Synthesis, characterization and photoluminescence properties of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ nanophosphors prepared by solution combustion method

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ABSTRACT

$\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ (0.5–8.0 mol%) nanophosphors have been prepared by low temperature solution combustion method using metal nitrates as oxidizers and oxalyl dihydrazide (ODH) as a fuel. The phosphors are well characterized by powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR) and photoluminescence (PL) techniques. PXRD patterns of as-formed and calcined (800 °C, 3 h) Gd_2O_3 powders exhibit monoclinic phase with mean crystallite sizes ranging from 20 to 50 nm. Eu^{3+} doping changes the structure from monoclinic to mixed phase of monoclinic and cubic. SEM micrographs shows the products are foamy, agglomerated and fluffy in nature due to the large amount of gases liberated during combustion reaction. Upon 254 nm excitation the photoluminescence of the $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ particles show red emission at 611 nm corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition. It is observed that PL intensity increases with calcination temperature. This might be attributed to better crystallization and eliminates the defects, which serve as centers of non-radiative relaxation for nanomaterials. It is observed that the optical energy gap (E_g) is widened with increase Eu^{3+} content.

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1. Introduction

During the last decade, much attention has been paid to nanomaterials due to their attractive electronic and optical properties. Among various nanomaterials, luminescent phosphors have been studied vigorously in recent years because of their significant properties that differ from the bulk [1]. Therefore, research on efficient and low cost phosphors is a challenging problem for new luminescence materials [2,3]. An extensive research has been carried out on different synthesis methods like solid state [4], co-precipitation [5], sol-gel [6,7], emulsion method [8], spray pyrolysis [9–11], chemical vapor deposition [12] and combustion to synthesize phosphors.

As a part of our programme on phosphor materials, in the present study, we attempt to synthesize Eu^{3+} doped Gd_2O_3 nanophosphors by a low temperature solution combustion method.

Gd_2O_3 is a useful host material because its crystallographic structure is similar to Y_2O_3 , a well known host lattice for efficient phosphors. Gadolinium is also a known contrast agent for magnetic resonance imaging (MRI) applications. Therefore, the rare-earth ion-doped Gd_2O_3 can be used for dual, MRI and fluorescence imaging applications [13–16].

Rare-earth sesquioxides have three different crystallographic structures: hexagonal, cubic and monoclinic phases. In cubic $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$, Eu^{3+} ions occupy two kinds of lattice sites (C_2 and S_6) after substituting the Gd^{3+} ions. In monoclinic Gd_2O_3 , the Eu^{3+} substitutes three nonequivalent sites of Cs symmetry [17]. Gd_2O_3 doped with Eu^{3+} exhibits strong UV absorption, which is useful in lamp and display applications [18,19]. Moreover, the typical narrow-band, long lifetime and large stokes shift of Eu^{3+} emission make the $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ a promising bio-fluorophore candidate in luminescence immunoassay [20,21]. Due to its wide and varied applications, we are interested in synthesizing Eu^{3+} doped Gd_2O_3 phosphors by a low temperature solution combustion method and studying the effect of temperature, doping on structure and luminescent properties. The prepared phosphors are well characterized by PXRD, SEM, FT-IR and optical and photoluminescence techniques.

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2. Experimental

2.1. Synthesis of Gd_2O_3 nano powders

The starting chemicals used for the preparation of $Gd_2O_3:Eu^{3+}$ nanophosphors were of Analar grade gadolinium nitrate [$Gd(NO_3)_3$] and europium nitrate [$Eu(NO_3)_3$]. The fuel oxalyl dihydrazide ODH ($C_2H_6N_4O_2$) is used for combustion synthesis and was prepared in our laboratory [22]. In the present study, an aqueous solution containing stoichiometric amounts of gadolinium nitrate and ODH (in the mole ratio 1:1.5) have been taken in a Petri dish of approximately 300 ml capacity. The excess water is allowed to evaporate by heating over a hot plate until a wet powder is left out. Then the Petri dish is introduced into a muffle furnace maintained at $500 \pm 10^\circ C$.

