

EFFECT OF LI⁺ IONS IN THE LUMINESCENCE STUDY OF ZrO₂:EU NANO-CRYSTAL MATERIALS

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Abstract:

Nano-crystal materials ZrO₂:Eu (5 %) and ZrO₂:Eu (5 %) / Li (2%) were prepared using chemical co-precipitation method in water medium. The materials were annealed at 1000 °C for 1 hour and then grained into powder form. The materials were characterized by recording XRD, showing monoclinic and tetragonal phases and their estimated crystalline sizes were approximated as recorded by TEM images. And, photoluminescence studies of as prepared materials were carried out at room temperature.

Keywords: Nanocrystal materials, Luminescence, Doping.

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Introduction:

Recently, the research work on the study of nanomaterials has been motivated because of their novel and promising physical and chemical properties as compared to their bulk counterparts, which are mainly due to quantum size effect as well as large surface to volume ratio [1]. Moreover, some workers have reported that the development in nanocomposites which are efficient ways for the development of new novel nanomaterials [2]. With the advanced development in material sciences, the study on luminescent nanomaterials has been intensively increased for their various potential applications in display, illumination industry, sensors, traffic signs, luminous paint etc. [3 & 4]. These scientific approaches are very essential in the present developing society. The commonly used luminescent materials are oxides, sulfides or oxysulfides based materials doped with lanthanide ions [5 & 6]. Among these, oxides based materials specially, ZrO_2 has been proposed as an excellent host because of its low photon energy, efficient luminescence of active ions [7], hardness, high refractive index and high optical transparency [8]. ZrO_2 matrix is chemically, photo-chemically and photo-thermally stable and has a broad optical transparency from the visible to the near IR so that it makes as an ideal medium for the preparation of highly luminescent materials [9&10]. Due to its high melting point, high thermal and mechanical resistance, high thermal expansion coefficient, low thermal conductivity, high dielectric constant and photo-thermal stability, it has extensively applied in photonics and other industries [10 &11]. And it is also widely used in the fabrication of structural ceramic devices, gas sensors, catalysts and optoelectronic devices etc. [12]

The main crystal phases of ZrO_2 are monoclinic (below $1170^\circ C$), tetragonal (1170 to $2370^\circ C$) and cubic (above $2370^\circ C$), and their respective main IR frequencies are 480, 435 and 270 cm^{-1} . It was reported that the crystal structures significantly influenced its physical properties [13]. And, ZrO_2 is a wide band gap (5.0 – 5.5 eV) transition metal oxide with excellent mechanical, thermal, optical and electrical characteristics [14]. A lot of research work has been reported such as $ZrO_2:Sm$ [15] $ZrO_2:Dy$ [16], $ZrO_2:Er$ [17]. Some workers have been reported $ZrO_2:Pr$ with a major focus on the laser area due to the possible applications in chemical, biological and medical fields, and new data storage and display techniques[18]. However, the lanthanide ions doped luminescent material has a limitation of luminescence intensity due to luminescent quenching. Generally, luminescent devices mainly depend on their intensities and hence to minimize the

quenching is the main problem in the luminescent research workers. Some workers reported that the intensity of quenched luminescent materials can be enhanced by co-doping with divalent ions to the lanthanide doped YVO_4 [19]. H.K. Yang et al reported that the co-doping of Li^+ ions can not only enhance the luminescence efficiency but also control the morphology and grain size of the lanthanide doped phosphors [20]. Thus, co-doping of suitable sensitizer is the important role in the enhancement of the luminescent efficient of phosphors. On the basis of the above facts, the authors aimed to study the role of Li^+ ions in the luminescence study $\text{ZrO}_2:\text{Eu}$ nano-crystal materials.

Experimental details:

The starting materials were Zirconium oxichloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ **Sigma** 99.99%), Europium Nitrate hydrate ($\text{Eu}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ **Sigma** 99.99%), Lithium Chloride (LiCl **Sigma** 99.99%) and double distilled water used as solution medium. In a typical synthesis of 5% of Eu doped ZrO_2 sample, 500 mg $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and 29 mg of $\text{Eu}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ were dissolved in 25ml of double distilled water and warmed at 40°C for 5 minutes and maintained pH value at 11 using sodium hydroxide (NaOH) pallet. With the introduction of NaOH , precipitation starts to form. The whole solution was stirred with a speed of 300 rpm at 40°C for 30 minutes to complete the reaction using magnetic stirrer. The precipitation was collected by centrifugation. The collected precipitation was annealed at 1000°C for 1 hour and made in powder form. Similar procedures were done for synthesis of other samples.

