

On the photoluminescence study of ZnO :Eu/Tm nano-crystal materials

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Abstract: ZnO:Eu(2%)/Tm(2%) nano-crystal materials were synthesized using chemical co-precipitation method in water medium. The materials were annealed at 800° C for 1 hour and then made into powder form. The solid state materials were structurally characterized by recording XRD data and TEM images. All the photoluminescence studies of as synthesized materials were carried out at room temperature.

Keywords: Nano-crystal materials, Photoluminescence, Doping.

Introduction:

With the increasing of population, the demand for energy consumption has been increasing gradually which starts to cause environmental pollution. In this context, research workers have been challenging to investigate new technological products having energy efficient, low cost, saving environmental pollution etc. In continuation of the above facts, the research work on metal oxide nanomaterials has been intensively increased due to their promising applications in light emitting diodes (LEDs) [1], Photocatalysis [2], Field emission display devices [3], solar cells [4], electroluminescent devices [5], electro-chromic windows, chemical sensors [6], ultraviolet laser diode [7]. For high-performance light emitting diodes, efficient emissions are required by applying low voltages to an optically active layer [8]. Among the metal oxide materials, zinc oxide is a promising candidate having a wide band gap of 3.37eV and rather large exciton binding energy (60 meV) and native defects [9]. ZnO is a technologically important phosphor as it exhibits two kinds of emission viz near band edge excitonic UV emission and visible deep level emission at room temperature [10]. Moreover, ZnO is an environmentally friendly material, which is desirable especially for bio-applications such as cancer detection and bio-imaging [11]. Generally, the optical properties of ZnO nanomaterials can be tuned by doping lanthanide ions because of 4f orbital of lanthanide ions are shielded by outer 6s, 5p and 5d, which are very important for the application in optoelectronic devices [12].

White light emitting diode (LED) has some excellent features such as energy efficient, mercury-free, low cost, long lifetimes etc.[13]. Due to these important features, white LED has been replacing the conventional lighting devices. Generally, white LED can be produced by mixing red, green, and blue lights [14]. To investigate white LED having high colour-rendering property, one needs to prepare a new phosphor emitting blue, green and red lights in the visible region. This multi-colours emitting phosphor can be obtained either by changing the composition of the host lattice through solid solution with similar crystal structure or to utilize the energy transfer between the co-doped activators [15]. In this matter, a lot of research work is essential to investigate new phosphors which can emit blue, green and red lights in the visible spectrum for the application of white LEDs. O. Lupan et al reported that Eu doped ZnO nanowire exhibits red and green emission [16]. A group of research workers led by N. F. Djaja reported that Ce-doped ZnO nanoparticles emit strong blue light [17]. Moreover, P. M. Aneesh et al reported that ZnO and Eu-doped ZnO nanoparticles exhibit broad green and strong red light respectively [3]. In the luminescence spectra, the peak positions of lanthanide ions are independent of the embedding matrix, but whose intensities and fine structure may vary [18]. In connection to the above matters, the authors are willing to synthesize and photoluminescence study of ZnO: Eu/ Tm nano-crystal materials and hope to perceive a new phosphor which can be used as white LED. However, to the best knowledge of the authors, the study on the photoluminescent property of this phosphor has not been reported.

Experimental details:

The starting materials were Zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ **Sigma** 99.99%), Europium Nitrate hydrate ($\text{Eu}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ **Sigma** 99.99%), Thulium Nitrate hydrate ($\text{Tm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ **Sigma** 99.99%) and double distilled water used as solution medium. In a typical synthesis of 2% of Eu and 2% of Tm doped ZnO, materials, 500 mg of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and 17 mg of $\text{Eu}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ and 21 mg of $\text{Tm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were dissolved in 50 ml of double distilled water and warmed at 40 °C for 5 minutes and maintained pH value at 12 using sodium hydroxide (NaOH) pallet. With the addition of NaOH, precipitation starts to form. The whole solution was stirred with a speed of 400 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 800 °C for 1 hour and made into powder form.

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 Å)

radiation with Ni filter. Transmission electron microscopy (TEM) images were recorded using JEM-2000 FX microscope at 160 KV. All the photoluminescence spectra were recorded in LS 55 Fluorometer (Perkin Elmer) at room temperature.

