Optical characterization of CdSe/Dy^{3+}-doped silica matrices

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Abstract. Cadmium selenide nanocrystals along with dysprosium ions are doped in silica matrices through sol–gel route. The optical bandgap and size of the CdSe nanocrystals are calculated from the absorption spectrum. The size of the CdSe nanocrystallites is also evaluated from the TEM measurements. The fluorescence intensities are compared for SiO_2–Dy^{3+} and CdSe-doped SiO_2–Dy^{3+}. The fluorescence intensity of Dy^{3+} is considerably increased in the presence of CdSe nanocrystals.

Keywords. Sol–gel synthesis; nanocrystallites; fluorescence; TEM.

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1. Introduction

Silica glasses doped with rare earth ions are of technological interest for a variety of applications in solid-state lasers, fibre optics and waveguide devices [1]. Compact and efficient solid-state lasers emitting in the visible spectral region are of great interest for a number of applications in medicine, biology, optical storage and display technology. Only a few solid-state lasers are currently commercially available in the visible wavelength range (400–700 nm). Laser oscillation observed in the rare earths such as trivalent praesodymium, neodymium, erbium, europium and terbium do not cover the entire visible range [2–4]. The dopant material dysprosium has the potential to fill the gaps that exist in the blue and yellow range because of the well-known strong fluorescence in the visible spectral range around 485 and 575 nm [5]. Nanoparticles have attracted great interest in recent years because of their unique physical and chemical properties, which are different from those of either the bulk materials or single atoms. The size- and shape-dependent optical properties of these nanoparticles render them attractive candidates as tunable light absorbers and emitters in optoelectronic devices [6] and more recently as fluorescent probes of biological systems [7]. Among them CdSe-doped glasses are found to be useful for optical communication and optical signal processing. Different physical

and chemical synthesis routes are adopted by different workers for the preparation of rare-earth ions along with semiconductor nanoparticle-doped glasses. But, sol–gel processing emerged as an attractive alternative for the fabrication of glasses utilizing combinations of II–VI semiconductors, rare earths and dielectrics like SiO_2. The sol–gel method can provide suitable host material via the transition states of viscous gels produced by polymerization of metal alkoxides under much more gentle conditions than the conventional high-temperature melting. The sol–gel technique has the ability for fabricating semiconductor nanocrystallites in glass matrices with high semiconductor concentration and relatively narrow size distributions.

2. Experimental

CdSe, Dy^{3+} and $CdSe/Dy^{3+}$-doped silica glasses are prepared by the sol–gel process with tetraethyl orthosilicate (TEOS) as precursor in the presence of ethanol and water. The dopants are added in the form of cadmium acetate, selenic acid and dysprosium nitrate. CdSe nanocrystallites are prepared from cadmium acetate and selenic acid by their decomposition reaction and incorporated into the SiO_2 matrix through annealing. Measured volume of 1 M HNO_3 is added as catalyst. The mixture (sol) is poured into polypropylene containers, which are sealed and kept to form gel. The following doped silica samples are prepared:

Sample A – Dy^{3+} (3 wt.%)
Sample B – Dy^{3+} (3 wt.%) CdSe (5 wt.%)
Sample C – CdSe (5 wt.%).

The variations in the annealing conditions of the samples result in the stabilization of final products and provide a high mechanical strength to them.

The excitation and emission spectra are taken using spectrophotofluorimeter (Shimadzu-RFPC 5301) and the absorption spectra with UV–visible spectrophotometer (Shimadzu-UVPC 2401) for samples heated to 500°C. The particle size is measured with Tecnai F 30 S-Twin transmission electron microscope (TEM) at 300 kV. All the measurements are done at room temperature.

3. Results and discussion

3.1 *Optical absorption studies*

The absorption spectrum corresponding to the CdSe-doped silica glass dried at 500°C (Sample C) is given in figure 1. The direct absorption band gap of the CdSe nanoparticles can be determined by fitting the absorption data to the equation

$$\alpha h\nu = B(h\nu - E_g)^{1/2} \tag{1}$$

in which $h\nu$ is the photon energy, α is the absorption coefficient, E_g is the absorption band gap and B is a constant relative to the material. The absorption coefficient can be obtained from the equation
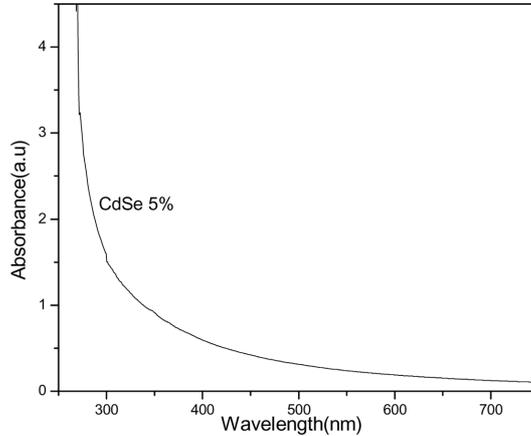
Figure 1. Absorption spectrum of CdSe-doped silica glass dried at 500°C.

$$\alpha = \frac{2.303A}{d}, \tag{2}$$

where A is the absorbance and d is the thickness of the sample.

