

PACS 42.55.Rz, 42.70.HJ, 78.60.Lc

Photoluminescent properties of crystalline solid solution $\text{Zn}_{1-x}\text{Mg}_x\text{Se}:\text{Cr}^{2+}$, a new active material for tunable IR lasers

N.O. Kovalenko, Yu.A. Zagoruiko, O.O. Fedorenko, E.A. Kuzminov

*Institute for Single Crystals STC "Institute for Single Crystals", NAS of Ukraine
60, Lenin Ave., 61001 Kharkiv, Ukraine*

Phone: 38(057) 341-03-49; e-mail: nazar@isc.kharkov.ua

Abstract. Considered in this work are the luminescent properties of new active material $\text{Zn}_{1-x}\text{Mg}_x\text{Se}:\text{Cr}^{2+}$ for tunable IR lasers. Measured in $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Se}:\text{Cr}^{2+}$ is the spectrum of IR luminescence excitation, and shown is the possibility of excitation in the visible spectral range. It is established that the luminescence band maximum is shifted by approximately 200 nm in comparison with that of $\text{ZnSe}:\text{Cr}^{2+}$. Presented are the measured time characteristics of photoluminescence excited in the visible (550 nm) and IR (1800 nm) spectral regions.

Keywords: ZnMgSe, solid solution, active media, IR luminescence, laser.

Manuscript received 17.09.09; accepted for publication 22.10.09; published online 04.12.09.

1. Introduction

By now there has been created a sufficient number of active laser materials on the base of compounds $\text{A}^{\text{II}}\text{B}^{\text{VI}}:\text{Cr}^{2+}$ ($\text{ZnS}:\text{Cr}^{2+}$, $\text{ZnSe}:\text{Cr}^{2+}$, $\text{ZnTe}:\text{Cr}^{2+}$, $\text{CdS}:\text{Cr}^{2+}$, $\text{CdSe}:\text{Cr}^{2+}$, $\text{CdTe}:\text{Cr}^{2+}$, $\text{CdZnTe}:\text{Cr}^{2+}$, $\text{CdMgTe}:\text{Cr}^{2+}$, $\text{CdMnTe}:\text{Cr}^{2+}$) [1, 2]. These materials operate in a wide generation band spreading from 1.9 μm (for $\text{ZnS}:\text{Cr}^{2+}$) up to 3.6 μm (for $\text{CdSe}:\text{Cr}^{2+}$). However, only narrow-band compounds $\text{CdSe}:\text{Cr}^{2+}$ and $\text{CdMnTe}:\text{Cr}^{2+}$ can be applied for the long-wave region of this band. Therefore, the search for new $\text{A}^{\text{II}}\text{B}^{\text{VI}}:\text{Cr}^{2+}$ compounds capable to operate in the mentioned region and have the working properties close to those of the best material $\text{ZnSe}:\text{Cr}^{2+}$ is a topical task. Reported in our paper [3] is a new active material $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Se}:\text{Cr}^{2+}$ with an absorption spectrum shifted towards the long-wave region. To continue the performed investigation, in this work we consider the excitation and photoluminescence spectra of $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Se}:\text{Cr}^{2+}$, as well as the time characteristics of IR luminescence at direct excitation in the IR region and indirect excitation in the visible region of the spectrum.

2. Experimental technique

Monocrystalline $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Se}:\text{Cr}^{2+}$ boules were grown from the melt by the Bridgman method under excessive inert gas pressure. The experimental samples with polished working surfaces were obtained from the boules by methods of mechanical treatment. The

luminescence excitation spectra were measured by a unit based on a monochromator of MDR-2 type, luminescence light being registered at an angle of 90° with respect to the excitation beam. As a sensitive element of the photodetector, there was used PbS photodetector. The spectra of IR luminescence were obtained using MDR-204 monochromator with a standard detector based on PbS photoresistor. The time dependences of IR luminescence were studied using a specialized unit EKSPLA, which allowed to measure the luminescence spectra in the range from 220 to 2500 nm at the excitation in 210-2299 nm range, and to register the luminescence decay time from 10 ns to 10 ms at an excitation time of 3-6 ns.

3. Experimental results

The obtained IR luminescence excitation spectra are shown in Fig. 1.

