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INSTITUTE OF GRADUATE STUDIES
Department of Chemistry



**THE IMPACT OF THERMAL PROCESSING ON THE
FABRICATION OF SOME NANOSIZED METAL BORATES
AND HYDROTALCITE MATERIALS**

DOCTOR OF PHILOSOPHY

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Liska FADLIYANI

ABSTRACT

THE IMPACT OF THERMAL PROCESSING ON THE FABRICATION OF SOME NANOSIZED METAL BORATES AND HYDROTALCITE

MATERIALS

PHD THESIS

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This work investigated the impact of thermal processing on the fabrication of some nanosized metal borates and layered double hydroxides (LDHs). Metal borates and hydrotalcite materials were prepared via solution combustion synthesis (SCS), and sol-gel method, respectively. X-ray diffraction and FTIR spectroscopy were conducted for structural analysis, while UV-Vis, FESEM, and EDX provided insights into optical properties, morphology, and elemental composition of the synthesized materials.

In the first part of this study, The XRD analysis revealed that rare earth-doped magnesium pyroborates, $\text{Mg}_2\text{B}_2\text{O}_5: \text{RE}^{3+}$ (RE: Ce^{3+} , Eu^{3+} , Tb^{3+}) crystallized in monoclinic phases at 800°C , transitioning to triclinic phases at higher temperatures. Tartaric acid was identified as the most effective fuel and the optical band gap energy found to be between 3.20-5.70 eV. The FESEM-EDX studies confirming the presence of all elements in irregular granular morphology.

In the second part, nanosized beta- $\text{Li}_4\text{B}_2\text{O}_5$ was successfully synthesized for the first time using SCS with tartaric acid and glycine fuel, achieving high crystallinity rhombus-like morphology at 640°C and decomposing into Li_3BO_3 and $\text{Li}_6\text{B}_4\text{O}_9$ at higher temperatures. The optical band gap calculated to be varied from 3.00-3.05 eV. Additionally, the lithium magnesium borate was also prepared for the first instances with tartaric acid fuel at 400°C .

In the last part, nanosized double-metal substituted, $\text{Mg}_{3-x-y}\text{Zn}_x\text{M}_y$ (M: Cu and Mn)/ Al_1 LDHs were fabricated in plate-like morphology through low-temperature processing. EDX analysis confirmed the presence of all elements, while DRS analysis revealed that MgZnMn/Al LDHs had smaller optical band gaps (2.24-2.51 eV) than MgZnCu/Al LDHs (2.98–3.02 eV).

KEYWORDS: SCS, Sol-Gel, Pyroborate, Rare Earth Metal, Layered Double Hydroxide

ÖZET

ISIL İŞLEMİN BAZI NANO BOYUTLU METAL BORATLAR VE HİDROTALSİT MALZEMELERİN FABRİKASYONU ÜZERİNDEKİ ETKİSİ

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Bu çalışma, ısıtıl işlemin bazı nano boyutlu metal boratlar ve katmanlı çift hidroksitlerin (KÇH) fabrikasyonu üzerindeki etkisini araştırmıştır. Metal boratlar ve hidrotalsit malzemeler sırasıyla çözeltide yanma sentezi (ÇYS) ve sol-jel yöntemi ile hazırlanmıştır. Sentezlenen malzemelerin yapısal analizi, X-ışını kırınımı (XRD) ve FTIR spektroskopisi ile gerçekleştirilirken, optik özellikleri, morfolojisi ve elementel bileşimleri hakkındaki bilgiler sırasıyla, UV-Vis, FESEM ve EDX teknikleri ile sağlanmıştır.

Bu çalışmanın ilk kısmında, XRD verilerinin analizi, nadir toprak metali katkılı nano boyutlu magnezyum piroboratların, $Mg_2B_2O_5: RE^{3+}$ ($RE: Ce^{3+}, Eu^{3+}, Tb^{3+}$), $800^{\circ}C$ 'de monoklinik fazda kristalleştğini ve daha yüksek sıcaklıklarda triklinik faza dönüştüğünü ortaya koymuştur. Tartarik asitin en etkili yakıt olduğu belirlenmiş ve hesaplanan optik bant aralığı enerjilerinin, 3.20-5.70 eV arasında olduğu bulunmuştur. FESEM-EDX çalışmaları, bileşiklerin, düzensiz granüler morfolojide olduğunu ve istenen tüm elementlerin varlığını doğrulamıştır.

İkinci kısımda, nano yapıları beta-lityum piroborat, tartarik asit ve glisin yakıtları kullanılarak ilk kez ÇYS yöntemi ile başarıyla sentezlenmiş, $640^{\circ}C$ 'de yüksek kristalliniteye sahip rombus benzeri morfoloji elde edilmiş ve daha yüksek sıcaklıklarda Li_3BO_3 ve $Li_6B_4O_9$ 'a dönüştüğü gözlenmiştir. Optik bant enerji aralığı 3.00-3.05 eV arasında hesaplanmıştır. Ayrıca, lityum magnezyum borat, $400^{\circ}C$ 'de tartarik asit yakıtı ile ilk kez ÇYS yöntemiyle sentezlenmiştir.

Son kısımda, çift metal değişimli $Mg_{3-x-y}Zn_xM_y$ ($M: Cu$ ve Mn)/ Al_1 KÇH'ler, düşük sıcaklıkta nano boyutta plaka benzeri yapılar olarak üretilmiştir. EDX analizi, tüm elementlerin varlığını doğrulamış, DRS analizi ise Mn içeren KÇH'lerin, Cu içerenlere (2.98–3.02 eV) kıyasla daha küçük optik bant aralıklarına (2.24-2.51 eV) sahip olduğunu ortaya koymuştur.

ANAHTAR KELİMELE: ÇYS, sol-jel, piroborat, nadir toprak metali, katmanlı çift hidroksit

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LIST OF ABBREVIATIONS AND SYMBOLS

CA	: Citric Acid
DRS	: Diffuse Reflectance Spectroscopy
EDS	: Energy Dispersive Spectroscopy
EDX	: Energy Dispersive X-ray
FESEM	: Field Emission Scanning Electron Microscope
FT-IR	: Fourier Transform Infrared
HMDA	: Hexamethylenediamine
HMTA	: Hexamethylenetetramine
ICDD	: International Centre for Diffraction Data
LDH	: Layered Double Hydroxide
Ref	: Reference
SCS	: Solution Combustion Synthesis
SEM	: Scanning Electron Microscopy
TA	: Tartaric Acid
TEM	: Transmission Electron Microscopy
UV-Vis	: Ultraviolet-Visible
wt	: weight
XRD	: X-ray Diffraction

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1. INTRODUCTION

Boron is the element belongs to the group III-A of periodic tables and has chemical symbol of B. Boron was discovered partially by Joseph L. Gay-Lussac and L. J. Thénard in 1808 and Sir Humphry Davy afterward. Gay-Lussac and Thénard firstly isolated boron by the boric acid reaction with magnesium or sodium. They declared that the grey solid obtained has characteristics similar to sulfur and phosphorus and named it as *bore*. On the other hand, Humphry Davy succesfully obtained a powdery substance of boron by treating the boric acid with the potassium in the hydrogen atmosphere. But neither of their works produced high purity boron which is only 60% pure. In early nineteenth century, Ezekiel Weintraub was succesfully synthesized 99% pure boron by reducing boron halides with hydrogen. Boron containing minerals have been utilized by human beings for many years even 300 years before century.

Boron has the most interesting and diverse chemistry of any element. It has played an important role in modern chemistry areas such as in organic synthetic methodology and the molecular orbital theory of chemical bonding (1). Boron which is the 5th element of periodic table has two stable isotope namely ¹⁰B and ¹¹B in ratio of 20:80% with atomic mass of 10.81 amu. Owing to its distinct location in the periodic table that separates the metal and nonmetal elements, boron has interesting properties which facilitated the formation of numerous compounds with diverse chemical and physical properties. Boron characteristics are known to be similar to its neighbouring elements such as silicon and carbon. Boron is a highly metalloid element that has larger covalent radius and less electronegativity than carbon as 0.085 nm (C: 0.77 pm) and 2.04 (C: 2.55), respectively.

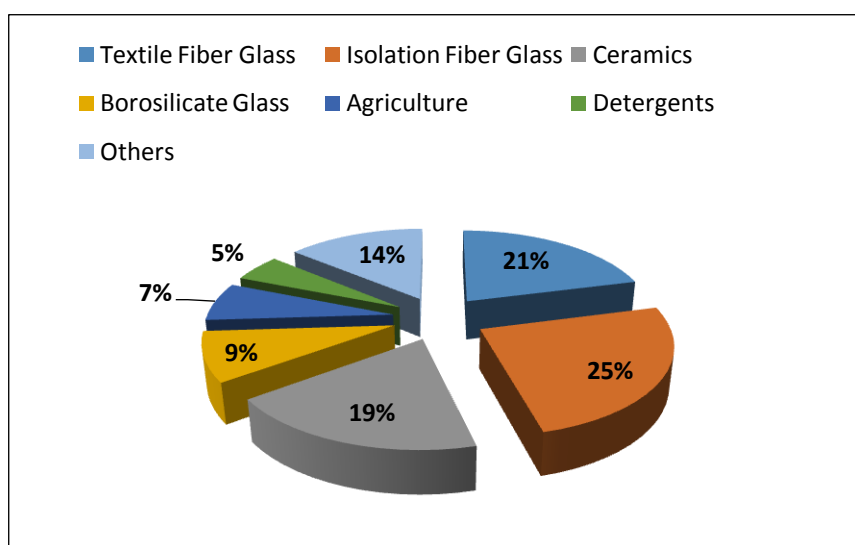
Boron is the element that does not appear in nature and occurs in environment through the natural process. Boron is generally found as boric acid and inorganic borates in soils, rocks, surfaces, and ocean waters. Although there are more than 200 types of boron minerals in earth's crust, only four minerals that commercially used for over 90% such as ulexite, $\text{NaCa}[\text{B}_5\text{O}_6(\text{OH})_6] \cdot 5\text{H}_2\text{O}$; the most dominant boron minerals that crystallize near hot springs alongside with tincal, kernite and colemanite (Table 1.1) (2,3).

Table 1.1. The most common boron minerals and their properties

Minerals	Formula	B ₂ O ₃	H ₂ O	Crystal Structures	Hardness
Ulexite	Na ₂ O-2CaO5B ₂ O ₃ .16H ₂ O NaCaB ₅ O ₉ .8H ₂ O NaCa[B ₅ O ₆ (OH) ₆] 5H ₂ O	42.95	35.57	triclinic	2.5
Tincal	Na ₂ B ₄ O ₇ 10H ₂ O Na ₂ O 2B ₂ O ₃ 10H ₂ O	36.51	47.24	monoclinic	2-2.5
Kernite	Na ₂ O 2B ₂ O ₃ 4H ₂ O Na ₂ B ₄ O ₇ 4H ₂ O Na ₂ [B ₄ O ₆ (OH) ₂] 3H ₂ O	50.95	26.37	monoclinic	2.5-3
Colemanite	2CaO 3B ₂ O ₃ 5H ₂ O Ca ₂ B ₆ O ₁₁ 5H ₂ O Ca[B ₃ O ₄ (OH) ₃] H ₂ O	50.80	21.92	monoclinic	4-5

Two main sources of boron minerals are found in Türkiye (45%) and USA (21%). Furthermore, Türkiye which known to be the largest borate producer in the world has been exporting mineral concentrates of tincal, ulexite and colemanite, borax pentahydrate (Na₂O-2B₂O₃-5H₂O), anhydrous borax (Na₂O-2B₂O₃), and boric acid (B[OH]₃).

Boron is a tough element and very resistant to heat. The boron-containing compounds have shown exceptional potential in wide range of application fields such as metallurgical, agricultural and also aerospace application. Boron also applied and used as optical data storage, gas storage, energy storage, molecular machines, energy conversion, wave guides, and multiphoton microscopy. Furthermore, the boron-containing compound also has a promising potential application as a catalyst in various organic transformations in medicinal chemistry which is essential in lives (2).

**Figure 1.1.** The major applied area of boron products (Ref. Eti Mining Co.)

1.1 BORATE

Naturally occurring boron is particularly found to be bound to oxygen as borates. The borates can be noticed as the salt of hydrated boron oxide which combines in B_2O_3 structural form where the ratio of the anion charge/boron atom is identical to the ratio of tetrahedral BO_4/B content. Due to its high affinity for oxygen, boron atom in the borate compounds are capable to form strong covalent of boron-oxygen bonds. The coordination of boron-oxygen can appear in two primary forms: triangular BO_3 and tetrahedral BO_4 . These configurations can be polymerized into diverse array of B_xO_y structures. Thus, it generally expressed in B_2O_3 form. According to the arrangement of their triangular BO_3 coordination, borates can be classified as orthoborates $[BO_3]^{3-}$, pyroborates $[B_2O_5]^{4-}$ and metaborate $[B_3O_6]^{3-}$.

Many borates with different compositions and crystal structures are considered to be promising among the research community in the past years (3). Owing to their appealing properties which are superb mechanical performance, high thermal and corrosive resisting, wide band gap semiconductor, significant industrial and mineralogical importance borates find application across various fields including ceramics, metal refining (especially gold and silver), anticorrosion compounds, pharmaceuticals, adhesives, abrasives, cosmetics, and also insecticides (2). Borates are also essential for further practical application in many fields of high technology such as mechanical strength, nonlinear optics, and laser technology. Because of its stability in different crystal structure and phases, borates compound has also been used as plasma display. Among all types of borates, metal borates have garnered particular attentions due to their exceptional mechanical strength, chemical inertness, low thermal expansion properties, excellent insulation, light weight, and outstanding corrosion resistance (4–9).

In this recent study, the works are focused on the pyroborates form of borates especially magnesium pyroborates and lithium pyroborates. Pyroborates were firstly characterized structurally by Berger in 1950 (10). The simplest triangular unit of borates is simplified as $B_2O_5^{4-}$ which comprises the anion of pyroborates. Within the pyroborate structure, B-O-B's angles are ranging between 111.8° to 138.7° and the coplanarity of terminal BO_2 torsion angles spanning from 1.6° to 67.0° . Also, the B-O bond length of triangular BO_3 lies between $1.28\text{\AA}$ to

1.43Å which is changed according to variation in the bond order within the coordinate arrangement (11).

The arrangement of $B_2O_5^{4-}$ in metal pyroborate varies based on the size of the alkali metal cations. The higher size of alkali metal cations lead to a more coplanar alignment of the B_2O_5 structure. The coplanarity of B_2O_5 increases with the size of the alkali metal cations and crystal structure of the pyroborate structure can be crystallized in monoclinic or triclinic symmetry with $P2_1/c$ or $P1$ of space group, respectively. The unit cell of monoclinic structure contains $Z = 4$ and $Z = 2$ formula units for the triclinic crystal structure.

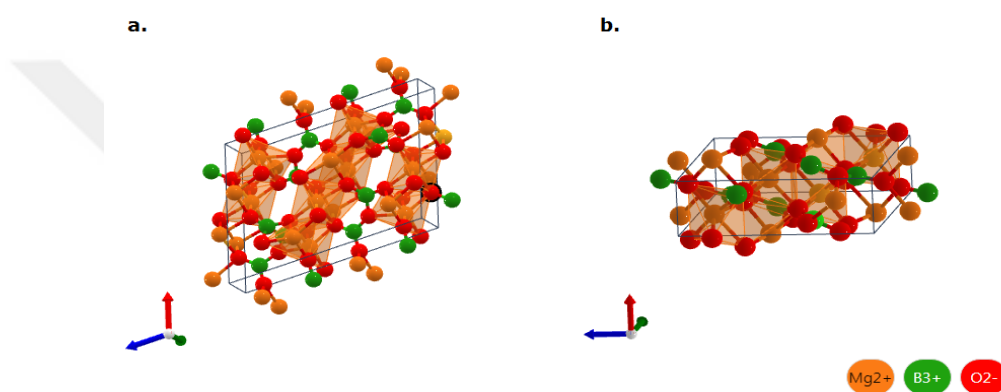


Figure 1.2. The crystal structure of magnesium pyroborates a) monoclinic
b) triclinic

The pyroborates can be categorized as alkaline-earth metal and transition metal based pyroborates. The pyroborates with alkaline earth metal based known as $A_2B_2O_5$ where A is an alkaline earth metal. The type of pyroborates has been studied and reported in different crystal structure such as $Ba_2B_2O_5$ crystallize in $P2_1/m$ space group (12), $Mg_2B_2O_5$, $Ca_2B_2O_5$ and $Sr_2B_2O_5$ isotopically crystallizing in $P2_1/c$ space group (13–15). In addition, Guo et al. stated $Mg_2B_2O_5$ also crystallize in $P1$ space group, triclinic magnesium pyroborates (16). The studies about naturally occurring minerals have also confirmed the presence of mixed alkaline-earth-based pyroborates ($AA'B_2O_5$). It is disclosed that kurchatovite and clinokurchatovite which are two polymorphs of $CaMgB_2O_5$ are crystalizing in space group types $Pc2_1b$ and $P2_1/c$, respectively (17,18). However, later in 2003, Callegary et.al reported that these two polymorphs crystallize in space group $Pbca$ for kurchatovite and type $P2_1/c$ space group for clinokurchatovite (19).

The pyroborates with transition metal based, $MM^I B_2O_5$ where M is the transition metal. If the transition metals are similar, $M = M^I$, the pyroborate is called homometallic pyroborates. The research on homometallic pyroborates have been done in the past years such as $Co_2B_2O_5$, $Cd_2B_2O_5$, $Mn_2B_2O_5$, and $Fe_2B_2O_5$ (11,20–23).

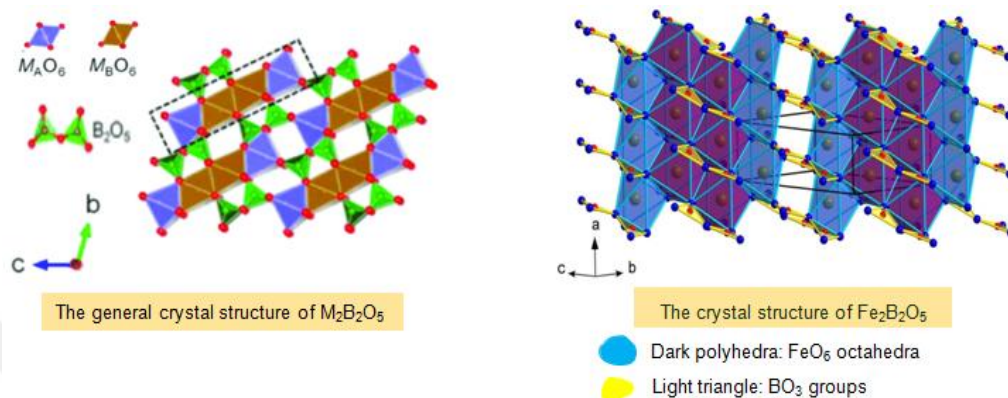


Figure 1.3. The general crystal structure of homometallic pyroborates

Pyroborates is known to be hetero-metallic when the transition metal that composed is different.. In the heterometallic compounds, the materials are intrinsically disordered because the metal ions occupy the both sites. The most strongly bonded pyroborate group $(B_2O_5)^{4-}$ is the bond that is formed by two trigonal $(BO_3)^{3-}$ groups. Each of the five oxygen ions simultaneously belongs to both octahedron and the pyroborate group. Many attempts have also been done in the preparation of heterometallic pyroborates or known as mixed metal pyroborates such as $BaCuB_2O_5$, $MnCoB_2O_5$ and $MnMgB_2O_5$, $BaMnB_2O_5$, $Mg_xMn_{2-x}B_2O_5$, $Co_{2-x}Ni_xB_2O_5$ (24–29).

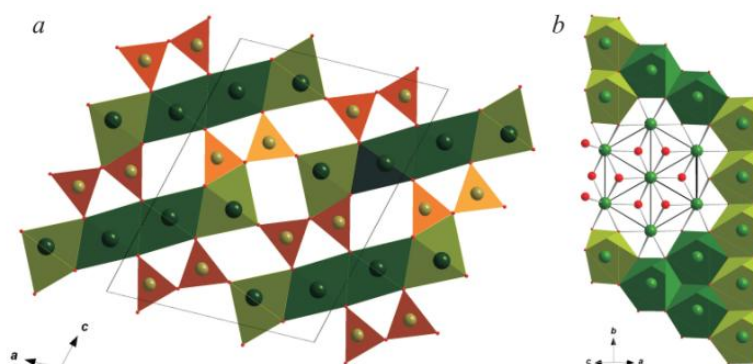


Figure 1.4. The general crystal structure of heterometallic pyroborates $CoNiB_2O_5$ (29).

1.1.1 Rare-Earth Metal Doped Borates Compounds

Metal borates gave remarkable potential in many optoelectronics, optical fibre and electronic materials due to their great luminescent properties. Rare Earth (lanthanide) doped metal borates have recently become a particularly active subject area of study due to their sharp fluorescence behavior in ultraviolet, visible and infrared regions, as well as their shielding effects on the 4f electrons by outer 5s and p orbitals. Hence, it also has reported that metal borates have good solubility of lanthanide metal ions and the addition of lanthanide metal ions as dopant within borate compounds can induced their magnetic and spectroscopic properties. The studies related to the metal borates doped rare-earth metal ions have been investigated in recent years, such as;

- **Ba₂Mg (BO₃)₂: Eu³⁺**

The structure of Ba_{1.98}Eu_{0.02}(BO₃)₂, a buetschliite derivative, has been elucidated using single-crystal X-ray diffraction, revealing the following crystal parameters: a = 5.343(2) Å, c = 16.520(3) Å, V = 408.4(2) Å³, Z = 3, and space group R3m. The compound Ba_{1.98}Eu_{0.02}(BO₃)₂, exhibits strong emission when excited by ultraviolet light, with excitation and emission maxima located at 359 nm and 608 nm, respectively(30).

- **InBO₃ and TbBO₃: Ce³⁺, Eu³⁺**

The change in the structural and luminiscence properties of the lanthanide metal ions doped TbBO₃ and InBO₃ were analyzed. The doping of cerium ion into Eu³⁺ doped TbBO₃ exhibited markedly different results in the absorption spectra due to the 4f-5d transition. It also noticed that the crystal structure of InBO₃ from calcite into veterite was observed in the inclusion of europium and terbium ions. The alteration in the crystal structure is also affecting the intensity of the Eu³⁺; ⁵D₀ → ⁷F₂ transition and the arise in the excitation band was also detected due to the existence of the rare earth metal, Eu³⁺ and Tb³⁺. In the TbBO₃: Eu³⁺, Ce³⁺, 4f-5d transition of Ce³⁺ were found at around 320-380 nm (31).

- **LiSr₄(BO₃)₃ : Ce³⁺, Eu³⁺, Tb³⁺**

Time-resolved and photoluminescence (PL) properties of cerium, europium and terbium doped LiSr₄(BO₃)₃ were investigated.

- In the excitation spectra of cerium doped $\text{LiSr}_4(\text{BO}_3)_3$, the two broad peak are detected at 280 nm and 340 nm whereas emission peak are noticed at 420 nm upon UV excitation at 350 nm. The luminescence also attributed to the transition of $5d-4f$ on Ce^{3+} .
 - The red emission of Eu^{3+} doped $\text{LiSr}_4(\text{BO}_3)_3$ were observed under the 260 and 393 nm excitation consisting the transition from the $^5\text{D}_0$ to $^7\text{F}_j$ levels. Five emission peaks are found at 578, 585, 613, 650 and 685 nm which are ascribed to the $^5\text{D}_0 \rightarrow ^7\text{F}_0$, $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$, $^5\text{D}_0 \rightarrow ^7\text{F}_3$, $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions, respectively. Broad excitation bands are observed at 260 nm with intense absorption peak of $f \rightarrow f$ absorption.
 - $\text{LiSr}_4(\text{BO}_3)_3: \text{Tb}^{3+}$ showed the strongest $^5\text{D}_4 \rightarrow ^7\text{F}_5$ emission peak at 540 nm. The intense absorption peak at 317, 351, 367, 377, and 485 nm are noticed due to the transition from $^7\text{F}_6$ to $^5\text{D}_j$, $^5\text{G}_j$, $^5\text{L}_{10}$, $^5\text{D}_3$, and $^5\text{D}_4$, respectively. Furthermore, The $^4\text{F}_8 \rightarrow ^4\text{F}_7$ $^5\text{D}_1$ transition of Tb^{3+} ion is observed at 280 nm (32).
- **$\text{LnAl}_3(\text{BO}_3)_4$ (Ln= Gd, Y, Lu): Ce^{3+}**
 Luminescence properties of cerium doped gadolinium and yttrium were compared with the $\text{LuAl}_3(\text{BO}_3)_4: \text{Ce}^{3+}$ which has been fabricated for the first time through solid state reaction method. Two bands of the emission spectra which belonged to the $^5\text{D}_1 \rightarrow ^2\text{F}_{5/2}$ and $^5\text{D}_1 \rightarrow ^2\text{F}_{7/2}$ transitions and five bands of the excitation spectra contributed to the crystal field levels at $^5\text{D}_1$ configuration were reported. The compounds of 0.5% doped $\text{LnAl}_3(\text{BO}_3)_4$ (Ln= Gd, Y, Lu) exhibit UV excitation at 4.6 eV, 270 nm and two emission bands in the 2.9–3.8 eV at 325–425 nm region. This phenomenon are due to the transition of Ce^{3+} $5d \rightarrow 4f$ (33).
- **$\text{LuBO}_3: \text{Ce}^{3+}$ and Eu^{3+}**
 In 2015, the rare earth metal doped LuBO_3 was acquired by the wet process where 0.5% mol of cerium and 5.0% mol of europium were applied. Reportedly, the $^7\text{F}_0 \rightarrow ^5\text{D}_0$ excitation spectra were detected for the 5 % mol Eu^{3+} doped at 300 K and the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ emission band at 610.5 nm (34).

- **MgB₄O₇: Ce³⁺, Li⁺**
This investigation on the optically stimulated luminescence (OSL) of magnesium tetraborate crystals doped with dysprosium (Dy) or cerium (Ce) and co-doped with lithium (Li), have been characterized through their OSL and radioluminescence emissions. The results show that MgB₄O₇: Ce, Li exhibits a strong emission peak at 420 nm, attributed to Ce³⁺ transitions, while MgB₄O₇:Dy, Li displays multiple peaks corresponding to Dy³⁺ transitions (35).
- **MgB₄O₇: Ce³⁺, Li⁺**
0.5% mol cerium doped MgB₄O₇ have been synthesized by Saoza L.F et.al via solid state reaction method and the dosimetric characteristics of the acquired sample were examined. An optical bleaching device which composed of six LED plates emitted blue light at 470 nm (35).
- **MgB₄O₇: Dy³⁺**
The thermoluminescence analysis on dysprosium doped MgB₄O₇ have been conducted by S. İflazoğlu et.al in 2019. It is stated that the crystal structure of the synthesized doped MgB₄O₇ are not altered by the addition of dysprosium and could be considered as neutron+gamma dosimeter. The TL neutron sensitivity of the samples was compared, and it was found that the MgB₄O₇ (1%) sample is more sensitive to neutron doses than the undoped MgB₄O₇, as well as the 0.1% and 0.5% Dy-doped MgB₄O₇ samples (36).
- **MgB₄O₇: Tb³⁺**
Polycrystalline MgB₄O₇ samples doped with various concentrations of terbium were synthesized using the solvent evaporation method. The 1 % mol of Tb-doped sample showed the highest luminescence intensity. Its glow curve featured a prominent TL peak at 220°C and a minor shoulder at approximately 330°C. Additionally, the TL spectra and fluorescence of the 1 mol% Tb-doped sample showed strong terbium emission lines at 489, 545, 588, and 622 nm (37).
- **MgB₄O₇: Eu³⁺**
This study explores the thermoluminescence (TL) dosimetric properties and density functional theory (DFT) analysis of Eu-doped MgB₄O₇

phosphor. The material, synthesized via a simple hydrothermal method, was irradiated with 100 MeV Ag^{7+} and Ni^{7+} ion beams across a fluence range of 1×10^{10} to 5×10^{12} ion/cm². Comparative investigations reveal that the photoluminescence emission, with peaks at approximately 593 nm and 625 nm, corresponds to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions of Eu^{3+} ions. The study also examines how ion beam fluence affects these photoluminescent properties (38).

- **$\text{Mg}_3\text{B}_2\text{O}_6: \text{Eu}^{3+}$**

Hierarchical microspheres of flower-like $\text{Mg}_3\text{B}_2\text{O}_6$ with average size of diameter of 2.0 to 2.5 μm were synthesized through a precipitation method, employing poly(vinyl pyrrolidone) as a template, followed by a heat treatment process. The structural, morphological, compositional, and photoluminescence (PL) characteristics of the synthesized and calcined samples were thoroughly analyzed (39).

- **$\text{Mg}_3\text{B}_2\text{O}_6: \text{Eu}^{3+}$**

The synthesis of europium doped magnesium orthoborates was first achieved by Uztetik Morkan, A. & Gul, E. (2018) via solution combustion method. The luminescence studies on doped compounds were examined by emission and excitation spectra. Based on the excitation spectra, the defining bands of europium ions were detected at 420 nm and 613 nm whereby the emission spectra of the highest intensity red emission peak were found at 630 nm in accordance with $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition (40).

- **$\text{NaBa}_4(\text{BO}_3)_3: \text{Ce}^{3+}$ and Eu^{3+}**

The luminescence properties of cerium and europium in the synthesized compound showed that the cerium doped gave the intense band at 350 nm and subtle peak at elevated energy level. The emission spectrum of cerium doped compound exhibit the blue band at 420 nm. Two emission band were also noticed at 410 nm and 445 nm belongs the lowest 5d excited state to $^2\text{F}_{5/2}$ and $^2\text{F}_{7/2}$ ground state, orderly. The excitation of the transition from $^5\text{D}_0$ to $^7\text{F}_J$ observed in the Eu^{3+} doped $\text{NaBa}_4(\text{BO}_3)_3$ which involved $^5\text{D}_0 \rightarrow ^7\text{F}_0$ (575 nm), $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (590 nm), $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (610 nm), $^5\text{D}_0 \rightarrow ^7\text{F}_3$ (650 nm), and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ (700 nm) transitions. Furthermore, the broad excitation bands also found at 270 nm in the excitation spectrum (41).

- **NaSr₄(BO₃)₃: Ce³⁺**

The solid state reaction method has also been utilized in the formation of cerium and manganese doped NaSr₄(BO₃)₃. The phosphor emit two different colors; Ce³⁺ emits a blue band with a peak at 435 nm and Mn²⁺ emits a red band at 660 nm. Additionally, two excitation bands belongs to Ce³⁺ were detected at 295 and 350 nm in the photoluminescence excitation spectrum contributed to the 4f¹–5d¹ transition (42).

- **NaSr₄(BO₃)₃ : Tb³⁺**

In 2014, the combustion synthesis has carried out for the fabrication of terbium (III) doped NaSr₄(BO₃)₃. The photoluminescence studies of the sample are also examined. The green characteristic emission band was observed under the 236 nm UV excitation. The sharp emission peak assigned at 486 nm, 544 nm, and 585 nm correspond to the transition from ⁵D₄ to ⁷F_J (J=3,4,5,6) in the 4f⁸ configuration of terbium ion (43).

- **Sr₂B₂O₆ : Ce³⁺, Eu³⁺**

The phosphors Sr_{2.955}B₂O₆:0.02Ce³⁺, 0.005Eu²⁺, 0.02A⁺ (where A = Li, Na, or K) were synthesized using a high-temperature solid-state reaction method. In these phosphors, Ce³⁺ emits in the blue region, while Eu²⁺ emits in the yellow region. The observed white light is a result of partial energy transfer from Ce³⁺ to Eu²⁺ in Sr₃B₂O₆, leading to the mixing of blue and yellow emissions. Additionally, the synthesized materials were characterized using PXRD and FT-IR analyses (44).

- **Sr₂B₂O₆ : Tb³⁺**

Strontium borates doped with terbium have been synthesized through combustion using urea as a fuel at 550 °C. The morphology of the phosphors reveals rod-like structures. Photoluminescence (PL) results indicate that the Sr₂B₂O₅ host is suitable for trivalent terbium emission, which peaks at wavelengths of 422 nm, 439 nm, 463 nm, 545 nm, 588 nm, and 625 nm when excited at 353 nm due to the 5d–4f transition. The strongest green emission occurs at 545 nm, corresponding to the ⁵D₄ → ⁷F₅ transition (45).

- **Zn₃B₂O₆: Ce³⁺**

The luminescence results revealed a strong emission in the 340 to 400 nm range for the synthesized Zn₃(BO₃)₂: Ce³⁺ sample. The sample doped with 0.5% Ce³⁺ (by mole) exhibits the maximum luminescent intensity. In this system, Ce³⁺ ions substitute for Zn²⁺ in the host material and function as emission centers, while Mn²⁺ acts as an activator. Although the position of the emission peak remains unchanged, the emission intensity of the Ce³⁺, Mn²⁺ co-doped samples is significantly altered with the addition of Ce³⁺ (46).

1.1.1.1 Rare-Earth Metal Doped Metal Pyroborates

Owing to their great optical properties, the studies of rare earth metal doped pyroborates have also been carried out by many research communities, namely;

- **Ba₅(BO₃)₂(B₂O₅): Ce³⁺**

Zhang. H et al has reported the preparation of Ba₅(BO₃)₂(B₂O₅):Ce³⁺ in 2016 by solid state reaction method. Near ultraviolet region a broad blue emitting phosphor are excited at 351 nm. With the increasing Ce³⁺ doping material, the emission intensities are observed and attained a maximum at 0.04 mol% (47).

- **Ba₂B₂O₅: Ce³⁺**

A blue emitting phosphor cerium doped Ba₂B₂O₅ have been fabricated by a high temperature solid state method. The investigation of its thermal stability and luminescent properties were done. It was reported that the broad blue emission band were detected below 350 nm and the transition of 5d¹–4f¹ was observed at 417 nm. Also, Ba_{1.97}B₂O₅:0.03Ce³⁺ has the emission intensity of 63.4% when turned up to 150°C (48).

- **Ba₂B₂O₅: Ce³⁺**

In the same year, Liu Q et.al has also synthesized and investigated a Ba₂B₂O₅:Ce³⁺ blue-emitting phosphor. The sample were fabricated by solid state reaction method. The sharp blue emission peaks of Ba₂B₂O₅:Ce³⁺ phosphor were assigned at around 423 nm consequent to 350 nm near-UV excitation. The Ce³⁺ critical quenching in the

$\text{Ba}_2\text{B}_2\text{O}_5$ was revealed to be 5 mol% with observed dipole-dipole interaction demonstrating great thermostability at about 200 °C (49).

- **$\text{Ba}_2\text{B}_2\text{O}_5: \text{Eu}^{3+}$**

High temperatures solid state reaction methods have applied in the synthesis of barium pyroborates doped europium ion. The final products were obtained after annealed and sintered for 3 hours at 900°C. The red emission was observed at 393 nm and the quenching concentration effects showed that europium doped $\text{Ba}_2\text{B}_2\text{O}_5$ have potential red phosphors for the white LEDs (50).

- **$\text{Ba}_2\text{B}_2\text{O}_5: \text{Ce}^{3+}, \text{Dy}^{3+}$**

Solid state reaction were applied in the preparation of $\text{Ba}_2\text{B}_2\text{O}_5$ codoped $\text{Ce}^{3+}/\text{Dy}^{3+}$. The luminescent properties and energy transfer were studied. Two intense peaks which belong to the transition of Dy^{3+} ions, $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ were found. It has been reported that the energy transfer of cerium to dysprosium in the $\text{Ba}_2\text{B}_2\text{O}_5$ host material resulting a broad peak with the addition of Ce^{3+} as sensitizer. Dy^{3+} presented a good thermal stability with Ce^{3+} blue-shift of emission (51).

- **$\text{Ca}_2\text{B}_2\text{O}_5: \text{Eu}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}$**

In 2016, calcium pyroborates doped europium; terbium and dysprosium rare-earth metal ions have been prepared by hydrothermal reaction methods. The luminescence properties of the compounds were observed to be in red, green and white for Eu^{3+} , Tb^{3+} and Dy^{3+} , respectively. It also stated the Dy^{3+} dopant gave the highest luminescence lifetime of 3.05 ms. The absolute quantum efficiency of Eu^{3+} , Tb^{3+} , Dy^{3+} are measured to be 65%, 35% and 37 %, respectively for the excitation in near ultraviolet region (52).

- **$\text{Ca}_2\text{B}_2\text{O}_5 \cdot \text{H}_2\text{O}: \text{Tb}^{3+}$**

The photoluminescence properties of pyroborates, $\text{Ca}_2\text{B}_2\text{O}_5 \cdot \text{H}_2\text{O}: \text{Tb}^{3+}$ was determined by AuSiO_2 hybridization through hydrothermal method. The distance between the pyroborates and the gold nanoparticles reported to be affecting its photoluminescence properties. Furthermore, the structural and

morphology of the synthesized products were also characterized by XRD, SEM, EDS, FESEM and also TEM (53).

- **Mg₂B₂O₅: Dy³⁺**
Dysprosium doped magnesium pyroborates have prepared by wet reaction method with various dopant concentrations. An exceptional gamma rays and thermoluminescence response were observed by 1% Dy³⁺ and the peaks' intensity fluctuates as the temperature rises (54).
- **Mg₂B₂O₅: Eu³⁺**
Magnesium pyroborate doped europium nanorods has been employed by calcining the as synthesized magnesium pyroborates nanowire with europium oxide, Eu₂O₃ at 930°C in air atmosphere. By SEM and TEM analysis, it reported that the nanowires Mg₂B₂O₅ and nanorod Mg₂B₂O₅: Eu³⁺ has diameter equal to 25-40 nm and 110-130 nm, respectively. Europium doped magnesium pyroborate has a great potential as green or orange phosphors (55).
- **Mg₂B₂O₅: Eu³⁺**
Very recently, the synthesis of Eu³⁺ doped triclinic magnesium pyroborate has been investigated by Kumar J. et al in 2020. The pyroborates were prepared in three different dopant concentrations such as 1%, 3% and 5% by low temperature combustion method. It is reported that the crystallite size of pyroborates decreases with europium doping and the sharp peak of excitation are detected at 325 nm during the photoluminescence analysis. The structural, luminescence and also diffuse reflectance analysis of triclinic magnesium pyroborates were also discussed (56,57).
- **Sr₂B₂O₅: Dy³⁺**
Solution combustion synthesis method has also been used in the synthesis of strontium pyroborates doped dysprosium (III) ion. The compounds are obtained at 900°C and crystallite sizes are between 45 and 49 nm for various compositions of Dy³⁺ ions. In the excitation spectrum of photoluminescence of the Dy³⁺ ions are detected in the ultraviolet and near ultraviolet regions. Four distinct emission peaks are observed such as blue emission at 485 nm (⁴F_{9/2} → ⁶H_{15/2}), yellow emission at 575 nm

($^4F_{9/2} \rightarrow ^6H_{13/2}$), red emission at 668 nm ($^4F_{9/2} \rightarrow ^6H_{11/2}$) and brownish red emission at 701 nm ($^4F_{9/2} \rightarrow ^6H_{9/2}$). The optical bandgap values of each dopants are also vary from 4.2 to 4.8 eV (58).

- **$Sr_2B_2O_5: Ce^{3+}, Tb^{3+}$**

Another lanthanides doped strontium pyroborates have been examined by solid state method applying Ce^{3+} and Tb^{3+} as dopant materials. It is showed the prepared phosphor can be excited effectively near-ultraviolet with double color at 392 nm which exhibit blue light emitting for Ce^{3+} (F-D transition) and emitted green light for Tb^{3+} (F-F transition) at 545 nm (59).

- **$Sr_2B_2O_5: Eu^{3+}$**

The luminescence properties and crystal structure of red phosphors $Sr_{1.93}B_2O_5$ doped $0.07Eu^{3+}$ was investigated. The sample was fabricated by high-temperature solid state reaction method at 1050°C with 2 h of heating time. The monoclinic strontium pyroborates consisted of six emission bands such as 579 nm, 592 nm, 611 nm, 620 nm, 650 nm and 700 nm with the highest band is marked at 611 nm which derived from the transition of $^5D_0 \rightarrow ^7F_2$. The sample also excited in near ultraviolet region with broad band at 260 nm and followed by the sharp excitation peaks at 320 nm, 362 nm, 382 nm, 394 nm, 416 nm and 466 nm (60).

- **$Sr_2B_2O_5: Tb^{3+}$**

The combustion synthesis method has been applied in the formation of terbium doped strontium pyroborates. Green emitting phosphors were obtained at 550°C in monoclinic crystal structure with $P2_1/c$ space group. Ensuing to the D-F transition at 545 nm ($^5D_4 \rightarrow ^7F_5$) the green emission was assigned, along with the excitation bands at 353 nm (45).

- **$Sr_2B_2O_5: Tm^{3+}, Na^+$**

Blue phosphor of lanthanide doped pyroborates has also been discussed by Lihan Cai et al. They have synthesized $Sr_2B_2O_5$ with Tm^{3+} and Na^+ doped via solid state method. The transitions of $^1D_2 \rightarrow ^3F_4$ and $^1G_4 \rightarrow H_6$ were detected for Tm^{3+} and Na^+ , respectively. At 457 nm, the emission spectra that specify the blue emitting of Tm^{3+} were observed whereas the bands were

observed at lower wavelength for Na^+ . It is claimed that $\text{Sr}_2\text{B}_2\text{O}_5$ doped Tm^{3+} and Na^+ are potentials phosphors for W-LED (61).

▪ **$\text{Sr}_2\text{B}_2\text{O}_5$: Tb^{3+} , Yb^{3+}**

The monoclinic phase of synthesized strontium pyroborates were fabricated by solid state reaction method and characterized. The photoluminescence spectrum showed three intense excitation peaks at 354, 374 and 487 nm monitored at intense absorption in near-UV region at wavelength of 543 nm and 980 nm. The excitation at 374 nm leads to a high visible emission intensity which is contributed to the $^5\text{D}_4 \rightarrow ^7\text{F}_j$ ($j=6, 5, 4, 3$) transition of Tb^{3+} and the emission observed near-infrared (NIR) were originated from $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ transition of Yb^{3+} (62).

▪ **$\text{Sr}_2\text{B}_2\text{O}_5$: Eu^{3+}**

Several borate phosphors (SrB_2O_4 , SrB_4O_7 , $\text{Sr}_2\text{B}_2\text{O}_5$ and $\text{Sr}_3\text{B}_2\text{O}_6$) doped Eu^{3+} doped were prepared by solid state reaction and sol-gel method. It is showed that all of the phosphor gave different luminescence properties. The red emission spectra was observed at 610 nm for $\text{Sr}_2\text{B}_2\text{O}_5:\text{Eu}^{3+}$ and $\text{Sr}_3\text{B}_2\text{O}_7:\text{Eu}^{3+}$ phosphors whereas the $\text{SrB}_2\text{O}_4:\text{Eu}^{3+}$ and $\text{SrB}_4\text{O}_7:\text{Eu}^{3+}$ has the orange emission at 593 nm (63).

1.1.2 Lithium Borates

The investigations on the $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ binary system have been studied by many research communities due to its great complexity and can be identified by the various formation lithium borate compounds, such as Li_3BO_3 , $\alpha\text{-Li}_4\text{B}_2\text{O}_5$, $\beta\text{-Li}_4\text{B}_2\text{O}_5$, $\text{Li}_6\text{B}_4\text{O}_9$, $\alpha\text{-LiBO}_2$, $\text{Li}_2\text{B}_4\text{O}_7$, $\text{Li}_3\text{B}_7\text{O}_{12}$, LiB_3O_5 and $\text{Li}_2\text{B}_8\text{O}_{13}$. Lithium borates have garnered significant attention due to their distinctive properties, including exceptional thermal stability, ionic conductivity, cost-effectiveness, environmental compatibility, and the ability to form a favorable solid electrolyte interface (64).

Lithium borate has potential for the applications in the development of new nonlinear optical materials, exhibits remarkable structural diversity, and serves as important components of glasses. Due to its importance in science and technology, it also applied as solid electrolytes in storage batteries, high-performance lithium batteries utilizing the Si/C composite anode, high voltage

cathodes, lithium metal anode or semi-solid lithium flowable electrodes. Furthermore, lithium borate glass finds wide-ranging application such as its use in identifying radiation dispersion of radiation which critical for homeland security and nonproliferation. Its high refractive index also makes it suitable for optical lenses.

Recently, ortho-borate compounds of the $MM'BO_3$ family (where M denotes alkali metals and M' signifies alkaline earth metals) have attracted significant interest due to their excellent properties. These compounds are recognized for their outstanding thermal stability, chemical robustness, significant thermal expansion, low thermal conductivity, effective UV absorption, impurities tolerance, and environmental sustainability. These characteristics make the borate compounds as promising candidates for applications in solid-state lighting, nonlinear optics, displays, and optoelectronics.

As a result, there has been active exploration of incorporating rare-earth and transition metal ions into these materials, either as luminescent centers or cathode materials. Various synthesis methods have been employed to evaluate their practical applicability. Specifically, alkali-alkaline ortho-borates of the $MM'BO_3$ type, where M = Li, Na, K and M' = Be, Mg, Ca, Sr, Ba) containing rare-earth and transition metal ions have been extensively studied.

$LiMgBO_3$ is a prominent member of the mixed metal borate family. It stands out as one of the lightest candidates within this group. The primary structural component of these borates is the planar $[BO_3]^{3-}$ unit, which imparts several advantageous properties, including highly localized valence electrons, superior optical quality, anisotropic polarizability, and low absorption at shorter wavelengths. These characteristics have driven research into the detailed crystal structure of $LiMgBO_3$ and its potential applications in deep ultraviolet non-linear optical (NLO) materials and phosphor-converted solid-state lighting.

The initial crystallographic study of $LiMgBO_3$ was conducted by Lehman et al. in 1962. More recent research has expanded on this groundwork, investigating both undoped and doped variants of $LiMgBO_3$. These studies have focused on its structural and electrical properties, luminescence behavior, and its utility in colored chromophores and red-light emitting diodes (65–68)

$LiMgBO_3: Tb^{3+}$ was fabricated by the sol-gel method. The crystal structure of the compound was determined through rietveld refinement of the X-ray

diffraction data. Diffuse reflectance spectroscopy analysis indicated that LiMgBO_3 exhibits excellent insulating properties with a high optical band gap of 6.3 eV, which is a critical attribute for thermoluminescence (TL) dosimetry applications (68).

The single-phase LiMgBO_3 phosphors doped with Tm^{3+} , Dy^{3+} , and their combinations, as well as with Li^+ , Na^+ , and K^+ , were synthesized using the solid-state reaction method. The energy transfer (ET) mechanisms between Tm^{3+} and Dy^{3+} were investigated through spectral overlap, emission spectra, and decay curves, with charge compensation mechanisms involving M^+ ions also examined. The thermal behavior was analyzed using TG/DTA, and X-ray diffraction technique confirmed the formation of single-phase monoclinic structure. Scanning electron microscopy revealed an irregular polygonal morphology, while EDS analysis displayed the presence of magnesium, boron, oxygen, thulium, and dysprosium. Upon the ultraviolet excitation, a blue peak at 456 nm was emitted by Tm^{3+} , and Dy^{3+} exhibited blue and dominant yellow peaks at 481 nm and 573 nm, respectively (69)

The investigation of 3d transition-metal ion substitution in LiMgBO_3 demonstrated the formation of isostructural single-phase materials with Fe^{3+} , Co^{2+} , Ni^{2+} , and Cu^{2+} . Notably, the materials containing Co^{2+} and Ni^{2+} , specifically $\text{LiMg}_{1-x}\text{Co}_x\text{BO}_3$ ($0 < x \leq 1.0$) and $\text{LiMg}_{1-x}\text{Ni}_x\text{BO}_3$ ($0 < x \leq 0.1$), exhibited distinct colors: purple-blue for Co^{2+} and beige-red for Ni^{2+} . Consequently, this study has identified TBP CoO_5 and NiO_5 as novel chromophores responsible for the purple-blue and beige-red hues, respectively (67)

Red emitting Mn^{4+} -doped LiMgBO_3 phosphors were synthesized using both solid-state and combustion methods to improve luminescence properties, with a fixed Mn^{4+} concentration of 0.5 mol%. The chemical state of the ion and the thermal stability of the material were evaluated through XPS and temperature-dependent photoluminescence analyses. Photoluminescence measurements demonstrated that these phosphors can be effectively excited by standard UV and blue LEDs, resulting in a vivid pure red emission. Rietveld refinement of X-ray diffraction data validated the phase-pure materials formation with high reliability factors. Furthermore, the crystal field parameters were examined to understand the impact of the surrounding environment on the phosphors' luminescence properties (70).

This report presents the first-time preparation of LiMgBO_3 using innovative and cost-effective combustion techniques. The study also investigates the thermoluminescence (TL) properties of dysprosium-doped LiMgBO_3 under X-ray irradiation. The focus of the research is on both the novel synthesis method and the detailed analysis of the TL characteristics of the material (71).

$\text{LiMg}_{1-x}\text{Mn}_x\text{BO}_3$ phases were synthesized at 800°C in an argon atmosphere via solid-state reactions. The monoclinic (C2/c) phase was formed for compositions with $0 \leq x \leq 0.5$, while the hexagonal phase was obtained for compositions with $0.75 \leq x \leq 1.0$. Mn^{2+} ions are coordinated by five oxygen atoms in an oxygen trigonal bipyramidal arrangement in the monoclinic phase. Red light emission with a peak wavelength between 682 and 696 nm, and decay times ranging from 0.4 to 24 ms was observed. This emission was induced by Mn d-d transitions (excited at $\lambda_{\text{ex}} = 428$ nm) and ultraviolet light irradiation (excited at $\lambda_{\text{ex}} = 200$ nm) (72).

1.1.2.1 Lithium Pyroborates

$\text{Li}_4\text{B}_2\text{O}_5$ was firstly investigated and studied by Sastry and Hummel. It was discovered in the region of $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ and Li_2O alongside with three compounds namely $3\text{Li}_2\text{O}-\text{B}_2\text{O}_3$, $2\text{Li}_2\text{O}-\text{B}_2\text{O}_3$, and $3\text{Li}_2\text{O}-2\text{B}_2\text{O}_3$ (73). As it is known, the lithium pyroborates has two polymorphic forms in a narrow temperature range between 600°C and 650°C which are known as α and β phase $\text{Li}_4\text{B}_2\text{O}_5$, respectively. These two polymorphs transform into each other at about 618°C as the low-temperature modification is named as α -phase $\text{Li}_4\text{B}_2\text{O}_5$ and high temperature know as β - $\text{Li}_4\text{B}_2\text{O}_5$. At higher temperature (>650), the $\text{Li}_4\text{B}_2\text{O}_5$ will dissociate into Li_3BO_3 and $\text{Li}_6\text{B}_4\text{O}_9$ (74,75).

In 1998, Matthew M.D et.al have prepared nine different lithium borates by melting the Li_2CO_3 and H_3BO_3 in a platinum crucible at 1223 K and followed by the Hg treatment at room temperature. The as-prepared products were annealed for 48 hours at 823 K and were heated depends on the composition of $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ at required temperatures in the range of 873 ± 1073 K. It reported that the final products of alpha and beta forms of lithium pyroborate were obtained after heating for 24 hours at 883 and 898 K, respectively. Mathew et.al additionally affirmed that the density of beta phase is marginally higher than that of alpha phase at room temperature. However, the substantial difference was noted in the

coefficient of the thermal expansion between α -phase and β -phase, which α -phase exhibiting a much larger coefficient. The difference in density becomes notably more pronounced at temperatures near to the phase transition (64,75).

Table 1.2. The properties of lithium pyroborates [Matthew M.D ,1998]

Pyroborate	Unit cell parameter/A			β°	Structure and Z	Density		Solubility g/100mL
	a	b	c			Obs	Cal	
α -Li ₄ B ₂ O ₅	10.15	17.58	4.729	--	Orthorombic Z=8	1.99	2.04	7.80
β -Li ₄ B ₂ O ₅	10.21	4.704	8.795	93.69	Monoclinic Z=4	1.98	2.04	7.86

The most recent study of lithium pyroborate was done by Meng He et.al which has synthesized the lithium pyroborates via quenched melt of Li₂CO₃ and H₃BO₃ as reactants for alpha modification and solid state reaction for the beta modification with Li:B=2:1 ratio. At 630°C and 635°C, the α -Li₄B₂O₅ and β -Li₄B₂O₅ forms were obtained respectively after heated for 3 hours. The results were compared to the Matthew's works and all the results were comparable. Furthermore, the longest B-O length on both polymorphic forms were also examined and stated to be 1.454 Å for orthorhombic crystal structure (α -Li₄B₂O₅) and 1.444 Å for monoclinic crystal structure (β -Li₄B₂O₅) (74).

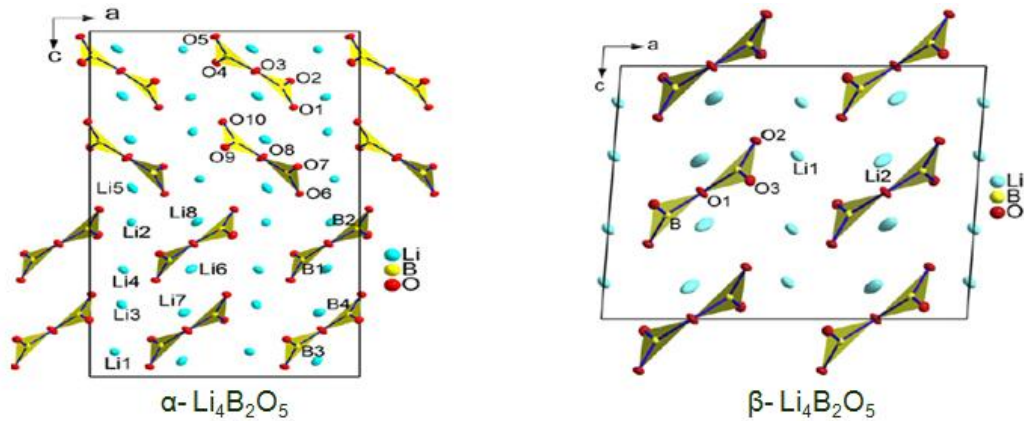


Figure 1.5. The crystal structure of alpha and beta Li₄B₂O₅ (74).

Lithium pyroborate is an intriguing compound due to its potential in various applications. However, the research on this compound remains limited because of its preparation process. The formation of lithium pyroborate can be

difficults for several reasons such as its thermal and chemical stability that hard to control during the synthesis.

Furthermore, to the best of our knowledge the examination on LiMgBO_3 and $\text{Li}_2\text{MgB}_2\text{O}_5$ was only done by the German-born biochemist. The borates were prepared by melting the starting materials of MgO and LiBO_2 . The decomposition of $\text{Li}_2\text{MgB}_2\text{O}_5$ into LiMgBO_3 and LiBO_2 by the normal cooling was also reported by H.A. Lehmann (65,76). In this study, efforts have been made in synthesizing the mixed metal lithium borates by simpler economic method and low heating temperature.

1.2 Layered Double Hydroxide (LDH)

Layered double hydroxides have been recognized for over 150 years. It was firstly discovered by Hochstetter in 1842 as natural mineral with hydrotalcite structure. Apparently, 100 years later the synthesized LDH was employed by Feitknecht. In his review, the Mg^{2+} cation is replaced by Al^{3+} and to maintained the electroneutrality of the materials in interlayered carbonate anion was observed between them (77).

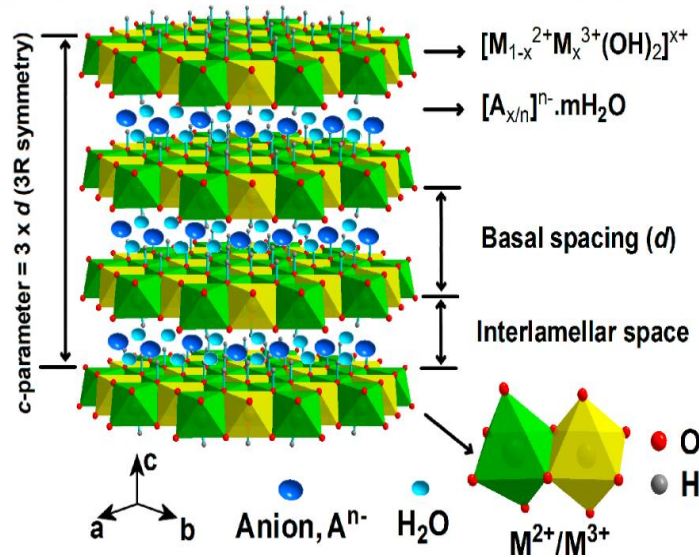
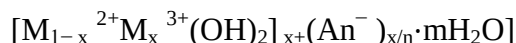


Figure 1.6. Crystal structure of Layered Double Hydroxides (LDHs), [Ref. Rives V, 1999]

Layered double hydroxides (LDHs) have attracted considerable attention owing to their unique structures and properties in recent years. LDHs are the 2D nanostructures materials that consist of cationic metal hydroxide-containing layers

with exchangeable interlayer anions and water molecules. LDHs are formed in brucite-like lamellar structure and are expressed by the general formula;



Where;

M^{2+} depict the divalent cations (Mg^{2+} , Ni^{2+} , Co^{2+} , Fe^{2+} or Zn^{2+})

M^{3+} depict the trivalent cations such as Al^{3+} , Cr^{3+} , Fe^{3+} , V^{3+} , or Ga^{3+} ;

An^- is the interlayer anion such as Cl^- , NO_3^- , CO_3^{2-} , SO_4^{2-} , PO_4^{3-} etc.

The structure of this compound is related to that of brucite which makes the presence of hydrotalcite is reduced in nature. Hence, the studies on LDH with variety of transition metals was done to acquire new layered structure of LDHs materials with great ability and basic character to intercalate anions in their structure. The charged of the lamellar layer depends on the ratio of cations M^{2+} and M^{3+} (77). According to Stanimirova and Kirov (2003), the effectiveness of LDH metal cation adsorption follows in order: $\text{Mg}^{2+} < \text{Mn}^{2+} < \text{Cd}^{2+} < \text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+} < \text{Zn}^{2+}$.

Additionally, different interlamellar layers of anion can be prepared by ion-exchange reaction and this variability could affect the physicochemical properties of the desired products. LDH materials have excellent properties of anion exchange which can assimilate the negatively charged anion into their interlamellar layer (78). Halides like chlorides and oxyanions such as nitrates and carbonates are the most common anions used in the LDH preparation. The anions in the interlayers of LDHs attach the main layer structure through electrostatic interactions or weak hydrogen. LDHs primarily bind to the heavy metal cations through anion exchange, physical adsorption, interlayer/surface complexation, electrostatic interaction and hydroxide precipitation (79).

The LDHs crystal structures depend on the double hydroxide layers formed by octahedral edge sharing of divalent and trivalent cations. The layers are generated by the derivation of the electroneutral layers present in brucite-like structure ($\text{Mg}(\text{OH})_2$) via the substitution of divalent M^{2+} with trivalent M^{3+} cations (80,81). The interlayer distance (d-value) of the brucite-like structure in LDH is equal to 4.77 Å and no additional cationic or anionic species existed in

the space of interlayer. According to X-ray diffraction, the structure of LDHs also varies according to their cations, molar ratio of cations and also the type of anions. In synthesizing LDH, the suitable range is around $0.2 \leq x \leq 0.33$ where the ratios of M^{2+}/M^{3+} must be between 2:1 and 4:1. If the value of $x < 0.2$, it will lead to the precipitate level of $M(OH)_2$ since M^{2+} consist of octahedral in their brucite sheets imposing high density. Concurrently, The increase in trivalent cation leads to the octahedral formation of $M(OH)_3$ (82).

In 2015, Zhitova E.S et al have investigated that the structure and the d-value of LDH are based on the molar ratio of cations metal. The $M^{2+}:M^{3+} = 2:1$ is revealed to be in quintinite group with ideal d-values equal to 7.56 whereas the $M^{2+}:M^{3+} = 3:1$ is found in hydrotalcite mineral group with 7.80 Å of d-value (83). Many types of LDHs with different structures have been synthesized and have been applied for several applications such as Ni-Fe, Ni-Al, Zn-Co, Ni-V, Co-Mn, Ni-Mn, and Ni-Co. Therefore, LDH samples that showed high efficacy in adsorbinng certain pollutants could potentially enhance their practical applications if proven to be multifunctional.

1.2.1 Application of Layered Double Hydroxide (LDH)

Layered double hydroxides (LDHs) have been applied in a variety of fields as they have remarkable properties such as high efficiency, environmental friendliness, and low cost (84). They are also known to have excellent ion exchange capacity, highly tunable interior architecture, interlayer space flexibility, and high porosity (85). Owing to their tunable and interesting capacity of anion exchange, LDHs materials are exceptionally utilized in many applications.

Based on literature studies of LDH in previous years, LDHs have been applied as energy storage (86,87), catalysis (88–90), drug delivery (91–95), remediation of the environment (96,97), waste water treatment and extraction of emerging sorbents, and fire retardant (98).

- For energy storage, LDHs developed as great materials for supercapacitor and battery applications.
- As catalysis, LDH based materials have shown substantial performance in several reactions namely pollutant degradation, water splitting, and carbon dioxide conversion.

- In the field of nano-adsorbents, LDHs showed a high removal efficiency for various inorganic species present in pollutants found in wastewater effluents such as metals, oxyanions, phosphate, and as well as organic pollutants, such as herbicides, pesticides, and dyes (99–102). In the water waste treatment, LDH can also serve as multiple purpose like wastewater disinfection, organic molecules photo degradation, and pollutant adsorption (77,99,103).
- As antimicrobial agents, LDH based materials were also believed to be promising as antimicrobial agents against several pathogens. Some antibacterial performances of LDH samples were reported in several mechanisms (104,105).

LDHs are used as an ideal sorbent owing to their unique physical and chemical characteristics including catalytic ability, high surface area, moderate space of interlayer, and good thermal stability. The surface area of LDH increased by its porous nature and enhanced the analyte physical absorption. Furthermore, the LDHs negatively charged allow the anion exchange and extract the anionic analytes. LDHs are promising sorbents for enriching anions and has been utilized as a sorbent in conventional solid-phase extraction (SPE) methods for extracting various analytes, such as polycyclic aromatic hydrocarbons iodate and fluoride. LDHs could also stably immobilize Cr(VI), Pb(II), As(III), and Cd(II) in the soil which reportedly could forbid the heavy metals biological transfer from soil to plants (106–108).

1.2.2 Preparation of Layered Double Hydroxide (LDH)

LDHs have been synthesized using diverse methods depending on the specific requirements of the desired materials, including high crystallinity, phase purity and porosity. The wide range combinations of cationic metals and anions can be employed to obtain the required properties. An enormous class of isostructural LDH materials with changeable physicochemical characteristics have been prepared by direct synthetic techniques, such as hydrothermal, coprecipitation (109), urea hydrolysis (110), microwave, mechanochemical and salt oxide sol–gel (111). Among these synthesis techniques, hydrothermal and

coprecipitation techniques are the most frequently applied methods in the preparation of LDH due to their simple process and great interlayer separation.

1. Hydrothermal Method

The fabrication of LDH by hydrothermal method has been done to enhance the particle size and the crystallinity of the final products. The process is usually carried out under mild conditions where the temperature is slowly raised at 150°C for a few days (112). The cationic metals are dissolved in water and transferred into the stainless-steel reactor. The solution is heated at a temperature range of 30-300°C with the steam pressure that is maintained accordingly based on the synthesis time (113). It has been stated that the products prepared with the hydrothermal method produced an increase in particle size, higher crystallinity and purity but it required more time-consuming and high energy compared to other techniques (114).

2. Coprecipitation Method

Another most commonly used method for the synthesis of LDH is coprecipitation method. This method is employed by dissolving the starting material inorganic salts into a medium of alkaline with constant pH. The pH are maintained above 8 to speed up the precipitation and are done to control the morphology and the molecular size of the LDH. Generally, the preparation with coprecipitation method consists of the mixture of metal ions and the hydroxyl anion that form the layers in the existence of the interlayer anion (115).

3. Urea hydrolysis

As it is known that urea is highly soluble in water and is a weak bronsted base. This characteristic allow urea to be applied as the precipitating agent to increase the pH through the decomposition of temperature. During the hydrolysis process, urea enables the pH control by the formation of interlayer CO_3^{2-} which produces the dispersed LDH materials with high crystallinity and particle size. Commonly, the urea hydrolysis is carried out alongside hydrothermal and coprecipitation methods (115,116).

4. Oxide Method

In this method, the metal of divalent metal oxide and anion are intercalated with the cationic of trivalent metal. some requirement are essentials for the moderate hydrolysis such as;

- The divalent metal have to be oxide to undergo the slow hydrolysis.
- The anion must be able to form the soluble salts with the trivalent metals.
- The medium must be acidic (117).

5. Microwave

The microwave method is the method where aging happens in the microwave. The speedy aging of irradiation with the microwave occurs in 15 to 60 minutes. It is reported that the particle size of LDH materials obtained by this method is smaller than the one from reflux maturation (118).

6. Mechanochemical Method

The mechanochemical method is grinding of the solid precursor in mortars, milling or crushing the solid in the planetary ball mills techniques that have been used in the preparation of LDH materials (119,120). The decarbonation of intercalated anions has been employed by Bhojarad et al via mechanochemical methods to perform the anion exchange of carbonate to nitrate anion (121). To increase the crystallinity of final products the hydrothermal methods with grounded starting materials were also applied by Mei-Gui et.al to acquire the LDH in monodispersed phase. Apparently, the mechanochemical methods are also environmentally friendly and not less requirements are needed in the drying and separation process.

7. Sol-Gel Method

Sol gel is the method that deals with the dissolutions of the metal salts in the water medium at room temperature. In the synthesis of nanoparticle materials with high purity and homogeneity, sol gel method is familiar for its reasonable cost, rapid synthesis time. Small alteration in temperature, pH, time, pressure, atmosphere and precursors can bring on the broad variations of compounds that have similar molecular structures. By only adjusting the type starting materials and changing annealing time, the structural properties of compound might be

varied throughout the sol gel method. Owing to its simplicity and resilience sol gel method is favored in the preparation of nonosized materials and widely used as coating method (122–125).

During the synthesis, the sol gel method comprise the usage of colloidal solution that derived a gel like solutions resulting from some chemical reactions. The sol-gel method can be classified as aqueous and non aqueous solution. The sol-gel method entails utilizing a colloidal solution (sol) which transforms into a gel-like network comprising both liquid and solid phases through several chemical reactions. The aqueous sol-gel method are involved five steps which are hydrolysis, condensation, aging, drying and crystalilization process (125,126).

Furthermore, the evaporation rate could also affected the gel structure of the synthesized materilas. This is caused due to the major changed in the network structure as the liquid is evaporated and formed the gel. The aerogel is formed when the network structure is maintained whereas on the contrary conditions the xerogel is formed. The differences between these two type of gels are the aerogel gives high surface area and high volume of pore while xerogel shows low pore volume and low surface area. xerogel results in low surface area and pore volume. Reportedly, the sol gel method sometimes required additional treatment namely hydrothermal method and mictrowave treatment to obtain final products with high surface area and purity (115,127).

As listed in Table 1.3, co-precipitation method is the most common method in the preparation of LDH materials. In this study, the fabrication of LDHs via sol-gel is rarely done in the past years. Consequently, triplet metal divalent cation will be firstly synthesis by sol-gel method owing to its high quality final products and simplicity.

Table 1.3. The recent studies of LDH in the past years

LDHs	Methods	Applications	Physicochemical Properties	References
Ca/Cr	Co-precipitation	Adsorbent of Congo red (carcinogenic and mutagenic) dye	adsorption capacity: 631.1 mg/g	(128)
Ca/Fe and Mg/Fe	Co-precipitation	Phosphorus removal in waste water treatment	phosphorus removal efficiency 99 % for FeCa-LDH: 1 min 82 % for FeMg-LDH: 10 min	(103)
CoZn/Fe and MgZn/Fe	Co-precipitation	Antimicrobial agents	Crystalline size: CoZn/Fe = 7.48 MgZn/Fe= 9.93	(129)
CoMn/Al	Electrospinning	Photothermal	evaporation rate= 3.06 kg/m ² h ¹ evaporation enthalpy = 1307.1 kJ/kg bandgap = 1.79 eV	(130)
Mg/Al and Co-/Ni-Mg-Al	Co-precipitation and hydrothermal	-	Crystallite size: Ni doped Mg-Al-LDHs = 25-27nm Co doped Mg-Al-LDHs = 20-26 nm	(131)
Mg/Al	Co-precipitation	Sorbent in dispersive SPE	limits of detection (0.03–1.47 µg/L) and good linearity ($r^2 > 0.9903$)	(132)
Ni/Al	Co-precipitation	Adsorbent of RE elements	d-spacing: 8.1 Å adsorption capacities Pr ³⁺ =18.13 mg/g, Sm ³⁺ =15.68 mg/g	(102)
Zn/Cr	Hydrothermal	Electrochemical sensor	crystallite size of ZnCr-LDH/VC : 76 nm	(133)
ZnMg/Al	Co-precipitation	Adsorbent	d-spacing: 7.60 Å crystalline size: 3.60 nm	(134)
Mg/Al	Coprecipitation method	Catalytic activity	d-spacing: 7.47-7.90	(135)

$Mg_{2-x}M_x/Al_1$ (M = Ca, Sr, Ba)	Sol-gel technique	-	d-spacing: 7.60-7.74 Å the average pore: Ca-MMO= ~ 2.5– 4.5 nm, Sr-MMO= ~ 3–7 nm, Ba-MMO =~ 3–8 nm	(136)
Mg/Al LDH	Co-precipitation method and hydrothermal	Polyester fabric coating	d-spacing : 7.72-7.77 Å crystallite Size : 13.76-15.29 nm	(137)
Mg/Fe LDH	ultrasonic-assisted hydrothermal method	Adsorbent	adsorption capacity reached 845.16 mg/g	(138)
$Mg_{3-x}Al_1$ LDH and $Mg_{3-x}Al_1$ Eu LDH	Sol-gel technique	-	SEM images: hexagonally shaped plate-like particles of LDHs of 200–600 nm in size.	(139)
$Mg_{3-x}M_x/Al_1$ (M= Mn, Co, Ni, Cu, Zn)	Sol-gel technique	-	average pore size is ~8–12 nm, ~9–11 nm and ~9–10 nm for the $Mg_{3-x}Co_x/Al_1$, $Mg_{3-x}Ni_x/Al_1$ and $Mg_{3-x}Zn_x/Al_1$ samples, respectively.	(140)
Ni/Mg/Al-LDH	Hydrothermal	Catalyst and adsorbent	adsorption capacities of CR (1250 mg/g) and Cr(VI) ions (103.4 mg/g). The microspheres: 2-3 µm	(141)
Zn/Al LDH	The Urea Method and Coprecipitation method	-	coprecipitation at controlled pH : local cation order and low crystallinity, urea method: highly crystalline but disordered LDHs	(142)
Zn-Cr LDH	coprecipitation method and urea hydrolysis process	Catalyst	FT-IR bands: Zn–Cr–SO ₂ ⁻⁴ : 1120 cm ⁻¹ Zn–Cr NO ⁻³ : 1380 cm ⁻¹ Zn–Cr CO ₃ ⁻² : 1380 cm ⁻¹ and 1450 cm ⁻¹	(143)
Zn/Al LDH	Urea Hydrolysis method	-	band gap value: 3.8–4.0 eV d-spacing: 7.48 Å	(144)
Mg/Fe LDH	Ion exchange methods	Adsorbent	d-spacing = 7.94 Å interlayer space = 3.09 Å adsorption capacity= 104,6 mg/g	(145)
NiCu/Al	Co-precipitation	Catalyst/ chelating agent for methanol	maximum methanol conversion = 82.6% H ₂ yield = 53.5%	(146)

2. AIM AND SCOPE OF THE STUDY

2.1 Rare-Earth Metal Doped Magnesium Pyroborates

The study of magnesium pyroborates have been done by many research communities due its unique properties and fascinating applications. To the best of my knowledge, the study about magnesium pyroborates doped rare earth element is still limited. For this reason, the aim of this study is to synthesize high purity rare-earth metal doped magnesium pyroborates with practical yet energy and time efficient method, Solution Combustion Synthesis (SCS). To evaluate the factors that influence the physicochemical properties of the magnesium pyroborates and to understand how the data behaves in different circumstances, various parameters are applied such as;

- Diverse doping materials: cerium (Ce^{3+}), europium (Eu^{3+}) and terbium (Tb^{3+}) in several molar ratios (0.5%, 1.0%, 1.5%, 2.0%, and 2.5%)
- Different organic fuels: citric acid, glycine, HMTA, tartaric acid and urea
- Various annealing temperature in the range of 400-1000°C

To asses the purity and the vibrational bands of the obtained products, FT-IR spectrophotometer is used. FT-IR analysis shows the unique chemical bonds of the sample material as absorption spectrum will give the characteristic peak which representing the existence of the desired components.

For the phase identification of doped magnesium pyroborates which form in triclinic and monoclinic phase, the X-ray Diffraction analysis will be employed. Using the given data, the crystallite size will be also calculated to confirm the formation of nanosized magnesium pyroborates using the equation of Debye-Scherrer.

The DRS studies will be also carried out to examine the optical properties by taking absorbance spectra into account. Furthermore, the band gap value will also be determined by Tauc's plot relation $[(\alpha h\nu)^{1/n} = C \times (h\nu - E_g)]$.

Furthermore, to determine the morphology and the elemental composition of the synthesized materials, the FESEM and EDX analysis will be conducted.

2.2 Lithium Pyroborates and Lithium Magnesium Borates

In the second part of this study, the fabrication of lithium pyroborates via SCS method will be done. The synthesis of lithium pyroborates is rarely done and not adequately reported because of its difficulty in forming the single phase of lithium pyroborates. Hence, the aim is to prepare a novel lithium borate especially lithium pyroborates with simpler method using different organic fuels and heating temperature. To identify and characterize the bond variation, structural properties, optical properties and morphology of the products, FT-IR spectroscopy, X-Ray diffraction, UV-Vis spectroscopy and Field Electron Scanning Electron Microscopy (FESEM) techniques are employed, respectively.

Furthermore, lithium magnesium borate and lithium magnesium pyroborates are also prepared via SCS method. Their properties will also be comparably characterized.

2.3 Layered Double Hydroxides (LDHs)

LDHs are one of the most popular subjects and have attracted significant attention due to its distinctive structures and application in many fields of area. In this study different concentrations of triplet metal divalent cation layered double hydroxide are prepared by using sol-gel method. The impact of various cations' concentrations on the characteristic of LDH materials will be analyzed. The characterization studies of the materials are done by:

- X-ray Diffraction (XRD) analysis, to provide the detailed information related to crystal structure, crystallinity and also the crystallite size of the materials.
- FT-IR Spectroscopy study, to identify the purity by determining the characteristic bond of the final products.
- Diffuse Reflectance Spectroscopy (DRS), to investigate the electronic absorption the optical properties of prepared materials.
- Field Emission Scanning Electron Microscopy (FESEM), to examine the surface morphology and structure of materials at the nanoscale providing the high-resolution images of the synthesized materials.
- Energy Dispersive X-ray Spectroscopy (EDX), to identify the element and their elemental compositions within the material.

3. MATERIALS AND METHODS

3.1 Materials

The chemicals that were used in this present work are listed as follows;

Magnesium nitrate hexahydrate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	: Merck, 99.00%
Lithium nitrate, LiNO_3	: Merck, 99.00%
Boric acid, H_3BO_3	: Merck, 99.00%
Carbohydrazide, $\text{CH}_6\text{N}_4\text{O}$	: Aldrich, 98.00%
Citric acid monohydrate, $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$	: Merck, 99.50%
Glycine, $\text{C}_2\text{H}_5\text{NO}_2$	: Merck, 99.70%
Hexamethylenediamine, $\text{C}_6\text{H}_{16}\text{N}_2$	: Merck, 99.90%
Hexamethylenetetramine, $\text{C}_6\text{H}_{12}\text{N}_4$	: Merck, 99.90%
Tartaric acid, $\text{C}_4\text{H}_6\text{O}_6$	: Merck, 99.00%
Urea, $\text{CH}_4\text{N}_2\text{O}$	: Merck, 99.50%
Cerium nitrate hexahydrate, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	: Aldrich, 99.00%
Europium nitrate pentahydrate, $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	: Aldrich, 99.00%
Terbium nitrate hexahydrate, $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	: Aldrich, 99.00%
Aluminium nitrate nonahydrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	: Merck, 99.00%
Zinc nitrate, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	: Merck, 99.00%
Copper nitrate hemi(pentahydrate), $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$	: Merck, 99.00%
Manganese (II) tetrahydrate, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	: Merck, 99.00%
Ethylene Glycol, $(\text{CH}_2\text{OH})_2$	: Merck, 99.00%
Potassium Bromide, KBr, for IR Spectroscopy	: Merck, 99.90%

3.2 Instruments

3.2.1 Fourier Transform Infrared Spectrophotometer

Perkin Elmer Fourier Transform Infrared (FT-IR) spectrophotometer was employed to record the infrared spectra of final products using Spectrum software in the range of 4000-400 cm^{-1} . The pellets were prepared in KBr: products ratio of 0.1500: 0.0010 (wt/wt).

3.2.2 X-ray Diffractometer

To determine the structural properties of the final products, The XRD analysis were done by Rigakuminiflex Goniometer and multiflex X-ray diffractometer in the arrangement of $\text{CuK}\alpha$ (30-40kV, 10-20mA, $\lambda=1.54056\text{\AA}$) radiation. The weighth of sample and the scan speed was tuned as 0.016 and 5°/minutes, respectively. The XRD diffractogram are plotted by Gnuplot software. The products purity is confirmed by comparing the obtained data with ICDD Data card of related compound.

3.2.3 Ultraviolet-Visible (UV-Vis) Spectrometer

The optical properties of the nanocompounds are determined by Perkin Elmer Lambda 35 UV-Vis Spectrometer. The absorbance spectra were recorded in wavelength range of 200-900 nm. The data was plotted by using Data Processor WinLab. The band gap energy values are assessed by correlating the curve of $[(\alpha h\nu)^{1/2}]$ againsts $h\nu$ photon energy] or known as Tauc's plot.

