



Germanosilicate glasses containing PbSe quantum dots for mid-infrared luminescence



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ABSTRACT

Lead selenide quantum dots (QDs) were precipitated in germanosilicate glasses to investigate the effect of GeO₂ content on the precipitation and optical properties. The absorption and photoluminescence (PL) bands red-shifted strongly as GeO₂ concentration increased. After heat-treatment at 470 °C for 10 h, the first excitonic absorption bands red-shifted from 801 nm to 2593 nm as GeO₂ content increased from 0 to 40 mol%, and thus PL at 2619 nm was achieved. The corresponding average QD diameters were 2.48–12.54 nm. The precipitation of large PbSe QDs resulted from the enhancement of diffusion with the increase of GeO₂ concentration, and is the main reason for these red-shifts.

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1. Introduction

Semiconductor quantum dots (QDs) made of lead chalcogenides offer access to the strong quantum confinement regime due to their narrow band-gap and large exciton Bohr radii [1–3]. Based on the strong quantum confinement effect, the dependence of the transition energy on QD size provides a wide tunability of the first exciton transition energy from visible to mid-infrared wavelengths, which cover most of the transmission windows of silica optical fibers, bio-tissues, and atmosphere. PbSe has a band gap in the mid-infrared (~4428 nm) and a small effective mass ($m_e^* \approx m_h^* \approx 0.05 m_0$) [4] and therefore, has potential for use as a material for near-infrared and mid-infrared applications in lasers, telecommunication, and fluorescence biological labels [5–7].

Glasses have good chemical and mechanical stability, so can be robust hosts of QDs; therefore various glasses containing PbSe QDs have been prepared, including silicate, borosilicate, and phosphate glasses [8–11]. However, due to the low solubility of Se and the limited mid-infrared transmittance of these glasses [12], absorption and photoluminescence from PbSe QDs were mainly limited in the near-infrared wavelength range ($\lambda < 2000$ nm). To realize mid-infrared emission from PbSe QDs in glasses, the Se solubility in them must be increased.

Germania (GeO₂) is a good glass-former and results in decrease melting temperature (T_m) and viscosity (η) of glasses [13–15]. Low T_m can reduce the evaporative loss of chalcogen, and thus maintain high

semiconductor concentration in the final glass; therefore, addition of GeO₂ can be expected to form large QDs. Decrease in η can facilitate diffusion of species that can also lead to precipitation of large PbSe QDs. This paper reports the precipitation and growth of PbSe quantum dots in germanosilicate glasses containing different GeO₂ concentrations. Absorption and photoluminescence were realized in the middle infrared $\lambda \sim 2.6$ μm . Effects of GeO₂ concentration on the growth of PbSe QDs were analyzed.

2. Experimental procedures

Glasses with nominal compositions (mol %) of (50 – x) SiO₂– x GeO₂–25Na₂O–8.2ZnO–10BaO–5Al₂O₃–1.2ZnSe–0.6PbO, $x = 0$ –40 (at 10 mol% interval), were prepared. PbO and ZnSe were used as precursors of Pb and Se, respectively instead of PbSe to reduce volatilization loss during melting. Starting powders were melted in alumina crucibles at 1100–1300 °C for 30 min. The melt was quenched by pouring onto a brass mold and pressing with another plate. The as-cast glasses were then annealed at ~380 °C for 2 h in a muffle furnace. Glasses were transparent yellow and turned dark brown or black after additional heat-treatment at temperatures slightly higher than the glass transition temperature (T_g).

The specimens were cut into square plates of 5 mm × 5 mm with ~1.5 mm thickness and optically polished for the spectroscopic measurements. Absorption spectra were recorded using a UV–vis–NIR spectrophotometer at 400 nm ≤ λ ≤ 3000 nm. Photoluminescence spectra were measured using an 800-nm excitation light source from a Ti-sapphire laser pumped by a Nd:YVO₄ diode laser. The spectra were

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registered using a lock-in amplifier, monochromator and InSb detector cooled with liquid N₂. High-resolution transmission electron micrographs (HR-TEM, JEOL JEM-2100 F) were used to identify the size and distribution of the QDs in glasses. X-ray diffraction patterns were recorded using an X-ray diffractometer (XRD, RIGAKU D/max-2500). Thermal analysis was conducted using a thermo-gravimetry/differential thermal analyzer (TG/DTA, SHIMADZU DTG-60). Temperature was recorded to 0.1 °C, and the overall accuracy of the instrument was estimated to be within ± 1 °C after calibration.

3. Results

Germanosilicate glasses heat-treated at 470 °C for 10 h contained nanocrystals (Fig. 1) and the X-ray diffraction (XRD) pattern of the glass (Fig. 2) had several peaks that match well with the peak positions of PbSe bulk crystals (JCPDF NO. 77-0245). The observation confirms that the nanocrystals are PbSe. PbSe QD diameters measured from TEM images vary between 8.4 and 13.8 nm with a mean value of ~11.2 nm. Diameter calculated from the XRD patterns in Fig. 2 using Scherrer formula [16] was ~11.6 nm. The results are smaller than that obtained from the absorption spectrum (~12.54 nm), due to the large size distribution.

