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Photoluminescence behavior of ZrO_2: Eu^{3+} with variable concentration of Eu^{3+} doped phosphor

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ABSTRACT

The ZrO_2 phosphor doped with Eu^{3+} was synthesized by solid state reaction method which is suitable for large scale production, and high temperature synthesis method. The prepared nanoparticles of ZrO_2 phosphor was characterized by X-ray diffraction technique (XRD) for Structural analysis and field emission gun scanning electron microscopy (FEGSEM)) for morphological details. The optical behavior of the prepared phosphor was determined by photoluminescence (PL) spectra recorded in room temperature. The PL excitation spectra was found at 311 nm range and the emission spectra in the range of 400–650 nm.

1. Introduction

Ultrafine zirconia (ZrO_2) particles or nano particles have been reported to have unique properties such as excellent refractoriness and chemical resistance, good mechanical strength, high ionic conductivity, low thermal conductivity at high temperature to get her with relatively high thermal expansion coefficient high refractive index, low phonon energy, high chemical and good thermal stability (Conga et al., 2007; Emeline et al., 1998; Ghosh & Patra, 2006; Meetei et al., 2012; Smits et al., 2010; Tamrakar, Bisen, Upadhyay and Tiwari, 2014; Tiwari, Kuraria, & Tamrakar, 2014; Xu et al., 2008), because of all these reasons Zirconia is an attractive material in both fundamental and application-oriented research. Red light emission from (600–630 nm) Eu^{3+} doped phosphors are extensively used in lamp and display applications. Many Eu^{3+} doped materials are being examined for use in new flat panel display technologies (Chen, Liu, & Li, 2004; Dubey, Tiwari, Pradhan, et al., 2014; Dubey, Tiwari, Tamrakar, et al., 2014; Meetei et al., 2012; Smits et al., 2010; Tamrakar, Dubey, Swamy, Tiwari, Pammi, Ramakrishna et al., 2013). Therefore, extensive amount of works have been reported on the properties of bulk and nanocrystalline ZrO_2 of different crystalline phases.

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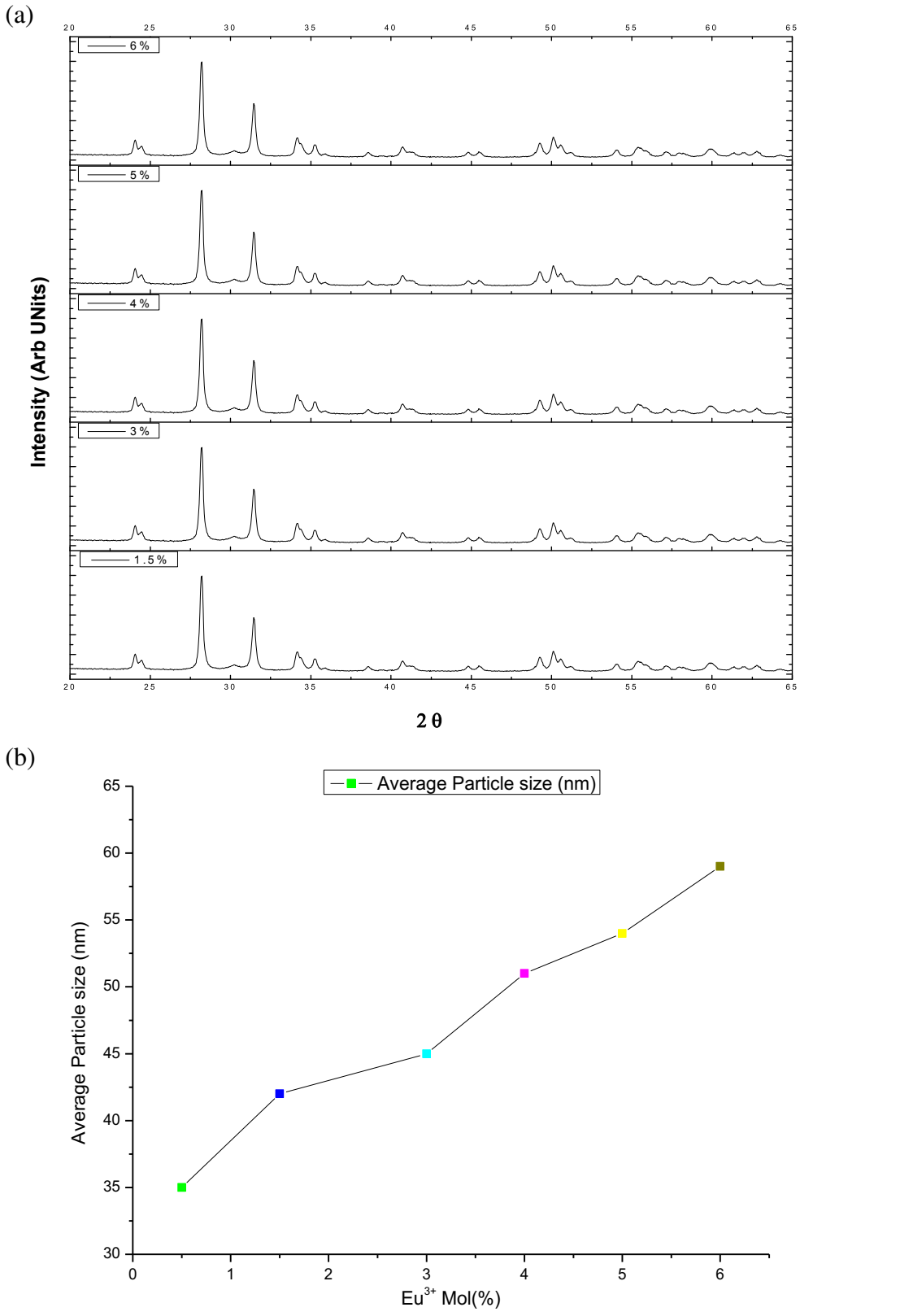

