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Citation: Sennaroglu, A. et al. "Chromium-doped zinc selenide gain media: from synthesis to pulsed mid-infrared laser operation." Optical Components and Materials VII. Ed. Shibin Jiang et al. San Francisco, California, USA: SPIE, 2010. 75981B-10. ©2010 SPIE.

As Published: <http://dx.doi.org/10.1117/12.847098>

Publisher: SPIE

Persistent URL: <http://hdl.handle.net/1721.1/58561>

Version: Final published version: final published article, as it appeared in a journal, conference proceedings, or other formally published context

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Chromium-doped zinc selenide gain media: From synthesis to pulsed mid-infrared laser operation

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ABSTRACT

This paper provides an overview of the experimental work performed in our research group on the synthesis, spectroscopic investigation, and laser characterization of chromium-doped zinc selenide ($\text{Cr}^{2+}:\text{ZnSe}$). By using diffusion doping, 40 polycrystalline $\text{Cr}^{2+}:\text{ZnSe}$ samples with ion concentration in the range of 0.8×10^{18} to 66×10^{18} ions/cm³ were prepared. From the absorption data, temperature-dependent diffusion coefficient of chromium and losses at the lasing wavelength were measured. In luminescence measurements, the concentration dependence of the fluorescence lifetime and fluorescence quantum efficiency was determined. During continuous-wave operation, the optimum concentration for lasing was determined to be 8.5×10^{18} ions/cm³ at an incident pump power of 2.1 W for 1800-nm pumping. During gain switched operation, intra-cavity pumping with a 1570-nm optical parametric oscillator resulted in continuous tuning between 1880 and 3100 nm. By employing dispersion compensation with a MgF_2 prism pair, Kerr-lens mode-locked operation was also demonstrated at 2420 nm, resulting in the generation of 95-fs pulses with an average output power of 40 mW and spectral bandwidth of 69 nm. The time-bandwidth product of the pulses was further measured to be 0.335 close to the expected value of 0.315 for sech^2 pulses.

Keywords: Tunable solid-state lasers, chalcogenide lasers, $\text{Cr}^{2+}:\text{ZnSe}$ lasers, diffusion doping, Kerr-lens mode locking, mid-infrared lasers, II-VI compound semiconductors, solid state spectroscopy.

1. INTRODUCTION

The spectroscopic properties of II-VI compound semiconductors (such as ZnSe, ZnS, CdTe, and others, also referred to as chalcogenides) doped with transition metal (TM) ions such as Cr^{2+} and Fe^{2+} have long been known¹⁻⁹. In particular, introducing TM ions into these hosts leads to the formation of strong absorption and emission bands in the mid infrared region of the electromagnetic spectrum. In late 1990s, pioneering work performed at the Lawrence Livermore National Laboratories further demonstrated laser action in $\text{Cr}^{2+}:\text{ZnSe}$ and $\text{Cr}^{2+}:\text{ZnS}$ ^{10, 11} near 2500 nm. Since then, lasing has been observed in numerous TM ion-doped chalcogenides¹²⁻²⁰. One of the most extensively studied members of this class of solid-state lasers is $\text{Cr}^{2+}:\text{ZnSe}$. It possesses several favorable spectroscopic properties that make it an important source of coherent radiation in the mid infrared region around 2.5 μm . These include 1) nearly unity luminescence quantum efficiency at room temperature, 2) broad absorption band near 1800 nm which allows optical pumping with Tm- and Er-based lasers, among others, 3) absence of excited-state absorption at the lasing wavelength around 2400 nm, and 4) presence of a vibronically broadened emission band extending over the 2-3 μm region which is suitable for the generation of mode-locked pulses with sub-20-fs duration. An additional unique feature of $\text{Cr}^{2+}:\text{ZnSe}$ is that diffusion doping can be employed to prepare doped, laser-active samples at very low cost by using commercially available ZnSe substrates²¹⁻²³.

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Cr²⁺:ZnSe lasers have several potentially important applications, one of which is high harmonic generation²⁴. Recent studies show that it is possible to increase the cut-off wavelength of harmonics in the deep ultraviolet and soft x-ray region by using femtosecond excitation lasers with longer central wavelengths in the mid infrared²⁵. Such wavelengths can be attained by using nonlinear wavelength conversion schemes²⁶⁻²⁹. Alternatively, Cr²⁺:ZnSe or other chalcogenide lasers can be employed to directly generate laser radiation at these long wavelengths. Other potential applications of Cr²⁺:ZnSe lasers include spectroscopy, pumping of optical parametric oscillators or Raman gain media to attain even longer wavelengths in the mid infrared and the development of mid-infrared optical combs for frequency metrology. Extensive review of the development and applications of chalcogenide lasers may be found in Refs.³⁰⁻³⁴.

