Broadband near-infrared luminescence and tunable optical amplification around 1.55 μm and 1.33 μm of PbS quantum dots in glasses

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ABSTRACT

Silicate glasses containing PbS quantum dots (QDs) with narrow size distribution were prepared through heat treatment. Transmission electron microscopy (TEM) results show that spherical PbS QDs are densely dispersed in the glassy matrix. Using ZnS–PbO to replace PbS as precursor of PbS QDs, the size distribution of PbS QDs in glasses becomes more uniform. Tunable infrared luminescence from 1100 to 2200 nm has been obtained by controlling the glassy matrix and preparation parameters. Obvious optical amplification at communication windows of 1.55 μm and 1.33 μm is probed, and the PbS QDs doped glasses using ZnS–PbO as precursor exhibit larger optical amplification. The PbS QDs doped glasses with intense optical amplification are considered to be promising candidate as gain medium for broadband fiber amplifier and tunable fiber laser.

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1. Introduction

Quantum dots (QDs) have attained considerable attention due to their unique electronic and optical properties. Based on their quantum confinement effect, QDs show a variety of size dependent properties, which exhibit potential applications in the areas of lasers, saturable absorbers, bio-labels, light emitting diodes (LED), etc. [1–8]. Among most II–VI and III–V QDs, although the exciton Bohr radii (a_B) is typically ∼10 nm or more, the Bohr radii of individual electron (a_e) is much larger than that of hole (a_h) due to the large difference in their effective masses [9]. Taking InSb QDs as an example, although its a_B is as large as 54 nm, a_h is only about 2 nm, so strong confinement of the hole will be impossible. However, for lead chalcogenide (i.e. PbS, PbSe, and PbTe) QDs, owing to their similarly small effective masses between electron and hole, the large confinement energy is split about equally between electron and hole carriers (e.g. $a_h = a_e = 10$ nm for PbS QDs, $a_h = a_e = 23$ nm for PbSe QDs) [1,9]. Based on the larger Bohr radii of both electron and hole, lead chalcogenide QDs show a much higher degree of confinement when their radii $R < a_e$, a_h. Therefore, lead chalcogenide (PbS) QDs are investigated in this work because the strong confinement effect can be obtained easily with large particles.

Among a variety of chemical and physical methods to prepare PbS QDs, preparation of QDs in glassy matrix by heat treatment has gained particular attention as it is a convenient and inexpensive way to precipitate QDs with excellent size and distribution control [9–15]. What is more important, synthesis of QDs in glassy matrix is beneficial for the fabrication of devices in planar and fiber forms, which is vital for their applications as amplifiers, lasers, waveguides, etc. Several efforts have been made on the synthesis and properties of PbS QDs embedded glasses, including nucleation and growth mechanism, tunable photoluminescence (PL), saturable absorbers, etc. However, the investigation on optical amplification (gain) of PbS QDs at optical communication window, which is one of the most important factors to estimate the practical application as gain medium in fiber amplifier and fiber laser, is scarce. Only a few works have been performed on the optical amplification at ∼1.3 μm [15]. So far, to our best knowledge, no any work has been carried out on the optical amplification at ∼1.55 μm window.

Herein, PbS QDs are precipitated in silicate glassy matrix by heat treatment. Tunable PL has been obtained by the control of QDs size and distribution in glass matrix. Optical amplification at third (1.55 μm) and second (1.33 μm) communication windows is characterized by traditional two-wave mixing configuration, which confirms obvious amplification at 1.55 μm and 1.33 μm, respectively.

2. Experimental details

In previous works, the SiO_2–B_2O_3–K_2O–BaO–ZnO glass system has demonstrated as an excellent matrix to form PbS QDs by heat treatment [13]. In this work, we used this system with an additional 1–1.5 mol% PbS for the formation

