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$Cr^{2+}-Fe^{2+}$ clusters formation in $Zn_{1-x}Mn_xSe$ crystal

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Spectroscopic properties of Cr2+ and Fe2+ ions in $Zn_{1-x}Mn_xSe$ solid solution with $x = 0.05$ content $x = 0.3$ and x=0.3 at low (77 K) temperature are investigated and their difference for crystals doped only by chromium ions and co-doped by chromium and iron ions is demonstrated. This difference is attributed to formation of $Cr^{2+}-Fe^{2+}$ clusters in co-doped crystals.

Keywords: $Zn_{1-x}Mn_xSe$ based solid solutions, $Cr^{2+}-Fe^{2+}$ ions co-doping, Spectroscopy, Clustering.

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Introduction

ZnSe crystals activated with divalent chromium or ferrous ions are widely used in the development of efficient tunable mid-IR lasers. Significant progress has recently been made in the maximum output power and efficiency of such lasers. Thus, for $ZnSe:Cr^{2+}$ crystals, the maximum demonstrated lasing efficiency exceeds 60%, and the CW lasing power was approximately 140 W. For $ZnSe:Fe^{2+}$ crystals, an output power of about 10 W has been demonstrated with an efficiency of over 40% [1]. In the pulse mode for $ZnSe:Fe^{2+}$ crystals, an output energy of over 1 J [2] was demonstrated. Such progress in the development of lasers based on $ZnSe:Fe^{2+}$ crystals allows to develop real devices on their basis, for example, laser spectrometers [3]. The main disadvantage of ferrous ions-based lasers, in addition to a significant shortening of the lifetime with increasing temperature, is the complexity of optical pump sources operating in the 3 μm region. Although the possibility of pumping ferrous ions with a fairly compact source based on the $ZBLAN:Er^{3+}$ fiber has already been demonstrated, for which the lasing of ferrous ions with an output power of more than 2 W and a differential efficiency of up to 59% [4] was realized. Another way to significantly simplify the sources of optical pumping of Fe^{2+} ions can be the co-doping of ZnSe crystals simultaneously with chromium and ferrous ions and the use of non-radiative $Cr^{2+} \rightarrow Fe^{2+}$ energy transfer process. In this case, it becomes possible to use the entire variety of commercially available optical pump sources for chromium ions (wavelength range 1500–2300 nm) and to implement long-wavelength (3500–5300 nm) tunable lasing of ferrous ions. The possibility of energy transfer from chromium ions to ferrous ions was shown for a ZnSe crystal back in [5–7]. Unfortunately, the use of the energy transfer process $Cr^{2+} \rightarrow Fe^{2+}$ in a ZnSe crystal to implement laser oscillation of ferrous ions has not yet been demonstrated. Moreover, in [5,8], ferrous ions fluorescence quenching and a decrease in power and lasing efficiency were observed when a ZnSe crystal was co-doped with chromium ions. However, this possibility has been successfully demonstrated for a number of solid solutions such as $Zn_{1-x}Mn_xSe{:}Cr^{2+}$, Fe^{2+} and $Zn_{1-x}Mg_xSe{:}Cr^{2+}$, Fe^{2+} [9–13].

The possibility of the formation of transition metal ions (Cr^{2+}, Fe^{2+}) clusters in zinc selenide (ZnSe) crystals has already been discussed in the literature. A noticeable change in the spectral-kinetic properties with an increase in the chromium ions concentration was shown (the maximum of the chromium ions fluorescence spectrum shifts to longer wavelengths, and the fluorescence decay time shortens) [14]. A similar situation can also be observed for ferrous ions in a ZnSe crystal, either with an increase in the concentration [15], or with a change in the excitation wavelength [16]. However, in co-doped crystals, the formation of $Cr^{2+}-Fe^{2+}$ clusters is also possible, leading to a change in the spectral properties of both chromium and ferrous ions in such clusters due to modification of the local environment. Moreover, such a transformation of the spectral-kinetic properties of chromium and ferrous ions in $Cr^{2+}-Fe^{2+}$ clusters can have a significant effect on the process of non-radiative $Cr^{2+} \rightarrow Fe^{2+}$ energy transfer. The proposed work is devoted to studying the possibility of the formation of such clustered centers as well as to determining their spectral properties in $Zn_{1-x}Mn_xSe:Cr^{2+}$, Fe^{2+} solid solution crystals with different contents of manganese ions.