Fig. 1 – (a). XRD Patterns of ZrO_2: Eu^{3+} (1.5–6%.). (b). Relation between particle size and Eu^{3+} (Mol %) concentration.

In this work, we present an experimental study of luminescence behavior of Eu^{3+} doped ZrO_2 under excitation of 311 nm generating overall luminescence emission. Supporting characterizations such as crystallographic analysis and particle size done by X-ray diffraction analysis (XRD), for determination of morphology of prepared phosphor Scanning electron microscope (SEM) and for chemical composition *Energy-dispersive X*-ray spectroscopy (EDX) was performed.

2. Synthesis of ZrO_2: Eu^{3+} phosphor by solid-state reaction method

The Eu^{3+} doped ZrO_2 samples containing variable Eu^{3+} (0.5–6 mol%) were prepared by conventional solid state synthesis method. ZrO_2 and Eu_2O_3 were used as precursor materials. The precursor materials were weighed in stoichiometric ratio and grounded by using mortar and pestle. The mixture were transferred into alumina crucible and placed in a muffle furnace followed by heating at 1200 °C for 3 h (Tamrakar, Bisen, & Brahme, 2014a, 2014c; Tamrakar, Bisen, Robinson, Sahu & Brahme, 2014; Tamrakar, Bisen, Sahu, & Brahme, 2014; Tamrakar, Bisen, Upadhyay & Brahme, 2014; Tamrakar, Upadhyay,Bisen, 2014).

The sample was characterized at the NIT, Raipur for X-ray diffraction by using the PAN-Analytical. XRD data were collected over the range 20–70° at room temperature. The X-rays were produced using a sealed tube, and the wavelength of the X-ray was 0.154 nm (Cu K-alpha). The particle size was calculated using the Debye–Scherer formula. The particle size and morphological investigations of ZrO_2: Eu^{3+}prepared by this process were carried out with a scanning electron microscope (SEM; LEO 440 system). The photoluminescence studies were carried out using RF5301 spectrophotofluorometer in the wavelength range 400–650 nm. All the PL spectra were recorded at room temperature (Tamrakar, 2013).

