

Synthesis and Characterization of Eu⁺⁺⁺ Doped Y₂O₃ (Red Phosphor) and Tb⁺⁺⁺ Doped Y₂O₃ (Green Phosphor) by Hydrothermal Processes

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ABSTRACT

Eu⁺⁺⁺ and Tb⁺⁺⁺ doped Y₂O₃ nanoparticles have been synthesized by hydrothermal process using yttrium oxo-isopropoxide Y₅O(OPrⁱ)₁₃ as precursor (OPrⁱ = isopropoxy). X-ray diffraction (XRD), transmission electron microscopy (TEM), nanoparticle size analyzer and photoluminescence (PL) spectroscopy have been used to characterize these powders. The as synthesized powders gave very sharp peak in the X-ray diffraction suggesting crystalline particles with average particle size between 28 - 51 nm for Eu⁺⁺⁺ doped Y₂O₃ nanoparticles and 43 - 51 nm for Tb⁺⁺⁺ doped Y₂O₃ nanoparticles annealed at 300°C for 3 h, 4 h and 5 h, which could be unique in comparison to other reports. Transmission electron micrograph investigation of the particles shows single dispersed particles along with agglomerates. The ratio of intensities of transitions in the europium and terbium emission spectrum have been used as structural probe to indicate the local environment around Eu⁺⁺⁺ and Tb⁺⁺⁺ in the Y₂O₃ particles.

Keywords: Yttrium Oxo-Isopropoxide; Nanophosphors; Y₂O₃:Eu⁺⁺⁺; Y₂O₃:Tb⁺⁺⁺; Hydrothermal Process

1. Introduction

The research of efficient and inexpensive nanoparticles is a challenging problem for the new materials generation [1]. The production of luminescent materials for technology applications requires strict control over their powder characteristics which include chemical homogeneity, low impurity levels and a sub micrometer particle size with a narrow distribution [2,3]. The conventional phosphor production through high temperature solid state reactions typically results in particle sizes of 5 - 20 nm [4]. Aiming at nanometer sized oxide particles, more advanced types of synthesis are then required [5,6]. Since the yttrium oxide presents good luminescent properties when doped with rare earth ions (Eu⁺⁺⁺, Tb⁺⁺⁺) [7-9], the oxide phosphor materials could be a good example to improve the luminescence properties and to extend the application field to a large domain [10,11].

Rare earth ions doped nanocrystalline metal oxides are a class of luminescent materials (also called upconverting phosphors) which have been proved to be excellent for applications such as in field emission displays (FEDs), cathode ray tubes (CRTs) and plasma display panels (PDPs), optoelectronic devices, biological fluorescence

labelling, luminescent paints and inks for security codes and many more [12]. Under UV irradiation Eu⁺⁺⁺ doped Y₂O₃ is a red phosphor and Tb⁺⁺⁺ doped Y₂O₃ is a green phosphor. It is possible that, due to their high quantum efficiency, they might serve as improved luminescent markers for identification of biomolecules, as already reported for CdSe and CdSe/ZnS nanocrystal [13]. However, for any biological applications these particle powders must be suspended in water while retaining their phosphorescence. Over the years a number of different routes, such as spray drying, freeze-drying, sol-gel, co-precipitation, self-sustaining combustion, emulsion technique, hydrothermal method, template method, electrochemical method or combinations thereof have been used to synthesize RE-doped Y₂O₃ nanophosphors [14-21]. We hereby report synthesis & characterization of Eu⁺⁺⁺ and Tb⁺⁺⁺ doped yttrium oxide nanoparticles by hydrothermal processes and compare its characteristics with the other reported methods for these nanoparticles. Eu⁺⁺⁺ and Tb⁺⁺⁺ doped Y₂O₃ nanoparticles have been synthesized by hydrothermal technique using yttrium oxo isopropoxide [Y₅O(OPrⁱ)₁₃] as precursor.