Optical absorption spectra (Fig. 3a) show absorption bands associated with PbSe QDs in glasses and their peak λ increased as GeO₂ concentration increased. Heat treatment condition (470 °C for 10 h) was the same for all specimens. Photoluminescence (PL) bands in Fig. 3b also showed similar changes; when GeO₂ concentration increased from 0 to 40 mol% the peak λ of the absorption bands shifted from 801 nm to 2593 nm, and the center λ of the PL bands shifted from 1122 nm to 2615 nm. Increase in the heat treatment temperature (T_H) resulted in similar changes. When glass with 40 mol% GeO₂ was heated at 450 °C–470 °C for 10 h, both the first exciton peak in the absorption and PL spectra shifted to longer λ ; this shift indicates that PbSe QDs size increased with temperature (Fig. 4). Peak λ of the PL band moved to ~2.6 μ m after heat treatment at 470 °C for 10 h; this is the longest λ observed from PbSe QDs in glasses. However, intensities of the PL band decreased considerably as the peak λ increased, possibly because the effectiveness of the strong confinement mode decreases as radius of nanocrystal approaches the exciton Bohr radius [17]. Decrease in the QD number density together with surface defect states and clustering of PbSe QDs also seem to contribute to this intensity decrease [18]. Similar decrease in intensity from PbS QDs has also been reported in silicate glasses [19].

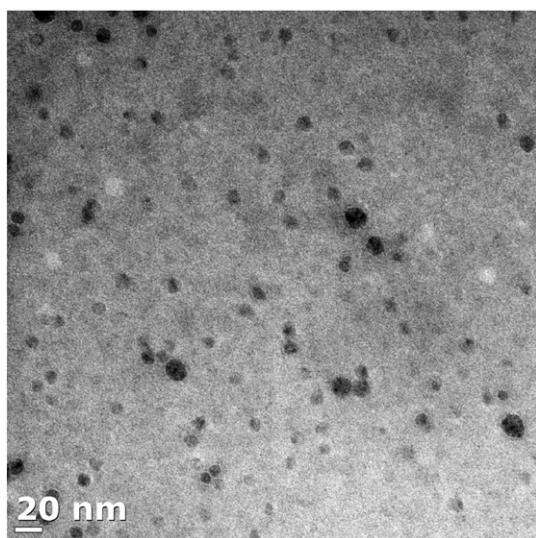


Fig. 1. TEM micrograph of germanosilicate glass (40 mol% GeO₂) after heat-treatment at 470 °C for 10 h.

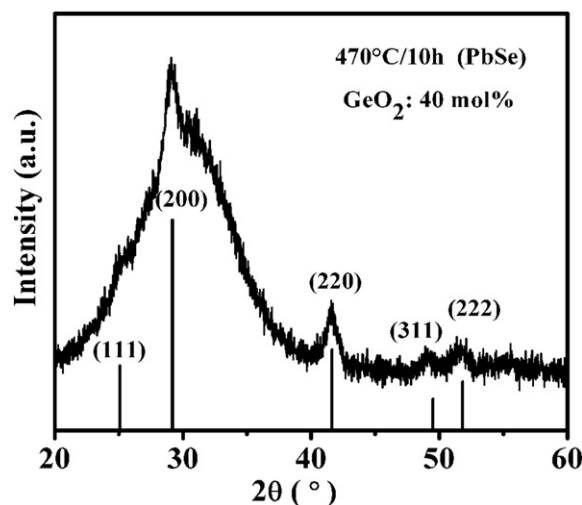


Fig. 2. X-ray diffraction pattern of germanosilicate glass (40 mol% GeO₂) after heat-treatment at 470 °C for 10 h.

The PL bands of PbSe QDs from glasses containing 0–40 mol% GeO₂ that were heat treated at 450 °C–520 °C for 10 h showed a similar red-shift in the peak λ of PL as T_H increased (Fig. 5). GeO₂ concentration has two effects on the formation of PbSe QDs. First, it affects the λ of the PL bands. For example, glasses heat treated glass at 470 °C, PL bands shifted from 1122 nm to 2615 nm when GeO₂ concentration increased to 40 mol%. Second, increase in GeO₂ concentration results in decrease in T_H required to obtain PbSe QDs of a given diameter. To obtain PL at ~1800 nm, T_H should be ~500 °C for a glass with 10 mol% GeO₂, whereas T_H ~450 °C appears to be high enough for a glass containing 40 mol% GeO₂.

4. Discussion

Average diameters D (nm) of PbSe QDs were calculated from the position of the 1S_e–1S_h peak maximum in Fig. 3(a) using [20]:

$$E_g(D) = E_g(\infty) + \frac{1}{0.0105D^2 + 0.2655D + 0.0667} \quad (1)$$

where, $E_g(D)$ is the first exciton transition energy, and $E_g(\infty)$ is the band gap of bulk PbSe semiconductor. Calculated diameters of QDs increased from 2.48 ± 0.14 nm to 12.54 ± 0.86 nm as GeO₂ concentrations increased from 0 to 40 mol% when all specimens were heat-treated at 470 °C for 10 h. The error bar was estimated from the width of the absorption peaks.

One of the major factors that affect the growth process of PbSe QDs is an increased diffusivity of ions in glasses as GeO₂ concentration increases [21]. Because GeO₂ substitutes for SiO₂ gradually, the number of [GeO₄] units increases. The length of the Ge–O bond is typically ~0.15 Å longer than the Si–O bond [22]. Assuming that [GeO₄] and [SiO₄] units are regular tetrahedra, the volume of a [GeO₄] unit is approximately ~8% larger than that of a [SiO₄] unit. This difference probably caused the increase in the molar volume of the glass from 25.03 cm³/mol to 26.30 cm³/mol as GeO₂ concentration increased from 0 to 40 mol%. This increase in molar volume would provide easy diffusion path to facilitate growth of PbSe QDs.

T_g of glasses with 0, 10, 20, 30, and 40 mol% GeO₂ was 471 °C, 465 °C, 459 °C, 452 °C and 442 °C, respectively. One can assume that at $T_H = 470$ °C, η of glasses would decrease as GeO₂ concentration increases. This reduced η will enhance the diffusion following the Stokes–Einstein equation $D = k_B T / 6\pi r \eta$, where D is the diffusion coefficient, k_B is the Boltzmann constant, T is the absolute temperature, and r is the moving

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