The plot of α^2 vs. $h\nu$ gives the value of the band gap as 3.6 eV. This is large compared to the bulk CdSe, a direct semiconductor, with a band gap energy of 1.7 eV. Semiconductor nanocrystals are known to have an absorption edge, which is shifted with respect to the bulk material, towards shorter wavelength. The blueshift of the absorption edge can be explained by the effective mass approximation model, developed by Brus [8] and Kayanuma [9]. In the strong exciton confinement regime of nanoparticles (particle radius $< a_b^*$), the energy $E(R)$ for the lowest 1S excited state as a function of cluster radius (R) is given by

$$E(R) = E_g + \frac{\pi e a_b^*}{8\varepsilon R^2} - \frac{1.786e^2}{4\pi\varepsilon R} + 2.48E_R. \tag{3}$$

Here a_b^* is the Bohr radius of the exciton (for CdSe, $a_b^* = 5.6$ nm), ε is the dielectric constant of the nanocrystallite (for CdSe, $\varepsilon = 8.98$) and E_R is the bulk exciton Rydberg energy (for CdSe, $E_R = 0.016$ eV). The band edge absorption is used to calculate the average size distribution of the CdSe nanoparticles in the silica matrix. The particle radius is estimated to be 4 nm from the absorption spectrum and using the Brus formula. The absorption spectra of samples A and B heated at 500°C is shown in figure 2. The prominent levels observed for dysprosium ions are assigned to the appropriate electronic transitions as follows:

^{6}H$_{15/2}$ → ^{6}P$_{7/2}$ (350 nm),
^{6}H$_{15/2}$ → ^{6}P$_{5/2}$ (364 nm),
^{6}H$_{15/2}$ → ^{4}I$_{13/2}$ (387 nm),
^{6}H$_{15/2}$ → ^{6}F$_{3/2}$ (757 nm),
^{6}H$_{15/2}$ → ^{6}F$_{5/2}$ (806 nm).

Figure 3 shows the TEM micrograph of CdSe-doped silica glass. We can see that the dark spots are scattered in the micrograph. The dark spots correspond to
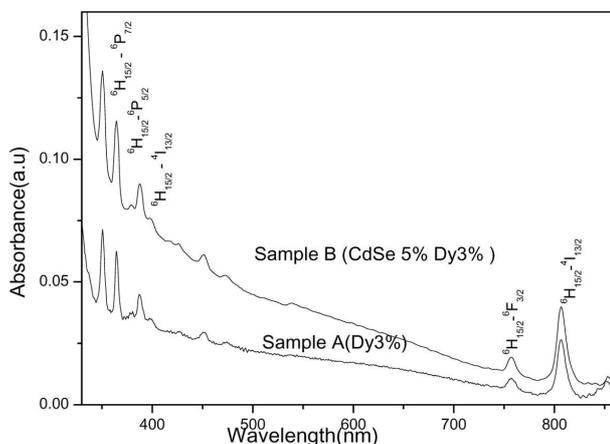
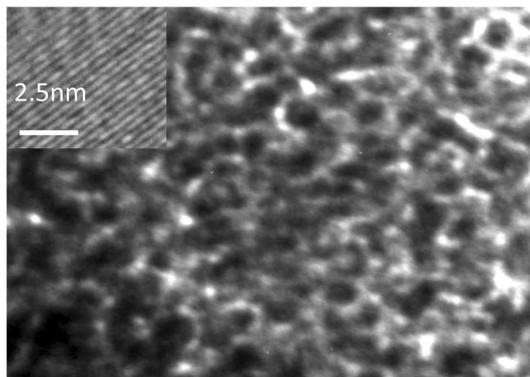**Figure 2.** Absorption spectra of samples A and B heated to 500°C.

Figure 3. TEM micrograph of CdS-doped glass.