3.2.4 Field Emission Scanning Eletron Microscope (FESEM)

The field emission scanning electron microscope, Hitachi SU-70 was utilized in this study for high-resolution analysis of the samples surfaces morphology. The analysis were performed using an accelerating voltage range of 5–10 kV under three different magnification (5000x to 20000x). Preceding to the analysis, the samples were coated with silver to a thickness of 10–15 nm using a Quorum Q150T ES sputter coater.

3.2.5 Scanning Electron Microscope (SEM)/Energy Dispersive X-Ray Spectrometer (EDX)

The elemental analysis of the synthesized materials was carried out using a Hitachi TM300 microscope, with data collected over a processing time of five

minutes. To achieve optimal results, spectra of each samples were recorded at three different points.

3.2.6 Furnace

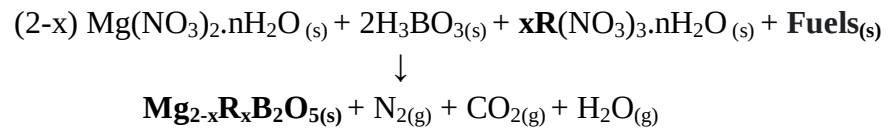
The reactions during the preparation of metal borates were carried out at heating range between 400-1000°C by the aid of Nuve MF 120 furnace.

3.2.7 Dry Heat Sterilizers

During the preparation of LDH compounds, the FN 055 Nuve sterilizers was used for drying the homogenous gel and LDH solutions at 105°C and 70°C, respectively.

3.3 The Combustion Reaction of Rare-Earth Metal Doped Magnesium Pyroborates

Magnesium pyroborates doped rare earth metal were synthesized via Solution Combustion Synthesis (SCS) using $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, H_3BO_3 , rare earth metal ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), and various fuels (citric acid, glycine, HMTA, tartaric acid and urea) as starting material. 5wt% excess of H_3BO_3 and different concentration of dopants (0.5%, 1.0%, 1.5%, 2.0% and 2.5%) were applied during the preparation process. The homogeneous solution were prepared by dissolving all the starting materials in minimum amount of distilled water and allowed it to evaporate by continuously stirring on the magnetic stirrer at 370°C until the gel-like solution were formed. The precursor gel was introduced to the preheated furnace at 400°C for 5 minutes. To obtained great crystallinity products the as-prepared powders were ground and heated at higher temperature in the range of 400-1000°C for an hour. The characterization studies of the prepared products were done by using XRD diffraction methods and also analyzed by FT-IR, UV-Vis, and FESEM-EDX techniques. The general theoretical reactions for the preparation of pyroborated can be expected as follow;



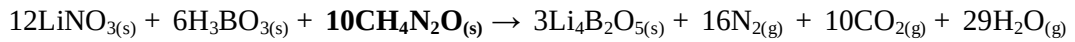
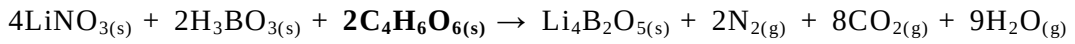
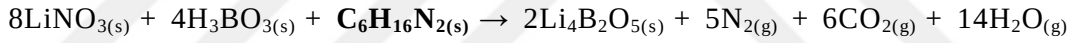
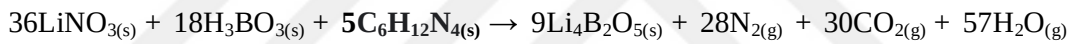
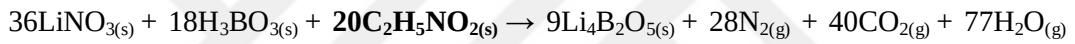
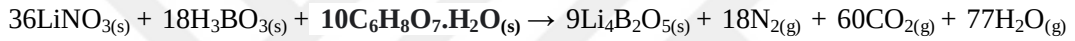
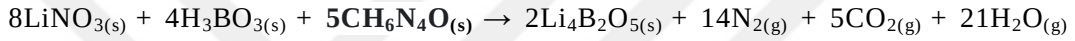
Where, R is dopants (Ce^{3+} , Eu^{3+} and Tb^{3+}), x is the concentration of dopant (0.005, 0.010, 0.015, 0.020 and 0.025), and fuels are citric acid, glycine, HMTA, tartaric acid and urea.

3.4 The Combustion Reaction of Lithium Borate

Several lithium borates such as $\text{Li}_4\text{B}_2\text{O}_5$, $\text{Li}_2\text{MgB}_2\text{O}_5$ and LiMgBO_3 have been also synthesized by SCS method. The starting materials namely lithium nitrate, magnesium nitrate hexahydrate, boric acid and various fuels are dissolved in minimum amount of distilled water. The solution was allowed to evaporate with continuous stirring at 370°C until the gel-like solution was formed. The precursor gel was introduced to the preheated furnace at 400°C for 5 minutes. The as-synthesized product was prepared for further annealing process.

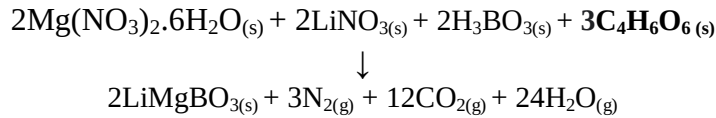
a) $\text{Li}_4\text{B}_2\text{O}_5$

Lithium pyroborates were prepared with various fuels and some excess of boric acid (5%, 10% and 15%) were also applied during this study. The expected reactions are presented as follow;



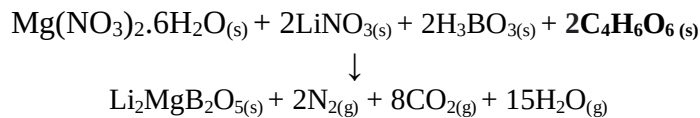
b) LiMgBO_3

The following reaction is the predicted reaction for the preparation of lithium magnesium borate. The borate is prepared by using the tartaric acid fuels and heated in interval of 100°C in the range of $400\text{-}650^\circ\text{C}$ for 1 hour.



c) $\text{Li}_2\text{MgB}_2\text{O}_5$

The attempt on the preparation of a novel lithium magnesium pyroborate via SCS method were done by using tartaric acid, glycine and urea as fuel. Stoichiometric amount of starting materials were applied.



3.5 The Synthesis of Layered Double Hydroxide (LDH)

In this recent studies, the first triplet divalent cation Mg_3/Al_1 LDH was synthesized by sol-gel method. Stoichiometric amounts of starting materials were dissolved in 50 mL distilled water under continuous stirring. The starting materials were dissolved in the order of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Then 10 mL of 0.2M citric acid solution was added into the homogeneous solution. After mixing for 1 hour at 80°C , 2 mL ethylene glycol was added. The solution was continuously stirred at 150°C for some hours (± 5 hours) until the gel-like solution was observed. The precursor gel was dried at 105°C for 24 hours and followed by annealing process at 650°C for 4 hours. The reconstruction process was then took place by dissolving the as-heated samples in 30 mL of distilled water and allows it to mix properly for 6 hours. To acquire the LDH powder products, the solution was dried at 70°C in oven for 12 hours. The detailed of the process were displayed in Figure 3.1.

The overall reactions in the formation of LDH are showed as follow:

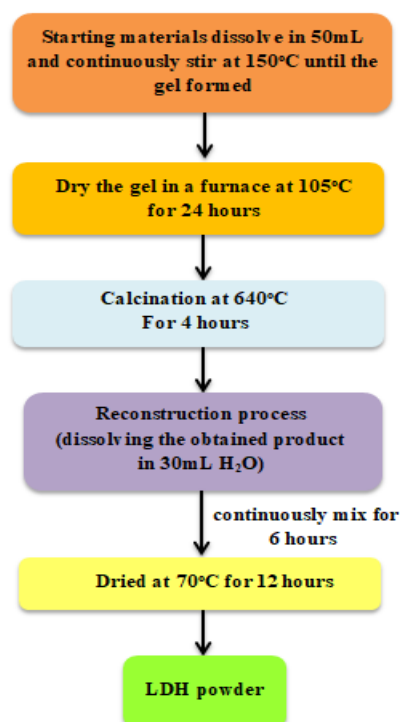
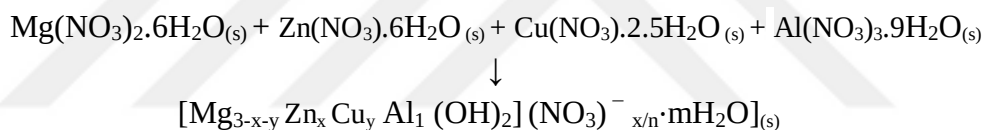


Figure 3.1. Schematic diagram of LDHs preparation process

4. RESULTS AND DISCUSSION

4.1. The Synthesis of Rare Earth Metal Doped Magnesium Pyroborates Nanocompounds

Rare earth metal doped $\text{Mg}_2\text{B}_2\text{O}_5$: Ce^{3+} (cerium), Eu^{3+} (europium), Tb^{3+} (terbium) were synthesized by Solution Combustion Synthesis (SCS) method with five different concentrations of dopants (0.5wt%, 1.0wt%, 1.5wt%, 2.0wt%, and 2.5wt %). Various fuels (citric acid, glycine, HMTA, tartaric acid and urea) were also used in the preparation process. The as-prepared products were heated at temperature range 400-1000°C for an hour with 100°C interval. The stoichiometric composition of the metal nitrates and the fuels is calculated based on the total oxidizing and reducing valences of the oxidizer (O) and fuel (F), $\text{O/F} = 1$ to get the maximum energy released during the reaction process. According to the concepts used in propellant chemistry, the element oxygen is considered as an oxidizing element with the valency -2 . The valency of nitrogen is known to be zero. The elements such as carbon, hydrogen, magnesium, or any other metal are considered as reducing elements with the corresponding valencies $+4$, $+1$, and $+2$, accordingly. Hence, the oxidizing and reducing valencies of the compounds used in the combustion mixtures can be calculated. In this study, fuel: oxidizer ratio and Mg:B ratio were applied in 1:1 and 1: 1.05 mole ratio, respectively where 5wt% excess of boric acid was applied. The obtained product was comparatively characterized.

The as-prepared powder of magnesium pyroborates prepared by using several fuels with different dopant concentrations are presented in picture 4.1 to 4.3. The synthesized materials produced different colors and textures depending on the fuel used during the preparation. The as-synthesized powder of magnesium pyroborates conduct with citric acid, glycine, and tartaric acid fuels give highly foamy powder with low density whereas HMTA and urea fuel formed harder product. Comparing the amount of powder products obtained, citric acid gave the most quantity of products followed by tartaric acid>glycine>urea>HMTA. This phenomenon might be due a great amount of gases, the porosity and also the increase of light scattering produces during the combustion reaction. Thus, the variation in the final colors of the products indicates that the color of the powders depends on the type of fuel used.

Fuels	0.5%Ce	1.0%Ce	1.5%Ce	2.0%Ce	2.5%Ce
Citric acid					
Glycine					
HMTA					
Tartaric acid					
Urea					

Picture 4.1. The as-synthesized magnesium pyroborates doped cerium

Fuels	0.5%Eu	1.0%Eu	1.5%Eu	2.0%Eu	2.5%Eu
Citric acid					
Glycine					
HMTA					
Tartaric acid					
Urea					

Picture 4.2. The as-synthesized magnesium pyroborates doped europium

Fuels	0.5%Tb	1.0%Tb	1.5%Tb	2.0%Tb	2.5%Tb
Citric acid					
Glycine					
HMTA					
Tartaric acid					
Urea					

Picture 4.3. The as-synthesized magnesium pyroborates doped terbium

4.2 Characterization Studies of Rare Earth Metal Doped Magnesium Pyroborates

4.2.1 The XRD Analyses of Rare Earth Metal Doped Magnesium Pyroborates

The products of $\text{Mg}_{2-x}\text{R}_x\text{B}_2\text{O}_5$ ($\text{R} = \text{Ce}^{3+}, \text{Eu}^{3+}, \text{Tb}^{3+}$, $x = 0.00, 0.005, 0.010, 0.015, 0.020, 0.025$) were characterized by X-ray Diffraction (XRD) technique. The as-prepared products were subjected to thermal treatment across a temperature range of 400–1000°C, with intervals of 100°C, for one hour at each temperature. Initial experiments at 400–700°C resulted in amorphous peaks with low crystallinity. These temperature ranges were selected based on earlier studies, which successfully synthesized monoclinic magnesium pyroborate at 700°C using the SCS method in 2019. This research also noted that the transition between monoclinic and triclinic phases occurs between 800–900°C, with triclinic phases observed at 1000°C (147). In more addition, Üçyıldız, A. and Girgin I (2010) stated that the monoclinic and triclinic forms of magnesium pyroborates is formed at 750°C and 1050°C, respectively and the transition between these two phases is observed at 950°C (148). The current study builds upon these findings, demonstrating that the optimal products, characterized by improved crystallinity and well-defined peaks, are achieved at temperatures between 800–1000°C. For this reason, all the XRD patterns obtained in these studies were compared with the ICDD Data Card No: 73-2232 and 73-2107 for triclinic and monoclinic phase, respectively.

4.2.1.1 Cerium Doped Magnesium Pyroborates

In these studies, the cerium doped magnesium pyroborates was successfully synthesized by solution combustion method with 5wt% excess of boric acid. The XRD pattern of undoped and cerium doped magnesium pyroborates with several fuels were presented in Figure (4.1 to 4.15). The XRD pattern has well defined peaks, which indicate high crystallinity of the synthesized samples at 800°C–1000°C. The samples have a monoclinic (space group, $P2_1/c$) and triclinic phase (space group, $P1$). The assignments of characteristic reflections of XRD pattern were also compared with ICDD card 73-2232 for triclinic $\text{Mg}_2\text{B}_2\text{O}_5$ and 73-2107 for monoclinic $\text{Mg}_2\text{B}_2\text{O}_5$. The patterns showed a great similarity with the undoped magnesium pyroborates which confirmed doping material was homogeneously

mixed into the magnesium pyroborates as host material. Furthermore, Ce_2O_3 was detected as the second phase in some patterns which proven the fuel effect on the formation of lanthanide doped magnesium pyroborates. This might be due to the large atomic radii of Cerium ions ($\text{Ce}^{3+}=1.02\text{\AA}$) whose bigger than the host materials ($\text{Mg}:0.72\text{\AA}$).

Citric Acid Fuel: The monoclinic crystal structure of $\text{Mg}_2\text{B}_2\text{O}_5$ can be distinguished easily by the existence of single reflection at $2\theta \approx 35^\circ$ obtained 800°C . For all fuels, the reflections are having a great compatibility with the ICDD card no 73-2107 which belongs to triclinic form of magnesium pyroborates. For citric acid fuels, the highest crystallinity belongs to 2.0% Ce^{3+} . The single sharp maximum d-line indicated the formation of monoclinic phase of magnesium pyroborates.

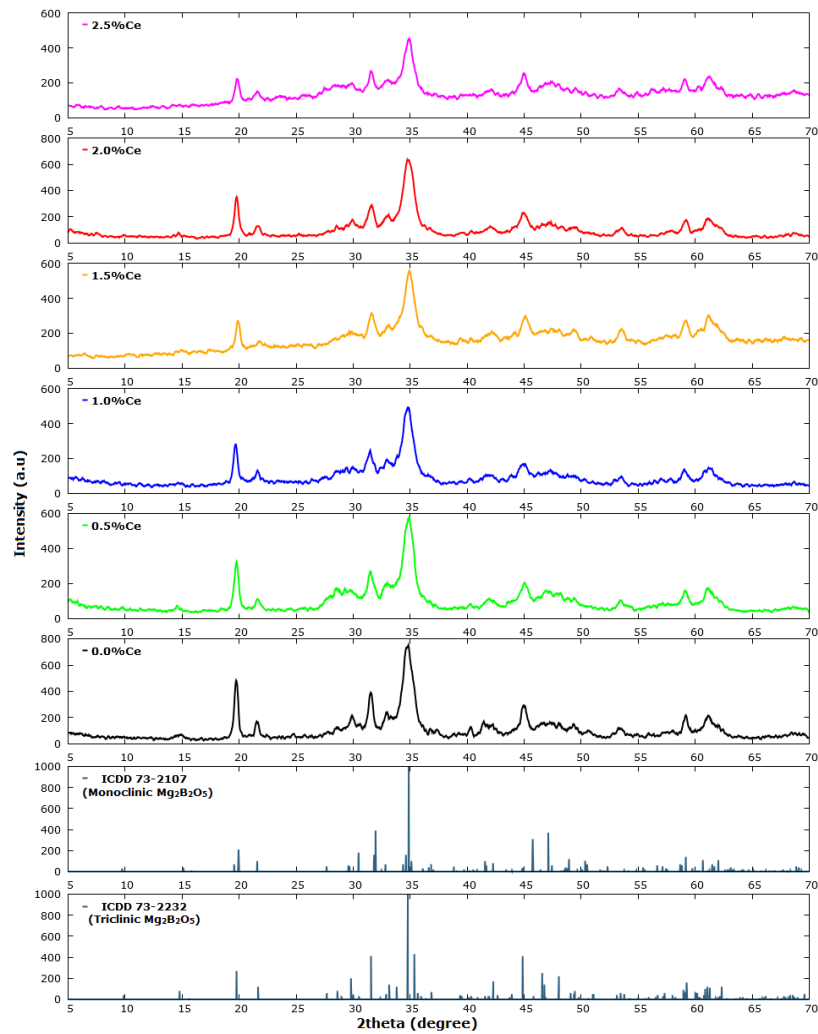


Figure 4.1. The XRD patterns of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x = 0.000- 0.025$) obtained at 800°C

At 900°C, the transition between two form was clearly seen at the XRD patterns of 1.5%wt and 2.5%wt Ce^{3+} where the split of maximum d-line at around $2\theta = \sim 35^\circ$ was detected. In these patterns, the impacts of heating temperature on the transition between two phases also observed. Additionally, the effect of doping concentration is also taken placed.

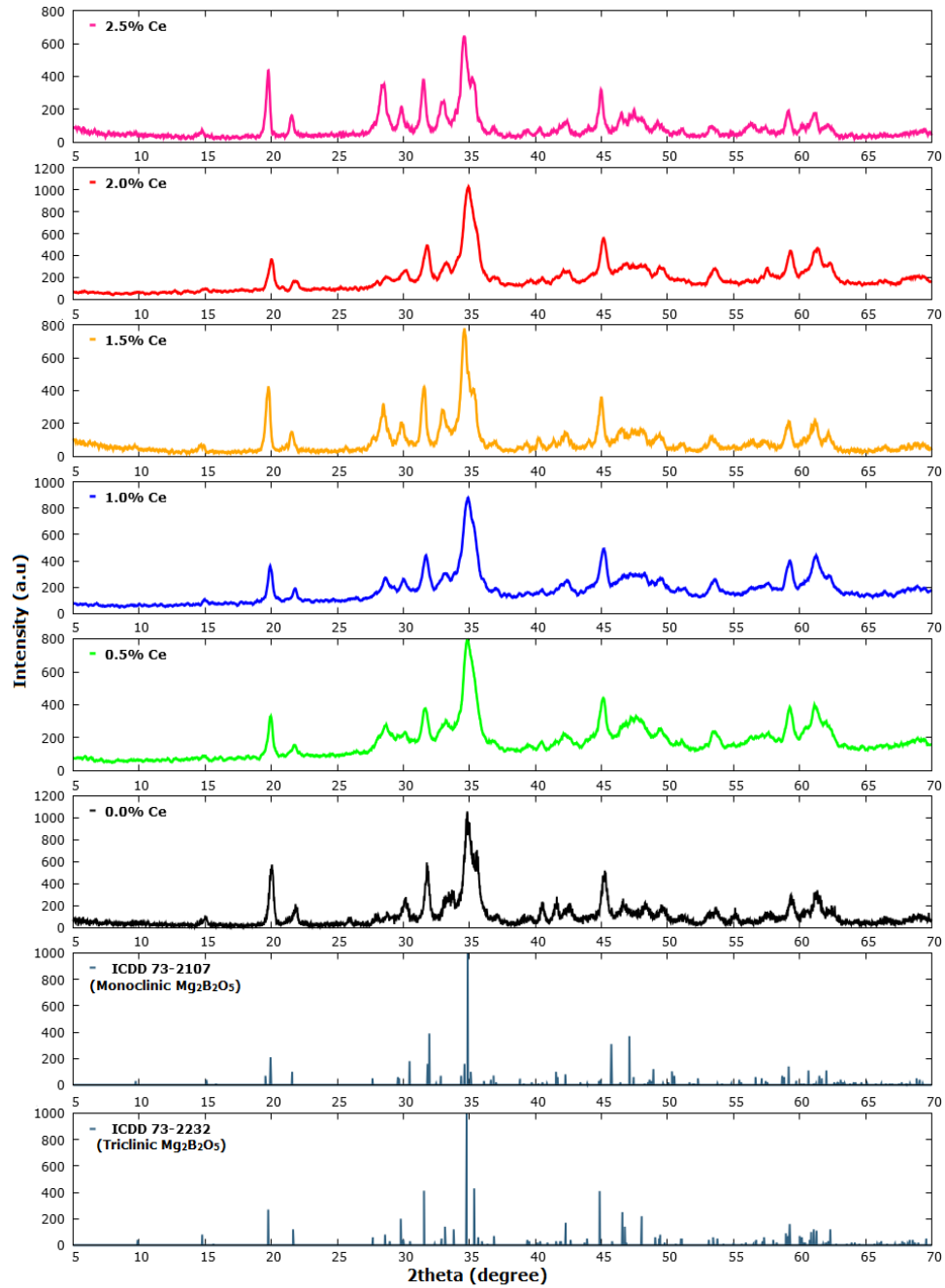


Figure 4.2. The XRD patterns of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x=0.000 - 0.025$) obtained at 900°C

Presented in the Figure 4.3, the single phase of cerium doped magnesium pyroborates in various concentrations are obtained at 1000°C. The compounds were prepared by applying 5% excess of boric acid and their formation was approved with the ICDD card no. 73-2232 which belongs to triclinic form of magnesium pyroborates. The addition of doping materials is slightly affecting the crystallinity of the magnesium pyroborates compounds and formed high purity triclinic phase at 1000°C.

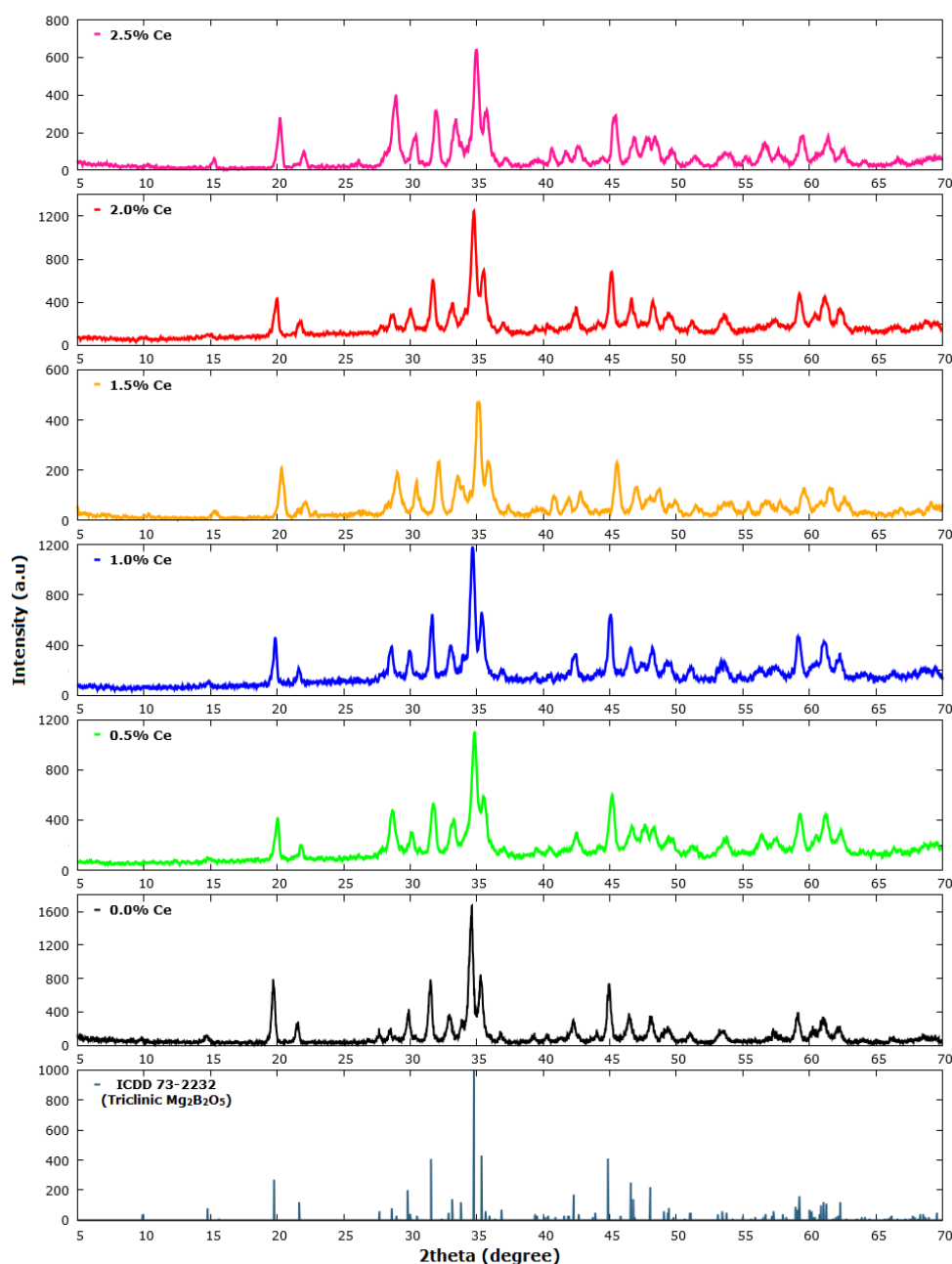


Figure 4.3. The XRD patterns of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 1000°C

Glycine Fuel: No significant different on the patterns which means there is no crystal structure changed by the addition of doping materials and change of fuel. The XRD patterns of the products obtained at 800°C and 900°C shown great competencies with the patterns of single phase undoped magnesium pyroborate. As it compared, the assignments of characteristic reflections of XRD pattern at 800°C has lower crystallinity than the products obtained at 900°C. Moreover, monoclinic phase were observed at lower temperature (Figure 4.4) and triclinic crystal structure were accomplished at 900°C (Figure 4.5).

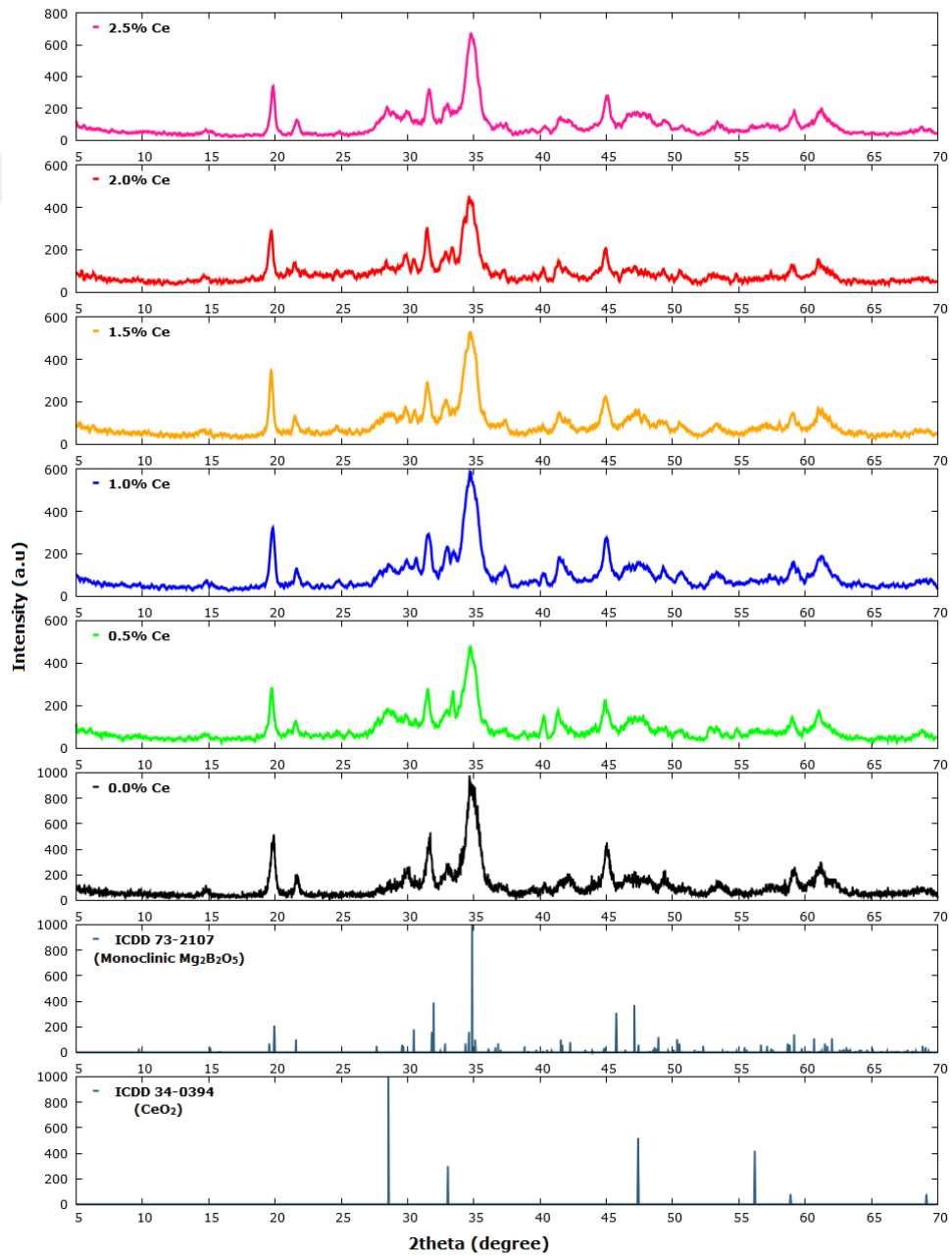


Figure 4.4. The XRD patterns of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x=0.000-0.025$) obtained at 800°C

The transformation from monoclinic form to triclinic form of magnesium pyroborates are observed between 800-900°C. The single d-line at $2\theta=34^\circ$ correspond to the characteristic d-line of monoclinic forms are split into two peak such as $2\theta=34.7^\circ$ and 35.4° which proven the formation of triclinic magnesium pyroborates. At higher annealing temperature, the additional peaks in the Figure 4.5. According to the ICDD card no. 34-0394, these peaks might be formed due to the incompleted combustion reaction during the synthesis process and belonged to CeO_2 .

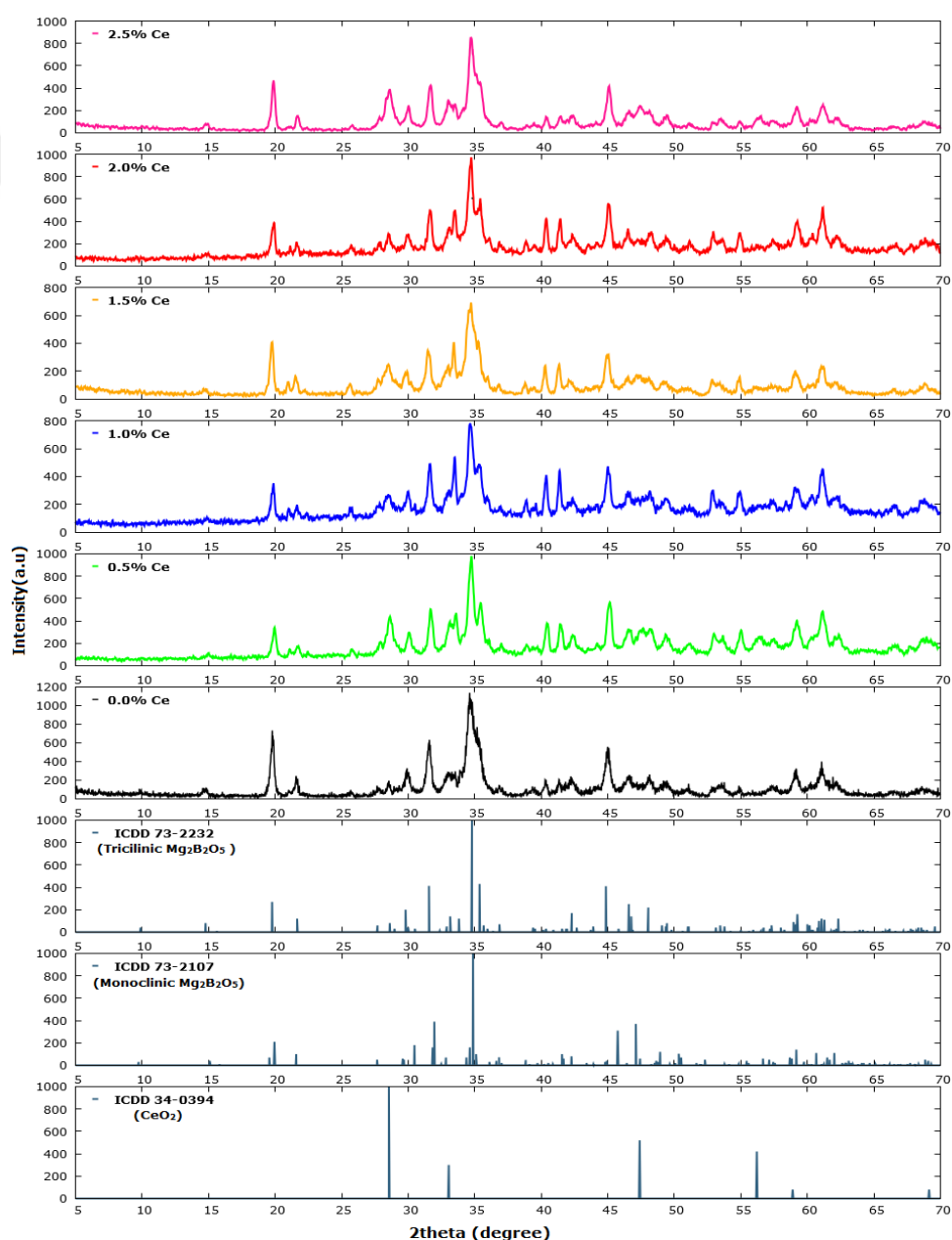


Figure 4.5. The XRD patterns of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 900°C

The formation of single phase magnesium pyroborates doped cerium ion was observed with 2.5% Ce^{3+} . High crystallinity was obtained and the formation of pure magnesium pyroborates was detected as it has a great accordance to ICDD card no. 72-2232 which belongs to triclinic phase of magnesium pyroborates, whereby the other concentrations of Ce^{3+} doped $\text{Mg}_2\text{B}_2\text{O}_5$ was formed alongside with cerium oxide. The existence of CeO_2 was assigned by intense peak at $2\theta=28.4^\circ$. Furthermore, the monoclinic phase was completely transformed into triclinic phase of magnesium pyroborates (Figure 4.6).

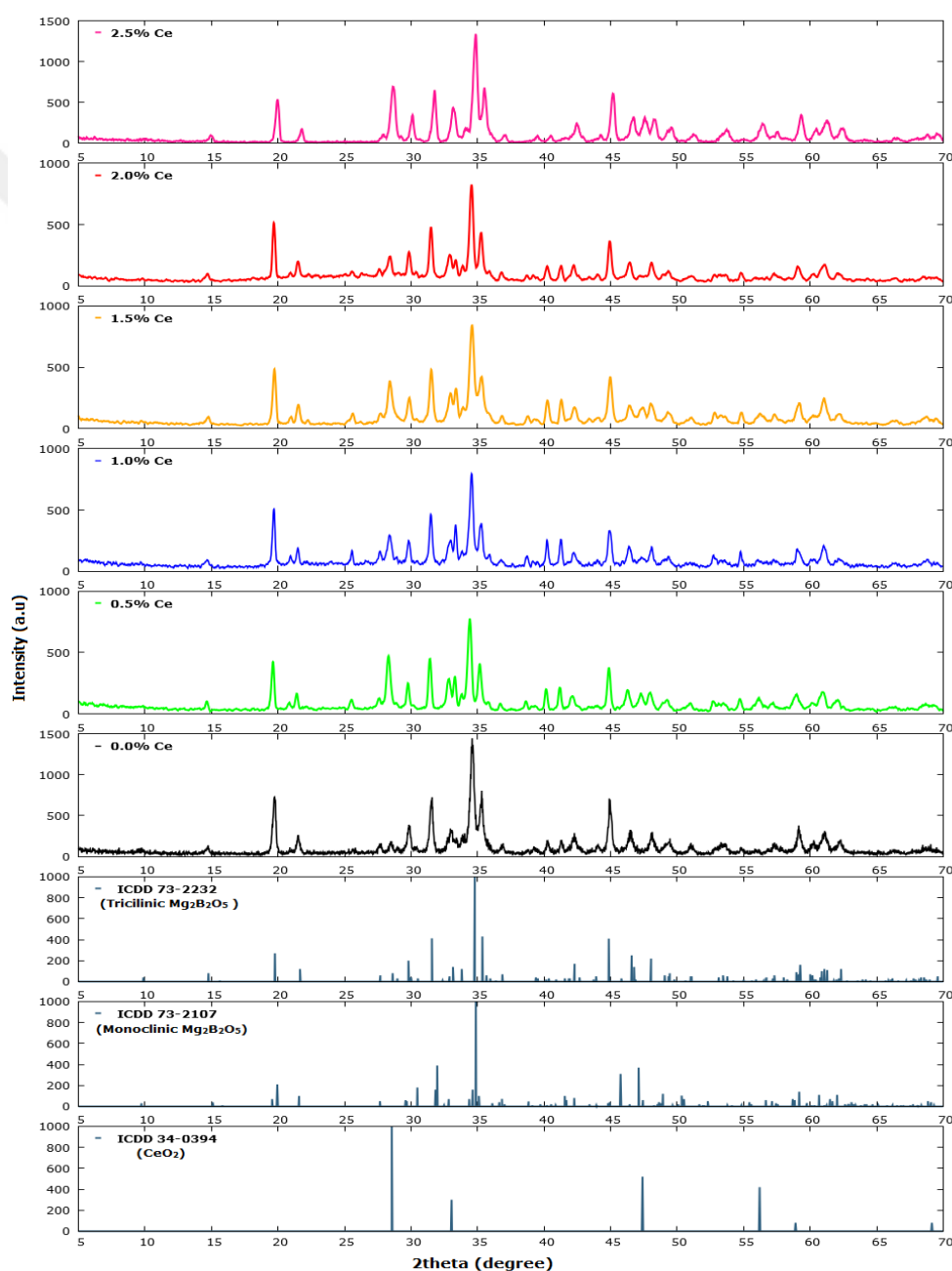


Figure 4.6. The XRD patterns of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 1000°C

HMTA Fuel: Single phase of both monoclinic and triclinic $\text{Mg}_2\text{B}_2\text{O}_5\text{:Ce}^{3+}$ were obtained at 800°C and 1000°C, respectively. The effect of temperature can be seen in these two patterns since the transformation of monoclinic phase to triclinic phase of $\text{Mg}_2\text{B}_2\text{O}_5$ were observed at 900°C. Single sharp peak at about $2\theta = 35^\circ$ is represent to the monoclinic $\text{Mg}_2\text{B}_2\text{O}_5$ whereas the separation of this peak into two at about $2\theta = 34.7^\circ$ and $2\theta = 35.3^\circ$ represent the formation of triclinic $\text{Mg}_2\text{B}_2\text{O}_5$.

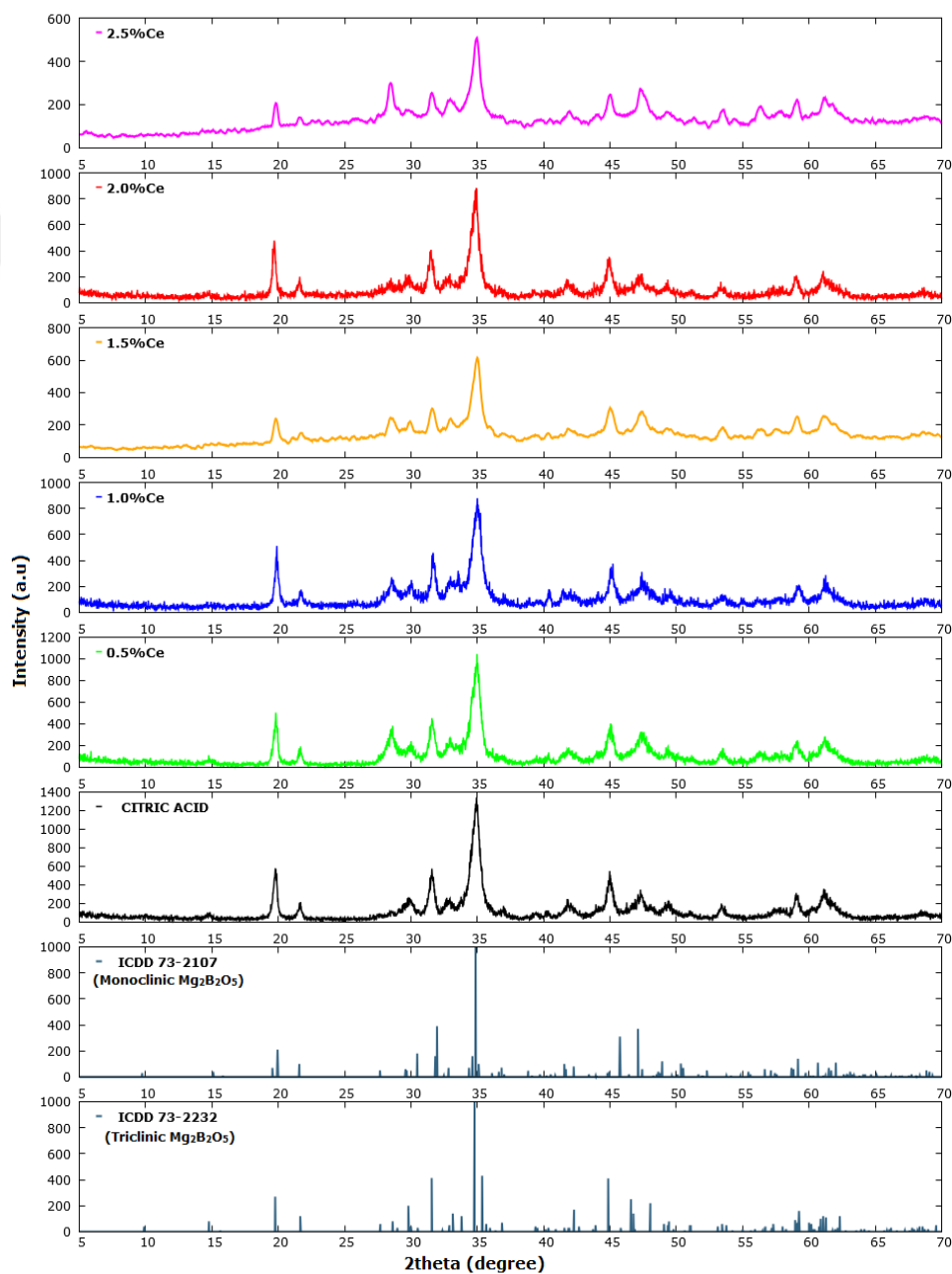


Figure 4.7. The XRD patterns of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 800°C

The XRD studies also examined initially the crystal structure of the obtained products at 900°C where the transformation of monoclinic phase toward triclinic phase were observed. At this temperature, the d-line of triclinic magnesium pyroborates are dominating but the major peaks at around $2\theta=35$ degree are not completely split. For this reason further heating process were taking placed to acquired a high crystallinity triclinic $\text{Mg}_2\text{B}_2\text{O}_5: \text{Ce}^{3+}$.

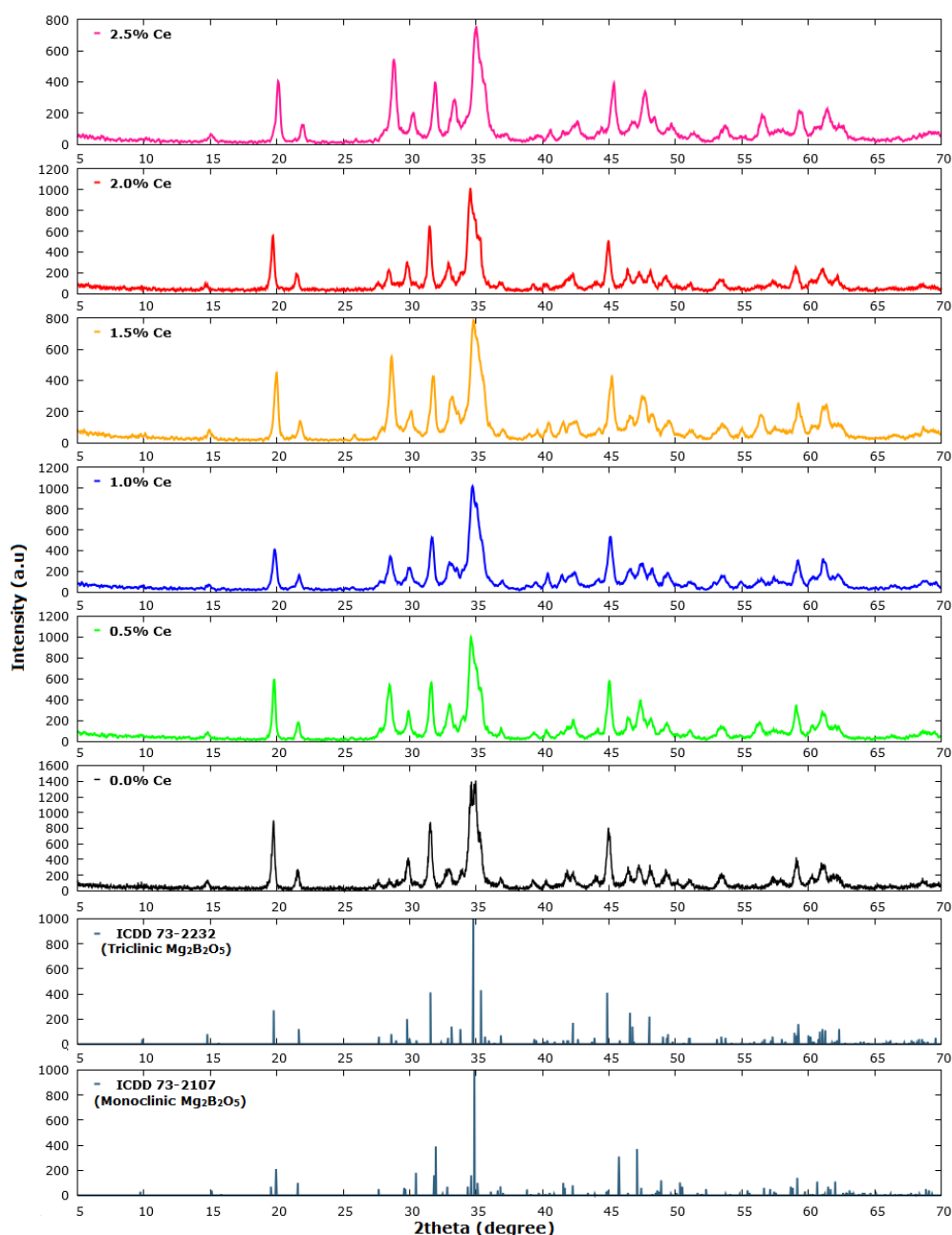


Figure 4.8. The XRD patterns of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x=0.000-0.025$) obtained at 900°C

The d-line of cerium doped magnesium pyroborates obtained at 1000°C are compatible with the ICDD card 73-2232 which belongs to triclinic magnesium pyroborates. An indication of Mg site successfully substituted with cerium dopant was clearly seen since there is no cerium reflection line was observed in the patterns. Additionally, the addition of cerium and temperature change is also affecting the peak intensity in the XRD patterns (Figure 4.9).

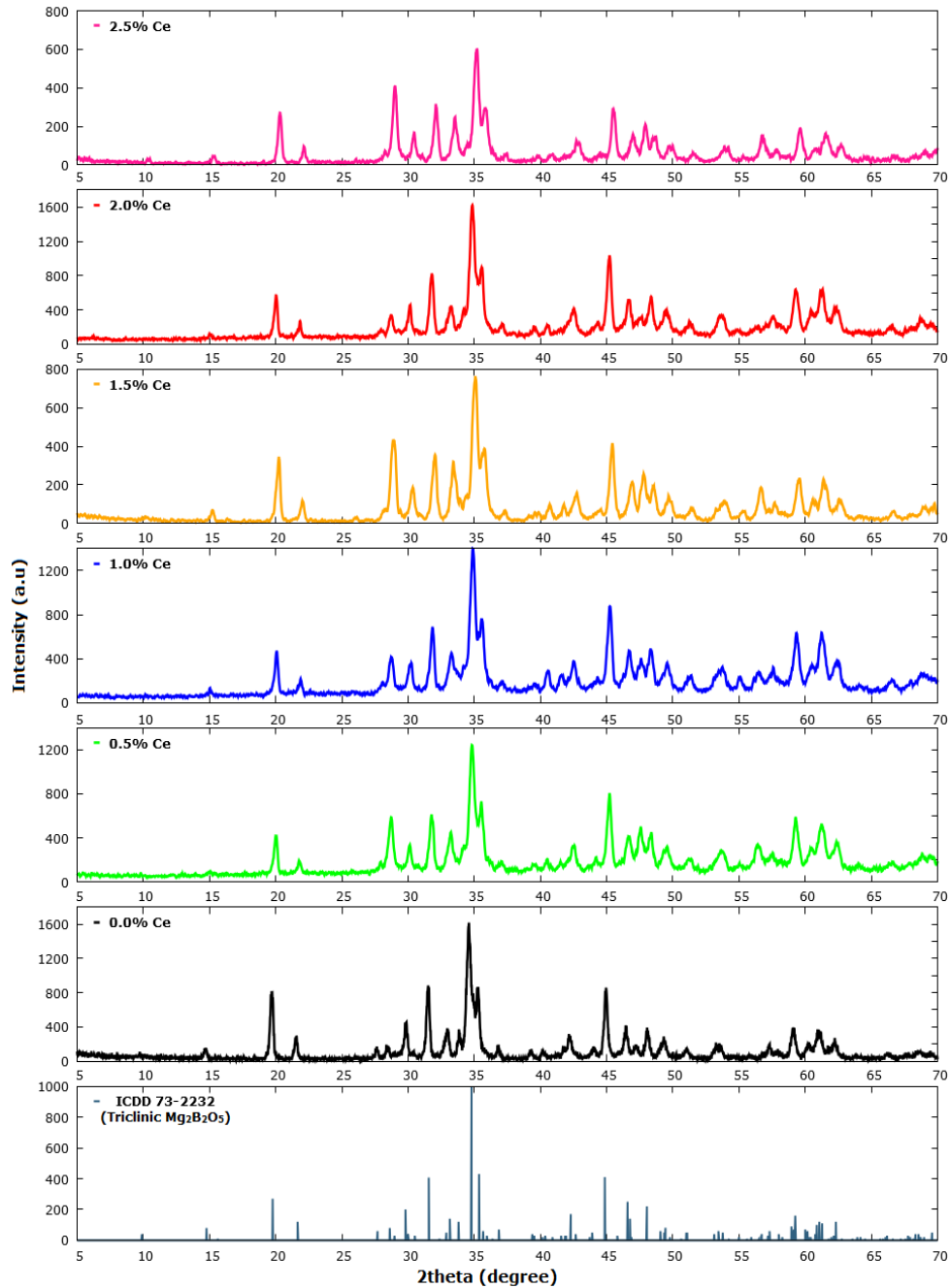


Figure 4.9. The XRD patterns of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 1000°C

Tartaric Acid Fuel: the monoclinic phases of $\text{Mg}_2\text{B}_2\text{O}_5$ were observed at 800°C for all concentration of Ce^{3+} and the diffractograms has a good accordance with ICDD card; 73-2107. Although the intensity of the patterns is low but the compounds are crystallized perfectly in monoclinic structure.

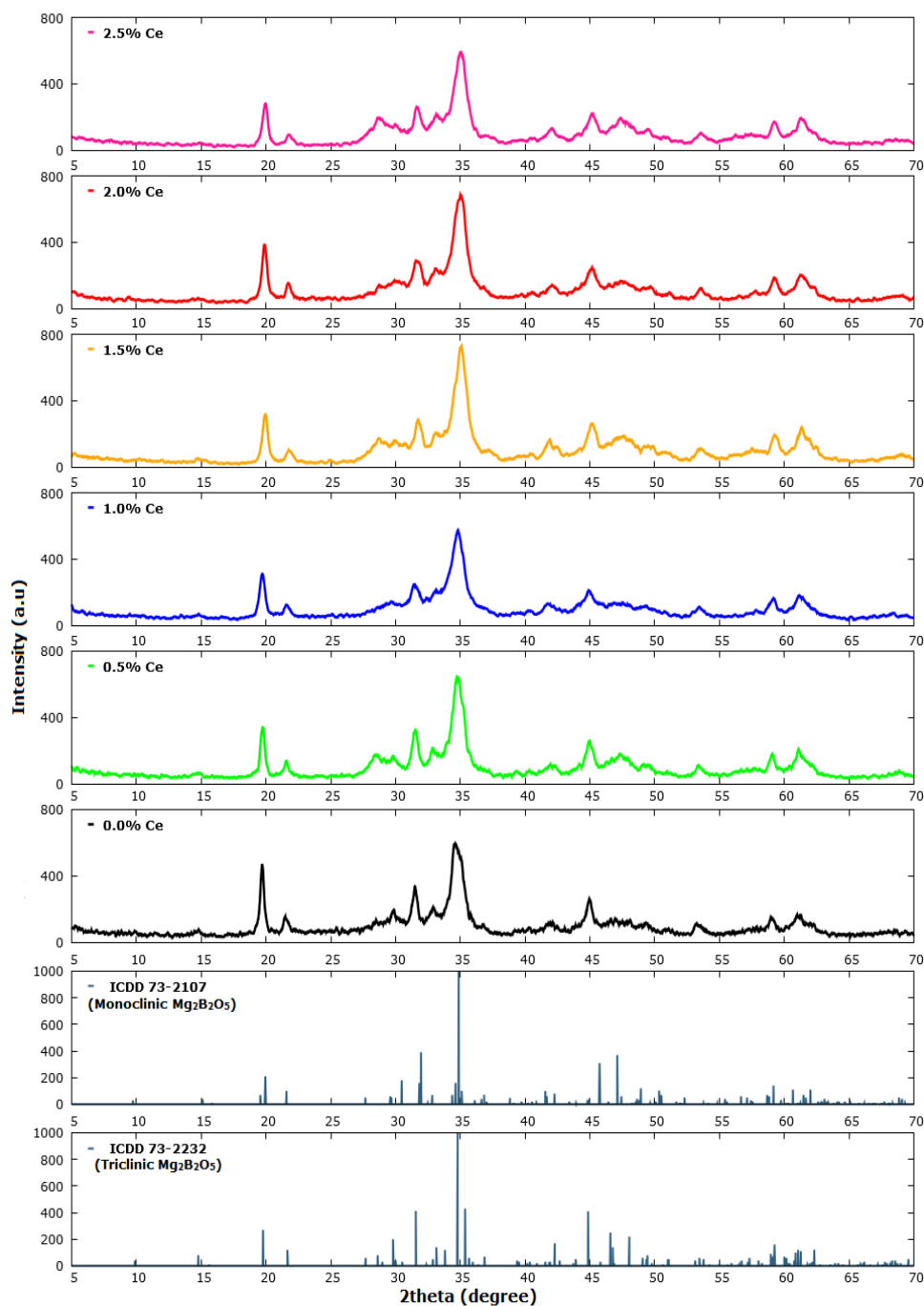


Figure 4.10. The XRD patterns of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 800°C

At 900°C, the d-lines that belong to triclinic magnesium pyroborates are found alongside with the monoclinic characteristic d-line. This phenomenon explained the transformation between two phases from the low temperature form (monoclinic) into high temperature form (triclinic) and impurities were observed (Figure 4.11).

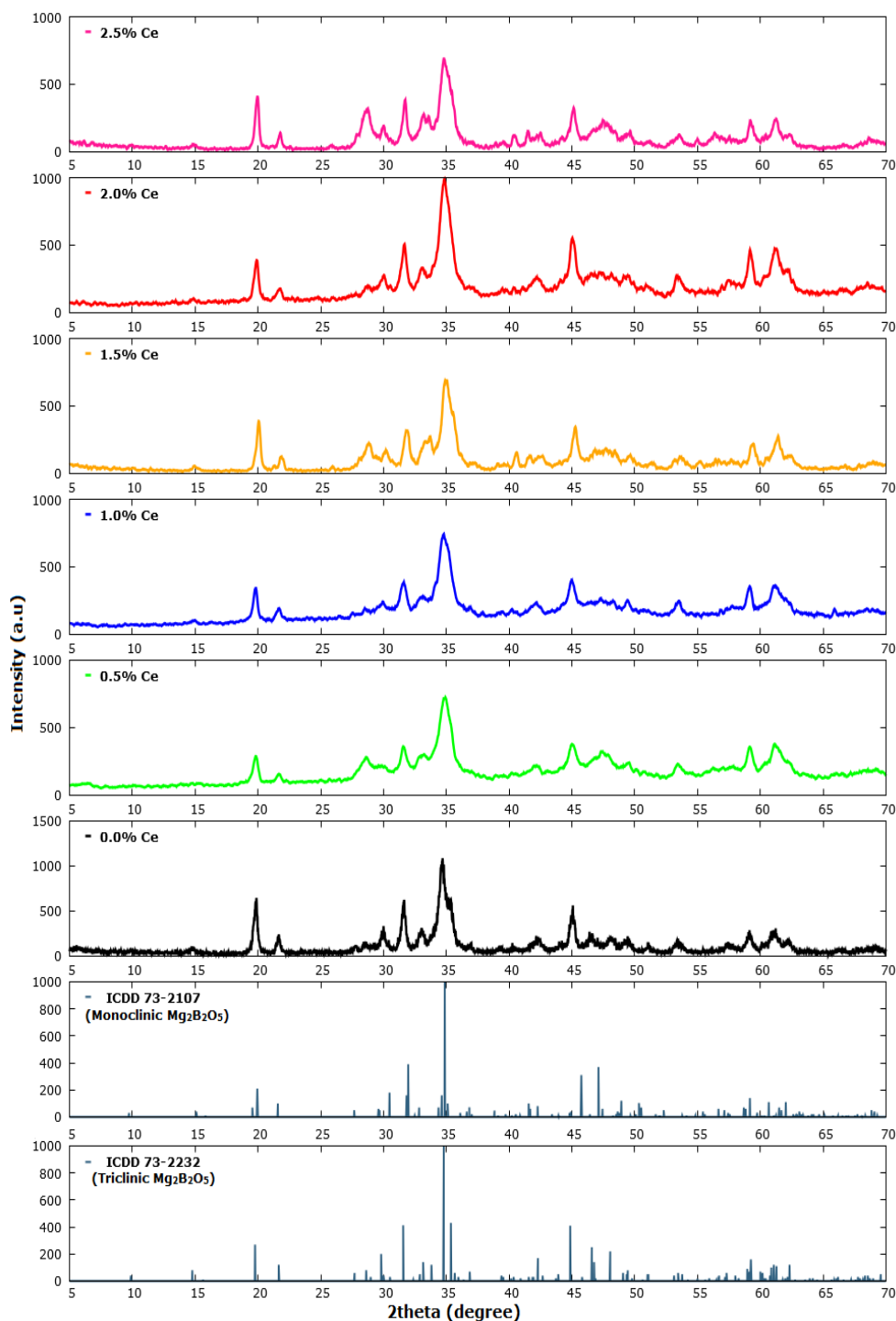


Figure 4.11. The XRD patterns of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 900°C

Presented in Figure 4.12, high crystalline single phase magnesium pyroborates are formed at 1000°C as all the d-lines have excellent compatibility with ICDD No. 72-2232 which belongs to triclinic form of magnesium pyroborates. Cerium (III) dopant is well-doped into $\text{Mg}_2\text{B}_2\text{O}_5$ as host materials or in other word it filled perfectly in the spaces between crystal lattices and expected to adjust the characteristics of host materials especially their semiconductor properties.

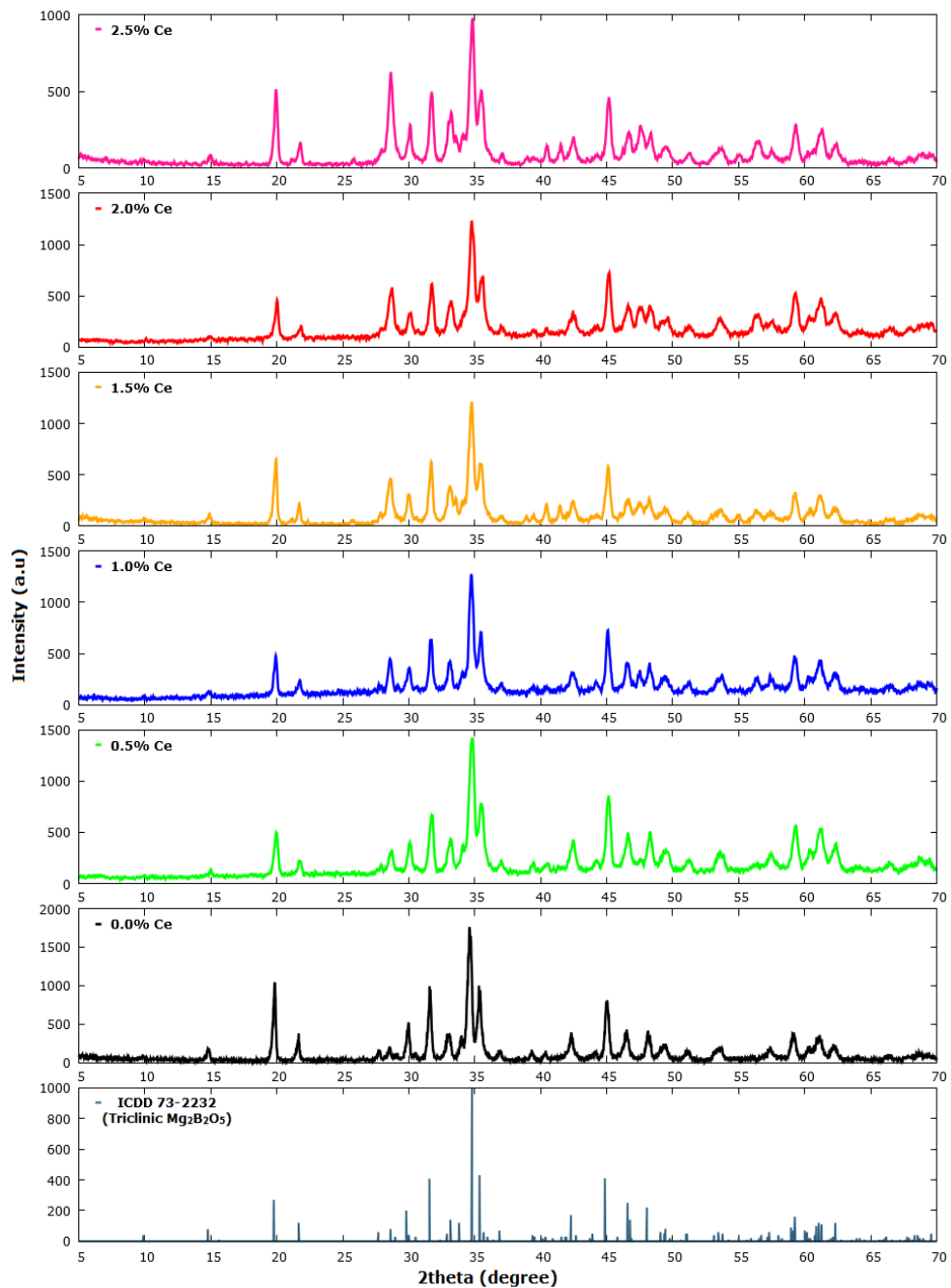


Figure 4.12. The XRD patterns of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 1000°C

Urea Fuel: In Figure 4.13 to 4.15, the assignments of characteristic reflections of the XRD pattern of Ce^{3+} doped $\text{Mg}_2\text{B}_2\text{O}_5$ products obtained at 800°C - 1000°C were also compared with the pure $\text{Mg}_2\text{B}_2\text{O}_5$ pattern and ICDD card. The reflection lines that belong to monoclinic forms of magnesium pyroborates were detected at 800°C as it has the same peaks given by ICDD card of m- $\text{Mg}_2\text{B}_2\text{O}_5$, 73-2107 (Figure 4.13).

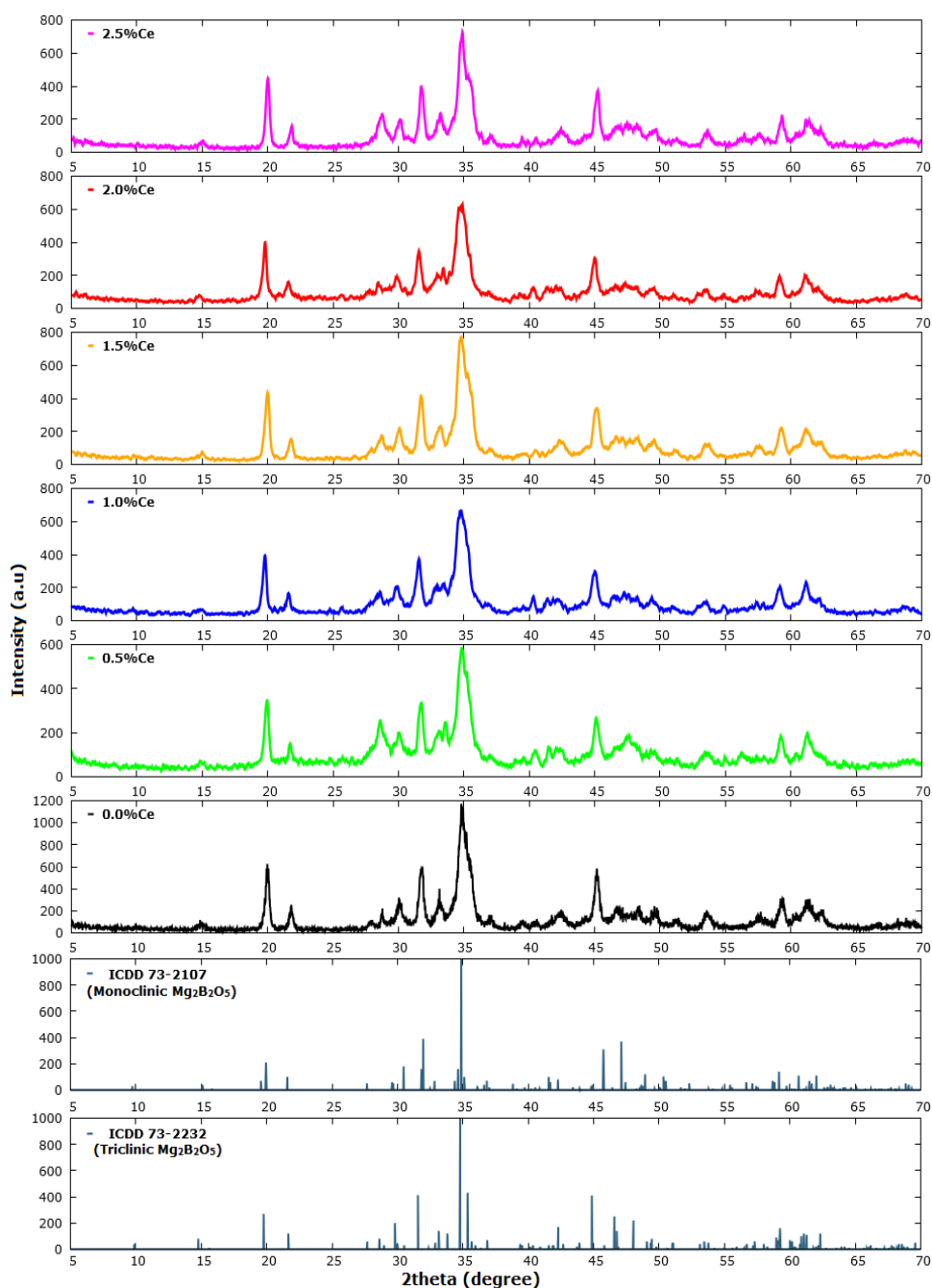


Figure 4.13. The XRD patterns of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x = 0.000$ - 0.025) obtained at 800°C

The transformation of monoclinic magnesium pyroborates into triclinic form were not observed at 900°C for the concentration of 0.5%, 1.0% and 1.5% of cerium dopant. The single maximum peak was observed. On the other hand the transformation of the samples into triclinic phase of magnesium pyroborates were recorded at the patterns of 1.5% and 2.5%. These behaviour shows the influence of heating temperature and also the concentration of doping materials on the structural properties of magnesium pyroborates (Figure 4.14).

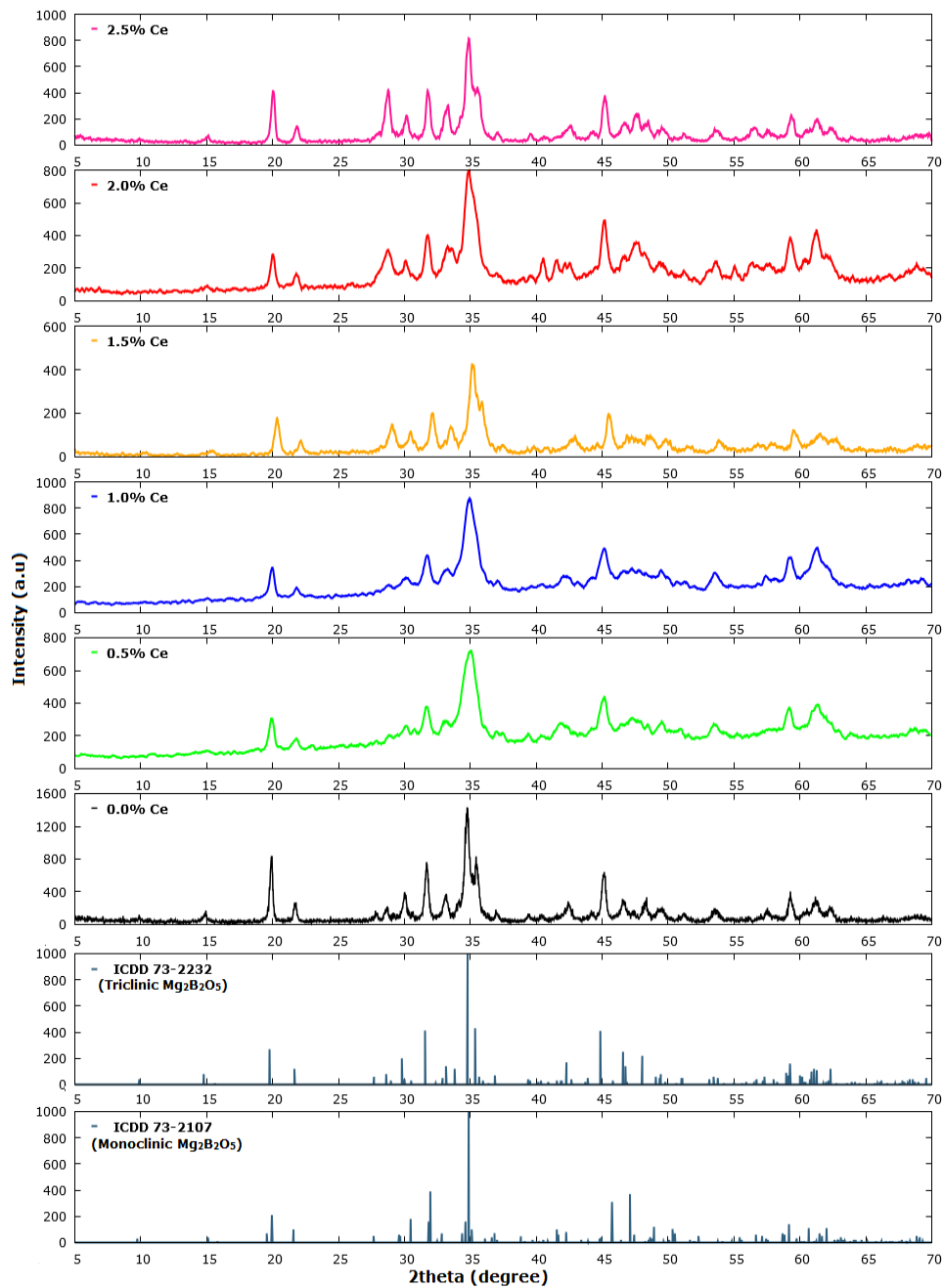


Figure 4.14. The XRD patterns of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 900°C

At 1000°C, the diffractograms showed that the complete transformation of magnesium pyroborates into triclinic form of magnesium pyroborates for all Ce³⁺ concentration. The intense peak at 2θ= 35° assigned the great crystallinity form of triclinic phases and all the d-lines have an excellent compatibility with the ICDD card no. 73-2232. The highest crystallinity is belonged to 2.0% with intensity of 1200 a.u.

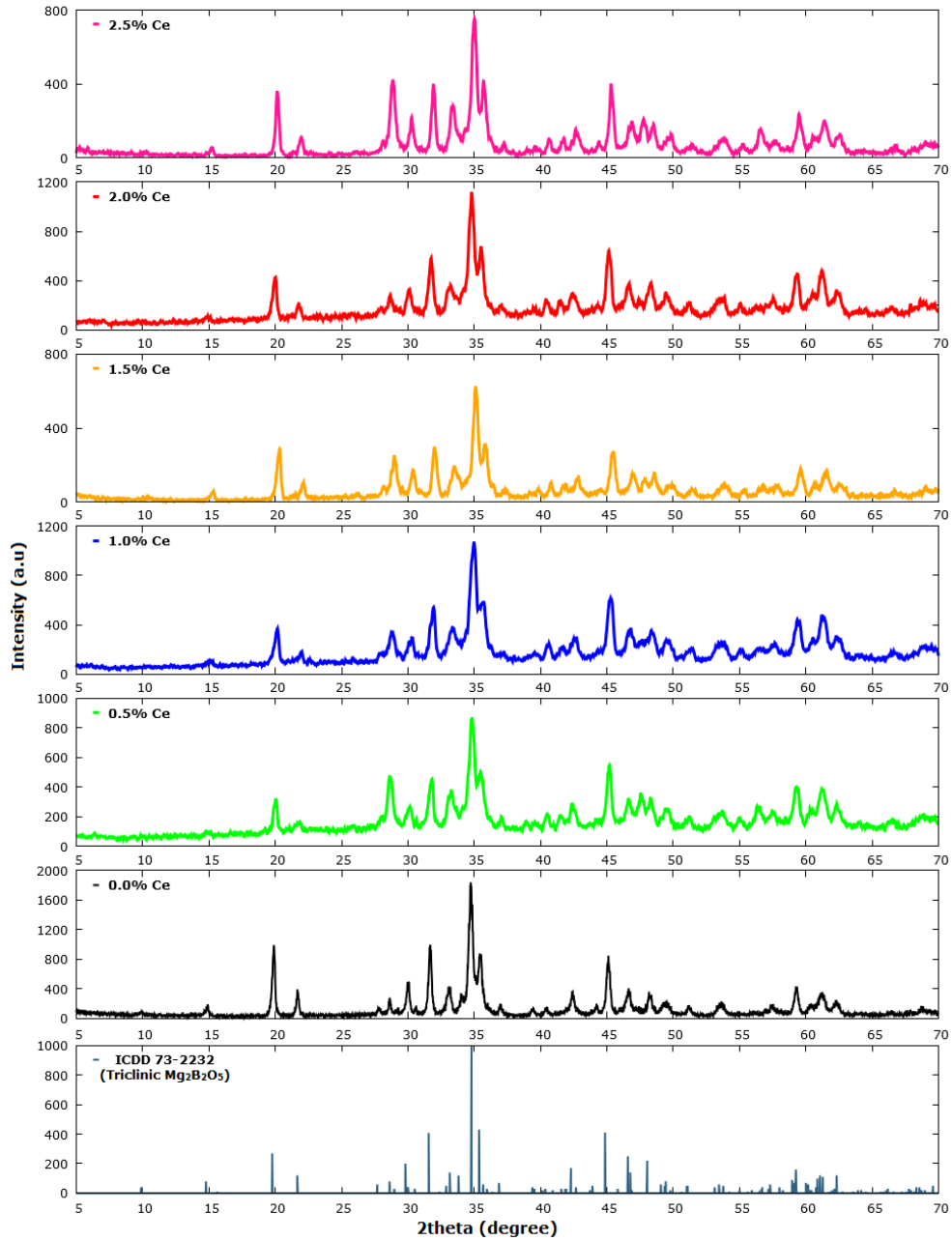


Figure 4.15. The XRD patterns of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 1000°C

4.2.1.2 Europium Doped Magnesium Pyroborates

According to the XRD patterns, the monoclinic and triclinic magnesium pyroborates doped europium metal ions were formed at 800°C and 1000°C, respectively. Regardless of the fuel types, the patterns show excellent compatibility with the respective ICDD card.

Citric Acid Fuel: The characteristic reflection which belongs to monoclinic magnesium pyroborates found at $2\theta \approx 35^\circ$ (Figure 4.16) and all the diffraction lines are in a good agreement with the ICDD cards of related crystal structures. These d-lines are similar to cerium doped magnesium pyroborates.

