ACTIVE MEDIA

Linear and nonlinear transmission of Fe²⁺-doped ZnSe crystals at a wavelength of 2940 nm in the temperature range 20–220 °C

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Abstract. The linear and nonlinear transmission of Fe^{2+}:ZnSe crystals is measured at a wavelength of 2940 nm in the temperature range 20–220 °C. It is found that, with increasing temperature from 20 °C to 150–220 °C, the transmission of Fe^{2+}:ZnSe crystals decreases in the case of incident radiation with an intensity of ~5.5 MW cm⁻² and increases in the case of radiation with an intensity of 28 kW cm⁻². At a temperature of 220 °C, the linear transmission almost coincides with the nonlinear transmission. The transmission spectra of Fe^{2+}:ZnSe crystals at temperatures of 22 and 220 °C in the wavelength range 500–7000 nm are presented.

1. Introduction

Recently, much attention has been paid to the study of zinc selenide single crystals doped with iron. This is explained by the possibility of lasing of this material in the wavelength range $\lambda = 3.8-5$ μm [1–5] at both low (100–200 K) and room temperatures. Radiation in this wavelength range is interesting from the viewpoint of its practical application.

One of the possible methods of doping ZnSe crystals with iron is the impurity diffusion through the crystal surface at high temperatures. In [5], one can find the results of investigation of a room-temperature superluminescent laser based on a diffusion-doped Fe^{2+}:ZnSe crystal. In the case of the diffusion method, the impurity is concentrated in a narrow subsurface region of the crystal. This circumstance makes it possible to efficiently use a transverse pumping scheme when the pump and laser beams are perpendicular to each other [5].

The diffusion doping of ZnSe crystals with Fe^{2+} ions was studied in [6, 7]. In particular, the diffusion coefficients of Fe^{2+} ions in zinc selenide single crystals as functions of temperature were measured in [7]. In [8], we studied the nonlinear transmission of diffusion-doped Fe^{2+}:ZnSe crystals at $\lambda = 2920$ nm. It was found that the samples have residual losses. Processing of the experimental data showed the best approximation when the lifetime of the upper level of the resonance

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transition in the Fe^{2+} ion was taken to be 100 ns. The Fe^{2+}:ZnSe crystal was successfully used as a passive Q-switch in an Er^{3+}:YAG laser [9, 10]. A review of recent investigations of iron-doped chalcogenide crystals can be found in [11].

The lasers based on Fe^{2+}:ZnSe crystals are usually pumped by radiation with $\lambda \sim 3000$ nm and operate at $\lambda \sim 4500$ nm. The difference in the energies of the pump and emission photons in this case is significant, i.e., 30%–40% of the pump energy is spent on heating of the Fe^{2+}:ZnSe active element. If this laser operates at room temperature, the active element can be heated to a temperature much higher than room temperature.

Another important reason for heat release in active elements is the low luminescence quantum yield at room temperature. In particular, the lifetime of the upper level of the Fe^{2+} ion in ZnSe crystals decreases from 105 μs at 120 K [2] to 355 ns at 300 K [4]. The possibility of creating an efficient Fe^{2+}:ZnSe laser operating at room temperature is to a large extent determined by the characteristics of this material at high temperatures. From this viewpoint, it is important to know the spectral and luminescent characteristics of the Fe^{2+}:ZnSe crystal at temperatures above room temperature. As far as we know, these studies have not been performed until now.

In the present work, we measure the linear and nonlinear transmission of the sample of diffusion-doped Fe^{2+}:ZnSe single crystals at $\lambda = 2940$ nm as a function of temperature. The transmission spectra of the samples in the wavelength range $\lambda = 500-7000$ nm at temperatures of 20 °C and 220 °C are also measured.

