

Synthesis and Characterization of White Light Emission of Dy³⁺ Doped Gd₂O₃ Phosphors

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Dy³⁺ ion doped Gd₂O₃ phosphors with varying concentrations were synthesized successfully by hydrothermal process. The XRD patterns and TEM images of prepared samples were well-studied. Upon the emission at $\lambda_{em} = 573$ nm, the excitation spectra consist of several peaks which denote the characteristic lines of the 4*f*-4*f* or 4*f*-5*d* intra-configurational transition of Gd³⁺ and Dy³⁺ ions. In the emission spectrum obtained by excitations at 234 nm and 273 nm, consist of two characteristic band obtained at 485 and 573 nm, which are attributed to ⁴F_{9/2}→⁶H_{15/2} (blue) and ⁴F_{9/2}→⁶H_{13/2} (yellow) transitions of Dy³⁺ ion, respectively. The photoluminescence lifetime are found to be at around 0.599-1.200 ms. The CIE Chromaticity coordinates showed the prepared samples could be used as a white light emitting phosphor applied in near UV region.

Keywords: White light emission, Dy³⁺, Phosphors, Gd₂O₃.

INTRODUCTION

Phosphors have intensive interest within the researchers in the past few years due to their technological importance and scientific applications. Lanthanide(III) oxide phosphor is one of the advanced materials which have large Stokes shifts, narrow band widths and suitable for multiphoton excitation and their applications in the field of optoelectronic devices, fluorescent labels, sensors, *etc.* [1-4]. Among all the lanthanide(III) oxide phosphors, Gd₂O₃ has been widely studied and applied due to its unique properties such as high chemical and thermal stability, low photonic energy, high luminescent efficiency and good dispersion [5,6]. Moreover, Gd³⁺ ion has seven unpaired electrons in 4*f*-electron layer with high spin magnetic moment, which interacts with water, it shortens the longitudinal relaxation time T₁ of proton in water to enhance the MRI imaging signal [7]. The combination Gd³⁺ ion with lanthanide ions can exhibit sharp emissions *via* intra-configurational *f-f* or 4*f*-5*d* transitions and so are used in nanoprobes, sensor device, display device, fluorescence detection, *etc.* [8-10]. Thus, Gd₂O₃ phosphor exhibits both fluorescent and MRI label properties [11].

Many researchers reported about the synthesis and optical properties of Eu³⁺ and Tb³⁺ doped Gd₂O₃ phosphor prepared *via* combustion, sol-gel, hydrothermal techniques, *etc.* [12-15]. However, few researchers reported about Dy³⁺ doped Gd₂O₃

phosphor. Sheng *et al.* [16] prepared cylindrical Gd₂O₃: Dy³⁺, Tb³⁺, Eu³⁺ particle, studied the tunable multi-colour emission and energy transfer within the dopant ions. Sangwarantee *et al.* [17] prepared the white light emission of gadolinium calcium phosphate oxide and oxyfluoride glasses doped with Dy³⁺. Similarly, Han *et al.* [18] prepared Gd₂O₃: Dy³⁺ nanocrystals, dealt the spectroscopic properties of the prepared samples. Samata *et al.* [19] reported the synthesis of Gd_{0.98}Eu_{0.02-x}Tb_xOOH and Gd_{1-y-z}Dy_yBi_zOOH, studied their yellow luminescence properties by excitation with near-ultraviolet radiation.

Hence, the present study deals with the hydrothermal synthesis of Dy³⁺ doped Gd₂O₃ phosphor with different dopant ions concentrations. Depending upon the dopant ion concentrations of the prepared samples, sizes, concentration quenching effect, luminescence properties, decay times and colour coordinates were studied. The structural and morphological behaviour of the prepared samples were also well-studied.

EXPERIMENTAL

All chemicals were of analytical grade and used as received. Gadolinium oxide (Gd₂O₃, 99.9%, Sigma-Aldrich, USA) and dysprosium acetate hydrate Dy(CH₃COO)₃·xH₂O, 99.9%, Sigma -Aldrich, USA) were used as a source of Gd³⁺ and Dy³⁺ ions, respectively. Nitric acid, sodium hydroxide, acetone were

procured from Merck, India and double distilled water were used in the preparation.

