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# Nanostructured CdS/CdSSe glass composite for photonic application

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**Abstract.** The present work describes the synthesis of CdS/CdSSe glass nanocomposites and its characterization. A few glass compositions were optimized and the optimized host glass was remelted along with different semiconductors like CdS and CdSSe at high temperature. The CdS/CdSSe is present in amorphous state in the glass matrix. The thermal treatments have been carefully optimized to obtain well-defined uniform crystal growth of CdS and CdSSe. The glasses with optimized conditions were fabricated and characterized thoroughly using UV, TG/DTA and TEM. The shift in absorption edge to the longer wavelength with heat treatment implies the increase in the crystal size. The band gap has been increased with decrease in the particle size. Crystal size of semiconductors obtained by TEM was 2.5–5 nm for the glass showing absorption edge cut-off at 475 nm (CM-475).

**Keywords.** Nanocrystal; glass; composite; photonics; nanotechnology.

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## 1. Introduction

Semiconductor-doped glasses (SDGs) have attracted great interest in the past few years due to their nonlinear optical characteristics [1–4]. The potential applications of these glasses are in the field of optoelectronics and optical cut-off filters. The optical properties of these glasses depend on the size and shape of the semiconductor nanocrystals. Semiconductor particles with diameters below 10 nm exhibit a well-known quantum size effect which is the origin of many linear and nonlinear optical properties useful in optoelectronics and optical switching devices [5–7]. The CdS-, CdSSe-doped glasses are colorless when made by the usual glass making process [7] and attain color only after reheating. The growth of semiconductor nanocrystals embedded in glass matrix occurs via the process of nucleation and crystal growth mechanism, which imparts color to the glasses.

In the present investigation, new glass composition has been tailored and the nanocrystals of CdS/CdSSe were grown thermally in glass matrix at different temperatures and time intervals. By using this composition, optical cut-off filters having sharp cut-off at 475 and 515 nm were fabricated keeping in view the possible photonic application of these glasses.

## 2. Experimental

The new glass composition $55SiO_2$, 2–7$Na_2O$, 20–30$K_2O$, 5–10ZnO, 1–8$B_2O_3$, 1$TiO_2$, 4–8BaO, was used for the study. The composition was homogenized with CdS (2%) for optical cut-off at 475 nm and CdS : Se (0.9 : 0.1) for 515 nm. The composition was weighed, mixed and was taken in recrystallized alumina crucible and melted in an electrically heated muffle furnace (Thermolyne-U3200) at 1300–1500°C. The melt was soaked for 3–4 h. During soaking time, the molten glass was stirred 3–4 times to achieve homogeneous distribution of semiconductors by using a special type of ceramic rod, which is thermally stable at high temperature. 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. 570–580°C and slowly cooled to room temperature to remove the stresses. The glass obtained was polished with emery papers of different grades, i.e. 120, 240, 320$\mu$ on glass polishing machine. The polished glass samples were heat treated at different temperatures (550, 575, 600°C) for crystal growth. The glass sample with the absorption edge cut off at 475 nm using CdS (doping) is termed as CM-475 and the glass sample with the absorption edge cut off at 515 nm using CdSSe (doping) is termed as CM-515.

The glasses obtained were characterized by different techniques. The optical characterization was carried out using UV-visible spectrophotometer (Hitachi, U-3210 Spectrophotometer). Thermal properties were studied by differential scanning calorimetry (Mettler Toledo DSC-7) to determine glass transition temperature ($T_g$) and thermomechanical analyzer (Perkin-Elmer TMA-7) was used to determine the thermal expansion coefficient of the glass. The particle sizes of CdS and CdSSe were measured using TEM (JEOL 100 CX).

## 3. Results and discussion

The melting of optical quality glasses for optical system is quite difficult because of its high requirement of homogeneity. Many compositions have been melted and few of them were optimized. Among the compositions optimized, the composition containing 55% (by weight) silica content has shown good homogeneity. The same composition has been selected for making optical cut-off filters CM-475 and CM-515.

