Concentration dependence of fluorescence and lasing efficiency in Cr\(^{2+}\):ZnSe lasers

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Abstract

We investigated the effect of Cr\(^{2+}\) concentration on the fluorescence lifetime, fluorescence efficiency, and lasing performance of Cr\(^{2+}\):ZnSe lasers. In the experiments, polycrystalline Cr\(^{2+}\):ZnSe samples with concentrations of \(0.34 \times 10^{18} - 66 \times 10^{18}\) ion/cm\(^3\) were prepared by diffusion doping. Spectroscopic measurements performed with Cr\(^{4+}\):YAG and Tm\(^{3+}\):fiber lasers show that the fluorescence efficiency decreases monotonically with increasing active ion concentration. Lifetime measurements and lasing characterization were also performed with a pulsed 1570-nm KTP optical parametric oscillator. In gain-switched operation, the highest output energy was obtained with the Cr\(^{2+}\):ZnSe sample having a Cr\(^{2+}\) ion concentration of \(14 \times 10^{18}\) cm\(^{-3}\). The power performance degrades with increasing concentration due to larger passive losses at the lasing wavelength. Furthermore, the pulse build-up time and the output pulsewidth decrease with pump energy and ion concentration. Finally, with a single set of optics, tunable output could be obtained in the 2520–3050 nm wavelength range.

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1. Introduction

First demonstrated by DeLoach et al. [1], chromium-doped zinc selenide (Cr\(^{2+}\):ZnSe) lasers provide broadly tunable radiation in the 2–3 \(\mu\)m range and can be used in numerous scientific and technological applications including vibrational spectroscopy, trace gas detection, atmospheric imaging [2–4], and so on. To date, extensive work has been performed on the development of Cr\(^{2+}\):ZnSe lasers and different modes of operation have been demonstrated to produce continuous-wave and pulsed laser output [1,5–10].

Due to the broad absorption band of the Cr\(^{2+}\):ZnSe medium extending from 1500 to 2000 nm, numerous lasers have been demonstrated as pump sources, including Co\(^{2+}\):MgF\(_2\) [1,5,11,12], Tm:YALO [7], NaCl:OH\(^{-}\) [13], laser diodes [14], and fiber lasers [15,16]. One drawback of these systems is that they are not as widely available as 1-\(\mu\)m solid-state pump lasers such as Nd:YAG. Therefore, an attractive alternative excitation scheme involves the use of 1064-nm-pumped nonlinear frequency converters such as Raman lasers or optical parametric oscillators (OPO). As an example, a BaNO\(_3\) Raman laser operating at 1598 nm has been used in previous studies to pump Cr\(^{2+}\):ZnSe lasers [17]. However, due to the hydroscopic nature of BaNO\(_3\), implementation of such a pump laser in practical systems faces several challenges. In our group, we have been exploring the possibility of exciting Cr\(^{2+}\):ZnSe lasers with 1064-nm-pumped KTP OPO’s at 1570 nm. The chemical stability and reasonably high damage threshold of the KTP crystal makes this source ideal for the construction of gain-switched Cr\(^{2+}\):ZnSe lasers. One important issue that needs to be addressed in this case has to do with the poor overlap of the pump wavelength...
(1570 nm) with the absorption band (1500–2000 nm) whose center is at 1775 nm. If the crystal lengths are kept fixed, this requires the use of gain media with higher active ion concentrations to absorb the same amount of pump power. Because high doping concentrations can lead to quenching effects or increased losses at the lasing wavelength, it is very important to investigate the variation in fluorescence and lasing efficiency as a function of active ion concentration.