Synthesis: $\text{Gd}_2\text{O}_3 \cdot x\text{Dy}^{3+}$ ($x = 1, 2, 3, 5, 7$) were successfully synthesized by hydrothermal method. In a typical preparation of 1 mol% Dy^{3+} doped Gd_2O_3 , 0.03 M of gadolinium oxide was dissolved in a minimum amount of conc. HNO_3 in 100 mL beaker. Evaporated at least three times by adding double distilled water to remove excess acid and then 40 mL of double distilled water was added. Then, 0.03 M of dysprosium acetate with 40 mL of water was added to another 100 mL beaker with constant stirring. Two reaction mixtures were mixed and stirred for 30 min at 300 rpm followed by the addition of NaOH solution dropwise to the reaction mixture with constant stirring till pH ~ 11 and then poured to the Teflon autoclave. The reaction mixture was carried out at 160°C by using Muffle furnace for 3 h. A white solid product of $\text{Gd}(\text{OH})_3 \cdot \text{Dy}^{3+}$ was then collected by centrifugation at around 12000 rpm and washed 3-4 times with double distilled water and finally acetone and then dried at 60°C . Subsequent dehydration of $\text{Gd}(\text{OH})_3 \cdot \text{Dy}^{3+}$ by heating at 700°C for 3 h to obtain $\text{Gd}_2\text{O}_3 \cdot \text{Dy}^{3+}$. The same process was repeated for all the samples.

RESULTS AND DISCUSSION

Structural and morphological studies: The phase purity and crystal structure of the prepared samples were analyzed by using Bruker D8 Advance X-ray diffractometer equipped with graphite monochromatized $\text{CuK}\alpha$ radiation ($\lambda = 0.15418$ nm) from 15° to 80° (2θ). Fig. 1 shows the XRD pattern of the prepared samples. All the peak patterns were well-matched with JCPDS card No. 86-2477, which could be indexed to the cubic phase with the space group $la\bar{3}$ (206). The peaks at 20.10° , 28.83° , 33.32° , 42.79° , 47.75° , 56.73° and 77.06° correspond to (2 1 1), (2 2 2), (4 0 0), (1 3 4), (4 4 0), (6 2 2) and (6 6 2) planes of cubic Gd_2O_3 , respectively. In all cases, sharp and strong diffraction peaks were found which indicates that the prepared samples possess a high crystallinity and also there is no extra phase found in the diffraction patterns. All the peaks were slightly shifted which means that the activator ions have been incorporated into the host matrix.

The morphological study was done by Transmission electron microscope (TEM), high resolution TEM (HRTEM) images and SAED pattern were taken from JEOL JEM-2100 TEM, operated at 200 kV. TEM images revealed that the prepared samples were found to be a nanorod and its diameter varies in the range of 15-30 nm with different lengths (Fig. 2). The SAED pattern of the prepared samples exhibit diffraction spots and ring which are associated to (4 0 0), (1 3 4) and (6 1 1) planes of Gd_2O_3 cubic phase. The lattice fringes in HRTEM image indicated that the prepared samples are highly crystalline. The measured space of lattice fringes of Gd_2O_3 : 1 mol% Dy^{3+} is 0.27 nm, which is accordance with interplanar distance of (4 0 0) plane of cubic phase, Gd_2O_3 , respectively.

Thermal studies: Thermogravimetric studies of 1 mol% Dy^{3+} doped Gd_2O_3 precursor shows the continuous weight loss steps A, B, C, and D as shown in Fig. 3. The first region A, ranges from 29°C to 130°C with the weight loss of 1.02% corresponding to the decomposition of water molecule. The second region

