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Broadly Tunable Chromium Doped Zinc Selenide Laser in the Mid-Infrared Region

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ABSTRACT

Cr^{2+}:ZnSe is one of the most studied and effective laser materials which meet all the previous mentioned requirements. The new active materials as well as new methods of other wavelengths generation are desired. One of the new materials investigated thoroughly in the past is ZnSe crystal doped with chromium ion. Recently, Cr^{2+} doped chalcogenide lasers have emerged as an attractive source of tunable laser radiation in the 2-3 μm region. In contrast to many other transition metal doped solids, Cr^{2+} ions in II-VI materials can exhibit significantly higher quantum yields at room temperature. Thermal diffusion doping is the widely used postgrowth technique for the preparation of Cr^{2+}:ZnSe samples. Further optimization of the materials preparation are needed to obtained laser quality samples for future mid-infrared laser performance testing. The important advantage of Cr^{2+}:ZnSe is the availability of the technologically developed and low cost polycrystalline material which makes the idea of the practical tunable diode pumped Cr^{2+}:ZnSe laser feasible. Solid state tunable mid-infrared laser radiation sources operating at room temperature are required for many applications in spectroscopy, including chemical monitoring, ranging, remote sensing, medical diagnosis, medical treatment, and also for coherent pumping of solid state lasers as well as nonlinear optical materials.

Keywords **– Cr^{2+}:ZnSe laser, Transition metal doped II-VI, Tunable mid-infrared, Solid state, Room temperature, Transition metal ion doped**

I. INTRODUCTION

Recently, transition metal ions (Cr^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, etc…) doped zinc and cadmium chalcogenides (ZnSe, ZnTe, CdSe, CdTe, etc…) have been evaluated as an innovative class of laser media. Divalent transition metal doped II-VI chalcogenide laser materials have recently attracted much attention due to their interesting features; room temperature operation between 2 and 5 μm, broad tenability, possibility of direct diode pumping and continuous wave (cw) operation [1]. Cr^{2+} doped broadband II-VI chalcogenide lasers, which were first suggested and later studied, represent nowadays the only room temperature, diode pump able, and simple alternative to the existing mid-infrared laser sources, based either on cryogenic crystalline lasers or on cascaded quantum well materials, or use of nonlinear frequency down conversion approaches [2].

The development of the diode pumped Cr^{2+}:ZnSe laser, better understanding of the earlier phenomena is important, since it allows optimization of the preparation techniques of the concentrated Cr^{2+}:ZnSe crystals used in the diode pumped systems with respect to their spectroscopic and laser quality [1]. The spectroscopic properties of transition metal doped II-VI compounds have been investigated for more than four decades now; technologically, these dopants were regarded as undesired impurities that acted as luminescence "killers" in visible emitting phosphors. Scientifically, highly resolved absorption spectra (usually obtained at low temperature) provided data for tests of crystal field theories. The need for a compact (diode pumped), efficient, room temperature operated broadly tunable mid-infrared solid state laser has proven a strong driving force for the investigation of transition metal doped chalcogenides as a new class of laser media [3, 4].

Chromium doped chalcogenides, and particularly Cr^{2+}:ZnSe have demonstrated to be extremely attractive for room temperature laser operation. Up to now, room temperature pulsed lasing has been demonstrated for Cr^{2+}:ZnSe [4, 5]. An all solid state Cr^{2+}:ZnSe pulsed laser using strained layer InGaAsP/InP laser diodes for direct laser diode pumping has also been demonstrated. More recently, the first cw room temperature operation of a broadly tunable Cr^{2+}:ZnSe laser has also been achieved, with a tuning range from 2138 to 2760 nm, the broadest wavelength tuning yet demonstrated from any room temperature cw laser [3].

The mid-infrared wavelength range, which is also often called a "molecular fingerprint" region, and in particular, the range between 2 and 5 μm is characterized by the presence of the strong fundamental and overtone vibrational absorption lines of atmospheric constituents, vapours and other gases. The crystalline solid state lasers which operate room temperature and have the largest relative bandwidth of the central wavelength of the laser can provide very high power levels retaining the good beam quality and narrow spectral linewidth at the wide tuning range. In combination with near infrared diode lasers as pump sources these lasers can offer stability, efficiency and compactness as well as the broad spectral coverage and tuning ranges, which are generally inaccessible for semiconductor lasers [6]. Cr^{2+} ions are incorporated in a tetrahedral coordination in II-VI semiconductor hosts, which is in contrast to the octahedral coordination of transition metal doped oxide and fluoride crystals. The tetrahedral coordination of transition metal ions in II-VI semiconductors directly effects the crystal field energy level splitting, electron-phonon interactions, emission quantum yields, and provides radiative emission further into the mid-infrared spectral region. Polycrystalline ZnSe and CdTe windows have proven to be promising candidates as host materials for Cr^{2+} ions. In addition, ternary Cd based II-VI materials are also being considered as novel Cr^{2+} laser hosts [7]. A typical feature of transition metal impurities in semiconductors in general, and of chromium in II-VI compounds in particular is the existence of several possible charge states of a given transition metal ion in a given host. Thus, although the neutral charge state of chromium in II-VI semiconductors is Cr^{2+}, both Cr^{1+} ($3d^5$) and Cr^{2+} ($3d^3$) may exist.

Presently available coherent mid-infrared sources include lead salt diode lasers, which produce milliwatt powers and require cryogenic techniques, some rare earth ion lasers, whose tenability is limited, and nonlinear optical devices like Raman shifters, frequency mixers, and optical parametric oscillator. The latter class offers the widest tunability but may require injection seeding with one or shorter wavelength lasers to obtain good wavelength stability, linewidth, and output mode quality. In spite of rapidly occurring improvements in materials properties and phase matching techniques, the nonlinear optical schemes remain too complex for many applications [4].

Besides basic research applications, such tunable lasers are of particular importance for environmental monitoring, military countermeasures, medical applications and remote sensing [3]. Availability, since recently, of the room temperature diode pumped broadband tunable solid state lasers as simple and compact alternative to semiconductor lasers and nonlinear optical frequency conversion devices in this wavelength region is a significant step forward in remote sensing and trace gas detection, as well as in other medical applications [6]. Currently available tunable sources in this spectral range often suffer from drawbacks such as cryogenic operation (the lead salt diode lasers), complexity (the broadly tunable optical parametric oscillators) or narrow tuning range.

High sensitivity spectroscopic detection is of special importance for trace gas sensing applications that have an increasing impact in numerous areas including fundamental spectroscopy, atmospheric chemistry, industrial process, and medical diagnostics. The infrared spectral region has the considerable advantage of being the location of relatively strong absorption molecular bands. The tunable lasers used in these techniques do not allow simultaneous coverage of broad spectral ranges. The broadband detection is required when there is a need to selectively detect several molecular gas species simultaneously by means of high sensitivity absorption spectroscopy [8].

