Optical properties of nanocrystalline Y$_2$O$_3$:Eu$^{3+}$

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Abstract

Optical properties of nanocrystalline red-emitting phosphor, Europium doped Yttria (Y$_2$O$_3$:Eu$^{3+}$), of average particle size 15 nm are investigated. The intensity of the strongest emission line at 612 nm is found to be highest in the nanocrystalline sample with 4 at. wt. % of Europium. The narrow electronic emission spectrum suggests a crystalline surrounding in this nanomaterial. We have estimated the strength of the crystal field parameter at the dopant site, which plays a crucial role in determining the appearance of the intense emission line. The equilibrium temperature of this system has also been calculated from the intensity ratio of Stokes and anti-Stokes Raman scattering. Though known for the bulk samples, our approach and consequent results on the crystalline nanomaterial of Y$_2$O$_3$:Eu$^{3+}$ provide a unique report, which, we believe, can be of considerable significance in nanotechnology.

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I. INTRODUCTION

The optical properties of rare-earth ions trapped in inorganic oxides continue to be a research attraction in terms of both their fundamental and technological importance. Yttrium oxide doped with Eu$^{3+}$ is one of the main red-emitting phosphors and is widely used in lighting industry and in solid-state-laser based devices. The unique optical properties of this material is based on the f- and d electrons of Europium ions. To enhance the brightness and resolution of displays in devices in the present nanotechnology regime, it is important to develop phosphors with controlled morphology and small particle size (nanoparticles). The potential of this low dimensional material in fabrication of modern micro/nano devices requires an understanding of their fundamental properties in detail. In particular, the origin and behavior of the strongest $^5D_0 - ^7F_2$ transition spectrum from Eu$^{3+}$ needs to be investigated because of its importance in designing laser devices. For example, permanent laser-induced gratings have been fabricated using crossed write beams in resonance with the $^7F_2 - ^5D_0$ absorption transition of Eu$^{3+}$.

Over the last couple of decades, a considerable amount of work on the spectral properties of bulk Y$_2$O$_3$:Eu$^{3+}$ has been reported in the literature. Additionally, we find several articles on nanoparticles of this material, though, the detailed study of their optical properties is, as far as we are aware, incomplete. In recent times, Schmechel et al. have reported luminescence properties of nanocrystalline Y$_2$O$_3$:Eu$^{3+}$. However, due to the presence of defect/disordered states in this low dimensional system, the quantum efficiency of this nanomaterial is much less than the corresponding bulk commercial sample. Furthermore, Konard et al. have synthesized and studied the luminescence properties of Y$_2$O$_3$:Eu$^{3+}$ nanoparticles, though they do not discuss the quantum efficiency of this material. In both these studies, one does not find the details of the optical emission spectrum of this low dimensional system.

Apart from optical properties, other characteristics of such inorganic, lanthanide-doped oxides also play an important role in using these materials in technology. Walsh et al. have recently demonstrated that the strength of the crystal field is crucial in improving the performance of solid-state lanthanide lasers. It may be noted that the doped Europium ions in these oxides provide the high-energy local mode phonons, which can produce structural modification of the host. Finally, the knowledge on the thermal properties of this material is...
required for efficient laser operation (for example, thermal lensing) as well as the stability of laser-induced gratings. Such gratings, designed from Europium ion doped glasses, are found to be stable up to a certain equilibrium temperature, but get erased with rising thermal energy.  

In this article, we have addressed optical properties of nanocrystalline Europium doped Yttria, prepared by soft chemical route. Section II covers the sample preparation and characterization of the nanomaterial by x-ray diffractometry and Transmission Electron microscopy (TEM). In Section III, we have reported the electronic emission spectrum for the range of 490 nm - 900 nm by Photoluminescence spectroscopy. The crystal field effect and equilibrium temperature in the nanocrystalline $Y_2O_3:Eu^{3+}$ have been discussed in Section IV. Finally, in Section V we have summarized our results with a few concluding remarks.

