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Size dependent effect of electron-hole recombination of CdS quantum dots on emission of Dy^{3+} ions in boro-silicate glasses through energy transfer

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ABSTRACT

The glass system SiO_2-B_2O_3-ZnO-Na_2O-K_2O-CdS with addition of Dy^{3+} ions was synthesized by using conventional melt-quench method. The CdS quantum dots in a glass matrix was studied using optimized heat treatment schedule. The growth of quantum dots was confirmed by optical absorption (UV–Vis), X-ray diffraction (XRD) and High resolution transmission electron microscopy (HRTEM). The optical absorption and luminescence were studied for these glasses. The photoluminescence spectra shows energy transfer between CdS quantum dots and Dy^{3+} ions. Because of quantum confinement, CdS QDs emits light as a result of electron hole recombination and some energy is transferred to nearest energy level of the Dy^{3+} ions to give combined emission due to recombination of electron-hole and electronic transitions (i.e. $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$) of Dy^{3+} ions.

1. Introduction

In recent years synthesis of isolated nanoparticles, clusters or doped particles in collides, polymers and glass matrix has been investigated. Nanoparticles with large surface area to volume ratio changes their optical properties by splitting continuous band structure into series of discrete states, increases surface states and takes part in photoluminescence process [1–3]. Glass matrix is useful host material for rare earth material as well as other impurities like semiconductor materials because of its high transparency, compositional variety, and easy mass production. Transparent glasses doped with nanoparticles promise for potential application in optical devices [4]. Growth of nanoparticles in glass matrix provides stability to nanoparticles by avoiding them to agglomerate at room temperature [5]. Among all glasses, boro-silicate glasses are excellent host matrices in which B_2O_3 acts as an excellent glass former, flux material and expand glass structure at low temperature [6] which support the growth of quantum dots in glass matrix. The choice of minimum adequate temperature and sufficient annealing duration offer favorable conditions for growth of nanoparticles in glass matrix. CdS quantum dots in glass matrix attracts more attention due to potential application in future optoelectronic devices due to tunable electronic band gap, direct band gap, high absorption coefficient, good emission efficiency, high thermal stability and easy to synthesis [2,7,8]. Recently, we have observed that optical properties of glasses can be tuned by controlled growth of CdS QDs in boro-silicate glass system [9]. The addition of rare-earth (RE) oxides in the glasses containing semiconductor quantum dots increases interest in spectroscopic properties because of energy transfer from QDs to RE^{3+} ions [10–12]. In rare earth, emission transitions occur as 4f-4f or 5d-4f and because of this characteristic they serve as an excellent activator [13]. However, direct and indirect band gap semiconductors can be good sensitizing centers due to efficient band to band absorption and their excitation cross sections are very high [14]. Since QDs of semiconductors like CdS, CdSe, ZnO etc. exhibit intrinsic electric dipole moment the energy transfer interactions are possible between QDs of these semiconductors and rare earth ions [11]. Among all rare earth ions, Dy^{3+} ion is known for blue ($^4F_{9/2} \rightarrow {}^6H^{15/2}$) and yellow ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) emissions which is due to 5d–4f transition and the 5d state can easily be affected by the glass matrix environment and on combination of both emissions it can give white light [15,16]. The growth of QDs in a glass matrix doped with rare earth ions changes their optical properties due to combined effect on electron-hole recombination and occurred electronic transitions in energy levels of QDs and rare earth ions respectively

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[7]. In the present work, we have added Dy_2O_3 in our recently reported CdS containing boro-silicate glass and their optical properties have been studied.

2. Experimental

The glass system 41.93 SiO_2: 12.66 B_2O_3: 15.89 Na_2O: 6.52 K_2O: 22.50 ZnO: 0.5 Dy_2O_3 (mole %) with 3 wt% CdS were prepared using a conventional melt quenching technique. All the chemicals were weighed using Shimadzu analytical balance and then mixed in agate mortar and pestle up to 8 h in order to enhance the homogeneity. After mixing thoroughly, the mixture was kept in a platinum crucible and melted in a furnace at 1200 °C for 2 h. The glasses were quenched at room temperature in aluminium mould to get transparent glass. To remove the thermal stresses, quenched glasses were annealed at 300 °C for 4 h and allowed to cool in the furnace up to room temperature. The differential thermal analysis (DTA) measurement of glass sample was carried out using Hitachi TG/DTA7200. The sample in powder form was put in platinum pan and heated up to 700 °C with heating rate of 10 °C/min in nitrogen flow. These glass samples were heat treated with optimized single step heat treatment schedule at 500 °C for 10, 35 and 60 h. The glass samples heat treated at different annealing time are given in Table 1. Growth of quantum dots were confirmed by X-ray diffraction studies using PAnalytical X'Pert Pro. Fourier Transform Infrared (FT-IR) was carried out by using Thermo Scientific Nicolet iS5 Spectrometer with iD5 ATR Accessory. Morphology and elemental analysis of the samples were characterized by field emission-gun scanning electron microscopy (FEG-SEM) and energy dispersive X-ray analysis (EDAX) (JEOL JSM-7600F). The field-emission transmission electron microscope (HR-TEM, JEOL/JEM 2100F) was used for determining the size of quantum dots (QDs) and lattice fringe observation. Optical absorption and PL spectra were recorded by JASCO V-670 Spectrophotometer and JASCO Spectroflurometer FP-8200 respectively.

