

Effect of Synthesis Conditions on the Photoluminescent Properties of Eu Doped Gadolinium Oxide Phosphors



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1 Introduction

Rare-earth activated phosphors have appealing applications in the optoelectronic and display devices as their emission spectra is sharp, intense, and narrow. The emission properties depend on various factors among which host lattice and dopant play a vital role. Rare-earth (RE) oxides are the promising host matrices. Among the various RE-oxides, Gd_2O_3 is an appropriate host matrix for the europium (Eu) ions [1–4]. This is for the reason that ionic radii of europium ions are close to gadolinium ions and both the elements have same valency [5–7].

$Gd_2O_3:Eu$ is a bi-probe as it can show paramagnetic as well as luminescent behavior. These properties make it useful in potential applications such as optoelectronic devices and biomedical applications. It exhibits sharp, narrow, and intense emission bands under UV excitation. Till now, synthesis of $Gd_2O_3:Eu$ has been reported by various routes. Among the various methods, co-precipitation route is a promising chemical method for the synthesis of pure cubic Gd_2O_3 phosphors. Earlier reports showed that cubic phase $Gd_2O_3:Eu$ has improved luminescent characteristics as compared to monoclinic crystal phase [8–10].

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In the present work, we have synthesized $\text{Gd}_2\text{O}_3:4\text{mol\%Eu}$ phosphors by co-precipitation route with the variation of temperature and pH during synthesis. The synthesized phosphors are characterized by various techniques.

2 Materials and Methods

Starting precursors such as gadolinium nitrate hexahydrate (99.99%), and europium nitrate hexahydrate (99.99%) have been purchased from Alfa Aesar. Ammonia solution (25 wt%,) and ethanol (99.9%) were used as solvents and acquired from Loba Chemie Pvt. Limited. Synthesis process involves the dissolution of stoichiometric quantities of gadolinium as well as europium precursors for the preparation of 0.1 M. To this solution, pH at 8 and 10 was maintained through dropwise addition of ammonia solution. The solution was aged for 24 h, centrifuged followed by water and ethanol washing using Whatman filter paper. After drying at 60 °C, precipitates were heat treated for 4 h at 800 °C in the programmed muffle furnace followed by grinding (to form uniform powder) to use for various characterizations respectively.

3 Characterization Techniques

X-ray diffraction (XRD) diffractograms were obtained with the help of XRD diffractometer (Panalytical X'Pert Pro) in the range from 10° to 80° with a step interval of 0.0131° at normal scan rate. Exstar TG/DTA 6300 was used to obtain thermographs corresponding to different samples in nitrogen environment. The heating rate was set to 10 °C/min. Field-emission scanning electron microscopic (FESEM) images were taken at operating voltage of 20 kV using Carl Zeiss FESEM. The emission spectrums of different phosphors were acquired with the help of Xenon lamp incorporated fluorescence spectrophotometer (Agilent Technologies- Model Cary Eclipse).

4 Results and Discussion

4.1 XRD Results

Figure 1a, b represents the XRD diffractograms of as-prepared precipitates at pH 8 and 10. All XRD peaks resemble to the standard ICDD card (01-083-2037) of $\text{Gd}(\text{OH})_3$ phase having hexagonal crystal structure. The space group symmetry of characterized sample is P63/m. Matching of all the diffraction peaks indicates the high purity of $\text{Gd}(\text{OH})_3$. High crystallinity of $\text{Gd}(\text{OH})_3$ phase is confirmed from sharp as well as intense diffraction peaks. Depending upon TG results, the obtained

samples are calcined at 800 °C to ensure the complete crystallization into the oxide phase.

XRD patterns of Gd_2O_3 prepared at pH 8 and 10 after calcining $Gd(OH)_3$ at 800 °C are presented in Fig. 2a, b. After careful investigation, diffraction patterns have been matched through standard ICDD card 03-065-3181, confirmed the establishment of pure Gd_2O_3 phase with BCC crystal structure having Ia-3 (206) group symmetry. Absence of impurity peak(s) due to $Gd(OH)_3$ infers the Gd_2O_3 single phase formation. Further, high crystallinity of prepared Gd_2O_3 was revealed from sharp as well as intense diffraction peaks. This shows that hydroxides are completely converted into oxides.

