Hydrothermal synthesis, characterization and Raman studies of Eu^{3+} activated Gd_2O_3 nanorods

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ABSTRACT

Eu^{3+} (8 mol%) activated gadolinium oxide nanorods have been prepared by hydrothermal method without and with surfactant, cetyl trimethyl ammonium bromide (CTAB). Powder X-ray diffraction (PXRD) studies reveal that the as-formed product is in hexagonal $\text{Gd}(\text{OH})_3:\text{Eu}$ phase and subsequent heat treatment at 350 and 600 °C transforms the sample to monoclinic $\text{GdOOH}:\text{Eu}$ and cubic $\text{Gd}_2\text{O}_3:\text{Eu}$ phases, respectively. The structural data and refinement parameters for cubic $\text{Gd}_2\text{O}_3:\text{Eu}$ nanorods were calculated by the Rietveld refinement. SEM and TEM micrographs show that as-obtained $\text{Gd}(\text{OH})_3:\text{Eu}$ consists of uniform nanorods in high yield with uniform diameters of about 15 nm and lengths of about 50–150 nm. The temperature dependent morphological evolution of $\text{Gd}_2\text{O}_3:\text{Eu}$ without and with CTAB surfactant was studied. FTIR studies reveal that CTAB surfactant plays an important role in converting cubic $\text{Gd}_2\text{O}_3:\text{Eu}$ to hexagonal $\text{Gd}(\text{OH})_3:\text{Eu}$. The strong and intense Raman peak at 489 cm^{-1} has been assigned to A_g mode, which is attributed to the hexagonal phase of Gd_2O_3 . The peak at $\sim 360\text{ cm}^{-1}$ has been assigned to the combination of F_g and E_g modes, which is mainly attributed to the cubic Gd_2O_3 phase. The shift in frequency and broadening of the Raman modes have been attributed to the decrease in crystallite dimension to the nanometer scale as a result of phonon confinement.

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1. Introduction

The research on efficient and inexpensive nanophosphors is a challenging problem for new luminescence materials [1–3]. The nanostructures such as nanospheres, nanorods, nanotubes and nanowires are of great interest due to their fundamental and technological importance [4,5]. As a part of our program on nanomaterials we are interested to synthesize and study the various properties of nano-structured materials. More recently [6,7] rare-earth oxide compounds such as Nd_2O_3 , Dy_2O_3 , Eu_2O_3 , Y_2O_3 , etc. and hydroxide compounds such as $\text{Y}(\text{OH})_3$, $\text{Dy}(\text{OH})_3$, $\text{Eu}(\text{OH})_3$, $\text{Tb}(\text{OH})_3$, etc. have been widely used as high-performance luminescent devices, catalysts and other functional materials based on the electronic, optical and chemical characteristics arising from their 4f electrons. Gd_2O_3 is a useful host material because its crystallographic structure is similar to that of Y_2O_3 , a

well-known host lattice for efficient phosphors. 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 C_s symmetry [8].

In the present study, Eu activated $\text{Gd}(\text{OH})_3$, GdOOH and Gd_2O_3 nanorods have been synthesized using the hydrothermal method without and with surfactant cetyl trimethyl ammonium bromide (CTAB). The phase dependent properties have been examined systematically by means of various spectroscopic techniques such as powder X-ray diffraction (PXRD), morphological (SEM and TEM), FTIR and Raman spectroscopies and the results are discussed in detail.

2. Experimental

2.1. Synthesis of Eu activated $\text{Gd}(\text{OH})_3$, GdOOH and Gd_2O_3 nanorods

All the chemical reagents used in the present experiments were obtained from commercial sources. In a typical synthesis, the

