

Optical and Morphological Studies of Doped Y_2O_3 Nanostructures

A
Thesis
Submitted for the award of degree of

Doctor of Philosophy

By

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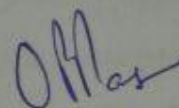


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October, 2016

CERTIFICATE

This is to certify that the thesis entitled “**Optical and Morphological Studies of Doped Y_2O_3 Nanostructures**” which is being submitted by **Deepak Kumar** (Regd. No. **950912012**) in fulfillment of the requirements for the award of the degree of **Doctor of Philosophy** in the **School of Physics and Materials Science, Thapar University, Patiala (Punjab)**, India is an exclusive record of candidate's own research work under my supervision. The thesis in part or in full has not been submitted in any other university or institute for the award of any degree. The thesis is fit to be considered for the award of degree of Doctor of Philosophy.



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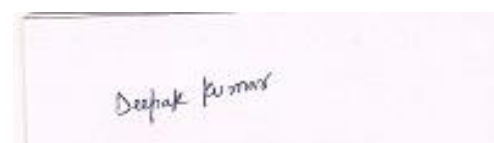
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A rectangular box containing a handwritten signature in dark ink. The signature appears to read 'Deepak Kumar'.

(Deepak Kumar)

LIST OF PUBLICATIONS

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1. Deepak Kumar, Manoj Sharma and O.P. Pandey “Effect of co-doping metal ions (Li^+ , Na^+ and K^+) on the structural and photoluminescent properties of nano-sized $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ synthesized by co-precipitation method” **D. Kumar, M. Sharma, O. P. Pandey Opt. Mater 36 (2014) 1131–1138.**
2. Deepak Kumar, Manoj Sharma and O.P. Pandey “Morphology controlled $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphors with enhanced photoluminescence properties”. **D. Kumar, M. Sharma, O.P. Pandey Journal of Luminescence 158, 268-274.**
3. Deepak Kumar, Manoj Sharma, H Haranath and O.P. Pandey “Facile route to produce spherical and highly luminescent Tb^{3+} doped Y_2O_3 nanophosphors” (**Journal of Alloys and Compounds**) (**In press**).
4. Deepak Kumar, Manoj Sharma, H Haranath and O.P. Pandey “Effect of Betacyclodextrin and Polyethylene glycol on the optical and morphological properties of Eu^{3+} doped Y_2O_3 nanophosphors” (**Journal of luminescence-under revision**).

LIST OF PAPERS PRESENTED IN CONFERENCES (INTERNATIONAL/ NATIONAL)

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PREFACE

The present work deals the optical and morphological properties of lanthanides ($\text{RE}^{3+} = \text{Eu}^{3+}$, Tb^{3+} and Dy^{3+}) doped Y_2O_3 nanophosphors prepared via co-precipitation method. Various techniques were used to enhance the PL characteristics of doped Y_2O_3 nanophosphors. Study of alkali metal ions (Li^+ , Na^+ , and K^+) co-doping with $\text{Y}_2\text{O}_3\text{:RE}^{3+}$ have been done. The main factors which affect the photoluminescence emission of the prepared phosphors are described in detail. Effect of various surfactants/polymers on optical and morphological properties of RE^{3+} doped Y_2O_3 have also been studied in detail.

Chapter 1 portrays the introduction of rare earth doped nanostructures. This chapter covers the various important topics explaining luminescence phenomenon of nanophosphors. Moreover, introduction to luminescence in lanthanide doped material have also been described in this chapter. At the end of this chapter a brief introduction of host Y_2O_3 and its applications in various fields of science is presented.

In **Chapter 2**, reported work which describes synthesis, structural, optical and photoluminescence (PL) studies of doped Y_2O_3 is reviewed. Effect of various parameters that affect the optical and morphological properties of Y_2O_3 has been described in detail. Besides this, other techniques developed to enhance the PL emission intensity has also been discussed. At the end of the chapter, the reasons for selecting main objectives behind this work are presented.

Chapter 3 describes the details of the synthesis procedure to prepare doped Y_2O_3 nanophosphors (NPs) using different chemicals. Details of different techniques which have been employed to characterize as prepared samples like X-Ray diffraction (XRD) technique, high resolution transmission electron microscopy (HRTEM), Fourier transfer infrared (FTIR) spectroscopy, UV-Vis spectroscopy and photoluminescence (PL) spectroscopy including their model number have been provided. Samples names and their codes have also been listed systematically in tabular form.

Chapter 4 describes the study of lanthanides ($\text{RE}^{3+} = \text{Eu}^{3+}$, Tb^{3+} and Dy^{3+}) doped Y_2O_3 nanophosphors (NPs) prepared via co-precipitation method. The effect of variation in annealing temperature and doping concentration has been studied on optical and morphological properties of doped Y_2O_3 . Moreover, $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ (red phosphor), $\text{Y}_2\text{O}_3\text{:Tb}^{3+}$ (green phosphor) and $\text{Y}_2\text{O}_3\text{:Dy}^{3+}$ (orange phosphor) are three types of phosphors which are

different from each other according to their optical characteristics. For simplicity these three systems have been presented separately.

Chapter 5 deals with the effect of alkali metal ions (Li^+ , Na^+ and K^+) co-doping on optical and morphological properties of $\text{Y}_2\text{O}_3:\text{RE}^{3+}$ ($\text{RE}^{3+}=\text{Eu}^{3+}$, Tb^{3+} & Dy^{3+}) doped nanophosphors (NPs) prepared via co-precipitation method. Enhancement of the luminescence of these phosphors further by co-doping them with alkali metal (Li^+ , Na^+ and K^+) ions have been discussed in detail. Various contributing factors that help in the luminescence enhancement of lanthanide ions (Eu^{3+} , Tb^{3+} & Dy^{3+}) in the presence of alkali ions (Li^+ , Na^+ and K^+) for Y_2O_3 (as host matrix) have also been presented systematically in this chapter.

Chapter 6 describes the effect of various surface modifiers (polymers and surfactants) on optical and morphological properties of doped Y_2O_3 nanophosphors. Samples of doped Y_2O_3 prepared with and without addition of polymers have been compared so as to explain the effect of polymers on optical and morphological properties of doped Y_2O_3 nanophosphors. Amount of polymers (at the time of synthesis) have been varied systematically to see their effect on optical and morphological properties of doped Y_2O_3 nanophosphors. Effect of pH of the solution during synthesis has also been described in this chapter.

Chapter 7 summarizes the results obtained from various experiments discussed in the previous chapters. Effect of various parameters (e.g. annealing temperature, doping of rare earth ions, co-doping of alkali metal ions, pH of the solution and use of surface modifiers at the time of synthesis) on optical and morphological properties of doped Y_2O_3 have been summarized. Results obtained from the variation of these parameters were studied in detail. Further, conclusions made from the study of these results have also been summarized in this chapter. Based on the observation of the present work, some suggestions to carry out more work in this field have been given at the end of this chapter.

Abbreviations

PL	Photoluminescence
NPs	Nanophosphors
Exc.	Excitation
Em.	Emission
β-Cyclo	Betacyclodextrin
PVP	Polyvinyl pyrrolidone
CTAB	Cetyl trimethylammonium bromide
TOPO	Trioctylphosphine oxide
TG	Thio-glycerol
PEG	Polyethylene glycol
λ_{ex}	Excitation wavelength
λ_{em}	Emission wavelength
XRD	X-ray Diffraction
JCPDS	Joint Committee on Powder Diffraction Standards
CI	Crystallinity index
FTIR	Fourier transformation infrared microscopy
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
SAED	Selected area electron diffraction
CIE	Commission International de L' Eclairage (chromaticity coordinates)
CCT	Correlated Color Temperature
Rwp	$R_{\text{weighted pattern}}$
Rexp	$R_{\text{experimental}}$

CHAPTER 1

INTRODUCTION

Overview

This chapter gives introduction to the luminescence and luminescent materials. First part of this chapter gives introduction to luminescence phenomenon and its types. The fundamental phenomenon involved during luminescence like excitation, emission, selection rules, stokes shift and concentration quenching process have been explained in this part. In the second section of this chapter, lanthanide ions and their unique properties have been covered. Various mechanisms involved during lanthanide luminescence are also explained in this part. In the third section of this chapter, a brief introduction of host Y_2O_3 and its applications in various fields of science is presented.

1.1 Introduction to Luminescence

Luminescence is a broad name given to the phenomenon where a material releases its additional energy as electromagnetic radiation either instantly or over a long period of time, once excited by a certain external energy. This external source can be an electromagnetic radiation (photon of light), an electric field, a high-energy electron or electrons beam. Undoubtedly, the luminescence process primarily involves the excitation, energy transfer and subsequent relaxation of the valence electrons from their excited states (emission). Depending upon different excitation sources, luminescence can be classified into photoluminescence, electroluminescence, cathodoluminescence, radioluminescence, chemiluminescence, thermoluminescence, triboluminescence, etc [1, 2], as given in Table 1.1. The material which shows this property of luminescence is called a luminescent material, or a phosphor. A phosphor can convert certain types of energy into electromagnetic radiation over and above thermal radiation. When you heat a solid to a temperature in excess of about 600 °C, it emits infrared radiation. This is thermal radiation (not luminescence). The electromagnetic radiation emitted by a luminescent material is usually in visible range, but can also be in other spectral regions, such as the ultraviolet or infrared [3]. These materials are of inorganic nature called “host lattice” that are purposely doped with a small amount of dopant called “activators” (rare earth ions/transition metal ions) as shown in Figure 1.1. During luminescence process, the effect of both host lattices and activators are involved. If the activator ions show too small absorption, a second kind of impurities can be added (sensitizers), which absorb the energy and then transfer the energy to the activators. This process involves transport of energy through the luminescent materials. Quite often, the emission color and its intensity can be adjusted by choosing the proper impurity ion, without changing the host lattice in which the impurity ions are incorporated. On the other hand, quite a few activator ions show emission spectra with emission at spectral positions, which are hardly influenced by their chemical environment. This is especially true for many of the rare-earth ions.

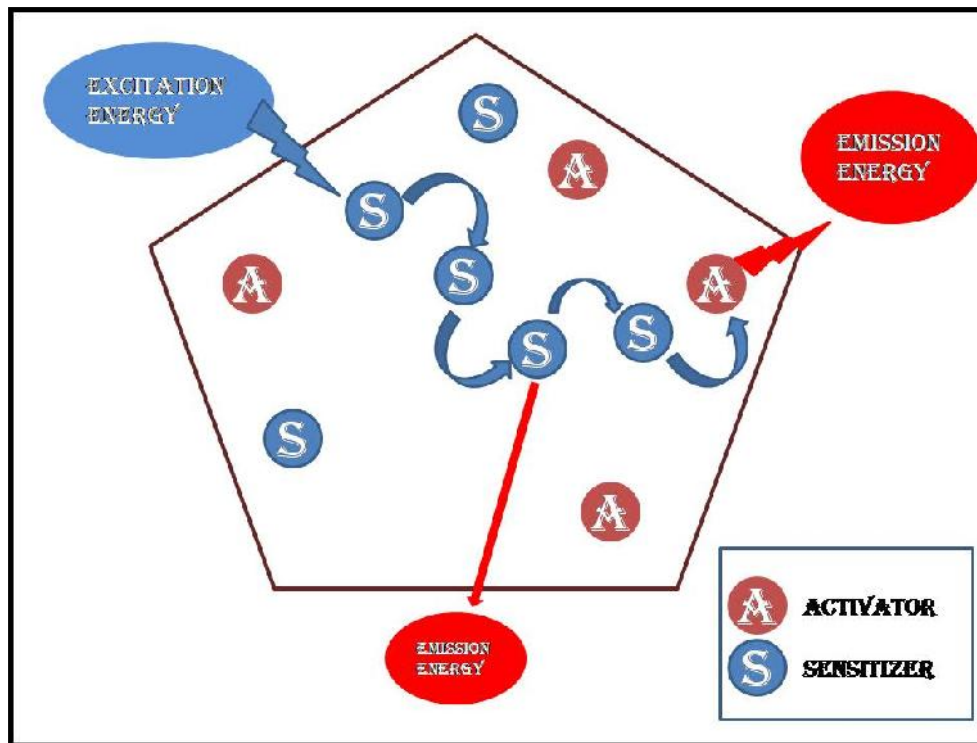


Figure 1.1: Luminescent material containing activator ions A (ions showing the desired emission) and sensitizing ions S (on which, e.g., UV excitation can take place) [4].

Table 1.1: Classifications of luminescent materials [4].

Type	Excitation Source	Application
Photoluminescence	Light	Fluorescent lamps, white LEDs, PDPs, afterglow
Electroluminescence	Electric current/ Electric field	LED, flat-panel displays, screens
Cathodoluminescence	Electron beam	FED, CRT
Radioluminescence	X-rays, α -, β -, γ -rays	X-ray detectors, scintillators
Chemiluminescence	Chemical reaction	Gas sensors, labeling
Thermoluminescence	Heating	Detectors, dosimeters
Triboluminescence	Mechanical energy	Remote sensing

1.2 Fundamentals of Luminescence

The physical processes involved in promoting atoms to an excited state by absorbing the excitation energy and dropping them down to the ground state by emitting photons are the main process in luminescence mechanism. Various excitation and de excitation processes occurring on absorption of radiation by a molecule are illustrated in energy level diagram in Figure 1.2. Initial absorption of radiation by a molecule results in its excitation from the ground state (S_0) to one of the excited singlet states (S_2 or S_1) [5]. The absorption of a photon of radiation is a very fast process ($\sim 10^{-15}$ s) [6]. The deexcitation of the excited molecule favors the route which

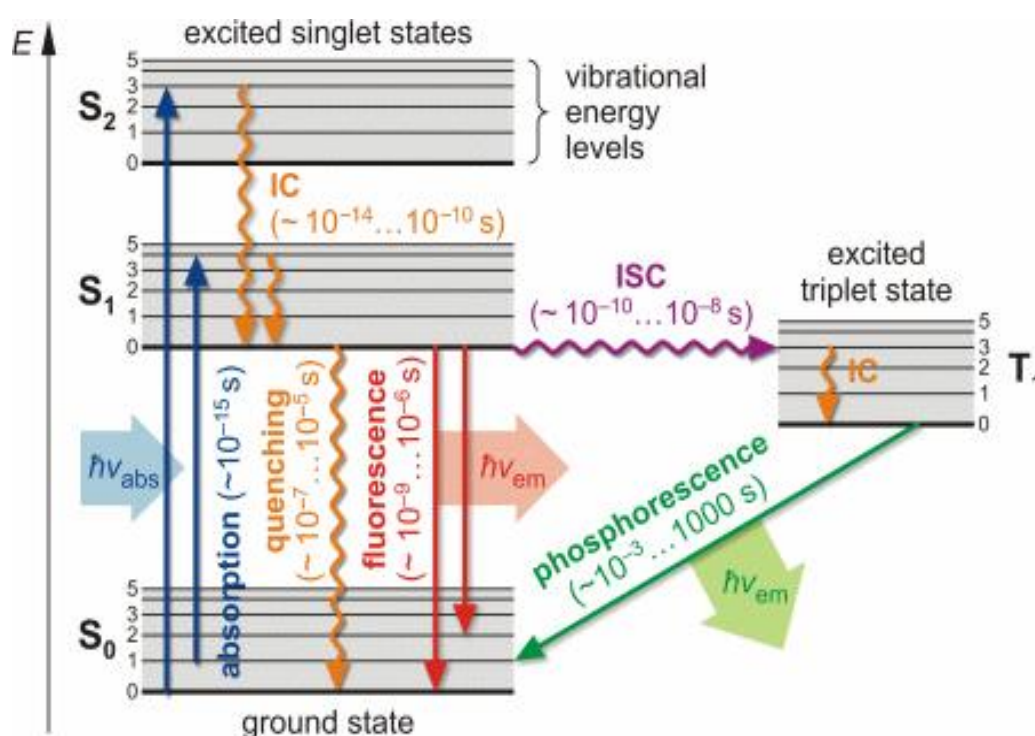


Figure 1.2: Energy diagram showing absorption of light and the processes involved in the emission of light as fluorescence and phosphorescence [4, 5].

minimizes the lifetime of the excited state. Depending upon different decay pathways, it can occur via radiative emission such as fluorescence or phosphorescence (indicated in Figure 1.2 as straight lines), or a non radiative decay, indicated in Figure 1.2 as curvy lines. The lifetime of the excited state for fluorescence emission is 10^{-9} to 10^{-6} s. After the excitation of a molecule from the ground state to a higher nondissociative excited state, radiationless internal conversion transitions to the lower excited states generally take place

before any radiative emission processes. Once the transition occurs, the molecule undergoes vibrational relaxations to the ground vibrational state of the S_1 electronic excited state at a significant rate. The time scale for internal conversion is 10^{-11} to 10^{-9} s [6]. Intersystem crossing is a process in which the spin of the excited electron is reversed and the electrons become unpaired. The time required for such a process is in the range of 10^{-10} to 10^{-8} s. Once intersystem crossing occurs from a singlet to a triplet excited state, the molecule undergoes deactivation by phosphorescence. The time scale for the radiative phosphorescence process is of the order of 10^{-3} to 10^3 s. Relaxation of the excited singlet and triplet states can also occur by decomposition of the excited species to form new chemical species. These photochemical reactions occur within 10^{-12} to 10^{-9} s [6]. The detailed study of few main processes i.e. excitation, emission, energy transfer, and non-radiative transitions is discussed below.

1.2.1 Excitation

A luminescent material does not emit light unless enough photons with suitable frequency are absorbed. This infers that, unlike emission, excitation is not a spontaneous process. The luminescent materials are blend of a host lattices and an activator (dopant). The excitation process is of two kinds, direct excitation and indirect excitation. In a direct excitation, activators absorb the excitation energy and promote its atoms to the excited state and in an indirect excitation host lattice first absorbs the excitation energy and then transfers it to the excited state of the activator ions. The energy levels of activator ions are in between the conduction band and valence band of the host material. The required energy for direct excitation is therefore smaller than that of indirect excitation. The efficiency of direct excitation is larger than that of indirect excitation. These are significant for phosphors in white LEDs, because the excitation sources in these devices are near ultraviolet or blue light that has lower energy than that in fluorescent lamps or cathode ray tubes (CRTs). Excitation spectrum of a luminescent material also depends on the activator species (dopant) and host lattice. The excitation spectrum shows that the emission of a phosphor can be observed if the activator ions (such as Ce^{3+} , Eu^{3+} , Eu^{2+} , Mn^{2+}) are directly excited, or if the energy absorbed by either the host lattice or the ligands is transferred to activator ions through the nonradiative transition process.

For example in the excitation spectrum of Eu^{3+} doped Y_2O_3 nanophosphor (Figure 1.3), different shapes and information from the excitation spectrum can be obtained. It has the following features:

- i. A very intense broad band with a maximum at ~ 260 nm.
- ii. An absorption peak at ~ 220 nm.
- iii. A number of weak sharp lines at 300, 323, 364, 382, 395, 468, and 532 nm.

The undoped Y_2O_3 only shows the host lattice absorption, which is located at ~ 220 nm [3]. The intense band and narrow spectral lines are associated with Eu^{3+} . The very strong broad band in the excitation spectrum is ascribed to a charge-transfer (CT) transition in which an electron is promoted from the highest-filled oxygen orbital to Eu^{3+} , and the groups of narrow line spectra are due to the Eu^{3+} absorption, resulting from the electronic transitions of $^7\text{F}_j \rightarrow ^5\text{D}_0$ of Eu^{3+} [3]. In the excitation spectrum of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, Eu^{3+} can be excited both directly (CT band and narrow lines) and indirectly (HL absorption). For indirect excitation, the energy is absorbed by the Y_2O_3 host lattice first, followed by transferring absorbed energy to Eu^{3+} . These observations show that the excitation spectrum of a luminescent material is greatly dependent on the activator species and host lattice.

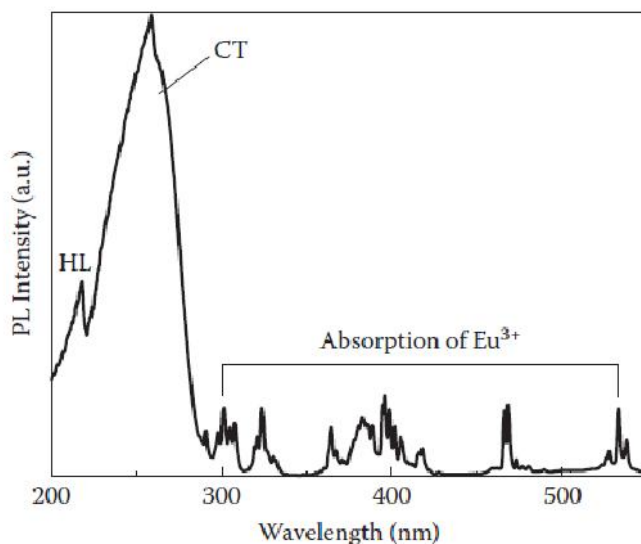


Figure 1.3: Excitation spectrum of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$. The narrow lines are transitions with the $^4\text{f}_6$ configuration of Eu^{3+} , CT is the charge transfer between O^{2-} and Eu^{3+} , and HL represents absorption of the host lattice [7].

Moreover, the excitation spectrum also shows that the emission of a phosphor can be observed if the activator ions (such as Ce^{3+} , Eu^{3+} , Eu^{2+} , Mn^{2+} , etc.) are directly excited, or if

the energy absorbed by either the host lattice or some ligands is transferred to activator ions through the nonradiative transition process [7].

1.2.1.1 Selection Rules

The disparity in intensity of an optical transition is very pronounced because all transitions between different energy levels do not occur with equal probability. Probability of electronic transitions from the ground state to the excited state is directed by selection rules that are derived from quantum mechanics. Selection rules decide which transitions are allowed or forbidden. Two important selection rules controlling the probability of electronic transitions are shown below [8].

a) The spin selection rule

Electronic transitions are only allowed between states of the same spin ($\Delta S = 0$). In other words, only those transitions are allowed that result in a conservation of the number of unpaired electrons in the d orbitals.

b) The orbital selection rule

Transitions involving only a redistribution of electrons within the same set of atomic orbitals are forbidden or allowed transitions that obey $\Delta l = \pm 1$ (l is the orbital angular momentum quantum number).

There are various factors that weaken these rules, because of these factors forbidden transitions still appear, but with reduced intensity. These factors are due to interaction between atoms that produce hybrid electronic states. Taking Eu^{3+} as an example in Figure 1.3, optical absorption transitions of Eu^{3+} occur within the f-shells ($4f_6$), so that they are strongly forbidden by the parity selection rule, but odd components of the crystal field make them partially allowed due to the admixture of sites with the opposite parity. The net effect of these selection rules is that forbidden transitions are weak, even for those partially allowed transitions. On the other hand, the charge-transfer transitions are allowed. The intensity of charge-transfer transitions arises from the movement of electronic charge across a typical interatomic distance, producing a large transition dipole moment and concomitant large oscillator strength for the absorption process [9]. So, the charge-transfer band has a higher intensity than the 4f-4f transition lines, as shown in Figure 1.3.

1.2.2 Emission

Figure 1.4 presents the configurational coordinate diagram for explaining the emission and relaxation process. The absorption of the excitation energy promotes the absorbing center to a higher vibrational level of the excited state (U'). Then the excited ion releases some of its energy to its surroundings and returns to the lowest vibrational level of the excited state. This process is also called “relaxation”, which brings the excited ions to their equilibrium state, with their interatomic distances corresponding to an equilibrium position. The relaxation process is nonradiative so no emission is observed. From the lowest vibrational level of the excited state, the excited ions can go back to the ground state (U) spontaneously through the radiative emission of photons. By this process, the ions then reach a higher vibrational level of the ground state, and finally relax to the lowest vibrational levels of the ground state non-radiatively.

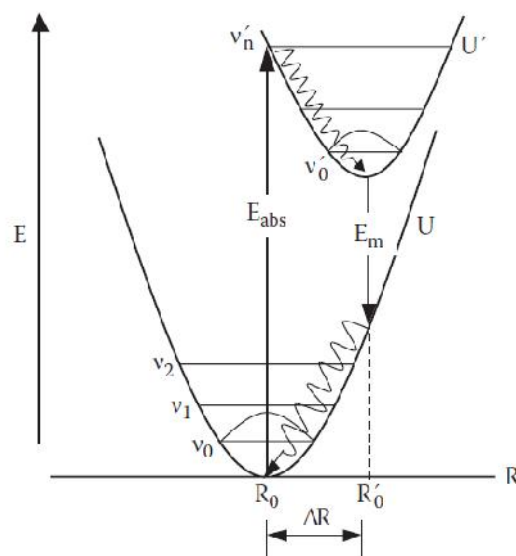


Figure 1.4: Configurational coordinate diagram showing the emission processes [7].

1.2.2.1 Stokes shift

Again, there is a distribution of probabilities for the starting points of the emission, with the greatest probability being at $R'0$. Because the relaxation process dissipates some of the energy of the excited ion, radiative decay to the ground state occurs at a lower energy than the absorption process (i.e., $E_{abs} > E_{em}$). This energy difference between positions of the band maxima of the excitation and emission spectra of the same electronic transition is known as

Stokes shift (in wavenumber or frequency unit). Assuming that the parabolas of the excited state and ground state have the same shape, the energy lost during relaxation is equal to S_{hv} per parabola. Then, the Stokes shift (SS) is expressed by [7]

$$SS = 2S_{hv} \quad (1.1)$$

where $h\nu$ is the energy difference between two vibrational levels, and S is the Huang-Rhys coupling factor that measures the strength of the electron-lattice coupling. S is proportional to $(\Delta R)^2$ [9]. The Stokes shift is an important feature of luminescence. It can be seen from Figure 1.4 and Equation 1.1 that a larger value for ΔR will cause a larger Stokes shift. A right small Stokes shift is desired, for achieving high luminescence, because it avoids strong overlap between the absorption and emission bands (otherwise, the emitted light would be reabsorbed by the emitting center), and it results in small thermal quenching (luminescence can be quenched with increasing temperature, called thermal quenching) [9].

1.2.2.2 Concentration Quenching of Luminescence

In principle, the emission intensity increases with an increase in concentration of a luminescent center (defects/dopant) in a host lattice. This is due to the reason that increase of the absorption efficiency results in increase of the luminescence intensity. However, such behavior is only observed when the concentration of a luminescent center reaches a certain limiting value. Above this value, the luminescence intensity decreases. This phenomenon is called “*concentration quenching of luminescence*”. The basis of concentration quenching is closely related to energy transfer among the luminescence centers. The quenching starts at a critical concentration where the distance between luminescent centers becomes so small, that the efficient energy transfer cannot occur any further. It is believed that donor-killer energy migration and cross-relaxation are two main mechanisms accountable for the concentration quenching of luminescence [1].

1.2.2.2.1 Donor-Killer Energy Migration Mechanism

The excitation energy can transfer to numerous centers before being released radiatively due to efficient energy transfer. A phosphor material has more or less a certain amount of defects or impurity ions that can act as acceptors. So with the increasing concentration of donors, the distance between the donors and acceptors becomes less and efficient energy transfer is easily

possible because of this, the excitation energy can also be transferred to these sites effectively. These acceptors release the absorbed energy to their ground state through nonradiative process, so they are called killers and act as an energy sink within the transfer chain to quench the luminescence, as shown in Figure 1.5.

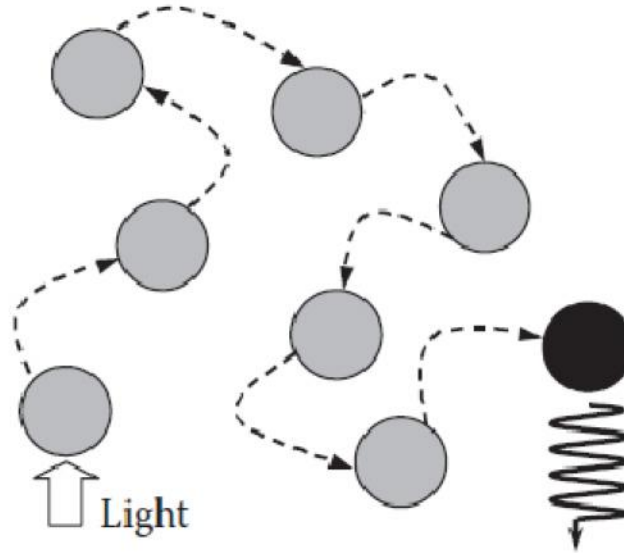


Figure 1.5: Donor-killer energy migration mechanism for concentration quenching of luminescence. The excitation energy is transferred to a killer center (black) along a chain of donors (grey) [7].

1.2.2.2.2 Cross-Relaxation Mechanism

Excitation energy does not travel to luminescent center completely. It can be lost via another mechanism called “cross relaxation”. It happens due to the resonant energy transfer between two same adjacent centers due to the special energy-level structure of these centers. The mechanism that explains for the concentration quenching of Tb^{3+} doped phosphors [10] is given in Figure 1.6. A possible energy-level scheme involving the $^5\text{D}_3$ - $^5\text{D}_4$ cross relaxation of Tb^{3+} is shown in this Figure 1.6. At a low concentration of Tb^{3+} , the radiative emissions from $^5\text{D}_3$ to $^7\text{F}_j$ dominate. But, with increasing the Tb^{3+} concentration, a resonant energy transfer occurs between two neighboring Tb^{3+} ions, reassigning part of the energy of $^5\text{D}_3$ - $^5\text{D}_4$ from excited ions (donors) to those ions in the ground state (acceptors), as labeled by ($^5\text{D}_3$, $^7\text{F}_6$)-($^5\text{D}_4$, $^7\text{F}_0$). Because of cross relaxation, the donor ions will be in the $^5\text{D}_4$ energy level, while the acceptor ions will be promoted to the ground state of $^7\text{F}_0$. Correspondingly, the

luminescence from the transition of ${}^5\text{D}_3 \rightarrow {}^7\text{F}_j$ is quenched, whereas emission from the transition of ${}^5\text{D}_4 \rightarrow {}^7\text{F}_j$ is enhanced.

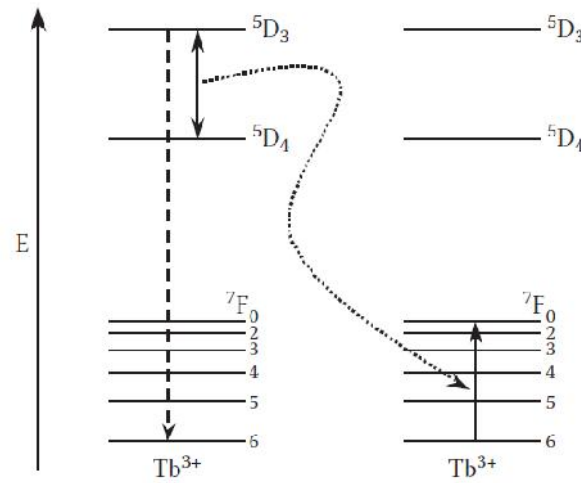


Figure 1.6: Quenching of higher levels of emission (${}^5\text{D}_3 \rightarrow {}^7\text{F}_j$) by the cross-relaxation mechanism in Tb^{3+} doped phosphors [7].

1.2.3 Nonradiative Transitions

The radiative de-excitation process (i.e., emission) occurs when the excited ions (luminescent center) go back to the ground state by releasing the excitation energy.

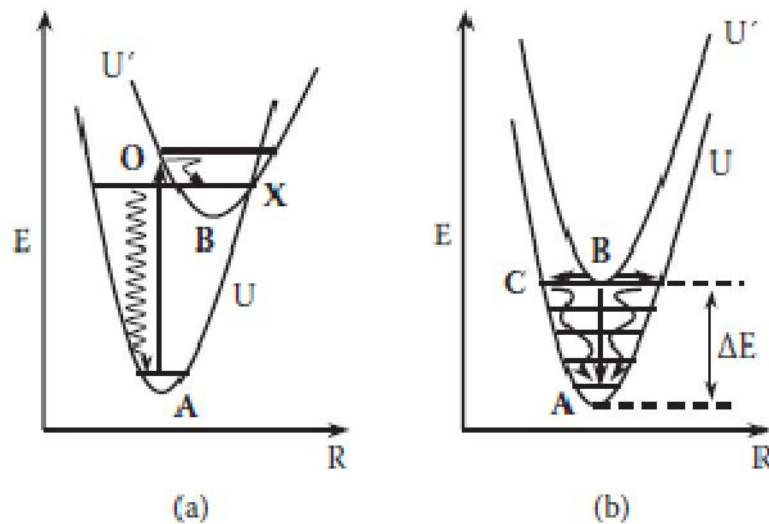


Figure 1.7: Configuration coordinate diagram illustrating the nonradiative de-excitation process of multiphonon emission: (a) strong electron-lattice coupling and (b) weak electron-lattice coupling ($S=0$) [7].

There is the possibility that a luminescent center returns to its ground state without emitting photons called nonradiative de-excitation process as explained in Figure 1.7.

1.3 Luminescent Centers

In this section different luminescent centers that can be induced in a host matrix by doping them with suitable dopant material. The key role of a luminescent center is to introduce new energy levels in between the energy gap of the solid crystals, creating new absorption and emission bands that are not characteristic of the perfect crystals. Not all the elements of the periodic table can be considered optically active centers, but only some of them can be accommodated into the lattice structure of crystals and produce suitable energy levels within the band gap of the crystals. The optically active centers are of technological and practical importance in luminescent materials is based on lanthanides ions (i.e., rare earth ions) and transition metal ions. The basic mechanisms involved in luminescence of lanthanides are discussed below.

1.3.1 Basics of lanthanide luminescence

The word lanthanide originated from the Greek word “lanthaneien” meaning lying hidden. The lanthanides are a clique of 15 chemically alike elements, from lanthanum to lutetium (atomic number 57 to 71), which holds electronic configuration $[\text{Xe}] 4f^n 5d^{0,1} 6s^2$ (where ‘n’ varies from 0–14) [11, 12] as given in Table 1.2. Scandium (21) and yttrium (39) (d-block elements) are always found in nature with lanthanides; so, lanthanides and these two elements altogether are known as the rare-earth elements. Lanthanide ions show fascinating optical properties, including the ability to convert near infrared photons to ultraviolet/visible photons (through an upconversion process) and vice versa (quantum-cutting process) [4, 11, 13, 14]. Due to their outstanding optical properties, many recent advances and developing applications such as lighting devices (light emitting diodes, cheap luminescent lamps), optical fibres, display devices, lasers and many biological researches depend heavily on them [4, 9, 13, 14]. Lanthanide ions have three types of optical changes in their energy levels: intra-configurational 4f–4f transition, inter-configurational 5d–4f transition and the charge transfer transition (ligand to metal or metal to ligand) [4, 11, 13]. Ce^{3+} and Eu^{2+} are widely used activator ions for phosphor applications [15–22]. Their characteristic transition is 4f–5d, which is an allowed transition and has a lifetime of the order of nanosecond. Since the 5d

orbitals are strongly affected by the crystal field and polarizability of the host crystal, these transitions (4f–5d transitions) can be easily tuned to the visible region by changing the crystal composition and structure [33-40]. In contrast, the 4f–4f transition in lanthanide(III) ions

Table 1.2: Electronic configurations and ground state of lanthanide ions [7].

Ions	4f Electrons	Ground state	Ions	4f electrons	Ground state
La ³⁺	0	¹ S ₀			
Ce ³⁺	1	² F _{5/2}			
Pr ³⁺	2	³ H ₄			
Nd ³⁺	3	⁴ I _{9/2}			
Pm ³⁺	4	⁵ I ₄			
Sm ³⁺	5	⁶ H _{5/2}	Sm ²⁺	6	⁷ F ₀
Eu ³⁺	6	⁷ F ₀	Eu ²⁺	7	⁸ S _{7/2}
Gd ³⁺	7	⁸ S _{7/2}			
Tb ³⁺	8	⁷ F ₆			
Dy ³⁺	9	⁶ H _{15/2}			
Ho ³⁺	10	⁵ I ₈			
Er ³⁺	11	⁴ I _{15/2}			
Tm ³⁺	12	³ H ₆			
Yb ³⁺	13	² F _{7/2}	Yb ²⁺	14	¹ S ₀
Lu ³⁺	14	¹ S ₀			

(viz. Pr³⁺, Nd³⁺, Ho³⁺, Er³⁺, Sm³⁺, Eu³⁺, Tb³⁺, Dy³⁺, Tm³⁺ and Yb³⁺), which is a forbidden transition, gives sharp and intense spectral lines (from UV to infrared region) with a lifetime of the order of microsecond [23]. Lanthanides are commonly in the +3 oxidation state (Ln³⁺), which is their most stable oxidation state (though Eu²⁺, Sm²⁺ and Cr⁴⁺ are also stable) and most of the optical properties of lanthanides are explored in this oxidation state. As the lanthanide ions feature an electron configuration of 4fⁿ, which proposes many possible arrangements, there are rather majority of electronic energy levels. The promotion of a 4f electron into the 5d sub-shell in lanthanide ions is allowed as suggested by the parity rule.

These transitions are quite active and observed only in Ce^{3+} , Pr^{3+} and Tb^{3+} ions. Since the 5d orbitals are external and interact directly with the ligand orbitals, their energy mainly hinges on the metal environment [23]. In Ce^{3+} ions, luminescence is observed from $^2\text{D}_{3/2}$ levels to $^2\text{F}_{5/2}$, $^2\text{F}_{7/2}$, whereas $^2\text{D}_{5/2}$ lies at high energy and luminescence from this level is not generally observed. The luminescence in Ce^{3+} can be tuned from about 290 to 450 nm, depending on the matrix into which the metal ion is inserted. Charge transfer transition in lanthanide ions is also allowed by Laporte's selection rule. Other and most studied transition in lanthanides is the 4f–4f transition. According to Laporte's rule, electric dipole transitions with the same parity are not allowed. Because of that, the 4f–4f transition in lanthanides is forbidden [9, 11]. However, when these ions are doped in a proper host matrix, due to influence of the ligand-field, non-centrosymmetric interactions, a mixing of the wave-functions of the states of opposite parity with 4f-wavefunctions, takes place. This relaxes somewhat the parity selection rule and 4f–4f transitions become partially allowed [9, 11].

The crystal field destroys the degeneracy of its energy levels. In fact, the ligand/crystal generates a ligand/crystal electrostatic field which interacts with the 4f electrons of the lanthanide ions generating a ligand field/crystal field (or Stark) splitting of the spectroscopic levels [9, 11]. The 4f orbitals of the lanthanide ions remain shielded by 5s and 5p orbitals, and so excitation of an electron into a 4f sub-orbital of higher energy does not change the binding pattern significantly. Thus, the inter-nuclear distance remains almost unaffected in the excited state which yields narrow emission lines. The long lifetime is because the 4f–4f transitions in the lanthanide ions are parity forbidden [9, 11].

Further, the ideal host matrix should also have low lattice phonon energies, to decrease non-radiative loss and maximize the radiative emission. The dopant concentration, which determines the average distance between neighboring dopant ions, has a strong influence on the optical properties of the lanthanide-based luminescence materials. In certain host matrices, luminescence of lanthanide ions increases appreciably with increasing crystallinity. This is because of the fact that as the crystallinity increases the particle size also increases due to which surface quenching centers (surface to volume ratio decreases) also decreases. The increased particle size is not required in many technological applications, which have been prompted due to the advancement in nanotechnology; so, researchers usually like to use a passive layer, by forming a core–shell structure, to reduce the surface quenching centers [24]. The co-doping of alkali ions in the matrix strongly affects the crystal structure, crystallinity, grain size, surface morphology, quenching centers (OH, NO^3 etc.) and

create distortion in the matrix [18, 23, 24]. Therefore, it would be interesting to study the effect of alkali ions (Li^+ , Na^+ & K^+), on the luminescence properties of lanthanide ions doped in various matrices and try to find out the meaningful information to understand the underlying mechanism, and to explore the future possibilities.

1.4 Introduction to host Y_2O_3

For many of these studies, nanocrystalline $\text{Y}_2\text{O}_3:\text{RE}^{3+}$ has been the material of choice because of its favorable physical properties and ease of synthesis in the nanometer regime [25]. The optical properties of yttrium oxide (single crystal and microcrystalline) doped with rare earth ions are well known. Yttria is a favorable host for rare earth ion substitution for several reasons. It is a refractory oxide having a high melting point ($\sim 2400^\circ\text{C}$) [26] and high thermal conductivity ($K_{\text{Y}_2\text{O}_3} = 27\text{W/mK}$) [27, 28]. Due to its chemical stability and refractoriness, yttria has been considered for many applications, such as high temperature chemical resistant substrates, crucibles for melting reactive materials, and nozzles for jet-casting molten rare earth–iron magnetic alloys [29]. Yttrium oxide is also optically isotropic, with refractive index of 1.91 [30].

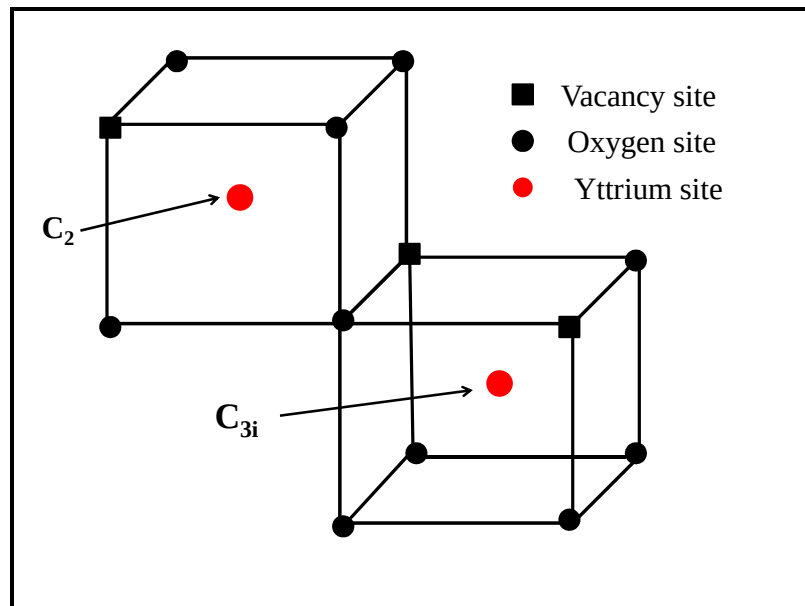


Figure 1.8: Cationic symmetry site for the $\text{Y}_2\text{O}_3:\text{Eu}^{+3}$ [3].

But the most important property of all is that yttrium oxide has low phonon energies. In fact, the dominant phonon energy is 380 cm, one of the smallest phonon energies among oxides [31]. This relatively small vibrational energy allows for efficient radiative transitions between electronic energy levels of the rare earth ions. The Y_2O_3 phosphor has a cubic structure with a space group Ia-3 and point-group symmetry m-3. The unit cell contains 16 formula units with 32 cations. This structure has two cation symmetry sites C_2 and C_{3i} , both coordinated six-fold with oxygen, as shown in Figure 1.8. These two cationic sites are allocated over two Wyckoff positions 8b with local symmetry C_{3i} and 24d with local symmetry C_2 . Oxygen ions are situated at 48e Wyckoff positions.

1.4.1 Applications of Y_2O_3

Yttrium oxide is a material with a wide range of applications. Some of the main applications of nano-crystalline Y_2O_3 is in optical, electrical, mechanical (refractories and ceramics), and catalytic fields. Some key applications of nano-crystalline Y_2O_3 in different fields of science are given below in table 1.3 [25],

Table 1.3: Some key applications of Y_2O_3 .

Optical Properties	Mechanical Properties	Catalysts Properties
▪ Display Devices ▪ Fluorescent Lamps ▪ Thin Films	▪ High temperature chemical-resistant substrates ▪ Crucibles for melting reactive metals ▪ Nozzles for jet-casting molten and Rare earth-iron magnetic alloys	▪ Catalytic Activity

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CHAPTER 2

LITERATURE REVIEW

Overview

In this chapter the earlier reported work on synthesis, properties and applications of rare earth (RE^{3+}) doped nano-sized yttrium oxide (Y_2O_3) is reviewed. The literature review is divided in three parts. First part summarizes the need of studying doped Y_2O_3 nanophosphors (NPs) among existing well studied inorganic NPs. In the second part numerous preparation techniques used to synthesize doped yttrium oxide nanocrystals has been discussed in detail. It also describes the effect of different surfactants and polymers (used during synthesis) on optical properties of doped Y_2O_3 . It also describes the effect of alkali metal ion on the luminescence of lanthanide ions in yttrium oxide (Y_2O_3) host matrices studied by other researchers. At last, thesis layout, existing gaps in literature and objectives of the work have been presented.

2.1 History of existing inorganic Nanophosphors

The memoirs of inorganic luminescent materials (phosphor) dates back to the era when the first phosphor, barium sulfide, was made in the nineteenth century. Later, phosphors covering many materials with different crystal structures and compositions have been significantly developed for lighting, display, sensing, and labeling. Over the past many years, countless advances in solid-state lighting technologies, especially in white light-emitting diodes (LEDs), which use phosphors as wavelength converters, have catalyzed the progress of a novel family of luminescent materials: inorganic phosphors. Since inorganic phosphors help in making white light LEDs brighter, more reliable, and natural, new researchers in this field are working on new synthesis techniques and understand the crystal chemistry, luminescence, and other applications of these nanophosphors.

Lanthanide based materials are favored over other luminescent materials due to their several applications. Researchers are more focused in using the unique luminescence features of lanthanide-based materials for multidisciplinary research and novel applications. Efforts are made to enhance the luminescence of lanthanide ions for their superior performance in various optical applications. There are two ways to enhance the luminescence of lanthanide ions. The first is to use an apt sensitizer, which can absorb excitation energy efficiently, and can transfer it to the lanthanide ions. This method is well described in the literature. The second method is to amend the host matrices in such a way that it favors radiative transitions. It is commonly reported in the literature that the presence of alkali ions, particularly Li^+ ions, in a matrix enhances the luminescence of lanthanide ions substantially.

2.2 Review of Nanometer-sized doped Y_2O_3

Y_2O_3 is a well explored host matrices for luminescence studies owing to its higher chemical and mechanical durability, higher thermal stability, excellent optical properties and relatively low phonon cut-off energy ($400\text{--}500\text{ cm}^{-1}$) compared to other host matrices [1-6]. Another advantage of using Y_2O_3 host matrices is that one can prepare phase pure samples by conventional solid state reaction (at lower temperatures) methods and also by many other routes [1-6]. Particle size, shape and surface morphology can be controlled and tuned by controlling different synthesis parameters. In this section we describe few major synthesis routes used to get yttrium oxide nanocrystals.

In 1999, Sharma *et al.* [7] used co-precipitation method to produce a gel in the presence of a surface modifier followed by the addition of Y_2O_3 seeds to the coprecipitated gel, which was then subjected to a hydrothermal treatment. Synthesis of nanocrystals via wet chemical methods requires control over the thermodynamics of the interfaces as particles have a tendency to minimize their surface energy by agglomerating or growing large particles. Using a surface modifier in highly alkaline media ($\text{pH} > 10$) is one of the approaches used to modify the surface of growing particles. Thus to control the particle size, addition of a surface modifier is necessary as it coats the surface of the particles and provides a barrier like protection against agglomeration [7].

Igarashi *et al.* [8] in the year 2000, synthesized nanometre $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ particles by firing a hydroxy carbonate precursor, which was prepared from two aqueous solutions [8]. One solution was composed of the metal nitrates $\text{Y}(\text{NO}_3)_3$ and $\text{Eu}(\text{NO}_3)_3$ while the other was an aqueous Na_2CO_3 solution. The two solutions were mixed and stirred for 10 minutes. The precipitate was separated by centrifugation at 3000 rpm for 15 minutes and then dried at 80 °C for 24 hours. The precursors were fired at 900 °C for 30 minutes in air and cooled rapidly to room temperature yielding particles with diameters of about 60 nm. In 2001, another group Wakefield *et al.* [2] synthesized nanocrystals of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ by colloidal chemical method involving precipitation of amorphous spherical precursor material, which was then fired to form the nanocrystalline material. Yttrium and europium chloride salts in water were adjusted to a pH of ~1 using HCl. An excess of urea, typically 15 times, was dissolved in the solution and then heated to >80 °C for 2 hours. The urea was decomposed slowly and a burst of particle nucleation was achieved when a certain pH was reached (pH 4–5). The particles continued to grow uniformly until the cation supply was exhausted. The obtained precipitate was washed, flocculated, dried, and fired in air for 3 hours at temperatures greater than 1000 °C. The material consisted of agglomerations of nanocrystals with the size of the agglomerates being defined by the drying stage. It was also possible to produce nanocrystals in the 2–10 nm range by colloidal methods which were defect-free. The surface of the nanocrystals can provide nonradiative recombination routes. However, by using a surface-capping agent, these effects can effectively be minimized. To a solution of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ in methanol, an equal amount of triocetylphosphine oxide (TOPO) solution was added. The TOPO binds to the surface and has three functions:

- It prevents particle agglomeration (steric passivation).
- It achieves electrical passivation.

- The ratio of TOPO to Eu^{3+} ions may be used to control the particle size.

Excitons migrating to the surface can de-excite, both radiatively and non-radiatively via surface dangling bonds, which may act as trap states. TOPO bound to the surface passivates these states and allows only recombination with the Eu^{3+} 4f shell. The solution was stirred for 10 minutes and the nanocrystals were precipitated by the addition of a controlled amount of methanolic NaOH solution (pH 5.5–6).

A gel combustion process was used by Roy *et al.* [9] to synthesise yttrium oxide nanocrystals with average particle size of 25 nm. They showed that a combination of citrate and nitrate ions in the precursor of a gel combustion process led to a low temperature combustion reaction with low reaction enthalpies. Normally employed chemical gelation route for synthesizing ceramic powders encounters following drawbacks:

- drying due to hygroscopy of the gels,
- adherence of the gels to glass surfaces,
- repetitive calcination due to swelling.

However, the gel combustion method directly yielded decomposed-intermediate powders and therefore overcame the difficulties discussed earlier. The gel was synthesized by gelling an aqueous solution of solid yttrium nitrate [$\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$] and anhydrous citric acid by evaporation of water at 80 ± 5 °C. A white precipitate was formed upon further heating under the identical conditions. The moment the precipitate was formed, the temperature of the hot plate was increased to 200 °C. The precipitates undergo a combustion process and yielded solid products along with the evolution of gases. The combusted products were calcinated at 750 °C in air for 2 hours at a heating rate of 6 °C per min.

In addition to these, numerous researchers have explored the photoluminescent properties of doped Y_2O_3 nanostructures with the aim to utilize this material effectively in the pertaining area. Work done by various research groups in the field, their main objectives and related outcomes have been summarized in Table 2.1.

Table 2.1: Summary of photoluminescent studies of doped Y_2O_3 nanostructures by various research groups and their main findings.

Investigator (Year) [ref.]	System	Method	Parameters studied	Outcomes
Zhang <i>et al.</i> (2003) [10]	Monodisperse array and nanowires of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphor (NPs).	Sol–gel method	Effect of template AAO (anodic aluminum oxide) was studied on optical and morphological properties of Y_2O_3 .	• The $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanowires are parallelly arranged in AAO template, all of which have uniform diameter of about 50nm having polycrystalline particles with cubic phase. • The red emission peak of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphor (NPs) at 611–616 nm is attributed to $^5\text{D}_0$-$^7\text{F}_2$ forced electric dipole transition of Eu^{3+}, this emission peak exhibited a broadened line width.
Vetrone <i>et al.</i> (2004) [11]	Nanocrystalline $\text{Y}_2\text{O}_3:\text{Er}^{3+}$	Wet chemical synthesis	Comparison between combustion and wet chemical studies were done in preparation of Er^{3+} doped Y_2O_3 nanophosphors.	• A broadening of both the reflectance spectrum and 77 K luminescence spectrum ($\lambda_{\text{exc}} = 488 \text{ nm}$) was observed in the nanocrystalline material compared to bulk $\text{Y}_2\text{O}_3:\text{Er}^{3+}$. • It was observed that the magnitude of the red enhancement in the bulk material and nanocrystals was nearly equal to the prepared via wet chemical process.
Dosev <i>et al.</i> (2006) [12]	Nanoparticles of europium doped yttrium oxide ($\text{Y}_2\text{O}_3:\text{Eu}^{3+}$)	Spray pyrolysis	Fluorescent and crystallinity were studied simultaneously to show their dependence on size of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphor.	• The nanoparticles of size 5–50 nm and 50–200 nm were prepared, which were separated using centrifugation technique. • It was found that particles larger than about 50 nm had a cubic Mn_2O_3-type structure that was typical of bulk material. Moreover, particles smaller than 50 nm exhibited a more complex structure which indicated the presence of the monoclinic phase with minor spectroscopic features that are consistent with this phase.

