

DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**INVESTIGATION OF OPTICAL PROPERTIES
AND STABILITIES OF SOME PHOSPHOR/
ORGANIC DYE/ COMBINATIONS IN
POLYMERIC MATRICES**

by

Beyza YILDIRIM

June, 2022

İZMİR

**INVESTIGATION OF OPTICAL PROPERTIES
AND STABILITIES OF SOME PHOSPHOR/
ORGANIC DYE/ COMBINATIONS IN
POLYMERIC MATRICES**

**A Thesis Submitted to the
Graduate School of Natural and Applied Sciences of Dokuz Eylül University
In Partial Fulfillment of the Requirements for the Degree of Doctor of
Philosophy in Chemistry**

by

Beyza YILDIRIM

June, 2022

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Ph.D. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled “**INVESTIGATION OF OPTICAL PROPERTIES AND STABILITIES OF SOME PHOSPHOR/ ORGANIC DYE/ COMBINATIONS IN POLYMERIC MATRICES**” completed by **BEYZA YILDIRIM** under supervision of **PROF. DR. KADRIYE ERTEKİN** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Doctor of Philosophy.

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Beyza YILDIRIM

**INVESTIGATION OF OPTICAL PROPERTIES AND STABILITIES
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IN POLYMERIC MATRICES**

ABSTRACT

Phosphors are commercially important chemicals because they are used as raw materials in mobile phones, personal computers, LCD screens, light emitting diode (LED) and white light emitting diode (WLED) technologies. In this thesis, commercially available phosphors of $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (LuAG: Ce^{3+}), $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (YAG: Ce^{3+}) and $\text{CaAlSiN}_3:\text{Eu}^{2+}$ (CASN: Eu^{2+}) were investigated to enhance their spectral properties rather than the known approaches. The green, yellow and red phosphors were chosen to represent a large spectral range available in the screen technologies as well as LED applications. All phosphors were prepared in thin film form in a polymethyl methacrylate (PMMA) matrix. The light harvesting materials of nano-scale ZnO and CuO, have been used to improve the spectral properties of the LuAG: Ce^{3+} and YAG: Ce^{3+} . In this process, fluorescence, phosphorescence, and excited state lifetimes were monitored and promising experimental results were obtained. Mechanisms indicating possible energy transfers between the species have been revealed. In the second part of the thesis, the energy transfer between phosphors and Tris (1,10-phenanthroline) ruthenium (II) hexafluorophosphate dye ($\text{Ru}(\text{phen})_3\text{PF}_6$) has been investigated. The binary blends of the LuAG: Ce^{3+} , YAG: Ce^{3+} and CASN: Eu^{2+} with the $\text{Ru}(\text{phen})_3\text{PF}_6$ exhibited promising results in the presence of the ionic liquid (IL). Long-term photo stabilities of the composites supported with the IL were investigated during 8 months. No significant effect of the IL on photo-stability levels was detected.

Keywords: LuAG: Ce^{3+} , YAG: Ce^{3+} , CASN: Eu^{2+} , phosphor, Ruthenium complex, ionic liquid, LED, WLED, photoluminescence, fluorescence, phosphorescence.

BAZI FOSFOR/ORGANİK BOYA KOMBİNASYONLARININ POLİMERİK MATRİKSLERDE OPTİK ÖZELLİKLERİNİN VE STABİLİTELERİNİN ARAŞTIRILMASI

ÖZ

Fosforlar cep telefonlarında, kişisel bilgisayarlarda, LCD ekranlarda, ışık yayan diyot (LED) ve beyaz ışık yayan diyot (WLED) teknolojilerinde hammadde olarak kullanıldığı için ticari olarak önemli kimyasallardır. Bu tez kapsamında, ticari amaçlarla kullanılan $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (LuAG: Ce^{3+}), $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (YAG: Ce^{3+}) ve $\text{CaAlSiN}_3:\text{Eu}^{2+}$ (CASN: Eu^{2+}) fosforlarının spektral özelliklerini geliştirmek için bilinen yaklaşımlar dışında farklı mekanizmalar araştırılmıştır. Yeşil, sarı ve kırmızı fosforlar, LED uygulamalarında olduğu kadar ekran teknolojilerinde de mevcut olan geniş bir spektral aralığı temsil edecek şekilde seçilmiştir. Tüm fosforlar, polimetil metakrilat (PMMA) matrisinde ince film şeklinde hazırlanmıştır. Işık hasadı yapabilen materyaller olarak da bilinen nano boyutlu ZnO ve CuO, LuAG: Ce^{3+} ve YAG: Ce^{3+} 'ın spektral özelliklerini geliştirmek için kullanılmıştır. Bu süreçte floresans, fosforesans ve uyarılmış hal ömürleri izlenmiş ve umut verici deneysel sonuçlar elde edilmiştir. Türler arasında olası enerji transferlerini gösteren mekanizmalar ortaya çıkarılmıştır. Tezin ikinci bölümünde, fosforlar ile Tris (1,10-fenantrolin) rutenyum (II) heksaflorofosfat boyası ($\text{Ru}(\text{phen})_3\text{PF}_6$) arasındaki enerji transferi incelenmiştir. LuAG: Ce^{3+} , YAG: Ce^{3+} ve CASN: Eu^{2+} ile $\text{Ru}(\text{phen})_3\text{PF}_6$ 'nın ikili karışımları, iyonik sıvının (IL) varlığında gelecek vadede sonuçlar sergilemiştir. IL ile desteklenen kompozitlerin 8 ay boyunca uzun süreli foto stabiliteleri araştırılmış ve IL'nin foto-stabilite seviyeleri üzerinde önemli bir etkisi saptanmamıştır.

Anahtar kelimeler: LuAG: Ce^{3+} , YAG: Ce^{3+} , CASN: Eu^{2+} , fosfor, Rutenyum kompleksi, iyonik sıvı, LED, WLED, fotoluminesans, floresans, fosforesans.

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CHAPTER ONE

INTRODUCTION

1.1 Phosphors; Inorganic Luminescent Materials

Phosphors are nano/micro-scale inorganic luminescent materials that emit light when excited by different types of energy covering the X- and gamma rays, UV-visible and even near infrared (NIR) region of the electromagnetic spectrum. They can also be excited by electrons, or an electric field.

Phosphors mainly consist of a host and small amounts of controlled levels of impurity ions activators or sensitizers. The activators or sensitizers are mainly group-B elements of the periodic table (transition metals) or the lanthanides or actinides which are also called as rare earths. These are responsible from the conversion of light or luminescence. The host part of a phosphor is generally in an oxide, nitride, sulfide and or in halide form. A wide variety of host-activator combinations provide many different colors from blue to red (Han, 2013).

The applications of phosphors are numerous including fluorescent lamps, LEDs, WLEDs, displays, cathode-ray tubes, X-ray screens, scintillators and sometimes paints exhibiting long persistent phosphorescence (Shionoya et al., 2018). Due to the longer lifetimes and lower energy consumption the LEDs and WLEDs are the promising light sources of the future. The white light emitting diodes include a LED chip, phosphor and the reflector cup in an epoxy resin whose critical material is the phosphor. In such a design the red-green-blue (RGB) phosphors are excited either by UV or blue light (Han, 2013). Therefore, most of the investigation focuses on these three colors and the yellow due to the wide range applications including the above mentioned technologies.

1.2 Classification of the Phosphors

Classification of phosphors can be made considering structure of the host (oxide, nitride, sulfide) or the emission color (blue, green, yellow, red) and sometimes according to the size of the regarding material (Sato et al., 2016). Herein we followed the classification performed according to the structure of the host. Table 1.1 indicates empirical formula and dopant information, excitation and emission maxima and quantum efficiency data of some of the green, yellow and red phosphors.

1.2.1 Oxide-type Phosphors

Examples of green ($\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}^{3+}$, $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, $\text{CaSc}_2\text{O}_4:\text{Ce}^{3+}$), yellow ($\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, $\text{Sr}_3\text{SiO}_5:\text{Eu}^{2+}$) and red ($\text{Sr}_2\text{ScAlO}_5:\text{Eu}^{2+}$, $\text{CsMgPO}_4:\text{Eu}^{2+}$) emitting oxide-type phosphors with different dopants are shown in Table 1.1. The production costs of oxide phosphors are less than their nitride-type correspondents due to low-cost precursors and low synthesis temperatures (Sato et al., 2016). They do not require the nitrogen atmosphere during their synthesis and provide chemically stable structure. (Jang and Jeon, 2007).

1.2.2 (Oxy)nitride-type Phosphors

Nitride-type phosphors activated with rare-earths provide chemical stability due to large covalence character of nitrogen compared with oxygen and strong chemical bonding with rigid networks. They also provide long wavelength excitation advantage due to larger crystal field splitting of the 5d orbitals of the activators in the nitride-type lattice (Shionoya et al., 2018; George et al., 2013). Examples of the nitride-type phosphors are yellow ($\text{Sr}_2\text{Si}_5\text{N}_8:\text{Ce}^{3+}$, $\text{CaAlSiN}_3:\text{Ce}^{3+}$, $\text{La}_3\text{Si}_6\text{N}_{11}\text{Ce}^{3+}$) and red ($\text{Ba}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$, $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$, $\text{SrAlSi}_4\text{N}_7:\text{Eu}^{2+}$, $\text{CaAlSiN}_3:\text{Eu}^{2+}$) emitting nitride-type phosphors with different dopants are shown in Table 1.1.

(Oxy)nitride phosphors can also be categorized as nitride-silicates and nitride-aluminosilicates consisting of the $\text{Si}(\text{N},\text{O})_4$ and $\text{Al}(\text{N},\text{O})_4$ tetrahedral sites in their

structure, respectively (Sato et al., 2016). Examples of green ($\text{BaSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$, $\text{Y}_4\text{Si}_2\text{O}_7\text{N}_2:\text{Ce}^{3+}$, $\beta\text{-SiAlON}:\text{Eu}^{2+}$) and yellow ($\text{CaSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$, $\text{Ca-}\alpha\text{-SiAlON}:\text{Eu}^{2+}$) forms can be encountered (See Table 1.1).

1.2.3 (Oxy)sulfide-type Phosphors

Alkaline earth containing phosphors of $\text{CaLaGa}_3\text{S}_7:\text{Eu}^{2+}$, $\text{Sr}_8\text{Al}_{12}\text{O}_{24}\text{S}_2:\text{Eu}^{2+}$ and $\text{CaZnOS}:\text{Eu}^{2+}$ are the examples of (oxy)sulfide phosphors. They may provide yellowish-green, orange and red colors (See Table 1.1). However, they suffer from instability due to the low water resistance (Sato et al., 2016).

1.2.4 (Oxy)halide-type Phosphors

The (oxy)halide-type phosphors are generally activated with rare earths. The $\text{Ca}_{10}(\text{Si}_2\text{O}_7)_3\text{Cl}_2:\text{Eu}^{2+}$, $(\text{Ca,Sr})_7(\text{SiO}_3)_6\text{Cl}_2:\text{Eu}^{2+}$ and $\text{Sr}_3\text{Al}_2\text{O}_5\text{Cl}_2:\text{Eu}^{2+}$ are the green, yellow and red emitting examples of the this group of phosphors and they are shown in Table 1.1 (Sato et al., 2016).

Table 1.1 Formula and dopant information, excitation and emission maximum ($\lambda_{\max}^{\text{ex}}$: excitation, $\lambda_{\max}^{\text{em}}$: emission maximum) and quantum efficiency data of some of the green, yellow and red phosphors (Most of the information given in this table was taken from (Sato et al., 2016))

Host material	Dopant	Concentration (mol%)	$\lambda_{\max}^{\text{ex}}$ (nm)	$\lambda_{\max}^{\text{em}}$ (nm)	Emission color	QE (in/ex)
Oxide						
Ba ₂ MgSi ₂ O ₇	Eu ²⁺	7	395	505	Green	92%/–
Ca ₃ Sc ₂ Si ₃ O ₁₂	Ce ³⁺	3	450	505	Green	41%/–
Lu ₃ Al ₅ O ₁₂	Ce ³⁺	6	450	508	Green	<100%/–
Ba ₉ Sc ₂ Si ₆ O ₂₄	Eu ²⁺	5	450	508	Green	–/–
CaSc ₂ O ₄	Ce ³⁺	1	450	510	Green	–/44%
Y ₃ Al ₅ O ₁₂	Ce ³⁺	3	450	545	Yellow	75%/–
Li ₂ SrSiO ₄	Eu ²⁺	0.5	450	562	Yellow	–/–
Sr ₃ SiO ₅	Eu ²⁺	3	400	580	Yellow	82%/–
Ba ₃ Sc ₄ O ₉	Ce ³⁺	0.1	437	583	Yellow	40%/–
Sr ₂ ScAlO ₅	Eu ²⁺	5	450	620	Red	48%/–
NaMgPO ₄	Eu ²⁺	2.5	450	628	Red	81%/–
CsMgPO ₄	Eu ²⁺	4	410	630	Red	10%/–

Table 1.1 Continues

Host material	Dopant	Concentration (mol%)	$\lambda_{\text{max}}^{\text{ex}}$ (nm)	$\lambda_{\text{max}}^{\text{em}}$ (nm)	Emission color	QE (in/ex)
Oxy(nitride)						
BaSi ₂ O ₂ N ₂	Eu ²⁺	5	450	495	Green	71%/–
Y ₄ Si ₂ O ₇ N ₂	Ce ³⁺	5	390	500	Green	–/–
β-SiAlON	Eu ²⁺	1.8	450	535	Green	70%/61%
SrSi ₂ O ₂ N ₂	Eu ²⁺	5	380	537	Green	91%/–
Sr ₂ Si ₅ N ₈	Ce ³⁺	0.1	397	560	Yellow	–/–
CaSi ₂ O ₂ N ₂	Eu ²⁺	2	400	560	Yellow	76%/–
CaAlSiN ₃	Ce ³⁺	10	460	575	Yellow	71%/50%
Ca-α-SiAlON	Eu ²⁺	7.5	450	590	Yellow	56%/75%
La ₃ Si ₆ N ₁₁	Ce ³⁺	10	460	595	Yellow	–/42%
Ba ₂ Si ₅ N ₈	Eu ²⁺	2	460	580	Red	79%/–
Ca ₂ Si ₅ N ₈	Eu ²⁺	1.4	460	610	Red	45%/–
Sr ₂ Si ₅ N ₈	Eu ²⁺	2	450	620	Red	87%/71%

Table 1.1 Continues

Host material	Dopant	Concentration (mol%)	$\lambda_{\text{max}}^{\text{ex}}$ (nm)	$\lambda_{\text{max}}^{\text{em}}$ (nm)	Emission color	QE (in/ex)
Oxy(nitride)						
SrAlSi ₄ N ₇	Eu ²⁺	2	450	635	Red	>53%/–
CaAlSiN ₃	Eu ²⁺	1.6	460	660	Red	83%/70%
(Oxy)sulfide						
KLuS ₂	Eu ²⁺	0.1	390	520	Green	–/–
CaLaGa ₃ S ₇	Eu ²⁺	15	460	554	Yellowish - green	–/–
Sr ₈ Al ₁₂ O ₂₄ S ₂	Eu ²⁺	8	450	605	Yellowish - orange	–/–
CaZnOS	Eu ²⁺	4	460	650	Red	36%/–
(Oxy)halide						
Ca ₁₀ (Si ₂ O ₇) ₃ Cl ₂	Eu ²⁺	30	395	508	Green	–/–
(Ca,Sr) ₇ (SiO ₃) ₆ Cl ₂	Eu ²⁺	4	400	580	Yellow	–/–
Sr ₃ Al ₂ O ₅ Cl ₂	Eu ²⁺	5	400	620	Red	>90%/–

1.3 Crystal Structure of Phosphors

Phosphors are generally made up of a host and small amount of activator and/or sensitizer ions, that are intentionally added into the structure. Luminescent properties of phosphors arise from the sensitizer and activator ions entrapped in the host which generally work together during the luminescence process (Shionoya et al., 2018). The host is made up of a crystalline structure; a three-dimensional network including repetitive structures and sometimes is called as “**lattice**”. The repetitive part of the crystal structure is known as “**unit cell**”. There are different types of crystal structures, depending on the unit cell geometry where the structure of the cell has been defined shortly by using the axial lengths and interaxial angles. There are seven basic unit cell types namely; **cubic**, **tetragonal**, **hexagonal**, **orthorhombic**, **rhombohedral**, **monoclinic** and **triclinic** (Callister & Rethwisch, 2018). Figure 1.1 indicates structure of these unit cell types in terms of their geometry axial lengths and interaxial angles.

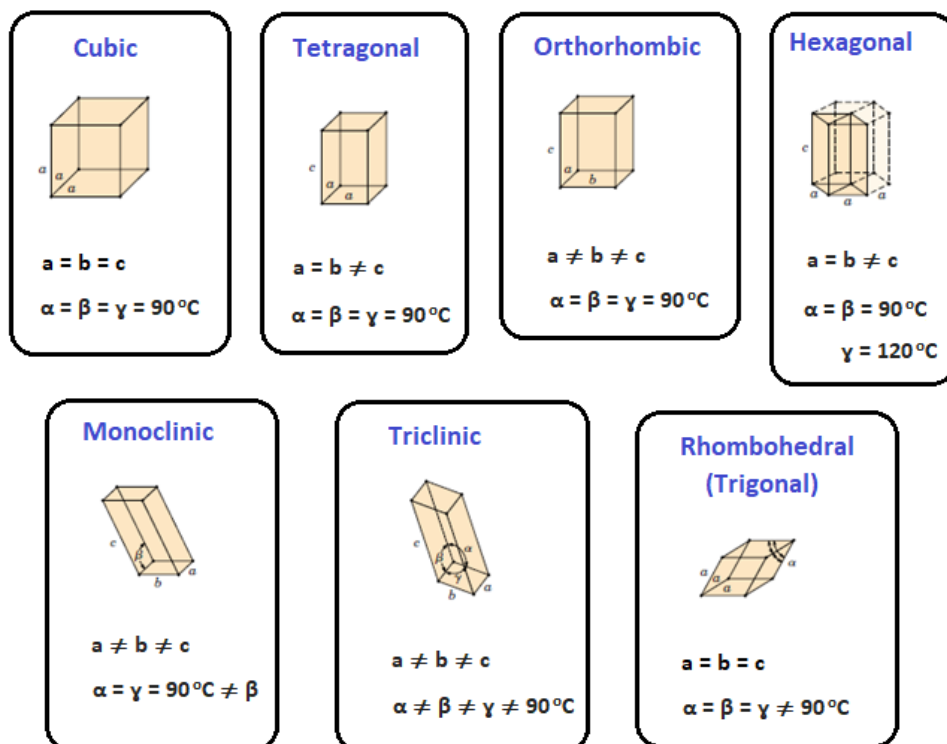


Figure 1.1 Structure of seven unit cell types with their geometry axial length and interaxial angle information (Was taken from (Callister & Rethwisch, 2018))

1.4 Luminescence of the Phosphors

In the crystalline structure of a phosphor, atoms of the unit cell, activator and/or sensitizer ions are interacting with each other. By the influence of these interactions, energy levels split to bands known as the “valence band” and the “conduction band” (See Figure 1.2) (Togay, 2012).

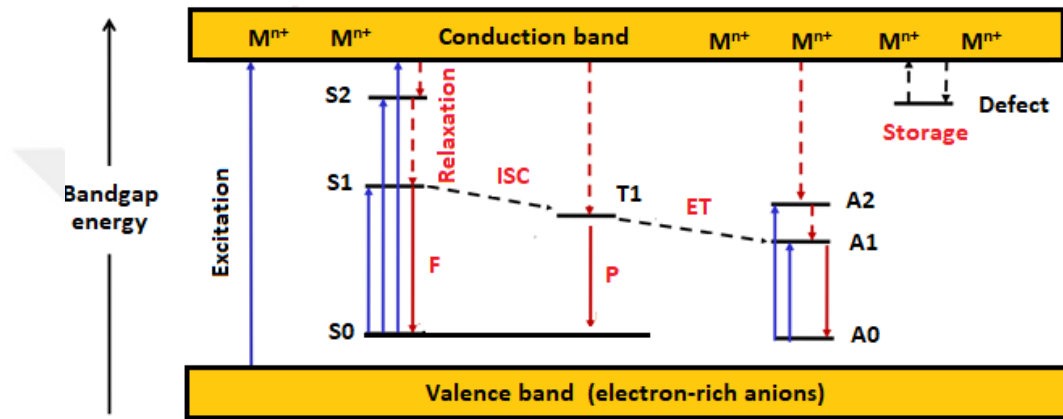


Figure 1.2 Valence band and the conduction band approach two explain the energy level splitting in a host. F: Fluorescence, P: Phosphorescence, S_0 : Ground singlet state, S_1 and S_2 : Excited singlet states, T_1 : Triplet level, A_0 , A_1 and A_2 : Energy levels of the activator ions, ISC: Intersystem crossing, ET: Energy transfer (Was taken from (Jüstel, 2022) and re-arranged)

Photoluminescence takes place upon the absorption of light which causes formation of an excited state, which then emits photon as it turns back to the ground state. Photoluminescence can be classified as fluorescence and phosphorescence. In case of fluorescence, an electron is excited one of the singlet excited states (S_1 or S_2) and then turns back into the S_1 level and following to the ground state (S_0). This phenomenon is known as fluorescence and takes place within nanoseconds. In case of phosphorescence however, the excited electron is relaxed into the S_1 state and then undergoes “intersystem crossing” spiking to the triplet excited state (T_1). Emission occurs via a “spin-forbidden transition” from the T_1 level to the ground state (S_0). This process is slower than that of the fluorescence and takes place on the order of “microsecond” or “millisecond” time scales (Lustig & Li, 2018).

Luminescent materials may have some defects in their structure including vacancies, interstitials and impurity ions. According to the position of energy level of the defect, they may be named as traps or luminescent centers. The defects lying near the conduction band are generally called “*traps*”, and the ones located near the valence band are named “*luminescent centers*” Luminescence may also be produced by these defects via radiative transitions including recombination of electrons with holes. (Krbetschek et al., 1997).

1.4.1 Quantum Yield and Lifetime

Besides the excitation and emission-based data, luminescence also can be quantified by **quantum yield** and **lifetime** measurements. **Lifetime**, is the time needed for the intensity of luminescence drops its approximately 37 percent (1/e) of its original intensity (Togay, 2012). Figure 1.3 illustrates monoexponential and multiexponential decay curves of a luminescent material. The decay of the fluorescence intensity as a function of time is an exponential function and can be defined by the following equation:

$$I(t) = I_0 \cdot e^{(-t/\tau)} \quad (1.1)$$

where $I(t)$ is the fluorescence intensity measured at any time t , $I(0)$ is the initial intensity, and τ is the fluorescence lifetime. However, this function sometimes may appear as bi-exponential or tri-exponential forms (Herman et al., 2022).

While the monoexponential decay takes place without energy transfer, the bi- and tri exponential decays may indicate presence of quenching process, energy transfer or afterglow (Jüstel, 2022).

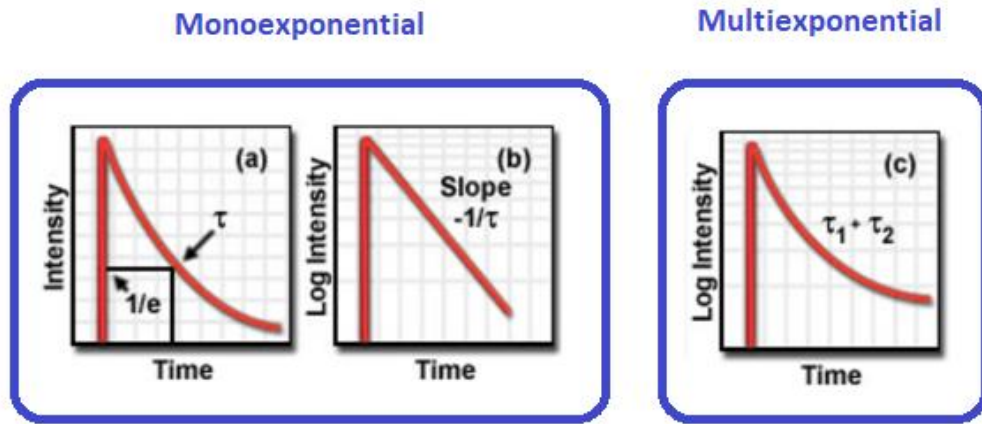


Figure 1.3 Schematic representation of monoexponential and bi-exponential decays (Was taken from (Herman et al., 2022) and re-arranged)

On the other hand, the **quantum yield (QY)** can simply be defined as “the ratio of number of emitted photons to number of absorbed photons” (Gaft et al., 2005). In case of solid state the quantum efficiency is mentioned as “external” and “internal” quantum efficiency. **External quantum efficiency (EQE)** includes re-absorbed photons. The **internal quantum efficiency (IQE)** however, is defined as the ratio of the number of photons emitted to the number of photons absorbed by the sample. Internal quantum efficiency is inversely proportional to decay time whereas external quantum efficiency has no correlation with the decay time. Therefore, the measurement of the IQE relies on the measurement of decay times, the radiative and nonradiative rates. In mathematical terms, it can be defined as;

$$\Phi = k_r / (k_{nr} + k_r) \quad (1.2)$$

where, Φ , k_r and k_{nr} are the quantum yield, radiative and non-radiative decay rates, respectively.

$$k_r = \Phi / \tau \quad (1.3)$$

$$k_{nr} = (1 - \Phi) / \tau \quad (1.4)$$

Herein, the Φ and τ can be extracted from the experimental data, and the k_r and k_{nr} can be calculated from the decay time (Lakowicz, 2006).

1.4.2 Stoke's Shift

Stoke's shift ($\Delta\lambda$) is simply the difference between the absorption and emission maximum in terms of wavelength or wave number. The energy of the emission is generally less than the energy of the absorption. Therefore, the emission maximum generally appears at further wavelengths with respect to the absorption or excitation maximum. This phenomenon is observed in the solution phase firstly. However, today it is adopted to the solid state (Lakowicz, 2006).

1.4.3 Energy Transfer (ET)

Energy transfer (ET) is a process where the excitation energy of an ion is transferred to another ion encapsulated in a crystal structure. A donor (D) (sometimes named as the sensitizer), and an acceptor (A), (also called activator), play role in the ET. This process is intentionally used in phosphors to enhance the quantum efficiency or to manipulate the emission maximum towards red or blue wavelengths (Sato et al., 2016).

1.4.4 Electronic Transitions in Rare Earth Ions

The typical spectral properties of the rare earth (RE) ions arise from the presence of 4f electrons in their structure which provide a number of discrete energy levels (Sato et al., 2016). The rare earths including Ce^{3+} , Pr^{3+} , Tb^{3+} , Er^{3+} and Eu^{2+} that can be excited directly from the $4f^n$ configuration to the $4f^{n-1} 5d^1$. The 4f-to-5d transitions are strongly dependent on the host and may exhibit wide variety throughout the electromagnetic spectrum between the UV and red wavelengths (Han, 2013).

1.4.5 Influence of Crystal Field

The micro-environment surrounding the activator ions is effective on the luminescence of phosphors. The surroundings also known as ligands. The crystal field on the other hand can be defined as the electric field inducing a particular ion and

arises from the surroundings. The orbital states of 5d electrons of rare earths and 3d electrons of transition metals split by the effect of crystal field. This crystal field is important on luminescence properties of phosphors and depends on the several factors including the number of electrons lying in the d orbitals, oxidation state of the metal, the geometry of the crystal and nature of the ligand (Han, 2013). Figure 1.4 indicates splitting of energy levels in tetrahedral, octahedral and square-planar fields.

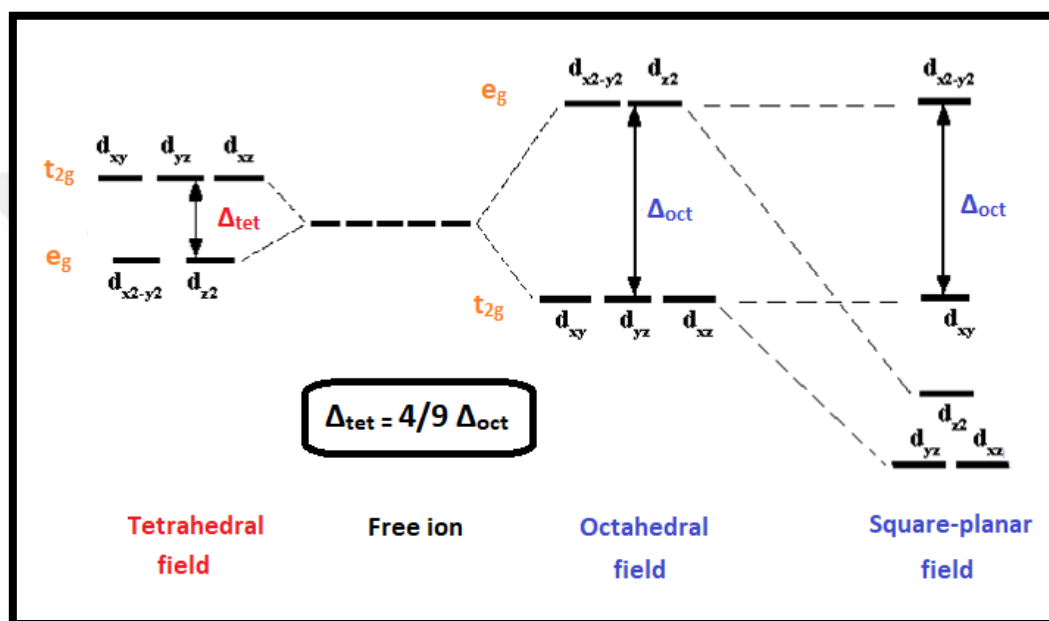


Figure 1.4 Schematic representation of energy levels in tetrahedral, octahedral and square-planar fields (Was taken from (Toppr, 2022) and re-arranged accordingly)

Effect of the surroundings on the potential 4f-5d electronic transitions has been summarized by Sato et al. (2016) with the following figure where nephelauxetic and crystal field splitting effects were shown schematically (Figure 1.5) (Sato et al., 2016). The nephelauxetic effect is largely concerned with covalency of the metal-ligand bond.

