

Recent progress in transition metal doped II-VI mid-IR lasers

Sergey Mirov, Vladimir Fedorov, Igor Moskalev, and Dmitri Martyskhin

Abstract— Recent progress in transition metal doped II-VI semiconductor materials (mainly Cr²⁺:ZnSe) makes them the laser sources of choice when one needs a compact system with continuous tunability over 2-3.1 μm, output powers up to 2.7 W, and high (up to 70%) conversion efficiency. The unique combination of technological (low-cost ceramic material) and spectroscopic characteristics make these materials ideal candidates for “non-traditional” regimes of operation such as microchip and multi-line lasing. This article reviews these non-traditional Cr-doped mid-IR lasers as well as describes emerging Fe²⁺:ZnSe lasers having potential to operate at room temperature over the spectral range extended to 3.7-5.1 μm. In addition to effective RT mid-IR lasing transition metal doped II-VI media, being wide band semiconductors, hold potential for direct electrical excitation. This work shows the initial steps towards achieving this goal by studying Cr²⁺, Co²⁺, and Fe²⁺ doped quantum dots. We have demonstrated a novel method of TM doped II-VI quantum dots fabrication based on laser ablation in liquid environment. TM doped II-VI quantum dots demonstrated strong mid-IR luminescence. It opens a new pathway for future optically and electrically pumped mid-IR lasers based on TM doped quantum confined structures.

Index Terms—Laser, mid-infrared, tunable, doped quantum dots.

I. INTRODUCTION

Transition metal (TM²⁺, e.g., Cr²⁺ or Fe²⁺) doped binary and ternary chalcogenides crystals represent relatively new class of solid state gain media with strong and ultra-broad absorption and emission bands in the middle-infrared (mid-IR) range of optical spectra. In 1996 Scientists from the Lawrence Livermore National Laboratory [1] were first to show that among different types of crystalline gain materials TM²⁺ doped wide bandgap II-VI semiconductor crystals could be very special for mid-IR lasing. These TM²⁺ doped II-VI compounds have a wide bandgap and possess several important features that distinguish them from other oxide and fluoride laser crystals. These features are as follows: (i) the heavy anions in the crystals provide a very low energy optical phonon cutoff that makes them transparent in a wide spectral region and decreases the efficiency of non-radiative decay,

which gives a promise of a high yield of fluorescence at room temperature (RT); (ii) II-VI compounds tend to crystallize as tetrahedrally coordinated structures, as opposed to the typical octahedral coordination at the dopant site. Tetrahedral coordination gives smaller crystal field splitting, placing the dopant transitions further into the IR. Active interest in TM doped II-VI compounds inspired by [1] was explained by the fact that these media are close mid-IR analogs of the titanium-doped sapphire (Ti-S) in terms of spectroscopic and laser characteristics and it was anticipated that TM²⁺ doped chalcogenides will lase in the mid-IR with a great variety of possible regimes of oscillation, similar to the Ti-S laser. Indeed, lasers based on Cr:ZnS, Cr:ZnSe, Cr:Cd_{1-x}Mn_xTe, and Cr:CdSe crystals working with efficiency exceeding 70% in 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 by several groups (see review [2] and references herein). It was also revealed that TM²⁺ doped II-VI lasers combine a unique versatility of the ion-doped solid-state lasers with the engineering capabilities of semiconductor lasers, paving the route to the future “non-traditional” regimes of oscillation.

II. NON-TRADITIONAL CR-DOPED MID-IR LASERS

A. Cr:ZnSe and Cr:ZnS microchip lasers

The unique combination of technological (low cost ceramic material) and spectroscopic characteristics (ultrabroadband gain bandwidth, high $\sigma\tau$ product and high absorption coefficients) make these materials ideal candidates for microchip lasing. First microchip laser experiments on both Cr²⁺:ZnS and Cr²⁺:ZnSe chemical vapor transport (CVT) grown crystals were performed and reported in [3]-[6].

After-growth doped Cr²⁺:ZnS and ZnSe crystals were prepared by a two-stage method. During the first stage, undoped single crystals were synthesized by a CVT reaction from the gas phase using an iodine gas transport scheme in a quartz tube of 20mm diameter and 200mm length placed in a two zone furnace. At the second stage, chromium was introduced into the crystalline host by thermal diffusion carried out in sealed ampoules under a pressure of 10⁻⁵ torr and temperature of 1000°C over 5-20 days. Some crystals, at the second stage of chromium introduction into the crystalline

Manuscript received November 7, 2006. This work was supported in part by the National Science Foundation under Grants No. ECS-0424310, EPS-0447675, and BEC 0521036.

The authors are with the Center for Optical Sensors and Spectroscopies of the Department of Physics, University of Alabama at Birmingham, CH 310, 1530 3rd Avenue South, AL 35294, USA (Tel. 205-934-8088; fax: 205-934-8042; e-mail: mirov@uab.edu).

host, were doped by thermal diffusion from a chromium thin film deposited by a Pulse Laser Deposition (PLD) method on a thin wafer of II-VI material. The mirrors were directly deposited on the parallel polished facets of a thin wafer of laser material. Two different pump arrangements were utilized. The first was with coupling optics between the fiber and the microchip. The second pump arrangement was without any coupling optics and was arranged by microchip laser mounting at a close ($\sim 20\ \mu\text{m}$) distance from the tip of the Er-fiber pump laser.

In a focused pump beam arrangement a laser threshold of 120 mW and a slope efficiency of 53% with respect to absorbed pump power were realized for the $\text{Cr}^{2+}:\text{ZnS}$ microchip laser. High, close to theoretical limit of 65%, slope efficiency of the microchip laser indicates the crystal to be of high quality with low loss. The maximum output power of $\text{Cr}^{2+}:\text{ZnS}$ microchip laser reached 150 mW at a slope efficiency of 43%. Maximum output power of the $\text{Cr}^{2+}:\text{ZnSe}$ microchip laser was reported to be 0.5 W (see Fig.1).

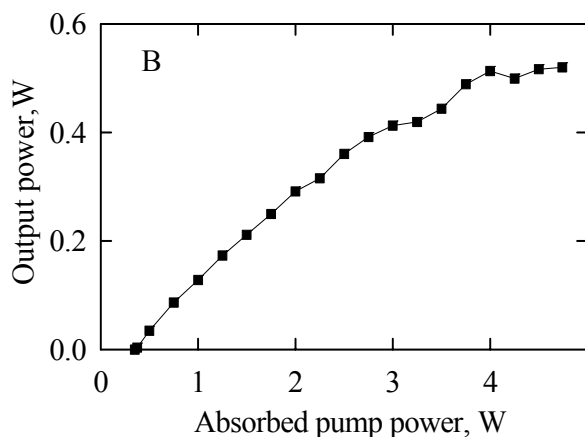


Fig. 1 Output-input characteristics of the $\text{Cr}^{2+}:\text{ZnSe}$ continuous wave microchip laser under Er-fiber laser excitation – focused pump beam arrangement.

Thermal effects provided cavity stabilization within the microchip crystals and are responsible for the slightly nonlinear character of output versus input laser performance.

In the second pump arrangement, when the microchip lasers were directly coupled to the fiber tip, laser thresholds of 150 mW and slope efficiencies of 36% with respect to absorbed pump power were realized for $\text{Cr}^{2+}:\text{ZnS}$ microchip laser. The maximum output power of the $\text{Cr}^{2+}:\text{ZnS}$ microchip laser was virtually unchanged in either pump arrangement. In the coupled cavity experiments the number of axial modes was decreased up to 3-4 modes. This can be further decreased to a single longitudinal mode oscillation in a coupled cavity configuration using a narrowband output coupler as it was successfully demonstrated for Tm:YLF in Ref [7].

Gain switched microchip laser experiments were performed with CVT grown ZnS and ZnSe crystals [5]-[6]. A maximum

slope efficiency of 6% with respect to pump energy and maximum output energy of 1 mJ were obtained.

