Materials Research Express

PAPER

Modulation of the optical properties of transition metal doped PbSe quantum dots in silicate glasses

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Keywords: lead chalcogenides, photoluminescence, blue-shift, bandgap, transition metal

Abstract

Optical properties of lead chalcogenide quantum dots (QDs) can be controlled by tuning its bandgaps. We prepared silicate glasses using the melt-quenching method and heat-treated 510 °C–540 °C for 10 h to precipitate transition metal ions into PbSe QDs. Transition metals oxide such as TiO, MnO & NiO were used in our experiment due to relative ease of incorporation of $\text{Ti}^{2+}$, $\text{Mn}^{2+}$, or $\text{Ni}^{2+}$ ions in PbSe crystal structure lattice compared to rare-earth ions. Emission spectra of PbSe QDs were tuned in a wide wavelength range through changing concentration of transition metals oxide in glasses. For instance, photoluminescence bands of $\text{Pb}_{1-x}\text{Ti}_x\text{Se}$ QDs moved from 1890 nm to 1625 nm with increasing TiO from 0.0 to 0.5 mol% at heat treatment 530 °C for 10 h. Absorption bands of QDs also shifted to shorter wavelength sides as concentration of TiO or MnO increased under constant thermal treatment conditions mainly due to the change in the bandgap of QDs. However, absorption & PL peaks moved to longer wavelength sides (red-shifted) with increasing the duration of thermal annealing while keeping the amount of transition metal oxides constant mainly due to enlargement of the QDs sizes with thermal treatment. Tunable optical properties of QDs make them a promising candidate for various photoelectric devices, for example, fiber-optics amplifiers in optical communication and fiber lasers.

1. Introduction

Semiconductor quantum dots (QDs) have attracted considerable attention due to their unique properties which are caused by quantum confinement effects. Typically, lead chalcogenide ($\text{PbX}$, where $X = \text{Se}, \text{S}, \text{Te}$) have given great attention for their tunable infrared luminescence in a wider range due to their narrow bandgap and strong quantum confinement effect [1–3]. Tunable optical properties of QDs make them useful in broad applications typically PbSe/PbS QDs doped glasses are a promising candidate for optical communication fiber amplifiers [4–8] and fiber lasers [9]. Organic-inorganic hybrid perovskite (CH$_3$NH$_3$PbX$_3$, $X = \text{Cl}, \text{Br},$ or I) quantum dots have also shown superior optoelectronic properties and huge potential for next-generation displays and lighting [10]. Diluted magnetic semiconductors (DMS) are also expected to be key materials for future spintronic devices [11–15]. For practical applications, QDs should be incorporated into glasses or solid matrices because they are chemically and mechanically stable. It is also a necessary accurate tune of QDs size and spatial distribution in glasses for a desire optical property. Precise control QDs size in the glass matrix is difficult using heat treatment process [16]. Thus, it is necessary to control the optical properties of QDs without large changing QDs size. Incorporation of transition metals (TM) ions into IV-VI QDs crystal structure can tune the bandgap of alloyed QDs [17–19] with sizes remained mostly unaffected. The bandgap of PbSe QDs increased with increasing transition metal ions in QDs at constant thermal treatment [20]. Thus, photoluminescence bands of alloyed QDs are shifted with a change of bandgap of QDs at a uniform thermal treatment schedule. The solubility limit of dopant transition metal ions in QDs might lead to limits the spectral range of QDs.
In this paper, we report the effect of transition metal ions (such as Ti$^{2+}$, Mn$^{2+}$, Ni$^{2+}$) incorporation in PbSe QDs on optical properties at constant thermal treatment, and also varying thermal treatment temperature. We expect transition metal ions (Oxidation $2^+$ ions) relatively easy to incorporate into PbSe quantum dots compared to rare-earth (RE) ions.

