

Effect of CdS nanoparticles on photoluminescence spectra of Tb^{3+} in sol–gel-derived silica glasses

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Abstract. CdS nanoparticles doped with Tb^{3+} were synthesized by sol–gel technique. The influence of CdS on the Tb^{3+} glass was studied by UV-Visible and luminescence spectroscopy. The luminescence intensity of the glasses increased significantly in the presence of CdS nanoparticles. Terbium ions excited into the 5D_3 level have a rich emission spectrum in the 400–700 nm range decaying to different 7F_J levels. The intensity of violet and blue luminescence from 5D_3 level is highly dependent on Tb^{3+} concentration, on presence of CdS co-dopant and annealing conditions.

Keywords. Glasses; sol–gel technique; nanoparticles; semiconductors; photoluminescence.

1. Introduction

Rare earth ions doped in glasses find uses in a wide variety of applications (Kelvin 1990; Lifshitz *et al* 1998). Luminescent nanomaterials in the form of nanoparticles or bulk nanocrystals are of interest not only for basic research but also for interesting application (Li and Nogami 1994; Gregorkiewicz and Langer 1999). Preparing nanoscale host materials can change the physical properties of the host materials which affects the luminescence and dynamics of the optically active dopants. High surface-to-volume ratio, local phenomenon such as absorption or change in the surface electronic state may contribute significantly to special properties. Semiconductors and nanoparticles are attractive because their physical properties are different from those of bulk due to quantum size effect. Various methods have been employed to synthesize nanomaterials (Selvan *et al* 1999; Hayakawa *et al* 2000; Mu *et al* 2006). M. Nogami's research group have examined the luminescence behaviour of lanthanide ions doped in sol–gel host. The luminescent complex into porous glasses opens up the possibility of using inorganic species ligands and increasing the luminescence by several orders of magnitude (Reisfeld *et al* 2000). Much studies have been carried out on the preparation and luminescence properties of Tb^{3+} and other rare-earth complexes in sol–gel-derived silica matrix (Silversmith *et al* 2006; Armellini *et al* 2009; Jyothy *et al* 2009). Among them, sol–gel technique is versatile and convenient method of preparing transparent optical material at low temperature. The process involves formation of a gel from liquid organic precursor and water,

and the subsequent drying and annealing of the materials. Glass doped with nanoparticles of semiconductor or metals have been used and are widely investigated for application in photonics. The RE doping with sol–gel glasses and the confinement of RE within nano-porous, interconnected structures in the materials make further attractive application in fabricating advanced nano-device. However, their tendency to cluster around non-bridging oxygen even at low doping level give rise to cross-relaxation between nearby excited ions resulting in non-radiative deexcitation of the ion pair, an effect which drastically reduces luminescence yield from the 5D_3 levels. The main observed consequence of clustering is the quenching of fluorescence proportional to the effective local concentration of RE drastically lowering the efficiency of RE materials. Clustering effect remains as one of the major practical problems keeping RE doped sol–gel glasses from industrial applications. Many rare-earth ions such as Eu^{3+} , Tb^{3+} , Pr^{3+} , Nd^{3+} and Tm^{3+} were doped as absorption and emission centres in glass hosts. Among the rare-earth ions, Tb^{3+} is the most popular efficient luminescent material. Particularly, Tb^{3+} could be used as phosphorous for fluorescent lamp and emission agents, or sensitizing agent for plasma displays. Tb^{3+} -doped phosphor films currently appear to be not only more environment friendly but also more energy efficient than mercury-containing fluorescent lamp. Some reports have observed that luminescence of Eu^{3+} ions can be highly enhanced by interaction of CdS nanoparticles (Selvan *et al* 1999; Hayakawa *et al* 2000; Mu *et al* 2006). Most of the works are based on adsorption of CdS nanoparticles at the surface of doped SiO_2 sol–gel materials after impregnation.

In this paper, we report the synthesis and optical properties of Tb^{3+} ions in the presence of CdS nanoparticles embedded in the silica xerogel. The dependence of the

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luminescence intensity as a function of dopant concentration and photoluminescence at different annealing temperatures are reported as well.

