

Study of the nonlinear transmission of Co^{2+} : ZnSe crystals at a wavelength of 1.54 μm

N.N. Il'ichev, P.V. Shapkin, S.E. Mosaleva, A.S. Nasibov

Abstract. The dependence of nonlinear transmission in Co^{2+} -doped ZnSe crystals at a wavelength of 1.54 μm on the incident energy density is studied under the $S_{\text{ZnSe}}\text{-}S_{\text{CoSe}}\text{-}L_{\text{Zn}}\text{-}V$ equilibrium conditions. The obtained results suggest that the residual losses in the crystal at high incident energy densities are not related to absorption from the excited state but are caused by losses appearing probably during sample growing and doping. The saturation energy and the ground-state absorption cross section are determined ($E_s = 0.12 \pm 0.03 \text{ J cm}^{-2}$ and $\sigma = (11 \pm 2) \times 10^{-19} \text{ cm}^2$).

Keywords: nonlinear crystals, saturation energy, passive switches.

1. Introduction

Co^{2+} -doped ZnSe crystals are used as passive switches in erbium-doped lasers emitting at $\sim 1.54 \mu\text{m}$ [1]. These lasers attract interest because their radiation is considered eye-safe, which provides their wide applications in laser range finders. The spectral and nonlinear properties of ZnSe crystals doped with Co^{2+} ions were studied in a number of papers [1–7]. A broad absorption band of these crystals in the region 1.4–1.9 μm is related to the transition from the ${}^4A_2({}^4F)$ ground state to the ${}^4T_1({}^4F)$ state [2, 7]. A broad luminescence band in the region 3–3.7 μm is caused by the transition from the ${}^4T_2({}^4F)$ state to the ${}^4A_2({}^4F)$ ground state [2].

The excited-state lifetime of Co^{2+} ions in ZnSe crystals at room temperature is 290 μs [2]. The experimental dependences of the nonlinear transmission in these crystals on the incident energy density obtained in papers [3–7] show that the transmission at high energy densities is substantially lower than 100%, which indicates to the presence of residual absorption. This fact is interpreted in the literature in two ways.

Thus, the residual losses were explained in [5] by absorption from the excited state. On the other hand, the authors of papers [3, 4] assume that these losses are caused by linear losses, for example, by absorption by

crystal defects appearing during the crystal growth and doping. This point of view is based on the fact that the Co^{2+} ion does not have appropriate higher resonance levels for the 1.54- μm transition from the upper excited state. There is no consensus on the origin of residual losses in Co^{2+} : ZnSe crystals so far.

The properties of nonlinear transmission in Co^{2+} : ZnSe crystals, in particular, the dependence of transmission on the incident radiation energy density do not allow one to distinguish residual losses caused by the excited-state absorption from linear losses. The dependence of the energy density on the longitudinal coordinate is described for these two cases by the same equation, in which only numerical coefficients are different. The experimental data can be described assuming the excited-state absorption or linear losses by fitting them with the properly selected coefficients. However, there is the case when the excited-state absorption is definitely absent – the case when no residual absorption is observed in a sample.

The values of absorption cross sections from the ground state for Co^{2+} : ZnSe crystals obtained by different authors are substantially different: $7.6 \times 10^{-19} \text{ cm}^2$ [3], $5.3 \times 10^{-19} \text{ cm}^2$ [4], $4.6 \times 10^{-19} \text{ cm}^2$ [5], $6.5 \times 10^{-19} \text{ cm}^2$ [6], and $11.5 \times 10^{-19} \text{ cm}^2$ [7]. In [3–7], the absorption cross sections were measured by processing numerically the experimental dependences of transmission on the incident energy density, so that such a large scatter in the data can be explained by the above-mentioned problem of interpretation of the residual losses observed in all these papers. For example, in [7] two ground-state absorption cross sections, 11.5×10^{-19} and $9.7 \times 10^{-19} \text{ cm}^2$, were reported for the same Co^{2+} : ZnSe crystal, which is, as pointed out in this paper, was determined by the model employed to interpret the experimental data.