For analyzing the broadband laser emission spectrum, Fourier transform spectrometers appear as the most efficient instruments. They need only one single detector. Furthermore, time resolved Fourier transform interferometers are available, which permit temporal sampling of the laser transient spectral dynamics observed in the repetitive pulsed operation mode. These results in the measurement of numerous spectra observed at different generation times under the same experimental sample conditions. This allows precise determination of equivalent absorbing paths by verifying the consistency of the time evolution of different spectral lines, making possible accurate line intensity measurement by intracavity laser absorption spectroscopy [9].

Since the first demonstrations in 1995 at Lawrence Livermore National Laboratory the laser related research largely focused around Cr^{2+}:ZnSe, Cr^{2+}:ZnS and Cr^{2+}:CdSe lasers. Namely, zinc chalcogenides doped with Cr^{2+}, Co^{2+}, Ni^{2+}, and Fe^{2+}, and demonstrated efficient, room temperature lasing action near 2.5 µm by using Cr^{2+}:ZnSe and Cr^{2+}:ZnS [4, 5]. Transition metal doped chalcogenide lasers are of high interest because of their versatility, broad room temperature wavelength tenability, demonstrated high optical efficiencies, potential to be scaled to high powers via direct diode pumping and relative novelty. To date, cw gain switched and mode locked laser operation has been demonstrated. Material advantages can include broad absorption and emission bands, high fluorescence quantum efficiencies at room temperature, moderate gain cross sections, and minimal susceptibility to loss mechanisms, such as excited state absorption or up conversion [10].

Additionally, cw Cr^{2+}:ZnSe laser has been shown to operate with greater than 50% optical to optical efficiency at room temperature and to be continuously tunable from 2.138 to 2.760 µm. Direct quasi cw diode pumping of a pulsed Cr^{2+}:ZnSe laser has also been demonstrated and describe cw mode locked operation of a Cr^{2+}:ZnSe laser [11]. However, in this case the gain element is made of a new Cr^{2+}:ZnSe laser material: hot pressed Cr^{2+}:ZnSe ceramic gain media. It is noteworthy that the technology of hot pressed Cr^{2+}:ZnSe ceramic is in the very early stage of development [12].

The used ceramic samples were fabricated with relatively low Cr concentration for spectroscopic characterization and optimization of the technological processes. For this reason in our current laser experiments with the Cr^{2+}:ZnSe ceramic media we used the available ceramic gain element with significantly lower Cr doping level as compared to the Cr^{2+}:ZnSe polycrystalline samples. This leads to much higher cw lasing threshold and much lower output power as compared to the polycrystalline Cr^{2+}:ZnSe. In this work, we describe broadly tunable chromium doped zinc selenide laser in the mid-infrared region.

II. TRANSITION METAL BASED SOLID STATE LASERS

Historically, the first tunable cw solid state lasers were those based on the divalent 3d transition metal ions. It should be noted that the existing transition metal ions, lasing on the 3d-3d transitions in the mid-infrared can be divided into two major groups: those ions, which occupy octahedral sites (Co^{2+} and Ni^{2+} in halides), and those, which can be found in tetrahedral positions (Cr^{2+}, Co^{2+}, Ni^{2+}, and Fe^{2+} in chalcogenides). The electric dipole transitions of the ions in octahedral sites (possessing inversion symmetry) are parity forbidden and have therefore generally low oscillator strength and long lifetime. The Cr^{2+} ions reside in II-VI hosts in tetrahedral sites. These sites do not posses inversion symmetry and are characterized by the high oscillator strength (high cross section) and short lifetime of typically a few microseconds [5]. The other distinguishing feature of the Cr^{2+} ions in tetrahedral sites is the relatively low crystal field splitting, placing optical transitions into infrared.

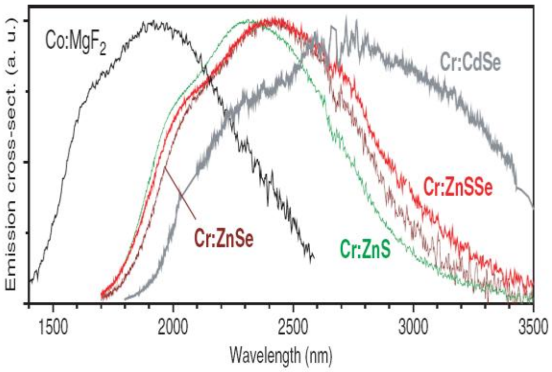

Figure 1. Gain curves of the existing ultra broadband mid-infrared lasers at room temperature [6]

The transition metal ions doped II-VI semiconductor compounds are promising materials for laser operation in the mid-infrared spectrum especially for the possibility of wavelength tuning in a broad range. Broadband transition metal ion doped solid state lasers are being frequently used as a constituent driving part of the optical parametric devices. At the same time they represent an attractive and simple alternative to these somewhat more complex and costly devices in the mid-infrared. In the recent years along with the Ti:sapphire based lasers systems, parametrically converting radiation to the mid-infrared, a lot of attention of researchers was devoted towards the alternative compact and cost effective cw and ultrashort pulsed sources based on Cr^{2+} doped crystals of the II-VI family. In the last decade a number of such sources have been developed in the "molecular fingerprint" range ~2 and 3.5 µm (Fig. 1).

At longer wavelengths (2 µm) the multiphonon relaxation processes set the fundamental limit for obtaining cw room temperature laser operation from vibronic transitions. Because of this the majority of the known vibronically broadened laser transitions in the mid-infrared are quenched at room temperature. At room temperature the latter is close to unity in Cr^{2+}:ZnSe and is comparably high in order chalcogenide materials. This provides Cr^{2+}:ZnSe the highest gain among vibronic lasers and enables efficient room temperature operation. It is not surprise that in the following years Cr^{2+}:ZnSe draw a lot attention as a room temperature broadly tunable cw laser operating around 2.5 µm [2, 13, 14]. Since all the higher lying states are singlets or triplets, the excited state absorption transitions from the upper state are spin forbidden. Altogether this ensures that Cr^{2+}:ZnSe has the highest gain among all vibronic solid state lasers and enables efficient broadband room temperature operation. One of the crystals of this family, Cr^{2+}:ZnSe, exhibited efficient room temperature diode pumped cw and mode locked operation also in the ceramic form. These lasers are nowadays probably the simplest and the most cost effective light sources in this wavelength region [11, 15, 16].

II.1. THE MATERIAL AND SPECTROSCOPIC PROPERTIES

The material and spectroscopic properties of the most important crystalline hosts for Cr^{2+} ion are summarized in Table 1 and Table 2 respectively. Among the listed crystals especially Cr^{2+}:ZnSe, Cr^{2+}:ZnS and Cr^{2+}:CdSe distinguished by their remarkable characteristics.

