Optical properties of Fe- and Nd-doped ZnSe crystals measured by pump-probe spectroscopy

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Abstract. We present the excited-state dynamics and optical properties of Fe- and Nd-diffusion doped zinc selenide polycrystals with different concentration measured by pump-probe spectroscopy in the visible and NIR range (400-1000 nm). The introduction of dopants allows one to control the optical properties of samples, which then can be used to create effective optoelectronic components for wide spectral ranges.

1. Introduction

The wide bandgap zinc-blende semiconductor crystals are attractive materials for various optoelectronic applications. ZnSe is transparent in a wide spectral range, it is a chemically inert, non-hygroscopic and high-purity product that is effective in many optical applications due to its extremely low volume loss, high resistance to thermal shock and stability in almost all environments, and is also easily processed. Zinc selenide with different dopants is a promising material for highly efficient, tunable [1] and pulsed [2] mid-infrared lasers. It is also used for spintronics applications [3] and pulsed terahertz radiation generation [4-5] and electro-optic sampling [6]. Doping with the transition and rare-earth elements provides the appearance of new crystal properties caused by changes in the energy levels. The better understanding of recombination processes and optical properties of newly synthesized materials is required. For characterization of excited-state dynamics, the pump-probe spectroscopy can be used. This powerful time-resolved technique allows measuring the sample absorbance variation after the excitation given by the pump pulse.

In this work, we observe the excited-state dynamics and optical properties of Fe- and Nd-diffusion doped zinc selenide polycrystals with different concentration measured by femtosecond pump – supercontinuum probe spectroscopy in the visible and NIR spectral range (400-1000 nm). The introduction of dopants (Fe\textsuperscript{2+} ions with a concentration 0.05-0.45 wt.\% and Nd\textsuperscript{3+} ions varying from 0.08 to 0.48 wt.\%) allows one to control the optical properties of samples which then can be used to create effective optoelectronic components for wide spectral ranges.

2. Experimental methods

2.1. The crystal growth and doping

The experiments were carried out on ZnSe plates alloyed with iron by thermal diffusion. The plates were cut from boules grown from the melt by the Bridgman method in graphite crucibles at a pressure of high-purity argon of 100 atm. The loading material was CVD grown ZnSe with 99.9996 wt. %...
purity which, as shown by ICP-MC analysis, provided an ingot of 99.9992 wt.% purity [7]. Impurities of Fe and Nd were introduced into ZnSe plates by thermal diffusion in a quasi-closed quartz reactor at a temperature of 1000 °C. The samples thickness varies around 1 mm.

The first group of samples was ZnSe crystals doped with an iron over the entire thickness of the plate. The concentration of iron, determined by x-ray fluorescence method was 0.23 wt.% and 0.15 wt.%. The measurements were carried out using a Bruker Mistral M-1 spectrometer.

The second group of samples consisted of ZnSe: Fe plates from the first group was additionally doped with Nd from the one side by thermal diffusion. The surface concentration of Nd, determined by the X-ray fluorescence method was 0.1 wt.%

The third group of samples consisted of undoped ZnSe plates was additionally simultaneously doped with Fe and Nd by thermal diffusion. The surface concentration of Fe and Nd, determined by the X-ray fluorescence method, was, respectively, 0.05 and 0.48 wt.%, 0.7 and 0.2 wt.%, 0.45 and 0.08 wt.%. The overview of all samples properties is shown in Table 1.

### Table 1. The ZnSe samples doping concentrations.

| Group   | Fe concentration, wt.% | Diffusion depth | Nd concentration, wt.% | Diffusion depth |
|---------|-------------------------|-----------------|-------------------------|-----------------|
| **Group 1** | 0.23                    | 0.15            | -                       | -               |
| **Group 2** | 0.23                    | 0.15            | 0.10                    | on surface      |
| **Group 3** | 0.05                    | 0.70            | 0.45                    | 0.20            | 0.08            | on surface |

2.2. The pump-probe spectroscopy setup

The experiments were carried out on the pump-probe supercontinuum spectrometer shown on Fig. 1. It is based on a Ti-sapphire regenerative amplifier (Ti:Sa RA) Regulas 35F1K (Avesta), which produces 30 fs pulses with energy up to 2.3 mJ and repetition rate of 1 kHz. The beam is split into two parts by BS1. One is used as a pump beam and its intensity is varied by the polarization attenuator (A) in the reflection geometry. The second part of the split beam is used for supercontinuum generation (SCG). To produce broad (350-1400 nm) SC in the visible – NIR spectral region, the water jet is applied [8-9]. The transmitted SC spectra are registered by the compact spectrometer ASP-100M (200-1000 nm).

![Figure 1. The femtosecond pump supercontinuum probe experimental set-up.](image-url)
3. Results and Discussions

To explain the optical absorption and changes in the band structure of undoped, Fe- and Nd-doped ZnSe samples pump-probe scans were recorded probing at different frequencies. The pump power at 800 nm was varied from 100 to 300 mW that corresponds to 3.6 and 10.9 GW/cm², respectively. The wavelength evolutions of induced absorption peaks extracted from various power dependences help to understand the energy levels’ positions in the band structure and the carrier redistribution in zinc selenide polycrystals with different dopant concentrations. The examples of typical pump-probe dynamics are presented in Fig. 2. The wavelength evolution of absorption peak position is used to extract the refractive index dispersion, as was shown in [10]. Relaxation of induced excitation wavelength evolution can be analyzed by the bandwidth of peak at half-maximum.

![Figure 2. Transmission dynamics of 700 nm probe wavelength for 10 GW/cm² pump pulse.](image)

Fig. 3 illustrates transmission of supercontinuum spectra by ZnSe and ZnSe:Fe crystals from Group1 after the pump beam excitation with different power levels. The effect of the short wavelength absorption edge shift for the doped sample confirms the known fact that this shift depends on the impurity concentrations and also on the annealing temperature during the diffusion of iron ions. Also, new absorption lines associated with the impurity level appear. The doping with iron change the transmitted supercontinuum spectra shifted to the red region.

![Figure 3. Transmission of supercontinuum spectra (normalized) after 150 and 300 mW pump beam excitation for Fe-doped ZnSe samples.](image)
Figure 4 shows the results for (a) 150 mW and (b) 300 mW pump power level excitation for samples from all three groups under study. It can be noticed that doping of Nd ions into the ZnSe:Fe samples sift the transmission spectra in the middle position between pure and doped samples shown in Fig.3. The increase of pump power also has an influence on the transmitted spectrum curve shape but not as strong as in the case of doping.

Figure 4(a, b). Transmission of supercontinuum spectra (normalized) after (a) 150 mW and (b) 300 mW pump beam excitation for Fe- and Nd-doped ZnSe samples.

The next study will help us to understand the way how we can vary the optical properties by doping ZnSe crystals with the transition and rare-earth elements. This can be used to create effective optoelectronic components for wide spectral ranges, for example, for improvement of terahertz electro-optical detection systems.

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