2. Measurement of the Fe²⁺:ZnSe crystal transmission as a function of temperature

Figure 1 shows the optical scheme for measuring the nonlinear transmission of Fe^{2+}:ZnSe samples as a function of temperature. We used three Fe^{2+}:ZnSe samples with the initial transmission $T_0 = 40\%$ (No. 464), 8.5% (No. 422), and 0.6% (No. 474) at $\lambda = 2940$ nm. The initial transmission of the samples depended on polishing removing a part of the diffusion layer doped with Er^{2+} ions. The thicker the removed layer, the higher the sample transmission. The samples were doped from both sides. Upon polishing, identically thick layers were removed from both sides.

Figures 2a–2c present the transmission spectra of the samples at temperatures of 22 °C and 220 °C. The measurements were performed using Shimadzu IR-460 and UV-3101PC spectrophotometers. One can see that, with increasing temperature, the absorption band of Fe^{2+} ions for all the samples broadens and the transmission in the absorp-
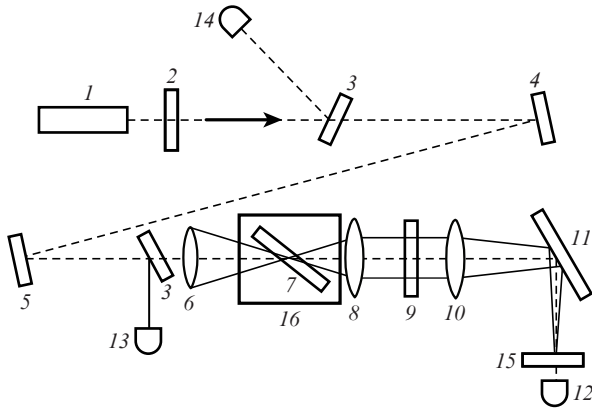
Figure 1. Optical scheme for measuring the nonlinear transmission of Fe^{2+}:ZnSe samples as a function of temperature: (*1*) passively Q-switched Er^{3+}:YAG laser ($\lambda = 2940$ nm, TEM_{00} mode, energy ~ 10 mJ, pulse duration ~ 200 ns, pulse repetition rate 0.8 Hz, linear polarisation); (*2, 9*) attenuating filters; (*3*) beam-splitters; (*4, 5, 11*) plane rotating mirrors; (*6, 8, 10*) CaF_2 lenses with focal distances of 80, 15 and 15 cm, respectively; (*7*) sample in the form of a plane-parallel plate (angle of the beam incidence $\sim 63°$, electric field vector of the incident beam lies in the plane of incidence); (*12, 13*) FSG-22-3a2 photodetectors for recording the transmitted and incident radiation, respectively; (*14*) PM-4 photodetector for measuring the radiation pulse energy (calibrated with a calorimeter); (*15*) scatterer (two glass plates with two frosted faces); (*16*) furnace for heating the sample to 220 °C (temperature measurement error ± 5 °C). Signals from the photodetectors were recorded by a DPO 7254 oscilloscope (input resistance 50 Ω).

tion maximum increases. In addition, it is noteworthy that there exists a continuous absorption, which changes from sample to sample and is clearly seen in the long-wavelength part of the spectrum. Probably, it is this absorption that manifests itself in the measurements of transmission at high radiation intensities. The origin of this absorption is unclear. Most probably, it relates to the insufficiently high purity of iron used for diffusion. It should also be noted that, with increasing temperature, no additional absorption lines appear in the spectral range in question. For comparison, Fig. 2d shows the transmission spectra of an undoped ZnSe sample at temperatures of 22 and 220 °C. It is seen that the spectra almost do not change as the temperature increases from 22 to 220 °C, while the transmission is determined by the reflection from the optical surfaces of the sample.