Table 1. Material properties of Cr^{2+} doped laser crystals [6]

	ZnSe	ZnS	CdSe
Crystal structure	cubic	Mixed-polytype	Cubic, uniaxial
Lattice constant (A˚)	5.67	5.4	6.05
Transparency range (µm)	0.5-20	0.4-14	0.8-18
Hardness	120	160	70
Refractive index	2.45	2.27	2.47
Thermal conductivity (W/mºC)	18	17	4
Thermal expansion (10^{-6}/ºC)	7.3	6.4	4.9
dn/dT (10^{-6}/ºC)	70	46	98
Bandgap (eV)	2.8	3.8	1.7

The materials can be produced by a variety of methods, including several direct growth techniques and diffusion doping. The principal material disadvantages include a high dn/dT (the change in refractive index with temperature) and, for some applications, a short energy storage time. The high dn/dT is an issue because it can lead to strong thermal lensing, which complicates high power laser designs. Cr^{2+}:CdSe has a somewhat larger lattice constant than Cr^{2+}:ZnSe and Cr^{2+}:ZnS (Table 1). The Cr^{2+} emission is therefore shifted by 100-200 nm towards the infrared and spreads out to over 3.5 µm. If not rather inferior to Cr^{2+}:ZnSe thermo optical properties, this laser crystal would be a perfect candidate for cw lasing beyond 3 µm. Similarly to Cr^{2+}:ZnSe and due to the same reason, the lifetime of 6 µs in Cr^{2+}:CdSe does not change between 60 and 300 K. The peak absorption and emission cross section were measured to be $3x10^{-18}$ cm^2 and $2x10^{-18}$ cm^2 respectively [17].

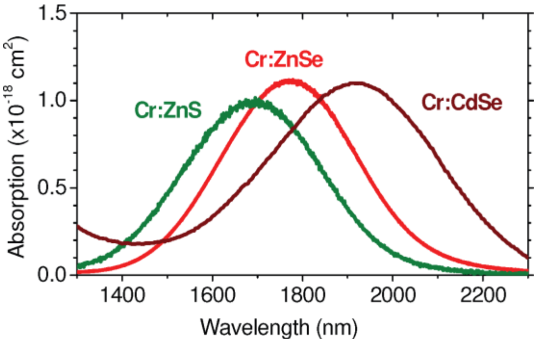

Figure 2. Absoption spectra of Cr^{2+}:ZnSe, Cr^{2+}:ZnS and Cr^{2+}:CdSe [6]

Table 2. Spectroscopic and laser characteristic of Cr^{2+} doped laser materials [6]

	ZnSe	ZnS	CdSe
Peak emission	130	140	200
Cross section $\sigma_{emission}$	90	75	-
Peak absorption	110	100	300
Cross section $\sigma_{absorption}$	87	52	-
Saturation intensity (kW/cm^2)	11	14	8
Luminescence bandwidth (nm)	900	800	550
Relative bandwidth	0.41	0.34	0.25
Optical quantum efficiency	1	0.73	1
Slope efficiency (%)	53	71	48
Cw output power (W)	1.8	0.7	-
Output energy (mJ-average pow.)	0.43	0.1	0.8
Mode locked output power (mW)	120	140	-
Pulse duration (fs)	80	$1x10^{-3}$	-
Diode pumping	yes	yes	no

The spectroscopic properties of Cr^{2+} (d^4) ion in II-VI compounds have been extensively studied since back in the sixties [18-20] and later in the seventies-eighties [21-25]. The absorption and emission spectra of Cr^{2+} ion in Cr^{2+}:ZnSe, Cr^{2+}:ZnS and Cr^{2+}:CdSe are depicted in Fig.1 and Fig. 2 respectively. A broad absorption band centered around ~1.8 μm in Cr^{2+}:ZnSe, around ~1.7 μm in Cr^{2+}:ZnS and around ~1.9 μm in Cd compounds allows pumping by Tm doped lasers, which are available as pulsed and cw sources of over 100 W average power and recently also as fiber lasers with even higher power [6]. It should be here that these media are characterized by high transition cross section, all being the results of inversion symmetry at the Cr^{2+} site (Table 2). Another important point is the additional broadening of the fluorescence spectrum due to the large Jahn-Teller splitting of the ground state, reaching 340 cm^{-1} and 300 cm^{-1} in Cr^{2+}:ZnSe and Cr^{2+}:ZnS respectively [20]. Among other II-VI compounds ZnS is distinguished by the largest energy gap of 3.8 eV, the smallest lattice constant and the correspondingly blue shifted fluorescence peaking around 2.1 μm (the corresponding emission cross section peaking around 2.3 μm). As in case of Cr^{2+}:ZnSe the measurements yielded decreased radiative lifetime of 5 μs and correspondingly corrected absorption and emission cross sections of ~$1x10^{-18}$ cm^2 and $1.4x10^{-18}$ cm^2 respectively. Cr^{2+}:ZnS, otherwise very similar to Cr^{2+}:ZnSe is characterized by a more rapid onset of the thermally activated nonradiative decay with temperature (Fig. 3). Relatively to the 77 K lifetime the room temperature lifetime drops by ~24%. The difference between Cr^{2+}:ZnSe and Cr^{2+}:ZnS may be explained by a higher maximum phonon frequency in this crystal (compare ~250 cm^{-1} in ZnSe and ~350 cm^{-1} in ZnS) [26, 27]. On the positive side there are the lowest dn/dT and the best hardness and the highest damage threshold among the Cr^{2+} doped media. All this makes Cr^{2+}:ZnS especially attractive for high power applications.

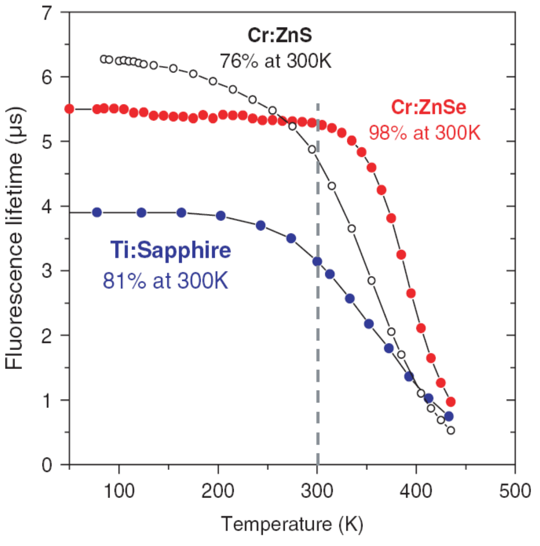

Figure 3. Temperature dependence of the active ion lifetime in Cr^{2+}:ZnSe, Cr^{2+}:ZnS and Ti:sapphire [6]