Hong <i>et al.</i> (2006) [13]	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanoparticles	Wet chemical synthesis	Addition of solvent (Methanol) and dispersing agent (Hydroxypropyl cellulose (HPC)) was used during synthesis to study their effect on optical and morphological properties of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ NPs.	- Particle size and specific surface area obtained was of 4 nm and 80 m²/g respectively. - The $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ NPs synthesized by using methanol solvent and hydroxypropyl cellulose (HPC) as a dispersing agent showed higher degree of crystallization than that without HPC.
Xu <i>et al.</i> (2006) [14]	Nanocrystalline $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphors	Combustion method	Sucrose was used as a chelating agent and fuel to study its effect on optical properties of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphor.	- It was found that cubic phase can be formed at a low temperature of 400 °C, and particles size of the annealed sample (at 1000 °C) was in the range of 30–50 nm. - The post-annealing treated $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphors yield intense red emission at 610 nm, corresponding to the $^5\text{D}_0\text{--}^7\text{F}_2$ transitions. - It was found that the luminescence properties of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ particles were strongly affected by the annealing temperatures and the sucrose to metal ion ratios.
Graeve <i>et al.</i> (2006) [15]	$\text{Y}_{(2-x-y)}\text{Tm}_x\text{Yb}_y\text{O}_3$ blue-emitting phosphors.	Combustion synthesis	Effect of Temperature on optical properties of the phosphor ($\text{Y}_{(2-x-y)}\text{Tm}_x\text{Yb}_y\text{O}_3$) were studied.	- From X-ray diffraction (XRD) it was determined that the powders in the as synthesized state were in a state of high strain. - Upon thermal treatment, the strain in the lattice decreased, which resulted in an improvement in the photoluminescence emission intensity of the $\text{Y}_{(2-x-y)}\text{Tm}_x\text{Yb}_y\text{O}_3$ phosphors.
Murugan <i>et al.</i> (2006) [16]	Eu^{3+} doped Y_2O_3 nanorods	Microwave hydrothermal route	Synthesis technique was studied to prepare Eu^{3+} doped Y_2O_3 nanorods.	- A facile synthesis of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphors by a two step route, which involves direct co-precipitation of Y^{3+}–Eu^{3+} ions from their nitrates by microwave assisted hydrothermal method and subsequent thermal decomposition of the precipitates to yield the nanocrystalline $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphors. - Time for synthesis of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanorods was very less (only 6 min were taken for completion of whole process).

Guixia <i>et al.</i> (2007) [17]	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ hollow spheres	Homogeneous precipitation method	Calcined silica as a template was used to prepare the $\text{SiO}_2/\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ core-shell structure material, and have dissolved silica cores with sodium hydroxide to obtain $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ hollow spheres	• The core-shell structure and hollow spheres of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ was crystalline in nature and the XRD patterns were broadened. • The size of the $\text{SiO}_2/\text{Y}_2\text{O}_3$ core-shell structure was about 100 nm, and the thickness of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ hollow spheres were less than 5 nm.
TranKim <i>et al.</i> (2007) [18]	Y_2O_3 nanomaterials doped with Eu^{3+} , Tb^{3+} , Tm^{3+} , Er^{3+} and Yb^{3+} ions	Direct precipitation route	• Luminescence, Energy transfer, and Upconversion mechanisms were studied for all the prepared samples. • The dependence of concentration of dopant and the influence of size on the luminescent properties were discussed in detail.	• Doped Y_2O_3 nanophosphor (NPs) was prepared in colloidal media. Average size of the obtained NPs was 5 nm. Particles were having narrow size distribution and were of spherical shape. • The luminescence in all the samples prepared was strong and energy transfer was observed in $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$, Eu^{3+} codoped sample. • The upconversion emission from $\text{Y}_2\text{O}_3:\text{Er}^{3+}$, Yb^{3+} nanophosphor is remarkable for developing an infrared display card.
Yin <i>et al.</i> (2007) [19]	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanosphere and nanowire	Solvothermal process	Different reaction mediums (water, ethanol, ethylene glycol and glycerol) were used to study their influence on photoluminescence and morphological properties of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor.	• The phosphor prepared in water and ethanol as medium possessed wire like morphology. However, the phosphor prepared in water showed high aspect ratio and that in ethanol showed low aspect ratio. • The powders prepared in ethylene glycol and glycerol possessed well-dispersed near-spherical powders, which showed almost the same level of photoluminescence emission intensity as that of submicron particles prepared without solvothermal treatment.
Zuoling <i>et al.</i> (2007) [20]	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanocrystals	Combustion process	Comparison between nanocrystals $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ and bulk $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ were done in order to study the influence of size on band	• The bond lengths of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanocrystals are shorter than those of the bulk counterpart and the bond covalency of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanocrystal also has an increasing trend as compared to bulk. • The blue-shift of CT (charge transfer) band in excitation

			gap and photo-luminescent properties of these nanophosphors.	spectra from bulk $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ to nanocrystalline $\text{Y}_2\text{O}_3::\text{Eu}^{3+}$ was observed. • The blue-shift of CT band is related to centroid shift and crystal-field splitting of Y_2O_3.
Tsuyoshi <i>et al.</i> (2008) [21]	Eu^{3+} doped yttrium oxysulfates ($\text{Y}_2\text{O}_2\text{SO}_4:\text{Eu}^{3+}$)	Homogeneous precipitation method	Effect of template agent (dodecylsulfate) and sintering temperature was studied on optical and morphological properties of $\text{Y}_2\text{O}_2\text{SO}_4:\text{Eu}^{3+}$ nanophosphors.	• It was found that Red emission due to Eu^{3+} ion in $\text{Y}_2\text{O}_2\text{SO}_4:\text{Eu}^{3+}$ nanophosphor is three times stronger in as compared to $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (for same Eu^{3+} ion concentration). • The abnormally enhanced emission is likely based on specific deformation of sulfate groups induced through the conversion of concentric dodecylsulfate-layers to straight sulfate-layers in the oxysulfate framework upon calcination.
Yunfeng <i>et al.</i> (2008) [22]	Li^+ and Er^{3+} codoped Y_2O_3 nanocrystals	Complex precursor method	Infrared-to-visible upconversion luminescence spectra are investigated in Li^+ and Er^{3+} codoped Y_2O_3 nanocrystals.	• By introducing Li^+ ions in $\text{Y}_2\text{O}_3:\text{Er}^{3+}$, the upconverted emission intensity is found to be greatly enhanced as compared to samples which were prepared without Li^+ doping. • The cause of the enhancement is believed to be the modification of the local symmetry of the Er^{3+} ion, which increases the intra 4f transitions of Er^{3+} ion, and the homogeneous distribution of Er^{3+} in Y_2O_3 nanocrystals.
Muresan <i>et al.</i> (2008) [23]	Eu^{3+} doped Y_2O_3 powder	Wet chemical process	• Various reagents, namely oxalic acid, ammonium oxalate, urea or ammonium carbonate were used as precipitating reagent to synthesis Eu^{3+} doped Y_2O_3 nanophosphor. • pH of the solution at the time of synthesis were also varied to study its effect on optical and	• Three types of as synthesised powder were obtained having variable particle shape (prismatic-lamellar, spherical, needle) and size (0.2–5 μm). • Thermal treatment of the as prepared precursors was performed at 1200 °C in order to generate $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor powders with emission intensity between 23.4% and 89.2%. • The study revealed that the nature of precipitating reagent and the precipitation pH have a strong influence on the PL properties, the microstructure and the morphology of phosphor particles.

			morphological properties of Eu^{3+} doped Y_2O_3 powder.	
Mukherjee <i>et al.</i> (2008) [24]	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}, \text{Tb}^{3+}$ co doped nanoparticles	Combustion Synthesis	Eu^{3+} co-doped $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ nanoparticles were prepared by the combustion method and characterized for their structural and luminescence properties as a function of annealing temperatures and relative concentration of Eu^{3+} and Tb^{3+} ions.	• It has been concluded that variation in the relative intensity of high spin (310 nm) and low spin (285 nm) $4f \rightarrow 5d$ excitation transitions of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}, \text{Tb}^{3+}$ nanoparticles arises due to the combined effect of distortion around YO_6/TbO_6 polyhedra and increased surface defect concentration. • For co-doped samples there exists strong energy transfer from Tb^{3+} to Eu^{3+} ions. However, the back energy transfer from Eu^{3+} to Tb^{3+} ions is found to be very weak. • Moreover, heat treatment temperatures and relative concentration of Eu^{3+} and Tb^{3+} ions strongly affect luminescence properties of Eu^{3+} co-doped $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ nanoparticles.
Zhang <i>et al.</i> (2009) [25]	BaSO_4 nanoparticles coated with $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$	Wet chemical method	Effect of temperature on optical properties of nanoparticles of BaSO_4 coated with $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor layers ($\text{BaSO}_4/\text{Y}_2\text{O}_3:\text{Eu}^{3+}$) had been studied.	• The obtained core-shell phosphors consist of well dispersed submicron spherical particles with narrow size distribution. • XRD result shows that the BaSO_4 cores and the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ shells were stable even after annealing at 1400 °C. • The $\text{BaSO}_4/\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ core-shell particles show a red emission corresponding to $^5\text{D}^0-^7\text{F}^2$ of Eu^{3+} under the excitation of ultraviolet.
Yuan <i>et al.</i> (2009) [26]	$\text{SiO}_2 @ \text{Y}_2\text{O}_3:\text{Eu}^{3+}$ and $\text{SiO}_2 @ \text{Y}_2\text{O}_3:\text{Eu}^{3+} @ \text{SiO}_2$ core-shell structure phosphor	Homogeneous precipitation method	Effect of Coating of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ on SiO_2 (core) was studied.	• Photoluminescence determination showed that both the phosphors ($\text{SiO}_2 @ \text{Y}_2\text{O}_3:\text{Eu}^{3+}$ and $\text{SiO}_2 @ \text{Y}_2\text{O}_3:\text{Eu}^{3+} @ \text{SiO}_2$) can be excited by ultra violet at 254nm which showed red-shift. • Under the excitation at 254 nm, the Eu^{3+} ion mainly shows its characteristic red (612 nm, $^5\text{D}_0-^7\text{F}_2$) emission in the particles from $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ shell.

Hao <i>et al.</i> (2009) [27]	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphor	Sol gel method	• Amount of chelating agents (citric acid and tartaric acid) were monitored during synthesis. • Amount of dopant (Eu^{3+}) was varied in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphor. • Effect of temperature was also studied on optical properties of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$.	• The particle size of the obtained phosphors varied from 1 to 6 μm (using citric acid as chelating agent) and from 20 to 30 nm (using tartaric acid as chelating agent). • The luminescent properties of Eu^{3+} doped Y_2O_3 as a function of Eu^{3+} concentration and sintering temperature have been investigated. The optimal Eu^{3+} concentration is 7 mol%. • The photoluminescent intensity of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ increases with the increase of sintering temperature up to 800 $^{\circ}\text{C}$ and 900 $^{\circ}\text{C}$ for the nanophosphors and microphosphors, respectively. Further increase in sintering temperatures resulting in reduction of the emission intensity.
Jadhav <i>et al.</i> (2009) [28]	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ spherical nanoparticles	Co-Precipitation method	Addition of additives like ethylenediaminetetraacetic acid (EDTA) and NaCl during synthesis were studied on optical properties of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphor.	• Photoluminescence emission of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphor had shown a drastically enhancement on the addition of NaCl and EDTA in the reaction mixture. • Increase in emission intensity of the nanophosphor was explained considering the nephelauxetic effect induced by the incorporated ions (Na^+ and Cl^-) in the reaction solution at the time of synthesis.
Ferrari <i>et al.</i> (2010) [29]	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (5 mol% Eu^{3+}) and $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (5 mol% Eu^{3+}) containing 1 mol% of Ag nanoparticles.	Citrate method	• Effect of citric acid was studied on optical properties of synthesized nanophosphors. • Effect of Ag nanoparticles was also studied on optical properties of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphors.	• The presence of the Ag nanoparticles in the Y_2O_3 host lattice might promote a decrease of the defects possibly present on the particle surface, which can affect the Eu^{3+} neighbourhood. • The metal-induced crystallization effect was observed which was responsible for the enhancement in PL of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$.
Xiaorui <i>et al.</i> (2010) [30]	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ $\text{Y}_2\text{O}_3:\text{Eu}^{3+}, \text{Li}^+$ nanoparticles.	Co-precipitation method	Effect on optical properties due to Li^+ ion co-doping in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ was studied.	• The quenching concentration of Eu^{3+} ions is 9.0 mol% in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ powders. • The results also showed that the incorporation of Li^+ ions in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ can greatly improve (79%) the luminescence intensity of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphor.

Zhilong <i>et al.</i> (2010) [31]	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ $\text{Y}_2\text{O}_3:\text{Tb}^{3+}, \text{Eu}^{3+}$ nanorodes	Hydrothermal method	The photoluminescence (PL) property of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}, \text{Eu}^{3+}$ phosphor was investigated by changing molar conc. of both dopants simultaneously.	- Both XRD and TEM results indicated that the size of these nanorods were micro-nano dimension in length 300-500nm and in diameter 20-40nm. - There was an energy transfer from Tb^{3+} to Eu^{3+} ions due to which tunable emission from $\text{Y}_2\text{O}_3:\text{Tb}^{3+}, \text{Eu}^{3+}$ nanophosphor was obtained.
Xiaoyong <i>et al.</i> (2010) [32]	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$	Surfactant assisted co- precipitation molten salt synthesis method.	The effects of surfactant(cetyl trimethyl ammonium bromide (CTAB)) content and annealing temperature on the structure and luminescence were investigated.	- It was found that the introduction of CTAB as a dispersing agent reduced the impurities attached on the surface of particles, promotes the reaction. As a result of this the crystallinity was highly improved which further resulted in strong emission intensity of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphors. - In PL spectra, the excitation spectra illustrate two rarely appeared strong lines located at 394 and 466 nm due to ${}^7\text{F}_{0,1}-{}^5\text{L}_6, {}^7\text{F}_{0,1}-{}^5\text{D}_2$ transitions of Eu^{3+} ions, respectively. Moreover, the as-synthesized samples have very strong red emission at 611 nm at the excitation wavelength of 394 or 466 nm.
Gomes <i>et al.</i> (2011) [33]	Eu^{3+} doped Y_2O_3 nanoparticles	Proteic sol-gel technique	Effect of pH and calcination temperature was studied on optical and morphological properties of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanoparticles.	- The average particle size was tunable from 4 to 50 nm by the control of the pH and calcination temperature of the samples. - The luminescent characterization of the samples has shown a dependence of the quantum yield on the particle size (PL intensity increases with increase in size from 4 nm to 50 nm) to the suppression of the charge transfer from the oxygen to the excited level of Eu^{3+}.
Hongfang <i>et al.</i> (2012) [34]	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ $\text{Y}_2\text{O}_3:\text{Tb}^{3+}, \text{Eu}^{3+}$	Homogeneous precipitation Technique	Doping concentration of Eu^{3+} and Tb^{3+} ions and synthesizing temperatures (700 °C to 1000 °C) were varied.	- The PL spectra indicate the Eu^{3+} and Tb^{3+} co-doped Y_2O_3 microspheres showed five main emission peaks: three at 591, 609 and 629 nm originate from Eu^{3+} and two at 482 and 541 nm originate from Tb^{3+}, under excitation of 250 – 340 nm irradiation. - The luminescence color could be changed by varying the excitation wavelength. - Different concentrations of Eu^{3+} and Tb^{3+} ions were

				induced into the Y_2O_3 lattice and the energy transfer from Tb^{3+} to Eu^{3+} ions in these phosphors was found.
Som <i>et al.</i> (2012) [35]	$Y_2O_3:Eu^{3+}$ $Y_2O_3:Tb^{3+}$ $Y_2O_3:Tb^{3+}, Eu^{3+}$	Combustion synthesis method	Doping concentration of Eu^{3+} and Tb^{3+} ions and synthesizing temperatures (500 °C to 1000 °C) were varied.	• A strong characteristic emission from Eu^{3+} and Tb^{3+} ions was identified and the influence of doping concentration and annealing temperature on PL properties was systematically studied. • Transfer of energy was observed from Tb^{3+} to Eu^{3+} ions in the codoped phosphor.
Gowd <i>et al.</i> (2012) [36]	Eu^{3+} doped Y_2O_3 nanophosphors	Simple colloidal precipitation method	Optical properties were studied with variation in sintering temperature. Conc. of Eu ion was also varied in $Y_2O_3:Eu^{3+}$ nanophosphor to study its effect on PL emission intensity. Effect of pH was also studied on PL emission intensity Eu^{3+} doped Y_2O_3 nanophosphors.	• The PL emission spectra of nanophosphors showed bright red emission at 612 nm due to hyper sensitive electric dipole (ED) $^5D_0-^7F_2$ transition of Eu^{3+} ions in Y_2O_3 lattice. • Photoluminescence studies indicated that optimum value of the Eu^{3+} to get best luminescence properties is 12 mol% as well as with increase in pH up to 12. • The enhancement of emission intensity of 612 nm peak at higher annealing temperature is also observed and attributed to improved crystallinity of the Eu^{3+} doped Y_2O_3 nanophosphor.
Yadav <i>et al.</i> (2013) [37]	$Yb^{3+}/Er^{3+}:Y_2O_3$	Combustion synthesis	Effect of addition of ZnO in $Yb^{3+}/Er^{3+}:Y_2O_3$ nanophosphor was studied.	• A strong green (525, 546 nm) with weak blue (411 nm) and red (657 nm) emissions through upconversion had been observed from the phosphor on excitation with 976 nm diode laser. • On addition of ZnO, the intensity of these emissions was enhanced several times. • The reason behind the enhancement was discussed with the help of the emitting level lifetime.
Liu <i>et al.</i> (2013) [38]	Eu^{3+} doped Y_2O_3 nanophosphors	Hydrothermal route.	Effect of chelating agent (sodium citrate) was studied on optical and morphological properties	• $Y(OH)_3:Eu^{3+}$ microcrystals with a variety of morphologies including nanoplate, microtube, microsphere, polyhedron, microdisk and microprism have been synthesized by simply changing the pH and

			of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphor.	amount of chelating agent during synthesis.
Gong <i>et al.</i> (2013) [39]	$\text{Y}_2\text{O}_3\text{-H}_3\text{BO}_3:\text{Eu}^{3+}$ powders	Mechanical alloying (MA) method	Effect of annealing temperature and time was studied on optical properties of $\text{Y}_2\text{O}_3\text{-H}_3\text{BO}_3:\text{Eu}^{3+}$ powders.	- The crystallite size of the powder mixture milling for 30 minutes (min) by the Willaimsone-Hall method was approximately 58.8 nm with strain of 0.00141; overall, the internal strain increased with the milling time (t_m). - The photoluminescence of the powder mixture excited to 240 nm by a zenon discharge lamp (20 kW) was detected near 592 nm ($^5\text{D}_0 / ^7\text{F}_1$), 613 nm, 628 nm ($^5\text{D}_0 / ^7\text{F}_2$), and 650 nm ($^5\text{D}_0 / ^7\text{F}_3$).
Boukerika <i>et al.</i> (2014) [40]	Eu^{3+} doped Y_2O_3 powders	Sol gel	Annealing temperatures	- The average crystallite size, found by XRD analysis, increases from 12 to 30 nm as annealing temperature increases. - Intense red emissions at 610 and 588 nm assigned to forced electric dipole $^5\text{D}_0 / ^7\text{F}_2$ and to magnetic dipole $^5\text{D}_0 / ^7\text{F}_1$ transitions, respectively, of Eu^{3+} ion are observed. - The emission becomes more intense for higher annealing temperature, which is related to the improvement of crystalline quality.
Ray <i>et al.</i> (2014) [41]	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphors	Complex based precursor solution method	Synthesis route was modified to synthesized uniform size nanophosphors.	- Undoped and Eu^{3+} doped cubic yttria nanoparticles with considerable good crystallinity had been synthesized by means of a complex-based precursor solution method. - Depending upon the temperature of the annealing treatment, nanophosphors with sizes between 6 and 37 nm, all showing narrow size distributions, had been obtained. - While nanoparticles of 37 nm had similar lattice parameters than bulk cubic yttria, the lattice parameter in the nanoparticles increases up to 0.26% (in undoped Y_2O_3) and 0.33% (in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$) as the particle size

				decreases from 37 to 6 nm.
Ajmal <i>et al.</i> (2014) [42]	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ $\text{Y}_2\text{O}_3:\text{Eu}^{3+}, \text{Gd}^{3+}$ nanophosphors	Homogeneous precipitation method	Bi-functional Y_2O_3 codoped with luminescent Eu^{3+} and paramagnetic Gd^{3+} system were synthesized.	• Partial replacing of Y^{3+} with Gd^{3+} linearly improved the strongest red 612 nm emission associated with $^5\text{D}_0\text{-}^7\text{F}_2$ transition of Eu^{3+}. • Co-doping yttria based red luminescent phosphors with Gd^{3+} resulted to enhancement of red luminescent emission together with paramagnetic functionality of the prepared composite particles.
Packiyaraj <i>et al.</i> (2014) [43]	Y_2O_3 (undoped), $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$	Hydrolysis assisted co- precipitation method	Effect of temperature was studied on structural and optical properties of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphor.	• The sample showed high crystallinity and average particle size was in the range of 10–16 nm and 20–25 nm when annealed at 600 and 900 °C respectively. • The 900 °C annealed $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ exhibited a stronger photoluminescence due to homogeneously occupied Eu^{3+} ions in the Y_2O_3 lattice and high crystallinity.
Mukherjee <i>et al.</i> (2014) [44]	Y_2O_3 nanoparticles doped with Dy^{3+} , Eu^{3+} and Tb^{3+} .	Gel combustion method	Effect of various amino acids namely, glycine, phenyl alanine, arginine, glutamic and aspartic acids were added during synthesis to study their effect on optical properties of $\text{Y}_2\text{O}_3:(\text{Dy}^{3+}$, Eu^{3+} and $\text{Tb}^{3+})$ nanophosphor.	• It was found that the nanoparticles prepared by using glycine and arginine as the fuels have smooth surface compared to those prepared using other amino acids. • For the nanoparticles prepared using glutamic and aspartic acids, there exist a diffused pore-grain interface due to the lesser extent of heat generated in the reaction which leads to smaller particle size, poor crystallinity and improper burning of the organic materials. • Lower surface area and smooth surface of the nanoparticles prepared using glycine leads to their improved luminescence properties of $\text{Y}_2\text{O}_3:(\text{Dy}^{3+}$, Eu^{3+} and $\text{Tb}^{3+})$ nanophosphor.
Jiamin <i>et al.</i> (2014) [45]	$\text{Y}(\text{OH})_3:\text{Eu}^{3+}$ nanotubes $\text{Au}/\text{Y}_2\text{O}_3:\text{Eu}^{3+}$	Hydrothermal method	Au particles were grown on the surface of Y_2O_3 : Eu^{3+} nanotubes to see its effect on optical	• In the excitation spectra of $\text{Au}/\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ monitored at 614 nm, the $^7\text{F}_0 \rightarrow ^5\text{H}_3$ transition from Eu^{3+} increased with increasing Au content, while the other sharp lines

			properties of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphor.	originating from Eu^{3+} f-f electron transitions almost vanished. • In the emission spectra, the spectral configurations of Eu^{3+} in $\text{Au}/\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ composite nanotubes varied with the excitation wavelengths. • When the excitation wavelength was 256 nm, the $^5\text{D}_4 \rightarrow ^7\text{F}_0$, $^5\text{D}_7 \rightarrow ^7\text{F}_0$, $^5\text{G}_2 \rightarrow ^7\text{F}_0$, $^5\text{L}_6 \rightarrow ^7\text{F}_0$, $^5\text{D}_0 \rightarrow ^7\text{F}_0$, $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$, $^5\text{D}_0 \rightarrow ^7\text{F}_3$, and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions from Eu^{3+} ions in $\text{Au}/\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ were observed.
Dubey <i>et al.</i> (2015) [46]	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphor	Modified solid state reaction method	Effect of europium concentration on photoluminescence and thermoluminescence behavior of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor was studied.	• The PL emission was observed in the range 417–632 nm ranges all visible regions for the Y_2O_3 phosphor doped with Eu^{3+}. • Excitation spectrum found at 254 nm. Sharp intense peaks found around 467, 534, 594, 612, and 632 nm with high intensity. • XRD data, using the Scherer's formula, the calculated average crystallite size of Eu^{3+}-doped Y_2O_3 phosphor is around 45 nm. • TL study was carried out for the phosphor with UV irradiation.
Ali <i>et al.</i> (2016) [47]	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ thin-film	Pulse laser deposition	Temperature dependence of structural and luminescence properties of Eu^{3+} -doped Y_2O_3 red-emitting phosphor.	• At lower annealing temperature of 600–700 °C, cubic bixbyite $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ was formed. As the annealing temperature was increased to 800 °C, hexagonal phase emerged. • Photoluminescence measurement indicates intense red emission around 612 nm due to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition.
Nigam <i>et al.</i> (2016) [48]	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$	Sol gel	Annealing effects	• It is observed that 1300 °C annealed samples show higher non-radiative contributions, poor lifetime and quantum efficiency in comparison to the samples annealed at lower temperatures (700 °C and 900 °C), even though the structural symmetry and emission

				profile remains almost unaffected by the increasing annealing temperature. • Based on empirical exploration it has been established that annealing at 1300 °C, reduces the average distance between Eu ions to ~ 6.7 Å on.
Yadav <i>et al.</i> (2016) [49]	$\text{Y}_2\text{O}_3:\text{Sm}^{3+}, \text{Tb}^{3+}$ $\text{Y}_2\text{O}_3:\text{Sm}^{3+}, \text{Tb}^{3+}, \text{Li}^+$	Solution combustion method	Effect of addition of Li^+ ion in $\text{Y}_2\text{O}_3:\text{Sm}^{3+}, \text{Tb}^{3+}$ nanophosphor.	• The Sm^{3+}-doped nano-phosphor gives off an orange-red emission whereas the Tb^{3+} doped nano-phosphor gives off blue and green emissions individually on excitation with 380 nm radiations. • When the Sm^{3+} and Tb^{3+} ions are doped together, the co-doped nano-phosphor emits white light with the CIE coordinates 0.33 and 0.37, due to the combined emissions of these two ions on excitation with 380 nm radiation. • The presence of Li^+ ions in the co-doped sample enhances the emission intensity of white light up to three times. The enhancement in the emission intensity is discussed in terms of a reduction in the optical quenching centers and an increase in the crystallite size.

2.3 GAPS IN THE STUDIES

1. The doping of Eu^{3+} in Y_2O_3 has been studied in detail by many workers where doping concentration has been varies from 3 to 10%. However, there is vast variation in their measured PL characteristics for the same concentration of dopants. This variation is because of occupancy of Eu^{3+} to different lattice site on Y_2O_3 (surface or interstitial site) which require further investigation.
2. From literature survey it is observed that sol gel process is an effective technique to synthesise nanodimensions Y_2O_3 : Eu^{3+} and Tb^{3+} doped nanoparticles with various surfactants (TOPO, oleic acid) which shows red and green emission with variable quantum yield. The correlation with morphological properties done by some workers suggests that aggregation of particles in aqueous solution in comparison to organic solvent occurs which is the basic cause for degradation in PL properties. So monodispersity in aqueous medium along with specified doping and surfactant concentration is needed for highly luminescent biomarkers.
3. To generate and characterize stable suspension for both red and green nanophosphors that should exhibit bright luminescence is required lacking in many studies discussed in this report. For biological sensing these nanoparticles have to be suspend in water while retaining their PL characteristics. Very less work till date is available for achieving considerable PL intensity in water. Synthesis and enhancement of PL characteristics in aqueous and non aqueous solution both is required.
4. Effect of multiple doping in host Y_2O_3 has been studied by some workers by using various methods. This co-doping results tunable colour as well as enhancement in PL intensity in prepared NPs. However, their PL properties are observed to vary with same doping concentration. Thus PL becomes a dependent parameter on occupancy of dopant site. Also energy transfer in between these dopants along with surfactant used is not done in detail. Since this colour tunability with enhanced emission output and monodispersity in aqueous medium is main concern for their end use in biosensors, so study of multiple doping like Eu^{3+} and Tb^{3+} in Y_2O_3 on PL characteristics is required.
5. The effect of pH during synthesis and doping of alkali metal ions were studied by many researcher but variation in pH during synthesis is still unclear and need to be addressed.

2.4 Plan of Work

Although incredible work has been made to control the size, enhance the PL emission intensity and tune the morphology of doped Y_2O_3 nanophosphors by many researchers yet some points are there which need to be explored in a systematic manner.

- ❖ A simple and economical synthesis method is required to produce doped highly luminescent Y_2O_3 nanophosphors (NPs). Moreover, synthesis of highly crystalline doped Y_2O_3 NPs with size in nano region is essential.
- ❖ It has been seen that pH of the solution (solution in which precipitation occurs) at the time of synthesis affect the morphology and PL emission of the final prepared phosphor (phosphor obtained after annealing) but still detailed study related to variation in pH of solution is required.
- ❖ Effect of different capping agents (with pH control) on morphology and optical behaviour of Y_2O_3 is still unclear.
- ❖ Effect of temperature (during annealing) of synthesised nanopowder on morphological and optical properties is still unclear.
- ❖ Effect of different dopants on optical properties of Y_2O_3 is still under speculation. Moreover, detailed study related to the effect of alkali metal ions (Li^+ , Na^+ and K^+) codoping with lanthanide dopants (Eu, Tb, Dy & etc.) on luminescent properties of Y_2O_3 is required.

Thus considering the above limitations or gaps, the main objectives behind the present work were as below:

1. To synthesize Eu^{3+} doped Y_2O_3 nanostructures using chemical precipitation routes.
2. To study the emission intensity of samples with variation in optical properties and doping concentration.
3. To study the optical and morphological properties of Y_2O_3 using multiple dopants (Eu^{3+} , Tb^{3+} , and Dy^{3+}).
4. To see the effect of surfactants like CTAB, TOPO etc. on photoluminescence characteristics.
5. To study the effect of thermal treatment on PL properties.

6. To characterize the synthesized nanomaterials with XRD, TEM, and SEM for morphological studies and with UV, PLE, and PL for optical and biological studies.

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CHAPTER 3

EXPERIMENTAL DETAILS

Overview

This chapter describes the details of the synthesis procedure to prepare doped Y_2O_3 nanoparticles (NPs) using different chemicals. The experimental procedure followed to prepare doped Y_2O_3 nanoparticles is given. Moreover, during synthesis of doped Y_2O_3 NPs the details (molar concentration) about different dopants, co-dopants and capping agents is also given. The characterization procedures along with instruments used to generate and analyze the data has been given. The details about each of the instruments, their model number, working and operating conditions have been given. The steps followed for different experiments have been discussed in detail. For simplicity, names of different sample prepared, along with their codes is also given in tabular form. This chapter concludes the whole scheme of events leading to successful completion of experimental work.

3.1 Raw materials

In the present study, raw materials used for preparing the samples were yttrium nitrate ($\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.99%, Sigma Aldrich); Europium nitrate ($\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 99.99%, Sigma Aldrich); Terbium nitrate ($\text{Tb}(\text{NO}_3)_3$, 99.99%, Sigma Aldrich); Lithium nitrate (LiNO_3 , 99.99%, Sigma Aldrich); Dysprosium nitrate ($\text{Dy}(\text{NO}_3)_3$, 99.99%, Sigma Aldrich); Sodium nitrate (NaNO_3 , 99.99%, Sigma Aldrich); Potassium nitrate (KNO_3 , 99.99%, Sigma Aldrich); ammonium hydrogen carbonate (NH_4HCO_3 , Himedia); Polyvinyl pyrrolidone (PVP, 99.99%, Sigma Aldrich); 1-Thioglycerol (TG, 99.99%, Sigma Aldrich); Cetyl trimethylammonium bromide (CTAB, 99.99%, Sigma Aldrich); Trioctylphosphine oxide (TOPO, 99.99%, Sigma Aldrich); Betacyclodextrin (β -cyclo, 99.99%, Sigma Aldrich); ethanol (Merk) and double distilled water. All these materials were used without any further purification.

3.2 Sample preparation

3.2.1 Synthesis of $\text{Y}_2\text{O}_3:\text{RE}^{3+}$ ($\text{RE}^{3+} = \text{Eu}^{3+}, \text{Tb}^{3+}$ and Dy^{3+}) nanophosphors.

Step I: Yttrium oxide (Y_2O_3) nanophosphors were synthesized by co-precipitation method [1-3]. $\text{Y}(\text{NO}_3)_3$ (99.99%), $\text{Eu}(\text{NO}_3)_3$ (99.9%), $\text{Tb}(\text{NO}_3)_3$ (99.9%) and $\text{Dy}(\text{NO}_3)_3$ (99.9%) (Sigma Aldrich) and ammonium hydrogen carbonate (NH_4HCO_3) (Himedia) were used as starting materials. Firstly, according to the formula of $(\text{Y}_{1-x}\text{Eu}_x)_2\text{O}_3$ ($x = 0.03$ to 0.13) mol%, stoichiometric amounts of $\text{Y}(\text{NO}_3)_3$, dopant ($\text{Eu}(\text{NO}_3)_3$) were dissolved in double distilled water and their nitrate solution of 0.2 mol/L was used as mother solution. The 1.5 mol/L solution of ammonium hydrogen carbonate was used as precipitant solution. The precipitates were obtained by drop wise addition of the ammonium hydrogen carbonate into mother solution with continuous stirring. After aging the suspension for 24 hours, the resultant suspensions were then centrifuged at $10,000 \text{ rpm}$ for 5 min . The precipitated particles were filtered using Whatman-40 filter paper. The particles were washed with hot water several times to remove the last traces of adhered impurities. The wet powders were dried at 80°C in vacuum oven for 24h.

Step II: Finally, these powders were annealed at 1000°C for 2 hours in a tubular furnace at a heating rate of 5°C per min in an alumina boat to get the corresponding nano crystalline powders. All chemicals used in this work were of analytical grade and were used as such without any further purification. Ultrapure water was used in the entire synthesis.

Similarly for the preparation of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ and $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ nanophosphors, formula used is $(\text{Y}_{1-y}\text{Tb}_y)_2\text{O}_3$ ($y = 0.02$ to 0.4) mol% and $(\text{Y}_{1-z}\text{Dy}_z)_2\text{O}_3$ ($z = 0.02$ to 0.4) mol%

respectively. All the other steps (i.e. Step I and II) were same in the preparation of $Y_2O_3:Tb^{3+}$ and $Y_2O_3:Dy^{3+}$ respectively.

3.2.1.1 Synthesis of doped Y_2O_3 nanophosphors at varying annealing temperature

After obtaining the optimizing concentration (PL emission intensity is maximum at this concentration of dopant) of all the dopants in Y_2O_3 , few samples of doped Y_2O_3 were also prepared at this optimum concentration of dopant and annealed at varying temperatures. These powders were annealed at temperatures starting from 300 to 1300 °C for 2 hours in a tubular furnace at a heating rate of 5 °C per min in an alumina boat to get the corresponding nano crystalline powders.

3.2.1.2 Synthesis of alkali metal ion (Li^+ , Na^+ and K^+) co-doped $Y_2O_3:RE^{3+}$ ($RE^{3+} = Eu^{3+}$, Tb^{3+} and Dy^{3+}) nanophosphor

Using similar method as discussed above (section - 3.2.1) $Y_2O_3:RE^{3+}$ nanophosphors codoped with alkali metal ions were also synthesized. In this case we have used $Y(NO_3)_3$ (99.99%), $Eu(NO_3)_3$ (99.9%), $LiNO_3$, $NaNO_3$, KNO_3 (99.99%) (Sigma Aldrich) and ammonium hydrogen carbonate (NH_4HCO_3) (Himedia) as starting materials. Firstly, according to the formula of $(Y_{1-x-y}Eu_xLi_y)_2O_3$ ($x = 0.12$, $y = 0$ to 0.07) mol%, $(Y_{1-x-y}Eu_xNa_y)_2O_3$ ($x = 0.12$, $y = 0$ to 0.05) mol% and $(Y_{1-x-y}Eu_xK_y)_2O_3$ ($x = 0.12$, $y = 0$ to 0.05) mol%, stoichiometric amounts of $Y(NO_3)_3$, $Eu(NO_3)_3$, $LiNO_3$, $NaNO_3$ and KNO_3 were dissolved in double distilled water and their nitrate solution of 0.2 mol/L was used as mother solution. All other process was similar as discussed earlier. Finally, these powders were sintered at 1000 °C for 2 hours in a tubular furnace at a heating rate of 5 °C per min in an alumina boat to get the corresponding nano crystalline powders.

Similarly samples

- $Y_2O_3:Tb^{3+}$ (1.0 mol%) co-doped with Li^+ (0.1 to 4 mol%)/ Na^+ (0.1 to 4 mol%)/ K^+ (0.1 to 4 mol%) and
- $Y_2O_3:Dy^{3+}$ (0.5 mol%) co-doped with Li^+ (0.2 to 4 mol%)/ Na^+ (0.2 to 4 mol%)/ K^+ (0.1 to 4 mol%) were also prepared by similar method as discussed above in section (3.2.1.2).

3.2.2 Synthesis of Eu^{3+} doped Y_2O_3 in the presence of polymers

3.2.2.1 Synthesis of Eu^{3+} doped Y_2O_3 using polymers (PVP, TG, PEG and β -cyclo) at the time of synthesis

STEP I: In order to prepare $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (5.0 mol%) the required amounts of rare-earth nitrates in defined stoichiometric ratio were dissolved in double distilled water and solution of 0.2 mol/L concentration and were used as mother solution.

STEP II: Similarly polymer (PVP and TG) solutions of certain mol% were prepared by adding proper amount of polymers in 30 mL of water. Polymer solution was added to mother solution and stirred for 30 min to get a homogeneous solution.

STEP III: The 1.5 mol/L solution of ammonium hydrogen carbonate was used as precipitant solution. Addition of ammonium hydrogen carbonate into the mother solution with continuous stirring resulted in the formation of precipitates. The pH of the solution was kept at 7 for all the samples.

STEP IV: The suspensions after aging for 12 hours were centrifuged, water washed, filtered and dried at 80 °C for 24 hours to obtain the white amorphous powders. Finally, these powders were fired at 1000 °C for 2 hours in a tubular furnace at a heating rate of 5 °C per min in an alumina boat to get the corresponding nano crystalline powders.

STEP V: Thereafter, few samples at pH 5 and 9 were also synthesised repeating steps I to IV at the obtained optimum concentration of polymer keeping all the other parameters constant. The amount of different polymers used during synthesis and corresponding sample's codes are given in Table 3.1.

Optimum concentrations of capping agents (at which sample has shown maximum luminescence) were determined to be 1.5 mol% for PVP and 1.5 mol% for TG.

Table 3.1: Name and codes to all samples prepared.

S. NO.	Sample Name	Sample Code
1	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (5.0 mol%) with pH 5, 7 and 9 at 1000 °C	S ₅ , S ₇ and S ₉
2	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (5.0 mol%), PVP (0.5, 1.0, 1.5 and 2.0 mol%) with pH 7 at 1000 °C	P _{a7} , P _{b7} , P _{c7} and P _{d7}
3	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (5.0 mol%), PVP (1.5 mol%) with pH 5 and 9 at 1000 °C	P _{c5} and P _{c9}
4	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (5.0 mol%), TG (0.5, 1.0, 1.5 and 2.0 mol%) with pH 7 at 1000 °C	T _{a7} , T _{b7} , T _{c7} and T _{d7}
5	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (5.0 mol%), TG (1.5 mol%) with pH 5 and 9 at 1000 °C	T _{c5} and T _{c9}
a=0.5, b=1.0, c=1.5 and d=2.0 mol% for both PVP and TG samples		

Sample codes are given according to the following Figure 3.1.

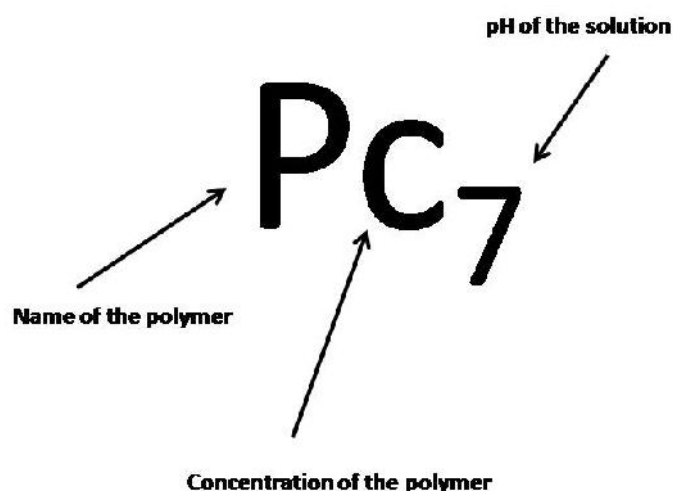


Figure 3.1: Sample Code Diagram

Similarly, samples of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (5.0 mol%) were also synthesised using PEG and β -cyclo as polymers in varying molar concentration which is listed below. All other conditions are kept same as discussed in step I to IV (section 3.2.2.1). Optimum concentrations of capping agents (at which sample has shown maximum luminescence) were determined to be 0.003 mol% for PEG and 0.015 mol% for β -cyclo. The amount of different polymers used during synthesis and corresponding sample's codes are given in Table 3.2.

Table 3.2: Name and codes to all samples prepared.

S. NO.	Sample Name	Sample Code
1	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (5.0 mol%) with pH 5, 7 and 9 at 1000 °C	S_5 , S_7 and S_9
2	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (5.0 mol%), PEG (0.001, 0.002, 0.003 and 0.004 mol %) with pH 7 at 1000 °C	G_{a7} , G_{b7} , G_{c7} and G_{d7}
3	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (5.0 mol%), PEG (0.003 mol%) with pH 5 and 9 at 1000 °C	G_{c5} and G_{c9}
4	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (5.0 mol%), β -cyclo (0.005, 0.010, 0.015 and 0.020 mol%) with pH 7 at 1000 °C	β_{a7} , β_{b7} , β_{c7} and β_{d7}
5	$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (5.0 mol%), β -cyclo (0.015 mol%) with pH 5 and 9 at 1000 °C	β_{c5} and β_{c9}
a= 0.001, b=0.002, c=0.003 and d=0.004 mol % for PEG, a=0.005, b=0.010, c=0.015 and d=0.020 mol% for β -cyclo		

3.2.2.2 Synthesis of Tb³⁺ doped Y₂O₃ using polymers (CTAB and TOPO) at the time of synthesis

STEP I: First, according to the formula (Y_{0.995}Tb_{0.005})₂O₃, stoichiometric amounts of rare-earth nitrates were dissolved in double distilled water and solution of 0.2 mol/L concentration was used as mother solution.

STEP II: Similarly, solutions of CTAB (0.001, 0.002, 0.003 and 0.004 mol%) and TOPO (0.005, 0.010, 0.015 and 0.025 mol%) as surfactant were prepared by adding proper amount of these surfactants in 30 mL of water. The surfactant solution was then added to mother solution and stirred for 30 minutes to form a homogeneous solution. 1.5 mol/L solution of ammonium hydrogen carbonate was used as precipitant. Under continuous stirring precipitating solution was added into the mother solution till pH of the solution reaches 7, resulting in formation of precipitates.

STEP III: The suspensions after 24 hours of aging were centrifuged, washed 2 times with ethanol and 3 times with hot deionized water. Then it was filtered and dried at 80 °C for 24 hours to get the white amorphous powders.

STEP IV: These powders were sintered at 700 °C for 2 hours in a tubular furnace at a heating rate of 1 °C per min in a recrystallized alumina boat to get the corresponding nano crystalline powders.

STEP V: Out of the above prepared samples, Y₂O₃:Tb³⁺ (0.5 mol%) have shown maximum luminescence at 0.003 mol% and 0.015 mol% concentration of CTAB and TOPO, respectively (discussed later in context). Interestingly we have prepared one more sample of Y₂O₃:Tb³⁺ (0.5 mol%) with both CTAB (0.003 mol%) and TOPO (0.015 mol%) together as surfactant using similar synthesis route as discussed above.

For better understanding we have given codes to all sample prepared above in Table 3.3.

Table 3.3: Name and codes to all samples prepared.

S. No.	Name of the sample	Code
1	Y ₂ O ₃ :Tb ³⁺ _(0.5 mol%) at 700 °C	S _P
2	Y ₂ O ₃ :Tb ³⁺ _(0.5 mol%) + CTAB _(0.003 mol%) at 700 °C	S _C
3	Y ₂ O ₃ :Tb ³⁺ _(0.5 mol%) + TOPO _(0.015 mol%) at 700 °C	S _T
4	Y ₂ O ₃ :Tb ³⁺ _(0.5 mol%) + CTAB _(0.003 mol%) + TOPO _(0.015 mol%) at 700 °C	S _{CT}

3.3 Morphological and Optical Characterization

The Y_2O_3 nanophosphors were characterized by X-ray diffraction (XRD) using Philips powder X-ray diffractometer (model PW 1071) with Ni filtered Cu K_α radiation in a wide range of Braggs angle 2θ ($15 \leq 2\theta \leq 85$). TEM images were recorded using JEOL 2100F (200 kV). For TEM analysis synthesized powder was dispersed in ethanol and ultra-sonicated for 15 minutes. One drop of the dispersed particles was put on a carbon-coated Cu grid and ethanol was allowed to evaporate. It was then mounted inside the sample chamber. Optical absorption spectra of the synthesized nanophosphors were recorded with double beam UV-Visible spectrophotometer using Hitachi U3900H in the range 200-700 nm. Photoluminescence study, calculation of Commission Internationale de l'Éclairage (CIE) color coordinates and Correlated Color Temperature (CCT) of the synthesized samples (in powder form) has been recorded with Edinburgh Instruments FLS920 spectrometer equipped with 450 W Xenon Arc Lamp and a cooled single photon counting photomultiplier (Hamamatsu R2658P). The lifetime measurement was carried out using a time-resolved luminescence spectrometer (model: F900 Edinburgh), equipped with a time correlated single photon counting system and microsecond xenon flash lamp as the source of excitation. FTIR spectra have been recorded in the range of $4,000\text{--}400\text{ cm}^{-1}$ with Perkin Elmer Spectrum BX(2). The pH value of the precipitating solution was monitored using a calibrated Elico LI 120 pH meter. All the measurements were performed at room temperature ($\sim 20^\circ\text{C}$).

References

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CHAPTER 4

RESULTS AND DISCUSSION

Optical and morphological properties of $\text{Y}_2\text{O}_3:\text{RE}^{3+}$ ($\text{RE}^{3+}=\text{Eu}^{3+}$, Tb^{3+} & Dy^{3+}) doped nano-phosphors

Overview

The present chapter describes the study of lanthanides ($\text{RE}^{3+} = \text{Eu}^{3+}$, Tb^{3+} and Dy^{3+}) doped Y_2O_3 nanophosphors (NPs) prepared via co-precipitation method. This chapter is divided into two parts. In these two parts, we have studied the effect of two parameters (temperature and doping concentration) on optical and morphological properties of doped Y_2O_3 . First part gives the effect on optical and morphological properties of doped Y_2O_3 NPs due to the variation in doping concentration of various dopants and the second part describes the effect on optical and morphological properties of doped Y_2O_3 NPs due to variation in annealing temperature. Moreover, $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (red phosphor), $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ (green phosphor) and $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ (orange phosphor) are three types of phosphors which are different from each other according to their optical characteristics. For simplicity we have studied the optical and morphological properties of these three systems separately. All the prepared samples were characterised by XRD, Rietveld refinement, FTIR and TEM to study the structural and morphological properties, PL spectroscopy was employed to study the optical properties of these samples. CIE color co-ordinates of the prepared NPs were also calculated to see the usefulness of the prepared phosphors for their various applications.

4.1 Effect of Eu^{3+} doping on optical and morphological properties of Y_2O_3 nanophosphors

Nanophosphors of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ have been synthesized by simple and economical co-precipitation method. Molar concentration of dopant (Eu^{3+}) was varied at the time of synthesis of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphors (NPs). These NPs have been synthesized with the aim to study the effect of doping concentration on their structural and photoluminescence properties. All the prepared samples were annealed at 1000 °C. The results of Eu^{3+} doped Y_2O_3 NPs are presented below.

4.1.1 XRD Studies

To investigate the structure of the prepared compounds, X-ray diffraction patterns for $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (3, 5, 6, 7, 9, 10, 12 and 13 mol%), nanoparticles annealed at 1000 °C were taken and are shown in Figure 4.1(a-g). The (h k l) values are labelled on the peaks. All the peaks are well matched with the JCPDS file No 83-0927 corresponding to body-centred cubic structure of Y_2O_3 with space group $Ia-3$. The sharp and single diffraction peaks of the XRD pattern confirm the formation of single phase compound, which is attributed to the high and uniform heating during the annealing process. The peak at $2\theta \sim 29^\circ$ was the strongest peak corresponding to the plane (2 2 2) and no peaks were observed for the dopants. The lattice parameter was calculated from the least square fitting of the diffraction peaks. With increase of dopants concentration there is a slight change in the lattice parameter for the all prepared samples. This is understandable as the radii of the dopant Eu^{3+} (0.91 Å) is of the order of radius of Y^{3+} (0.90 Å). The systematic increase in the lattice parameter also reveals that Eu^{3+} ions have substituted at the Y^{3+} site in the lattice. The lattice parameters for all the prepared samples are listed in Table 4.1.

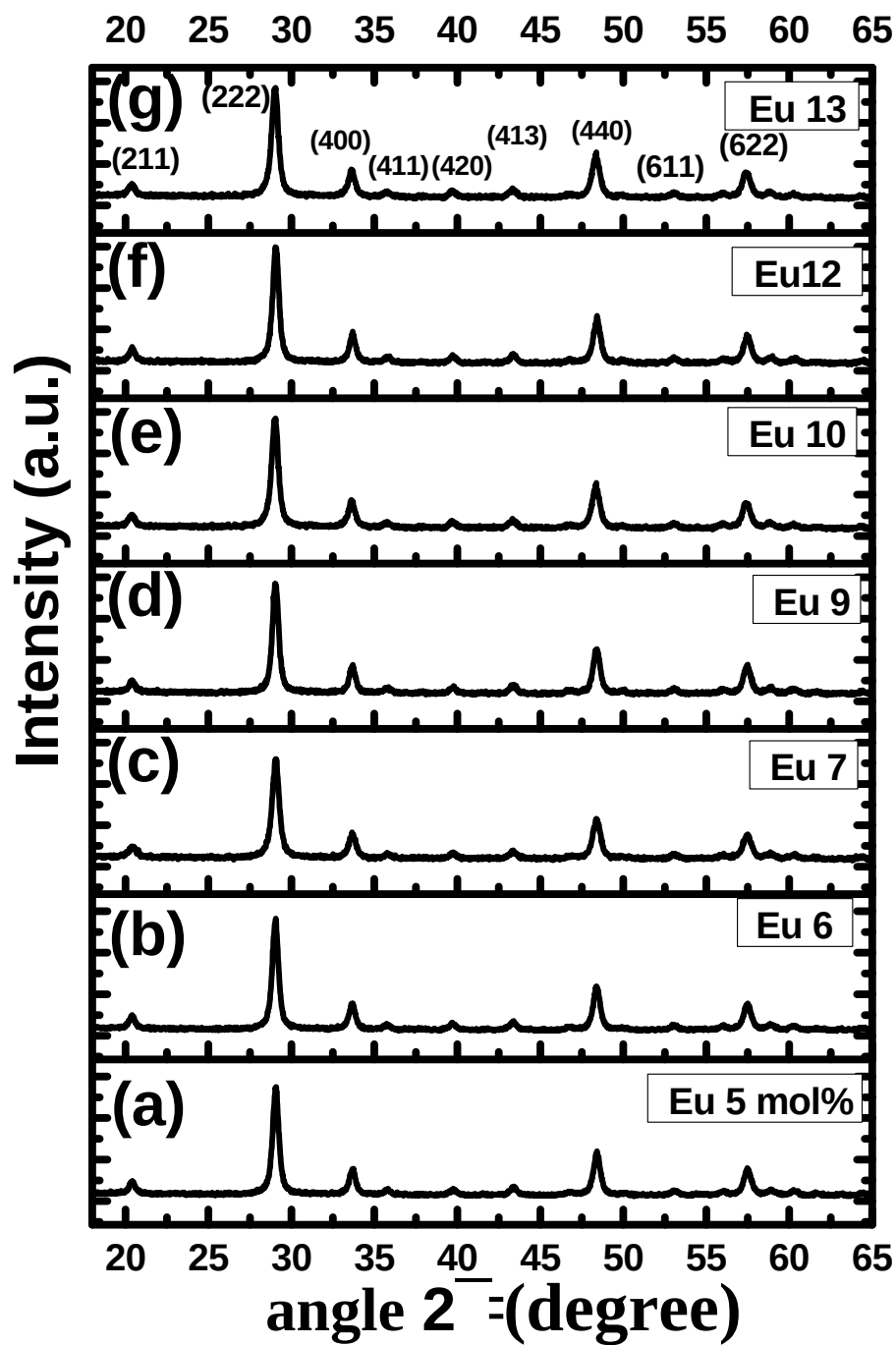


Figure 4.1: $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (5.0-13.0 mol%) annealed at 1000°C .