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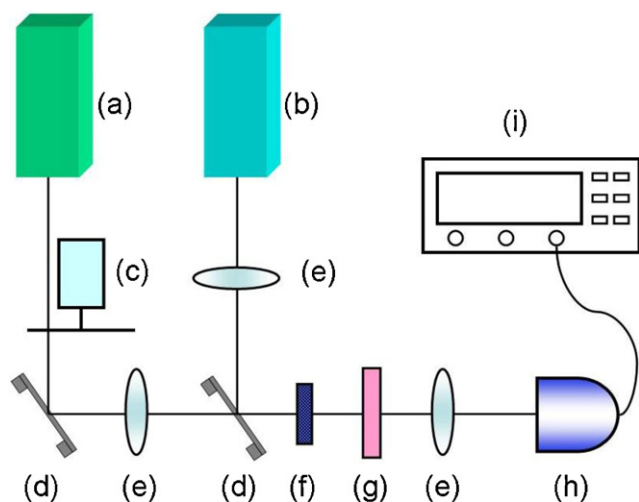
Fig. 1. Schematic diagram of optical amplification experimental system. (a) 1330 nm or 1550 nm LD as probe beam, (b) 808 nm LD as excitation source, (c) chopper, (d) mirror, (e) lens, (f) sample, (g) filter, (h) InGaAs *p-i-n* detector, and (i) digital oscilloscope.

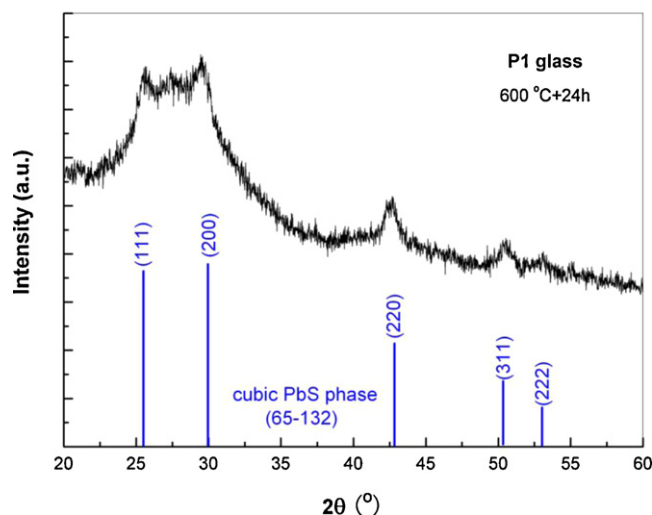**Fig. 2.** XRD pattern of P1 glasses heat treated at 600 °C for 24 h.

of PbS QDs. Another glass system, which was using ZnS–PbO to replace PbS as starting materials, was also prepared to compare the infrared luminescence and optical amplification properties of PbS QDs doped glasses. Analytical grade SiO_2, B_2O_3, K_2CO_3, $BaCO_3$, ZnO and PbS (or ZnS and PbO) were used as raw materials to prepare precursor glasses through the melt-quenching method. The stoichiometric starting powders were melted at 1400 °C for 60 min in a closed alumina crucible to alleviate the volatilization of sulfur. The glass melts were then quenched on a stainless steel mold at room temperature. To precipitate PbS QDs in glasses, the glasses were thermally treated at 525–620 °C for 24 h. After heat treatment, the PbS QDs doped glasses were then cut into the thickness of 3 mm and optically polished for optical and amplification characterizations. The glasses with a normal composition (in mol%) of $66SiO_2$–$8B_2O_3$–$18K_2O$–$4BaO$–$4ZnO$–$1.5PbS$, $66SiO_2$–$8B_2O_3$–$18K_2O$–$4BaO$–$4ZnO$–$1PbS$ and $66SiO_2$–$8B_2O_3$–$18K_2O$–$6ZnO$–$2ZnS$–$1PbO$ were labeled as P1.5, P1 and Z2, respectively.

The morphology and crystallization of PbS QDs in glass was characterized by high resolution transmission electron microscopy (HR-TEM, Philips-FEI, Netherlands). The accelerating voltage was as high as 300 kV. X-ray diffraction (XRD) of the samples was performed using a Rigaku D/MAX X-ray diffractometer with CuKα radiation. Absorption spectra of specimens were recorded on Lambda 900 (Perkin Elemer, USA) spectrophotometer. PL spectra of QDs doped glasses were measured on Triax 320 (Jobin Yvon, France) fluorescence spectrofluorometer. An 808 nm laser diode (LD) with a power density of ∼48 W/cm² was used as an excitation source. All the measurements were performed at room temperature.

