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Growth of lead selenide quantum dots in silicate glasses

Jing Wang[a,b], Wei Zhang[a], Chao Liu[a], Jianjun Han[a,*]

[a] State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, 122 Luoshi Road, Hongshan, Wuhan, Hubei 430070, China
[b] State Key Laboratory of Advanced Technology for Float Glass, 751 Donghai Road, Longzihu, Bengbu 233018, China

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ABSTRACT

Glass with the composition of $50SiO_2$-$25Na_2O$-10ZnO-10BaO-$5Al_2O_3$ (in mol%) was used as the matrix for the growth of PbSe QDs. The viscosity-temperature relations of the glass were obtained through Vogel-Tammann-Fulcher equation. PbSe QDs were precipitated in this silicate glasses with the heat-treatment temperatures (T_H) ranging from 490 to 540 °C for fixed duration of 10 h, corresponding to the glass-viscosity $10^{11.2}$–$10^{8.9}$ Pa·s. Meanwhile, the absorption peaks from PbSe QDs shifted from 872 nm to 2134 nm, and the PL peaks shifted from 1104 nm to 2185 nm. To study the PbSe QDs growth kinetics, the glasses were heat treated at 500, 520 and 540 °C for 1–20 h. Changes in diameter of PbSe QDs exhibited strong time dependencies (i.e. $D \sim t^{0.17}$, T_H = 520 °C), while the time dependencies were much smaller than that predicted by the classical Lifshitz-Slyozov-Wagner (LSW) theory ($D \sim t^{1/3}$) and the higher T_H leads to the smaller growth exponent.

1. Introduction

Quantum dots (QDs) made of lead chalcogenide semiconductors have shown potential for wide range applications in the areas of biosensors, lasers and photovoltaic cells [1,2,3]. For the practical applications, QDs should be incorporated into solid matrices. Lead chalcogenide QDs doped glasses offer simple technological process of synthesis, chemical stability and the possibility to create all-solid and compact devices. Lead chalcogenide QDs have been prepared in phosphate [4], fluorophosphates [5], lead-phosphate [6], germanosilicate [7], borosilicate [8], silicate [9] and nanoporous silicate glasses [10]. To realize the desired optical characteristics, the size and spatial distribution of QDs in glasses must be controlled. Previously, many new methods were used to control the growth of QDs in glasses, such as doping some rare-earth ions as nucleation agents [11–12], ion-implantation [13], femtosecond laser irradiation [14], etc. While, optimizing temperatures and durations of thermal treatments is still the mainly method to control the crystallization of QDs in matrix glasses. The growth of QDs in glass matrix governed by heat-treatment has been attempted to understand in terms of diffusion-controlled growth process using the classical Lifshitz-Slezov mode [15–16]. It describes the average QDs radius is proportional to the cube root of diffusion coefficient of the semiconductor and the growth time [17]. Although the growth mechanism of cadmium chalcogenides QDs in glasses seems to agree well with this dependence, very few other semiconductors have been tried [18–19]. To achieve desirable optical properties, precise control of growth of the QDs in glass matrices is required, and the fundamental mechanisms of QDs growth should be well understood.

To form the QDs in the glass, heat treatment of samples should be conducted at temperature high enough to cause effective diffusion and low enough to maintain solution oversaturation.

Usually, heat-treatment is carried at temperature slightly higher than transition temperature T_g, corresponding to the viscosity at 10^{12} Pa·s. The viscosity of glass matrix plays an important role in the growth of QDs through the dependence of diffusion coefficient on the glass viscosity, which can be used to optimize heat treatment temperature. Another important viscosity point is at 10 Pa·s which corresponds to the melting temperature. The boiling point of bulk PbSe semiconductor is around ~1100 °C, the use of low melting temperature glass can decrease the loss of semiconductor compounds due to evaporation, and help to maintain more semiconductor species [20–21]. This promotes the nucleation and growth of semiconductor QDs. In this research, the viscosity of silicate glasses with PbSe precursors (PbO and ZnSe) were studied to determine the heat treatment temperatures (T_H) and to estimate the glass-forming ability. PbSe QDs were precipitated from the glass upon thermal treatments. We studied the effects of the T_H on the absorption and photoluminescence characteristic of the glasses containing PbSe QDs and discussed the growth kinetics at different T_H for 1–24 h.

2. Experimental procedures

The nominal composition of glass was $50SiO_2$-$25Na_2O$-10ZnO-10BaO-$5Al_2O_3$ (in mol%), with excess PbO (0.6 mol%) and ZnSe

* Corresponding author.
E-mail address: hanjj@whut.edu.cn (J. Han).

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(1.2 mol%), which were along with PbSe to compensate the vaporization losses. Starting powders were melted in alumina crucibles at 1300 °C for 30 min. A part of melt was quenched by pouring onto a brass mold and pressed with another plate, and the residual melt was quenched in the water for viscosity measurement. The glass frits were measured with a rotating crucible viscometer (Model RheotronicII, THETA, USA) above the glass soften point. Characteristic temperatures of glass such as transition temperature, T_g, and dilatometric softening point, T_d, were measured by using a horizontal dual-rod dilatometer (Model DIL 402, Netzsch, Germany). The as-cast glasses were annealed at the temperature of ~380 °C for 2 h in the muffle furnace. To tune the quantum dot sizes and distributions, the glass samples were heat-treated at various temperatures between T_g and T_d with different durations Glass samples thus obtained were characterized by X-ray diffraction (XRD, RIGAKU D/max-2500, Japan), optical absorption (Perkin Elmer Lambda), photoluminescence (PL, Mellennia Pro 6Sj, Spectra Physics) and high-resolution transmission electron microscope (HR-TEM, JEOL JEM-2100F, Japan).

