



Structural and Spectroscopic Study of CdS Quantum Dots in Glass Matrix

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Abstract

The present work is the investigation of quantum dot–glass nanosystems by confining nano cadmium sulfide in designated glass. The CdS quantum dots were grown in a special glass matrix, which involved a sequence of steps. The obtained glass was of uniformly bright yellow in color. X-Ray diffraction pattern confirms the amorphous nature of glass samples. We report the synthesis of the CdS doped silica glass, growth of semiconductor nanocrystallites which is essentially striking temperature dependent. We also present the change in the optical property and the corresponding band gap variations. It has been observed that the steepness in the UV cut off is dependent on thermal treatment, crystal size and distribution of semiconductor nanocrystals.

Keywords: Cadmium sulfide, doping, nanocrystals, glass, UV-Vis, semiconductor

INTRODUCTION

Today nanostructured materials and quantum dots have immense importance in the field of optoelectronics and biomedical. The quantum dots in solution have been effectively used in LED, solar systems and biomedical applications. Quantum dots are generally unstable and attempts have been made to stabilize these quantum dots using glass and polymer matrix. Semiconductor doped glasses (SDGs) have become



interesting in the past few years due to their nonlinear optical characteristics¹⁻⁴. The optical and thermal properties of semiconductor nanoparticles can differ dramatically from those of bulk material of the same composition. Semiconductor particles with diameter in the order of 10nm or less are small enough to confine the electron and holes in all three directions and are referred to as quantum dots. When the particle size is reduced below the bulk exciton diameter, quantum confinement and size dependent Coulomb interactions, affect both optical transition energies and matrix elements. The properties of such nanoparticles are intrinsically interesting, allowing us to test models for size-dependent electronic and structural effects. Semiconductor nanoparticles also have potential applications for linear and nonlinear optical devices⁵⁻⁷. Kale et al.,⁸ have reported the preparation of confinement of nano CdS in designated glass a novel functionality of quantum dot-glass nanosystems in solar hydrogen production. Chemical leaching with HCl studies demonstrate that the 2.5 nm size CdS quantum dots distribute homogeneously in a mono dispersed form in the glass domain and on the surface with a "partially embedded exposure" configuration. This disposition imparts an excellent photo stability against photo corrosion and also a facile catalytic function. In the past, CdS/CdSSe embedded silicate glasses have been studied but their application is limited to its optical and photonic properties⁹⁻¹⁴. They have been used for fabrication of integrated optical structures, optical circuits with fast switching time (below 10^{-14} s), planar channel waveguides, optical modulators and electro-optical switches¹⁵⁻¹⁹. In literature emphasis was given on the characterization of the glasses rather than compositional study. The dissolution of semiconductors in glass matrix is a critical phenomenon which entirely depends on the base glass compositions. These glasses are colourless after glass making process and obtain their colour only after reheating. The size and shape of the tiny microcrystals depends on the glass composition. Here, we have investigated new glass composition and studied the size quantization effect. In the present investigation, new glass composition has been tailored and the tiny nanocrystals of CdS were developed thermally in glass matrix at different temperatures. The glasses obtained were characterized for optical cut offs using UV-Visible spectrophotometer and the optical properties were studied accordingly.

EXPERIMENTAL

Raw Materials :

The CdS doped glasses of various compositions were prepared by conventional melt-quench technique using analytical grade compounds SiO_2 , H_3BO_3 , MgO , Na_2CO_3 , K_2CO_3 , ZnO , TiO_2 , CdS and Starch as starting materials.

Synthesis :

The new glass composition 54SiO_2 , $08\text{Na}_2\text{O}$, 04MgO , $08\text{B}_2\text{O}_3$, $08\text{K}_2\text{O}$, 12ZnO , 06TiO_2 , 01Starch , CdS dopant 0.5-0.8% was used for the study. The different raw materials were weighed as per the above composition and mixed in pestle mortar to



obtain homogeneous charge. The amount of semiconductor dopants like CdS were selected depending on the type of filter and added into the composition followed by further mixing. The composition prepared was taken in recrystallized alumina crucible and melted in an electrically heated muffle furnace at 1200-1300°C. The melt was soaked for the period of 3-4 hrs. After refining, the glass melt was quenched in air on hot brass plate and processed immediately for annealing. The glass was annealed in programmable furnace at its transition temperature (T_g) i.e. 470-480°C and slowly cooled to room temperature to remove the residual stresses. The glass samples were heat treated at 550, 575 and 600°C for time 6hrs for crystal growth. The glass obtained was polished with emery papers of different grades. The melting of optical quality glasses for optical system is quite difficult because of its high requirement of homogeneity. To achieve good homogeneity, good melting facility is essential. The melting of the semiconductor doped glasses is quite critical than the normal optical glasses. Many compositions have been melted and few of them were optimized. Among the compositions optimized, the composition containing silica content 54% has shown good homogeneity. The same composition has been selected for making glasses. The glass were prepared by following the above method and characterized by various techniques.

