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ScienceDirect
Journal of Non-Crystalline Solids 353 (2007) 1195–1200
JOURNAL OF NON-CRYSTALLINE SOLIDS
www.elsevier.com/locate/jnoncrysol

Nonlinear optical properties of PbS quantum dots in boro-silicate glass

Alexander M. Malyarevich [a], Maxim S. Gaponenko [a,*], Vasili G. Savitski [a], Konstantin V. Yumashev [a], Galina E. Rachkovskaya [b], Galina B. Zakharevich [b]

[a] *Institute for Optical Materials and Technologies, Belarussian National Technical University, Bldg.17, #65 Nezavisimosti Ave, 220013 Minsk, Belarus*
[b] *Belarussian State Technological University, Minsk, Belarus*

Received 3 May 2006
Available online 13 March 2007

Abstract

PbS quantum dots synthesis in boro-silicate glass is presented. Absorption bleaching of PbS quantum dots of ≈4 and ≈7 nm in diameter dispersed in this glass has been studied. Bleaching relaxation time of 20–30 ps, absorption saturation fluence of ≈5 mJ/cm^2 and ground-state absorption cross-section of $2 \div 6 \times 10^{-17}$ cm^2 at the wavelengths corresponding to the first excitonic absorption band maxima are measured.

PACS: 78.47.+p; 78.67.Hc; 78.67.−n

Keywords: Nanocrystals; Quantum wells, wires and dots; Optical spectroscopy; Ultrafast processes and measurements; Boro-silicates

1. Introduction

Quantum dots (QDs) of lead sulfide, PbS have been recently introduced as potential material for various optical applications: saturable absorbers for mode-locking and Q-switching of near IR lasers [1–7], ultrafast signal switches or routers [8], light converters [9,10] and possible waveguide amplifiers for telecommunications [11]. The possibility to synthesize PbS QDs in a glassy matrix (in contrast to solutions) transfers research from pure fundamental interest to the practical field. The necessity of coupling of such elements with other parts to construct devices outlines relevance of doping solid matrices with these QDs. Moreover application reasons demand to grow QDs of definite size with narrow size distribution, to vary QDs doping concentration, to engineer elements of different sizes and shapes. Glasses are quite valid media for such purposes taking into account the possibility to grow QDs with narrow size distribution in them and also their long-term stability and high optical damage threshold. QDs of PbS were firstly grown in silicate glass matrix [12] and later – in phosphate one [13]. Recently synthesis of PbS QDs in boro-silicate glass was demonstrated [14]. Glasses contained QDs of 3.4 ÷ 7.2 nm in mean diameter were synthesized. PbS QDs of such sizes demonstrate first excitonic peak position in the range from 0.86 to 1.67 μm. This corresponds that saturable absorption of the first excitonic absorption band can be used for pulse shaping of emission from lasers emitting in this spectral range or for signal switching at wavelengths from this region.

In this paper we present details of synthesis conditions of PbS QDs in boro-silicate glass and comparative study of their nonlinear optical properties at 1.1 and 1.5 μm with PbS QDs in silicate and phosphate glasses.

2. Synthesis and characterization

Our boro-silicate glasses have been prepared using Na_2O–ZnO–Al_2O_3–B_2O_3–SiO_2 glass system. The amount of B_2O_3 in the glass batch has been controlled at the level of 10–20 wt%. Structure of boro-silicate glass, in contrast

* Corresponding author. Fax: +37 5172926286.
E-mail address: gap@ilc.by (M.S. Gaponenko).

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doi:10.1016/j.jnoncrysol.2007.01.018

to usual silicate one, is formed with groups of [BO_3], [BO_4] and [SiO_4]. Energy of B–O bond is of 89 kcal which is less than for Si–O one (106 kcal). So that structure of boro-silicate glass is less stable in comparison with silicate glass and consequently addition of B_2O_3 leads to weakening of internal glass net and to decrease of the glass sintering temperature. We have put up to 2 wt% of fluorine into the glass raw as an aggregator and for decrease of glass viscosity. This facilitates stabilizing of PbS crystallites forming on the glass body and prevents their recurrent dissolution in the batch. As the result of boron oxide and fluorine addition the well-known problem of sulfur evaporation from the melt during prolonged, high-temperature glass formation is easier solved for the boro-silicate system.