Note also that the maximum incident energy densities used in [1–7] were from 1.2 J cm^{-2} [6] up to 4 J cm^{-2} [3] and the pulse durations were from 10 to 75 ns. The maximum energy density was restricted by the radiation damage threshold of samples. Such relatively low energy densities cannot provide accurate measurements of residual losses. The radiation damage threshold for pulses of such durations is known to depend on the radiation power density [8]. Because the excited-state lifetime is 290 μs [2], an increase in the pulse duration, for example, by an order of magnitude will not virtually affect the dependence of transmission on the energy density but will provide a substantial increase in the incident energy density.

In this paper, we investigated the dependence of transmission in Co^{2+} : ZnSe crystals at 1.54 μm on the energy

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density. We measured losses in the crystals at high (up to 10 J cm^{-2}) incident energy densities and calculated the ground-state absorption cross section at $1.54 \mu\text{m}$.

2. Experimental setup

Figure 1 shows the setup used for the measurements of nonlinear transmission in crystals. We employed a Q -switched $1.54\text{-}\mu\text{m}$ erbium-doped glass laser with a lithium niobate electro-optical switch. The pulse duration was $200\text{--}300 \text{ ns}$ and the output energy was $3\text{--}5 \text{ mJ}$ in the TEM_{00} mode. Pulses of such duration allowed us to perform measurements at incident energy densities on samples up to 10 J cm^{-2} without the sample damage. After propagation through Glan prism (1), beamsplitter (2), and lens (3), laser radiation was incident on sample (4). The energy of transmitted radiation was measured with photodiode (5). The energy of a radiation pulse incident on a sample and reflected from mirrors (2) and (6) was measured with reference photodiode (7). The output signal from the photodiode was calibrated with the help of a calorimeter placed instead of a sample. The FD-7g photodiodes were used, and an integrating chain was used in the detection circuit, so that the output signal was proportional to the pulse energy. The output signal of the photodiode was measured by means of an ADC-14 in the CAMAC standard. The control of the setup, data acquisition and preliminary processing were performed with a PC. The pulse duration was measured with an LFD-2a photodiode and a Tektronix 7104 oscilloscope with the total time resolution of about 1 ns .

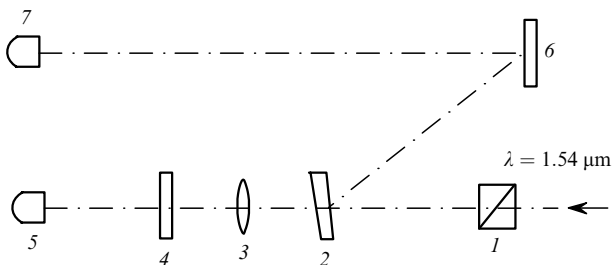


Figure 1. Scheme of the experimental setup for measuring transmission in $\text{Co}^{2+} : \text{ZnSe}$ crystals: (1) Glan prism; (2) beamsplitter; (3) lens; (4) sample; (5) photodiode; (6) mirror; (7) reference photodiode.

The energy density incident on a crystal was changed by moving the crystal along the laser beam near the caustic waist. Radiation incident on a sample was linearly polarised in Glan prism (1) (the degree of polarisation was $\sim 1 : 1000$). To avoid variations in the output signal from photodiodes, caused by the possible motion of the radiation spot on the input window of the photodetector, opal glasses were placed in front of photodiodes. When the $3\text{--}4\text{-mm}$ radiation spot on the input window of the photodiode was displaced by $\pm 4 \text{ mm}$, a change in the ratio of the output signals from photodiodes was $0.1\% \text{--}0.2\%$.

The transmission in crystals was measured in the following way. A sample was removed, and the output signals U_1 and U_2 from photodiodes (5) and (7) were measured (Fig. 1) and the ratio $g = U_1/U_2$ for each pulse was calculated. Then, the ratio $\langle g \rangle = g_0$ averaged over 30

pulses and the average output signal of the reference photodiode were found. After that, the sample was put into the beam and the value of g_1 was measured in the same way. The transmission was determined by the expression $T = g_1/g_0$. Such a measurement procedure reduced substantially the effect of a pulse-to-pulse energy variation, so that the root-mean-square deviation of T was no worse than $0.1\% \text{--}0.2\%$ and for U_2 no worse than $2\% \text{--}4\%$.