3. Results and discussion

3.1. Glass properties (viscosity)

Viscosity is one of the most important properties of glasses which depends on the chemical compositions and temperatures. The viscosities (in Pa·s) for the glass containing PbSe QD precursors are illustrated as a function of the temperature, as shown in Fig. 1. The viscosity of most silicate melts are well described by the empirical equation of Vogel-Tammann-Fulcher (VTF) equation [22] corresponding to wide temperature range from T_g to temperatures above T_m:

$$log\eta = A + \frac{B}{T - T_0} \quad (1)$$

where A, B and T_0 are empirical parameters, and T represents temperature in °C. The viscosities (in Pa·s) for the glass containing PbSe QD precursors are illustrated as a function of the temperature, as shown in Fig. 1. The T_g and T_d were determined by the dilatometer. The parameters A, B and T_0 are determined by fitting VFT Eq. (1) to the viscosity data, and the corresponding constants are − 2.59, 3484.26, and 235.82 respectively. The reference temperature points determined by the viscosity-temperature curve (Fig. 1) are shown in Table 1.

In this work, the target is to precipitate PbSe QDs in silicate glass matrix. Therefore, for the silicate glass host itself, a high glass stability is preferable. The Hruby parameter K_H, is used to measure the glass stability against devitrification on heating and estimate the glass-forming ability on cooling [23].

$$K_H = \frac{T_c - T_g}{T_m - T_c} \quad (2)$$

where the T_c, T_g and T_m are the onset crystallization temperature (on heating), glass transition and melting temperatures. According to Hruby, the higher value of K_H, the higher its stability against crystallization on heating and, presumably, the higher its vitrifiability on cooling [24]. In our glass system, the K_H is calculated to be 0.458, which is higher than the glass systems in $Na_2O{\cdot}CaO{\cdot}SiO_2$, $BaO{\cdot}2SiO_2$, $Li_2O{\cdot}2SiO_2$ [25]. Therefore, this glass has a good stability to avoid phase separation or glass crystallization during heat treatment for precipitating QDs.

Table 1
Viscosity reference temperatures.

Name of reference temperature	Viscosity (Pa·s)	Temperature (°C)
Melting temperature (T_m)	10	1208
Crystallization temperature (T_c)	10^3–10^5	700–861
Dilatometric softening point (T_d)	10^8–10^9	536–565
Transition temperature (T_g)	10^{12}	471

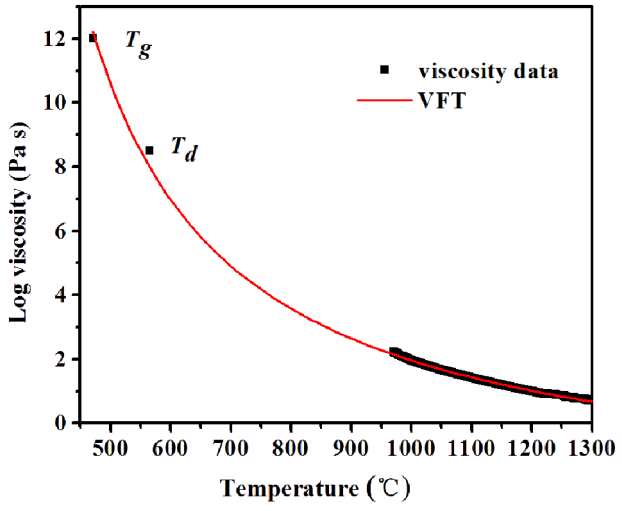

Fig. 1. The viscosity data (solid symbols) fitted using the VFT equation for the glass containing PbSe precursors.

3.2. Formation of PbSe QDs

Structure of the as-prepared glass and heat-treated glass were measured using XRD. No detectable nanocrystals were present in the as-cast glass. After heat treatment at ~540 °C for 10 h, color of as-prepared glasses changed from light yellow to black due to the formation of PbSe QDs upon heat treatment, which was further confirmed by the XRD patterns (Fig. 2) and TEM images (Fig. 3). One typical HR-TEM image of PbSe nanocrystals showed the d = 0.31 nm, corresponding to the (200) plane of PbSe crystal (JCPDF # 06-0354).

3.3. Optical properties

Fig. 4 represents absorption and normalized PL spectra of synthesized PbSe-QD-doped silicate glasses heat treated at 490–540 °C for 10 h. The temperatures correspond to the viscosity from $10^{11.2}$–$10^{8.9}$ Pa·s. A weak absorption peak at ~872 nm occurred after heat treatment at 490 °C for 10 h. As elevating the T_H from 490 °C to 540 °C, the peak wavelengths of absorption bands shifted from 872 nm to 2134 nm. Such absorption spectrum confirms the formation of PbSe QDs in the glass matrix, and the average diameter of QDs is small enough to induce the quantum confinement effect. Average diameters of

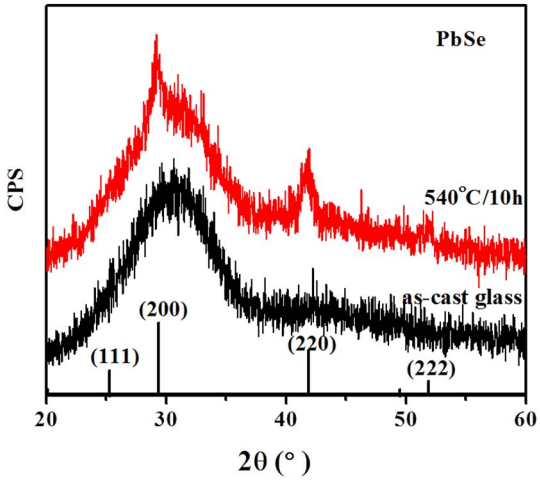

Fig. 2. XRD patterns of PbSe QDs embedded glass and as-cast glass.