

**INVESTIGATION OF PHASE EVOLUTION DURING
CRYSTALLIZATION OF LONG AFTERGLOW STRONTIUM
ALUMINATE PHOSPHOR ($\text{Sr}_4\text{Al}_{14}\text{O}_{25}$): THE B_2O_3 EFFECT**

by

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ABSTRACT

INVESTIGATION OF PHASE EVOLUTION DURING CRYSTALLIZATION OF LONG AFTERGLOW STRONTIUM ALUMINATE PHOSPHOR ($\text{Sr}_4\text{Al}_{14}\text{O}_{25}$): THE B_2O_3 EFFECT

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Strontium aluminate ceramics, when doped with rare earth elements, have an impressive capability for temporary storage and slow release of light, making them attractive for zero-energy consumption lighting. While persistent luminescence has been well known in Eu^{2+} and Dy^{3+} co-doped $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ (S4A7ED) as the most efficient luminescing compound in strontium aluminate family, the addition of B_2O_3 , initially merely as a sintering flux, increases the brightness and dramatically extends the afterglow persistence from several minutes to > 14 hours. Previous works, centered on the influence of boron on electronic structure, suggested that the extended afterglow might be attributed to clustering of ionic defects induced by presence of B_2O_3 . However, the results were solely based on indirect experimental evidences obtained by global characterizations. The objective of this dissertation is to understand the pivotal role played by B_2O_3 through

investigating its effect on microstructural evolution that supports long afterglow. To set the stage, we have systematically analyzed the impact of B_2O_3 content on microstructural evolution of stoichiometric $Sr_4Al_{14}O_{25}$ compounds processed by a modified Pechini method under thermal and kinetic control. Spatially resolved analyses based on advanced electron microscopy techniques were used to elucidate the nature of boron incorporation by investigation of local coordination of B, as well as the influence of B_2O_3 on diffusion kinetics and dopant distribution in the microstructure, giving rise to persistent luminescence. Our key results demonstrate that, incorporation of B_2O_3 facilitates the evolution of the long afterglow $Sr_4Al_{14}O_{25}$ phosphors through reducing the migration energy of the Sr^{2+} diffusing species in between the aluminum polyhedra. In the absence of B_2O_3 , the mechanism of phase evolution from amorphous state is controlled by a diffusion-limited solid-state reaction. However, evolution of $Sr_4Al_{14}O_{25}$ phase from the thermodynamically meta-stable phases is facilitated by a liquid phase assisted diffusion due to precipitation of a borate glassy phase in between the grains. At very high concentration of B_2O_3 , our results suggest that, the crystallization mechanism completely changes to precipitation from liquid phase. Our study reveals that B plays another role in the evolution of the microstructure that supports persistent afterglow—optimizing the Eu^{2+} and Dy^{3+} concentration below the solubility limit of the $Sr_4Al_{14}O_{25}$ phase—in addition to fostering their energy-transfer interactions. The experimental evidences obtained in this work, based on spatially resolved assessment of the B_2O_3 effect in the microstructure of $Sr_4Al_{14}O_{25}$: Eu, Dy compound, contributes significantly to the knowledge in the field and provides new insights for rational design of afterglow behavior in strontium aluminate pigments.

ÖZET

UZUN FOSFOR IŞIMA SÜRELİ STRONSIYUM ALÜMİNAT FOSFORUN KRİSTALİZASYONU SIRASINDA FAZ EVRİMİNİN İNCELENMESİ ($\text{Sr}_4\text{Al}_{14}\text{O}_{25}$): B_2O_3 ETKİSİ

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Anahtar Kelimeler: Stronsiyum Alüminat, Uzun fosfor Işıma, Mikroyapısal Evrim, B_2O_3 , Dopant Dağılımı, Katodoluminesans, EELS, Atomik Çözünürlük STEM Görüntüleme

Stronsiyum alüminat seramikler, nadir toprak elementleri ile katkılındıklarında, geçici depolama ve ışığın yavaş salınımında etkileyici kapasiteye sahiptir ve bu da onları sıfır enerji tüketimli aydınlatma için çekici kılar. Stronsiyum alüminat ailesindeki en etkili lüminesan olan Eu^{2+} ve Dy^{3+} katkılı $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ (S4A7ED) bileşiğinde ısrarlı ışıldama iyi bilinirken, başta sinterleme ajanı(flux) olarak kullanılan B_2O_3 ilavesi parlaklığı artırır ve ısrarlı ışıma süresini önemli ölçüde uzatır, birkaç dakikadan > 14 saate kadar. Borun elektronik yapı üzerindeki etkisine odaklanan önceki çalışmalar, uzun süreli parlamanın B_2O_3 varlığından kaynaklanan iyonik kusurların kümelenmesine bağlanabileceğini öne sürdü. Bununla birlikte, sonuçlar yalnızca küresel karakterizasyonlarla elde edilen dolaylı deneysel kanıtlara dayanıyordu. Bu tezin amacı, B_2O_3 'ün uzun süreli parlamayı

destekleyen mikro yapısal evrim üzerindeki etkisini araştırarak oynadığı önemli rolü anlamaktır.

Termal ve kinetik kontrol altında geliştirilmiş modifiyeli Pechini metodu ile üretilmiş stokiometrik $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ bileşiklerinin mikroyapısal evriminde B_2O_3 etkisi sistematik olarak çalışıldı ve çalışmanın zemini oluşturuldu. Bor katkılanmasının doğasını aydınlatmak için, gelişmiş elektron mikroskobu tekniklerine dayanan uzaysal çözümlenmiş analizler ile B'nun lokal koordinasyonu incelendi. Bunun yanı sıra, ısrarlı ışımaya neden olan, B_2O_3 'ın mikro yapıda difüzyon kinetiği ve katkı maddelerinin dağılımı üzerindeki etkisi araştırıldı.

Temel sonuçlarımız, B_2O_3 katkılanmasının, Sr^{2+} difüzör türlerinin alüminyum polyhedraller arasındaki göç enerjisini azaltarak uzun süreli parlak $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ fosforlarının evrimini kolaylaştırdığını göstermektedir. B_2O_3 yokluğunda, amorf durumdan faz evrim mekanizması,

difüzyonla sınırlı katı hal reaksiyonu ile kontrol edilir. Bununla birlikte, $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ fazının termodinamik olarak meta-kararlı fazlardan evrimi, taneler arasında borat camı bir fazın çökmesinden dolayı sıvı faz destekli difüzyonla kolaylaştırılır. Çok yüksek B_2O_3 konsantrasyonunda, sonuçlarımız gösteriyor ki kristalleşme mekanizması sıvı fazdan çökelmeye dönüşüyor. Çalışmamız, B'nun, enerji transferi etkileşimlerini teşvik etmenin yanı sıra, sürekli parlamayı destekleyen mikroyapının evriminde başka bir rol oynadığını ortaya koyuyor - Eu^{2+} ve Dy^{3+} konsantrasyonunu $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ fazının çözünürlük sınırının altında optimize edilmesine etki ediyor. $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$: Eu, Dy bileşiğinin mikroyapısındaki B_2O_3 etkisinin uzaysal çözümlü değerlendirmesine dayanan bu çalışmada elde edilen deneysel kanıtlar, bu alandaki çalışmalara önemli ölçüde katkı da bulunmaktadır ve stronsiyum alüminat pigmentlerinde uzun ışıma davranışının rasyonel tasarımı için yeni anlayışlar sağlamaktadır.

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*To the Innocent Victims of
Flight PS752...*

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LIST OF ABBREVIATIONS

ABF	Annular Bright Field
ADF	Annular Dark Field
AEM	Analytical Electron Microscopy
Al	Aluminum
Ar	Argon
AR-STEM	Atomically Resolved Scanning Transmission Electron Microscope
B	Boron
CA	Citric Acid
CB	Conduction Band
CIF	Crystallographic Information File
CL	Cathodoluminescence
COD	Crystallography Open Database
CS	Conventional Sintering
DP	Diffraction Pattern
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
Dy	Dysprosium
EDS	Energy Dispersive X-ray Spectroscopy
EELS	Electron Energy Loss Spectroscopy
EG	Ethylene Glycol
ELNES	Energy Loss Near Edge Spectrum
Eu	Europium
FIB	Focused Ion Beam
HAADF	High Angle Annular Dark Field
HRTEM	High Resolution Transmission Electron Microscopy
ICSD	Inorganic Crystal Structure Database
JEMS	Java Electron Microscopy Software
JCPDS	Joint Committee on Powder Diffraction Standards
O	Oxygen
PCA	Principle Component Analysis
PL	Photoluminescence
RGB	Red, Blue, Green Additive Color Mixing
ROI	Region of Interest
SA phosphors	Strontium Aluminate phosphors
SA	SrAl_2O_4
SA ₂	SrAl_4O_7
SA ₆	$\text{SrAl}_{12}\text{O}_{19}$
S ₄ A ₇	$\text{Sr}_4\text{Al}_{14}\text{O}_{25}$
SAB	Strontium Aluminoborate
S ₄ A ₇ ED	$\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ co-doped with Europium and Dysprosium
S ₄ A ₇ EDB	$\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ co-doped with Europium and Dysprosium with Boron
SEM	Scanning Electron Microscope
SPS	Spark Plasma Sintering
STEM	Scanning Transmission Electron Microscope
TEM	Transmission Electron Microscope

TG	Thermogravimetry
UV	Ultra-Violet
VB	Valence Band
V''_{Ca}	Calcium Vacancy
V_o	Oxygen Vacancy
V''_{Sr}	Strontium Vacancy
WDS	Wavelength Dispersive X-ray Spectroscopy
XRD	X-Ray Diffraction
ZA	Zone Axis
ZLP	Zero-Loss Peak



CHAPTER 1: INTRODUCTION

1.1 History and Background

The initial observations of afterglow phenomenon can be traced back as old as 1000 years ago attributed to a painting – a cow pasturing in a stable – recorded in the Chinese Song dynasty (960–1279 A.D.). The raw materials used as the ink for drawing is said to be a mixture of calcium extracted from pearl shell, and sulfide compounds obtained from volcanic activities [1]. The painting remained visible at night and it was supposed to have an unfathomable magic behind it.

The preliminary scientific reports on the “*glow in dark*” phenomenon was however, attributed to the Bologna stone which was documented as the first persistent luminescence material, discovered by the Italian shoemaker and alchemist, Vincenzo Cascariolo in the early 17th century [1, 2]. The stone was synthesized by calcination of the mineral, baryte, which is an impure barium sulfate (BaSO_4). After exposure of the heat-treated stone to the sunlight, the stone demonstrated an orange and reddish afterglow in darkness. The phosphorescence behavior of the stone was ascribed to alchemy, during which the “*golden light of the Sun*” was attracted by the stone. 400 years later, it was revealed by Hölsa *et al.* [3] that the afterglow of the Bologna stone is due to electronic transition of $3d^9 4s^1 \rightarrow 3d^{10}$ of Cu^+ cations present as the impurity (dopant) in the structure of the reduced product of baryte *e.g.* BaS.

The term *afterglow* (also known as *phosphorescence*) as one of the classes of photoluminescence, is generally referred to emission of light at room temperature, due to relaxation of excited electronic state in an insulator substance that is detectable for a long period of time, from a few seconds to several hours after excitation source cut-off [1, 2, 4].

1.2 Strontium Aluminate Compounds

Strontium aluminate ceramics, when doped with Eu^{2+} , are considered as efficient and stable long afterglow materials due to their excellent capability of temporarily storing energy upon UV and or visible light illumination, and slow release of the energy as visible light. Due to high quantum efficiency in the visible light range, chemical stability, no radio-active irradiation and long-lasting phosphorescence, strontium aluminate compounds are attractive for zero-energy consumption lighting applications.

Stable hosts for the Eu^{2+} ion in strontium aluminate ceramics includes five different thermodynamically stable stoichiometries according to the phase diagram of $\text{SrO} - \text{Al}_2\text{O}_3$ [5]. These phases include $\text{Sr}_3\text{Al}_2\text{O}_6$ (S3A), SrAl_2O_4 (SA), $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ (S4A7), SrAl_4O_7 (SA2) and $\text{SrAl}_{12}\text{O}_{19}$ (SA6), arranged in the order of increasing Al_2O_3 to SrO ratio[6].

Each phase is composed of chains of negatively charged aluminum polyhedral units of AlO_x (with $x = 4, 5$ and 6) that are corner, edge or face sharing depending on the crystal structure. The alumina scaffolds define cavities of negative charge, into which Sr^{2+} sublattice ions are incorporated to provide charge compensation for charge neutrality [6]. Among all the strontium aluminate phases, it is well-know that only SA and S4A7 support long afterglow at room temperature [6-8].

1.2.1 Crystal Structure of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$

The $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ phase crystallizes into orthorhombic crystal structure with the space group of Pmma symmetry with lattice parameters of $a = 2.4785 \text{ nm}$, $b = 0.8487 \text{ nm}$ and $c = 0.4886 \text{ nm}$ [9, 10]. The unit cell of S4A7 (**Figure 1.1-a**) consists of edge-shared columns of AlO_6 which are separated by double layer of corner sharing AlO_4 polyhedral units [6, 8-12]. The negative charge of the cavities built up by Al polyhedral units are compensated by Sr^{2+} cations. There are two non-equivalent crystallographic sites for Sr^{2+} cations in the unit cell which form distorted polyhedral with oxygen ions (**Figure 1.1-b**). Sr1 site, coordinated with 10 oxygen ions forms a wider cage with the average Sr – O bond length of $2.77 \text{ \AA}$ while Sr2 site is coordinated with 7 oxygen ions and the average bond length of $2.62 \text{ \AA}$ [6, 8-10, 12]. The ionic radii of Sr^{2+} cations in Sr1 and Sr2 sites are $1.26 \text{ \AA}$ and

1.21 Å, respectively [13]. It should be noted that, because the average Sr – O bond length in the tenfold coordinated Sr1 sites are longer than that of sevenfold coordinated Sr2 sites, the interaction between Sr^{2+} cations and the surrounding oxygens, *i.e.* the crystal field of the Sr1 sites at the 10-fold Sr polyhedron is weaker than that of 7-fold Sr2 sites [6, 12].

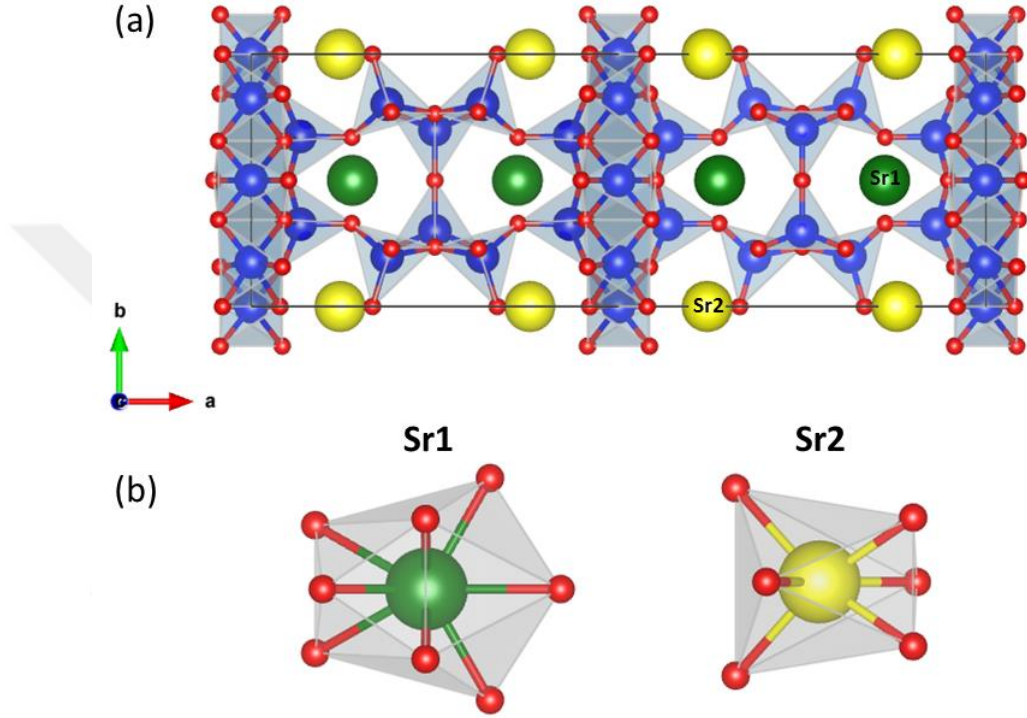


Figure 1.1. a) Unit cell of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ along the c projection b) Local coordination of non-equivalent Sr^{2+} sites in the crystal structure of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$.

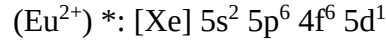
1.2.2 Effect of Eu^{2+} Dopant

Rare earth ions have been used as dopants in strontium aluminates to create optically active centers which introduce new energy levels inside the energy gap of the crystal [14-16]. The electronic transitions between such levels generate photon emission, which do not occur in the original host prior to doping. Eu^{2+} , as one of the most efficient activators used in phosphor materials has the following electronic configuration:



There are seven f-shell electrons in the ground state of Eu^{2+} . When Eu^{2+} in the host lattice is irradiated by external photons, the absorbed energy results in increasing the orbital

configuration energy of the electrons. This rearrangement in electron density distribution becomes:



When divalent Eu^{2+} is incorporated into the structure of the host strontium aluminates, it serves as an optically emitting center and shows a broad band emission due to electronic relaxation from the lowest excited state of $4f^6 5d^1$ to the ground state ($4f^7$) ($4f^7 \rightarrow 4f^6 5d^1$) [6, 17-19]. Eu^{2+} ions doped in the host lattice are substitutionally replaced for Sr^{2+} sublattice sites because of similar ionic radii [4, 6, 20], and the wavelength of the emission is strongly dependent on the interaction of the 5d electrons of the luminescence center with its surrounding oxygen ions, e.g. the crystal field [6]. In the case of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ when doped with Eu^{2+} , because there are two crystallographically non-equivalent Sr sites in the structure with different local environments, Eu^{2+} ions can occupy Sr1 and Sr2 lattice positions and thus, there are two Eu^{2+} luminescent centers. In addition, due to shorter average Sr – O bond length in Sr2 sites, there is a higher degree of covalency in Sr2 site polyhedron. Consequently, a larger crystal field splitting will be applied on the Eu^{2+} ions incorporating into 7-fold coordinated Sr site. The energy difference between the ground state $4f^7$ level and the excited $4f^6 5d^1$ level of Eu^{2+} is narrower, giving rise to emission of light with longer wavelength (in the green region of the visible spectrum) from the Sr2 sites. Similarly, the band gap of Eu^{2+} substituting into Sr1 site (10-fold coordinated) is larger, leading to emission of light with higher energy (shorter wavelength in the blue region of the visible spectrum) upon relaxation by $4f^6 5d^1 \rightarrow 4f^7$ transition [6, 12].

1.2.3 Effect of Dy^{3+} Co-doping

Besides the luminescent centers in the structure of the host strontium aluminate compounds, long afterglow phenomenon necessitates the presence of localized energy levels in the forbidden bandgap of the host material to serve as trap states for charge carriers [4]. These trap levels could be associated with structural defects including co-dopants and/or vacancies in the host material. During excitation of the emitting center, the excited charge carriers could be trapped in such discrete levels. Consequently, due to spatial separation between the trap states and the luminescent centers, the trapped charge carriers will be temporarily maintained in a metastable state and direct recombination of

the excited electrons are hindered. The excited electronic charges that are captured by trap levels generated by incorporating the co-dopants can then be thermally released and this thermally stimulated detrapping is accompanied by extended afterglow time in the Eu^{2+} -activated strontium aluminates [21-24].

It has been shown that, when strontium aluminates are codoped with Dy^{3+} , the duration of luminescence is extended to several minutes [22]. The excited states of Dy^{3+} are close in energy to the excited states Eu^{2+} . When the electronic energy level of the two ions are sufficiently close to each other, the excited electrons of the emitting center (Eu^{2+}) can transition to the trap states provided by Dy^{3+} by energy transfer. Because Dy^{3+} ($r = 0.97 \text{ \AA}$) co-dopant is also close in the ionic radius to that Sr^{2+} ($r = 1.21 \text{ \AA}$) [13], they can occupy Sr^{2+} sites in the crystal structure of strontium aluminates. However, in order to maintain the charge neutrality in the lattice, two Dy^{3+} cations must replace three Sr^{2+} which means that, the incorporation trivalent co-dopants would generate structural defects *e.g.* the cation and oxygen vacancies in the host lattice [4, 14, 23, 25]. In fact, Dy^{3+} provides auxiliary trap states including structural defects, in close spatial proximity of the $4f^6 5d^1$ levels in the excited state of Eu^{2+} and delays the de-excitation process [18, 26].

Several mechanisms have been proposed to describe the persistent luminescence phenomenon in inorganic phosphors that are activated by rare earth elements. Generally speaking, there are two types of structural defects, also known as the activation centers, that contribute to persistent luminescence in the materials exhibiting long afterglow. The emitting centers and the trap centers which are located in the band gap of the phosphor material [1]. The former are ions that are capable of undergoing electronic transition in their outer most electronic arrangement by external photoexcitation, such as lanthanide ions (with $5d \rightarrow 4f$ or $4f \rightarrow 4f$ transitions) or transition metal ions (with $d \rightarrow d$ transitions). Trap centers are either intrinsic lattice defects such as oxygen vacancies or the intentionally introduced impurities incorporated into the structure of the material as co-dopants [1, 15, 27-29]

In general, the basic physical principles behind the delayed light emission during persistent phosphorescence can be summarized as follow [1]:

1. Excitation of the charge carriers (including electrons or holes) via illumination of at certain wavelength (**Excitation**).
2. Non-radiative capture of the charge carriers by electron/hole traps during which the energy of the excitation is stored (**Trapping**).

3. Thermally assisted liberation of the charge carriers after the removal of the excitation source (***Detrapping***).
4. Delayed emission of photon (with a shorter wavelength compared to the exciting beam) due to recombination of electrons and holes at the emission center (***Recombination***).

Although the general principles behind the afterglow phenomenon is well understood by now, the detailed mechanism of persistent luminescence in phosphor materials is still an unresolved issue among researchers. Several models centered on the electronic band structure of the long afterglow materials have been proposed to explain the correct mechanism of long afterglow in such materials consistent with global analysis of powders. Before reviewing the proposed mechanisms of persistent luminescence in strontium aluminates codoped with Eu^{2+} and Dy^{3+} suggested in the literature, we first briefly present an introduction to the basics of luminescence and then the major difference between fluorescence and phosphorescence will be reviewed.

1.3 Luminescence

The term *luminescence* is defined as the spontaneous emission of light from a cold body when the electronic state of the material is excited by an external source of energy. The absorption of the excitation energy by the substance promotes the atoms to an excited state followed by de-excitation to the ground state upon which the absorbed energy is released in the form of electromagnetic waves in the range of visible light [2, 30, 31]. In the definition of luminescence phenomenon, the emphasis is on the fact that the emission of the light is not caused by the rise in temperature as opposed to the incandescence where light radiation occurs from hot bodies and is conditioned by rise in temperature.

In inorganic materials, luminescence is predominantly occurred due to the presence of impurities and point defects which are called activators. Transition between the electronic states during luminescence can thus be attributed to the perturbation of the energy levels of the impurity ions under the influence of surrounding crystal field or it can be related to the band structure of the host matrix disturbed by the impurity ion [31].

Luminescence can be categorized into several classes based on the type of the excitation energy. In particular, photoluminescence is the light emission when the electronic transitions are activated by photon. Other important types of luminescence include cathodoluminescence, thermoluminescence, triboluminescence, sonoluminescence and chemiluminescence where the source of the excitation energy is electron beam, thermal energy, mechanical energy, sound waves and chemical reactions, respectively [31].

1.4 Fluorescence vs Phosphorescence

Among all the luminescence categories, photoluminescence is the main concern of this work and can be further divided into *fluorescence* and *phosphorescence*. The distinction between the two is commonly known on the basis of duration of light emission after extinguishing the excitation source. In fact, fluorescence is characterized as the emission of light that terminates simultaneously with the excitation source cut-off and its lifetime is short and in the range of nano-second (10^{-8} to 10^{-9} s). Thus, fluorescence is considered as short-live luminescence [2, 32].

In phosphorescence however, the absorbed energy during excitation is not immediately emitted and the emission of light persists after the end of excitation with a lifetime of 10^{-6} to 1 second [2, 32] and thus is considered as long-lived luminescence. In addition, the intensity of the emitted light during phosphorescence is much lower compared to fluorescence [1, 2, 32].

It should be noted that, discrimination between fluorescence and phosphorescence merely based on the lifetime of the emission might be misleading since physical phenomena such as long-lived fluorescence and short-lived phosphorescence have comparable durations [2]. Therefore, the physics behind the two type of luminescence must be elucidated in more detail.

1.5 Mechanism of Persistent Phosphorescence (Afterglow) in Inorganic Solids

As mentioned earlier, for the long afterglow phosphors, two types of structural defects *e.g.* emitting centers and trap centers play the main role in delaying the light emission. Both activation centers are located in the band gap of the phosphor material. The trap centers can be generally divided into two groups; 1) the electron traps with energy levels of a few electron volts (less than 1 eV) just below the bottom of conduction band (CB) and 2) hole traps with energy levels located at a few electron volts just above the top of the valence band (VB) [1, 33].

The emission wavelength of the long afterglow materials is strongly dependent on the energy levels of the emitting center, as well as the interaction of the emitting center with its surrounding environment, *e.g.* the crystal field applied by the host lattice on the luminescent ion. On the other hand, the duration and the intensity of the afterglow is determined by the trap characteristics including the type of the trap, the trap depth and the density of trap energy levels [1, 31].

The mechanisms for long afterglow phenomenon in phosphor materials is governed by charge carrier trapping-detrapping through a thermally stimulated process. The charge carriers could be either electrons or holes, and all the proposed mechanisms for the persistent phosphorescence will be categorized in either electron or hole trapping – detrapping procedure. In the following section, we briefly review the general models involved in long afterglow phosphors.

1.5.1 Electron Trapping – Detrapping: Band to Band Excitation

Depending on the absorption energy during illumination of the phosphor material, the electronic transition can be initiated by exciting an electron from the VB to CB leaving a hole in the VB (**process 1 in Figure 1.2**). The electron the generated hole can move through the CB and VB, respectively, possibly due to vibronic relaxation. The mobile electron will be captured by the electron traps located just below the bottom of CB in the forbidden band gap of the phosphor material while the generated hole is trapped by the ground state of the emitting center, leading to increase in the oxidation state of the emitting center (**process 2 in Figure 1.2**). After the excitation source was cut-off, the trapped electron can be thermally liberated provided that the trap depth (ΔE) *e.g.* the

energy difference between the bottom of CB and the trap state can be overcome by the thermal activation energy at room temperature. In this case, the stuck electron can be gradually released from the trap state to the excited state of the emitting center (**process 3 in Figure 1.2**). Once the excited electron returns to the excited state of the emitting ion, it recombines with the waiting hole present in the ground state of the emitting ion and as a result, a delayed photon emission occurs (**process 4 in Figure 1.2**).

In fact, during band to band electron transition, the electron is excited from the valence band of the host crystal and ends up in the ground state of the luminescent center. In addition, the electron trap depth plays a vital role in long afterglow phenomenon. The depth must be shallow enough so that electron detrapping can occur at room temperature.

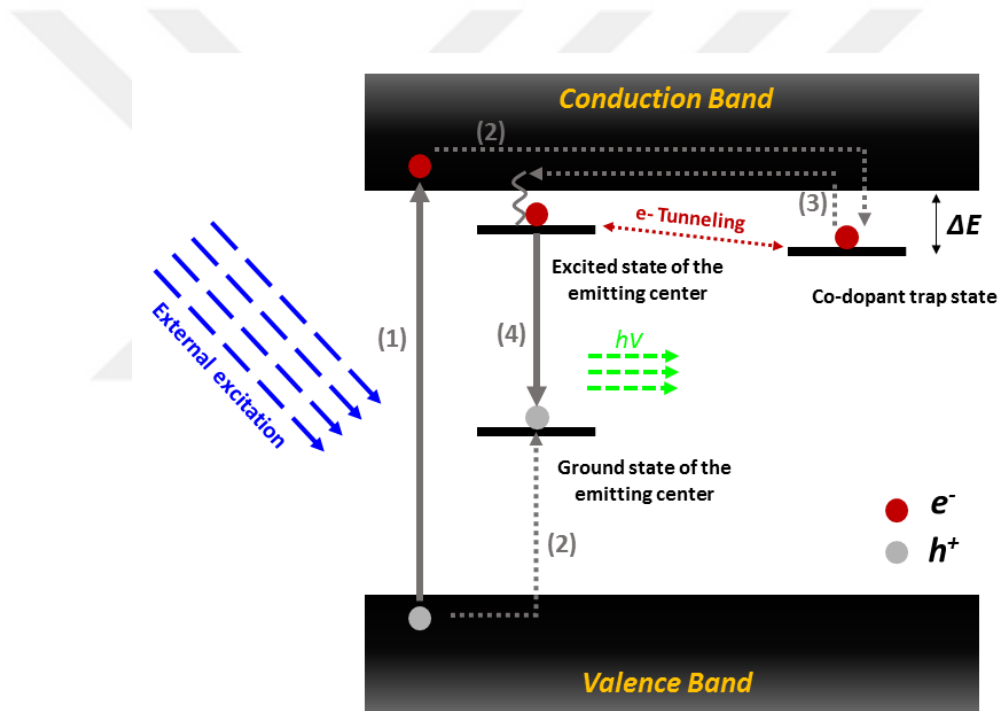


Figure 1.2. Electron trapping-detrapping process in a band to band transition in long afterglow materials.

1.5.2 Electron Trapping – Detrapping: Emission Center Excitation

This situation occurs when the excitation source has a lower energy (usually low energy UV or even visible light) compared to band to band transition and the excited electron is directly pumped from the emitting center ion. In this model, the electron is excited directly from the ground state of the emitting center during illumination, leaving a hole in the

ground state. The excited electron can then transition into the CB via a thermally assisted process, if the energy difference between the excited state for the emitting center and CB is sufficiently small (**process 1 in Figure 1.3**). The detrapping and recombination steps are similar to what was described in for the case of band to band transition in *section 1.5.1*.

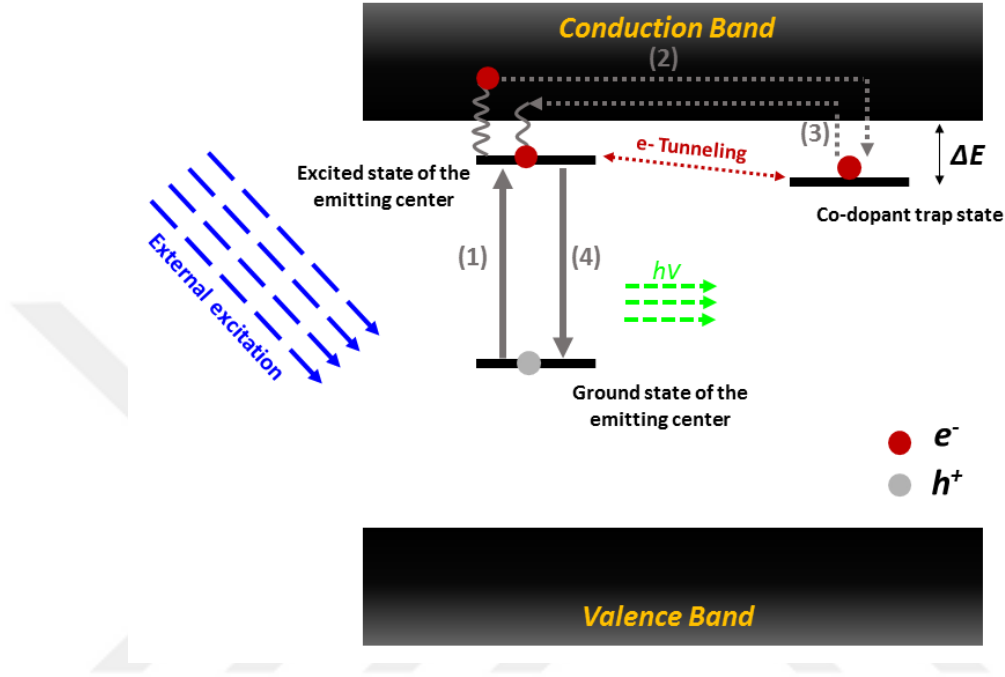


Figure 1.3. Electron trapping-detrapping process from the emitting center in long afterglow materials.

It should be noted that, in both cases, the detrapping of the electron from the trap state to the excited state of the luminescent center can also be accomplished through an electron tunneling procedure in the forbidden band gap of the host material if the vibrational state of the trap center overlaps with the electronic excited state of the emitting center [1, 33]

1.5.3 Hole Trapping – Detrapping: Band to Band Excitation

The hole trapping – detrapping initiated by a band to band transition is exactly the mirror of what was discussed in the case of electron counterpart as discussed in section 1.5.1. Here, instead of electron being released from an electron tarp through CB and final recombination at the emitting center, this is the hole that is released from a trap center through the VB. Under high energy excitation, the electron-hole pair is generated in the

CB and VB, respectively (**process 1 in Figure 1.4**). The generated hole can move through the VB and be captured by the hole trap state while at the same time the excited electron in CB will be trapped with the excited state of the luminescence center (**process 2 in Figure 1.4**). When external illumination is ceased, the captured hole can be first thermally bridged to the VB if the thermal vibration energy is comparable to the energy difference (ΔE) between the hole trap electronic state and the top of the VB and then returns to the ground state of the emitting center (**process 3 in Figure 1.4**). Finally, the recombination of the returned hole with the initially excited electron captured by the excited state of the emitting center takes place and consequently, a photon is emitted (**process 4 in Figure 1.4**).

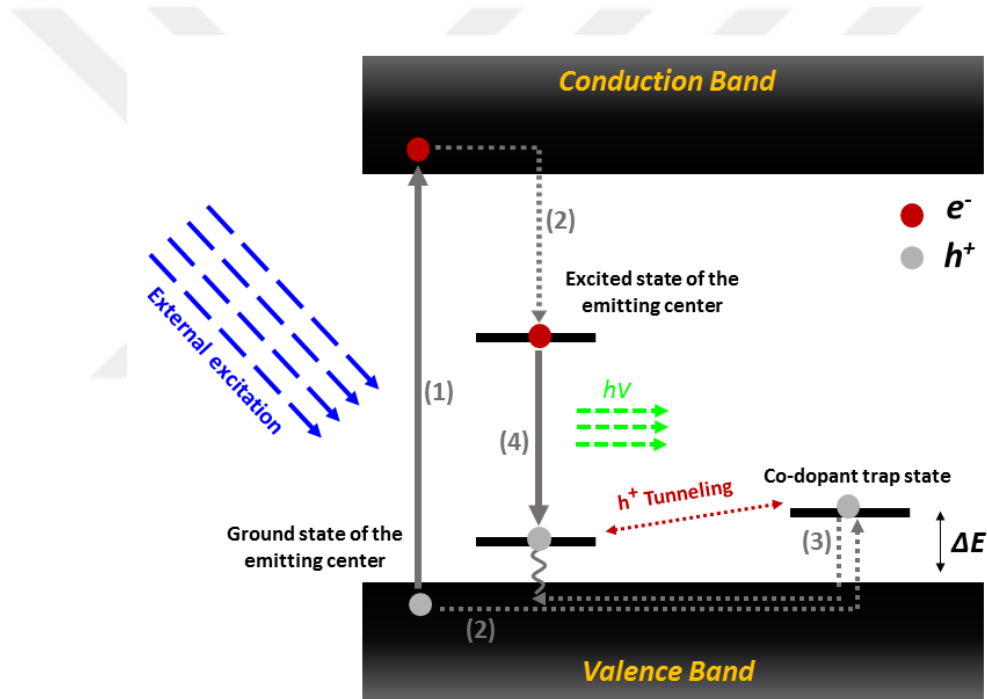


Figure 1.4. Hole trapping-detrapping process in a band to band transition in long afterglow materials.

1.5.4 Hole Trapping – Detrapping: Emission Center Excitation

In this mechanism, similar to that of electron, the hole is directly generated in the electronic ground state of the luminescence center. Again, through a thermally stimulated process, the hole can jump to the VB if there is an overlap between the vibrational level of the ground state of the emitting center (**process 1 in Figure 1.5**). The hole detrapping

followed by recombination at the emitting center location completes the persistent phosphorescence mechanism via hole trapping-detraping model.

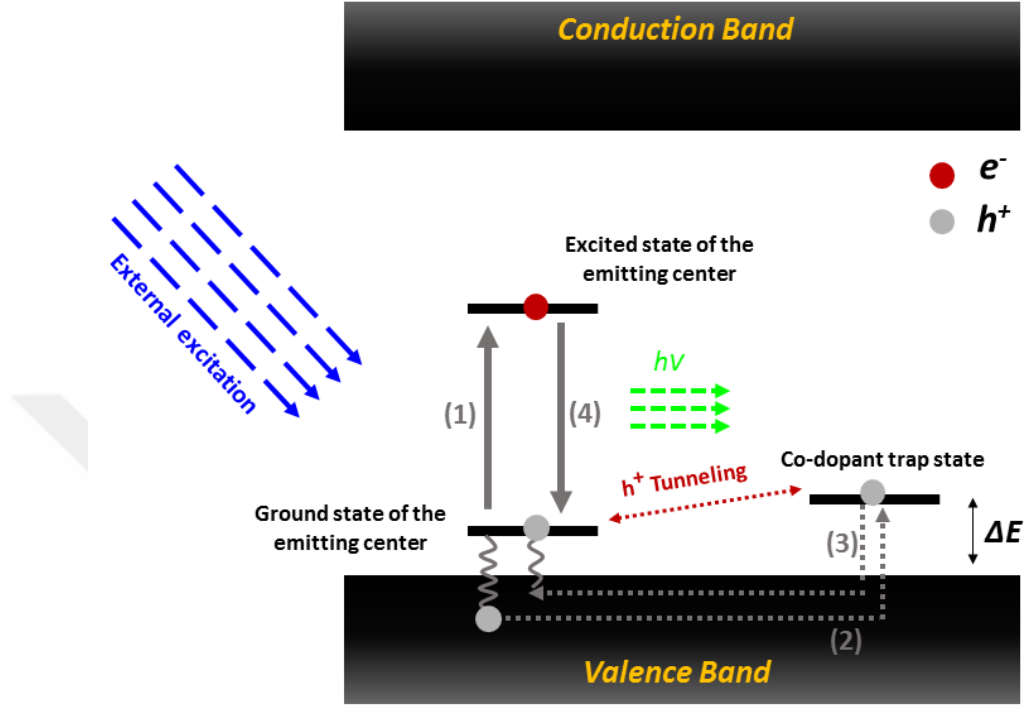


Figure 1.5. Electron trapping-detraping process from the emitting center in long afterglow materials.

1.6 Mechanism of Persistent Phosphorescence in Strontium Aluminates

The long afterglow mechanism of the inorganic phosphor materials, in particular - strontium aluminate compounds activated by rare earth ions have been described in the literature. In all the proposed mechanisms, the general idea that after the excitation, the charge carriers could be captured by the so-called traps inside the forbidden band gap of the host materials, followed by slow release from the trap states and recombination at the activator sites was agreed.

However, although the purposed mechanisms were supported by some experimental proofs by their own time, there is a lack of consistency in terms of the nature and the origin of the traps and the charge carrier. In this course of the study, the well-known mechanisms suggested for justifying the persistent phosphorescence phenomenon in

strontium aluminate phosphors, specifically SrAl_2O_4 codoped with Eu and Dy rare earth elements will be overviewed.

1.6.1 The Matsuzawa Model

The explanation of the mechanism for long afterglow behavior in phosphor materials doped with rare earth ions was revolving around the hole trapping model after of Matsuzawa asserted the discovery of an extraordinary long lasting phosphorescence material, the SrAl_2O_4 activated by codoping of Eu^{2+} and Dy^{3+} in 1996 [22]. Based on the photoconductivity experiment of $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$ powder, Matsuzawa concluded that, the mobile charge carriers in the phosphor material are holes. This model assumes that, the ground state energy level of $4f^7$ electronic configuration of Eu^{2+} is located in the close proximity of the top of the valence band [4, 16, 22].

Matsuzawa proposed that, upon UV excitation, Eu^{2+} is excited from the $4f^7$ ground state to $4f^6 5d^1$ excited state ($4f^7 \rightarrow 4f^6 5d^1$). This would generate a hole in the $4f^7$ energy level, which can then escape to the VB of SrAl_2O_4 and thereby, Eu^+ specie is generated. The hole as the charge carrier then moves through the VB and is captured by the trivalent Dy^{3+} , leading to formation Dy^{+4} species. After the cessation of the UV illumination, the trapped holes are thermally released back to the VB again. The released hole can return to the Eu^+ ion followed by recombination with the excited electron, by which Eu^{2+} relaxes to its ground state by emission of a photon (**Figure 1.6**) [22].

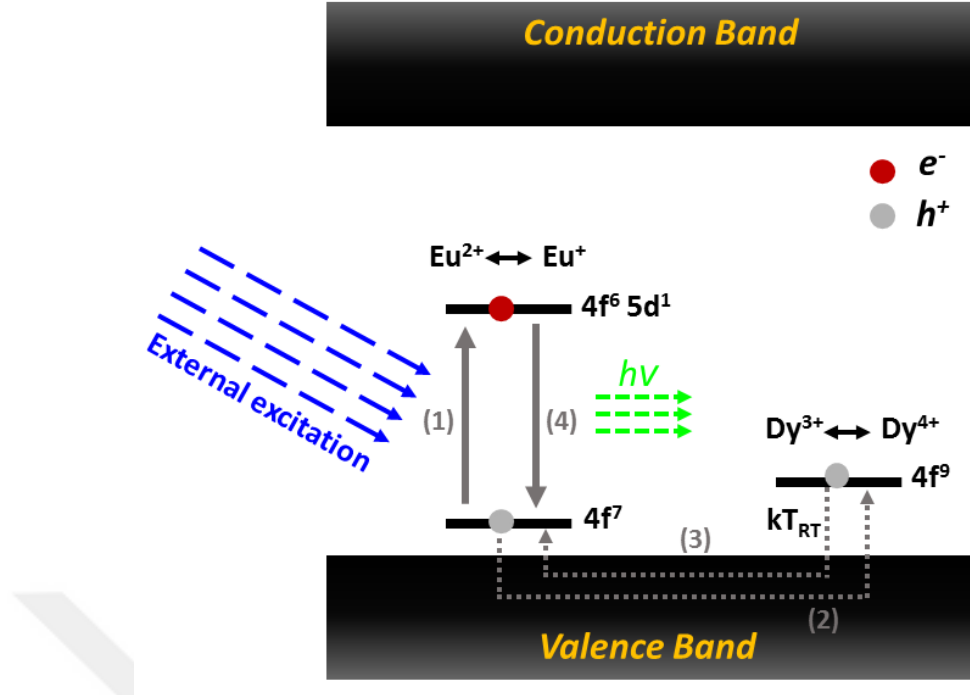


Figure 1.6. The energy level diagram for the long persistent phosphorescence mechanism proposed by Matsuzawa et al. for $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$.

However, the proposed mechanism is based on questionable assumptions. First, the formation of Eu^+ species is highly improbable because the reduction of Eu^{2+} to Eu^+ requires a high energy [4] and the oxidation of Dy^{3+} to Dy^{4+} ($\text{Dy}^{3+} + h^+ \rightarrow \text{Dy}^{4+}$) in the hole trap centers is unrealistic due to the chemical instabilities Dy^{4+} ions [4, 25]. Furthermore, the calculation of band structure for the Eu^{2+} - doped SrAl_2O_4 revealed that the Eu d-block lie just below the CB bottom and 4f-block of Eu at approximately 3 eV above the top of VB [4].

1.6.2 The Aitasalo Model

In this model (**Figure 1.7**), Aitasalo et al. suggested that, the structural defects including oxygen vacancies (V_o) and cation vacancies in the structure of the host alkaline earth aluminates are served as electron and hole traps, respectively [14].

Based on this mechanism, electrons are excited from VB to discrete energy levels with unknown origin in the bandgap upon UV illumination. The holes that are generated in the VB, can then be trapped by the negative effective charge of the cation vacancies such as V''_Sr or V''_Ca located a few electron volts just above the VB in the alkaline earth

aluminates. The excited electrons stuck in the unknown energy levels are then transferred to the positively charged oxygen vacancies that are close to the CB via thermal stimulation. Consequently, the recombination of electrons in oxygen vacancy defects with holes in the cation vacancy sites gives rise to emission of a photon, whose energy is transferred to the emitting center, *e.g.* Eu^{2+} ions. Therefore, this assumption requires close proximity of the vacancies to the luminescent centers [16]. This energy transfer excites Eu^{2+} from $4f^7$ electronic state to $4f^6 5d^1$ configuration. The electronic relaxation of Eu^{2+} to its ground state completes the long afterglow phenomenon in strontium aluminate phosphors [14]. They showed that, because the trivalent lanthanide ions occupy the divalent alkaline earth sites, it results in spontaneous defect creation for charge compensation [16]. Thus the presence of trivalent co-dopants can increase the number of cation vacancy structural defects, which are considered as the hole traps [4, 14].

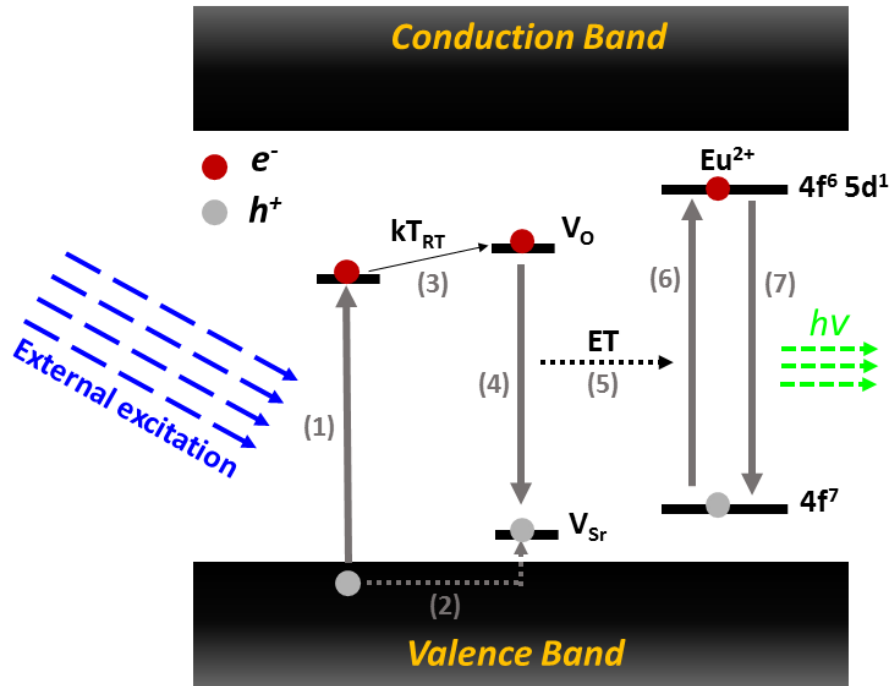


Figure 1.7. The energy level diagram for the long persistent phosphorescence mechanism proposed by Aitasalo et al. for $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$.

1.6.3 The Dorenbos Model

This model was centered on the previous determination of the location of energy levels of the divalent and trivalent lanthanides with respect to the VB and CB in inorganic

compounds [34, 35]. Dorenbos *et al.* [15, 34] stated that, when lanthanide ions with the possibility of undergoing $4f^n \rightarrow 4f^{n-1} 5d^n$ transition in their electronic configuration are incorporated into the crystal structure of inorganic compounds, the electrons of the $4f^n$ orbitals are shielded from the surrounding crystal field [34]. This means that, the variation in the energy level of $4f^n$ in the band structure of the host lattice is almost independent from the crystal field imposed by the host material and is determined by the properties of the lanthanide ion. On the contrary, a 5d electron strongly interacts with the crystal field, and the location of its energy level is determined by the crystal field and not by the type of the lanthanide ion [15, 34]. In the crystal structure of $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$, they showed that the 5d energy level of Eu^{2+} is located very close to the bottom of conduction band, while the excited energy state of Dy^{3+} stays between the ground and excited state of Eu^{2+} [15, 34, 35]

The model proposed by Dorenbos [35] relies on the fact that, the persistent luminescence in strontium aluminate phosphors follows an electron trapping – detrapping mechanism, including electron transport via CB, as opposed to the hole transport model suggested by Matsuzawa and Aitasalo. According to this model, Eu^{2+} is excited to 5d energy level, which is very close to the bottom of CB. These excited electrons can then move easily through the CB until they are trapped by the trivalent rare earth co-dopant. The captured electron can return to the CB again by a thermally stimulated process and reach the excited state energy level of Eu^{2+} followed by relaxation at the emitting center and light emission as schematically shown in **Figure 1.8**.

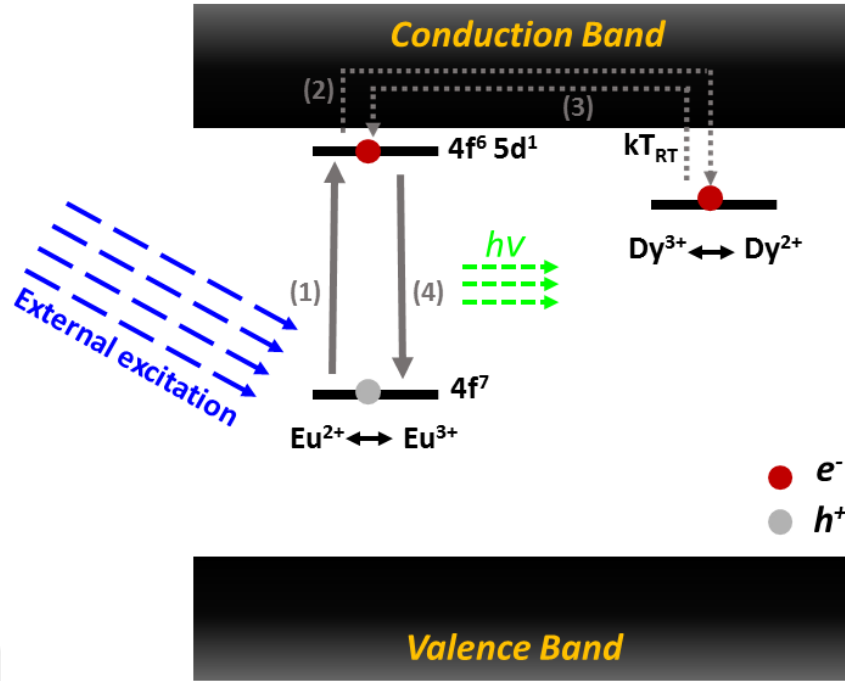


Figure 1.8. The energy level diagram for the long persistent phosphorescence mechanism proposed by Dorenbos for strontium aluminate compounds.

1.6.4 The Clabau Model

The mechanism proposed by the Clabau et al. [4, 25] is based on the fact that, the electronic state of the d orbital for the excited Eu^{2+} is very close to the bottom of the CB in SrAl_2O_4 . They also observed from electron paramagnetic resonance (EPR) measurements that, under UV illumination of SrAl_2O_4 : Eu^{2+} , Dy^{3+} , the concentration of Eu^{2+} species decreases continuously, and it increases again when the excitation source is terminated until the end of afterglow. Therefore, Eu^{2+} is involved in the trapping process and the idea of energy transfer to Eu^{2+} [14] was ruled out. In addition, they assumed that, the strontium aluminate phosphors have always some amount of Eu^{3+} because complete reduction of Eu^{3+} to Eu^{2+} during synthesis is not possible.

According to this model (**Figure 1.9**), under UV excitation, electrons are promoted from the 4f to 5d energy levels of Eu^{2+} and from the VB to the 4f level of residual Eu^{3+} by a charge transfer process. It is important to note that, during charge transfer from VB to the residual Eu^{3+} ions, the Eu^{3+} species are reduced to Eu^{2+} .

The excited electron in the 5d level are then trapped by the structural defects, the oxygen vacancies, which are located close to the energy levels of Eu^{3+} . By this electron trapping, the Eu^{2+} are oxidized to Eu^{3+} . At the same time, the holes that are generated in the VB, can be captured by the energy levels of cation vacancies including both V_{Sr} and V_{Al} .

The captured electrons in V_{O} defects are then thermally detrapped to the 5d excited state of Eu^{3+} and the relaxation of $4f^6 5d^1 \rightarrow 4f^7$ gives rise to green light emission (520 nm). The transfer of liberated electrons to the excited state of the emitting center occurs directly and thus requires close proximity of oxygen vacancy to the excited state of the Eu^{2+} .

On the other hand, charge transfer from the $4f^7$ level of Eu^{2+} (the already residual Eu^{3+}) back to the VB leads to emission of blue phosphorescence (450 nm). As for the role of Dy^{3+} co-dopants, this model suggests that, the incorporation of Dy^{3+} into the structure, enhance the density and the depth of the electron traps e.g. the oxygen vacancies, leading to improvement of the afterglow property of the strontium aluminate phosphors.

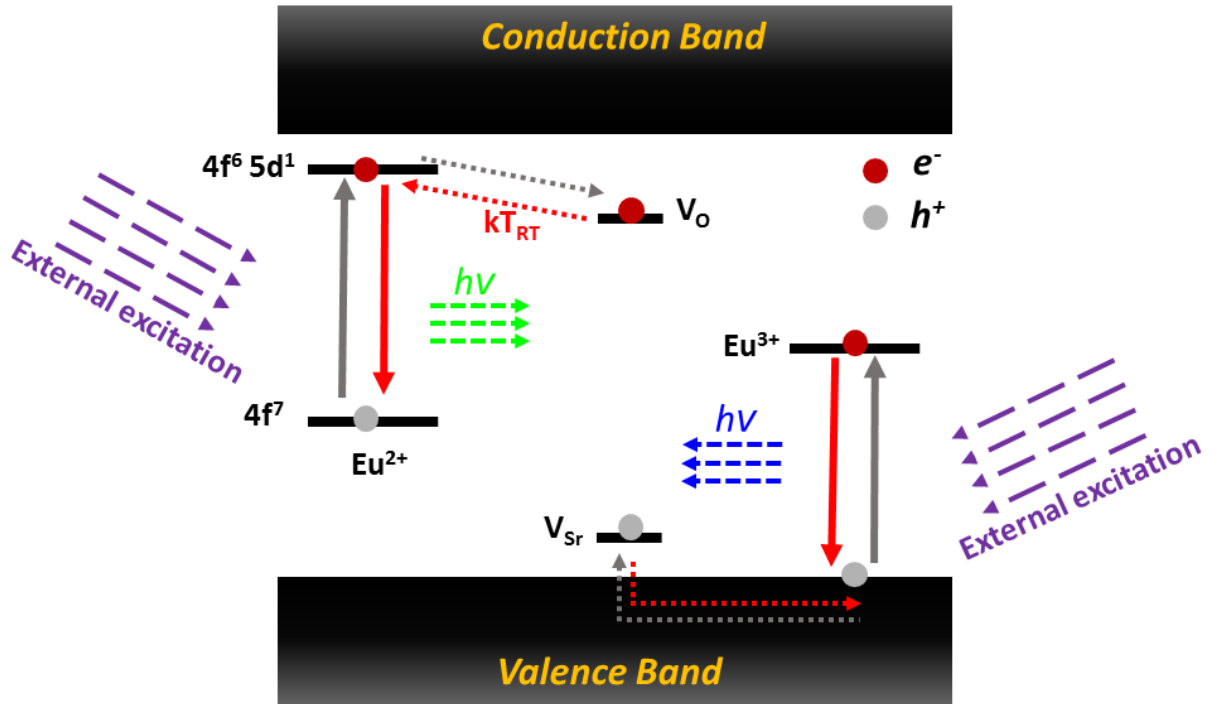


Figure 1.9. The energy level diagram for the long persistent phosphorescence mechanism proposed by Clabau et al. for $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$.

1.7 The Effect of B³⁺ Doping

During the ceramic processing of strontium aluminate (SA) phosphors, the addition of B₂O₃ as a sintering flux agent promotes the grain growth and densification of the host material via facilitating diffusion, as well as decreasing the processing temperature of the target phase [36-38]. In addition, it has been observed that when B₂O₃ is incorporated into the Eu and Dy codoped strontium aluminate compounds, it dramatically extends the afterglow persistence time from the order of minutes to several hours as well as enhanced afterglow intensity [36]. Although the effect of B₂O₃ doping on extremely long afterglow of the Eu²⁺ and Dy³⁺ codoped strontium aluminate ceramics has not been clearly understood, the most widely accepted mechanism induced by B³⁺ incorporation is suggested to be the clustering of the ionic defects in the structure [4, 25]. In other words, the long afterglow behavior in B-doped SAED phosphors is ascribed to spatial and energetic proximity of the point defects in the crystal (including the oxygen vacancies and substitutional co-dopants) which allows direct energy transfer between the charge carrier trap levels.

From an electronic structure point of view, the effect B₂O₃ addition on extended persistence phosphorescence is related to increasing the number of electron and hole traps by the formation of BO₃ and BO₄ units, respectively. [4, 39, 40]. The oxygen vacancies in the host lattice generated by formation of BO₃ trigonal units, have a positively charged field which requires some electron density from the adjacent cations to be stabilized. Because the ionization potential of the Eu²⁺ is the lowest among all the cations present, the propensity for electron density delocalization in Eu²⁺ cations is higher than that in the other species. Oxygen vacancies are strongly attracted to Eu²⁺ and can serve as electron traps [4, 25]. The Dy³⁺ cations present nearby, can also be associated with oxygen vacancies and can reinforce the effect of electron trap attraction by Eu²⁺. Thus, incorporation of B³⁺ can promote the aggregation of the structural defects that support long afterglow.

Furthermore, the addition of B₂O₃ as a sintering flux promotes the diffusion of rare earth activators into the strontium aluminate host through facilitating grain boundary diffusion enhances the afterglow properties via tuning the distribution of rare earth dopants in the crystal lattice [37].

1.8 The Aim of The Thesis

Although an efficiently luminescing phase in strontium aluminate compounds, the Eu^{2+} and Dy^{3+} co-doped $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ (S4A7ED) phosphors exhibit phosphorescence behavior, it only lasts on the order of minutes. However, use of B_2O_3 during ceramic processing extremely extends the duration of phosphorescence duration up to several hours [7, 8]. As discussed earlier, there is still a lack of consensus on the exact role of B_2O_3 that contributes to extremely extended afterglow in strontium aluminates compound, in particular $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}, \text{Dy}^{3+}$.

Previous work in our group concerning the nano-scale effects of boron incorporation into the microstructure of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}, \text{Dy}^{3+}$ revealed that, the addition of B_2O_3 improves the homogenous distribution of the optically active center *e.g.* Eu^{2+} cations into the lower symmetry Sr1 sites in the crystal structure of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ as well as facilitating the evolution of large single crystal of S4A7 equiaxed grains with uniform distribution of Dy^{3+} and Eu^{2+} [7]. In addition, by using atomic resolution HAADF-STEM imaging of atomic columns in the structure of boron incorporated $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}, \text{Dy}^{3+}$, the role of B in persistent afterglow was related to facilitating the clustering of the rare earth activators during crystallization of S4A7 ceramic [8].

We believe that B_2O_3 plays an important role in microstructural evolution from amorphous state through modifying the crystallization kinetics that supports afterglow. Because previous results in our group, based on spatially resolved analyses of the microstructure of the B-doped S4A7ED, suggests that B_2O_3 doping induces the aggregation of ionic defects in the microstructure, the goal of this dissertation is to investigate the impact of B_2O_3 on crystallization kinetics, microstructural evolution and dopant distribution that support afterglow in S4A7EDB. Because materials properties, in this case persistent luminescence, strongly depends on the microstructural evolution in the atomic scale, the hypothesis in this work was built on the fact that, the addition of B_2O_3 as the sintering flux in differing amounts during crystallization of amorphous precursor of S4A7ED would modify the activation energy of phase formation, as well as distribution of the rare earth dopants during microstructural development.

Although crystallization of thermodynamically stable phases in $\text{SrO} - \text{Al}_2\text{O}_3$ from an amorphous state have been previously reported by Douy *et al.* [11, 41], there is still a lack of detailed systematic study, correlating the influence of B_2O_3 on the kinetics of

microstructural evolution and afterglow properties during the synthesis of long afterglow $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ co-activated by Eu and Dy.

With this goal in mind, we sought to understand the mechanisms by which B extends the afterglow, from the microstructural evolution perspective. Hence, the microstructural evolution was analyzed under thermal and kinetic control by a series of experiments. Globally averaged and spatially resolved material characterization techniques were employed to elucidate the role of diffusion kinetics under the influence of boron on microstructural evolution, dopant distribution and luminescence behavior of S4A7ED compounds.

In this work, we first present the methodology considered for investigation of the impact of B_2O_3 on phase evolution during crystallization of S4A7ED from the amorphous state. The details of the Pechini processing for preparation of amorphous pre-ceramic of S4A7ED which allows better control over the phase purity is described in detail. In addition, the experimental procedure and characterization tools that were used to extract the structural information after ceramic processing is also discussed (**Chapter 2**).

In the first study, we systematically investigated the phase evolution from amorphous precursor of Pechini processed B_2O_3 -free S4A7ED compounds. The sequence of phase formation, the mechanism of microstructural evolution and the crystallization kinetics of the amorphous preceramic material was determined by the insights obtained from a detailed thermal analysis (DTA-TG) accompanied by structural investigation (X-ray diffraction) and quantitative Rietveld phase analysis. Once crystallization path in B_2O_3 -free S4A7ED was fully identified, the effect of B_2O_3 content on microstructural evolution and kinetics of phase formation was elucidated by comparing the phase analysis results and microstructural analyses of 10, 20, 30 and 40 mol% B_2O_3 -doped S4A7ED amorphous precursor against that of B_2O_3 -free ceramic powder (**Chapter 3**).

In the second study, the effect of B_2O_3 and sintering rate on diffusion kinetics of rare earth dopant that supports persistent afterglow in S4A7EDB ceramic pigments was investigated. Because the spark-plasma sintering (SPS) technique offers the means to limit diffusion kinetics, it would enable the increase of rare-earth content in the crystalline grains by suppressing diffusion and segregation of the rare-earth dopants to the exterior of the crystalline grains. Thus, the ceramic microstructure and dopant distribution resulting from SPS was compared against that of produced by conventional sintering (CS) with and without B_2O_3 sintering flux. Spatially resolved analyses based on SEM-WDS, SEM-CL,

and STEM-EELS was used to evaluate the diffusivity and segregation of Eu and Dy dopants under a combination of kinetically different regimes, dictated by the heating rate and B₂O₃ content (*Chapter 4*).

In the third study, the microstructure of B₂O₃ incorporated S4A7ED sintered specimen was investigated by using advanced electron microscopy techniques including atomic resolution HAADF-STEM imaging, selected area electron diffraction pattern (SAED), electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDS). We acquired EELS spectrum images to elucidate the nature of boron incorporation into the microstructure of Eu²⁺ and Dy³⁺ co-doped strontium aluminate ceramics processed by sol-gel (Pechini) methods. The pivotal role played by B on microstructural evolution as well as its influence on the electronic structure giving rise to persistent luminescence was evaluated through investigating its distribution in the microstructure by spatially resolved spectroscopic techniques. we evaluated the distribution of the B-K core-loss edge in the microstructure, focusing on both crystalline grains and intergranular pockets. By mapping the B-K ELNES, we also investigated differences in local coordination of B, comparing the ELNES from intergranular pockets and grains. In addition, the distribution of rare earth dopants in the microstructural features was elucidated by spectrum imaging of Eu-M and Dy-M ionization edges. Furthermore, the position of rare earth dopants incorporated into Sr sublattice sites in the host lattice of S4A7 crystal was examined by HAADF-STEM (Z-contrast) atomic resolution imaging (*Chapter 5*).

CHAPTER 2: EXPERIMENTAL TECHNIQUES

To understand the mechanisms by which boron oxide would affect the evolution of microstructural features in the stoichiometric $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ precursor doped with Eu and Dy (S4A7ED), the actual sequence of phase formation during crystallization in the absence of B_2O_3 upon increasing temperature must be determined first. The crystallization path and microstructural features, the phase formation mechanism, and the kinetics of crystallization in the B_2O_3 free S4A7ED was then taken as the reference state for comparison with the B_2O_3 doped ceramic powders. In the next step, similar analyses were carried out on the amorphous precursor doped with various B_2O_3 contents to investigate the effect of B_2O_3 on phase evolution and structural transformations.

In order to examine the effect of B_2O_3 on the crystallization of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ phase that supports persistent phosphorescence, the ceramic powders were synthesized by using modified Pechini (sol-gel) method. The pre-ceramic samples were then analyzed initially by global characterization tools with an emphasis on thermal analysis techniques – to specify the required processing parameters for further investigations. General and spatially resolved material characterization techniques were employed to elucidate the role of diffusion kinetics under the influence of boron on microstructural evolution, dopant distribution and luminescence behavior of S4A7ED compounds.

In this chapter, the methodology and the experimental procedures will be discussed for investigating the effect of B_2O_3 on microstructural development and kinetics of phase formation. In addition, global and local characterization techniques that were used for elucidating the aim of this work will be introduced. The characterization tools for analysis of the globally averaged properties included differential thermal analysis (DTA), thermogravimetry (TG), dilatometry, X-ray diffraction analysis (XRD), Rietveld refinement of the XRD data, Raman spectroscopy, photoluminescence spectroscopy and afterglow decay time measurements. In addition, scanning electron microscopy (SEM)

imaging techniques including secondary electron imaging (SE), electron backscattered imaging (BSE) and energy dispersive X-ray spectroscopy (EDS) were used to characterize the microstructural features of the S4A7 compounds.

For the spatially resolved analyses of the microstructural features, cathodoluminescence analysis in the scanning electron microscope (SEM-CL) and wavelength dispersive X-ray spectroscopy (SEM-WDX) was used. Furthermore, advanced TEM techniques, including sample preparation by focused ion beam (FIB), TEM-bright field imaging, selected area electron diffraction (SAED), atomic resolution imaging by HAADF-STEM, electron energy loss spectroscopy (STEM-EELS), EELS spectrum imaging and energy dispersive X-ray spectroscopy (STEM-EDX) were used to evaluate the influence of boron doping on structural evolution of the $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ phosphors.

2.1 Chemical Processing of Strontium Aluminate Compounds

2.1.1 The Sol-Gel Method

Sol-gel processing is a wet chemical method, which is extensively used for the synthesis of nano structured materials and ceramic processing [42-47]. In general, the process involves the transformation of an aqueous precursor solution of metal salts or metal alkoxides (sol) into an inorganic solid (gel) through an inorganic polymerization reaction [47-49]. The metal precursors are chosen such that they can readily react with water to form a solution. In the case of metal salts, for example metal nitrates, water is used as the solvent, because nitrates dissolve in water easily. However, if a metal alkoxide with a general chemical formula of M-OR (where R stands for alkyl group e.g $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7$) [50] is used as the cation source, the metal precursor is usually dissolved in an organic solvent (usually an alcohol) which is miscible in water [47]. In general, ceramic oxide processing by a sol-gel technique is governed by two fundamental reactions: hydrolysis and condensation reactions.

2.1.1.1 Hydrolysis Reaction

In the first step of the process, a colloidal suspension of metal precursor is formed as a result of *hydrolysis reaction*. Because water molecules have a polar nature as a result of

considerable difference between the electronegativity of oxygen and hydrogen atoms, the center of positive charge and negative charge in the molecule do not coincide and consequently a permanent dipole moment is present. The oxygen atom in water molecule with a higher electronegativity with respect to hydrogen therefore carry a partial negative charge as illustrated in **Figure 2.1**.

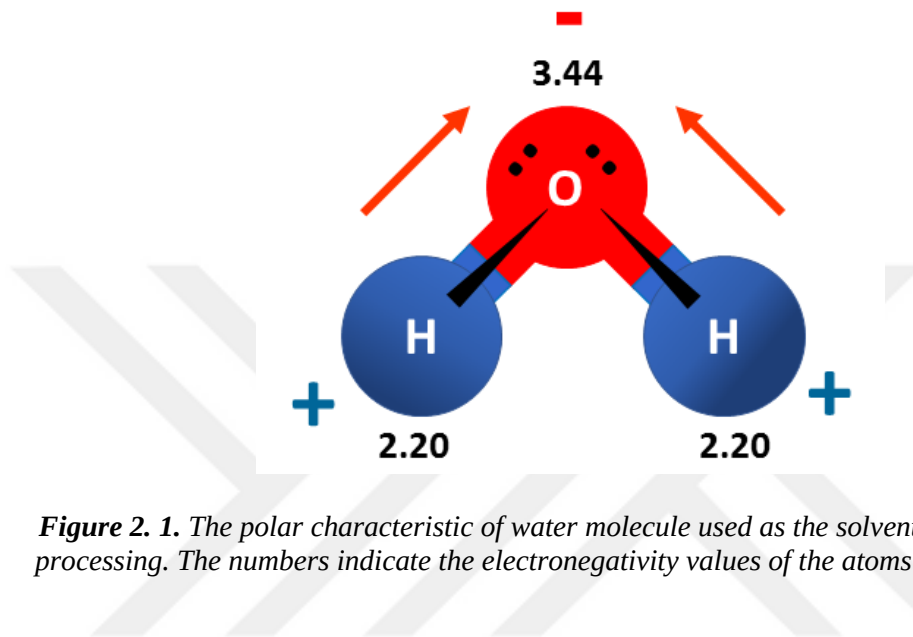


Figure 2. 1. The polar characteristic of water molecule used as the solvent during Sol-Gel processing. The numbers indicate the electronegativity values of the atoms in the molecule.

During the hydrolysis reaction in sol-gel processing, the negatively charged oxygen atom in the water molecule would interact with the cation center in a metal salt (known as nucleophilic attack) [47, 49, 51], leading to the replacement of the alkoxide groups with hydroxyl groups as demonstrated in **Figure 2.2-a**. At the end of the hydrolysis reaction, a “Sol” is formed which is in fact a homogeneous aqueous colloidal suspension of metal hydroxide [45, 47, 48]. The agglomeration of fine particles in the solvent for formation of sol particles is conducted due to the presence of van der Waals forces in order to minimize the total interfacial energy of the system [49] . It should be noted that, because hydrolysis reaction in a neutral environment is kinetically limited and the reaction may proceed very slow, it is common to accelerate the reaction by using acid or basic catalysts [47].

2.1.1.2 Condensation Reaction

Once sol particles were formed, the colloidal suspension of metal cations will be preserved for a particular period of time without any further agitation. During this period, a *condensation reaction* will take place in which the sol will transform to a *gel* through reaction between metal hydroxide units as shown in **Figure 2.2-b**. The result of condensation reaction is the formation of the amorphous chains of *metal-oxide-metal* (M-O-M) species [42, 45, 47, 52]. In fact, monomers of metal cation oxides that were already formed during the hydrolysis reaction, would join to each other in order to constitute an interconnected inorganic polymer network of three-dimensional metal cation polyhedra [53]. The final gel is therefore a biphasic solid-state amorphous network inside a liquid.

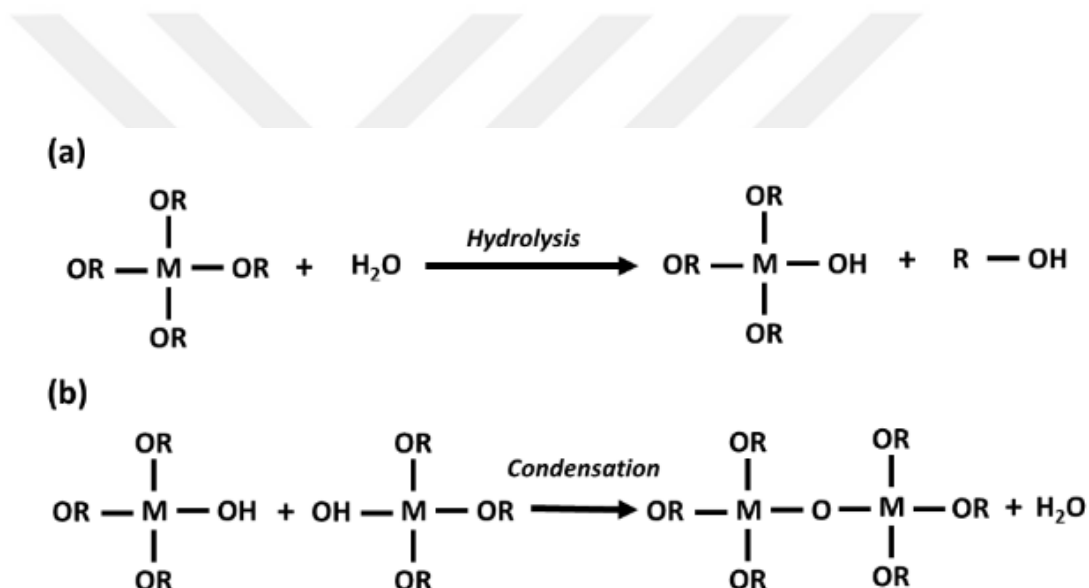


Figure 2. 2. The main reactions involved in sol-gel chemistry starting with a metal alkoxide precursor a) hydrolysis reaction b) condensation reaction. *M* and *R* stand for metal cation and alkyl group, respectively.

2.1.1.3 Formation of Aerogel and Xerogel

Once the condensation reaction is completed throughout the solution, the liquid solvent should be removed for further processing. Different approaches for drying the gel have been reported in literature [50, 52, 54]. An aerogel will be formed upon drying if the removal of the liquid from the gel network takes place under hyper critical conditions without destroying the gel network. In fact, when supercritical conditions are applied for the elimination of the solvent, generation of surface tensions on the gel will be suppressed.

Consequently, no capillary forces will be established during drying and the actual form of the gel network will be preserved. Due to the processing conditions for gel drying, an aerogel contains a high degree of porosity up to 95% [47, 50].

On the other hand, if the liquid phase is evaporated at ambient conditions, this will lead to a remarkable shrinkage of the gel. The resulting gel after drying is known as a *xerogel* which contains a uniform size distribution of pores and is thus denser with respect to an aerogel. Because xerogel has very fine particulates and pores, the subsequent sintering for ceramic processing starting from a xerogel will be facilitated and the final microstructure will be more uniform with small grain size distribution [47, 50].

In addition to the fundamental reactions involved in the preparation of a sol-gel precursor described above, the key steps during ceramic processing by sol-gel technique is schematically shown in **Figure 2.3** and can be summarized as follow:

- i. Preparation of homogeneous solution of ions from hydrolysis of metal salts in water under vigorous string. **(Sol)**
- ii. Formation of localized M-O-M bonds in the aqueous solution via condensation reaction. **(Gel)**
- iii. Continuous growth of the M-O-M bonds by further condensation resulting in the formation of short-range order metal polyhedral within the gel network followed by expulsion of the solvent. **(Aging)**
- iv. Removal of the liquid phase from the gel network to form either a dense xerogel or a porous aerogel. **(Drying)**
- v. Fully decomposition of the gel by heat treatment at elevated temperatures (800°C) resulting in complete collapse of the gel network into powder particles. **(Calcination)**

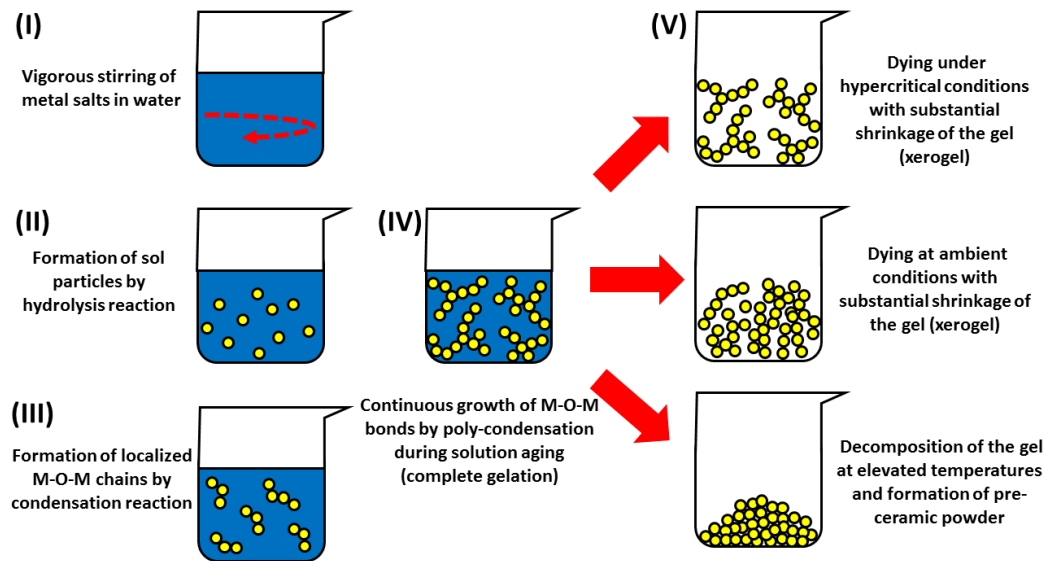


Figure 2. 3. Schematic of the sol-gel process.

2.1.2 The Advantage of Sol-Gel Technique for Ceramic Processing

Although conventional solid-state reaction between the constituent metal oxide powders followed by subsequent thermal treatment is a commonplace method for synthesis of ceramic materials, it has been shown that the final product usually suffers from some deficiencies. The most fundamental problem regarding the solid-state methods is the inhomogeneity of the starting mixture. Because a perfect homogenous mixing between powder particles based on the stoichiometric values is unlikely, complete conversion of the starting precursors to the desired equilibrium phase will be limited by mass transport [47, 51]. In fact, due to inhomogeneity of the starting mixture, the reaction between the adjacent powder particles as the reactants, may not be completed because of limited diffusion. Consequently, obtaining a phase pure ceramic material by using conventional ceramic processing methods is challenging and some unreacted starting materials or metastable phases will be present as the by-products. In addition, control over the morphology of powder particles is limited in conventional ceramic processing methods [47].

Because the sol-gel technique offers the advantage of formation of a chemically homogenous gel network, the amorphous pre-ceramic material is in fact a framework of uniformly dispersed ions in an amorphous state in which mixing of the cations and anions as the reactants in the atomic level is guaranteed. Therefore, ceramic processing at

relatively lower temperatures can be achieved by sol-gel method. More importantly, the homogenous mixing of initial precursors facilitates the formation of phase pure ceramics [47]. To produce ceramic specimen for our studies, we chose the sol-gel route.

2.1.3 Modification of Sol-Gel Method for Synthesis of Complex Ceramics

It should be noted that, hydrolysis and condensation reactions in sol-gel chemistry is limited by the number of elements present in the solution. This limitation stems from the fact that the reaction rates for precipitation of the sol and for gelation process is different for each metal precursor. For single cation systems, for example, during the sol-gel processing of metal oxides such as Al_2O_3 [43, 55, 56], TiO_2 [53, 57] and SiO_2 [45, 58, 59], hydrolysis followed by condensation reactions produce a uniformly dispersed arrangement of cations. On the contrary, in the case of processing of binary, ternary and quaternary ceramics in which multiple-cations oxides are involved, there is always a strong tendency for phase separation, due to a disparity in reaction rates for dissociation of the cations from the initial metal salts during hydrolysis and sol-to-gel transition during condensation [47]. In the case of ceramics with complex crystal structures, such as perovskites and strontium aluminate compounds doped with rare earth elements, where the production of the final ceramic material requires the involvement of multi-cation oxides, obtaining a stoichiometric and homogeneously distributed mixture of cations during the synthesis of mixed oxide powders is troublesome. Therefore, routine sol-gel processing might still give rise to segregation of ions and consequently formation of multi-phase binary oxides. One solution to this drawback is stabilization of metal cations in a polymeric network by using the so-called “steric entrapment” method. This way, all the cations will be immobilized upon release from the corresponding metal salts. Once the hydrolysis and condensation reactions were accomplished for the whole mixture, further heat treatment can be applied for preparation of an amorphous preceramic.

Likewise, although sol-gel technique provides the advantage of a perfect randomness of ions in the case of single cation systems, the existence of some degree of structural ordering would be beneficial for the production of complex ceramics [47].

Hence, synthesis of mixed oxide powders by using sol-gel chemistry needs some modifications.

2.1.4 The Pechini Method

Pechini method uses functionalizing organic molecule carriers to form metal-organic ligands, to stabilize the metal cations of different types in solution. To avoid aggregation of sol particles, a chelating agent like citric acid is used to sterically entrap the metal cations. The stabilization action originates from the columbic attraction forces between the functional groups of the organic carrier materials and metal cations [47, 50, 60]. The main principle of Pechini modified sol-gel method is centered on polyesterification reaction between carboxylic groups of hydrocarboxylic acids (like citric acid) and hydroxyl end of polyhydroxy alcohols (like ethylene glycol) [47, 61-63]. By using organic macro molecule chains as the carrier for different cations, the Pechini modified sol-gel method is able to form a homogenously distributed cation network when a number of metal cations are present. Bellow, the role of organic carrier materials during the Pechini processing will be discussed in more detail.

2.1.4.1 The Role of Citric Acid

The molecular structure of citric with the general chemical formula of $C_6H_8O_7$ is shown in **Figure 2.4-a**. There are three carboxylic groups in the citric acid molecule. When citric acid is dissolved in water during Pechini processing, a reaction occurs upon which the hydrogen ions in the carboxylic ends of the acid are released as shown in **Figure 2.4-b**. Consequently, the single bonded oxygen atoms in the carboxyl heads of the molecule will have an extra electron in the outer become negatively charged.

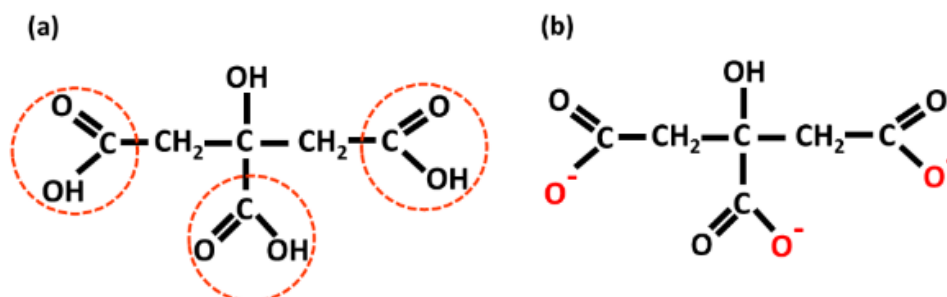


Figure 2. 4. Molecular structure of citric acid a) before dissolving in water and b) after dissolution in water. The carboxylate groups are highlighted with dashed lines in a).

The cation precursor to be used for Pechini synthesis should be soluble in water and common salts are thus including nitrates, hydroxides, chlorides and acetates [62]. When a metal salt is dissolved in water along with citric acid, a so-called steric barrier is formed, and the citric acid molecule encompasses the cation due to electrostatic attraction between the negatively charged carboxyl groups and the positively charged metal cation. As a result, a chelated-metal complex will be formed. Therefore, citric acid is used as the chelating agent during Pechini processing. The chelating effect of citric acid stabilizes the cations in the solution and prevents their aggregation [47, 60, 62-64]. It is worthy of note that, for the processing of complex ceramics including multiple cations by Pechini-type sol-gel method, the order of mixing of the metal salts to the chelating agents is important and the cation that forms the most stable chelate ligands must be added first, and the one that forms the least stable chelate at the end [62, 65]. **Figure 2.5** shows the schematic of citric acid chelating effect for a divalent metal cation such as Sr^{2+} in the solution. As a result of metal-citrate complex, metal cations are stabilized in the solution and will be homogeneously distributed in the pre-ceramic mixture[47, 63, 64, 66].

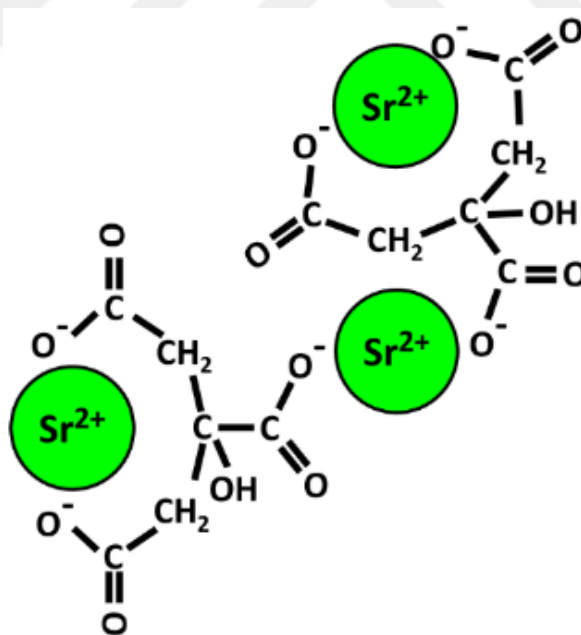


Figure 2. 5. Stabilization of divalent Sr^{2+} cations by chelating effect of citric acid molecules during Pechini processing.

2.1.4.2 The Role of Ethylene Glycol

The molecular structure of ethylene glycol with a chemical formula of $C_2H_6O_2$ is shown in **figure 2.6**. The molecule has two hydroxyl groups.

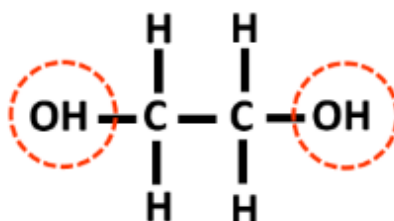


Figure 2. 6. Molecular structure of ethylene glycol. The hydroxyl ends of the molecule are highlighted in with dashed lines.

Ethylene glycol is used as a polymerization agent to build up the polymeric network during Pechini synthesis. Once the metal cations were surrounded by the chelating agent in the solution, the metal-chelate complexes will be immobilized as a result of formation of a very viscous polymer network due to polyesterification reaction between the citric acid (CA) and ethylene glycol (EG). **Figure 2.7** shows the principle of the esterification reaction between CA and EG and formation of a polyester in the solution, respectively.

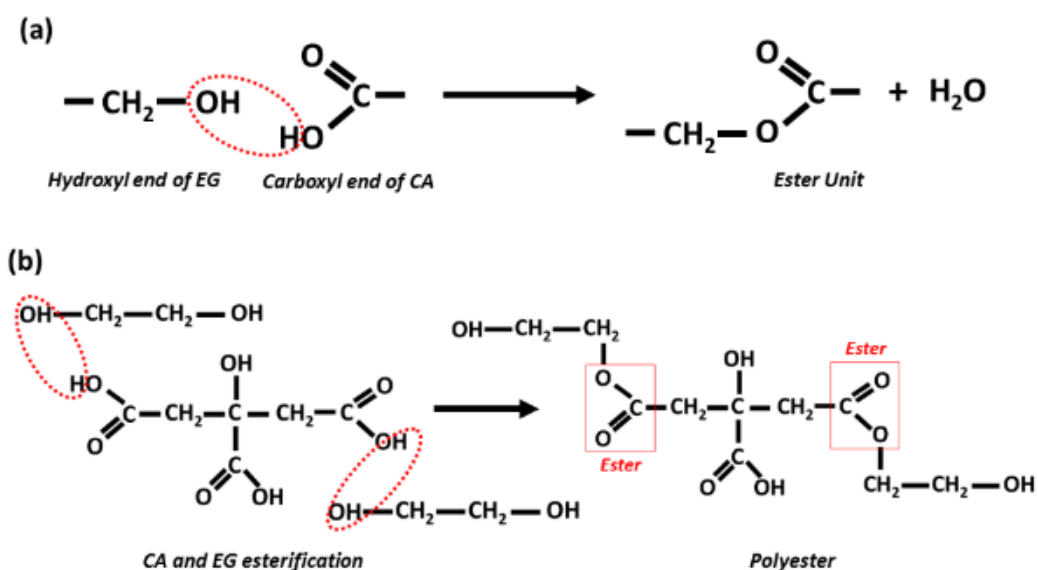


Figure 2. 7. The mechanism of esterification reaction between CA and EG a) formation of an ester unit b) formation of polyester.

In fact, by polyesterification reaction between carboxylic groups of the chelating agent (CA) and the hydroxylic groups of the ethylene glycol, the cation-citrate molecules are cross linked to each other [63, 64, 66]. The polymer macromolecular chains obtained by the polyesterification process will produce a covalent network [47] that contain uniformly dispersed and very stable metal-organic ligands in the solution. **Figure 2.8** summarizes the steps involved in ceramic precursor processing by Pechini method for synthesis of strontium aluminate compounds doped with Eu, Dy and B.

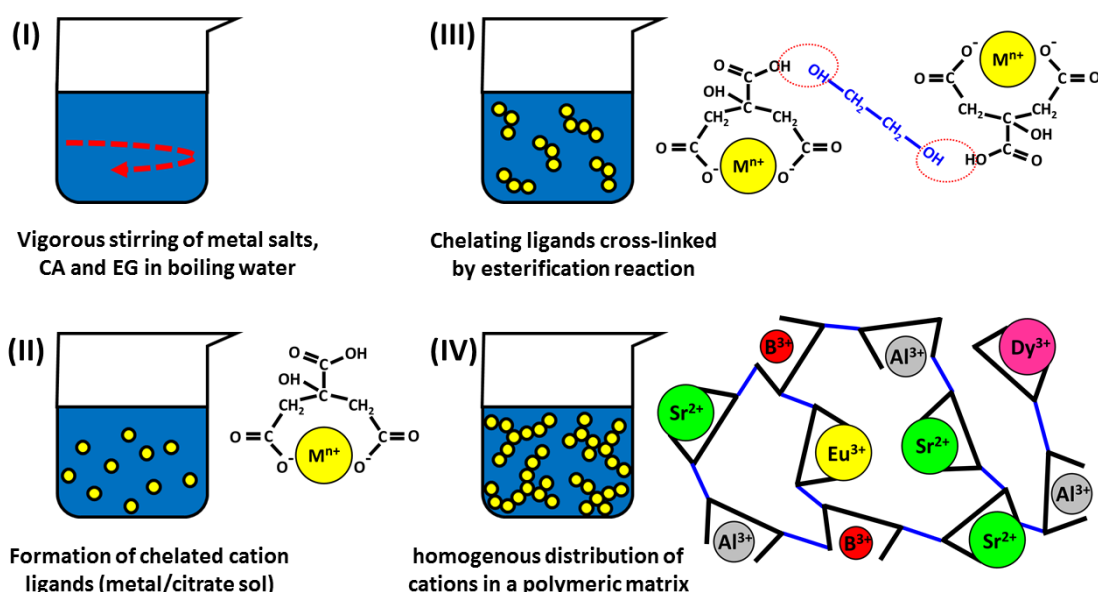


Figure 2.8. Schematic of Pechini modified sol-gel synthesis of a pre-ceramic precursor containing multiple cation.

The mixture will then be heated in a furnace under an oxidizing atmosphere to fully combust the polymeric matrix, and an amorphous preceramic powder is obtained. Cross-linking between chelating ligands in Pechini method would delay the thermal decomposition of the polymeric matrix and provide better control in holding the cations in close vicinity until the desired ceramic processing temperature is reached [47]. Because the viscosity of the organic networks that chemically bind the metal cations is relatively high, the segregation of cations upon solvent removal is also suppressed [64, 66].

There are several advantages for the processing of multi-cation oxides by using Pechini method compared to traditional solid-state reaction technique. First, the diffusion of cations during calcination is facilitated, because of shorter migration distance between

cations of different types during crystallization from amorphous state. The reduced diffusion distance originates from homogenous nature of cation distribution from different types throughout the solution, after organics burn-out. Therefore, the processing temperature for crystallization of the ceramic is substantially decreased compared to that of solid state reaction. In addition, combustion of the polymeric matrix gives rise to a local temperature increase which can assist the diffusion process.

Moreover, because the nucleation sites are uniformly distributed in the amorphous pre-ceramic material, the final ceramic product will be of smaller grain size [47, 63, 64, 66].

2.1.5 Materials and Precursors

Strontium aluminate powders with the nominal stoichiometry of $(\text{SrO})_4 \cdot (\text{Al}_2\text{O}_3)_7$ doped with 1 mole % of Europium and 1 mole % of Dysprosium (S4A7ED) with various B_2O_3 contents as the sintering flux were prepared by using a modified sol-gel Pechini method. Nitrate salts of each constituent cation were selected as the cation source. The chemicals that were used for synthesizing the precursors of S4A7ED with and without B_2O_3 are summarized in **Table 2.1**.

Table 2.1. Chemical list used for synthesis of strontium aluminate with the stoichiometry of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$: Eu, Dy, X %mol B.

Material	Chemical Formula	Provider
Aluminum nitrate nonahydrate	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	Merck / 99.9%
Strontium nitrate anhydrous	$\text{Sr}(\text{NO}_3)_2$	Merck / Extra pure
Europium (III) nitrate hexahydrate	$\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	Alfa Aesar /99.99%
Dysprosium (III) nitrate pentahydrate	$\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	Alfa Aesar /99.99%
Boron trioxide	B_2O_3	Alfa Aesar /99.98%
Citric acid monohydrate	$\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$	Merck / 99.5%
Ethylene glycol	$\text{C}_2\text{H}_6\text{O}_2$	Carlo Erba/99.5%

2.1.6 Calculation of the Precursor Amounts for Synthesis of Stoichiometric $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$: 1 %mole Eu, 1 %mole Dy, X %mol B (S4A7EDXB)

In order to synthesize stoichiometric $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$: 1 mol% Eu, 1 mol% Dy doped with various contents of B in this work, it is assumed that the rare earth dopants, (Eu^{3+} and Dy^{3+}) would most probably substitute for Sr^{2+} sublattice sites during microstructural evolution due to close proximity in their ionic radii to Sr^{2+} . However, because the ionic radius of B^{3+} is substantially smaller than the crystal constituent cations *e.g.* Sr^{2+} and Al^{3+} , it is possible that B enters the crystal lattice either interstitially between the crystal polyhedral or, substitutionally for Al^{3+} sites. **Table 2.2** lists the ionic radii of the cations [4] to be used during the Pechini synthesis of strontium aluminate compounds in this study.

Table 2.2. The ionic radii of the cations present in the structure of strontium aluminate phosphor ceramics.

Cation	Ionic Radii ($\text{\AA}$)
Sr^{2+}	1.21
Al^{3+}	0.39
Eu^{3+}	1.01
Dy^{3+}	0.97
B^{3+}	0.11

Therefore, the general stoichiometry of $(\text{Sr}_4\text{Al}_{14}\text{O}_{25})_{[1-(0.02+X)]} \text{Eu}_{0.01} \text{Dy}_{0.01} \text{B}_X$, was considered where the number 0.02 in the chemical formula is the summation of the concentration of rare earth dopants in terms of mol% which was determined to be fixed and equal to 1 mol% for both europium and dysprosium in this work. The value X in the stoichiometric formula also represents the concentration of boron in mol% which would range from 0 mol% up to 40 mol% in this work.

The total moles of the S4A7EDXB to be synthesized can be calculated according to equation (2-1).

$$\text{Total Mole} = \frac{\text{Target mass for synthesis (gr)}}{\text{Molecular weight of S4A7EDXB } \left(\frac{\text{gr}}{\text{mole}}\right)} \quad \text{Eq (2-1)}$$

The molecular weight of the S4A7EDXB compound in the denominator in Equation (2-1) can be obtained from the following equation.

$$\text{M.wt. of S4A7EDXB} = [(4 \times \text{Sr}) + (14 \times \text{Al}) + (25 \times \text{O})] \times \left[\frac{(100 - \text{mol\% Eu} - \text{mol\% Dy} - \text{mol\% B})}{100} \right] + \left(\text{Eu} \times \frac{\text{mol\% Eu}}{100} \right) + \left(\text{Dy} \times \frac{\text{mol\% Dy}}{100} \right) + \left(\text{B} \times \frac{\text{mol\% B}}{100} \right) \quad \text{Eq (2-2)}$$

Where the element symbols represent the atomic weights of each element according to the periodic table and mol% Eu, mol% Dy and mol% B are the concentration of dopants in terms of mole percent. For example, in the case of synthesis of S4A7 doped with 1 mol% Eu and 1 mol% Dy and 10 mol% B₂O₃, the molecular weight of S4A7ED10B compound would be calculated as follow:

$$\begin{aligned} \text{Molecular weight}_{(\text{S4A7EDXB})} &= [1128.48] \times \left[\frac{(100 - 1 - 1 - 10)}{100} \right] + \\ &\left(151.96 \times \frac{1}{100} \right) + \left(162.5 \times \frac{1}{100} \right) + \left(10.81 \times \frac{10}{100} \right) = 997.288 \left(\frac{\text{gr}}{\text{mol}} \right) \end{aligned}$$

By determining the molecular weight of the S4A7EDXB compound depending on the boron concentration to be used as the sintering flux from equation (2-2), and by knowing the target mass for synthesis, the total mole of the S4A7EDXB compound will be obtained from equation (2-1). The target mass of individual nitrate precursors can then be calculated as follow:

$$\text{Sr(NO}_3)_2(\text{gr}) = \text{Total mole} \times [\text{Sr(NO}_3)_2 (\text{gr/mol})] \times \left(4 \times \left[\frac{(100 - \text{mol\% Eu} - \text{mol\% Dy} - \text{mol\% B})}{100} \right] \right) \quad \text{Eq (2-3)}$$

$$\text{Al(NO}_3)_3.9\text{H}_2\text{O}(\text{gr}) = \text{Total mole} \times [\text{Al(NO}_3)_3.9\text{H}_2\text{O}(\text{gr/mol})] \times \left(14 \times \left[\frac{(100 - \text{mol\% Eu} - \text{mol\% Dy} - \text{mol\% B})}{100} \right] \right) \quad \text{Eq (2-4)}$$

$$Eu(NO_3)_3 \cdot 6H_2O (gr) = \text{Total mole} \times [Eu(NO_3)_3 \cdot 6H_2O (gr/mol)] \times \left(\left[\frac{(mol\% Eu)}{100} \right] \right) \quad Eq (2-5)$$

$$Dy(NO_3)_3 \cdot 5H_2O (gr) = \text{Total mole} \times [Dy(NO_3)_3 \cdot 5H_2O (gr/mol)] \times \left(\left[\frac{(mol\% Dy)}{100} \right] \right) \quad Eq (2-6)$$

$$B_2O_3 (gr) = \text{Total mole} \times [B_2O_3 (gr/mol)] \times \left(\left[\frac{(mol\% B)}{100} \right] \right) \quad Eq (2-7)$$

In order to calculate the target mass of the chelating agent (CA) and the complexing agent (EG), We considered the molar ratio of CA:EG:1. Moreover, the molar mass of the individual organic precursors should be equal to the summation of the molar mass of all the metal cation precursors that are present in the aqueous solution to guarantee the stabilization of metal cations during Pechini processing. To account for this, the target mass of the metal cations that were obtained by equations (2-3) to (2-7), were initially converted to the corresponding mole values. The total molar mass for each of the organics were then considered to be equivalent to the sum of the molar mass of the cation salts. Once the molar mass of the citric acid and ethylene glycol were obtained, the corresponding weights for the organics were calculated by converting the mole contents to mass values.

The above-mentioned calculations were summarized in a dynamic excel spread sheet to facilitate the measurements of the target mass of the precursors for the synthesis of nominal stoichiometric S4A7 composition with various dopant concentrations. **Figure 2.9** shows the dynamic excel spread sheet used for calculations of target masses of the starting material for the Pechini synthesis of 5 gr stoichiometric S4A7 codoped with 1 mol% Eu, 1 mol% Dy and 10 mol% B₂O₃.

	A	B	C	D	E	F	G	H	I	J	K
20	Al(NO ₃) ₃ ·9H ₂ O	375									
21	Eu(NO ₃) ₃ ·6H ₂ O	446.06									
22	Dy(NO ₃) ₃ ·5H ₂ O	438.5									
23	B ₂ O ₃	69.62									
24	CA	210.14									
25	EG	62									
26											
27	Sr4Al14O25	1128.48 g/mol			Amounts used	Target Mass (g)	mole %	moles total			cat%
28	S4A7EDXB	997.29 g/mol			S4A7	5	100	0.0050			
29					Sr(NO ₃) ₂	3.734640	20		0.01765	22%	
30					Al(NO ₃) ₃ ·9H ₂ O	23.162818	68		0.06177	78%	
31	N	14			Eu(NO ₃) ₃ ·6H ₂ O	0.022364	1 target amount		0.00005		
32	O	16	22		Dy(NO ₃) ₃ ·5H ₂ O	0.021985	1 target amount		0.00005		
33	H	1			B ₂ O ₃	0.034905	10 target amount (Boron percentage)		0.00050		
34	Sr	87.62	3.52		CA	16.81			0.08002		
35	Al	27	12.32		EG	4.96			0.08002		
36	Eu	151.96	0.01								
37	Dy	162.5	0.01								
38	B	10.81	0.1								
39	NO ₃	62									
40	H ₂ O	18									
						total [g] =	26.98	100 = total [mole %]			

Figure 2.9. Calculations of the target mass of the starting nitrate precursors for the synthesis of stoichiometric S4A7ED10B compound by Pechini method.