2. Experimental procedures

2.1. Glass specimens preparation
The nominal composition of silicate glass specimens [20] with addition of transition metal oxides (such as TiO, MnO/NiO) up to 0.5 mol% was prepared by conventional melt-quenching method at 1300 °C for 30 min under ambient atmosphere. Glasses were heat-treated from 510 °C to 540 °C for 10 h to precipitate QDs. Glass specimens size of 5 mm × 5 mm × 1.5 mm were prepared and then polished all their surfaces for optical and structural measurements.

2.2. Characterization of optical & magnetic properties of alloyed QDs doped glasses
UV/Vis/NIR spectrophotometer (Lambda 750S, Perkin Elmer, Shelton, CT) and $\lambda = 800$ nm excitation beam from Ti-Sapphire laser pumped by a 532 nm laser were used to measure the optical absorption and photoluminescence (PL) spectra respectively. X-ray diffractometer (D/MAX-2500/PC) and High-Resolution Transmission Electron Microscope (HRTEM, JEOL, JEM-2200FS) measurements were used to analyze the formation of QDs in the as-prepared & heat-treated glasses, and characterize its nanostructure. Precipitation of transition metal ions incorporated QDs in a glass was verified using a Magnetic Force Microscopy (MFM) image, a Scanning Probe Microscopy (SPM) system (AFM/MFM/STM Base, VEECO dimension 3100 + Nanoscope Version 7.0). MFM measurement was also used to study the magnetic moments of transition metal ions into NCs in glasses, namely: Pb$_{1-x}$MnxSe NCs or Pb$_{1-x}$Co$_x$Se NCs [21, 22]. Thus, we prepared glass specimens with addition of 0.5 mol% titanium oxide (TiO) and then heat-treated 530 °C for 10 h for MFM measurement. Titanium ions (Ti$^{2+}$) ([Ar] 3d$^2$ configuration) migration into host PbSe QDs was assessed by Electron Paramagnetic Resonance (EPR) technique. Absorption of electromagnetic radiation was measured by placing these powder samples into a strong magnetic field region of the EPR spectrometer, constant frequency ($v$) 9.12 GHz, and power 0.998 mW by varying magnetic field ($B_0$).

3. Results and discussion

3.1. Optical properties of glass contain Pb$_{1-x}$TM$_x$Se QDs, (TM = Ti, Mn, Ni)
As-prepared glass specimens’ colors were yellow; they were changed to black after heat-treated from 510 °C to 540 °C for 10 h. At HT 530 °C for 10 h, optical absorption bands of QDs blue-shifted from 1774 nm to 1467 nm with increasing titanium oxide concentration, [TiO], from 0.0 to 0.5 mol% (figure 1(a)). Similarly, photoluminescence (PL) bands of QDs also shifted from 1890 nm (without TiO) to 1625 nm at [with

![Image](image.jpg)
TiO = 0.5 mol% (figure 1(b)). In our previous study [20], we reported PL intensities of Pb₁₋ₓTiₓSe QDs increased with increasing [TiO] in glasses.

We calculated the diameter of QDs using the Brus equation [23] and its diameter decreased slightly from 6.74 nm to 5.22 nm with [TiO] increased from 0.0 mol% to 0.5 mol% in glasses (table 1). These results infer the shifting of absorption bands from 1774 nm to 1467 nm is not mainly due to a decrease in QDs sizes. However, absorption bands shifted mainly due to the change in the bandgap of Pb₁₋ₓTiₓSe QDs with TiO addition. A similar observation was also observed in previous articles [20, 24].

The results show the center wavelengths of absorption and PL bands moved to shorter wavelength sides as [TiO] increased from 0.0 to 0.5 mol% at constant HT 530 °C/10 h. However, absorption & PL bands moved to longer wavelength sides (red-shifted) with increasing thermal annealing while keeping the amount of transition metal oxides constant mainly due to enlargement of the QDs sizes with thermal treatment (figures 2(a)–(c)). For instance, optical absorption bands of Pb₁₋ₓTiₓSe QDs with [TiO] = 0.2 mol% shifted from 1417 nm to 1703 nm.
with HT increased from 510 °C to 540 °C for 10 h. Similarly, PL bands red-shifted to 1801 nm with HT increased to 540 °C/10 h (figure 2(a)). Likewise, optical absorption bands of Pb1-xMnxSe QDs with Manganese oxide [MnO] = 0.2 mol% shifted from 1476 nm to 1831 nm as HT increased from 510 °C to 540 °C for 10 h, and PL bands also red-shifted to 1894 nm as HT increased to 540 °C/10 h; this shift indicates that QDs size increased with thermal treatment (figure 2(b)).

