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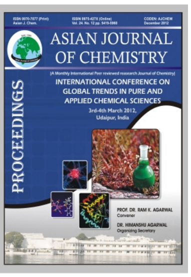

Enhanced Red Emission from Europium Doped Yttrium Oxide Nano Phosphor†

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Facile combustion method has been utilized for the synthesis of europium-doped yttrium oxide red nano phosphor with the inclusion of alkali metal. The red nano phosphor having the general formula $(Y_{1-x}Eu_x)_{2-y}Na_yO_{3-y}$, where $0.004 \leq x \leq 0.2$ and Na^+ is in the mole ratio 0.025 to 0.2 mol has been reported. Luminescence intensity of nano phosphor greatly enhanced with the inclusion of Na^+ ions along with the doping of europium. The materials are soft with fine crystal size less than the 30 nm. X-ray diffraction spectrum and scanning electron micrograph of the materials are also taken for further studying the morphology of the luminescent compound.

Key Words: Nano phosphor, Red Luminescence, Combustion method.

INTRODUCTION

Phosphors are found to be applied in various technological applications such as cathode ray tubes used in medical imaging, projection television, fluorescent lights, graphics, electroluminescent panels and field emission display[1-7]. These luminescent materials especially contained with lanthanides as doped centers, provide high luminescence due to the electronic transition mainly due to the $4f \rightarrow 4f$ transition of the activator ions. Disadvantage of cathode ray tubes for many applications are due to its size and power consumption. However, field emission display solves many problems over the conventional cathode ray tubes displays. For field emission display system however, very small particle size is required instead of the larger.

Oxide phosphors has been prepared with various methods such as solid state reactions, sol-gel techniques[8], hydroxide precipitation[9], hydrothermal synthesis[10], spray pyrolysis[11], laser evaporation[12] and combustion synthesis[13,14]. These methods have their rewards as well as restrictions. In multi step processes like heating at high temperatures and long processing time are required. The combustion is a novel technique through which a voluminous, foamy nano crystalline powder can be prepared within a few minutes. This technique is ideal for producing the fine, pure and single-phase powders.

Small amounts of Li ions as co-dopant frequently play an imperative role in increasing the luminescent efficiency of the $(Y_{1-x}Eu_x)_2O_3$ phosphors[15] producing fascinating red colour. It is also expected that the co-doping of the Na^+ ions into the nano sized phosphors may also improve the luminescence intensity. In the present work, synthesis and spectral characterization of the Na^+ co-doped $(Y_{1-x}Eu_x)_2O_3$ nano phosphor are described.

EXPERIMENTAL

Preparation: Stoichiometric amounts of yttrium nitrate hexahydrate (Aldrich 99.99 %), europium nitrate pentahydrate (Aldrich 99.99 %) and sodium nitrate ($NaNO_3$, Aldrich 99.99 %) were mixed in minimum doubly distilled water. Proportionate amount of the fuel (carbohydrazide, Aldrich) was also calculated as reported by Ekambaram and Patil[16] and was added to the concentrated solution. This mixture was heated in a crucible on a hot plate to form a viscous gel. After evaporating most of the water contents, crucible was placed into a preheated furnace maintained at 500 ºC for 5-10 min to promulgate for the combustion reaction. The reaction initiated immediately in furnace with flame appearing on the surface that spread over the entire volume of the crucible, leaving a white powder of an extreme porosity. The materials obtained were powdered using a ball mill having zirconia balls.

Thus a series of phosphor materials with general formula $(Y_{1-x}Eu_x)_2O_3$: Na ($0.004 < x < 0.2$ and $0.025 \leq Na \leq 0.2$) was prepared by dissolving the mixtures in proportionate amounts as stated above.

Morphology of the phosphor was determined by the scanning electron microscope using a Philips XL series. Elemental analyses were made by the Philips EDAX PV 9900

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series. Photoluminescence spectrum was recorded with a Minolta CS 1000 series spectrophotometer (USA). X-ray diffraction (XRD) spectrum of the materials was taken using a Rigaku spectophotometer model D/max 2000 (Japan) with CuK_α radiation.

