CdS/CdSSe quantum dots in glass matrix

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Abstract. The compositions containing 55 and 60% of silica have been formulated for preparation of glass filters having sharp cut-off at 475 and 575 nm. To achieve cut-off at these wavelengths, the glasses have been doped with CdS/CdSSe and melted at 1200–1300°C. The glass samples were transparent and pale yellow in colour due to presence of CdS/CdSSe tiny nano crystal (Q-dots). *In situ* growth of CdS/CdSSe nano crystals imparts the yellow/orange/red colour to these glasses. Optical study shows that as prepared glasses have optical cut-off in the range 350–370 nm. The linear crystal growth of CdS/CdSSe in glasses exhibits red shift in optical cut-off. The optical filter having cut-off at 475 nm can be prepared by doping CdS and cut-off filter of wavelength 575 nm by CdSSe. The TEM results show that the CdS/CdSSe nano crystals (Q-dots) ranging from 2–5 nm are uniformly distributed into the glass matrix.

Keywords. CdS; CdSSe; nanocrystals; glasses; optical filters.

1. 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 attracted great interest in the past few years due to their nonlinear optical characteristics. The potential application of these glasses are in the field of optoelectronics and optical cut-off filters (Ekimov and Onushchenko 1981; Borrelli *et al* 1987; Potter and Simmons 1988; Hache *et al* 1989; Santhi and Trojanek 2005). The optical properties of these glasses depend on the size and shape of the semiconductor nanocrystals. Semiconductor particles below 10 nm in diameter exhibits a well known quantum size effect which is the origin of many linear and nonlinear optical properties useful in optoelectronics and optical switching devices. The CdS, CdSSe-doped glasses are colourless when made by the usual glass making process (Persans *et al* 2001) and obtain their colour only after reheating. The growth of semiconductor nanocrystals embedded in glass matrix occurs via the process of nucleation and crystal growth mechanism, which imparts colour to the glasses. 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 devices (Ekimov *et al* 1993; Norris *et al* 1994; Persans *et al* 2001). Many researchers have given emphasis on the characterization of the glasses rather than compositional study. However, very few of them have studied the crystal growth kinetics of these types of glasses with different glass compositions. The dissolution of CdS and CdSSe in glass matrix is a critical phenomenon, which entirely depends on the base glass composition. In the present investigation, new glass composition has been tailored and the tiny 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 575 nm in UV-visible were fabricated in order to study the possible photonic application of these glasses.

2. Experimental

2.1 Glass preparation

The new glass composition, 55 SiO₂, 2–7 Na₂O, 20–30 K₂O, 5–10 ZnO, 1–8 B₂O₃, 1 TiO₂, 4–8 BaO, was used for the study. The different raw materials were weighed as per the above composition and mixed in pestle mortar to obtain homogeneous mixture. The amount and type of dopants like CdS, Se, S 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 (Thermolyne-U3200) at 1300–1500°C. The melt was soaked for 3–4 h. During soaking

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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 μ on glass polishing machine. The polished glass samples were heat treated at different temperatures for crystal growth and repolished again.

2.2 Characterization

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

3. Results and discussion

The melting of optical quality glasses for optical system is quite difficult because of its 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 have optimized. Among the compositions optimized, the composition containing silica content 55% and 60% (by weight) has shown good homogeneity (Persans *et al* 2001). In the present study these same compositions have been selected for making optical cut-off filters.

At optimized conditions the glasses were prepared, polished and filters having cut-off at 475 and 575 nm were fabricated. The glass filter (samples) having cut-off wavelength of 475 nm are hereafter referred to as CM-475 and samples having cut-off wavelength of 575 nm are referred to as CM-575. The results of these glasses are summarized in table 1. DSC showed T_g of these glasses at 575–580°C and TMA showed thermal expansion at around $11 \times 10^{-6}/K$. There was no significant change in thermal properties after growth of semiconductors. This may be because of the low concentration of semiconductors i.e. <1%. The density of the glasses observed in the range 2.5–3 g/cc where there was no change after crystal growth.