In this study, we employed different experimental techniques to investigate the effect of Cr$^{2+}$ concentration on the fluorescence lifetime, fluorescence efficiency, and lasing performance in Cr$^{2+}$:ZnSe lasers. In the experiments, polycrystalline Cr$^{2+}$:ZnSe samples with varying concentration were prepared by diffusion doping. In fluorescence measurements, we measured the fluorescence efficiency at 2400 nm as a function of doping concentration by using a 1510-nm Cr$^{4+}$:YAG and a 1800-nm Tm-fiber laser as pump sources. In both cases, the fluorescence efficiency decreases monotonically with increasing active ion concentration. Lifetime measurements and lasing characterization were also performed with a pulsed 1570-nm KTP OPO. The fluorescence lifetime and the laser efficiency of the samples were found to decrease with increasing Cr$^{2+}$ ion concentration. The best power performance was obtained with a Cr$^{2+}$:ZnSe sample containing an estimated Cr$^{2+}$ ion concentration of $14 \times 10^{18}$ ion/cm$^3$. Measurements were also performed to investigate the dependence of the pulse build-up time and output pulsewidth on pump energy, ion concentration, and output coupler transmission.

2. Experimental

The Cr$^{2+}$:ZnSe samples used in our study were prepared by diffusion doping. Cylindrical polycrystalline ZnSe samples (diameter = 10 mm and thickness = 2–3 mm) were placed inside silica ampoules with 0.35 g of CrSe dopant. The dopant and the host were placed in different compartments separated by open pointings so that deposition of the dopant on the host occurred only during gas phase. The ampoule was then evacuated and sealed under high-vacuum ($P < 10^{-5}$ mbar). The samples were placed in a tube furnace and subjected to thermal diffusion between 800 and 1100 °C for periods ranging from 1 to 43 days. Fig. 1 shows the measured absorption coefficient at 1500 nm as a function of diffusion time for 10 different Cr$^{2+}$:ZnSe samples prepared at 1000 °C. By assuming an peak absorption cross-section of $1.15 \times 10^{-18}$ cm$^2$ (at 1775 nm) [18], the Cr$^{2+}$ doping concentrations of the samples were estimated to be in the range of $0.34 \times 10^{18}$–$6.6 \times 10^{18}$ ion/cm$^3$ (corresponding peak absorption coefficients at 1775 nm are $0.4$–$7.6$ cm$^{-1}$). Note that due to the nature of the diffusion process, there is a spatial variation in the doping concentration across the cross-section of the samples. The values shown in Fig. 1 correspond to the absorption coefficients measured near the center of the samples.

Fluorescence efficiency measurements were carried out with two different pump sources: a home-built cw Cr$^{4+}$:YAG laser operating at 1510 nm and a commercial thulium-doped fiber laser (IPG) at 1800 nm. In each case, the pump beam was focused at the center of the Cr$^{2+}$:ZnSe samples to a spot size of around 50 μm using a converging lens (focal length = 5 cm). The pump beams were also chopped to provide reference signal for lock-in detection. In the fluorescence measurements, the incident powers from the Cr$^{4+}$:YAG and thulium-doped fiber lasers were 40 mW and 0.5 W, respectively. The emitted fluorescence was collected with a concave gold mirror (diameter = 7.6 cm, f = 7.6 cm) and imaged at the entrance slit of a 0.5-m Czerny–Turner type monochromator, after passing through a high-pass optical filter that blocked the pump radiation. The fluorescence signal was detected with a PbS detector and amplified in two stages by using a pre-amplifier and a lock-in amplifier. As an example, the measured variation of the detected fluorescence intensity as a function of wavelength is shown in Fig. 2 for Cr$^{2+}$:ZnSe samples with concentrations of (a) $3 \times 10^{18}$ ion/cm$^3$ and (b) $14 \times 10^{18}$ ion/cm$^3$ (corresponding peak absorption coefficients at 1775 nm are (a) 3.4 cm$^{-1}$ and (b) 16 cm$^{-1}$, respectively). The fluorescence spectra were not corrected for the detector and grating response. In addition, the monochromator was not purged during the fluorescence measurements. Here, the Cr$^{4+}$:YAG laser was used as the pump source. In order to assess the role of doping concentration, the fluorescence efficiency $\eta_F$ at 2400 nm, defined as

$$\eta_F = \frac{I_{2400}}{P_{abs}},$$

($I_{2400}$ = measured fluorescence intensity at 2400 nm and $P_{abs}$ = absorbed pump power at the excitation wavelength) was measured for different doping levels.