### 3.1 *Optical properties*

Figure 1 shows the behavior of the absorption edge of CM-475 glass, depending upon the striking process. The sample of glass (CM-475) was treated at different temperatures. Curve ‘a’ corresponds to a sample without heat treatment; curves ‘b–d’ correspond to heat treatments at 550, 575 and 600°C respectively for 20 h. It can be clearly seen that, the shape of the absorption edge becomes steeper with higher temperature and that the edge is shifted to the red. It was also observed that the striking conditions depend on the quenching time of the glass. The glass without heat treatment shows optical cut-off at 397 nm. This is because of the slight crystallization of the CdS nanocrystallites during quenching. The glasses doped with CdSSe (not shown) show similar absorption edge behavior even though the shapes of the edges differ slightly. Figure 2 shows a sharp cut-off at 475 nm for CM-475 glass (unpolished) which is prepared at a little larger scale (3 inch dia.). From the absorption edges of CM-475 at different temperatures, the band gaps were calculated which are summarized in table 1. From the results of CM-475, it was clearly seen that the band gap is decreasing with the temperature. Since the crystal size increases with striking temperature the band gap also decreases. In the case of CdS-doped glass, the absorption cut-off attained up to 495 nm beyond which there was a precipitation. There must be an optimum time at a particular temperature where a semiconductor does not grow beyond a particular size. But it is observed that the particle density and uniformity are better if samples are

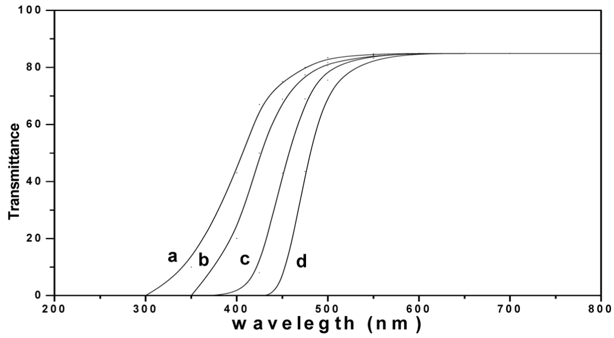


**Figure 1.** UV–visible spectra of the glass filter CM-475 heat treated at various temperatures (a: As-prepared, b: 550°C, c: 575°C, d: 600°C).

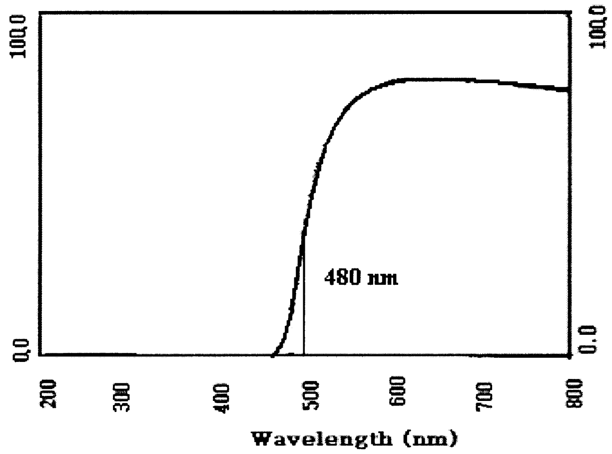


**Figure 2.** UV–visible spectra of the unpolished glass filter CM-475 (3 inch dia.).

**Table 1.** Effect of striking temperature on UV-cut off and band gap of CdS.

| Glass filter | Striking temperature (°C) | Wavelength (nm) | Band gap (eV) |
|---|---|---|---|
| | Without striking | 397 | 3.0158 |
| CM-475 | 550 | 418 | 2.864 |
| (CdS) | 575 | 450 | 2.660 |
| | 600 | 475 | 2.530 |
| CM-515 | 550–575–600 | 515 | 2.40 |

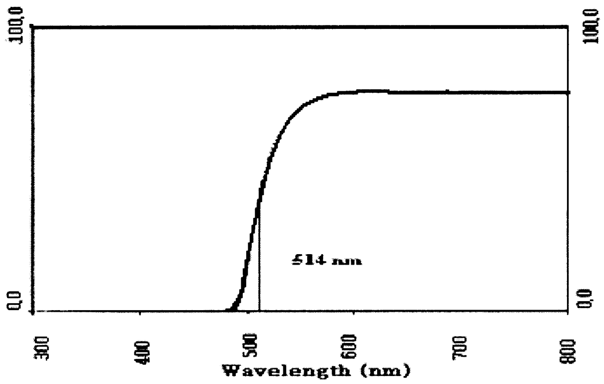


**Figure 3.** UV–visible spectra of the glass filter CM-515.

heat treated for longer duration. Figure 3 shows UV–visible spectrum of CM-515 glass. This glass was prepared using CdS and Se in host glass composition. The absorption cut-off is obtained at 515 nm due to *in-situ* growth of CdSSe after the complete heat treatment cycle. The steepness of the absorption curve indicates uniform size distribution of the embedded semiconductor nanocrystallites. The shift in the energy of onset of absorption is consistent with the band-gap shift that varies with selenium fraction within the $CdS_xSe_{1-x}$ mixed anion system.