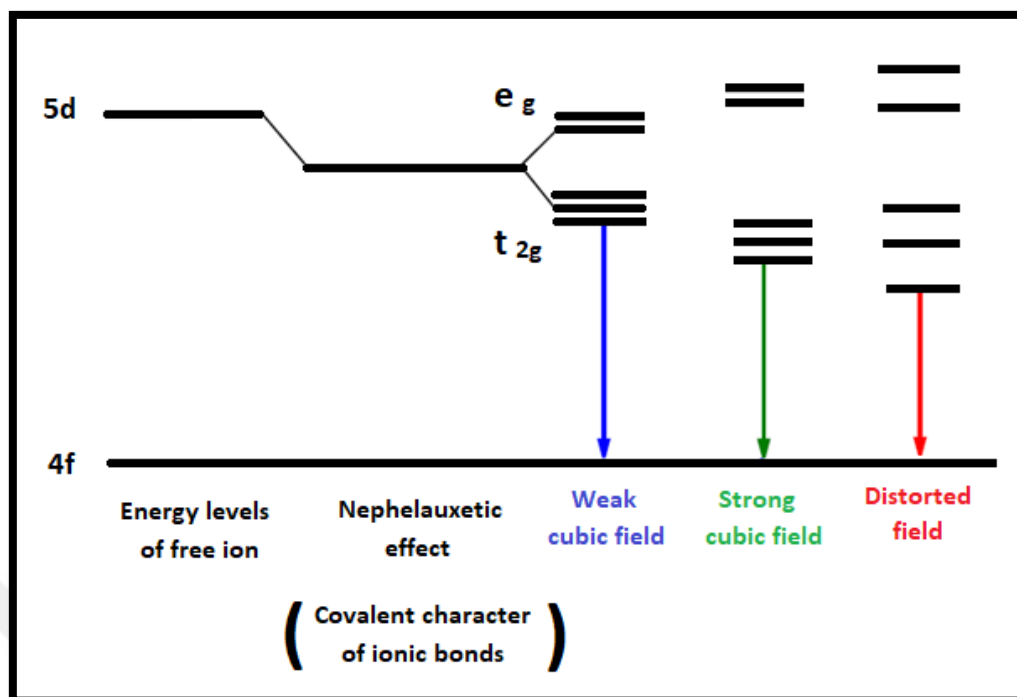


Figure 1.5 Schematic representation of potential effects on 5d energy levels of the rare earth ions like Eu^{2+} and Ce^{3+} (Was taken from (Sato et al., 2016) and re-arranged)

1.5 Aim of this Thesis

The green, yellow and red emitting phosphors are intensively used in the production of light emitting diodes (LEDs), white light emitting diodes (WLEDs), plasmas, LCD, cathode ray tubes and other lightening applications including fluorescent lamps. In this thesis we investigated three representative pigments of Ce^{3+} activated $\text{Lu}_3\text{Al}_5\text{O}_{12}$ ($\text{LuAG}:\text{Ce}^{3+}$) and $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}$ ($\text{YAG}:\text{Ce}^{3+}$) and Eu^{2+} activated CaAlSiN_3 ($\text{CASN}:\text{Eu}^{2+}$) which were green, yellow and red colored phosphors, respectively. Due to the intensive utilization of the phosphors in the electronic and lightening industry, synthesis of the cost effective and robust phosphors is a target research field. In order to provide, high quantum efficiency and brightness in the desired region some rare earths are intentionally added into their structure. Sometimes one type of rare-earth may be enough. However, in some cases, a dopant and a co-dopant are used at the same time to perform an energy transfer within the crystal to provide higher efficiency. However, the rare earths used in the structure of the phosphors are expensive and

probably are not sustainable. Therefore, alternative ways should be discovered to enhance the performance of phosphors rather than the rare-earths. Utilization of the light harvesting nano-scale metal oxides together with the phosphors or preparation of dye-phosphor blends may be promising to obtain higher brightness. By this way, the effective band width or the emission maximum of the phosphor can be manipulated.

In this thesis, we intended to use the commercially available phosphors of the LuAG:Ce³⁺ and YAG:Ce³⁺ along with the nano-scale metal oxides of zinc oxide (ZnO) and copper (II) oxide (CuO) to improve the spectral properties of the phosphors in polymeric matrices. We also used the Ruthenium dye; Tris (1,10-phenanthroline) ruthenium (II) hexafluorophosphate (Ru(phen)₃PF₆) together with the LuAG:Ce³⁺, YAG:Ce³⁺ and CASN:Eu²⁺ to understand the potential spectral interactions to enhance the brightness of the phosphors. Herein we tested the composites in the absence and presence of the ionic liquid during 8 months to understand its effect on long-term photostability of the dye.

The chosen phosphors are the most intensively used materials of lightening industry as well as optoelectronics. On the other hand, the Ruthenium dye is one of the dopant materials used in “organic light emitting diodes; OLEDs”. We prepared our phosphor blends with nano-scale metal oxides or Ru(phen)₃PF₆ in a poly (methyl methacrylate) (PMMA) matrix which is also a desired polymer in screen technologies.

Therefore, we aimed to enhance optical properties of the phosphors with cost-effective and/or sustainable materials rather than expensive rare earths. Because the light emitting diodes or white light emitting diodes will be the light source of the future. Additionally, today the screen of a mobile phone or computer looks like the most expensive component of a PC or smartphone. Utilization of the cost-effective materials may provide a way to make these devices more accessible.

CHAPTER TWO

EXPERIMENTAL METHODS AND INSTRUMENTATION

2.1 Reagents

The green and yellow phosphors; $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (LuAG: Ce^{3+}) and $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (YAG: Ce^{3+}) were provided from Mitsubishi Chemical Corporation. Metal oxides of ZnO and CuO were synthesized by our co-workers. The synthesis chemicals; zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and copper(II)acetate ($\text{Cu}(\text{CO}_2\text{CH}_3)_2 \cdot \text{H}_2\text{O}$) were purchased from Sigma-Aldrich and Merck, respectively. Triethanolamine (TEA) was from Riedel-de Haen. The isopropyl alcohol, acetic acid, and ethanolamine were provided from Merck. The polymeric matrix material of polymethylmethacrylate (PMMA) and its solvent Tetrahydrofuran (THF ≥ 99) were supplied from Sigma Aldrich. The ruthenium dye Tris (1,10-phenanthroline) ruthenium (II) hexafluorophosphate ($\text{Ru}(\text{phen})_3\text{PF}_6$) and the ionic liquid 1-Butyl-3-methyl-imidazolium-tetrafluoroborate (BMIM BF_4) were provided from Sigma-Aldrich. The Mylar (TM type) substrate was purchased from DuPont Teijin Films Company.

2.2 Structural Specification of the Utilized Phosphors and the Ruthenium Complex

The phosphors of LuAG: Ce^{3+} , YAG: Ce^{3+} and CASN: Eu^{2+} were purchased from Mitsubishi Chemicals and used without further purification or treatment to modify their size. We recorded the XRD and XPS spectra of the phosphors only to verify the composition and purity levels of them. Therefore, we did not present interpretation of the spectral data in this thesis. Similarly, the Tris (1,10-phenanthroline) ruthenium (II) hexafluorophosphate ($\text{Ru}(\text{phen})_3\text{PF}_6$) was also provided commercially and used without further purification.

2.2.1. Specification of $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (LuAG: Ce^{3+})

The XRD and XPS spectra of the commercially available LuAG: Ce^{3+} were recorded to control the potential impurities as well as crystal structure (See Figure 2.1 and 2.2 and Table 2.1 and 2.2). The XRD spectra supported the cubic garnet crystal structure of the LuAG: Ce^{3+} ($\text{Lu}_3\text{Al}_5\text{O}_{12}$) and was found to be in accordance with the JCPDS card No. 00-056-1464. The XPS analysis of the phosphor revealed all of the elements and presence of the Lu^{3+} . However, trace amount of Ce^{3+} was not appeared on the XPS analysis. Additionally, trace amount of Ca^{2+} and some C appeared in the spectrum can be attributed to the presence of some extent of CaCO_3 and contamination from the adhesives, respectively.

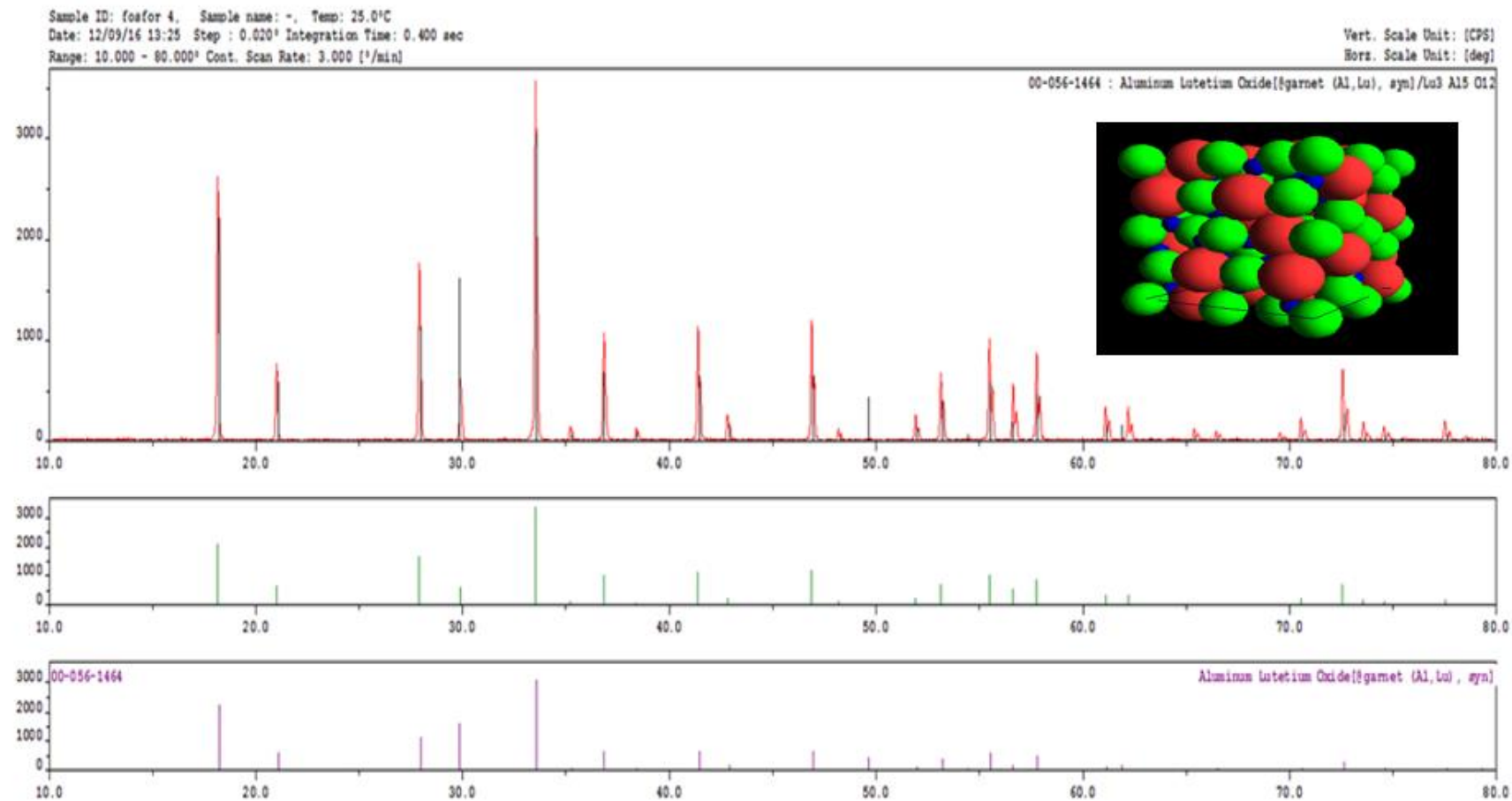


Figure 2.1 The XRD data of the LuAG:Ce³⁺ phosphor

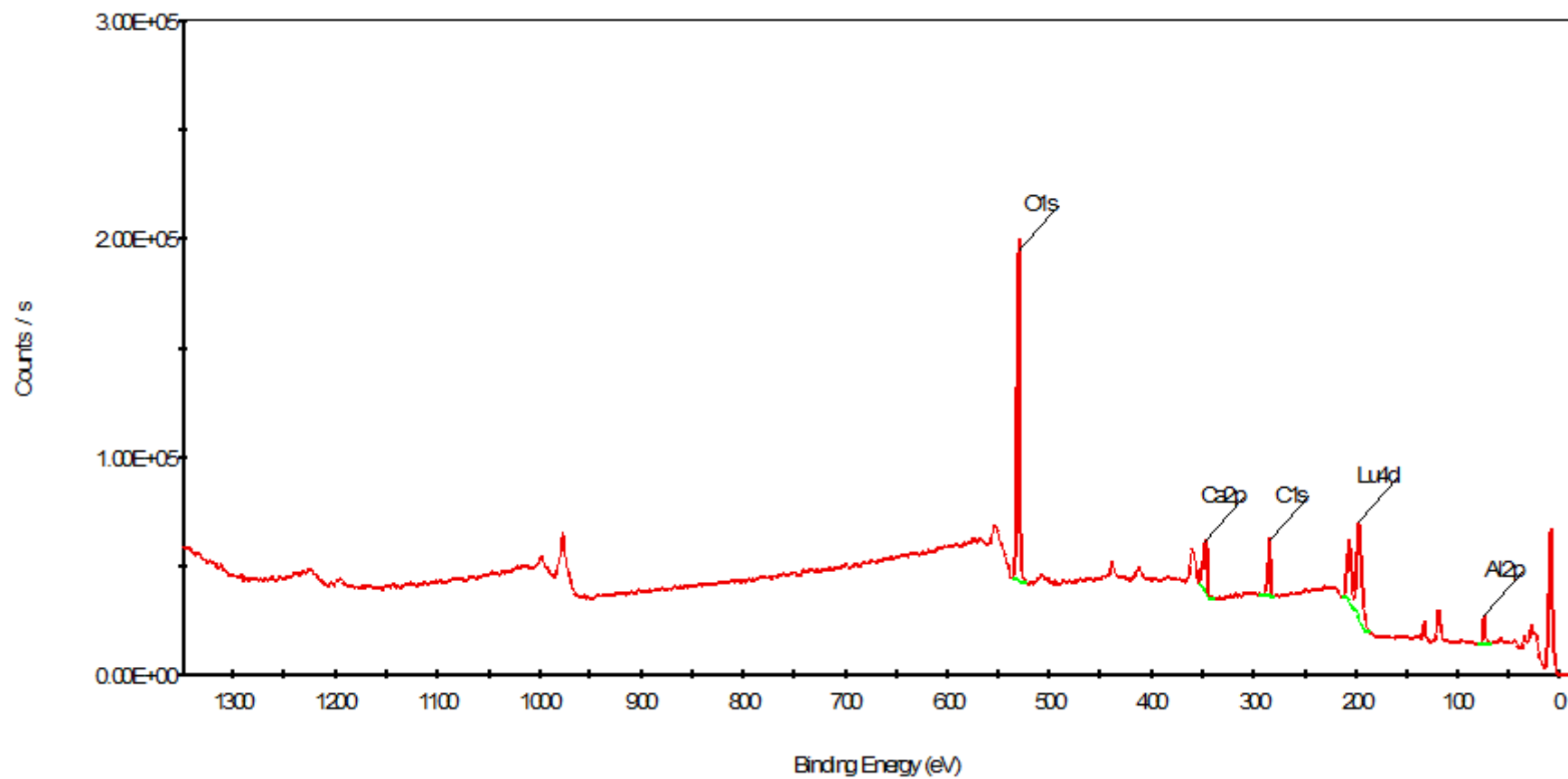


Figure 2.2 The XPS spectra of the LuAG:Ce³⁺ phosphor

Table 2.1 The XPS Parameters for LuAG:Ce³⁺ phosphor

Parameter	
Total acquisition time	2 mins 16.1 secs
Number of Scans	10
Source Gun Type	Al K Alpha
Spot Size	400 μ m
Lens Mode	Standard
Analyser Mode	CAE: Pass Energy 150.0 eV
Energy Step Size	1.000 eV
Number of Energy Steps	1361

Table 2.2 The binding energies, FWHM values and detailed chemical properties of the peaks of the elements in LuAG:Ce³⁺ phosphor

Name	Peak BE	FWHM eV	Area (P) CPS.eV	Atomic %	Q
O1s	530.23	3.059	484956.73	47.85	1
Lu4d	196.34	4.920	395637.05	6.67	1
Al2p	73.79	2.909	42272.60	18.01	1
C1s	284.36	2.988	87682.70	22.10	1
Ca2p	346.51	1.831	104548.88	5.37	1

2.2.2 Specification of (Y,Gd)₃Al₅O₁₂:Ce³⁺ (YAG:Ce³⁺)

Similarly, both the XRD and XPS spectra of the commercial YAG:Ce³⁺ were recorded and depicted in Figure 2.3 and 2.4 and Table 2.3 and 2.4, respectively. The XRD spectra revealed the cubic garnet crystal structure of the tri yttrium dialuminum tris(aluminate) (Y₃Al₁₂(AlO₄)₃) and was found to be in accordance with the JCPDS card No. 01-082-0575. The XPS analysis of the YAG: Ce³⁺ revealed all of the elements including Ce³⁺. However, the Gd³⁺ was not appeared on the XPS analysis.

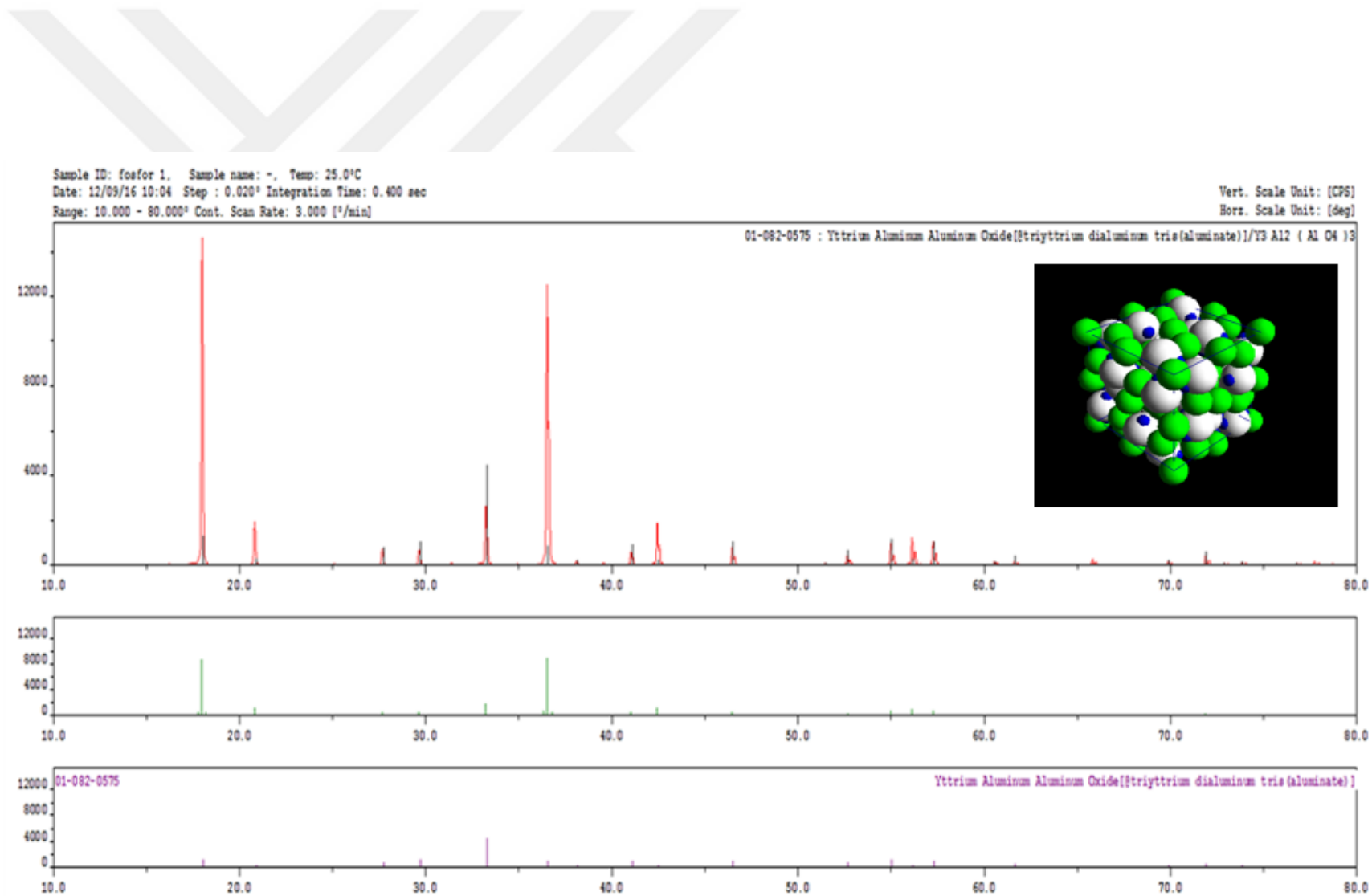


Figure 2.3 The XRD data of the YAG:Ce³⁺ phosphor

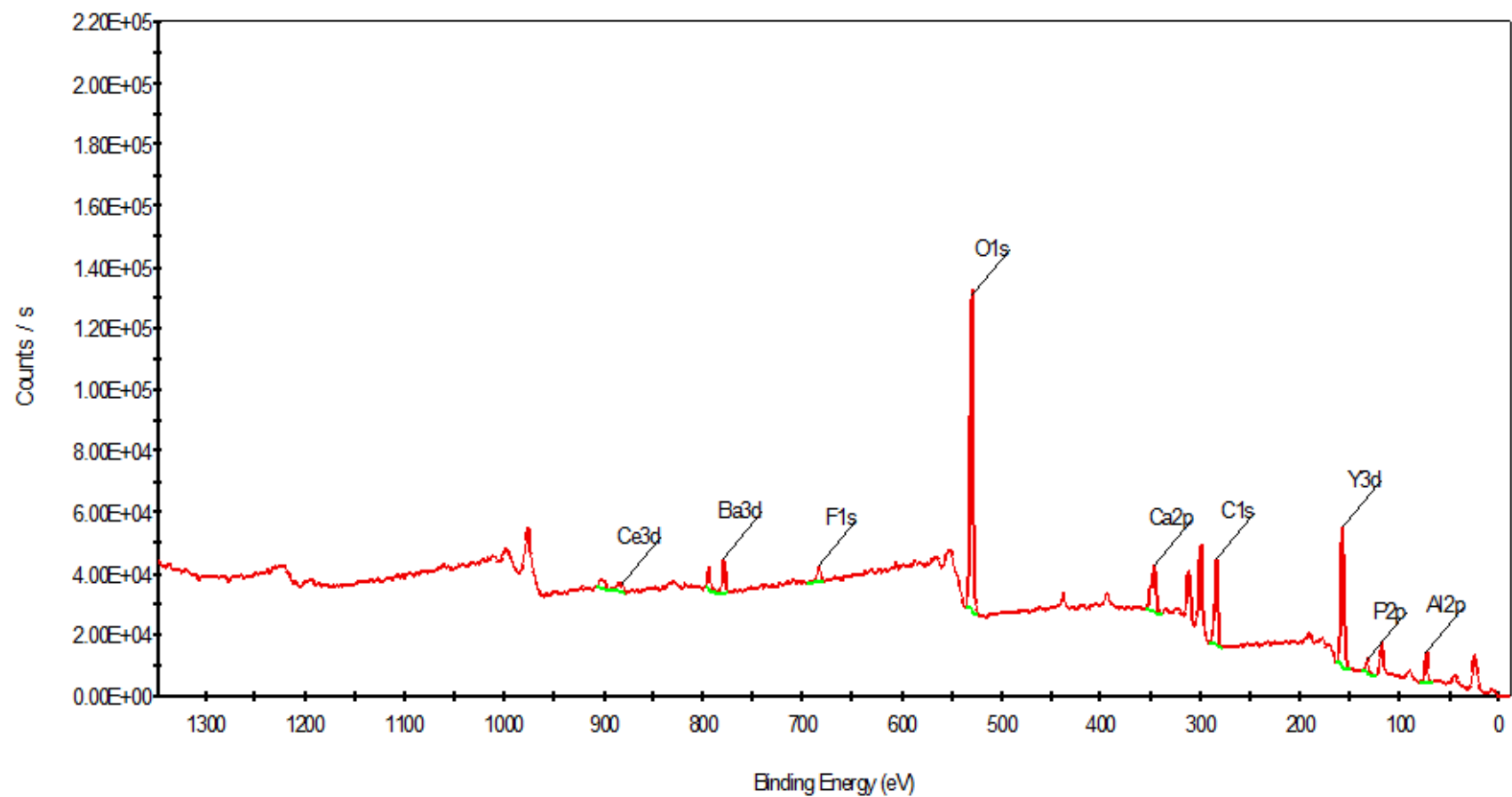


Figure 2.4 The XPS spectra of the YAG:Ce³⁺ phosphor

Table 2.3 The XPS Parameters for YAG:Ce³⁺ phosphor

Parameter	
Total acquisition time	2 mins 16.1 secs
Number of Scans	10
Source Gun Type	Al K Alpha
Spot Size	400 μ m
Lens Mode	Standard
Analyser Mode	CAE: Pass Energy 150.0 eV
Energy Step Size	1.000 eV

Table 2.4 The binding energies, FWHM values and detailed chemical properties of the peaks of the elements in YAG:Ce³⁺ phosphor

Name	Peak BE	FWHM eV	Area (P) CPS.eV	Atomic %	Q
O1s	529.49	2.209	373898.06	38.73	1
Y3d	157.02	4.239	205273.42	8.55	1
C1s	283.50	1.957	103845.75	27.47	1
Ba3d	778.90	3.402	69219.73	0.58	1
Al2p	72.46	1.892	32259.75	14.42	1
Ca2p	346.23	3.196	76651.57	4.13	1
P2p	131.92	3.221	18246.51	3.77	1
F1s	683.60	3.677	26470.47	2.01	1
Ce3d	881.18	3.119	42963.38	0.33	1

2.2.3 Specification of CaAlSiN₃:Eu²⁺ (CASN:Eu²⁺)

The XRD and XPS spectra of the commercial CASN:Eu²⁺ were recorded and shown in Figure 2.5 and 2.6 and Table 2.5 and 2.6. The XRD spectra indicated existence of the dmisteinbergite, (CaAl₂Si₂O₈) and meta-sillimanite (Al₂SiO₄)O phases and was found to be in accordance with the JCPDS card No. of 00-051-0064 and 01-070-7056. The XPS analysis of the CASN:Eu²⁺ supported presence of all of the elements expect that of Eu²⁺.