2.1.7 The Synthesis Procedure

400 mL deionized water was boiled in a glass beaker on a hot plate for 10 min. The precursors were precisely weighted according to the stoichiometric amounts corresponding to S4A7EDXB composition and were added to the boiling water. The solutions were continuously mixed by using a magnetic stirrer for 20 minutes to assure complete mixing of the metal salts and organic materials. The aqueous solution was then placed into a box furnace and were maintained at a temperature of 120 °C for 24 hours to accelerate the gelation process and to evaporate the water. After dehydration, a yellowish sponge-like amorphous material was obtained. The amorphous precursor of S4A7 compositions codoped with Eu and Dy and various concentrations of B were thus prepared as described above. **Figure 2.10** shows the amorphous foam-like and highly porous S4A7EDXB pre-ceramic material after dehydration. The amorphous precursors were then ground into powders in an agate mortar with pestle for further analyses and thermal treatments to investigate the effect of boron content on microstructural evolution which is described in detail in section 2.2.1.



Figure 2.10. Strontium aluminate pre-ceramic material after dehydration at 120°C for 24 hours.

In order to obtain fully crystalline strontium aluminate compounds with persistent luminescence, several heat treatment steps were applied in the following order:

- i. Because most of the organic materials decompose at temperatures around 600-700°C, after dehydration of the Pechini processed S4A7EDXB compounds, the dried and ground pre-ceramic mixture was pre-calcined in a box furnace from room temperature to 600°C for 6 hours and then 700°C for 2 hours with a heating rate of 10 °C/min in an alumina crucible under oxidizing atmosphere. This pre-calcination burns off the organics that were used during Pechini synthesis for stabilization of cations. **Figure 2.11** shows the state of the ceramic amorphous precursor after pre-calcination step. The dark color of the powder is indicative of oxidation of polymeric matrix. The amorphous pre-ceramic precursor at the end of this step is free of nitrate and organic materials.
- ii.



Figure 2.11. Strontium aluminate compounds after organics burn out by pre-calcination at 600 °C for 6h and then 700°C for 2h.

Because one of the aims of this work is to investigate the effect of sintering rate on diffusion kinetics and distribution of rare earth dopants under the influence of boron in the microstructure, we sintered the amorphous pre-ceramic powder under two different sintering methods. More details on the second process will be discussed in chapter 4. The organics free mixture at the end of this step was used as the pre-ceramic material for sintering.

- iii. After organics burn-out, the powder was calcined in a box furnace in air at the appropriate calcination temperature for a long time (*ca.* 10 hours) to complete crystallization of the equilibrium phase.
- iv. In order to activate the luminescent centers i.e Eu cations in the structure of S4A7EDXB compounds, the powder was calcined under a reducing atmosphere of varigon gas (96 wt% Ar and 4 wt% H₂) with a flow rate of 120 mL/min at the same target calcination temperature for 3 hours in a tube furnace as shown in **Figure 2.12**. After reduction, the powder was cooled down in the furnace to room temperature.

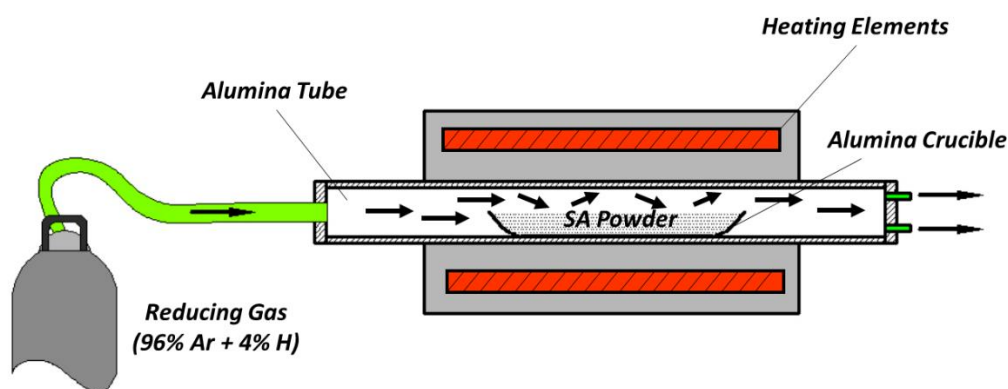


Figure 2. 12. Schematic of the tube furnace set up used for the reduction process of strontium aluminate powders.

This reduction step was considered to convert Eu^{3+} to Eu^{2+} so that the energy transfer between the ground state of Eu^{2+} and the excited state of Eu^{2+} ($4f^7 \leftrightarrow 4f^6 5d^1$) can occur. At the end of the reduction process the color of the ceramic powders became a pale green.

Previous work in our group [67, 68] revealed that SA compositions without boron require shorter reduction time (about 1 hour) while the optimized reduction duration for the boron-doped compounds is 3 hours. In fact, prolonged reduction time to more than 3 hours will increase the concentration of oxygen vacancies in the ceramic powder during the reduction process and the powder will be over reduced. As a result, the blackening of powder particles was observed, which substantially decrease the brightness and the afterglow time of the phosphor ceramics. **Figure 2.13** compares the state of the S4A7EDXB ceramic powder before and after the reduction step.

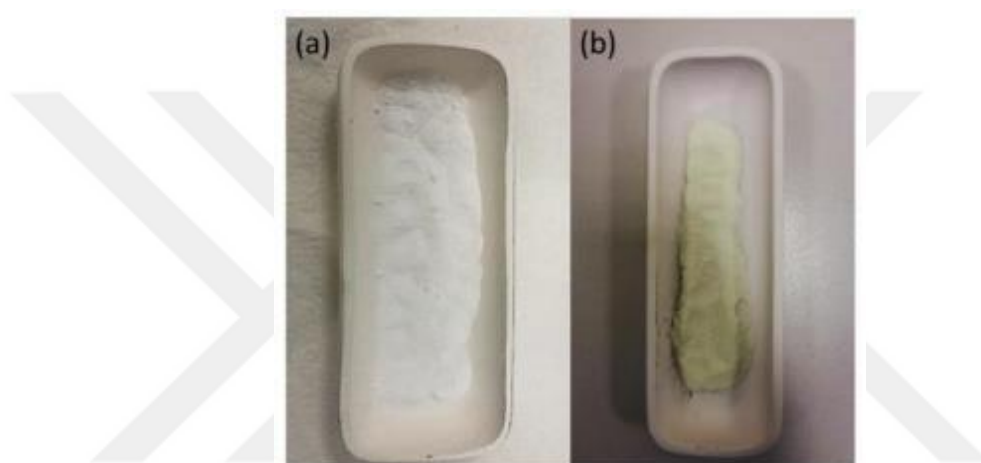


Figure 2.13. Comparison between the state of the strontium aluminate powders a) after 10h heat treatment at the target calcination temperature and b) after reduction at the calcination temperature under vacuum atmosphere for 3h.

2.2 Characterization Tools

2.2.1 Thermal Analysis

2.2.1.1 Thermal Analysis for Crystallization Study

Because thermal analysis offers insight into structural transformations and chemical reactions, we have applied differential thermal analysis (DTA) and thermogravimetry analysis (TGA) to investigate the microstructure evolving in stoichiometric $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ during Pechini processing, i.e., from the amorphous gel formed by polymerization of ethylene glycol and citric acid-chelated cations. In order to investigate the effect of B_2O_3 on microstructural evolution, the thermal behavior of amorphous precursor of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$

codoped with 1 mol% Eu, 1 mol% Dy and nominal with nominal 0, 5, 10, 20, 30 and 40 mol% B₂O₃ concentration upon increasing temperature were compared.

2.2.1.1.1 Thermogram of The Dehydrated Gel

We first started with the B₂O₃- free S4A7ED composition to fully monitor the thermal events during crystallization from the amorphous state. After dehydration of the gel at 120 °C for 24 hours, the powder was slightly ground in an agate mortar with pestle to obtain a homogenous powder in terms of particle size. The thermogram of about 100 mg from of the dehydrated pre-ceramic material was then recorded by using a simultaneous DTA-TG set up (Netzsch STA 449C Jupiter, Selb, Germany) from room temperature to 1400 °C with a ramping rate of 10 °C/min under air atmosphere with flow rate of 40 mL/min.

2.2.1.1.2 Thermal Analysis of The Individual Precursors

Because during the Pechini synthesis of the ceramic powders, nitrate precursors along with polymeric chelating and polyesterification agents were used, the dehydrated amorphous gel after drying at 120 °C for 24 hours would still contain nitrate materials and organics. In order to interpret the thermogram of the amorphous pre-ceramic, the DTA-TG traces of individual constituents were also recorded with identical conditions, and the thermal fingerprints related to decomposition of the initial precursors were compared against that of S4A7ED mixture. By following a stepwise strategy of adding precursor components to evaluate their influence on crystallization, the sequence of thermal events including decomposition of nitrate materials, organics burn out and crystallization peaks during phase evolution from an amorphous state was elucidated.

2.2.1.1.3 Obtaining an Organics-Free Amorphous Gel – Elucidating the Crystallization Peaks in DTA

In order to determine the calcination temperatures for further investigation of crystallization sequence during phase evolution of the amorphous precursor based on

thermal analysis data, it was necessary to focus on the crystallization and/or phase transition temperature ranges in the thermogram in more detail. However, due to presence nitrate compounds and organic materials, the thermal fingerprints attributed to crystallization events, including the crystallization onset, crystallization maximum and crystallization endpoint temperature, might not have been resolvable in the DTA-TG of the pre-ceramic material dried at 120 °C. Therefore, based on the thermal analysis of the dehydrated gel, a pre-calcination thermal treatment was designed to decompose the nitrate materials and organics in the amorphous pre-ceramic powders. The pre-calcination temperature for obtaining an organic-free amorphous S4A7ED mixture was thus determined based on DTA-TG results of the dehydrated gels such that it was high enough and sufficiently long to decompose all the nitrates and organics while did not induce any crystallization in the system yet, maintaining the amorphous nature of the ceramic precursor for crystallization study. In fact, the appropriate pre-calcination step was determined to remove the thermal history of the S4A7ED amorphous mixture and enable resolution of crystallization and/or phase transformation peaks in DTA signals.

2.2.1.1.4 Determination of Calcination Temperatures Based on Thermal Analysis Data

Once an amorphous and mostly organics-free precursor of stoichiometric S4A7ED composition was obtained by pre-calcination at elevated temperature, 50 mg of the organic-free pre-ceramic material was again analyzed by DTA-TG from room temperature to 1400 °C with heating rate of 10 °C/min. Because we aimed to investigate the actual phase evolution of S4A7ED composition which occurs in a box furnace in air, thermal analysis of the organic-free pre-ceramic powder was conducted under air atmosphere. By obtaining clear and resolvable peaks, the critical temperatures around the crystallization peaks *i.e* the onset, the maximum and the endpoint temperatures were accurately determined by using the first and second derivatives of in DTA signals [69]. Similar approach was applied for investigation of phase evolution sequence in S4A7ED doped with 10, 20, 30 and 40 mol% B₂O₃.

2.2.1.2 Thermal Analysis for Kinetics Study

In order to further elucidate the crystallization mechanism of S4A7ED_xB compounds, where $x = 0, 10, 20, 30$ and 40 mol% B₂O₃, from an amorphous precursor under the influence of boron concentration, we performed kinetics experiments by using DTA. Because crystallization of amorphous pre-ceramic precursor occurs with nucleation and growth [70], kinetics analysis would give insight into the activation energies of crystallization (E) and phase transitions along with information about the growth mode (also known as Avrami exponent) of the evolving phases. The activation energy of crystallization is actually the sum of activation energy for nucleation and the activation energy for growth [71-73]. However, it is common to report an activation energy representative for the whole crystallization process. The growth mode during crystallization is related to the mechanism by which the evolving microstructure develops, i.e whether it is a diffusion-controlled growth, or the growth of the crystal is governed by an interface-controlled mechanism. Moreover, information about the dimensionality of the growing phase can be obtained through kinetics studies [74-76].

There are two well-known methods for obtaining the kinetics information for crystallization from an amorphous state by thermoanalytical techniques, the so-called isothermal [71, 72, 76] and non-isothermal [73, 77-79] crystallization kinetics, which can be applied to both DTA and differential scanning calorimetry (DSC) data [72, 80].

2.2.1.2.1 Isothermal Kinetics

The isothermal kinetics study involves rapid increase of the temperature of the amorphous material close to the crystallization temperature and then isothermally heating at several desired temperatures to complete the crystallization as a function of time. The extraction of the kinetics parameters will be centered on Johnson-Mehl-Avrami equation [70-72, 76]

$$X = 1 - \exp [-(kt)^n] \quad \text{Eq (2-8)}$$

Where X is the time dependent fraction crystallized after time t , K is the reaction rate constant, and n is the Avrami exponent. The exponent n reflects the nucleation and growth

mechanism and represents the dimension of growth. The reaction rate constant K , is dependent on temperature through an Arrhenius equation as follow [70-72, 76, 81] :

$$k(T) = k_0 \exp \left[-\frac{E}{RT} \right] \quad \text{Eq (2-9)}$$

In equation (2-9), K_0 is a pre-exponential constant, E is the activation energy of crystallization, R is the gas constant and T is the absolute temperature.

Equation (2-8) can be rearranged as:

$$\ln [-\ln(1 - x)] = n \ln k + n \ln t \quad \text{Eq (2-10)}$$

Therefore, according to equation (2-10), the plot of $\ln [-\ln(1 - x)]$ versus $\ln t$ would be linear and the slope will yield the Avrami exponent n . Under isothermal conditions, the fraction transformed from amorphous state to crystalline state can be obtained from the ratio between the area of the peak from t_s to time t (A) and the total area of the peak from t_s to t_f (A_0) of an exothermic DTA peak as shown in **Figure 2.14**.

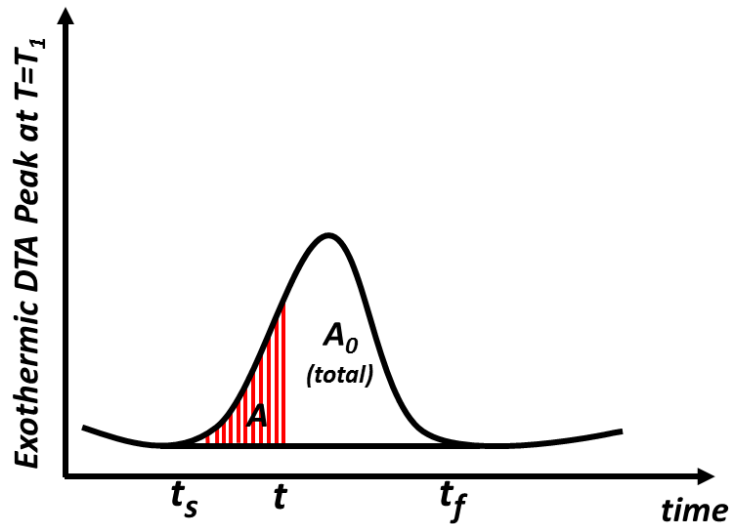


Figure 2. 14. A typical crystallization peak in DTA under isothermal condition. t_s , t and t_f stand for the times of transformation start, a given time during transformation and transformation finish, respectively.

Once the Avrami exponent n was obtained, the intercept in equation (2-10) would determine the reaction rate constant k for successive isothermal calcination temperatures.

Moreover, the rate constant equation (2-9) can be written as:

$$\ln k(T) = \ln k_0 - E/RT \quad \text{Eq (2-11)}$$

Therefore, according to equation (2-11), activation energy of crystallization can be obtained from the slope of the plots of $\ln k$ versus $1/T$.

2.2.1.2.2 Non-Isothermal Kinetics

For non-isothermal crystallization kinetics, the kinetics of transformation from an amorphous system is investigated by recording DTA scans at different heating rates. In fact, the crystallization process including nucleation and growth is investigated as temperature is increasing. Because the Johnson-Mehl-Avrami model (equation 2-8) has been derived under isothermal conditions [70, 72, 76], it is assumed that the crystallization initiates under a site-saturated situation, in which the nucleation process is completed before crystal growth commences, and the number of nuclei during crystallization is constant [70, 72, 76]. Therefore, because the formation of new nuclei during evolution from the amorphous state or upon phase transformation is negligible, the complicated dependence of nucleation frequency on temperature is ignored, and the crystallization rate is independent of the thermal history [72, 76]. However, in the case of complex systems such as Pechini-derived strontium aluminates, which may contain multiple competing phases evolving from amorphous precursor, the completion of the nucleation process prior to crystal growth is not guaranteed.

Therefore, in the case of non-isothermal conditions, other models should be used to determine the fraction crystallized and the kinetics parameters under a linear increase in temperature.

2.2.1.2.2.1 Kissinger Method

In this model, it is assumed that the temperature, at which the maximum rate of crystallization occurs at a fixed heating rate, is related to the activation energy of crystallization [82-84]. Because the crystallization peak temperature (T_p) shifts to higher temperature by increasing the heating rate, Hence, the activation energy of crystallization can be obtained based on the variation of the peak maximum temperature in DTA exotherms with heating rate through the following relationship:

$$\ln \left[\frac{\beta}{T_p^2} \right] = - \frac{E}{RT_p} + \text{Constant} \quad \text{Eq (2-12)}$$

Where β is the heating rate, T_p is the crystallization peak temperature measured at various heating rates in Kelvin, E is the activation energy for crystallization (J/mol) and R is the gas constant ($R = 8.314 \text{ J. mol}^{-1}. \text{ K}^{-1}$). The mathematical derivation of the so-called Kissinger equation (equation 2.12) can be found in references [85, 86].

According to the Kissinger equation, the activation energy of crystallization in non-isothermal kinetics study can be calculated from the slope of the linear fit function of the plot of $\ln \left[\frac{\beta}{T_p^2} \right]$ versus $1/T_p$.

The Kissinger equation is also valid for calculating of the activation energy of glass transition temperature in some reports [87-92].

2.2.1.2.2.2 Ozawa Method

In this method, the fraction transformed, the so-called Avrami exponent n that reflects information about the growth mode during crystallization, and the heating rate are related according to the following relationship:

$$\ln[-\ln(1 - x_T)] = -n \ln \beta + \text{Constant} \quad \text{Eq (2-13)}$$

Where x_T is the fraction crystallized at temperature T that can be obtained from the ratio $\frac{A}{A_0}$ as shown in **Figure 2.15**. The area A_0 is regarded as the total area under the DTA exotherm between the T_s at which crystallization peak begins and T_f at which crystallization is completed while the area A is considered as the area under DTA exotherm subtended between T_s and the temperature T . β denotes the heating rate in $^{\circ}\text{C}/\text{min}$ and n is the Avrami exponent.

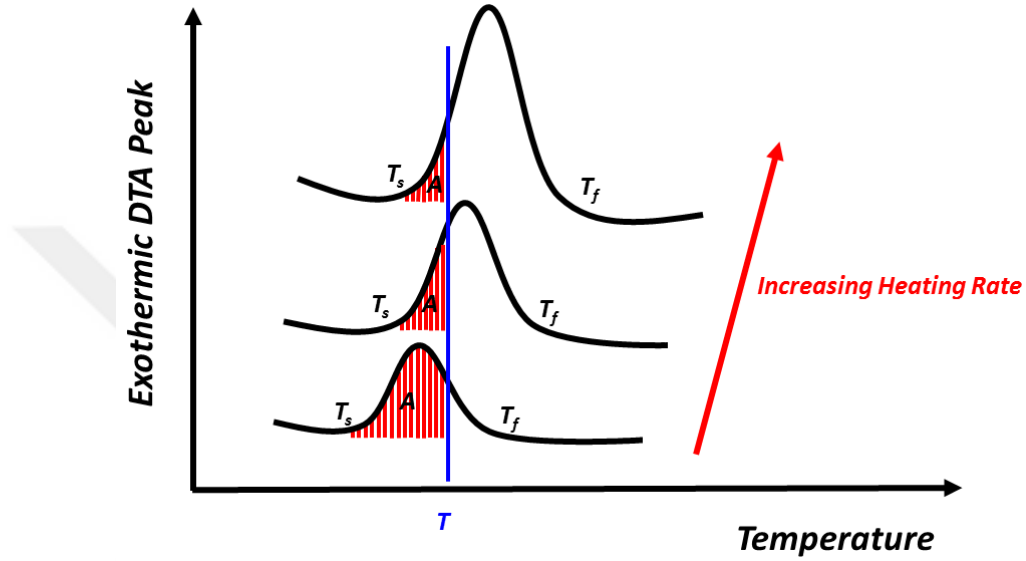


Figure 2.15. Extraction of the fraction crystallized in non-isothermal crystallization kinetics.

On the basis of the Ozawa model (equation 2.13), the plots of $\ln[-\ln(1 - x_T)]$ vs $\ln \beta$ would be fitted by a straight line where the slope of the line would yield $-n$, which physically corresponds to the growth mode. The mathematical derivation of the Ozawa equation can be found in reference [93].

2.2.1.2.3 Non-Isothermal Crystallization Kinetics in S4A7EDxB Compounds

Because crystallization from an amorphous precursor of strontium aluminate ceramics involves the evolution of multiple competing phases, the kinetics analysis experiments during crystallization were performed under non-isothermal conditions. In fact, based on the previous works in our group [67, 68] the trend of crystallization events in strontium aluminate compounds might occur too fast to be measured under time-resolved isothermal

conditions. Instead, non-isothermal kinetics approaches is more appropriate for temperature-resolved reactions during crystallization process [78].

For non-isothermal kinetics study, the stoichiometric S₄A₇ amorphous pre-ceramic powder codoped with 1 mol% Eu, 1 mol% Dy and nominal 0, 5, 10, 20, 30 and 40 mol% B₂O₃ contents were prepared by Pechini method. After calcination of the pre-ceramic powders at 800 °C for 3h in a box furnace in air atmosphere, nitrate materials during processing were fully decomposed, verified by DTG of zero slope, and organic-free amorphous ceramic precursors were obtained. DTA scans at the heating rates of 3, 5, 10, 15, 20 and 30 °C/min were recorded for the organic-free powders with different B₂O₃ contents by using DTA-TG instrument (Netzsch STA 449C Jupiter, Selb, Germany) from room temperature to 1400 °C under air atmosphere. The activation energy (E) of crystallization and/or phase transformation events in addition to nucleation and growth mechanisms (n), were investigated by using Kissinger and Ozawa methods, respectively. The values of activation energy and the growth modes were compared for S₄A₇ED compositions containing different concentrations of B₂O₃ to elucidate the exact role of boron on crystallization kinetics.

2.2.2 Sintering of Strontium Aluminate Compounds

In order to investigate the effect of diffusion kinetics on distribution of rare earth dopants (Eu²⁺ and Dy³⁺) in the microstructure of strontium aluminate ceramics by spatially resolved electron microscopy techniques, we aimed to understand the role of sintering rate and boron content in tuning the diffusion kinetics during phase evolution from amorphous precursor of Pechini processed stoichiometric S₄A₇ED composition. For this purpose, sintered specimens of S₄A₇ED compound were prepared under two sintering method with and without B₂O₃ as the sintering flux. For slow heating rates during sintering, the ceramic powders were conventionally sintered (CS) while for achieving high heating rates for sintering, spark plasma sintering (SPS) technique was used. The microstructural evolution during sintering and the distribution of rare earth elements in microstructural features were then compared for sintered specimens produced by conventional method against that of SPS.

To produce the amorphous pre-ceramic material for sintering with CS and SPS method the following steps were undertaken:

- i. The nominal $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ compound doped with 1 mol% Eu and 1 mol% Dy was synthesized by a sol-gel Pechini process, as described in Section 2.1.7, both without B_2O_3 and with 30 mol% B_2O_3 .
- ii. The sponge-like and dried powder product (Figure 2.10) was slightly ground in an agate mortar with pestle to breakdown the agglomerated particles and obtain a homogenous powder. The precursor at this stage still contains nitrate materials and organics used during Pechini processing.
- iii. The amorphous powder was then pre-calcined in an alumina crucible at 600 °C in air for 6 h and then at 700 °C for 2 h at a heating rate of 10 °C/min in a box furnace under air to fully decompose the nitrate precursors and oxidize the organics materials, followed by cooling at room temperature in the furnace. At the end of this pre-calcination step, an organic-free amorphous pre-ceramic powder was produced.

The organic free and amorphous powder was considered as the starting materials for sintering.

2.2.2.1 Spark Plasma Sintering

To produce the sintered specimens under high heating rates, the amorphous powder was sintered in an SPS furnace (SPS-615E, Dr. SINTER; SPS Syntex Inc., Kawasaki, Japan). The pre-ceramic powder was loaded into a graphite die with a punch diameter of 10 mm. Sintering was conducted under vacuum, a contact load of 3 kN, and a heating rate of 100 °C/min. A regulated, 4 V DC pulsed current was gradually increased to 2000 mA, to achieve a final sintering temperature with different SPS dwell times, for both B_2O_3 -incorporated and B_2O_3 -free amorphous pre-ceramic. **Figure 2.16** shows the schematic of a spark plasma sintering furnace and Table 2.3 summarizes the SPS parameters for producing the sintered pellets by spark plasma sintering in this work.

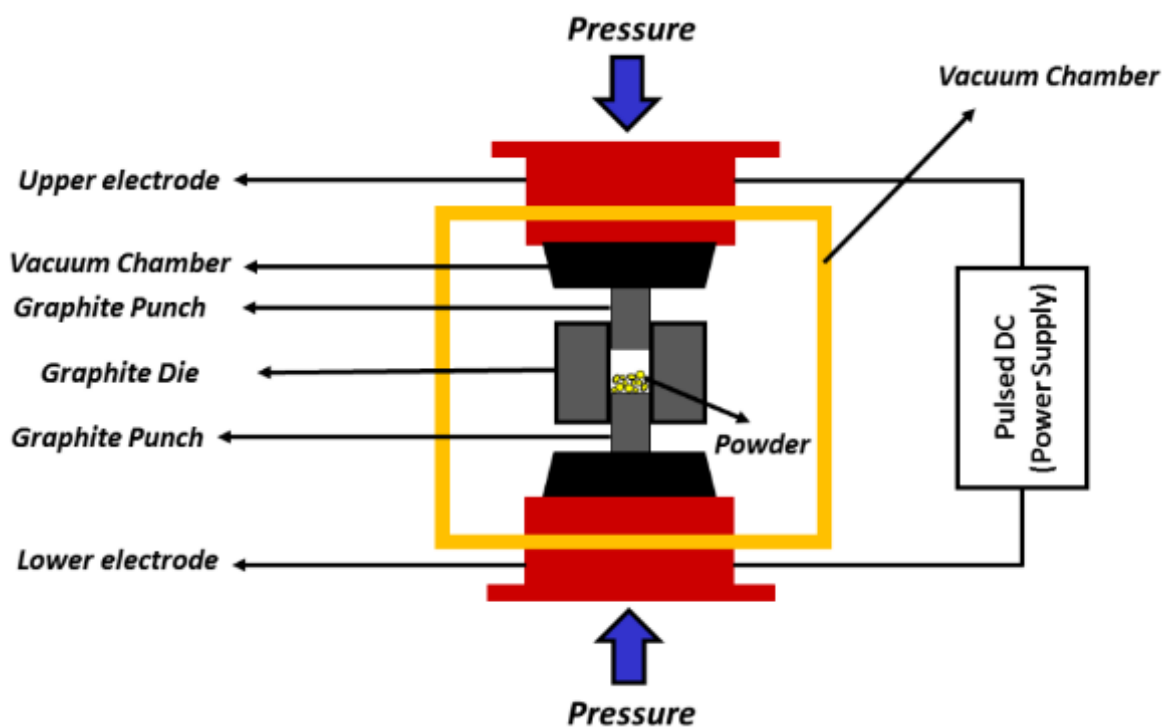


Figure 2.16. Schematic of spark plasma sintering set up.

Table 2.3. SPS parameters and B_2O_3 concentration used for sintering of amorphous $Sr_4Al_{14}O_{25}$: 1 mol% Eu, 1 mol% Dy compound.

Sintering Temperature (°C)	Sintering Dwell Time (min)	B_2O_3 content (mol%)
1100	3	30
1100	10	30
1100	20	30
1150	10	30
1300	3	30
1300	10	30
1300	10	0
1500	3	30
1600	3	30

2.2.2.2 Conventional Sintering

For comparison of the effect of sintering heating rate on rare earth dopant distribution, the amorphous pre-ceramic with and without B_2O_3 were also processed by conventional sintering. To produce conventionally sintered specimens, the following steps were done:

- i. A portion of organic free powder both was placed in alumina crucible and the temperature was increased first from room temperature to 1300 °C with a heating rate of 10 °C/min and calcined for 10 hours in a box furnace under ambient atmosphere to fully crystallize the powder. The powder was then allowed to be cooled down in the furnace.
- ii. The crystalline powders were then fully ground in an agate mortar with pestle in pure ethanol for about one hour to obtain a uniform small particle size. The grinding step was considered to assist the final sintering step.
- iii. After drying the powder and removal of the ethanol, the powders were uniaxially pressed into a pellet under a pressure of 70 bar for 2 min.
- iv. The pellet was then sintered for 5h at 1300 °C, under a heating rate of 10 °C/min and a varigon mixture (96% Ar + 4% H_2 , 120 ml/min) in a tube furnace.

2.2.3 Raman Spectroscopy

To elucidate the crystallization of Pechini processed S4A7EDxB compounds from the amorphous state, it is important to investigate the structural changes of the amorphous alumina during crystallization. In fact, the crystal structure of the stable phases in SrO- Al_2O_3 binary system is constructed by corner-sharing or edge-sharing alumina polyhedral with Sr^{2+} cations incorporating into the large cavities, producing charge compensation [6, 11, 81, 94]. Because the nature of alumina polyhedral, e.g. the formation AlO_4 tetrahedral and AlO_6 octahedral units upon increasing temperature may influence the sequence of phase formation of strontium aluminates, we investigated the phase evolution of the alumina precursor (aluminum nitrate) used in Pechini processing of strontium aluminate compounds.

However, it should be noted that before formation of the most stable alumina phase, the α - Al_2O_3 , a number of metastable transition phases including, χ , γ , δ , η and θ might form [95-97]. In addition, it is possible that some of the transition phases are simultaneously

present during structural evolution of amorphous alumina to α -Al₂O₃. Unfortunately, identification of the metastable phase of alumina polymorphs by diffraction methods is challenging, due to the fact that the transition alumina phases provide similar diffraction patterns [97, 98].

We thus considered the characterization of alumina polymorphs obtained from the calcination of aluminum nitrate through vibrational modes of the structural polyhedron units. Because Raman spectroscopy uses the shift in frequency of an inelastically scattered incident photon, due to excitation of structural units of the specimen to different virtual vibrational energy levels [99-101], it provides very useful information in characterization of transition alumina phases.

For this purpose, aluminum nitrate nonahydrate (Al (NO₃)₃ · 9H₂O) was pre-calcined at 600 °C for 6 hours to fully decompose the nitrate materials. The nitrate-free amorphous alumina powder was calcined in a box furnace at the onset and endpoint temperatures of the exothermic peaks determined from thermograms of the amorphous alumina; and the powders were immediately quenched to room temperatures in air.

Raman analysis of the powders was carried out with a *Renishaw inVia* Raman system. The excitation source was 532 nm wavelength laser with a laser power of 5%. A 50× objective lens with numerical aperture of 0.75 was used in the micro-Raman measurements, and the spot size of the 532 nm-laser was estimated to be *ca.* 865 nm. 4 different points in the powder specimens were analyzed to ensure that the obtained Raman spectra were statistically representative of the sample analyzed.

2.2.3.1 Principle Component Analysis (Finger Printing) by Raman Spectroscopy

In addition, we investigated the presence of a glassy phase in the conventionally sintered specimen doped with 30 mol% B₂O₃ by micro-Raman spectrum mapping. For hyperspectral Raman analysis of the sintered pellet, the sintered specimen was embedded in epoxy and the cross-section of the pellet was polished down to 4000 grit size.

By using an excitation of 532 nm – wavelength from a laser source with a laser power of 5% and 50× objective lens with numerical aperture of 0.75, the spot size of was estimated to be *ca.* 865 nm, and a minimum step size of 1.3 μm was achieved. Raman spectra were recorded at every point over the mapping area.

Because principle component (PC) analysis method uses the whole range of the Raman spectrum collected at individual pixels, we applied this technique for precise discrimination of the phases present in the B₂O₃-doped sintered pellet in Raman spectral images.

For principle component analysis of the Raman mapping data, the Raman reference spectrum of pure SrAl₁₂O₁₉ (SA₆), Sr₄Al₁₄O₂₅ (S₄A₇), B₂O₃ powders and the epoxy was first collected. The corresponding representative spectra for each principle component were then compared against the reference spectra for precise discrimination of the phases present in the B₂O₃-doped sintered pellet.

2.2.4 X-Ray Diffraction

The sequence of phase formation during structural evolution of Pechini processed amorphous precursor of S4A7EDXB ceramic powders was confirmed by X-ray diffraction. Diffraction patterns were recorded by using a Cu-K α source ($\lambda = 1.54056 \text{ \AA}$) which was generated under 30 mA current and 30 kV in the X-ray tube (D2 Phaser diffractometer, Bruker, Germany). Data acquisition was carried out in the 2θ range of 5–90° with an increment of 0.02° step size at a counting time of 1 s per step over the scan range.

To identify the crystalline phases during phase evolution, the experimental diffraction patterns were compared to that PDF card files in Joint Committee on Powder Diffraction Standards (JCPDS) database by using *DIFRACT.SUITE EVA* software (AXS Bruker, Germany).

2.2.4.1 X-ray Diffraction Phase Analysis During Structural Evolution

For crystallization study (chapter 3), a systematic phase analysis by XRD was carried out for understanding the structural evolution under the influence of B₂O₃ for all the S4A7EDxB compositions ($x = 0, 10, 20, 30$ and $40 \text{ mol\% B}_2\text{O}_3$). For each composition, the amorphous pre-ceramic was calcined in a box furnace at a heating rate of 10 °C/min in air at the several temperatures based on thermal analysis data including 50 °C before the onset of the exotherm, the onset temperature, the temperature of the exotherm maximum, the endpoint temperature of the crystallization exotherm, and 50 °C above the

exothermic peak. The specimens were immediately air quenched from high temperature to the room temperature to freeze the actual structure at the corresponding calcination temperature. The crystal structure of the powders at every step was then examined by XRD to determine the sequence of phase formation upon increasing temperature.

For the compositions that exhibited two crystallization peaks, similar approach was considered to investigate the phase evolution at the second exothermic peak too.

Moreover, phase analysis was carried out for all the S4A7EDxB compositions calcined at 1300 °C for calcination durations of 1, 5, 10 and 20 hours, to evaluate the formation of the equilibrium phase by time. In all cases, the specimens were air-quenched and the diffraction patterns were analyzed. **Figure 2.17** shows a typical example of the strategy that was considered for phase analysis during structural evolution based on the thermal analysis data.

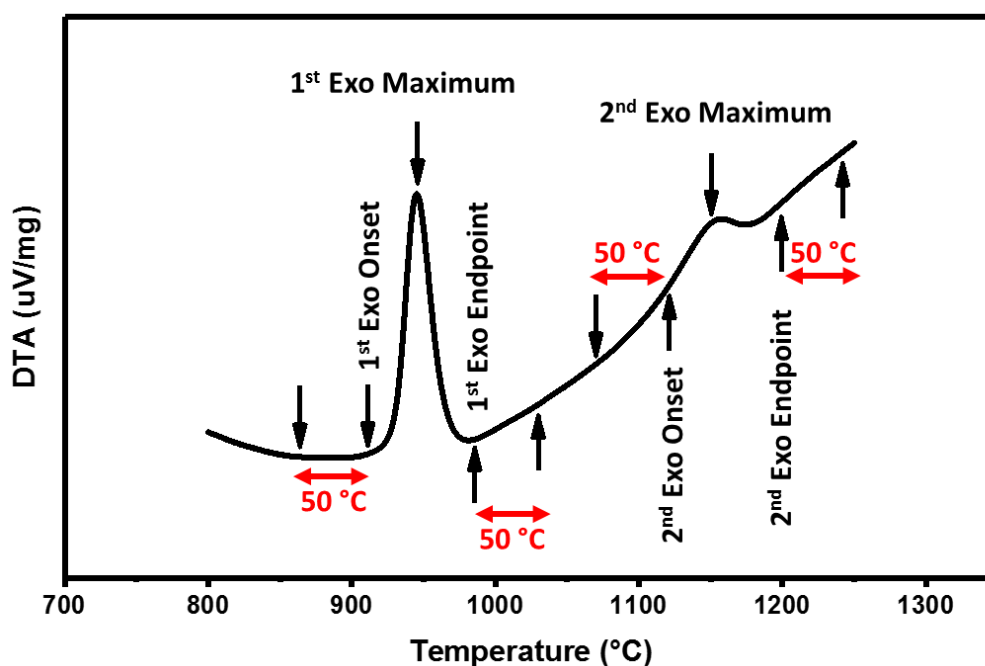


Figure 2.17. A typical DTA curve for strontium aluminate compounds. Phase analysis by XRD were carried out on the powder specimens calcined at the temperatures specified by arrows on the thermogram.

In addition, the same approach was considered to investigate the structural evolution in amorphous alumina precursor to correlate the alumina polyhedral units present with phase evolution in strontium aluminate phosphors.

The fraction of evolving phases at each step was investigated by Rietveld phase analysis method [102, 103].

2.2.4.2 Rietveld Quantitative Analysis of XRD Data

The fundamentals of Rietveld refinement method and its application in phase evolution studies can be found in the references [103, 104].

Rietveld refinement of X-ray diffraction data was performed using the TOPAS-Academic V5 [105, 106] in the lunch mode joint with the *Jedit* text editor. After phase analysis of the diffraction pattern through search/match in *DIFRACT.SUITE EVA* software, the corresponding crystallographic information file (CIF) attributed to all the identified phases was collected from FindIt crystal database software and/or crystallography open database (COD).

During Rietveld analysis, the CIF files of the identified phases were used as the structural models for refinement [103]. The background contribution to the diffraction pattern was described by using a 6-coefficient polynomial function. Because the shape of the diffraction peaks in XRD pattern is a function of both the sample (due to probable existence of structural defects, stress and strain), and the instrument (through the instrument geometry, the source of X-ray photons and the slits used), it is important to describe the shape of the diffraction peaks properly during the refinement. For this purpose, the shape of the diffraction peaks was fitted by using a TCHZ peak shape profile which accounts for the Gaussian and the Lorentzian components of the peak shapes as a function of 2θ .

Before the structural refinement for each phase (including the atomic fractional coordinates and thermal coefficients), the contribution of instrumental parameters to the shift of diffracting peaks was considered through the refinement of zero-point offset (illumination of the sample by X-ray photons at $2\theta = 0^\circ$) and sample displacement from the center of the goniometer, respectively [103].

After the refinement of the instrumental parameters, the parameters related to the specimen, *i.e.* the structural parameters, were refined for each of the phases. Initially, the lattice parameters of all phases present were refined. This will account for the correction of peak positions that originates from the specimen. Next, for the most dominant phase,

the atomic fractional coordinates were refined starting with the atoms with the highest atomic number. For example, in the case of structural refinement of a strontium aluminate phase consisting of Sr, Al and O atoms, the atomic fractional coordinates were refined in the order of Sr^{2+} , Al^{3+} and O^{2-} , respectively.

Equation 2 – 14 is the general representation of the structure factor that reflects the interference among the atoms located within a unit cell:

$$F_{(hkl)} = \sum_j f_j \exp \{ -i2\pi (hx_j + ky_j + lz_j) \} \quad \text{Eq (2-14)}$$

where f_j is the scattering power (also known as the form factor) of the j^{th} atom, h, k , and l are the Miller indices of the (hkl) atomic plane and x_j , y_j and z_j are the fractional coordinates of the j^{th} atom in the unit cell. According to Equation 2-14, the structure factor $F_{(hkl)}$ is the summation of scattering from all the atoms in the unit cell that contribute to constructive interference giving rise to a diffraction peak from the hkl atomic planes.

The intensity of the reflection peaks in the X-ray diffraction pattern is proportional to the structure factor as

$$I_{(hkl)} \propto |F_{(hkl)}|^2 \quad \text{Eq (2-15)}$$

Therefore, because the structure factor is directly dependent on both the type of the atoms present in the unit cell through f_j and the position of atomic sites in the unit cell through (x_j, y_j, z_j) , refining the atomic positions during the Rietveld analysis changes the magnitude of structure factor, and the relative peak intensities of the calculated data will be adjusted to match and the experimental data.

At the end, the atomic displacement factors (also known as thermal vibration coefficients), which are represented by *B-factor* values in the CIF files, were refined. The difference plot between calculated data and the experimental data, as well as the R-values, were constantly checked during the refinement to assure a realistic fit. The procedure of structural refinement was repeated for the next dominant phase, until all the identified phases during phase analysis were refined. At the end of the refinement, the fraction of

the phases, which is basically obtained by considering the ratio of relative reflection intensities, were reported.

2.2.4.3 Fraction of Amorphous Phase from XRD Data

To quantify the fraction of amorphous phase in the XRD data, the X-ray diffraction pattern was analyzed in the *DIFRACT.SUITE EVA* software as follows:

- i. The contribution of incoherent X-ray scattering to the XRD patterns was first eliminated.
- ii. By removing the effect of incoherent scattering, the remainder would be scattering from crystalline and amorphous phases only.
- iii. The residual background, indicative of the amorphous diffuse scattering, was subtracted from the diffraction pattern, revealing the contribution of crystalline reflections to the XRD.
- iv. The raw area under the “*crystalline peaks*” only and the raw area of the “*amorphous + crystalline*” contribution were calculated, and the fraction of the amorphous phase was obtained as follows:

$$\begin{aligned} \text{Fraction of crystalline (\%)} & \quad \text{Eq (2-16)} \\ &= \frac{\text{Raw area of "crystalline peaks"}}{\text{Raw area of "amorphous + crystalline"}} \times 100 \end{aligned}$$

$$\text{Fraction of amorphous phase (\%)} = 100 - \text{crystalline (\%)} \quad \text{Eq (2-17)}$$

2.2.5 Fluorescence Spectrophotometry

Optical behavior of the S4A7ED phosphors containing 0 and 30 mol% B₂O₃ produced by conventional and spark plasma sintering methods at 1300 °C was analyzed by using fluorescence spectrophotometry (*Agilent Cary Eclipse Spectrofluorometer*). The excitation wavelength for the boron-incorporated, sintered pellets was 371 nm. For boron-

free CS and boron-free SPS specimens the efficient excitation wavelength was chosen to be 334 nm and 347 nm, respectively.

2.2.6 Afterglow Decay Measurement

To investigate the effect of sintering heating rate on distribution of rare earth elements within the microstructure that control the extending the luminescence, we compared the afterglow decay curves for the sintered specimens prepared from the amorphous pre-ceramic with nominal stoichiometry of Sr_4Al_7 doped with 1 mol% Eu, 1 mol% Dy and 30 mol% B_2O_3 by CS (slow heating rate) and SPS (high heating rate) at 1300 °C . For this purpose, the sintered pellets were first illuminated by a UV lamp ($\lambda = 365$ nm) for 10 minutes. The excited pellets were then immediately placed in front of the photon counter (*Hamamatsu PMT head Model H7421-40, photon counting module C8855-01*) on an optical bench, and the decay curve was recorded for each of the pellets.

2.2.7 Scanning Electron Microscopy

Scanning electron microscopy techniques were used to investigate the evolving microstructural morphology during phase formation from an amorphous pre-ceramic of strontium aluminate compounds and understanding the distribution of elements within the microstructural features in sintered specimens. Due to interaction of electron beam with the specimen in a scanning electron microscope, various signals are produced (**Figure 2.18**) [107, 108]. The generated signals were used to obtain information about the morphology and compositional analysis of the microstructure in this work.

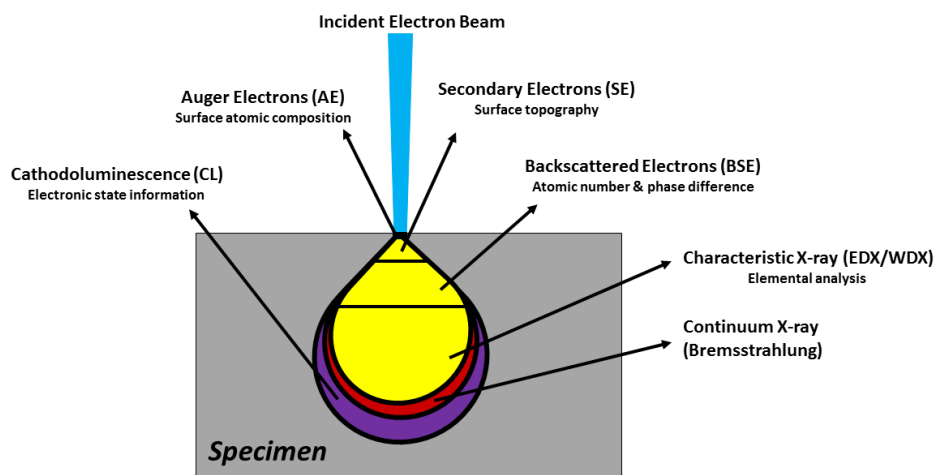


Figure 2.18. Signals emitted from different parts of the interaction volume and their relative locations.

For investigation of microstructural evolution from an amorphous pre-ceramic of the S4A7ED compositions doped with various B_2O_3 contents, a field-emission scanning electron microscope (FE-SEM, LEO Supra VP-55, Carl Zeiss, Germany) equipped with an energy dispersive X-ray spectrometer (EDS; QUANTAX, Xflash 6100, Bruker, Germany) was used. First, the morphological investigation of the specimens was performed by secondary electron (SE) imaging. Because the backscattered electron signals (BSE) in SEM are the result of elastic scattering events between the electron incident beam with atoms in the specimen, larger atoms can scatter the electron beam more strongly with respect to atoms with smaller atomic number [107]. The dependence of BSE signals on the atomic number provides useful information about the phase composition. The compositional variation throughout the microstructure of the specimens was investigated by BSE imaging. Using the phase contrast in BSE images to identify the grains of different phases, the elemental distribution within each phase was analyzed by energy dispersive X-ray spectroscopy.

For the sintered specimens, BSE imaging and the analysis of elemental distributions were performed in a field-emission gun scanning electron microscope (FEG-SEM JEOL JSM-7600F) equipped with a wavelength dispersive X-ray spectrometer (WDS; Microspec WDX-400; Oxford Instruments INCA Wave system).

2.2.7.1 Sample Preparation for Microstructural Analysis in SEM

For microstructural analysis of the powder specimens, the powder particles were embedded in resin epoxy first, in order to be able to polish the cross section of the powder particles. For this purpose, a small piece of carbon tape was pasted at the bottom of a plastic mold, and small amount of powders was deposited on top of the carbon tape. The resin solution was prepared by mixing 15 mL of epoxy precursor and 2.5 mL of hardener as the curing agent, and the solution was vigorously mixed until a viscous liquid was obtained. The resin-epoxy mixture was poured on top of the powder specimens fixed by carbon tape at the bottom of the plastic mold. The molds were left for about 12 hours at room temperature to allow the resin to be cured. The mounted powder was extracted from the mold, then taken out from the mold and the surface of the powders were polished down to 4000 size grit, followed by diamond polishing of the sample cross section. The polished surface was then chemically etched in dilute phosphoric acid (15 mL phosphoric acid + 85 mL distilled water) for 10 seconds. The surface of the polished powder was then coated with carbon by sputter coating to avoid electrostatic charging during imaging and microstructural analysis in the SEM.

For microstructural analysis of the sintered pellets in the SEM, the pellet cross-sections were also polished down to 4000 grit and etched in phosphoric acid for 10 seconds. The same sample preparation for polishing of the powder specimens was also applied to the sintered pellets. However, it should be noted that, in the case of the powder specimens, starting with very coarse grit sizes should be avoided during surface polishing. Otherwise, the powder particles will be completely removed.

2.2.7.2 X-ray Spectroscopy Techniques in the SEM

The presence and the quantity of the elements in the specimen can be determined through detecting the characteristic X-rays that are emitted as a result of the interaction between the primary electron beam with the atoms in the sample. When the electron beam irradiates the sample, it knocks out an electron from inner shell of the atom. As a result, the atom becomes temporarily ionized. The electron vacancy will be refilled by another electron from higher energy outer shells, and the atom relaxes back to its original state. To compensate for the energy of this electron transition, an X-ray photon will be

generated. **Figure 2.19** shows the mechanism for generation of a characteristic X-ray photon as a result of electron beam-specimen interaction.

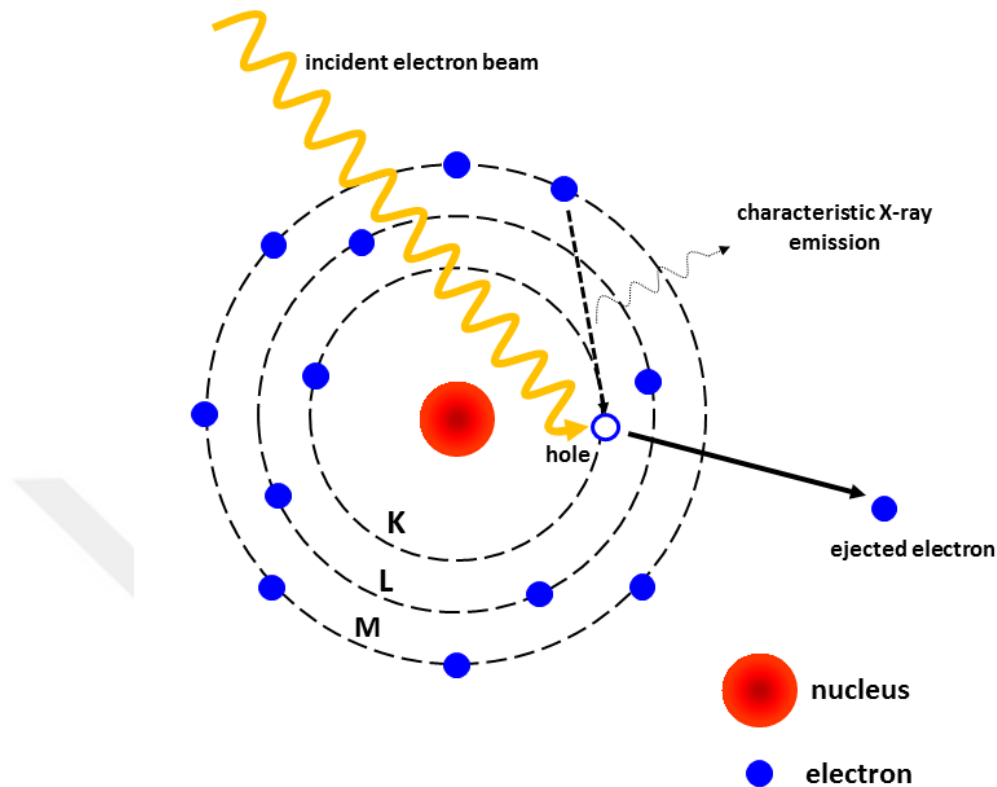


Figure 2.19. Generation of characteristic X-ray as a result of interaction between electron beam and a particular atom in the specimen.

The energy of the emitted X-ray photon is equal to the difference between the energy level of the inner shell electron and the outer shell electron. Because the difference in the energy levels of electrons is known for each element, the generated X-ray is a fingerprint for individual atoms and is known as the characteristic X-ray. Therefore, qualitative and quantitative information about the chemical elements that exist in the specimen can be obtained either from the energy of the X-rays as in EDS or from the analysis of the wavelength of the X-rays, as in WDS .

2.2.7.2.1 Energy Dispersive X-ray Spectroscopy (EDS)

In EDS spectroscopy technique, the detection of characteristic X-rays of atoms occurs through the generation of the electron-hole pairs in a lithiated silicon detector. Because the band gap of Si is 1 eV, the number of electron-hole pairs generated is practically the

energy of the incoming X-ray that is absorbed by the detector. By applying a bias across the semiconductor, the electrical current flow generates a pulse. The pulses are then amplified and binned into many channels representative of the spectrum of X-ray energies. However, the detection of light elements with atomic number less than that of sodium is troublesome in EDS technique, due to the absorption of low energy X-rays, because of the presence of a thin protective window (usually made of beryllium or carbon) at the surface of the detector. Moreover, the energy resolution of an EDS spectrum is on the order of 100-200 eV which means that the X-ray lines will appear as peaks of some width in the spectrum. The poor energy resolution makes it difficult to resolve the characteristic X-rays that energy differences approaching 200 eV. In addition, because the detection of X-rays relies on the electronics in the detector, the signal-to-noise ratio is relatively poor. Because of this, quantitative analysis of the elements in the specimen is accompanied with some degree of uncertainty [107-109].

In this work, EDS point analysis as well as EDS elemental distribution mapping was done for the polished powders calcined at different temperatures. In order to be able to collect the characteristic X-rays efficiently, EDS analysis was performed at a working distance of 9 mm with an accelerating voltage of 15 kV and an objective aperture size of 30 μm . This combination of the X-ray microanalysis parameters was considered such that, the spot size of the beam for point analysis fell within the microstructural features analyzed. The estimated value of electron beam penetration depth into the specimen (the depth of the interaction volume) was approximately between 2-3 microns, depending on the average atomic number of the region being analyzed. This way, we could assume that the characteristic X-rays were almost collected from the grain of interest, but not from the neighboring microstructures. In addition, these operating parameters allowed a reasonable number of X-rays to be detected by the EDS detector (5-6 kcps) simultaneously with BSE imaging of the microstructure.

The elemental distribution maps and EDS point spectra from individual grains and intergranular phases were collected over a sufficiently long time until the signal-to-noise ratio was of acceptable quality, i.e. EDS spectra became smooth, or the distribution map was sufficiently populated without specimen drift under the electron beam.

For quantitative analysis of the microstructural features in sintered specimens, EDS spectra were collected from several points for each of the microstructural features for statistical analysis of elemental distribution. The mean values were calculated for the

Al:Sr ratio, at% Eu, and at% Dy, based on the number of point-beam analyses performed. The standard error of the mean values was then calculated based on the number of point-beam analyses performed. The corresponding standard deviation was extracted from the data spread around the mean value.

2.2.7.2.2 Wavelength Dispersive X-ray Spectroscopy (WDS)

The main principle of WDS technique is centered on detection of characteristic X-rays of the element of interest by using a single crystal diffraction (also known as analyzing crystal) as a filter according to the Bragg's diffraction law:

$$n\lambda = 2d\sin\theta \quad \text{Eq (2-18)}$$

According to the equation (2-18), the single crystal with certain lattice d-spacing that is placed right before the detector (**Figure 2.20**), can diffract only specific wavelength of the incoming characteristic X-ray beam emitted from the specimen.

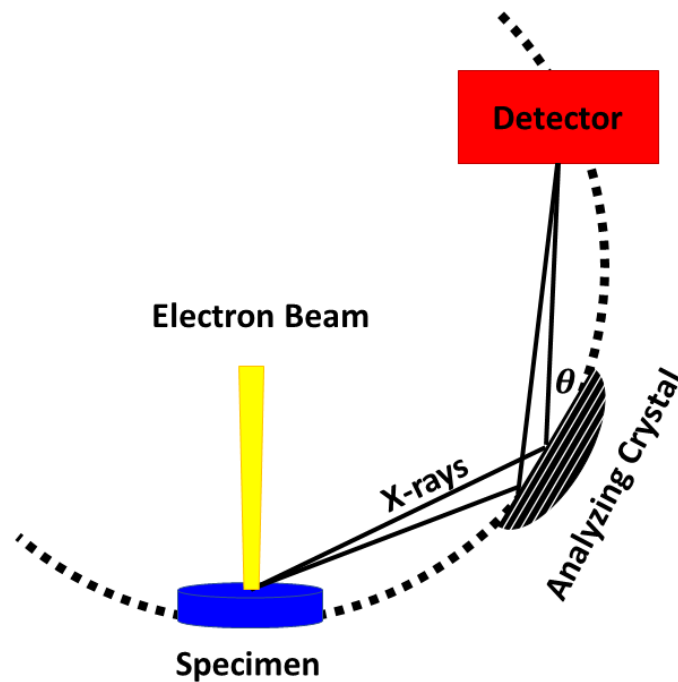


Figure 2.20. The geometry of WDS spectrometer.

The d-spacing of the single crystal spectrometer determines the range of detectable atomic number. Therefore, detection of light elements is possible through careful choice of the diffracting crystal. For detecting the characteristic X-rays of light elements having longer wavelengths, single crystals with a larger d-spacing should be used; while for detection of heavy elements with shorter wavelength of characteristic X-rays, single crystals with smaller atomic d-spacing should be selected. In addition, since X-ray spectroscopy in WDS solely depends on diffraction of a specific wavelength rather than electronics (as in EDS), the energy resolution and signal-to-background ratio in the spectrum are substantially improved, and quantitative elemental analysis is more statistically significant and reproducible [107, 109].

In this work, WDS point-beam analyses was performed to determine the distribution of Sr, Al, Eu and Dy within the microstructure of the sintered specimen. The analysis was operated at an accelerating voltage of 18 kV and a beam current of 30 nA. The standards used for quantification were SrTiO_3 , Al_2O_3 , Eu_2O_3 and Dy_2O_3 . The WDS procedure was optimized to achieve high analytical sensitivity and precision for all elements, thus allowing us to determine very low dopant (Eu, Dy) concentrations with high accuracy.

2.2.7.3 Cathodoluminescence in SEM (SEM-CL)

SEM-cathodoluminescence is a useful technique to investigate the distribution of intrinsic and extrinsic defects in the microstructure. When the specimen is rastered by electron beam, the emission of photons with characteristic wavelengths will be produced by electronic transitions. In fact, the electrons of the atoms that are temporarily promoted to an excited state, might be trapped by the structural defects, such as point defects, and then return to the ground state as a result of electron beam – specimen interaction. Consequently, the energy released, due to this transition, will be emitted as a photon, which usually falls in the visible portion of electromagnetic spectrum (wavelengths of 400-700 nm) [109].

We investigated the correlation between microstructural features with optical properties in the CS and SPS amorphous precursor of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ doped with 1 mol% Eu, 1 mol% Dy and 30 mol% B_2O_3 . The distribution of Eu^{2+} and Dy^{3+} were confirmed by measuring the spatially resolved, monochromated cathodoluminescence distribution in an SEM

(Gatan MonoCL4 mounted on a JEOL JSM-7100F, 10 kV, 3 nm bandwidth, system response-correction applied).

2.2.8 Transmission Electron Microscopy (TEM)

Because transmission electron microscopy techniques are capable of revealing the structural properties of the specimens down to atomic level, we employed a combination of TEM analyses methods to elucidate the crystal structure of strontium aluminate compounds doped with Eu, Dy and B at the nanoscale level.

In conventional TEM analysis, parallel beam of high energy electron (*e.g.* 200 kV) strikes an ultrathin electron transparent specimen with thickness of less than 100 nm. As a result, a significant portion of the beam is transmitted through the specimen, while several signals as result of scattering events will be produced, due to interaction of the electron beam and the ultrathin specimen.

In scanning transmission electron microscopy (STEM), the electron beam is converged into a probe which is comparable to the size of atoms. This way, it is possible to extract localized structural information at the scale of atomic columns, such as atomic resolution imaging, dopant positions, chemical composition and electronic structure of the material.

2.2.8.1 Sample Preparation for TEM Analysis

For transmission electron microscopy analyses including diffraction analysis, STEM atomic resolution imaging and compositional analysis by analytical methods (STEM-EDX and EELS), it is necessary to prepare an ultrathin electron transparent specimen. The following general steps were undertaken for sample preparation for TEM analysis in this work:

- i. Synthesis of Eu, Dy and B doped amorphous precursor of S_4A_7 composition as described in *section 2.1.7*
- ii. Preparation of a sintered specimen as described in *section 2.2.2.2*.
- iii. The sintered specimen cross-section was then polished down to 4000 grit size followed by diamond polishing of the pellet surface as described in *section (sample preparation for SEM analysis)*

- iv. Investigation of the microstructure of the S4A7EDB sintered pellet by electron backscatter imaging in SEM to locate a region of interest where different compositional variations are present adjacent to each other.
- v. Preparation of a thin lamella by cutting through the region of interest using focused ion beam (FIB) milling.

2.2.8.1.1 Focused Ion Beam Milling

The thin foil specimen was prepared by focused ion beam milling (FIB) on an SEM platform, (JIB 4601F Multi-Beam, JEOL Ltd.). To prevent charging, the pellet was coated with an Au/Pd thin film by sputter coating, prior to FIB processing, as well as to protect the surface from direct exposure to high energy electron-ion bombardment during processing. An ion energy of 30 keV and different ion currents (from 10 nA, down to 100 pA) were used for different stages of milling, until an electron-transparent section of ca. 100 nm-thickness is reached. **Figure 2.21** shows the thin lamella preparation procedure by focused ion milling technique.

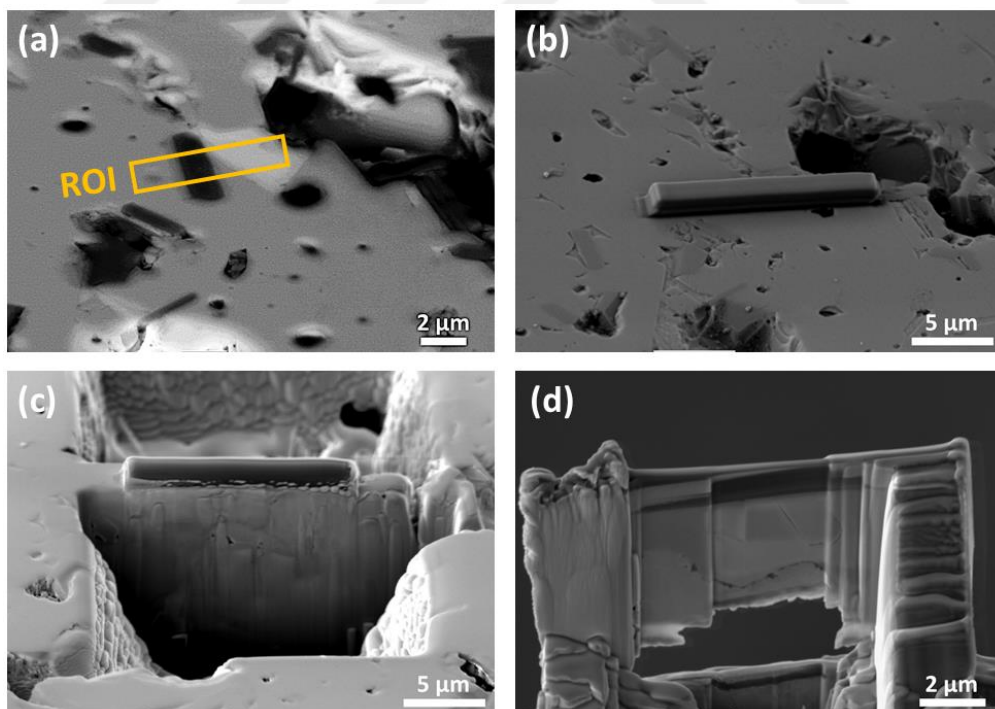


Figure 2. 21. Sample preparation procedure by FIB a)BSE image of the microstructure for locating the region of interest on the sintered pellet b)deposition of a carbon layer on the region of interest prior to FIB milling to protect the sample from gallium implantation c)ion milling to achieve a 1-2 μm thick cross-section sample d) mounting the FIB lamella on top of the TEM grid platform and further thinning to obtain an electron transparent specimen.

2.2.8.2 Structural Analysis by Electron Diffraction Pattern

We used selected area electron diffraction pattern (SAED) technique to evaluate the crystal structure of the microstructure that were developed during the sintering of amorphous precursor Eu, Dy and B codoped S4A7 ceramics by SPS and CS. The microstructure of ultrathin FIB lamella prepared from the specimens were first previewed by bright field (BF) imaging in TEM mode. The distinct crystalline grains were tilted onto a low-indexed zone axis of the crystal, and SAED patterns were recorded for each individual microstructural feature with a camera length of 100 cm. The selected area aperture size used for electron diffraction analysis was chosen according to the relative size of the microstructure being analyzed, in the range of 10 μm to 50 μm in diameter.

The diffraction patterns were collected from the extremely thin regions of the grains to allow spot patterns to be formed. Formation of spot SAED patterns in diffraction mode enabled us to precisely tune the tilting of the crystal very close to the zone axis of interest.

The experimental SAED patterns were then indexed by using JEMS software to specify the geometry of the zone axis that the crystal was tilted. By simulating the diffraction patterns from different projections of a crystal and comparing the simulated SAED pattern with the experimental ones, we were able to identify the phase that formed the spot diffraction pattern. In fact, the analysis of the SAED pattern enabled us to perform localized phase analysis while providing the projection at which the crystal lattice was imaged at the atomic scale.

2.2.8.2.1 Simulation of Electron Diffraction Patterns in JEMS

In order to simulate the SAED patterns of the strontium aluminate compounds on different zone axes, it is necessary to obtain the CIF files of the related phases. The CIF files contain the spatial position of all the atoms in the unit cell, the corresponding site occupancy and the Wyckoff positions. The CIF file was then loaded in the JEMS software as shown in *Figure 2.22*.

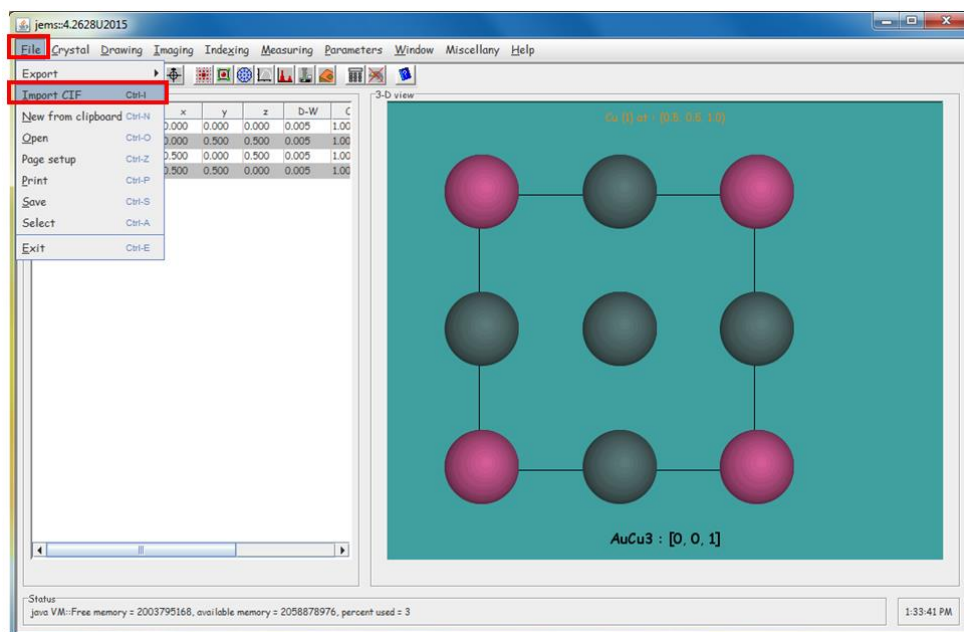


Figure 2. 22. The graphical user interface of the JEMS software and loading the CIF file into the software.

Once the CIF file of the phase of interest was loaded, the crystal structure of the phase should appear on the screen as shown in **Figure 2.23**. In this example, the CIF file for $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ (ICSD # 27744) is shown. To start the simulation, a projection for visualization of the structure was be selected.

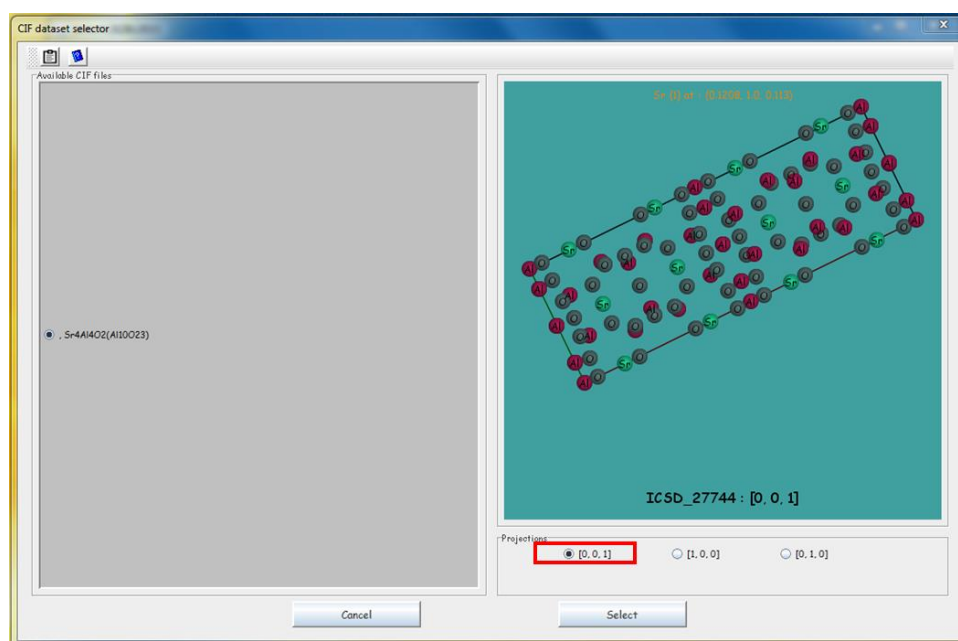


Figure 2. 23. Visualization of the crystal structure of S4A7 phase in JEMS.

When the crystal structure was defined, the spot patterns of the loaded crystal was generated along several zone axes by choosing the tab “draw diffraction pattern”. By doing so, a list of projections with their corresponding SAED pattern appeared as shown in **Figure 2.24**. By scrolling through the list, it is possible to visualize the diffraction patterns of the crystal from different zone axes.

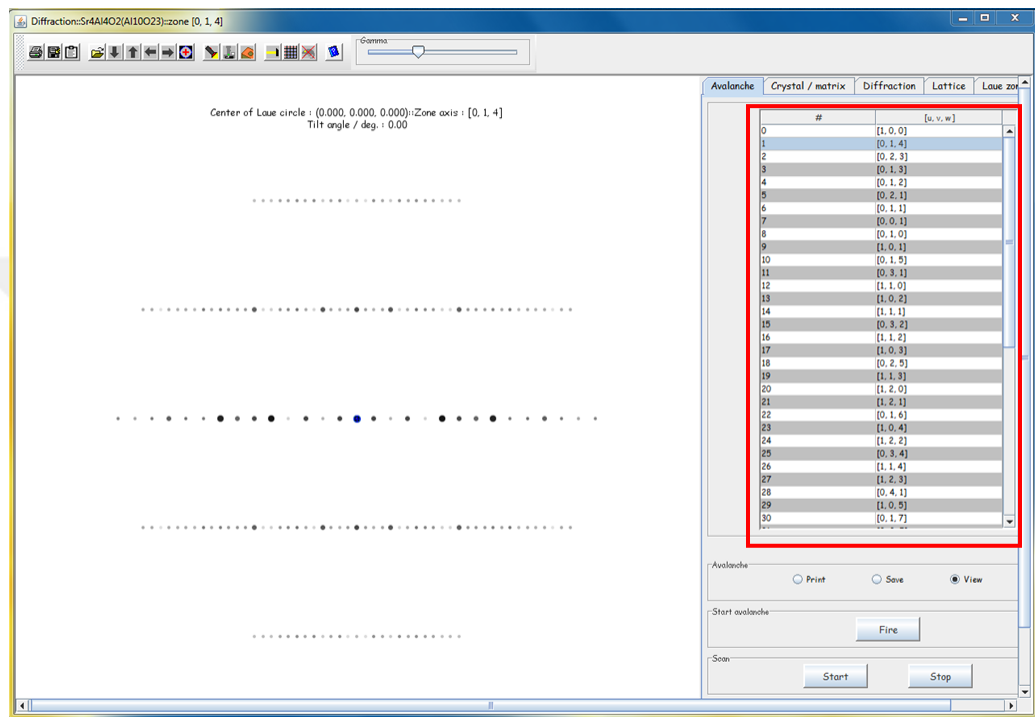


Figure 2. 24. List of several projections with their corresponding SAED pattern.

In the next step of the simulation, the experimental diffraction patterns (DP) recorded at the microscope was loaded in the software to start comparing the experimental DP with simulated ones for phase analysis and identification of the zone axis to which the crystal had been tilted and the experimental DP was recorded. Once the experimental DP was loaded, the color of the simulated spot pattern was changed under the “Option tab” to discriminate the between the experimental spots and the simulated ones (**Figure 2.25**).

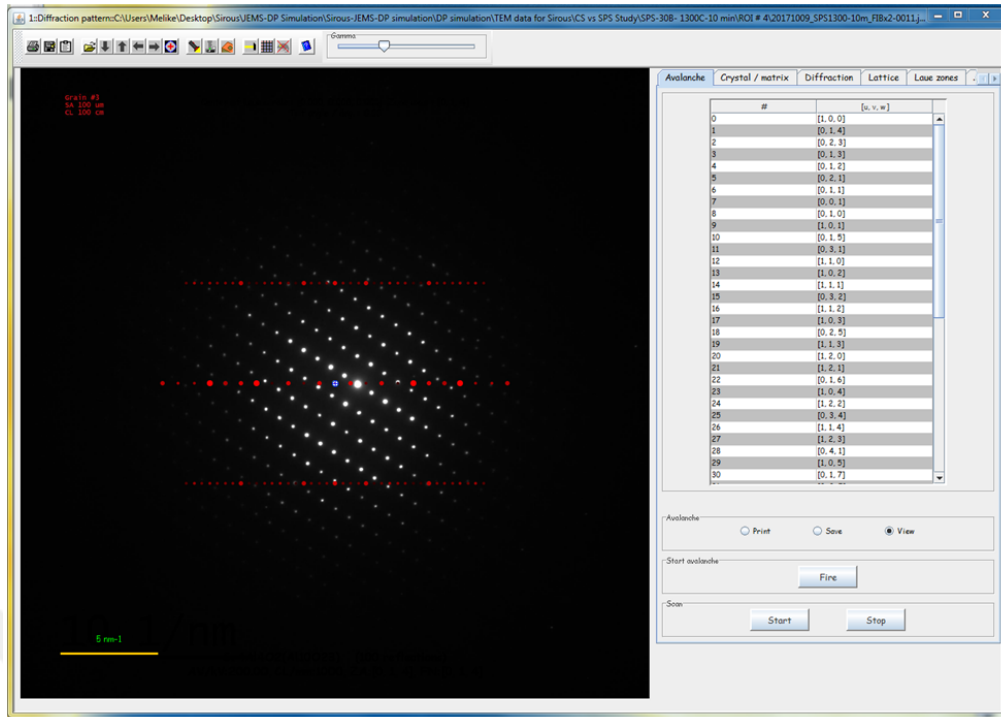


Figure 2. 25. Superimposition of experimental DP on the simulated spot patterns. The red dots represent the simulated pattern.

Before starting to compare the experimental DP with the simulated one, it is necessary to define the microscope configuration parameters, including the accelerating voltage and the camera length etc. by which the SAED pattern was collected. In addition, the scale calibration was adjusted by using the scale bar of the experimental DP. This step was done under the “Diffraction” tab in JEMS as displayed in **Figure 2.26**.

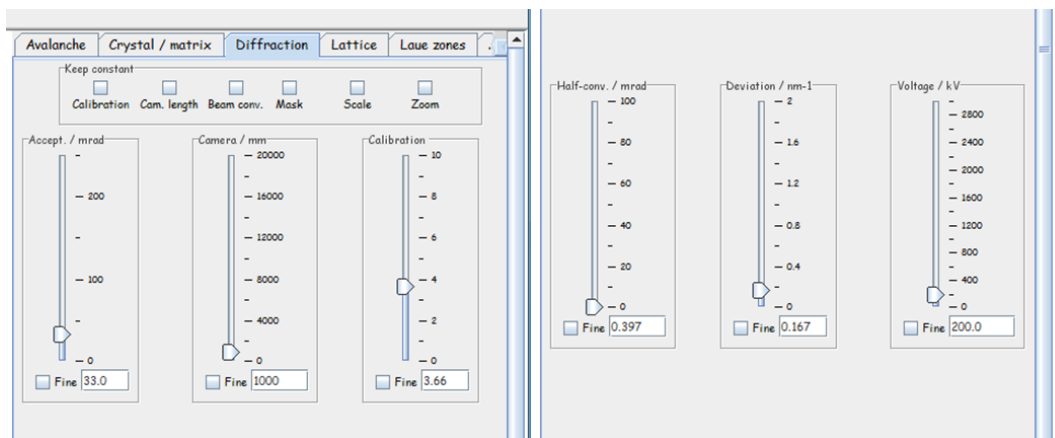


Figure 2. 26. Setting the microscope configuration parameters for simulating the DP in JEMS.

In order to start the search/match between the simulated diffraction patterns and our experimental DP, the center of the two (e.g. the transmitted spot) must coincide to facilitate the comparison. The center of the simulated patterns was aligned on top of the experimental pattern. Moreover, the orientation of the simulated pattern was adjusted to the orientation of the experimental data under the “Normal tab” in JEMS as shown in **Figure 2.27**.

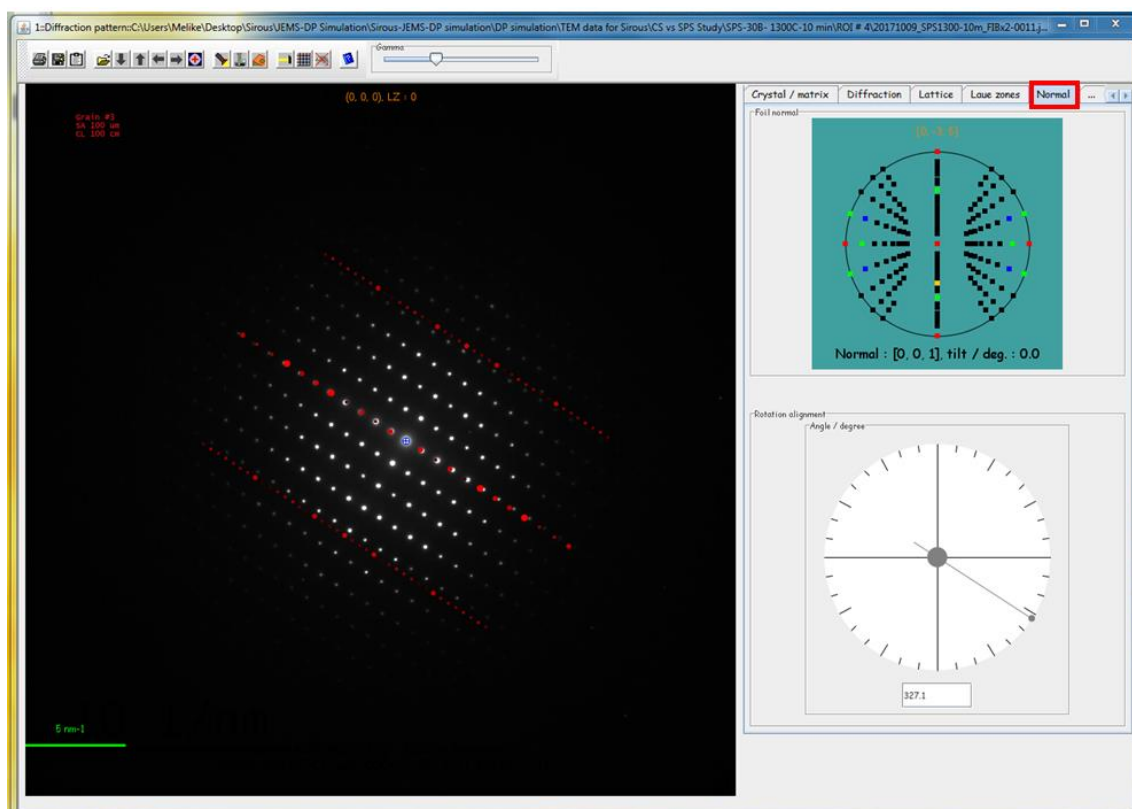


Figure 2. 27. Aligning the simulated DP (red dots) with the experimental DP (white dots) for investigation of zone axis.

After aligning the simulated pattern with the experimental DP, we compared the generated SAED patterns from different zone axes of the S4A7 crystal to find the best match with the experimental DP. **Figure 2.28** shows a perfect match between experimental SAED pattern with that of S4A7 viewed from $[0\ 0\ 1]$ projection in this example. This means that the microstructure in the specimen that formed the SAED pattern is S4A7 phase, which had been tilted to $[0\ 0\ 1]$ zone axis. The procedure could be repeated with the CIF files of the other strontium aluminate phases to confirm the phase analysis by electron diffraction.

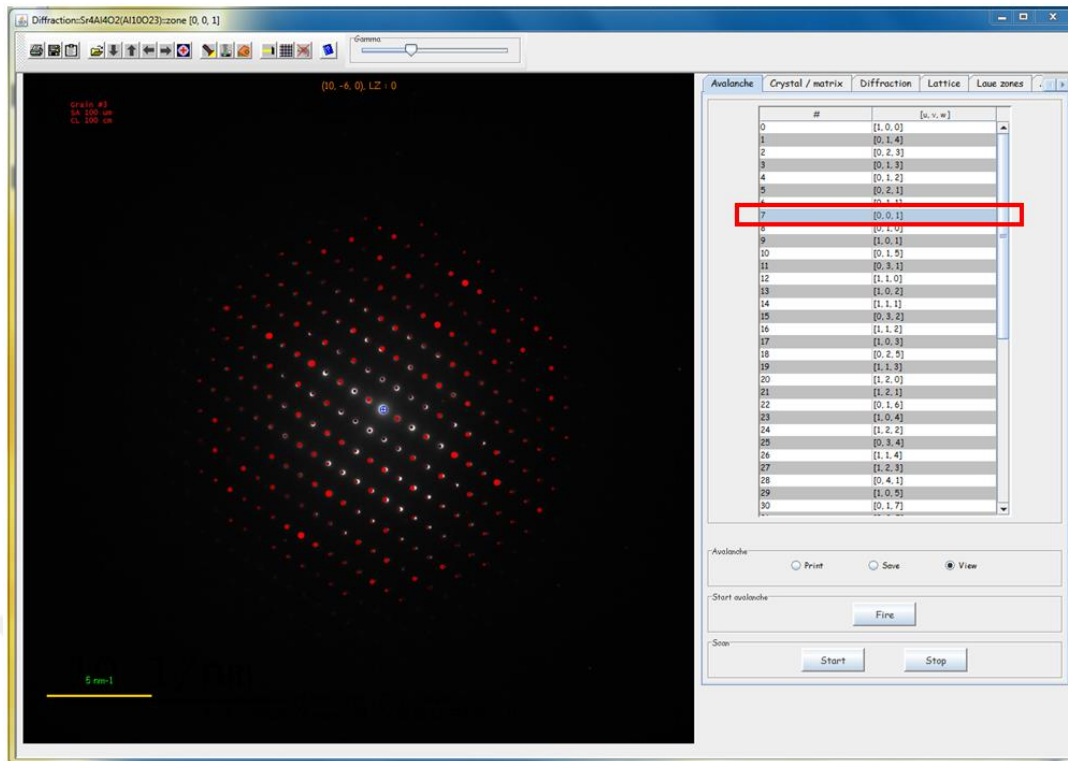


Figure 2. 28. Matching the experimental DP with those of simulated spot patterns in DP database.

2.2.8.3 Atomic Resolution Imaging by Scanning Transmission Electron Microscopy (STEM)

After confirmation of crystalline and/or amorphous nature of the microstructural features by electron diffraction pattern, and tilting a crystalline grain along a zone axis, we switched to the scanning mode where the electron beam is converged to form a sub-angstrom spot size to probe the specimen. The signals generated after the interaction between the electron beam with an ultrathin specimen and the relative location of the STEM detectors are illustrated in **Figure 2.29-a** and **Figure 2.29-b**, respectively. As can be seen, the generated signals after passing through the specimen will be scattered over a broad range of semi-angles.

The bright field detector (BF) is a solid disk that collects the central transmitted beam along with those scattered electrons that have been scattered slightly off-axis (up to *ca.* 11 mrad) to form bright field images. The origin of intensity variation in the STEM-BF image (contrast) is due to attenuation of transmitted beam in the atomic positions, where the image is a dark sample on a bright background [110].

The annular dark field detectors (ADF) are ring-shaped each with certain inner and outer collection semi-angles θ_2 set by the camera length (see Figure 2.29). Dark field imaging in STEM mode is accomplished by using an annular detector that is positioned below the specimen such that it collects the forward scattered electrons. When two annular detectors are present, the one closer to the optic axis, the low-angle annular dark field (LAADF), may also capture diffracted beam. The intensity variation in the LAADF images arises from diffraction contrast and scales with the amplitude of diffraction.

The high-angle annular dark field (HAADF) detector collects the electrons that are highly scattered incoherently and inelastically off axis more than 50 mrad. Since the angle of scattering to such a high degree is directly proportional to the atomic number of the atoms present in the specimen [111], the contrast of the images produced by HAADF detector reveals direct interpretable information about the atomic number of the chemical elements present in the specimen. In other words, strong scatterers in a column of atoms appear bright while lighter elements appear darker in the HAADF image. It is important to note that, due to the incoherent nature of the scattered electron probe, the HAADF detector is not sensitive to neither the thickness variation nor phase shift between the electron waves [8, 111, 112]. This allows direct correlation of intensity variation in the image to the atomic mass and resolving the structural features including the location of dopant atoms in the crystal.

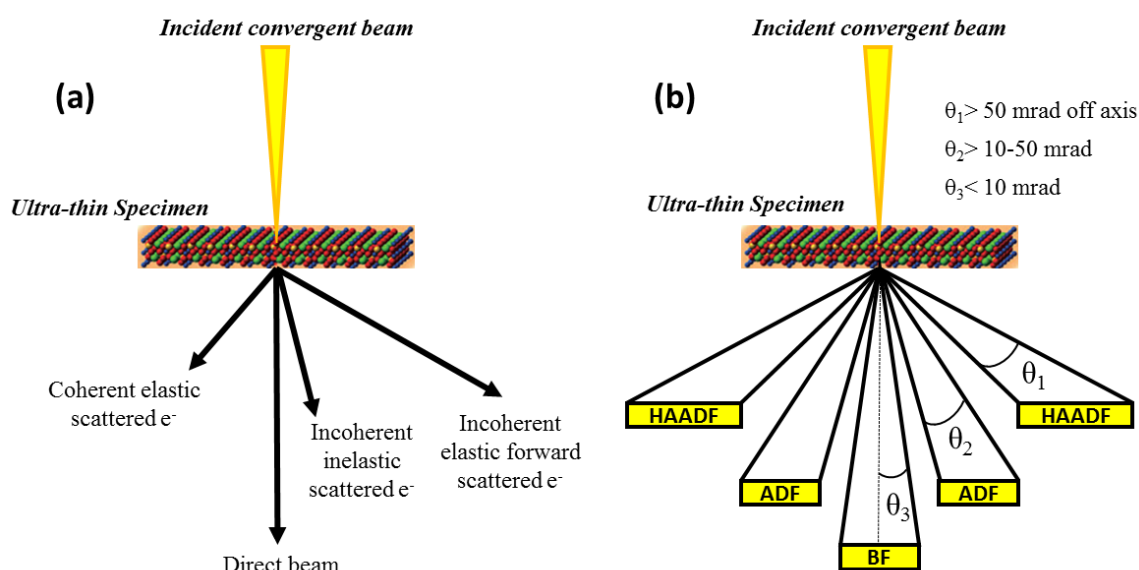


Figure 2. 29. Signal generation and signal detection in STEM mode a) interaction between convergent beam and thin specimen b) relative locations of the detectors in STEM mode.

We performed atomic resolution STEM imaging in an aberration-corrected scanning transmission electron microscope (STEM; JEOL JEM-ARM-200CF) at an accelerating voltage of 200 kV using a 40 μm condenser aperture and a 1 Å probe size and BF, ADF and HAADF images were simultaneously collected.

2.2.8.4 Spectroscopy Techniques in STEM

Analytical electron microscopy (AEM) techniques in the TEM were used to elucidate the chemical information with nanoscale spatial resolution. Inelastic scattering events resulted in generation of characteristic X-ray photons as well as the loss of energy in the primary high energy electron beam after it ionizes atoms. Detection of these signals by spectroscopy methods in the TEM provides very useful chemical and compositional information, elemental mapping and electronic properties of crystalline and amorphous phase in S4A7EDxB ceramic materials with atomic scale spatial resolution. They offer the potential to correlate atomic arrangements with globally measured optical properties.

2.2.8.4.1 Energy Dispersive X-ray Spectroscopy in STEM (STEM-EDS)

To assess the distribution of chemical elements across the microstructure of S4A7ED doped with 30 mol% B₂O₃ produced by CS and SPS methods, we performed STEM-EDX analysis. The sample preparation for STEM-EDX analysis of the sintered specimens was carried out by FIB technique as described in *Section 2.2.8.1.1*.

In general, EDS analysis in TEM provides better energy spatial resolution compared to SEM. This is mostly due to the fact that in SEM, the beam size that probes the specimen, the penetration depth and the spread of the electron beam in the bulk specimen is substantially larger (*ca.* 1-3 μm). Therefore, the characteristic X-rays of the elements are generated from a volume of *ca.* 1 μm^3 . In contrast, the analyzed volume in a TEM sample is in the order of a few nanometers from the section of an ultrathin specimen. Due the very small probe size in the STEM mode (0.1 – 10 nm), higher accelerating voltage and extremely small thickness of the specimen (5-150 nm), the beam spread in the specimen is suppressed and the interaction volume is significantly smaller (**Figure 2.30**). Therefore, the source of the characteristic X-rays is limited to a few atomic columns, and the spatial resolution of the EDS spectrum is improved [110]. The improved energy resolution in

STEM-EDS analysis allowed us to analyze the actual distribution of dopants in nanoscale within the crystalline grains and at the grain boundaries.

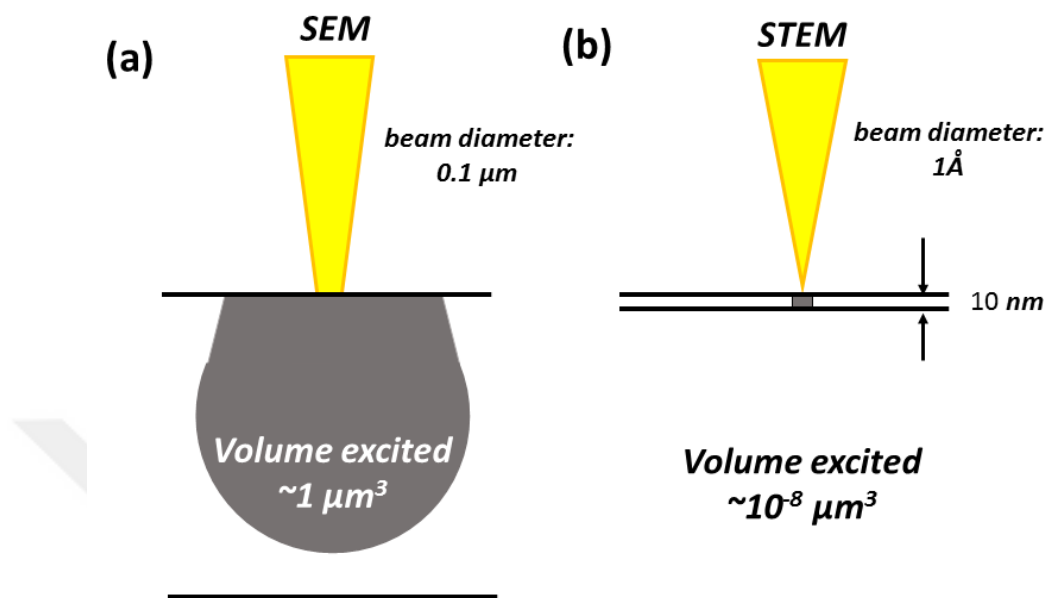


Figure 2. 30. Comparison between the beam size, penetration depth and the analyzed volume in a) SEM and b) STEM.

We performed EDS analysis in the TEM to investigate the distribution of Eu, Dy. Elemental distribution mapping with nanoscale spatial resolution was performed in a scanning transmission electron microscope with a C_s -aberration-corrected probe (STEM; JEOL JEM-ARM 200CF) equipped with an energy dispersive x-ray spectrometer (EDXS, Jeol Centurio, $100\ \text{mm}^2$ EDXS detector). The accelerating voltage, the probe size and the probe current were 200 kV, *ca.* $2\ \text{\AA}$ and *ca.* 700 pA, respectively.

2.2.8.4.2 Electron Energy Loss Spectroscopy (EELS)

When a high energy-electron beam irradiates a thin specimen in TEM, a portion of the incident beam energy will be lost due to inelastic scattering events. This loss of energy can provide a wealth of information about the material properties including electronic structure, local bonding as well as oxidation state and quantitative and qualitative analysis of the elements with spatial resolution at the atomic level [110, 113]. Therefore, electron energy loss spectroscopy (EELS) measures the energy distribution of the electrons of the primary beam after undergoing inelastic interaction as it passes through the specimen.

Figure 2.31 shows a typical EEL spectrum which includes three main regions: the zero-loss peak (ZLP), the low loss region and the core loss region.

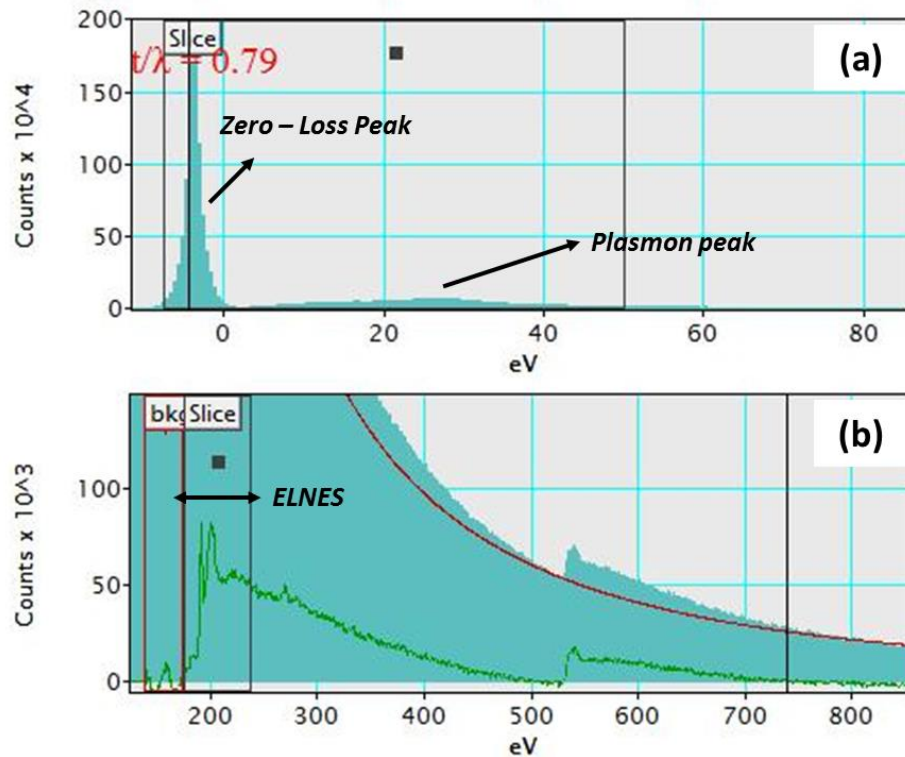


Figure 2. 31. A typical example of EEL spectrum.

The intense zero-loss peak located at 0 eV (**Figure 2.31-a**) in the spectrum is the result of the incident electrons that pass through the specimen either without any interaction with the atoms (so no loss in the energy) or with forward elastic scattering without any major change in the initial energy. The full width at half maximum (FWHM) of the ZLP which is typically in the order of 0.3 – 1 eV, determines the energy resolution of the spectrum [114].

The low energy loss region appears after the zero-loss peak and it is extended to up to ca. 50 eV of the energy loss in the spectrum (Figure 2.31-a). The low loss region of the spectrum is the result of the inelastically scattering events of the incident beam by the weakly bonded valence electrons in the atoms present in the specimen. In fact, when the electron beam interacts with the outer shell electrons of the atoms, it induces a collective oscillation of the valence electrons. This collective excitation of the valence electrons – known as *plasmon* - reduces the energy of the electron beam and this energy loss will appear as a broad peak at energy loss values less than 50 eV. The analysis of the low loss

region of the spectrum can provide information about the local thickness of the specimen, inter and intra band transitions and thus band gap values, optical properties and dielectric constant of the material [110, 114, 115].

In a typical EEL spectrum, the energy losses beyond 50 eV, which are characterized by a smoothly decaying background is known as core loss (high loss) region (**Figure 2.31-b**). The core loss region in the spectrum is a result of inelastic scattering of the electron beam by the ionization of inner shell electrons of the constituent atoms. When the electron beam strikes the electrons that are present in the inner shell electrons of an atom, the inner shell electrons will be ejected. This ionization process requires that the core electrons receive enough energy to overcome the binding energy to the atom nucleus. When this energy is absorbed by the core electrons, the core electron would be excited to unoccupied available energy levels in the outer shells and the transmitted beam has lost a corresponding amount of energy. The energy loss equivalent to the ionization energy (E_c) of the atom will appear in the EEL spectrum, which is known as the ionization edge. Because the binding energies of the core electrons and the energy required for their inter-band transition are uniquely defined for each element, the ionization edge energies can be used as a fingerprint for each element [110, 113, 116, 117]. Investigation of the ionization edges in the core loss region of the spectrum can be used to investigate the presence of atoms qualitatively at very high spatial resolution. In other words, identification of trace amounts of a chemical elements at the dopant concentration level is possible through investigation of their characteristic ionization edges. Moreover, the intensity of the ionization edge is directly representative for the amount of the element present in the specimen, and quantitative analysis of chemical species can be performed by looking at the high loss region of the EEL spectrum. Furthermore, because EELS technique involves the ionization edges of the atoms for qualitative analysis, it is sensitive to light elements such as boron that cannot be detected by EDS spectroscopy.

In addition, the core-loss ionization edge is associated with fine structures within a few electron volts of the edge. Intensity fluctuations in close vicinity above the ionization edges, *i.e.* the energy loss near edge fine structure (ELNES), is highly dependent on the electronic structure of the material. During the ionization process, the core electrons are in fact excited to unoccupied energy states above the Fermi level. The density of the unfilled energy levels is directly related to the electron density distribution between the ionized atom and the nature of bonding to its nearest neighbor atoms [110, 114]. In fact,

there is a direct correlation between the shape of the ELNES features and the unfilled electron energy levels, i.e. the density of the state (DOS).

Because subtle changes in number and in spatial arrangement of the atoms in the first nearest neighbor shell around the ionized atom result in characteristic differences in the shape of ELNES features, the ELNES can be interpreted as the coordination fingerprints. Therefore, the analysis of near edge structures can reveal information about changes in the crystal field around the ionized atom, including coordination number and the type of bonding.

In this study, the distribution of dopants including B, Eu and Dy through the microstructure of the sintered specimen was evaluated by electron energy loss spectrum imaging in an aberration-corrected scanning transmission electron microscope (STEM; JEOL JEM-ARM-200CF—200 kV, 0.08 nm spot size—equipped with a post-column energy filter (Gatan GIF Quantum ER). A 5 mm entrance aperture of the spectrometer and a camera length of 30 mm were used, resulting in a collection semi-angle of 83 mrad. A dispersion of 0.1 eV/channel was used, leading to a FWHM of 0.7 eV of the zero-loss peak.

CHAPTER 3: EFFECT OF B_2O_3 ON MICROSTRUCTURAL EVOLUTION DURING CRYSTALLIZATION OF PECHINI PROCESSED LONG AFTERGLOW $Sr_4Al_{14}O_{25}$

3.1 Introduction

The presence of B dramatically extends afterglow to >8 hours in Eu and Dy co-doped strontium aluminate ceramics, making such pigments very attractive potential for energy – saving applications[7, 39, 40, 118]. While B clearly modifies the crystallization kinetics, due its well-known role as a sintering flux agent, exactly how it modifies the energy transfer between Eu and Dy in these long afterglow ceramics is still not as clearly understood. We believe that B also plays a role in the evolution of microstructural features that support long afterglow.

Because thermal analysis offers insight into structural transformations and chemical reactions, we have applied differential thermal analysis (TG-DTA) to investigate the microstructure evolving in stoichiometric $Sr_4Al_{14}O_{25}$ during Pechini processing, *i.e.*, from the amorphous gel formed by polymerization of ethylene glycol and citric acid-chelated cations.

In this chapter, we present a detailed TG-DTA study to determine the actual sequence of phase formation during crystallization from amorphous state. By following a stepwise strategy of adding precursor components to evaluate their influence on crystallization, we first seek to determine the influence of B_2O_3 content on phase formation from amorphous precursor of S4A7ED composition doped with various B_2O_3 content.

Moreover, because one of the goals of this study is to investigate the crystallization kinetics under the influence of B_2O_3 , non-isothermal kinetics study based on DTA

analysis with different heating rates will be applied to observe the kinetics of the phase formation.

For investigating the effect of B_2O_3 on crystallization kinetics during microstructural evolution of Pechini processed strontium aluminate compounds, we considered our physical model as a homogenous disordered box of Sr^{2+} , Al^{3+} and O^{2-} ions according to the stoichiometry of $Sr_4Al_{14}O_{25}$ composition. The starting mixture of ions is amorphous, containing short range order of Sr – O and Al – O bonds. Crystallization from amorphous is expected to initiate with nucleation followed by growth of the stable nuclei.

