PbSe quantum dots grown in a high-index low-melting-temperature glass for infrared laser applications

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ABSTRACT

PbSe quantum dots (QDs) were grown in high-refractive-index low-melting-temperature lead-phosphate glass. QDs with various sizes ranging from 2 nm to 5.3 nm were grown by controlling the growth parameters, heat-treatment temperature and time. The corresponding room-temperature exciton absorption was tuned within the infrared region from 0.93 μm to 2.75 μm. Photoluminescence was measured for samples with absorption peaks above 0.95eV. Real time quantum dot growth was demonstrated by monitoring the evolution of exciton absorption with temperature and time duration. As a demonstration of the use of QDs in laser applications, the saturation fluence (F_{sat}) of one of the QDs was evaluated and found to be ~2.1 μJ/cm^2 at 1.2 μm.

Keywords: Quantum dots, exciton absorption, saturable absorbers, high-index glass, lead-phosphate glass

1. INTRODUCTION

Semiconductor quantum dots (QDs) are of interest for optoelectronics since they demonstrate active properties including the modulation of light, optical nonlinearity, optical gain, and lasing [1-3]. These properties are observed at wavelengths close to the quantum optical transitions in the QDs. The dependence of the transition energy on QD size allows tuning of these effects to the wavelength of a specific light source, and resonance tuning is possible if the QDs have a narrow size-distribution. QDs of IV–VI materials such as PbS and PbSe offer access to the regime of strong quantum confinement due to their relatively large exciton Bohr radii. The electron and hole masses are almost identical in the bulk, so the electron and hole wave functions will be similar, approximating an ideal quantum dot in the strong-confinement limit. For PbSe, the exciton Bohr radii is ~ 46 nm, which is much larger than in any other semiconductors. These large radii allow strong confinement to be achieved in relatively large nanostructures, providing a wide tunability of the first exciton transition energy.

Growing QDs in glasses offers attractive applications such as saturable absorbers for passive Q-switching and mode-locking in solid-state lasers[1,2] and active media for lasers[3], in a robust all solid-state format. Present research work on integrated photonics such as integrated photonic circuits [4, 5] and on realizing compact ultrashort sources [6], provides a motivation for the fabrication of QD-containing glasses with a wide range of refractive indices so as to have proper index matching for reduced reflection losses and/or as part of a guided-wave index structure. Though there are reports on growing QDs in high-index lead-silicate glass[7], the melting point of lead-silicate glass (~1400 ^oC) is much higher than the boiling point of PbSe/PbS semiconductors (~1100 ^oC), which results in loss of semiconductor due to evaporation. Therefore the use of a low-melting temperature glass should help to maintain high semiconductor concentration in the final glass matrix. This encourages the nucleation and growth of semiconductor QDs. Lead-phosphate glass [8, 9] offers the required low melting temperature and a high refractive index and indeed the PbO-ZnO-P_2O_5 glass system provides refractive index tunability from 1.5 to 1.8 [10] to allow matching the index of specific laser crystal. In particular, they offer the additional advantage of including higher concentrations of PbSe by substitution of

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the PbO already within the glass, while at the same time maintaining a constant relative concentration of lead and other glass components and hence limits the change in refractive index due to PbSe doping once a desired refractive index has been achieved [8].

In this work, narrowly size-distributed PbSe QDs were grown in high-index low-melting-temperature lead-zinc-phosphate glass ($PbO\text{-}ZnO\text{-}P_2O_5$). Through controlled heat treatment the QD size was varied between 2nm and 5.3nm and the corresponding exciton peak of the QD was tuned within the infrared region between 0.93 µm and 2.75 µm. QD growth was monitored in real time for the precise control of the QD exciton absorption. The saturation fluence (F_{sat}) of one of the QDs was evaluated.

2. EXPERIMENTAL DETAILS

Glass batches of 20 g of (50-x) PbO - 10ZnO - $40P_2O_5$ - xPbSe (named here as PZPx) (x=0, 10 mol%) were prepared by a standard melting-quenching approach in a dry atmosphere[8]. The glasses were melted at 900 ^oC for 3 hours (hrs), casted onto a brass mould and subsequently annealed at 350^oC to release the strain. QDs were grown in PZP10 glass by heat treating the sliced glasses between 370 ^oC and 400 ^oC with dwelling time varying from 2 hrs to 24 hrs. Thermal analysis was carried out using a Perkin Elmer Thermo Gravimetry/Differential Thermal Analyser (TG/DTA). The refractive indices were measured with a white light ellipsometer over the range 300 nm-1600 nm. Transmission electron microscope (TEM) images were recorded with a Jeol 3010 and absorption spectra of heat treated samples and real time absorption spectra during heat treatments were recorded using a Cary 500 (from Varian) spectrophotometer. Photoluminescence (PL) was measured for samples with absorption peaks below 1500 nm by pumping with an 808 nm diode laser and an optical spectrum analyser.