Optical amplification of PbS QDs doped glasses was performed by traditional two-wave mixing configuration, as shown in Fig. 1 [16]. An 808 nm laser diode (LD) was acted as an excitation source, while a 1330 nm (or 1550 nm) LD was used as a probe beam. The coupled input beam was focused onto the surface with a focal spot of ∼0.7 mm in diameter. The optical gain, g is defined as $g = I/I_0$, where I and I_0 represent the intensity of probe signal with and without an excitation source.

3. Results and discussion

Fig. 2 shows the XRD pattern of P1 glasses heat treated at 600 °C for 24 h. Based on the broad diffraction background ascribed to amorphous silicate glass, a series of peaks appear, which are consistent with the standard XRD cards of cubic PbS phase. Fig. 3(a) and (b) illustrates the TEM images of P1 and Z2 glasses heat treated at 580 °C for 24 h. The particles are approximately spherical, which are densely distributed in both glasses. Fig. 3(c) shows the size distribution of PbS QDs corresponding to TEM image in Fig. 3(a). The diameter of QDs in P1 glasses is between 3 and 8 nm, with an average diameter of ∼5.7 nm. HR-TEM image of one single PbS QD is also given in the insert of Fig. 3(a). A group of lattice fringe can be clearly observed in the image. The lattice constant is calculated to be 0.21 nm, which is assigned to the (2 2 0) plane of cubic PbS crystals. The result agrees well with the XRD pattern in Fig. 2, which indicates that PbS QDs with high density have been formed in P1 glasses after heat treatment at 580 °C for 24 h. For Z2 glasses in

Fig. 3(b), a large number of spherical PbS QDs are also found in TEM image. The average diameter of PbS QDs is ∼4.6 nm in Fig. 3(d), and the size distribution of PbS QDs in Z2 glasses is more uniform than that of P1 glasses.

Fig. 4 shows the absorption spectra of P1.5 glass heat treated at various temperatures for 24 h. For the as-prepared P1.5 glass, no obvious absorption peak is observed in the spectrum. When the glass is heat treated at 550 °C for 24 h, a new absorption peak appears at 1280 nm, which is due to the generation of electron and hole pairs in PbS QDs induced by the excitation photon. With the temperature increases to 575 °C and 600 °C, the absorption peak of PbS QDs shifts to the longer wavelength region. This is due to the larger size of PbS QDs formed at higher heat treatment temperature. The large blue-shift from the bandgap of bulk PbS crystal demonstrates the strong quantum confinement effect of PbS QDs in glasses. The absorption spectra of P1 and Z2 glasses heat treated at various temperatures are similar with those in Fig. 4. When the glasses are heated at 580 °C, 600 °C and 620 °C for 24 h, the absorption peaks owing to PbS QDs in P1 glass shift from 1490 nm to 1645 nm and 1820 nm, while those of Z2 glasses shift from 1100 nm to 1280 nm and 1520 nm.

From previous works, the average radius of the PbS QDs in glasses can be estimated by the following equation [17,18]:

$$(E_g(R))^2 = E_g^2 + \left(\frac{2h^2E_g}{m^*} \right) \left(\frac{\pi}{R} \right)^2, \tag{1}$$

where R is the average radius of PbS QDs, h is Planck's constant, m^* is the reduced mass, $E_g(R)$ is the effective energy of PbS QDs, and E_g is the bandgap energy of bulk PbS semiconductor ($E_g = 0.41$ eV). From the absorption spectra of PbS QDs doped glass, the average radius of PbS QDs in P1 and Z2 glasses heat treated at 580 °C for 24 h is calculated to be ∼3.2 nm and ∼2.6 nm, which agrees with the TEM result in Fig. 3. And the average radius of other PbS QDs doped P1.5, P1 and Z2 glasses heat treated at various temperatures is between 2.5 and 5 nm.