II. SAMPLE PREPARATION AND CHARACTERIZATION

The nanomaterial has been prepared by soft-chemical method using TEA (Tri-ethanolamine) as complexing (chelating) agent. Solid powder of Europium Oxide and Yttrium Oxide (both from ALDRICH) are boiled with concentrated nitric acid in water bath to get clear solutions of Europium Nitrate and Yttrium Nitrate, respectively. The addition of nitric acid is continued until the solution reached a pH of 3.0. Europium Nitrate and Yttrium Nitrate solutions are taken in different stoichiometric ratios in order to vary the $Eu^{3+}$ concentration by 1-7 at. wt. % with respect to $Y^{3+}$. These nitrate solutions and TEA are taken in a beaker and then heated on a hot plate at a temperature of about 180-200 °C. TEA helps to keep the metal ions in homogenous solution through the reaction without precipitation. Due to complete dehydration of the complex precursor and decomposition of the metal complexes upon heating the mixture, we get a fluffy mass. It is calcined at 900 °C for four hours. A white powder is obtained. In the rest of this article, we denote the nanomaterial of $Y_2O_3$ doped with 4 at. wt. % $Eu^{3+}$ (in stoichiometric ratio) as Sample A. The micron-sized particles (Sample B) are prepared by heating a part of the above sample at 1200 °C for six hours, after which white bulk $Y_2O_3:Eu^{3+}$ phosphor is obtained.

Samples for Transmission Electron Microscopy are deposited onto 300 mesh copper TEM grids coated with 50 nm carbon films. Nanocrystals, dissolved in Acetone, are placed on the grid drop-wise. The excess liquid is allowed to evaporate in air. The grids are examined in
JEOL 2010 microscope with Ultra-High Resolution (UHR) pole-piece using a LaB$_6$ filament operated at 200 kV. The high resolution transmission electron microscopy (HRTEM) image for Sample A, shown in Fig. 1(a), clearly demonstrates the lattice fringes for the cubic phase of Y$_2$O$_3$: Eu$^{3+}$. From the micrograph we have determined the lattice spacing in the particle to be 0.29 nm, which corresponds to (222) plane of cubic phase of this material. The frequency plot of the size distribution, shown in Fig. 1(b), is obtained by measuring the size of many particles per sample. Size distribution for the nanoparticles are usually found to be log-normal:

$$P(d) = \frac{1}{d\sigma\sqrt{2\pi}} e^{\frac{-\ln^2(d/\bar{d})}{2\sigma^2}}. \tag{1}$$

Here $\bar{d}$ and $\sigma$ are related to the average size and the size distribution of the particles. By fitting the frequency plot using Eq. (1) [solid line in Fig. 1(b)], the average particle size of Sample A has been estimated to be 15 nm with a very narrow size distribution ($\sigma = 0.14$). The average particle size of Sample B is found to be 500 nm with a wider size distribution.

Samples have been characterized by x-ray diffraction at room temperature using Philips PW1710 X-ray Diffractometer, equipped with a vertical goniometer and CuK$_\alpha$ radiation source of wavelength ($\lambda = 1.514 \, \text{Å}$). X-ray diffraction patterns for both Sample A and B are shown in Fig. 2. The observed values of the diffraction angles ($2\theta$) match quite well with the reported data and the patterns exhibit cubic symmetry (space group $Ia3$). Identical diffraction patterns of both Sample A and Sample B indicate that the lattice constants in both the materials are same i.e. there is no distortion in the structure of Sample A because of lowering of dimension of the system. We have calculated the average nanocrystallite size ($L$) using Scherrer’s equation:

$$\Gamma = \frac{0.94\lambda}{L \cos \theta}, \tag{2}$$

where $\Gamma$ (expressed in radians) is the full width at the half maxima (FWHM) of the x-ray diffraction peak. $\theta$ is the diffraction peak position. Taking the diffraction resolution function (DRF) to be Gaussian and the diffraction line to be Lorentzian, the line-width correction for the x-ray instrumental broadening can be taken into account by using the empirical expression.
\[ \eta = \eta_e - \left( \frac{1}{\eta_e} \right)^\beta, \]  

(3)

where, \( \beta = 1 - 0.1107/\eta_e \). \( \eta_e \) is the ratio of observed FWHM (\( \Gamma_e \)) and the FWHM (\( \Gamma_d \)) of the DRF, whereas, \( \eta \) is the ratio of the true FWHM (\( \Gamma \)) of the diffraction line and \( \Gamma_d \). For our instrument \( \Gamma_d = 0.10^\circ \). For the diffraction peak at \( 2\theta = 28.974^\circ \) of the Sample A, \( \Gamma_e = 0.326^\circ \), which gives \( \Gamma = 0.254^\circ \). From Eq. (2), the crystallite size has been estimated, which is close to what we have observed from the HRTEM images of the particles, discussed earlier. The narrow diffraction pattern from the nanoparticles implies the crystalline nature of Sample A.