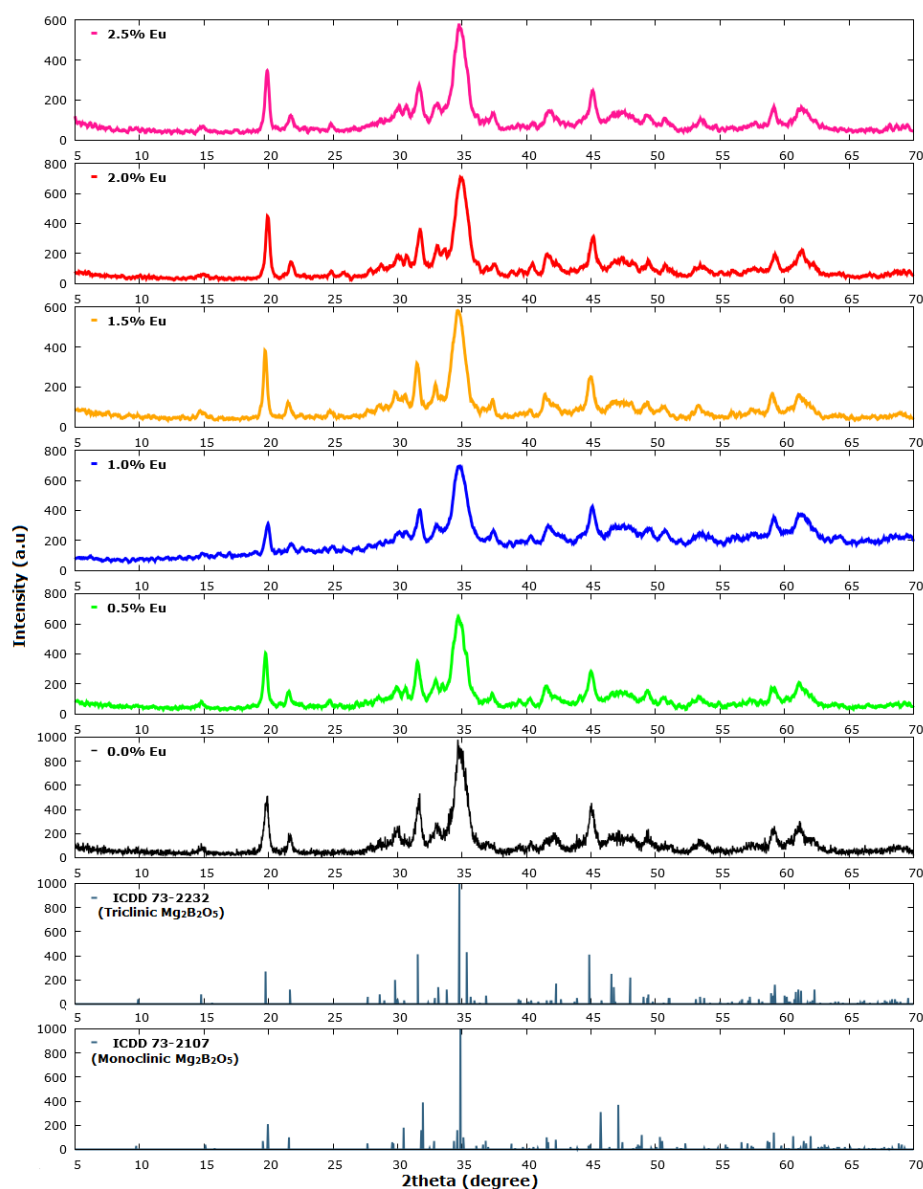


Figure 4.16. The XRD patterns of $\text{Mg}_{2-x}\text{Eu}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 800°C

There is no distinctive changes were observed in the diffractogram of the products obtained at 900°C. Presented in Figure 4.17, only 1.5% Eu and 2.5% transformed from monoclinic to triclinic phase. The chemical composition and temperature range of heating might be the factors that lead to the alterations in this behavior.

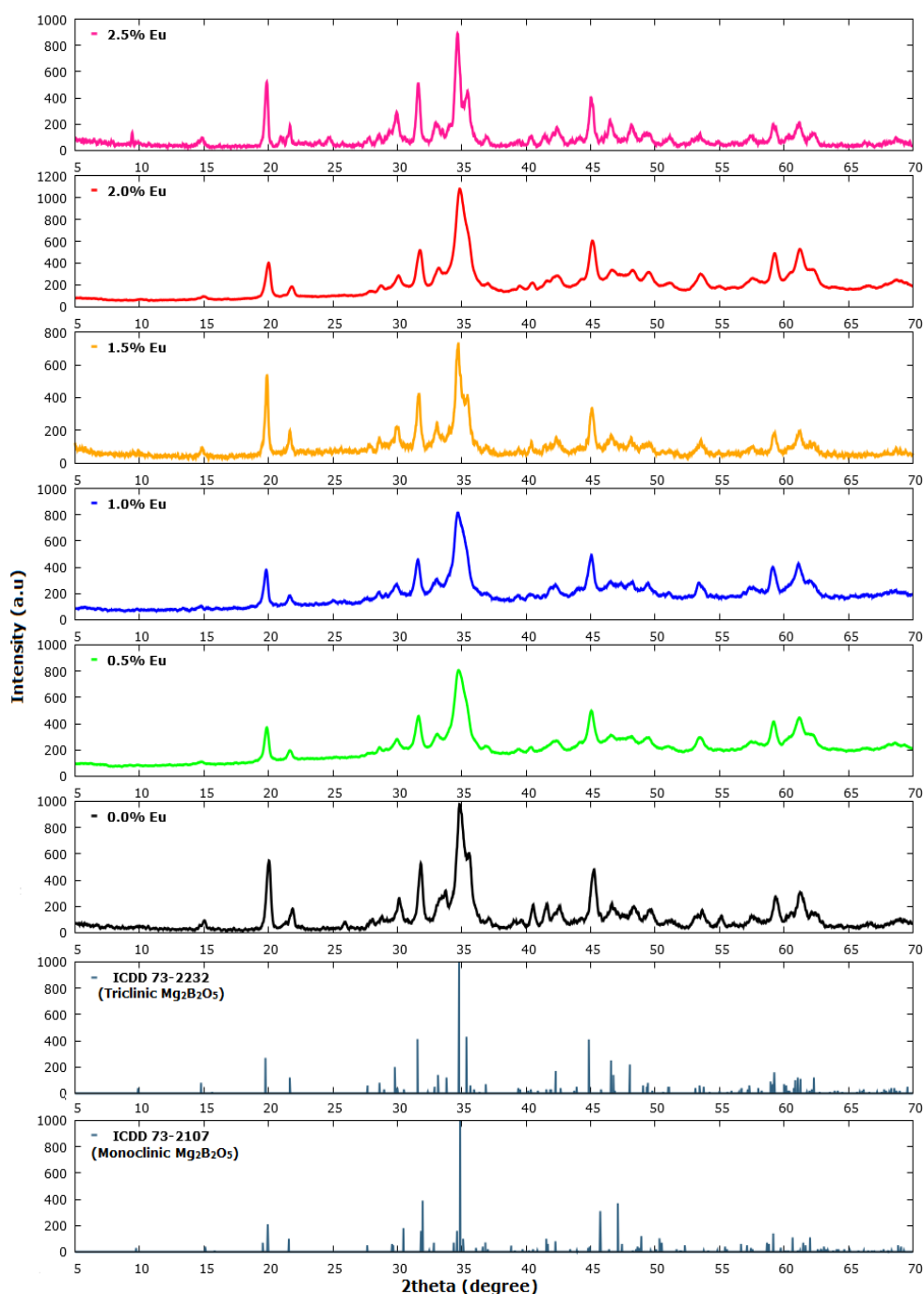


Figure 4.17. The XRD patterns of $\text{Mg}_{2-x}\text{Eu}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 900°C

According to the Figure 4.18, higher annealing temperature will direct the structural change towards triclinic forms of magnesium pyroborate, indicated by XRD peaks splitting at $2\theta \sim 34.8$ degree. A secondary phase is observed in the patterns for 1.5% Eu^{3+} and 2.5% Eu^{3+} doping concentrations, while the other patterns correspond to the triclinic form of magnesium pyroborates. The highest intensity belongs to 1.0% Eu^{3+} at around 1495 (a.u) which makes this compound has the highest crystallinity compares to others.

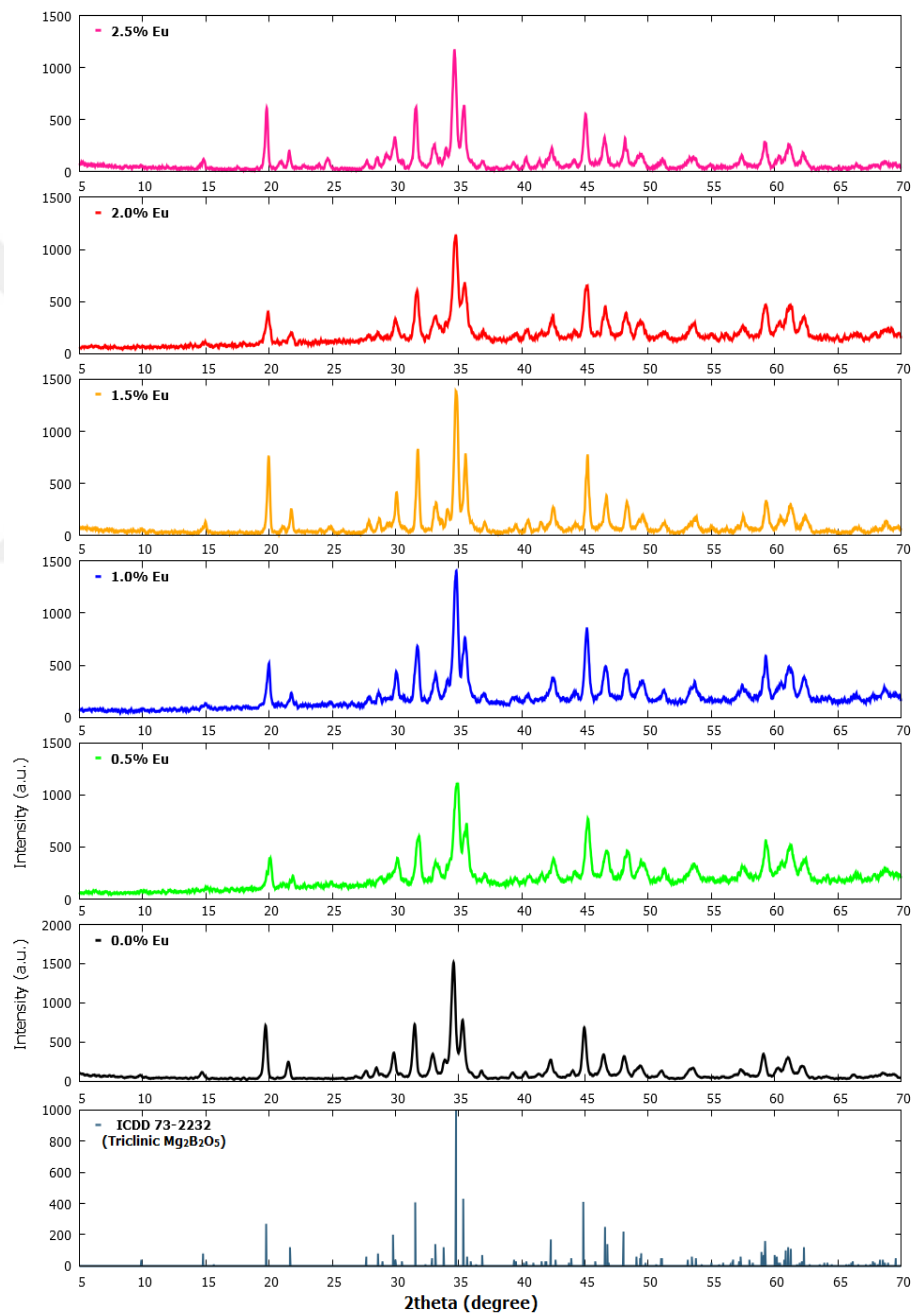


Figure 4.18. The XRD patterns of $\text{Mg}_{2-x}\text{Eu}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 1000°C

Glycine Fuel: $\text{Mg}_2\text{B}_2\text{O}_5: \text{Eu}^{3+}$ showed very similar spectra with the pure $\text{Mg}_2\text{B}_2\text{O}_5$ obtained at the same temperatures which are 800°C, 900°C and 1000°C. All the obtained products were compared. In the XRD patterns of different quantities of Eu^{3+} , similar to Ce^{3+} doped single phase monoclinic magnesium pyroborates were successfully obtained at 800°C (Figure 4.19). This behavior confirmed the type of doping materials does not alter the crystal structure of the host materials and are completely mixed with the host magnesium pyroborates materials. The crystal structure was found to be monoclinic at 800°C and triclinic at higher temperature.

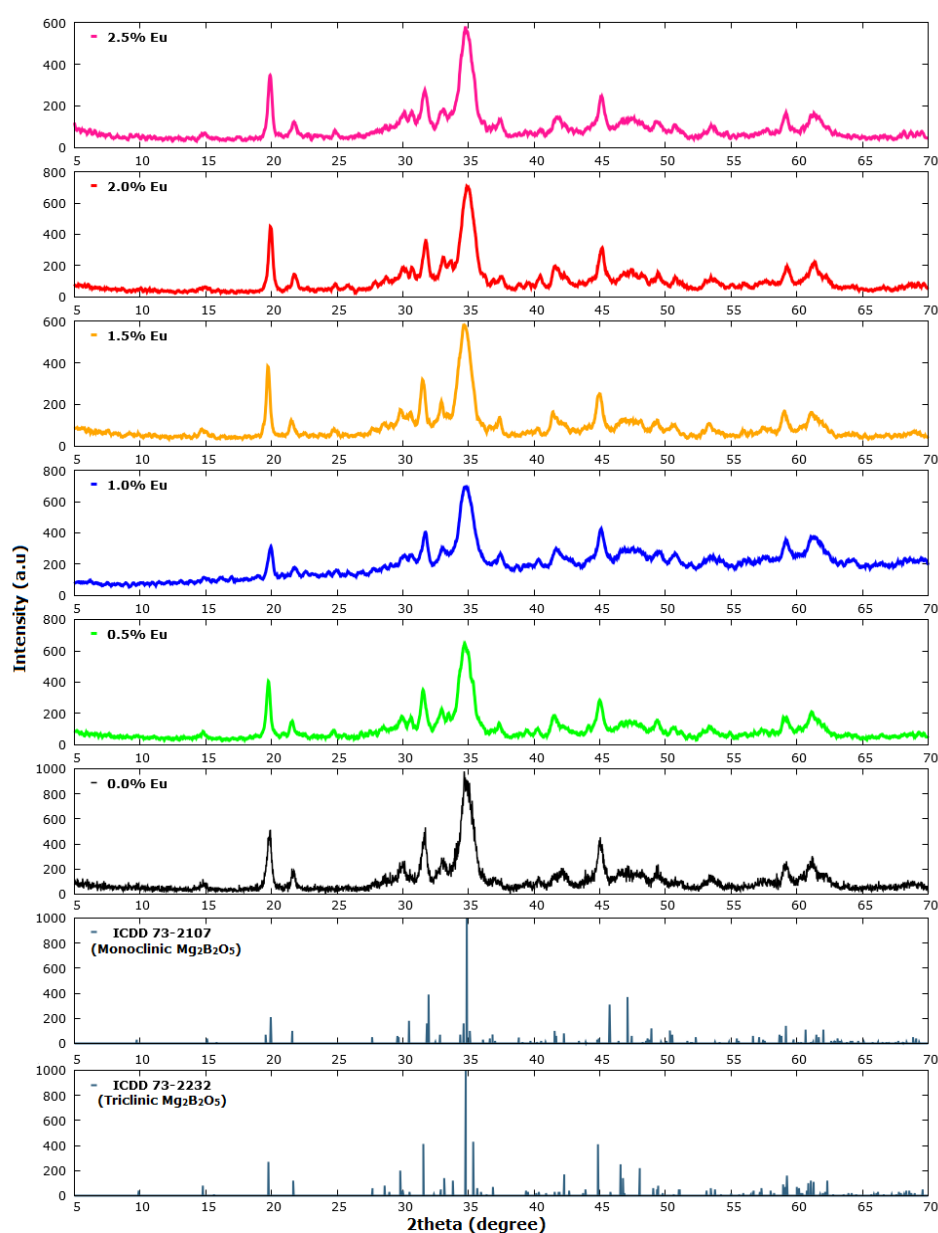


Figure 4.19. The XRD patterns of $\text{Mg}_{2-x}\text{Eu}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 800°C

Given in Figure 4.20, the monoclinic europium doped magnesium pyroborate with different concentrations were transformed into triclinic forms at 900°C. At this temperature, the d-line of triclinic form magnesium pyroborates start to dominate except for 2.5% Eu^{3+} doped which still crystallized in monoclinic phase. The formation of triclinic magnesium pyroborates was confirmed by the existense of doublet sharp maximum peak at $2\theta = \sim 34.6^\circ$. Furthermore, the additional d-line belong to secondary phase was noticed that belongs to Eu_2O_3 with ICDD No: 34-0392.at patterns of 1.5% Eu^{3+} around $2\theta = 28.4^\circ$ and 32.7° .

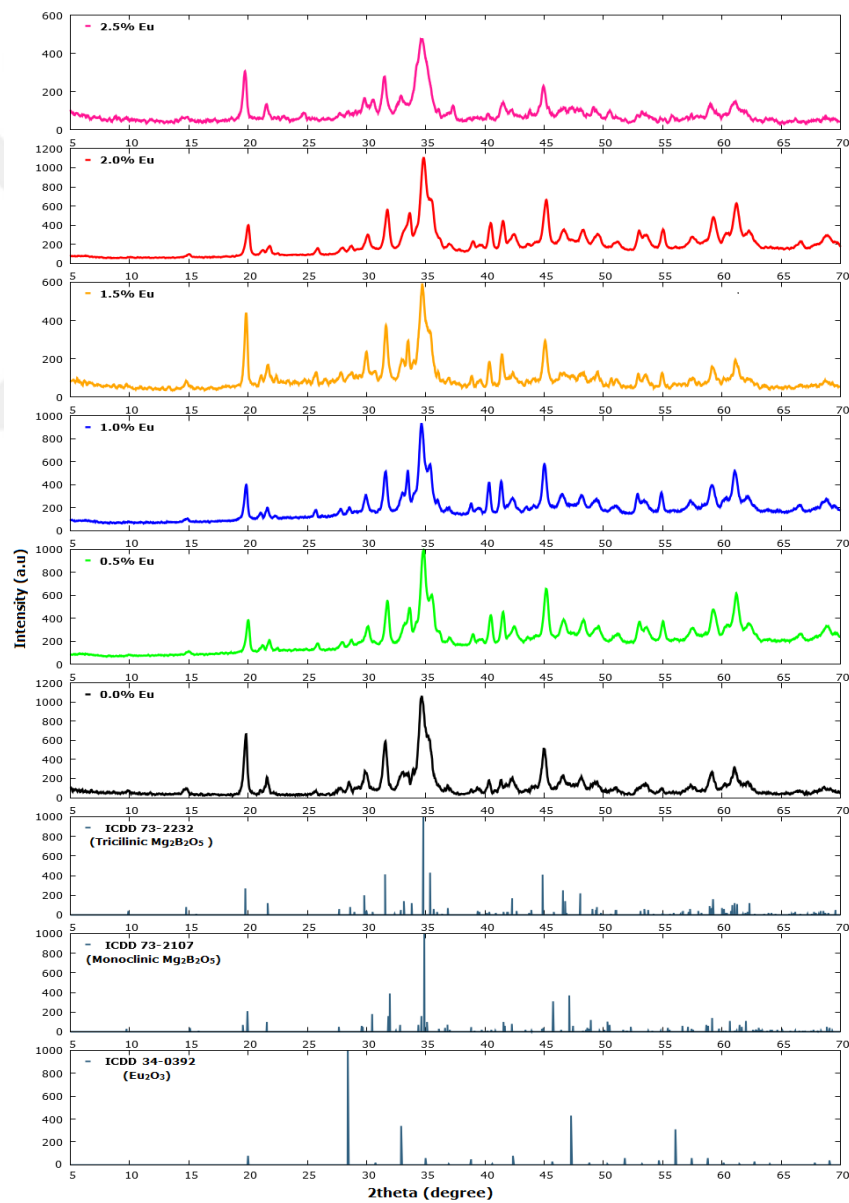


Figure 4.20. The XRD patterns of $\text{Mg}_{2-x}\text{Eu}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 900°C

The XRD data at 1000°C are consistent with the standard ICDD card no: 73-2232, predominantly showing peaks characteristic of the triclinic phase of magnesium pyroborate. Additionally, two minor reflections corresponding to secondary phases are present in all patterns observed at this temperature. The secondary phase, identified at 2θ angles of approximately 21° , 28.6° , and 33.1° , is attributed to Eu_2O_3 (ICCD Card No. 34-0392). Unlike the other concentrations, where additional reflection lines began to appear at 900°C, the 2.5% Eu-doped sample displayed extra lines only at 1000°C. The pure monoclinic phase was obtained at 900°C (Figure 4.20).

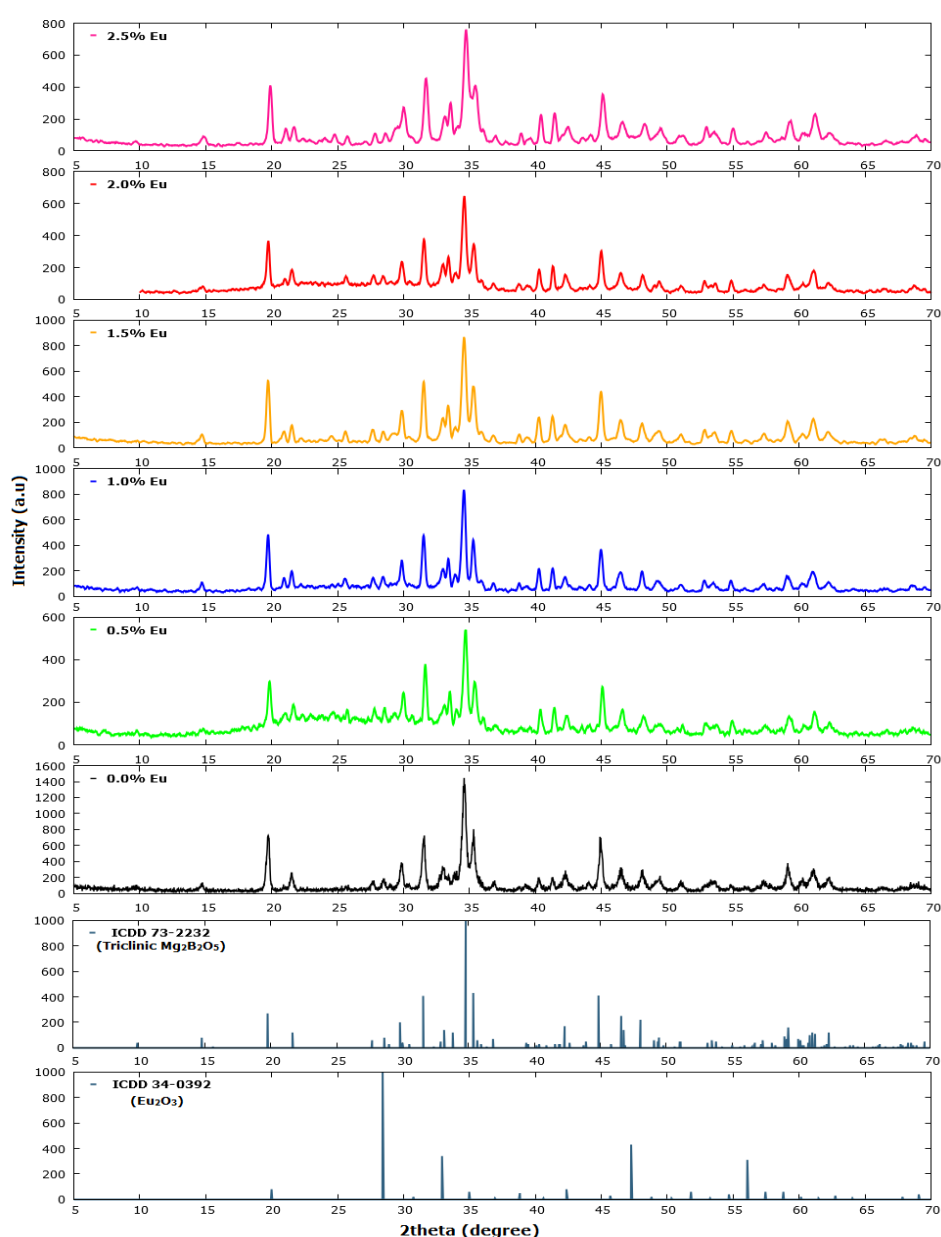


Figure 4.21. The XRD patterns of $\text{Mg}_{2-x}\text{Eu}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 1000°C

HMTA Fuels: The XRD patterns of the products obtained at 800°C and 900°C using various concentration of europium (III) are shown in Figure 4.21 and 4.22. The assignments of characteristic reflections of XRD pattern were also compared with the pure $\text{Mg}_2\text{B}_2\text{O}_5$ data and ICDD card data (73-2232 and 73-2107). All the reflections on the diffractogram gave a great compatibility with the reflections to the pure $\text{Mg}_2\text{B}_2\text{O}_5$ and have high crystallinity.

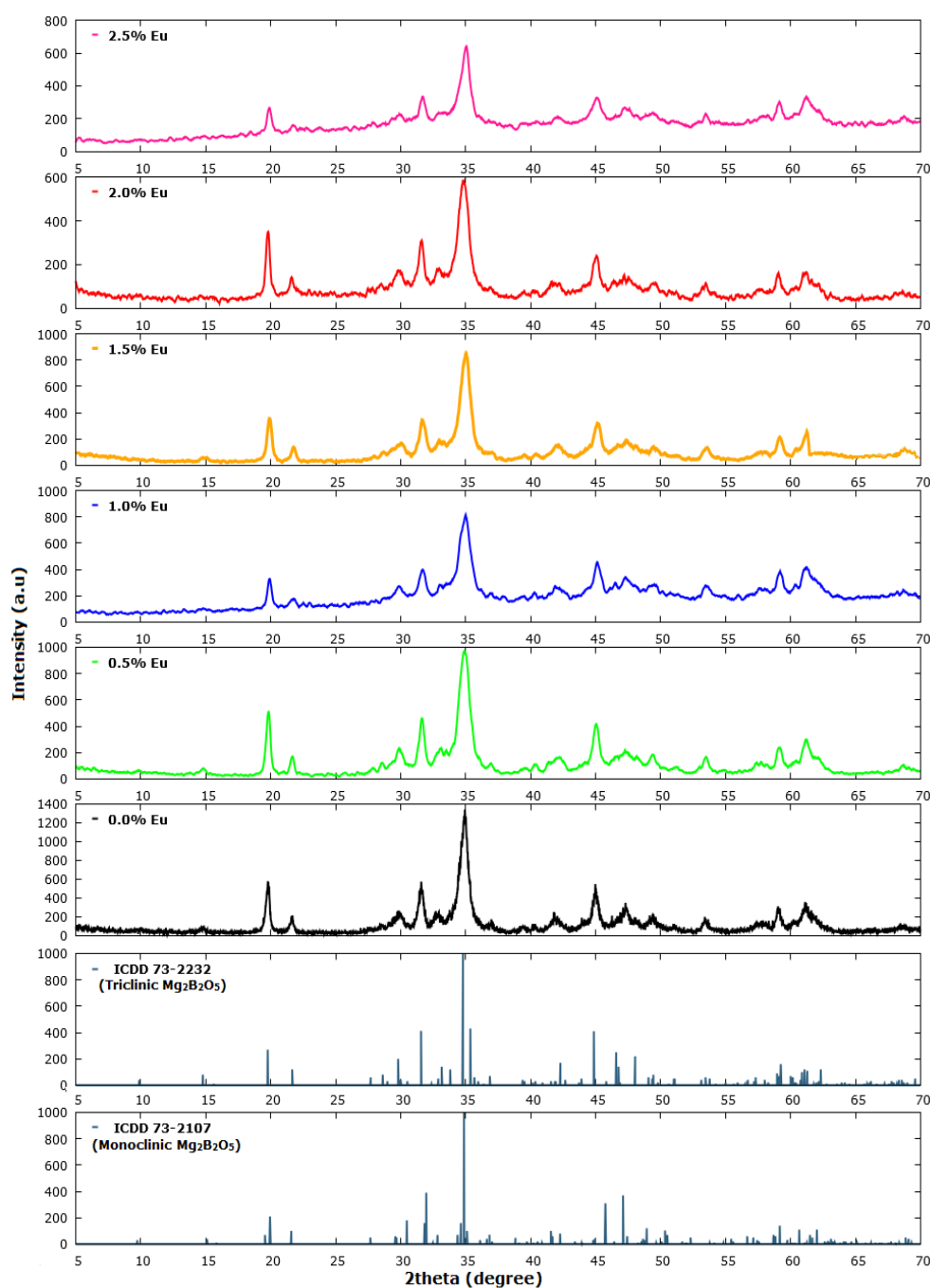


Figure 4.22. The XRD patterns of $\text{Mg}_{2-x}\text{Eu}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 800°C

The transformation of single-phase magnesium pyroborates obtained at 900°C was observed. The d-lines of the triclinic phase of magnesium pyroborates are dominated and have a great compatibility with ICDD card no: 72-2232. These confirmed that the addition of doping is not significantly altering the transformation's temperature of monoclinic into triclinic phases at higher 900°C.

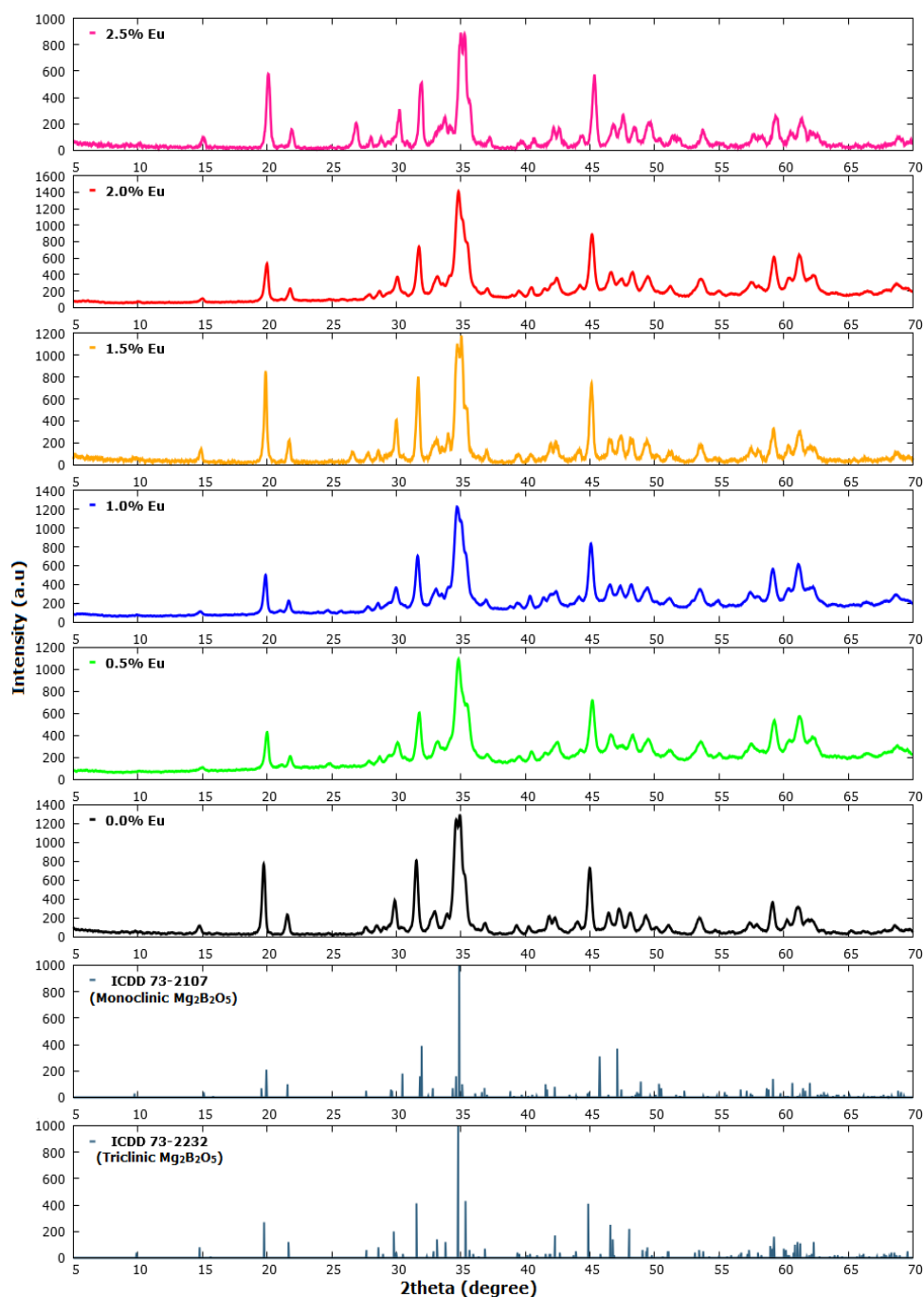


Figure 4.23. The XRD patterns of $\text{Mg}_{2-x}\text{Eu}_x\text{B}_2\text{O}_5$ ($x = 0.000$ - 0.025) obtained at 900°C

Single phase magnesium pyroborates doped europium ion was obtained at 1000°C. The secondary phase was observed in the patterns of 1.5% and 2.5% of Europium concentrations. The secondary phase was detected by the existence of small d-lines in the range of $2\theta = 21$ -30 theta degree. The other concentrations known as 0.5%, 1.0% and 2.0% was found to be single phase magnesium pyroborates (Figure 4.24). The second phase might be caused due to the side reactions of high heating temperature or the phase transition which induce change in the morphology of the products.

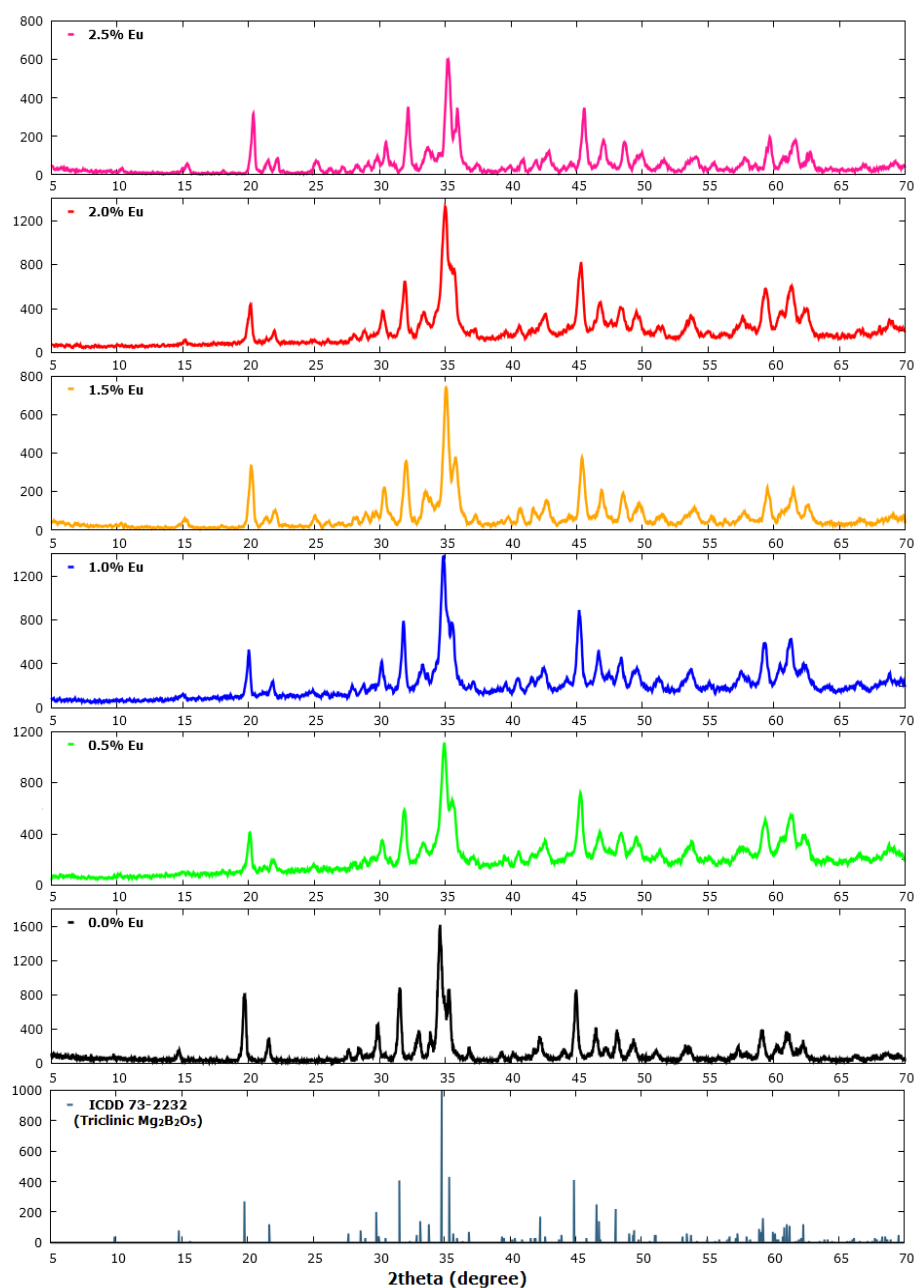


Figure 4.24. The XRD patterns of $\text{Mg}_{2-x}\text{Eu}_x\text{B}_2\text{O}_5$ ($x = 0.000$ - 0.025) obtained at 1000°C

Tartaric Acid : Presented in Figure 4.25 to 4.27, single phase magnesium pyroborates with europium (III) with various concentrations were acquired. Tartaric acid was used as fuels and it observed that the europium is successfully doped into $\text{Mg}_2\text{B}_2\text{O}_5$ as no secondary phases e.g Eu_2O_3 was found. The patterns displayed a great crystallinity of products and the m- $\text{Mg}_2\text{B}_2\text{O}_5$ was formed at 800°C (Figure 4.25). The transition between two phases of magnesium pyroborates were detected at 900°C (Figure 4.26).

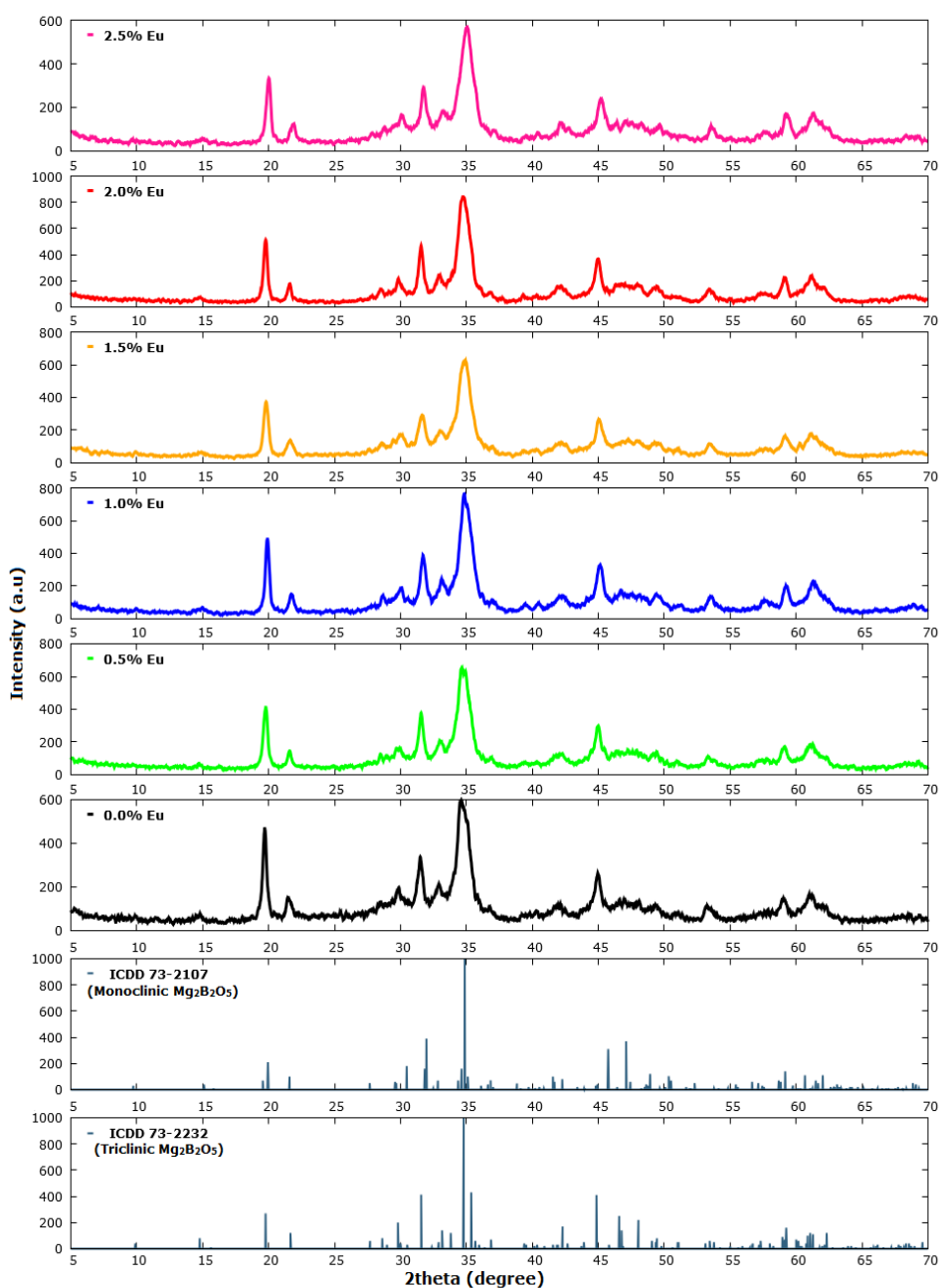


Figure 4.25. The XRD patterns of $\text{Mg}_{2-x}\text{Eu}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 800°C

The influence on the amount of dopant materials used were clearly noticed in the patterns obtained at 900°C. The transformation of m-Mg₂B₂O₅ to t-Mg₂B₂O₅ were observed. At concentrations greater than 1.0% Eu³⁺, triclinic magnesium pyroborates are fully formed, as evidenced by the detection of two characteristic reflections corresponding to the triclinic phase of Mg₂B₂O₅ at 2θ = 34.5° and 35.2°. These patterns are consistent with ICDD card no: 73-2232.

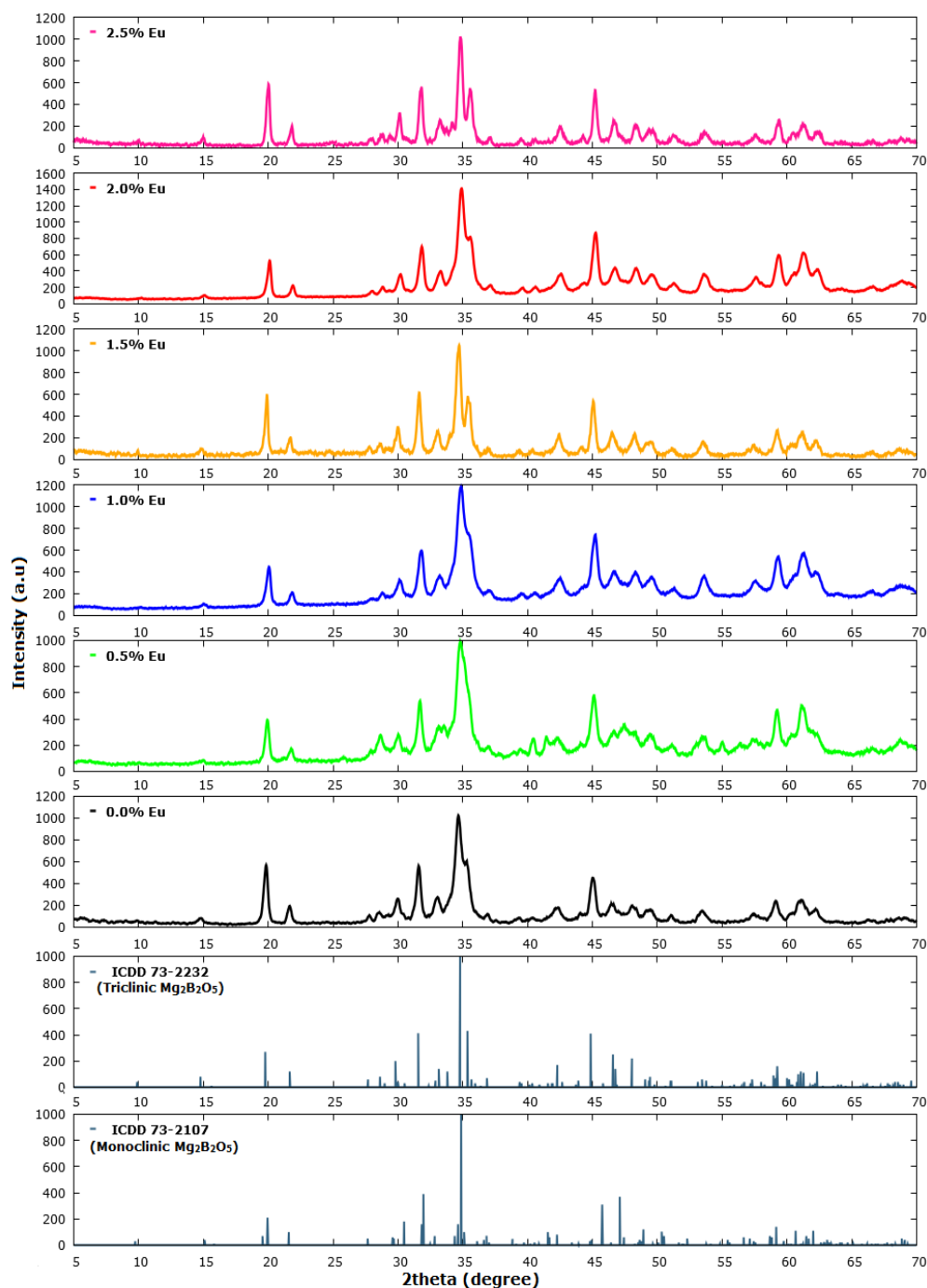


Figure 4.26. The XRD patterns of Mg_{2-x}Eu_xB₂O₅ (x= 0.000-0.025) obtained at 900°C

The patterns displayed in Figure 4.27 characterized the single phase triclinic magnesium pyroborates in high crystallinity. All the diffractograms show a great compatibility with the triclinic magnesium pyroborates' ICDD data card. Furthermore, 1.0% Eu^{3+} are considered as the best concentration in the formation of pure magnesium pyroborates as it has the highest crystallinity among the other concentrations.

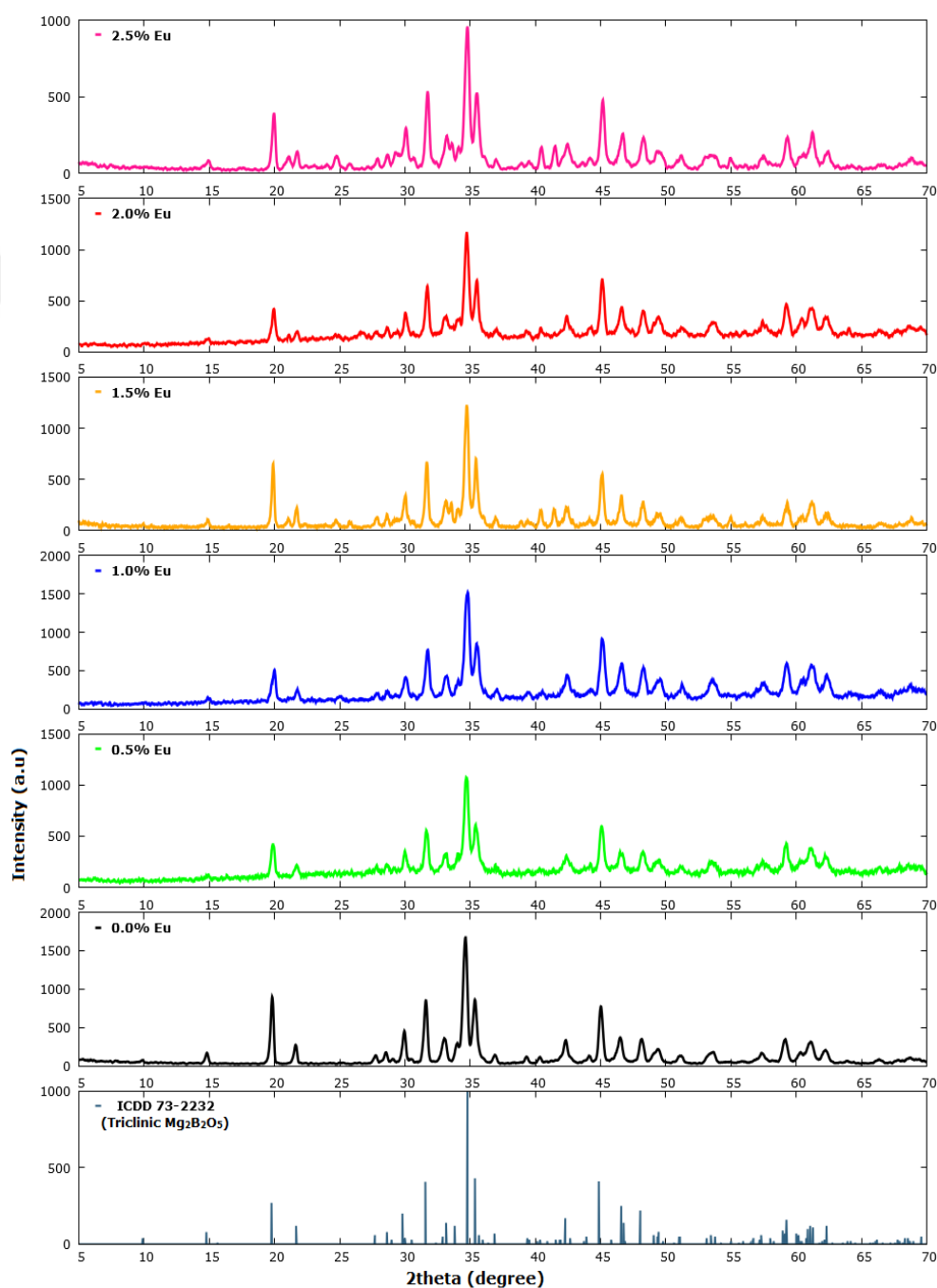


Figure 4.27. The XRD patterns of $\text{Mg}_{2-x}\text{Eu}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 1000°C

Urea Fuels : The XRD patterns of europium (III) doped magnesium pyroborates were given in Figures below. Similar to the other patterns, the monoclinic phase of magnesium pyroborates was acquired at 800°C. The formation of monoclinic phase are confirmed by the presence of single maximum peak at $2\theta = 35^\circ$. Furthermore, the transformation between two phases of magnesium pyroborates were expected to be observed at higher temperature as the characteristic peaks of triclinic phase magnesium pyroborates are observed in the patterns of 2.5% europium. In these patterns the m-Mg₂B₂O₅ d-lines are pre-dominated (Figure 4.28).

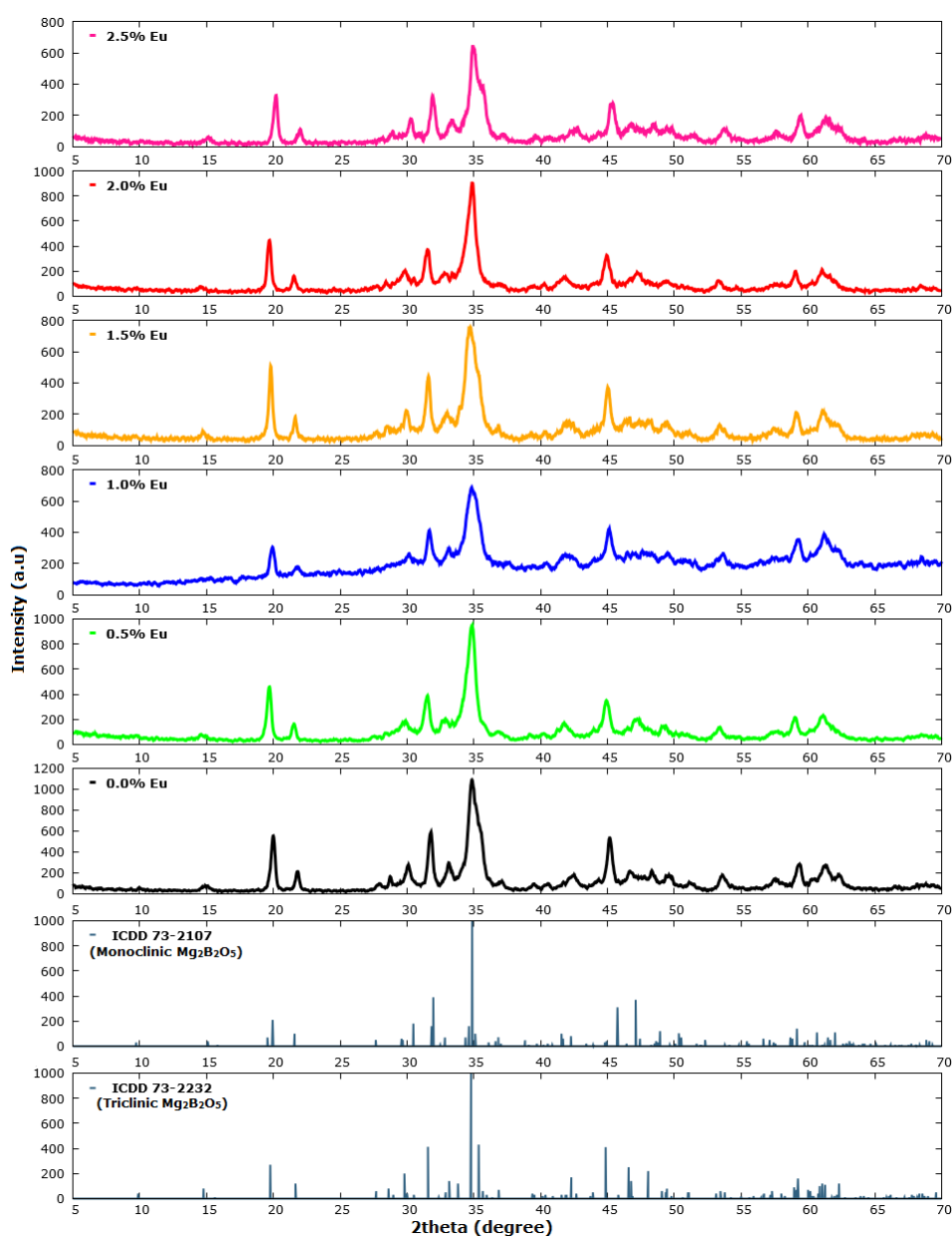


Figure 4.28. The XRD patterns of Mg_{2-x}Eu_xB₂O₅ (x= 0.000-0.025) obtained at 800°C

Differ from the XRD patterns of the undoped magnesium pyroborates, the transformation to the triclinic magnesium pyroborate phase has not yet occurred at 900°C. All the diffraction lines are in excellent agreement with the ICDD card no: 73-2107, corresponding to the monoclinic phase of magnesium pyroborate. This also proposed the temperature and also the dopant's concentration effects on the crystal structure of the host materials. Additionally, single phase magnesium pyroborates was obtained by the additions of 2.5% europium(III).

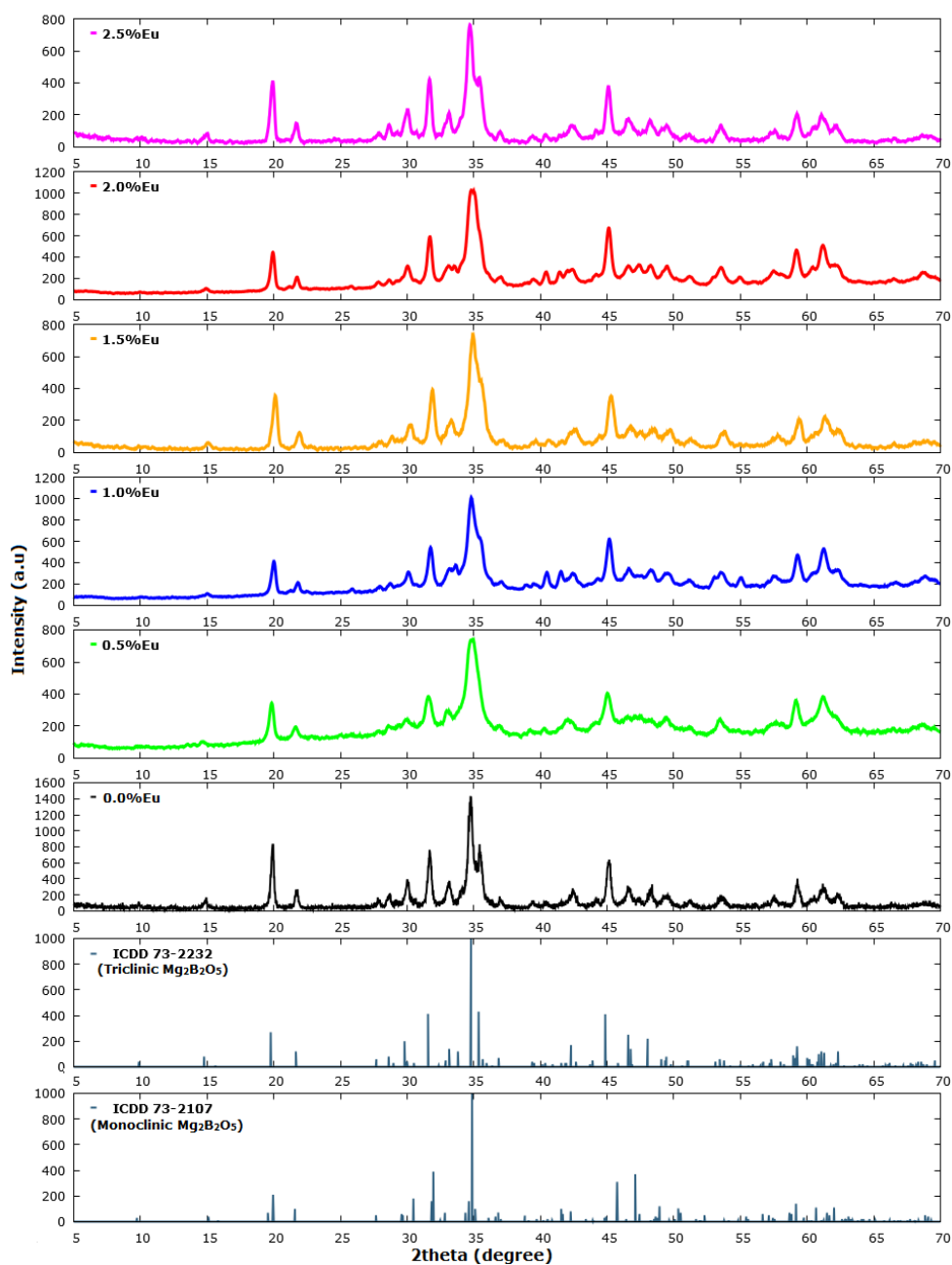


Figure 4.29. The XRD patterns of $\text{Mg}_{2-x}\text{Eu}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 900°C

As shown in Figure 4.30, the multiple phases in magnesium pyroborates indicated by the detection of small peaks at $2\theta = 21^\circ$ in the patterns of 1.5% Eu^{3+} and 2.5% Eu^{3+} . In contrast, the single-phase magnesium pyroborates were successfully synthesized with high crystallinity at 0.5%, 1.0%, and 2.0% europium (III) doping. The diffraction lines in these three diffractograms are in good agreement with the ICDD card for triclinic $\text{Mg}_2\text{B}_2\text{O}_5$ (ICDD Card: 73-2232).

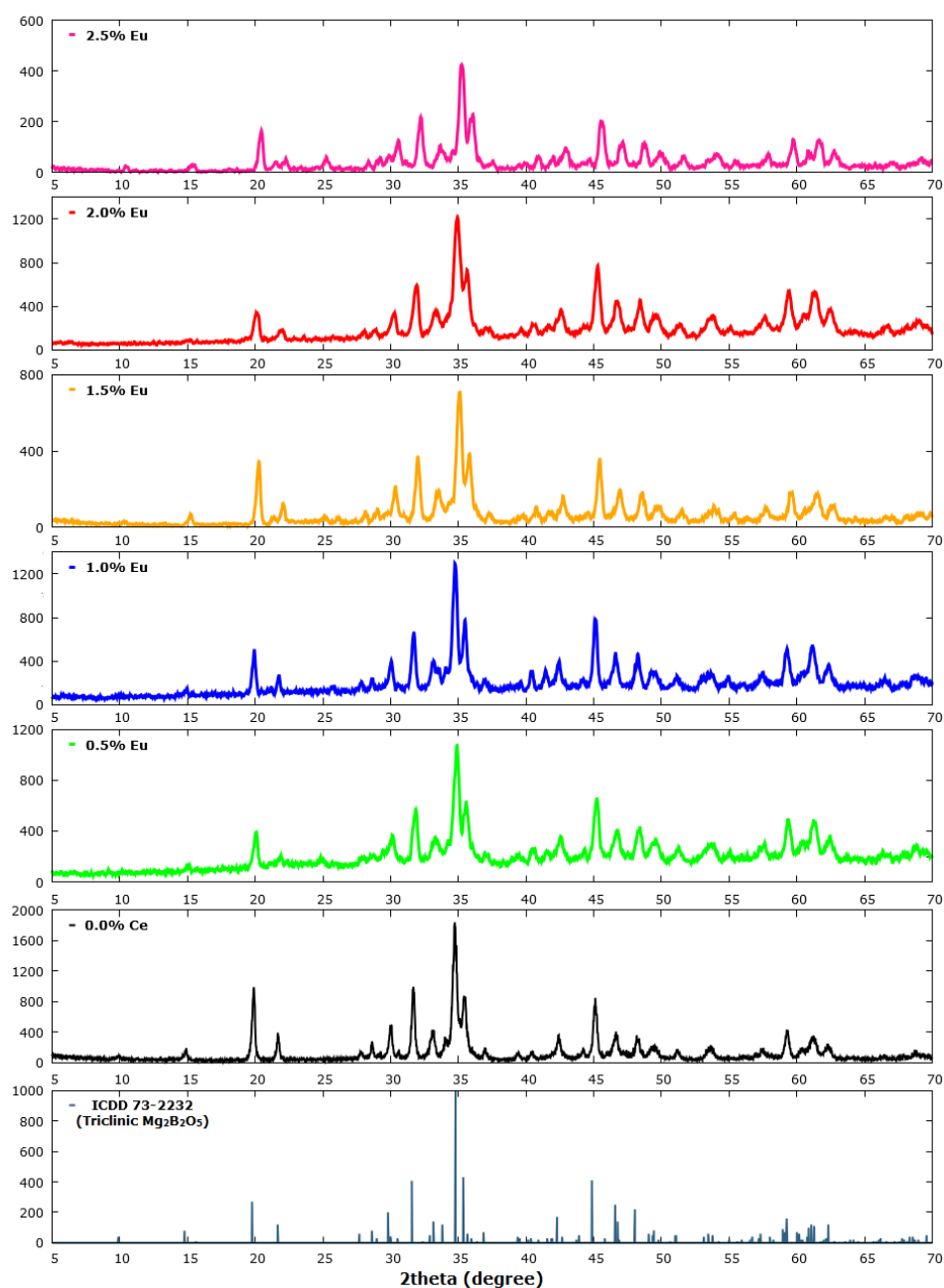


Figure 4.30. The XRD patterns of $\text{Mg}_{2-x}\text{Eu}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 1000°C

4.2.1.3 Terbium Doped Magnesium Pyroborates

The XRD patterns of terbium doped magnesium pyroborates have also defined in the range of 5-70 theta degree. The results showed similar behavior with the previous dopant materials, cerium and europium doped. In some products terbium oxide was detected as second phase which might form due to the increase of terbium's concentration. This second phase can be form during the synthesis and also annealing process.

Citric Acid Fuel: In The XRD patterns of $\text{Mg}_2\text{B}_2\text{O}_5:\text{Tb}^{3+}$ and undoped $\text{Mg}_2\text{B}_2\text{O}_5$ shown below (Figure 4.31-4.33). The assignments of characteristic reflections of XRD pattern were analyzed based on ICDD card 73-2232 and 73-2107. Monoclinic phase and triclinic phase of $\text{Mg}_2\text{B}_2\text{O}_5$ were observed at 800°C and $\geq 800^\circ\text{C}$, respectively.

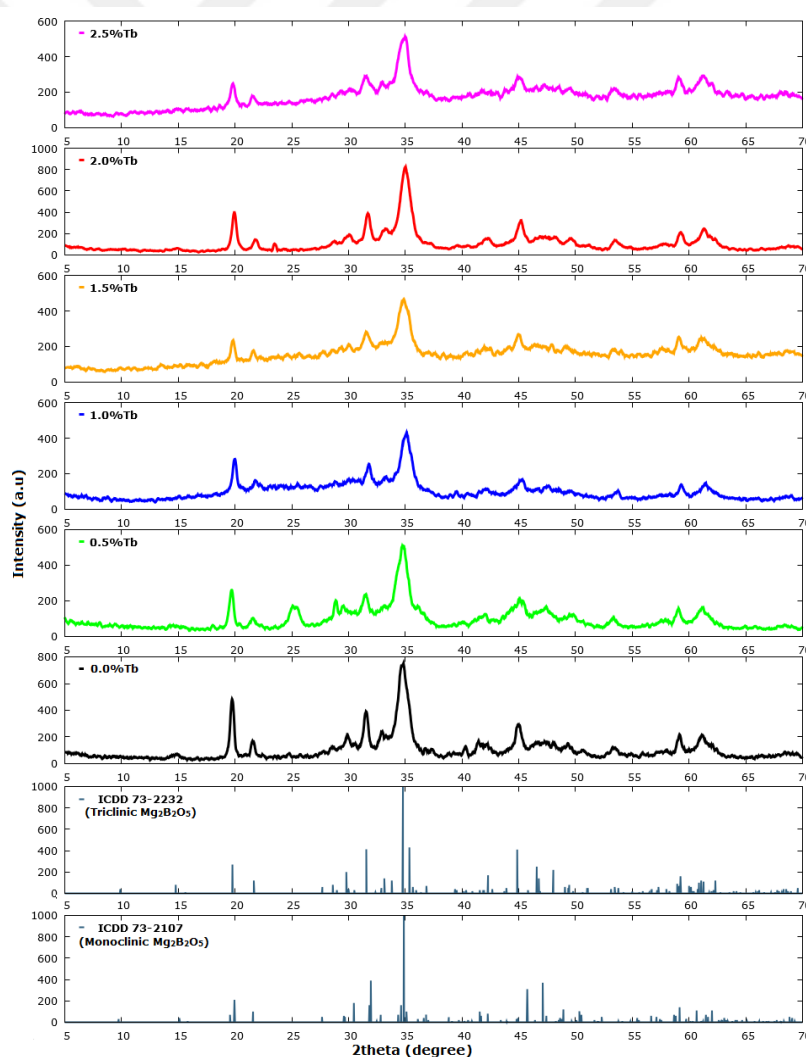


Figure 4.31. The XRD patterns of $\text{Mg}_{2-x}\text{Tb}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 800°C

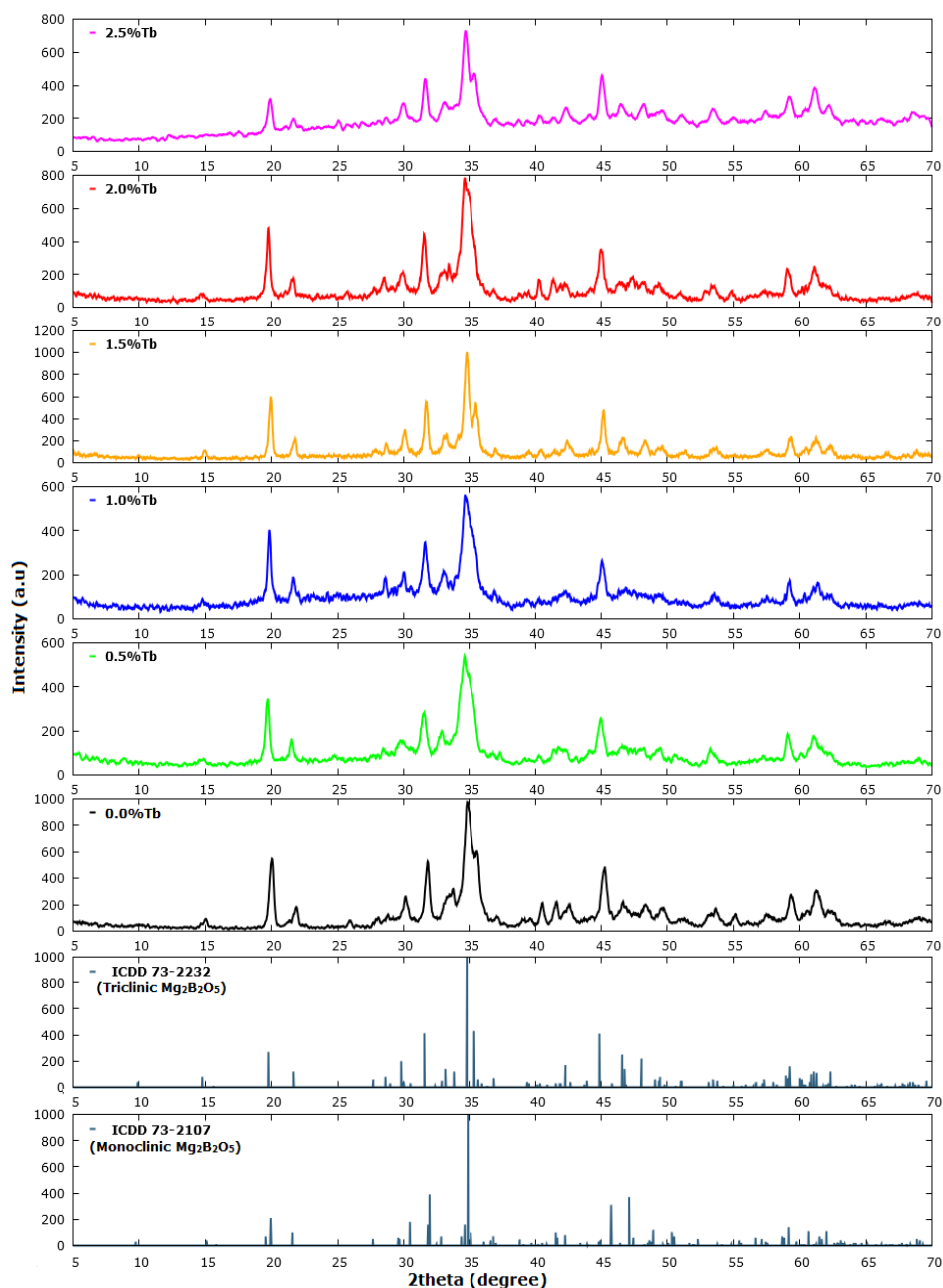


Figure 4.32. The XRD patterns of $\text{Mg}_{2-x}\text{Tb}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 900°C

Compared to the standard ICDD card data and the patterns of other samples, two additional small peaks were observed at $2\theta = 20^\circ$ and 50° in the patterns of the 2.5% Tb-doped sample attained at 1000°C . These impurities may have arisen due to an incomplete reaction during the preparation process or during the phase transformation. Due to this secondary phase, the intensity of the 2.5% Tb^{3+} pattern is found to be the lowest among all concentrations. In contrast, the other dopant concentrations (0.5–2.0% Tb^{3+}) formed a single phase with a triclinic form of magnesium pyroborates (Figure 4.33).

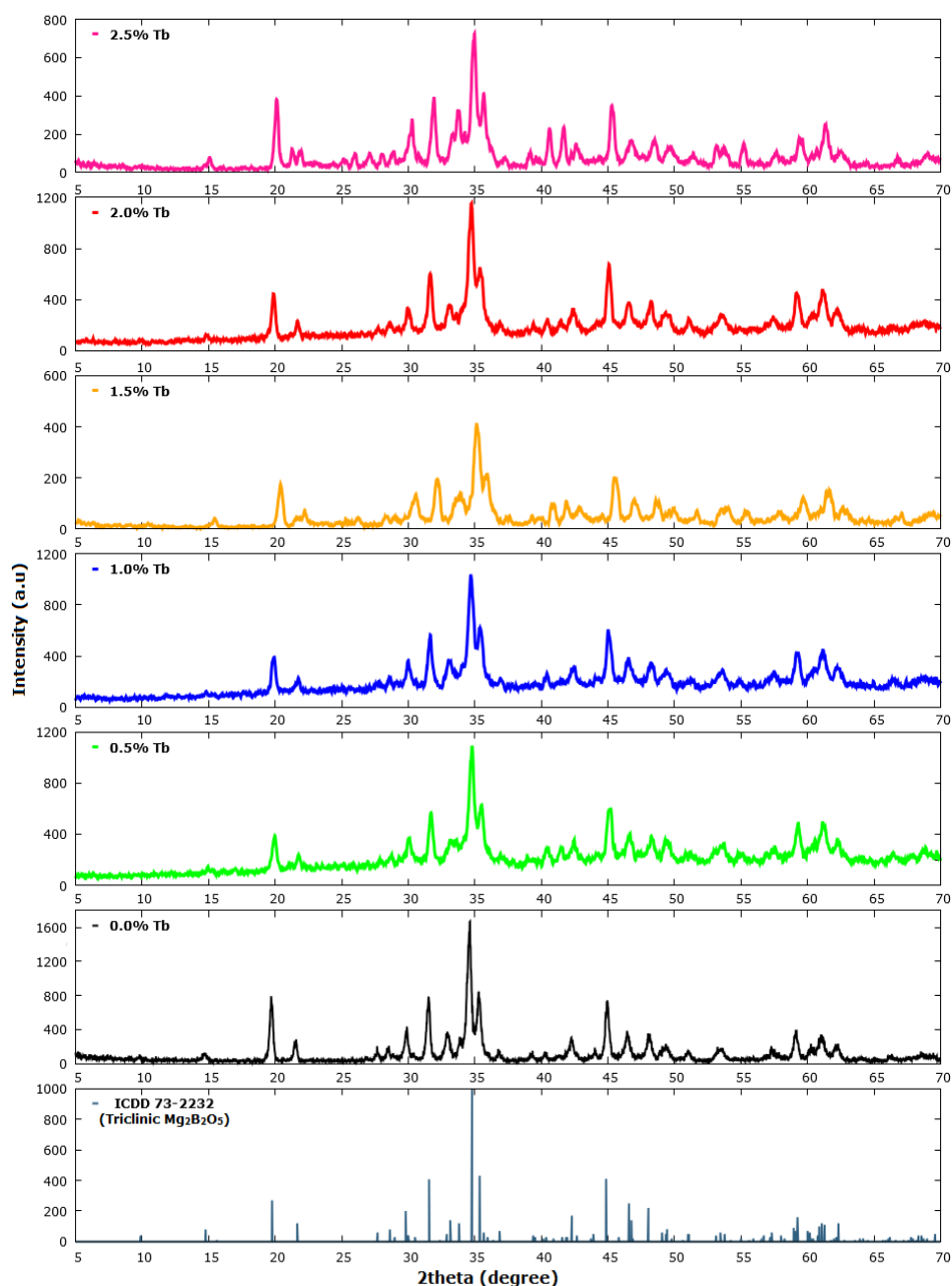


Figure 4.33. The XRD patterns of $\text{Mg}_{2-x}\text{Tb}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 1000°C

Glycine Fuel: The patterns shown in Figure 4.34 to 4.35 emphasized the temperature and doping effect on the formation of single phase $\text{Mg}_2\text{B}_2\text{O}_5$. Similar to Eu^{3+} doped $\text{Mg}_2\text{B}_2\text{O}_5$, Tb^{3+} doped magnesium pyroborates also produced secondary phase. The products obtained at 900°C have higher crystallinity than the one obtained at 800°C which indicate more order and arrangement of atom in the compound. These facts showed the impact of temperature on the structural properties of the examined materials.

