Optical properties of phosphate glass with CdSe quantum dots in terahertz frequency range

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Abstract. Optical properties and spectral characteristics of phosphate glasses with CdSe QDs were studied using time-domain terahertz spectroscopy in transmission mode in the frequency range of 0.2 - 1.0 THz. Concentration and size of QDs were varied by changing heat treatment conditions of initial glass samples containing components of the semiconductor phase. The change of refractive index and absorption coefficient at the high frequency edge of the investigated range at variation of secondary processing parameters was observed.

1. Introduction
Terahertz (THz) is the frequency range of the electromagnetic spectrum lying between the microwave band and the far infrared band. This frequency range isn’t enough safe for human [1],[2] and it is often referred to as the last frontier for electromagnetic waves, since historically there has been comparatively little work observing the science and develop the applications of THz waves. Among all the applications of THz waves, the THz tunable metamaterial components, which may precisely control and manipulate THz waves, are essential for THz imaging systems and high-speed communication with THz rays [3] - [9]. Quantum dots (QDs) are nanoparticles with sizes in the range of nanometers, in which charge carriers are limited by the three coordinate axes, making the particles have discrete energy levels like an atom, that can be changed by varying the size of nanoparticles. Over recent years, semiconductor quantum dots (QDs) have attracted much attention of researchers due to the dependence of properties on size, and the creation of optoelectronic and photonic devices with tunable characteristics [10]. Currently, the QDs are being used used in the development of high-speed filters for signal processing, optical fiber amplifiers, low-threshold lasers, solar cells, etc [11]. The study of the properties of QDs in the terahertz frequency range is of special scientific interest [12]. In this experimental work, samples of barian-phosphate glasses grown in their volume QDs CdSe were studied for the development of new components and devices with tunable characteristics in THz frequency range.

2. Method of samples fabrication
The original glass was synthesized in silit furnace in a quartz crucible at a temperature range of 1380 - 1420 °C. Components of semiconductor compounds were introduced into the batch in excess of 100% in form of CdO and elemental phosphorus. Fusion was produced in heated
graphite form. Annealing of the obtained casting at a temperature close to the glass transition temperature $T_g$ was carried out. The original glass was transparent and had no absorption at wavelengths greater than 300 nm. The selection of the semiconductor phase was carried out as a result of secondary heat treatment at the isothermal conditions. In contrast to previous work [13], in which a QDs of CdSe were grown in a silicate matrix using the complicated two-stage heat treatments, in this paper we used a one-step heat treatment at a predetermined temperature in the range of 490 - 530 °C and a fixed time of isothermal heating for 3 hours, one sample at a temperature of 530 °C and a heating time of 7 hours and one sample at 550 °C and heating time 30 hours.

3. Experimental setup

![Scheme of pulsed broadband THz time-domain spectrometer (TDS). FL-1 — femtosecond infrared laser, M — mirror, BS — beam splitter, DL — delay line, G — generator (crystal InAs) THz radiation, PM — parabolic mirror, L — lens, F — Teflon filter, od — modulator, NC — nonlinear crystal CdTe, W — Wollaston prism, BD — balanced photodiodes, LIA — Lock-in-amplifier, ADC — analog-to-digital Converter, PC — personal computer](image)

