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Temperature dependence of the spectral properties of chromium ions in $Zn_{1-x}Mn_xSe$ solid solution crystals

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The temperature dependence of the spectroscopic properties of Cr^{2+} ions in $Zn_{1-x}Mn_xSe$ solid solution crystals with varying manganese ion content ($x = 0$, 0.05, and 0.3), was studied over a temperature range from 77 to 380 K. It was found that as the temperature increases, the maxima of the absorption ($^5T_2 \rightarrow {}^5E$) and luminescence ($^5E \rightarrow {}^5T_2$) spectra of Cr^{2+} ions shift to shorter wavelengths almost linearly, at a rate of approximately 0.3 nm/K. The width of the absorption and luminescence lines increases at a rate of about 0.2 nm/K. For the crystal with $x = 0.05$, the lifetime of Cr^{2+} ions remains virtually independent of temperature up to 300 K ($\tau \approx 5.5\,\mu$s) and decreases to 2.1 μs at 380 K. In the crystal with manganese content $x = 0.3$, the lifetime is stable ($\tau \approx 5.2\,\mu$s) up to 250 K and then drops to approximately 1.1 μs at 380 K.

Keywords: $Zn_{1-x}Mn_xSe$ solid solution, Cr^{2+} ions, spectroscopy, temperature dependence.

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Introduction

The current interest in lasers based on ZnSe crystals doped with chromium Cr^{2+} ions stems from their demonstrated high output parameters in continuous wave operation (over 140 W [1]) at room temperature, as well as their ability to generate ultrashort pulses (as short as 43 fs [1]) in the mid-infrared (IR) 2–3 μm wavelength range. The key benefits of divalent chromium as an active ion in $A^{II}B^{VI}$ group crystals include high absorption and fluorescence cross-sections, negligible absorption from the excited state, and a sufficiently long lifetime at temperatures up to room temperature. Successful lasing has been demonstrated in a number of $A^{II}B^{VI}$ group crystals, such as ZnS, ZnSe, ZnMnSe, CdSe, and CdMnTe. A thorough investigation of the spectroscopic properties of Cr^{2+} ions in a wide range of $Zn_{1-x}Mn_xSe$ ($x = 0 - 0.4$) solid solutions at room temperature has been carried out recently, and the possibility of achieving tunable Cr^{2+} lasing in such crystals under diode pumping has been demonstrated [9,10]. However, to the best of our knowledge, the temperature dependences of spectroscopic properties of Cr^{2+} ions in $Zn_{1-x}Mn_xSe$ crystals, such as the position and magnitude of the maximum and the HWHM values of absorption and fluorescnece spectra, have not been examined in detail. Moreover, such studies performed for the ZnSe:Cr^{2+} crystal within a wide temperature range are also scarce [11,12]. Therefore, the aim of the present study was to investigate the temperature dependence of spectroscopic parameters of Cr^{2+} ions in $Zn_{1-x}Mn_xSe$ solid solution crystals.

Materials and equipment

The spectroscopic properties of Cr^{2+} ions in $Zn_{1-x}Mn_xSe$ crystals with a manganese ion concentration close to the minimum ($x = 0.05$) and maximum ($x = 0.3$) levels at which the structure of the solid solution remains cubic [13] were examined within a wide temperature range of 77 – 380 K. For comparison, measurement data for the ZnSe:Cr^{2+} crystal (manganese concentration $x = 0$) were used.

In the studies, crystalls with similar Cr^{2+} ion concentrations and approximately the same thickness, were used. The absorption spectra were measured using a Cary 5000 spectrophotometer across the 1000 – 2500 nm range. The samples were placed into a cryostat cooled with liquid nitrogen, with temperature control within the range of 77 – 380 K. Fluorescence spectra and fluorescence decay curves were measured in a similar cryostat under excitation by nanosecond pulses from a Solar LP 603 parametric oscillator operating at a wavelength of 1700 nm. The measurements were performed using a single-grating MDR-2 monochromator (300 lines/mm) and a Thorlabs PbS-based photodetector connected to a Tektronix digital oscilloscope. The signal from the digital oscilloscope was fed to a personal computer.