B. Hot pressed ceramic Cr:ZnSe lasers

Currently the state of the art in TM:II-VI laser systems relies either on single crystal, or vapor grown polycrystalline materials. Both of these materials have particular drawbacks in terms of crystal doping. The commonly used doping methods are in melt [8], vapor growth [9]-[10] or after growth thermo-diffusion doping [11]. Under atmospheric pressure ZnSe sublimation occurs at a temperature above $\sim 400\ \text{°C}$ which is lower than that of the melting point [10]. Therefore to use melt growth techniques, in addition to high temperature ($1515\ \text{°C}$), it is necessary to apply high pressure ($75 \times 10^2\ \text{KPa}$) [10]. High temperature melt growth is often accompanied by uncontrolled contamination. This contamination can lead to undesirable and parasitic absorptions. Control of the amount of Cr^{2+} ions incorporated in the crystal is difficult when using vapor growth techniques [9], [11]. Doping of host crystals/polycrystals that are already grown allow for another method of TM incorporation, thermal diffusion. This technique utilizes thermally activated diffusion of transition metal ions into the II-VI crystals [11]. However this technique has several drawbacks as well. These drawbacks include non-uniform doping, large concentration gradients, and the procedure has poor repeatability. These problems with the control of dopant concentration are not appropriate for fabrication of low cost, large-scale samples for high-energy mid-IR applications. Thus another method of crystal growth is required that will allow for large-scale crystal production in a timely and efficient manner. In the 1960's researchers hypothesized that a dense polycrystal of a pure material will be optically indistinguishable from a single crystal of the same composition [12]. Since then many advances have been made in Nd:YAG ceramics [13]-[15]. It has been recently demonstrated that hot-pressed ceramics are a promising and viable "alternative route" for the synthesis of large-scale mid-IR laser media based on chromium doped ZnSe [16]-[17]. Hot-Pressed Cr:ZnSe laser materials can be made quickly, with any dopant concentration, and many varied geometries. The preparation of the powder for hot-pressing was performed by mixing pure ZnSe and a preliminary prepared mixture of ZnSe-CrSe (1 mol %). This final mixture was subjected to grinding in a "Fritch" spherical agate mortar. The grinding yields particles with a size less than $10\ \mu\text{m}$. Prior to the hot pressing, the samples were first briquetted at room temperature with a pressure of 60 MPa. The internal diameter of the press-form was $\sim 15\text{mm}$. The mass of the powder used to prepare a pellet was chosen such that the final height of the pellet will be 20-25 mm. These sample pellets, contained 0.01, 0.03, 0.05, and 0.1 mol % of CrSe were further hot-pressed.

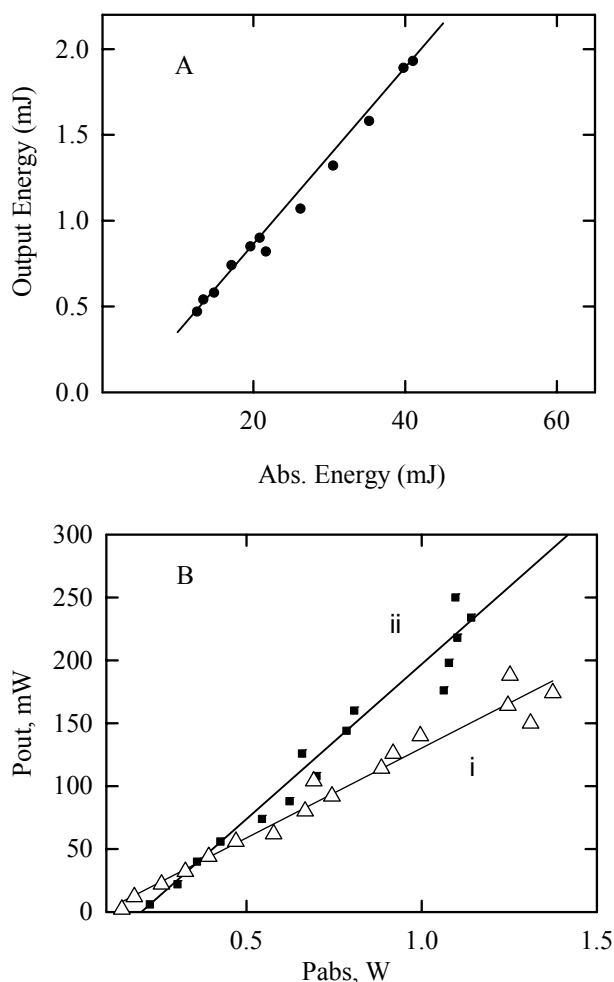


Fig. 2. The output-input characteristics of the hot-pressed ceramic $\text{Cr}^{2+}:\text{ZnSe}$ lasers operating in gain-switched (A); and cw regimes for 10% (i) and 5% (ii) output couplers.

Pyrolytically densed graphite “MPG” was used for preparation of the press-form and punch. Initial heating was performed in a resistive heating furnace and the temperature reached 900K. Further heating was achieved by applying a direct electric current through the sample. This current heated the samples to 1400-1500 K. In conjunction with the heating, the samples were subjected to axial compression with a pressure of 30-35 MPa. After 10-15 minutes of this hot-pressing, samples were cooled to room temperature. Then final cutting and polishing was performed. The final samples had a diameter of 15 mm and a height of 10.5 mm.

XRD measurements demonstrated that the Hot-Pressed ceramic samples are indeed polycrystalline ZnSe in the cubic crystal form. A broad absorption band centered at 1.78 μm indicates that chromium is indeed in the optically active 2+ state. Photoluminescence measurements show that the decay constant corresponding to the ceramic samples is in good agreement with that for the conventionally thermally defused polycrystalline samples.

In the gain-switched laser experiments the laser cavity consisted of a single flat high reflectivity mirror (99.5%) and

the Fresnel reflection from the front face of the ceramic sample. The ceramic crystals were pumped at the Brewster angle from the front surface with a pump spot diameter of 6.5mm. The pumping was achieved using the 1st Stokes (1.907 μm) of the H_2 Raman shifted single frequency Nd:YAG laser. The input-output characteristic of the gain-switched laser is shown in Fig. 2 [16]-[17]. The slope efficiency of 5% and maximum output energy of 2 mJ were achieved.

Laser studies of the hot-pressed ceramic sample under cw Er-fiber excitation were performed in a Kogelnik cavity with 10 and 5 % output couplers (see Fig. 2B). For the first time cw lasing of hot-pressed ceramic $\text{Cr}:\text{ZnSe}$ was achieved with maximum output power of 0.25 W with 20% efficiency with respect to absorbed power.

The described results demonstrate the feasibility of the mid-IR laser systems based on hot-pressed ceramics.

C. Multi-line and ultrabroadband $\text{Cr}:\text{ZnSe}$ laser

There are many practical applications where a source of radiation combining spatial coherence and high intensity with continuous or discrete ultrabroadband, multiwavelength spectrum is required. Since 1970s, there have been many attempts to build multiwavelength and ultrabroadband laser sources. All these attempts are based on the idea to suppress mode competition in the cavity, which is responsible for output spectrum narrowing.

There are two possible ways for implementation of this idea: mode separation in temporal or spatial domain (see review [18] and references herein). $\text{Cr}:\text{ZnSe}$ crystals featuring ultrabroadband gain bandwidth are ideal candidates for ultrabroadband and multiline lasing in spatially-dispersive cavities. The spatially dispersive cavity [19] provides a spatial dispersion of different frequency components of the laser gain profile in the active medium, thus enforcing each frequency to be amplified in its own region of the laser crystal. As a result, the mode competition, natural for conventional lasers, is eliminated and the laser operates at many wavelengths simultaneously.

First demonstration of a continuous-wave, multiwavelength, ultrabroadband, broadly tunable mid-IR (2200—2800 nm) laser source based on 1.55 μm Er-fiber-laser pumped, polycrystalline $\text{Cr}^{2+}:\text{ZnSe}$ gain medium, utilized in a Littrow-mounted grating spatially-dispersive cavity was done in [19]-[20]. A dual-wavelength operation of the laser, tunable over a 600 nm spectral range (2200—2800 nm), an ultrabroadband operation of the laser, producing a continuous 135 nm wide spectrum centered at 2500 nm, and show a 200 nm wide (2400—2600 nm) multiline, tunable output spectra, consisting of up to 40 spectral lines was achieved. A simultaneous tuning of a 20-lines ultrabroadband spectrum over a spectral range of 2200—2800 nm was shown.