Methods

$Zn_{1-x}Mn_xSe:Cr^{2+}$, Fe^{2+} crystals with low ($x = 0.05$) and high ($x = 0.3$) contents of manganese ions were used in the experiments. Studies were carried out at a low

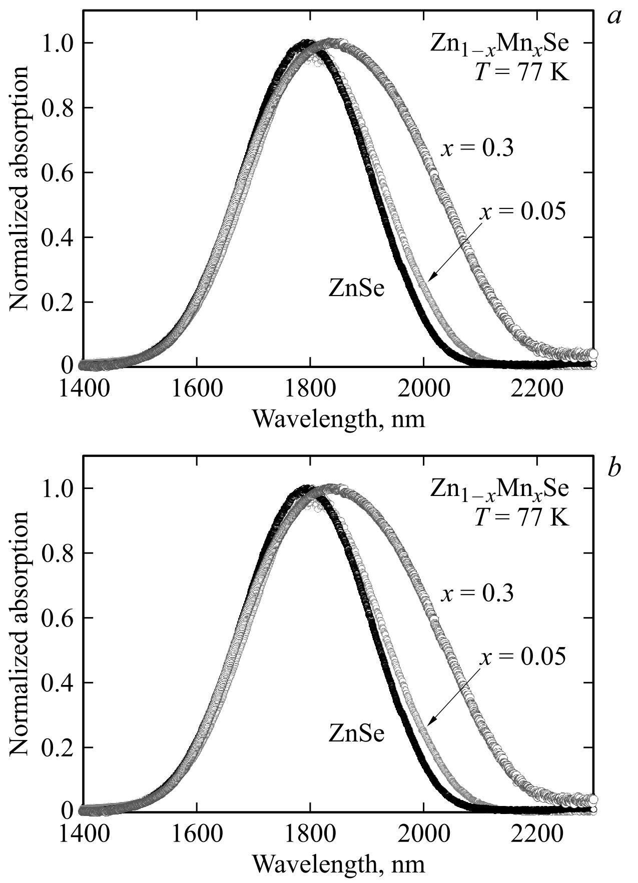

Figure 1. Low-temperature chromium ions absorption spectra in $Zn_{1-x}Mn_xSe$ solid solutions with different manganese contents x doped only with chromium ions (a) and co-doped with chromium and ferrous ions (b).