The transmission at $\lambda = 2940$ nm was recorded as follows. The amplitude ratio of the pulses from photodetectors (*12*) and (*13*) (Fig. 1) was measured in the absence and presence of a sample in the measurement path. This ratio determined the transmission. The results were averaged over 32 pulses. To measure the transmission at a low radiation intensity, we placed a filter (*9*) (NS9 with a transmission of ~ 0.5%) in front of the lens (*6*) and repeated the described procedure. The transmission at each temperature was measured at low and high radiation intensities. The main experimental problem was that the sample was heated (moreover, heated inhomogeneously) due to a significant heat release under the action of high-power radiation, which led to the formation of
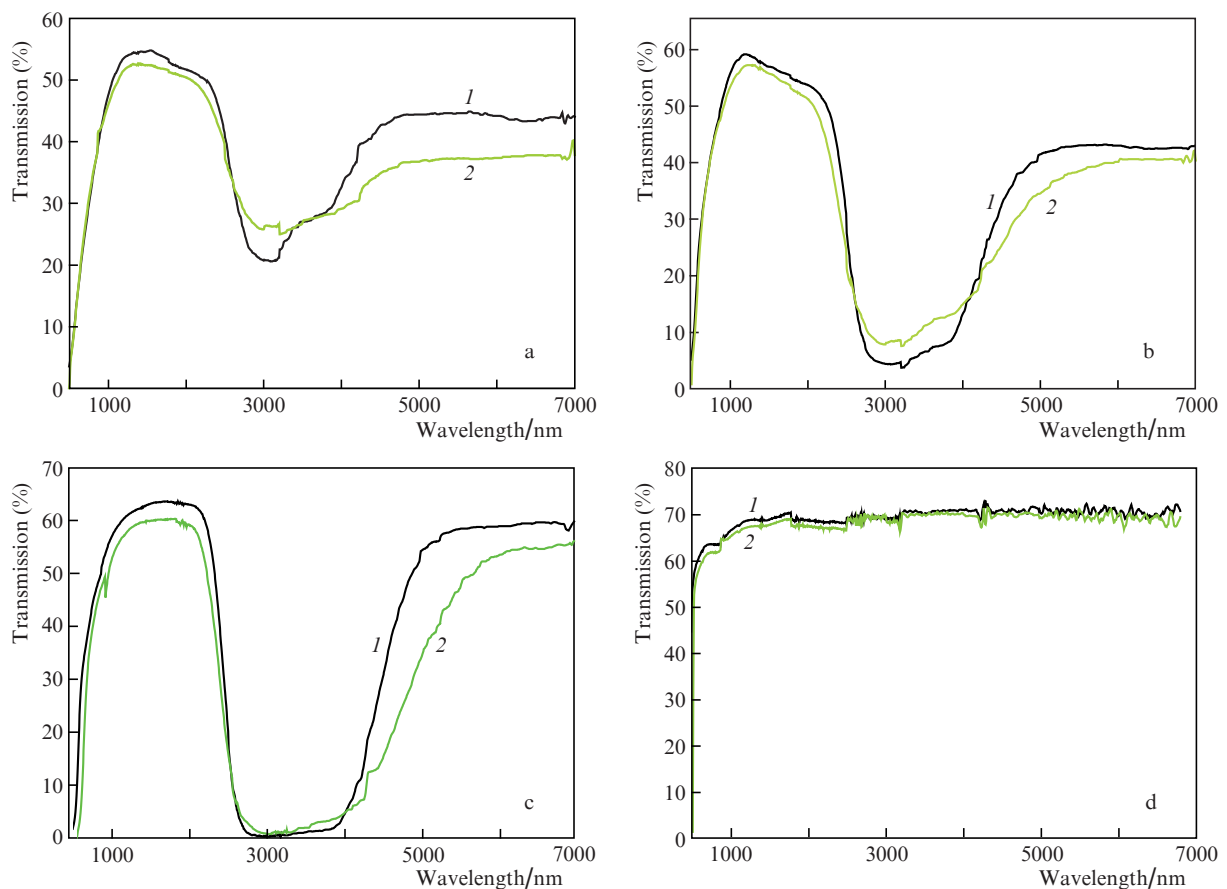

Figure 2. Transmission spectra of Fe^{2+}:ZnSe samples Nos 464 (a), 422 (b) and 474 (c), as well as of an undoped ZnSe sample (d) at temperatures of 22 °C (*1*) and 220 °C (*2*) in the case of normal incidence of the probe radiation.

