

International Journal of Luminescence and applications Vol5 (4) December, 2015, pages 500-505

Luminescence of Eu Doped Y₂O₃ Nanophosphor Prepared from Different Synthesis methods: Effect of synthesis Temperature on Luminescence Intensity Nikhil R Jha^{1*}, R K Kuraria², S R Kuraria² and P D Sahare³

¹Department of Physics, Takshshila Institute of Engineering and Technology, Jabalpur, MP, India ²Department of Physics, Government Autonomous Model Science college, Jabalpur, MP, India - 482001 ³Department of Physics & Astrophysics, University of Delhi, Delhi, India - 110 007 Corresponding author: <u>nikhilr_jha@rediffmail.com</u>: UD0001 08277222240

H/P0091 9827733240

Abstract

 Y_2O_3 :Eu nanophosphors are prepared from different synthesis viz. Combustion synthesis, Precipitation Method, Sol-Gel. The samples are annealed from 600-1400°C temperature. Effect of Temperature on luminescence intensity of Europium Doped Y_2O_3 phosphor prepared from different synthesisroutes is studied in the presented paper. Prepared samples are found to have monoclinic structure when compared with JCPDS standard data. The luminescence intensity increases with the increase of particle size and is affected by synthesis route. Eu doped Y_2O_3 particle shows sharp emission at 611nm at UV excitation. The samples are excited with different UV wavelength and maximum emission intensity is found when excited with 234nm wavelength. Powder X-Ray Diffraction (XRD) results indicated that high temperature leads to increase in the particle size. TEM photographs show the agglomeration of the samples at higher temperature.

Keywords: Different synthesis methods; Temperature dependence luminescence intensity; Emission for different excitation wavelength.

1.0 INTRODUCTION

 Y_2O_3 :Eu discovered decades ago, is still considered to be one of the best red inorganic phosphors, due to sharp emission (λ =611nm) of the europium ion activator (Eu³⁺) in the host lattice (Y₂O₃). This material has been utilized for some time due to its efficient luminescence under ultraviolet (UV) and electron beam excitation[1]. Commercial phosphor of this material is generally synthesized by solid state reaction or precipitation method, the particle size of which is in the range of µm scale. Y₂O₃:Eu with micrometer size was used as red component in trichromatic lamps, and projection color television. Application of nanometer phosphors for display has gathered great interest, since Bhargava et al. [2] reported the optical properties of ZnS:Mn nanocrystal with high quantum efficiency in 1994. Recently, numerous studies have focussed on optical properties of nano-dimensioned Y₂O₃:Eu. Europium doped yttrium oxide is commonly used in lighting and display applications in fluorescent lamp [3,4]. For enhanced display luminescence and resolution, phosphor particles with controlled morphology and smaller sizes are needed. Numbers of attempt were made to prepare different Nanosized Y₂O₃:Eu³⁺. In many of these methods, the prepared material were annealed to attain a preferred phase and to improve the crystallinity for the highest luminescence efficiency [5]. Chemical Vapor technique used by Konrad et al. [6] to obtain nanophosphor of 10nm size. Sol-Gel method [7,8,9], Combustion synthesis [10,11], Spray combustion synthesis[12] Flame spray pyrolysis [13], Co-precipitation method[14] and other methods were reported to prepare different Nanocrystalline Y2O3:Eu phosphor with different morphology. In 1995, Hergen Eilers and Brian M Tissue obtained nanocrystalline

Y2O3:Eu3+ particles condense in monoclinic crystal structure after CO₂-Laser vaporization[15] of metal oxide ceramics. Lei Yang et al. made Y₂O₃ nanotube arrays embedded in anodic alumina membranes (AAMs) prepared by an electronic field-assisted deposition method [16]. Guoping Dong et al. [17] reported to synthesis Nanofibers composed of pure body centered cubic (bcc) Y₂O₃ phase prepared by electrospinning. Many Photo Luminescence (PL) studies of Y₂O₃:Eu has been done for different UV excitation. J. Zhang et al[18] showed the comparative study of Y2O3:Eu3+ prepared from sol-gel and solid state reaction method and excitation spectrum of the red fluorescence (λ =612nm) at 233.5nm which is attributed to transition toward the charger transfer state (CTS) due toEu-O interaction. Comparative PL studies of Y₂O₃:Eu³⁺ prepared by urea combustion and precipitation method was done by Dhoble et al.[19] at 247nm excitation. Gareth Wakefield et al. [20] studied Luminescence spectra of Eu doped metallic oxide exciting it with 254nm UV source. Dosi Dosev et al. [21] reported PL Emission for 260nm excitation. L Robindro Singh et al.[22] have shown effect of doping on PL intensity at 394 excitation.