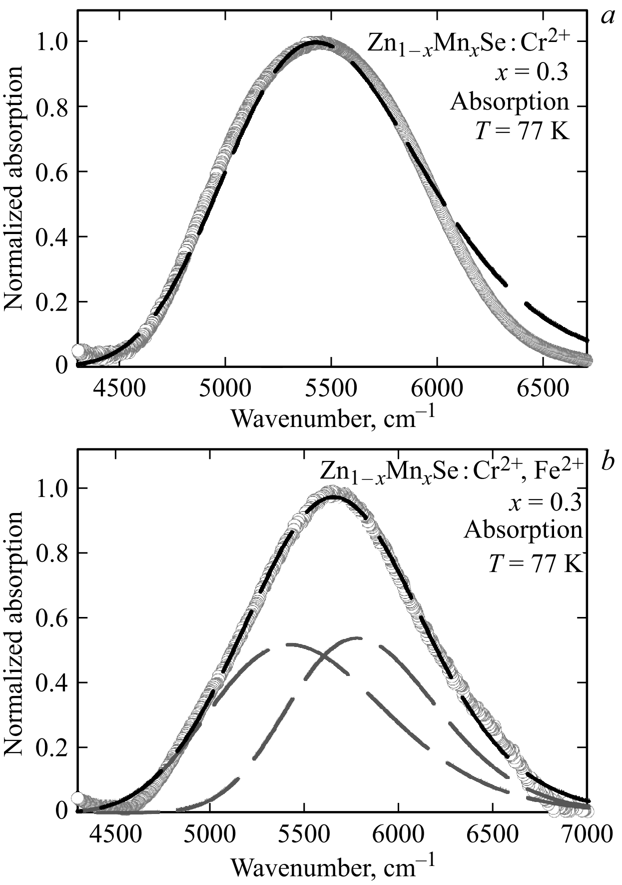

Figure 2. Decomposition into Gaussian contours of low-temperature absorption spectra of chromium ions in the $Zn_{1-x}Mn_xSe$ ($x = 0.3$) solid solution, doped only with chromium ions (a) and co-doped with chromium and ferrous ions (b).

temperature (77 K). The absorption spectra of chromium and ferrous ions were recorded using a tSTAT335x cryostat (RTI Ltd.) in an Infralum FT-08 FTIR spectrophotometer. Fluorescence spectra and fluorescence decay kinetics were measured in a Janis VPF-100 nitrogen cryostat or under excitation into the absorption band of chromium ions by a pulsed nanosecond YLF:Er laser with a wavelength of 1735 nm, or under direct excitation of ferrous ions by a pulsed nanosecond YAG:Er laser with a wavelength of 2940 nm. To detect the radiation, we used: in the chromium ion fluorescence region ~ 2300 nm IBSG PD36 05, and in the ferrous ion fluorescence region ~ 4400 nm – Vigo PVI-6, connected to a digital oscilloscope. All signals were recorded in digital form using a computer.

Results and Discussion

Fig. 1, a shows the experimentally measured low-temperature (77 K) absorption spectra of chromium ions in $Zn_{1-x}Mn_xSe:Cr^{2+}$ solid solution crystals with different contents of manganese ions. For comparison, the figure shows the absorption spectrum of chromium ions measured under similar conditions in a ZnSe crystal. As can be seen from the figure, for crystals containing only chromium ions as a dopant, the absorption spectra with an increase in manganese content (x) differ mainly in the long-wavelength part of the spectrum, and the short-wavelength edges for all crystals practically coincide. As was also observed earlier [17], the higher the content of manganese x in the solid solution, the more the spectrum shifts to the long-wavelength region. Fig. 1, b shows the absorption spectra of chromium ions for $Zn_{1-x}Mn_xSe$ crystals with different manganese ions contents co-doped with chromium and ferrous ions. The absorption spectrum of the $ZnSe:Cr^{2+}$ crystal here is similar to that shown in Fig. 1, a and is presented for comparison. As follows from the figure, for the crystals co-doped with ferrous ions, the shape of the chromium ions absorption spectra differs from that for non-co-doped crystals. Here, in addition to changes in the long-wavelength part of the absorption spectrum, as in Fig. 1, a, changes are also well observed in the short-wavelength part, which are especially noticeable for the $Zn_{1-x}Mn_xSe$ ($x = 0.3$) crystal with a higher manganese content.

As shown in Fig. 2, a, the simplest approximation of the low-temperature (77 K) absorption spectrum of chromium ions in a $Zn_{1-x}Mn_xSe$ ($x = 0.3$) crystal is possible using a single Gaussian contour (Fig. 2, *a*, dashed line). For a co-doped crystal, the absorption spectrum can be approximated by two Gaussian contours, one of which, in all its parameters (line width, position of the maximum), except for the amplitude, corresponds to the Gaussian contour obtained for a crystal doped only with chromium ions. The additional band has a maximum at a higher frequency (a shorter wavelength line in the absorption spectrum) while the linewidth is close. The difference in the positions of the maxima between these lines is quite significant, measuring around $350\,cm^{-1}$. This additional short-wavelength absorption line is apparently associated with the formation of chromium ions with a modified local environment in the co-doped $Zn_{1-x}Mn_xSe:Cr^{2+}$, Fe^{2+} crystal [18], associated with the presence of additional ferrous ions in the crystal.