2. Experimental

2.1 Preparation of silica glass co-doped with Tb^{3+} and CdS nanoparticles

Silica gel containing Tb^{3+} and varying concentrations of CdS were prepared by sol-gel process using tetraethylorthosilicate (TEOS) as a glass precursor in the presence of distilled water, methanol and nitric acid (Hazarika and Rai 2004; Bokatial and Rai 2010). The ratio of TEOS to other constituents used in the preparation, viz. doubly distilled water, methanol and dilute HNO_3 was 16:10:70:4 ml, respectively. Firstly, 0.02 M-terbium oxide was dissolved in a mixture of distilled water, methanol and dilute HNO_3 and stirred till terbium oxide got dissolved completely. To this solution 1.6 ml TEOS was added and further stirred. Then $Cd(NO_3)_2$ methanol solution was doped into the solution in first step followed by $SC(NH_2)_2$ methanol solution into the solution as second step and was further stirred till gelation started. Finally, these xerogel were heated in air at different temperature ranges from $100^\circ C$ to $250^\circ C$. Fluorescence and excitation spectra were measured using spectrofluorometer (Horiba Jobin Yvon, FluoroMax-4) and absorption spectra were performed using PD UV-VIS spectrophotometer (S-3100). All recorded spectra were performed at room temperature.

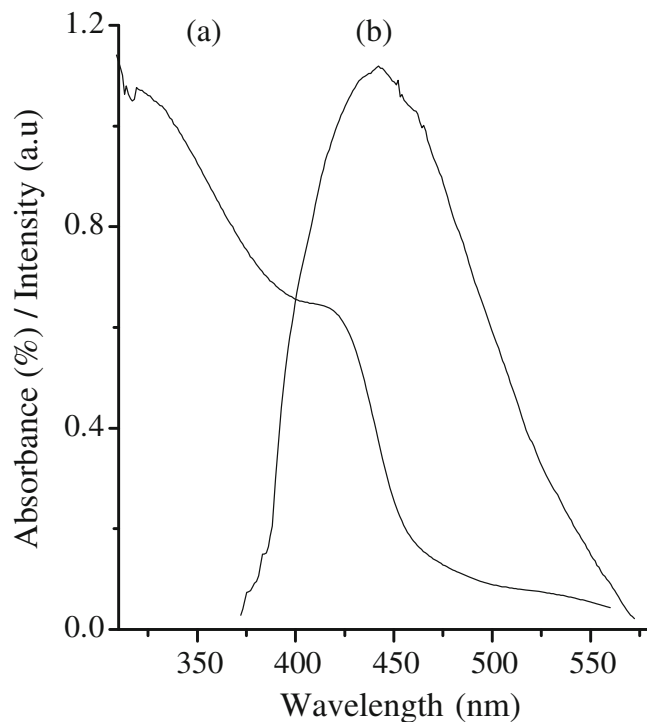


Figure 1. (a) Optical absorption and (b) PL spectra of CdS alone doped glass.

3. Results and discussion

3.1 Absorption and emission spectra of CdS alone doped sol-gel glass

Figures 1(a) and (b) show the absorption and photoluminescence spectra of pure CdS nanoparticles. The absorption band at 424 nm is consistent with the formation of CdS nanoparticles. It is well known that the diameter of the particles is related to the absorption edge. Particles in nanosize regime exhibit quantum confinement effect, the evidence of which is a blue shift in the optical spectrum. The blue shift of the bandgap energy is described by effective mass approximation (Brus 1986; Kayanum 1988). Bulk CdS is reported to have a broad emission with emission maximum in the 500–700 nm region of luminescence spectrum. The emission is due to recombination from surface defect. The photoluminescence (PL) is shown close to the band edge emission with the maximum at 445 nm. The calculation of the CdS diameter using effective mass approximation (EMA) model gives a value of 4.8 nm. Figure 2 shows the SEM image of CdS nanoparticles. It gives spherical shape, and particles distributed homogeneously.

