Down conversion luminescence behavior of Er and Yb doped Y₂O₃ phosphor

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Abstract

We have studied downconversion luminescence behaviour of Y₂O₃ phosphor doped with Er 1 mol% and 1 mol% of Yb. The sample was prepared by modified solid state reaction method. Using inorganic material like (Y₂O₃), Flux Calcium Fluoride (CaF₂) and Er₂O₃ as well as Yb₂O₃ with molar ratio 1 mol% of dopant. The prepared phosphor sample was characterized using Powder X-Ray Diffraction (PXRD), Field Emission Gun Scanning Electron Microscopy (FEGSEM), High Resolution Transmission Electron Microscopy (HRTEM), Photoluminescence (PL), Thermoluminescence (TL) and CIE techniques. The obtained sample shows an intense greenish-white emission (ranging from 350 to 600 nm, centered at 565 nm) under a wide range of UV light excitation (220–400 nm).

Keywords:
Downconversion
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Thermoluminescence

1. Introduction

Since a short-wavelength UV light of mercury vapor plasma is commonly used as an excitation source in most commercially available lamps, the optimization of luminescence quantum efficiency of phosphors is required for the 254 nm excitation in the fluorescent light products (Sato, Takahashi, & Sato, 1996). Nevertheless, the disposing of the used vapor junk causes environmental contamination. Recent investigation on deep violet light-emitting devices and lasers quite possibly provides an alternative excitation in the range of 340–400 nm (Ohashi et al. 2005; Piao, Horikawa, Hanzawa, & Machida, 2006; Park, Kim, Park, Park, & Choi, 2004; Xie, Hirosaki, Sakuma, Yamamoto, & Mitomo, 2004; Sagawa & Uchino, 2005; Liu, Shi, & Qi, 2005). Yttrium sesquioxide (Y₂O₃) ceramics have been intensively investigated for different technological purposes. For decades, yttrium oxide has been an important material in the ceramic industry, from being a constituent of ceramic super-conductors (Regnier, Sapin, & deMontprevill, 1989), to well-known YSZ ceramics (Boaro, Vohs, & Gorte, 2003). Y₂O₃ is used in electronic applications as a part of metal–oxide–semiconductor hetero structures in Metal Oxide Semiconductor (MOS) transistors (Chambers and Pearson, 2001). It also plays an important role in the preparation of novel light – emitting materials (Vetrone, Boyer, Capobianco, Speghini, & Bettinelli, 2003a, 2003b; and Wang, Lin Liu, Lin, & Yu, 2005; Konrad, Herr, Tidecks, Kummer, & Samwer, 2001). Host materials with a wide band gap are attractive for optical applications in the visible and UV spectral ranges (Patra, Friend, Kapoor, & Prasad, 2002; and Salas et al. 2005), because the rare earths can emit within its optical window and do not suffer of quenching effects inherent to semiconductor hosts (Vetrone, et al., 2003a, 2003b and Matsuura, 2002).

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2. Experimental

To prepare Y$_2$O$_3$ with erbium and ytterbium (1 mol %) consists of heating stoichiometric amounts of reactant mixture is taken in alumina crucible and is fired in air at 1300 °C for 4 h in a muffle furnace. Every heating is followed by intermediate grinding using agate mortar and pestle. The Er and Yb activated Y$_2$O$_3$ phosphor was prepared via high temperature modified solid state diffusion. The starting materials were as follows: Y$_2$O$_3$, Er$_2$O$_3$, Yb$_2$O$_3$ and CaF$_2$ (as a flux) in molar ratio were used to prepare the phosphor (Dubey, Kaur, & Agrawal, 2013 and Dubey, Kaur, & Agrawal, 2014; Dubey, Kaur, Suryanarayana, & Murthy, 2014; Dubey, Kaur, Agrawal, Suryanarayana, & Murthy, 2014).

