Near-infrared photoluminescence of PbS QDs precipitated in the glass matrix

Chao LIU, Yong Kon KWON and Jong HEO†

Center for Information Materials, Department of Materials Science and Engineering, Pohang University of Science and Technology, Pohang, Gyeongbuk, 790–784, Korea

Optical properties of PbS quantum dots (QDs) precipitated inside the oxide glass matrix were investigated. Photoluminescence (PL) spectra were recorded with peak wavelengths located at 1170–1680 nm with peak width of 150–500 nm. Radii of QDs in glasses were 2.0–3.7 nm depending upon the thermal treatment conditions. Changes in temperatures and excitation intensities resulted in the shift of photoluminescence bands as large as 70 nm, due to the laser-induced local heating. Photoluminescence from PbS QDs showed darkening and brightening behavior. Intensity of the photoluminescence increased with time at low temperature (< 150 K) especially when the excitation intensity was low. Photo-darkening was observed when temperature and/or illumination intensities increased. Competition between the photo-brightening and photo-darkening determined the final steady-state photoluminescence intensity.

Key-words : PbS quantum dots, Photoluminescence, Local heating, Photo-brightening, Photo-darkening

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1. Introduction

Semiconductor nanocrystals (quantum dots or QDs) have been extensively investigated because of their unique optical and electronic properties compared to their bulk counterparts.1,2) For some narrow band gap semiconductors, near IR luminescence that covers the important wavelength region for the fiber-optic communication can be obtained by tuning the band gap energy of the QDs through the size control. In particular, narrow band gap IV–VI semiconductors such as PbS and PbSe due to the large bulk exciton Bohr radii of 18 nm and 46 nm, respectively.3) In addition, it is well known that PbS nanoparticles can provide the luminescence over the whole transmission window (1.2–1.7 μm) of silica optical fibers. Photoluminescence bands of PbS QDs with a proper size distribution can be significantly broader than that of rare-earth ions and therefore, can be potentially used for the broadband optical amplifiers.4)

Current work reports the near infrared photoluminescence of PbS QDs within the transmission window of silica fiber by the thermal treatment of glasses. Peak wavelength of the photoluminescence can be tuned not only by controlling the size of QDs but also by changing the excitation intensities and temperatures. Upon the excitation, photoluminescence also showed reversible darkening and brightening.

2. Experimental procedures

Host glass with the nominal composition (mol%) of 66SiO2·8B2O3·18K2O·4BaO·4ZnO (abbreviated as BZ glass, hereafter) with additional 1.0 PbS was prepared. Starting powders were melted under the ambient atmosphere in an alumina (hereafter) with additional 1.0 PbS was prepared. Starting powders were melted under the ambient atmosphere in an alumina crucible at 1350°C for 90 min. The melt was quenched by pouring onto a brass mold at room temperature. The glass was cut into several pieces and then heat-treated at various temperatures to facilitate the formation of PbS QDs. Transmission electron microscope (TEM) images and diffraction patterns were used to identify the size, shape and crystal structure of PbS QDs. Absorption spectra of the glasses were recorded using an UV/Vis/NIR spectrophotometer over the wavelength region of 300–2400 nm. Photoluminescence (PL) spectra recorded by pumping the specimens with an 800 nm laser beam from a continuous wave Ti: Sapphire laser. Photoluminescence from the specimen was collected at the direction perpendicular to excitation beam using a focusing lens and a 1/4 meter monochromator. The intensity of photoluminescence was measured by an InGaAs detector with a lock-in amplifier. The changes of PL intensities with time were recorded under the continuous excitation condition. Low temperature PL spectra were recorded with an additional cryostat system cooled by compressed helium gas.

