3.9-4.8 μm gain-switched lasing of Fe:ZnSe at room temperature

J. Kernal*, V. V. Fedorov, A. Gallian, S. B. Mirov

Department of Physics, University of Alabama at Birmingham, CH 310, 1530 3rd Avenue South,
Birmingham, Alabama 35294, USA,
vfedorov@uab.edu

V. V. Badikov

Kuban State University, 149 Stavropolskaya str., Krasnodar, 350040, Russia
ntlab@kubsu.ru

Abstract: We report a room temperature Fe:ZnSe laser in gain-switched operation and tuning over the 3.9 - 4.8μm spectral range. Mid-IR emission of Fe^{2+}:ZnSe was studied under three regimes of excitation: ordinary optical (2.92μm) excitation of $^5T_2$ excited state of Fe^{2+}; excitation via ^5E level of Cr co-dopant (1.56μm); and excitation via photo-ionization transition of Fe^{2+} (0.532μm). The energy transfer from Cr^{2+} (^5E level) to Fe^{2+} ($^5T_2$ level) under 1.56μm wavelength excitation was observed and resulted in simultaneous room temperature emission of Fe:Cr:ZnSe crystal over ultra-broadband spectral range of 2-3 and 3.5-5μm. We also report the observation of mid-IR emission at 3.5-5μm induced by 2+->3+->2+ ionization transitions of the iron ions in Fe:ZnSe.

OCIS codes: (140.3580) Lasers, Solid-State; (140.5680) Rare earth and transition-metal solid-state lasers

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1. Introduction

There is a growing demand for affordable mid-infrared sources for use in a variety of applications including eye-safe laser radar, remote sensing of atmospheric constituents, trace gas analysis, environmental monitoring, industrial control, eye-safe medical laser sources for non-invasive medical diagnostics, optical communication, and numerous military applications such as target designation, obstacle avoidance and infrared counter measures.

DeLoach et al. [1] and Page et al. [2] have performed detailed spectroscopic studies of several II –VI chalcogenides with different divalent transition metal (TM) ions as potential mid-IR laser materials. These publications [1, 2] introduced to the laser community a new class of mid-IR laser media. Since then, lasers based on Cr:ZnS, Cr:ZnSe, Cr:$Cd_{1-x}Mn_xTe$, and Cr:CdSe crystals working with efficiency exceeding 60% in CW, free-running long pulse, Q-switched and mode-locked regimes of operation and tunable over the 2-3.5 μm spectral region were reported (see review [3] and references herein).

Similar to Cr^{2+} ($3d^4$) ions, the ground and first excited levels of Fe^{2+} ($3d^6$) ions have the same spin, and therefore will have a relatively high cross-section of emission. Furthermore, higher lying levels of Cr^{2+} and Fe^{2+} - have spins that are lower than the ground and first excited levels, greatly reducing the probability for significant excited state absorption at the pump or laser transition wavelengths. The lowest term ^5D of the Fe^{2+} ($3d^6$) free ion is split into an orbital doublet ^5E (ground state) and an orbital triplet $^5T_2$ (higher level) by the tetrahedral symmetry crystal field (point group T_d) when the Fe^{2+} ion substitutes for a Zn ion in the lattice. The Jahn-Teller, spin-orbit interactions further provide 15-fold and 10-fold splitting of the $^5T_2$ and ^5E states, respectively. The crystal field splitting for Fe^{2+} ions in the tetrahedral fields of the II-VI crystals is smaller than for Cr^{2+} ions, so for a Fe^{2+} doped crystal, the laser operates in a longer wavelength range (3.7-5.0 μm), which is important for many applications.

Unfortunately, mid-IR transition in Fe^{2+}:ZnSe crystal demonstrates multi-phonon quenching at room temperature, as a result untill now the lasing of Fe^{2+}:ZnSe crystals have been achieved only for temperatures below 180K. The first lasing action from an Fe-doped semiconductor at 2K was demonstrated by Klein *et al.*[4], who observed laser oscillations at 3.53 μm in *n*–InP crystal. The first tunable lasing of Fe:ZnSe crystal in 3.98-4.5 μm spectral range was demonstrated in [5] for temperatures ranging from 15 to 180 K. Recently an IR Fe:ZnSe laser continuously tunable over 3.98-4.5 μm spectral range was demonstrated in [6,7] at 255K.