To date, different modes of operation have been demonstrated with Cr²⁺:ZnSe lasers. These include gain switched^{10, 11}, continuous-wave (cw) tunable³⁵, actively mode-locked^{36, 37}, passively mode-locked³⁸⁻⁴⁰ and microchip laser⁴¹ operations with as high as multi-watt cw output powers^{42, 43}. Furthermore, by employing intra-cavity pumping, the broadest tuning range reported to date spans the 1.88-3.1 μm region⁴⁴.

This paper provides an overview of the experimental work conducted in our research group at Koç University, İstanbul, Turkey aimed at the synthesis and characterization of Cr²⁺:ZnSe for laser applications. Section 2 first describes the preparation of polycrystalline Cr²⁺:ZnSe samples by using the method of thermal diffusion doping. Spectroscopic characterization involved the measurement of the absorption/emission spectra, passive losses at the lasing wavelength, determination of the temperature dependence of the diffusion coefficient in ZnSe, fluorescence quantum efficiency as a function of doping concentration, and fluorescence lifetime as a function of concentration. In Sections 3 and 4, we discuss the cw and gain-switched operations of Cr²⁺:ZnSe lasers at room temperature. In particular, intra-cavity pumping with an optical parametric oscillator (OPO) resulted in a broad tuning range extending from 1880 to 3100 nm. Furthermore, we experimentally determined the optimum ion concentration for cw lasing. Finally, Section 5 summarizes our recent ultrashort pulse generation experiments where 95-fs pulses were generated at 2420 nm by using the method of Kerr-lens mode locking.

2. SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF POLYCRYSTALLINE Cr²⁺:ZnSe

Thermal diffusion doping was employed to prepare the Cr²⁺:ZnSe samples used in this study²³. In particular, in each doping run, a polycrystalline ZnSe substrate with a diameter of 10 mm and thickness of 2.0 mm was placed together with CrSe dopant powder inside an evacuated (pressure < 10⁻⁵ mbar) silica ampoule and heated to temperatures in the 800-1100 °C range. The diffusion time of samples was varied between 6 hours and 43 days. Altogether, about 40 Cr²⁺:ZnSe samples were prepared with different peak absorption coefficients (at 1775 nm) in the range of 0.9-76 cm⁻¹. The average Cr²⁺ ion concentration of each sample was estimated by using the absorption cross-section value reported by Vallin ($\sigma_{\text{abs}} = 1.15 \times 10^{-18}$ cm² at 1775 nm)⁶. The average Cr²⁺ ion concentration of the samples varied in the range of 0.8x10¹⁸-66x10¹⁸ ions/cm³.

Thermal diffusion doping leads to a non-uniform dopant distribution inside the crystal. By measuring the variation of the absorption coefficient as a function of position and by using a three-dimensional diffusion model, we further determined the diffusion coefficient D for chromium ions inside ZnSe for samples prepared at different temperatures. At 1000 °C, D was determined to be 5.4 x 10⁻¹⁰ cm²/s for Cr²⁺:ZnSe. The temperature dependence of D was further measured between 800 and 1100 °C²³.

By using the absorption spectra and by subtracting the Fresnel losses, we further determined the variation of the passive losses near 2500 nm as a function of active ion concentration. This is a very important parameter to characterize in an actual laser since the lasing threshold as well as the slope efficiency of the laser depend on the level of passive losses. From the absorption measurements performed with more than 10 polycrystalline samples, the differential loss coefficient α_{2500} at 2500 nm (in units of cm⁻¹) of the Cr²⁺:ZnSe samples was found to increase approximately linearly with average Cr²⁺ concentration (denoted as N_{Cr} (ions/cm³)) according to the empirical relation⁴⁵

$$\alpha_{2500} \approx (0.04 \pm 0.02) + \{(0.02 \pm 0.01) \times 10^{-18}\} N_{\text{Cr}}. \quad (1)$$

The concentration dependence of losses could be due to defects introduced during diffusion, other impurities such as Fe in the dopant, or self absorption⁴⁶⁻⁵⁰. Note that there is a residual loss of $0.04 \pm 0.02 \text{ cm}^{-1}$ at low doping levels possibly due to scattering.