3.1 Optical properties

Figure 1(a and b) depicts the behaviour of the optical absorption of glasses, CM-475 and CM-575, at different temperatures. The glass, CM-475, was heat treated at different temperatures for 8 h.

Table 1. Properties of glass filters.

Properties	CM-475	CM-575
Density (g/cc)	2.5–3	2.5–3
Transition temperature (T_g in °C)	580	574
Thermal expansion ($10^{-6}/K$)	11	11
Refractive index	1.563	1.563
Absorption edge cut-off (nm)	475	575
Chemical stability	Good	Good

Figure 1. UV-visible transmission spectra of glass filter **A.** CM-475 nm, heated at various temperatures: a. RT, b. 550°C, c. 575°C and d. 600°C for 8 h and **B.** CM-575 nm heated at various temperatures: a. RT, b. 550°C, c. 575°C and d 600°C.

Table 2. Optical cut-offs and bandgap at different striking conditions.

Glass filter	Striking temperature (°C)	Wavelength (nm)	Bandgap (eV)
475 nm (CdS)	Before striking	397	3.12
	550	418	2.97
	575	450	2.76
	600	475	2.61
575 nm (CdSSe)	Before striking	450	2.76
	550	497	2.49
	575	549	2.26
	600	575	2.16

Curve 'a' in the UV spectra corresponds to sample that was without heat treatment; curves b–d correspond to glass sample heated to 550, 575 and 600°C, respectively. It can be clearly seen that the shape of the absorption edge becomes steeper with increasing striking temperature. This suggests that the crystal size of CdS was increasing with temperature. The steepness also shows uniform growth of the crystals. The non-uniform growth with different shape crystallites generally gives broad absorption (Murgan *et al* 2001). It also reduces the optical transmittance, which ultimately hampers the optical properties. It was also observed that the striking conditions are dependent on the quenching time of the glass. The absorption edge at 397 nm was observed for the glass without heat treatment. Such absorption can be attributed to slight crystallization of the CdS nanocrystallites that occurs during quenching. The glasses doped with CdSSe i.e. CM-575 (figure 1b) shows similar absorption edge behaviour even though shapes of the edges differ slightly. In case of pure CdS doped glass, the absorption cut-off attained up to 495 nm beyond which there was a precipitation leading to decrease in the optical transmittance. The longer heat treatment at lower temperatures had no significant effect. There must be an optimum time at a particular temperature where CdS does not grow beyond a particular size. However, it was observed that the glass samples with initial low temperature (520–550°C) heat treatment at longer time exhibited better particle density and uniformity, which may be due to the homogeneous nucleation. This was observed in all types of the glass samples. This is the first time we are reporting the sharp absorption edge cut-offs at a lower striking temperature as compared with the high striking temperature (up to 700°C) reported in the literature (Persans *et al* 2001). This novel base glass composition, in general, exhibits chemical and thermal stability which made us to study their structural and optical properties.

The nucleation of new particles ends when the supply of either Cd or S/Se in the glass matrix begins to deplete. At this time, smaller particles will become less stable resulting in dissolution back into the glass matrix and large particles grow at the expense of small particles. This final stage is known as coarsening or ripening stage (Lifshitz and Slyozov 1961; Potter and Simmons 1988).

Figure 2. TEM images of glass filter a. CM-475 nm and b. CM-575 nm.

The fact that the magnitude of the absorption peak begins to decrease after a few hours (550°C) of heat treatment and becomes steady at 600°C (20 h) and is consistent with the ripening phenomenon. The sharp leading edge of the absorption shoulder is consistent with the large-particle cut-off in the Lifshitz–Slyozov distribution (Lifshitz and Slyozov 1961; Potter and Simmons 1988) and the crystal size dependence of excited energy states.

The effect of striking temperature on the UV-visible absorption edge at various temperatures has been studied and the results are summarized in table 2.