RESULTS AND DISCUSSION

Homogenous samples of the red phosphor of europium doped yttrium oxide could be prepared by combustion method within a few minutes with nitrogen based fuel *i.e.* carbohydrazide. In general a good fuel should react non-violently and produces nontoxic gases. Reaction of fuel with metal nitrates at *ca.* 400 ºC produces combustible gases, finally producing non-toxic gases like N_2, CO_2 in situ that make the product fluffy[16]. The flame temperature increases with increase of fuel/oxidizer ratio[17]. According to the basics of the propellant chemistry[18], the oxidizing and reducing valencies of the element are: C = 4, H = 1, O = -2, N = 0, M = 1, 2 or 3 depending on the valency of the metal. Therefore the oxidizing valency of the trivalent metal nitrate $M(NO_3)_3$ is -15 and the reducing valency of the carbohydrazide (m.f. $N_2H_3CON_2H_3$), the fuel in the present case is +8. The ratio of carbohydrazide to the trivalent metal nitrates (fuel/metal nitrate) comes out to be 15/8 *i.e.* 1: 1.875. During the combustion the metal nitrates were impregnated into polymeric product in the gel form, the reaction initiated somewhere in the interior, flame appeared on the surface and proceeded rapidly throughout the whole volume, leaving a voluminous product with a high porous structure. The gases librated during the reaction were responsible to make the materials porous, henceforth particles size smaller. The product obtained had good phase purity and homogeneity over the entire volume of the oxide phosphor material.

Effect of the activator concentration: The effect of concentration of activator *i.e.* europium varied from 0.004 to 0.2 mol in the Y_2O_3 matrix on luminescence property was studied. The photoluminescence intensity of the phosphor increased up to 0.06 mol of Eu_2O_3 per mol of the Y_2O_3 and then decreased above this level due to the concentration quenching[19]. The best results for luminescence were obtained if europium concentration was taken between 0.02 to 0.06 mol for the yttrium oxide lattice.

Effect of Na^+ ions: Inclusion of Na^+ ions between 0.025 to 0.2 mol with respect to the phosphor material in the above-said series greatly increased the intensity of the luminescence of the material. It was noticed that the amount of Na^+ should be between 0.05 to 0.1 mol where luminescence intensity more than twice was observed, if the phosphor was without Na^+ ions. Lower concentrations of Na^+ ions < 0.05 produced less luminescence while maximum was observed with 0.1 mol of Na^+, but material lost its softness above 0.1 mol. The inclusion of the Na^+ ions in the lattice was confirmed by the elemental analysis technique (EDAX).

Crystal size and morphology: Scanning electron micrographs of the material showed the particle size to be smaller then 25 nm (Fig. 1). The average size of the crystallite was *ca.* 30 nm as estimated from the full width at half maximum of the peaks using the Scherrer's equation. This confirmed that the material made by the present method was highly fragile and fluffy and produced nano crystalline material on grinding. Fig. 2 is the XRD patterns obtained for red nano phosphor composition (a) $(Y_{0.95}Eu_{0.05})_2O_3$ without adding sodium (Na^+); (b) $(Y_{0.95}Eu_{0.05})_2O_3 : 0.01\ Na^+$ with sodium. XRD patterns as shown in Fig. 2 conclude that the peaks of material synthesized by gel combustion method further sharpened with the addition of the Na^+ and showed the crystalline nature of the phosphor material. The morphology of the crystalline powder confirmed a cubic structure that resembled with the pattern card of JCPDS-No 43-1036[20].