In order to investigate the effect of doping concentration on fluorescence strength, we measured the fluorescence lifetime and fluorescence efficiency of the $\text{Cr}^{2+}:\text{ZnSe}$ samples. In the lifetime measurements, a 1570-nm, KTP optical parametric oscillator (OPO) was used. The OPO generated 65-ns pulses at a pulse repetition rate of 1 kHz. The time-dependent fluorescence of the samples was monitored by using an InGaAs detector with a response time of 3 ns. Measurements performed with twenty-six $\text{Cr}^{2+}:\text{ZnSe}$ samples of varying active ion concentration show that the fluorescence lifetime decreases monotonically with active ion concentration as was observed in earlier studies^{21, 51}. Furthermore, the concentration dependence of the fluorescence lifetime (τ_F) could be fitted to an empirical formula of the form⁴⁵

$$\tau_F = \frac{\tau_{F0}}{1 + \left(\frac{N_{Cr}}{N_0} \right)^2}, \quad (2)$$

where τ_{F0} is the fluorescence lifetime at low doping levels, N_{Cr} is the chromium ion concentration, and N_0 is the concentration where τ_F is reduced to $\tau_{F0}/2$. The best-fit values of τ_{F0} and N_0 were determined to be $5.56 \text{ } \mu\text{s}$ and $17 \times 10^{18} \text{ ions/cm}^3$. Since the reduction in the fluorescence lifetime stems from non-radiative decay that increases with concentration, we see that samples with Cr^{2+} concentration less than approximately $10 \times 10^{18} \text{ ions/cm}^3$ (corresponding peak absorption coefficient of 11.5 cm^{-1} at 1775 nm) are less susceptible to non-radiative losses during cw operation.

Phonon-assisted non-radiative decay is another source of unwanted loss during lasing. To characterize this further, we also measured the temperature dependence of the fluorescence lifetime for a $\text{Cr}^{2+}:\text{ZnSe}$ sample with Cr^{2+} concentration of $5.7 \times 10^{18} \text{ ions/cm}^3$, where concentration-dependent non-radiative decay is minimal. For temperatures above $60 \text{ }^\circ\text{C}$, we observed a sharp increase in nonradiative decay rates similar to previous studies^{10, 21, 51}. The temperature dependence of the fluorescence lifetime at low doping concentrations could be obtained from the empirical equation⁴⁵

$$\frac{1}{\tau_F(T)} = \frac{1}{\tau_R} + \frac{1}{\tau_{NR}(T)} = \frac{1}{\tau_R} + \frac{1}{\tau_{NR0}} \text{Exp}\left(-\frac{\Delta E}{k_B T}\right), \quad (3)$$

where $\tau_F(T)$ is the temperature-dependent fluorescence lifetime, τ_R^{-1} is the spontaneous radiative decay rate, $\tau_{NR}(T)^{-1}$ is the temperature-dependent nonradiative decay rate, τ_{NR0} is the high temperature limit of the nonradiative decay rate, ΔE is the activation energy, k_B is Boltzmann's constant and T is the absolute temperature in degrees Kelvin. The best-fit values of τ_{NR0} and ΔE were determined to be 0.63 ps and 4260 cm^{-1} , respectively, for $\text{Cr}^{2+}:\text{ZnSe}$. Furthermore, the critical temperature (defined as $T_{1/2}$ in ref⁵²) at which the fluorescence lifetime drops to half of the radiative lifetime comes to $115 \text{ }^\circ\text{C}$. Hence, for local temperatures below 100°C and doping levels less than $10 \times 10^{18} \text{ ions/cm}^3$, undesirable effects due to non-radiative decay should be relatively low.