Fig. 1 Diffraction patterns of samples synthesized at **a** pH = 8, and **b** pH = 10, respectively

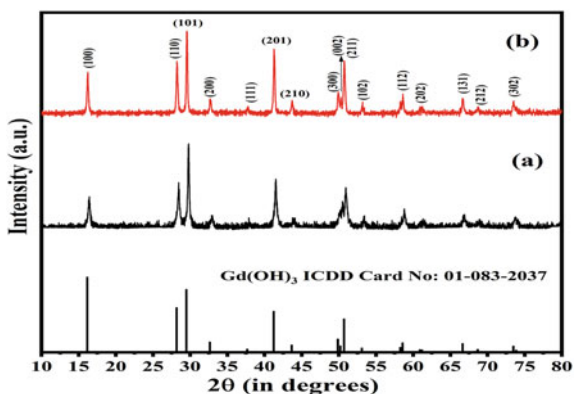
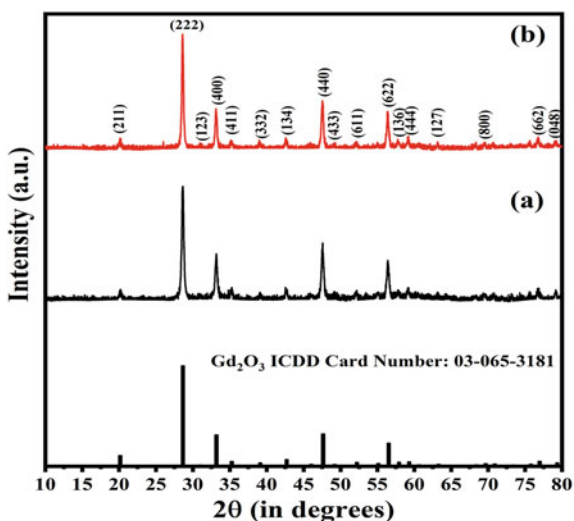
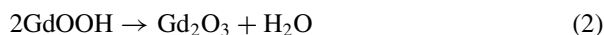
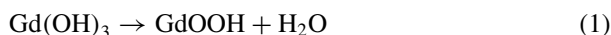


Fig. 2 XRD patterns of Gd_2O_3 calcinated samples synthesized at **a** pH = 8, and **b** pH = 10



4.2 Thermal Behavior of As-Synthesized Samples

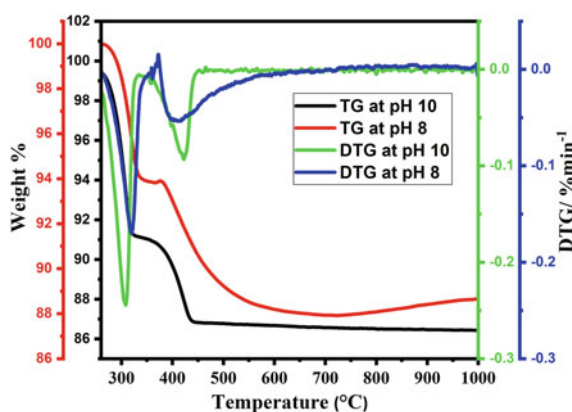
The thermal behavior of prepared $\text{Gd}(\text{OH})_3$ powders at different pH values are analyzed via TG/DTG curves, as shown in Fig. 3. The TG curves represent two stages at which weight loss can be clearly seen. The sample synthesized at pH 8 shows different weight loss stages around 323.24 and 410.81 °C, respectively. The weight losses corresponding to these temperatures are ~6.08 and ~6.71%, respectively. However, in the case of sample synthesized at pH 10, weight losses are observed at 306.21, and 419.41 °C, and the corresponding weight losses are ~8.95 and ~4.11%, respectively. The variation in the temperature and weight losses in the TG curves indicates the formation of intermediate products during calcination. In literature, it is reported that lanthanide hydroxides have the LnOOH phase as an intermediate product when dehydration of $\text{Ln}(\text{OH})_3$ takes place [11]. Based on this, dehydration of the synthesized $\text{Gd}(\text{OH})_3$ is considered to following dehydration steps:



The total experimental weight loss for $\text{Gd}(\text{OH})_3$ prepared at pH = 8 and 10 is 12.79% and 13.1%, respectively. These experimentally determined values are very close to the theoretical value of weight loss of $\text{Gd}(\text{OH})_3$, i.e. 12.97% [12, 13].

The micrographs of $\text{Gd}_2\text{O}_3:4\text{mol}\%\text{Eu}$ calcined at 800 °C and synthesized at pH (8 and 10) are shown in Fig. 4a, b. Samples prepared at pH 8 do not have particular morphology, as shown in Fig. 4a. The sample consists of irregular shape particles having rod-like features. The length of the rods is found to be in the range 200–400 nm and diameter around 90–150 nm. The average size of the particles lies in the range 55–90 nm. However, samples synthesized at pH 10 (Fig. 4b) have uniform