During nucleation, as thermal energy is introduced to the homogeneously distributed ions, the ions start to rearrange their previous bonds in the short-range order, coming together and, forming new bonds to lower their energy by forming crystalline phases with long range order. Nucleation initiates by formation of meta-stable embryos. Formation of nucleation sites of the crystalline phases in the amorphous box would lead to formation of an interface between the embryos and the surrounding disordered amorphous phase, which imposes an energy penalty to the system due to creation of new surfaces with high surface energy. Under such circumstances, if the embryos size are small, and the localized increase in the energy by formation of new surfaces is greater than the energy lowering effect by formation of the new bonds, the embryos will be unstable and they re-dissolve back to the amorphous state. However, if the embryos reach to a critical size upon which the energy lowering effect due to formation of new crystalline bonds can overcome the surface energy effect contribution, the embryos will be stable and are termed as nuclei.

During the nucleation process in the amorphous mixture of Sr^{2+} , Al^{3+} and O^{2-} with the starting stoichiometry of $Sr_4Al_{14}O_{25}$ composition, the diffusivity of the ions determines the probability of conversion of embryos of the crystalline phases to stable clusters. In this model, we assume that, the diffusivity of the ionic species is not similar. In addition, the driving force for diffusion of ions in the amorphous box, is the chemical potential gradient as well as the Columbic interaction between the charged ions. The parameters controlling the nucleation process in such a model can be listed as follow:

1. The conversion rate of embryos to the stable clusters.
2. The localized concentration and stoichiometry of cations distributed in the amorphous box.
3. Relative diffusivity of the ionic species.

After the formation of stable nuclei, crystallization is proceeded by growth. It is well-known that crystallization in such systems can occur through either surface or bulk (internal) crystallization mechanisms or a mixture of the two processes [73, 77]. In surface crystallization, the nuclei form only on the outer surface of the amorphous particle followed by crystal growth on the surface. During internal crystallization however, after the formation of nucleation sites, crystalline grains grow 3-dimensionally inside the bulk of the amorphous particle.

In this study, we seek to understand the way by which B_2O_3 modifies the crystallization kinetics during microstructural evolution from the amorphous state. By applying non-isothermal kinetics models, the effect of B_2O_3 addition on activation energy of crystallization, as well as the parameters controlling the nucleation and growth, including nucleation rate and the mechanism of growth for the evolving crystals during phase evolution will be discussed.

3.2 Thermal Analysis of the Precursors: The Preceramic Constituents

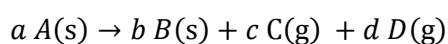
3.2.1 Aluminum Nitride Nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$)

Figure 3.1 shows the thermal decomposition of $Al(NO_3)_3 \cdot 9H_2O$. From the DTA curve (figure 3.1-a), two endothermic peaks with onsets at 76 °C and 134°C can be observed, respectively. The first endotherm can be related to evaporation of water from $Al(NO_3)_3 \cdot 9H_2O$ and the second endotherm is attributed to decomposition of $Al(NO_3)_3$ to form amorphous Al_2O_3 . The two endotherms are accompanied by a sharp weight loss in the TG curve. Moreover, at high temperature in the range of 800°C-1200°C, there are two exothermic peaks with onsets at 852 °C and 1050°C, respectively. These two exotherms are ascribed to crystallization of Al_2O_3 from amorphous alumina and a subsequent phase transition between alumina phases [41].

Figure 3.1-b displays the thermogravimetry (TG) analysis and the derivative of the TG curve (DTG) for thermal decomposition of $Al(NO_3)_3 \cdot 9H_2O$. There are four resolvable peaks in DTG curve which is indicative of four decomposition steps in the TG curve. Except for the first peak in DTG which is related to evaporation of the water, the other three steps of during decomposition of aluminum nitrate can be attributed to formation of water-acid azeotrope, thermal decomposition of nitrate specie and decomposition of

aluminum hydroxide to aluminum oxide, respectively [119, 120]. The main decomposition step happens between 130°C - 400°C with a maximum rate of weight loss at 154°C. The total weight loss during decomposition of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to render amorphous Al_2O_3 , according to the TG curve is 86.16% (residual mass is 13.84%).

In general, the theoretical weight loss of a decomposition reaction which involves the production of gaseous species during thermal decomposition, can be obtained from the ratio of the sum of the molecular weight of the gaseous products to the molecular weight of the starting material that undergoes thermal decomposition as follow:



$$(\text{weight loss})_{th} = \frac{[(c \times \text{M. wt of material C}) + (d \times \text{M. wt of material D})]}{[(a \times \text{M. wt of material A})]}$$

Where a, b, c and d represent the stoichiometric coefficients of reactant A and reaction product B, C and D substances.

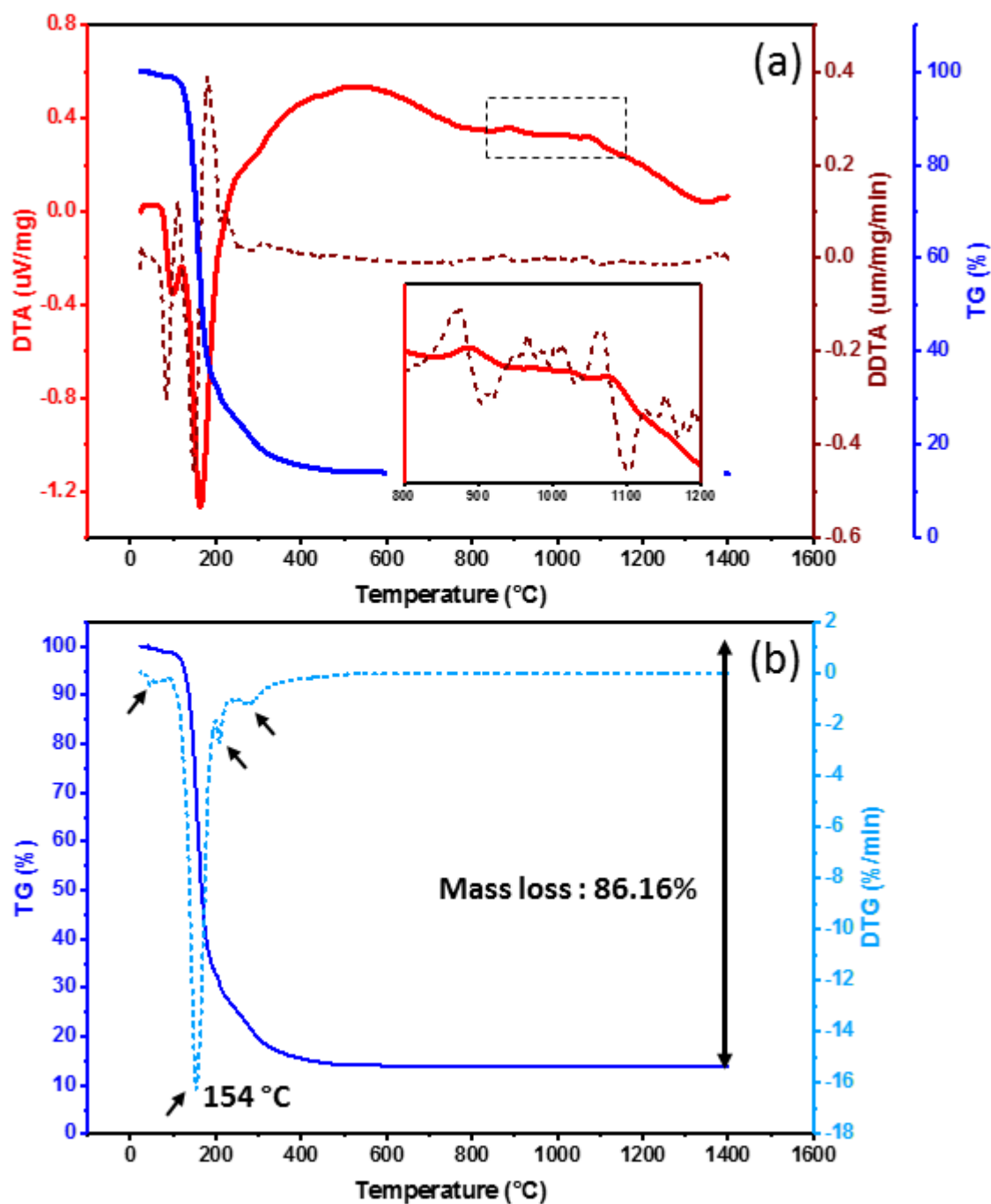
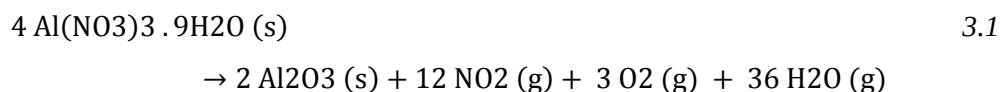


Figure 3.1. Thermal decomposition of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ at a heating of $10^\circ\text{C}/\text{min}$ under air atmosphere a) DTA-TG-DDTA curves. The inset image shows the DTA and DDTA curves in the range of 800 - 1200°C which corresponds to the crystallization temperature of amorphous alumina b) TG-DTG curves. Arrows in b specify the resolvable peaks in DTG plots indicative of the temperatures at which rate of weight loss steps is maximum.

The experimental weight loss of decomposition (86.16%) is in excellent agreement with the theoretical weight loss for decomposition of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ according to the following reaction [120]:

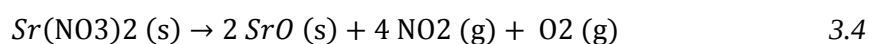
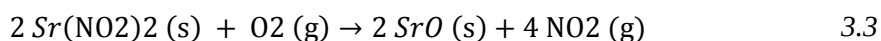
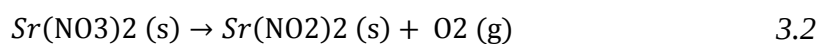


$$(\text{weight loss})_{th} = \frac{[(12 \times 46) + (3 \times 32) + (36 \times 18)]}{[(4 \times 374.98)]} = 86.40 \%$$

3.2.2 Strontium Nitrate ($\text{Sr}(\text{NO}_3)_2$)

The thermograms for thermal decomposition of $\text{Sr}(\text{NO}_3)_2$ precursor is shown in **figure 3.2**. From the DTA curve, two endothermic peaks with onsets at 560 °C and 670°C can be observed, respectively. The two endotherms are accompanied by a sharp weight loss in the TG curve (figure 3.2-a). TG curve revealed that the main decomposition step occurs at the temperature range of 580-750 °C. The overall decomposition reaction seemed to involve two steps as indicated by a sharp peak at 732 °C which is preceded by a peak shoulder at 720 °C (figure 3.2-b). Therefore, the maximum rate of the weight loss during the first and second step of thermal decomposition reaction happens at 720 °C and 732 °C, respectively. In addition, the total weight loss during decomposition of $\text{Sr}(\text{NO}_3)_2$ to render SrO, according to the TG curve is 51.4% (residual mass is 48.6%).

Based on the experimental observations, the thermal decomposition reaction of $\text{Sr}(\text{NO}_3)_2$ can be described by the following successive reactions [121]:



Where reaction 3.4 is the overall decomposition reaction of $\text{Sr}(\text{NO}_3)_2$ and is in fact the summation of the two sub-reactions of 3.2 and 3.3. The theoretical weight loss for decomposition of $\text{Sr}(\text{NO}_3)_2$ to SrO according to equation 3.4 can be calculated as:

$$(\text{weight loss})_{th} = \frac{[(4 \times 46) + (1 \times 32)]}{[(2 \times 211.42)]} = 51.03 \%$$

The experimental mass loss 51.4% is consistent with the theoretical value of 51.03% indicative of the correctness of the purposed decomposition steps for $\text{Sr}(\text{NO}_3)_2$.



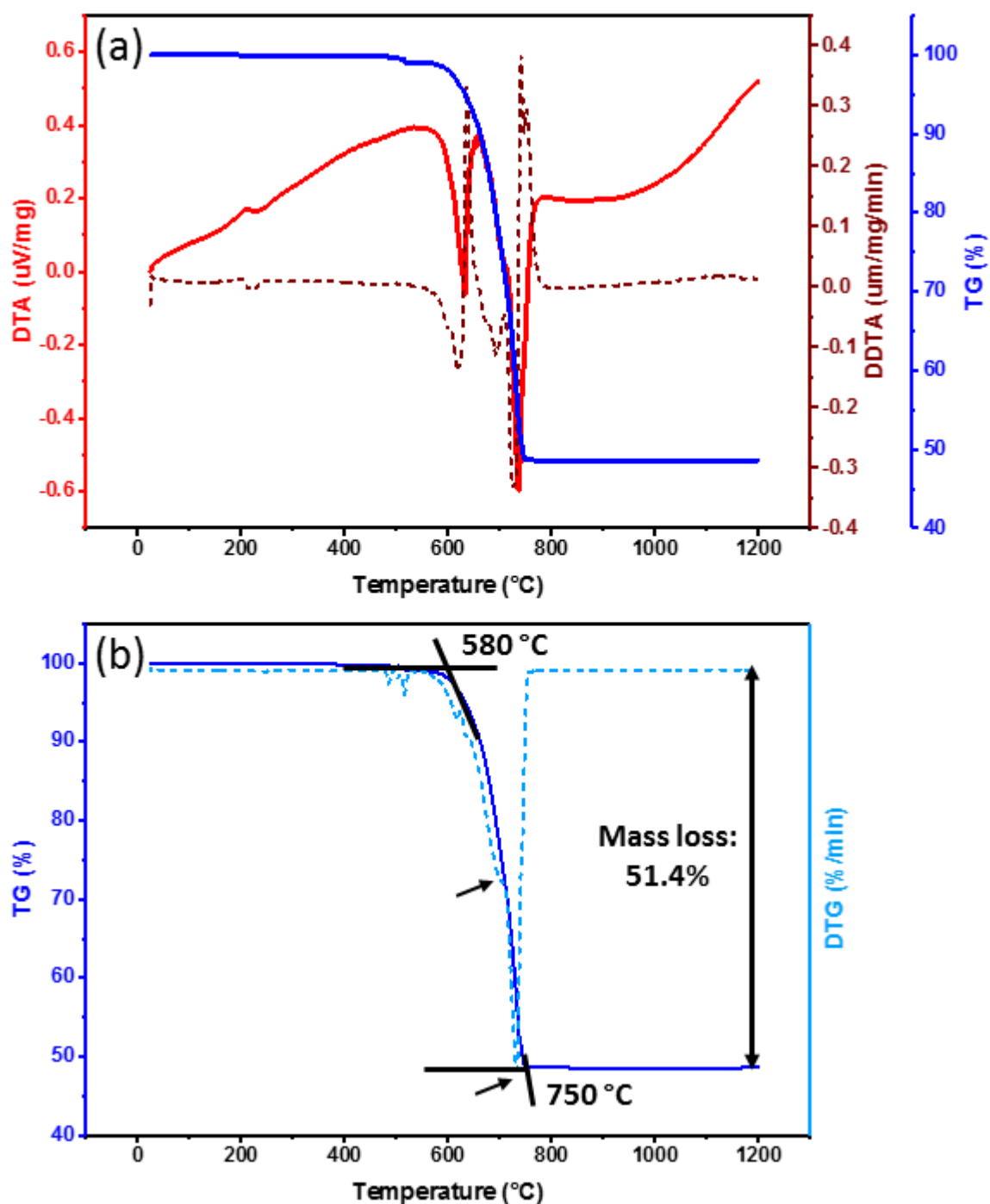


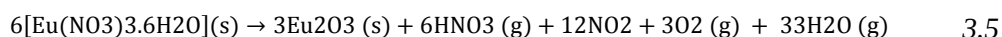
Figure 3.2. Thermal decomposition of $\text{Sr}(\text{NO}_3)_2$ under air atmosphere at a heating rate of 10 $^\circ\text{C}/\text{min}$ a) DTA-TG-DDTA curves and b) TG-DTG curve. Arrows in b specify the resolvable peaks in DTG plots indicative of the temperatures at which the rate of weight loss steps is maximum.

3.2.3 Europium Nitrate Hexahydrate (Eu (NO₃)₃. 6H₂O)

Thermal decomposition behavior of Eu (NO₃)₃. 6H₂O under air atmosphere with heating rate of 10 °C/min is shown in **Figure 3.5**. The decomposition process for europium nitrate hexahydrate is rather complex due to its molecular structure. In the structure of Eu (NO₃)₃.6H₂O, the Eu cation is coordinated by three NO₃ molecules and four water in the first coordination shell. The second coordination shell contains two lattice water molecules [122].

From the DTA curve in figure 3.3-a, the first endothermic peak occurs at 75°C which corresponds to simultaneous dehydration of the crystallization water molecules present in the 2nd coordination shell and hydrolysis of Eu(NO₃)₃.6H₂O. As a result of the hydrolysis reaction, nitric acid (HNO₃) forms. The onset of the second endothermic peak is at 155°C is related to further evaporation of water and evaporation of nitric acid. The small exothermic peak with an onset at about 250°C corresponds to formation of intermediate oxynitrides. The intense endothermic peak with an onset at 370°C which is accompanied by a sharp mass loss can be ascribed to complete decomposition of nitric acid by which H₂O, NO₂ and O₂ gases are liberated. The endothermic peak at 453°C can be attributed to degradation of oxynitrates. At this step, a complete denitrification is achieved by further losing NO₂ and only a hydrated europium oxide remains. Finally, after having lost lattice water, the hydrated Europium oxide will transform to Eu₂O₃ (above 600°C) [122].

From DTG curve in Figure 3.3-b, there are six visible peaks (highlighted by the arrows) which means that the mass loss profile contains six sequential steps as indicated in the TG plot. In addition, there is a good correspondence between the peaks in DTG curve (figure 3.3-b) with the endothermic peaks in DTA signal (Figure 3.3-a). Furthermore, the TG plot comes to a plateau at about 700°C which means that the decomposition process is completed. At the end of thermal decomposition, the experimental mass loss value of 59.2% was observed. The overall decomposition reaction for Eu(NO₃)₃.6H₂O can thus be described as :



The theoretical weight loss for reaction 3.5 was calculated as:

$$(\text{weight loss})_{th} = \frac{[(6 \times 63) + (12 \times 46) + (3 \times 32) + (33 \times 18)]}{[(6 \times 445.96)]} = 60.3 \%$$

The experimental mass loss 59.2% is consistent with the theoretical value of 60.3%.

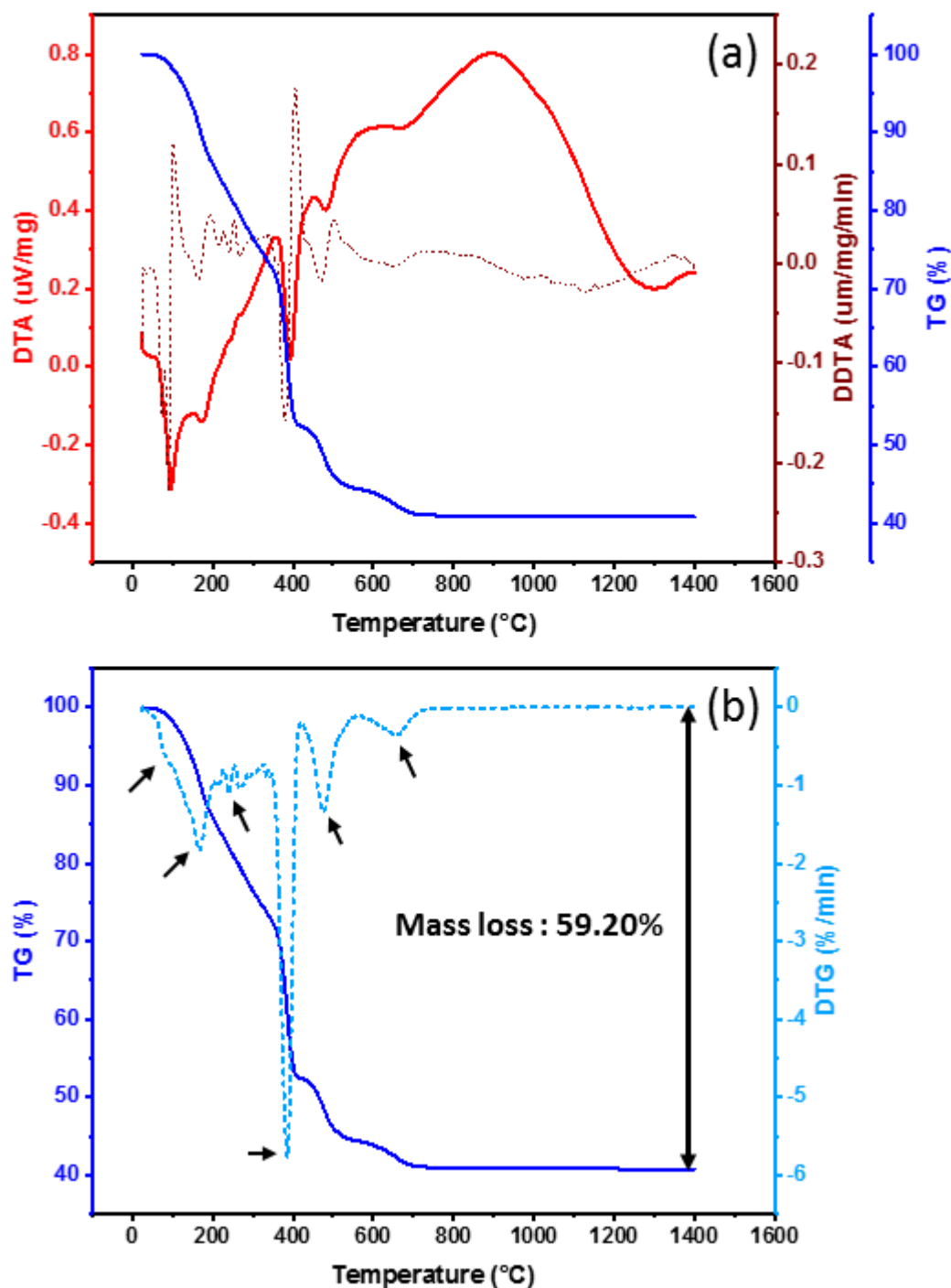


Figure 3.3. Thermal decomposition of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ under air atmosphere at a heating rate of 10 °C/min a) DTA-TG-DDTA curves and b) TG-DTG curve. Arrows in b specify the resolvable peaks in DTG plots indicative of the temperatures at which the rate of weight loss steps is maximum.

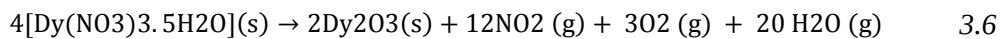
3.2.4 Dysprosium Nitrate Pentahydrate ($\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$)

Figure 3.4 shows the thermal decomposition of $\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ upon increasing temperature from room temperature to 1400°C at a heating rate of $10^\circ\text{C}/\text{min}$ under air atmosphere. The DTA-TG traces for $\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ is very identical to that of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ indicating that the two rare earth dopant nitrate precursors decompose with similar mechanism.

Thermal decomposition of dysprosium nitrate starts with condensation of the initial monomer $\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ to form a cluster of $6[\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ [123]. From the DTA signal in figure 3.4-a, the endothermic effect with an onset of 85°C corresponds to the fusion of crystallization water, hydrolysis of $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and formation of nitric acid and evaporation of the molten water. The second endotherm with an onset of 150°C is mostly related to evaporation of HNO_3 . The exothermic peak starting at 230°C is attributed to crystallization of intermediate unstable oxynitrates $3\text{Dy}_2\text{O}_3 \cdot 2\text{N}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$ and/or $3\text{Dy}_2\text{O}_3 \cdot \text{N}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$. The very intense endothermic peak at 358°C which is concurrent with a sharp mass loss is related to thermal decomposition of HNO_3 . The endotherm at 456°C is attributed to decomposition of intermediate oxynitrates to form a hydrated dysprosium oxide. The last endothermic effect at 608°C corresponds to dehydration of the dehydrated dysprosium oxide to form Dy_2O_3 [123].

Figure 3.4-b displays the TG-DTA signals during decomposition of $\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. The presence of five peaks in DTG plot represents the presence of five different slopes in the TG curve indicative of different stages of thermal decomposition. The experimental mass loss of 58.6% was obtained at the end of thermal decomposition where the TG curves flattened (above 700°C) and no further weight loss was observed.

The overall decomposition reaction for $\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ can thus be described as :



The theoretical weight loss for the decomposition reaction of 3.6 was obtained as:

$$(\text{weight loss})_{th} = \frac{[(12 \times 46) + (3 \times 32) + (20 \times 18)]}{[(4 \times 438.5)]} = 57.46 \%$$

The experimental mass loss value of 58.6% is fairly consistent with the theoretical value of 57.46% which confirms the validity of the suggested decomposition reaction.

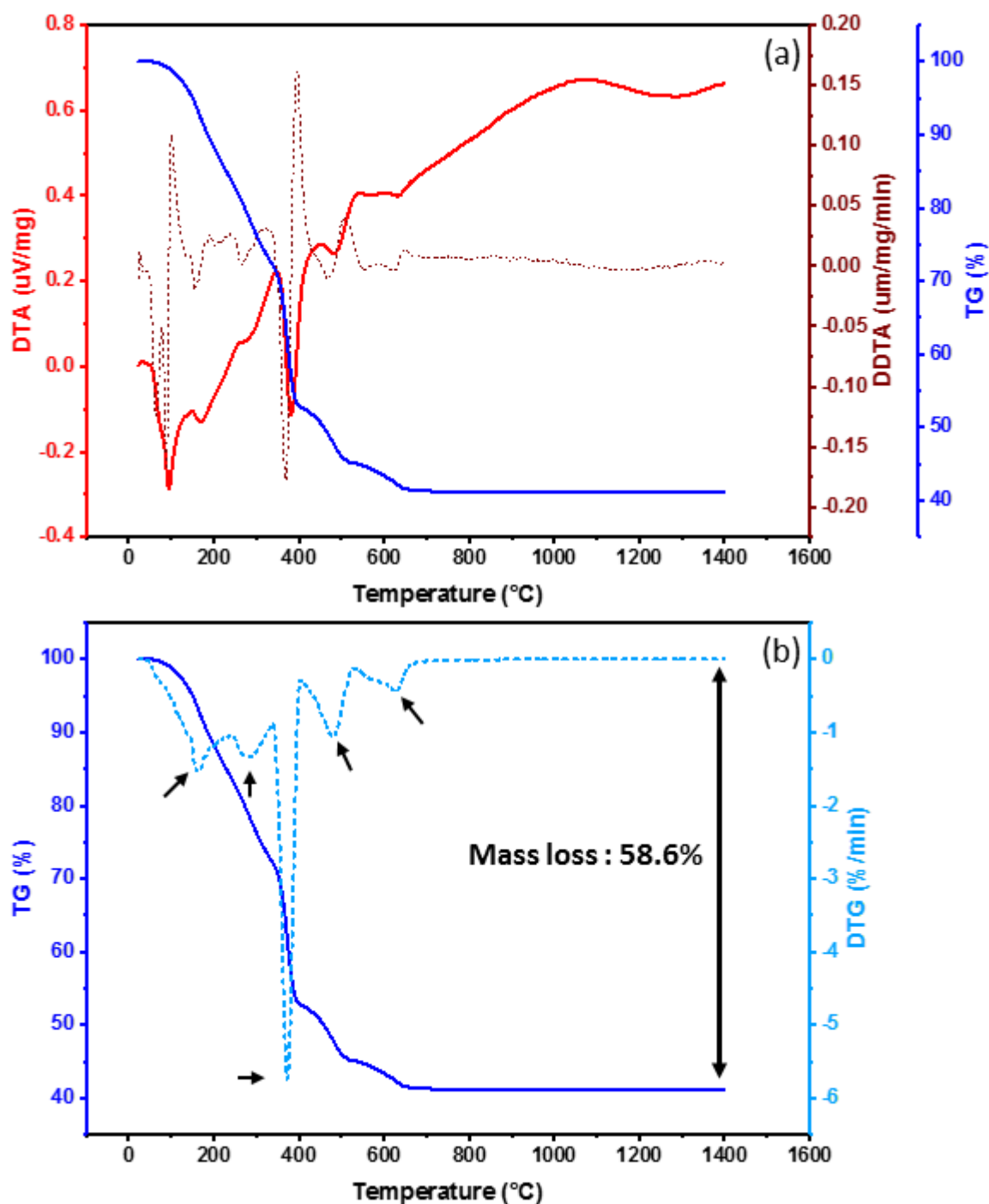


Figure 3.4. Thermal decomposition of $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ under air atmosphere at a heating rate of 10 °C/min a) DTA-TG-DDTA curves and b) TG-DTG curve. Arrows in b specify the resolvable peaks in DTG plots indicative of the temperatures at which the rate of weight loss steps is maximum.

3.2.5 Citric Acid Monohydrate ($C_6H_8O_7 \cdot H_2O$)

DTA-TG analysis of citric acid monohydrate is shown in **Figure 3.5**. From DTA signal in figure 3.5-a, the first endothermic effect with an onset at about 70°C was due to the removal of the absorbed moisture. The second endothermic peak with an onset at around 120°C was related to evaporation of water molecules from citric acid monohydrate. These two endotherms were accompanied by a shallow mass loss step in TG curve.

The intense endothermic peak with an onset at about 170°C, which was concurrent with a sharp mass loss, was related to the melting of citric acid, followed by dehydration of the molten material. This melting, which was followed by dehydration, formed aconitic acid [124, 125]. These two processes *e.g.* melting, and dehydration of citric acid occurred almost simultaneously, and it is difficult to resolve the endothermic peaks for melting and dehydration of the melt at a heating rate of 10 °C/min during thermal analysis. Decomposition of citric acid is known to be preceded by its melting [124, 125]. However, the two endothermic events appeared as an asymmetric endotherm in the DTA curve, and the corresponding intense peak in DTG signal in Figure 3.5-b showed a small shoulder, which indicates the presence of two thermal events ongoing at that temperature range.

The aconitic acid is the product of dehydration of citric acid and has two types of isomers: trans-acnitic acid and cis-acnitic acid. Upon further heating, the two isomer molecules will lose another unit of water and form anhydrate intermediate products. The small exothermic peak at slightly above 300°C is attributed to the isomerization reaction between aconitic acid isomers during which the cis-acnitic anhydride isomer is then transformed to the trans-type, due to the more thermodynamically stable arrangement of trans-type molecule [125]. The isomerization reaction was accompanied by a small weight loss step as indicated by a shallow peak in DTG signal slightly above 300°C (figure 3.5-b).

Finally, the broad exothermic peak that started slightly above 400°C and continued up to 600°C was related to the decarboxylation reaction, upon which carboxyl groups were fully decomposed and CO₂ gas was liberated. When all the carboxylic groups were completely burnt, the TG curves become flat, which means that the thermal decomposition of citric acid finished above 600°C. The experimental mass loss value of 100% was obtained above 600°C indication of complete decomposition of citric acid. In addition, the DTA signal suddenly dropped due to complete burn out of the carboxyl groups.

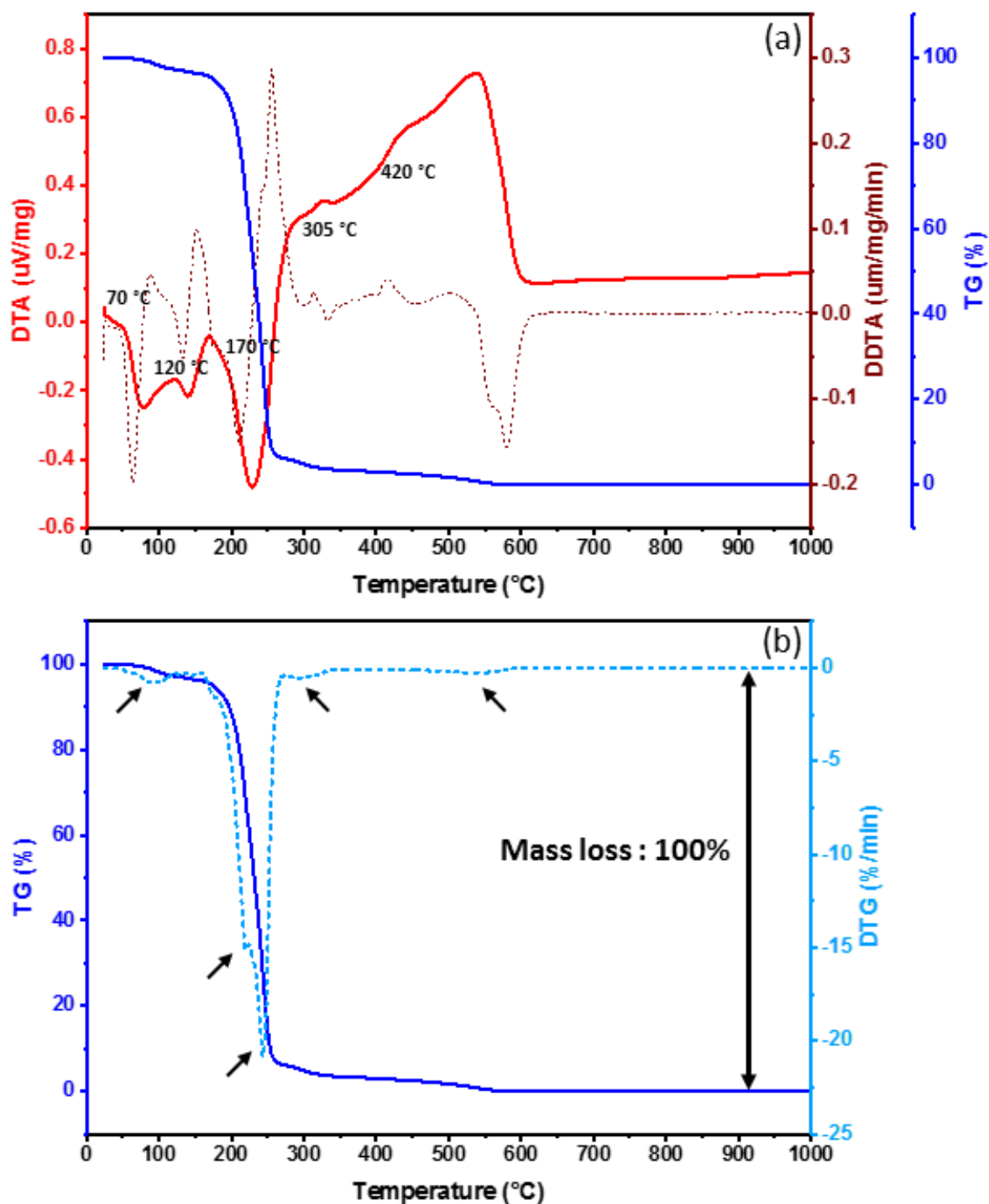
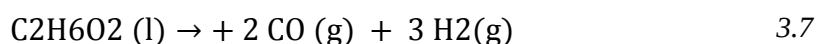


Figure 3.5. Thermal decomposition of citric acid monohydrate under air atmosphere at a heating rate of 10 °C/min a) DTA-TG-DDTA curves and b) TG-DTG curves. Arrows in b specify the resolvable peaks in DTG plots indicative of the temperatures at which the rate of weight loss steps is maximum.

3.2.6 Ethylene Glycol (C₂H₆O₂)

The thermogram related to thermal decomposition of liquid ethylene glycol is shown in **Figure 3.6**. From DTA curve, there was a sharp endothermic peak with an onset at about 150°C which was accompanied by a sharp mass loss. This endotherm was attributed to the boiling of ethylene glycol. The mass loss started at 155°C and finished at 330 °C. Therefore, EG was completely burnt at temperatures as low as 330 °C.

The global decomposition reaction for ethylene glycol can be expressed as [126]:



Therefore, upon thermal decomposition of EG, CO gas was released.

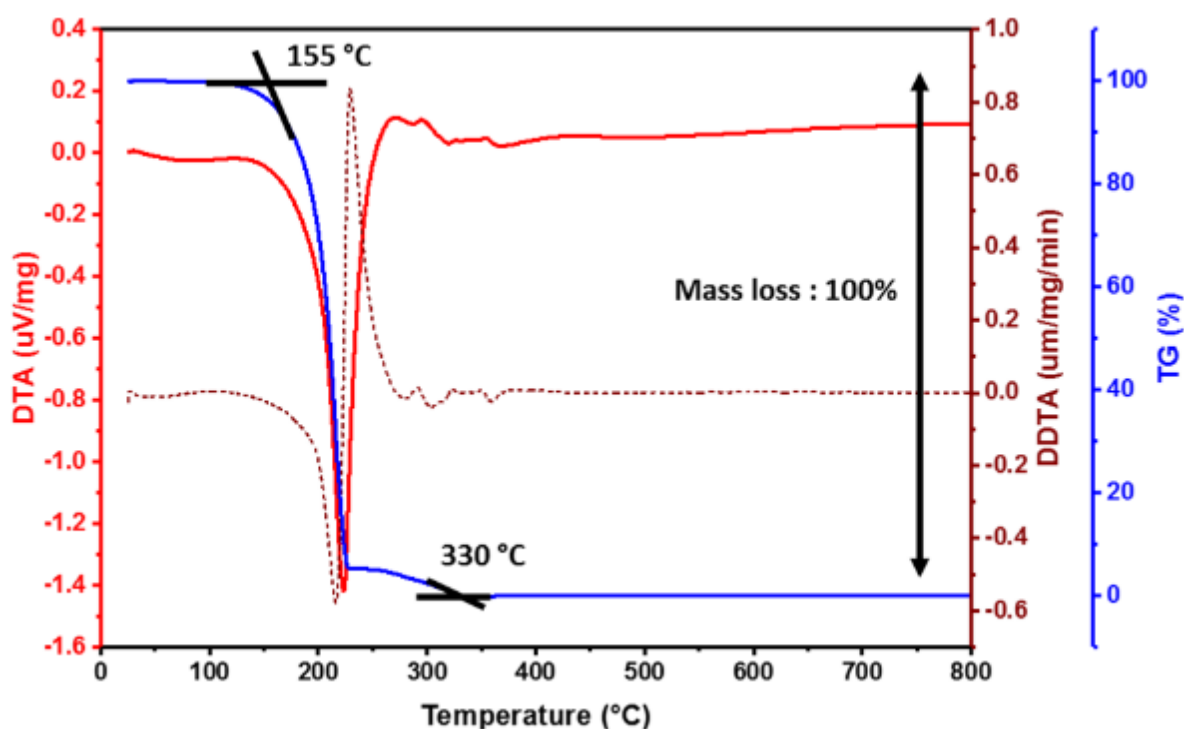


Figure 3.6. DTA-TG-DDTA curves obtained during thermal decomposition of ethylene glycol at a heating rate of 10 °C/min under air atmosphere.

3.2.7 CA + EG Mixture

Because during the Pechini processing, citric acid units used to stabilize the metal cations were cross-linked to each other through polyesterification reaction by ethylene glycol, we also investigated the thermal decomposition of citric acid and ethylene glycol mixture. Citric acid and ethylene glycol were mixed to a 1:1 mole ratio in boiling water. The solution was stirred for 30 minutes to obtain a homogenized viscose liquid. The mixture was then poured into a petri dish and cured in a box furnace at 120°C for 24 hours to allow the esterification reaction occurs. A transparent gel of CA + EG was obtained and was analyzed with DTA-TG technique at a heating rate of 10 °C/min under air, to monitor its thermal decomposition behavior. **Figure 3.7** shows the thermal decomposition of CA+EG against that of CA and EG. The DTA signal for CA + EG mixture is in fact a superimposition of thermal decomposition of the two organic materials with two major differences.

First, from the DTA signal in Figure 3.7-a, there is an exothermic peak with an onset of 155°C, which is probably related to polyesterification reaction between CA and EG. In addition, the wide exothermic peak attributed to the complete burn out of the CA spanned over a longer temperature range and decomposition of the carboxylic groups was delayed to about 800 °C (Figure 3.7-a).

Moreover, the comparison of the thermogravimetric analysis in figure 3.7-b showed that thermal decomposition of EG and CA were completed at about 300 °C and 600°C, respectively. However, the TG curve for the CA+EG leveled off at slightly below 800°C. Therefore, due to polyesterification between the CA and EG, an extended covalent polymer network form. These covalent bonds would delay the thermal decomposition of the organic mixture with respect to its constituents, making the Pechini processing capable of rendering a more homogenously dispersed metal cations throughout the polymer network as described in *Section 2.1.4*.

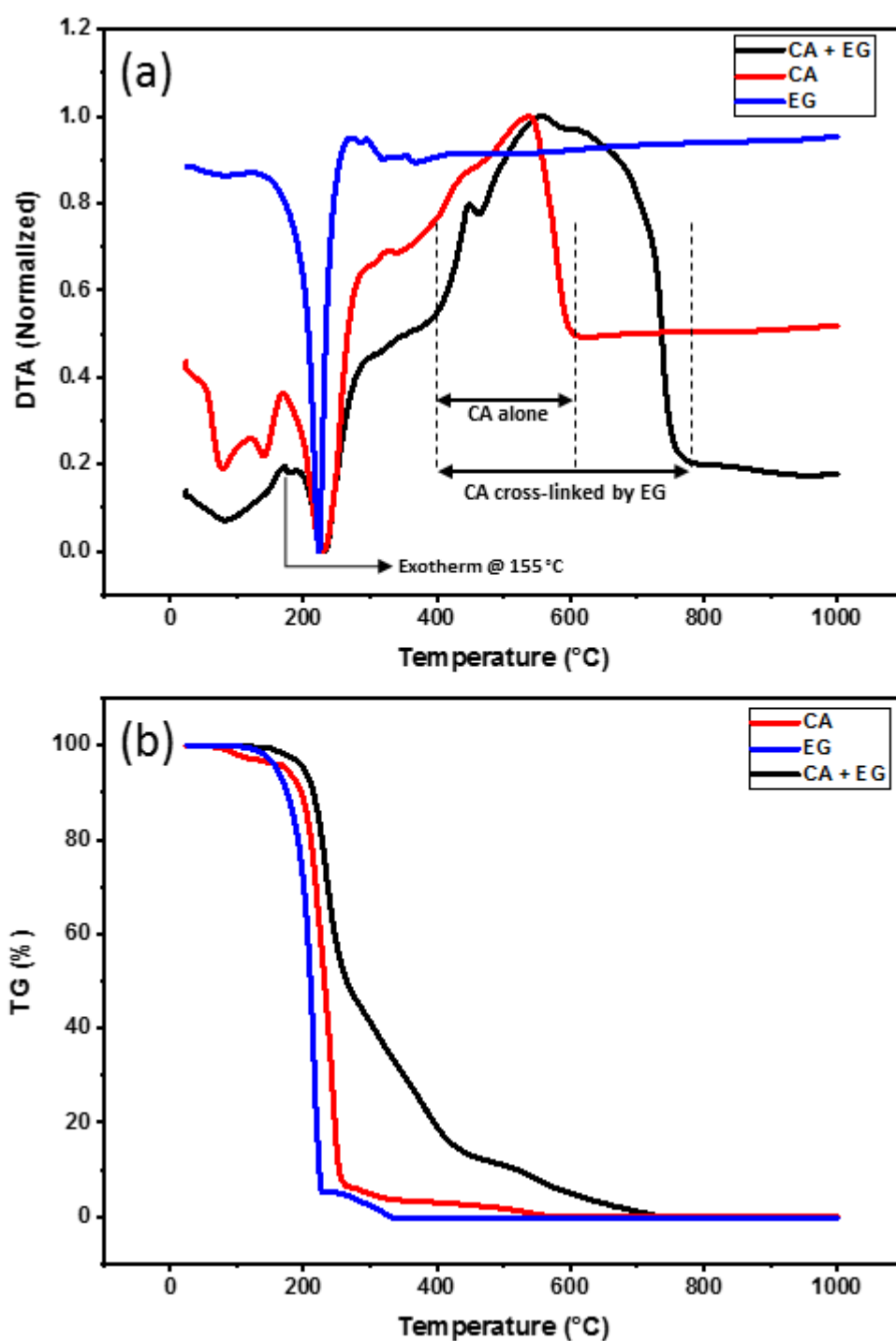


Figure 3.7. Comparison between thermal decomposition of CA, EG and CA+EG mixture
a) DTA signals b) TG signals.

3.3 Thermal Analysis of The Pechini-Processed S₄A₇ED Without B₂O₃

After understanding the thermal behavior of the individual precursors upon increasing temperature, we investigated the thermal behavior of the stoichiometric Sr₄Al₁₄O₂₅ doped with 1 mol% Eu and 1 mol% Dy during Pechini processing, *i.e.*, from the amorphous gel formed by polymerization of ethylene glycol and citric acid-chelated cations. The amorphous pre-ceramic material with the stoichiometry of S₄A₇ED without B₂O₃ was prepared as described in chapter 2 section 2.1.7. **Figure 3.8** shows the thermogram including DTA-DDTA signals (Figure 3.8-a) and the corresponding TG-DTG curves (Figure 3.8-b) for S₄A₇ED composition after dehydration of the mixture at 120 °C for 24 h (see Figure 2.10) at a heating rate of 10°C/min under air atmosphere. The thermal events upon increasing temperature of the S₄A₇ED amorphous mixture were identified by comparing the thermogram with that of individual precursors.

From the DTA curve in figure 3.8-a, the wide endothermic peak, which started at about 50°C continued up to 180 °C (labeled as #1), was the superimposition of several endothermic effects. When compared to the thermograms of the individual nitrate precursors, the main thermal events attributed to this endotherm were evaporation of the absorbed moisture, decomposition of nitrates in aluminum nitrate and the commencement of thermal decomposition of CA by evaporation of water molecules from citric acid monohydrate. In addition, partial decomposition of rare earth dopant nitrate precursors, including the evaporation of their water of crystallization, as well as evaporation of nitric acid due to nitrate pyrolysis occurred at this temperature range.

The sharp endothermic peak in the DTA signal (labeled as #2) that started at about 180°C and spanned up to 300°C (figure 3.8-a), was related to the overlay of endothermic boiling of EG along with partial degradation of CA including the melting followed by dehydration of the molten CA. It should be reminded that, during the thermal decomposition of EG, CO gas was liberated in the mixture as indicated by equation 3.7. This step was accompanied by a sharp mass loss as indicated by TG-DTG curves shown in figure 3.8-b.

The broad exothermic peak with an onset slightly around 380°C that extended up to approximately 500°C (labeled as #3), was attributed to decarboxylation reaction; during the thermal decomposition of CA and CO₂ gas was released. In addition, the evaporation of nitric acid as well as decomposition of oxynitrates that formed during the pyrolysis of

nitrate precursors, occurred at this temperature range and H₂O, NO₂ and O₂ gases were liberated. Due to the release of gaseous species, the exotherm was concurrent with an intense step of weight loss as indicated in the TG curve, and confirmed by the sharp DTG signal at the corresponding temperature range in figure 3.8-b.

At this point, it is worth mentioning that, due to the liberation of CO and CO₂ gases as a result of combustion of organic materials at the temperature range of 200-500°C, charring of the polymeric materials was highly possible. Because Sr²⁺ cations have a high reactivity towards the char as well as CO₃ species [127], it was possible that they have preferentially link themselves to the polymeric materials and become trapped as Sr-char complex and/or form SrCO₃ to some extent [127].

The very wide exothermic effect (labeled as #4) that started at around 550°C and extended to about 800°C, was identical to the exotherm that appeared during complete burn out of the polymeric materials during thermal decomposition of EG + CA mixture (see figure 3.7-a for comparison). However, in thermal analysis of the Pechini processed S4A7ED amorphous precursor, complete removal of the organics was shifted to slightly higher temperatures compared to CA + EG polymeric network without the presence of metallic cations. This was probably due to the fact that, when chelated divalent and trivalent cations are present, the decomposition of carboxylic groups of CA that have surrounded the metal cations by coulombic attraction, as described in *Section 2.1.4.1*, required more thermal energy to break the bonds between the chelating agent and the cations. Therefore, the broad exothermic between 550-800°C in DTA signal corresponded to pyrolysis of the polymeric network in the amorphous gel. This DTA peak was also accompanied by a separate step of mass loss as shown in the TG curve. The occurrence of a peak in the DTG plot at the corresponding temperature range also confirmed the change in the slope of TG curve, indicative of a step of mass loss related to this exotherm.

In addition, decomposition of Sr (NO₃)₂ alone occurred in the temperature range of 580-750 °C, as discussed in *Section 3.2.2* and shown in figure 3.2. However, the temperature range related to thermal decomposition of Sr (NO₃)₂ overlaps with the wide exothermic peak attributed to combustion of the organics materials, and thermal fingerprint for decomposition of Sr(NO₃)₂ was not resolvable in DTA signal of amorphous S4A7ED gel. In fact, the nitrate precursors of the metal cations dissolved in water during the Pechini processing of the pre-ceramic material and the metal-chelated ligands formed at the early

stage of powder synthesis. The nitrate species and oxynitrate by-products mainly decomposed at temperatures below 500°C [41, 127, 128].

The small exothermic peak with an onset of about 850°C (labeled as #5) was crystallization peak, most probably attributed to the crystallization of amorphous alumina precursor present in the S4A7ED mixture.

The exothermic effect with an onset at around 920°C (labeled as #6), which was concurrent with a small mass loss of about 3% (figure 3.8-b), and a wide peak in the DTG curve (figure 3.8-b), were attributed to char burn out during Pechini processing, *i.e.*, from the amorphous gel formed by polymerization of ethylene glycol and citric acid-chelated cations [127].

Finally, from the variation of the derivative of DTA signal in the temperature range labeled as #7, it seems that there is an exothermic event present above 1000 °C, most likely related to a phase transition in the amorphous alumina precursor. In addition, at the temperature range of 1200-1400°C (labeled as #8), there might be a very broad and faint exothermic peak, which can be an indication of a continuous reaction at elevated temperatures. The sequence of thermal events upon increasing temperature during crystallization of S4A7ED mixture processed by modified Pechini sol-gel method is summarized in **Table 3.1**.

Table 3.1. The sequence of thermal events obtained from thermal analysis of the Pechini processed stoichiometric S_4A_7ED from amorphous precursor after dehydration at 120°C for 24h.

No.	Peak Type	Temperature Range (°C)	Thermal Fingerprint
#1	Endo.	50 – 180	evaporation of absorbed moisture decomposition of Al-Nitrate partial decomposition of CA
#2	Endo.	180 – 300	decomposition of EG melting and dehydration of molten CA
#3	Exo.	380 – 500	decarboxylation of CA decomposition of nitrates and oxynitrate
#4	Exo.	550 – 800	burn out of the polymeric matrix
#5	Exo.	850 – 910	crystallization of amorphous alumina
#6	Exo.	920 – 950	char burn out
#7	Exo.	1000 - 1150	structural transformation of alumina
#8	Exo.	1150 - 1400	phase evolution reaction of strontium aluminate

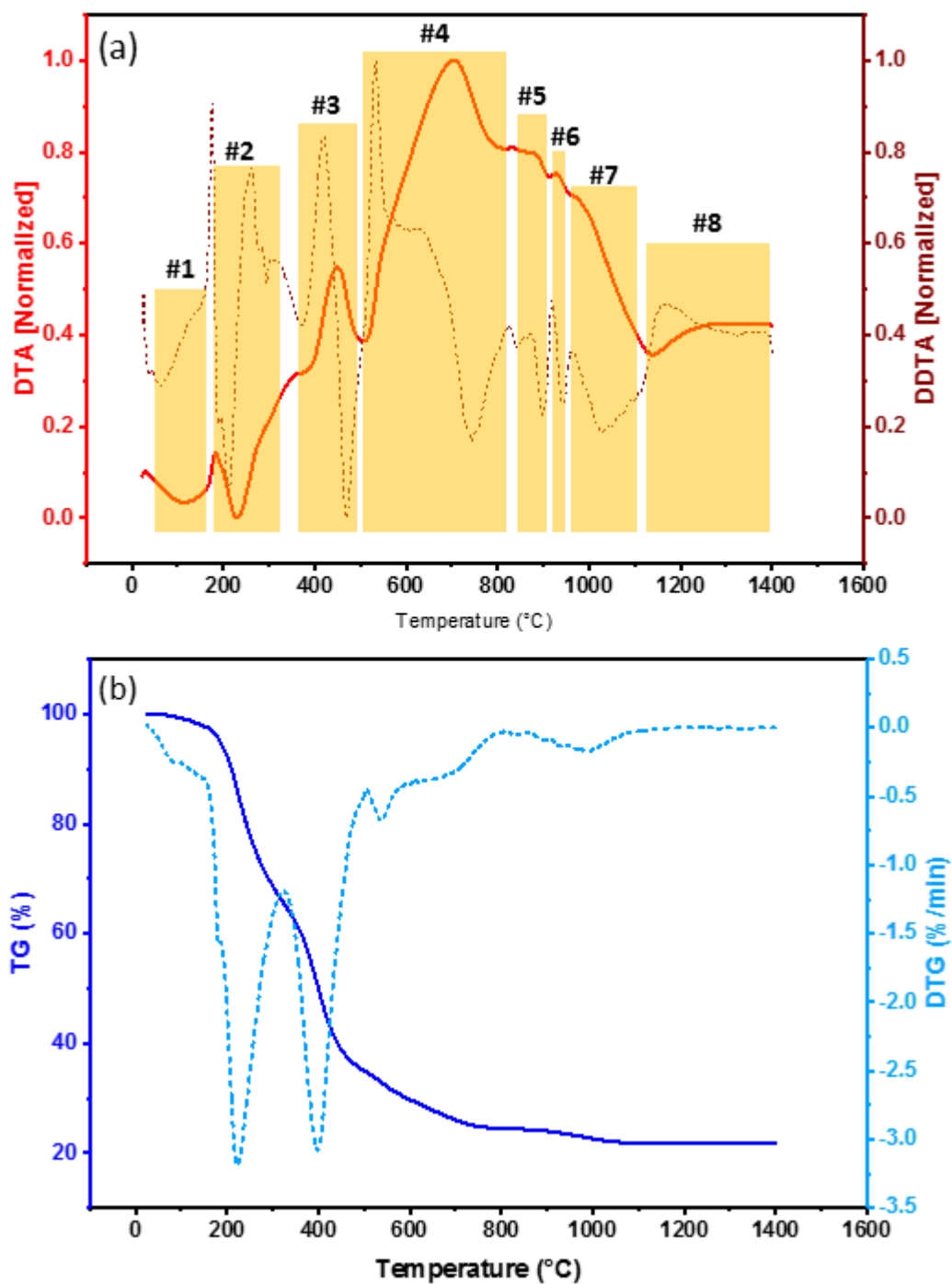


Figure 3.8. Thermal analysis of the Pechini processed S4A7ED mixture without B_2O_3 after dehydration at 120°C for 24h at a heating rate of 10°C/min under air atmosphere a) DTA-DDTA b) TG-DTG signals.

3.4 Crystallization of The Amorphous Alumina Precursor

Stable phases in the strontium aluminate system are composed of chains of corner, edge or face sharing alumina polyhedral units with general formula of AlO_x . In fact, the alumina scaffolds in the structure of strontium aluminates define the negatively charged sites with different spatial symmetry, and the charge deficiency between the Al^{3+} in tetrahedra and octahedra units is compensated for by incorporation of Sr^{2+} cations into the sub-lattice sites. Eu^{2+} as the emitting center is then substitutionally incorporated into the Sr^{2+} sites during ceramic processing. Because the optical properties of the strontium aluminates are directly dependent on the crystal field defined by site coordinating oxygens, the way in which alumina scaffold matrix is built up during phase evolution is of great importance. Therefore, before investigating the sequence of phase evolution during crystallization in the amorphous pre-ceramic with stoichiometric $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ doped with Eu and Dy, it is useful to evaluate the phase evolution of the alumina precursor alone, which is used during the synthesis of the pre-ceramic material.

In this course of the work, we present a study on the phase evolution of amorphous alumina obtained from decomposition of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as the alumina source in our system.

3.4.1 Thermal Analysis of The Nitrate-Free Al_2O_3

Thermal analysis of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (figure 3.1) revealed that at temperatures above 400 °C, most of the nitrates were decomposed. In addition, two small exothermic peaks related to crystallization amorphous Al_2O_3 and phase transition between alumina polymorphs were detected in the temperature range 800-1200°C. However, due to very intense endothermic effect caused by pyrolysis of nitrate materials, the crystallization peak at elevated temperatures were not well-resolved.

In order to investigate the phase evolution of amorphous alumina, it is necessary to start with an amorphous precursor, which is free of nitrates. This way, it is possible to look at the temperature range corresponding to the atomic arrangement of crystallizing alumina in more details. Based on the thermogram obtained during thermal decomposition of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (figure 3.1), the alumina nitrate precursor was calcined at 600 °C for 6 h at a heating rate of 10 °C/min in a box furnace to allow complete removal of the nitrates.

The nitrate free alumina precursor was then analyzed by differential thermal analysis at a heating rate of 10 °C/min under an air atmosphere.

Figure 3.9 shows the DTA signal of the nitrate- free alumina precursor after nitrate decomposition. The thermogram of amorphous alumina obtained from aluminum nitrate precursor after nitrate decomposition exhibited two exothermic peaks. The first exotherm onset appeared at 825°C and finished at 910°C. The second exothermic peak was sharper and started at 1090°C and transformation finished at 1150°C. This result was consistent with the thermogram of the spray-dried aluminum nitrate recorded by differential scanning calorimetry (DSC), reported by Douy *et al.* [41, 128].

The specified temperatures in the DTA signal were used to evaluate the sequence of phase evolution during crystallization of amorphous alumina.

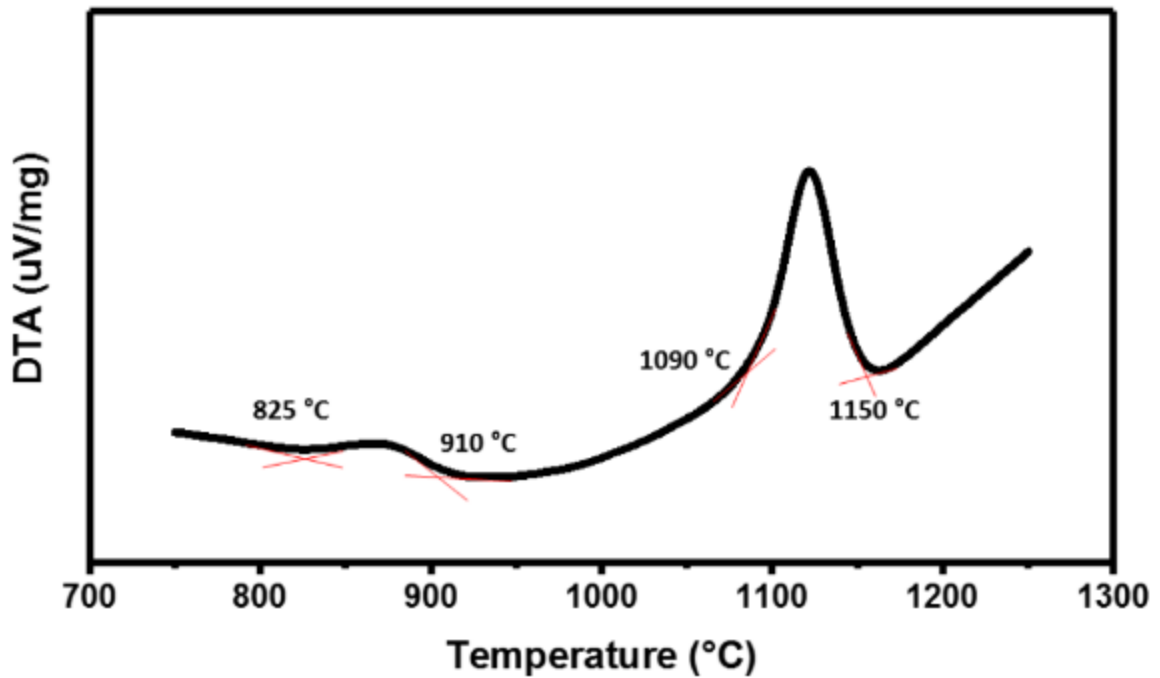


Figure 3.9. DTA signal of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ after calcination at 600C for 6 h at a heating rate of 10 °C/min under air atmosphere. The temperature range corresponding to crystallization region is shown.

3.4.2 Phase Evolution

In order to understand the sequence of phase formation during crystallization of the amorphous alumina obtained by the removal of the nitrates from the $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ precursor, we applied a systematic phase analysis study based on the DTA results shown

in figure 3.9. The nitrate-free amorphous alumina was heated at different temperatures at a heating rate of 10°C/min, from which the DTA signal in Figure 3.9 was obtained. The specimens were immediately removed from the furnace and allowed to cool to room temperature, to quench in the microstructure that had found. This strategy allowed us to characterize the actual phase that evolved at the temperature of interest. **Table 3.2** summarizes the calcination temperatures considered for investigation of phase evolution during crystallization of amorphous alumina precursor.

Table 3.2. Calcination temperatures considered for investigation of phase evolution during crystallization of amorphous alumina precursor based on DTA data.

Calcination temperature (°C)	DTA characteristic
825	1 st Exo. onset
910	1 st Exo. endpoint
1090	2 nd Exo. onset
1150	2 nd Exo. endpoint

Figure 3.10 shows the XRD patterns of the amorphous alumina heat treated at different temperatures. Phase analysis was performed by comparing the experimental XRD patterns against the reference PDF cards of α -Al₂O₃ (46-1212 JCPDS file), θ -Al₂O₃ (23-1009 JCPDS file), δ -Al₂O₃ (16-0394 JCPDS file) and γ -Al₂O₃ (50-0741 JCPDS file).

XRD analysis revealed that, the Al(NO₃)₃ · 9H₂O powder was X-ray amorphous after calcination at 600°C for 6 h. When the amorphous alumina precursor was heated to 825°C, the XRD pattern showed broad diffraction peaks, which is characteristics of metastable alumina transition phases with poor crystallinity. For the specimen that was calcined beyond the temperature of the first exothermic peak at 910 °C, the diffraction peaks became slightly sharper without any considerable change in the phase composition. The XRD patterns obtained from the specimens that were calcined at the onset and endpoint of the first exotherm, are in good agreement with the reference pattern attributed to γ -Al₂O₃ [98, 129, 130]. Douy *et al.* [41, 128, 131] reported that the spray dried aluminum nitrate, after annealing at 750°C for 3h, was amorphous, and it crystalized into a highly disordered, metastable γ -Al₂O₃ transition phase at temperature ranges of 840-880 °C. In addition, it has been shown that during the phase evolution of (Al, Fe)₂O₃ processed

by solution-based synthesis method using nitrate precursors, all compositions had first crystallized into a distorted solid solution of Fe^{3+} incorporated $\gamma\text{-Al}_2\text{O}_3$ at around 800 °C, regardless of the concentration of Fe^{3+} ions [132].

By increasing the temperature to the onset of the second DTA peak, reflections of the most stable alumina polymorph, the $\alpha\text{-Al}_2\text{O}_3$, started to appear and coexisted with a mix of metastable δ - and $\theta\text{-Al}_2\text{O}_3$ phases and a small residue of $\gamma\text{-Al}_2\text{O}_3$. The transition phases completely transformed to pure $\alpha\text{-Al}_2\text{O}_3$ as the specimen was heated to 1150 °C beyond the second exothermic peak.

Therefore, from phase analysis by XRD, it was observed that the amorphous alumina precursor obtained from aluminum nitrate, first crystallized to a meta-stable transition phase of highly disordered $\gamma\text{-Al}_2\text{O}_3$ at the temperature range of the first exothermic peak and then transformed into the thermodynamically stable α -phase through the second exotherm, as indicated by the DTA signal in Figure 3.9. The temperature range between the two exothermic peaks probably corresponded to phase transition from γ to α phase though conversion to δ and θ [96-98, 130]. Thus, a mixture of the transition phases is simultaneously present between the two exotherms.

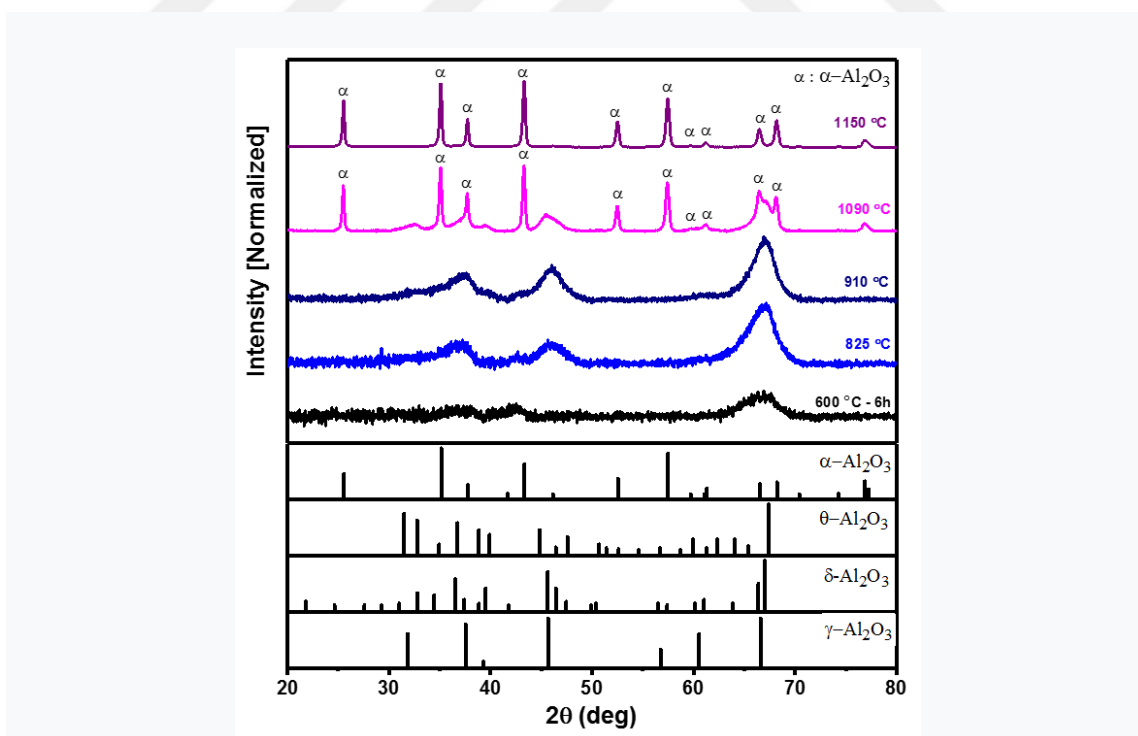


Figure 3.10. XRD patterns of the amorphous alumina powder obtained from decomposition of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ after calcination at 600°C for 6 h and heated to different temperatures of 825°C (1st exotherm onset), 910°C (1st exotherm endpoint), 1090°C (2nd exotherm onset) and 1150°C (2nd exotherm endpoint).

Because transition alumina structures including γ , δ and θ - Al_2O_3 have similar diffraction patterns, as shown in the reference patterns obtained from the JCPSD database in Figure 3.10, XRD analysis of these phases cannot be considered as a tool for precise determination of the exact metastable phases present. This is more problematic if the formation of transition phases occurred simultaneously during microstructural phase evolution. Under such circumstances, it is better to characterize the metastable phases by using vibrational spectroscopy techniques.

In order to complement the XRD results, we investigated the phase evolution of amorphous alumina at the temperature of the first and the second exothermic peaks in DTA profile by Raman spectroscopy. **Figure 3.11** shows the micro Raman spectra for the specimens that were heat treated according to the conditions in Table 3.2. For the specimen heated to 825 °C, the Raman spectrum showed a peak at about 468 cm^{-1} . When the amorphous alumina powder was heated to 910°C, the Raman peak at 468 cm^{-1} became more intense. This Raman band corresponded to the bending vibration mode of O – Al – O angle in tetrahedral units [133-135].

As the temperature approached to the onset temperature of the second exothermic peak at 1090°C, the Raman peak at 468 cm^{-1} disappeared, and the spectrum showed the seven well-known Raman-active modes at 378, 417, 430, 448, 576, 644 and 750 cm^{-1} , that are characteristic of the vibrational modes of AlO_6 octahedral units in α - Al_2O_3 [136-140]. For the specimen calcined at 1150 °C, the Raman peaks attributed to vibrational modes of six-fold coordinated Al^{3+} became slightly sharper. In addition, the Raman peak at 468 cm^{-1} was also observed in this specimen, possibly due to the presence of remnant metastable alumina phases containing tetrahedral units that had not completely transformed to α - Al_2O_3 during calcination.

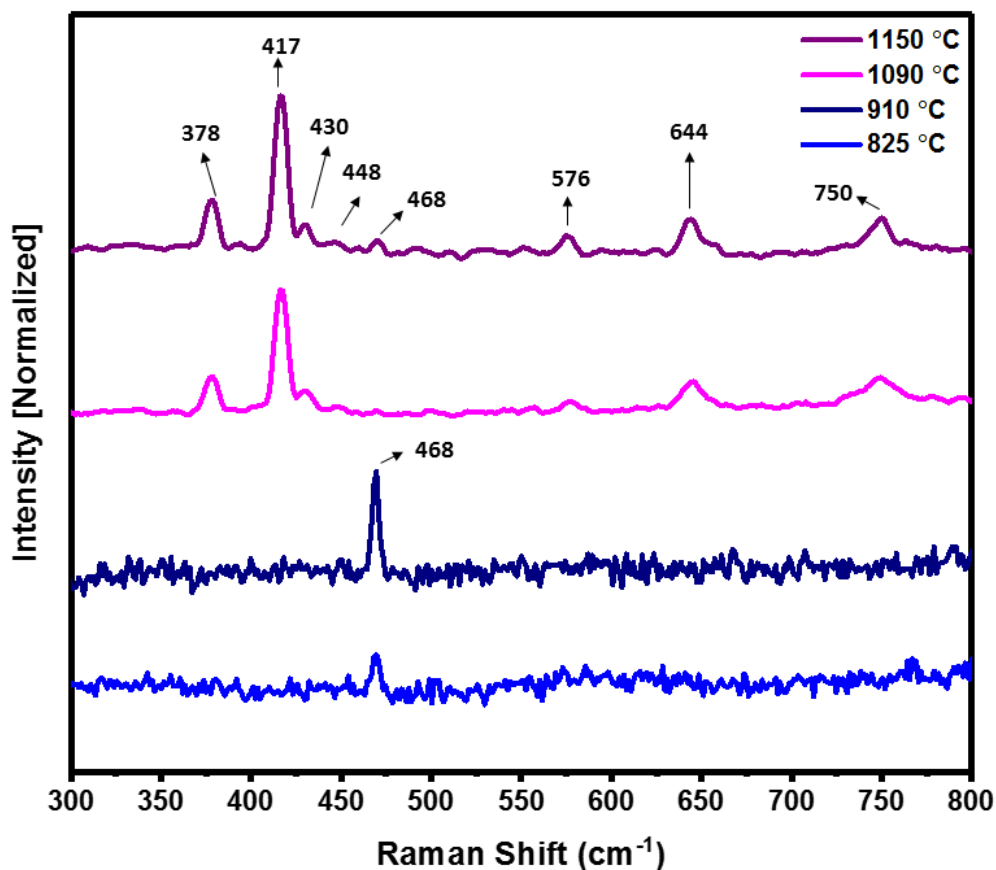


Figure 3.11. Raman spectra of the amorphous alumina powder obtained from decomposition of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ after calcination at 600°C for 6 h and heated to different temperatures of 825°C (1st exotherm onset), 910°C (1st exotherm endpoint), 1090°C (2nd exotherm onset) and 1150°C (2nd exotherm endpoint).

Figure 3.12 shows the schematic of the crystal structure of $\gamma\text{-Al}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$, respectively. The crystal structure of $\gamma\text{-Al}_2\text{O}_3$ is a defect spinel structure with Al^{3+} cations occupying 30% of the tetrahedral sites and 70% of the octahedral sites [141]. The chains of edge-sharing AlO_6 octahedrons are linked to each other through the corner-shared AlO_4 tetrahedral units (figure 3.12-a). The $\alpha\text{-Al}_2\text{O}_3$ however, is composed of Al^{3+} cations coordinated by six oxygens, and the structure contains Al^{3+} only in octahedral sites (Figure 3.12-b).

As a comparison between XRD and Raman analysis, X-ray diffractograms showed that, at temperatures close to the temperature range of the first exothermic peak in DTA (Figure 3.9), $\gamma\text{-Al}_2\text{O}_3$ with a distorted spinel structure evolved from the amorphous state. Although the crystal structure of γ polymorph contains Al^{3+} in both octahedral and tetrahedral sites, Raman spectra showed the fingerprint of the bending vibration mode attributed to

tetrahedral units at the onset and endpoint temperature of the first exotherm. This observation suggests that, during the phase evolution of amorphous alumina, the AlO_4 units were stabilized first as a rigid unit in the structure of metastable $\gamma\text{-Al}_2\text{O}_3$. Moreover, XRD and Raman analyses revealed that, the phase transformation from $\gamma\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$ had started around the onset temperature of the second exothermic peak. The transformation was then completed by passing through the second exotherm, as indicated by the X-ray diffractograms and the dominance of vibrational modes of Al^{3+} purely in 6-fold coordination, characteristic of corundum structure.

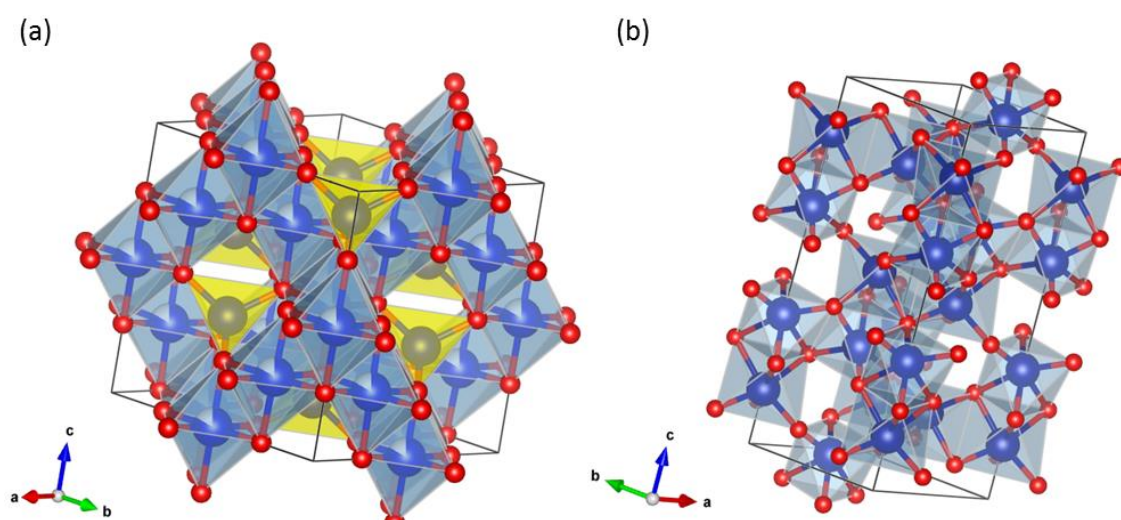


Figure 3.12. Schematic representation of alumina polymorphs a) crystal structure of $\gamma\text{-Al}_2\text{O}_3$ containing both tetrahedral and octahedral sites. The Al^{3+} in tetrahedral sites are highlighted in yellow b) crystal structure of $\alpha\text{-Al}_2\text{O}_3$ composed of Al^{3+} cations only in octahedral sites.

3.4.3 Crystallization Kinetics During Phase Evolution of Amorphous Alumina

In order to investigate the kinetics of crystallization, in particular the activation energy and the Avrami exponent, of amorphous alumina, we performed a non-isothermal kinetics study as describes in Section 2.2.1.2.2. DTA of the nitrate-free alumina precursor (obtained from calcination of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ at 600°C for 6 h) was carried out at heating rates of 3, 5, 10, 20 and $30^\circ\text{C}/\text{min}$ in air atmosphere. The DTA temperature calibration was conducted by using the melting point of pure metal standards. **Figure 3.13** summarizes the DTA signals from nitrate-free amorphous alumina at different heating rates and the crystallization peak temperatures (T_p) for the two exotherms under various

heating rates as listed in **Table 3.3**. It was observed that, by increasing the heating rate, the crystallization peak temperatures (T_p) of the exothermic peaks shifted to higher temperatures.

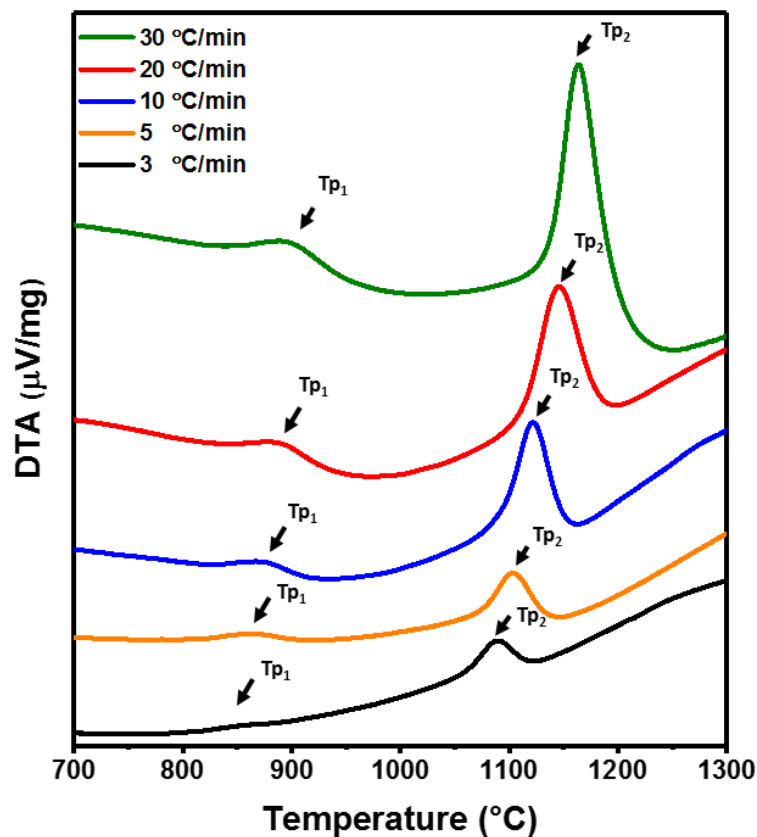


Figure 3.13. Non-isothermal DTA curves of amorphous alumina precursor obtained at different heating rates. The arrows specify the crystallization peak temperatures T_{p1} and T_{p2} for the first and second exothermic peaks, respectively.

Table 3.3. Crystallization peak temperatures for amorphous alumina obtained under different heating rates.

Heating Rate (°C/min)	Crystallization Peak Temperature (°C)	
	1 st Exo. (T_{p1})	2 nd Exo. (T_{p2})
3	852	1090
5	860	1103
10	872	1122
20	892	1146
30	899	1164

The activation energy (E) of crystallization and phase transformation was obtained based on the variation of the maximum temperature of the exothermic peak by heating rate, using the Kissinger model that was described in detail in *Section 2.21.2.2.1* and *Equation 2.12* in chapter 2. Moreover, the values of the Avrami exponent (n) were determined from the fraction crystallized at a specific temperature, according to DTA traces recorded at different heating rates and based on the Ozawa model as discussed in *Section 2.21.2.2.2* and *Equation 2.13*.

Figure 3.14-a shows the plots of $\ln \left(\frac{\beta}{T_p^2} \right)$ versus $\frac{1}{T_p}$ for calculation of the activation energies for crystallization of γ -Al₂O₃ from the amorphous state (first exothermic peaks) and for evolution of α -Al₂O₃ phase (second exothermic peaks), according to the Kissinger method. It is worth mentioning that in this case, β is the heating rate and T_p is considered as absolute temperature of the crystallization peak maximum in Kelvin. The line fitted to the data points in the plot is expected to be linear, and the slope of the straight line is proportional to the activation energy (E) of the reaction that takes place at the corresponding exothermic peak in DTA signal. The uncertainty in the activation energy values were obtained by means of calculation of uncertainty in the slope using the T-test method.

From Figure 3.14-a, it was observed that the fitted lines for the two exothermic peaks during crystallization of amorphous alumina was almost parallel, indicative of similar activation energies found for the two thermal events. The activation energy obtained for crystallization of γ -Al₂O₃ from amorphous precursor was 496.81 ± 31 kJ/mol. As confirmed by Raman spectroscopy, the formation of aluminum tetrahedral units was dominant around the first exothermic peak. Therefore, the activation energy of 496.81 ± 31 kJ/mol was attributed to the stabilization of AlO₄ sites in the defect spinel structure of γ -Al₂O₃ from the amorphous state.

For the phase transformation of $\gamma \rightarrow \alpha$ -alumina, the activation energy of 486.93 ± 23 kJ/mol was observed. Because the value of activation energy obtained for this transformation was comparable to the enthalpy of Al – O, i.e. the energy for breaking the bond, of 512 kJ/mol [142], the evolution of α - Al₂O₃ appeared to involve changes in ionic bonds accompanied by diffusion of Al³⁺ and O²⁻ ions into the structure of metastable γ -alumina [143, 144].

Figure 3.14-b shows the plots of $\ln [-\ln (1 - \alpha_T)]$ against $\ln \beta$ for determining the Avrami exponent n and the growth mode during phase evolution of alumina amorphous precursor. In this case, α_T represents the fraction transformed under exothermic peaks at a specific temperature and β is the heating rate. In evaluating n for the first exothermic peak, α_T was considered as the area under the peak at 900 °C, and for the second exothermic peak, α_T was set to the fraction crystallized up to 1135 °C for the DTA peaks recorded at the heating rates of 5, 10, 20 and 30°C/min in air.

The value of n for crystallization of amorphous alumina into $\gamma\text{-Al}_2\text{O}_3$ at the first exothermic peaks was determined to be 0.85. For the evolution of α phase at the second exothermic peak, a value of 2.45 was obtained for n . Much effort has been dedicated to interpreting the value of Avrami exponent. It is well-known that for the crystallization processes that are controlled by nucleation and growth, $n \sim 1$ is characteristics for surface crystallization, which is governed by the growth of the previously formed nuclei. When $0 < n < 3$, crystallization takes place from both surface and the bulk. For $n \geq 3$, the internal nucleation and growth dominates the crystallization with increasing nucleation rate [145, 146]. Therefore, formation of $\gamma\text{-Al}_2\text{O}_3$ from amorphous precursor initiates from the pre-existing nuclei formed on the surface. In addition, the evolution of α phase at the second exothermic peak with a $n = 2.45$ implies that the transformation occurs simultaneously from both the surface and the interior of the pre-existing metastable phase.

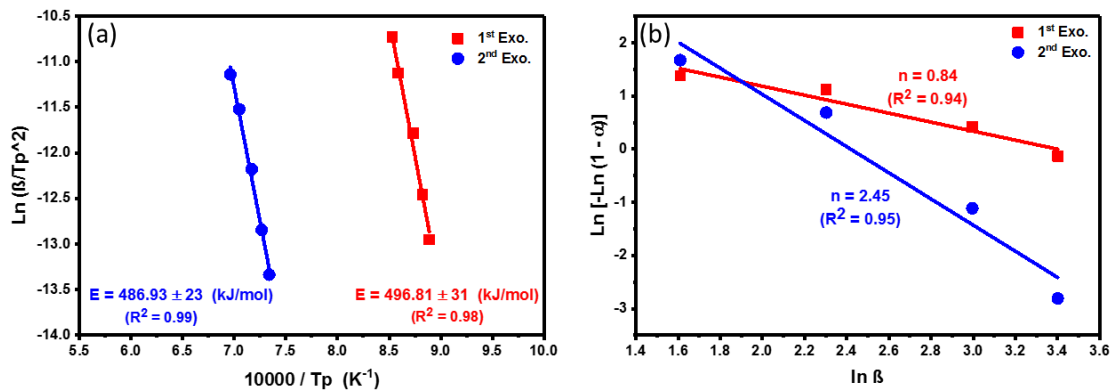


Figure 3.14. Plots used for determination of kinetics parameters based on non-isothermal kinetics a) Kissinger plots for determination of activation energy during crystallization and phase transformation of amorphous alumina and b) The Ozawa-type plots for determination of Avrami exponent. The straight lines in red corresponds to the first exothermic peak and the ones in blue is related to the second exotherm.

3.5 Crystallization of Pechini-Processed S4A7ED Without B₂O₃

After investigating the phase evolution of alumina, which forms the scaffold in the crystal structure of strontium aluminate ceramics, in this section, we evaluated the crystallization of amorphous pre-ceramic of (SrO)₄·(Al₂O₃)₇ doped with 1 mol% Eu and 1 mol% Dy without the presence of B₂O₃ as the sintering flux. A similar approach as discussed in evaluation of phase formation during crystallization of amorphous alumina was considered, which is presented in this section.

3.5.1 Thermal Analysis of The Formation of Organics-Free S4A7ED Without B₂O₃

In *Section 3.3*, we discussed the sequence of the thermal events, when the amorphous precursor of the Pechini processed S4A7ED after gel dehydration, was heated from room temperature to 1400 °C. Except for the thermal events that were listed in *Table 3.1*, it was observed that the decomposition of the nitrate materials and the combustion of the organics were completed at temperatures close to 800°C. In addition, from *Figure 3.8* and *Table 3.1*, it can be seen that the crystallization fingerprints that were reflected in the high temperature regime of the thermogram (above 850 °C), were not well-resolved, due to the presence of intense endothermic and exothermic effects attributed to nitrate decomposition and organics burn-out. In order to investigate the sequence of phase evolution, it was necessary to obtain a clear thermogram, in which the temperature range concerning the crystallization of the strontium aluminate phases were visible. We thus pre-calcined the dehydrated amorphous powder of S4A7ED at 800°C for 3 h in a box furnace at a heating rate of 10 °C/min in an oxidizing atmosphere, to fully decompose the nitrates and to remove the organics materials used during the synthesis by Pechini method. The pre-calcined powder was analyzed by DTA-TG from room temperature to 1400 °C at a heating rate of 10 °C/min in air.

Figure 3.15 shows the DTA signal of the S4A7ED amorphous pre-ceramic material after pre-calcination at 800 °C for 3 h. The first observation was that, after pre-calcination step, the crystallization peaks were clearly characterized with two exothermic peaks and heating the dehydrated sponge-like gel to 800 °C at a ramping rate of 10 °C/min and soaking time of 3 h was sufficient for complete removal of the organic components and the nitrates. XRD analysis of the pre-calcined powder (not shown here) also revealed that

the specimen was still amorphous and pre-calcination at 800 °C for 3 h did not induce detectable crystallization. We thus considered *dehydration of the gel at 120 °C for 24 h followed by pre-calcination at 800 °C for 3 h* as our basic recipe for investigation of phase evolution during crystallization of Pechini processed S4A7ED composition with and without B₂O₃ in this work.

The DTA trace of the B₂O₃-free compound showed two exothermic peaks. The first exotherm was sharper, starting at 930 °C and finishing at 965°C and was followed by a less intense and broader peak that has an onset and endpoint of 1110°C and 1180°C, respectively. Similar results had been observed during crystallization of amorphous precursor of spray-dried amorphous precursor of S₄A₇ composition processed by using aluminum nitrate and strontium nitrate as the starting materials by DSC [41] .

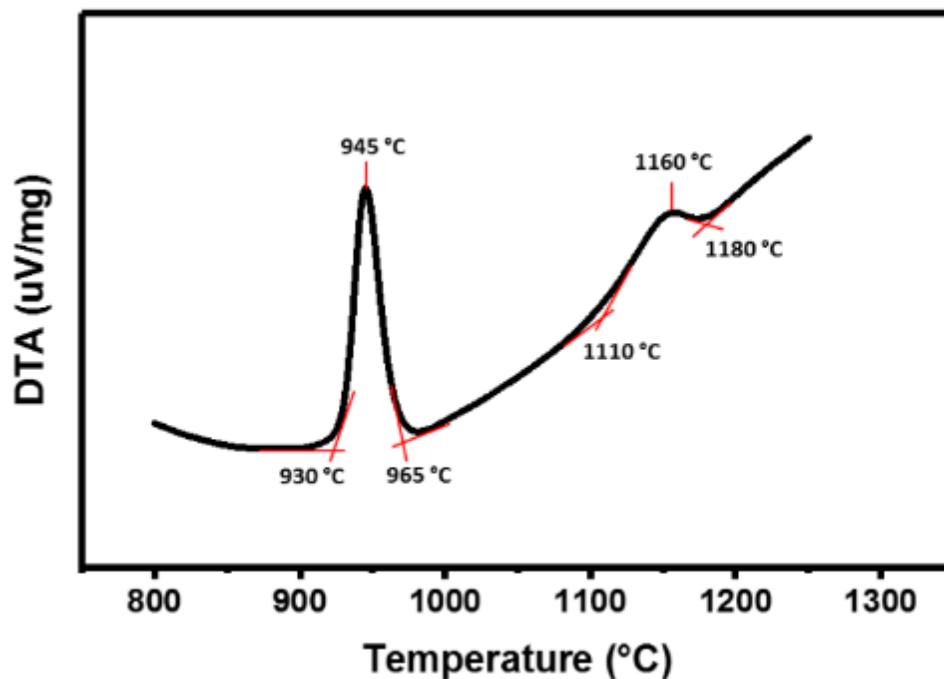


Figure 3.15. DTA plot of the Pechini processed S4A7ED composition after pre-calcination at 800°C for 3h at a heating rate of 10 °C/min under air atmosphere.

3.5.2 Phase Evolution of B₂O₃ – Free S4A7ED Compound

To evaluate the sequence of phase formation in the amorphous pre-ceramic of S4A7ED composition, the DTA signal shown in figure 3.15 was used as a road map to determine the appropriate calcination temperatures. Because DTA was performed on the pre-

calcined powder precursor with a heating rate of 10 °C/min under the flow of air, all heat treatments to the desired temperatures were implemented with the same ramping rate in a box furnace, to keep the experimental conditions as similar as possible to that of DTA. After heating to the target temperature, all the specimens were rapidly cooled (air-quenched) to allow the actual microstructure to be preserved, minimizing the possibility of any reversible reaction upon cooling under equilibrium. We also investigated the effect of calcination dwell time at 1300 °C, at which S4A7 composition is the thermodynamic equilibrium phase. The calcined powders were then characterized by globally averaged characterization methods, including XRD and microstructural investigation by SEM. The calcination temperatures and dwell times considered for the study of phase evolution sequence from amorphous S4A7ED under conditions listed in **Table 3.4**.

Table 3.4. Calcination temperatures and dwell times used for investigation of phase evolution in amorphous S4A7ED – 0% B₂O₃ composition.

Calcination conditions (°C)	DTA characteristic
880 °C	50 °C below the 1 st Exo. onset
930 °C	1 st Exo. onset
965 °C	1 st Exo. endpoint
1015 °C	50 °C above the 1 st Exo. endpoint
1060 °C	50 °C below the 2 nd Exo. onset
1110 °C	2 nd Exo. onset
1180 °C	2 nd Exo. endpoint
1230 °C	50 °C above the 1 st Exo. endpoint
1300 °C – 0 h	-
1300 °C – 1 h	-
1300 °C – 5 h	-
1300 °C – 10 h	-
1300 °C – 20 h	-

Figure 3.16 displays the XRD patterns of the S4A7ED – 0% B₂O₃ pre-ceramic powder specimens that were heated to the characteristic temperatures of the first exothermic peak *e.g.* 880, 930, 965 and 1015°C. The specimen heated to 880°C below the first DTA peak

showed a very broad and diffuse peak indication of amorphous nature with short range order. As the temperature increased to the onset temperature of the first exothermic peak at 930°C, the crystalline peaks attributed to SrAl_2O_4 (SA) phase in both hexagonal (31-1336 JCPDS file) and monoclinic (34-0379 JCPDS file) polymorphs along with SrAl_4O_7 (SA_2) phase (25-1289 JCPDS file) started to appear. However, the crystallinity of the specimen was still poor. For the specimen heated to the endpoint temperature of the first DTA peak, the XRD pattern showed that the diffuse amorphous hump decreased, and the crystallinity of the specimen was improved. In addition, the intensity of the peaks related to SA_2 phase did not change significantly, while the peaks attributed to SA phases became more intense, as highlighted in the XRD patterns. The presence of $\gamma\text{-Al}_2\text{O}_3$ phase was also detected in this specimen, as reflected by a shallow broad peak at $2\theta = 67^\circ$ (not shown here) and confirmed by Rietveld phase analysis of the XRD pattern. When the temperature was increased beyond the first exothermic peak to 1015 °C, the diffraction pattern did not show any significant compositional change, while monoclinic and hexagonal SA, SA_2 and $\gamma\text{-Al}_2\text{O}_3$ phases coexisted.

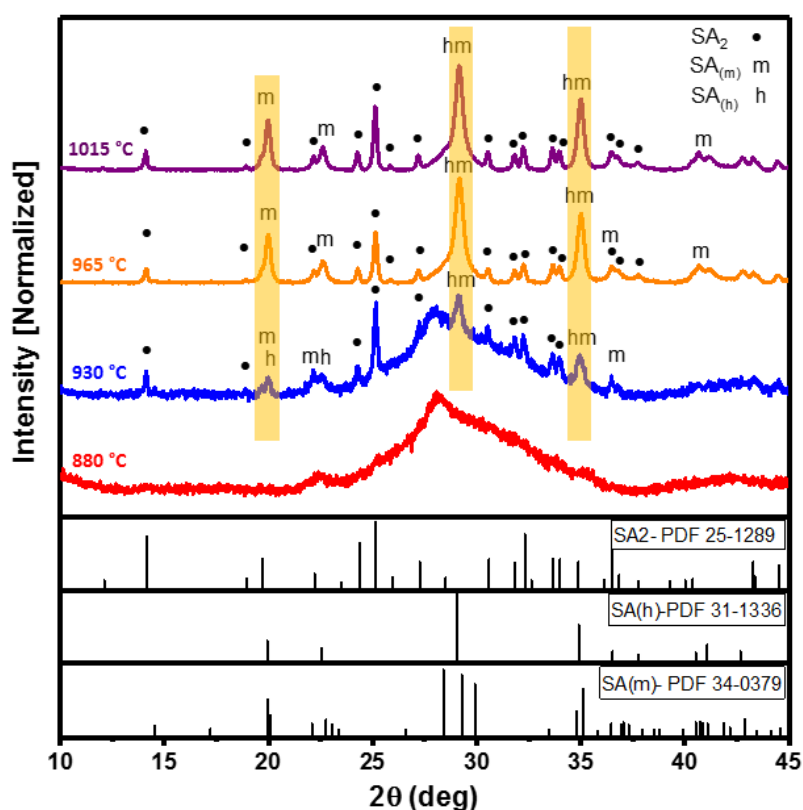


Figure 3.16. XRD patterns of the amorphous pre-ceramic of S4A7ED – 0 mol% B_2O_3 composition heated to the characteristic temperatures of the first DTA exotherm at 880, 930, 965 and 1015 °C.

Figure 3.17 shows the diffractograms for the amorphous pre-ceramic of S4A7ED compound that were calcined to the characteristic temperatures of the second exothermic peak in the DTA signal. As the temperature increased to 50°C below the second exothermic peak, *e.g.* at 1060 °C, the SA phases, consisting of both hexagonal and monoclinic structures, still dominated the phase composition. At the onset temperature of the second exotherm at 1110 °C, XRD analysis implied that the intensity of the diffraction peaks corresponding to SA₂ phase increased at the expense of SA phase, and SA₂ became the dominant phase. Further heating to the temperature of the second DTA peak endpoint at 1180 °C, resulted simultaneously in the appearance of the S₄A₇ (74-1810 JCPDS file) phase and the increase in the phase fraction of SA₂, while the reflections related to the metastable SA phase had decreased. It should be noted that at this temperature only the monoclinic SA (SA_m) phase was detected. In addition, the γ -Al₂O₃ phase disappeared, as confirmed by Rietveld quantitative analysis of the XRD pattern. The composition of the specimen heated to beyond the second exothermic peak at 1230 °C did not undergo a significant change, and SA₂ dominated the phase composition, while S₄A₇ and the metastable SA_m phases were also present.

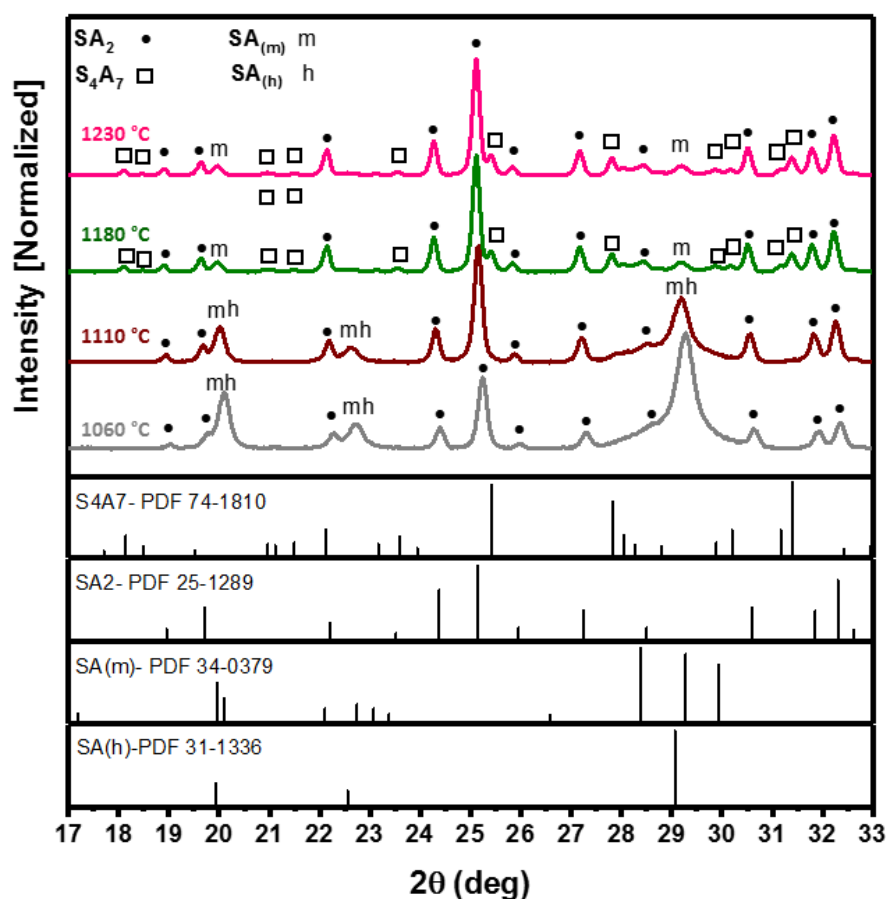


Figure 3.17. XRD patterns of the amorphous pre-ceramic of S4A7ED – 0 mol % B₂O₃ composition heated to the characteristic temperatures of the second DTA exotherm at 1060, 1110, 1180 and 1230 °C.

The results of Rietveld quantitative phase analysis of the XRD patterns obtained from the calcination of S4A7ED – 0 mol% B₂O₃ pre-ceramic material is summarized in **Table 3.5**.

Table 3.5. Phase composition revealed by Rietveld quantitative analysis of the XRD data from specimens processed under different calcination temperatures. R_{wp} and R_{exp} are weighted profile and expected R -factors, respectively.

Temperature (°C)	Phase Composition (wt%)					Goodness of Fit (R_{wp}/R_{exp})
	SA _m	SA _h	SA ₂	γ -Al ₂ O ₃	S4A ₇	
965	30.47	30.89	22.84	15.80	-	2.26
1015	30.02	28.52	26.30	15.16	-	2.34
1060	34.03	26.09	27.15	12.73	-	2.11
1110	26.27	12.78	50.27	10.68	-	2.25
1180	12.77	-	65.59	-	21.63	2.16
1230	12.34	-	65	-	22.66	2.13

To facilitate comparison of trends in phase fraction change, the results of quantitative phase analysis is also presented in **Figure 3.18**.

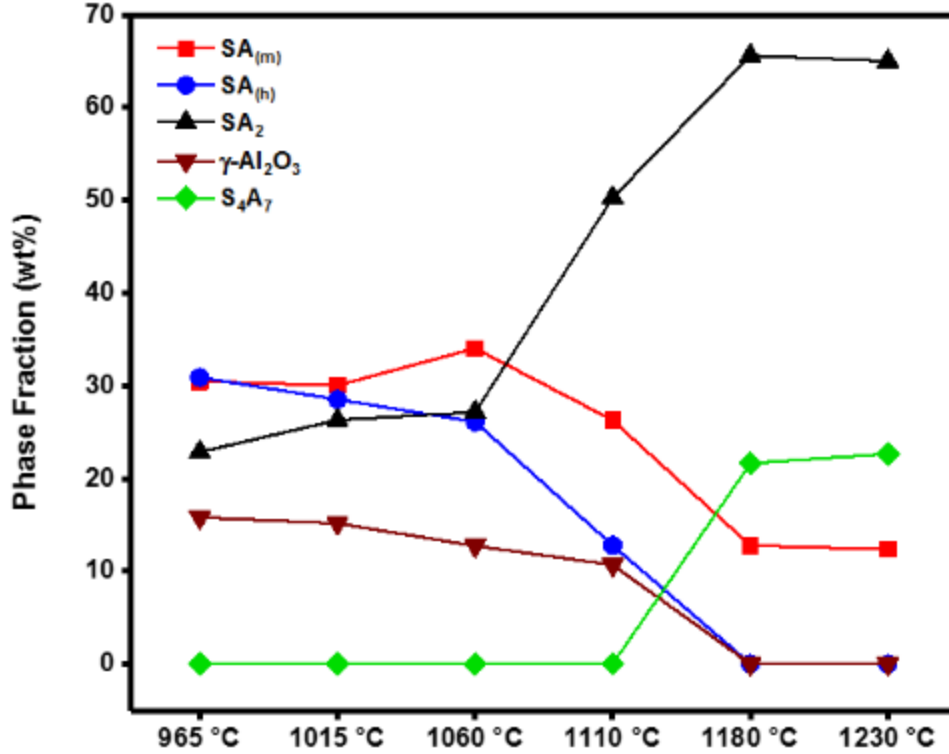


Figure 3.18. Phase fractions obtained by Rietveld quantitative phase analysis of XRD data during phase evolution of amorphous S4A7ED – 0 mol% B₂O₃ pre-ceramic upon increasing temperature. The lines are provided as visual guide.

