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Energetics of CdS_xSe_{1-x} quantum dots in borosilicate glasses

Riham M. Morcos [a,b], Christoph Mitterbauer [b], Nigel Browning [b], Subhash Risbud [b], Alexandra Navrotsky [a,b,*]

[a] Theromochemsitry Facility and NEAT ORU, University of California at Davis, Davis, CA 95616, USA
[b] Department of Chemical Engineering and Materials Science, University of California at Davis, Davis, CA 95616, USA

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Abstract

The thermodynamics of CdSe quantum dots embedded in a glass matrix is of great interest because of the numerous applications as optical materials. In this study, the energetics and stability of CdSe quantum dots in a borosilicate glass matrix is investigated as a function of size using high-temperature oxide melt solution calorimetry. $CdS_{0.1}Se_{0.9}$ nanoparticles (1–40 nm) embedded in glass were analyzed by photoluminescence spectroscopy, electron microprobe, X-ray fluorescence, high-energy synchrotron X-ray diffraction, and (scanning) transmission electron microscopy using both electron energy loss and energy dispersive X-ray spectroscopy. As CdSe particles coarsen, their heat of formation becomes more exothermic. The interfacial energy of CdSe QDs embedded in a borosilicate glass, determined from the slope of enthalpy of drop solution versus calculated surface area, is 0.56 ± 0.01 J/m^2.

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1. Introduction

Semiconductor quantum dots (QD) represent an emerging area of research in nanomaterials. The CdS_xSe_{1-x}, CdS, and CdSe nanoparticles or quantum dots (diameter $\leqslant$20 nm) embedded in glass matrices exhibit quantum confinement, which leads to numerous potential technological applications. Since the early 1980s, numerous and extensive studies of QD electronic, optical and structural properties have been made, using techniques such as optical absorption, photo-modulation (PM), Raman scattering, electromodulation (EM), photoluminescence (PL), photo-thermal deflection spectroscopy (PDS), X-ray absorption fine structure spectroscopy (XAFS), small angle X-ray and neutron scattering (SAXS and SANS), X-ray fluorescence (XRF), electron microprobe (EMP), and nuclear magnetic resonance (NMR) [1–9]. Hayes et al. [8] reported, using XAFS, that both oxygen and sulfur were found as the nearest neighbors of cadmium. Cadmium is either octahedrally coordinated to oxygen or tetrahedrally coordinated to sulfur. In the un-struck samples (containing dissolved CdS with no nucleation of sulfide particles), the nearest neighbors of cadmium are consistent with a 50–50 mixture of oxygen and sulfur sites. After long heat treatments this becomes a 20:80 mixture, favoring sulfur [2,10].

Nanoparticles lie in the realm between dissolved molecular clusters and crystalline macroscopic solids but their properties are different from those of either [11,12]. Studies on the energetics of titania, zirconia, and silica nanoparticles show that their heat of formation depends on size and polymorph type. Calorimetry has proven to be a

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[*] Corresponding author. Address: Theromochemsitry Facility and NEAT ORU, University of California at Davis, Davis, CA 95616, USA. Tel.: +1 530 752 3292; fax: +1 530 752 9307.
E-mail address: anavrotsky@ucdavis.edu (A. Navrotsky).

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valuable technique for determination of heats of formation and surface energies of nanomaterials [11]. However, the heats of formation of nanoparticles that are stabilized or embedded in glass media have not yet been explored.

In this paper we report calorimetric determination of the energetics of CdS_xSe_{1-x} QD contained in glass. The motivation of this study is to address the following scientific questions. When the glass is initially doped with several percent CdSe or CdS, and no quantum dots are detected, is the CdS truly dissolved or is it present as nanoclusters? As the particles coarsen, how does their enthalpy depend on size? At what size is their enthalpy the same as that of bulk CdS? Can one obtain the interfacial energy of the QD-glass interface? The main goal of this study is to clarify how enthalpy of nano-CdSe in glass depends on particle size. Research has shown that single quantum dots are typically energetically unstable [13–15]. However, if quantum dots are embedded in glass, interactions with the matrix may stabilize them, and slow diffusion rates may prevent coarsening. To address these questions; a combination of thermodynamic and structural tools was used, including drop solution calorimetry in a molten oxide solvent, differential scanning calorimetry, X-ray diffraction, (scanning) transmission electron microscopy, and photoluminescence spectroscopy.