The sample was characterized using Photoluminescence (PL), Thermoluminescence (TL), FEGSEM and HRTEM. Observation of particle morphology was investigated by FEGSEM (field emission gun scanning electron microscope) (JEOL JSM-6360). The photoluminescence (PL) emission and excitation spectra were recorded at room temperature by use of a Shimadzu RF-5301 PC spectrofluorophotometer. The excitation source was a xenon lamp. Thermally stimulated luminescence glow curves were recorded at room temperature by using TLD reader I1009 supplied by Nucleonix Sys.Pvt.Ltd. Hyderabad (Tamrakar & Bisen 2013a, 2013b; Tamrakar, Bisen, & Brahme, 2014, Tamrakar, Bisen, Robinson, Sahu, & Brahme, 2014, Tamrakar, Bisen, Sahu, & Brahme, 2014). The obtained phosphor under the TL examination is given UV radiation using 254 nm UV source (Dubey, Kaur, Agrawal, & Suryanarayana, 2010; Dubey, Kaur, Agrawal, & Suryanarayana, 2012).

3. Results and discussions

X-ray diffraction pattern was already published with cubic structure (Dubey, Kaur, & Agrawal, 2014).

FEGSEM and HRTEM: Field emission gun scanning electron microscopy and high resolution transmission electron microscopy images are shown in Figs. 1 and 2. From the above images that confirms the formation of phosphor. The prepared sample shows a compact distribution over the surface and good connectivity between grains. Similarly the HRTEM image is the diffraction pattern that is similar as XRD pattern (Dubey, Kaur, & Agrawal, 2014). The particles had a narrow size distribution, a rugby-like shape and a diameter of 70–100 nm.

4. Photoluminescence study

Fig. 3 shows the PL excitation spectra of prepared phosphor (Y$_2$O$_3$: Er), excitation spectra recorded at 565 nm excitation. Peaks found 258 nm, 368 nm, 380 nm and 392 nm. Here the emission found at visible region at 365 nm due to crystal field effect of the sample. (Fig. 4) Broad emission band 400–500 in blue region and some narrow peaks at red region.

The visible emission bands in the region 409–565 nm (Fig. 5), are observed, which can be attributed to the transitions of $^3H_{11/2} \rightarrow 4I_{15/2}$, $^4S_{3/2} \rightarrow 4I_{15/2}$ of Er$^{3+}$, respectively. The red emission at 612 and 722 nm is much weaker than other emissions, which can be not seen by naked eyes. Also, the obvious splits are observed from the emission bands of $^3H_{11/2} \rightarrow 4I_{15/2}$, $^4S_{3/2} \rightarrow 4I_{15/2}$ transitions, different from previous reports (Dong, Li, & Lei, 2007 and Guo et al., 2006). It is well known that the crystal field has a strong effect on the emissions of the rare earth doped ions. The results show that the crystal field in Y$_2$O$_3$ is stronger than that in other hosts.

To explore the effects of Yb$^{3+}$ doping concentration on the emissions, Fig. 6 shows the integral intensity of 452, 468, 493 and 613 nm. Fig. 7 shows the excitation spectra of Er, Yb doped Y$_2$O$_3$ phosphor for both have 1 mol% concentration. It show downconversion properties in various reports that Er and Yb for upconversion here it has downconversion and more intense and broad emission at 254 nm for 565 nm excitation that is charge transfer band to Y$_2$O$_3$ to Yb.
Fig. 3 – Excitation Spectra of Er (1 mol %) doped Y₂O₃ phosphor.

Fig. 4 – Emission Spectra of Er (1 mol %) doped Y₂O₃ phosphor.

Fig. 5 – Emission Spectra of Er (1 mol %) doped Y₂O₃ phosphor excitation with 380 nm.

Fig. 6 – Emission Spectra of Yb (1 mol %) doped Y₂O₃ phosphor excitation with 254 nm.

Fig. 7 – Excitation Spectra of Er and Yb (1 mol %) doped Y₂O₃ phosphor excitation with 565 nm.

