

Thermoluminescence and Photoluminescence of Eu^{3+} doped Y_2O_3 Nanophosphors

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Abstract

Rare earth doped Y_2O_3 nanophosphors were prepared with different doping concentration of Eu^{3+} and synthesizing temperature 600°C by the combustion method. In this method urea is employed as a fuel. The particle size is estimated to be in the range of 10-20 nm as determined by X-ray diffractometry. The Photoluminescence Spectra are ascribed by the well known ${}^5D_0{}^-F_2$ transition (J=0,1,2,...etc)of Eu ${}^{+3}$ ion with the strongest emission for j=2.. The TL property of Eu doped Y_2O_3 nanophosphors have been investigated for different UV irradiation time and TL kinetic parameter were caculated. TL Spectra show intense peak around 600nm ,which shows Eu^{+3} emission. The red emission of Eu doped Y_2O_3 nanophosphors are promising materials not only in high resolution screen but also in radiation dosimetry.

Keywords: YttriumOxide, Nanophosphor, CombustionMethod

1.0 Introduction

Inorganic luminescence materials are crystalline compounds that absorb energy and subsequently emit this absorbed energy as light [1]. Phosphors are composed of an inert host lattice and an optically excited activator, typically a 3d or 4f electron metal such as Ce³⁺, Cr³⁺, Eu³⁺, and Tb³⁺. Oxide phosphors were found to be suitable for field emission display (FED), vacuum fluorescent display. (VFD), electroluminescent (EL) devices, and plasma panel display (PDP) devices. Y₂O₃ is an advanced ceramic due to its stable physical and chemical properties, which has been widely used as a host material in various luminescent applications.[2-4] It also presents the advantage of highly saturated color, which makes it a promising material for various industrial applications.

A number of studies have been reported on the luminescent properties of Y_2O_3 :Eu⁺³ nanoparticles and luminescence was found to depend strongly on the nature of synthesis method and condition employed. Luminescence efficiency increases as the size of the phosphor particle is decreased. The preparation process of phosphor powders becomes very important in the technological procedure [5]. To achieve better quality of small particle size powders, low temperature synthesizing is desired. In this study, we attempted a combustion synthesis process to produce Y_2O_3 :RE phosphors powders.

Red phosphor of Y_2O_3 doped with trivalent ions such as Eu has particularly attracted considerable interest in terms of high chemical durability and thermal stability [6].Tissue and coworkers have thoroughly investigated and reported Size Dependence of the Luminescence Spectra and Dynamics in Eu³⁺:Y₂O₃ Nanocrystals .They found no changes in the luminescent spectra and life time of red transition with decreasing the particle size.[7].Nanocrystalline europium doped yttrium oxide, synthesized using a chemical vapor deposition with an average particle size of only 10 nm showing blue shifted absorption band were studied by konrad et al.

The TL phenomenon is the result of releasing electrons trapped by some defects within the material lattice when exposed to any type of ionizing radiation. The stimulation energy to release these electrons trapped is usually thermal and those defects are in the form of electrons or holes traps. If these traps are energetically deep enough, charge carriers may remain trapped for an extended period of time until they acquire enough thermal-energy to increase the probability to escape, producing electromagnetic radiation after a radiative recombination process takes place. The relationship between the TL signal intensity and the irradiation dose provides the sample the potential application in dosimetry. Yeh et al [9] have reported the UV induced thermoluminescence in rare earth doped oxide Phosphor and its possible use in UV dosimetry and they found that Eu doped Y_2O_3 is sensitive enough to measure background UV



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radiation such as sun light, bulb light etc. We have also studied the TL and ML of Eu doped Y_2O_3 nanophosphor[10]. In this paper, we obtain the Y_2O_3 : Eu, nanocrystalline phosphors by combustion method. The luminescence properties of Y_2O_3 : Eu were investigated by changing the concentration of doping materials.

