



Synthesis and photoluminescence study of $Gd_2O_3:Dy^{3+}$ nanophosphors for white light applications

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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 ${}^4F_{9/2}-{}^6H_{15/2}$, ${}^4F_{9/2}-{}^6H_{13/2}$ and ${}^4F_{9/2}-{}^6H_{11/2}$ 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'éclairage) 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

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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 nano-optic 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^{3+}) doped phosphors has been studied in the white light applications because of its intense blue (484nm) and yellow (575nm) emissions corresponding to ${}^4F_{9/2}-{}^6H_{15/2}$ and ${}^4F_{9/2}-{}^6H_{13/2}$ [1-3]. Many works have been reported for the white light emitting Dy^{3+} 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_2O_3) is a promising host matrix. It possesses low phonon

energy ($\sim 600\text{ cm}^{-1}$) and has its first excited state at 32000 cm^{-1} (4eV) and can easily be doped with rare earth ion(s)[7]. The high thermal stability, good chemical durability of Gd_2O_3 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^{3+} doped Gd_2O_3 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^{3+} , Er^{3+} and Tm^{3+} codoped Gd_2O_3 nanotube has been reported by Kezhi et al.[1] And also Bedekar and co-et 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 sol-gel 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

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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 $DyCl_3 \cdot 6H_2O$ (Aldrich), NaOH (MERK) as precipitator.

At first, 250mg of $Gd(NO_3)_3$ was dissolved in 25 ml of water by stirring for 10 minutes. 0.5at.%, 1at.%, 1.5at.%, 2at.% of $DyCl_3$ 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 $600^\circ C$ 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 $Cu K_\alpha$ 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

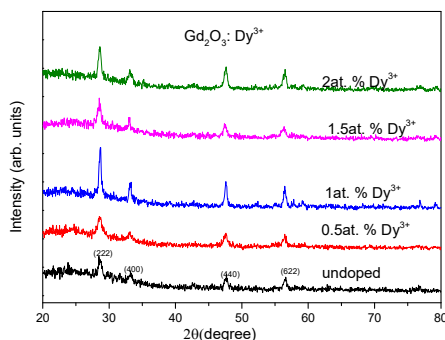


Fig. 1 XRD patterns of the samples

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, λ is the X-ray wavelength, β is the fullwidth at half maximum and θ 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.

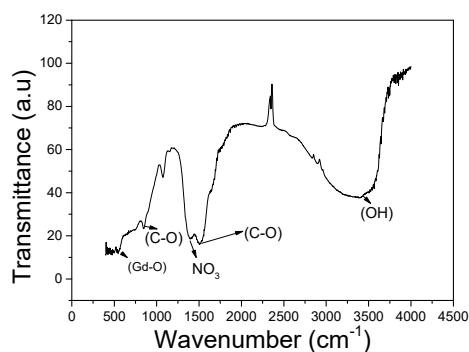
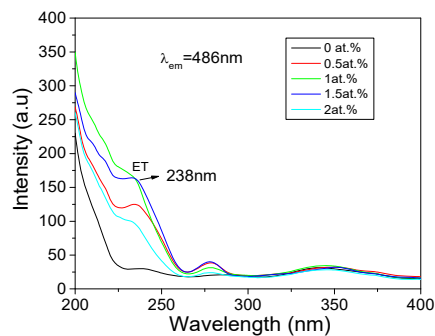


Fig.2 FT-IR spectra of Dy^{3+} doped Gd_2O_3 phosphors

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 $600^\circ C$. The absorption peak at 540 cm^{-1} is associated with the vibration of Gd-O bond [10,16]. The peaks at 850 cm^{-1} and in the range $1400\text{--}1600\text{ cm}^{-1}$ indicate carbonate groups which originate from the absorption of atmospheric CO_2 [15]. The peak at 1380 cm^{-1} are associated with vibration modes of NO_3 groups [7,10, 15]. Presence of NO_3 groups is probably from the precursor we used. The broad band at $3000\text{--}3500\text{ cm}^{-1}$ correspond to OH stretching of H_2O molecular absorbed from the atmospheric air [7,10, 15].



