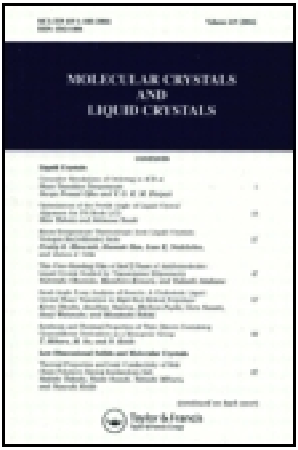

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Size Dependence of the Third-Order Optical Nonlinear Susceptibility of PbS Nanocrystals in PVA

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We have synthesized a composite material containing semiconductor nanocrystals with a high third-order optical nonlinear susceptibility $\chi^{(3)}(\omega) = (6.5 \pm 2.3) \cdot 10^{-16}\,m^2/V^2$ *(PbS-18 nm) at* $\lambda = 1.064\,nm$ *in the case where the nanocrystal size approaches the Bohr radius of an exciton in the material.*

Keywords: composite material; nanoparticles; nonlinear optical susceptibility

INTRODUCTION

Composite materials based on semiconductor (SC) nanocrystals (NCs) and organic polymers have a number of unusual optical and electrophysical properties and are promising materials for optoelectronics and nonlinear optics. Such materials exhibit a high nonlinear optical (NLO) response due to the local electric field amplification induced by an input light wave in the small volume of nanocrystals. It was experimentally shown [1] that the use of semiconductor nanoparticles in composite materials leads to an increase in the NLO sensitivity. The

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theoretical calculations [2] showed that, under some conditions, the third-order optical nonlinear susceptibility $\chi^{(3)}(\omega)$ is proportional to $(1/R)^3$, where R is the crystallite radius. That is, a decrease in the particle size leads to a strong increase in the nonlinear susceptibility. It was also shown [3,4] that the third-order optical nonlinear susceptibility $\chi^{(3)}(\omega)$ in the visual spectral range in the composites with nanocrystals of narrow-band semiconductors can be much higher than that for wide-band ones. It should be noted that, from the practical point of view, NLO devices based on such materials have to work with widespread lasers Nd:YAG ($\lambda = 1064\,\text{nm}$) and Al_2O_3:Ti ($\lambda = 800\,\text{nm}$). The main purpose of these studies was to synthesize a polymer composite with narrow-band semiconductor nanocrystals, namely PbS, and to study the NC size effect on $\chi^{(3)}(\omega)$ using a pulsed Nd:YAG laser ($\lambda = 1064\,\text{nm}$).

EXPERIMENTAL

PbS NCs were synthesized in an aqueous solution in the presence of PVA. Equimolar solutions of $Pb(NO_3)_2$ with a concentration of 10^{-2} mole/l and Na_2S were mixed. As a result of the mixing and stirring, a colloidal solution of PbS particles stabilized by PVA together with the product of the substitution reaction (sodium nitrate, $Pb(NO_3)_2 + Na_2S \rightarrow PbS + 2NaNO_3$) was obtained. $NaNO_3$ was removed from the solution by dialysis. The diffusion acceleration taking place at a higher temperature of the reactive mixture leads to the increase of both the reaction speed and the particle size due to the Ostwald ripening effect, when the size of larger particles grows at the expense of smaller ones. To obtain samples with different particle sizes, we heated the colloidal solutions of PbS during 12, 48, and 72 h. At higher temperatures, PVA loses its stabilizing abilities, so large particles precipitate very quickly. Such a behavior of PVA is connected with the fact that the glass transition temperature T_g of PVA is about 70°C [5]. So, the thermally stimulated mobility of polymer chain fragments takes place at temperatures higher than T_g. Thin films of the material in question were prepared by spreading the solution onto the surface of 30×30-mm glass plates. The amount of the solution was taken in such a way to obtain films with a thickness of 3 to 30 μm. The number of samples with different thicknesses was from 8 to 12 for each time of heating (12, 48, and 72 h).