The optical properties and spectral characteristics of the samples were measured using time-domain terahertz spectrometer (Fig. 1). Infrared (IR) femtosecond laser beam is divided into a pump beam and a probe beam at 90% and 10% intensity, respectively. The pump beam passes through the delay line and falls onto the semiconductor indium arsenide (InAs) crystal surface. In this crystal, the Dember effect is observed: mobility of electrons in semiconductor is more than mobility of holes, thereby forming electric dipoles. The dipoles excite the radiation in terahertz frequency range. Next, the THz beam is focused into sample and passes through it and then incidents on the nonlinear crystal (NC) surface. The probe beam passes through: optomechanical modulator to remove acoustic noise and electromagnetic oscillations AC, $\lambda/2$ plane to rotate probe beam polarization on 45°, Glan prism to remove unwanted polarization. Then it falls into NC surface. The nonlinear crystal of cadmium tellurium is used to detect terahertz radiation due the Pockels effect. Without THz radiation the nonlinear crystal is isotropic for the IR probe beam. Otherwise, the crystal becomes anisotropic, the polarization of the probe beam becomes elliptical. Further the probe beam is collimated and it passes through $\lambda/4$. The changes of the degree of ellipticity of beam polarization are used in measuring process.
Further, the probe beam passes the Wollaston prism, after which it splits into two orthogonal components with vertical and horizontal polarization. These beams fall onto diodes of the balanced detector. The signal from the detector is analog signal of the difference of the beams intensities. THz spectrometer has the following parameters: the wavelength of femtosecond laser of 1046 nm, the IR pulse duration of 200 fs, the IR average power of ≥1 W; the THz pulse duration of 2.7 ps, the modulation frequency of 663 Hz, the frequency range from 0.2 to 0.8 THz, the dynamic range of ≥50 dB.

4. Results
Using the method of time-domain terahertz spectroscopy, the waveforms of terahertz pulses, which passed through the samples and air (Fig. 2) were obtained.

![Figure 2. Waveform of terahertz pulses passed through the air (AIR - black line) and the reference sample (REF - red line).](image)

The reference sample (REF) was without crystal phase CdSe QDs. The Fast Fourier transform (FFT) was used to obtain spectral characteristics and optical properties of the samples using magnitude \(A(f)\) and phase \(\phi(f)\). From these data we calculated the refractive index \(n_{re}(f)\), the permittivity \(\varepsilon_{re}(f)\) and the absorption coefficient \(\alpha(f)\) of the samples.

\[
n_{re}(f) = 1 + \frac{c}{2\pi d} \frac{\phi_s(f) - \phi_r(f)}{f}
\]

\[
\alpha(f) = \frac{1}{d} \ln \left( \frac{A_r(f)}{A_s(f)} \right)^2
\]

\[
\varepsilon_{re}(f) = n_{re}^2 - \left( \frac{c}{4\pi f} \alpha(f) \right)^2
\]

where \(d\) — is the sample thickness, \(c\) — the speed of light. The dispersions of refractive index, permittivity, absorption coefficient of the samples are shown in Fig. 3—5.

Also, if we make approximation that glass with QDs is effective medium, knowing the absorption coefficients of glasses with QDs and without them, it is possible to calculate concentration of QDs in the glass.

\[
C_{CdSe}(f) = \frac{n_{re s}(f) - n_{re \text{ REF}}(f)}{n_{re \text{ REF}}(f) - n_{re \text{ CdSe}}}
\]
where \( n_{rc}(f), n_{rc\text{ REF}}(f), n_{rc\text{ CdSe}} \approx 3.335 \) — the refractive index of the sample, the reference sample and the bulk CdSe respectively. The dependence of CdSe concentration on the temperature of secondary processing for \( f = 0.7345 \text{ THz} \) is shown in Fig. 6.

**Figure 3.** Dispersion of the refractive index of the investigated glasses

**Figure 4.** Permittivity dispersion of samples

**Figure 5.** Dispersion of the absorption coefficient of the samples

**Figure 6.** Dependence of concentration ratio on temperature of secondary processing of glass for \( f = 0.7345 \text{ THz} \) with indicated refractive indices

### 5. Conclusion

We observed that CdSe QDs concentration varies from 4.21 to 1.11 % at the change of parameters of secondary treatment, that results in the increase of the refractive index of glass and the enhancement of the absorption coefficient. For the samples treated at the different temperatures but with the same exposure time, there is a linear dependence of the concentration on the temperature of secondary processing of glass. Based on this phenomenon it is possible to create terahertz component on the basis of glass with CdSe QDs, the characteristics of which can be controlled in the manufacturing process.
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