Characterization :

The glasses thus obtained were characterized further. Prepared glasses were characterized by X-ray diffraction technique to check for possible crystallinity of glasses. Using X-ray diffractometer (model, Rigaku Miniflex II Desktop) with CuK radiation the XRD patterns were recorded in the 2θ range 20-80 degree with scanning rate 10/mint. The UV visible optical transmission for glass samples were measured by using double beam spectrophotometer (UV-3600, SHIMADZU, UV-VIS-NIR-Spectrophotometer) covering the range 200-800nm.

RESULTS AND DISCUSSION

Structural Study :

X-ray diffraction patterns were obtained using Rigaku Model and Diffraction scans over a range of 2θ from 20– 80° for CdS doped glass striked at 600°C are shown in fig.1. The overall XRD pattern illustrates the broad peak at $2\theta \sim 27^\circ$ which confirms the amorphous nature of the glass. There is slight shift observed which may be due to the higher content of ZnO and B₂O₃. In this glass, one relatively diffuse peak was observed on a sloping background, which implies the nanocrystalline nature of CdS. Since silica is a major constituent in the glass, the growth of quartz is quite obvious. This is the clear indication of amorphous nature within the resolution limit of XRD instrument.

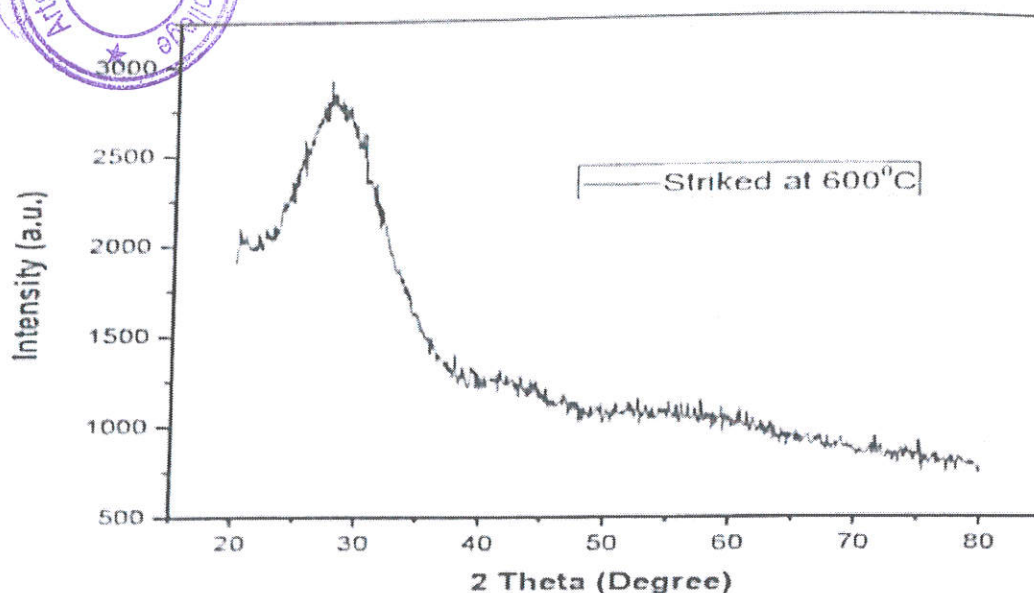
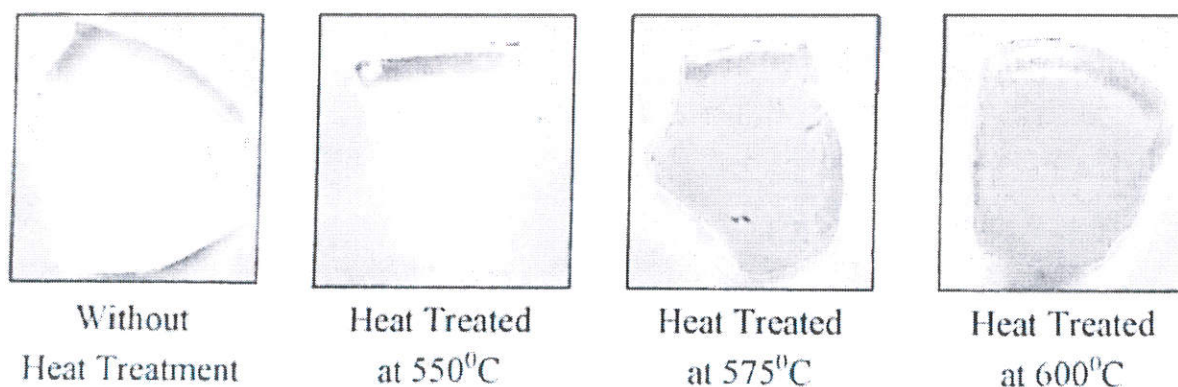