Table 4.1: Structural parameters of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ with variation in Eu^{3+} concentration.

Sample Name	2θ (degree)	Calculated	Calculated	Approx Crystallite Size XRD (nm)	Chi square value
$\text{Y}_2\text{O}_3:\text{Eu}_{5\text{mol}\%}$	29.1580	10.600557	3.060	44 nm	1.45
$\text{Y}_2\text{O}_3:\text{Eu}_{6\text{mol}\%}$	29.1470	10.604383	3.061		1.35
$\text{Y}_2\text{O}_3:\text{Eu}_{7\text{mol}\%}$	29.1150	10.605845	3.064		1.21
$\text{Y}_2\text{O}_3:\text{Eu}_{9\text{mol}\%}$	29.1370	10.608251	3.062		1.34
$\text{Y}_2\text{O}_3:\text{Eu}_{10\text{mol}\%}$	29.1350	10.610502	3.062		1.35
$\text{Y}_2\text{O}_3:\text{Eu}_{12\text{mol}\%}$	29.1300	10.610845	3.063		1.30

The crystallite size (D) was determined using the Debye-Scherer formula [1] as given below:

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (4.1)$$

Here, β represents the full-width at half-maximum (FWHM) in radians, λ (0.154 nm) is the wavelength of X-rays.

4.1.2 Rietveld Refinement

To confirm that the structure is truly of cubic type, a structural refinement by the Rietveld method was performed using the Fullprof Program [2]. The structural refinement results for the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%) phosphor annealed at 1000 °C are illustrated in Figure 4.2. The calculated structural parameters for all the other samples are shown in Table 4.1. The results are in good agreement between the observed and calculated XRD patterns. The quality of structural refinement data was checked by measuring a parameter called goodness of fit (GOF), which is defined as $\text{GOF} = R_{\text{wp}}/R_{\text{exp}}$ [3, 4]. For perfect refinement the GOF must approach unity. In the present case, the GOF was found to be 1.3, which is nearer to ideal GOF (i.e. $\text{GOF} = 1$) and is very good in comparison to earlier reports [5].

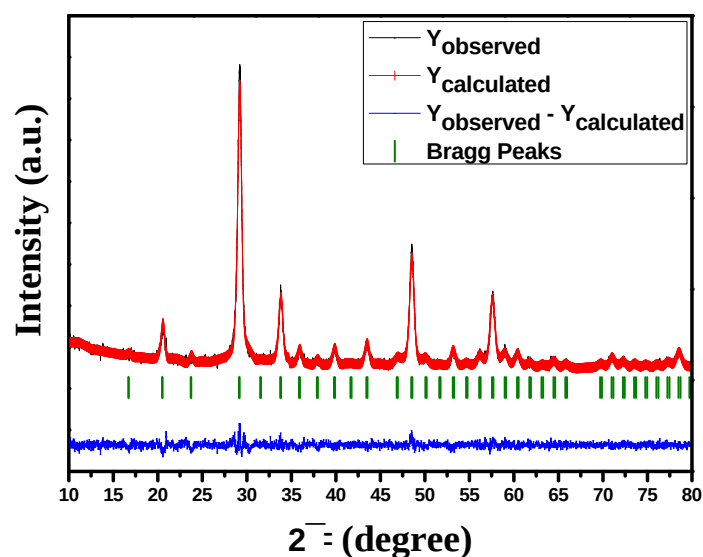


Figure 4.2: Refinement data of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%).

4.1.3 FT-IR analysis

FT-IR Spectra of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%), annealed at 1000 °C phosphors are illustrated in Figure 4.3. The absorption band centred at 567 cm^{-1} is attributed to Y–O lattice vibration [6]. The peaks at 849 cm^{-1} and the ones at 1014 , 1396 and 1518 cm^{-1} are due to C–O bond bending and stretching vibration, respectively [6]. These peaks were due to residual carbon in the prepared samples as precipitation is done by ammonium bicarbonate or absorption of CO_2 from the ambient atmosphere. The broad band at 3450 cm^{-1} is assigned to O–H stretching vibration [6]. This band in the prepared doped samples was probably due to the adsorbed molecular water from the KBr pellet used for the preparation of samples, or may be absorption of H_2O from the ambient atmosphere. The residual hydroxyl groups (–OH) at 3450 cm^{-1} are responsible for the quenching of rare earth emission and thereby decreasing the luminescence intensity. This band becomes weaker with increase in annealing temperature (discussed later in section 4.2) and disappears at higher temperatures [5]. Moreover, the Y–O band at 567 cm^{-1} is stronger as the annealing temperature is high (1000 °C).

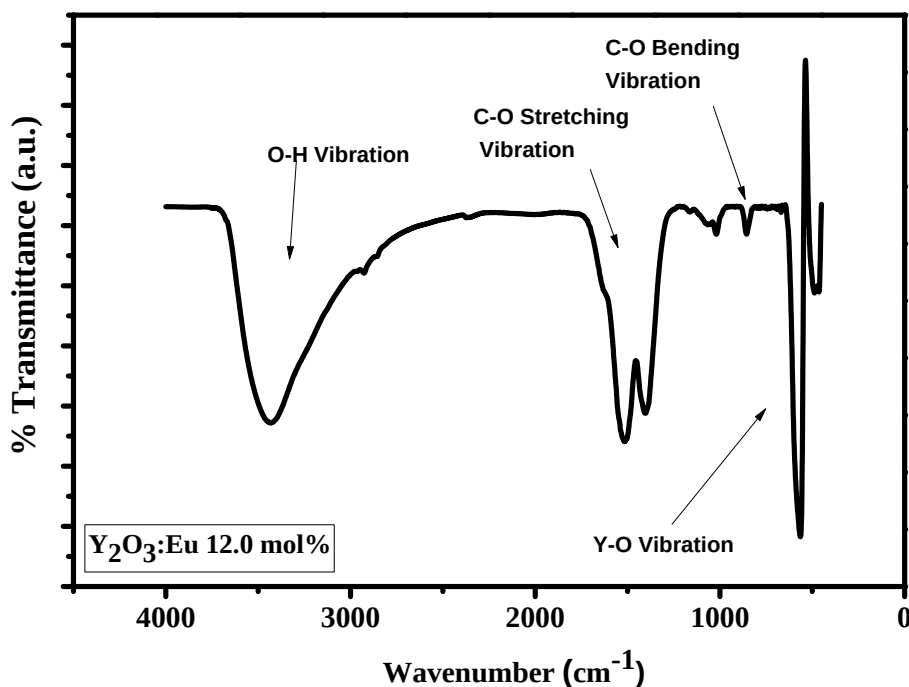


Figure 4.3: FT-IR spectra of Y_2O_3 phosphor Eu^{3+} .

So, both these facts support that a high annealing temperature is required to prepare a good luminescent Y_2O_3 phosphor.

4.1.4 Optical properties

4.1.4.1 UV visible spectrum

The band gap has been calculated by using Tauc's formula which shows relationship between absorption coefficient (α) and incident photon energy ($h\nu$) that can be written as [7, 8]

$$\alpha h\nu = A(h\nu - E_g)^n \quad (4.2)$$

where A is constant, α is the absorption coefficient and n depends on the type of transition having values $1/2$, 2 , $3/2$ and 3 corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect respectively [9, 10]. The exact value of the band gap has been determined by extrapolating the straight line portion of the $(\alpha h\nu)^{1/n}$ versus $h\nu$ graph. Figure 4.4 shows the graphs between $(\alpha h\nu)^2$ and $h\nu$ for $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%) annealed at 1000°C . The band gap value has been found to be 5.84 eV respectively.

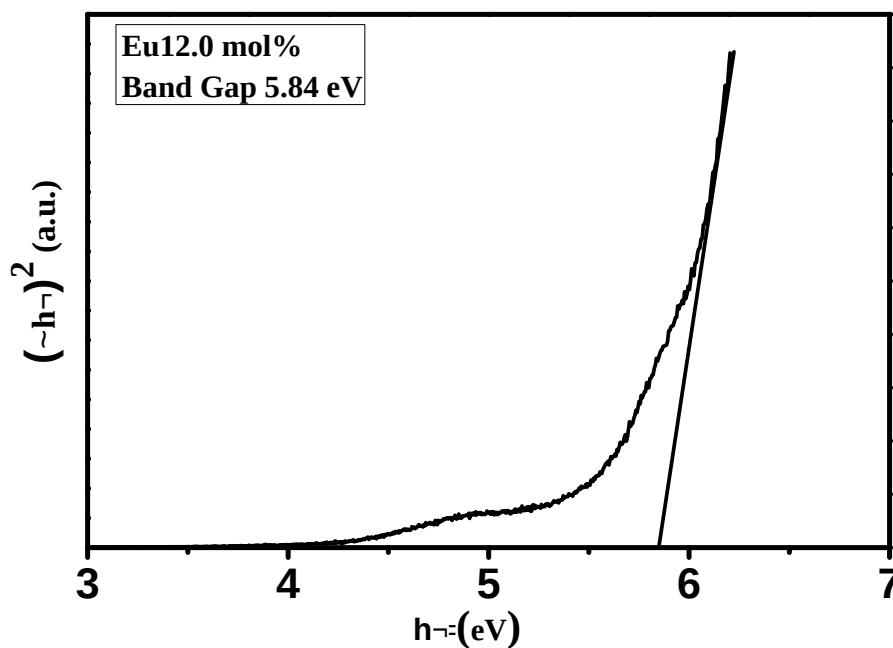
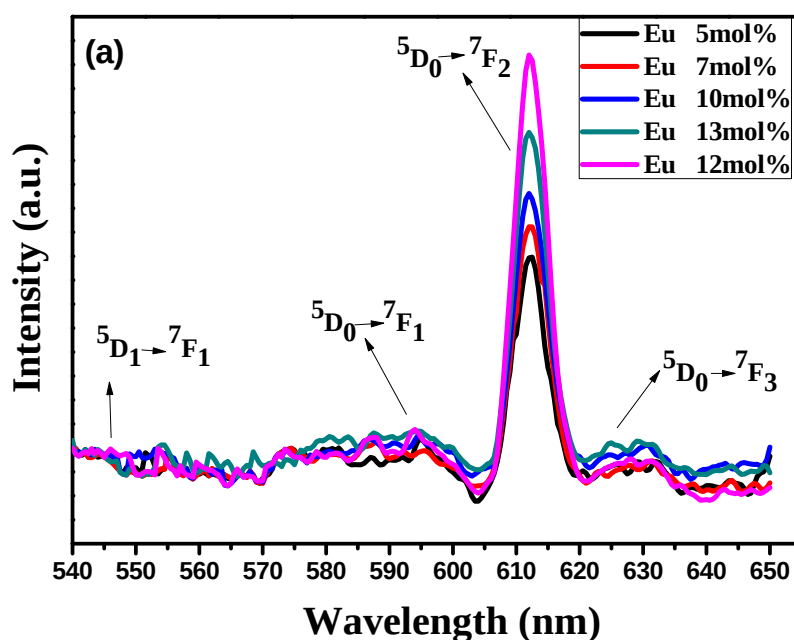


Figure 4.4: Tauc's plot for band gap calculations of $\text{Y}_2\text{O}_3: \text{Eu}^{3+}$ (12.0 mol%).

4.1.4.2 Photoluminescence

The performance of luminescent materials is influenced by the doping concentration and it is very important to determine the optimum concentration for luminescence applications. Figure 4.5 shows the emission spectra of the Eu^{3+} doped Y_2O_3 nanophosphor at an excitation wavelength of 254 nm. The distinct emission lines lying between 550 nm and 650 nm were observed due to transitions from the excited $^5\text{D}_1 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($j = 0 - 3$) levels of Eu^{3+} ions. The origin of these transitions (electric dipole or magnetic dipole) from emitting levels to terminating levels depends on the location of Eu^{3+} ion in the Y_2O_3 lattice and the type of transition is determined by selection rules [11]. The most intense peak at 611 nm and a small peak at 630 nm correspond to the hypersensitive transition between the $^5\text{D}_0$ and $^7\text{F}_2$ levels of Eu^{3+} ion in the yttrium oxide host caused by the forced electric dipole transition mechanism. The weak emission in the vicinity of 590 nm (590 nm – 600 nm) is ascribed to the magnetic dipole transition of $^5\text{D}_0 \rightarrow ^7\text{F}_1$. Generally, when Eu^{3+} is located at a low symmetry (without an inversion centre), the 611 nm emission is dominant whereas the 590 nm emission is stronger when Eu^{3+} is located at a high symmetry (with an inversion centre). In the present case, the emission at 611 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) is dominant suggesting that the location of Eu^{3+} deviates from the inversion symmetry, i.e. at low symmetry positions. The emission intensity increases with increase in Eu^{3+} concentration up to 12.0 mol% as shown in

Figure 4.5 which is higher than the micron scale where the quenching concentration is nearly 6.0 mol% [5]. Due to the defects produced during the preparation process and impurities contained in the raw materials, the samples inevitably have quenching centers (traps) which induce non-radiative transitions and decrease the luminous efficiency. Higher quenching concentration of nanopowders is mainly due to the unique properties of the nanostructures where the quenching centers (traps) are distributed randomly between particles. Some particles may contain many traps while others may contain fewer traps. Due to the hindering effect of the particle boundaries, the Eu^{3+} luminescence quenching occurs first in particles containing many traps. However, in those particles containing few traps Eu^{3+} luminescence quenches at high concentration. Therefore, luminescence quenching occurs at higher concentration in nano-sized materials than in normal ones [12]. In addition, owing to the small increase in the lattice constant of nanopowders (as discussed earlier and given in Table 4.1), the phonon density may decrease. Accordingly, the non-radiative process weakens and the quenching concentration increases [13]. The CIE parameter such as color coordinates was calculated in order to know the photometric characteristics of the prepared phosphors. The values of CIE parameters (Figure 4.6) for the ($\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol %)) phosphors are CIE (x) = 0.65 CIE (y) = 0.34, which is very close to coordinates of ideal red (0.67, 0.33) [14-16].



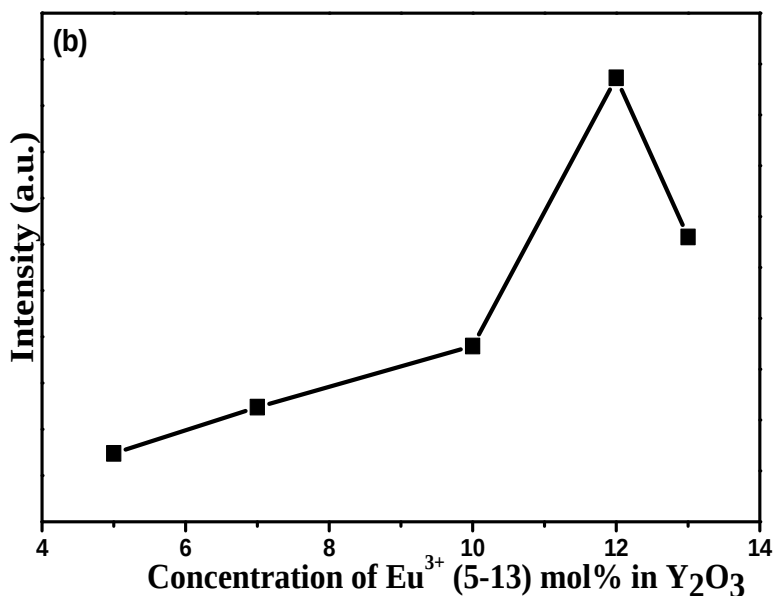


Figure 4.5: (a) Emission spectra of Y₂O₃: Eu³⁺ with different Eu³⁺ concentration and (b) Variation of luminescence emission intensity with Eu³⁺ concentration.

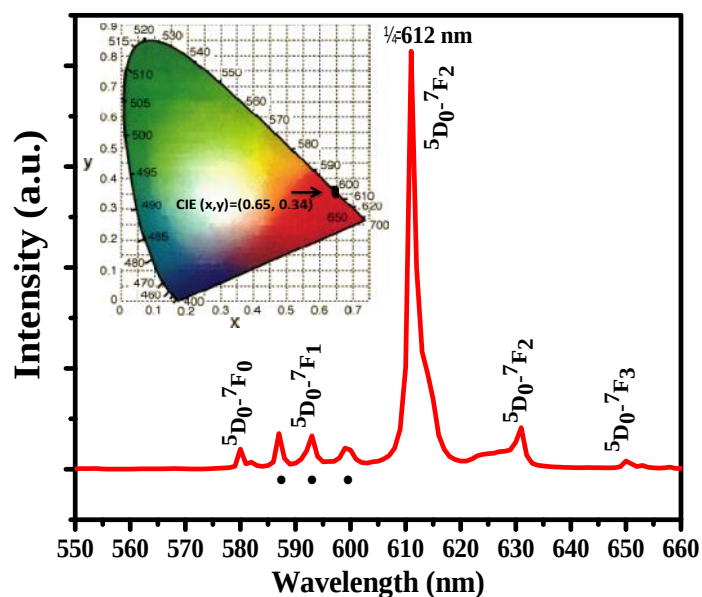


Figure 4.6: Chromaticity diagram of Y₂O₃:Eu³⁺ (12.0 mol%).

In addition the calculated CIE chromaticity coordinates are rather close to edge of CIE diagram (shown in inset of Figure 4.6), indicating that this kind of phosphor shows better color purity in solid state lightning. From the above study we can conclude that the maximum luminescence from Y₂O₃ can only be enhanced to certain limit i.e. below quenching

concentration of Eu^{3+} which in our case is 12.0 mol% . Doping of Eu^{3+} above 12.0 mol % in Y_2O_3 resulted in decrease of luminescence. Now in next section, in order to see the effect of temperature on $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, annealing temperature of the prepared phosphor is varied systematically. The results are presented below.

4.2 Effect of annealing temperature on optical and morphological properties of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphors

In this section annealing temperature of the samples were varied systematically to see its effect on optical and morphological properties of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphors. The concentration of the dopant was kept constant i.e. 12.0 mol% and annealing temperature was varied from 300 °C to 1300 °C. The observed results are presented below.

4.2.1 XRD studies

Figure 4.7 (a-f) shows the XRD pattern of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ after annealing at different temperatures from 300 to 1000 °C. No change in peak position was observed for all the annealed samples. The 1000 °C annealed phosphor showed more narrow peaks compared with the 300 °C annealed phosphor. Moreover, the intensities of all the peaks corresponding to 1000 °C sample are also high with respect to 300 °C sample, which indicated the increase in of crystallinity of the samples at high temperatures. The crystallite size of the phosphor also increased with increase in temperature of annealing. Table 4.2 shows the variation of crystallite size as a function of annealing temperature.

Table 4.2: Variation of crystallite size as a function of annealing temperature.

S.No.	Crystallite size (nm)	Temperature (°C)
1	10 nm	500
2	18 nm	700
3	27 nm	900
4	42 nm	1000

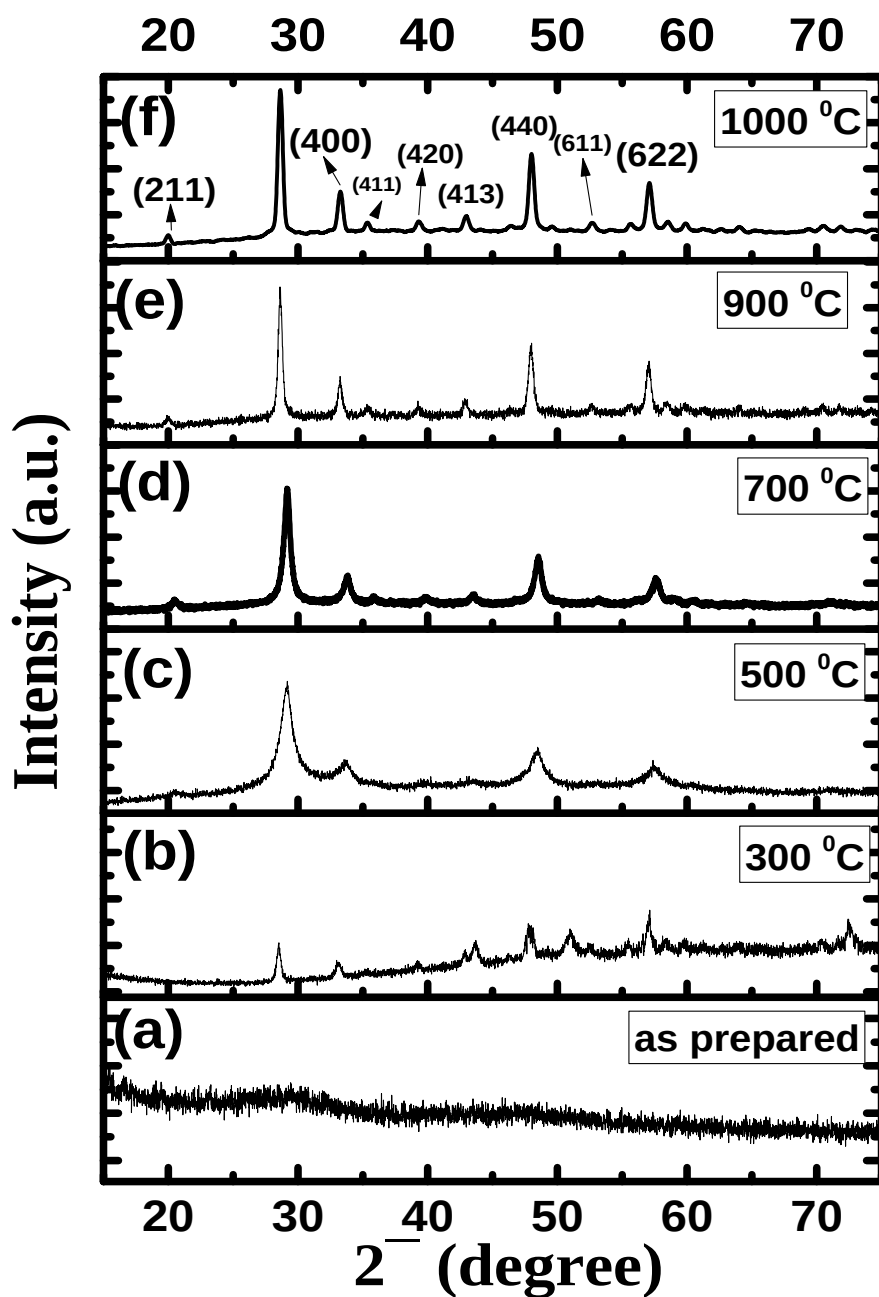


Figure 4.7: XRD pattern of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ samples prepared at different annealing temperatures.

4.2.2 FT-IR studies

FT-IR Spectra of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%) phosphors, annealed at 300, 700 & 1000 °C are illustrated in Figure 4.8. The absorption band centred at 567 cm^{-1} is attributed to Y–O lattice vibration [6]. The Y–O band at 560 cm^{-1} becomes stronger with increase in annealing temperature (Figure 4.8). As discussed earlier in Figure 4.3, the broad band at 3450 cm^{-1} is

assigned to O–H stretching vibration [12, 15]. This band in the prepared doped samples was probably due to the adsorbed molecular water from the KBr pellet used for the preparation of samples, or may be absorption of H₂O from the ambient atmosphere. The residual hydroxyl groups (–OH) at 3450 cm^{–1} are responsible for the quenching of rare earth emission and thereby decreasing the luminescence intensity. This band becomes weaker for 1000 °C as compared to sample annealed at 300 °C. The decrease of –OH band at 3450 cm^{–1} and the increase of Y–O band at 560 cm^{–1} with increase in annealing temperature (Figure 4.8) support that a high annealing temperature is required to prepare a highly crystalline luminescent Y₂O₃ phosphor.

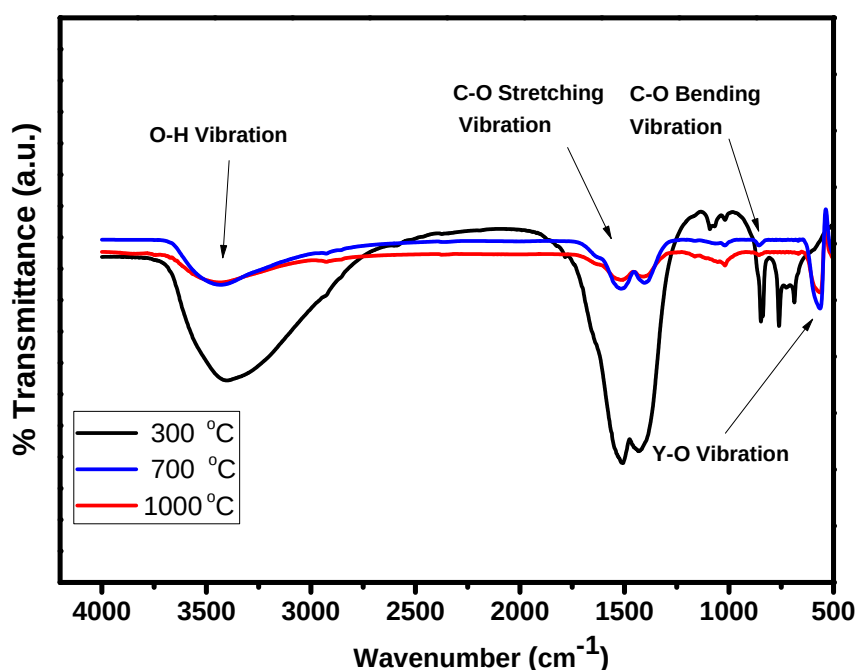


Figure 4.8: FTIR spectra of Y₂O₃:Eu³⁺ (12.0 mol%) prepared at different annealing temperatures.

4.2.3 SEM and TEM analysis

The morphology of prepared samples was analyzed under scanning electron microscope (SEM). SEM micrograph of the as prepared sample Y₂O₃:Eu³⁺ (12.0 mol%) shows two types of morphology as shown in Figure 4.9 (a). One is bigger size faceted structure and other is feathery rod type. The growth of the rod is taking place in a bunch like brush. Figure 4.9 (b) is SEM images of the same powder annealed at 1000 °C in which rods with continuous, long and sharp bends can be seen. Apart from this there is another feature where clustered nanoparticles can be seen. For detailed morphological study, TEM images of Y₂O₃: Eu³⁺

annealed at 1000 °C were also recorded as shown in figure 4.10. These TEM micrographs also show the rod like morphology of the prepared samples as was seen in the SEM images.

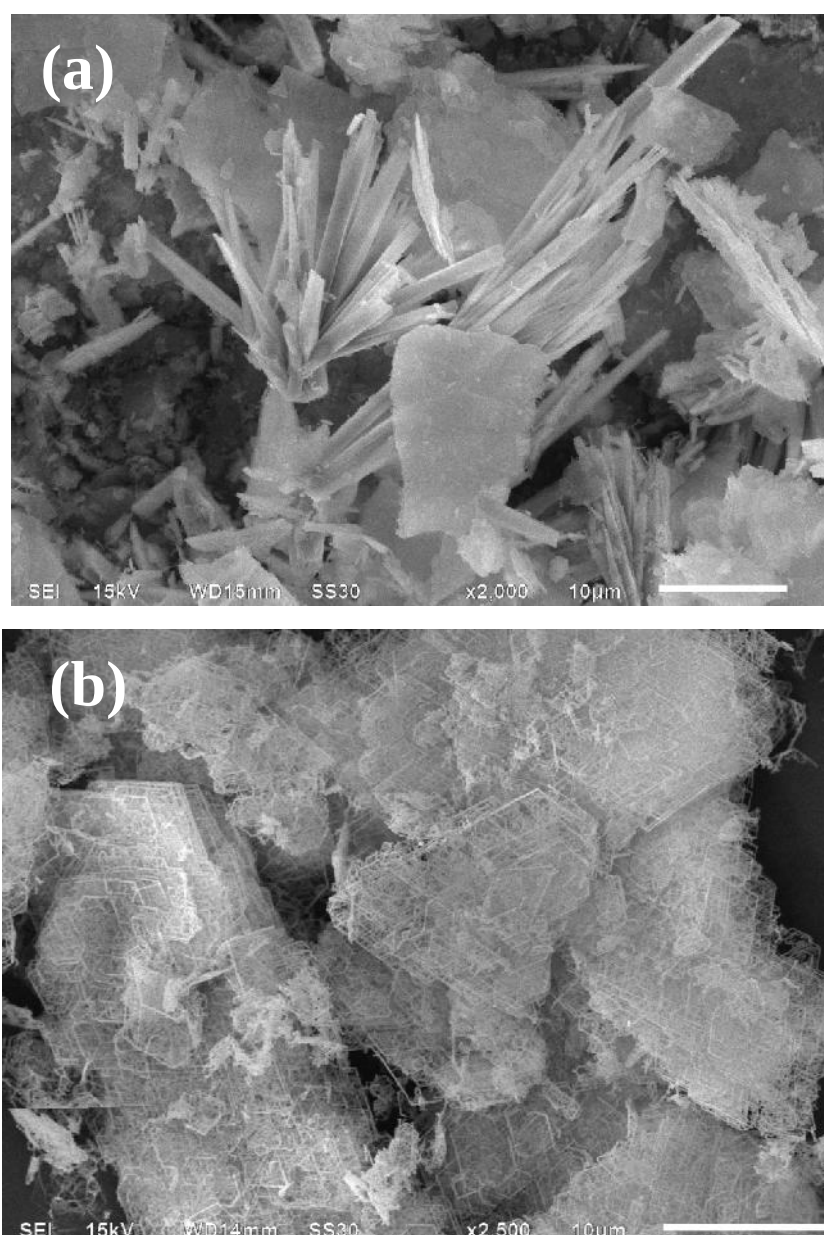


Figure 4.9: SEM micrographs of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (a) as prepared & (b) annealed at 1000 °C.

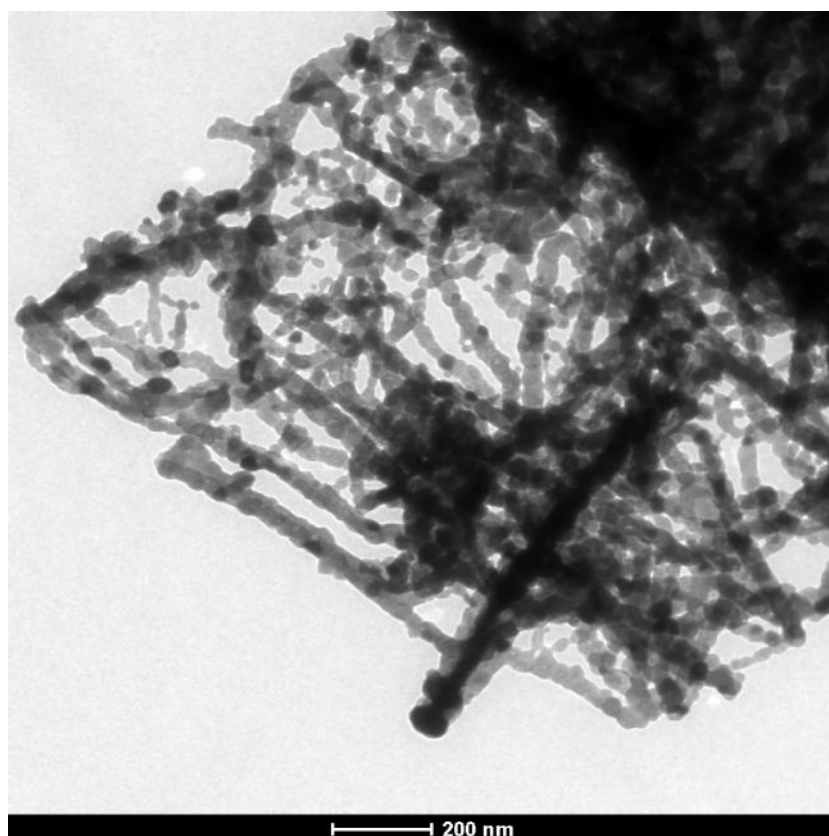


Figure 4.10: TEM micrographs of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ annealed at 1000 °C.

4.2.4 Photoluminescence study

Figures 4.11 illustrate the emission spectra of the doped phosphors at different annealing temperatures keeping the optimum concentration of Eu^{3+} (12.0 mol %). The emission intensity increases with the annealing temperature. Annealing below 700 °C does not increase the emission intensity significantly but above 700 °C, the emission intensity increases remarkably. This result is consistent with that obtained from the XRD and FTIR. In the XRD, the prepared nanophosphors had shown good crystallinity for annealing temperatures >700 °C and FTIR studies show the reduction of –OH band with annealing temperature [17]. Both these properties are also responsible in enhancing the luminescence intensity of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphor. However, the PL emission intensity increases till 1000 °C and decreases with further increase in the annealing temperature as shown in Figure 4.11.

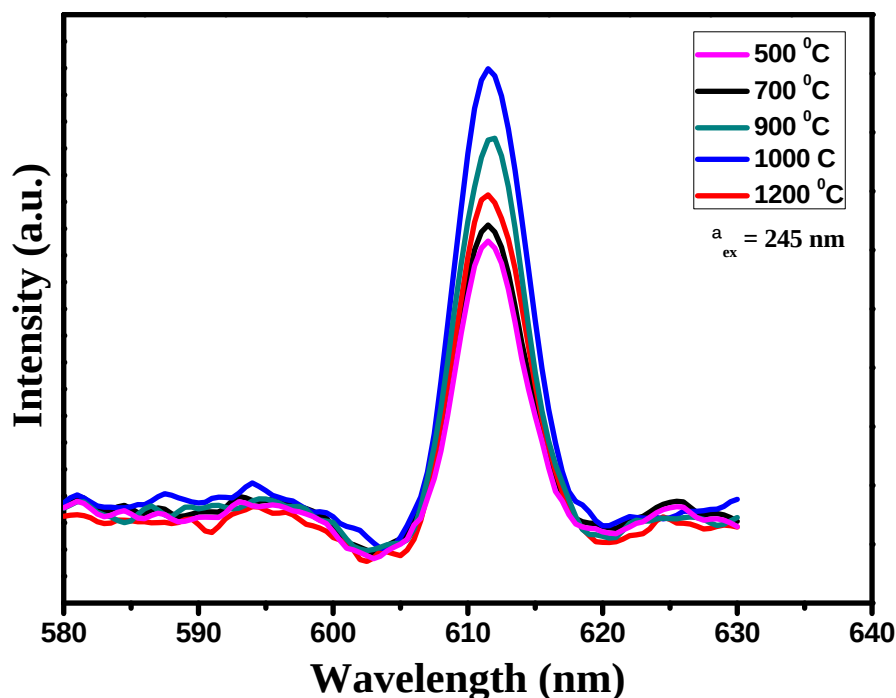


Figure 4.11: Emission spectra of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ at different annealing temperatures.

4.3 Study of Terbium (Tb^{3+}) and Dysprosium (Dy^{3+}) doped Y_2O_3 nanophosphor

This section describes the photoluminescent properties of Tb^{3+} and Dy^{3+} doped Y_2O_3 . As discussed earlier in section 4.1 and 4.2 doping concentration and annealing temperature has drastically changed the structural and morphological properties of Eu^{3+} doped Y_2O_3 and due to which optical properties i.e. emission intensity of the dopant gets changed. To get the highest luminescence from Terbium (Tb^{3+}) and Dysprosium (Dy^{3+}) doped Y_2O_3 nanophosphor, same synthesis techniques were also used to prepare these NPs. As atomic radii of Terbium (Tb^{3+}) and Dysprosium (Dy^{3+}) are similar to that of Eu^{3+} as a result of this, the structural changes which we have observed earlier in the case of nanophosphors $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ are almost similar. Below structural and the optical properties of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ and $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ are presented.

4.3.1 XRD of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ and $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$

To investigate the structure of the prepared compounds, X-ray diffraction patterns for $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ (1.0 mol%) and $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ (0.5 mol%) annealed at 1000 °C were taken and are shown in Figure 4.12. The (h k l) values are labelled on the peaks. All the peaks are well matched with

the JCPDS file No 83-0927 corresponding to body-centred cubic structure of Y_2O_3 with space group $Ia-3$. The sharp and single diffraction peaks of the XRD pattern confirm the formation of single phase compound, which is attributed to the high and uniform heating during the annealing process. The peak at $2\theta \sim 29^\circ$ was the strongest peak corresponding to the plane (2 2 2) and no peaks were observed due to dopants.

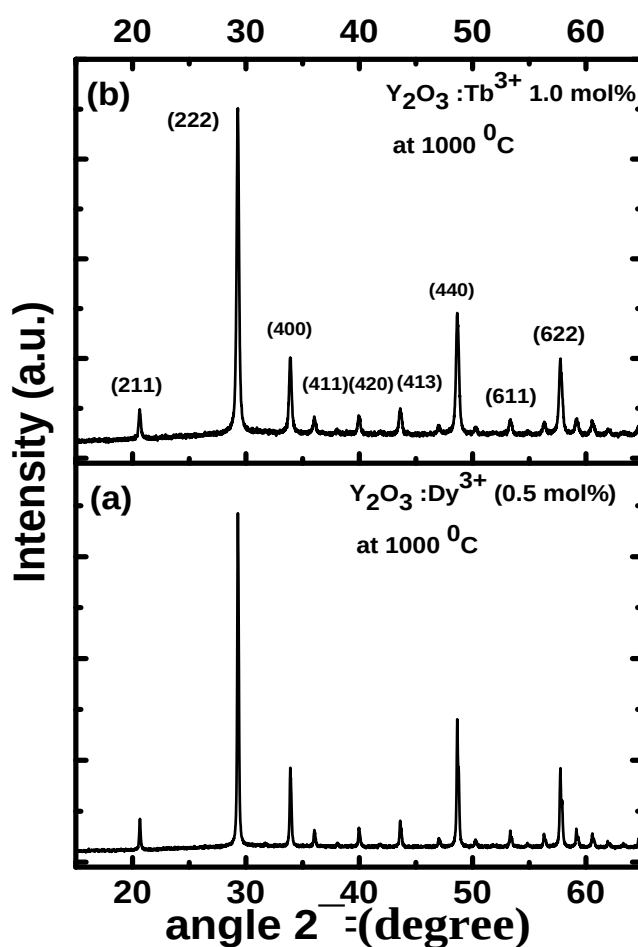


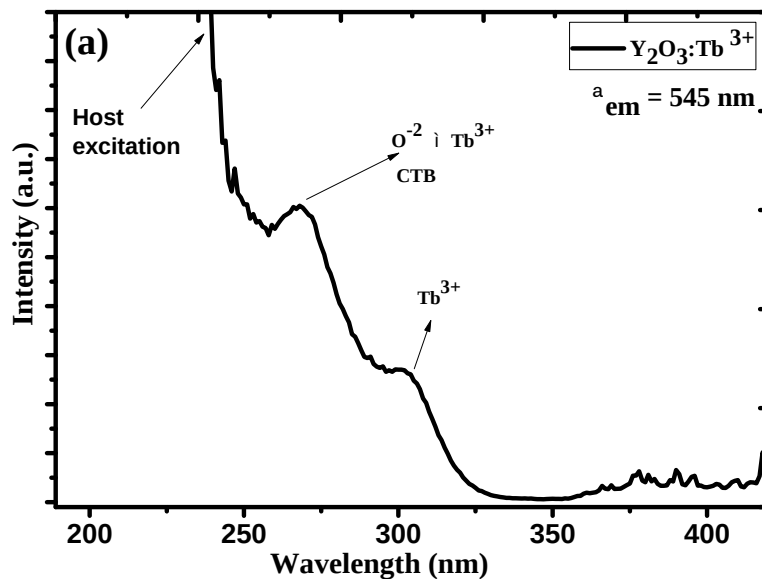
Figure 4.12: XRD of (a) $Y_2O_3:Tb^{3+}$ (1.0 mol%) and (b) $Y_2O_3:Dy^{3+}$ (0.5 mol%) annealed at $1000^\circ C$.

Average crystallite size for $Y_2O_3:Tb^{3+}$ (1.0 mol%) and (b) $Y_2O_3:Dy^{3+}$ (0.5 mol%) annealed at $1000^\circ C$ are 44 nm and 45 nm respectively.

4.3.2 Photoluminescence Studies of Tb^{3+} doped Y_2O_3 nanophosphors

To understand the effect of Tb^{3+} concentration on optical properties of Tb^{3+} doped Y_2O_3 , photo luminescence excitation and emission spectra of various synthesized samples was

recorded (All the samples were synthesized at 1000 °C). Figure 4.13 (a & b) represents the (a) excitation and (b) emission spectra of Tb^{3+} doped Y_2O_3 as a function of Tb^{3+} ion concentration. Enhancement in PL emission intensity at 545 nm (under an excitation of 267 nm) due to increase in doping concentration is observed. The obtained optimal Tb^{3+} concentration for maximum luminescence in $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ is 1.0 mol%. Moreover, peak position in the excitation and emission spectra (Figure 4.13 (a & b)) does not change with increase in dopant's concentration suggesting that the nature of Tb^{3+} ion remains unchanged with increase in its concentration. Figure 4.13 (a) shows the excitation spectrum recorded at $\lambda_{\text{em}} = 545$ nm. Two overlapping bands having maxima at 267 and 301 nm [18, 19] were observed. The band at around 267 nm is ascribed to the $\text{O}^{2-}/\text{Tb}^{3+}$ charge transfer band (CTB), which corresponds to the electronic transitions from the 2p orbital of O^{2-} to the 4f orbital of Tb^{3+} . Origin of the band at 301 nm results from absorption of incident radiation by Tb^{3+} ions and leads to excitation of electrons from Tb^{3+} ground state to one of its excited 4f levels [5]. However, due to the parity forbidden character of the transition within the 4f configuration, the peaks beyond 301 nm were weak [19, 20]. However, emission spectra of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ (Figure 4.13 (b)) is composed of several sharp lines resulting due to the $^5\text{D}_4 \rightarrow ^7\text{F}_J$ transitions where $J = 3, 4, 5$ and 6. Strongest emission occurs at 545 nm due to the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ characteristic transition of green emission for Tb^{3+} [5, 19]. The other peaks at 485 nm, 585 nm and 625 nm arise from the $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$ and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ transitions, respectively.



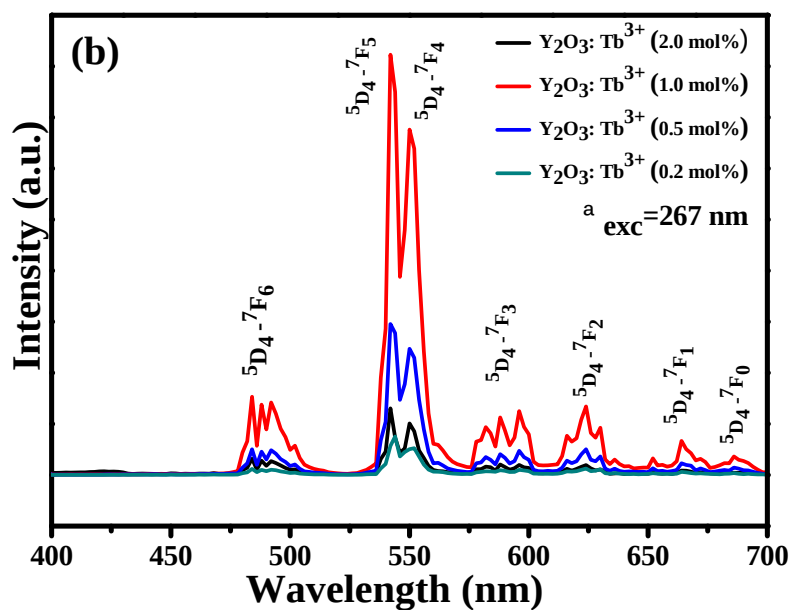
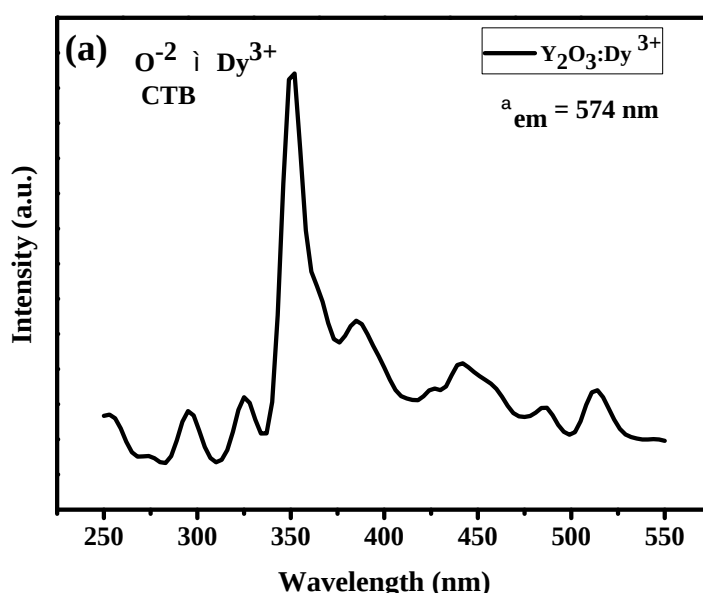


Figure 4.13: (a) Excitation and (b) emission spectra of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ with variation in doping concentration.

4.3.3 Photoluminescence Studies of Dy^{3+} doped Y_2O_3 nanophosphors

Figure 4.14 (a & b) represents the (a) excitation and (b) emission spectra of Dy^{3+} doped Y_2O_3 as a function of Dy^{3+} ion concentration. The concentration of Dy^{3+} in $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ sample was varied from 0.2 mol% to 4.0 mol%.



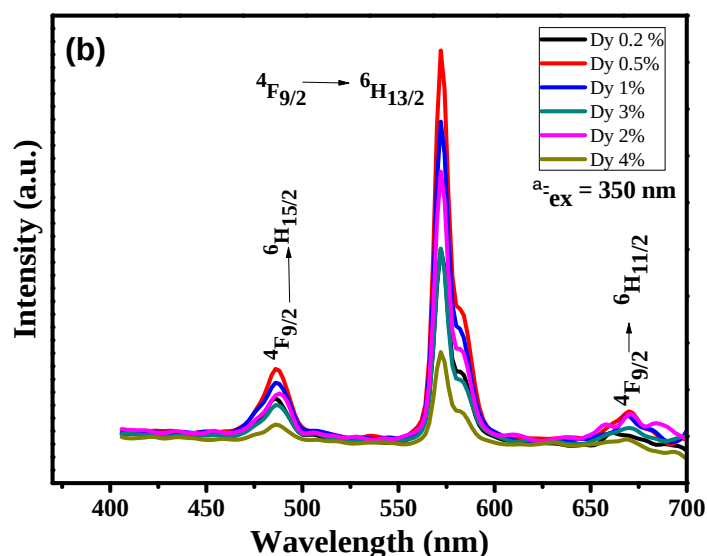


Figure 4.14: (a) Excitation and (b) emission spectra of $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ with variation in doping concentration.

As the concentration of Dy^{3+} increases, the emission intensity increases, and it reaches to maximum at 0.5 mol% of Dy^{3+} molar concentration, which was taken as the optimum concentration. Figure 4.14 (a) shows the excitation spectrum of $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ (0.5 mol%) (monitored under emission 574 nm) in the range 250–550 nm that consists of different excitation bands centered at 303 (${}^6\text{H}_{15/2}-{}^4\text{D}_{7/2}$), 351 (${}^6\text{H}_{15/2}-{}^6\text{P}_{7/2}$), 389 (${}^6\text{H}_{15/2}-{}^4\text{M}_{21/2}$), 450 (${}^6\text{H}_{15/2}-{}^4\text{J}_{15/2}$) [21]. The remaining peaks at 482 and 526 nm correspond to 4f–4f transitions of Dy^{3+} ions. However, Figure 4.14 (b) shows a typical emission spectra of synthesized $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ (0.2–4.0 mol%) nanophosphors under different excitation wavelengths (350 nm). The emission spectra of $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ under 350 nm excitation exhibits small band at blue region 486 (${}^4\text{F}_{9/2}-{}^6\text{H}_{15/2}$ transition), Yellow region (${}^4\text{F}_{9/2}-{}^6\text{H}_{13/2}$ transition) 574, 582 nm and weak red region (${}^4\text{F}_{9/2}-{}^6\text{H}_{11/2}$ transition) 667 nm [21]. From the Figure 4.14 (b), it was observed that the yellow emission at 574 nm was prominent compared to blue (486 nm) and red (667 nm) emissions. The transition corresponding to blue emission was magnetically allowed and hardly varies with the crystal field strength around the Dy^{3+} ion [22–24]. Whereas, the transition corresponding to yellow emission belongs to the hypersensitive (forced electric dipole) transition with the selection rule $D_J = 2$, which was strongly influenced by the outside surrounding environment. When Dy^{3+} ion was located at a low-symmetry local site (without inversion center), yellow emission is often dominant. In the present study, since the yellow emission was dominant, the Dy^{3+} ions occupies lower

symmetry local site in host matrix. The shape and position of Dy^{3+} emission peaks was found to be similar for $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ (0.2 – 4.0 mol%) nanophosphors with change in Dy^{3+} concentration. Moreover, emission intensity reaches a maximum value at $x = 0.5$ mol% and then decreases with increasing their Dy^{3+} concentration which can be attributed to concentration quenching phenomenon [25].

4.4 Effect of annealing temperature on Photoluminescent properties of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ and $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$

4.4.1 XRD studies

Figure 4.15 and Figure 4.16 shows the XRD pattern of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ and $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ nanophosphors prepared and annealed at 500 °C, 800 °C and 1000 °C. The XRD pattern of these phosphors is similar to the XRD as discussed earlier in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (section 4.1.2.5). Peak position for all the samples were not affected by the annealing temperature. The 1000 °C annealed phosphor showed more narrow peaks compared with the 500 °C annealed phosphor. Moreover, the intensities of all the peaks corresponding to 1000 °C sample are also high with respect to 500 °C sample, which is an indication of higher crystallinity of the samples annealed at 1000 °C. The crystallite size of the phosphor also increases with increase in annealing temperature. The size of the annealed samples for $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ at 500, 800 and 1000 °C are 25 nm, 35 nm and 44 nm respectively. In case of annealed samples for $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ at temperature 500, 800 and 1000 °C the crystallite size are 27 nm, 32 nm and 45 nm respectively. The above observations show that with increase in annealing temperature the crystallinity of the phosphor gets improved and the size of the crystallite also increases.

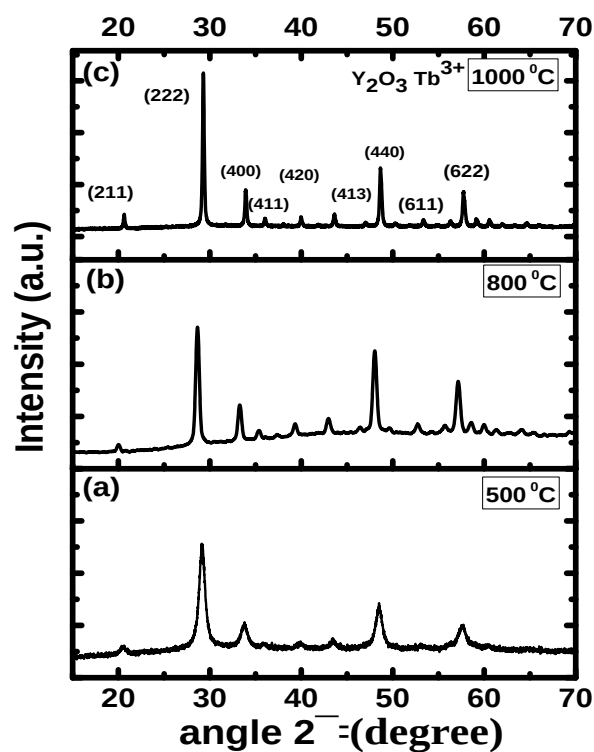


Figure 4.15: Shows the XRD pattern of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ (1.0 mol%) nanophosphors prepared by annealing at 500, 800 and 1000 °C.