3.2 Structural characterization

X-ray diffraction patterns were obtained using Rigaku Model and reflection parameters are in good agreement with the reported values (Borrelli *et al* 1987; Murugan *et al* 2001). Diffraction scans over a range of 2θ from 20° – 80° are shown in figures 2(a) and (b) for the glasses, CM-475 and CM-575, respectively. In both these glasses, one relatively diffuse peak was observed on a sloping background that is the portion of the broad 'halo' characteristic of diffraction of nanocrystals in glass. This peak was observed in both types of glasses at same theta values ($2\theta \sim 23$ – 37°), which implies the nanocrystalline nature of CdS and CdSSe. The other three peaks were identified as a reflection from (102), (110) and (103) planes of hexagonal structure (Hache *et al* 1989; Murugan *et al* 2001). The other peaks obtained might be because of the growth of the quartz crystals. Since silica is a major constituent in the glass, the growth of quartz is quite obvious. The particle size was calculated using Scherrer formula (Hache *et al* 1989) using the prominent peak. From XRD, the

glasses, CM-475 and CM-575, were found to have crystallite sizes 5 and 7 nm, respectively.

3.3 Surface morphology of glasses

The TEM images of the CM-475 and CM-575 glass filters is as shown in figures 3a and b. In both the images, careful observation of images shows that spherical shaped particles can be easily seen in the glass matrix. These spherical particles are nothing but the CdS nanocrystals in CM-475 and CdSSe nanocrystals in CM-575 types of glasses. The particle size of semiconductors obtained by TEM was 2.5 and 5 nm for the glass, CM-475 and CM-575, respectively. TEM pictures also give an idea about uniform distribution of CdS and CdSSe crystallites into the glass matrix.

4. Conclusions

One of the potential applications for nanoparticle composites such as CdS/CdSSe in glass is as a non-linear absorbing element in optical switches. The objective of the materials development is to concentrate as much oscillator strength as possible into a narrow energy range. One path of this goal is to make a narrow size distribution of small particles. This will be dependent on the ideal glass composition favourable to uniform and controlled crystal growth. In view of this, the new glass composition was optimized and the nano-crystals of CdS/CdSSe were grown thermally in glass matrix at different temperatures. There was no appreciable change observed in thermal properties after striking process. In X-ray pattern of all glass samples, one relatively diffuse peak was observed on a sloping background that is the portion of the broad 'halo' characteristic of diffraction of nanocrystals in glass, which implies the nanocrystalline nature of the CdS and CdSSe. The particle size of semiconductors obtained by TEM was 2.5 and 5 for the glasses, CM-475 and CM-575, respectively. TEM pictures clearly indicate that all crystallites of CdS and CdSSe are uniformly distributed in the glass matrix. Since the crystal size increases with striking temperature the bandgap also decreases with increasing crystal size, implying quantum confinement. The steepness of the absorption edge is related to crystal size of the CdS/CdSSe and its uniform distribution in the glass matrix.

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Figure 3. XRD patterns of glasses a. CM-475 and b. CM-575.

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References

- Borrelli N F, Hall D W, Holland H J and Smith D W 1987 *J. Appl. Phys.* **61** 5399
- Ekimov A I and Onushchenko A A 1981 *Pis' ma Zh. Eksp. Teor. Fiz.* **34** 363
- Ekimov A I *et al* 1993 *J. Opt. Soc. Am.* **B10** 100
- Hache F, Richard D and Flytzanis C 1989 *Appl. Phys. Lett.* **55** 1504
- Lifshitz I M and Slyozov V V 1961 *J. Phys. Chem. Solids* **19** 35
- Murugan A V, Sonawane R S, Kale B B, Apte S K and Kulkarni A 2001 *Mater. Chem. & Phys.* **71** 98
- Norris D J, Sacra A, Murray C B and Bawendi M G 1994 *Phys. Rev. Lett.* **72** 2612
- Persans P D, Lurio L B, Pant J, Lian G D and Hayes T M 2001 *Phys. Rev.* **B63** 5320
- Potter Jr B G and Simmons J H 1988 *Phys. Rev.* **B37** 10838
- Santhi S and Trojanek F 2005 *Physica* **E27** 38