

Spectroscopy and tunable continuous-wave operation of $\text{Cr}^{2+}:\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ single crystal around $2.5\ \mu\text{m}$

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Abstract. Hexagonal single crystals of the $\text{Cr}^{2+}:\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ solid solution are grown by the Bridgman–Stockbarger technique. We study their optical and photoluminescent characteristics and determine the temperature dependences of the photoluminescence kinetics within the range 5–440 K. The crystals possess a broad gain band in the range from 2 to $3.5\ \mu\text{m}$ and exhibit a weak quenching of luminescence with a quantum yield exceeding 80% at room temperature. Tunable continuous-wave oscillation is demonstrated in the region of $2.5\ \mu\text{m}$.

Keywords: II–VI compounds, solid solution, tunable laser, mid-IR region.

1. Introduction

Solid-state mid-IR lasers tunable around $2.5\ \mu\text{m}$ are of great interest for spectroscopy, medicine, ecological monitoring of the atmosphere, communication systems, etc. Since their invention in 1996 [1], a number of lasers based on binary and ternary II–VI crystalline compounds doped with bivalent chromium ions have been reported [2–6]. These lasers are tunable within a wide wavelength range and can operate at room temperature. To date, the most widely used compounds are Cr:ZnSe and Cr:ZnS [2], which are commercially available in the form of ceramics. Such characteristics as pump and laser wavelength regions, tuning range, metastable level lifetime, luminescence quantum efficiency at room temperature and thermo-optical parameters of tunable IR lasers depend, first of all, on the chemical composition of the host crystal [4], which makes it possible to purposefully change the mentioned parameters of laser materials.

However, important factors for practical applications of laser materials are not only high technological efficiency and production reproducibility but also high optical quality and

ability to efficiently operate at room temperature. At present, the long-wavelength tuning edge of lasers based on II–VI crystalline compounds doped with Cr^{2+} ions in the cw regime reaches $3.45\ \mu\text{m}$ for $\text{Cr}^{2+}:\text{CdSe}$ [7] and $3.34\ \mu\text{m}$ for $\text{Cr}^{2+}:\text{ZnSe}$ [8]. Extension of the tuning range of $\text{Cr}^{2+}:\text{A}^{\text{II}}\text{B}^{\text{VI}}$ lasers to longest possible wavelengths ($\lambda > 3\ \mu\text{m}$), i.e., to the region of many vibrational molecular frequencies, is an interesting but very difficult problem.

One of the possible ways to extend a laser tuning range is to use ternary II–VI compounds as crystalline matrices. As was shown in [5], the use of $\text{Cr}^{2+}:\text{ZnS}_x\text{Se}_{1-x}$ solid solution crystals extends the tuning range compared to binary compounds, but the structural and optical quality of the first samples of this crystal was rather low. It is especially important that this material was found to have a stronger temperature dependence of luminescence lifetime (temperature quenching of the metastable level), which is typical for sulphide compounds due to high phonon frequencies.

Another approach consists in the substitution of a part of ions of the anion sublattice of II–VI crystalline materials. In [6], this approach was applied to Cd-containing compounds, which *a priori* have a strong temperature quenching of luminescence and poor thermo-optical properties.

In the present work, we study the $\text{Cr}^{2+}:\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ ternary compounds grown for the first time by authors of [9] using the Bridgman–Stockbarger method in a high-pressure inert gas atmosphere. This solid-solution single crystal has good mechanical and optical characteristics, which allowed the authors of [10, 11] to obtain pulsed lasing in this material for the first time. In contrast to the well-known $\text{Cr}^{2+}:\text{ZnSe}$ material, which has a cubic structure, the new compound with a magnesium fraction $x > 0.12$ has an anisotropic wurtzite structure [12]. Its intrinsic birefringence decreases the thermal depolarisation loss thus enabling a higher output power. Therefore, it is of interest to determine the influence of the crystal lattice anisotropy of the studied material on the luminescence of Cr^{2+} ions, the temperature dependence of the lifetime of the metastable level of active ions and the tuning range limits.

The studied $\text{Cr}^{2+}:\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ ($0.2 \leq x \leq 0.3$) single crystals were grown by the vertical Bridgman–Stockbarger method in a high-pressure inert gas atmosphere. The crystals were doped with chromium directly during the growth process. The measurements were performed on the samples with a chromium concentration of $3.5 \times 10^{18}\ \text{cm}^{-3}$, which corresponds to the peak absorption of $5\text{--}7\ \text{cm}^{-1}$ at a wavelength of about $1800\ \text{nm}$. The samples were $2.3\ \text{mm}$ thick.