The described spatially-dispersive $\text{Cr}^{2+}:\text{ZnSe}$ laser can operate at many wavelengths simultaneously, producing any pre-assigned output spectral composition as well as a

continuous ultrabroadband spectrum within 2-3 μm spectral range. These lasers could find important practical application for free space optical communication, information coding, multi-analyte remote sensing, and numerous wavelength specific military applications.

D. Tunable single-frequency Cr:ZnSe laser

We have developed an Er-fiber laser pumped Cr:ZnSe laser operating in a single longitudinal mode regime. The laser design is very compact (the total optical length of the folded laser cavity is 10 cm), as one can see in Fig. 3, and is based on a folded Kogelnik/Littman scheme utilizing two concave mirrors with $R_1=25$ mm and $R_2=50$ mm radii of curvature, 600 g/mm gold coated grating with reflectivity 50%

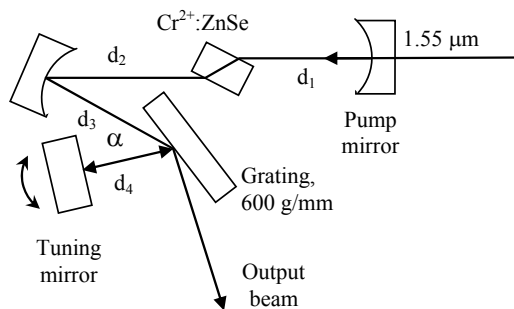


Fig. 3. Cr²⁺:ZnSe tunable, single-frequency laser based on Kogelnik/Littman cavity.

at an angle of incidence 75° , and thermo-diffusion doped Cr:ZnSe crystal absorbing $\sim 70\%$ of pump at $1.55 \mu\text{m}$. Cr:ZnSe of the size $4 \times 8 \times 1$ mm was mounted at Brewster angle into a thermoelectric cooling unit, providing temperature stabilization at $20 \pm 0.1^\circ\text{C}$. The radiation of the single transverse mode linearly polarized Er-fiber laser (IPG Photonics, ELM-10-LP) was focused into the crystal by a 50 mm lens. The lasing wavelength was controlled with precision wavemeter EXFO WA-1500, and the spectral structure and laser linewidth was monitored with a home-made scanning FP interferometer. The output radiation had a linewidth of 120 MHz (measurement limit of the available FPI) over a 120 nm tuning range around $2.5 \mu\text{m}$, and

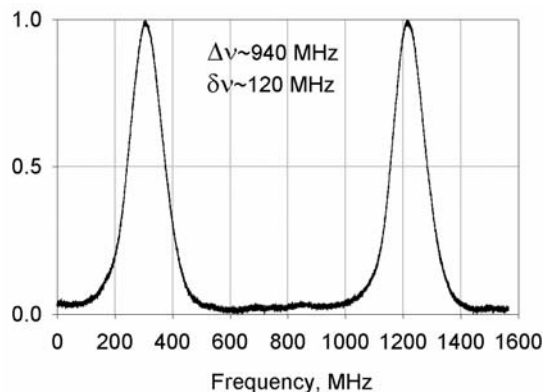


Fig. 4. Interference pattern of the SLM output spectrum from a 160 mm FPI. The spectral resolution is limited by the interferometer finesse of 7.7, which gives the upper limit on the laser linewidth of 120 MHz.

maximum output power was up to 150 mW. The output spectrum of the laser is shown in Fig. 4. The tuning range of the laser in the single-frequency regime was limited due to low diffraction efficiency of the grating at grazing angles.

Figure 5 demonstrates preliminary results on practical utilization of single-frequency Cr:ZnSe laser in Doppler limited resolution intracavity laser absorption spectroscopy of ro-vibrational transitions of the ν_3 and ν_1 bands of H_2O . Minimum detectable absorption coefficient of $\sim 3 \times 10^{-7} \text{ cm}^{-1}$, has been achieved, which corresponds to 9 parts per billion by volume water vapor detection limit. It must be noted here that the output wavelength of the laser was scanned by tilting the

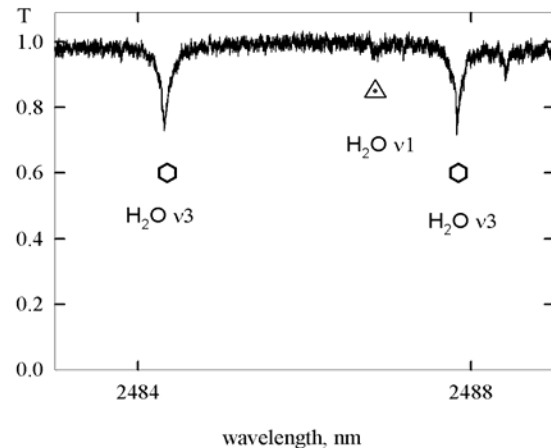


Fig. 5. Weak ro-vibrational transitions of the ν_1 and ν_3 bands of water measured with a single-frequency Cr:ZnSe laser at a scan speed of $4 \mu\text{m/s}$.

mirror around an axis lying in its plane with a piezo-driven home-made mirror shaker with repetition rate of 220 Hz. Thus, the complete wavelength scan over about 9 nm range was performed in $1/440$ s (2.3 ms). Simultaneous monitoring of the output laser spectrum with a fixed-length FPI showed that the laser was operating in the single-mode regime during this entire wavelength scan, which allowed us to acquire the absorption spectrum in Fig. 5.

E. Power scaling of continuous wave Cr:ZnSe laser

Power scaling of the Cr:ZnSe laser output to multi-watt level requires special geometry designed for maximum suppression of thermal effects. In [21] utilization of water cooled thick slab of ~ 12 mm long Cr:ZnSe resulted in 18.5 W of output power under gain switched pumping with the 33 W of Tm:YALO laser radiation and ~ 3 W at 7 W of pumping. This record output power was achieved due to utilization of pump duty cycle of $\sim 10^{-3}$, effective heat removal from the slab, and utilization of $1.94 \mu\text{m}$ pump radiation enabling small quantum defect in the gain medium. Another attractive approach was demonstrated in [22], where face cooled disk design enabled power scaling of Cr:ZnSe 1 mm and 0.5 mm disk laser outputs to 4.2 W in 10 kHz repetition rate gain switched, and 1.4 W cw regimes, respectively. It was revealed in [22] that for single face cooling geometry thermal lensing is proportional to disk thickness and absorbed pump power, but

disk temperature is proportional primarily to absorbed pump power and cannot be reduced by using thinner disks. Attempts to reduce thermal lensing by reducing disk thickness below 0.5 mm runs into a problem of insufficient pump absorption because utilization of heavily doped crystals is not feasible due to high losses and increase in concentration quenching [23].

To mitigate these problems we utilize different geometry with the gain medium in the form of a thin and long parallelepiped which is pumped transversely and cooled through two large polished faces. In this case, the Cr ions are concentrated in a very thin ($\sim 200 \mu\text{m}$) layer near one of the large crystal facets and parallel to it. The crystal is wrapped into a $100 \mu\text{m}$ Indium foil and fixed on a copper cold plate, which is cooled by water or a TEC cooler. This method allows for very efficient heat removal from the laser crystal and strongly reduces the thermal lensing effects. With this approach, we have built the first to our knowledge multi-watt (2.7 W at 7.0 W pump), pure CW $\text{Cr}^{2+}:\text{ZnSe}$ laser, which is briefly described below.

The laser is based on a standard Kogelnik cavity. The laser is pumped by a single mode Er-fiber laser (IPG Photonics, ELM-10-LP), which delivers maximum of 7 W pump power at $1.55 \mu\text{m}$. In this series of laser experiments we have tested 10 Cr:ZnSe samples with the sizes of $10 \times 10 \times 1.5 \text{ mm}$ (Cr layer was parallel to $10 \times 10 \text{ mm}$ surface). The average coefficient of absorption at $1.55 \mu\text{m}$ along the optimal path in the crystal was about 2.0 cm^{-1} (measured with the pump laser at low powers). In these experiments we utilized two output couplers with 50% and 18% reflectivities.