As seen from this figure, the long-wave part of the spectrum for $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Se}:\text{Cr}^{2+}$ is shifted towards longer wavelengths approximately by 70 nm with respect to that of $\text{ZnSe}:\text{Cr}^{2+}$ spectrum, and this correlates with the shift of the absorption band reported in [3]. The short-wave band of the excitation spectrum is shifted towards shorter wavelengths. In [4] the boundaries of the short-wave band are shown to be bound up with the presence of an impurity energy level in the forbidden band formed by Cr^{1+} center. As seen from the comparison of the position of these bands in $\text{ZnSe}:\text{Cr}^{2+}$

and ZnMgSe:Cr²⁺, in the latter material the depth of the impurity level Cr¹⁺ is larger by 0.16 eV and makes 2.16 eV from the valence band top.

The presented curves have pronounced peaks in the short-wave range. The positions of these peaks correspond to 470 nm for ZnSe:Cr²⁺ and 423 nm for ZnMgSe:Cr²⁺, or to 2.64 and 2.92 eV, respectively. These data almost coincide with the known values of forbidden band widths for the considered materials, and make it possible to attribute the presence of the peaks to the “band-to-band” electron transitions, or to creation of exciton pairs followed by the formation of the excited center Cr²⁺.

Fig. 2 presents the normalized and smoothed photoluminescence spectra for ZnSe:Cr²⁺ (curve 2) and ZnMgSe:Cr²⁺ (curve 1). It is seen that the presence of magnesium impurity leads to an essential (of about 200 nm) shift of the luminescence band towards longer wavelengths.

This shift of the luminescence band is explained in the following way. When Cr²⁺ ion penetrates into the site of the cationic sublattice in ZnSe crystal, the ground level of chromium ⁵D becomes split into the ground level ⁵T₂ and the excited ⁵E level under the influence of the electric field of Se²⁻ surrounding ions. The value of the energy gap between these levels defines the position of the luminescence band in the spectrum and the lasing band of Cr²⁺ ion in ZnSe crystalline matrix. It is known [5] that incorporation of magnesium in concentrations exceeding 7 at.% into ZnSe crystals leads to the change of the type of the crystal lattice from “sphalerite” to “wurtzite” and to the increase of distances between the sites in the tetrahedron formed by Se²⁻ ions. Therefore, the said changes caused by the incorporation of Mg into ZnSe:Cr²⁺ lattice decrease the intensity of electric crystalline field and make the energy gap between the levels ⁵T₂ and ⁵E narrower, thus resulting in the shift of the luminescence band and the generation band towards longer wavelengths.

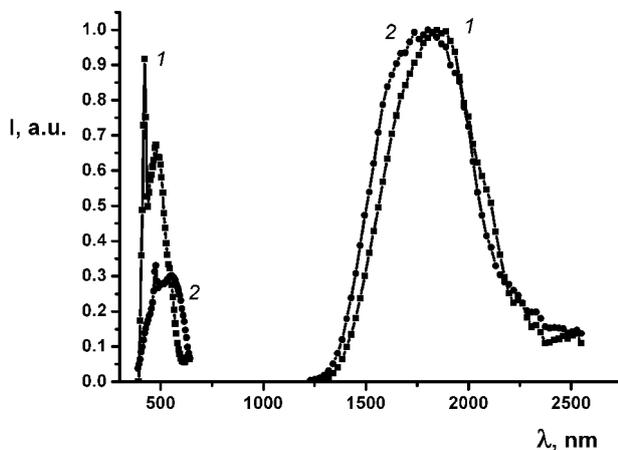


Fig. 1. Photoluminescence excitation spectra: 1 – Zn_{0.75}Mg_{0.25}Se:Cr²⁺; 2 – ZnSe:Cr²⁺.

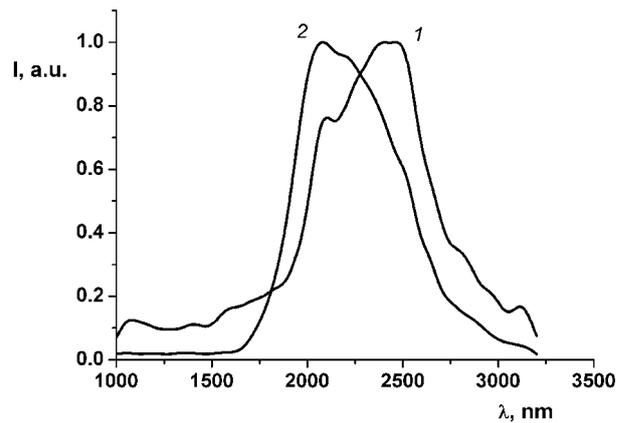


Fig. 2. Photoluminescence spectra: 1 – Zn_{0.75}Mg_{0.25}Se:Cr²⁺; 2 – ZnSe:Cr²⁺.