III. OPTICAL EMISSION SPECTRA

Luminescence spectra are obtained using a 1200 g/mm holographic grating, a holographic supernotch filter, and a Peltier cooled CCD detector. We use a 488 nm Argon ion laser as our excitation source.

The electronic transition spectra for the range 490 nm to 900 nm are shown in Fig. 3. Many of these transitions satisfy the magnetic dipole selection rules (\( \Delta J = 0, \pm 1 \) with \( J = 0 \leftrightarrow J' = 0 \)) in an intermediate coupling scheme (shown in Fig. 4).\(^{24} \) In free Eu\(^{3+} \), the \( ^{5}D_0 - ^{7}F_2 \) transition is forbidden (for both magnetic and electric dipoles). This holds true in a crystalline environment, which has inversion symmetry. \( \text{It is well established that in the body centred cubic structure of Yttria, Eu}^{3+} \text{ replaces Y}^{3+} \) in two different sites. 75% of these sites are with \( C_2 \) and the other 25% are with \( S_6 \) symmetry. Between these two the former does not have the inversion symmetry.\(^{25,26,27,28,29} \)

According to the theory of Judd\(^{30} \) and Ofelt\(^{31} \) the \( ^{5}D_0 - ^{7}F_2 \) transition becomes electric dipole type, due to an admixture of opposite parity \( 4f^{n-1}5d \) states by an odd parity crystal field component. \( ^{5}D_0 - ^{7}F_{3,5} \) transitions have a mixed character - magnetic dipole intensity usually to first order and electric dipole intensity to second order.\(^{32} \) The \( ^{5}D_0 - ^{7}F_3 \) transition exhibits a relatively larger intensity than what is expected because of its large induced electric dipole character. The large oscillator strength of the \( ^{5}D_0 - ^{7}F_3 \) transition may be attributed to significant crystal-field induced mixing of the \( ^{7}F_3 \) state to \( ^{7}F_2 \) state, leading to the transfer of energy from \( ^{5}D_0 - ^{7}F_2 \) to \( ^{5}D_0 - ^{7}F_3 \) transition.\(^{33} \) \( ^{5}D_0 - ^{7}F_{4,6} \) transitions are electric dipole in character and have appreciable intensities.\(^{32} \) The
magnetic dipole and electric quadrupole transitions are forbidden for $J_0 - J_0$ line. The theory of Judd and Ofelt does not explain the $^5D_0 - ^7F_0$ fluorescence of Eu$^{3+}$ ion because the $J_0 - J_0$ transition is forbidden even in the presence of non-centrosymmetric potential. The origin of this emission line may be explained by the variation in crystal field potential, which causes the mixing of odd parity $J = 1$ states into the $^7F_0$ and $^5D_0$ states. However, from the fluorescence line-narrowing experiment, it has been shown that the $^5D_0 - ^7F_0$ borrows its intensity from $^5D_0 - ^7F_2$ line through the $J$-mixing in this material. Other than the above transitions, direct band to band transition and excitonic emission appear at 6.2 eV and 5.9 eV, respectively, in this system. We could not study these emission lines because of our experimental limitations (recall that we have used 488 nm as the wavelength of our excitation source). No bands are reported below 490 nm. However, electronic transitions from $^5D_3$ to $^7F_J$ is known to occur in this region. In Fig. 4 we have shown the energy level diagram of the low-lying states of the Eu$^{3+}$ ion in nanocrystalline $Y_2O_3$:Eu$^{3+}$, as obtained in our experiment.