3. RESULTS AND DISCUSSIONS

3.1 Growth of PbSe quantum dots in high-index low-melting-temperature glass

Before QDs were grown within the PZP10 glass, the glass transition temperature (T_g) and the crystallization temperature (T_x) were identified by performing differential thermal analysis (DTA) for PZP10 glass at a scan rate of 10 ^oC/min (Fig. 1). The T_g and T_x were identified from the DTA curve as ~370 ^oC and ~465 ^oC respectively.

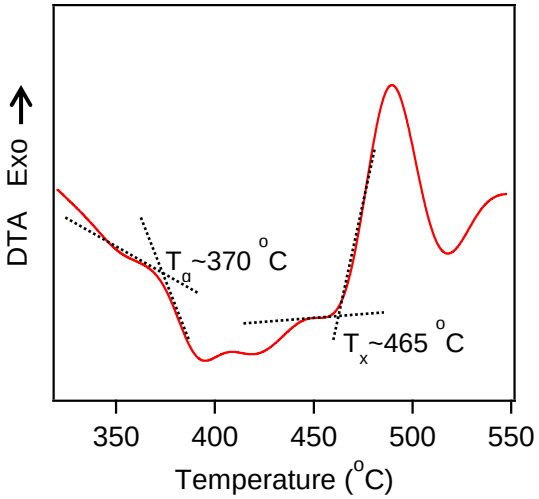

Figure 1: DTA curve of PZP10 glass

Quantum dots were grown inside PZP10 glass by heat treatments within the temperature range 370 ^oC to 420 ^oC for dwelling times varying between several minutes and 24 hrs. As the dwelling time increased at a fixed temperature, the colour of the glass samples gradually changed from dark red to brown and then to black. The formation of PbSe QDs within the glass matrix was then confirmed by recording absorption spectra and TEM images. For heat treatment at 370

°C, QD nucleation and growth was observed for dwelling times above 6 hrs. For higher temperatures, e.g. 400 °C, QD nucleation and growth were observed for dwelling times as short as 30 minutes.

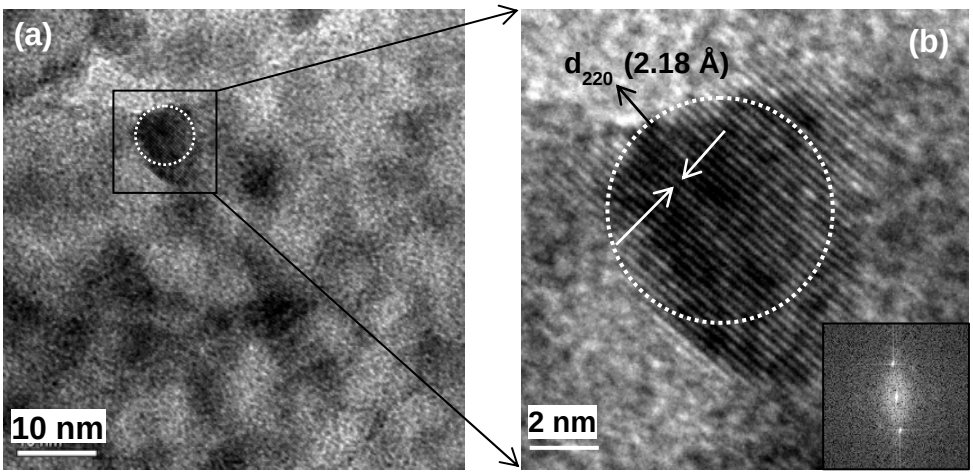

Figure 2: (a) High-resolution TEM image of PZP 10 glass heat treated at 380 °C for 12hrs, (b) Magnified TEM image showing fringe pattern of PbSe QDs embedded in PZP glass (PZP10) heat-treated at 380 °C for 12 hrs. Inset is the Fourier transform of d_{220} plane.