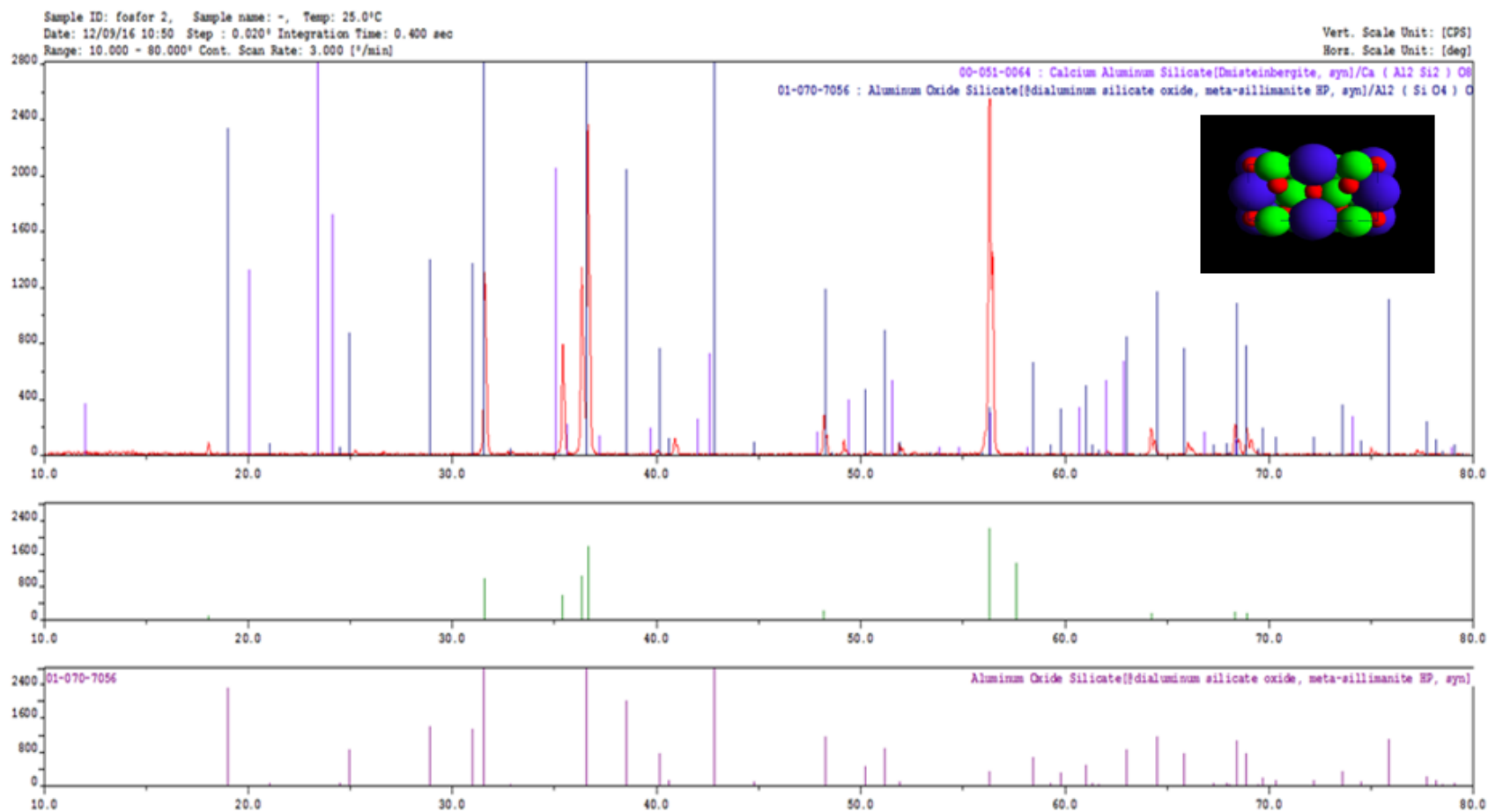


Figure 2.5 The XRD data of the CASN:Eu²⁺ phosphor

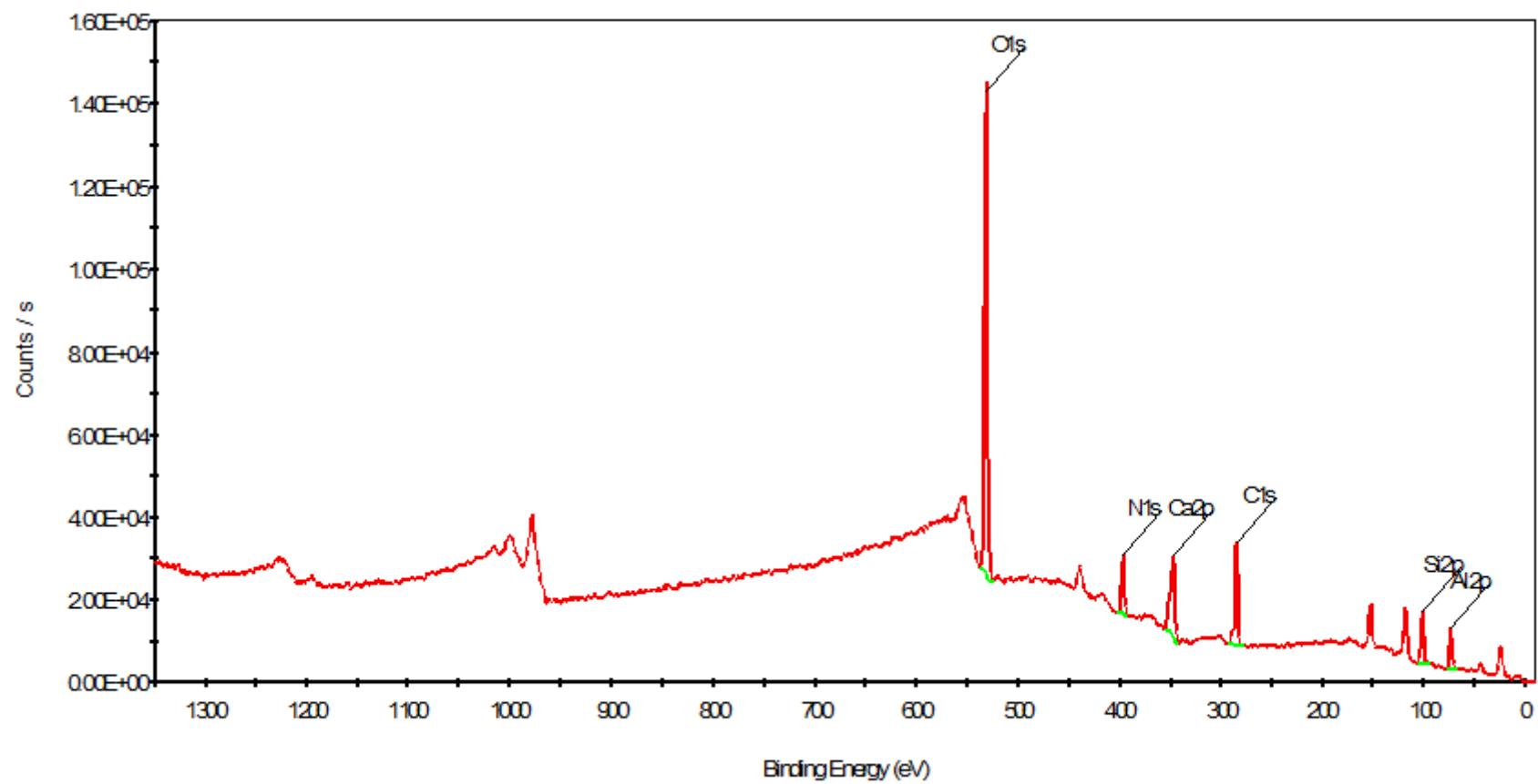


Figure 2.6 The XPS spectra of the CASN:Eu²⁺ phosphor

Table 2.5 The XPS Parameters for CASN:Eu²⁺ phosphor

Parameter	
Total acquisition time	2 mins 16.1 secs
Number of Scans	10
Source Gun Type	Al K Alpha
Spot Size	400 μm
Lens Mode	Standard
Analyser Mode	CAE: Pass Energy 150.0 eV
Energy Step Size	1.000 eV
Number of Energy Steps	1361

Table 2.6 The binding energies, FWHM values and detailed chemical properties of the peaks of the elements in CASN:Eu²⁺ phosphor

Name	Peak BE	FWHM eV	Area (P) CPS.eV	Atomic %	Q
O1s	531.19	3.200	395943.37	39.97	1
C1s	284.41	2.807	84949.56	21.89	1
Al2p	73.76	2.931	31421.85	13.69	1
N1s	396.33	3.109	47108.34	7.15	1
Si2p	101.36	3.104	42172.12	12.22	1
Ca2p	347.10	5.402	96656.30	5.07	1

2.3 Instruments and Apparatus

A **spectrofluorometer** equipped with a Xenon light source from Edinburgh Instruments (FLS920) was used throughout the excitation/emission-based measurements (See Figure 2.7). The decay times were recorded by the same instruments in mode of time-correlated single-photon counting (TCSPC) by using a pulsed laser or a microsecond flash lamp as the excitation source. The excitation and emission slits were adjusted prior to each measurement, optimized each time. The Instrument Response Function (IRF) correction was performed by using a suspension

of colloidal silica (LUDOX 30%, Sigma Aldrich) in water. Thermo-Scientific Evolution 600 Instrument was used for **the UV–VIS transmittance and reflectance spectra** of the samples which was equipped with a “diffuse reflectance accessory” and an “integrating sphere”.

X-ray diffraction instrument (XRD, Thermo-Scientific, ARL K α) equipped with a Cu K α radiation source was used for the identification of the crystal structures of the solid samples. A Thermo-Scientific instrument including an Al-K α irradiation source was used for **the XPS analysis** of the phosphors and metal-oxides. **Field emission scanning electron microscope (SEM)** of Zeiss Sigma 500 was used to determine the particle morphologies of the samples.

A spin on device was used for the preparation of the thin films. Thicknesses of the films were measured by using surface profilometer (Ambios Technology XP-2).

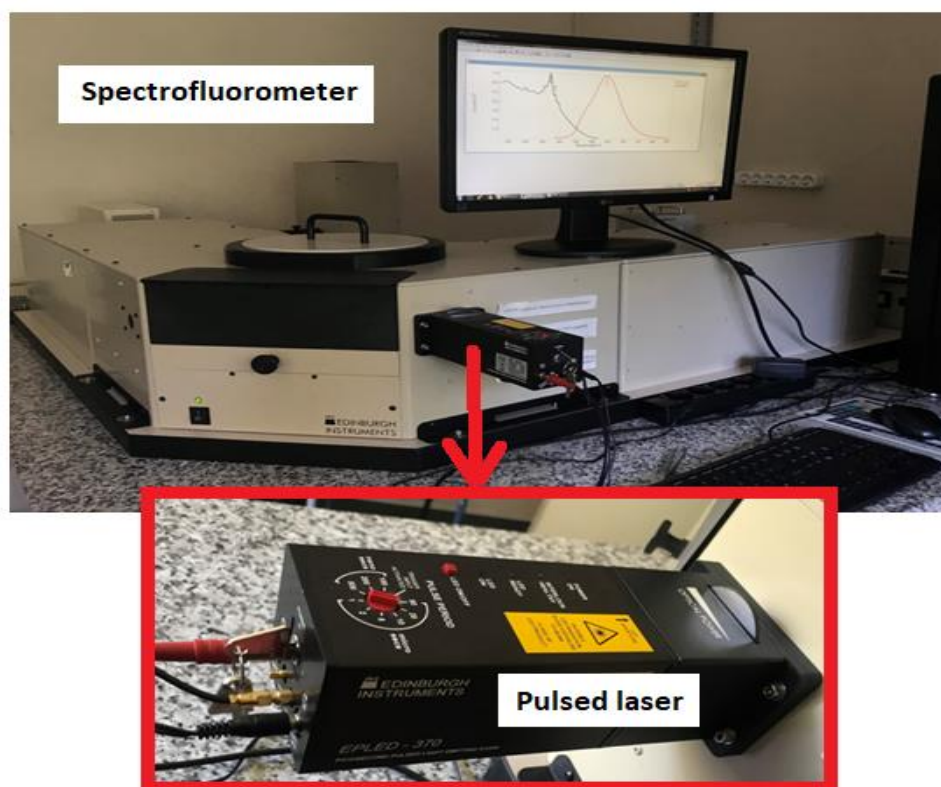


Figure 2.7 Photograph of the the spectrofluorometer instrument and pulsed laser light source (Personal archive, 2022)

CHAPTER THREE

MANIPULATION OF BRIGHTNESS AND DECAY KINETICS OF LuAG:Ce³⁺ AND YAG:Ce³⁺ BY SIMPLE METAL OXIDES IN POLYMERIC MATRICES

3.1 Introduction

Today, production of new, long-life, and efficient phosphors continues to be the research target of scientists due to their wide range of applications including optoelectronic, lighting and screen technologies (Bardsley et al., 2014; Birkel et al., 2012; Jin et al., 2016; Li, Y. Q. et al., 2013; Li Y. et al., 2015; Ronda et al., 2007; Wu et al., 2013; Xu et al., 2019; Yen et al., 2004; Zorenko et al., 2016; Zych et al., 1997).

Among these production processes, efforts on synthesis of the lutetium and yttrium aluminum garnets (LuAG:Ce³⁺ and YAG:Ce³⁺) doped by trivalent cerium ions are more intensive due to their indicated fast and efficient scintillation potentials, short decay times, and utilization potential in the detection of high energy particles; X and gamma-rays in addition to other applications (Ronda et al., 2007; Zych et al., 1997).

Relevantly their arising economic importance, sometimes synthesis efforts in the production of these materials resulted in new patent applications (Li, Y. Q. et al., 2013; Li, Y. et al., 2015; Wu, et al., 2013; Xu et al., 2019). Intematix Corp. developed lutetium-aluminum-garnet type phosphors with various types of dopants exhibiting similar crystal structure to YAG phosphors emitting in the green or yellow band of the electromagnetic spectrum (Li, Y. Q. et al., 2013; Wu, et al., 2013). Dow Electronic Materials presented new nitride and oxynitride type phosphors where partial substitution of carbon by nitrogen has been performed to tune the color. A study indicating scintillating screens of Ce-doped multi-component garnets of Lu_{3-x}Gd_xAl_{5-y}Ga_yO₁₂, Lu_{3-x}Tb_xAl_{5-y}Ga_yO₁₂ and Tb_xGd_xAl_{5-y}Ga_yO₁₂ and their decay times was presented by Zorenko et al. (2016). The authors reported increased light yield in single crystalline films comparison with that LuAG:Ce³⁺ and YAG:Ce³⁺ scintillators extending to 3.8- and 1.85-fold (Zorenko et al., 2016). In most of these studies, the

main motivation point has been to improve the optical performance of the phosphors. Variations including lattice structure, size, and concentration of the activator ions through compositional modification of the LuAG:Ce³⁺ phosphors have been reported earlier (Hansel et al., 2009; Li, J. et al., 2013). Similarly, the yttrium aluminum garnet (Y₃Al₅O₁₂ or YAG) and its compositional derivatives doped with Ce³⁺ have also been studied extensively (Babin et al., 2007; Yuan et al., 2020). To tune the color, some strategies including changing the electronic microenvironment of the activator ion and to create structural diversity have been tested. In these works, the intense yellow emission of the Ce³⁺ has been explained by a strong crystal field splitting arising from its host. Although many strategies have been tried to obtain effective phosphorus, studies on composites where phosphors are used in combination with other absorbers and emissive materials are rare (Hu et al., 2012; Sun et al., 2016).

On the other hand, ZnO and CuO can strongly absorb and emit in a wide spectrum, and, because of these characteristics, they are effectively used in solar cell applications. It is also known that both oxides exhibit very interesting optical properties when they are in nanoscale. If there have been a few publications indicating utilization of the ZnO to improve emission efficiency of GaN-based LEDs (Jeon et al., 2014; Park et al., 2016; Soh et al., 2010), the ZnO nanoparticles have rarely been used along with YAG-type phosphors (Amara et al., 2020; Chao et al., 2011; Hsu et al., 2014). As far as we know, there is no study in which ZnO and CuO were used together to increase the luminescence efficiency of phosphors. Therefore, we focused our work on to investigate how these two metal oxides will affect the emission of phosphors. Usually, the optical properties of the ZnO nanostructures are attributed to the presence of defects in the crystal. The underlying mechanism of the strong absorption and emission capability of the ZnO comprises the bandgap excitation of the crystal with energetic photons generating exciton pairs with holes in the valance band, and electrons in the charge band. These charge carriers may recombine dissipating the energy as emission or undergo a charge transfer process with the chromophores. The yellow and blue emissions have been observed in samples produced in oxygen-rich (Kar et al., 2009; Li et al., 2004; Qiu et al., 2009; Tam, et al., 2006) and zinc-rich (Zeng, et al., 2012) environments, respectively. Similarly, the nano-scale CuO particles also exhibit

broadband photoluminescence centered at 540 nm arising from electronic transitions from the conduction to the valence band and by the transitions between the defective energy levels or between the defect levels and the conduction or valence band, which is referred to as defect-related emission (Xu et al., 2018).

Herein we investigated photoluminescence of the two commercially available phosphors, lutetium aluminum garnet (LuAG:Ce³⁺) and yttrium aluminum garnet (YAG:Ce³⁺) in detail by steady-state photoluminescent and decay time measurements when they are entrapped together with nano-scale metal oxides, which can absorb and emit light in a large spectrum. Besides, we have excited these phosphors, which have been generally stimulated with high energy wavelengths due to their stopping properties, with the blue wavelength commonly used in LED or display applications. Upon excitation, the phosphors exhibited interesting interactions with the metal oxides yielding enhanced quantum yield and a longer excited-state lifetime compared to their additive-free forms. When the LuAG:Ce³⁺ was entrapped along with the ZnO and CuO in a polymethyl methacrylate matrix, both the absorption and emission efficiency of the phosphor enhanced 59-fold. Similarly, when the yttrium aluminum garnet (YAG:Ce³⁺) incorporated with the ZnO and ZnO-CuO respectively, exhibited 6- and 4-fold enhancement in the emission intensity. We recorded the decay curves at nanosecond and microsecond time scales to clarify the mechanism lying behind the enhancement in the intensity. In nanosecond regime measurements, polymer-free and polymer embedded phosphors and their composites exhibited their typical average decay times around 50–60 ns. However, the microsecond scale steady-state and decay time based experimental studies supported that metal oxides act as donors and phosphors as acceptors when encapsulated in the PMMA in an appropriate ratio. Average excited-state lifetime of the LuAG:Ce³⁺ extended from 181 to 397 microseconds when embedded along with the ZnO-CuO in the PMMA. Similarly, the life span of the YAG:Ce³⁺ extended from 49 to 477 microseconds for the YAG:Ce³⁺-ZnO composite films.

3.2 Experimental

3.2.1 Synthesis of ZnO and CuO Nanoparticles

Synthesis of the ZnO and CuO nanoparticles (NPs) was performed by our co-workers (Keskin, O. Y., Birlik, I. & Azem, F. A.). The ZnO and CuO NPs were synthesized by the conventional sol-gel method by using following procedure: 0.65 and 0.75 M solutions of $(\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$ and of $(\text{Cu}(\text{CO}_2\text{CH}_3)_2 \cdot \text{H}_2\text{O})$ were prepared by 20 mL of isopropyl alcohol under magnetic stirring at room temperature. Stoichiometric amounts of acetic acid and triethanolamine were added into the zinc solution. Similarly, the solution of copper (II) acetate was dissolved in isopropyl alcohol and stirred at room temperature for an hour. The pH of the copper solution was adjusted by ethanolamine. After the reaction, both products were dried at 100 °C for 24 h and calcinated at 550 °C for one hour.

3.2.2 Preparation Protocols of the Composites

Phosphor based emissive composites were prepared in 5 mL of glass vials by mixing 120 mg of PMMA in 2 mL of THF under magnetic stirring. Then 10 mg of phosphor and equal amount of ZnO or CuO or their blend were added into the vial. The obtained viscous mixture was cast on a 125 μm Mylar (TM type) substrate by spin-coating technique. Photographs of the glass vials containing test material were shown in Figure 3.1.

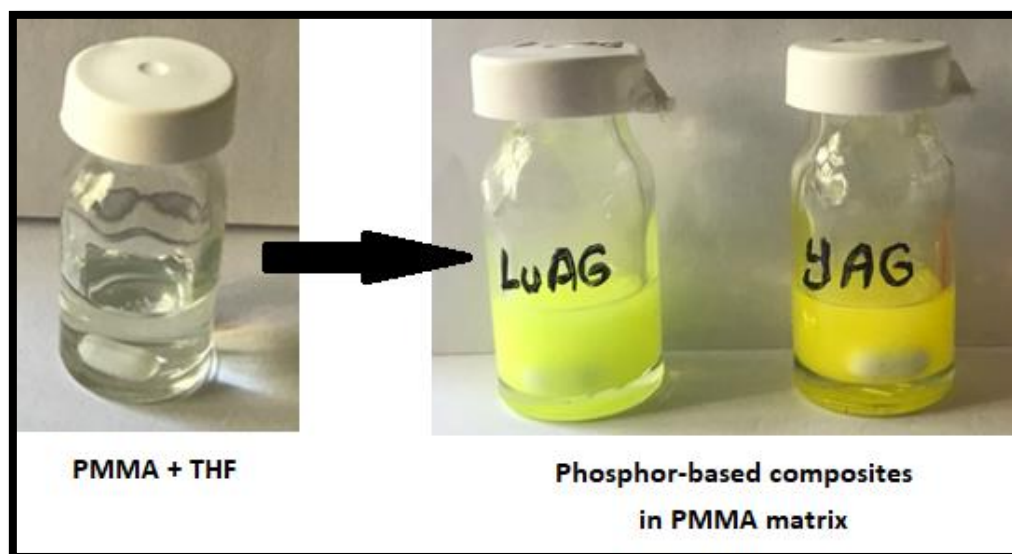


Figure 3.1 Preparation of phosphor-based composites in PMMA matrix under magnetic stirring (Personal archive, 2022)

The average thickness of the films was found to be $15.76 \pm 0.1 \mu\text{m}$ ($n = 10$). The side and front microscopic images of the sample particles in the dispersed form were shown in the SEM photographs in Figure 3.2 and 3.3.

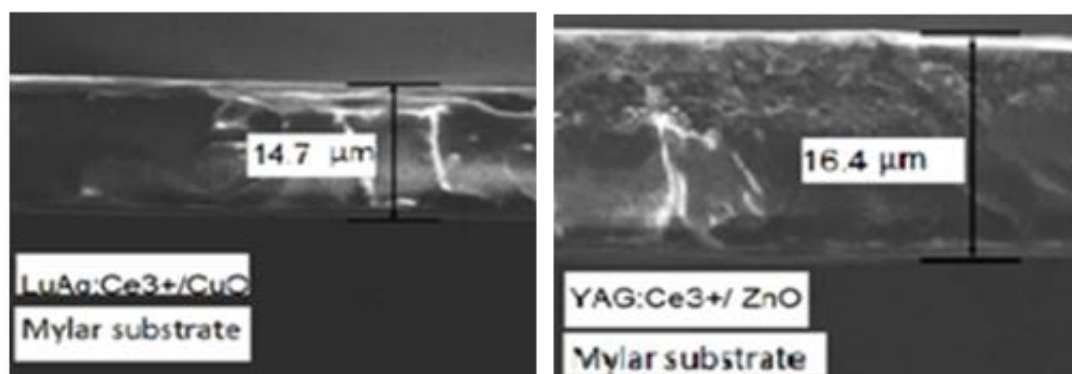


Figure 3.2 Side view of the composite thin films prepared by phosphors and metal oxide NPs

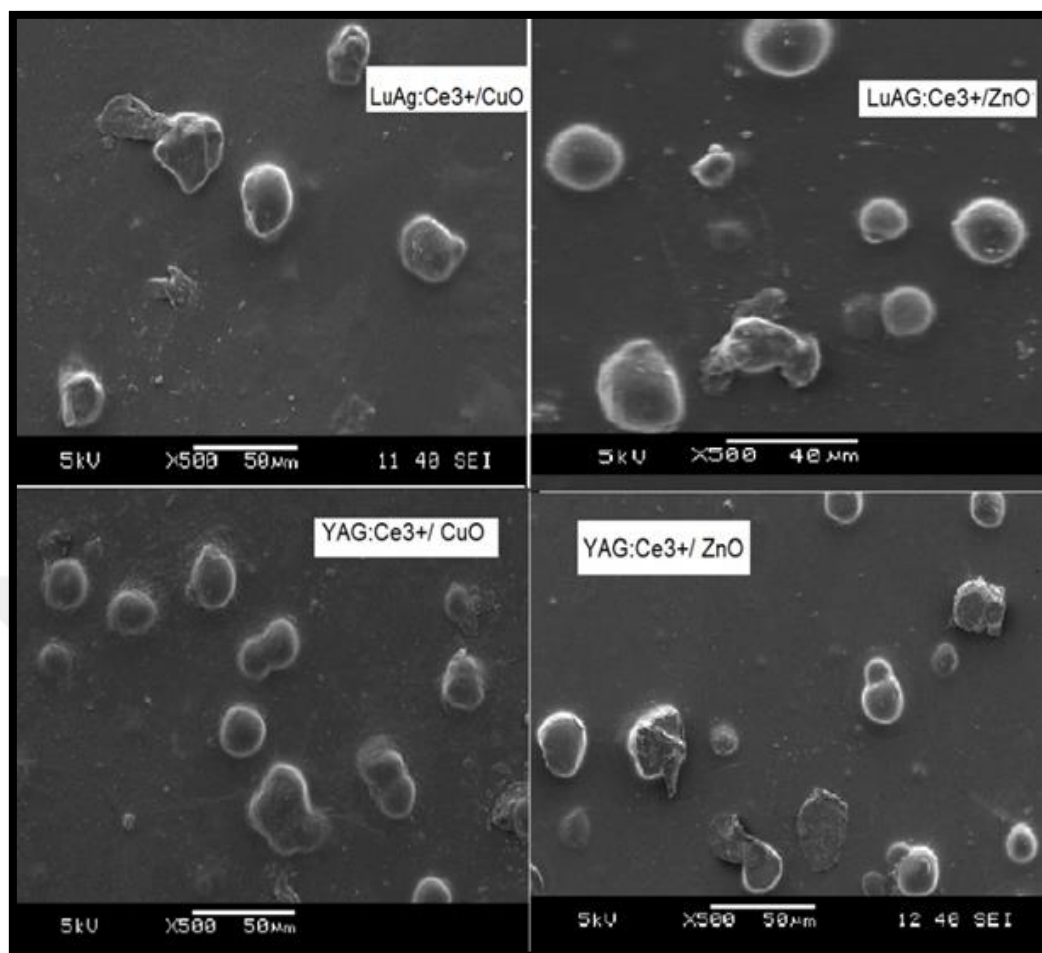


Figure 3.3 Front picture of the composite thin films prepared by phosphors and metal oxide NPs

The thin films were cut to an appropriate size and placed diagonally onto the solid sample holder or the cuvette of the spectrofluorometer for the spectral scans. Exact compositions of the used phosphors and additives were shown in Table 3.1.

Table 3.1 Composition of the luminescent materials

Sample	Phosphor: 10 mg	Additive: 10 mg	Matrix: 120 mg	Solvent: 2 mL
LuAG:Ce ³⁺	LuAG:Ce ³⁺	-	PMMA	THF
LuAG:Ce ³⁺ -ZnO	LuAG:Ce ³⁺	ZnO	PMMA	THF
LuAG:Ce ³⁺ -CuO	LuAG:Ce ³⁺	CuO	PMMA	THF
LuAG:Ce ³⁺ -ZnO-CuO	LuAG:Ce ³⁺	ZnO-CuO (5 mg-5 mg)	PMMA	THF
YAG:Ce ³⁺	YAG:Ce ³⁺	-	PMMA	THF
YAG:Ce ³⁺ -ZnO	YAG:Ce ³⁺	ZnO	PMMA	THF
YAG:Ce ³⁺ -CuO	YAG:Ce ³⁺	CuO	PMMA	THF
YAG:Ce ³⁺ -ZnO-CuO	YAG:Ce ³⁺	ZnO-CuO (5 mg-5 mg)	PMMA	THF

3.3 Results

3.3.1 X-Ray Diffraction Analysis of the ZnO and CuO Nanoparticles

The XRD patterns of the ZnO and CuO nanoparticles are shown in Figure 3.4. Diffraction peaks located at 31.90, 34.57, 36.41, 47.70, 56.76, 62.97, 66.58, 68.07, 69.21, 72.75, 76.98, and 81.51°, are in accordance with the hexagonal wurtzite structure of the ZnO (JCPDS card No. 89-7102). The peaks observed at 32.47, 35.49, 38.68, 48.65, 53.36, 58.25, and 61.45°, can be concluded as evidence of the monoclinic structure of the sol-gel synthesized CuO (JCPDS card No. 48-1548) (Dalmis et al., 2019; Jayalakshmi et al., 2018; Keskin et al., 2020; Poloju et al., 2018).

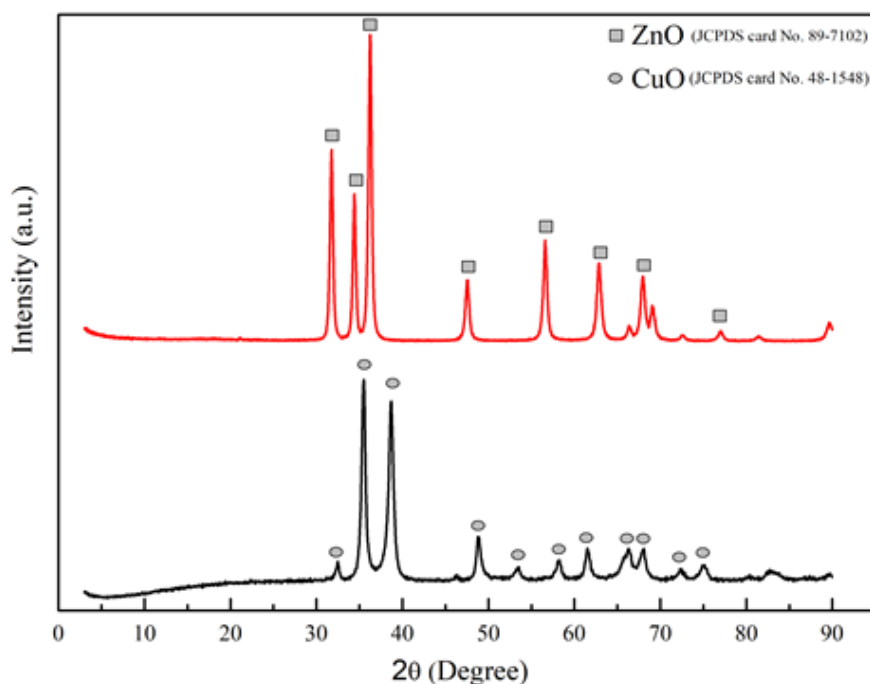


Figure 3.4 XRD spectra of the ZnO and CuO NPs

Figure 3.4 also evidences the formation of both forms, without other phases or impurities. The average crystalline sizes of the ZnO and CuO were determined by using XRD patterns in accordance with the Scherrer equation ($D = (0.89 \times \lambda) / (\beta \times \cos \theta)$), where; D is the crystalline size, β is full width half maximum of the 2θ , λ is the wavelength of radiation, and, θ is the Bragg angle (Alexander & Klug, 1950). The

average crystalline sizes of the samples were found to be 31.70 and 20.74 nm for the CuO and ZnO, respectively (Table 3.2).

Table 3.2 Crystal size parameters of the newly synthesized the ZnO and CuO NPs

Sample	Crystalline size (nm)	FWHM (Deg)	a [Å]	b [Å]	c [Å]
ZnO	20.74	0.421	3.2507	3.2507	5.2065
CuO	31.70	0.275	3.0440	6.2230	6.2793

3.3.2 XPS Analysis of the ZnO and CuO Nanoparticles

The overlaid XPS spectra of the CuO and ZnO NPs evidence the existence of the Zn, Cu, O, and C without other elements or impurities (See Figure 3.5a). Figure 3.5b shows the high-resolution spectra of the CuO NPs. The parent peaks located at 934.7 and 954.7 eV corresponds to Cu2p_{3/2} and Cu2p_{1/2}, respectively, and the difference between these peaks with ~20 eV well matches with the 2⁺ oxidation state of the copper. Also, the satellites located at 942.32 and 962.88 eV with 20.5 eV difference, coherent with the parent peaks, and indicate 2⁺ oxidation state of the copper. The high-resolution scan of ZnO NPs. is shown in Figure 3.5c. The two parent peaks located at 1021.79 and 1044.84 eV corresponding to the Zn2p_{3/2} and Zn2p_{1/2}, respectively, evidences the 2⁺ valance state of the Zn. Besides, differences between two-parent peaks with ~ 23 eV, consistent with the literature and confirm the oxidation state of the Zn as in 2⁺ (Jiang et al., 2018; Wang et al., 2011; Xu et al., 2013). The O 1s spectra of the ZnO and CuO particles were illustrated in Figure 3.5d. The peaks centered at 532.13 and 531.01 eV can be assigned to the O²⁻ state in the zinc and copper oxides and can be attributed to the presence of the Zn-O and Cu-O bonds (Wang et al., 2011; Xu et al., 2013). The peak that appeared at 284.6 eV (C1s) arises from carbon which is an ingredient of the adhesive used for analysis or absorbed from the atmosphere (Annathurai et al., 2019).