It is well known that a strong energy transfer takes place from $S_6$ to $C_2$ site, which gets stronger with increase in Europium content. Consequently, the ratio of the emission intensity of $C_2$ site to the emission intensity of $S_6$ site also increases with increase in Europium concentration in the sample. Previous emission study on cubic bulk $Y_2O_3$:Eu$^{3+}$ has shown that only the transitions $^5D_0 - ^7F_1$ originate from $S_6$ site, whereas nearly all of the other features in the electronic spectrum are due to Eu$^{3+}$ ion in $C_2$ sites. The different behaviour of Eu$^{3+}$ ion in two different lattice sites is most probably due to the large diameter (0.95 Å) of Eu$^{3+}$ ion, which fills the lattice sites of the host, and gets affected by nearby atoms. Fig. 5 shows the change in ratio of the peak intensities of emission spectra for $^5D_0 - ^7F_0$ (581 nm) transition of $C_2$ site and $^5D_0 - ^7F_1$ transitions (587 nm) of $S_6$ site for nanocrystalline $Y_2O_3$:Eu$^{3+}$ with different Europium ion concentration. Due to the energy transfer from $S_6$ site to $C_2$ site, the ratio increases till the dopant concentration is 4 at. wt. % of the host material, but decreases with further increase in mole concentration of Europium ion. This drop in the ratio with concentration of Eu$^{3+}$ beyond 4 at. wt. % can be attributed to fluorescence quenching, which arises due to the energy transfer or electron transfer process between the two nearest excited Eu$^{3+}$ and dominates over the spontaneous emission process. In the above analysis we have compared $^5D_0 - ^7F_1$ transition of $S_6$ site with $^5D_0 - ^7F_0$ transition of $C_2$ site, as these two lines are of comparable intensity. Justifying the above discussion,
we now show that the effect of fluorescence quenching becomes dominant in the case of the most intense emission line at 612 nm for the sample doped with more than 4 at. wt. % of Eu$^{3+}$. We have fitted the emission spectrum at 612 nm for all the samples with Lorentzian line shape. In the inset of Fig. 5 we have shown the variation in intensity of this emission spectrum with concentration of Eu$^{3+}$ in nanocrystalline Y$_2$O$_3$. The sample with 4 at. wt. % of dopant concentration (Sample A) shows highest emission intensity for 612 nm transition line. Hence, we have taken this particular material as a standard nanocrystalline sample and compared its physical properties with bulk (Y$_2$O$_3$:Eu$^{3+}$).

In Fig. 6, we have compared the most intense electronic transition line at 612 nm in the spectra for both nanomaterial (dashed-dotted line : Sample A) and the bulk system (solid line : Sample B). Both the spectra have been fitted with three Lorentzian line shapes. In the non-linear least square fit the width of the spectral line and its intensity have been kept as varying parameters. We have not observed any shift in the luminescence peak position due to quantum size effect. As shown in Fig. 6, the luminescence intensity of 612 nm transition from Sample A is slightly less than that observed in Sample B. Surface states are the sources of non-radiative recombination centers. Due to high surface to volume ratio in nanoparticles compared to the corresponding bulk material the non-radiative recombination processes dominate in the former. Moreover, there is a possibility of absorption by impurities in nanostructured materials. These, in turn, decrease the luminescence efficiency in nanoparticles. However, here we would like to point out that the drop in intensity in nanocrystalline sample compared to the corresponding bulk material, prepared by us, is much less than what has been reported before in the literature due to the absence of impurities and defects in Sample A (as we have observed from our x-ray measurements).

We note that (i) the half-widths of the 612 nm line for sample A and sample B have been obtained as 0.5 ± 0.2 nm and 0.4 ± 0.2 nm, respectively. The sharp transition spectrum for Sample A suggests nearly crystalline surrounding and (ii) the appearance of all lines from $^5D_2$ and $^5D_1$ signify absence of too many non-radiative cross-relaxation processes in Sample A.
The most intense forced electric dipole $^5D_0 - ^7F_2$ transition line, discussed in the previous section, is expected to be hypersensitive to the crystal field at the dopant site. The crystal field Hamiltonian can be written as

$$H_{CF} = \sum_{l,m} \sum_i B_{lm} C_{lm}(\theta_i, \phi_i),$$  \hspace{1cm} (4)

where $B_{lm}$, the crystal field parameter, which describes the effect of the crystal field on the free ion Hamiltonian, satisfies

$$B_{lm} = (-1)^m B_{l,-m}$$  \hspace{1cm} (5)

and $C_{lm}$ are spherical tensors defined in terms of spherical harmonics according to

$$C_{lm}(i) = \left( \frac{4\pi}{2l+1} \right)^{1/2} Y_{l,m}(\theta_i, \phi_i).$$  \hspace{1cm} (6)