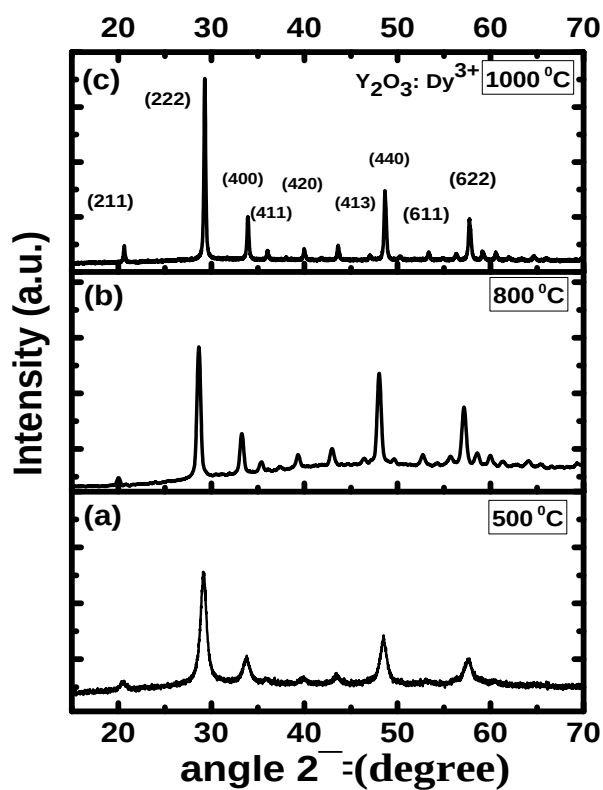
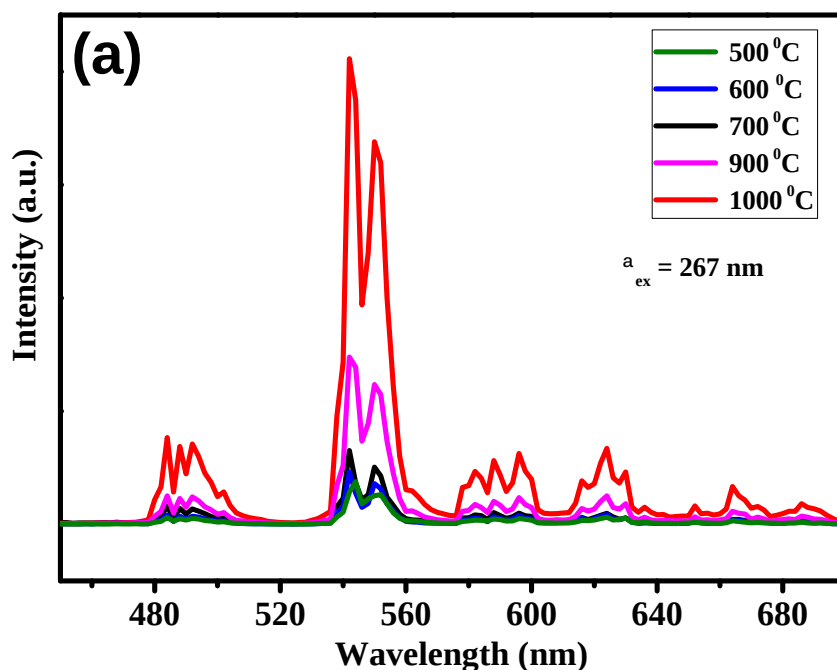


Figure 4.16: Shows the XRD pattern of $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ (0.5 mol%) nanophosphors prepared by annealing at 500, 800 and 1000 °C.

4.4.2 Photoluminescence studies

Figures 4.17 (a & b) represents the emission spectra of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ (1.0 mol%) and $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ (0.5 mol%) annealed at different temperatures. Excitation wavelength for $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ and $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ are 267 nm and 350 nm respectively. The emission intensity increases with increase in the annealing temperature for both $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ and $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$. The maximum luminescence was obtained at 1000 °C for both $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ and $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$. This result is consistent with the results obtained from the XRD pattern for both the samples (Figure 4.15 and 4.16). In the XRD, the prepared nanophosphors shows good crystallinity which ultimately increases the emission intensity of the nanophosphor [17]. CIE color coordinates of the prepared $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ (1.0 mol%) and $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ (0.5 mol%) are (0.357, 0.584) and (0.32, 0.48) as given in Figure 4.18 (a & b).



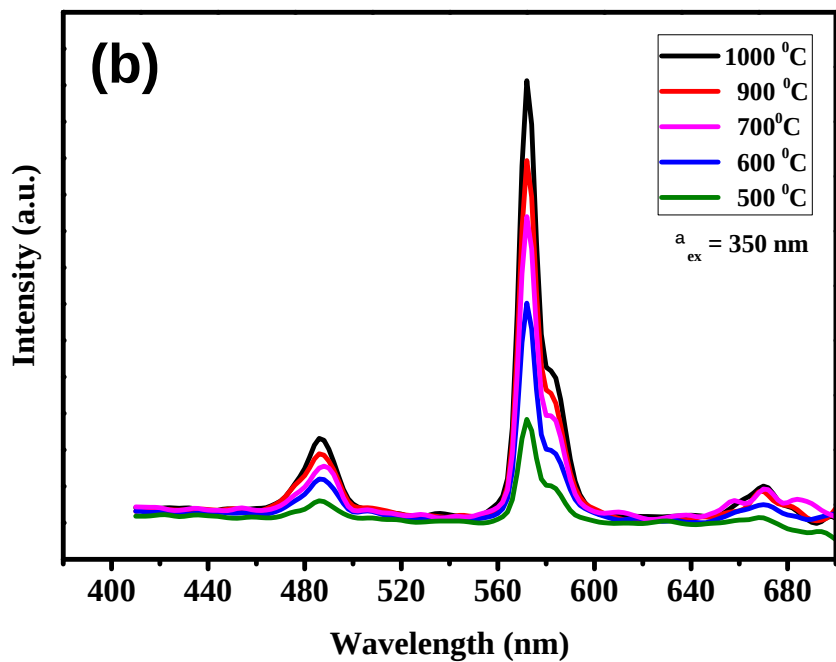
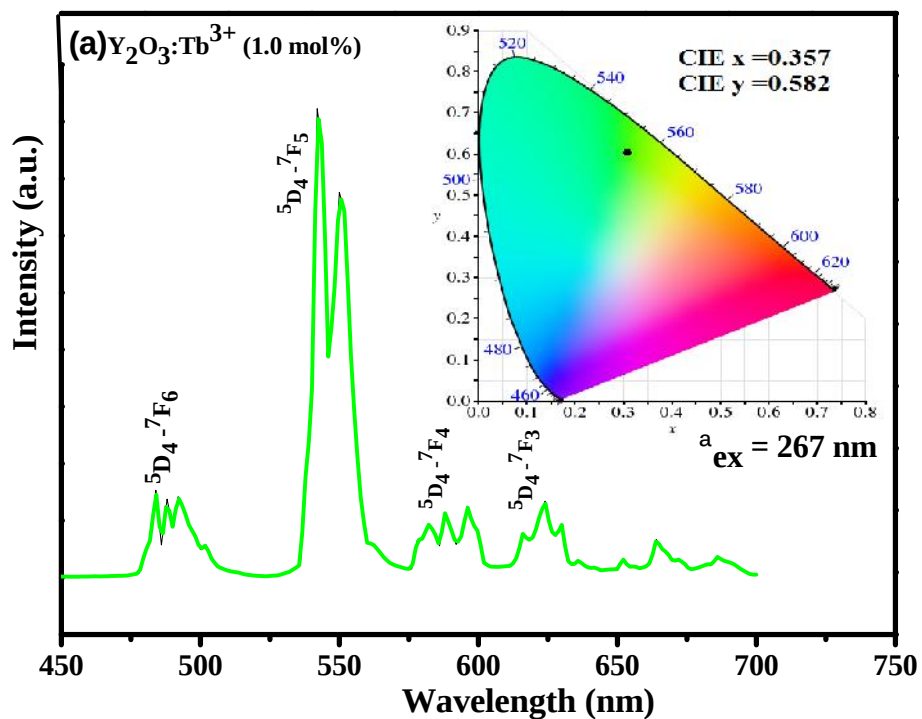


Figure 4.17: (a) Emission spectra of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ (1.0 mol%) and (b) emission spectra of $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ (0.5 mol%) at different annealing temperatures.



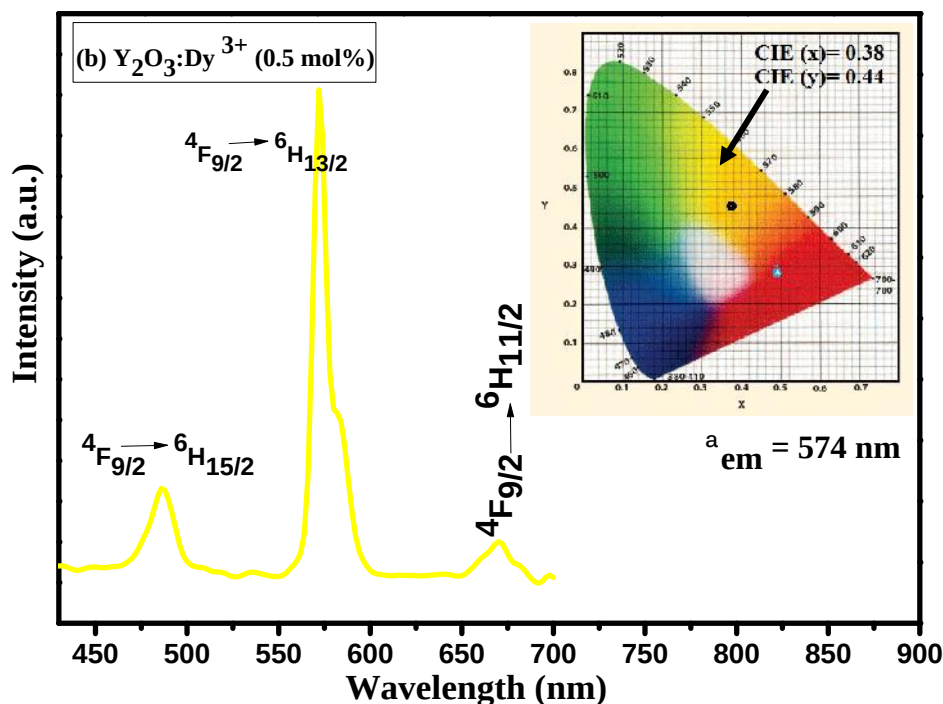


Figure 4.18: Chromaticity diagram of (a) $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ (1.0 mol%) and (b) $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ (0.5 mol%).

In this chapter we have discussed the effect of doping concentration and annealing temperature on optical and morphological properties of lanthanide (Eu^{3+} , Tb^{3+} and Dy^{3+}) doped Y_2O_3 nanophosphors. The aim for the study was to obtain maximum luminescence from lanthanide doped Y_2O_3 NPs by varying two parameters (i.e. doping concentrations of the dopants and annealing temperature) during synthesis. From above discussion we can conclude that both doping concentration and annealing temperature affect the optical and morphology of Y_2O_3 . However both parameters have some limitations. First, the doping concentration of a dopant increase the luminescence of Y_2O_3 but up to certain limit i.e. we cannot increase luminescence beyond the quenching concentration of dopants which in our case are found to be 12.0 mol%, 1.0 mol% and 0.5 mol% for $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ and $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ respectively. Second, is the annealing temperature i.e. with increase in annealing temperature the luminescence of the prepared NPs increases however, the crystallite size of the NPs also increases which restricts their use in many applications. That means we have to think out of the box and to enhance the luminescence of doped Y_2O_3 further beyond the obtained optimum concentration of dopants which will be the topic of study in our next chapter.

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CHAPTER 5

RESULTS AND DISCUSSION

Effect of alkali metal ions (Li^+ , Na^+ and K^+) co-doping on optical and morphological properties of $\text{Y}_2\text{O}_3:\text{RE}^{3+}$ ($\text{RE}^{3+}=\text{Eu}^{3+}$, Tb^{3+} & Dy^{3+}) doped nanophosphors

Overview

The present chapter describes the effect of alkali metal ions (Li^+ , Na^+ and K^+) co-doping on optical and morphological properties of $\text{Y}_2\text{O}_3:\text{RE}^{3+}$ ($\text{RE}^{3+}=\text{Eu}^{3+}$, Tb^{3+} & Dy^{3+}) doped nanophosphors (NPs) prepared via co-precipitation method. In previous chapter the variation in doping concentration and annealing temperature to get maximum luminescence from RE^{3+} doped Y_2O_3 has been presented. The aim of work is to enhance the luminescence of these phosphors further by co-doping them with alkali metal (Li^+ , Na^+ and K^+) ions and to study the various contributing factors that help in the luminescence enhancement of lanthanide ions (Eu^{3+} , Tb^{3+} & Dy^{3+}) in the presence of alkali ions (Li^+ , Na^+ and K^+) for Y_2O_3 (as host matrix). As discussed earlier, $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (red phosphor), $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ (green phosphor) and $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ (orange phosphor) are three types of phosphors which are different from each other according to their optical characteristics. Moreover, the optimum concentration of each dopant in Y_2O_3 for maximum luminescence is also different (discussed in chapter 4). However, for simplicity we have studied the optical and morphological properties of these three systems separately. All the prepared samples were characterized by XRD, FTIR, SEM and TEM to study the structural and morphological properties, PL spectroscopy was employed to study the optical properties of these samples. CIE color co-ordinates of the prepared NPs were also calculated to see the usefulness of the prepared phosphors for their various applications.

5.1 Effect of alkali metal ions (Li^+ , Na^+ and K^+) co-doping on optical and morphological properties of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ doped nanophosphors

5.1.1 Introduction

Lanthanide based materials are preferred over other luminescent materials for various applications. Furthermore, efforts are going on to enhance the luminescence of lanthanide ions for better performance. In a broader sense, there are few ways to enhance the luminescence of lanthanide ions. The first is to use a suitable sensitizer, which can absorb excitation energy efficiently, and can transfer it to the lanthanide ions. The second way is to modify host matrices in such a way that it favors radiative transitions. Another way is to co-dope the lanthanide ion along with of alkali metal ions (mainly Li^+ , Na^+ and K^+ ions) in a matrix (e.g. Y_2O_3) that results in enhancement of the luminescence of lanthanide ions significantly. But there are no comprehensive reports available in the literature that summarize how alkali metal ions help in the luminescence enhancement of lanthanide ions in various host matrices[1-13].

As discussed in chapter 4 (section 4.1.4.2) the optimum concentration of dopant Eu^{3+} to obtain maximum luminescence emission intensity from $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ is 12.0 mol%. Beyond this concentration of Eu^{3+} the emission intensity of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ decreases due to concentration quenching process. In this present chapter, sample of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%) was further codoped by Li^+ or Na^+ or K^+ (separately). The concentration of alkali metal ions were also varied systematically to obtain maximum luminescence from $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$. The obtained highest luminescent phosphors were than compared with each other to get highly luminescent $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor.

5.1.2 XRD studies

Figure 5.1 shows the XRD pattern of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ codoped with Li^+ , Na^+ and K^+ annealed at 1000 °C. To investigate the structure of the prepared compounds, X-ray diffraction patterns for $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%); $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%), Li^+ (1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0 mol%); $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%), Na^+ (1.0, 2.0, 3.0, 4.0, 5.0 mol%) and $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%), K^+ (1.0, 2.0, 3.0, 4.0, 5.0 mol%) nanoparticles annealed at 1000 °C were recorded. However, in Figure 5.1 only the XRD pattern for NPs synthesized at highest level of doping and co-doping concentration have been compared. The (hkl) values are labeled on the peaks.

All the peaks are well matched with the JCPDS file No. 83-0927 corresponding to body-centered cubic structure of Y_2O_3 with space group Ia-3. The sharp and single diffraction peaks of the XRD pattern confirm the formation of single phase compound, which is attributed to the high and uniform heating during the annealing process. The peak at $2\theta \approx 29^\circ$ was the strongest peak corresponding to the plane (222) and no peaks were observed for the dopants. The lattice parameter was calculated from the least square fitting of the diffraction peaks. With increase of dopants concentration there is a slight change in the lattice parameter for the all prepared samples. This is understandable, as the radii of all the dopants (Table 5.1(d)) are of the order or less than the radius of Y^{3+} (0.90 Å). One of the interesting observations is that the crystallite sizes are not disturbed by insertion of these ions in the Y_2O_3 lattice. Table 5.1 (a–c) gives the structural parameters for the most intense diffraction peak of the annealed samples at 1000 °C. The average crystallite size for all the prepared samples was found to be around 45 nm.

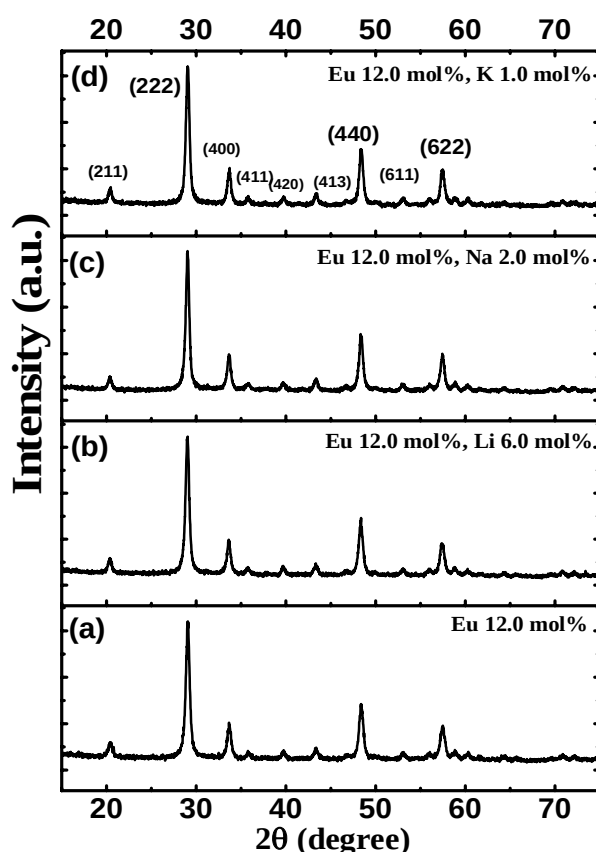


Figure 5.1: XRD pattern of (a) Y_2O_3 : Eu 12.0 mol%, Li 0.0 mol%, (b) Y_2O_3 : Eu 12.0 mol%, Li 6.0 mol%, (c) Y_2O_3 : Eu 12.0 mol%, Na 2.0 mol% (d) Y_2O_3 : Eu 12.0 mol%, K 1.0 mol% at 1000 °C.

Table 5.1(a): Structural parameters of Y₂O₃:Eu_{12 mol%}Li_{(1-7) mol%} nanophosphors.

Sample Name	2θ (deg.)	(h k l)		Lattice Constants a (Å ⁰)		Interplaner spacing d _{h, k, l} (Å ⁰)		Appr. Crysta llite Size (nm)	Chi squa re
		JCPD S	Calcul at-ed	JCP DS	Calculat e-d	JCP DS	Calcula t-ed		
Y ₂ O ₃ :Eu _{12mol%}	29.130 0	(2 2 2)	(2 2 2)		10.6101		3.062	45 nm	1.32
Y ₂ O ₃ :Eu _{12mol%} Li _{1mol%}	29.130 0	(2 2 2)	(2 2 2)		10.6105 28		3.063		1.30
Y ₂ O ₃ :Eu _{12mol%} Li _{2mol%}	29.142 0	(2 2 2)	(2 2 2)	10.60	10.6063 48	3.06	3.061		1.33
Y ₂ O ₃ :Eu _{12mol%} Li _{3mol%}	29.142 0	(2 2 2)	(2 2 2)	4	10.6063 75		3.061		1.36
Y ₂ O ₃ :Eu _{12mol%} Li _{4mol%}	29.135 0	(2 2 2)	(2 2 2)		10.6087 23		3.062		1.35
Y ₂ O ₃ :Eu _{12mol%} Li _{5mol%}	29.135 0	(2 2 2)	(2 2 2)		10.6087 23		3.062		1.35
Y ₂ O ₃ :Eu _{12mol%} Li _{6mol%}	29.130 0	(2 2 2)	(2 2 2)		10.6105 55		3.063		1.30
Y ₂ O ₃ :Eu _{12mol%} Li _{7mol%}	29.135 0	(2 2 2)	(2 2 2)		10.6087 34		3.062		1.35

Table 5.1(b): Structural parameters of Y₂O₃:Eu_{12 mol%}Na_{(1-5) mol%} nanophosphors.

Sample Name	2θ (degree)	(h k l)		Lattice Constants a (Å ⁰)		Interplaner spacing d _{h, k, l} (Å ⁰)		Appro x Crysta llite Size XRD(nm)	Chi squa re valu e
		JCPD S	Calculat ed	JCPD S	Calculat ed	JCP DS	Calculat ed		
Y ₂ O ₃ :Eu _{12mol%} N a _{1mol%}	29.0610	(2 2 2)	(2 2 2)	10.60 4	10.6351 63	3.06	3.070	45	1.21
Y ₂ O ₃ :Eu _{12mol%} Na _{2mol%}	29.1220	(2 2 2)	(2 2 2)		10.6132 49		3.063		1.35
Y ₂ O ₃ :Eu _{12mol%} Na _{3mol%}	29.0070	(2 2 2)	(2 2 2)		10.6544 79		3.075		1.29
Y ₂ O ₃ :Eu _{12mol%} Na _{4mol%}	29.0860	(2 2 2)	(2 2 2)		10.6262 41		3.067		1.42
Y ₂ O ₃ :Eu _{12mol%} Na _{5mol%}	29.0868	(2 2 2)	(2 2 2)		10.6244 79		3.067		1.41

Table 5.1(c): Structural parameters of $\text{Y}_2\text{O}_3:\text{Eu}_{12 \text{ mol}\%} \text{K}_{(1-5) \text{ mol}\%}$ nanophosphors.

Sample Name	2 θ (degree)	(h k l)		Lattice Constants a ($\text{\AA}$)		Interplaner spacing $d_{h, k, l}$ ($\text{\AA}$)		Appr ox Cryst allite Size XRD (nm)	Chi squa re value
		JCP DS	Calcula ted	JCP DS	Calcula ted	JCP DS	Calcul ated		
$\text{Y}_2\text{O}_3:\text{Eu}_{12 \text{ mol}\%} \text{K}_{1 \text{ mol}\%}$	29.1840	(2 2 2)	(2 2 2)		10.617 607		3.065		1.20
$\text{Y}_2\text{O}_3:\text{Eu}_{12 \text{ mol}\%} \text{K}_{2 \text{ mol}\%}$	29.1190	(2 2 2)	(2 2 2)	10.6 04	10.614 566	3.06	3.064	45	1.96
$\text{Y}_2\text{O}_3:\text{Eu}_{12 \text{ mol}\%} \text{K}_{3 \text{ mol}\%}$	29.1290	(2 2 2)	(2 2 2)		10.611 079		3.063		1.96
$\text{Y}_2\text{O}_3:\text{Eu}_{12 \text{ mol}\%} \text{K}_{4 \text{ mol}\%}$	29.1010	(2 2 2)	(2 2 2)		10.620 942		3.066		1.17
$\text{Y}_2\text{O}_3:\text{Eu}_{12 \text{ mol}\%} \text{K}_{5 \text{ mol}\%}$	29.1018	(2 2 2)	(2 2 2)		10.611 079		3.063		1.60

Table 5.1(d): Ionic radii of all the dopants

Name	Ionic radii ($\text{\AA}$)
Y^{3+}	0.90
Eu^{3+}	0.91
Tb^{3+}	0.92
Dy^{3+}	0.93
Li^+	0.76
Na^+	0.95
K^+	1.33

5.1.3 FT-IR analysis

FT-IR spectra of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%) (as prepared) and $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%), $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%), Li^+ (6.0 mol%), $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%), Na^+ (2.0 mol%) and $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%), K^+ (1.0 mol%) annealed at 1000 °C phosphors are illustrated in Figure 5.2.

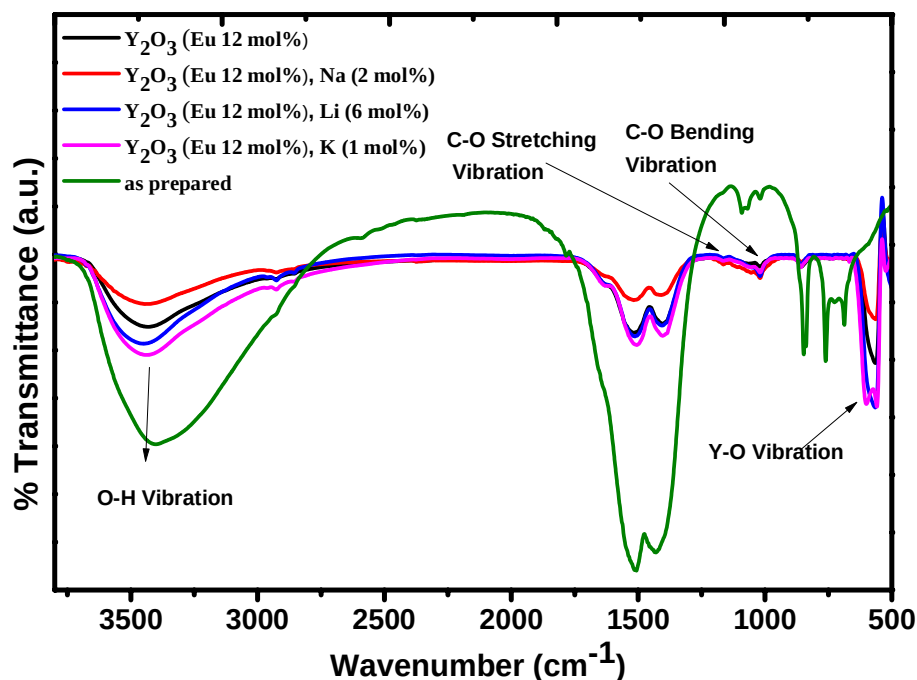


Figure 5.2: FT-IR spectra of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%) (as prepared) and $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%), $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%), Li^+ (6.0 mol%), $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%), Na^+ (2.0 mol%) and $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%), K^+ (1.0 mol%) annealed at 1000°C.

The peaks at 849 cm^{-1} and 1014 cm^{-1} are due to C–O bond bending and stretching vibration. These peaks were due to residual carbon in the prepared samples as precipitation is done by ammonium bicarbonate or may be due to the absorption of CO_2 from the ambient atmosphere [14]. Peaks at 1396 and 1518 cm^{-1} are due to N–O asymmetric stretch and N–O symmetric stretch respectively as nitrate precursors were used at the time of synthesis. The broad band at 3450 cm^{-1} is assigned to O–H stretching vibration [14]. This band in the prepared doped samples was probably due to the adsorbed molecular water from the KBr pellet used for the preparation of samples, or may be absorption of H_2O from the ambient atmosphere. Moreover, all these samples are annealed at same temperature i.e. 1000 °C (except as prepared sample) and the characterization was also done using same physical conditions.

However, there is difference between the peak width and intensity corresponding to peaks around 3450, 1500 and 567 cm^{-1} in all the samples as shown in Figure 5.2. Sample $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12 mol%), Na^+ (2 mol%) has shown smallest OH^- band and weakest band at 1500 cm^{-1} for asymmetric and symmetric nitro group. The residual hydroxyl groups ($-\text{OH}$) at 3450 cm^{-1} and the N-O group at 1396 and 1518 cm^{-1} are responsible for the quenching of rare earth emission and thereby decreasing the luminescence intensity [15]. Since as prepared sample was not annealed so a large OH^- band at 3450 cm^{-1} is natural. The absorption band centered at 567 cm^{-1} is attributed to Y–O lattice vibration is more for $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12 mol%), Li^+ (6 mol%) which also is a sign of better phase purity of Y_2O_3 in this sample as compared to others samples. All these conditions are good for synthesis of a novel phosphor.

5.1.4 TEM study

The morphology of prepared samples was analyzed with the help of TEM. TEM images of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%), Li^+ (6.0 mol%) and $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%), Na^+ (2.0 mol%) annealed at 1000 $^\circ\text{C}$ were recorded and are shown in Figure 5.3 (a & b) and 5.4 (a & b). In Figure 5.3 (a) TEM micrograph shows the rod like morphology of the prepared samples as was seen in the SEM images (discussed earlier in chapter 4 section 4.2.3). Here the particles seem to be encapsulated and have spherical feature. However, most of the particles are embedded within the rods. The bright and dark field view of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, Na^+ is shown in Figure 5.4 (a & b). Here one can see the spherical particles embedded uniformly inside and on the surface of the rods. The size of these rods varies from 500 nm to 800 nm in length and 80 nm to 100 nm in diameter. Particle size as calculated from TEM is the range 40–60 nm which is in good agreement with XRD in which calculated average crystallite size is of the range of 45 nm. The SAED pattern in Figure 5.3(b) shows a set of sharp rings corresponding to diffraction from different planes of the nanocrystallites instead of spots due to the random orientation of the crystallites. The three rings corresponding to the (211), (222) and (400) lattice planes of the cubic phase of Y_2O_3 have been marked.

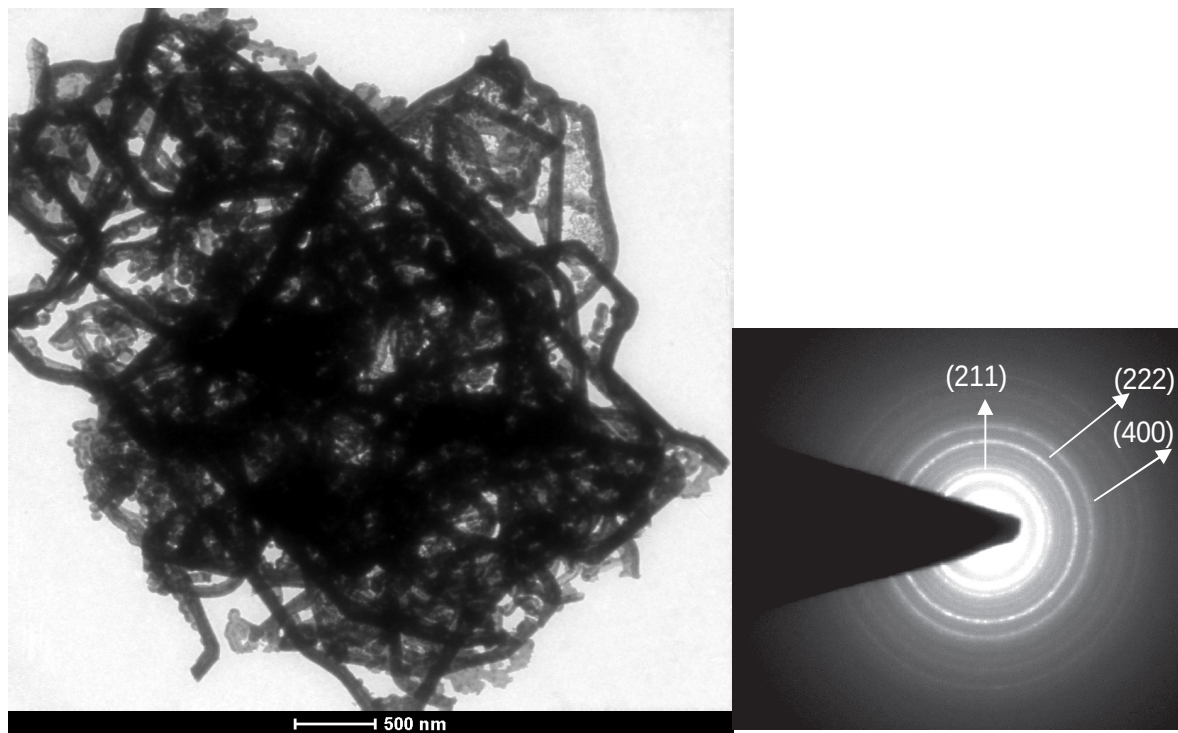


Figure 5.3: (a) TEM micrograph of $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ (12.0 mol%), Li^+ (6.0 mol%) and (b) SAED of $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ (12.0 mol%), Li^+ (6.0 mol%) annealed at 1000 °C.

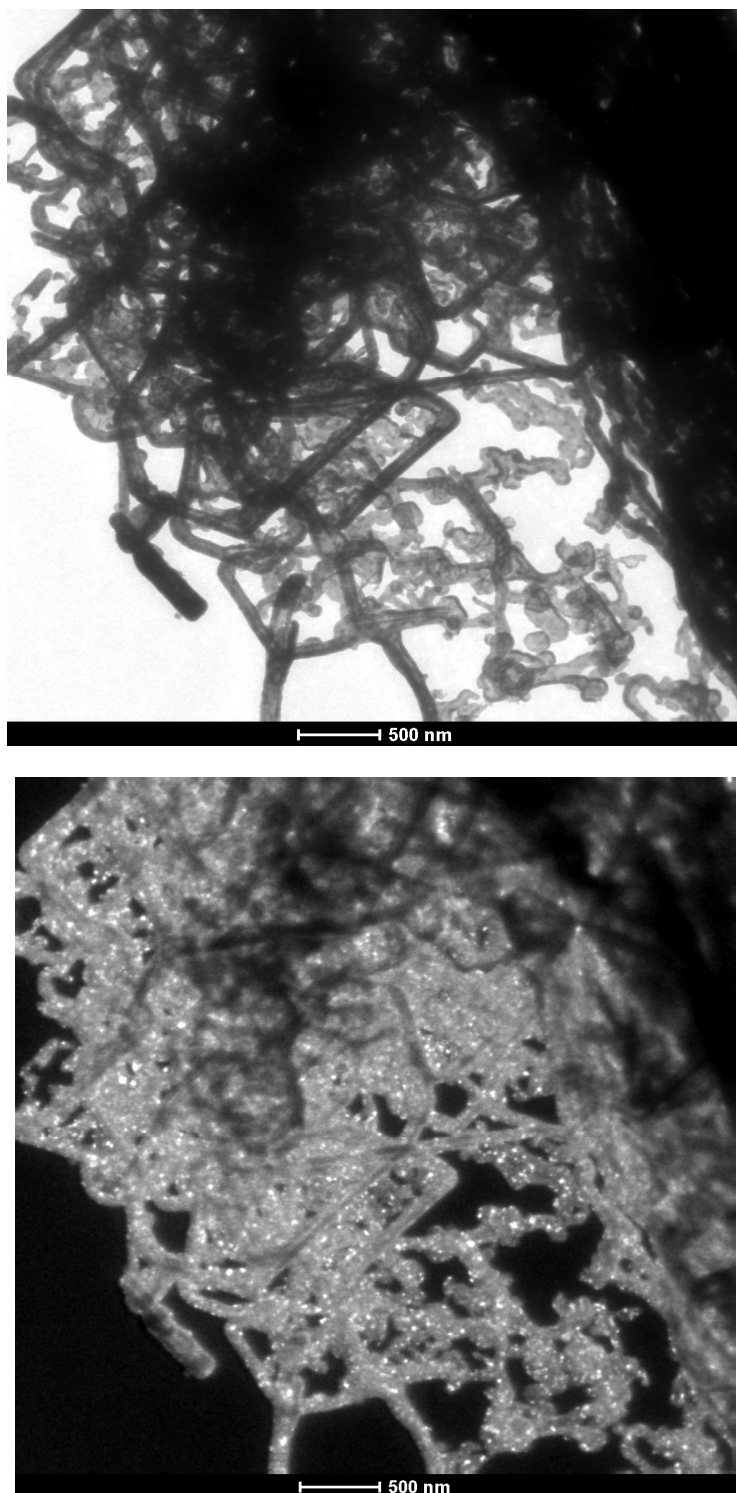


Figure 5.4: TEM micrograph (a) Bright and (b) dark field view of $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ (12.0 mol%), Na^+ (2.0 mol%) annealed at 1000 °C.

5.1.5 Photoluminescence study

Once the optimum concentration of Eu^{3+} was determined which is 12.0 mol%, the effect of metal ions ($\text{M}^+ = \text{Li}^+, \text{Na}^+$ and K^+) co-doping was also studied. Figure 5.5 (a & b), 5.6 (a & b), 5.7 (a & b) gives the effect of M^+ ion concentration on PL intensity of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%) NPs. The luminescence intensity further increases from $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%) (quenching concentration with only Eu^{3+}) and along with 6.0 mol% of Li^+ , 2.0 mol% of Na^+ and 1.0 mol% of K^+ ions co-doping respectively. In all the obtained emission spectra of the M^+ codoped $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ with different M^+ concentration, emission intensity increases with increase in M^+ concentration up to certain percentage (6.0 mol% for Li^+ , 2.0 mol% for Na^+ and 1.0 mol% for K^+). The distinct emission lines lying between 550 nm and 650 nm were observed due to transitions from the excited $^5\text{D}_1 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($j = 0-3$) transitions of Eu^{3+} ions. The origin of these transitions (electric dipole or magnetic dipole) from emitting levels to terminating levels depends on the location of Eu^{3+} ion in the Y_2O_3 lattice and the type of transition is determined by selection rules [16]. The most intense peak at ~ 611 nm and a small peak at 630 nm correspond to the hypersensitive transition between the $^5\text{D}_0$ and $^7\text{F}_2$ levels of Eu^{3+} ion in the yttrium oxide host caused by the forced electric dipole transition mechanism. The weak emission in the vicinity of 590 nm (590 nm – 600 nm) is ascribed to the magnetic dipole transition of $^5\text{D}_0 \rightarrow ^7\text{F}_1$. Generally, when Eu^{3+} is located at a low symmetry (without an inversion centre i.e. C_2 site), the ~ 611 nm emission is dominant whereas the 590 nm emission is stronger when Eu^{3+} is located at a high symmetry (with an inversion centre i.e. C_{3i} site) as shown in Figure 5.8 [17]. In the present case, the emission at 611 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) is dominant suggesting that the location of Eu^{3+} deviates from the inversion symmetry, i.e. at low symmetry positions (C_2 site). Due to the defects produced during the preparation process and impurities contained in the raw materials, the samples inevitably have quenching centers (traps) which induce non-radiative transitions and decrease the luminous efficiency.

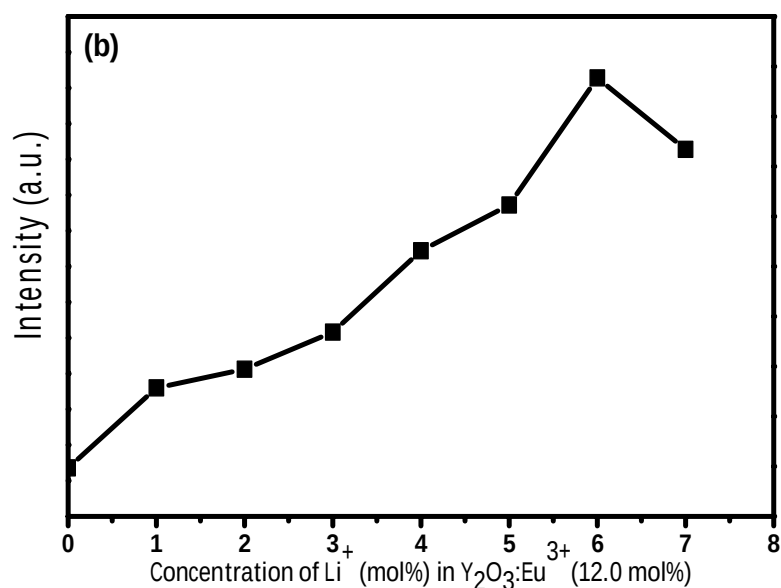
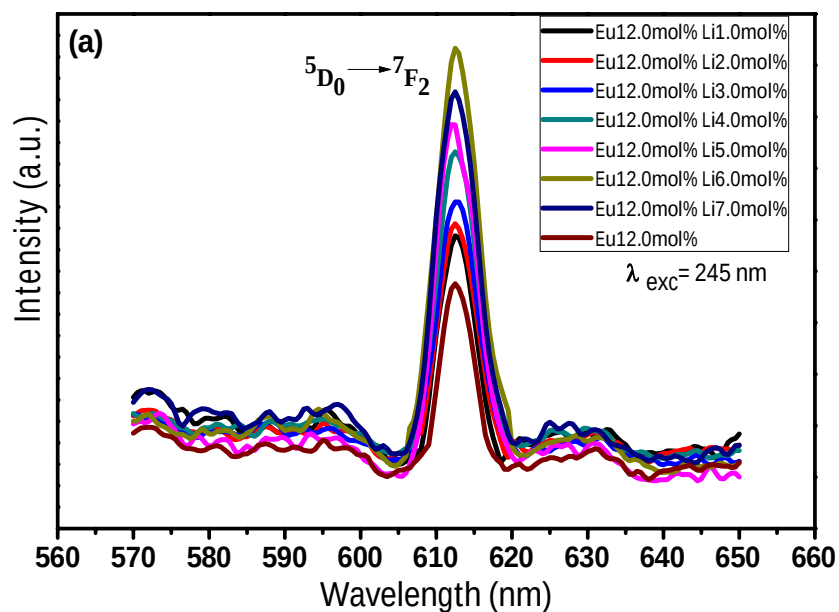


Figure 5.5: (a) Spectra of $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ 12.0 mol%, Na^+ ion concentration (1.0 – 4.0 mol%); (b) Variation in luminescence intensity with Na^+ ion concentration in $(\text{Y}_{0.88-y}\text{Eu}_{0.12}\text{Na}_y)_2\text{O}_3$.

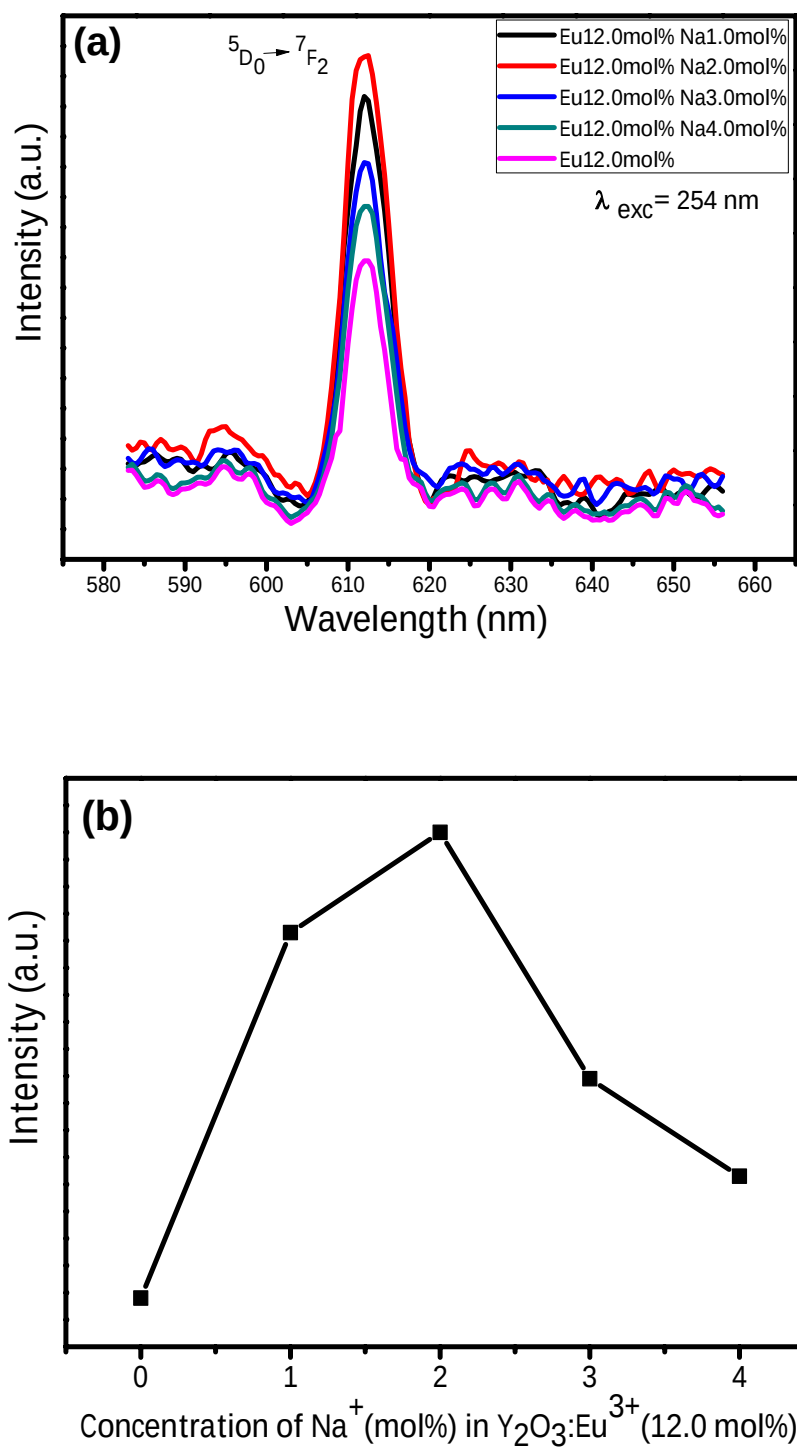


Figure 5.6: (a) Spectra of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ 12.0 mol%, Na^+ ion concentration (1.0 – 4.0 mol%); (b) Variation in luminescence intensity with Na^+ ion concentration in $(\text{Y}_{0.88-y}\text{Eu}_{0.12}\text{Na}_y)_2\text{O}_3$.

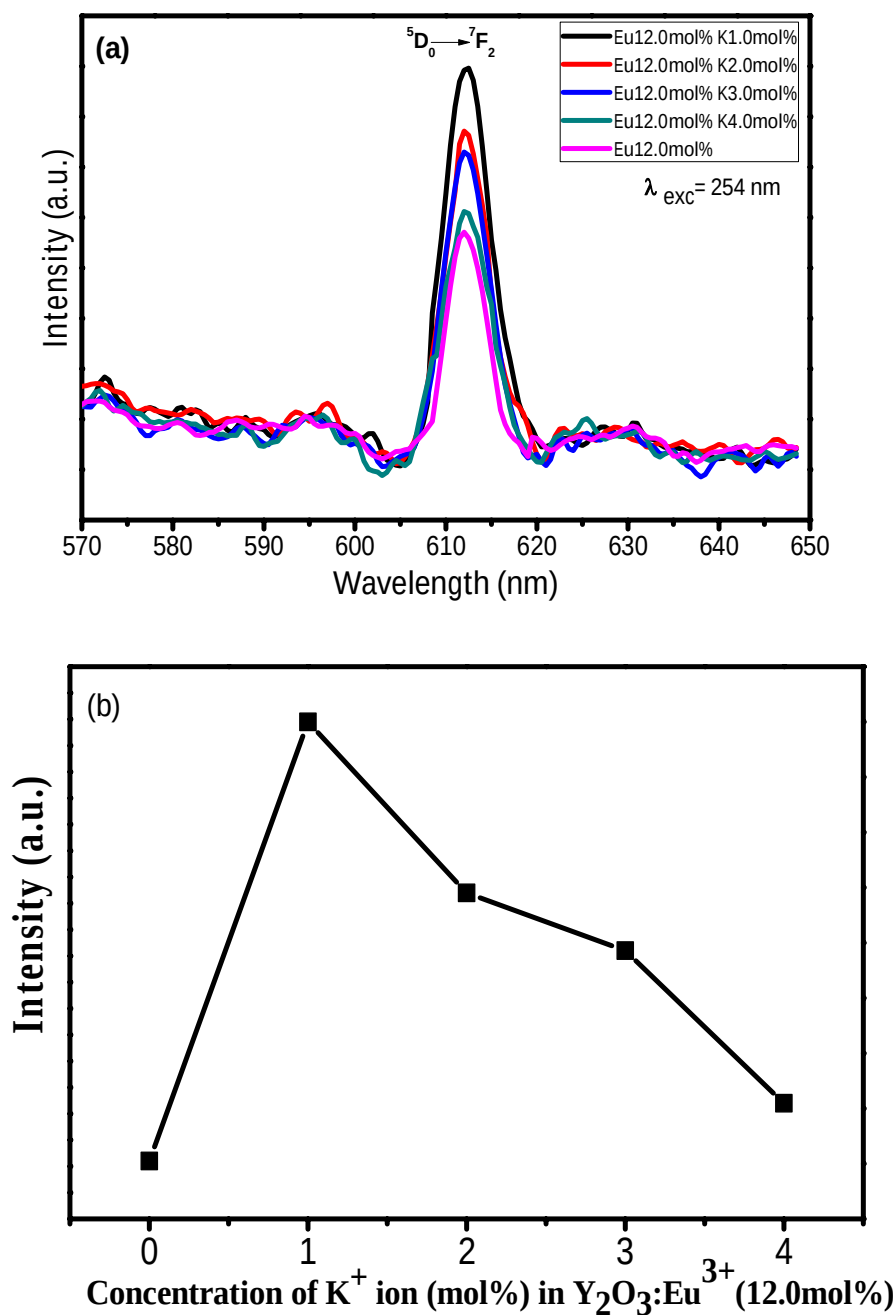


Figure 5.7: (a) Spectra of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ 12.0 mol%, Na^+ ion concentration (1.0 – 4.0 mol%); (b) Variation in luminescence intensity with Na^+ ion concentration in $(\text{Y}_{0.88-y}\text{Eu}_{0.12}\text{Na}_y)_2\text{O}_3$.

Earlier it was reported that addition of Li^+ ion in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ NPs increases the PL intensity to some extent [11]. However, in our case we have co-doped $\text{Li}^+/\text{Na}^+/\text{K}^+$ ions individually in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ doped NPs. It shows further increase in PL intensity of singly doped $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%) which is the optimum concentration of Eu^{3+} in Y_2O_3 . These metal ions (M^+) are

likely to occupy the C_2 sites (Figure 5.8) of the Y_2O_3 lattice, which relates with the red luminescence emission at 611 nm approximately [18].

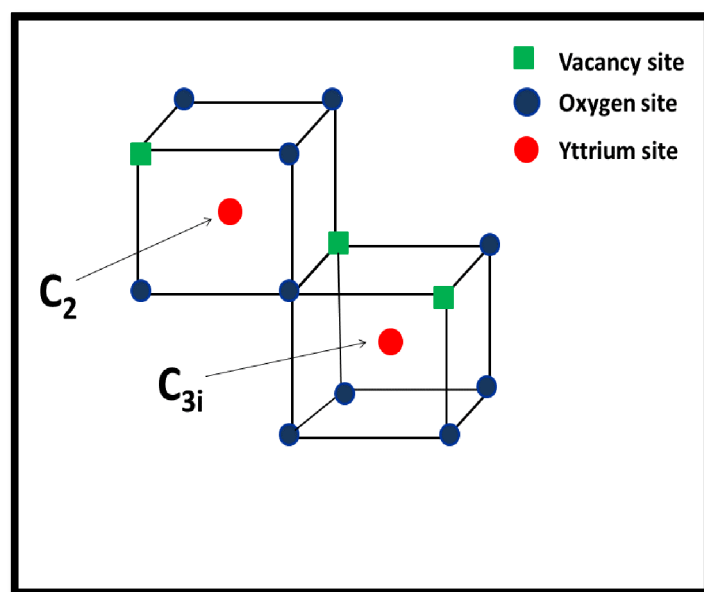


Figure 5.8 Yttrium ion site in the cubic form of Y_2O_3 .

As the ionic radii of these metal ions are smaller or nearly equal to that of Y^{3+} (90 pm), the incorporation of these ions reduces the symmetry of C_2 sites (Figure 5.8), as metal ions have +1 charge in comparison to +3 charge of Y^{3+} . So this creates oxygen vacancy which suggests that parity selection rule is broken and luminescence intensity increases further[19]. However, when the content of these metal ions increases further beyond certain limit, the oxygen vacancies of host lattice increase accordingly, which may destroy the powder crystallization and lead to the decrease of luminescence intensity. In case of Na^+ and K^+ doping, the luminescence of the samples has been enhanced but the percentage of doping concentration for these metal ions is less (2.0 mol% for Na^+ and 1.0 mol% for K^+) than in case of Li^+ (6.0 mol%). This may be due to the larger size of Na^+ and K^+ ions as compared to Li^+ . With further increase in dopant ion concentration beyond above mentioned values for Li^+ , Na^+ and K^+ the crystallinity reduces which shows that Na^+ and K^+ ions have quenched the PL emission intensity even at low doping concentration compared to Li^+ of these ions. However, they have shown the increased luminescence intensity even for this small doping concentration. Figure 5.9 shows the PL emission spectra of $Y_2O_3:Eu^{3+}$ (12.0 mol%), $Y_2O_3:Eu^{3+}$ (12.0 mol%), Li^+ (6.0 mol%), $Y_2O_3:Eu^{3+}$ (12.0 mol%), Na^+ (1.0 mol%) and $Y_2O_3:Eu^{3+}$ (12.0 mol%), K^+ (1.0 mol%) under an excitation of 254 nm. Emission intensity of

$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%), Na^+ (1.0 mol%) sample is higher than the earlier reported which may be due to better crystalline behavior as discussed in XRD and FTIR studies. The CIE parameter such as color coordinates was calculated in order to know the photometric characteristics of the prepared phosphors. The values of CIE parameters for the ($\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12 mol%), Na^+ (2.0 mol%)) phosphors are CIE (x)= 0.65 CIE (y)= 0.34, which is very close to coordinates of ideal red (0.67, 0.33) [20].