Although the pre-ceramic was processed according to the nominal stoichiometry of long afterglow S₄A₇ doped with Eu and Dy, the fraction of this phase was not dominant up to temperatures as high as 1230°C, and metastable SA and SA₂ phases were also present.

Therefore, it can be deduced that the formation of S₄A₇ phase was controlled by a diffusion process, which required time to allow the equilibrium phase to form. We thus investigated the effect of calcination time at 1300 °C on the phase evolution during crystallization from the amorphous precursor of S4A7ED – 0% B₂O₃.

Figure 3.19 shows the XRD patterns of the amorphous pre-ceramic material after calcination at 1300°C for 0, 1, 5, 10 and 20 hours. It was observed that, when the amorphous powder was calcined at 1300 °C without any holding time, metastable SA₂ was the predominant phase, while the long afterglow S₄A₇ and a minor amount of SA

phase were also present. By prolonging the calcination dwell time to 1 and 5 h, the diffraction peaks of S_4A_7 became more intense at the expense of SA_2 meaning that S_4A_7 was evolving from SA_2 . After 10 hours of annealing at 1300°C , S_4A_7 phase dominated the composition and SA_2 phase diminished in amount continuously, and the magnitude of SA phase did not change significantly. Finally, the XRD pattern of the specimen calcined for 20 hours showed that the composition of the specimen was mainly composed of S_4A_7 , and the non-equilibrium SA and SA_2 phases were still present.

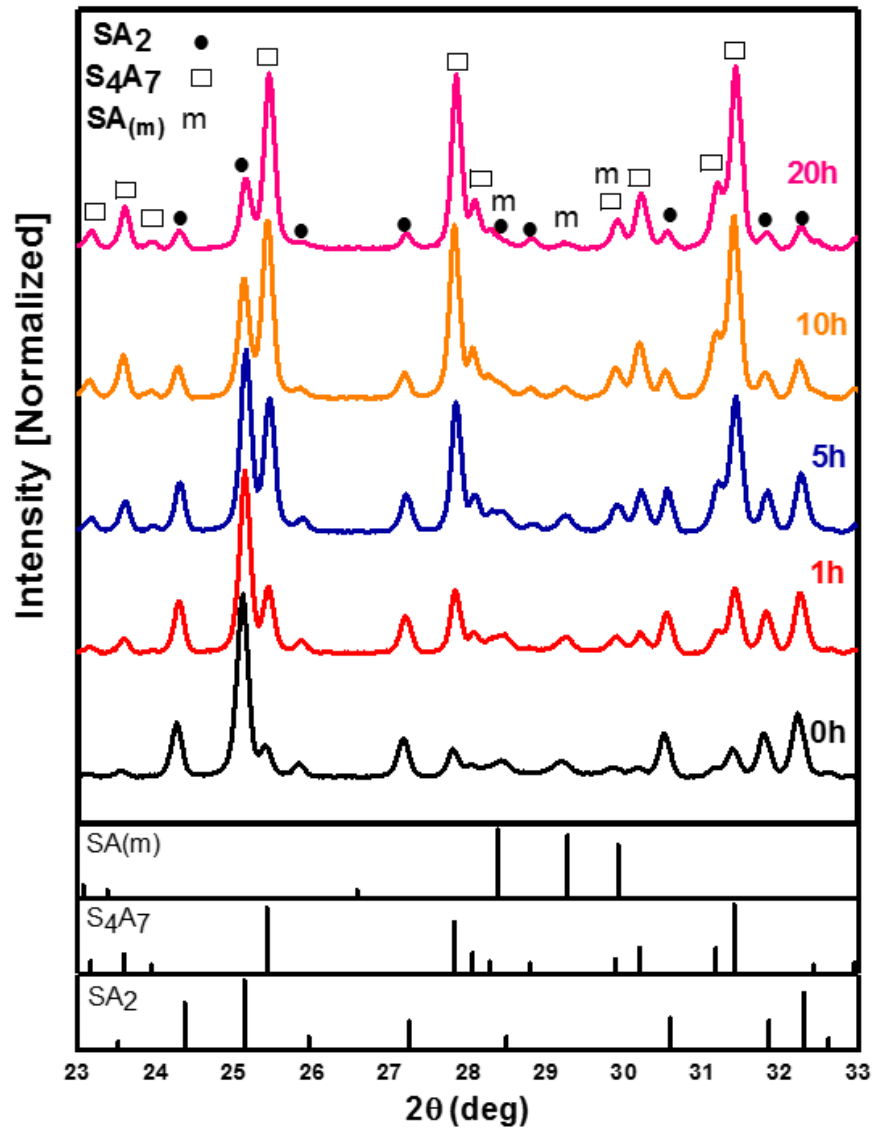


Figure 3.19. XRD patterns of the amorphous precursor of $S_4A_7ED - 0 \text{ mol\% } B_2O_3$ composition calcined at 1300°C for various times.

The phase fractions obtained by structural refinement of the XRD data for the specimens calcined at 1300 °C for various times are listed in **Table 3.6** and **Figure 3.20**, respectively.

Table 3.6. Phase composition revealed by Rietveld quantitative analysis of the XRD data from specimens processed at 1300 °C under different time. R_{wp} and R_{exp} are weighted profile and expected R -factors, respectively.

Calcination Time (h)	Phase Composition (wt%)			Goodness of Fit (R_{wp}/R_{exp})
	SA _m	SA ₂	S ₄ A ₇	
0	16.51	68.17	15.32	2.11
1	16.20	65.91	17.89	2.10
5	7.92	20.85	71.23	2.85
10	7.62	13.5	78.88	2.94
20	7.17	9.51	83.33	2.38

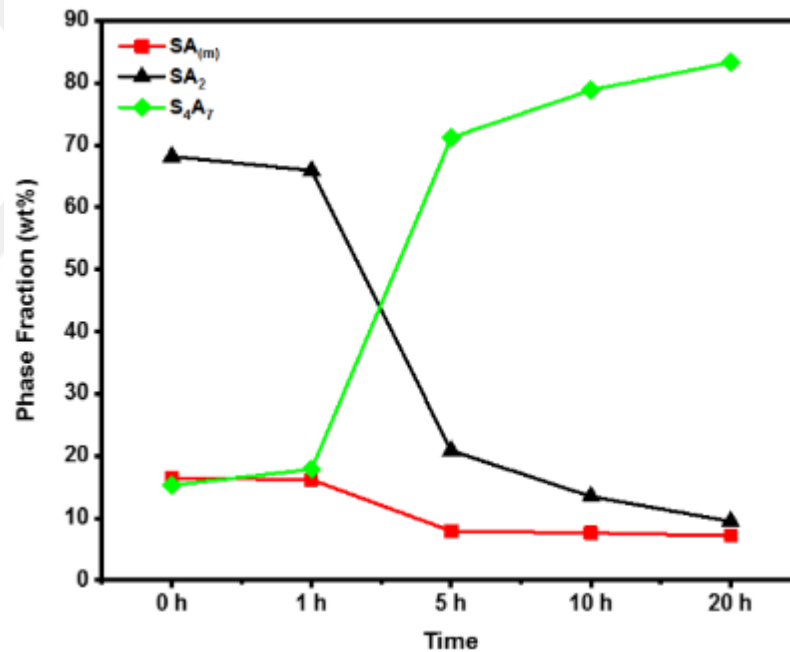


Figure 3.20. Phase fractions obtained by Rietveld quantitative phase analysis of XRD data for the amorphous S4A7ED – 0 mol% B₂O₃ pre-ceramic calcined at 1300°C for various time. The lines are provided as visual guide.

The results of phase analysis by XRD and Rietveld analysis revealed that, starting from an amorphous precursor with a nominal stoichiometry of S4A7ED without the presence of B₂O₃ as the sintering flux, the S₄A₇ phase as the equilibrium composition did not predominantly form upon increasing temperature. Instead, it evolved from the metastable SA₂ phase by calcination at elevated temperatures as high as 1300 °C over long annealing

times, suggesting that the long afterglow S_4A_7 phase had formed most likely by a diffusion-controlled mechanism.

To compare the phase evolution induced by increasing temperature at the characteristic temperatures of the exothermic peaks (*Figure 3.15*), we recorded backscattered electron (BSE) images of the amorphous pre-ceramic of $S_4A_7ED - 0 \text{ mol\% } B_2O_3$ heated to different temperatures determined by thermal events according to the DTA signal. The powders were embedded in resin and epoxy and polished as described in *Chapter 2* to minimize the effect of surface topography contribution to the contrast in the backscattered electron images. Therefore, the variation of contrast in the images originated merely from compositional difference, in particular, between phases with significant difference in their content of high atomic number elements.

For the specimen heated to 930°C (1st DTA exotherm onset) (*Figure 3.21 a-c*), two different contrast levels were distinguished from the powder particles. The brighter contrast was attributed to the phases that were richer in Sr^{2+} . Because the XRD pattern of this specimen (*Figure 3.16*) contained small crystalline peaks of SA and SA_2 phases, superimposed on a broad diffuse amorphous hump, it can be deduced that the dark contrast was related to the non-crystalline portion of the powder particles, which involves randomly distributed Sr^{2+} cations in between the short range ordered Al^{3+} polyhedra, possibly a solid solution of Sr in defect structure of $\gamma - Al_2O_3$. For the specimen heated to 965°C (1st DTA exotherm endpoint) (*Figure 3.21 d-f*), the BSE images still showed two distinct contrast levels. However, the bright contrast was the prevailing microstructure in the powder particles and the dark regions had diminished substantially, compared to that of 930°C . X-ray diffraction analysis of the powders heated to 965°C (*Figure 3.16*) showed that the amorphous hump almost disappeared. In addition, Rietveld analysis (Table 3.5 and *Figure 3.18*) implied that at 965°C , the SA phase dominated the phase composition. Therefore, the microstructure with brighter contrast was attributed to the SA phase, and the dark regions to the SA_2 phase. The microstructure observed during phase evolution at the onset and endpoint temperatures of the 1st exothermic in DTA trace supported the results of XRD phase analysis.

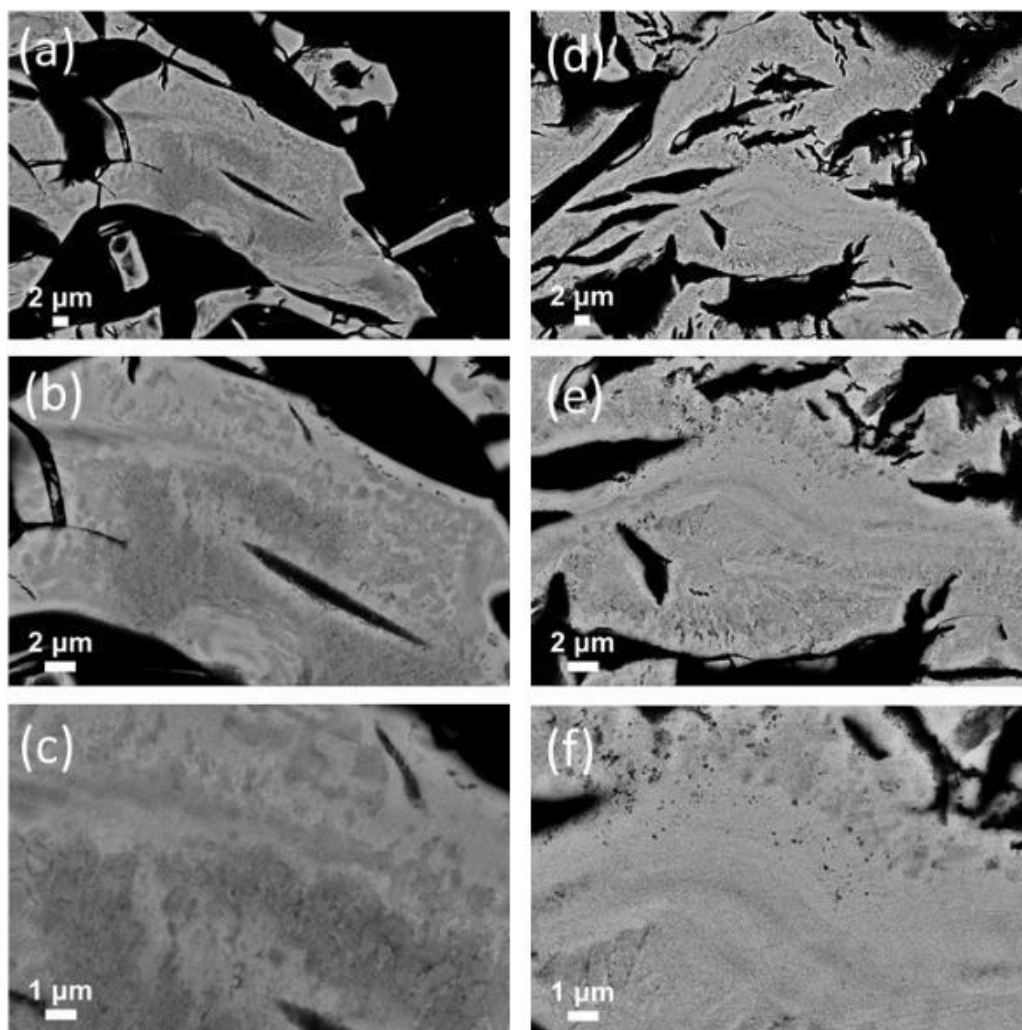


Figure 3.21. The microstructure produced during phase evolution of amorphous precursor of S4A7ED – 0 mol% B₂O₃ at (a-c) onset of the first DTA peak at 930 °C and (d-f) endpoint of the first DTA peak at 965 °C at different magnifications.

The microstructure of the specimen calcined up to the onset and endpoint of the second DTA exothermic peak is shown in **Figure 3.22**. When the amorphous pre-ceramic was heated to 1110 °C, the BSE images revealed a porous microstructure, and two different phase contrast levels were distinguished (*Figure 3.22 a-c*). Since Rietveld analysis of the XRD data confirmed that at this temperature SA₂ had formed as the major phase (50.27 %) along with SA (39.05 %) and minor quantities of γ -Al₂O₃, it can be inferred that the crystallites with bright contrast, which are rich in Sr²⁺, are SA phases while the pale gray grains in the powder particles with higher magnitude are the SA₂ crystals.

At the endpoint of the second exothermic peak (1180 °C), the BSE images (*figure 3.22 d-e*) showed three distinct microstructural features, the very bright and small grains of SA

phase with Al:Sr ratio of 2 (denoted by #1), the equiaxed large grains of SA_2 phase with Al:Sr ratio of 4 (denoted by #2) and long aspect ratio grains with a mid-gray contrast representative for S_4A_7 phase with a Al:Sr ratio of 3.5 (denoted by #3). The microstructural analysis of the specimen heated to 1180°C was consistent with the results of the phase analysis by XRD, where the diffractogram exhibited the formation of long afterglow S_4A_7 phase (21.63%) coexisted with small values of SA phase (12.77%) and SA_2 (65.6%) as the dominant phase. In addition, it was observed that the evolved S_4A_7 grains were highly porous at one end of the grains as highlighted by dashed lines in *Figure 3.21-f*.

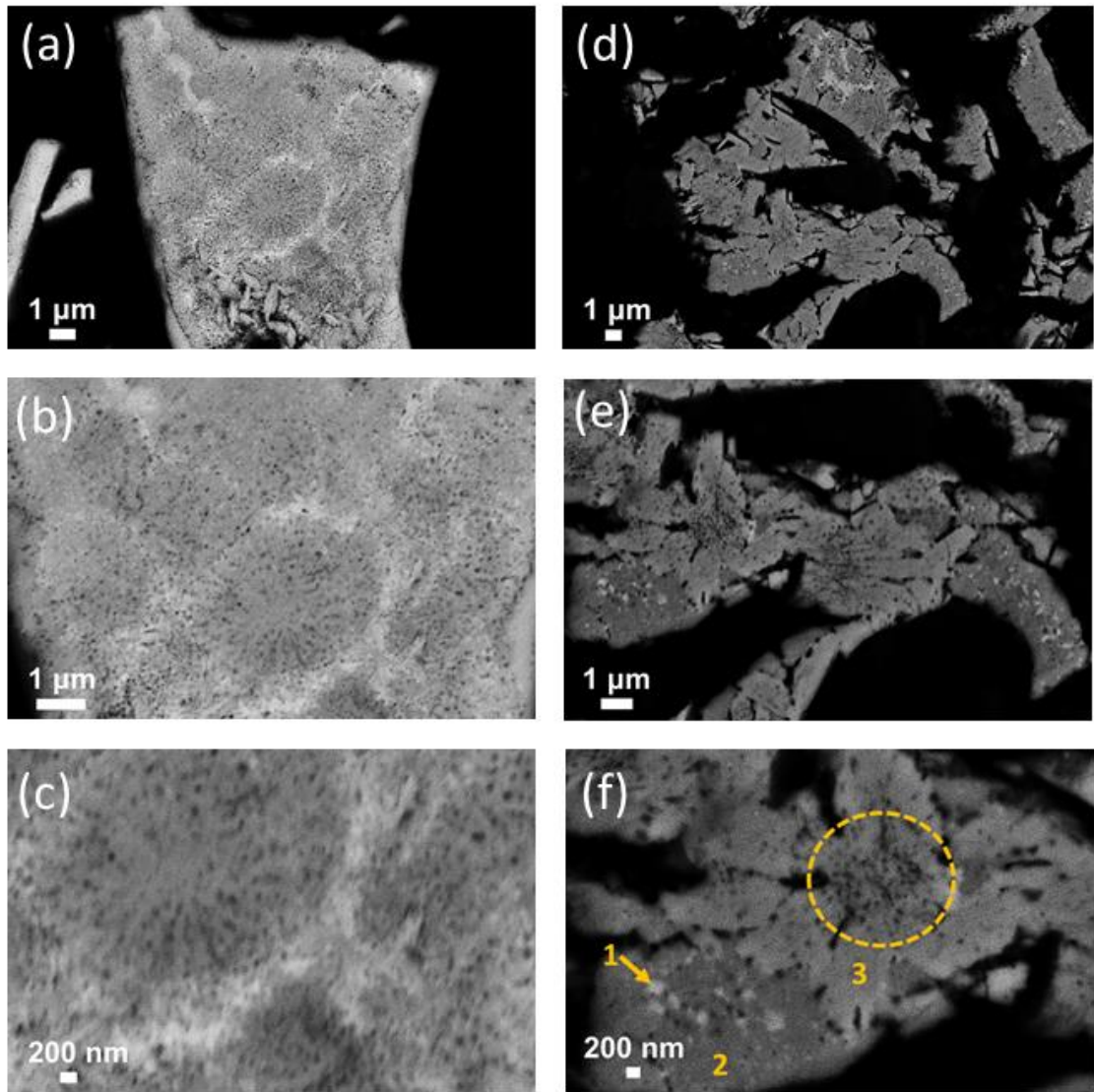


Figure 3.22. The microstructure produced during phase evolution of amorphous precursor of $S_4A_7ED - 0 \text{ mol\% } B_2O_3$ at (a-c) onset of the second DTA peak at 1110 °C and (d-f) endpoint of the second DTA peak at 1180°C at different magnifications.

The evolution of S_4A_7 phase at 1300°C over time from meta-stable SA and SA_2 phases was demonstrated in BSE images in **Figure 3.23**. When the amorphous precursor of $S_4A_7ED - 0 \text{ mol\% } B_2O_3$ is calcined at 1300°C for 1 h, the microstructure involved three distinct types of contrast (Figure 3.23 a-b). The phase distribution according to Rietveld analysis (*Table 3.6*) showed that after 1 h calcination, SA and S_4A_7 phases were almost equal in terms of phase fraction and SA_2 is the major phase. Because the Al:Sr ratio for the mentioned phases in descending order of $SA_2 > SA > S_4A_7$, the grains labeled as #1, #2 and #3 are SA, SA_2 and S_4A_7 , respectively based on the contrast resulting from the concentration of high atomic number Sr content. The distribution of the phases shown in the BSE images for the specimen calcined at 1300°C for 1h was in good agreement with Rietveld quantitative phase analysis.

When the calcination time was prolonged to 5 h, BSE images (Figure 3.23 c-d) clearly showed that S_4A_7 grew at the expense of the SA_2 phase, while infinitesimal amounts of SA phase were still present in the microstructure as revealed by Rietveld analysis. Over longer calcination time of 20 h, the thermodynamically stable S_4A_7 phase dominated the microstructure (Figure 3.23 e-f), and SA and SA_2 phases became rarely detected in electron micrographs.

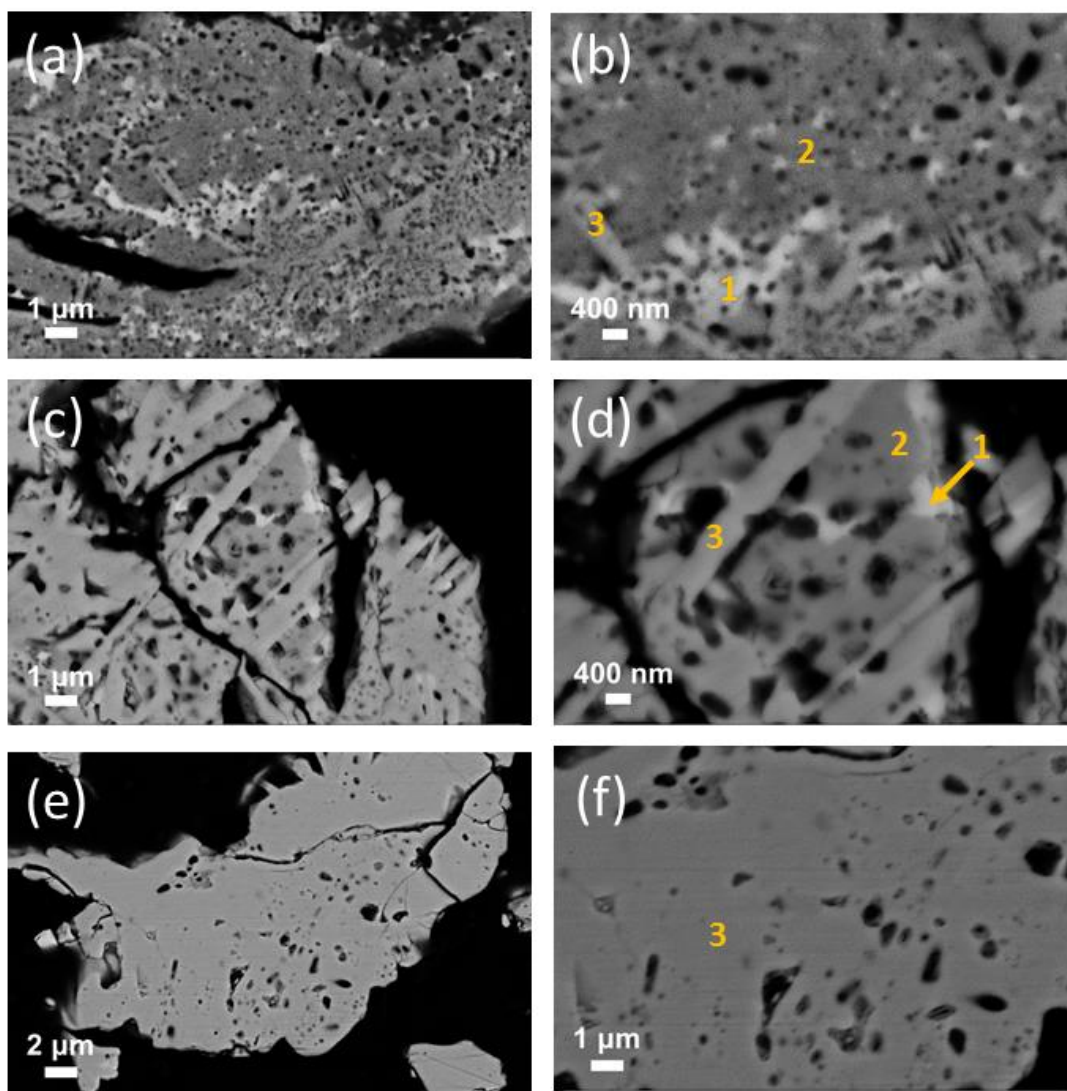


Figure 3.23. The microstructure produced during phase evolution of amorphous precursor of S4A7ED – 0 mol%B₂O₃ at 1300 °C over various calcination times of (a-b) 1h (c-d) 5h and (e-f) 20h at different magnifications.

3.5.3 Crystallization Kinetics During Phase Evolution of B₂O₃ – Free S4A7ED Compound

To evaluate the kinetics of crystallization during phase evolution in the amorphous precursor of S4A7ED – 0%B₂O₃, we conducted non-isothermal kinetics study on the organics – free pre-ceramic obtained by pre-calcination of the dehydrated gel at 800 °C for 3h. DTA scans were performed on the amorphous precursor at different heating rates of 5, 10, 20 and 30 °C/min in air (flow rate of 40 mL/min), from room temperature up to

1400 °C. The activation energy of crystallization at the first and second exothermic peaks were determined through the variation in maximum temperatures of the DTA exotherms, based on Kissinger plots. The Avrami exponent for each crystallization events was extracted through calculation of fraction transformed at a specific temperature (α_T) by the ratio of the area under the exothermic peaks at temperature T (A_0) relative to the total area of the DTA exotherm (A) at different heating rates based on Ozawa model. More details on the non-isothermal crystallization kinetics were discussed in *Chapter 2* and *Section 2.2.1.2.2*.

Figure 2.24 displays the DTA traces of the amorphous precursor of S4A7ED – 0 mol% B₂O₃ recorded at various heating rates. The crystallization peak temperatures (T_{p1} and T_{p2}) of the exothermic peaks were shifted to higher temperatures as the heating rate increased.

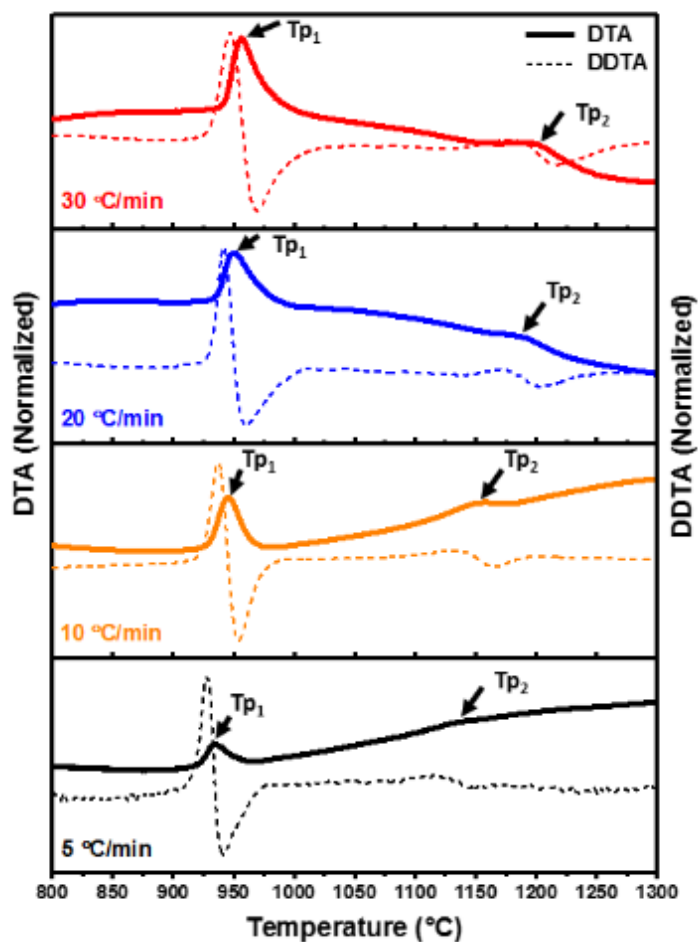


Figure 3.24. Non-isothermal DTA curves of amorphous pre-ceramic of S4A7ED-0 mol% B₂O₃ obtained at different heating rates. The arrows specify the crystallization peak temperatures T_{p1} and T_{p2} for the first and second exothermic peaks, respectively.

The values of T_p for the two exotherms under different heating rates are listed in **Table 3.7**.

Table 3.7. Crystallization peak temperatures obtained from DTA analysis of the amorphous pre-ceramic of S4A7ED-0 mol% B_2O_3 under different heating rates.

Heating Rate ($^{\circ}C/min$)	Crystallization Peak Temperature ($^{\circ}C$)	
	1 st Exo. (T_{p1})	2 nd Exo. (T_{p2})
5	935	1137
10	945	1154
20	950	1192
30	956	1201

Figure 3.25-a shows the results of calculation of the activation energy during crystallization of amorphous S4A7ED precursor without the presence of B_2O_3 for reactions occurring as a result of the first and second exothermic peaks in DTA signals. For the phase evolution that happened at the temperature range of the first exothermic peak, an activation energy of 1034.34 (± 97) kJ/mol was obtained. In addition, the activation energy for the process that occurred through the second exothermic peak, an activation energy of 413 (± 52) kJ/mol was obtained.

In general, the activation energy for crystallization is determined by 2 underlying processes: The energy required for dissociation of the ionic bonds and diffusion/migration of ions and coordination polyhedra [79, 147, 148]. The value of activation energy for the processes at the first exothermic peak is greater than the dissociation energy of Al – O ionic bonds (512 kJ/mol) and that of Sr – O ionic bonds (454 kJ/mol) [142]. This suggests that the phase evolution that takes place through the first exothermic peak involved the breakdown of the alumina network as well as Sr – O bonds. The margin of activation energy with respect to the bond dissociation energies was attributed to the migration of ions during structural transformation. For the second exothermic peak, the activation energy of 413 kJ/mol for phase transformation was less than the bond dissociation energy of Al – O bonds but comparable to that of Sr – O ionic bonds. This implies that, the phase evolution did not involve significant bond breakage in the alumina scaffolding around the

second exothermic peak. However, the process required dissociation and/or migration of Sr^{2+} for the phase transforming at the second exotherm.

Figure 3.25-b shows the Ozawa plots used to determine the Avrami exponent n for the phase evolution of the amorphous S4A7ED pre-ceramic occurring at the first and second exothermic peaks. For each exothermic peak, the fraction transformed (α_T) was determined at three different specific temperatures within the exotherms, and the Avrami exponents obtained for each peak was reported as the average value of three measurements. From the slope of the linear fit functions, the Avrami exponent values were determined to be $1.53 (\pm 0.2)$ for the 1st DTA peaks and $2.90 (\pm 0.05)$ for the 2nd exotherms.

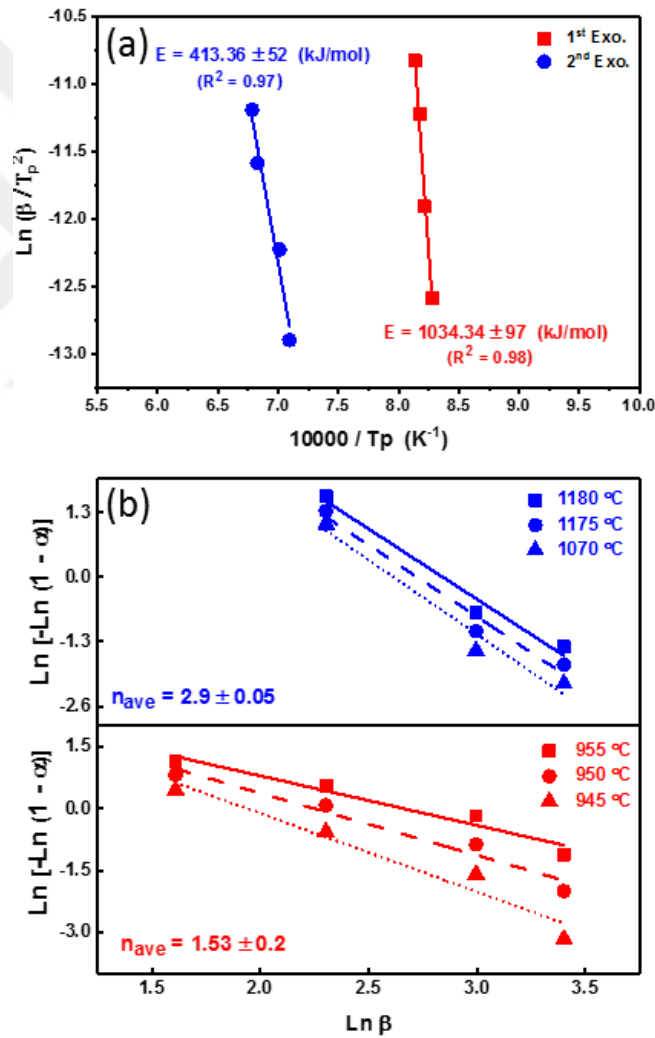


Figure 3.25. Plots used for determination of kinetics parameters during crystallization of amorphous pre-ceramic of S4A7ED – 0 mol% B_2O_3 based on non-isothermal kinetics a) Kissinger plots for determination of activation energy and b) The Ozawa-type plots for determination of Avrami exponent. The straight lines in red corresponds to the first exothermic peaks and the ones in blue is related to the second exotherms in the DTA scans at various heating rates.

For determining the physical model for crystallization, different interpretations of the Avrami exponent have been proposed. Crystallization is a 2-step process – nucleation followed by growth. In the simplest, (where the rate limiting step is reaction at the surface of the crystalline nuclei,) $n \sim 1$ represents the surface crystallization. For $1 < n < 3$, the crystallization is governed by simultaneous surface and internal crystallization while for $n \geq 3$, bulk crystallization is dominant [145, 149].

Furthermore, a more detailed interpretation of the Avrami exponent was provided by Henderson *et al.* [146] for different transformation conditions. For crystallization that is controlled by cation diffusion, the values of n are interpreted according to the characteristics of the nucleation rate during crystallization, as categorized in **Table 3.8**.

Table 3.8. Values of Avrami exponent n and the mechanism proposed for nucleation and growth for diffusion-controlled phase transformation [146, 150].

Avrami exponent (n)	Mechanism of phase transformation
$0 < n < 1.5$	growth of pre-existing nuclei
$n = 1.5$	growth of nuclei with zero nucleation rate (site saturation)
$1.5 < n < 2.5$	growth of nuclei with decreasing nucleation rate
$n = 2.5$	growth of nuclei with constant nucleation rate
$n > 2.5$	growth of nuclei with increasing nucleation rate

Therefore, the value of $n = 1.53$ for the first peak means that during phase transformation at the first DTA peak both surface and bulk crystallization contributes. However, surface crystallization is dominant under site saturation conditions (zero nucleation rate). For the phase transformation at the second peak, the n value of 2.9 indicates that internal crystallization is more prevailing than surface crystallization because the value is closer to 3 and nucleation proceeds by increasing nucleation rate during the phase transformation.

Likewise, it is common to express the n value as

$$n = a + mb$$

where a represents the nucleation rate, m indicates the dimensionality of the growing crystal and b stands for the mechanism of the growth. The combination of a , m and b

parameters can be is used to determine the nucleation and crystal growth mode during crystallization and phase transformations as listed in **Table 3.9**.

Table 3.9. Values of a , m and b parameters in determining the nucleation and growth modes from Avrami exponent [79, 81, 147, 148].

$n = a + mb$		
parameter	value	crystallization characteristic
a	0	zero nucleation rate
	1	constant nucleation rate
	< 1	decreasing nucleation rate
	>1	Increasing nucleation rate
m	1	1D growth
	2	2D growth
	3	3D growth
b	0.5	diffusion – controlled
	1	Interface – controlled

To interpret our results about the growth modes at the first and second exothermic peaks with the criteria indicated in table 3.9, we evaluated the morphology of the powder particles for the specimens at temperatures corresponding to the 1st and 2nd DTA peak onsets recorded at a heating rate of 10 °C/min (see figure 3.15) by secondary electron (SE) SEM images.

Figure 3.26 shows the SE images of the powder particles for the amorphous precursor of S4A7ED -0% B₂O₃ heated to the onset of the first exothermic peak at 930 °C and onset of the second exothermic peak at 1110 °C in the DTA signal, respectively.

For the specimen heated to the onset of the 1st exotherm, the SEM image (figure 3.26 a-b) revealed the formation spherical shape crystallites on the surface of the amorphous particle ($m = 3$).

In addition, the XRD analysis (Figure 3.16) showed that at this temperature, SA and SA₂ phases start to evolve simultaneously from amorphous state as discussed in *section 3.5.2*. Further XRD analyses (not shown here) revealed that by prolonging the calcination time up to 20 hours at the temperature ranges of the 1st DTA peak, pure SA₂ phase was formed. Therefore, although initially SA and SA₂ started to form together upon increasing temperature, SA₂ is in fact the more stable phase around the first DTA peak. Beside this, the analysis of the activation energy at the location of the first exotherm implied that the crystallization process involves the migration of both Al³⁺ and Sr²⁺ cations. So, the process is a diffusion-controlled mechanism ($b = 0.5$)

Regarding to the criteria listed in table 3.9, for $n = 1.5$ for the first exothermic peak, and considering the above observations for $m = 3$ and $b = 0.5$, it can be concluded that $a = 0$ which is an indication of zero nucleation rate. To sum up, the mechanism of crystallization through the first DTA peak is surface crystallization, accompanied by zero nucleation rate and controlled by diffusion process.

For the specimen heat treated at the onset of the 2nd exothermic peak, SE images (figure 3.26 c-d) shows the spherical crystallites ($m = 3$) with substantially higher nucleation sites. XRD analysis (figure 3.17) showed that the evolution of S₄A₇ phase starts at the temperature range of the 2nd DTA peak and the equilibrium S₄A₇ phase forms upon long calcination times (figure 3.19) by diffusion process. In addition, the activation energy calculations showed that the transformation around the second peak involves the diffusion of Sr²⁺ ($b = 0.5$).

For $n = 2.9$ related to the second exothermic peak, by considering the values of $m = 3$ and $b = 0.5$, the value for the parameter a , representative for nucleation rate is $a = 1.4$, indicative of increasing nucleation rate. The higher nucleation rate for the phase transformation at the 2nd DTA peak with respect to crystallization at 1st DTA peak is obvious from the SEM images. Therefore, the mechanism of phase transformation at the second exothermic peak with $n = 2.9$ is dominated by internal crystallization with an increasing nucleation rate under a diffusion-controlled mechanism.

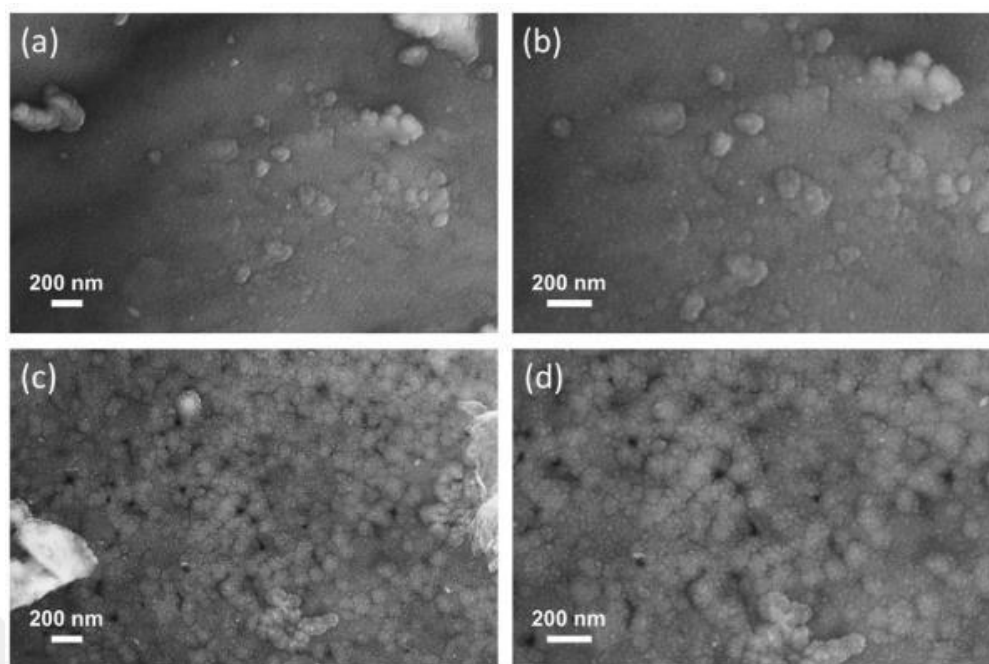


Figure 3.26. The morphology of the growing crystals on the surface of the powder particles heat treated at (a-b) first DTA peak onset and (c-d) second DTA peak onset.

3.6 Crystallization of Pechini-Processed S4A7ED Doped with B₂O₃

After investigation of phase evolution in B₂O₃-free amorphous pre-ceramic of (SrO)₄(Al₂O₃)₇ doped with 1 mol% Eu and 1 mol% Dy, in this course of the study, we evaluated the effect of B₂O₃ content on crystallization of S4A7ED compounds. Different concentrations of B₂O₃ (5, 10, 20, 30 and 40 mol%) as the sintering flux were used during Pechini processing of the pre-ceramic as described in *Chapter 2*. The effect of B₂O₃ on crystallization was studied by using the globally averaged characterization tools including thermal analysis by DTA, XRD phase analysis and microstructural analysis in the SEM.

3.6.1 Thermal Analysis of The Organics-Free S4A7ED Doped with Various B₂O₃ Contents

For all the compositions, the Pechini processed amorphous gel was calcined at 800 °C for 3h in order to allow complete decomposition of the nitrate precursors and organic components. DTA scans were conducted on the organics-free amorphous pre-ceramic for different B₂O₃-doped compositions at a heating rate of 10 °C/min in air (flow rate of 40 ml/min). The results of DTA of the S4A7ED composition doped with different contents

of B_2O_3 are shown in **Figure 3.27**. For comparison, the DTA curve for B_2O_3 -free composition is also provided. We observed that by increasing the B_2O_3 content, the first exothermic peak shifted to lower temperatures. This effect was more pronounced for the second exotherm, when the concentration of B_2O_3 was increased to 10 mol%. Beyond 10 mol% B_2O_3 , the second exothermic peak was barely discernable, and a step-like feature appeared instead in the DTA traces of 20, 30 and 40 mol% B_2O_3 -doped samples, indicating a possible glass transition, due to the presence of high concentrations of B_2O_3 , which is a glass former.

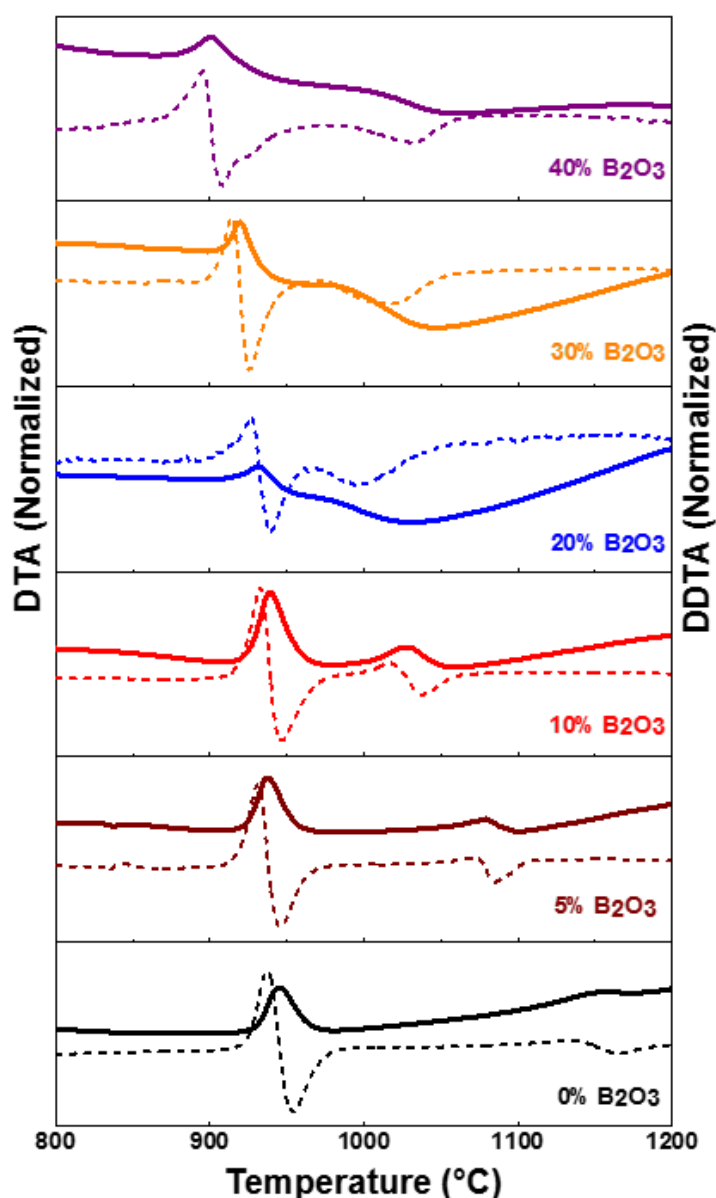


Figure 3.27. Effect of B_2O_3 content on DTA curves of the Pechini processed S4A7ED – x mol% B_2O_3 compositions. All the DTA curves were recorded at a heating rate of 10 °C/min under air atmosphere.

3.6.2 Phase Evolution in S4A7ED – 10 mol% B₂O₃

Figure 3.28 shows the DTA signal of the S4A7ED doped with 10 mol% B₂O₃ after pre-calcination at 800 °C for 3h. Similar to that of B₂O₃-free composition, DTA showed a sharp crystallization peak with an onset of 925°C, which was immediately followed by a broad exotherm with an onset at 1000°C. The characteristic temperatures of the exothermic peaks were used for elucidating the phase formation sequence during crystallization of the 10 mol% B₂O₃ – doped composition.

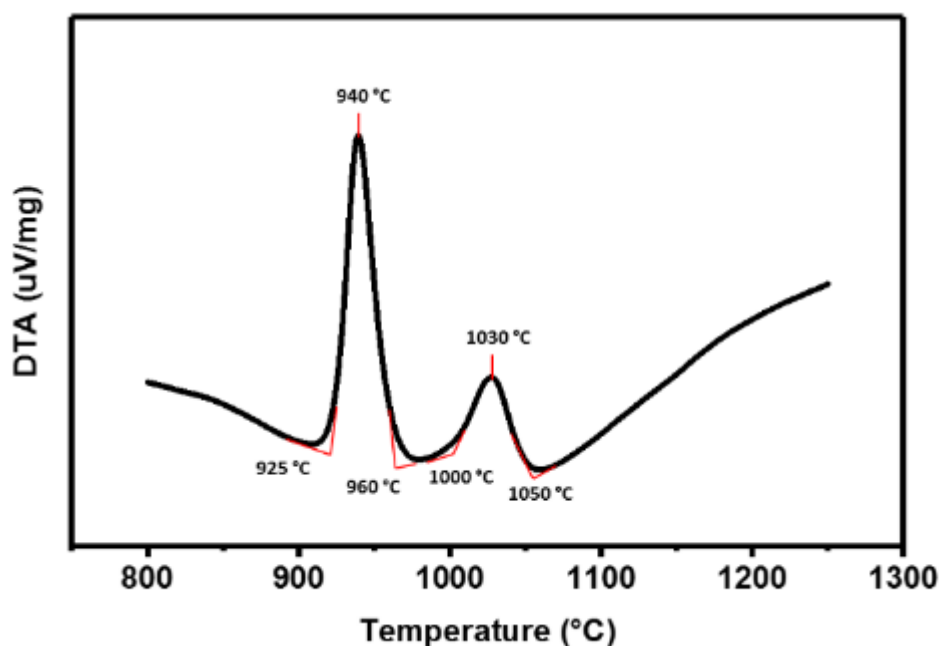


Figure 3.28. DTA curve of the Pechini processed S4A7ED doped with 10 mol% B₂O₃ after pre-calcination at 800°C for 3h at a heating rate of 10 °C/min under air atmosphere.

To evaluate the phase evolution in S4A7ED – 10 mol% B₂O₃ compound, we preformed the heat treatment of the amorphous preceramic based on the temperatures obtained from DTA of the preceramic as listed in **Table 3.10**. It is worth noting that, because the temperatures chosen for investigation of phase evolution were determined based on the DTA signal recorded at a heating rate of 10 °C/min in air, all heat treatments on the amorphous powder of 10 mol% B₂O₃-incorporated S4A7ED were conducted at a heating rate of 10 °C/min.

Table 3.10. Calcination temperatures and dwell times used for investigation of phase evolution in amorphous S4A7ED – 10 mol% B₂O₃ composition.

Calcination conditions (°C)	DTA characteristic
875 °C	below the 1 st Exo. onset
925 °C	1 st Exo. onset
960 °C	1 st Exo. endpoint
1000 °C	2 nd Exo. onset
1050 °C	2 nd Exo. endpoint
1100 °C	above the 1 st Exo. endpoint
1300 °C – 0 h	-
1300 °C – 1 h	-
1300 °C – 5 h	-
1300 °C – 10 h	-
1300 °C – 20 h	-

Figure 3.29 shows the phase evolution of the amorphous precursor of S4A7ED when 10 %mol B₂O₃ was added as the sintering flux around the first exothermic peak. Despite the B₂O₃ – free composition (Figure 3.16), where the state of the powder at 50 °C below the onset of the first DTA exotherm was amorphous, when 10 mol% B₂O₃ was present, small reflections of the crystalline phase of SA (both hexagonal and monoclinic polymorphs) and SA₂ started to appear at 875 °C, although a wide diffuse halo, representative for amorphous nature was present in the diffraction pattern. At the onset of the first exothermic peak at 925°C, the XRD pattern showed substantial improvement in crystallinity, where sharp diffraction peaks of SA₂ and SA phases along with γ -Al₂O₃ (with a characteristic peak at $2\theta = 67^\circ$ confirmed by Rietveld refinement) evolved. By increasing the temperature to the endpoint of the 1st exotherm, the phase composition of the specimen did not undergo a substantial change, and only the fraction of SA₂ phase increased slightly at the expense of SA.

The most important observation during phase evolution of amorphous precursor starting with the nominal stoichiometry of S4A7ED doped with 10 mol% B₂O₃, compared to that B₂O₃-free composition, was that, in the absence of B₂O₃ as the sintering flux, the state of the specimen was mostly amorphous with small reflections of crystalline phases of SA₂

and SA at the onset of the first exothermic peak. However, in the presence of 10 mol% B_2O_3 , sharp diffraction peaks of SA_2 and SA phases were formed at the onset temperature. In addition, the phase composition of the B_2O_3 -free specimen at the endpoint temperature of 1st exotherm was dominated by meta-stable SA phases; by contrast in the preceramic containing 10 mol% B_2O_3 , the transformation of SA to SA_2 was accelerated, and SA_2 phase was the major phase at the endpoint temperature of the 1st exothermic peak.

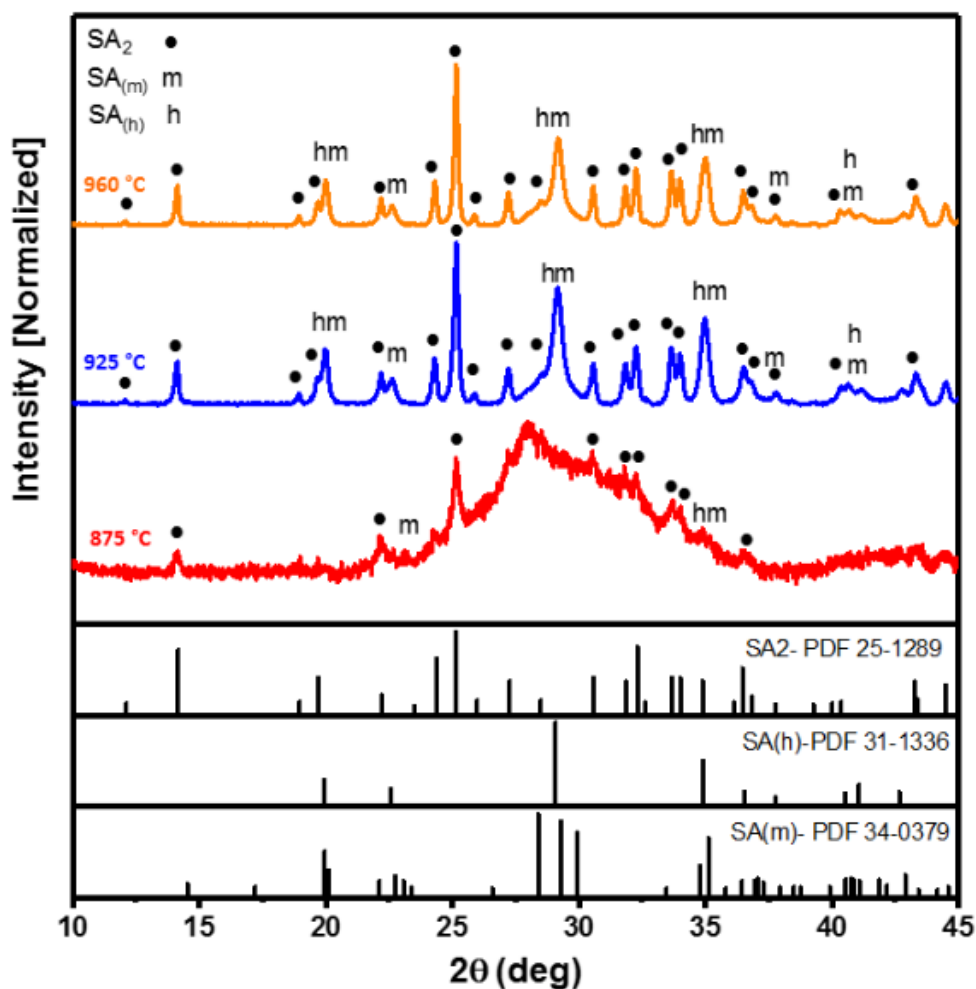


Figure 3.29. XRD patterns of the amorphous pre-ceramic of S4A7ED – 10 mol% B_2O_3 composition heated to the characteristic temperatures of the first DTA exotherm at 875, 925 and 960 °C.

In **Figure 3.30**, XRD patterns of the 10 mol% B_2O_3 -doped S4A7ED composition heated to the temperature range of the second exothermic peak are presented. At the onset of the 2nd exotherm at 1000 °C, the SA phase with hexagonal structure, as well as alumina phase, had completely disappeared, and the SA_2 phase increased in fraction. This suggests that the SA_2 phase was formed as a result of reaction between $SA_{(h)}$ and $\gamma-Al_2O_3$. Increasing

the temperature to 1050 °C did not have a significant effect in phase composition, as revealed by Rietveld phase analysis of the XRD data. Low intensity diffraction peaks attributed to the S_4A_7 phase appeared beyond the second exotherm at 1100 °C.

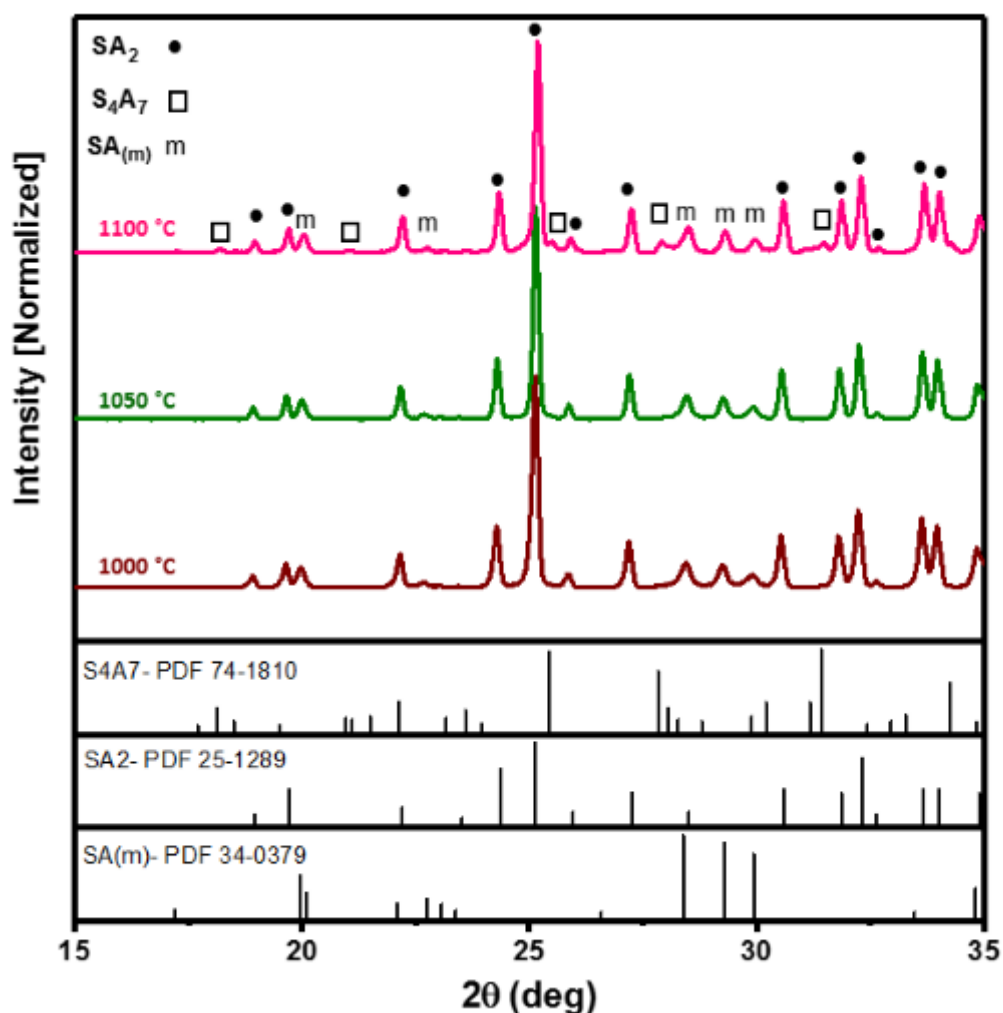


Figure 3.30. XRD patterns of the amorphous pre-ceramic of S_4A_7ED – 10 mol% B_2O_3 composition heated to the characteristic temperatures of the second DTA exotherm at 1000, 1050 and 1100 °C.

XRD patterns of the 10 mol% B_2O_3 containing pre-ceramic of S_4A_7ED calcined at 1300 °C for different times is summarized in **Figure 3.31**. The diffraction patterns showed the formation of S_4A_7 phase at the expense of SA_2 , by increasing the calcination from 0 h to 20 h. However, after 20 h small amounts of SA and SA_2 were still detectable.

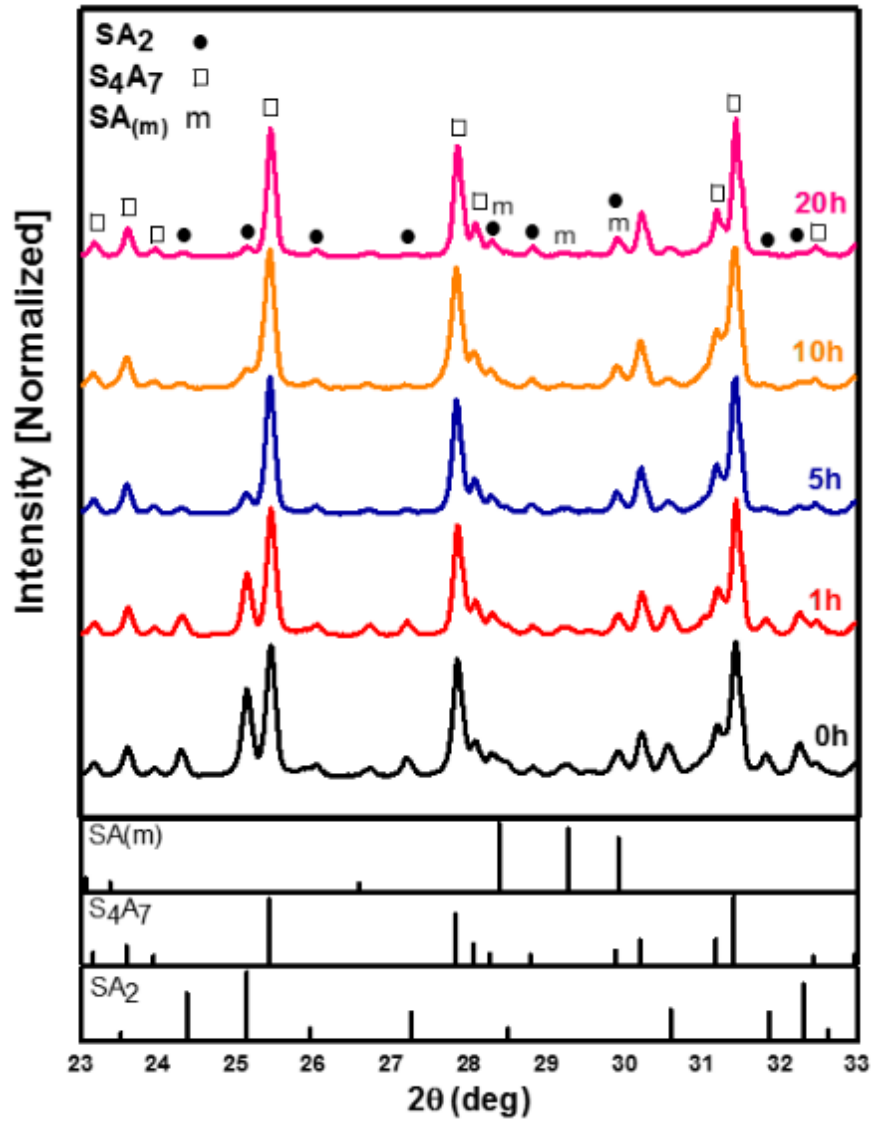


Figure 3.31. XRD patterns of the amorphous precursor of S4A7ED – 10 mol% B₂O₃ composition calcined at 1300 °C for various times

The results of Rietveld quantitative phase analysis of the XRD data for the amorphous pre-ceramic of S4A7ED – 10 %mol B₂O₃ specimens heated to the characteristic temperatures of the first and second exothermic peak (Figure 3.28) are presented in **Table 3.11**, and the trend of the change in the phase fractions are plotted in **Figure 3.32**.

Table 3.11. Phase composition of S4A7ED – 10 mol% B₂O₃ pre-ceramic material revealed by Rietveld quantitative analysis of the XRD data for the specimens heated to the onset, endpoint and beyond the endpoint temperatures of the 1st and 2nd exothermic peaks in the DTA signal. R_{wp} and R_{exp} are weighted profile and expected R-factors, respectively.

Temperature (°C)	Phase Composition (wt%)					Goodness of Fit (R_{wp}/R_{exp})
	SA _m	SA _h	SA ₂	γ -Al ₂ O ₃	S ₄ A ₇	
925	22.70	20.12	46.95	10.23	-	1.97
960	23.28	18.77	48.07	9.88	-	2.176
1000	17.61	-	82.39	-	-	2.35
1050	15.5	-	84.5	-	-	2.42
1100	12.44	-	67.89	-	19.67	2.57
1300 – 0 h	5.54	-	21.76	-	72.70	3.12
1300 – 1 h	5.33	-	18.57	-	76.10	3.30
1300 – 5 h	3.92	-	7.08	-	89	2.78
1300 – 10 h	4.37	-	7.63	-	88	2.84
1300 – 20 h	2.47	-	5.25	-	92.28	2.84

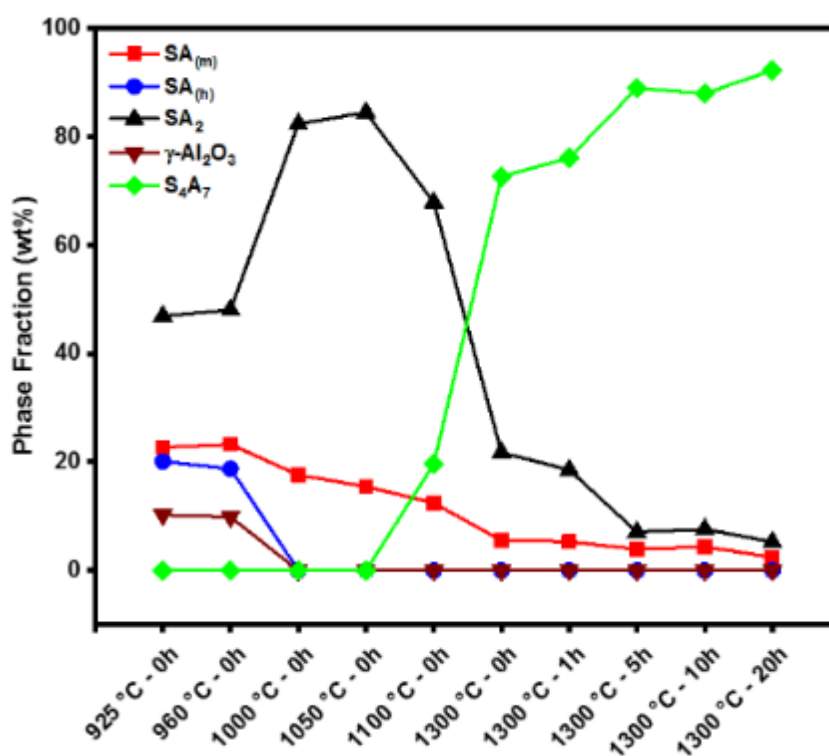


Figure 3.32. Phase fractions obtained by Rietveld quantitative phase analysis of XRD data during phase evolution of amorphous S4A7ED – 10 mol%B₂O₃ pre-ceramic upon increasing temperature and calcination at 1300 °C over various dwell time. The lines are provided as visual guide.

3.6.3 Phase Evolution in S4A7ED – 20 mol% B₂O₃

The DTA signal corresponding to the Pechini processed S4A7ED composition doped with 20 mol% B₂O₃ is shown in **Figure 3.33**. In contrast to the DTA traces for 0, 5 and 10 mol% B₂O₃ doped compositions, we did not observe two resolvable exothermic peaks during crystallization of the amorphous pre-ceramic with increasing temperature, and the shape of the thermogram had changed significantly. This indicates that in the presence of large amounts of sintering flux, the microstructure evolves differently than the processes under low B₂O₃ conditions. The strontium aluminate phases appeared to be forming by precipitation from liquid, rather than by solid state reaction.

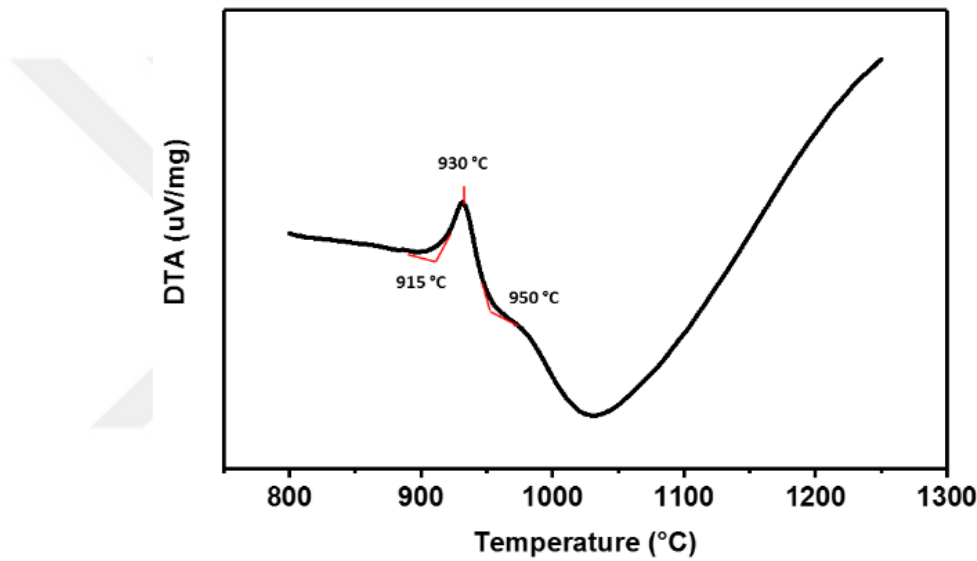


Figure 3.33. DTA curve of the Pechini processed S4A7ED doped with 20 mol% B₂O₃ after pre-calcination at 800 °C for 3 h at a heating rate of 10 °C/min under air atmosphere.

Because only one exothermic peak was observed in the thermogram, the phase evolution in 20 mol% B₂O₃-doped specimens was monitored at the characteristic temperatures of the first exotherm, as well as 1300 °C, for different calcination times. **Table 3.12** lists the temperatures obtained, based on DTA in Figure 3.33, that were used to investigate the phase evolution in S4A7ED composition doped with 20 mol% B₂O₃.

Table 3.12. Calcination temperatures and dwell times used for investigation of phase evolution in amorphous S4A7ED – 20 mol% B₂O₃ composition.

Calcination conditions (°C)	DTA characteristic
865 °C	below the 1 st Exo. onset
915 °C	1 st Exo. onset
950 °C	1 st Exo. endpoint
1100 °C	beyond the 1 st Exo. endpoint
1300 °C – 0 h	-
1300 °C – 1 h	-
1300 °C – 5 h	-
1300 °C – 10 h	-
1300 °C – 20 h	-

Figure 3.34 shows the XRD pattern obtained from the calcination of the S4A7ED – 20 mol% B₂O₃ pre-ceramic at different temperatures related to the exothermic peak in DTA. From the XRD pattern attributed to the specimen annealed at 865 °C, we observed that crystallization from the amorphous state was initiated before the exothermic reaction started. At the onset temperature of 915 °C, the SA₂ phase was dominant. However, it seems that the magnitude of SA phases was smaller than that of 10 mol% B₂O₃ and B₂O₃ – free compounds at the onset temperature of the first exothermic peak. In fact, by increasing the B₂O₃ content, decomposition of the meta-stable SA phase, including both hexagonal and monoclinic structure, was accelerated. At 950 °C, the hexagonal SA phase had completely vanished, and the fraction of SA₂ increased. When the temperature reached 1100 °C, a simultaneous decrease in fraction of SA₂ (about 5 %) and SA_(m) (about 3%) and formation of S₄A₇ (about 8%) was observed from Rietveld analysis of the XRD data. This implies that initial nucleation of S₄A₇ had occurred through reaction between SA₂ and SA.

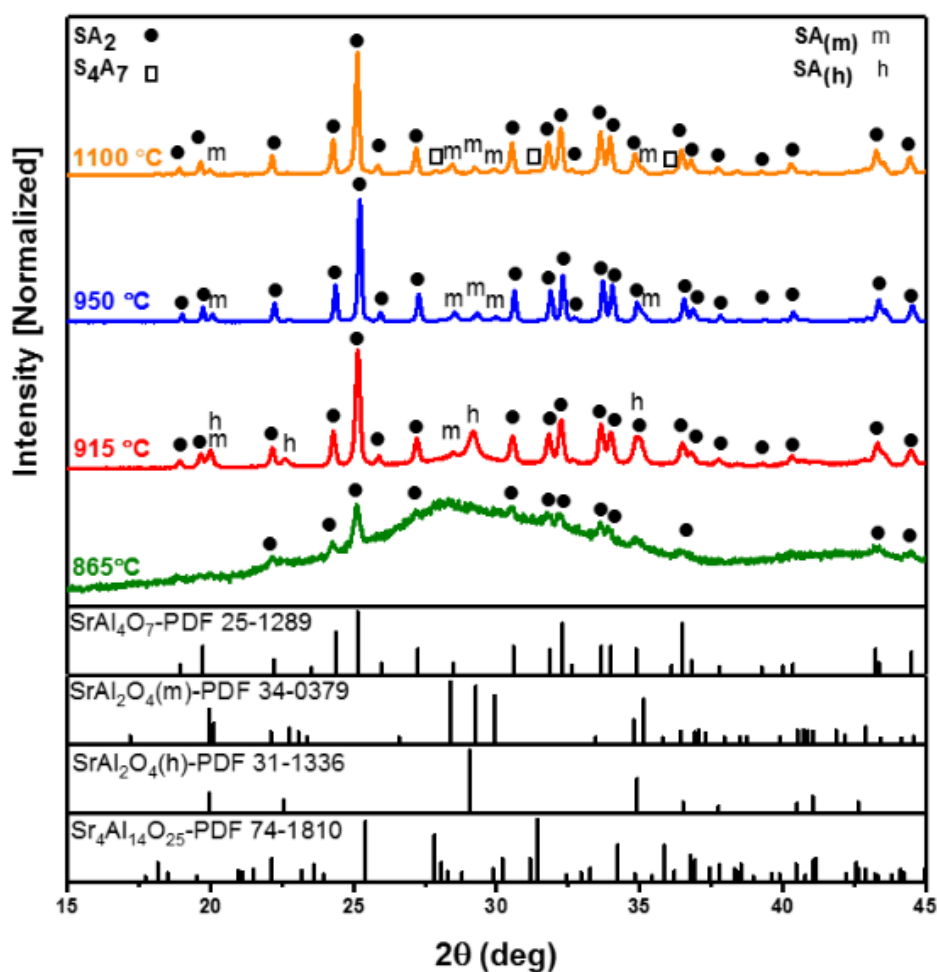


Figure 3.34. XRD patterns of the amorphous pre-ceramic of S4A7ED – 20 mol% B_2O_3 composition heated to the characteristic temperatures of the DTA exothermic peak at 865, 915, 950 and 1100 °C.

The phase evolution over different calcination times at 1300 °C for the 20 mol% B_2O_3 composition is shown by X-ray diffraction analysis in **Figure 3.35**. For the specimen with 20 mol% B_2O_3 that was immediately quenched at 1300 °C, in contrast to 0 and 10 mol% B_2O_3 -doped compositions, the diffraction peaks of SA phase were barely detectable. Increasing the calcination time to 1 h and 5 h, resulted in further formation of S_4A_7 at the expense of SA_2 . By prolonging the dwell time to 10 h, a trace amount of SA_2 (1.66%) had remained, along with S_4A_7 . Further calcination for 20 h, produced pure S_4A_7 without traces of the meta-stable SA_2 phase. The results of Rietveld quantitative analysis for 20 mol% B_2O_3 -doped compound during phase evolution are summarized in **Table 3.13** and **Figure 3.36**, respectively.

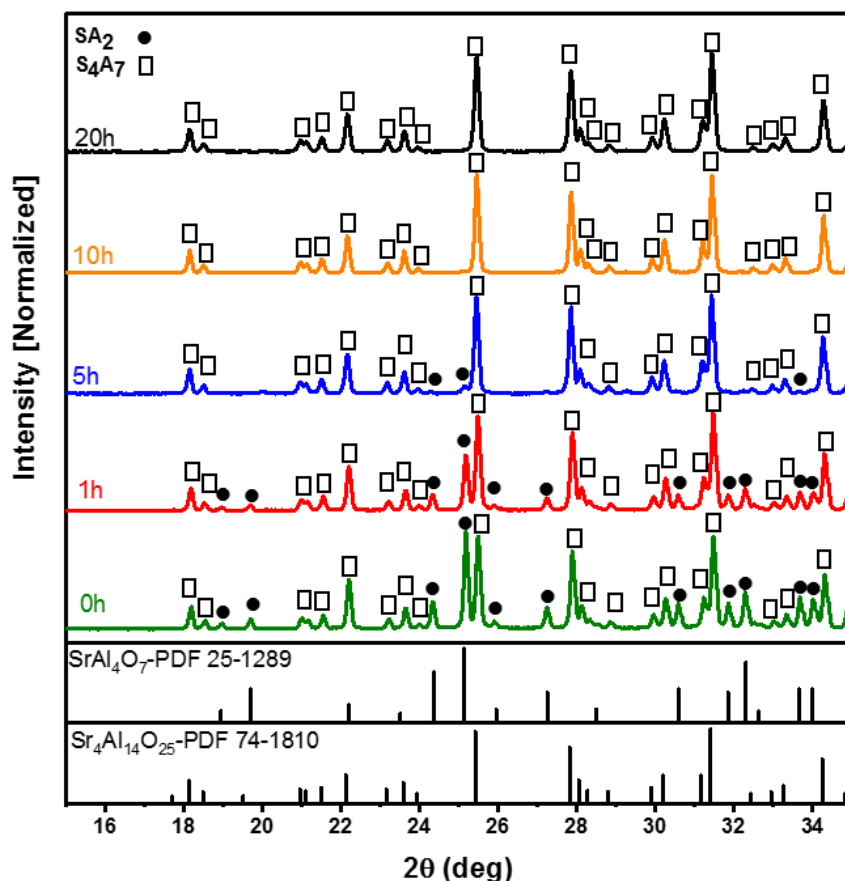


Figure 3.35. XRD patterns of the amorphous precursor of S4A7ED – 20 mol% B₂O₃ composition calcined at 1300 °C for various times.

Table 3.13. Phase composition of S4A7ED – 20 mol% B₂O₃ pre-ceramic material revealed by Rietveld quantitative analysis of the XRD data for the specimens heated to the onset, endpoint and beyond the endpoint temperatures of the exothermic peaks in the DTA signal. R_{wp} and R_{exp} are weighted profile and expected R-factors, respectively

Temperature (°C)	Phase Composition (wt%)				Goodness of Fit (R_{wp}/R_{exp})
	SA _m	SA _h	SA ₂	S ₄ A ₇	
915	21.90	11.89	66.21	-	1.92
950	11.46	-	88.66	-	2.40
1100	8.13	-	83.20	8.67	2.60
1300 – 0 h	2.27	-	31.10	66.63	1.73
1300 – 1 h	-	-	20.95	79.05	2.00
1300 – 5 h	2.44	-	2.87	94.37	2.17
1300 – 10 h	-	-	1.66	98.34	2.06
1300 – 20 h	-	-	-	100	1.91

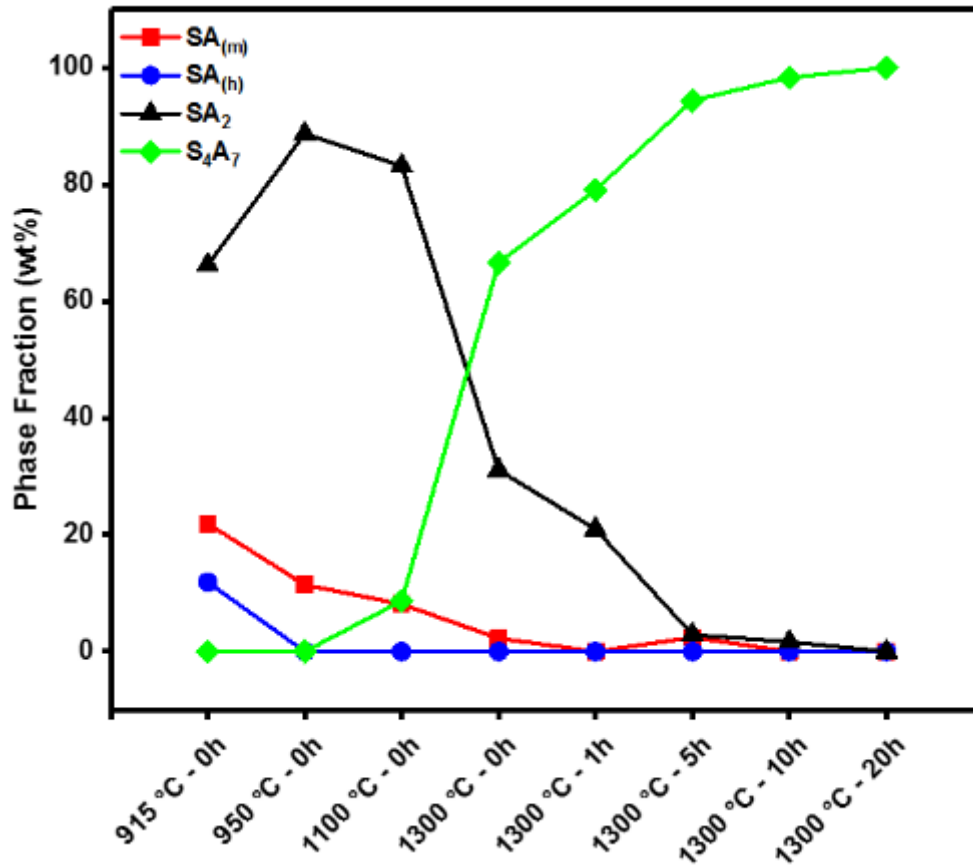


Figure 3.36. Phase fractions obtained by Rietveld quantitative phase analysis of XRD data during phase evolution of amorphous S4A7ED – 20 mol% B₂O₃ pre-ceramic upon increasing temperature and calcination at 1300 °C over various dwell time. The lines are provided as visual guide.

The shape of the thermogram for the composition with 20 mol% B₂O₃ (Figure 3. 33) was different with those of 0 mol% (Figure 3.15) and 10 mol% B₂O₃ (Figure 3.28), which we attributed to the effect of larger concentration of B₂O₃ glass former. We investigated the microstructure produced at every step of phase evolution from the amorphous pre-ceramic of S4A7ED – 20 mol% B₂O₃.

Figure 3.37 shows the SEM – EDX microstructural analysis of the specimen that was air quenched from 915 °C. The BSE images (Figure 3.37 a-c) showed two major compositional contrasts. Because the XRD data confirmed the coexistence of SA₂ as the major phase with SA phases, the large grains that were richer in Al (Figure 3.37 d and e) were SA₂ grains while small bright and spherical grains, which were richer in high atomic number Sr cations (Figure 3.37 d and f) were SA phases.

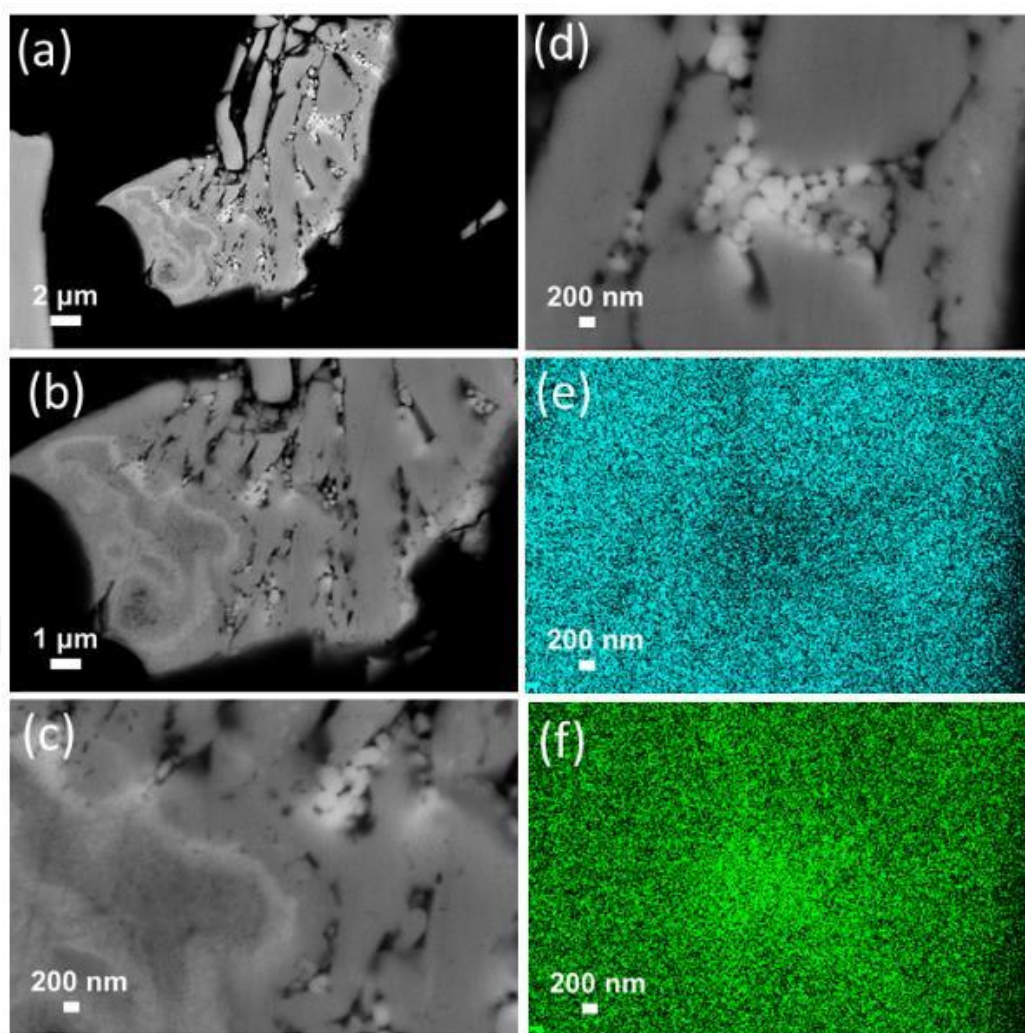


Figure 3.37. SEM – EDX microstructural analysis of the pre-ceramic amorphous S4A7ED -20 mol% B₂O₃ heated to the onset of the DTA exothermic peak at 915 °C (a-c) back-scattered electron images at different magnifications (d) region of interest for EDX elemental distribution mapping (e) elemental distribution map of Al-Kα (f) elemental distribution of Sr-L

The microstructure produced by heating the amorphous precursor of S4A7ED -20 mol% B₂O₃ to 950 °C (DTA exotherm endpoint) is shown in **Figure 3.38**. Three distinct microstructural features with different compositional contrast were observed in BSE images as labeled by #1, #2 and #3, respectively. Grains type #1, which were poor in Al and rich in Sr were SA phase (with Al:Sr = 2), while Grains type # 2, which were the most rich phase in Al were SA₂ phase (with Al:Sr = 4). Grains type #3, which formed between SA and SA₂ grains, were possibly related to formation of S₄A₇ phase (with Al:Sr = 3.5), although it was not detected during phase analysis by XRD (table 3.13). It is possible that global phase amount was below the detection limit of XRD.

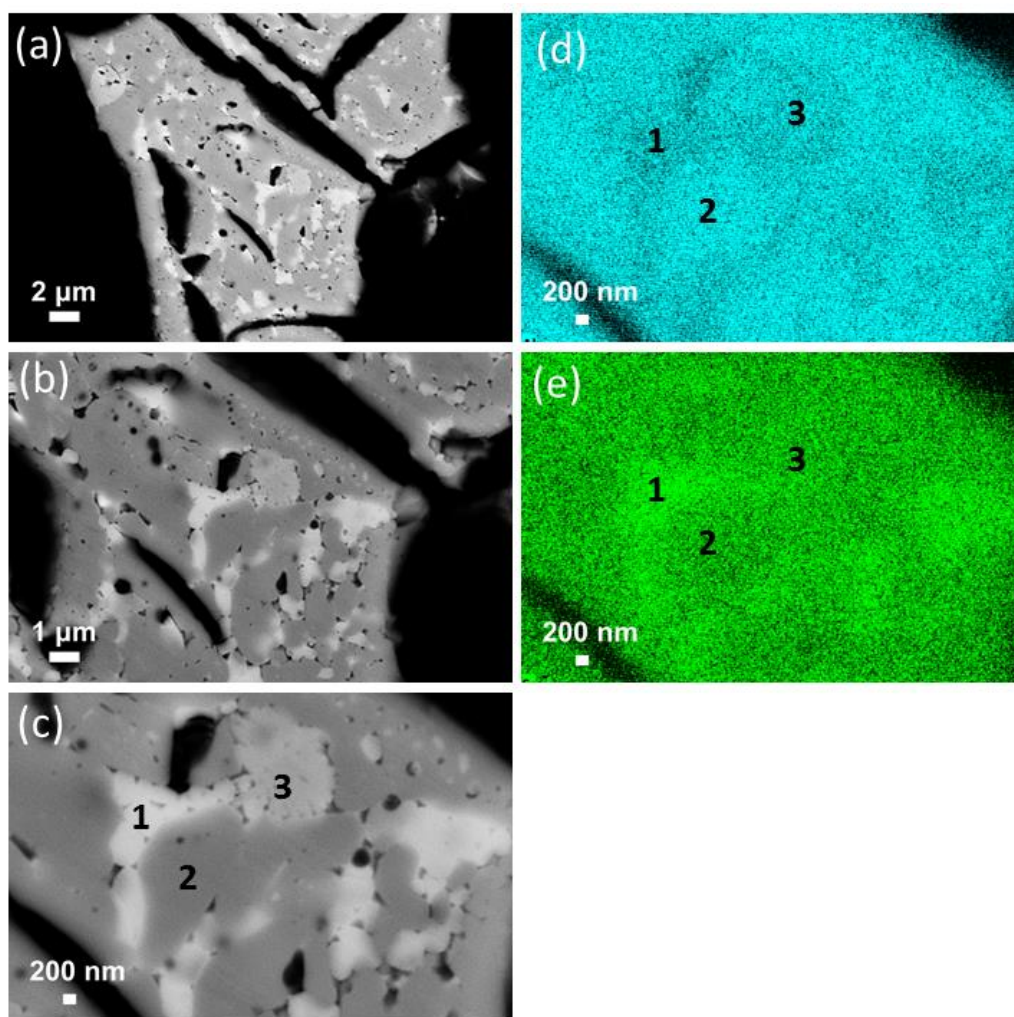


Figure 3.38. SEM – EDX microstructural analysis of the pre-ceramic amorphous S4A7ED -20 mol% B₂O₃ heated to the endpoint of the DTA exothermic peak at 950 °C (a-c) back-scattered electron images at different magnifications (d) elemental distribution map of Al-K α (e) elemental distribution of Sr-L.

The SEM-EDX analysis of the specimen heated to 1100 °C beyond the step-like thermal feature indicative of a glassy transition temperature in the DTA trace (Figure 3.33) is shown in **Figure 3.39**. The formation of S₄A₇ grains (denoted by #3) dominated the microstructure, confirming the results of Rietveld quantitative phase analysis of the specimen heated to 1100 °C. In addition, the elemental distribution maps of Sr and Al (Figure 3.39 e-f) obtained from the region of interest (Figure 3.39 - d) correlated nicely with Sr-rich SA grains (#1) and Al-rich large, equiaxed grains of SA₂ (#2) and elongated S₄A₇ grains (#3).

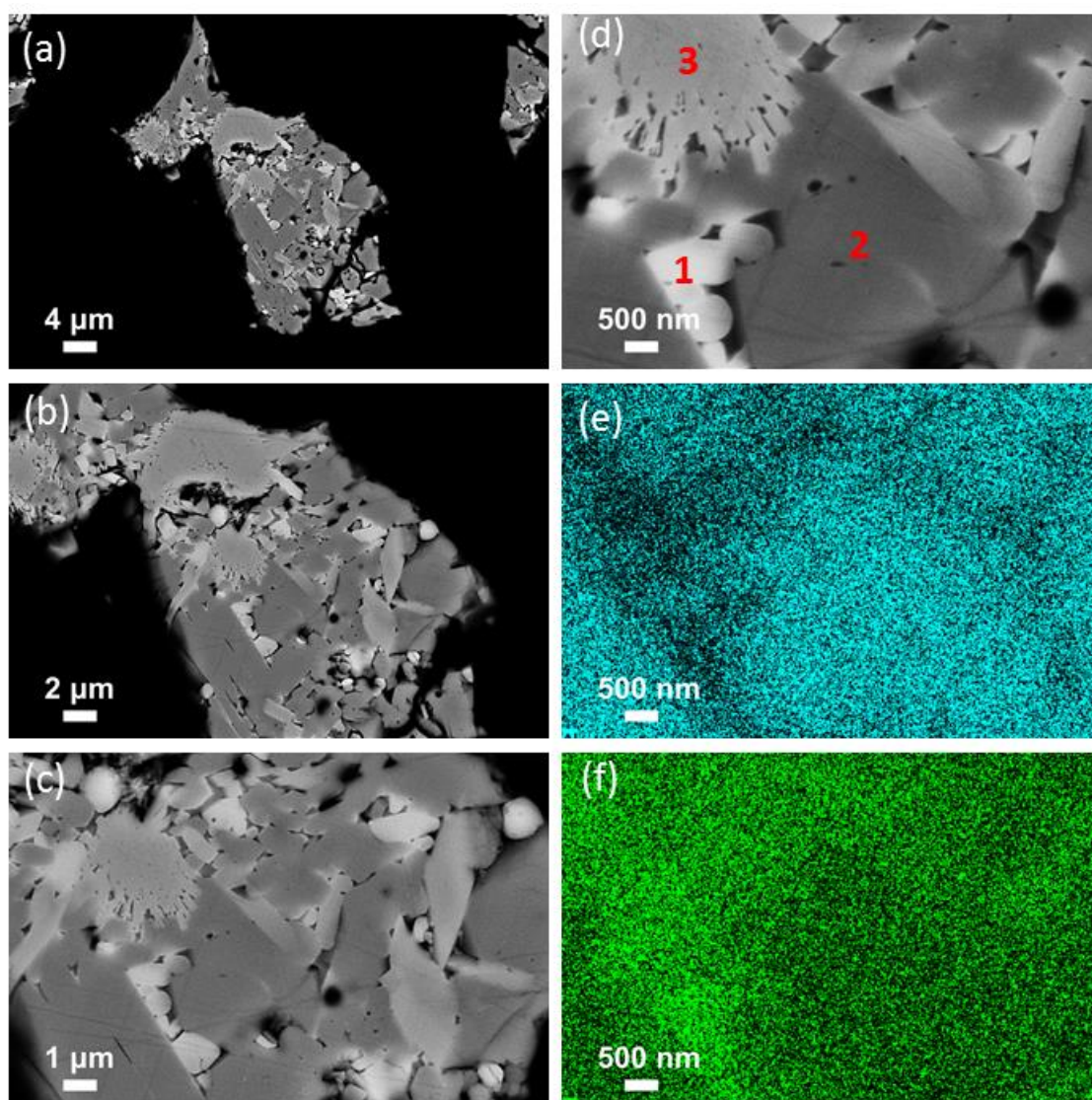


Figure 3.39. SEM – EDX microstructural analysis of the pre-ceramic amorphous S4A7ED -20 mol% B₂O₃ heated to 1100 °C (a-c) back-scattered electron images at different magnifications (d) region of interest for EDX elemental distribution mapping (e) elemental distribution map of Al-K α (f) elemental distribution of Sr-L.

In addition to the microstructural features related to SA, SA₂ and S₄A₇ phases, which were verified by XRD phase analysis at 1100 °C, we also noticed the existence of an intergranular phase for the 20 mol% B₂O₃ incorporated specimen, when the temperature was above the glass transition feature in DTA curve. In order to understand the elemental composition of this microstructural feature (Figure 3.40), we applied EDX point analysis on the intergranular phase (IGP). The ratio of Al:Sr obtained for IGP phase was 1.89, which was not consistent with any equilibrium strontium aluminate phases in SrO – Al₂O₃ binary system, indicative of the glassy nature of the intergranular phase.

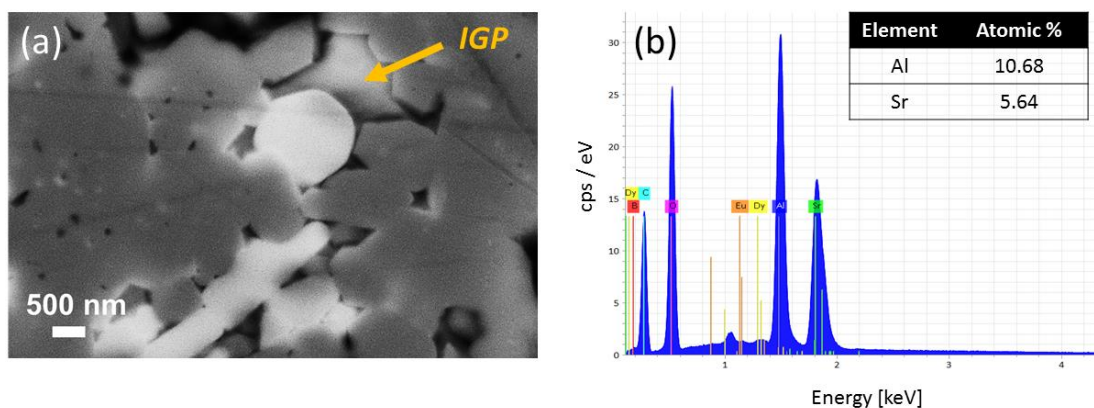


Figure 3.40. SEM – EDX analysis of the intergranular phase produced during phase evolution of S4A7ED – 20 mol% B₂O₃ at 1100 °C. a) BSE image b) EDX spectrum obtained from point analysis of the intergranular phase.

Figure 3.41 shows the comparison of the BSE images from the microstructure of the powder particles heated to 950 °C and 1100 °C, without polishing and chemical etching, respectively. The microstructure of both specimens shows the presence of large, equiaxed SA₂ grains and SA grains. However, we observed that in the specimen heated beyond the glass transition temperature at 1100 °C, all the grains were coated by an intergranular phase at the grain boundaries. The crystalline grains surfaces had been wetted by a high melting temperature glassy phase. Therefore, it can be postulated that for high concentration of B₂O₃, at the temperature range close to the glass transition, the phase evolution occurred by precipitation from the glassy liquid rather than solid state reaction between the grains.

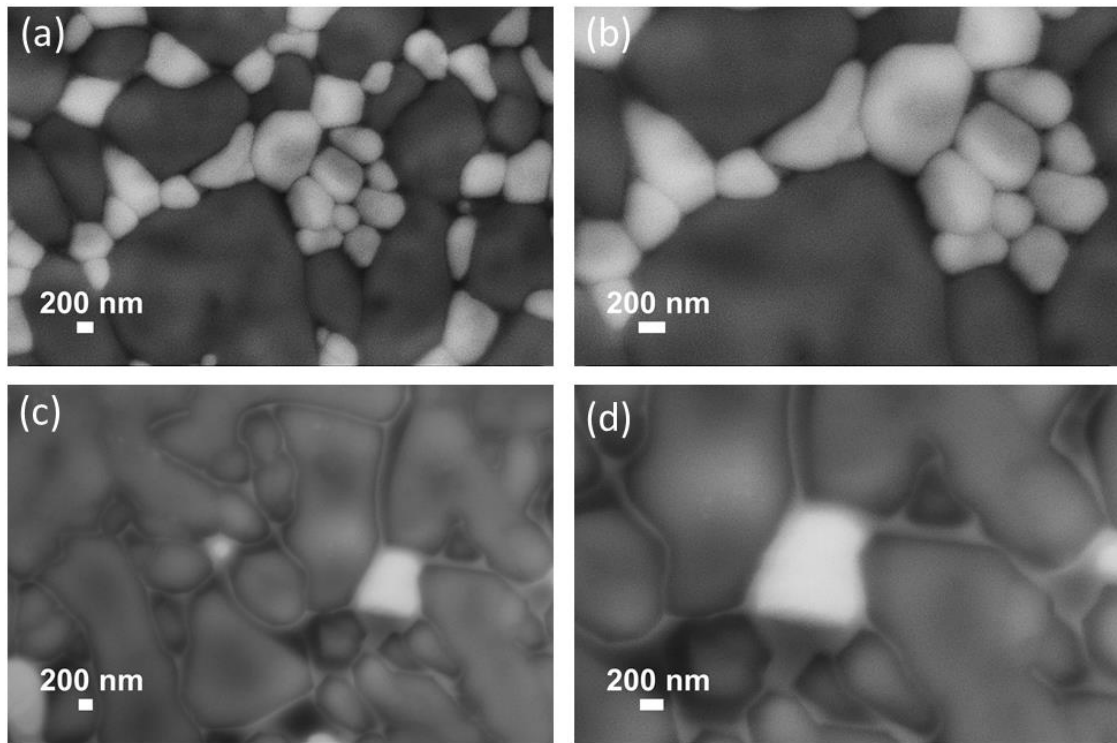


Figure 3.41. Microstructure of $S_4A_7ED - 20 \text{ mol\% } B_2O_3$ preceramic powders (unpolished) at (a-b) $950^\circ C$ and (c-d) $1100^\circ C$.

The microstructural analysis of the 20 mol% B_2O_3 doped specimen heated to $1300^\circ C$ and then air-quenched to the room temperature is shown in **Figure 3.42**. It can be seen that large, equiaxed grains of S_4A_7 phase coexists with darker SA_2 grains, in agreement with XRD phase analysis. In addition, between the two phases, the presence of the intergranular phase is evident, as indicated by arrows (Figure 3.42 a-b). Furthermore, there is a compositional variation at the interface between the S_4A_7 and SA_2 gains, which is discernable by a bright contrast at the grain boundary shown in the high magnification BSE image in Figure 3.42 – c. This feature maybe due to wetting of the glassy phase or preferential segregation inside the grains during microstructural evolution. Elemental distribution maps (Figure 3.42 d-e), revealed that, the intergranular phase between neighboring S_4A_7 and SA_2 grains is highly rich in Sr while deficient in Al.