CdSe nanocrystals. Inset shows the $(1\,1\,0)$ plane with a d value of 2.210 Å which is consistent with the d_{110} value of the bulk CdSe (JCPDS file) having 2.149 Å. The average size of the CdSe nanoparticles is estimated to be 6 nm.

3.2 *Excitation studies*

The excitation spectra give the characteristic rare-earth absorption lines corresponding to intraconfigurational $4f^n$-$4f^n$ transitions of the rare-earth ions, but not the semiconductor host lattice excitation band. The excitation spectrum taken with an emission wavelength of 570 nm gives a clear picture of the different transitions associated with the Dy^{3+} ions and is given in figure 4. The excitation spectrum shows strong excitation bands with the co-doping of CdSe nanocrystallites.

Table 1. Yellow to blue ratio (Y/B), for the transitions of Dy^{3+} ions in samples A and B.

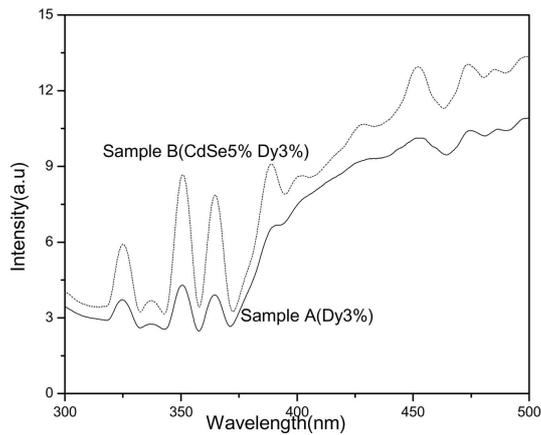| Sample	Asymmetric ratio (Y/B)
A	0.352
B	0.482

Figure 4. Excitation spectra of samples taken at an emission wavelength ($\lambda_{\text{eff}} = 570$ nm).

3.3 *Fluorescence studies*

Figure 5 presents the fluorescence spectra of the samples heated to 500°C with an excitation wavelength of 350 nm. The Dy^{3+}-doped sol–gel silica glass shows two fluorescence bands which belong to the ^{4}F$_{9/2}$ →^{6}H$_{15/2}$ (480 nm) and ^{4}F$_{9/2}$ →^{6}H$_{13/2}$ (570 nm) transitions. A considerable enhancement in the emission intensity is observed for CdSe/Dy^{3+}-doped silica glass. The calculated asymmetric ratio (table 1) also substantiates the fluorescence enhancement. The structural features play a critical role on the fluorescence enhancement, as the complex dielectric function of the composite medium depends directly on the structural features of the particles involved. In the case of Dy^{3+}, the main emission lines occur between the ^{4}F$_{9/2}$ levels to the ^{6}H$_j$ multiplets. The incorporation of CdSe to the Dy^{3+}-doped matrix provides a relative softening of the crystal field strength and also distorts the anion symmetry around the rare earth and therefore increases the transition rates.

4. Conclusion

CdSe nanoparticles along with Dy^{3+} ions are incorporated in silica matrix by sol–gel processing. The nanocrystallite size estimated from the absorption spectrum agrees with that obtained from the TEM micrograph. The excitation spectrum shows
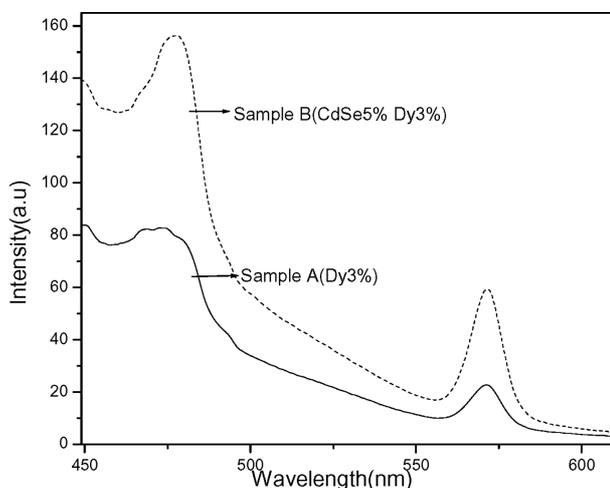
Figure 5. Fluorescence spectra of samples taken at an excitation wavelength ($\lambda_{\text{exc}} = 480$ nm).

strong f–f transitions of dysprosium ions in the presence of CdSe nanoparticles. The fluorescence intensity of Dy^{3+} increases in the presence of CdSe nanocrystallites. This enhancement is attributed to the nonradiative energy transfer of electron–hole recombination of the CdSe nanoparticles to Dy^{3+} ion.

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