3. Experimental results

3.1 Room temperature absorption and photoluminescence spectra

Spherical PbS QDs with rock-salt structure was formed in the glasses through the thermal treatment, as evidenced from the transmission electron microscopy image.5) One typical image taken from glass with different glass composition was shown here for the clear presentation purpose (Fig. 1). Color of glasses changed from yellow to black as a result of the quantum dots formation. Fig. 2(a) shows the absorption spectra of precursor and heat-treated glasses. The broad absorption bands were found at the wavelengths of 1050, 1180 and 1450 nm for glasses heat-treated at 600°C/20 h, 600°C/50 h and 620°C/20 h, respectively.6) The band gap energy of a bulk PbS crystals at room temperature is 0.41 eV and therefore, appearance of the absorption bands in the 1–2 μm wavelength region clearly demonstrated the quantum confinement effect. The average radii of PbS QDs formed in the glasses as calculated from the peak positions of absorption bands were 2.0, 2.3, and 3.0 nm for the heat-treatment conditions described above, respectively. Photoluminescence spectra of heat-treated glasses also
changed with thermal treatment. As the size of the PbS QDs increased, peak wavelength of the photoluminescence bands shifted from 1166, 1318 to 1620 nm as shown in Fig. 2(b). They also showed Stokes shifts of approximately 100 meV from the position the corresponding absorption bands. These large Stokes shifts were most probably induced by the defects on the surface of PbS QDs. In addition, the PL band showed full width at half maximum (FWHM) PL intensity values of 150–500 nm and they are considerably larger than the value usually observed from the emission of Er$^{3+}$ ions. The large FWHM was probably induced by the large size distribution of PbS QDs in the glasses. Large FWHM and tunability of absorption and PL bands indicates that PbS QDs in glasses have potentials for the amplification over the whole transmission window of silica fibers.

3.2 Effect of excitation intensity on the photoluminescence spectra

It is known that the band gap energy of lead chalcogenide quantum dots increases when the temperature increases, especially for the large size quantum dots. Figure 3(a) shows the photoluminescence spectra of 2.3 nm PbS QDs recorded at various temperatures under 800 nm laser excitation with an intensity of 70 W/cm$^2$. As the temperature increased from 50 K to 294 K, PL bands shifted to the short wavelength side with a magnitude of ~70 nm. This phenomenon is consistent with the results reported previously. In addition, PL bands also blue-shifted approximately 70 nm when the excitation power increased from 70 to 850 W/cm$^2$ at a temperature of 50 K (Fig. 3(b)).
It is apparent that temperatures and excitation intensities had a similar effect on the peak energies of the PL bands. When the temperature or the excitation intensities were increased further, the magnitude of the shift of PL bands slowed down, while the values of FWHM intensities increased continuously. Similar phenomena were also observed from the photoluminescence recorded from the PbS QDs with average radii of 2.0 and 3.0 nm PbS QDs.

3.3 Brightening and darkening of photoluminescence from PbS QDs

Intensity of the photoluminescence from PbS QDs also showed brightening (increase) and darkening (decrease) behaviors with time while the intensities of the excitation beam remained constant. In fact, darkening has long been observed for quantum dots. Figure 4 shows the brightening and darkening of PbS photoluminescence intensity recorded at various temperatures under the constant excitation intensities of 283 and 850 W/cm². At temperatures higher than 200 K, the steady state PL intensity was lower than that observed at the onset of excitation regardless of the excitation intensities. It was also observed that the degree of photo-darkening increased with increasing temperature. On the other hand, photoluminescence of PbS QDs recorded at low temperatures below 200 K showed an increase in the PL intensities with time. Photo-darkening and photo-brightening states can be reversed simply by changing the temperatures and the excitation intensities. These results indicated that photoluminescence properties of PbS QDs were closely related to the temperatures in the vicinity of QDs.

4. Discussion

4.1 Origin of excitation intensity dependent photoluminescence properties

Since excitation intensities and experimental temperatures \((T_{\text{exp}})\) had similar effects on the photoluminescence of PbS QDs (Fig. 3), it is reasonable to expect that the increase in excitation intensity led to the increase of the local temperature around the QDs. Therefore, the effective local temperature was calculated using the procedures described in our last report. It was found that \(T_{\text{Eff}}\) increased as the excitation intensities increased, and the difference between \(T_{\text{Eff}}\) and \(T_{\text{exp}}\) increased with increasing excitation intensity. These two features suggested that laser beam used for the excitation induced the local heating and it was responsible for the shift of the PL bands.

To verify the laser induced local heating effect, these calculated effective temperatures were further used to simulate the values of full width at half maximum intensity of photoluminescence bands using the following equation:

\[
W(T_{\text{Eff}}) = W_0 + \alpha \left[ \exp \left( \frac{\hbar \omega}{k_B T_{\text{Eff}}} \right) - 1 \right]^{-1}
\]

Here, \(W(T_{\text{Eff}})\) is the measured FWHM values at the effective temperatures, \(W_0\) is the value due to the size dispersion only. \(\alpha\) is the electron-phonon coupling strength, \(\hbar \omega\) is the energy of the optical phonon (215 cm\(^{-1}\)) and \(k_B\) is the Boltzmann’s constant. The results of fitting using Eq.(1) was shown in Fig. 5(a) and the

![Fig. 4](image1.png)

**Fig. 4.** Changes in the photoluminescence intensities of 2.3 nm PbS QDs in BZ glass recorded at different temperatures with illumination intensity of (a) 283 W/cm² and (b) 850 W/cm².