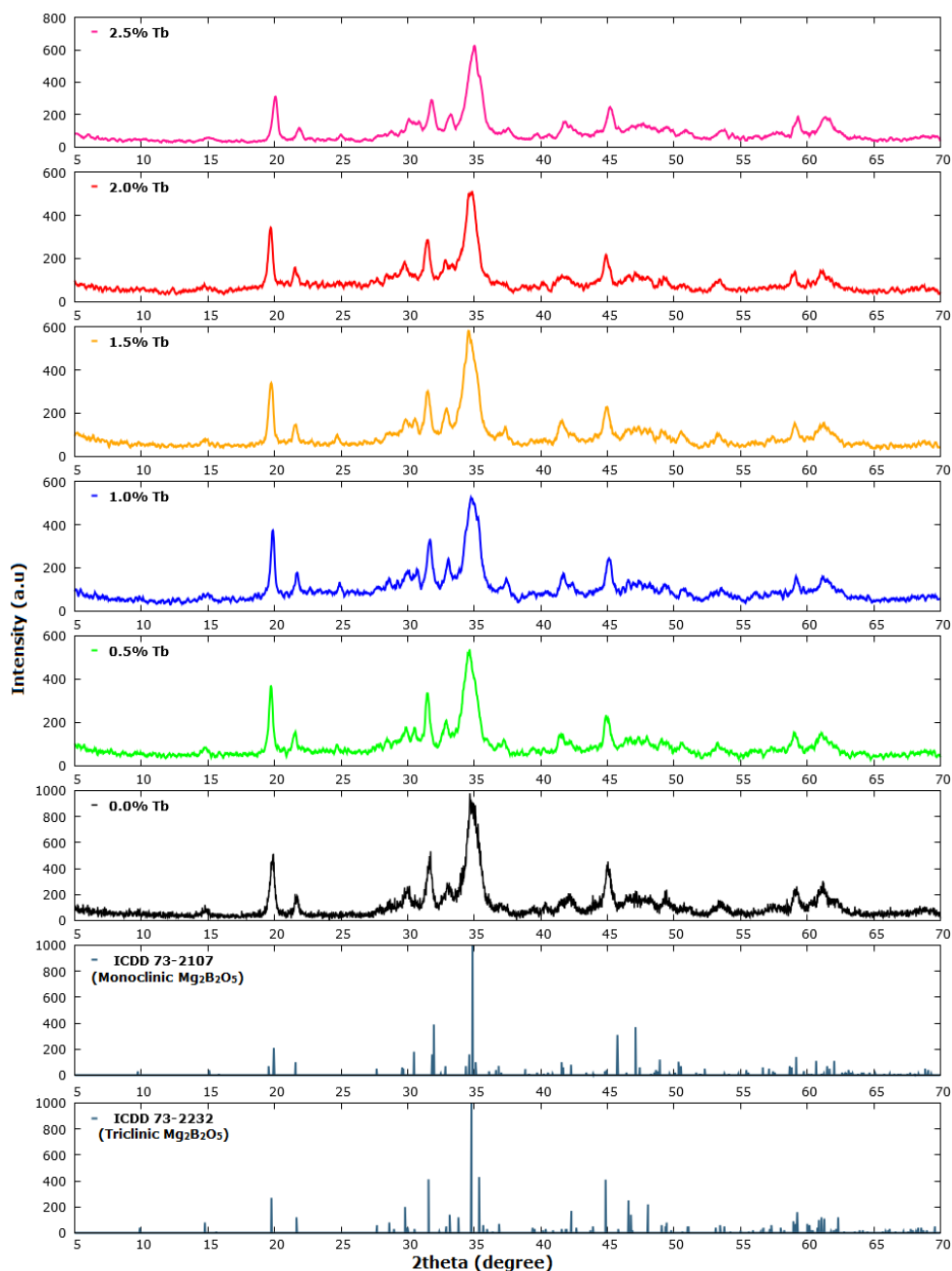


Figure 4.34. The XRD patterns of $\text{Mg}_{2-x}\text{Tb}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 800°C

Higher intensity patterns were obtained at 900°C and 1000°C , respectively but due to the existence of secondary phase at the lower temperature the formation of impurities at 1000°C can not be avoided. Although the d-line of triclinic phase are dominating and most of them have excellent accordance to ICDD card no: 73-2232, some additional peak were detected between $2\theta = \sim 21^\circ-30^\circ$ (Figure 4.35). Terbium oxide was found to be the secondary phase during the preparation of terbium doped magnesium pyroborates.

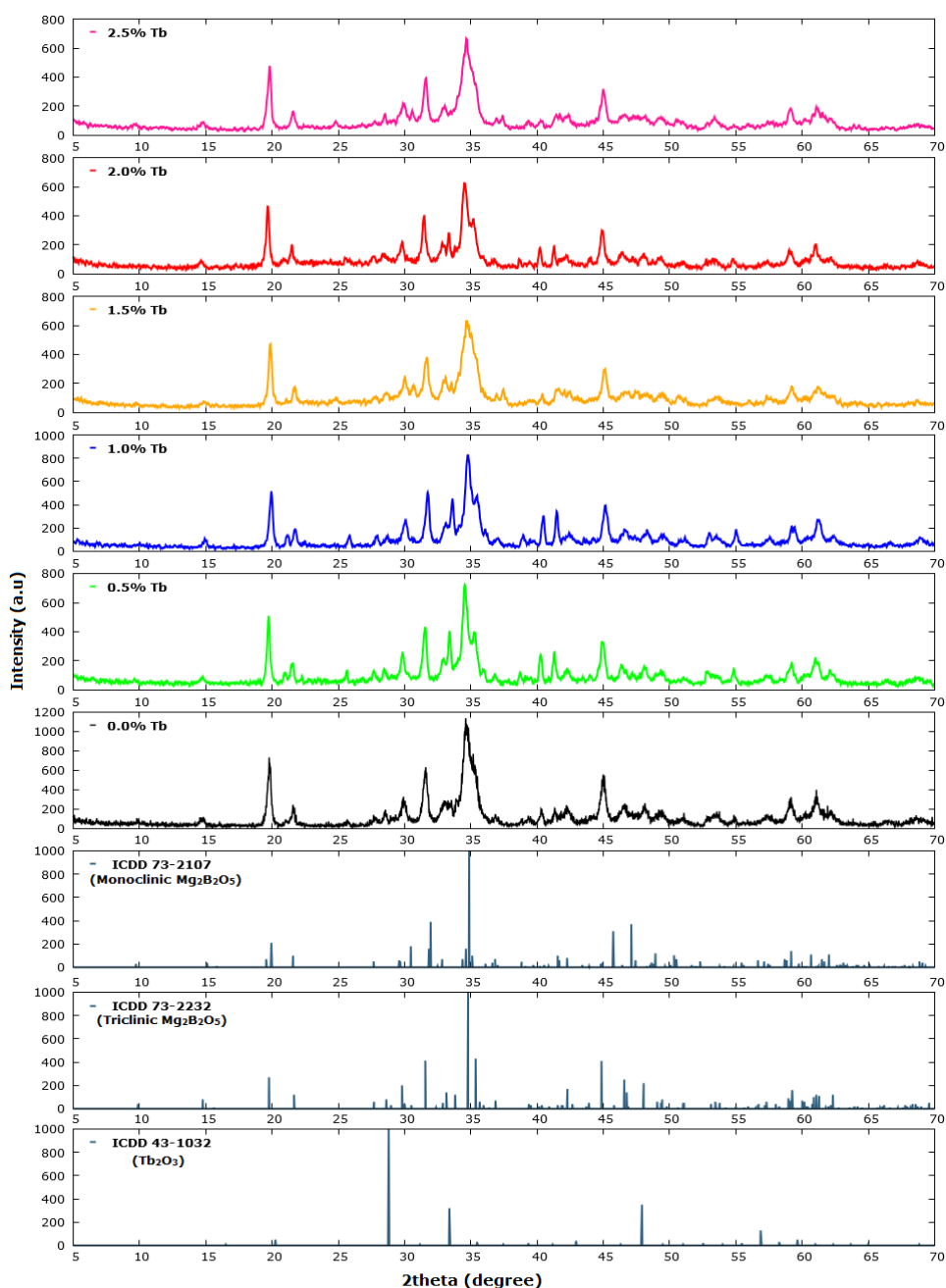


Figure 4.35. The XRD patterns of $\text{Mg}_{2-x}\text{Tb}_x\text{B}_2\text{O}_5$ ($x = 0.000\text{--}0.025$) obtained at 900°C

Given the high heating temperature ($>800^\circ\text{C}$), terbium ions might undergo oxidation during the transformation process, leading to the formation of terbium oxide. Although the triclinic phase of magnesium pyroborates is dominant, the presence of terbium oxide diffraction lines cannot be overlooked. These impurities may form during the synthesis or heating process. The formation of terbium oxide could also influence the properties of the final products, including their optical characteristics.

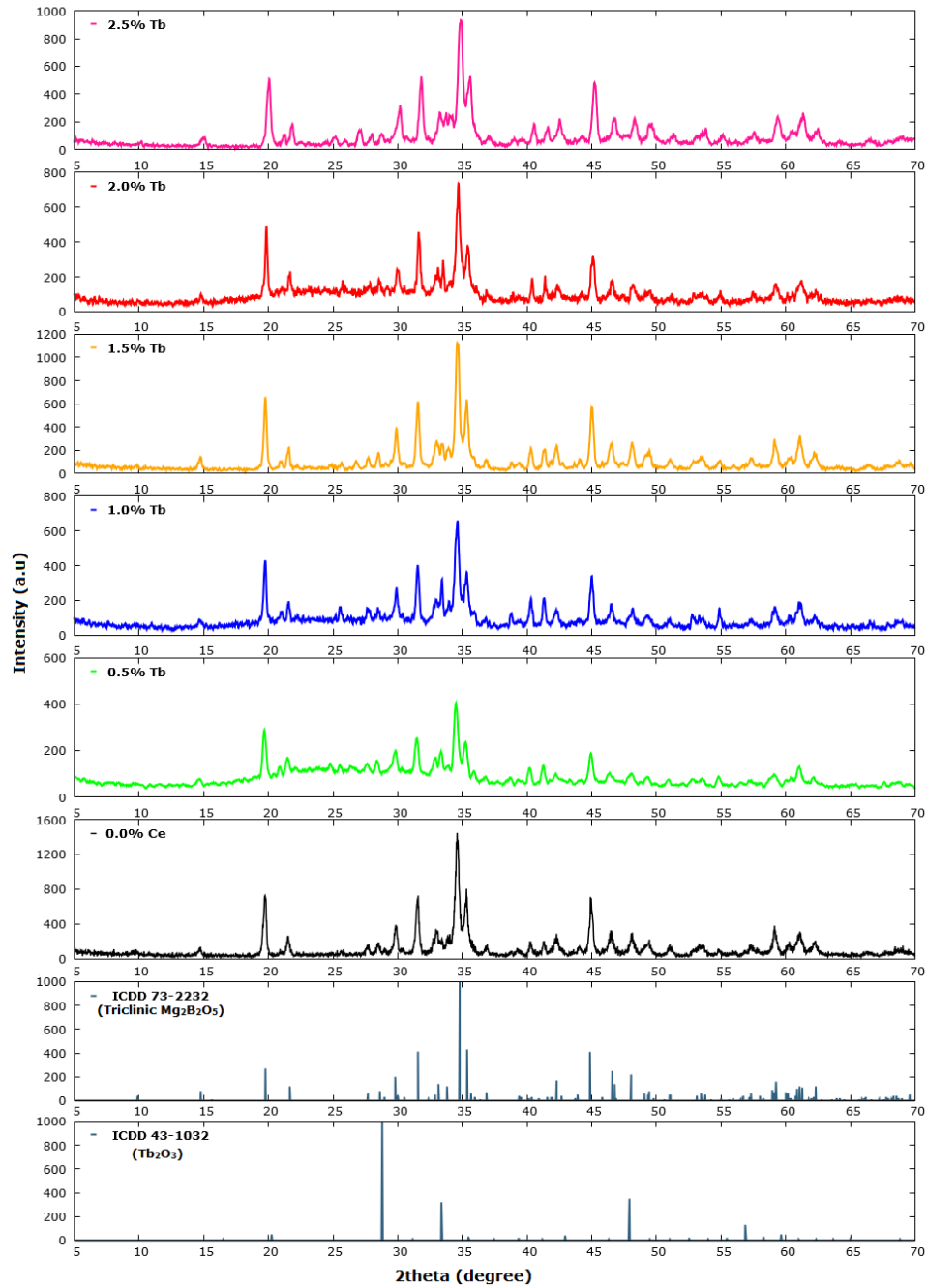


Figure 4.36. The XRD patterns of $\text{Mg}_{2-x}\text{Tb}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 1000°C

HMTA Fuels: The XRD patterns of $\text{Mg}_2\text{B}_2\text{O}_5:\text{Tb}^{3+}$ are presented in Figure 4.37-4.39. Some additional peaks belong to monoclinic $\text{Mg}_2\text{B}_2\text{O}_5$ were observed. Unlike the impurities obtained in glycine fuel products that have high intensities and can be differentiated easily, the peaks of secondary phase are detected in the patterns of product obtained in 900°C as shown in Figure 4.37 are very small and are hardly to distinguish in some patterns. Regardless of these

minor impurities, it obviously showed that the patterns in 800°C were monoclinic phases of $\text{Mg}_2\text{B}_2\text{O}_5$ and triclinic phases were dominated in the product obtained at 900°C and 1000°C.

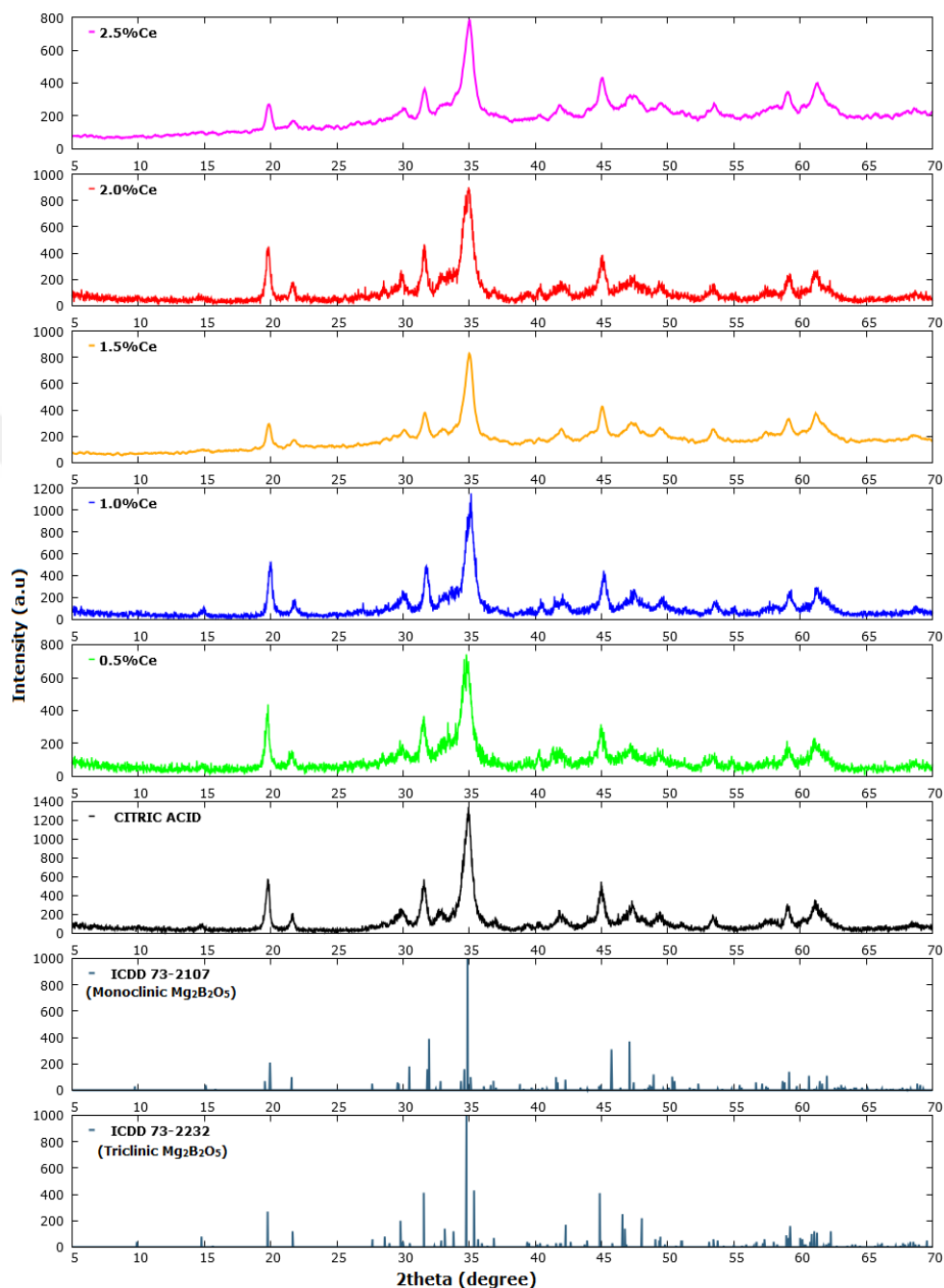


Figure 4.37. The XRD patterns of $\text{Mg}_{2-x}\text{Tb}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 800°C

Presented in Figure 4.38, different with the examination of XRD patterns of magnesium pyroborates synthesized with glycine, the transformation between two phases of magnesium pyroborates yet to be detected at 900°C. All the

reflection lines in the XRD patterns are dominated by monoclinic lines of magnesium pyroborates.

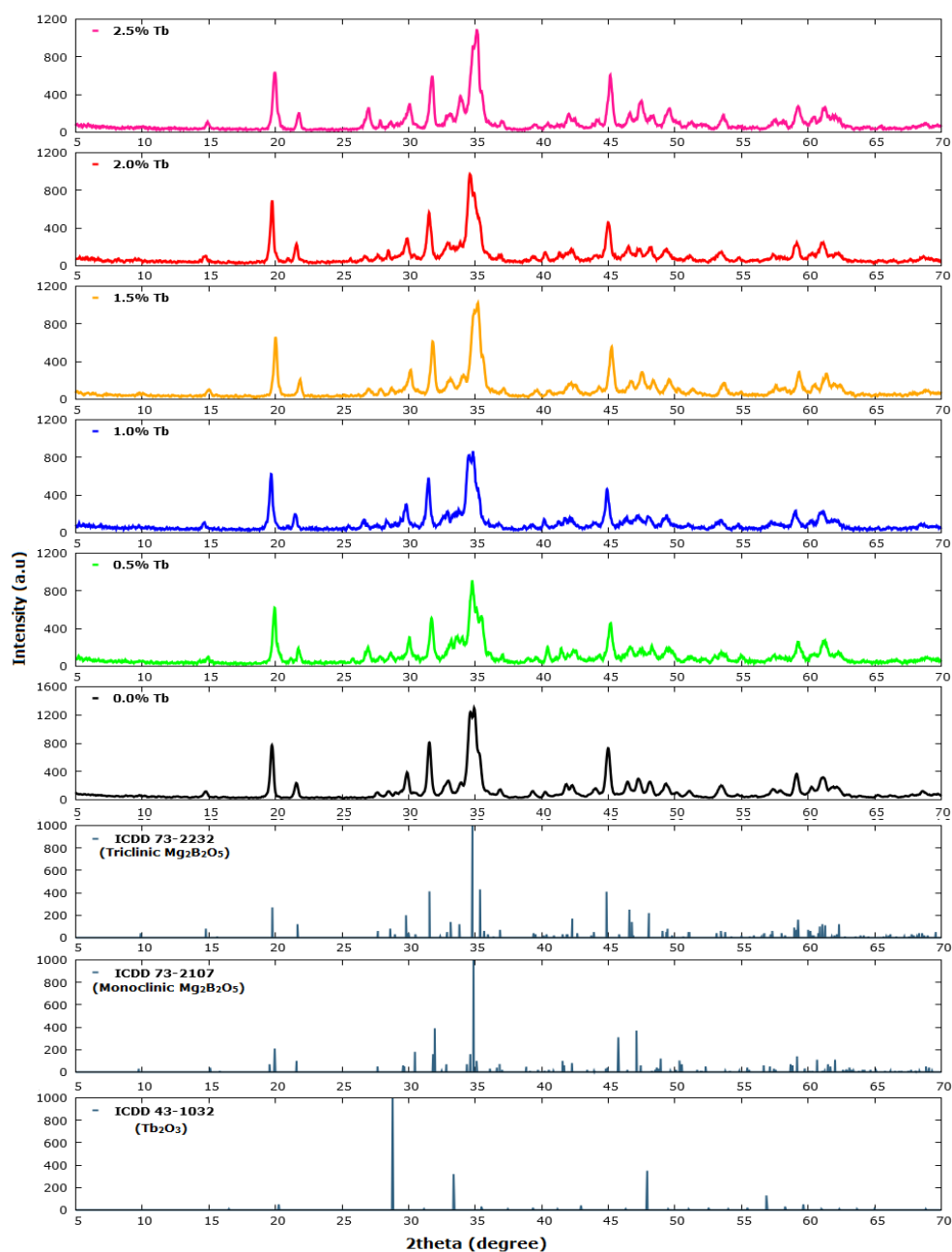


Figure 4.38. The XRD patterns of $\text{Mg}_{2-x}\text{Tb}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 900°C

High crystalline triclinic magnesium pyroborates have successfully obtained at 1000°C and has a great compatibility with the ICDD card no 73-2232. While the other concentrations showed no secondary phase, 1.5% and 2.5% Eu^{3+} formed Eu_2O_3 at 1000°C . This showed the doping concentrations effect on the formation of single phase magnesium pyroborates. At very high dopant

concentrations, there's a possibility of dopant aggregation or clustering within the crystal lattice. This can have complex effects on the material's properties, potentially leading to deviations from the behavior observed at lower dopant concentrations.

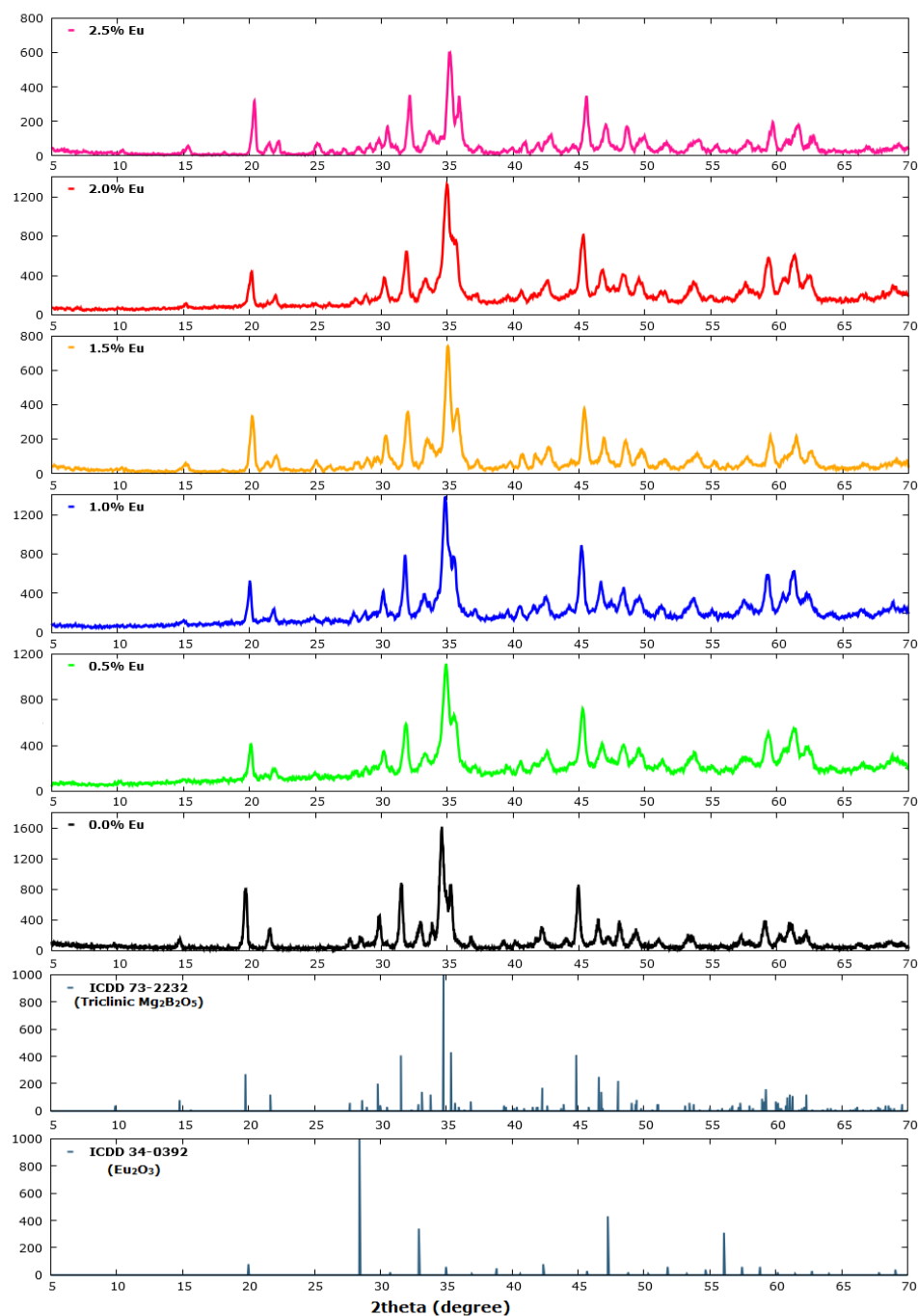


Figure 4.39. The XRD patterns of $\text{Mg}_{2-x}\text{Tb}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 1000°C

Tartaric Acid Fuels: Undoped and doped magnesium pyroborates compounds with tartaric acid fuel were compared and the monoclinic phase of $\text{Mg}_2\text{B}_2\text{O}_5$ was observed in the products at 800°C (Figure 4.40). The reflection lines have very great accordance to each other and have a low crystallinity. However, by further heating the higher crystallinity products were obtained.

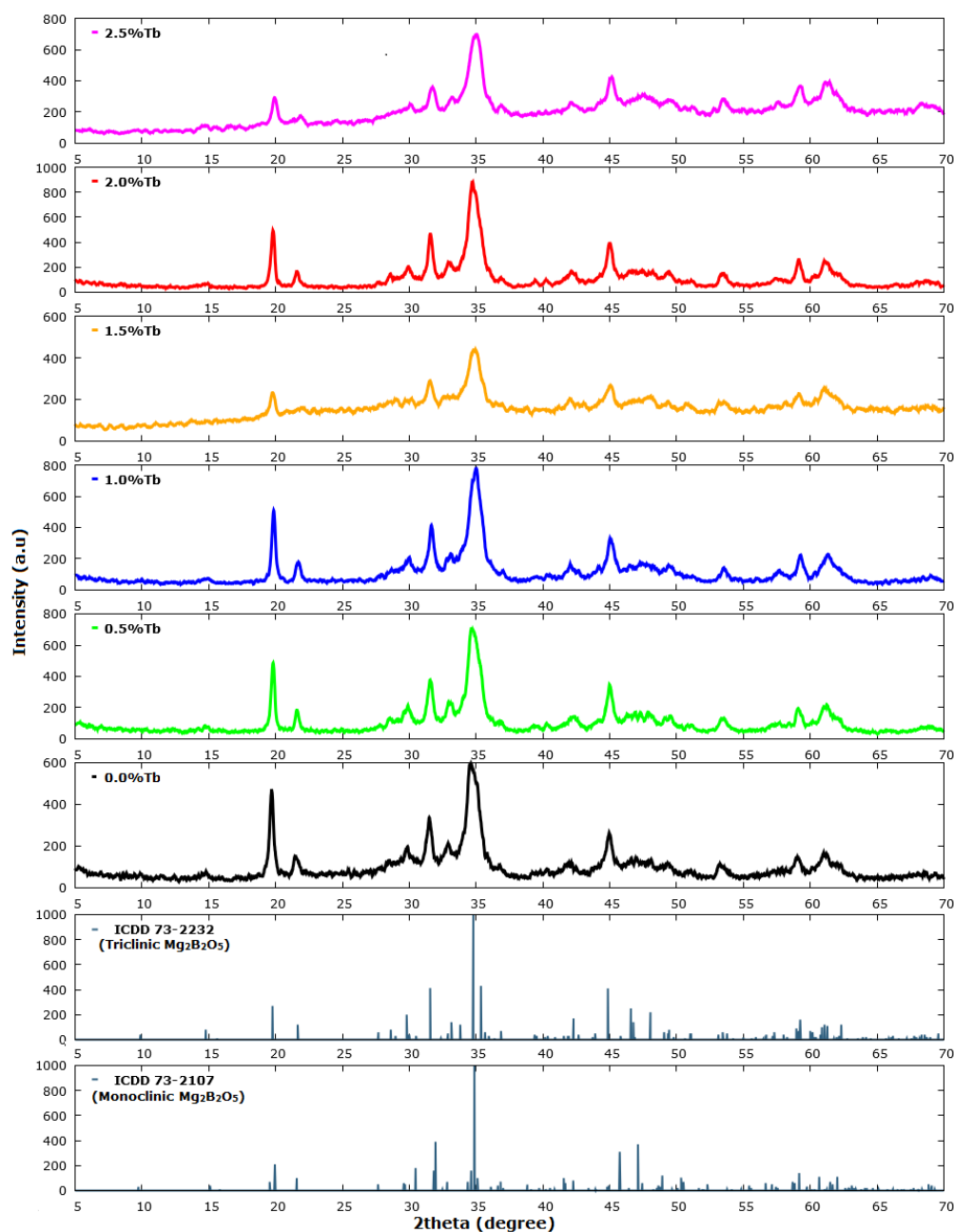


Figure 4.40. The XRD patterns of $\text{Mg}_{2-x}\text{Tb}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 800°C

The presence of the doublet maximum diffraction lines were started to noticed between $2\theta = 35-37^\circ$ which provide the information of the magnesium

pyroborates formation. The diffraction lines are in a good accordance to the ICDD card 72-2232 as shown in Figure 4.41. The highest intensity was belonged to 1.0% Tb³⁺ denoted to have highest crystallinity compared to the other concentrations. Unlike other fuel, no additional peak is observed and single phase terbium doped magnesium pyroborates were succesfully achieved.

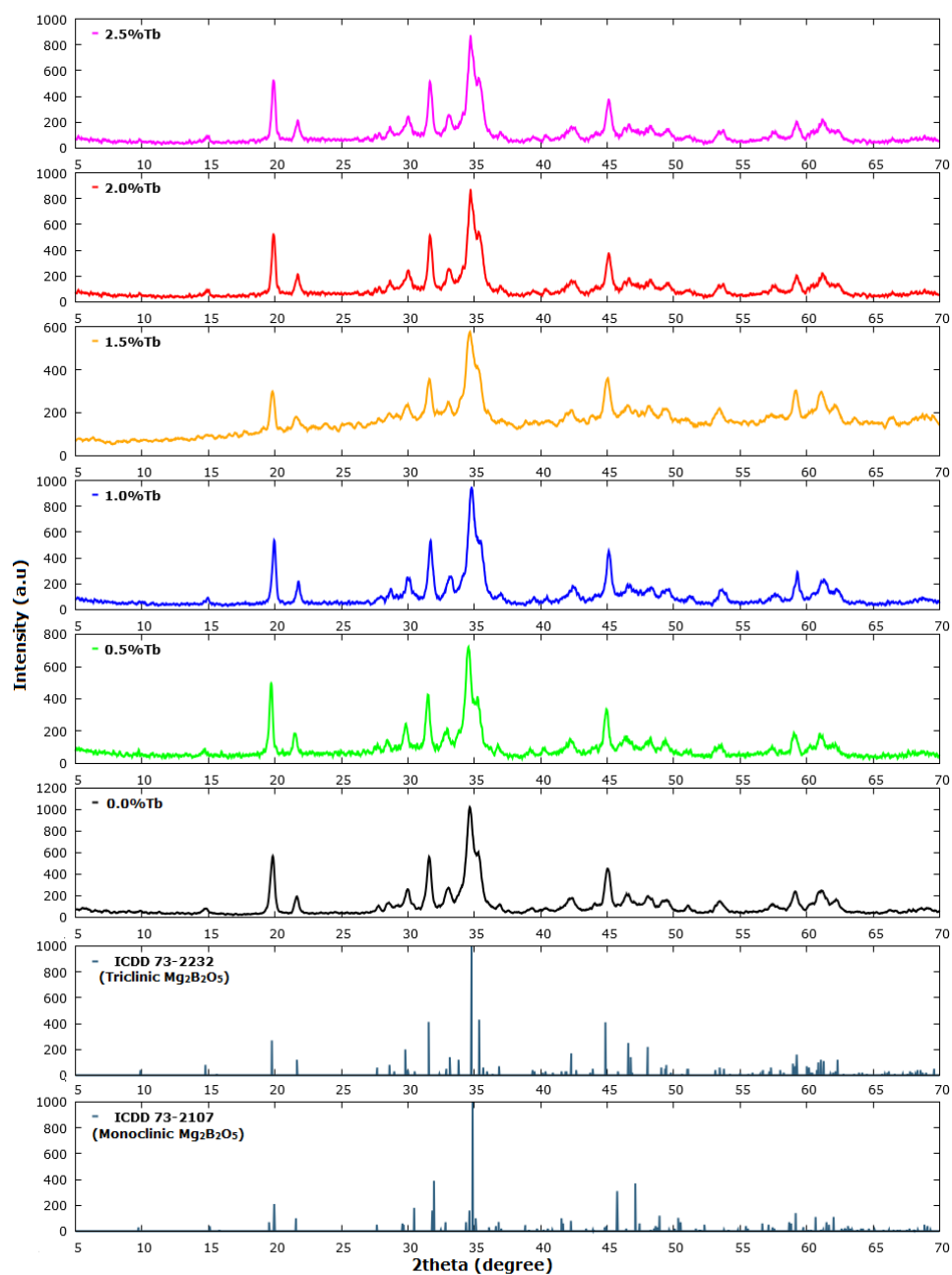


Figure 4.41. The XRD patterns of $\text{Mg}_{2-x}\text{Tb}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 900°C

Presented in Figure 4.42, magnesium pyroborate doped with terbium ions obtained at 1000°C was also identified by XRD analysis. The diffraction patterns indicate that the reflection lines correspond to the triclinic phase of magnesium pyroborate, except in the case of the 2.5% terbium (III) doped sample. Also, it has been noticed that there is no alteration on the crystal structure of host lattice magnesium pyroborates upon the addition of terbium (III) as dopant materials which suggested that the terbium ion is completely incorporated in the host lattice.

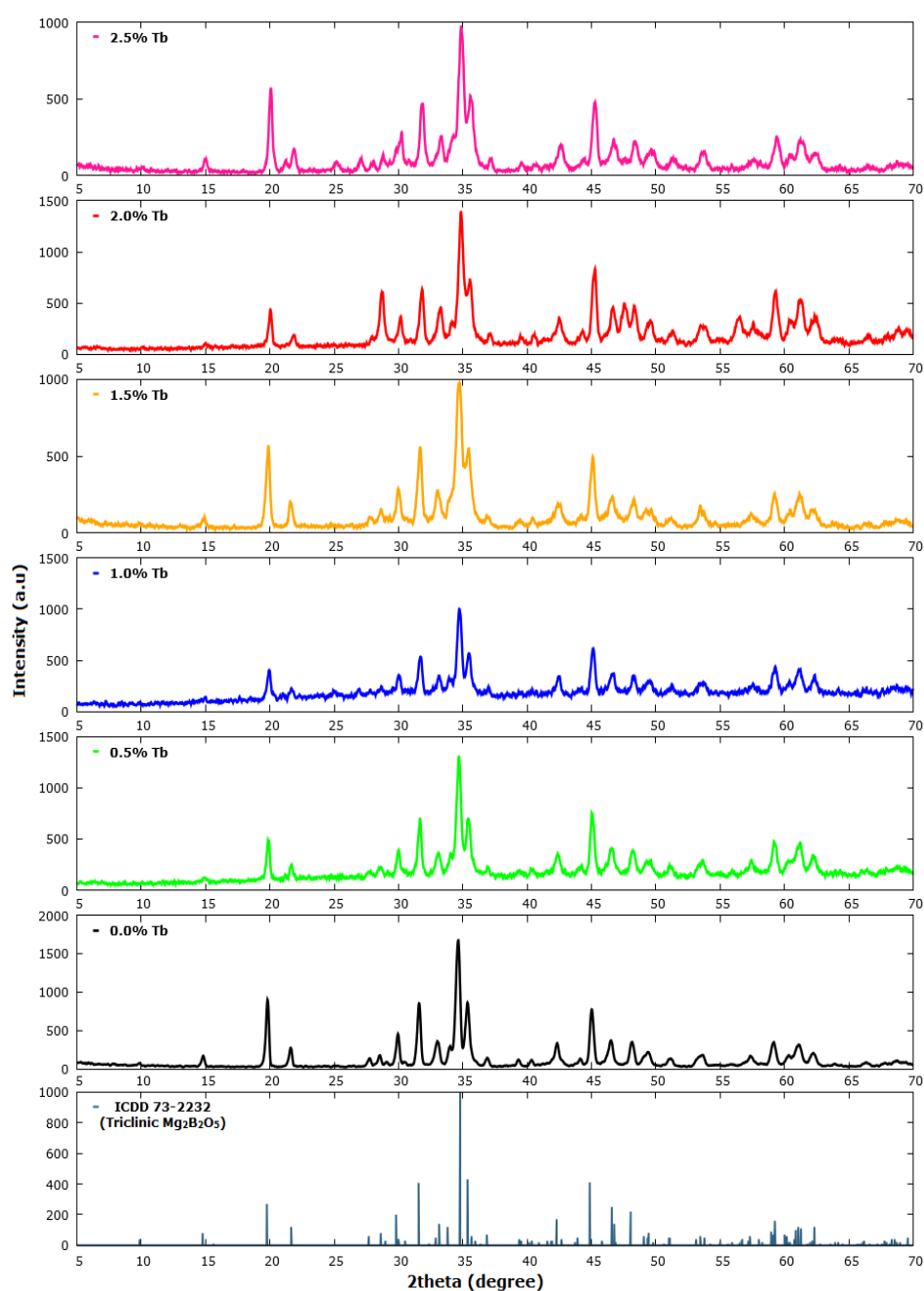


Figure 4.42. The XRD patterns of $\text{Mg}_{2-x}\text{Tb}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 1000°C

Urea Fuels: The XRD patterns of terbium doped magnesium pyroborates was also examined between $2\theta = 5-70^\circ$. The reflection lines of monoclinic magnesium pyroborates are dominated and have a great compatibility with ICDD card no: 73-2107. All the patterns are similar except for 2.5% Tb^{3+} where the doublet maximum peaks ($2\theta = 34-36^\circ$) confirming the formation of triclinic magnesium pyroborates.

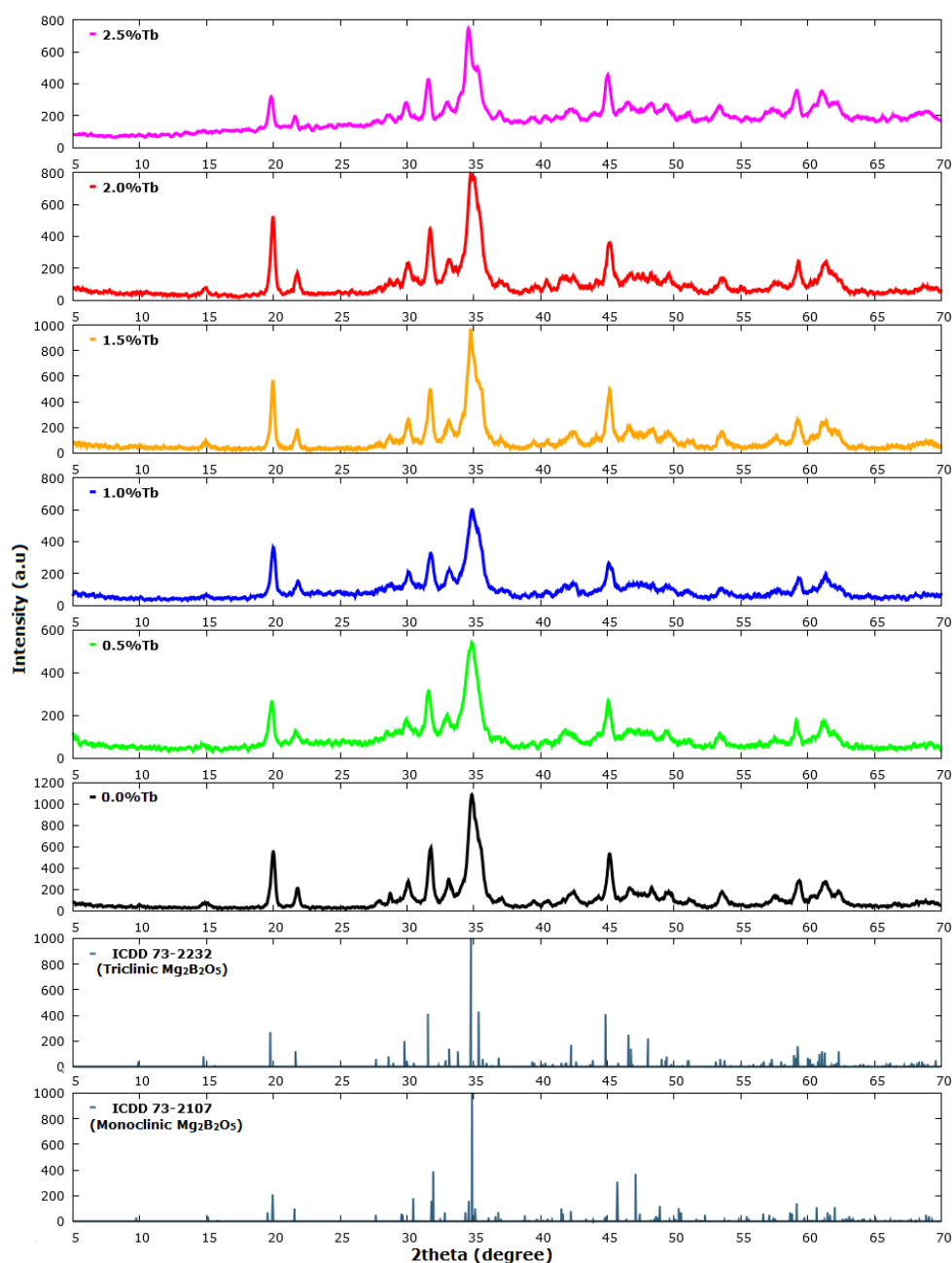


Figure 4.43. The XRD patterns of $\text{Mg}_{2-x}\text{Tb}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 800°C

At 900°C, the transformation into triclinic magnesium pyroborates was observed. The high crystallinity single phase triclinic magnesium pyroborates was obtained and there is no secondary phase was found. All the reflection lines are compatible with the ICDD card no: 72-2232, confirming the addition of a very small amount of dopants does not affect the crystal structure of the compound, as the dopants are fully incorporated into the Mg sites of the host material.

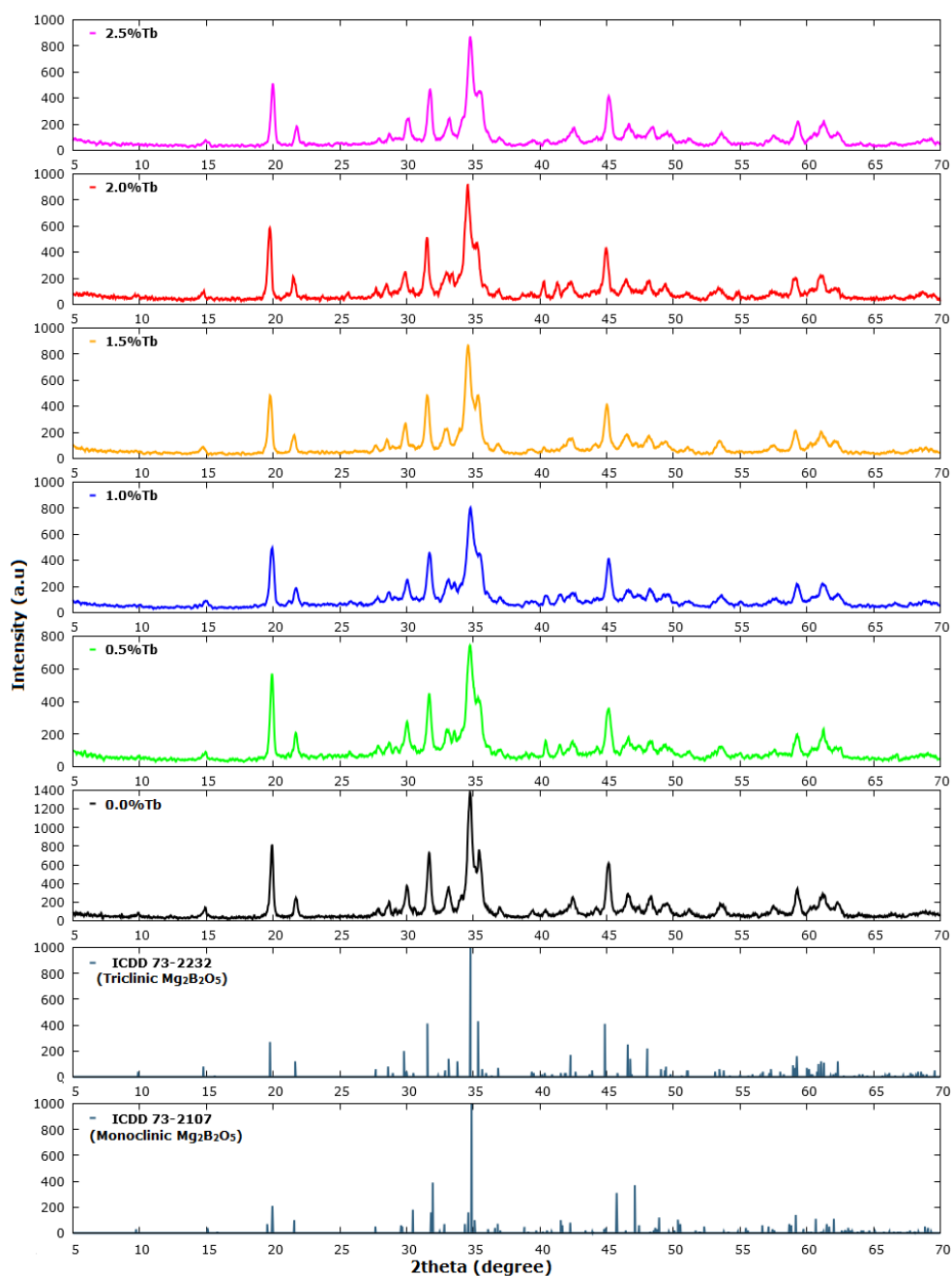


Figure 4.44. The XRD patterns of $\text{Mg}_{2-x}\text{Tb}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 900°C

Compared to the XRD patterns of Ce^{3+} and Eu^{3+} doped $\text{Mg}_2\text{B}_2\text{O}_5$ synthesized with urea fuel, terbium doped magnesium pyroborates gave the highest crystallinity of products. The highest intensity was detected at 1600 a.u. For all concentrations of terbium (III), the reflection lines resemble to ICDD card that belong to triclinic magnesium pyroborates (Figure 4.45). As it is known, different fuels have different combustion temperatures. Higher temperatures can promote faster reaction rates and more vigorous combustion, which might influence the kinetics of crystal formation and growth during the synthesis process. This can affect the size, shape, and distribution of crystalline domains in the resulting products.

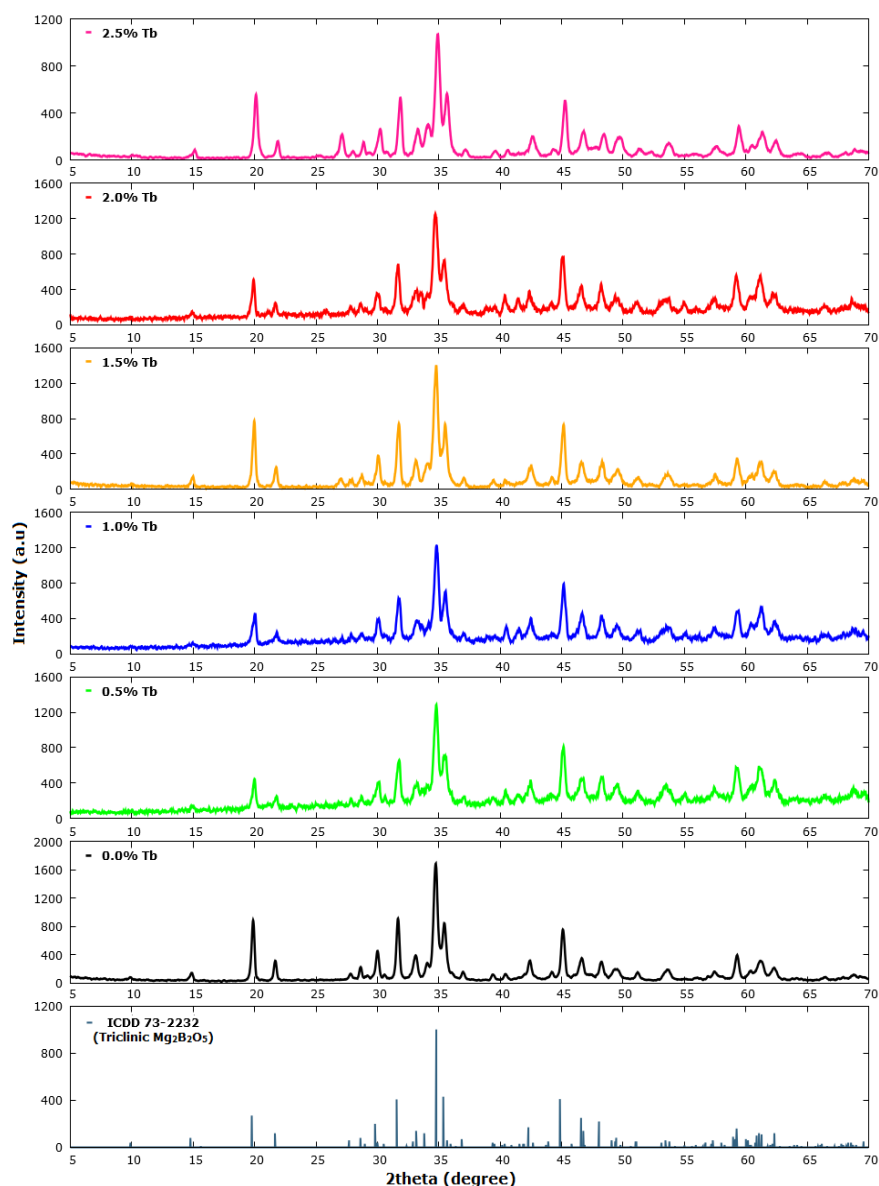


Figure 4.45. The XRD patterns of $\text{Mg}_{2-x}\text{Tb}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 1000°C

Analyzing all these XRD data, it can be stated that the selection of fuel in combustion synthesis significantly influences the crystallinity of the resulting products. Fuels with varying carbon content and combustion temperatures can affect reaction kinetics, phase formation, and the size and distribution of crystal domains. Oxygen balance is crucial for achieving complete combustion and preventing unwanted byproducts. Heat release profiles, residue formation, and gas-phase reactions also play roles in determining crystallinity during the heating process. Therefore, the choice of fuels can have complex effects on the formation and properties of the synthesized products.

4.2.2 The XRD Shift and Crystallite Size of Rare Earth Metal Doped Magnesium Pyroborates

The XRD peaks shifting of magnesium pyroborates products were also determined by plotting the graph using Origin Lab 2017 Software with respect to the pattern of undoped magnesium pyroborates. Accordingly, the shift of peak (0-21) and (021) for triclinic phase of magnesium pyroborates with access of different fuels were shown in Figure 4.46. It is observed that the d-line shift mostly toward the higher diffraction angle at higher annealing temperature.

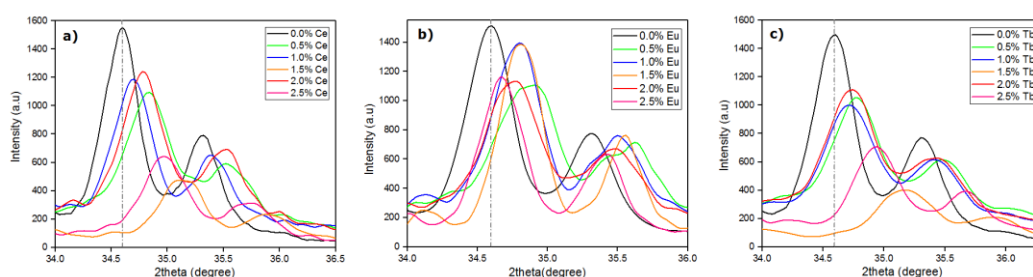


Figure 4.46. The XRD shift of doped $\text{Mg}_2\text{B}_2\text{O}_5$ at 1000°C a) cerium, b) europium, c) terbium with citric acid fuel

With respect to the pattern of undoped magnesium pyroborates, rare earth metal doped magnesium pyroborates with citric acid, HMTA, tartaric acid and urea as fuel showed the shift of the diffraction peaks to the longer theta degree at 1000°C . These behaviors show how fuel variation and temperature affect the synthesized materials. Magnesium pyroborates doped with 1.0% Eu^{3+} and tartaric acid shift to higher 2θ degree compared to other concentrations. Similarly, the highest dopant levels in Ce^{3+} and Tb^{3+} -doped magnesium pyroborates also shift to higher 2θ degree.

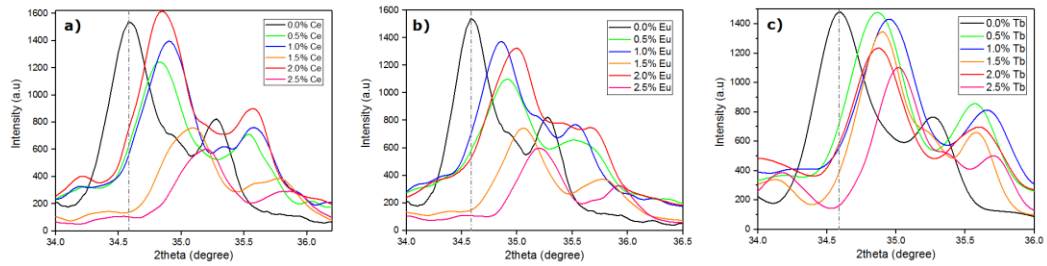


Figure 4.47. The XRD shift of doped $\text{Mg}_2\text{B}_2\text{O}_5$ at 1000°C a) cerium, b) europium, c) terbium with HMTA fuel

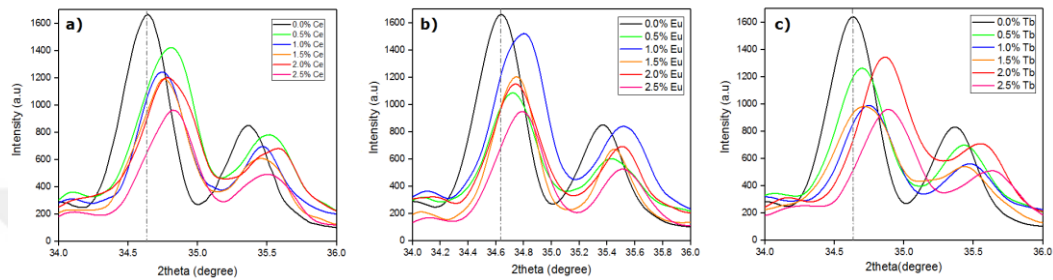


Figure 4.48. The XRD shift of doped $\text{Mg}_2\text{B}_2\text{O}_5$ at 1000°C a) cerium, b) europium, c) terbium with tartaric acid fuel

In more additions, no significant shifts were detected for the peak of 1.0% Eu^{3+} and 2.0% Tb^{3+} , as it remains nearly in the same position as the undoped magnesium pyroborates synthesized with urea fuel.

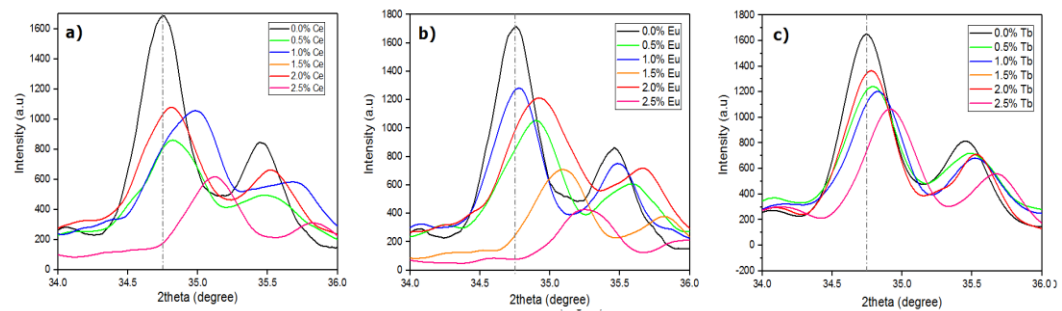


Figure 4.49. The XRD shift of doped $\text{Mg}_2\text{B}_2\text{O}_5$ at 1000°C a) cerium, b) europium, c) terbium with urea fuel

Unlike the other fuels, the shifting of diffraction peak was observed toward the shorter/longer angle by the addition of doping materials which respected to the undoped magnesium pyroborates for the products synthesized by glycine. For Ce^{3+} doped, the peaks are shifting toward lower angle except for 2.5% Tb^{3+} , whereas there is no significant shifting observed at peak of $\text{Mg}_2\text{B}_2\text{O}_5$: Eu^{3+} . Furthermore, most of peaks are shifting toward the larger angle for the products

prepared by terbium doped. The shift of angle in XRD pattern strongly depends on doping concentration and ionic size in the samples, which is directly affecting the unit of the unit cell. It also depends on the site which doping ion occupies.

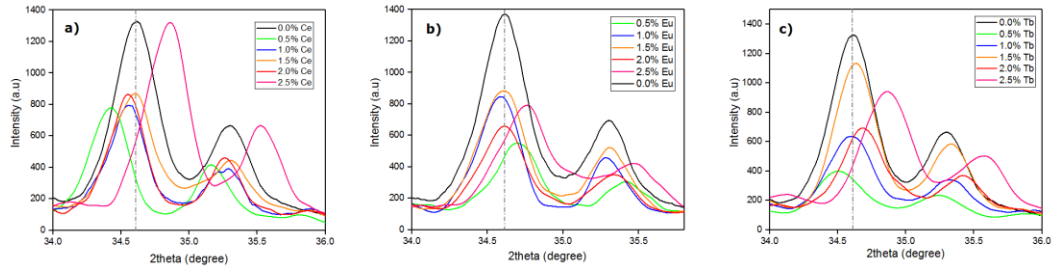


Figure 4.50. The XRD shift of doped $\text{Mg}_2\text{B}_2\text{O}_5$ at 1000°C a) cerium, b) europium, c) terbium with glyine fuel

Applying the data from the XRD analyses, the crystallite size of the nanocompound are quantitatively determined by Debye-Scherrer's equation.

$$D = \frac{K\lambda}{\beta \cos\theta}$$

Where D is the average crystallite size (nm), K is the constant shape factor that generally taken as 0.94, λ is the radiation wavelength (CuK α) which is λ equal to 1.54056 Å, β is the full width at half of the maximum (radians) and θ is the diffraction angle.

Examining the crystallite size values, it reveals that the crystallite size increase. For all the RE doped magnesium pyroborates prepared with citric acid, the smallest crystallite size belongs to 0.50% as they found in the range of 15-19 nm. The addition on different concentration of dopant materials observely influenced the structural properties of magnesium pyroborates such as crystallite size. The crystallite size decreases in the presence of doping materials. In average, the crystallite size of magnesium pyroborate doped Tb^{3+} (15-19 nm) < Eu^{3+} (15-26 nm) < Ce^{3+} (19-24 nm). The variation in the crystallite size values can be assigned to the substitutions of doping materials (Ce^{3+} , Eu^{3+} and Tb^{3+}) to the host material site (Mg) has a larger ionic radius (1.14 Å, 1.06 Å, 0.923 Å) than Mg^{2+} (0.72 Å) (74). The effect of doping on the reduction in the crystallite size was reported by Jadhav et al and they stated that the doping materials changed the crystallinity and also caused an increase in FWHM, which directed to the decreases the crystallite size.

Table 4.1. The crystallite size of doped magnesium pyroborates

Pyroborates	Concentration of dopant	Crystallite Size (nm)				
		Citric Acid	Glycine	HMTA	TA	Urea
$\text{Mg}_2\text{B}_2\text{O}_5$	0.00%	24.92	27.76	25.35	28.64	26.31
$\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$	0.50%	19.54	30.38	21.95	20.68	20.19
	1.00%	24.34	34.54	21.53	22.95	20.74
	1.50%	20.84	28.38	21.37	21.79	19.63
	2.00%	20.35	31.58	20.84	21.41	18.46
	2.50%	23.01	26.56	20.16	22.62	21.76
$\text{Mg}_{2-x}\text{Eu}_x\text{B}_2\text{O}_5$	0.50%	15.14	22.74	15.61	17.93	14.87
	1.00%	17.74	26.80	18.54	17.47	18.32
	1.50%	25.87	26.42	18.69	24.92	17.80
	2.00%	15.44	21.96	17.29	18.22	14.68
	2.50%	24.15	24.33	19.17	21.06	16.53
$\text{Mg}_{2-x}\text{Tb}_x\text{B}_2\text{O}_5$	0.50%	15.63	18.39	17.99	19.04	17.63
	1.00%	15.92	22.66	17.31	17.93	17.42
	1.50%	16.26	23.20	23.90	17.90	18.99
	2.00%	16.95	23.24	16.76	17.55	17.35
	2.50%	18.70	23.44	23.73	17.10	18.81

4.2.3 FT-IR Analyses of Rare-Earth Doped Magnesium Pyroborates

The FT-IR spectra of the synthesized $\text{Mg}_{2-x}\text{R}_x\text{B}_2\text{O}_5$ were also analyzed. The identification was done in the range of $4000\text{--}400\text{ cm}^{-1}$. The attained vibrational bands confirmed the presence of $\text{Mg}_2\text{B}_2\text{O}_5$. Comparison with pure $\text{Mg}_2\text{B}_2\text{O}_5$ revealed that the spectra were identical, and no additional peaks were observed. These FT-IR spectra have a great compatibility with the previous studies which ensured the formation of magnesium pyroborates (147,149,150).

4.2.3.1 FT-IR Analyses of Cerium Doped Magnesium Pyroborates

The FT-IR spectra of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ with various concentrations and fuels were recorded. The FT-IR spectra analysis of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ synthesized with citric acid as a fuel are closely resemble to pure $\text{Mg}_2\text{B}_2\text{O}_5$ key vibrational modes include B-O-B bending of BO_3 ($679\text{--}723\text{ cm}^{-1}$), asymmetric stretching of BO_4 and BO_3 in the ranges $839\text{--}1173\text{ cm}^{-1}$ and $1290\text{--}1500\text{ cm}^{-1}$, respectively. This analysis provides valuable insights into the structural composition and bonding characteristics of the synthesized material.

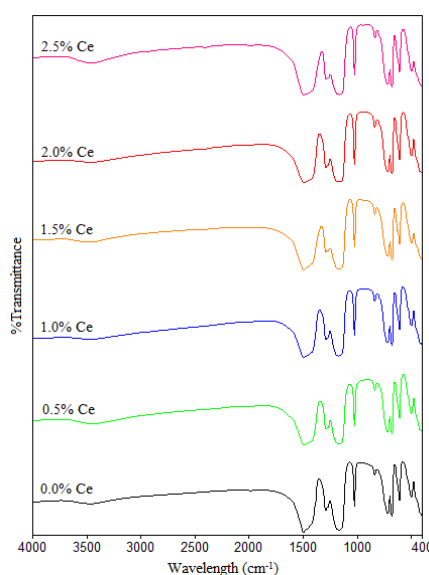


Figure 4.51. The FT-IR spectra of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x = 0.000\text{--}0.025$) obtained at 800°C

The peaks are identical to pure $\text{Mg}_2\text{B}_2\text{O}_5$ and there is no additional peaks were observed, indicating that the Ce^{3+} doping did not induce noticeable changes in the vibrational bands. Several factors, such as the similar chemical structure, substitutional doping, low doping concentrations, limited sensitivity of FT-IR, and

a homogeneous distribution of Ce^{3+} , could contribute to the lack of changes observed in the vibrational bands.

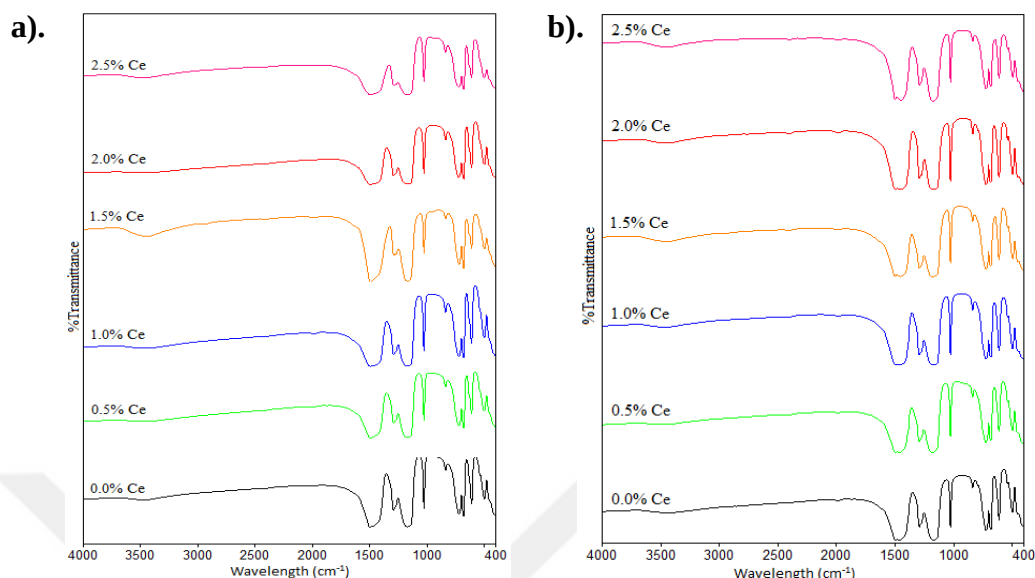


Figure 4.52. The FT-IR spectra of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at a) 900°C and b) 1000°C

The FT-IR spectra of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x = 0.005, 0.010, 0.015, 0.020$ and 0.025) with glycine fuel revealed that the spectra were resembled to the pure $\text{Mg}_2\text{B}_2\text{O}_5$ as shown in Figure 4.53 and 4.54. The B-O bending of trigonal BO_3 was observed at around 720 cm^{-1} and 682 cm^{-1} whereas the asymmetric B-O stretching of BO_3 was observed at the region $1290-1500\text{ cm}^{-1}$. In more addition, B-O stretching of the tetrahedral BO_4 was discovered at around 840 cm^{-1} and 1180 cm^{-1} .

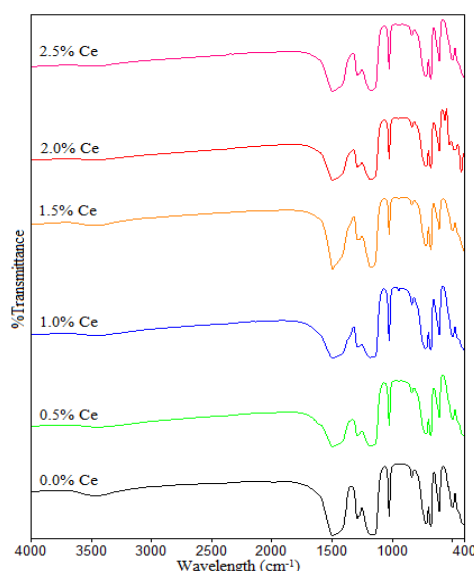


Figure 4.53. The FT-IR spectra of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 800°C

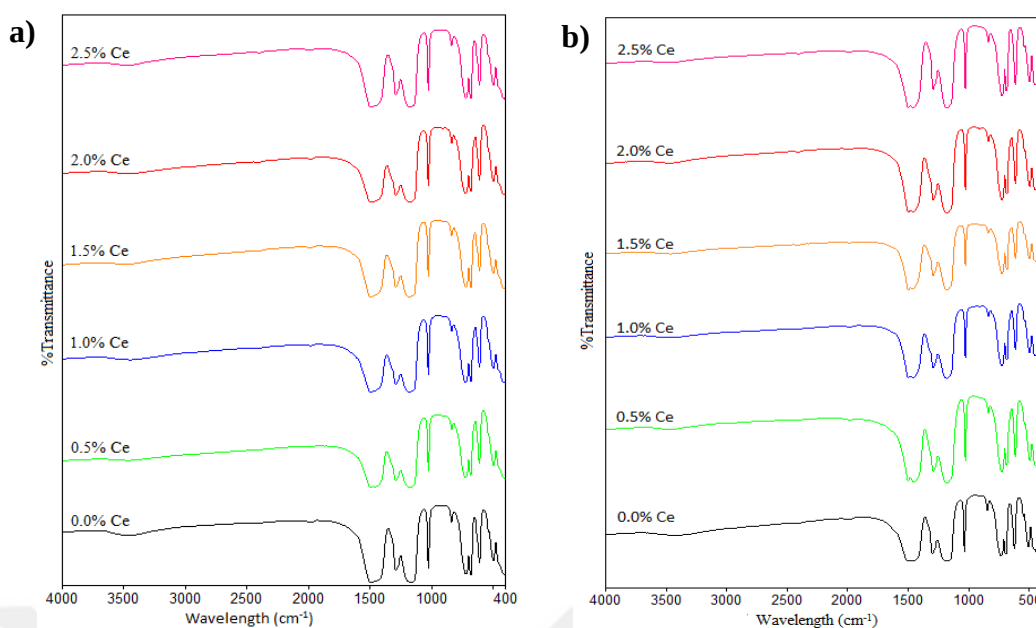


Figure 4.54. The FT-IR spectra of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at a) 900°C and b) 1000°C

The vibrational bands of Ce^{3+} doping $\text{Mg}_2\text{B}_2\text{O}_5$ using HMTA as fuel are found to be similar to the spectra of pure $\text{Mg}_2\text{B}_2\text{O}_5$. The bands of the products obtained at $800-1000^\circ\text{C}$ are observed at around 680cm^{-1} and 715cm^{-1} represent the B-O-B bending of BO_3 , at 840cm^{-1} , 1026cm^{-1} and 1180cm^{-1} correspond to the B-O stretching vibration of BO_4 and $1200-1450\text{cm}^{-1}$ indicate the B-O stretching vibrations of BO_3 . No impurities or second phases are shown.

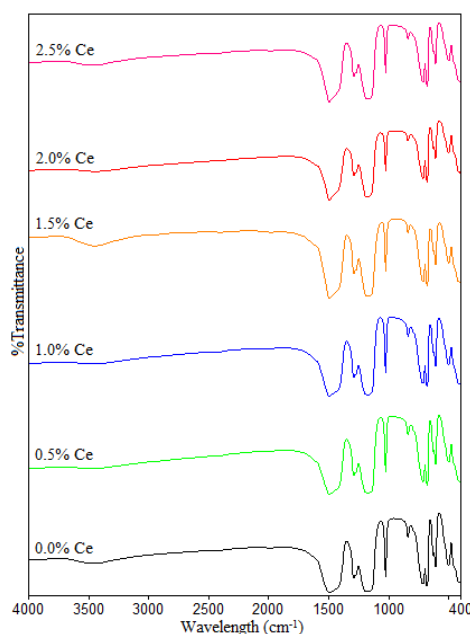


Figure 4.55. The FT-IR spectra of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 800°C

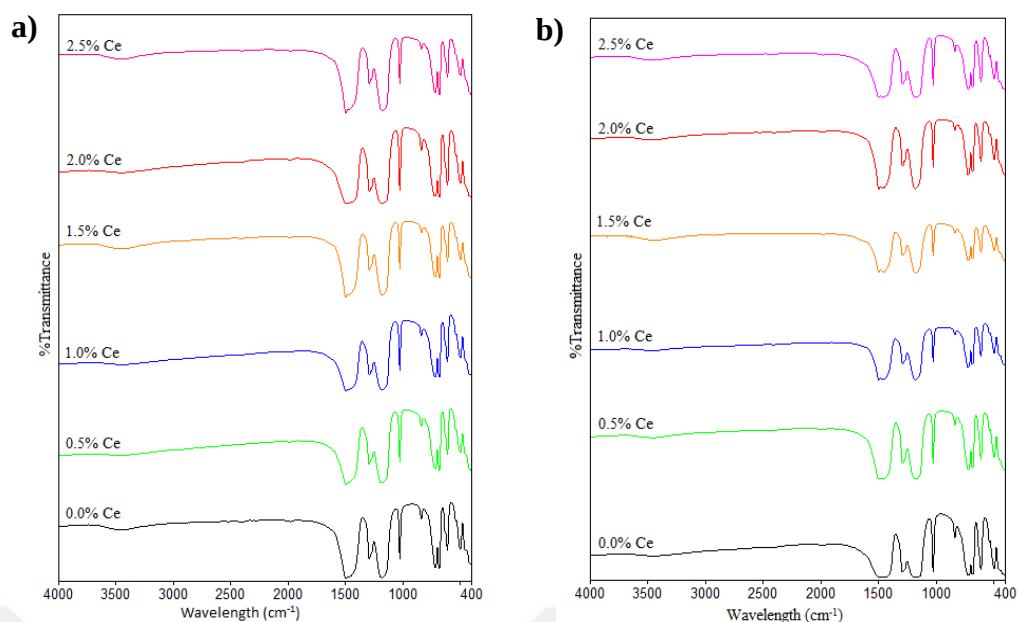


Figure 4.56. The FT-IR spectra of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at a) 900°C b) 1000°C

The infrared spectra of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x = 0.005, 0.01, 0.02$) synthesized with tartaric acid fuels was also give a characteristic peaks of magnesium pyroborates at around 683 cm^{-1} , 720 cm^{-1} , 839 cm^{-1} , 1026 cm^{-1} , 1165 cm^{-1} , 1290 cm^{-1} and 1490 cm^{-1} as shown in Figure 4.57 to 4.58 for the products heated at 800-1000°C, respectively.

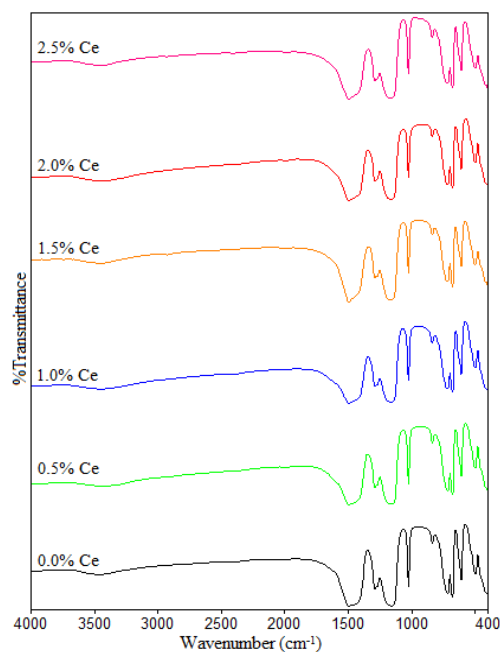


Figure 4.57. The FT-IR spectra of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 800°C

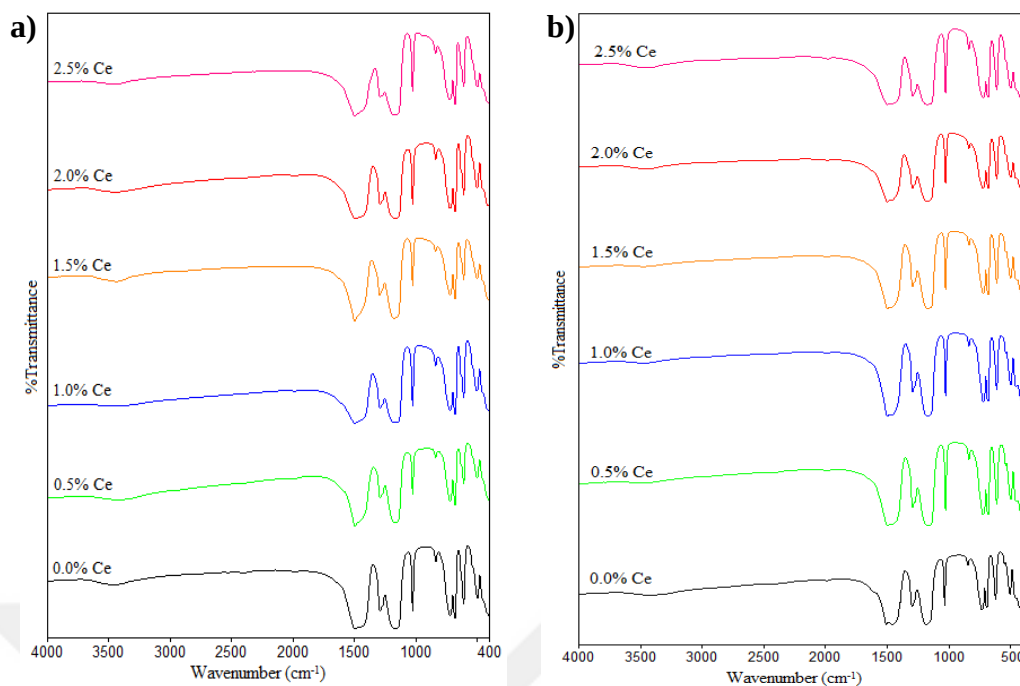


Figure 4.58. The FT-IR spectra of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at a) 900°C and b) 1000°C

In the FT-IR spectra of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x = 0.005-0.025$) using urea as fuel, similar to other fuels the vibrational bands are observed at 682 cm^{-1} , 720 cm^{-1} , 839 cm^{-1} , 1026 cm^{-1} , 1175 cm^{-1} , 1290 cm^{-1} and 1490 cm^{-1} vibrational bands are confirmed the existence of $\text{Mg}_2\text{B}_2\text{O}_5$.

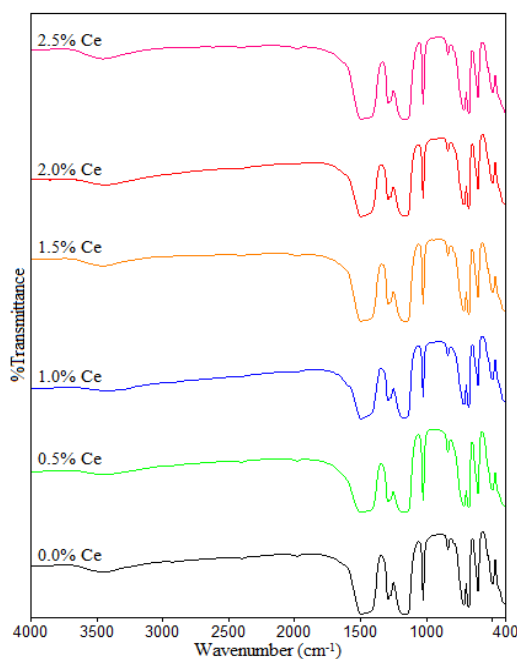


Figure 4.59. The FT-IR spectra of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 800°C

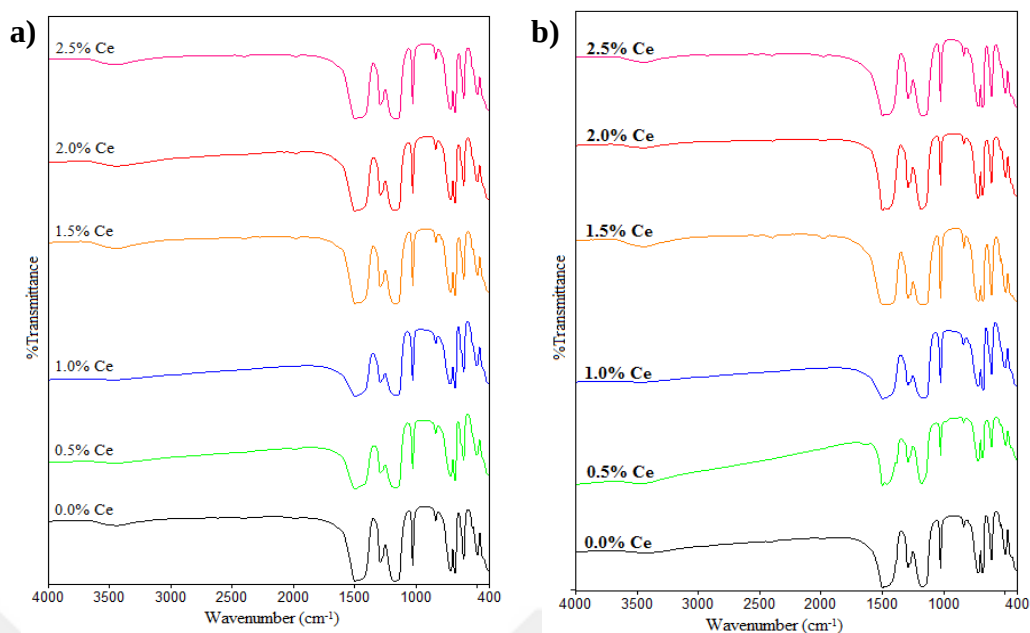


Figure 4.60. The FT-IR spectra of $\text{Mg}_{2-x}\text{Ce}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at a) 900°C and b) 1000°C

4.2.3.2 FT-IR Analyses of Europium Doped Magnesium Pyroborates

The FT-IR analyses of europium doped magnesium pyroborates with various types of fuels were also determined in the range of $400-4000\text{ cm}^{-1}$. Using citric acid as fuels, the FT-IR spectra of $\text{Mg}_2\text{B}_2\text{O}_5:\text{Eu}^{3+}$ were detected to be consisted of the main vibrational modes of suanite, $\text{Mg}_2\text{B}_2\text{O}_5$.