Results and Discussion:

Fig. 1 shows the XRD patterns of ZnO:Eu(2%)/Tm(2%) materials annealed at 800° C for 1 hour. The diffraction peaks show the nanocrystalline nature of the materials. From X' pert High Score's search match analysis the ZnO:Eu(2%)/Tm(2%) materials show the presence of hexagonal structure according to JCPDS-36-1451. By the application of Scherrer formula : $t = (0.9\lambda)/(\beta \text{ Cos } \theta)$, 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 synthesized materials were in the range 70-75 nm. The sizes of as synthesized nano crystal materials were approximately confirmed by TEM images as shown in Fig. 2

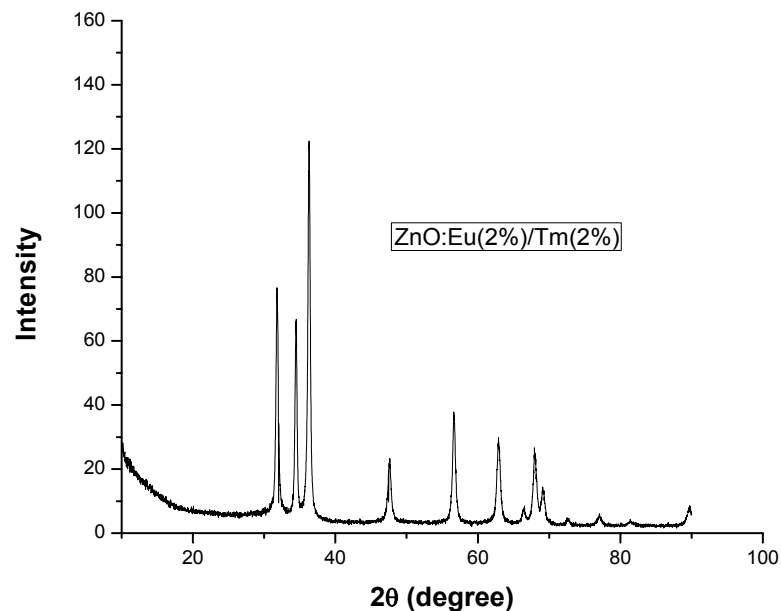


Fig.1 XRD patterns of ZnO:Eu(2%)/Tm(2%) nano-crystal materials

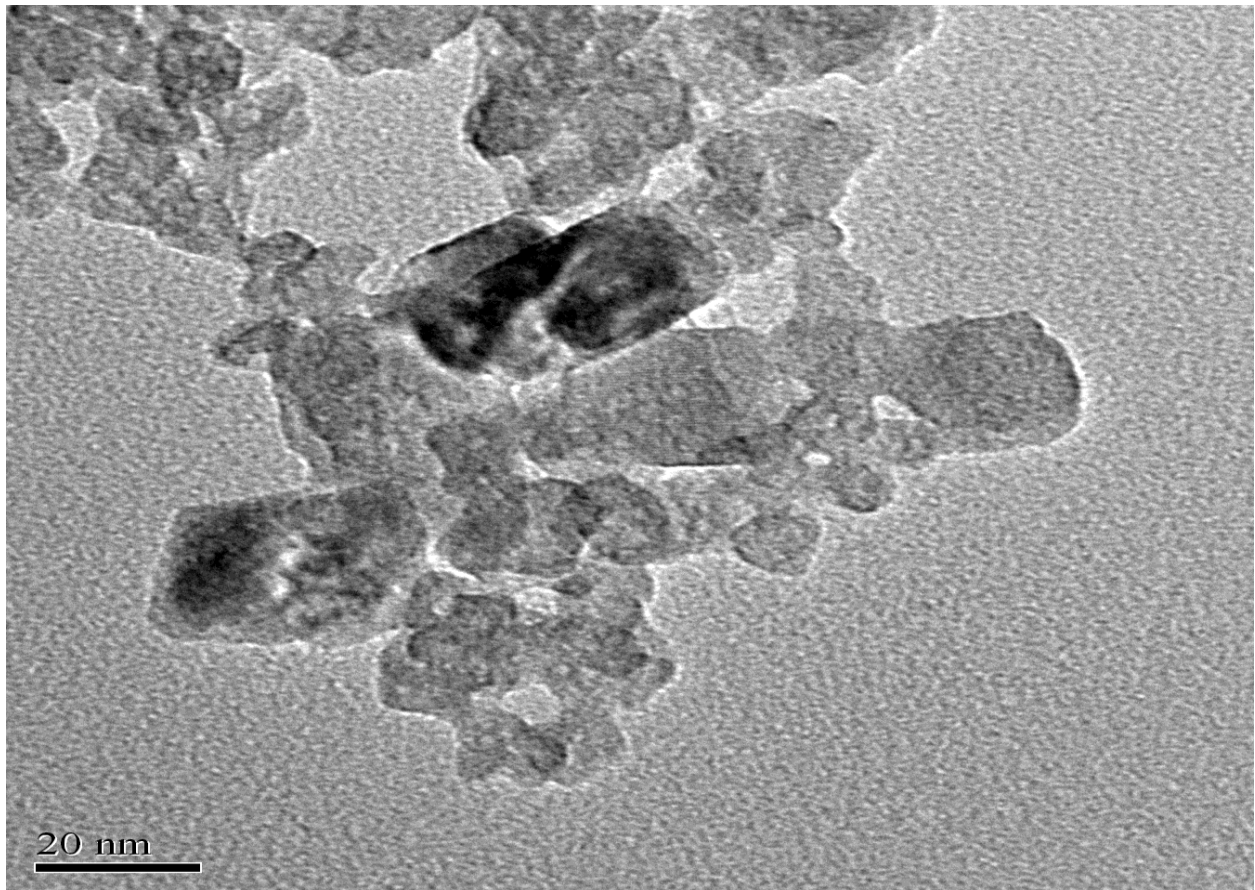


Fig. 2 TEM image of ZnO:Eu(2%)/Tm(2%) nanocrystal materials at 20 nm scale

Fig. 3 shows excitation spectra of as-synthesized ZnO:Eu(2%)/Tm(2%) nanocrystal materials annealed at 800° C for 1 hour by monitoring the emission at 618 nm recorded at room temperature. The spectra show a broad absorption at range of 225-400 nm consisting of a broad peak at around 278 and a small peak at 395 nm. The broad peak at around 278 nm is attributed mainly due to charge transfer transition between lanthanide ions and O^{2-} . The small peak at 395 nm is mainly originated from the f-f transitions of lanthanide ions.