All tested Cr:ZnSe active elements demonstrated same output characteristics within 20% margin. The Input-Output characteristics for the best sample for the two output couplers are shown in Fig. 6. This pure CW $2.5\text{-}\mu\text{m}$ laser delivers up to 2.7 W of output power at 7 W pump, which corresponds to 39% real efficiency. We believe that the laser performance can further be significantly increased by using single crystalline ZnSe host material.

III. FE-DOPED MID-IR LASERS

Mid-IR transitions in the $\text{Fe}^{2+}:\text{ZnSe}$ crystal have multi-phonon quenching at RT. This has prevented RT lasing using Fe:ZnSe as a gain medium. The first tunable lasing of a Fe:ZnSe crystal in $3.98\text{-}4.5 \mu\text{m}$ spectral range was demonstrated in [24] for temperatures ranging from 15 to 180 K. After this pioneering work, where laser effect was realized with output energy of $5 \mu\text{J}$ at 150 K, a much more efficient lasing of Fe:ZnSe has been achieved in [25]-[26] in the 85-255 °K temperature range. For 733 mJ pump energy of Er:YAG laser operating at $2.94 \mu\text{m}$ in free running regime, the maximum output energy of Fe:ZnSe laser at 85 K reached 187 mJ. The maximum slope efficiency of the laser in nonselective cavity was 43 % The output spectrum of the $\text{Fe}^{2+}:\text{ZnSe}$ laser at $T=85\text{K}$ was continuously tuned between 3.77 and $4.40 \mu\text{m}$ in a dispersive resonator with a CaF_2 prism.

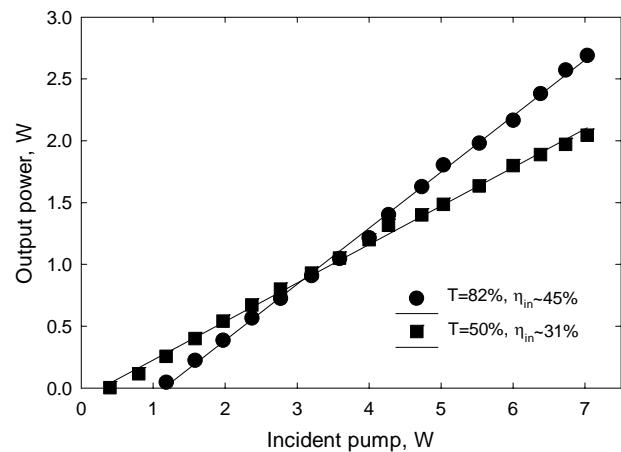


Fig.6. CW Cr:ZnSe laser output power as a function of incident pump power. This is the highest power (2.7 W) demonstrated today for Cr:ZnSe CW laser.

High output energy of the Er:YAG pumped Fe:ZnSe laser was achieved in [26]-[27] at 255K when the ZnSe crystal was cooled with a two-stage thermoelectric unit. The output energy reached 142 mJ with 21% efficiency with respect to the incident pump energy.

Fe:ZnSe has a large emission cross-section $\sigma_{em}=2\text{-}3 \times 10^{-18} \text{ cm}^2$ at $4.4 \mu\text{m}$, however, the luminescence lifetime of Fe:ZnSe at RT ($370 \pm 25 \text{ ns}$ [27]) 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 good chance to obtain RT lasing of Fe:ZnSe in a gain-switched regime with pump pulses shorter than 300 ns. The first RT gain-switched lasing of Fe:ZnSe crystal at $4.4 \mu\text{m}$ in microchip configuration as well as in a nonselective cavity under $2.92 \mu\text{m}$ excitation with a pulse duration of 5 ns was demonstrated in [28]. Selective cavity experiments were also performed in a Littrow mount configuration and tunable oscillation of Fe:ZnSe crystal over $3.9\text{-}4.8 \mu\text{m}$ spectral range was demonstrated at RT. Maximum output energy was relatively small – of the order of several micro-Joules. However, this level of output power is sufficient for injection seeding of optical parametric oscillators (OPO) and amplifiers (OPA). First parametric amplification of $4.4 \mu\text{m}$ microchip gain-switched Fe:ZnSe laser radiation in ZnGeP_2 based OPA was reported in [29]. The single-pass amplification factor of 2 at $4.4 \mu\text{m}$ was achieved with $2.92 \mu\text{m}$ pump intensity of 20 MW/cm^2 .

Output energy and efficiency of Fe:ZnSe lasing at RT in gain switched regime was further improved in [27] where output energy reached 0.4 mJ at $4.4 \mu\text{m}$ with 20% quantum efficiency of lasing with respect to pump energy. The output spectrum of the dispersive $\text{Fe}^{2+}:\text{ZnSe}$ laser was continuously tuned in the spectral range $3.95\text{-}5.05 \mu\text{m}$.

Further improvements of Fe^{2+} lasing at RT require improvements in fabrication of high optical density ZnSe gain media as well as search for new low-phonon-energy hosts.

IV. FUTURE ELECTRICALLY PUMPED TM:II-VI MID-IR LASERS

In addition to effective RT mid-IR lasing transition metal

doped II-VI media, being wide band semiconductors, hold potential for direct electrical excitation. The initial steps towards achieving this goal were performed in [30]-[31] by studying Cr^{2+} ion excitation into the upper laser state 5E via direct electrical excitation as well as excitation and lasing via photoionization transitions. It was also shown that MBE and PLD provide optically active chromium and iron in different chalcogenides and represent a viable route for fabrication of future optically and possibly electrically pumped waveguide confinement laser structures, broadly tunable in the mid-IR spectral region [32]-[36].

In [30] two promising routes for achieving TM:II-VI mid-IR lasing under electrical excitation were envisioned: 1) utilization of TM doped quantum well II-VI heterostructures, and 2) utilization of thin films based on TM-doped nanocrystalline quantum dots (NCD), or NCD dispersed in a conductive matrix. Below we will describe our first steps towards fabrication and characterization of TM doped NCD.

A. Why TM:II-VI NCD are so special for mid-IR?

There are numerous publications related to preparation, luminescence properties and potential applications of Mn^{2+} :II-VI nanoparticles. The interest to this phosphor was stimulated by Bhargava [37] whose most fundamentally interesting result was luminescence enhancement resulting from efficient energy transfer from the ZnS nanocrystals to Mn^{2+} ions facilitated by mixed electronic states. Regarding Cr and Fe doped II-VI nanocrystals their photo-physical properties have not yet been addressed. It is believed that similarly to Mn doped ZnS nanocrystals, one can expect an efficient energy transfer from the low dimensional II-VI structures to Cr^{2+} and Fe^{2+} . Fast energy transfer from the low-dimensional host to Cr^{2+} and Fe^{2+} can be qualitatively explained by the increase of the exciton oscillator strength bound to the impurity center. First of all, quantum size confinement should increase the oscillator strength of the free exciton due to an increase of the electron-hole overlap factor. Secondly, the oscillator strength of the exciton bounded to the impurity center depends on the oscillator strength of the free exciton and electron-hole exchange interaction term which is also supposed to be large due to the carrier's confinement. Thus, one may expect a large enhancement of the oscillator strength of the exciton bound to the impurity embedded in nanostructured materials with respect to bulk hosts. Another important issue that was successfully proven by Tanaka [38] for Mn doped II-VI nanocrystals relates to remarkable differences in thermal quenching of TM d-d PL in nanocrystals and bulk materials. First of all, the density of states for both electron and phonons decreases with size. This is likely to result in weaker electron-phonon coupling opening a pathway for development of a mid-IR light emitting nanostructured material with high RT quantum efficiency of PL under intra-shell IR optical excitation. Hence, Fe^{2+} doped nanostructured materials might efficiently lase at RT. On the other hand, the increased overlap

between the electron and hole wave functions decreases the exciton-phonon coupling. Analogously to Mn in ZnS, such nanostructured materials are supposed to provide much weaker thermal quenching of Fe^{2+} in nanocrystals than that of the bulk crystals. This analysis provides a background for the remarkable differences that could be expected in excitation of Cr^{2+} and Fe^{2+} ions in nanostructures with respect to the bulk crystals and thus the motivation for studies of these nanostructures.

