3.77–5.05-μm Tunable Solid-State Lasers Based on Fe^{2+}-Doped ZnSe Crystals Operating at Low and Room Temperatures

Vladimir V. Fedorov, Sergey B. Mirov, Andrew Gallian, Dmitri V. Badikov, Mikhail P. Frolov, Yuri V. Korostelin, Vladimir I. Kozlovsky, Alexander I. Landman, Yuri P. Podmar'kov, Vadim A. Akimov, and Artem A. Voronov

Abstract—Spectroscopic properties and lasing of Fe:ZnSe and co-doped Fe:Cr:ZnSe crystals in the mid-infrared spectral range were studied at room and low temperatures. Using a free-running Er:YAG laser as a pump source, the output energy of the thermoelectrically cooled Fe:ZnSe laser was 142 mJ with 30% slope efficiency at $T = 220$ K. Passive Q-switched oscillation of Er:YAG laser with Fe:ZnSe crystal was demonstrated and used as a pump source for a Fe:ZnSe laser system. Room-temperature (RT) gain-switched lasing of Fe:ZnSe was achieved in microchip and selective cavity configurations using Q-switched Er:YAG and Raman-shifted Nd:YAG lasers as pump sources. The microchip laser threshold of 100 mJ/cm^2 was demonstrated using a Fe:ZnSe crystal without any reflection coatings. A slope efficiency of 13%, oscillation threshold of 1.3 mJ, and tunable oscillation of Fe:ZnSe laser systems over 3.95–5.05 μm spectral range were realized at RT.

Index Terms—Mid-infrared (Mid-IR) lasers, transition metal lasers, tunable solid-state lasers.

I. Introduction

THERE is a continuously growing demand for affordable compact room-temperature (RT) mid-infrared (IR) sources for use in a variety of spectroscopic and other applications including: eye-safe laser radar, remote sensing of atmospheric constituents, trace gas analysis, environmental monitoring, industrial control, eye-safe medical laser sources for noninvasive medical diagnostics, optical communication, and numerous military applications such as target designation, obstacle avoidance and IR counter measures.

One of the reliable and promising approaches is using II-VI chalcogenides with different divalent transition metal (TM) ions as an active material for tunable mid-IR lasers. In 1996 and 1997 , DeLoach *et al.* [1] and Page *et al.* [2] performed a detailed spectroscopic study of several II-VI chalcogenide hosts with different TM dopants as potential mid-IR laser materials. Since then, lasers based on Cr:ZnS, Cr:ZnSe, Cr:Cd$_{1-x}$Mn$_x$Te, and Cr:CdSe crystals working with efficiency exceeding 60% in continuous-wave (CW), free-running long pulse, Q-switched and mode-locked regimes of operation as well as being tunable over the 2–3.5-μm spectral region have been reported (see [3] and references herein).

Unfortunately, mid-IR transitions in the Fe^{2+}:ZnSe crystal have multiphonon quenching at RT. Until now this has prevented RT lasing using Fe:ZnSe as a gain medium. The first lasing action from an Fe-doped n-InP semiconductor crystal at 2 K was demonstrated by Klein *et al.* [4], who observed laser oscillations at 3.53 μm. The first tunable lasing of a Fe:ZnSe crystal in 3.98–4.5 μm spectral range was demonstrated in [5] for temperatures ranging from 15 to 180 K. The first RT lasing of a Fe:ZnSe was demonstrated in [8].

In this study we extended our effort to develop high optical density and high quality Fe^{2+}:ZnSe crystals for improving low temperature output characteristics and demonstrating the feasibility of Fe^{2+}:ZnSe crystals for efficient gain-switched lasing at RT.

II. Sample Preparation

In our experiments we used iron doped ZnSe crystals prepared by two different techniques. In the first technique, the undoped polycrystalline samples of ZnSe were grown by chemical vapor deposition. Doping of the 1–3-mm-thick ZnSe polycrystalline wafers was performed by after growth thermal diffusion of Fe and/or Cr. Doping of ZnSe samples was achieved by inserting ZnSe crystals together with FeSe and/or CrSe powder into quartz ampoules that were evacuated and then sealed, under 10^{-4} torr pressure. The thermal diffusion coefficient of Cr^{2+} in ZnSe single crystal and polycrystalline materials was studied in [6]. This paper shows that a maximum chromium concentration of about 8×10^{19} cm^{-3} with a penetration depth of 0.5 mm can be achieved in polycrystalline ZnSe by thermal diffusion at 907°C for 1.75 days. In [7], the diffusion coefficient for iron and

chromium ions were estimated to be 7.95×10^{-10} cm^2/s and 5.45×10^{-10} cm^2/s, respectively, at 1000 °C. Thermal diffusion was performed in [7] at 1000 °C for 4 days and a Fe:ZnSe polycrystal with absorption coefficient of 18 cm^{-1} at 3.3 μm was produced. In our preparation [8], the sealed ampoules were placed in a furnace and annealed at 820–1120 °C for 5–14 days. Once removed from the furnace and cooled, doped crystals were extracted from the ampoules and polished.

Using the second method for generating Fe doped ZnSe crystals, ZnSe single crystals were doped with Fe^{2+} ions directly during growth. The free growth method developed for growing the II-VI compound single crystals was used [9]–[11]. According to this method, the growth is performed from separate sources containing polycrystalline ZnSe and FeSe. Calibrated orifices were installed in each source to control the output of ZnSe and FeSe vapors. The doping level is regulated by changing the growth temperature in the 1100°C–1250°C range and/or the ratio of source orifice areas. The crystals can be grown by either physical vapor transport with helium or chemical transport with hydrogen.

A series of single crystal Fe^{2+}:ZnSe samples were grown utilizing this method, with the Fe^{2+} concentration spanning the range from 0.9×10^{18} to 2.9×10^{18} cm^{-3}. The majority of these samples were used for luminescence measurements. The concentration of Fe^{2+} ions in the samples was estimated using a value of the absorption cross-section, $\sigma = 0.95 \times 10^{-18}$ cm^2 at 2.9364 μm [5]. For laser experiments a 10-mm-long single crystal Fe^{2+}:ZnSe active element of transverse dimensions 17×10 mm^2 with Fe^{2+} concentration of 0.9×10^{18} cm^{-3} was fabricated.

III. SPECTROSCOPIC METHODS

Unpolarized absorption spectra were measured at low temperatures with a close-cycle helium cryostat and a computer-controlled 0.75-m Acton Research SpectraPro-750 spectrometer. RT absorption measurements in the visible and mid-IR spectral regions were performed with a Shimadzu UV-VIS-NIR-3101PC and a Bruker Tensor-27 FTIR spectrophotometers.

The fluorescence spectra were measured using an (Acton Research ARC-300i) spectrometer and a liquid nitrogen cooled (EG&G Optoelectronics J15D14-M200-S01M-10-WE) HgCdTe detector-amplifier—(Stanford Research SR250) boxcar averager—(Acton Research NCL) Spectral Measurement System combination. The fluorescence spectra were corrected with respect to the spectral sensitivity of the recording system using a Newport-Oriel Infrared element (Model #6580) as a calibration source. Kinetic measurements were performed either with an InSb (EGG Judson J10D-M204-R04M-60) detector coupled to an amplifier (Perry PA050) (rise-time 300 ns), or a liquid nitrogen cooled Au doped Ge photo-resistor (rise-time 10 ns). Mid-IR emission of Fe^{2+} in ZnSe was studied under three regimes of excitation: optical (2.92 μm, second D$_2$ Raman Stokes of the Nd:YAG laser with 5-ns pulse duration or 2.94 μm of the Er:YAG laser with pulse duration of 60 ns) excitation of ^{5}T$_2$ excited state of Fe^{2+}; excitation via 5E level of Cr co-dopant (1.56 μm, first D$_2$ Raman Stokes of the Nd:YAG laser); and excitation via a photo-ionization transition

of Fe^{2+} (0.532 μm, second harmonic of the Nd:YAG laser). The major advantage of the described second D$_2$ Raman Stokes of Nd:YAG laser pump system is a short pulse duration (less than 5 ns).

We also studied lasing of Fe^{2+}:ZnSe crystals utilizing several different pump sources: Q-switched and free-running Er:YAG laser pumping at 2.94 μm, and pumping from the second D$_2$ Raman Stokes of Nd:YAG laser at 2.92 μm.