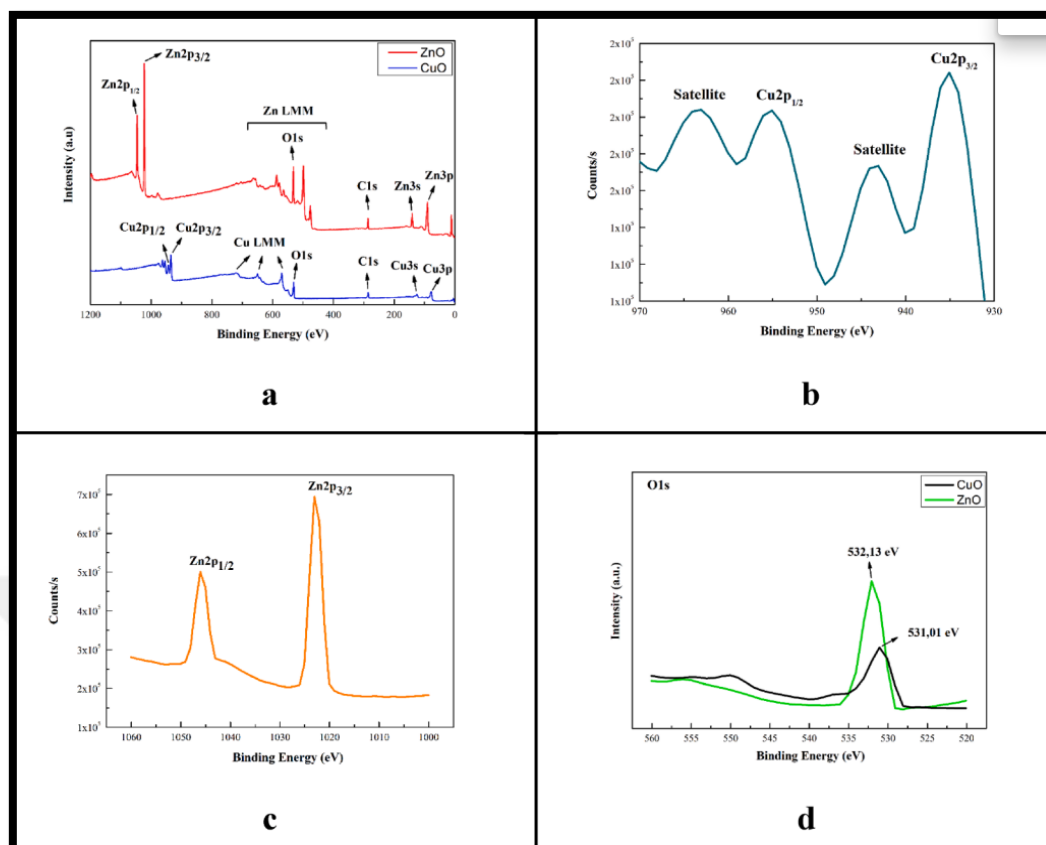


Figure 3.5 a: Overlaid XPS spectra of the CuO and ZnO b: High-resolution spectra of the CuO c: High-resolution spectra of the ZnO d: The O1s spectra of the ZnO and CuO particles

3.3.3 Absorption-based Properties of the ZnO and CuO Nanoparticles

Figure 3.6 indicates the gathered absorption spectra of the sol–gel synthesized ZnO and CuO NPs. Prior to UV–Vis measurements, the samples were dispersed in water, sonicated for 15 min and put into a quartz cuvette for the spectral scan. While the ZnO NPs strongly absorbing around 380 nm, the absorption maximum of the CuO appeared at shorter wavelengths, around 250 nm. The absorption maximum centered at 376 nm is the characteristic for the ZnO and arises from electronic transitions of the valance band electrons of the oxygen to the 3d levels of Zn^{2+} ions at the conduction band (Al-Gaashani et al., 2013). Both the ZnO and CuO, strongly absorbed between 200 and 500 nm. The absorption band observed at 376 nm in the spectrum of the ZnO can be assigned to ligand–metal charge transfer (LMCT) from 2p orbitals of the oxygen lying

in the valance band (VB), to the 3d levels of the Zn^{2+} ions at the conduction band (CB). The underlying mechanism of the strong absorption (and following emission) of the ZnO comprises the bandgap excitation of the crystal with photons generating exciton pairs with holes in the VB and electrons in the CB. These charge carriers may recombine dissipating the energy as emission or may undergo a charge transfer with other acceptors taking place its close proximity. Similarly, the strong absorption band is associated with charge transfer from the O2p to Cu3d. The copper oxide, the last compound in the series of the simplest oxides of transition metals with a nearly filled 3d-shell, exhibited the absorption maximum at a shorter wavelength with respect to the ZnO (Al-Gaashani et al., 2013; Fu et al., 2011). Herein, both oxides act as UV–visible light-harvesting agents in their absorption range. In the case of the nano-scale metallic particles which is generally smaller than the wavelength of the excitation light, collective electronic oscillations (Mie-plasmons) may be subjective where collective excitations of conduction band electrons occur and mainly results in pronounced absorption in the UV or visible range of the electromagnetic spectrum.

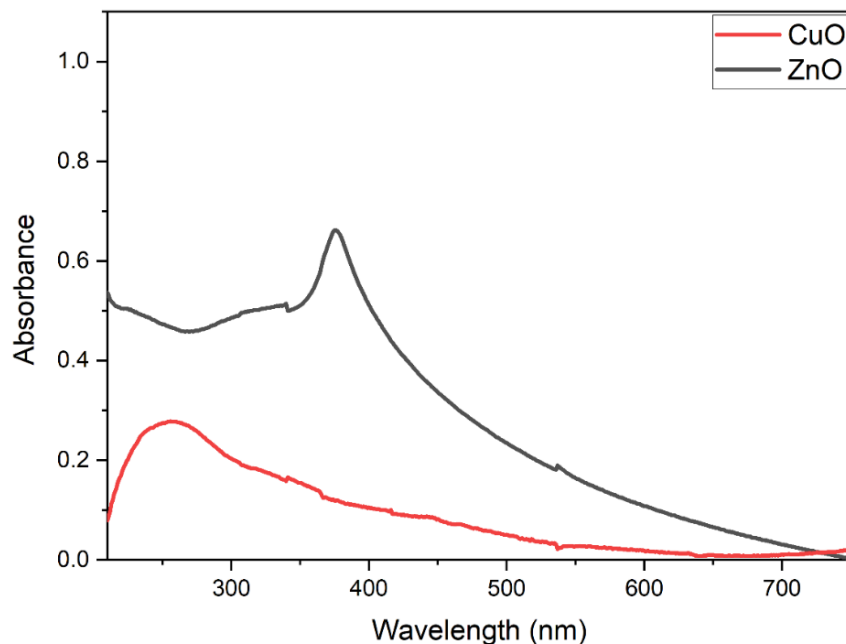


Figure 3.6 Absorption spectra of the ZnO and CuO in dispersed form in water

3.3.4 Transmittance and Reflectance Spectra of the CuO, ZnO, and LuAG:Ce³⁺ and YAG:Ce³⁺ and their Composites

Transmittance and reflectance spectra of the CuO, ZnO, and LuAG:Ce³⁺ and YAG:Ce³⁺ and their ternary composites were recorded to verify the absorption based data when the particles were encapsulated in form of thin films in PMMA matrix on fused silica substrate and were shown in Figure 3.7, 3.8 and 3.9, respectively.

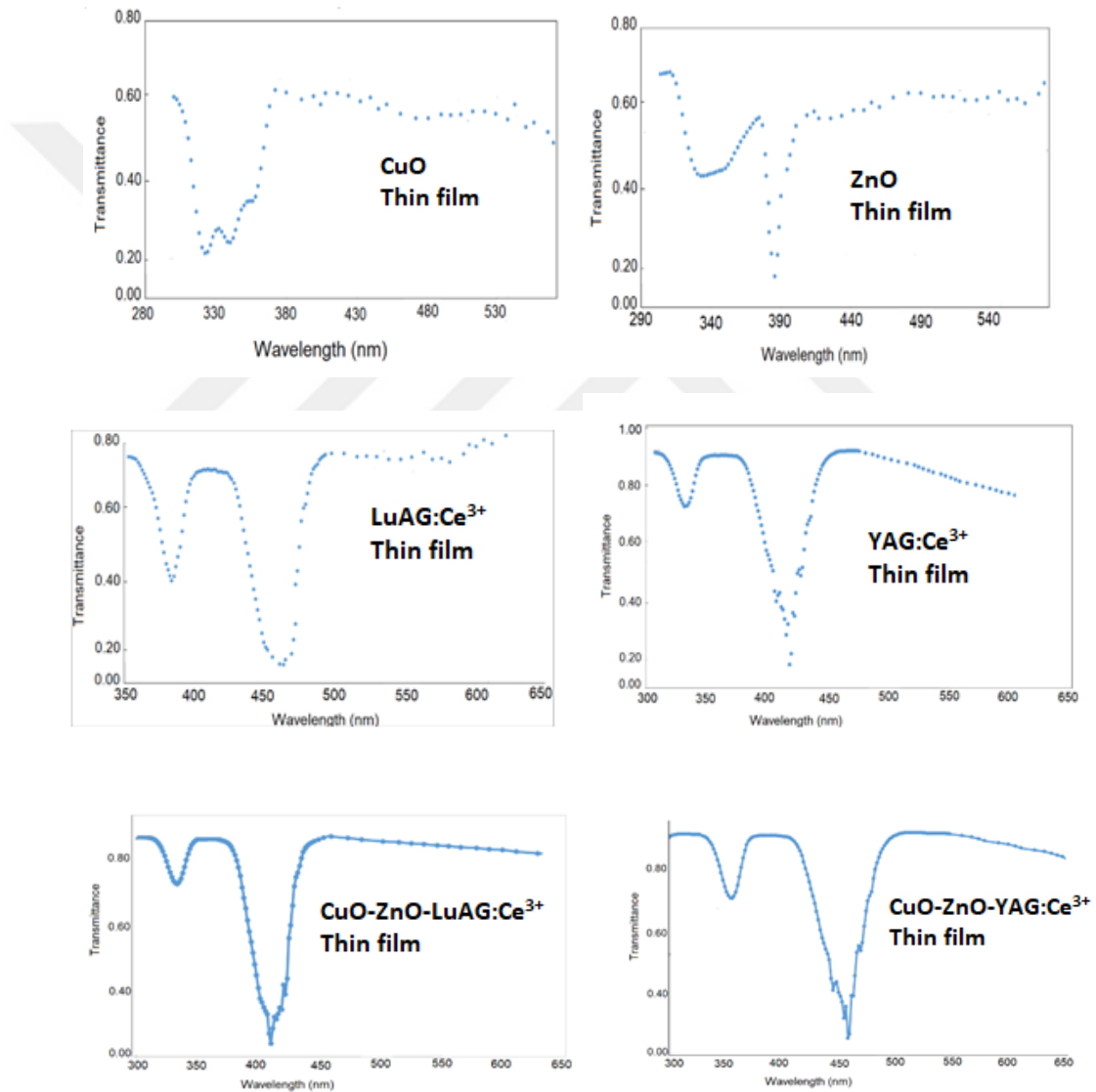


Figure 3.7 Transmittance spectra of the CuO, ZnO, and LuAG:Ce³⁺ and YAG:Ce³⁺ based composites. Spectra were recorded on fused silica substrate in thin form for the samples

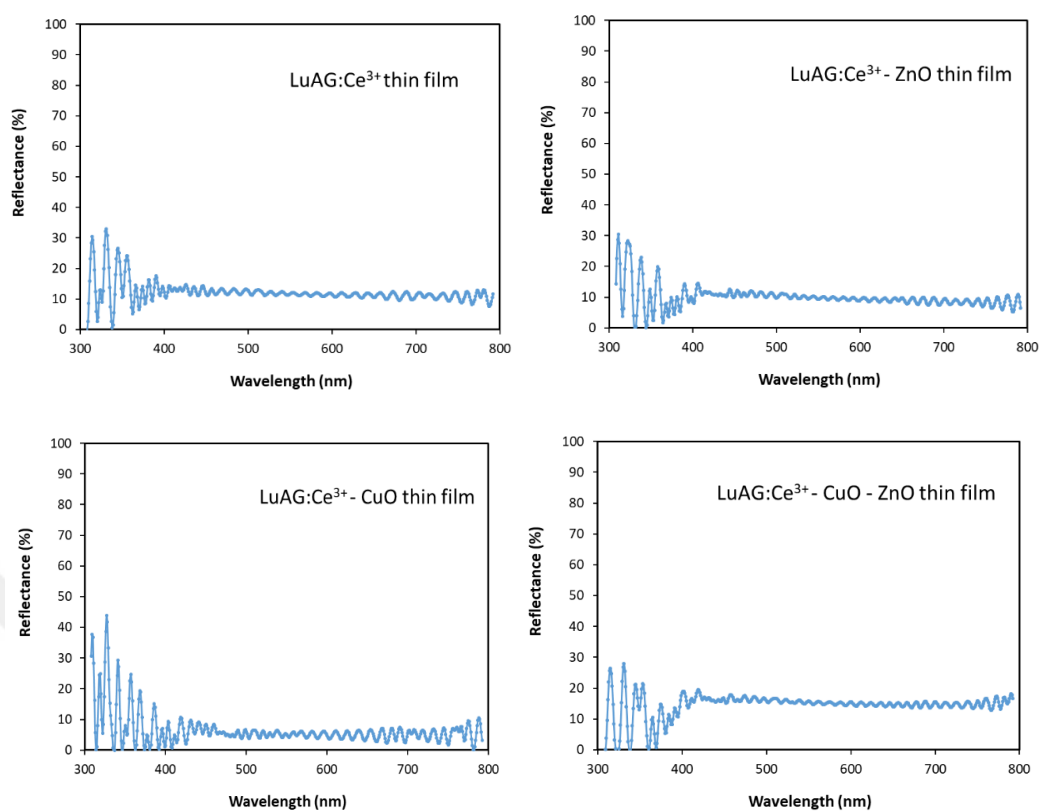


Figure 3.8 Reflectance spectra of the LuAG:Ce³⁺ based thin films

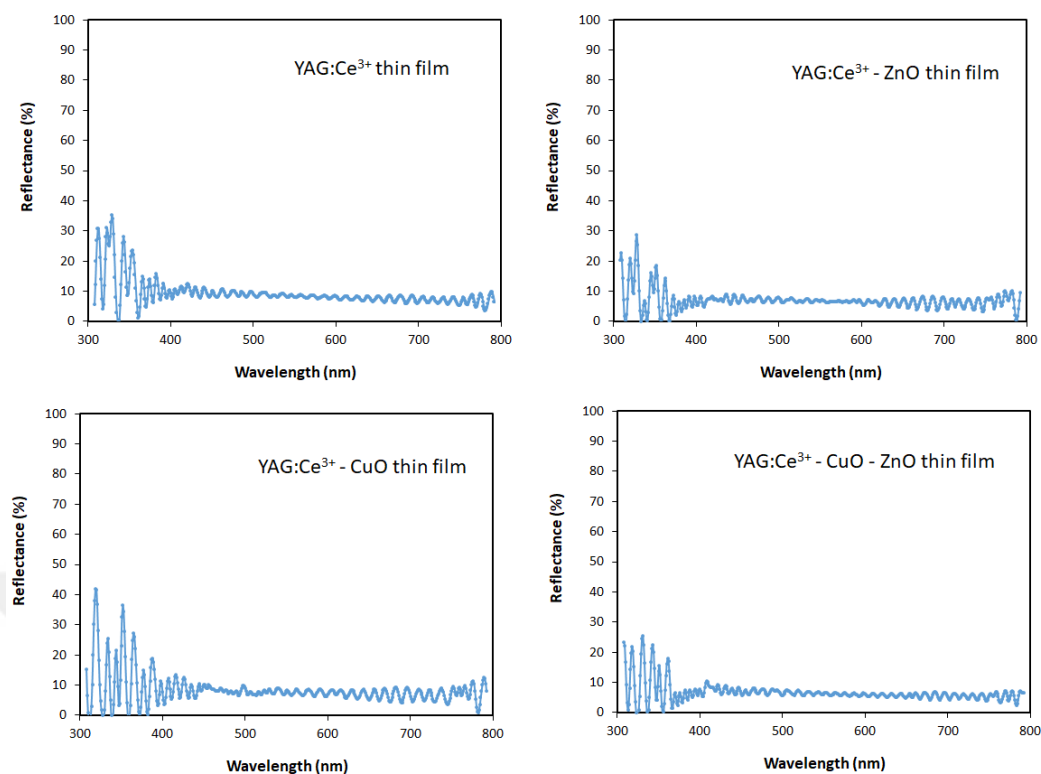


Figure 3.9 Reflectance spectra of the YAG:Ce³⁺ based thin films

3.3.5 Morphology and Size of the Utilized Particles

Average sizes and morphologies of the utilized particles were characterized by size distribution analysis and/or SEM images. The ZnO and CuO particles exhibited a nano-scale buddy and porous structure in accordance with the literature (Al-Gaashani et al., 2013; Annathurai et al., 2019; Dhineshbabu et al., 2016; Fu et al., 2011; Sukhorukov et al., 1995). Size distribution analysis results supported the SEM images of the oxides exhibiting 110 and 362 nm average particle size for the ZnO and CuO, respectively. SEM images of the LuAG:Ce³⁺ and YAG:Ce³⁺ indicated well-shaped spherical morphology and micro-scale size distribution; 17 and 15 μm , respectively. Traces of a mechanical process on the surface of the garnets is also observable (Figure 3.10). The nano-scale size of the zinc and copper oxides which is much smaller than the phosphors may be concluded as an advantage for the better interaction of these light-harvesting agents with the LuAG:Ce³⁺ and YAG:Ce³⁺. The glittering layer around the phosphor particles observed in the SEM images of the composites (Figure

3.2 and 3.3) can be attributed to the co-action of the homogenously distributed ZnO and CuO NPs and the garnets, which is not visible for the oxide-free phosphors (See Figure 3.10).

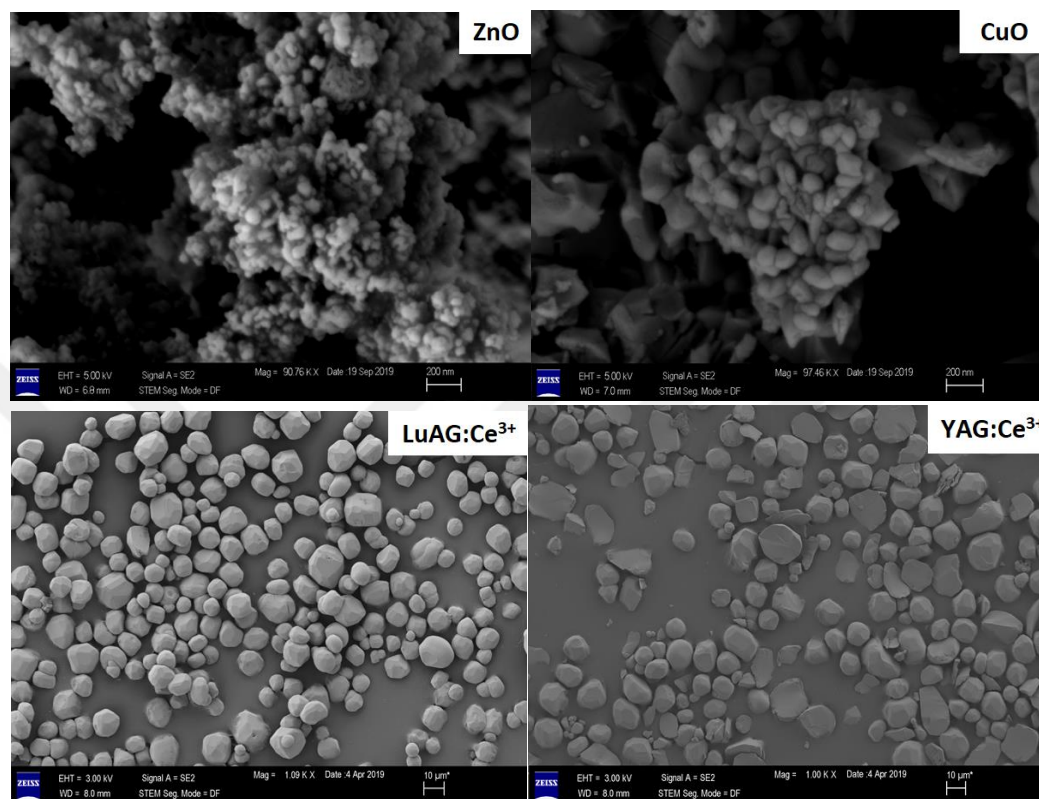


Figure 3.10 SEM images of the ZnO, CuO, LuAG:Ce³⁺ and YAG:Ce³⁺

3.3.6 Spectral Properties of the Ce³⁺-activated LuAG and YAG in the PMMA Matrix

Excitation and emission spectra of the LuAG:Ce³⁺ and YAG:Ce³⁺ were recorded individually, and along with the metal oxides of ZnO, CuO and ZnO-CuO blend in the entrapped form in the polymethylmethacrylate. Figure 3.11 reveals excitation/emission spectra of the green and yellow phosphors and corresponding electronic transitions of the LuAG:Ce³⁺ and YAG:Ce³⁺ when excited at 450 and 466 nm, respectively. Two bands observed at 346 and 450 nm in the excitation spectrum of the LuAG:Ce³⁺ at room temperature corresponds to transitions to the two lowest energy levels of the five crystal field components in D₂ symmetry (Figure 3.11 I)

(Bárta et al., 2012; Liu et al., 2015; Praveena et al., 2011; Setlur & Srivastava, 2007; Wu et al., 2007). Corresponding photoluminescence spectra of the 5d-4f transition exhibited broad emission bands centered at 514 and 540 nm in the green region for the LuAG:Ce³⁺ and YAG:Ce³⁺, respectively. The 4f⁰5d¹ configuration electrons undergo ²D term split (²D_{3/2} and ²D_{5/2}), and the 4f electron of the ground 4f¹ configuration forms ²F_{7/2} and ²F_{5/2} states by spin-orbit coupling. Therefore, the broad-band emissions observed in the room temperature spectra of Ce³⁺ doped LuAG and YAG can be assigned to the sum of the two overlapping sub-bands arising from the splitting of the 2F state to the ²F_{7/2} and ²F_{5/2} states, respectively. The presence of radiative recombination of electron-hole pairs on Ce³⁺ ions is also evidenced by electron paramagnetic resonance experiments which suggest the presence of LuAG defects in the vicinity of Ce³⁺ ions (Ahn & Kim, 2016; Liu et al., 2015). The Stoke's shift of the LuAG:Ce³⁺ was simply determined to calculate the energy difference between excitation (450 nm) and emission (514 nm) band maxima, which yields a value of 64 nm (See Table 3.3).

Similarly, the YAG:Ce³⁺ exhibited characteristic excitation bands arising from the presence of the Ce³⁺, at 340 and 466 nm. The emission maximum appeared at 568 nm (See Figure 3.11 II). The YAG:Ce³⁺ exhibited a larger Stoke's shift (102 nm) with respect to the LuAG:Ce³⁺ (64 nm) which can be attributed to room temperature phosphorescence at 568 nm which occurs from comparatively lower energy excited triplet states compared to the LuAG:Ce³⁺ (See Table 3.3) (Nikl et al., 2007; Ogiegło et al., 2012). Additionally, the covalency of Ce³⁺ in the YAG lattice is larger than for the Ce³⁺ in the LuAG. The Ce³⁺ emission may appear between the ultraviolet and blue spectral region in the oxides, depending on the surroundings. In the presence of higher covalency and strong crystal field, the 5d orbital shifts to lower energies, resulting in emission in the yellow and even red wavelengths. Therefore, the lower energy and large-band emission of the Ce³⁺ in the YAG (568 nm) with respect to the LuAG (514 nm) can be attributed to the lowering of the lowest energy emitting the 5d state of Ce³⁺ by a combined effect of a large crystal field splitting and a high covalency.

Table 3.3 Absorption and emission-based characteristics of the utilized phosphors and additives when embedded in PMMA matrix. $\lambda_{\max}^{\text{abs}}$: absorption maximum, $\lambda_{\max}^{\text{ex}}$: excitation maximum, $\lambda_{\max}^{\text{em}}$: emission maximum and $\Delta\lambda$: Stoke's shift in nm

Sample	$\lambda_{\max}^{\text{abs1}}$ (nm)	$\lambda_{\max}^{\text{ab2}}$ (nm)	$\lambda_{\max}^{\text{ex}}$ (nm)	$\lambda_{\max}^{\text{em}}$ (nm)	$\Delta\lambda$ (nm)
LuAG:Ce ³⁺	346	450	450	514	64
LuAG:Ce ³⁺ -ZnO	344	450	450	510	60
LuAG:Ce ³⁺ -CuO	346	450	450	542	62
LuAG:Ce ³⁺ -ZnO-CuO	346	450	450	514	64
YAG:Ce ³⁺	340	466	466	568	102
YAG:Ce ³⁺ -ZnO	340	466	466	556	90
YAG:Ce ³⁺ -CuO	340	466	466	554	88
YAG:Ce ³⁺ -ZnO-CuO	340	466	466	558	92

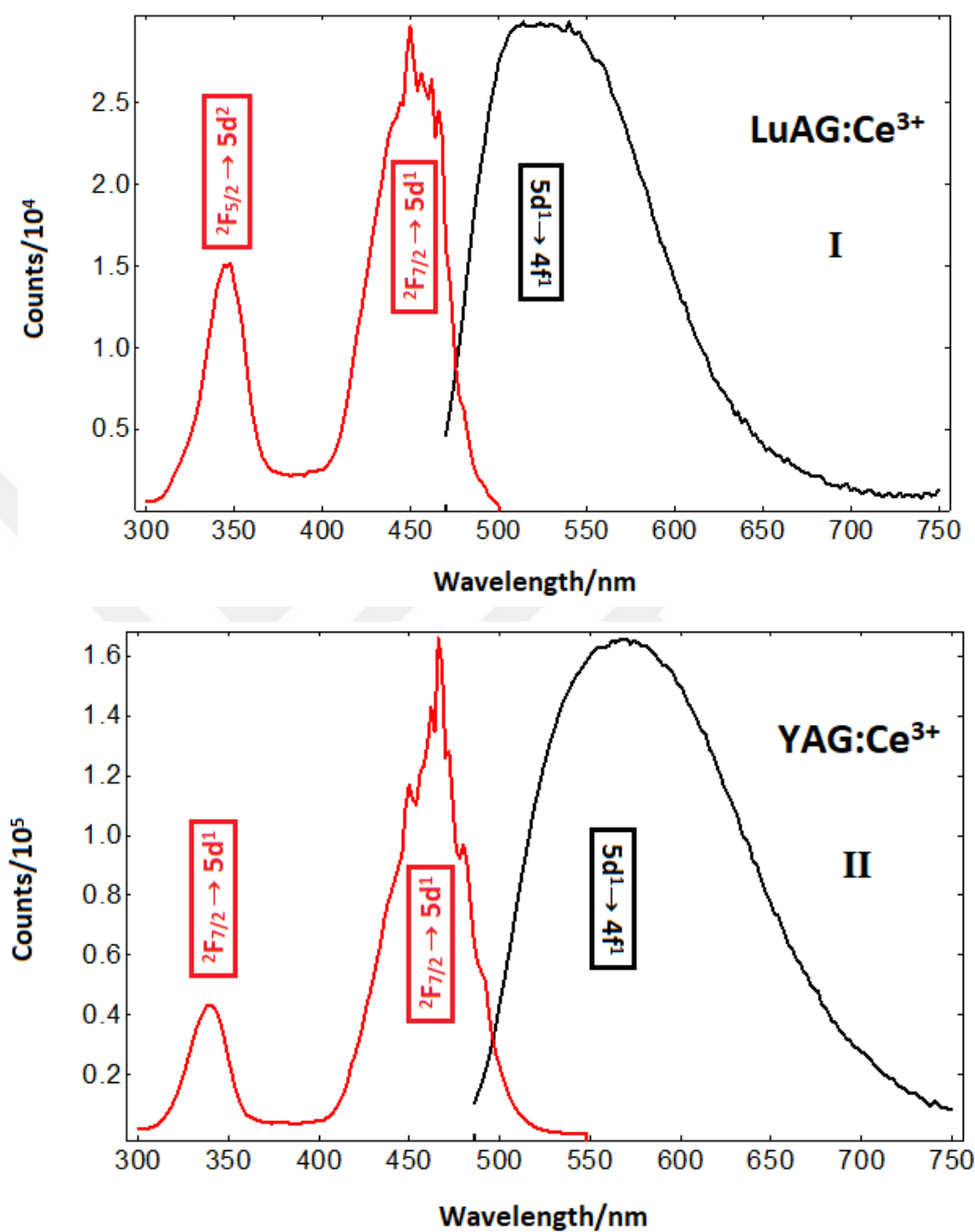


Figure 3.11 Excitation and emission spectra of the green and yellow phosphors in the PMMA and corresponding electronic transitions (I: LuAG:Ce³⁺; λ_{ex} =450 nm λ_{em} =514 nm, II: YAG:Ce³⁺; λ_{ex} =466 nm λ_{em} =568 nm)

3.3.6.1 Spectral Properties of the LuAG:Ce³⁺-based Composites

Comparative excitation and emission spectra of the additive-free LuAG:Ce³⁺ and LuAG:Ce³⁺-metal oxide composites were shown in Figure 3.12, respectively. In all cases, excitation has been performed at 450 nm. The LuAG:Ce³⁺-ZnO-CuO based composites exhibited an extraordinary brightness in the emission intensity which is 59-fold higher compared to the individual form of the LuAG:Ce³⁺ without any spectral shift. The LuAG:Ce³⁺-CuO based films exhibited 6-fold enhancement in the brightness, in contrast, the intensity of the LuAG:Ce³⁺-ZnO composites slightly decreased. 4 nm of blue shift and 2 nm of redshift was observed in the emission maximum of the composites for the CuO and ZnO blended forms, respectively. To clarify the interactions lying behind the enhancement of the emission intensity we recorded individual spectra of the PMMA embedded LuAG:Ce³⁺, ZnO, and CuO respectively.