Figure 2a shows the high-resolution TEM image of PZP10 glass heat treated at 380 °C for 12 hrs. The observed fringe patterns of different planes of QD crystals, whose physical extent is indicated by the dotted rings, were well resolved at higher magnifications (Fig. 2b). The interplanar distances (*d*-spacing) calculated from the Fourier transform of the fringe patterns are d_{111}= 3.53 Å, d_{200}= 3.08 Å and d_{220}= 2.18 Å. One such Fourier transform is shown as the inset of Fig. 2b (of the *220* plane). The calculated *d*-spacings are well-matched to the *d*-spacings of PbSe planes [11]. The measured QD radii vary between 3.1 nm and 3.5 nm peaking at ~3.3 nm (± 0.2 nm variation in QD radius).

Figure 3 shows the measured refractive indices of PZP0, PZP10 and 5.2 nm QD containing PZP10 glass over the wavelength range 300 nm to 1600 nm. Though there are variations in refractive index of PZP0 and PZP10 glasses in the visible region, the index variation above 800 nm is < $7x10^{-3}$. The indices of both the glasses are very similar at near infrared wavelengths from which it can be concluded that the substitution of PbO with PbSe gives the advantage of maintaining a nearly constant refractive index even at high PbSe doping concentrations. Glass containing QD of radius 5.2 nm shows slightly higher refractive index compared to the glasses without QD growth, which might be due to the effects of the larger QD size resulting in a higher crystallinity.

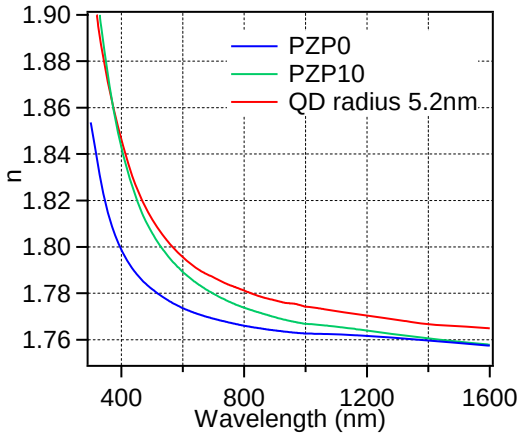

Figure 3: Refractive index profile of PZP0, PZP10 and 5.2 nm QD containing PZP10 glass over the wavelength range 300 nm to 1600 nm

3.2 Absorption and emission spectra of PbSe quantum dot containing glass

Absorption spectra of QDs grown by heat treating at 380 °C for different times are shown in Fig. 4. Absorption spectra show the first exciton transition of the QDs. These transitions are blue shifted with respect to the band gap of bulk PbSe (~0.27 eV) due to the quantum-confinement effect [12]. The first exciton transition was tuned from 0.93 µm to 2.75 µm by the heat treatment of the PZP10 glasses from 2 hrs to 24 hrs at 380 °C. The saturation of the exciton transitions of the QDs forms the basis of the passive saturable absorption useful for pulsed laser devices. From the transition energy, QD size can also be estimated from the equation (1) [13]:

$$E_n = E_g + \frac{n^2 h^2}{8R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.8e^2}{\varepsilon R} \quad (1)$$

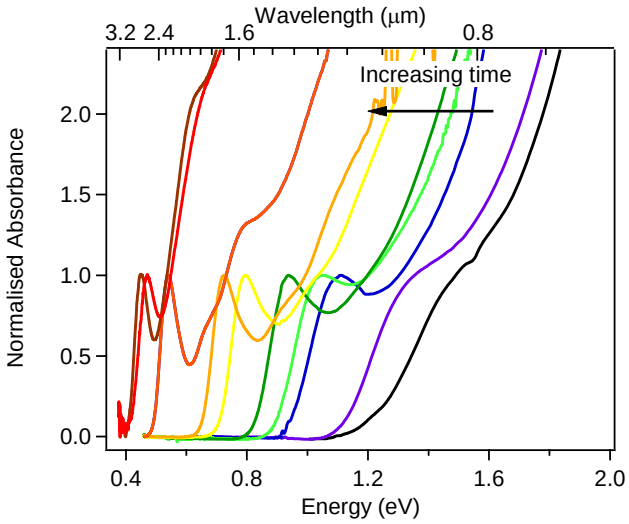

Figure 4: Normalised absorption spectra of PbSe-containing (PZP10) glasses heat-treated at 380 °C from 2 to 24 hrs.

where n is the order of exciton transition, E_n is the exciton transition energy, E_g is the bulk PbSe semiconductor band gap, R is the radius of QD, h is Planck's constant, ε is the dielectric constant, and m_e^* and m_h^* are the effective masses of electron and hole respectively and e is the charge of an electron.