PL spectra of PbS QDs doped glasses are illustrated in Fig. 5. Broadband near-infrared peaks are observed in the spectra, which is due to the recombination of electron and hole pairs created by the excitation source. For the P1.5 glasses heat treated at 550 °C, 575 °C, and 600 °C for 24 h, the central wavelength of emission band shifts from 1370 → 1705 → 1795 nm. While the full width at half-maximum (FWHM) increases from 220 → 300 → 350 nm. With the increase of heat treatment temperature, PbS QDs grows larger, which will result in the red-shift of PL emission band. The size distri-
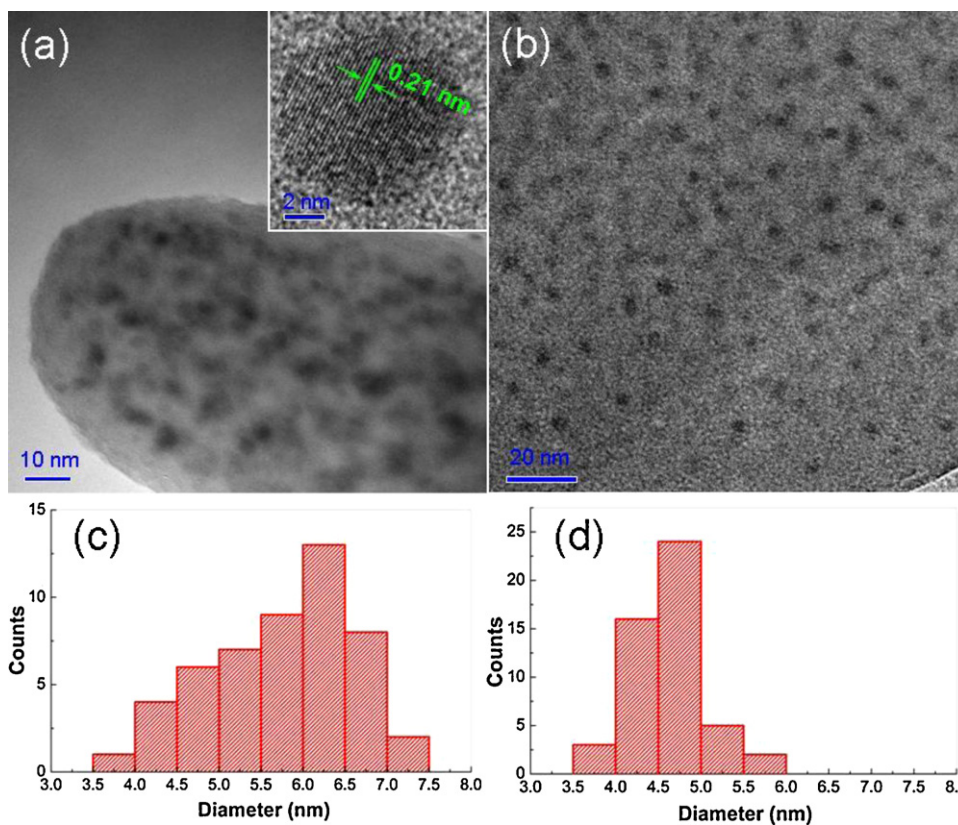
Fig. 3. TEM image of (a) P1 glasses and (b) Z2 glasses heat treated at 580 °C for 24 h. The insert of (a) shows the HR-TEM image of a single PbS QD. (c and d) The size distribution of PbS QDs in P1 and Z2 glasses corresponding to TEM image (a) and (b), respectively.

bution of PbS QDs in glasses also becomes wider. This will broaden the FWHM of emission band. In P1 glasses with less concentration of PbS, red-shift and broadening of emission band is also observed when the heat treatment temperature increases from 580 °C to 620 °C. However, comparing with the emission band of P1.5 glasses heat treated at the same condition (e.g. 600 °C for 24 h), the emission band of P1 glasses is located at lower wavelength, which is probably due to the lower starting concentration of Pb and S source in P1 glasses. In this work, we also replace PbS with ZnS + PbO as Pb and S source to prepare PbS QDs doped glasses (Z2 glasses), and the PL spectra are shown in Fig. 5. Besides the red-shift and broadening of emission band with the increase of heat treatment