Results and discussion

The examples of the absorption spectra of $Zn_{1-x}Mn_xSe$ crystals with manganese ion concentration $x = 0$ (ZnSe),

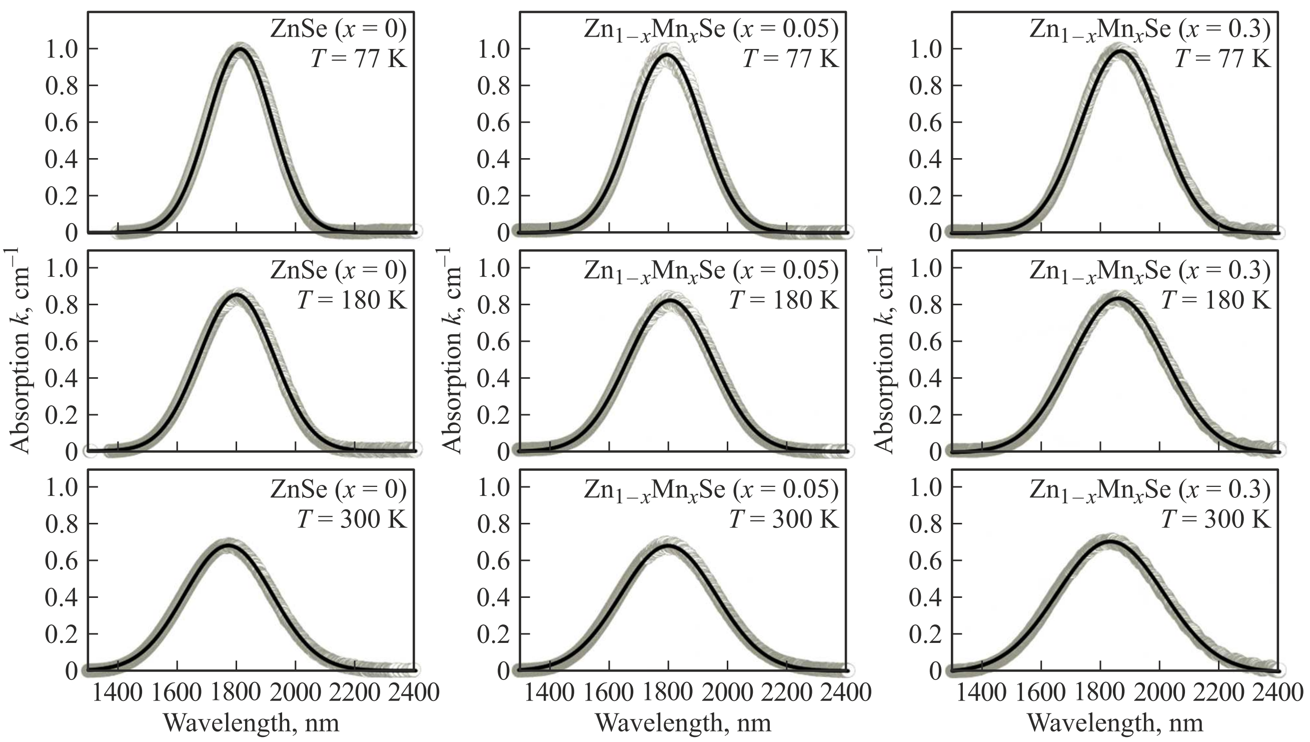

Figure 1. Absorption spectra of Cr^{2+} ions in $Zn_{1-x}Mn_xSe$ solid solutions with varying manganese concentration x measured at different temperatures.

0.05, 0.3 measured at different temperatures are shown in Fig. 1. It is clear that as temperature increases, all samples exhibit a noticeable short-wave shift in the maximum of the absorption spectrum, an increase in the spectrum width, and a decrease in the maximum absorption coefficient value. To determine these three parameters (magnitude, half-width at half-maximum (HWHM), and spectral position of the maximum) more accurately, each of the recorded spectra was approximated with a Gaussian curve (solid lines in Fig. 1). It can be seen that a single Gaussian curve provides a fine fit to the absorption spectrum across the entire examined range of temperatures. The configuration diagram of Cr^{2+} ions presented in Fig. 2 [14,15] also suggests that a single line is to be expected in the absorption spectrum, while two lines should be present in the fluorescence spectrum.