IV. IRON IONS IN II–VI MATERIALS

Energy structure of TM ions in II–VI compounds has been extensively studied since the 1960s (see, for example, [12] and [13]). The ^{5}D ground states of the Fe^{2+}($3d^6$) and Cr^{2+}($3d^4$) in the tetrahedral crystal field (T_d) of ZnSe crystal are split into the doublet ^{5}E and triplet ^{5}T$_2$, respectively. The ratio of the degeneracies of these multiplets is equal to $g(^5\mathrm{E})/g(^5\mathrm{T}_2) = 2/3$ (total degeneracy of the ^{5}D level is equal to $g = 25$). The energy difference between the ^{5}E state and the ^{5}T$_2$ state for Fe^{2+} ions in ZnSe crystal field corresponds to the mid-IR spectral region [12], [14]–[16]. The doublet ^{5}E is the ground state of the iron ions, and the triplet ^{5}T$_2$ is first excited state. For Fe^{2+} ions, the second order spin-orbit coupling results in splitting of the ^{5}E ground state on five equidistant levels (Γ_1-singlet, Γ_4-triplet, Γ_3-doublet, Γ_5-triplet, and Γ_2-singlet) with energy splitting $K = 6\lambda^2/\Delta = 10 - 20$ cm^{-1} ($\lambda \approx 100$ cm^{-1}, $\Delta \approx 3000$ cm^{-1}). First order spin-orbit interaction does not split the ^{5}E multiplet. Most of the experimental results for an iron doped crystal agreed with a K value equal to ~ 15 cm^{-1} ($\lambda = 92$ cm^{-1}, $\Delta = 3400$ cm^{-1} in Fe:ZnS [17]). Spin-orbit interaction predicts that, the triplet ^{5}T$_2$ level is split by first order spin-orbit interactions into three multiplets separated with an energy gap of 2λ and 3λ. Second order spin-orbit interaction further splits these levels as shown in Fig. 1. According to the selection rules, transitions between ground level Γ_1 and upper levels Γ_5 are allowed by electric-dipole interactions. So crystal field theory predicts that at low temperatures two narrow lines separated by $5\lambda \sim 500$ cm^{-1} should exist in the absorption spectrum. The first strong narrow absorption line is observed in all chalcogenides, but a second line has never been observed in II–VI materials. Therefore, most of the theoretical speculations consider the Jahn–Teller effect as the mechanism responsible for ^{5}T$_2$ splitting. According to [18] the zero-phononline transition (transition between the lowest sublevels of the ^{5}T$_2$ and ^{5}E states) corresponds to 2747 cm^{-1}, and second and third sublevels of ^{5}T$_2$ are separated from the lowest one by 24 and 50–80cm^{-1}.

A photo-induced electron spin resonance of chromium and iron ions in ZnSe was reported in [19]. The position of the $2+/3+$ donor level of iron in the forbidden gap of ZnSe crystal was measured as 1.1 eV above the valence band. The photoluminescence spin forbidden transitions from high energy levels ^{3}T$_1$ (^{3}T$_1 \rightarrow ^5$E for iron and ^{3}T$_1 \rightarrow ^5$T$_2$ for chromium ions in ZnSe crystal) were reported in [20]–[22]. The schematic energy diagrams of Fe and Cr ions in ZnSe are shown in Fig. 2.

V. SPECTROSCOPIC RESULTS

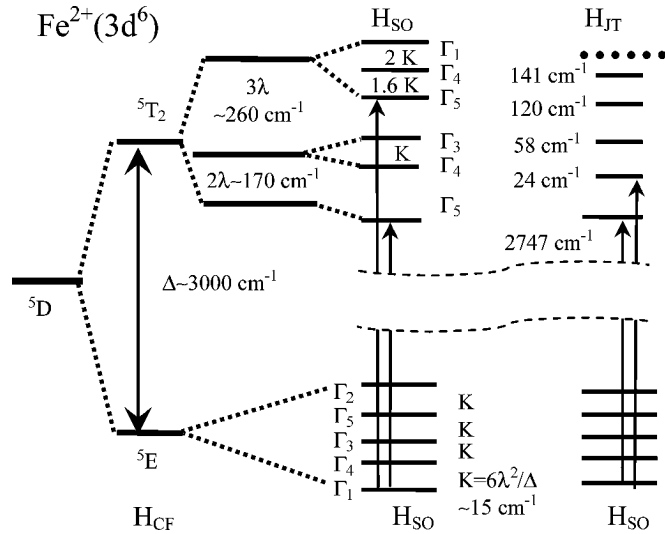The absorption spectra of iron- and chromium-doped ZnSe crystals are depicted in Fig. 3. The maximum absorption coef-

Fig. 1. Schematic energy diagram of Fe^{2+} ions in the tetrahedral crystal field according to crystal field theory (left part) and in presence of Jahn–Teller splitting (right part) [18].
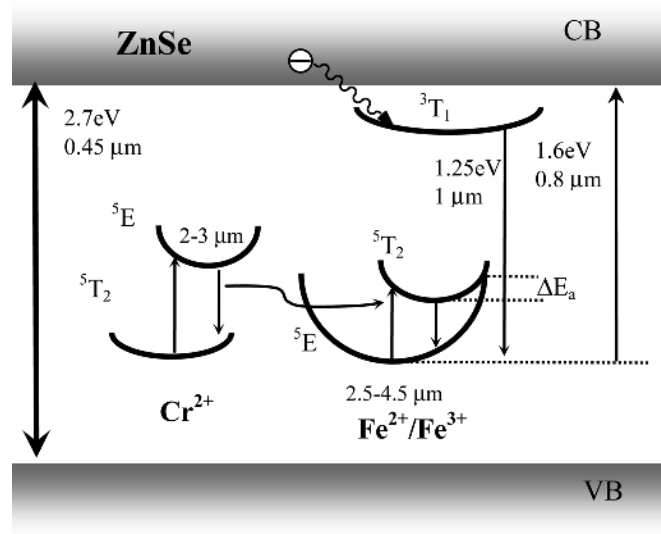

Fig. 2. Schematic energy diagrams of Fe and Cr ions in ZnSe.

Fig. 3. (i) RT and (ii) low temperature T = 20 K absorption spectra of Fe:Cr:ZnSe crystals.

ficient of the Fe^{2+} ions at RT was $k = 9$ cm^{-1} (at $\lambda = 3.2$ μm) in the crystals prepared by the thermal diffusion technique. The dopant concentration in the samples was estimated using the absorption cross section ($\sigma_{ab} = 0.65 \times 10^{-18}$ cm^2) at 2.698 μm reported in [5]. The calculated Fe concentration in these crystals was about $(6-9) \times 10^{18}$ cm^{-3} and varied in some crystals from 10^{18} to 10^{20} cm^{-3}. Curve (i) shows the absorption spectrum of Fe and Cr co-doped ZnSe crystals. As one can see, in addition to the absorption band of Fe these crystals feature a characteristic Cr^{2+} $^5T_2 \rightarrow ^5E$ band at 1.77 μm with a maximum absorption coefficient of 1.8 cm^{-1}. At T = 20 K the absorption spectrum of Fe^{2+} reveals the structure of the $^5E \rightarrow ^5T_2$ transition with a zero-phonon line near 2725 cm^{-1}.

The RT emission spectrum over the 3.5–5.2-μm spectral range is shown in Fig. 4, curve (i). As one can see, at RT Fe^{2+}:ZnSe features a broadband (3.5–5.2 μm) luminescence
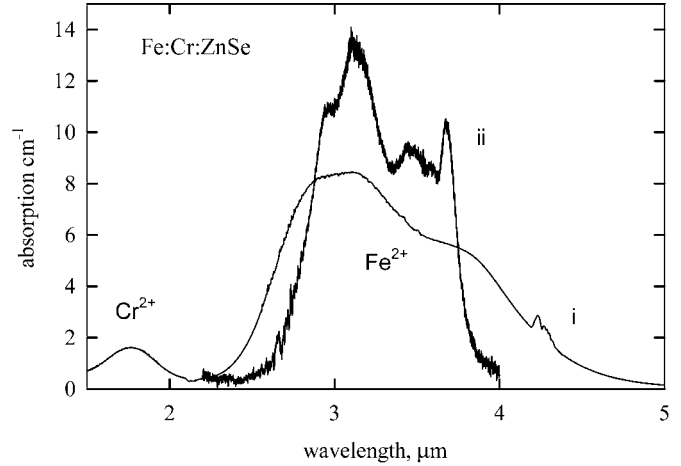
with a dip at 4.25 μm caused by absorption of atmospheric CO_2. We also studied mid-IR luminescence of Fe:Cr:ZnSe under excitation of the first Stokes (1.56 μm) of the D_2 Raman shifted radiation of a Nd:YAG laser (1.06 μm). This excitation overlaps with the absorption band of Cr^{2+} (see Fig. 3) and results in strong RT luminescence of Cr^{2+} over the 2.0–3.3-μm spectral range detected in Fe:Cr:ZnSe crystals (see Fig. 5). Interestingly, in addition to Cr^{2+}, the Fe^{2+} luminescence under 1.56 μm excitation was observed in Fe:Cr:ZnSe crystals. There was no Fe^{2+} luminescence detected in Fe:ZnSe crystals under 1.56 μm excitation. Absence of the Fe^{2+} luminescence in the Fe:ZnSe crystals under 1.56-μm pumping coupled with the existence of the Fe^{2+} luminescence in the Fe:Cr:ZnSe samples indicate that Fe^{2+} in ZnSe could be excited via a $Cr^{2+} \rightarrow Fe^{2+}$ energy transfer process (depicted in Fig. 2). Chromium and iron mid-IR luminescence in Fe:Cr:ZnSe crystals were also measured under 532 nm excitation at cryogenic temperatures ($\sim$107 K). We believe that this luminescence is induced by photo-ionization excitation of TM ions in ZnSe (see Fig. 4, curve ii). Recently the ionization mechanisms of chromium ions under 532-nm excitation leading to strong mid-IR emission, were discussed in [23] and [24]. The ionization of the iron ions from a 2+ to a 3+ state under the 532-nm radiation and then recombination with an electron from the conduction band will eventually leave the Fe ion in an 2+ $^5T_2$ excited state that will be the same as with direct intra-shell excitation [4]. A similar technique was used with Cr:ZnSe and at RT resulted in mid-IR lasing under green excitation [24].

The radiative lifetime was estimated from the absorption measurements as follows:

$$\tau_{\text{rad}} = \frac{g_u}{g_l} \frac{1}{8\pi n^2 c} \frac{1}{\int \lambda^{-4} \sigma_{ab}(\nu) d\lambda}. \tag{1}$$

The low temperature radiative lifetime was calculated to be 26 μs, this value is close to luminescence lifetime measured at 14 K ($\tau = 33$ μs) [5].

