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Spectroscopy of PbS and PbSe Quantum Dots in Fluorine Phosphate Glasses[1]

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Abstract—Transmission spectra of the narrow-bandgap semiconductor quantum dots PbS and PbSe in the fluorine phosphate glass are experimentally studied at different temperatures. Energies of 1s exciton transitions observed in the absorption spectra are used to determine characteristic sizes of the quantum dots under study. A nontrivial temperature behavior of the ground and excited quantum confined states in the quantum dots of different sizes are observed.

1. INTRODUCTION

Semiconductor PbS and PbSe quantum dots (QDs) have been widely investigated because of their unique optical and electronic properties. The PbS and PbSe crystals are typical narrow-bandgap (E_g = 0.41 eV and E_g = 0.29 eV) semiconductors with the large Bohr exciton radii, R_B = 20 nm for PbS and 46 nm for PbSe. These quantum dots provide strong quantum confinement effect for excitons, which can be easily realized in wide range of QD [1, 2].

Optical composite materials with the PbS and PbSe QDs are used for optical and photonic applications. For example, PbS(Se) QDs have potential applications in near-infrared photodetectors, photovoltaics, broadband optical amplifiers and luminophors as well as saturable absorbers [3, 4]. The PbS(Se) QDs can also provide near infrared (IR) (1−2 μm) photoluminescence with high absolute quantum yield ≥60% [5, 6] tunable by controlling the size of QDs, which matches well with the whole optical communication window [4, 7, 8].

The operation spectral range of such devices is determined, first of all, by the bandgap of these semiconductors.

A specific property of bulk crystals PbS and PbSe, which differ them from other semiconductors, is an unusual temperature dependence of the bandgap. In most semiconductors, the bandgap energy increases with decreasing temperature, however, the semiconductors PbS and PbSe show the opposite behavior, namely, the bandgap energy increases with increasing temperature [9]. The origin of such behavior is most probably related to specific of the band structure of these crystals, which is not studied in detail so far. Studies performed by several research groups [10, 11] have shown that the bandgap in these QDs is strongly rises due to the effect of the quantum confinement that further complicates the temperature dependence.

Here we report on the temperature dependence of transmission spectra of the semiconductor QDs PbS and PbSe formed in the fluorine phosphate glass. We used a fluorine phosphate (FP) glass as a matrix for the QDs characterized by a number of advantages compared to conventional silicate glasses, including low temperature of the synthesis, accurate control of the size, homogeneity, and concentration of the QDs, as well as shorter time of the heat treatment. In addition, the glass matrix protects the QDs from effects of ambient conditions and their optical properties remain very stable for a long time.

2. EXPERIMENTAL

We have measured the transmission spectra of a set of samples with the PbS and PbSe QDs at different temperatures in the range 4−300 K in the spectral range 600−2500 nm (0.5−2 eV). The QD size is varied in the range 3−15 nm. For determination of the QDs sizes we have used the empirical model proposed in

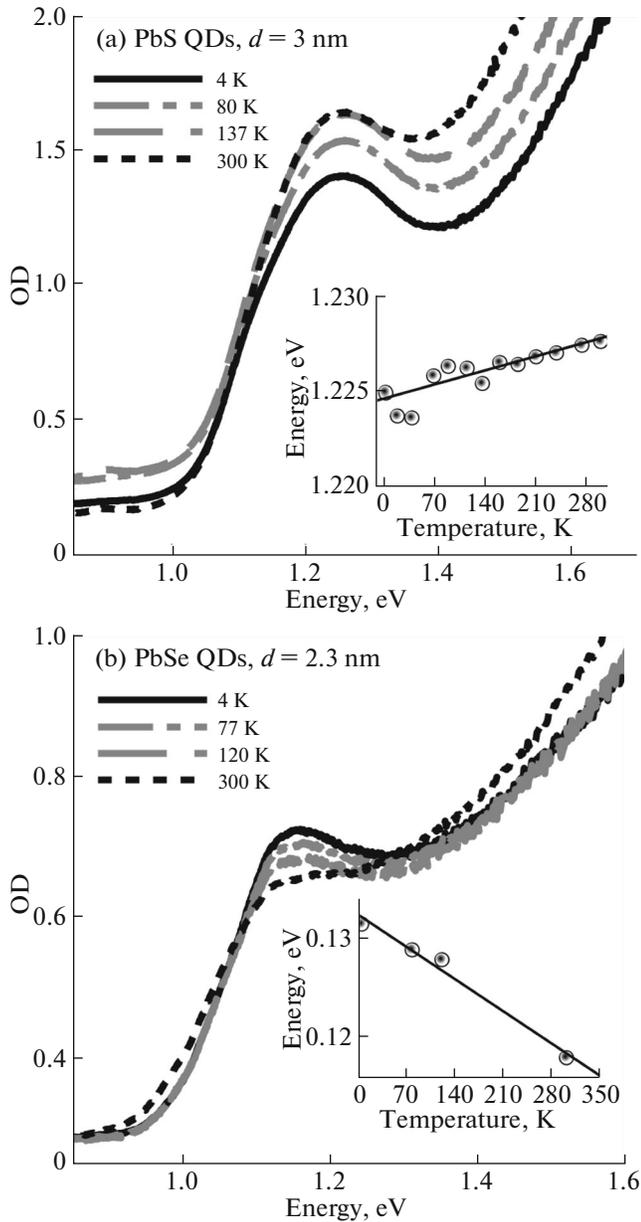---

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Fig. 1. Spectra of optical density for the samples with small PbS (a) and PbSe (b) QDs measured at different temperatures. Insets show the energy shift of the ground states with increasing temperature.