We further carried out fluorescence efficiency measurements to estimate the optimum doping concentration for cw lasing. In these measurements, a home-built cw $\text{Cr}^{4+}:\text{YAG}$ laser at 1510 nm and a commercial cw thulium fiber laser at 1800 nm (IPG Photonics) were used as excitation sources. In both cases, lock-in detection was employed together with a 0.5-m Czerny-Turner type monochromator and a PbS detector to measure the variation of the fluorescence as a function of wavelength. To obtain a quantitative measure for the emission strength of the samples, we experimentally determined the fluorescence efficiency η_F at 2400 nm, defined as

$$\eta_F = \frac{I_{2400}}{P_{abs}}, \quad (4)$$

where I_{2400} is the measured fluorescence intensity at 2400 nm and P_{abs} is the absorbed pump power at the excitation wavelength (1510 nm or 1800 nm). Note that although the measured fluorescence signal here is in arbitrary units, this method allows for a comparison of the fluorescence efficiency from different samples. Results showed that a sharp decrease in the fluorescence efficiency occurred with increasing Cr^{2+} concentration in agreement with the lifetime data. We could obtain a good fit to the fluorescence efficiency data by using the following empirical formula for η_F ⁴⁵:

$$\eta_F = a \ln \left[\frac{N_F}{N_{Cr}} \right]. \quad (5)$$

Clearly, the above formula is valid for doping concentrations below N_F . The fitting parameters a and N_F were determined to be 0.1725 and 68.4×10^{18} ions/cm³ (corresponding peak absorption coefficient at 1775 nm = 78.5 cm^{-1}), respectively.

Spectroscopic data presented so far can be used to estimate the optimum chromium concentration N_{opt} which maximizes the fluorescence power at the lasing wavelength for a given pump power. N_{opt} also depends on the sample length. The total emitted power at the lasing wavelength will be proportional to $A\eta_F$, where A is the absorption in a sample of length ℓ and is given by $A = 1 - \exp(-\sigma_a N_{Cr} \ell)$. Here, σ_a is the absorption cross section and N_{Cr} is the chromium ion concentration. As N_{Cr} increases, A monotonically increases and approaches unity at large doping levels. The product $A\eta_F$, on the other hand, attains a local maximum and then decreases to zero as N_{Cr} is varied. By using the best-fit parameters obtained from the experimentally measured fluorescence efficiency data, our simple model predicts that for a 2-mm-long sample, the optimum chromium concentration is about 6×10^{18} ions/cm³ (corresponding peak absorption coefficient at 1775 nm = 6.9 cm^{-1}). Furthermore, we find that the calculated optimum ion concentration decreases as the sample length is increased as can be seen from Fig. 1. Physically, this makes sense because as the sample length is increased, lower ion concentration still provides enough absorption and at the same time, the fluorescence efficiency remains high.

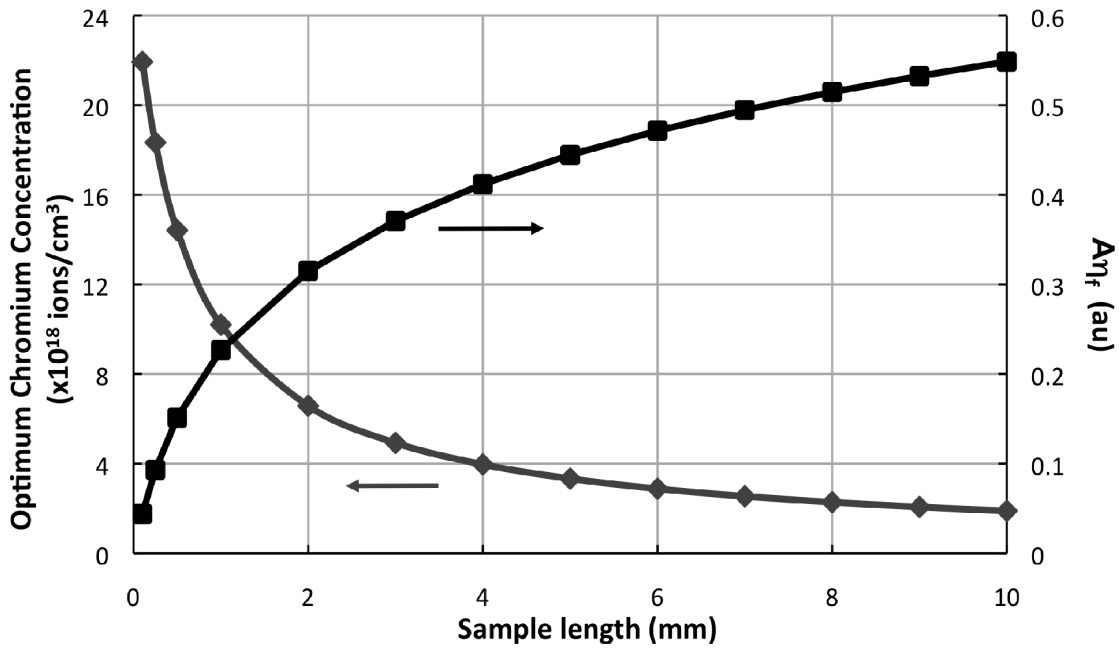


Figure 1. Calculated variation of the optimum chromium concentration and the corresponding fluorescence strength $A\eta_F$ (in arbitrary units) as a function of the sample length for polycrystalline $\text{Cr}^{2+}:\text{ZnSe}$.