The luminescence lifetime in the 15–220 K temperature range was studied in [5], where it was demonstrated that from 12 to

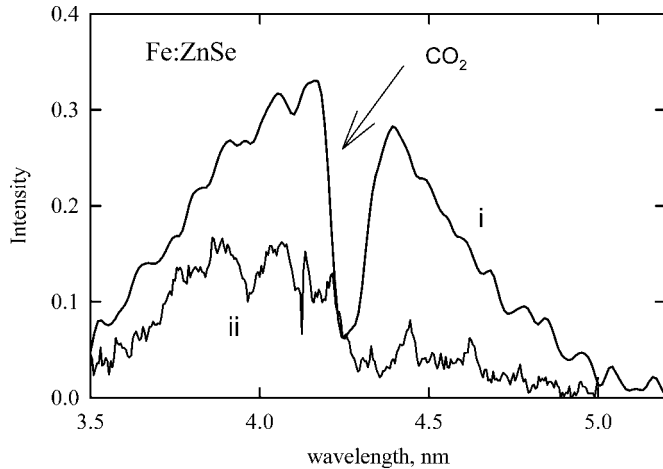Fig. 4. (i) RT emission of Fe:ZnSe crystal under 2.92 μm excitation. (ii) Low temperature T $=$ 107 K emission of Fe:ZnSe crystal under 0.53 μm excitation .
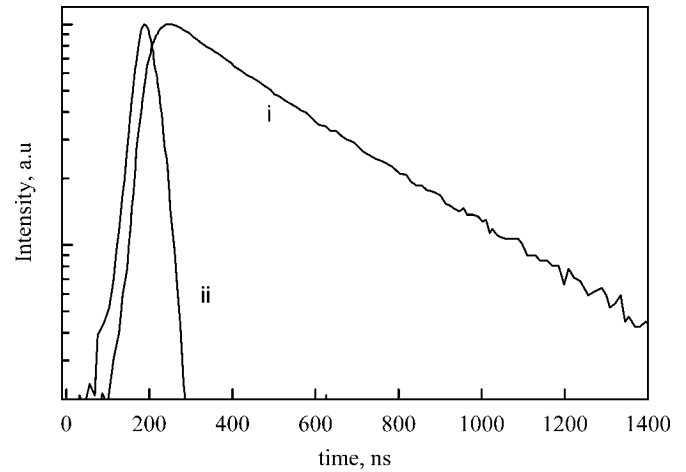

Fig. 5. Emission of Fe:Cr:ZnSe crystal under 1.56-μm excitation.

120 K, the lifetime increases from 33 to 105 μs and then decreases down to 5 μs at 220 K.

The experimental photoluminescence lifetime measurements of the $^5T_2$ level of Fe^{2+} in single crystal Fe^{2+}:ZnSe samples at RT (293 K) were performed in the current work using pulsed excitation with 2.94 μm radiation from a passively Q-switched Er:YAG laser (pulsewidth 60 ns FWHM) described in more details in Section VI-C. In this study, three Fe^{2+}:ZnSe samples with Fe^{2+} concentrations of 0.9×10^{18}, 1.2×10^{18} and 2.9×10^{18} cm^{-3} were examined. The excitation pulse energy was $\sim$7 mJ and the beam size at the sample was about 2 mm in diameter. We observed the Fe^{2+} luminescence in the direction perpendicular to the exciting beam. A long-pass filter (cut-off wavelength $\approx$ 3.3 μm) was used to cut the scattered exciting radiation. We did not observe a concentration dependence of the luminescence decay time for the samples with Fe^{2+} concentrations from 0.9×10^{18} cm^{-3} to 2.9×10^{18} cm^{-3}. The temporal profiles of the pump pulse and the luminescence signal are presented in the Fig. 6. The luminescence decay for all samples reveals an exponential dependence (1/e) with a lifetime of

Fig. 6. (i) Decay of the $^5T_2 \rightarrow {}^5E$ Fe^{2+} luminescence in single crystal Fe^{2+}:ZnSe sample at 293 K after pulsed excitation with 2.94-μm light on logarithmic scale. (ii) Excitation pulse profile is also presented.
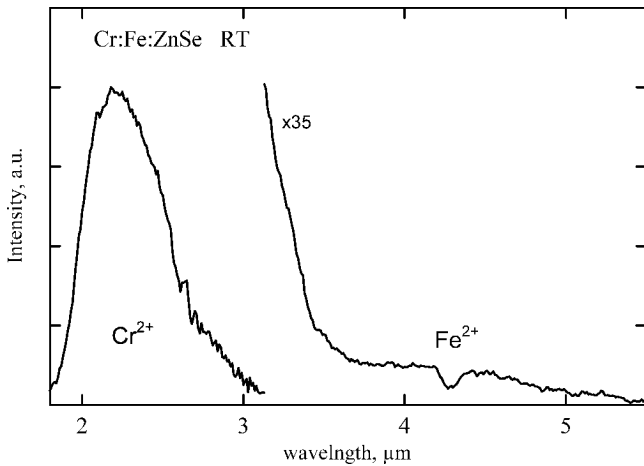
370 $\pm$ 25 ns at 293 K. The RT quantum yield of fluorescence was estimated to be 0.01 using the following relationship:

$$\eta = \frac{\tau_{\mathrm{em}}}{\tau_{\mathrm{rad}}} \approx 0.01. \qquad (2)$$

Two different processes could explain the unusual behavior of the temperature dependence of the Fe:ZnSe luminescence lifetime. In the first stage, (12–110 K) the luminescence lifetime increase is due to the thermal population of levels with smaller oscillator strength. The energy gaps between the lowest sublevels of $^5T_2$ manifold are only 24 and 50–80 cm^{-1} [18]. Therefore, these levels will be effectively populated at a temperature range of 20–100 K. As it was shown in [18] using the low temperature absorption measurements, the transitions from these levels feature oscillator strength smaller (longer radiative lifetime) than that found between the lowest levels. Therefore, the population of these levels should result in an increase of the luminescence lifetime. However, a large difference between the luminescence lifetimes at 12 and 120 K requires a large set of sublevels of $^5T_2$ manifold to be used for fine fitting. Unfortunately, a complete energy level diagram for Fe:ZnSe crystals is not known in it's entirety. In our work fine fitting was realized for five energy sublevels within 20–80 cm^{-1} energy gap. On the other hand, decreasing luminescence lifetime at a temperature higher than 120 K is mainly due to thermally activated nonradiative decay. A single configuration-coordinate model with linear coupling can be considered as a first approximation for the theoretical description of the nonradiative decay. In the case of strong coupling (Huang−Rhys factor $>$ 1) and high temperature (kT greater than effective phonon energy) the radiationless transition rate is described by the Mott equation. This process is typical for nonradiative relaxation in optical centers with a strong electron–phonon coupling. This approach leads to a fluorescence lifetime and radiationless rate given by the following equations (see, for example, [25]):

$$\tau^{-1} = \tau_{\mathrm{rad}}^{-1} + \tau_{\mathrm{NR}}^{-1} \qquad (3)$$

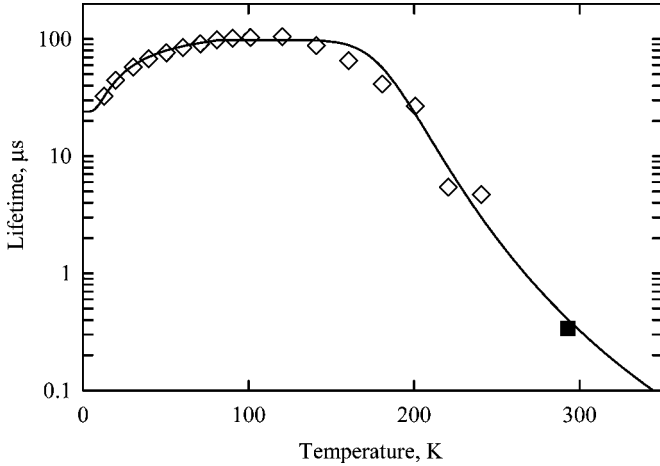$$\tau_{\mathrm{NR}}^{-1} = W_a \exp(-\Delta E_a / kT) \qquad (4)$$

Fig. 7. Luminescence lifetime versus temperature for Fe:ZnSe crystals. ($\Diamond$): experimental data according to [5]; ($\blacksquare$): current work; solid line: theoretical fit according to (4).
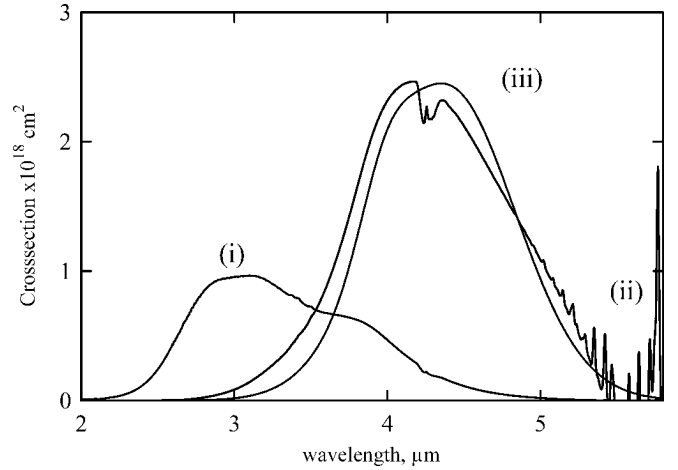

Fig. 8. (i) RT absorption and (ii)–(iii) emission cross-sections. Emission cross section calculated using (ii) reciprocity method and (iii) Fuchtbauer–Landenburg equation.

where ΔE_a-energy gap between the intersection of the adiabatic potential energy curves and the minimum of the excited state curve (see Fig. 2). The best fit (of the data in Fig. 7) was obtained with parameters $\Delta E_a = 1900$ cm^{-1} and $1/W_a = 5$ ns.