temperature, the growth speed of PbS QDs is much slower than that of P1 and P1.5 glasses. The FWHM of Z2 glasses heat treated at 580 °C, 600 °C, and 620 °C for 24 h is about 220 nm, 260 nm and 285 nm, respectively, which is also narrower than that of P1.5 and P1 glasses. The change of emission band of Z2 glasses can be elucidated from the role of ZnO (ZnS) in glasses during the formation and growth of PbS QDs. Firstly, when the glass is melted at high temperature, the volatilization of sulfur is unavoidable. ZnO is usu-
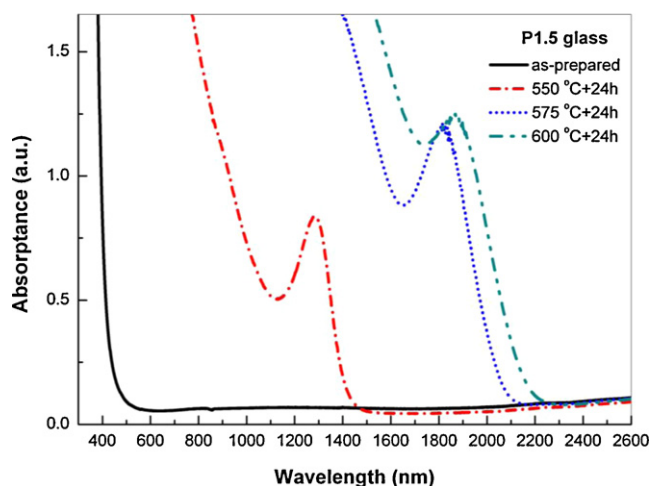
Fig. 4. Absorption spectra of P1.5 glasses heat treated at different temperatures for 24 h.
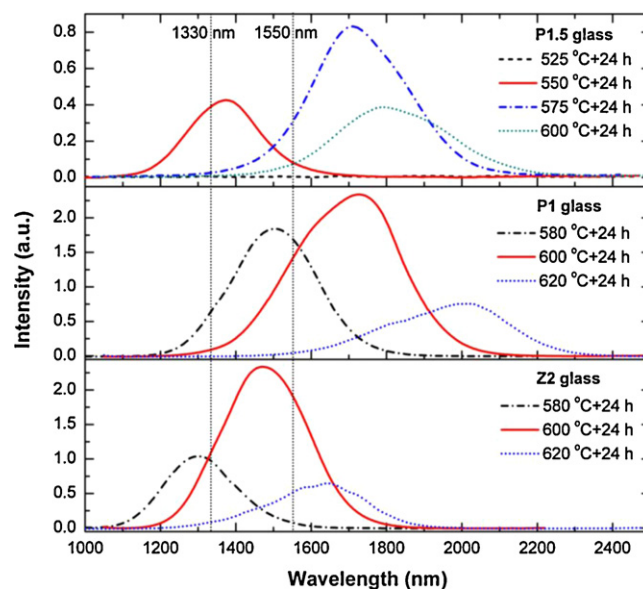
Fig. 5. PL spectra of P1.5, P1 and Z2 glasses heat treated at different temperatures for 24 h. An 808 nm LD was using as an excitation source.
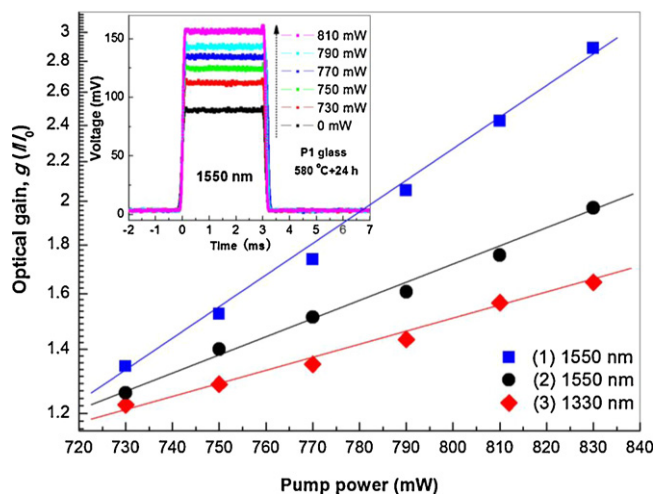
Fig. 6. Optical gain (I/I_0) of PbS QDs doped glasses collected as a function of pumping power. (1) Z2 glasses heat treated at 600 °C for 24 h, (2) P1 glasses heat treated at 580 °C for 24 h, and (3) P1.5 glasses heat treated at 550 °C for 24 h. The insert shows the amplified signals of P1 glasses heat treated at 580 °C for 24 h.