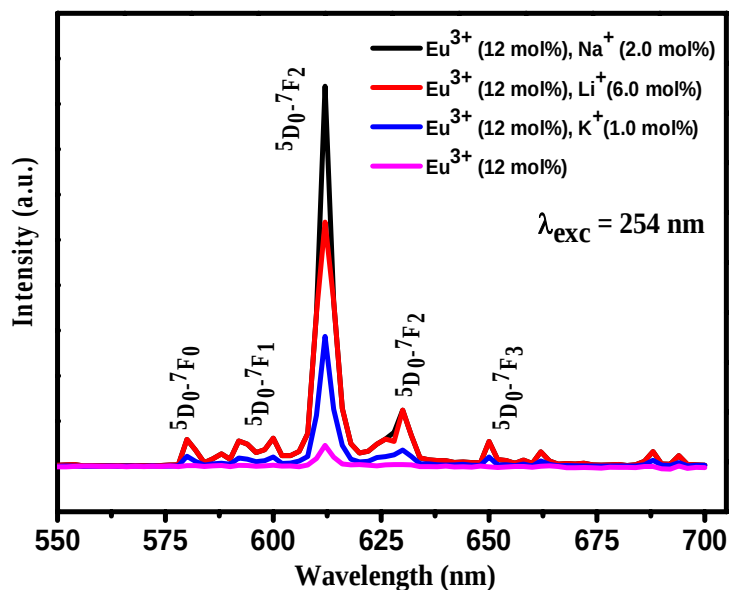


Figure 5.9: Emission spectra $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%), $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%), Li^+ (6.0 mol%), $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%), Na^+ (1.0 mol%) and $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%), K^+ (1.0 mol%) annealed at 1000 °C.

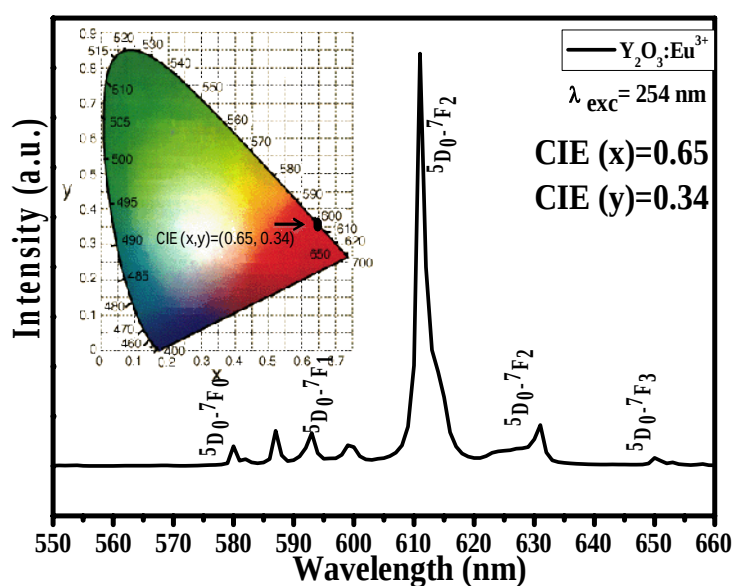


Figure 5.10: CIE color coordinates of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (12.0 mol%), Na^+ (2.0 mol%).

In addition, the calculated CIE chromaticity coordinates are rather close to edge of CIE diagram (shown in inset of Figure 5.10), indicating that this kind of phosphor shows better color purity in solid state lighting.

5.2 Effect of alkali metal ions (Li^+ , Na^+ and K^+) co-doping on optical and morphological properties of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ doped nanophosphors

5.2.1 Introduction

As discussed in chapter 4 (section 4.3.2) the optimum concentration of dopant Tb^{3+} to obtain maximum luminescence emission intensity from $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ was 1.0 mol%. Doping above this concentration of Tb^{3+} in Y_2O_3 leads to decreases in emission intensity due to concentration quenching process. This sections describes the effect of coping of alkali metal ions ($\text{Li}^+/\text{Na}^+/\text{K}^+$) on optical and structural properties of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ (1.0 mol%) NPs. The concentration of alkali metal ions were varied systematically to obtain maximum luminescence from $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ (1.0 mol%). The obtained highest luminescent phosphors were than compared with each other to get highly luminescent $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ nanophosphor.

5.2.2 XRD studies

Figure 5.11 shows the XRD pattern of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ codoped with Li^+ , Na^+ and K^+ annealed at 1000 °C. To investigate the structure of the prepared compounds, X-ray diffraction patterns for $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ (1.0 mol%); $\text{Y}_2\text{O}_3:(\text{Tb}^{3+}$ 1.0 mol%, Li^+ 0.2, 0.5, 1.0, 1.5 and 2.0 mol%); $\text{Y}_2\text{O}_3:(\text{Tb}^{3+}$ 1.0 mol%, Na^+ 0.2, 0.5, 1.0, 1.5 and 2.0 mol%) and $\text{Y}_2\text{O}_3:(\text{Tb}^{3+}$ 1.0 mol%, K^+ 0.2, 0.5, 1.0, 1.5 and 2.0 mol%) nanoparticles annealed at 1000 °C were recorded. However, in Figure 5.11 only the XRD pattern for NPs synthesized at highest level of doping and co-doping concentrations are compared. The (hkl) values are labeled on the peaks. All the peaks are well matched with the JCPDS file No. 83-0927 corresponding to body-centered cubic structure of Y_2O_3 with space group Ia-3. The sharp and single diffraction peaks of the XRD pattern confirm the formation of single phase compound, which is attributed to the high and uniform heating during the annealing process. The peak at $2\theta \approx 29^\circ$ was observed as the strongest peak corresponding to the plane (222). Moreover, with increase of dopants concentration there is a slight change in lattice parameter for all the prepared samples. However, the crystallite sizes are not disturbed by insertion of these ions in the Y_2O_3 lattice.

The average crystallite size (D) calculated using Debye–Scherer formula [21] was found to be around 46 nm.

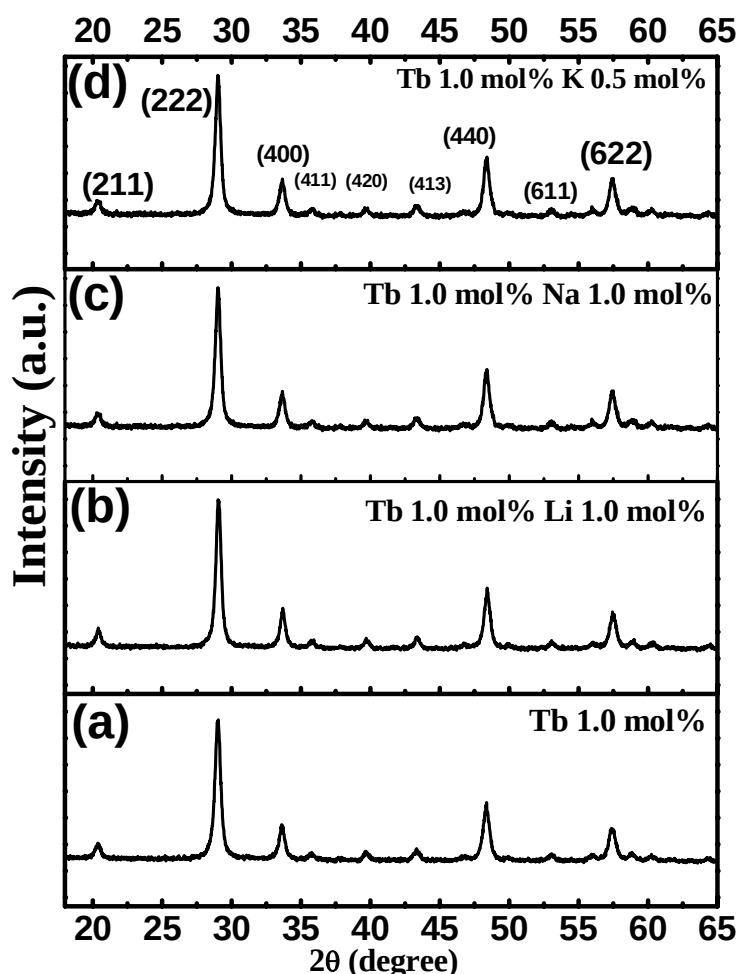


Figure 5.11: XRD pattern of (a) $\text{Y}_2\text{O}_3: \text{Tb}^{3+}$ (1.0 mol%), (b) $\text{Y}_2\text{O}_3: (\text{Tb}^{3+} 1.0 \text{ mol}\%, \text{Li}^+ 1.0 \text{ mol}\%)$ (c) $\text{Y}_2\text{O}_3: (\text{Tb}^{3+} 1.0 \text{ mol}\%, \text{Na}^+ 1.0 \text{ mol}\%)$ (d) $\text{Y}_2\text{O}_3: (\text{Tb}^{3+} 1.0 \text{ mol}\%, \text{K}^+ 0.5 \text{ mol}\%)$ annealed at 1000 °C.

5.2.3 Photoluminescence Study

After the optimum concentration of Tb^{3+} was determined which is 1.0 mol%, the effect of metal ions ($\text{M}^+ = \text{Li}^+, \text{Na}^+$ and K^+) co-doping was also studied. Figure 5.12 (a & b), 5.13 (a & b) and 5.14 (a & b) gives the effect of M^+ ion concentration on PL intensity of $\text{Y}_2\text{O}_3: \text{Tb}^{3+}$ (1.0 mol%) NPs. The luminescence intensity further increases from $\text{Y}_2\text{O}_3: \text{Tb}^{3+}$ (1.0 mol%) (quenching concentration with only Tb^{3+}) and along with 1.0 mol% of Li^+ , 0.5 mol% of Na^+ and 0.2 mol% of K^+ ions co-doping respectively. In all the excitation spectra (Figure 5.12(a),

5.13(a) and 5.14(a)) recorded at $\lambda_{\text{emi}} = 545$ nm emission, is composed of two overlapping bands having maxima at 276 and 307 nm [22]. The peak position in the emission spectra does not change with Tb^{3+} concentration suggesting that the nature of dopant (Tb^{3+}) remains unchanged with concentration. The band located at around 276 nm is attributed to the $\text{O}^{2-}-\text{Tb}^{3+}$ charge transfer band (CTB), which corresponds to the electronic transitions from the 2p orbital of O^{2-} to the 4f orbital of Tb^{3+} . The origin of the band at 302 nm results from the absorption of incident radiation by Tb^{3+} ions and leads to the excitation of electrons from the Tb^{3+} ground state to one of its excited 4f levels. However, due to the parity forbidden character of the transition within the 4f configuration, the peaks beyond 307 nm were too weak to observe here [16].

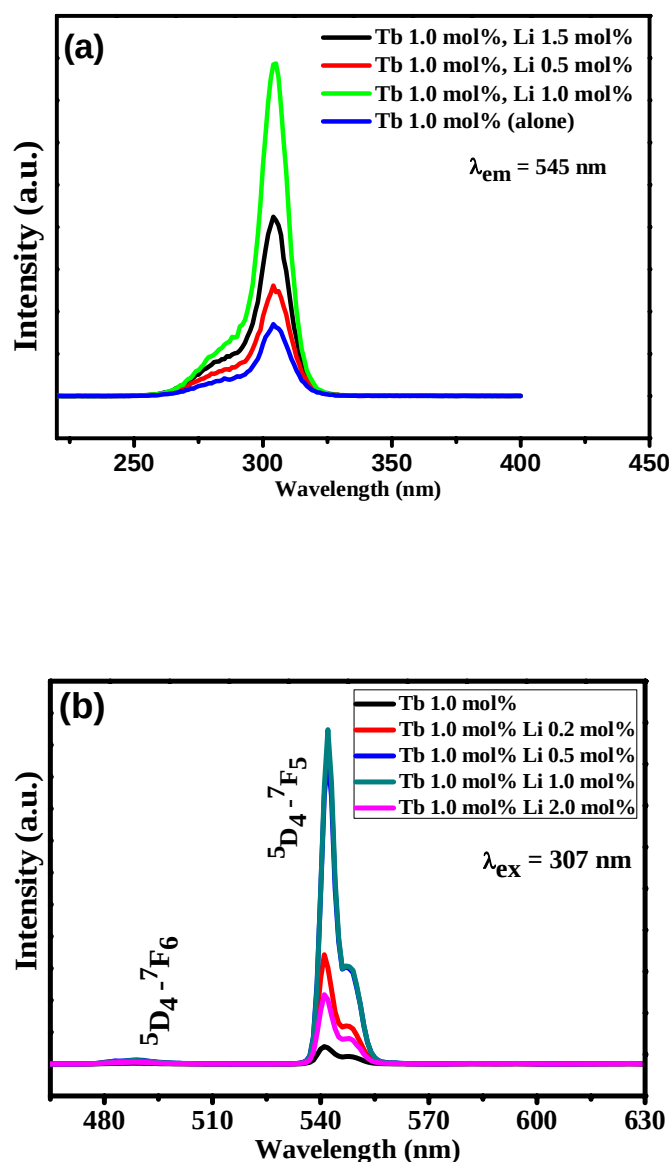


Figure 5.12: (a) Excitation and (b) emission spectra of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}/\text{Li}^+$ annealed at 1000 °C.

With the doping of metal ions in $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ (1.0 mol%) the emission intensity corresponding to Tb^{3+} increases further from optimum concentration of Tb^{3+} in Y_2O_3 . These metal ions (M^+) are likely to occupy the C_2 sites (Figure 5.8) of the Y_2O_3 lattice, which relates with the green luminescence emission at 545 nm approximately [16]. As the ionic radii of these metal ions are smaller or nearly equal to that of Y^{3+} (90 pm) (Table 5.1(d)), the incorporation of these ions reduces the symmetry of C_2 sites (Figure 5.8), as metal ions have +1 charge in comparison to +3 charge of Y^{3+} . So this creates oxygen vacancy which suggests that parity selection rule is broken and luminescence intensity increases further.

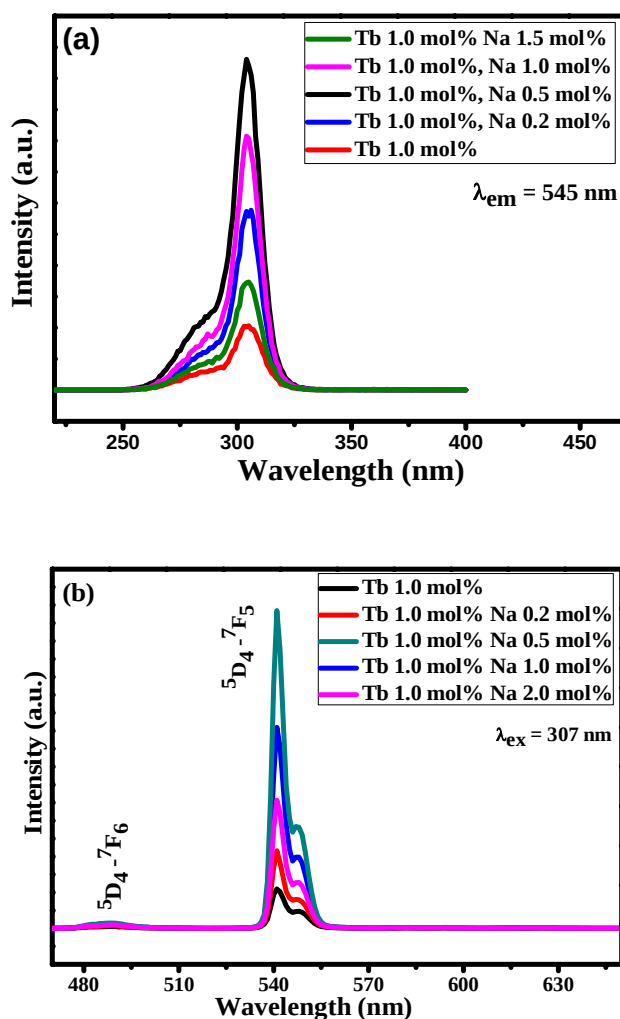


Figure 5.13: (a) Excitation and (b) emission spectra of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}/\text{Na}^+$ annealed at 1000 °C.

However, when the content of these metal ions increases further beyond certain limit, the oxygen vacancies of host lattice increase accordingly, which may lead to instability in the crystal and cause in decrease of luminescence intensity.

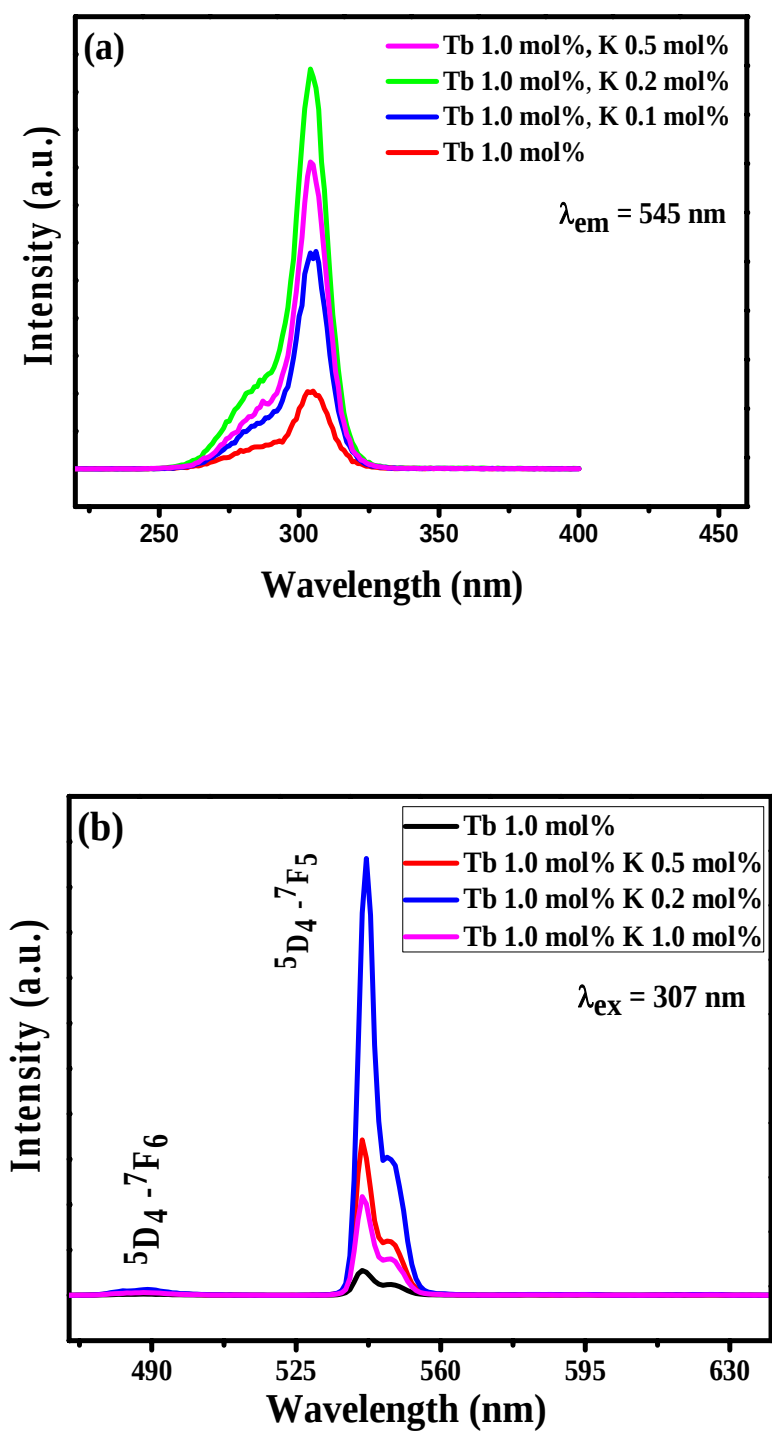


Figure 5.14: (a) Excitation and (b) emission spectra of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}/\text{K}^{+}$ annealed at 1000 °C.

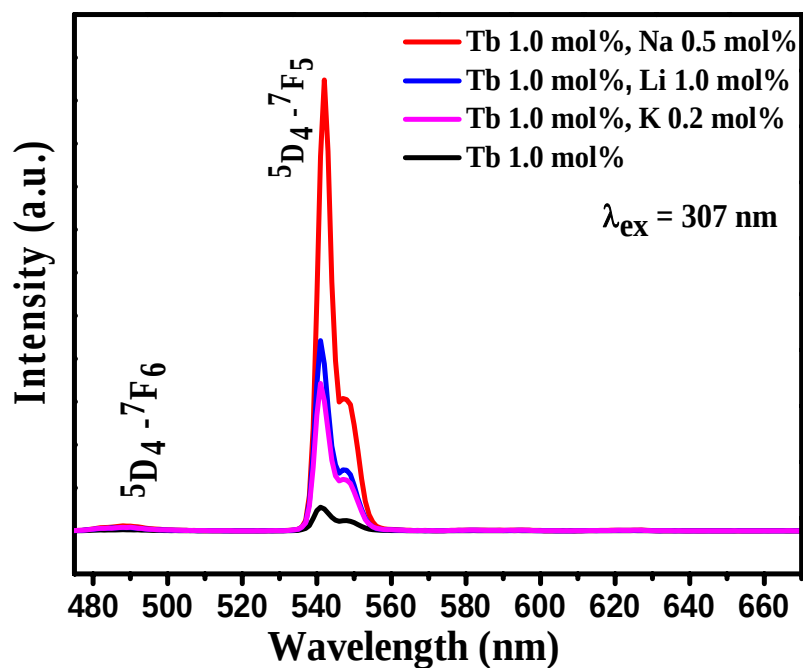


Figure 5.15: Emission spectra of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ (1.0 mol%); $\text{Y}_2\text{O}_3:(\text{Tb}^{3+}$ 1.0 mol%, Li^+ 1.0 mol%); $\text{Y}_2\text{O}_3:(\text{Tb}^{3+}$ 1.0 mol%, Na^+ 0.5 mol%) and $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ (1.0 mol%, K^+ 0.2 mol%) annealed at 1000 °C.

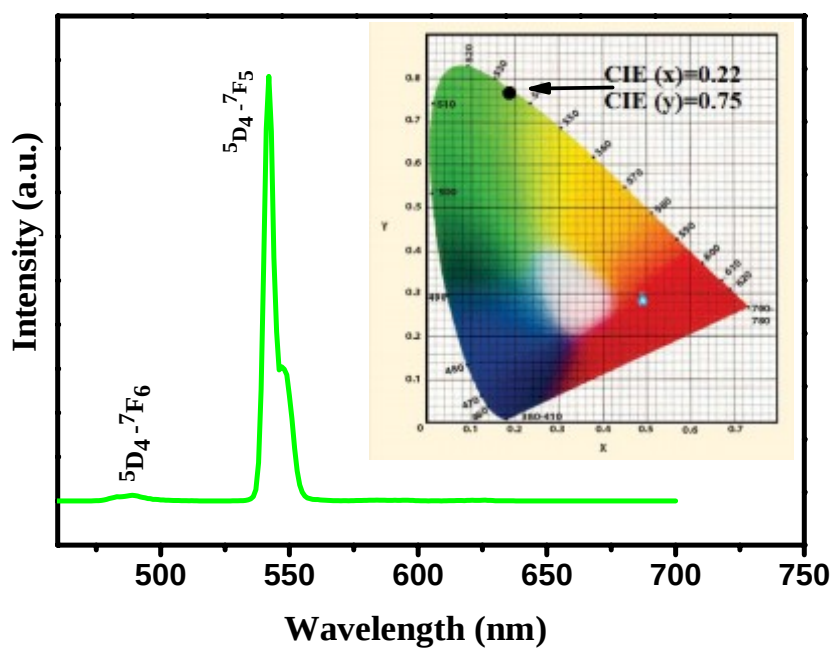


Figure 5.16: CIE color co-ordinates of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ (1.0 mol%, Na 0.5 mol%) annealed at 1000 °C.

Figure 5.15 shows the comparative PL emission spectra of $\text{Y}_2\text{O}_3:(\text{Tb}^{3+} 1.0 \text{ mol}\%); \text{Y}_2\text{O}_3:(\text{Tb}^{3+} 1.0 \text{ mol}\%, \text{Li}^+ 1.0 \text{ mol}\%); \text{Y}_2\text{O}_3:(\text{Tb}^{3+} 1.0 \text{ mol}\%, \text{Na}^+ 0.5 \text{ mol}\%)$ and $\text{Y}_2\text{O}_3:(\text{Tb}^{3+} 1.0 \text{ mol}\%, \text{K}^+ 0.2 \text{ mol}\%)$ under an excitation of 307 nm. Emission intensity of $\text{Y}_2\text{O}_3:(\text{Tb}^{3+} 1.0 \text{ mol}\%, \text{Na}^+ 0.5 \text{ mol}\%)$ sample is maximum. The CIE parameter such as color coordinates was calculated in order to know the photometric characteristics of the prepared phosphors. The values of CIE (x, y) parameters (Figure 5.16) for the $\text{Y}_2\text{O}_3:(\text{Tb}^{3+} 1.0 \text{ mol}\%, \text{Na} 0.5 \text{ mol}\%)$ phosphors are (0.22, 0.75).

5.3 Effect of alkali metal ions (Li^+ , Na^+ and K^+) co-doping on optical and morphological properties of $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ doped nanophosphors

5.3.1 Introduction

As discussed in chapter 4 (section 4.3.3) the optimum concentration of dopant Dy^{3+} to obtain maximum luminescence emission intensity from $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ was 0.5 mol%. Beyond this concentration of Dy^{3+} the emission intensity of $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ decreases due to concentration quenching process. In this present chapter NPs of $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ (0.5 mol%) was codoped by $\text{Li}^+/\text{Na}^+/\text{K}^+$. The concentration of alkali metal ions were also varied systematically to obtain maximum luminescence from $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$. The obtained highest luminescent phosphors were than compared with each other also to get highly luminescent $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ phosphor.

5.3.2 XRD studies

Figure 5.17 shows the XRD pattern of $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ codoped with Li^+ , Na^+ and K^+ annealed at 1000 °C. To investigate the structure of the prepared compounds, X-ray diffraction patterns for $\text{Y}_2\text{O}_3:(\text{Dy}^{3+} 0.5 \text{ mol}\%); \text{Y}_2\text{O}_3:(\text{Dy}^{3+} 0.5 \text{ mol}\%, \text{Li}^+ 0.2, 0.5, 1.0, 1.5 \text{ and } 2.0 \text{ mol}\%); \text{Y}_2\text{O}_3:(\text{Dy}^{3+} 0.5 \text{ mol}\%, \text{Na}^+ 0.2, 0.5, 1.0, 1.5 \text{ and } 2.0 \text{ mol}\%)$ and $\text{Y}_2\text{O}_3:(\text{Dy}^{3+} 0.5 \text{ mol}\%, \text{K}^+ 0.2, 0.5, 1.0, 1.5 \text{ and } 2.0 \text{ mol}\%)$ nanoparticles annealed at 1000 °C were recorded. However, in Figure 5.17 only the XRD pattern for NPs synthesized at highest level of doping and co-doping concentration have been compared. The (hkl) values are labeled on the peaks. All the peaks are well matched with the JCPDS file No. 83-0927 corresponding to body-centered cubic structure of Y_2O_3 with space group Ia-3. The sharp and single diffraction peaks of the XRD pattern confirm the formation of single phase compound, which is attributed to the high and uniform heating during the annealing process. The peak at $2\theta \approx 29^\circ$ was observed as the

strongest peak corresponding to the plane (222). The lattice parameter was calculated from the least square fitting of the diffraction peaks. The crystallite size (D) was determined to be around 44 nm (using Debye–Scherer formula) [16].

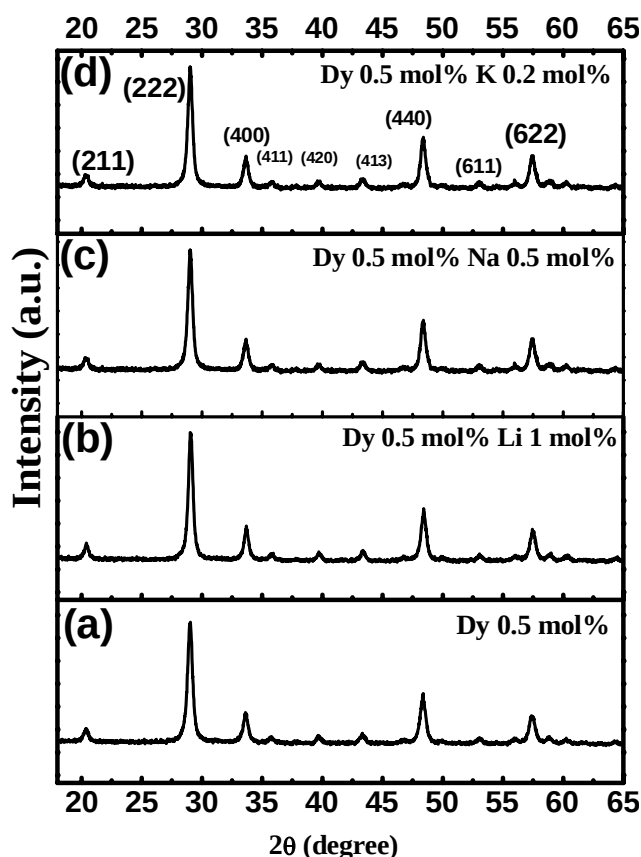


Figure 5.17: XRD pattern of $\text{Y}_2\text{O}_3:(\text{Dy}^{3+} 0.5 \text{ mol}\%)$; $\text{Y}_2\text{O}_3:(\text{Dy}^{3+} 0.5 \text{ mol}\%, \text{Li}^+ 0.2, 0.5, 1.0, 1.5 \text{ and } 2.0 \text{ mol}\%)$; $\text{Y}_2\text{O}_3:(\text{Dy}^{3+} 0.5 \text{ mol}\%, \text{Na}^+ 0.2, 0.5, 1.0, 1.5 \text{ and } 2.0 \text{ mol}\%)$ and $\text{Y}_2\text{O}_3:(\text{Dy}^{3+} 0.5 \text{ mol}\%, \text{K}^+ 0.2, 0.5, 1.0, 1.5 \text{ and } 2.0 \text{ mol}\%)$ nanoparticles annealed at 1000 °C.

5.3.3 Photoluminescence Study

After the optimum concentration of Dy^{3+} was determined which is 0.5 mol%, the effect of metal ions ($\text{M}^+ = \text{Li}^+, \text{Na}^+$ and K^+) co-doping was also studied. Figure 5.18 (a & b), 5.19, 5.20 gives the effect of M^+ ion concentration on PL intensity of $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ (0.5 mol%) NPs. The luminescence intensity further increases from $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ (0.5 mol%) (quenching concentration with only Dy^{3+}) and along with 1.0 mol% of Li^+ , 0.5 mol% of Na^+ and 0.2 mol% of K^+ ions co-doping respectively. Figure 5.18 (a & b) represents the (a) excitation and (b) emission spectra of Li^+ codoped Dy^{3+} doped Y_2O_3 as a function of Li^+ ion concentration.

The concentration of Dy^{3+} in $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ sample was varied from 0.2 mol% to 2.0 mol%. As the concentration of Li^+ increases, the emission intensity increases, and it reaches to maximum at 1.0 mol% of Li^+ molar concentration, which was taken as the optimum concentration. Figure 5.18 (a) shows the excitation spectrum of $\text{Y}_2\text{O}_3:(\text{Dy}^{3+} 0.5 \text{ mol}\%, \text{Li}^+ 1.0 \text{ mol}\%)$ excited at 574 nm in the range 250–550 nm that consists of different excitation bands centered at 351 ($^6\text{H}_{15/2}-^6\text{P}_{7/2}$) and 389 ($^6\text{H}_{15/2}-^4\text{M}_{21/2}$) [23]. However, Figure 5.18 (b) shows a typical emission spectra of synthesized $\text{Y}_2\text{O}_3:(\text{Dy}^{3+} 0.5 \text{ mol}\%, \text{Li}^+ 0.2\text{--}2.0 \text{ mol}\%)$ nanophosphors under excitation wavelengths of 350 nm. The emission spectra ($\lambda_{\text{ex}}=350 \text{ nm}$) exhibits small band at blue region 486 ($^4\text{F}_{9/2}-^6\text{H}_{15/2}$ transition) and a large Yellow region ($^4\text{F}_{9/2}-^6\text{H}_{13/2}$ transition) 574 [23]. The transition corresponding to blue emission was magnetically allowed and hardly varies with the crystal field strength around the Dy^{3+} ion [24-26]. Whereas, the transition corresponding to yellow emission belongs to the hypersensitive (forced electric dipole) transition with the selection rule $D_J = 2$, which was strongly influenced by the outside surrounding environment. When Dy^{3+} ion was located at a low-symmetry local site (without inversion center), yellow emission is often dominant. In the present study, since the yellow emission was dominant, the Dy^{3+} ions occupies lower symmetry local site in host matrix. The shape and position of Dy^{3+} emission peaks was found to be similar when $\text{Y}_2\text{O}_3:(\text{Dy}^{3+} 0.5 \text{ mol}\%, \text{Li}^+ (0.2\text{--}2.0 \text{ mol}\%))$ nanophosphors with change in Li^+ concentration.

It shows further increase in PL intensity of singly doped $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ (0.5 mol%) which is the optimum concentration of Dy^{3+} in Y_2O_3 . These metal ions (M^+) are likely to occupy the C_2 sites (Figure 5.8) of the Y_2O_3 lattice, which relates with the yellow luminescence emission at 574 nm approximately [23]. As the ionic radii of these metal ions are smaller or nearly equal to that of Y^{3+} (90 pm) (Table 5.1(d)), the incorporation of these ions reduces the symmetry of C_2 sites (Figure 5.8), as metal ions have +1 charge in comparison to +3 charge of Y^{3+} . So this creates oxygen vacancy which suggests that parity selection rule is broken and luminescence intensity increases further [38]. However, when the content of these metal ions increases further beyond certain limit, the oxygen vacancies of host lattice increase accordingly, which may destroy the powder crystallization and lead to the decrease of luminescence intensity.

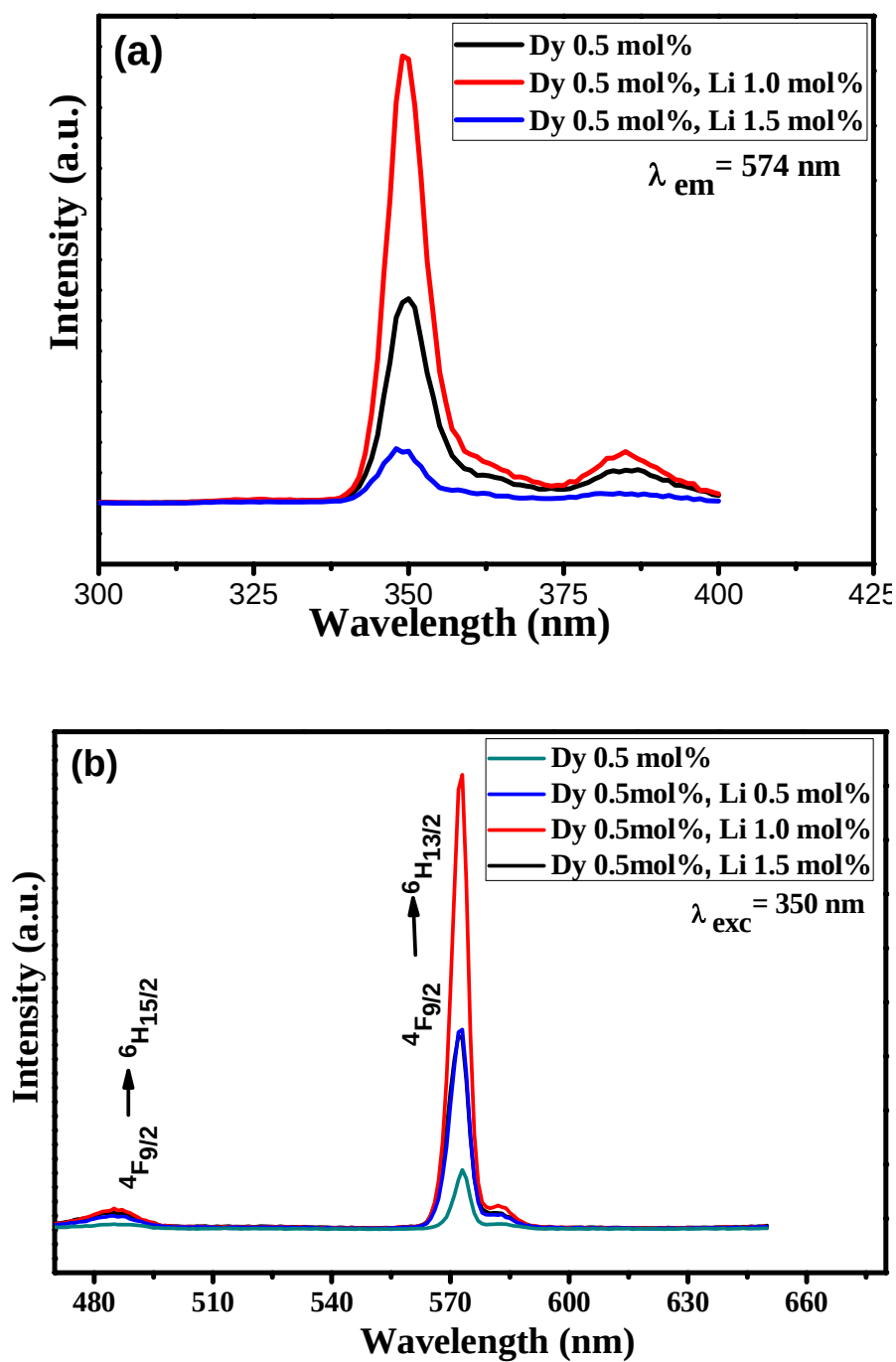


Figure 5.18: PL (a) excitation and (b) emission spectra of $\text{Y}_2\text{O}_3:(\text{Dy}^{3+} 0.5 \text{ mol}\%, \text{Li } 0.2 - 1.5 \text{ mol}\%)$.

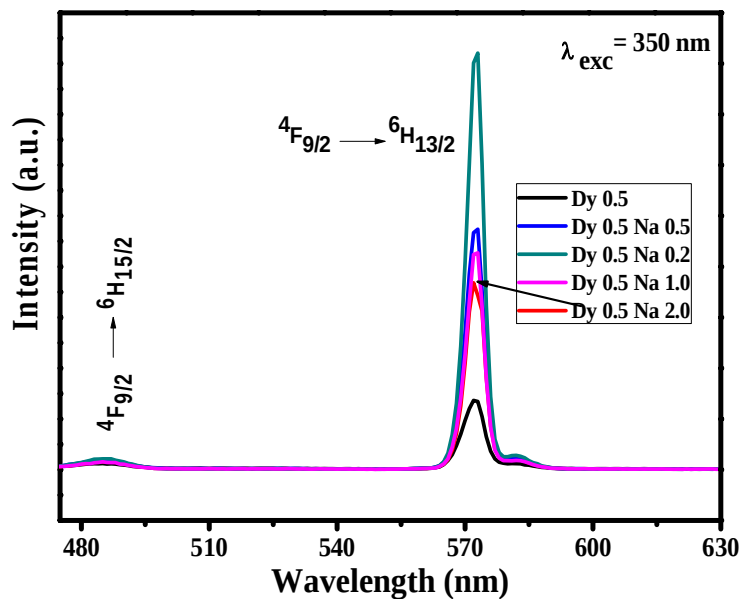


Figure 5.19: PL emission spectra of $\text{Y}_2\text{O}_3:(\text{Dy}^{3+} 0.5 \text{ mol}\%, \text{Na}^+ (0.2-2.0 \text{ mol}\%))$.

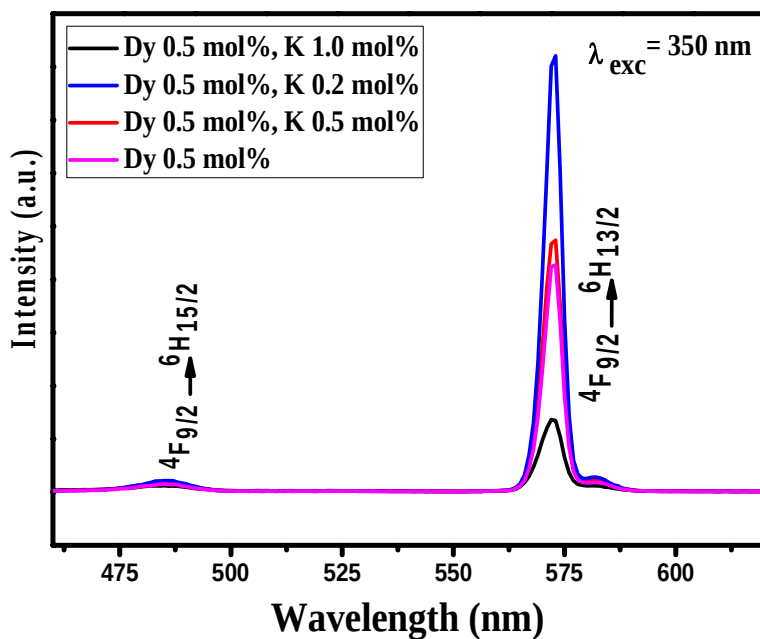


Figure 5.20: PL emission spectra of $\text{Y}_2\text{O}_3:(\text{Dy}^{3+} 0.5 \text{ mol}\%, \text{K}^+ (0.2-1.0 \text{ mol}\%))$.

Figure 5.21 shows the PL emission spectra of $\text{Y}_2\text{O}_3:(\text{Dy}^{3+} 0.5 \text{ mol}\%)$, $\text{Y}_2\text{O}_3:(\text{Dy}^{3+} 0.5 \text{ mol}\%, \text{Li}^+ 1.0 \text{ mol}\%)$, $\text{Y}_2\text{O}_3:(\text{Dy}^{3+} 0.5 \text{ mol}\%, \text{Na}^+ 0.5 \text{ mol}\%)$ and $\text{Y}_2\text{O}_3:(\text{Dy}^{3+} 0.5 \text{ mol}\%, \text{K}^+ 0.2 \text{ mol}\%)$ under an excitation of 350 nm. Emission intensity of $\text{Y}_2\text{O}_3:(\text{Dy}^{3+} 0.5 \text{ mol}\%, \text{Na}^+ 0.5 \text{ mol}\%)$ annealed at 1000 °C under excitation of 350 nm sample is maximum.

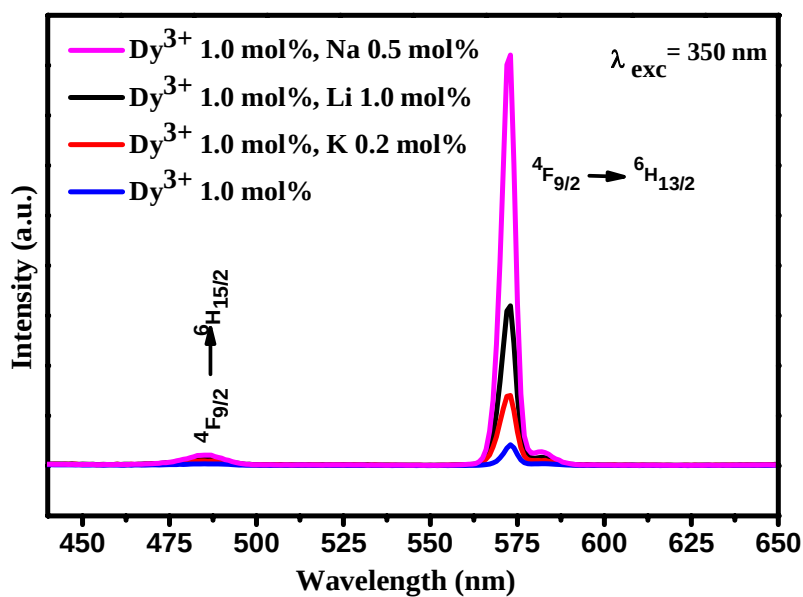


Figure 5.21: Emission spectra of $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$, $\text{Y}_2\text{O}_3:\text{Dy}^{3+}/\text{Li}^+$, $\text{Y}_2\text{O}_3:\text{Dy}^{3+}/\text{Na}^+$ and $\text{Y}_2\text{O}_3:\text{Dy}^{3+}/\text{K}^+$ annealed at 1000 °C.

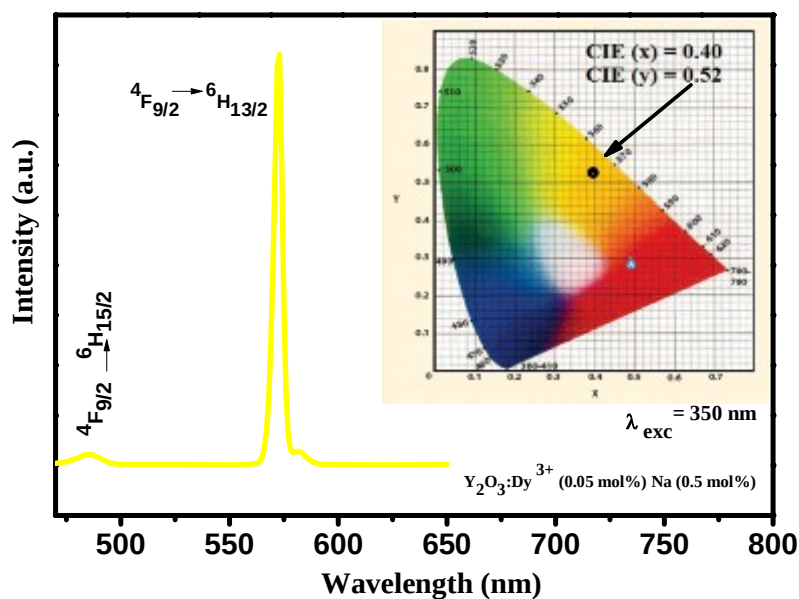


Figure 5.22: Chromaticity diagram of (a) $\text{Y}_2\text{O}_3:(\text{Dy}^{3+} 0.5 \text{ mol}\%, \text{Na}^+ 0.5 \text{ mol}\%)$ annealed at 1000 °C.

The CIE parameter such as color coordinates was calculated in order to know the photometric characteristics of the prepared phosphors. The values of CIE (x, y) parameters (Figure 5.22) for the $\text{Y}_2\text{O}_3:(\text{Dy}^{3+} 0.5 \text{ mol}\%, \text{Na}^+ 0.5 \text{ mol}\%)$ phosphors are (0.40, 0.52).

This chapter describes the optical and morphological properties of $\text{Y}_2\text{O}_3:\text{RE}^{3+}$ codoped with alkali metal ions ($\text{M}^+ = \text{Li}^+, \text{Na}^+$ and K^+). In the detail description of this chapter

few points are important that need to be summarized systematically at the end. The basic aim of this chapter is to study the effect on optical properties of RE^{3+} doped Y_2O_3 due to the co-doping of alkali metal ions. In chapter 4, we have seen that due to concentration quenching phenomenon amount of activator in a host is limited, i.e. doping can enhance the emission intensity to a confined amount. In this chapter we have enhanced the emission intensity of RE^{3+} doped Y_2O_3 beyond the quenching concentration of the dopant without increasing dopant's concentration using metal ions at the time of synthesis. Addition of alkali metals has greatly enhanced emission intensity of red ($\text{Y}_2\text{O}_3:\text{Eu}^{3+}$), green ($\text{Y}_2\text{O}_3:\text{Tb}^{3+}$) and yellow ($\text{Y}_2\text{O}_3:\text{Dy}^{3+}$) phosphor (discussed in various section of this chapter). One more interesting observation is the effect of Na^+ ion doping on Y_2O_3 . Due to the presence of Na^+ ion the hydroxyl (OH^-) and nitro groups (NO_2^-) that are also called luminescent quenchers reduced to large extent which ultimately results in highest emission intensity of various $\text{Y}_2\text{O}_3:\text{RE}^{3+}$ nanophosphors which were codoped with Na^+ ion at the time of synthesis. In this chapter, the effect of alkali metals (Li^+ , Na^+ & K^+) ions on morphology and optical properties of Y_2O_3 has been described and effect of surface modifier (surfactant and polymer) at the time of synthesis has not been studied. As a result the morphology and the particle size could not be controlled which resulted in uncontrolled growth of rod like morphology in the prepared samples as shown in TEM (Figure 5.3 & 5.4). In the next chapter, different surface modifiers were used to observe their effect on optical and morphological properties of doped Y_2O_3 nanophosphor.

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CHAPTER 6

RESULTS AND DISCUSSION

Effect of surface modifiers (surfactants and polymers) on optical and morphological properties of doped Y_2O_3 nanophosphors

Overview

This chapter describes the effect of various surface modifiers (polymers and surfactants) on optical and morphological properties of doped Y_2O_3 nanophosphors. In the previous chapters' effect of various parameters (e.g. doping, annealing temperature and co-doping metal ions) were studied on optical properties of doped Y_2O_3 nanophosphors. However, in all the prepared samples since no surface modifier was used at the time of synthesis, uncontrolled growth of nanophosphors were observed as studied from TEM and SEM. Many researchers have used various polymers/surfactants to control the growth of nanoparticles during synthesis. However detailed study in this direction is still required. This chapter describes the use of various polymers and surfactants at the time of synthesis and explains the effect of these modifiers on optical and morphological properties of Y_2O_3 doped nanostructures. All the prepared samples were characterized by XRD, FTIR, SEM and TEM to study the structural and morphological properties, PL spectroscopy was employed to study the optical properties of these samples. CIE color co-ordinates of the prepared NPs were also calculated to see the usefulness of the prepared phosphors for their various applications.

6.1 Introduction

Nanocrystalline particles exhibit many novel physical properties not found in bulk materials [1, 2]. These nanoparticles are of significant interest from the fundamental point of view for the phosphor's technological applications. Among various rare-earth oxides, yttrium oxide (Y_2O_3) is a promising alternative host matrix for luminescence, which has a great application prospect in commercial lighting and display devices, due to its high chemical stability, low thermal expansion and phonon energy [3, 4]. Luminescent properties of an optical host strongly depend on the structure and morphology of the crystals. By adjusting different morphologies of the host material, the relative intensity of the emission peaks can be effectively controlled. Therefore, the controllable synthesis of Y_2O_3 with well-defined morphology and narrow size distribution via a rapid, simple, and mass production method is a great challenge.

From previous chapters, it is concluded that PL emission intensity of doped Y_2O_3 nanophosphors depends upon crystalline behavior of the host Y_2O_3 . To achieve better crystallinity, the as prepared powder of Y_2O_3 needs to be annealed at higher temperature ($> 600\text{ }^\circ\text{C}$). With increase in annealing temperature the crystallite size of the Y_2O_3 also increases gradually. This behavior of the phosphor restricts its use in many applications. The urge to overcome this shortcoming has turned the study towards the use of surface modifiers (SMs) at the time of synthesis. Moreover, synthesized 'as prepared' nanopowders must be annealed to get higher crystallinity. However, control on crystallite size during annealing is not possible. Considering these facts to control the size of NPs during synthesis i.e during the time of precipitation of NPs different SMs have been used.

To date, numerous efforts have been made to explore various convenient and efficient approaches for the preparation of different inorganic crystals in nano-dimensions with different shapes [5-7]. In these techniques, the use of organic additives as the shape modifier is a common strategy to adjust and control the morphology and size of the products. Organic molecules are known to either promote or inhibit crystal growth by modifying its surface. By properly choosing organic additives that might have specific molecular complementarity with their inorganic counterparts, the growth of the crystals can be rationally directed to yield products with desirable morphologies and/or hierarchical structures [8]. Therefore, for improving the interaction of the dopant impurities with the host matrix, quantum confined nanostructures are desired, which is the main focus of in this work. In the current work,

doped Y_2O_3 nanophosphor was synthesized by modified co-precipitation method. Different SMs (Poly vinyl pyrrolidone (PVP), 1-Thio-glycol (TG), Betacyclodextrin (β -cyclo), Polyethylene glycol (PEG), Cetyl trimethylammonium bromide (CTAB) and Trioctylphosphine oxide (TOPO)) with varying molar concentration have been used during synthesis in order to improve the morphology and luminescence of the doped Y_2O_3 nanophosphor. The structural, morphological and luminescent properties were studied using X-ray diffractometer (XRD), Fourier transform infrared spectroscopy (FT-IR), High resolution transmission electron microscope (HRTEM), steady state and time resolved photoluminescence (PL) measurement techniques. XRD studies and Rietveld refinement confirmed the body-centered cubic structure of doped phosphors. With systematic structural and optical characterizations it has been observed that addition of SMs has enhanced the luminescent intensity of doped Y_2O_3 nanophosphors. These modifications in the synthesis route have resulted to achieve enhanced luminescence from Y_2O_3 nanophosphors along with high crystallinity and almost spherical morphology which increases the potentiality of this phosphor in biological fields and innovative display applications.