The luminescence lifetime of Fe:ZnSe at RT (370 ± 25 ns) is too short for effective CW pumping but still longer than the typical pulse duration of Q-switched lasers (1–100 ns). Hence, there is hope to obtain RT lasing of Fe:ZnSe in a gain-switched regime with pump pulses shorter than 300 ns.

The absorption cross section spectra was obtained from absorption measurements and using the known absorption cross section at 2.698 μm [5]. Emission cross sections at RT are determined using either the reciprocity method (RM) or the Fuchtbauer–Landenburg (FL) equation [6], [27]. Using a fundamental relationship between spontaneous and stimulated processes, the FL equation can be written as

$$\sigma_{\mathrm{em}}(\lambda) = \frac{\lambda^5 I(\lambda)}{8\pi c n^2 \tau_{\mathrm{rad}} \int I(\lambda)\lambda d\lambda} \tag{5}$$

where $\sigma_{\mathrm{em}}(\lambda)$ is emission cross section, λ is the emission wavelength, n is the refractive index, c is the speed of light, τ_{rad} is the radiative emission lifetime, and I is the energy per area per unit time. The emission cross section can be also obtained from the absorption spectra by the RM. According to this method the absorption and emission cross sections are related as

$$\sigma_{\mathrm{em}}(\nu) = \sigma_{ab}(\nu)\frac{Z_l}{Z_u}\exp\left([E_{zl} - h\nu]/kT\right) \tag{6}$$

where E_{zl} is the energy separation between the lowest crystal field components of the upper and lower states, Z_u, Z_l are partition functions that can be obtained using the energy gap (E_i, E_j) from the lowest crystal field level of each manifold and (g_i, g_j) energy-level degeneracies by the following equations:

$$Z_u = \sum_j g_j \exp(-E_j/kT) \tag{7}$$

$$Z_l = \sum_i g_i \exp(-E_i/kT). \tag{8}$$

The Z_l/Z_u factor depends on temperature but does not contain any spectral dependence. The emission cross section calculated according to RM with factor $Z_l/Z_u = 1.5$ is shown in the Fig. 8. The difference in the Z_l/Z_u factor from g_l/g_u ratio is caused by larger upper level splitting ($^5\mathrm{T}_2$) in comparison to the ground state level ($^5\mathrm{E}$) and thermal energy $E = kT$. As one can see from Fig. 8, both methods (FL and RM) demonstrate a wide amplification band at RT with maximum at ~ 4.3 μm and a bandwidth of ~ 1.1 μm. However, the spectral shapes of the curves are not identical. This difference can be explained with several reasons. First of all, RM is very sensitive to the accuracy of the absorption measurements for transitions with a large Stocks shift due to an exponential factor. From the other side, the FL method is valid when all the transitions have the same strength regardless of the components involved. But according to [5], the measured Fe^{2+} lifetime increases in the 12–120 K temperature range and this increase could be a result of very different radiative lifetimes of the components of the $^5\mathrm{E} \leftrightarrow {}^5\mathrm{T}_2$ transition. In addition, measured emission spectra can be of slightly suppressed intensity at the short wavelength tail of the spectrum due to a re-absorption process. In spite of the minor differences, both techniques demonstrate close values for the position of the maximum and linewidth of the amplification band of Fe^{2+} ions at RT.

So one can see from this analysis Fe:ZnSe has a large emission cross section $\sigma_{\mathrm{em}} = 2 - 3 \times 10^{-18}$ cm^2 and a 370 ns lifetime at RT, hence, lasing of the Fe:ZnSe crystal at RT could be feasible in a gain-switch regime. Indeed, RT lasing is shown in subsequent Sections VI-B and VI-D.

VI. LASER EXPERIMENTS

Lasing of Fe:ZnSe has been achieved in several different regimes of operation. First low temperature Fe:ZnSe lasing has been achieved using two different cooling methods in conjunction with pumping from a free-running 2.94-μm flashlamp pumped Er:YAG laser. The Fe:ZnSe active elements in these laser systems were either cooled utilizing a cooled copper heat sink (85–255 K) or dual stage thermoelectric coolers (220 K).

The second regime of operation is for a microchip active element configuration. This microchip system obtained lasing utilizing two schemes: A simple cavity defined by purely Fresnel reflection from crystal facets or using a flat high reflecting gold mirror attached to the crystal and Fresnel reflection as the output coupler. In both of these schemes a D_2 second Stokes shifted Q-switched Nd:YAG laser was the pump source.

The final regime of operation was tunable RT operation using the novel Q-switched Er:YAG laser as a pump source. This pump source is a passively Q-switched Er:YAG laser. The Q-switching element is a sample of Fe:ZnSe.

A. Low-Temperature Lasing

The lasing characteristics of the Fe^{2+}:ZnSe laser at low temperatures of the active element were studied in the 85–255 K temperature range. The resonator of the Fe^{2+}:ZnSe laser was formed by a spherical mirror (with radius of curvature 50 cm) with reflectivity ∼100% and a plane output coupler with reflectivity 70% at 4 μm. The cavity length was 32 cm. The single crystal active element was mounted at the Brewster angle on a copper heat sink inside a cryostat with CaF_2 Brewster windows. A more detailed description of this experimental setup can be found in [28] and [29].

The Fe^{2+}:ZnSe laser was pumped by a flashlamp-pumped free-running Er:YAG laser lasing at 2.94 μm. The Er:YAG laser operated at 750 mJ output energy and a 200-μs pulse duration. The linearly polarized pump radiation was incident on the crystal at a small angle ($\sim 2°$) to the resonator axis. The pump beam was focused so that its cross section on the front surface of the crystal was an ellipse with axes 3 and 3.5 mm. The pump energy was varied utilizing a set of calibrated optical filters. The pump pulses had an irregular spike structure, which is typical for multimode pulsed solid-state lasers. The Fe:ZnSe laser output pulse also consisted of spikes, which at the sufficiently high pump energy followed the pump spikes with a 0.2–0.5 μs delay depending on the excess pump energy over the threshold pump energy.

We studied the laser characteristics of the Fe:ZnSe crystal in the active element temperature range of T = 85–255 K. The temperature of the Fe:ZnSe element in the laser was fixed using a liquid nitrogen cryostat or two-stage thermoelectric cooler and controlled with 3 K accuracy.

Fig. 9 shows the dependences of the output energy of the laser obtained at different temperatures. The slope efficiency and threshold absorbed pump energy were determined from a linear fit to the experimental points using the method of least squares. The maximum slope efficiency of the laser amounting to 43% (the quantum efficiency was 59%) was obtained at T = 85 K. For pump energy of 733 mJ, we obtained the maximum output energy of 187 mJ (the absorbed pump energy was 470 mJ).

One can see from Fig. 9 that the slope efficiency decreases with temperature over the entire temperature range of 85–186 K, however not dramatically. This contradicts the results obtained in [5], where lasing was observed only for $T < 180$ K and the maximum efficiency was obtained at T = 150 K. One can see from Fig. 9 that the threshold pump energy of the laser is 15 mJ at T = 85 K.
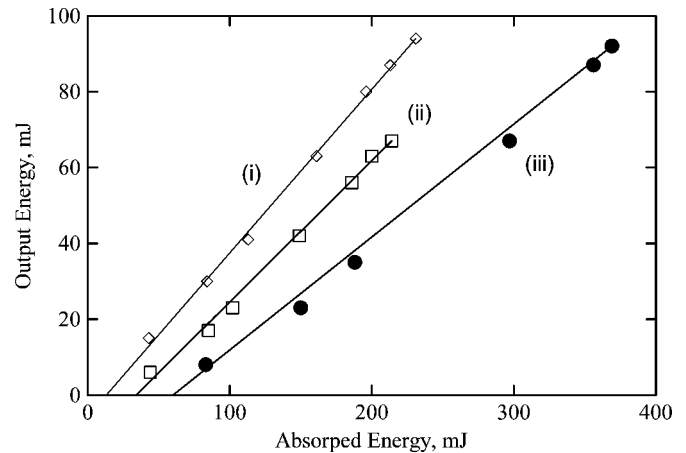

Fig. 9. Input–output characteristics of the Fe^{2+}:ZnSe laser at different temperatures of the active elements (i: 85 K; ii: 186 K; iii: 220 K, obtained with thermoelectric cooler).

We observed with increasing temperature, a red shift of the oscillation wavelength. The shift is caused by the red temperature shift of the long-wavelength edge of the absorption spectrum of the Fe:ZnSe crystal [5]. The laser wavelength increased from 4.1 μm at 85 K to 4.17 μm at 255 K, which differs from the spectral shift from 3.98 to 4.54 μm observed in [5] for the temperature change from 15 till 180 K. This can be explained by the spectral dependence of the reflectivity of our output mirror, which decreased from 70% at 4.1 μm down to 59% at 4.5 μm.

The output spectrum of the Fe^{2+}:ZnSe laser at $T = 85$ K was continuously tuned between 3.77 and 4.40 μm in a dispersive resonator with a 70° CaF_2 prism [28].