In this study we extend our effort to develop high optical density and high quality Fe^{2+}:ZnSe and demonstrate the feasibility of Fe^{2+}:ZnSe crystals for gain-switched lasing at room temperature (RT).

2. Experimental procedures

The undoped polycrystalline samples ZnSe were grown by chemical vapor deposition and 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 or CrSe powder into quartz ampoules that were evacuated and sealed under 10^{-4} Torr pressure. The sealed ampoules were then 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.

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

A schematic of experimental set-up for spectroscopic and laser characterization of Fe:ZnSe is depicted in Fig. 1. 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)

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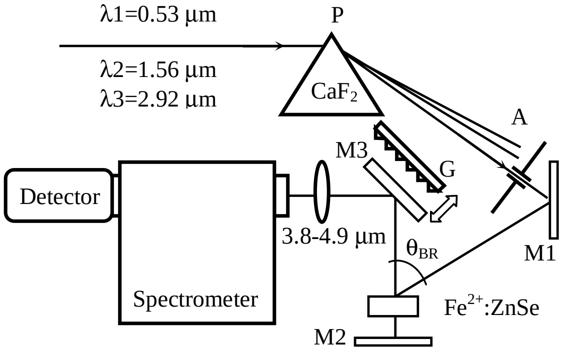

Fig. 1. Experimental set-up for spectroscopic and laser characterization of Fe:ZnSe.

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 Newport-Oriel Infrared element (Model # 6580). Kinetic measurements were performed with (EGG Judson J10D-M204-R04M-60) InSb detector coupled to an amplifier (Perry PA050). This InSb detector-amplifier combination featured a temporal resolution of 0.4 µs. The radiation of the single frequency, Q-switched Nd:YAG laser with a repetition rate of 10Hz, and pulse duration of 7ns was used as a basic laser source. Mid-IR emission of Fe^{2+} in ZnSe was studied under three regimes of excitation: optical (2.92 µm, 2nd D_2 Raman Stokes of Spectra Physics GCR 230 Nd:YAG laser) excitation of $^5T_2$ excited state of Fe^{2+}; excitation via ^5E level of Cr co-dopant (1.56µm, 1st D_2 Raman Stokes of Spectra Physics GCR 230 Nd:YAG laser); and excitation via photo-ionization transition of Fe^{2+} (0.532µm, 2nd harmonic of Spectra Physics GCR 230 Nd:YAG laser). The Nd:YAG laser radiation was directed into a 1 m (Light Age, Inc.) Raman Convertor filled with D_2 ($\Delta\nu$=2991 cm^{-1}). In the single-longitudinal mode regime the pump 1.06 µm radiation was effectively converted into the 1st Stokes and the 2nd Stokes radiations. Using 1.06 µm radiation with ~700 mJ of pump energy, the 1st Stokes radiation with ~ 200 mJ @ 1.56µm and 2nd Stokes radiation with output energy of up to 45 mJ @ 2.92µm were achieved. Output radiation of 1.56, 2.92, or 0.53 µm was selected using CaF_2 prism-aperture combination, and was further attenuated by neutral filters. One of the advantages of the described pump system is short pulse duration (less than 5 ns). This is important for room temperature studies of Fe:ZnSe. The duration of the excitation is shorter than the lifetime of the $^5T_2$ excited state being significantly quenched by nonradiative relaxation processes.