The phase purity and crystal structure of as prepared samples were examined by powder X-ray diffraction (XRD) technique using **Philips Powder Diffractometer** with $\text{CuK}\alpha$ (1.5405 \AA) radiation with Ni filter. Transmission electron microscopy (TEM) images were recorded using JEM-2000 FX microscope at 160 KV. All the luminescence spectra were recorded in LS 55 Fluorometer (Perkin Elmer) at room temperature.

Results and Discussion:

Fig. 1 shows the XRD patterns of $\text{ZrO}_2:\text{Eu}$ (5%) and Li^+ (2 %) co-doped $\text{ZrO}_2:\text{Eu}$ samples annealed at 1000°C for 1 hour. The diffraction peaks show the nanocrystalline nature of the samples. From X'pert High Score's search match analysis the sample $\text{ZrO}_2:\text{Eu}$ (5%) show the

presence of both monoclinic phase (Ref. code: 01-083-0944) and tetragonal phase (Ref. code:01-079-1770). However, with the introduction of Li^+ ions in $\text{ZrO}_2:\text{Eu}$ (5%) nanocrystals do not change in the crystal structure. By the application of Scherrer equation: $t = (0.9\lambda)/(\beta \text{ Cos } \theta)$, where λ is the X-ray wavelength, β is line broadening at half at the maximum intensity in radians and θ is the Bragg angle, the crystallite sizes of as prepared samples were 56 and 62 nm respectively. The sizes of as prepared nano crystal materials were approximately confirmed by TEM images as shown in Fig. 2

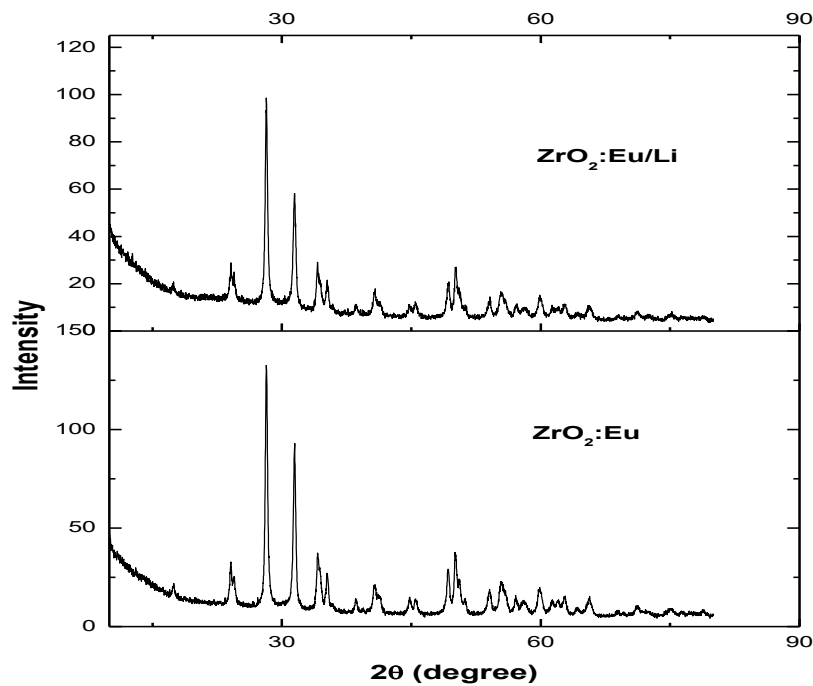


Fig.1 XRD patterns of $\text{ZrO}_2:\text{Eu}$ (5%) and Li^+ (2 %) co-doped $\text{ZrO}_2:\text{Eu}$ samples