Our preliminary study with cryostat cooling demonstrated that the slope efficiency of the laser exceeded 30% at crystal temperatures below 220 K. Because the temperature 220 K can be easily achieved using a two-stage thermoelectric cooler, we studied the Fe^{2+}:ZnSe laser with a thermoelectric cooler.

The dependence of the output energy of the laser obtained by cooling the crystal with the two-stage thermal module is shown in Fig. 9 curve (iii). For an absorbed pump power 370 mJ, the maximum output energy was 91 mJ (the incident pump energy was 718 mJ). The slope efficiency of the laser with respect to the absorbed energy was 30%. To increase the output energy, we mounted two additional aluminum mirrors, which returned the unused transmitted pump radiation back to the laser crystal so that it intersected the optical axis of the resonator at an angle of 4° at the crystal center. The more efficient use of the pump radiation resulted in an increase in the output energy of this laser system design utilizing thermoelectric cooling to 142 mJ for incident pump energy of 746 mJ. The slope efficiency of this thermoelectrically cooled laser with respect to the incident pump energy was 21%. Therefore, with further optimization of the laser resonator (selection of the optimal reflectivity of the output mirror, elimination of intracavity losses at chamber windows, better matching of the pump and lasing modes) will provide even higher output energy and better slope efficiency for the Fe^{2+}:ZnSe laser.

B. RT Microchip Lasing

Efficient continuous wave and pulse microchip oscillation in Cr:ZnSe and Cr:ZnS crystal were previously demonstrated in [30], [31]. To realize this regime of oscillation highly doped samples are required. Therefore, in these experiments we used polycrystalline iron doped samples prepared by the thermal diffusion technique. The thickness of crystal plate was $h = 2$ mm. The Fe^{2+} ion concentration was $\sim 10^{19}$ cm^{-3}. As a pump source for laser experiments we used the second Stokes output of the Nd^{3+}:YAG laser in a D_2 cell. The pump radiation at 2.92 μm with a beam diameter of 1.5 mm excited the Fe^{2+}:ZnSe crystal at the Brewster angle of incidence. The crystal temperature remained 300 K during all laser measurements. One of the advantages of the described pump system is short pulse duration (less than 5 ns). This is important for RT studies of Fe:ZnSe.

In our experiments stimulated emission was observed at RT without any coatings on crystal surfaces when oscillation feedback was due only to Fresnel reflection from the crystal surfaces ($R \sim 17\%$). As one can see from the Fe:ZnSe emission spectra depicted in Fig. 10, an increase of pump energy density above the threshold level of 170 mJ/cm^2 results in Fe stimulated emission at 4.4 μm accompanied by a sharp line narrowing from 1.1 down to 0.2 μm. In spite of the poor feedback due to Fresnel reflection, the required gain may be achieved. Indeed at $\sigma_{em} = 2 - 3 \times 10^{-18}$ cm^2 and a Fe^{2+} concentration of $(6 - 9) \times 10^{18}$ cm^{-3} the gain may be as high as 12–27 cm^{-1} while the cavity loss is $h^{-1} \cdot \ln(1/R) = 10$ cm^{-1}. In subsequent experiments we set the laser crystal on the surface of gold mirror. The cavity in this case was formed by a gold mirror and Fresnel reflection from the output facet of the Fe^{2+}:ZnSe crystal. Fig. 11 shows the Fe^{2+}:ZnSe laser output as a function of pump energy density. A linear approximation of the experimental data estimates the threshold value of the pump energy density to be 50 mJ/cm^2. In this experiment the laser spectral line was centered at 4.35 μm with a linewidth of 0.15 μm. The maximum output energy was estimated to be ~ 1 μJ. Obtaining high output energy at RT was not the goal of this initial experiment. The lasing efficiency was small due to the following reasons. First, the low optical density of the crystal resulted in a poor efficiency of pump absorption. Second, the use of an output coupler formed by Fresnel reflection from the crystal facet was not optimal. Indeed at threshold, gain on the order of 10 cm^{-1} and the lateral size of excited area being larger than 1 mm, the amplified spontaneous emission is too high to achieve effective lasing along the plate normal. Later experiments will optimize crystal geometry, doping densities, and the output coupler reflectivity to increase the output energy.

C. Passive Q-Switching of the Er:YAG Laser at 2.94-μm Wavelength for Pumping a Mid-IR Fe:ZnSe RT Laser System

Passive Q-switching of mid-IR lasers has attracted much attention in recent years. Q-switching of a 1.54-μm Er:glass laser was demonstrated using Cr^{2+}:ZnSe and Co^{2+}:ZnSe crystals [32]. A Cr^{2+} : $Cd_{0.55}Mn_{0.45}$Te crystal was used for the Q-switching of a 2.09-μm Ho:Tm:Cr:YAG laser [33]. However, effective passive solid-state Q-switches for the 3-μm spectral range are not currently available [34]. A 2.94-μm
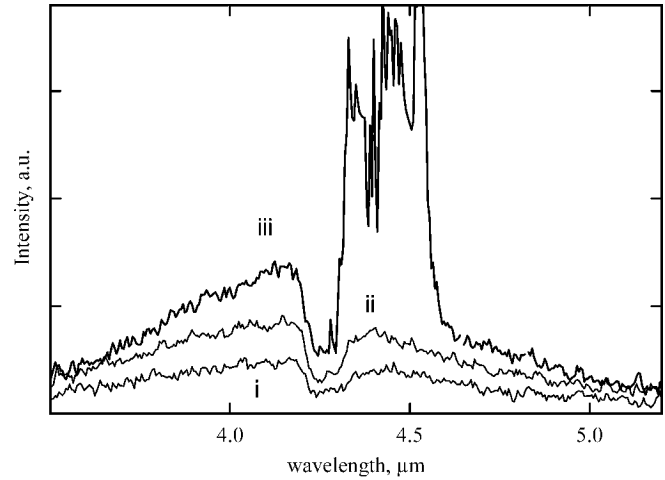

Fig. 10. Emission spectra of Fe:ZnSe crystal versus pump density at RT under pump energy density (i) 40 mJ/cm^2; (ii) 110 mJ/cm^2; (iii) 170 mJ/cm^2.
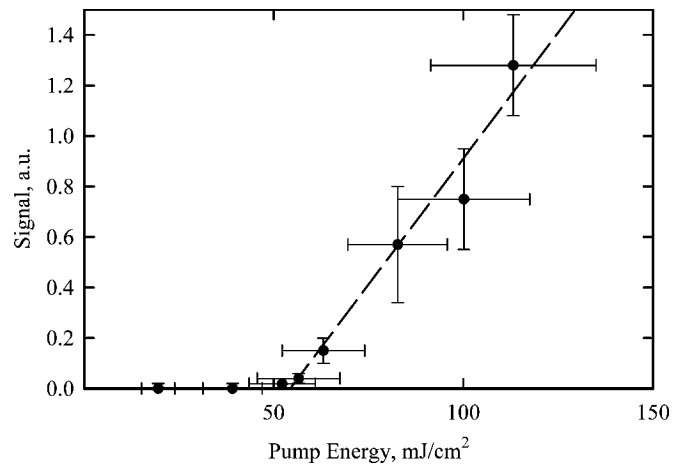

Fig. 11. Output of RT microchip oscillation of Fe:ZnSe crystal at RT.

Er:YAG laser was Q-switched using a rotating mirror as reported in [35], electro-optic Q-switch in [36], and a passive water and ethanol Q-switch in [37]. In this paper (see also [38]), passive Q-switching of an Er:YAG laser is demonstrated using a Fe^{2+}:ZnSe single crystal as the saturable absorber.

As one can see from Fig. 8 the absorption cross section of Fe^{2+} ion in the ZnSe crystal at $\lambda = 2.94$ μm is 9.5×10^{-19} cm^2, which is approximately 35 times higher than the cross section for the laser transition in the Er^{3+} ion in yttrium-aluminum garnet.

A flashlamp-pumped Er:YAG laser was used for studying the Fe^{2+}:ZnSe as a passive Q-switch. The flashlamp pump-pulse had a pulse duration of 100 μs [full-width at half-maximum (FWHM)]. The laser cavity (23 cm long) had a 1-m radius high reflector and a flat 82% reflectivity output coupler. The 4-mm-diameter × 105-mm-long Er:YAG laser rod (Er^{3+} concentration 50%) was pumped by 90 mm arc-length xenon flashlamp. The laser emitted the fundamental transverse mode, which was achieved by placing a ⌀2.4-mm aperture between the high reflector and laser rod. The passive Q-switch in the form of 1.5-mm-thick plane-parallel plate Fe:ZnSe sample with initial transmission 85% was placed at the Brewster angle between the
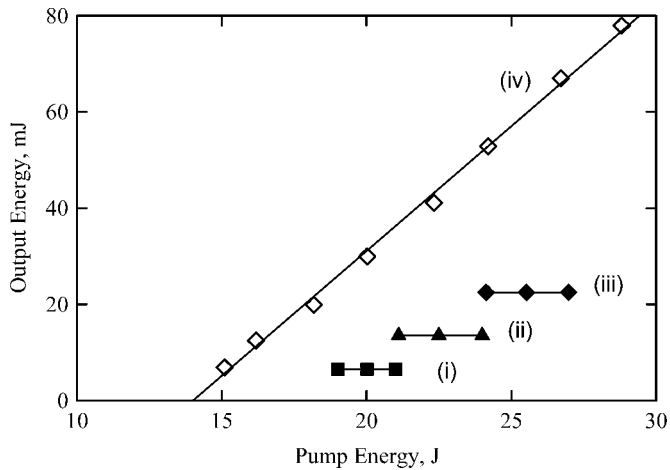
Fig. 12. (iv) Input–output characteristics of the free-running Er:YAG laser and passively (Fe^{2+}:ZnSe) Q-switched Er:YAG laser. (i): 1 pulse; (ii): 2 pulses; and (iii): 3 pulses.

