

International Journal of Luminescence and applications Vol5 (4) December, 2015, pages 380-383

# Synthesis and photoluminescence study of Gd<sub>2</sub>O<sub>3</sub>:Dy<sup>3+</sup> nanophosphors for white light applications

Sh. Dorendrajit Singh\*, Sonia Nambram, S. Dhiren Meetei

Department of Physics, Manipur University, Canchipur, Manipur - 795003, India

#### Abstract

 $Gd_2O_3$  is a promising host matrix for optical studies due to its low phonon energy, high thermal stability and good chemical durability. A series of  $Gd_2O_3$  nanophosphors doped with different concentration of  $Dy^{3+}$  was synthesized by chemical precipitation method. The undoped and doped samples were found to be in cubic phase from the X-ray diffraction (XRD) study suggesting that  $Dy^{3+}$  atoms remain in the crystallite lattice of the host. The particle sizes were found to be in the range of 14-21 nm. Photoluminescence emission peak of  $Dy^{3+}$  in doped samples were observed at 487 nm, 575 nm and 672 nm corresponding to the  ${}^{4}F_{92}$ - ${}^{6}H_{152}$ ,  ${}^{4}F_{92}$ - ${}^{6}H_{132}$  and  ${}^{4}F_{92}$ - ${}^{6}H_{112}$ transition respectively. Effective energy transfer from  $Gd^{3+}$  to  $Dy^{3+}$  was observed yielding efficient emission under UV excitation. The maximum emission intensity was found for 1.5 at.%  $Dy^{3+}$  doped  $Gd_2O_3$  sample. The enhancement in the emission intensity with the increase of  $Dy^{3+}$  was due to the increase in energy transfer from  $Gd^{3+}$  ions of host to  $Dy^{3+}$ ions. The CIE (Commission Internationale de l'e' clairage) co-ordinates of the doped samples were found to be very close to that of white light (0.33, 0.33).

Keywords: nanophosphors; cubic; photoluminescence; chromaticity

PACS Code: 42.70-a; 82.80.Ej; 85.60.Jb

# **1.0 INTRODUCTION**

Recently there has been a tremendous interest on the production of white light emitting nanophosphors which will be a more preferable replacement for conventional lighting sources. White emitting nanophosphors can serve as lighting sources in nanooptic devices as well as variety of applications such as displays, backlight and alternatives to general lighting. White light can be produced by mixing red, green, blue phosphors in an appropriate proportion or using single phosphor containing the combination of RGB emission or yellow or blue emission [1,2]. Recently trivalent dysprosium ions (Dy<sup>3+</sup>) doped phosphors has been studied in the white light applications because of its intense blue (484nm) and vellow (575nm) emissions corresponding to  ${}^{4}F_{9/2}$ - ${}^{6}\text{H}_{15/2}$  and  ${}^{4}\text{F}_{9/2}{}^{-6}\text{H}_{13/2}$  [1-3]. Many works have been reported for the white light emitting Dy3+ doped phosphors having different hosts such as borates,

vanadates, molybdates, oxides etc [4-6]. Among these hosts, oxides phosphors specially lanthanide oxide phosphors offer potential advantages because of their large Stokes shift, sharp emission spectra, long life times and resistance against photo-bleaching . For instance gadolinium oxide (Gd<sub>2</sub>O<sub>3</sub>) is a promising host matrix. It possesses low phonon energy (~600 cm<sup>-1</sup>) and has its first excited state at~ 32000 cm<sup>-1</sup> (4eV) and can easily be doped with rare earth ion(s)[7]. The high thermal stability, good chemical durability of Gd<sub>2</sub>O<sub>3</sub> makes it as one of the promising host for the preparation of highly luminescent phosphors.

