Journal of Non-Crystalline Solids 482 (2018) 177–182

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Optical properties of $Pb_{1-x}Sn_xSe$ quantum dots (QDs) in silicate glasses dictated by GeO_2 concentrations

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ARTICLE INFO

Keywords:
Quantum dots
$Pb_{1-x}Sn_xSe$
Band gap
Viscosity
Diffusion coefficient

ABSTRACT

Effects of SnO addition on the optical properties of $Pb_{1-x}Sn_xSe$ quantum dots (QDs) were investigated as a function of GeO_2 content [GeO_2] in germanosilicate glasses. Addition of SnO resulted in a red-shift of the absorption bands from QDs at [GeO_2] < 20 mol%, but in a blue-shift at [GeO_2] ≥ 20 mol%. Addition of GeO_2 to the glass caused a large decrease in its viscosity, so it increased diffusion coefficient (D); as a result the amount of Sn in $Pb_{1-x}Sn_xSe$ QDs increased. D of Sn^{2+} was ~560 times higher in the glasses with [GeO_2] = 40 mol% than in the glass with no GeO_2. The differences in Sn content in QDs affected their bandgap.

1. Introduction

Nano-sized semiconductors called quantum dots (QDs) show tunable optical and electrical properties when the QDs are smaller than the Bohr exciton radius r_B [1–3]. In particular, lead chalcogenides (PbS, PbSe and PbTe) QDs have a strong quantum confinement effect because of their large r_B (PbS 18 nm, PbSe 46 nm) [4–5]. Therefore, they are candidate materials for fiber-optic amplifiers, mode-locked lasers and thermal imaging using the infrared light [6–8].

QDs have been synthesized in various media such as glasses, zeolites and organic solutions [9–11]. QDs precipitated in solutions are called colloidal QDs (CQDs) and they show high photoluminescence efficiencies with a narrow size distribution [11]. However, these QDs must be immersed in solution to prevent agglomeration and therefore, are difficult to integrate with other optical components [12]. Glass matrices can prevent the undesired agglomeration, and can also provide high chemical durability and mechanical stability [6]. QDs inside glasses have been precipitated by heat treatment process, ion implantation and laser irradiation [13–15]. Heat treatment is the most convenient method and is, therefore, widely used. In this case, wavelengths of the emission bands are entirely dependent on the size of the QDs. However, precise control of the size of the QDs by adjusting only the heat-treatment conditions is a difficult or impossible task [15].

Recently, doping of a third element such as Ti^{4+}, Sn^{2+} or Sr^{2+} into PbSe QDs in silicate glass matrices has been assessed as a way to control the optical bandgap E_G, and thereby the optical properties of the QDs [16–18]. In particular, E_G of the $Pb_{1-x}Sn_xSe$ QDs significantly decreased with SnO addition in silicate glasses without any remarkable changes in the diameters of the QDs [18]. It is known that bandgaps of the Sn-doped lead chalcogenide semiconductors ($Pb_{1-x}Sn_xSe$ and $Pb_{1-x}Sn_xTe$) change anomalously; E_G values of $Pb_{1-x}Sn_xSe$ approach to 0 eV when the Sn concentration in $Pb_{1-x}Sn_xSe$ approaches at 0.15 and then increase again with a further Sn addition [19–21]. However, these changes have been realized from bulk materials only. Therefore, the control of Sn concentration in $Pb_{1-x}Sn_xSe$ QDs can provide a good alternative method for the modulation of optical properties by changing values of E_G.

Optical properties of QDs can also be modulated by carefully controlling the host glass compositions [22–24]. Addition of GeO_2 to silicate glasses greatly decreases their melting temperatures and viscosities η [23]. The low η seemed to facilitate the diffusion of species [25–27] and resulted in the formation of large QDs. This work reports the effect of GeO_2 on the formation of $Pb_{1-x}Sn_xSe$ QDs and proved the incorporation of Sn changed with GeO_2 concentration.