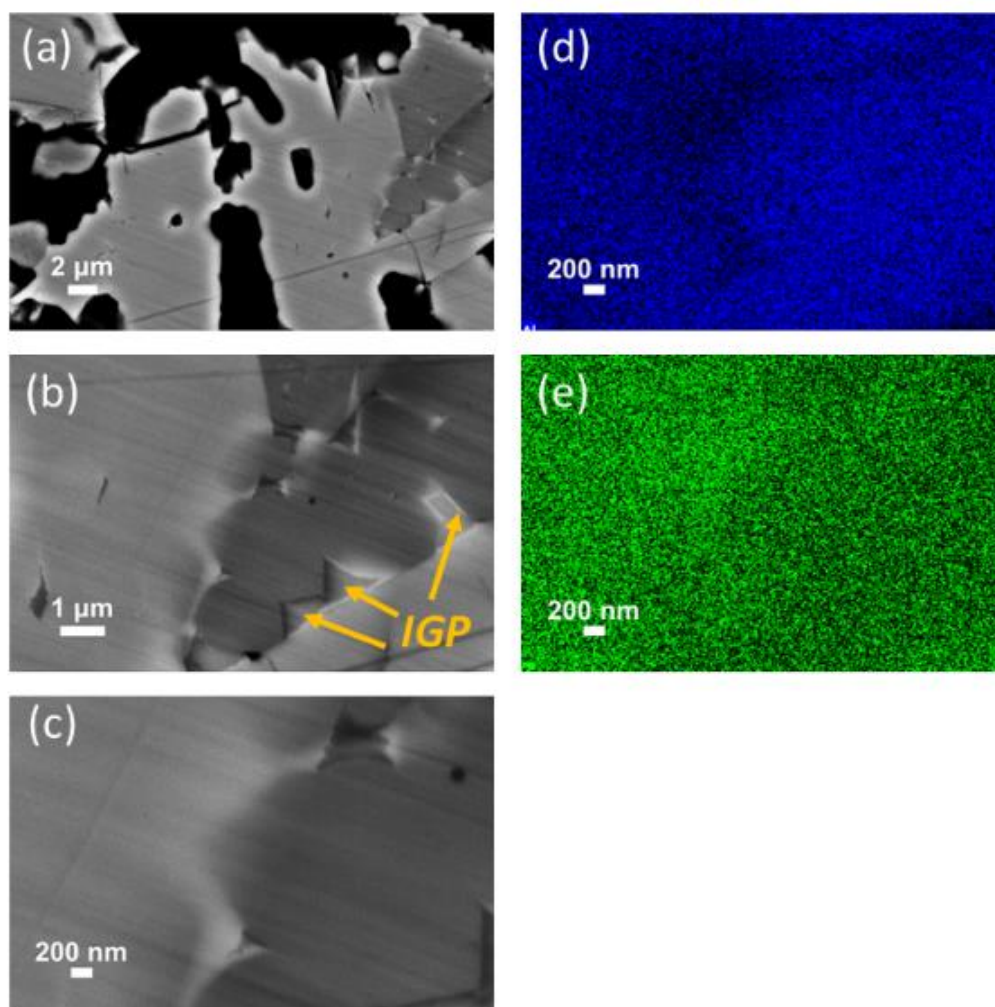


Figure 3.42. SEM – EDX microstructural analysis of the pre-ceramic amorphous S4A7ED -20 mol% B₂O₃ heated to 1300 °C (a-c) back-scattered electron images at different magnifications (d) elemental distribution map of Al-K α (e) elemental distribution of Sr-L.

We further investigated the distribution of the elements along the interface of S₄A₇ / IGP / SA₂ by applying line profile analysis in energy dispersive X-ray spectroscopy. The line of interest was chosen such that it started from the center of the S₄A₇ grain, passed through the intergranular phase at the interface and extended up to the center of the adjacent SA₂ grain (**Figure 3.43 -a**). The distribution of the elements throughout the line (**Figure 3.43 -b**) showed that, by moving from the center of the S₄A₇ grain towards the IGP, the Al content decreased. By entering the IGP, the concentration of Al continuously decreased until it met a minimum at the interface of IGP and SA₂. Inside the SA₂ grain, the Al content increased close to the interface and then flattened at the center of the grain. This situation is the reverse of the segregation profile of Sr cations. As for the rare earth dopants, we observed that, the dopant concentrations were more uniform inside the S₄A₇

grain. At middle of the IGP, the magnitude of Eu and Dy was slightly higher than the neighboring S_4A_7 grains. However, the concentrations of both Eu and Dy dropped inside the SA_2 phase. Furthermore, it is important to note that, the content of rare earth dopants was higher inside the S_4A_7 compared to that in SA_2 , meaning that S_4A_7 phase can accommodate more Eu and Dy in its crystal structure relative to SA_2 . In the case of B, the EDX line profile showed almost no variation along the line of analysis, possibly due to the poorer detection statistics for B in SEM-EDX.

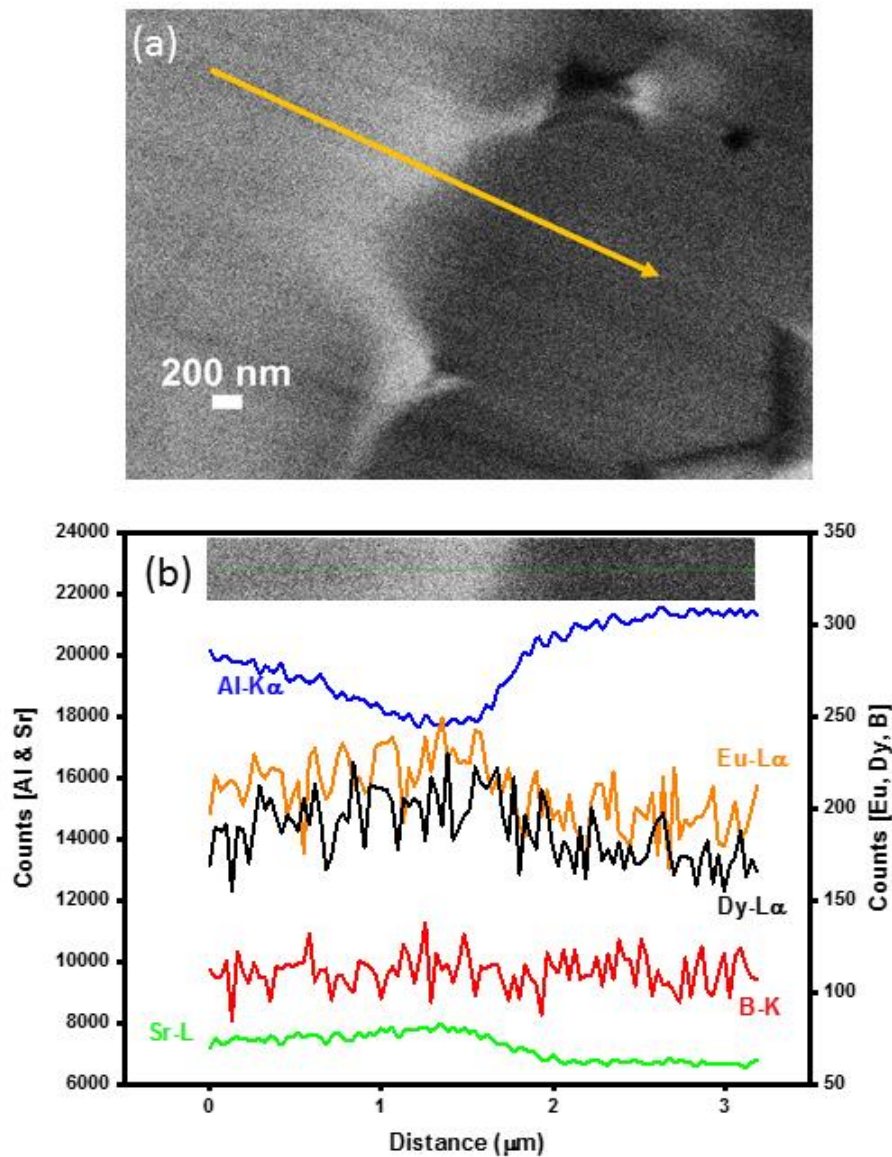


Figure 3.43. SEM-EDX line profile analysis of the S_4A_7 / IGP / SA_2 interfaces in the pre-ceramic amorphous S_4A_7ED -20 mol% B_2O_3 heated to 1300 °C. a) the distance analyzed in the region of interest b) concentration profiles of the elements along the indicated line in a.

Figure 3.44 shows the microstructure produced by calcination of S4A7ED – 20 mol% B₂O₃ pre-ceramic powder at 1300 °C for 10h. According to Table 3.13, the specimen was almost pure in S₄A₇ (98.34%). Thus, the large equiaxed grains in BSE images were characterized as S₄A₇ phase. Moreover, the amount of the intergranular phase with very bright contrast had increased, compared to the specimen calcined at 1300 °C without any holding time. This indicates that by prolonging the calcination time, phase segregation was increased, due to slow diffusion kinetics. In addition, the elemental distribution maps (Figure 3.44 d-f) revealed that the glassy intergranular phase was deficient in Al and O and highly rich in Sr species.

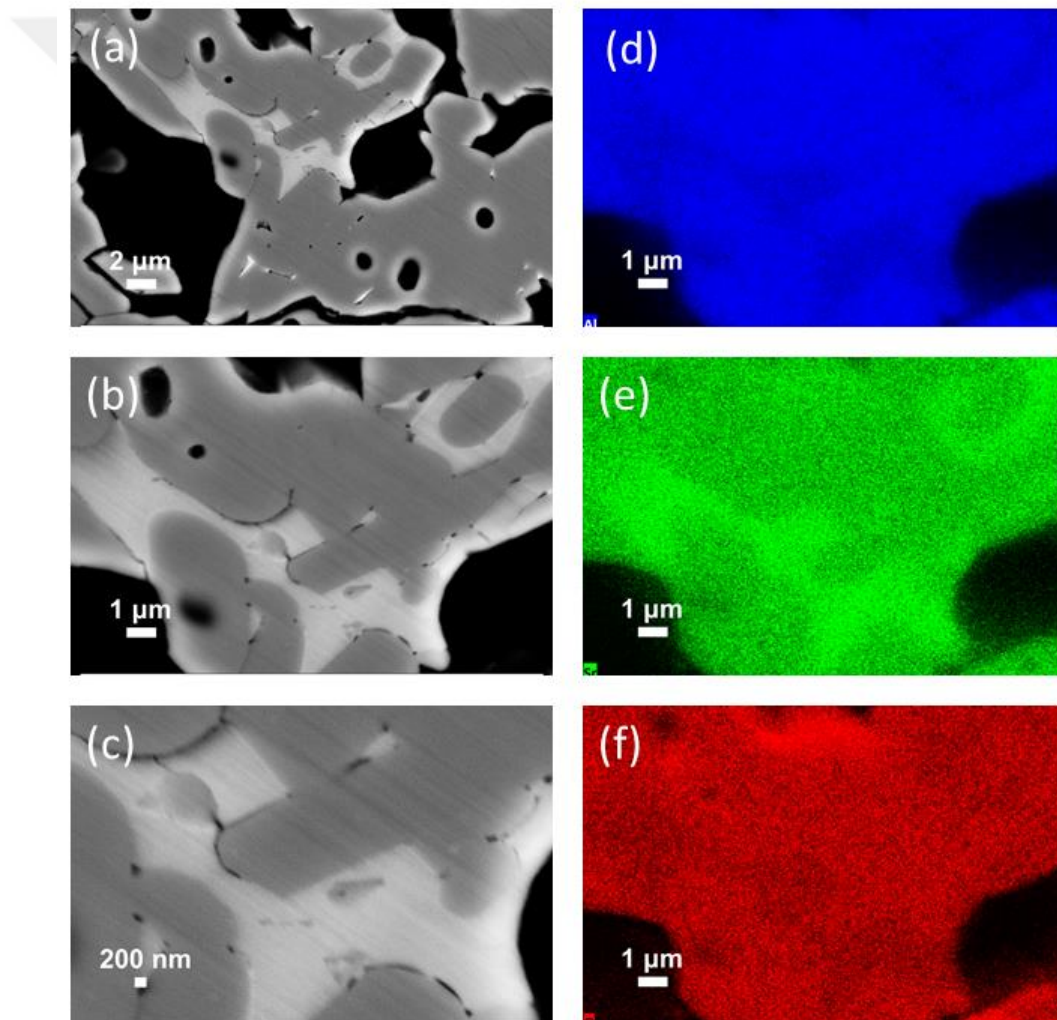


Figure 3.44. SEM – EDX microstructural analysis of the amorphous pre-ceramic of S4A7ED -20 mol% B₂O₃ calcined at 1300 °C for 10h (a-c) back-scattered electron images at different magnifications (d) elemental distribution map of Al-K α (e) elemental distribution of Sr-L (f) elemental distribution of O-K.

In **Figure 3.45**, the results of EDX line profile analysis are reported as indicated in the microstructure shown in Figure 3.45-a. The glassy phase that coated the $SrAl_2O_4$ grain, was not compositionally homogenous, and was rich in Sr and poor in Al, as implied by enhanced concentrations of Sr and Al at the two sides of the crystalline grain (Figure 3.45-b). Along the line of analysis, the concentration of Eu and Dy in Figure 3.45-c showed almost a uniform distribution between the neighboring $SrAl_2O_4$ and IGP microstructural features. However, for the concentration profile of B, it seems that the glassy phase is richer in B relative to the crystalline adjacent grains as can be seen by a shallow increase in B content in the range of *ca.* 3 – 3.5 μm along the line profile. Therefore, the IGP microstructural feature can be a borate phase although we did not detect any crystalline borate phase by XRD analysis and Rietveld refinement.



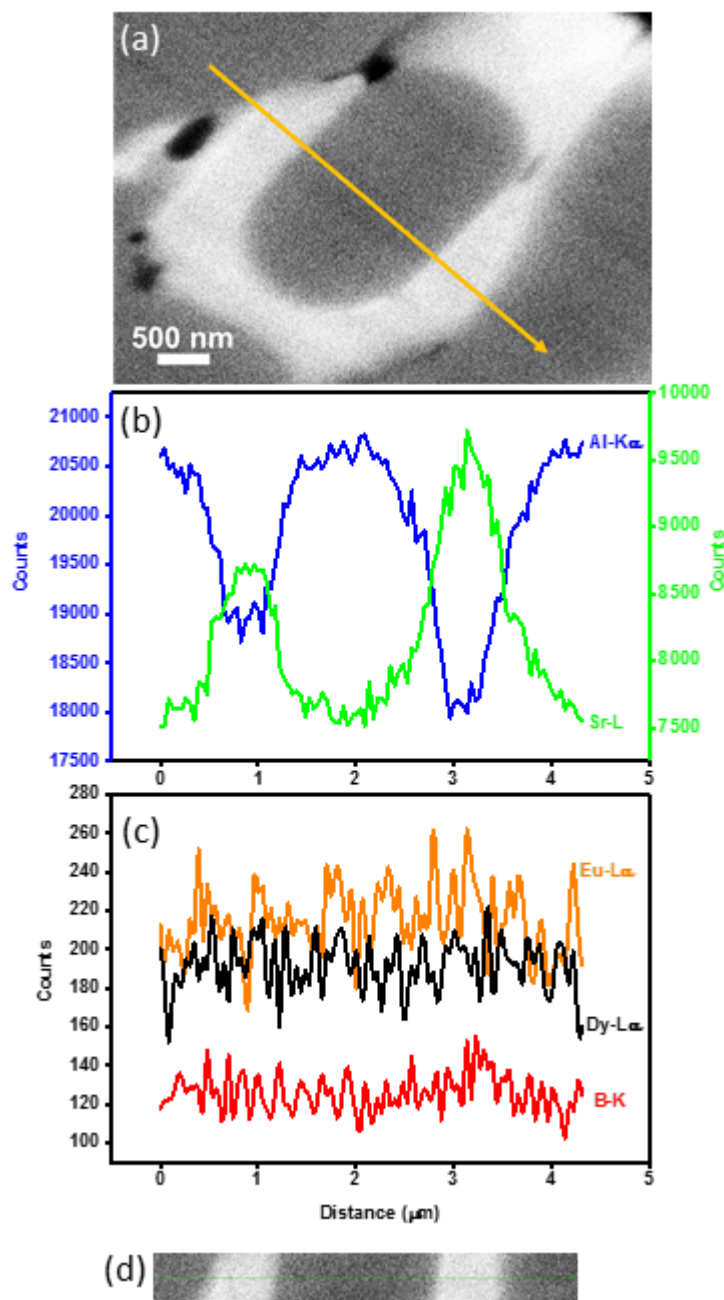


Figure 3.45. SEM-EDX line profile analysis of the S₄A₇ / IGP / S₄A₇ interfaces in the amorphous pre-ceramic of S₄A₇ED -20 mol% B₂O₃ calcined at 1300 °C for 10h a) the distance analyzed in the region of interest and concentration profiles of b) Al and Sr c) Eu, Dy and B dopants along the indicated line in a d) the scanned region of interest for line profile analysis.

3.6.4 Phase Evolution in S₄A₇ED – 30 mol% B₂O₃

Differential thermal analysis of the Pechini processed S₄A₇ED pre-ceramic when doped with 30 mol% B₂O₃ is shown in **Figure 3.46**. The thermogram was recorded at a heating rate of 10 °C/min under air atmosphere (flow rate of 40 mL/min). The DTA curve for 30

mol% B₂O₃ doped specimen resembles the DTA plot for 20 mol% B₂O₃ specimen. Again, only one exothermic peak was observed, and the crystallization peak was followed by the step-like thermal fingerprint as for the case of 20 %mol B₂O₃ sample (see figure 3.33). Before the crystallization peak, the DTA baseline is almost constant. Because in DTA analysis the same amount of thermal energy is input to a reference material (in this case empty alumina crucible) and the material of interest, and the temperature difference between the two is measured upon increasing temperature, the change in the baseline is directly representative for thermal heat capacity of the material that is being thermally scanned with respect to a reference. Thus, the constant baseline level before the crystallization peak is an indication of no substantial change in the state of the pre-ceramic, which was amorphous. As the temperature increased, the pre-ceramic underwent an exothermic crystallization at an onset temperature of 910 °C. This means that at 910 °C, the state of the pre-ceramic material starts to change. The peak maximum occurring at 920 °C is the maximum temperature difference between the S4A7ED-30 mol% B₂O₃ pre-ceramic material with the reference crucible. After undergoing the first crystallization event, it was observed that the baseline did not flatten and immediately underwent a step-like change, which is characteristic of a glass transition in the material. It was observed that in the case of 20 mol% B₂O₃-doped specimen, when the temperature was around this thermal feature, the microstructure contained a glassy liquid, which wetted the surface of the growing crystalline grains. The phase evolution was accompanied by dissolving of the reactants in the liquid and the precipitation of the products from the liquid phase. Moreover, DTA analysis in Figure 3.46 also revealed that the baseline changes continuously above 1050 °C, which means that phase transformation was continuous and consequently, the thermal heat capacity changed continuously at elevated temperatures.

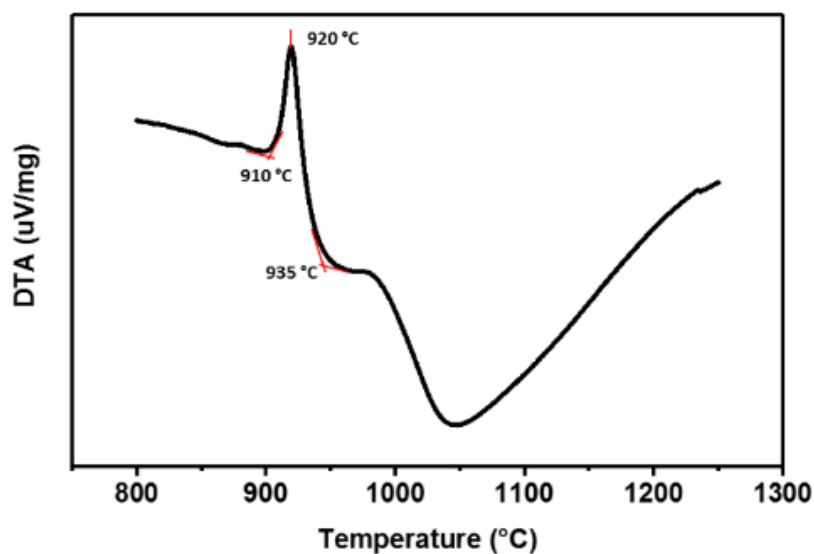


Figure 3.46. DTA trace of the Pechini processed S4A7ED doped with 30 mol% B₂O₃ after pre-calcination at 800 °C for 3 h at a heating rate of 10 °C/min under air atmosphere.

The phase evolution of the amorphous pre-ceramic containing 30 mol% B₂O₃ sintering flux was evaluated based on the critical temperatures in thermogram and according to the temperatures listed in **Table 3.14**.

Table 3.14. Calcination temperatures and dwell times used for investigation of phase evolution in amorphous S4A7ED – 30 mol% B₂O₃ composition.

Calcination conditions (°C)	DTA characteristic
860 °C	below the Exo. onset
910 °C	Exo. onset
935 °C	Exo. endpoint
1000 °C	beyond the 1 st Exo. endpoint
1300 °C – 0 h	-
1300 °C – 1 h	-
1300 °C – 5 h	-
1300 °C – 10 h	-
1300 °C – 20 h	-

Figure 3.47 shows the XRD patterns of the S4A7ED amorphous precursor doped with 30 mol% B_2O_3 , which were heated to the characteristic temperatures of the exothermic peak in Figure 3.46. We observed that the state of the powders was amorphous up to the endpoint temperature of the DTA exothermic peak. Among the strontium aluminate phases, only small reflections attributed to SA_2 phase were detected at the endpoint temperature. When the temperature was increased to 1000 °C, sharp crystalline peaks of SA_2 phase appeared. Small residuals of monoclinic SA phase were also detected. As opposed to lower B_2O_3 -content specimens, it was observed that the formation of intermediate SA phase, especially hexagonal polymorph was substantially suppressed, and the amorphous powder had primarily crystallized into the SA_2 phase directly.

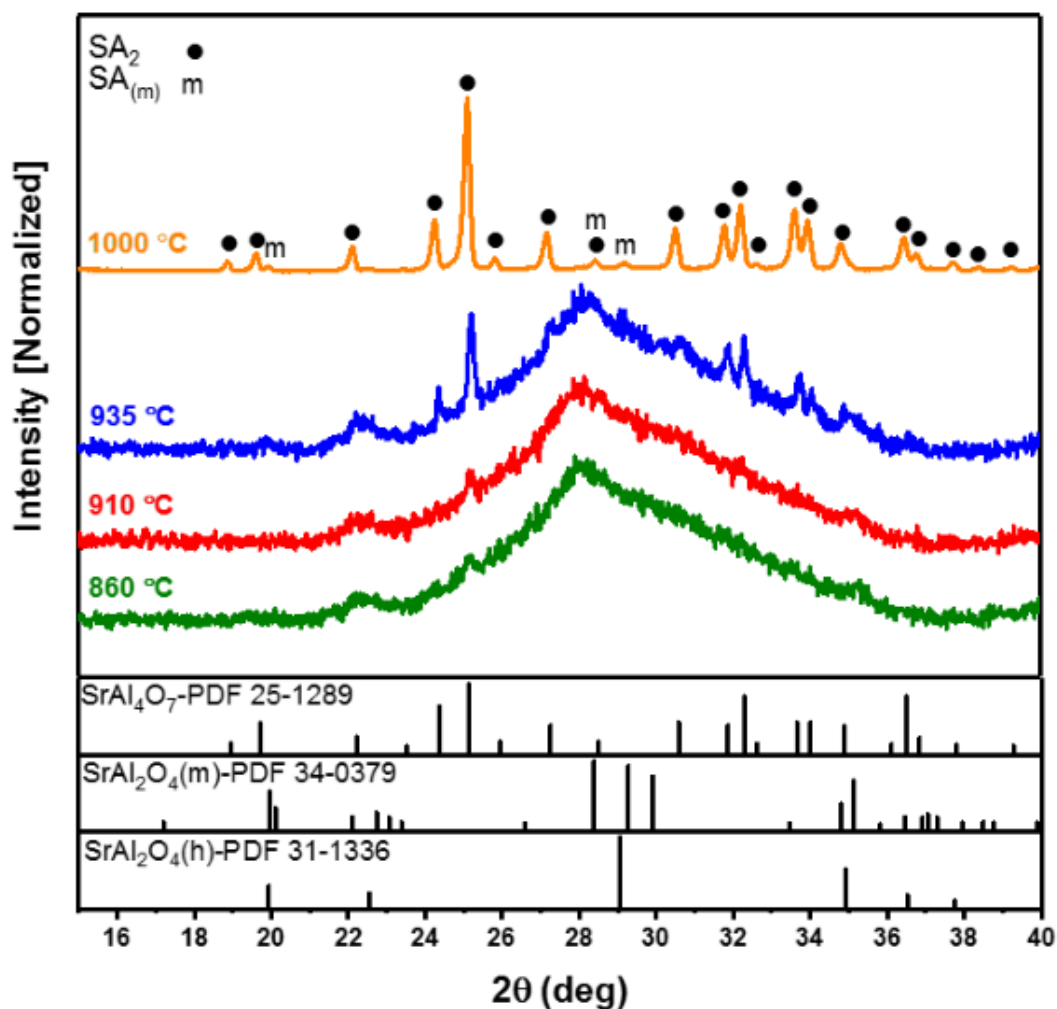


Figure 3.47. XRD patterns of the amorphous pre-ceramic of S4A7ED – 30 mol% B_2O_3 composition heated to the characteristic temperatures of the DTA exothermic peak at 860, 910, 935 and 1000 °C.

Figure 3.48, shows the phase evolution of the amorphous compound of S4A7ED – 30 mol% B₂O₃ upon increasing the calcination duration at 1300 °C. The trend of phase evolution by time is analogous to that of previously reported compositions with lower B₂O₃ contents. However, it was observed that the SrAl₁₂O₁₉ (SA₆) phase had also formed to an extent of *ca.* 3 – 4 wt% and remained constant in phase fraction, regardless of the calcination duration.

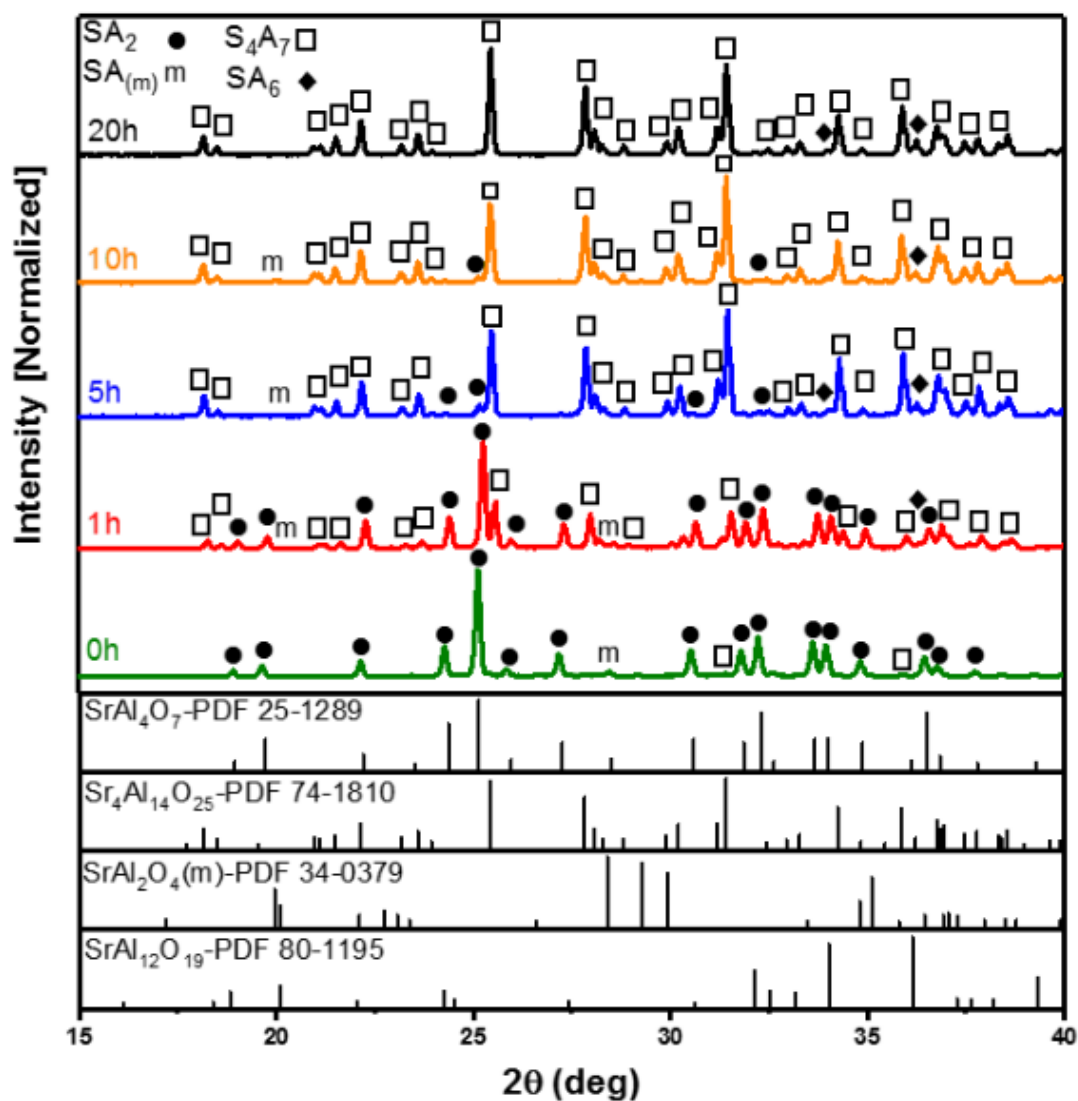


Figure 3.48. XRD patterns of the amorphous precursor of S4A7ED -30 mol% B₂O₃ composition calcined at 1300 °C for various times.

The results of Rietveld quantitative analysis for 30 mol% B₂O₃-doped compound during phase evolution are summarized in **Table 3.13** and **Figure 3.36**, respectively.

Table 3.15. Phase composition of S4A7ED – 30% B₂O₃ pre-ceramic material revealed by Rietveld quantitative analysis of the XRD data for the specimens calcined under different conditions based on the DTA signal. R_{wp} and R_{exp} are weighted profile and expected R-factors, respectively.

Temperature (°C)	Phase Composition (wt%)				Goodness of Fit (R_{wp}/R_{exp})
	SA _m	SA ₂	SA ₆	S ₄ A ₇	
1000	12.08	87.82	-	-	2.69
1300 – 0 h	3.14	90.72	-	6.14	1.96
1300 – 1 h	2.30	58.50	3.00	36.20	2.27
1300 – 5 h	2.82	5.01	3.90	88.28	2.61
1300 – 10 h	2.58	3.16	3.38	90.89	2.80
1300 – 20 h	-	-	3.77	96.23	2.76

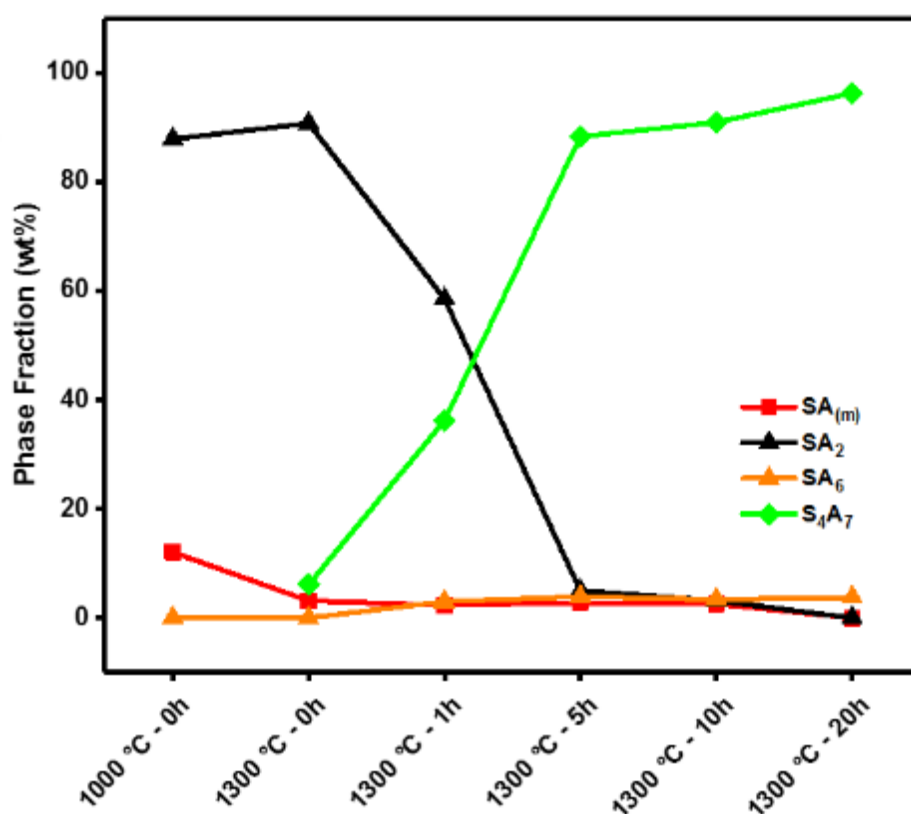


Figure 3.49. Phase fractions obtained by Rietveld quantitative phase analysis of XRD data during phase evolution of amorphous S4A7ED – 30 mol% B₂O₃ pre-ceramic upon increasing temperature and calcination at 1300 °C over various dwell times. The lines are provided as visual guide.

3.6.5 Phase Evolution in S4A7ED – 40 mol% B₂O₃

The DTA trace of the strontium aluminate compound with nominal stoichiometry of S₄A₇ doped with 1 %mol Eu, 1 %mol Dy and 40 %mol B₂O₃, after pre-calcination at 800 °C for 3h, at a heating rate of 10 °C/min under air atmosphere (flow 40 mL/min) is shown in **Figure 3.50**. The thermogram showed a sharp exothermic peak with an onset of 880 °C, which extended up to the endpoint temperature of 930 °C. The onset and endpoint temperatures were obtained by extrapolation of the tangents applied to the baseline and the exothermic peak tails as shown in Figure 3.50. Similar to the compositions doped with 20 and 30 mol% B₂O₃, and in contrast to the ones without or with lower concentration of B₂O₃ e.g. 0, 5 and 10 mol% B₂O₃, the thermogram did not exhibit a well resolved second exothermic peak on a flat baseline. Instead, a drop in the DTA signal in the range of 950 – 1050 °C was observed.

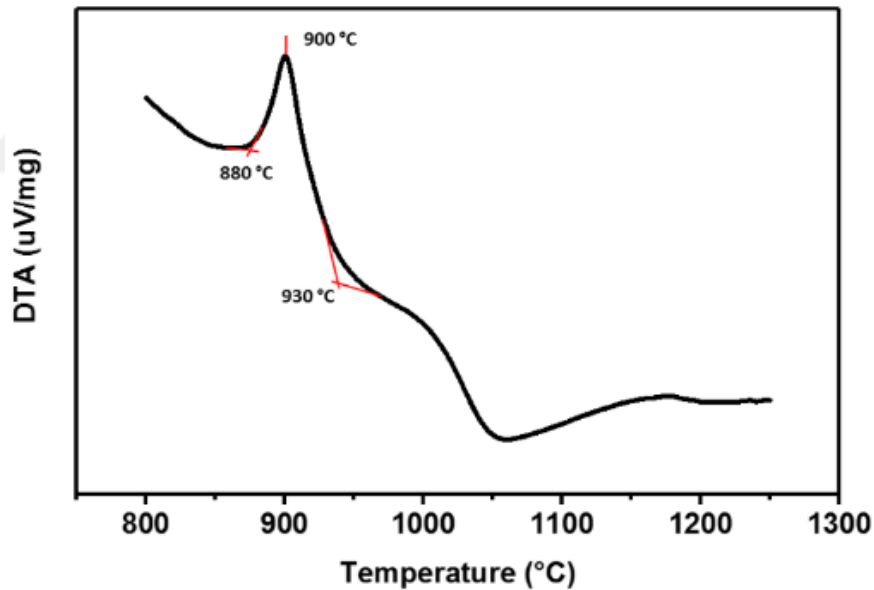


Figure 3.50. DTA trace of the Pechini processed S4A7ED doped with 40 mol% B₂O₃ after pre-calcination at 800 °C for 3h at a heating rate of 10 °C/min under air atmosphere.

The phase evolution of the amorphous pre-ceramic containing 40 mol% B₂O₃ sintering flux was evaluated based on the critical temperatures in the thermogram and according to the temperatures listed in **Table 3.16**.

Table 3.16. Calcination temperatures and dwell times used for investigation of phase evolution in amorphous S4A7ED – 40 mol% B₂O₃ composition.

Calcination conditions (°C)	DTA characteristic
830 °C	below the Exo. onset
880 °C	Exo. onset
930 °C	Exo. endpoint
1000 °C	beyond the 1 st Exo. endpoint
1300 °C – 0 h	-
1300 °C – 1 h	-
1300 °C – 5 h	-
1300 °C – 10 h	-
1300 °C – 20 h	-

XRD patterns related to the amorphous pre-ceramic of S4A7ED-40 mol% B₂O₃ which were heated to the temperatures before and after the exothermic reaction are shown in **Figure 3.51**. Before the DTA peak onset, the powder was mainly amorphous and only diffraction peaks attributed to SA₂ phase with very low intensity was observed. In fact, the evolution of SA₂ crystalline phase is accelerated before the peak onset temperature, when the B₂O₃ content was increased to 40 mol%. At the onset temperature, the composition of the specimen did change. Upon increasing the temperature to the endpoint of the DTA exotherm, the crystallinity of the specimen was improved, and diffraction peaks of SA₂ became more intense. However, no peak attributed to the SA phase was detected, opposite to observations in the lower B₂O₃ concentrations. Beyond the exothermic peak at 1000 °C, the residual amorphous portion of the specimen had crystallized into SA₂ phase only. Therefore, it seems that by increasing the content of B₂O₃, formation of SA phase was completely suppressed.

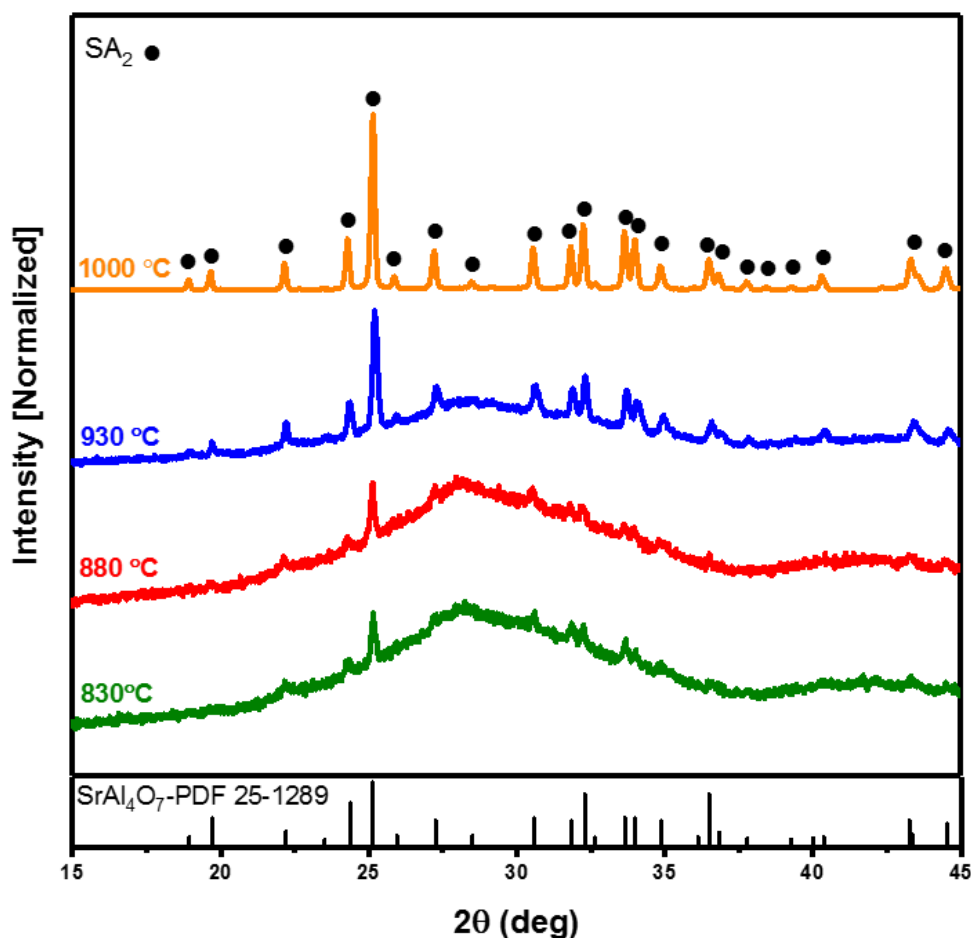


Figure 3.51. XRD patterns of the amorphous pre-ceramic of S4A7ED – 40 mol% B₂O₃ composition heated to the characteristic temperatures of the DTA exothermic peak at 830, 880, 930 and 1000 °C.

X-ray diffraction analysis of the 40 mol% B₂O₃ doped amorphous precursor of S4A7ED calcined at 1300 °C for various times is shown in **Figure 3.52**. At 1300 °C without any soaking time, SA₂ was still the major phase, while small fractions of SA₆ also appeared. When the calcination time was increased to 1 h, crystalline peaks attributed to the long afterglow S₄A₇ phase appeared abruptly and SA₂ peaks were diminished in intensity. In addition, the fraction of SA₆ was also increased as confirmed by Rietveld refinement of the XRD data. By further prolongation of the calcination time to 5, 10 and 20 h, the meta-stable SA₂ phase was completely decomposed, and the thermodynamically stable S₄A₇ was present as the major phase along with SA₆. The magnitude of the fraction of S₄A₇ and SA₆ did not change significantly by increasing the calcination time, and the phase composition remained constant.

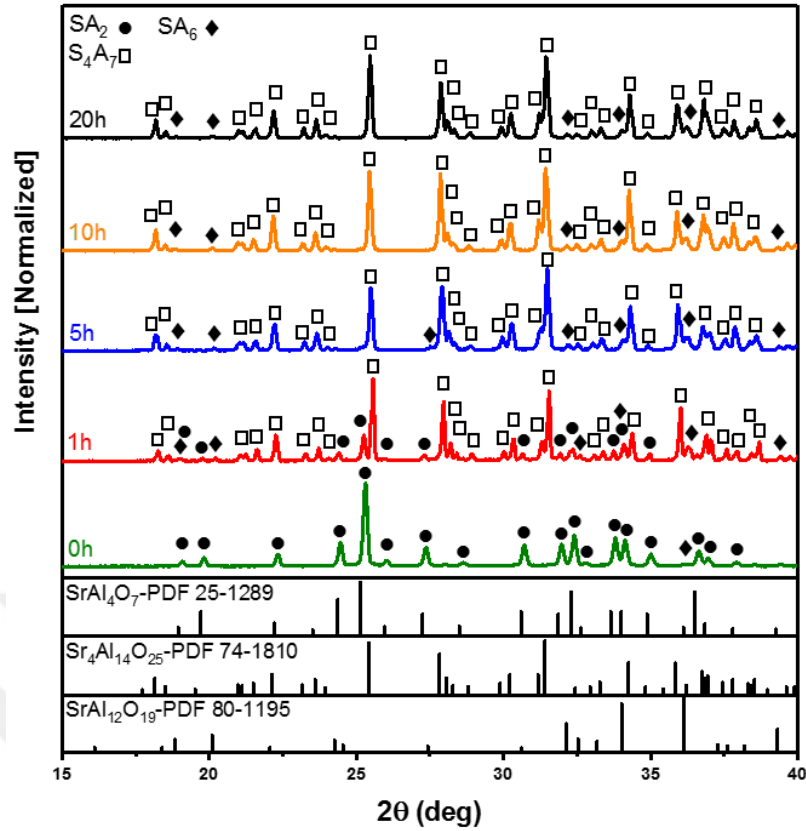


Figure 3.52. XRD patterns of the amorphous precursor of S4A7ED-40 mol% B₂O₃ composition calcined at 1300 °C for various times.

The results of Rietveld quantitative analysis for 40 mol% B₂O₃-doped compound during microstructural evolution are summarized in **Table 3.13** and **Figure 3.36**, respectively.

Table 3.17. Phase composition of S4A7ED – 40 mol% B₂O₃ pre-ceramic material revealed by Rietveld quantitative analysis of the XRD data for the specimens calcined under different conditions based on the DTA signal. R_{wp} and R_{exp} are weighted profile and expected R-factors, respectively.

Temperature (°C)	Phase Composition (wt%)			Goodness of Fit (R_{wp}/R_{exp})
	SA ₂	SA ₆	S ₄ A ₇	
1000	100	-	-	2.27
1300 – 0 h	96.59	3.41	-	2.28
1300 – 1 h	15.69	9.97	74.35	2.90
1300 – 5 h	-	10.36	89.64	3.12
1300 – 10 h	-	9.00	91.00	2.85
1300 – 20 h	-	9.83	90.17	3.22

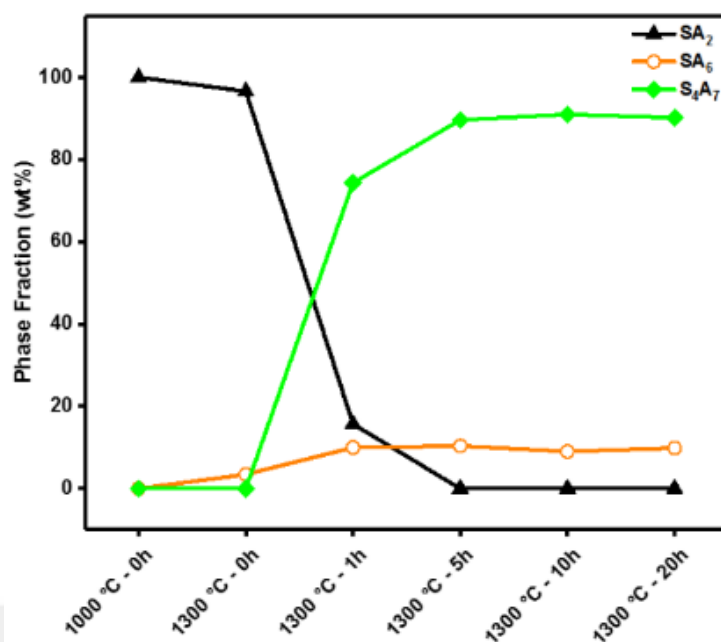


Figure 3.53. Phase fractions obtained by Rietveld quantitative phase analysis of XRD data during phase evolution of amorphous S4A7ED – 40 mol% B₂O₃ pre-ceramic upon increasing temperature and calcination at 1300 °C over various dwell times. The lines are provided as visual guide.

The microstructure of the S4A7ED – 40 mol% B₂O₃ pre-ceramic material, heated to 1000°C and then air-quenched, as revealed by BSE imaging of the polished powder particles, is shown in **Figure 3.54**. The microstructure consisted of large, equiaxed grains with average Al:Sr ratio of 3.88 (± 0.02), obtained by EDX point analyses on several grains as indicated in Figure 3.54 – a, which was consistent with the Al:Sr ratio of the SA₂ phase. These results agreed with as was also confirmed by XRD phase analysis of the powders at 1000°C.

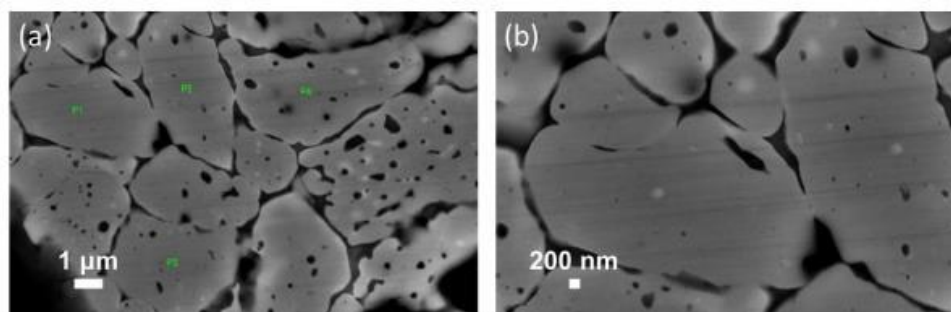


Figure 3.54. BSE images of the microstructure of S4A7ED – 40 mol% B₂O₃ pre-ceramic compound after heating to 1000 °C.

In the S4A7ED – 40 mol% B₂O₃ amorphous precursor calcined at 1300 °C without any soaking time, we detected three distinct microstructural features as illustrated in **Figure 3.55**. In region #1, the microstructure showed large equiaxed grains with intergranular phase (figure 3.55-a). In this case, most of the IGP phase was chemically etched away during sample preparation by etching the polished powders in dilute phosphoric acid, resulted in formation of the empty spaces between the crystalline grains. The corresponding elemental distribution maps for region #1 revealed that the IGP was highly deficient in Al (Figure 3.55-b). However, a correlation between Sr map and barely discernable Eu and Dy maps with the intergranular phase was obtained (Figure 3.55 c-e). The EDX point analyses of the microstructure in region #1, revealed an Al:Sr ratio of 3.88 (± 0.03) for the crystalline grains and 1.86 for the intergranular phase. The equiaxed grains were close to the stoichiometry of SA₂ phase, as was also confirmed by XRD results.

In region #2, the microstructure showed the presence of SA₂ grains with intergranular phase which was not completely removed by chemical etching (Figure 3.55-k). Because the IGP was not completely etched, the elemental distribution map of aluminum still showed Al deficiency in the IGP phase (Figure 3.55-g) but to a less extent compared to Figure 3.55-b. In addition, the IGP phase in this case was rich in Sr, while the correlation of Eu and Dy cations with the intergranular phase was clearly visible, when the IGP phase was not completely etched (Figure 3.55 h-j). This suggests that the IGP phase was a glassy phase of strontium aluminoborate phase containing Eu and Dy complexes.

We also detected the presence of perfectly hexagonal grains (with a salty habit) in the microstructure along with SA₂ grains in region #3 which are rich in Al and poor in Sr. Because XRD results confirmed the presence of the SA₆ phase (3.41 wt%) in this specimen (see Table 3.17), and by considering the elemental maps of Sr and Al, the hexagon grains can be attributed to the SA₆ phase with hexagonal crystal structure. No substantial change was observed in the distribution of rare earth elements between the SA₂ large equiaxed grains and the SA₆ grains (Figure 3.55 k-o).

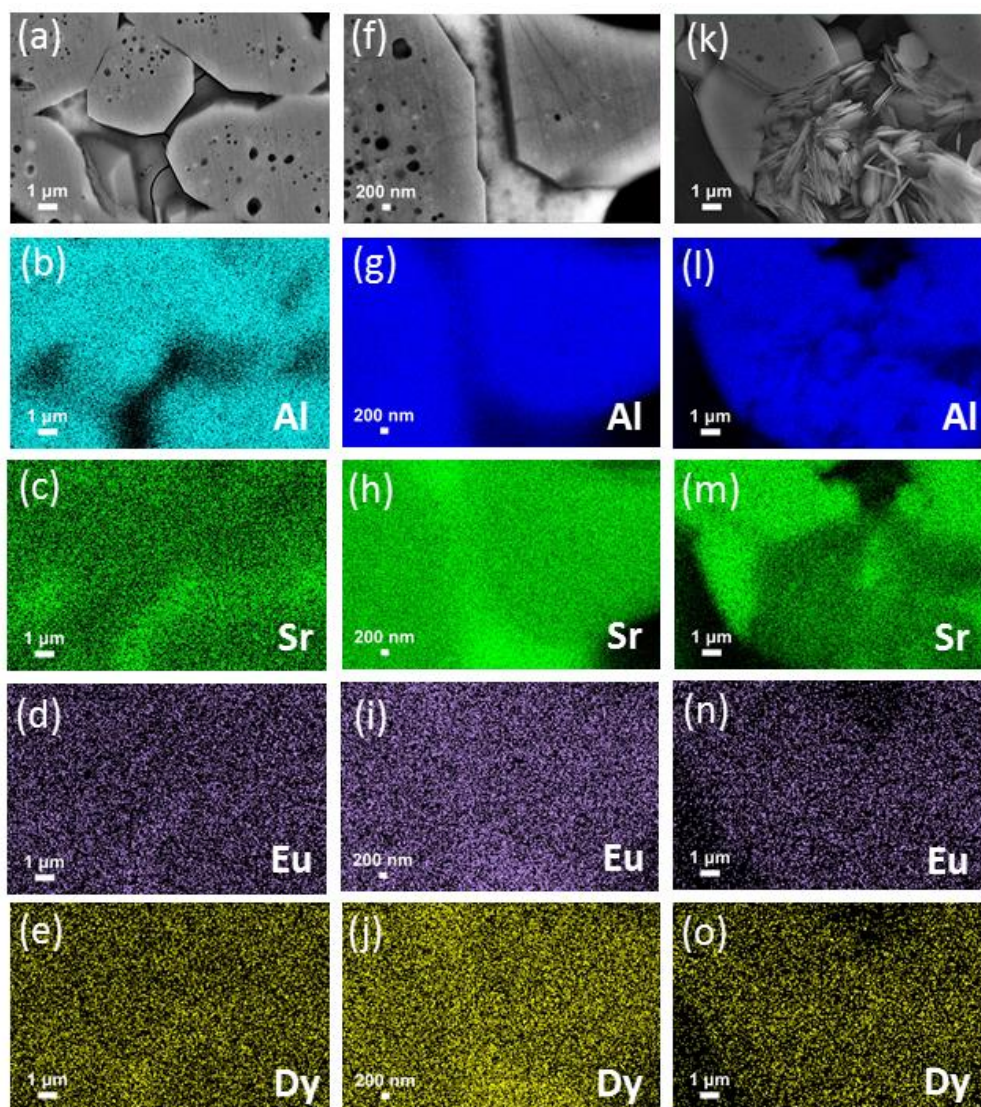


Figure 3.55. SEM – EDX microstructural analysis of S4A7ED – 40 mol% B₂O₃ pre-ceramic compound calcined at 1300 °C a) microstructure at region #1 (b-e) elemental distribution maps corresponding to Region #1 f) microstructure at region #2 (g-j) elemental distribution maps corresponding to Region #2 k) microstructure at region #3 (l-o) elemental distribution maps corresponding to Region #3.

The microstructure produced after calcination of S4A7ED – 40 mol% B₂O₃ pre-ceramic at 1300°C for 1h is presented in **Figure 3.56**. The microstructure showed the coexistence of four different characteristic features, phases as revealed by compositional contrast due to variation of average Z-number in the microstructure in BSE micrographs. In ROI#1 (Figure 3.56-b), the porous, equiaxed grains of SA₂ were surrounded by the intergranular pockets. Moreover, large S₄A₇ crystals with brighter contrast (with respect to SA₂ grains) were also observed. In addition, microstructure in ROI#2 and ROI#3 revealed the abundant formation of the Al-rich grains of SA₆ phase, evolved from the intergranular

phase and inside the S_4A_7 grains (Figure 3.56 c-d). The microstructural observations for the specimen calcined at 1300 °C for 1h were consistent with the results of Rietveld quantitative analysis of the XRD data (Table 3.17), indicating the multiphase nature of the specimen.

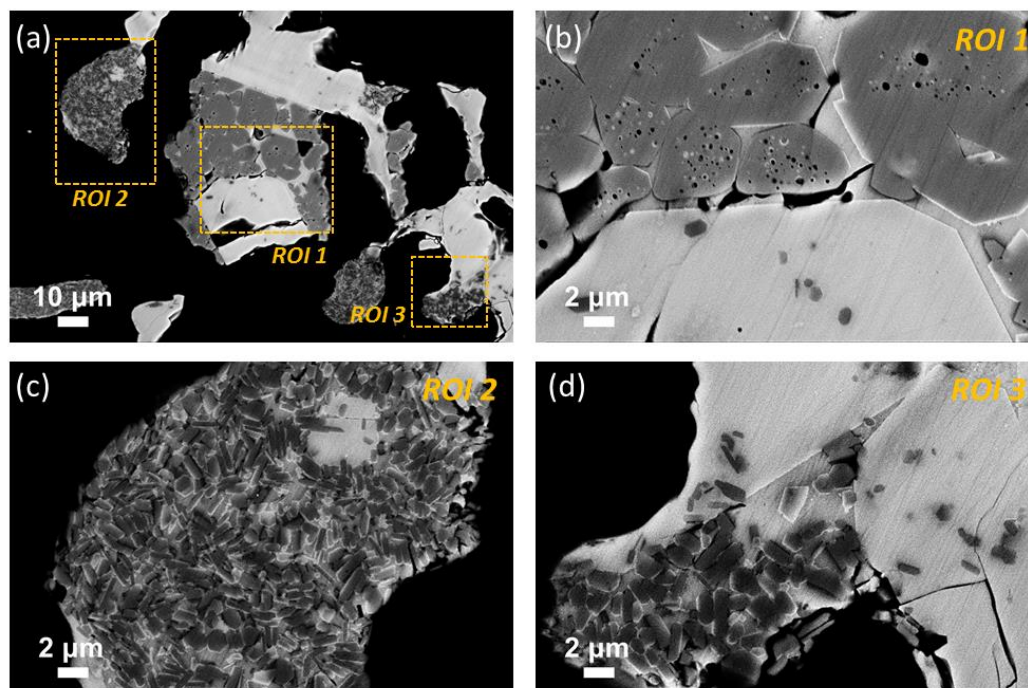


Figure 3.56. The microstructure produced during phase evolution of amorphous precursor of $S_4A_7ED - 40 \text{ mol\% } B_2O_3$ at 1300 °C after calcination for 1h at different magnifications.

In order to verify the phase composition of in the microstructure including crystalline grains and intergranular pockets displayed in Figure 3.56, we performed SEM-EDX point analysis on each characteristic microstructural feature under identical experimental conditions. For all the point analyses, a working distance of 9 mm, accelerating voltage of 15 KeV and objective aperture size of 30 µm, resulted in final prob size diameter of 0.75 µm. Under this set up, the interaction volume depth was estimated to be 2.8 µm. The 0.75 µm spot size was sufficiently small compared to the size of microstructural features on the polished surface of the specimen to make sure that data collection is solely limited to the feature of interest and the probe size does not rater the neighboring phases. Data acquisition time for all the spectra was 5 minutes for all the analyzed points.

The results of SEM-EDX point analysis of the microstructure in S_4A_7ED with 40 mol% B_2O_3 after calcination at 1300 °C for 1h is shown in **Figure 3.57**. For the crystalline grain

denoted by P1, the point analysis revealed an Al:Sr ratio of 3.56, which was consistent with that of $SrAl_2O_7$ phase. The intergranular phase labeled with P2, showed an Al:Sr ratio of 1.45, which was not close to any of the strontium aluminate stable phase, possibly an indication of amorphous nature of the intergranular phase. The EDX spectrum attributed to the grains denoted by P3 showed an Al:Sr ratio of 3.95, which was close to the stoichiometry of $SrAl_4O_7$ (SA_2) phase. Finally, the Al:Sr ratio of 8.04 was obtained for the small hexagonal grains with dark contrast labeled as P4, which was close to the composition of SA_6 phase.

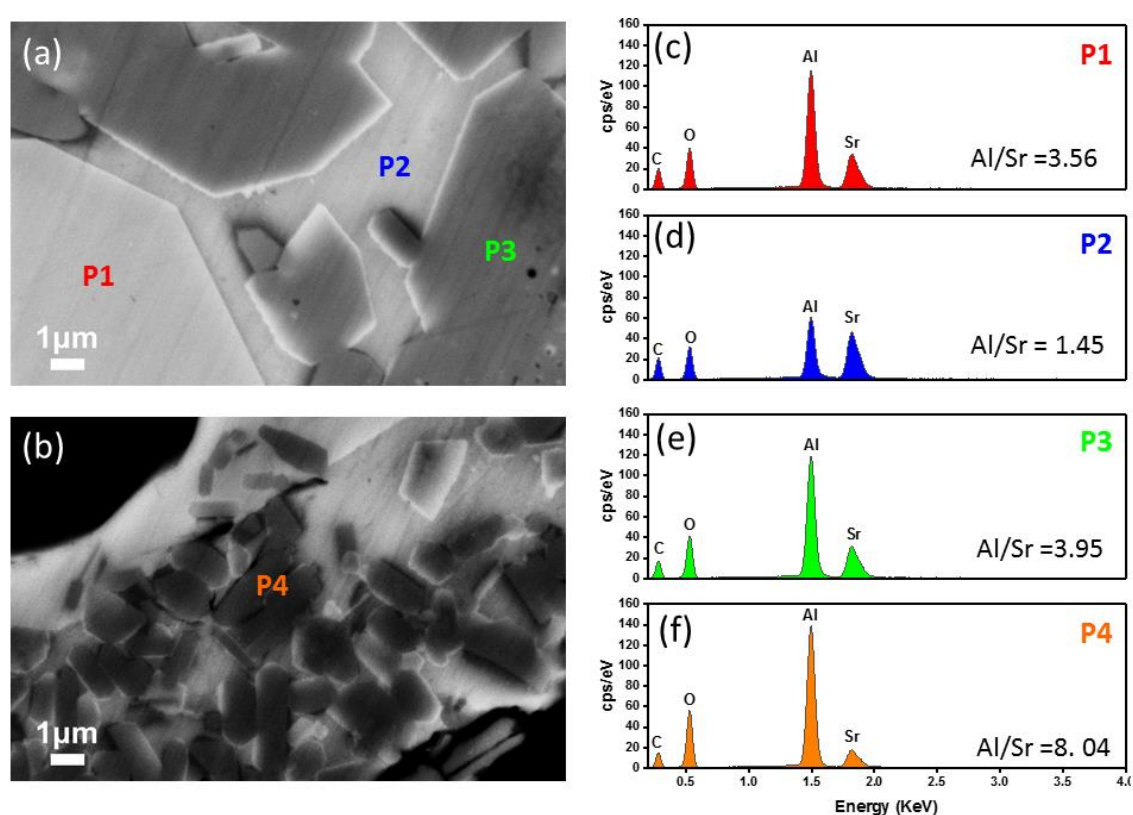


Figure 3.57. SEM-EDX point analysis of the microstructural features of $S4A7ED$ with 40 mol% B_2O_3 pre-ceramic after calcination at 1300 °C for 1h. (a-b) BSE image of four different microstructural features and (c-f) EDX spectra corresponding to P1, P2, P3 and P4, respectively.

We also investigated the elemental distribution maps of the microstructure presented in ROI#1 and ROI#2 in Figure 3.56 (**Figure 3.58**). We observed that, while the intergranular phase was highly Al deficient, the Al-rich SA_6 grains had precipitated inside the intergranular phases. This means that a phase separation occurred in the glassy intergranular phase during phase evolution from the amorphous state upon which SA_6

grains had formed, and the IGP phase became depleted from Al and enriched in Sr. In addition, it was observed that some of the SA_6 grains had also formed inside the S_4A_7 grains, but not inside the SA_2 crystals.

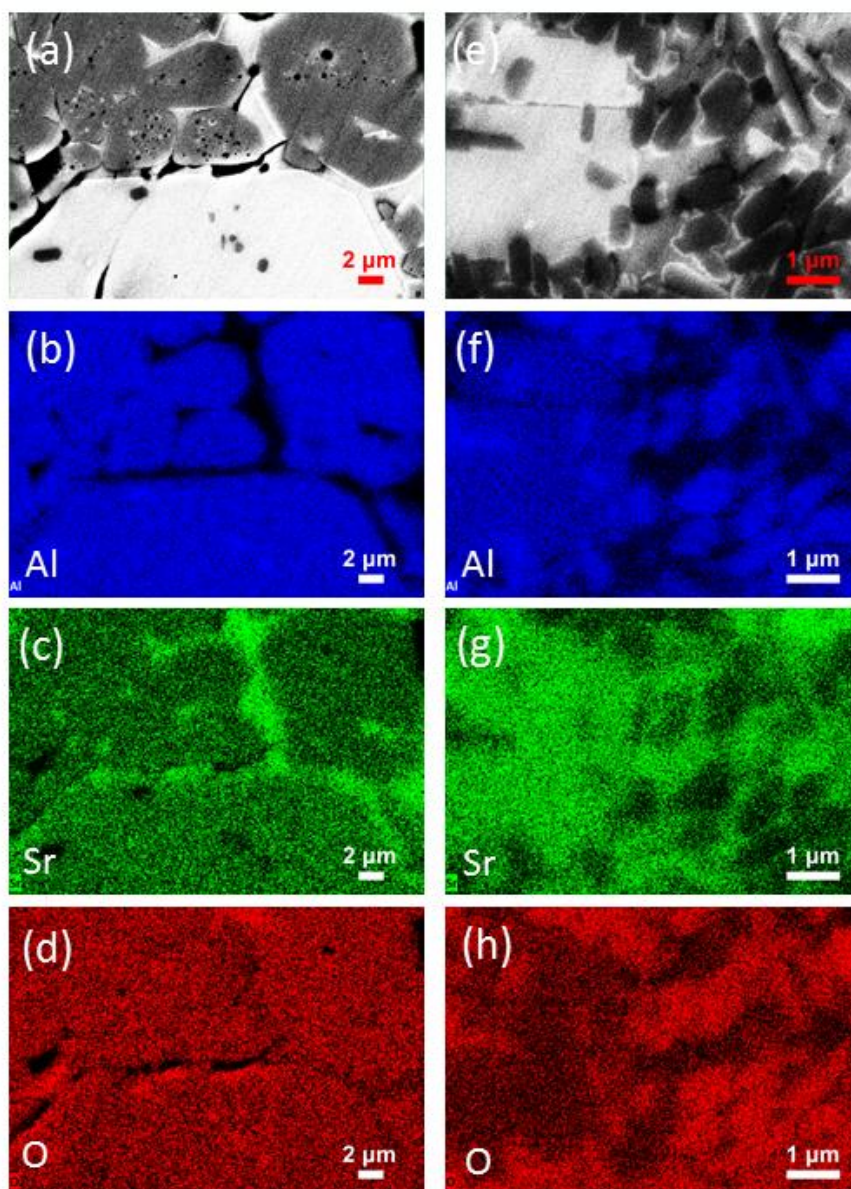


Figure 3.58. SEM – EDX microstructural analysis of S_4A_7ED – 40 mol% B_2O_3 pre-ceramic compound calcined at 1300 °C for 1h a) BSE image of ROI #1 (b-d) elemental distribution maps corresponding to ROI #1 e) BSE image of ROI #2 (f-h) elemental distribution maps corresponding to ROI #2.

The microstructure produced after 5 h and 10 h of calcination at 1300 °C, resembled that of 1h except that the large equiaxed SA_2 grains were not present as confirmed by XRD

phase analysis and thus not shown here. However, when the pre-ceramic powder of S4A7ED doped with 40 mol% B_2O_3 was calcined for 20 h at 1300 °C, we noticed the presence of a super-bright phase in between the SA_6 grains, which was replaced by the intergranular glassy phase reported previously in the specimen calcined at 1300 °C for 1h, as shown in **Figure 3.59**. Furthermore, the EDX mapping analysis of the microstructure implied that the super-bright phase (indicated by red arrow) is rich in both rare earth dopants of Eu and Dy, and is depleted in Sr and Al, while the intergranular phase that was described previously (indicated by orange arrow) was also rich in Sr (Figure 3.59 d-f). Thus, it seems that the super-bright phase produced over 20 h calcination at 1300 °C was different in composition compared to the glassy phase that was already identified. From the elemental distribution maps of Eu and Dy (Figure 3.59 g-h), we observed that the rare earth elements were segregated between the SA_6 phase at the expense of intergranular pockets.

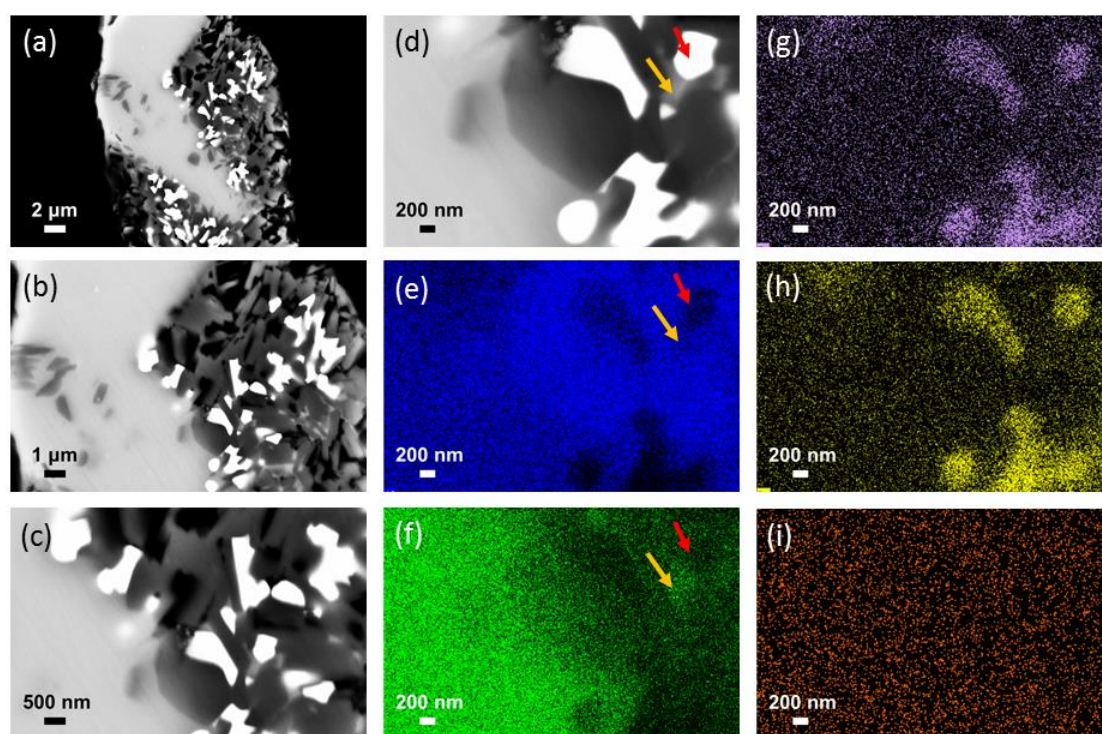


Figure 3.59. SEM-EDX analysis of the S4A7ED – 40 mol% B_2O_3 pre-ceramic compound calcined at 1300 °C for 20h (a-c) BSE image at different magnifications d) BSE image of the region of interest for elemental distribution mapping e) elemental map of Al-K α f)) elemental map of Sr-L g)) elemental map of Eu-L α h)) elemental map of Dy-L α and i)) elemental map of B-K.

In order to verify the compositional difference between the two types of intergranular phase, we acquired EDX spectra from individual points representative for each type of intergranular pockets and the results of EDX point analysis are shown in **Figure 3.60**. EDX spectrum acquisition for both points was obtained under identical experimental conditions (prob diameter size of 0.75 μm , with penetration depth of 2.5 μm , and collection time of 5 minutes). For the intergranular phase denoted by P_1 (Figure 3.60 – a), a Al:Sr ratio of 1.95 was obtained and the EDX spectrum did not exhibit any distinguishable peak for the rare earth dopants. However, the Al:Sr ratio for the super-bright phase denoted by P_2 (Figure 3.60 – a) was 0.45 and visible peaks attributed to Eu and Dy characteristic X-rays was detected in EDX spectrum which implied that the compositional nature of the two phase were substantially different.

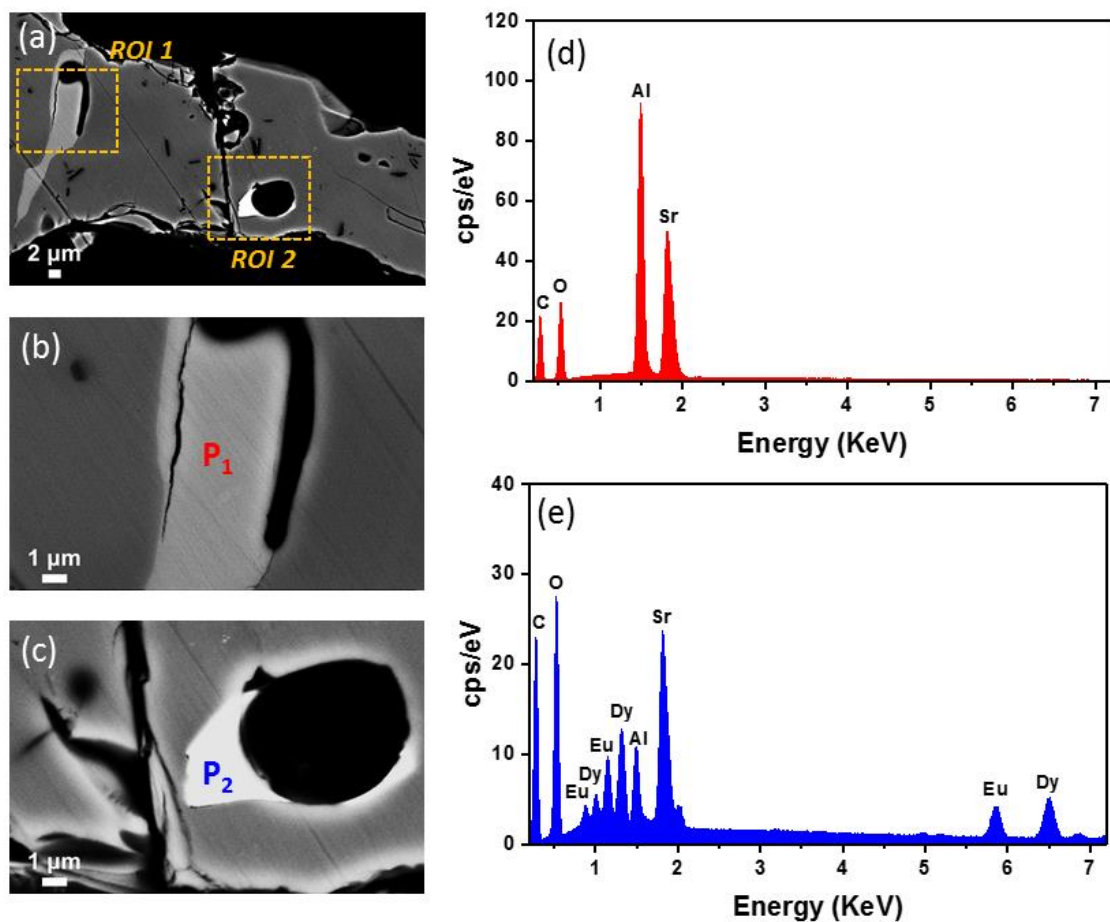


Figure 3.60. EDX point analyses of the regular intergranular and super bright phases a-c) BSE images of the microstructural features in S4A7ED-40 mol% B_2O_3 amorphous powder after calcination at 1300°C for 20h d) EDX spectrum related to P_1 in ROI#1 and e) EDX spectrum corresponding to P_2 in ROI#2.

3.6.6 Crystallization Kinetics in B₂O₃-Doped S4A7ED Compounds

To understand the effect of B₂O₃ content on crystallization of amorphous precursor of Pechini processed S4A7ED, we evaluated the influence of B₂O₃ concentration on the kinetics parameters, the activation energy of crystallization and the growth mode by performing non-isothermal kinetics study. As described in *Chapter 2*, the Pechini-processed powders with different B₂O₃ contents, were first pre-calcined at 800 °C for 3 hours to eliminate the nitrate materials and organics. The pre-calcined amorphous powders were then subjected to DTA at different heating rates to extract the kinetics data from the differences in thermal response.

Figure 3.61 shows the DTA thermograms of the amorphous pre-ceramic S4A7ED – x mol% B₂O₃ at different heating rates. We observed that, when the B₂O₃ content was low *e.g.* up to 10 mol%, the DTA signals at all the heating rates revealed 2 exothermic peaks identified by the shape of the first derivative curve of the DTA trace (DDTA) at the location of the two peaks (Figure 3.61 – a) . However, upon increasing the B₂O₃ concentration o (20, 30 and 40 mol% B₂O₃), the first exothermic peak became broader, and the second peak was replaced by a glass transition feature in the thermograms (Figure 3.61 b-d). For the 40 mol% B₂O₃ containing specimens at high heating rates of 20 and 30 C/min, we again observed a wide second exothermic peak (Figure 3.61-d).

Based on these observations, because only the 10 mol% B₂O₃-doped specimen exhibited two exothermic peaks at all the heating rates, we were able to estimate the activation energy for crystallization and the Avrami exponent *n* for both exothermic peaks, only in this composition. For the higher level of B₂O₃ doping, the kinetic parameters were evaluated for the first exothermic peak only. The values of crystallization peak temperatures (*T*_{P1} and *T*_{P2}) for the exothermic peaks and glass transition temperature (*T*_g) under different heating rates are listed in **Table 3.18**. It should be noted that the value of *T*_g for compositions that exhibited glass transition, was obtained from the inflection point of the DTA trace in the step-like thermal event, which coincided with the minimum point in the corresponding DDTA curve, as illustrated in Figure 3.61.

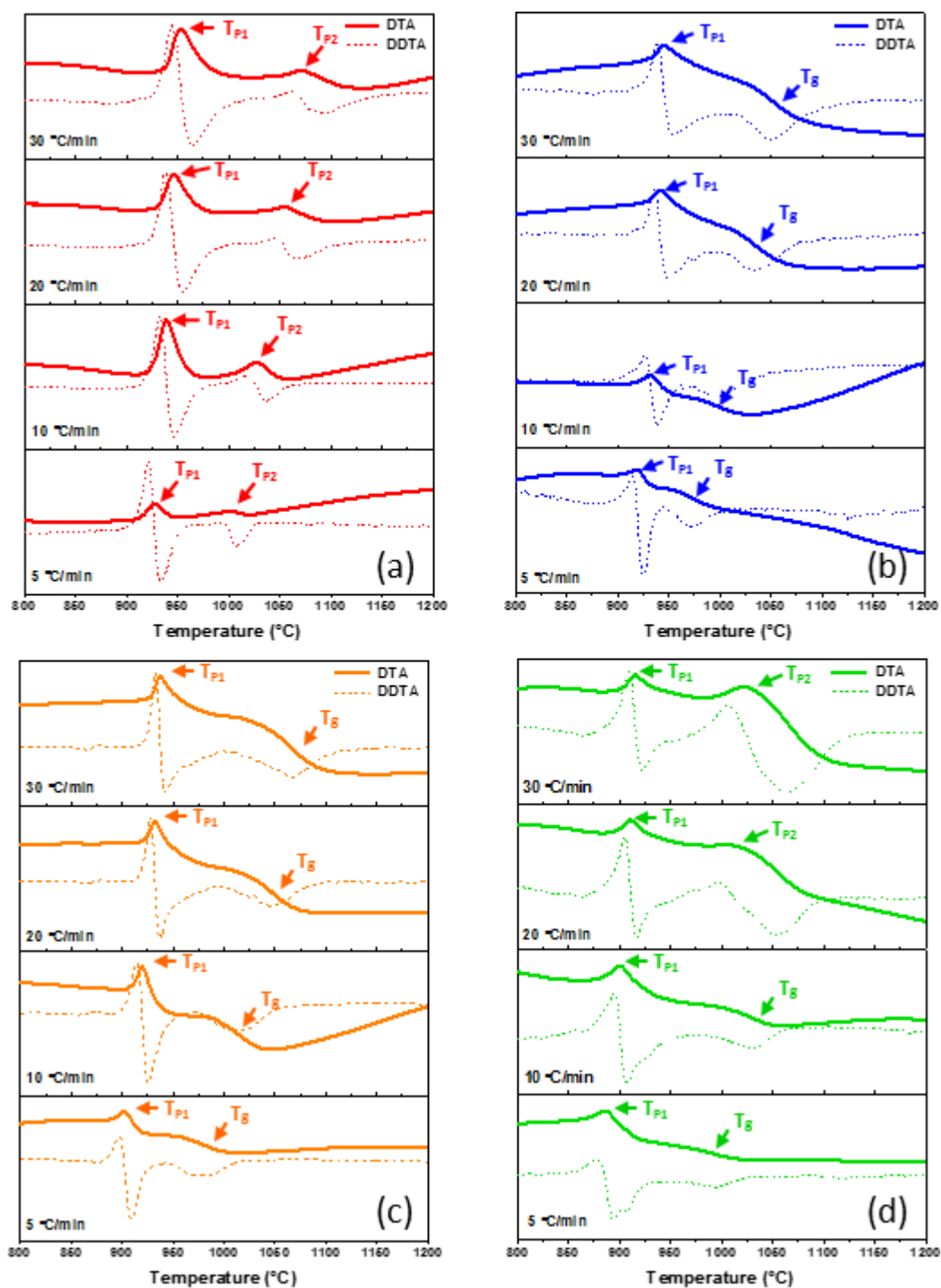


Figure 3.61. DTA scans different heating rates of 5, 10, 20 and 30 °C/min for the amorphous S4A7ED pre-ceramic material doped with a) 10 mol% b) 20 mol% c) 30 mol% and d) 40 mol% B_2O_3 .

Table 3.18. Crystallization peak and glass transition temperatures and obtained from DTA analysis of the amorphous pre-ceramic of S4A7ED doped with different B₂O₃ contents under different heating rates.

Composition	Heating Rate (°C/min)	Tp ₁ (°C)	Tp ₂ (°C)	Tg (°C)
S4A7ED – 10% B ₂ O ₃	5	927	1003	-
	10	940	1030	-
	20	946	1054	-
	30	954	1070	-
S4A7ED – 20% B ₂ O ₃	5	919	-	970
	10	930	-	995
	20	942	-	1033
	30	946	-	1047
S4A7ED – 30% B ₂ O ₃	5	906	-	968
	10	920	-	1007
	20	930	-	1037
	30	935	-	1060
S4A7ED – 40% B ₂ O ₃	5	886	-	994
	10	900	-	1030
	20	911	1010	-
	30	915	1022	-

Figure 3.62 shows the effect of B₂O₃ concentration on activation energy of crystallization during phase evolution of amorphous pre-ceramic of S4A7ED composition doped with different B₂O₃ contents for the first and second exothermic peaks. The values of activation energies determined by applying the Kissinger analysis (*Equation 2.12*) of the variation in maximum temperature of the DTA exotherms. For comparison, activation energies for the crystallization peaks related to the 0 mol% B₂O₃ specimen is also presented. We observed that, while the activation energy around the first crystallization peak was greater than that of second peak, with increasing the B₂O₃ content the activation energy for both 1st and 2nd crystallization exotherms was reduced. This can be related to the fact that, by increasing the B₂O₃, due to formation of the liquid glassy phase the three-dimensional connectivity among the ions was reduced, and migration of the cations occurred through

a liquid phase. In the case of solid-state reaction, diffusion would be slower through the grains but also along the surfaces, reducing the energy barrier for atom migrations and phase formation.

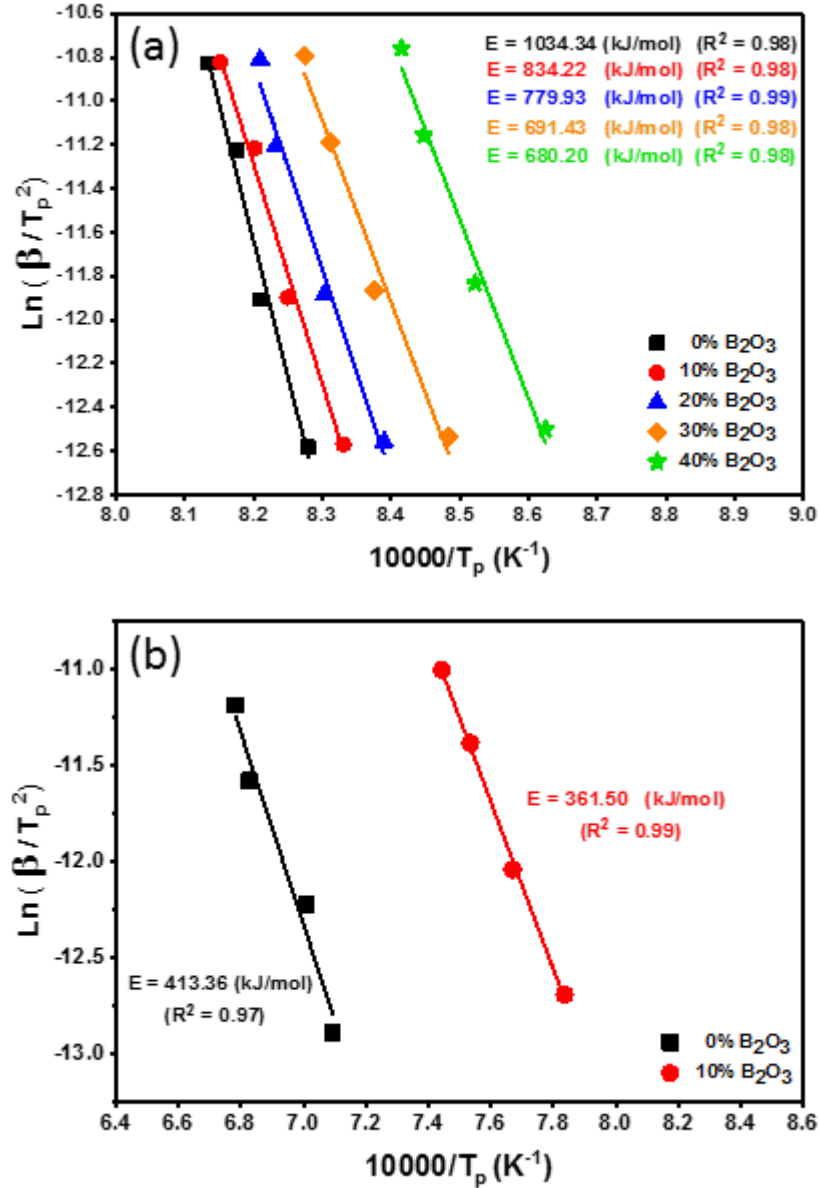


Figure 3.62. Kissinger-type plots summarizing the effect of B_2O_3 content on activation energy of crystallization for a) first exothermic peaks b) second exothermic peaks

Figure 3.63 represents the Ozawa-type plots used for determination of Avrami exponent (n) for the first DTA exothermic peaks of crystallization by using Ozawa plots (Equation 2.13). For each exothermic peak, the fraction transformed (α_T) were determined up to three different fixed temperatures within the exotherms giving rise to n_1 , n_2 and n_3 values

and the Avrami exponents obtained for each peak was reported as the average value of the three measurements. As shown in Figure 3.63, when there was no B_2O_3 present, the value of n for the 1st exotherm was $1.5 (\pm 0.2)$, indicative of surface crystallization where the nucleation rate is negligible as described in Section 3.5.3. When B_2O_3 was added to the system, the value of n for crystallization for the first exotherm increased to *ca.* $n = 2$, regardless of the B_2O_3 content, which means that the internal crystallization also contributes during phase crystallization from amorphous state.

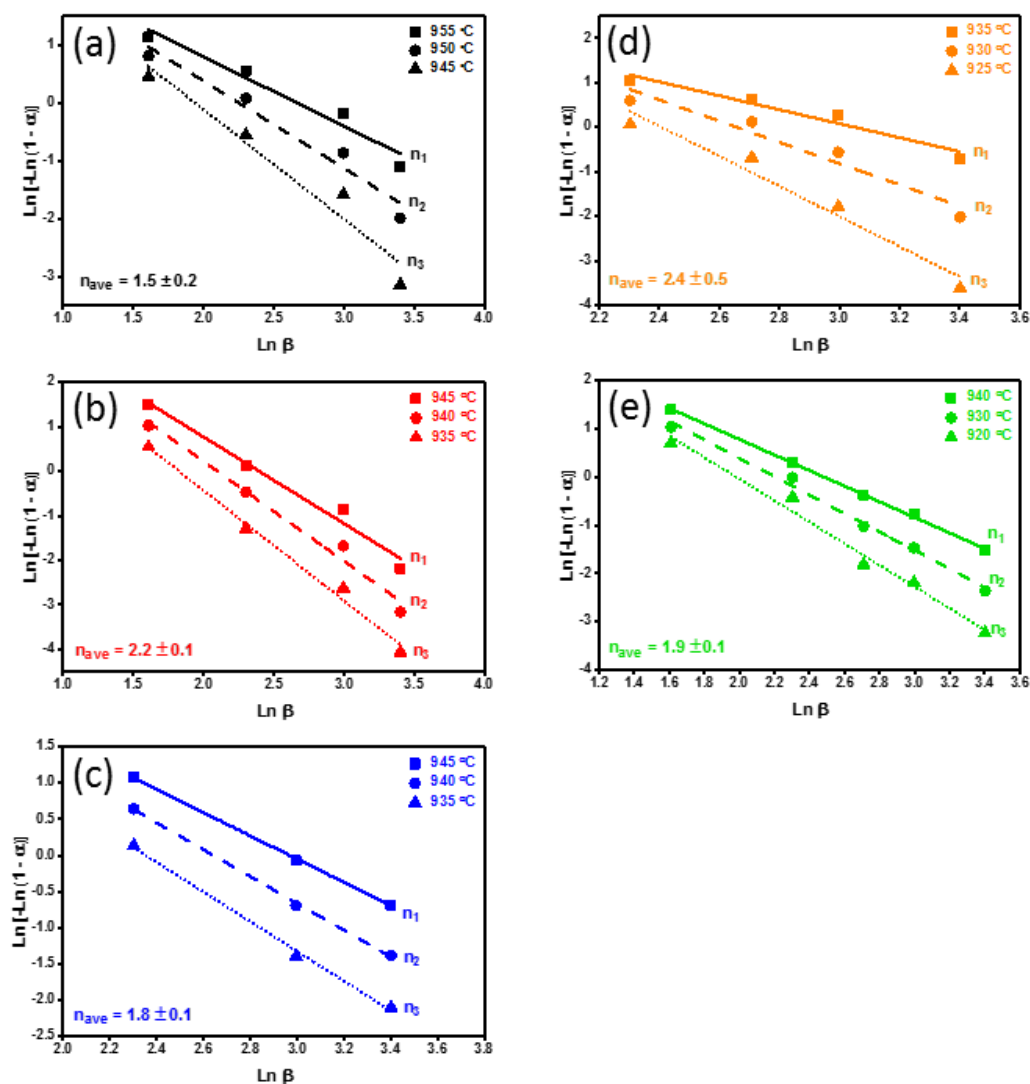


Figure 3.63. Ozawa-type plots demonstrating the effect of B_2O_3 content on the value of Avrami exponent for the first exothermic peak during crystallization of amorphous pre-ceramic of S4A7ED with a) 0 b) 10 c) 20 d) 30 and e) 40 mol% B_2O_3 .

Figure 3.64 compares the effect of B_2O_3 addition on the growth mode related to phase evolution around the second exothermic peaks during crystallization of S4A7ED

amorphous precursor. The value of n for the second DTA peaks was greater than that of the first peak for both 0 and 10 mol% B_2O_3 which means that the phase transformation occurring at the second peak was highly dominant by bulk crystallization accompanied by increasing nucleation rate. However, when B_2O_3 increased to 10 mol%, it was observed that the average value of n was also increased from $2.9 (\pm 0.05)$ to $4.94 (\pm 0.4)$ which means that the crystal growth was done at much faster nucleation rate.

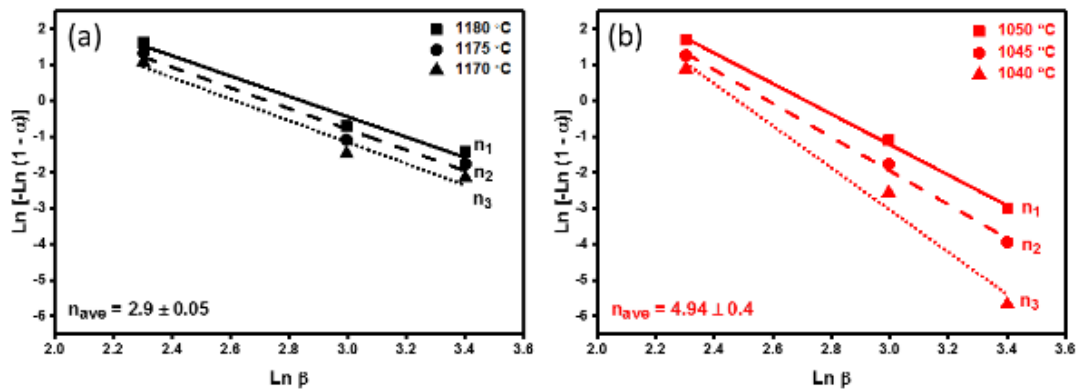


Figure 3.64. Ozawa-type plots demonstrating the effect of B_2O_3 content on the value of Avrami exponent for the first exothermic peak during crystallization of amorphous pre-ceramic of S4A7ED with a) 0 and b) 10 mol% B_2O_3 .

The results of Avrami exponent determination for crystallization DTA peaks for S4A7ED doped with different B_2O_3 contents are summarized in **Table 3.19**.

Table 3.19. Determination of Avrami exponent for DTA exothermic peaks during crystallization of the S4A7ED pre-ceramic material doped with different B_2O_3 contents.

B_2O_3 (%mol)	1 st Exothermic Peak				2 nd Exothermic Peak			
	n_1	n_2	n_3	n_{ave}	n_1	n_2	n_3	n_{ave}
0	1.19	1.50	1.89	1.53	2.83	2.88	3.00	2.90
10	1.94	2.23	2.47	2.22	4.24	4.69	5.86	4.93
20	1.61	1.85	2.05	1.84	-	-	-	-
30	1.56	2.38	3.38	2.44	-	-	-	-
40	1.61	1.91	2.23	1.92	-	-	-	-

In order to elucidate the effect of B_2O_3 content on the growth mode during crystallization from the amorphous state of S4A7ED compound, we compared the morphology of the powder particles for 0 mol% B_2O_3 versus that of 10 mol% B_2O_3 , at the first and second DTA crystallization peaks, respectively. When no B_2O_3 was present, the growth mode for phase evolution at the first exothermic peak (**Figure 3.65-a**) occurred mostly from surface with zero nucleation rate ($n = 1.5$). When 10 mol% B_2O_3 was incorporated in the amorphous matrix, for the phase evolution at the first DTA peak ($n = 2.2$) nucleation rate was much faster as reflected in the SEM image with much higher nucleation sites (**Figure 3.65-b**). As for the second exothermic peak, by increasing the B_2O_3 content from 0 to 10 mol%, the value of Avrami exponent was increased from 2.90 to 4.94. The SEM images showed a dramatic difference in the growth rate between the B_2O_3 -free specimen (**Figure 3.65 -c**) and B_2O_3 -doped sample (**Figure 3.65 -d**). In fact, the grain growth at the onset temperature of the 2nd DTA peak (1000 °C) in the B_2O_3 -containing specimen was much faster than that of S4A7ED – 0 mol% B_2O_3 composition.

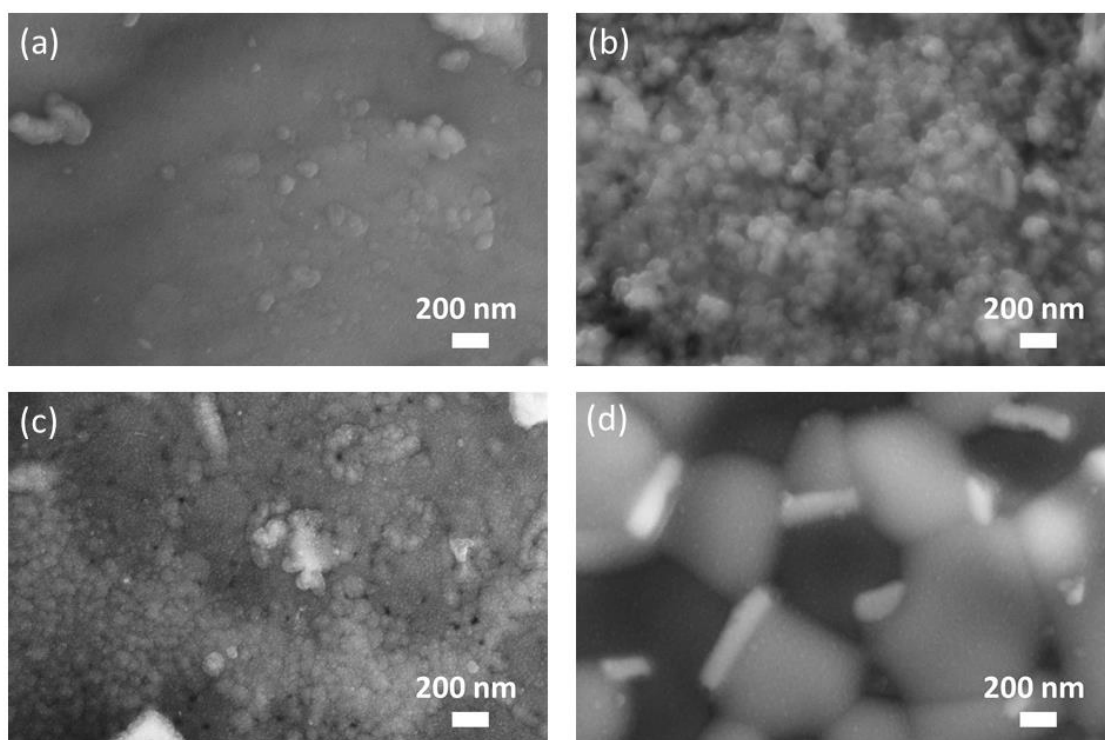


Figure 3.65. Secondary electron SEM images of a) S4A7ED – 0 mol% B_2O_3 calcined at the onset temperature of the 1st exothermic peak b) S4A7ED – 10 mol% B_2O_3 calcined at the onset temperature of the 1st exothermic peak c) S4A7ED – 0 mol% B_2O_3 calcined at the onset temperature of the 2nd exothermic peak d) S4A7ED – 10 mol% B_2O_3 calcined at the onset temperature of the 2nd exothermic peak.

3.7 Discussion

Because alumina polyhedral provide the matrix scaffolds in the structure of strontium aluminate ceramics, the characteristic of the Al polyhedra play a vital role during the phase development in amorphous S4A7ED pre-ceramic. The DTA trace of amorphous alumina (Figure 3.9) used during Pechini processing of S₄A₇ compound, resembles the DTA trace of the B₂O₃-free S4A7ED compound (Figure 3.15). In fact, the presence of two exothermic peaks of crystallization during microstructural evolution of amorphous S4A7ED mixture is attributed to formation of the alumina scaffold based on coordination units of tetrahedra and octahedra units. The state of the amorphous alumina transforms to a transition γ -Al₂O₃ through the first exothermic peak. At this temperature range, scaffolds of 4-fold coordinated Al cations are abundant while the presence of 5-fold alumina scaffolds are inevitable. with increasing temperature through the second DTA peak, all the transition alumina polymorphs included 4 and 5-fold coordinated Al with the material structure reached most thermodynamically stable atomic arrangement of alumina, α -Al₂O₃, which consists of only octahedral units. In the mixture of amorphous S4A7ED processed by the Pechini method, we assumed that the cations were homogenously distributed in the amorphous mixture. When Sr²⁺ cations are present, we observed that the exothermic reactions were shifted to higher temperatures than those in the evolution of phase pure amorphous alumina (**Figure 3.66-a**). In fact, in the presence of Sr²⁺, structural ordering for amorphous alumina appeared to be more difficult, possibly due to repulsion between Sr²⁺ and Al³⁺ hindering the easy diffusion of Al³⁺ and O²⁻ ions. Thus, formation of the first crystalline alumina required more thermal energy. Similarly, more thermal energy was required for the γ to α transition, and the transformation of $\gamma \rightarrow \alpha$ phase was also retarded when Sr²⁺ was present. Okada *et.al* [143] reported that the presence of divalent cations such as Ca²⁺, Sr²⁺ and Ba²⁺ have a stabilizing effect on the γ -Al₂O₃ transition phase and this stabilizing effect is directly proportional to the difference in the ionic radius of the divalent cation with Al³⁺ [41, 143].

During the phase evolution of amorphous pre-ceramic starting with nominal stoichiometry of (SrO)₄.(Al₂O₃)₇ doped with 1 %mol Eu and 1 %mol Dy and in the absence of B₂O₃, initially SA and SA₂ phases start to evolve simultaneously from amorphous state at the onset of the first exothermic reaction. By passing the first DTA peak, at the endpoint temperature of the first DTA peak and even slightly beyond the

exotherm (Figure 3.15), it is the SA phase that evolved as the major phase, and the intensity of diffraction peaks attributed to SA₂ did not change significantly (Figure 3.16). In the crystal structure of the SA phases (both hexagonal and monoclinic polymorphs), the Al cations are present only in 4-fold coordinated tetrahedron (**Figure 3.66 b-c**). Therefore, as the temperature approached to the temperature range attributed to the formation of 4-fold alumina, the Sr²⁺ cations present nearby would fill the interstitial cavities in the alumina scaffold for charge compensation [81], and the SA phase started to develop. This finding was consistent with the results of high-resolution ²⁷Al NMR reported by Capron *et al.*, implying that during the phase evolution of spray-dried amorphous precursor of S₄A₇ composition, a solid solution of Sr²⁺ cations in γ-Al₂O₃ had formed at temperature ranges around 1000 °C [11, 41] . As the amount of alumina tetrahedral units increased upon reaching temperatures at the end of the first exothermic reaction. These observations were supported by the 4-fold alumina characteristic Raman peaks, consistent with increased SA phase fraction.