(a)

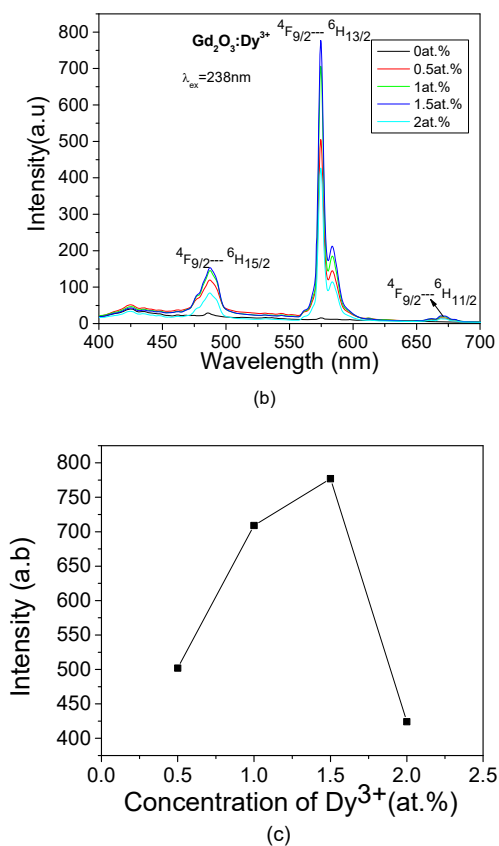


Fig. 3. (a) excitation spectra of Gd₂O₃ doped with different concentration of Dy³⁺; (b) emission spectra of Gd₂O₃ doped with different concentration of Dy³⁺ and (c) Concentration of Dy³⁺ Vs intensity graph

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 Gd₂O₃ lattice resulting in an energy transfer from ⁶P_{7/2} level of Gd³⁺ ions of host to Dy³⁺ ions [2,15]. A peak at 280 nm also corresponds to Gd³⁺ absorption (⁸S-⁶I) transition. The excitation peak at 350 nm shows absorption bands originating from f-f transitions in Dy³⁺ (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 Dy³⁺ 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 ⁴F_{9/2}-⁶H_{15/2}, ⁴F_{9/2}-⁶H_{13/2} and ⁴F_{9/2}-⁶H_{11/2} transitions respectively [1-3]. The ⁴F_{9/2}-⁶H_{13/2} transition corresponds to electric dipole transition which is allowed in the case that Dy³⁺ ions locate at the local sites with non-inversion symmetry. Thus, the more intense emission at 575 nm shows that Dy³⁺ 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 Dy³⁺, 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 Dy³⁺ concentration. The increase in energy transfer from Gd³⁺ of host to Dy³⁺ ions i.e. the increase in the absorption efficiency with the increase of Dy³⁺ concentration in Gd₂O₃ 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 non-radiative cross-relaxation occur and hence luminescence quenching takes place. The optimum doping concentration of Dy³⁺ 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 l'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 Dy³⁺ doped Gd₂O₃ 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 co-ordinates of 0.5-2at.% Dy^{3+} doped Gd_2O_3 samples respectively. The CIE co-ordinates of the Dy^{3+} doped samples are in the white light region. Hence Dy^{3+} doped Gd_2O_3 nanophosphor will be a promising phosphor for white light application.

4. CONCLUSION

Dy^{3+} 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_2O_3 nanophosphors has been studied. The maximum emission intensity is found at 1.5 at.% Dy^{3+} doped Gd_2O_3 sample. The CIE co-ordinates of the samples are found to be close to the standard co-ordinate of white light (0.33,0.33). Thus the Dy^{3+} doped Gd_2O_3 nanophosphors will be a promising phosphor for white light applications.

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