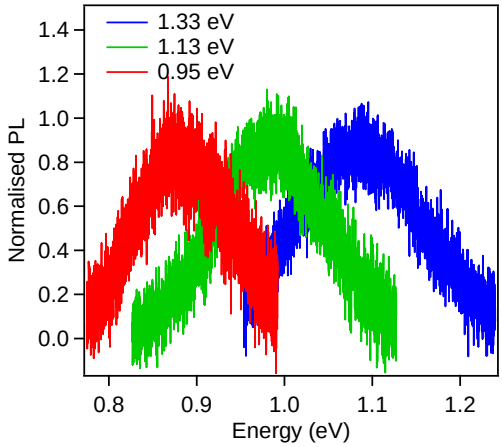

Figure 5: Normalised photoluminescence spectra of PbSe-containing (PZP10) glasses having absorption at 1.33 eV, 1.13 eV and 0.95 eV.

For PbSe, at T=300 K, E_g=0.27 eV, m_e^*=0.12m and m_h^*=0.07m, where m is the mass of electron [13]. The known refractive indices of bulk PbSe and the glass matrix were used to calculate the dielectric constant, $\varepsilon=(n_{PbSe}/n_{PZP10})^2$. The calculated QD radius, ~ 3.23 nm for the QD containing glass peaked at ~0.73 eV, is in close agreement with the direct measurements from TEM (Fig. 2). Photoluminescence were recorded for samples with absorption peaks above 0.95 eV by pumping with 808 nm (1.53 eV) diode laser delivering upto 150 mW (see Fig. 5). The emissions peaks for QD absorptions at 1.33 eV, 1.13eV and 0.95 eV were at 1.08 eV, 0.98 eV and 0.87 eV respectively. The Stokes shift was found to decrease with the increase in QD size.

3.3 Real time quantum dot growth monitoring.

Experiments were performed on a QD containing glass to monitor the QD growth in real time and hence to precisely control the exciton peak position. A Cary 500 spectrophotometer was modified to incorporate a heating system so that absorption spectra were recorded from room temperature (RT) to 420 ^oC in real time. Surface polished QD containing glass with an exciton peak at 0.74 eV (at RT) was heated from RT to 420 ^oC at 5 ^oC/min and the absorption spectra were recorded at regular intervals. With increasing temperature the exciton peak intensity diminished with an accompanying increase in the full width half maximum (FWHM) of the peak (Fig. 6a). The peak also blue shifted with increasing temperature. The shift in the peak is presented in Fig. 6b. A shift of 45 meV was observed on heating the sample from RT to 420 ^oC. This shift is temporary and retraces the peak positions with temperature as the temperature is reduced to RT, which is due to the variation in the confinement energy of the QDs [14].

The peak can be shifted permanently by increasing the dwelling time at temperatures above T_g. To monitor the permanent peak shift in real time, the above QD containing glass was heat treated at 420 ^oC by increasing the dwelling time from 0 min to 50 min. The evolution of absorption spectra with increase in dwelling time, at 420 ^oC, was recorded and is presented in Fig. 7a. With an offset of 45 meV in the exciton absorption peak (temporary peak shift shown in Fig. 6) at 420 ^oC as compared to RT, the peak also shifts with the dwelling time. This shift is due to the growth of QDs within the glass. On heating the glass containing QDs with radius ~3.23 nm, the QD absorption peak (recorded at 420 ^oC) was tuned from 0.695 eV to 0.56eV (see Fig. 7b and c). Considering the fact that the temporary peak shift of 45 meV with temperature (from RT to 420 ^oC) is constant for QDs of all sizes [14], the calculated RT exciton absorption peak after heat treatment is 0.56 eV (at 420 ^oC) + 0.045 eV (offset) = 0.605 eV (at RT), which is in agreement with the measured RT absorption spectra (red dotted curve in Fig. 7c). The corresponding QD radius, calculated using eq. 1, is ~3.82 nm. Thus by increasing or decreasing the dwelling times and by monitoring the exciton peak shift in real time gives the advantage of controlling the exciton peak to a desired position.