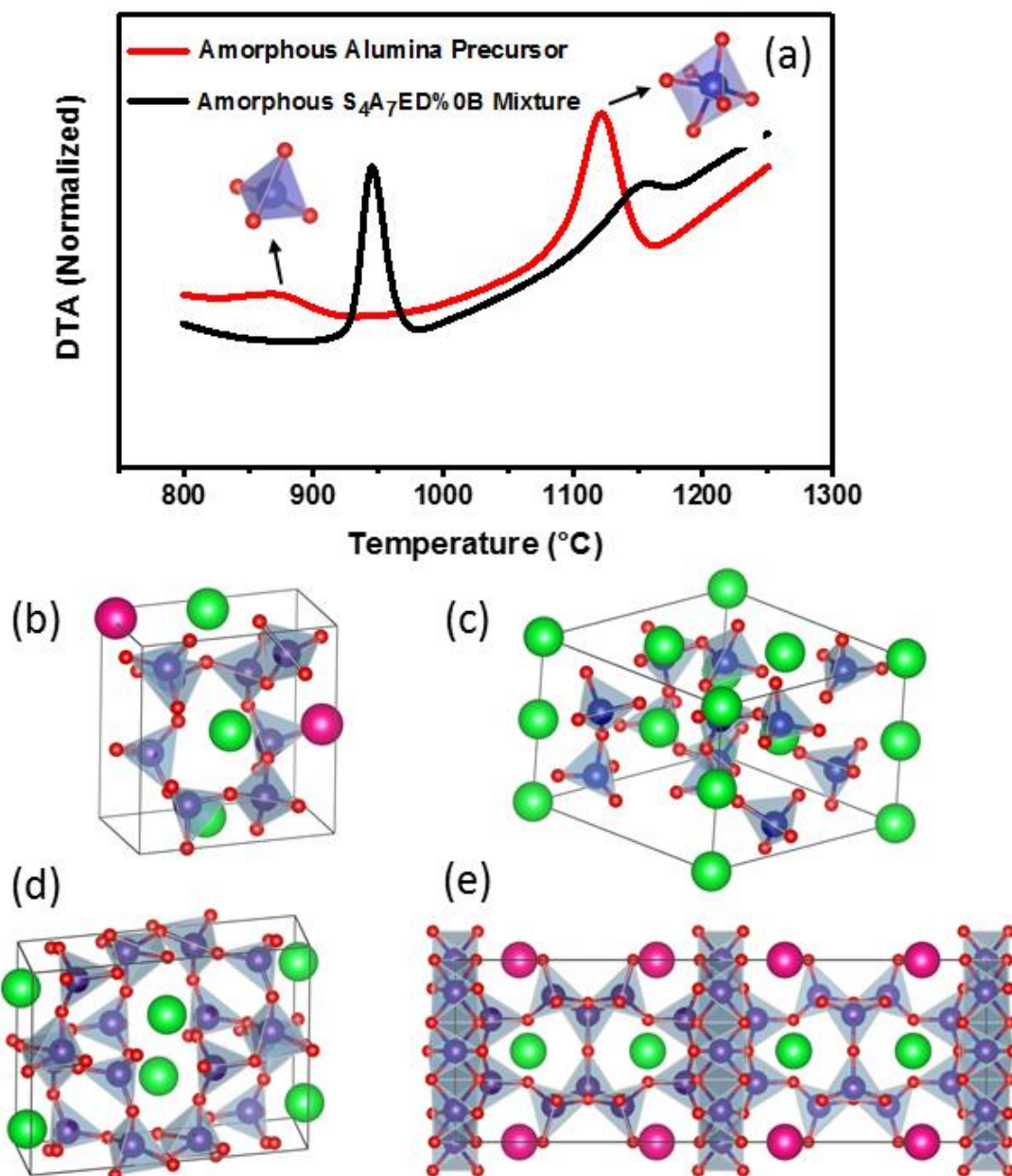
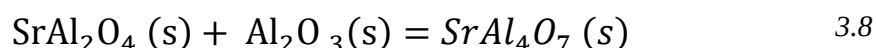


Figure 3.66. Correlation between structural evolution in the amorphous alumina precursor and that in strontium aluminate ceramics a) comparison the DTA trace of amorphous alumina (red) with the DTA trace of B_2O_3 -free S4A7ED amorphous pre-ceramic and crystal structure of strontium aluminate phases b) monoclinic SA c) hexagonal SA d) SA2 and e) S4A7. Green, purple blue and red balls stand for Sr_1 , Sr_2 , Al and O atoms, respectively.

The evolution of SA phase as the first major meta-stable phase during crystallization from amorphous precursor with the starting composition of $(SrO)_4.(Al_2O_3)_7$ was due to the fact that the formation of $(SrO).(Al_2O_3)$ phase is energetically favorable. The enthalpy of mixing between the two oxides is the minimum at equimolar fractions, regardless of the concentration of SrO and Al_2O_3 present [151, 152].

In addition, the crystal structure of the SA₂ phase is composed of both AlO₄ and AlO₅ units (**Figure 3.66-d**). Therefore, starting with the stoichiometry of the S4A7, when SA phase formed as the first crystalline phase, Sr²⁺ and Al³⁺ were removed from the amorphous pre-ceramic at a 1:1 ratio, leaving the amorphous pre-ceramic surrounding them enriched in Al³⁺. Thus, the local stoichiometry became favorable for forming SA₂, and small quantities of SA₂ phase initially formed directly from amorphous precursor. As indicated earlier, by increasing the temperature from the onset of the first exotherm to the endpoint temperature of the first DTA peak during phase evolution of S4A7ED – 0 mol% B₂O₃, the diffraction peak intensity attributed to SA₂ phase remained intact. This suggests that that SA₂ at the endpoint temperature are same as SA₂ that evolved from the amorphous matrix. Upon further increase in temperature beyond that of first exotherm, the fraction of amorphous phase diminished. The phase fraction of SA and γ – Al₂O₃ crystalline phases also decreased, and the amount of SA₂ phase increased. This compositional change continued up to 1110°C, the onset temperature of second exothermic processes (Figure 3.15). We compared the phase fraction obtained from Rietveld quantitative analysis in the temperature range between 965°C to 1110°C (from end point of the first exotherm to the onset of the second exotherm), where amount of SA₂ phase was continuously increasing, with the stoichiometry ratio of the solid-state reaction between SA and γ -Al₂O₃ to check if the evolution of SA₂ up to 1110°C is the result of the reaction between the meta-stable SA phase and alumina, according to the following equation:

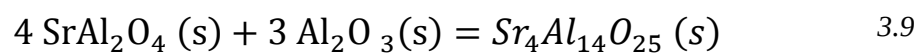


According to Rietveld quantitative phase analysis, a total decrease of 22.31 wt% and 5.12 wt% was observed in the phase fraction of SA and γ -Al₂O₃, respectively. On the other hand, in this temperature range, the quantity of SA₂ phase increased by 27.43 wt%. However, based on the molar ratio between the reactants and the product in Equation 3.8, the production of 27.43 wt% of SA₂ phase was not consistent with the consumed quantities of SA and alumina. We concluded that, the evolution of SA₂ by solid-state reaction indicated in equation 3.8 is ruled out at this temperature range and it directly

formed from amorphous preceramic through the diffusion of cations to the interface of the growing nuclei of SA₂, as was the case for formation of SA.

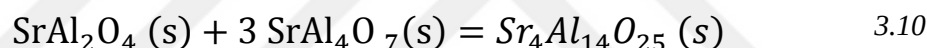
When the temperature passes the second exothermic reaction peak (Figure 3.15), as mentioned earlier, the octahedrally coordinated aluminum cations (AlO₆) are abundant. At this temperature, e.g. the endpoint temperature of the second DTA peak at 1180 °C, the first crystalline peaks attributed to the S₄A₇ phase appeared. The crystal structure of S₄A₇ is composed of parallel columns of edge sharing AlO₆ units, which are interconnected by corner-shared AlO₄ units. Sr²⁺ cations in two crystallographically non-equivalent sites, provide charge balance in the interstitial cavities in the alumina scaffolds [6, 67] (**Figure 3.66 – e**). As the 6-fold coordinated Al³⁺ forms in the system, the structural conditions necessary for formation of S₄A₇ phase is facilitated. It is interesting to note that, the first diffraction peaks attributed to S₄A₇ phase appeared at the endpoint temperature of the second exothermic peak.

Upon increasing the temperature from 1110°C (onset of the second peak), where no S₄A₇ has been formed yet, to 1180 °C (endpoint of the second peak), where the first reflections of S₄A₇ was observed, the phase fraction of Al₂O₃ decreased from 10 wt% to completely disappearing (10 wt% decrease). In addition, the SA phase decreased by 27 wt%, accompanied by simultaneous increase in SA₂ at the endpoint temperature by about 15 wt% (with respect to 1110°C) and 21 wt% increase in S₄A₇ (Table 3.5 and Figure 3.18). In fact, the total amount of decrease in the fraction of SA and Al₂O₃ (c.a. 37 wt%) at the endpoint temperature with respect to the onset temperature of the second peak was consistent with the total increase in the magnitude of SA₂ and S₄A₇ phase (c.a. 36 wt%). This quantification of the XRD data suggests that, because SA₂ phase fraction increased simultaneously with the evolution of S₄A₇, it is unlikely that SA₂ participated in the formation of S₄A₇ in this temperature range. Instead, by increasing the temperature from 1110°C to 1180°C, the solid-state reaction between SA and Al₂O₃ contributed to both further evolution of SA₂ (according to Eq. 3.8) and simultaneously lead to formation of S₄A₇ phase according to the following equation:



Capron *et al.* [41] reported that the formation of S₄A₇ crystalline phase was accomplished by reaction between a solid solution of γ -Al₂O₃ stabilized by Sr²⁺ cations and a solid solution of SA phase in the hexagonal structure stabilized by excess alumina.

However, we noticed during phase evolution of Pechini-processed amorphous preceramic of S₄A₇ composition, that the formation of S₄A₇ was not merely generated by the reaction indicated in equation 3.9. The results of XRD analysis of the S4A7ED – 0 %mol B₂O₃ at 1300°C over various calcination times (Figure 3.19 and 3.20 and Table 3.6) implied that, the formation of S₄A₇ as the major phase occurred over a long calcination duration which indicated a diffusion-controlled mechanism. In fact, from quantitative Rietveld analysis of the XRD data at 1300 °C, we observed that the phase fraction of S₄A₇ phase increased abruptly when the calcination time was prolonged from 1h to 5h. Over this dwell time, the amount of S₄A₇ phase fraction increased by 53 wt%. At the same time, SA and SA₂ phase fractions decreased by ca. 8 wt% and 45 wt%, respectively. These values are in good agreement with the reaction proposed in equation 3.10 as follow:



By further prolonging the calcination duration from 5 h to 10 h and then 20 h, the phase fraction of meta-stable SA phase remained intact, while the SA₂ appeared to be consumed in the formation of S₄A₇. However, this decrease in SA₂ and increase in S₄A₇ fraction becomes less intense. Slow development of S₄A₇ at the expense of SA₂ phase without any change in the amount of SA and over long calcination time implies that evolution of S₄A₇ occurred through diffusion of Sr²⁺ cations into the neighboring SA₂ grains. Taking the above discussion into consideration, the following mechanism is proposed for isothermal evolution S₄A₇ at 1300 °C under equilibrium conditions:

In the temperature range of the second exothermic peak in the DTA curve of S4A7ED – 0 mol% B₂O₃, when SA and SA₂ grains are in contact (**Figure 3.67 – a**), Sr²⁺ cations diffuse from the Sr-rich SA phase towards the interface, due to the chemical potential gradient (**Figure 3.67 – b**). At the interface, a layer of S₄A₇ phase forms as a result of solid-state reaction, according to Equation 3.10 (**Figure 3.67 – c**). As the thickness of the product layer increases, the diffusion distance for Sr²⁺ through the layer becomes too long, and the process terminates, and the SA phase no longer contributes to the formation of

S₄A₇ (**Figure 3.67 – d**). That is the reason for the presence of residual SA phase over long calcination time at 1300 °C, revealed by Rietveld quantitative analysis of XRD data.

Because the formation of S₄A₇ still continues at the expense of SA₂ only, and since SA₂ and S₄A₇ have similar compositions, and Al³⁺ cations are too strongly bonded to their coordinating oxygens, it is likely that transformation from SA₂ to S₄A₇ occurs via diffusion-less small rotations of alumina polyhedra, accompanied by diffusion of Sr²⁺ cations in order to compensate for charge deficiency resulting in the alumina scaffolding. This process will continue until complete transformation of the grains.

The microstructure in **Figure 3.67 – e** demonstrating the growth of S₄A₇ grains into the SA₂ grains is consistent with the proposed mechanism. It should be noted that the porous nature of the microstructure can be attributed to the collapse of vacancies due to cations migration or as a result of evolved gas due to either char burn out produced during organics removal [127] or the release of residues of hydroxyl groups entrapped in between the amorphous matrix [131].

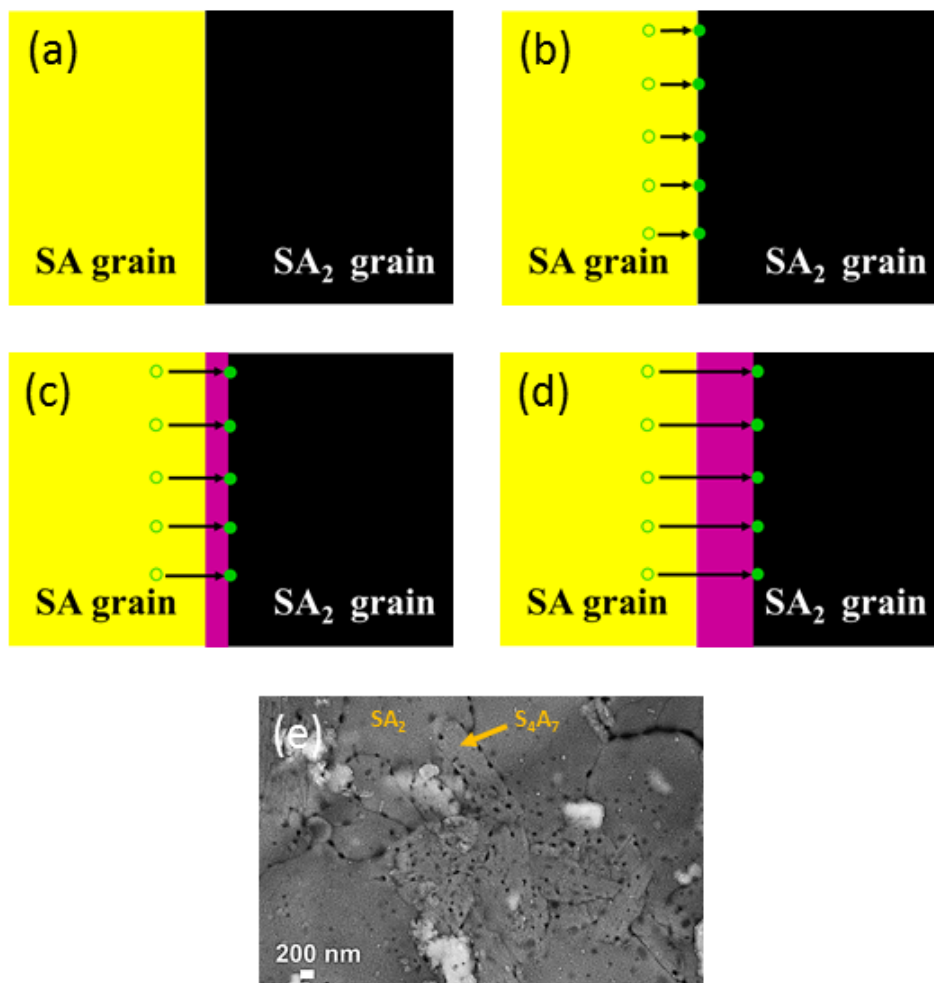


Figure 3.67. The mechanism of S_4A_7 evolution through diffusion of Sr^{2+} cations (a-d) as result of solid-state reaction between SA and SA₂ and h) the microstructure showing the development of S_4A_7 grains into SA₂ crystals. The empty and solid green balls represent the cation vacancies and Sr^{2+} cations, respectively.

Furthermore, the shape of the DTA curve and non-isothermal kinetics study of S4A7ED – 0 mol% B₂O₃ composition illuminates further details on the mechanism of phase development and the type of the diffusing species during crystallization from the amorphous state. The first crystallization peak was sharp while the second exothermic peak was wide and shallow (Figure 3.15). The maximum intensity of the DTA peak was proportional to the number of nuclei present in the amorphous preceramic because the crystallization peak intensity always increased with increasing amount of sample [153]. In other words, the intensity of the DTA exotherm reflects the amount and strength of the bonds in the amorphous state broken and then reformed during crystallization. The first exotherm was sharp, indicative of the high and well-defined thermal energy required for

breaking of the bonds followed by rearrangement of bonds for the first crystallization. During this thermal event, the meta-stable phases of SA and SA₂ were formed. Thus, the first crystallization peak must involve substantial bond breakage and bond reformation. The broad and low intensity second exothermic peak also suggests that, phase transformation occurring at the second DTA peak (formation of S₄A₇) involved less energy consumed for breaking bonds compared to the first exothermic reaction. The transformation most likely proceeds by rotational – i.e. diffusion-less – rearrangement of the already formed polyhedra, thus does not require thermal energy as high as that required to initiate crystallization in the first exothermic process.

The values obtained for the activation energy barriers for crystallization and phase transformation, *i.e.* for the first (1034.34 kJ/mol) and second (413.36 kJ/mol) exothermic peaks, further support the model being proposed, elucidating the type of the diffusing species during phase evolution from amorphous state in S4A7ED – 0 %mol B₂O₃. At the first exothermic peak where both SA and SA₂ phases start to evolve, comparison of the value of activation energy with dissociation energies of Al – O ionic bonds (512 kJ/mol) and that of Sr – O ionic bonds (454 kJ/mol) implies that, for crystallization of SA and SA₂, which took place around the first peak, both Al³⁺ and Sr²⁺ were the diffusing species. However, for phase transformation at the second peak, *i.e.* the formation of S₄A₇, only Sr²⁺ diffuses through the matrix. These results are consistent with the mechanism proposed for evolution of S₄A₇ at high temperature at the expense of SA₂, as described in Figure 3.67.

Figure 3.68 displays the ternary equilibrium phase diagram and the glass forming region for the Al₂O₃-SrO-B₂O₃ system [154]. Different compositions of S4A7ED doped with different B₂O₃ contents that were investigated in this work, are also indicated on the ternary diagram. As can be seen, all the compositions lay outside of the glass forming region. However, when the amount of B₂O₃ increases, the stoichiometry of the starting S4A7ED pre-ceramic approaches the glass forming region, promoting the formation of a glass phase to a larger extent. This explains the change in the shape of the thermogram upon increasing the concentration of B₂O₃ (Figure 3.27).

When B₂O₃ is added to the amorphous pre-ceramic material at low concentrations (5 and 10 mol%), the second exothermic peak undergoes a pronounced shift to lower temperatures, when compared to the composition without B₂O₃ (Figure 3.27). However, the onset of the first exothermic peak does not change significantly. Since the second

DTA exotherm was assigned to formation of AlO_6 octahedral units by [11, 41, 128], therefore, the addition of boron oxide appears to accelerate the rearrangement of meta-stable alumina polyhedral units of AlO_4 and AlO_5 to octahedrally coordinated Al^{3+} . While it was reported by Okada *et al.* [143] that the presence of divalent alkaline earth cations delays the formation of AlO_6 during phase evolution, our work shows that when B^{3+} and Sr^{2+} are simultaneously present, the accelerating effect of B^{3+} overcomes the retarding effect of Sr^{2+} in formation of stable, 6-fold Al^{3+} . In addition, at low B_2O_3 concentration (up to 10 mol%), the thermal behavior of the amorphous pre-ceramic, *e.g.* the phase evolution at elevated temperatures beyond the first DTA peak seems to follow the same mechanism described for the 0 mol% B_2O_3 specimen, but slightly modified by the presence of liquid phase.

When B_2O_3 concentration increases to 20 mol% and higher, the second DTA exothermic peak was replaced by a glass transition fingerprint in thermograms recorded at 10 °C/min (Figure 3.27). In fact, due to presence of excess B_2O_3 sintering flux, a liquid phase formed at the temperatures above the first exothermic reaction, and the meta-stable crystalline phases formed during phase evolution at the first exothermic peak were partially dissolved in the liquid (Figure 3.41) [154, 155]. Due to formation of the glassy phase, the shape of the thermogram changed indicating that, the phase evolution at elevated temperatures attributed to formation of S_4A_7 phase, was a completely different mechanism than that of the 0 mol% B_2O_3 compound.

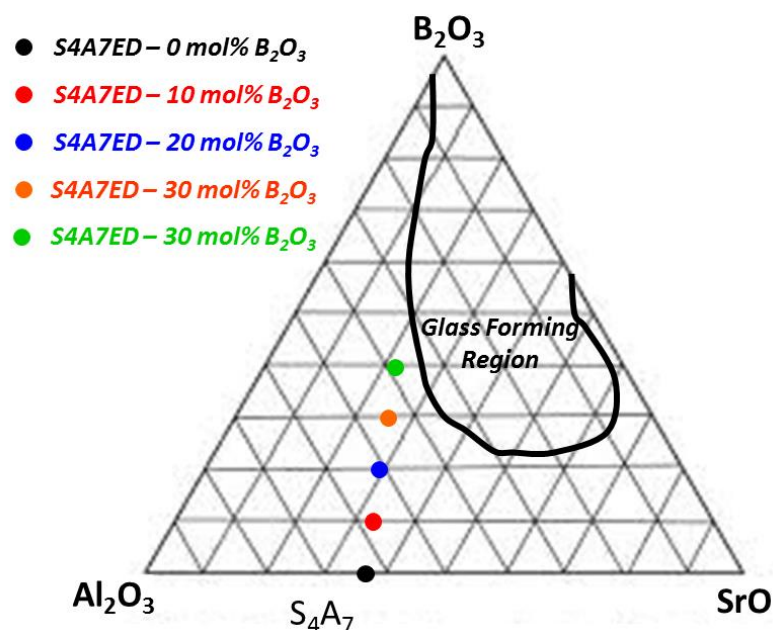


Figure 3.68. Ternary phase diagram for the Al_2O_3 - SrO - B_2O_3 system. The glass forming region and the composition of S4A7ED pre-ceramic doped with various B_2O_3 contents are shown on the phase diagram.

During the phase evolution, the amorphous pre-ceramic in the B_2O_3 -free specimen first crystallized into a mixture of SA and SA_2 phases with SA as the dominant phase, as discussed earlier (Figure 3.16). When B_2O_3 was increased to 10 and 20 mol%, the first crystals to evolve from the amorphous state were still SA and SA_2 with SA_2 being the dominant phase (Figure 3.29 and 3.34). In the case of 30 mol% B_2O_3 , the SA phase was barely detectable as the crystalline phase evolving from amorphous pre-ceramic (Figure 3.47). When the B_2O_3 content reached to 40 mol%, we observed that the amorphous precursor of S_4A_7 had initially crystallized into SA_2 phase only. In fact, the formation of SA phase was suppressed at high concentrations of B_2O_3 (Figure 3.51).

To elucidate the effect of B_2O_3 addition on phase evolution mechanism, we investigated the temperature range, in which an extensive quantity of S_4A_7 phase was formed in all compositions $\text{S}_4\text{A}_7\text{ED} - x \text{ mol}\% \text{B}_2\text{O}_3$ quantitatively in greater detail.

In the B_2O_3 -free composition, significant formation of S_4A_7 phase had occurred between 1300°C -0h and 1300°C -5h, where the formation of S_4A_7 phase was mainly due to solid-state reaction between SA and SA_2 according to Equation 3.10.

For the $\text{S}_4\text{A}_7\text{ED} - 10 \text{ mol}\% \text{B}_2\text{O}_3$ composition, substantial formation of S_4A_7 phase was obtained, when the temperature was increased from 1100°C to 1300°C without any

holding time (Figure 3.32). Upon this increase in temperature, the quantities of SA and SA₂ phases decreased by 6.9 wt% and 46.13 wt%, respectively, and 53.03 wt% of S₄A₇ was produced, (Table 3.11). According to the solid-state reaction between SA and SA₂ (eq. 3.10), production of 53.03 wt% S₄A₇ necessitates consumption of 9.66 wt% SA and 43.37 wt% of SA₂, respectively. Although, the individual changes in phase fraction obtained by Rietveld analysis were slightly different from the theoretical values required by solid-state reaction, the deviations were small. We assume that the main mechanism for S₄A₇ formation still follows the same solid-state mechanism, which has been modified by diffusion facilitated by the presence of a liquid phase. Furthermore, we observed that the SA phase did not remain un-reacted. It continuously decreased in fraction under prolonged calcination time, in contrast to the case for the B₂O₃-free compound, where the solid state reaction was limited, due to significantly lower diffusivity in the solid.

For the composition with nominal stoichiometry of S₄A₇ED – 20 mol% B₂O₃, S₄A₇ had formed primarily when the temperature was increased from 1100°C to 1300°C (Figure 3.36). The results of Rietveld analysis (57.96 wt% increase in S₄A₇ against 5.86 wt% and 52.1 wt% decrease in SA and SA₂, respectively) contradicts the requirements of the solid-state reaction (reaction of *ca.* 10.5 wt% SA with *ca.* 47.4 wt% SA₂). This significant deviation indicates that the mechanism of phase evolution during formation of S₄A₇ is no longer solid-state reaction, and instead a liquid-mediated reaction mechanism dominates. In fact, SA and SA₂ crystals are dissolved in a strontium aluminoborate (SAB) liquid phase that had formed due to the high concentration of B₂O₃.

For the compositions doped with 30 and 40 mol% B₂O₃, SA does not participate in microstructural evolution and the pre-ceramic material crystallizes directly into SA₂ and amorphous intergranular SAB phase. The mechanism for S₄A₇ formation is no longer solid-solid reaction facilitated by liquid-phase diffusion. Instead, everything dissolves in the liquid at once, and S₄A₇ phase precipitates out from the liquid phase, as evident in the microstructure shown in Figure 3.56. Therefore, the addition of boron oxide as a sintering flux, changes the mechanism of phase evolution in strontium aluminate compounds from a solid-state reaction to a solid-liquid crystallization or precipitation from liquid, when more than 10 mol% B₂O₃ is used in the Pechini synthesis. In addition, at high concentrations of B₂O₃ (30 and 40 mol%), crystalline SA₆ grains were also formed in addition to S₄A₇.

The amorphous precursor after organic's removal is assumed to be homogenous. It is composed of oxygen coordinated cation polyhedral units, with only short-range order. When thermal energy is absorbed by this amorphous network, crystallization starts to occur through breaking and re-forming of the bonds between polyhedral units of all cations (nucleation), followed by diffusion of the mobile species (growth). For evolving the pre-ceramic powder into a monophasic crystal structure, the chemical potential of all ionic species must be equal across the entire microstructure at thermodynamic equilibrium. However, the microstructure obtained during phase evolution of S₄A₇ED compounds, initially forms metastable phases, due to diffusion-limited and localized stoichiometry variations. The metastable phases were then transformed into the global thermodynamic equilibrium S₄A₇ phase, obliged by the stoichiometry of the starting composition. On the other hand, at high B₂O₃ concentrations and at temperatures as high as 1300°C, the presence of an intergranular phase rich in B, Sr, Eu and Dy, as well as SA₆, was detected along with S₄A₇.

The addition of B₂O₃ in small amounts results in a liquid phase that facilitates mass transport through the liquid and along surfaces, coarsening, densification, and dopant segregation [37, 154]. When the concentration of B₂O₃ is low, it forms glassy borate phases (including strontium borate and/or strontium aluminoborate) as by-products. However, at very high concentration of B₂O₃, crystalline borate phases are formed [39, 118, 156]. Regardless of amorphous or crystalline nature, the formation of borate phases clearly indicates that B₂O₃ is not merely acting as an inert sintering flux to promote the grain growth, but it also interacts with the cations present in the mixture, preferentially, with more reactive components e.g. Sr²⁺ [39], changing the special variation in chemical potential of the cations. Because the amorphous intergranular phase was enriched in Sr and rare earth dopants, the changes in chemical potential of Sr can affect the gradient relative to the other crystalline phases as well.

The multiphase nature of the evolving microstructure indicates that, the chemical potential energy landscape has hills and valleys, where the valleys correspond to metastable equilibria for SA, SA₂, SA₆, SB, etc., in addition to S₄A₇. In fact, the diffusivity of the ions is kinetically limited, and each different phase can be considered as regions with local energy minima which limits the diffusion of ions homogeneously. This gives rise to formation of meta-stable phases other than the thermodynamically stable phase e.g. S₄A₇.

In fact, formation of the liquid SAB phase, which is rich in Sr cations, forces the remaining preceramic to be Al-rich. Therefore, during the first exothermic reaction, where the first crystalline strontium aluminates (SA and SA₂) start to appear, increasing the concentration of B₂O₃ encourages the formation of the Al-rich phase (SA₂) and suppresses the formation of SA phase, due to the higher diffusivity of Sr²⁺ cations to diffuse in the liquid. In very high boron oxide compounds *e.g.* the compositions doped with 30 and 40 mol% B₂O₃, and prolonged calcination duration at 1300°C, *e.g.* 20h, the phase evolution in the glass-ceramic composite is controlled by dissolution and precipitation from liquid phase. We observed that a lot of SA₆ grains have been formed inside the Sr-rich intergranular phase, along with S₄A₇ (Figure 3.56 c-d). This implies that during phase evolution, diffusion of Sr cations into the liquid phase is facilitated at higher temperatures and longer durations, and the liquid borate phase accommodates a lot of Sr to form amorphous SAB. The much poorer diffusivity of Al³⁺ under all calcination conditions results in local enrichment, allowing SA₆ crystals to nucleate and grow.

It is worthy to comment that, the intergranular borate phase is rich in heavy elements of Sr, Eu and Dy but is poorer in Al as shown by the results of EDX elemental distributions map (Figure 3.43 and 3.55). Because Al³⁺ cations form stable bonds with oxygen [157], Al-coordination polyhedra are stable. This means that it requires significant energy to break up the bonds and thus they are more likely to remain coherent polyatomic species. By contrast, Sr coordination polyhedra are relatively unstable [157] and easily allow Sr cations to diffuse as individual cations. During formation of strontium aluminate crystals, if the concentration of the dopants is above the solubility limit of the growing crystals, the cations segregate out, accumulating in the surrounding liquid phase. In addition, since $r_{B^{3+}} < r_{Al^{3+}}$, the effective charge carried by B polyhedral units are more negative than that of Al polyhedral [39]. Hence, rare earth dopants with relatively high positive charge, prefer to associate themselves with the borate phase.

Furthermore, it was observed that in S4A7ED composition doped with 40 mol% B₂O₃, after calcination at 1300C for 20h (Figure 3.59 and Figure 3.60), the regions extremely rich in Dy and Eu appeared in the microstructure, corresponding to regions with super bright contrast in BSE images. The composition of these super-bright regions is totally different with the intergranular phase and, depleted from Sr cations. In fact, it seems that a new IGP rich in trivalent cations has developed over long calcination time at elevated temperatures. Since trivalent cations bring more non-bridging oxygens (1.5 oxygen per

cation according to the chemical formula of Eu_2O_3 and Dy_2O_3) compared to divalent cations (1 oxygen per cation as in SrO), more bond breaking is achieved in the structure of the glass by incorporating of Eu^{3+} and Dy^{3+} , leading to higher stability. Thus, Eu and Dy further segregate out of the Sr-rich intergranular phase to form complexes of Eu borate and/or Dy-borate [39, 118].

The activation energy of crystallization for DTA exothermic peaks is substantially reduced by increasing the B_2O_3 content. That can be attributed to the fact that the mechanism of phase evolution changes from one of solid-state reaction (0 mol% B_2O_3) to one of solid-state evolution assisted by liquid phase (10 and 20 mol% B_2O_3) and finally precipitation from liquid (30 and 40 mol% B_2O_3). It is well-known that boron oxide can occur in both BO_4 tetrahedral coordination polyhedra and planar BO_3 triangles [39, 67, 158, 159]. However, in the oxide glass, B^{3+} forms mostly two-dimensional BO_3 units. Thus, when it melts into a liquid, the three-dimensional connectivity among the cations is reduced, resulting in decreased activation energy of crystallization. Consequently, the thermal energy for atomic migration is reduced, and the crystallization onset temperature will decrease [147].

Phase transformation requires the diffusion of ionic species. Due to lower dissociation energy of Sr – O bonds, Sr^{2+} cations can be easily dissociated from the amorphous phase and migrate as an isolated cation to join the growing nuclei of the crystal. In contrast, the energy of Al – O bonds are relatively high, and thus, it is less likely that Al^{3+} cations migrate as an isolated ion. Instead, the Al atoms would remain in the form of alumina polyhedra. The structural evolution of S4A7 phase is thus accomplished by both diffusion of Sr^{2+} cations as well as diffusionless change in the connectivity of Al – O bonds, including rotation of bond angles from tetrahedral sites to octahedral units.

Furthermore, because at the temperature range of the first and second exothermic peaks, multiple phases, with different crystal structures were evolving simultaneously, it can be deduced that, different facets with different surface energies were generated during the initial stage of microstructural evolution. The density of the dangling bonds and the absorption of the ionic species on the facets with different surface energies for the growing crystals are different. Therefore, the growth of the evolving microstructure is determined by the competition between facets of high surface energy. The possible phases competing with orthorhombic S4A7 are monoclinic SA, monoclinic SA2 and in the case of high B_2O_3 -doped compositions, hexagonal SA6. This is very well reflected in the values of the

Avrami exponent obtained for the 1st and 2nd exothermic peaks in the DTA signals. The dimensionality of growth revealed by the Avrami exponents is not an integer number, meaning that due to presence of facets with different surface energies, imposed by complex crystal structures of strontium aluminate phases, the absorption probability to the growth front of the growing crystals is not uniform and thus, growth does not occur with regular one, two or three dimensionality.

3.8 Conclusion

In this chapter, the effect of B₂O₃ on phase evolution from Pechini processed amorphous precursor of (SrO)₄(Al₂O₃)₇ doped with 1 mol% Eu and 1 mol% Dy (S4A7ED), prepared by polymerization of ethylene glycol and citric acid-chelated cations was systematically investigated by using thermal analysis (DTA-TG) and Rietveld quantitative analysis of the XRD data.

Primary results of DTA-TG analysis of the amorphous gel after Pechini processing showed that, the thermal behavior of the starting gel is rather complex and includes successive decomposition steps of the nitrate materials as well as polymeric matrix built by esterification of citric acid and ethylene glycol. It was shown that most of the organics and nitrate materials were decomposed at temperatures as high as 800°C. Therefore, pre-calcination of the dehydrated gel at 800°C for 3h was chosen as the suitable heat treatment to render an amorphous pre-ceramic free of nitrates and organics as a model starting material, on which we based studies of its microstructural evolution.

When B₂O₃ is not present, the thermogram of the organics-free pre-ceramic of S4A7ED showed two exothermic peaks. Comparison of the DTA trace related to amorphous alumina with amorphous pre-ceramic of S4A7 mixture revealed that, the phase evolution in S4A7ED compound strongly correlated with the state of alumina polyhedra. During the phase evolution, over the temperature range corresponding to the first exothermic peak, where AlO₄ forms abundantly, SA and SA₂ phases evolved simultaneously from the amorphous precursor as the first crystalline strontium aluminate phases. By increasing the temperature to the temperature range of the second exothermic peak, when octahedrally coordinated Al⁺³ polyhedra were formed, and form a 3-D interconnected network that serves as the scaffolding for S4A7 formation.

Our results showed that the initial formation of S_4A_7 is due to solid state reaction between SA and $\gamma\text{-Al}_2\text{O}_3$. with increasing temperature, S_4A_7 evolves as a consequence of solid-state reaction between meta-stable SA and SA_2 . However, the solid-state reaction will be limited, due to low diffusivity of Sr^{2+} cations through solids. The microstructural evolution is terminated by rendering a multiphase composition consisting of SA and SA_2 , coexisting with S_4A_7 .

The addition of B_2O_3 to the mixture, changes the chemical potential of the ions, encouraging the formation of a liquid borate phase rich in Sr, Eu and Dy. Doping of B_2O_3 , at low concentrations (up to 10 mol%) changes the mechanism of microstructural evolution from a diffusion-controlled solid-state reaction to a diffusion-controlled, liquid phase facilitated reaction. In this case, the liquid phase between the grains wets the surface of the meta-stable SA and SA_2 crystals, increasing diffusivity of the mobile cations during evolution of S_4A_7 .

When B_2O_3 is incorporated in the mixture at high concentrations (above 20 mol%), the starting composition is closer to the glass forming region in the ternary diagram of $SrO\text{-}Al_2O_3\text{-}B_2O_3$. This promotes the formation of Sr-rich borate phase, forcing the amorphous preceramic to be slightly Al-rich, thus the formation of SA phase is suppressed. In this case, everything dissolves in the liquid glassy phase, and the mechanism of phase evolution is governed by precipitation of S_4A_7 phase out of the liquid. At elevated temperatures and over long calcination times, a phase separation occurs in the amorphous borate phase due to high affinity of Sr cations to the glass. Local enrichment in Al occurs in the glass and SA_6 grains also evolve in addition to S_4A_7 . The formation of the glassy phase and change in the mechanism of phase evolution was reflected in the thermogram through the appearance of glass transition thermal fingerprint in DTA signal.

The results of non-isothermal kinetics study revealed that, the activation energy of crystallization at the first exothermic peak involves dissociation and migration of both Sr^{2+} and Al^{3+} cations. However, the value of activation energy for phase transformation was comparable to dissociation and migration of Sr^{2+} cations only. Therefore, the evolution of S_4A_7 phase at high temperatures is accomplished by diffusion of Sr^{2+} cations and changes in bond angle and orientation upon absorbing thermal energy, resulting in network modification.

CHAPTER 4: EFFECT OF SINTERING RATE AND BORON CONTENT ON RARE EARTH DOPANT DISTRIBUTION AND PHASE FORMATION IN LONG AFTERGLOW STRONTIUM ALUMINATE

4.1 Introduction

Certain phases of strontium aluminate— $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ (S_4A_7) and SrAl_2O_4 (SA), when doped with rare-earth and transition metal dopants in ceramic crystals—are well known to support persistent luminescence [11, 33, 160-162]. In fact, the addition of B extends afterglow duration from minutes to > 10 hours in Eu and Dy co-doped strontium aluminate compounds prepared by the Pechini method [36, 39], although there is still a lack of consensus on the direct role of B on dramatically extending the afterglow [25, 37, 39]. In previous work, we have shown that B influences the most stable atomic arrangements [8] and the relative distribution of the Eu and Dy dopants in the microstructure of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ doped with 1 mol% Eu, 1 mol% Dy, ($\text{S}_4\text{A}_7\text{ED}$) and 30 mol% B_2O_3 ($\text{S}_4\text{A}_7\text{EDB}$) [7].

When an amorphous pre-ceramic of $\text{S}_4\text{A}_7\text{EDB}$ is sintered, the dominant phase in the microstructure that forms is S_4A_7 , although $\text{SrAl}_{12}\text{O}_{19}$ (SA_6), SrAl_4O_7 (SA_2) and SA may also appear [41, 151]. In all of these phases, Eu and Dy are incorporated into the Sr cation sub-lattice [6, 8, 37]. Eu^{2+} is the optically active ion, while Dy^{3+} in close proximity offers trap states for thermally stimulated de-trapping and relaxation of the excited Eu^{2+} ion [6, 33, 37]. An optimal concentration of 1 mol% has been reported for Eu^{2+} for long afterglow [21, 163] ; above that concentration, the probability for concentration quenching is increased [9, 164].

Compounds of boron oxide are commonly used as sintering flux agents in the preparation of ceramic oxides, including in the initial reports of long afterglow in strontium aluminate [161]. With a low melting point relative to that of aluminates (450–468 °C), B₂O₃ in particular lowers the temperatures at which high liquid diffusivities occur [165]. Because it was also reported to influence the extremely long afterglow duration [36], the role of B in extending persistent luminescence may be related to tuning diffusion kinetics, i.e., facilitating the distribution of the rare-earth dopants, in addition to the formation of the phases exhibiting room temperature afterglow, S₄A₇ and SA.

We have previously reported the measured Eu and Dy content in the strontium aluminate grains to be well below 1 mol% [7]. When the concentration of Eu and Dy in the crystalline strontium aluminate phases exceeds the solubility limit for thermodynamic equilibrium, these ions would segregate to the surface of the precipitating crystals [37, 166, 167]. To limit this thermodynamically driven diffusion, spark-plasma sintering (SPS) can be applied to induce crystallization of the amorphous S₄A₇EDB precursor under high heating rates.

During SPS, a low voltage, pulsed electrical current (ca. 4 V DC, a few milliseconds) is applied simultaneously with continuous uniaxial loading. When the sintering specimen are electrically non-conductive powders, the graphite die and punches undergo Joule heating, which is also transferred from the die to the powder-like pellet [168]. Through the bulk of the particles and at contact points between particles, heat is transferred only in a conductive and radiative manner. In contrast, the convective nature of heat transfer in conventional sintering (CS) allows surface diffusion to dominate.

Because the powder particles are exposed to heating from both inside and outside, high heating rates can be achieved, accelerating heat and mass transport and in-situ chemical reactions [169]. Heating rates of ca. 1000 °C/min and cooling rates of ca. 150 °C/min allow the by-passing of grain coarsening in the early sintering stages, while the uniaxial compression accelerates densification. The sintered products are highly dense compacts of fine-grained powder [169, 170]. In addition, such processing can kinetically stabilize otherwise metastable phases [168] and allow separation of grain growth from densification [169]. Because densification occurs by pore elimination and grain growth, the high diffusivity through the limited contact area causes high stress on necks between grains producing additional vacancies that further enhance densification. High heating

rates of polymer-mediated ceramics also give rise to foaming, from the burn-off of residual organic moieties and chemical and adsorbed water [171].

Due to containment in a graphite die, powders are sintered in a reducing environment in SPS, leading to oxygen deficiency in the final microstructure [172]. In contrast, the environment in CS ranges from oxidizing to inert to slightly reducing. In the glasses, oxygen deficiency leads to trapping of some dopants and favoring mobility for others. With B present, for example, its strong affinity for bonding with oxygen restricts the diffusivity of B, compared to the other cations [172]. Meanwhile in solids, oxygen vacancies reduce electrostatic screening locally in the lattice, contributing to non-uniform incorporation of cations into lattice and interstitial sites, perturbation to diffusivity paths [165], and electronic trap states for non-radiative transitions [161].

To elucidate the role of diffusion kinetics under the influence of B on dopant distribution, microstructure, and luminescence behavior, we produced S4A7ED by SPS against that of CS, with and without B_2O_3 as sintering flux as described in chapter 2 and compared the microstructural evolution by dilatometry, and characterized the phase composition by XRD, the elemental distribution by wavelength-dispersive spectroscopy and cathodoluminescence spectroscopy in the scanning electron microscope (SEM-WDS and SEM-CL), and the distribution and local environment of B by electron energy loss spectroscopy in a scanning transmission electron microscope (STEM-EELS).

4.2 Results

The densification behavior was monitored for the amorphous powder precursor including 30 mol% B_2O_3 in the SPS furnace under a constant pressure of 3 kN, a 100 °C/min heating rate, and a dwell time from 3 to 10 min (**Figure 4.1a**). During the 5-minute pre-heating step to 575 °C, which was necessary to raise the temperature into the sensitivity range of the optical pyrometer controlling the heating, the sample underwent initial densification. Upon application of the pulsed current, the dilatograms showed 3 densification stages: 575-750 °C, 800-900 °C, and 1225-1300°C. At 750 °C, the non-densification, indicative of a phase transformation, was most likely the activation of the liquid-phase. A second, more pronounced densification occurred between 800-900 °C at a much faster rate. At *ca.* 950 °C, the system reached a long stagnant period of non-densification, most likely the

formation of SA and SA₂ phases. A slower final densification followed, until the system reached a phase transformation onset at 1300 °C, consistent with the formation of S₄A₇.

Densification in the amorphous powder precursor for CS specimen was characterized using dilatometry (**Figure 4.1b**). The pellet held between 2 alumina plates was heated to 1300 °C with a 5-minute dwell at 575 °C. In the B-free specimen, densification of the amorphous precursor was observed up to *ca.* 700 °C, followed by a second densification at a more pronounced rate up to *ca.* 925 °C. The phase transformation occurring over the temperature range of 925-1275 °C was most likely the formation of crystalline strontium aluminate phases. In the specimen containing 30 mol% B₂O₃, the amorphous pre-ceramic underwent 2 phase transformations at *ca.* 1000 °C and at 1300 °C. The first crystalline phase to form underwent thermal expansion followed by a final transformation.

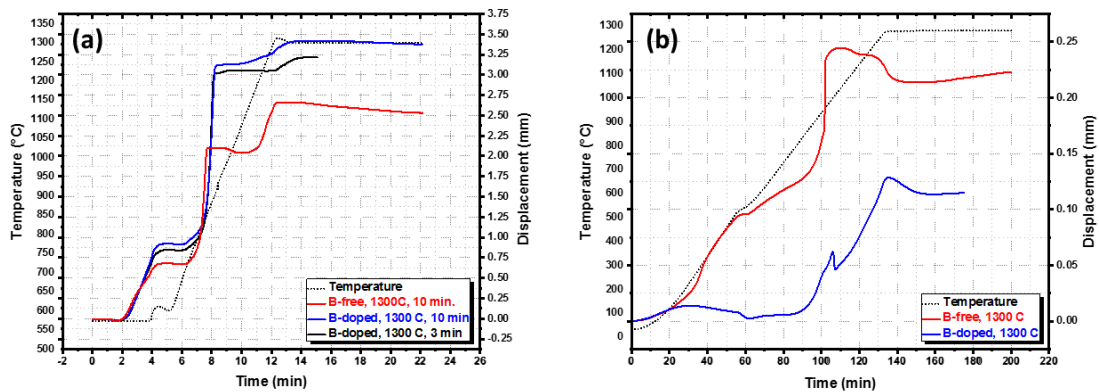


Figure 4.1. (a) Displacement and temperature profile vs. time, during SPS at a heating rate of 100 °C/min and for two different dwell times at the final sintering temperature, i.e., 3 min and 10 min; (b) dilatograms for the CS specimen at a heating rate of 10 °C/min.

The Archimedes' density for all specimen is summarized in **Table 4.1**.

Table 4.1. Archimedes density of final SPS and CS specimen.

Processing	Heating Rate [°C/min]	mol% B ₂ O ₃	Density [g-cm ⁻³]
SPS-10 min	100	0	2.75
SPS-10 min	100	30	3.06
SPS-3 min	100	30	2.94
CS-5 h	10	0	2.83
CS-5 h	10	30	2.80

To determine phase composition, the samples produced by SPS and CS were analyzed using XRD (**Figure 4.2**). Rietveld phase analysis of the XRD patterns revealed a phase composition of 89.58% S_4A_7 , 6.21% SA_2 and 4.21% SA for the CS S_4A_7ED powder (without B_2O_3). When the B_2O_3 -free amorphous precursor of S_4A_7ED was sintered by SPS with a dwell time of 10 min, we obtained a phase distribution of 41.74% S_4A_7 , 25.65% SA_2 , 10.98% SA and 21.63% graphite. Graphite contamination was present, due to use of a graphite die for compressive loading of the powders during SPS. The goodness-of-fit for the quantitative analyses were 1.69 and 2.59 for the CS and SPS samples, respectively.

Table 4.2 summarizes the results of quantitative analysis of the XRD data. For the B_2O_3 -doped specimens, Rietveld quantitative analysis showed a phase composition of 64.39% S_4A_7 , 4.74% SA_6 , 13.18% SA_2 , and 17.69% graphite for SPS dwell time of 3 min. An increase in SPS dwell time to 10 min resulted in a phase composition of 83.43% S_4A_7 , 10.65% SA_6 , and 5.92% graphite. The compositions were determined with a goodness-of-fit of 1.65 and 1.63, respectively. In the CS specimen, there was 8.80% of SA_6 and 91.20% of S_4A_7 . Despite the high B_2O_3 content, crystalline borate phases were not detected.

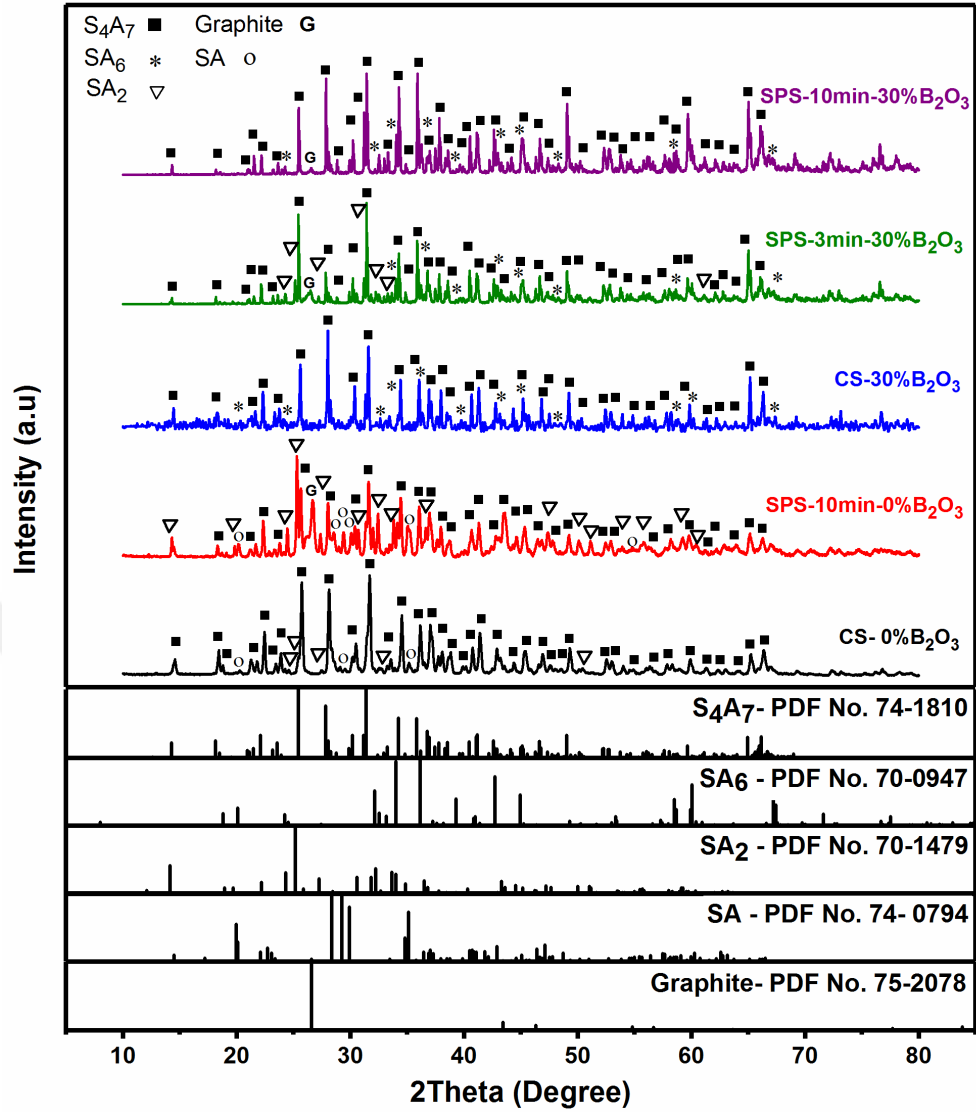


Figure 4.2. XRD patterns of the powders produced by SPS and CS from an amorphous S4A7ED(B) precursor revealed the phase evolution under different restriction of diffusion kinetics.

Table 4.2. Phase composition revealed by Rietveld quantitative analysis of the XRD data from specimens processed under different sintering conditions. R_{wp} and R_{exp} are weighted profile and expected R-factors, respectively.

Sintering Condition	mol% B_2O_3	Phase Composition (wt%)					Goodness of Fit (R_{wp}/R_{exp})
		S_4A_7	SA_6	SA_2	SA	Graphite	
Conventional - 1300 °C	0	89.58	-	6.21	4.21	-	1.69
SPS – 1300 °C – 10 min	0	41.74	-	25.65	10.98	21.63	2.59
Conventional – 1300 °C	30	91.20	8.80	-	-	-	2.00
SPS – 1300 °C – 3 min	30	64.39	4.74	13.18	-	17.69	1.65
SPS – 1300 °C – 10 min	30	83.43	10.65	-	-	5.92	1.63

In the absence of B_2O_3 , there was no liquid in the system, and diffusivity was limited only by the heating rate. CS at 1300 °C allowed the microstructure to evolve along conditions closer to equilibrium. Under SPS, the restricted diffusion over longer distances hindered the development of equilibrium phases, and local stoichiometric variations led to the formation of metastable phases. The addition of B_2O_3 to the amorphous precursor increased diffusivity, accelerating the formation of SA_2 in SPS and enabled development of the equilibrium S_4A_7 phase across the microstructure in both CS and SPS. With increasing SPS dwell time from 3 to 10 min, the metastable SA_2 phase transformed to S_4A_7 .

Due to the 30 mol% B_2O_3 sintering flux used, it is possible that boron-containing compounds may have formed. Thus, we evaluated the experimental XRD patterns of the B_2O_3 -containing sintered specimens by applying Rietveld quantitative analysis. To elucidate the presence of overlapping reflections from crystalline borate phases, possible crystalline borate compounds—including strontium borates (orthorhombic SrB_2O_4 JCPDS 15-0779, cubic SrB_2O_4 JCPDS 22-1419, and SrB_4O_7 JCPDS 15-0801), aluminum borates ($Al_2B_2O_6$ JCPDS 75-1108 and $Al_4B_2O_9$ JCPDS 79-1477) and strontium aluminoborate phases ($SrAl_2B_2O_7$ JCPDS 46-0621 and $Sr_2Al_2B_2O_8$ JCPDS 77-0397)—were considered simultaneously, in addition to strontium aluminate phases. **Figure 4.3** shows the results of Rietveld refinement of the B_2O_3 -containing sintered specimens. Crystalline borate phases did not contribute to the calculated XRD pattern for the CS and SPS specimens. Nag et al. [39] reported that the presence of B_2O_3 as the sintering flux up to 40 mol% did not induce crystallization of borate phases during processing of the strontium aluminate ceramic powders. They showed that when the concentration of B_2O_3 was increased to 100 mol%, crystalline strontium aluminoborate phase had formed. Therefore, we conclude that boron-containing compounds in B_2O_3 -doped sintered specimens remained amorphous and contributed to the shallow bump of diffuse scattering in the XRD patterns.

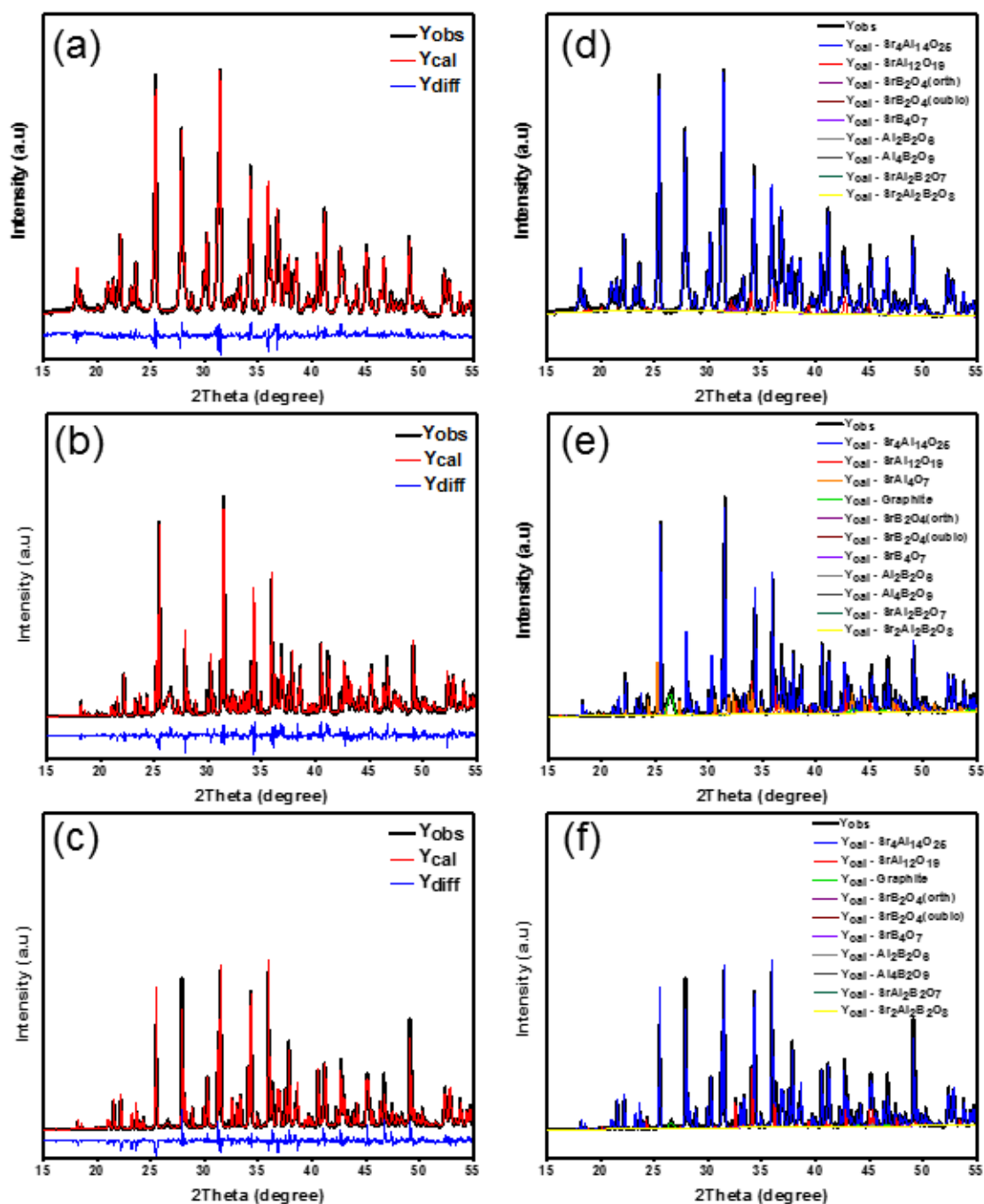


Figure 4.3. Figure S1. Rietveld refinement plots for B₂O₃ doped a) conventionally, b) SPS-3 min, and c) SPS-10 min sintered specimens. Black lines represent acquired intensities, red lines for calculated intensities; difference between acquired and calculated intensities shown below diffractograms in blue. Contribution of individual phases to acquired XRD data in d) conventionally, e) SPS-3 min, and f) SPS-10 min sintered specimens.

The presence of amorphous (glassy) boron containing compounds was revealed by quantifying the fraction of amorphous phase present. Quantification of the amorphous phase content in the B₂O₃-doped sintered specimens is summarized in **Table 4.3**.

Table 4.3. Percent crystallinity and amorphous phase fraction determined from the XRD data of B₂O₃-doped sintered specimens.

Sintering Condition	B ₂ O ₃ Content (mole %)	Fraction of crystalline phase (%)	Fraction of amorphous phase (%)
Conventional–1300 °C	30	61.23	38.77
SPS – 1300 °C – 3 min	30	82.35	17.65
SPS – 1300 °C – 10 min	30	87.07	12.93

The presence of glassy borate phase in the conventionally sintered specimen (S4A7ED – 30 mol%B₂O₃) was further investigated by principal component of micro-Raman maps. To evaluate the crystalline and amorphous nature of the microstructural features, we analyzed the sintered pellet of CS-B by hyperspectral Raman imaging (**Figure 4.4**). We applied principle component (PC) analysis to the full range of Raman-shift spectra collected. Three physically significant principle components were determined, and their corresponding representative spectra were then compared against the reference spectra collected from pure SrAl₁₂O₁₉ (SA₆), Sr₄Al₁₄O₂₅ (S₄A₇), and B₂O₃ powders, as well as the epoxy. **Figure 4.4-a** shows the visible light image of the CS-B specimen, on which the region of interest for Raman spectral imaging is indicated. **Figure 4.4-b** shows the scan area at higher magnification, where crystalline grains and an intergranular phase coexist. The spectral image constructed by PC1 (**Figure 4.4-c**) shows that PC1 originates from the needle-like grains in the scan area (**Figure 4.4-d**). The representative Raman spectrum from PC1 shown in green (**Figure 4.4-i**) is consistent with the reference Raman spectrum obtained from the pure SA₆ phase. In addition, a peak at *ca.* 868 cm⁻¹ is also present in PC1 Raman spectrum, consistent with the Raman vibrational mode of B₂O₃, and confirms the presence of a borate glassy phase in between the high aspect ratio SA₆ grains. The spectral image formed by PC2 (**Figure 4.4-e**) strongly correlates with the large crystalline grain in the overlay image (**Figure 4.4-f**). Comparison of PC2 Raman spectrum shown in blue (**Figure 4.4-i**) with those of the reference spectra reveals that PC2 arises from the

S₄A₇ phase. Similarly, spectral images stemming from PC3 (**Figure 4.4-g and 4.4-h**) which itself is shown in red (**Figure 4.4-i**), are in fact a superposition of S₄A₇, SA₆, B₂O₃ and the epoxy. Due to the limited spatial resolution of the micro-Raman system, it was not possible to detect an individual principle component arising solely from intergranular glassy phase.

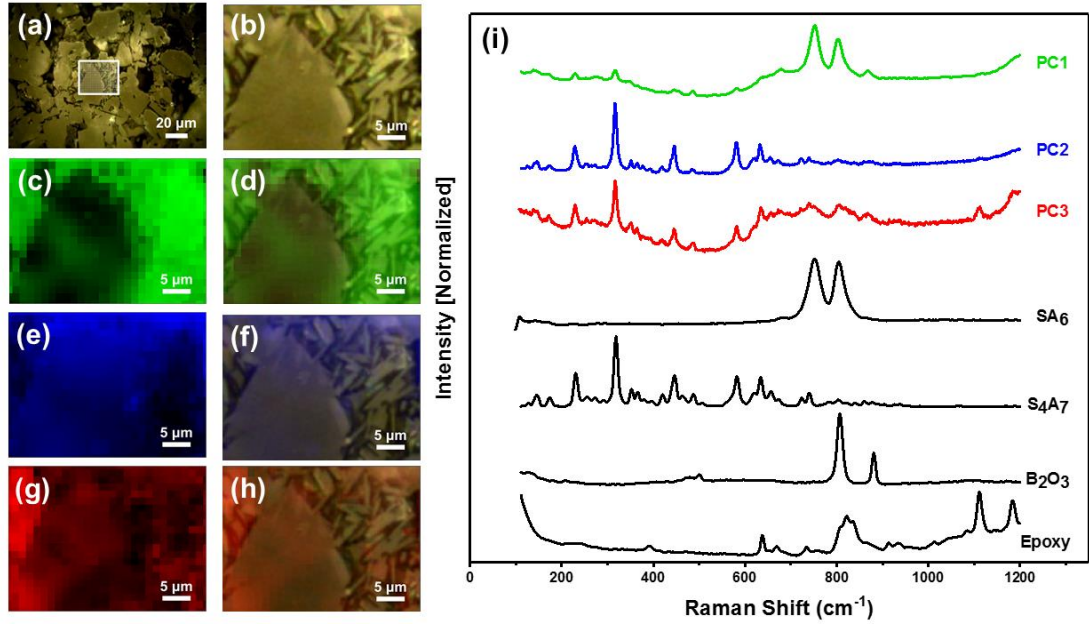


Figure 4.4. Raman mapping analysis of the CS-B specimen a) visible light image of specimen b) region of interest for Raman mapping c) PC1 spectral image d) PC1 superimposed on the scan area e) PC2 spectral image f) PC2 superimposed on the scan area g) PC3 spectral image h) PC3 superimposed on the scan area i) representative Raman spectra of the 3 principle components compared to reference Raman spectra from pure SA₆, S₄A₇, B₂O₃ and the epoxy.

To compare the effect of sintering method and B₂O₃ content on microstructural evolution, we recorded BSE images of SPS (@1300 °C, 10 min) and CS (@1300 °C) pellets in the presence of B₂O₃ and without B₂O₃, respectively. In the B₂O₃-doped specimens, three distinct features were observed—equiaxed matrix (Type 1) grains, an intergranular phase (IGP) and dark high aspect ratio (Type 2) crystals. The microstructure of the SPS pellet containing 30 mol% B₂O₃ (**Figure 4.5, a-c**) resembled the one produced by conventional sintering (**Figure 4.5, d-f**). Variation in contrast in the BSE images is indicative of compositional variations between different phases, particularly between phases with significant difference in their content of high atomic number elements [107].

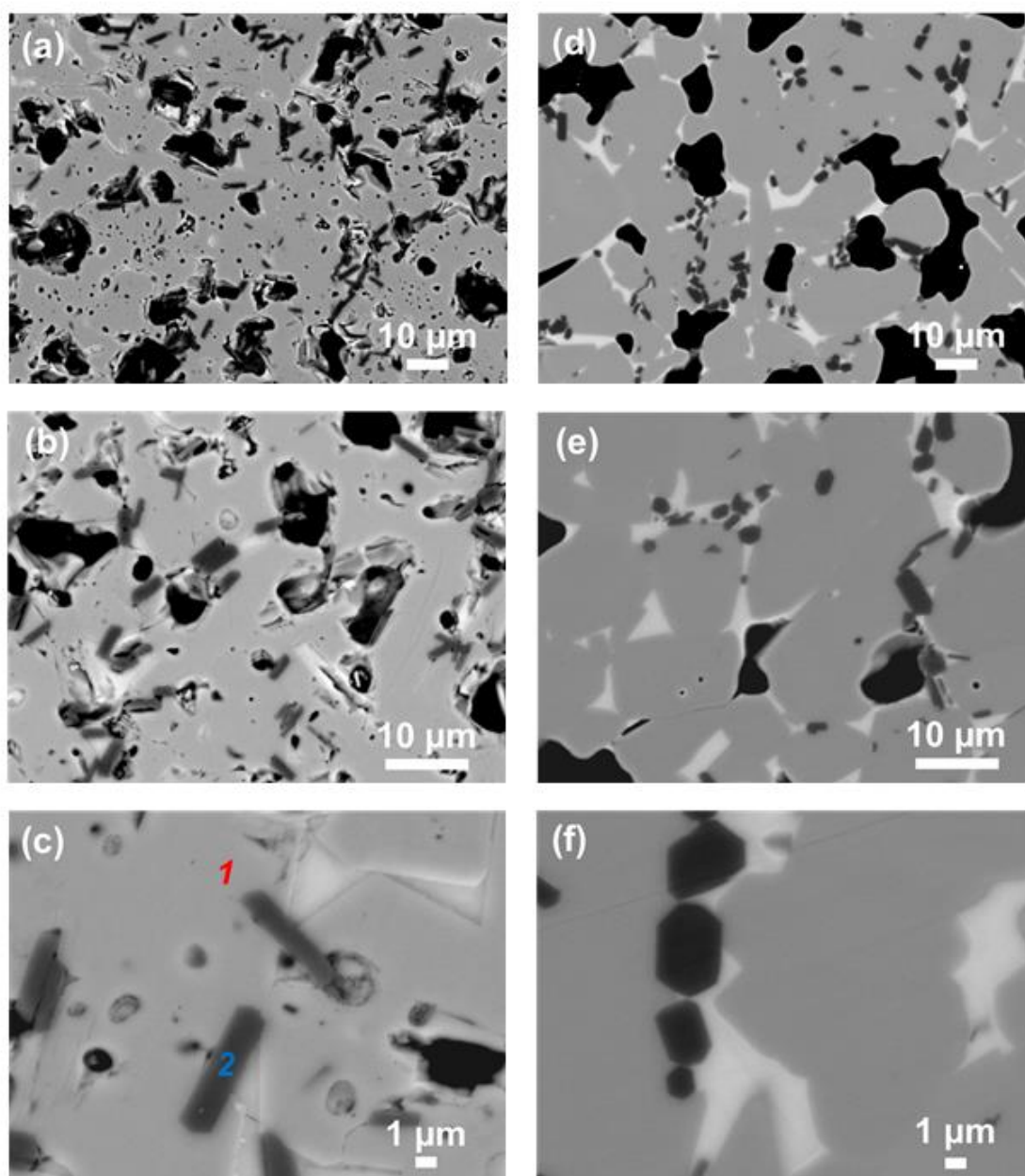


Figure 4.5. B-doped S4A7ED microstructure produced (a-c) by SPS at 1300 °C for 10 min. and (d-f) by CS at 1300 °C for 5 h, at different magnifications. Numbers 1 and 2 in figure 3c refer to equiaxed type 1 and high aspect ratio Al-rich crystals, respectively.

SPS of the B_2O_3 -free powder also produced three distinct features in the microstructure—equiaxed Type 1 grains with an Al:Sr ratio of 3.5, a Type 3 grains with an Al:Sr ratio of 2.2 and equiaxed Type 4 grains with an Al:Sr ratio of 4.0 (**Figure 4.6, a-c**). By contrast, only crystalline features with an Al:Sr ratio of 3.5 was observed in the B_2O_3 -free CS specimen (**Figure 4.6, d-f**). The BSE micrographs also show that when B_2O_3 is not

present, the microstructure of the pellets sintered by both SPS and CS techniques has a high degree of porosity compared to those of B_2O_3 doped specimens.

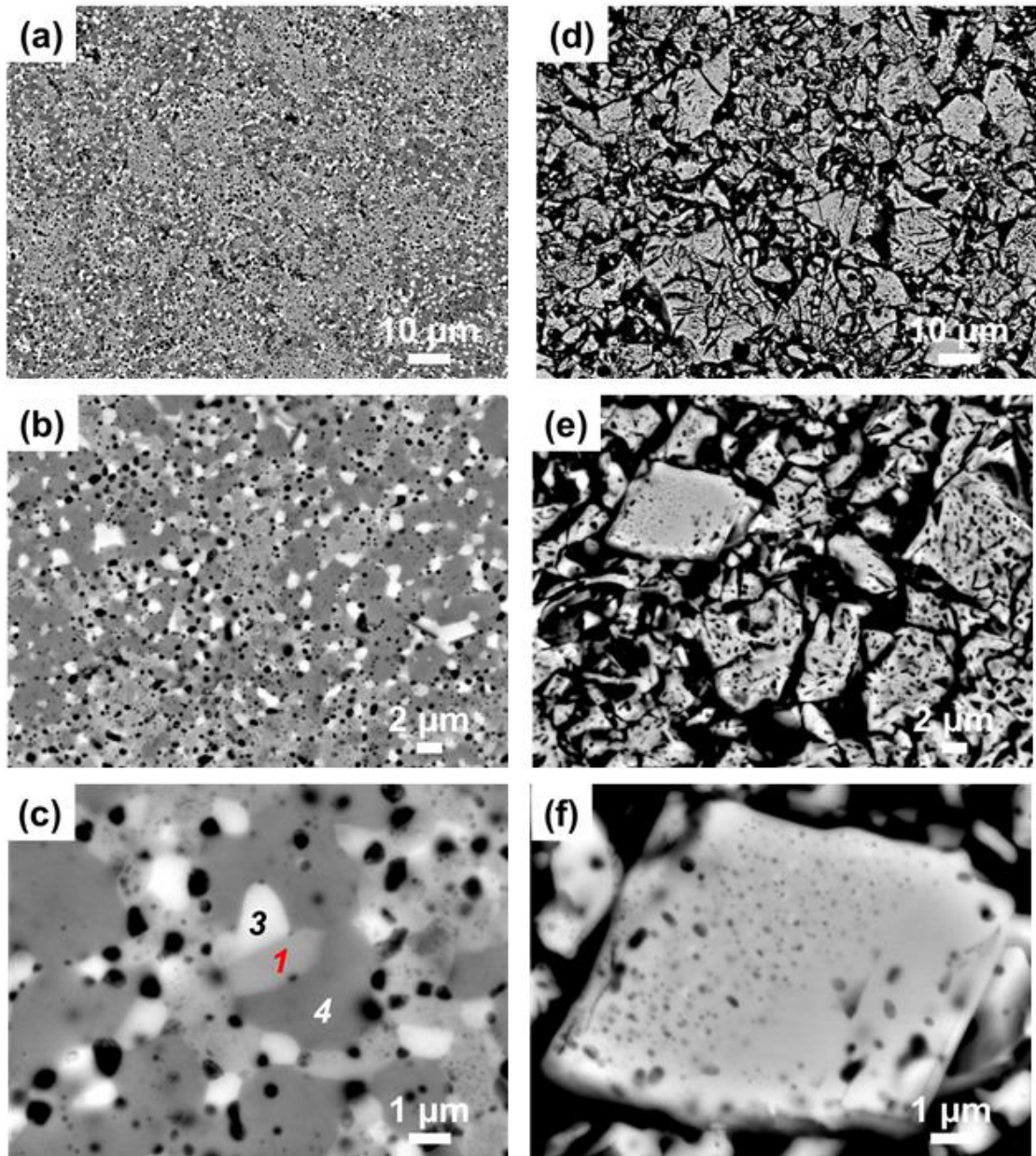


Figure 4.6. B-free S4A7ED microstructure produced by spark plasma sintering (a-c) SPS at 1300 °C for 10 min and (d-f) CS @ 1300 °C for 5 h, at different magnifications. Numbers 1, 3 and 4 in figure 4c refer to equiaxed type 1 grains, Sr-rich type 3 grains and equiaxed type 4 microstructures, respectively.

Selected area diffraction analysis (**Figure 4.7**) of the CS and SPS-10 min specimens doped with 30 mol% B_2O_3 in the TEM revealed that the equiaxed Type 1 grains are of S_4A_7 phase, while the high aspect ratio Type 2 grains are of SA_6 , and the IGP is amorphous. SEM-CL spectra (**Figure 4.8**) from the Type 1 grains are also consistent with

Eu^{2+} luminescence in an S_4A_7 matrix, while luminescence from the high aspect ratio Type 2 grains is from Eu^{2+} in an SA_6 matrix [6, 7].

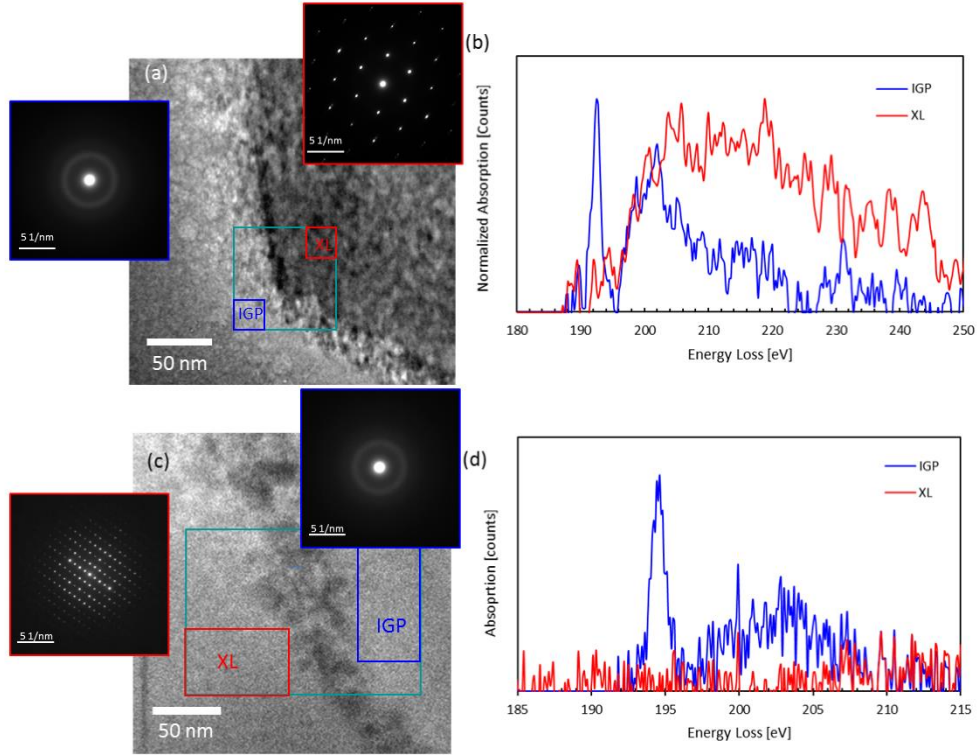


Figure 4.7. CS specimen of $\text{S}_4\text{A}_7\text{EDB}$ a) bright-field TEM image of the intergranular phase (IGP) and a grain with insets of corresponding selected area diffraction patterns—amorphous IGP and SA_6 crystal; the turquoise box indicates the region selected for STEM EELS spectrum image analysis; b) normalized electron energy loss spectrum showing the K ionization edge of boron with characteristic ELNES of [4]B in the grain and [3]B in the IGP; SPS specimen of $\text{S}_4\text{A}_7\text{EDB}$ c) bright-field TEM image of the intergranular phase (IGP) and a grain with insets of corresponding selected area diffraction patterns—amorphous IGP and S_4A_7 crystal; the turquoise box indicates the region selected for STEM EELS spectrum image analysis; d) normalized electron energy loss spectrum showing the K ionization edge of boron with characteristic ELNES of [3]B in the IGP and not detectable in the crystal (XL).

To evaluate the correlation between luminescence, B-content, and regions of increased RE content, the spatial distribution of CL was analyzed in an SEM. **Figure 4.8** summarizes the typical microstructure observed by BSE imaging in the B_2O_3 -doped SPS-10min (Figure 4.8-a) and CS (Figure 4.8-e) specimen, accompanied by the corresponding monochromatic CL images (Figure 4.8 b-d and f-h). In each set of CL images, the detector brightness and contrast levels were held constant within the set, to enable comparison between the relative CL emission intensity. These images show microstructural features containing emitters of specific wavelengths. CL spectra, shown in Figure 6i, were

recorded from Type 1 and Type 2 grains, as labeled in Figure 6a. CL signals were emitted at *ca.* 420 nm and *ca.* 490 nm, due to Eu^{2+} transitions [67], from the equiaxed Type 1 grains, but predominantly at *ca.* 410 nm from the high aspect ratio Type 2 grains (Figure 4.8-i). CL emission at 574 nm, associated with Dy^{3+} transitions [173], was generated from the intergranular pockets (*i.e.*, the IGP phase labeled in Figure 4.8-a), grain boundaries surrounding the high aspect ratio Type 2 grains, and from the interior of the Type 2 grains. In the CS specimen, strong emission at *ca.* 490 nm appeared from the IGP coating the surface of some grains. In the SPS specimen, the emission from 574 nm within a grain—indicated by the red arrow in Figure 4.8-d—was not homogeneous, indicating a non-uniform distribution of Dy^{3+} between the surface layer of the grains and their interior. Such a core-shell distribution was not observed in the CS microstructure.

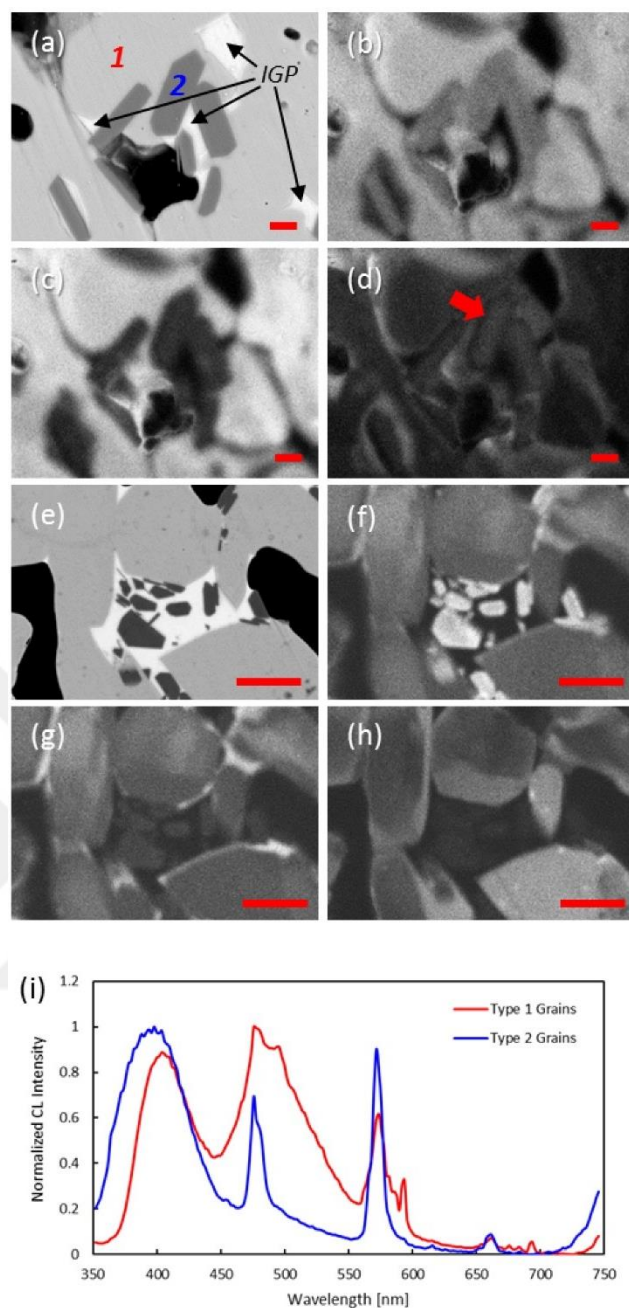


Figure 4.8. Microstructure of S4A7EDB specimen processed by SPS (1300 °C, 10 min) revealed by SEM images formed from a) backscattered electrons and monochromatic CL at b) 410 nm, c) 490 nm, d) 574 nm. For images a-d, scale bar is 2 μm . Microstructure of CS specimen e) backscattered electrons and monochromatic CL at f) 410 nm, g) 490 nm, and h) 574 nm. For images e-h, scale bar is 10 μm . i) CL spectra for Type 1 grains and high aspect ratio Type 2 grains in the SPS sample, labeled in part a.

Fluorescence (FL) spectra were recorded from the sintered pellets and are summarized in **Figure 4.9** with peak characteristics listed in **Table 4.4**. The sintered specimen showed strongest absorption at ca. 371 nm (i.e., containing 30 mol% B_2O_3) and at ca. 334 nm

(i.e., 0 mol% B₂O₃). In the CS specimen containing 30 mol% B₂O₃, the characteristic peaks of Eu²⁺ incorporated into the 2 crystallographically non-equivalent Sr sites of S₄A₇ appeared at *ca.* 420 nm and 490 nm (Figure 4.9-a). Emission around 490 nm was the highest intensity and spanned a broad spectral range. In the 0 mol% B₂O₃ CS pellet, the FL spectrum was dominated by a narrower band of emission at 490 nm, with weaker emission bands at *ca.* 475 nm and at 520 nm. In the SPS specimen, additional peaks appeared, as listed in Table 4.4. Aside from the emission bands centered around 420 nm and 490 nm (Eu²⁺ in S₄A₇) and around 574 nm (Dy³⁺ in S₄A₇), the additional bands are consistent rare-earth dopants incorporating into other phases in the SrO-Al₂O₃ system—S₃A, SA, SA₂, and SA₆ [6]. These spectra highlight the limitation of FL for spatially resolved spectroscopy studies and the advantages offered by SEM-CL. Due to the absence of spatial resolution in the FL analysis, we believe that the SEM-CL data is more relevant to studying the correlation between the spatial distribution of dopants in persistent afterglow S₄A₇EDB compounds.

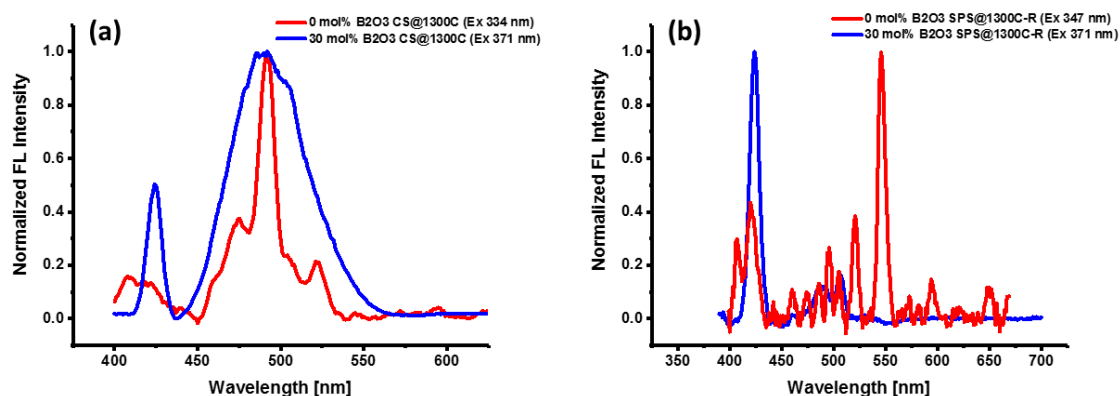


Figure 4.9. Fluorescence spectra from a) CS-B and CS-no B and b) SPS-B and SPS-no B specimen.

Table 4.4. Summary of FL peak characteristics

Spectrum Name	$\lambda_{\text{excitation}}$ [nm]	Peak Center [nm]	Peak Height
CS1300 S4A7ED30B	371 nm	424	0.5
		486	1.0
		492	1.0
CS1300 S4A7ED0B	334 nm	408	0.2
		419	0.1
		475	0.4
		492	1.0
		504	0.2
		521	0.2
SPS1300 S4A7ED30B	371 nm	424	1.0
		487	0.2
		506	0.2
SPS1300 S4A7ED0B	337 nm	407	0.3
		420	0.4
		486	0.1
		496	0.3
		505	0.2
		521	0.4
		546	1.0
		594	0.1

Electron energy-loss spectrum imaging (EELS-SI) of the B-K ionization edge enabled spatially resolved detection of B [174]. **Figure 4.7** summarizes the results for an SPS and a CS specimen. The presence of B is verified in both the amorphous IGP and in the crystalline grains in CS S₄A₇EDB. However, although the B-K edge was detected in the amorphous pocket in SPS S₄A₇EDB, it was not present in the crystalline grain. Moreover, B in the IGP was 3-fold coordinated, as evidenced by the $\pi \rightarrow \pi^*$ transition in the electron

energy-loss near-edge fine structure (ELNES). The ELNES showed that when incorporated into the crystal, B is 4-fold coordinated.

The results of WDS point-beam quantitative microanalysis are summarized in **Table 4.5** for the CS and SPS specimen. To facilitate comparison of trends in composition and morphology, the Al:Sr ratio and the distribution of rare earth dopants are plotted in **Figure 4.10** for each distinct microstructural feature: equiaxed grains, dark grains, and IGP. For statistical analysis of elemental distribution obtained from the WDS, the standard error of the mean values was calculated for the Al:Sr ratio, at% Eu, and at% Dy, based on the number of point-beam analyses performed on each of the distinct microstructural features. The corresponding standard deviation was extracted from the data spread around the mean value.

The Al:Sr ratio in the equiaxed Type 1 grains was *ca.* 3.5, which is consistent with the stoichiometry of $SrAl_4O_7$ in all CS and SPS specimens (with and without B_2O_3). To determine this ratio of atomic percentages, we had assumed that there were 25 oxygen atoms per unit cell, when calculating the atomic percentages from the mass percentages. Sufficient counting statistics were ensured for achieving a statistical precision with standard counting deviation of $\leq \pm 1\%$ relative. In the case of the IGP, which were richer in strontium ions, the Al:Sr ratio (see Table 4.5) did not correspond to the stoichiometry of any stable phase in $SrO-Al_2O_3$ system, possibly indicative of an amorphous phase in between the $SrAl_4O_7$ grains. In the case of SPS and CS specimens doped with B_2O_3 , the high aspect ratio Type 2 grains in the micrographs (Figure 4.5) were richer in aluminum. With an Al:Sr ratio of 10.826 ± 0.910 (for SPS) and 8.722 (for CS), these slab-like grains are most likely the SA_6 phase. The Type 3 grain in the SPS pellet without B_2O_3 with an Al:Sr ratio of 4.017 is consistent with the stoichiometry of $SrAl_4O_7$ (SA_2).

The high analytical sensitivity of WDS enables measurement of elemental rare earth content with high accuracy [107, 109], suggesting that the relatively low Eu and Dy concentrations were determined with high confidence and are true, real and significant. In the B_2O_3 -containing specimens, the WDS results revealed a significant increase in concentration of rare earths in the IGP over the relatively lower amounts detected in both Type 1 and Type 3 grains. This increase was even more pronounced in the CS specimen, when compared with the SPS one. For the B_2O_3 -free SPS specimen, the distribution of rare earth dopants within the three microstructures is relatively uniform with no

significant difference in the concentration of Eu and Dy between the IGP and the neighboring crystal.

Table 4.5. The results of WDS microanalysis for the conventionally sintered and spark-plasma sintered specimen.

Specimen	B ₂ O ₃ (mol%)	Structural Feature	Element Distribution (at%)					
			Al/ Sr		Eu		Dy	
			value	error	value	Error	value	error
SPS-10 min	30%	Type 1 Grains	3.487	0.043	0.029	0.002	0.017	0.004
		Intergranular Pockets	1.095		0.092		0.295	
		Type 2 Grains	10.826	0.910	0.024	0.002	0.035	0.001
CS	30%	Type 1 Grains	3.551	0.040	0.016	0.001	0.010	0.002
		Intergranular Pockets	0.829	0.033	0.285	0.009	0.472	0.018
		Type 2 Grains	8.722		0.028		0.019	
SPS-10 min	0%	Type 1 Grains	3.396	0.030	0.024	0.002	0.035	0.001
		Intergranular Pockets	2.310	0.079	0.039	0.002	0.038	0.002
		Type 3 Grains	4.017	0.038	0.022	0.003	0.016	0.0008
CS	0%	Type 1 Grains	3.578	0.052	0.028	0.001	0.029	0.001

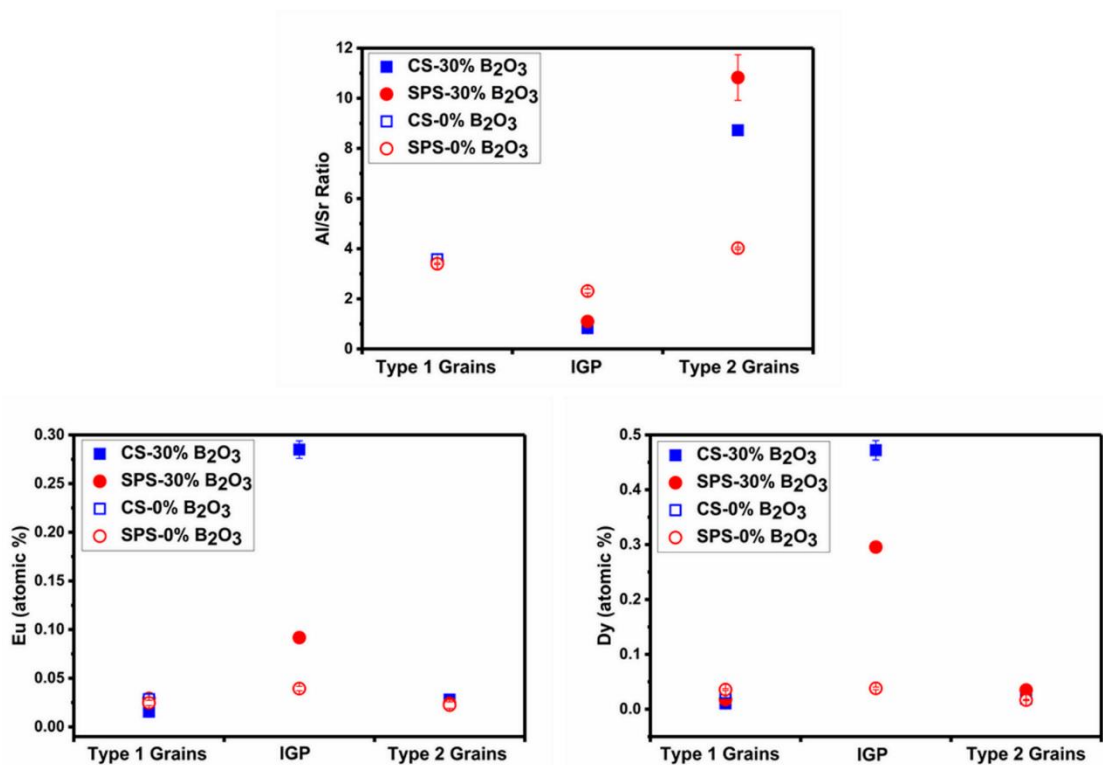


Figure 4.10. Elemental content distributed across different microstructural features, as determined by WDS analysis of conventionally sintered (blue markers) and spark-plasma sintered (red markers) 1 at% Eu and 1 at% Dy doped Sr₄Al₁₄O₂₅ ceramic powders, processed without B₂O₃ and with 30 mol% B₂O₃.

Afterglow decay was measured for both the CS and SPS specimen with 30 mol% B₂O₃. As shown in **Figure 4.11**, the CS pellet decayed to 1/e in 331 min., whereas the SPS pellet only required 153 min.

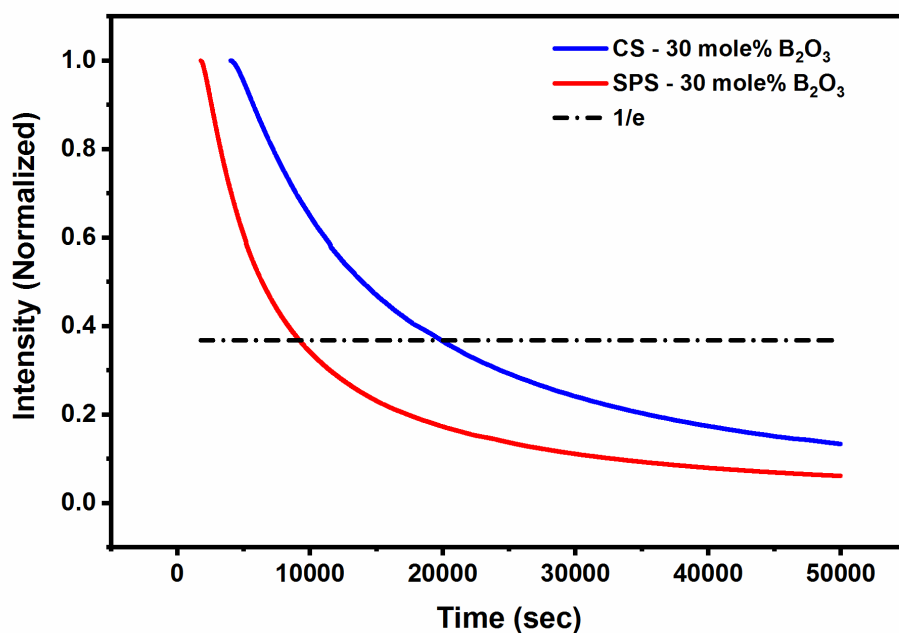


Figure 4.11. Afterglow decay curves for CS and SPS-10 min specimen with 30 mol% B.

To compare the effect of re-oxidation and controlled reduction at 1150 °C, SEM-EDS analyses were performed on the Type 1 grains, the Type 2 grains, and the IGP between a pellet directly from SPS and a re-oxidized one. The re-oxidized pellet is shown in **Figure 4.12-a** and **b**, where points 1-4 (P1-P4) correspond to Type 1 grains; points 5-9 (P5-P9) correspond to the IGP; and points 10-13 (P10-P13) correspond to Type 2 grains. The pellet directly from SPS is shown in **Figure 4.12-c**, where points 1-3 (P1-P4) correspond to Type 1 grains; points 5-8 (P5-P8) correspond to the IGP; and points 10-12 (P10-P12) correspond to Type 2 grains. The results shown in Figure 4.12 reveal that the change in elemental concentration lies within the error bars, indicating that the change in dopant distribution was negligible.

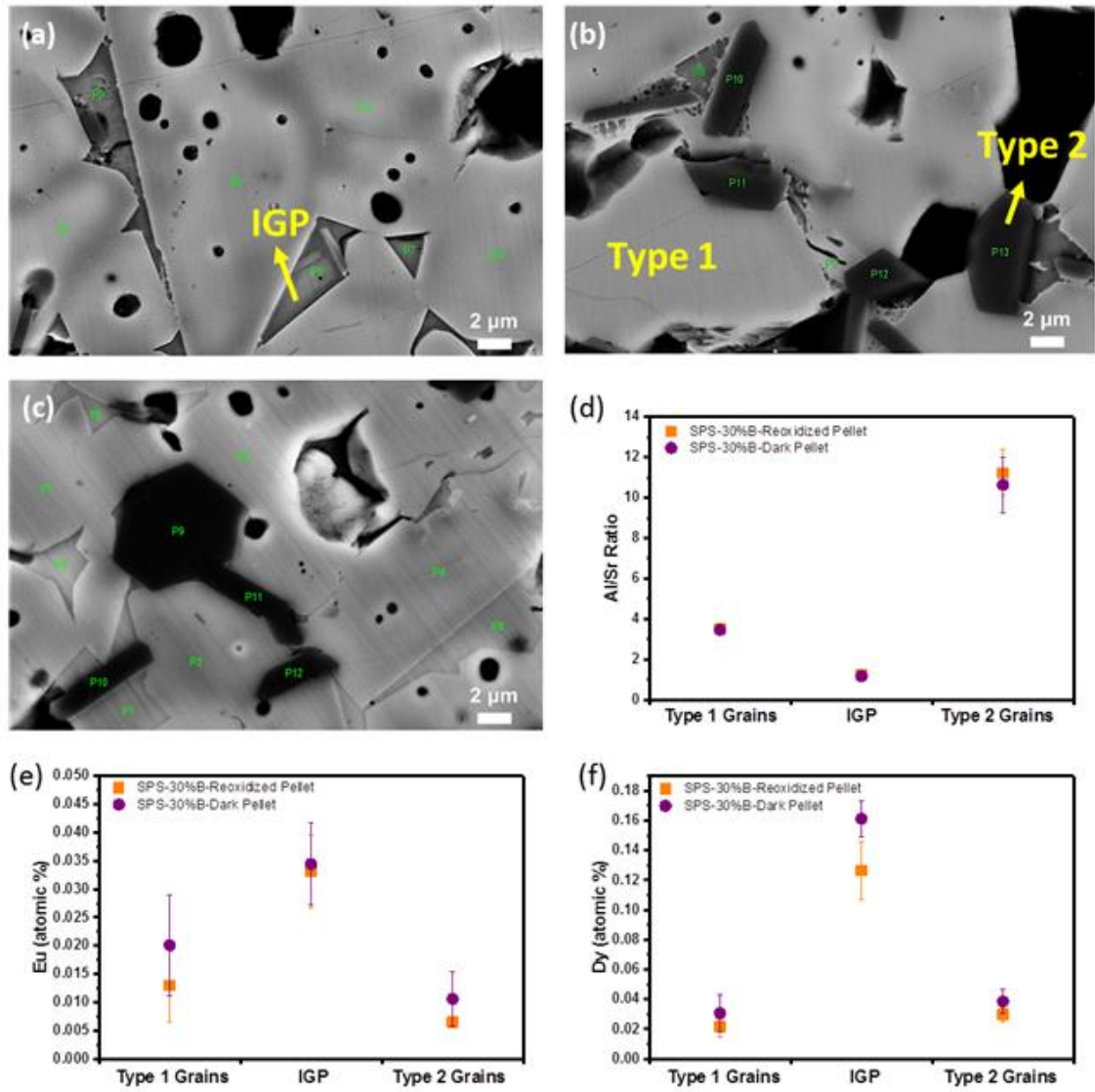


Figure 4.12. Effect of re-oxidation @ 1150 °C on elemental distribution in SPS-10 min. The “dark pellet” is the SPS-10 min. product, while “Reoxidized pellet” is the SPS-10 min pellet after re-oxidation and controlled reduction at 1150 °C.

4.3 Discussion

While prior work [7, 8] suggested that B facilitates clustering of Eu and Dy ions in persistent afterglow $\text{S}_4\text{A}_7\text{EDB}$, it also revealed the development of a substantially different microstructure compared to B-free $\text{S}_4\text{A}_7\text{ED}$: lower porosity, dominance of micron-scale, equiaxed Type 1 grains, and high aspect ratio Type 2 grains in the IGP [7]. To elucidate the effect of the modified microstructure on extending persistent afterglow, we now consider 2 parameters for tuning diffusion kinetics in Pechini processed

S₄A₇EDB: i) heating rates for sintering at 1300 °C, by SPS and CS, and ii) the addition and omission of B₂O₃. By the 4 distinct combinations of these 2 parameters, we examined their effects on the morphology and chemistry of the S₄A₇ED microstructure. In all cases, the starting pre-ceramic was chemically homogenous and of the stoichiometry Sr₄Al₁₄O₂₅ doped with 1 mol% Eu, 1 mol% Dy and with either 0 or 30 mol% B₂O₃. Based on the microstructure revealed by micrographs, we rank the 4 different levels of diffusion kinetics tested, in order of increasing restriction for diffusivity: CS for 5 h with B₂O₃ (CS-B), SPS for 10 min. with B₂O₃ (SPS-B), SPS for 10 min. without B₂O₃ (SPS-no B), and CS for 5 h without B₂O₃ (CS-no B).