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stoichiometric amounts of Gd_2O_3 and Eu_2O_3 (2.51 g (6.9 mmol) of Gd_2O_3 and 0.10 g (0.29 mmol) of Eu_2O_3) were dissolved in 1:1 HNO_3 . A clear solution was obtained by uniform stirring and thereafter the solution is heated on the sand bath to evaporate excess HNO_3 . The aqueous KOH (1.0 N) solution was added into the mixture until the pH of solution was adjusted to be around 12. The resulting colloidal mixture was put into a Teflon-lined stainless steel autoclave with a capacity of 60 mL. The autoclave was then sealed and maintained at 120 °C for 18 h and thereafter naturally cooled to room temperature. A white solid product of $\text{Gd}(\text{OH})_3\text{:Eu}$ was collected by filtration and washed several times with distilled water and ethyl alcohol and then dried at 80 °C. Subsequent dehydration of $\text{Gd}(\text{OH})_3\text{:Eu}$ by heat treatment at 350 and 600 °C for 3 h results in monoclinic $\text{GdOOH}\text{:Eu}$ and cubic $\text{Gd}_2\text{O}_3\text{:Eu}$, respectively. Further the effect of CTAB (1 mol%) surfactant on each phase was studied by maintaining similar synthesis conditions (120 °C for 18 h) as well as heat treatments.

Cetyl trimethyl ammonium bromide (CTAB) is a cationic surfactant and it plays a key role in controlling the growth and production of Gd_2O_3 nanorods. The growth process of Gd_2O_3 in the presence of CTAB is different; the surface tension of solution is reduced to the existence of surfactant, which lowers the energy needed for the formation of a new phase. CTAB is an ionic compound, which ionizes completely in water. The resultant CTA^+ is a positively charged tetrahedron with a long hydrophobic tail; the resulting cation is also a tetrahedron with a long hydrophobic tail [9]. Therefore, ion pairs between gadolinium hydroxide anion and CTA^+ could form due to electrostatic interaction [9]. In the crystallization process, surfactant molecules adsorbed on the crystal nuclei serve not only as a growth director but also as a protector to prevent from aggregation of the product. As a result, Gd_2O_3 nanorods were produced.

2.2. Instruments used

A powder X-ray diffractometer (Siemen's D5005) using CuK_α radiation with Ni filter was used to estimate the crystallinity of the phases. The recorded powder XRD patterns were used to estimate the lattice parameters using the Fullproff program [10]. The surface morphology of the samples was studied using scanning electron microscopy (JEOL JSM 840A) by sputtering technique with gold as the covering contrast material. For Transmission Electron Microscope (TEM) analysis, Hitachi H-8100 (accelerating voltage up to 200 kV, LaB6 filament) equipped with EDS (Kevex Sigma TM Quasar, USA) was used. The FTIR studies have been performed on a Perkin Elmer Spectrometer (Spectrum 1000) with KBr pellets. Raman spectroscopic studies were performed using a Renishaw In-via Raman spectrometer equipped with a CCD (charge coupled device) with 633 nm (He–Cd laser power set at 30 mW) and a Leica DMLM optical microscope equipped with 50× objective, thus providing a laser spot of 2 μm in diameter.

3. Results and discussion

Fig. 1 shows the powder X-ray diffraction patterns (PXRD) of $\text{Gd}(\text{OH})_3\text{:Eu}$, $\text{GdOOH}\text{:Eu}$ and $\text{Gd}_2\text{O}_3\text{:Eu}$ samples prepared without CTAB. The diffraction peaks (Fig. 1(a)) can be indexed as hexagonal $\text{Gd}(\text{OH})_3$ with space group $P6_3/m$ and lattice constants $a=b=0.63$ nm and $c=0.36$ nm (JCPDS Card No. 83-2037) [11]. No impurity peaks were observed demonstrating a high purity of the final product. The product calcined at 350 °C for 3 h was not able to fit the JCPDS cards within the GdOOH system, indicating that a mixed phase was obtained. Since most of the lanthanide compounds have the form of MOOH, this unidentified phase was assumed to have the composition of GdOOH . The dehydration

Fig. 1. PXRD patterns of $\text{Gd}(\text{OH})_3\text{:Eu}$ prepared (without CTAB) (a) as-formed (b) calcined at 350 °C and (c) calcined at 600 °C for 3 h.

process therefore was assumed to be

On calcination at 600 °C for 3 h, it transforms to cubic $\text{Gd}_2\text{O}_3\text{:Eu}$, which is in good agreement with that of JCPDS Card No. 86-2477. Fig. 1(c) shows the X-ray diffraction pattern of cubic $\text{Gd}_2\text{O}_3\text{:Eu}$ observed in the present study. The dehydration process can therefore be written as

The results are in good agreement and well reported in the literature [12].