In Eq. (4) - (6) $l$ runs over 2, 4, 6..... and $m = 0, \pm 2, \pm 4..... \pm l$. The sum on $i$ runs over the number of electrons in the $4f^n$ configuration. $\theta_i$ and $\phi_i$ are the angular coordinates of the $i$th electron. The reason for the presence of only even $l$ in the sum is related to the fact that even $l$ terms in the expansion of Eq. (4) contribute to the shifting and splitting of energy levels. On the other hand, the odd $l$ terms in Eq. (4), if included, would represent the mixing of opposite parity states from higher lying configuration into the $4f^n$ one. The usual analysis with the crystal field potential, in Eq. (4), does not take into account the mixing of different $J$-states. $l=0$ is always ignored because it corresponds to spherically symmetric crystal field that shifts all energy levels equally without affecting the energy level splitting. However, as discussed before, $J$-mixing plays an important role in explaining the optical emission spectrum of the material. Assuming that the $D_0 - F_0$ transition is allowed only by $J$-mixing, the intensity variation of $^5D_0 - ^7F_0$ line is ascribed to the effect of mixing of $^7F_2$ into $^7F_0$ states. This can be taken into account by considering the second-order term (crystal field parameter $B_{20}$) in the above local field potential. The transition strength of $^5D_0 - ^7F_0$ line is known to be proportional to $\alpha B_{20}^2$, where $\alpha = 4/75\Delta_{20}$ and that of $^5D_0 - ^7F_2$ line is independent of $B_{20}$. Here, $\Delta_{20}$ is the energy separation between the $^7F_2$ and $^7F_0$ states. Thus, the intensity ratio of $^5D_0 - ^7F_0$ and $^5D_0 - ^7F_2$ transitions is given by
\[
\frac{I_{0-0}}{I_{0-2}} = \frac{4B_{20}^2}{75\Delta_{20}^2}.
\]

Taking \(\Delta_{20} = 900\, \text{cm}^{-1}\), variation of crystal field parameter, \(B_{20}\), with increase in concentration of Eu\(^{3+}\) is shown in Fig. 7. Its value for Sample A and Sample B are estimated to be 1077 cm\(^{-1}\) and 995 cm\(^{-1}\), respectively. These values of \(B_{20}\) are found to be in good agreement with the reported value 1260 cm\(^{-1}\) for the commercial bulk system\(^\text{25}\). Indirectly, it also reveals that the crystal field effect is similar in both Sample A and Sample B and match very well with the commercial bulk material.

Fig. 8 shows both Stokes and anti-Stokes side of the Raman line at 375 cm\(^{-1}\), typical of cubic Y\(_2\)O\(_3\):Eu\(^{3+}\) lattice. Local heating produced by the vibrational modes can give rise to a change in structure of the local environment of the Eu\(^{3+}\) by causing ions to move from one equilibrium position to another. Stokes (\(I_S\)) and anti-Stokes (\(I_{AS}\)) Raman scattering intensities are related to a very good approximation by the relation\(^\text{42}\)

\[
n(\omega)I_S = [n(\omega) + 1]I_{AS},
\]

where \(n(\omega)\) is the Bose-Einstein thermal factor, explicitly given by

\[
n(\omega) = \frac{1}{exp(h\omega/k_BT) - 1},
\]

where \(k_B\) is Boltzmann’s constant and \(T\) is the equilibrium temperature of the sample. From the intensity ratio of the Stokes (\(I_s\)) and anti-Stokes (\(I_{AS}\)) Raman line one can calculate the equilibrium temperature \(T\) of the material by using the equation\(^\text{42}\)

\[
\frac{I_s}{I_{AS}} = exp\left(\frac{h\omega}{k_BT}\right),
\]