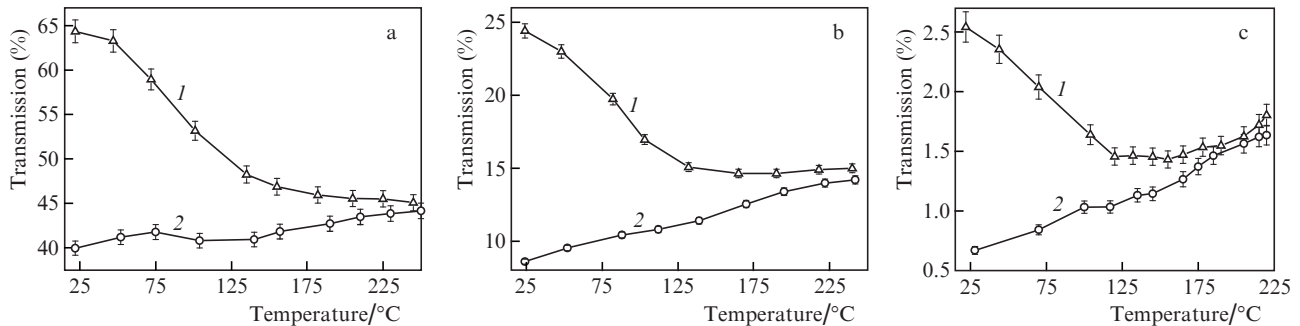

Figure 3. Transmission of Fe^{2+}:ZnSe samples Nos 464 (a), 422 (b) and 474 (c) at λ = 2940 nm as a function of temperature at incident radiation intensities of ~5.5 MW cm⁻² (*1*) and 28 kWcm⁻² (*2*).

a lens in the crystal. The focal length of this lens changed during the radiation action, which could affect the shape of the recorded signal due to vignetting at the apertures of optical elements upon beam propagation to the photodetector (*12*). Lenses (*8*), (*10*) and a scatterer (*15*) served to eliminate the effect of the thermal lens on the shape of the signal recorded by the photodetector (*12*).

Figure 3 presents the temperature dependences of the transmission of the samples at λ = 2940 nm for high- and low-intensity radiation. The high-power radiation intensity at the entrance to the sample was 5.5 MW cm⁻² (energy density ~1.1 J cm⁻²), and the attenuated radiation intensity was 28 kW cm⁻² (0.005 J cm⁻²).

3. Discussion

The transmission of high-power radiation by sample No. 464 decreases as the temperature increases from 20 to 220 °C. For samples Nos 422 and 474, the transmission of high-power radiation decreases until the temperature reaches 130--150 °C and then either almost does not change (sample No. 422) or slightly increases (No. 474) similar to the case of low-intense radiation. This behaviour is most probably related to additional heating of the thin iron-enriched diffusion layer by high-power radiation, since the maximum absorption coefficient at the entrance to these samples is estimated to be 200–250 cm⁻¹. Note that the high-power radiation heats all the samples, but to different extents. The transmission of low-intense radiation by all the samples increases with increasing temperature. This is caused by a decrease in the absorption coefficient at the radiation wavelength, as is seen from the transmission spectra at different temperatures given in Figs 2a–2c.

At a temperature of 220 °C, all the samples cease to bleach under the used radiation intensity. This can be explained by the fact that the lifetime of the upper level of Fe^{2+} in the ZnSe crystal decreases with increasing temperature, because of which the incident radiation intensity turns out to be not high enough to bleach the sample.