Jia et al. [12] synthesized highly uniform $\text{Gd}(\text{OH})_3$ and $\text{Gd}_2\text{O}_3\text{:Eu}^{3+}$ nanotubes by wet chemical route without any surfactant. Uniform nanorods of $\text{Gd}(\text{OH})_3$ with diameter of ~40 nm and length of 200–300 nm were observed. After calcinations at 600 °C, $\text{Gd}(\text{OH})_3$ hexagonal phase was converted to cubic phase without achieving intermediate monoclinic GdOOH phase.

Fig. 2 shows the effect of CTAB surfactant (1 mol%) on hexagonal $\text{Gd}(\text{OH})_3\text{:Eu}$, monoclinic $\text{GdOOH}\text{:Eu}$ and cubic $\text{Gd}_2\text{O}_3\text{:Eu}$ was studied by maintaining 120 °C for 18 h. No change is observed in hexagonal and monoclinic phases, whereas cubic phase transforms into hexagonal $\text{Gd}(\text{OH})_3\text{:Eu}$ phase. Further, we studied the effect of CTAB surfactant and hydrothermal temperature on cubic $\text{Gd}_2\text{O}_3\text{:Eu}$ obtained by without CTAB. It is observed cubic $\text{Gd}_2\text{O}_3\text{:Eu}$ transform to hexagonal $\text{Gd}(\text{OH})_3\text{:Eu}$ for all the temperatures, and find no change in intensity of PXRD profiles and results are depicted in Fig. 3. It was observed that the particle size does not vary much in the studied range. The structural data and refinement parameter for cubic $\text{Gd}_2\text{O}_3\text{:Eu}$ nanorods were calculated by Rietveld refinement of the experimental powder XRD pattern (Fig. 1c) as given in Table 1. Fig. 4 shows the cubic crystal structure for the above refined data. The values are in good agreement with those in the reported literature [13].

Fig. 5(a), (b) and (c) shows SEM micrographs of $\text{Gd}(\text{OH})_3\text{:Eu}$, $\text{GdOOH}\text{:Eu}$ and $\text{Gd}_2\text{O}_3\text{:Eu}$ phases, respectively, maintained at 120 °C for 18 h. It can be seen from the micrographs that the particles are fused and agglomerated. However, when CTAB was added to the respective phases (Fig. 5(d–f)) agglomeration was almost retained in $\text{Gd}(\text{OH})_3\text{:Eu}$ phase. For other two phases, less agglomeration with more irregular shape and tapered end nanorods was observed.

The temperature dependent (120–210 °C for 18 h) morphological evolution of $\text{Gd}_2\text{O}_3\text{:Eu}$ with CTAB was investigated by SEM and the images are shown in Fig. 6(a–d). The nanorods of irregular shape, branching with sharp tips, have been observed. As the temperature is raised to 180 °C for 18 h, nanorods of smooth and uniform diameter with varying lengths from 100 to 150 nm have been obtained. In this condition sharp edges are almost completely

decomposed. With further increase in temperature to 210 °C for 18 h the nanorods obtained were non-uniform and irregular in shape. In the present investigation hydrothermal temperature of 180 °C for 18 h is more suitable to obtain the smooth uniform nanorods.

Fig. 7 shows the typical TEM image of the $\text{Gd}(\text{OH})_3\text{:Eu}$ Phosphors without CTAB. The $\text{Gd}(\text{OH})_3\text{:Eu}$ nanorods exhibit relatively straight, smooth and uniform diameter of about 15 nm and lengths varying from 50 to 150 nm. The inset of Fig. 7 shows the selected area diffraction (SAED) pattern of the nanorods, which indicates that the nanorods are well crystallized. The nominal composition of $\text{Gd}(\text{OH})_3\text{:Eu}$ phase was analyzed using energy dispersive X-ray spectroscopy (EDX) as shown in Fig. 8 (inset shows the elemental percentage).