1.1 Experimental

In Yttrium nitrate (99.99%), nitric acid, urea (90%) were used as starting raw material. To prepare Y_2O_3 : RE ⁺³, RE(NO₃)₃ stock solutions was prepared by dissolving RE₂O₃ in nitric acid .These two solution of Y(NO₃)₃ and RE(NO₃)₃ were mixed according to the formula (Y_{.95}RE_{.05})₂O₃ in a beaker and then a suitable amount of urea was added. An urea to metal nitrate was employed to prepare the precursor solution. Finally this sample was transferred to crucible and fired in a furnace at 600^oC.The synthesis reaction is

(2-2x) Y (NO₃)₃ + 2x RE(NO₃)₃ +5NH₂CONH₂ → (Y_{1-x}RE_x)₂O₃+5CO₂+8N₂+10H₂O

The morphologies and sizes of the Eu doped Y_2O_3 were determined by X-ray diffraction studies with Cu K α radiation (λ =1.5418 A°).XRD data were collected over the range 20°-80° at room temperature. The Xray diffraction patterns have been obtained from Xray Powder diffractometer .The particle size was determined using the sherrer's formula. The Shimadzo 1700 UV-VIS spectrometer is used to obtain the optical absorption spectra of Eu doped Y₂O₃. For recording TL, samples were exposed to UV radiations at different time. TL glow curves were recorded with the help of TLD reader (Model 1009I).TL spectra were recorded by using interference filters. .The resulting products were characterized by FTIR spectra to evaluate the vibrational feature of the sample.

1.2 Results and Discussion

1.2.1 Optical Absorption

The study of optical absorption is important to understand the behavior of nano-crystals. A fundamental property is the band gap-the energy separation between the filled valence band and the empty conduction band. Optical excitation of electrons across the band gap is strongly allowed, producing an abrupt increase in absorption at the wavelength corresponding to the band gap energy. This feature in the optical spectrum is known as the optical absorption edge. Figure 1.1 shows the optical absorption spectra of Y_2O_3 :Eu(3 mol%) powder .



Fig 1.1 Optical absorption spectra of Y₂O₃: Eu(3 mol%)

The absorption edge was obtained at 230 nm for Eu doped Y_2O_3 and corresponding band gap energy is found 5.4 eV for Y_2O_3 : Eu phosphor

1.2.2 X-RayDiffraction



Fig 1.2 X-ray diffraction patterns of Y₂O₃:Eu(3 mol%)

Figure 1.2 shows the X-ray diffraction patterns of Y_2O_3 :Eu(3 mol%) powder . The XRD patterns are well matched with the characteristic peaks of the standard cubic Y_2O_3 structure (JCPDS no. 41- 1105), which belongs to Ia3 space group with lattice constant a=10.608 nm. The peak at 2θ = 29.1501 was observed as the strongest peak corresponding to the plane (222) for Eu doped Y_2O_3 . The mean crystallite sizes (D) of nanophosphors were calculated based on the peak widths from the Debye–Scherrer equation, given as D=0.89 λ / β Cos θ where D is the crystalline



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size in nanometers, λ is the X-ray wavelength (1.54056 A°), β is the full-width at half maximum in radians, and θ is the Bragg angle. The crystallite sizes for the as-prepared Y₂O₃: Eu (3 mol %) powder was around 14 nm.

1.2.3 FTIR



Fig1.3 Infrared spectra of Eu doped Y_2O_3 :Eu(3 mol %)

FT-IR was used to investigate the functional groups on the surface of as prepared RE doped Y₂O₃ nanocrystals. FTIR spectra of Y2O3: Eu (3 mol %) is shown in Figure 1.3. A broad absorption band around 3340 cm^{-1} can be ascribe to the stretching vibration of the hydroxyl group (-OH) of the absorbed water molecules. Absorption at around 1500- 1380 cm⁻¹ might originated from C-H bend and C-C stretching. These peaks were due to residual carbon in the prepared samples or absorption of CO₂ from the ambient atmosphere. The absorption bands at around 570 cm⁻¹ are characteristic of the metal oxide (Y–O) stretching vibrations of cubic Y₂O₃, which is in accordance with the report 11. The absorption peaks resulted by bonding of metal ions usually appears at short wave numbers [12].