The X-ray structure analysis was performed using a DRON-4.07 diffractometer (CuK_α-radiation, $\lambda = 1.54178\,\text{Å}$). The electronic absorption spectra were obtained with a spectrophotometer SF-20M. The nonlinear refraction in the samples was studied by the dynamic

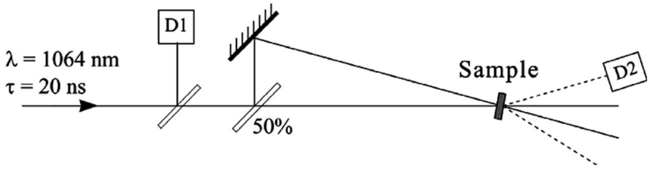

FIGURE 1 Experimental setup for the degenerate four-wave mixing (self-diffraction). $D_{1,2}$ are the detectors.

holographic grating recording in the scheme of degenerate two-wave mixing (Fig. 1). A one-mode frequency-doubled YAG:Nd^{+3} laser ($\tau = 10\,\mathrm{ns}$, $\lambda = 1064\,\mathrm{nm}$, TEM_{00}) was used as a light source. The time resolution of our registering system was about 10 ns. The read out of the dynamic gratings was carried out by using a cw He-Ne laser. The interference field of two interacting coherent light beams from a pulsed laser induced a dynamic grating based on the refractive index modulation in the sample, on which the self-diffraction of recording beams was observed. The dynamic gratings were recorded on the basis of the third-order optical nonlinearity characterized by the nonlinear optical susceptibility $\chi^{(3)}$ (ω;ω,-ω,ω). The value of $\chi^{(3)}$ (ω;ω,-ω,ω) was evaluated by means of the diffraction efficiency of recorded gratings measurements using the Eq. (6)

$$|\chi^{(3)}(\omega)|[\mathrm{m}^2/\mathrm{V}^2] = \frac{4}{3}\varepsilon_0 \mathrm{c} \mathrm{n}_0^2 \mathrm{n}_2 = \frac{4\varepsilon_0 \mathrm{c}\mathrm{n}_0^2 \lambda \sqrt{\eta}}{3\pi\ell \mathrm{I}_0}, \tag{1}$$

where n_0 is the refractive index of the sample, n_2 is the nonlinear refractive index coefficient, ℓ is the sample thickness, I_0 is the total intensity of the recording light, λ is the light wavelength, η is the diffraction efficiency, c is the speed of light, and ε_0 is the absolute dielectric constant of vacuum.

RESULTS AND DISCUSSION

Determination of the Particle Sizes

It is known that a decrease in the NC size leads to broadening the X-ray diffraction peaks. This broadening relatively to the peaks of a reference monocrystal with a half-width B_S makes it possible to define the NC size. A silicon monocrystal with $B_S = 0.38^0$ was used as a reference sample. The peak broadening $\Delta = (\mathrm{B}^2 - \mathrm{B}_S^2)^{1/2}$ is related to the particle mean diameter $2R$ by the Scherrer equation:

$$2R = \frac{K\lambda}{\Delta \cdot \cos \vartheta}, \tag{2}$$

where $\lambda = 1.542\,\text{Å}$ is the X-ray wavelength, θ is the scattering angle, Δ is a half-width of the diffraction peak in units of 2θ, K is the geometric factor taken to be 1 for the cubic rock-salt structure of PbS.

Using Equation (2) and the data obtained by X-ray diffraction for our samples, we have determined that the mean size of PbS NC at the heating of a colloidal solution during 12, 48, and 72 h at 70°C was 9, 14, and 18 nm, respectively. Figure 2 shows X-ray diffraction traces for samples of PbS NC with sizes of 9 and 18 nm. One can see the large diffraction peak spreading for the samples with 9-nm PbS NCs.

The absorption spectrum of the composite material film PbS/PVA with a thickness of 3 μm and the PbS density of 4 vol. % for particles with sizes of 9, 14, and 18 nm is presented in Figure 3. From the figure, it is seen that the absorption spectrum is shifted towards the short-wave region with decrease in the particle size. This shift is determined by the quantum dimensional effect which takes place at particle sizes less than 18 nm [7] for PbS NCs. The vertical line in Figure 3 shows the spectral position of the exciting wavelength $\lambda = 1064$ nm.