Lifetime and laser efficiency measurements were carried out with a home-built KTP OPO operating at 1570 nm. A Q-switched Nd:YAG laser at 1064 nm was used as the pump source. As can be seen from Fig. 3, the OPO could produce up to 880 µJ of output at 1570 nm with 2.6 mJ of 1064-nm pump in double-pass pumping configuration. The pulsewidth and the pulse repetition rate were 65 ns
In lifetime measurements, a converging lens with a focal length of 5 cm was used to focus the output of the OPO into the Cr\textsuperscript{2+}:ZnSe samples. The fluorescence decay signal was separated from the OPO signal by using several high-pass filters and collected with a MgF\textsubscript{2} lens (focal length = 8 cm) at 90° with respect to the direction of excitation beam. The time-dependent fluorescence decay signal was measured with a fast InGaAs detector that had extended spectral response up to 2.6 μm, and recorded with a digital sampling oscilloscope. The response time of the InGaAs detector was 3 ns.

In lasing experiments, Cr\textsuperscript{2+}:ZnSe samples were positioned at Brewster’s angle inside a folded x-cavity containing two highly reflective concave focusing mirrors (R = 10 cm). The resonator was terminated with a flat high reflector at one end and a flat output coupler at the other end. The high reflectors had a reflectivity larger than 98% between 2600 and 3200 nm. Output couplers with 5.5%, 17.5%, and 26% transmission were used in the experiments. The length of each resonator arm was 15 cm. The estimated pump and laser waist radii were 135 and 110 μm, respectively. In the experiments, the variation of the output power was measured as a function of the pump power for different output couplers and for samples with Cr\textsuperscript{2+} ion concentrations of 3.6 × 10\textsuperscript{18}, 14 × 10\textsuperscript{18}, and 25 × 10\textsuperscript{18} ion/cm\textsuperscript{3}. Tuning of the laser was achieved by using an intracavity sapphire prism oriented at Brewster incidence.

### 3. Results and discussions

Fig. 4 shows the measured variation of the fluorescence efficiency at 2400 nm as a function of doping concentration. Measurements performed with 1510-nm Cr\textsuperscript{4+}:YAG and 1800-nm Tm-fiber laser are both shown in Fig. 4. Note that the fluorescence efficiency shows a strong monotonic decrease due to concentration quenching. For example, η\textsubscript{F} is reduced to half of its low-concentration value at the doping concentration of 4 × 10\textsuperscript{18} cm\textsuperscript{-3} (corresponding peak absorption coefficient of about 4.6 cm\textsuperscript{-1} at 1775 nm). This suggests that samples with Cr\textsuperscript{2+} concentrations of less than
4 × 10^{18} \text{cm}^{-3} \) are more suitable for lasing applications. Also note that very similar trends were observed in the case of 1510- and 1800-nm pumping. Lifetime measurements displayed in Fig. 5 show a similar, expected trend. However, note that the fluorescence efficiency shows a sharper decrease with increasing concentration. This may be attributed to the increase in the losses at 2400 nm at higher doping levels. The effect of doping on losses is further discussed below in laser experiments. The concentration dependence of the fluorescence lifetime \( \tau_F \) can be fitted to an empirical formula of the form

\[
\tau_F = \frac{\tau_{F0}}{1 + \left( \frac{N}{N_0} \right)^2},
\]

(2)

where \( \tau_{F0} \) is the low-concentration value of the fluorescence lifetime, \( N \) is the doping density of the \( \text{Cr}^{2+} \) ions, and \( N_0 \) is the critical concentration where \( \tau_F \) is reduced to \( \tau_{F0}/2 \). The least-squares fit to the experimental lifetime data by using Eq. (2) is also shown in Fig. 5. The best-fit values of \( \tau_{F0} \) and \( N_0 \) were determined to be 5.6 \( \mu \text{s} \) and \( 14 \times 10^{18} \text{ion/cm}^3 \), respectively.