The reaction mixture undergoes thermal dehydration and ignites at one spot with liberation of gaseous products such as oxides of nitrogen and carbon. The combustion of ODH is exothermic and releases the energy required for the synthesis. The combustion reaction may be written as

The combustion propagates throughout the reaction mixture without further need of any external heating, as the heat of reaction is sufficient for the decomposition of redox mixture. The flame temperature was found to be $1000 \pm 50^\circ C$, which persists for few seconds, and was measured by a thermocouple placed inside the glass dish without touching the solution. Similarly the europium doped Gd_2O_3 phosphors have been prepared by adding a calculated quantity of $Eu(NO_3)_3$. This process lasted for about 5 min and results in voluminous powder.

2.2. Instruments used

The phase formation and crystallinity of the phosphors have been examined using a powder X-ray diffractometer (Siemens D5005) with $Cu K\alpha$ radiation and Ni filter. The surface morphology, and size distribution of the grains were examined on a JEOL (JSM-840A) scanning electron microscope (SEM). The FT-IR spectral studies have been performed on a Perkin Elmer Spectrometer (Spectrum 1000) with KBr pellets. The photoluminescence measurements were performed on a Shimadzu Spectrofluorometer (Model RF 510) equipped with 150 W xenon lamp as an excitation source. The emission spectra were studied using an excitation of 254 nm UV lamp.

3. Results and discussion

Fig. 1 shows the powder X-ray diffraction pattern of (a) as-formed and (b) calcined ($800^\circ C$, 3 h) Gd_2O_3 nanopowders both indexed to monoclinic structure and in good agreement with JCPDS file no. 43-1015. The diffraction intensity of the sample is increased with calcination temperature due to better crystallization. The sharp and intense peaks clearly show the crystalline nature of the sample. The crystallite size was calculated from the XRD pattern following the Scherer equation [23]

$$d = \frac{0.9\lambda}{\beta \cos \theta} \quad (2)$$

where d is the average grain size of the crystallites, λ the incident wavelength, θ the Bragg angle and β the diffracted full-width at half-maximum (FWHM) in radians caused by the crystallites.

Fig. 1. Powder X-ray diffraction pattern of Gd_2O_3 phosphors (a) as-formed and (b) calcined at $800^\circ C$ (3 h).

Fig. 2. Powder X-ray diffraction pattern of (a) as-formed Gd_2O_3 , (b) 0.5 mol% Eu^{3+} , (c) 1.0 mol% Eu^{3+} , (d) 4.0 mol% Eu^{3+} and (e) 8.0 mol% Eu^{3+} (*cubic phase) phosphors calcined at $800^\circ C$ (3 h).

The mean crystallite sizes thus calculated for the as-formed and calcined samples are found to be 20 and 50 nm, respectively.

For the complex matrix Gd_2O_3 , the Eu^{3+} ions substitute Gd^{3+} ions in the lattice, which make the structure change from monoclinic to mixed phase of monoclinic and cubic. In Fig. 2, XRD patterns of (a) as-formed Gd_2O_3 phosphor crystallize in the monoclinic structure similar to the reported in JCPDF card no. 43-1015. The lattice parameters are in good agreement with the reported value having the lattice parameters $a=14.081(\text{\AA})$, $b=3.556(\text{\AA})$, $c=8.779(\text{\AA})$. On increasing Eu^{3+} content, the monoclinic phase transforms to the cubic like phase. In Fig. 2(d), the intense lines correspond to the cubic phase of Gd_2O_3 (2 2 2), (4 0 0), (4 4 0) and (6 2 2). No extra peaks are (due to Eu addition) observed in XRD pattern since the amount of dopant is very less and there is no shift in XRD peaks because of the similar atomic radii of Eu (1.01 $\text{\AA}$) and Gd (1.00 $\text{\AA}$). However the photoluminescence study on Eu^{3+} doped Gd_2O_3 phosphors showed an increase in PL intensity with increase in the

Fig. 3. Powder X-ray diffraction pattern of Gd_2O_3 : 0.5 mol% Eu^{3+} phosphor calcined at (a) 800 °C, (b) 1000 °C and (c) 1200 °C.

concentration of Eu^{3+} ion; this implies the Eu^{3+} incorporation within the Gd_2O_3 structure. It is observed that as the Eu ion concentration increases, the ratio of the peak values, $I_C(2\ 2\ 2)/I_M(4\ 0\ 2)$ increased from 0.27 to 1.12. Bae et al. [24] have observed the ratio of the peak values $I_C(2\ 2\ 2)/I_M(4\ 0\ 2)$ increased from 1.96 to 2.48 in a mixture of cubic and monoclinic phases in $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ thin film phosphors with increased pressure from 100 to 200 m Torr.

