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Synthesis and Studies of Optical Properties of Eu^{3+} Doped Gd_2O_3 Phosphor Prepared via Hydrothermal Process

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ABSTRACT

Eu^{3+} ion doped Gd_2O_3 phosphors with varying concentrations were synthesized successfully by hydrothermal process. The XRD pattern of prepared samples was in good agreement with cubic system of pure Gd_2O_3 (JCPDS No. 86-2477) with no extra phase. The TEM and HRTEM images also revealed the prepared samples are highly crystalline nanorods having the diameter in the range of 20 – 30 nm with different length. Vibrational modes are also studied using FT-IR Spectroscopy. Upon the emission at λ_{em} = 612 nm, a broad absorption band observed around at 220 – 300 nm is due to overlap of O^{2-} to Eu^{3+} charge transfer (CT) band, Gd^{3+} to Eu^{3+} CT band and host lattice absorption band and other weak bands observed at longer wavelength regions are attributed to the f-f transitions of the Eu^{3+} ions. In the emission spectrum obtained by excitations at 258 nm, consists of the characteristic transition lines between Eu^{3+} levels. The emission spectrum was dominated by the red $^5D_0 \rightarrow {}^7F_1$ (612 nm) transition of the Eu^{3+} ion which is an electric-dipole allowed transition and hypersensitive to the environment. The photoluminescence lifetime of the prepared samples are found to be 2.88 – 1.24 ms ranges.

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Introduction

In recent few years, rare-earth doped inorganic materials have been widely used as luminescent devices, catalysts, display devices and optical telecommunications etc.[1-3]. Such compounds show excellent properties due to the presence of f – orbital electrons. Lanthanide ions exhibit sharp fluorescent emission via intra configurational f-f and 4f - 5d transitions. Because of these transitions, lanthanide ions are used as light emitting device or phosphors. The intensity of 4f-4f transition is weak since these transitions are not allowed by Laporte selection rule. And also the 4f shell is shielded by the outer filled 5s and 5p orbitals since the energy of the 4f electrons are not influenced by the surrounding environment of the lanthanide ions. However, the promotion of a 4f electron into the 5d sub-shell is parity allowed; the corresponding transitions are broader than f-f transitions and their energy depends largely on the metal environment since the 5d – orbital are external and interact directly with the ligand orbitals [4-6].

To get enhanced luminescence properties of lanthanide ions, the chosen of appropriate host materials were required. Here, we have chosen Gd_2O_3 host because of its low photonic vibration, high transparency in the visible range, high capability of energy transfer and large band gap [7-9]. Gd_2O_3:Eu^{3+} exhibit strong paramagnetic behaviour (S = 7/2) as well as strong UV and also a promising candidate material for improving luminescent properties [10-12]. Many researchers have synthesized a variety of rare earth doped multi color phosphors such as Gd_2O_3: (Eu^{3+}, Dy^{3+}, Tb^{3+}), GdF_3: (Yb^{3+}, Er^{3+}), $20Gd_2O_3$-10CaO-$69P_2O_5$:Dy^{3+} , $20GdF_3$-$10CaF_2$-$69P_2O_5$ etc. [13-16]

Some gadolinium compounds ie., gadolinium oxides and chelates of gadolinium (III) with diethyletriamine pentaacetic acid (DTPA) etc., have been used as T1-weighted magnetic resonance imaging (MRI) contrast agents due to small r_2/r_1 ratio. Due to high biocompatibility, rare earth doped Gd_2O_3 nanocrystal becomes a promising material in biological fluorescence labeling, disease diagnosis and treatment [17-19]. Recently, Single phase multi-functional bio-probes are attractive field in research. Gadolinium based nanoparticles such as Gd_2O_3, lanthanides (Yb, Er, Tm) doped Gd_2O_3, $GdPO_4$ and GdF_3 are reported as an examples of single phase multi-functional bio-probes [20-23].

Experimental

Materials

All chemicals are of analytical grade and used as received. Gadolinium oxide (Gd2O3, 99.9%, Aldrich), europium oxide (Eu2O3, 99.9%, s Aldrich), were used as a source of Gd3+ and Eu3+ respectively. Nitric acid (HNO3, Merck), potassium hydroxide (KOH, Merck), ethylene glycol (Merck), acetone (CH3COOH) and double distill water were used in the preparation.