Fig. 3 TG/DTG curves of as-prepared samples at pH 8 and 10



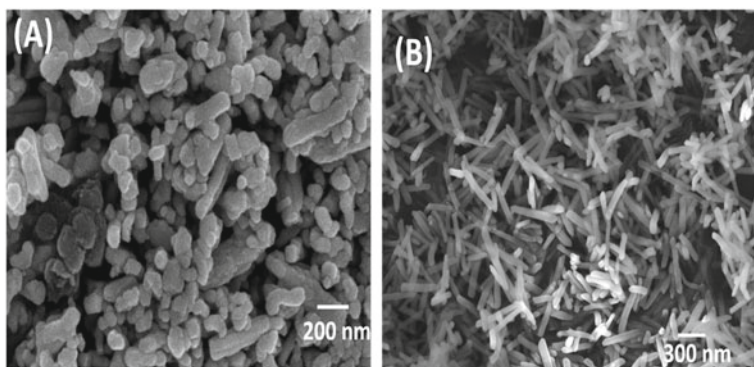


Fig. 4 FESEM micrographs of $\text{Gd}_2\text{O}_3:4 \text{ mol}\% \text{Eu}$ phosphors obtained at **a** pH 8 and **b** pH 10

rod-like morphology with nano dimensions. The rod-like morphology is related to the self or induced scrolling mechanism [14]. The diameter of the rods is found in the range 70–120 nm, and the length around 200–500 nm.

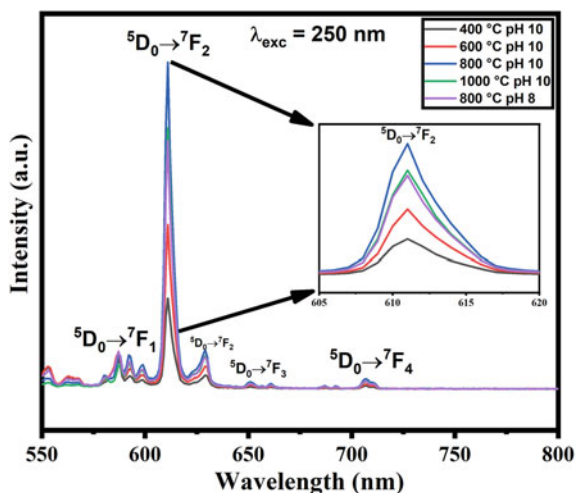
4.3 Photoluminescence Results

The effect of pH as well as calcination temperature on luminescent characteristics of $\text{Gd}_2\text{O}_3:4 \text{ mol}\%$ is also investigated. Emission spectra of $\text{Gd}_2\text{O}_3:4 \text{ mol}\%$ with respect to pH and calcination temperature are shown in Fig. 5. The obtained spectrums comprise sharp, intense, and narrow emission peaks. Emission bands observed at approximately 592, 612, 625, 650, and 705 nm correspond to europium ion transitions, i.e., ${}^5\text{D}_0 \rightarrow {}^7\text{F}_{1,2,3,4}$ respectively [15]. Among all the peaks, the peak observed at 612 nm (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$) has the highest intensity, which is hypersensitive and dominant emission transition.

Cubic Gd_2O_3 exhibits two symmetry sites, i.e., C_2 and S_6 , having 3:1 ratio respectively. From which non-inversion symmetry is possessed C_2 symmetry sites whereas inversion symmetry is occupied by S_6 symmetry sites. As soon as europium occupies S_6 sites, peak corresponding to the 592 nm dominates. The emission peak at 612 nm dominates if europium ions occupy C_2 sites in Gd_2O_3 lattice [16].

Figure 5 also cleared that PL emission increases with rise in calcination temperature and is found maximum at 800 °C. Further increase in calcination temperature, i.e., 800 °C beyond leads to decrease in the PL intensity due to enlargement of non-radiative transitions. On the other hand, emission intensity is observed maximum at pH 10 compared to the sample synthesized at pH 8. The fall in PL intensity at low pH is attributed to the non-uniform morphology, irregular shapes, and agglomeration observed in the samples. The maximum PL is obtained for the sample, which is synthesized at pH 10, and calcined at 800 °C.

Fig. 5 PL emission spectra of $\text{Gd}_2\text{O}_3:4 \text{ mol\%Eu}$ phosphors synthesized at different pH and temperature values



5 Conclusion

The uniform shape, phase pure, and crystalline $\text{Gd}_2\text{O}_3:4 \text{ mol\%Eu}$ samples were synthesized via co-precipitation route. XRD patterns confirmed the cubic phase of Gd_2O_3 samples. FESEM results revealed the rod type morphology of the samples synthesized at pH 10, while mixed particle and rod-like morphology was obtained at pH 8. Moreover, PL emission intensity was found higher for samples prepared at pH 10, which is due to the uniform morphology of the samples. Moreover, with increase in temperature, PL intensity was found to increase and was maximum for samples calcined at 800 °C.

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