The radius of a radiation spot on a sample was determined from the dependence of the transmission through an aperture with the known diameter on its coordinate along the laser beam. The transverse energy distribution in pulses was assumed Gaussian. The fitting parameters in the data processing were the beam waist radius and the waist position. The validity of such an approach was confirmed by the special measurements of the dependence of the transmission through a narrow slit (0.15 mm) on its position in the direction perpendicular to the laser beam. Figure 2 shows the measured transverse distribution of the energy density in the laser pulse. The radius of this distribution $w = 0.86 \text{ mm}$ was measured from the dependence of transmission through an aperture of diameter 0.385 mm on its position along the laser beam. Our calculations showed that the radii of the Gaussian beam determined with the help of the aperture and slit coincide with accuracy better than 3% . The measurement error of the cross sectional area $s = \pi w^2/2$ is estimated as 6% .

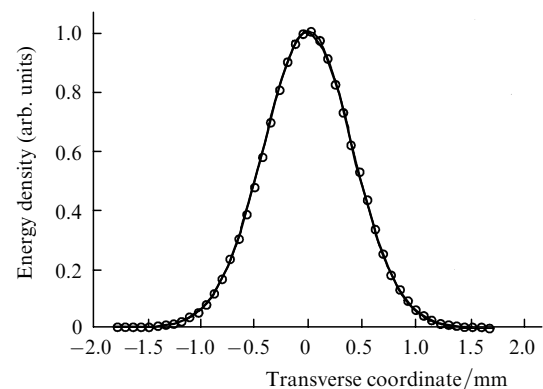


Figure 2. Transverse distribution of the energy density in the laser pulse normalised to the maximum. Circles are measurements, the solid curve is the function $\exp[-2(r/w)^2]$, where $w = 0.86 \text{ mm}$.

By measuring transmission, we measured simultaneously the pulse energy, which allowed us to take into account a pulse-to-pulse energy variation, thereby improving the accuracy of measurements. The energy density in the maximum of the transverse distribution (peak energy density) was found from the radiation pulse energy and the beam radius, and the dependence of transmission in the sample on the peak energy density was measured. In this method for measuring nonlinear transmission, the range of variation in the output signal of a photodiode is usually much narrower than in the measurements based on a change in the pulse energy, which also improved the measurement accuracy. For example, if the sample transmission increases from 70% to 100% , the output signal of photodiode (5) (Fig. 1) changes only by a factor of 1.5, whereas the energy density incident on a crystal can change in this case by a few orders of magnitude.

3. Measurement of nonlinear transmission

We studied several ZnSe crystals doped with different amounts of Co^{2+} . The crystal were doped by the diffusion method under the $\text{S}_{\text{ZnSe}}\text{-S}_{\text{CoSe}}\text{-L}_{\text{Zn}}\text{-V}$ equilibrium condition. This technology differs from the used earlier methods for preparing Co^{2+} : ZnSe crystals: the modified diffusion method [4, 7] described in [9] and the Bridgman method [6].

The optical faces of crystals Nos 343 and 356 had AR coatings for 1.54 μm , and radiation was incident on them almost normally. Sample No. 365 had no AR coating and was mounted at the Brewster angle to the incident radiation, the radiation electric field vector lying in the plane of incidence.

Figure 3 shows the transmission spectra of ZnSe crystals with the 1.54- μm AR coatings, two of which were doped with Co^{2+} and one was pure. The transmission in crystals Nos 343 and 356 at 1.54 μm in a weak field was 29.5 % and 69.5 %, respectively. The AR coating was deposited simultaneously on these crystals, which were mounted alongside in a vacuum deposition apparatus. The transmission spectra shown in Fig. 3 demonstrate the absence of any significant losses. It is difficult to estimate the reflectivity of faces of the doped crystals at 1.54 μm from these spectra because of the absorption in this region. However, the quality of the AR coating of doped crystals can be estimated by comparing their transmission spectra and the transmission spectrum of the pure crystal in the spectral regions $\lambda < 1200$ nm and $\lambda > 2200$ nm, where the absorption of impurity centres is absent. One can see from Fig. 3 that all the spectra in these regions are almost identical, the transmission coefficient for the pure crystal at 1.54 μm being equal to 99 %.