Synthesis

Gd2O3: xEu3+ (x = 1, 3, 5, 7, 10, 15 mol %) were successfully synthesized by hydrothermal method at 1600C for 3hrs, maintained at ~ 11pH.

In a typical preparation, 0.03 M of Gadolinium oxide and 0.03 M of europium oxide were dissolved in a minimum amount of concentrated nitric acid in a 100 mL beaker. Evaporated at least three times by adding double distill water to remove excess acid and 40 mL of double distill water was added. Then, 40 mL of water was added to another 100 mL beaker with stir constantly. Two reaction mixtures were mixed and stirred 30 minutes. KOH solution were added drop wise to the reaction mixture with constant stirring till pH ~ 11 and then added to the Teflon autoclave. The reaction mixture was carried out at a temperature 1600C by using Muffle furnace for three hours. A white solid product of Gd(OH)3:Eu3+ was then collected by centrifugation at around 12000 rpm and washed three/four times with water and finally acetone and then dried at 600C. Subsequent dehydration of Gd(OH)3:Eu3+ by heating at 7000C for 3hrs results

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Gd2O3:Eu3+. The same process was repeated for the preparation of the other doped samples.

Characterization

Structural studies of all samples were carried out using Bruker D8 Advance X-ray diffractometer equipped with graphite monochromatized Cu Ka radiation (λ=0.15418 nm) from 100 to 800 (2θ). Infrared spectra were recorded on a Fourier transform infrared (FT-IR) spectrophotometer of Shimadzu (model: 8400S) using thin pellets of the samples made with KBr (1:3 ratio). Transmission electron microscope (TEM), high resolution TEM (HRTEM) images, and SAED pattern were taken from JEOL JEM-2100 TEM, operated at 200kV. 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. All the measurements were carried out at room temperature.

Results and Discussion

Structural Analysis

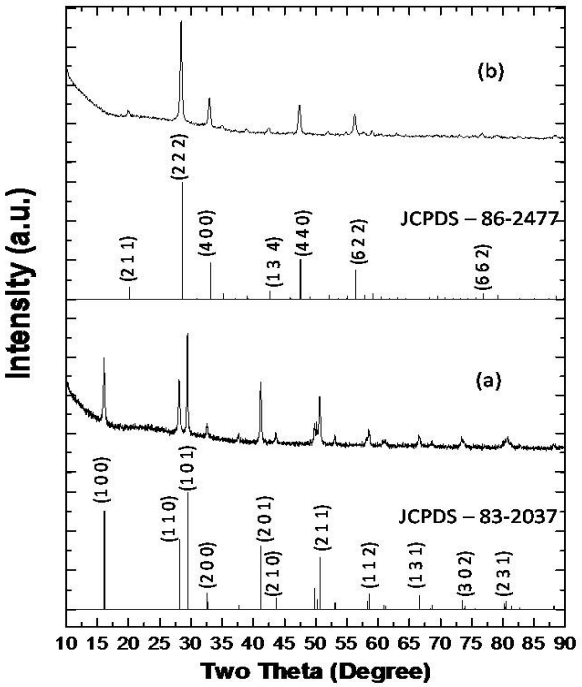

Figure 1: XRD spectra of (a) $Gd(OH)_3$: 7 mol% Eu^{3+} and (b) Gd_2O_3: 7 mol% Eu^{3+}

The phase purity and crystal structure of the prepared samples were analyzed from XRD patterns. Figure 1(a) & 1(b) show the XRD pattern of 7 mol% Eu^{3+} ion doped $Gd(OH)_3$ and Gd_2O_3 phosphor respectively. In the Fig. 1(a), all the peak patterns were well matched with JCPDS Card No. 83 – 2037 which could be indexed to the hexagonal phase of the $Gd(OH)_3$ with the space group $P6_3/m$. Whereas, all the peaks in the Fig. 1(b) were matched with JCPDS card no. 86 – 2477 which could be indexed to the cubic phase of Gd_2O_3 with the space group Ia-3. In both cases, sharp and strong diffraction peaks were found which indicates the prepared samples posses a high crystallinity and also there is no extra phase found in the diffraction patterns which means that the Eu^{3+} ion have been incorporated into the host matrix. By applying the Debye – Scherer formula, the crystallite size of the prepared samples were determined and it was found to be 20 – 30 nm ranges.