The parameters obtained as a result of approximation within the entire studied temperature range for $Zn_{1-x}Mn_xSe$ solid solutions with manganese ion concentration $x = 0$ (ZnSe), 0.05, 0.3 are presented in Fig. 3. It is evident that the absorption spectra maxima shift toward longer wavelengths depending on concentration x of manganese ions in the crystal, similar to the findings in [8]. It can also be seen that the temperature dependences of the position of the maximum, the half-width of the spectrum, and the maximum absorption coefficient of all crystals with different concentrations of manganese ions x may be approximated fairly well by straight lines with close slopes. The maximum absorption coefficient decreases at a rate of approximately 0.0013 cm^{-1}/K, the

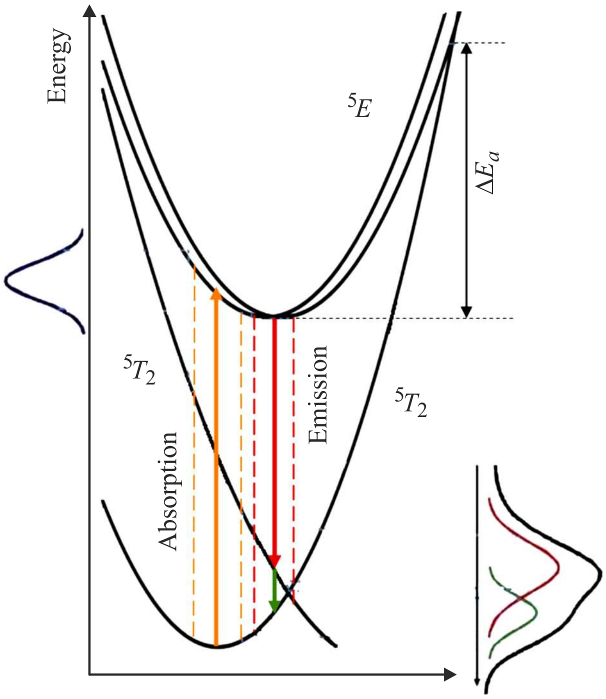

Figure 2. Configuration diagram of the energy level splitting of Cr^{2+} ions in a tetrahedral configuration [14,15].

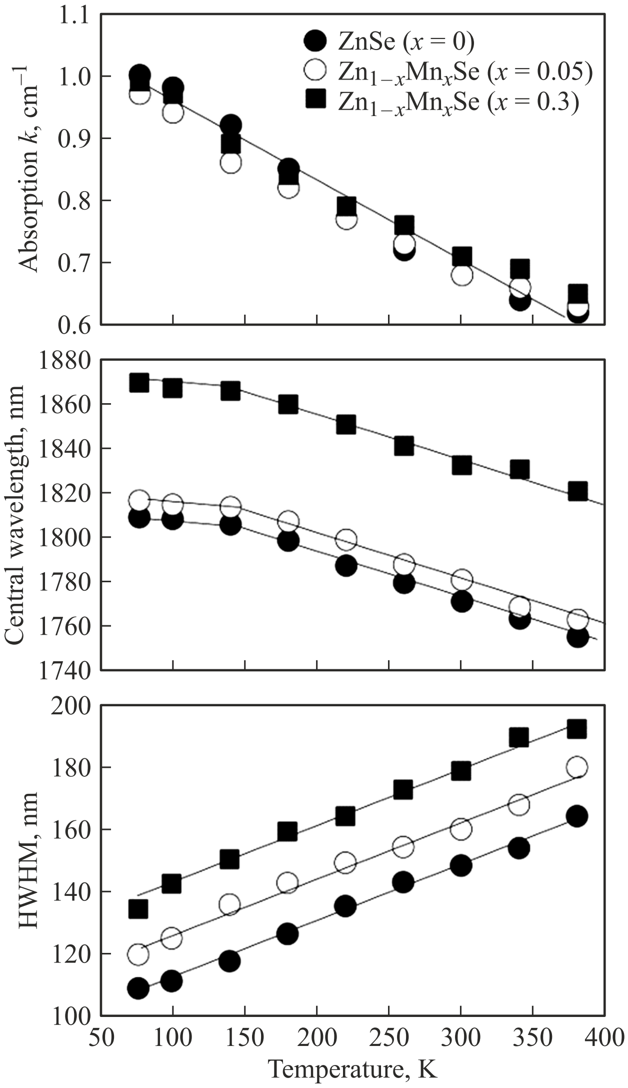

Figure 3. Dependences of the maximum absorption coefficient, the central wavelength, and the HWHM value of the spectra measured at different temperatures for Cr^{2+} in $Zn_{1-x}Mn_xSe$ solid solutions with varying manganese concentration x.