B. Fabrication of TM:II-VI NCD

The majority of methods of metal and semiconductor nanoparticles synthesis is based on chemical approaches in which a variety of functional groups are used to stabilize nanoparticles and serve as a capping agents. A various byproducts of a chemical reaction may also interact with nanoparticles and are difficult to remove from nanoparticles surface. An entirely physical approach of fabrication of metal and semiconductor nanoparticles, such as laser ablation, enables synthesis of pure uncapped nanoparticles. Recently laser ablation was used to prepare various semiconductor nanoparticles in liquid environment [39]-[40]. However, formation of semiconductor nanoparticles doped with transition metal ions under laser ablation was not reported so far to the best of our knowledge. Here we report the fabrication of II-VI NCD doped with TM (Cr, Co and Fe) ions by laser ablation method.

TM doped ZnSe and ZnS nanoparticles were prepared using multi-stage process. Initially, polycrystalline ZnSe and ZnS samples were grown using CVD and were TM (Cr, Co, Fe) doped by post-growth thermal diffusion. During the thermo-diffusion the ZnSe and ZnS samples were annealed in sealed evacuated ampoules with CrSe (CoSe, FeSe) or CrS powder for seven days at 950°C. The average TM ions concentration was 10^{18} - 10^{19} cm^{-3} .

At the first stage of NCD preparation, bulk polycrystalline TM doped ZnS and ZnSe samples were ablated in pure distilled and deionizer water by the radiation of fundamental harmonic radiation of Nd:YAG laser (EXPLA PL2143) with pulse duration 30 ps, repetition rate 10 Hz, and pulse energy of 10 mJ. Laser radiation was slightly focused on the surface of the bulk samples to the spot size of 2 mm. The formation of nanoparticles was observable due to creation of colloidal suspension and coloration of the solution.

At the second stage of preparation, ZnS or ZnSe nanoparticles suspension was sonicated in order to break large aggregates. The suspension was further irradiated by the radiation of the third harmonic (355nm) of the Nd:YAG laser (EXPLA PL2143) with pulse duration 30 ps, repetition rate 10 Hz, and pulse energy of 15 mJ. The laser beam with 1 cm in diameter was directed in to the optical cell without focusing. Initially blurry nanoparticles suspension became clear after 10 minutes of irradiation.

For mid-IR spectroscopic characterization, precipitated nanoparticles were extracted from aqueous solution, washed with distilled-deionizer water and dried naturally under ambient condition.

C. XRD characterization of TM:II-VI NCD

The NCD samples were investigated using x-ray diffraction (XRD) to determine the crystalline grain size range. This XRD measurements were performed using (θ - 2θ) angle x-ray diffraction (Philips X-Pert MPD, The Netherlands) with a Cu K-alpha anode. Spectra were taken from 20° to 60° 2-theta. The XRD pattern shown in Fig. 7-A (a) corresponds to the initial Cr doped polycrystalline ZnS sample used for ZnS-NQD preparation. The most prominent diffraction peaks located at $2\theta = 28.6^\circ$; 47.5° and 56.4° coincide with (111); (200); (220) and (311) reflections of the zinc-blend structure. Cr:ZnS nanocrystals obtained after the first stage of laser irradiation exhibit XRD pattern (Fig. 7A-b) with several additional peaks characteristic to the wurtzite ZnS (100); (101); (102); (110) and (103). The other peaks of the wurtzite structure (002); (110) and (112) overlap with main peaks of the zinc-blend structure (111); (220) and (311). These results indicate that after the first stage of nanoparticles preparation they have mixed wurtzite and zinc-blend structure. From the width of the XRD peak, mean crystalline size can be calculated using Scherrer's equation: $D = k\lambda/B\cos(2\theta)$, where λ is X-ray wavelength (for Cu K α , $\lambda=0.154$ nm), 2θ - diffraction angle; B is the measured full width at half max (FWHM) of the XRD peak, and $k=0.9$. XRD pattern (see Fig.7A-c) of ZnS NQD prepared after the second stage of laser UV treatment exhibits significant peak broadening. After the first stage and second stages of preparation, the mean crystal sizes of doped ZnS nanoparticles were estimated to be 11 and 3 nm, respectively.

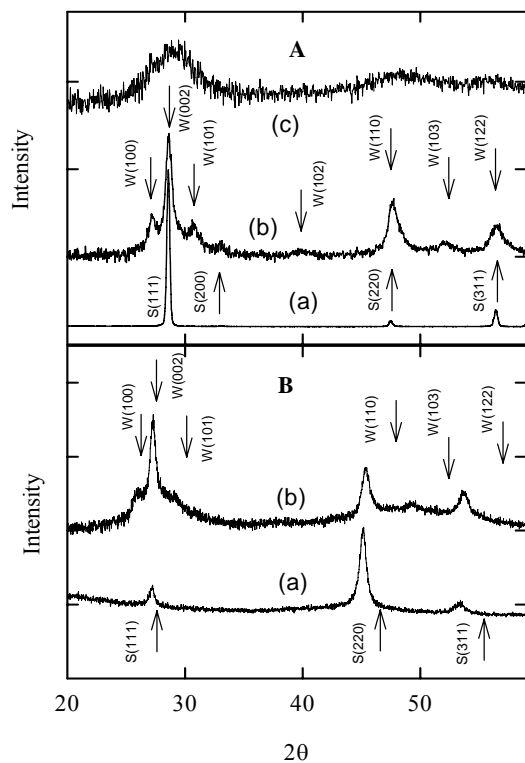


Fig. 7. XRD diffraction pattern of Cr^{2+} doped ZnS (A) and ZnSe (B) NCDs after first (b) and second (c) stages of preparations. The XRD patterns of the bulk ZnS and ZnSe used polycrystals (a) are shown for comparison at the bottom.

Similar results were obtained in the case of ZnSe nanocrystals prepared by 1064 nm laser ablation. Polycrystalline ZnSe target (see Fig. 7 B-a) has XRD peaks at $2\theta = 27.2^\circ$; 45.1° and 53.4° corresponding to (111), (220) and (311) planes reflection of cubic ZnSe. As one can see in Fig. 7-B (b), ZnSe nanocrystals had peaks corresponding to wurtzite structure and peaks width was broadened due to formation of relatively small nanocrystals. An average nanocrystal size after the first stage of fabrication was estimated to be ~ 13 nm. It is noteworthy that we have not observed any additional peaks associated with ZnO or other impurities that could be produced at the stage of laser ablation.

D. Optical characterization of TM:II-VI NCD

After the first stage of preparation, absorption spectrum of the ZnS NQD reveals two minor absorption shoulders peaking at 295 and near 350 nm. After the second stage, the absorption peak at 350 nm disappears while the first peak is slightly blue shifted to 290 nm. We assume that this band is associated with excitonic absorption of ZnS NQD. The blue shift of absorption band indicates strong quantum size effect. The sizes of the NCD could be estimated using the approximation equation [41] and is approximately equal to 3 nm, which is quite consistent with the XRD analysis.

Spectroscopic characteristics of Cr and Co doped NCDs in mid-IR spectral region were studied under 1.6 μm laser excitation. Room-temperature fluorescence spectra of Cr:ZnS and Cr:ZnSe NCDs are shown in the Fig. 8A and 9A. The luminescence spectra of bulk crystals obtained at the same experimental conditions are shown on the same graphs for comparison. Luminescence bands of ZnS and ZnSe NCDs were blue shifted compared to the bulk crystals as can be seen in the Fig 8A and 9A.