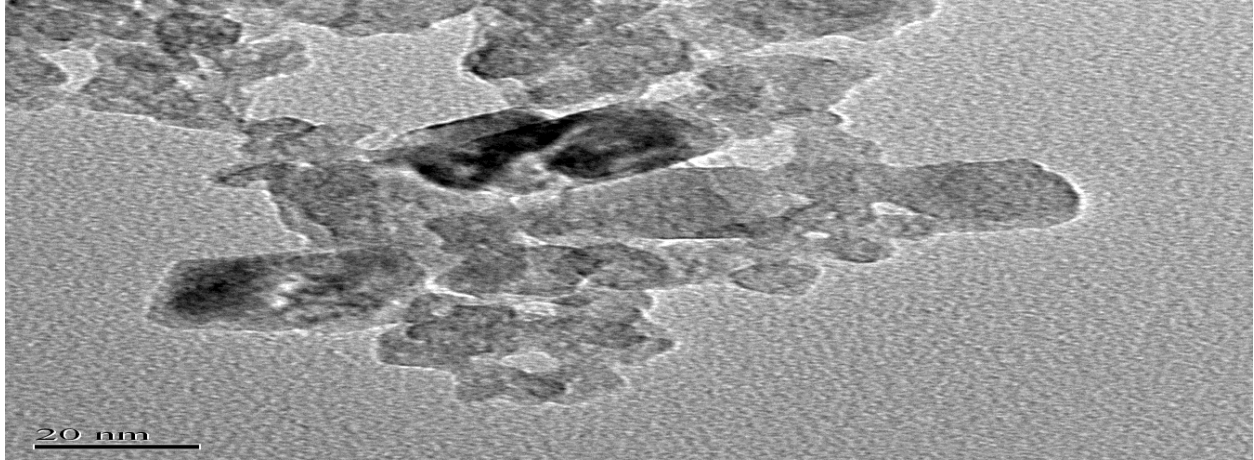


Fig. 2 TEM image of as prepared $ZrO_2:Eu$ (5%) nanocrystal materials at 20 nm scale

Fig. 3(a) shows excitation spectra of as-prepared $ZrO_2:Eu$ (5%) nanocrystal materials annealed at $1000^\circ C$ for 1 hour by monitoring the emission at 615 nm recorded at room temperature. The spectra show a broad absorption at range of 220-400 nm consisting of a broad peak at around 238, a hump peak at 380 nm and a small peak at 395 nm. The broad peak at around 238 nm is attributed mainly due to charge transfer transition between Eu^{3+} and O^{2-} [21]. The hump peak at 380 nm and the small peak at 395 nm are mainly originated from the f-f transitions of Eu^{3+} . The excitation spectra of Li^+ doped $ZrO_2:Eu$ (5%) nanocrystal materials annealed at $1000^\circ C$ for 1 hour by monitoring the same emission wavelength 615 nm is shown in Fig 3 (b). The spectra show the same peak positions but their intensities decrease.

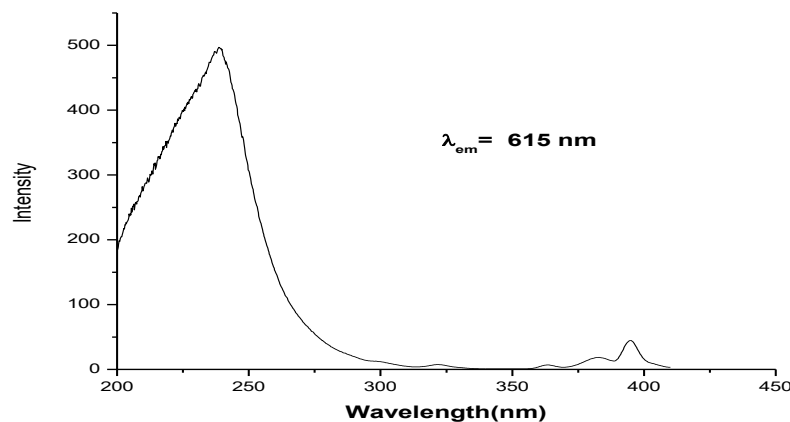


Fig. 3 (a) Excitation spectra of $ZrO_2:Eu$ (5%) nanocrystal materials

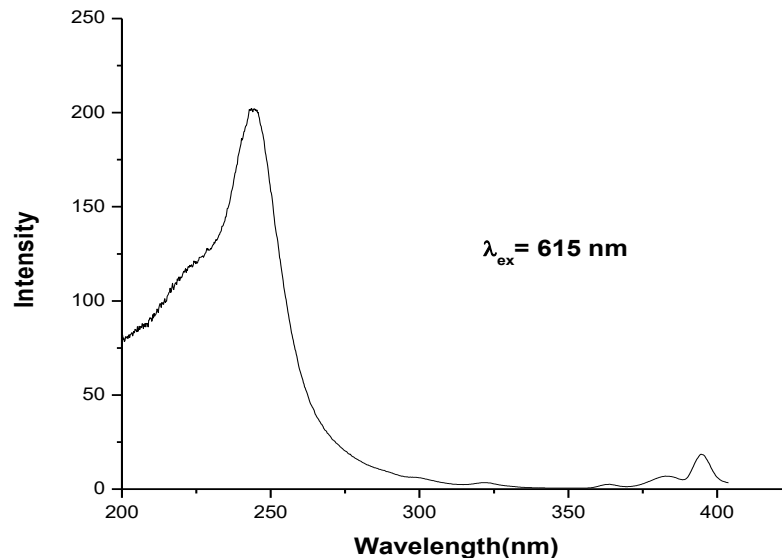


Fig. 3 (b) Excitation spectra of $\text{ZrO}_2:\text{Eu}$ (5%) /Li(2%) nanocrystal materials