3. CONTINUOUS-WAVE LASER PERFORMANCE

A more direct way to determine the optimum ion concentration involves evaluating the cw laser performance of the samples with different concentrations. The setup shown in Fig. 2 was used for this purpose. The astigmatically compensated x-cavity containing each $\text{Cr}^{2+}:\text{ZnSe}$ sample was end pumped with a cw 5-W thulium fiber laser (IPG Photonics) at 1800 nm. An input converging lens (L1, $f=10 \text{ cm}$) focused the pump beam inside the gain medium. The resonator consisted of two curved high reflectors (M1 and M2, $R=10 \text{ cm}$) around the gain medium, a flat end high reflector (HR), and a 3 % flat output coupler (OC). Each sample was held in a copper holder and water cooled at 15°C . Laser operation was obtained in the free-running mode with a center wavelength near 2500 nm.

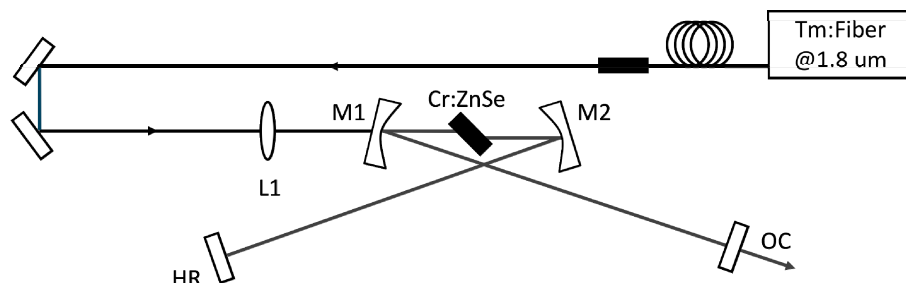


Figure 2. Schematic of the continuous-wave thulium-fiber pumped $\text{Cr}^{2+}:\text{ZnSe}$ laser.

We experimentally investigated the cw power performance of nine $\text{Cr}^{2+}:\text{ZnSe}$ samples with Cr^{2+} concentration in the $0.8\text{--}23.2 \times 10^{18}$ ions/cm³ range. The thickness of each sample was around 2 mm. For consistency, only those samples prepared at the diffusion temperature of 1000 °C were used. Different diffusion times were used to vary the active ion concentration from sample to sample. Results showed that laser performance depends strongly on the active ion concentration as was expected from the spectroscopic results. It is important to note that in a practical laser system, the optimum concentration also depends on the pumping level since thermal effects are related to the amount of non-radiative decay. For example, pumping at 2.1 W of incident pump power, the sample producing the maximum output power of approximately 165 mW had a Cr^{2+} concentration of 8.5×10^{18} ions/cm³. Detailed experimental measurements of threshold power, slope efficiency, and output power showed that for samples with chromium concentration outside the range of $4\text{--}10 \times 10^{18}$ ions/cm³, the chromium concentration is either too low to have sufficient pump absorption, or too high to produce efficient fluorescence, in reasonable agreement with the spectroscopic predictions. This range corresponds to a peak absorption coefficient of $4.6\text{--}11.5$ cm⁻¹ at 1775 nm⁴⁵. In the cw regime, continuous tuning could be obtained from 2240 to 2900 nm by using a Brewster-cut MgF_2 prism⁵³.

