

Photoluminescence and Electroluminescence of Y₂O₃: Tb Nanophosphor

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Abstract-

The characteristics and luminescent properties of nanophosphors, Y_2O_3 : Tb, are reviewed and summarized in this work, with focus on the results obtained. In this work, Trivalent Terbium (Tb)-doped cubic Yttrium oxide (Y_2O_3) nanophosphors for different concentration of doping material were synthesized by combustion synthesis method using urea as fuel. The prepared sample were characterized by X-ray diffraction (XRD), Transmission electron microscopy (TEM),Scanning electron microscopy(SEM), Fourier transform infrared spectroscopy (FTIR) In the optical properties, emission spectra comprise several groups of lines corresponding to the ${}^5D_4 \rightarrow {}^7F_J(=1-6)$ 4f electronic transitions of the Tb ${}^+3$ ions. EL intensity was measured with the help of photomultiplier tube.

Keywords:Nanophosphor, *combustion method*, *photoluminescence*(*PL*), *Electroluminescence*(*EL*)

Introduction

Over past few years, the synthesis and characterization of nanomaterials have attracted much attention in display and lighting technology. Nanostructured materials possess properties, which are often uniquely different from those exhibited by their macroscopic counterparts due to perturbations of the electronic distribution induced by reduced dimensionality. The development of nanocrystalline phosphors has become pivotal due to the ever-shrinking size of today's technology.In particular, this oxide is chosen as host because it is characterized by a low-phonon frequency, which makes the nonradiative relaxation of excited states inefficient. Moreover, it has excellent refractory properties with a melting point of 2450 °C and a high thermal conductivity [1].

As regards the doping ions, REs are considered to be the most promising elements as activator of nanophosphors since they have particular optical properties because of their special electronic configuration. The characteristic luminescence of RE ions is attributed to the 4f shell, which is not entirely filled [2]. In the case of Tb³⁺, there are eight 4f-electrons; the 4f shell readily releases an electron, and the intraionic transition $4f^8-4f^75d$ absorption takes place at relatively low energy. Moreover, the 5d orbit, being the outer orbit of the ion, is strongly influenced by the electric field of the surrounding ions (the crystalfield), creating efficient absorption bands.

Particular attention has been drawn to trivalent Tb ions $(4f^8)$ as a doping element in hosts as yttrium or

gadolinium oxide because of its narrow green bands originating from intra 4f-transitions. Soo et al.,[3] investigated the local structure of Tb-doped Y_2O_3 nanocrystals. Meng et al [4] reported the influence of size confinement on the energy transfer between Tb⁺³ ions in Y_2O_3 nanopowders. Incorporation of rare earth in the nanocrystalline yttrium oxide matrix can be done by several techniques, such as the, polyol method [5], hydrothermal [6,7], liquid phase reaction [8], aerosol pyrolysis[9], and sol–gel techniques[10], Pechini method[11]. In recent works, Combustion method has been successfully used in the synthesis of dielectrics networks doped with Respect to prepare luminescent powder materials [1, 12-15].

EXPERIMENTAL DETAILS-

In this study Europium oxide (99.99%), Yttrium nitrate (99.99%), nitric acid, urea (90%) were used as starting raw material. To prepare Y_2O_3 : Tb⁺³, RE(NO₃)₃ stock solutions was prepared by dissolving Tb₂O₃ in nitric acid .These two solution of Y(NO₃)₃ and Tb(NO₃)₃ were mixed according to the formula $(Y_{.95}Tb_{.05})_2O_3$ in a beaker and then a suitable amount of urea was added. A urea to metal nitrate was employed to prepare the precursor solution. Finally this sample was transferred to crucible and fired in a furnace at 600⁰C.The Synthesis reaction is

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



Characterization of the sample

All the samples were characterized by Transmission electron microscopy (TEM), X-ray techniques (XRD) and Scanning electron microscopy(SEM). X-ray diffraction of the prepared phosphors were recorded in a wide range of Bragg angle 2θ using a Bruker D8 advanced X-ray diffraction (XRD) measuring instrument with Cu target radiation ($\lambda = 0.154$ nm). The Fourier transform infrared (FTIR) spectra were recorded in the wavenumber range 4000-400 cm⁻¹ using a Shimadzu FTIR spectrometer.TEM of the prepared phosphors were done by using Philips CM10 microscope. SEM of the prepared phosphors were done by using Zeiss EVO40 microscope. The PL measurements (absorption ,excitation and emission) were performed on the synthesized samples of Tb doped Y2O3 nanophosphor using Shimadzu Spectroflurophotometer RF 5301 PC. and EL intensity was measured with the help of photomultiplier tube.