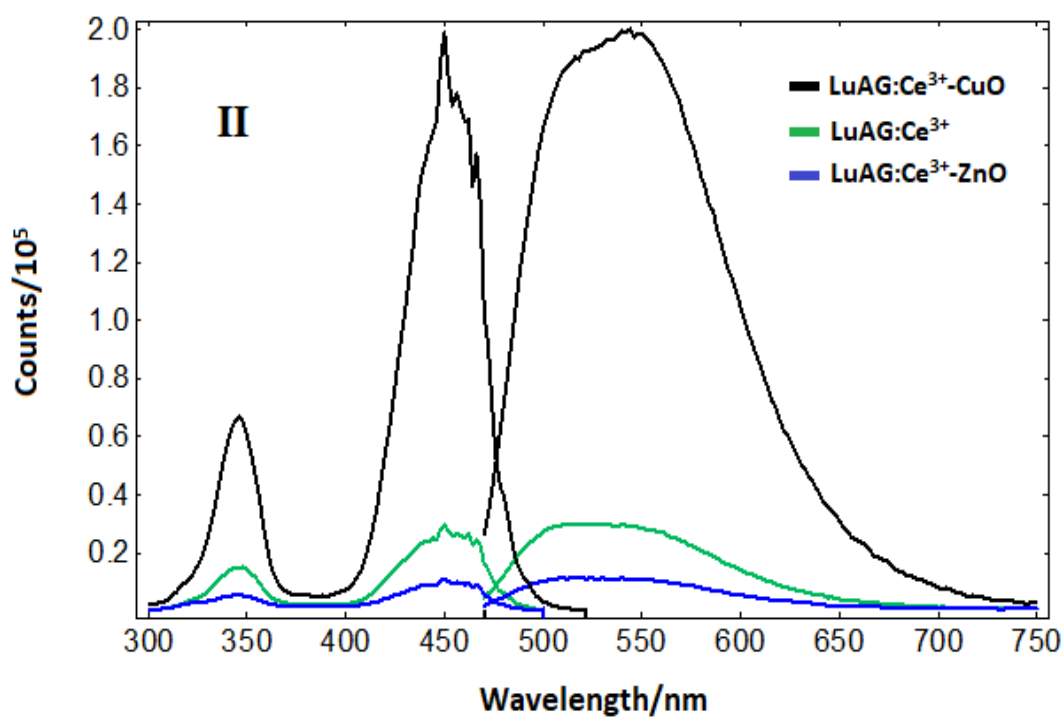
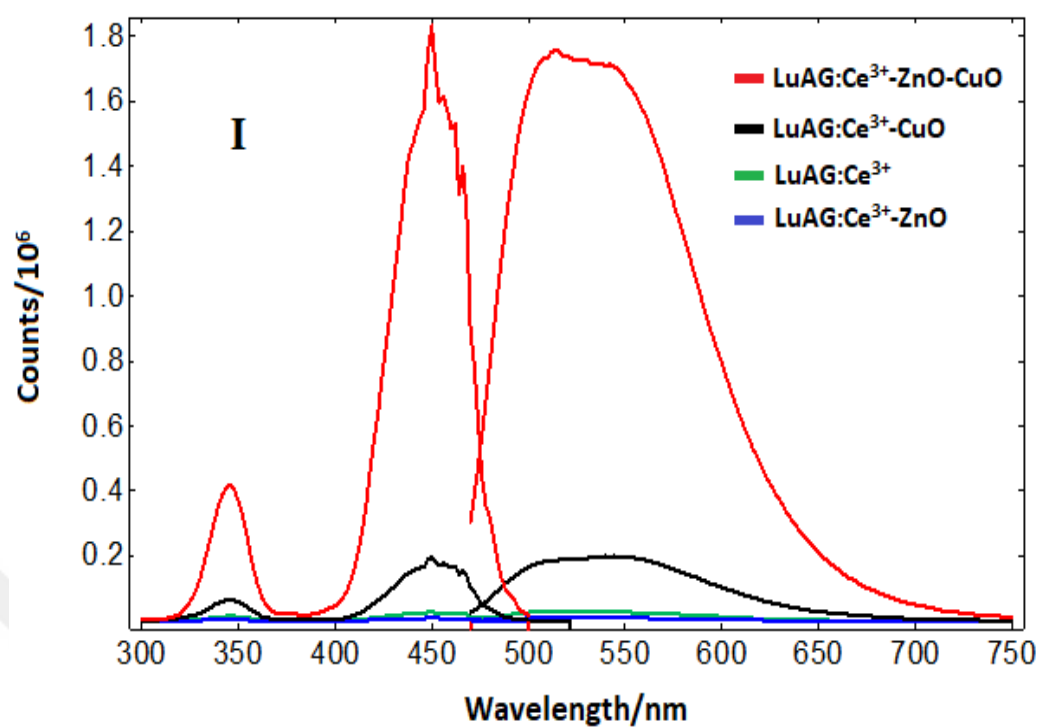


Figure 3.12 I: Excitation-emission spectra of the additive-free LuAG:Ce³⁺ and ZnO or CuO or ZnO-CuO doped forms. Excitation has been performed at 450 nm. II: Enlarged luminescence spectra of the LuAG:Ce³⁺ and doped forms

Figure 3.13 I and II show separately recorded but gathered in luminescence spectra of the LuAG:Ce³⁺-CuO and LuAG:Ce³⁺-ZnO, respectively. Both the CuO and ZnO strongly absorbed between 300 and 500 nm and emitted at a large wavelength range extending from 450 to 700 nm covering the excitation band of the LuAG:Ce³⁺ which makes an energy transfer between the nano-scale metal oxides and the phosphor particles, possible (See Figure 3.13. I and II). Although energy transfer effects are observable in the emission spectra of the copper oxide containing composites (Figure 3.12 I), this effect is absent or in a negative direction in the zinc oxide containing forms (See Figure 3.12 II). However, the coexistence of the CuO and ZnO nanocrystals at the same time in the composite resulted in a synergistic effect creating a very strong and unexpected enhancement in the emission intensity of the phosphor. The absorption and emission capability of the ZnO nanostructures can be assigned to the presence of defects in the oxides. The excitation bands observed at 340 and 392 nm arises from electronic transitions of the ligand–metal charge transfer from 2p orbitals of the oxygen lying in the valance band to the 3d levels of Zn²⁺ ions at the conduction band. The mechanism of the absorption and emission abilities of the ZnO comprises the bandgap excitation of the oxide with energetic photons generating exciton pairs with holes in the VB and electrons in the CB. These charge carriers may recombine dissipating the energy as emission or undergo a charge transfer process with the LuAG:Ce³⁺ particles taking place in its appropriate proximity. On the other hand, large band emission extending from 420 to 690 nm of the CuO NPs can be attributed to the direct transition of the electrons between the conduction band and the valence band as well as the electron transitions between the defect levels in the forbidden band or between the defect levels and the conduction band or valence band (Ekuma et al., 2014; Jayalakshmi et al., 2018; Poloju et al., 2018; Wang et al., 2019; Xu et al., 2018). The optical properties of the CuO are in many ways typical of the oxides of 3d elements. However, due to the 3d9 structure, electronic interactions resulting in the splitting of the energies of different configurations into terms and the interactions of multielectron configurations make it difficult to describe correctly within the traditional band approaches (Ekuma et al., 2014; Wang et al., 2019).

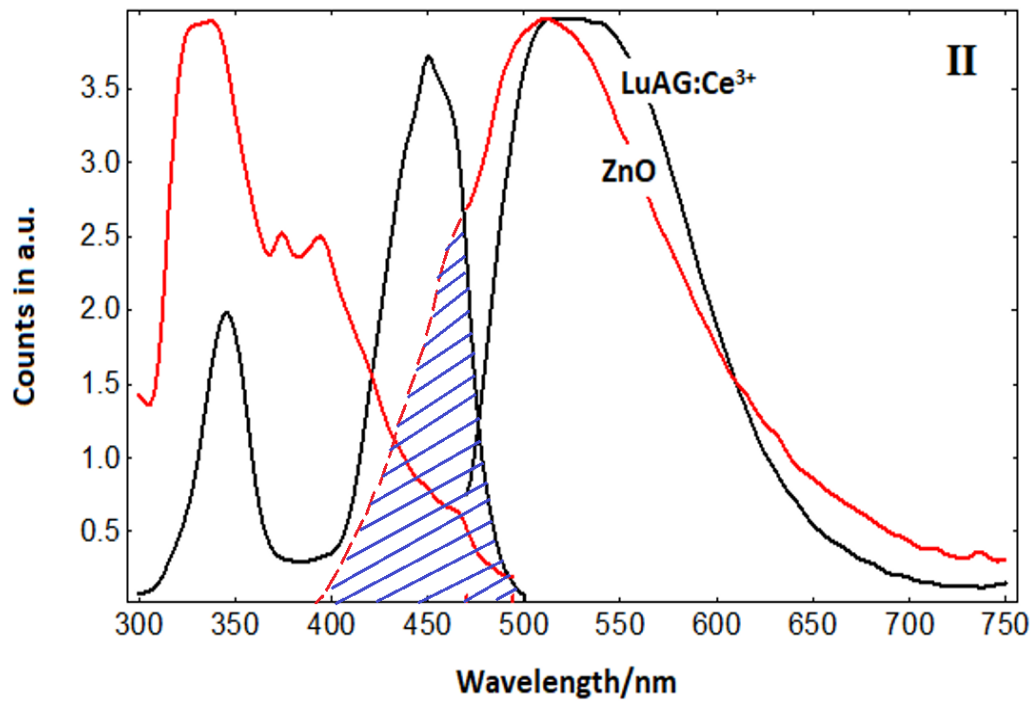
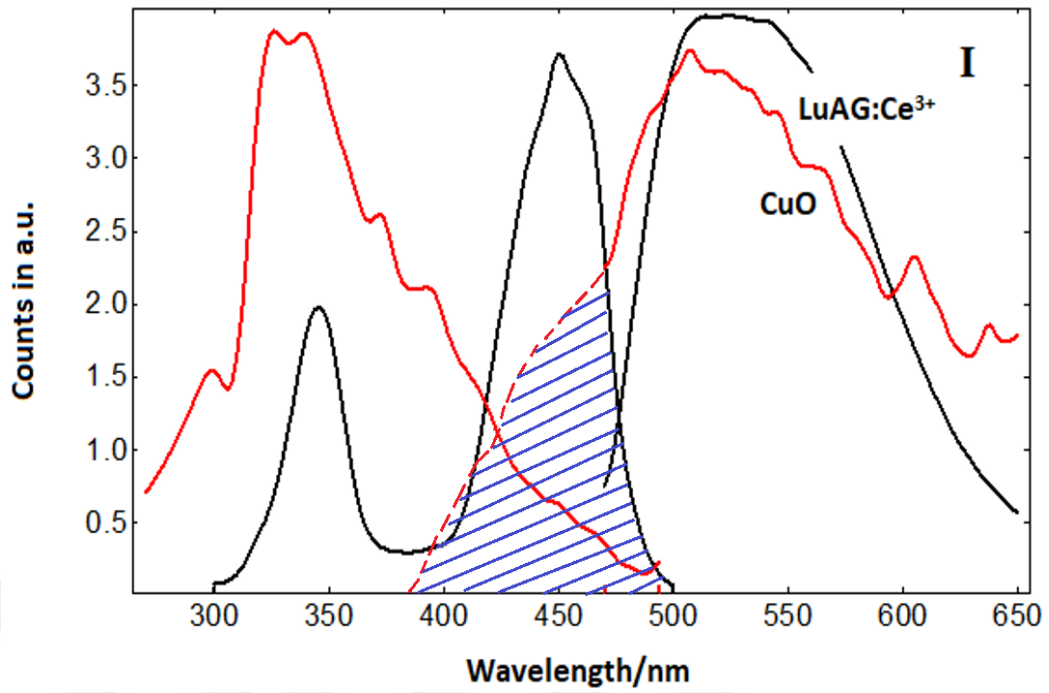


Figure 3.13 I: Normalized luminescence spectra of the LuAG:Ce³⁺ and CuO in the PMMA. (LuAG:Ce³⁺; $\lambda_{ex}=450$ nm $\lambda_{em}=514$ nm, CuO; $\lambda_{ex}=450$ nm $\lambda_{em}=506$ nm) II: Normalized spectra of the LuAG:Ce³⁺ and ZnO (LuAG:Ce³⁺; $\lambda_{ex}=450$ nm $\lambda_{em}=514$ nm, ZnO; $\lambda_{ex}=450$ nm $\lambda_{em}=510$ nm)

On the other hand, since the absorption spectrum of the CuO is well-matched with the spectrum of the sunlight, it is considered to have potential application in solar cells in combination with the ZnO, and results demonstrated that the absorption intensity of the Cu₂O/ZnO thin film heterojunction is significantly enhanced in the visible region compared with the ZnO thin films (Ekuma et al., 2014). In Cu₂O/ZnO thin film heterojunctions prepared on ITO glass substrates, because of the different carrier concentration, electrons of the ZnO flow towards Cu₂O at the interface, at the same time, the Cu₂O holes move to ZnO, which causes the bands to bend and the heterojunction is in equilibrium until the Fermi levels of the ZnO and Cu₂O are equal. Understanding of these photoelectric interactions taking place on the heterojunction can be a guide in explaining the remarkable increase in the spectrum. Such kind of interaction may also take place between the ZnO and CuO nano crystals leading to an efficient energy transfer from the nanoscale metal oxides to the LuAG. To provide more evidence, we investigated the decay characteristics of the particles in detail which will be explained in the following chapters.

3.3.6.2 Spectral Properties of the YAG:Ce³⁺-based Composites

Like the LuAG:Ce³⁺ based materials, spectroscopic behavior of the YAG:Ce³⁺-metal oxide composites were also investigated. Figure 3.14 reveals excitation-emission spectra of the additive-free YAG:Ce³⁺; ZnO, CuO, and their blended forms upon excitation at 450 nm. While the YAG:Ce³⁺ exhibiting a broad-band emission centered at 568 nm, when blended with the ZnO, yielded a 6-fold more intense and 12 nm blue-shifted emission at 556 nm. When the YAG:Ce³⁺ blended with the ZnO-CuO nanoparticles at the same time, the enhancement in the signal intensity was four-fold. The YAG:Ce³⁺-CuO blends exhibited 6 nm of blue-shift and a slight decrease in the emission intensity. Figure 3.15 I and II reveals individually recorded excitation and emission spectra of the YAG:Ce³⁺-CuO and YAG:Ce³⁺-ZnO pairs, respectively. From a careful examination of both spectra, evidence indicating the potential of an energy transfer between the YAG:Ce³⁺ and metal oxides can be seen. In both forms, the tail of the emission spectrum of the metal oxide largely overlaps with the excitation bands

of the YAG:Ce^{3+} . However, further evidence is necessary to explain the enhancement in the emission intensity.

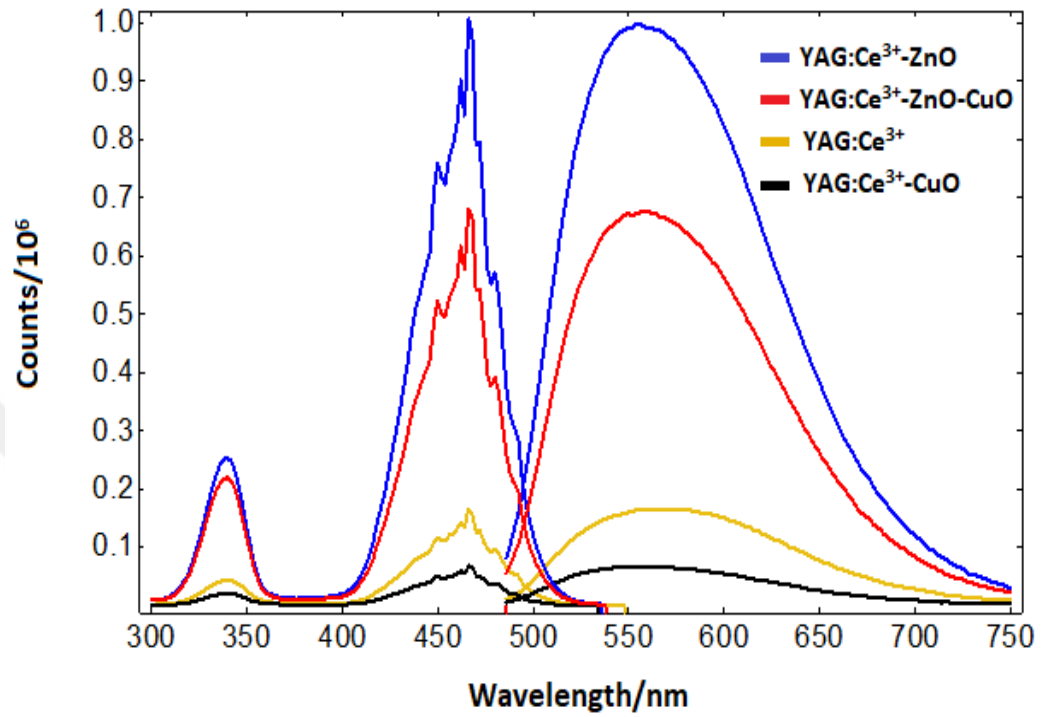


Figure 3.14 Excitation-emission spectra of the additive-free YAG:Ce^{3+} and ZnO, CuO or ZnO-CuO blended forms. Excitation has been performed at 450 nm

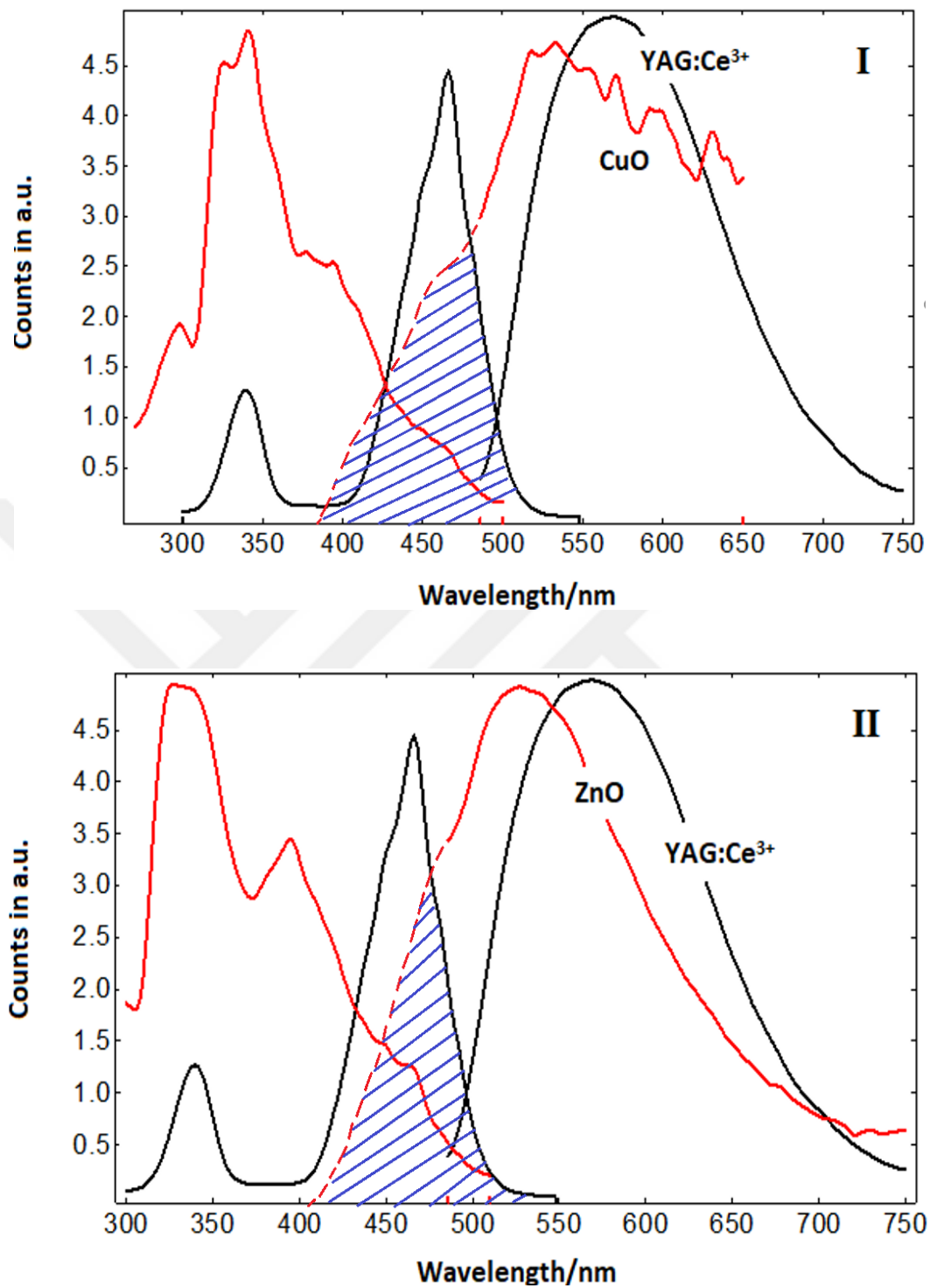


Figure 3.15 I: Normalized luminescence spectra of the YAG:Ce³⁺ and CuO in the PMMA (YAG:Ce³⁺; $\lambda_{ex}=466$ nm $\lambda_{em}=568$ nm, CuO; $\lambda_{ex}=466$ nm $\lambda_{em}=516$ nm) II: Normalized spectra of the YAG:Ce³⁺ and ZnO (YAG:Ce³⁺; $\lambda_{ex}=450$ nm $\lambda_{em}=568$ nm, ZnO; $\lambda_{ex}=466$ nm $\lambda_{em}=528$ nm)

3.3.7 Decay Kinetics of the LuAG:Ce³⁺, YAG:Ce³⁺ and their Blends with Metal Oxides

In most of the previous studies, Ce³⁺ activated LuAG and YAG have been investigated many times in terms of optical properties including decay times. In most of these studies, short lifetimes have been reported for garnets activated by the Ce³⁺. In just a few studies, measurements were made on both the nanosecond and microsecond scale. Some afterglow observed in these studies points out the role of defects in the garnets (Ekuma et al., 2014; Nikl et al., 2007; Ogiegło et al., 2012). In a recent work, Ogiegło and co-workers reported decay curves measured at different time scales (nanosecond, microsecond, and millisecond) for the Ce³⁺ emission in the samples co-doped with different Tb³⁺ concentrations in a LuAG host where the complexity of the microsecond time scale results has been discussed (Shiang et al., 2003). Herein we report nanosecond and microsecond time scale decays of the PMMA entrapped LuAG:Ce³⁺, YAG:Ce³⁺, and their blends with metal oxides. Generally speaking, sub-nanosecond decay times can be assigned to photo-excitation of free excitons and their trapping at defect sites. Photoluminescence arising from normal defects and free excitons occurs on nanosecond timescales, and the presence of the deeply trapped holes results in microsecond lifetimes. Herein, due to the presence of the free charge carriers (electrons and holes) and their efficient migration, and recombination in the phosphors and composites, we recorded short and long luminescence decay time components both in the nanosecond and microsecond time scale. Our decay time-related findings covering a large time scale can be attributed to the existence of the many different kinds of traps and energy depths, and the competing contributions of the charge carriers, excitons, and defects to the luminescence. For the measurements performed in the nanosecond time scale, the sample is exposed to a pulse of laser ($\lambda_{\text{max}}^{\text{ex}} = 467 \text{ nm}$), where the pulse width was dramatically shorter (118.2 ps) than the decay times of the samples (62 and 65 ns for the LuAG:Ce³⁺ and YAG:Ce³⁺). The intensity decay is recorded with a high-speed detection system that permits the measurement of the decay time on the ns timescale with high accuracy. During the measurements performed in the microsecond regime, we used a microsecond flash lamp. The photoluminescence decay curves of the LuAG:Ce³⁺ and

YAG:Ce³⁺ based samples recorded both in nanosecond and microsecond time regime were shown in Figure 3.16, 3.17, 3.18 and 3.19, respectively.

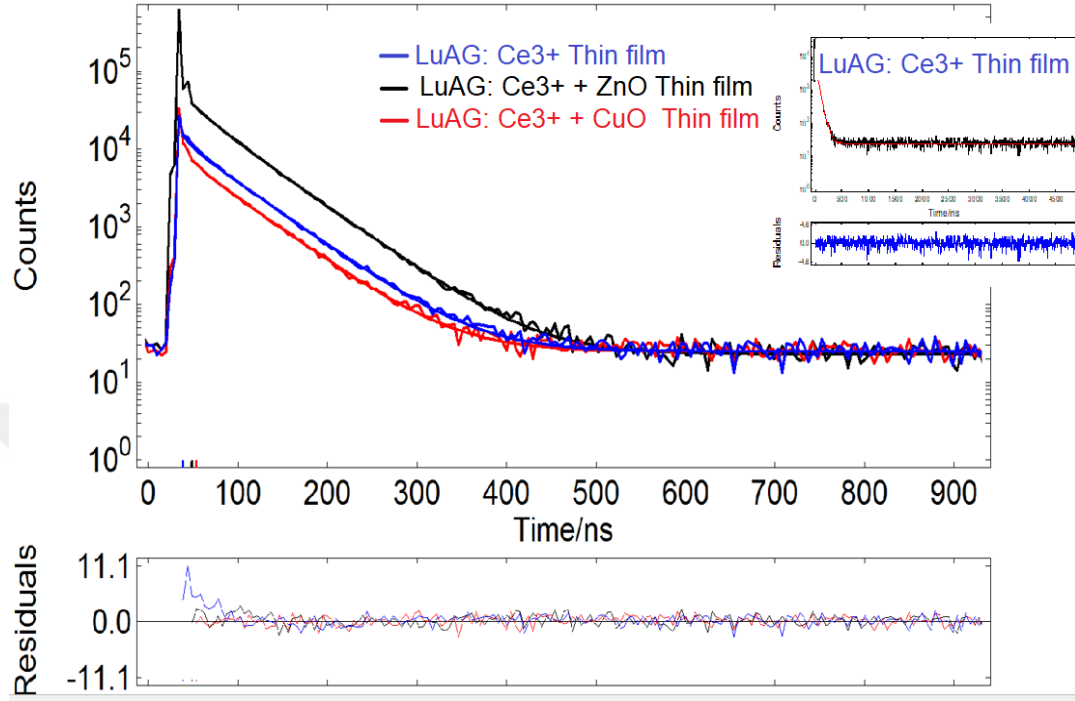


Figure 3.16 Nanosecond regime decay curves of the LuAG:Ce³⁺ based composites

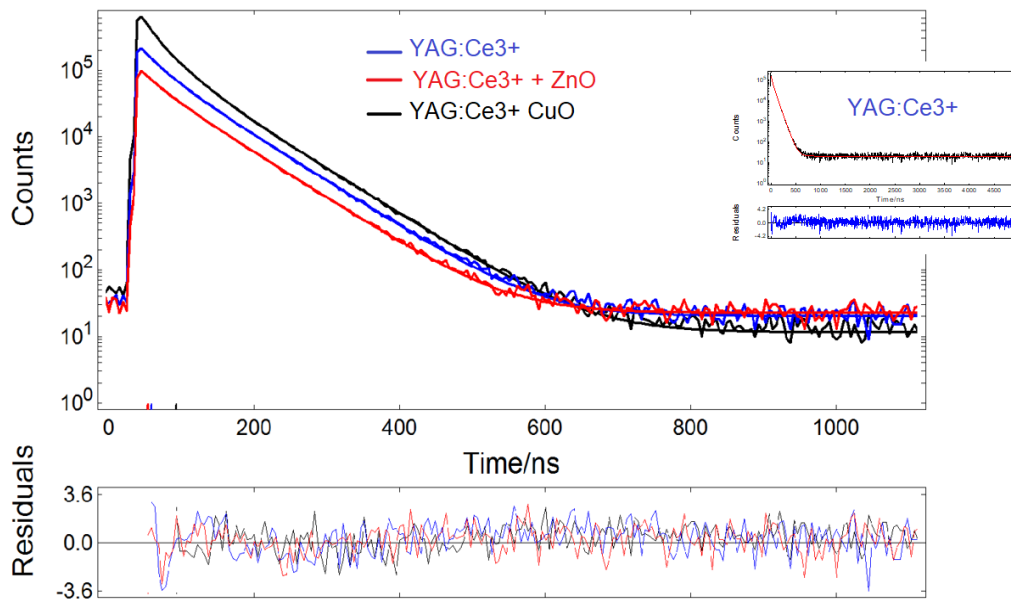


Figure 3.17 Nanosecond regime decay curves of the YAG:Ce³⁺ based composites

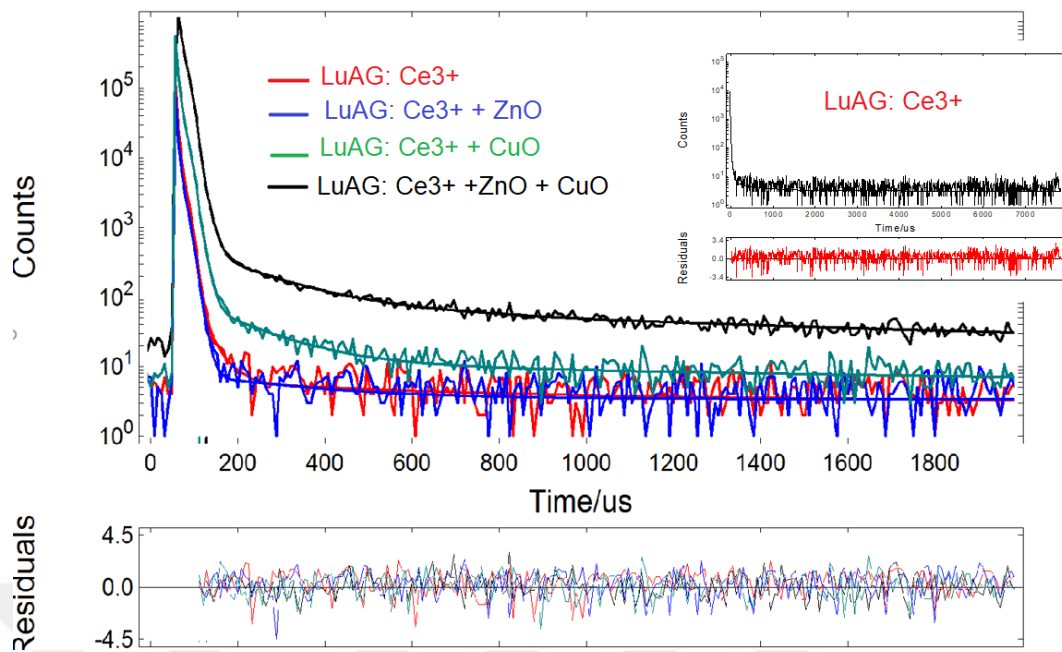


Figure 3.18 Microsecond regime decay curves of the LuAG:Ce³⁺ based composites

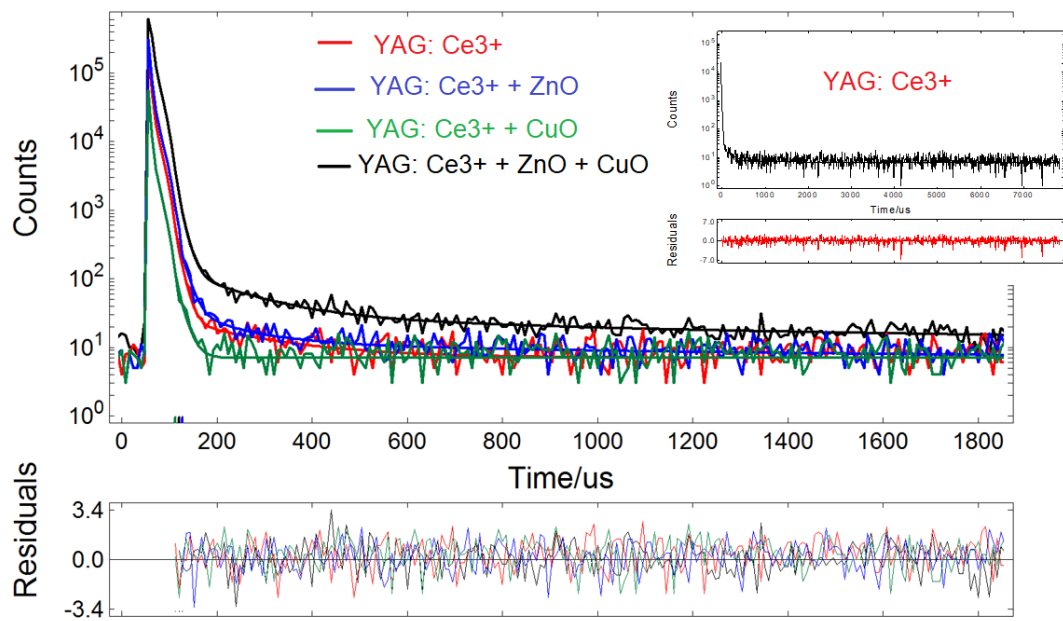


Figure 3.19 Microsecond regime decay curves of the YAG:Ce³⁺ based composites

3.3.7.1 Nanosecond-time Scale Decay Time Measurements

During excitation studies, intensity of the excitation light was kept at 467 nm which is lower than that of the excitation band of the related host. Under these conditions, upon excitation, the polymer-free LuAG:Ce³⁺ exhibited its typical average decay time of 52 ns arising from the 5d-4f transitions of the Ce³⁺. The long and short lifetime components of this decay were 55 (89%) and 26 (11%) ns, respectively. When embedded into the PMMA no significant difference has been observed neither in duration nor in the distribution of the decay components. The phosphor exhibited 53 (93%) and 10 ns (7%) of biexponential decay times. When blended with ZnO and CuO the average decay times of 50 and 51 ns were recorded, respectively. Further details of these measurements were shown in Table 3.4. The Ce³⁺ activated YAG exhibited similar results to the LuAG:Ce³⁺. 62 and 56 ns of average decay times were calculated for the polymer-free and polymer encapsulated forms of the YAG:Ce³⁺, respectively. 58 and 54 ns were measured for the ZnO and CuO blends. In all cases decay times were bi-exponential. Unlike nanosecond time scale results, where the decay time of the Ce³⁺-related emission was about 50–60 ns, the microsecond time scale measurement results were completely different for both the phosphors and phosphor blends. The observed spectral improvement may also be arising from the nanosecond, microsecond and even afterglow properties of the species in question. The size of the nano-scale zinc and copper oxides which is much smaller than the wavelength of the excitation light may also be influential in the performance of the excited states of the phosphors due to the local field effects.