2. Experimental procedures

Glasses with nominal compositions (mol%) of $(50-x)SiO_2 - xGeO_2 - 25Na_2O - 8.2ZnO - 10BaO - 5Al_2O_3 - 1.2ZnSe - 0.6PbO$ (x = 0, 10, 20, 30 and 40) were prepared by conventional melt quenching. Glasses containing x = 0, 10, 20, 30 and 40 will be referred to as Ge0, Ge10, Ge20, Ge30 and Ge40, respectively. SnO was added up to 0.6 mol%,

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https://doi.org/10.1016/j.jnoncrysol.2017.12.034
Received 8 September 2017; Received in revised form 15 December 2017; Accepted 18 December 2017
Available online 21 December 2017

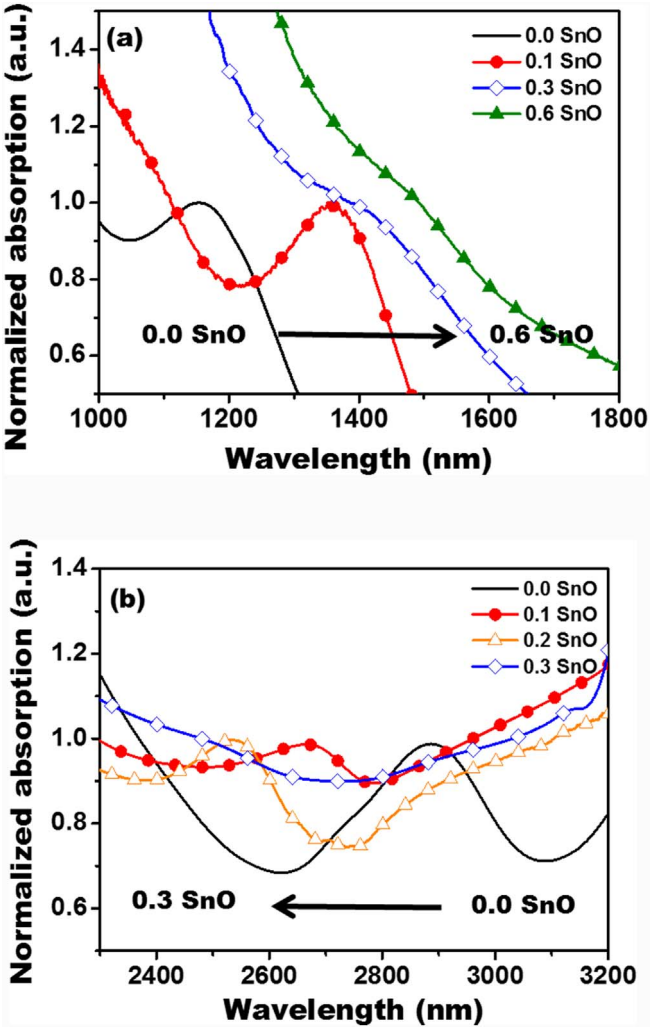

Fig. 1. Normalized absorption spectra of PbSe QDs with SnO addition (a) in Ge0 glasses heat treated at 510 °C for 10 h and (b) in Ge40 glasses heat treated at 480 °C for 10 h.

Table 1
Addition of SnO into Ge0 and Ge10 resulted in the red-shift of the absorption bands while the opposite is true for glasses with $GeO_2 \geq 20$ mol%.

Absorption [nm]			
Composition	0.0 mol% SnO	0.1 mol% SnO	Δ λ
Ge0	1153 (± 52)	1352 (± 59)	+ 194
Ge10	1380 (± 62)	1627 (± 56)	+ 247
Ge20	1379 (± 53)	1282 (± 33)	− 97
Ge30	2012 (± 90)	1880 (± 76)	− 132
Ge40	2889 (± 120)	2676 (± 67)	− 213

replacing ZnO. High-purity powders (> 99.9%) were weighed, mixed with ethanol and milled in a ZrO_2 ball-miller for 15 h. Mixtures were dried in an oven at 75 °C for 3 h to remove ethanol, then further heated at 105 °C for 3 h to evaporate water. Powders were then melted in an alumina crucible at 1100–1300 °C for 30 min. The melts were poured onto a preheated brass mold and quenched by pressing with another brass plate before annealing at 380 °C for 2 h. The glass specimens were then heated at 480 °C, 500 °C or 510 °C for 10 h to precipitate QDs. An additional specimen was heat-treated at 520 °C for 10 h for use in