1.2.4 Thermoluminescence



Fig 1.4 The TL glow curve of UV irradiated Y₂O₃:Eu(1 mol %)



Fig 1.5 The TL glow curve of UV irradiated Y_2O_3 :Eu(3 mol %)



Fig1.6 The TL glow curve of UV irradiated Y₂O₃:Eu(5 mol %)





1.7 The TL glow curve of UV irradiated Y₂O₃:Eu(7 mol %)

In the TL glow curve of Y_2O_3 : Eu nanophosphor for different concentration of doping material, two peaks have been observed. The maximum TL intensity have been found at 20 min UV irradiation time for 1 mole % concentration of doping material (figure 1.4), at 10 min UV irradiation time for 3 mole % concentration of doping material (figure 1.5), at 15 min UV

S. No.	Concentration 10 minutes irradiation time	Integral Count	First Peak Intensity	Second Peak Intensity
1.	Pure Y ₂ O ₃	1688	0	26
2.	1 mole %	3873	1	42
3.	3 mole %	7517	15	87
4.	5 mole %	3001	3	48
5.	7 mole%	2515	1	33

Table 1.1: Integral count, first and second peak intensity of Y_20_3 :Eu nanophosphors for different concentration at particular irradiation time 10 minutes



Fig 1.8 Total TL intensity Vs concentration of doping material

irradiation time for 5 mole % concentration of doping material (figure 1.6) and at 10 min UV irradiation time for 7 mol % concentration of doping material (1.7). From these figures, It is clear that the TL intensity increases with increasing in UV irradiated time and attains a maximum value for particular irradiation time and then it seems to be saturated for higher irradiation time.

Eu³⁺ ion acts as a recombination center affecting the TL response of the Y_2O_3 material. As the particle become smaller, ions at the surface are not saturated in coordination. Electrons or holes may be excited easily and escape from the ions and they are trapped at surface states located in the forbidden gap. When the sample is heated the electrons are detrapped and their subsequent recombination with holes gives rise to the light emission. The TL intensity is increased for higher exposed time because the new trapping center is created by increasing exposure time of UV radiation. The trapping centers provide energy states available between valance band and conduction band responsible for radiative recombination. As the radiation dose is increased the color centers increase so initially the intensity increases with increasing UV dose. After the color center get saturated so that TL intensity saturated for higher UV dose.



Fig 1.9 The first peak intensity Vs concentration of doping material.

From figure 1.8, figure 1.9 and 1st peak intensity, it is seen that the total TL intensity firstly increases, attains a peak value at 3 mol% and further decreases with increasing concentration of doping material and this reduction in total TL intensity has been attributed to concentration quenching. Similar case occurs for second peak intensity .There is no considerable change found in first and second peak temperature with variation in concentration.





Fig 2.0 Thermoluminescence spectra of UV irradiated Eu doped Y₂O₃ (3 mol %)

Fig 2.0 shows the TL spectrum of Y_2O_3 : Eu nanophosphor (for 3 mole% concentration). Spectra shows one peak at 600nm which shows Eu emission.

A complete characterization of thermoluminescent materials can not be done without concerning the kinetic parameters , such as order of kinetics (b),the activation energy (E) of the trap involve in the TL emission and frequency factor. The knowledge of these parameter is essencial ,due to its connection with thermal and optical stability of traps as well as further application. Here we are using two following methods for calculating kinetic parameters of Eu doped Y_2O_3 nanophosphor.

1.2.4.1 Initial Rise Method

The initial-rise is based on the fact that as the glow curve initially begins to rise, the density of unoccupied recombination centers and the density of trapped electrons remain approximately constant, and hence the TL intensity is strictly proportional to exp(-E/kT).



Fig 2.1 IR method for First peak of Y₂O₃:Eu (3mole%)

concentration)



Fig 2.2 IR method for second peak of Y₂O₃:Eu (3mole% concentration)

S.No	Sample name (mol	For	Ist	For	2 nd
	%)	peak		peak	
1.	Y ₂ O ₃ : Eu (3 mol %)	.51ev		1.05 ev	

Table 1.2: The activation energy of Eu doped Y₂O₃ by IR method

1.2.4.2 Chen's Peak Shape Method

The order of kinetics and the activation energy of glow curve was found using Chen's empirical formulae [13]. Theoretically the form factor μ_g is found using formula

 $\mu_{\rm g} = (T_2 - T_{\rm m})/(T_2 - T_1).$

Where, T_m is the peak temperature at the maximum and T_1 and T_2 are respectively, the temperatures on either side of T_m , corresponding to half intensity. The trap depth or the thermal energy needed to free the trapped electrons can be calculated using the

following equation $E_{\alpha}=c_{\alpha} (kT_m 2/\alpha)-b_{\alpha} (2kT_m) \qquad \alpha=\tau, \, \delta, \, \omega,$