Fig. 9(a) shows the FTIR spectra of $\text{Gd}(\text{OH})_3\text{:Eu}$ without CTAB. The spectrum shows the absorption peaks of H_2O at 3410 cm^{-1} and OH groups at 703 and 3616 cm^{-1} . The CO_3^{2-} anion groups were observed at 1374 and 1586 cm^{-1} , which indicate that the precursor may be hydroxyl carbonate. In GdOOH:Eu (Fig. 9(b)) phase, the absorption peaks of H_2O at 3410 cm^{-1} and the CO_3^{2-} anion groups at 1498 , 1383 , 847 and 694 cm^{-1} are shown [14,15]. Fig. 9(c) shows the strong absorption peak near 540 cm^{-1} , which is associated with the vibration of the $\text{Gd}-\text{O}$ bond and the absorption peaks of H_2O at 3410 cm^{-1} . The CO_3^{2-} anion group was found at 1489 cm^{-1} . Fig. 10(a) and (b) shows the FTIR spectra of $\text{Gd}(\text{OH})_3\text{:Eu}$ and GdOOH:Eu with CTAB, respectively. It is noted that there is no change in the $\text{Gd}(\text{OH})_3\text{:Eu}$ and GdOOH:Eu phases after CTAB surfactant was added. Further, it is observed that CTAB surfactant plays an important role in converting cubic $\text{Gd}_2\text{O}_3\text{:Eu}$ to hexagonal $\text{Gd}(\text{OH})_3\text{:Eu}$ (Fig. 10(c)). The effect of temperature on $\text{Gd}_2\text{O}_3\text{:Eu}$ phase with CTAB surfactant (Fig. 11(a)–(d)) shows no

Fig. 2. PXRD patterns of $\text{Gd}(\text{OH})_3\text{:Eu}$ prepared (with CTAB) (a) as-prepared (b) calcined at 350 °C and (c) calcined at 600 °C for 3 h.

Fig. 3. PXRD patterns of hexagonal $\text{Gd}(\text{OH})_3\text{:Eu}$ phases obtained from cubic $\text{Gd}_2\text{O}_3\text{:Eu}$ (with CTAB) at (a) 120 °C , (b) 150 °C , (c) 180 °C and (d) 210 °C for 18 h.

Fig. 4. PXRD pattern of $\text{Gd}_2\text{O}_3\text{:Eu}$ nanorods prepared by without CTAB along with a Rietveld refined fit.

Table 1

Rietveld refined structural parameters for cubic $\text{Gd}_2\text{O}_3\text{:Eu}^{3+}$ nanorods synthesized by the hydrothermal method without CTAB.

Atoms	Oxidation state	Wyckoff notation	x	y	z	occupancy
Gd1/Eu1	+3	8b	0.250	0.250	0.250	1
Gd2/Eu2	+3	24d	−0.027(6)	0.000	0.250	1
O1	−2	48e	0.395(4)	0.169(4)	0.414(3)	1
O2	−2	16c	0.380(9)	0.380(9)	0.380(9)	1

Crystal system: cubic; space group: I_{a3} (no. 206). Lattice parameters: $a=10.816(7)\text{ Å}$; cell volume: $V=1265.41(9)\text{ Å}^3$. R_{factors} : $R_p=0.173$, $R_{\text{wp}}=0.229$, $R_{\text{Bragg}}=0.12$ and $R_F=0.112$.

Fig. 5. SEM micrographs of (a) $\text{Gd}(\text{OH})_3\text{:Eu}$, (b) GdOOH:Eu and (c) $\text{Gd}_2\text{O}_3\text{:Eu}$ prepared without CTAB and (d) $\text{Gd}(\text{OH})_3\text{:Eu}$, (e) GdOOH:Eu and (f) $\text{Gd}_2\text{O}_3\text{:Eu}$ prepared with CTAB for 18 h.

