Hydrothermal synthesis, characterization and Raman studies of Eu$^{3+}$ activated Gd$_2$O$_3$ nanorods

N. Dhananjaya a,b, H. Nagabhushana c, B.M. Nagabhushana d, B. Rudraswamy a, C. Shivakumara a,e, R.P.S. Chakradhar f,1,*

a Department of Physics, J.B. Campus, Bangalore University, Bangalore 560 056, India
b Department of Physics, B.M.S. Institute of Technology, Bangalore - 560 064
c Department of PG studies & Research in Physics, University Science College, Tumkur University, Tumkur-572 103, India
d Department of Chemistry, M.S. Ramaiah Institute of Technology, Bangalore - 560 054, India
e Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore - 560 012, India
f Glass Technology Lab, Central Glass and Ceramic Research Institute (CSIR), Kolkata - 700031, India

ARTICLE INFO

Available online 14 October 2010

Keywords:
Hydrothermal synthesis
Nanorods
Gd$_2$O$_3$:Eu
XRD
SEM
TEM
FTIR
Raman

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$_2$O$_3$, Dy$_2$O$_3$, Eu$_2$O$_3$, Y$_2$O$_3$, etc. and hydroxide compounds such as Y(OH)$_3$, Dy(OH)$_3$, Eu(OH)$_3$, Tb(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$_2$O$_3$ is a useful host material because its crystallographic structure is similar to that of Y$_2$O$_3$, a well-known host lattice for efficient phosphors. Rare-earth sesquioxides have three different crystallographic structures: hexagonal, cubic and monoclinic phases. In cubic Gd$_2$O$_3$:Eu$^{3+}$, Eu$^{3+}$ ions occupy two kinds of lattice sites (C and S) after substituting the Gd$^{3+}$ ions. In monoclinic Gd$_2$O$_3$, the Eu$^{3+}$ substitutes three nonequivalent sites of Cs symmetry [8].

In the present study, Eu activated Gd(OH)$_3$, GdOOH and Gd$_2$O$_3$ 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 Gd(OH)$_3$, GdOOH and Gd$_2$O$_3$ nanorods

All the chemical reagents used in the present experiments were obtained from commercial sources. In a typical synthesis, the
stochiometric amounts of Gd₂O₃ and Eu₂O₃ (2.51 g (6.9 mmol) of Gd₂O₃ and 0.10 g (0.29 mmol) of Eu₂O₃) were dissolved in 1:1 HNO₃. A clear solution was obtained by uniform stirring and thereafter the solution is heated on the sand bath to evaporate excess HNO₃. 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 Gd(OH)₃:Eu was collected by filtration and washed several times with distilled water and ethyl alcohol and then dried at 80 °C. Subsequent dehydration of Gd(OH)₃:Eu by heat treatment at 350 and 600 °C for 3 h results in monoclinic GdOOH:Eu and cubic Gd₂O₃: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 Gd₂O₃ nanorods. The growth process of Gd₂O₃ 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, Gd₂O₃ nanorods were produced.

2.2. Instruments used

A powder X-ray diffractometer (Siemen’s D500S) using CuKα 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 Fullprof program [10]. The surface morphology of the samples was studied using scanning electron microscopy (JEOL JSM 840A) by sputtering technique with gold as a coating 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 (HeCd 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 Gd(OH)₃:Eu, GdOOH:Eu and Gd₂O₃:Eu samples prepared without CTAB. The diffraction peaks (Fig. 1(a)) can be indexed as hexagonal Gd(OH)₃ with space group P 6\text{3} \text{m} and lattice constants \(a=0.63 \text{ nm and } c=0.36 \text{ nm} \) (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 process therefore was assumed to be

\[
\text{Gd(OH)}_3: \text{Eu} \leftrightarrow \text{GdOOH}: \text{Eu} + \text{H}_2\text{O}
\]

On calcination at 600 °C for 3 h, it transforms to cubic Gd₂O₃: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 Gd₂O₃:Eu observed in the present study. The dehydration process can therefore be written as

\[
2\text{GdOOH}: \text{Eu} \leftrightarrow \text{Gd}_2\text{O}_3: \text{Eu} + \text{H}_2\text{O}
\]