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2. Results and discussion

Absorption and luminescence spectra of $\text{Cr}^{2+}:\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ samples were studied for two polarisations, parallel (π) and perpendicular (σ) to the optical axis of the crystal, at temperatures from 5.6 to 440 K. Typical absorption and luminescence spectra for both polarisations are shown in Fig. 1.

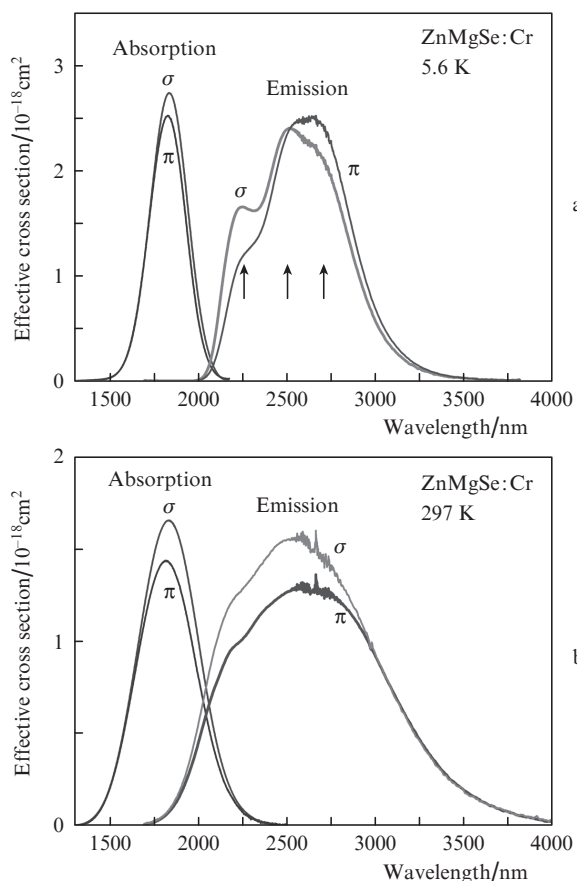


Figure 1. Effective absorption and emission cross sections of $\text{Cr}^{2+}:\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ single crystals in the case of the polarisation plane parallel (π) and perpendicular (σ) to the optical axis of the crystal at temperatures of (a) 5.6 K and (b) 297 K. The noise in the emission spectra in the range 2.6–2.8 μm is related to the absorption by water vapour in the spectrometer. The arrows mark the approximate positions of the Jahn–Teller components of luminescence cross section.

The luminescence spectra were measured using a Fourier-transform IR spectrometer with corrections for the detector response and atmospheric transmission; the effective cross sections were calculated using the Füchtbauer–Ladenburg formula [1] taking into account the anisotropy [13]. The correctness of the obtained data was checked by comparing the total integral cross sections of absorption and luminescence. This discrepancy, taking into account the degeneracies of the lower and upper levels of Cr^{2+} (formula (3) in [1]), was less than 20%.

From Fig. 1 one can see that the anisotropy of the effective cross section spectra does not exceed 20%, because of which the product of the peak luminescence cross section σ_{lum} and the lifetime τ for both polarisations will be close to that for the isotropic crystal [13]. Since the lasing threshold is proportional to $(\sigma_{\text{lum}}\tau)^{-1}$, we can expect that the lasing threshold

for the considered material will be comparable with the thresholds for isotropic $\text{Cr}^{2+}:\text{ZnSe}$ or $\text{Cr}^{2+}:\text{ZnS}$ crystals. At room temperature, we observed a slight shift of the spectral peaks, the absorption and luminescence peaks shifting in opposite directions for the σ - and π -polarisations. However, the luminescence spectra at a low temperature clearly show that no shift really occurs, but this effect is caused by intensity redistribution between the three Jahn–Teller components of the luminescence (marked by arrows in Fig. 1a), which are not resolved at high temperatures. At the same time, the apparent shift is considerably smaller than the width of the peaks and, hence, can be ignored for practical purposes.

The effective emission cross section spectra and the measured temperature dependence of the luminescence lifetime of $\text{Cr}^{2+}:\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ single crystals are studied in comparison with the corresponding characteristics of $\text{Cr}^{2+}:\text{ZnSe}$ and $\text{Cr}^{2+}:\text{ZnS}_y\text{Se}_{1-y}$ single crystals (Fig. 2).