3. Results and discussion

3.1. X-ray diffraction (XRD) results

From the XRD pattern, it was found that the prominent phase formed in ZrO_2: Eu^{3+}, after diffraction peaks were well indexed based on JCPDS no. 30–1468 indicating the cubic phase structure. The main peaks were founded around 24.02°, 28.14°, 31.48°, 34.18° and 50.57°. Direct size measurements obtained from images are often used in conjunction with other measurements such as powder, X-ray diffraction (XRD). Fig. 1(a) is the. XRD pattern of ZrO_2: Eu^{3+} (1.5–6%). The crystallite size was calculated using the Scherrer equation $D = k\lambda/\beta \cos\theta$[Tamrakar et al., 2014]. Where the constant $k = (0.9)$, λ the wavelength of X-rays (1.54060 A°), β the full-width at half maxima (FWHM) and θ the Bragg angle of the XRD peak. The calculated average crystallite size of Eu^{3+} doped ZrO_2 ranging from 35 nm to 59 nm (Fig. 1(b) & Table 1) (Bisen et al., 2009; Tamrakar, 2012; Tamrakar, Bisen, Sahu, & Brahme, 2014; Tamrakar & Bisen, 2013, Tamrakar, Bisen, & Sahu, 2014; Tamrakar, Bisen, Sahu & Bramhe, 2014; Tamrakar et al., 2014a; Tamrakar, Bisen, & Brahme, 2014b; Tamrakar et al., 2013).

Table 1 – Effect of Eu^{3+} concentration on Particle size

S. No.	Eu^{3+} Concentration (Mol%)	Particle size (nm)
1.	.5	35
2.	1.5	42
3.	3	45
4.	4	51
5.	5	54
6.	6	59

3.2. Scanning electron microscope (SEM) & Energy-dispersive X-ray spectroscopy (EDX) results

Characterization of particles, surface morphology and size of nano crystals is done routinely using scanning electron microscope. The main advantage of SEM is that they can be used to study the morphology of prepared nano particles and nano composites. From the Scanning Electron Micrographs of ZrO_2: Eu^{3+} (1.5%) phosphors (Fig. 2A), it is found the particles are irregular in shape with various sizes in nano range and also clusters are found. In EDX analysis, the existence of Zr, O and Eu in the samples proves the formation of ZrO_2: Eu^{3+} (Fig. 2B).

3.3. Photoluminescence results

3.3.1. PL excitation spectra

The excitation and emission spectra of the prepared ZrO_2: Eu^{3+} phosphor was recorded. The excitation spectra was monitored under 615 nm excitation, which corresponds to the $^7F_2 \rightarrow {}^5D_0$ transition. The excitation spectra have peaks around 311 nm. The emission peaks attributed to transition from 2p orbital of O_2- to 4f orbital of Eu^{3+}, known as ligand to metal charge transfer band (CTB) transition (Quan, Wang, & Lin, 2005). The emission spectra were recorded at 311 nm excitation. In emission spectra, the strongest emission peaks near 613 nm correspond to a forced electron dipole transition of Eu^{3+} ($^5D_0 \rightarrow {}^7F_2$) which is allowed only when Eu^{3+} is occupied in low symmetries with no inversion center. It is also hypersensitive to environmental effects. The peak near 592 nm corresponds to the $^5D_0 \rightarrow {}^7F_1$ transition, which is mainly magnetically allowed and is not dependent on the site symmetry at which europium is situated. The ratio between the electron dipole and the magnetic dipole is a measure of the site symmetry at which europium is situated. In addition, we can see other energy transitions of Eu^{3+} corresponding to $^5D_0 \rightarrow {}^7F_0$ near 585 nm and $^5D_0 \rightarrow {}^7F_3$ near 628 nm (Chen et al., 2004; De la Rosa, Diaz-Torres, Salas, & Rodríguez, 2005; Jia et al., 2009; Liu, Hong, & Sun, 2004; Meza et al., 2014; Xu et al., 2008) in all the emission luminescence spectra. The $^5D_0 \rightarrow {}^7F_3$ transition which is magnetic dipole transition remains independent from the chemical environment of dopant ions whereas the $^5D_0 \rightarrow {}^7F_2$ transition which is electric dipole transition. $^5D_0 \rightarrow {}^7F_2$ transition depends upon the chemical environment of Eu^{3+} ion. This transition can be observed only when Eu^{3+} ions are present at inversion centers inside the crystal lattice Fig. 3(a–d).