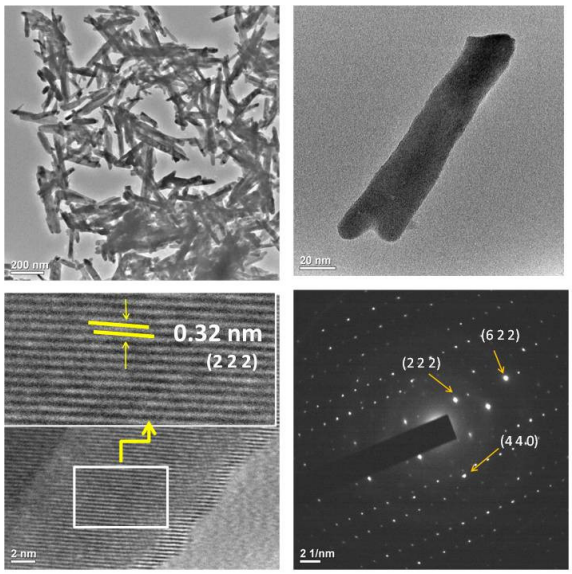

Figure 2: TEM images, HRTEM image and SAED pattern of 7 mol% Eu^{3+} doped Gd_2O_3 phosphor respectively

Figure 2 shows the typical TEM images, HRTEM image and selected area electron diffraction (SAED) pattern of 7mol% Eu^{3+} doped Gd_2O_3 phosphor. TEM images reveal that the prepared samples are found to be a nanorod having smooth surface and its diameter varies in the range of 20 – 30 nm with different lengths. The SAED pattern in Fig. 2 exhibits diffraction spots and ring which are associated to (2 2 2), (6 2 2) and (4 4 0) planes of Gd_2O_3 cubic phase. The lattice fringes in HRTEM image indicate that the prepared samples are highly crystalline. The measured space of lattice fringes is 0.32 nm which is accordance with interplannar distance of (2 2 2) plane of cubic phase, Gd_2O_3. FT-IR spectra of 7mol%Eu^{3+} doped $Gd(OH)_3$ and Gd_2O_3 phosphor are given in the Fig. 3. The band at 3595 cm^{-1} and 1632 cm^{-1} are attributed to O – H stretching and bending vibration of $Gd(OH)_3$ respectively [24-25]. The absorption peak at 541 cm^{-1} is assigned to Gd – O stretching vibration [26-27]. The peak at 1506 cm^{-1} and 1393 cm^{-1} are assigned to C – O stretching and bending vibration of CO_2 absorbed from the atmosphere [28].