position of the absorption line maximum shifts toward shorter wavelengths at a rate of approximately 0.3 nm/K with an increase in temperature, and HWHM value increases at a rate of approximately 0.2 nm/K. It should be noted that similar linear dependences of the position of the maximum, the HWHM value of the spectrum, and the maximum absorption coefficient on temperature for Cr^{2+} ions in a ZnSe crystal have also been observed in [11,12].

It can be seen from Fig. 3 that the spectral position of the absorption line maximum features a different dependence at temperatures below 140 K. The initial region may also be approximated by a linear function, but the one with a significantly (approximately 4 times) lower slope of 0.05 nm/K. A similar deviation from the linear dependence in the low-temperature region in ZnSe crystals has also been observed in [11,12]. It should be noted that the temperature dependence of the position of the absorption line maximum in [16] also had two different slopes at the initial stage $8 - 120$ K and above 140 K, which was attributed to the temperature dependence of the density of phonon states.

Since it was impossible to maintain absolutely identical conditions in the measurements of temperature dependences of fluorescence spectra, the recorded spectra for all three studied crystals were normalized to the peak value of the fluorescence spectrum at each temperature. The examples of measured and normalized fluorescence spectra for $Zn_{1-x}Mn_xSe$ solid solutions with manganese ion concentration $x = 0$ (ZnSe), 0.05, 0.3 at different temperatures are shown in Fig. 4. Since the fluorescence spectra of Cr^{2+} ions correspond to two transitions (Fig. 2), each recorded spectrum is expected to contain two lines [15]. Therefore, all the recorded spectra were approximated with two Gaussian curves (solid lines in Fig. 4) in order to determine the parameters of each spectrum (magnitude, HWHM value, and spectral position of the maximum) more accurately. It can be seen that a sum of two Gaussian curves provides a fine fit to the fluorescence spectra of all three studied samples across the entire examined temperature range. Similar to the previously measured absorption spectra, both maxima in the fluorescence spectra shift toward shorter wavelengths with increasing temperature, and the fluorescence line broadens at higher temperatures.

The parameters for two Gaussian curves obtained as a result of approximation across the entire studied temperature range for $Zn_{1-x}Mn_xSe$ solid solutions with manganese ion concentration $x = 0$ (ZnSe), 0.05, 0.3 are presented in Fig. 5. The presented results clearly show that, similar to the absorption spectra and to the reported in [8], both maxima of the fluorescence spectra shift toward longer wavelengths depending on manganese ion concentration x. This shift for both maxima is independent of temperature. It can also be seen that the temperature dependences of the maximum position and the HWHM of the spectra for all the studied crystals may be approximated fairly well by a linear function, with a slope that does not depend on the manganese ion concentration. As the temperature increases, the position of the maximum of both fluorescence lines shifts toward shorter wavelengths at a rate of approximately 0.3 nm/K, while the HWHM value increases at a rate of approximately 0.2 nm/K. Notably, the mentioned parameters are completely consistent with the values obtained above for the absorption spectra, indicating that the dependences are similar in nature. It should also be noted that, in contrast to the absorption spectra, the fluorescence spectra reveal virtually no difference in the width of the lines corresponding to different concentrations of manganese ions x across the entire examined temperature range.

The measured dependences of the lifetime of Cr^{2+} ions in $Zn_{1-x}Mn_xSe$ solid solution crystals with varying manganese ion concentration $x = 0$ (ZnSe), 0.05, 0.3 are shown in Fig. 6. It can be seen that this temperature dependence for the crystal with a low manganese concentration ($x = 0.05$)