3.2 Excitation spectrum of Tb^{3+} : CdS

Figure 3 shows the excitation spectra of Tb^{3+} : CdS doped sol-gel glass. We observed five band peaks at 342, 351, 359, 369 and 379 nm and they correspond to the electronic

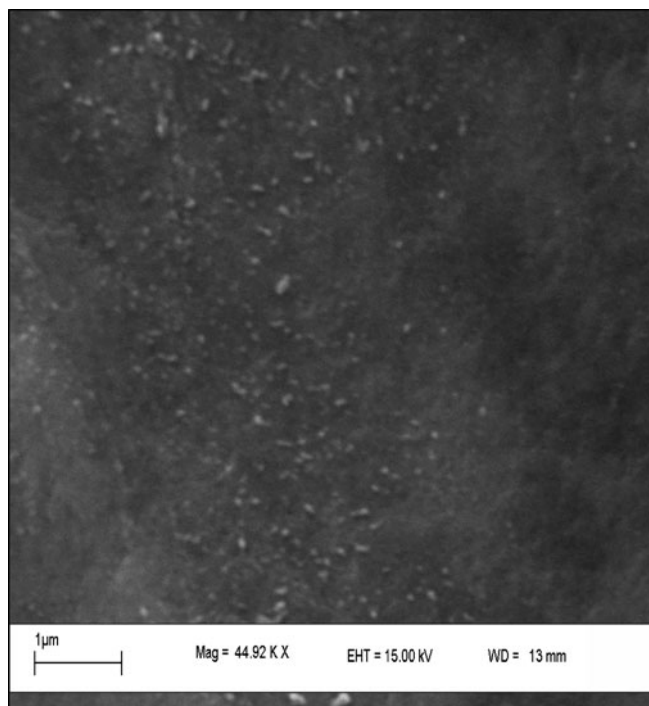


Figure 2. SEM image of CdS nanoparticles.

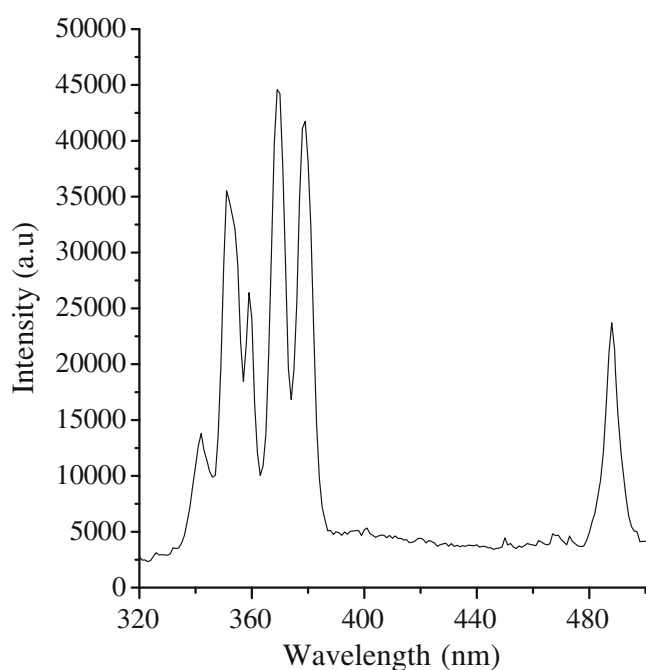


Figure 3. Excitation spectra of Tb³⁺: CdS.

transition of Tb³⁺ ions from the ground state ⁷F₆ to excited states ⁵G₄, ⁵D₂, ⁵L₁₀, ⁵D₃ and ⁵D₄, respectively. The excitation was monitored at 544 nm.