Generally the metal oxides derived by sol-gel method are required to be annealed to temperature ranging from 400°C - 800°C in order to develop crystalline phases [22].

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However, this annealing also results in development of aggregates which are undesirable for bio-conjugation experiments. But in our case the crystallinity was achieved at 300°C by hydrothermal process. The average particle sizes as calculated from XRD were found between 28 nm to 51 nm in case of Eu⁺⁺⁺ doped Y₂O₃ and 43 nm to 50 nm in case of Tb⁺⁺⁺ doped Y₂O₃ nanoparticles at 300°C for 3 h, 4 h and 5 h. The TEM investigations showed the presence of single particles along with agglomerates.

2. Experimental

2.1. Synthesis and Characterization of (Y₅O(OPrⁱ)₁₃ Precursor

The precursor Y₅O(OPrⁱ)₁₃ was synthesized and characterized by the method of Ashutosh Pandey *et al.* [22]. Y₅O(OPrⁱ)₁₃ was used as precursor in hydrothermal process for making yttrium oxide nanoparticles. The manipulation pertaining to synthesis of Y₅O(OPrⁱ)₁₃ precursor was performed under dry argon atmosphere using Schlenck techniques. The solvent were dried and purified by standard procedures. Water was doubly distilled, deionized and purified by standard procedures. Yttrium chips (Aldrich), toluene, isopropanol, Hg(OAc)₂ (all qualigens) were used to perform the chemical reaction which gave the precursor in 70% yield. It was characterized by elemental analysis (Found (%) C 38.15, H 7.70; calculated C 38.12, H 7.12) and NMR spectroscopy {¹H NMR in ppm}, 1.29 (doublet), 4.30 (septet) in dry CDCl₃ and found in accordance with reported values.

2.2. Synthesis of Eu⁺⁺⁺ and Tb⁺⁺⁺ Doped Nanoparticles by Hydrothermal Method

83 ml of 0.1 M HNO₃ was added dropwise to Y₅O(OPrⁱ)₁₃ (13.0 g) with vigorous stirring. At the same time a mixture of 4.51 g Eu(NO₃)₃·5H₂O (for 0.2 M doping) and 0.945 g water was added dropwise to it under stirring. After the addition was completed, white precipitate formed instantaneously. The slurry was refluxed and stirred vigorously for 8 h, to achieve peptization. The colloidal solution was introduced in a rotary evaporator and evaporated (50°C, 30 mbar) to get desired volume of suspension. The growth of these particles was achieved under hydrothermal condition and sedimentation occurred during the hydrothermal condition. After the decantation of above milky liquid portion, we got colloidal suspension of europium doped yttrium nanoparticles. The colloidal suspension was dried in oven at 100°C to achieve a white powder. It was subjected to heat treatment at 300°C for 3 h, 4 h and 5 h respectively. Upon heating to different time, the Eu⁺⁺⁺ doped (0.2 M doped) material did not show any discernable change in white color of the starting powder.

A similar procedure was applied for Tb⁺⁺⁺ doped powders for which 4.51 g Tb(NO₃)₃·5H₂O was used for

0.2 M doping. The resulting suspension was dried in an oven at 100°C to give white powder. It was subjected to heat treatment at 300°C for 3 h, 4 h and 5 h respectively. Tb⁺⁺⁺ doped Y₂O₃ powder did not undergo any colour change upon heat treatment to different time.

2.3. Characterization

The proton and C13 NMR spectra were recorded by GEOL-300 MHz spectrometer at BHU Varanasi, X-ray diffraction pattern were recorded on Seifert powder diffractometer using Cu-Kα X-rays. The surface morphology of samples was studied by the transmission electron microscopy on model Tecnai G20-twin. The secondary particle size of TiO₂ nanoparticles were measured by Nanotrak particle size analyser. The photoluminescence spectra were recorded on an ocean optics system with range 200 - 1800 nm using an excitation wavelength of 440 nm.