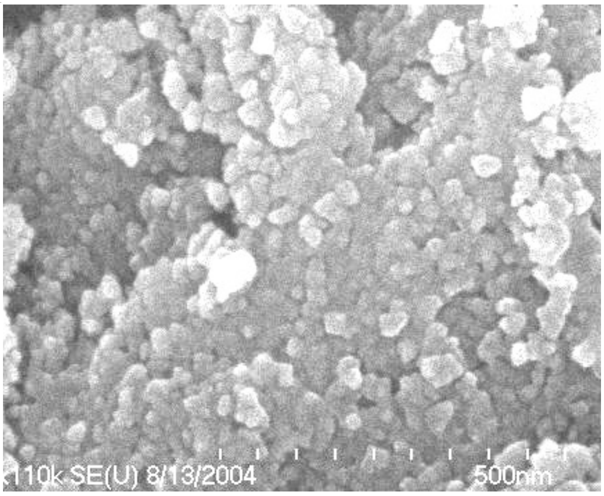

Fig. 1. Scanning electron micrograph of $(Y_{0.95}Eu_{0.05})_2O_3 : 0.01$ Na

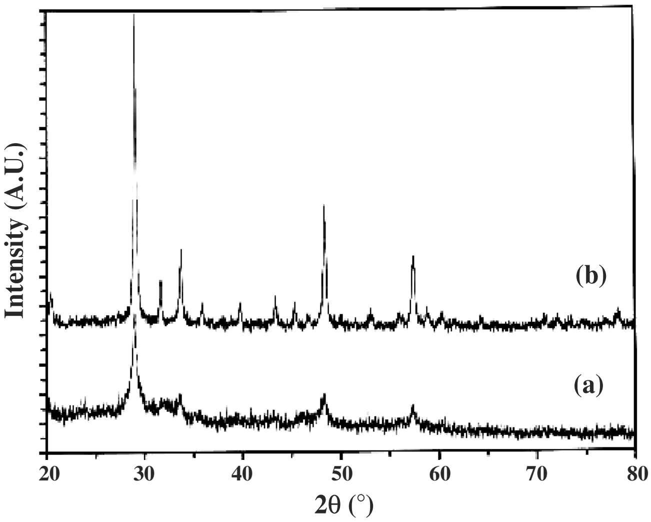

Fig. 2. XRD patterns of (a) $(Y_{0.95}Eu_{0.05})_2O_3$ without sodium ions; (b) $(Y_{0.95}Eu_{0.05})_2O_3 : 0.01$ Na

There were no peaks of Na_2O in the product combusted in presence of Na^+ ions. The co-dopant, Na^+ ions therefore did not destroy the crystallinity reflected by the diffraction intensity. For the complex matrix the Na^+ ions substitute yttrium ions in the lattice and that is why no extra phase of Na_2O existed. Usually, doping into space among crystal lattice may cause lattice distortion resulting in change of the cell parameters[21]. From the XRD results it may be assumed that Na^+ ions could not occupy the space among the crystal lattice, but they replaced Y^{3+} ions and occupied the sites of lattice. Therefore the most probable lattice structure equals to $(Y_{1-x}Eu_x)_{2-y}Na_yO_{3-y}$.

Spectral properties: The prepared material showed the uniform bright red colour emitting maximum at 612 nm when exposed to a 254 nm UV source. The photoluminescence spectrum of the nano red phosphor $(Y_{0.95}Eu_{0.05})_2O_3$: 0.01 Na^+, showed the λem at 612 nm. The emission at 612 nm can be assigned due to the hypersensitive transition of europium from $^5D_o \rightarrow {}^7F_2$. The brightness of the material enhanced almost to double due to the inclusion of the sodium as shown in Fig. 3. The CIE chromaticity coordinates of the above prepared nano phosphor fall in the red region of the colour triangle with x = 0.5078, y = 0.3137.

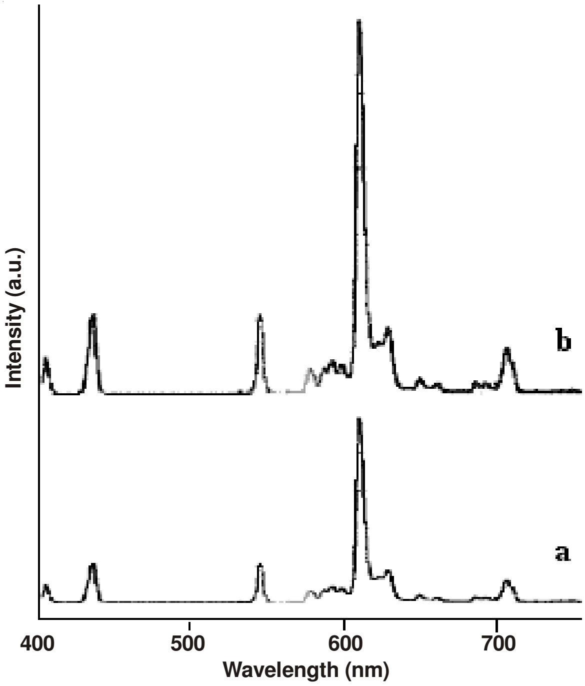

Fig. 3.