We have prepared our PbS QDs-doped glasses in a flame pot furnace without special conditions preventing sulfur evaporation. Synthesis of the glass using batch melting technique takes place at 1350 ± 50 °C during 2 h at the maximal temperature. In order to create PbS microcrystalline phase Pb_3O_4 and S have been added into glass batch directly. The glass has been poured onto a metal plate and annealed at 450 °C. The variations of subsequent heat treatment regimes allow obtaining a high volume of PbS QDs dispersed in the glass body with a certain dot size. PbS QDs start to form when heat treatment temperature rises up to 480 °C. The smallest QDs (of 3.2 nm in diameter) have been synthesized under double stage heat treatment: first stage – at 480 °C during 24 h, the second one – during 5 h at 525 °C. Bigger QDs can be grown by prolonging heat treatment procedure at 525 °C. The biggest size of PbS QDs in our glass system – 8.0 nm – has been achieved by us at the procedure duration of 35 h. Fig. 1(a) shows QDs' mean size dependence on time of thermal treatment. These data are well fitted with $\propto t^{1/2}$ function that is typical for independent growth of dots.

Room-temperature absorption spectra of PbS QDs-doped glasses with different dots sizes are presented in Fig. 1(b). It is seen that absorption due to imperfections of and impurities in (except on PbS QDs) glass matrix, α_b (estimated at wavelengths much longer than the first excitonic peak position) amounts ≈0.25 cm^{-1} for samples #1–3 (at wavelengths 1800–2000 nm), ≈0.4 cm^{-1} for sample #4 (2000–2200 nm) and ≈0.6–0.8 cm^{-1} for samples #5, #6 (2200–2300 nm). Higher values of α_b for bigger dots are registered obviously because the estimations are made at wavelengths longer 2000 nm where absorption of water residue in glass may exhibits. Nonlinear optical properties of some of these glasses will be discussed below (samples #1, #2 have been studied at ~1.1 μm and samples #4, #5 – at ~1.5 μm).

Fig. 2 presents X-ray diffraction patterns of powdered glass measured using Cu Kα radiation with a Ni filter. Positions of the main patterns for the glass (0.342; 0.297; 0.209 nm) correspond to that ones registered for the single crystal of PbS [15]. It is known that sizes of PbSe QDs (relative compound for PbS) obtained from X-ray measurements are usually overestimated, particularly for smaller

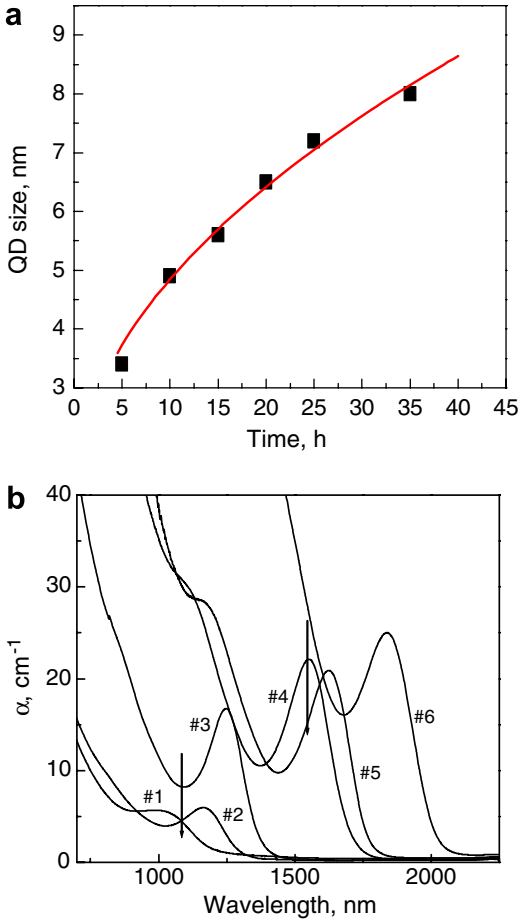

Fig. 1. (a) Dependence of PbS QDs mean diameter on heat treatment time in boro-silicate glass. Solid line is a $t^{1/2}$ function. (b) Linear absorption spectra of boro-silicate glass with PbS QDs of mean diameter 4.0 (#1), 4.6 (#2), 4.9 (#3), 6.5 (#4), 6.8 (#5), 8.0 (#6) nm. Arrows show wavelength positions at which nonlinear optical properties for these glasses have been studied.

dots (see e.g. [16]). That is why here we use the dependence between first excitonic absorption peak position and PbS QDs size derived in the Ref. [17] for estimation of dots' sizes in our glasses.

3. Experimental

Kinetics of bleaching relaxation have been measured using a standard picosecond pump-probe technique. A fifteen picosecond pulse from the passively mode-locked Nd:$YAlO_3$ laser ($\lambda = 1.08$ μm) has been employed as a pump radiation. A delayed part of this pulse has been used as a probe. The pump intensity in the samples is ≈0.2 GW/cm^2. The bleaching value was defined as the differential absorption $\Delta OD = -\log(T/T_0)$, where T_0 and T are the transmission of the probe beam without and with pump beam present, respectively.

The laser mentioned above has been applied for the absorption saturation measurements at 1.08 μm. The transmittance of the probe pulses has been measured after 15-ps time delay of the pump pulse (i.e. measurements of the