Fig. 8 – Emission Spectra of Er and Yb (1 mol %) doped Y₂O₃ phosphor excitation with 254 nm.
We have prepared the Y$_2$O$_3$:Er, Yb samples with 1 mol% Yb$^{3+}$ and Er$^{3+}$ doping concentration. Under 254 nm UV excitation, the blue, green and red downconversion emissions are observed at around 406, 469, 565 and 612 nm, which are attributed to the transitions of $^4$S$_{3/2}$ $\rightarrow$ $^4$I$_{15/2}$ and $^4$F$_{9/2}$ $\rightarrow$ $^4$I$_{15/2}$ of Er$^{3+}$ ions. It is shown that a two-photon process populates the $^4$S$_{3/2}$ and $^4$F$_{9/2}$ levels for the Y$_2$O$_3$ powders. (see Fig. 8).

For the various transition of Er$^{3+}$ transition level diagram (Fig. 9) presents for the 406, 469, 565, and 612 nm emission peaks due to transitions of $^4$S$_{3/2}$ $\rightarrow$ $^4$I$_{15/2}$ and $^4$F$_{9/2}$ $\rightarrow$ $^4$I$_{15/2}$ of Er$^{3+}$. The CIE coordinates were calculated by Spectrophotometric method using the spectral energy distribution of the Y$_2$O$_3$:Er$^{3+}$, Yb$^{3+}$ sample (Fig 10). The color co-ordinates for the Er$^{3+}$, Yb$^{3+}$ doped sample are $x = 0.147$ and $y = 0.185$ (for blue emission (in web version)), $x = 0.311$ and $y = 0.520$ (for green emission (in web version)) and $x = 0.640$ and $y = 0.307$ (for red emission (in web version)) (these coordinates are very near to the blue, green and red light emission). Hence this phosphor having excellent color tenability from white light emission composed with three band. However, the relative intensity of the emission bands which provide the fundamental colors balance for blue, green and red-light emission was achieved providing the CIE 1931 chromaticity coordinates much closer to the equal-energy white-light (Dubey, Kaur, Suryanarayana, et al., 2014; Dubey, Kaur, Agrawal, Suryanarayana, et al., 2014).

5. Thermoluminescence study

The glow curve is characteristic of the different trap levels that lie in the band gap of the material. A reliable dosimetric study of a thermoluminescent material should be based on a good knowledge of its kinetic parameters that include trap depth (E), order of kinetics (b) and frequency factor (s). The study of relatively deep trapping defect-states in various phosphors, as well as TL dating of solid state materials, is closely related to the position of the trapping levels within the forbidden gap. Although there are various methods to obtain the number of glow peaks in the complex glow curves and their kinetic parameters that best describe the peaks (McKeever, 1985; Tamrakar, Bisen, & Brahme, 2014, Tamrakar, Bisen, Robinson, et al., 2014, Tamrakar, Bisen, Sahu, et al., 2014).

To gain some idea of the characteristic glow curves of the synthesized Y$_2$O$_3$:Er samples, the TL glow curves were obtained by heating samples from 50 up to 400 °C at a heating rate of 6.7 °C s$^{-1}$. The glow curves of synthesized Y$_2$O$_3$:Er (Fig. 11) with the variation of UV exposure time 5–20 min. Prominent peak found at 98 °C and sample shows the second order kinetics which is determined by shape factor. The values of kinetic parameters for Y$_2$O$_3$:Er (1 mol%), Y$_2$O$_3$:Yb (1 mol%) and Y$_2$O$_3$:Er, Yb (1 mol%) are given in Tables 1–3.
respectively. The peak shape factor for the TL glow curve of the prepared phosphor was found to be ~0.5 (for maximum peaks). In Figs. 12 and 13 represents the TL glow curve of Y2O3:Er, Yb (1 mol%) in the single peak was found for both the sample (Tamrakar, Bisen, Sahu, et al., 2014, Tamrakar & Bisen 2013a, 2013b, Tamrakar, 2012).

### 6. Conclusion

The results can be helpful for the design and applications of low-cost light emitting diode (LED) applications. Here the PL emission spectra found in all visible region so that these phosphor can act a single host for white light emitting diode phosphor material. The thermo luminescence glow curve shows the two or more traps from the material because the value of order of kinetics is two. Relative activation energy found at .51–.55 eV and frequency factor found at 2 × 10^8 to 5 × 10^8.

### References