2. Experimental procedure

2.1.1. Sample synthesis and characterization

The samples in this study were prepared from commercial RG695 filter glass from Schott Glass Technologies. The borosilicate base glass has major components SiO_2, B_2O_3, Na_2O, ZnO, K_2O in the following weight percent ratios: 60:1:11:20:6 (mol percent ratios: 71:1:11:13:5). The glass composition was determined by both electron microprobe and X-ray fluorescence analysis as shown in Table 1. The CdSe content was determined to be 1.0 ± 0.02 wt% in doped glass sample.

Seven samples were initially prepared from the commercial filter glass containing CdSe. The as received (unstruck) starting glass sample had been homogenized as a high temperature melt, quenched and heat treated to relieve stress. The seven samples representing different growth stages were prepared by isothermal heat treatment at temperatures ranging from 600 to 1100 °C. These samples were analyzed by electron microprobe, photoluminescence spectroscopy, X-ray diffraction and drop solution calorimetry. A single as-received filter was cut into pieces and re-melted in a Pt crucible under atmospheric conditions in a furnace at 1100 °C and then quenched to room temperature; the dark reddish brown colored sample became transparent indicating the CdSe had dissolved into the matrix. The sample was then annealed at 550 °C to initiate nucleation and at 600, 650, 700 °C for 2 h, 750 °C for 20 h and at 1000 °C for 30 min to grow crystals. The annealing temperatures were higher than the glass transition temperature, which was determined by differential scanning calorimetry. Each sample was initially heated at 100 °C for 1 h to remove any adsorbed water and the furnace ramp rate was 10 °C/min until the desired temperature was reached, annealed for 2 h and lastly cooled to 100 °C at 10 °C/min. No weight change was detected for any sample. This suggests that loss of chalcogenide by vaporization and/or oxidation was not a problem. The above annealing temperatures and sequences were established to maximize the crystal volume fraction. Samples of varying average crystallite size were obtained adjusting the annealing temperatures and growth times. Annealing the glasses produced yellow to orange to red to dark brown coloration, indicating the development of a new phase (as shown in Fig. 1). The color changes indicate the formation of crystalline nanostructures QD's. The particle size increases with longer annealing and/or higher temperature, as expected. All the glass samples were photoluminescent under a high energy (low wavelength of 350 nm) black-light source. The slight yellow to red luminescent colors under the black light were homogenous. Structural and optical measurements were carried out on pieces of the same glass samples.

Additionally, based on the analyzed composition of the commercial filter glass; the base glass without any CdS or CdSe was prepared. SiO_2 (alpha-quartz, 99.95%), carbonates Na_2CO_3 (99.95%), K_2CO_3 (99.7%), B_2O_3 (99.95%), ZnO (99.99%, all on purity on a metal basis) were used as starting materials (Alfa Aesar, Ward Hill, MA). The SiO_2 was dried at 500 °C, and the carbonates were all dried at 110 °C for 24 h. After heating, the stoichiometric amounts of the carbonates and oxides were first mixed

Table 1
Composition of glasses used for drop solution calorimetry

Samples	Na_2O	SiO_2	CdSe	K_2O	ZnO	Total[a]
A	12.23 ± 0.13	66.45 ± 0.20	0.33 ± 0.01	3.95 ± 0.03	17.03 ± 0.18	100 ± 0.30 (8)[b]
B	12.18 ± 0.23	67.07 ± 0.22	0.34 ± 0.02	3.99 ± 0.06	16.43 ± 0.14	100 ± 0.40 (10)
C	12.32 ± 0.08	66.34 ± 0.19	0.33 ± 0.02	3.92 ± 0.04	17.08 ± 0.10	100 ± 0.23 (10)
D	12.20 ± 0.07	66.46 ± 0.19	0.35 ± 0.01	3.96 ± 0.04	16.95 ± 0.07	100 ± 0.25 (10)
E	12.36 ± 0.08	66.65 ± 0.17	0.33 ± 0.01	3.91 ± 0.04	16.75 ± 0.10	100 ± 0.28 (10)

(mol percent of oxides and CdSe).

[a] The associated measurement error represents two standard deviations (2σ) of the mean.

[b] The value in ( ) represents the number of experiments.