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The study of the optical nonlinear properties of bulk ZnSe for immersion applications

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In this work, we study the nonlinear absorption of ultrashort laser pulses of variable duration (0.3−10 ps) in a bulk polycrystalline ZnSe dielectric. The transmission of the sample was measured for two wavelengths, 515 and 1030 nm, in a wide range of intensities. A nonlinear behavior of the transmission is found when the sample is irradiated with laser radiation at a wavelength of 515 nm with absorption saturation in the region of 3−5 TW/cm^2. Surface damage thresholds were obtained for a wavelength of 1030 nm for pulse durations of 0.3−10 ps.

Keywords: nonlinear ZnSe absorption, solid-state immersion, two-photon absorption, chalcogenide glass surface ablation, ZnSe ablation thresholds.

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Introduction

ZnSe is a commercially-available material that has been widely used in infrared optics as optical elements (lenses and optical windows), due to its good radiation transmission in the range $\approx 0.5-21\,\mu$m [1]. Absorption of radiation in this region is practically absent for this material, and at normal incidence of radiation, losses occur only due to Fresnel reflection. In this case, the refractive index of ZnSe ($n \approx 2.48$) practically coincides with the refractive index of diamond, which opens up prospects for using ZnSe as immersion medium in which the uncut diamond will be placed. This will make it possible to focus the laser beam almost without distortion in the volume of the sample for its micro-marking [2,3] or for studying the internal structure using IR spectroscopy. In this case, the processing of diamond requires laser radiation with intensities of the order of terawatts, focused into a spot up to $10\,\mu$m in size. For such problems, it is necessary to take into account how the optical properties of the immersion medium will change under such laser exposure.

The nonlinear properties of semiconductors have been studied for many years [4,5]. As is known, if the incident photon energy $h\upsilon$ is less than the band gap E_g, the multiphoton absorption mechanism [4] can be realized. For ultra-short pulses (USPs), other nonlinear processes are also added to nonlinear absorption, such as multiphoton ionization, defocusing, filamentation, etc.

To date, there are a number of works in which nonlinear absorption in ZnSe [6–8] is studied. Measurement of the nonlinear absorption coefficient is performed using various methods of scanning with a focused beam along the sample i.e. the so-called z-scanning [7–10]. At the same time, at high intensities, when the focus is shifted to the sample boundary, the ablation process is possible, which is extremely undesirable for the measurement data; there are also a number of conditions for focusing the laser beam, which should not be too strong; therefore, high intensities are not used in these techniques. For laser marking, on the contrary, it is important to use sharp focusing and high intensities of laser radiation. Therefore, the study of the nonlinear properties of this immersion material at high intensities is an urgent task.

In this work, the study of the nonlinear absorption of ZnSe for ultrashort pulses of variable duration for wavelengths of 1030 and 515 nm, was made. The use of different durations made it possible to study nonlinear transmission in a wide range of intensities. The possibility of using ZnSe as a solid-state immersion medium for laser marking of diamond volumes by focused picosecond laser pulses is shown.

Experimental part

As a sample, the plane-parallel ZnSe wafer polished on both sides with a thickness of 4 mm was used. The absorption spectrum of the sample is shown in Fig. 1, *c*. Satsuma ytterbium fiber laser (by Amplitude Systemes) with wavelengths of the first and second harmonics of laser radiation of 1030 and 515 nm, respectively, was used as a radiation source in the work. The pulse duration was changed using a built-in compressor in the range 0.3−10 ps [10]. The laser radiation was focused through the object lens (NA 0.25) into the sample volume at depth of $750\,\mu$m, taking into account the refractive index ≈ 2.48. The laser radiation energy was monitored using an Ophir PD10-C energy meter (Fig. 1, *a*).