II.2. Cr^{2+}:ZnSe LASER COMPONENTS

Active material, Cr^{2+}:ZnSe crystal grown by the special Bridgman method was prepared in the form of 6 mm thick block. The concentration of Cr^{2+} active ions in ZnSe matrix was ~$1.0x10^{19}$ cm^{-3}. The measured single pass absorption of Cr^{2+}:ZnSe crystal in rectangular position was ~36% and ~33% for the wavelength 1.66 μm and 1.97 μm, respectively. The setup for testing laser properties Cr^{2+}:ZnSe crystal is shown in Fig. 4. Here, the test crystal is a thin, uncoated slab with parallel faces near the center of a confocal cavity. Test crystals were placed at the center of a confocal resonator whose dielectric coated mirrors had 20 cm radii of curvature. Coatings were centered at ~2350 nm and covered the 2200-2520 nm range. So far, most of the laser testing has been done with crystals grown by the Bridgman technique. Inspection with a microscope shows that these samples are not homogeneous, but have inclusions and/or voids which are tentatively attributed to selenium rich or metal rich precipitates [28]. With no tuning elements in the laser cavity, both the Cr^{2+}:ZnSe and Cr^{2+}:ZnS lasers operated at the emission peak of ~2350 nm with a bandwidth ~40 nm. In that wavelength region, the mirror reflectivities were fairly constant, and ground state absorption from Cr^{2+} appears to be nonexistent.

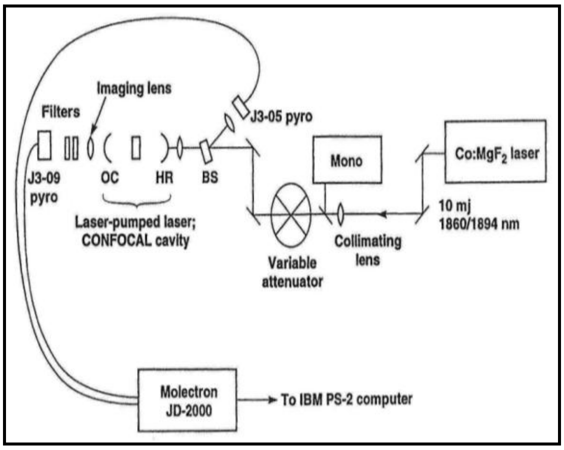

Figure 4. Experimental setup for testing Cr^{2+} laser [4]

We review the fluorescence properties of the Cr^{2+}:ZnSe medium. In particular, we present data that show how the lifetime and the fluorescence efficiency vary with the active ion concentration. An empirical fit is also obtained for the concentration dependence of the lifetime. We further discuss the models used for the determination of the absorption cross section from cw and pulsed absorption saturation measurements. Since lifetime data are needed in the cw analysis of saturation.

Cr^{2+}:ZnSe is attractive for room temperature cw laser applications because of a near unity fluorescence quantum efficiency at 300 K, a high gain cross section ($\sigma_{emission}$ ~$9x10^{-19}$ cm^2), and extremely wide vibronically broadened absorption and emission bands. Additionally, the Cr^{2+} ion in the ZnSe host effectively has a two term electronic structure (transitions to higher lying levels are spin forbidden and, presumably, very weak) that precludes losses that are due to excited state absorption or upconversion but allows four level laser action [13]. All of them report Cr^{2+} lifetime in various chalcogenides to be a few microseconds and not quenched up to ~300 K. The extensive lifetime measurements were carried out in the last years for mainly polycrystalline as well as for single crystalline Cr^{2+}:ZnSe crystals [29]. The latter study report only negligible increase of the lifetime from 5.4 µs at 77 K to 5.6 µs at 300 K.

To summarize, the advantages of Cr^{2+} doped chalcogenide materials include:

- Broad absorption bands (relaxed pump wavelength constraints)
- Broad emission bands (enables very broad laser tuning)
- Large emission cross sections (for instance, $\sigma_{emission}$ ~8x3 10^{19} cm^2 in ZnSe)
- Minimal problems of excited state absorption (no spin allowed excited state transitions from the upper laser level)
- High fluorescence quantum efficiencies at 300 K (enables efficient room temperature laser operation)
- High thermal conductivities (18 Wm^{-1} K^{-1} for ZnSe, 17-27 Wm^{-1} K^{-1} ZnS, and 6-7 Wm^{-1} K^{-1} for CdSe)
- Ability to produce material by several techniques (modified Bridgman growth technique and by diffusion doping)
- Readily available host material (polycrystalline material can be diffusion doped) [10].

III. EXPERIMENTAL PROCEDURE

The fundamental reason for the lack of tunable solid state mid-infrared lasers is the paucity of known materials luminescent in that region; the usual explanation for the long wavelength cutoff in the luminescence is the rapid onset of radiation less decay associated with multiphonon emission. As the electronic transition energy gap declines with increasing emission wavelength, the multiphonon emission rate overtakes and ultimately overwhelms the radiative transition rate, quenching the luminescence. Naturally, when solid state host dopant systems are considered, the long wavelength emission properties depend crucially on the choices of host and dopant [4]. Recently we undertook a spectroscopic study to search for potential laser materials for the 2-5 µm range. Here, in finding a new class of tunable mid-infrared lasers Cr^{2+} ions in II-VI hosts (ZnSe). This class of lasers shows potential for high slope efficiency at room temperature, use of long wavelength laser diodes as pump sources, and coverage of most of the 2-3 µm range.

The low phonon frequencies of heavy ion host materials give rise to infrared transparency, such that low loss windows, lenses, etc., for high power 10.6 µm operation are conveniently fabricated from ZnSe and other II-VI compounds. As the energy gap law tell us, the multiphonon emission rate for a given is reduced as the phonon frequency is lowered. So, the tendency for luminescence quenching is reduced on this account as well [4].

To our knowledge, based on the scientific literature, the potential for laser action went unrecognized in spite of spectroscopic research spanning three decades. Our recent spectroscopic characterization focused on properties relevant to laser performance: absorption and emission cross sections, emission lifetimes, emission quantum yields, and the likelihood of significant excited state absorption. Most of the measurements were made at room temperature (Fig. 5), without regard to spectroscopic fine structure or detailed spectral assignments [5]. In this experiment tenability between 2.1 µm and 2.85 µm was achieved at up to 10 W output power. Based on the analysis of the mechanical, thermal, spectroscopic, and laser properties of Cr^{2+}:ZnSe, the output powers over 10 W in cw regime and several Watts in the mode locked or amplifier regime can be anticipated. A representative room temperature optical absorption spectrum for Cr^{2+} doped ZnSe is shown in Fig. 5. The Cr^{2+} concentration in this particular sample was determined to be $5x10^{18}$ cm^{-3}. For reference, the fundamental (band to band) absorption of an undoped ZnSe sample at ~440nm is also shown (see dotted line).