There are several possible explanations of this phenomenon. One of the most probable reasons affecting the shape of luminescence spectrum is absorption of OH groups that possibly present on the surface of nanoparticles. A strong NCD luminescence signal suppression of wavelengths longer

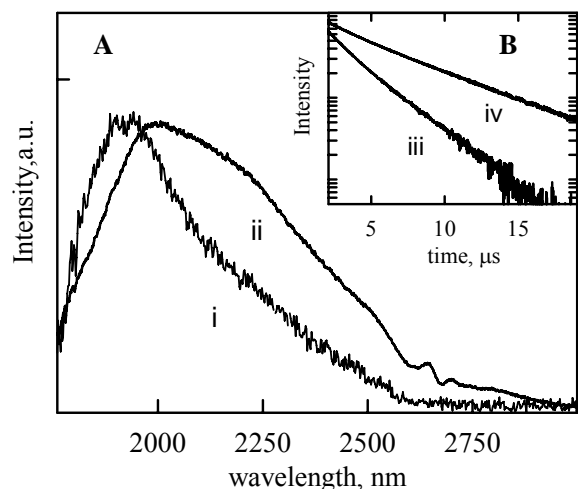


Fig. 8. (A) RT luminescence spectra of Cr doped ZnS NCD (i) and bulk (ii) samples. (B) Kinetics of fluorescence of the chromium doped ZnS NCD dots measured at room (iii) and 77K (iv) temperatures.

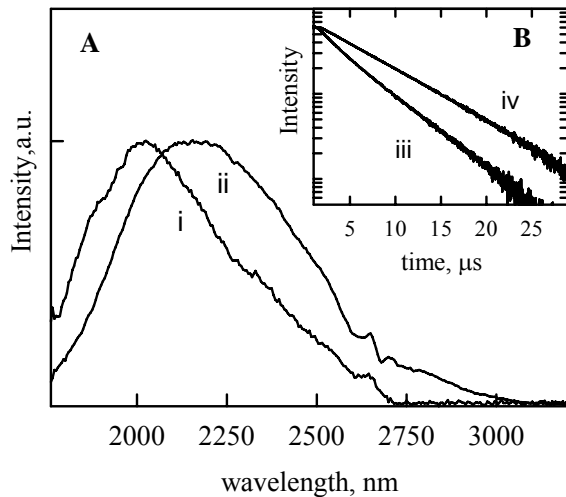


Fig. 9. (A) RT luminescence spectra of Cr doped ZnSe NCD (i) and bulk (ii) samples. (B) Kinetics of fluorescence of the chromium doped ZnSe NCD dots measured at room (iii) and 77K (iv) temperatures.

then 2600 nm comparing to bulk crystals strongly supports this hypothesis.

Another fact that further supports influence of OH group absorption is that luminescence maximum shift is more prominent in ZnSe nanoparticles since luminescence band of bulk ZnSe is located closer to the absorption band of OH group. Another cause of luminescence shift could be alteration of the strength of the crystal field in nanoparticles.

Luminescence kinetics of ZnS and ZnSe NCDs at RT and 77K are given in Fig. 8-B and Fig. 9-B, correspondingly. ZnS nanoparticles luminescence lifetime was smaller, down to 2.6 μs, comparing to 6μs typical to the bulk crystals. However, at 77 K NQD luminescence lifetime was 5μs, which is close to one in bulk sample. Thus we conclude that the major factor responsible for shorter Cr^{2+} excited state lifetime in nanoparticles is increased probability of non-radiative relaxation.

We have observed shorter Cr^{2+} excited state lifetime in the Cr:ZnSe NCDs as well.

Absorption spectra of Co^{2+} (d^7) doped II-VI semiconductors in middle IR region have two bands associated with transitions ${}^4A_2 \rightarrow {}^4T_1$ (~1500 nm) and ${}^4A_2 \rightarrow {}^4T_2$ (~3000 nm) [1]. ${}^4A_2 \rightarrow {}^4T_2$ transition is relatively weak since it is symmetry-forbidden [1]. Luminescence spectra of ${}^4A_2 \rightarrow {}^4T_2$ transition in Co:ZnSe quantum dots and bulk crystal excited to ${}^4A_2 \rightarrow {}^4T_1$ (~1600 nm) at room temperature are shown in Fig. 10A. It can be seen that Co^{2+} luminescence is strongly suppressed in 2800 nm region, which is another confirmation of OH group absorption influence to the TM luminescence in 3000 nm region. The lifetime of the excited 4T_2 state at room temperature in bulk crystal was ~200 μs. Cooling of the sample down to 77K led to increase of excited state life time to 1.1 ms (see Fig. 10 B), which is in good agreement with previously reported values [1]. We have not observed buildup of luminescence due to population of 4T_2 state, which is evident to fast excitation relaxation from 4T_1 to 4T_2 states. Luminescence kinetics of Co:ZnSe nanoparticles at room temperature (see Fig. 10B) was similar to kinetics in bulk and

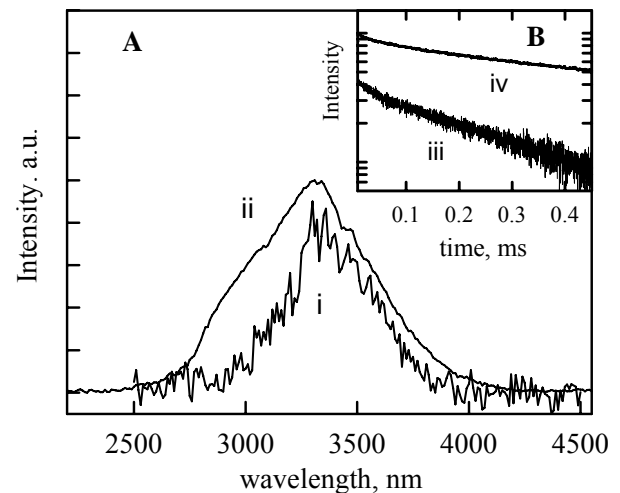


Fig. 10. (A) RT luminescence spectra of Co doped ZnSe bulk (ii) and NCD samples (i). (B) Kinetics of fluorescence of the Co doped ZnSe NCDs measured at room (iii) and bulk sample measured at T=77K (iv) temperatures.

the decay time was 220 μs. Thus we conclude that in Co ions doped samples there was no increase of non-radiative relaxations.

V. CONCLUSION

There is a significant progress in development of room temperature mid-infrared lasers based on Cr^{2+} doped chalcogenides (mainly Cr^{2+} :ZnSe and ZnS). These lasers have already become sources of choice for those who need a compact CW system with continuous tunability over 2-3.1 μm, output powers up to 2.7W, and high (up to 70%) conversion efficiency. This chapter has attempted to focus on specific regimes of operation of these lasers.

The unique blend of ultrabroadband gain bandwidth, high $\sigma\tau$ product and high absorption coefficients make these materials ideal candidates for microchip regime of operation. Future improvements in technology of hot-pressed ceramic Cr:ZnSe and ZnS materials could stimulate further cost reduction of fabrication process and scale up the output power and energy.

In addition, Cr^{2+} doped chalcogenide crystals featuring ultrabroadband gain bandwidth are ideal candidates for ultrabroadband and multiline lasing in spatially-dispersive cavities. These lasers can operate at many wavelengths simultaneously, producing any pre-assigned output spectral composition as well as a continuous ultrabroadband spectrum within 2-3 μm spectral range.

This article reviews these non-traditional Cr-doped mid-IR lasers as well as describes emerging Fe^{2+} :ZnSe lasers having potential to operate at room temperature over the spectral range extended to 3.7-5.1 μm. Recent progress in Fe^{2+} :ZnSe materials demonstrate that lasers on their basis can operate in gain-switched regime at room temperature with efficiencies of dozens of percents generating output energies from mJ level at RT till hundreds of mJ under thermoelectric cooling of the crystal. Future progress in developing pure cw Fe^{2+} lasers

depends on success of a search of new, less quenched bulk materials. Utilization of low-dimensional Fe^{2+} :ZnSe and ZnS structures with reduced phonon density of states could suppress thermal quenching of Fe^{2+} ions and make possible RT lasing over 3-5 μm spectral range under cw optical excitation.