Low-temperature (77 K) fluorescence spectra of chromium ions in a $Zn_{1-x}Mn_xSe:Cr^{2+}$ ($x = 0.05$) crystal for the cases of doping with chromium ions and co-doping with chromium and ferrous ions simultaneously are shown in Fig. 3, *a*. The figure also shows the edge of the absorption spectrum of ferrous ions in a $Zn_{1-x}Mn_xSe:Fe^{2+}$ ($x = 0.05$) crystal. It can be seen that the fluorescence spectra, as well as the absorption spectra of chromium ions, for the co-doped crystal again differ significantly from the non-co-doped one. The difference in the long-wavelength part of the fluorescence spectrum can be explained by the partial absorption of the chromium ions fluorescence by ferrous ions (it can be seen from the figure that the fluorescence spectrum of chromium ions overlaps with the absorption spectrum of ferrous ions), however the changes in the short-wavelength part of the fluorescence spectrum, as well as for the absorption spectrum are apparently related to a change in the local environment of chromium ions in the co-doped crystal. With an increase in the manganese ions content in the solid solution to $x = 0.3$ (Fig. 3, *b*), in addition to the previously observed shift of the maximum of the chromium ions fluorescence spectrum to the long wavelength region with an increase in x [17], one can also see much more significant changes in the short-wavelength part of the fluorescence spectrum when the crystal is co-doped with ferrous ions. It is noticeable that the shift of the absorption spectra of chromium ions to the long wavelength region with an increase in the content of manganese ions (x) increases the degree of their overlap with the absorption spectrum of ferrous ions in the $Zn_{1-x}Mn_xSe:Fe^{2+}$ crystal (Fig. 3, *b*), which should provide conditions for more efficient $Cr^{2+} \rightarrow Fe^{2+}$ energy transfer.

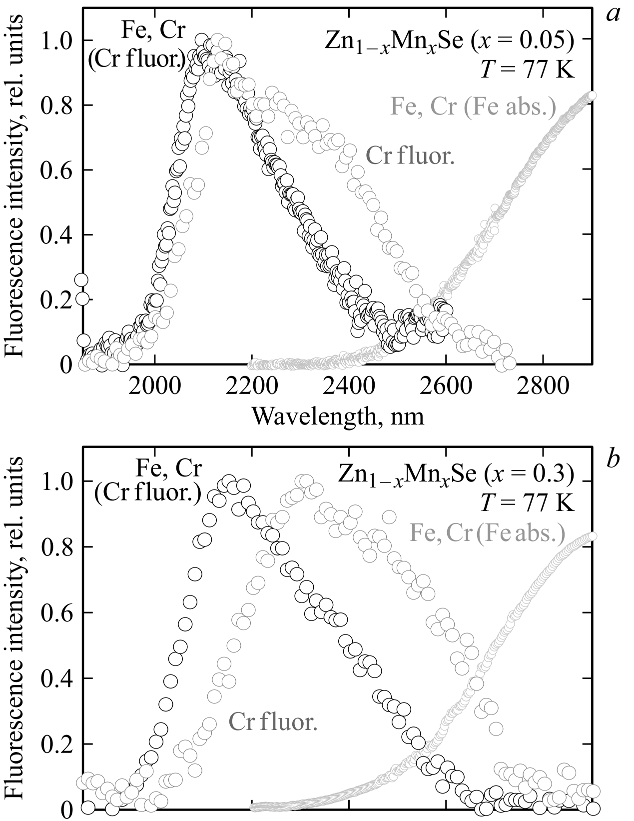

Figure 3. Low-temperature fluorescence spectra of chromium ions in $Zn_{1-x}Mn_xSe$ solid solutions with different manganese contents $x = 0.05$ (*a*) and $x = 0.3$ (*b*), doped only with chromium ions and co-doped with chromium and ferrous ions, and also fragments of the corresponding absorption spectra of $Zn_{1-x}Mn_xSe:Fe^{2+}$ crystals.