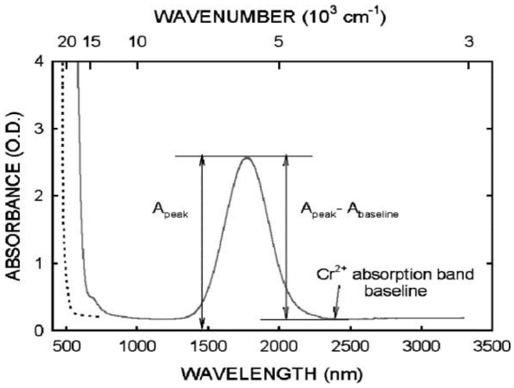

Figure 5. Room temperature absorption spectrum of a Cr^{2+} doped ZnSe sample [3]

The following achievements so far have been demonstrated with Cr^{2+} doped ZnSe laser: cw TEM_{00} output power over 1.7 W, as well as over 1100 nm tunability and narrow linewidth operation (A laser schematic is shown in Fig. 6).

Crystals were longitudinally pumped and placed in a three mirror resonator. Laser crystals were 2-3 mm thick and oriented at Brewster's angle. A key feature of this design is the use of a gold mirror to double pass the pump light through the laser crystal while maintaining good pump and cavity mode overlap. This enabled the laser to produce higher output power and use more of the pump beam than a single pass device, without sacrificing efficiency. Laser line widths were on the order of 35-50 nm, similar to the pulsed lasers described previously.

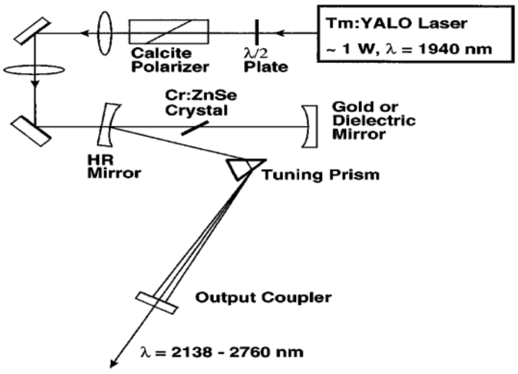

Figure 6. Schematic of the optical system and laser cavity used for most of the Cr^{2+}:ZnSe laser experiments [13]

Diode pumping has been realized in a quasi cw regime in transversal pumped scheme, and recently, the cw operation of the diode end pumped Cr^{2+}:ZnSe laser has been reported

[1]. They present the diode pumped room temperature cw Cr^{2+}:ZnSe laser, which is tunable over 350 nm. The laser delivered around 2.5 mm up to 70 mW of polarized radiation in a single transverse mode.

Cr^{2+}:ZnSe is one of the most studied and effective active laser materials which meet all the previous mentioned requirements. So far the Cr^{2+}:ZnSe crystal samples were produced mainly by the diffusion doping technique. In their study they have investigated Cr^{2+}:ZnSe bulk crystal samples grown by the special Bridgman method. The Cr^{2+} ion concentration was lx10^{19} cm^{-3}. Cr^{2+}:ZnSe crystal bulks with a diameter up to 50 mm and a length up to 100 mm were produced. From the bulk the Cr^{2+}:ZnSe dispersive prism was polished. This Cr^{2+}:ZnSe dispersive prism was utilized as a laser active material and simultaneously as a wavelength tuning element inside the laser resonator [30].

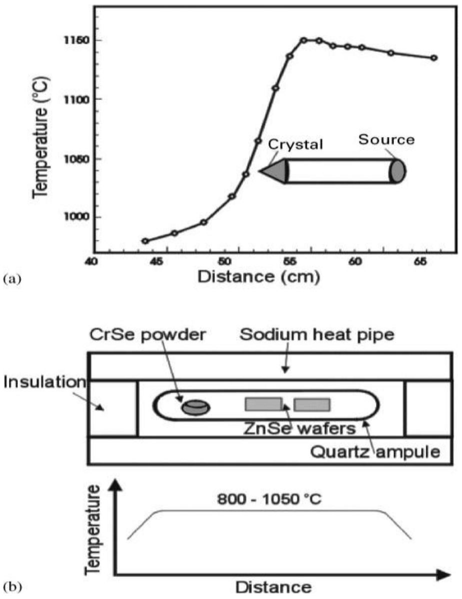

Figure 7. Experimental setup for the preparation of Cr^{2+}:ZnSe samples by (a) physical vapor transport, (b) solid state diffusion doping [3]

In general, dopant concentration levels of the order of 10^{18}-10^{19} cm^{-3} are usually needed to provide device required characteristics. Compared with melt grown and post growth diffusion doped ZnSe crystals, physical vapor transport grown chromium doped ZnSe possesses the highest optical quality and lowest loss [4]. Concentrations in excess of 10^{19} Cr^{+2} ions/cm^3 comparable to the previously reported values for melt grown Cr^{+2} doping ZnSe material, have been obtained by diffusion doping and physical vapor transport growth. The setup for both the physical vapor transport growth and diffusion doping methods are shown in Fig. 7.

However, the reported luminescence lifetimes varied considerably from sample to sample. A specific goal of the present study was to perform a systematic study that will comparatively evaluate the luminescent properties of ZnSe samples doped with chromium during growth by physical vapor transport with samples doped post growth by thermal diffusion.

We report the experimental observation of the significant change of the upper laser level population under low power visible excitation, which is explained by the enhanced charge transfer process. For laser experiments, three laser crystals were available, two of them grown by physical vapor transport and one by chemical vapor transport methods. The crystals were diffusion doped with Cr^{2+} ions reaching concentration between 5x10^{18} cm^{-3} and 2x10^{19} cm^{-3}. The crystal thickness varied between 1.5mm and 3 mm, providing over 80% absorption at the pump wavelength of 1600 nm.

III.1. SPECTROSCOPIC MEASUREMENTS

Transmission and absorption measurements were performed using Bruken Equinox 55 Fourier transform FTIR spectrophotometer (Department of Physics, METU, Ankara-Turkey). A selective group of Cr^{2+} doped ZnSe and CdTe windows possessing different absorption coefficients and Cr^{2+} concentration were further evaluated for mid-infrared laser applications.