In addition to effective RT mid-IR lasing transition metal doped II-VI media, being wide band semiconductors, hold potential for direct electrical excitation. This work shows the initial steps towards achieving this goal by studying Cr^{2+} , Co, and Fe doped quantum dots. We have demonstrated a novel method of TM doped II-VI NCD fabrication based on laser ablation in liquid environment. This technique has considerable advantage over chemical synthesis of doped II-VI NCDs due to possibility of doping nanocrystals with a variety of TM ions using laser ablation of thermo-diffusion doped polycrystalline II-VI targets. For the first time to our knowledge TM doped II-VI NCD demonstrated strong mid-IR luminescence. It opens a new pathway for future optically and electrically pumped mid-IR lasers based on TM doped quantum confined structures.

ACKNOWLEDGMENT

The authors would like to thank Andrew Gallian and Changsu Kim for help with experiments. We are also grateful to our colleagues and collaborators V. Badikov and D. Badikov (Kuban State University, Russia), E. Dianov and A. Zabezhailov (General Physics Institute, Russian Academy of Sciences), I. Kazakov, M.P. Frolov, Y.V. Korostelin, V.I. Kozlovsky, A.I. Landman, Y.P. Podmar'kov, V.A. Akimov, A.A. Voronov (P.N.Lebedev Physics Institute, Russian Academy of Sciences), I. Sorokina and E. Sorokin (Vienna University of Technology).

REFERENCES

- [1]. L. D. DeLoach, R.H. Page, G.D. Wilke, S. A. Payne, W. F. Krupke, "Transition Metal-Doped Zinc Chalcogenides: Spectroscopy and Laser Demonstration of a New Class of Gain Media", *IEEE J. QE* **32** 885-895 (1996).
- [2]. I. T. Sorokina, "Cr²⁺-doped II-VI materials for lasers and nonlinear optics," *Opt. Mater.*, vol. 26, pp. 395-412, 2004.
- [3]. S.B.Mirov, V.V.Fedorov, K. Graham, I.S.Moskalev, V.V.Badikov, V. Panutin, "Mid-IR Cr²⁺:ZnS and ZnSe microchip lasers", *Advanced Solid State Lasers*, Martin E. Fermann and Larry R. Marshall, eds. (Optical Society of America, Washington DC, 2002), pp.364-370.
- [4]. S.B.Mirov, V.V.Fedorov, K.Graham, I.Moskalev, V.Badikov, V. Panyutin, "Er-fiber laser pumped continuous-wave microchip Cr²⁺:ZnS and Cr²⁺:ZnSe lasers", *Optics Letters*, **27**, 909-911, (2002).
- [5]. S.B.Mirov, V.V.Fedorov, K.Graham, I.S.Moskalev, V.V.Badikov, V.Panutin, "CW and pulsed Cr²⁺:ZnS and ZnSe microchip lasers", in *OSA Trends in Optics and Photonics (TOPS) Vol. 73, Conference on Lasers and Electro-Optics*, OSA Technical Digest, Postconference Edition (Optical Society of America, Washington DC, 2002), pp.120-121.
- [6]. S.B. Mirov, V.V. Fedorov, K. Graham, I. S. Moskalev, I.T. Sorokina and E. Sorokin, V. Gapontsev, D. Gapontsev, V.V. Badikov, V. Panyutin "Diode and fiber pumped Cr²⁺:ZnS mid-IR external cavity and microchip lasers", *IEE Optoelectronics*, **150** (4), 340-345 (2003). This article has been awarded with the Snell Premium by the IEE, UK.
- [7]. J.Izawa, H.Nakajima, H. Hara, Y.Arimoto, "A tunable and longitudinal mode oscillation of a Tm,Ho:YLF microchip laser using an external etalon", *Opt.Comm.*, **180**, 137-140 (2000).
- [8]. H.Kukimoto, S. Shionoya, T. Koda, T. and R.Hioki, "Infrared absorption due to donor states in ZnS crystals", *J. Phys. Chem. Solids*, **29**, 935-940, 1968.
- [9]. C-H.Su, S. Feth, M.P. Voltz, R. Matyi, M.A. George, K. Chattopadhyay, A. Burger, S.L. Lehoczky, "Vapor growth and characterization of Cr-doped ZnSe crystals", *J. Crystal Growth* **207**, 35-42, 1999.
- [10]. D.R.Vij, N. Singh, "Luminescence and related properties of II-VI semiconductors" (Nova Science Publishers, Inc, Commack, NY, 1998).
- [11]. J.-O.Ndap, K. Chattopadhyay, O.O. Adetunji, D.E. Zelmon, A. Burger, "Thermal diffusion of Cr²⁺ in bulk ZnSe", *J. of Crystal Growth*, **240**,176-184 (2002).
- [12]. E. Carnall, S. E. Hatch, and W.F. Parsons, "Optical Studies on Hot-Pressed, Polycrystalline CaF₂ with Clean Grain Boundaries," *Mater. Sci. Res.* **3**, 165-173 (1966)
- [13]. A. Ikesue, T. Kinoshita, and K. Kamata, "Fabrication of polycrystalline, transparent YAG ceramics by a solid-state reaction method," *J. Am. Ceram. Soc.* **78**, 225-228 (1995).
- [14]. J. Lu, M. Prabhu, J. Song, C. Li, J. Xu, K. Ueda, A.A. Kaminskii, H. Yagi, and T. Yanagitani, "Optical properties and highly efficient laser oscillation of Nd:YAG ceramics," *Appl. Phys. B* **71**, 469-473 (2000).
- [15]. J. Lu, T. Murai, K. Takaichi, T. Uematsu, K. Misawa, M. Prabhu, J. Xu, K. Ueda, H. Yagi and T. Yanagitani, A. A. Kaminskii, and A. Kudryashov, "72 W Nd:Y₃Al₅O₁₂ ceramic laser," *Appl. Phys. Lett.* **78**, 3586-3588 (2001).
- [16]. A.Gallian, V.V.Fedorov, S.B.Mirov, V.V. Badikov S.N. Galkin, E.F. Voronkin, A.I. Lalayants, "Hot-Pressed Ceramic Cr²⁺:ZnSe Gain-Switched Laser", *Technical Digest, CLEO'05*, Baltimore, MD, May 22-27, 2005.
- [17]. A. Gallian, V.V. Fedorov, Sergey B. Mirov, V. V. Badikov, S. N. Galkin, E. F. Voronkin, A. I. Lalayants "Hot-Pressed Ceramic Cr²⁺:ZnSe Gain-Switched Laser," *Optics Express*, 2006 to be published.
- [18]. I.S.Moskalev, V.V.Fedorov, T.T.Basiev, P.G.Zverev, S.B.Mirov, "Application of laser beam shaping for spectral control of "spatially dispersive" lasers" Chapter 7, pp.241-267, in *Laser Beam Shaping Applications*, Dickey, Holswade, Shealy - Eds., Taylor & Francis, ISBN 0-8247-5941-9, 2005.
- [19]. I.S.Moskalev, V.V.Fedorov and S.B.Mirov, "Multiwavelength mid-IR spatially-dispersive CW laser based on polycrystalline Cr²⁺:ZnSe", in *Advanced Solid State Photonics 2005 Technical Digest on CD-ROM* (The Optical Society of America, Washington, DC, 2005), presentation number TuB12, ISBN: 1-55752-781-4.
- [20]. I.S. Moskalev, S.B. Mirov, V.V. Fedorov, "Multiwavelength mid-IR spatially-dispersive CW laser based on polycrystalline Cr²⁺:ZnSe", *OPTICS EXPRESS* **12**, 4986-4992 (2004).
- [21]. T.J.Carrig, G.J.Wagner, W.J.Alford, and A.Zakel, "Chromium-doped chalcogenides lasers", in *Solid State Lasers and Amplifiers*, Proc. SPIE, vol.5460, Bellingham, WA, 2004, pp. 74-82.
- [22]. K.L.Schepler, R.D.Peterson, P.A.Berry, J.B.McKay, "Thermal effects in Cr²⁺:ZnSe thin disk laser", *IEEE J.QE* **11** 713-720 (2005).
- [23]. A.Sennaroglu, U.Demirbas, N. Vermeulen, H.Ottevaere, H.Thienpont, Continuous-wave broadly tunable Cr:ZnSe laser pumped by a thulium fiber laser" *Optics Comm.*, **268** 1150120 (2006).
- [24]. 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.*, **24**, 1720-1722 (1999).
- [25]. V. A. Akimov, A. A. Voronov, V. I. Kozlovskii, Yu. V. Korostelin, A. I. Landman, Yu. P. Podmar'kov, M. P. Frolov, "Efficient IR Fe:ZnSe laser continuously tunable in the spectral range from 3.77 to 4.40 μm ," *Quantum Electron.*, **34**(10), 912-914 (2004).
- [26]. A. A. Voronov, V. I. Kozlovskii, Yu. V. Korostelin, A. I. Landman, Yu. P. Podmar'kov, M. P. Frolov, "Laser parameters of a Fe:ZnSe laser crystal in the 85-255K temperature range," *Quantum Electron.*, **35**(9), 809-812 (2005).
- [27]. V.V. Fedorov, S.B. Mirov, A. Gallian, D. V. Badikov, M.P. Frolov, Y.V. Korostelin, V.I. Kozlovsky, A.I. Landman, Y.P. Podmar'kov, V.A. Akimov, A.A. Voronov, "3.77-5.05- μm Tunable Solid State Lasers based on Fe²⁺-doped ZnSe Crystals Operating at Low and Room Temperatures", *IEEE J. of Quantum Electronics* **42** (9), 907-917 (2006).
- [28]. J.Kernal, V.V.Fedorov, A.Gallian, S.B.Mirov, V.Badikov, "3.9-4.8 μm gain-switched lasing of Fe:ZnSe at room temperature", *Optics Express*, **13**, n 26, 10608-10615 (2005).
- [29]. A.Gallian, I.S. Moskalev, V.V.Fedorov, S.B.Mirov, and K.L. Vodopyanov, "Parametrically Amplified Room Temperature 4.4 μm