Fig. 13. Input–output characteristics of the gain switched Fe^{2+}:ZnSe laser at RT.

Fig. 14. Tuning curve of RT Fe^{2+}:ZnSe laser with intracavity prism obtained at absorbed pump energy of 4.5 mJ.

high reflector and the aperture. The input-output characteristics of Er:YAG laser operating in Q-switched and in free-running regimes are presented in Fig. 12. The threshold pump energy for the Q-switched Er:YAG laser was 19 J. Under the pump energy $E_p =19$–21 J the laser produced single 6.5-mJ, 50-ns (FWHM) giant pulses. Under $E_p =21$–24 J the laser produced two similar giant pulses with a total energy 13–14 mJ, which followed each other after 30 μs. Under higher pump energies the laser produced three giant pulses separated by intervals of ~ 25 μs with the total output energy of 22–23 mJ. The output laser energy in free-running mode (without the passive Q-switch) was 30 mJ for a pump energy of $E_p = 20$ J. It means that the conversion efficiency (the ratio of energy of single giant pulse to the respective free-running energy) exceeded 20%.

The broad absorption band of Fe^{2+}:ZnSe crystal (2.5–4.2 μm) makes it a promising material for passive Q-switching of mid-IR laser cavities.

D. Tunable RT Oscillation

Efficient RT Fe^{2+}:ZnSe laser oscillation was achieved using a 2.94-μm passively Q-switched Er:YAG laser as a pump source (see Section VI-C). With a more transparent output coupler (50%) this laser was able to produce 10-mJ output pulses of 60-ns pulse duration (FWHM).

The nonselective 17-cm-long Fe^{2+}:ZnSe laser cavity had a 0.5-m radius high reflector ($\sim$100%) and a flat, 90.5% reflectivity ($\lambda = 4.4$ μm) output coupler. The Fe^{2+}:ZnSe single crystal was placed at the Brewster angle close to the output coupler. The pump radiation was incident on the crystal at an angle $\sim 2°$ to the resonator axis and the beam size in front of the crystal was about 1.4 mm in diameter. The pump energy was varied by using a set of calibrated optical filters.

Fig. 13 shows the RT Fe^{2+}:ZnSe laser output as a function of absorbed pump energy. Maximum output energy and slope efficiency were 0.37 mJ and 13%, respectively. The threshold absorbed pump energy was 1.4 mJ. The 0.1 μm width-output spectrum was centered at a wavelength of 4.4 μm.

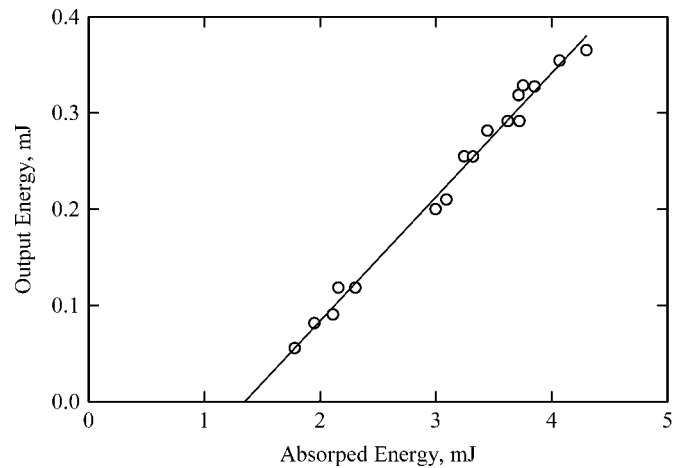Under the high pump energy, the leading edge of the laser pulse was delayed with respect to the maximum of pump pulse by 20–30 ns, and the laser pulse duration did not exceed 40 ns. The laser pulse duration and delay increased with the decrease of pump energy and were 60 and 200 ns, respectively, just above the threshold.
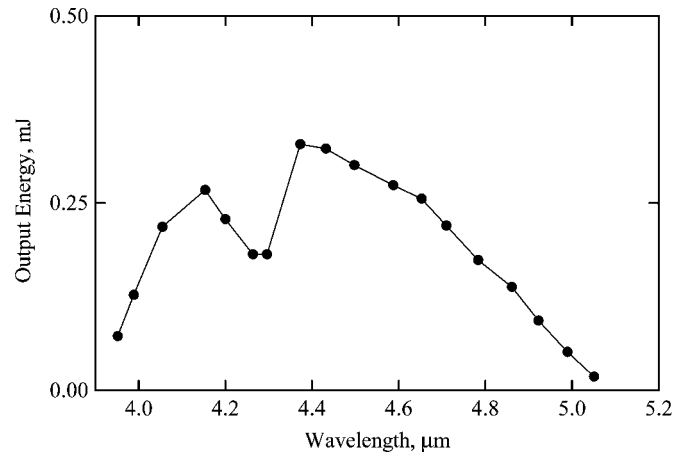
The output spectrum of the RT Fe^{2+}:ZnSe laser was continuously tuned using an intracaviy dispersive element (70° CaF$_2$ prism) placed in front of the high reflector. The tuning curve (Fig. 14) spans the spectral range 3.95–5.05 μm and on the short-wavelength edge is probably limited by the output coupler reflectivity, which sharply decreased for wavelengths shorter then 4.2 μm. The output spectrum width was 0.05 μm in this dispersive resonator.

As it was mentioned above short pump pulses are required for RT operation of a Fe^{2+}:ZnSe laser because of high rate of thermally induced nonradiative decay of the upper laser level.

VII. CONCLUSION

In conclusion, the absorption and luminescence properties of Fe:ZnSe and Fe:Cr:ZnSe crystals in the mid-IR spectral range were studied at room and low temperatures. The RT emission cross section of ^{5}E $\leftrightarrow$ ^{5}T$_2$ transition of iron ions was estimated from spectroscopic measurements. Mid-IR emission of Fe^{2+} in

ZnSe was studied under three different regimes of excitation: ordinary optical (2.92 μm) excitation of $^5T_2$ first excited state of Fe^{2+}; excitation via ^5E level of Cr co-dopant (1.56 μm); and excitation via photo-ionization transition of Fe^{2+} (0.532μm). For the energy transfer from Cr^{2+} (^5E level) to Fe^{2+} ($^5T_2$ level) under 1.56-μm wavelength excitation was observed and resulted in simultaneous RT emission of Fe:Cr:ZnSe crystal over ultra-broadband spectral range of 2–5 μm. We also report the first observation of mid-IR emission at 3.5–5 μm induced by $2 + -3 + -2+$ ionization transitions of iron ions in Fe^{2+}:ZnSe. This result is essential for optical pumping of Fe^{2+}:ZnSe by easily available and efficient visible lasers, and, most importantly, opens a pathway for Fe^{2+}:ZnSe broadband mid-IR lasing under direct injection of free electrons and holes.

We have studied the free-running Fe^{2+}:ZnSe laser in the 85–255 K temperature range. The slope efficiency of the laser with respect to absorbed energy decreased with temperature from 43% (at 85 K) to 9% (at 255 K), and its emission spectrum shifted from 4.0 to 4.17 μm. In a dispersive resonator the output spectrum of the Fe^{2+}:ZnSe laser at 85 K was continuously tuned between 3.77 and 4.40 μm. We have observed the oscillation of the Fe^{2+}:ZnSe laser by cooling the laser crystal with a thermoelectric element. In this case, the slope efficiency of the laser with respect to absorbed energy was 30% and with respect to the incident pump energy can exceed 20%.

The microchip lasing of Fe:ZnSe crystal at 4.4 μm was demonstrated at RT in a nonselective cavity under 2.92 μm excitation with a pulse duration of 5 ns. Efficient external cavity RT Fe^{2+}:ZnSe laser oscillation was demonstrated with the quantum efficiency of 20%. The output spectrum of the RT Fe^{2+}:ZnSe laser was continuously tuned in the spectral range 3.95–5.05 μm. Thus, the total range of the Fe^{2+}:ZnSe laser tuning spans from 3.77 to 5.05 μm.

REFERENCES

[1] L. D. DeLoach, R. H. Page, G. D. Wilke, S. A. Payne, and W. F. Krupke, "Transition metal-doped zinc chalcogenides: Spectroscopy and laser demonstration of a new class of gain media," *IEEE J. Quantum Electron.*, vol. 32, no. 6, pp. 885–895, Jun. 1996.

[2] R. H. Page, K. I. Schaffers, L. D. DeLoach, G. D. Wilke, F. D. Patel, J. B. Tassano, S. A. Payne, W. F. Krupke, K. T. Chen, and A. Burger, "Cr^{2+}-Doped zinc chalcogenides as efficient, widely tunable mid-infrared lasers," *IEEE J. Quantum Electron.*, vol. 33, no. 4, pp. 609–617, Apr. 1997.

[3] I. T. Sorokina, "Cr^{2+}-doped II-VI materials for lasers and nonlinear optics," *Opt. Mater.*, vol. 26, pp. 395–412, 2004.