Prepration of EL Cell and EL measurement

EL was investigated using a single layer structured EL device. The Phosphor emission layer was placed between two electrode layers. One electrode was SnO_2 coated transparent glass plate and aluminium was used as



Fig 1 : EL Set up

Results and Discussion

second electrode deposited. The thickness of the aluminium electrode was of the order of 1µm. The transparent electrode has been prepared by depositing thin film of SnO_2 layer by chemical vapor deposition on clean glass substrate heated to 500°C. When $SnCl_2.2H_2O$ (Stannous Chloride) was thermally decompose in atmosphere, which after reaction, form SnO_2 layer on the heated glass slides. The light emission was observed from EL cell by applying frequency, ac voltage from mains and the emitted light intensity was

measured by increasing the applied voltage with the help of variac.

Morphological Analysis



Fig 2 XRD result for nanophosphor Y₂O₃: Tb

Fig 2 presents the XRD result for nanophosphor Y_2O_3 : Tb. Four different peaks are obtained at 2 Θ values of 29.12° , 33.78 °, 48.46° and 57.56 ° and the peaks correspond to diffraction at (222),(400), (440) and (622) planes, respectively .The spectrum clearly shows the expected body centered cubic crystalline phase for the nanopowders in agreement with (ICSD #160890).Crystallite size estimated based on a simple debye scherrer method yield value of around 30-40 nm.

Optical Absorption Spectra

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. The study of optical absorption is important to understand the behavior of nano-crystals. Fig. 3 shows the absorption spectra of Y_2O_3 : Tb phosphor in the range of 190 nm -700 nm. The absorption edge is found at 223 nm. The band gap was calculated corresponding to absorption edge (223 nm). The band gap was found to be 5.5 eV for Y_2O_3 : Tb phosphor.



Figure 3 Absorption spectra of Y_2O_3 : Tb phosphor.

FTIR Analysis

FTIR spectra of Y_2O_3 :Tb that was synthesized at the heating temperature peak of 600 °C are shown in Figure 4. A broad peak (A) at around 3000 cm⁻¹ is originated from O-H stretching in



Figure 4 FTIR spectra of Y2O3:Tb

hydroxyl groups.Overtone or combination band[B] located in the range 2000–1650 cm⁻¹ [16]. Absorption at around[C] 1500– 1350 cm⁻¹ might originated from C-H bend and C-C stretching. Y-O stretching [D] at around 562 cm⁻¹ [17]. The absorption peaks resulted by bonding of metal ions usually appears at short wave numbers [18].

TEM (Transmission electron microscopy)

Fig:5 shows the TEM image of the Tb doped Y_2O_3 . The TEM image exihibits uniform ,spherical morphology and significantly aggregated. The aggregated particles sizes



Figure 5 TEM image of Y₂O₃:Tb(3 mol %)

are found to be in the range of 100 -150 nm. The particle size obtained from the TEM image is larger than that obtained from XRD linewidths and this has been attributed to the fact that linewidths depend on the presence of coherent domains in the sample, wheras the TEM technique does not have that requirement and measures the actual particle size.

SEM (Scanning electron microscopy)



Figure 6 SEM picture of Y₂O₃:Tb(3 mol%) nanophosphor

The SEM observation(fig 6) shows that the size distribution was broad and particles are agglomerated and forms a continuous network .Few pores and voids can be seen. Particles are porous an irregular that is often the case for powders derived from metal nitrates . The Eu doped Y_2O_3 and Tb doped Y_2O_3 samples consist hollow spheres, many of which are fractured with mean size 268 ± 300 nm.

Photoluminescence

The excitation spectra are composed of two overlapping bands. The maxima are centered at 275 and 302 nm,in agreement with previous reports[19]. The excitation



spectra (fig 7) are composed of two overlapping bands. The maxima are centered $(4f^8-4f^75d^1)$ transition of Tb⁺³. The emission at 275 and 302 nm, corresponding to 4f-5d



Fig:7:Excitation spectra of Tb doped $Y_2O_3(3 \text{ mole}\%)$



Fig 8:emission spectra of Tb doped $Y_2O_3(3 \text{ mole}\%)$



Fig 9: Quenching curve of nanopowder Y_2O_3 doped with different Tb concentrations

spectra are complex, containing several groups of sharp line associated with electronic transitions of the Tb^{+3} ion.The classification of the emission lines from the

 ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$ manifold follows Flores-Gonzalez et al[20],and is in agreement with results on Tb⁺³ ions in other hosts,Lu₂O₃[21],and Y₃Al₅O₁₂[22].