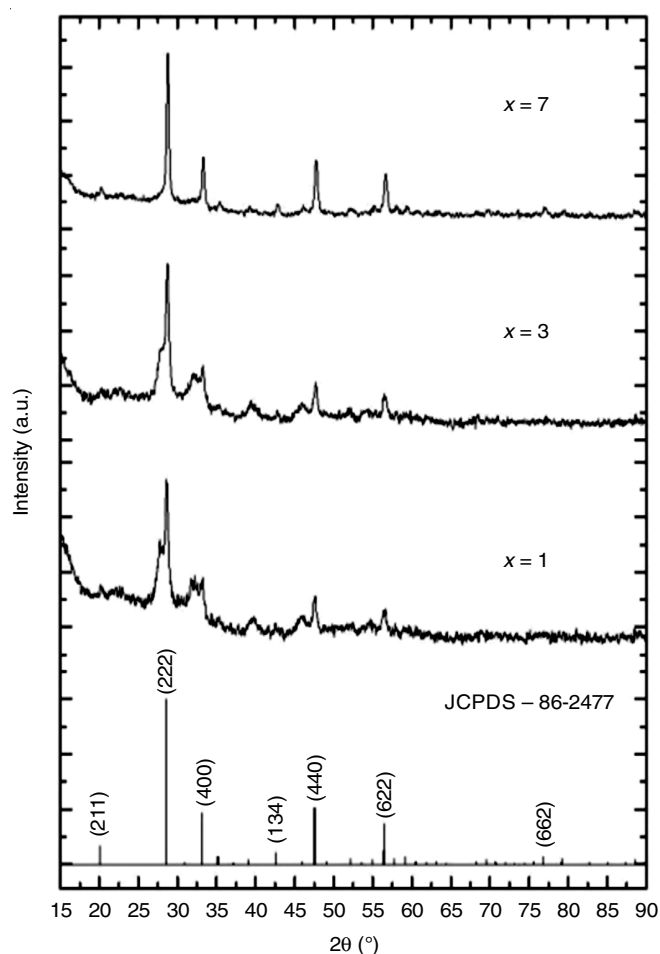


Fig. 1. XRD pattern of the Gd_2O_3 : x mol% Dy^{3+} ($x = 1, 3, 7$)

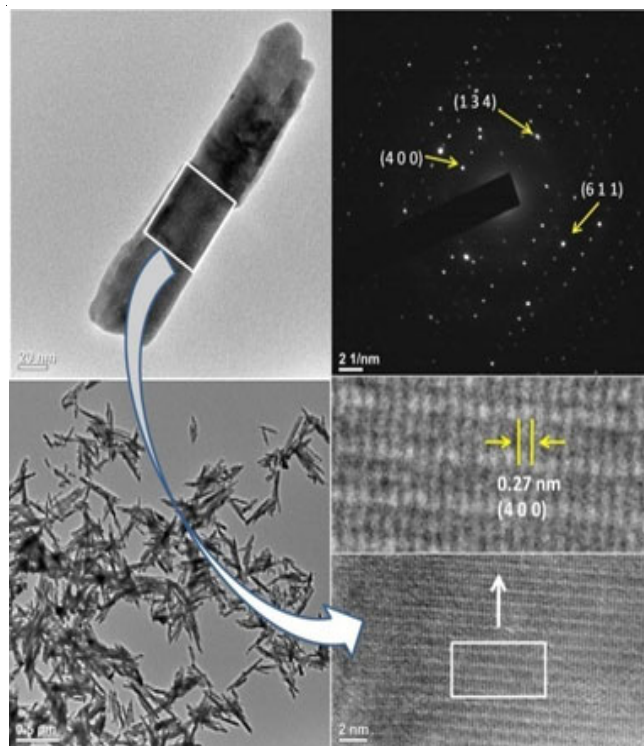


Fig. 2. TEM images, HRTEM images and SAED patterns of Gd_2O_3 : 1 mol% Dy^{3+}

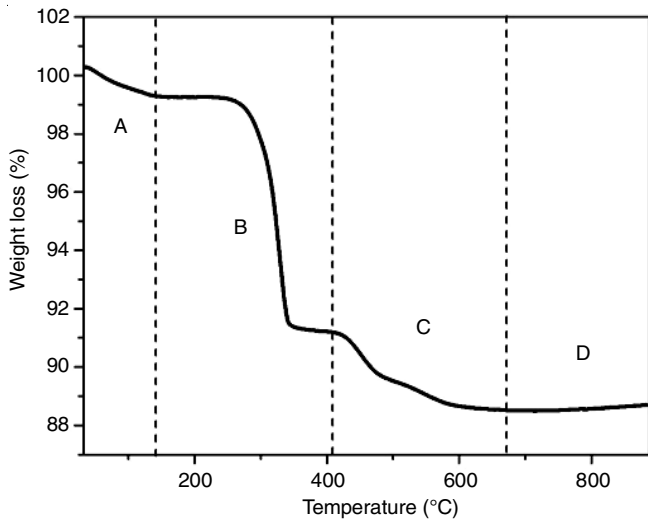


Fig. 3. TGA profile of 1 mol% Dy³⁺ doped Gd₂O₃

B, ranges from 130 °C to 410 °C with the weight loss of 8.03%, it is due the combustion of residual organic molecules. The third region C ranges from 410 °C to 650 °C with the weight loss of 2.68% corresponding to the oxidation of further residual organic molecules and water molecules and to form Gd₂O₃. The last region D, ranges from 650 °C to 900 °C, there is no appreciable weight loss which reveals that the complete formation of stable crystalline phase of Gd₂O₃. The weight loss percentage of the precursor is about 11.73% which accounts for the final Gd₂O₃ precursor.