6.2 Effect of PVP and TG on optical and morphological properties of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphors

6.2.1 Introduction

RE^{3+} doped $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ is prepared by facile yet modified co-precipitation method. In this section we have used different molar concentration of Poly vinyl pyrrolidone (PVP) and 1-Thio-glycol (TG) as capping agents to study their effect on optical and morphological properties of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphors. In addition, variation of pH was studied to control the particle size of the synthesized product. The polymer concentration (TG and PVP) was also optimized at different pH to get higher luminescence of Eu^{3+} doped Y_2O_3 NPs. For simplicity we have given codes to prepared samples as discussed in chapter 3 (experimental techniques) and is briefly given here. The results of various characterized samples are discussed below.

6.2.2 XRD studies

Figure 6.1 shows X-ray diffraction patterns for (a) S₅, (b) P_{c5} and (c) T_{c5} NPs. It shows that all of the samples prepared are in good agreement with the standard data of the pure body-centered cubic phase of Y₂O₃. The XRD peaks were identified and indexed according to the JCPDS file No 83-0927.

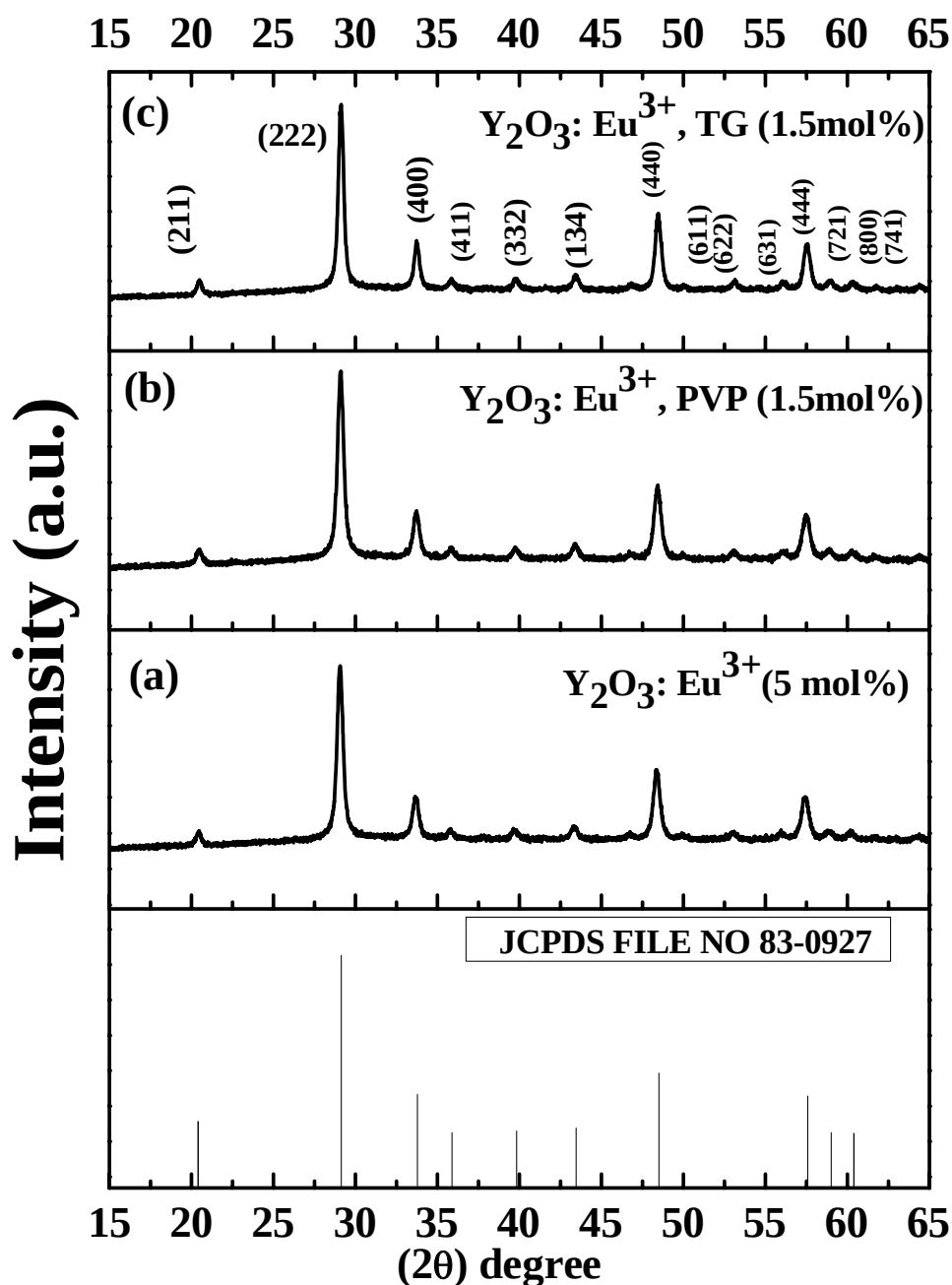


Figure 6.1: XRD pattern of (a) S₅, (b) P_{c5} and (c) T_{c5} samples annealed at 1000 °C.

The sharp diffraction peaks in XRD confirm the formation of single phase Y_2O_3 , which is attributed to the high and uniform heating during the annealing process. Moreover, all the prepared samples are having body-centered cubic structure of $Y_2O_3:Eu^{3+}$ with space group (Ia-3). The peak at $2\theta \sim 29.5^\circ$ is the strongest peak corresponding to the plane (2 2 2).

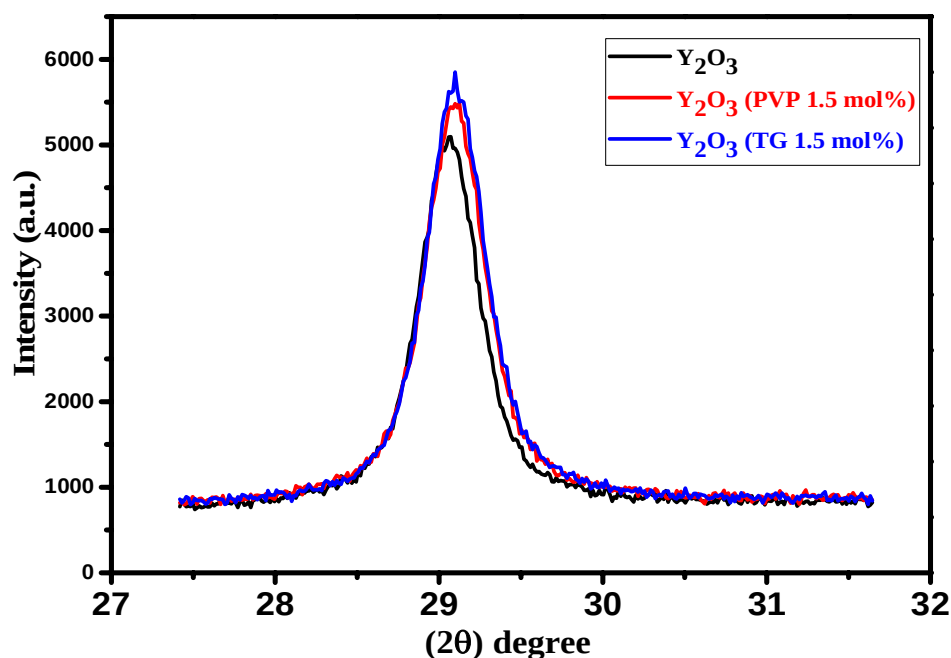


Figure 6.2: XRD pattern of (a) S_5 , (b) P_{c5} and (c) T_{c5} samples around 29° corresponding to peak 222.

However, the lattice parameter of the doped samples slightly increased. This is understandable as ionic radius of Eu^{3+} ($0.91\text{\AA}$) is greater than that of Y^{3+} ($0.90\text{\AA}$) [25]. However, systematic increase in the lattice parameter also reveals that these ions are substituted at the Y^{3+} site in the lattice. Figure 6.2 gives the detail description of polymer effect on crystallite size of Y_2O_3 . By studying peak (222) position around 29° it is clear that sample prepared by adding TG has shown high peak intensity and peak width. This means that samples prepared by adding TG showed better crystallinity and smaller crystallite size as compared to other samples. Similar characteristics were also seen in other peaks of sample prepared by TG. The average crystallite size calculated from Debye-Scherrer relation for sample S_5 , P_{c5} and T_{c5} are 45.2 nm, 37.3 nm and 24.6 nm respectively.

6.2.3 Rietveld Refinement

To affirm that the structure is truly of cubic type, a structural refinement by the Rietveld method [9] using the Fullprof Program was performed [10]. The structural refinement results for the sample P_{c7} is shown in Figure 6.3.

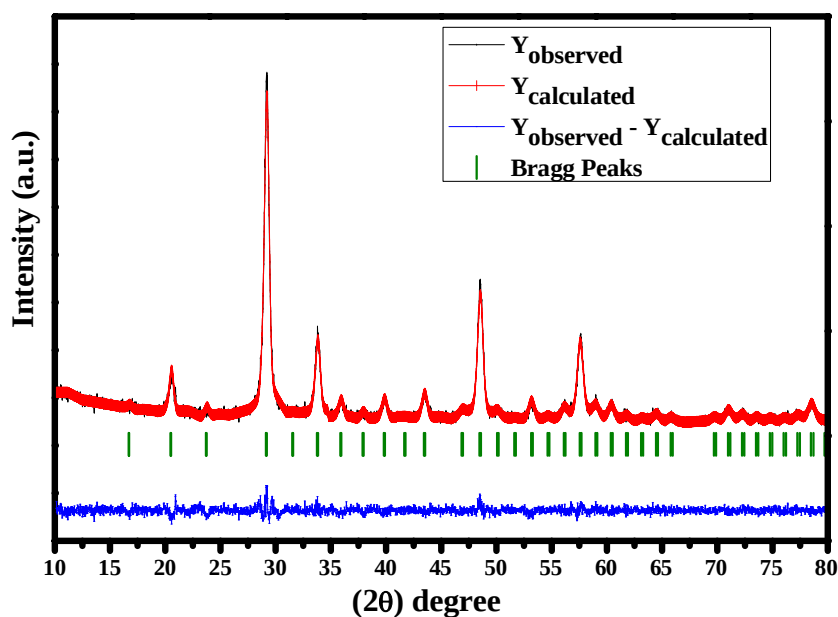


Figure 6.3: Refinement data of P_{c7} sample.

The results are in good agreement with the observed and calculated values. The superiority of structural refinement data [10, 11] was checked by determining a parameter called goodness of fit (GOF), which is given as $GOF = R_{wp}/R_{exp}$ [12]. For errorless refinement the GOF essentially approaches unity. In the present case, the GOF was found to be 1.31 for P_{c7} .

6.2.4 FT-IR analysis

FT-IR spectra of the prepared phosphors are shown in Figure 6.4. It corresponds to sample (a) T_{c5} , (b) P_{c5} , (c) S_5 and (d) as-prepared $Y_2O_3: Eu^{3+}$ (at room temperature). The absorption band centered at 560 cm^{-1} is attributed to Y–O lattice vibration [13]. The peaks at 850 cm^{-1} and the others at 1021,

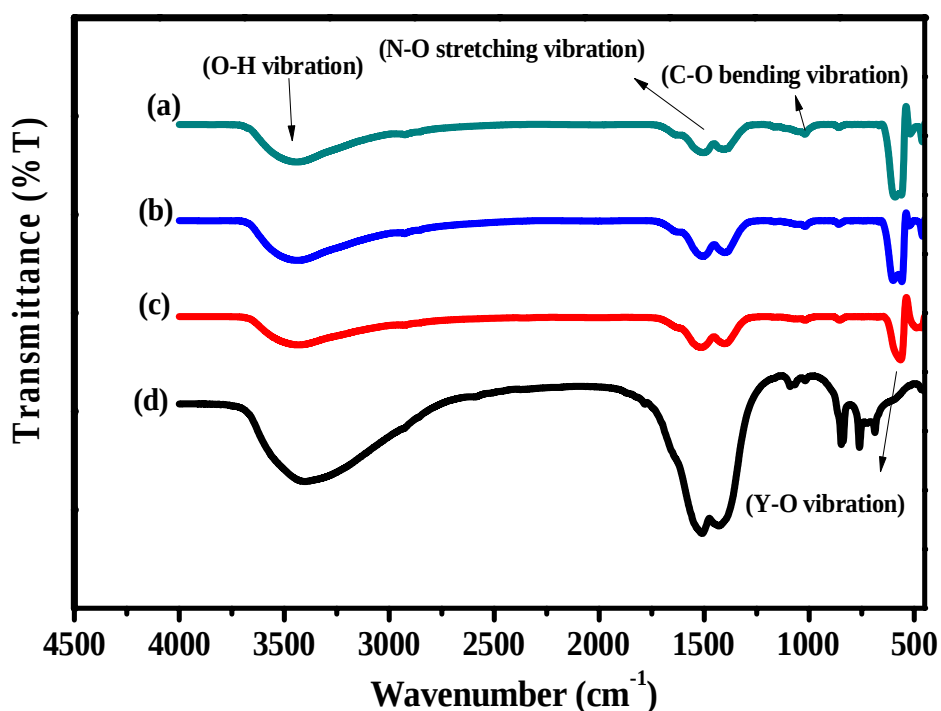


Figure 6.4: FT-IR spectra of (a) T_{c5} (b) P_{c5} (c) S₅ annealed at 1000 C° and (d) Y₂O₃:Eu³⁺ (as prepared).

1395 and 1520 cm⁻¹ are due to N–O symmetric and un-symmetric bending vibration respectively [13]. The broad band at 3430 cm⁻¹ is assigned to O–H stretching vibration [13]. The residual hydroxyl groups (–OH) at 3550 cm⁻¹ and the nitro group (1395 and 1520 cm⁻¹) are responsible for the quenching of rare earth emission and thereby decreasing the luminescence intensity. However, this band becomes weaker with increase in annealing temperature and disappears at higher temperatures [13]. From Figure 6.4 it is clear that both these bands in sample T_{c5} are small as compared to other samples. Moreover, the Y–O band at 560 cm⁻¹ is also strong for sample T_{c5} as compared to other samples. Strong Y–O band at 560 cm⁻¹ band support the fact that Y₂O₃ crystal is highly crystalline. From these observations it is concluded that addition of TG during synthesis helped in getting better crystallinity and phase purity for Y₂O₃ phosphor.

6.2.5 TEM micrographs

For detailed morphological studies TEM micrographs were recorded. Figure 6.5 represents TEM micrograph of sample S₅. Since capping agent was not used at the time of synthesis so

agglomeration of particles can be observed in this case. Figure 6.6 (a, b) shows bright and dark field TEM micrograph of sample P_{c5} . Both these micrographs show fine size particles exhibiting spherical to faceted morphology with little agglomeration in the sample. Particle size calculated from TEM micrograph varies from 25-35 nm which matches well with XRD data. Figure 6.7 shows (a) bright and (b) dark field view of TEM micrograph of P_{c9} sample annealed at 1000 °C. Large agglomerated particles can be seen in both these micrographs due to increase in pH (pH 9) of the sample P_{c9} . Figure 6.8 (a, b) shows bright and dark field TEM micrograph of sample T_{c5} showing nanoparticles with size range varying from 15-25 nm. Figure 6.9 shows the TEM micrograph of sample T_{c9} . Hefty agglomeration of particles can be observed due to increase in pH of the solution at the time of synthesis. The SAED pattern of sample P_{c5} as shown in Figure 6.10 exhibits sharp rings corresponding to diffraction from different planes of the nanocrystallites instead of spots due to the random orientation of the crystallites. The observed three rings correspond to (211), (222) and (400) lattice planes of the cubic phase Y_2O_3 , which is in good agreement with the XRD patterns discussed earlier.

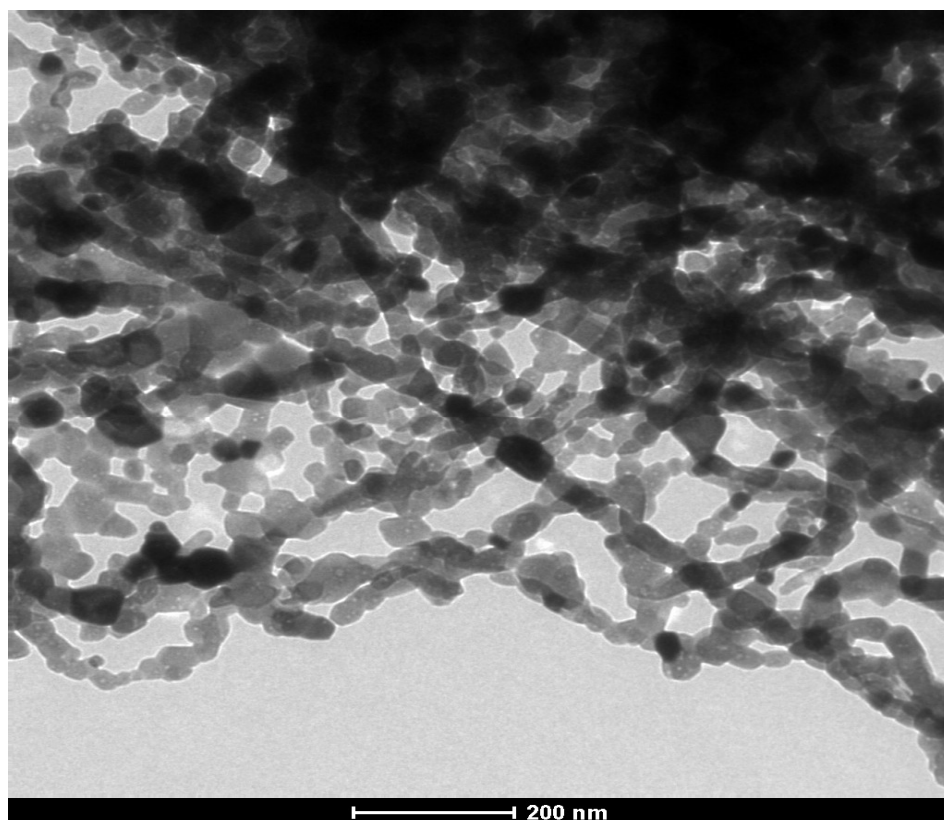


Figure 6.5: TEM image of S_5 sample annealed at 1000 °C.

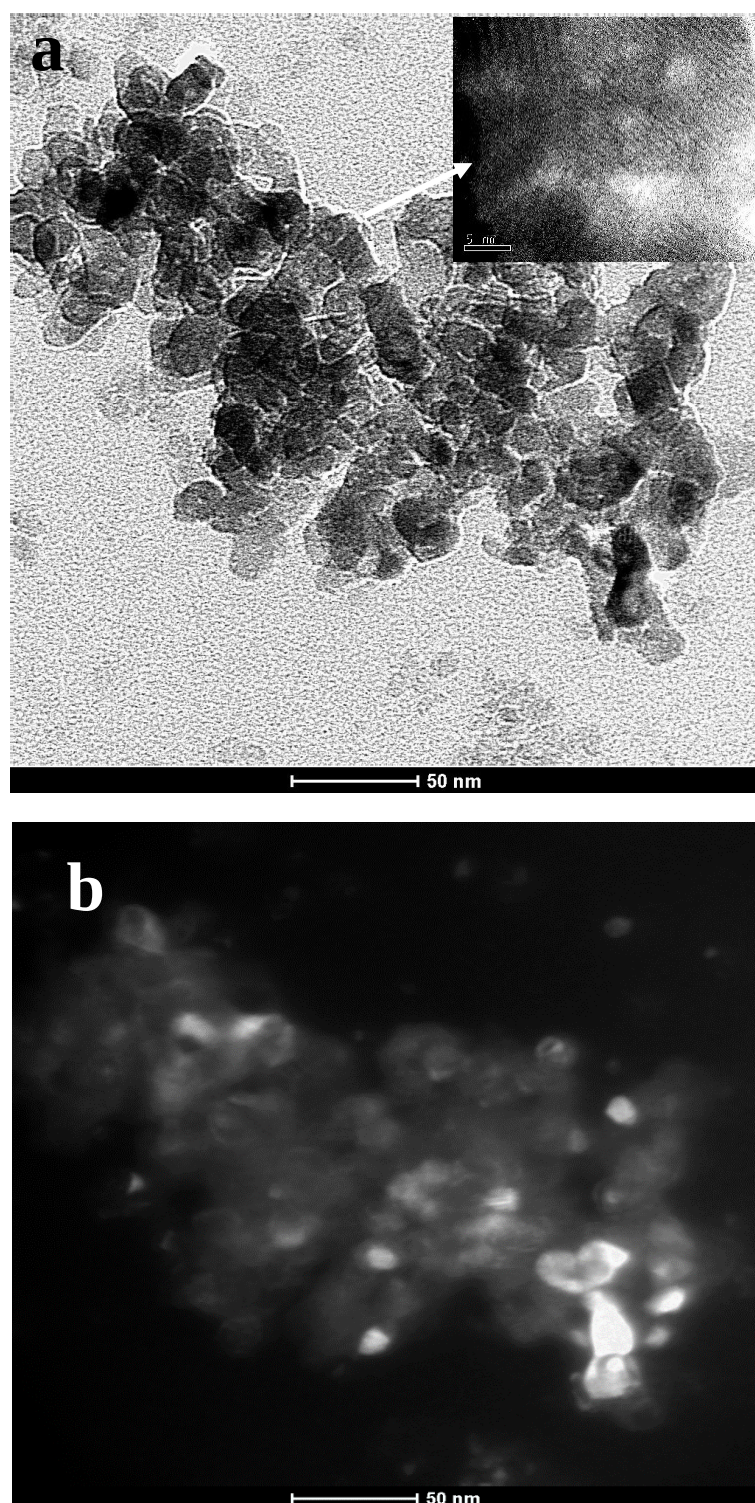


Figure 6.6: (a) Bright and (b) dark field view of TEM micrograph of P_{c5} sample annealed at 1000 °C.

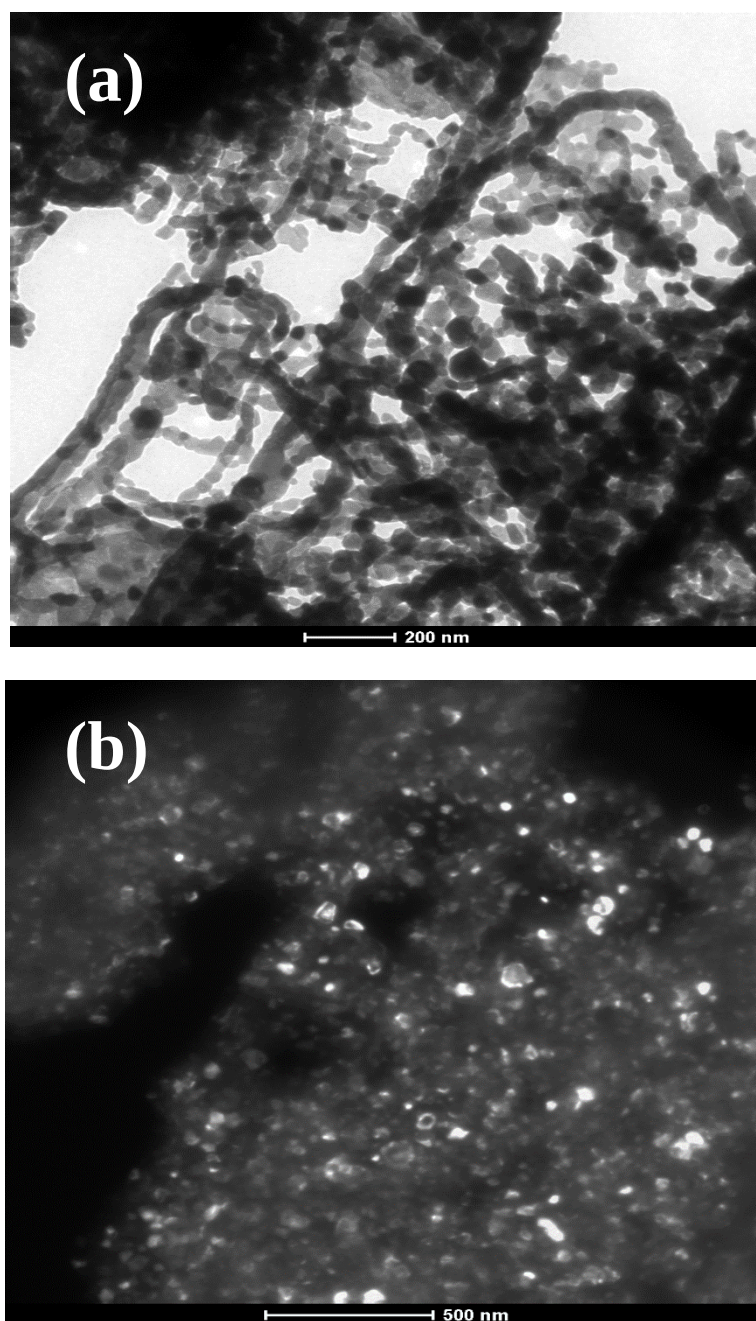


Figure 6.7: (a) Bright and (b) dark field view of TEM micrograph of P_{C9} sample annealed at 1000 °C.

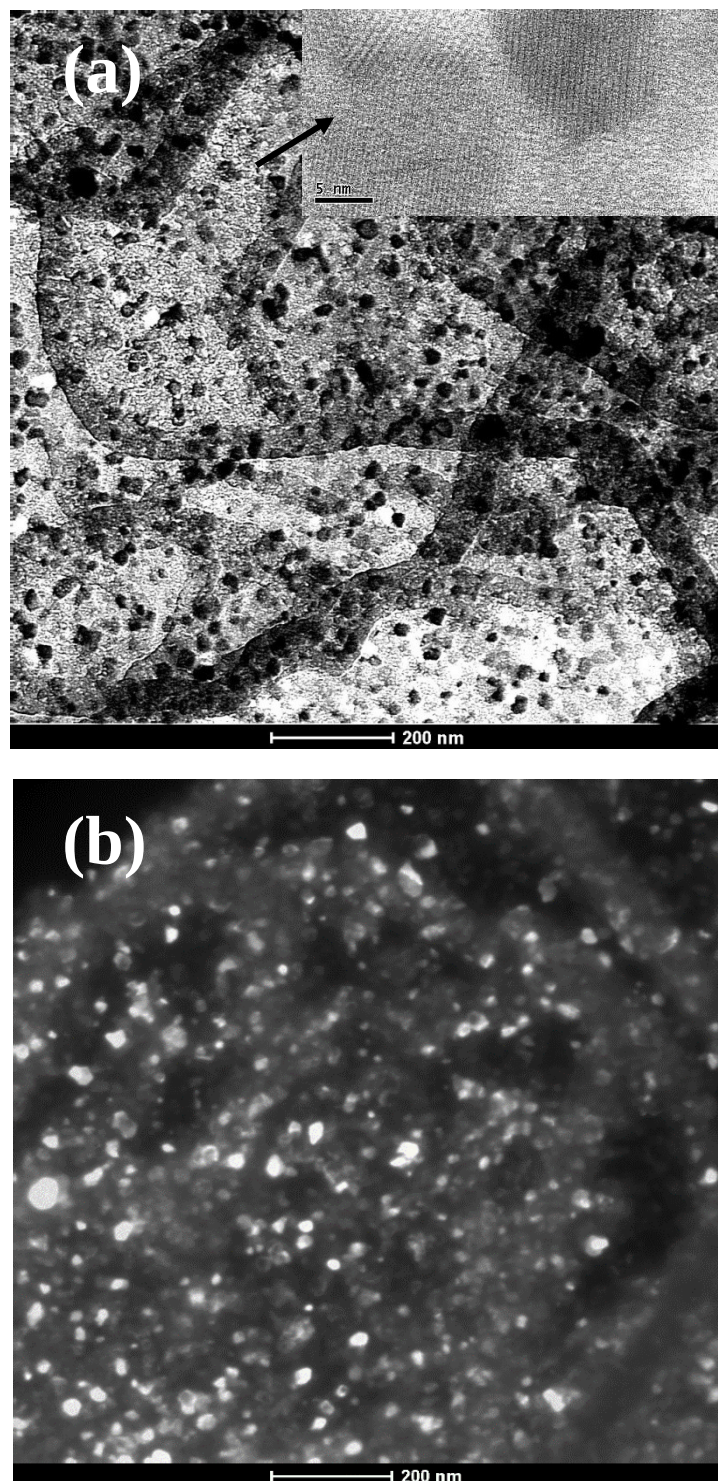


Figure 6.8: (a) Bright and (b) dark field view of TEM micrograph of T_{c5} sample annealed at 1000 °C.

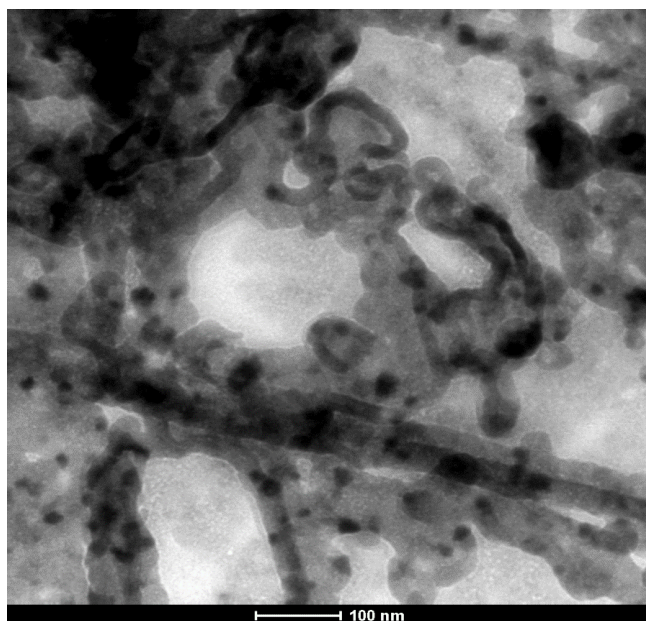


Figure 6.9: TEM micrograph of T_{c9} sample annealed at 1000 °C.

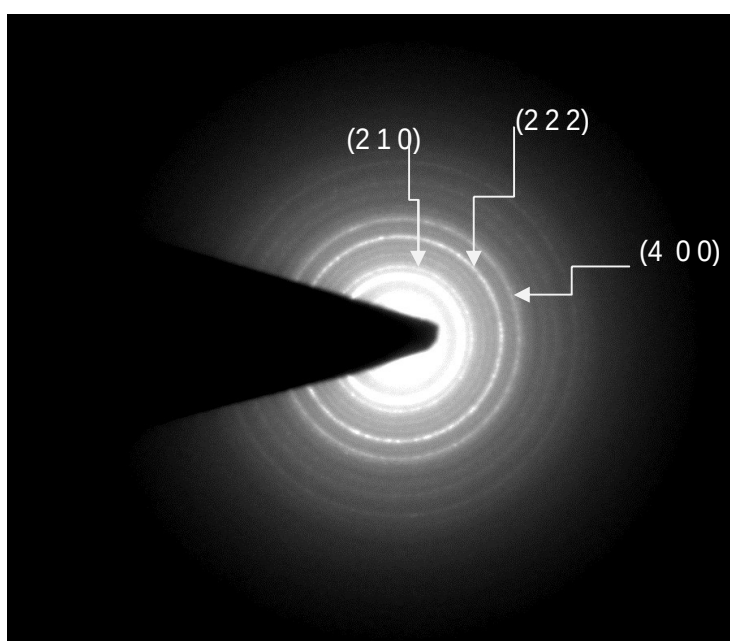
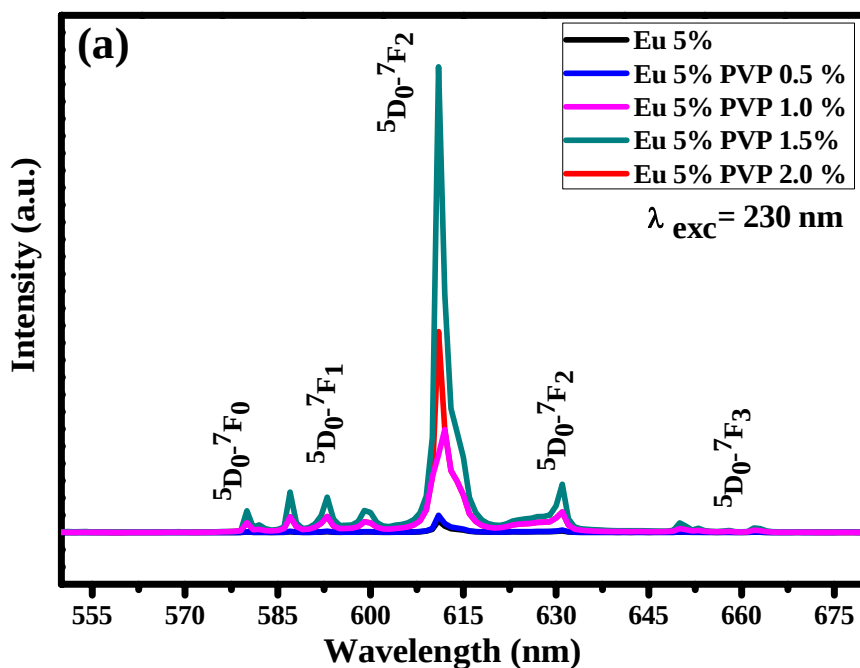


Figure 6.10: SAED pattern of P_{c5} sample.

6.2.6 Photoluminescence

Room temperature PL emission spectra of the prepared phosphors in powder form annealed at 1000 °C at excitation wavelength (λ_{exc}) of 230 nm are shown in Figure 6.11 and 6.12. Figure 6.11 shows the PL emission spectra of sample S₇ along with (a) P_{a7}, P_{b7}, P_{c7} and P_{d7} and (b) T_{a7}, T_{b7}, T_{c7} and T_{d7} samples. It is noteworthy that the addition of polymer during synthesis has increased the Eu³⁺ emission intensity ($\lambda_{\text{em}} = 611$ nm) in Y₂O₃ to nearly two to three times as compared to samples prepared without polymer content at constant pH 7. Samples P_{c7} and T_{c7} have shown maximum luminescence as shown in Figure 6.11 (a & b). Moreover, to study the effect of pH during synthesis on luminescence of Y₂O₃:Eu³⁺ (5.0 mol %) fired at 1000 °C, samples of Y₂O₃:Eu³⁺ (5.0 mol %) annealed at 1000 °C with pH 5 and 9 at the optimum concentration of polymers (PVP - 1.5 mol% and TG - 1.5 mol %) were also prepared. Figure 6.12 (a & b) shows the PL emission spectra of samples (a) P_{c5}, P_{c7}, P_{c9} and (b) T_{c5}, T_{c7}, T_{c9} respectively. Highest luminescence intensity is for samples P_{c5} and T_{c5} as shown in Figure 6.12 (a & b). Moreover, the PL intensity emission spectra of sample S₅, P_{c5} and T_{c5} are also shown in Figure 6.13. In all the above recorded PL emission spectra of Y₂O₃:Eu³⁺, the distinct emission lines lying between 550 nm and 650 nm were observed due to transitions from the excited ⁵D₁ to the ⁷F₁ and ⁵D₀ to the ⁷F_j (j = 0 – 3) levels of Eu³⁺ ions.



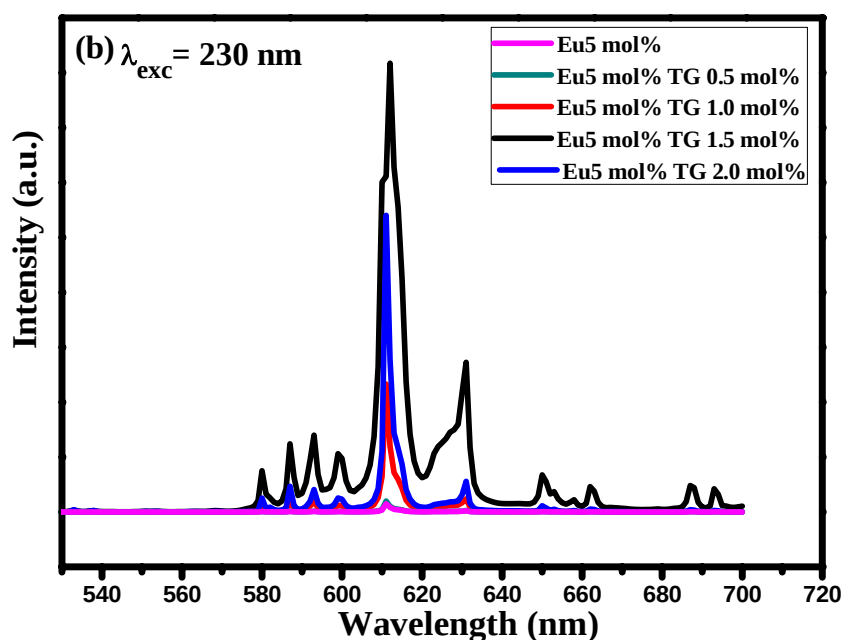


Figure 6.11: PL emission spectra of (a) P_{a7}, P_{b7}, P_{c7} and P_{d7} (b) T_{a7}, T_{b7}, T_{c7} and T_{d7} samples annealed at 1000 °C.

The origin of these transitions (electric dipole or magnetic dipole) from emitting levels to terminating levels depend on the location of Eu³⁺ ion in the Y₂O₃ lattice and the type of transition is determined by selection rules [14]. The strongest peak at 611 nm and a small peak at 630 nm correspond to the hypersensitive transition between the ⁵D₀ and ⁷F₂ levels of Eu³⁺ ion in the yttrium oxide host caused by the forced electric dipole transition mechanism. The feeble emission in the vicinity of 590 nm (590 nm – 600 nm) is ascribed to the magnetic dipole transition of ⁵D₀ to ⁷F₁. Generally, when Eu³⁺ is located at a low symmetry (without an inversion center), the 611 nm emission instead of 590 nm emission is dominant.

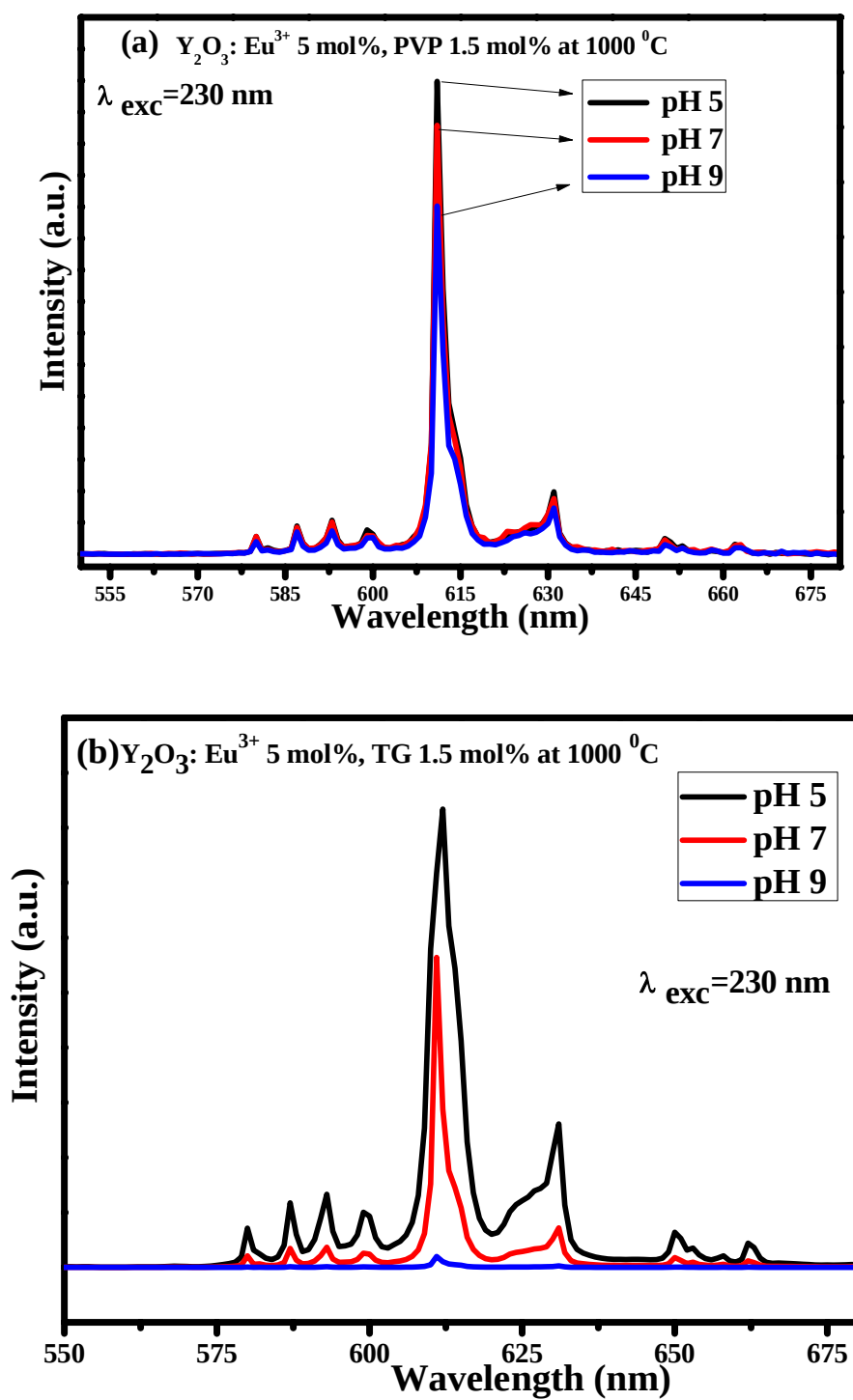


Figure 6.12: PL emission spectra of (a) P_{c5}, P_{c7}, and P_{c9} samples, (b) T_{c5}, T_{c7}, and T_{c9} samples annealed at 1000 °C.

However, the 590 nm emission is stronger than 611nm when Eu^{3+} is settled at a high symmetry (with an inversion center). In the present case, the emission at 611 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) is dominant suggesting that the location of Eu^{3+} diverts from the inversion symmetry, i.e. at low symmetry positions [15]. Earlier we have shown that emission intensity corresponding to 611 nm emission increases with increase in Eu^{3+} concentration up to certain percentage and then decreases due to quantum quenching effect [12]. Due to the defects produced during the synthesis process and impurities contained in the raw materials, the samples inevitably have quenching centers (traps) which stimulate non-radiative transitions and decrease the overall luminous efficiency. The quenching concentration of nano powders is mainly due to the unique properties of nanostructure that is, the quenching center traps are spread out randomly between particles. Some particles may contain many traps while others may contain no one. Due to the hindering effect of the particle boundaries, the Eu^{3+} luminescence quenching occurs first in particles bearing many traps. However, in particles containing fewer traps, Eu^{3+} luminescence quenches at high concentration. This indicates that doping concentration cannot be increased beyond certain limit for the enhancement in PL intensity.

In this investigation, water soluble polymers PVP and TG are used as capping agents. The role of these polymers is to control the growth of the precipitating particles and to prevent agglomeration by steric effect due to repulsive force acting among their groups. Therefore, these polymers try to encapsulate the precipitating particles by creating a restricted environment around the NPs [16]. To get pure crystalline phase, $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ NPs were heated at 1000 °C owing to which the organic polymers were removed forming nearly mono-dispersed NPs. Moreover, addition of extensive amount of PVP/TG on precipitating particle surface may induce the attraction among their polymeric chains due to the osmotic pressure. This phenomenon is known as “depletion flocculation”. It may create destabilization and hence decrease in luminescence of NPs [17]. For both PVP and TG, PL intensity of S_7 sample increases greatly with the increase in polymer concentration from 0.5 to 1.5 mol% and decreases considerably as the concentration of the polymer exceeds to 1.5 mol% as indicated in Figure 6.11 (a & b). In the presence of polymer the optimum luminescence of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (5.0 mol%) was obtained at pH 5. Here the particle size was of the order of 20-50 nm and agglomeration was also negligible as confirmed by TEM (Figure 6.6 and 6.8). Synthesis of NPs at higher pH (pH >7) with the optimum concentration of polymer have shown increase in agglomeration (Figure 6.7 & 6.9) and decrease in PL intensity (Figure 6.11 (a & b)). Moreover, T_{c5} has shown the maximum luminescence as compared to P_{c5} (Figure 6.13). This

may be due to nearly monodisperse nature of NPs synthesized with TG in comparison to PVP where few agglomerated particles are observed as can be seen in TEM (Figure 6.6 & 6.8). Moreover, XRD and FTIR studies reveal that this sample has shown better crystalline behavior, purity and smaller crystallite size as compared to other prepared samples. Many researchers have observed that luminescence of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ increases with decrease in particle size [18, 19]. In order to get highly luminescent particles of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ two things are necessary (a) small particle size with narrow size distribution and (b) spherical symmetry. However, to obtain pure crystalline phase of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ NPs, heat treatment above 600 °C is required [20]. With increase in temperature, size of the particles starts to increase from nano to micro range. This restricts their application in medical diagnostic, targeted therapeutics and in other display applications (due to decrease in luminescence). In this work, an attempt has been made to control the growth of NPs at the time of synthesis by optimizing polymer concentrations (PVP and TG) and pH (5, 7 and 9) to get maximum luminescence from $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (5.0 mol%) NPs. Moreover, by optimizing these conditions we have successfully shown improvement in the morphology and PL emission intensity of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (5.0 mol%). So far the study of PVP and TG molar concentration along with pH control on morphological and PL properties of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ were not done. In order to get maximum luminescence we have tried to optimize both these conditions systematically.

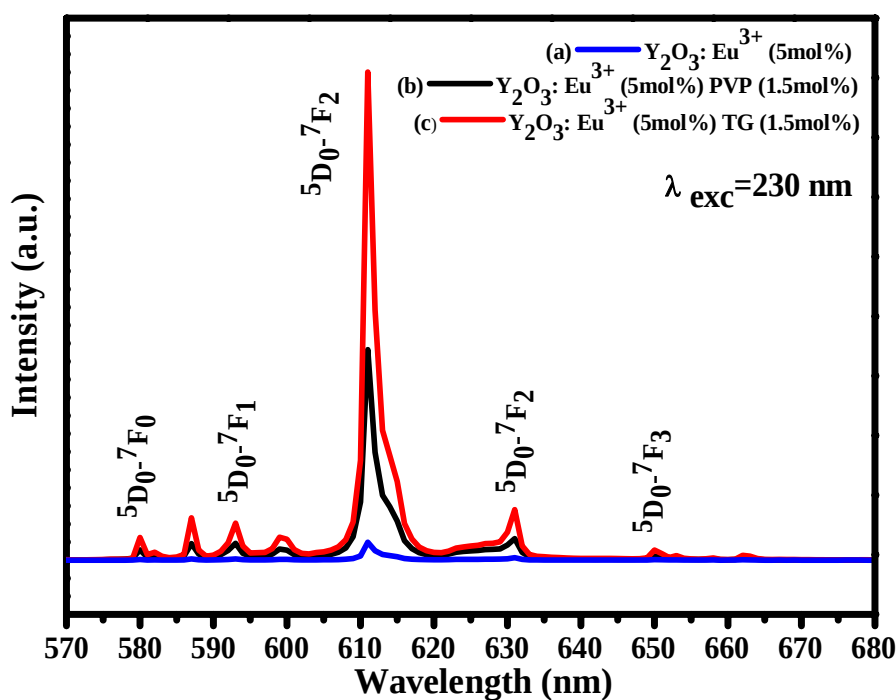


Figure 6.13: PL emission spectra of (a) S_5 , (b) P_{c5} and (c) T_{c5} samples annealed at 1000 °C.

The CIE chromaticity coordinates were calculated in order to know the photometric characteristics of the prepared phosphors. The values of CIE (x, y) parameters for the samples T_{c5} and P_{c5} are (0.66, 0.33) and (0.66, 0.34) respectively, which is very close to coordinates of ideal red (0.67, 0.33) [44]. In addition, the calculated CIE chromaticity coordinates are rather close to edge of CIE diagram (shown in inset of Figure 6.14), indicating that these kinds of phosphors shows better color purity in solid state lighting and are promising red phosphors.

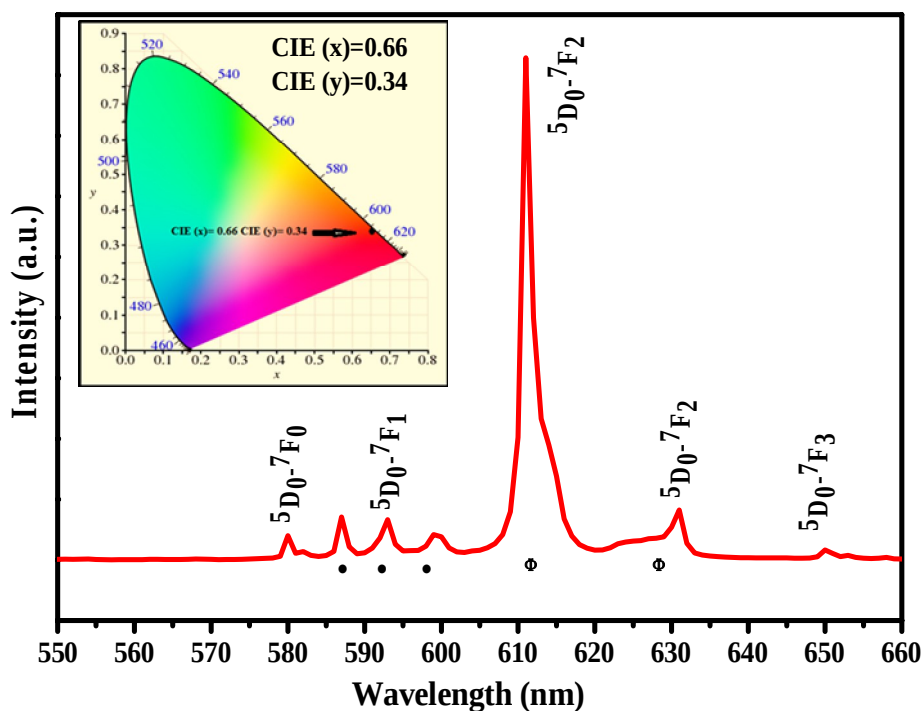


Figure 6.14: Chromaticity diagram of P_{c5} sample.

6.3 Effect of PEG and Betacyclodextrin on optical and morphological properties of $Y_2O_3:Eu^{3+}$ nanophosphors.

6.3.1 Introduction

Europium doped yttrium oxide ($Y_2O_3:Eu^{3+}$) is a promising red-emitting phosphor and is widely used in display devices, security inks, fluorescent lamps, and bio-imaging applications. In the current study, nano-sized and highly luminescent Eu^{3+} doped Y_2O_3 has been prepared. It has been observed that luminescence of the nanophosphors improved significantly when capping was done by betacyclodextrin (β -cyclo) and polyethylene glycol

(PEG). It got improved further by controlling the pH of the solution during synthesis. Hence, in the current work, we report the synthesis of highly luminescent $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ red-emitting nanophosphor by modified co-precipitation method in the presence of polyethylene glycol (PEG) and betacyclodextrin (β -cyclo) polymer. In order to enhance the luminescent properties the reaction conditions were varied systematically. The results are as discussed below.

6.3.2 XRD studies

Figure 6.15 shows the X-ray diffraction pattern of (a) S_5 (b) G_{c5} and (c) β_{c5} nanophosphor (NP) samples annealed at 1000 °C, respectively. The XRD peaks were identified and indexed according to the JCPDS file No 83-0927. The sharp diffraction peaks of the XRD pattern confirm the formation of single phase Y_2O_3 , which has been observed after uniform annealing. Moreover, all the prepared samples were found to be body-centered cubic structure of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ with space group Ia-3. The peak at $2\theta \sim 29.5^\circ$ was observed as the strongest peak corresponding to the plane (2 2 2). However, the lattice parameter of the doped samples was found to be slightly increased. This is understandable, as ionic radius of Eu^{3+} (0.91 Å) is more than that of Y^{3+} (0.90Å) [21]. However, systematic increase in the lattice parameter also reveals that these ions have successfully substituted for Y^{3+} site in the lattice. The mean crystallite sizes calculated from Debye-Scherrer relation for samples S_5 , G_{c5} and β_{c5} are 46.2 nm, 39.3 nm and 29.6 nm respectively. The decrease in the crystallite size of samples G_{c5} and β_{c5} as compared to S_5 may be due to presence of polymer at the time of synthesis whereas no polymer was added when S_5 samples were prepared.