Fig. 6. SEM micrographs of hexagonal $\text{Gd}(\text{OH})_3\text{:Eu}$ phases obtained from cubic $\text{Gd}_2\text{O}_3\text{:Eu}$ (with CTAB) at (a) 120 °C, (b) 150 °C, (c) 180 °C and (d) 210 °C for 18 h.

Fig. 7. (a) TEM images of $\text{Gd}(\text{OH})_3\text{:Eu}$ nanorods. (b) SAED patterns of the $\text{Gd}(\text{OH})_3\text{:Eu}$ nanorods.

Fig. 8. EDX image of $\text{Gd}(\text{OH})_3\text{:Eu}$. The inset shows the elemental percentage of $\text{Gd}(\text{OH})_3\text{:Eu}$ nanorods.

change in peak positions except that the CO_3^{2-} group vanishes when the temperature is increased from 120 to 210 °C.

Fig. 12(a) and (b) shows the Raman spectra of hexagonal $\text{Gd}(\text{OH})_3\text{:Eu}$ and cubic $\text{Gd}_2\text{O}_3\text{:Eu}$ nanorods recorded at room temperature with an excitation wavelength of 633 nm He–Cd laser. Raman spectroscopy is a potential tool for characterizing materials because it is an in situ and non-destructive method. Well defined Raman peaks (Fig. 12(a)) were observed at ~ 137 , 308, 389 and 489 cm^{-1} . The strong and intense peak at 489 cm^{-1} has been assigned as the A_g mode, which is attributed as the hexagonal B-type structure of Gd_2O_3 [16]. The peak at $\sim 360\text{ cm}^{-1}$ (Fig. 12(b)) has been assigned to the combination of F_g and E_g modes and this peak is mainly attributed to the cubic C-type Gd_2O_3 structure [17]. These peaks are in good agreement with those reported in the literature [7].

Fig. 9. FTIR spectra of $\text{Gd}(\text{OH})_3\text{:Eu}$ prepared (without CTAB) (a) as-prepared, (b) calcined at 350 °C and (c) calcined at 600 °C for 3 h.

Fig. 10. FTIR spectra of the $\text{Gd}(\text{OH})_3\text{:Eu}$ prepared (with CTAB) (a) as-prepared, (b) calcined at 350 °C and (c) calcined at 600 °C for 3 h.

Geo Rajan and Gopchandran [17] studied the micro-Raman spectrum of $\text{Gd}_2\text{O}_3\text{:Eu}^{3+}$ thin films under 633 nm and observed two Raman peaks at 358 and 463 cm^{-1} . The major peak at 358 cm^{-1} has been assigned to $F_g + E_g$ mode with C-type Gd_2O_3 structure and space group I_{a3} . The strong and intense Raman peak at 463 cm^{-1} has been assigned to A_g mode and is attributed to monoclinic B-type Gd_2O_3 structure. Dilawar et al. [7] studied the Raman measurements of various commercially available spectroscopic grade rare-earth sesquioxides. They observed four Raman peaks at ~ 307 , 364, 421 and 468 cm^{-1} in C-type Gd_2O_3 structure. According to the factor group theory investigations [18], 22 Raman modes have been predicted for the C-type bixbyite structures rare-earth sesquioxides. These are expected to be 4 A_g , 4 E_g and 14 F_g Raman active modes. In the present study, there is a shift in the frequency of Raman peaks of $\sim 10\text{ cm}^{-1}$; this can be attributed to the decrease in crystallite dimension to the nanometer scale. This can cause the frequency shift and broadening of Raman peaks as a result of phonon confinement.

Fig. 11. FTIR spectra of $\text{Gd}_2\text{O}_3:\text{Eu}$ prepared (with CTAB) at (a) 120 °C, (b) 150 °C, (c) 180 °C and (d) 210 °C.