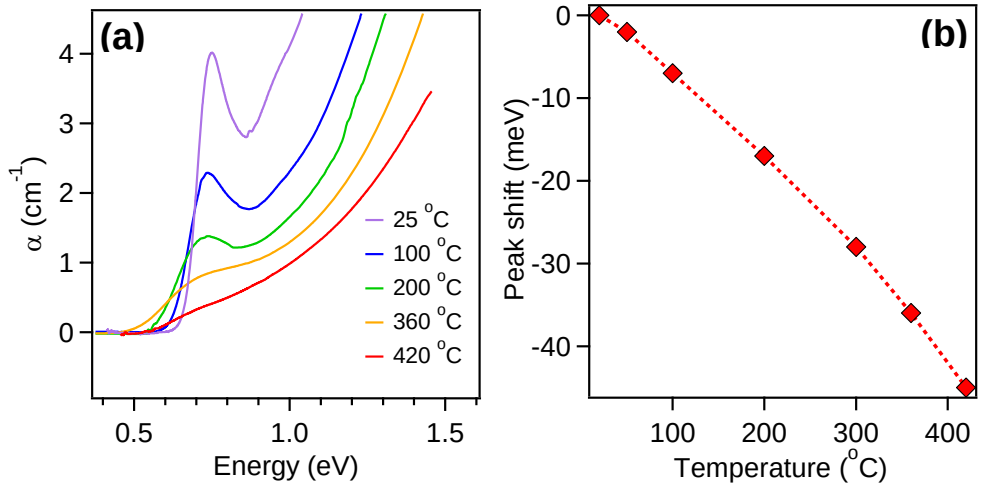

Figure 6: (a) Shift in the exciton absorption peak of PbSe QD (QD radius ~3.23 nm) with temperature (RT exciton peak is at 0.74 eV) and (b) peak shift with increase in temperature.