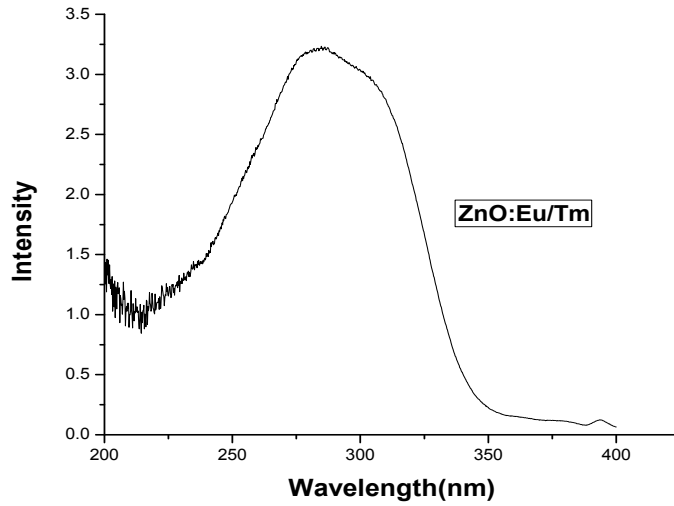


Fig. 3 Excitation spectra of ZnO:Eu(2%)/Tm(2%) nanocrystal materials

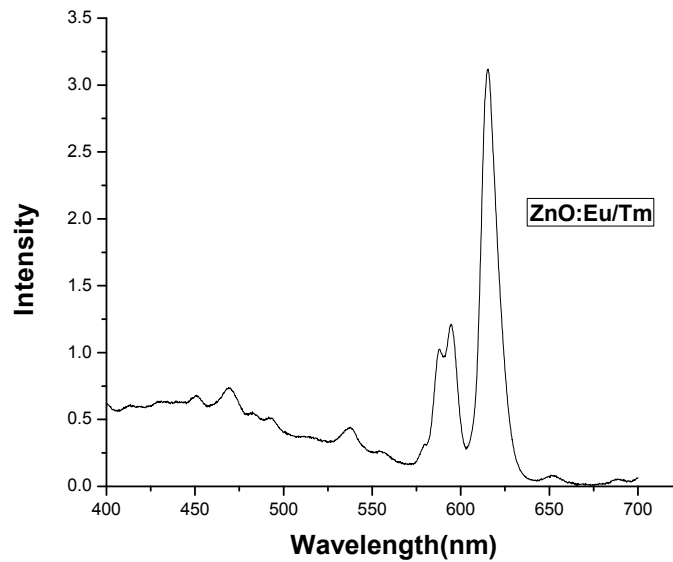


Fig. 4 Emission spectra of ZnO:Eu(2%)/Tm(2%) nanocrystal materials

Fig. 4 shows the emission spectra of as-synthesized ZnO:Eu(2%)/Tm(2%) nanocrystal materials annealed at 800° C for 1 hour by monitoring the excitation at 278 nm recorded at room temperature. The emission spectra exhibit the main characteristic emission lines of (i) Eu³⁺ in the red region of spectrum at 592 and 618 nm corresponding to ⁵D₀ – ⁷F₁ and ⁵D₀ – ⁷F₂ transitions respectively (ii) Tm³⁺ in the blue region at 472 nm corresponding to ¹G₄ – ³H₆ transition and there exists a small green emission peak at 540 nm corresponding to ⁵D₄ – ⁷F₅ transition.

Conclusions ZnO:Eu(2%)/Tm(2%) nanocrystal materials were synthesized by co-precipitation method in water medium with particle sizes in the range 70-75 nm. These sizes were critically confirmed by XRD data and TEM images and also showing hexagonal phases. Photoluminescence study of as prepared nanocrystal materials were carried out with the emission of strong red, small green and small blue lights, which is much closed to white light.

Acknowledgements: N. Bhmeshwar Singh thanks University Grants Commission, NERO, for providing financial support for Minor Research Project [File No. F.5-280/2015-16/MRP/NERO/1139 dated 29 March 2016]. N. John Singh also thanks University Grants Commission, NERO, for providing financial support for Minor Research Project [File No. F.5-234/2015-16/MRP/NERO/ 1060 dated 29 March 2016]. We acknowledged MU, Canchipur, NIT, Imphal, SAIF, NEHU, Sillong, Meghalaya, for providing XRD, PL, TEM measurement facilities.