4. GAIN-SWITCHED OPERATION OF $\text{Cr}^{2+}:\text{ZnSe}$ LASERS

We also investigated gain-switched operation of $\text{Cr}^{2+}:\text{ZnSe}$ lasers⁵⁴. Here, to obtain the broadest tuning range possible, we employed intra-cavity pumping inside the resonator of a pulsed KTP OPO operating at 1570 nm⁴⁴. The KTP OPO was end-pumped with a Q-switched Nd:YAG laser which generated 145-ns pulses at a pulse repetition rate of 1 kHz at 1064 nm. The output of the OPO was then focused inside a 2-mm-long $\text{Cr}^{2+}:\text{ZnSe}$ sample which was prepared by using diffusion doping at 1000°C. The diffusion time was 6 days, resulting in a doping concentration of 5.7×10^{18} ions/cm³, fluorescence lifetime of 5 μs, and a small signal absorption of 43 % at 1570 nm. Low pump absorption was necessary for obtaining simultaneous oscillation at 1570 nm and for tuning below 2000 nm where re-absorption is a limiting factor. The $\text{Cr}^{2+}:\text{ZnSe}$ laser was an astigmatically compensated x-cavity in which a Brewster-cut sapphire prism was used to tune the output. The pump beam at 1570 nm transmitted through the $\text{Cr}^{2+}:\text{ZnSe}$ sample was retroreflected to extend the resonator of the OPO and to include the $\text{Cr}^{2+}:\text{ZnSe}$ gain medium. When properly aligned, intracavity-pumped lasing could be obtained with this composite cavity. At the output wavelength of 2.6 μm, up to 145 μJ of energy was obtained per pulse with a 25 % output coupler. The repetition rate was 1 kHz. The total incident Nd:YAG pump energy used was 1.8 mJ. By using 4 different sets of optics and the sapphire tuning prism, the output wavelength could be continuously tuned from 1880 to 3100 nm.

5. KERR-LENS MODE-LOCKED OPERATION OF $\text{Cr}^{2+}:\text{ZnSe}$ LASERS

In recent experiments, we also demonstrated Kerr-lens mode-locked operation of a $\text{Cr}^{2+}:\text{ZnSe}$ laser and generated femtosecond pulses near 2400 nm⁵⁵. Different from the studies described in the previous sections, a commercial, 2.4-mm-long $\text{Cr}^{2+}:\text{ZnSe}$ single crystal was used as the gain medium. A schematic of the experimental setup is shown in Fig. 3. The astigmatically compensated x-cavity containing the $\text{Cr}^{2+}:\text{ZnSe}$ crystal at Brewster incidence was end-pumped with a thulium fiber laser at 1800 nm. The total small-signal absorption of the gain medium was 94% at 1800 nm. In the mode locking experiments, an output coupler with a transmission of 1% (at 2400 nm) was used. The total cavity length was 159 cm. Dispersion compensation was achieved with a pair of Brewster-cut MgF_2 prisms.

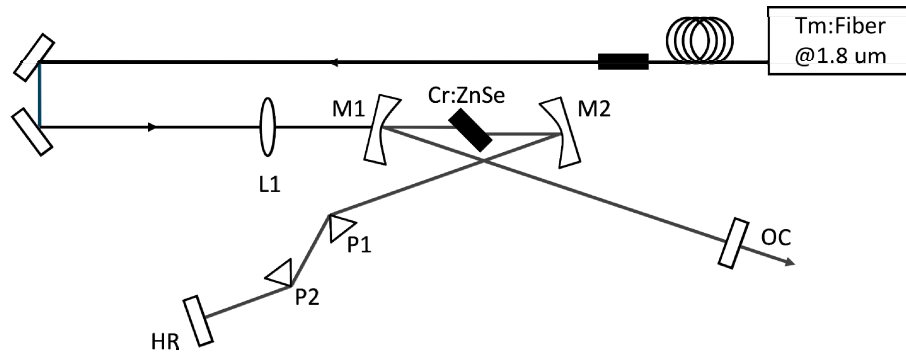


Figure 3. Schematic of the Kerr-lens mode-locked femtosecond $\text{Cr}^{2+}:\text{ZnSe}$ laser.

Figure 4 further shows the cw power performance of the $\text{Cr}^{2+}:\text{ZnSe}$ laser in the free-running mode and with the MgF_2 prism pair. With the 1% output coupler, the laser produced up to 150 mW of output power in the free-running mode at an incident pump power of 2.67 W. The slope efficiency was 6.7%. The estimated round-trip passive loss due to the crystal and resonator optics was further determined to be 3.65 %. Inclusion of the prism pair reduced the maximum available output power to about 100 mW due to the poor surface quality of the prisms. The tip-to-tip separation of the prisms was set to 8.5 cm during mode locking experiments. The overall round-trip dispersion of the resonator including the gain medium, prism pair, and prism insertion was estimated to be -1700fs^2 at 2420 nm. Note that the zero-dispersion wavelength for MgF_2 is around $1.35\text{ }\mu\text{m}$ and at 2420 nm, the dispersion contribution coming from the prism material is also negative. Dispersion estimates were made by using the Sellmeier equations for ZnSe and MgF_2 from Ref.⁵⁶.