Fig. 3 shows the PXRD patterns of Eu^{3+} (0.5 mol%) doped Gd_2O_3 with different calcination temperatures (800–1200 °C). It is observed that the intensity of the PXRD peaks increases with calcination temperature. It is noticed that the ratio of peak values, $I_C(2\ 2\ 2)/I_M(1\ 1\ 1)$, increased from 0.62 to 0.944 with increase in calcination temperature from 800 to 1200 °C.

For the combustion method, it is well known that the morphological characteristics of the prepared powders are strongly dependent on the heat and gases generated during the complex decomposition. Large amount of gases are suitable for preparation of tiny particles while the heat released is an important factor for crystal growth. Fig. 4 shows the SEM photographs of as-prepared and 4 mol% Eu^{3+} doped Gd_2O_3 . The as-prepared phosphors are agglomerated from few microns to a few tens of microns, fluffy and porous in nature. The agglomeration of nanoparticles is usually explained as a common way to minimize their surface free energy. The voids and pores present in the sample are due to the large amount of gases produced during combustion synthesis [25].

Fig. 5 shows the FT-IR spectra of as-formed, Eu^{3+} doped (0.5 and 4.0 mol%) Gd_2O_3 phosphor calcined at 800 °C for 3 h. The peak at 3416 cm^{-1} for as-formed sample is due to $-\text{OH}$ vibration. A decrease of the band at 3416 cm^{-1} in doped samples with calcination temperature can be attributed to the release of water molecules trapped inside the solid matrix. The peaks at around 400 and 540 cm^{-1} are due to stretching vibrations of the Gd–O bond [26].

Fig. 6 shows the emission spectra of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ phosphor calcined at 800 °C (3 h), when excited with 254 nm. The emission spectra of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ (0.5–8.0 mol%) phosphor consist of sharp lines ranging from 525 to 650 nm, which are associated with the transitions from the excited $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($j=0, 1, 2$ and 3) state of Eu^{3+} ions [27]. In the emission spectra, the peaks at 611 and 586 nm are assigned to $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transitions of the

Fig. 4. SEM micrographs of Gd_2O_3 phosphor calcined at 800 °C, 3 h (a) undoped and (b) 4.0 mol% Eu^{3+} doped samples.

Fig. 5. FT-IR spectra of Gd_2O_3 phosphor calcined at 800 °C (3 h) (a) undoped, (b) 0.5 mol% Eu^{3+} and (c) 4.0 mol% Eu^{3+} doped samples.

Fig. 6. PL spectra of Gd_2O_3 phosphor calcined at 800°C . 3 h (a) undoped, (b) 0.5 mol% Eu^{3+} , (c) 1.0 mol% Eu^{3+} , (d) 4.0 mol% Eu^{3+} and (e) 8.0 mol% Eu^{3+} doped samples.

Eu^{3+} ions, respectively. It denotes that Eu^{3+} ions occupy the Gd^{3+} sites with C_2 or S_6 symmetry. The emissions from $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_1 \rightarrow ^7\text{F}_2$ are detected at 535 and 555 nm, respectively. In all of the transitions, the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions are of particular interest because they represent the local environment of Eu^{3+} ion. The $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition is magnetic-dipole allowed and its intensity shows very little variation with the crystal field strength surrounding the Eu^{3+} ions. The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ hypersensitive transition obeys the selection rule ($\Delta J=2$), is electric-dipole allowed and its intensity is sensitive to the local structure acting on the Eu^{3+} ion [28,29]. It is observed that the PL intensity increases with increase of Eu content (0.5–8.0 mol %). Further, it is observed that the PL intensity is improved, as a result of an increase in the number of luminescent centers. If the Eu^{3+} activator concentration exceeds a certain threshold concentration (4 mol% in the present study), the PL intensity generated by excess Eu^{3+} ions is reduced (Fig. 7). Since the excitation transitions by resonant energy transfer among activators are very efficient, they reduce the PL intensity by transferring the absorbed energy to quenching centers that exist on the surface of the phosphor particles.