When heating from the amorphous pre-ceramic, residual organic moieties from the Pechini processing and adsorbed water were eliminated from the stoichiometrically uniform polymeric gel, which was revealed by dilatometry to undergo glass transformation at *ca.* 750 °C. The amorphous network consisted of interconnected polyhedral units of cations coordinated by oxygen. Between *ca.* 850 °C and 1300 °C, nucleation and growth of crystalline phases occurred. The Sr and Al cations were subjected to a chemical driving force, the volumetric Gibbs free energy, for precipitation as SA, SA₂, S₄A₇, and SA₆ crystal structures; concurrently, network viscosity decreased, and cation diffusivity increased.

Although the thermodynamically preferred state at 1300 °C appeared to be the S₄A₇ phase with limited solubility of Eu and Dy for a nominal stoichiometry of S₄A₇ED, the amorphous pre-ceramic did not melt in CS-no B. The network viscosity had decreased at 1300 °C, facilitating cation diffusivity. The resulting local variation in cation concentration enabled metastable phases to form and stabilize, as indicated by phase analysis of the XRD data (Figure 4.2, Table 4.2).

With B₂O₃ present (as in CS-B), a liquid glass formed by incongruent melting at around 750 °C, significantly lowering viscosity and increasing diffusivity. As shown in **Figure 4.13-a**, the amorphous pre-ceramic had the composition indicated by the red dot at 25SrO-45Al₂O₃-30B₂O₃ (doped with 1 mol% Eu and 1 mol% Dy), which lay outside the glass-forming region. At 1300 °C, the system was in the 2-phase liquid-solid field. Because the melting temperature was above 1700 °C, the amorphous pre-ceramic did not melt directly. Instead, crystallization and coarsening at 1300 °C occurred inside a liquid of composition different from that of the amorphous pre-ceramic. According to EDX analysis of the final microstructure, the liquid was rich in Sr, B, Eu, and Dy, albeit with some Al present. The

S_4A_7 grains dominated the microstructure in the form of equi-axed, Type 1 grains of up to microns in diameter. The next most stable phase at 1300 °C, SA_6 , also appeared (Table 4.2), while an amorphous IGP was frozen in at grain boundaries, intergranular pockets, and the surfaces of pores.

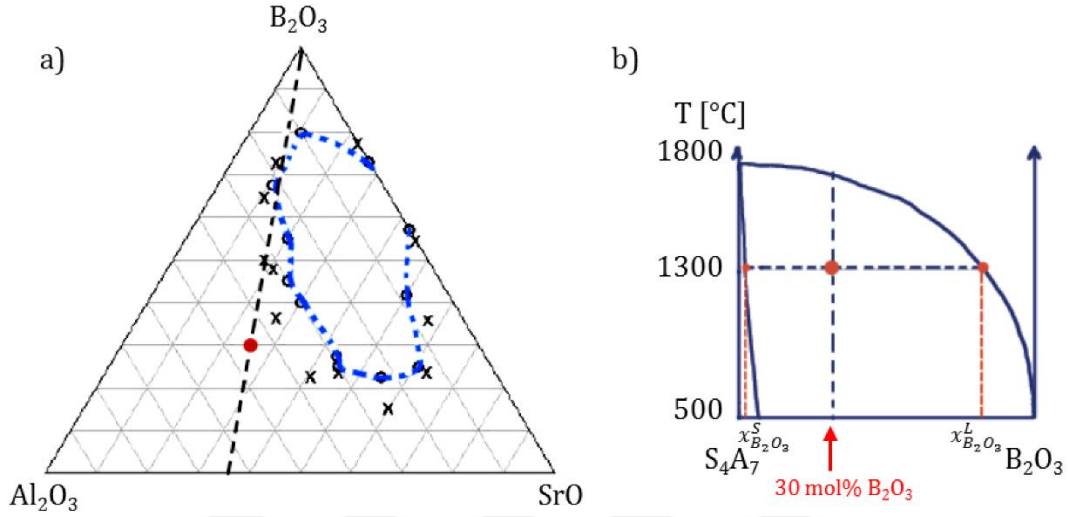


Figure 4.13. a) The ternary SrO-Al₂O₃-B₂O₃ phase diagram showing the glass-forming region and the composition of S4A7EDB investigated in this study; b) the pseudo-binary phase diagram proposed for S4A7-B₂O₃, corresponding to the dashed line in part a; the red dot indicates the composition in this study, S4A7ED doped with 30 mol% B₂O₃.

In the case of SPS-no B, SEM micrographs revealed a fine-grained microstructure consistent with conductive heat and cation transport at high rates over limited distances. Due to kinetic limitations, additional metastable phases appeared in the microstructure, as exemplified by the Type 3 grains (Figure 4.6). Another effect of the high heating rates was evident in the microstructure, in the form of fine porosity, which can be attributed to foam formation during elimination of residual organics and adsorbed water in vapor form [171]. With B₂O₃ present (in SPS-B), S_4A_7 grains crystallized and coarsened in the liquid phase as Type 1 grains, while the localized non-stoichiometry enabled stabilization of another phase at 1300 °C, SA_6 , as Type 2 grains. Due to the increased liquid phase diffusivity, the gas bubbles were able to coalesce or escape, resulting in a marked reduction in porosity.

The equilibrium phase S_4A_7 [11] dominated under the least restrictive conditions, in CS-B, while the metastable SA_2 and SA phase content was elevated at the expense of

S₄A₇ under SPS-no B (Table 4.2). Under the most limited diffusion conditions for Sr and Al cations, in SPS-no B, the S₄A₇ content was 41.74%, and the stoichiometry was stabilized locally for the metastable SA₂ and SA phases—confirmed by WDS-measured Al:Sr ratios. Independent of the initial SrO-Al₂O₃ solution stoichiometry, SA was the first phase to form, due to its lowest enthalpy of formation [151]. With SA present, it may have also reacted with Al₂O₃ to form SA₂. However, with increased diffusivity of Sr and Al, metastable SA₂ and SA would likely have transformed to S₄A₇.

Both the CS and SPS microstructures (Figure 4.5 and 4.6) showed that the use of B₂O₃ promoted viscous-flow sintering by lowering viscosity of the glassy phase, lowering sintering temperature and enhancing densification—increasing grain size and minimizing porosity. The microstructure in B-doped S₄A₇ED was dense with large grains, while that without B₂O₃ was fine-grained and contained a high degree of porosity. In Pechini processing, the nitrate precursors were dissolved in ethylene glycol with a chelating agent, citric acid, and bubbles of CO₂ gas were likely to have evolved. The gas bubbles remained trapped in the developing microstructure without B₂O₃ present, regardless of sintering conditions—*i.e.*, in CS-no B and SPS-no B. On the other hand, in CS-B, the gas bubbles had enough time to coalesce or escape, while in SPS-B, porosity was still present, albeit noticeably reduced.

Further insight into phase development during SPS was revealed by comparing phase content under SPS dwell times of 3 minutes and 10 minutes (Table 4.2). During the initial 3 minutes, in addition to formation of the equilibrium S₄A₇ phase, metastable phases were present—SA₆ (4.74%), SA₂ (13.18%), and graphite (17.69%). Over an additional 7 minutes of dwell time at 1300 °C, the S₄A₇ phase content increased from 64.39% to 83.43% and SA₆ to 10.65%, due to transformation from SA₂.

The combined effects of localized variation in stoichiometry and kinetically limited diffusion also enabled crystallization of the SA₆ phase. Because such crystals tended to be *i*) surrounded by a Sr-rich IGP and *ii*) clustered inside the IGP, it's likely that S₄A₇ formed before SA₆—*i.e.*, as the surrounding solution became depleted in Sr, the resulting stoichiometry led to the development of SA₆ grains.

The IGP was also enriched in Sr, Eu, and Dy, according to WDS analyses (Figure 4.10), revealing the effect of diffusion limitations on rare earth dopant distribution. In the absence of B₂O₃, both the SPS and CS microstructures contained relatively uniform distributions of Eu and Dy. However, there was a substantial difference in Eu and Dy

content in the grains vs. the IGP (Figure 4.10) in CS-B. In the case of SPS-B (10 min. dwell), the difference in RE content in the grains vs. the IGP was less pronounced. These results suggest that there is a driving force for segregation of the RE ions out of the crystallizing grains, due to their initial levels in the amorphous phase exceeding the solubility limit in the grains. It is possible that the evolving crystal structure, which is a dense scaffold of corner- and edge-sharing Al polyhedral with Sr^{2+} providing charge balance, was not able to easily accommodate the size difference between Eu, Dy, and Sr for their incorporation into the Sr sub-lattice [8]. Despite the higher diffusivities under the highest heating rates, RE segregation was still limited and a relatively uniform composition was preserved across the microstructure—*i.e.* in both the IGP and the grains. However, under the less kinetically limiting conditions in CS-B, the higher diffusivity enabled segregation of the RE ions to the surface of the grains.

SEM-CL maps of the B_2O_3 -containing SPS and CS microstructure provided additional insight with higher spatial resolution into the distribution of Eu^{2+} and Dy^{3+} . Emission at *ca.* 410 nm arises from Eu^{2+} incorporating into Sr^{2+} sites in SA_6 grains [6] mapped solely to the Type 2 grains. Emission at *ca.* 420 nm and *ca.* 490 nm, characteristic of Eu^{2+} emission in S_4A_7 grains [7], arose from the Type 1 grains in the BSE images, in both SPS and CS microstructures. From the luminescence at *ca.* 574 nm in the interior of grains and in the IGP in both types of microstructure, we conclude that Dy^{3+} is distributed across the entire microstructure.

In the SPS microstructure, changes in CL distribution were abrupt at the grain boundaries (Figure 4.8 *a-d*). The presence of a depletion zone suggests that there was a segregation tendency from the interior of the crystal, but only the ions in the sub-surface layer were able to diffuse to the IGP. The dopant ions in the grain interior were kinetically trapped. Although the Eu and Dy concentrations as measured by WDS were similar in the grain interior and in the IGP, the intensity variation in the CL maps of the microstructure indicates diffusion-limited conditions and is representative of other regions analyzed in the sample. In contrast, maps of the elemental distribution in the CS specimen reveal more gradual changes in contrast between grains and IGP, consistent with the CL maps. Finally, we note that the CL intensity from the IGP at 490 nm and at 574 nm was higher in the SPS-B microstructure than in the CS-B one. Because the Eu and Dy concentrations were elevated by more than an order of magnitude in the IGP of CS-B, it is possible that their emission was absorbed by the high density of neighboring Eu and Dy ions—a

phenomenon known as concentration quenching [175] . In the IGP of SPS-B, the Eu and Dy concentrations were lower, and the CL emission intensity was higher.

Closer inspection of the 574 nm monochromatic CL map of the SPS-B specimen (Figure 4.8-d) revealed a pronounced core-shell structure in the Type 2 grains. Because emission at 574 nm arose from the Dy^{3+} dopant [173] , this map suggested a non-uniform distribution in Dy in those grains, particularly a depletion of Dy in the surface layer. The 490 nm monochromatic CL map also showed a less pronounced depletion layer at the surface of the Type 2 grains, also suggesting depletion of Eu^{2+} at the grain surface, albeit to a lesser extent than of Dy^{3+} . As we only observed this depletion shell in SPS-B, we attribute the depletion layers to diffusion limited by the high cooling rates occurring in SPS. In contrast, the Type 2 grains in the CS-B did not show the core-shell structure in the monochromated SEM-CL maps. Although the core-shell structure may be an imaging artefact due to a tilted grain facet or enhanced scattering from grain boundaries, Nakanishi et al. [176] had reported SEM-EDX elemental maps showing a similar Eu-depleted shell in Eu- and Dy-doped SA (SAED) crystals produced by the frozen sorbet method, a processing approach strongly resembling the SPS-B system. Further cross-section analysis of the SA_6 grains would be necessary to assess the significance of the core-shell structure, which is beyond the scope of this study.

The rich variation in FL emission bands highlights the limitation of FL for spatially resolved spectroscopy studies, emphasizing the advantages offered by SEM-CL. Due to the absence of spatial resolution in the FL analysis, we believe that the SEM-CL data is more relevant for studying the correlation between the spatial distribution of dopants in persistent afterglow $\text{S}_4\text{A}_7\text{EDB}$ compounds.

To determine the distribution of B in the microstructure, we analyzed the K ionization edge of B at *ca.* 188 eV, via STEM-EELS spectrum images—representative ones shown in Figure 4.7. We specifically chose thin (< 100 nm-thick) regions of the FIB lamella to characterize, where there was an amorphous IGP region in contact with a crystalline grain. The B-K signal was not detected in the SPS crystal, although it was detected in the IGP. It is likely that B may be present deeper into the grain, but not in the sub-surface layer of the grain, where it was also depleted. Because the ionization edge is sensitive to multiple scattering losses in thicker specimen, we were not able to detect the B-K edge deeper in the core of the grain. By contrast, the B-K signal was present in both the IGP and in the crystal in the CS-B specimen. Because the B-K ELNES is sensitive to the local

coordination environment, it indicates if the symmetry is 3-fold or 4-fold [174]. The B-K ELNES of the IGP showed a peak corresponding to the $\pi \rightarrow \pi^*$ transition characteristic of trigonal coordination. When B was incorporated into the CS grain, the B-K ELNES was present, but lacked the $\pi \rightarrow \pi^*$ peak, indicating that it was tetrahedrally coordinated.

The final amorphous IGP indicated that the glassy melt was uniformly enriched in B, driven by the inclusion of boron oxide in the glassy structure. Because solidification in the CS-B system occurred closer to equilibrium conditions, it appears that the S_4A_7 grain was able to accommodate some B (Figure 4.7). On the other hand, while the B distribution in the SPS-B microstructure was present in the amorphous IGP, it was not detected at least in the shell layer of SA_6 grain.

Because crystallization occurs in a strongly reducing atmosphere in SPS, unlike the oxidizing one of CS, we analyzed the data for SPS-B and CS-B, to determine the influence of oxygen deficiency on dopant re-distribution. In the competition between cations for oxygen, the relative oxygen affinity can be estimated from the free energy of oxide formation, as summarized in **Table 4.6** [177]. Because the oxygen affinity of Sr, Eu, and Dy are the strongest, those cations are the most likely to bond with the available oxygen in the glass in SPS-B, compared to Al and B. The WDS and EDX analyses confirmed that the glass was poorer in Al, but rich in Sr, Eu, and Dy, in addition to B. Because B is less likely to bond with oxygen in the glass, it has the highest mobility. However, there was negligible trace of B-K ionization edge in the ELNES (Figure 4.7-d) of SPS-B, indicating that all B remained in the IGP. In contrast, B was detectable in CS-B grains as well as in the IGP. Overall, these results suggest that the sintering atmosphere had minimal impact on the microstructural evolution.

Table 4.6. Comparison between oxygen affinity between cations [177].

Compound	ΔG_f [kJ/mol]	moles of O_2	ΔG_f [kJ/mol of O_2]
SrO	-710.346	0.5	-1421
Al_2O_3	-1837.194	1.5	-1225
Eu_2O_3	-1970.417	1.5	-1314
Dy_2O_3	-2137.433	1.5	-1425
B_2O_3	-1445.962	1.5	-964

4.4 Conclusion

In this study, we sought to determine if the B-modified diffusion kinetics of Eu and Dy play a role in extending afterglow persistence in S_4A_7EDB . We compared the microstructure and dopant distributions produced by sintering via SPS and CS of S_4A_7ED , with and without B_2O_3 . While we verified that B_2O_3 facilitates dominance of the equilibrium long afterglow phase, S_4A_7 , in the microstructure, we also showed that B is incorporated into conventionally sintered grains but not the SPS ones. Its presence in the overall microstructure additionally tuned partitioning of the RE dopants and their distribution—in both grains and the IGP—ensuring incorporation of an optimal concentration of Eu and Dy in the host crystals. The results of SEM-WDS, SEM-CL, and STEM-EELS analyses suggest that B plays an additional role in determining the material structure supporting persistent luminescence—optimizing the concentration of Eu^{2+} and Dy^{3+} incorporating into S_4A_7 grains—in addition to inducing interaction between Eu^{2+} and Dy^{3+} ions within those grains.

CHAPTER 5: SPATIALLY RESOLVED INVESTIGATION OF THE MICROSTRUCTURE IN THE SINTERED AMORPHOUS PRE-CERAMIC OF B, Eu AND Dy DOPED Sr₄Al₁₄O₂₅: ELECTRON ENERGY LOSS SPECTROSCOPY AND ATOMIC RESOLUTION STEM-IMAGING

5.1 Introduction

Strontium aluminate powders, when codoped with Eu²⁺ and Dy³⁺, have distinctive optical properties because of their ability to temporarily store energy and slow release of energy in the form of light which makes them good candidates for long afterglow applications. It has been reported that the addition of boron can enhance the afterglow duration and intensity of strontium aluminate powders through the tuning of electronic structure in the crystal lattice [7, 8, 39].

Persistent luminescence of the host material, in our case, strontium aluminate phosphors, is directly dependent on the crystal field around the emitting center (the Eu²⁺ ions). Because incorporation of co-dopants into the microstructure influences the density of the available energy states in the host material through formation of molecular bonds, the way by which boron enters the microstructure can thus play a vital role in distribution of electron energy states of the ionized atom and its nearest neighbors, resulting in modification of the crystal field which is applied on the Eu²⁺ ions. In addition to this, understanding the distribution homogeneity of the dopants in the microstructural features within a sub-nanometer spatial resolution is an important parameter to elucidate the correlation between the optical properties of the strontium aluminate phosphors with the microstructure. However, understanding the true mechanism of persistent luminescence

in such materials through investigation of dopant distribution and coordination polyhedral units of the dopant ions in the microstructure have been limited to globally averaged characterization tools and indirect observations [37, 39, 118] and only a few works have been dedicated to spatially-resolved investigations [7, 8, 67].

Because during ionization process, the core electron of an atom is excited to the unoccupied available electronic energy states and the density of the empty levels is related to the type of bonding between the ionized atom and its nearest neighbors [159] *e.g.* the molecular orbitals in the material, the ELNES features located at *ca.* 30-50 eV above the edge onset is highly sensitive to local environment of the ionized atom. This means that, the difference in the spatial arrangement of the atoms in the nearest neighbor shell around the ionized atom would result in characteristic shapes of the ELNES signal which is termed as coordination fingerprint. Therefore, different ELNES fingerprint of an ionized atom can be interpreted as electronic transition between molecular orbitals that are formed due to interaction of the atomic orbitals of the central atom and its surrounding atoms [113, 178].

To elucidate the nature of boron incorporation in the microstructure, we used coordination fingerprinting of B-K ionization edge through electron energy loss near-edge structure (ELNES) measurements by using electron energy loss spectroscopy technique. By comparing the measured ELNES fingerprint of B-K edge in the microstructure of strontium aluminate compounds with the ELNES spectra of boron, obtained from standard reference materials containing pure 3-fold and/or 4-fold coordinated boron, the site symmetry of boron between two different phases in the strontium aluminate phosphors can be identified. Sauer et al. [159] determined the ELNES fingerprint of boron in planar trigonal BO_3 units by analysis the near edge structure of B-K edge in vonsenite as a reference mineral sample where boron is only coordinated by three oxygen atoms. In their work, they also characterized the ELNES shape of tetrahedral BO_4 units in rhodizite, a mineral where boron is merely three dimensionally coordinated by four oxygens. The main difference between the near-edge structure of BO_3 and BO_4 structures lies in the difference between the molecular orbital formed around the central B atom [158, 159].

When boron is coordinated with three oxygen, the bonding electrons of boron are located in sp^2 hybridized orbitals [67], that is the atomic orbitals involved in bonding are 2s atomic orbital and two of the p atomic orbitals ($2p_x$ and $2p_y$). The ELNES fingerprint of the B-K edge shows a sharp peak at *ca.* 194 eV followed by a broader peak at about ~ 204 eV. In

addition, a shallow rarely discernable intermediate peak located at *ca.* 199 eV might be present (**Figure 5.1-a**). In fact, when boron is trigonally coordinated in BO_3 arrangement, the structure of the molecular orbitals is such that the lowest unoccupied molecular orbital (LUMO), is a π^* (π -antibonding) which is derived from the boron 2p atomic orbital. Thus, the sharp peak in near edge structure is the result of transition of excited electron to π^* character (A in Figure 5.1-a) [158, 159]. The broader peak at *ca.* 203 eV is known to be due to transition from 1s to a σ^* (σ -antibonding) which is predominantly derived from boron 2p atomic orbital [158](C in Figure 5.1-a). The peak with the intermediate energy loss in the ELNES features for three-fold coordinated boron (B in Figure 5.1-a) is known to be the result of transition to another σ^* with predominant boron 2s character [158] or less likely, might be related to the states attributed to boron 3p or 4p [159].

When boron is in tetrahedral site coordinated by four oxygen atoms, the central B atom in the BO_4 configuration, uses the 2s atomic orbital along with three p atomic orbitals ($2p_x$, $2p_y$ and $2p_z$) for delocalizing of the bonding electrons, leading to formation of sp^3 hybridized orbital [67]. Under this circumstance, the LUMO is a σ^* antibonding orbital and dominated by boron 2p character and the wide peak located at *ca.* 199 eV in the ELNES spectra of 4-fold boron (**Figure 5.1-b**) is attributed to transition from σ to σ^* . The wide shoulder located at about 5-10 eV higher is known to be due to transition to another σ^* predominantly made of boron 2s atomic orbital. [158, 159]. Nevertheless, for the case of 4-fold coordinated boron, all the ELNES features are a consequence of transition to σ^* antibonding molecular orbital.

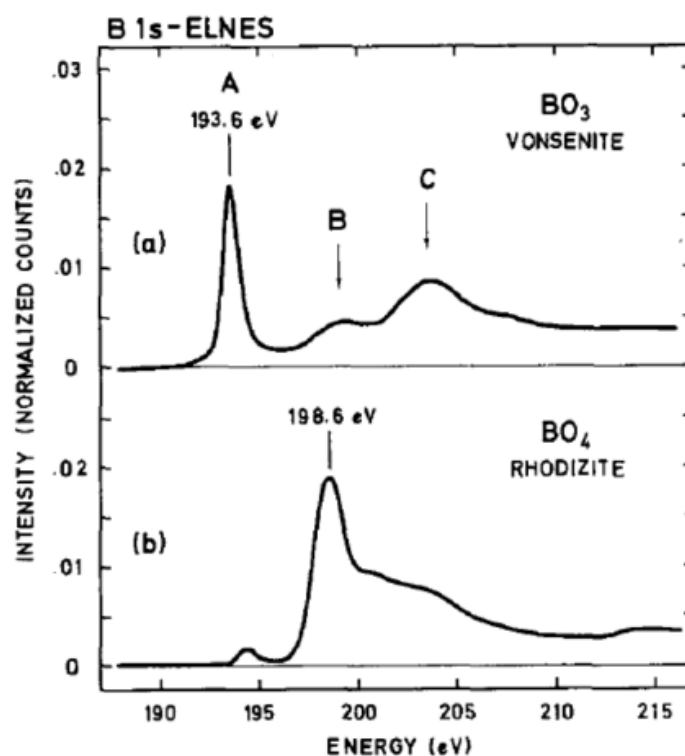


Figure 5.1. ELNES fingerprints of boron in a) vonsenite containing pure 3-fold coordinated B in BO_3 trigonal planar units and b) rhodizite containing pure 4-fold coordinated B in BO_4 tetrahedral units (reprinted from Ref.[159], copyright (1993), with permission from Elsevier).

In addition, because the change in the distribution of dopants might occur over very small distances along the interface of the two adjacent phase, characteristic ionization edge with high spatial resolution down to atomic level can be used to identify the presence of the rare earth dopants in the nanoscale throughout the microstructure.

As discussed earlier, the information provided by the ELNES features are the very useful if it is obtained at the nanoscale. The elemental mapping at the atomic level by using electron energy loss spectroscopy can be acquired by two approaches. First, energy filtered TEM (EFTEM) technique in which a region of the specimen is illuminated by the parallel beam of incident electrons followed by recording a set of filtered images using specific energy-selecting window. Second, spectrum imaging (SI) by using a focused electron beam in the STEM mode, rastering on the region of the interest on the specimen and recording a full EEL spectrum at each point [179, 180]. The former technique is not the subject of this study and thus, only STEM-EELS spectral imaging will be discussed. In spectrum imaging technique, a data cube (**Figure 5.2**) is generated which is indeed a 3D matrix made of single pixels scanned by the electron probe on the specimen and every

pixel is assigned to a point with (x, y, E) where x and y correspond to spatial information and the third dimension is a complete electron energy loss spectrum [179-181]. The most important advantage of the spectrum imaging technique is high spatial and energy resolution which makes it possible to map the ELNES features at the nanoscale in the microstructure.

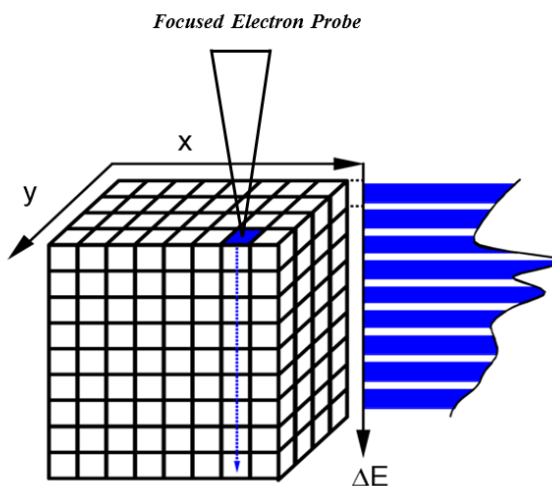


Figure 5.2. Creation of data cube in STEM-spectrum imaging mode.

In this chapter, we used spectrum imaging as a nanoscale characterization tool to map the ionization edge and the ELNES features of the dopant elements within the microstructural features produced during phase evolution of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ doped with 1 mol % Eu, 1 mol% Dy and 30 mol% B_2O_3 ($\text{S}_4\text{A}_7\text{ED30B}$). Because we are aiming to understand the effect of boron, and since ELNES fingerprint of an atom is very sensitive to changes in the crystal field, the EEL spectrum imaging is one of the most efficient ways to detect the structural perturbations of boron upon structural changes during phase evolution. Furthermore, despite energy dispersive X-ray spectroscopy, ELNES analysis is also a useful tool in the qualitative and quantitative detection of low weight elements ($Z < 4$) in a localized region as small as phase interfaces. Likewise, incorporation of rare earth dopants Eu and Dy into the crystal structure could also be analyzed with high spatial resolution.

Finally, in order to image the crystal structure and elucidating the position of dopants in the crystal lattice, we used the state of the art of atomic resolution STEM imaging by using a sub-angstrom probe in an aberration corrected microscope. The atomic

arrangements in the microstructure of the sintered specimens of S₄A₇ED30B were qualitatively investigated by HAADF, ADF and BF imaging in the STEM mode.

5.2 Experimental

In order to investigate the local bonding of the elements in the microstructure of strontium aluminate phosphors, the ceramic foil was prepared with a nominal composition of Sr₄Al₁₄O₂₅ co-doped with 1 mol% Eu, 1 mol% Dy, and 30 mol% B₂O₃ using a modified Pechini process as described in chapter 2. The powder produced was pressed into a pellet, sintered and reduced in a varigon environment at 1300 °C and a thin lamella was prepared by FIB milling as described in chapter 2. We then identified the local environment of boron and the distribution of rare earth dopants as well as Al and Sr cations between amorphous intergranular phase and the neighboring crystalline grains by analyzing B-K, Eu-M, Dy-M, Al-K and Sr-L ionization edges and the ELNES features through performing electron energy loss spectrum imaging on a localized region in the microstructure.

The spectrum images were recorded in a spherical aberration (Cs) - corrected scanning transition electron microscope (JEOL JEM-2010 F), equipped with a post-column energy filter operating at 200 kV beam energy with a prob diameter of 0.08 nm and a convergence semi angle (α) of 22 mrad. The entrance aperture of the EEL spectrometer was 5 mm and a camera length of 30 mm was used. This set up resulted in a collection semi-angle (β) of 83 mrad as is schematically shown in **Figure 5.3**.

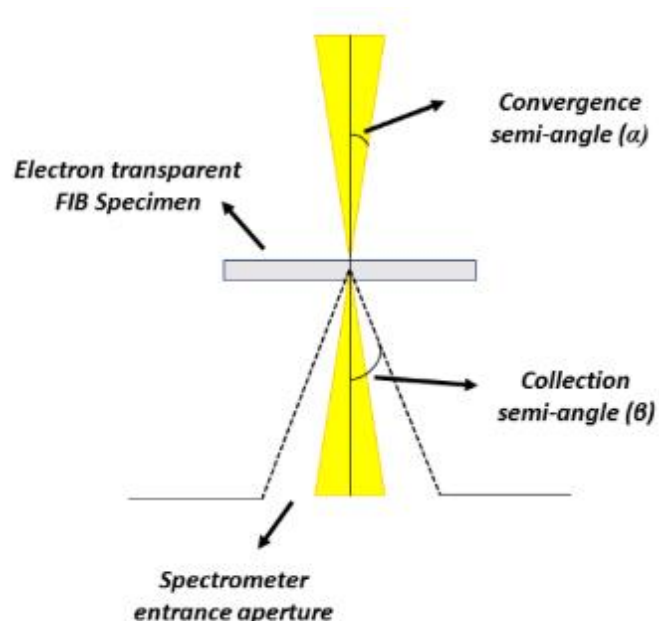


Figure 5.3. Convergence semi-angle (α) and collection semi-angle (β) in the STEM mode.

To acquire the spectrum image, a dispersion of 0.1 eV/channel was used. The FWHM of the zero-loss peak, indicative of the energy resolution of the spectrum was *ca.* 0.7 eV. The final spectrum image was recorded under the dual EELS mode where the exposure time and the energy for the low-loss spectra were set to investigate the B-K edge ELNES features while the high-loss spectra were adjusted to examine the Eu-M, Dy-M, Al-K and Sr-L ionization edges. These parameters are summarized in **Table 5.1**. The scan area was set to 11×11 pixels with a step size of 10 nm and acquisition time of 1 second per pixel.

Table 5.1. Spectrum imaging parameters used for investigation of ionization edges and the ELNES fingerprints of the elements.

Energy Loss Range	Exposure Time (s)	Energy (eV)	Ionization Edge
Low loss	0.02	50	B-K, Al-L
High loss	10	1080	Eu-M, Dy-M, Al-K, Sr-M

In addition, STEM-EDX analysis was also performed as a complement to the EELS data. The elemental distribution of Al, Sr, Eu and Dy were mapped in the microstructure by

using a condenser lens aperture size of 50 μm , camera length of 80 mm and time constant of T4 in the STEM mode.

In order to image the atomic columns in the crystal structure and elucidating the location of rare earth dopants in the crystalline grains of strontium aluminate phosphors evolved during the sintering of Pechini processed S4A7EDB, we performed STEM atomic resolution imaging on the ceramic lamella prepared by FIB milling. The crystalline grain of the interest was initially tilted to a zone axis of the grain and selected area electron diffraction pattern of was recorded in the TEM mode. Using a Cs-aberration corrected probe microscope (JEM-ARM 200CF, JEOL Ltd.) operating at 200 keV which provides a resolution in the order of 1 Å in the image mode, we then recorded the HAADF, ADF and BF images of the atomic arrangements in the crystal lattice. The zone axis was then indexed to identify the projection by which the atomic columns were imaged. By comparing the experimental images with the visualized supper lattice obtained from VESTA software as well as intensity profile analysis of the atomic columns, qualitative interpretation of the HAADF images were obtained.

5.3 Results

5.3.1 Specimen Overview

Figure 5.4 shows the HAADF image of the FIB lamella prepared from strontium aluminate phosphor (S4A7EDB) and the corresponding selected area electron diffraction patterns of the microstructural features present in the FIB specimen. From SAED patterns, ROI#1 in the specimen is a single crystalline grain and ROI#2 is an amorphous intergranular phase stuck between the crystalline grains. Therefore, this region is suitable for investigation of electronic structure of B as well as localized distribution of rare earth element by EELS analysis.

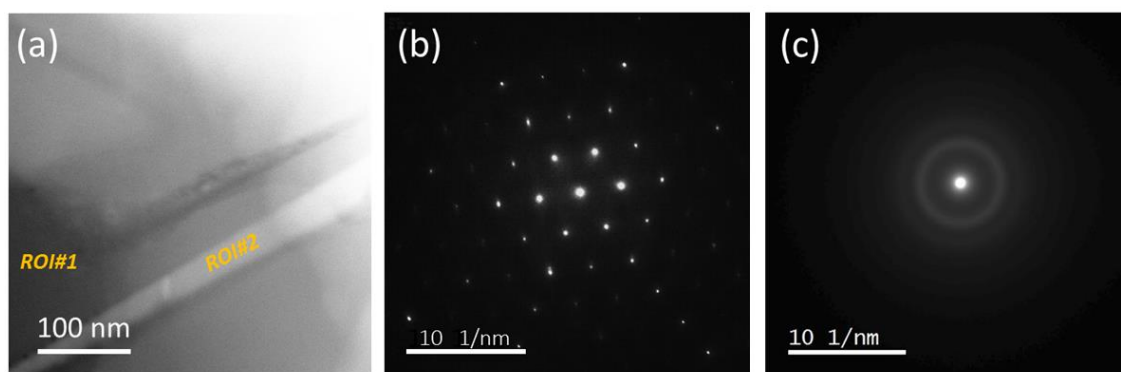


Figure 5.4. Overview of the FIB specimen prepared from sintered S4A7EDB pellet a) HAADF image of the microstructure and selected area electron diffraction pattern analysis of b) crystalline grain (ROI#1) and c) amorphous IGP (ROI#2).

We used STEM-EDX analysis of the microstructure as a complementary technique for EEL spectrum imaging (SI). **Figure 5.5** shows the elemental distribution map of the microstructure. It can be deduced that the intergranular phase is depleted from Al while it is clearly rich in Sr and Dy. For Eu, the elemental map does not show a clear correlation to the intergranular phase, indication of a more uniform distribution between the crystals and the glassy phase. The quantification (without using standard materials) obtained from the crystals surrounding the amorphous region (specified by a circle in Figure 5.5 – a) shows that the composition of the neighboring grains is of SA₆ phase.

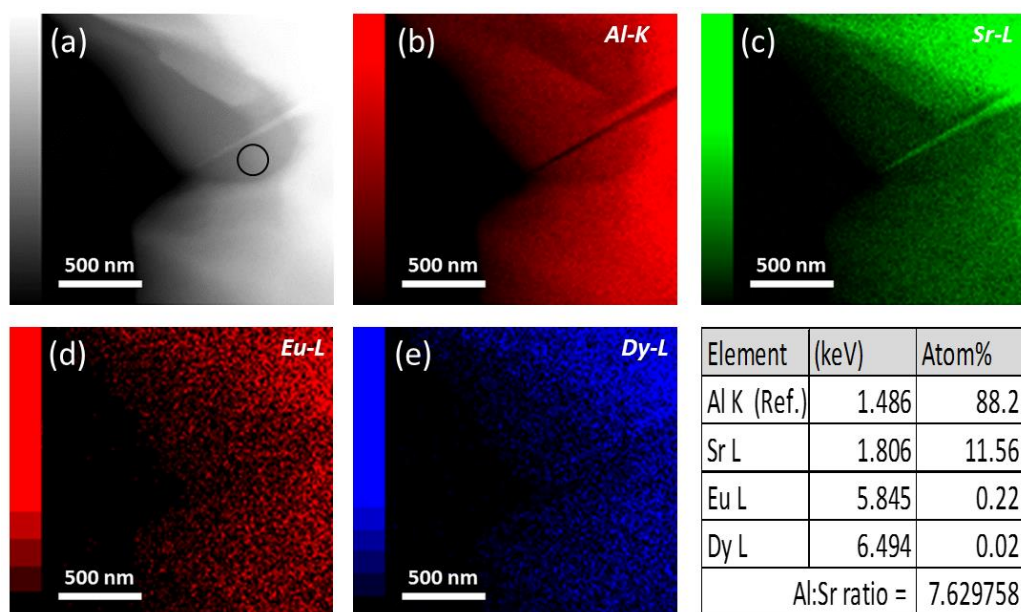


Figure 5.5. Elemental distribution maps in the region of interest. a) HAADF image and distribution of b) Al c) Sr d) Eu and e) Dy. The table shows the quantification of the elements in terms of atomic% obtained from the region specified by the black circle on the crystalline grain in a).

In order to make sure that the effect of plural scattering on the ELNES features are negligible, it is important to acquire the final spectrum image from a substantially thin region of the FIB specimen. The thickness of the region of interest was analyzed by using the ratio of the plasmon peak height to the zero-loss peak [182] as shown in **Figure 5.6**. In a typical thickness map spectrum image (**Figure 5.6-b**), the z-axis in the data cube is representative for the intensity of the sample. Thus, the uniformity in contrast in the thickness map image implies that the thickness of the specimen is almost uniform in the crystalline grains while it is smaller in the IGP phase. The mean free pass (MFP) measured from a low-loss spectrum from a representative pixel (**Figure 5.6-b**) was 0.69 which indicates that the thickness of the specimen is good enough for performing the ultimate spectrum imaging analysis.

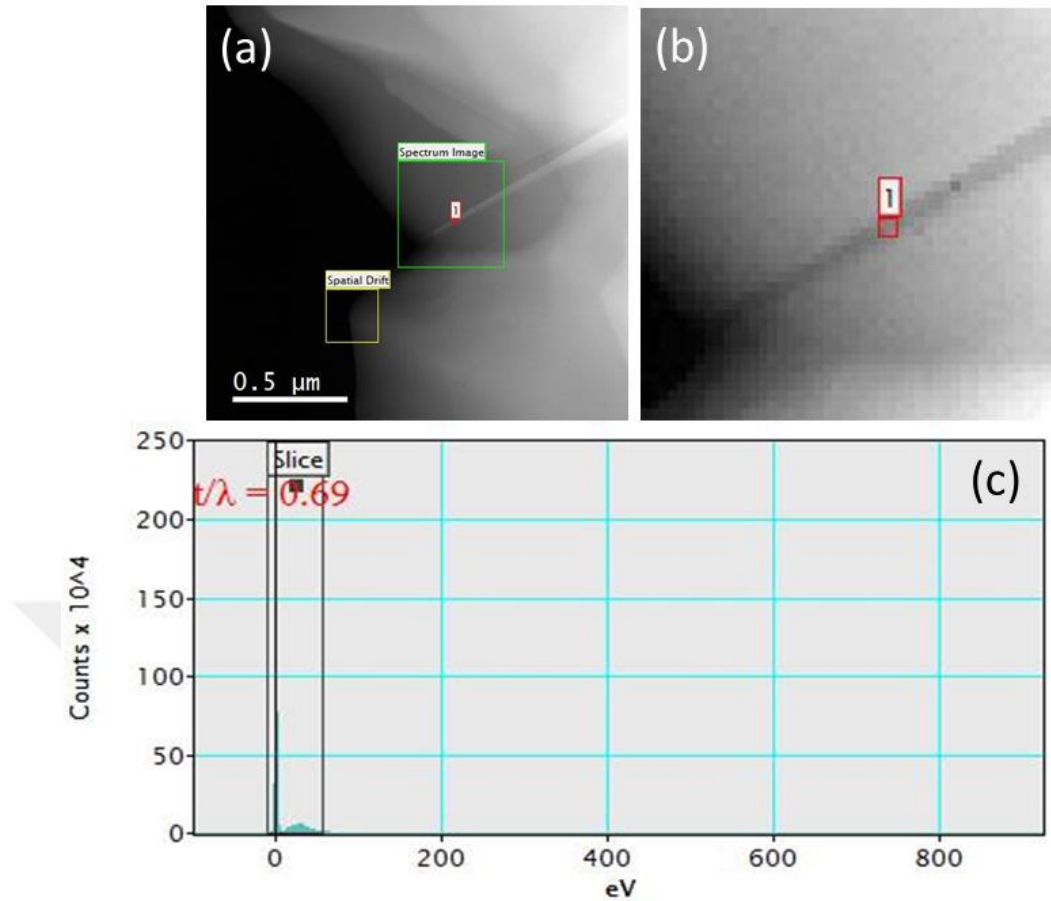


Figure 5.6. Investigation of the thickness of the specimen for spectrum imaging a) ADF image of the FIB sample with the scanned region b) thickness map and c) the low-loss EELS spectrum obtained from the integration of several pixels denoted by “1” in b.

5.3.2 Spectrum Image of The Microstructure

The spectral images recorded from S4A7EDB lamella is shown by the green square in **Figure 5.7-a**. The low loss SI (Figure 5.7-b) is used for investigation of B-K edge ELNES fingerprints while the high loss SI (Figure 5.7-c) is used for the analysis of the local environment and electronic structure of Al-K, Sr-L and rare earth dopants M-edge. In order to compare the ELNES features of the elements in different microstructure *e.g.* local bonding in various crystal fields, integrated pixels #1 and #2 in the amorphous phase and the crystalline grains were chosen. SAED patterns (Figure 5.7 d-e) are provided to emphasize that the integrated pixels #1 and that of #2 are corresponding to amorphous phase and crystalline grains, respectively.

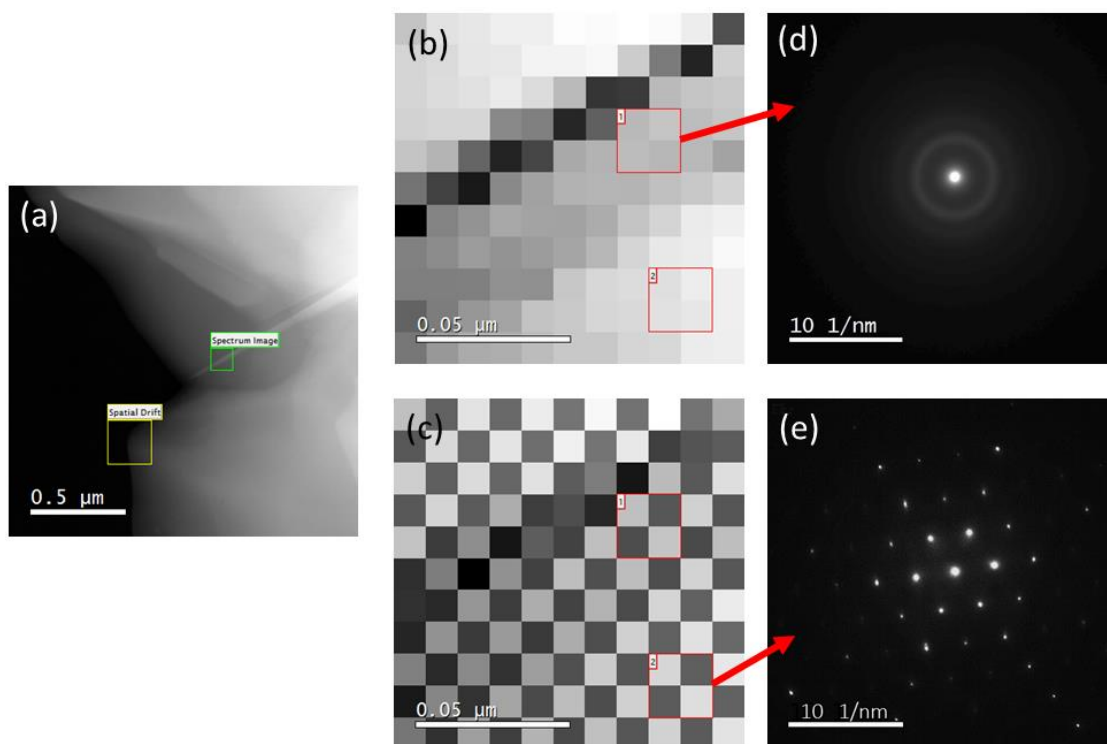


Figure 5.7. Spectrum image analysis of the microstructure a) The survey image b) raw low-loss SI c) raw high-loss SI d) SAED pattern corresponding to integrated pixels #1 from IGP e) SAED pattern corresponding to integrated pixels from crystal.

5.3.2.1 B-K Ionization Edge

Figure 5.8 shows the background subtraction from the EEL spectrum obtained from the integration of four pixels on the low-loss spectrum image. Due to multiple inelastic scattering events of the incident electrons, the ionization edges are superimposed on a rapidly decreasing background. To examine the B-K ionization edge, the background was determined and removed using a power law model [114, 179]. For removing the background, we used a double background window fitting. A first background window ($\Delta E = 5$ eV) was located just before the B-K ionization edge at 188 eV. The second window ($\Delta E = 7.5$ eV) was placed before the next ionization edge in a way that the deconvoluted signal (shown in green) stays positive through the entire spectrum. The ionization edges at ca. 188 eV and 530 eV are the B-K and O-K edges, respectively.

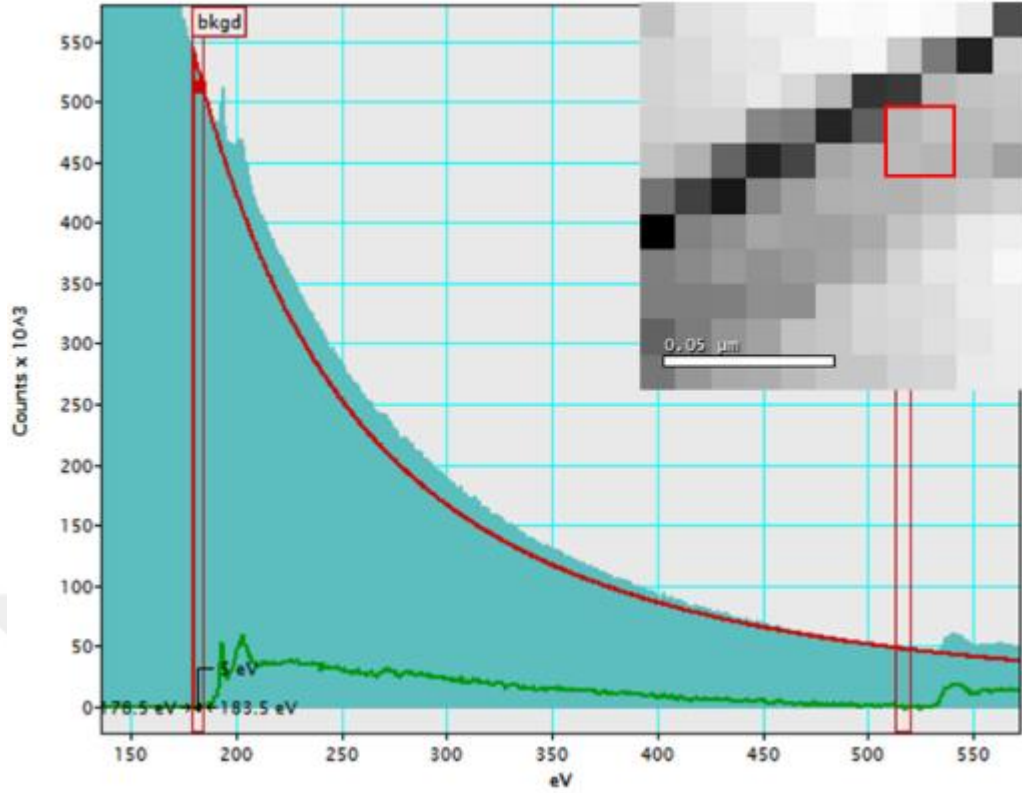


Figure 5.8. Background subtraction procedure from the low-loss EEL spectrum for B-K ionization edge. The inset image is the raw low loss spectrum image with the integrated pixels corresponding to the spectrum.

After background removal, we investigated the nature of boron incorporation into the microstructure by mapping the B-K ELNES fingerprint between the neighboring crystals and intergranular glassy phase. The ELNES spectra of B-K obtained from intergranular phase (ROI#1 on the SI image) is shown in **Figure 5.9-b**. It can be observed that, the ELNES fingerprint demonstrated a sharp pre-peak at *ca.* 192 eV attributed to $\pi \rightarrow \pi^*$ transition which followed by a broader peak at 203 eV corresponding to $\sigma \rightarrow \sigma^*$ electronic state. Thus, by comparing the ELNES fingerprint from the reference materials [158, 159], boron is present in the IGP in a trigonal planar BO_3 coordination. Because the pre-peak ELNES feature in figure 5.9-a is characteristic of 3-fold coordinated boron ($^{[3]}\text{B}$), the slice window in the energy range of 190 – 195 eV ($\Delta E = 5$ eV) in figure 5.9-a was chosen to map the $^{[3]}\text{B}$ over the entire low loss spectrum image. **Figure 5.9-b** shows the $^{[3]}\text{B}$ -contrast throughout the spectrum image with meaningful and interpretable contrast. It was observed that boron is 3-fold coordinated in the IGP while the intensity level of the pixels in the crystalline grains low which is indicative of no $^{[3]}\text{B}$ in the crystals.

Figure 5.9-c shows the B-K edge ELNES features obtained from integrated pixels in the crystal (ROI#2). When the ELNES signal was compared to the reference materials, it was found that boron is mainly tetrahedrally incorporated in the crystals in the form of BO_4 and the ELNES features is characteristic of only $\sigma \rightarrow \sigma^*$ transition [158, 159]. In order to map the four-fold coordinated boron (^{14}B) over the entire spectrum image, the slice window in the range of 187.5 – 247.7 eV ($\Delta E = 62$ eV) was selected (figure 5.9-c). The localized distribution of ^{14}B between the crystalline grains and IGP is shown in **Figure 5.9-d**. Since the contrast in figure 5.9-d indicates the intensity of the slice window in figure 5.9-c, the ^{14}B contrast in the spectrum image revealed that boron enters the crystals in the tetragonal sites.

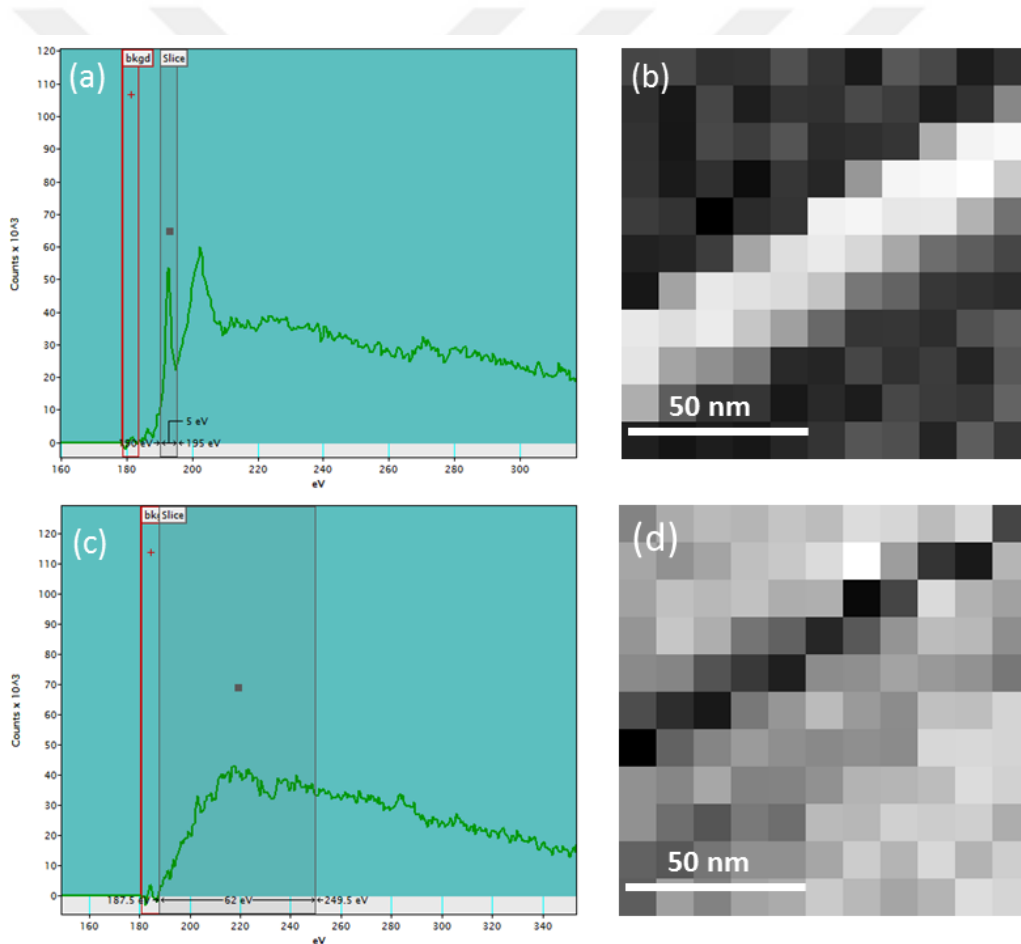


Figure 5.9. Analysis of B-K edge ELNES fingerprint in the low-loss spectrum image.

Therefore, although elemental distribution map of boron in the microstructure by STEM-EDX is not conclusive due to limitation of detection of light elements, the EEL spectrum

imaging technique provided useful information not only about the distribution of B, but also the local environment of the boron in the strontium aluminate phosphor was also elucidated.

5.3.2.2 Eu-M Ionization Edge

To investigate the distribution of Eu, we used the Eu-M edge which is typically characterized with a sharp ionization edge located at *ca.* 1132 eV followed by a shallower peak at 1160 eV. The raw high loss spectrum image was thus analyzed to elucidate the distribution of Eu. **Figure 5.10** shows the background subtraction in the core loss spectrum obtained from the integration of four pixels as shown in the inset image. The double peak in the range of 1120 – 1170 eV in the background subtracted signal (green curve) is attributed to Eu-M ionization edge. The small ionization edge located at 1280 eV is related to the ionization peak of Dy-M edge while the rapid increase in the intensity located between 1500-1600 eV corresponds to Al-K ionization edge which will be discussed later.

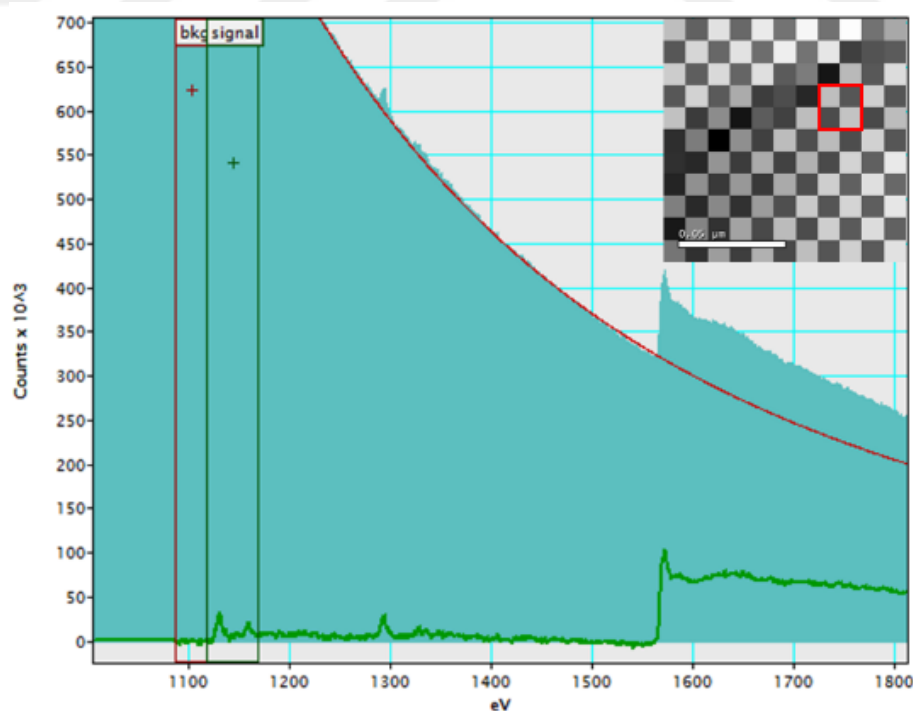


Figure 5.10. Background subtraction procedure from the high-loss EEL spectrum for Eu-M ionization edge. The inset image is the raw high-loss spectrum image with the integrated pixels corresponding to the spectrum.

Figure 5.11 compares the intensity of Eu-M edge between pixels which are representative for intergranular phase (ROI#1) and that of crystal (ROI#2) (Figure 5.11-a). For both set of pixels on the raw high loss spectrum image, the background window ($\Delta E=14$ eV) for signal deconvolution was identical and the ionization edge was compared over a similar slice window ($\Delta E=48$ eV) (Figure 5.11 b-c) to allow a reasonable comparison between the intensity of the ionization peaks. Because the edge intensity is directly and quantitatively related to the amount of the element present [113], it was observed that Eu-M edge is more intense in the IGP which implies that, the concentration of Eu is higher in the intergranular glassy phase with respect to crystals.

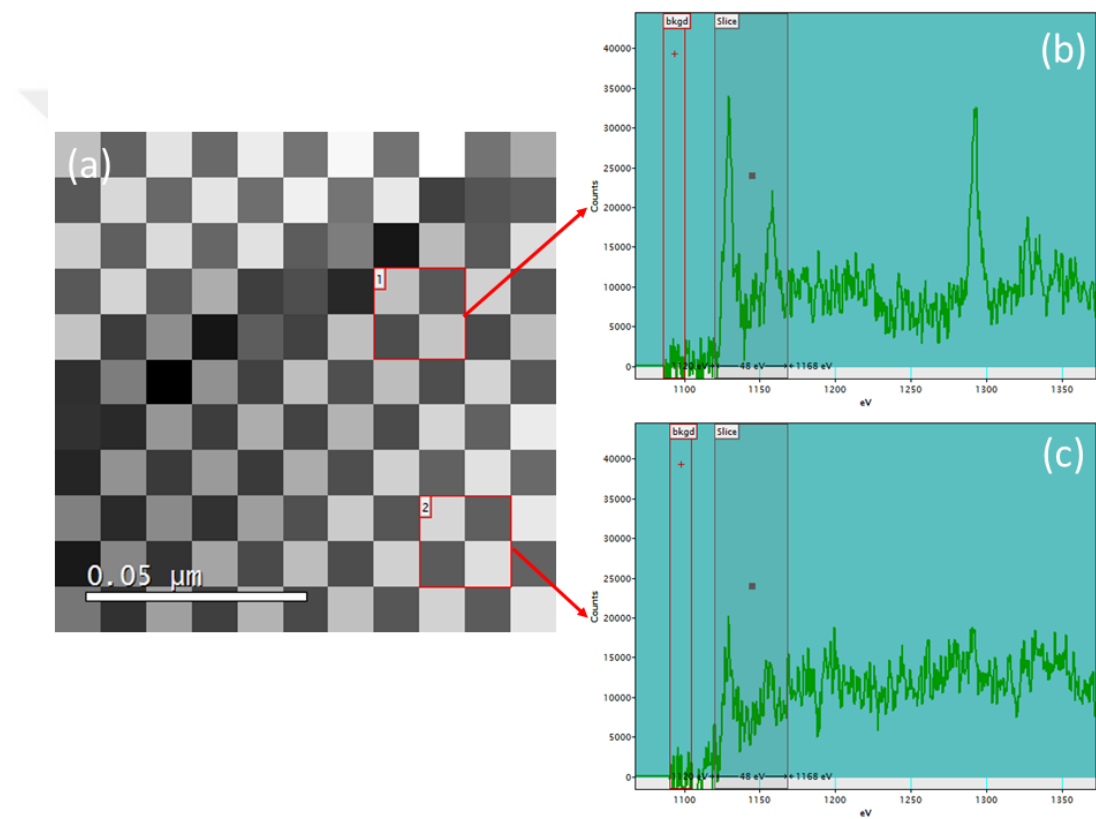


Figure 5.11. Comparison of Eu-M edge in intergranular phase and crystalline grain a) Raw high-loss spectrum image with integrated pixels #1 corresponding to IGP and integrated pixels#2 corresponding to crystalline grain and representative Eu-M ionization edge in b) intergranular phase and c) crystalline grain. The ionization peak and the ELNES features are highlighted by the slice window in b and c.

In order to map the Eu-M edge through the entire high loss spectrum image in the scanned area, the slice window with the energy loss range of 1120 – 1168 eV (**Figure 5.12-a**) was selected in high loss spectrum. The intensity of pixels in the raw high loss SI (**Figure 5.12-b**) was thus modified to interpretable Eu-M edge contrast (**Figure 5.12-c**). The

Intensity level of the pixels in figure 5.12-c indicated that the distribution of Eu-M was more random throughout the microstructure albeit the concentration of Eu seemed to be higher in the IGP strip compared to the adjacent crystals. The results of Eu-M ELNES analysis of the high-loss spectrum image was consistent with the STEM-EDX elemental distribution map of Eu (Figure 5.5 – d).

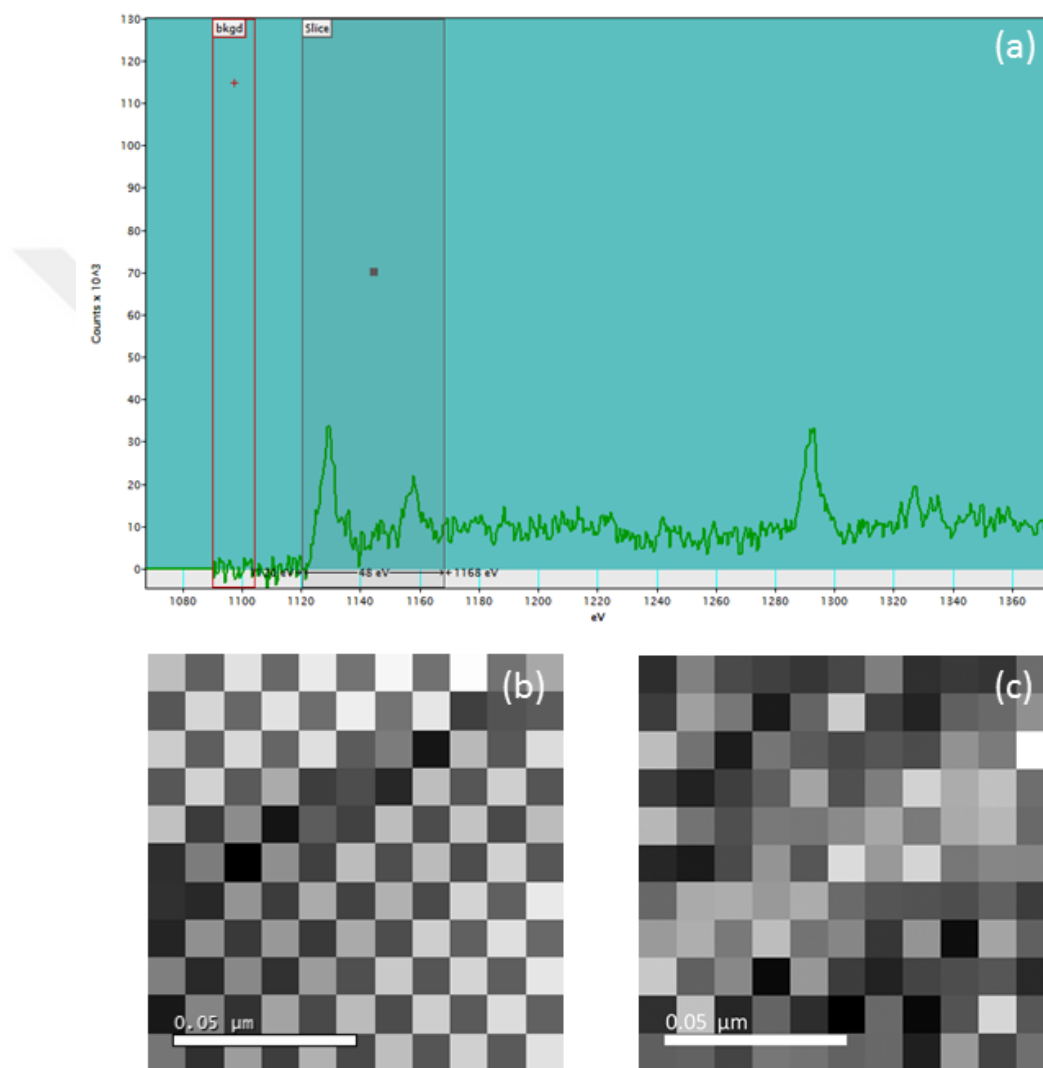


Figure 5.12. Analysis of Eu-M edge ELNES fingerprint in the high-loss spectrum image.

5.3.2.3 Dy-M Ionization Edge

To investigate the distribution of Dy by spectrum imaging technique, the Dy-M edge which is ideally characterized with a sharp ionization edge at *ca.* 1295 eV followed by a shallower peak at 1332 eV was investigated using the raw high loss spectrum image.

Figure 5.13 shows the background subtraction in the core loss spectrum obtained from the integration of four pixels shown in the inset image. The ionization edge and ELNES fingerprints in the range of 1280 – 1340 eV in the background subtracted signal (green curve) is attributed to Dy-M ionization edge in this specimen.

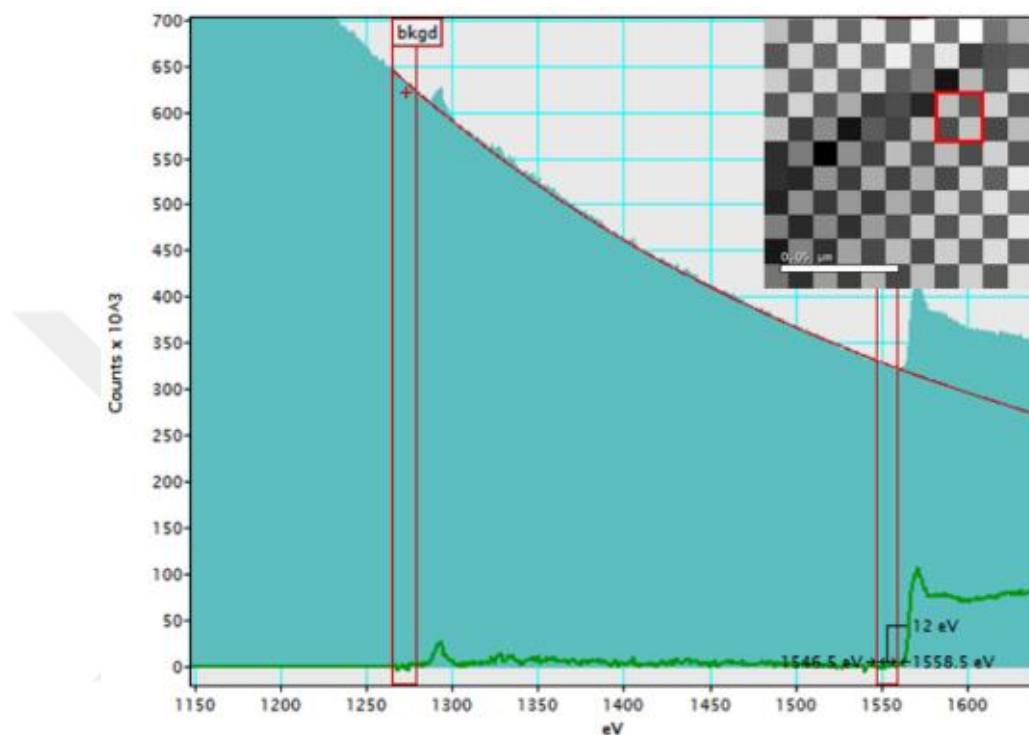


Figure 5.13. Background subtraction procedure from the high-loss EEL spectrum for Dy-M ionization edge. The inset image is the raw high-loss spectrum image with the integrated pixels corresponding to the spectrum.

The intensity of Dy-M edge obtained from pixels in the intergranular phase (ROI#1) against that of crystal (ROI#2) is shown in **Figure 5.14**. For both set of pixels on the raw high loss spectrum image, the background window ($\Delta E=14$ eV) for signal deconvolution was identical and the ionization edge was compared over a similar slice window ($\Delta E=58$ eV) to allow a reasonable comparison between the intensity of the ionization peaks in different microstructure. It was observed that the intensity of Dy-M ionization edge is rather high in the intergranular phase while in the crystals, it is rarely detectable (Figure 5.14 b-c).

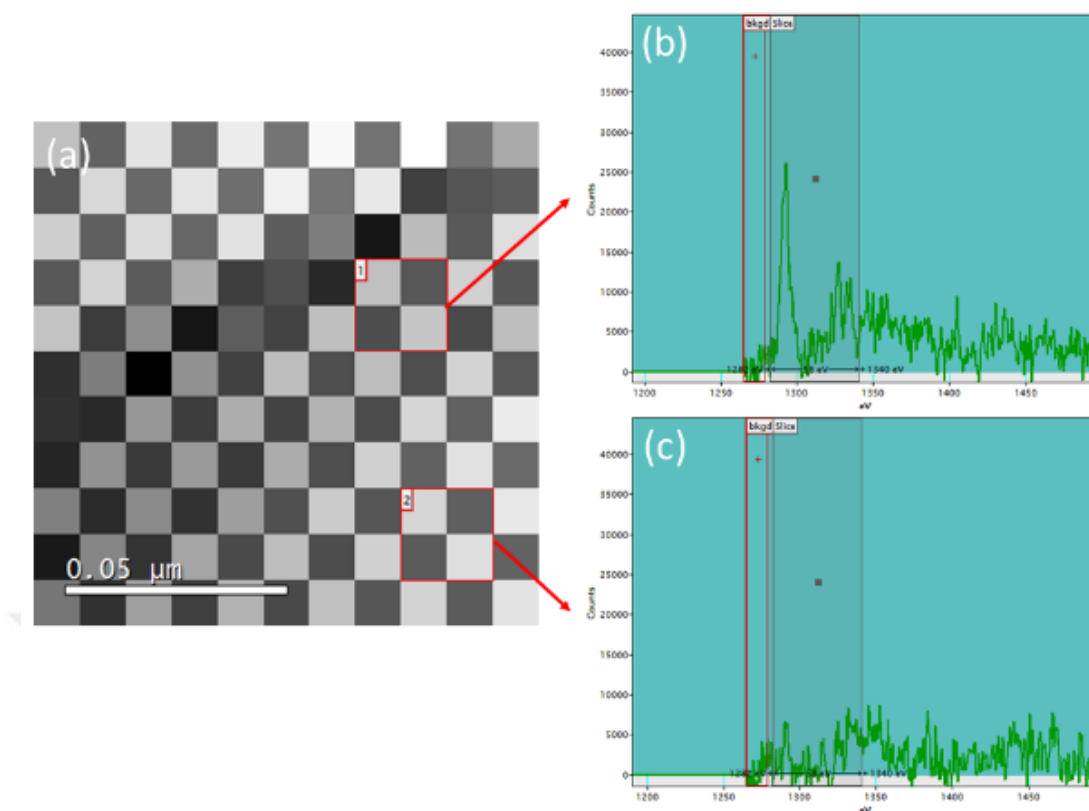


Figure 5.14. Comparison of Dy-M edge in intergranular phase and crystalline grain a) Raw high-loss spectrum image with integrated pixels #1 corresponding to IGP and integrated pixels#2 corresponding to crystalline grain and representative Dy-M ionization edge in b) intergranular phase and c) crystalline grain. The ionization peak and the ELNES features are highlighted by the slice window in b and c.

We also mapped the Dy-M edge over the high-loss spectrum image by selecting a slice window with energy loss range of 1282-1340 eV (**Figure 5.15-a**). The intensity of the pixels in the raw high-loss SI (**Figure 5.15-b**) was filtered by the energy loss corresponding to Dy-M ionization edge and the distribution of Dy-M edge in the scanned area was obtained (**Figure 5.12-c**). This result was consistent with the elemental map distribution of Dy cations obtained STEM-EDX analysis (Figure 5.5-e).

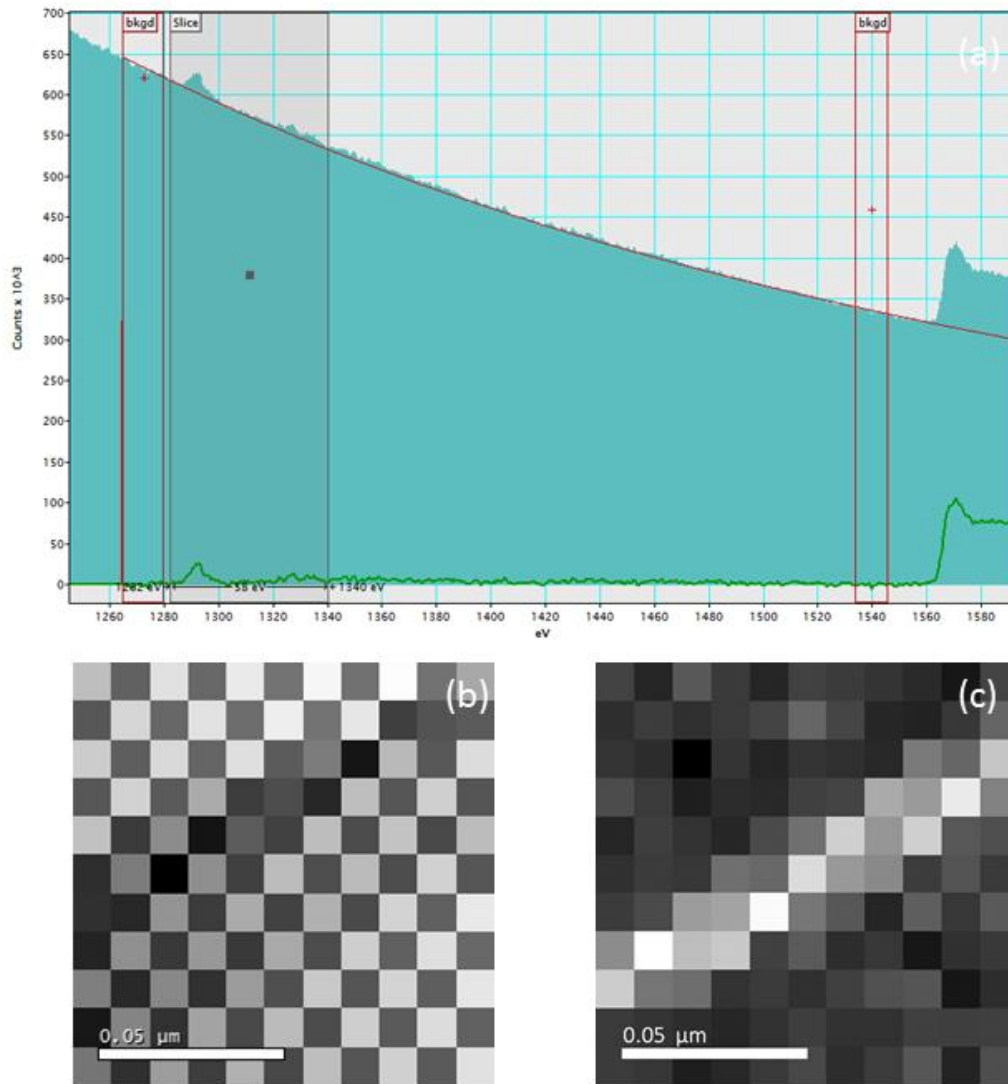


Figure 5.15. Analysis of Dy-M edge ELNES fingerprint in high-loss spectrum image.

5.3.2.4 Al-K Ionization Edge

After investigation of Eu-M and Dy-M edges, the next ionization edge in the high-loss spectrum is Al-K edge. Although it is possible to look at the Al-L edge located at *ca.* 73 eV from the low-loss spectrum, we focus on the Al-K ELNES features in the high-loss spectrum. **Figure 5.16** shows the background subtraction for investigation of Al-K ELNES in the microstructure of strontium aluminate FIB specimen. The sharp rise in the energy loss intensity at slightly above 1550 eV followed by small fluctuations in intensity up to 1650 eV is related to Al-K edge. To evaluate the local bonding of Al in the spectrum image, the background of the spectrum was fitted by a double background subtraction where the first window ($\Delta E = 10$ eV) was placed just before the Al ionization edge and

the second background window ($\Delta E = 12$ eV) was located just before the next ionization event. The ionization edge with a peak located at ca. 1950 eV and the ELNES features extended above 2000 eV is attributed to Sr-L ionization edge which will be discussed in the next section.

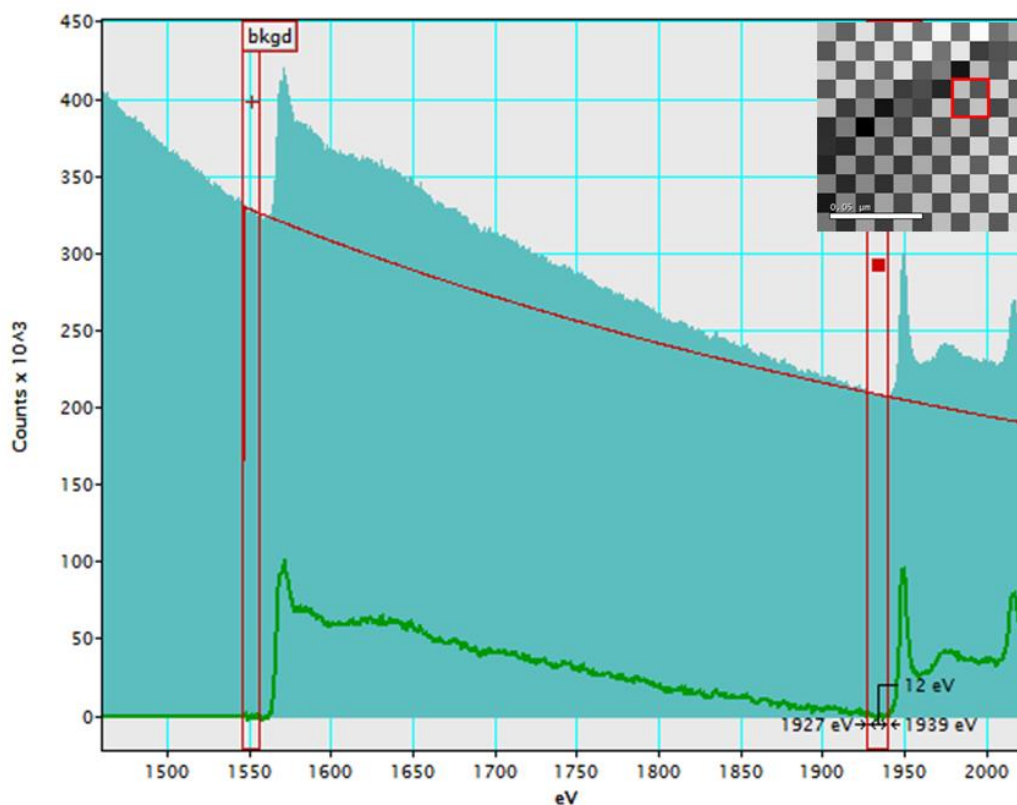


Figure 5.16. Background subtraction procedure from the high-loss EEL spectrum for Al-K ionization edge. The inset image is the raw high-loss spectrum image with the integrated pixels corresponding to the spectrum.

When the Al-K edge obtained from intergranular glassy phase *e.g.* pixels in ROI#1 was compared to that of crystal in pixels in ROI#2 (**Figure 5.17-a**), it was revealed that, the intensity of Al-K edge is substantially lower in the IGP which means that the amount of Al cations in the glassy phase between the two grains is small. In addition, the shape of ELNES features just above the edge is completely different which implies that, the electron density distribution of the Al core shell electron, i.e. the crystal field, is different in the glassy phase and the SA₆ crystal. The ELNES fingerprint of Al-K in IGP phase (**Figure 5.17-b**) is similar to four-fold coordinated Al as reported by Cabaret *et al.* [183] and Henderson *et al.* [184] by looking at X-ray absorption near-edge structure (XANES)

of berlinite and natrolite, the minerals containing pure Al tetrahedral sites. Because in the crystal structure of SA₆ Al cation is present in different coordinations including ^[4]Al, ^[5]Al and ^[6]Al, the ELNES features of the Al-K edge in the SA₆ crystal (**Figure 5.17-c**) resembles a superimposition of 4-fold and 6-fold and possibly 5-fold Al cations [183, 184].

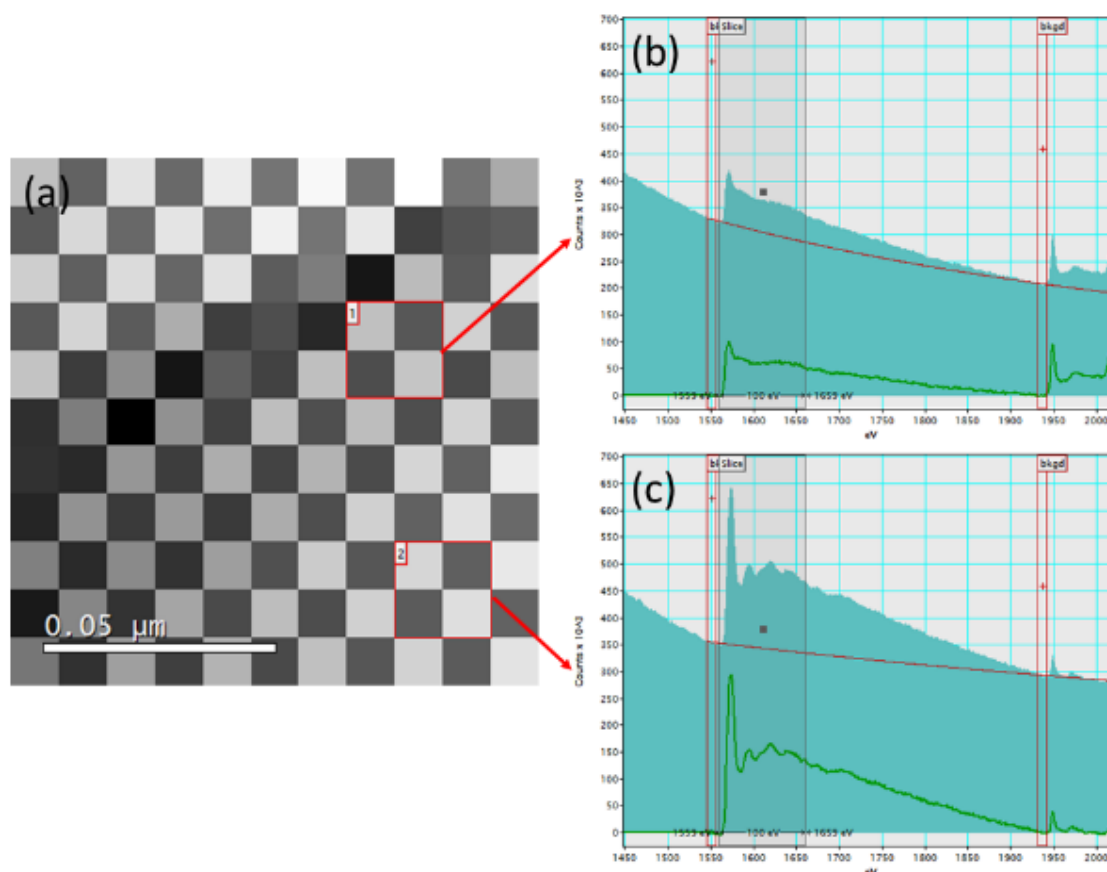


Figure 5.17. Comparison of Al-K edge in intergranular phase and crystalline grain a) Raw high-loss spectrum image with integrated pixels #1 corresponding to IGP and integrated pixels#2 corresponding to crystalline grain and representative Al-K ionization edge in b) intergranular phase and c) crystalline grain. The ionization peak and the ELNES features are highlighted by the slice window in b and c.

Figure 5.18 shows the raw high-loss spectrum image and the Al-K edge ELNES map over the entire SI. To map the Al-K ELNES fingerprint, a slice window with an energy loss range of 1559 – 1569 eV ($\Delta E = 100$ eV) was selected. A clear correlation was observed between the presence of Al-K ELNES features in the crystalline SA₆ grains while the intensity of the pixels related to the IGP region is dark, indicative of low concentration of Al cations in the amorphous phase. Moreover, the alternate bright and dark pixels in the two sides of the amorphous strip clearly reflected the crystalline nature

of the grains and is most likely due to Al polyhedral units repeating on a long – range order in the crystals. The results of Al-K ELNES analysis of the high-loss spectrum image was consistent with the STEM-EDX elemental distribution map of Al (Figure 5.5 – b).

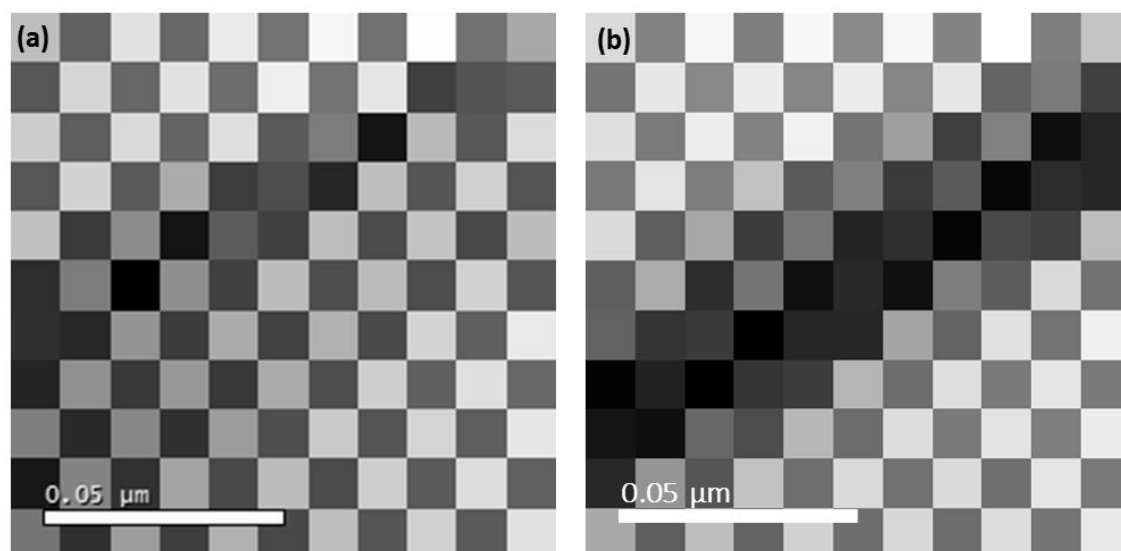


Figure 5.18. Analysis of Al-K edge ELNES fingerprint in high-loss spectrum image.

5.3.2.5 Sr-L Ionization Edge

Figure 5.19 shows the analysis of Sr-L edge and its ELNES features in the high-loss spectrum image. The intensity of Sr-L edge obtained from ROI#1 is more pronounced relative to that of ROI#2 when the background was removed under identical conditions (Figure 5.19 a-b). The map of Sr-L edge ELNES features constructed by a slice window in the range of 1940 – 2024 eV (Figure 5.19 d) demonstrated that the amorphous intergranular phase is also rich in Sr as well as B, Eu and Dy. The results of Sr-L ELNES analysis of the high-loss spectrum image was consistent with the STEM-EDX elemental distribution map of Sr (Figure 5.5 – c).

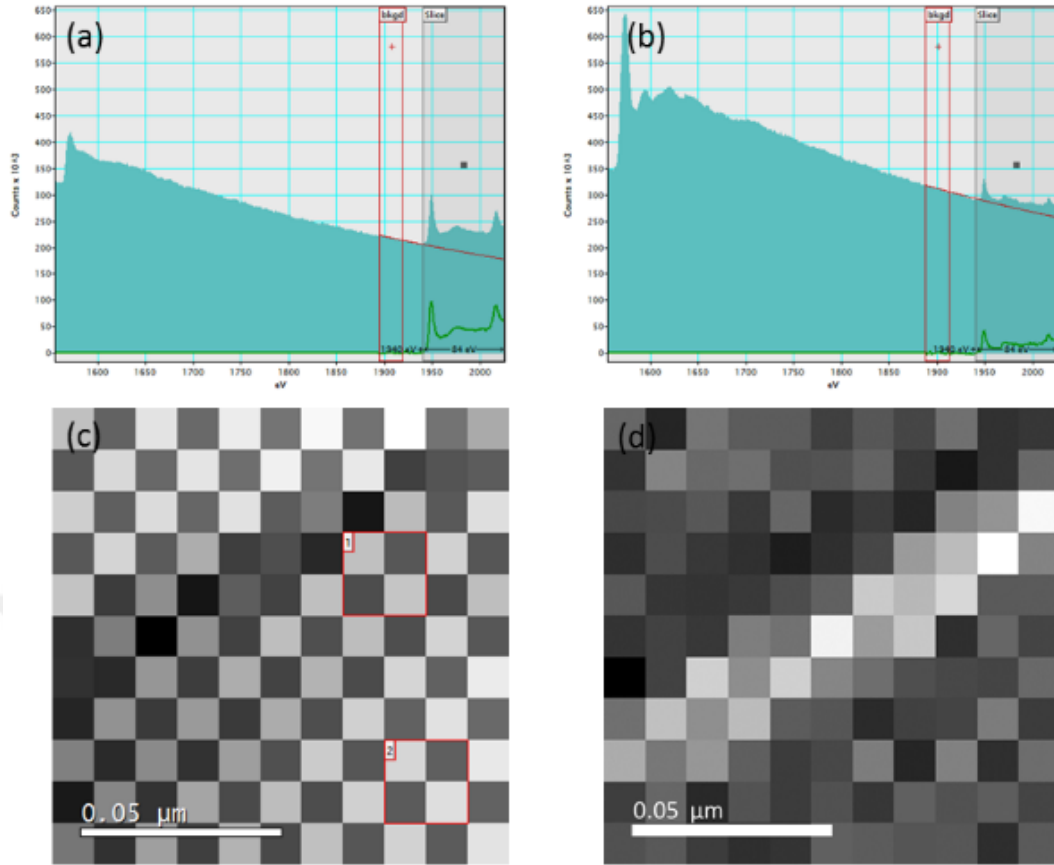


Figure 5.19. Analysis of S-L edge ELNES fingerprint in high-loss spectrum image.

5.3.2.6 Visualizing Variation in Elemental Distribution

In order to investigate the correlation between the distribution of cations in the microstructure by using electron energy loss spectrum imaging technique, we constructed RGB image from the combination of B-K, Eu-M, Dy-M, Al-K and Sr-L ELNES maps as discussed in the previous sections. **Figure 5.20** shows the RGB spectrum image constructed from dopants where B-K, Dy-M and Eu-M edges were assigned to red, green and blue colors, respectively.

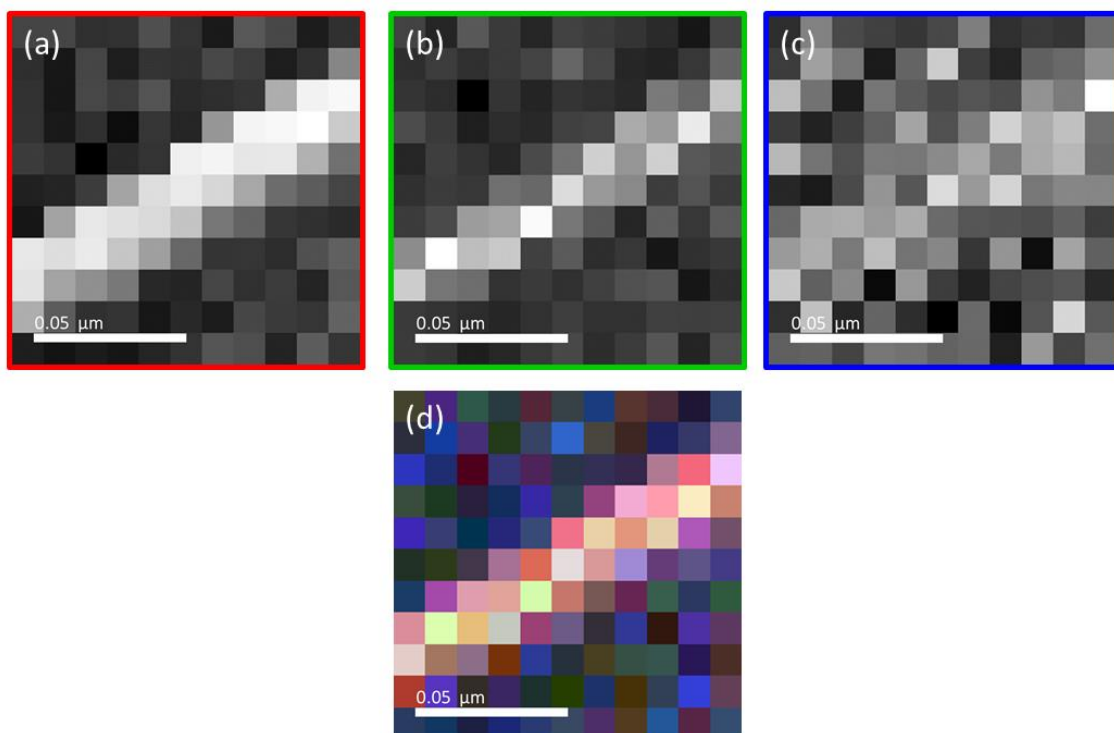


Figure 5.20. RGB construction of spectrum image with a) Red assigned to B-K b) Green assigned to Dy-M c) Blue assigned to Eu-M and d) the RGB image.

Figure 5.21 shows the RGB correlation between the Al^{+3} and rare earth dopants where Al-K, Dy-M and Eu-M edges were assigned to red, green and blue colors, respectively. From the RGB image, it was observed that, blue-greenish pixels resulting from the overlap between green channels originating from Dy-M and blue channels representative for Eu-M are concentrated in the amorphous phase between the two crystalline grains. In addition, there are some violet pixels as a result of combination of red channels from Al-K edge and blue from Eu-M edge) distributed in the SA_6 crystals, indication of incorporation of Eu^{2+} cations between the Al polyhedral units.

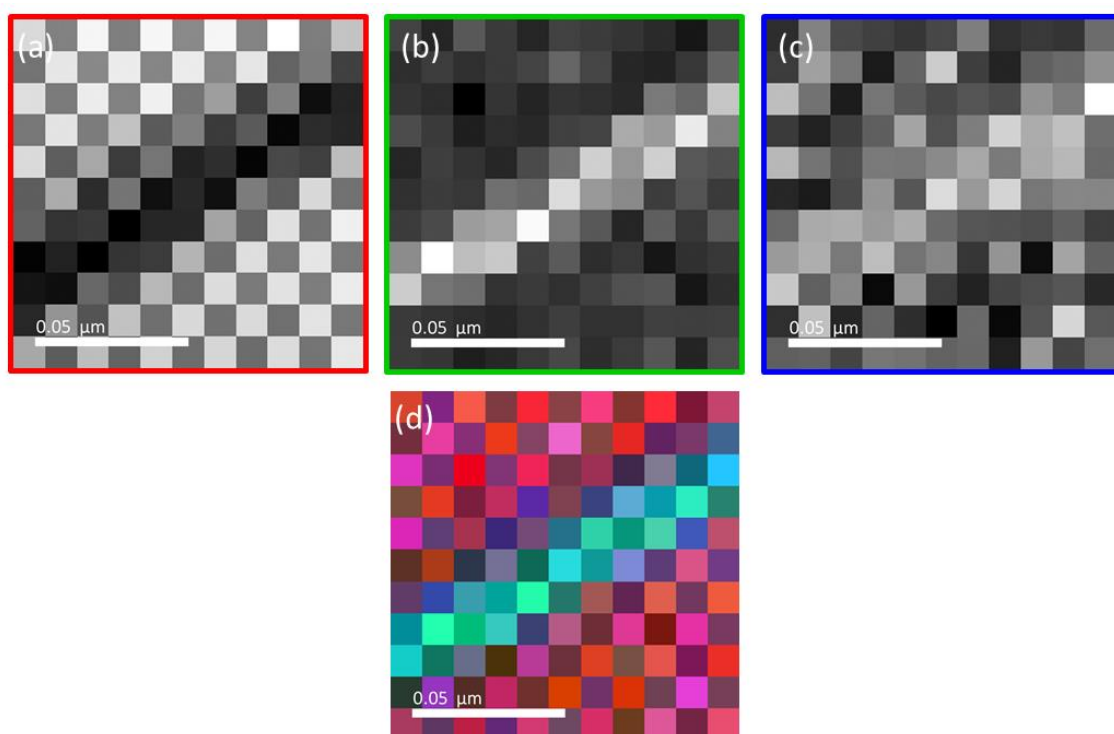


Figure 5.21. RGB construction of spectrum image with a) Red assigned to Al-K b) Green assigned to Dy-M c) Blue assigned to Eu-M and d) the RGB image.

Figure 5.22 shows the RGB correlation between the strontium aluminate matrix components *e.g.* Al^{+3} , Sr^{2+} and B^{3+} dopants where B-K, Al-K and Sr-L ionization edges were assigned to red, green and blue colors, respectively.

In the RGB image, the combination of B-K and Sr-L edges creates pinkish pixels at the amorphous intergranular pocket and no contribution from green channel was observed. This suggests that the intergranular phase is in fact a strontium borate phase. On the contrary, the grains are highly dominated by green pixels with a few pixels in blue-greenish hue. The presence of blue-greenish pixels distributed in the green regions is possibly indicative of Sr polyhedral units between the Al sites in the structure of SA_6 grains.

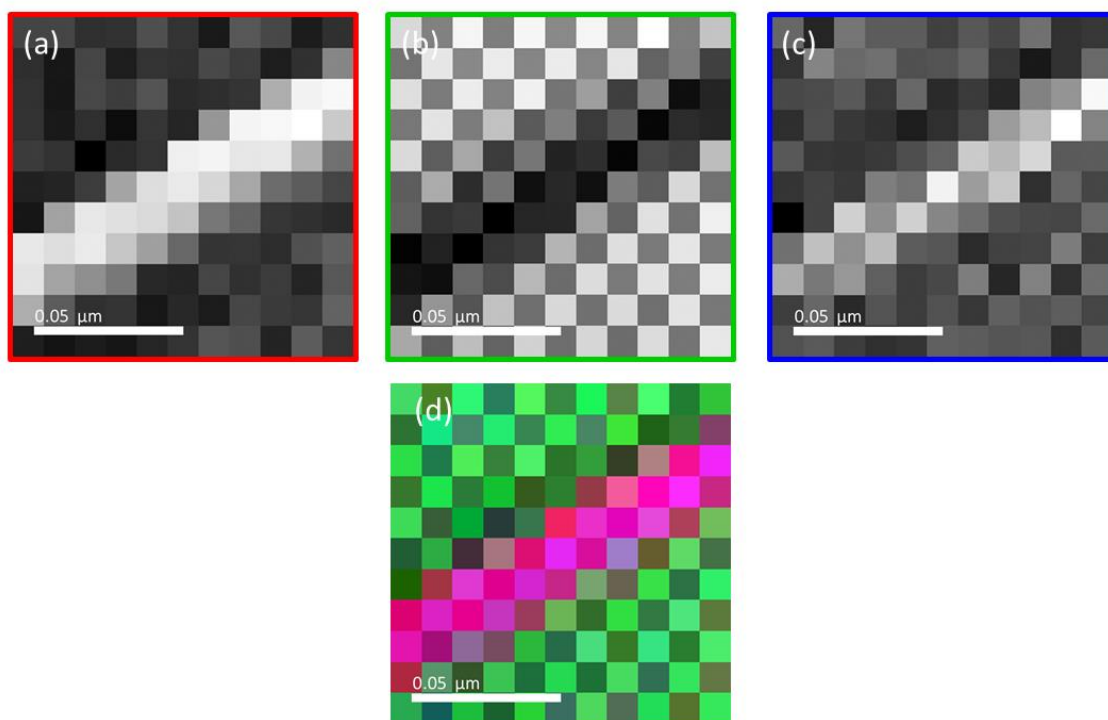


Figure 5.22. RGB construction of spectrum image with a) Red assigned to B-K b) Green assigned to Al-K c) Blue assigned to Sr-L and d) the RGB image.

5.3.3 Investigation of Crystal Structure of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$: 1 mol% Eu, 1 mol% Dy, 30 mol% B_2O_3 by Atomic Resolution Imaging

In this course of the study, we present the results of STEM atomic resolution imaging of the single crystal of S4A7 compound. The amorphous pre-ceramic with the stoichiometry of S4A7ED30B was synthesized by using a sol-gel Pechini method as described in chapter 2. The amorphous pre-ceramic was sintered by spark plasma sintering (SPS) method. **Figure 5.23** shows the lamella preparation by focused ion beam milling technique from the spark plasma sintered S4A7ED-30 %mol B_2O_3 compound. The region of interest was first determined from back-scattered electron SEM image and the FIB specimen was prepared from the ceramic pellet as described in chapter 2 for further TEM analyses.

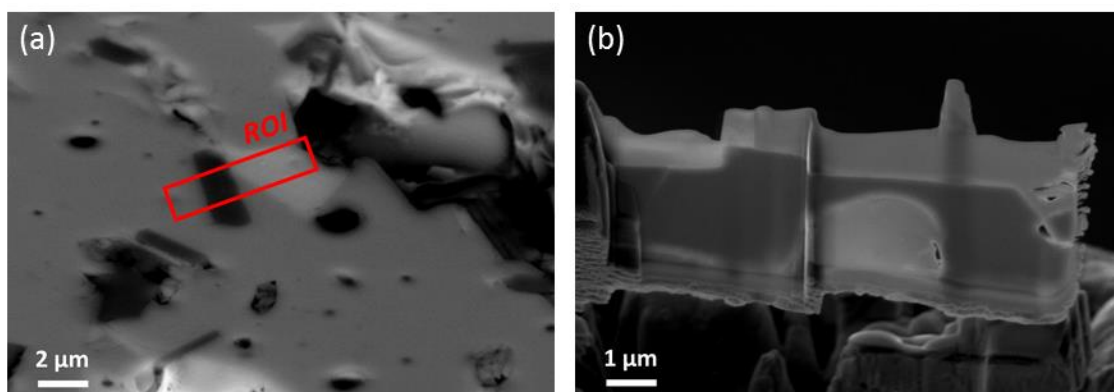


Figure 5.23. FIB sample preparation from the SPS specimen. a) BSE image from the SPS pellet and determination of the region of interest b) FIB lamella prepared from the region of interest.