Tb³⁺ emission usually consists of a series of transitions around an intense emission at 544 nm and hence promises as green phosphors (Shionoya 1999). With an atomic number of 65, neutral terbium (Tb) has an electronic configuration of [Xe]4f⁹6s². The 4f shells remain unfilled, which means that the electrons in the 4f shell are optically active. This shielding produces narrow spectral lines, long fluorescence lifetimes and energy level that are relatively insensitive to their host environment because the optically active electrons interact weakly with the ions environment. Figure 4(a) shows a partial energy level diagram of Tb³⁺ with level transition that corresponds to observed fluorescence line between 400 and 650 nm (as in figure 4(b)). Terbium ions excited to ⁵D₃ level have a rich emission spectrum in the 400–470 nm region; decaying to the different ⁷F_J levels that make up the ground state (see figure 5). To measure the emission spectrum we excite ions to the level directly by using 370 nm, but observed a large ⁵D₄ population, due to cross-relaxation. The observed emission spectrum indicates that the probability of cross-relaxation is higher than the probability of radiative emission since the integrated intensity of the ⁵D₄ transition is significantly greater than the integrated intensity of ⁵D₃ transitions. There are, in particular, two quenching processes that are characteristic problem of using sol-gel glasses, i.e. concentration quenching via cross-relaxation and non-radiative vibrational excitation of hydroxyl (OH) groups.

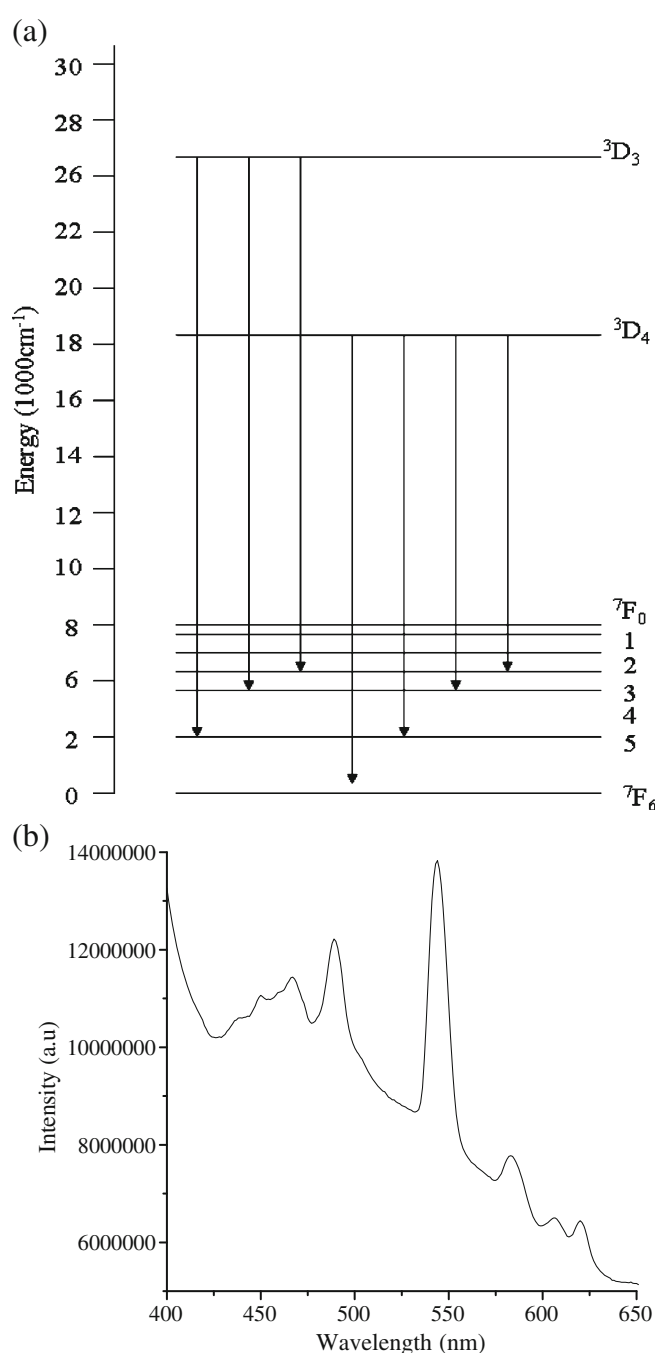


Figure 4. (a) Partial energy level diagram of Tb³⁺ with levelled transitions and (b) fluorescence spectrum of Tb³⁺ transitions.

3.3 Effect of CdS nanoparticles on PL of Tb³⁺ doped silica glass

In order to investigate the effect of CdS concentration on photoluminescence properties of the sample, different concentrations of CdS were co-doped with Tb³⁺. The emission spectra of Tb³⁺ with and without CdS doped sample having different concentrations of CdS were measured under the excitation wavelength of 370 nm, as shown in figure 5.