Fig. 4 (a) shows the emission spectra of as-prepared $\text{ZrO}_2:\text{Eu}$ (5%) nanocrystal materials annealed at 1000°C for 1 hour by monitoring the excitation at 395 nm recorded at room temperature. The emission spectra exhibit the main characteristic emission lines of Eu^{3+} consisting of magnetic dipole transition, ${}^5\text{D}_0 - {}^7\text{F}_1$ at 592 nm emitting orange-red light and electric dipole moment transition, ${}^5\text{D}_0 - {}^7\text{F}_2$ at 615 nm emitting red light[22]. The emission spectra of Li^+ doped $\text{ZrO}_2:\text{Eu}$ (5%) nanocrystal materials annealed at 1000°C for 1 hour by monitoring the same excitation wavelength 395 nm is shown in Fig 4 (b). The emission spectra exhibit the same characteristic emission lines of Eu^{3+} as that of $\text{ZrO}_2:\text{Eu}$ (5%) nanocrystal materials but their intensities decrease.

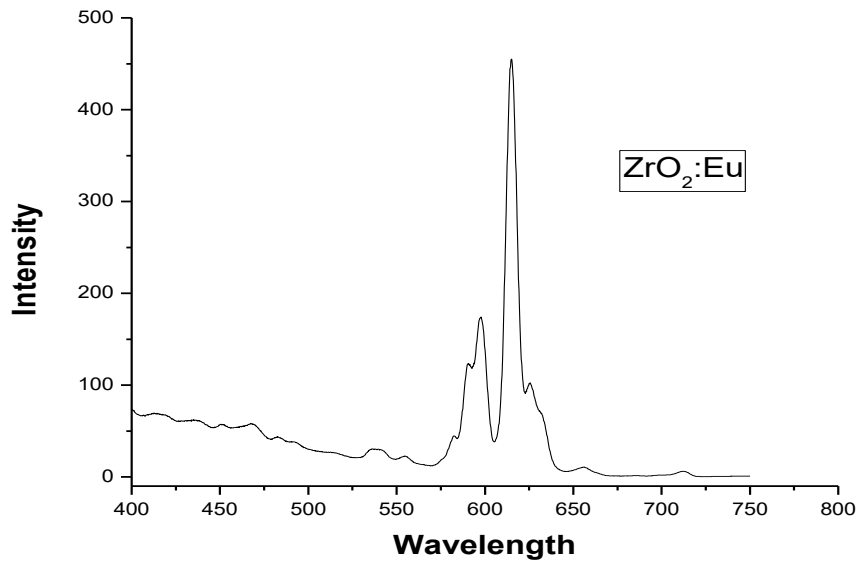
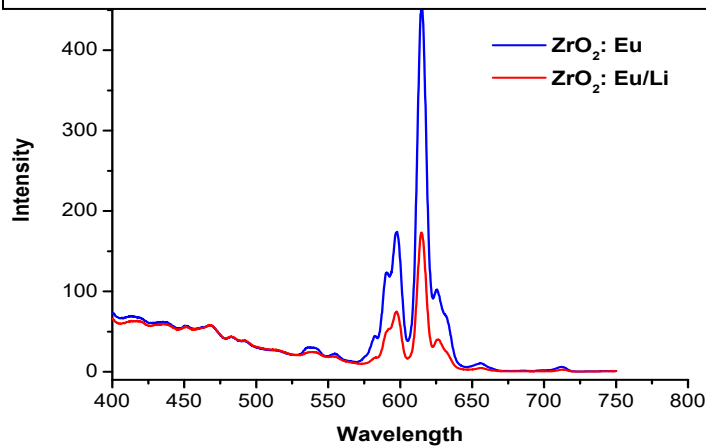


Fig. 4 (a) Emission spectra of $ZrO_2:Eu$ (5%) nanocrystal materials

Fig. 4 (b) Emission spectra of $ZrO_2:Eu$ (5%) and $ZrO_2:Eu$ (5%) /Li(2%) nanocrystal materials



Conclusions: $\text{ZrO}_2:\text{Eu}$ (5%) and $\text{ZrO}_2:\text{Eu}$ (5%) /Li(2%) nanocrystal materials were synthesized by co-precipitation method in water medium with particle sizes in the range 50-70 nm. These sizes were critically confirmed by XRD data and TEM images and also showing monoclinic and tetragonal phases. Photoluminescence study of as prepared nanocrystal materials were carried out with the emission of orange-red and strong red lights. However, co-doping of Li^+ at a particular dopant concentration (2%) decreased to the peak intensities of $\text{ZrO}_2:\text{Eu}$ (5%). Therefore, luminescence study on $\text{ZrO}_2:\text{Eu/Li}$ of different concentrations of Li^+ will be carried out in future.

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