[12, 13] which relates the 1s exciton absorption peak to the QDs diameter.

Typical spectra of two of the samples measured at several temperatures are shown in the Fig. 1.

One can see the peculiarities corresponding to the optical transition to the 1s exciton state (1sh–1se optical transition) for the samples with PbS QDs, E = 1.2 eV, with diameter, d = 3 nm and PbSe QDs, E = 1.1 eV, with diameter, d = 2.3 nm. For the PbS QDs, the transition energies are shifted to the higher ener-

gies with increasing temperature, which is typical behavior for bulk PbS crystals [13]. However, the energy band for the PbSe QDs is shifted to the opposite side. As it is seen from the inset in the Fig. 1b, the energy of the 1s exciton state decreases with increasing temperature. This behavior is similar to that for many wide-bandgap bulk semiconductors.

In the Fig. 2 the absorption spectra for the samples with PbS(Se) QDs with larger diameter of 7 nm for PbS QDs and 4.3 nm for PbSe QDs are shown. Due to the smaller quantization energy, one can see two peculiarities for the both the samples in the spectral range studied. The low-energy absorption band, of about 0.8 eV for PbS QDs and 0.6 eV for PbSe QDs, corresponds to optical transition to the 1s exciton state. This band is shifted in both samples to the higher photon energies (the blue shift) with increasing temperature, as in bulk materials. The temperature behavior of the second (excited) spectral band attributed to the optical transition to the 1p-state is found to be more complicate.

To determine the sign and magnitude of the temperature shifts of both the spectral bands, we performed an accurate analysis of the experimental data. Namely, an exponentially growing with energy background was subtracted from the spectra and the absorption bands were fitted by Gaussians. Results of the data processing are shown in Figs. 3 and 4.

It is seen in Fig. 3 that the position of the high-energy absorption band, lying in the range of about 1.1−1.2 eV for PbS QDs and attributed to optical transition ph−pe, is almost unchanged within experimental error with increasing temperature (see insert in Fig. 3). For the sample with the PbSe QDs, similar high-energy absorption band in the range of about 1.0−1.1 eV (see Fig. 4) is shifted to the low energies (see insert in Fig. 4) that is to the opposite side than the ground state in this sample and in the bulk crystals PbS(Se).

To fit the temperature shift of the 1p exciton state in PbS(Se) QDs, we use a model proposed in [13]:

$$E_{\mathrm{g}}(T) = E_0 + E_1 [2(\exp(f_1/kT) - 1)^{-1} + 1] \\ - E_2 [2(\exp(f_2/kT) - 1)^{-1} + 1], \qquad (1)$$

where f_1 = 6.06 meV is the "Pb-like" phonon frequency, f_2 = 29.1 meV is the "S-like" phonon frequency, f_2 = 15.5 meV is the "Se-like" phonon frequency. The values E_0, E_1, and E_2 are the fitting parameters. The authors of this paper fitted in such way the temperature dependent energy shift only the 1s-transition. We used this approximation to fit the temperature shift of the 1p-transition and received the reasonable values for parameters E_0, E_1, and E_2. A theoretical modeling of this unusual temperature behavior the states requires further study.
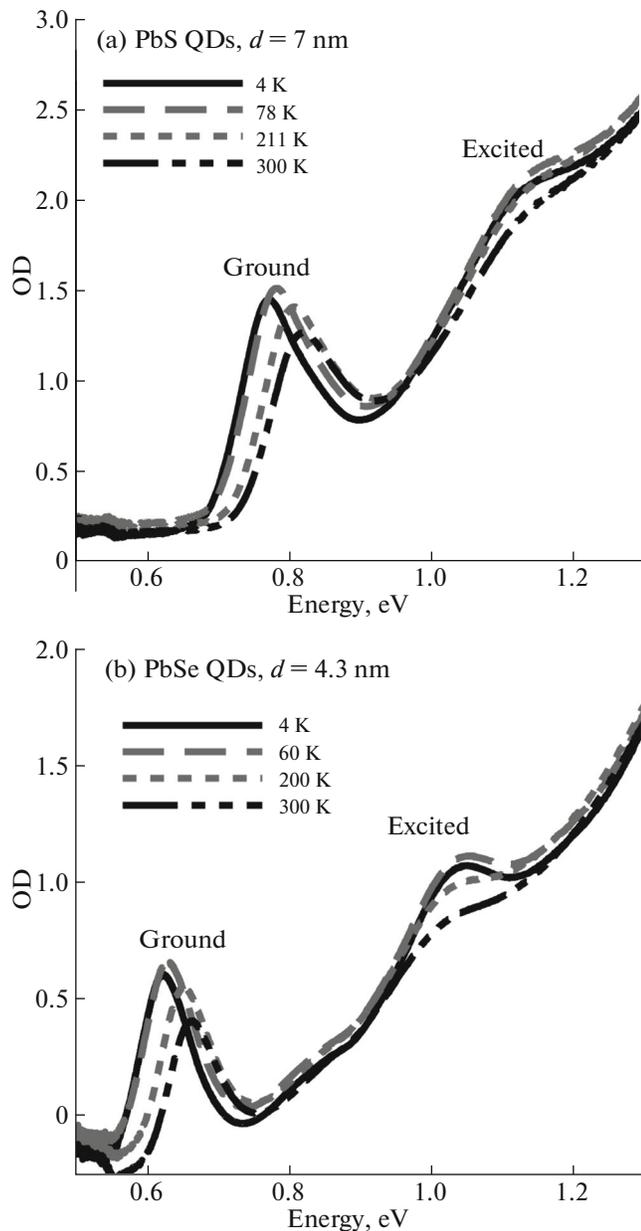
Fig. 2. Spectra of optical density for the samples with large PbS (a) and PbSe (b) QDs measured at different temperatures.