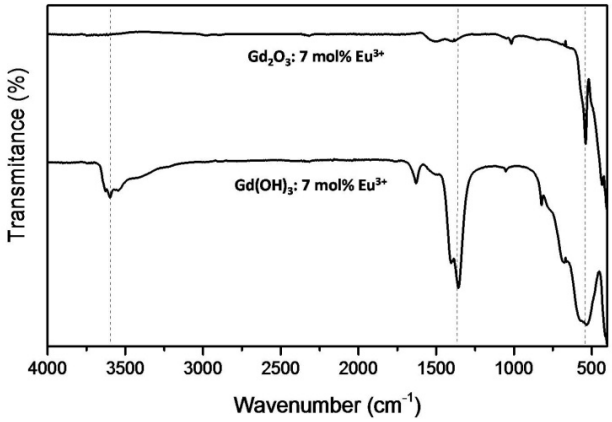

Figure 3: FT-IR spectra of 7 mol% Eu^{3+} doped $Gd(OH)_3$ and Gd_2O_3 phosphor

Optical Analysis

Figure 4 and 5 shows the excitation spectra of Gd_2O_3:Eu^{3+} with different concentrations monitoring emission wavelength at 612 nm. A broad/strong absorption band observed around at 220 – 300 nm is due to overlap of O^{2-} to Eu^{3+} charge transfer (CT) band, Gd^{3+} to Eu^{3+} CT band and host lattice absorption band. The other weak bands at 362 nm, 381 nm, 394 nm are due to f-f transition of Eu^{3+} ions [29-32]. The emission spectra are recorded under UV excitation at 258 nm wavelength in the range of 400 – 750 nm as given in the Fig. 6. A sharp peak observed at 612 nm is due to $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ion. Those peaks observed at longer wavelength 652 nm and 709 nm are assigned as $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_2$ transition respectively. And other peaks observed at shorter wavelength are attributed to 467 nm, 499 nm, 511 nm ($^5D_2 \rightarrow {}^7F_{j=0,1,2}$), 535 nm, 553 nm, 568 nm, 580 nm ($^5D_1 \rightarrow {}^7F_{j=0,1,2,3,4}$) and 591 nm ($^5D_0 \rightarrow {}^7F_1$) transitions. Emission intensity increases as Eu^{3+} ion concentration increases upto 7mol% and then decreases with a further increase of Eu^{3+} ion concentrations is due the concentration quenching effect [11]. In body centred cubic Gd_2O_3, there are two types of symmetry sites i.e., C_2 (no inversion symmetry) and S_6 (inversion symmetry) present in the ration of 3:1. The sharp peak at 612 nm ($^5D_0 \rightarrow {}^7F_2$) is hypersensitive electrical dipole transition which is located in C_2 symmetry. This transition is highly dependent on the local environment of Eu^{3+} ions in the host lattice surrounding. The other peak at 591 nm ($^5D_0 \rightarrow {}^7F_1$) is magnetic dipole transition and located in S_6 symmetry site which is independent on the local environment [8,33-34]. The variation of the relative intensity and asymmetry ratio with a function of Eu^{3+} ion concentrations as shown in Fig. 7, give information about the symmetry of Eu^{3+} ions in the host matrix.

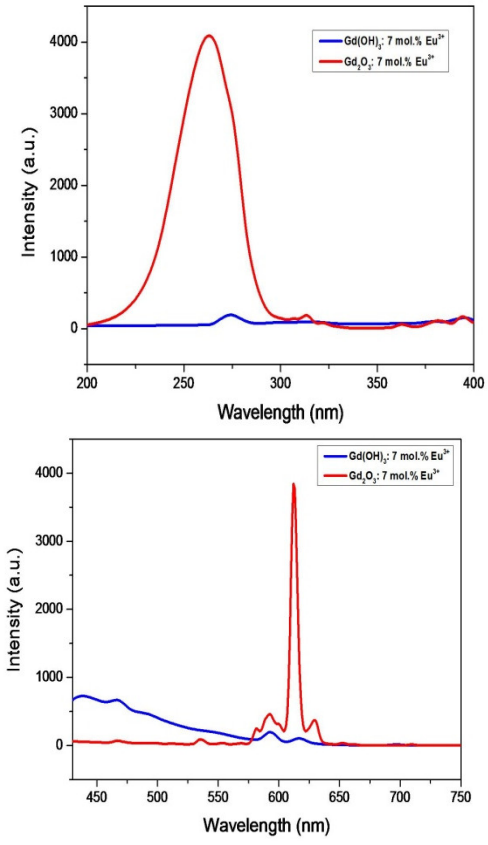

Figure 4: Excitation and emission spectra of 7 mol% Eu^{3+} doped $Gd(OH)_3$ and Gd_2O_3