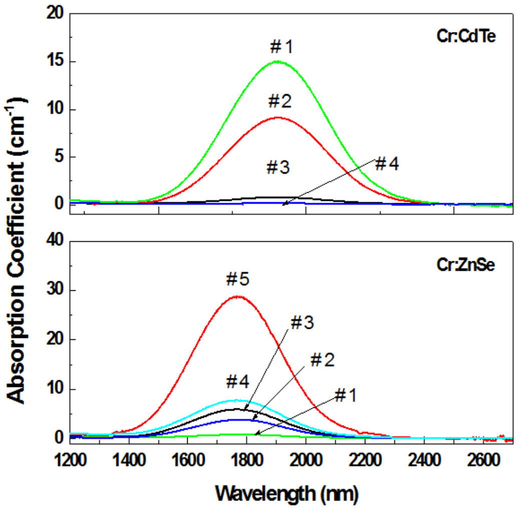

Figure 8. Absorption spectra of Cr^{2+}:ZnSe and Cr^{2+}:CdTe polycrystalline window materials [31]

In addition, the absorption and emission properties of a series of Cr^{2+} doped single crystals including CdTe. The Cr^{2+}:ZnSe and Cr^{2+}:CdTe series was evaluated for possible compositional effects, which may alter the spectroscopic properties of Cr^{2+} ions. The mid-infrared emission measurements were performed using a Tm fiber laser operating at 1907 nm. The emission was detected with an InSb detector and dispersed by a 0.3 m spectrometer with a 150 g/mm grating blazed at 2000 nm. A series of samples with different Cr^{2+} concentrations was prepared for Cr^{2+}:ZnSe and Cr^{2+}:CdTe windows. The background corrected absorption spectra of Cr^{2+}:ZnSe and Cr^{2+}:CdTe windows are shown in Fig. 8.

The successful incorporation of Cr^{2+} ions into the II-VI materials (windows) is evidenced by the strong absorption bands centered at ~1750 nm for Cr^{2+}:ZnSe and at ~1900 nm for Cr^{2+}:CdTe [10, 31]. All samples exhibited the characteristic absorption and emission features of tetrahedral coordinated ions. The mid-infrared emission properties of these materials are promising for solid state laser development in the 2-3 µm spectral region.

III.2. NANOCRYSTALLINE Cr^{2+}:ZnSe LASER

The Cr^{2+} doped laser materials are characterized by high gain and an intrinsically low lasing threshold, as well as by such remarkable spectroscopic features as the absence of excited state absorption and high quantum yield. The active media can be obtained by diffusion doping of metallic chromium into the ceramic ZnSe. Along with several other techniques of producing ceramic ZnSe, the latter is often obtained by hot pressing the micro and nanocrystalline ZnSe powder. Cr^{2+}:ZnSe lasers can be operated in pulsed mode by using a second pulsed pump laser whose wavelength overlaps with the absorption band. The peak powers obtainable from pulsed pump sources are typically high and lasing can thus be achieved at lower average pump powers than those needed for cw pumping.

An important feature, distinguishing the Cr^{2+} doped materials from all the other solid state lasers combines the properties of semiconductors with that of the traditionally used in solid state lasers dielectric materials. Cr^{2+} doped materials possess the excellent laser properties along with the interesting physics as well as optical and nonlinear properties, distinguishing them from the traditionally used dielectric laser media. This opens up an exciting white field of research and new opportunities for the use of these materials in laser and nonlinear optical applications, as well as for direct electrical pumping.

Because of the semiconductor nature of II-VI compounds the charge transfer processes play an important role in these materials. The most important features of these materials, which distinguish them from other oxide and fluoride laser crystals:

1. Noncentrosymmetric tetrahedral sites for Cr^{2+} ions. This leads to the partially allowed electric dipole transitions and large absorption and emission cross sections (10^{-18} cm^2).
2. Covalent rather than ionic type of bonding leads to the fact that intraionic laser processes are not purely intracentral in these materials, which results in high probability of charge transfer processes and explains multiple valency of transition metal ions, especially in highly concentrated samples (~10^{19} cm^{-3}), as required for diode pumping.
3. Semiconductor nature of the crystals implies that charge transfer processes generate free carriers leading to photorefractive phenomena, it also leads to the high second and third order nonlinearity of the host crystal.

As it has been recently shown, the charge transfer processes in some cases may affect the laser performance of Cr^{2+}:ZnSe and Cr^{2+}:ZnS lasers with the active ions in tetrahedral sites [1, 32]. In both these lasers we observed a novel effect of sensitization (modulation) of the induced radiation around 2.5 μm with only a few milliwatt of the visible and near infared radiation (470-770 nm). The reported phenomenon is of the photorefractive nature and involves charge transfer to chromium ions, similar to the mechanism of photorefraction, which takes place in other transition metal doped chalcogenides.

Summarizing, the described effect of sensitization of induced radiation can be used for both, electrical pumping of Cr^{2+} laser, and for opto-optical switching. Indeed, the “zero to one” switching was realized in Cr^{2+}:ZnSe laser by switching on and off the probe beam, whereas the laser changed its condition from the state with no lasing to the state with laser operation. This was a proof of principle demonstration of using a diode pumped solid state laser as an alternative type of switching device. Maybe one of the most exciting developments in Cr^{2+} doped lasers recently was the demonstration of the first Cr^{2+}:ZnSe random nanolaser, based on nanometer (down to 200 nm) sized Cr^{2+}:ZnSe powder emitting around 2.4 μm.

High quality transparent ceramic laser gain media have a number of potential advantages over conventional solid state gain elements: absence of internal stress typical for single crystals; negligible scattering losses common for polycrystalline media such as ZnSe; flexibility in the spatial distribution of the gain centers, which allows for efficient compensation of thermal lensing effects (which are very problematic for conventional Cr^{2+}:ZnSe media). Therefore, fabrication of high quality Cr^{2+}:ZnSe ceramic gain media is of a great interest for development of advanced mid-infrared laser systems.

IV. CONCLUSION

We have provided a comprehensive review of the work on the development of Cr^{2+}:ZnSe lasers. A detailed account of the preparation methods and spectroscopic characterization techniques was presented. Diffusion doping was described in detail and various methods for the determination of the diffusion coefficient were discussed. Pulsed, cw, and mode locked operations of the Cr^{2+}:ZnSe lasers were also reviewed.

Summarizing, Cr^{2+} doped lasers have come of age and already entered several real world applications, such as gas analysis, ultra sensitive spectroscopy, and quantum optics. As an extension of previous work, we present the results of a systematic study which investigates the synthesis of Cr^{2+}:ZnSe and Fe^{2+}:ZnSe samples by thermal diffusion. In particular, we have measured how the diffusion parameters such as temperature and time influence the chromium and iron concentrations inside the host and determined the diffusion coefficient for both Cr^{2+}:ZnSe and Fe^{2+}:ZnSe. In the case of Cr^{2+}:ZnSe, we have further characterized the spatial transverse uniformity of the diffusion doped samples.

The results of the absorption and room temperature luminescence measurements are given in Fig. 9 and summarized in Table 3. As seen in Fig. 1, the high quality absorption due to predominantly Cr^{2+} ions could be obtained in this crystal with peak absorption coefficient of 9.5 cm^{-1} the maximum around 1.69 μm. The room temperature lifetime was measured to be 3.7 μs, which is close to the corresponding value measured in concentrated Cr^{2+}:ZnSe and Cr^{2+}:ZnS, as are the corresponding values for absorption and emission cross sections. However, emission bandwidth is noticeably broader than in Cr^{2+}:ZnSe or Cr^{2+}:ZnS and is peaked at the same wavelength as in Cr^{2+}:ZnSe (Fig. 9).