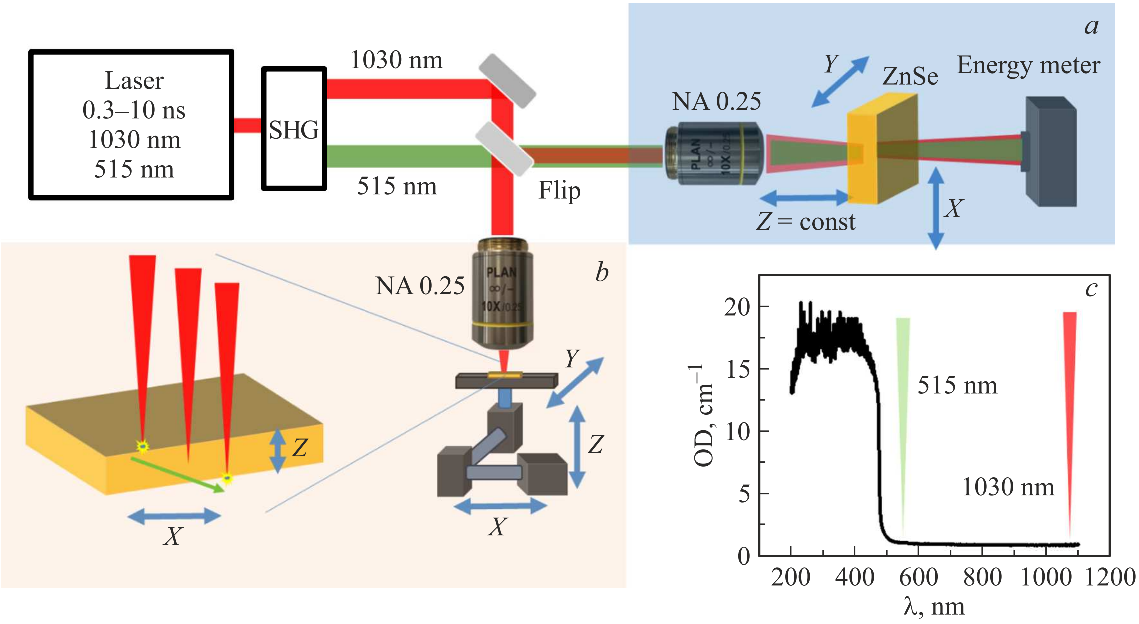

Figure 1. Experimental scheme. (*a*) Measuring the transmission of ultrashort laser pulses. (*b*) Ablation of the target when scanning through the entire sample. (*c*) ZnSe absorption spectrum with indication of the wavelengths of the laser radiation used.

During the transmission measurement, the sample was displaced by motorized three-coordinate shifting XYZ, and each new pulse was incident on a fresh section of the sample surface, the laser pulse repetition rate was 10 Hz, and the signal was averaged over 100 pulses. The Rayleigh length for a given focusing can be calculated using the formula $\pi n_0 w_0^2/\lambda$, where w_0 is the focal spot radius equal to for our system $2\,\mu$m (515 nm) and $4\,\mu$m (1030 nm) [11], n_0 is refractive index of the medium, into which the radiation is focused, λ is the wavelength of the laser radiation. The Rayleigh length calculated by this formula for the object lens used is $120\,\mu$m for a wavelength of 1030 nm and $60\,\mu$m for 515 nm.

The target was ablated for the first harmonic of laser radiation in the sample scanning mode simultaneously along two coordinates X and Z at a speed $5\,\mu$m/s and a laser pulse repetition rate 100 kHz (Fig. 1, *b*). The number of pulses arriving at one point was calculated by the formula $N = Df/V$, where $D = 4\,\mu$m is the characteristic diameter of the ablation region, and amounted to $8 \cdot 10^4$. The choice of this scanning mode was due to the fact that at lower exposures on the rear side of the target for 0.3 ps, ablation was absent.

Results and discussion

To study the absorption of a ZnSe wafer, dependences of transmission through the sample of laser pulses of various durations on the intensity of laser radiation were obtained (Fig. 2),

$$T = \frac{I}{I_0}, \qquad (1)$$

where I_0 is the intensity incident on the sample, I is the intensity transmitted through the sample. When measuring the intensity of light transmitted through the sample, the Fresnel reflection from two faces $(1-R)^2$ was taken into account. The important fact that we observe from these dependences is the absence of an effect of the duration of laser radiation on transmission, which depends only on the intensity of laser radiation.