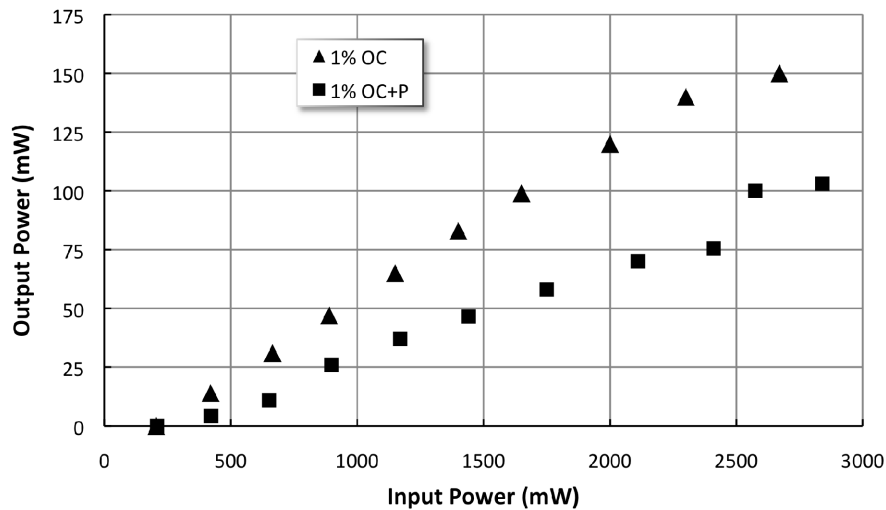


Figure 4. Continuous-wave power efficiency curves for the $\text{Cr}^{2+}:\text{ZnSe}$ laser in the free running mode and with the MgF_2 prism pair. The output wavelength is near 2400 nm.

After the focusing within the gain medium was optimized, Kerr-lens mode-locked operation could be obtained by translating the output coupler. Sample autocorrelation and spectrum of the generated pulses are shown in Figs.5 and 6, respectively. The collinear autocorrelation of the pulses was measured via two-photon absorption in a germanium detector. For this particular example, the autocorrelation width (τ_{AC} in Fig. 5) was 156 fs, giving a pulse duration (FWHM) of 103 fs by assuming a sech^2 pulse profile. The spectral width was 66 nm, resulting in a time-bandwidth product of 0.347. This is in good agreement with what is expected (0.315) for a transform-limited sech^2 pulse. Further optimization of the focusing and cavity dispersion resulted in the generation of pulses as short as 95 fs with a time-bandwidth product of 0.335 at 2420 nm⁵⁵.

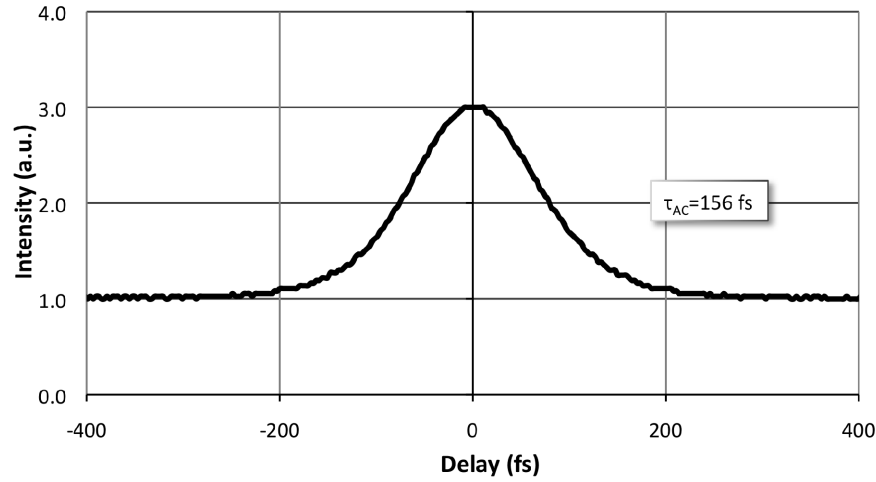


Figure 5. Collinear autocorrelation of the mode-locked femtosecond pulses generated at 2414 nm with the Cr²⁺:ZnSe laser.