Using the absorption cross section at λ = 2940 nm (~10^{-18} cm², see, for example, [2]) and the upper level lifetime (~355 ns [4]), the saturation intensity at room temperature can be estimated to be 0.2 MW cm⁻². Since the crystal almost does not bleach at a temperature of 220 °C and a radiation intensity of 5.5 MW cm⁻², then, taking this intensity as the saturation intensity at 220 °C and ignoring the decrease in the absorption cross section at this temperature, we find that the lifetime of the upper level of the Fe^{2+} impurity centre in the

ZnSe crystal at 220 °C must be shorter than 12 ns. Note that the lifetime of the upper level of Fe^{2+} in the ZnSe crystal is rather difficult to measure from the luminescence decay above room temperature due to a low luminescence quantum yield at high temperatures.

4. Conclusions

(1) It is found that, for high-power (incident radiation intensity ~5.5 MW cm⁻²) pulsed radiation with λ = 2940 nm, the transmission of Fe^{2+}:ZnSe crystals decreases as the crystal temperature increases from 20 °C to 150–220 °C. This is most probably explained by a decrease in the lifetime of the upper level of the Fe^{2+} ion with increasing temperature. At a temperature of 220 °C and an incident radiation intensity of ~5.5 MW cm⁻², all the samples almost cease to bleach. This circumstance allows us to conclude that the lifetime of the upper level of the Fe^{2+} ion at a temperature of 220 °C does not exceed 12 ns.

(2) The linear transmission of the Fe^{2+}:ZnSe crystal increases as the temperature increases from 20 °C to 220 °C due to a decrease in the absorption cross section of the Fe^{2+} impurity centre with increasing temperature. The absorption spectra of the samples at temperatures of 20 °C and 220 °C within the spectral range 500–7000 nm are presented.

(3) The temperature dependence of the nonlinear optical characteristics of Fe^{2+}-doped ZnSe crystals must be taken into account when developing high-power lasers based on this material, especially for lasers operating at room temperature.

References

1. DeLoach L.D., Page R.H., Wilke G.D., Payne S.A., Krupke W.F. *IEEE J. Quantum Electron.*, **32** (6), 885 (1996).
2. Adams J.J., Bibeau C., Page R.H., Krol D.M., Furu L.H., Payne S.A. *Opt. Lett.*, **24** (23), 1720 (1999).
3. Kernal J., Fedorov V.V., Gallian A., Mirov S.B., Badikov V.V. *Opt. Express*, **13** (26), 10608 (2005).
4. Akimov V.I., Voronov A.A., Kozlovskii V.I., et al. *Kvantovaya Elektron.*, **36** (4), 299 (2006) [*Quantum Electron.*, **36** (4), 299 (2006)].

5. Il'ichev N.N., Danilov V.P., Kalinushkin V.P., Studenikin M.I.,
    Shapkin P.V., Nasibov A.S. *Kvantovaya Elektron.*, **38** (2), 95
    (2008) [*Quantum Electron.*, **38** (2), 95 (2008)].
6. Demirbas U., Sennaroglu A., Somer M. *Opt. Mater.*, **28**, 231
    (2006).
7. Il'ichev N.N., Shapkin P.V., Gulyamova E.S., Kulevskii L.A.,
    Nasibov A.S. *Neorg. Mater.*, **46** (2), 149 (2010).
8. Il'ichev N.N., Shapkin P.V., Kulevsky L.A., Gulyamova E.S.,
    Nasibov A.S. *Laser Phys.*, **18** (2), 130 (2008).
9. Voronov A.A., Kozlovskii V.I., Korostelin Yu.V., Landman A.I.,
    Podmar'kov Yu.P., Polushkin V.G., Frolov M.P. *Kvantovaya
    Elektron.*, **36** (1), 1 (2006) [*Quantum Electron.*, **36** (1), 1 (2006)].
10. Samokhin A.A., Vovchenko V.I., Il'ichev N.N., Shapkin P.V.
    Kvantovaya Elektron., **38** (12), 1141 (2008) [*Quantum Electron.*, **38**
    (12), 1141 (2008)].
11. Mirov S.B., Fedorov V.V., Martyshkin D.V., Moskalev I.S.,
    Mirov M.S., Gapontsev V.P. *Opt. Mater. Express*, **1** (5), 898
    (2011).