Table 3. Main spectroscopic data of Cr^{2+} doped laser materials [6]

	ZnSe	**ZnS**	**ZnSSe**
Absorption peak (nm)	1770	1695	1696
Absorption width (nm)	355	350	400
Gain peak (nm)	2400	2315	2410
Gain bandwidth (nm)	850	800	930
Lifetime at 300 K (μs)	4.8	4.3	3.7

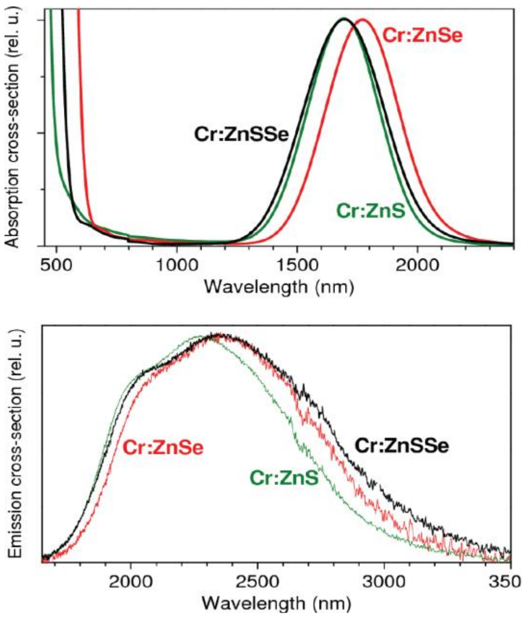

Figure 9. Comparison of the absorption (upper graph) and fluorescence (lower graph) spectra of Cr^{2+}:ZnSe, Cr^{2+}:ZnS, and Cr^{2+}:ZnSSe [6]

The most impressive results have been obtained so far using the Cr^{2+}:ZnSe crystals. The Cr^{2+}:ZnS crystal was less studied as a laser material due to the lack of good optical quality single crystals. Having similar spectroscopic properties to Cr^{2+}:ZnSe, Cr^{2+}:ZnS is known to have a larger band gap, better hardness, a higher thermal shock parameter (5.3 $W/m^{1/2}$ and 7.1 $W/m^{1/2}$ in Cr^{2+}:ZnSe and Cr^{2+}:ZnS, respectively [33]), and the lower dn/dT than in Cr^{2+}:ZnSe (Table 1). At the same time, the temperature quenching of the Cr^{2+}:ZnS lifetime starts at lower temperatures, than in Cr^{2+}:ZnSe (Fig. 3), which might be a serious disadvantage, especially in cw applications. With proper cooling, however, the power handling capability of this material should be on par or better than that of Cr^{2+}:ZnSe, making Cr^{2+}:ZnS attractive for high power applications.

It is noteworthy that as a result of numerous experiments with Cr^{2+}:ZnSe gain media we found that there are no significant advantages of using single crystalline over the polycrystalline ZnSe host material. However, from practical point of view, the technology for polycrystalline active elements is much cheaper, and high quality undoped polycrystalline ZnSe material is widely available in various sizes for further thermal diffusion Cr^{2+} doping. For these reasons, all the experiments with high power Cr^{2+}:ZnSe lasers, where relatively long gain elements are required, were conducted with the polycrystalline Cr^{2+}:ZnSe gain media. There are several reasons why the Cr^{2+}:ZnS a laser system performs much better than the Cr^{2+}:ZnSe laser in our arrangement. First of all, the emission wavelength of the pump diode is ~1685 nm, which is practically at the maximum of absorption curve of Cr^{2+}:ZnS gain media. Secondly, the Cr^{2+}:ZnS gain element has about 1.70 times higher Cr^{2+} concentration that the Cr^{2+}:ZnSe gain element used in the experiments. As a result of these two factors more pump power is absorbed by the Cr^{2+}:ZnS gain crystal than by the Cr^{2+}:ZnSe gain element and we observe higher overall efficiency on the incident pump for the Cr^{2+}:ZnS laser system. Undoubtedly, more careful design of the Cr^{2+}:ZnSe gain element will allow one to obtain similar output characteristics as for the Cr^{2+}:ZnS diode pumped laser.

Nowadays, femtosecond pulses in this wavelength range are being produced by multi stage parametric frequency converters based on Ti:sapphire laser, which are rather bulk and inefficient in comparison to the directly diode pumped Cr^{2+}:chalcogenide lasers, emitting in this wavelength region. In the last few years picosecond mode locking, both active and passive, has been achieved in Cr^{2+}:ZnSe and Cr^{2+}:ZnS laser [11]. The first works used an acousto optic modulator to mode lock the laser with the shortest pulses being 4 ps at up to 400mW output power. Later, the first semiconductor saturable absorber mode locked Cr^{2+}:ZnSe laser generating 11 ps pulses at 2.5 μm at 400mW output power was demonstrated [11]. The pulse duration was presumed to be limited by some intrinsic limitation like an etalon. For some time the reported pulse durations were in the picosecond range. To overcome a picosecond barrier in Cr^{2+} lasers became therefore a highly desirable, but also a very challenging task. Recently we could finally identify the physical cause of this picosecond barrier, which was due to the water absorption lines in the resonator around 2.5 μm. Finally we should note that Cr^{2+}:ZnSe is capable of power scaling and producing up to 1 μJ pulses directly from the oscillator. Looking into the future one can envisage broadband tunable and high power Cr^{2+}:ZnSe based nanocrystalline doped fiber lasers, operating in the very interesting for remote sensing and trace gas sensing applications wavelength region around 2.5 μm. Development of such a laser, which would be complementary to the existing Tm fiber laser at 1.9 μm, will be a leap forward in the fiber laser technology. Therefore, medical applications as ophthalmology, tissue cutting and welding, neurosurgery, dermatology and bioimaging would benefit from broadband and rapidly tunable coherent sources in this wavelength region.

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REFERENCES

[1] E. Sorokin and I.T. Sorokina, Tunable diode-pumped continuous-wave Cr^{2+}:ZnSe laser, *Applied Physics Letters, 80(18)*, 2002, 3289-3291.

[2] I.T. Sorokina, E. Sorokin, A.D. Lieto, M. Tonelli, R.H. Page and K.I. Schaffers, Efficient broadly tunable continuous-wave Cr^{2+}:ZnSe laser, *Journal of the Optical Society of America B, 18(7),* 2001, 926-930.

[3] A. Burger, K. Chattopadhyay, J.O. Ndap, X. Ma, S.H. Morgan, C.I. Rablau, C.H. Su, S. Feth, R.H. Page, K.I. Schaffers and S.A. Payne, Preparation conditions of chromium doped ZnSe and their infrared luminescence properties, *Journal of Crystal Growth, 225(2-4),* 2001, 249-256.

[4] 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 Journal of Quantum Electronics, 33(4),* 1997, 609-619.