Inclusion of Na^+ ions in Y_2O_3 : Eu nanoparticles may replace Y^{3+} that may develop defects in the lattice structure. The accompanied increase in the emission intensity might be accordingly attributed to the increased Na^+ deficiency and therefore the oxygen vacancies. With the gradual increase in the Na^+ content, probably the oxygen vacancies of host lattice greatly increased which destroyed the crystallinity and lead to the luminescence quenches.

Conclusion

Nano crystalline $(Y_{0.95}Eu_{0.05})_2O_3$: 0.01 Na^+ red phosphor could be prepared utilizing the facile combustion synthesis technique. The luminescence of the nano phosphor greatly enhanced almost twice when prepared by adding of sodium ions. The phosphor produced the bright red luminescence at the 612 nm having the average nano crystalline particle size - 30 nm.

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REFERENCES

1. G. Blasse and B.C. Grabmair, Luminescent Materials, Springer Verlag, Berlin (1994).
2. S. Shionoya and W.M. Yen, Phosphor Handbook, CRC, Boca Roton, Boslin (1999).
3. S.M.J. Smets, *Mater. Chem. Phys.*, **16**, 238 (1989).
4. C.R. Ronda, *J. Lumin.*, **49**, 72 (1997).
5. C.R. Ronda, *J. Alloys Comp.*, **225**, 534 (1997).
6. C.-H.g Kim, I.-E. Kwon, C.-H. Park, Y.-J. Hwang, H.-S. Bae, B.-Y. Yu, C.-H. Pyun and G.-Y. Hong, *J. Alloys Comp.*, **311**, 33 (2000).
7. O.A. Serra, S.A. Cicillini and R.R. Ishiki, *J. Alloys Comp.*, **303-304** 316 (2000).
8. C.N. Rao, *Mater. Sci. Eng.*, **B18**, 1 (1993).
9. K.M. Kinsman, J. Mckittrick, E. Sluzky and K. Hesse, *J. Am. Ceram. Soc.*, **77**, 2866 (1994).
10. C.D. Vietch, *J. Mater. Sci.*, **26**, 6527 (1991).
11. Y.C. Kang, H.S. Roh and S.B. Park, *Adv. Mater.*, **12**, 451 (2000).
12. D.K. Wilams, B. Bhihari and B.M. Tissue, *J. Phys. Chem., B,* **102**, 916 (1998).
13. Y. Tao, G.W. Zhao, W.P. Zhang and S.D. Xia, *Mater. Res. Bull.*, **32**, 501 (1997).
14. L.D. Sun, J. Yao, C.H. Liu, C.S. Liao and C.H. Yan, *J. Lumin.*, **87-89**, 447 (2000).
15. T. Takeda, D. Koshiba and S. Kikkawa, *J. Alloy. Comp.*, **879**, 408 (2006).
16. S. Ekambaram and K.C. Patil, *J. Alloys Comp.*, **248**, 7 (1997).
17. J.J. Kingsley and L.R. Pederson, *Mater. Res. Soc. Symp., Proc.*, **296**, 361 (1993).
18. S. Ekambaram and K.C. Patil, *Bull. Mater. Sci.*, **18**, 921 (1995).
19. F.S. Kao, *Mater. Chem. Phys.*, **76**, 295 (2002).
20. Joint Commission on Powder Diffraction Spectroscopy (JCPDS)-International Centre for Diffraction Data, Swarthmore, U.S.A., Card No. 43, 1036.
21. B. Allieri, L.E. Depero, A. Marino, L. Sangaletti, L. Caporaso, A. Speghini and M. Bettinelli, *Mater. Chem. Phys.*, **66**, 164 (2000).