Since the fluorescence spectrum of chromium ions in the ZnSe crystal and ZnSe-based solid solutions contains two lines, the fluorescence absorption spectrum in the $Zn_{1-x}Mn_xSe:Cr^{2+}$ ($x = 0.3$) crystal was approximated by two Gaussian contours, as shown in Fig. 4, *a*. To approximate the fluorescence spectrum of chromium ions in a co-doped crystal similarly to the absorption spectra, in addition to these two lines (the approximation parameters of the two contours, except for the amplitude, did not change), it is necessary to add a third, higher frequency one (Fig. 4, *b*). As can be seen from Fig. 4, *b*, the amplitude of the lowest-frequency (long-wavelength) component in the decomposition for a co-doped crystal is much smaller than for a non-co-doped one. Such a decrease in the amplitude can be associated both with a better overlap of the fluorescence spectrum of chromium ions with the absorption spectrum of ferrous ions on the long-wavelength wing (Fig. 3, *b*), and with a lower concentration of chromium ions in the unchanged local environment in the case of a $Zn_{1-x}Mn_xSe:Cr^{2+}$, Fe^{2+} ($x = 0.3$) crystal. Since the fluorescence spectrum of chromium ions in both the standard (unchanged) and modified local environments should contain two bands, the line with a maximum at a frequency of about $4380\,cm^{-1}$(2280 nm) is apparently a superposition of chromium ion fluorescence lines which frequencies vary slightly in different local environments. The shift between the high-frequency fluorescence maxima of chromium ions in this case can be estimated as $\sim 330\,cm^{-1}$, which is close to the value obtained above for the absorption spectra.

The analysis of the process of energy transfer from chromium ions to ferrous ions in $Zn_{1-x}Mn_xSe$ crystals with different manganese contents, carried out in [19,20], showed a 4-fold difference in the energy transfer rates at the initial ordered and subsequent disordered (Förster) stages, despite a significant difference in the distances between the donor (chromium ion) and nearby acceptors (ferrous ions) in the first case and statistically distributed distant acceptors in the second case, and the distance dependence of the non-radiative transfer efficiency as R^6. From the decompositions of the fluorescence spectra of chromium ions shown in Fig. 4, it follows that for co-doped crystals (in the case of a changed local environment of chromium ions), the value of the overlap integral of the fluorescence spectra of chromium ions (donors) and the absorption spectra of ferrous ions (acceptors) is smaller than in the case „of the standard“ environment. This can lead to a deterioration in the conditions for resonant non-radiative energy transfer from chromium ions to ferrous ions located in the nearest environment (such a close location leads to a change in the local environment), and, conversely, to an improvement in resonance conditions in the case when the chromium ions are in a „standard“ environment, and ferrous ions are sufficiently isolated.

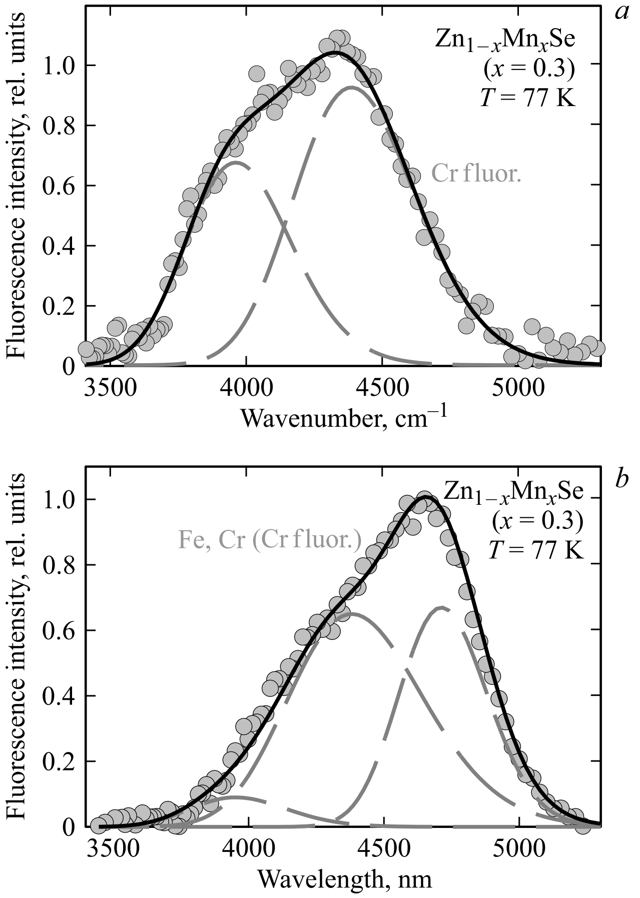

Figure 4. Decomposition into Gaussian contours of low-temperature fluorescence spectra of chromium ions in the $Zn_{1-x}Mn_xSe$ ($x = 0.3$) solid solution, doped only with chromium ions (*a*) and co-doped with chromium and ferrous ions (*b*).