where, \(\omega\) is the phonon frequency. We have fitted both Stokes and anti-Stokes Raman spectra from the sample with Lorentzian line shape. In the non-linear least square fit the intensity, width, and the peak position have been kept as fitting parameters. From the intensity ratios of the Stokes and anti-Stokes Raman lines and using Eq. (10), the equilibrium temperatures of Sample A and Sample B have been estimated to be 247 K and 257 K, respectively. In other words, the material is stable till its equilibrium temperature is within this value. The equilibrium energy \((k_BT)\) of a system is a thermodynamic property. Thus, we expect both Sample A and Sample B to have an equivalent local environment, which
again is an important fact to be kept in mind while using these nanocrystalline $Y_2O_3:Eu^{3+}$ in nanotechnology.

V. CONCLUSION

In this article, we have reported optical properties of cubic nanocrystalline rare-earth doped inorganic oxide, $Y_2O_3:Eu^{3+}$, of average particle size 15 nm. The electronic energy levels of this material are obtained from the photoluminescence measurements. The analysis of the variation in intensity of the luminescence spectrum at 612 nm for nanocrystalline $Y_2O_3:Eu^{3+}$ as a function of Eu$^{3+}$ concentration in the host lattice leads to the observed fact that the dopant concentration of 4 at. wt % exhibits maximum intensity of the emission peak. We have discussed the crystalline nature of the material and the local field effect around the Europium ion, both of which influence the emission spectrum of this system. The equilibrium temperature, which affects the local field at the dopant site, has been estimated from the intensity ratio of Stokes and anti-Stokes Raman line. Table 1 summarizes the physical properties of the nanocrystalline $Y_2O_3:Eu^{3+}$, doped with 4 at. wt. % of Eu$^{3+}$ (Sample A), as obtained in our experiment and analysis. We claim that such nanocrystalline rare-earth doped oxides, with known characteristics can be used commercially as a red-emitting phosphor in nanotechnology.

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Figure Captions

Fig. 1. (a) HRTEM image of Sample A and (b) the frequency plot.

Fig. 2. X-ray diffraction pattern for Sample A (dotted line) and Sample B (solid line).

Fig. 3. Emission spectrum of nanocrystalline Y$_2$O$_3$:Eu$^{3+}$ for $\lambda_{\text{exc}} = 488$ nm. Intensities of (a) and (b) are not in the same scale.

Fig. 4. A schematic diagram of the energy level of Eu$^{3+}$ in nanocrystalline Y$_2$O$_3$:Eu$^{3+}$.

Fig. 5. Filled squares are the variation of the ratio of the intensities of $^{5}D_{0} - ^{7}F_{0}$ to $^{5}D_{0} - ^{7}F_{1}$ emission spectrum with at wt. % of Eu ion in nanocrystalline Y$_2$O$_3$:Eu$^{3+}$. The solid line is the guide to the eye. The variation in intensity for $^{5}D_{0} - ^{7}F_{2}$ emission peak with dopant concentration is shown in the inset.

Fig. 6. Emission spectrum of 612 nm line for bulk (solid line) and nanocrystalline (dashed-dotted line) of Y$_2$O$_3$:Eu$^{3+}$. The non-linear fit of the data for Sample A is shown in the inset.

Fig. 7. Variation of $B_{20}$ with concentration of Eu ion.

Fig. 8. Stokes and anti-Stokes Raman spectra for Y$_2$O$_3$: Eu$^{3+}$. The squares are experimental data points. The solid lines are non-linear least square fit to the data.
TABLE I: Physical properties of nanocrystalline Y\(_2\)O\(_3\):Eu\(^{3+}\)

| Property                                               | Remark                                      |
|--------------------------------------------------------|---------------------------------------------|
| Size of the particle                                   | 15 nm                                       |
| Size distribution                                      | ± 5 nm                                      |
| Phase                                                  | Cubic (corresponds to space group \(Ia3\)) |
| Intensity of the strongest emission line at 612 nm     | Maximum for 4 at. wt. % doped Eu\(^{3+}\)ion |
| Crystal field parameter \((B_{20})\)                   | 1077 cm\(^{-1}\)                           |
| Equilibrium temperature                                | 247 K                                       |