References:

1. A. Sharma, S. Dhar, B. P. Singh, T. Kundu, M. Spasova, M. Farle, *J. Nanopart Res* **14** (2012) 676.
2. E. Pelizzetti, C. Minero, P. Piccinini and M. Vincenti, *Coord. Chem. Rev.* **125** (1993) 183.
3. P. M. Aneesh and M. K. Jayaraj, *Bull. Mater. Sci.* **33**,3 (2010) 227-231.
4. O'Regan B and Graetzel M, *Nature* **353** (1991)737-740.
5. Haque S A, Koops S, Tokmoldin N, Durrant J R, Huang J, Bradley D D C and Palomares E, *Adv. Mater*,**19** (2007)683-687
6. Granqvist C G, *Sol. Energy Mater Sol Cells*, **60** (2000) 201-223
7. J.C. Johnson, H. Yan, R.D. Schaller, L.H. Haber, R.J. Saykally, P. Yang, *J. Phys.Chem. B* **105** (2001)11387-11390.
8. O. Lupan, T. Pauporte, B. Viana, *Advanced Materials* **22** (2010)3298-3302.
9. M.D. McCluskey, S. J. Jokela, *Journal of Applied Physics*, **106** (2009)071101.

10. S. Chakrabarti, D Ganguli and S Chaudhari *J. Phys. D:Appl. Phys*, 36 (2003) 146-151.
11. Y.L. Wu,A.I.Y. Tok, F.Y. C. Boey, X.T. Zeng. X.H. Z Hang, *Applied Surface Science* 253 (2007) 5473-5479.
12. C. Jayachandraiah and G. Krishnaiah, *Advanced Materials Letters DOI: 10.5185 (2015)5801*.
13. S. Nakamura and G. Fasol, **Springer-Verlag, Berlin, 1997**.
14. H. Daicho, T. Iwasaki, K. Enomoto, Y. Sasaki, Y. Maeno, Y. Shinomiya, *Nature Communicationms*, 3 (2012) 1132.
15. M. Upasani, B. Butey, S. V. Moharil, *IOSR-JAP*, 6,2(2014) 28-33.
16. O. Lupan, T. Pauporte, B. Viana, P. Aschehoug, et al, *Applied Surface Science* 282 (2013) 782-788.
17. Nadia Febiana Djaja and Rosari Saleh, *Materials Sciences and Applications*, 4 (2013) 145-152.
18. Matrinus H.V. Werts, *Science Progress*, 88, 2 (2005) 101-131.