[4] P. B. Klein, J. E. Furneaux, and R. L. Henry, "Laser oscillation at 3.53 um from Fe^{2+} in n-InP:Fe," *Appl. Phys. Lett.*, vol. 42, pp. 638–640, 1983.

[5] J. J. Adams, C. Bibeau, R. H. Page, D. M. Krol, L. H. Furu, and S. A. Payne, "4.0–4.5 μm lasing of Fe:ZnSe below 180 K, a new mid-infrared laser material," *Opt. Lett.*, vol. 24, pp. 1720–1722, 1999.

[6] J. O. Ndap, K. Chattopadhyay, O. O. Adetunji, D. E. Zelmon, and A. Burger, "Thermal diffusion of Cr^{2+} in bulk ZnSe," *J. Cryst. Growth*, vol. 240, pp. 176–184, 2002.

[7] U. Demirbas, A. Sennaroglu, and M. Somer, "Synthesis and characterization of diffusion-doped Cr^{2+}:ZnSe and Fe^{2+}:ZnSe," *Opt. Mater.*, vol. 28, pp. 231–240, 2006.

[8] J. Kernal, V. V. Fedorov, A. Gallian, S. B. Mirov, and V. V. Badikov, "3.9–4.8 μm Gain-switched lasing of Fe:ZnSe at room temperature," *Opt. Exp.*, vol. 13, no. 26, pp. 10608–10615, 2005.

[9] Y. V. Korostelin, V. I. Kozlovsky, A. S. Nasibov, and P. V. Shapkin, "Vapour growth of II-VI solid solution single crystals," *J. Cryst. Growth*, vol. 159, pp. 181–185, 1996.

[10] Y. V. Korostelin and V. I. Kozlovsky, "Vapour growth of II-VI solid solution single crystals by contact-free technique," *J. Alloys Compounds*, vol. 371, pp. 25–30, 2004.

[11] V. A. Akimov, M. P. Frolov, Y. V. Korostelin, V. I. Kozlovsky, A. I. Landman, Y. P. Podmar'kov, and A. A. Voronov, "Vapour growth of II-VI single crystals doped by transition metals for mid-infrared lasers," *Phys. Stat. Sol. (C)*, vol. 3, no. 4, pp. 1213–1216, 2006.

[12] W. Low and M. Weger, "Parametric resonance and optical spectra of divalent iron in cubic fields. I. Theory," *Phys. Rev.*, vol. 123, pp. 1188–1203, 1961.

[13] R. Pappalardo and R. E. Dietz, "Absorption spectra of transition ions in CdS crystals," *Phys. Rev.*, vol. 118, pp. 1119–1130, 1960.

[14] G. Grebe and H.-J. Schulz, "Luminescence of Cr^{2+} centers and related optical interactions involving crystal field levels of chromium ions in zinc sulfide," *Z. Naturforsch*, vol. 29a, pp. 1803–1819, 1974.

[15] J. T. Vallin, G. A. Slack, and S. Roberts, "Infrared absorption in some II-VI compounds doped with Cr," *Phys. Rev. B*, vol. 2, no. 11, pp. 4313–4333, 1970.

[16] G. A. Slack, F. S. Ham, and R. M. Chrenko, "Optical absorption of tetrahedral Fe^{2+} (3d6) in Cubic ZnS, CdTe, and $MgAl_2O_4$," *Phys. Rev.*, vol. 152, pp. 376–402, 1966.

[17] G. Grebe, H. Zimmermamm, and H.-J. Schulz, "Jahn-Teller interaction at Cr^{2+} (d4) centers in tetrahedrally coordinated II-VI lattices studied by optical spectroscopy," *Z. Phys. B*, vol. 91, pp. 429–436, 1993.

[18] O. Mualin, E. E. Vogel, M. A. de Orúe, L. Martinelli, G. Bevilacqua, and H.-J. Schulz, "Two-mode Jahn–Teller effect in the absorption spectra of Fe^{2+} in II-VI and III-V semiconductors," *Phys. Rev. B*, vol. 65, p. 035211-9, 2002.

[19] M. Surma, M. Godlewski, and T. P. Surkova, "Iron and chromium impurities as centers of nonradiative recombination," *Phys. Rev. B*, vol. 12, pp. 8319–8324, 1994.

[20] M. T. P. Surkova, P. Kaczor, A. J. Zakrzewski, K. Swiatek, V. Y. Ivanov, M. Godlewski, A. Polimeni, L. Eaves, and W. Giriat, "Optical properties of ZnSe, ZnCdSe, and ZnSSe alloys doped with iron," *J. Cryst. Growth*, vol. 214/215, pp. 576–580, 2000.

[21] M. U. Lehr, B. Litzenburger, J. Kreissl, U. W. Pohl, H. R. Selber, H.-J. Schulz, A. Klimakow, and L. Worschech, "Identification of near-infrared luminescence in ZnSe," *J. Phys.: Condens. Matter*, vol. 9, pp. 753–763, 1997.

[22] V. Y. Ivanov, A. A. Shagov, A. Szczerbakow, and M. Godlewskic, "Excitation mechanism of blue antistokes and 2.4 μm infrared emission in ZnSe:Cr," *Physica B*, vol. 308–310, pp. 942–944, 2001.

[23] V. Y. Ivanov, M. Godlewski, A. Szczerbakow, A. Omel'chuk, A. Davydov, N. Zhavoronkov, and G. Raciukaitis, "Optically pumped mid—infrared stimulated emission of ZnSe:Cr crystals," *Acta Physica Polonica A*, vol. 105, no. 6, pp. 553–558, 2004.

[24] A. Gallian, V. V. Fedorov, J. Kernal, S. B. Mirov, and V. V. Badikov, "Laser oscillation at 2.4 μm from Cr^{2+} in ZnSe optically pumped over Cr ionization transitions," Advanced Solid-State Photonics 2005 Technical Digest on CD-ROM The Optical Society of America. Washington, DC, 2005, MB12.

[25] B. Henderson and R. H. Bartran, *Crystal-Field Engineering of Solid-State Laser Materials*. Cambridge, U.K.: Cambridge Univ. Press, 2000.

[26] D. E. McCumber, "Einstein relations connecting broadband emission and absorption spectra," *Phys. Rev.*, vol. 136, no. 4A, pp. 954–957, 1964.

[27] S. A. Payne, L. L. Chase, L. K. Smith, W. L. Kway, and W. Krupke, "Infrared cross section measurements for crystals doped with Er^{3+}, Tm^{3+}, and Ho^{3+}," *IEEE J. Quantum Electron.*, vol. 28, no. 11, pp. 2619–2630, Nov. 1992.

[28] V. A. Akimov, A. A. Voronov, V. I. Kozlovskii, Y. V. Korostelin, A. I. Landman, Y. P. Podmar'kov, and M. P. Frolov, "Fe:ZnSe laser continuously tunable in the spectral range from 3.77 to 4.40 μm," *Quantum Electron.*, vol. 34, no. 10, pp. 912–914, 2004.

[29] A. A. Voronov, V. I. Kozlovskii, Y. V. Korostelin, A. I. Landman, Y. P. Podmar'kov, and M. P. Frolov, "Laser parameters of a Fe:ZnSe laser crystal in the 85–255 K temperature range," *Quantum Electron.*, vol. 35, no. 9, pp. 809–812, 2005.

[30] S. B. Mirov, V. V. Fedorov, K. Graham, I. Moskalev, V. Badikov, and V. Panyutin, "Er-fiber laser pumped continuous-wave microchip Cr^{2+}:ZnS and Cr^{2+}:ZnSe lasers," *Opt. Lett.*, vol. 27, pp. 909–911, 2002.

[31] S. B. Mirov, V. V. Fedorov, K. Graham, I. S. Moskalev, I. T. Sorokina, E. Sorokin, V. Gapontsev, D. Gapontsev, V. V. Badikov, and V. Panyutin, "Diode and fiber pumped Cr^{2+}:ZnS mid-IR external cavity and microchip lasers," *Proc. IEE Optoelectron.*, vol. 150, no. 4, pp. 340–345, 2003.

[32] A. V. Podlipensky, V. G. Shcherbitsky, N. V. Kuleshov, V. P. Mikhailov, V. I. Levchenko, and V. N. Yakimovich, " Cr^{2+}:ZnSe and Co^{2+}:ZnSe saturable absorber Q switches for 1.54- μm Er:glass lasers," *Opt. Lett.*, vol. 24, no. 14, pp. 960–963, 1999.

[33] A. V. Podlipensky, V. G. Shcherbitsky, M. I. Demchuk, N. V. Kuleshov, V. I. Levchenko, V. N. Yakimovich, S. Girard, and R. Moncorge, " Cr^{2+} : $Cd_{0.55}Mn_{0.45}Te$ crystal as a new saturable absorber for 2 μm lasers," *Opt. Commun.*, vol. 192, pp. 65–68, 2001.

[34] K. L. Vodopyanov, A. V. Lukashev, and C. C. Phillips, "Nano- and picosecond 3 μm Er:YSGG lasers using InAs as passive Q-switchers and mode-lockers," *Opt. Commun.*, vol. 95, pp. 87–91, 1993.

[35] K. S. Bagdasarov, V. P. Danilov, V. I. Zhekov, T. M. Murina, A. A. Manenkov, M. I. Timoshechkin, and A. M. Prokhorov, "Pulsed laser utilizing $Y_3Al_5O_{12}$: Er^{3+} crystals with a high activator concentration under repetitive conditions," *Sov. J. Quantum Electron.*, vol. 8, no. 1, pp. 83–85, 1978.