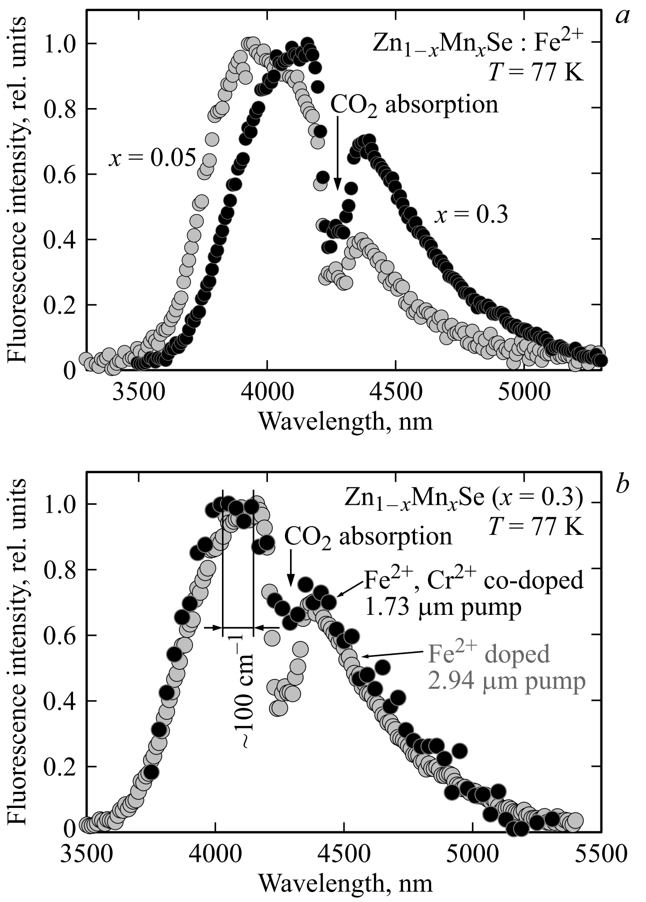

Figure 5. Low-temperature fluorescence spectra of ferrous ions in $Zn_{1-x}Mn_xSe$ solid solutions with different contents of manganese $x = 0.05$ and $x = 0.3$ doped only by ferrous ions (*a*) and fluorescence spectra of ferrous ions in a $Zn_{1-x}Mn$ crystal co-doped with chromium and ferrous ions $_x$Se ($x = 0.3$) under direct excitation of ferrous ions ($\lambda = 2940$ nm) and under excitation via chromium ions ($\lambda = 1730$ nm) (*b*).

The shift of the maximum of the ferrous ions fluorescence spectrum (as well as for chromium ions) in low-temperature (77 K) spectra in a crystal of the $Zn_{1-x}Mn_xSe:Fe^{2+}$ solid solution with increasing manganese content is shown in Fig. 5, *a* and corresponds to the previously demonstrated results [21]. In the co-doped $Zn_{1-x}Mn_xSe:Cr^{2+}$, Fe^{2+} ($x = 0.3$) crystal, the fluorescence spectrum of ferrous ions obtained under excitation into the absorption band of ferrous ions (2940 nm) practically did not differ from the spectrum of the non-co-doped crystal. However, under excitation into the absorption band of chromium ions (1730 nm), the fluorescence of ferrous ions was still observed, which indicates the presence of $Cr^{2+} \rightarrow Fe^{2+}$energy transfer, but the fluorescence spectrum was slightly different (Fig. 5, *b*). In the maximum of the fluorescence spectrum of ferrous ions in the co-doped crystal, a small short-wavelength shift (about $100\,cm^{-1}$) was observed compared to the non-