3. Spectroscopic characterization

The absorption spectra of $^5E \rightarrow {}^5T_2$ transition are depicted in Fig. 2. The maximum absorption coefficients of the crystals at room temperature were $k=6\text{-}9\ cm^{-1}$ (at λ=3200 nm). The concentration in the doped samples was estimated using absorption cross section (σ_{ab}=0.65 x10^{18} cm^2) at 2.698 µm reported in [5]. The calculated Fe concentration in these crystals was about (6-9)x10^{18} cm^{-3} and varied in some crystals from 10^{18} to 10^{20} cm^{-3}. Figure 2 curve (ii) demonstrates the absorption spectrum of Fe and Cr co-doped ZnSe crystals. As one can see, these crystals feature a characteristic Cr^{2+} $^5T_2 \rightarrow {}^5E$ band at 1770 nm with a maximum absorption coefficient of 1.8 cm^{-1} in addition to the absorption band of Fe. At T=20K (Fig. 2, curve (iii)) the absorption spectrum of Fe:ZnSe reveals structure of the $^5E \rightarrow {}^5T_2$ transition with a zero-phonon line near 2725 cm^{-1}.

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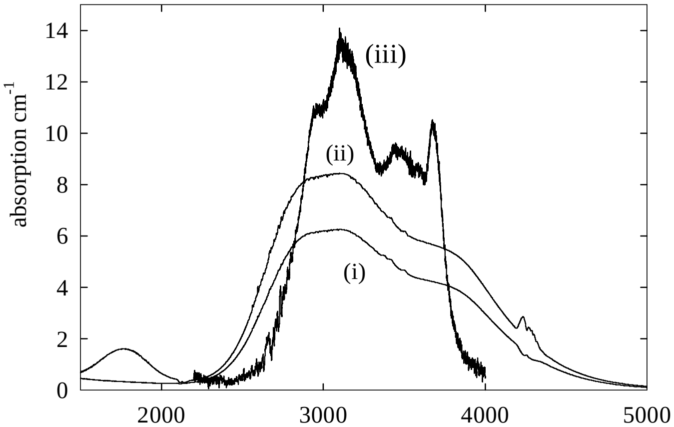

Fig. 2. Absorption spectra of Fe:ZnSe (i) at RT, Fe:Cr:ZnSe (ii) at RT and Fe:ZnSe (iii) at 20K.

The room temperature emission spectra (measured in units proportional to $\left(W \times nm^{-1} \times m^{2} \times srad^{-1}\right)$ over 3100-5500 nm spectral range are shown in Fig. 3.A. As one can see, at room temperature all the samples feature a broadband (3500-5500 nm) luminescence with a dip in the middle of the emission spectra around 4300 nm, caused by absorption of atmospheric CO_2. The radiative lifetime measurement at room temperature was limited by the temporal response of the InSb detector and was estimated to be less than 1μs.

We also studied mid-IR luminescence of Cr:ZnSe, Fe:Cr:ZnSe, as well as Fe:ZnSe under excitation with the D_2 Raman shifted radiation (1st Stokes 1.56μm) of a Nd:YAG laser. This excitation overlaps with the absorption band of Cr^{2+} (see Fig. 2) and results in a strong room temperature luminescence of Cr^{2+} over the 2000-3300 nm spectral range detected in both Cr:ZnSe and Fe:Cr:ZnSe crystals. There was no Fe^{2+} luminescence detected in Fe:ZnSe crystals under 1.56μm excitation. Interestingly, in addition to Cr^{2+}, the Fe^{2+} luminescence under 1.56μm excitation was observed in Fe:Cr:ZnSe crystals. Figure 3.B demonstrates room temperature luminescence spectra of Cr:ZnSe and Fe:Cr:ZnSe crystals under 1.56μm wavelength excitation measured in the same experimental conditions. Absence of the Fe^{2+} luminescence in the Fe:ZnSe and Cr:ZnSe crystals and existence of the Fe^{2+} luminescence in the Fe:Cr:ZnSe samples indicate that Fe^{2+} in ZnSe could be excited via $Cr^{2+}\rightarrow Fe^{2+}$ energy transfer process.

Chromium and iron mid-IR luminescence in Fe:ZnSe crystals were also measured under 532nm excitation at cryogenic temperatures (~20K). We believe that this luminescence is induced by photo-ionization excitation of TM ions in ZnSe. The ionization mechanisms of chromium ions under 532 nm excitation leading to strong mid-IR emission and lasing has been recently discussed in [8, 9]. The ionization of the iron ions from a 2+ to a 3+ state under the 532nm radiation and then a 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 [9].