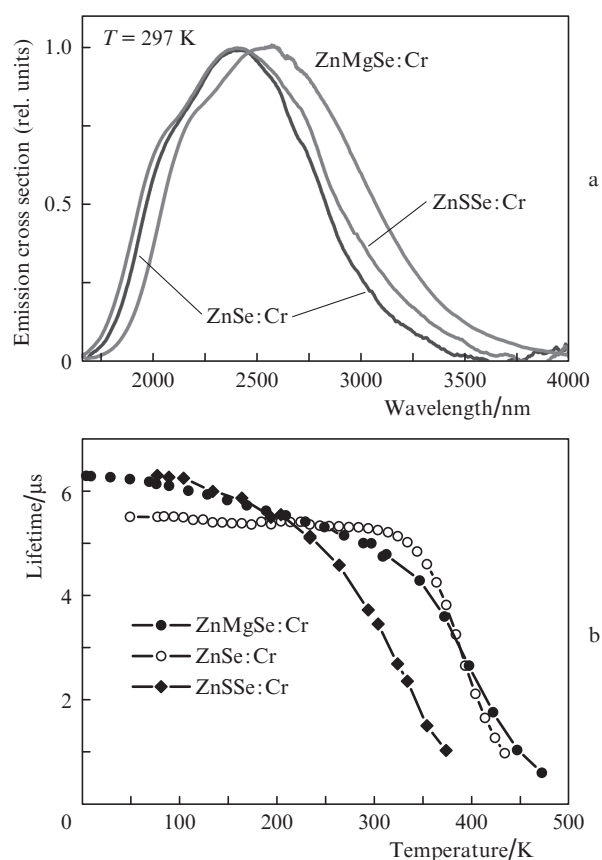


Figure 2. Spectrum of the effective emission cross section (σ -polarisation) (a) and temperature dependence of the luminescence of $\text{Cr}^{2+}:\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ (b) in comparison with the corresponding characteristics for $\text{Cr}^{2+}:\text{ZnSe}$ and $\text{Cr}^{2+}:\text{ZnS}_y\text{Se}_{1-y}$ [14].

One can see (Fig. 2a) a noticeable (by 200–250 nm) broadening of the long-wavelength wing of the $\text{Cr}^{2+}:\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ emission cross section spectrum, which suggests that the tuning range of lasers based on the new material can be extended to the long-wavelength spectral region. It should be especially noted that the broadening of the spectrum is not accompanied by enhancement of temperature quenching of luminescence as observed, for example, in $\text{Cr}^{2+}:\text{ZnS}_y\text{Se}_{1-y}$ (Fig. 2b).

The measured lifetimes (see Fig. 2b) demonstrate only a slight decrease in the quantum yield with temperature (up to

300 K). At high temperatures, the parameter $\tau(T)$ of the new crystal is even better than that of $\text{Cr}^{2+}:\text{ZnSe}$. This feature is important for the development of high-power lasers and for the extension of frequency tuning ranges, because these purposes require high pump levels, which leads to strong heating of active elements. Based on the possibility of wavelength tuning in $\text{Cr}^{2+}:\text{ZnSe}$ crystals to 3.34 μm [5], we can expect that lasers based on $\text{Cr}^{2+}:\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ active crystals of high optical quality will allow one to extend the tuning range to ~ 3.5 μm .

As a pump source in laser experiments, we used an erbium fibre laser emitting at a wavelength of 1607 nm. The studied sample absorbs 43% of this radiation. The experimental scheme is shown in Fig. 3.

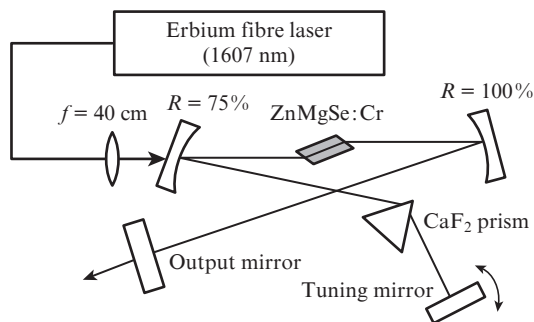


Figure 3. Scheme of the experimental setup for laser experiments. The $\text{Cr}^{2+}:\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ sample $5 \times 5 \times 2.3$ mm in size is attached to a passive heat sink (room temperature) at the Brewster angle for the σ -polarisation (the pump and laser radiation polarisation plane is perpendicular to the c axis of the crystal). The distance between the concave and plane mirrors is 30 cm.