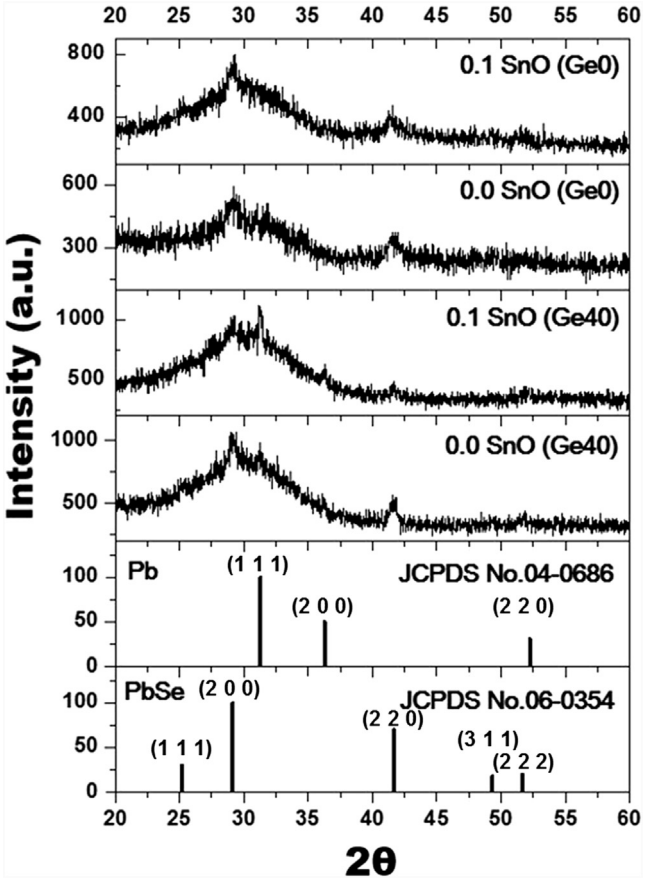

Fig. 2. XRD patterns of Ge0 and Ge40 glasses with 0.0 and 0.1 mol% SnO. Ge0 glasses were heat treated at 560 °C for 10 h and Ge40 glasses were heat treated at 480 °C for 10 h.

electron energy loss spectroscopy (EELS) analysis to clearly identify incorporation of SnO into PbSe QDs. The glass specimens were cut and polished for optical measurement. Absorption spectra were measured at $1000 \leq \lambda \leq 3300$ nm using a spectrophotometer (Lambda UV/Vis/IR spectrometer, Perkin-Elmer). X-ray diffraction (XRD) patterns were recorded by an X-ray diffractometer (D/MAX-2500/PC, Rigaku) using Cu-K_α radiation (λ = 1.54 Å).

Specimens for transmission electron microscope (HR-TEM, JEM-2200FS, JEOL, Kyoto, Japan) were prepared by ion-milling using a focused ion beam (FIB, Helios-Pegasus, FEI) and coated with carbon to reduce charging and potential damage by the electron beam. TEM images were recorded to investigate the size and spatial distribution of QDs in the glass matrix. The energy losses associated with the Pb ($O_{2,3}$), Se ($M_{4,5}$), Sn ($M_{4,5}$), Ge (L_3, $M_{4,5}$) and O (K) shell electrons were recorded to analyze the distribution of each element in the specimens. A three-window technique with one post-edge image and two pre-edges images for the background correction was used to visualize the distribution of Pb, Se and Sn. Energy dispersive X-ray spectroscopy (EDS) analysis was performed using HR-TEM with an accelerating voltage of 200 keV to analyze the amount of Sn incorporation into PbSe QDs. All measurements were conducted at room temperature.

η of the glasses were measured by a thermomechanical analyzer (TMA) using a beam-bending method. Specimens of 1 mm width × 0.5 mm height × 8 mm length were inserted into a vitreous silica tube, then a 20-g load was applied to the top of specimen [28–29]. The specimen was heated to 550 °C at 5 °C/min, and changes in deflection during heating were monitored.