Photoluminescence study: The excitation and emission spectra of all samples were carried out using a F7000 Hitachi spectrophotometer with xenon discharge lamp as the excitation source. Luminescence lifetime was taken by using μs flash lamp attached to F7000 Hitachi spectrophotometer. The excitation spectrum consists of several peaks. Among these peaks, the peak at 234 nm (⁸S_{7/2}→⁶D₁), 273 nm (⁸S_{7/2}→⁶I₁) and 310 nm (⁸S_{7/2}→⁶P₁) are originated from Gd₂O₃ host matrix (Fig. 4). It reveals that the excitation is mainly from Gd₂O₃ host lattice

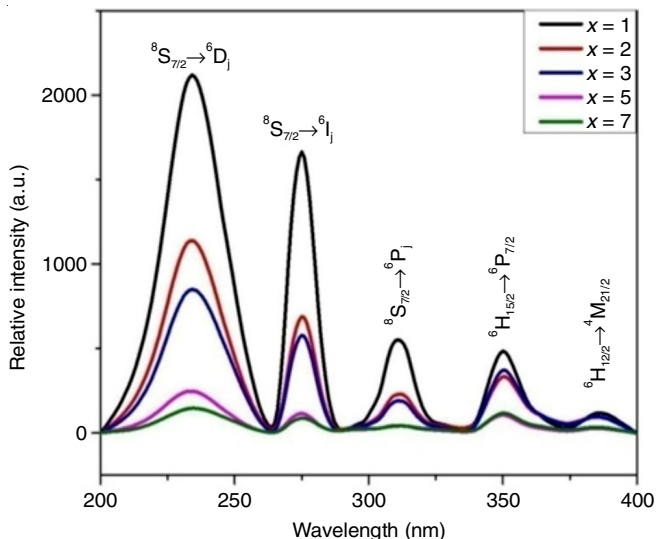


Fig. 4. Excitation spectra of Gd₂O₃: x mol% Dy³⁺, where, x = 1, 2, 3, 5, 7 (monitoring λ_{em} at 573 nm)

and it has higher energy than the excited state of ⁴F_{9/2} of Dy³⁺ ion. The other two peaks found at 350 nm and 386 nm are attributed to ⁶H_{15/2}→⁶P_{7/2} and ⁶H_{12/2}→⁴M_{21/2} transitions of Dy³⁺ ion, respectively [18,20-21]. Upon the excitation at 234 nm, the emission spectra consist of four peaks at 425 nm, 485 nm (blue), 573 nm (yellow) and 668 nm, which are ascribed to ⁴G_{11/2}→⁶H_{15/2}, ⁴F_{9/2}→⁶H_{15/2}, ⁴F_{9/2}→⁶H_{13/2} and ⁴F_{9/2}→⁶H_{11/2} transition of Dy³⁺ ion, respectively. The transition ⁴F_{9/2}→⁶H_{15/2}, originates due to the magnetic dipole transition (ΔJ = 1) which is independent on the local environment whereas the transition ⁴F_{9/2}→⁶H_{13/2} (dominated) are electric dipole transition (ΔJ = 2), which is hypersensitive to the structural environment and surrounding which shows that Dy³⁺ ions occupy the sites without inversion symmetry in the host lattice. Hence, Dy³⁺ doped Gd₂O₃ host lattice can also serve as a very efficient and sensitive structural probe [17,22,23].