Table 3.4 Decay times of the polymer-free LuAG:Ce³⁺ and YAG:Ce³⁺ and their PMMA embedded blends with ZnO and CuO recorded in nanosecond scale

Sample		Decay Time (ns)	Std. Dev. (ns)	Rel. (%)
LuAG:Ce ³⁺ (Polymer-free)	τ_1	26.22	2.59	11.42
	τ_2	55.28	0.55	88.58
	τ_{avr}		51.96	
LuAG:Ce ³⁺ Thin Film	τ_1	10.00	0.82	7.04
	τ_2	53.31	0.25	92.96
	τ_{avr}		50.26	
LuAG:Ce ³⁺ - ZnO Thin Film	τ_1	21.17	1.20	11.13
	τ_2	53.96	0.29	88.87
	τ_{avr}		50.31	
LuAG:Ce ³⁺ - CuO Thin Film	τ_1	11.13	2.12	4.68
	τ_2	53.06	0.41	95.32
	τ_{avr}		51.10	
YAG:Ce ³⁺ (Polymer-free)	τ_1	29.24	3.84	9.32
	τ_2	65.34	0.71	90.68
	τ_{avr}		61.97	
YAG:Ce ³⁺ Thin Film	τ_1	25.38	0.39	19.32
	τ_2	63.52	0.17	80.68
	τ_{avr}		56.15	
YAG:Ce ³⁺ - ZnO Thin Film	τ_1	24.13	0.68	13.39
	τ_2	63.31	0.21	86.61
	τ_{avr}		58.06	
YAG:Ce ³⁺ - CuO Thin Film	τ_1	27.96	0.35	29.04
	τ_2	64.36	0.20	70.96
	τ_{avr}		53.79	

3.3.7.2 Microsecond-regime Decay Time Measurements

The nanosecond regime studies did not present any evidence for an energy transfer or other potential events taking place within the polymeric matrix. That is due to the

complexity and different character of the three-component composites than that of the previously published RE co-doped phosphors. However, in the microsecond time scale, we observed an increase in the decay times in parallel to the observed enhancements in the emission intensities. Further details of the microsecond-regime decay times and measurement parameters for the LuAG:Ce³⁺, YAG:Ce³⁺ and ZnO, CuO, and ZnO-CuO blended composites are shown in Table 3.5.



Table 3.5 Decay times of the LuAG:Ce³⁺ and YAG:Ce³⁺ and their blends with ZnO, CuO, or ZnO-CuO

Sample	$\lambda_{\max}^{\text{ex}}$ (nm)	$\lambda_{\max}^{\text{ex}}$ (nm)	χ^2		Decay time (μs)	Std. Dev. (μs)	Rel. (%)
LuAG:Ce ³⁺	450	514	1.237	τ_1	7.82	2.01	46.48
				τ_2	33.60	10.65	27.40
				τ_3	647.07	215.02	26.12
				τ_{avr}		180.95	
LuAG:Ce ³⁺ - ZnO	450	510	1.281	τ_1	10.50	0.98	74.29
				τ_2	272.59	87.78	25.71
				τ_{avr}		78.67	
LuAG:Ce ³⁺ - CuO	450	542	1.217	τ_1	11.06	0.33	64.07
				τ_2	134.77	13.65	16.69
				τ_3	1613.72	303.26	19.24
				τ_{avr}		336.20	
LuAG:Ce ³⁺ - ZnO -CuO	450	514	1.089	τ_1	13.17	0.34	38.09
				τ_2	150.12	7.92	27.79
				τ_3	1030.71	59.25	34.12
				τ_{avr}		397.17	

Table 3.5 Continues

Sample	$\lambda_{\max}^{\text{ex}}$ (nm)	$\lambda_{\max}^{\text{ex}}$ (nm)	χ^2		Decay time (μs)	Std. Dev. (μs)	Rel. (%)
YAG:Ce ³⁺	466	568	1.245	τ_1	11.84	0.59	77.93
				τ_2	180.58	27.45	22.07
				τ_{avr}		48.96	
YAG:Ce ³⁺ - ZnO	466	556	1.217	τ_1	15.01	1.77	38.18
				τ_2	114.39	42.70	19.76
				τ_3	1067.91	315.21	42.05
				τ_{avr}		476.83	
YAG:Ce ³⁺ - CuO	466	554	1.170	τ_1	2.05	0.21	29.22
				τ_2	14.71	4.75	70.78
				τ_{avr}		11.00	
YAG:Ce ³⁺ - ZnO - CuO	466	558	1.098	τ_1	12.27	0.41	54.54
				τ_2	129.36	15.91	19.96
				τ_3	954.98	130.02	25.50
				τ_{avr}		275.94	

The decay curves of the LuAG:Ce³⁺ were well fitted by three exponential decay function when excited at 467 nm. The distribution of the short (7.8 μs) mid (33.6 μs) and long lifetime (647 μs) components were found to be 47, 27, and 26%, respectively. The average decay time of the LuAG:Ce³⁺ in the embedded form in PMMA was 181 microseconds. When incorporated with CuO and ZnO-CuO, the LuAG:Ce³⁺ exhibited average decay times of 336 and 397 microseconds, respectively. The YAG:Ce³⁺, exhibited a bi-exponential decay when entrapped individually. The average of the short (11.84 μs, 78%) and long (181 μs, 22%) lifetime components was found to be 49 microseconds. Similar to the decay patterns of the LuAG:Ce³⁺ based composites, both, the YAG:Ce³⁺-ZnO and YAG:Ce³⁺-ZnO-CuO yielded longer average decay times of 476.8 of 275.9 microseconds, compared to the YAG:Ce³⁺. Increases observed in the decay times of the YAG:Ce³⁺ based composites were parallel to the enhancement recorded in the emission intensities. To identify the reasons for the enhancement in the emission intensity of the phosphors when embedded along with the nano-scale metal oxides, we focused on the donor–acceptor approach considering the metal oxides as the donor and the phosphors as the acceptor. According to the theory, if both donor and acceptor are emitting particles, energy transfer manifests itself through quenching of donor fluorescence and a reduction of the fluorescence lifetime, accompanied also by an increase in acceptor emission. Table 3.6 indicates potential donor–acceptor pairs and their decay behavior for different composites prepared by keeping the amount of the donor constant and increasing the amount of the acceptor, gradually. The CuO exhibited decreasing decay times when entrapped along with the gradually increasing amounts of the LuAG:Ce³⁺ in the PMMA which can be concluded as evidence of an energy transfer from the CuO nanoparticles towards the micro-scale phosphors in embedded form when used in critical concentration. Similarly, the ZnO exhibited parallel behavior to the CuO in decay characteristics manifesting decreasing decay times when encapsulated with increasing amounts of both phosphors. Table 3.6 indicates the detailed decay characteristics of the studied composites.

Table 3.6 Decay times of the composites prepared by donors; ZnO, CuO, and their blends including varying amounts of the acceptor counterparts; LuAG:Ce³⁺ or YAG:Ce³⁺

Sample	Donor	Acceptor	$\lambda_{\text{max}}^{\text{ex}}$ (nm)	$\lambda_{\text{max}}^{\text{em}}$ (nm)	χ^2	Decay Time (μs)	Std.Dev. (μs)	Rel. (%)	
CuO	CuO (5 mg)	-	350	532	1.253	τ_1	8.37	0.87	28.12
						τ_2	125.84	20.28	26.32
						τ_3	1033.08	166.04	45.56
						τ_{avr}		499.90	
CuO-LuAG:Ce ³⁺	CuO (5 mg)	LuAG:Ce ³⁺ (5 mg)	350	532	1.236	τ_1	10.12	0.17	37.10
						τ_2	149.42	6.00	22.55
						τ_3	881.03	20.61	40.35
						τ_{avr}		389.76	
CuO-LuAG:Ce ³⁺	CuO (5 mg)	LuAG:Ce ³⁺ (10 mg)	350	532	1.167	τ_1	9.93	0.14	55.85
						τ_2	155.62	6.92	19.49
						τ_3	952.93	37.53	24.66
						τ_{avr}		274.13	
CuO-YAG:Ce ³⁺	CuO (5 mg)	YAG:Ce ³⁺ (5 mg)	350	532	1.229	τ_1	10.81	0.17	38.37
						τ_2	141.69	4.47	24.82
						τ_3	994.63	23.52	36.81
						τ_{avr}		407.52	
CuO-YAG:Ce ³⁺	CuO (5 mg)	YAG:Ce ³⁺ (10 mg)	350	532	1.163	τ_1	10.52	0.59	38.19
						τ_2	112.13	15.83	20.66
						τ_3	861.43	84.58	41.14
						τ_{avr}		380.74	

Table 3.6 Continues

Sample	Donor	Acceptor	$\lambda_{\text{max}}^{\text{ex}}$ (nm)	$\lambda_{\text{max}}^{\text{em}}$ (nm)	χ^2	Decay Time (μs)		Std.Dev. (μs)	Rel. (%)
ZnO	ZnO (5 mg)	-	374	502	1.228	τ_1	15.58	0.99	19.94
						τ_2	172.14	14.66	30.62
						τ_3	983.12	57.46	49.44
						τ_{avr}	538.11		
ZnO-LuAG:Ce ³⁺	ZnO (5 mg)	LuAG:Ce ³⁺ (5 mg)	374	502	1.123	τ_1	11.82	0.52	30.58
						τ_2	156.87	10.97	30.95
						τ_3	1064.74	81.59	38.47
						τ_{avr}	456.75		
ZnO-LuAG:Ce ³⁺	ZnO (5 mg)	LuAG:Ce ³⁺ (10 mg)	374	502	1.103	τ_1	11.55	0.39	32.74
						τ_2	152.18	9.09	29.95
						τ_3	950.10	56.24	37.31
						τ_{avr}	400.93		
ZnO-YAG:Ce ³⁺	ZnO (5 mg)	YAG:Ce ³⁺ (5 mg)	374	502	1.141	τ_1	12.91	0.49	32.08
						τ_2	165.63	12.62	28.37
						τ_3	930.72	57.36	39.55
						τ_{avr}	418.20		
ZnO-YAG:Ce ³⁺	ZnO (5 mg)	YAG:Ce ³⁺ (10 mg)	374	502	1.273	τ_1	10.31	0.18	51.94
						τ_2	141.68	6.78	22.31
						τ_3	939.92	45.65	25.75
						τ_{avr}	278.11		

3.3.8 Quantum Yield Measurements

Acquisition of photons from an integrating sphere can only measure the external quantum efficiency (EQE) including re-absorbed photons. The internal quantum efficiency is defined as the ratio of the number of photons emitted to the number of photons absorbed by the sample. The correct measurement of the QY relies on the measurement of decay times, the radiative and nonradiative rates. In mathematical terms, it can be written as

$$\Phi = k_r / (k_{nr} + k_r) \quad (3.1)$$

where, Φ , k_r and k_{nr} are the quantum yield, radiative and non-radiative decay rates, respectively.

$$k_r = \Phi / \tau \quad (3.2)$$

$$k_{nr} = (1 - \Phi) / \tau \quad (3.3)$$

Herein, the Φ and τ were extracted from the experimental results, and the k_r and k_{nr} were calculated from the decay time data. In previous works, investigators followed the decay times obtained from nanosecond regime measurements of the Ce^{3+} ions arising from the 5d-4f transitions of the Ce^{3+} , due to the effects of trapping, internal reflection, and scattering between air and material interfaces (Gorrotxategi et al., 2015; Silva et al., 2019). Therefore, herein we considered nanosecond regime decay times of the Ce^{3+} ions in QY calculations as a robust comparison parameter. The external and internal quantum efficiencies of the studied forms shown in Table 6, are in agreement with the EQEs obtained with previous measurements performed with integrating sphere systems, with values lying between 0.80 and 0.98 for the additive-free-LuAG: Ce^{3+} and YAG: Ce^{3+} based samples. We observed a distinct enhancement from 88.4 to 116.4% in the external quantum yield of LuAG: Ce^{3+} -ZnO-CuO composite, with respect to the additive free-LuAG: Ce^{3+} . Similarly, in the case of YAG: Ce^{3+} based samples, presence of the ZnO in the composite resulted in enhancement of the EQE from 80.6 to 98.1 which can be attributed to the inclusion of the ZnO, CuO, and/or ZnO-CuO into the phosphors (See Table 3.7).

Table 3.7 External and internal quantum efficiencies of the studied samples

Sample	External Quantum Efficiency (%)	Internal Quantum Efficiency (%)
LuAG:Ce ³⁺	88.4	96.0
LuAG:Ce ³⁺ -ZnO	79.6	93.4
LuAG:Ce ³⁺ -CuO	96.0	99.9
LuAG:Ce ³⁺ -ZnO-CuO	116.4	-
YAG:Ce ³⁺	80.6	99.7
YAG:Ce ³⁺ -ZnO	98.1	111.4
YAG:Ce ³⁺ -CuO	76.9	99.3
YAG:Ce ³⁺ -ZnO-CuO	89.2	97.8

3.4 Conclusion

In this work, photoinitiated luminescence of the two commercially available phosphors, lutetium aluminum garnet (LuAG:Ce³⁺), and yttrium aluminum garnet (YAG: Ce³⁺), and their blends with nano-scale metal oxides have been investigated in detail by steady-state and decay time measurements. In contrast to most of the former studies, the phosphors and their blends with metal oxides have been excited with the blue wavelength commonly used in LED or display applications. When the phosphors are embedded along with the nano-scale metal oxides; which can absorb and emit the light in a large spectrum; they displayed an unexpected enhancement in the emission intensities. Both phosphors exhibited interesting interactions with the metal oxides yielding enhanced brightness and a longer excited lifetime with respect to their additive-free forms. When the LuAG:Ce³⁺ was entrapped in a poly methyl methacrylate matrix along with ZnO-CuO nanoparticles, both the absorption and emission efficiency of the phosphor enhanced 59-fold. Similarly, when yttrium aluminum garnet (YAG:Ce³⁺) incorporated with ZnO and ZnO-CuO composites, exhibited 6- and 4-fold enhancement in the emission intensity when excited by the blue light. The steady-state and decay time based experimental studies have confirmed that metal oxides act as donors and phosphors as acceptors when encapsulated in the

PMMA in an appropriate ratio. The microsecond timescale excited-state lifetime of the LuAG:Ce³⁺ extended from 181 to 397 μ s when embedded along with the ZnO-CuO NPs in the PMMA. Similarly, the life span of the YAG:Ce³⁺ extended from 49 to 477 microseconds for the YAG:Ce³⁺-ZnO composite films. The external quantum yield of the LuAG:Ce³⁺-ZnO-CuO based composite enhanced from 88.4 to 116.4% with respect to the additive free-LuAG:Ce³⁺. In YAG:Ce³⁺ based samples, the presence of the ZnO in the matrix resulted in the enhancement of the EQE from 80.6 to 98.1. Increased brightness, quantum yield, and long luminescence times observed in this study obtained with low-cost metal oxides may be a promising strategy for the production of more effective phosphors in the future.



CHAPTER FOUR

MANIPULATION OF BRIGHTNESS AND DECAY KINETICS OF LuAG:Ce³⁺, YAG:Ce³⁺ AND CASN:Eu²⁺ BY (Ru(phen)₃PF₆) IN PMMA MATRIX

4.1 Introduction

In this chapter, we investigated the interactions between the green, yellow and red phosphors of **LuAG:Ce³⁺**, **YAG:Ce³⁺** and **CASN:Eu²⁺** and the ruthenium complex of Tris (1,10-phenanthroline) ruthenium (II) hexafluorophosphate (**(Ru(phen)₃PF₆)**) in terms of excitation and emission characteristics as well as decay times. Binary blends of the phosphors together with the Ru(phen)₃PF₆ were prepared both in the absence and presence of the ionic liquid 1-Butyl-3-methyl-imidazolium-tetrafluoroborate (**BMIM BF₄**), respectively. Phosphors are generally photostable and thermally stable for a long time duration. However, photo and thermal stability of the dyes is sometimes questionable. Therefore, we used the ionic liquid; BMIM BF₄ to enhance the long term photostability of the dye which is evidenced in earlier studies many times for the HPTS dye and others (Aydogdu et al., 2011; Oter et al., 2006, 2016; Topal et al., 2008). Composition information of the LuAG:Ce³⁺, YAG:Ce³⁺ and CASN:Eu²⁺ and the ruthenium complex of the Ru(phen)₃PF₆ composites were given in Table 4.1.

The LuAG:Ce³⁺-Ru(phen)₃PF₆ based composite exhibited 50 nm of red-shift and slight enhancement in the emission intensity. However, when prepared in the presence of the ionic liquid the LuAG:Ce³⁺-Ru(phen)₃PF₆ yielded 92 nm of red-shift and 2.78 fold enhancement in the emission intensity.

Similarly, the YAG:Ce³⁺-Ru(phen)₃PF₆ based composite exhibited 18 nm and 54 nm of red-shift in the absence and presence of the ionic liquid, respectively. 2.24 and 4.00 fold increase in the emission intensity was observed for both of the above mentioned composites.

Binary blends of the CASN:Eu²⁺ and Ru(phen)₃PF₆ resulted in 1.75 and 3.15 fold enhancement in the emission intensity for the IL-free and IL-doped blends, respectively. 4 and 8 nm of blue-shift was accompanied to the increase in the intensities.

In all cases, we observed a significant enhancement in the emission characteristics of the phosphors due to the presence of the Ru(phen)₃PF₆ within the matrix. Addition of the ionic liquid into the matrix increased the interactions between the phosphor particles and the dye in direction of enhancement in terms of the brightness and red-shift. In order to clarify, the role of the ionic liquid on the brightness of the composites we also tested the binary mixtures of the phosphors an ionic liquid only. However, the phosphor-IL blends did not exhibit any spectral shift or increased signal intensity. Therefore, we attributed the enhancement of the brightness observed for the phosphor-ruthenium based blends to the synergistic effect of the ionic liquid on ruthenium complex only, and investigated these interactions into detail on bases of excitation and emission spectra as well as the decay times in further chapters.

Table 4.1 Composition of the used luminescent materials and additives

Sample	Phosphor: 5mg	Organic Dye: 2 mg	Ionic liquid: 48 mg	Matrix: 120 mg	Solvent: 2 mL
LuAG:Ce ³⁺	LuAG:Ce ³⁺	-	-	PMMA	THF
LuAG:Ce ³⁺ - Ru(phen) ₃ PF ₆	LuAG:Ce ³⁺	Ru(phen) ₃ PF ₆	-	PMMA	THF
LuAG:Ce ³⁺ - Ru(phen) ₃ PF ₆ – IL	LuAG:Ce ³⁺	Ru(phen) ₃ PF ₆	BMIM BF ₄	PMMA	THF
YAG:Ce ³⁺	YAG:Ce ³⁺	-	-	PMMA	THF
YAG:Ce ³⁺ - Ru(phen) ₃ PF ₆	YAG:Ce ³⁺	Ru(phen) ₃ PF ₆	-	PMMA	THF
YAG:Ce ³⁺ - Ru(phen) ₃ PF ₆ – IL	YAG:Ce ³⁺	Ru(phen) ₃ PF ₆	BMIM BF ₄	PMMA	THF
CASN:Eu ²⁺	CASN:Eu ²⁺	-	-	PMMA	THF
CASN:Eu ²⁺ - Ru(phen) ₃ PF ₆	CASN:Eu ²⁺	Ru(phen) ₃ PF ₆	-	PMMA	THF
CASN:Eu ²⁺ - Ru(phen) ₃ PF ₆ – IL	CASN:Eu ²⁺	Ru(phen) ₃ PF ₆	BMIM BF ₄	PMMA	THF

4.2 LuAG:Ce³⁺- Ru(phen)₃PF₆ based Blends

The LuAG:Ce³⁺ yielded excitation maximum of 344 and 450 nm arising from the electronic transitions of the Ce³⁺; $^2F_{5/2} \rightarrow 5d^2$ and $^2F_{7/2} \rightarrow 5d^1$, respectively. The broad and intense emission band centered at 516 and 538 nm can be assigned to the back transitions of the excited 5d electrons of the Ce³⁺ to the 4f orbitals. The LuAG:Ce³⁺-Ru(phen)₃PF₆ based composite exhibited similar excitation spectra to the LuAG:Ce³⁺ exhibiting the excitation maxima at the same wavelengths of 346 and 450 nm. However, the emission spectrum varied both in shape and maximum exhibiting a shoulder at 516 nm and a maximum at 566 nm. 50 nm of red-shift and slight enhancement in the emission intensity accompanied to this variation.

The LuAG:Ce³⁺-Ru(phen)₃PF₆-IL based composite exhibited completely different excitation spectrum then that of the LuAG:Ce³⁺ and LuAG:Ce³⁺-Ru(phen)₃PF₆ yielding two intense excitation bands at 396 and 466 nm. When excited at 450 nm the ternary composite yielded a well-shaped, broad and intense emission spectrum centered at 608 nm. We observed 92 nm of red-shift and 2.78 fold enhancement in the emission intensity. In order to identify, the reasons lying behind this enhancement, we investigated the potential interactions between the dye and phosphor recording their excitation and emission spectra, individually. Then we recorded the overlaid spectra to reveal the energy transfer possibilities between the phosphor and the dye. Table 4.2 indicates excitation-emission maximum and Stoke's shift information of the used luminescent forms.

Table 4.2 Absorption ($\lambda_{\max}^{\text{abs}}$), excitation ($\lambda_{\max}^{\text{ex}}$), emission ($\lambda_{\max}^{\text{em}}$) maximum and Stoke's shift ($\Delta\lambda$) information of the used luminescent forms

Sample	$\lambda_{\max}^{\text{abs1}}$ (nm)	$\lambda_{\max}^{\text{abs2}}$ (nm)	$\lambda_{\max}^{\text{ex}}$ (nm)	$\lambda_{\max}^{\text{em}}$ (nm)	$\Delta\lambda$ (nm)
LuAG:Ce ³⁺	344	450	450	516	66
LuAG:Ce ³⁺ - Ru(phen) ₃ PF ₆	346	450	450	566	116
LuAG:Ce ³⁺ - Ru(phen) ₃ PF ₆ - IL	396	450	450	608	158

4.2.1 Spectral Behavior of the LuAG:Ce³⁺

Spectral behavior of the LuAG:Ce³⁺ has been explained in chapter two. As previously mentioned, the two bands observed at 346 and 450 nm in the excitation spectrum of the LuAG:Ce³⁺, corresponds to transitions to the two lowest energy levels of the five crystal field components lying in D₂ symmetry (Bárta et al., 2012; Liu et al., 2015; Praveena et al., 2011; Setlur & Srivastava, 2007; Wu et al., 2007). Corresponding emission spectra of the 5d-4f transition resulted in broad emission bands centered at 514 in the green region for the LuAG:Ce³⁺. The 4f⁰5d¹ configuration electrons undergo ²D term split (²D_{3/2} and ²D_{5/2}), and the 4f electron of the ground state 4f¹ configuration, forms ²F_{7/2} and ²F_{5/2} states by spin-orbit coupling. Therefore, the broad-band emissions observed in the room temperature spectra of Ce³⁺ doped LuAG can be assigned to the sum of the two overlapping sub-bands arising from the splitting of the 2F state to the ²F_{7/2} and ²F_{5/2} states, respectively. The presence of radiative recombination of electron-hole pairs on Ce³⁺ ions is also evidenced by electron paramagnetic resonance experiments which suggest the presence of LuAG defects in the vicinity of Ce³⁺ ions (Ahn & Kim, 2016; Liu et al., 2015). The Stoke's shift of the LuAG:Ce³⁺ was simply determined to calculate the energy difference between excitation (450 nm) and emission (514 nm) band maxima, which yields a value of 64 nm.

4.2.2 Spectral Behavior of the Ruthenium Complex

The excitation and emission spectra of the ruthenium complex recorded in PMMA were presented in Figure 4.1. The absorption band observed around 382 nm which is at the UV side of the spectrum can be attributed to the Π - Π^* transitions of the Phenanthroline (phen) rings and singlet intra ligand charge transfer (ILCT) transitions. The intense excitation band appeared 466 nm is due to the metal ligand charge transfers (MLCT). Therefore, the large excitation band extending from 300 to 550 nm can be considered as a result of the overlap of the ILCT and MLCT bands (Ji et al., 2010; Leung et al., 2016; Song et al., 2003). The emission band centered at 578 nm which is very bright and highly photostable, arises from phosphorescence process lying on metal-to-ligand charge transfer (Demas et al., 1968; Rosenzweig et al., 1996).

When the ruthenium complex embedded with the IL in the PMMA matrix, the emission maximum observed at 578 nm shifts to 606 nm. Additionally, an increase in the emission intensity and a band broadening occurs. The variation observed in the emission spectrum of the ruthenium complex when embedded together with the ionic liquid (IL) can be attributed to the influenced energy levels of the phen ligand lying in the complex due to the electron-donating imidazolium ring of the IL. Figure 4.1 indicates excitation-emission spectra of the PMMA embedded $\text{Ru(phen)}_3\text{PF}_6$ in the absence and presence of the ionic liquid.

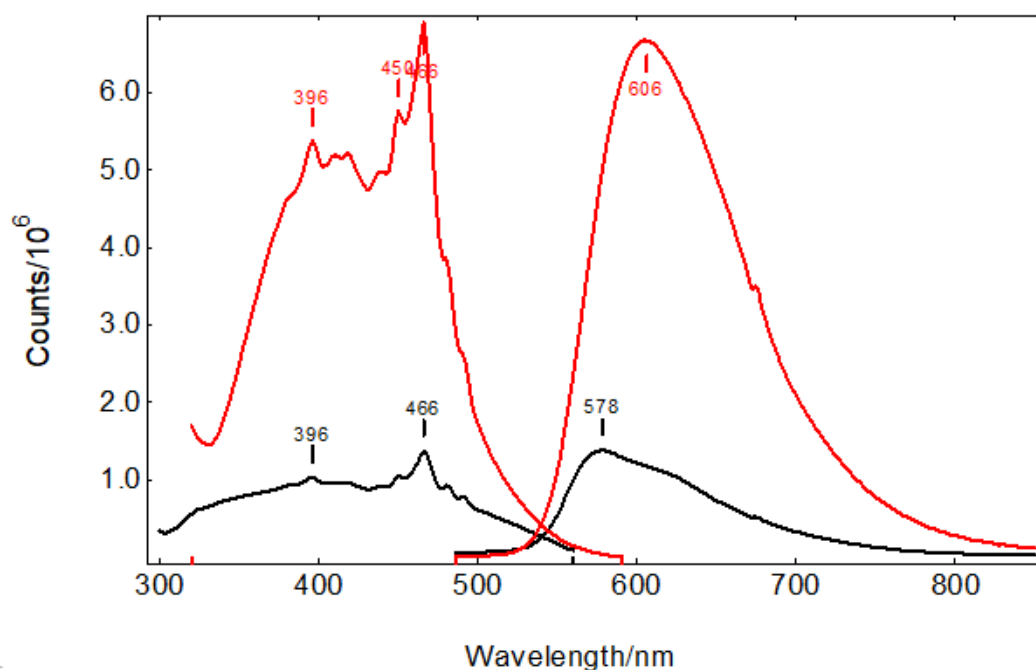


Figure 4.1 Excitation-emission spectra of the additive-free Ru(phen)₃PF₆ dye (black) and binary blend of Ru(phen)₃PF₆ - IL (red) upon excitation at 466 nm

4.2.3 Spectral Behavior of the Ternary Blends of LuAG:Ce³⁺, Ru(phen)₃PF₆ and Ionic Liquid

Spectral behavior of the Ternary blends of LuAG:Ce³⁺, Ru(phen)₃PF₆ and ionic liquid was shown in Figure 4.2. The LuAG:Ce³⁺-Ru(phen)₃PF₆-IL based ternary composites exhibited completely different excitation spectrum then that of the excitation band of the LuAG:Ce³⁺ and LuAG:Ce³⁺-Ru(phen)₃PF₆ yielding two intense excitation bands at 396 and 466 nm. When excited at 450 nm the ternary composite yielded a well-shaped, broad and intense emission spectrum centered at 608 nm. We observed 92 nm of red-shift and 2.78 fold enhancement in the emission intensity with respect to the individually recorded spectra of the LuAG:Ce³⁺.