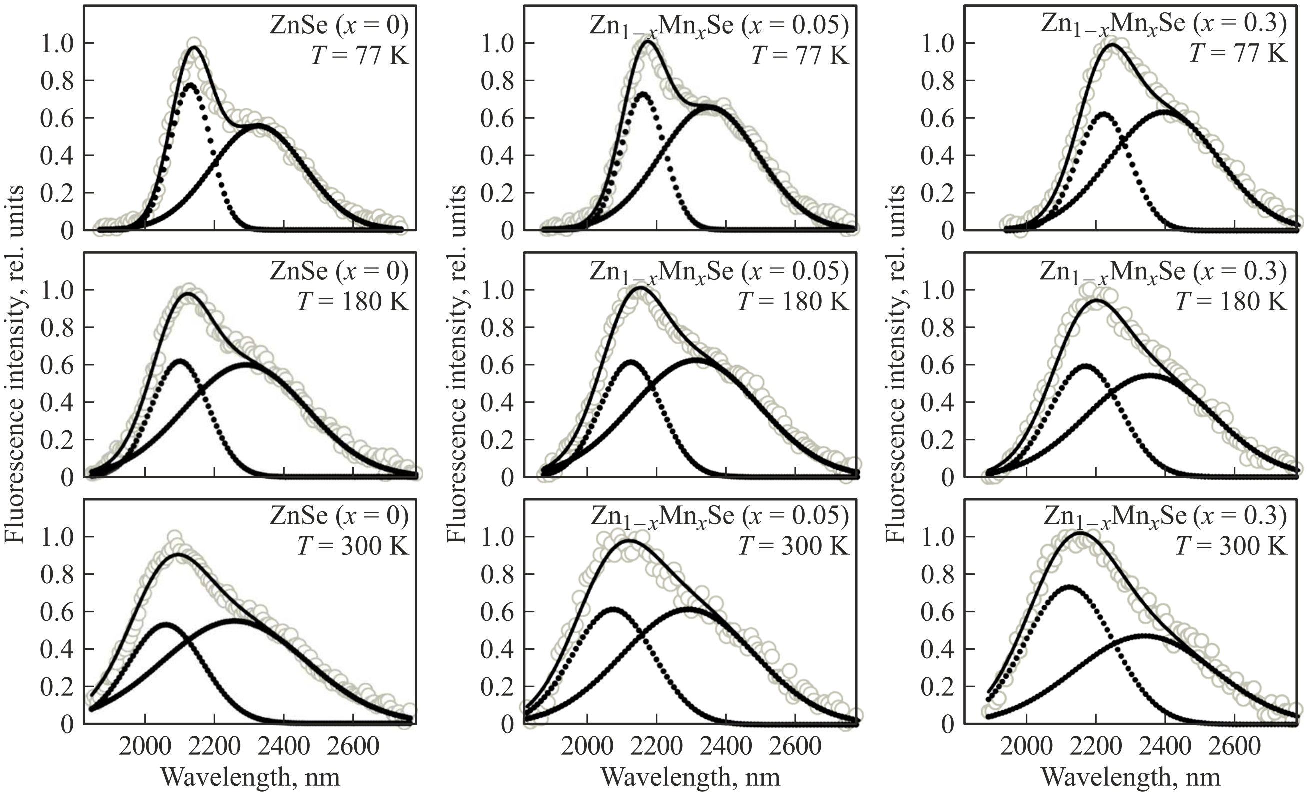

Figure 4. Fluorescence spectra of Cr^{2+} ions in $Zn_{1-x}Mn_xSe$ solid solutions with varying manganese concentration x measured at different temperatures.

is close to the one of ZnSe ($x = 0$). The lifetime for both crystals remains virtually independent of temperature up to room temperature (300 K). The lifetime of Cr^{2+} ions in the crystal with a high concentration of manganese ($x = 0.3$) starts decreasing earlier, at a temperature of about 250 K. As was proposed in [8], this is attributable to stronger quenching due to a smaller gap ΔE_a between the minimum of the adiabatic curve for level $^5T_2$ and the point of intersection of the adiabatic curves for levels $^5T_2$ and ^5E in the configuration diagrams (Fig. 2).