3. Results and Discussion

Europium (Eu⁺⁺⁺) and terbium (Tb⁺⁺⁺) doped Y₂O₃ is a well-known and efficient red emitting luminescent material finding extensive application in displays, *in vivo* biological imaging and as a luminescent security ink for detecting any counterfeiting, alteration and unauthorized trading [23]. It is an insulator with a bulk band gap of 5.6 eV and hence strongly absorbs at energies with wavelengths of less than 230 nm.

In the present investigation, we have successfully synthesized a Eu⁺⁺⁺ and Tb⁺⁺⁺ doped Y₂O₃ nanophosphors of average size 28 - 51 nm using hydrothermal technique and finally developed highly transparent and nonaqueous-stable nanophosphors for bio-conjugation applications. In order to understand the stability of colloids, which has a direct relation to particle size, we carefully monitored the morphology of selective experiments. Slow and controlled heat treatments to the nanoparticles were performed to tailor the Y₂O₃:Eu⁺⁺⁺ and Y₂O₃:Tb⁺⁺⁺ nanophosphors for enhanced brightness level. Europium and terbium doped (0.2 M concentration) Y₂O₃ white powder, were derived by hydrothermal methods and warmed to 100°C.

The obtained nanoparticles were annealed to 300°C for 3 h. X-ray diffraction patterns for the Eu⁺⁺⁺/Y₂O₃ doped particles are shown in **Figure 1**. All peaks in **Figure 1(a)** correspond to that cubic structure of Y₂O₃, indicating that crystallinity was achieved at 300°C. However, the solvent molecules were completely expelled after annealing at 400°C to achieve the crystallinity [22]. So the obtained nanoparticles were further heated to 4 h and 5 h at the same temperature *i.e.* 300°C to observe the effect of further annealing on the particle size of these nanoparticles. These show that our samples achieved crystallinity at

300°C when annealed for 3 h in hydrothermal process which differentiates these nanoparticles from several techniques, such as sol-gel technique [22] and alkali reduction method [24]. The crystallinity was achieved at 500°C and above in case of alkali reduction and 400°C in case of sol-gel technique. The peak positions of the entire specimen showed (222) peak with highest intensity in the XRD patterns. The diffraction peak in the patterns is indexed to cubic equilibrium structure for $\text{Eu}^{+++}/\text{Y}_2\text{O}_3$ and $\text{Tb}^{+++}/\text{Y}_2\text{O}_3$ nanoparticles. The average particle size (d) was calculated using the Scherer's formula.

$$d = 0.9 \lambda / (B \cos \theta)$$

The average particles sizes with respect to sharp peaks are 28, 32, 34 nm in case of $\text{Eu}^{+++}/\text{Y}_2\text{O}_3$ nanoparticles and 43, 46, 50 nm in case of $\text{Tb}^{+++}/\text{Y}_2\text{O}_3$ nanoparticles respectively at 300°C for 3 h, 4 h and 5 h.

The morphological aspect of the resulting powders synthesized by hydrothermal technique was examined by TEM, as shown in **Figure 2**. The micrographs revealed the formation of agglomerates, along with single dispersed particles. An X-ray diffraction indicated that all of these agglomerates consisted of Y_2O_3 doped with $\text{Eu}^{+++}/\text{Tb}^{+++}$ ions.