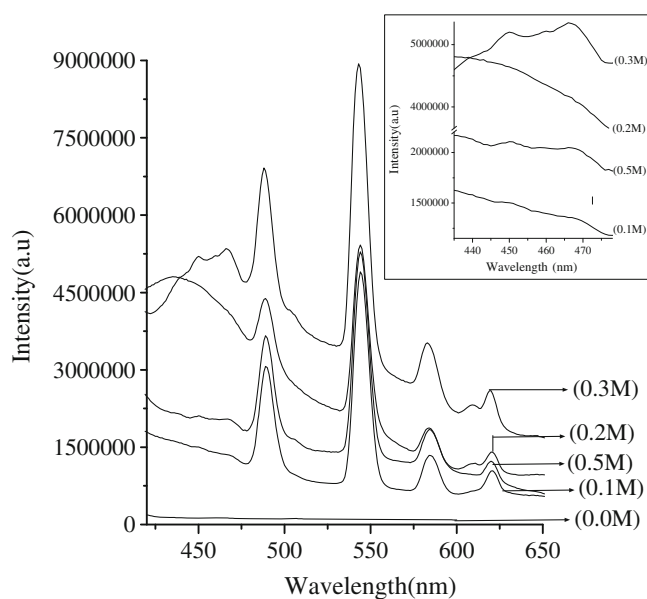


Figure 5. PL spectra of $\text{Tb}^{3+}:\text{CdS}$ with different concentrations of CdS.

Emission spectra of $\text{Tb}^{3+}:\text{CdS}$ ions in silica glass consist of two groups of emission band: transition from the 5D_4 excited level to the 7F_J manifold of the ground state, and the transition from 5D_3 excited level to the 7F_J manifolds of the ground state. Because of multiphonon relaxation from higher excited level 5D_3 to 5D_4 has a high probability; the emission intensity from 5D_4 level to the 7F_J manifolds of the ground state is much higher than that from the 5D_3 level to the 7F_J manifolds. The $\text{Tb}^{3+}:\text{CdS}$ doped xerogel shows different luminescence bands belonging to the $^5D_3 \rightarrow ^7F_4$ (450 nm), $^5D_3 \rightarrow ^7F_3$ (466 nm), $^5D_4 \rightarrow ^7F_6$ (489 nm), $^5D_4 \rightarrow ^7F_5$ (544 nm), $^5D_4 \rightarrow ^7F_4$ (585 nm) and $^5D_4 \rightarrow ^7F_3$ (621 nm). We observed drastic changes in the luminescence intensity as we varied the CdS concentration. Increasing the CdS concentration from 0.1 M% to 0.3 M% increases the luminescence intensity, whereas increasing the concentration of CdS further decreases the intensity. The possible explanation is that CdS nanoparticles doped in the network of $\text{SiO}_2\text{-Tb}^{3+}$ xerogel would increase the concentration of Si dangling and oxygen vacancy in the network of the silica xerogel (Yang *et al* 2001). In this way, more electron or hole can be easily excited and radiant recombinations are increased. Subsequently the emission intensity of the doped sample markedly increased. Moreover, the band edge emission of CdS nanoparticles themselves should be one of the contributing factors. The intensity of 5D_3 emission relative to 5D_4 lines decreases dramatically with increase in the concentration of CdS, as shown in the inset of figure 5, confirming the presence of stronger cross relaxation induced quenching. When the concentration of CdS nanoparticles were increased further (0.5 M), we observed that emission intensity declined, which may be due to the clustering of CdS nanoparticles. The weak

emission of $\text{Tb}^{3+}:\text{SiO}_2$ above 0.3 M concentration of CdS was probably due to defect concentration in the network of silica xerogel which blocked the energy transfer between the defect and Tb^{3+} ion. Similar result was observed by Mu *et al* (2006) in $\text{Eu}^{3+}\text{-SiO}_2$ sol-gel glass.

