Experimental study of THz electro-optical sampling crystals ZnSe, ZnTe and GaP

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Abstract. The application of optoelectronic techniques to the generation and detection of THz radiation is now well established. Wide gap semiconductor crystals of groups II-VI, III-V and III-VI are abundantly used. However, some limitations are occurred while using powerful laser systems. In this paper we introduce experimental results of two-photon absorption (2PA) in ZnSe, ZnTe and GaP studied with femtosecond pump-probe supercontinuum spectroscopy. Using of supercontinuum helps us to measure 2PA absorption dynamics and nonlinear index of refraction in wide frequency ranges. Besides influence of Fe concentration in ZnSe:Fe crystals on transmitted THz radiation is described.

1. Introduction
Semiconducting crystals of groups II-VI, III-V and III-VI are widely used as sources and detectors of terahertz radiation. In time domain spectroscopy systems, that are very popular in different fields of applied research [1], electro-optical method for the detection of THz radiation is often used. The main advantage of this method is a wide dynamic range [2]. The process is based on measuring the change in polarization of probe optical pulse under the influence of terahertz field in electro-optic media [3].

There are several ways to increase the efficiency of THz spectroscopy. The first one is to use more powerful laser sources in the optical and near-IR range to generate and detect the THz radiation. However, it leads to a non-linear response of electro-optic semiconductor crystals. Second way, is to increase the emission of THz radiation by raising the number and mobility of the electron-hole pairs that can be implemented with crystal impurities.

Consequently, we presented two main ideas: to investigate the dependence of crystal response and nonlinear processes arising from the source power improvement [4], as well as to study the efficiency of THz radiation by changing the crystal structure, for example, by densify impurities [5].

2. Investigation of two-photon absorption and refractive index dispersion
One of the main processes influencing on response of semiconductor crystals is a two-photon absorption (2PA). 2PA reduces the intensity of light propagated through the crystal and the ultra-fast response [6] of semiconductor materials. Here we introduce experimental results of 2PA studied with femtosecond pump-probe supercontinuum spectroscopy. By usage of supercontinuum, 2PA absorption dynamics and nonlinear index of refraction variation with wavelength could be detected.
The experiments were carried out on pump-probe supercontinuum spectrometer (figure 1). It was based on a Ti:Sapphire regenerative amplifier Regulas 35F1K, which produces 30 fs pulses with energy up to 2.3 mJ and repetition rate of 1 kHz. Beam was split into two parts.

One was sent through the delay line and used as a probe beam, while the second part of the beam was used for supercontinuum (SC) generation. To produce high-intensity ultra-wide SC in the IR and UV spectral regions the water jet was used [7]. The range of frequencies generated in SC was 350-1400 nm. By using pump-probe technique, we recorded pump-probe scans, pumping at 800 nm and probing at different frequencies and power levels of beams. Variation of probe beam characteristics results on change of the width and the position of 2PA peak. Shift of band peak dependence on probe wavelength can be used to quantify refractive index dispersion. Band width at half-maximum wave dependence helps to determine the relaxation of induced excitation in material.

2.1. Femtosecond pump-probe supercontinuum spectroscopy experiment results
Using wavelength evolutions of 2PA absorption bands at half-maximum for ZnSe, ZnTe [8] and GaP crystals, extracted from various power dependences, and with knowledge of sample thickness, we obtained the dispersion of refractive index (figure 2). Here we present results only ZnTe crystal. It follows that the laser intensity on the order of 10 GW/cm² doesn’t lead to non-linear response in ZnTe, ZnSe and GaP crystals in considered frequency range. However, radiation with the intensity on the order of more than 20 GW/cm² may cause nonlinear response of detection systems and make experimental findings unreliable.

![Figure 1](image1.png)

**Figure 1.** Scheme of pump-probe supercontinuum spectrometer.

![Figure 2](image2.png)

**Figure 2.** Dispersion of refractive index for different pump power levels for ZnTe (black dot values given in [9]).

3. Influence of crystal impurities on transmitted THz radiation
The next studies will help us to understand the way how to increase the THz emission from doped crystals. As it was shown in [5], increase in the concentration of impurities can both enhance and reduce THz transmission through the sample.

In our experiment we investigate two samples: pure ZnSe and ZnSe:Fe* Fe=[0.23%] wafers. The orientation of samples was the same (111), as well as thickness ~ 610 μm. To find out the influence of crystal impurities on transmitted THz radiation typical THz spectrograph was use. The experimental setup can be seen in figure 3.
Figure 3. Experimental setup of THz time-domain spectrometer.

The light source is the same as in the pump-probe supercontinuum spectrometer. THz generator (Tera-AX Avesta) has the central frequency of 1 THz with the spectrum width of 1.5 THz, pulse duration <1 ps and THz pulse energy up to 1 uJ. Detection of THz radiation is performed by an electro-optical method using a ZnTe crystal and a balanced photodetector. As a detector Nirvana Auto-Balanced Photoreceiver is used with an operating wavelength range of 400–1070 nm and rise time <3 μs.

3.1. Terahertz time-domain spectroscopy experiment results

With the help of terahertz time-domain spectrometer we were able to get transmitted THz signals through two different samples and to compare their waveforms (figure 4). Fe impurities presence of course increase absorption of the sample, but on some time regions incensement of transmittance can be seen. It is our belief that because of low concentration of imputes this incensement is negligible.

Then the forward Fourier transformation was used to obtain spectral information. Figure 5 shows the amplitude of the terahertz spectrum.

Figure 4. Temporal shapes of THz pulses for reference, transmitted through ZnSe and ZnSe:Fe signals.
If we compare the THz spectra of reference and transmitted through ZnSe and ZnSe:Fe signals, it is seen that at certain frequencies the transmission of ZnSe:Fe increases, as was shown in [5]. The presence of impurities in the sample makes the medium more transparent in the THz range. As it was mentioned before, because of low concentration of impurities this increase is negligible. This effect can increase the generation of THz radiation. This can be explained in such way: when the ZnSe:Fe is doped to a certain concentration, the polarizability of the molecule increases. For more accurate descriptions and conclusions, further research is needed.

![THz spectra](image)

**Figure 5.** THz spectra of reference and transmitted through ZnSe and ZnSe:Fe signals.

4. Conclusion
With the help of femtosecond supercontinuum pump probe spectroscopy we were able to study nonlinear response of electro-optical semiconductor crystals at several excitation intensities ranging from 5 to 50 GW/cm² and in frequency range of 500-1000 nm. This enables to measure refractive index dispersion and to determine the optimum intensity at which no nonlinearity arises – it’s around the order of 20 GW/cm². We also carried out experiments to study the transmission of THz radiation through ZnSe and ZnSe:Fe crystals using THz time-domain spectrometer. The presence of impurities in the sample makes the medium more transparent on some frequencies of THz range. Dependencies obtained from the experimental data matches well with one from previous works.

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