Conclusion

Thus, to our knowledge, these are the first detailed temperature studies on the dependence of spectral characteristics of Cr^{2+} ions in $Zn_{1-x}Mn_xSe$ solid solution crystals with widely varying manganese ion concentration $x = 0$ (ZnSe), 0.05, 0.3 to have been carried out. It was demonstrated that the maxima of absorption and fluorescence spectra of all the studied crystals shift toward shorter wavelengths almost linearly at a rate of approximately 0.3 nm/K with an increase in temperature. The widths of absorption and fluorescence lines also have a near-linear dependence and increase in virtually the same manner with temperature at a rate of 0.2 nm/K. The temperature dependence of the lifetime of Cr^{2+} ions in crystals with low and high concentrations of manganese ions remains weak up to room temperature and to 250 K, respectively. The earlier and faster temperature quenching of the fluorescence decay time of Cr^{2+} ions at higher concentrations of manganese ions x may be attributed to a reduction in ΔE_a value ($4250\,\mathrm{cm}^{-1}$ for $x = 0.05$ and 3050 cm for $^{-1}$. $x = 0.3$ [8]).

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] S.B. Mirov, I.S. Moskalev, S. Vasilyev, V. Smolski, V.V. Fedorov, D. Martyshkin, J. Peppers, M. Mirov, A. Dergachev, V. Gapontsev. IEEE J. Sel. Top. Quant. Electron., **24** (5), 1601829 (2018).
DOI: 10.1109/JSTQE.2018.2808284

[2] L.D. De Loach, R.H. Page, G.D. Wilke, S.A. Payne, W.F. Krupke. IEEE J. Quant. Electron., **32** (6), 885 (1996).
DOI: 10.1109/3.502365

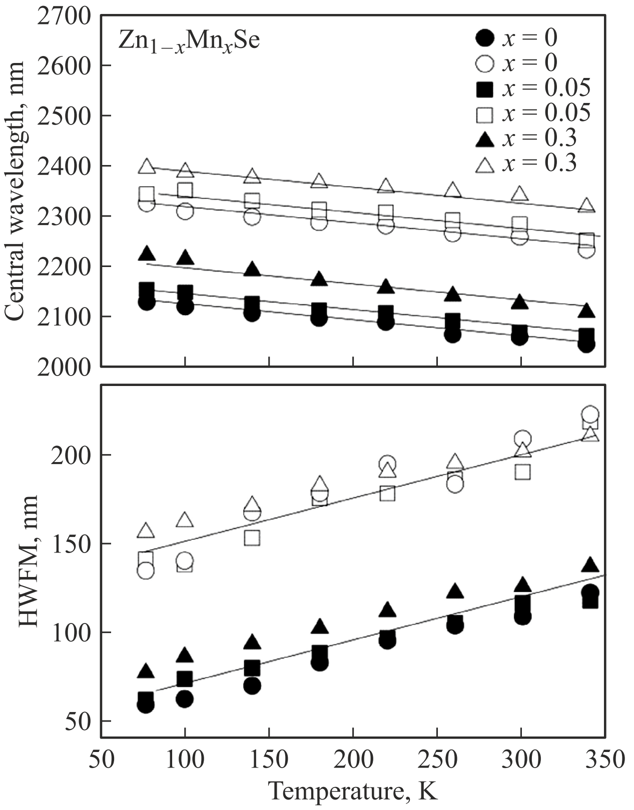

Figure 5. Dependences of the central wavelength and the HWHM values for two Gaussian curves of the fluorescence spectra of Cr^{2+} ions measured at different temperatures in $Zn_{1-x}Mn_xSe$ solid solutions with varying manganese concentrations x.

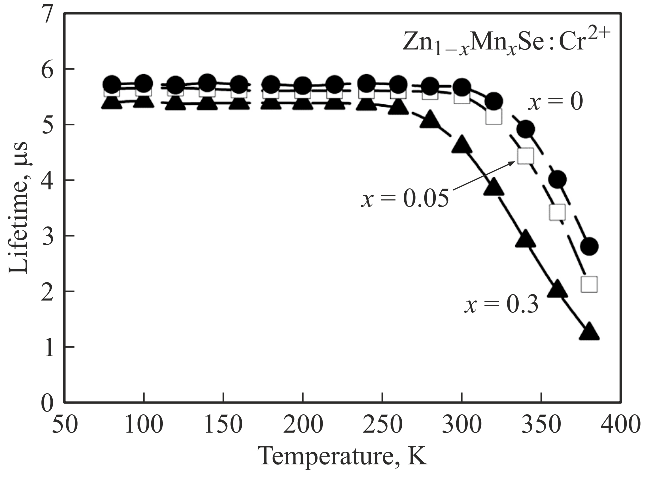

Figure 6. Temperature dependences of the lifetime of Cr^{2+} ions in $Zn_{1-x}Mn_xSe$ solid solutions with varying manganese concentration x.