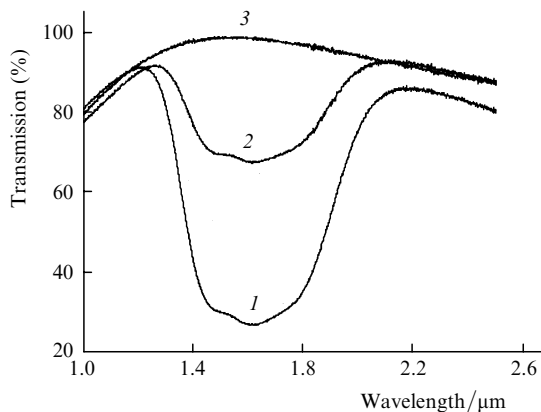


Figure 3. Transmission spectra of AR coated samples Nos 343 (1) and 356 (2) and of a pure ZnSe crystal (3).

Figure 4 shows the dependences of the transmission in samples Nos 343, 356, and 365 on the incident energy density.

4. Discussion of results

The calculation for a medium with absorption saturation was performed by solving numerically the Avizonis–Grotbeck equation [10]

$$\frac{dx}{dz} = -\alpha(1 - e^{-x}) - \gamma x, \quad (1)$$

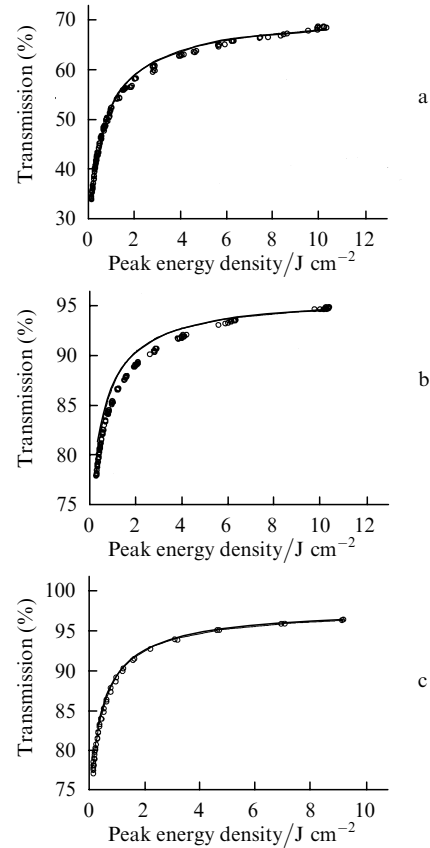


Figure 4. Transmission of crystals Nos 343 (a), 356 (b), and 365 (c) as a function of the peak energy density incident on a crystal. Circles are measurements, the solid curves are calculations. Sample No. 365 is oriented at the Brewster angle.

where x is the radiation pulse energy density normalised to the saturation energy density $E_s = \hbar\omega/\sigma$; σ is the ground-state absorption cross section at 1.54 μm ; $\hbar\omega$ is the photon energy; z is the coordinate along the propagation of radiation; α is the absorption coefficient related to absorption saturation; and γ is the absorption coefficient related to linear losses or (and) excited-state absorption. It was assumed that α and γ are independent of z and that the transverse distribution of the radiation energy density on a sample is $x(r) = x_{\text{max}} \exp[-2(r/w)^2]$. We solved numerically Eqn (1) at the crystal exit for each value of $x(r)$ at the crystal entrance and, by integrating over the cross sectional area, found the energy at the crystal exit as a function of the incident peak energy density. We took into account in the calculations the reflection from crystal faces. Transmission was measured as the ratio of energies at the exit and entrance of the crystal.