3.4 Annealing temperature effect

The photoluminescence (PL) emission spectra of $\text{Tb}^{3+}:\text{CdS}$ doped SiO_2 glasses annealed at different temperatures were measured by excitation wavelength of 370 nm as shown in figure 6. The emission transition attributed to the $^5D_{3,4} \rightarrow ^7F_J$ ($J = 1, 2, 3, 4, 5, 6, 7$) transition of Tb^{3+} ions. The most intense band at 544 nm is assigned to be $^5D_4 \rightarrow ^7F_J$. This band is usually much strongly affected by host. It is found that the PL line positions are not affected by annealing temperature. This is because the PL lines caused by transitions have $4f-4f$, and $4f$ -orbital electrons are well shielded by the $5s, 5d$ outer shells. Thus, the PL position originated from $f-f$ transitions are hardly affected by external factors.

In addition, the intensity of $\text{Tb}^{3+}:\text{CdS}$ emission increases with annealing temperature and reaches to a maximum at 150°C , and then decreases as the annealing temperature increases. This result can be explained as follows. In the process of heat treatment, the concentration of hydroxyl groups (OH) that are present in the glass will decrease; also during the annealing process various defect centres were formed by the hydrolysis and condensation of alkoxy silane precursor. On the one hand, a strong electron-photon coupling caused the emission. As the CdS particles are in nanometer size, we cannot ignore the existence of the electron or hole-trapped surface level on CdS particles. Because most of the ions of

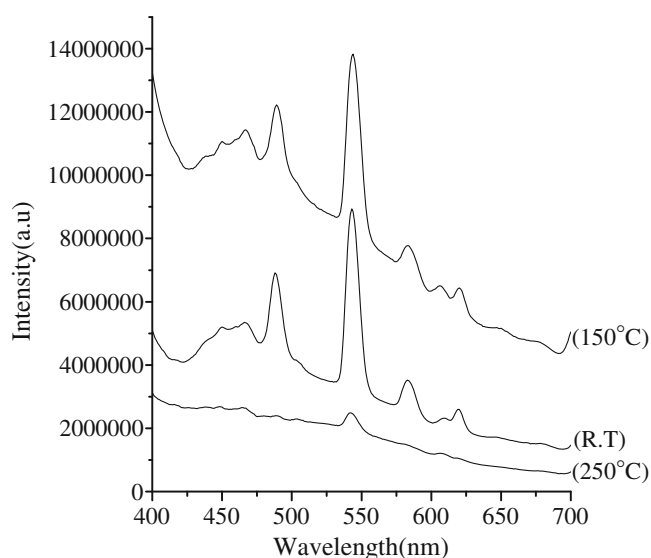


Figure 6. PL spectra of $\text{Tb}^{3+}:\text{CdS}$ with different annealing temperatures.

the nanoparticles are located on the surface and they are non-saturated in coordination, electrons or holes may be excited easily and escape from the ions. On the other hand, the influence of high energy vibration of hydroxyl group on the emission of Tb³⁺ ions was decreased and the releasing energy from electron and hole produced by defect recombination was transferred to the Tb³⁺ ions that were embedded in the network of silica xerogel and thus led to the improvement of Tb³⁺:CdS surroundings. As a result, more efficient luminescent centre is formed and the emission intensity increases with annealing temperature (Mu *et al* 2006). With increasing annealing temperature an extra unassigned peak of low intensity appeared at 610 nm at 150°C. Further increase in the annealing temperature may result in the formation of Tb³⁺ cluster or may decrease the defect concentration in the network of silica xerogel, which blocked the energy transfer between the defects and Tb³⁺ ions, and this effect may be predominant in high annealing temperature, and the emission intensity decreased.

4. Conclusions

By means of photoluminescence spectroscopy we observed enhanced luminescence of Tb³⁺-doped CdS nanoparticles embedded in SiO₂ amorphous matrices. This might be of interest for potential applications such as phosphor materials for light emitting devices. We observed drastic changes in luminescence characteristic as we vary CdS concentrations and annealing temperature. On increasing CdS from 0.1 M% to 0.3 M%, the luminescent intensity increases and on changing the concentration above 0.3 M% the intensity decreases.

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