Figure 3 shows the particle size distribution corresponding to sample $\text{Eu}^{+++}/\text{Tb}^{+++}$ doped Y_2O_3 nanoparticles soluble in chloroform. The graph shows the uniform

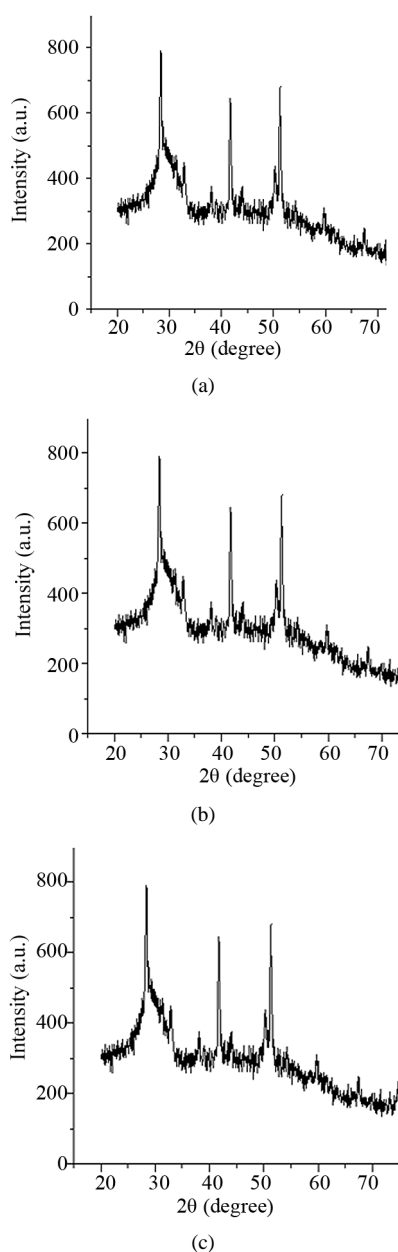


Figure 1. XRD pattern of 0.2 M Eu^{+++} doped Y_2O_3 nanoparticles synthesized by hydrothermal method annealed at 300°C for 3 h, 4 h and 5 h (a-c).

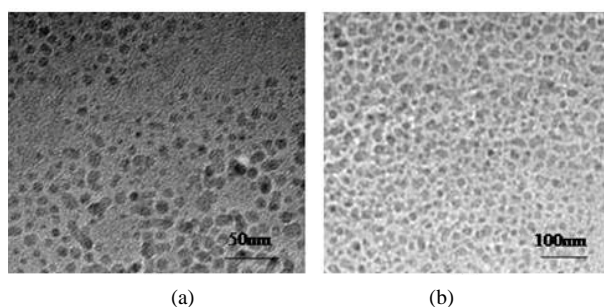


Figure 2. TEM images of (a) 0.2 M Eu^{+++} (b) 0.2 M Tb^{+++} doped Y_2O_3 synthesized by hydrothermal process.

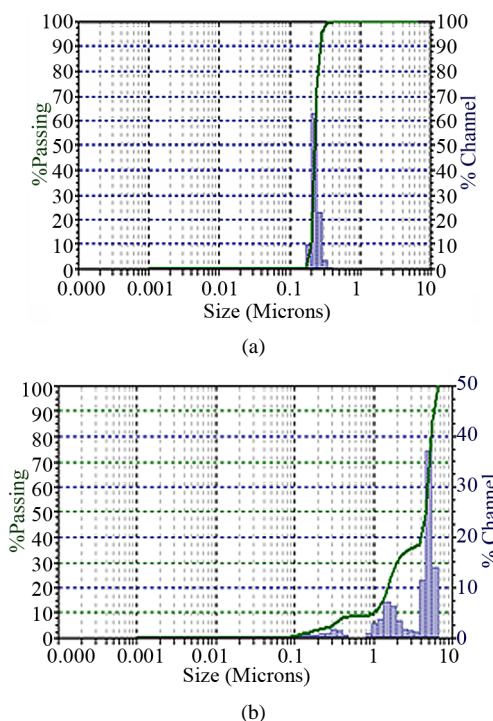


Figure 3. Particle size distribution corresponding to samples [1] 0.2 M $\text{Eu}^{+++}/\text{Y}_2\text{O}_3$ and [2] 0.2 M $\text{Tb}^{+++}/\text{Y}_2\text{O}_3$ nanoparticles soluble in chloroform.

stability and improved homogeneity of nanoparticles in case of Eu^{+++} doped Y_2O_3 suitable for bioconjugation. The particle size analysis showed that these are nonaggregated and spherical in shape. But in case of Tb^{+++} doped Y_2O_3 nanoparticles, a group of nanoparticles are present with various sizes because of agglomeration of nanoparticles. The average secondary particle sizes calculated by nanotracer particle size analyzer were 110 nm and 140 nm for Eu^{+++} Tb^{+++} doped Y_2O_3 nanoparticles.