The strongest emission (fig 8) occurs at 544 nm due to the ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ characteristic transition of green emission for Tb⁺³.The other peaks at 485nm, 585nm and 625 nm arises from the ${}^{5}D_{4} \rightarrow {}^{7}F_{6}, {}^{5}D_{4} \rightarrow {}^{7}F_{4}$ and ${}^{5}D_{4}$ to ${}^{7}F_{3}$ transitions respectively. Unfortunately, reliable PL spectra could not be obtained between 350 and 450nm due to the inability to filter the background light from the excitation source, thus the possibility of ${}^{5}D_{3} \rightarrow {}^{7}F_{J}$ emission could not be determined by our measurements.

No Shift in the position of the ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$ PL emission maximum at 544 nm was observed as a function of Tb concentrations suggesting that the nature of Tb⁺³ activator remains unchanged with concentrations. On the other hand, the intensity changed dramatically for different Tb concentrations. This is shown in Fig 9, which presents the emission intensity measured at 544 nm as a function of the Tb concentrations(from 1 mol% to 7 mol%), higher light output are obtain due to the large number of luminescent centers, up to critical concentration(3 mol%), beyond which a decrease in the output may have caused by the concentration quenching phenomena, which were due to energy transfer between adjacent centers is observed.

 Tb^{3+} (${}^{5}D_{3}$) + Tb^{3+} (${}^{7}F_{6}$) $\rightarrow Tb^{3+}$ (${}^{5}D_{4}$) + Tb^{3+} (${}^{7}F_{0}$).(cross-relaxation between neighbouring Tb^{3+} ions)

Electroluminescence



Fig 10 EL brightness curve of Tb doped Y₂O₃ for different frequency Voltage brightness characteristics

The voltage (V) Vs EL brightness (B) characteristics of Y_2O_3 :Tb(3 mole %) nanocrystals for different frequencies of the applied electric field has shown in fig(10).The brightness was observed between 400 volts



to 500 volts for Y_2O_3 :Tb(3 mole%) at different frequencies (from 290 Hz to 310 Hz)and between 350 V to 600 V for Y_2O_3 :Eu,Tb at different frequencies (from 290 Hz to 350 Hz).It is observed that light emission starts as a threshold voltage and then it increases with increasing value of the applied voltage. The electroluminescent efficiency depends on the carrier life time of the injected charge carriers.



Fig 11: Voltage current charecteristics of the Tb doped Y₂O₃

The voltage current charecteristics of the Y_2O_3 : Tb (3 mole %) at particular frequency 330 Hz is shown in fig 11 .It is clear from the observation made that as the input voltage increases there is continuous increase in the current .In the present study linear relation is obtained between voltage and current for both samples . These indicate the ohmic nature, ie there is ohmic contact between sample and the electrodes .I-V properties of the devices depend on the strength of the electric field.



Fig 12 EL brightness curve of Y₂O₃ :Tb(3 mole%) for different voltage

Fig 12 shows the frequency dependence of the EL brightness (B) of the Y_2O_3 :Tb(3 mole %) nanophosphor for different voltages of the applied electric field and it is found that on increasing the frequency of the input signal ,EL brightness increases. and then attains a saturation value. A possible explanation for this may be as follows: As the number of cycles per second increases, the energy supplied to the device also increases, reinforce the EL brightness. When frequency is further increased beyond the optimum, the extra energy starts dissipating as heat,

leading to decrease in brightness and finally damage of EL device.

Conclusion

- XRD studies confirmed the body-centred cubic structure of doped phosphors. FTIR studies also confirmed the formation of these compounds.
- The optimum concentration of impurities for both Y_2O_3 : Tb³⁺ was achieved for photoluminescence emission as 3 mole%.
- EL brightness of Y_2O_3 :Tb(3 mole%) with voltage ,while the voltage current characteristics shows straight line indicating ohmic nature. Relation between voltage and brightness indicate that EL Intensity is produced by acceleration collision mechanism.
- For a fixed voltage, the EL brightness initially increases linearly with the frequency of the applied voltage and then nonlinearty occurs at higher frequencies.

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