Earlier in the works [7,8] the nonlinear part of the refractive index n_2 was obtained, which for 1030 nm has the positive value $\approx 2.3 \cdot 10^{-14}$ cm^2/W, whereas near the fundamental absorption edge it changes sign and for wavelength of 515 nm takes on the negative value $\approx -4 \cdot 10^{-14}$ cm^2/W. This may be the reason for such different behavior of radiation transmission through the sample (Fig. 2). If for the first harmonic the monotonic change in transmission is observed, then for the second harmonic one can note several segments with different slopes of the transmission curve versus intensity with absorption saturation in the region 3–5 TW/cm^2, which was not previously reported in works on measuring the nonlinear properties of ZnSe.

For positive value of the nonlinear refractive index, filamentation will occur when the critical self-focusing power $P_{cr} = \approx 0.02 \pm 0.01$ MW, calculated by the formula $P_{cr} = 3.77\lambda^2/8\pi n_0 n_2$, is reached.

When scanning through the sample, ablative damage to the surface occurred on the front and back sides. Damage in the volume could not be detected using an optical polarizing microscope. Scanning of the sample began when the focus of the laser radiation was above the surface and ended when the focus was below the sample. Examples of the topology

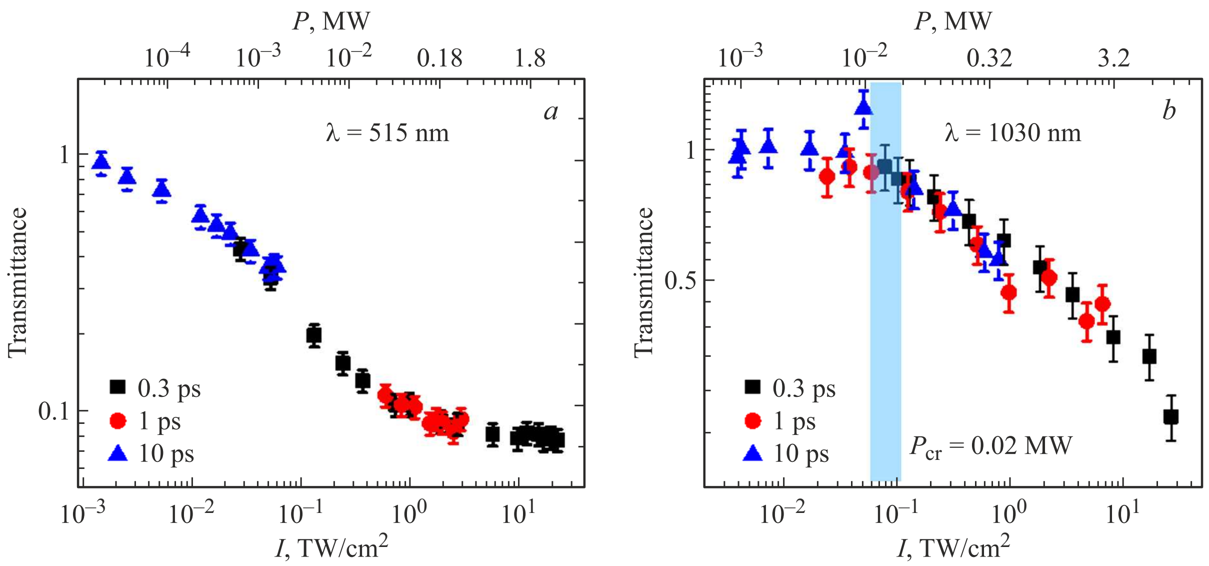

Figure 2. Transmission of a ZnSe sample over a length of (*a*) 515 nm, (*b*) 1030 nm. The blue area marks the critical self-focusing power.