At constant HT 540 °C/10 h, absorption & PL spectra of PbSe QDs were also shifted as a function of transition metals ions (Ti²⁺/Mn²⁺/Ni²⁺) embedded into the crystal structure QDs (table 2). We expected bandgap of alloyed QDs were changed depending on the solubility limit of these dopant ions in host QDs.

N.B. The concentration of transition metal oxides (0.2 mol%) & heat treatment (540 °C/10 h) constant for all glasses.

Table 2. Optical absorption & PL spectra of Pb1-xTMxSe QDs in glasses with a different type of transition metal oxides (such as TiO/MnO/NiO) addition.

| Type of Pb1-xTMxSe QDs       | Abs. (nm) | PL (nm) | Calculated diameter (nm) |
|-----------------------------|-----------|---------|-------------------------|
| PbSe QDs                    | 1850      | 1900    | 7.26                    |
| PbSe QDs with 0.2% Ti²⁺     | 1703      | 1801    | 6.46                    |
| PbSe QDs with 0.2% Mn²⁺     | 1831      | 1894    | 7.16                    |
| PbSe QDs with 0.2% Ni²⁺     | 1956      | 1991    | 7.87                    |

with HT increased from 510 °C to 540 °C for 10 h. Similarly, PL bands red-shifted to 1801 nm with HT increased to 540 °C/10 h (figure 2(a)). Likewise, optical absorption bands of Pb1-xMnxSe QDs with Manganese oxide [MnO] = 0.2 mol% shifted from 1476 nm to 1831 nm as HT increased from 510 °C to 540 °C for 10 h, and PL bands also red-shifted to 1894 nm as HT increased to 540 °C/10 h; this shift indicates that QDs size increased with thermal treatment (figure 2(b)).

At constant HT 540 °C/10 h, absorption & PL spectra of PbSe QDs were also shifted as a function of transition metals ions (Ti²⁺/Mn²⁺/Ni²⁺) embedded into the crystal structure QDs (table 2). We expected bandgap of alloyed QDs were changed depending on the solubility limit of these dopant ions in host QDs.

N.B. The concentration of transition metal oxides (0.2 mol%) & heat treatment (540 °C/10 h) constant for all glasses.