Gain-Switched Fe:ZnSe Laser” Technical Digest on CD-ROM, CLEO’06, Long Beach, CA, May 21-26, 2006.

- [30]. V.V. Fedorov, A. Gallian, I. Moskalev, S.B. Mirov, “En route to electrically pumped broadly tunable middle infrared lasers based on transition metal doped II-VI semiconductors” J. of Luminescence, to be published (2006), doi:10.1016/j.jlumin.2006.08.010.
- [31]. L.Luke, V.V.Fedorov, I.Moskalev, A.Gallian, S.B.Mirov, “*Middle-infrared electroluminescence of n-type Cr-doped ZnSe crystals*” in Solid State Lasers XV: Technology and Devices, edited by Hanna J.Hoffman and Ramesh K. Shori, Proc. Of SPIE Vol. 6100 (SPIE, Bellingham, WE, 2006) 61000Y-1-8 (ISBN 0-8194-6142-3).
- [32]. A.Gallian, V.V.Fedorov, J.Kernal, J.Allman, S.B.Mirov, E.M.Dianov, A.O.Zabechaylov I.P.Kazakov, “Spectroscopic studies of Molecular-Beam Epitaxially Grown Cr²⁺-doped ZnSe thin films”, Appl. Phys. Lett., 86, 091105 (2005).
- [33]. S. Wang, S. B. Mirov, V. V. Fedorov, R. P. Camata, “*Synthesis and spectroscopic properties of Cr doped ZnS crystalline thin films*” in Solid State Lasers XIII: Technology and Devices, Proceedings of SPIE (2004) Vol. 5332, 13-20 Editors: Richard Scheps, Hanna J. Hoffman (ISBN 0-8194-5240-8)
- [34]. M. Luo, B.L. VanMil, R.P. Tompkins, T.H. Myers, N.C. Giles, “Photoluminescence of ZnTe and ZnTe: Cr grown by molecular-beam epitaxy” Appl. Phys. Lett 97, 013518-1-8 (2005).
- [35]. B.L. VanMil, A.J. Ptak, L. Bai, L.J. Wang, M.Chirila, N.C. Giles, T.H. Myers, L.Wang, “Heavy Cr doping of ZnSe by molecular beam epitaxy”, J. of Electronic Materials, 31, 770-775 (2002).
- [36]. M. S. Vitiello, F. Rizzi, G. Scamarcio, A. Colli, F. Martelli, “Intra-Atomic Mid-IR (3.7 μm) Luminescence In ZnSe:Fe Grown By Molecular Beam Epitaxy” AIP Proceedings 709, 446-447 (2004)
- [37]. R.N.Bhargava, D.Gallagher, XHong, A Nurmikko, “Optical properties of manganese-doped nanocrystals of ZnS”, Phys. Rev. Lett. 72(3), 416-419 (1994).
- [38]. M.Tanaka, “Photoluminescence properties of Mn²⁺ doped II-VI semiconductor nanocrystals”, J. of Luminescence 100, 163-173 (2002).
- [39]. K.V. Anikin, N.N. Melnik, A.V. Simakin, G.A. Shafeev, V.V. Voronov, A.G. Vitukhnovsky, “Formation of ZnSe and CdS quantum dots via laser ablation in liquids”, Chemical Physics Letters 366, 357-360 (2002).
- [40]. T. Sasaki, Y. Shimizu, N. Koshizaki, Journal of Photochemistry and Photobiology A: Chemistry, “Preparation of metal oxide-based nanomaterials using nanosecond pulsed laser ablation in liquids”, 182, 335-341 (2006).
- [41]. V.T.Liveri, M. Rossi, G.D.Arrigo, D.Manno, G.Micoccim Synthesis and characterization of ZnS nanoparticles in water/AOT/n-heptane microemulsions”, Appl. Phys. A 69 (4), 369-373 (1999).



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, 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 of the Russian Academy of Sciences. His early work in 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. He 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.

Since 1993 Dr. Mirov is a faculty member at the Department of Physics of the University of Alabama at Birmingham (UAB), USA. Currently, he is a professor of physics at the 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. In 2004 the Institute of Electrical Engineers in the United Kingdom has named Dr. Mirov and his team recipients of the Snell Premium award for the input in optoelectronics

and development of Cr²⁺: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. He has authored or co-authored over two hundred seventy scientific publications in the field of quantum electronics, has published 1 book, several book chapters, and holds thirteen patents.



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 joint 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 of the University of Alabama at Birmingham (UAB), USA. During the last 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.



Igor S. Moskalev was born in Belarus, USSR in 1973. He received his bachelor degree in physics from Novosibirsk State University, Russia in 1986 and till 1998 he worked as a research assistant in the Institute of Laser Physics, Novosibirsk, Russia, where he was involved in development of a highly stable, single frequency, diode pumped Nd:YAG laser with intracavity frequency doubling. Since 1998 till 1999 he worked as a research assistant in Hong Kong University of Science and Technology where he studied algal motility using a modified laser PIV system. He joined the Department of Physics of the University of Alabama at Birmingham (UAB), USA in 2000 and received his M.S. degree in physics in 2002, and his Ph.D. degree in physics in 2004 from UAB for his work on development of ultrabroadband, multiwavelength, tunable semiconductor and Cr²⁺:ZnSe solid-state lasers. Currently he is involved in development of novel laser systems based on semiconductor materials with transition metals impurities. Dr. Moskalev is a member of the Optical Society of America. With colleagues, he received the "Snell Premium" of the Institute of Electrical Engineers of the United Kingdom in 2004 for development of Cr²⁺:ZnS mid-IR external cavity and microchip lasers.



Dmitri V. Martyshkin was born in Russia in 1973. He received his bachelor degree from Novosibirsk State University, Russia in 1996. He received his master degree and his Ph.D in Physics from University of Alabama at Birmingham, USA in 2000 and 2004 respectively. Dr. Martyshkin is involved in application of laser spectroscopy such as Raman, fluorescence, surface enhanced Raman spectroscopy (SERS), laser induces breakdown spectroscopy (LIBS), and cavity ring-down spectroscopy (CRDS) for biomedical applications. He is also involved in development and characterization of novel materials designed for construction of photonic devices as well as for biomedical application.