4. Effect of Eu^{3+} ion concentration

Emission spectra was recorded as function of Eu^{3+} ion concentration to understand the effect of ion concentration on emission intensity. The intensity of emission peaks corresponds to $^5D_0 \rightarrow {}^7F_2$ transition which increases with increasing Eu^{3+} concentration. This increases in intensity may be due to energy transfer between nearby ions due to decrease

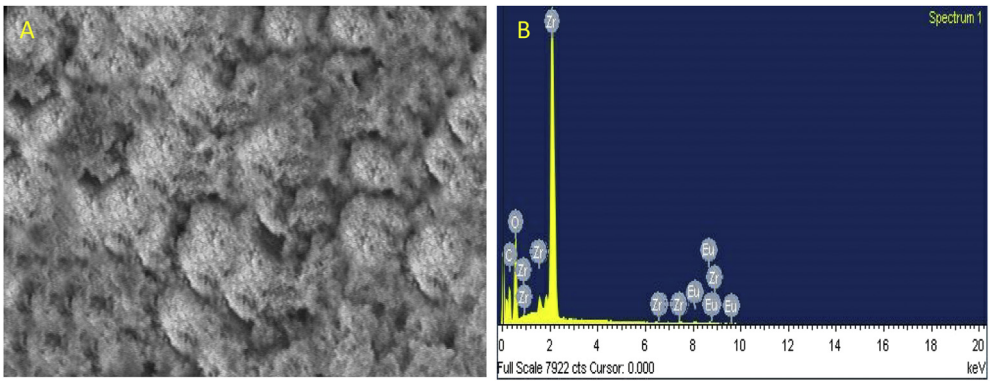

Fig. 2 – (A) SEM image & (B) EDX spectra of ZrO_2: Eu^{3+}.

in inter-ionic distance. The intensity of emission peaks increases upto 5 mol% of Eu^{3+} ion after this concentration intensity decreases due to concentration quenching. This concentration quenching is due to the increase in the ion–ion interaction provoked by the shorter distance between interacting activators as the concentration increases.

4.1. *CIE coordinated*

The spectrophotometric determination of PL emission spectra were measured by CIE 1931 coordinate system. Here four points were calculated by PL emission spectra peaking at 585 (A), 592 (B), 613 (C) and 628 (D) nm (Fig. 4). The intense red