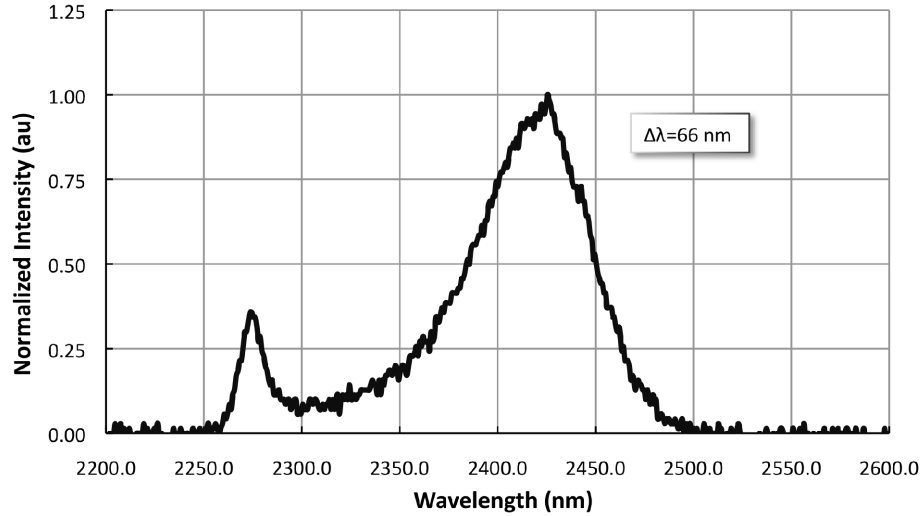


Figure 6. Spectrum of the mode-locked pulses generated at 2414 nm with the Cr²⁺:ZnSe laser.

By using the optimized pulsewidth (95 fs) and energy data obtained during mode-locked operation, we also estimated the nonlinear refractive index of the Cr²⁺:ZnSe gain medium from the equation^{57, 58}

$$\tau = \frac{4|D|}{W\delta}. \quad (6)$$

Above, τ is the pulse duration (FWHM) divided by 1.76 (54.1 fs), $|D|$ is the magnitude of group delay dispersion (GDD \sim 1700 fs²), W is the intra-cavity pulse energy (42 nJ), and the nonlinearity coefficient δ is given by

$$\delta = \frac{2\pi}{\lambda} \frac{n_2 \ell}{A_{eff}}. \quad (7)$$

In Eq. (7), n_2 is nonlinear refractive index, ℓ is the crystal length, λ is the vacuum wavelength, and A_{eff} is the effective beam area which we approximately took as $\pi(\omega_0)_{rms}^2$, $((\omega_0)_{rms}$ =rms spot size in the gain medium=32 μ m). From this

simple analysis, n_2 for $\text{Cr}^{2+}:\text{ZnSe}$ was determined to be $1.4 \times 10^{-14} \text{ cm}^2/\text{W}$, in good agreement with previously reported value ($1.7 \times 10^{-14} \text{ cm}^2/\text{W}$)³¹.

6. CONCLUSIONS

In conclusion, we provided a brief review of the work conducted in our reserach group on the synthesis and characterization of diffusion-doped $\text{Cr}^{2+}:\text{ZnSe}$ for mid-infrared laser applications. Spectroscopic analysis shows that samples with dopant concentration in the $4\text{-}10 \times 10^{18} \text{ ions/cm}^3$ range are less immune to non-radiative decay porcesses and should be suitable for a wide range of laser applications. Diffusion-doped polycrystalline samples were used to demonstrate cw and gain-switched lasing. Intra-cavity pumping with a 1570-nm KTP OPO resulted in continuous tuning from 1880 to 3100 nm. Kerr-lens mode locking was further demonstartred with a single-crystal $\text{Cr}^{2+}:\text{ZnSe}$ sample and 95-fs pulses were generated at 2420 nm. These studies demonstrate the versatility of the $\text{Cr}^{2+}:\text{ZnSe}$ gain medium for different regimes of laser operation in the 2-3 μm wavelength region.

ACKNOWLEDGMENTS

This project was supported by the Network of Excellence in Micro-Optics (NEMO) funded by the European Union 6th Framework program (2004-2008) and by the Scientific and Technological Research Council of Turkey (TUBITAK) under projects TBAG-2030 and 108T028.

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