![Fig. 5](image2.png)

**Fig. 5.** Fitting results of the values of FWHM intensities with (a) calculated effective local temperatures or (b) experimental temperatures using Eq.(1). The solid line represents the fitting results, and dots are measured values of FWHM intensities at various conditions.
values of $W_0$ and $\alpha$ were found to be 75.47 ± 0.16 meV and 52.65 ± 0.43 meV, respectively.\(^5\) The value of $W_0$ was comparable to that obtained from PbS QDs capped with thiol ($W_0 = 90 ± 10$ meV).\(^6\) However, calculated value of $\alpha$ was smaller than the reported value of 110 ± 20 meV, most probably due to the different surface states and sizes of QDs. In addition, fitting of the FWHM values were difficult when the values of experimental temperatures $T_{\text{exp}}$ were used instead of the effective local temperatures $T_{\text{eff}}$. and this was especially true when the experimental temperatures were low, as shown in Fig. 5(b).

4.2 Brightening and darkening of photoluminescence from PbS QDs

It has been speculated that photo-induced oxidation of PbS QDs can result in irreversible brightening and darkening of photoluminescence recorded from the powders.\(^6\) However, the darkening-brightening behavior and laser-induced shift of PL bands observed in the present work completely reversible.\(^5\)

Therefore, photo-induced surface oxidation of PbS QDs cannot explain the darkening or brightening of the photoluminescence. Ionization of the QDs due to the thermal ejection of charge carriers or through Auger process was proposed to explain the photo-darkening effect.\(^11\) Thermal ejection is strongly dependent on temperatures and excitation intensities while Auger ionization process depends only on the squares of the excitation intensities. Therefore, both process appeared to be responsible for the photo-darkening effect although thermal ejection of charge carriers seemed to be dominant. These thermally ejected charge carriers were trapped by the defects either on the surface of PbS QDs or inside the host glass and these charges trapping has led to the darkening of photoluminescence. These trapped carriers were then relaxed to the initial state to neutralize the ionized PbS quantum-dots and recovered to the initial luminescent state, leading to the reversibility of darkening behavior.

Defects in the matrix also have important effect on the photoluminescence properties of QDs. CdS,Se$_x$, QDs were known to exhibit photo-brightening upon UV irradiation.\(^15\) Irradiation of UV first induced the defects in the matrix and charge carriers trapped at these defects site can be further excited into the conduction band of glasses by absorbing another photon from the excitation light. Afterwards, they recombined with the surface defects of QDs and neutralized the surface defects, resulting in the photo-brightening. Since glasses are rich in defects even without UV irradiation, carriers can be trapped at those defect centers and neutralized the surface defects of QDs in a similar fashion. This recombination of carriers and surface defects led to the increase of photoluminescence intensities. Specifically, it is well known that E$_1$ and H$_1$ centers are present in alkali-silicate glasses with their binding energies dependent on temperature.\(^13\) For example, binding energy of E$_1$-like centers in potassium-silicate glasses increases from ~1.49 eV at 77 K to 1.61 eV at 210 K. In this work, precursor silicate glass is rich potassium, and photon energy of excitation is 1.55 eV (800 nm). Thus, charge carriers trapped by the E$_1$ or H$_1$-like centers in the host glasses were excited by the illumination at low temperatures. Relaxation of these excited carriers to the surface defects of PbS QDs neutralized the quantum-dots, and resulted in the brightening of the photoluminescence.

5. Conclusion

Optical properties of PbS quantum dots (QDs) in the glass matrices were investigated. Photoluminescence of PbS QDs within 1–2 μm wavelength region was achieved by precipitating the QDs with radii of 2.0–3.0 nm throughout the heat-treatment. The photoluminescence intensities of PbS QDs were sensitive to the temperatures and excitation intensities. Peak wavelengths of the photoluminescence shifted as much as 70 nm when temperatures and excitation intensities changed. These shifts were due to the changes in the band gap energies of PbS QDs induced by the local heating. Photoluminescence of PbS QDs also exhibited reversible darkening and brightening behaviors and competition between these two processes determined the final steady-state PL intensities. Switching between photo-darkened and photo-brightened states can be achieved by controlling the temperatures and excitation intensities.

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