The laser wavelength was tuned within 385 nm using a calcium fluoride prism (Fig. 4a). With the use of a 2% output mirror, we obtained an absorbed pump power threshold of 345 mW, a slope efficiency of 8% and an output power of 54 mW (Fig. 4b).

These parameters are far from the record values demonstrated by $\text{Cr}:\text{ZnSe}$ and $\text{Cr}:\text{ZnS}$ laser [2, 5], which is explained by an admixture of Fe^{2+} ions. Bivalent iron has a broad absorption band in the region $\lambda > 2.5$ μm (Fig. 4a, dashed line) with absorption losses about 5% per cavity roundtrip at 2500 nm, which is twice as high as the output mirror transmission.

These factors explain the high threshold, the low slope efficiency and the narrow tuning range of the given sample. At the same time, the spectroscopic data and the measured thermal conductivities ($\kappa_{\text{ZnMgSe}} \approx 1.1\kappa_{\text{ZnSe}}$ [15]) make clear that the characteristics of crystals with better quality (free of iron ions) can be closer to that obtained for $\text{Cr}:\text{ZnSe}$ and other materials.

3. Conclusions

Our study of the absorption, emission and temperature dependences of the luminescence lifetime of $\text{Cr}^{2+}:\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ single crystal allows us to conclude that this material is promising as an active laser medium for superbroadband tunable and high-power mid-IR lasers.

This material is optically uniaxial and exhibits a broad luminescence band with a weak temperature quenching of luminescence up to 300 K. Based on the detailed comparison

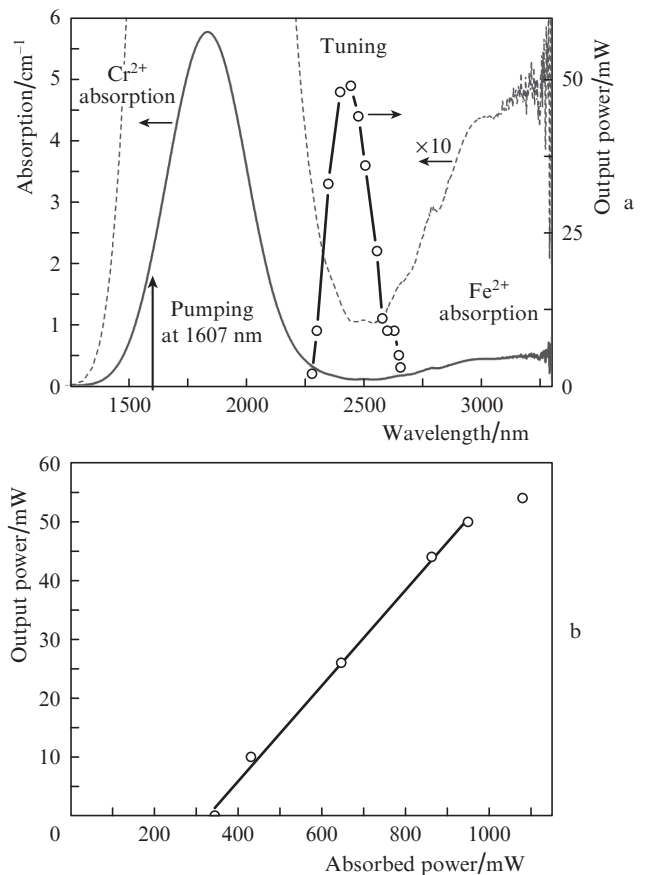


Figure 4. Wavelength tuning range and total optical absorption curve of $\text{Cr}^{2+}:\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ in the σ -polarisation (a) and output power of the $\text{Cr}^{2+}:\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ laser (b). The slight transmission modulation seen in the tenfold-magnified absorption curve (dashed line) is related to birefringence in the imperfectly oriented sample. The lasing threshold is 345 mW (at an incident power of 800 mW), the slope efficiency is 8% and the tuning range is 2275–2660 nm.

with the well-known laser material $\text{Cr}:\text{ZnSe}$, we expect that optimisation of the impurity composition of the studied crystal will allow one to obtain an average output power of several watts and to extend the tuning range up to 3.5 μm .

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