It is convenient to characterise residual losses by the parameter $\Delta = \alpha/(\alpha + \gamma)$. If γ is caused by excited-state absorption, the value of Δ should be independent of the impurity concentration in samples. The transmission obtained for samples Nos 356 and 343 in the case of saturation was 97 % and 71 %, respectively. We assumed in the calculations that the initial transmission for crystal No. 343 was $T_0 = 29.5$ %, transmission caused by reflection from crystal faces was $T_r = 99$ %, the crystal thickness was $L_s = 0.81$ mm, $\alpha = 10.2$ cm^{-1} , $\gamma = 4.0$ cm^{-1} , $\Delta = 0.73$, $E_s = 0.115$ J cm^{-2} , and $\sigma = 11.2 \times 10^{-19}$ cm^2 , and for crystal

No. 356 – $T_0 = 69\%$, $T_r = 99\%$, $L_s = 0.58$ mm, $\alpha = 5.6$ cm⁻¹, $\gamma = 0.5$ cm⁻¹, $\Delta = 0.92$, $E_s = 0.115$ J cm⁻², and $\sigma = 11.2 \times 10^{-19}$ cm².

Similar measurements were performed for several Co²⁺:ZnSe crystals. Table 1 presents the initial transmission, maximum transmission, and the parameter Δ for different crystals. We assumed in calculations that $E_s = 0.115$ J cm⁻², and $\sigma = 11.2 \times 10^{-19}$ cm². These values of the saturation energy density and cross section provide the best fit of the experimental data.

Table 1.

	T_0 (%)	T_{\max} (%)	Δ
343	29.5	74	0.73
344	86.0	94	0.66
355	39.0	89	0.88
356	69.5	97	0.92
358	81.0	97	0.92
365*	73.6	98	1.00

*Radiation is incident on a crystal at the Brewster angle.

To calculate transmission in crystal No. 365 mounted at the Brewster angle, we measured transmission in pure ZnSe samples mounted at the Brewster angle, which proved to be 98%. Such a considerable difference from 100% is caused by reflection of light from crystal faces, which is probably explained by the formation of a distorted layer upon polishing. The initial transmission in sample No. 365, measured at normal incidence of radiation at 1.54 μ m, was 75% (taking reflection from crystal faces into account), the sample thickness being $L_s = 0.67$ mm. We assumed that the distances propagated by radiation in the ZnSe crystal with the refractive index $n = 2.45$ [11] was 0.74 mm, and transmission in the crystal mounted at the Brewster angle was 73.6%. We also assumed in calculations that the transverse distribution of the radiation energy density in the sample was proportional to $\exp[-2(x/w_x)^2 - 2 \times (y/w_y)^2]$, where $w_x = w$, $w_y = un$, and w is the measured radius of this distribution. The energy density at the distribution maximum was assumed to be E_{\max}/n , where E_{\max} is the energy density at the distribution maximum in the site of sample location in a plane perpendicular to the radiation propagation direction. The solid curve in Fig. 4c is calculated for $\Delta = 1$ ($\gamma = 0$).

The data obtained for the crystals show that the parameter Δ is different for different samples, which means that residual losses cannot be caused by excited-state absorption. This conclusion is even more convincingly confirmed by the results obtained for crystal No. 365, where residual losses are absent at all.

The origin of large residual losses in some samples, for example, crystal No. 343, where the maximum transmission is 74%, remains unclear.

The value of E_s obtained to the third decimal place after processing the data is presented above. In our case, the error of determining E_s is limited by the calibration error of the output signal from photodiode (7) (Fig. 1), which is determined by the error of energy measurement with an IMO-2N calorimeter and does not exceed 15% according to the specification. The error of measuring the cross sectional area of the beam was estimated as 6%. The contributions from the measurement errors for other parameters to the error of measuring E_s are significantly smaller. Therefore,

we received the estimates $E_s = 0.12 \pm 0.03$ J cm⁻² and $\sigma = (11 \pm 2) \times 10^{-19}$ cm².

5. Conclusions

We have found that residual losses are different in different sample, the parameter Δ varying from unity (residual losses are absent) up to 0.66, which indicates the absence of excited-state absorption. The residual losses are most likely related to the technology of crystal growth and doping. The saturation energy and the ground-state absorption cross section measured in our experiments are ($E_s = 0.12 \pm 0.03$ J cm⁻² and $\sigma = (11 \pm 2) \times 10^{-19}$ cm², respectively).

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