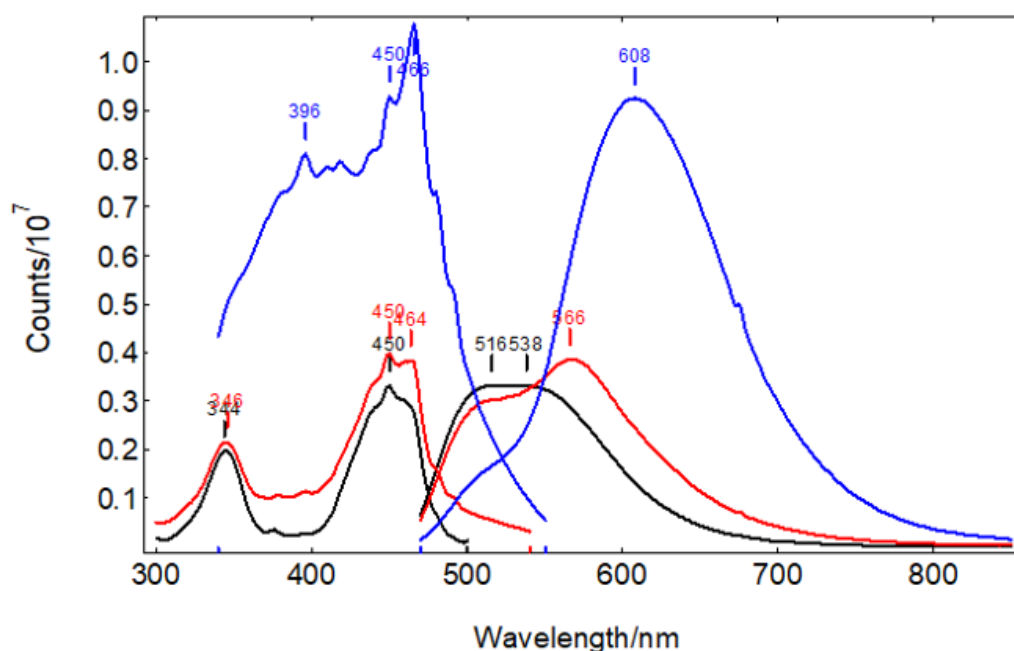


Figure 4.2 Excitation-emission spectra of the additive-free LuAG:Ce³⁺ (black), binary blend of LuAG:Ce³⁺-Ru(phen)₃PF₆ (red) and ternary blend of LuAG:Ce³⁺-Ru(phen)₃PF₆-IL (blue)

In order to understand, the reasons of this enhancement we gathered the individually recorded excitation and emission spectrum of the LuAG:Ce³⁺ and the Ru(phen)₃PF₆ on the same graph. As mentioned earlier according to the theory, if both donor and acceptor species are emitting forms, energy transfer indicates itself by an increase in acceptor emission and a quenching of donor fluorescence. A reduction of the fluorescence lifetime of the donor supports presence of the energy transfer between the counterparts.

Figure 4.3 indicates the overlaid spectra of the singly recorded LuAG:Ce³⁺ and the Ru(phen)₃PF₆ in the absence of the ionic liquid. The figure indicates potential overlap area between the emission spectra of the LuAG:Ce³⁺ and excitation spectrum of the Ru(phen)₃PF₆ when each chromophore has been excited its own excitation wavelength.

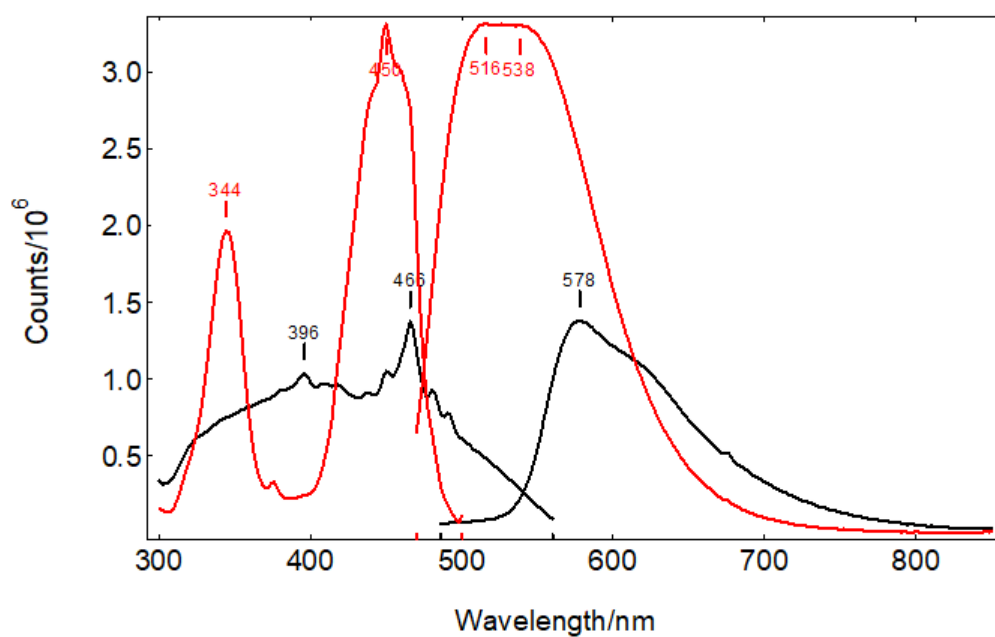


Figure 4.3 Excitation-emission spectra of the additive-free LuAG:Ce³⁺ upon excitation at 450 nm (red) and Ru(phen)₃PF₆ (black) when excited at 466 nm

We also recorded the normalized form of this spectrum to clarify the overlap area and to understand the extent of the interaction between the potential donor of LuAG:Ce³⁺ and the acceptor counterpart; Ru(phen)₃PF₆ dye (See Figure 4.4). We evidenced existence of the energy transfer from the phosphor to the Ru(phen)₃PF₆ dye by decay time measurements.

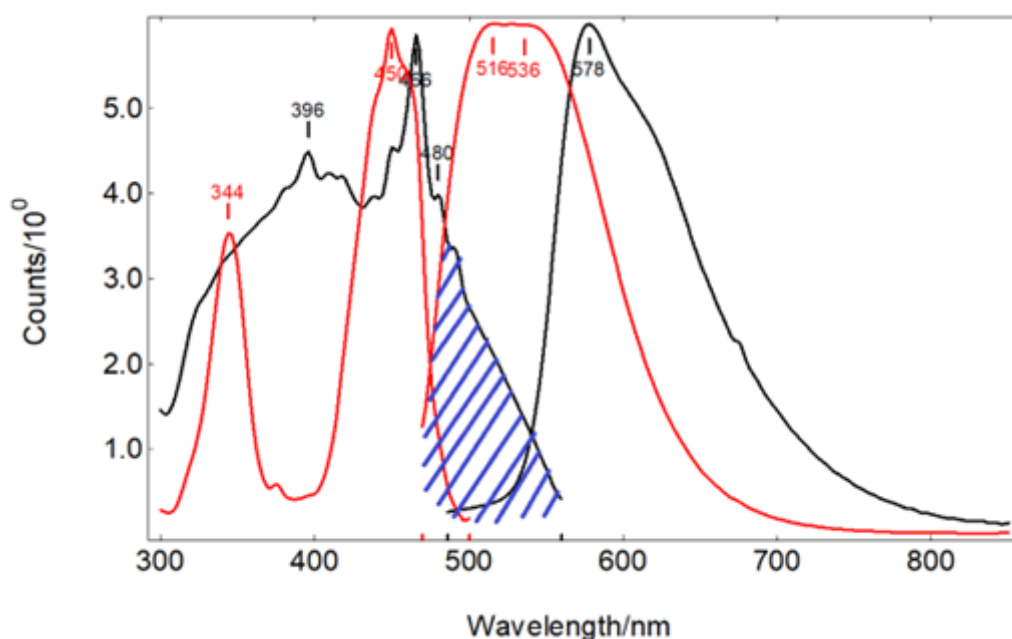


Figure 4.4 Normalized Excitation-emission spectra of the additive-free LuAG:Ce³⁺ upon excitation at 450 nm (red) and Ru(phen)₃PF₆ (black) when excited at 466 nm

4.2.4 Decay Time Measurements of IL-free and IL-doped LuAG:Ce³⁺ and LuAG:Ce³⁺-Ru(phen)₃PF₆

Decay time measurements of the IL-free and IL-doped LuAG:Ce³⁺ and LuAG:Ce³⁺-Ru(phen)₃PF₆ were performed for nanosecond and microsecond time regions, respectively. In nanosecond time regime the PMMA embedded Ru(phen)₃PF₆ exhibited bi-exponential decays of 13.75 (3.12%) and 359.16 ns (96.88%) corresponding to an average 348.63 ns (See Table 4.3). However, in microsecond time scale the dye yielded a tri-exponential decay consisting of 12.12 (67.00%), 176.9 (14.89%) and 1198.00 μ s (18.00%) components. The average decay time of the Ru(phen)₃PF₆ has been evaluated as 250.2 μ s (See Table 4.4). Results of the both of the nanosecond and microsecond time scale measurements can be assigned to the existence of the triplet excited states and intra-ligand and/or metal to ligand charge transfer transitions in the complex and its micro-environment.

Similarly, the LuAG:Ce³⁺ also exhibited bi-exponential and tri-exponential decays for the nanosecond and microsecond time scales, respectively. Components of the

50.05 ns bi-exponential decay were recorded as 9.89 (5.73%) and 52.76 ns (94.27%). The average decay time of 50.05 ns can simply be attributed to the 5d-4f transitions of the Ce^{3+} which is in accordance with the literature (Yildirim et al., 2020; Yildirim et al., 2021). Distribution of the tri-exponential decay was in the form of 9.97 (96.04%), 105.51 (12.61%) and 976.97 μs (18.35%). Average decay time for the microsecond time scale was calculated as 196.30 μs . The three exponential decays observed for the phosphor can be assigned to the native defects in the host lattice including vacancies, antisites and dislocations, which trap the electrons delaying recombination with the holes within the crystal (Yildirim et al., 2019).

Binary or ternary blends of the $\text{LuAG}:\text{Ce}^{3+}$ exhibited different behavior for the nanosecond and microsecond time scales. While the $\text{LuAG}:\text{Ce}^{3+}$ exhibiting 50.05 ns of excited state lifetime when blended with the $\text{Ru}(\text{phen})_3\text{PF}_6$ and $\text{Ru}(\text{phen})_3\text{PF}_6$ and IL, yielded 167.23 and 256.80 ns of decay times exhibiting an increase in the duration (See Table 4.3). The observed increase in the decay time cannot be concluded as an evidence of the energy transfer from the phosphor to the Ru complex. However, in the microsecond time scale, addition of the $\text{Ru}(\text{phen})_3\text{PF}_6$ and $\text{Ru}(\text{phen})_3\text{PF}_6$ and IL into the composite resulted in a decrease in the excited triplet lifetimes from 196.30 to 165.97 and 173.00 μs , respectively which can be an indicator of an energy transfer between these two luminescent materials (See Table 4.4).

Table 4.3 Decay times of the LuAG:Ce³⁺, Ru(phen)₃PF₆ and their blends recorded in nanosecond time scale

Sample	$\lambda_{\text{max}}^{\text{ex}}$ (nm)	$\lambda_{\text{max}}^{\text{em}}$ (nm)	χ^2		Decay time (ns)	Std. Dev. (ns)	Rel. (%)
LuAG:Ce ³⁺	450	516	1.278	τ_1	9.89	0.58	5.73
				τ_2	52.76	0.17	94.27
				τ_{avr}		50.05	
Ru(phen) ₃ PF ₆	466	578	1.302	τ_1	13.75	1.12	3.12
				τ_2	359.16	3.05	96.88
				τ_{avr}		348.63	
LuAG:Ce ³⁺ - Ru(phen) ₃ PF ₆	450	566	1.480	τ_1	52.75	0.26	63.47
				τ_2	372.59	4.91	36.53
				τ_{avr}		167.23	
LuAG:Ce ³⁺ - Ru(phen) ₃ PF ₆ – IL	450	608	1.107	τ_1	77.56	3.45	12.41
				τ_2	284.52	2.49	87.59
				τ_{avr}		256.80	

Table 4.4 Decay times of the LuAG:Ce³⁺, Ru(phen)₃PF₆ and their blends recorded in microsecond time scale

Sample	$\lambda_{\max}^{\text{ex}}$ (nm)	$\lambda_{\max}^{\text{em}}$ (nm)	χ^2	Decay time (μs)		Std. Dev. (μs)	Rel. (%)
LuAG:Ce ³⁺	450	516	1.304	τ_1	9.97	0.10	69.04
				τ_2	105.51	4.93	12.61
				τ_3	976.97	38.34	18.35
				τ_{avr}		196.30	
Ru(phen) ₃ PF ₆	466	578	1.289	τ_1	12.13	0.31	67.20
				τ_2	176.91	24.19	14.89
				τ_3	1198.05	228.16	17.91
				τ_{avr}		250.20	
LuAG:Ce ³⁺ - Ru(phen) ₃ PF ₆	450	566	1.257	τ_1	9.76	0.10	75.39
				τ_2	103.77	5.70	10.51
				τ_3	1059.15	59.77	14.10
				τ_{avr}		165.97	
LuAG:Ce ³⁺ - Ru(phen) ₃ PF ₆ – IL	450	608	1.271	τ_1	9.76	0.08	72.14
				τ_2	91.68	3.68	11.35
				τ_3	977.03	32.19	16.52
				τ_{avr}		173.00	

4.2.5 Investigation of Donor-Acceptor Relationship between the LuAG:Ce³⁺ and Ru(phen)₃PF₆ in terms of Decay Time Measurements

Herein we considered the LuAG:Ce³⁺ as the donor and the Ru(phen)₃PF₆ as the acceptor counterparts, on basis of the steady-state measurements, respectively. To verify the theory, we prepared composites including increasing amounts of the acceptor counterpart. Decay times of the composites were investigated by microsecond time scale measurements (See Table 4.5). As can be concluded from Table 4.5 decay time of the LuAG:Ce³⁺ exhibited a decrease when blended with the increasing amounts of the Ru(phen)₃PF₆ providing evidence for a potential energy transfer from the LuAG:Ce³⁺ to the Ru complex. However, this variation is only observable for the microsecond time scale measurements rather than the nanosecond time scale excited state lifetime of the LuAG:Ce³⁺ arising from the 5d to 4f transitions of the Ce³⁺. The donor-acceptor interaction therefore relies on the electron transitions from the vacancies, antisites and dislocations of the crystal to the long lifetime triplet states of the Ru(phen)₃PF₆.

Table 4.5 Decay times of the composites prepared by varying amounts of the acceptor (Ru(phen)₃PF₆) versus constant amount of the donor (LuAG:Ce³⁺) in microsecond scale

Sample	Donor	Acceptor		Decay Time (μs)	Std.Dev. (μs)	Rel. (%)
LuAG:Ce ³⁺	LuAG:Ce ³⁺ (5 mg)	-	τ ₁	9.94	0.09	75.73
			τ ₂	104.16	4.92	10.20
			τ ₃	1209.89	66.75	14.07
			τ _{avr}		187.20	
LuAG:Ce ³⁺ -Ru(phen) ₃ PF ₆	LuAG:Ce ³⁺ (5 mg)	Ru(phen) ₃ PF ₆ (2 mg)	τ ₁	9.71	0.10	75.44
			τ ₂	97.27	5.64	10.39
			τ ₃	993.66	53.71	14.17
			τ _{avr}		156.13	
LuAG:Ce ³⁺ -Ru(phen) ₃ PF ₆	LuAG:Ce ³⁺ (5 mg)	Ru(phen) ₃ PF ₆ (5 mg)	τ ₁	8.81	0.05	88.93
			τ ₂	51.10	2.31	5.62
			τ ₃	694.57	26.76	5.45
			τ _{avr}		45.30	

4.3 YAG:Ce³⁺ - Ru(phen)₃PF₆ based Blends

The YAG:Ce³⁺ yielded excitation maximum of 338 and 466 nm arising from the electronic transitions of the Ce³⁺; ²F_{5/2}→5d² and ²F_{7/2}→5d¹, respectively. The broad and intense emission band centered at 562 nm which is sum of the two overlapping sub-bands arising from the splitting of the 2F state to the ²F_{7/2} and ²F_{5/2} states, can be assigned to the back transitions of the excited 5d electrons of the Ce³⁺ to the 4f orbitals. Radiative recombination of electron-hole pairs on Ce³⁺ ions which is evidenced by electron paramagnetic resonance experiments (Ahn & Kim, 2016; Liu et al., 2015), also causes band broadening in the spectrum.

The YAG:Ce³⁺-Ru(phen)₃PF₆ blend exhibited two excitation maxima at 338 and 466 nm. However, the emission spectrum varied both in shape and maximum exhibiting 18 nm of red shift and accompanying band broadening. The emission maximum appeared at 580 nm. 2.24-fold enhancement in the emission intensity was also observed.

The YAG:Ce³⁺-Ru(phen)₃PF₆-IL based composite exhibited similar excitation behavior but considerably red shifted emission spectrum in comparison to the YAG:Ce³⁺ and YAG:Ce³⁺-Ru(phen)₃PF₆ yielding a very broad and intense emission band centered at 616 nm when excited at 466 nm. We reported 54 nm of red-shift and 4.00-fold enhancement in the emission intensity.

To clarify the theoretical facts lying behind this enhancement, we investigated the potential interactions between the dye and phosphor recording their excitation and emission spectra, individually. Then we recorded the overlaid spectra to reveal the energy transfer possibilities between the phosphor and the dye. Table 4.6 indicates excitation-emission maximum and Stoke's shift information of the used luminescent forms.

Table 4.6 Absorption ($\lambda_{\max}^{\text{abs}}$), excitation ($\lambda_{\max}^{\text{ex}}$), emission ($\lambda_{\max}^{\text{em}}$) maximum and Stoke's shift ($\Delta\lambda$) information of the used luminescent forms of YAG:Ce³⁺, YAG:Ce³⁺ - Ru(phen)₃PF₆ and YAG:Ce³⁺ - Ru(phen)₃PF₆ – IL

Sample	$\lambda_{\max}^{\text{abs1}}$ (nm)	$\lambda_{\max}^{\text{abs2}}$ (nm)	$\lambda_{\max}^{\text{ex}}$ (nm)	$\lambda_{\max}^{\text{em}}$ (nm)	$\Delta\lambda$ (nm)
YAG:Ce ³⁺	338	466	466	562	96
YAG:Ce ³⁺ - Ru(phen) ₃ PF ₆	338	466	466	580	114
YAG:Ce ³⁺ - Ru(phen) ₃ PF ₆ – IL	340	466	466	616	150

4.3.1 Spectral Behavior of the Ternary Blends of YAG:Ce³⁺, Ru(phen)₃PF₆ and Ionic Liquid

Spectral response of the ternary blends of YAG:Ce³⁺, Ru(phen)₃PF₆ and ionic liquid was shown in Figure 4.5. The YAG:Ce³⁺-Ru(phen)₃PF₆-IL containing ternary composites exhibited broadened excitation spectrum then that of the excitation band of the YAG:Ce³⁺ and YAG:Ce³⁺-Ru(phen)₃PF₆ yielding a very broad and intense excitation band between 350-550 nm. When excited at 466 nm the composite yielded a well-shaped, broad and intense emission spectrum centered at 616 nm. We observed 54 nm of red-shift and 4.00 fold enhancement in the emission intensity with respect to the individually recorded spectra of the YAG:Ce³⁺.

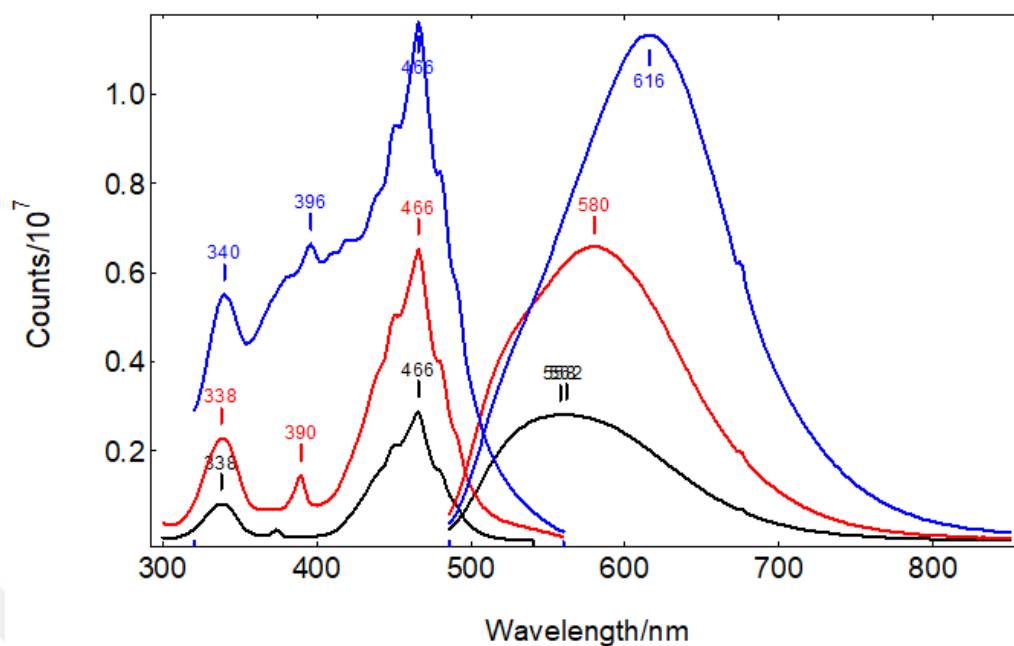


Figure 4.5 Excitation-emission spectra of the additive-free YAG:Ce³⁺ (black), binary blend of YAG:Ce³⁺-Ru(phen)₃PF₆ (red) and ternary blend of YAG:Ce³⁺-Ru(phen)₃PF₆-IL (blue)

The individually recorded excitation and emission spectrum of the YAG:Ce³⁺ and the Ru(phen)₃PF₆ were gathered on the same graph to understand the potential donor and acceptor species. Figure 4.6 indicates the overlaid spectra of the singly recorded YAG:Ce³⁺ and the Ru(phen)₃PF₆ in the absence of the ionic liquid. The figure indicates potential overlap area between the emission spectra of the YAG:Ce³⁺ and excitation spectrum of the Ru(phen)₃PF₆ when each chromophore has been excited its own excitation wavelength.

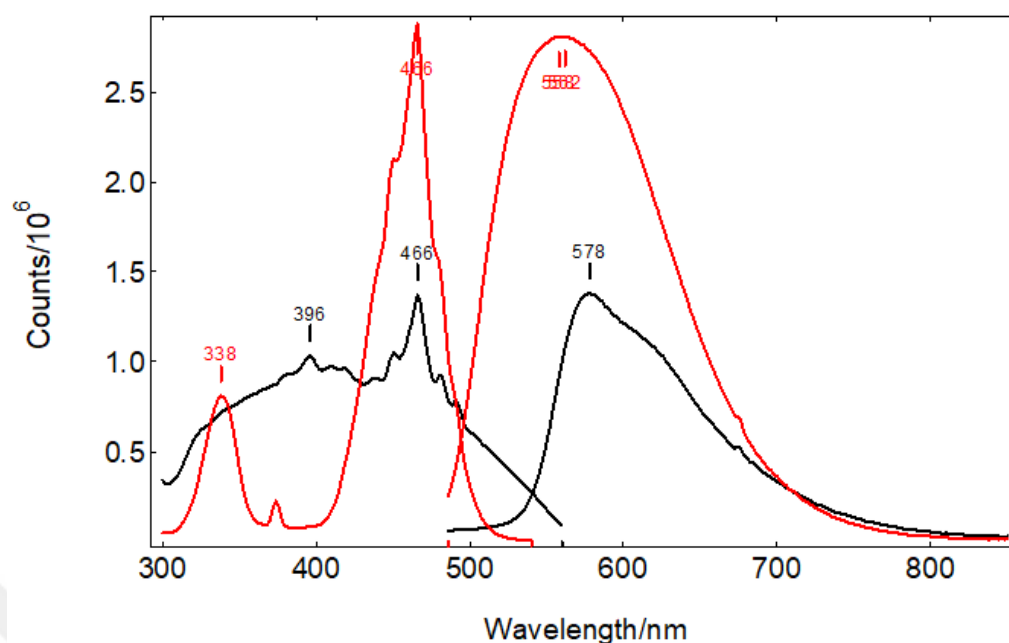


Figure 4.6 Excitation-emission spectra of the additive-free YAG:Ce³⁺ (red) and Ru(phen)₃PF₆ (black) when excited at 466 nm

We also recorded the normalized form of this spectrum to show the overlap area and to understand the extent of the interaction between the YAG:Ce³⁺ and the Ru(phen)₃PF₆ dye (See Figure 4.7). According to the figure, there is a possibility of an energy transfer from the YAG:Ce³⁺ to the Ru(phen)₃PF₆. In addition to the steady-state measurements, we also evidenced existence of the energy transfer from the phosphor to the Ru(phen)₃PF₆ dye by decay time measurements.

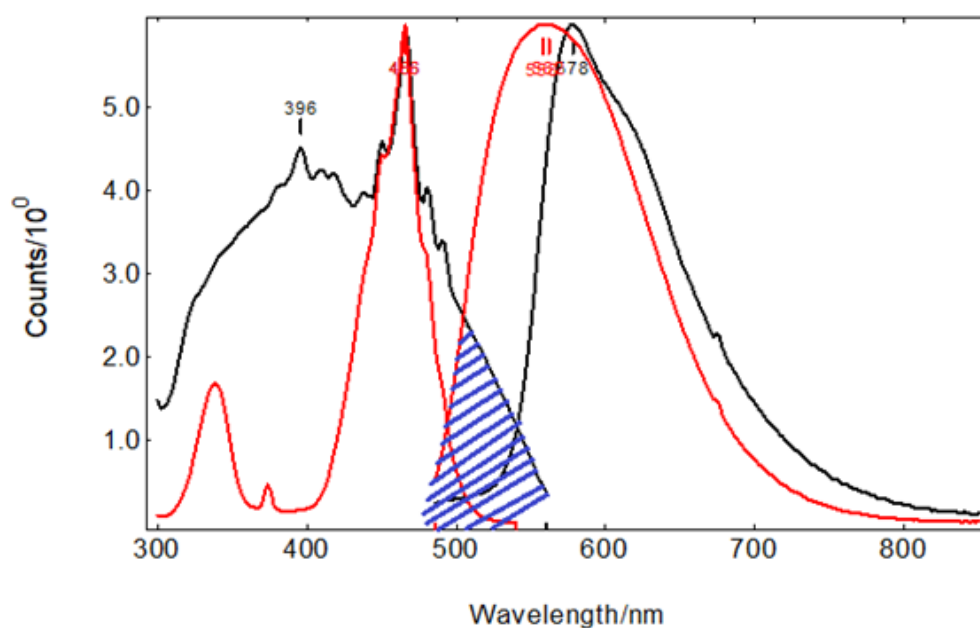


Figure 4.7 Normalized excitation-emission spectra of the additive-free YAG:Ce³⁺ (red) and Ru(phen)₃PF₆ (black) when excited at 466 nm

4.3.2 Decay Time Measurements of IL-free and IL-doped YAG:Ce³⁺ and YAG:Ce³⁺-Ru(phen)₃PF₆

Similar to the previous work, the decay time measurements of the IL-free and IL-doped YAG:Ce³⁺ and YAG:Ce³⁺-Ru(phen)₃PF₆ blends were performed for nanosecond and microsecond time regions, respectively (See Table 4.7). In nanosecond time regime, the YAG:Ce³⁺ exhibited bi-exponential decay times of 26.62 (12.14%) and 63.85 ns (87.86%) corresponding to 59.30 ns of average time. The recorded excited state lifetimes observed in nanosecond time scale arise from fast 5d-4f transitions of the Ce³⁺. The tri-exponential excited state decays were recorded in the microsecond time scale measurements. The YAG:Ce³⁺ exhibited 11.56 (74.80%), 92.74 (10.08%) and 640.92 (15.12%) μ s of decay times corresponding to the average decay time of 113.95 μ s. The slower decays can be attributed to the native defects in the host lattice including vacancies, antisites and dislocations, which trap the electrons, delaying recombination with the holes within the crystal structure of the YAG:Ce³⁺.

Table 4.7 Decay times of the YAG:Ce³⁺, Ru(phen)₃PF₆ and their blends recorded in nanosecond and microsecond time scale

Sample	$\lambda_{\max}^{\text{ex}}$ (nm)	$\lambda_{\max}^{\text{em}}$ (nm)	χ^2		Decay time (ns)	Std.Dev. (ns)	Rel. (%)
YAG:Ce ³⁺	466	562	1.185	τ_1	26.62	0.69	12.14
				τ_2	63.85	0.17	87.86
				τ_{avr}		59.30	
YAG:Ce ³⁺ - Ru(phen) ₃ PF ₆	466	580	1.535	τ_1	59.92	0.18	67.95
				τ_2	410.62	4.24	32.05
				τ_{avr}		172.10	
YAG:Ce ³⁺ - Ru(phen) ₃ PF ₆ – IL	466	616	1.043	τ_1	65.98	0.75	40.04
				τ_2	278.64	2.44	59.96
				τ_{avr}		193.16	
Sample	$\lambda_{\max}^{\text{ex}}$ (nm)	$\lambda_{\max}^{\text{em}}$ (nm)	χ^2		Decay time (μs)	Std. Dev. (μs)	Rel. (%)
YAG:Ce ³⁺	466	562	1.122	τ_1	11.56	0.20	74.80
				τ_2	92.74	1.82	10.08
				τ_3	640.92	50.92	15.12
				τ_{avr}		113.95	
YAG:Ce ³⁺ - Ru(phen) ₃ PF ₆	466	580	1.238	τ_1	10.38	0.08	85.27
				τ_2	62.86	4.35	6.28
				τ_3	727.22	31.88	8.45
				τ_{avr}		74.34	
YAG:Ce ³⁺ - Ru(phen) ₃ PF ₆ – IL	466	616	1.477	τ_1	9.32	0.04	89.09
				τ_2	58.16	2.05	5.34
				τ_3	787.97	21.91	5.57
				τ_{avr}		56.10	

Binary or ternary blends of the YAG:Ce³⁺ exhibited different behavior for the nanosecond and microsecond time scales. While the YAG:Ce³⁺ exhibiting 59.30 ns of excited state lifetime when blended with the Ru(phen)₃PF₆ and Ru(phen)₃PF₆ and IL, yielded 172.10 and 193.16 ns of decay times exhibiting an increase in the excited state lifetimes. However, in the microsecond time scale, addition of the Ru(phen)₃PF₆ and Ru(phen)₃PF₆ and IL into the composite resulted in a decrease in the excited triplet lifetimes from 113.95 to 74.34 and 56.10 μ s, respectively which can be an indicator of an energy transfer between these two luminescent materials. Further details of the distribution of the short and long lifetime components were shown in Table 4.7.

4.3.3 Investigation of Donor-Acceptor Relationship between the YAG:Ce³⁺ and Ru(phen)₃PF₆ in terms of Decay Time Measurements

Considering the steady-state measurements, the YAG:Ce³⁺ can be accepted as the donor and the Ru(phen)₃PF₆ as the acceptor counterparts. To verify the theory, we prepared composites including increasing amounts of the Ru(phen)₃PF₆. Decay times of the composites were investigated by microsecond time scale measurements (See Table 4.8). As can be concluded from Table 4.8 decay time of the YAG:Ce³⁺ exhibited a decrease when blended with the increasing amounts of the Ru(phen)₃PF₆ providing an evidence for a potential energy transfer from the YAG:Ce³⁺ to the Ru(phen)₃PF₆. However, this variation is only observable for the microsecond time scale measurements rather than the nanosecond time scale. The donor-acceptor interaction therefore relies on the electron transitions from the vacancies, antisites and dislocations of the crystal to the long lifetime triplet states of the Ru(phen)₃PF₆ because the excited state lifetime of the YAG:Ce³⁺ arising from the 5d to 4f transitions of the Ce³⁺ is too fast.