In lasing experiments, the \( \text{Cr}^{2+}:\text{ZnSe} \) laser described in the previous section was end-pumped by the KTP OPO at 1570 nm. Table 1 lists the optical properties of the three samples used. Fig. 6 shows the variation of the output pulse energy as a function of the absorbed pump energy for different output coupler transmissions. The highest output energy was obtained with sample 2 which had a peak absorption coefficient of 16 cm\(^{-1}\) at 1775 nm and a corresponding

\[
y = 0.16x - 4.96
\]

\[
y = 0.11x - 2.66
\]

\[
y = 0.05x - 0.99
\]

For Cr\(^{2+}\) concentration of \( 14 \times 10^{18} \text{cm}^{-3} \). The length of the sample was 3 mm with a total absorption of 75% at the pump wavelength of 1570 nm. With 341 \( \mu \text{J} \) of absorbed pump energy, the resonator produced 52 \( \mu \text{J} \) of output energy with the 26% output coupler. The threshold pump energy was 50 \( \mu \text{J} \). Furthermore, the output wavelength was near 2600 nm and the pulse width varied between 10 and 30 ns.

The role of active ion concentration on the lasing performance was also studied by using the three samples listed in Table 1. Each sample had approximately the same length (3 mm) with \( \text{Cr}^{2+} \) concentrations of \( 3.6 \times 10^{18}, 14 \times 10^{18}, \) and \( 25 \times 10^{18} \text{ion/cm}^3 \). Fig. 7 shows the energy efficiency curves with the 26% output coupler. Note that the power performance degrades monotonically with increasing ion concentration. In particular, the slope efficiency of the resonator decreases from 25% to 12% when the ion concentration increases from \( 3.6 \times 10^{18} \) to \( 25 \times 10^{18} \text{ion/cm}^3 \). This could be mainly attributed to an increase in passive losses at the lasing wavelength. Although the slope efficiency was higher with sample 1, higher output energy was obtained with sample 2 due the larger absorption of the latter.

The passive loss analysis of the samples was also performed by using the power efficiency data. Fig. 8 shows

\[
y = 0.25x - 7.81
\]

\[
y = 0.16x - 4.96
\]

\[
y = 0.12x - 6.31
\]
the variation of the inverse slope efficiency \((1/\eta)\) as a function of the inverse transmission \((1/T)\) of the output coupler for the three samples. \(\eta\) and \(T\) are related according to

\[
\frac{1}{\eta} = \frac{1}{\eta_0} \left( 1 + \frac{L}{T} \right),
\]

where \(L\) is the passive round trip cavity loss, and \(\eta_0\) is the quantum defect-limited value of the slope efficiency. By using Eq. (3), the single-pass loss was estimated to be 11%, 15%, and 31% for samples 1, 2 and 3, respectively. Here, atmospheric and mirror losses were neglected.

Pulse formation dynamics in the gain-switched Cr\(^{2+}\):ZnSe laser was also studied. In particular, the variation of the pulse build-up time (the delay between the 1570-nm pump pulse and the 2600-nm laser pulse) and the output pulsewidth were measured as a function of absorbed pump energy, chromium concentration, and output coupler transmission. As an example, Fig. 9 shows the temporal profile of the pump and laser pulses, obtained with the Cr:ZnSe sample 1. The output coupler transmission and the incident pump energy were 26% and 90 \(\mu\)J (absorbed pump energy = 50 \(\mu\)J), respectively. At this pumping level, the resonator produced 28-ns-long pulses with 4 \(\mu\)J of energy and the pulse build-up time was 210 ns. Fig. 10 shows the measured variation of the pulse build-up time and the output pulsewidth as a function of the incident pump energy. As expected, both the build-up time and the output pulsewidth decrease with increasing pump energy until saturation of the pump pulse dominates. With this configuration, the shortest pulsewidth (16 ns) and build-up time (70 ns) were obtained at the highest incident pump energy of 470 \(\mu\)J (absorbed pump energy = 150 \(\mu\)J).