The absorption cross section was obtained from absorption measurement and using the known absorption cross section at 2.698 μm [5]. Emission cross sections at room temperature are determined using either the reciprocity method (RM) or the Fuchtbauer-Landenburg (FL) equation [10, 11]. Using a fundamental relationship between spontaneous and stimulated processes, the FL equation can be written as

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$$\sigma_{em}(\lambda)=\frac{\lambda^5 I(\lambda)}{8\pi c n^2\tau_{rad}\int I(\lambda)\lambda d\lambda}, \qquad (1)$$

where $\sigma_{em}(\lambda)$ is emission cross section, λ-emission wavelength, n - refractive index, c-speed of light, τ_{rad}- radiative emission life-time, and I -energy per area per time. The radiative lifetime was estimated from the absorption measurements as follows:

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

The radiative lifetime was calculated to be 26μs, that value is close to luminescence lifetime measured at 14K (τ=33μs) [5]. The emission cross section as a function of wavelength calculated according to relationship (1) is shown in Fig. 4. The emission cross section can be also obtained from the absorption spectra by so-called reciprocity method (RM). According to

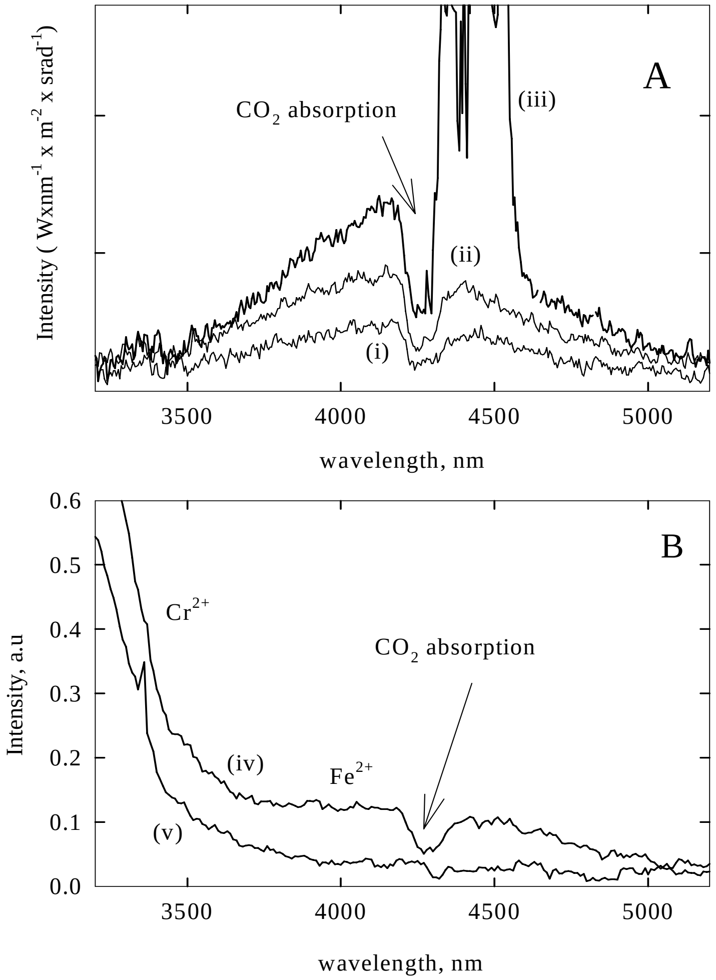

Fig. 3. (a) Room temperature emission of Fe:ZnSe crystal under 2.92 μm excitation ((i) E_{pump}= 2 mJ, (ii) E_{pump}=5 mJ, (iii) E_{pump}=8 mJ); (b) Emission of Fe:Cr:ZnSe (iv) and Cr:ZnSe (v) crystal under 1.56 μm excitation.