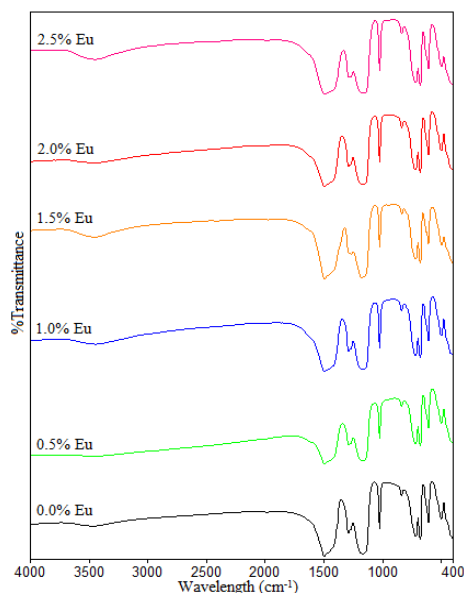


Figure 4.61. The FT-IR spectra of $\text{Mg}_{2-x}\text{Eu}_x\text{B}_2\text{O}_5$ ($x = 0.005-0.025$) obtained at 800°C

In the Figure 4.61 and 4.62 presented that the band at 839-1177 cm^{-1} assign to the B-O stretching of the tetrahedral BO_4 whereas the broad band at around 1290 cm^{-1} and 1500 cm^{-1} correspond to the asymmetric B-O stretching of Trigonal BO_3 . Furthermore, the two bands at around 725 cm^{-1} and 680 cm^{-1} are due to the B-O-B bending of trigonal BO_3 . All these bands of $\text{Mg}_2\text{B}_2\text{O}_5: \text{Eu}^{3+}$ is identical with pure magnesium pyroborates and no additional bands are observed.

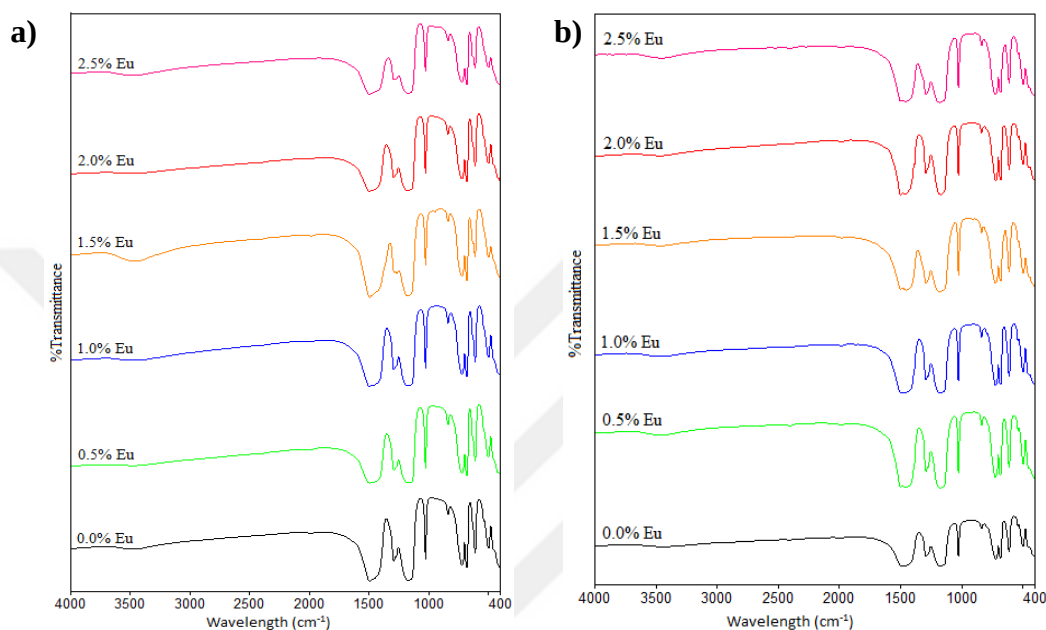


Figure 4.62. The FT-IR spectra of $\text{Mg}_{2-x}\text{Eu}_x\text{B}_2\text{O}_5$ (x= 0.005-0.025) obtained at a) 900°C and b) 1000°C

Glycine Fuels: Given in Figure 4.63, the spectra are identical and almost hardly distinguished from pure $\text{Mg}_2\text{B}_2\text{O}_5$. As mention in previous section, the spectra were observed at the range of 400-1500 cm^{-1} is the characteristics bands of magnesium pyroborates. A small extra band was detected in the spectra of 1.5% and 2.5% Eu^{3+} (800°C and 900°C) located at at around 909-948 cm^{-1} .

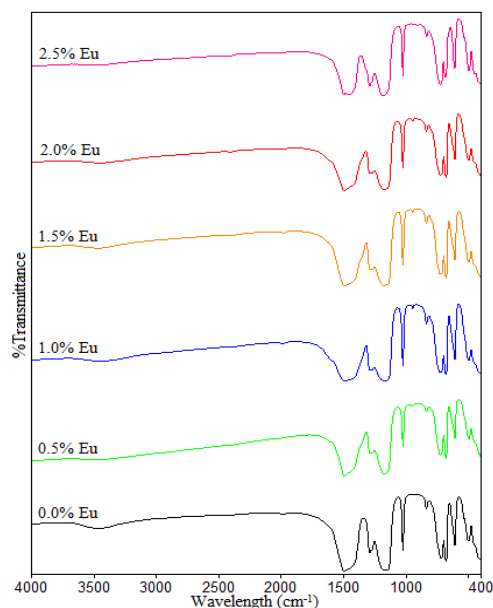


Figure 4.63. The FT-IR spectra of $\text{Mg}_{2-x}\text{Eu}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at a) 800°C

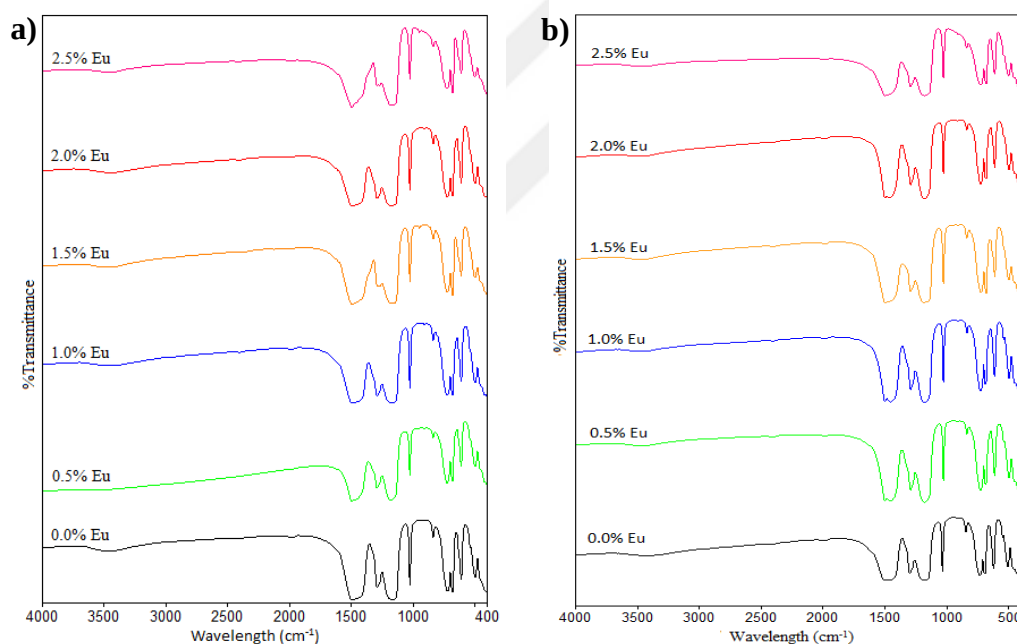


Figure 4.64. The FT-IR spectra of $\text{Mg}_{2-x}\text{Eu}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at a) 900°C and b) 1000°C

HMTA Fuels : The spectra of $\text{Mg}_2\text{B}_2\text{O}_5:\text{Eu}^{3+}$ using HMTA with various dopants' concentrations were also determined. The vibrational bands were turned out to be similar to the bands mentioned in previous section. All the bands are observed in the finger print region of $1500-400\text{ cm}^{-1}$. Based on the FT-IR spectra, there is no secondary phase is detected. Purportedly, the FT-IR spectra of the

powder products obtained at 800-1000°C are very much alike to one another which verified the formation of magnesium pyroborates at 800°C.

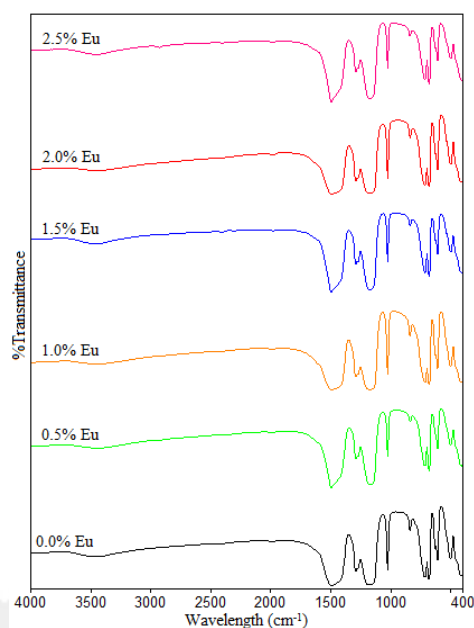


Figure 4.65. The FT-IR spectra of $\text{Mg}_{2-x}\text{Eu}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 800°C

The FT-IR spectra of the products obtained at 900°C and 1000°C are shown in Figure 4.66. The bands observed are all the characteristic bands of magnesium pyroborates.

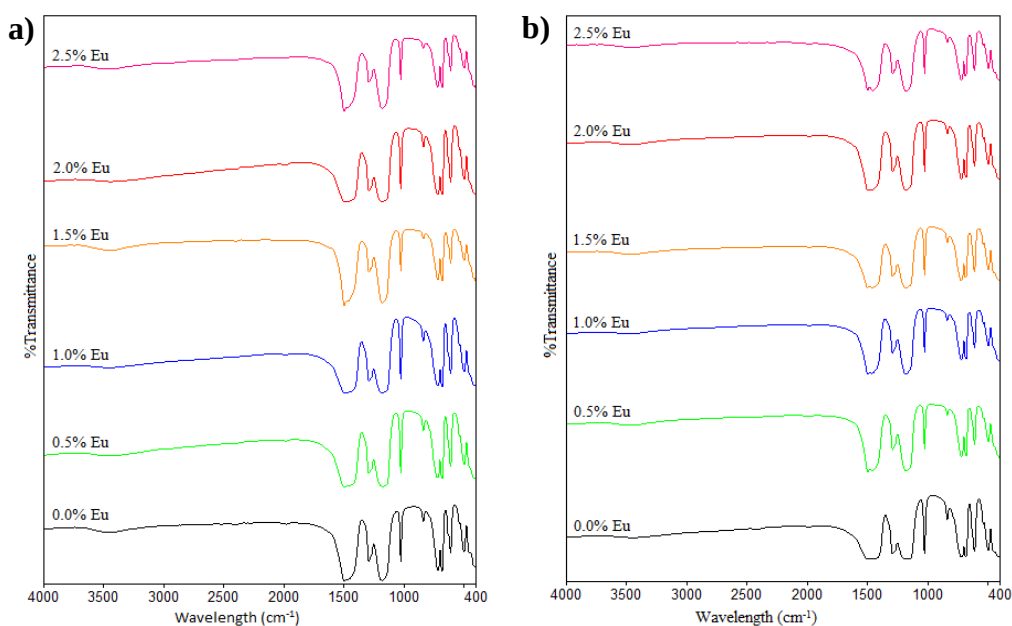


Figure 4.66. The FT-IR spectra of $\text{Mg}_{2-x}\text{Eu}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at a) 900°C b) 1000°C

Tartaric Acid Fuels: The FT-IR spectra of $\text{Mg}_{2-x}\text{Eu}_x\text{B}_2\text{O}_5$ ($x= 0.005$ - 0.025) are given in Figure 4.67 and 4.68. The comparison with undoped magnesium pyroborates compound revealed that the spectra of all products have a great compatibility to each other. Eight characteristics bands of magnesium pyroborates which contributed to different bond variations were recorded.

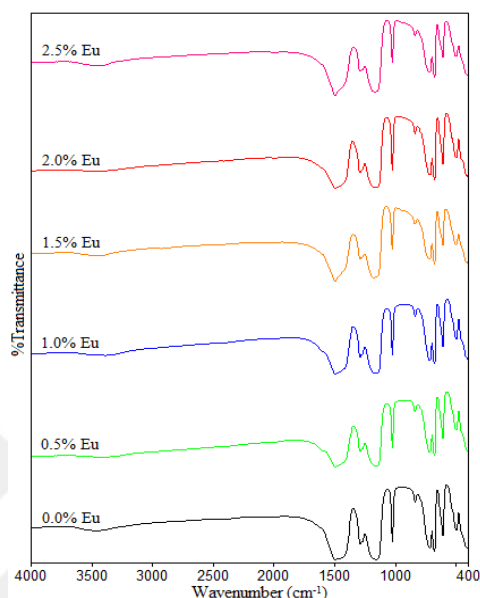


Figure 4.67. The FT-IR spectra of $\text{Mg}_{2-x}\text{Eu}_x\text{B}_2\text{O}_5$ ($x= 0.000$ - 0.025) obtained at 800°C

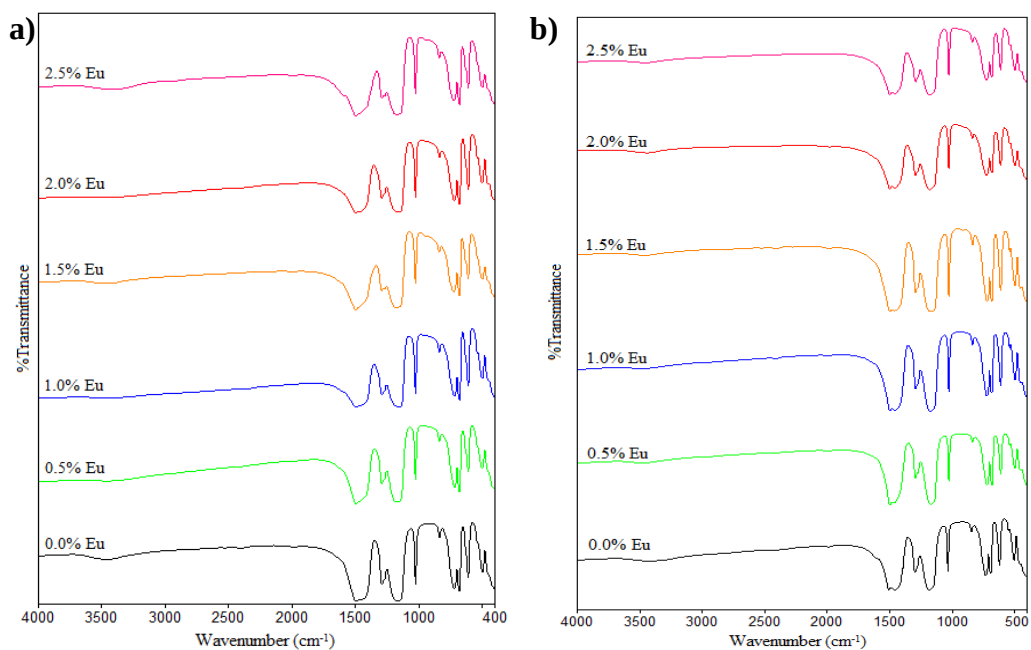


Figure 4.68. The FT-IR spectra of $\text{Mg}_{2-x}\text{Eu}_x\text{B}_2\text{O}_5$ ($x= 0.000$ - 0.025) obtained at a) 900°C and b) 1000°C

Urea Fuels: The B-O bending of trigonal BO_3 , B-O stretching vibrations of trigonal BO_3 and tetrahedral BO_4 are detected at region around $1290\text{--}1500\text{ cm}^{-1}$ and 682 cm^{-1} , 715 cm^{-1} and at region around $840\text{--}1190\text{ cm}^{-1}$, respectively which belong to the vibrational bands of $\text{Mg}_2\text{B}_2\text{O}_5$. Similar to the previous section (4.2.3.1) the products are pure without impurities since no extra bands observed.

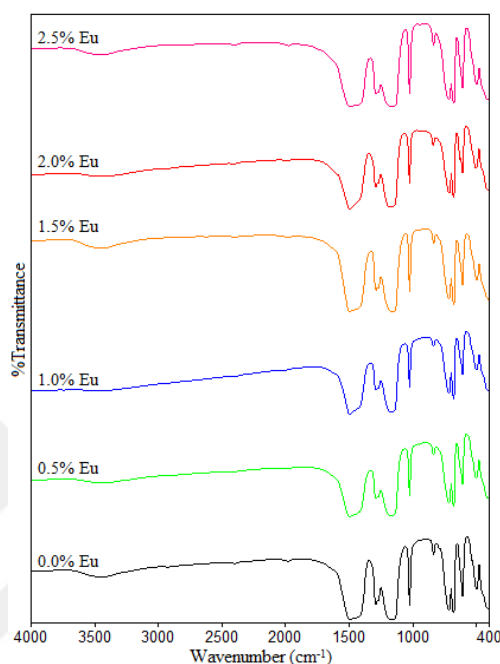


Figure 4.69. The FT-IR spectra of $\text{Mg}_{2-x}\text{Eu}_x\text{B}_2\text{O}_5$ ($x = 0.000\text{--}0.025$) obtained at 800°C

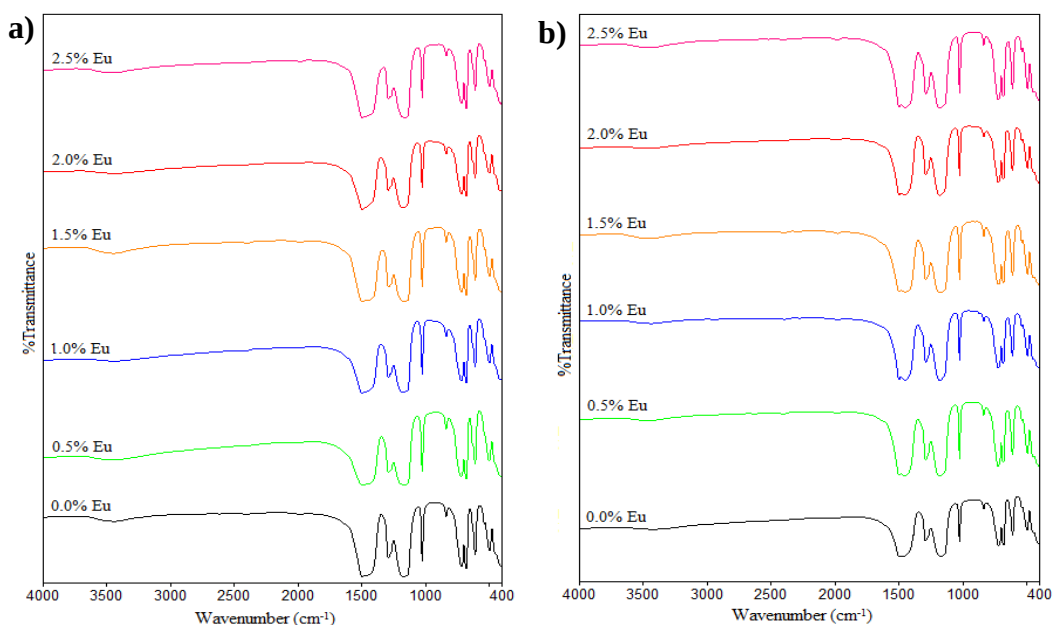


Figure 4.70. The FT-IR spectra of $\text{Mg}_{2-x}\text{Eu}_x\text{B}_2\text{O}_5$ ($x = 0.000\text{--}0.025$) obtained at a) 900°C and b) 1000°C

4.2.3.3 The FT-IR Analyses of Terbium Doped Magnesium Pyroborates

The FT-IR spectra of magnesium pyroborate doped with various concentration of Tb^{3+} at 800°C, 900°C and 1000°C are presented. The spectra showed similar behavior with pure $\text{Mg}_2\text{B}_2\text{O}_5$ at certain temperature. Moreover, the same spectra that were mentioned in previous section (Section 4.3.2.1) are also observed in the spectra of Tb^{3+} doped $\text{Mg}_2\text{B}_2\text{O}_5$.

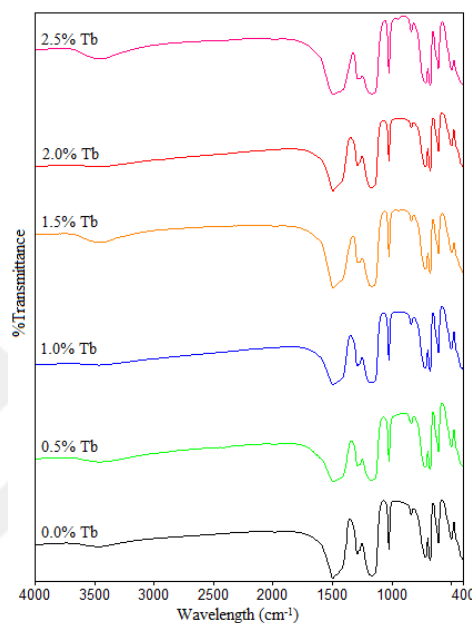


Figure 4.71. The FT-IR spectra of $\text{Mg}_{2-x}\text{Tb}_x\text{B}_2\text{O}_5$ ($x = 0.005-0.025$) obtained at 800°C

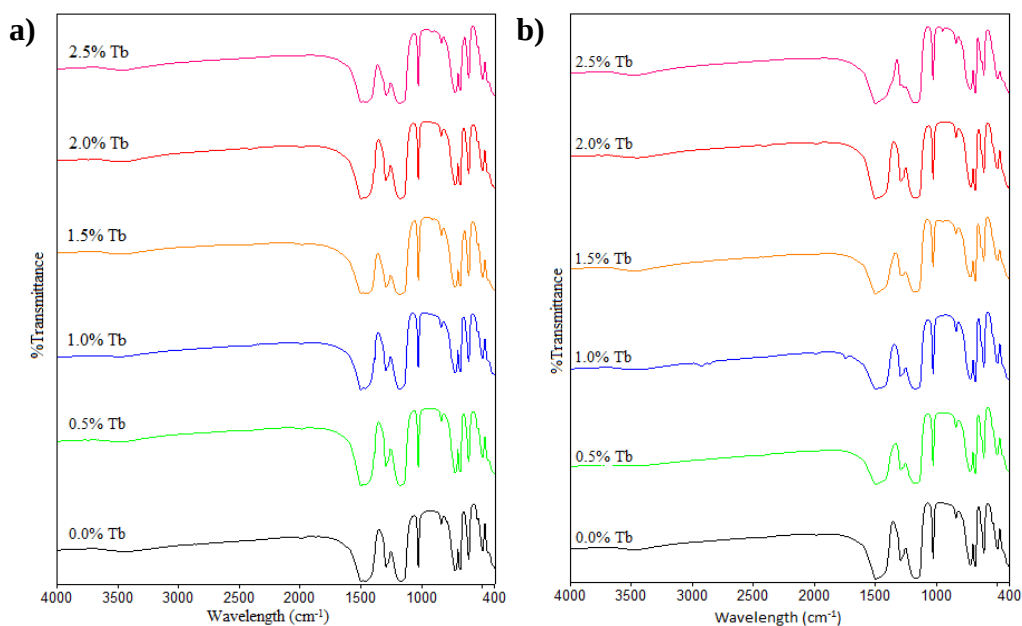


Figure 4.72. The FT-IR spectra of $\text{Mg}_{2-x}\text{Tb}_x\text{B}_2\text{O}_5$ ($x = 0.005-0.025$) obtained at a) 900°C and b) 1000°C

Glycine Fuels: Each of terbium doped magnesium pyroborates compound also have a good accordance with undoped magnesium pyroborates compound (Figure 4.73 and 4.74) and the band wave numbers of each temperature are shown in Table 4.8. Additional peaks that belong to the secondary phase were found at 948 and 1272 cm^{-1} (800°C and 900°C).

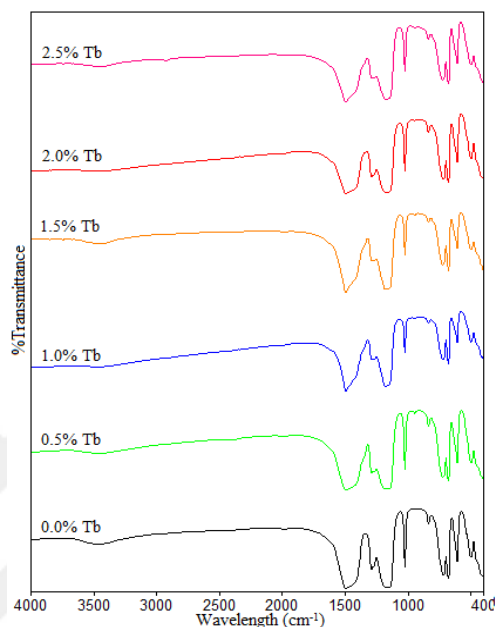


Figure 4.73. The FT-IR spectra of $\text{Mg}_{2-x}\text{Tb}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 800°C

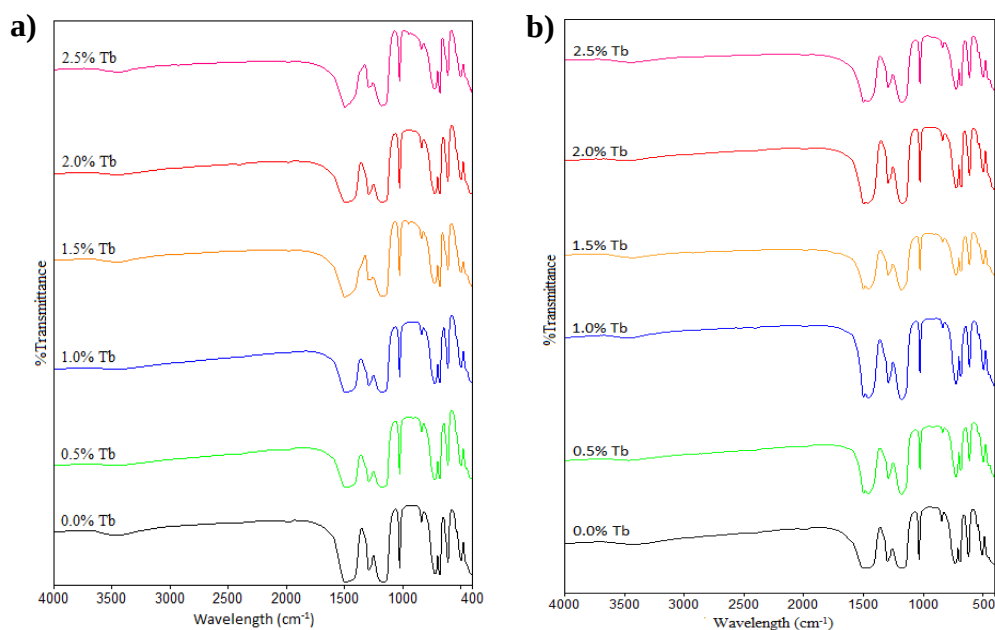


Figure 4.74. The FT-IR spectra of $\text{Mg}_{2-x}\text{Tb}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at a) 900°C and b) 1000°C

Corresponding to the XRD results, triclinic magnesium pyroborates are obtained at 1000°C. The characteristic bands of magnesium pyroborates was also observed in the FT-IR analysis where the bands at 1290-1500 cm^{-1} are contributed to the asymmetric B-O stretching of trigonal BO_3 , at 720 cm^{-1} and 682 cm^{-1} are assigned to the B-O-B bending of trigonal BO_3 . Furthermore, the stretching of B-O of tetrahedral BO_4 was observed at 840 cm^{-1} and 1180 cm^{-1} (Figure 4.74).

HMTA Fuels: The vibrational bands corresponded to the characteristic bands of $\text{Mg}_2\text{B}_2\text{O}_5$ are observed at 680 cm^{-1} , 715 cm^{-1} , 839 cm^{-1} , 1026 cm^{-1} , 1185 cm^{-1} , 1290 cm^{-1} and 1465 cm^{-1} . Additional peaks were noticed in the spectra of 2.0%Tb and 2.5%Tb around 918.75 and 868.75 cm^{-1}) at 1000°C.

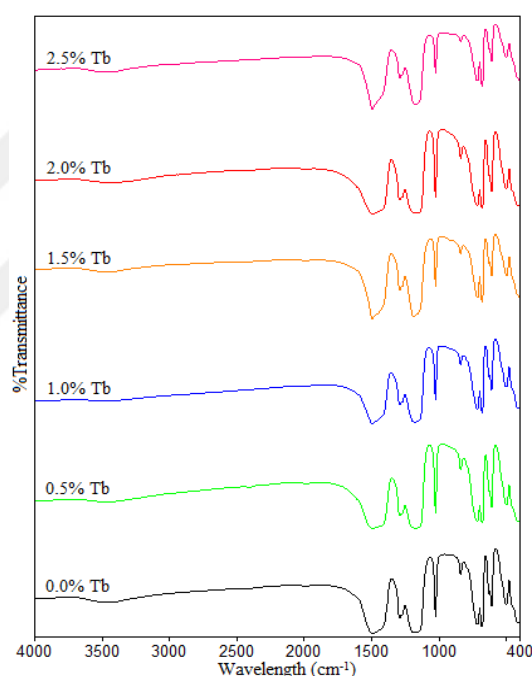


Figure 4.75. The FT-IR spectra of $\text{Mg}_{2-x}\text{Tb}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at 800°C

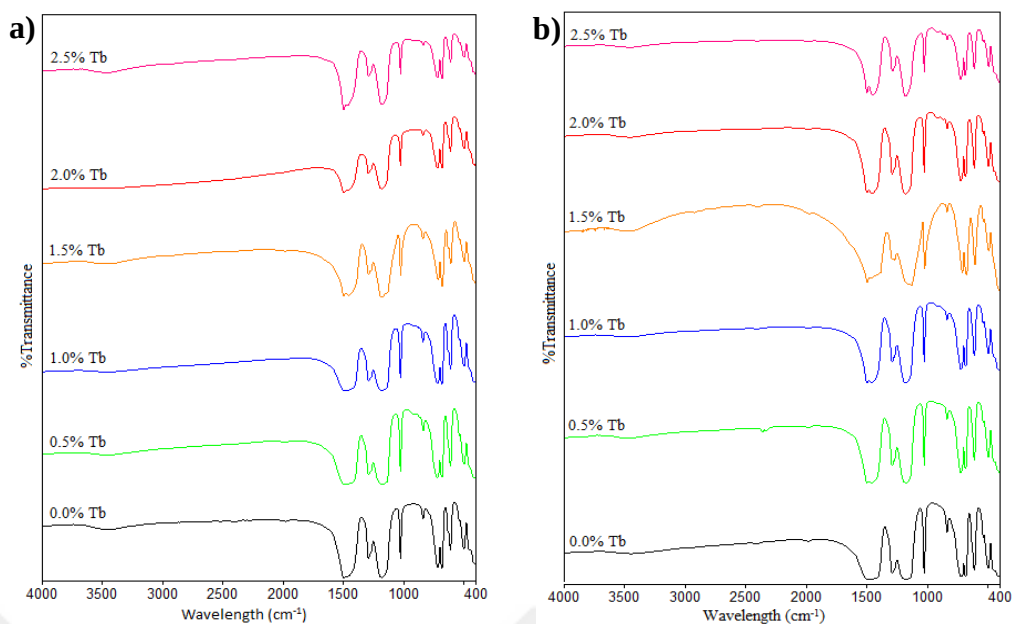


Figure 4.76. The FT-IR spectra of $\text{Mg}_{2-x}\text{Tb}_x\text{B}_2\text{O}_5$ ($x=0.000-0.025$) obtained at a) 900°C and b) 1000°C

Tartaric Acid Fuels: Similarly, the FT-IR spectra of $\text{Mg}_2\text{B}_2\text{O}_5: \text{Tb}^{3+}$ gave similar assignments with the other dopants and each concentration has great accordance with undoped magnesium pyroborates products (Figure 4.77 and 4.78).

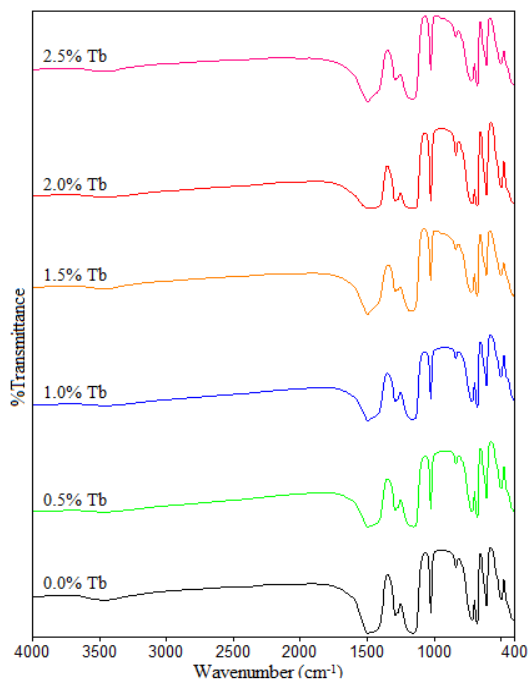


Figure 4.77. The FT-IR spectra of $\text{Mg}_{2-x}\text{Tb}_x\text{B}_2\text{O}_5$ ($x=0.000-0.025$) obtained at 800°C

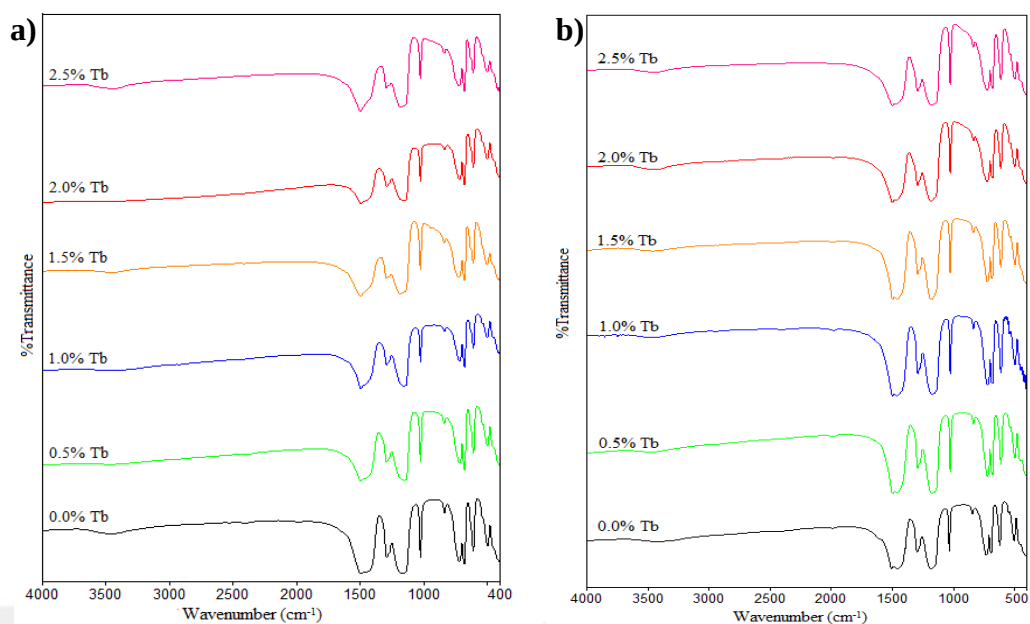


Figure 4.78. The FT-IR spectra of $\text{Mg}_{2-x}\text{Tb}_x\text{B}_2\text{O}_5$ ($x= 0.000\text{-}0.025$) obtained at a) 900°C and b) 1000°C

Urea Fuels: The characteristic bands of magnesium pyroborates were noticed in the spectra of terbium doped magnesium pyroborates. These similarities indicate that Tb-doped magnesium pyroborate are pure. The bands are found at around 683 cm^{-1} , 720 cm^{-1} , 839 cm^{-1} , 1026 cm^{-1} , 1170 cm^{-1} , 1290 cm^{-1} and 1490 cm^{-1} .

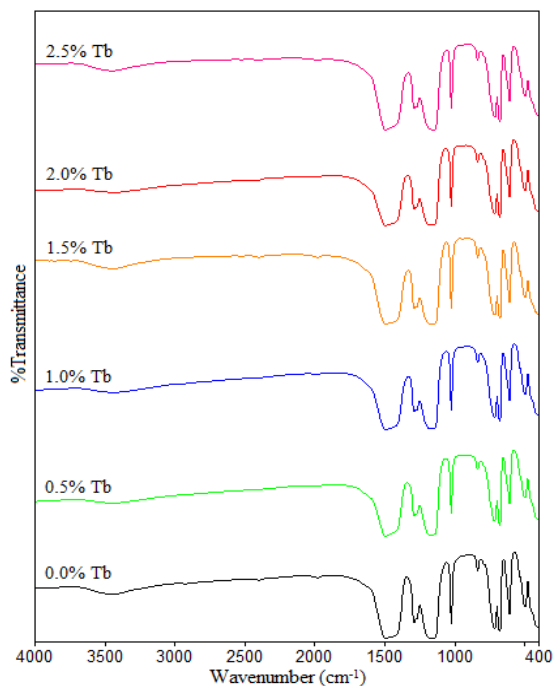


Figure 4.79. The FT-IR spectra of $\text{Mg}_{2-x}\text{Tb}_x\text{B}_2\text{O}_5$ ($x= 0.000\text{-}0.025$) obtained at 800°C

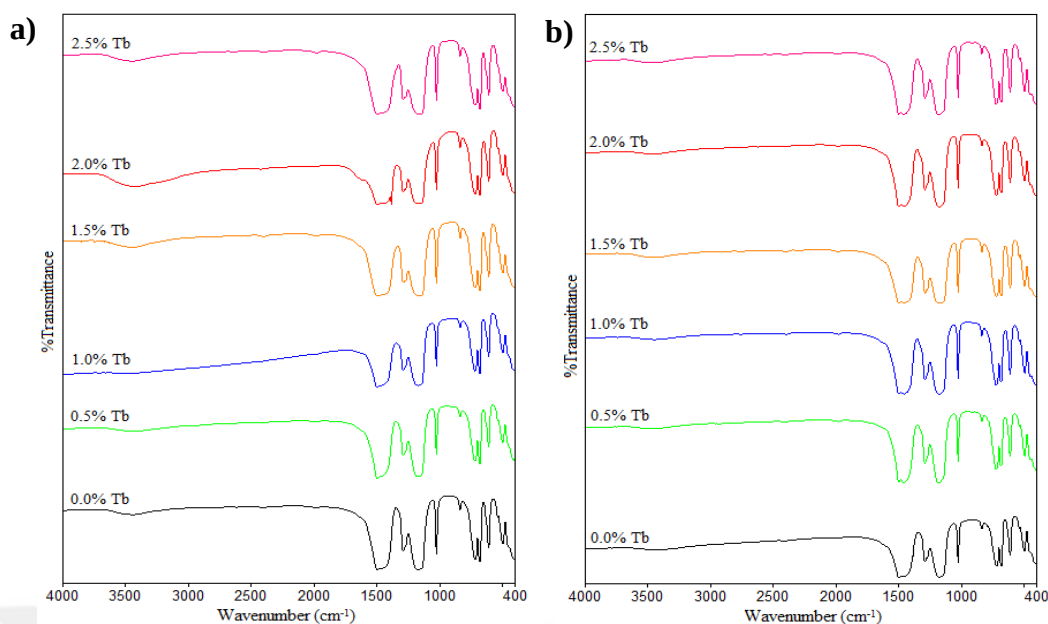


Figure 4.80. The FT-IR spectra of $\text{Mg}_{2-x}\text{Tb}_x\text{B}_2\text{O}_5$ ($x = 0.000-0.025$) obtained at a) 900°C and b) 1000°C

4.2.4 UV-Vis Studies of Rare Earth Metal Doped Magnesium Pyroborates

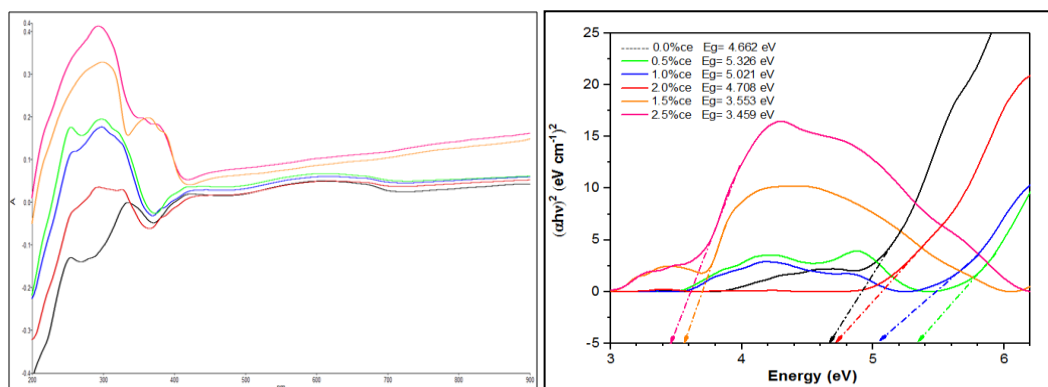
The spectra of rare-earth-doped magnesium pyroborates were recorded in the range of 200-900 nm using Diffuse Reflectance Spectroscopy (DRS). The effects of the dopants were observed during this analysis, and the optical band gap energy of the resulting products was determined.

4.2.4.1 UV-Vis Studies of Cerium Doped Magnesium Pyroborates

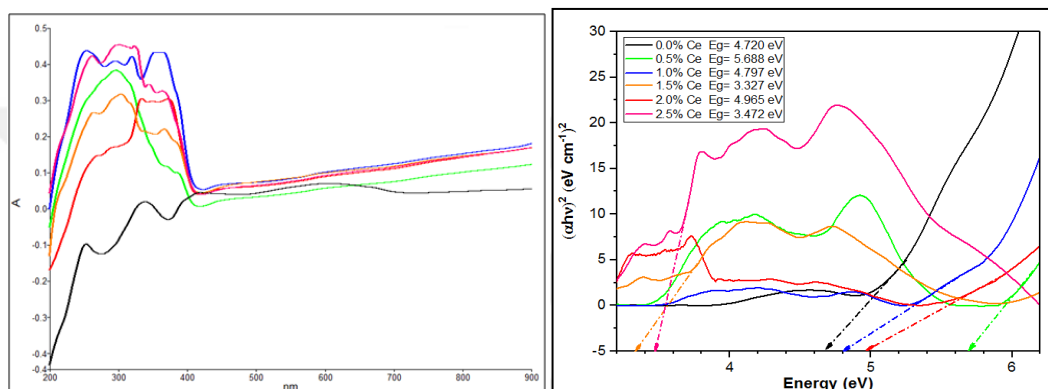
The absorbance spectra of the magnesium pyroborates acquired at 1000°C showed two peaks in the UV region were observed for all concentrations of dopant materials. For cerium doped magnesium pyroborates, the band gap energy of obtained products at 1000°C has also been determined using tauc plot ($(\alpha h\nu)^2$ versus energy) by taking the intercept of the curve on the energy in the x-axis. The optical band gap of the $\text{Mg}_2\text{B}_2\text{O}_5:\text{Ce}^{3+}$ are in the range of 3.10-5.69 eV.

The peaks were observed at wavelength below 400 nm in the spectra of cerium-doped magnesium pyroborate for all synthesized products with different fuels. The absorbance spectra were detected at the range of 200-400 nm. In comparison with the undoped magnesium pyroborates, the addition of cerium (III) ions as dopants to the host magnesium pyroborates compound has resulted in a clear and distinctive change in the optical properties of the host materials.

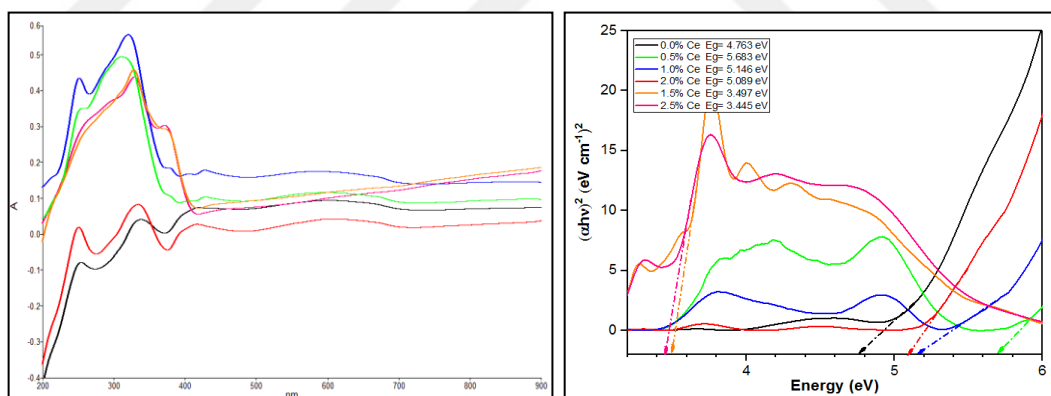
a) $\text{Mg}_2\text{B}_2\text{O}_5 : \text{Ce}^{3+}$ with Citric Acid



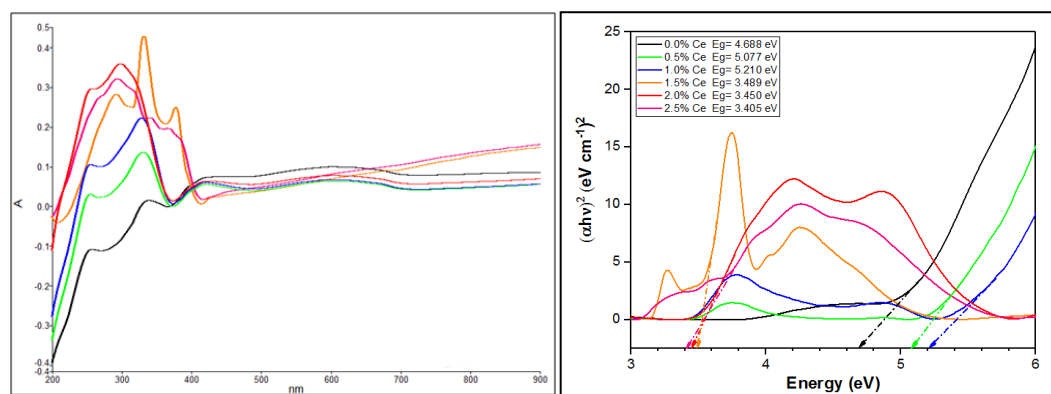
b) $\text{Mg}_2\text{B}_2\text{O}_5 : \text{Ce}^{3+}$ with Glycine



c) $\text{Mg}_2\text{B}_2\text{O}_5 : \text{Ce}^{3+}$ with HMTA



d) $\text{Mg}_2\text{B}_2\text{O}_5 : \text{Ce}^{3+}$ with Tartaric Acid



e) $\text{Mg}_2\text{B}_2\text{O}_5 : \text{Ce}^{3+}$ with Urea

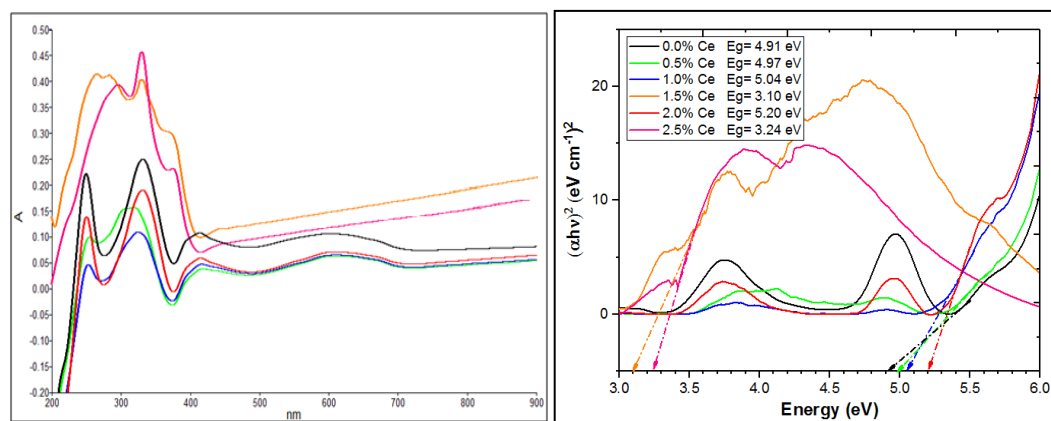


Figure 4.81. The absorbance spectra and optical band gap energy of cerium doped $\text{Mg}_2\text{B}_2\text{O}_5$ obtained at 1000°C with all fuels

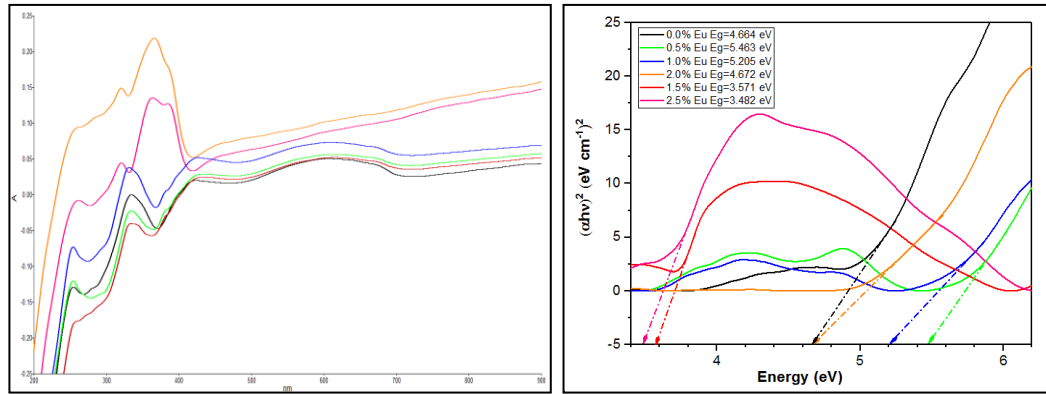
When Ce^{3+} is doped into magnesium pyroborate, the observed absorption peaks in the ultraviolet (UV) region are primarily attributed to the 4f-5d electronic transitions of the Ce^{3+} ions. These transitions occur at high energy levels, corresponding to UV light absorption. While the magnesium pyroborate host lattice can affect the exact position and intensity of these peaks, the UV absorption is fundamentally due to the intrinsic electronic properties of the Ce^{3+} ions, which dominate the spectral characteristics even within the host matrix.

This alteration in optical properties is likely attributed to the incorporation of cerium ions into the crystal structure of magnesium pyroborates, influencing how the material interacts with light. The study demonstrates that the introduction of cerium as a dopant during the synthesis of magnesium pyroborates using different fuel has notable effects on the optical properties and band gap energy of the resulting materials. The absence of cerium peaks in the visible regions suggests successful substitution, and the calculated band gap values indicate a significant alteration due to the doping process.

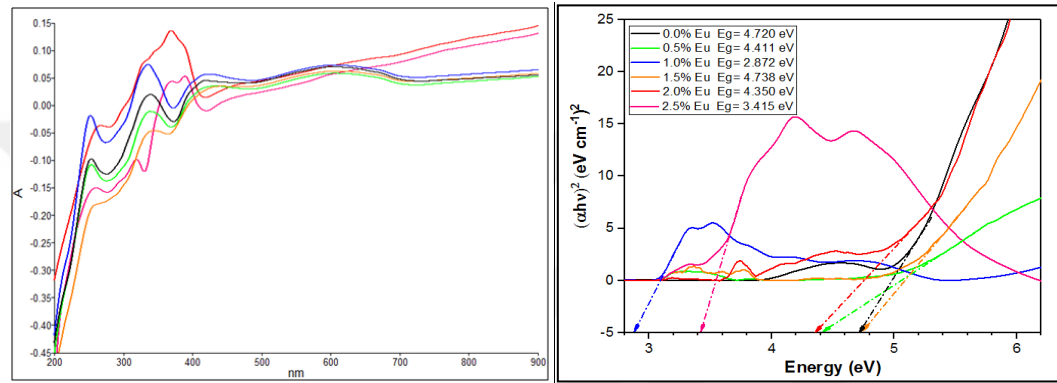
4.2.4.2 UV-Vis Studies of Europium Doped Magnesium Pyroborates

The absorbance spectra of $\text{Mg}_2\text{B}_2\text{O}_5 : \text{Eu}^{3+}$ were also examined between 200-900 nm. The peaks are found in the UV region and there is no peaks were detected in the visible region. Unlike the spectra of cerium doped magnesium pyroborates, the spectra of europium doped gave the maximum peak with maximum sharp absorptions at approximately 390 nm (Figure 4.82).

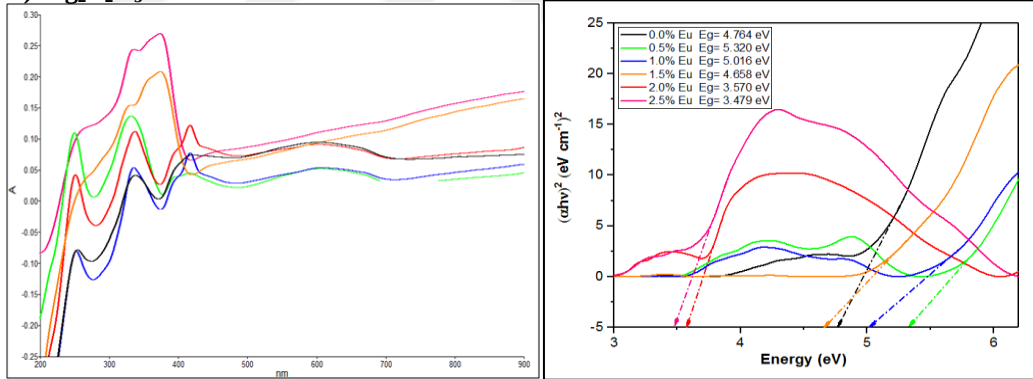
a) $\text{Mg}_2\text{B}_2\text{O}_5: \text{Eu}^{3+}$ with Citric Acid



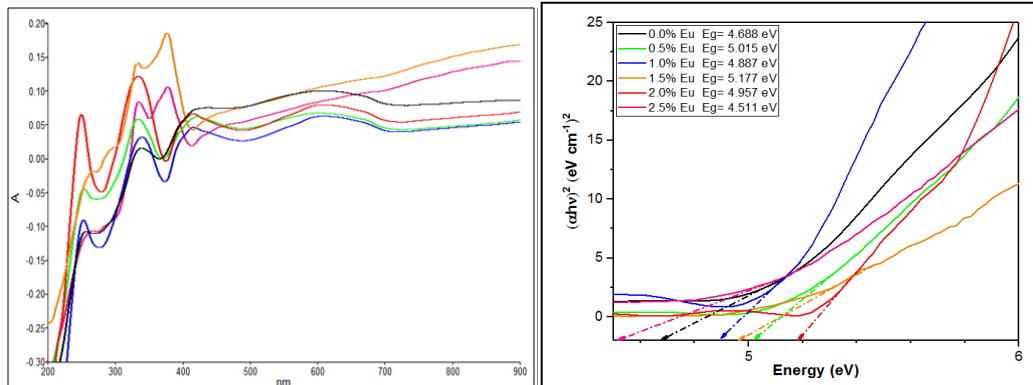
b) $\text{Mg}_2\text{B}_2\text{O}_5: \text{Eu}^{3+}$ with Glycine



c) $\text{Mg}_2\text{B}_2\text{O}_5: \text{Eu}^{3+}$ with HMTA



d) $\text{Mg}_2\text{B}_2\text{O}_5: \text{Eu}^{3+}$ with Tartaric Acid



e) $\text{Mg}_2\text{B}_2\text{O}_5:\text{Eu}^{3+}$ with Urea

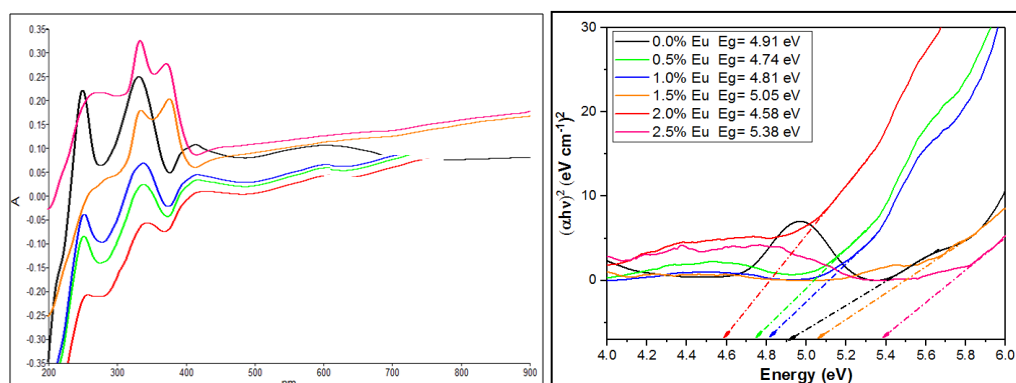


Figure 4.82. The absorbance spectra and optical band gap energy of europium doped $\text{Mg}_2\text{B}_2\text{O}_5$ obtained at 1000°C with all fuels

When europium is doped into magnesium pyroborate, the spectral features are primarily characterized by the 4f-4f electronic transitions of the europium ions, which typically result in sharp emission lines in the visible region, particularly in the red or orange wavelengths. However, the host matrix, magnesium pyroborate, might influence the specific spectral characteristics, including the intensity and exact positioning of these emission lines detected in the ultraviolet region. The spectra of every dopants concentration are resemble to each other and confirms the substitution of Mg^{2+} as host materials with dopant europium (III) ion.

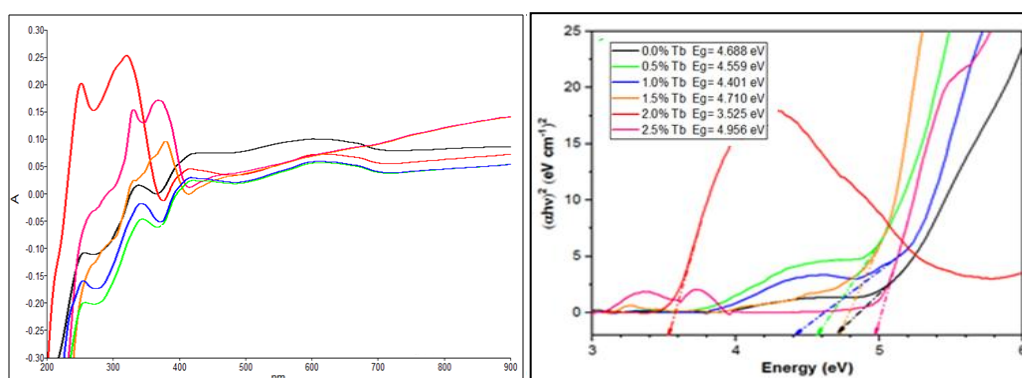
The optical band gap energy of $\text{MgB}_2\text{O}_5:\text{Eu}^{3+}$ with different concentrations were also examined by taking the intercept of the Tauc plot. At 1000°C , the absorbance intensity of the compounds is varied as the concentrations of each dopant are different. This showed their effect on the properties of the desired compound. Based on the band gap values given by the europium doped magnesium pyroborates it observed that the additions of doping materials affected the band gap values of the magnesium pyroborates. The optical band gap energy was found to range from 3.43 to 5.21 eV, decreasing with increasing dopant concentrations in all products synthesized using citric acid, glycine, HMTA, and tartaric acid. The highest band gap value, 3.479 eV, was observed for the product obtained with 2.5% europium using urea as the fuel, indicating that the optical properties are influenced by the type of fuel used.

4.2.4.3 UV-Vis Studies of Terbium Doped Magnesium Pyroborates

The optical band gap values of terbium doped magnesium pyroborates approximately 3.52-4.96 eV. These band gap energy values at 1000°C were much closed to the result obtained by Došler et al. (2010), 4.72 eV. The variety of band gap energy values also proved the impact of doping materials and their concentrations on the optical band gap energy of the products. The band gaps are acquired in the ranges of 4.30 to 5.50 eV.

Presented in Figure 4.83, the spectra of terbium doped magnesium pyroborates which is formed in triclinic structure gave two peaks at the range of 200-400 nm. The presence of terbium ions typically introduces new absorption bands due to the electronic transitions of terbium. However, the absence of absorption peak in the visible region may be due to the intrinsic properties of the host lattice magnesium pyroborates and the specific doping concentration of terbium which is very low. Additionally, the observed behavior confirms that terbium ions have been successfully incorporated into the magnesium pyroborate host lattice. The peaks are similar to each other except for 1.5% Tb and 2.5% Tb which formed boarder peaks at higher absorbance values. Taking the intercept of the Tauc plot, it is reported that the highest band gap value is belong to the lowest dopant concentrations (0.5% Tb) with 5.424 eV. In another words, the band gap values is inversely proportional to concentration of dopants. The band gap energy is decreasing by the additions of Terbium (0.5%Tb, 1.0%Tb and 2.0%Tb).

a) $\text{Mg}_2\text{B}_2\text{O}_5: \text{Tb}^{3+}$ with Citric Acid



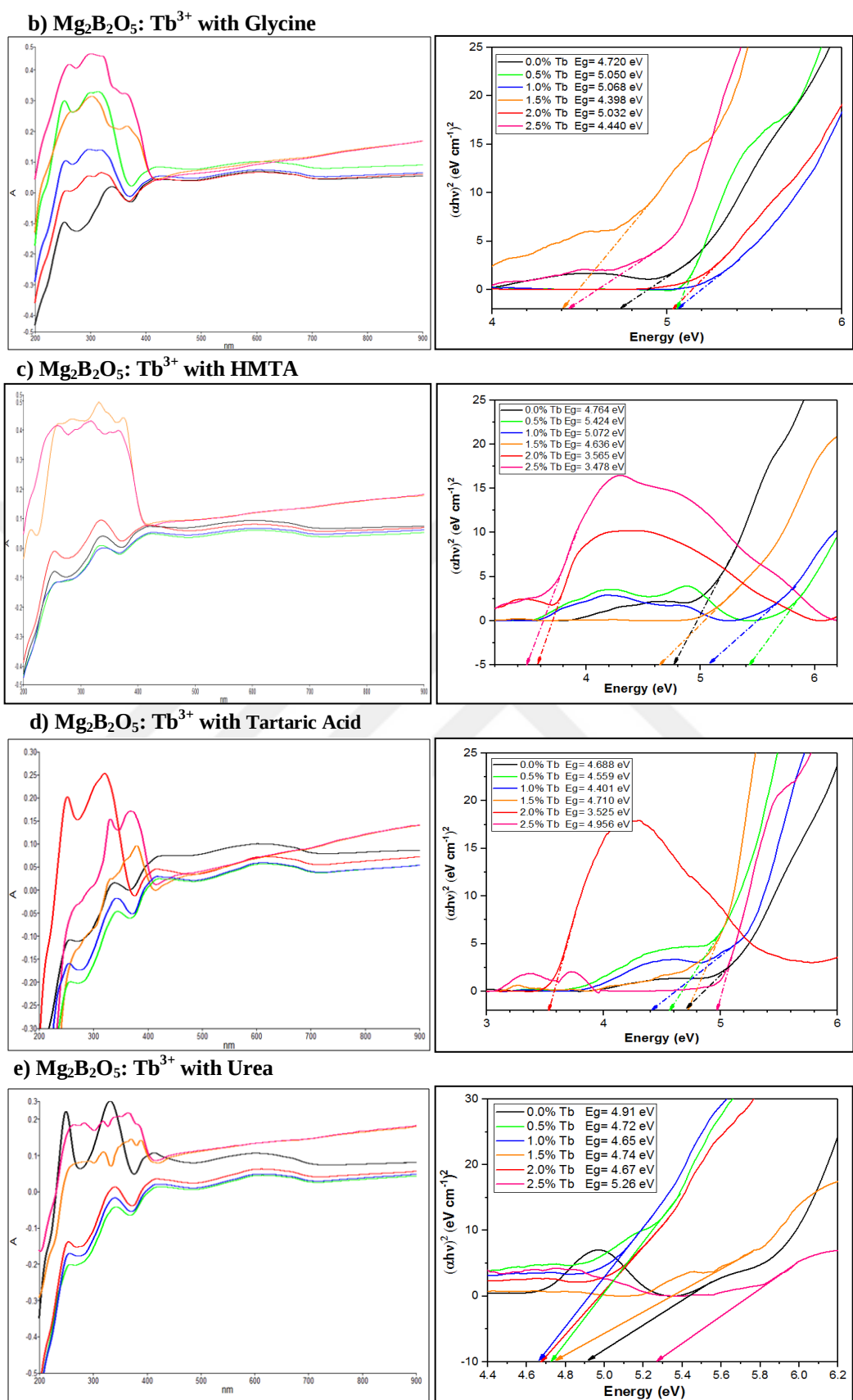
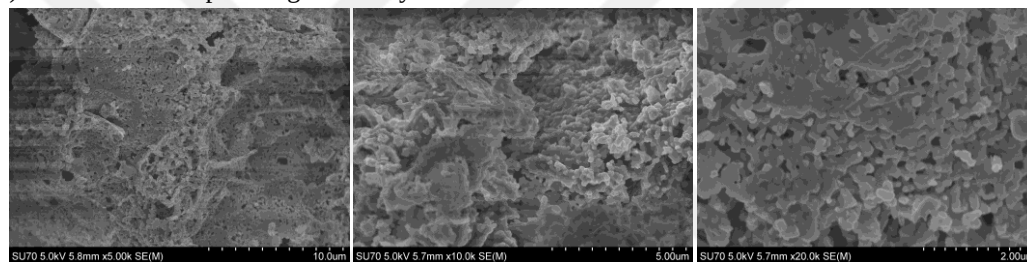


Figure 4.83. The absorbance spectra and optical band gap energy of terbium doped $\text{Mg}_2\text{B}_2\text{O}_5$ obtained at 1000°C with all fuels

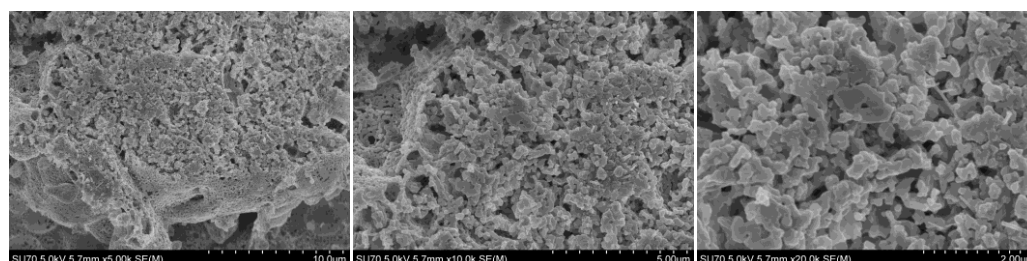
4.2.5 Field Emission Scanning Electron Microscopy (FESEM) Analyses of Rare Earth Metal Doped Magnesium Pyroborates

The morphology of the synthesized lanthanide-doped magnesium pyroborates was investigated using a high-resolution field emission scanning electron microscope (FESEM). The study focused on samples synthesized using the tartaric acid fuel method, known for producing fine, homogeneously mixed powders with 1.0% dopant concentrations. The samples were prepared by dispersing a small quantity of the powder onto conductive carbon tape, followed by sputter-coating with a thin layer of silver to enhance electrical conductivity and reduce charging effects. The FESEM images were acquired at magnifications of 5000x, 10000x, and 20000x.

a) 1.0% Cerium Doped Magnesium Pyroborates



b) 1.0% Europium Doped Magnesium Pyroborates



c) 1.0% Terbium Doped Magnesium Pyroborates

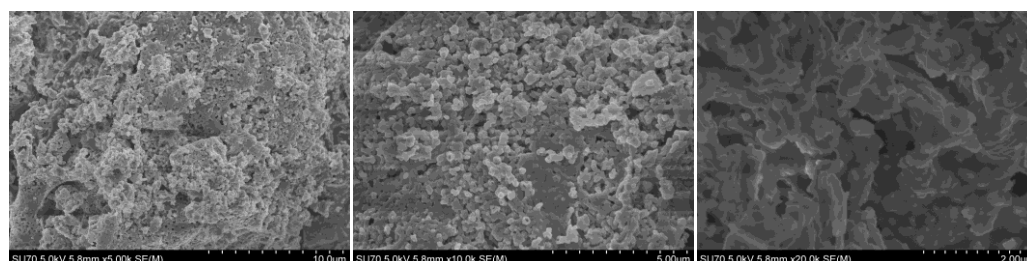


Figure 4.84. The FESEM images of 1.0% RE-Mg₂B₂O₅ obtained at 1000°C with tartaric acid fuel

The FESEM analysis at various magnifications revealed the following morphological characteristics of the lanthanide-doped magnesium pyroborates:

- **5000x magnification:** at 5000x magnification, the overall morphology of the particles is observed. The material exhibits a relatively homogeneous particle distribution with evidence of agglomeration. The particles are observed to be irregular in shape.
- **10000x magnification:** closer examination at 10000x magnification reveals more detailed surface features. The particles exhibit rough surfaces, indicative of the formation of the pyroborate phase.
- **20000x magnification:** at 20000x magnification, fine nanoscale features are discernible. The nanostructured nature of the material is confirmed, with individual crystallites forming larger aggregates.

This nanostructuring is consistent with the expected outcome of the calculated crystallite size that found in the range of 10-35 nm. It was also observed that the morphology of the cerium-doped samples has porous structure, irregular and granular shapes with larger particle sizes and more ordered compared to other dopant materials, in order cerium>europium >terbium.

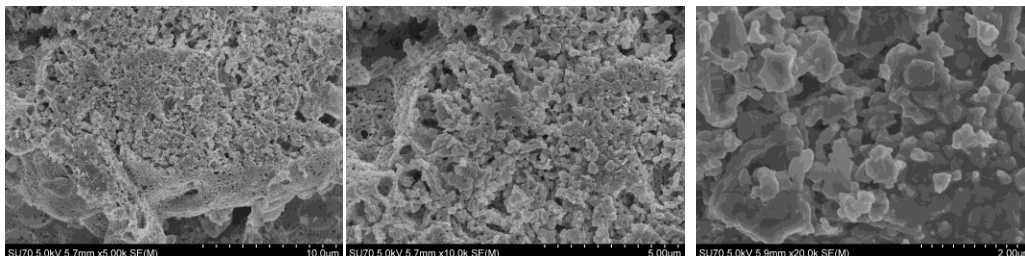
The FESEM images of europium-doped magnesium pyroborates synthesized by tartaric acid fuel (1000°C) were also analyzed at different europium concentrations to assess their impact on particle morphology and size. The analysis revealed how varying dopant levels influence particle distribution and agglomeration, providing insights into the relationship between europium concentration and the resulting structural characteristics of the material.

The FESEM images demonstrate that varying europium concentrations significantly affect the particle size of the synthesized magnesium pyroborates, though the overall morphology remains consistent. Specifically, increasing the europium concentration leads to noticeable changes in particle size, indicating that the dopant concentration influences the degree of particle growth and agglomeration. Despite these changes in size, the morphology of the particles across different concentrations appears largely uniform, with the particles predominantly exhibiting an irregular, column-round like agglomerated structure. This suggests that while europium concentration impacts particle dimensions, it does not substantially alter the fundamental morphology of the material.

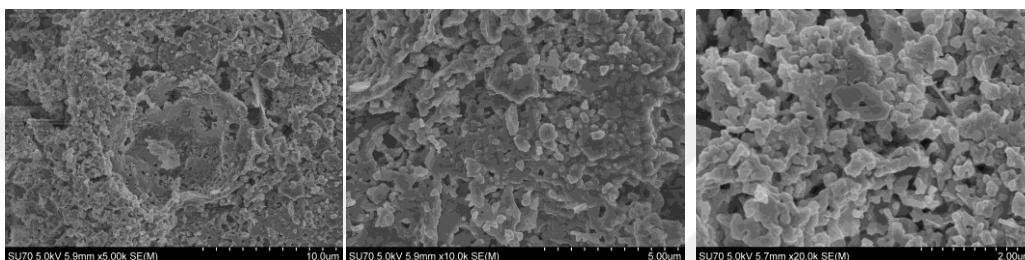
Furthermore, all the samples are found to be nanosized, with their dimensions aligning closely with the calculated crystallite size. Notably, the

samples with 0.5% Eu^{3+} doping exhibit the smallest particle size and 1.5% Eu^{3+} observed to have clear borders between each particle compared to the others.

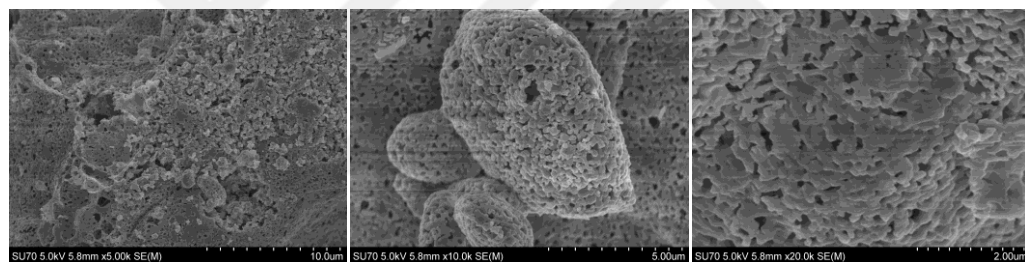
a) 0.5% Europium Doped Magnesium Pyroborates



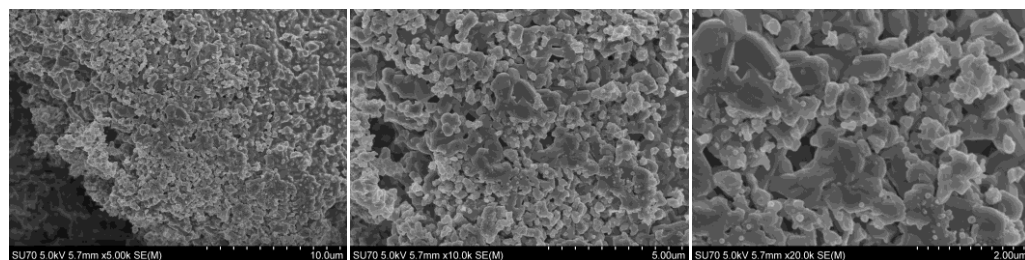
b) 1.0% Europium Doped Magnesium Pyroborates



c) 1.5% Europium Doped Magnesium Pyroborates



d) 2.0% Europium Doped Magnesium Pyroborates



e) 2.5% Europium Doped Magnesium Pyroborates

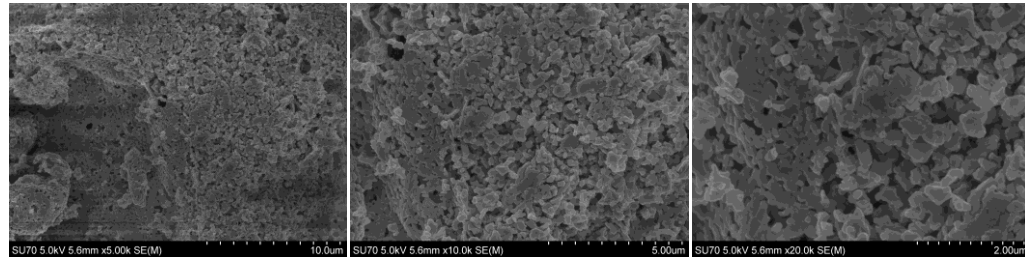


Figure 4.85. The FESEM images of $\text{RE-Mg}_2\text{B}_2\text{O}_5$ with various concentrations

4.2.6 Energy Dispersive X-Ray Spectroscopy (EDX) Analyses of Rare Earth Metal Doped Magnesium Pyroborates

Energy dispersive X-ray spectroscopy (EDX) is a widely used technique for determining the elemental composition of nanoparticle samples. The EDX spectrum, which displays energy versus relative counts of detected X-rays, is analyzed to ascertain both the qualitative and quantitative composition of the elements in a sample, providing valuable insights into their chemical makeup. In the EDX spectra for rare earth metal doped $\text{Mg}_2\text{B}_2\text{O}_5$ nanoparticles, as shown in Figures 4.86-4.88, the elements such as carbon (C), silicon (Si), silver (Ag), oxygen (O), magnesium (Mg), and lanthanide metal ions (Ce, Eu and Tb) are identified in varies intensity. The spectrum indicates that magnesium and oxygen are present in higher concentrations compared to other elements. Carbon peak might be introduced from environmental contamination or adsorption from the substrate, as well as phytochemical interactions with the nanoparticles' surface. The silicon and silver peaks result from the substrate and coating process applied during the analysis.