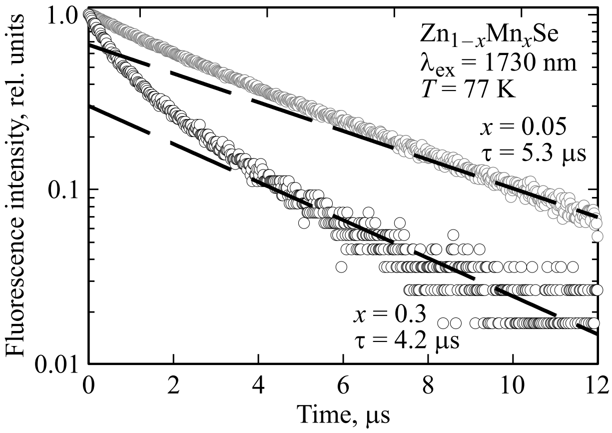

Figure 6. Low-temperature fluorescence decay curves of chromium ions in $Zn_{1-x}Mn_xSe$ solid solutions with different manganese contents $x = 0.05$ and $x = 0.3$ co-doped by chromium and ferrous ions.

co-doped crystal. Apparently, such a short-wavelength shift, as well as for chromium ions, corresponds to a changed local environment of ferrous ions. Since similar changes in the spectra are observed for both chromium and ferrous ions, it is quite reasonable to assume the formation of clustered $Cr^{2+}-Fe^{2+}$ optical centers in co-doped $Zn_{1-x}Mn_xSe$ crystals.

The fluorescence decay curve of chromium ions in non-co-doped $Zn_{1-x}Mn_xSe$ crystals with different manganese contents under excitation by nanosecond pulses with a wavelength of 1730 nm at a temperature of 77 K had a single-exponential form with a lifetime of 5.3 μs and 4.2 μs for $x = 0.05$ and $x = 0.3$ respectively [20,19]. In co-doped crystals, the fluorescence decay curve was non-exponential (Fig. 6), which indicates the presence of non-radiative energy transfer from chromium ions to ferrous ions. The measured fluorescence decay kinetics in this case at the far stage of decay had a form close to exponential with times 5.3 μs and 4.2 μs (Fig. 6), which corresponds to the lifetime of chromium ions in non-co-doped crystals.

Conclusions

Thus, the study of crystals of the $Zn_{1-x}Mn_xSe$ solid solution with different contents of manganese ($x = 0.05$ and $x = 0.3$) has shown that, when the crystals are co-doped with divalent chromium and ferrous ions, there is a change in the measured low-temperature (77 K) absorption and fluorescence spectra of chromium ions. In contrast to the changes associated with manganese content (x) in the crystal, there are alterations in the short-wavelength region of the spectra caused by the presence of additional short-wavelength lines in the absorption and fluorescence spectra. For a crystal with a high manganese content ($x = 0.3x = 0.3$the position of the shortest wavelength band in both spectra (absorption and fluorescence) turns out to be significantly shifted to the blue area by approximately 350 cm^{-1}compared to a non-co-doped crystal. When ferrous ions are excited via chromium ions by radiation with a wavelength of 1730 nm, in such a crystal, the low-temperature (77 K) fluorescence spectrum of Fe^{2+}also turns out to be shifted to the short-wavelength region by approximately 100 cm^{-1} compared to direct excitation of ferrous ions by radiation with a wavelength of 2940 nm. Such changes in the absorption and fluorescence spectra of chromium and ferrous ions suggest the formation of clustered optical centers containing fairly closely spaced chromium and ferrous ions with a changed local environment. Due to the smaller value of the overlap integral between the fluorescence spectra of chromium ions and the absorption spectra of ferrous ions in such clustered centers, the resonance conditions for non-radiative $Cr^{2+} \rightarrow Fe^{2+}$ energy transfer worsen. Apparently, this leads to a 4-fold difference in the rate of energy transfer from chromium ions to ferrous ions at the first ordered and subsequent disordered (Förster) stages in both crystals.

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Conflict of interest

The authors declare that they have no conflict of interest.

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