

J. Synchrotron Rad. (1999), **6**, 495–496

Growth and dissolution of CdS nanoparticles in glass

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We have employed x-ray absorption spectroscopy to study the local bonding of Cd atoms in CdS doped glasses after heat treatment at various temperatures. Optical spectroscopy was used to characterize particle size and composition. We discuss crystalline quality and the balance between growth and dissolution as functions of temperature.

Keywords: nanocrystals; phase stability; cadmium sulfide; optical absorption, semiconductor, quantum dots

Semiconductor nanocrystals exhibit remarkable crystallite-size related stability and optical effects (Brus 1991, Alivisatos 1995, Schroeder and Persans 1996). For example, quantum confinement of electrons and holes leads to a blue shift of the optical absorption edge of CdS particles by several tenths of an electron-volt when particle size is varied from several nanometers down to a few nanometers (Ekimov and Onushchenko 1982). Precipitation in silicate glass is a commercially established approach to the bulk production of optically useful nanoparticles in a robust, stable form (Borrelli *et al* 1987, Yükselici *et al* 1996). Better control of particle-size distribution and composition in such particle/glass composites will lead to improved optical properties. Such control requires an understanding of phase segregation and dissolution on a molecular scale.

The growth of CdS semiconductor particles in a glass matrix is based on a thermodynamic process of precipitation from a supersaturated solution. In glasses, the supersaturated solution can be formed by dissolving the reactants in the glass at high temperature and then quenching. The concentration of reactants available for particle formation is limited by supply and reactant solubility in the high-temperature melt. Particles are typically grown by diffusion-limited precipitation at temperatures from 600 to 800°C.

We have employed x-ray absorption spectroscopy to study the local bonding of Cd atoms in borosilicate glasses doped with Cd and S after heat treatment at temperatures from 550 to 900°C. Varying temperature and time can form CdS particles with average size from a few to several nanometers, with higher temperatures and longer times leading to larger particles. Optical absorption and resonant Raman spectroscopies are used to characterize particle size and composition (Yükselici *et al* 1996).

The starting material was a glass consisting of SiO₂:B₂O₃:Na₂O:CaO:K₂O:ZnO in the approximate ratios 61:20:8.5:6.2:3.6:0.4, as determined by electron microprobe, and doped with Cd and S. As received ("unstruck"), the glass had been homogenized in the melt, quenched, and heat-treated to initiate nucleation. It was a pale yellow-green color in transmission. We subjected 35×5×2 mm slices of this starting

material to isothermal heat treatment for intervals between 0.25 and 14 h.

The unstruck glass is characterized by a very gradual onset of absorption starting at ~2.9 eV. The spectrum evolves monotonically with heat treatment at 625°C to one characterized by a well-defined peak at ~3.3 eV (0.25 to 1 h), consistent with an average particle diameter $d \approx 3$ nm. For heat treatment times greater than one hour at 625°C, the peak evolves into a shoulder and the edge shifts slowly down to ~2.75 eV. After 14 h at 625°C the spectrum is characterized by a relatively sharp edge beginning at 2.75 eV (and no peak), consistent with $d \approx 4$ nm. Treatment at higher temperatures leads to a faster evolution of the peak and edge and can reduce the edge position after 14 h treatment to ~2.6 eV. Note that the edge of bulk CdS is at 2.45 eV. We have attributed the residual blue shift of particles in glass to Zn substitution for Cd in the nanocrystals, which we have quantified from the Raman shift (Yükselici *et al* 1996). Taking this into account, the radius of the predominant particles in each sample can be deduced from the edge positions.