Many works has been reported on the synthesis of Eu<sup>3+</sup> doped Gd<sub>2</sub>O<sub>3</sub> red phosphor by different methods and its application in optoelectronic devices and in the field of biotechnology, biomedical [7-13] etc. A bright white upconversion emission from Yb<sup>3+</sup>, Er<sup>3+</sup> and Tm<sup>3+</sup> codoped Gd<sub>2</sub>O<sub>3</sub> nanotube has been

Email address: dorendrajit@yahoo.co.in

reported by Kezhi et al.[1] And also Bedekar and coet al[2]. reported the generation of white emission from  $Dy^{3+}$  and  $Tb^{3+}$  codoped  $Gd_2O_3$  phosphors. White light emitting monoclinic phase  $Gd_2O_3:Dy^{3+}$ phosphors by combustion method is reported by Mula et al[14]. Further synthesis of multicolour emitting  $Gd_2O_3:Dy^{3+}$  phosphor by citrate-based solgel method has been reported recently [15].

In this work,  $Dy^{3+}$  doped  $Gd_2O_3$  nanophosphors have been synthesized by chemical precipitation method. Effective energy transfer from  $Gd^{3+}$  to activator  $Dy^{3+}$  is observed yielding a high efficiency emission coming from  $Dy^{3+}$ . Difference in the emission intensity with different concentrations of  $Dy^{3+}$  is also observed. The chromatic properties of the phosphors are also discussed.

#### 2. Experiment

The samples  $Gd_2O_3$  doped with different concentration of  $Dy^{3+}$  namely 0.5at.%, 1at.%, 1.5at.% and 2at.% were prepared using precipitation method, using NaOH. The starting materials were  $Gd(NO_3)_3$  (Acros Organics) and  $DyCl_3.6H_2O$  (Aldrich), NaOH (MERK) as precipitator.

At first, 250mg of Gd(NO<sub>3</sub>)<sub>3</sub> was dissolved in 25 ml of water by stirring for 10 minutes. 0.5at.%, 1at.%, 1.5at.%, 2at.% of DyCl<sub>3</sub> was added to the solution and stirred for another 10 minutes. Equal amount of NaOH was added for all the samples and stirred for 30 minutes. Upon introduction of NaOH, white precipitate is formed. White precipitate so formed was centrifuged and washed with acetone and dried it in open air and grind it. The white powder so obtained was annealed at 600<sup>o</sup>C for 4 hours to grow the crystallites.

For determination of crystalline structure and average size, samples were investigated by X-ray diffraction (XRD) patterns using PANalytical instrument operating with Cu K<sub>a</sub> radiation (1.5406Å). Fourier transform infra-red (FT-IR) spectra were recorded in Shimadzu FTIR 8400S in order to know different molecular species present in the phosphor along with the rare earth ions. The fluorescence excitation and emission spectra of all the samples were recorded on LS55 (Perkin Elmer) instrument at room temperature to study the luminescent properties of the samples.

# 3. Results and discussion



Fig. 1 XRD patterns of the samples

Fig.1 gives the XRD patterns of the samples. The peak position and intensity agreed with the ICSD reference no. 00.011.0604, which is cubic phase. The average crystallite size of the samples were calculated from the diffraction linewidth based on Scherrer's relation

# $t=0.9\lambda/\beta \cos\theta$

where t is the crystallite size,  $\lambda$  is the X-ray wavelength,  $\beta$  is the fullwidth at half maximum and  $\theta$  is the Bragg's angles.

The crystallite size of the samples are found to be in the range of 14-21 nm. The lattice constant of the undoped  $Gd_2O_3$  sample is found to be 10.780 Å which is in close agreement with the literature value of a= 10.809 Å.



Fig.2 FT-IR spectra of Dy3+ doped Gd2O3 phosphors

In order to analyse the different molecular species present in the samples, Fourier transform infra-red (FT-IR) spectra are recorded. Fig. 2 shows the FT-IR spectra of  $Dy^{3+}$  doped  $Gd_2O_3$  samples annealed at  $600^{0}$ C. The absorption peak at 540 cm<sup>-1</sup> is associated with the vibration of Gd-O bond [10,16]. The peaks at 850 cm<sup>-1</sup> and in the range 1400-1600 cm<sup>-1</sup> indicate carbonate groups which originate from the absorption of atmospheric CO<sub>2</sub> [15]. The peak at 1380 cm<sup>-1</sup> are associated with vibration modes of NO<sub>3</sub> groups [7,10, 15]. Presence of NO<sub>3</sub> groups is probably from the precursor we used. The broad band at 3000-3500cm<sup>-1</sup> correspond to OH stretching of H<sub>2</sub>O molecular absorbed from the atmospheric air [7,10, 15].