It is also important to note that the doping process of lanthanide materials has been successful, as peaks corresponding to cerium, europium, and terbium are observed in the EDX analysis and detected at the related X-ray energies. The absence of boron detection in the EDX spectrum of lantahnide doped magnesium pyroborates can be attributed to several factors related to the limitations of the EDX technique. EDX has relatively poor energy resolution, which often results in peak overlaps, especially for elements with X-ray emission lines in the low-energy range. Boron, in particular, has its K-alpha peak below 1 keV (0.1833 keV), where it is prone to interference from other light elements such as carbon, oxygen, and heavier elements' L- and M- family peaks. These overlaps make it challenging to distinguish and accurately measure the intensity of Boron's X-ray emission, leading to its non-detection in the spectrum (151).

Despite these EDX limitations, the presence of Boron in the synthesized materials have been validated through complementary analytical technique such as FT-IR and XRD analysis, which provide robust evidence of magnesium pyroborates nanoparticle's formation and its constituent elements.

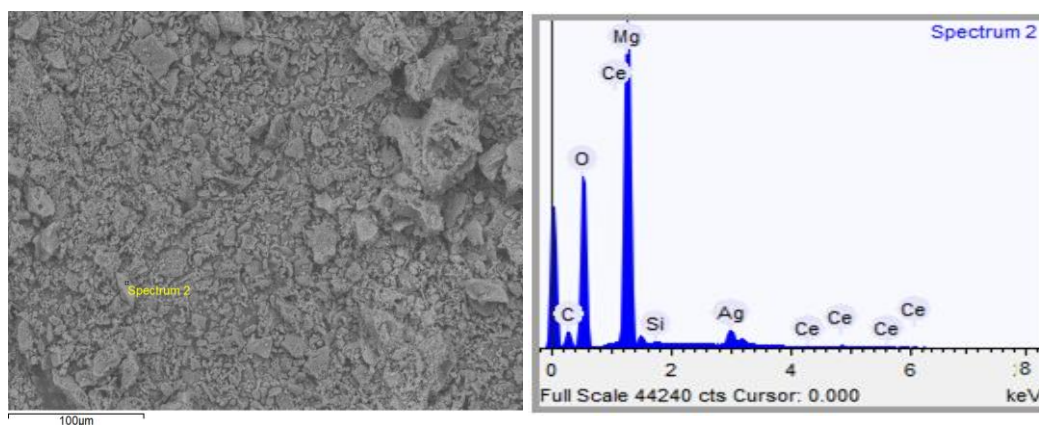


Figure 4.86. The EDX spectrum of 1.0% Ce^{3+} doped magnesium pyroborates

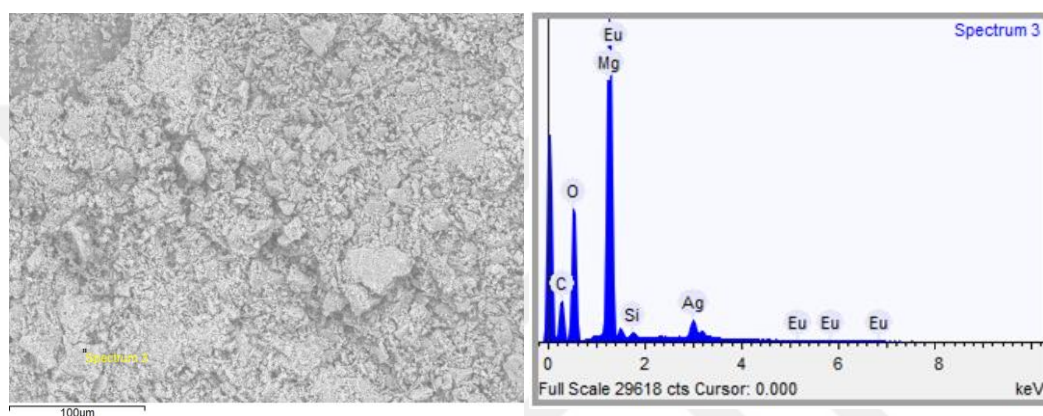


Figure 4.87. The EDX spectrum of 1.0% Eu^{3+} doped magnesium pyroborates

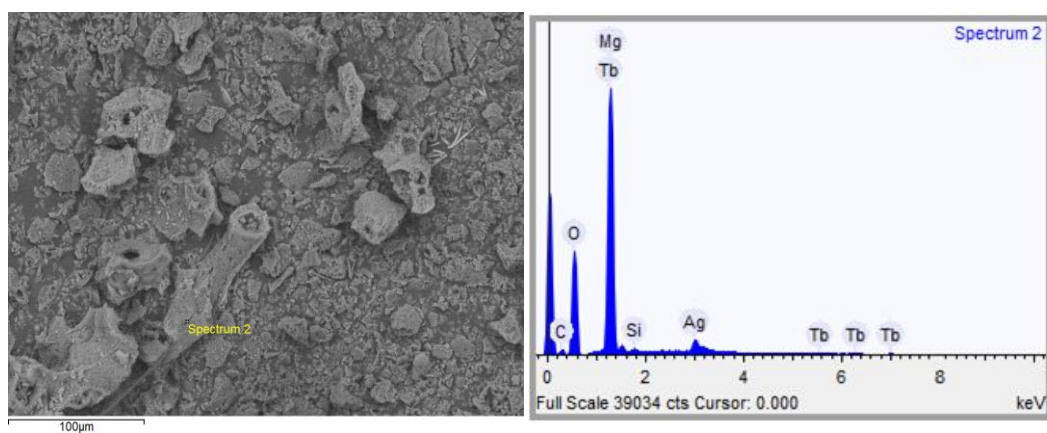


Figure 4.88. The EDX spectrum of 1.0% Tb^{3+} doped magnesium pyroborates

Energy dispersive X-ray spectroscopy (EDX) analysis was also performed on the synthesized europium doped magnesium pyroborates with various concentrations to identify their elemental makeup and composition. The compositions of magnesium and europium ions are expected to be directly proportional to each other (Figure 4.89).

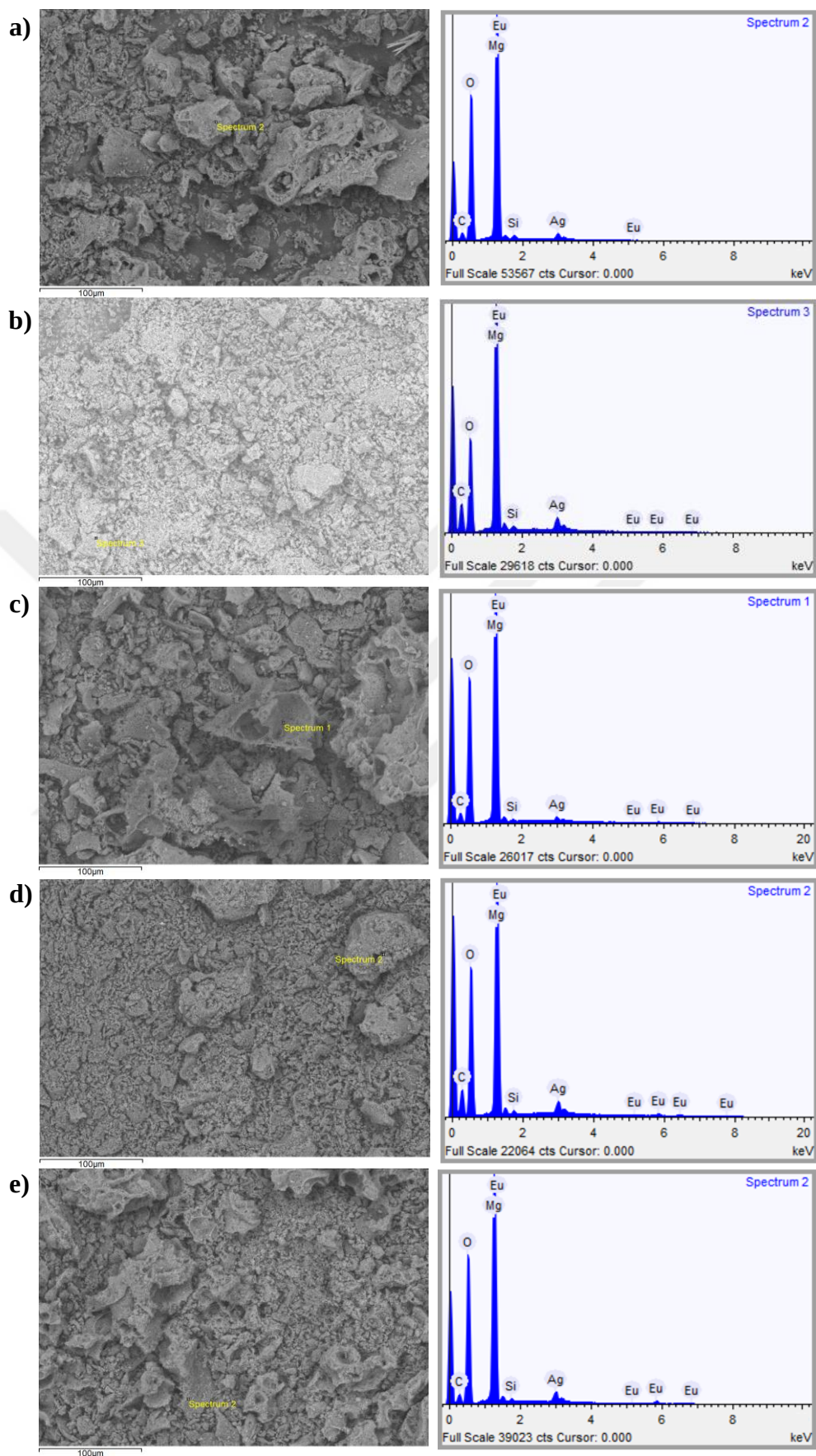


Figure 4.89. The EDX spectrum of a) 0.5%, b) 1.0%, c) 1.5%, d) 2.0% and e) 2.5% Eu^{3+} doped magnesium pyroborates

Theoretically, the atomic weight percentages of each element in magnesium pyroborate are as follows: Mg: 32.37%, B: 14.39%, and O: 53.25%. These values provide a baseline expectation for the elemental composition of the pure, undoped material. Zhu W. et.al also found the composition of element in undoped magnesium pyroborates are Mg: 36.8% of, B: 12.7% and O: 50.5% (152).

Table 4.2. The elements' atomic weight percentage of EDX analyses

Element	Atomic Weight %				
	0.5% Eu ³⁺	1.0% Eu ³⁺	1.5% Eu ³⁺	2.0% Eu ³⁺	2.5% Eu ³⁺
C	11.895	8.694	12.006	14.647	12.608
O	62.871	56.791	64.434	60.772	62.148
Mg	24.302	32.712	22.461	23.805	23.612
Si	0.399	0.564	0.288	0.231	0.327
Ag	0.482	1.063	0.620	0.345	0.807
Eu	0.051	0.176	0.192	0.201	0.498

The atomic weight percentages obtained from EDX analysis, are closely match the theoretical compositions of the synthesized materials when adjusted for the undetectable boron. This alignment between theoretical calculations and experimental data confirms that the doping process was successful. The EDX spectrum of magnesium pyroborates doped europium with various concentrations also observed to verify its element compositions, as presented in Figure 4.87. When europium ions are doped into the host material, the atomic weight percentages of the detectable elements vary depending on the concentration of the dopant. The elemental composition obtained may not match the exact desired values, which could be attributed to variations in the synthesis process and the distribution of elements within the materials. The introduction of dopant ions alters the overall composition of the material. The magnesium weight mostly decreased as the concentration of doping materials is increases.

4.3 The Synthesis and Characterization of Lithium Pyroborates Nanocompounds

As far as our knowledge, the study about lithium pyroborate was rarely done due to its difficulty in forming single crystal structure products. In the recent years only few studies about preparation of lithium pyroborates. It the review of

Meng He et.al, it was reported that both crystal structure alpha and beta lithium pyroborates were acquired at different temperature by solid state reaction method. Consequently, to obtain pure lithium pyroborates via simpler method, many trials and errors were done as follows:

4.3.1 Synthesis of Lithium Pyroborate Stoichiometrically With Tartaric Acid

The first study of Lithium pyroborate was done by quick and easy synthetic method, solution combustion synthesis (SCS) method using tartaric acid as fuel. Tartaric acid was used because of its reasonable cost, chemical stability, basic stoichiometric calculation and produce high amount of final products. The starting materials such as lithium nitrate (LiNO_3), boric acid (H_3BO_3) and tartaric acid was dissolved into minimum amount of distilled water. The solution was allowed to evaporate at 370°C until the gelatinous solution was observed. The gel was then introduced to pre-heated furnace at 400°C for 10 minutes. The color appearance of the as-prepared powder products and annealed materials is differentiated. The as-prepared product of lithium pyroborates was black in colour (Picture 4.4) which might be resulting from the unreacted organic compound.



Picture 4.4. The as-synthesized lithium pyroborate with tartaric acid

The as-prepared product was annealed at the temperature range of 400 - 650°C for an hour. Since the temperature is a crucial parameter in the formation of lithium pyroborates, the heating temperatures was raised in interval of 10°C for each heating process to get the desired products. It also observed that the

annealing (at $>400^{\circ}\text{C}$) treatment enhances the nanocrystalline nature with the formation of pure lithium pyroborates.

By the analysis of XRD, it showed that the mix of α and β polymorph of $\text{Li}_4\text{B}_2\text{O}_5$ was started to form at 630°C (overnight). Compared to Meng He et al whose formation of lithium pyroborates was obtained after several days of annealing process, the SCS method is way better and suitable method for the formation of lithium pyroborates (74). Additionally, the formation of lithium pyroborates is formed at temperature range of $600\text{--}650^{\circ}\text{C}$. Above or below that temperature, the compound dissociated into Li_3BO_3 and $\text{Li}_6\text{B}_4\text{O}_9$ (64,75). This statement is also confirmed in this study as decomposition of $\text{Li}_4\text{B}_2\text{O}_5$ into $\text{Li}_6\text{B}_4\text{O}_9$ was observed by further heating at higher temperature at 650°C (Figure 4.90).

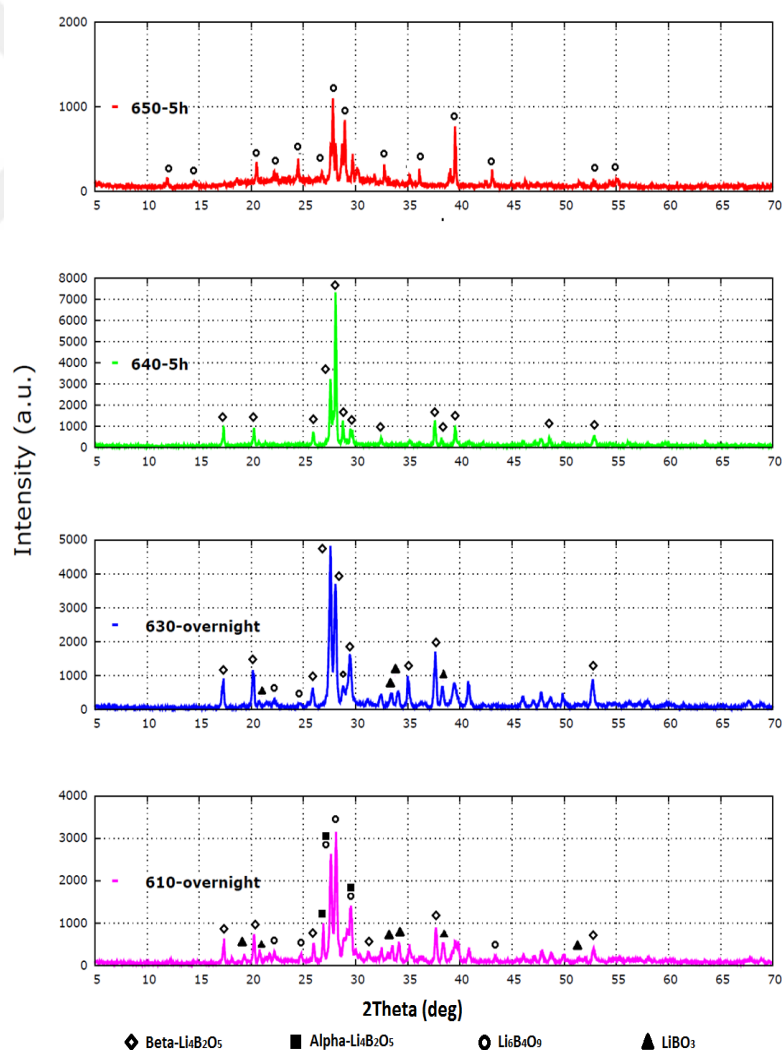


Figure 4.90. The XRD patterns of single phase lithium pyroborate with tartaric acid fuel

Single phase of lithium pyroborates was formed at 640°C for 5 hours as it has great compatibility with the ICDD Card No 18-0720 which belongs to β - $\text{Li}_4\text{B}_2\text{O}_5$ (Figure 4.91). The single phase powder product was also acquired in high crystallinity products and has high intensity of diffractogram, 8000 a.u.

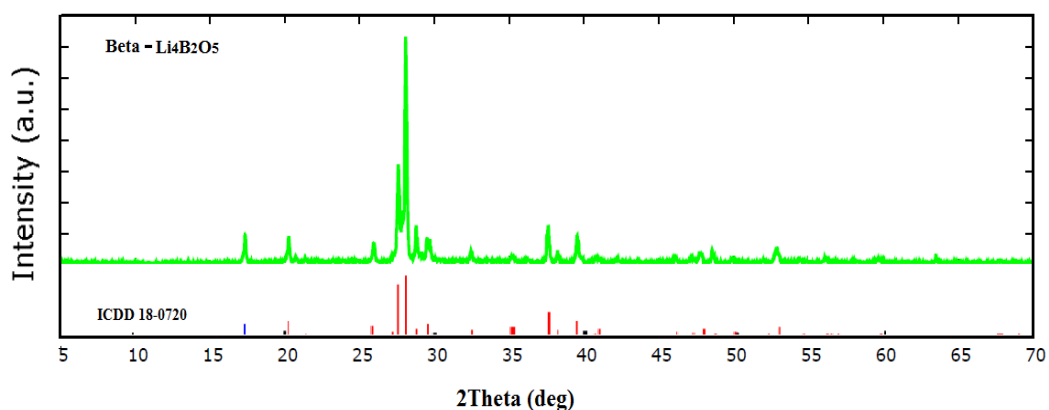


Figure 4.91. The XRD patterns of lithium pyroborate with tartaric acid fuel

4.3.2 The Fabrication of Lithium Pyroborates With Various Fuels via SCS

Based on the previous result, various fuels were applied in the fabrication of lithium pyroborates such as carbonylhydrazide, citric acid, glycine, HMDA, HMTA, tartaric acid and urea. The desired products were prepared by Solution Combustion Synthesis (SCS) method. The synthesis procedure and overall the reactions were written in Section 3.4. During the synthesis process, the results showed that the product varies in texture and color depending on the type of fuel used.



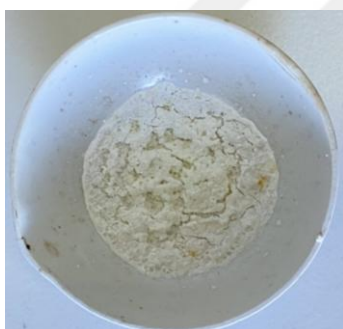
Lithium pyroborate synthesized with **HMDA fuel** showed the hardest texture among all the products obtained. It boasts a pure white color.



The powder product attained by glycine fuel is slightly firm in texture. Upon grinding the product become light brown hue in color and the quantity is relatively small compare to other products.



Volumous powder product with black color is obtained by using tartaric acid as fuel source. In comparison to the alternative fuels, tartaric acid yields the highest volume of as-synthesized product.



Similar to the other fuels, lithium pyroborates synthesized by using urea fuel produced hard products with white in color.

The products were ground by using mortar and pestle followed by annealing process at high temperature to get rid of organic impurities traces and to obtain higher crystallinity products. The choice of the fuels expected to affect the parameters such as combustion temperature, reaction kinetics and the final products characteristics. The synthesis by using TA as fuel also took place to confirm the repeatability of the perfect single phase products in the previous studies. According to the XRD analysis, only glycine and tartaric acid fuels formed the single-phase beta form of lithium pyroborates at 640°C whereas the other fuels produced mixed-phases of alpha-beta crystal structure of $\text{Li}_4\text{B}_2\text{O}_5$, $\text{Li}_6\text{B}_4\text{O}_9$, and Li_3BO_3 .

According to the XRD patterns shown in Figure 4.92, the alpha and beta forms of lithium pyroborates were found after the as-prepared with carbohydrazide fuel sample was heated overnight at 630°C. The beta form was dominating as it has great accordance with ICDD card No 18-0720. The existence of alpha-lithium pyroborates was confirmed by the d-line located at $2\theta = 25-27^\circ$. Furthermore, the decomposition of lithium pyroborates into $\text{Li}_6\text{B}_4\text{O}_9$ and Li_3BO_3 was observed at higher temperatures, 640°C.

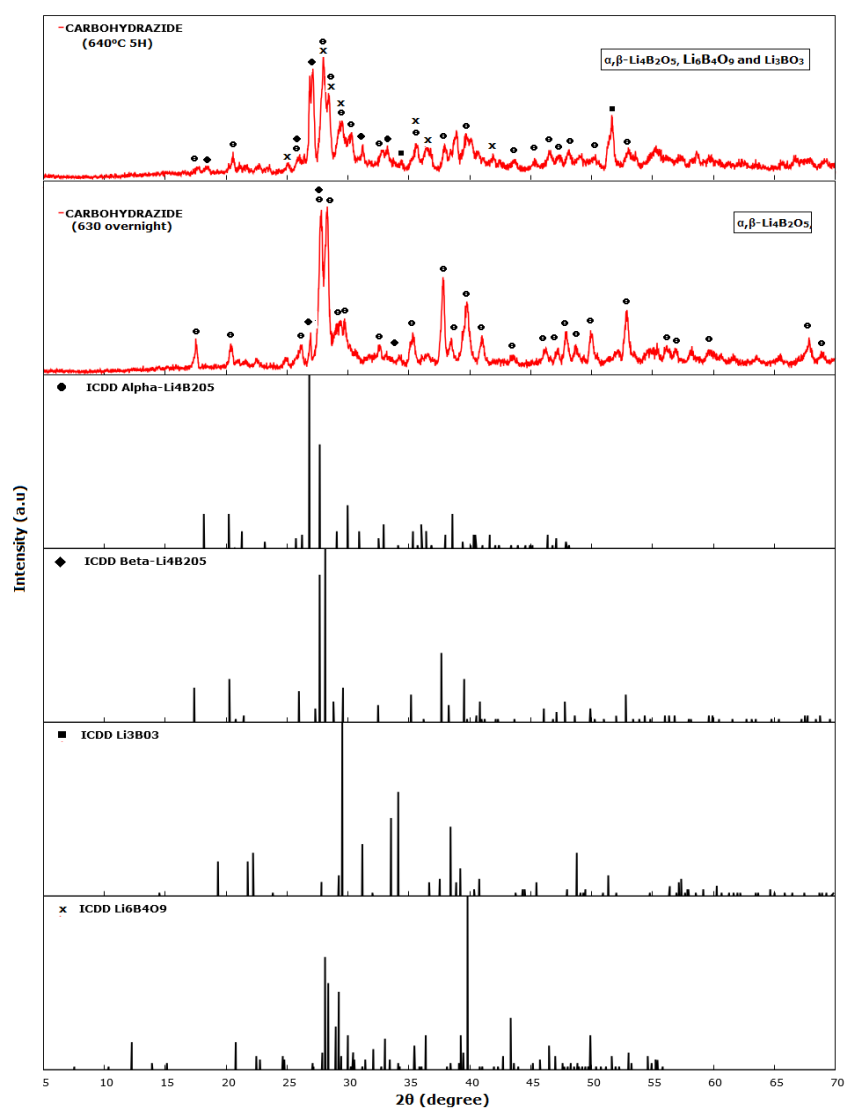


Figure 4.92. The XRD patterns of $\text{Li}_4\text{B}_2\text{O}_5$ with carbohydrazide fuel

Unlike carbohydrazide fuels, no decomposition of pyroborates into $\text{Li}_6\text{O}_4\text{B}_9$ was observed in the XRD analysis of lithium pyroborates with citric acid fuel. It revealed that the citric acid fuel produced Single phase lithium pyroborates after heated at 630°C for overnight (~12 hours) which then

transformed into multiphase of alpha and beta lithium pyroborates alongside with Li_3BO_3 (ICDD No: 18-0718) at higher temperature.

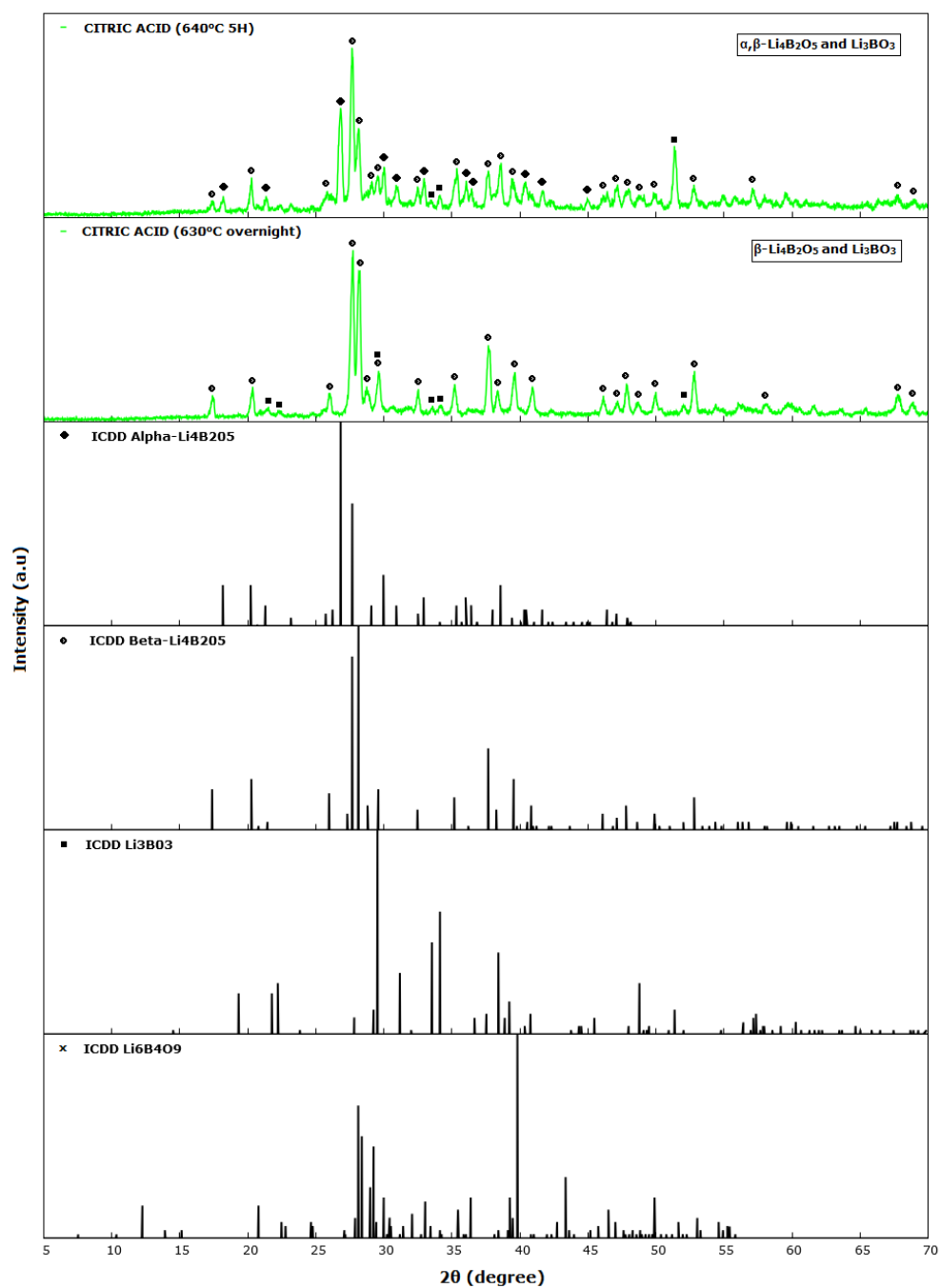


Figure 4.93. The XRD patterns of $\text{Li}_4\text{B}_2\text{O}_5$ with citric acid fuel

Single-phase Lithium pyroborates with glycine as fuels were successfully synthesized as all reflection peaks in the XRD patterns obtained at 640°C have great compatibility with beta-lithium pyroborates. The pattern was also believed to be in excellent crystal structure since it has high intensity. Interestingly, the lower temperature formed of lithium pyroborates was dominating at 630°C which then transformed into a pure compound at higher temperature form after further heating. This shows the temperature sensitivity of our desired products.

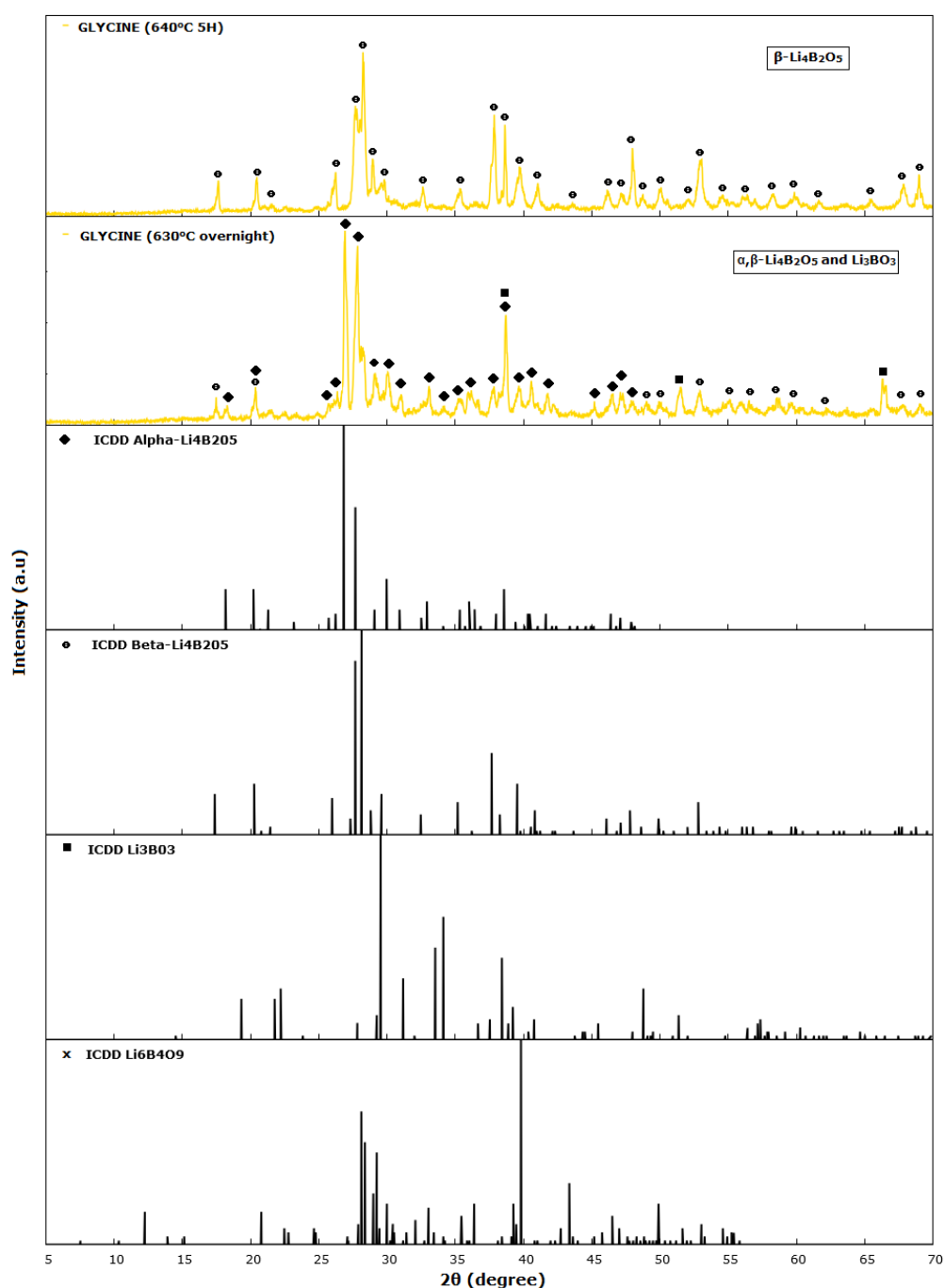


Figure 4.94. The XRD patterns of $\text{Li}_4\text{B}_2\text{O}_5$ with glycine fuel

The experiments were also carried out by using HMDA fuels. The XRD results gave the multiphase products of α - β $\text{Li}_4\text{B}_2\text{O}_5$, $\text{Li}_6\text{B}_4\text{O}_9$, and Li_3BO_3 were obtained where the primary reflection line belongs to beta-lithium pyroborates.

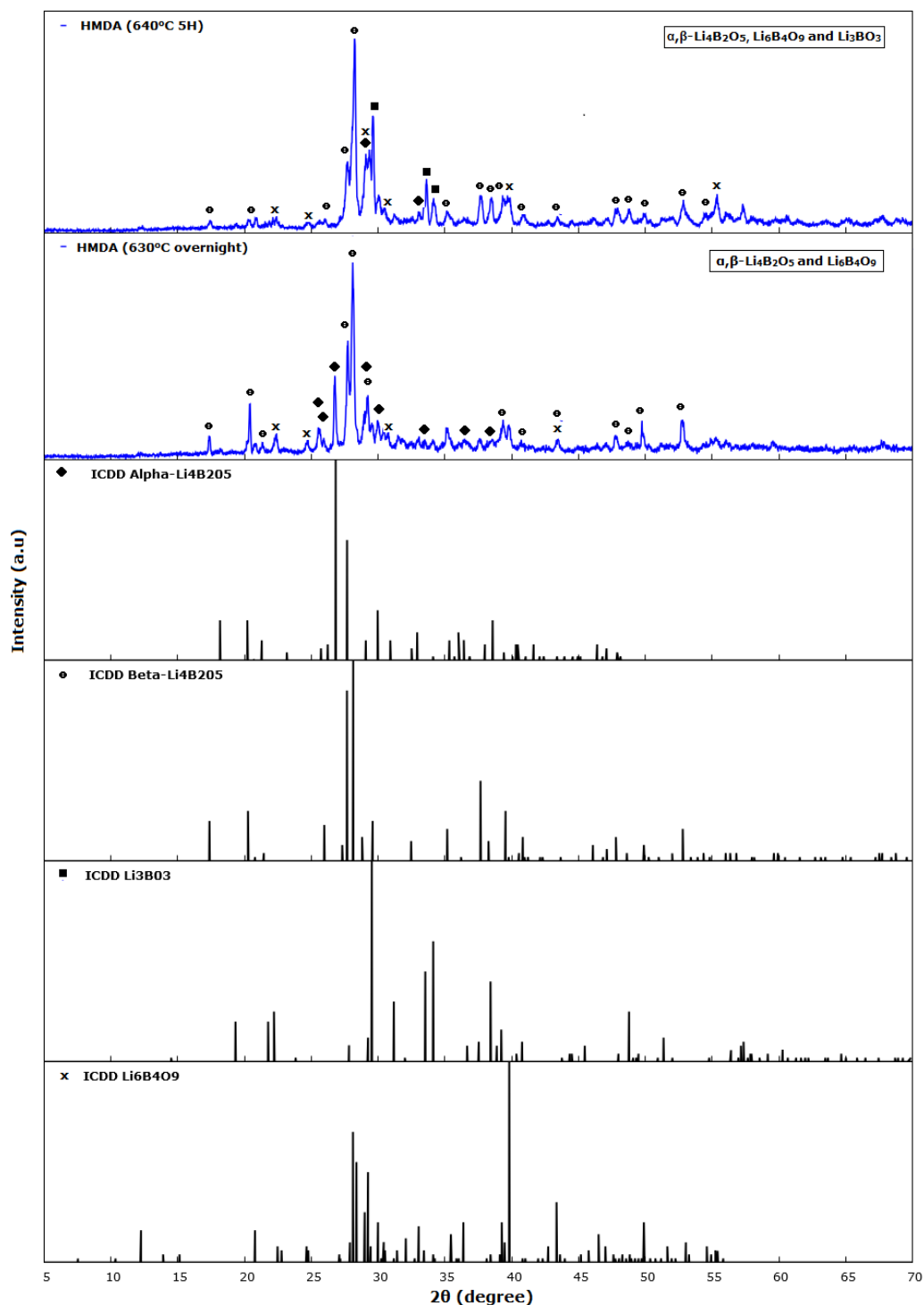


Figure 4.95. The XRD patterns of $\text{Li}_4\text{B}_2\text{O}_5$ with HMDA fuel

The mixed phase of the beta form of lithium pyroborates with $\text{Li}_6\text{B}_4\text{O}_9$ was observed in the patterns of lithium pyroborates synthesized with HMTA fuel. It was much closed to the formation of pure product but unfortunately, several d-lines of $\text{Li}_6\text{B}_4\text{O}_9$ were detected.

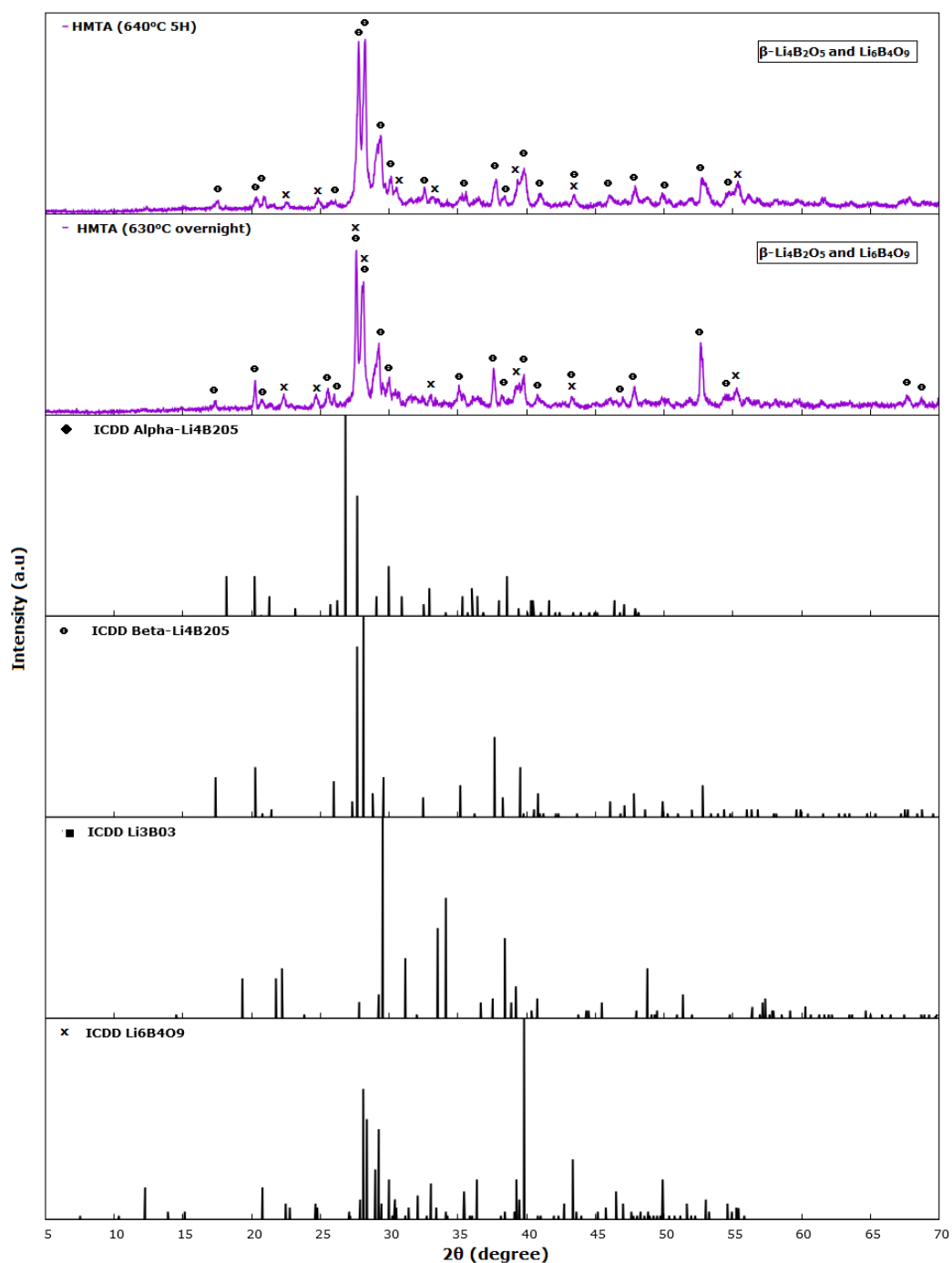


Figure 4.96. The XRD patterns of $\text{Li}_4\text{B}_2\text{O}_5$ with HMTA fuel

As expected, the lithium pyroborates with tartaric fuels gave single-phase lithium pyroborates at 640°C. It showed that the annealing process enhance the formation of pure lithium pyroborate as several impurities compounds such as $\text{Li}_6\text{B}_4\text{O}_9$ and Li_3BO_3 were disappeared at higher annealing temperature.

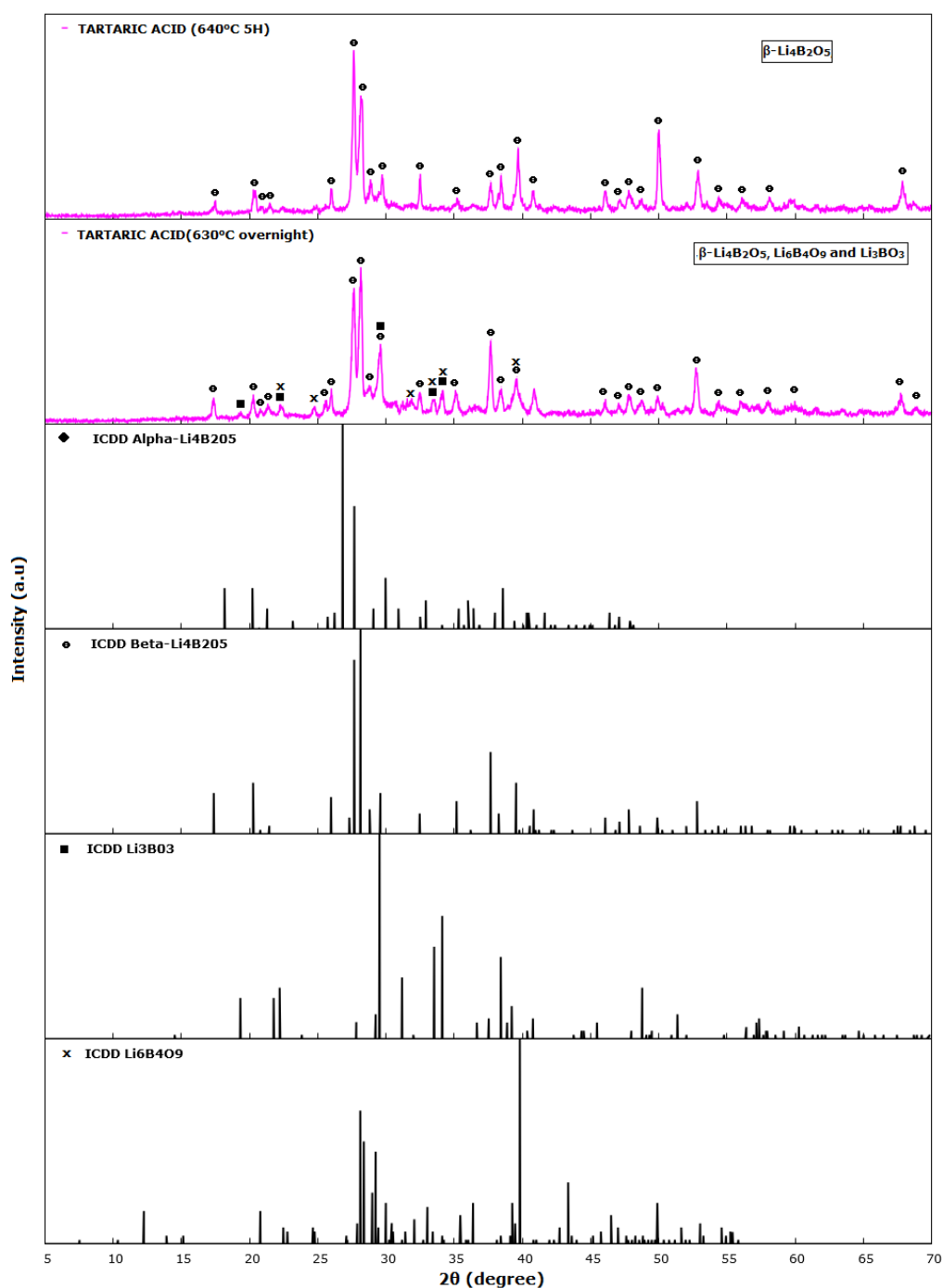


Figure 4.97. The XRD patterns of $\text{Li}_4\text{B}_2\text{O}_5$ with tartaric acid fuel

Although few d-lines of beta lithium pyroborates were disclosed at 640°C, the peaks that belong to $\text{Li}_6\text{B}_4\text{O}_9$ were dominating and observed together with Li_3BO_3 . Examining all these XRD analysis results, the importance of fuels used and applied temperature in the fabrication of single-phase lithium pyroborates was approved. The type of fuels and temperature played a crucial role in the formation and decomposition of the desired compound.

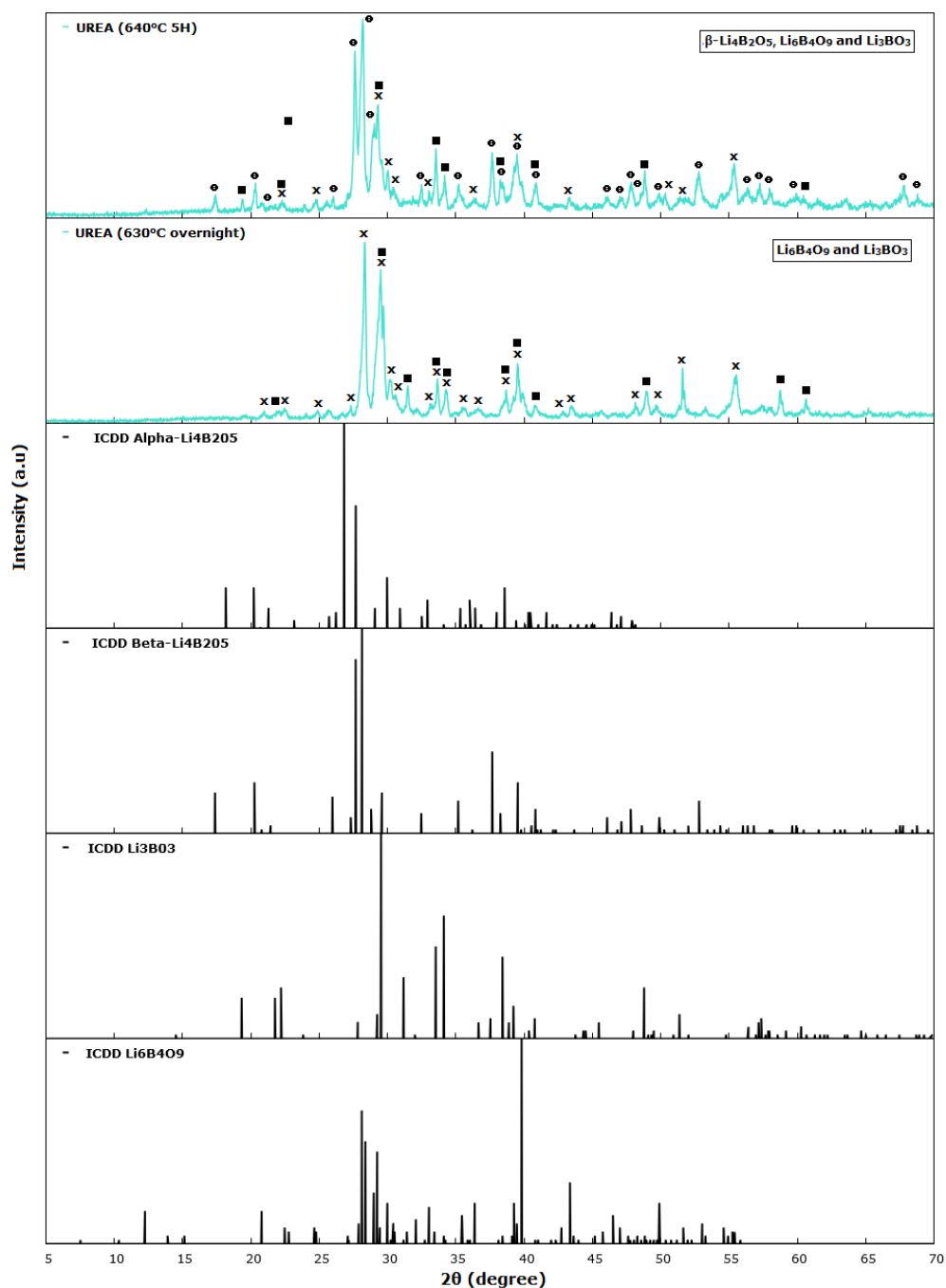


Figure 4.98. The XRD patterns of $\text{Li}_4\text{B}_2\text{O}_5$ with urea fuel

The crystallite sizes of synthesized single-phase lithium pyroborates using glycine and tartaric acid fuels were calculated using Debye-Scherrer's equations. The obtained crystallite sizes for lithium pyroborates were 28.14 nm and 27.35 nm, respectively, indicating the formation of nanosized lithium pyroborates. To ensure the precision of our results, our investigation exclusively targeted the calculation of crystallite size within single-phase lithium pyroborates, deliberately disregarding any potential influences stemming from impurities. These findings illuminate the critical role of purity in delineating crystallite size, offering valuable perspectives for the synthesis and utilization of lithium pyroborates across diverse domains.

Additionally, a shift in the XRD peak of glycine and tartaric acid was observed, with glycine exhibiting a higher wavelength compared to tartaric acid, as shown in Figure 4.99.

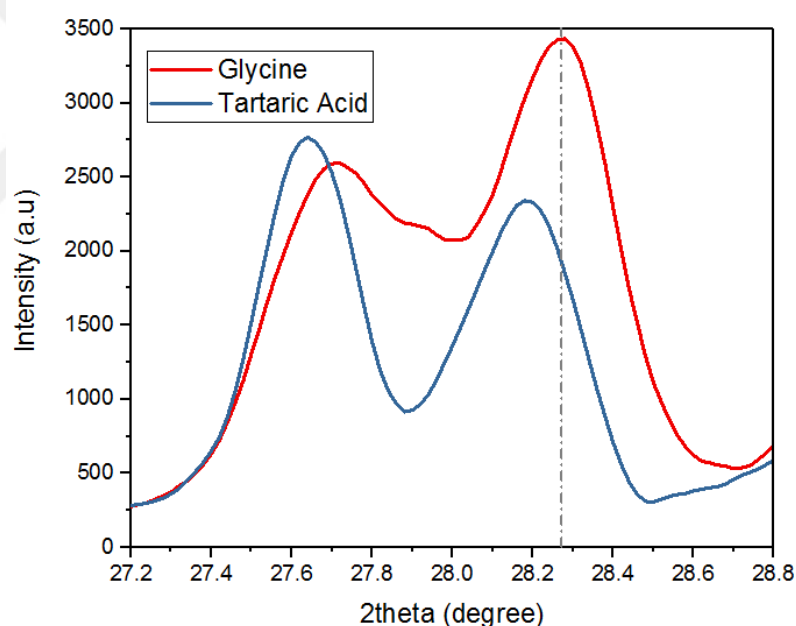


Figure 4.99. The XRD shift of synthesized single phase lithium pyroborate

Peak shifting in X-ray diffraction (XRD) analysis occurs due to a combination of factors influencing the crystal lattice and scattering behavior of materials, variations in particle size, chemical composition, temperature, and pressure can all influence the XRD pattern by altering the arrangement of atoms within the crystal lattice. Presence of amorphous phases alongside crystalline ones also contributes to peak shifts due to differences in scattering behavior between the two phases. Furthermore, instrumental factors like broadening and calibration

errors can introduce additional complexities. Recognizing and understanding these factors is crucial for accurately interpreting XRD patterns and determined the effect of different parameters on the structural properties of synthesized products.

Followed by the XRD results, the FT-IR analyses were also carried out to ascertain the bond vibration of the synthesized products. These analyses revealed the presence of characteristic peaks of corresponding to lithium pyroborates. The peaks found at 1440 cm^{-1} is attributed to the BO_3 asymmetric stretching vibrations, whereas the peaks at 1175 cm^{-1} should originate from the BO_3 symmetric stretch, and also, the small peak observed at 1325 cm^{-1} are attributed to B-O-H in-plane bending modes and the one at 1048 and 948 cm^{-1} is attributed to the asymmetric stretching modes of tetrahedral boron. The peak at 866 cm^{-1} is symmetric stretching vibrations of B-O bonds in the BO_3 unit. The peaks nearby 732 , 689 and 633 cm^{-1} assigned to out-of-plane bending modes of the BO_3 groups, and the bands at 539 cm^{-1} belong to bending vibration of B-O bonds in the triangular BO_3 units. Furthermore, the bands observed at $\sim 3000\text{ cm}^{-1}$ might be attributed to the OH groups stretching vibrations of the water molecules.

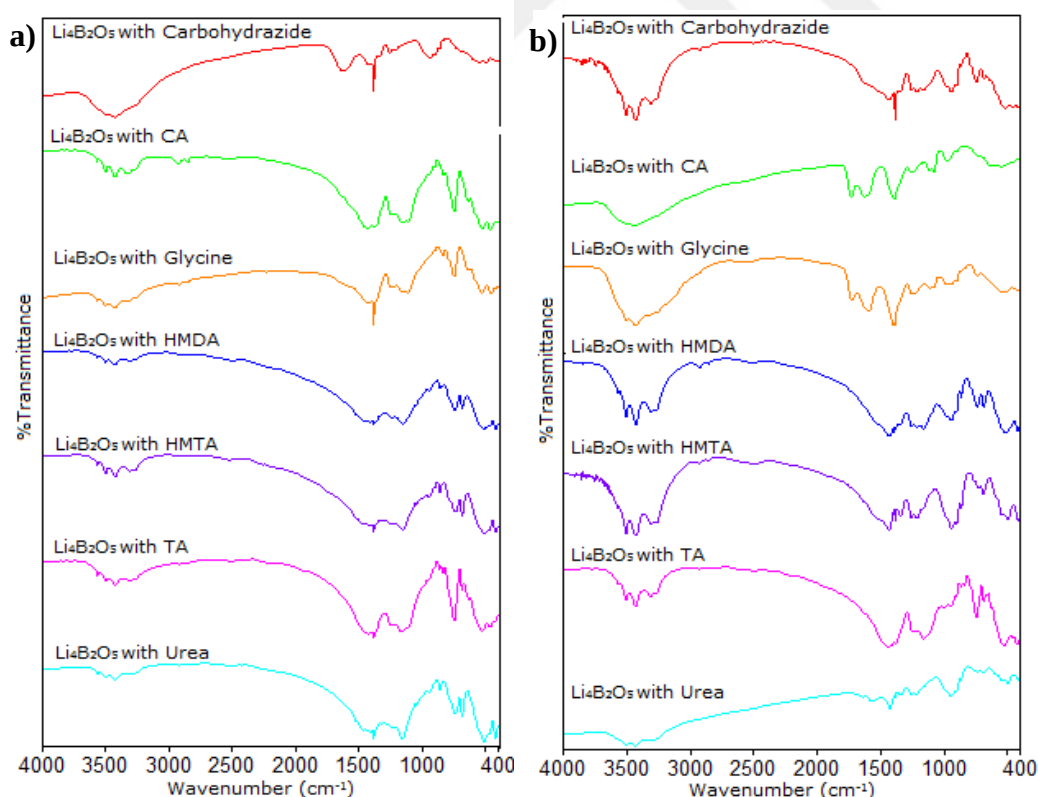


Figure 4.100. The FT-IR spectra of $\text{Li}_4\text{B}_2\text{O}_5$ at a) 630°C and b) 640°C

The DRS Studies on the synthesized single phase lithium pyroborates has also carried out and the optical band gap energy of the compounds were also determined.

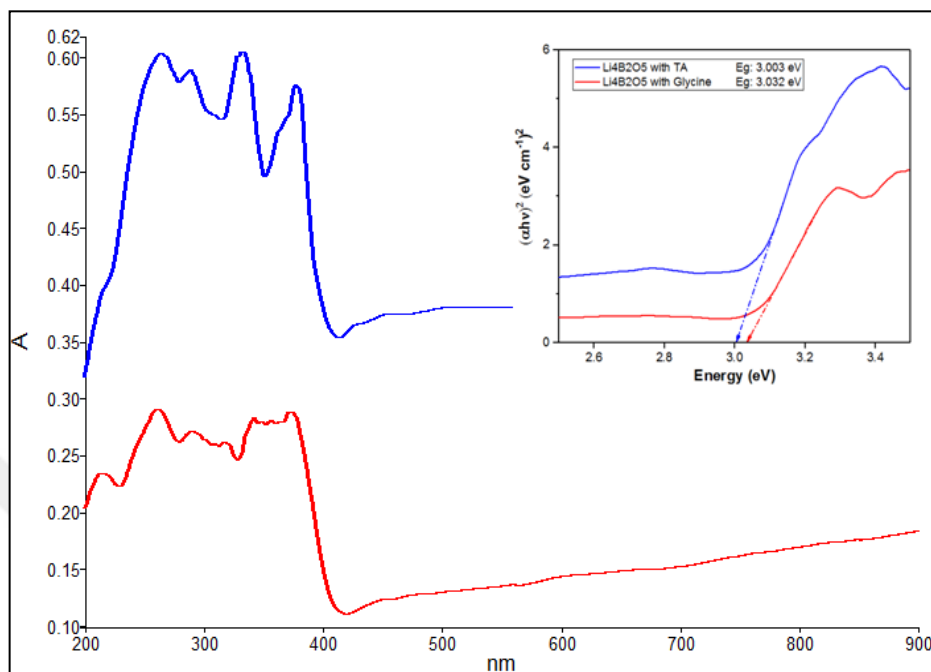


Figure 4.101. The UV-Vis spectra of single phase $\text{Li}_4\text{B}_2\text{O}_5$

Presented in Figure 4.101 the spectra are observed in the UV region, < 400 nm and there are no absorption observed at the higher wavelength. The optical and gap energy are in the range of 3.00-3.05 eV. The product prepared with glycine has higher band gap compared to the one synthesized by tartaric acid. This again proves the effect of fuel on the optical properties of the materials.

To determine the morphology of the synthesized single phase lithium pyroborates, FE-SEM analysis was carried out with three different magnifications. It revealed that, the change in fuel affecting the morphology of the products, presented in Figure 4.102 and 4.103.

The FESEM image of lithium pyroborates synthesized with glycine reveals a smooth, continuous surface with interconnected structures. Although the crystals observed to exhibit a rhombus-like shape, their interconnected nature and lack of distinct porosity make the individual shapes difficult to discern clearly.

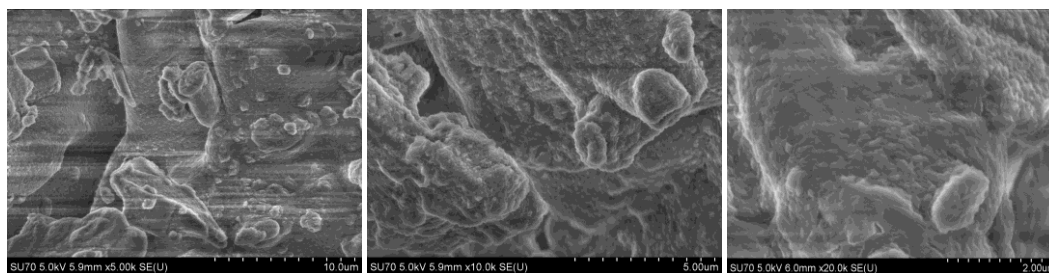


Figure 4.102. The FESEM images of $\text{Li}_4\text{B}_2\text{O}_5$ with glycine fuel

The synthesis of lithium pyroborates using tartaric acid resulted in a distinctive morphology compared to the one synthesized with glycine fuel. Specifically, the crystals formed were rhombus-shaped characterized by their well-defined sharp edges. This indicates a high degree of structural order and purity in the material.

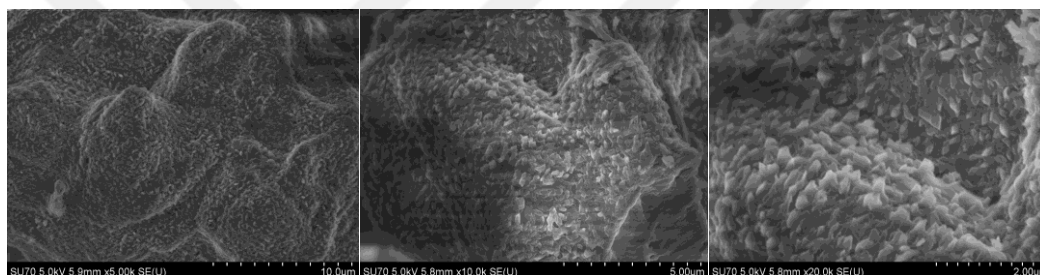


Figure 4.103. The FESEM images of $\text{Li}_4\text{B}_2\text{O}_5$ with tartaric acid fuel

4.3.3 The Synthesis and Characterization Studies Lithium Pyroborates with excess of H_3BO_3

The formation of alpha and beta forms of lithium pyroborates known to be occurred at 618°C and 630°C , respectively. For this reason, lower annealing temperatures were paired with varying concentrations of boric acid (5%, 10%, and 15%) in order to assess their combined effect on reducing impurities and forming of single phase alpha lithium pyroborates. By systematically testing different conditions, the study aimed to determine the most effective combination for the formation of single phase alpha lithium pyroborates.

The preparation process was carried out by SCS method with tartaric acid fuel. In this section, tartaric acid was chosen as fuel due to its effectiveness in synthesizing lithium pyroborates, as discussed earlier. This choice reflects its superior performance compared to other fuels for this specific purpose. Utilizing

tartaric acid ensured optimized conditions for the synthesis of lithium pyroborates, highlighting its suitability for the desired outcome.

4.3.3.1 The XRD Studies of Lithium Pyroborates With H_3BO_3 Excess

Presented in Figure 4.104, the synthesis yielded single-phase beta lithium pyroborates exclusively at 618°C, while at lower and higher temperatures, multiphase products were obtained. Furthermore, the initial setback occurred when the excess of boric acid was found to be unnecessary, leading to the failure to achieve a single phase of alpha-lithium pyroborates.

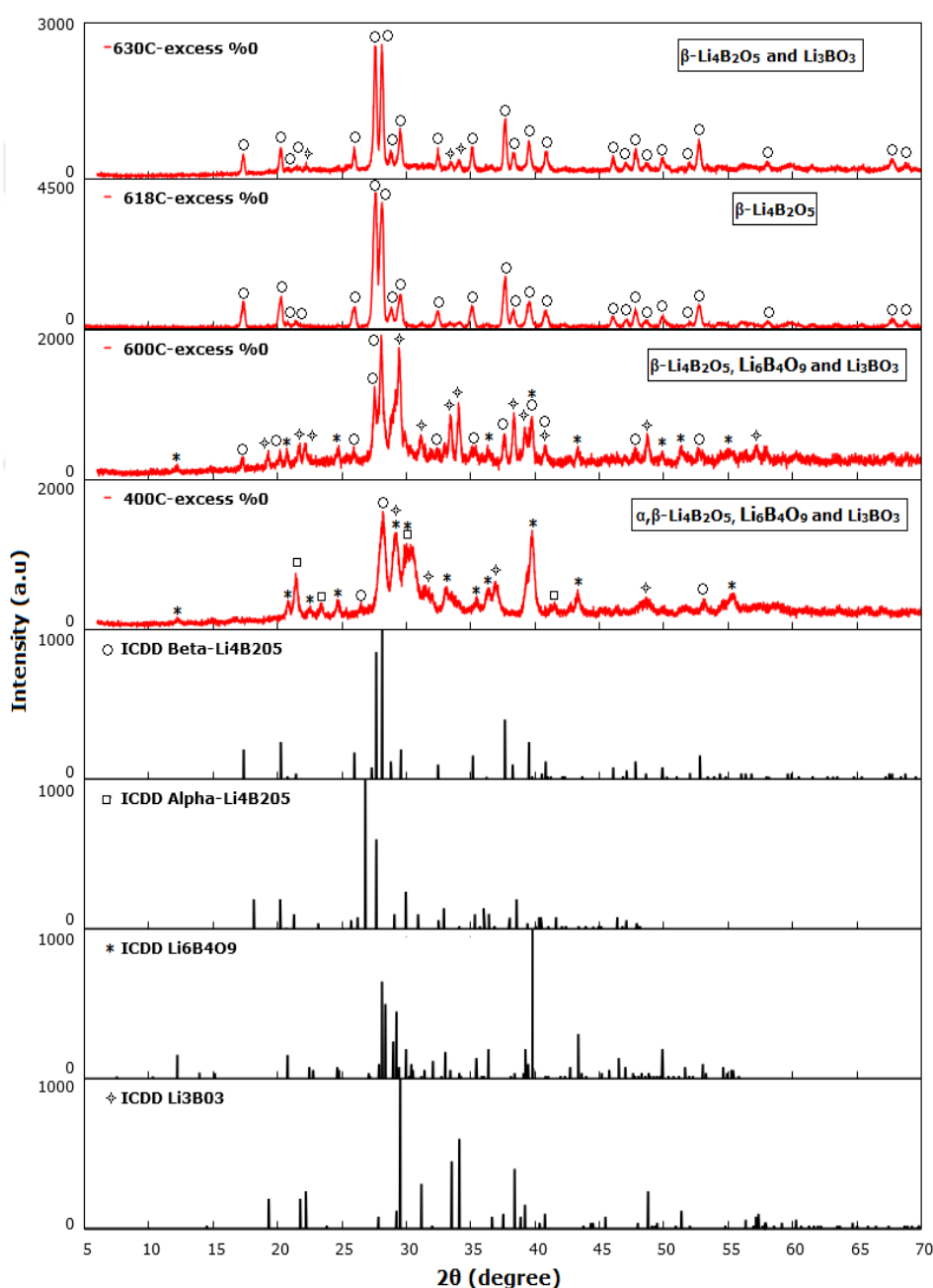


Figure 4.104. The XRD patterns of $\text{Li}_4\text{B}_2\text{O}_5$ with no excess of boric acid

The introduction of 5% excess of boric acid resulted in the formation of multiphase products. Initial observation revealed various diffraction lines characteristics of alpha lithium pyroborates at lower temperature, 400°C which later dissociated into $\text{Li}_6\text{B}_4\text{O}_9$ at elevated temperature. Notably, the diffraction lines of $\text{Li}_6\text{B}_4\text{O}_9$ became predominant at 630°C.

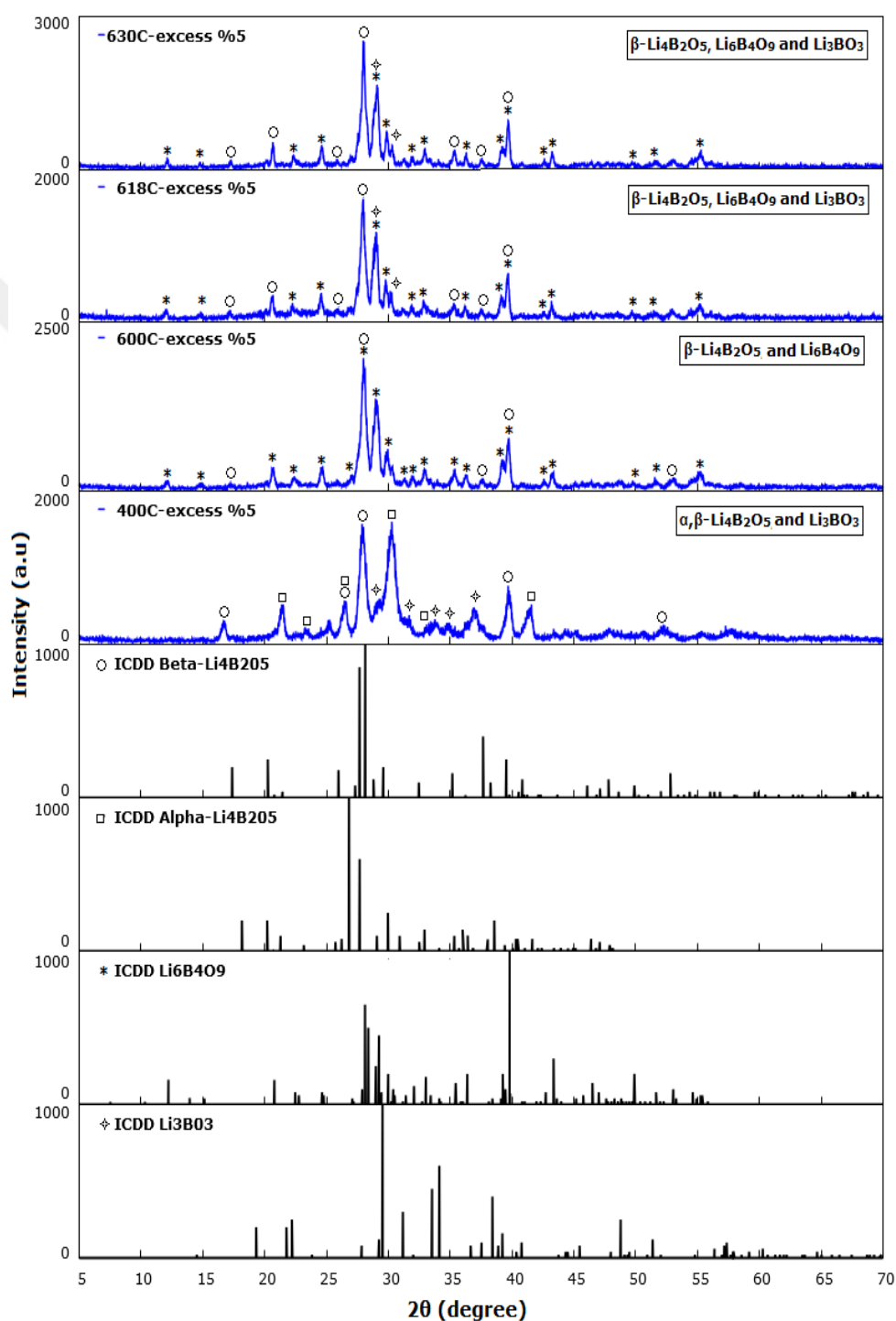


Figure 4.105. The XRD patterns of $\text{Li}_4\text{B}_2\text{O}_5$ with 5% excess of boric acid

With 10% excess of boric acid, beta phase lithium pyroborates were predominantly observed at 630°C alongside with $\text{Li}_6\text{B}_4\text{O}_9$ and Li_3BO_3 . The formation of alpha lithium pyroborates was initially detected during the first annealing process at 400°C but diminished as the temperature increased. Additionally, fewer reflection lines of impurities were observed with the higher excess of boric acid (Figure 4.106).

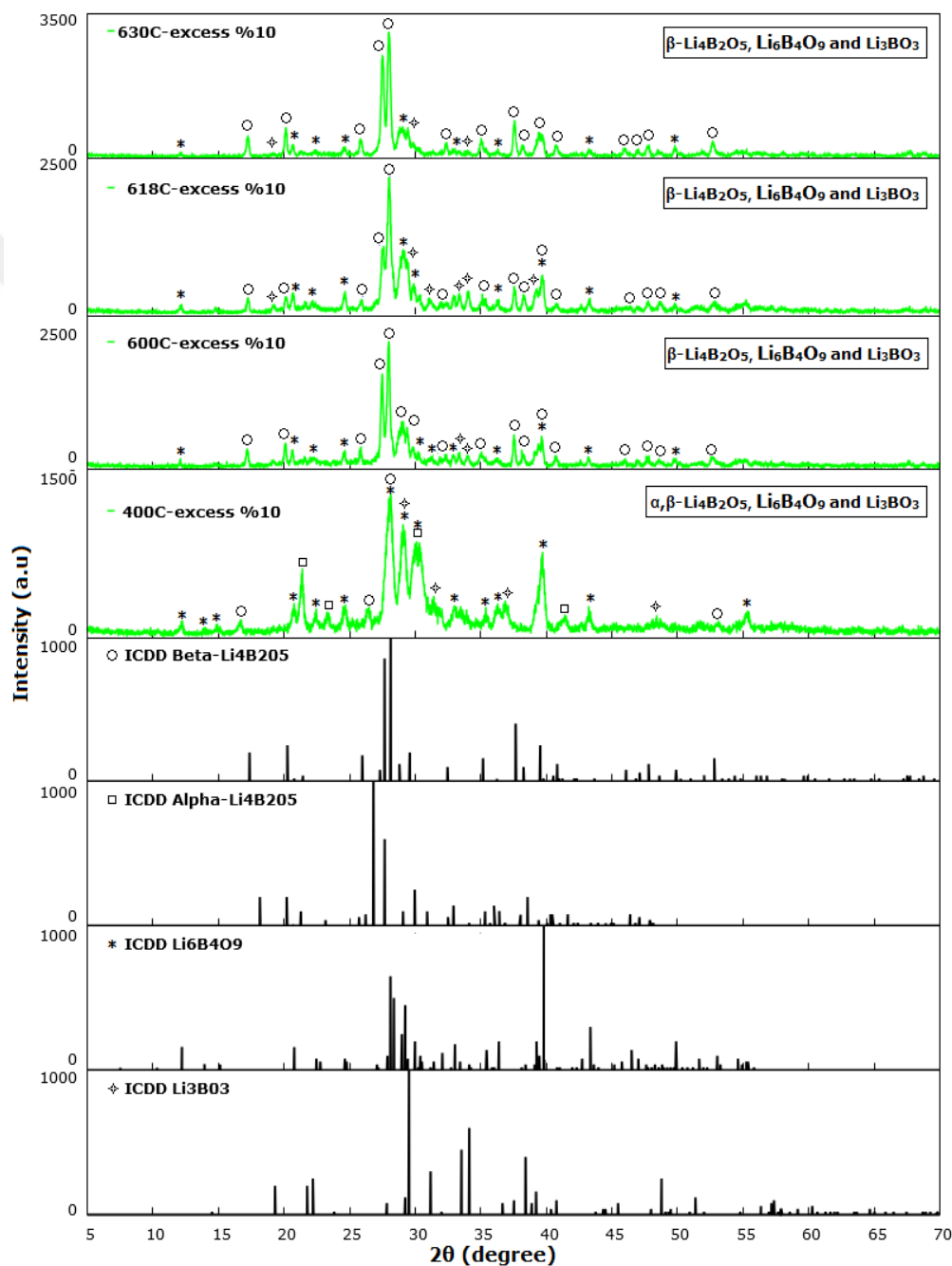


Figure 4.106. The XRD patterns of $\text{Li}_4\text{B}_2\text{O}_5$ with 10% excess of boric acid

Increasing the amount of boric acid leading to the formation of multiphase of products at all heating temperature. At 400°C, the d-lines of alpha lithium pyroborates were observed but its diminished instantly at higher temperature. At 630°C, the multiphase of beta lithium pyroborates and $\text{Li}_6\text{B}_4\text{O}_9$ was observed. several d-line with high compatibility with ICDD card belongs to $\text{Li}_6\text{B}_4\text{O}_9$ were found and the patterns are dominated by the reflection lines of beta lithium pyroborates.