3. Results and discussion

Synthesized glass samples were characterized with Differential thermal analysis (DTA) to determine the thermal behavior of glass sample. The DTA curve (Fig. 1) of glass sample GR1 shows endothermic (T_g) and exothermic (T_c) curves at 485 °C and 583 °C respectively. The single step heat treatment was optimized and glass sample was heat treated at 500 °C for different time duration to favor the growth of CdS QDs via Ostwald ripening.

Inset of Fig. 2 shows images of as made glass and glass samples heat treated for several hours doped with Dy_2O_3. It is observed from the images that, as made glass sample (GR1) is clear and transparent and the glass samples heat treated at 500 °C for different time duration (i.e. GR2, GR3, GR4 for 10, 35 and 60 h respectively) turned dark yellowish with increase in annealing time. Change in color of glasses with increase in annealing time are due growth of quantum dots in glasses.

Table 1
Experimental and calculated crystallite size of CdS QDs embedded in glass matrix from XRD pattern and band gap.

Sample Name	Heat treatment duration	Crystallite size from XRD (nm)	Optical Band Gap (E_g^{opt}) eV	Crystallite size from Band gap (nm)
GR1	As made glass	–	3.59	1.27
GR2	500 °C for 10 Hrs	2.92	2.78	2.05
GR3	500 °C for 35 Hrs	3.22	2.69	2.30
GR4	500 °C for 60 Hrs	5.65	2.44	4.70

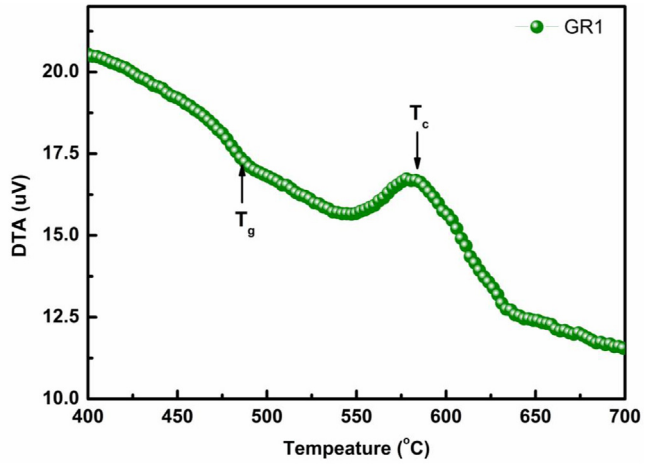

Fig. 1. DTA curve of glass sample.

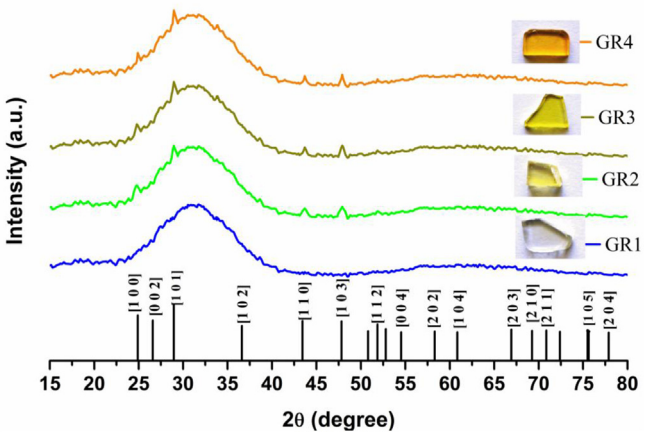

Fig. 2. X-ray diffraction (XRD) pattern of glass samples.

Fig. 2 shows XRD plots of glass samples containing Dy_2O_3. The XRD pattern for GR1 does not show any diffraction peak except halo shape around 20° to 40° because of their amorphous nature. However, CdS phases found to be developed with less intensity in heat treated glasses as amorphous nature dominates the crystalline phases of CdS. XRD results of these samples shows [100], [101], [110] and [103] phases of CdS at 2θ positions around 24.80, 28.96°, 43.71° and 47.97° respectively which are well matched with reference code 01-075-1545. It is also observed that full-width half-maximum (FWHM) decreases and peak intensity increases with increase in heating duration due to the improved crystallinity and grain growth. The crystallite size of the grown crystals as an effect of heating duration is calculated by using Scherer equation and depicted in Table 1.

Among all glasses borate glasses have good ability of structural modifications. The addition of alkali oxides (i.e. Na_2O and K_2O) in borate glasses leads to change in glass network as well as increase in free charge carriers as a function of temperature [6,17]. The glass network containing different size interstices can easily accommodate different size of alkali ions (mixed alkali) than alkali ion of same size (single alkali). The alkali ions in glass sits in more favorable positions therefore more energy required for their movement [18]. In mixed alkali glasses, larger alkali ion (Na^+) jump