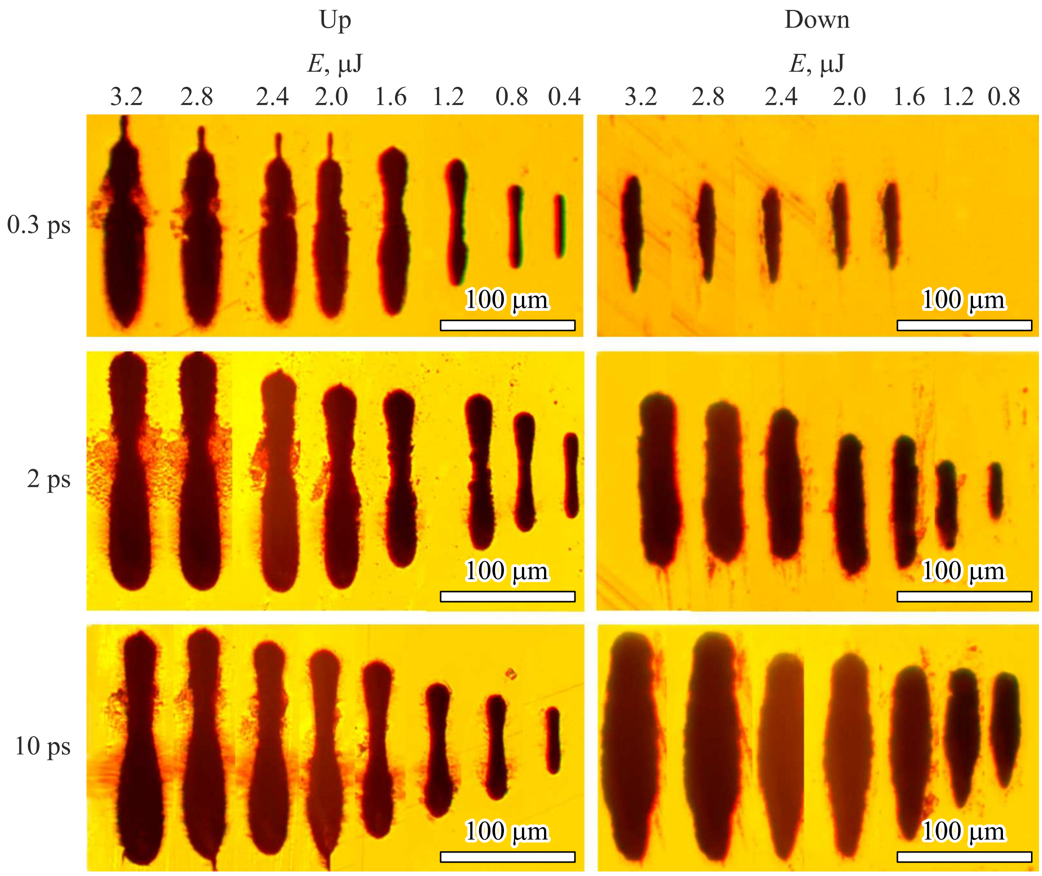

Figure 3. Visualization of damage to the front (upper) and rear (lower) surfaces of the ZnSe target, obtained at the specified duration and energy of laser radiation with wavelength of 1030 nm.

of surface damages depending on the duration and energy of laser radiation are shown in Fig. 3.

For the front surface, we observe the most accurate damage for 0.3 ps, for 2 and 10 ps they are approximately equal. Whereas for the rear side, the decrease in the size of the damaged region with decrease in the duration of laser radiation is noticeable, which is associated with nonlinear absorption in the sample. For this sample, the values of

Table

τ, ps	0.3	2	10
F_{th1}/F_{th2}, J/cm^2 w_{abl1}/w_{abl2}, μm	$(0.13 \pm 0.03)/(1.6 \pm 0.4)$ $(3.5 \pm 0.5)/(10 \pm 1)$	$(0.28 \pm 0.05)/(1.2 \pm 0.2)$ $(3.7 \pm 0.5)/(7.2 \pm 2)$	$(0.4 \pm 0.07)/(1.45 \pm 0.22)$ $(3.8 \pm 0.3)/(7.3 \pm 0.3)$