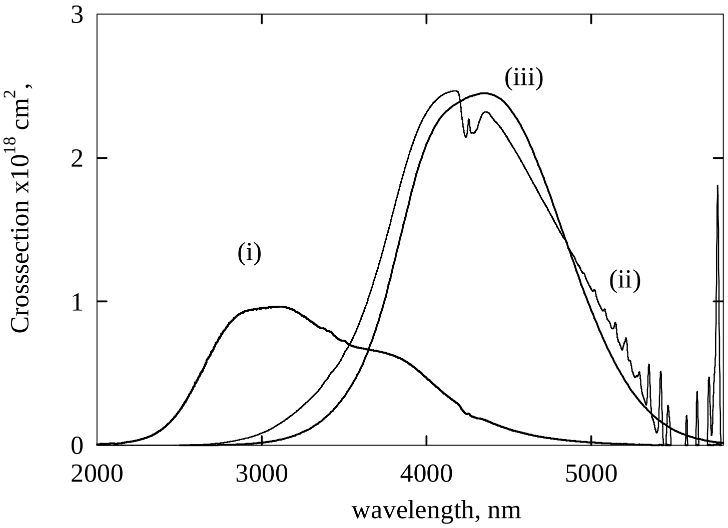

Fig. 4. Room temperature absorption (i) and emission cross-sections (ii) and (iii). Emission cross-section calculated using reciprocity method (ii) and Fuchtbauer-Landenburg equation (iii)

this method absorption and emission cross sections are related as:

$$\sigma_{em}(\nu) = \sigma_{ab}(\nu)\frac{Z_l}{Z_u} exp([E_{zl} - h\nu]/kT), \tag{3}$$

where E_{zl}-is 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:

$$Z_u = \sum_j g_j \, exp(-E_j/kT) \tag{4}$$

$$Z_l = \sum_i g_i \, exp(-E_i/kT) \tag{5}$$

The Z_l/Z_u factor depends on temperature but does not contain any spectral dependence. Emission cross section calculated according to RM with factor $Z_l/Z_u=1.5$ is shown in the Fig. 4. The difference in the Z_l/Z_u factor from g_l/g_u ratio is caused by bigger upper level splitting ($^5T_2$) in comparison to the ground state level (^5E) and thermal energy $E=kT$. As one can see from Fig. 4, both methods (FL and RT) demonstrate a wide amplification band at RT with maximum at ~4300nm and a bandwidth of ~1100nm. However, the spectral shapes of the curves are not identical. This difference can be explained by 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 12K-120K temperature range and this increase could be a result of very different radiative lifetimes of the components of the $^5E \rightarrow {}^5T_2$ transition. In addition, measured emission spectra can be of slightly suppressed intensity at the short wavelength tail of the spectrum due to the 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 room temperature.

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4. RT gain-switched lasing

As one can see from the Fe:ZnSe emission spectra depicted in Fig. 3 curve-(iii), an increase of pump energy above the threshold level of 7-8 mJ results in Fe stimulated emission at 4400nm accompanied by a sharp line narrowing from 1100nm down to 200nm. This threshold corresponds to lasing due to Fresnel reflections from the crystal surfaces. A setup for room temperature laser experiments is shown in Fig. 1. As a pump source we used the 2nd Stokes output of the Nd^{3+}:YAG laser described above. The pump radiation at 2.92 μm with a beam diameter of 1.5mm excited the Fe^{2+}:ZnSe crystal at Brewster angle of incidence. The crystal temperature remained 300K during all laser measurements. In nonselective laser experiments the cavity was formed by a gold mirror (M2) and Fresnel reflection from the output face of the Fe^{2+}:ZnSe crystal. Figure 5 shows the Fe^{2+}:ZnSe laser output as a function of pump energy. A linear approximation of the experimental data estimates the threshold value of the pump energy to be 2.5mJ. In this experiment the laser spectral line was centered at 4350nm with a linewidth of 150nm. The maximum output energy measured with a J3-02 Molectron Joule meter was estimated to be ~ 1μJ. 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, small optical density of the crystal resulted in a small efficiency of pump absorption. Second, output coupler formed by Fresnel reflection from the crystal facet was not optimal. Later experiments will optimize crystal geometry, doping densities, and the output coupler to increase the output energy.