Figure 5.24 shows the bright field TEM image of the FIB specimen. Several microstructural features were identified in the FIB lamella and were labeled as *ROI#1* to *ROI#6* for performing selected area electron diffraction (SAED) pattern analysis.

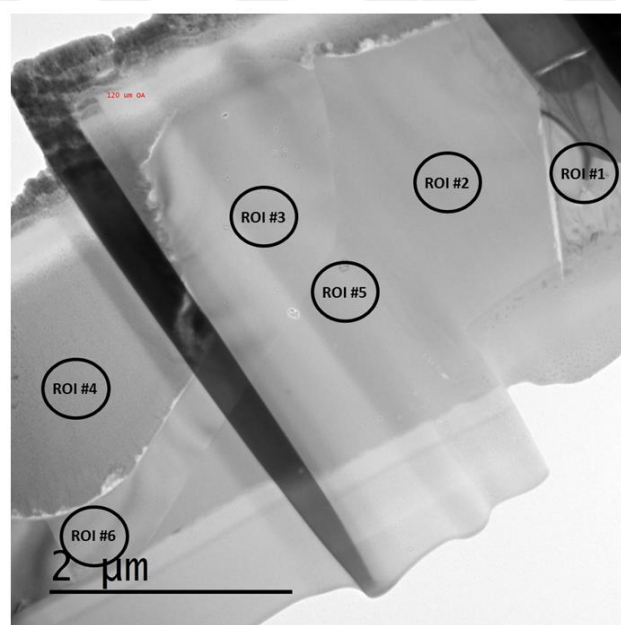


Figure 5.24. TEM-BF image of the FIB specimen prepared from the spark plasma sintered S4A7ED30B composition.

The results of SAED pattern analysis of the microstructural features are shown in **Figure 2.25**. The electron diffraction patterns of the crystalline grains were indexed by using JEMS software as described in chapter 2. The diffraction pattern attributed to ROI # 1

(**Figure 5.25 – a**) was indexed to S_4A_7 phase when the grain is tilted to $[0\ 1\ 0]$ zone axis. SAED pattern corresponding to ROI # 2 (**Figure 5.25 – b**) is attributed to the zone axis of $[3\ 1\ 0]$ of SA phase. The analysis of SAED pattern of ROI #3 (**Figure 5.25 – c**) revealed that, this grain is of S_4A_7 phase when tilted to $[0\ 0\ 1]$ projection. Electron diffraction patterns of ROI # 4 and ROI # 5 (**Figure 5.25 – c-e**) showed diffuse rings, characteristic of amorphous nature. Finally, ROI#6 (**Figure 5.25 – f**) showed a similar SAED pattern to that of ROI# 3 which was also indexed as S_4A_7 phase tilted to $[0\ 0\ 1]$ projection. In fact, a strip-like S_4A_7 grain (ROI#3 and ROI#6) had surrounded an amorphous intergranular region (see Figure 5.24).

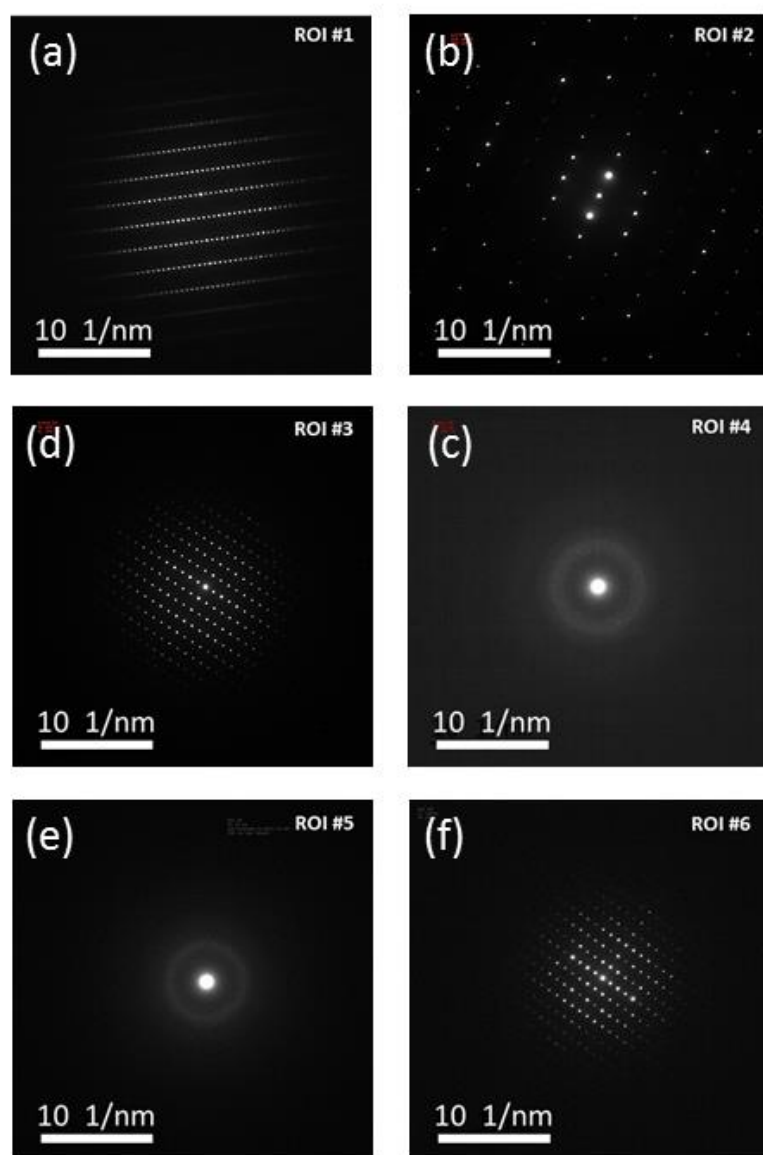


Figure 5.25. SAED pattern analysis of the microstructural features corresponding to a) ROI#1 b) ROI#2 c) ROI#3 d) ROI#4 e) ROI#5 and f) ROI#6 in figure 5.24.

Because the S_4A_7 phase is considered as long afterglow phase, capable of phosphorescence at room temperature [6], we sought to image the atomic columns in the crystal structure to elucidate the position of point defects – the rare earth dopants in the crystal lattice. Since the low index zone axis of S_4A_7 grain *e.g.* $[0\ 0\ 1]$ was accessible for ROI # 6 in figure 2.24, we chose to perform the STEM atomic resolution imaging of the crystal lattice on S_4A_7 crystal from $[0\ 0\ 1]$ projection.

Figure 5.26 shows the comparison between the experimental and simulated electron diffraction pattern of S_4A_7 crystal from $[0\ 0\ 1]$ projection. It was observed that there is a good fit between the experimental data and simulated point pattern (red dots).

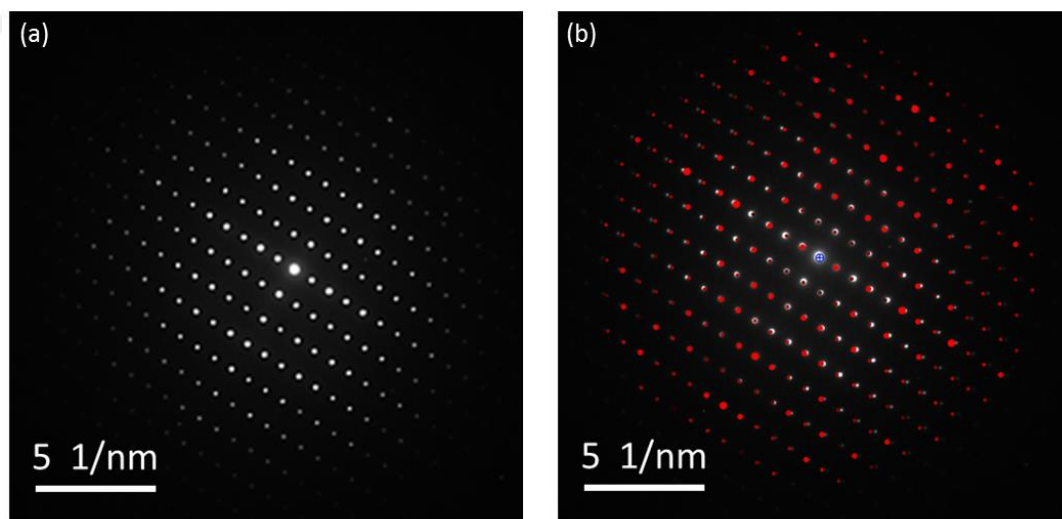


Figure 5.26. Selected area electron diffraction pattern of S_4A_7 single crystal tilted to $[0\ 0\ 1]$ projection. a) experimental DP b) superimposition of simulated DP (red dots) on the experimental DP.

We thus set up the stage for imaging the atomic columns of Eu and Dy codoped $Sr_4Al_{14}O_{25}$ compound by tilting the S_4A_7 grain to the $[0\ 0\ 1]$ zone axis. **Figure 5.27** displays the unit cell of S_4A_7 phase along the $[0\ 0\ 1]$ projection. The crystal structure of $Sr_4Al_{14}O_{25}$ is composed of parallel columns of 6-fold coordinated Al^{3+} (AlO_6 units) interconnected by corner sharing 4-fold coordinated Al^{3+} (AlO_4 units). The charge deficiency in the cavities between the Al-polyhedral units are compensated by Sr^{2+} cations. In the unit cell of S_4A_7 phase, there two non-equivalent Sr sites which are located in low symmetry distorted polyhedral units. In the first strontium site (Sr_1), Sr^{2+} is coordinated with 10 oxygens and the average Sr-O bond length is 2.77 Å while in the second strontium site, Sr^{2+} is 7-fold

coordinated by oxygens ions with an average bond length of 2.62 Å [6, 26, 163, 185] (**Figure 5.27**).

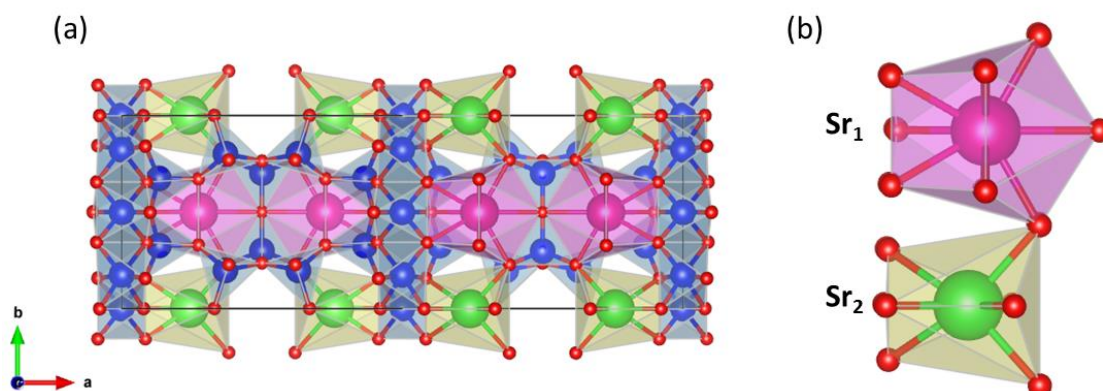


Figure 5.27. a) Unit cell of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ projected on $[0\ 0\ 1]$ axis b) Sr_1 and Sr_2 polyhedral sites in crystal structure of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$.

In addition, because Eu^{2+} and Dy^{3+} have similar ionic radii to Sr^{2+} , the rare earth dopants replace the strontium sites upon doping [6, 163]. **Figure 5.28** shows the super-cell of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ projected on $[0\ 0\ 1]$ zone axis. It can be observed that, from this projection, Sr^{2+} cations in both Sr_1 and Sr_2 sites are very well separated and resolvable. It is important to note that, looking at the crystal along this projection, it can be seen that Sr_1 and Sr_2 sites are slightly mis-placed relative to each other in the alternating row, creating a zig-zag arrangement as shown by the black dash line. Therefore, HAADF images of S_4A_7 crystal from $[0\ 0\ 1]$ projection can give insight about the position of point defects in the crystal lattice.

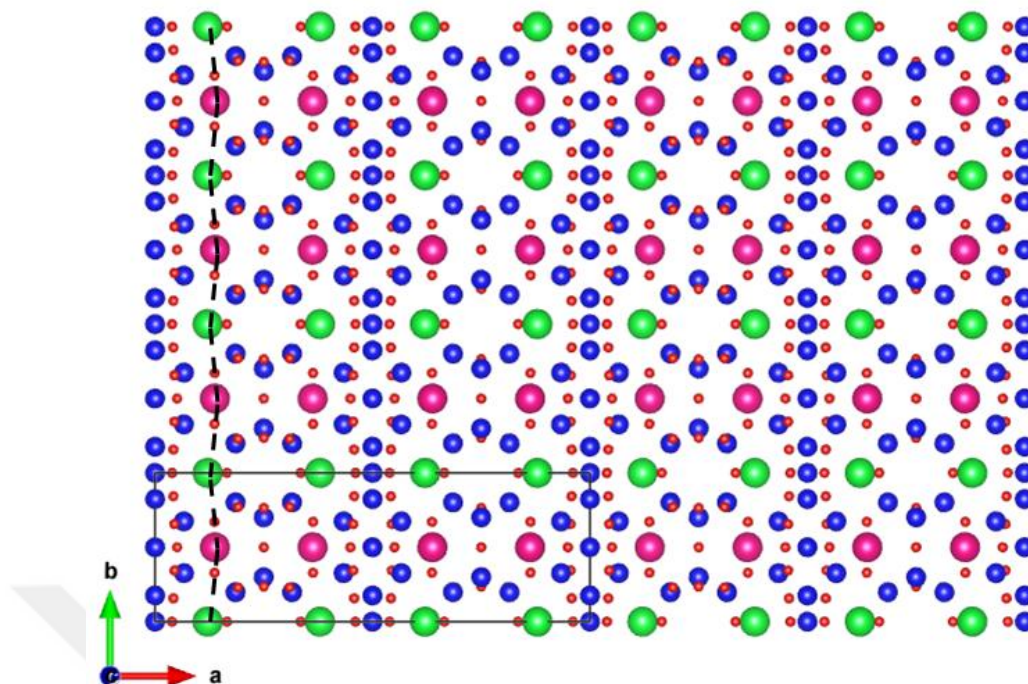


Figure 5.28. super cell of S4A7 viewed from $[0\ 0\ 1]$ projection. The pink and green balls correspond to Sr1 and Sr2 sites, respectively. Al and O ions are also shown in blue and red, respectively.

Figure 5.29 shows the experimentally obtained BF and HAADF images of the crystal lattice of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ grain doped with Eu, Dy and B which was tilted onto the $[0\ 0\ 1]$ zone axis. Because in BF image (Figure 5.29 – a) the electrons that transverse the specimen, leave the sample at very low angle with respect to the optic axis, they produce overlapping Bragg's disk on the BF detector. Thus, there would be a phase shift in the wave of electrons after interaction with the sample. Because Sr^{2+} cations are larger in size, the phase shift applied to the electron wave front is greater and Sr columns appear as dark spheres in the BF image.

In the STEM-HAADF image (Figure 5.29 – b), The contrast variations correspond to the differences in the atomic numbers of the Sr and Al and O (38, 13 and 8, respectively), with the Sr atomic columns producing higher intensity. In fact, since the Sr atoms are heavier compared to Al and O ions, the electrons are scattered at higher angles. Therefore, the very bright columns in the HAADF images represents the Sr sites in the structure.

The Al atoms in the less dense atomic columns (denoted by black arrow in Figure 5.29 – c) are form alternative rings which are partially visible in the HAADF images. However,

in the denser columns (denoted by red arrow in Figure 5.29 – c), Al atoms are hardly discernable.

The O ions are invisible in this case due to the small distances and vicinity of the heavier Sr and Al columns that produce higher intensity in this projection. Therefore, direct visualization of the O/Al ligand atomic columns was not possible neither by HAADF nor by BF STEM-imaging due to overlap of the oxygen ions with Sr or Al sites observed in the $[0\ 01]$ zone axis (Figure 5.29 – c). In order to image Al and O ions, annular bright field (ABF) imaging from another projection combined with STEM image simulation techniques are more appropriate [8]. Superimposition of Sr and Al atoms on the highlighted region in Figure 5.29 – b is shown on the HAADF image in Figure 5.29 – d.

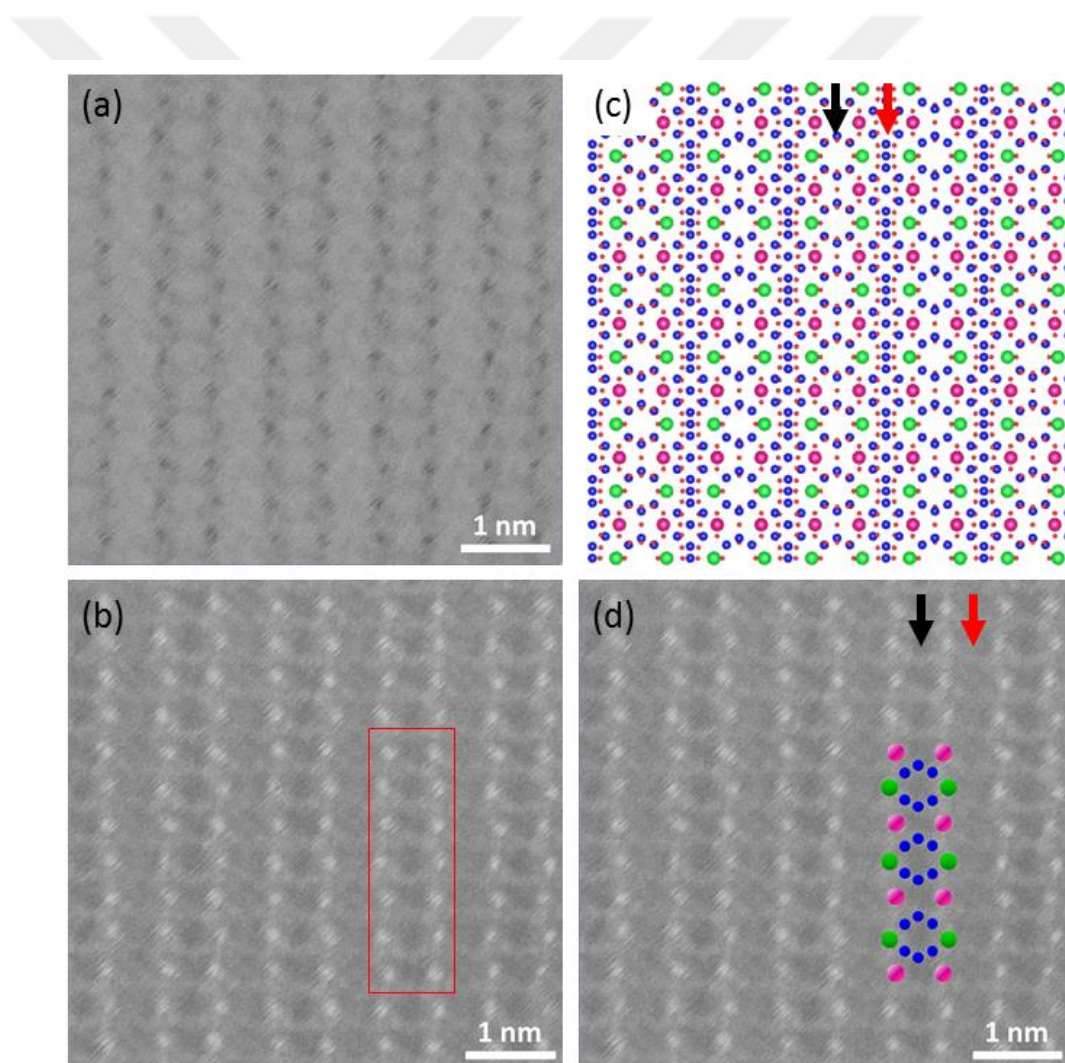


Figure 5.29. Atomic resolution STEM images of S4A7 crystal from $[0\ 0\ 1]$ projection. a) BF b) HAADF c) visualized crystal structure of S4A7 crystal from projected on $[0\ 0\ 1]$ zone axis in VESTA and d) superimposition of Sr and Al atoms on the atomic columns in the HAADF image. Pink, green, blue and red balls in c and d correspond to Sr_1 , Sr_2 , Al and O ions, respectively.

In order to detect the position of point defects *e.g.* rare dopants incorporated into strontium sub-lattice sites, we investigated the intensity line profile of the Sr cations in the contrast inverted HAADF image recorded from [0 0 1] projection (**Figure 5.30**). Because from this projection, along the direction shown by the dashed box alternate columns of Sr cations in Sr₁ site and Sr₂ sites are slightly displaced with respect to each other, the investigation of line profile would be misleading. Therefore, to analyze the contrast difference in the Sr site columns, the intensity profile was investigated along ROI#1 which includes only the columns of Sr₁ and along ROI#2 which is built only by Sr₂ sites atoms (see Figure 5.28 for comparison with the visualized lattice). A closer inspection of the intensity profile in ROI#1 and ROI#2 revealed that, the atoms specified by the arrows have relatively higher intensity compared to the others. Since the rare earth dopants have higher atomic number compared to Sr atoms, it is reasonable to assume that the higher intensity observed in the line profiles is attributed to the presence of a point defect in the atomic arrangement of the crystal lattice *e.g.* incorporation of Eu or Dy ions into the Sr sublattice sites.

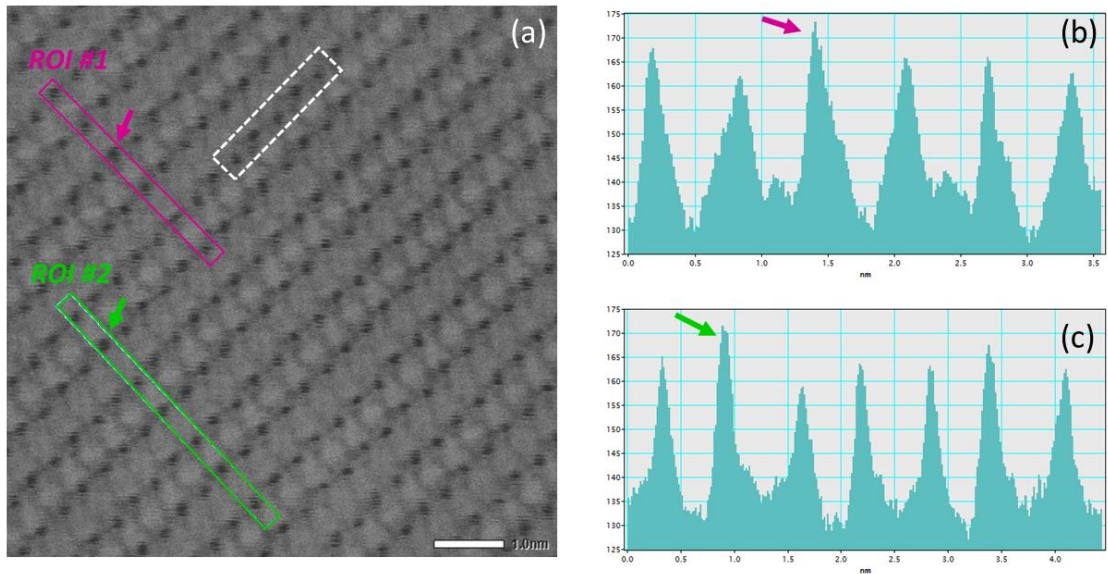


Figure 5.30. a) contrast inverted HAADF image of S4A7 crystal doped with Eu, Dy and B from [0 0 1] projection b) Intensity line profile along ROI #1 corresponding to Sr₁ atomic sites c) Intensity line profile along ROI 21 corresponding to Sr₂ atomic sites. The arrows specify the atoms with higher intensity in HAADF images and line profiles.

5.4 Discussion

Analysis of local coordination of boron via comparing the B-K ELNES fingerprints in the microstructure of sintered S4A7EDB compound to that reference minerals reported in the literature [158, 159] revealed that, boron predominantly remains in the amorphous intergranular phase as 3-fold coordinated. In the crystalline grain, boron enters four-fold coordinated. The analysis of electron energy loss spectrum image confirmed that the amorphous phase in the intergranular phase is rich trigonal 3-fold coordinated boron (Figure 5.9-b). When the ELNES of 4-fold boron was mapped throughout the microstructure, a uniform distribution of ^{14}B was observed in the crystalline grains, albeit the intensity of B-K edge was small (Figure 5.9-d). The high content of trigonal BO_3 units in the amorphous intergranular phase suggests that this phase is in fact a borate glass.

In addition, the map of Sr-L edge in the high-loss spectrum image correlates strongly with B-K ELNES features attributed to 3-fold coordinate boron (Figure 5.19). On the other hand, the Al-K ionization edge fingerprint was not found in the intergranular strip (Figure 5.18). These results imply that, the borate glassy phase is indeed Sr-borate phase and formation of strontium alumino borate phase is ruled out (Figure 5.22). Therefore, B_2O_3 is not merely an inert sintering flux but it also interacts with the cations present in the mixture, specifically, with more reactive component e.g. Sr-O polyhedral units. Because Al^{3+} cations form very stable bonds with oxygen, therefore, Al-coordination polyhedral are very stable. This means that it requires significant energy to break up the bonds and thus they are more likely to remain coherent polyatomic species. By contrast, Sr coordination polyhedra are relatively unstable and easily allow Sr cations to diffuse as individual cations.

In terms of the distribution of rare earth dopants, spatially resolved analysis of Eu-M, Dy-M and B-K edges in the spectrum images confirmed that, while the amorphous IGP is enriched in all the dopant elements, Eu^{2+} cations are more uniformly distributed in the crystalline grains compared to B^{3+} and Dy^{3+} (see Figure 5.20). This suggests that there is a higher affinity for Dy to stay in the borate phase leading to formation of Dy-borate complexes [39, 118]. furthermore, because the ionic radius of B^{+3} is smaller than that of Al^{+3} , the effective charge carried by B polyhedral units are more negative than that of Al polyhedral, the rare earth dopants with high positive charge density, would prefer to be accommodated inside the borate phase.

The analysis of the selected area electron diffraction pattern on the S_4A_7 crystal in the microstructure of the spark plasma sintered S_4A_7ED30B specimen showed that, from $[0\ 0\ 1]$ projection, Sr atoms on Sr_1 and Sr_2 sites are very well separated (Figure 5.28). On the other hand, the ionic radii of rare earth dopants are comparable to Sr atoms and therefore, it is less likely that they enter the structure of S_4A_7 interstitially. Instead, Eu and Dy would replace the Sr atoms substitutionally [18]. Thus, by HAADF (Z-contrast) imaging of the Sr atomic columns, it is possible to detect the position of rare dopants that substitutionally replace the Sr sublattice sites.

STEM-HAADF images recorded from $[0\ 0\ 1]$ projection of S_4A_7 crystal was then analyzed in order to identify possible atomic positions that may be occupied by rare earth elements. Since the origin of contrast in the HAADF image is Z-contrast, variation in contrast should be investigated in order to detect a substitutional atomic species with a higher atomic number than the host lattice. The intensity profile along a line cut from the HAADF image obtained along $[0\ 0\ 1]$ zone axis (Figure 5.30) revealed that in the atomic columns corresponding to strontium sites, there exist one atom with higher intensity compared to other ones. This implies that, the emitting center Eu (or Dy) have been substitutionally replaced by Sr atoms in both Sr_1 and Sr_2 sites. The fact that point defects were detected in both Sr sites, explains the presence of two significant emission band at 420 nm and 490 nm [7] in the PL spectra of the S_4A_7 grain codoped with Eu Dy and B.

5.5 Conclusion

In this study, we investigated the microstructure of long afterglow strontium aluminate compounds by using spatially resolved electron microscopy techniques. While investigation of boron distribution by energy dispersive X-ray spectroscopy is not possible due to limitation of the EDX technique, investigation of B-K ionization edge by EELS spectrum imaging clearly showed the distribution of boron in the microstructure. Furthermore, analysis of the ELNES fingerprint of B-K edge revealed that the intergranular amorphous phase is rich in 3-fold coordinated boron while in the crystalline grains, B enters 4-fold coordinated by oxygen. By mapping the Al-K, Sr-L, Eu-M and Dy-M edges in the high-loss spectrum image, we showed that the boron doping results in formation of Sr-borate glassy phase which is rich in rare earth dopants. The incorporation

of rare earth dopants in Sr sublattice sites was confirmed by atomic resolution STEM-HAADF imaging of the crystal structure of S4A7EDB.



CHAPTER 6: PERSPECTIVES FOR FFUTURE WORK

Resolving ionic sub-lattices into which boron might have been incorporated (interstitially or substitutionally) will explain the role of boron in extended afterglow. In this work, we considered performing atomic resolution STEM imaging of the microstructural features produced during conventional sintering of amorphous pre-ceramic of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$: 1 %mol Eu, 1%Dy and 30 %mol B_2O_3 (S4A7EDB). Because the stage is already set up for further investigation of the microstructure with atomic-scale resolution to correlate the position of structural point defects with optical properties in strontium aluminate ceramics, herein we present the preliminary results of advanced TEM analyses of the microstructure. The continuation of this line of the study is planned for the future work.

A region of interest (ROI) in the microstructure of the S4A7EDB sintered specimen was chosen based on the phase composition contrast revealed by SEM backscatter electron image (**Figure 6.1-a**). A FIB lamella was prepared from the region of interest (ROI) for further advanced TEM analyses (**Figure 6.1-b**)

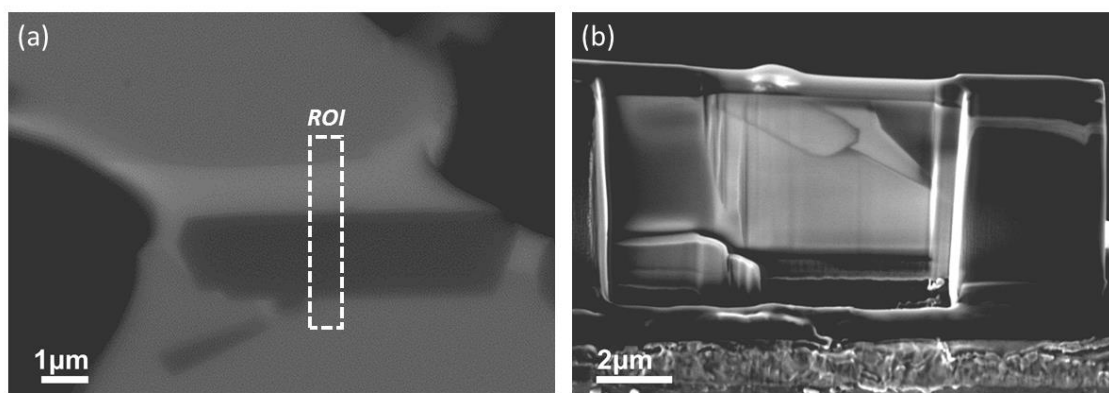


Figure 6.1. a) backscatter electron SEM image of the microstructure of S4A7EDB sintered sample b) FIB specimen prepared from ROI in (a).

Selected area electron diffraction patterns of the microstructural features were recorded and then indexed to identify the phases present in the microstructure (**Figure 6.2**). Diffraction pattern indexing revealed the presence of equiaxed S_4A_7 single crystal grain which is one of the two long persistence afterglow phases in the strontium aluminates phosphor family coexisted with that of SA6 grains that does not exhibit persistent phosphorescence at room temperature [6, 7].

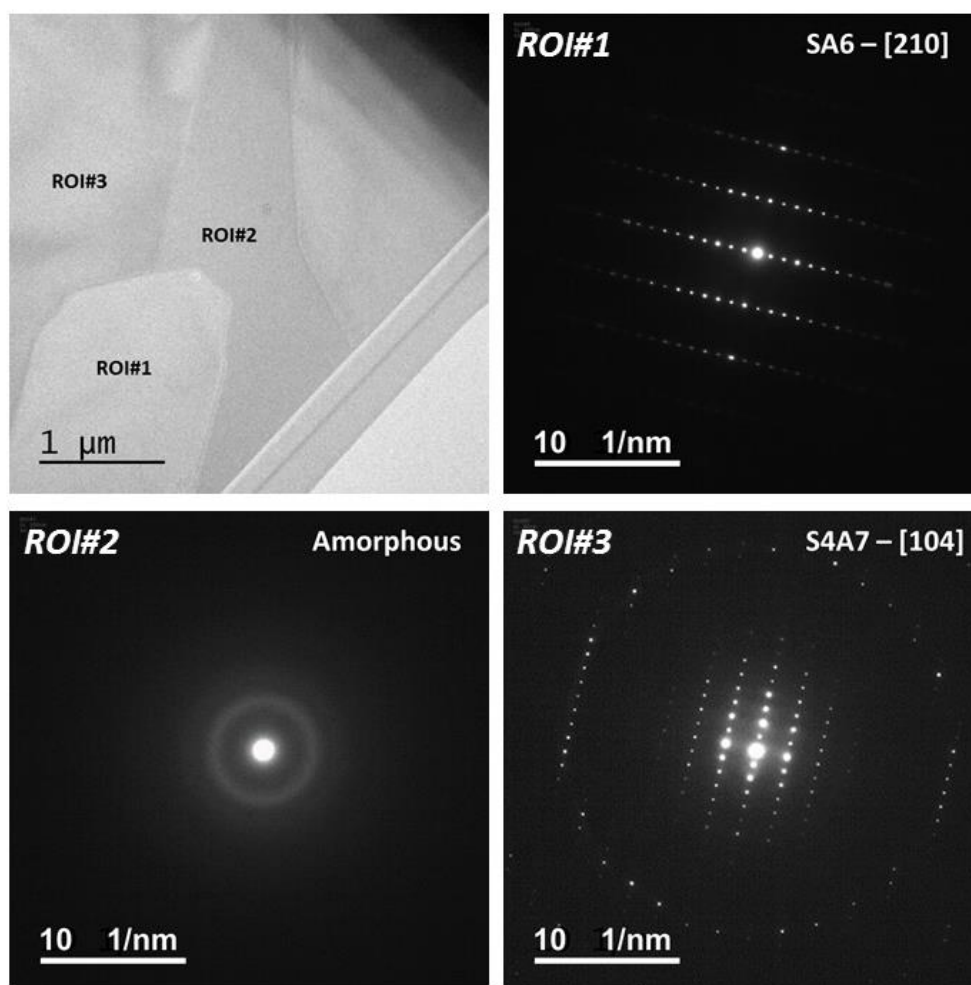


Figure 6.2. TEM-BF image of the FIB sample with corresponding SAED pattern of the microstructural features.

After tilting the crystalline grains to a nearby zone axis, the projection of the crystal was identified by comparing the simulated and experimental diffraction patterns. The atomic resolution STEM images of the SA6 crystal (ROI#1) and S_4A_7 grain (ROI#3) are shown **Figure 6.3** and **Figure 6.4**, respectively.

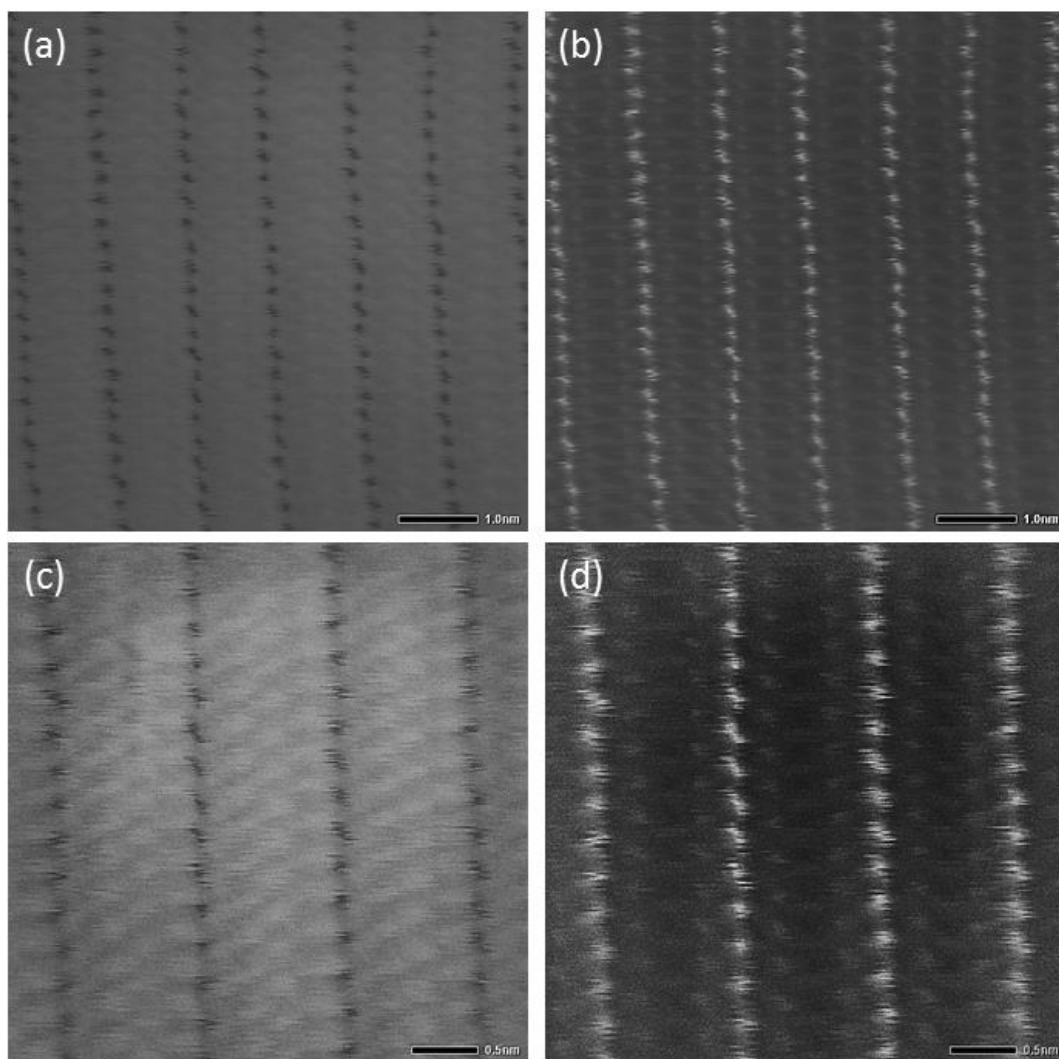


Figure 6.3. Atomic-scale STEM images of the SA6 (ROI#1) crystal. (a) and (c) are the BF images at different magnifications and (b) and (d) are the corresponding HAADF images projected on $[2\ 1\ 0]$ zone axis.

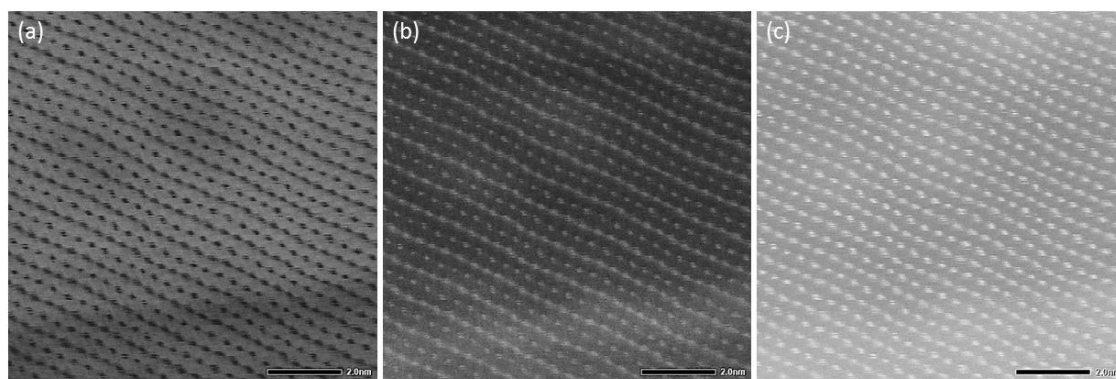


Figure 6.4. Atomic-scale STEM images of the S4A7 (ROI#3) crystal. (a) BF (b) Low angle annular dark field (LAADF) and (c) High angle annular dark field (HAADF) images projected on $[1\ 0\ 4]$ zone axis.

Although the position of ionic sublattice in the atomic arrangement of strontium aluminates for the heavy elements can be assessed qualitatively by direct interpretation of Z-contrast in HAADF-STEM images, the imaging of point defects with rarely discernable intensity variation still requires a deeper investigation. In order to reliably interpret the atomic resolution images obtained from the crystalline grains, quantification of the variation of intensity levels (contrast) in atomic resolution images by quantitative image simulation of the atomic-scale STEM images is the next obvious step.

Through quantitative STEM image simulation, one can combine the crystal structure model, (including the thickness of the crystal lattice and the projection of atomic planes) with imaging conditions to obtain a directly interpretable simulated image of the atomic arrangement in the lattice. Therefore, the experimentally obtained AR-images from different strontium aluminate compositions discussed in this chapter can be compared with the simulated ones to resolve the ionic sub-lattices which may contain rare earth dopants and boron. This way, the spatial correlation between the position of B with optically active center Eu and the auxiliary co-dopant Dy can be validated which can provide a clearer insight about the point defect clustering mechanism that supports afterglow.

In addition, by comparing the clustering effect of dopants atom inside the host lattice of S_4A_7 and SA_6 through STEM image simulation, the reason for superior persistent phosphorescence property in S_4A_7 at room temperature compared to that of SA_6 can be elucidated.

Furthermore, because annular bright field (ABF) imaging enables the simultaneous detection of light and heavy atoms as opposed to HAADF which is more sensitive to high atomic number elements, the imaging of lighter elements like Al and B by ABF technique from a suitable zone axis where Sr, Al and O atoms are sufficiently resolvable is of interest for the future work.

APPENDIX A: TRANSFER PRINTING GOLD NANOPARTICLE ARRAYS BY TUNING THE SURFACE HYDROPHILICITY OF THERMO-RESPONSIVE POLY N- ISOPROPYLACRYLAMIDE (pNIPAAm)

For the transfer of 2-D gold nanoparticle arrays between different substrates, we have developed a new method using thermo-responsive poly-*N*-isopropylacrylamide (pNIPAAm). By tuning the degree of surface hydrophilicity of pNIPAAm between 5 °C and 50 °C, we demonstrate the transfer of arrays extending over micron-scale areas with preservation of array properties.

Processes for preparing 2-D arrays of colloidal nanoparticles tend not to be universally suitable across the variety of substrates used in electronic devices—posing a challenge for the integration of precise planar arrangements of colloidal nanoparticles into the device fabrication of organic electronics. To circumvent this obstacle, we have developed a new method for transfer printing an array of such nanoparticles from a sacrificial substrate using a film of thermosensitive polymer, poly-*N*-isopropylacrylamide (pNIPAAm), as a coating on a polydimethylsiloxane (PDMS) stamp. Successful stamping transfer of particles between substrates depends strongly on the particle size; hence no universal stamp material has yet been identified. Rogers *et al.* have demonstrated the efficacy of a bare polydimethylsiloxane (PDMS) surface, when used under two kinetically distinct regimes, to pick up and release micron scale-sized particles [186, 187]. For manipulating nanoscale-sized objects, poly methymethacrylate (PMMA) coatings have been effective [188-191]. However, this transfer approach requires additional chemical treatments and elevated temperatures for peeling the PMMA/nanomaterials off from the source substrate, and for releasing the transfer objects onto the target substrate, followed by complete removal of the PMMA film. Recently, a more versatile approach was

demonstrated by Zhang et al. in the transfer printing of various nanostructures, including nanoparticles, nanowires and nanosheets, onto a variety of target substrates with broader variation in surface properties. In their approach, they employed poly (L-lactic acid) (PLLA) as the carrier and dichloromethane (DCM) for removing the polymeric matter. The drawback of this process, though, remains in the form of potential chemical incompatibility between the DCM solvent and the transfer substrate.

Although polymeric micelle nanoreactors are particularly useful for producing size-monodisperse inorganic colloidal nanoparticles with controllable 2-D dispersion on a surface [192-195] removal of the polymeric matter necessitates the use of a plasma etch treatment [194-196], which may be detrimental to the underlying support layers, in particular, for plasma-sensitive organic device processing. Preliminary work by our group to transfer a 2-D gold nanoparticle array between substrates involved the use of bare PDMS [197], following the kinetically controlled approach. However, this process was not successful, most likely due to the roughness of PDMS compared to the feature size of the nanoparticles. Although this approach has been successfully applied to micro-scale objects [186, 187] the non-uniformity of the surface made it difficult to reliably pick and release nano-scale objects.

As thermo-responsive polymers enable control and manipulation of their properties by temperature changes, we considered the thermo-sensitive polymer, pNIPAAm, which undergoes rapid, reversible changes in molecular conformation at a lower critical solution temperature (LCST) [198-200]. When fully immersed in water, the LCST occurs at 32–35 °C [198-200], and the pNIPAAm surface can easily switch between a hydrophilic swollen state and a hydrophobic collapsed state [200-202]. Thus, with an LCST near room temperature, the surface of pNIPAAm can be tuned for manipulating arrays of nanoparticles, and we investigated tuning the character of the pNIPAAm surface in ambient humidity for transfer printing.

The pNIPAAm molecule has both a hydrophilic secondary amine group (–N–H) and a hydrophobic group (isopropyl), and depending on the temperature, the surface of a pNIPAAm film may be dominated by either the hydrophilic moieties or the hydrophobic ones [203, 204]. When the temperature is below the LCST, the hydrophobic isopropyl groups in pNIPAAm molecule prefer the interior of the film, while the hydrophilic –NH groups are predominantly exposed toward the exterior for solvation by ambient water molecules, facilitating intermolecular hydrogen bonding. In water, the polymer is in its

swollen state. At temperatures above the LCST, the intermolecular hydrogen bonds of pNIPAAm reversibly transform to intramolecular bonding, and the change in molecular conformation leads to hydrophobic isopropyl groups exposed to the exterior, thus imparting both hydrophobic surface properties [203] and a reported nonlinear increase in elasticity [205, 206]. Thus, with a local stiffness more than 100 times higher in the collapsed state at 35 °C, in contrast to the swollen state at 10 °C [205, 207], pNIPAAm has thermo-responsive properties that may even be suitable for transfer printing nanoparticle arrays.

Herein transfer printing was demonstrated for gold nanoparticle arrays (GNPs) using thermo-responsive pNIPAAm coatings exposed only to ambient humidity (**Figure 7.1**). We elucidated the particle pick-up mechanism and the particle release mechanism by characterizing the temperature-dependent changes in pNIPAAm via contact wetting angle measurements, atomic force microscopy (AFM), and ellipsometry.

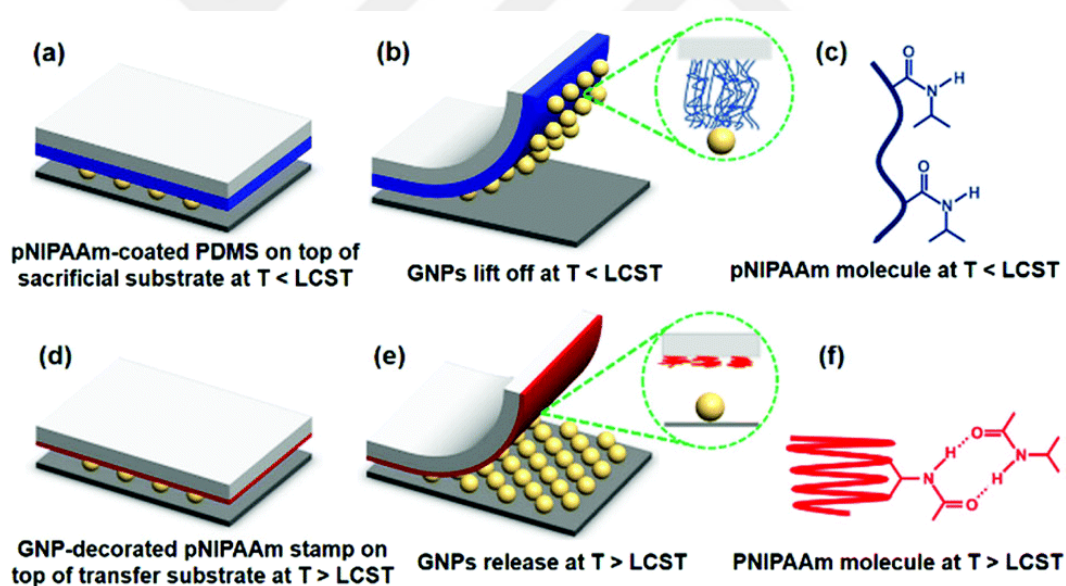


Figure 7.1. The transfer printing process using a PDMS stamp coated with the thermo-responsive polymer, pNIPAAm.

The stamps were prepared by initiated chemical vapor deposition (iCVD) growth of a pNIPAAm coating onto a PDMS substrate [208-210]. For developing the transfer printing process, we chose to use arrays of GNPs and silicon wafer substrates. The array geometry facilitated quantitative assessment of the degree of successful array transfer. Silicon wafer substrates have sufficiently low roughness, which minimized interference with picking

up and releasing the GNPs, while their contrast in electronic structure with that of gold facilitated imaging in the scanning electron microscope (SEM). The gold nanoparticles (GNP) were formed in reverse diblock copolymer micelles, which were assembled in a monolayer on sacrificial silicon wafer substrates, and exposed to an oxygen plasma for removal of the polymeric matter, as well as reduction of the gold precursor [194-196, 211].

To exploit the temperature dependence of the surface structure and energy of pNIPAAm, the stamp was placed in direct contact with a sacrificial silicon substrate containing a gold nanoparticle layer, and the entire assembly was cooled to 5 °C—relative humidity (RH) 85%—for 2 hours, ensuring equilibration well below the LCST of pNIPAAm. The stamp was then peeled off from the sacrificial substrate, and the exposed GNP-decorated surface was placed on top of the transfer silicon substrate and held at 50 °C for 2 hours. To ensure a conformal contact between pNIPAAm and the substrates at both temperatures, a uniaxial load of 23 kPa was applied.

The stamping transfer of the GNP arrays was validated by comparing the quantitative spatial pattern characteristics of secondary electron images of the nanoparticle arrays. The images recorded in a field-emission SEM (LEO Supra VP-55) were processed (i.e. amplifying the difference in image contrast), in order to allow the use of the ImageJ software [212] for quantifying the array characteristics—the average interparticle spacing and particle size distribution—by spatial point pattern analysis [213].

Figure 7.2-a shows a secondary electron image of the post-plasma etched gold nanoparticle array on the sacrificial substrate, which confirmed that the use of diblock copolymer micelle reactors (**Figure S1a**) enabled the formation of a two-dimensional, quasi-periodic hexagonal array of size-monodisperse GNPs on a Si wafer substrate and also that the exposure of the GNP-loaded micelles to a 29.6 W oxygen plasma for 90 minutes was sufficient for a complete removal of the polymeric matter (**Figure S1b**). From a spatial point pattern analysis of the array in **Figure 7.2-a**, an average particle size of 16 ± 3 nm, an average interparticle spacing of 65 ± 2 nm, and particle areal density of $2 (\pm 0.2) \times 10^{-4} \text{ nm}^{-2}$ for the array assembled on a sacrificial substrate could be determined from the radial distribution function (**Figure S1c**) and particle size distribution of the GNP array (**Figure S1d**).

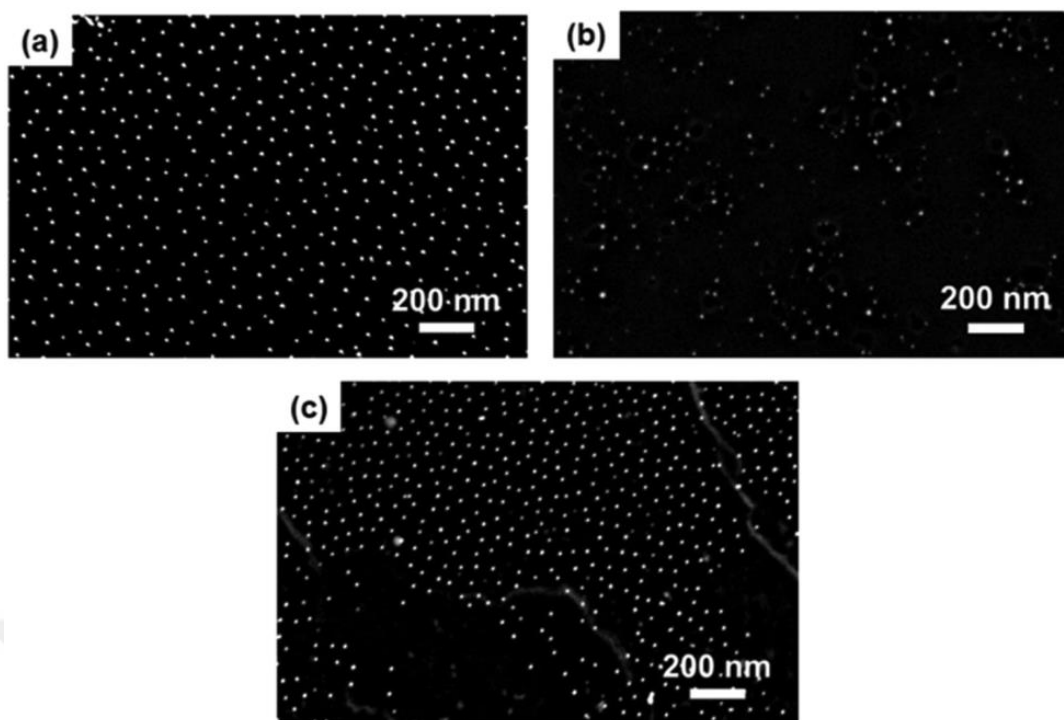


Figure 7.2. Secondary electron images of (a) the post-plasma etched GNP array on the sacrificial substrate (the image processed for pattern analysis)—the raw image can be found in Figure S1; (b) the sacrificial substrate after transfer printing (processed image, manipulated for spatial point pattern analysis—original raw data in Figure S2) and (c) the target transfer substrate (processed image, manipulated for spatial point pattern analysis—original raw data in Figure S3).

After peeling the pNIPAAm stamp off from the sacrificial substrate at 5 °C, bald patches were observed in the SEM images of the sacrificial substrate (**Figure 7.2-b**) (see also **Figure S2** for the corresponding raw data). After the GNP-decorated pNIPAAm stamp (**Figure S3**) was pressed onto the transfer silicon substrate at 50 °C, the GNP array was observed on the transfer substrate (**Figure 7.2-c** for the processed image, manipulated for spatial point pattern analysis from the original raw data in **Figure S3a**) with an average particle size of 16 ± 3.3 nm, an average interparticle spacing of 55 ± 1 nm, and a particle areal density of $3 (\pm 0.5) \times 10^{-4} \text{ nm}^{-2}$ (**Figure S3c and d**). Compared with the GNP array characteristics on the sacrificial substrate (**Figure 7.2-a**), the values for the average particle size were identical, while the interparticle distance was reduced by 15%, both indicating that the pNIPAAm surface had effectively transferred the GNP array between the two substrates, albeit with slight changes in array registry, due to the increase in areal density over a $2 \mu\text{m} \times 1.25 \mu\text{m}$ area.

The preservation of characteristics in the transferred array was further analyzed by spatial point pattern analysis of the SEM images [213] (**Figure S4**), for the sacrificial substrate

before transfer printing and for the target substrate after transfer printing. Comparing the degree of ordering revealed only a small change in the degree of short-range order in the quasi-hexagonal pattern (**Figure S4a**), as well as preservation of the pattern regularity (**Figure S4b**). Moreover, the pair correlation function (**Figure S4c**) shows both first and second order peaks for the two substrates, indicating predominantly more regularity than complete spatial randomness. These results are further supported by the consistency in nearest neighbor distribution analysis (**Figure S4d**)—resolved into three nearest neighbor peaks for both the sacrificial (before) and transfer (after) substrate—confirming the transfer of the GNP array.

To evaluate the temperature-dependent changes in surface energy of pNIPAAm above and below its LCST, we measured the advancing wetting contact angle at 5 °C and at 50 °C (**Figure S5**). For the pNIPAAm surface immediately upon removal from 5 °C, the average wetting angle was measured to be $\theta = 39.6^\circ \pm 5.7^\circ$. When the pNIPAAm was heated to 50 °C, the wetting angle increased to $\theta = 64.5^\circ \pm 4^\circ$, indicating that the pNIPAAm surface had become significantly less hydrophilic in character between the pick-up and release temperatures. Such a magnitude in change for the wetting behavior is consistent with the thermally tunable surface wetting properties of pNIPAAm in the literature, when crossing the LCST [214].

To verify that pick-up only occurred at 5 °C and release only occurred at 50 °C using pNIPAAm, we also evaluated pick-up at 50 °C and release at 5 °C, and the results are summarized in **Figure 7.3**. The GNP array remained intact on the sacrificial substrate, when contacted by pNIPAAm at 50 °C (comparison between **Figure 7.3 a and b**). PNIPAAm did not release the array at 5 °C (**Figure 7.3-c**), but instead only at 50 °C (**Figure 7.3-d**). These results were further confirmed upon inspection of the images of the pNIPAAm surface after transfer printing at 5 °C, on which GNPs remained, and at 50 °C, which was devoid of the released GNPs. Evidently array pick-up required that the pNIPAAm/substrate system be at 5 °C and release only at 50 °C. It should be noted that reversing the temperature sequence resulted in no transfer printing.

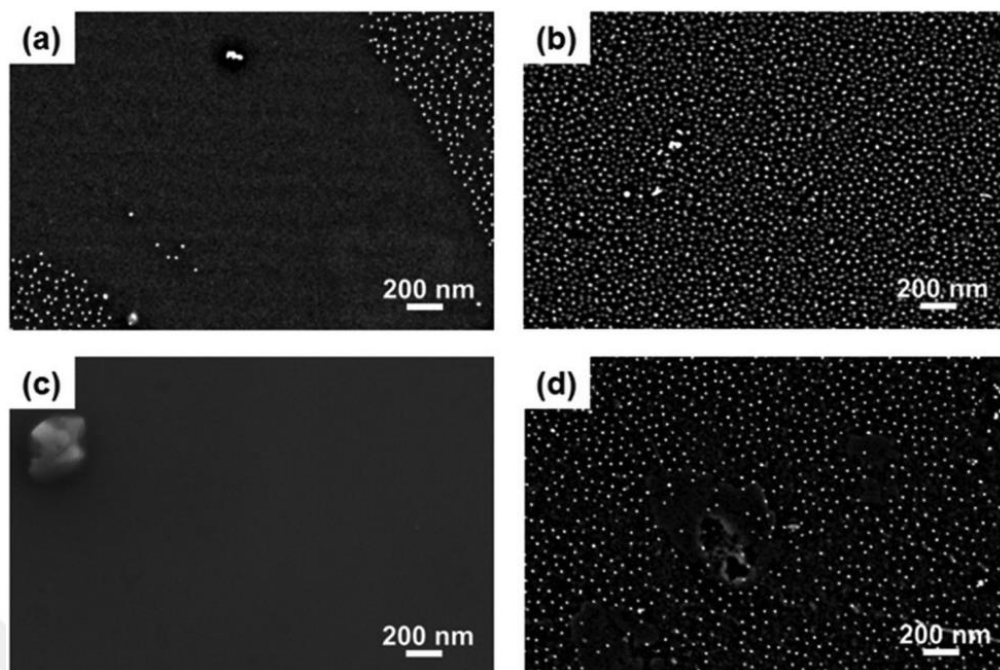


Figure 7.3. FE-SEM images of (a) the sacrificial substrate after transfer printing at 5 °C (processed image—original raw data in Figure S6a); (b) the sacrificial substrate after transfer printing at 50 °C (processed image—original raw data in Figure S6b); (c) the transfer substrate after transfer printing at the pick-up temperature of 5 °C; (d) the transfer substrate after transfer printing at 50 °C (processed image—original raw data in Figure S6c).

Because surface energy is also influenced by surface roughness, we also evaluated the influence of topography and of lateral variation in the elastic modulus of pNIPAAm surface by atomic force microscopy (**Figure S7**). The root mean square (rms) surface roughness of the pNIPAAm coating was 11.3 ± 1 nm, which was comparable to the average particle size of gold nanoparticles on the sacrificial substrate (16 nm). However, this degree of roughness did not appear to interfere with conformal contact between the pNIPAAm surface and the GNPs during pick-up, nor with the transfer of the particles. From the elastic modulus distribution (Figure S7b), the average elastic modulus was 5.23 ± 1 MPa over the $10 \mu\text{m} \times 10 \mu\text{m}$ scan area of 256×256 points, indicating that the stiffness of the pNIPAAm coating was uniform on the size scale of the nanoparticles in the plane of the substrate, indicating no interference during pick-up and release from nanoscale pNIPAAm deformation.

Also evident in the AFM imaging is the morphology of the wrinkles in the pNIPAAm-coated stamp surface. Although as-cast PDMS had an RMS roughness of 7.66 nm, deposition of pNIPAAm introduced wrinkles with micron-scale lateral variation (**Figure S8**). The gold nanoparticles were picked up only by the “ridges”, hence the bald patches

on the sacrificial substrate (**Figure 7.2-b**). The transfer of the gold nanoparticles decorating only the wrinkle ridges resulted in bald patches on the target substrate (**Figure 7.2-c**). Nonetheless, it appears that virtually all of the GNPs picked-up by pNIPAAm were successfully transferred (Figure S8)—the areal density generally increased by 150% with 22% variation.

Temperature-dependent changes in film thickness were analyzed by ellipsometry measurement of the pNIPAAm coating in ambient humidity of 70% RH (**Figure S9**). The pNIPAAm thickness was reduced from 100 ± 3.3 nm to 89.5 ± 4 nm upon heating from room temperature to 50 °C, due to temperature-dependent changes in refractivity [215]. At 20 °C in 90% RH, the pNIPAAm molecules readily form hydrogen bonds with water molecules and are fully hydrated, taking in up to 8 wt% of water [216]. However at temperatures above the LCST, the intrinsic hydrophobicity of the pNIPAAm molecule dominates over hydrogen bonding, resulting in separation of the water phase and deswelling of the surface layer of the dehydrating pNIPAAm film [215, 216]. This thermal shrinkage of $10.4 \pm 1.8\%$ revealed by ellipsometry is therefore consistent with the temperature-dependent volume expansion in the surface layer of pNIPAAm [215] and the reported order of magnitude in volume expansion over the temperature range 22–50 °C [217]. Moreover, the surface layer contraction at the release temperature of 50 °C is consistent with an increased areal density of transferred particles on the target substrate.

We thus attributed the success of transfer printing the GNP array by pNIPAAm to thermo-responsive changes in surface energy. Even though the pNIPAAm films in our studies remained below the LCST across the entire temperature range investigated—5–50 °C, there is clearly a temperature-dependent tuning in solvation behavior of the adsorbed water molecules from the humid ambient. When pNIPAAm is in its swollen state below the LCST, the hydrophilic –NH groups in the molecule are pre-dominantly exposed toward the surface, making the surface of the stamp hydrophilic. This situation is consistent with analysis of the pNIPAAm properties measured in the dry state at 5 °C. Thus, the chemical nature of the surface enables the pNIPAAm coating to adhere conformally to the gold nanoparticles and pick up the array from sacrificial substrate. When the temperature is raised to 50 °C, the hydrophobic isopropyl groups are exposed to the outer layer to impart decreased hydrophilicity to the pNIPAAm surface; the change in hydrophilicity may also be augmented by the surface roughness. This situation also appeared to be consistent with our pNIPAAm coatings at 50 °C, leading to release of the

gold nanoparticle array onto a target transfer substrate. Although the transfer-printed array characteristics showed a 15% reduction in interparticle spacing, the array characteristics were reasonably well-preserved.

Moreover, uniaxial loading (≤ 900 kPa) (**Figure S10**) of a PDMS stamp on sacrificial silicon wafer substrate did not result in the pick-up of the gold nanoparticle array. Therefore, although a load of 23 kPa was applied to the pNIPAAm-coated PDMS stamp during pick-up, in order to ensure the conformal contact between the stamp and the particle array on the silicon substrate, this force did not affect the pick-up process, and we attribute transfer printing of the GNP array solely to manipulating the temperature-dependent surface energy of the pNIPAAm film.

To demonstrate the feasibility of actual integration into device processing, we compared the performance of the transfer-printed GNP array on the ITO anode of a conventional bulk heterojunction organic photovoltaic OPV device against that of a polymer-templated GNP array prepared directly on the ITO anode from plasma-etching a micelle monolayer. Both types of devices showed an improvement in power conversion efficiency (PCE) over their respective control devices, i.e. ones without the GNP interlayer, which can be attributed to the plasmonic enhancement [218]. OPVs containing a transfer-printed GNP array on the ITO anode had a PCE improved by ca. 32% (Fig. S11[†]), while the devices, in which the polymer-templated GNP array on the ITO was exposed to the oxygen plasma, had improved by only ca. 17% [211].

Stamping transfer of GNP arrays from a sacrificial silicon wafer substrate and to a target silicon wafer substrate was achieved by using thermo-responsive pNIPAAm-coatings on PDMS stamps. The pick-up and release mechanisms were controlled by the thermally sensitive changes in surface energy of pNIPAAm. Well below the LCST temperature of pNIPAAm at 5 °C, the more hydrophilic nature of the pNIPAAm surface enabled adhesion to the gold nanoparticle array, while at 50 °C, the decreased hydrophilicity of the pNIPAAm surface enabled release of the array. The original short-range array characteristics were preserved to within $20 \pm 6\%$ in the transferred array. With the pick-up and release mechanism being driven solely by physical changes in the surface energy of pNIPAAm, the stamping transfer of nanostructured arrays by pNIPAAm is likely to be universally applicable to a broad diversity of material systems, provided that they are chemically inert to pNIPAAm up to 50 °C.

7.1 Supporting Information to APPENDIX A

7.1.1 Details of the Materials Synthesis Procedures

Preparation of the gold nanoparticle arrays: The gold precursor, $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ (Aldrich, 254169), was loaded into PS-*b*-P2VP diblock copolymer (Polymer Source, P10491-S2VP, M_w 183k-*b*-52k) reverse micelles dispersed in a toluene solvent. The loaded micelles were deposited onto silicon wafer substrates by spin coating (5500 rpm, 40 seconds). The polymeric matter was removed by oxygen plasma etching (O_2 at 30 sccm, 29.6 W RF power, 90 minutes; Harrick PDC-002, Ithaca, New York), and the gold precursor was reduced to elemental gold. In order to remove residual polymer on the sacrificial substrates, the post-etch substrates were subjected to further sonication processing in acetone, methanol and isopropyl alcohol (IPA) each for 10 minutes, respectively.

Deposition of the pNIPAAm films: PNIPAAm films were deposited by initiated chemical vapor deposition. The monomer N-Isopropylacrylamide (NIPAAm), the cross-linker ethylene glycol dimethacrylate (EGDMA) and the initiator tert butyl peroxide (TBPO) were used without further purification. The NIPAAm and the EGDMA were heated to 75 °C and 85 °C, respectively, to achieve sufficient vapor pressure, while the TBPO was kept at room temperature. The vapors were introduced into the evacuated deposition chamber at 1 mTorr. The optimized flow rates for pNIPAAm and EGDMA were 1 sccm and 0.075 sccm, respectively, while the flow rates of TBPO and N_2 were fixed at 1 sccm. The substrate and filament temperatures were set at 25 °C and 300 °C. Depositions were carried out under a reactor pressure of 200 mTorr. The films thickness was monitored in-situ using a laser interferometry system to reach the target thickness of 100 nm.

PDMS stamp preparation: PDMS stamps (Sylgard 184, SIGMA-ALDRICH No. 761036) were prepared by mixing 8 g of base and 0.8 g of curing agent for 20 minutes. The solution was then degassed in an evacuated desiccator for 24 hours, cast into a glass petri dish, and then cured at 80 °C for 4 hours.

7.1.2 Spatial Point Pattern Analysis for Quantifying The Array Characteristics on The Sacrificial Substrate Before Transfer Printing

The array of gold nanoparticles on a silicon substrate was imaged using secondary electrons in a field-emission scanning electron microscope (FE-SEM, LEO Supra VP-

55). The images were processed (*i.e.* difference in image contrast amplified), in order to allow the use of the ImageJ software [212] to quantify the array characteristics—the average interparticle spacing and particle size distribution—by spatial point pattern analysis [213].

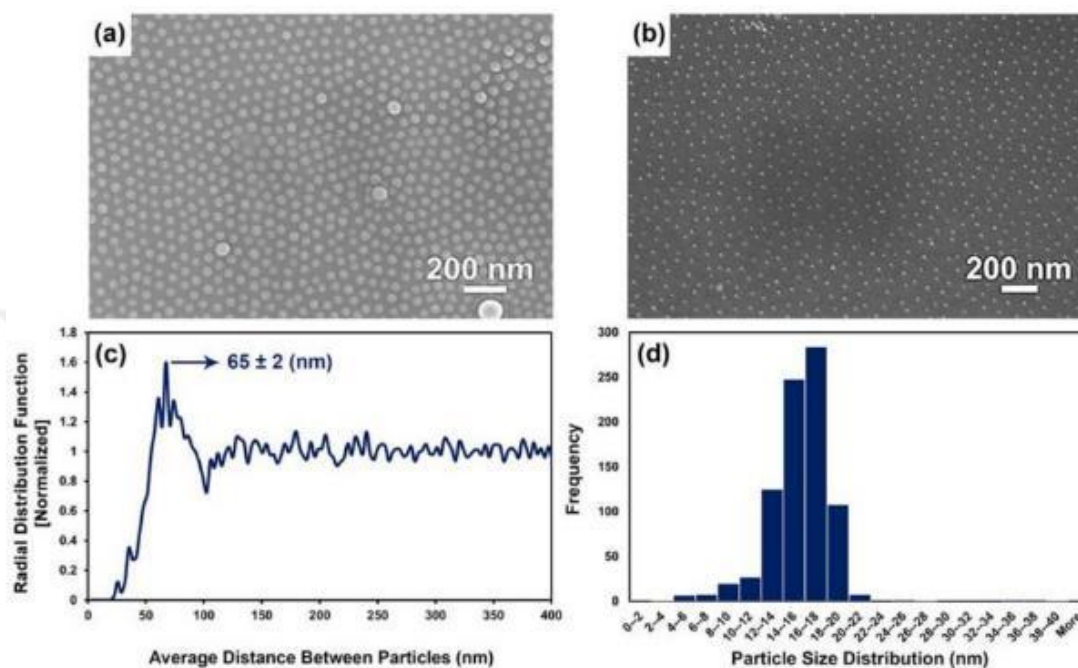


Figure 7.4. Original raw secondary electron images of a) gold precursor loaded diblock copolymer micelles; b) the post plasma-etched GNP array on the sacrificial substrate; c) Radial distribution function and d) Particle size (diameter) distribution of GNPs on the sacrificial substrate (**Figure S1**).

7.1.3 Sacrificial Substrate After Pick-up at 5 °C

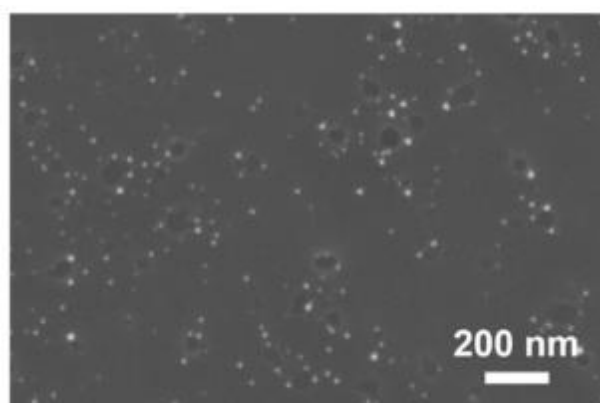


Figure 7.5. Original raw secondary electron image of the sacrificial substrate after picking up at 5 °C (**Figure S2**).

7.1.4 pNIPAAm Surface and Spatial Point Pattern Analysis of The Array Transfer-Printed onto The Target Substrate After Transfer Printing

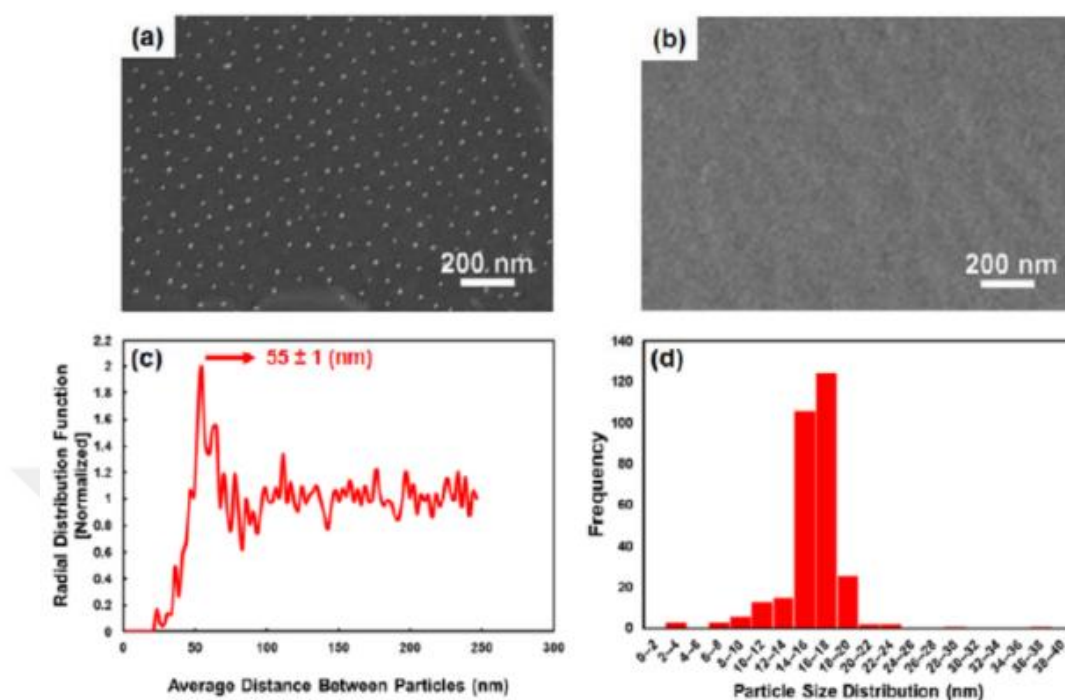


Figure 7.6. Original raw secondary electron images of a) the target transfer substrate; b) pNIPAAm surface after transfer to the target substrate at 50°C; c) the radial distribution function and c) the particle size (diameter) distribution of the transfer printed gold nanoparticle array (Figure S3).

7.1.5 Summary of Array Characteristics Quantified by Spatial Point Pattern Analysis

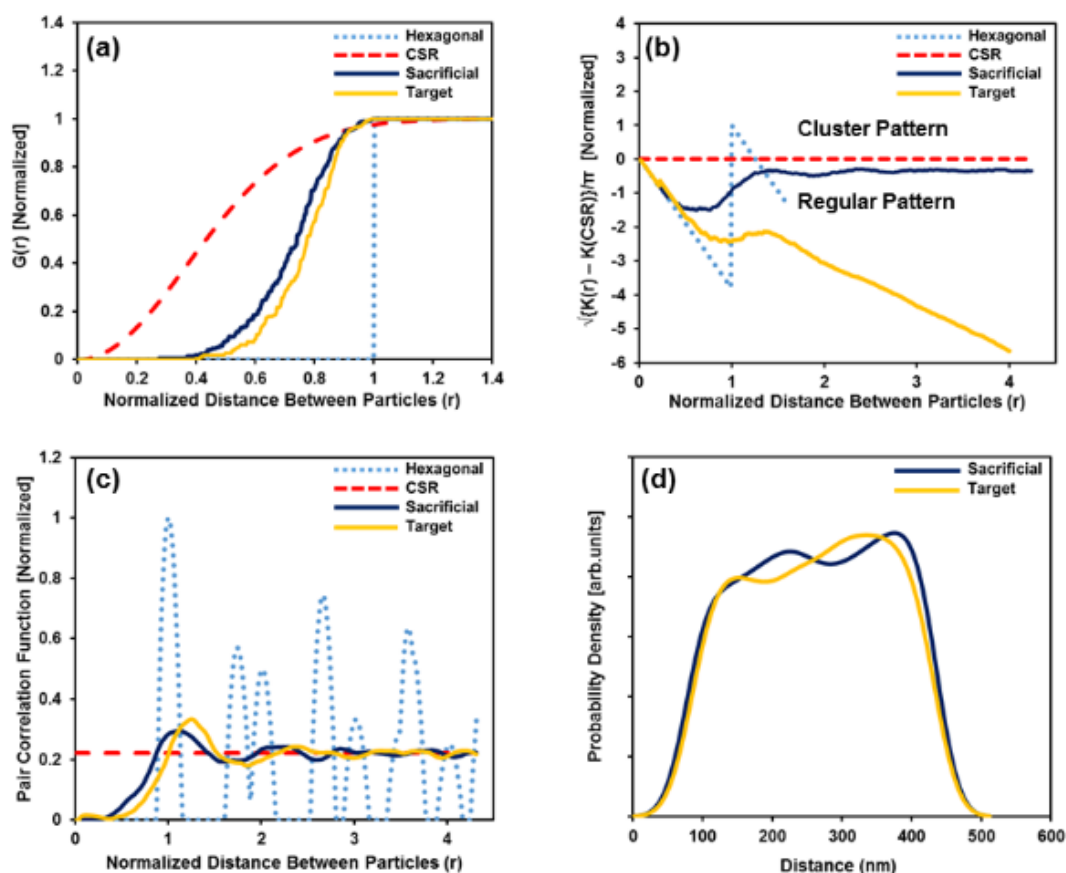


Figure 7.7. Spatial point pattern functions for sacrificial and transfer substrate. All are normalized to a hexagonal lattice dispersion with similar interparticle distances and density of particles per unit area. Expected values for complete spatial randomness (CSR) and the 2D hexagonal close packed lattice are also given for comparison. a) Cumulative nearest neighbor distribution function ($G(r)$); b) Difference spectrum for the linearized Ripley's K function compared to CSR (dotted red line); clustered patterns lie above the CSR line, while ordered regular patterns fall below the line; c) pair correlation function; d) Distribution of nearest neighbors showing the three nearest neighbor peaks for the sacrificial and target substrates, which indicate the preservation of the same order after transfer printing (**Figure S4**).

7.1.6 Wetting Contact Angle Measurements of pNIPAAm at 5 °C and 50 °C

We measured the wetting contact angle of sessile drops by using an optical tensiometer (Attension Theta Lite, Biolin Scientific AB, Stockholm, Sweden). Images were continuously recorded of the deionized water droplet from initial contact until it became stable, at a rate of 15 frames per second for 10 seconds, in the OneAttension version 2.3

software. To determine the contact angle, the captured images were automatically analyzed in the software by fitting

the drop profiles. The mean wetting contact angle was then calculated from the average contact angle extracted from all images captured during those ~10 seconds. The contact angle was measured on pNIPAAm at room temperature and at 50 °C. In order to perform the measurement of pNIPAAm at 50 °C, an electrically controlled heating plate (ThermoPlate, TOKAI HIT, Shizuoka-Ken, Japan) was mounted onto the sample stage, and the pNIPAAmcoated substrate was placed on top of the stage plate, once the plate had reached a stable 50 °C. These images show that the degree of surface wetting on the pNIPAAm at room temperature is more hydrophilic (Figure S5a) than pNIPAAm at 50 °C (Figure S5b).

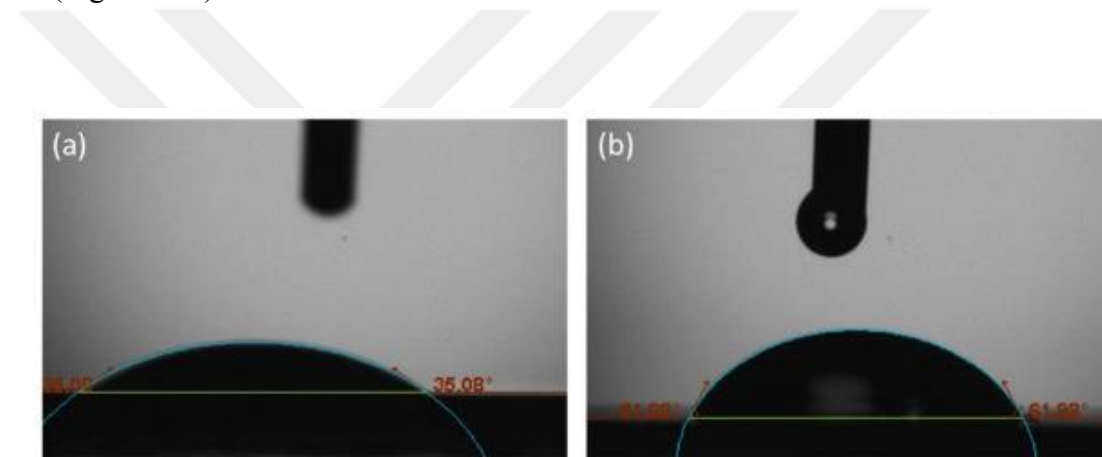


Figure 7.8. Contact angle measurements on different regions of the pNIPAAm deposited on PDMS stamp. a) below the LCST at 25 °C and b) above the LCST at 50 °C (Figure S5).

7.1.7 Unprocessed SEM Images of The Confirmation Experiments

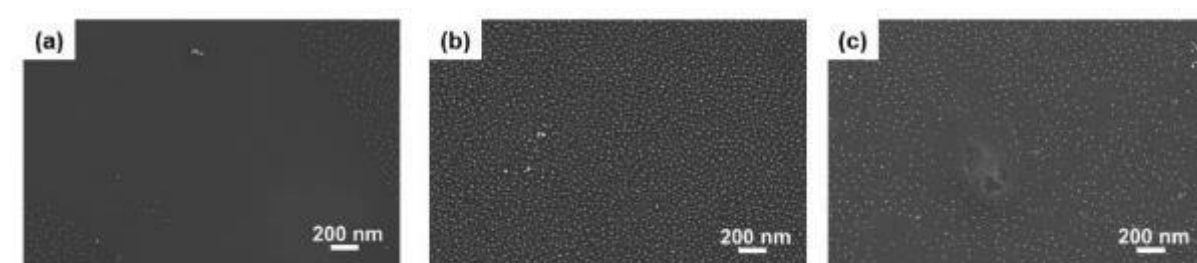


Figure 7.9. Original raw secondary electron images of a) sacrificial substrate after transfer printing at 5 °C; b) sacrificial substrate after transfer printing at 50 °C and c) target substrate after transfer printing at 50 °C, indicative of GNPs pick up only at 5 °C and GNPs release only at 50 °C (Figure S6).

7.1.8 Atomic Force Microscopy of the pNIPAAm Film: Lateral Uniformity of Surface Morphology and Elasticity

Samples of 10 mm x 10 mm size were mounted onto magnetic disks using double-sided adhesive tape. PeakForce QNM (Quantitative Nanomechanical Mapping) atomic force microscopy (AFM) mode and Bruker Multimode 8 was used to record surface topology, elastic modulus and adhesion maps. AFM measurements were performed using standard ScanAsyst-Air tips with resonant frequency of 70 kHz and spring constant of 0.4 N/m. Tip parameters were extracted from rough Ti reference substrate for tip shape and radius, sapphire reference substrate for cantilever deflection sensitivity using Nanoscope Analysis 1.40 software. The parameters further confirmed using low density polyethylene and polystyrene substrates. pNIPAAm surfaces were imaged using a scan size of 10 μm and a scan rate of 0.5 Hz. For validity of elastic modulus measurements, a minimum of 2 nm deformation is provided by adjusting peak force set point. All measurements were made under ambient conditions at room temperature and relative humidity of 50-60%. Gwyddion 2.44 and Nanoscope Analysis 1.40 software were used to process the obtained maps.

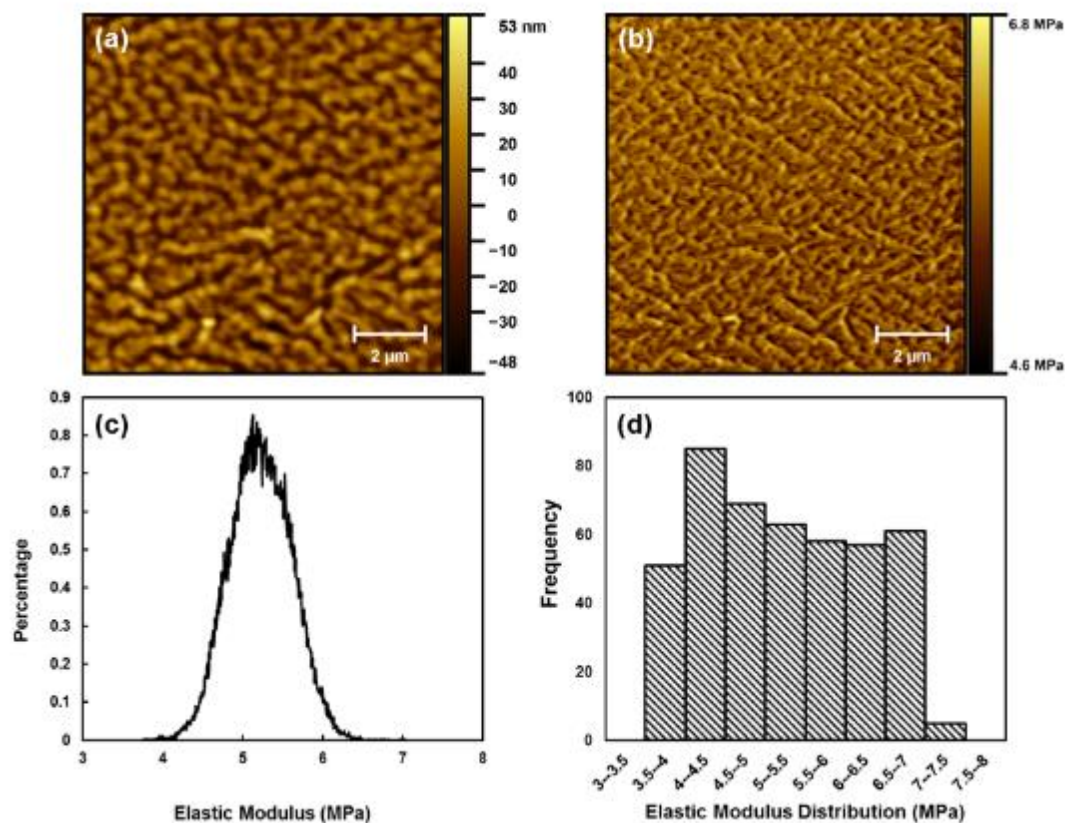


Figure 7.10. Atomic force microscopy images of the pNIPAAm at room temperature: a) topography map and b-d) elastic modulus distribution (**Figure S7**).

FFT of the images allow semi-quantitative comparison of spatial frequencies present in the images. To correlate the wrinkles on the stamp with the regions of transferred GNP arrays, the spatial frequencies in the AFM height image of the stamp (**Figure S8a and b**) is compared with those in a processed version of the SEM image of the transfer-printed, target substrate (**Figure S8c and d**). Represented by the limits of frequency distribution in the 2-D FFT patterns, the spread in spatial frequencies in the area covered by the GNPs is consistent with the spread of the same in the wrinkles on the stamp surface.

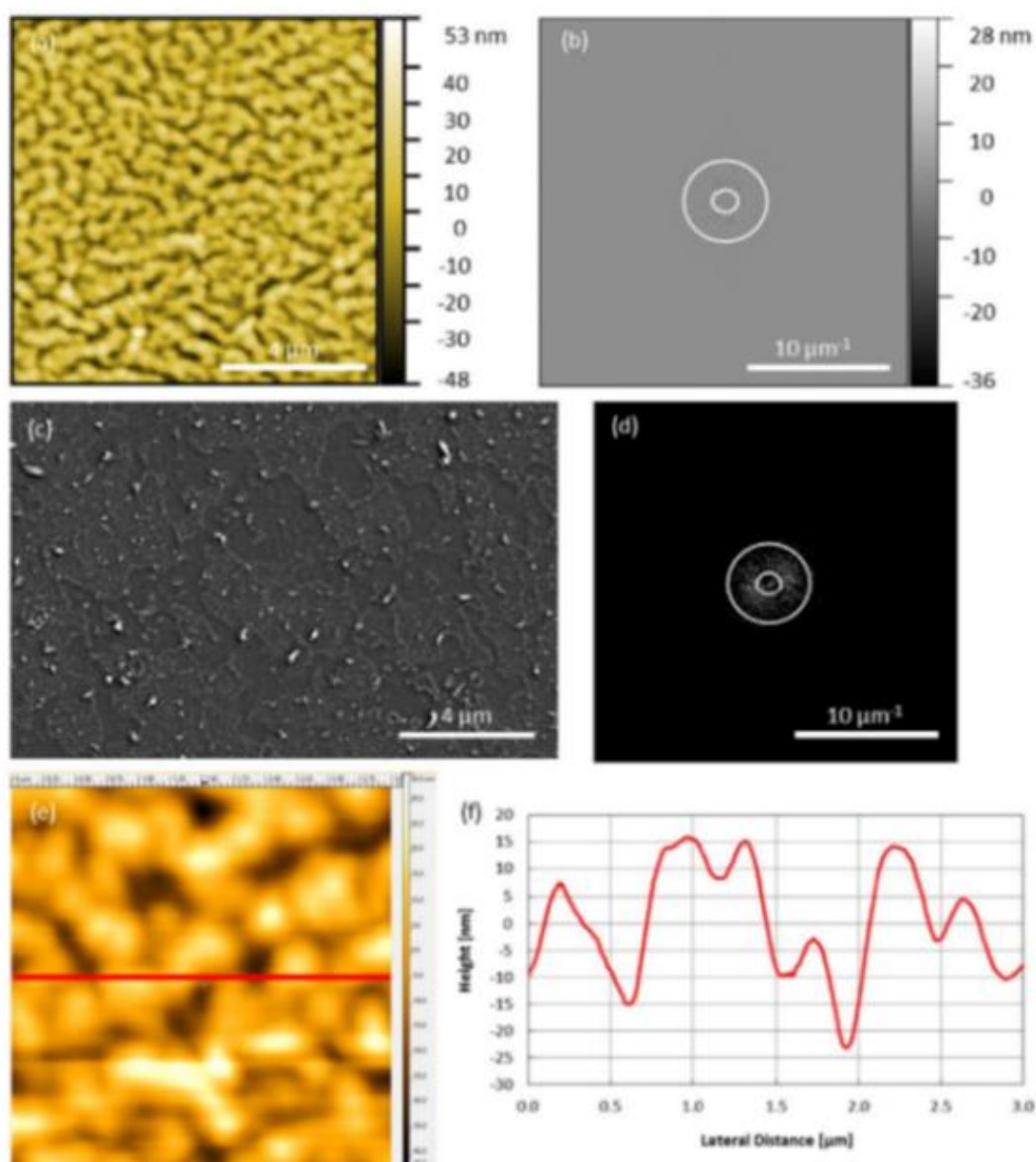


Figure 7.11. a) AFM height image of the pNIPAAm surface, b) FFT of AFM height image, c) SEM micrograph of a target substrate containing GNPs, d) FFT of the processed SEM image in part c; e) AFM height image of the pNIPAAm surface at higher magnification with f) line profile of height variation as indicated by the red line (**Figure S8**).

7.1.9 Ellipsometric Thickness Measurements of The pNIPAAm Stamp upon Heating up to 50 °C

Ellipsometry analysis (M2000 Spectroscopic Ellipsometer, J.A. Woollam Co., Inc.) was also carried out to confirm the volumetric transition of the pNIPAAm upon heating in the dry state in an ambient humidity of 70% RH.

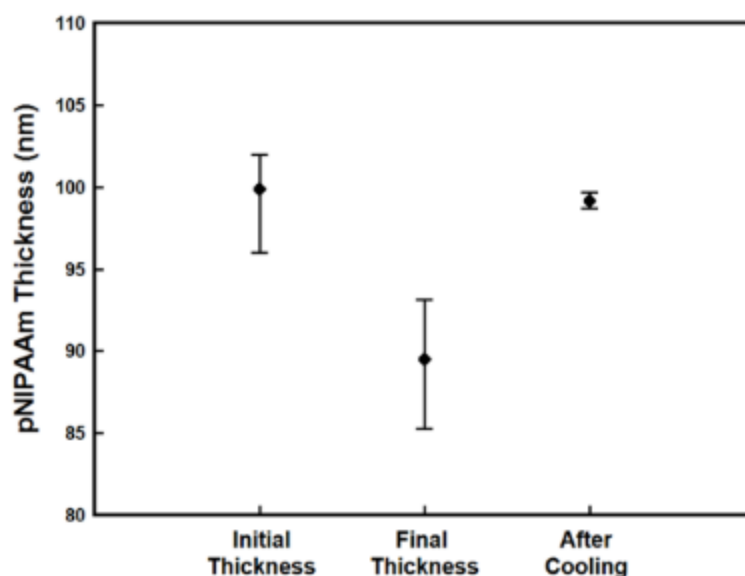


Figure 7.12. Variation in the thickness of pNIPAAm film upon heating from 25 °C up to 50 °C measured at three different locations on the same pNIPAAm film surface at ambient pressure (Figure S9).

7.1.10 Uniaxial Loading of a Bare PDMS Stamp on Sacrificial Silicon Wafer Substrate

A dynamometer was placed beneath the upper plate of a custom-built uniaxial loading system and a PDMS film deposited onto a silicon wafer substrate. The dimensions of both PDMS and silicon wafer were 2 cm x 1 cm. Pressure was applied constantly up to the fracture point of silicon wafer substrate and the normal force versus time was monitored on the screen. At the fracture point, a force of 180 N was recorded by the dynamometer.

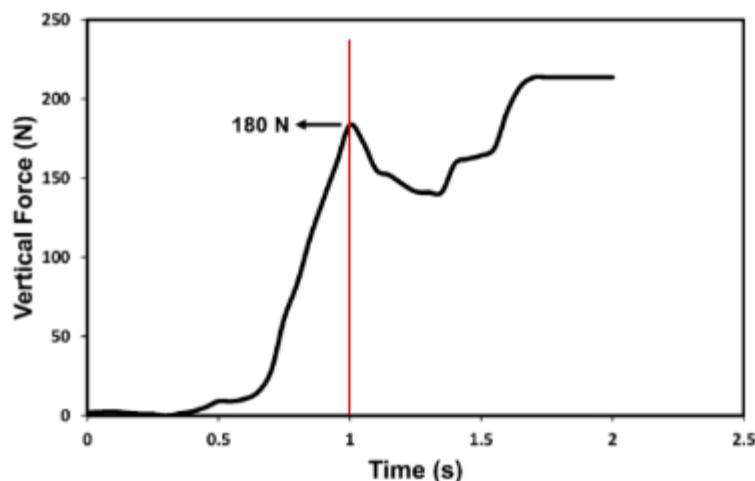


Figure 7.13. Vertical force of a home-made pressure device versus time for a PDMS stamp (1×2 cm) on a sacrificial silicon wafer substrate (1×2 cm). Sudden decrease in force indicates the fracture of silicon wafer substrate at a pressure of 900 kPa (**Figure S10**).

7.1.11 The Incorporation of Transfer Printed of Gold Plasmonic Particles into PCDTBT: PC70BM Bulk Heterojunction (BHJ) Polymer Solar Cells

We integrated the transfer-printed GNP array interlayers into poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]:[6,6]-Phenyl-C71-butyric acid methyl ester (PCDTBT:PC₇₀BM) bulk heterojunction (BHJ) devices. Pre-patterned indium tin oxide anode substrates (ITO, Ossila S101, Sheffield, UK) with and without GNP arrays were sonicated in acetone, methanol and isopropanol baths for 10 min each, prior to 30 min. UVozone treatment. A thin layer of diluted poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT: PSS, Heraeus Clevious™ PVP AI 4083, filtered at 0.45 μ m) was deposited by spin-coating (6000 rpm, $\sim$ 30 nm thickness) and annealed at 150 $^{\circ}$ C for 15 min under ambient conditions. PCDTBT (Ossila M137, Sheffield, UK; M_w 42200) and PC₇₀BM (Ossila M113, Sheffield, UK; 95%) were mixed in a 1:4 weight ratio in chlorobenzene.

PCDTBT: PC₇₀BM (20 mg/mL) solution was deposited by spin-coating at 3000 rpm for 60 s, resulting in a $\sim$ 70 nm thick layer. Layer thicknesses were measured using a surface profiler (KLA-Tencor P6, Milpitas, CA, USA). The samples were fabricated in ambient clean room conditions and immediately transferred to a thermal evaporator chamber and placed under high vacuum ($< 2 \times 10^{-6}$ mbar). To make the back-side electrical contact, we performed thermal evaporation of a 1.3 nm-thick LiF layer, followed by a 100 nm-thick

Al cathode layer on the organic active layers. The samples were then annealed at 80 °C for 15 min. after cathode evaporation under vacuum. The devices were subsequently encapsulated using UV-curable epoxy (Ossila E131, Sheffield, UK) and cured under 365 nm UV illumination.

GNPs show plasmonic behavior, which lead to field amplification, light scattering and light absorption—i.e., enhancing the interaction between incident sunlight and the active layers in photovoltaics. When nanostructures are significantly smaller than the wavelength of the incoming light, collective oscillations of electrons formed over the surfaces of nanostructures become localized, rather than propagating. Thus, the localized surface plasmon resonance (LSPR) behavior in GNP arrays can be exploited in light-trapping and field transmission amplification strategies in photovoltaics in order to improve device performance [211, 218].

We evaluated the performance of bulk heterojunction polymer solar cells containing the transfer-printed GNP array at the ITO anode. **Figure S11** shows the J-V characteristics of PCDTBT: PC₇₀BM solar cells under 1 sun illumination with and without transfer printed GNPs incorporated on the ITO anode. The transfer-printed GNPs improved the power conversion efficiency (PCE) of PCDTBT: PC₇₀BM solar cells by 32.2%. The open circuit voltage (V_{oc}) was improved by 50 mV, and the photogenerated short circuit current (J_{sc}) was increased by 27.6%. Both parameters combined contributed to a slight reduction in fill factor (FF) from 48% to 47% (**Table S1**).

Table 7.1. Characteristics of the PCDTBT: PC₇₀BM solar cells with and without transfer printed GNPs on the organic active layer (**Table S1**).

OPV	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF	PCE [%]
Control	0.844	-7.39	0.48	2.98
GNPs Incorporated	0.890	-9.43	0.47	3.94

As a proof-of-concept, we have demonstrated the transfer printing of a plasmonic particle array onto the ITO anode of a PCDTBT: PC₇₀BM BHJ OPV, during the device fabrication. The device performance was compared to one with an ITO anode, on which the plasmonic particle array was deposited directly in micelles and plasma etched. **Figure S11**, summarizing the device characteristics, shows that the performance was not

adversely impacted by the transfer printing process. In the device containing a transfer-printed GNP array, the plasmonic enhancement led to a 32.2% improvement in PCE.

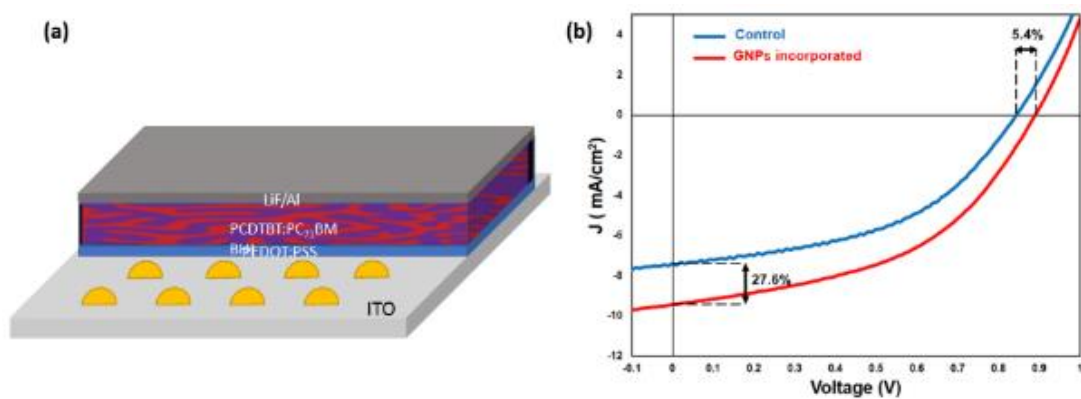


Figure 7.14. (a) Cross-sectional schematic of the plasmonic enhanced PCDTBT:PC₇₀BM solar cells, with a cut-away showing the location of the GNP layer; and (b) their J-V characteristics under 1 sun illumination, in comparison with devices without transfer printed GNPs, incorporated on ITO anode (**Figure S11**).

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