[5] 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 Journal of Quantum Electronics, 32(6),* 1996, 885-895.

[6] I.T. Sorokina, Broadband mid-infrared solid-state lasers, *Topics in Applied Physics, 79*, 2003, 255-350.

[7] U. Hömmerich, J.T. Seo, A. Bluiett, M. Turner, D. Temple, S.B. Trivedi, H. Zang, S.W. Kutcher, C.C. Wang, R.J. Chen and B. Schumm, Mid-infrared laser development based on transition metal doped cadmium manganese telluride, *Journal of Luminescence, 87-89,* 2000, 1145-2000.

[8] N. Picque, F. Gueye and G. Guelachvili, Time-resolved Fourier transform intracavity spectroscopy with a Cr^{2+}:ZnSe laser, *Optics Letters, 30(24),* 2005, 3410-3412.

[9] V.M. Baev, T. Latz and P.E. Toschek, Laser intracavity absorption spectroscopy, *Applied Physics B: Lasers and Optics, 69(3),* 1999, 171-202.

[10] T.J. Carrig, Transition-metal-doped chalcogenide lasers, *Journal of Electronic Materials, 31(7),* 2002, 759-769.

[11] T.J. Carrig, G.J. Wagner, A. Sennaroglu, J.Y. Jeong and C.R. Pollock, Mode-locked Cr^{2+}:ZnSe laser, *Optics Letters, 25(3),* 2000, 168-170.

[12] S. Mirov, V. Fedorov, I. Moskalev and D. Martyshkin, Recent progress in transition metal doped II-VI mid-IR lasers, *Journal of Specification Topics in Quantum Electronics, 13(3),* 2007, 810-827.

[13] G.J. Wagner, T.J. Carrig, R.H. Page, K.I. Schaffers, J.O. Ndap, X. Ma and A. Burger, Continuous-wave broadly tunable Cr^{2+}:ZnSe laser, *Optics Letters, 24(1),* 1999, 19-21.

[14] A. Sennaroglu, A.O. Konza and C.R. Pollock, Continuous-wave power performance of a 2.47 µm Cr^{2+}:ZnSe laser: experiment and modelling, *IEEE Journal of Quantum Electronics, 36(10),* 2000, 1199-1205.

[15] E. Sorokin, S. Naumov and I.T. Sorokina, Ultrabroadband infrared solid-state lasers, *IEEE Journal of Selected Topics in Quantum Electronics, 11(3),* 2005, 690-712.

[16] E. Sorokin, I.T. Sorokina, A.D. Lieto, M. Tonelli and P. Minguzzi, Mode-locked ceramic Cr^{2+}:ZnSe laser, *OSA Trends in Optics and Photonics, 83, (Advanced Solid-State Lasers),* 2003, Optical Society of America, Washington, pp. 227-230.

[17] K.L. Schepler, S. Kueck and L. Shiozawa, Cr^{2+} emission spectroscopy in CdSe, *Journal of Luminescence, 72-74,* 1997, 116-117.

[18] J.T. Vallin, G.A. Slack, S. Roberts and A.E. Hughes, Near and far infrared absorption in Cr doped ZnSe, *Solid State Communications, 7(17),* 1969, 1211-1214.

[19] J.T. Vallin, G.A. Slack, S. Roberts and A.E. Hughes, Infrared absorption in some II-VI compounds doped with Cr, *Physical Review B, 2(11),* 1970, 4313-4333.

[20] M. Kaminska, J.M. Baranovski, S.M. Uba and J.T. Vallin, Absorption and luminescence of Cr^{2+} (d^4) in II-VI compounds, *Journal of Physics C: Solid State Physics, 12(11),* 1970, 2197-2214.

[21] G. Grebe and H.J. Schulz, Luminescence of Cr^{2+} centers and related optical interactions involving crystal field levels of chromium ions in ZnS, *Zeitschrift für Naturforschung A, 29(12),* 1974, 1803-1809.

[22] G. Grebe, G. Roussos and H.J. Schulz, Infrared luminescence of ZnSe:Cr crystals, *Journal of Luminescence, 12-13*, 1976, 701-705.

[23] R. Renz and H.J. Schulz, Temperature dependence of the lifetime of excited states for 3d transition element centers in II-VI crystals, *Journal of Luminescence, 24-25(1),* 1981, 221-224705.

[24] G. Goetz and H.J. Schulz, Decay of internal luminescence transitions of 3d-impurities in II-VI compounds-recent experiments and refined interpretations, *Journal of Luminescence, 40-41,* 1988, 415-416.

[25] H. Pradella and U.W. Pohl, Luminescence of the Cr^{+} center in ZnSe, *Physica Status Solidi B, 141(2),* 1987, K143-K146.

[26] A.K. Arora, E.K. Suh, U. Debska and A.K. Ramdas, Raman-scattering study of the high-pressure phase transition in $Zn_{1-x}Mn_xSe$, *Physical Review B, 37(6),* 1988, 2927-2932.

[27] O. Brafman and S.S. Mitra, Raman effect in wurtzite and zinc-blende-type ZnS single crystals, *Physical Review, 171(3),* 1968, 931-934.

[28] K.T. Chen, M.A. George, Y. Zhang, A. Burger, C.H. Su, Y.G. Sha, D.C. Gillies and S.L. Lehoczky, Selenium precipitation in ZnSe crystals grown by physical vapor transport, *Journal of Crystal Growth, 147(3-4),* 1995, 292-296.

[29] U. Demirbas, A. Sennaroglu and M. Somer, Synthesis and characterization of diffusion-doped Cr^{2+}:ZnSe and Fe^{2+}:ZnSe, *Optical Materials, 28(3),* 2006, 231-240.

[30] P. Koranda, M.E. Doroshenko, H. Jelinkova, J. Sulc, M. Nemec, T.T. Basiev, V.K. Komar and M.B. Kosmyna, Broadly tunable Cr:ZnSe laser, *2007 and the International Quantum Electronics Conference.* CLEOE-IQEC 2007, European Conference on, 17-22 June 2007.

[31] I.T. Sorokina, Cr^{2+} -doped II-VI materials for lasers and nonlinear optics, *Optical Materials, 26(4),* 2004, 395-412.

[32] I.T. Sorokina, E. Sorokin, S. Mirov, V. Federov, V. Badikov, V. Panyutin and K. Schaffers, Broadly tunable compact continuous-wave Cr^{2+}:ZnS laser, *Optics Letters, 27(2),* 2002, 140-142.

[33] R.H. Page, L.D. DeLoach, G.D. Wilke, S.A. Payne, R.J. Beach and W.F. Krupke, Cr^{2+} -doped II-VI crystals: new widely tunable, room-temperature mid-IR lasers, *Lasers and Electro-Optics Society Annual Meeting (8th Annual Meeting Conference Proceedings), 1,* 1995, 449-450.