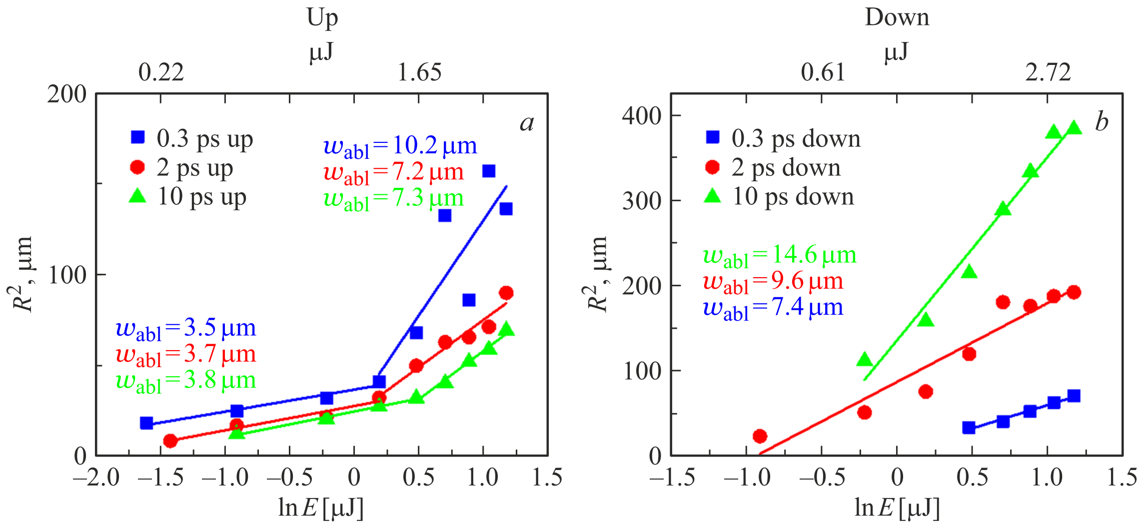

Figure 4. Dependences of the squared ablation radius near the focus on the upper and lower surfaces of the target on the logarithm of the energy.

the laser radiation waist region were measured, presented in the form of dependences $R^2 - \ln E$ (Fig. 4). From the approximation of the obtained dependences, the values of the threshold damage density of the sample surface F_{th} [12] were obtained.

During ablation of the upper surface, we observe two segments with different slopes of the dependences $R^2 - \ln E$, where the root of the slope of the curve corresponds to the experimental value of the laser spot radius in the focusing region w_{abl} (by level 1/e). For the mode with low radiation energies, the good agreement between the obtained values of the focusing spot and the theoretical value $4\,\mu$m is observed. Whereas, for energies above $1.5\,\mu$J, nonlinear effects related to plasma shielding, filamentation, etc. contribute to the size, so the value w_{abl} significantly exceeds the value of the geometric focusing for a given optical system.

Interestingly, when focusing on the lower surface, the spots are larger than on the upper one, which is also associated with the nonlinear interaction in the medium. In this case, all values lie on the same curve.

Calculated values of the threshold energy density of ablation and the radius of the focusing spot of laser radiation at different pulse durations, obtained from the dependences $R^2 - \ln E$.

The table shows the threshold values of the ablation energy density on the upper surface of the target, calculated by the formula $F_{th} = E_{abl}/\pi w_{abl}^2$, where E_{abl} is the ablation threshold energy, which is determined by extrapolating the curve to zero ordinate. F_{th1} and w_{abl1} correspond to the low energy mode, while the values F_{th2} and $w_{abl\,2}$ correspond to the mode with high intensities. As the pulse duration increases from 0.3 to 10 ps, the threshold value F_{th1} increases by approximately 3 times, while the value F_{th2} remains within 1.2–1.5 J/cm^2 and depends weakly on the duration.

Conclusion

In the course of this work, the nonlinear optical properties of a 3D- polycrystalline ZnSe sample were studied. The dependences of the sample transmission for ultrashort laser pulses focused in the sample volume by an NA 0.25 objective with a variable pulse duration 0.3–10 ps for wavelengths 1030 and 515 nm are obtained in a wide range of intensities 0.001–20 TW /cm^2, were obtained. The absence of a dependence of transmission on the duration of laser radiation was found. The nonlinear behavior of the transmission is found when the sample is irradiated with laser radiation with a wavelength of 515 nm with absorption saturation in the region 3–5 TW/cm^2 was found. The thresholds of ablation damage to the surface in the multi-pulse ablation regime are obtained, the values of which increase with the duration of the laser pulse.

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Conflict of interest

The authors declare that they have no conflict of interest.

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