In this paper, we have reported Comparative PL of $Y_2O_3:Eu^{3+}$ made by different synthesis routes viz. Combustion synthesis (Urea, Glycine), Sol-Gel (Citric Acid, Tartaric Acid), precipitation and solid state Reaction method. Excitation and Emission Spectra of $Y_2O_3:Eu^{3+}$ derived from different synthesis routes, effect of synthesis on particle size for different methods at definite temperature and comparative change in particle size due to increase in temperature is also studied in the paper.

2.0 EXPERIMENTAL PROCEDURE

 Y_2O_3 (99.99%), E_2O_3 (99.99%), Nitric Acid (80% A.R.), Urea, Glycine, Citric Acid, Tartaric Acid, Oxalic Acid are taken as starting raw materials. $Y(NO_3)_3$ and $Eu(NO_3)_3$ stock solutions were prepared by dissolving Y_2O_3 and Eu_2O_3 in nitric acid and warming these solutions at 70-80°C over the electric heater. Initially brown fumes evolve from the solution and after 10-15 mins vivid transparent solutions of nitrates are obtained.

2.1 Combustion synthesis

For Combustion synthesis, the solution of $Y(NO_3)_3$ and $Eu(NO_3)_3$ were mixed according to the formula $(Y_{0.94}, Eu_{0.06})_2O_3$ in a beaker and suitable amount of Urea or Glycine is added taking U/N molar ratio unity. The solution was then heated with continuous stirring till the excess water evaporates leaving brownish yellow gel. The Gel is transferred into silica crucible and placed under preheated $600^{\circ}C$ furnace for an hour.

 $6Y(NO_3)_3 + NH_2CH_2COOH \rightarrow 3Y_2O_3 + 20CO_2 + 20H_2O + 14N_2$

Initially Y_2O_3 :Eu phosphor is made through urea combustion synthesis for different Eu mole concentration. The maximum PL intensity is found at 6 mol% (x=0.06) doping. Therefore, further preparation of samples were made for 6 mol% of Eu concentration.

2.2 Sol-Gel synthesis

 Y_2O_3 :Eu³⁺ nanoparticles were synthesized according to the flow chart presented in Fig.1. Tartaric acid was dissolved in Distilled water and the individual solutions of $Y(NO_3)_3$ and Eu(NO₃)₃ were mixed under constant stirring. Molar ratio of metal ions to tartaric acid takenwas 1:2. The mixture was then stirred for 24 h at room temperature. The mixture was



Fig 1. Flow Chart for Sol-gel synthesis

heated under constant stirring at 80° C for 2 h, which made the mixture denser forming the 'sol'. Then, the sol was heated at 120° C until a gel was formed and dried subsequently to get a fluffy powder. The dried gel was collected and heated in a preheated furnace at 600° C for 1h.

The citric acid is added in $Y(NO_3)_3$ and $Eu(NO_3)_3$ solution with 2:1 molar ratio of the metal ions and citric acid. The concentration of metal ions in the so-obtained solution is 1 mol/l, and pH is about 0.5. The solution was heated at 80°C while stirring till we get transparent gel. The gel was dried Study of Luminescence of Eu Doped Y₂O₃ Nanophosphor Prepared from Different Synthesis and Effect of Temperature on Luminescence Intensity, Nikhil R Jha et al

at 120°C to get a gray fluffy powder. The dry gel was then kept for heating at 600° C for 1 hr.