We measured the XAS spectra at the Cd K edge for these samples using fluorescence detection. The data were acquired at

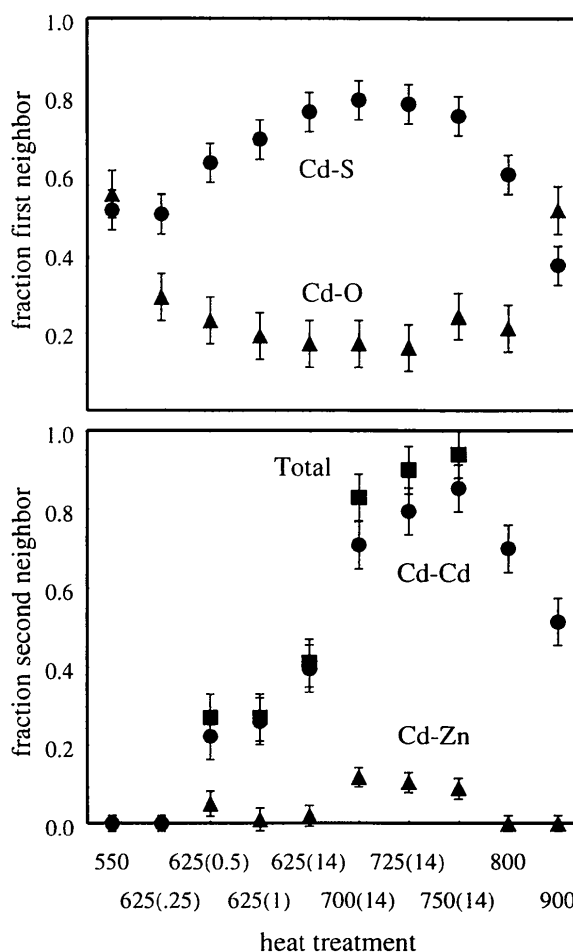


Figure 1 First- and second-nearest neighbor coordination of Cd atoms in a Cd- and S-doped borosilicate glass after heat treatment at temperatures (in °C) and for times (in hours) as shown, as deduced from the analysis of x-ray and optical data.

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20 K using a Si(220) "two-bounce" monochromator on beamline 4-2 at the Stanford Synchrotron Radiation Laboratory. Our optics yielded a measured resolution of 12 eV FWHM at the Cd K edge. The XAS spectra were reduced and analyzed using standard techniques (Hayes and Boyce 1982). Numerical analysis of the spectra using real-space signatures calculated by FEFF3 (Rehr *et al* 1991) or extracted from the CdS data yielded the Cd nearest and second-nearest neighbor coordinations summarized in Fig. 1.

In all the samples, both oxygen and sulfur were found as the nearest neighbors of Cd. Due to the significant differences in the bonding of these elements to Cd, we presume this to represent a mixture of sites coordinated with either six O or four S. In Fig. 1 we plot the fraction of Cd atoms bonded to S and O for various heat treatments. In the as-received unstruck sample, the nearest neighbors of Cd are consistent with a 50-50 mixture of (6)O and (4)S sites. After heat treatment at 625°C for 14 h, this becomes a 75:25 mixture, favoring S. For 14 h treatment at 700 to 725°C, the mixture rises slightly to ~80:20. At heat treatment temperatures above 750°C, O begins replacing S as the nearest neighbor. We believe this to be indicative of the dissolution of CdS particles back into the glass.

Nearest-neighbor analysis and optical absorption spectra suggest that the four samples heat treated at 625 to 750°C for 14 hours are quite similar, with ~75% of the Cd having S neighbors and with relatively large particles ($d > 4$ nm). The amplitude of the second neighbor shows, however, that these samples are actually quite different. In all samples we find Cd as the predominant second neighbor with a small amount of Zn, consistent with optical and Raman analysis. For the samples heat-treated at 625°C, the second neighbor amplitude is only ~30% of the bulk CdS value. We have previously suggested that this deficiency is due to static disorder (Hayes *et al* 1995). The degree of crystalline order is much greater for the three samples heat-treated at 700 to 750°C, approaching 100% coordination for the 750°C sample. When the heat-treatment temperature exceeds 750°C, the second neighbor amplitude decreases, implying decreased crystalline order.

We thank Schott Glass Technologies for providing the unstruck doped glass. We gratefully acknowledge support of this research by DOE grant no. DE-FG02-97ER45662. The XAS measurements were made at SSRL, which is funded by the DOE Office of Basic Energy Sciences and the NIH Biotechnology Resource Program.

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(Received 10 August 1998; accepted 25 January 1999)