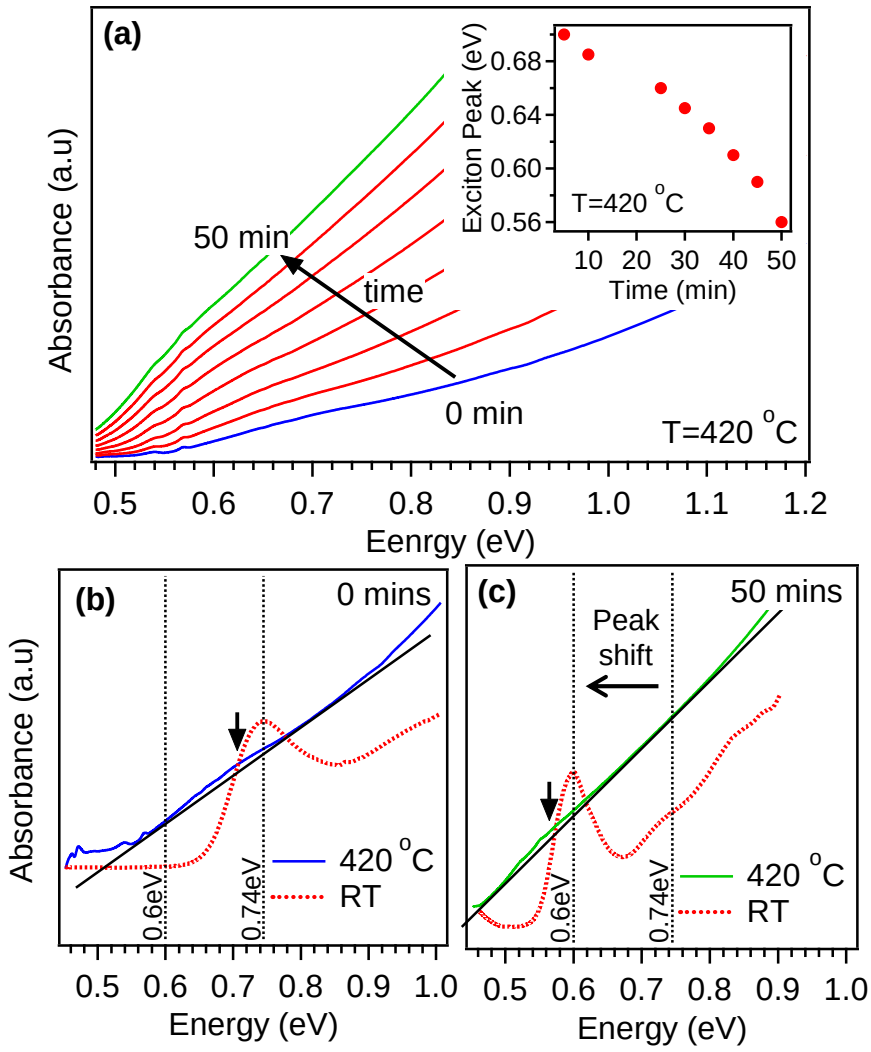

Figure 7: (a) Absorption spectra of PbSe QDs at various heat treatment times (temperature maintained at 420°C) monitored in real time. Inset: Exciton peak shift with heat treatment time (at 420°C) (b) and (c) Absorption spectra of PbSe QDs at RT and 420 °C for heat treatment times (b) 0 min and (c) 50 min. (Black solid lines and arrows in b and c are the base lines and the exciton peak positions at 420 °C respectively).

3.4 Saturable absorption.

QD-containing glasses are promising materials as saturable absorbers for mode-locking [1,2]. The QD-containing glasses fabricated by the method described above should be of interest for optical applications over the infrared spectral region from as low as 0.93 μm to as high as 2.75 μm. Furthermore, growing QDs in high-index glasses could pave the way for integrated photonic devices based on materials with similarly high index. For example, Ti:Sapphire, a material commonly used for bulk ultrafast lasers [15], has a refractive index of 1.76 at 800 nm, comparable to the present glass system, and several methods of creating waveguides in these materials have been previously reported [16].

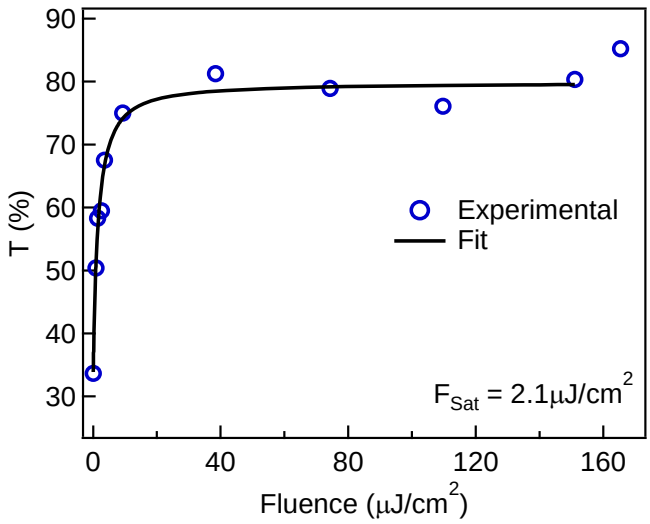

Figure 8: transmission versus fluence at 1.2 μm for QD absorption peak at 1.3μm

Saturable absorption properties was demonstrated in one of the QDs peaked near 1.3 μm. The saturation fluence (F_{sat}) was evaluated by measuring the intensity dependent transmission at 1.2 μm, pumped by a femtosecond (fs) laser with pulse duration of 150 fs, average power of up to 70 mW, and repetition rate of 1 kHz. The incident energy fluence on the sample was varied using neutral density filters and the transmission was calculated from the ratio of the pulse energy with and without the sample. This has been plotted against the input energy fluence in Fig. 8. Using a least squares fit[17] (see Fig. 8) the saturation fluence and the non-saturable absorption coefficient were estimated to be ~2.1 μJ/cm^2 and ~0.85 cm^{-1} respectively. The estimated value of saturation fluence is comparable to a previously reported QD-containing glass used as a saturable absorber for mode-locking at 1.3 μm [2].

4. CONCLUSIONS

PbSe quantum dots (QDs) were grown in high-refractive-index low-melting-temperature lead-phosphate glass. QDs with various sizes ranging from 2 nm to 5.3 nm were grown by controlling the growth parameters, heat-treatment temperature and time. The corresponding room-temperature exciton absorption was tuned within the infrared region from 0.93 μm to 2.75 μm. Photoluminescence was measured for samples with absorption peaks above 0.95 eV. Real time quantum dot growth was demonstrated by monitoring the evolution of exciton absorption with temperature and time duration. These high-index QD-containing glasses are promising for optical devices such as ultrafast integrated lasers. As an example, the QDs saturable absorption properties were measured at 1.2 μm, giving a saturation fluence of 2.1 μJ/cm^2, demonstrating its promise as a saturable absorber in pulsed laser systems.

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