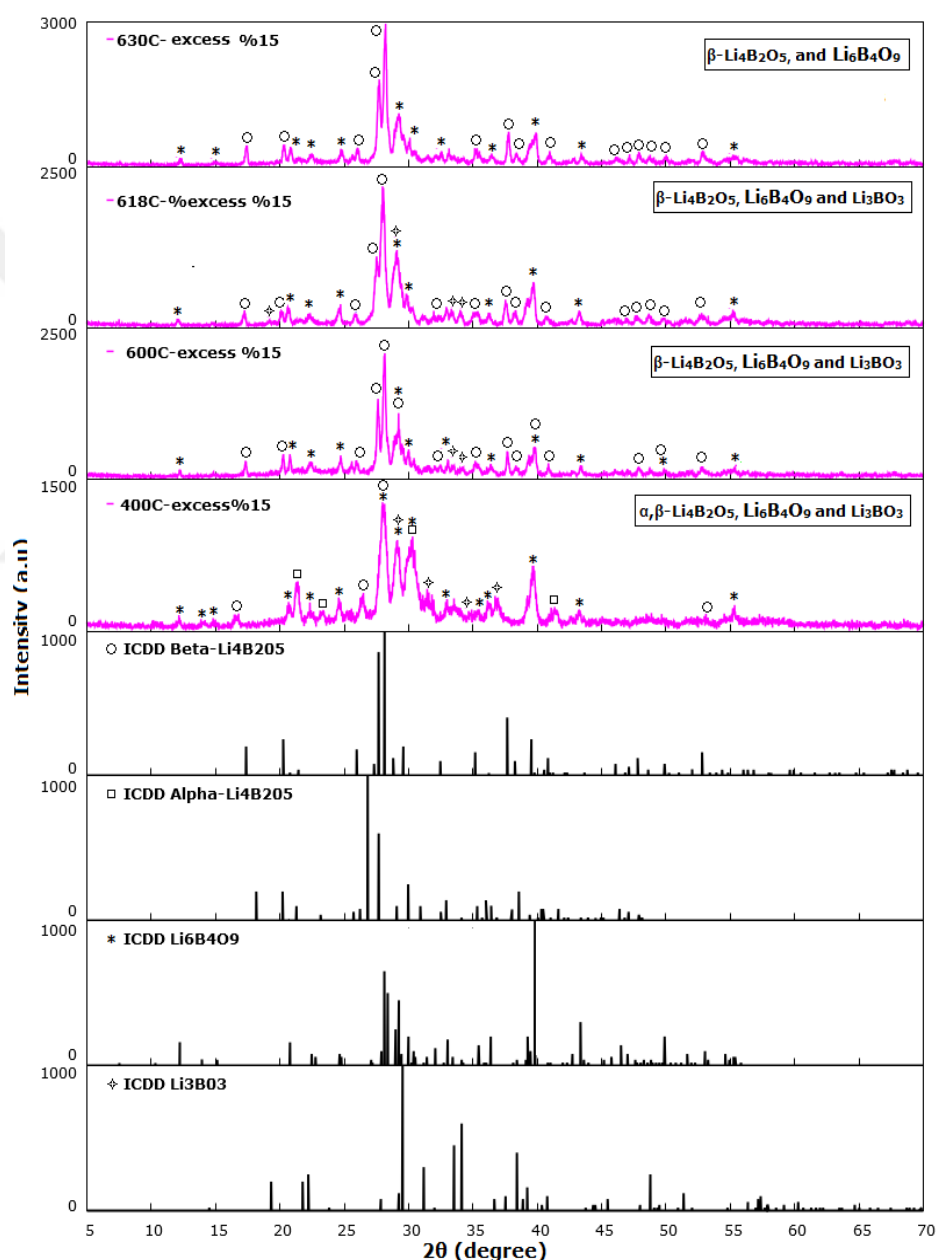


Figure 4.107. The XRD patterns of $\text{Li}_4\text{B}_2\text{O}_5$ with 15% excess of boric acid

The observation of all these results underscores the importance of precise control over synthesis parameters to achieve desired material properties and phase purity. This outcome underscores the importance of carefully considering the stoichiometry and composition of reactants in the synthesis process. Additionally, the temperature specificity highlights the critical role of thermal conditions in dictating the crystalline phase composition of the final products.

4.3.3.2 The FT-IR Analysis of Lithium Pyroborates with H_3BO_3 Excess

The FT-IR analysis of lithium pyroborates nanocompounds were also done to determined their chemical bond. The vibration bands of lithium pyroborates were examined by FT-IR spectrometer ranging $4000\text{--}400\text{ cm}^{-1}$. The spectra of $\text{Li}_4\text{B}_2\text{O}_5$ with different excess of H_3BO_3 at different temperature are shown in the Figure 4.108. It is observed that the characteristic bands of lithium borates were observed in the fingerprint region and the FT-IR spectra of each temperature shows similar infrared active bands.

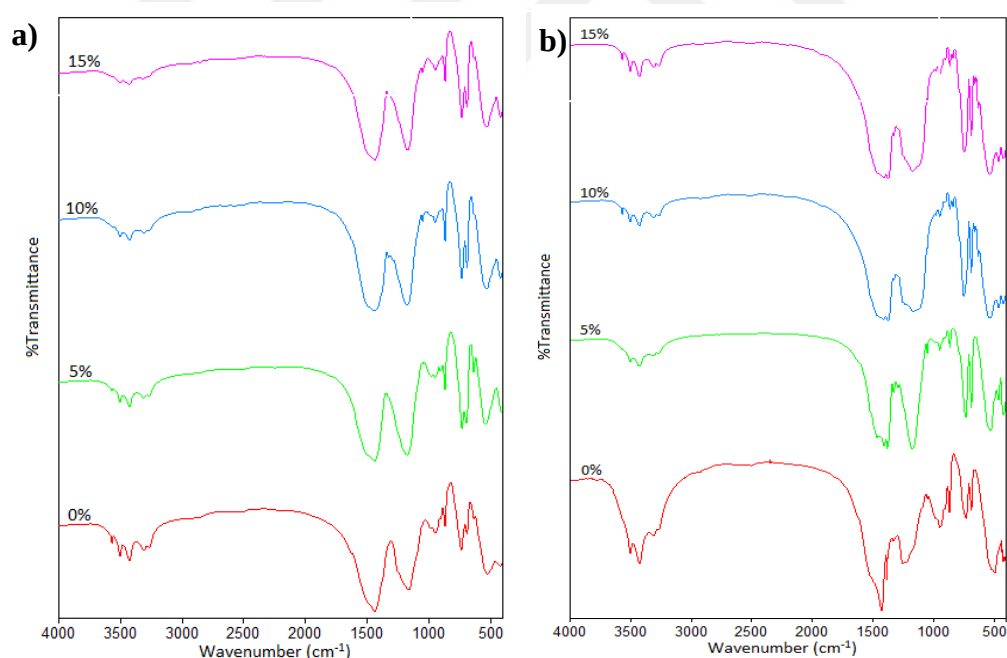


Figure 4.108. The FT-IR spectra of $\text{Li}_4\text{B}_2\text{O}_5$ with H_3BO_3 excess at a) 400°C and b) 600°C

According to the IR spectra, the higher excess of boric acid give the smaller peaks at $>3000\text{ cm}^{-1}$ which might attributed to OH groups stretching vibrations of the water molecules and the impurities bands. The peak found at

1440 cm^{-1} attributed to the BO_3 asymmetric stretching vibrations. The small peaks observed at around 1375 and 1329 cm^{-1} should originate from the organic compound (impurities) whereas the ones noticed in the range of 1050-1172 cm^{-1} ascribed to the BO_3 symmetric stretch. The symmetric stretching vibrations of B-O bonds in the BO_3 unit are detected at 950-866 cm^{-1} . Furthermore, the peaks nearby 732-748 and 688-689 cm^{-1} assigned to out-of-plane bending modes of the BO_3 groups, and the bands at 527-535 cm^{-1} and 418-461 cm^{-1} belong to bending vibration of B-O bonds in the triangular BO_3 units.

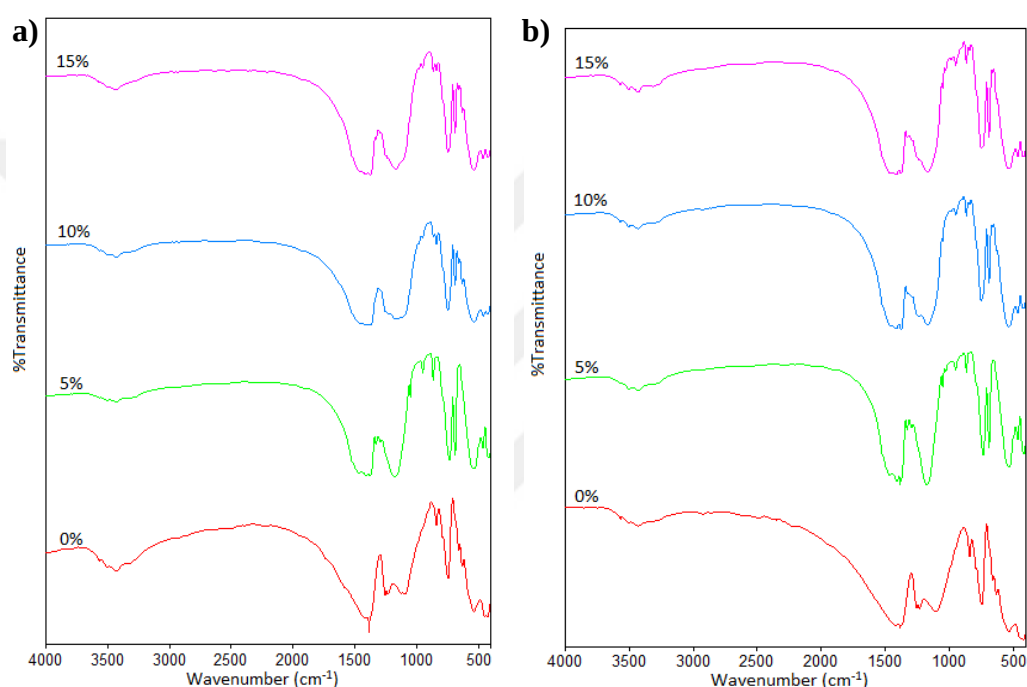


Figure 4.109. The FT-IR spectra of $\text{Li}_4\text{B}_2\text{O}_5$ with H_3BO_3 excess at a) 618°C and b) 630°C

Presented in Figure 4.109, the FT-IR spectra of lithium magnesium borates gave the prominent absorption in 1600-400 cm^{-1} region. At 618°C, the characteristic bands of pure lithium pyroborates were observed. The broad peak found at 1408 cm^{-1} is attributed to the BO_3 asymmetric stretching vibrations, whereas the peaks at 1376 and 830 cm^{-1} should originate from the organic compound that used during the preparation of the product. The broad peak observed at 1171 cm^{-1} assigned to the BO_3 symmetric stretch. The small peak observed at 1325 cm^{-1} and 948 cm^{-1} are attributed to B-O-H in-plane bending and asymmetric stretching modes of tetrahedral boron, respectively. The peaks nearby 745, 688 and 631 cm^{-1} assigned to out-of-plane bending modes of the BO_3

groups, and the bands at 536 cm^{-1} belong to bending vibration of B-O bonds in the triangular BO_3 units.

Examining all the peaks in the FT-IR spectra of lithium pyroborates, it's evident that the sample with zero excess of boric acid exhibited peaks consistent with lithium pyroborates which similar to the FT-IR spectra presented by Chen Zou et al. in 2018 (76).

4.3.4 The Synthesis and Characterization of Mixed Metal Borate

Metal mixed Borates of lithium and magnesium such as LiMgBO_3 and $\text{Li}_2\text{MgB}_2\text{O}_5$ were also synthesized via solution combustion synthesis. There are several fuels applied during this preparation such as glycine, tartaric acid and urea. The substitution of lithium by magnesium is a feasible process due to their similar physicochemical properties and ionic radii, Mg: 0.72 and Li: 0.76. Therefore, the studies on $\text{Li}_2\text{O-MgO-B}_2\text{O}_3$ system were employed to obtain the novel mixed metal borates of lithium and magnesium.

4.3.4.1 Lithium Magnesium Borate (LiMgBO_3)

Lithium magnesium borate, LiMgBO_3 was prepared stoichiometrically by using lithium nitrate, magnesium borate, boric acid and tartaric acid as starting materials. The synthesis was carried out as mentioned in section 3.4b. During the synthesis process it was observed that the precursor gel was yellow and produced dark brown powder products after heated at 400°C for 5 minutes (Picture 4.5). The annealing process was conducted at temperature ranging from $400\text{-}650^\circ\text{C}$ effectively to eliminate the organic impurities and enhance the crystallinity of powder products.



Picture 4.5. The precursor gel and as-synthesized lithium magnesium borate

The crystalline phase of prepared lithium magnesium pyroborstes was characterized by XRD diffractometer in the range of $2\theta=5-70^\circ$. Single-phase lithium magnesium borates were attained at 400-650°C in a great agreement with ICDD No: 79-1996 and were found in high crystallinity (Figure 4.110). Based on this result, the SCS is the best method in the formation of LiMgBO_3 . The similarity with the standart ICDD patterns indicated the formation of pure polycrystalline LiMgBO_3 powder at relatively low temperature, 400°C.

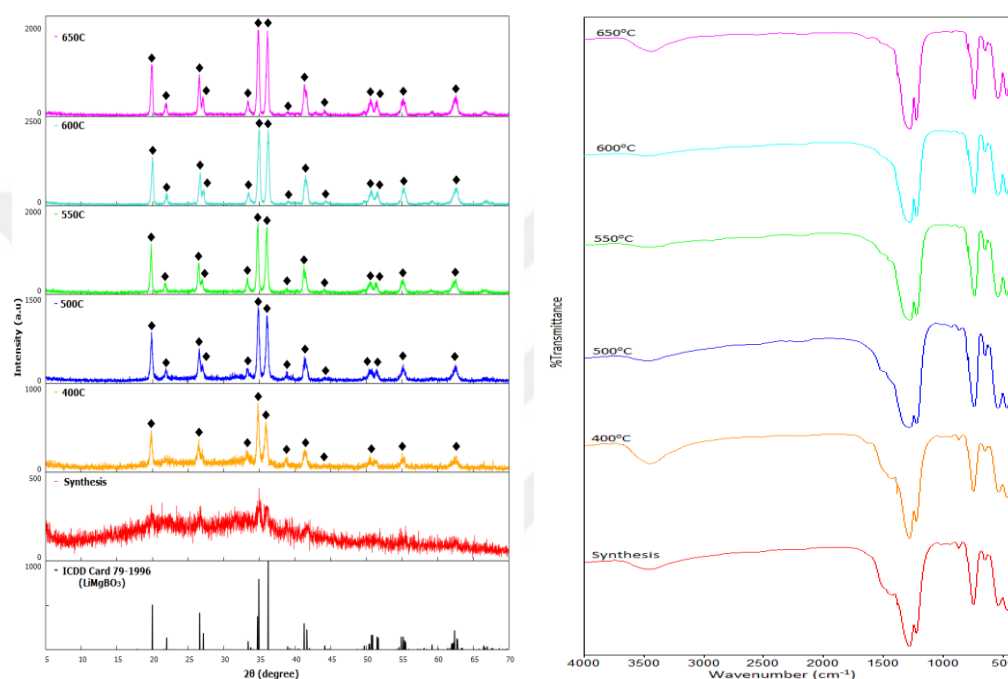


Figure 4.110. The XRD patterns and FT-IR spectra of lithium magnesium borate obtained at various temperatures

The pattern also shows reflection lines consistent with those reported by Wu et al. and N.S. Bajaj et al., corresponding to the monoclinic phase of LiMgBO_3 with the space group $P2_1/c$ (71,153). Further heating treatment was carried out to enhance the nanocrystalline nature of the products. The formation of sharp peaks indicates the good crystallinity of the synthesized powder products. Consequently, the highest degree of crystallinity was achieved at 600°C.

To determine the chemical bond interaction of lithium magnesium borates, the FT-IR analysis was carried out. The infrared spectra of the fabricated samples gave the the strong bands detected at 1100 cm^{-1} contributed to the stretching mode of B–O in the triangular $[\text{BO}_3]^{3-}$ groups, while the sharp bands at around $700\text{--}900\text{ cm}^{-1}$ is assigned to the B–O bending (out of plane), which verify the

presence of the $[\text{BO}_3]^{3-}$ groups in synthesized powder products. The absence of the band in the region of $1500\text{--}2000\text{ cm}^{-1}$ validated the complete removal of organic matter and residual nitrates. The band found at 3500 cm^{-1} attributed to the O–H stretching mode water molecules (Figure 4.110)

4.3.4.2 Lithium Magnesium Pyroborate ($\text{Li}_2\text{MgB}_2\text{O}_5$)

The preparation of lithium magnesium pyroborates ($\text{Li}_2\text{MgB}_2\text{O}_5$) has also been made via solution combustion synthesis using tartaric acid as fuel. The detailed steps on the synthesis have explained in the synthesis method part of this studies mentioned in section 3.4c. The as-synthesized product was annealed at $400\text{--}700^\circ\text{C}$ to enhance the structural properties of the nanosized compound.

Figure 4.111 showed the XRD patterns and FT-IR spectra of the $\text{Li}_2\text{MgB}_2\text{O}_5$ sample. The XRD patterns of $\text{Li}_2\text{MgB}_2\text{O}_5$ displayed along with the patterns of $\text{Li}_2\text{MgB}_2\text{O}_5$ (ICDD No: 17-0808), LiMgBO_3 (ICDD No: 79-1996), and LiBO_2 (ICDD No: 76-2212). The XRD pattern depicts the pattern belongs to the monoclinic phase of LiMgBO_3 with LiBO_2 which very consistent with the standard ICDD pattern of the related compound. Reportedly, the $\text{Li}_2\text{MgB}_2\text{O}_5$ phase exists within a limited temperature range up to 650° . However, due to the stable formation of the LiMgBO_3 compound, the detection of $\text{Li}_2\text{MgB}_2\text{O}_5$ was elusive. The characterization of the $\text{Li}_{2.45}\text{Mg}_{0.3}\text{BO}_{3.025}$ and $\text{Li}_{3.366}\text{Mg}_{0.317}\text{B}_2\text{O}_5$ were successfully done by Wu et.al and Zhou et.al, respectively. However, they failed to obtain $\text{Li}_2\text{MgB}_2\text{O}_5$ crystal structure (76,153)

According to the FT-IR spectra, the broad IR peaks in the regions of $3500\text{--}2700\text{ cm}^{-1}$ might be corresponded to stretching and bending vibrational modes of O–H of molecular water. The peak located around $1500\text{--}1300\text{ cm}^{-1}$ are attributed to the BO_3 asymmetric stretching vibration whereas the peaks found at $1200\text{--}1000\text{ cm}^{-1}$ might belonged to the BO_3 symmetric stretching. The peak found around 840 cm^{-1} is assigned to symmetric stretching vibrations of B–O bonds in the BO_3 group. The peaks around $680\text{--}630\text{ cm}^{-1}$ should originate to out-of-plane bending modes of the BO_3 groups, while the bands located around 510 cm^{-1} are assigned to the bending vibration of B–O bonds in the triangular BO_3 units. The peaks at the range of $450\text{--}400\text{ cm}^{-1}$ might be due to the vibrations of Li–O and Mg–O. Lastly, The IR peaks that observed in the region of 2300 cm^{-1} (600°C) might be assigned to the asymmetric stretching of carboxylates from tartaric acid (fuel).

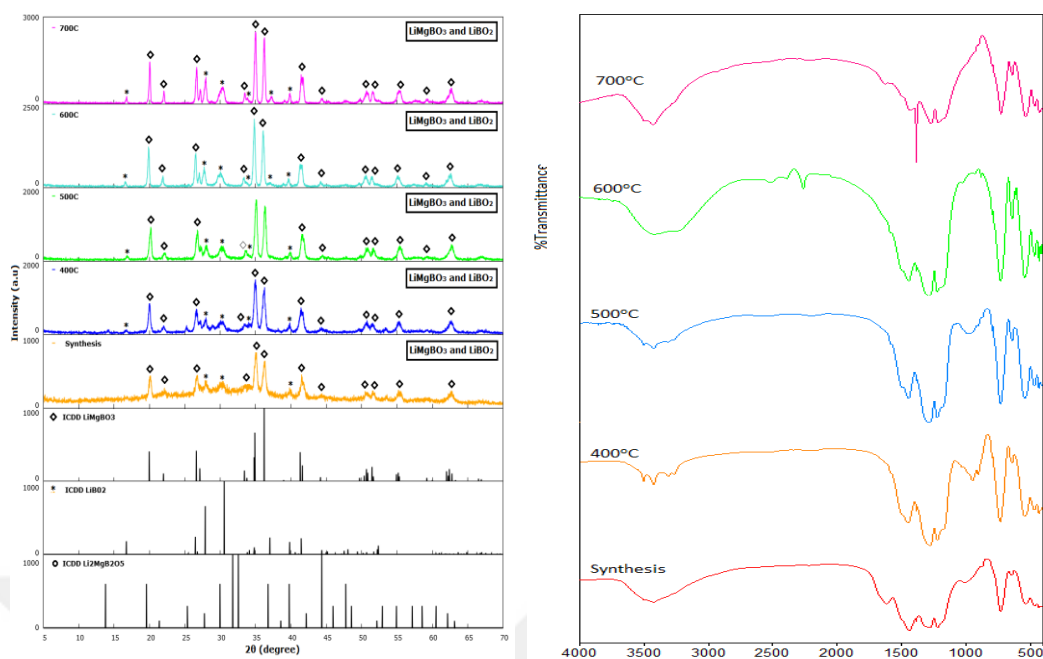
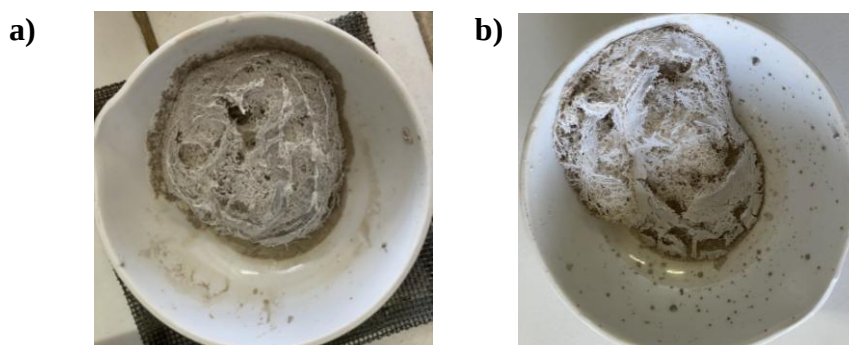


Figure 4.111. The XRD patterns and FT-IR spectra of lithium magnesium pyroborates obtained at various temperatures

Following the observation of characteristic vibration bands for LiMgBO_3 in the previous analysis, rather than for $\text{Li}_2\text{MgB}_2\text{O}_5$, different approach was taken to enhance the formation of the pyroborates phase. To achieve this, the excess amount of H_3BO_3 (5% and 10% wt) were applied, while using tartaric acid as the fuel. This modification was intended to optimize the boron source concentration and fuel-oxidizer ratio, thereby facilitating the formation of $\text{Li}_2\text{MgB}_2\text{O}_5$. However, FT-IR studies revealed the excess of boric acid does not prove to be advantageous in the formation of pure $\text{Li}_2\text{MgB}_2\text{O}_5$ as the primary vibrational bands observed were belonged to LiMgBO_3 . During the synthesis process the light grey products with porous-light structure were obtained (Picture 4.6).



Picture 4.6. The as-synthesized lithium magnesium pyroborate with a) 5% excess and b) 10% excess of H_3BO_3

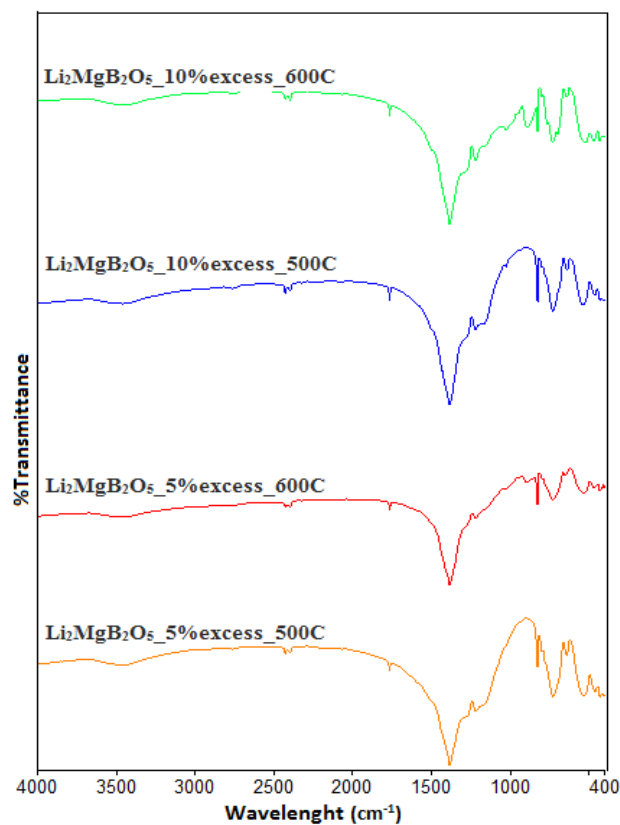
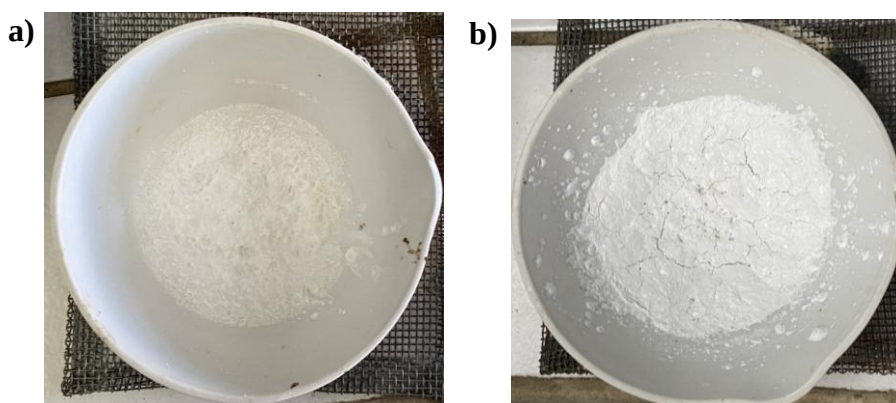


Figure 4.112. The FT-IR spectra of $\text{Li}_2\text{MgB}_2\text{O}_5$ excess H_3BO_3 at various temperatures

An experimental effort was undertaken to synthesis single phase lithium magnesium pyroborates through the utilization of distinct fuels, namely glycine and urea. Both fuel produce fluffy white powder products as shown in Picture 4.7.



Picture 4.7. The as-synthesized lithium magnesium pyroborates with a) glycine and b) urea

Figure 4.113 represents The FT-IR spectra of the $\text{Li}_2\text{MgB}_2\text{O}_5$ sample synthesized by glycine and urea fuel. The broad IR peaks in the regions of $3500\text{--}3000\text{ cm}^{-1}$ and the peak nearby 1600 cm^{-1} might be corresponded to stretching and bending vibrational modes of O-H of molecular water. The peak located around 1450 cm^{-1} might attributed to the BO_3 asymmetric streatching vibration whereas the peaks found at $1200\text{--}1000\text{ cm}^{-1}$ assigned to the BO_3 symmetric stretching. The peaks around $750\text{--}630\text{ cm}^{-1}$ should originate to out-of-plane bending modes of the BO_3 groups, while the bands located around 510 cm^{-1} are assigned to the bending vibration of B-O bonds in the triangular BO_3 units. The peak observed around 840 cm^{-1} is assigned to symmetric stretching vibrations of B-O bonds in the BO_3 group and is not the active peak of $\text{Li}_2\text{MgB}_2\text{O}_5$.

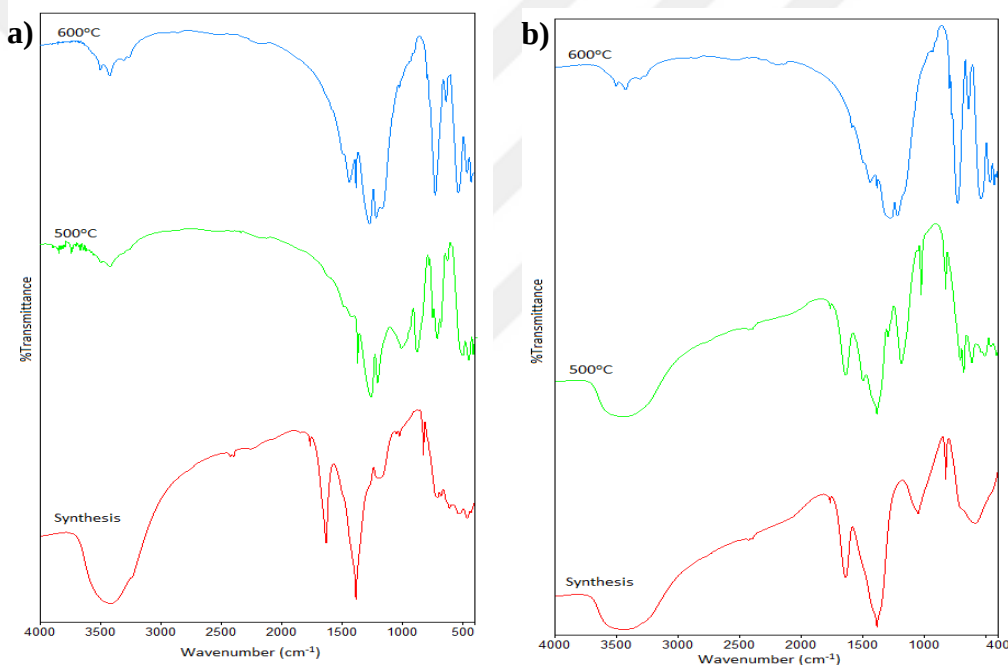


Figure 4.113. The FT-IR spectra of $\text{Li}_2\text{MgB}_2\text{O}_5$ with a) glycine and b) urea as fuel

Following this methodology, the resulting FT-IR spectra analyses revealed a notable challenge in the formation of lithium magnesium pyroborates as no distinct peak around 1520 cm^{-1} and 1196 cm^{-1} which are characteristic peaks of $\text{Li}_2\text{MgB}_2\text{O}_5$. Further investigation is necessary to clarify the optimal condition for the successful fabrication of single-phase $\text{Li}_2\text{MgB}_2\text{O}_5$.

4.4 The Synthesis of Layered Double Hydroxides (LDHs)

4.4.1 The Preparation of $\text{Mg}_{3-x-y}\text{Zn}_x\text{M}_y/\text{Al}_1$

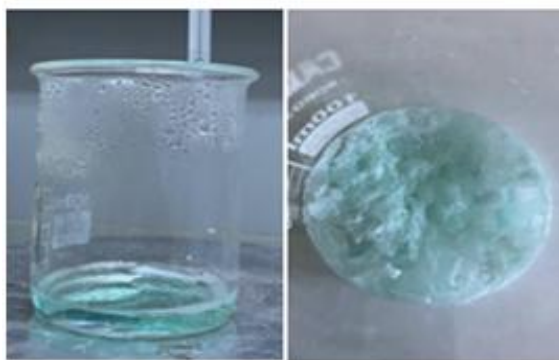
The synthesis of $\text{Mg}_{3-x-y}\text{Zn}_x\text{M}_y/\text{Al}_1$ LDH (**M**: Cu and Mn) was done by dissolving the stoichiometric amounts of starting materials in 50 mL distilled water under continuous stirring. The starting materials were dissolved sequentially as follows; $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Then 10 mL of 0.2 M citric acid solution was added. The resulting solution was stirred continuously for an hour at 80°C and then 2 mL ethylene glycol was added. The solution was agitated constantly at 150°C for some hours (± 5 hours) to ensure complete evaporation, until the gel-like solution was acquired.

a) $\text{Mg}_{3-x-y}\text{Zn}_x\text{Cu}_y/\text{Al}_1$ LDHs

Throughout the preparation process of $\text{Mg}_{3-x-y}\text{Zn}_x\text{Cu}_y/\text{Al}_1$ LDHs, it was noted that the light blue solution deepened in color and transformed into a turquoise gel-like consistency with an increase in the composition of copper (II). The precursor gel was introduced to oven and dried at 105°C for 24 hours. The gel and dried gel was showed in Picture 4.8-4.14.



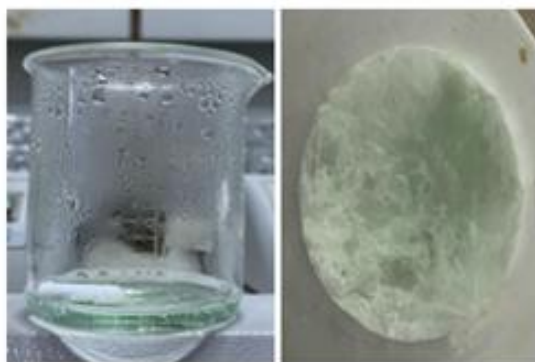
Picture 4.8. The gel and dried gel of $\text{Mg}_{2.94}\text{Cu}_{0.06}/\text{Al}_1$



Picture 4.9. The gel and dried gel of $\text{Mg}_{2.94}\text{Zn}_{0.01}\text{Cu}_{0.05}/\text{Al}_1$



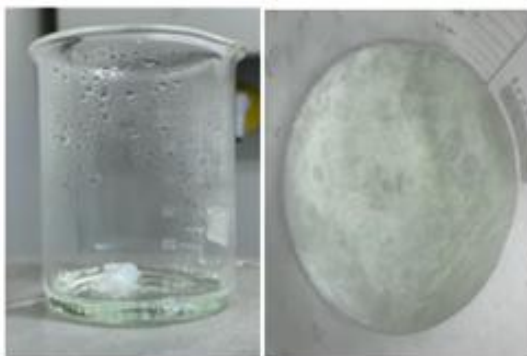
Picture 4.10. The gel and dried gel of $\text{Mg}_{2.94}\text{Zn}_{0.02}\text{Cu}_{0.04}/\text{Al}_1$



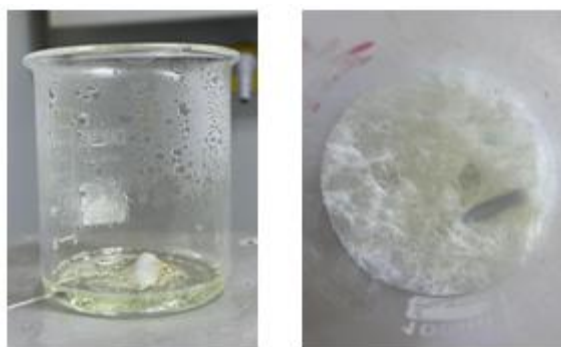
Picture 4.11. The gel and dried gel of $\text{Mg}_{2.94}\text{Zn}_{0.03}\text{Cu}_{0.03}/\text{Al}_1$



Picture 4.12. The gel and dried gel of $\text{Mg}_{2.94}\text{Zn}_{0.04}\text{Cu}_{0.02}/\text{Al}_1$

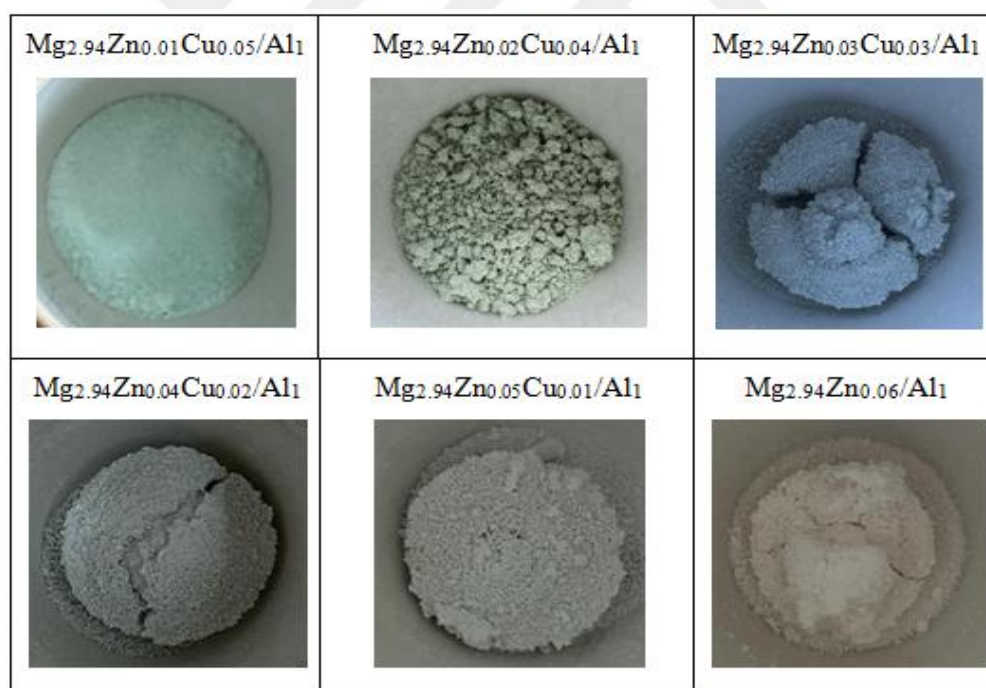


Picture 4.13. The gel and dried gel of $\text{Mg}_{2.94}\text{Zn}_{0.05}\text{Cu}_{0.01}/\text{Al}_1$



Picture 4.14. The gel and dried gel of $\text{Mg}_{2.94}\text{Zn}_{0.06}/\text{Al}_1$

The dried gel or known as xerogel were ground by using mortar and pestle for the next annealing process. It is observed that the color of the products become lighter as the concentration of copper (II) decreases. The annealed process was done at 650°C for 4 hours (Picture 4.15). The powder products were attained and used for the reconstruction process. The powder products were expected to be mixed metal oxide (MMO) compounds.



Picture 4.15. The products obtained after annealed at 650°C for 4 hours

The hydrotalcite materials were obtained by reconstruction of MMO powders in 30 mL of water under stirring at 50°C for 6 hours. The resulting solution was dried in the oven for 12 hours at 70°C and the obtained product was

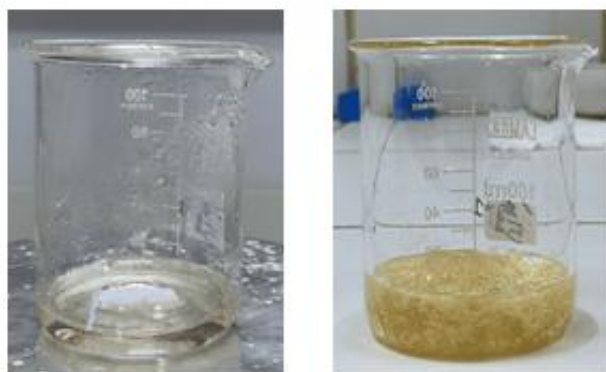
then characterized by several techniques. The light blue powder products were obtain as shown in Figure 4.16.



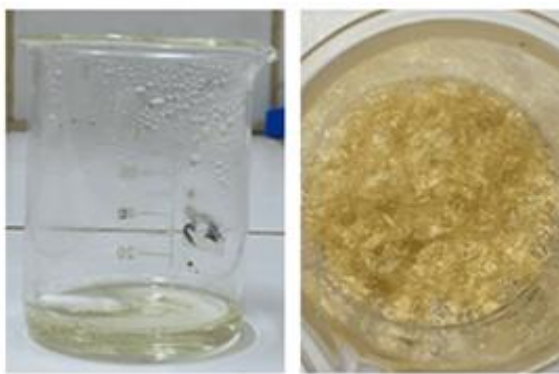
Picture 4.16. The final LDH products after dried at 70°C for 12 hours

b) $\text{Mg}_{3-x-y}\text{Zn}_x\text{Mn}_y/\text{Al}_1$ LDHs

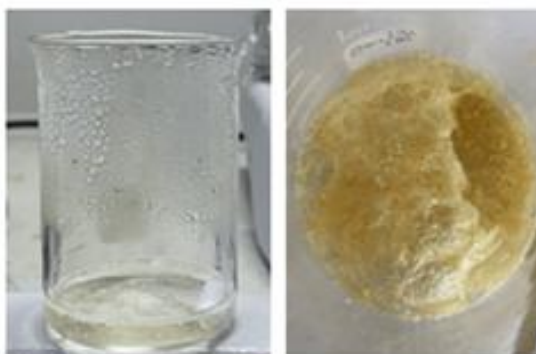
The preparation of Mn-containing LDHs at different concentrations was also carried out using the same procedure. It was observed that the solutions turned into a very light yellow gel as the concentration of manganese decreased. At the highest concentration of manganese, the xerogel took on a turmeric-like color. The gel and xerogel before and after the drying process are depicted in Pictures 4.17-4.22.



Picture 4.17. The gel and dried gel of $\text{Mg}_{2.94}\text{Mn}_{0.06}/\text{Al}_1$



Picture 4.18. The gel and dried gel of $\text{Mg}_{2.94}\text{Zn}_{0.01}\text{Mn}_{0.05}/\text{Al}_1$



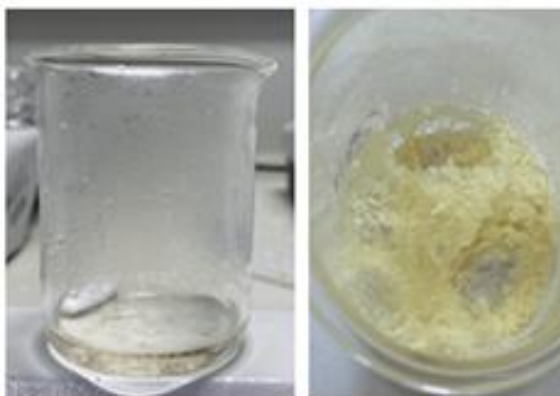
Picture 4.19. The gel and dried gel of $\text{Mg}_{2.94}\text{Zn}_{0.02}\text{Mn}_{0.04}/\text{Al}_1$



Picture 4.20. The gel and dried gel of $\text{Mg}_{2.94}\text{Zn}_{0.03}\text{Mn}_{0.03}/\text{Al}_1$



Picture 4.21. The gel and dried gel of $\text{Mg}_{2.94}\text{Zn}_{0.04}\text{Mn}_{0.02}/\text{Al}_1$



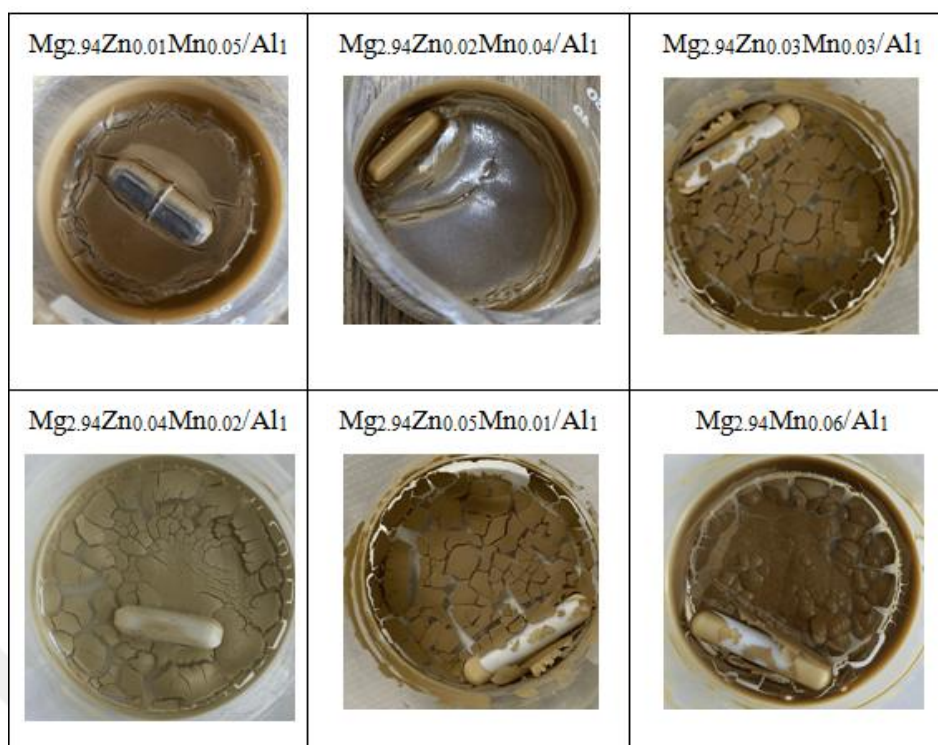
Picture 4.22. The gel and dried gel of $\text{Mg}_{2.94}\text{Zn}_{0.05}\text{Mn}_{0.01}/\text{Al}_1$

Similar to MgZnCu/Al , the annealing process was also applied to MgZnMn/Al . The dried gel then was ground and annealed at 650°C for 4 hours. From the Figures 4.23, it showed that the color of the powder products was become darkened as the amount of manganese concentration increases.



Picture 4.23. The products obtained after annealed at 650°C for 4 hours

After the annealing process, the light pink powder was obtained and dissolved in 30mL for the reconstruction process which carried out for 6 hours by continuous stirring at 50°C . After dried at 70°C for 12 hours, the brown color powder products were attained, as shown in Picture 4.24.



Picture 4.24. The final LDH products after dried at 70°C for 12 hours

It is observed that the change in the color of the LDH depends on the heating temperature. At room temperature, the sample is turquoise-white color; further heating to 650 °C leads to a change in the color of the sample to lightblue-white, which is most likely associated with the onset of the reduction of Copper.

Various $\text{Mg}_{3-x-y}\text{Zn}_x\text{M}_y$ (**M**: Cu and Mn)/ Al_1 with different concentrations ($x,y=0.01-0.06$) were synthesized via sol-gel method. The characterization processes were carried out by X-ray Diffraction (XRD), Fourier Transform Infrared (FTIR) Spectroscopy, Diffuse Reflectance Spectroscopy (DRS), Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-Ray (EDX) Spectroscopy.

4.4.2 The Characterization Studies of $\text{Mg}_{3-x-y}\text{Zn}_x\text{Cu}_y/\text{Al}_1$

The XRD patterns and FT-IR spectra of $\text{Mg}_{3-x-y}\text{Zn}_x\text{Cu}_y/\text{Al}_1$ LDHs ($x, y = 0.00 - 0.06$) are very similar to each other. The transformation of MMO to LDH can be determined in the XRD patterns and the FT-IR Spectra (Figure 4.114-120); the MMO was formed after the gel dried at 105°C 24 hours and annealed in a furnace at 650°C for 4 hours.

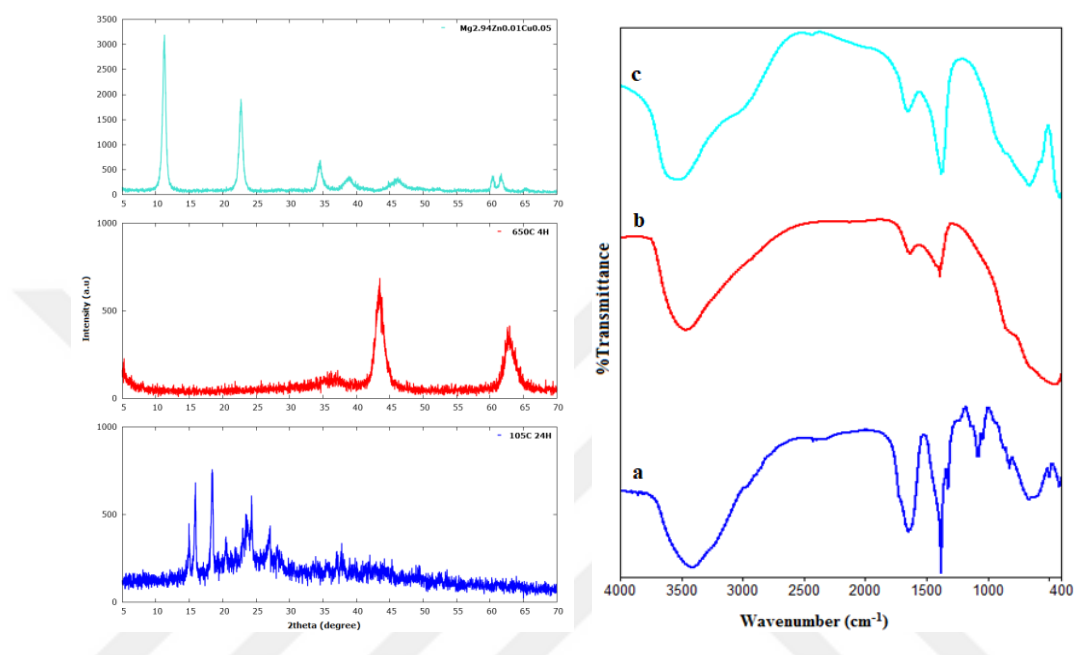


Figure 4.114. The XRD patterns and FT-IR spectra of $\text{Mg}_{2.94}\text{Zn}_{0.01}\text{Cu}_{0.05}/\text{Al}_1$ a) xerogel b) MMO c) LDH

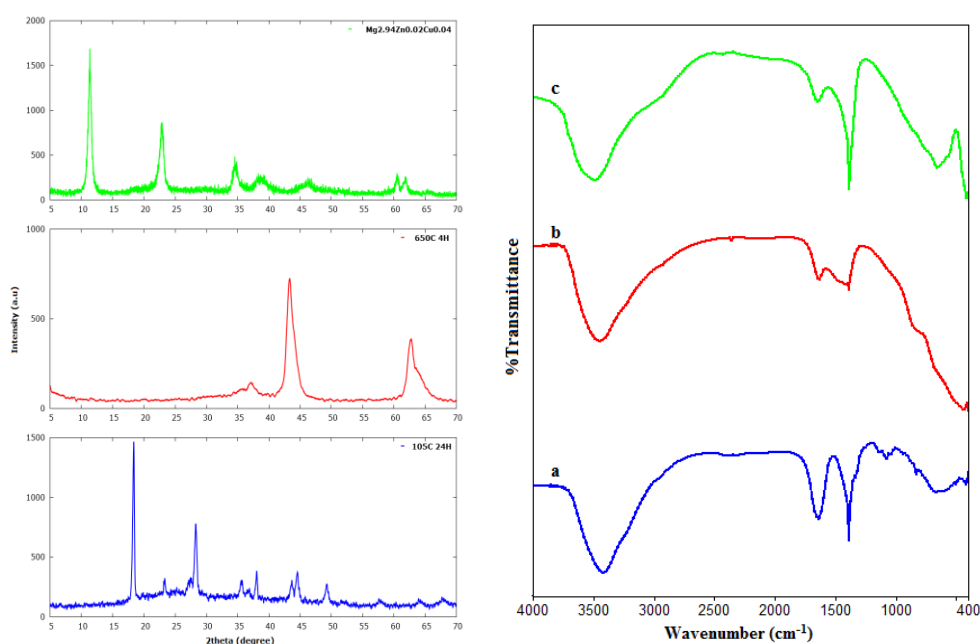


Figure 4.115. The XRD patterns and FT-IR spectra of $\text{Mg}_{2.94}\text{Zn}_{0.02}\text{Cu}_{0.04}/\text{Al}_1$ a) xerogel b) MMO c) LDH

A broad absorption band at around $3600\text{--}3100\text{ cm}^{-1}$ is assigned to the O–H stretching vibrations of the hydroxyl groups and interlayer water molecules. The water bending vibration occurs at 1629 cm^{-1} . Compared to the other spectra, the broad peak observed at around $750\text{--}400\text{ cm}^{-1}$ is attributed to the enhanced M–O vibrations which also confirmed the formation of MMO at 650°C . After the reconstruction process, the medium absorption band at about $658\text{--}655\text{ cm}^{-1}$ attribute to the lattice vibration modes corresponding to the translation vibration of M–OH whereas the band at approximately 415 cm^{-1} arises from metal–oxygen bonds M–O vibrations. This implies that MMO have transformed into LDH by the presence of these bands (Figure 4.114-115).

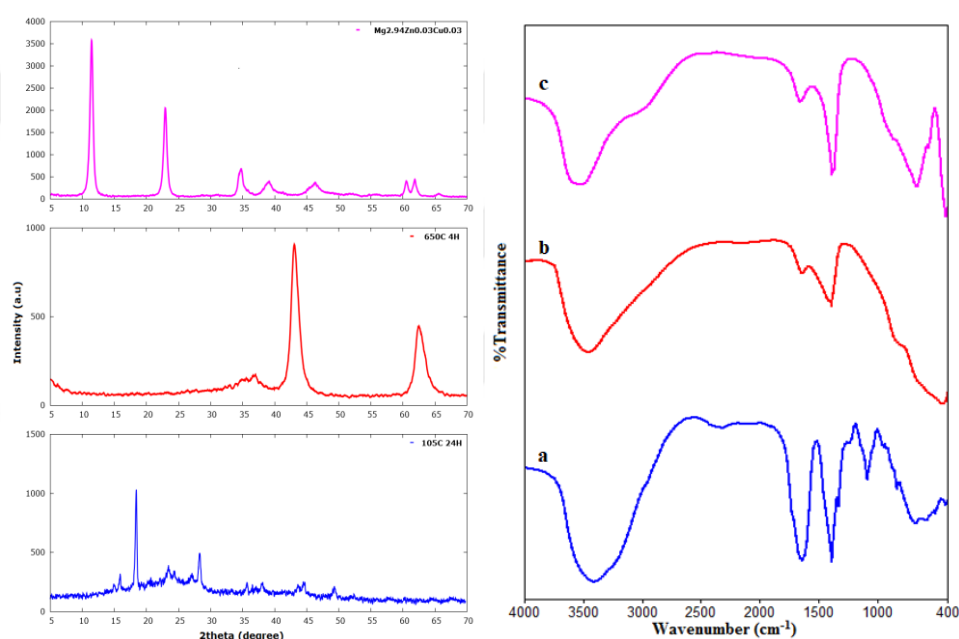


Figure 4.116. The XRD patterns and FT-IR spectra of $\text{Mg}_{2.94}\text{Zn}_{0.03}\text{Cu}_{0.03}/\text{Al}_1$ **a)** xerogel **b)** MMO **c)** LDH

The characteristic vibration bands of Layered Double Hydroxides (LDHs) have also been observed in the synthesized $\text{Mg}_{2.94}\text{Zn}_{0.03}\text{Cu}_{0.03}/\text{Al}_{1.00}$ (Figure 4.116) and $\text{Mg}_{2.94}\text{Zn}_{0.04}\text{Cu}_{0.02}/\text{Al}_{1.00}$ (Figure 4.117). The peak at 1634 cm^{-1} arose from the bending vibration of water in the interlayer, and the strong band at 1361 cm^{-1} clearly identified the presence of the NO_3^{2-} ion in the sample. Meanwhile, the M–O and M–O–M lattice vibrations (M = Mg or Al) caused the adsorption peaks to appear at $658\text{--}790\text{ cm}^{-1}$. These five peaks confirmed the formation of layered double hydroxide. The disappearance of organic trace was clearly seen by the spectrum of drying gel which completely transform in to MMO at 650°C .

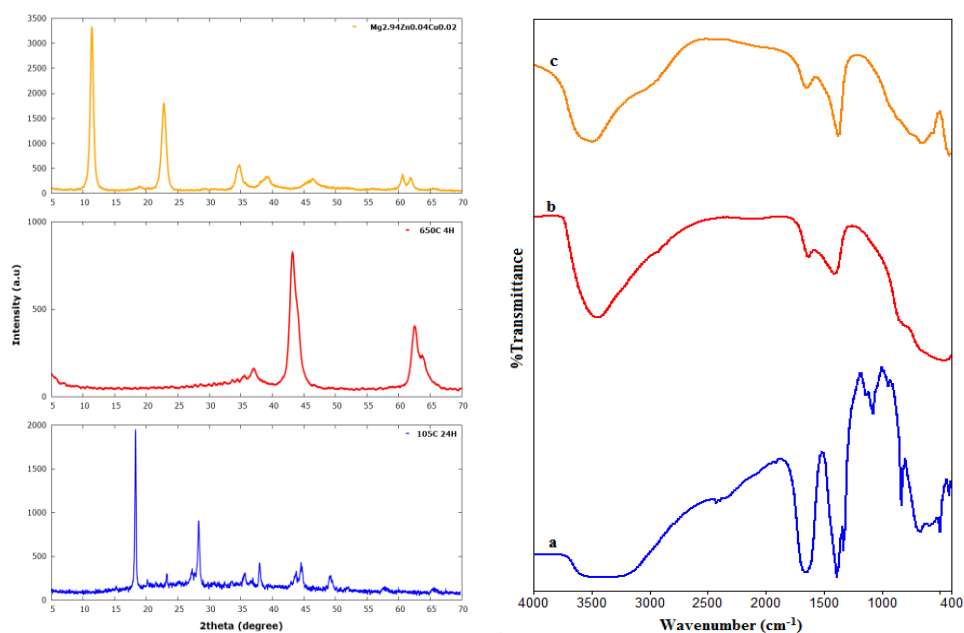


Figure 4.117. The XRD patterns and FT-IR spectra of $\text{Mg}_{2.94}\text{Zn}_{0.04}\text{Cu}_{0.02}/\text{Al}_1$ **a)** xerogel **b)** MMO **c)** LDH

The FT-IR $\text{Mg}_{2.94}\text{Zn}_{0.05}\text{Cu}_{0.01}/\text{Al}_1$ and $\text{Mg}_{2.94}\text{Zn}_{0.06}/\text{Al}_1$ LDH is shown in Figure 4.118 and 4.119, respectively. The presence of three bands that indicate the formation of the layered double hydroxide are observed at 3470 cm^{-1} , 1640 cm^{-1} and 815 cm^{-1} , which correspond to the various stretching modes of OH groups of intercalated and adsorbed H_2O molecules and/or hydroxyl groups of the lamellar lattice.

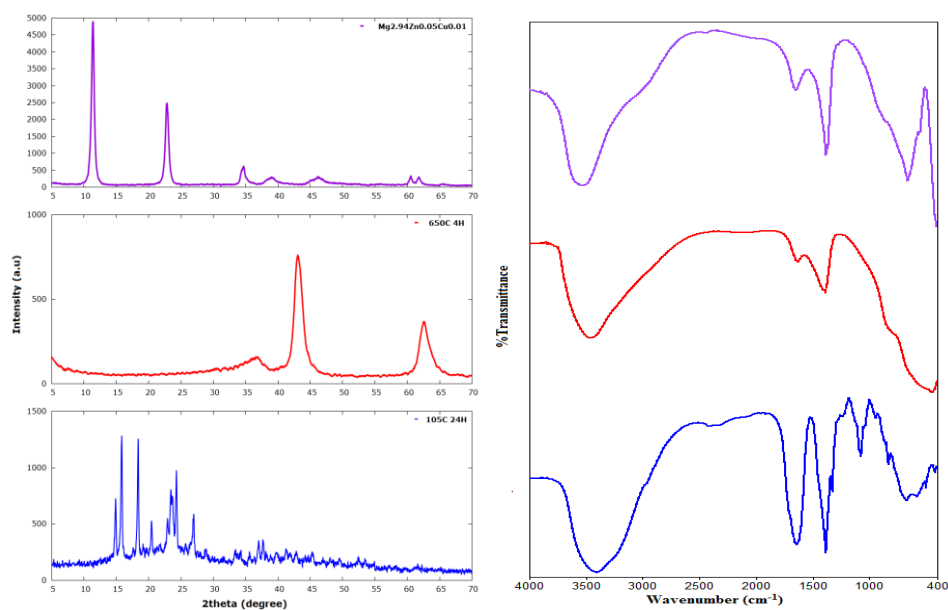


Figure 4.118. The XRD patterns and FT-IR spectra of $\text{Mg}_{2.94}\text{Zn}_{0.05}\text{Cu}_{0.01}/\text{Al}_1$ **a)** xerogel **b)** MMO **c)** LDH

The high intensity thin sharp band located at 1350 cm^{-1} can be associated with the antisymmetric stretching of N-O vibration of free nitric ions. The FT-IR spectra confirmed that the synthetic process was very critical since the vibration of nitric ions is detected from the beginning of the preparation process. Furthermore, the transformation of LDH from MMO can also be clearly seen from the spectra where the FT-IR spectrum of LDH (c) had one more peak than MMO (b) at 660 cm^{-1} .

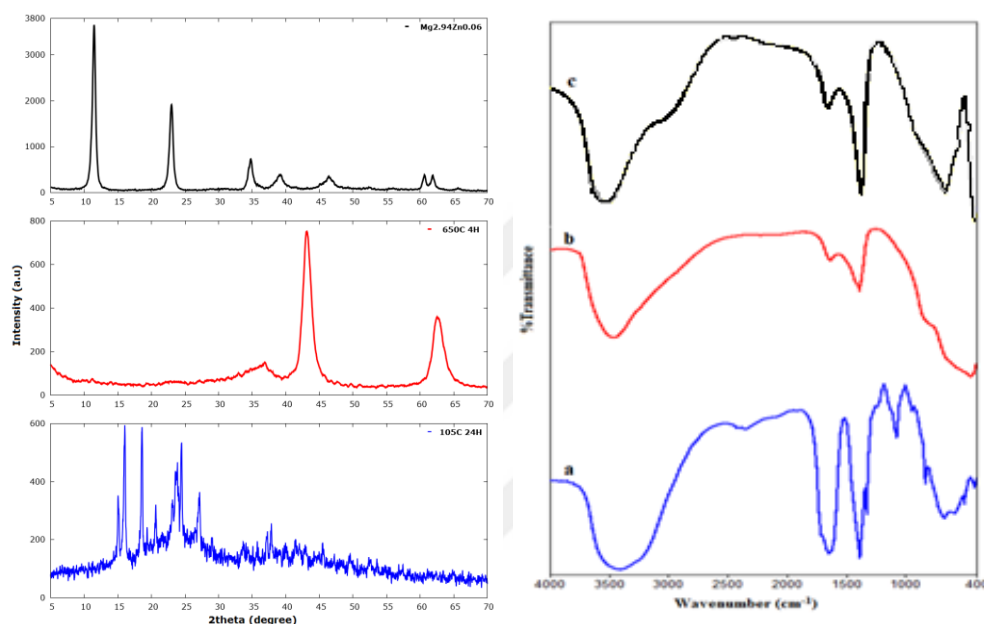


Figure 4.119. The XRD Patterns and FT-IR spectra of $\text{Mg}_{2.94}\text{Zn}_{0.06}/\text{Al}_1$ **a)** xerogel **b)** MMO **c)** LDH

The FT-IR spectra confirmed the formation of LDH with NO_3^{2-} as interlayer anion, resembling to the FT-IR spectra reported by Hirata et.al (143). Analyzing all of these results, single phase LDH samples with double metal effect with high crystallinity were obtained. Thus, it also confirms the high reproducibility of sol-gel processing used in this study for the preparation of mixed-metal LDH samples.

4.4.2.1 The X-Ray Diffraction (XRD) Analyses of $\text{Mg}_{3-x-y}\text{Zn}_x\text{Cu}_y/\text{Al}_1$

The structural properties of LDH were executed by XRD analysis in the 2θ range of 5 to 70° with a scan speed of $5^\circ/\text{min}$. There is no variation and also no secondary phase detected in the patterns. The XRD showed characteristic reflections corresponding to the (003), (006), (101), (015), (018), (110), and (113)

diffraction lines of the typical layered double hydroxide structure. The sharp intense peak indicated the high crystallinity of the products.

According to the patterns showed in Figure 4.120, the basal peaks for the (003), (006) (101), (015), (018) planes were observed and the (110) and (113) planes assign to the non-basal peaks at higher $2\theta=60^\circ$ values. The peak detected at around 11° is the highest peak that indexed as (003) and attributed to the basal reflection and the of LDH interlayer anion whereas the doublet reflection detected at approximately 60° theta is due to the orientation from the (110) plane. This indicated that the single phase LDH layered structure are well crystallized and have the highest degree of crystallinity. The doublet reflection also due to spacing between the brucite-like layer corresponds to the lattice parameter a, which coincides with the distance of the closest M-M.

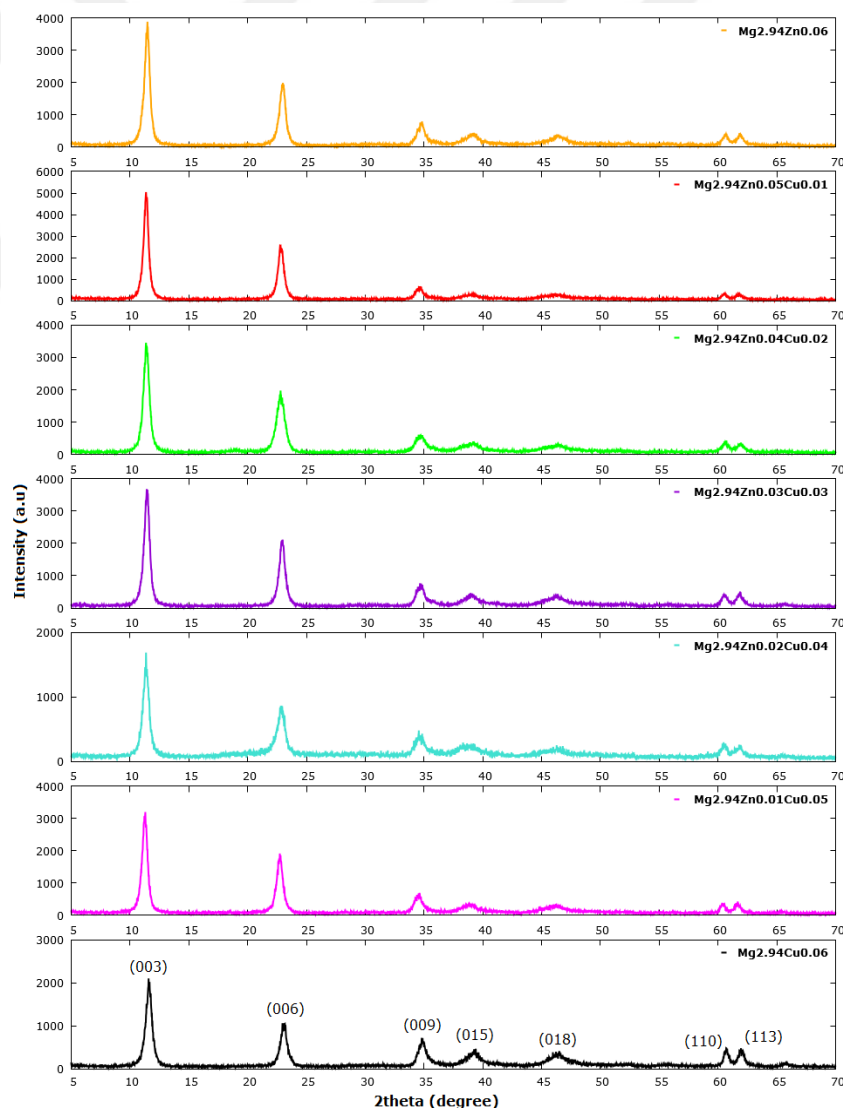


Figure 4.120. The XRD patterns of $\text{Mg}_{3-x-y}\text{Zn}_x\text{Cu}_y/\text{Al}_1$

The shifting on the XRD patterns of LDH was also examined and it observed that the peaks are shifting toward the longer theta degree upon the additions of Cu cationic ion in the LDH materials.

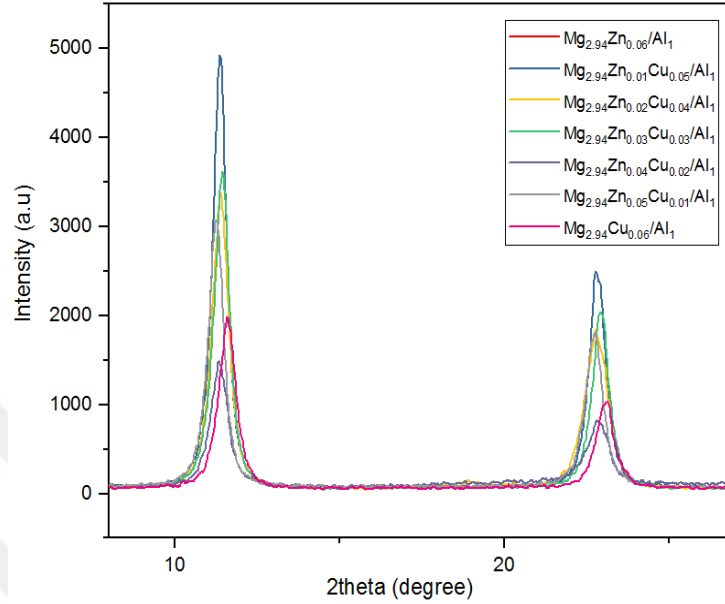


Figure 4.121. The XRD Shift of Mg_{3-x-y}Zn_xCu_y/Al₁

The unit cell parameters of *a* and *c* are determined by the reflections of 110 and 003, respectively. The obtained parameters are presented in Table 4.2. These lattice parameters agree well with those reported for hydrotalcite-like compounds. The lattice constant and volume of the samples were calculated by using the following Bragg's equations (Eq. 1);

$$\frac{1}{d^2} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2} \quad \text{Equation 1}$$

For (0 0 3) and (1 1 0) planes, the lattice constant for *a* and *c* are $c = 3d$ and $a = b = 2d$, while the equation to determine the volume (Eq. 2), the positional parameter (Eq. 3) and also the dislocation density that cause of LDH are written below (154).

Volume:

$$V = \frac{\sqrt{3}}{2} a^2 c \quad \text{Equation 2}$$

Positional Parameter:

$$u = \frac{a^2}{3c^2} + 0.25 \quad \text{Equation 3}$$

From these data, it can be stated that the d-value for LDH materials obtained are well-sustained and are in the range of 7.62-7.85 Å, which is very close to the values reported by Zhitova E.S. et al (155). The c/a ratio for LDH materials found in the range of 7.50-7.70. The positional parameter are varied at 71-73 where the maximum value is belong to Cu =0.05 mol.

Table 4.3. The d-spacing, unit-cell parameters, positional parameter (u) and volume of LDH materials

LDH	d	a (Å)	c (Å)	c/a	u	V (Å ³)
Mg _{2.94} Cu _{0.06}	7.6204	3.049	22.86	7.50	71.054	183.95
Mg _{2.94} Zn _{0.01} Cu _{0.05}	7.8535	3.062	23.56	7.70	73.859	191.24
Mg _{2.94} Zn _{0.02} Cu _{0.04}	7.7844	3.057	23.35	7.64	73.000	189.01
Mg _{2.94} Zn _{0.03} Cu _{0.03}	7.7341	3.055	23.20	7.59	72.438	187.55
Mg _{2.94} Zn _{0.04} Cu _{0.02}	7.7612	3.052	23.28	7.63	72.566	187.88
Mg _{2.94} Zn _{0.05} Cu _{0.01}	7.7783	3.056	23.33	7.64	72.903	188.76
Mg _{2.94} Zn _{0.06}	7.7205	3.052	23.16	7.59	72.151	186.81

The dislocational density of LDH that cause by stress or strain are determined. The amounts of defect are calculated by the equation below, where D is the crystallite sizes of the materials.

$$\delta = \frac{1}{D^2} \quad \text{Equation 5}$$

Furthermore, the the microstrain of the LDH materials were also examined by the equations below, where ε is the microstrain, β is the FWHM value and θ is the peak position in radians.

$$\varepsilon = \frac{\beta}{4 \tan \theta} \quad \text{Equation 6}$$

Table 4.4. The crystallite size (D), dislocation density (δ), average microstrain (ϵ), dielectric constant and bond length (L) of LDH

LDH	D (nm)	$\delta \cdot 10^{-3} (\text{nm}^{-2})$	$\epsilon \cdot 10^{-3}$	L (Å)
$\text{Mg}_{2.94}\text{Cu}_{0.06}$	10.11	9.78	15.83	1.613
$\text{Mg}_{2.94}\text{Zn}_{0.01}\text{Cu}_{0.05}$	10.21	9.59	16.45	1.728
$\text{Mg}_{2.94}\text{Zn}_{0.02}\text{Cu}_{0.04}$	8.33	14.4	20.97	1.693
$\text{Mg}_{2.94}\text{Zn}_{0.03}\text{Cu}_{0.03}$	9.89	10.22	16.00	1.669
$\text{Mg}_{2.94}\text{Zn}_{0.04}\text{Cu}_{0.02}$	8.28	14.58	19.67	1.677
$\text{Mg}_{2.94}\text{Zn}_{0.05}\text{Cu}_{0.01}$	10.58	8.93	15.57	1.689
$\text{Mg}_{2.94}\text{Zn}_{0.06}$	10.15	9.71	15.04	1.659

The crystallite size of all samples was calculated by Debye-Scherrer's equation. Analyzing the crystallite sized value, the formation of nanosized LDH materials were confirmed. The crystallite sized is in the range of 8-11 nm. Also, the microstrain is calculated in the range of $15\text{-}20 \times 10^{-3} \epsilon$. Crystallite size and microstrain is inversely proportional. Smaller crystallite size gives the highest value of microstrain. This relationship might happen due to the existences of defects in the crystal lattice, which increases as the crystallite size decreases. It also shown that the values are found at maximum with $\text{Cu}=0.04$. It also noticed the structural lattice parameters decrease with increasing crystallite size and the crystallite size decreases as peaks in the XRD broaden.

The relationships of these parameters are plotted into graphs as shown in Figures 4.122. The parameter a and c are directly proportional to each other. The value of a and c parameters depends on the specific crystal structure and alter the values of a and c accordingly due to the interatomic forces and strain in the overall symmetry of the crystal lattice.

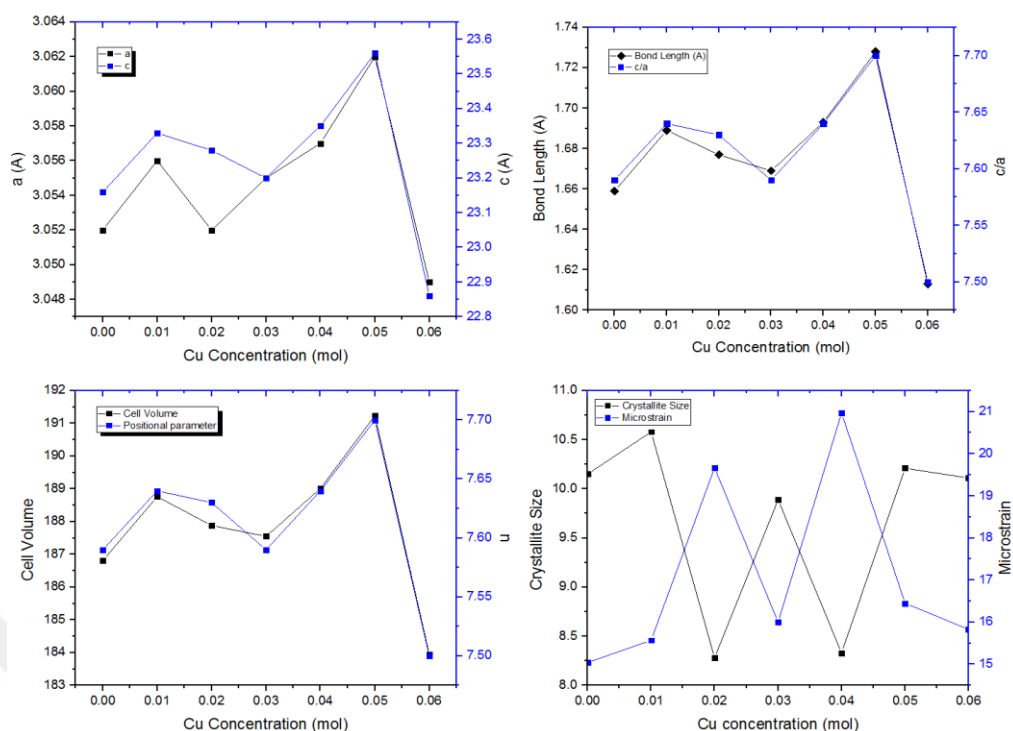


Figure 4.122. The relationship of some parameters of $Mg_{3-x-y}Zn_xCu_y/Al_1$

The bond length and the c/a ratio in crystal structure are related. As c/a ratio increases the bond length along the c-axis become longer relative to those in basal plane and vice versa. The bond length is found to be maximum at Cu= 0.05 mol and minimum at Cu=0.06 mol. The addition of Zinc concentration alongside the reduction of copper is affecting the bond length of LDH materials as the bond lengths are increasing with addition of zinc composition. Moreover, it also showed that the change in positional of atoms within the unit cell affect the overall volume of the cell. For instances, the changes in the c/a ratio, the height of atoms, the positional and the cell volume are directly proporsional and related to each other (Figure 4.122).

4.4.2.2 The Diffuse Reflectance Spectroscopy (DRS) Analyses of $\text{Mg}_{3-x-y}\text{Zn}_x\text{Cu}_y/\text{Al}_1$

The absorbance spectra and the optical band gap energy values of the synthesized materials are shown in the Figures 4.123. The optical properties of the synthesized hydrotalcite materials of the various substituents' concentrations were determined by the DRS analysis. Although the samples have varying concentrations of zinc and copper, all the samples exhibited light absorption in the visible region within the range of 200–400 nm. These absorbance spectra might be detected due to the successful substitution of d-block metals in the interlayer spaces of the LDH. The bands that observed at around 250 nm could be attributed to the d-d transitions of the metal ions.

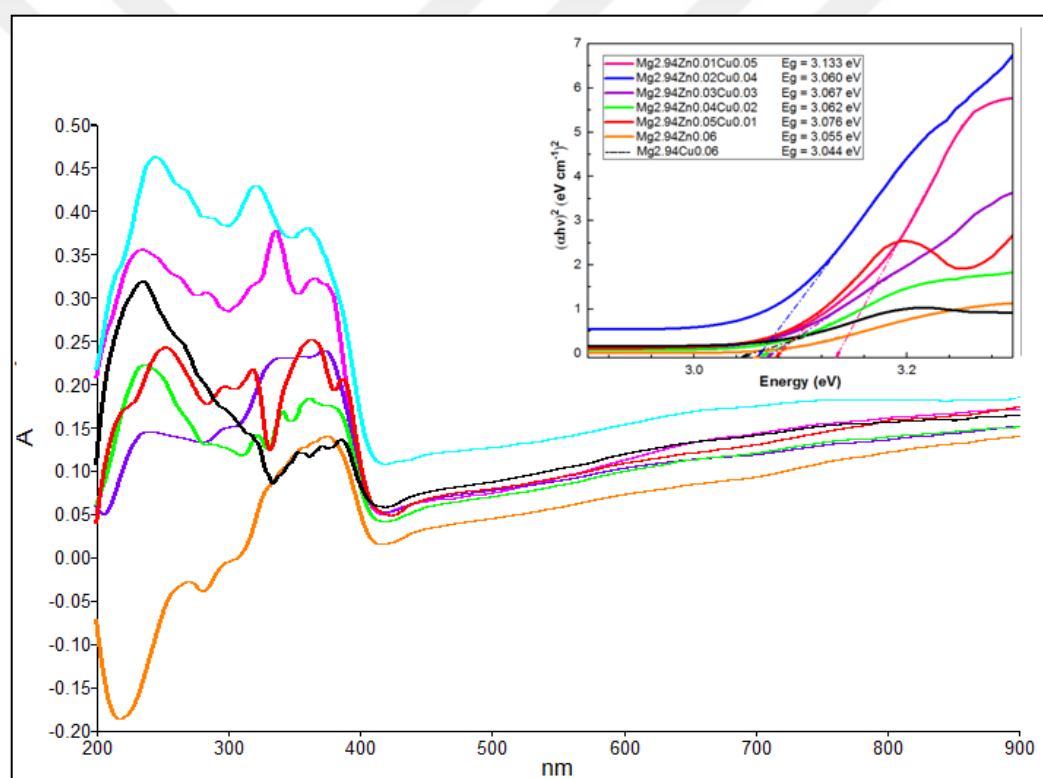


Figure 4.123. The absorbance spectra and optical band gap energy of the synthesized material

Additionally, the optical band gap energy values are applied to calculate the dielectric constants of the synthesized materials. It is showed that the dielectric constants are in the range of 7.80-7.94 with highest dielectric constant belong to $\text{Cu}=0.06$ mole when the composition of zinc is in lowest values. The change in the optical band gap energy of materials altered the dielectric constant values. The relationship between these two parameters is indirectly proportional

to each other, since the the higher band gap values the lower the value of the dielectric constant.

