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 4f-electron layer with high spin magnetic moment, which interacts with water, it shorten 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 4f-5d 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 Gd0.98Eu0.02-xTbxOOH and Gd1-y-zDyzyBi2O3OH, 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 \( \text{Gd}_2\text{O}_3 \), 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 Gd(OH)\(_3\):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 Gd(OH)\(_3\):Dy\(^{3+}\) by heating at 700 °C for 3 h to obtain Gd\(_2\)O\(_3\):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 Cu\(\alpha\) radiation (\(\lambda = 0.15418\) nm) from 15° to 80° (2\(\theta\)). 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\(_2\)O\(_3\), respectively. In all cases, sharp and strong diffraction peaks were found which indicates that the prepared samples posses 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\(_2\)O\(_3\) cubic phase. The lattice fringes in HRTEM image indicated that the prepared samples are highly crystalline. The measured space of lattice fringes of Gd\(_2\)O\(_3\): 1 mol% Dy\(^{3+}\) is 0.27 nm, which is accordance with interplanar distance of (4 0 0) plane of cubic phase, Gd\(_2\)O\(_3\), respectively.

**Thermal studies:** Thermogravimetric studies of 1 mol% Dy\(^{3+}\) doped Gd\(_2\)O\(_3\) 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...
B, ranges from 130 °C to 410 °C with the weight loss of 8.03%, it is due to 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 ºC, 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 (8S7/2 → 6Dj), 273 nm (8S7/2 → 6Ij) and 310 nm (8S7/2 → 6Pj) are originated from Gd2O3 host matrix (Fig. 4). It reveals that the excitation is mainly from Gd2O3 host lattice and it has higher energy than the excited state of 4F9/2 of Dy3+ ion. The other two peaks found at 350 nm and 386 nm are attributed to 4H15/2 → 6Pj, 4H13/2 → 6Dj 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 4G11/2 → 6H13/2, 4F9/2 → 6H15/2, 4F9/2 → 6H15/2 and 4F9/2 → 6H13/2 transition of Dy3+ ion, respectively. The transition 4F9/2 → 6H15/2, originates due to the magnetic dipole transition (ΔJ = 1) which is independent on the local environment whereas the transition 4F9/2 → 6H13/2 (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,
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 label diagram of the prepared sample is shown in Fig. 7. The CIE coordinates of Gd\(_2\)O\(_3::\)xmol% Dy\(^{3+}\) where x = 1, 2, 3, 5 and 7 monitored \(\lambda_{ex}\) 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 label diagram showing the energy transfer between Gd$^{3+}$ and Dy$^{3+}$ ions in the host matrix

Fig. 8. CIE chromaticity diagram of Gd$_2$O$_3$:x mol% Dy$^{3+}$ where, x = 1, 2, 3, 5, & 7

Conclusion

Dy$^{3+}$ ion doped Gd$_2$O$_3$ phosphors with different concentrations were successfully synthesized by hydrothermal method. All the prepared samples were found to be cubic phase with the space group la3 (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% Dy$^{3+}$ doped Gd$_2$O$_3$ phosphor. The luminescent properties decreases gradually with increase in Dy$^{3+}$ 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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