3.2. Size distribution of QDs in glasses

The structural & size distributions of QDs in glasses were characterized using X-Ray Diffraction (XRD) measurements. As-prepared glasses (with & without TMO addition) showed no XRD peaks. However, diffraction peaks have appeared at (200) and (220) planes after HT 530 °C for 10 h which confirms the formation of QDs in glasses (figure 3). Crystallite sizes of NCs are calculated using Scherrer equation, measuring x-ray Diffraction [25], \( R = \frac{b \lambda}{\beta \cos \theta} \) where \( R \) is the crystallite size assuming they were cubes, monodisperse in size. XRD image shows that Pb1-xTi2-Se QDs precipitated in glasses at 530 °C/10 h and Full-Width Half Maximum at (220) is slightly broad with more TiO addition which is an indication of lower crystal size based on Scherrer equation. There might be a slight lattice distortion of Pb1-xTi2-Se crystal structure with incorporation of Ti²⁺ ions. The lattice parameter of PbSe crystal structure more likely decreased due to the replacement of Pb²⁺ ions having larger ions (~112 pm) by smaller ionic radius such as Ti²⁺ (100 pm) or Mn²⁺ (~83 pm) or Ni²⁺ (~69 pm). A similar thought was also reported with the incorporation of Manganese (Mn²⁺) ions in PbSe crystal structure [15, 21 and 26]. In TEM images, we observed several black spots in glasses with [TiO] = 0.0 mol% and
with $[\text{TiO}] = 0.4 \text{ mol\%}$. Thus, QDs were precipitated in both glasses after 530 °C/10 h (figures 4 and 5). The contrast observed in the magnetic image mainly due to the magnetic response of the precipitated semimagnetic Pb$_{1-x}$Ti$_x$Se QDs with a magnetic tip. Dark fields of the MFM image indicate Pb$_{1-x}$Ti$_x$Se NCs have magnetization in a parallel direction to the tip magnetization. Whereas bright fields of the MFM image indicate QDs have magnetization in an antiparallel direction to the tip magnetization (figure 5). The 3D morphology of Pb$_{1-x}$Ti$_x$Se NCs in a glass is shown in figure 5(b). A similar observation was explained in Pb$_{1-x}$Mn$_x$Se QDs and Pb$_{1-x}$Co$_x$Se QDs in glasses [17, 18, 26]. We also reported Pb, Se, Ti ions more highly concentrated inside QDs than in the glass matrix from EELS image in previously published paper [20]. This probably an indication of Ti$^{2+}$ incorporated in Pb$_{1-x}$Ti$_x$Se QDs by replacing some of the positive ions of QDs precursor ions, i.e. Pb$^{2+}$ ions.

### 3.3. Evidence Pb$_{1-x}$Ti$_x$Se NCs in glass using electron paramagnetic resonance (EPR)

EPR spectra shown in figure 6 indicate divalent Ti$^{2+}$ ions ([Ar] 3d2) have been doped in PbSe crystals. Pb$_{1-x}$Ti$_x$Se QDs embedded silicate glass with $[\text{TiO}] = 0.5 \text{ mol\%}$ reveals –double quantum line pattern. It was matched with
the spectroscopic splitting factor \( g \) value of unheated-treated silicate glass contains TiO 0.5 mol%. From EPR spectra measurement, free Ti\(^{2+} \) resonance absorption has occurred between the two split spin levels \([27–29]\). Resonance condition is given by, \( h\nu = g\beta B_\text{o} \), where \( g \) is splitting factor, \( \beta \) Bohr magneton, \( B_\text{o} \) a magnetic field (G). Figure 6 shows, at 300 K, the spectroscopic splitting factor \( g \) value from the EPR spectrum of Ti\(^{2+} \) in pristine silicate glass and Pb\(_{1-x}\)Ti\(_x\)Se NCs embedded silicate glass at low microwave power was 2.163 56 and 2.157 40 respectively. This confirms that Ti\(^{2+} \) ions substitute some Pb\(^{2+} \) ions of host PbSe NCs.

4. Conclusion

Silicate glasses containing Pb\(_{1-x}\)Ti\(_x\)Se QDs were prepared adding small amount transition metals oxide at constant and varying heat-treatment temperature. Optical properties of Pb\(_{1-x}\)Ti\(_x\)Se QDs such as absorption and PL wavelength of QDs moved to a shorter wavelength side with increasing 0.0%–0.5% [TiO] at 530 °C/10 h. Pb\(_{1-x}\)Ti\(_x\)Se QDs with 0.2% transition metal ions (such as Ti\(^{2+} \), Mn\(^{2+} \), Ni\(^{2+} \)) have different optical properties as that of pure PbSe QDs. With increasing heat-treatment temperature from 510 °C to 540 °C, optical absorption and PL spectra moved to longer wavelength sides keeping transition metal oxide concentration constant. This is mainly due to a change in temperature that often leads to the uncontrolled growth of QDs.

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Figure 6. EPR spectra of the 0.5% TiO addition in silicate glasses (a) As-prepared glass contains 0.5% TiO, (b) Pb\(_{1-x}\)Ti\(_x\)Se QDs precipitated in glass.
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