2.3 Precipitation method

For Precipitation method, the solution of dehydrated oxalic acid was made in double distilled water and warmed for 15-20min, with continuous stirring till transparent solution is obtained. $Y(NO_3)_3$ and $Eu(NO_3)_3$ were mixed in beaker and solution of oxalic acid was added drop by drop in the mixture and stirrer it well. The precipitate was obtained and filtered out. The precipitate then kept in preheated furnace at 600^oC for an hour.

2.4 Solid State Reaction

Also, $Y_{2-x}O_3$:Eu_x³⁺ (x = 6 mol%) was synthesized at 1300 °C for 3h by usual solid-state reaction technique for comparative studies. Stoichiometric amounts of Y_2O_3 , Eu₂O₃ and H₃BO₃ (Boric Acid, 2 wt.%) were mixed and finely grinded in an agate mortar. The powder was fired for 1h at 1000°C and 1300° C in air.

Y₂O₃:Eu nanophosphors were also prepared by Combustion synthesis for definite combinations of Citric Acid + Glycine and Oxalic Acid + Glycine reported in the present work. Same Synthesis procedure is adopted as used for Urea and Glycine Combustion synthesis.

The morphology and particle size of prepared samples were observed using X-Ray Diffraction Spectroscopy. The XRD measurements were carried out using Bruker D8 Advance X-ray diffractometer. The x-rays were produced using a



Fig. 2

sealed tube and the wavelength of x-ray was 0.154 nm (Cu K-alpha). The X-rays were detected using a fast counting detector based on Silicon strip technology (Bruker LynxEye dtector). PL was recorded on "Varian-CARY ECLIPSE Fluorescence Spectrophotometer" (for Excitation and Emission slit width 1.5 micron).

3. RESULT AND DISCUSSION

Y₂O₃:Eu nano phosphors were prepared wih different doping percentage 2,5,6,7,8,10,12 and 15 mol % through Urea Combustion syntheses; photo Luminescence emission spectra of these samples for excitation at 260nm is shown in Fig 2. It is found that the luminescence intensity initially increases with increase in doping percentage and attains



Fig. 3 Excitation Spectrum for 611nm Emission

highest peak at 6 mol% concentration. Further increase in doping percentage leads in decreasing luminescence intensity. This value is chosen as the optimum europium concentration and is consistent with the results given by other authors[22,23]Therefore all experimental samples are made with 6mol% Eu doping.





fixed emission 611nm and are shown in Fig. 3. Notable Excitation peaks were found at 228, 234, 242, 260, 325 and 374 nm wavelength for 611nm emission. It is observed that all samples show prominent peak at 234nm UV excitation which on vice-versa matched with emission spectra with maximum luminescence intensity at 611nm comparative to

other excitation wavelength. The strong red emission at 611nm is ascribed to the forced electric dipole transition $({}^{5}D_{0} \rightarrow {}^{7}F_{2})$, which is allowed in this case as the europium does not occupy a center of symmetry in yttrium[24].

Comparative PL study of samples annealed at 600^{0} C is shown in Fig.4. It is found that the luminescence intensity of sample (Glycine) is Maximum in comparison with other samples. The Luminescence intensity of precipitation method > Sol-gel (Tartaric Acid) > Combustion synthesis



Fig. 5 (a) XRD Pattern of Y2O3:Eu at 600°C

of Oxalic Acid (OA)+ Glycine > Sol-Gel (Citric Acid) > Combustion (Urea) > Combustion synthesis of Citric Acid (CA)+ Glycine is found in descending order at the same temperature. On annealing the samples at 1000° C, intensity of sample prepared by precipitation method was found maximum with respect to other samples. Respective descending intensity of samples at 1000° C is found to be precipitation method > Combustion (Urea) > Sol-gel (Tartaric Acid) > Combustion synthesis of Oxalic Acid (OA)+ Glycine > Combustion (Glycine)> Combustion synthesis of Citric Acid (CA)+ Glycine > Sol-Gel (Citric Acid).