The variation of relative intensity and asymmetric ratios with Dy³⁺ ions was compared by considering the area under emission band of Dy³⁺ ion, particularly at 486 nm and 573 nm. This was done by using Gaussian distribution,

$$I = I_B + \sum_{i=1}^n \frac{A_i}{w_i \sqrt{\frac{\pi}{2}}} e^{-\frac{(\lambda - \lambda_{ci})^2}{w_i^2}} \quad (1)$$

where, I is the intensity, I_B is the background intensity, w_i is the width at half-maximum intensity of curve, and A_i is the area under the curve, λ is the wavelength and λ_{ci} is the mean wavelength value corresponding to the transition. The curves are fitted in the ranges from 462 nm to 506 nm and 552 nm to 600 nm for ⁴F_{9/2}→⁶H_{15/2} and ⁴F_{9/2}→⁶H_{13/2} transitions, respectively. From the emission spectra, it is observed that emission intensity decreases with increase in Dy³⁺ ion concentration, it is due to the concentration quenching effect. As increase in Dy³⁺ ion concentration, the dipole-dipole interaction among the Dy³⁺ ion increase and thus cross-relaxation among Dy³⁺ ion occurs leading to quenching of luminescence intensity [24]. The optimum luminescence intensity is found at 1 mol% of Dy³⁺ ion doped Gd₂O₃. The asymmetry ratio shows the symmetry around the dopant ions in the host matrix. From Fig. 5b and d, the asymmetric ratio gradual decreases with increase of Dy³⁺ ion concentrations, which means that firstly the dopant ions are occupied at low symmetry locate site *i.e.* no inversion symmetry site upto 3 mol% of Dy³⁺ ion doped and then move towards the inversion symmetry locate site. This is responsible for the colour coordinate shifting from light yellow to light blue through white colour in the CIE chromaticity co-ordinate profile.

The luminescence decay time of the prepared samples were analyzed by using F-7000 Hitachi fluorescence spectrophotometer. All the decay curves of the prepared samples (Fig. 6) were well fitted using bi-exponential decay equation:

$$I = I_1 \exp^{-t/\tau_1} + I_2 \exp^{-t/\tau_2} \quad (2)$$

where, I₁ and I₂ are the luminescence intensities at different time intervals and τ₁ and τ₂ their corresponding lifetimes. The average decay lifetime values were calculated by using eqn. 3 and Table-1 gives the calculated average life time of Gd³⁺ in Gd₂O₃: xmol% Dy³⁺ (x = 1, 2, 3, 5, & 7).