The dependence of the pulse width and pulse build-up time on chromium ion concentration was also investigated. For a fixed output coupler transmission and pumping level, both were found to decrease with increasing concentration due to an increase in the overall absorption and hence the gain of the samples. The shortest pulse width and pulse build-up time were obtained with the highly doped Cr:ZnSe sample 3. In this case, at the same incident pump energy and output coupler transmission, pulses as short as 11 ns in duration were obtained with a corresponding build-up time of 60 ns. Note that in this case, the absorbed pump energy was 410 \(\mu\)J. Finally, we investigated the variation of the pulsewidth and build-up time with output coupler transmission. Whereas the pulsewidth was fairly insensitive, the delay increased due to larger resonator losses. In particular, the pulse delay increased from 82 ns to 94 ns when the output coupler transmission went from 1% to 26% at an incident pump energy of 210 \(\mu\)J (sample 1). In the same transmission range, output pulsewidth increased from 17 to 20 ns.

Finally, the tuning characteristics of the Cr\(^{2+}\):ZnSe laser were also studied. Fig. 11 shows the measured variation of the output energy as a function of the emission wavelength for sample 2 with the 26% output coupler and with an absorbed pump energy of 340 \(\mu\)J. An intracavity Brewster-cut sapphire prism was used for tuning. The cavity was not purged during the experiments. Laser output could be tuned between 2520 and 3050 nm. The obtained tuning range was optics limited below 2500 nm. Tuning below 2500 has been reported in other studies [19].

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**Fig. 8.** Dependence of inverse slope efficiency on the inverse output coupler transmission, for samples 1, 2, and 3. Output coupler transmissions were 5.5%, 17.5%, and 26%.

**Fig. 9.** Temporal profiles of the OPO pump pulse (pulsewidth = 65 ns) and the output laser pulse (pulsewidth = 28 ns). The pulse build-up time is 210 ns. Intensities of the pump and the laser pulse are not to scale.

**Fig. 10.** Variation of laser pulse build-up time and output pulsewidth as a function of the incident pump energy for sample 1. The output coupler transmission was 26%.
In conclusion, we provided a detailed analysis of the effect of Cr\textsuperscript{2+} concentration on the fluorescence efficiency and lasing performance in Cr\textsuperscript{2+}:ZnSe lasers. In experiments, polycrystalline Cr\textsuperscript{2+}:ZnSe samples with concentrations in the $0.34 \times 10^{18} - 66 \times 10^{18}$ ion/cm\textsuperscript{3} range were prepared by diffusion doping. Spectroscopic measurements show that the fluorescence efficiency monotonically decreases with increasing Cr\textsuperscript{2+} concentration due to the enhancement of nonradiative decay processes and that samples with ion concentrations of less than $4 \times 10^{18}$ cm\textsuperscript{-3} ions/cm\textsuperscript{3} are more suitable for lasing applications. In lifetime measurements, the critical concentration at which the fluorescence lifetime decreases to half of its low-concentration value was determined to be $14 \times 10^{18}$ ion/cm\textsuperscript{3}. The gain-switched lasing of the samples were further investigated by using a 1570-nm KTP OPO. Highest output energy was obtained with the sample having an active ion concentration of $14 \times 10^{18}$ cm\textsuperscript{-3}. Measurements showed that both the pulse build-up time and the output pulsewidth decreased with increasing pump energy and ion concentration. Finally, with a single set of optics, the output wavelength of the laser could be tuned from 2520 to 3050 nm.

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