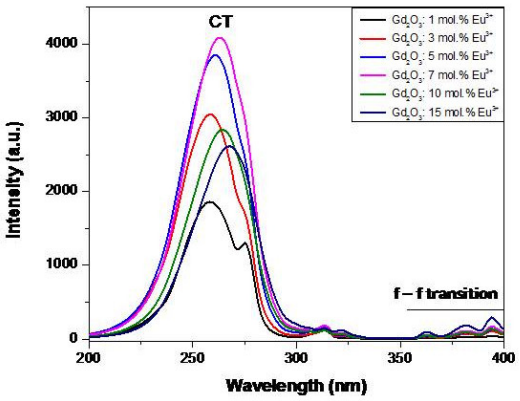

Figure 5: Excitation spectra of Gd_2O_3:Eu^{3+} with different concentrations

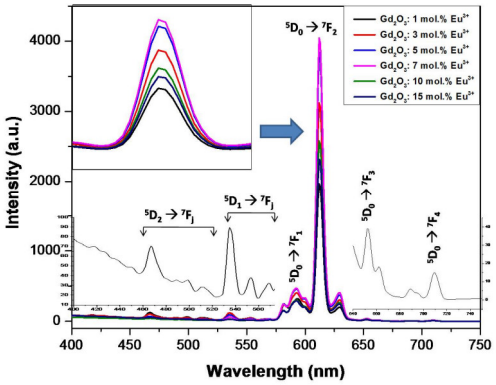

Figure 6: Emission spectra of Gd_2O_3:Eu^{3+} with different concentrations

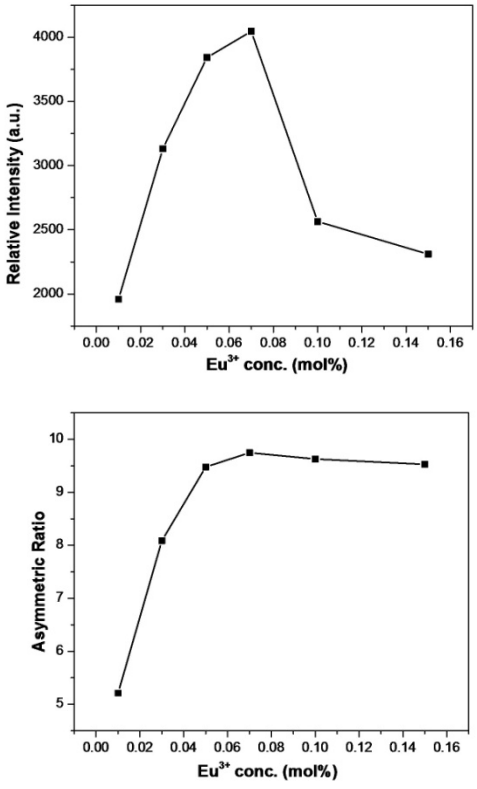

Figure 7: Variation of relative emission intensity and asymmetry ratio Vs concentration of Eu^{3+} ions respectively

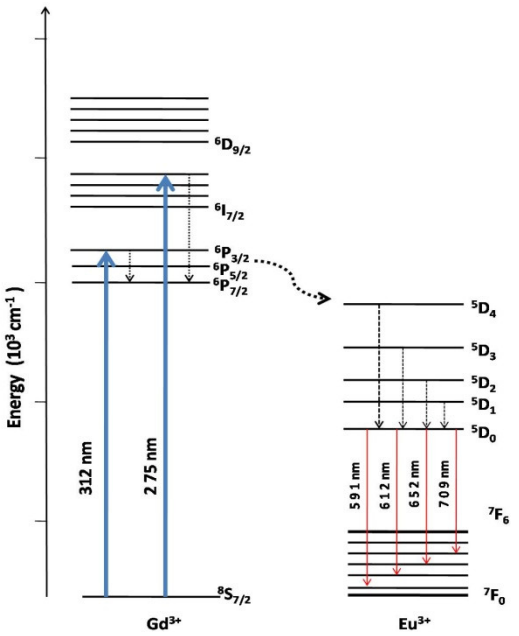

Figure 8: Schematic energy label diagram showing the energy transfer between Gd^{3+} and Eu^{3+} ions in the host matrix

The luminescence decay time of Gd_2O_3:Eu^{3+} phosphor with different Eu^{3+} ions concentrations were analyzed by using F-7000 Hitachi fluorescence spectrophotometer. The excitation and emission wavelength are fixed at 258 nm and 612 nm, respectively [Fig 8].