Fig. 3. (a) excitation spectra of  $Gd_2O_3$  doped with different concentration of  $Dy^{3+}$ ; (b) emission spectra of  $Gd_2O_3$  doped with different concentration of  $Dy^{3+}$  and (c) Concentration of  $Dy^{3+}$  Vs intensity graph

Fig. 3(a) shows PL excitation spectra of the undoped and 0.5at.%-2at.% of Dy3+ doped samples under 486 nm emission. The excitation spectra show a sharp peak at 238 nm due to the host absorption of Gd<sub>2</sub>O<sub>3</sub> lattice resulting in an energy transfer from  $^{6}P_{7/2}$  level of Gd<sup>3+</sup> ions of host to Dy<sup>3+</sup> ions [2,15]. A peak at280 nm also corresponds to Gd3+ absorption (8S-6I) transitionThe excitation peak at 350 nm shows absorption bands originating from f-f transitions in  $Dy^{3+} \ (^6H_{15/2} - \,^4M_{15/2} + {}^6P_{7/2}).$  Fig. 3(b) shows the PL emission spectra of the undoped and 0.5at.%-2at.% of Dy<sup>3+</sup> doped samples with excitation wavelength 238 nm. In emission spectra there are two dominating emissions at 487nm and 575 nm and as well as one weak emission at 672 nm, corresponding to <sup>4</sup>F<sub>9/2</sub>- ${}^{6}H_{15/2}$ ,  ${}^{4}F_{9/2}{}^{-6}H_{13/2}$  and  ${}^{4}F_{9/2}{}^{-6}H_{11/2}$  transitions respectively[1-3]. The <sup>4</sup>F<sub>9/2</sub>-<sup>6</sup>H<sub>13/2</sub> transition corresponds to electric dipole transition which is allowed in the case that Dy<sup>3+</sup> ions locate at the local sites with non-inversion symmetry. Thus, the more intense emission at 575 nm shows that Dy<sup>3+</sup> ions lie in the host lattice without inversion centre [3,4,15].

From the emission spectra, it can also be seen that the profile of the emission spectra of doped samples is independent of the concentration of the dopant Dy<sup>3+</sup>, but the emission intensity changes with the change in the concentration of the dopant. The concentration of dopant vs intensity graph (fig.3c) shows that the emission intensity increases with the increase of Dy3+ concentration upto 1.5at.% and decreases with further increase of Dy<sup>3+</sup> concentration. The increase in energy transfer from Gd3+ of host to  $Dy^{3+}$  ions i.e. the increase in the absorption efficiency with the increase of  $Dy^{3+}$  concentration in  $Gd_2O_3$ leads to the increase of emission intensity. However such behavior occurs only upto a certain critical concentration of dopants. The luminescence intensity starts to decrease above this critical concentration. Further increase in Dy3+ concentration results in reducing the distance between Dy3+ ions and noncross-relaxation occur and radiative hence luminescence quenching takes place. The optimum doping concentration of Dy<sup>3+</sup> for obtaining maximum emission intensity is found to be 1.5at.%.

For evaluating phosphors' performance, study of color co-ordinates is one of the important factors. Hence the color co-ordinates for the samples are calculated using the PL emission spectra data and the chromatic standard issued by the Commission International de I'Eclairage in 1931 (CIE 1931).

The color co-ordinates of the doped samples are found to be very close to that of the standard white light (x=0.33, y=0.33) [4]. In fig.4 the dotted regions

are the calculated CIE co-ordinates of the undoped and  $Dy^{3+}\ doped\ Gd_2O_3\ samples.$  The dotted regions



Fig.4. CIE color co-ordinates for  $Gd_2O_3$  samples doped with different concentration of  $Dy^{3+}$ 

surrounded by black circle represent CIE coordinates of 0.5-2at.%Dy<sup>3+</sup> doped Gd<sub>2</sub>O<sub>3</sub> samples respectively. The CIE co-ordinates of the Dy<sup>3+</sup> doped samples are in the white light region. Hence Dy<sup>3+</sup> doped Gd<sub>2</sub>O<sub>3</sub> nanophosphor will be a promising phosphor for white light application.