XRD patterns of Y_2O_3 :Eu nanophosphor are shown in shown in Fig 5(a) and 5(b) for different prepared samples for different temperatures respectively. Comparing the XRD data with standard JPDS it is found that samples belongs to cubic crystal system. The broadening of the peaks (at FWHM) of prepared powders suggests particle size in nm range. The size of the sample is estimated using Sherrer's formula: $D = (0.89\lambda)/(\beta \cos\theta)$, where D is the average diameter of the grains, λ is the wavelength of X-Ray (= 0.1541nm), β is Full Width at Half Maximum (FWHM) of X-Ray diffraction lines and θ is Braggs angle. The average particle sizes vary drastically with the synthesis of preparation, but remain almost definite size range for particular synthesis irrespective of doping percentage. In our study, we found particle size of Y₂O₃:Eu prepared by urea combustion synthesis is of definite nm range and had no effect of doping percentage viz. Particle

Comparative XRD Pattern of Y2O3:Eu phosphor





size between 11-13nm (6 sample sets, heated at 600° C for 10 mins) and 13-15nm (10 sample sets, heated at 600° C for 1 hrs) and so on, irrespective of doping percentage.

The Particle size for different synthesis temperatures is calculated by Sherrer's formula for different samples are tabulated in Table 1. It is found that nanophosphor prepared by the combination of Citric Acid and Glycine combustion synthesis has smallest particle size, hence least luminescence intensity. It is reported elsewhere that larger the particle size larger the intensity or smaller the particle size lesser the intensity. This fact is also evident from nanophosphor prepared by Glycine combustion synthesis that shows maximum luminescence intensity among all samples treated at 600^oC as its particle size is 21.2nm in the set shown in the table.

Precipitation method is found to be the most efficient method with respect to the temperature change, that means it is found showing maximum intensity. Also its particle Study of Luminescence of Eu Doped Y₂O₃ Nanophosphor Prepared from Different Synthesis and Effect of Temperature on Luminescence Intensity, Nikhil R Jha et al

size to intensity ratio is maximum in comparison to other synthesis.

Comparative Luminescence Intensity of Different Y_2O_3 :Eu Nanophosphors prepared form different synthesis at different temperature are shown in Fig 6. It is found that the particle size of Glycine (for Glycine/Nitrate = 1) initially give higher intensity with larger particle size for 600° C and when annealed its comparative intensity decreases with increase in particle size. Also on annealing it at 1000° C give an average particle size of that range, which was not seen at 600° C. Particle obtained from Urea synthesis shows second best particle size to intensity ratio after precipitation method.

Citric Acid when combined with Glycine in Combustion synthesis yields smallest particle size. Even after treating at 1000°C again, the same sample shows smallest particle size among all samples from which we conclude that CA in combination with Glycine works as capping leading to smaller particle size for different temperatures as compared with other synthesis methods.

4.0 CONCLUSION

Comparative study of different synthesis methods was done and effect of synthesis on Luminescence intensity and particle size is reported. It is found that maximum luminescence intensity is found at 6 mol%. Particle size of phosphors increases with increase in temperature. Sample prepared by precipitation method shows best luminescence properties and particle size to intensity ratio is maximum in comparison to samples from other synthesis. Combustion of CA+Glycine shows noticeable smallest particle size in comparison with other synthesis methods. This shows that CA combined with Glycine in combustion synthesis acts as cap in increasing particle size.

ACKNOWLEDGEMENT

We gratefully acknowledge the Government Model Science College, Jabalpur, MP, India and University of Delhi, New Delhi, India for providing their Lab facilities. We also express our thanks to UGC, DAE Consortium for Scientific Research, Indore, India for XRD and TEM Characterization facilities. We also extend our thanks to Disha Institute of Management and Technology (DIMAT), Raipur, CG, India for providing there laboratory facilities without which the research work could not be accomplished. We are also thankful to Dr B P Chandra for his valuable guidance in sample preparation.