The energy diffracted into the first diffraction order versus the recording pulse energy for a PbS/PVA film (4 vol. %, 18-nm PbS particles) is shown in Figure 4. The experimental data (dots) and the approximation (line) show that the diffraction dynamical gratings are recorded upon the

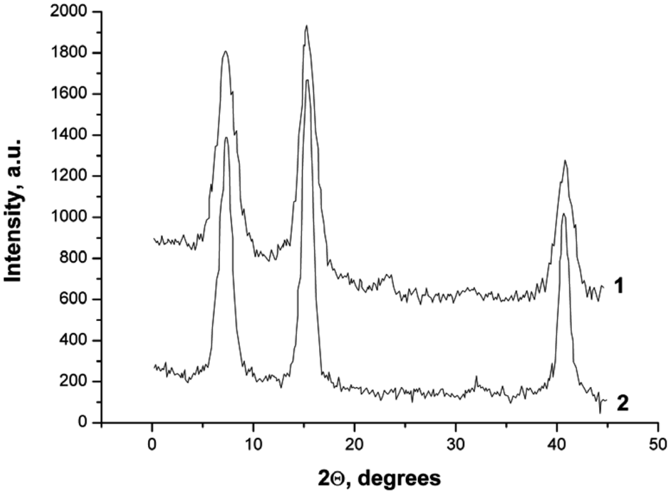

FIGURE 2 X-ray diffraction pattern for a PVA film containing 4 vol. % of 9-nm PbS particles (1) and 18-nm ones (2).

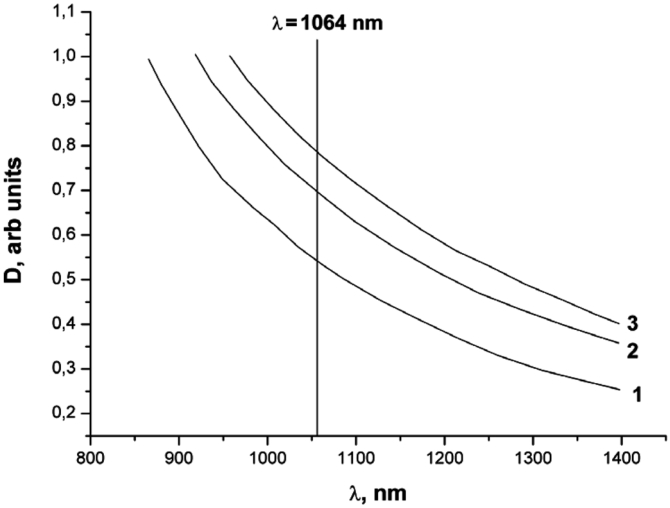

FIGURE 3 Absorption spectrum of a PVA/PbS composite film (4 vol. % of PbS) with a thickness of 3 μm and the particle size of 9 nm (1), 14 nm (2), and 18 nm (3).

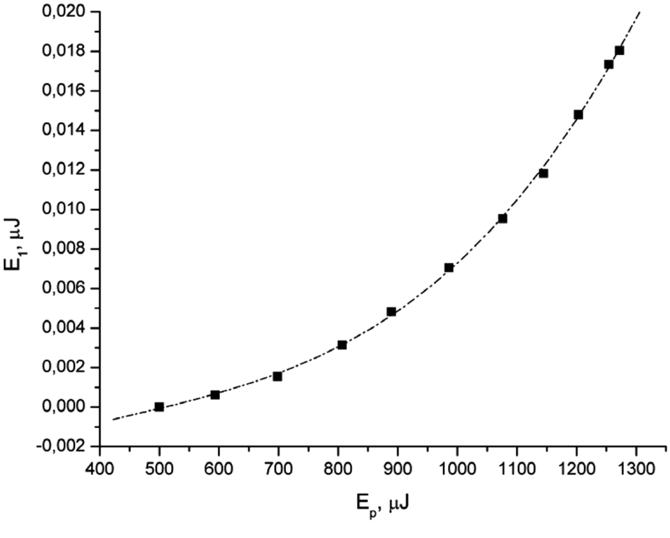

FIGURE 4 First-order diffraction pulse energy versus the writing pulse energy of PVA/PbS particles). Experimental data (dots) and the line which presents the approximation by a cubic equation are shown.

third order in the electric field nonlinearity which is described by the third-order optical nonlinear susceptibility $\chi^{(3)}$ $(\omega;\omega,\text{-}\omega,\omega)$.

In the sample with a thickness of $3\div30\,\mu\text{m}$, we manage to write the phase dynamical gratings with the response time less than 10 ns in the scheme of degenerate two-wave mixing. That is, our composite material exhibits the strong fast nonlinear refraction.