#### 4. CONCLUSION

Dy<sup>3+</sup> doped  $Gd_2O_3$ nanophosphors were successfully synthesized by simple chemical precipitation method. The effect of the luminescence intensity with the concentration of dopant  $Dy^{3+}$  in Gd<sub>2</sub>O<sub>3</sub> nanophosphors has been studied. The maximum emission intensity is found at 1.5 at.% Dy<sup>3+</sup> doped Gd<sub>2</sub>O<sub>3</sub> sample. The CIE co-ordinates of the samples are found to be close to the standard coordinate of white light (0.33, 0.33). Thus the Dy<sup>3+</sup> doped Gd<sub>2</sub>O<sub>3</sub> nanophosphors will be a promising phosphor for white light applications.

## ACKNOWLEDGEMENT

The authors gratefully acknowledged the University Grant Commission for financial support (sanction no. 41-860/2012(SR)).

## **References:**

- K. Zheng, D. Zhang, D. Zhao, N. Liu, F. Shi and W. Qin Phys Chem. Chem. Phy. 12 (2010), 7620-7625
- V.Vedekar, D.P.Dutta, M.Mohapatra, S.V. Godbole, R.Ghildiyal and A.K. Tyagi Nanotechnol. 20 (2009)125707
- J.C.G.Bu<sup>"</sup>nzli and S.V. Eliseeva Lanthanide Springer series of Fluorescence 7 Pekka Hanninen, Harri Harma (12-24)
- L.Cheng, X.Li, J. Sun, H. Zhong, Y.Tian, J. Wan, W. Lu, Y.Zheng, T.Yu, L. Huang, H.Yu, B. Chen, Physica B, 405(2012) 4457
- L.A.Diaz-Torres, E.D.Rosa, P.Salas, V.H. Romero, C.A.Chaviz Journal of Solid State Chemistry, Volume 181, (2008) 75-80
- N.S.Singh, R.S.Ningthoujam, N.Yaiphaba, S.D. Singh and R.K. Vatsa J. Appl. Phys. 105 (2009) 064303
- G.Kaur, S.K. Singh and S.B.Rai J. Appl. Phys. 107 (2010) 073514
- 8. K.H. Lee, Y.J. Bae and S.H. Byeon Bull. Korean Chem. Soc. 29 (2008) 2161
- O.Milosevic, L.Mancic, M.E.Ralanal, J.M. Torralba, B.Yang and P. Townsend, Journal of the Electrochemical Society, 152 (2005) 6707-6713
- J. Chandradass, M. Balasubramanian, D.S.Bae and H.Kim, Materials and Manufacturing Processes, 27 J.W. Lee, J. Korean Ceramic Society, 47(2010) 177-182
- L.Yanhong, L.Guixia and H.Guangyan J. Rare Earths 22 (2004) 70
- In Yong Park and Jong Won Lee, J. Korean Ceramic Society, 47(2010) 177-182
- E. Hemmer, N. Venkatachalam, H. Hyodo and K. Soga, Adv.Mater. Sci. Eng. 2012 Article ID 748098, 15 pages
- M. Jayasimhadri, B. V. Ratnam, K. Jang, H. S. Lee, B.Chen, S.S. Yi, J. H. Jeong and L. Rama Moorthy Journal of Applied Ceramic Technology, 8 (2011) 709-717
- T.Selvalakshmi, S. Sellaiyan, A. Uedono and A. Bose RSC Adv. 4 (2014) 34257
- S.D. Meetei, S.D. Singh, N.S. Singh, V. Sudarsan, R.S. Ningthoujam, M. Tyagi,., Journal of Luminescence, 132 (2012) 537-544