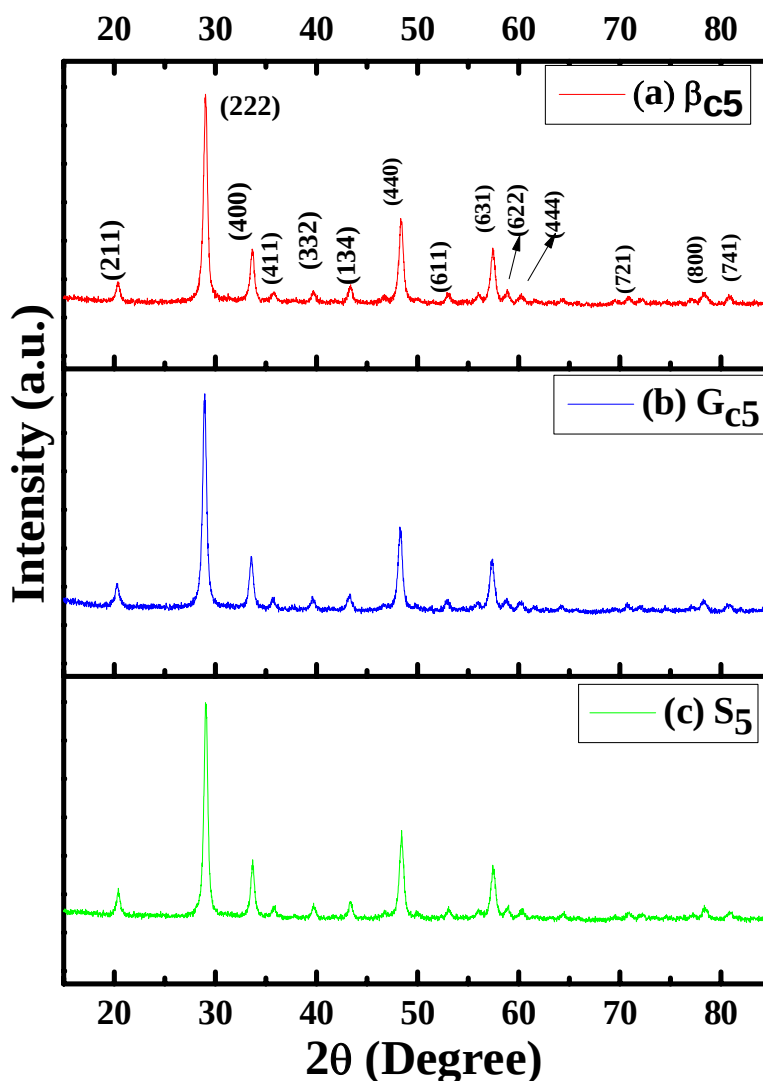


Figure 6.15: XRD pattern of (a) S_5 , (b) G_{c5} and (c) β_{c5} samples annealed at 1000 °C.

6.3.3 Rietveld Refinement

To affirm that the structure is truly cubic, the structural refinement by the Rietveld method [9] was performed using the Fullprof Program [10]. The structural refinement result for the β_{c5} sample is shown in Figure 6.16. The results are in good agreement between the observed and calculated values. The dominance of structural refinement statistics [10, 11] was tested by calculating a factor called goodness of fit (GOF), which is given as $GOF = R_{wp}/R_{exp}$. For accurate refinement the GOF should approach unity. In the present case, the GOF was found to be 1.27 for β_{c5} sample.

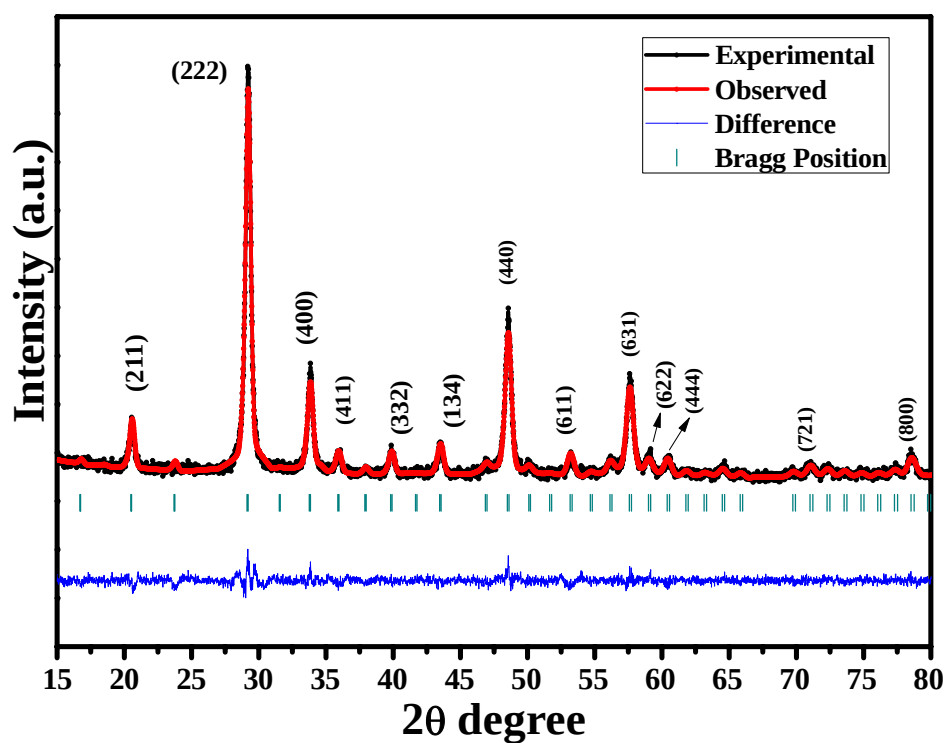


Figure 6.16: Refinement data of β_{c5} sample annealed at 1000 °C.

6.3.4 TEM study

For detailed morphological studies TEM micrographs of various samples were recorded. Figure 6.17 shows TEM micrograph of S_5 sample. Since no capping agent was used during the synthesis, highly agglomerated particles are observed in the micrograph.

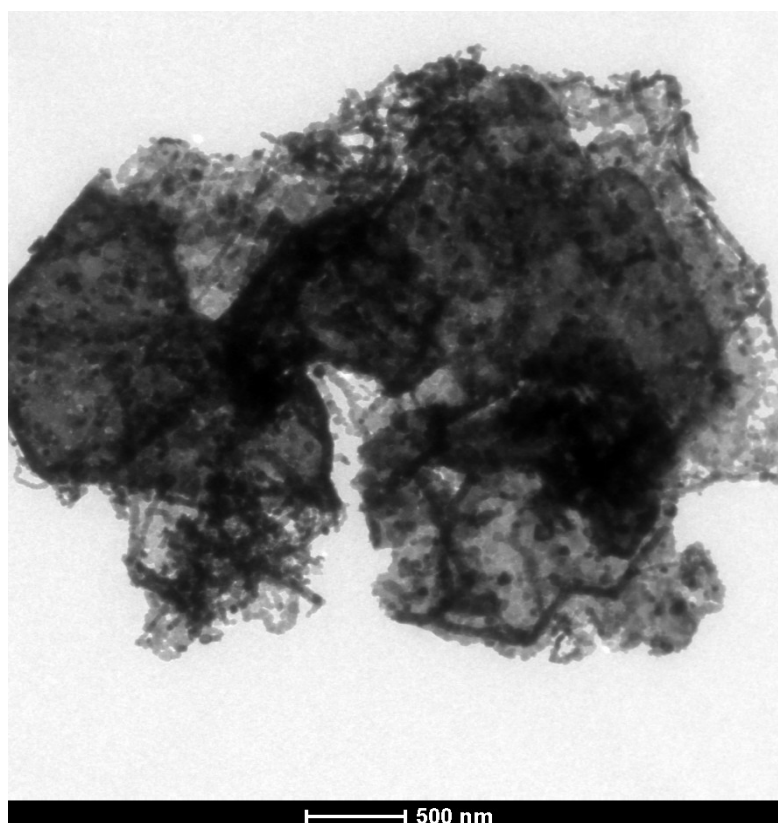


Figure 6.17: TEM image of S₅ sample annealed at 1000 °C.

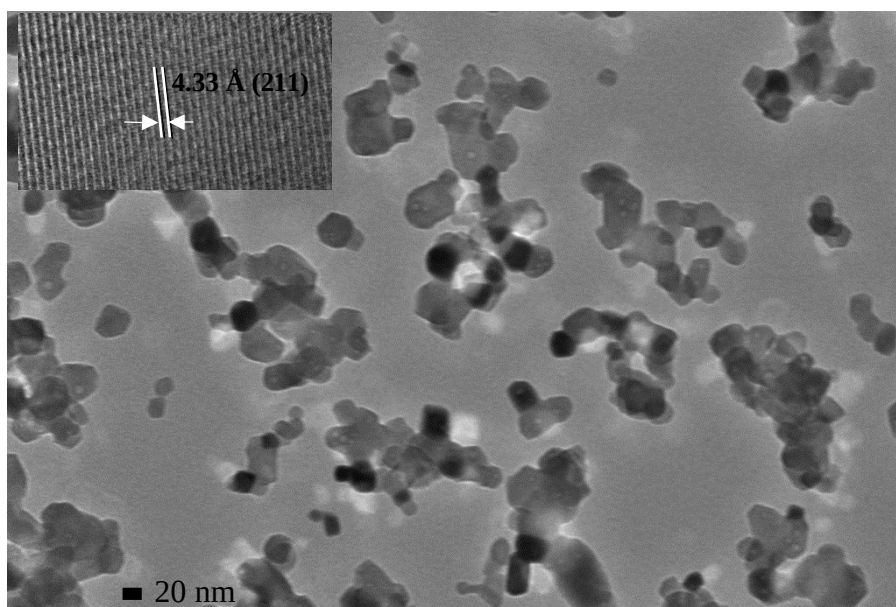


Figure 6.18: TEM micrograph of β_{c5} sample annealed at 1000 °C.

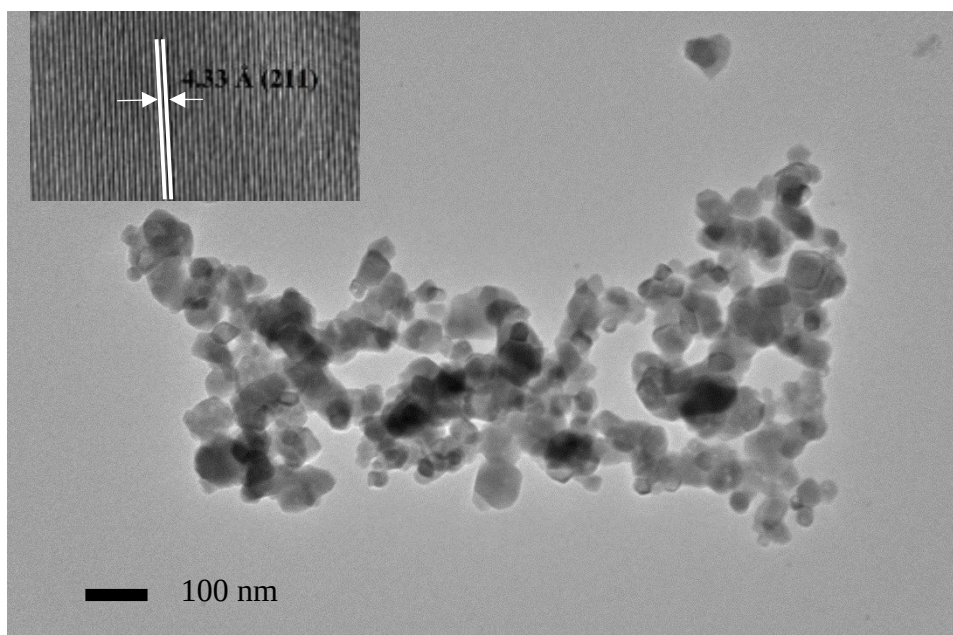


Figure 6.19: TEM micrograph of G_{c5} sample annealed at 1000 °C.

Figure 6.18 represents TEM micrograph of β_{c5} sample, which shows that the nanoparticles are nearly mono-disperse with size ranging between 20-40 nm. Figure 6.19 shows TEM micrograph of G_{c5} sample, where uniform sized particles exhibiting spherical to faceted morphology with petite agglomeration is observed. Particle size calculated from TEM micrograph varied between 20 to 50 nm, which is in consistent with the sizes calculated from XRD peak broadening. The inset of Figure 6.18 and 6.19 shows lattice fringes of 4.33 Å corresponding to (211) plane of Y_2O_3 , which further confirms the presence of highly crystalline phase of Y_2O_3 obtained after annealed at 1000°C.

6.3.5 UV visible spectrum

UV visible studies were done by determining the absorbance of the samples in wavelength range 200–800 nm. By analysing the transmittance data using the Manifacier Model [22, 23], the absorption coefficient (α) was calculated in the zone of intense absorption. To determine the band gap of synthesized NPs, the major absorption, which corresponds to the transition from valence band to the conduction band, was used. The relation between absorption coefficient (α) and incident photon energy ($h\nu$) is given by the relation

$$\alpha h\nu = A (h\nu - E_g)^n \quad (6.1)$$

where A is constant, α is the absorption coefficient and n depends on the type of transition

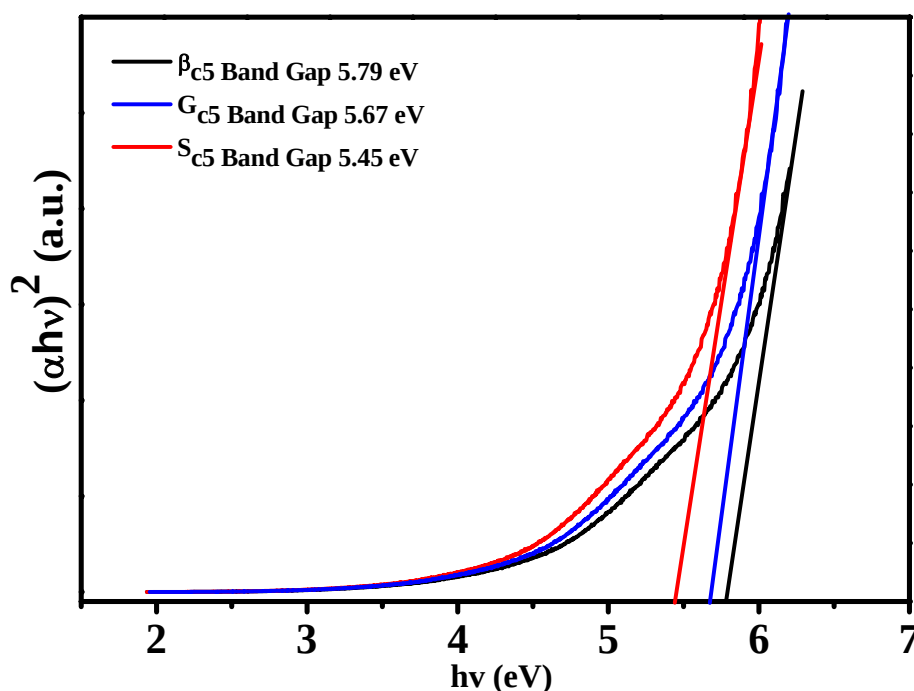


Figure 6.20: UV visible spectra of (a) S₅ (b) β_{c5} and (b) G_{c5} samples annealed at 1000 °C.

having values 1/2, 2, 3/2 and 3 corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect respectively [24]. The band gap was calculated by extrapolating the straight line portion of the $(\alpha h\nu)^{1/n}$ versus $h\nu$ graph. Figure 6.20 shows the graphs between $(\alpha h\nu)^2$ and $h\nu$ for samples S_{c5}, G_{c5} and β_{c5}. The band gap value for samples S_{c5}, G_{c5} and β_{c5} has been found to be 5.45, 5.67 and 5.79 eV respectively. Since the known band gap of the Eu³⁺ doped Y₂O₃ is 5.6 eV [25], the nominal increase in the band gap in samples G_{c5} and β_{c5} might be due to the decrease in size of NPs as polymers (PEG and β-cyclo) were added to control the growth of NPs at the stage of precipitation.

6.3.6 Photoluminescence

Room temperature photoluminescence (PL) excitation and emission spectra of the prepared phosphors in powder form are shown in Figure 6.21 (a & b) and 6.22 (a & b), respectively. The excitation spectrum (Figure 6.21(a) and 6.22 (a)) of Y₂O₃:Eu³⁺ at an emission wavelength of 611 nm corresponding to transition ⁵D₀ → ⁷F₂ of Eu³⁺ has been recorded.

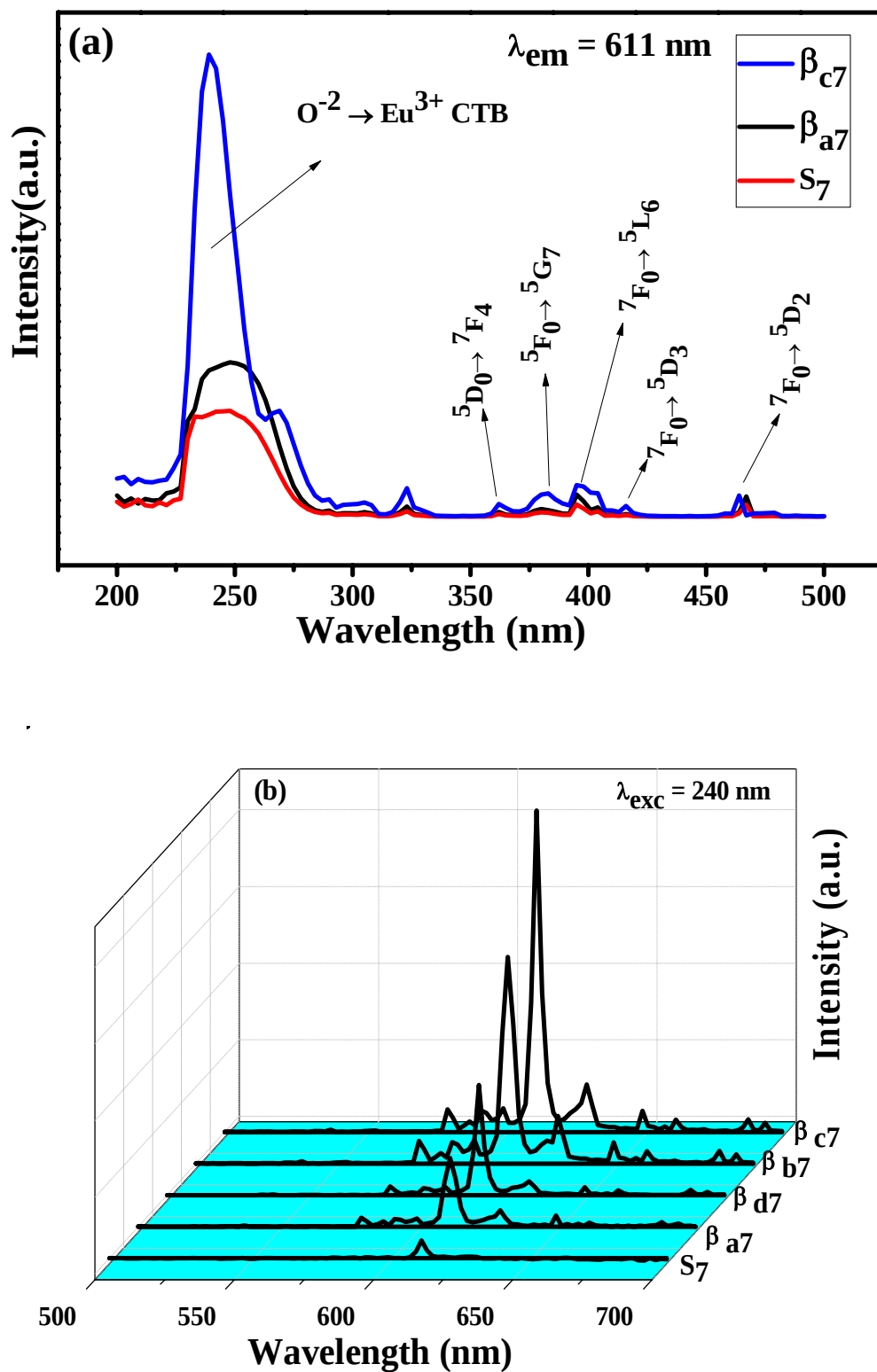


Figure 6.21: PL (a) excitation and (b) emission spectra of S_7 , β_{a7} , β_{b7} , β_{c7} and β_{d7} samples.

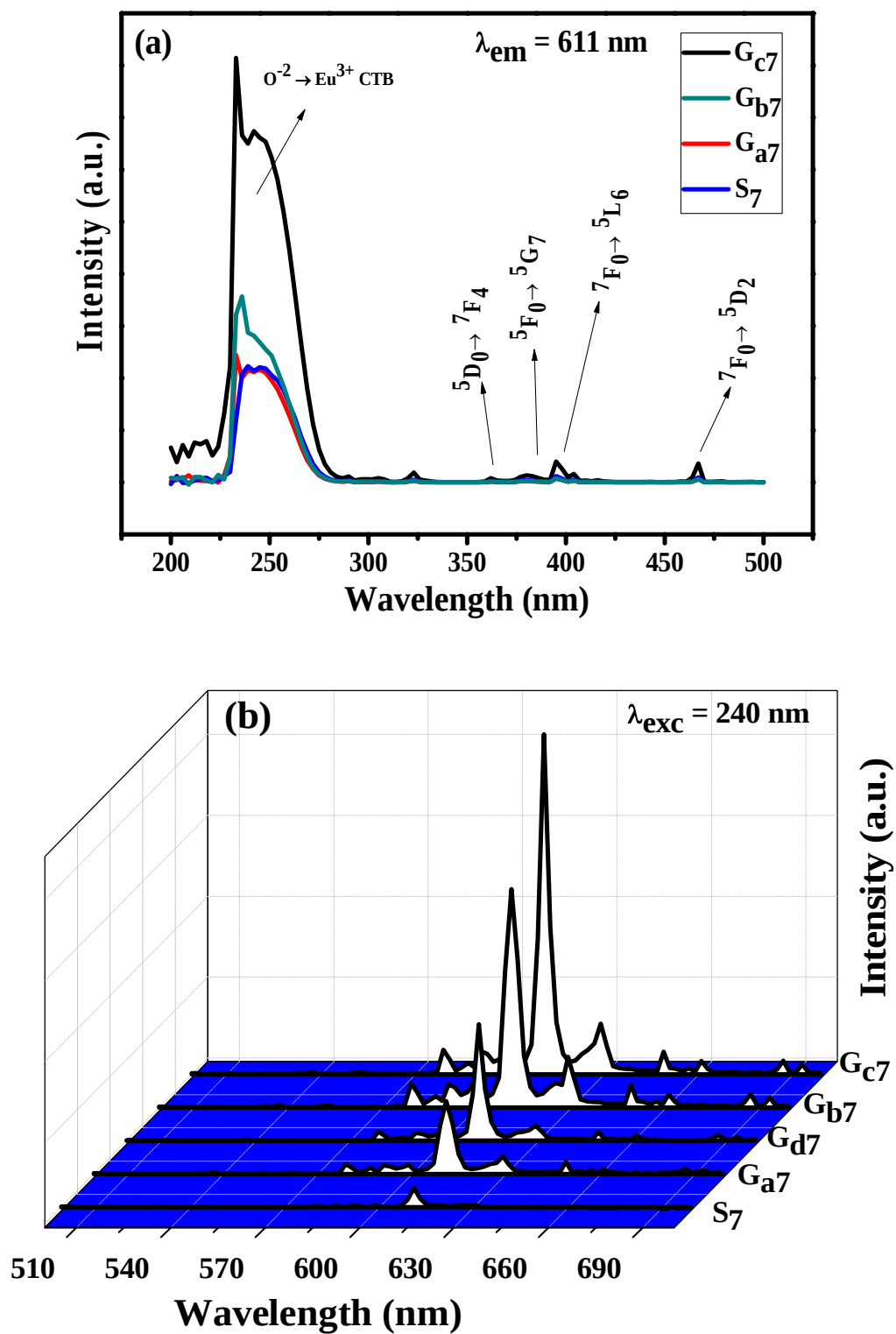


Figure 6.22: PL (a) excitation and (b) emission spectra of S_7 , G_{a7} , G_{b7} , G_{c7} and G_{d7} samples.

The wide band around 240 nm originates from the excitation of the O^{2-} to Eu^{3+} charge transfer band (CTB) and some very weak peaks observed at 362, 380, 394, 414 and 464 nm are attributed to ${}^7F_0 \rightarrow {}^5D_4$, ${}^7F_0 \rightarrow {}^5G_7$, ${}^7F_0 \rightarrow {}^5L_6$, ${}^7F_0 \rightarrow {}^5D_3$ and ${}^7F_0 \rightarrow {}^5D_2$ to the intra-configurational $4f^6-4f^6$ transitions of Eu^{3+} , respectively [26]. Figure 6.21 (b) and 6.22 (b) shows the emission spectra of samples (a) β_{a7} , β_{b7} , β_{c7} and β_{d7} ; (b) G_{a7} , G_{b7} , G_{c7} and G_{d7} respectively, under an excitation of $\lambda = 240$ nm.

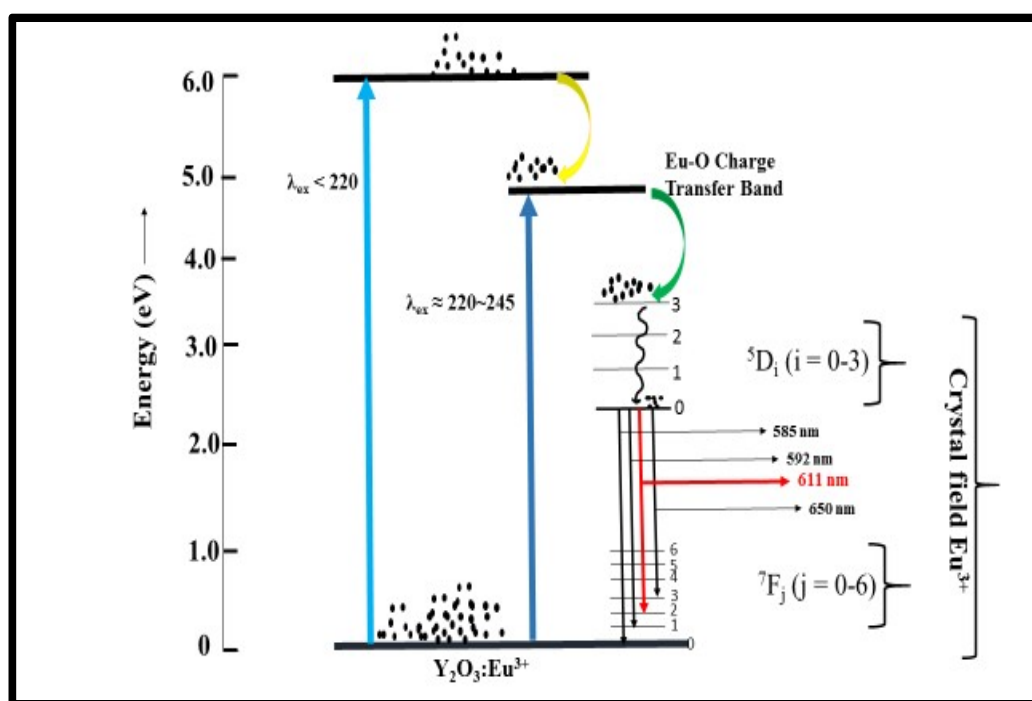


Figure 6.23: Band Gap diagram of Eu^{3+} doped Y_2O_3 .

The addition of polymer during synthesis has increased the Eu^{3+} emission intensity around $\lambda_{em} = 611$ nm in Y_2O_3 which is nearly two to three times as compared to samples prepared without polymer at a constant pH value of 7. As shown in Figure 6.21(b) and 6.22 (b), the samples G_{c7} and β_{c7} exhibited the optimum luminescence. Figure 6.23 represents the energy level diagram of Eu^{3+} doped Y_2O_3 . This diagram shows the various possible electronic transitions in $Y_2O_3:Eu^{3+}$. Figure 6.24 (a & b) shows the PL emission spectra of nanophosphors synthesized at pH 5, 7 and 9 for the samples (a) G_{c5} , G_{c7} and G_{c9} and (b) β_{c5} , β_{c7} and β_{c9} . Maximum luminescence intensity for both G_{c5} and β_{c5} can be seen in Figure 6.24 (a & b). Moreover, the relative PL intensity emission spectra of sample G_{c5} and β_{c5} is also shown in Figure 6.25 indicating that β_{c5} is better phosphor in comparison to G_{c5} . When

excited at 240 nm, all the emission spectra exhibited characteristic transition lines between Eu^{3+} levels (Figure 6.21(b) and 6.22(b)). The emission spectrum depicts five main groups of emission lines at 583, 593, 611, 632 and 650 nm, which are assigned to the $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($j = 1-5$) transitions of Eu^{3+} , respectively. Moreover, the strongest peak at 611 nm and a minor peak at 632 nm correspond to the hypersensitive transition between the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ levels of Eu^{3+} ion in the yttrium oxide host caused by the forced electric dipole transition mechanism. The insignificant emission in the locality of 590 nm (590 nm – 600 nm) is caused by the magnetic dipole transition of $^5\text{D}_0$ to $^7\text{F}_1$. In general, when Eu^{3+} is located at a low symmetry (without an inversion center), the 611 nm emission instead of 590 nm emission is dominant. However, the 590 nm emission is stronger than 611 nm when Eu^{3+} is situated at a high symmetry (with an inversion center) [27]. In the present case, the emission at 611 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) is dominant suggesting that the location of Eu^{3+} diverts from the inversion symmetry, i.e. at low symmetry positions.

In the current work, water soluble polymers PEG and β -cyclo are used as capping agents during synthesis. PEG is a straight chain polymer and β -cyclo is a cyclic polymer. In order to study the effect of these polymers on optical properties of Eu^{3+} doped Y_2O_3 , a comparative study has been done. The role of these polymers is identified to control the growth of the precipitating particles and to decrease agglomeration by steric effect due to repulsive force acting among their groups. Therefore, these polymers try to encapsulate the precipitating particles by forming a closed environment all over the nanoparticle boundaries during synthesis [16]. Also to get pure crystalline phase of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, the obtained nanoparticles were heated at 1000°C due to which these organic polymers were removed and pure NP powder in highly crystalline form having high emission intensity is obtained. Moreover, addition of large quantity of PEG/ β -cyclo on precipitating particle surface may lead to the attraction among their polymeric chains due to the osmotic pressure causing depletion flocculation which may produce destabilization [17] and hence a steep decrease in luminescence of NPs is observed. PL intensity of S_7 first increases significantly with an increase in polymer concentration for both PEG and β -cyclo and then decrease gradually with further increase in polymer amount at the time of synthesis (Figure 6.22 (a & b)). Moreover, investigation of pH showed that in the presence of the required concentration of polymer, optimum luminescence of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (5.0 mol%) was obtained at pH 5, where particle size was of the order of 20-50 nm and agglomeration was also negligible as confirmed by TEM observations (Figure 6.18 & 6.19). However, synthesis of nanoparticles at higher pH >7 at the

required concentration of polymer have shown decrease in PL intensity (Figure 6.24 (a & b)). Moreover, sample β_{c5} has shown the maximum luminescence as compared to sample G_{c5} (Figure 6.25). This may be due to better morphology of NPs synthesized with β -cyclo as compared to PEG where some agglomeration with larger particle size can be seen in TEM micrographs (Figure 6.18 & 6.19).

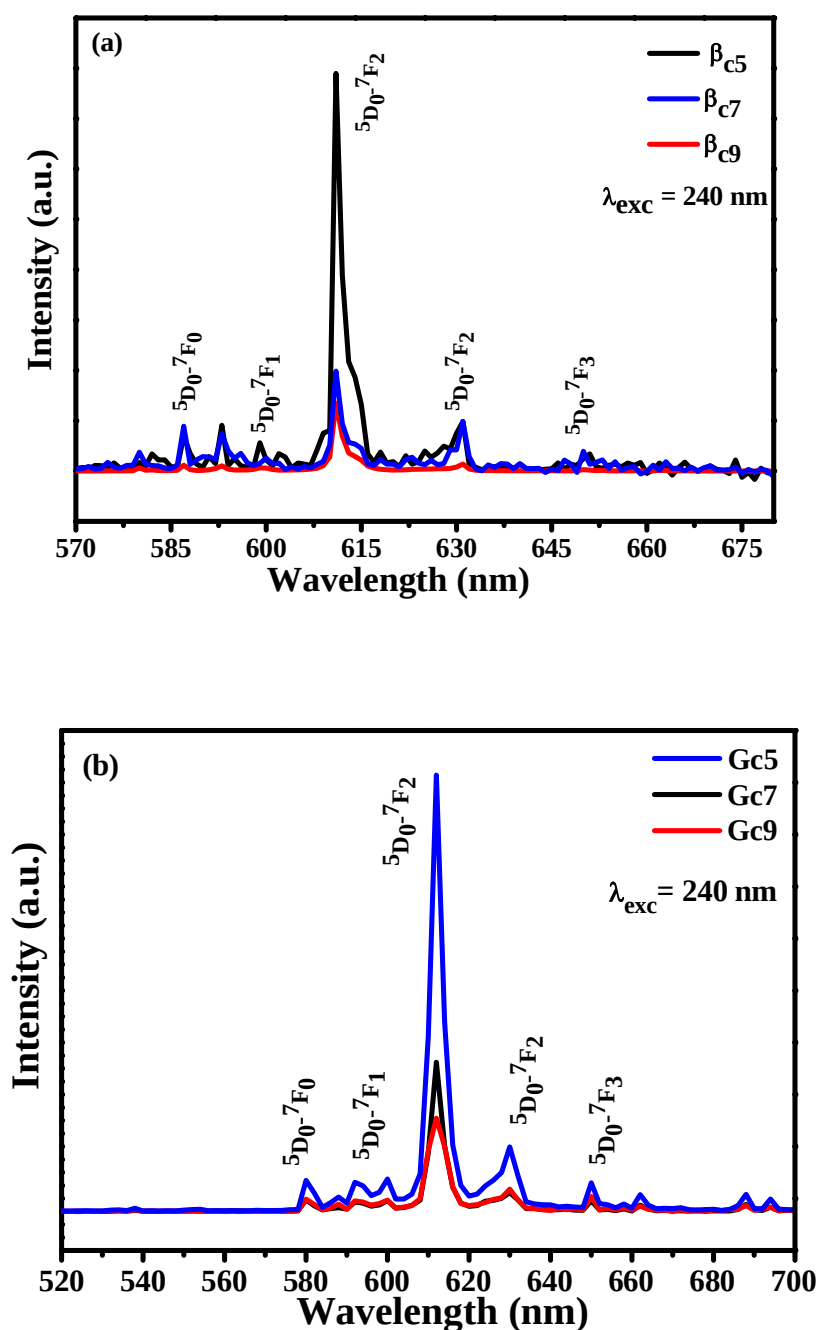


Figure 6.24: PL emission spectra of (a) G_{c5} , G_{c7} , and G_{c9} samples, (b) β_{c5} , β_{c7} , and β_{c9} samples.

In the past literature, it has been observed by many researchers that luminescence of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ increases with decrease in particle size [18, 19]. However, in order to get highly luminescent particles of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ usually researchers increase the pH of the solution at the time of synthesis [28].

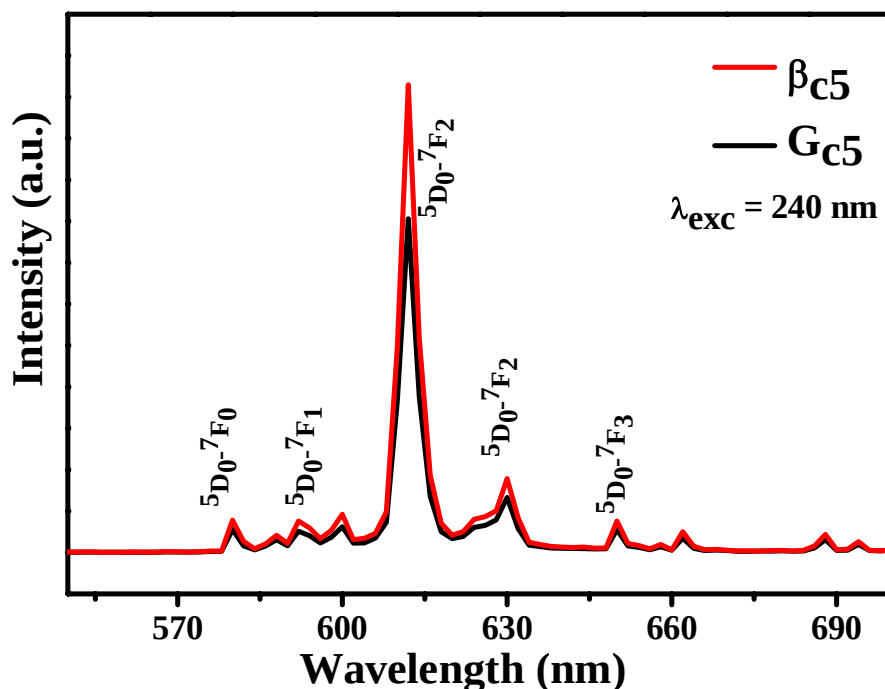


Figure 6.25: PL emission spectra of (a) G_{c5} and (b) β_{c5} samples.

It is known that an increase in particle size and the degree of agglomeration are the two factors that affect the morphology with increase in pH of the solution at the time of precipitation. In addition to this for obtaining pure crystalline phase of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ NPs heat treatment above 600 °C should be given [20]. With an increase in annealing temperature the size of particles start increasing from nano to micro range and hence restrict their application in medical diagnostics, targeted therapeutics and in other display devices (due to decrease in luminescence). In this work, an attempt has been made to control the growth of NPs at the time of synthesis by optimizing polymer concentrations (PEG and β -cyclo) and pH (5, 7 and 9) to get maximum luminescence with narrow size distribution of nanoparticles of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (5.0 mol%). Moreover, by optimizing these conditions we have successfully shown

improvement in the morphology and PL emission intensity of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (5.0 mol%). In order to know the photometric characteristics of the prepared phosphors the CIE chromaticity coordinates were also calculated.

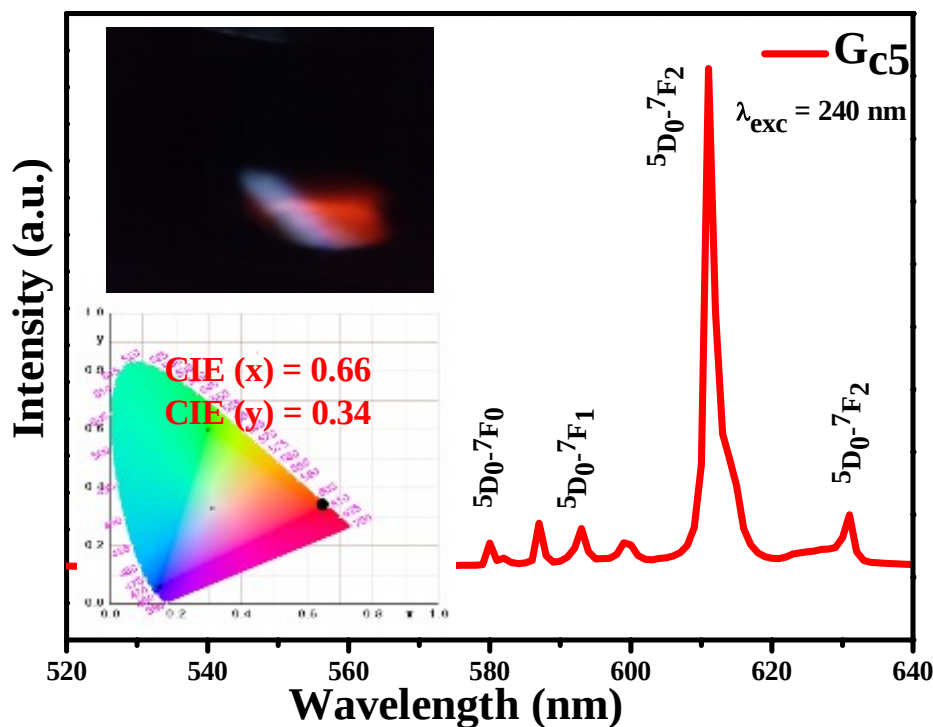


Figure 6.26: Chromaticity diagram of G_{c5} sample.

The values of CIE parameters (x, y) for the samples β_{c5} and G_{c5} are (0.66, 0.33) and (0.66, 0.34) respectively, which is very close to coordinates of ideal red (0.67, 0.33) [29, 30]. In addition, the measured CIE chromaticity coordinates are near the edge of CIE diagram (shown in inset of Figure 6.26), suggesting that such type of phosphors have better color purity and can be useful in solid-state lighting and other applications of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ as a promising red-emitting phosphors.

From above discussed results of this chapter it has been observed that there is a considerable effect of pH and capping agent on the morphological and optical properties of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$. Moreover, by optimizing pH and polymer amount during synthesis of nanoparticles narrow size, higher crystallinity and enhanced photoluminescent properties of doped Y_2O_3 can be achieved. In next section of this chapter effect of Cetyl trimethylammonium bromide (CTAB) and Trioctylphosphine oxide (TOPO) at the time of synthesis has been studied on $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$. It has been seen in literature that CTAB at the time

of synthesis helps in achieving better crystallinity and TOPO helps in controlling size of the nanoparticles [31, 32]. The main idea of using both the surfactants is to use both of them simultaneously at the time of synthesis to achieve highly crystalline and nanosized $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ phosphor at relatively low temperature (i.e. at 700 °C).

6.4 Effect of TOPO and CTAB on optical and morphological properties of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ nanophosphors

6.4.1 Introduction

Taking the considerations in mind to see the beneficial effect of both CTAB and TOPO on optical and morphological properties both SMs were used together at the time of synthesis. The basic aim of this study is to get highly luminescent and highly crystalline $\text{Y}_2\text{O}_3:\text{RE}^{3+}$ nanophosphor at comparatively low temperature (700 °C). Terbium doped yttrium oxide ($\text{Y}_2\text{O}_3:\text{Tb}^{3+}$) nanophosphor has been synthesized via a modified co-precipitation method. To get maximum luminescence output from $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ nanophosphors, surfactants namely, Cetyl trimethylammonium bromide (CTAB) and Trioctylphosphine oxide (TOPO) were added during synthesis. Further, it has been observed that combined addition of surfactant (CTAB + TOPO) at the time of synthesis has resulted in nearly spherical morphology of the nanophosphor. Furthermore, these optimized materials are observed to have enhanced integrated photoluminescence (PL) intensity of ~23% higher as compared to the one synthesized without the addition of any surfactant. The results are further supported by detailed structural and optical studies. Optimum use of surfactants during synthesis shows that both nano-sized distribution and high crystallinity can be achieved simultaneously which has resulted in bright green emission in Tb^{3+} doped Y_2O_3 nanophosphors.

6.4.2 XRD studies

The phase and purity of the samples were studied by X-ray powder diffraction (XRD) measurement and Figure 6.27(a-d) presents the XRD profiles of (a) S_P , (b) S_C , (c) S_T and (d) S_CT annealed at 700 °C. For comparison purpose we have also given the XRD profile of pure cubic phase Y_2O_3 (JCPDS 83-0927) [33]. From these profiles one can see that samples prepared were in good agreement with the standard data of the pure cubic phase Y_2O_3 with space group Ia3 [33]. No impurity peak was observed in these XRD patterns, indicating high

purity of the synthesized samples [12]. The (hkl) values of most prominent peaks are shown in the XRD pattern (Figure 6.27(a-d)).

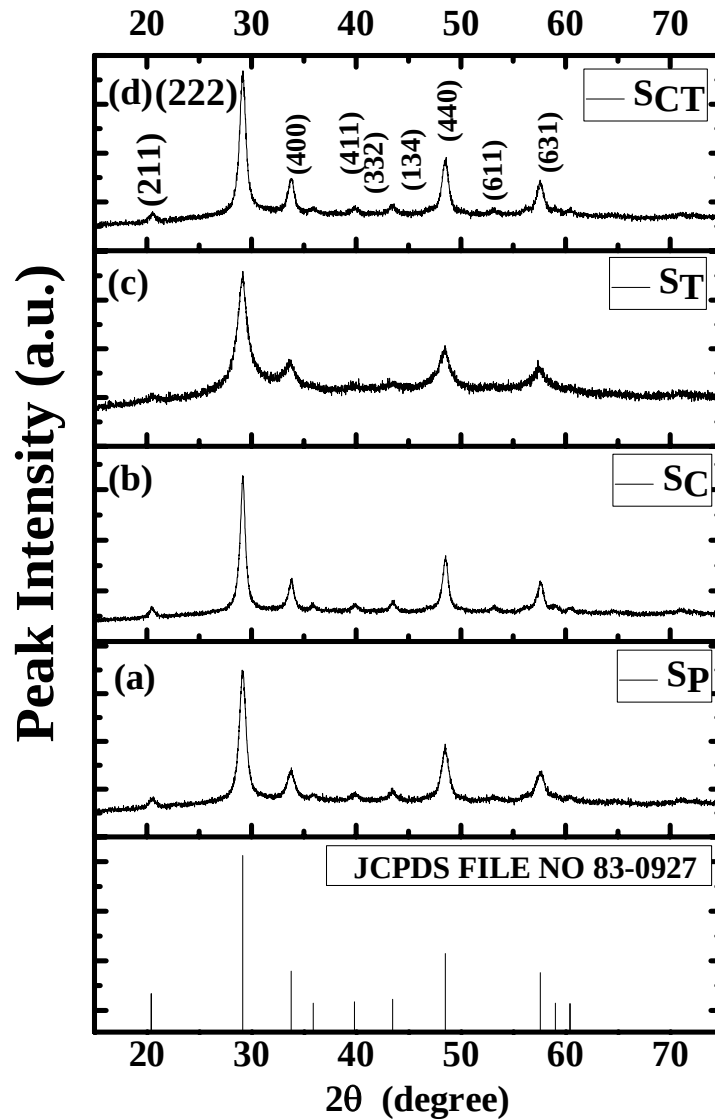


Figure 6.27: XRD pattern of (a) S_p , (b) S_c , (c) S_t and (d) S_{CT} samples.

To study the effect of surfactant on crystallite size and crystallinity of $Y_2O_3:Tb^{3+}$, the highest intensity peak (2 2 2) of samples (S_p , S_c , S_t and S_{CT}) from Figure 6.27(a-d) were selected and compared them in Figure 6.28(a). A careful comparison of the (2 2 2) diffraction peaks between $2\theta = 27^\circ - 32^\circ$ (Figure 6.28(a)) have shown the following observation.

- The presence of TOPO at the time of synthesis in the samples (S_T) has caused broadening in this peak (2 2 2) with smaller peak intensity as compared to sample S_P .
- In the sample containing CTAB as surfactant i.e. (S_C) has shown enhancement in peak intensity of this peak (2 2 2) whereas broadening is less as compared to sample S_P .

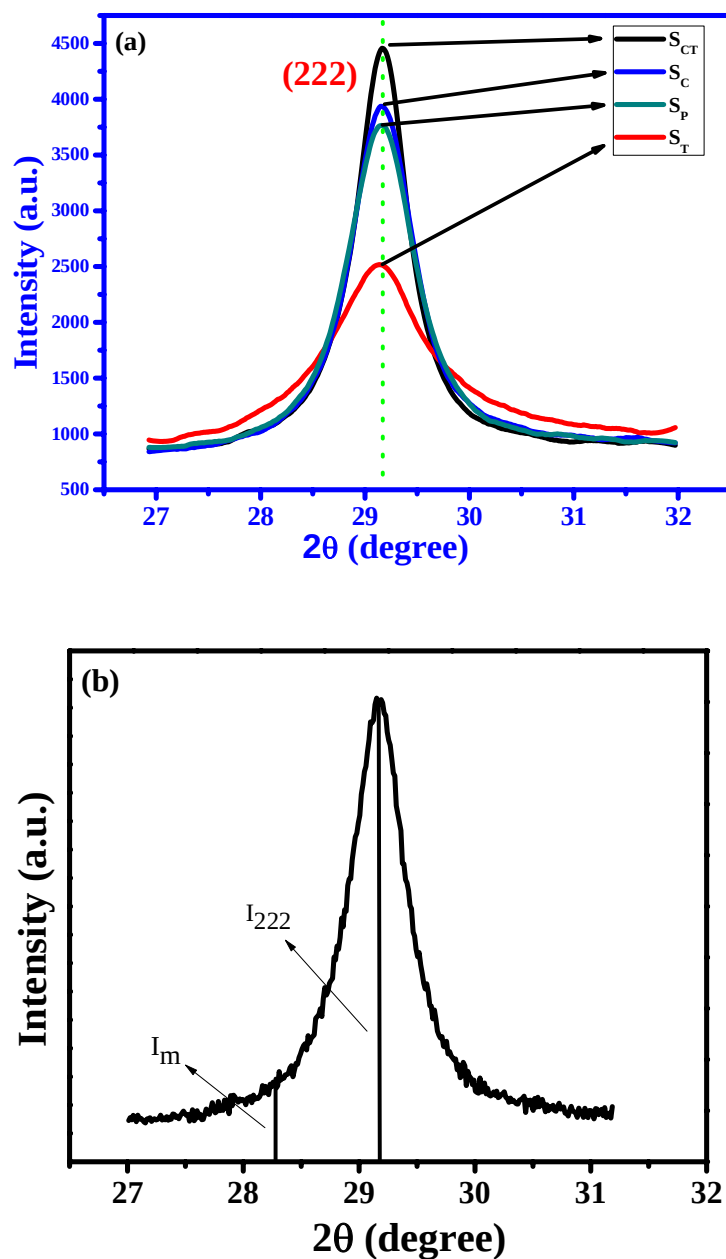


Figure 6.28: (a) Comparative intensity of (2 2 2) diffraction peaks in the range of $2\theta = 27^\circ$ - 32° of these samples S_P , S_C , S_T and S_{CT} . (b) Crystallinity index (C.I. %) calculation from (222) peak.

Table 6.1: FWHM and Peak intensity of the samples (a) S_P, (b) S_C, (c) S_T and (d) S_{CT}.

SAMPLE CODES	(h k l)					
	(222)			(400)		
	FWHM (radian)	Peak intensity (a.u.)	2θ (degree)	FWHM (radian)	Peak intensity (a.u.)	2θ (degree)
S _C	0.67305	4568	29.16	0.67855	1711	33.78
S _T	1.17373	2606	29.16	1.55304	1288	33.49
S _{CT}	0.76162	4100	29.16	0.71828	1600	33.77
S _P	0.43922	3620	29.15	0.36903	1544	33.76

Both these samples (S_T and S_C) were heated at same temperature (700 °C), for same time (2 hours) under same physical condition and XRD measurements were also done under similar conditions. So based on the above observations it shows that CTAB surfactant during annealing helps in vanishing unwanted phases in the samples which are prior present before annealing [15]. However, TOPO has decreasing the crystallite size of the samples which results in the broadening of (222) peak. We have also observed the same behavior in all other peaks present in XRD of these samples (S_C and S_T). Interestingly in samples (S_{CT}) prepared by adding CTAB and TOPO together, both the broadening and peak intensity of diffraction peaks were high i.e. this sample (S_{CT}) has smaller crystallite size and better crystallinity than the other prepared samples (S_T, S_C and S_P). From Table 6.1 we can see that for the sample S_T, FWHM is more and peak intensity is less and for S_C sample FWHM as well as and peak height is high as compared to S_P sample, which was prepared adding no surfactant at the time of synthesis.

To compare the crystallinity of the prepared samples, XRD crystallinity index (CI_{XRD}) were calculated from the following peak height method developed by Segal *et al.* [34]

$$CI_{XRD}(\%) = \frac{I_{222} - I_m}{I_{222}} \times 100 \quad (6.2)$$

where, I₂₂₂ was the intensity of the (222) crystalline peak at 29° and I_m the height of the minimum of peak (222), as shown in Figure 6.28(b) [34].

To investigate further, crystallite size (D in nm) was calculated using the Debye–Scherer formula [35] and the Hall–Williamsons method (equation 6.3) [36]

$$\frac{\beta \cos \theta}{\lambda} = \frac{1}{D} + \frac{\varepsilon \sin \theta}{\lambda} \quad (6.3)$$

Here, β represents the full-width at half-maximum (FWHM) in radians, θ is the angle of the corresponding diffraction peak and λ (0.154 nm) is the wavelength of X-rays, ε represents the microstrain present in the samples. The crystallite size from the Hall–Williamsons equation (equation 6.3) was calculated from the reciprocal of the intercept of its straight line plot, as shown in Figure 6.29(a-d) for samples (a) S_P , (b) S_T , (c) S_C and (d) S_{CT} . The slope of this equation ε implies the microstrain (ε) present in the samples. Table 6.2 illustrates the values of D (crystallite size in nm) and CI_{XRD} (%) of synthesized samples using above mentioned methods. Gaussian fitting was used to calculate the FWHM and peak intensity of all the samples using origin pro software [37].