Fig. 12. Raman spectra of $\text{Gd}(\text{OH})_3:\text{Eu}$ prepared (without CTAB) (a) as-prepared and (b) calcined at 600 °C for 3 h.

4. Conclusions

We present a hydrothermal method for the preparation of various phases of Eu^{3+} activated Gd_2O_3 nanorods without and with

CTAB surfactant. The as-formed product has hexagonal $\text{Gd}(\text{OH})_3:\text{Eu}$ phase. Subsequent heat treatment at 350 and 600 °C produced monoclinic $\text{GdOOH}:\text{Eu}$ and cubic $\text{Gd}_2\text{O}_3:\text{Eu}$ phases, respectively. SEM and TEM micrographs indicate that the as-obtained $\text{Gd}(\text{OH})_3:\text{Eu}$ product entirely consists of uniform nanorods in high yield with uniform diameters of about 15 nm and lengths of 50–150 nm. It is observed that the temperature at 180 °C for 18 h is more suitable to obtain the smooth uniform nanorods. The strong and intense Raman peak at 489 cm^{-1} has been assigned to A_g mode, which is attributed to the hexagonal phase of $\text{Gd}_2\text{O}_3:\text{Eu}$. The peak at $\sim 360\text{ cm}^{-1}$ has been assigned to the combination of F_g and E_g modes, which is mainly attributed to the cubic Gd_2O_3 phase. It is observed that the shift in frequency and broadening of Raman modes could be attributed to the decrease in crystallite dimension to the nanometer scale as a result of phonon confinement.

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References

- [1] M.J. Weber, J. Lumin. 100 (2002) 35.
- [2] D.W. Cooke, B.L. Bennett, R.E. Muenchausen, J.K. Lee, M.A. Nastasi, J. Lumin. 106 (2004) 125.
- [3] E. Zych, C. Brecher, A. Lempicki, Spectrochim. Acta A 54 (1998) 1763.
- [4] A.M. Rao, E. Richter, S. Bandow, Science 275 (1997) 187.
- [5] G. Adachi, N. Imanaka, Chem. Rev. 98 (1998) 1479.
- [6] N. Zhang, R. Yi, Z. Wang, R. Shi, H. Wang, G. Qiu, X. Liu, Mater. Chem. Phys. 111 (2008) 13.
- [7] Shalini Mehrotra Nita Dilawar, D. Varandani, B.V. Kumaraswamy, S.K. Haldar, A.K. Bandyopadhyay, Mater. Charact. 59 (2008) 462.
- [8] J. Dexpert Ghys, M. Faucher, P. Caro, Phys. Rev. B 23 (1981) 607.
- [9] X.M. Sun, X. Chen, Z.X. Deng, Y.D. Li, Mater. Chem. Phys. 78 (2002) 99.
- [10] D.B. Wiles, R.A. Young, J. Appl. Crystallogr. 14 (1981) 149.
- [11] Chengkang Chang, Fumiko Kimura, Tsunehisa Kimura, Hitoshi Wada, Mater. Lett. 59 (2005) 1037.
- [12] Guang Jia, Kai Liu, Yuhua Zheng, Yanhua Song, Mei Yang, Hongpeng You, J. Phys. Chem. C 113 (2009) 6050.
- [13] V. Grover, S.N. Achary, A.K. Tyagi, J. Appl. Crystallogr. 36 (2003) 1082.
- [14] A.M. Pires, M.R. Davolos, E.B. Stucchi, J. Inorg. Mater. 3 (2001) 785.
- [15] G. Liu, G. Hong, J. Wang, X. Dong, J. Alloys. Compd. 432 (2007) 200.
- [16] C. Le Luyer, A. Garcia-Murillo, E. Bernstein, J. Mugnier, J. Raman Spectrosc. 34 (2003) 234.
- [17] Geo Rajan, K.G. Gopchandran, Appl. Surf. Sci. 255 (2009) 9112.
- [18] W.B. White, V.G. Keramidas, Spectrochim. Acta A 28 (1972) 501.