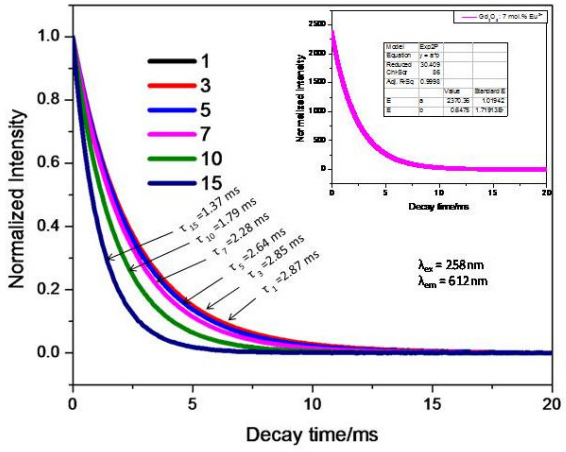

Figure 9: The normalized decay curve of Gd_2O_3:Eu^{3+} with different Eu^{3+} ions concentrations

The decay curve of the prepared samples are well fitted using the single exponential equation,

$$I = I_0 \exp^{-t/\tau}$$

Where, I and I_0 are the luminescence intensities at time 0 and t respectively and τ is the decay lifetime.

The decay lifetime values of the prepared samples are found to be 2.87, 2.85, 2.64, 2.28, 1.79 and 1.37 ms. A fitting parameter is shown in inset of the Fig. 9. The decay lifetime values decease with increase in Eu^{3+} ions concentrations is due to quenching effect i.e. cross-relaxation among the Eu3+ ions is dominant over the non-radiative relaxation which arises from the surface or near the surface of the host.

The CIE colour coordinate analysis of the prepared samples is shown in the Fig.10. The values of X and Y coordinates for 258 nm excitation wavelength of different Eu^{3+} ions concentrations i.e., 1, 3, 5, 7, 10 and 15 mol% are found to be (0.52, 0.33), (0.56, 0.33), (0.59, 0.33), (0.60, 0.33), (0.58, 0.33) and (0.56, 0.31), respectively. These results indicate the probable visible colours of the prepared samples are approached from orange to deep red.

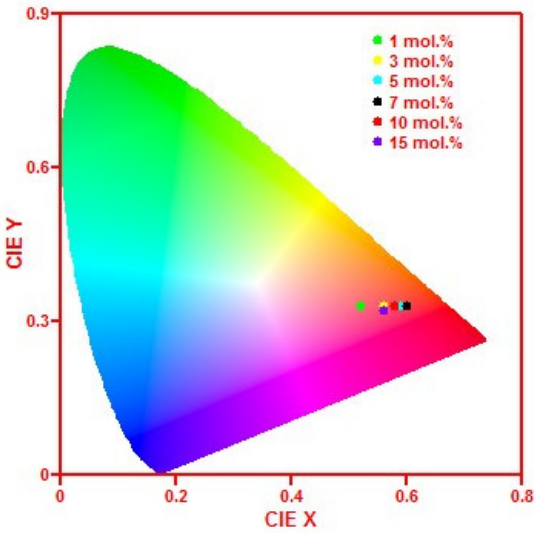

Figure 10: CIE diagram for Gd_2O_3:Eu^{3+} phosphor with different concentrations (λ_{ex} = 258 nm)

Conclusions

Eu^{3+} ions doped Gd_2O_3 phosphors with different concentrations were successfully synthesized by hydrothermal method. The XRD analysis confirmed the cubic structure of Gd_2O_3. The TEM and HRTEM images also revealed the prepared samples are highly crystalline nanorods having the diameter in the range of 20 – 30 nm with different length. The presence of oxides and hydroxides in the samples are shown by FT-IR study. The photoluminescence studies indicated the highest luminescence intensity is found at 7 mol% Eu^{3+} ions doped sample. The emission intensity increases up to 7 mol% of Eu^{3+} ions and then decreases for further increase and its decay lifetime are found in the range 1.37 – 2.87 ms. The CIE chromaticity coordinates of 7 mol% Eu^{3+} ions doped Gd_2O_3 phosphor show the deep red emission which makes some applications in the solid state lighting devices.

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