Fig. 3. Absorption bands extracted from the spectra shown in Fig. 2a for the PbS QDs. Insert shows the energy shift of the excited state with increasing temperature.

Fig. 4. Absorption bands extracted from the spectra shown in Fig. 2b for the PbSe QDs. Insert shows the energy shift of the excited state with increasing temperature.

Besides two main absorption bands there is a relatively small peculiarity at about 0.83 eV, see Fig. 4. Two possible origins of the peculiarity are discussed in literature [11, 14]. The first model assumes that it is due to the phonon-assisted processes allowing for the initially forbidden direct s−p transition [10]. The second model takes into account the very strong anisotropy of the bands so that the 1p transition is splitted to the transverse and longitudinal components [14]. Our experimental data do not allow us to verify, which model is applicable for this additional absorption band.
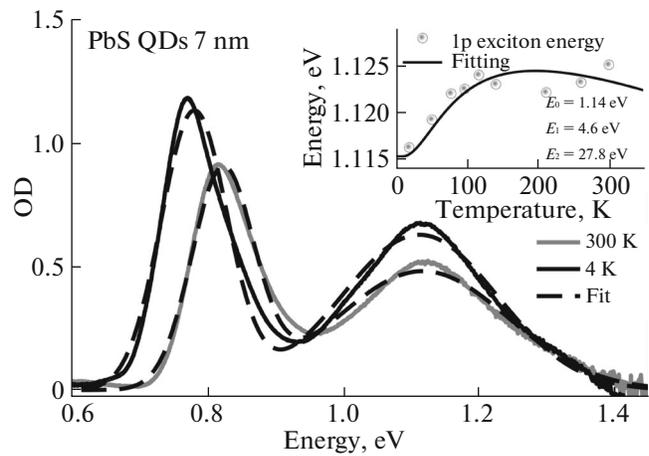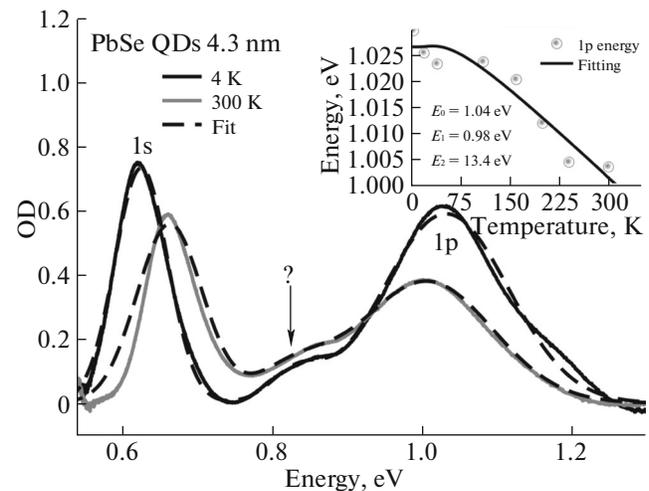
3. CONCLUSION

In conclusion, we have measured the temperature dependences for the samples with the PbS and PbSe QDs of different sizes in the fluorine glass matrix. For the small sizes of the PbS QDs, the energy shift of the bandgap increases with increasing temperature as it is observed in the corresponding bulk PbS crystal. For the PbSe QDs of small sizes, the energy shift of the bandgap changes sign leading to a decrease of the bandgap with increasing temperature.

For the larger sizes of the PbS(Se) QDs, we have measured the absorption spectra for several optical transitions. For both types of the samples, the 1s transition is found to depend on the temperature by a standard way, namely, the energy of bandgap decreases

with decreasing temperature. The excited state for the sample with PbS QDs is almost unchanged with the temperature variations within the experimental error, in contrast to the case of the sample with the PbSe QDs, where the 1p transition demonstrates the red shift. The absorption spectra of the sample with the PbSe QDs contain also the peculiarity, which can appear due to the QD asymmetry-related splitting of the 1p transition or the phonon-assisted 1s−1p transitions.

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