Fig.1 XRD pattern of 0.6% CdS doped glass struck at 600°C for 6 hr



Photographs of Cadmium Sulfide (CdS) Doped Glass Nanocomposite

Spectroscopic Study :

Fig.2 show the behavior of all glass samples heat treated at 550, 575 and 600°C at for time 6hrs respectively. It can be clearly seen that the striking conditions are dependent on the quenching time of the glass. It is also observed that the shape of the absorption edge becomes steeper with time and the edge is shifted to the red. UV- cut off at 441nm was obtained for the glass without heat treatment. This is because of slight crystallization of the CdS nanocrystallites occurring during quenching time. The CdS may be in the semi-amorphous state which is confirmed by the XRD. The glasses doped with CdS (Fig.2) shows absorption edge behavior even though the shapes of the edges differ slightly. At striking temperature 550, 575 and 600°C, the absorption cut off reaches up to 427nm, 464 and 482nm respectively in 6hrs. The longer heat

treatment at lower temperatures has no significant effect. The red shift in the band gap is due to quantum confinement effect. There must be optimum time at particular temperature where a semiconductor doesn't grow beyond particular size. But it was observed that the particle density and uniformity is better if samples are heat treated for longer time, initially at low temperature, which can be attributed to better nucleation. This has been observed in all type of glass samples. Fig 2 shows that with striking temperature, the absorption edge is shifted to longer wavelength. From the absorption edges at different temperatures the band gap was calculated which has been summarized in table.1. From the results it was clearly seen that the band gap is decreasing with shift in absorption edge at longer wavelength. The steepness is due to uniform size of the crystallites of semiconductors. The growth of nanocrystals is well known in glass matrix. Semiconductor micro crystallites grown in the glass matrix impart strong optical nonlinearities to the glass. Due to this interesting property these glasses are gaining wider acclamation in the field of optoelectronics. Their much emphasized application is as an optical cut off filter. Band gap values at the respective UV cut offs and %T given in table 1.

Table 1. Band gap of different CdS Doped Glass Nanocomposite

Sr. No	Sample Code	Composition X Mole %	% T	UV cut off (nm)	Band Gap in eV
1	SCdS-2D	0.6	86	441	2.811
2	SCdS-2D-550°C	0.6	84	427	2.903
3	SCdS-2D-575°C	0.6	87	464	2.672
4	SCdS-2D-600°C	0.6	82	482	2.572

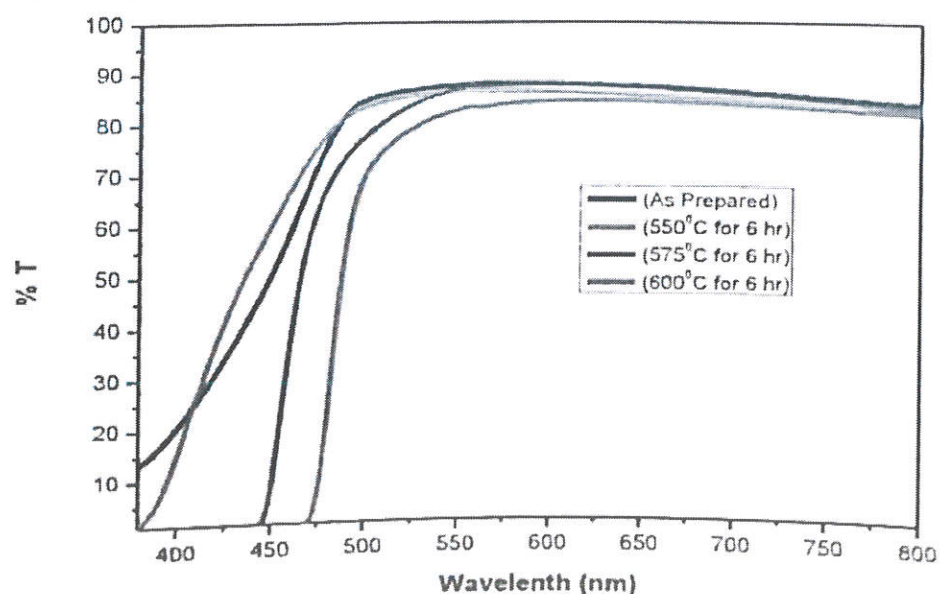


Fig.2. UV-Vis Spectra of CdS Doped Glass Nanocomposite

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