The distribution of the Eu^{+++} ions within the host Y_2O_3 matrix has been worked out by examination of the photoluminescence spectra, which is shown in **Figure 4** for both the 0.2 M Eu^{+++} :1 M Y_2O_3 (a) and 0.2 M Tb^{+++} :1 M Y_2O_3 (b).

PL spectra of all the samples were recorded using an excitation wavelength of 440 nm. The most characteristic peaks at 592 nm, 612 nm and 675 nm, which correspond to $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions in case of europium while in case of terbium the most characteristic peaks at 486, 481, 470, 456, 436, 414, and 381 nm, which correspond to $^5\text{D}_3 \rightarrow ^7\text{F}_0$, $^5\text{D}_3 \rightarrow ^7\text{F}_1$, $^5\text{D}_3 \rightarrow ^7\text{F}_2$, $^5\text{D}_3 \rightarrow ^7\text{F}_3$, $^5\text{D}_3 \rightarrow ^7\text{F}_4$, $^5\text{D}_3 \rightarrow ^7\text{F}_5$ and $^5\text{D}_3 \rightarrow ^7\text{F}_6$ transitions have been reported [25].

In our study, the photoluminescence spectrum for the nanoparticles synthesized and annealed at 300°C for 3 h bears a completely different look which is similar to powder synthesized by sol-gel method and annealed at

800°C [22]. In general, the sharp emission lines point towards occupation of Eu^{+++} ions in these crystallographic site that are situated in the interior of the nanocrystal. In particular, the 0.2 M Eu^{+++} samples show slightly broadened peak in the corresponding region indicating that in them some of the Eu^{+++} ions might have gone to particle boundaries. It may be due to sudden onset of thermodynamic process which extracts europium from the symmetrical octahedral sites in Y_2O_3 lattice and places them at the particle boundary and show simultaneous emission from site with different crystal field splitting. The powder which was annealed at 300°C for 3 h, showed the presence of $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$ as well as the $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transition lines, each with a large broadening so that they have merged together confirming the presence of europium ions in unsymmetrical environments (**Table 1**).

Similarly PL spectrum for 0.2 M doping concentration of Tb^{+++} within the Y_2O_3 matrix is showed in **Figure 4**. The $\text{Tb}^{+++}/\text{Y}_2\text{O}_3$ nanoparticles showed following transitions *i.e.* $^5\text{D}_3 \rightarrow ^7\text{F}_1$, $^5\text{D}_3 \rightarrow ^7\text{F}_2$ and $^5\text{D}_3 \rightarrow ^7\text{F}_3$ which overlapped together. All of these peaks have a very large broadening so that they merged together confirming the presence of terbium ions in unsymmetrical environments. A very broad peak indicates simultaneous emission from site with different crystal field splitting [26]. Therefore, the present investigation claims the synthesis of Eu^{+++} and Tb^{+++} doped Y_2O_3 phosphor nanoparticles for their potential applications with continuous emission properties.

4. Conclusion

Europium and terbium ions have been incorporated into Y_2O_3 matrix by hydrothermal process using yttrium oxo

Table 1. Comparative study of $\text{Eu}^{+++}/\text{Y}_2\text{O}_3$ and $\text{Tb}^{+++}/\text{Y}_2\text{O}_3$ nanoparticles synthesized by hydrothermal method.