Table 6.2: Illustrates the values of CI_{XRD} (%).and D (crystallite size in nm).

Sample Code	CI_{XRD} (%) (Crystallinity Index)	D (nm) (Crystallite Size)	
		Debye Scherer $\pm$ error	Hall–Williamson's $\pm$ error
S_{CT}	80.1	18.00 $\pm$ 0.30	20.00 $\pm$ 0.24
S_T	64.3	17.00 $\pm$ 0.15	15.00 $\pm$ 0.21
S_C	77.2	25.00 $\pm$ 0.22	24.00 $\pm$ 0.37
S_P	70.2	36.00 $\pm$ 0.38	34.00 $\pm$ 0.51

From above observations in Table 6.1 and 6.2, it can be concluded that by adding TOPO as surfactant, sample (S_T) has small crystallite size and using CTAB as surfactant sample, S_C have shown a better phase and crystalline behavior than pure sample S_P . Further, we conclude that sample (S_{CT}) which was prepared in the presence of CTAB + TOPO has shown better phase formation with smaller crystallite size then S_P . It has been observed by many

coworkers [12] that to get pure crystalline phase and better crystallinity of Y_2O_3 , samples of Y_2O_3 need to be heated at higher temperatures in the range of 600 °C to 1400 °C.

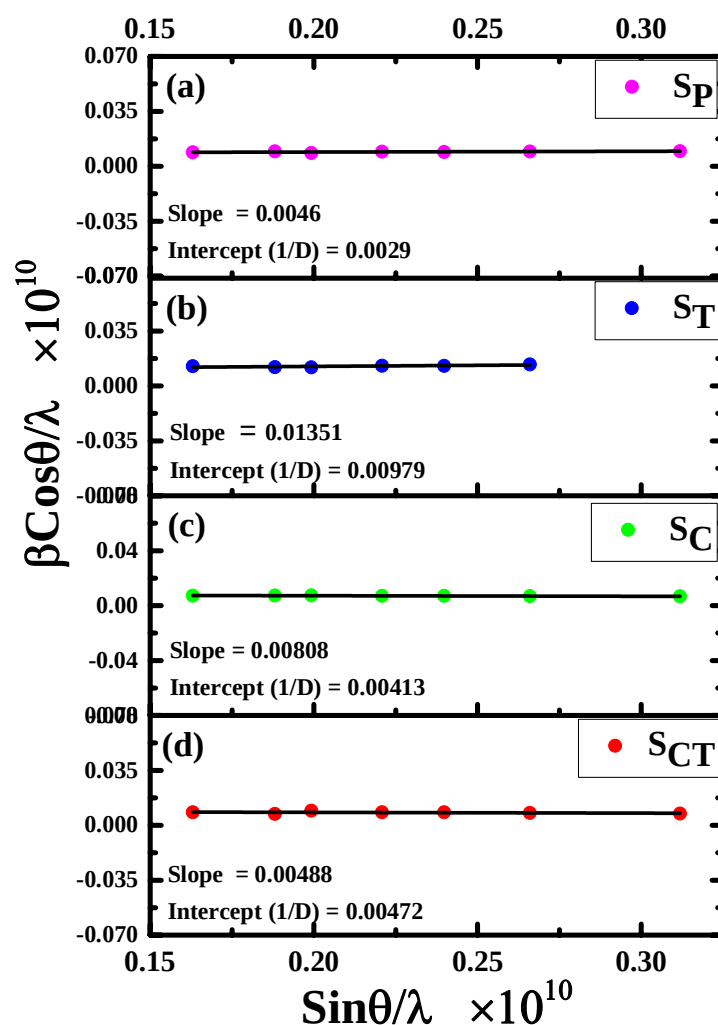


Figure 6.29: Hall–Williamsons Plots for samples (a) S_P , (b) S_T , (c) S_C and (d) S_{CT} .

The main idea to gain better crystalline behavior and small crystallite size of phosphor is because both these properties upsurge the optical properties of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ phosphor [26]. However, with increase in temperature the luminescence increase but crystallite size also increase [38]. This property of phosphor is useful in many applications yet restricts its use in many other applications related to biological use of this phosphor. Hence, it is required to prepare nano-sized particles having high crystallinity. From XRD studies discussed above we conclude that samples of Tb^{3+} doped Y_2O_3 prepared by adding CTAB and TOPO as additives helps in getting better phase stability, crystallinity and smaller crystallite size.

6.4.3 Rietveld refinement

The structural refinement results for the samples (a) S_P , (b) S_C , (c) S_T and (d) S_{CT} phosphor annealed at 700 °C are shown in Figure 6.30 (a-d) and are presented in Table 6.3. Results show good agreement between the observed and calculated XRD patterns. In the present case, the GOF for samples (a) S_P , (b) S_C , (c) S_T and (d) S_{CT} was found to be 1.20, 1.24, 1.21 and 1.33.

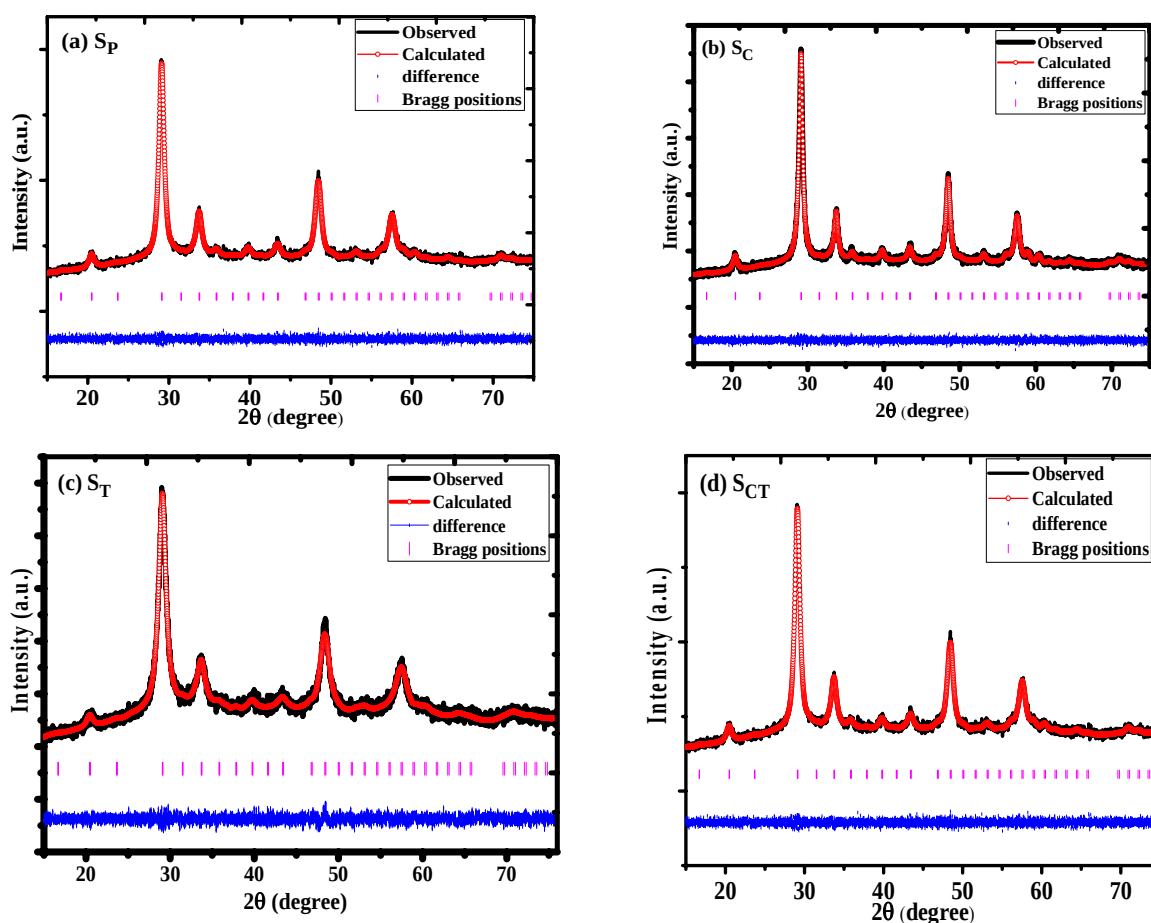


Figure 6.30: Refinement data of (a) S_P , (b) S_C , (c) S_T and (d) S_{CT} sample.

6.4.4 Unit cell representation

Figure 6.31(a) illustrates an Y_2O_3 unit cell. This unit cell was modeled through a program called Diamond- Visualization of crystal and molecular structure [39] using Rietveld refinement data (lattice constants and atomic positions) (Table 6.3). The Y_2O_3 phosphor has a cubic structure with a space group Ia-3 and point-group symmetry m-3. The unit cell contains 16 formula units with 32 cations. This structure contains two cation symmetry sites C_2 and

C_{3i} , both coordinated six-fold with oxygen, as shown in Figure 6.31(b). These two cationic sites were allocated over two Wyckoff positions 8b with local symmetry C_{3i} and 24d with local symmetry C_2 . Oxygen ions are situated at 48e Wyckoff positions.

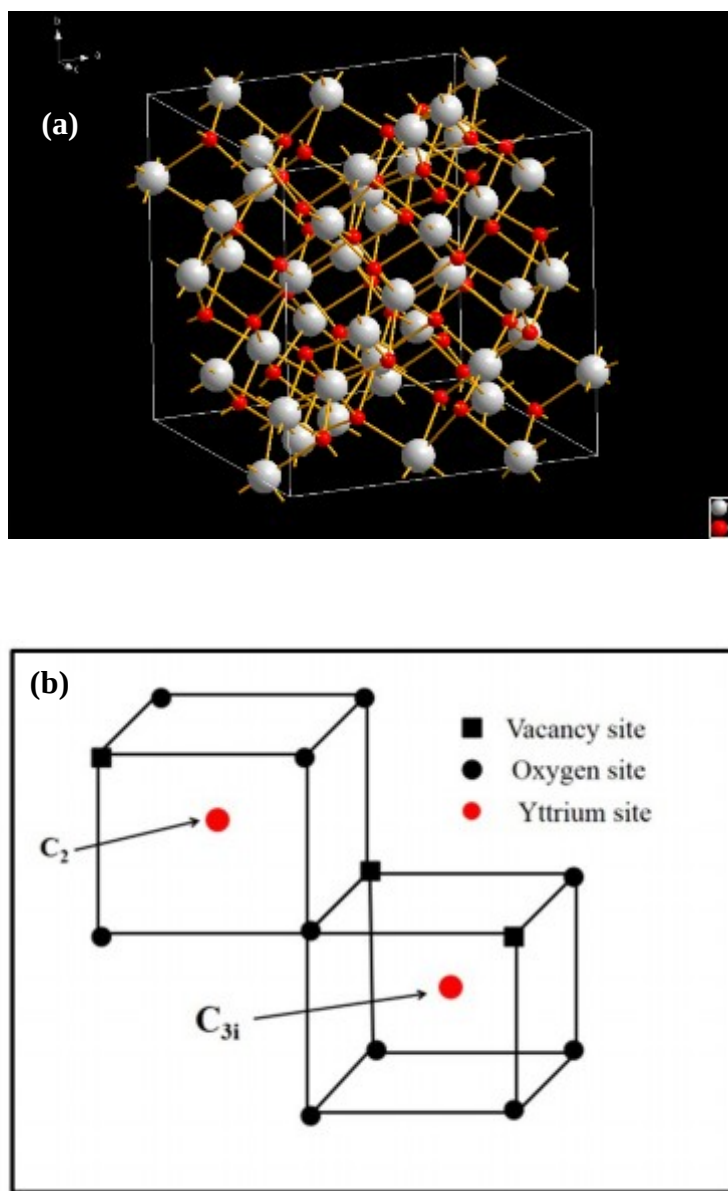


Figure 6.31: (a) Schematic representation of the unit cell and (b) Cationic symmetry site for the $Y_2O_3:Tb^{3+}$.

Table 6.3: Calculated crystallographic data of samples (a) S_C , (b) S_T and (c) S_C and (d) S_{CT} by Rietveld refinement method.

Sample Name →		S_P	S_T	S_C	S_{CT}
Space Group		Ia-3	Ia-3	Ia-3	Ia-3
$\left. \begin{array}{l} a \text{ (Å)} \\ b \text{ (Å)} \\ c \text{ (Å)} \end{array} \right\}$		10.5953 ± 0.0000125	10.5892 $\pm$ 0.000234	10.6739 $\pm$ 0.000534	10.6265 $\pm$ 0.000235
		90°	90°	90°	90°
Volume (Å) ³		1189.432	1187.379	1216.1	1200.0
R_{wp} (%)		16.0	14.5	14.6	16.9
R_p (%)		21.0	15.1	17.2	20.5
R_{exp} (%)		14.64	13.22	13.13	14.61
χ^2		1.20	1.21	1.24	1.33
(Occupancy)	Y1	0.09201	0.08822	0.09711	0.08984
	Y2	0.32340	0.31365	0.31336	0.29585
	O	0.78423	0.77073	0.78584	1.02129

The rare earth cations (Tb^{3+}) were replaced at the Y^{3+} symmetry site. The ionic radii of Y^{3+} (0.90 Å) and Tb^{3+} (0.92 Å) are close and therefore, Y^{3+} is fit to be substituted by Tb^{3+} ions in Y_2O_3 matrix. By incorporating Tb^{3+} ions in Y_2O_3 , no significant change in peak position of XRD patterns were observed, as shown in Figure 6.27 (a-d) showing that Tb^{3+} ions cause no change in the cubic structure of the Y_2O_3 matrix. Cation site occupancy is a substantial structural factor that can adjust the optical and other physical properties. From an optical stance, the C_{3i} site has a center of inversion symmetry so according to selection rules, only the magnetic dipole transitions are allowed whereas the C_2 site does not have inversion symmetry and hence both electric and magnetic dipole transitions are allowed [40]. The C_{3i}/C_2 site occupancies were found from the Fullprof. program The estimated values of C_{3i}/C_2 site occupancies of Tb^{3+} are given in Table 6.3.

6.4.5 FT-IR Analysis

FT-IR study has been performed for the samples S_P and S_{CT} as shown in Figure 6.32. A broad IR band at 3442 cm^{-1} corresponds to OH stretching vibration [41]. This band for S_{CT} sample becomes comparatively small. The absorption band due to O–H vibration is absent in the commercial undoped Y_2O_3 phosphor [12]. The residual hydroxyl groups ($-OH$) at 3442 cm^{-1} quenches emission intensity in rare earth emission and decreasing the luminescence intensity. This band becomes weaker with increase in annealing temperature and disappears at higher temperatures. During synthesis since both these samples were annealed at same temperature ($700\text{ }^\circ\text{C}$) so this difference between the peaks may be due to better crystallinity of the S_{CT} sample as compared to S_P (discussed in XRD earlier). This band becomes weaker with increase in annealing temperature [41] (disappears at higher temperatures) and by modifications during synthesis (washing the sample several time by ethanol and water before annealing) [42]. The nitro group around 1519 cm^{-1} and 1404 cm^{-1} has also displayed a decrease in S_{CP} sample as compared to S_P . The residual nitro group around 1500 cm^{-1} are called luminescence quenchers for rare earth emission and decreases the luminescence emission intensity [43-46]. These facts discussed above support that, addition of polymers (i.e. CTAB and TOPO) at the time of synthesis as well as during annealing have decreased the luminescent quenchers to a greater extent which can result in synthesizing highly luminescent $Y_2O_3:Tb^{3+}$ phosphors.

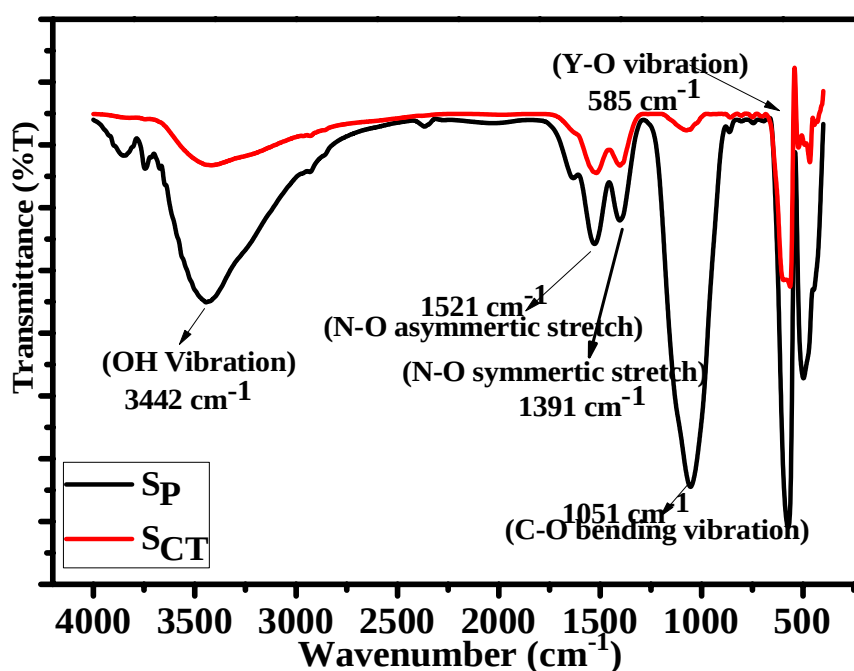


Figure 6.32: FT-IR of samples S_P and S_{CT} .

6.4.6 TEM micrographs

Figure 6.33(a-d) shows the TEM micrographs of (a) S_P , (b) S_T , (c) S_C and (d) S_{CT} annealed at 700 °C. In Figure 6.33(a) agglomerated particles can be seen as no additive was used at the time of synthesis. For sample S_T flake like morphology can be observed in Figure 6.33(b). Few folded flakes can be seen as samples that were annealed at 700 °C. Spherical morphology of the particles can be seen in samples S_C as shown in Figure 6.33(c). Average particle diameter calculated from micrograph 6.33(c) lies between 30-40 nm which matches well with XRD measurements discussed earlier. Figure 6.33(d) represents TEM micrographs corresponding to sample S_{CT} . Since both the surfactants (CTAB+TOPO) were present at the time of synthesis, this sample (S_{CT}) has shown almost spherical morphology having particle diameter lying between 15 to 25 nm which agrees well with XRD data. The inset of Figure 6.33(c) shows Selected Area Electron Diffraction (SAED) pattern of S_C sample. Ring pattern corresponding to diffraction from different planes of the nanocrystalline, instead of spots due to the random orientation of the crystallites can be seen. The observed rings correspond to (211), (222) and (400) lattice planes of the cubic phase of Y_2O_3 as shown in Figure 6.33(c), which is in good agreement with the XRD patterns discussed before. Inset of Figure 6.33(d) for sample S_{CT} shows lattice fringes (0.308 nm) corresponding to (222) which further defends its crystalline behavior.

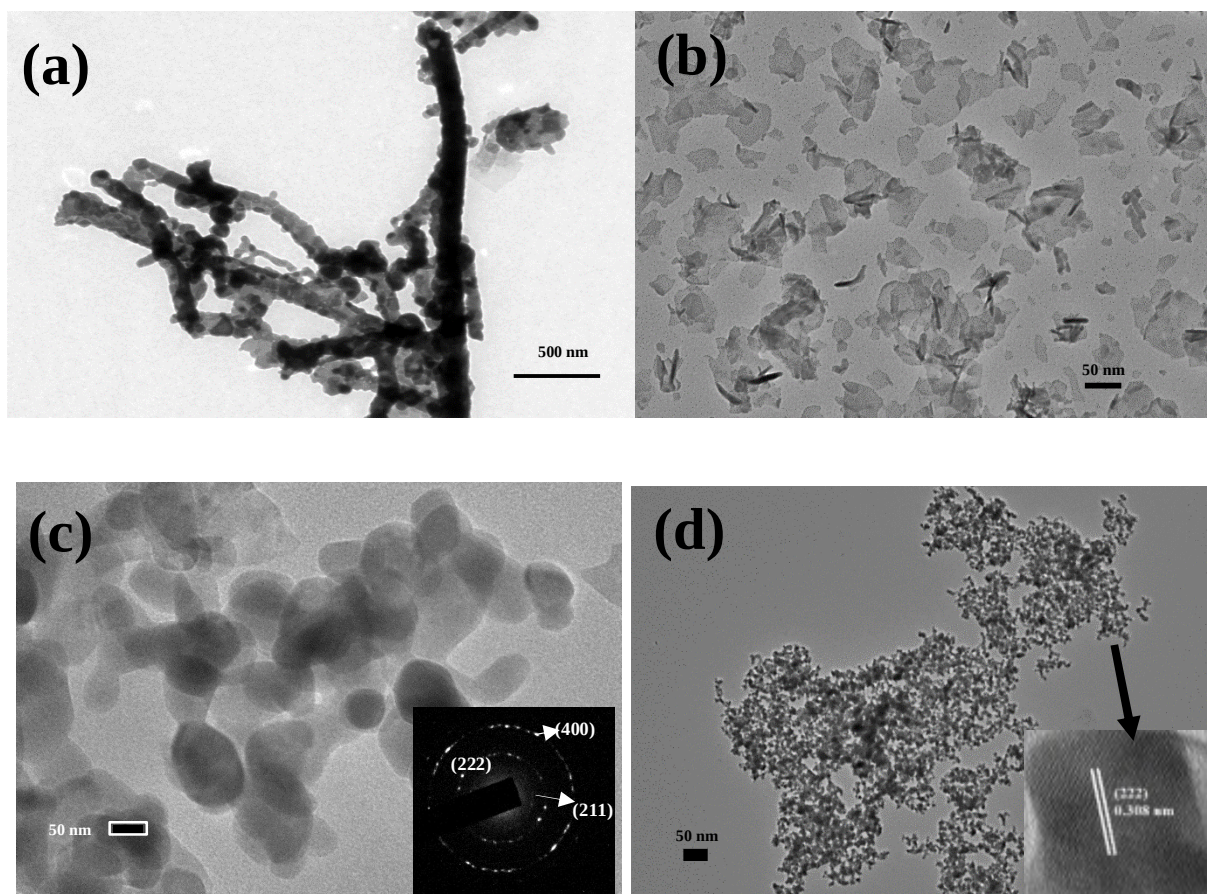


Figure 6.33: TEM micrograph of (a) S_P , (b) S_T , (c) S_C and (d) S_{CT} sample.

6.4.7 Photoluminescence studies

To understand the effect of surfactant on optical properties of Tb^{3+} doped Y_2O_3 , we have recorded Photo luminescence excitation and emission spectra of various prepared samples. Figure 6.34 (a & b) represents the comparative emission spectra of samples S_P vs S_T and S_P vs S_C under excitation of 267 nm. In the inset part of Figure 6.34 (a & b) shows the intensity relation with concentration of corresponding surfactant. Enhancement in PL emission intensity due to addition of surfactant at the time of their synthesis as compared to sample S_P can be observed. The obtained optimal concentration for maximum luminescence in sample S_C and S_T is 0.003 mol% (CTAB) and 0.010 mol% (TOPO) respectively as shown in inset of Figure 6.34 (a & b). Peak position in the emission spectra (Figure 6.34 (a & b)) does not change with surfactant concentration suggesting that the nature of Tb^{3+} activator remains unchanged with concentration of surfactant. Percentage increase in PL emission intensity of S_T and S_C samples with respect to pure sample S_P is 2.34% and 1.49% respectively. It has

also been seen (inset of diagram 6.34 (a & b)) that as the concentration of surfactant increases above its optimum concentration, PL intensity decreases thereafter [17].

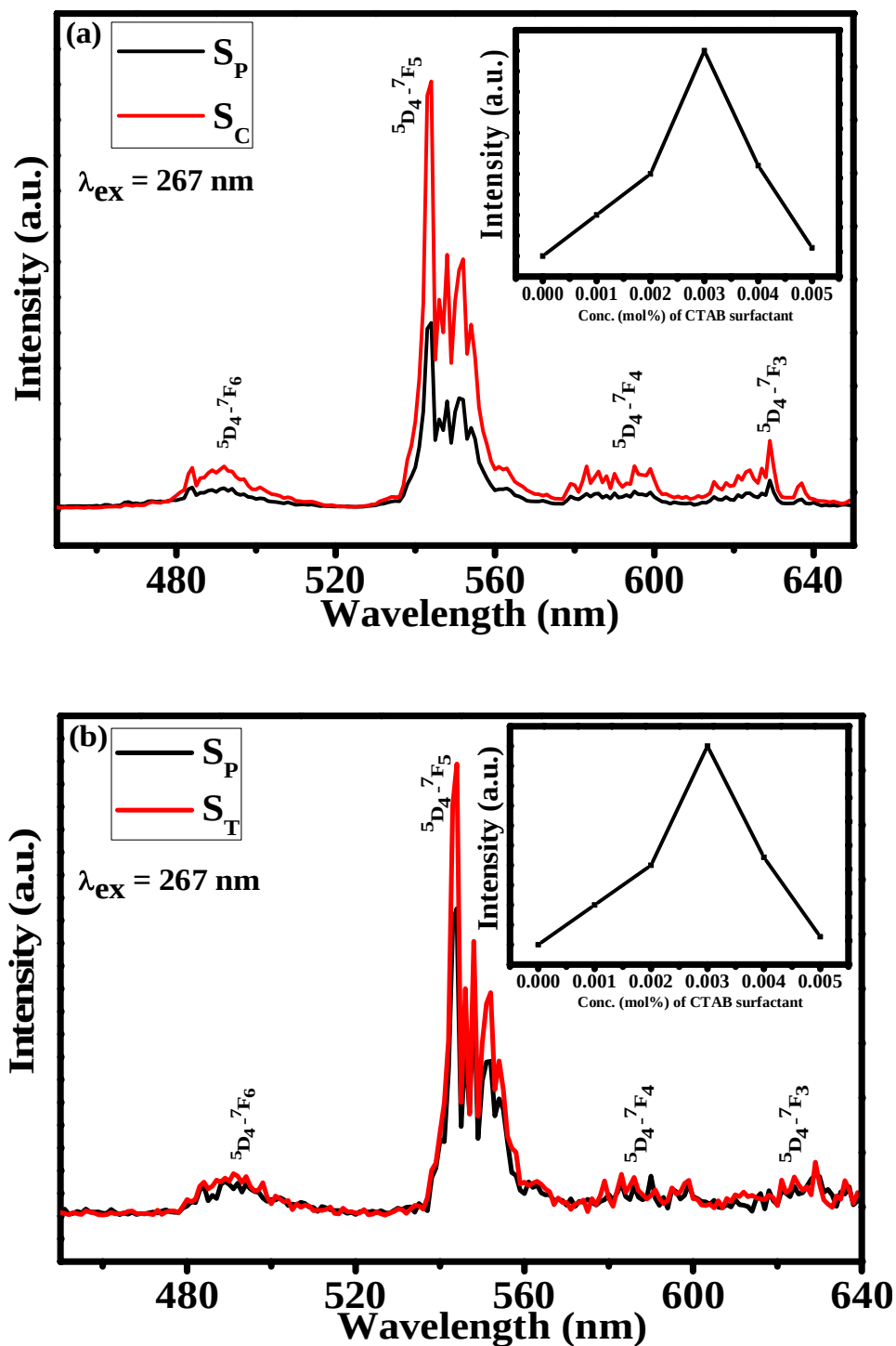


Figure 6.34: Comparative PL emission spectra of (a) S_P and S_C , (b) S_P and S_T sample.

Figure 6.35 (a & b) represents excitation and emission spectra of S_P , S_C , S_T and S_{CT} . Excitation spectrum recorded at $\lambda_{em} = 545$ nm emission is the overlapping bands having maxima at 267 and 301 nm [47, 48]. The band at around 267 nm is ascribed to the $O^{2-} - Tb^{3+}$ charge transfer band (CTB), which corresponds to the electronic transitions from the 2p orbital of O^{2-} to the 4f orbital of Tb^{3+} .

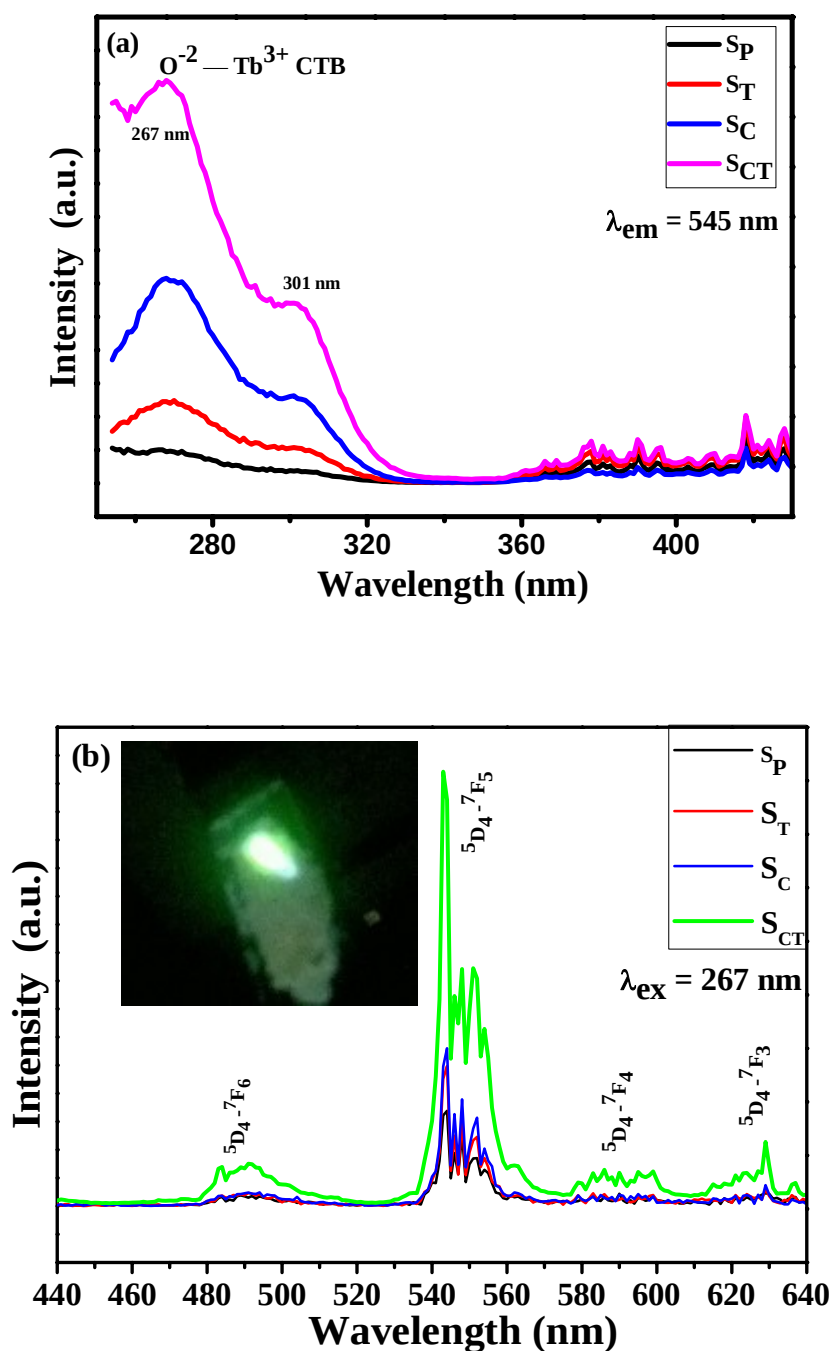


Figure 6.35: PL (a) excitation and (b) emission spectra of (a) S_P , (b) S_C , (c) S_T and (d) S_{CT} sample.

Origin of the band at 301 nm results from absorption of incident radiation by Tb^{3+} ions and leads to excitation of electrons from Tb^{3+} ground state to one of its excited 4f levels [12]. However, due to the parity forbidden character of the transition within the 4f configuration, the peaks beyond 301 nm were weak [19, 48]. Emission spectra of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ (1.0 mol%) (Figure 6.34 (a & b), 6.35 (b)) is composed of several sharp lines resulting due to the $^5\text{D}_4 \rightarrow ^7\text{F}_J$ transitions where $J = 3, 4, 5$ and 6. Strongest emission occurs at 545 nm due to the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ characteristic transition of green emission for Tb^{3+} [12, 48]. The other peaks at 485 nm, 585 nm and 625 nm arise from the $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$ and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ transitions, respectively. Band-gap diagram of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ is given in Figure 6.36.

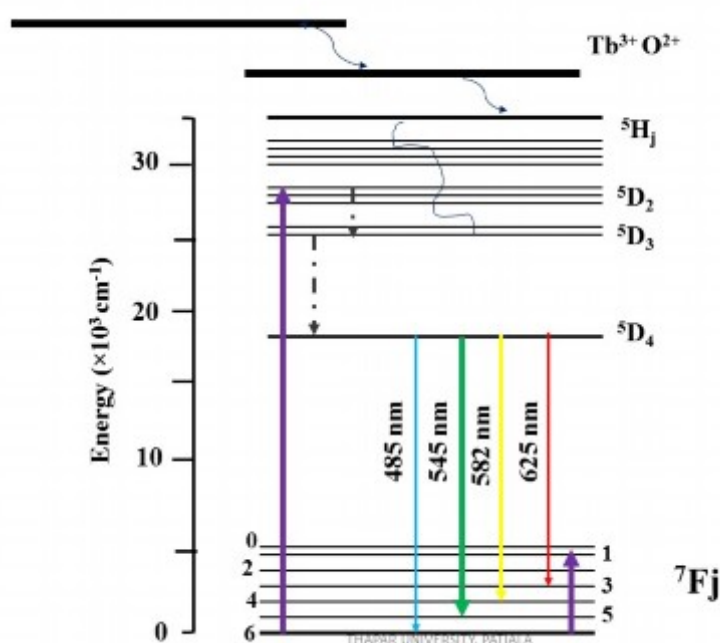


Figure 6.36: Band Gap diagram of Tb^{3+} doped Y_2O_3 .

The emission intensity of S_{CT} sample has shown large enhancement. Percentage improvement in PL intensity in this sample S_{CT} is 23% higher as compared to sample S_{P} which was prepared without addition of any surfactant. The increase in PL emission intensities of S_{C} , S_{T} and S_{CT} as compared to pure sample S_{P} is due to many factors discussed earlier in XRD, TEM and FTIR studies. XRD studies favors enhancement in PL intensity as samples prepared by adding CTAB surfactant (S_{C}) has better crystalline behavior as compared to pure sample S_{P} . Samples prepared by adding TOPO additive (S_{T}) have shown smaller crystallite size. Both these properties i.e. better crystalline behavior and smaller crystallite size can be

observed in sample prepared by adding both TOPO and CTAB samples. TEM studies have shown that better morphology in S_C , S_T and S_{CT} plays the major role in defending the reason of enhancement in PL emission intensity of these samples as compared to S_P sample. FTIR studies shows that sample of CTAB + TOPO (S_{CT}) has fewer amount of nitro (NO_2^-) and hydroxyl (OH^-) ions present on its surface, which is also an one of the reason for increase in PL intensity of S_{CT} sample as both these ions play as luminescent quenchers (increases non-radiative transitions) whose absence results in better PL emission intensity corresponding to S_{CT} sample.

6.4.8 Decay Analysis

Further, to understand behavior of luminescent decay, the decay data was fitted with different decay equations (Figure 6.37 (a-d)). It was found that curve follow second order exponential decay for the prepared samples [49-51].

$$I(t) = I_0 + I_1 e^{-t/\tau_1} + I_2 e^{-t/\tau_2} \quad (6.4)$$

Where I_1 and I_2 are intensities at different times and their corresponding lifetimes are τ_1 and τ_2 respectively. The average lifetime can be calculated using the relation [51]

$$\tau_{avg} = \frac{I_1 \tau_1^2 + I_2 \tau_2^2}{I_1 \tau_1 + I_2 \tau_2} \quad (6.5)$$

On the basis of equation (6.4 & 6.5), the average lifetimes of samples S_P , S_T , S_C and S_{CT} are 0.70, 1.47, 1.27 and 2.14 μs respectively. Decrease in structural defects due to presence of surfactant during synthesis and lower doping concentration of Tb^{3+} sites in the matrix may affect the $^5D_4 - ^7F_2$ level emission (when excited under 302 nm wavelength), leading to τ_{avg} little higher than expected. It is clear from the results that addition of surfactant and their mixture has increased the lifetime of Tb^{3+} doped Y_2O_3 significantly. Presence of surfactants at the time of synthesis has decreased the surface defects, which further decreases the non-radiative decay paths for excited Tb^{3+} related emission. This decreases the non-radiative transition probability which decreases the radiative luminescence emission rate [52]. The

decrease in the total transition probability enhances the lifetime of samples prepared by surfactant addition as the lifetime is inverse of the total transition probability [52].

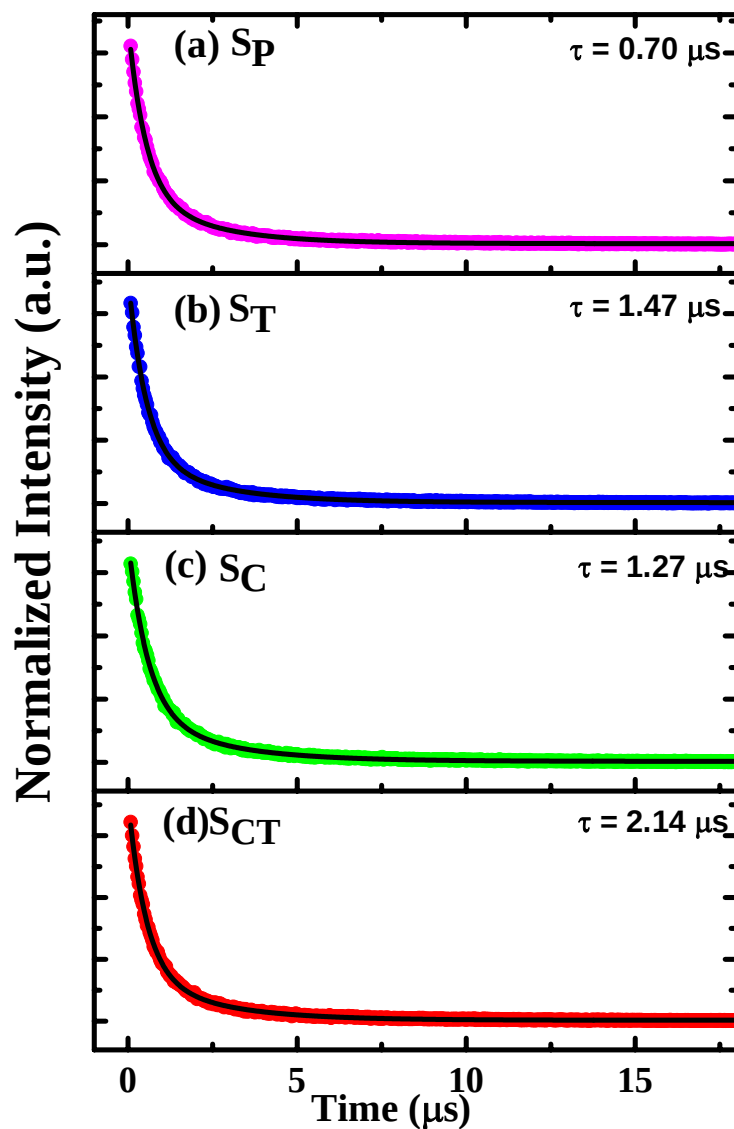


Figure 6.37: Luminescence decay curve ($\lambda_{em}=545$ nm) of (a) S_P , (b) S_C , (c) S_T and (d) S_{CT} sample.

6.4.9 Colorimetric studies

The color of any object (self-luminous or reflecting) can be conveniently specified via Commission International de L' Eclairage (CIE) chromaticity coordinates marked on a chromaticity diagram [53]. Figure 6.38 shows the CIE chromaticity coordinates for the optimized sample (S_{CT}) calculated from the emission spectra measured under 272 nm

excitation wavelength. The CIE chromaticity coordinates (Figure 6.38) for phosphor S_{CT} were found to be (0.340, 0.590) which are very near to ideal green color (0.29, 0.60) [54].

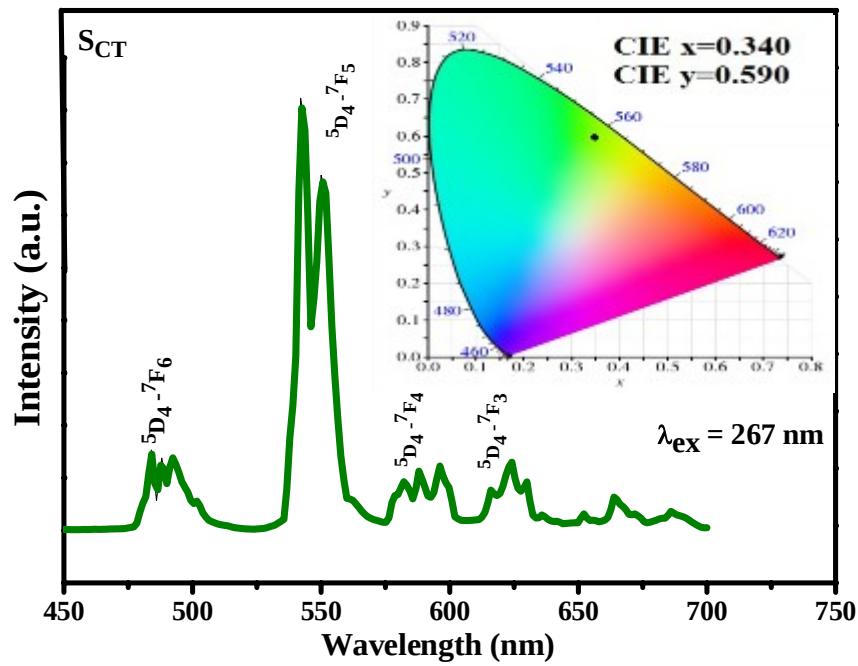


Figure 6.38: CIE chromaticity diagram of S_{CT} sample.

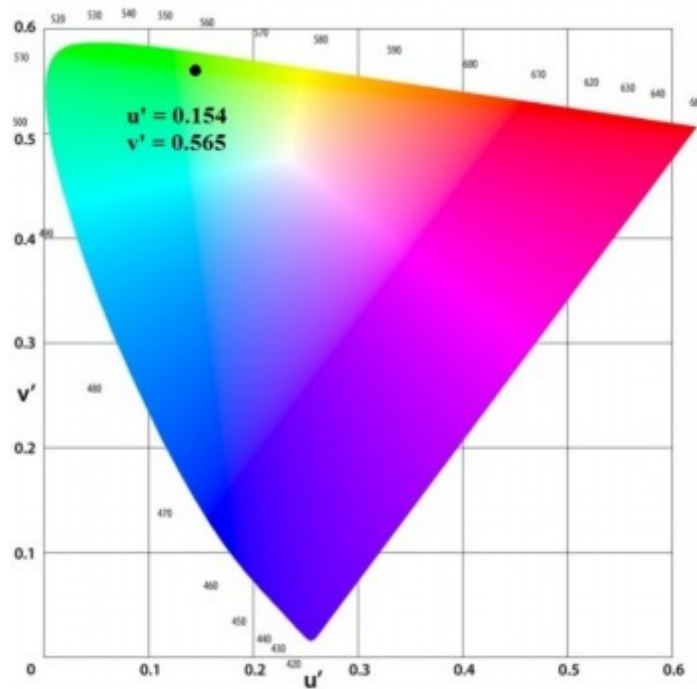


Figure 6.39: (u' , v') chromaticity diagram of S_{CT} sample.

CIE YUV (1960) is a linear transformation of Yxy, to create a chromaticity diagrams in which a vector of unit magnitude (difference between two points signifying two colors) is equally visible at all colors [54]. Y is unchanged from XYZ or Yxy. Difference in non-uniformity is reduced considerably, but not enough. A third co-ordinate, w', can also be defined but is dismissed.

$$u' = \frac{2x}{(6y-x+1.5)} \quad (6.6)$$

$$v' = \frac{4.5y}{(6y-x+1.5)} \quad (6.7)$$

the value of u' and v' for sample S_{CT} are (0.154, 0.565) and are shown in Figure 6.39. Further, the quality of white light is evaluated from the chromaticity coordinates using McCamy's relation [55] by first evaluating ratio between inverse slope line and chromaticity epicenter as:

$$n = \frac{(x-x_e)}{(y-y_e)} \quad (6.8)$$

where $x_e = 0.3320$ and $y_e = 0.1858$. Here value of n is 0.06. The Correlated Color Temperature (CCT) was evaluated as:

$$CCT = -449n^3 + 3525n^2 - 6823.3n + 5520.33 \quad (6.9)$$

this was found to be 5123.2 for SCT sample.

The color purity or color saturation of a light source is the distance in the chromaticity diagram between the (x, y) color coordinate point of the test source and the coordinate of the equal energy point divided by the distance between the equal-energy point and the dominant wavelength point. The color purity is thus given by [56]

$$\text{Color Purity (\%)} = \frac{\sqrt{(x-x_i)^2 + (y-y_i)^2}}{\sqrt{(x_d-x_i)^2 + (y_d-y_i)^2}} \times 100 \quad (6.10)$$

where, (x, y), (x_i, y_i) and (x_d, y_d) represent the chromaticity coordinates of the light source under test, equal-energy reference illuminant and dominant-wavelength point, respectively. The CIE coordinates (x, y) of S_{CT} are (0.340, 0.590). (x_i, y_i) is the CIE of equal energy illuminant with a value of (0.3101, 0.3162). The dominant wavelength point of S_{CT} are

determined to be 559 nm and we can obtain, chromaticity coordinates (x_d , y_d) for S_{CT} are (0.365, 0.631), respectively. By substituting the coordinates of (x , y), (x_d , y_d) and (x_i , y_i) to Eq. (6.10), the color purities of S_{CT} are determined to be nearly 75%. This result indicates that S_{CT} phosphor is a deep green phosphor and features as a high color purity phosphor, which signifies that this green-emitting phosphor is a suitable candidate for different color conversion and bio-labeling applications.

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CHAPTER 7

CONCLUSIONS AND FUTURE SCOPE

Overview

The present chapter summarizes the results obtained from various experiments discussed in the previous chapters. Effect of various parameters (e.g. annealing temperature, doping of rare earth ions, co-doping of alkali metal ions, pH of the solution and use of surface modifiers at the time of synthesis) on optical and morphological properties of doped Y_2O_3 have been summarized. Results obtained from the variation of these parameters were studied in detail. Further, conclusions made from the study of these results have also been summarized. Based on the observation of the present work, some suggestions to carry out more work in this field have been given at the end of this chapter.

7.1 Conclusions

In the present work, rare earth (Eu^{3+} , Tb^{3+} and Dy^{3+}) doped Y_2O_3 nanophosphors (NPs) with varying experimental conditions are synthesized. Effect of various parameters were studied to establish a route for the synthesis of highly luminescent doped Y_2O_3 NPs. Firstly various doping concentration and annealing temperature on optical and morphological properties of rare earth ($\text{RE}^{3+} = \text{Eu}^{3+}$, Tb^{3+} and Dy^{3+}) doped Y_2O_3 nanophosphors were studied. It was found that both doping concentration and annealing temperature affect the optical and morphology of Y_2O_3 . However, both parameters have some limitations. With increase in dopant's concentration in Y_2O_3 the PL emission intensity increases up to a certain limit. This limit is called quenching concentration of the corresponding dopant. In our case it was found to be 12.0 mol%, 1.0 mol% and 0.5 mol% for $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ and $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ phosphors respectively. Further increase in doping concentration of the dopant results in overall decrease in PL emission intensity of the phosphor. Moreover, with the increase in temperature during annealing, the luminescence intensity of the NPs increases. However, the crystallite size of the NPs also increases. The increase in crystallite size of nanophosphors restricts their use in many applications.

In order to overcome these limitations in prepared NPs, $\text{Y}_2\text{O}_3:\text{RE}^{3+}$ were then synthesized by codoping of alkali metal ions. Effect of codoped alkali metal ions ($\text{M}^+ = \text{Li}^+$, Na^+ and K^+) on optical and morphological properties of $\text{Y}_2\text{O}_3:\text{RE}^{3+}$ were studied. Further enhancement in the emission intensity of RE^{3+} doped Y_2O_3 beyond the quenching concentration of the dopant was observed using codoping of alkali metal ions at the time of synthesis. Addition of alkali metals has greatly enhanced the emission intensity of red ($\text{Y}_2\text{O}_3:\text{Eu}^{3+}$), green ($\text{Y}_2\text{O}_3:\text{Tb}^{3+}$) and yellow ($\text{Y}_2\text{O}_3:\text{Dy}^{3+}$) phosphor. One more interesting observation is the effect of Na^+ ion doping on Y_2O_3 . Due to the presence of Na^+ ion the hydroxal (OH^-) and nitro groups (NO_2^-) that are also called luminescent quenchers reduced to large extent which ultimately resulted in highest emission intensity of various $\text{Y}_2\text{O}_3:\text{RE}^{3+}$ nanophosphors which were codoped with Na^+ ion at the time of synthesis. However, considerable enhancement in PL emission intensity was also seen for codoping of Li^+ ion and K^+ ions. The morphology of the samples containing metals ions was almost same in all the samples. Since this study was to see the effect of metals ions on morphology and optical properties of Y_2O_3 so, the effect of surface modifiers (surfactant or polymer) at the time of

synthesis was not studied. As a result of this the morphology was not controlled by any other factor which results in uncontrolled growth of rod like morphology in almost all the samples.

To control the morphology of synthesized phosphors effect of various surface modifiers (SMs) were also studied. It was observed that there is a considerable effect of pH and capping agent on the morphological and optical properties of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$. Moreover, by optimizing polymer amount during synthesis of nanoparticles narrow size, higher crystallinity and enhanced photoluminescent properties of doped Y_2O_3 has been achieved. However, for spherical morphology with smaller diameter of the nanoparticles, the pH of the solution should be maintained at low value ($\text{pH} < 7$). One more interesting observation was the effect of CTAB surfactant. It was seen that the addition of CTAB at the time of synthesis helps in improving the crystallinity of the final product. The samples prepared by CTAB were more crystalline than the samples which were prepared without CTAB. Moreover the samples prepared by adding TOPO showed better spherical morphology and smaller crystallite size even in samples which were annealed at higher temperatures ($> 600^\circ\text{C}$). However, effect on optical and morphological properties of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ NPs were also studied by adding both these surface modifiers at the time of synthesis. It was observed that the samples of $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ prepared by adding both CTAB and TOPO i.e. ($\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ @ CTAB+TOPO) were highly crystalline, narrow size distribution and highly luminescent.

The concluding remarks of this discussion are that for the synthesis of doped Y_2O_3 co-precipitation is an economical and easy method. The aim of the present work is to synthesize highly luminescence and narrow sized nanophosphor of rare earth doped Y_2O_3 . In order to accomplish this aim various parameters were studied. Doping and annealing temperature has enhanced the photoluminescence properties greatly. Further enhancement beyond quenching concentration of the dopants has been achieved by co-doping of alkali metal ions in doped Y_2O_3 effectively. Effect of doping and codoping can be easily seen from PL excitation and emission spectra of prepared nanophosphors of Y_2O_3 . Morphology and narrow particle size distribution has been obtained by maintain pH ($\text{pH} < 7$) of the solution and by adding suitable surface modifiers in certain amount successfully. Clear spherical morphology can be seen in TEM micrographs of the prepared samples using above synthesis modifications. All these above discussed synthesis modification can be useful in synthesizing highly luminescent nano-sized $\text{Y}_2\text{O}_3:\text{RE}^{3+}$ for its applications in various fields as a promising phosphor.

7.2 Future scope

Although extensive study has been done to improve photoluminescence properties of doped Y_2O_3 , still there are many more possibilities of further investigations. Based on the present work, the suggested possibility to further improve the efficiency of these phosphors can be undertaken. These are listed below.

- Based on above study, combined effect on red, blue and green part of these phosphors, white light can be generated and further improvement in white light can be done using all the techniques can be achieved.
- Based on the above studies, effect of UV irradiation can be investigated on optical and morphological properties of doped Y_2O_3 nanophosphors.
- It has been seen from primarily study (discussed above) that $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$ can be a potential candidate for emitting white light as three types of emission can be seen in its PL emission spectra. Further work in this direction can be promising one to obtain white light from a single dopant system.
- In our work we have used CTAB and TOPO together simultaneously to improve the crystallinity, morphology and luminescence of doped Y_2O_3 nanophosphors similarly other combinations of various surfactants can be studied to achieve better crystalline behaviors and high luminescence at low temperature.
- Highly luminescent doped Y_2O_3 nanophosphors obtained by our synthesis methods can be used in biological fields. Biological use of these phosphors is the main future scope of this study.