Furthermore, it is also clear that the luminescence intensity strongly depends on the calcination temperatures (Fig. 8). It was observed that the PL intensity of the $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ increased calcinations up to 1200°C and beyond this there was no observable change in the PL intensity. This is mainly due to the improvement in doping, good activation and high crystallinity.

The emission intensity of the sample depends strongly on the temperature (Fig. 8), since the higher temperature would lead to large particles and better crystallization and would help to eliminate defects, which can serve as centers of non-radiative relaxation for nanomaterials. The excitation spectra of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ phosphor having different Eu^{3+} (0.5–8 mol%) concentration for 611 nm emission were studied. It is observed that a broadband with a maxima at 254 nm corresponds to $\text{O}^{2-} \rightarrow \text{Eu}^{3+}$ charge transfer (CT) band. The weak lines observed at 278 and 310 nm are related to internal Gd^{3+} f–f transitions, which are possible to detect due to $\text{Gd}^{3+} \rightarrow \text{Eu}^{3+}$ energy transfer.

Fig. 9 shows the UV–vis absorption spectra of un-doped and Eu^{3+} doped (4 mol %) phosphor measured by using UV–vis diffuse reflectance. An intense absorption band at 265–275 nm is

Fig. 7. The variation of PL intensity for 611 nm emission, as a function of Eu^{3+} content in Gd_2O_3 matrix.

Fig. 8. PL spectra of Gd_2O_3 : 0.5 mol% Eu^{3+} phosphor calcined at (a) 800°C (b) 1000°C and (c) 1200°C .

observed. The optical energy gaps E_g of commercial, as-prepared un-doped and as-prepared un-doped but calcined at 800°C were calculated using the Tauc relation [30]:

$$\alpha(h\nu) \sim (h\nu - E_g)^{1/n} \quad (3)$$

where $h\nu$ is the photon energy and α is the optical absorption coefficient near the fundamental absorption edge. The absorption coefficient α was calculated from these optical absorption spectra. The values of the optical band gap energy are obtained by plotting $(\alpha h\nu)^n$ vs $h\nu$ in the high absorption range followed by extrapolating the linear region of the plots to $(\alpha h\nu)^n = 0$ (not shown in the figure). The analysis of the present data showed that the plots of $(\alpha h\nu)^n$ against $h\nu$ give linear relations, which are most

Fig. 9. UV-vis absorption spectra of Gd_2O_3 (a) commercial, (b) as-formed and (c) 4 mol% Eu^{3+} doped phosphor.

fitted for the above equation with $n=2$ for both un-doped and Eu doped samples. This indicates that the allowed direct transition is responsible for the interband transitions in un-doped and doped samples. The optical energy band gaps for commercial, as-prepared un-doped and as-prepared un-doped calcined at 800°C are found to be 5.10, 5.26 and 5.53 eV respectively. These values are in good agreement with those reported in the literature [31]. It is observed that the band gap is less commercial when compared to as-prepared Eu undoped and calcined Gd_2O_3 sample.

4. Conclusions

$\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ powder phosphors have been successfully prepared by a low temperature solution combustion method from a mixed solution of rare-earth nitrates and ODH. X-ray diffraction pattern reveals that the undoped sample is in pure cubic phase whereas Eu doped samples are in mixed phase of monoclinic and cubic. The as-prepared $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ phosphors are agglomerated and have a fluffy, fine and porous morphology. The PL emission peak centered at $\sim 611\text{ nm}$ is due to $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} ions. In the PL spectra, the concentration of Eu has a significant effect on the luminescence efficiency, and the highest luminescence efficiency was obtained for 4.0 mol% Eu^{3+} . The PL peak intensity increases with increase in calcination temperature. This might be due to the improved lattice imperfection. Broad band excitation and high luminescence efficiency in the red region indicate that this powder is a potential candidate for use in phosphor industry. The band gap is more in the nanocrystalline

Gd_2O_3 compared to the commercial one and it is also found that the band gap increases when calcined.

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