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

Jia et al. [12] synthesized highly uniform Gd(OH)₃ and Gd₂O₃:Eu²⁺ nanotubes by wet chemical route without any surfactant. Uniform nanorods of Gd(OH)₃ with diameter of ~40 nm and length of 200–300 nm were observed. After calcinations at 600 °C, Gd(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 Gd(OH)₃:Eu, monoclinic GdOOH:Eu and cubic Gd₂O₃:Eu was studied by maintaining 120 °C for 18 h. No change is observed in hexagonal and monoclinic phases, where as cubic phase transforms into hexagonal Gd(OH)₃:Eu phase. Further, we studied the effect of CTAB surfactant and hydrothermal temperature on cubic Gd₂O₃:Eu obtained by without CTAB. It is observed cubic Gd₂O₃:Eu transforms to hexagonal Gd(OH)₃:Eu for all the temperatures, and find no change in intensity of PXRD profiles and results are dipicted 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 Gd₂O₃:Eu nanorods were calculated by Rietveld refinement of the experimental powder XRD pattern (Fig. 1(c)) 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 Gd(OH)₃:Eu, GdOOH:Eu and Gd₂O₃: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 Gd(OH)₃: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 Gd$_2$O$_3$: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 Gd(OH)$_3$:Eu Phosphors without CTAB. The Gd(OH)$_3$: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 Gd(OH)$_3$: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 Gd(OH)$_3$:Eu without CTAB. The spectrum shows the absorption peaks of H$_2$O 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$_2$O 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 Gd – O bond and the absorption peaks of H$_2$O 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 Gd(OH)$_3$:Eu and GdOOH:Eu with CTAB, respectively. It is noted that there is no change in the Gd(OH)$_3$:Eu and GdOOH:Eu phases after CTAB surfactant was added. Further, it is observed that CTAB surfactant plays an important role in converting cubic Gd$_2$O$_3$:Eu to hexagonal Gd(OH)$_3$:Eu (Fig. 10(c)). The effect of temperature on Gd$_2$O$_3$:Eu phase with CTAB surfactant (Fig. 11(a)–(d)) shows no significant change.

---

Table 1

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

Crystal system: cubic; space group: Ia3 (no. 206). Lattice parameters: \(a=10.816(7)\) Å; cell volume: \(V=1265.41(9)\) Å$^3$. \(R_{text{factor}}=0.173\), \(R_{wp}=0.229\), \(R_{text{merge}}=0.12\) and \(R_{I}=0.112\).
Fig. 5. SEM micrographs of (a) Gd(OH)$_3$:Eu, (b) GdOOH:Eu and (c) Gd$_2$O$_3$:Eu prepared without CTAB and (d) Gd(OH)$_3$:Eu, (e) GdOOH:Eu and (f) Gd$_2$O$_3$:Eu prepared with CTAB for 18 h.

Fig. 6. SEM micrographs of hexagonal Gd(OH)$_3$:Eu phases obtained from cubic Gd$_2$O$_3$:Eu (with CTAB) at (a) 120 °C, (b) 150 °C, (c) 180 °C and (d) 210 °C for 18 h.
change in peak positions except that the $\text{CO}_3^{2-}$ group vanishes when the temperature is increased from 120 to 210 °C.

**Fig. 12** (a) and (b) shows the Raman spectra of hexagonal Gd(OH)$_3$:Eu and cubic Gd$_2$O$_3$: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$_2$O$_3$ [16]. The peak at $\sim$ 360 cm$^{-1}$ (Fig. 12(b)) has been assigned to the combination of $E_g$ and $F_g$ modes and this peak is mainly attributed to the cubic C-type Gd$_2$O$_3$ structure [17]. These peaks are in good agreement with those reported in the literature [7].

Geo Rajan and Gopchandran [17] studied the micro-Raman spectrum of Gd$_2$O$_3$: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$_2$O$_3$ structure and space group Ia$_3$. 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$_2$O$_3$ structure. Dilawar et al. [7] studied the Raman measurements of various commercially available spectroscopic grade rare-earth sesquioxides. They observed four Raman peaks at $\sim$ 307, 364, 421 and 468 cm$^{-1}$ in C-type Gd$_2$O$_3$ 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 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.
4. Conclusions

We present a hydrothermal method for the preparation of various phases of Eu$^{3+}$ activated Gd$_2$O$_3$ nanorods without and with CTAB surfactant. The as-formed product has hexagonal Gd(OH)$_3$:Eu phase. Subsequent heat treatment at 350 and 600 °C produced monoclinic GdOOH:Eu and cubic Gd$_2$O$_3$:Eu phases, respectively. SEM and TEM micrographs indicate that the as-obtained Gd(OH)$_3$: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 Gd$_2$O$_3$:Eu. The peak at ~360 cm$^{-1}$ has been assigned to the combination of $F_g$ and $E_g$ modes, which is mainly attributed to the cubic Gd$_2$O$_3$ 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.

Acknowledgments

The authors are grateful to TEQIP Laboratory of M.S. Ramaiah Institute of Technology, Bangalore, for providing the facilities for preparation of materials. One of the authors N.D acknowledges Management, Principal and HOD, B.M.S. Institute of Technology, Bangalore for the support and encouragement.

References