[3] T.J. Carrig. J. Electron. Mater., **31** (7), 759 (2002). DOI: 10.1007/s11664-002-0233-1

[4] M. Mond, D. Albrecht, E. Heumann, G. Huber, S. Kück. Opt. Lett., **27** (12), 1034 (2002). DOI: 10.1364/OL.27.001034

[5] A.G. Bluiett, U. Hömmerich, R.T. Shah, S.B. Trivedi, S.W. Kutcher, C.C. Wang. J. Electron. Mater., **31** (7), 806 (2002). DOI: 10.1007/s11664-002-0241-1

[6] V.I. Kozlovsky, Y.V. Korostelin, Y.P. Podmar'kov, Y.K. Skasyrsky, M.P. Frolov. J. Phys.: Conf. Ser., **740**, 012006 (2016). DOI: 10.1088/1742-6596/740/1/012006

[7] M.E. Doroshenko, H. Jelínková, P. Koranda, J. Šulc, T.T. Basiev, V.V. Osiko, V.K. Komar, A.S. Gerasimenko, V.M. Puzikov, V.V. Badikov, D.V. Badikov. Las. Phys. Lett., **7** (1), 38 (2010). DOI: 10.1002/lapl.200910111

[8] M.E. Doroshenko, H. Jelinkova, A. Riha, K. Pierpoint. Mater. Today Commun., **37**, 107048 (2023). DOI: 10.1016/j.mtcomm.2023.107048

[9] A. Říha, M. Němec, H. Jelínková, M. Čech, D. Vyhlídal, M.E. Doroshenko, V.K. Komar, A.S. Gerasimenko. In: *Photonics, Devices, and Systems VII*, ed. by K. Fliegel, P. Páta, V. 10603 (SPIE, 2017), p. 243–250. DOI: 10.1117/12.2292196

[10] A. Říha, H. Jelínková, M. Němec, R. Švejkar, M.E. Doroshenko, V.V. Osiko, N.O. Kovalenko, A.S. Gerasimenko. In: *2018 International Conference Laser Optics* (ICLO) (IEEE, 2018), p. 5. DOI: 10.1109/LO.2018.8435767

[11] S.B. Mirov. *Transition Metal and Rare Earth Doped II–VI Chalcogenides for Optically and Electrically Pumped Broadly Tunable Mid-IR Lasers.* AFRL-AFOSR-VA-TR-2018-0389 Final Report, 2018. URL: https://apps.dtic.mil/sti/pdfs/AD1062813.pdf

[12] A. Říha, H. Jelínková, M. Němec, M. Čech, D. Vyhlídal, M.E. Doroshenko, V.V. Badikov. In: *High-Power, High-Energy, and High-Intensity Laser Technology IV*, V. 11033 (SPIE, 2019), p. 111–118. DOI: 10.1117/12.2520722

[13] M. Hetterich, B. Daniel, C. Klingshirn, P. Pfundstein, D. Litvinov, D. Gerthsen, K. Eichhorn, D. Spemann. Phys. Stat. Sol., **1** (4), 649 (2004). DOI: 10.1002/pssc.200304143

[14] E. Sorokin. *Solid-State Materials for Few-Cycle Pulse Generation and Amplification.* In: Kärtner, F.X. (eds) Few-Cycle Laser Pulse Generation and Its Applications. Topics in Applied Physics. V. 95. DOI: 10.1007/978-3-540-39849-3_1

[15] I.T. Sorokina. In: *Mid-Infrared Coherent Sources and Applications*, ed. By M. Ebrahim-Zadeh, I.T. Sorokina. NATO Science for Peace and Security. Series B: Physics and Biophysics. (Springer, Dordrecht, 2008), p. 225–260. DOI: 10.1007/978-1-4020-6463-0_7

[16] A.I. Belogorokhov, M.I. Kulakov, V.A. Kremerman, A.L. Natadze, Yu.B. Rozenfel'd, A.I. Ryskin. Zh. Eksp. Teor. Fiz., **94** (6), 174 (1988).

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