Table 4.5. The band gap and dielectric constants of LDH materials

LDH	band gap (eV)	dielectric constant
$\text{Mg}_{2.94}\text{Cu}_{0.06}$	3.044	7.931
$\text{Mg}_{2.94}\text{Zn}_{0.01}\text{Cu}_{0.05}$	3.133	7.805
$\text{Mg}_{2.94}\text{Zn}_{0.02}\text{Cu}_{0.04}$	3.060	7.908
$\text{Mg}_{2.94}\text{Zn}_{0.03}\text{Cu}_{0.03}$	3.067	7.898
$\text{Mg}_{2.94}\text{Zn}_{0.04}\text{Cu}_{0.02}$	3.062	7.905
$\text{Mg}_{2.94}\text{Zn}_{0.05}\text{Cu}_{0.01}$	3.076	7.885
$\text{Mg}_{2.94}\text{Zn}_{0.06}$	3.055	7.915

In contrast to the inverse proportionality between the dielectric constant and band gap, the relationship between cell volume, crystallite size, and band gap energy values exhibits direct proportionality, which is notably influenced by variations in Zn/Cu composition (Figure 4.124).

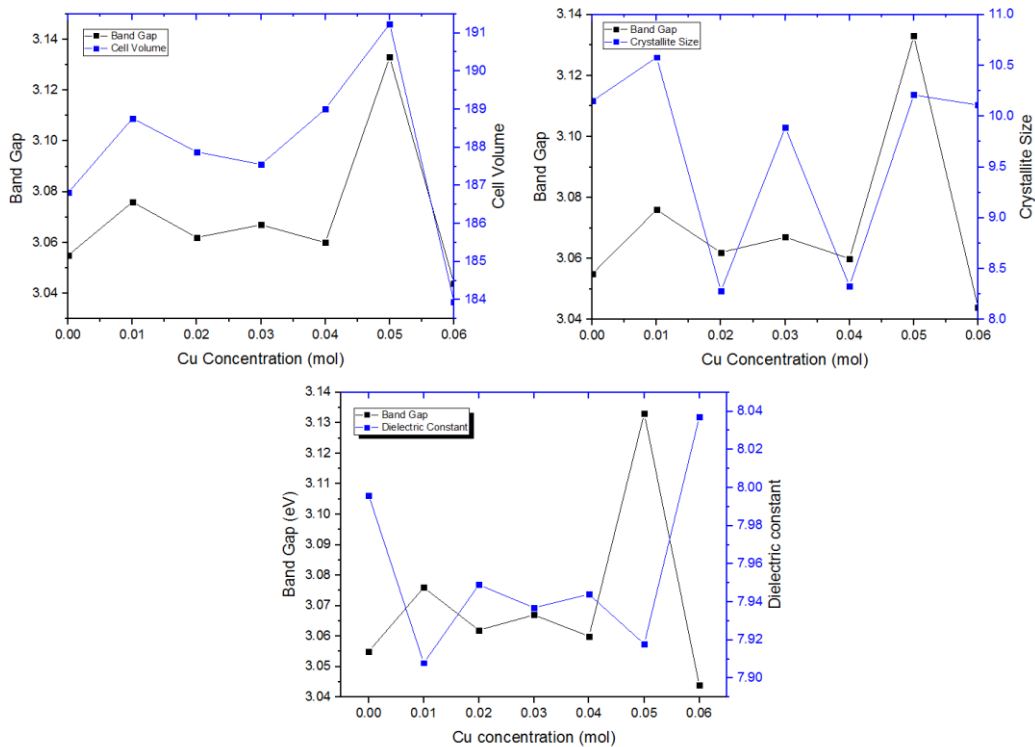


Figure 4.124. The relationship of the LDH materials related to their optical band gap energy

In the application of optoelectronic and sensor, there is significant interest in the materials with high refractive index and wide band gap. These two

characteristics are crucial for enhancing the optical properties such as optical sensor and the performance of the optical interference filter. There are some models used to calculate the refractive index of the materials such as Hervé and Vandamme (156), Kumar and Singh (157), Ravindra et al. (158), Reddy and Anjayenulu (159) and Moss (160). The refractive indexes of the mixed metal LDH material $\text{Mg}_{2-x-y}\text{Zn}_x\text{Cu}_y/\text{Al}_1$ are found between 2.18-2.75 which varied according to related calculation methods.

Table 4.6. The calculated refractive indexes of MgZnCu/Al LDH Materials

LDH	Hervé and Vandamme	Kumar and Singh	Moss	Ravindra et al.	Reddy and Anjayenulu
$\text{Mg}_{2.94}\text{Cu}_{0.06}$	2.32	2.35	2.36	2.20	2.75
$\text{Mg}_{2.94}\text{Zn}_{0.01}\text{Cu}_{0.05}$	2.30	2.33	2.35	2.14	2.73
$\text{Mg}_{2.94}\text{Zn}_{0.02}\text{Cu}_{0.04}$	2.31	2.35	2.36	2.19	2.75
$\text{Mg}_{2.94}\text{Zn}_{0.03}\text{Cu}_{0.03}$	2.31	2.35	2.36	2.18	2.75
$\text{Mg}_{2.94}\text{Zn}_{0.04}\text{Cu}_{0.02}$	2.31	2.35	2.36	2.19	2.75
$\text{Mg}_{2.94}\text{Zn}_{0.05}\text{Cu}_{0.01}$	2.31	2.34	2.36	2.18	2.74
$\text{Mg}_{2.94}\text{Zn}_{0.06}$	2.31	2.35	2.36	2.19	2.75

4.4.2.3 The FESEM Analyses of $\text{Mg}_{3-x-y}\text{Zn}_x\text{Cu}_y/\text{Al}_1$

The FESEM images of MgZnCu/LDH materials reveal detailed information about their surface morphology and structural characteristics. The analysis was carried out by coating all the samples with 10-15 nm thickness of silver. The morphology of LDH materials are reported to be in the hexagonally nanosheet and 3D nanoflower structures (139,161,162). Presented the Figure 4.125- 4131, a clear view of surface morphology of the LDH materials was observed. The growth process of 3D flowerlike structures was observed prior the increasing in the zinc concentration of LDH materials. At the highest copper concentration, an interconnected nanoplate structures were observed (Figure 4.125). Upon adjusting the composition to $\text{Zn} = 0.01$ and $\text{Cu} = 0.05$ resulted in a higher density of plate-like structures and a gradual increase in their size, as depicted in Figure 4.126.

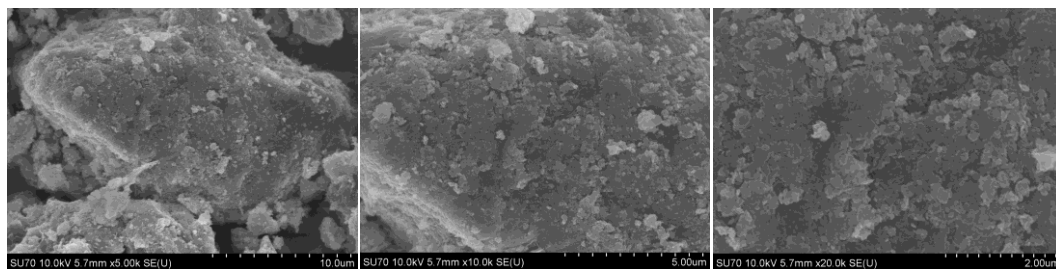


Figure 4.125. The FESEM images of $\text{Mg}_{2.94}\text{Cu}_{0.06}/\text{Al}_1$

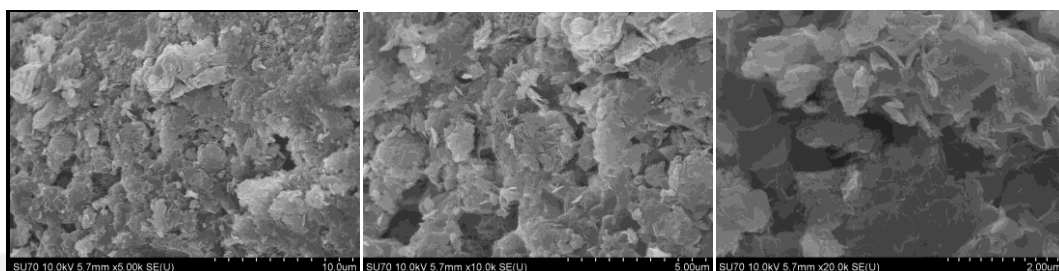


Figure 4.126. The FESEM images of $\text{Mg}_{2.94}\text{Zn}_{0.01}\text{Cu}_{0.05}/\text{Al}_1$

At higher zinc concentrations, the FESEM images show a morphology characterized by randomly stacked, plate-like structures. When the concentrations of zinc and copper are equal, the plate-like structures become more pronounced.

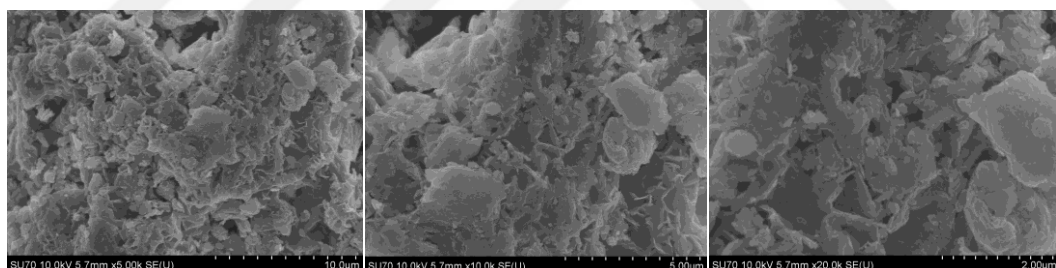


Figure 4.127. The FESEM images of $\text{Mg}_{2.94}\text{Zn}_{0.02}\text{Cu}_{0.04}/\text{Al}_1$

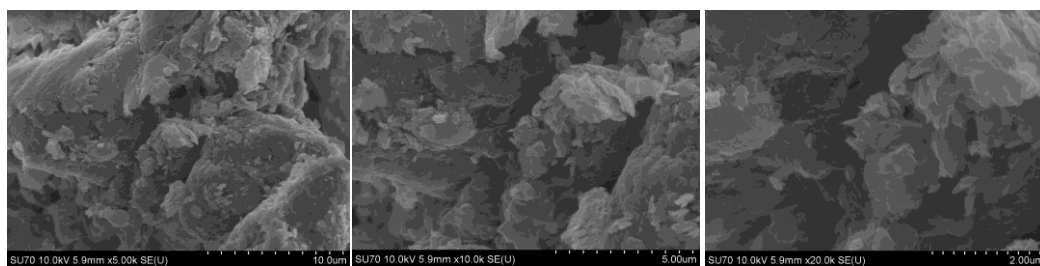


Figure 4.128. The FESEM images of $\text{Mg}_{2.94}\text{Zn}_{0.03}\text{Cu}_{0.03}/\text{Al}_1$

The interconnected plate-like morphology are gradually diminished and become more order which form flower like three dimensional structures build by dozen nanosheets that were connected to each other (Figure 4.129).

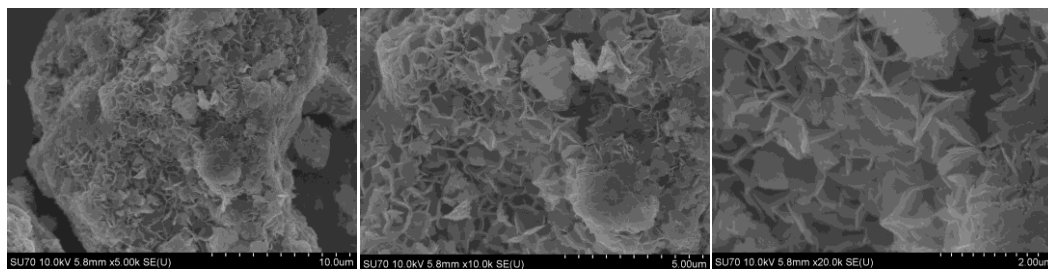


Figure 4.129. The FESEM images of $\text{Mg}_{2.94}\text{Zn}_{0.04}\text{Cu}_{0.02}/\text{Al}_1$

When the concentration of copper is very low ($\text{Cu}=0.01$), the plate-like structures stack together but do not form a three-dimensional flower-like morphology. Instead, they exhibit a well-defined and ordered arrangement.

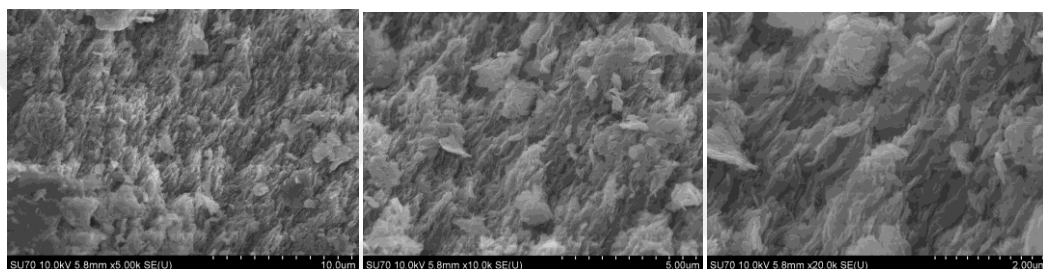


Figure 4.130. The FESEM images of $\text{Mg}_{2.94}\text{Zn}_{0.05}\text{Cu}_{0.01}/\text{Al}_1$

Figure 4.131 presents the FESEM images of $\text{Mg}_{2.94}\text{Zn}_{0.06}/\text{Al}_1$, revealing a well-defined 3D flower-like morphology. This formation is attributed to the interconnected nanoplates that assemble into a spherical structure. The image also shows the presence of hexagonal-shaped plates.

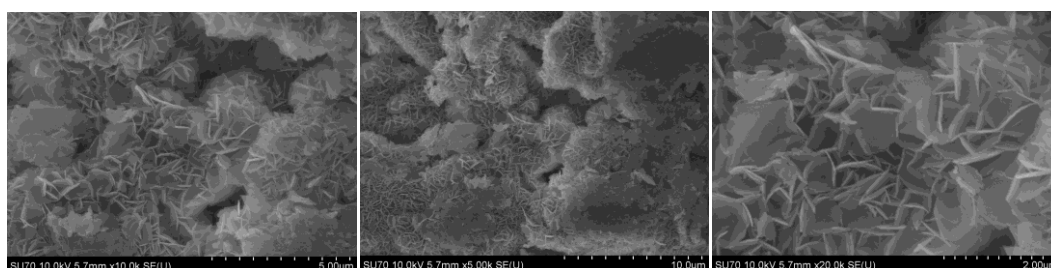


Figure 4.131. The FESEM images of $\text{Mg}_{2.94}\text{Zn}_{0.06}/\text{Al}_1$

4.4.2.4 The EDX (Energy Dispersive X-Ray) Analyses of $\text{Mg}_{3-x-y}\text{Zn}_x\text{Cu}_y/\text{Al}_1$

The Energy Dispersive X-Ray (EDX) analysis was conducted to assess the elemental identification and quantitative composition of the synthesized hydrotalcite Layered Double Hydroxide (LDH) materials. The EDX analysis

showed a good agreement between the experimental elemental ratios and the theoretical values. The EDX spectrum provides clear evidence of the successful synthesis of Mg/Al LDH through the presence of prominent peaks for oxygen (O), magnesium (Mg), and aluminum (Al). These peaks are indicative of the expected elemental composition of the Mg/Al LDH structure, confirming that the synthesized LDHs exhibit high purity and consistent composition. (Figure 4.132-138).

Table 4.7. The elements' atomic weight percentage of EDX analyses

Element	Atomic weight %						
	Zn6	Zn5Cu1	Zn4Cu2	Zn3Cu3	Zn2Cu4	Zn1Cu5	Cu6
O	66.763	60.268	67.332	63.234	69.323	55.336	67.228
Mg	15.912	15.150	14.365	13.704	12.004	13.047	13.810
Al	5.264	4.862	4.740	4.607	3.915	4.306	4.493
Cu	0.000	0.019	0.031	0.104	0.185	0.145	0.428
Zn	0.253	0.112	0.111	0.077	0.062	0.068	0.000
Si	0.058	0.349	0.051	0.094	0.098	0.103	0.062
C	11.750	19.240	13.370	18.180	14.413	26.995	13.978

The detection of characteristic peaks for copper (Cu) and zinc (Zn) further supports the incorporation of these elements into the hydrotalcite material. The specific X-ray energy peaks corresponding to Cu and Zn verify their successful integration and confirm their present close to the expected quantities and composition.

Notably, hydrogen (H) is not detected in the EDX spectrum. This absence is due to hydrogen's very low atomic number and its X-ray emission being below the detection limit of standard EDX instrumentation. Although hydrogen is a crucial component in the LDH structure, its presence has been confirmed by the previously applied FT-IR analysis. Furthermore, the presence of carbon (C) and silicon (Si) peaks in the EDX spectra attributed to the substrate material that were used during the analysis process and potential contamination from the environment, such as carbon dioxide in the air or silicon from the sample holder. These peaks are common in EDX spectra and do not affect the primary analysis of the sample's composition.

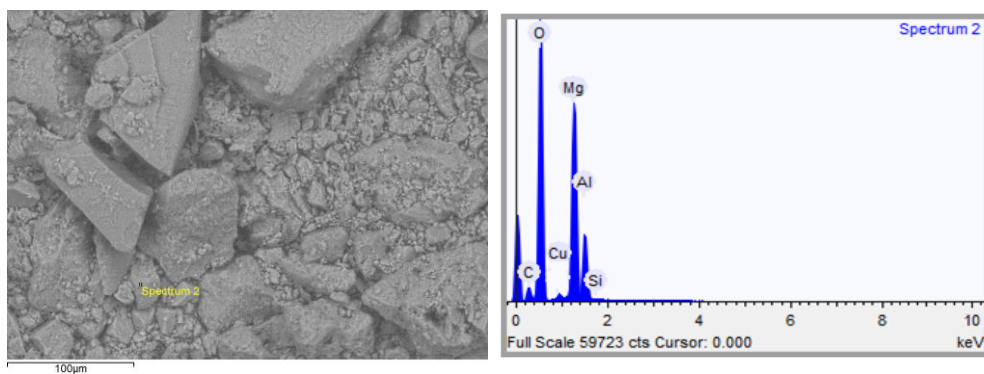


Figure 4.132. The EDX spectrum of $\text{Mg}_{2.94}\text{Cu}_{0.06}/\text{Al}_1$

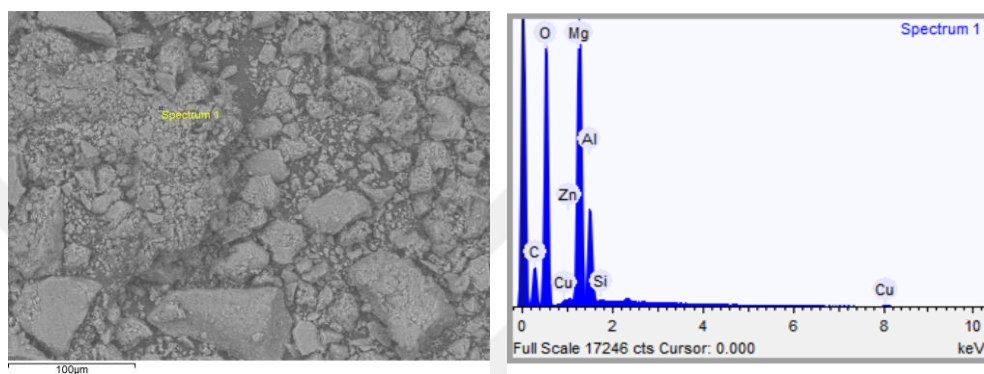


Figure 4.133. The EDX spectrum of $\text{Mg}_{2.94} \text{Zn}_{0.01}\text{Cu}_{0.05}/\text{Al}_1$

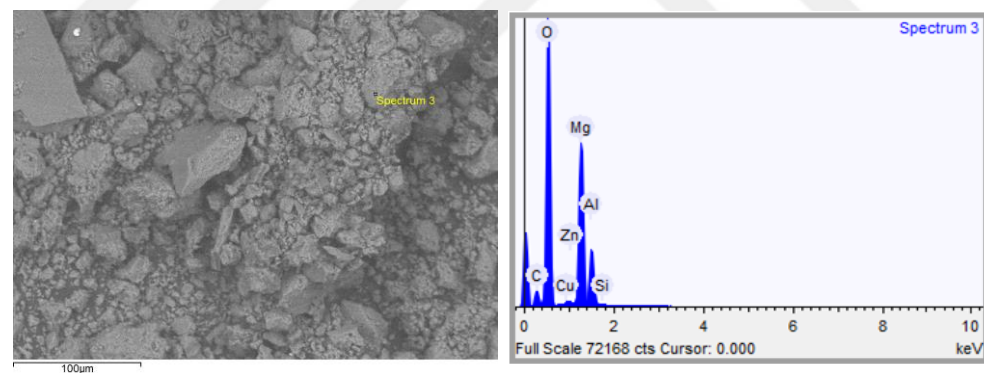


Figure 4.134. The EDX spectrum of $\text{Mg}_{2.94} \text{Zn}_{0.02}\text{Cu}_{0.04}/\text{Al}_1$

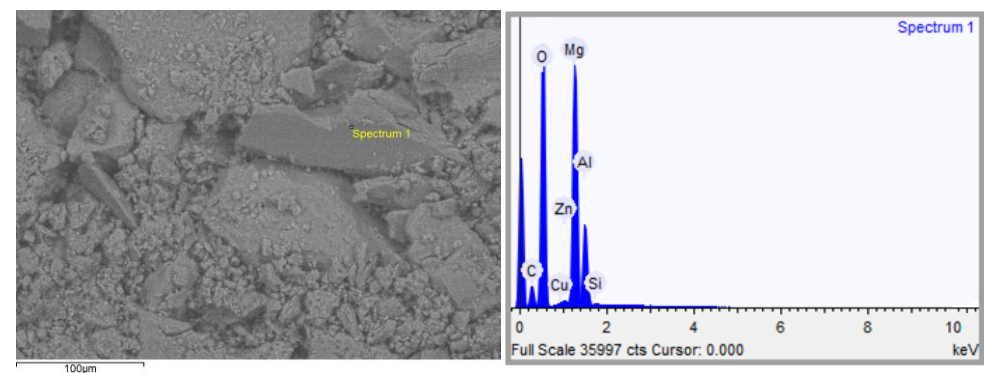


Figure 4.135. The EDX spectrum of $\text{Mg}_{2.94} \text{Zn}_{0.03}\text{Cu}_{0.03}/\text{Al}_1$

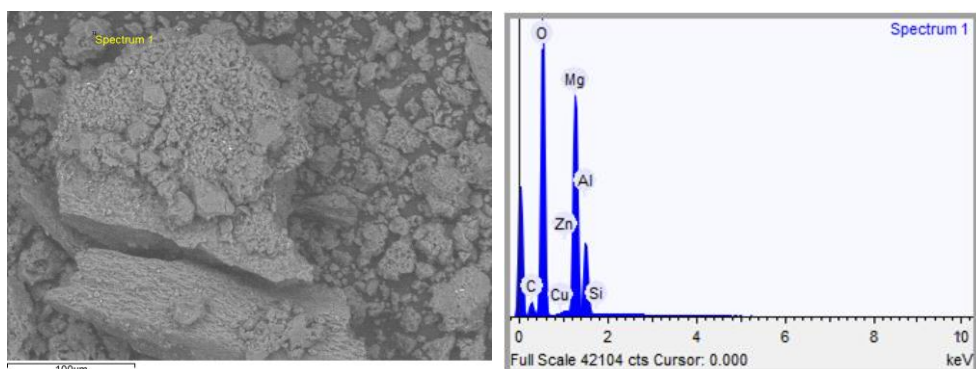


Figure 4.136. The EDX spectrum of $\text{Mg}_{2.94} \text{Zn}_{0.04} \text{Cu}_{0.02} / \text{Al}_1$

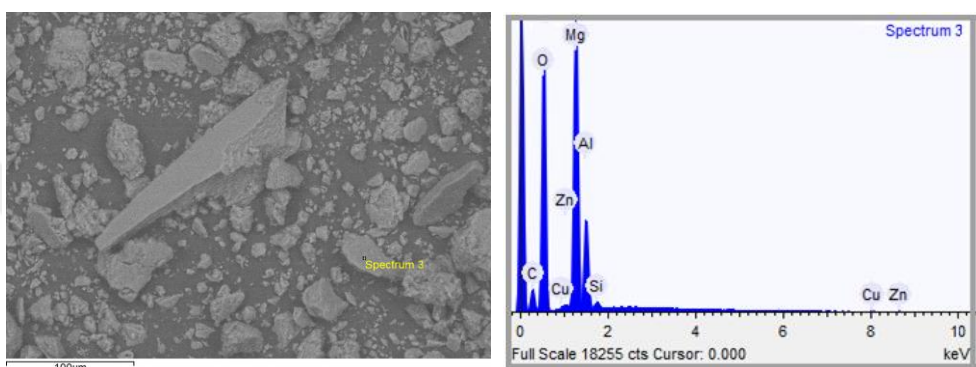


Figure 4.137. The EDX spectrum of $\text{Mg}_{2.94} \text{Zn}_{0.05} \text{Cu}_{0.01} / \text{Al}_1$

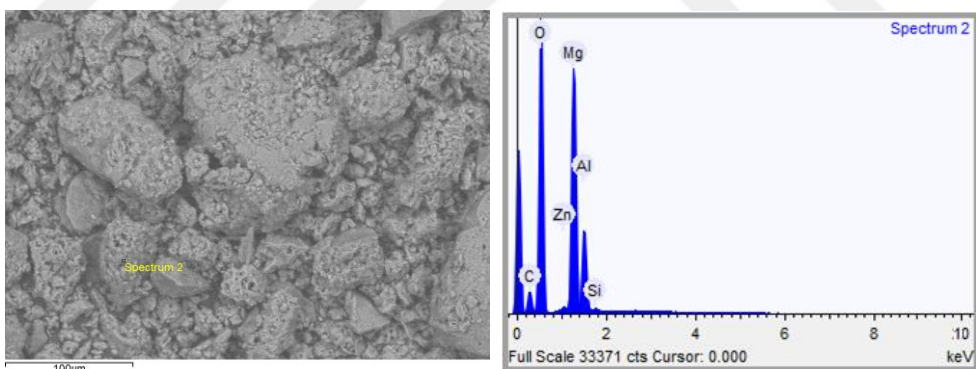


Figure 4.138. The EDX spectrum of $\text{Mg}_{2.94} \text{Zn}_{0.06} / \text{Al}_1$

Analyzing all the acquired data, the EDX analysis effectively confirms the successful synthesis of the MgZnCu/Al LDH, with all expected elements incorporated as intended. The Mg:Al ratio is found to be close to the expected 3:1 for all synthesized hydrotaalcite materials, validating the intended composition. Additionally, the data shows that an increase in the percentage atomic weight of copper element is associated with a decrease in zinc element composition.

4.4.3 The Characterization Studies of $\text{Mg}_{3-x-y}\text{Zn}_x\text{Mn}_y/\text{Al}_1$

The characterization studies of Mn containing LDH materials have been carried out by using various techniques such as XRD technique, FT-IR analysis, DRS studies, FESEM and EDX analysis to determine their structural properties, optical properties, morphology and elemental composition, respectively.

4.4.3.1 The X-Ray Diffraction (XRD) and FT-IR Analyses of $\text{Mg}_{3-x-y}\text{Zn}_x\text{Mn}_y/\text{Al}_1$

The characterization studies of $\text{Mg}_{3-x-y}\text{Zn}_x\text{Mn}_y$ LDH materials were done by XRD techniques and FT-IR analyses. The XRD was recorded at the range of 5-70° and high crystallinity products were observed. The characteristic peaks of LDH materials corresponding to (003), (006), (110), (113) plane which are indicative to Mg/Al LDH characteristic structure. The (003) plane is observed as the most intense peak, located at approximately $2\theta=11$ degree. The formation of LDH materials were further assured by the existence of doublet peak at 60-65 2θ degree which attributed to the orientation of the (110) plane. The high-intensity XRD patterns obtained validate the formation of high-crystalline hydrotalcite MgZnCu/Al LDH materials.

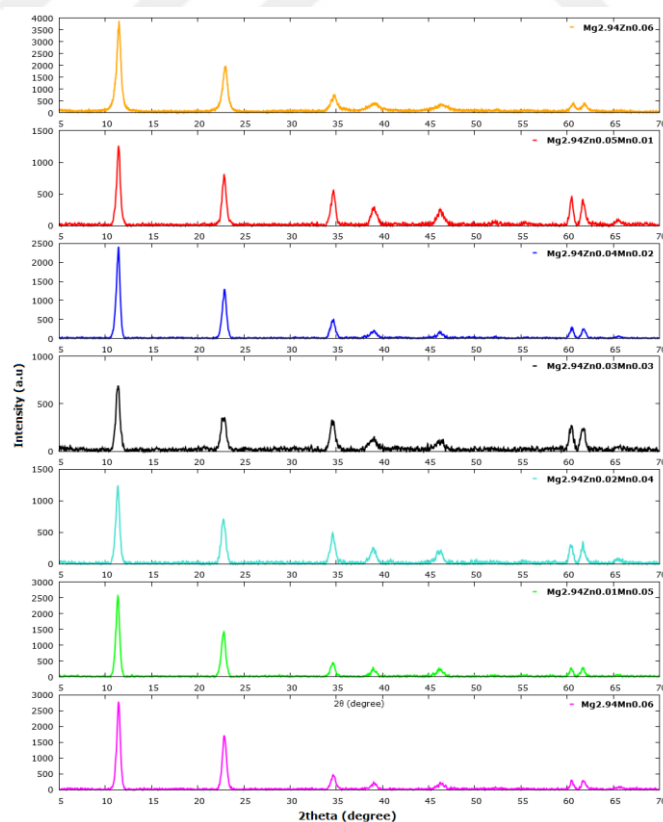


Figure 4.139. The XRD Patterns of $\text{Mg}_{3-x-y}\text{Zn}_x\text{Mn}_y/\text{Al}_1$

Analyzing the XRD shift of the two maximum peaks in the patterns revealed a trend towards lower theta degrees with increasing manganese concentration, while the addition of more zinc concentration led to a shift towards longer wavelengths.

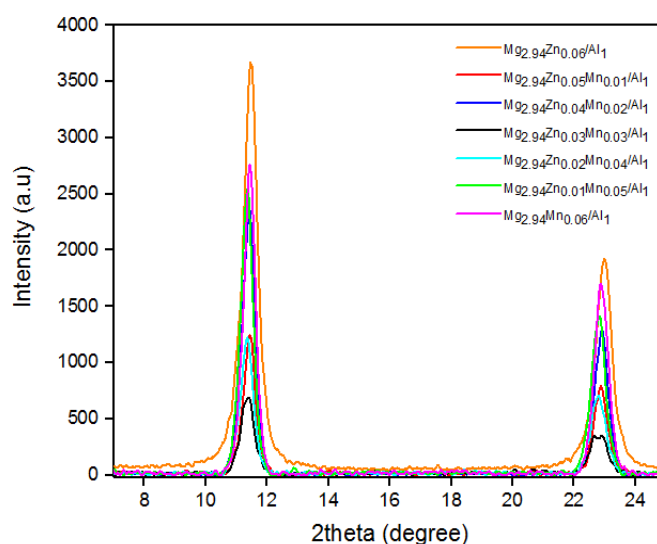


Figure 4.140. The XRD shift of $\text{Mg}_{3-x-y}\text{Zn}_x\text{Mn}_y/\text{Al}_1$

The unit cell parameter and crystallite size of products have also been calculated using the equations given in previous section (4.4.2.1). It is showed that the change in the metal type in the LDH materials does affect the parameter of the products. Accompanying the data listed in the Table 4.8, it's observed that the volume and positional parameter of synthesized materials are found between the ranges of $187\text{-}190 \text{ \AA}^3$ and $72.5\text{-}73.5$, respectively.

Table 4.8. The d-spacing, unit-cell parameters, positional parameter and volume of LDH materials

LDH	d (Å)	c (Å)	a (Å)	c/a	u	V (Å ³)
$\text{Mg}_{2.94}\text{Mn}_{0.06}$	7.737	23.21	3.057	7.59	72.58	187.92
$\text{Mg}_{2.94}\text{Zn}_{0.01}\text{Mn}_{0.05}$	7.740	23.22	3.059	7.59	72.69	188.20
$\text{Mg}_{2.94}\text{Zn}_{0.02}\text{Mn}_{0.04}$	7.763	23.29	3.058	7.61	72.83	188.56
$\text{Mg}_{2.94}\text{Zn}_{0.03}\text{Mn}_{0.03}$	7.783	23.35	3.060	7.63	73.16	189.42
$\text{Mg}_{2.94}\text{Zn}_{0.04}\text{Mn}_{0.02}$	7.797	23.39	3.061	7.64	73.32	189.84
$\text{Mg}_{2.94}\text{Zn}_{0.05}\text{Mn}_{0.01}$	7.793	23.38	3.060	7.64	73.26	189.68

The decrease in crystallite size was observed with the addition of zinc, reaching its minimum when the composition of manganese and zinc equaled 0.03 mol. The crystallite sizes are found within the range of $12.93\text{-}15.40 \text{ nm}$.

Table 4.9. The crystallite size (D), dislocation density (δ), microstrain (ϵ) and bond length (L) of LDH Materials

LDH	D (nm)	$\delta * 10^{-3} \text{ (nm}^{-2}\text{)}$	$\epsilon * 10^{-3}$	L ($\text{\AA}$)
$\text{Mg}_{2.94}\text{Mn}_{0.06}$	15.39	4.22	9.37	1.672
$\text{Mg}_{2.94}\text{Zn}_{0.01}\text{Mn}_{0.05}$	14.98	4.46	9.55	1.676
$\text{Mg}_{2.94}\text{Zn}_{0.02}\text{Mn}_{0.04}$	14.55	4.72	9.82	1.684
$\text{Mg}_{2.94}\text{Zn}_{0.03}\text{Mn}_{0.03}$	12.93	5.98	11.23	1.696
$\text{Mg}_{2.94}\text{Zn}_{0.04}\text{Mn}_{0.02}$	14.26	4.91	9.96	1.703
$\text{Mg}_{2.94}\text{Zn}_{0.05}\text{Mn}_{0.01}$	15.13	4.37	9.55	1.701

The relationship between various parameters of manganese-containing layered double hydroxides (LDHs) was analyzed and presented graphically. The analysis revealed that the cell volume and positional parameter are directly proportional to each other. Similar trends were observed in the graphs plotting the lattice parameter a versus c, as well as the bond length versus c/a ratio. Additionally, the crystallite size was found to be inversely proportional to the microstrain value. The different of Mn concentration also influenced these parameters, affecting both the crystallite size and microstrain values.

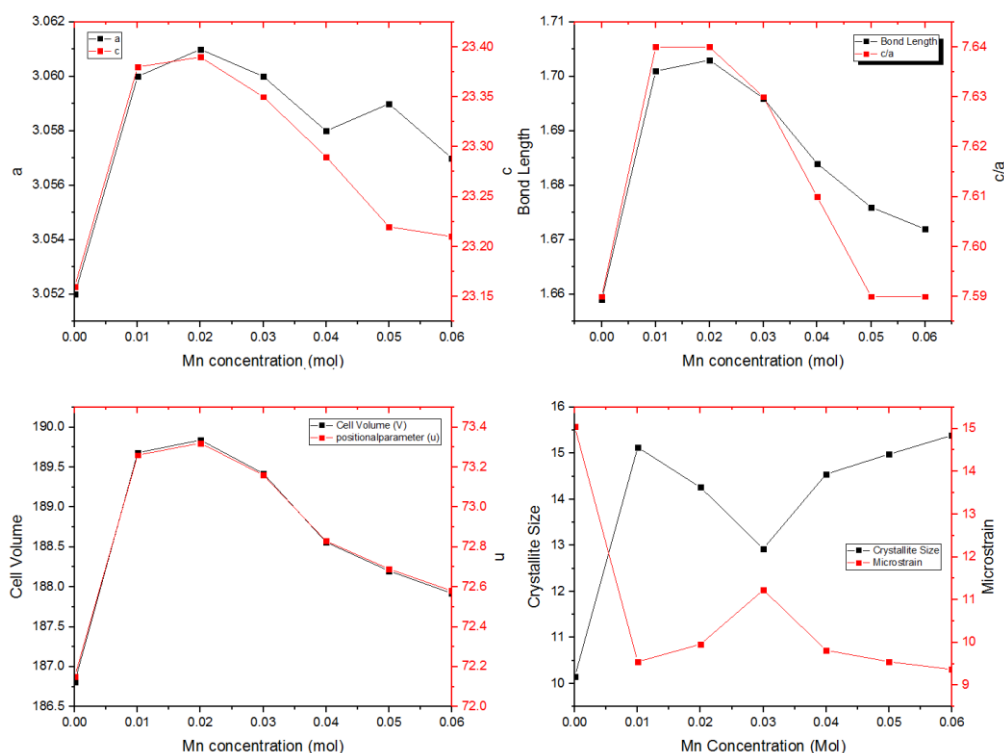


Figure 4.141. The relationship of some parameters of $\text{Mg}_{3-x-y}\text{Zn}_x\text{Mn}_y/\text{Al}_1$ LDH

The vibration bands of the LDH materials were also determined by FT-IR analyses between 4000-400 cm^{-1} . Similar to the spectra of MgZnCu/Al LDH, the characteristic peaks of LDH are clearly observed on Figure 4.142 such as 3489 cm^{-1} , 1687 cm^{-1} , 1371 cm^{-1} , 860 cm^{-1} , 765 cm^{-1} , 659 cm^{-1} , 556 cm^{-1} and 417 cm^{-1} . The peak detected around 3500 and 1650 cm^{-1} attributed to the stretching and bending vibration of water, respectively. The sharp strong band at ~ 1360 cm^{-1} identified the presence of the NO_3^{2-} ion in the sample. Whereas, the peaks between 760-400 cm^{-1} are belong to the M-O and M-O-M lattice vibrations (M = Mg, Zn, Mn or Al).

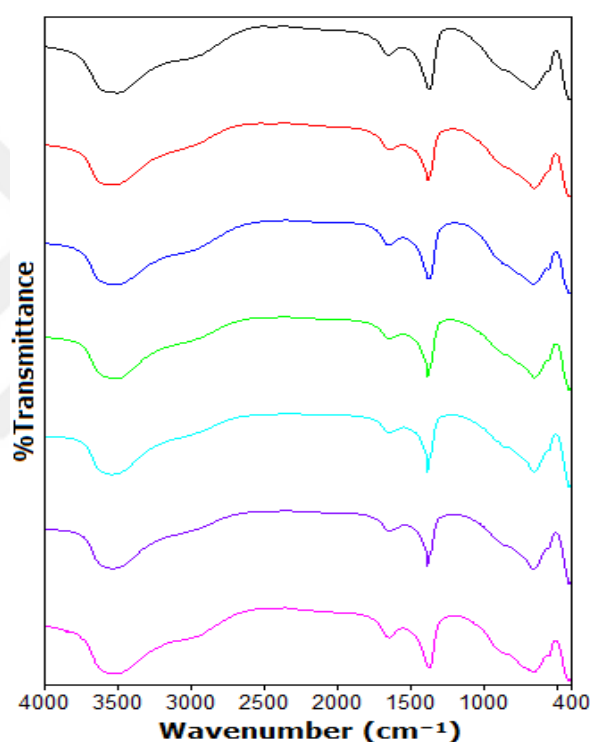


Figure 4.142. The FT-IR spectra of $\text{Mg}_{3-x-y}\text{Zn}_x\text{Mn}_y/\text{Al}_1$ LDH

4.4.3.2 The Diffuse Reflectance Spectroscopy Analyses of $\text{Mg}_{3-x-y}\text{Zn}_x\text{Mn}_y/\text{Al}_1$ LDH

The DRS analysis was conducted in the range of 200-900 nm to determine the optical properties of synthesized $\text{Mg}_{3-x-y}\text{Zn}_x\text{Mn}_y/\text{Al}_1$ hydrotalcite materials. Based on their absorbance spectra, the absorbance peaks of each sample with different concentrations were observed in the ultraviolet region, at approximately below 400 nm. The highest absorbance peaks belongs to $\text{Mg}_{2.94}\text{Mn}_{0.06}$ which does

not contain Zn in its composition. In more additions, the increase in Zn concentration caused the decreases in absorbance value, as shown in Figure 4.143.

The optical band gap energy of Mn-based LDH materials are lower Compare to MgZnCu/Al LDH. The optical band gap energy values are determined to be in the range of 2.24-2.51 eV. The optical band gap energy is observed to increase as the composition of the zinc increases (Table 4.10).

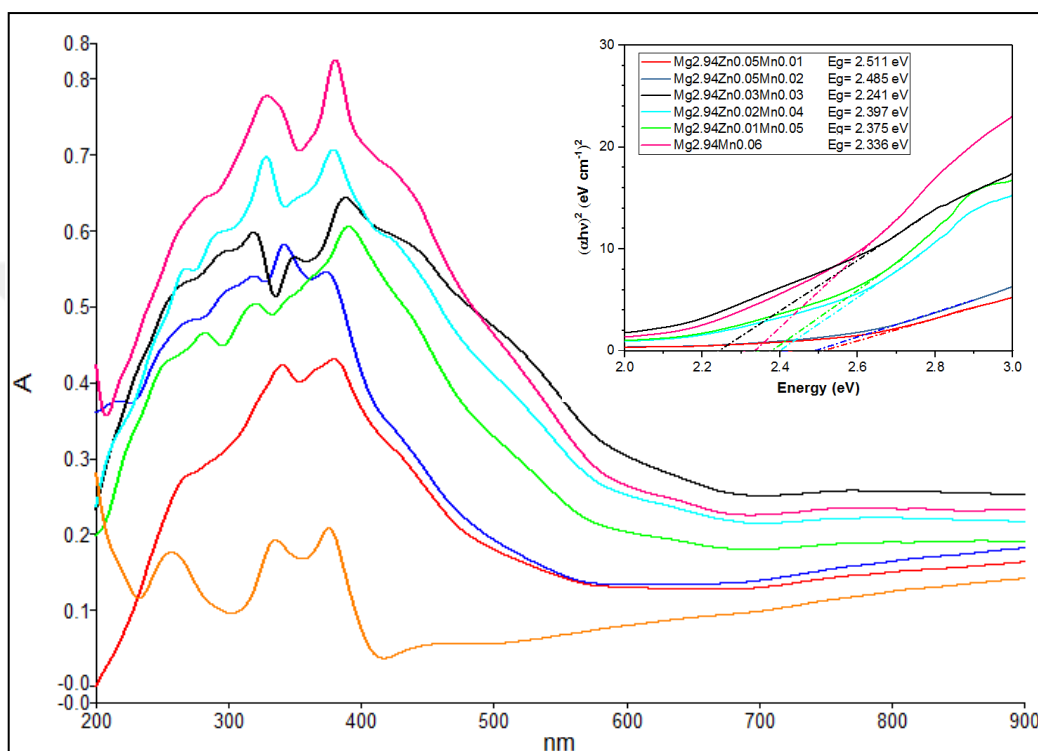


Figure 4.143. The absorbance spectra and optical band gap energy of the synthesized material

As depicted in Table 4.10, the lower the band gap energy the higher the dielectric constant of the LDH materials. Comparing the dielectric constants of layered double hydroxide (LDH) materials containing different transition metals, it was observed that the Mn-based LDH materials exhibit a higher dielectric constant compared to the Cu-based LDH materials. This might happen because manganese (Ar: 197 pm) has higher atomic radii than copper (Ar: 128 pm). As is known, materials with higher atomic radii exhibit increased polarizability, thereby enhancing their ability to store electrical energy.

Table 4.10. The Band Gap and Dielectric Constants of MgZnMn/Al LDH Materials

LDH	Band Gap (eV)	Dielectric Constant
$\text{Mg}_{2.94}\text{Mn}_{0.06}$	2.336	9.276
$\text{Mg}_{2.94}\text{Zn}_{0.01}\text{Mn}_{0.05}$	2.375	9.181
$\text{Mg}_{2.94}\text{Zn}_{0.02}\text{Mn}_{0.04}$	2.397	9.129
$\text{Mg}_{2.94}\text{Zn}_{0.03}\text{Mn}_{0.03}$	2.241	9.521
$\text{Mg}_{2.94}\text{Zn}_{0.04}\text{Mn}_{0.02}$	2.485	8.929
$\text{Mg}_{2.94}\text{Zn}_{0.05}\text{Mn}_{0.01}$	2.511	8.873
$\text{Mg}_{2.94}\text{Zn}_{0.06}$	3.055	7.915

The relationship of the band gap with cell volume, crystallite size, and dielectric constant of the prepared materials has been compared. The band gap versus cell volume shows a complex relationship: an inverse relationship is observed at low Mn concentrations, while at higher concentrations, the relationship becomes more complicated, with instances of direct correlation and varying behavior (Figure 4.144).

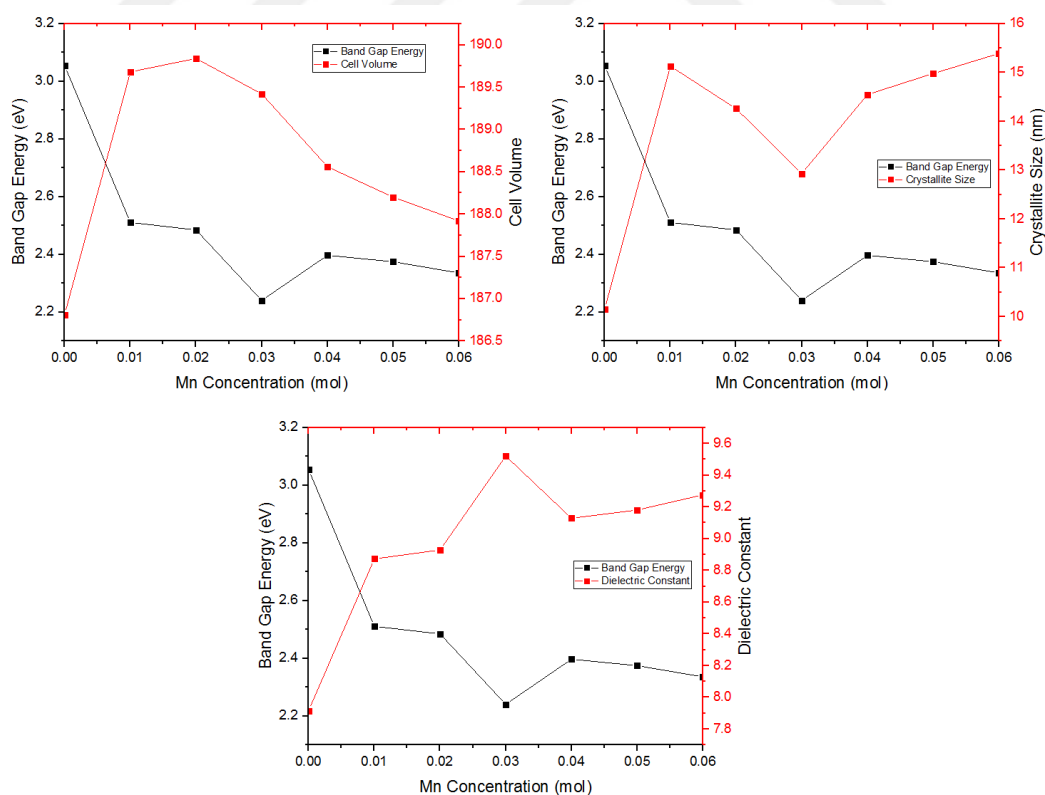


Figure 4.144. The relationship of the LDH materials related to their optical band gap energy

As shown in Figure 4.144, the band gap energy is inversely proportional to the crystallite size, but this relationship is not strictly linear and varies with Mn concentration. Additionally, the band gap energy versus dielectric constant reveals a directly proportional relationship, where an increase in band gap energy resulting in a decrease in the dielectric constant.

The refractive indexes of LDH materials are calculated using these five different models (132-136) and are listed in Table 4.11. It showed that the manganese containing LDH materials has higher refractive indexed compared to copper containing materials. The refractive indexes of $\text{Mg}_{3-x-y}\text{Zn}_x\text{Mn}_y/\text{Al}_1$ are 2.50-3.02.

Table 4.11. The calculated refractive indexes of MgZnMn/Al LDH materials

LDH	Hervé and Vandamme	Kumar and Singh	Moss	Ravindra et al.	Reddy and Anjayenulu
$\text{Mg}_{2.94}\text{Mn}_{0.06}$	2.56	2.57	2.53	2.66	2.98
$\text{Mg}_{2.94}\text{Zn}_{0.01}\text{Mn}_{0.05}$	2.55	2.56	2.52	2.64	2.97
$\text{Mg}_{2.94}\text{Zn}_{0.02}\text{Mn}_{0.04}$	2.54	2.55	2.52	2.62	2.96
$\text{Mg}_{2.94}\text{Zn}_{0.03}\text{Mn}_{0.03}$	2.60	2.61	2.56	2.72	3.02
$\text{Mg}_{2.94}\text{Zn}_{0.04}\text{Mn}_{0.02}$	2.52	2.54	2.50	2.59	2.95
$\text{Mg}_{2.94}\text{Zn}_{0.05}\text{Mn}_{0.01}$	2.52	2.53	2.50	2.59	2.94
$\text{Mg}_{2.94}\text{Zn}_{0.06}$	2.31	2.35	2.36	2.19	2.75

4.4.3.3 The FESEM Analyses of $\text{Mg}_{3-x-y}\text{Zn}_x\text{Cu}_y/\text{Al}_1$

The morphology of MgZnMn/Al with various concentrations are done by using Field Emission Scanning Electron Microscope (FESEM) Analysis. Prior the analysis process, the samples were coated by silver-sputter with the thickness around 10-15 nm. The FESEM image of the $\text{Mg}_{3-x-y}\text{Zn}_x\text{Mn}_y/\text{Al}_1$ LDH were depicted in Figure 4.145 to 4.150. The FESEM image was recorded in three different magnifications namely, 10000x, 5000x and 2000x.

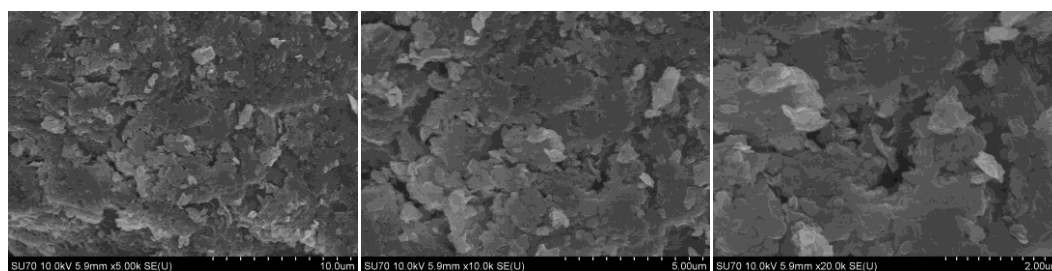


Figure 4.145. The FESEM images of $\text{Mg}_{2.94}\text{Mn}_{0.06}/\text{Al}_1$

The LDH materials with Mn=0.06 showed a round-platelet like structure where the features are densely packed, making them difficult to distinguish. The stacking of the structures creates overlapping regions with porous surface (Figure 4.145).

The addition of Zn into the Mn-based LDH materials leads to a noticeable increase in the nanosheet size distribution. The platelet structures become more distinct and well-defined compared to the FESEM image of $\text{Mg}_{2.94}\text{Mn}_{0.06}/\text{Al}_1$ LDH. This reveals that the addition of Zn composition plays a significant role in altering the morphology and enhancing the clarity of the synthesized hydrotalcite materials.

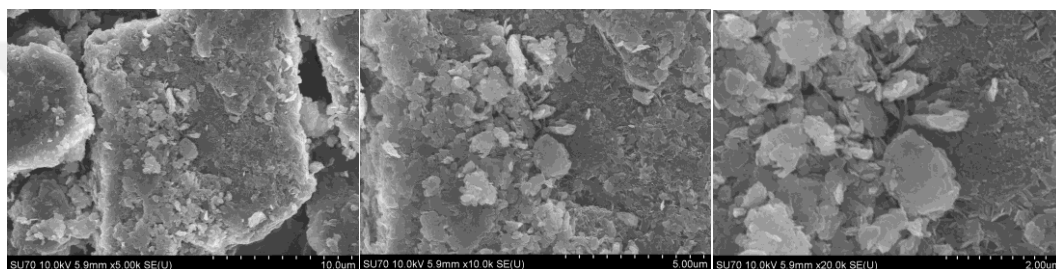


Figure 4.146. The FESEM images of $\text{Mg}_{2.94}\text{Zn}_{0.01}\text{Mn}_{0.05}/\text{Al}_1$

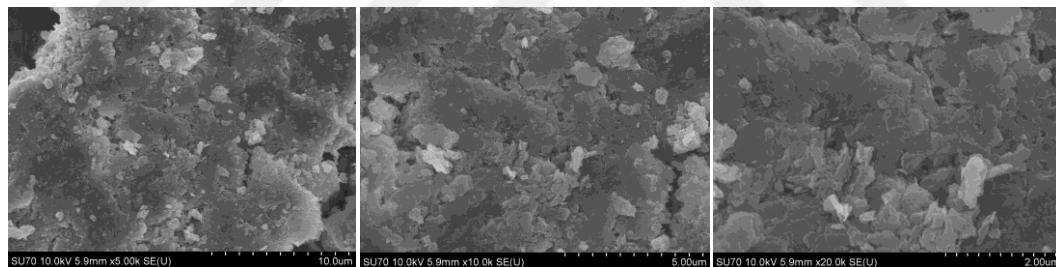


Figure 4.147. The FESEM images of $\text{Mg}_{2.94}\text{Zn}_{0.02}\text{Mn}_{0.04}/\text{Al}_1$

Hexagonal platelet-like structures were observed, exhibiting a more uniform size distribution and a higher degree of order. Despite the nanoplates being layered and interconnected, their individual boundaries remain clearly distinguishable (Figure 4.148).

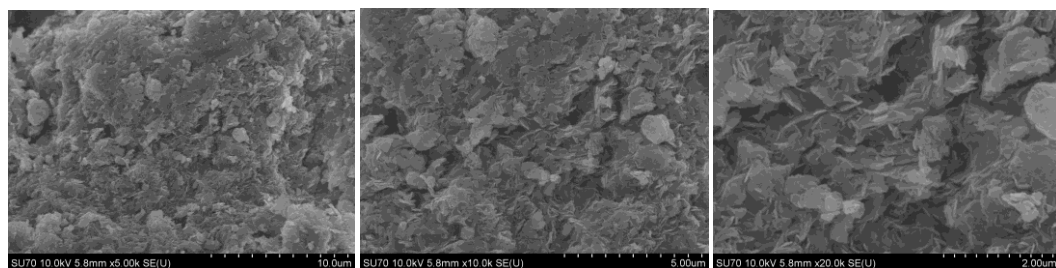


Figure 4.148. The FESEM images of $\text{Mg}_{2.94}\text{Zn}_{0.03}\text{Mn}_{0.03}/\text{Al}_1$

Depicted in Figure 4.149, higher concentration of Zn resulted in the formation of nanoplate-like structures that interconnect with each other, forming a 3D flower-like structure with sharp edges, confirming the high crystallinity of the synthesized material.



Figure 4.149. The FESEM images of $\text{Mg}_{2.94}\text{Zn}_{0.04}\text{Mn}_{0.02}/\text{Al}_1$

The FESEM image of the $\text{Mg}_{2.94}\text{Zn}_{0.05}\text{Mn}_{0.01}/\text{Al}_1$ LDH displays platelet-like structures with sharp edges and a porous surface. These structures are closely stacked upon one another, forming a lamellar arrangement rather than exhibiting a three-dimensional flower-like configuration (Figure 4.150).

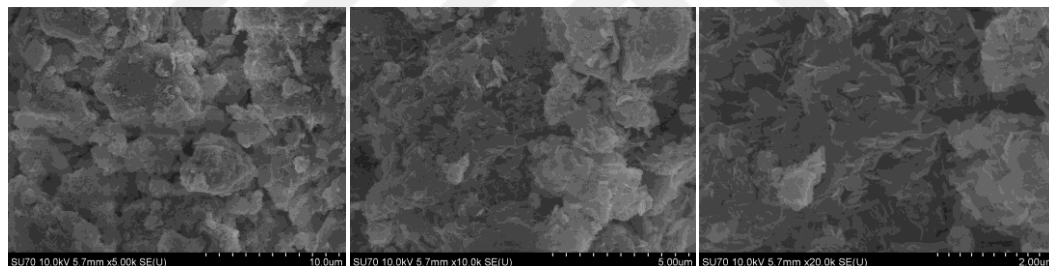


Figure 4.150. The FESEM images of $\text{Mg}_{2.94}\text{Zn}_{0.05}\text{Mn}_{0.01}/\text{Al}_1$

4.4.3.4 The EDX (Energy Dispersive X-Ray) Analyses of $\text{Mg}_{3-x-y}\text{Zn}_x\text{Mn}_y/\text{Al}_1$

The elemental analysis of synthesized hydrotalcite materials was done using Energy Dispersive X-ray Spectroscopy (EDX) techniques. To ensure a representative analysis, the spectrum was collected at three different points on the sample with 5 minutes process time. The EDX spectra indicated the presence of the desired elements, including magnesium (Mg), zinc (Zn), aluminum (Al), and manganese (Mn). According to all spectra depicted in Figure 4.151-4.157, the most intense peaks in the spectra corresponded to oxygen and magnesium, which are characteristic of LDH structures. The presence of aluminum at the relevant X-ray energy values confirmed the successful formation of LDH materials. The

existence of carbon and silicon peak in the EDX spectra are resulted from the substrate used during the characterization process, as well as the contributions of surrounding air environment.

Table 4.12. The elements' atomic weight percentage of EDX analyses

Element	%Atomic weight					
	Mn6	Zn5Mn1	Zn4Mn2	Zn3Mn3	Zn2Mn4	Zn1Mn5
O	69.189	68.102	66.163	61.232	65.215	67.779
Mg	12.826	14.291	12.029	14.616	16.790	14.215
Al	4.174	4.620	3.786	4.695	5.879	4.804
Mn	0.197	0.143	0.114	0.180	0.079	0.051
Zn	0.000	0.025	0.045	0.101	0.101	0.087
Si	0.000	0.000	0.055	0.082	0.163	0.229
C	13.613	12.820	17.808	19.094	11.773	12.834

Listed in Table 4.12, the elemental ratios of magnesium (Mg) and aluminum (Al) were found to be in close agreement with the anticipated values, validating the effective incorporation of the elements into the hydrotalcite framework. However, the concentrations of zinc (Zn) and manganese (Mn) were observed to be significantly lower than expected. This deviation may be attributed to several factors intrinsic to the synthesis and characterization processes. Elemental losses may also occur during the synthesis process, particularly during the drying stages of preparation. These drying processes can expose the materials to conditions that promote the volatilization of certain elements, potentially leading to a reduced concentration of zinc and manganese in the final product. Additionally, both zinc and manganese are present in low concentrations within the hydrotalcite structure ranging from 0.00-0.06 moles, rendering them more difficult to detect accurately using EDX due to the technique's inherent detection limits. Furthermore, these lower apparent concentrations of zinc and manganese might also be attributed to the inhomogeneous distribution of element distribution within the hydrotalcite structure.

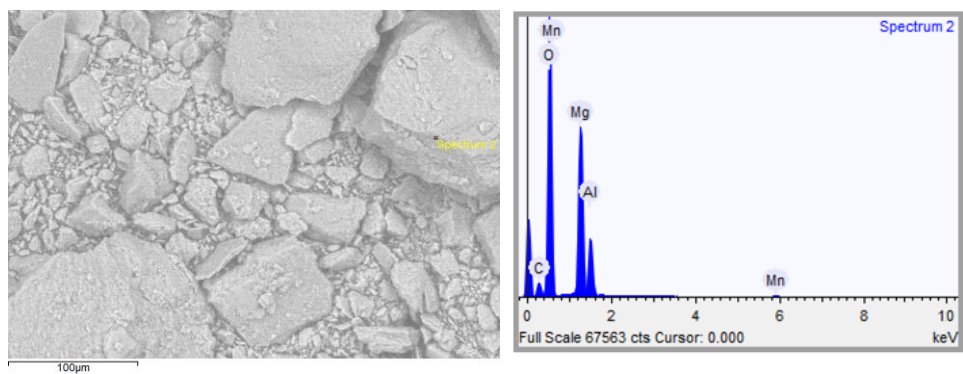


Figure 4.151. The EDX spectrum of $\text{Mg}_{2.94}\text{Mn}_{0.06}/\text{Al}_1$

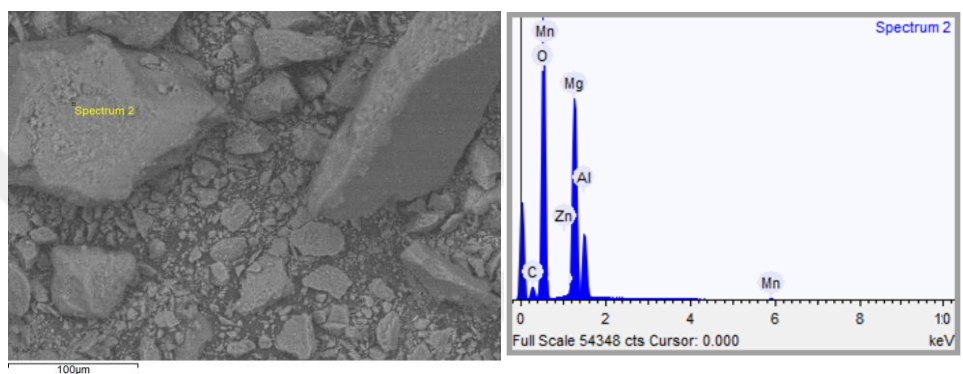


Figure 4.152. The EDX spectrum of $\text{Mg}_{2.94}\text{Zn}_{0.01}\text{Mn}_{0.05}/\text{Al}_1$

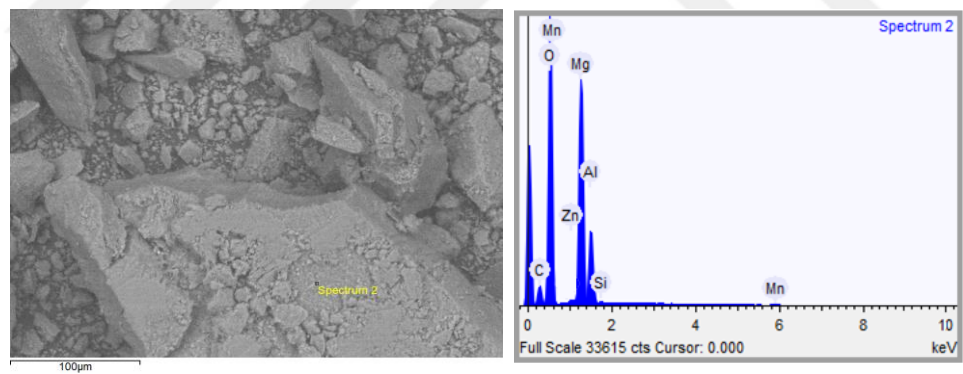


Figure 4.153. The EDX spectrum of $\text{Mg}_{2.94}\text{Zn}_{0.02}\text{Mn}_{0.04}/\text{Al}_1$

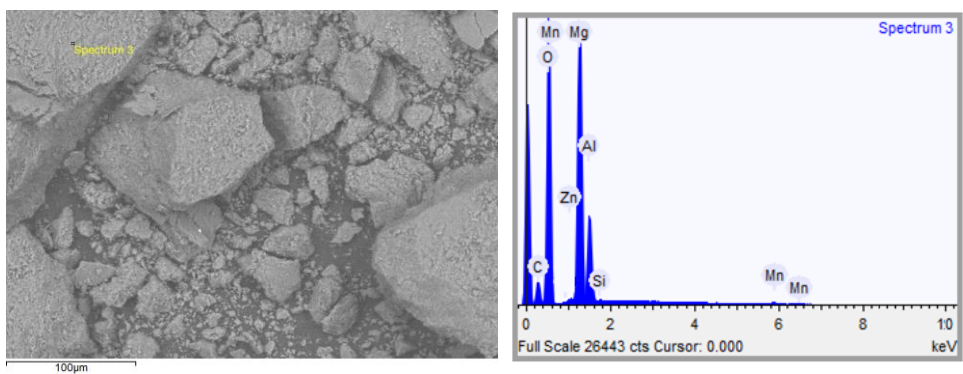


Figure 4.154. The EDX spectrum of $\text{Mg}_{2.94}\text{Zn}_{0.03}\text{Mn}_{0.03}/\text{Al}_1$

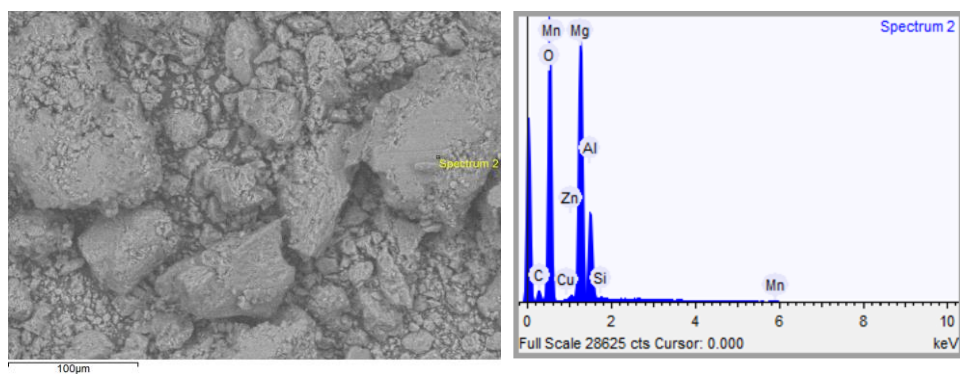


Figure 4.155. The EDX spectrum of $\text{Mg}_{2.94}\text{Zn}_{0.04}\text{Mn}_{0.02}/\text{Al}_1$

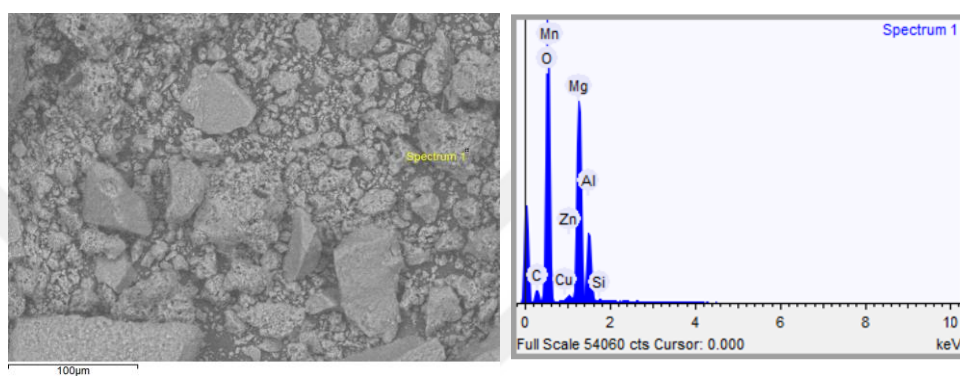


Figure 4.156. The EDX spectrum of $\text{Mg}_{2.94}\text{Zn}_{0.05}\text{Mn}_{0.01}/\text{Al}_1$

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Rare-Earth Metal Doped Magnesium Pyroborates

This study aimed to synthesize nanosized pyroborates more effectively by the fast and self-sustaining method, Solution Combustion Synthesis (SCS) method. Throughout the process, it is obvious that the method is the best in the preparation of pyroborates due to its simplicity, low annealing temperature, and high-purity products. Single-phase magnesium pyroborates doped with three different doping materials (Ce^{3+} , Eu^{3+} , and Tb^{3+}) are successfully acquired and compared.

By analyzing the results and collective data obtained by FT-IR, XRD, DRS, FESEM and EDX techniques, the final products were observed to form in the monoclinic phase at 800°C and transform into the triclinic phase at a higher temperature, 1000°C . The transformation between these two phases is believed to happen at around 900°C . It is also observed that the additions of dopants do not significantly affect the crystal structure of the host materials, $\text{Mg}_2\text{B}_2\text{O}_5$. In the some synthesized compounds, secondary phases are observed which belongs to the oxide of the related rare earth metals (e.g CeO_2 , Eu_2O_3 and Tb_2O_3). According to the fuels used during the synthesis process, the results are described as:

▪ Citric Acid Fuel

The Synthesis is carried out successfully and produced brown fluffy powder products. The monoclinic phase of the products was observed at 800°C followed by transition at 900°C and perfectly forms into triclinic crystal structure at 1000°C . The impact of heating temperature, dopant types and their concentration are observed. Highest crystallinity products are obtained.

▪ Glycine Fuel

The powder products of lanthanide metals doped magnesium pyroborates with glycine fuel is light grey in color which become lighter as it's annealed at higher temperature. Although the reflection lines of magnesium pyroborates dominating, the oxides of dopant materials are observed as secondary phase at 900°C . CeO_2 was detected clearly at 1000°C during the preparation of cerium doped magnesium pyroborates.

▪ **HMTA Fuel**

High crystallinity products were obtained by applying HMTA as fuel. The products are light cream in color. The formation of monoclinic phase, transition between two phase and triclinic phase of magnesium pyroborates are formed at 800°C, 900°C and 1000°C, respectively. Small impurities are found when the Eu^{3+} and Tb^{3+} dopant concentration is at the highest (2.5% dopant).

▪ **Tartaric Acid Fuel**

Tartaric acid is considered as the best fuel in the fabrication of magnesium pyroborates due to its ability to produce large quantity of powder products in high crystallinity. Only 1.5% and 2.5% europium doped products formed small impurities while the rest of synthesized products have high purity.

▪ **Urea**

Urea is found to be the best fuel in the formation of terbium doped magnesium pyroborates as high purity single phase products was observed in both phases of magnesium pyroborates. During the formation of $\text{Mg}_2\text{B}_2\text{O}_5:\text{Eu}^{3+}$ small d-lines of europium oxide are detected at 900°C.

Based on the XRD analysis, the peak shifting of the maximum d-line of magnesium pyroborates at 1000°C showed different behavior. When using citric acid, HMTA, tartaric acid, and urea as fuel in the synthesis process, the maximum peak of rare earth metal doped magnesium pyroborates showed a shifting as their diffraction peaks shifted to higher angle at 1000°C, respected to the d-line of magnesium pyroborates. However, with glycine as fuel the diffraction peak shifted in a different direction respected to the undoped magnesium pyroborates, especially noticeable shifted toward to longer and shorter angle depending to the applied dopant material.

Additionally, to confirm the formation of doped magnesium pyroborates as nanosized compounds the crystallite sizes are also calculated. Indeed, the crystallite sizes are varied and found to be between 15.10-35.6 nm. It is also noticed that the crystallite size is differ according to the type of dopants in order of $\text{Ce}^{3+} > \text{Eu}^{3+} > \text{Tb}^{3+}$. In particular, the final products showed distinctive optical behavior upon the DRS analysis. The one with cerium doped gave abroad peak whereas the other dopants showed two vibrational bands at the ultraviolet regions. It also reported that the band gap values of the products vary based on their

dopants and their concentrations. The band gaps are in the range of 3.20-5.70 eV. These results indicated that the additions of different doping materials in several concentrations and fuel type variations in the synthesis of magnesium pyroborates host materials do affect the physiochemical properties of the final products.

To determine the impact of dopant concentrations and types on the morphology and elemental composition of the synthesized products, FESEM-EDX analyses were performed on samples prepared by the most effective fuels, tartaric acid. FESEM analysis revealed that the dopant materials (cerium, europium and terbium) affect particle morphology and size of the magnesium pyroborates. The morphology of RE-doped magnesium pyroborates with 1.0% dopant concentrations exhibit a porous structure with irregular and granular shapes, demonstrating larger particle sizes and greater ordering in the order of cerium > europium > terbium. Furthermore, increasing the europium concentration leads to significant changes in particle size, indicating that dopant concentration plays a critical role in influencing particle growth and agglomeration. Despite the variations in size, the morphology across different concentrations remains largely uniform, characterized by an irregular, column-round structure. Notably, the samples with 0.5% Eu^{3+} doping display the smallest particle size, while the 1.5% Eu^{3+} samples exhibit clear borders between particles.

The presence of key elements, including oxygen (O), magnesium (Mg), and lanthanide metal ions (Ce, Eu, and Tb), was identified by EDX spectroscopy analysis showing varying intensities. The EDX spectrum confirms the elemental composition of magnesium pyroborates doped with cerium, europium, and terbium, with Mg and O exhibiting the most intense peaks. At varying concentrations of europium, the atomic weight percentages of the detectable elements are observed to fluctuate. Importantly, as the concentration of doping materials increases, a decrease in the magnesium weight percentage was observed.

5.2 Lithium Pyroborates and Lithium Magnesium Borates

This study also challenged the idea about the difficulty of the preparation of single-phase lithium pyroborates which is known to be the lightest solid metal and its sensitivity. In doing so, the synthesis of $\text{Li}_4\text{B}_2\text{O}_5$ via the SCS method with five different fuels (citric acid, glycine, HMTA, tartaric acid, and urea) is carried out for the first time. At low annealing temperature (400-700°C), low crystallinity

and amorphous characteristics were observed. The monoclinic lithium pyroborates are successfully obtained at 640°C in a higher degree of crystallinity with tartaric acid and glycine fuel. The decomposition of lithium pyroborates into Li_3BO_3 and $\text{Li}_6\text{B}_4\text{O}_9$ is observed at temperatures >640°C. Subsequently, the stoichiometric ratio is proven to be the most suitable proportion in the synthesis of lithium pyroborates. The crystallite size of single-phase lithium pyroborates was determined to be 28.14 nm (with glycine fuel) and 27.35 nm (with tartaric acid fuel). Additionally, optical band gap energies were determined by plotting a Tauc plot and found to be in the range of 3.00-3.05 eV.

The morphology of synthesized lithium pyroborates utilizing tartaric acid formed distinctly rhombus-shaped crystals with well-defined sharp edges, indicative of a high degree of structural order and purity within the material. In contrast, the synthesis employing glycine results in a smooth, continuous surface characterized by interconnected structures. Although the crystals exhibit a rhombus-like morphology, their interconnected nature and the absence of distinct porosity obscure the clarity of individual crystal shapes. These differences highlight the impact of the fuel choice on the crystalline structure and overall characteristics of lithium pyroborates.

To obtain the mixed metal borates in the $\text{Li}_2\text{O-MgO-B}_2\text{O}_3$ system, two different mixed metal borates of lithium and magnesium are fabricated namely LiMgBO_3 and $\text{Li}_2\text{MgB}_2\text{O}_5$. Pure LiMgBO_3 was firstly synthesized via SCS using tartaric acid and glycine as fuel. The synthesized materials were obtained at a lower temperature, 400°C in a well-crystallized crystal structure. The best nanosized monoclinic LiMgBO_3 compound was obtained at 600°C with a higher degree of crystallinity. The attempts on the preparation of lithium magnesium pyroborates have also been made however multiphase products are acquired. Instead of forming pyroborates, lithium magnesium borate is formed alongside with lithium diborate. Based on these results, further research with a different approach is needed to synthesize the single-phase lithium magnesium pyroborates.

5.3 Layered Double Hydroxide (LDH)

Owing to its simplicity and resilience sol-gel method is favored in the preparation of layered double hydroxide. The double metal substituted Mg_3/Al_1

LDHs were synthesized and the high crystalline single-phase compounds were successfully acquired. The LDH materials were synthesized by varying the metal composition and types which are copper (II) and manganese (II). According to the XRD analysis, the LDHs are crystallized in nanosized in the range of 8-11 nm and 12-15.4 nm for Cu and Mn consisting materials, respectively. Moreover, the d-values for LDH materials obtained are well-maintained and varied in the range of 7.62-7.85 Å. The various d-values are the consequence of the variations in the cationic ratio. The shifting in the XRD patterns of LDH was also examined. The shifting toward the longer wavelength was observed under the additions of Cu and Mn cationic ions in the LDH materials. As indicated by the UV-Vis spectra, the spectra vary depending on the type of doping materials. No peaks were observed in the visible region, indicating the complete replacement of transition metals Zn^{2+} , Cu^{2+} and Mn^{2+} into the Mg^{2+} site of LDH materials.

It is also noted that LDH materials containing Mn have smaller optical band gap energies compared to those containing Cu. Specifically, the optical band gap energies of MgZnCu/Al range from 2.98 to 3.02 eV, while those of MgZnMn/Al range from 2.24 to 2.51 eV. These findings confirm the influence of metal cationic additions on both the optical and structural properties of LDH materials.

Based on their morphology analysis, the structure of Cu- and Mn-based layered double hydroxides exhibits an irregular, plate-like morphology when the concentration of Zn is lower than that of the metal (Cu and Mn) concentrations. As the zinc composition increases, the morphology transitions to a more defined hexagonal plate-like structure, ultimately forming a 3D flower-like configuration.

The EDX analysis of the synthesized $\text{Mg}_{3-x-y}\text{Zn}_x\text{M}_y/\text{Al}$ (**M**: Cu and Mn; x,y: 0.00-0.06 mol) LDHs materials confirmed the presence of all desired elements, with the expected ratios of magnesium (Mg) and aluminum (Al) aligning with theoretical predictions. However, the concentrations of zinc (Zn), copper (Cu), and manganese (Mn) were observed to be lower than the desired values. This variation may be due to the low concentrations of these elements or their inhomogeneous distribution within the hydrotalcite structure. To achieve the desired composition, an increase in the concentration of the dopant elements is recommended.

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