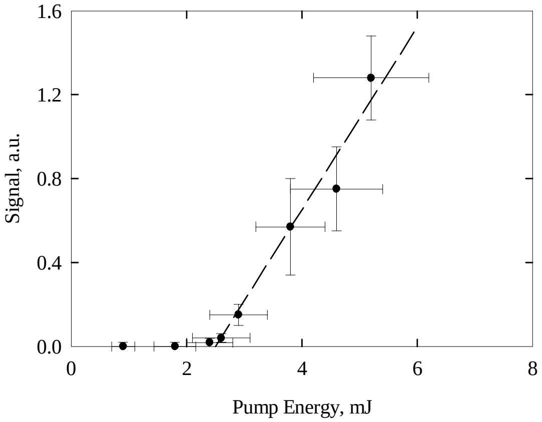

Fig. 5. Input-output curve for RT gain-switched Fe:ZnSe lasing in nonselective cavity.

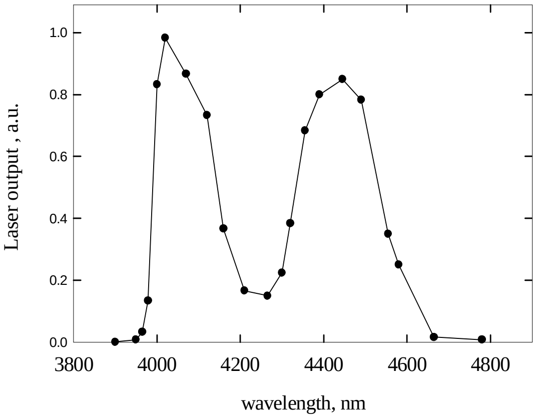

Fig. 6. Tuning curve of RT gain-switched Fe:ZnSe laser.

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In the laser wavelength tuning experiment a Littrow mount cavity of 10 cm length was utilized (see Fig. 1). Wavelength tuning was realized using a diffraction grating with 150 grooves/mm blazed at 2 μm and operating in an auto-collimation regime for the first diffraction order. Zero order of diffraction served as an output coupler. A wavelength tuning over the 3.9- 4.8 μm spectral region was realized (see Fig. 6). The output of the Fe^{2+} laser oscillation had a linewidth of approximately 70nm (FWHM) and was limited by nonselective reflection from the crystal surfaces. The peak efficiency of the tunable output was centered at 4150 nm and was shifted to a shorter wavelength when compared to the non-selective regime. This shift could be due to higher diffraction grating efficiency at shorter wavelength. As one can see from the Fig. 6, the measured tuning curve has a deep dip around 4300 nm due to atmospheric absorption of CO_2. So, to achieve continuous wavelength tuning at this spectral range the laser cavity should be purged with N_2 or other gases. A sharp drop of stimulated emission at the short wavelength tail of the tuning curve could be due to an increase of absorption losses in this part of spectral region.

5. Summary

In conclusion, the absorption and luminescence properties of Fe:ZnSe and Fe:Cr:ZnSe crystals in the middle infrared spectral range were studied at room and low temperatures. Room temperature emission cross-section of $^5E \rightarrow ^5T_2$ transition of iron ions was estimated from spectroscopic measurements. Middle infrared 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+} (0.532 μm). For the first time the energy transfer from Cr^{2+} (^5E level) to Fe^{2+} ($^5T_2$ level) under 1.56μm wavelength excitation was observed and resulted in simultaneous room temperature emission of Fe:Cr:ZnSe crystal over ultra-broadband spectral range of 2-3 and 3.5-5 um. We also report the first observation of middle infrared emission at 3.5-5 um 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 middle-infrared lasing under direct injection of free electrons and holes. The first room temperature gain-switched lasing of Fe:ZnSe crystal at 4.4 um was demonstrated in a nonselective cavity under 2.92 um excitation with a pulse duration of 5 ns. Selective cavity experiments were also performed in a Littrow mount configuration. Tunable oscillation of Fe:ZnSe crystal over 3.9-4.8 μm spectral range was demonstrated at room temperature.

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