Hydrothermal Process	$\text{Eu}^{+++}/\text{Y}_2\text{O}_3$ (0.2M)	$\text{Tb}^{+++}/\text{Y}_2\text{O}_3$ (0.2M)
Time	XRD [Particle size (nm)] PL [Transition Peaks (nm)]	XRD [Particle size (nm)] PL [Transition Peaks (nm)]
3 h	28 $^5\text{D}_0 \rightarrow ^7\text{F}_1$ $^5\text{D}_0 \rightarrow ^7\text{F}_2$ $^5\text{D}_0 \rightarrow ^7\text{F}_4$	43 $^5\text{D}_3 \rightarrow ^7\text{F}_1$ $^5\text{D}_3 \rightarrow ^7\text{F}_2$ $^5\text{D}_3 \rightarrow ^7\text{F}_3$
4 h	32 $^5\text{D}_0 \rightarrow ^7\text{F}_1$ $^5\text{D}_0 \rightarrow ^7\text{F}_2$ $^5\text{D}_0 \rightarrow ^7\text{F}_4$	46 $^5\text{D}_3 \rightarrow ^7\text{F}_1$ $^5\text{D}_3 \rightarrow ^7\text{F}_2$ $^5\text{D}_3 \rightarrow ^7\text{F}_3$
5 h	34 $^5\text{D}_0 \rightarrow ^7\text{F}_1$ $^5\text{D}_0 \rightarrow ^7\text{F}_2$ $^5\text{D}_0 \rightarrow ^7\text{F}_4$	50 $^5\text{D}_3 \rightarrow ^7\text{F}_1$ $^5\text{D}_3 \rightarrow ^7\text{F}_2$ $^5\text{D}_3 \rightarrow ^7\text{F}_3$

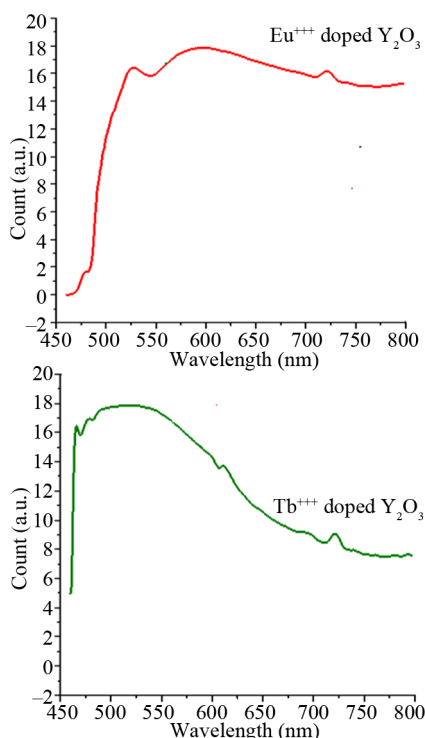


Figure 4. Photoluminescence spectra of Eu^{+++} (0.2 M) and Tb^{+++} (0.2 M) doped Y_2O_3 prepared by hydrothermal method, annealed at 300°C for 3 h.

isopropoxide as precursor. In hydrothermal process the particle size increased as the heating time increased but less than other process. The crystallinity was achieved at 300°C that is unique in comparison to other synthetic methods. The morphological aspect of the resulting powders was examined by TEM which showed single dispersed particles along with agglomerates. X-ray diffraction indicated that all of these agglomerates consisted of Y₂O₃ doped with Eu⁺⁺⁺ ions and Tb⁺⁺⁺ ions. The location of rare earth (Eu⁺⁺⁺ and Tb⁺⁺⁺) in the particles has been probed by examining the PL spectra of particles. The powders annealed at 300°C for 3 h, 4 h and 5 h, showed the occupancy of Eu⁺⁺⁺ ions and Tb⁺⁺⁺ ions in both symmetrical and unsymmetrical lattice positions by the ions. In case of hydrothermal process, the broadened peaks were observed which is similar to sample synthesized by sol-gel method [22] and annealed at 800°C.

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