[36] K. S. Bagdasarov, V. I. Zhekov, L. A. Kulevskii, V. A. Lobachyov, T. M. Murina, and A. M. Prokhorov, "Giant pulses of laser radiation from yttrium-erbium-aluminum garnet crystals," *Sov. J. Quantum Electron.*, vol. 10, no. 9, pp. 1127–1131, 1978.

[37] K. L. Vodopyanov, L. A. Kulevsky, P. P. Pashinin, and A. M. Prokhorov, "Water and ethanol as bleachable absorbers of radiation in an yttrium-erbium-aluminum garnet laser ($\lambda = 2.94$ μm)," *Sov. Phys.-JETP*, vol. 82, no. 6, pp. 1820–1824, 1982.

[38] A. A. Voronov, V. I. Kozlovskii, Y. V. Korostelin, A. I. Landman, Y. P. Podmar'kov, V. G. Polushkin, and M. P. Frolov, "Passive Fe^{2+}:ZnSe single-crystal Q-switch for 3- μm lasers," *Quantum Electron.*, vol. 36, no. 1, pp. 1–2, 2006.

Vladimir V. Fedorov was born in Moscow, Russia, in 1961. He received the M.S. degree in physical and quantum electronics from the Moscow Institute of Physics and Technology, in 1985 and the Ph.D. degree in physics from the General Physics Institute of the Russian Academy of Sciences, Moscow, for his work on color center lasers and laser spectroscopy of the rare earth aggregate centers in the fluoride crystals.

He joined General Physics Institute of the Russian Academy of Sciences, as a Research Fellow in 1987. His research interest include coherent and laser spectroscopy of doped solids; nonlinear optics; color center physics; and solid-state lasers. Since 2000, he has a been working as a Research Associate at the Department of Physics, University of Alabama at Birmingham (UAB). During the last few years, his research was concentrated on studying of laser media based on semiconductor materials with transition metals impurities.

Dr. Fedorov is a member of the Optical Society of America, and the International Society for Optical Engineering. Dr. Fedorov with colleagues received "Snell Premium" of the Institute of Electrical Engineers of the United Kingdom in 2004.

Sergey B. Mirov was born in Moscow, Russia, on December 4, 1955. He received the M.S. degree in electronic engineering from the Moscow Power Engineering Institute-Technical University, in 1978, and the Ph.D degree in physics in 1983, from the P. N Lebedev Physical Institute of the Russian Academy of Sciences, Moscow, for his work on tunable color center lasers.

He served as a Staff Research Physicist, at P. N. Lebedev Physical Institute, and a Principal Research Associate and a Group Leader at the General Physics Institute, Russian Academy of Sciences. His early work at the Russian Academy of Sciences involved physics of color centers formation under ionizing irradiation, color center's photo chemistry, laser spectroscopy of solids and led to the development of the first room temperature operable commercial color center lasers, passive Q-switches and nonlinear filters for various types of neodymium lasers from mini lasers to powerful laser glass systems. Since 1993, he has been a faculty member at the Department of Physics, University of Alabama at Birmingham (UAB). Currently, he is a Professor of physics at UAB and Co-Director of the Center for Optical Sensors and Spectroscopies. His main fields of interest include tunable solid-state lasers, laser spectroscopy, and quantum electronics. He has authored or co-authored over two hundred seventy scientific publications in the field of quantum electronics, has published one book, several book chapters, and holds 13 patents.

Dr. Mirov was awarded the USSR First National Prize for Young Scientists in 1982, for the development of LiF color center saturable absorbers. He received Distinguished Research Awards from the General Physics Institute in 1985 and 1989, and from the P N. Lebedev Physical Institute in 1980. In 2004, the Institute of Electrical Engineers in the United Kingdom has named him and his team recipients of the Snell Premium award for the input in optoelectronics and development of Cr^{2+}:ZnS mid-IR external cavity and microchip lasers. Dr. Mirov is a member of the Optical Society of America, the American Physics Society, and the International Society for Optical Engineering.

Andrew Gallian was born in Springfield, MO, on September 23, 1977. He received the B.S. degree in physics from The University of the South, Sewanee, TN, in 1999. He received the B.S. and M.S. degrees in electrical engineering in 2000 and 2003, respectively. In 2003, he joined the Physics Department, University of Alabama at Birmingham and received the M.S. degree in 2005 and is currently working towards his Ph.D. in physics.

His research interests include transition metal doped II–VI semiconductors as a laser gain media in the mid-infrared as well as the feasibility of electrically pumping Cr:ZnSe laser systems.

Dmitri V. Badikov was born in Krasnodar, Russia, in 1982. He received the B.S. degree in physics from Kuban State University, Krasnodar, in 2005.

He is currently engaged in growing and characterization of chalcogenide laser and nonlinear materials for mid-IR spectral range as a Graduate Fellow, Physics and Technology Department, Kuban State University. He was the first to grow $PbGa_2S_4 : Dy^{3+}$ laser crystal operating at room temperature at 4.3 μm.

Mikhail P. Frolov was born in Vladimir, Russia, in 1951. He received the M.S. and Ph.D. degrees, both in physics, from Moscow Institute of Physics and Technology, in 1974 and 1977, respectively. His thesis research involved a study of the intracavity laser spectroscopy using dye lasers.

Since 1977, he has been with Quantum Radiophysics Division, P. N. Lebedev Physical Institute, Russian Academy of Sciences, Moscow, Russia, where he is currently a Leading Staff Scientist. Since 1995, he has been with Moscow Institute of Physics and Technology, where he is currently an Assistant Professor. His work included the development of intracavity laser spectroscopy and experimental research of chemical HF lasers, oxygen-iodine lasers and a spectroscopic study of potential visible chemical laser systems initiated by powerful UV laser radiation. He has authored over 100 journal articles and conference presentations. His current research interests are mid-IR solid-state lasers and the mid-IR intracavity laser spectroscopy.

Yuri V. Korostelin was born in Ufa, Russia, in 1956. He was a scholar at the Faculty of Semiconductor Materials and Devices, Moscow Steel and Alloys Institute, Moscow, Russia, where he received the certificate of engineer degree in electronic technique in 1979. In 1994, he received the Ph.D. degree in semiconductor technology from General Physical Institute of the Russian Academy of Sciences, Moscow, Russia.

In 1979, he joined the P.N. Lebedev Physical Institute, Moscow, where he carried out the investigation

of crystallization of II–VI compound single crystals from the vapor phase and developed growth technology of high uniform II–VI compound solid solution single crystal for laser cathode-ray tubes and other optoelectronics devices. Last time his research involves the growth of both substrate-quality II–VI compound single crystals for epitaxy of low-dimension II–VI compound heterostructures and transition metal-doped II–VI compound single crystals for mid-infrared solid-state lasers.

Vladimir I. Kozlovsky was born in Berdichev, Ukraine, in 1948. He received the certificate of engineer degree in acoustics from Moscow Institute of Physics and Technology, Moscow, Russia, in 1972 and the degree of Candidate of Physico-Mathematical Sciences from P.N. Lebedev Physical Institute of Russian Academy of Sciences, Moscow, Russia, in 1979.

He joined the staff of P. N. Lebedev Physical Institute where he carried out experimental studies of electron beam pumped semiconductor lasers based on II–VI compound single crystals and developed a laser cathode-ray tube. In recent years his research interests have been in investigations of low-dimension II–VI heterostructures for the e-beam pumped semiconductor lasers emitting in visual and ultraviolet spectral ranges and in applications of II–VI compound single crystals doped by transition metals for mid-infrared solid-state lasers.

Alexander I. Landman was born in Alabino, Moscow region, Russia, in 1980. He received the diploma in solid-state physics from the Moscow Engineering-Physics Institute in 2003.

In 2003, he joined the P. N. Lebedev Physical Institute, Moscow, Russia, as a Scientific Employee. His research has involved setting up an II–VI compound crystal growth. His primary interests lie in growth of II–VI compound crystals doped by transition metals for mid-IR lasers.

Yuri P. Podmar'kov was born in Kuyman, Lipetsk region, Russia, in 1957. He received the M.S. degree in physics from the Moscow State University, Moscow, Russia, in 1980.

He joined the staff of P. N. Lebedev Physical Institute, Russian Academy of Sciences, Moscow, Russia, in 1980, where he is currently a Senior Staff Scientist. His work included research and development of chemical lasers and optical diagnostics of laser active media. Other research interests included the investigations of solid-state lasers and a wide variety of lasers for intracavity laser spectroscopy.

Vadim A. Akimov was born in Tula, Russia, in 1982. He received the M.S. degree in laser physics from the Moscow Insititute for Physics and Technology, Moscow, Russia, in 2005, where he is currently pursuing the Ph.D. degree.

He is currently with Lebedev Physical Institute, Moscow, as an Associate Researcher. His research interests include characterization of solid-state mid-infrared lasers based on transition metal-doped chalcogenides, studying its spectral dynamics with respect to intracavity laser spectroscopy (ICLS), and practical application of ICLS in the mid-infrared region.

Artem A. Voronov was born in Chelyabinsk, Russia, in 1980. He received the B.S. and M.S. degrees in applied physics and mathematics from the Moscow Institute of Physics and Technology, Dolgoprudny, Moscow Region, Russia, in 2001 and 2003, respectively. He is currently pursuing the Ph.D. degree at the Moscow Institute of Physics and Technology, Moscow, Russia, investigating Fe:ZnSe-laser properties

His research interests include IR solid-state lasers, IR spectroscopy, intracavity laser spectroscopy.