 $\omega = T_2 - T_1$ is the total half-width

 $\mu\text{=}~\delta/~\omega$ is so called geometrical shape or symmetry factor

$$c_{\tau} = 1.51 + 3.0 \ (\mu_g - 0.42), \qquad c_{\delta} = 0.976 + 7.3 \ (\mu_g - 0.42)$$

 $\tau = T_m - T_1$ is the half width at the low temperature side of the peak

 $\delta = T_2 - T_m$ is the half width toward the fall-off side of the glow peak

 $c_{\omega} = 2.52 + 10.2 \ (\mu_g - 0.42), \ b_{\tau} = 1.58 + 4.2(\mu_g - 0.42)$ $b_{\delta} = 0, \ b_{\omega} = 1$

frequency factor [14] was calculated from equation $\beta E \ / \ kT_m = s \ exp\{-E/kT_m \ \} [1+(b-1)T_m \ Where$

(



 β = Heating rate

E = The activation energy or trap depth (eV)

T = The absolute temperature (K)

Y ₂ 0 ₃ :E u	Maximum peak temperature (T _m)	Order of kinetics(b)	Activation energy (E)			Frequen cy factor (s)	
3mol %			E _δ	Eω	Eτ	E_{avg}	
First peak	400.68	2 nd order	0.59 8	0.552 8	0.4959	0.54	4.3* 10 ¹⁰
Secon d peak	568	1st order	1.09	1.09	1.08	1.08	1.09*10 ⁹

Table 1.3: The TL parameters of Eu doped Y₂O₃ by Chen's empirical method

From the above results(table 1.3), it is seen that the first trap is 0.54 eV below conduction band and the second trap is 1.08 eV below conduction band. The intensity of first peak is less then the intensity of second peak. Therefore we can say that the concentration of first trap is less than the concentration of second trap. Since the frequency factor (s) is also called attempt to escape frequency and it is directly proportional to absolute temperature so for higher temperature glow peak frequency factor is high.

1.2.4 Photoluminesce



Fig 2.3: Excitation spetra of Y₂O₃: Eu



Fig 2.4: Emission spectra of Y₂O₃: Eu

Fig: 2.3 and fig 2.4 displayed the excitation and emission spectra of Y₂O₃: Eu (3 mol %) phosphors powder. For photoluminescence measurements, Y_2O_3 : Eu phosphors powder was excited with 260 nm wavelengths from a UV lamp. The characteristic line at 611 nm appeared in the spectra of Y2O3: Eu phosphors powder with 3 mol% of europium concentration. The strong and narrow emission feature is an indication of presence of Eu³⁺ in a highly crystalline cubic Y₂O₃ environment. From the luminescence spectrum, we can observe that the Y_2O_3 : Eu phosphors powder shows a red emission. The emission of strong red emission at 611 nm is ascribed to the forced electric dipole transition (${}^{5}D_{0}$ - $^{7}F_{2}$), which is allowed in this case as the europium does not occupy a center of symmetry in yttria [15]. According to previous reports, Y₂O₃has a cubic space group with two crystallographically different sites C₂ and C_{3i} . Eu³⁺ ions reside in both sites with equal probability. However, the strong red emission at about 611 nm caused then ${}^{5}D_{0}$ - ${}^{7}F_{2}$ transition of Eu³⁺ in the C_2 site [16].

2.0 CONCLUSION

In Summary ,we have shown that nanocrystalline Y₂O₃:Eu can be prepared via combustion synthesis between metal nitrate and urea.X-ray diffractometry indicate that the particle diameter is in the range of 10-20 nm.The Photoluminescent spectra of as prepared samples were measured and show the red emission. The TL property of Eu doped Y₂O₃ nanophosphors have been investigated for UV irradiation and it is seen that at particular irradiation time, high intensity glow peaks were found. The trapping parameters are calculated. The 1st peak of Eu doped Y₂O₃ is found to have 2nd order of kinetics suggesting retrapping of charge carriers. The 2nd peak of Eu doped Y_2O_3 is found to first order kinetics in TL emission Suggesting large electron-hole recombination. .TL Spectra show intense peak around 600 nm, which shows Eu^{+3} emission.

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