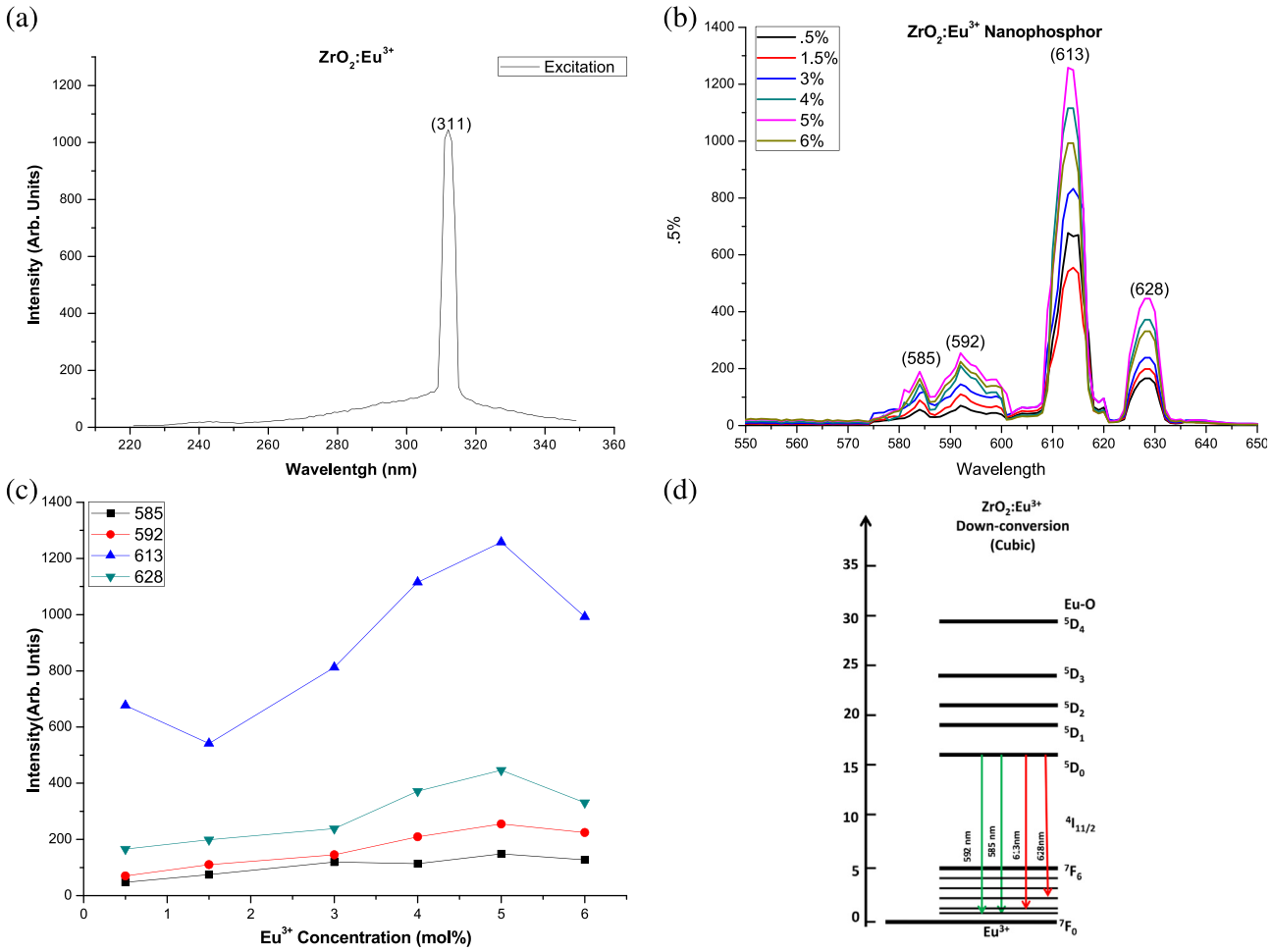

Fig. 3 – (a) PL Excitation spectra of ZrO_2: Eu^{3+} (.5–6%) monitored with 625 nm excitation. (b) PL Emission spectra of ZrO_2: Eu^{3+} (.5–6%) monitored with 311 nm excitation. (c) Eu^{3+} concentration Vs Peak position plot of ZrO_2: Eu^{3+} (.5–6%). (d) shows the energy level diagram for various transition of Eu^{3+} ion in.

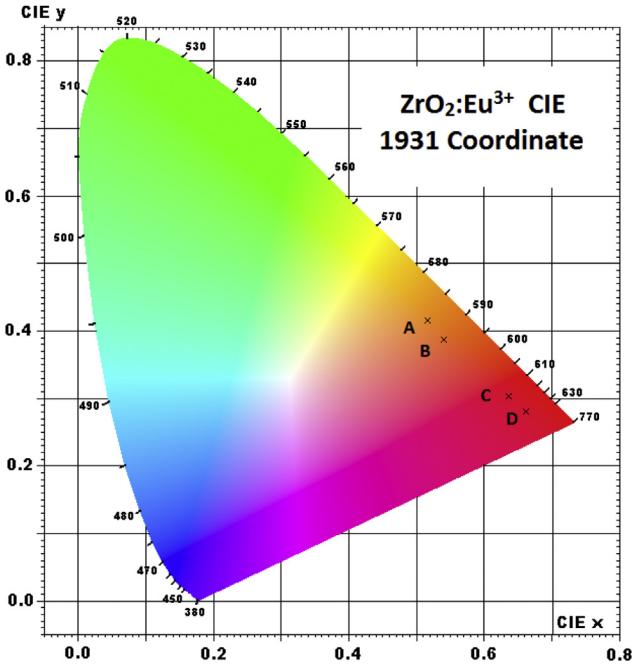

Fig. 4 – CIE coordinates depicted on 1931 chart of Eu^{3+} (5%) doped ZrO_2 phosphor.

emission was found which is dominates over all the peaks so the prepared phosphor useful for red emitting material for display device application. The color coordinates for the Eu^{3+}doped ZrO_2 phosphor are A ($x = 0.517$ and $y = 0.415$), B ($x = 0.541$ and $y = 0.387$), C ($x = 0.637$ and $y = 0.303$) and D ($x = 0.662$ and $y = 0.280$); these coordinates belongs to Orange-Red (in web version) and Red (in web version) light emission.

4.2. *Conclusion*

From the above studies it is concluded that the Eu^{3+} doped ZrO_2 phosphor with different concentration europium were prepared by solid state reaction method. This method is suitable for large scale production. The sample was characterized by XRD, SEM and PL studies. From XRD pattern it is confirmed that prepared phosphor has cubic structure and average particle size was determined by Debye- Scherer formula. SEM micrographs also confirmed formation of nano-phosphor which is in good agreement with XRD pattern. The photoluminescence study shows that the main characteristic emission peak is due to electric dipole transition ($^5D_0 \rightarrow {}^7F_2$) at 613 nm. The emission intensity increases with increasing Eu^{3+} ion concentration and shows concentration quenching after 5 mol%.

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