### 3.2 *Morphology*

The size and morphology of the semiconductor nanocrystals such as CdS were demonstrated by FESEM and TEM techniques. Figure 4 represents the FESEM of the polished CM-475 glass filter. Since the particle size of CdS nanocrystals was less than 10 nm, TEM analysis was undertaken. Figure 5 represents the TEM micrograph of the CM-475 glass filter. TEM shows the presence of CdS crystallites with the sizes ranging from 2.5 to 5 nm [8,9].

### 3.3 *Other properties of filters*

The other properties of CM-475 together with the undoped glass are summarized in table 2. DSC showed that $T_g$ of these glasses are 580 and 575°C respectively and

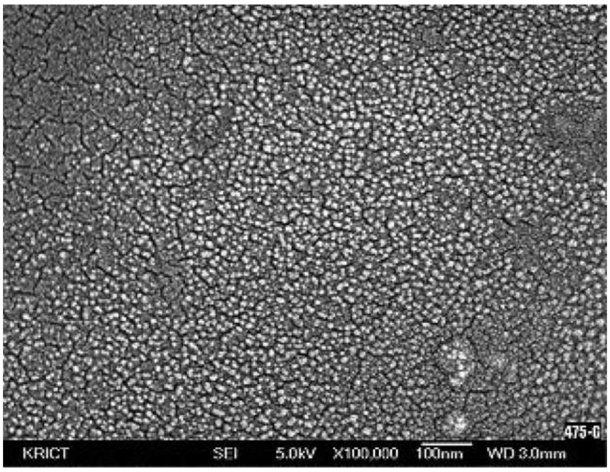


**Figure 4.** FESEM image of the glass filter CM-475.

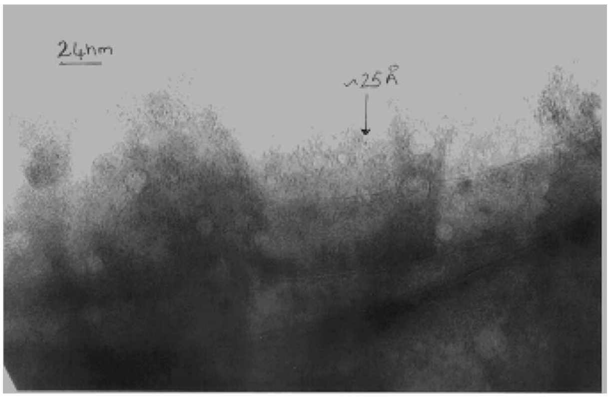


**Figure 5.** TEM image of the glass filter CM-475.

**Table 2.** Properties of host glass and glass filter.

| Properties | Host glass | CM-475 |
|---|---|---|
| Density (g/cc) | 2.5–3 | 2.5–3 |
| Transition temperature ($T_g$ in °C) | 575 | 580 |
| Thermal expansion ($10^{-6}$/K) | 10.5 | 11 |
| Refractive index | 1.543 | 1.563 |
| Absorption edge cut-off (nm) | – | 475 |
| Chemical stability | Good | Good |

TMA showed thermal expansion at around $11 \times 10^{-6}$/K. There was no significant change in thermal properties after the growth of semiconductors. This may be because of the low concentration of semiconductors, i.e. <1%. The density of the glasses observed is in the range 2.5–3 g/cc where there was no change after crystal growth. Since the same host glass has been used for CM-515 filter, we have not measured the other properties of CM-515.

## 4. Conclusions

The glass composition was optimized and the nanocrystals of CdS/CdSSe were grown thermally in glass matrix at different temperatures. No appreciable change was observed in thermal properties after crystal growth in the glass when compared to host glass. The crystal size of semiconductors obtained by TEM was 2.5–5 nm for the glass filter CM-475. From the TEM picture, it is quite clear that all crystallites of CdS are uniformly distributed in the glass matrix. From the results of CM-475, it was clearly seen that the band gap is decreasing with the striking temperature and time. Since the crystal size increases with striking temperature the band gap also decreases [8,9]. The steepness of the UV cut-off is related to a uniform crystal size and uniform distribution of nanocrystals of semiconductors in the glass matrix. CM-515 was fabricated using CdS and Se and steep absorption edge was observed at 515 nm.

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