Table 4.8 Decay times of the composites prepared by varying amounts of the acceptor (Ru(phen)₃PF₆) versus constant amount of the donor (YAG:Ce³⁺) in microsecond scale

Sample	Donor	Acceptor		Decay Time (μ s)	Std.Dev. (μ s)	Rel. (%)
YAG:Ce ³⁺	YAG:Ce ³⁺ (5 mg)	-	τ_1	11.73	0.18	74.97
			τ_2	116.63	13.03	10.99
			τ_3	773.28	74.10	14.04
			τ_{avr}		129.70	
YAG:Ce ³⁺ - Ru(phen) ₃ PF ₆	YAG:Ce ³⁺ (5 mg)	Ru(phen) ₃ PF ₆ (2 mg)	τ_1	10.23	0.08	85.30
			τ_2	64.05	3.58	7.05
			τ_3	765.03	37.29	7.66
			τ_{avr}		71.31	
YAG:Ce ³⁺ - Ru(phen) ₃ PF ₆	YAG:Ce ³⁺ (5 mg)	Ru(phen) ₃ PF ₆ (5 mg)	τ_1	8.95	0.06	88.68
			τ_2	32.96	1.41	7.37
			τ_3	562.72	18.00	3.95
			τ_{avr}		32.40	

4.4 CASN:Eu²⁺- Ru(phen)₃PF₆ based Blends

The CASN:Eu²⁺ yielded a broad band excitation spectrum exhibiting two maximum at 340 and 466 nm arising from the electronic excitation of the Eu²⁺ ion. The intense emission band observed at 640 nm arises from the allowed 4f⁶ 5d¹ → 4f⁷ parity-allowed transitions of the Eu²⁺ ion located in the lattice which exhibit highly efficient and broad 5d–4f transition absorption and emission bands (Yang et al., 2012; Yildirim et al., 2019).

The CASN:Eu²⁺- Ru(phen)₃PF₆ blend exhibited two excitation maxima at 340 and 466 nm, respectively. The emission maximum appeared at 636 nm exhibiting 4 nm of blue-shift in comparison to the emission maximum of the dye-free CASN:Eu²⁺. Additionally, 1.75-fold enhancement in the emission intensity was also observed.

In case of the CASN:Eu²⁺- Ru(phen)₃PF₆ - IL compromising composite similar excitation behavior was observed. We reported 8 nm of blue-shift and 3.15-fold enhancement in the emission intensity.

Table 4.9 indicates excitation-emission maximum and Stoke's shift information of the used luminescent forms.

Table 4.9 Absorption ($\lambda_{\max}^{\text{abs}}$), excitation ($\lambda_{\max}^{\text{ex}}$), emission ($\lambda_{\max}^{\text{em}}$) maximum and Stoke's shift ($\Delta\lambda$) information of the used luminescent forms of CASN:Eu²⁺, CASN:Eu²⁺ - Ru(phen)₃PF₆ and CASN:Eu²⁺ - Ru(phen)₃PF₆ - IL

Sample	$\lambda_{\max}^{\text{abs1}}$ (nm)	$\lambda_{\max}^{\text{abs2}}$ (nm)	$\lambda_{\max}^{\text{ex}}$ (nm)	$\lambda_{\max}^{\text{em}}$ (nm)	$\Delta\lambda$ (nm)
CASN:Eu ²⁺	340	466	466	640	174
CASN:Eu ²⁺ - Ru(phen) ₃ PF ₆	340	466	466	636	170
CASN:Eu ²⁺ - Ru(phen) ₃ PF ₆ - IL	340	466	466	632	166

4.4.1 Spectral Behavior of the Ternary Blends of CASN:Eu²⁺, Ru(phen)₃PF₆ and Ionic Liquid

Spectral response of the ternary blends of CASN:Eu²⁺, Ru(phen)₃PF₆ and ionic liquid was shown in Figure 4.8. The CASN:Eu²⁺-Ru(phen)₃PF₆-IL containing composites exhibited broadened excitation spectrum then that of the excitation band of the CASN:Eu²⁺ and CASN:Eu²⁺ - Ru(phen)₃PF₆ yielding a very intense excitation band between 350-600 nm. When excited at 466 nm the ternary blends yielded a well-shaped, broad and intense emission spectrum centered at 632 nm. We observed 8 nm of red-shift and 3.15 fold enhancement in the emission intensity with respect to the individually recorded spectra of the CASN:Eu²⁺.

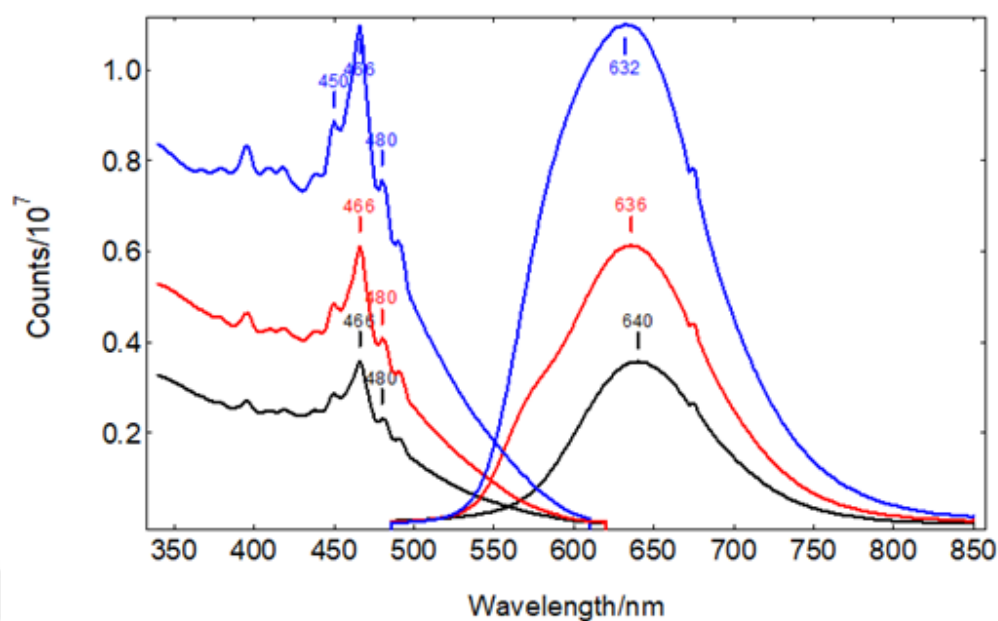


Figure 4.8 Excitation-emission spectra of the additive-free CASN:Eu²⁺ (black), binary blend of CASN:Eu²⁺ - Ru(phen)₃PF₆ (red) and ternary blend of CASN:Eu²⁺ - Ru(phen)₃PF₆-IL (blue)

We recorded the excitation and emission spectra of the Ru(phen)₃PF₆ dye and the CASN:Eu²⁺ phosphor individually and overlaid them to reveal the energy transfer possibilities between the phosphor and the dye. Figure 4.9 indicates the gathered spectra of the singly recorded CASN:Eu²⁺ and the Ru(phen)₃PF₆ in the absence of the ionic liquid. The Figure indicates potential overlap area between the emission spectra of the Ru(phen)₃PF₆ and excitation spectrum of the CASN:Eu²⁺ when each chromophore has been excited at 466 nm.

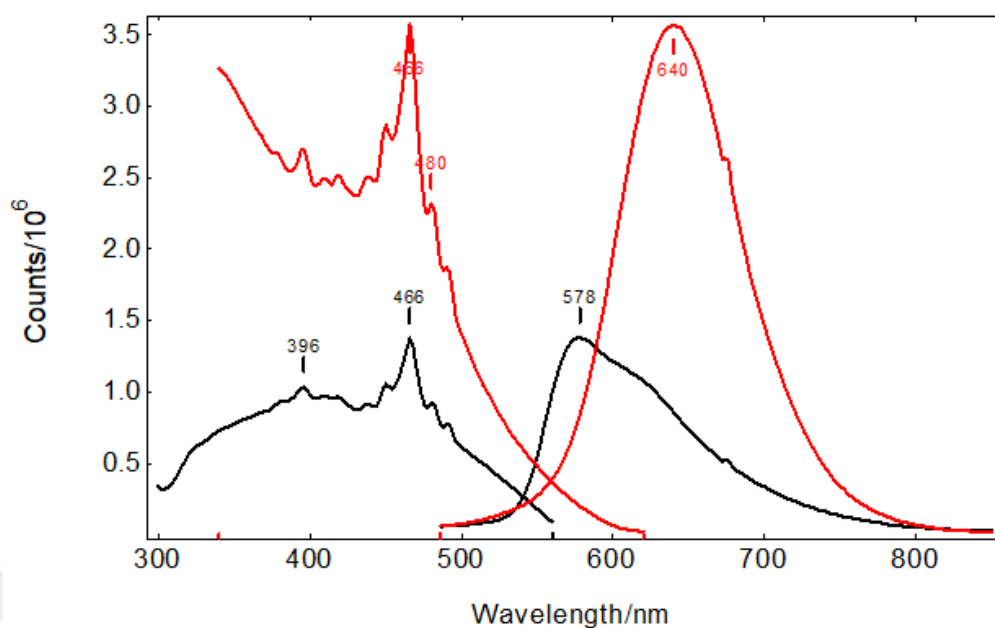


Figure 4.9 Excitation-emission spectra of the additive-free CASN:Eu²⁺ (red) and Ru(phen)₃PF₆ (black) when excited at 466 nm

We also recorded the normalized form of this spectrum to show the overlap area and to understand the extent of the interaction between the donor (Ru(phen)₃PF₆) and the acceptor (CASN:Eu²⁺) forms (See Figure 4.10). According to the figure, there is a possibility of an energy transfer from the Ru(phen)₃PF₆ to the CASN:Eu²⁺. In addition to the steady-state measurements, we also evidenced existence of the energy transfer from the Ru(phen)₃PF₆ dye to the phosphor by decay time measurements.

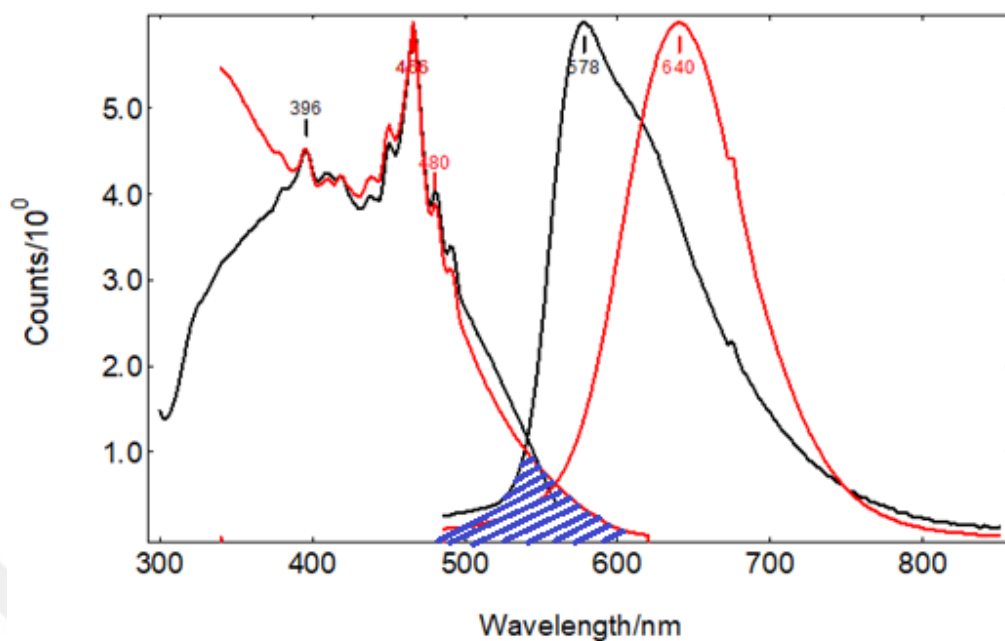


Figure 4.10 Normalized excitation-emission spectra of the additive-free CASN:Eu²⁺ (red) and Ru(phen)₃PF₆ (black) when excited at 466 nm

4.4.2 Decay Time Measurements of IL-free and IL-doped CASN:Eu²⁺ and CASN:Eu²⁺- Ru(phen)₃PF₆ Comprising Blends

The decay time measurements of the IL-free and IL-doped CASN:Eu²⁺ and CASN:Eu²⁺- Ru(phen)₃PF₆ blends were performed for nanosecond and microsecond time regions, respectively. In nanosecond time regime, the CASN:Eu²⁺ exhibited bi-exponential decay times of 1.11 (22.84%) and 655.17 ns (77.16%) corresponding to 504.60 ns of average time. The recorded excited state lifetimes observed in nanosecond time scale arise from fast 4f⁶ 5d¹ → 4f⁷ transitions of the Eu²⁺. The tri-exponential excited state decays were recorded in the microsecond time scale measurements. The CASN:Eu²⁺ exhibited 9.31 (87.48%), 84.42 (5.44%) and 883.26 (7.08%) μs of decay times corresponding to the average decay time of 74.10 μs (See Table 4.10). The slower decays can be attributed to the native defects in the host lattice including vacancies, antisites and dislocations, which trap the electrons, delaying their recombination with the holes within the crystal structure.

Table 4.10 Decay times of the CASN:Eu²⁺, Ru(phen)₃PF₆ and their blends recorded in nanosecond and microsecond time scale

Sample	$\lambda_{\text{max}}^{\text{ex}}$ (nm)	$\lambda_{\text{max}}^{\text{em}}$ (nm)	χ^2		Decay time (ns)	Std. Dev. (ns)	Rel. (%)
CASN:Eu ²⁺	466	640	1.084	τ_1	1.11	0.01	22.84
				τ_2	655.17	8.56	77.16
				τ_{avr}		504.60	
CASN:Eu ²⁺ - Ru(phen) ₃ PF ₆	466	636	1.214	τ_1	17.93	1.67	0.92
				τ_2	553.12	3.67	99.08
				τ_{avr}		547.65	
CASN:Eu ²⁺ - Ru(phen) ₃ PF ₆ -IL	466	632	1.282	τ_1	170.10	13.73	22.47
				τ_2	410.22	16.72	77.53
				τ_{avr}		353.26	
Sample	$\lambda_{\text{max}}^{\text{ex}}$ (nm)	$\lambda_{\text{max}}^{\text{em}}$ (nm)	χ^2		Decay time (μs)	Std. Dev. (μs)	Rel. (%)
CASN:Eu ²⁺	466	640	1.191	τ_1	9.31	0.09	87.48
				τ_2	84.42	7.41	5.44
				τ_3	883.26	73.90	7.08
				τ_{avr}		74.10	
CASN:Eu ²⁺ - Ru(phen) ₃ PF ₆	466	636	1.204	τ_1	10.46	0.13	77.63
				τ_2	93.37	6.28	9.56
				τ_3	945.74	58.74	12.81
				τ_{avr}		130.00	
CASN:Eu ²⁺ - Ru(phen) ₃ PF ₆ -IL	466	632	1.185	τ_1	10.58	0.10	78.58
				τ_2	90.91	5.18	9.12
				τ_3	960.07	45.35	12.30
				τ_{avr}		131.70	

Binary or ternary blends of the CASN:Eu²⁺ exhibited different behavior for the nanosecond and microsecond time scales. While the solely CASN:Eu²⁺ exhibiting 504.60 ns of excited state lifetime when blended with the Ru(phen)₃PF₆ and then with the Ru(phen)₃PF₆-IL, yielded 547.65 and 353.26 ns of decay times in the excited state. The decrease observed in the decay time in the presence of the IL in nanosecond region can be attributed to the change of donor acceptor counterparts with respect to the phosphor blends investigated in former chapters. Herein the donor is the Ru(phen)₃PF₆ and its decay dynamics has been effected from the presence of the IL rather than the phosphor. However, in the microsecond time scale, addition of the Ru(phen)₃PF₆ and Ru(phen)₃PF₆-IL into the composite resulted in increase in the excited triplet lifetimes from 74.10 to 130.00 and 131.70 μ s, respectively (See Table 4.10).

4.4.3 Investigation of Donor-Acceptor Relationship between the CASN:Eu²⁺ and Ru(phen)₃PF₆ in terms of Decay Time Measurements

Considering the steady-state measurements, the Ru(phen)₃PF₆ can be accepted as the donor and the CASN:Eu²⁺ as the acceptor counterparts. To verify the theory, we prepared composites including increasing amounts of the CASN:Eu²⁺. Decay times of the composites were investigated by microsecond time scale measurements (See Table 4.11). As can be concluded from Table 4.11 decay time of the Ru(phen)₃PF₆ presented a decrease when blended with the increasing amounts of the CASN:Eu²⁺ providing an evidence for a potential energy transfer from the Ru(phen)₃PF₆ to the CASN:Eu²⁺. However, this variation is only observable for the microsecond time scale measurements rather than the nanosecond time scale. Therefore, the donor-acceptor interactions promotes on bases of the initial emission of the Ru(phen)₃PF₆ and acceptance of this energy by the phosphor. As mentioned earlier in the microsecond time scale, the electron transitions from the vacancies, antisites and dislocations of the crystal are responsible from the lifetime components of the phosphor. Therefore, this kind of transitions have been effected from the presence of the dye rather than the nanosecond lifetime of the phosphor arising from the fast 5d-4f transitions of the Eu²⁺.

Table 4.11 Decay times of the composites prepared by varying amounts of the acceptor (CASN:Eu²⁺) versus constant amount of the donor (Ru(phen)₃PF₆) in microsecond scale

Sample	Donor	Acceptor		Decay Time (μ s)	Std.Dev. (μ s)	Rel. (%)
Ru(phen) ₃ PF ₆	Ru(phen) ₃ PF ₆ (2 mg)	-	τ_1	12.13	0.31	67.20
			τ_2	176.91	24.19	14.89
			τ_3	1198.06	228.16	17.91
			τ_{avr}		250.20	
CASN:Eu ²⁺ - Ru(phen) ₃ PF ₆	Ru(phen) ₃ PF ₆ (2 mg)	CASN:Eu ²⁺ (5 mg)	τ_1	10.98	0.29	71.28
			τ_2	55.24	7.18	11.65
			τ_3	568.35	34.34	17.07
			τ_{avr}		110.40	
CASN:Eu ²⁺ - Ru(phen) ₃ PF ₆	Ru(phen) ₃ PF ₆ (2 mg)	CASN:Eu ²⁺ (10 mg)	τ_1	8.84	0.09	86.32
			τ_2	33.46	2.02	8.51
			τ_3	487.28	20.88	5.17
			τ_{avr}		34.85	

4.5 Long Term Photostability Studies of the Dye-Phosphor Blends

Photo and thermal stability of the dyes is sometimes questionable due to the environmental effects including corrosive vapors or oxidizing agents and sometimes the sunlight. Therefore, we used the ionic liquid; BMIM BF₄ to enhance the long term photo-stability of the dye whose effect is evidenced in earlier studies many times for the HPTS dye and others (Aydogdu et al., 2011; Oter et al., 2006, 2016; Topal et al., 2008). We prepared the IL-free and IL-doped composites of the Ru dye as well as their phosphor blends and tested their fluorescence intensities after certain time periods by steady state and kinetic measurements. However, long term photo-stabilities of the (Ru(phen)₃PF₆) based composites did not exhibit any significant difference due to the presence of the IL during 8 months with respect to the IL-free composites. Our photostability tests are still ongoing. Figure 4.11, 4.12, 4.13 and 4.14 reveal long term photo stability test results of the materials under investigation in a PMMA matrix in form of thin film, for 8 months.

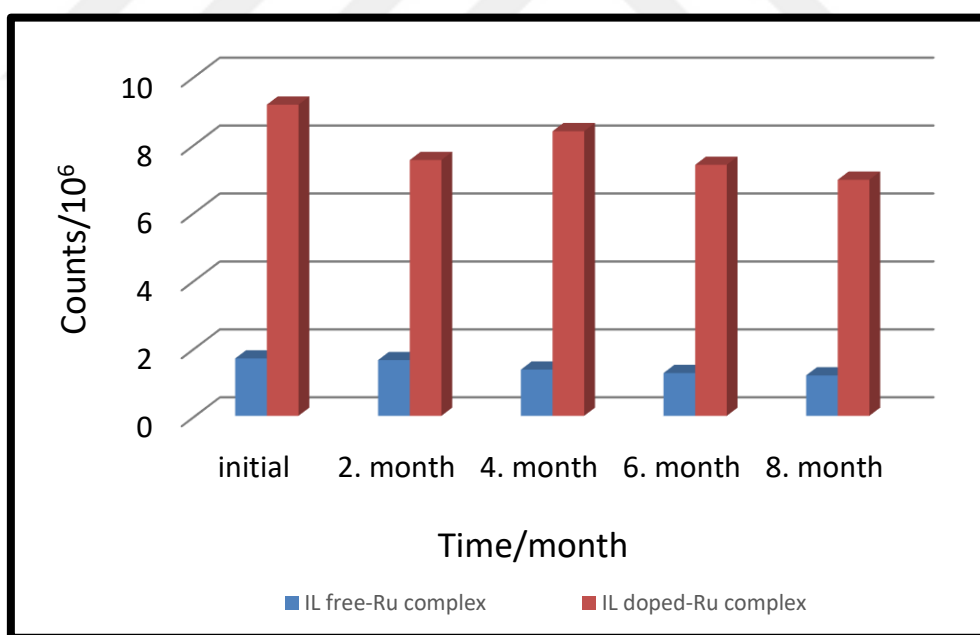


Figure 4.11 Long term photostability tests of the IL-free and IL-doped Ru(phen)₃PF₆

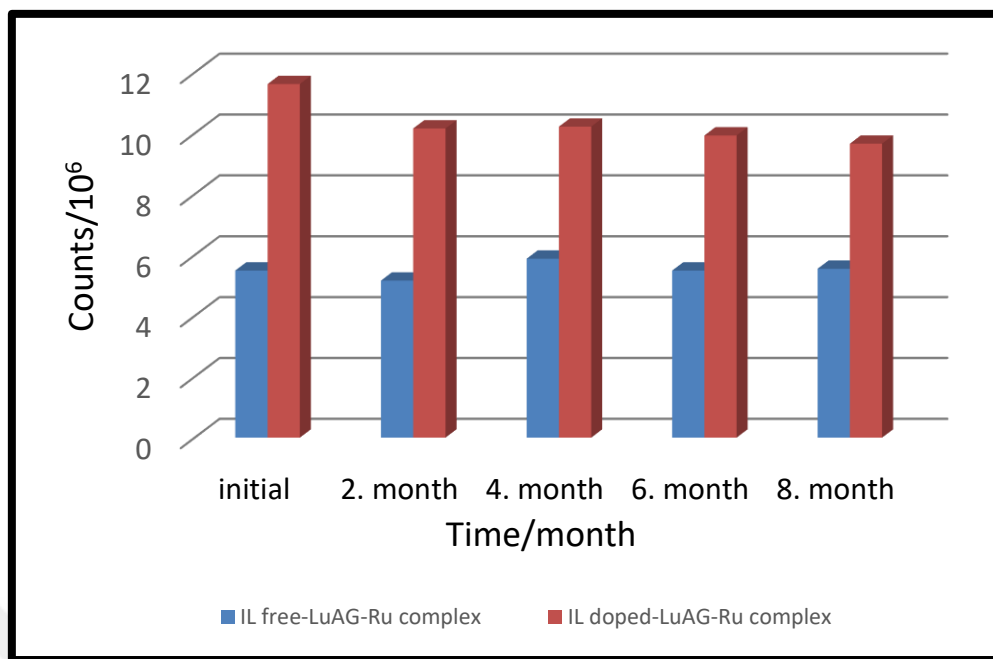


Figure 4.12 Long term photostability tests of the IL-free and IL-doped LuAG:Ce³⁺- Ru(phen)₃PF₆ composites

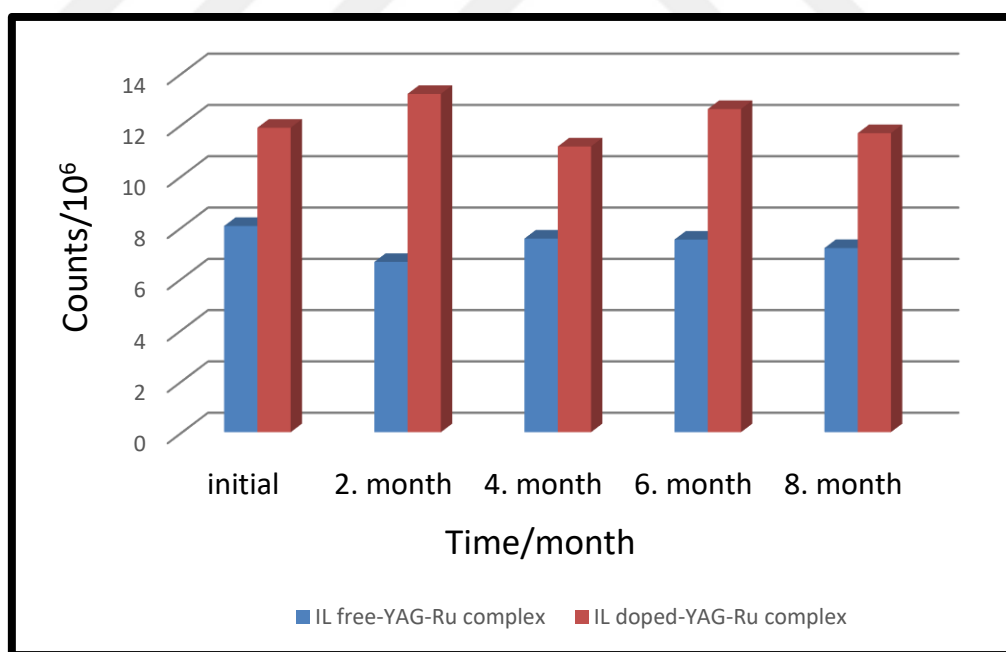


Figure 4.13 Long term photostability tests of the IL-free and IL-doped YAG:Ce³⁺- Ru(phen)₃PF₆ composites

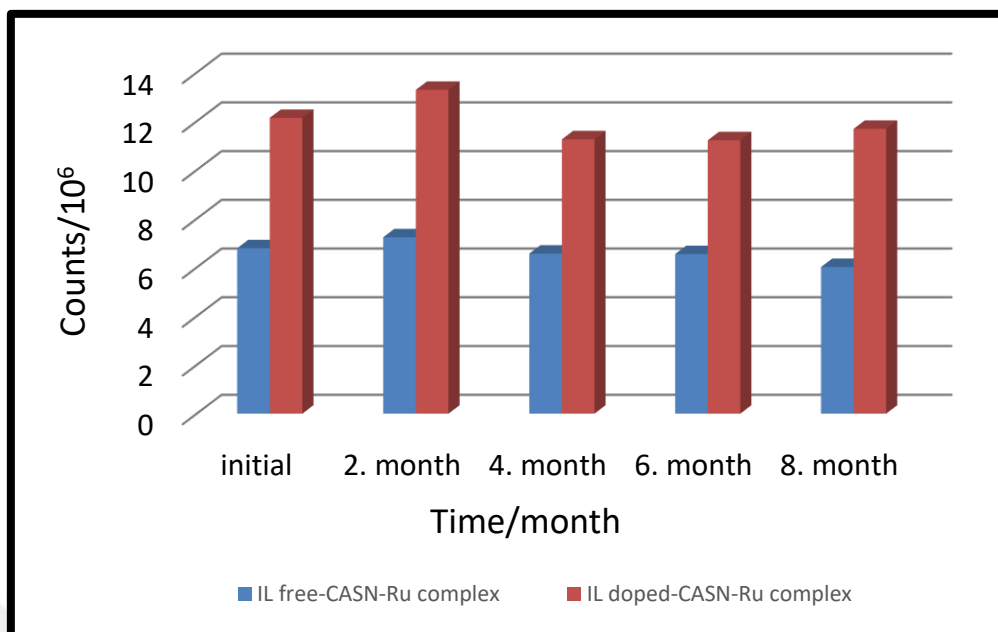


Figure 4.14 Long term photostability tests of the IL-free and IL-doped CASN:Eu²⁺- Ru(phen)₃PF₆ composites

4.6 Conclusion

In this chapter, we focused on the interactions between the green, yellow and red phosphors of LuAG:Ce³⁺, YAG:Ce³⁺ and CASN:Eu²⁺ and the Tris (1,10-phenanthroline) ruthenium (II) hexafluorophosphate (Ru(phen)₃PF₆) dye in terms of excitation and emission characteristics as well as decay times. Binary blends of the phosphors together with the Ru(phen)₃PF₆ were prepared in the absence and presence of the IL, respectively. Phosphors are generally photostable and thermally stable for a longtime duration. However, photostability of the dyes may sometimes be questionable. Therefore, we tested effect of the ionic liquid; BMIM BF₄ to enhance the long term photo-stability of the dye.

The IL-free LuAG:Ce³⁺- Ru(phen)₃PF₆ based composite exhibited 50 nm of red-shift and slight enhancement in the emission intensity. However, when prepared in the presence of the ionic liquid the LuAG:Ce³⁺-Ru(phen)₃PF₆ yielded 92 nm of red-shift and 2.78 fold enhancement in the emission intensity. Similarly, the YAG:Ce³⁺-

Ru(phen)₃PF₆ based composite exhibited 18 nm and 54 nm of red-shift in the absence and presence of the ionic liquid, respectively. 2.24 and 4.00 fold increase in the emission intensity was observed for the IL-free and IL doped YAG:Ce³⁺-Ru(phen)₃PF₆. Binary blends of the CASN:Eu²⁺ and Ru(phen)₃PF₆ resulted in 1.75 and 3.15 fold increase in the emission intensity for the IL-free and IL-doped blends, respectively. 4 and 8 nm of blue-shift was accompanied to the increase in the intensities. Addition of the ionic liquid into the matrix increased the interactions between the phosphor particles and the dye in direction of enhancement of the brightness and red-shift which can be attributed to the synergistic effect of the ionic liquid on ruthenium complex only, as a consequence of the above mentioned steady-state and decay time based experimental results.

According to our preliminary test results the long term photo-stabilities of the (Ru(phen)₃PF₆) based composites did not affect from the presence of the IL with respect to the IL-free composites.

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