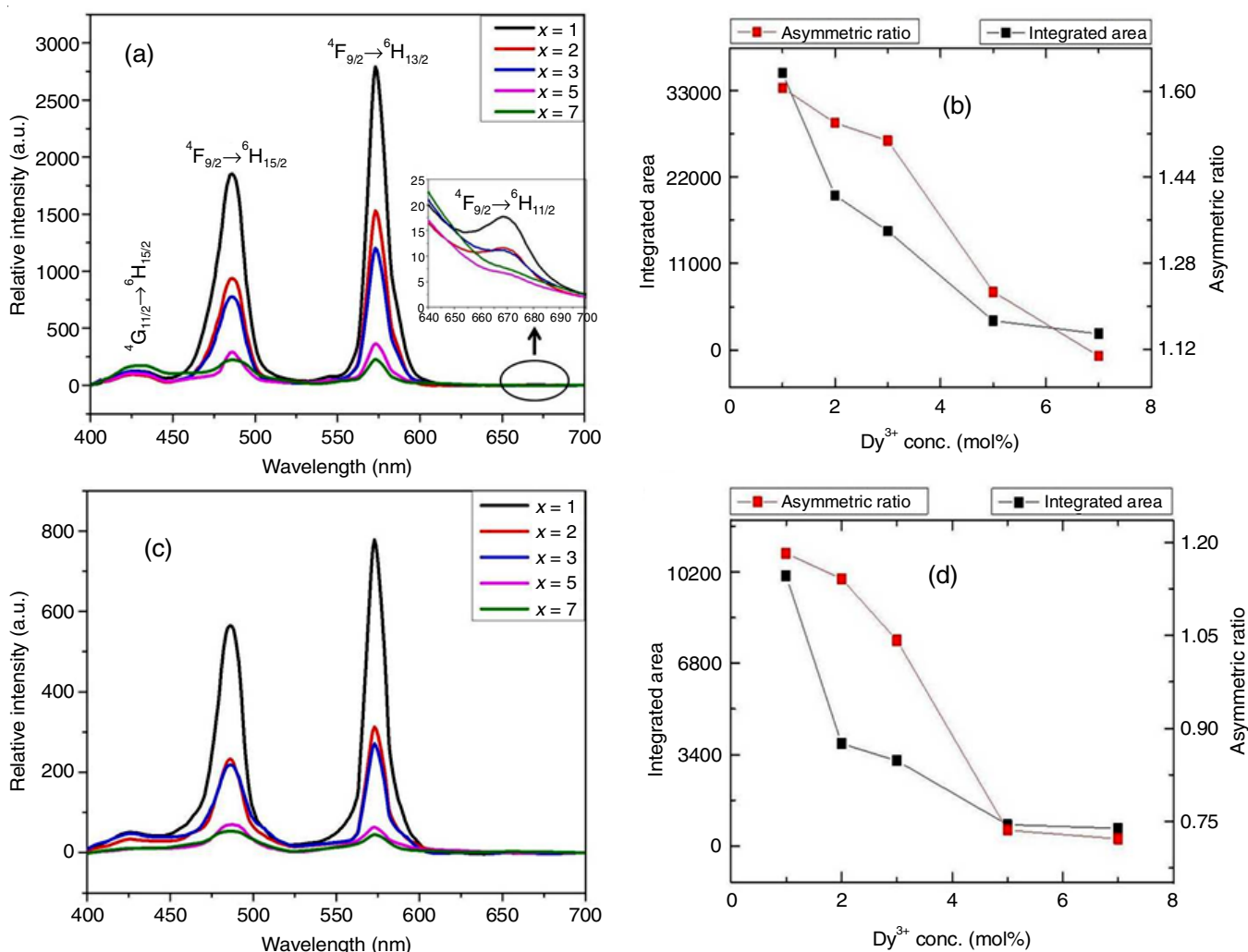


Fig. 5. (a&c) Emission spectra of $\text{Gd}_2\text{O}_3: x \text{ mol\% Dy}^{3+}$, where, $x = 1, 2, 3, 5, 7$ (monitoring λ_{ex} at 234 nm and 273 nm) and (b&d) variation of relative emission intensity and asymmetric ratios with Dy^{3+} ion concentrations, respectively

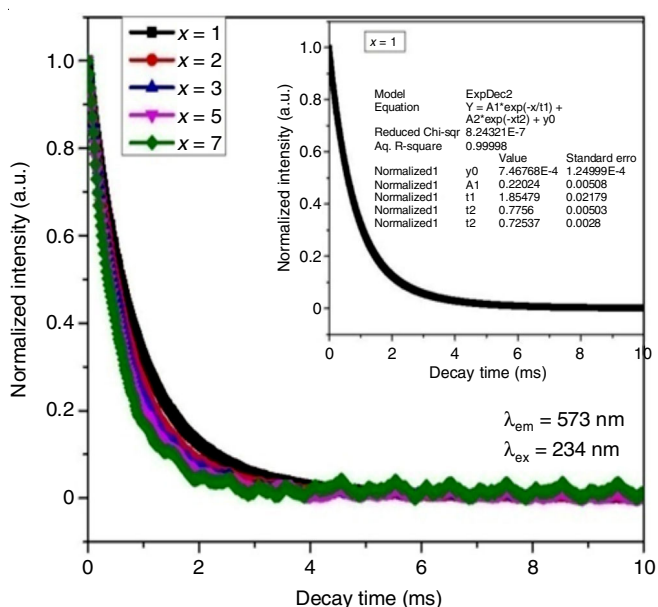


Fig. 6. Decay profile of $\text{Gd}_2\text{O}_3: x \text{ mol\% Dy}^{3+}$ where, $x = 1, 2, 3, 5, 7$ (inset shows the decay profile of 1 mol% Dy^{3+} doped Gd_2O_3 phosphor with its fitting parameter)

TABLE-1
CALCULATED DECAY LIFE TIME
OF THE PREPARED SAMPLES

| Dy^{3+} conc. (mol%) | R^2 value | Lifetime (ms) |
|-------------------------------|-------------|---------------------|
| 1 | 0.99998 | 1.200 ± 0.00012 |
| 2 | 0.99992 | 1.126 ± 0.00015 |
| 3 | 0.99948 | 0.965 ± 0.00024 |
| 5 | 0.99911 | 0.753 ± 0.00036 |
| 7 | 0.99705 | 0.599 ± 0.00046 |

$$\tau_{\text{av}} = \frac{I_1 \tau_1^2 + I_2 \tau_2^2}{I_1 \tau_1 + I_2 \tau_2} \quad (3)$$