References:

- T. Guo, Z. Huang, X. Wu, J. Lin, Y. Zeng, Z. Liu, D. Zhang, Society for information Display, International n Digest of Technical Papers 2000, 31, 416
- 2. R. N. Bhargava, D. Gallagher, X. Hong, A. Nurmikko, Phys. Rev. :ett. 72 (1994) 416
- 3. G. Blasse and B.C.Grabmaier, Luminescent Materials. Springer, Berlin (1994)
- 4. T. Justel, H. Nikol and C. Ronda, New developments in the field of luminescent materials for lighting and displays, Angew. Chem. Int. Ed. 37, 3085 (1998).
- J. McKittric, C.F. Bacalski, G.A. Hirata, K.M. Hubbard, S.C. Pattillo, K.V.Salazar, M.Trkula, J. Am. Ceram. Soc. 83 (2000) 1081
- A. Konrad, T.Fries, A. Gahn, F.Kummer, U.Herr, R.Tidecks, K.Samwer, J. Appl. Phys. 86 (1999) 3129
- Junying Zhang, Zilong Tang, Zhongtai Zhang, Wangyang Fu, Jin Wang, Yuanhua Lin, Materials Science and Engineering A334 (2002) 246–249
- 8. M.K. Chong, K. Pita, C.H. Kam, Journal of Physics and Chemistry of Solids 66 (2005) 213–217
- V.B. Taxak, S.P. Khatkar, Sang-Do Han, Rajesh Kumar, Mukesh Kumar, Journal of Alloys and Compounds 469 (2009) 224–228
- R.V. Mangalaraja, J. Mouzon, P. Hedstrom, I. Kero, K.V.S. Ramam, Carlos P. Camurri, M.Oden, J. materials processing technology, 208 (2008), 415-422
- Tao Ye, Zhao Guiwen, Zhang Weiping and Xia Shangda, Materials Research Bulletin, Vol. 32, No. 5, pp. 501-506,1997
- Gang Yao, Liangbi Su, Jun Xu, Xiaodong Xu, Lihe Zheng, Yan Cheng, Journal of Crystal Growth 310 (2008) 404–409
- Dosi Dosev, Bing Guo, Ian M. Kennedy, J. Aerosol Science 37 (2006) 402 – 412
- Xiaorui Hou, Shengming Zhou, Yukun Li, Wenjie Li, J. of Alloys and Compounds 494 (2010) 382–385
- Hergen Eliers, Brian M Tissue, Chemical Physics Letters 251 (1996) 74-78
- Lei Yang, Yuanhong Tang, Xiaohua Chen, Yan Li, Xueli Cao, Materials Chemistry and Physics 101 (2007) 195–198
- Guoping Dong, Yingzhi Chi, Xiudi Xiao, Xiaofeng Liu, Bin Qian, Zhijun Ma, E Wu, Heping Zeng, Danping Chen, and Jianrong Qiu, 7 December 2009 / Vol. 17, No. 25 / OPTICS EXPRESS 22515
- Junying Zhang, Zilong Tang, Zhongtai Zhang, Wangyang Fu, Jin Wang, Yuanhua Lin, Materials Science and Engineering A334 (2002) 246–249
- S.J. Dhoble,, I. M. Nagpure, J.G. Mehakhode, S. V. Godbole, M. K. Bhinde, S. V. Moharil, Iucl. Instr. And Meth. In Phys. Res. B 266 (2008) 3437-3442
- 20. Gareth wakefield, Edward holland, Peter J. Dobson, and John L. Hutchison, Adv. Mater. 2001, 13, No. 20, October 16.

INTERNATIONAL JOURNAL OF LUMINESCENCE AND ITS APPLICATIONS Vol.I(1) April.2011 ISSN No.

- 21. D. Dosev, B. Guo, I. M. Kennedy, Aerosol Science 37 (2006) 402-412
- L. Robindo Singh, R S Ningthoujam, V Sudarsan, Iti Srivastava, D Dorendrajit Singh, G K Dey and S K Kulshreshtha, Nanotechnology 19 (2008) 055201
- 23. M. Kottaisamy, D. Jeyakumar, R. Jagannathan, M.M. Rao, Mater. Res. Bull. 31 (1996) 1013
- 24. G. Wakefield, E. Holland, P. J. Dobson, J. L. Hutchison, Adv. Mater. 13 (2001) 1557