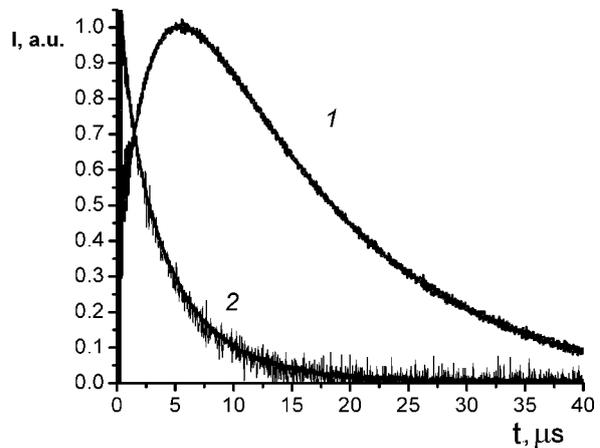


Fig. 3. IR luminescence decay at the excitation in the visible (550 nm) and IR (1800 nm) regions (curves 1 and 2, respectively).

Shown in Fig. 3 are the curves of IR photoluminescence decay at indirect excitation in the visible spectral region (550 nm) and direct excitation in the IR region (1800 nm).

As seen from this figure, the luminescence decay time at the excitation in the visible region of the spectrum (curve 1) is 15 μs. These results testify to the presence of another luminescence mechanism different from the direct transition ⁵E → ⁵T₂ in Cr²⁺ ion. A detailed study of this experimental fact will be performed in our future works.

The exponential approximation of luminescence decay at the excitation in the IR region of the spectrum (curve 2) gives the time constant equal to 4 μs, which is less in comparison with that of ZnSe:Cr²⁺ (8 μs). However, we hope that further work aimed at optimization of the methods for the growth of ZnMgSe:Cr²⁺ crystals will allow to improve this characteristic.

4. Conclusions

The influence of magnesium impurity on the photoluminescence spectrum of the ions Cr^{2+} in $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ matrix is considered. It is established that the spectrum of IR photoluminescence excitation for the active medium $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Se}:\text{Cr}^{2+}$ is shifted by ~ 200 nm towards longer wavelengths. In $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Se}:\text{Cr}^{2+}$ crystals, the efficiency of IR luminescence at the excitation in the visible region of the spectrum is shown to be higher in comparison with that for $\text{ZnSe}:\text{Cr}^{2+}$. It is shown that in $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{Se}:\text{Cr}^{2+}$ the decay of IR luminescence at pumping in the visible spectral region has a larger time constant (~ 15 μs) in comparison with that at direct pumping (~ 4 μs). Such a fact points to the presence of another luminescence mechanism different from the direct transition ${}^5\text{E} \rightarrow {}^5\text{T}_2$ in Cr^{2+} ion.

Acknowledgement

The authors are grateful to I.M. Solsky and A.P. Luchechko from the Scientific Research Company "Carat", Lviv for affording an opportunity to investigate the kinetics of photoluminescence.

References

1. U. Hommerich, A.G. Bluiett, I.K. Jones et al., Crystal growth and infrared spectroscopy of $\text{Cr}:\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ and $\text{Cr}:\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ // *J. Cryst. Growth* **287**, p. 243 (2006).
2. M. Mond, D. Albrecht, E. Heumann et al., 1.9 – m and 2.0 – m laser diode pumping of $\text{Cr}^{2+}:\text{ZnSe}$ and $\text{Cr}^{2+}:\text{CdMnTe}$ // *Opt. Lett.* **27**, p. 1034 (2002).
3. Yu.A. Zagoruiko, N.O. Kovalenko, O.A. Fedorenko, V.A. Khristyan, $\text{ZnMgSe}:\text{Cr}^{2+}$ single crystal: a novel material for active elements of tunable IR region lasers (rapid communication) // *Functional Materials* **15**, p. 247 (2008).
4. M. Godlewski, M. Surma, V.Yu. Ivanov, T.P. Surkova, Mechanizms of radiative and nonradiative recombination in $\text{ZnSe}:\text{Cr}$ and $\text{ZnSe}:\text{Fe}$ // *Fizika nizkikh temperatur* **30**, p. 1187 (2004), in Russian.
5. Yu.A. Zagoruiko, O.A. Fedorenko, N.O. Kovalenko, M.A. Rom, P.V. Mateichenko, Physical properties of $\text{ZnSe}:\text{MgSe}$, $\text{ZnSe}:\text{CdS}$ solid solution and possibilities of their application in IR engineering // *Semiconductor Physics, Quantum Electronics & Optoelectronics* **3**(2), p. 165-169 (2000).