With increase in Dy^{3+} ion concentration, the average life of Gd^{3+} ion decreases which reveals that the energy transfer occurs in between Gd^{3+} and Dy^{3+} ion. The schematic energy level diagram of the prepared sample is shown in Fig. 7. The CIE coordinates of $\text{Gd}_2\text{O}_3: x \text{ mol\% Dy}^{3+}$ where $x = 1, 2, 3, 5$ and 7 monitored λ_{ex} at 234 nm were found to be (0.33, 0.39), (0.32, 0.38), (0.30, 0.36), (0.27, 0.32), and (0.24, 0.24), respectively. This results clearly suggested that 1, 2, 3 mol% Dy^{3+} ion doped samples can be used as white light emitting phosphor (Fig. 8).

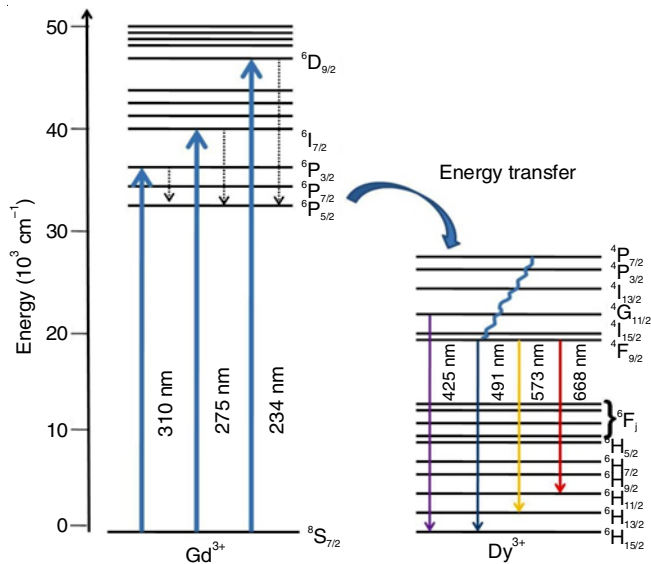


Fig. 7. Schematic energy level diagram showing the energy transfer between Gd³⁺ and Dy³⁺ ions in the host matrix

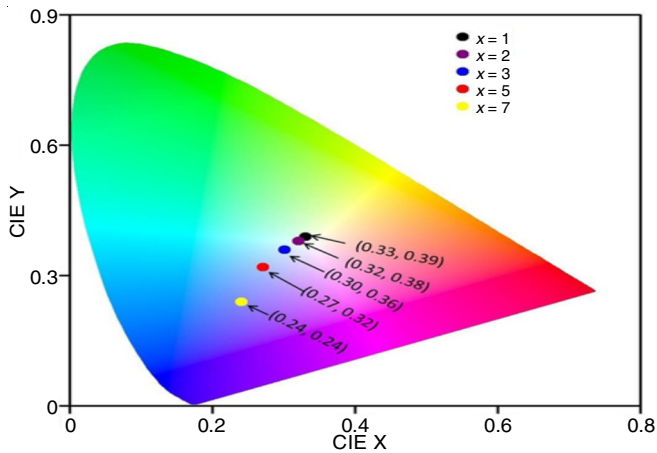


Fig. 8. CIE chromaticity diagram of Gd₂O₃: x mol% Dy³⁺ where, x = 1, 2, 3, 5, & 7

Conclusion

Dy³⁺ ion doped Gd₂O₃ phosphors with different concentrations were successfully synthesized by hydrothermal method. All the prepared samples were found to be cubic phase with the space group *la* $\bar{3}$ (206). The TEM and HRTEM images revealed the prepared samples were found to be a nanorod and its diameter varies in the range of 15-30 nm with different lengths. The luminescence studies indicated the highest luminescence intensity was found at 1 mol% Dy³⁺ doped Gd₂O₃ phosphor. The luminescent properties decreases gradually with increase in Dy³⁺ ions concentration and its decay life time are found in the range from 0.599 ms to 1.200 ms. The CIE Chromaticity coordinates showed the prepared samples could be used as a white light emitting phosphor applied in near UV region.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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