Using our experimental data for ℓ, I_0, and η, as well as $n_{0(PVA)} = 1.5$, $\lambda = 1.064\,\mu\text{m}$, we obtain the mean value for $\chi^{(3)}$ (ω) and the possible range of deviations from the mean value with the probability 2σ as

$$\chi^{(3)}(\omega) = (2.2 \pm 0.6) \cdot 10^{-16}\text{m}^2/\text{V}^2(\text{PbS-9nm});$$
$$\chi^{(3)}(\omega) = (6.2 \pm 1.8) \cdot 10^{-16}\text{m}^2/\text{V}^2(\text{PbS-14nm});$$
$$\chi^{(3)}(\omega) = (6.5 \pm 2.3) \cdot 10^{-16}\text{m}^2/\text{V}^2(\text{PbS-18nm}).$$

It should be noted that the obtained values of $\chi^{(3)}$ (ω) for PbS at the 1064-nm excitation increase with the NC size and are by a factor of 1.5 higher than that for 5-nm PbS NCs at the 532-nm excitation.

Figure 5 shows the dependence of the forbidden band energy E_g on the PbS NC size from [8] and our data on the nonlinear optical susceptibility $\chi^{(3)}$ (ω). The increase of the forbidden energy band gap E_g with decrease in the particle size (for PbS, it is less than 18 nm [7]) induces the quantum size effect. However our results showed that, when the size of particles is less than the PbS Bohr exciton radius (about 21 nm [3]), $\chi^{(3)}$ (ω) was not increased, as was predicted in [2], but decreased. The double decrease of the PbS particle size from 18 to 9 nm leads to the three-time decrease of $\chi^{(3)}$ (ω). In our opinion, the reason for such a behavior can be two counteracting factors related to the decrease in the size of particles:

1) increase in the localization of an excitation in the NC and the electric field amplification induced by an input light wave;
2) decrease in the absorption due to the quantum size effect at NC sizes less than the exciton Bohr radius.

As our data show, for the NC size less than the Bohr radius, the negative effect of the second factor prevails upon the positive effect of the first factor.

Earlier, it was shown in [3] at $\lambda = 532\,\text{nm}$ and in [9] at $\lambda = 780\,\text{nm}$ by means of the Z-scan technique that, in 5-nm PbS NCs, the nonlinear change of the refractive index is negative ($n_2 < 0$).

The negative sign of the refractive index change observed in our material can be attributed to the contribution of non-equilibrium free carriers generated in PbS NC under excitation.

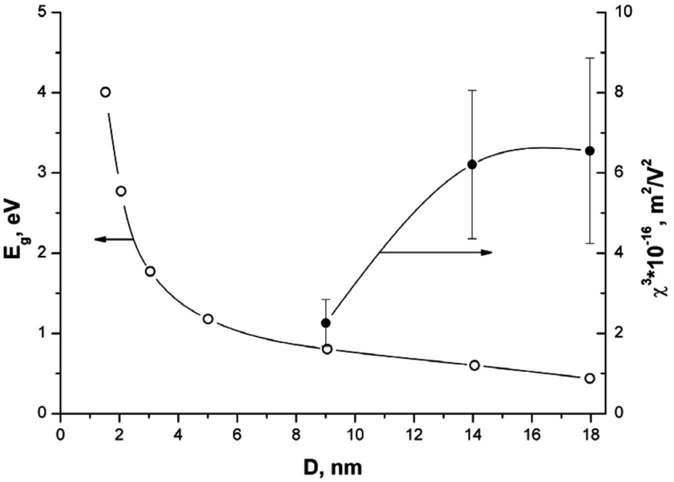

FIGURE 5 Dependence of the energy band gap E_g (1) and the optical nonlinear susceptibility $\chi^{(3)}$ (2) on the PbS nanoparticle size.

The experimental method described above allows us to observe the fast NLO response ($\tau \leq 10\,\text{ns}$) due to the most rapid and practically important electronic mechanism.

CONCLUSION

In conclusion, we have shown the possibility to synthesize the composite material with semiconductor nanocrystals with the high third-order optical nonlinear susceptibility $\chi^{(3)}$ $(\omega) = (6.5 \pm 2.3)\cdot 10^{-16}$ m^2/V^2 (PbS-18nm) at $\lambda = 1.064\,\text{nm}$ in the case where the NC size approaches the Bohr radius of an exciton in the material.

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