ally added to inhibit the volatilization of sulfur [19]. During the glass melting process, sulfur prefers to bonding with zinc at high melting temperature, which will inhibit the volatilization of sulfur. When the glasses are heat treated to form PbS QDs, ZnS then releases sulfur to lead to facilitate the precipitation of PbS QDs. Secondly, the melting and volatilization temperature of ZnS (∼1800 °C and 1180 °C) is higher than that of PbS (1114 °C and 860 °C). Therefore, compared with PbS, using ZnS + PbO as the precursor is more beneficial to inhibiting the volatilization of sulfur. Furthermore, in P1.5 and P1 glasses, due to the volatilization of sulfur during glass melting, the final glasses are always lead rich. While in Z2 glasses, due to the inhibition of sulfur volatilization and the compensation of sulfur by increasing the S/Pb ratio (ZnS:PbO = 2:1) in the starting materials, the stoichiometry between sulfur and lead can reach a balance. Therefore, when the glasses are heat treated at 550–620 °C, the release and migration of sulfur to precipitate PbS QDs in Z2 glasses is more stable than that in P1.5 and P1 glasses. Additionally, due to a majority of sulfur is bonding with zinc in Z2 glasses, the growth rate of PbS QDs in Z2 glasses is slower than that in P1.5 and P1 glasses. Both the factors discussed above result in the smaller diameter and uniform size distribution of PbS QDs in Z2 glasses (see Fig. 3).

For the practical application as gain medium in fiber amplifier and fiber laser, the optical amplification of PbS QDs doped glasses is one of the most important factors. However, the estimation of the optical amplification character of PbS QDs doped glasses at 1.55 μm communication window has not been processed yet. Herein, the optical amplified signals at 1.55 μm of PbS QDs doped glasses are measured by the traditional two-wave mixing configuration in this work. Owing to the intensive PL and excellent peak match, P1 glasses heat treated at 580 °C for 24 h is chosen as the representative sample for 1.55 μm optical amplification measurement. The insert in Fig. 6 shows the amplified signals of P1 glasses. No obvious spurious mode is detected in the vicinity of the signal. When the excitation power is directed as 730 mW, the optical gain, g is about 1.26. With the increase of excitation power, the g value increases linearly in logarithmic form. When the excitation power reaches 830 mW, the optical gain is as large as 1.97. For Z2 glasses heat treated at 600 °C for 24 h, which is using ZnS + PbO as the precursor of PbS QDs, the optical gain is about 1.34 and 2.89 with the excitation power of 730 mW and 830 mW, respectively. Both the optical gain, g and the slope efficiency (vs. excitation power) of Z2 glasses are obviously larger than those of P1 glasses. It can be ascribed to

the uniform size distribution of PbS QDs in Z2 glasses, which has been confirmed by the TEM results in Fig. 3. Due to the uniform size distribution of QDs, the PL intensity will enhance while the optical loss decreases. Therefore, PbS QDs doped Z2 glasses will exhibit a higher optical gain.

From the works reported previously [20,21], it can be found that the PL spectra can be influenced by the excitation power, which can result in the heating of the glass and change the effective bandgap energy of the QDs. To confirm the possible heating effect induced by the excitation laser, P1 glass heat treated at 580 °C for 24 h is choosing as a representative sample, and no obvious change is observed in the PL spectra with different excitation powers. Therefore, it can be deduced that the influence of the possible heating effect induced by excitation laser in optical amplification measurement can be neglected.

In this work, choosing P1.5 glasses heat treated at 550 °C for 24 h as a representative sample, we also estimate the optical amplification property of PbS QDs doped glasses. Obvious optical gain is detected at 1.33 μm, which confirms that the PbS QDs doped glasses can exhibit multi-wavelength amplification by controlling the size and distribution of PbS QDs. And the optical amplification property can also be further enhanced through the improvement of glassy matrix and synthesized parameters.

4. Conclusions

PbS QDs with an average diameter of 3–8 nm, which show strong quantum confinement effect, have been precipitated in silicate glasses by heat treatment. By replacing PbS with ZnS–PbO as precursor, the size distribution of PbS QDs in glasses became more uniform and narrower. Tunable near-infrared luminescence covered communication windows were achieved by controlling the size of PbS QDs. The optical amplification at 1.55 μm and 1.33 μm of PbS QDs doped glasses was detected in PbS QDs doped glasses. Due to the optical amplification is obtained at the exciton ground state transitions, it can be deduced that the ultrabroad band optical amplification can be achieved in PbS QDs doped glasses by controlling the size of QDs.

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