The influence of iron concentration on the cathodoluminescence kinetics in the mid-IR range in ZnSe:Fe crystals

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Abstract. Integral intensity and kinetics dependences of cathodoluminescence of ZnSe:Fe crystals in mid-IR spectral range was studied. Concentration of iron varied from 0.01 to 14 wt.%. The experiments were carried out in 77 - 300 K temperature range. It is established that the luminescence pulse rise time is longer than excitation pulse at low iron concentration at 77 K temperature. The increasing ones lead to shortening of the luminescence pulse rise time, decreasing of the luminescence lifetime and increasing of the luminescence intensity in mid-IR. The annealed ZnSe:Fe concentration series in vapour Zn are reproduced the same trends. The nature of observed experimental effects is discussed.

1. Introduction
Zinc selenide crystals doped with iron are of interest as active laser media for the mid-IR range 3-5 μm [1]. The ZnSe:Fe crystals demonstrate high lasing characteristics with optical pumping by HF or Er:YAG lasers [2-4]. However, the practical implementation of laser systems with such method is a difficult due to dimension and weight of excitation systems. The alternative pumping method of activator atoms is impact excitation with hot (dozen of keV) electrons. In [5] was reported the first study of cathodoluminescence (CL) spectral characteristics of ZnSe:Fe samples in the range of 3-5 μm. The CL spectrum coincides with luminescence spectrum obtained with optical pumping and is associated with 3T2 и 1E intracenter transition of Fe2+ ions [6]. In present investigation we demonstrated the influences of Fe concentration and annealing process in Zn atmosphere on the mid-IR CL kinetics of ZnSe:Fe.

2. Samples and experimental technique
The sample investigated were ZnSe plates doped with iron by thermal diffusion. The initial undoped ZnSe plates were cut of ingots produced using Bridgman method in graphite crucibles at the pressure of high-purity argon of 100 atm. The purity of ingot was 99.9992 wt.% observed by ICP-MC analysis.

The doping based on thermal diffusion of Fe from the surface. The thickness of the iron layer on the surface was about 150 μm. The doping carried out in quasi-closed quartz reactor at a temperature of 1000 °C for 20 hours.
In experiments we used the 2.5 mm thick ZnSe plate with the Fe concentration of 14 wt. % on the surface after diffusion. The concentration of iron was determined by the XRF using the Bruker Mistral M-1 spectrometer.

The samples with Fe concentration in the range of $5 \cdot 10^{18}$ to $3 \cdot 10^{21}$ cm$^{-3}$ were produced by mechanical polishing of the doping surface controlled by 5-point concentration measurements within standard deviation of 0.05.

Thus, the studied range of iron concentrations was significantly expanded, since, the investigation with optical excitation of ZnSe:Fe are carried out at iron concentrations lower than $8 \cdot 10^{19}$ cm$^{-3}$ [6, 8]. It should be noted that iron clusters and inclusions of other phases could be formed at concentrations higher than 0.5 wt. %.

After CL experiments the samples were annealed in a quasi-closed volume in Zn atmosphere at a temperature of 1000 °C for 20 hours. The CL of crystals was excited by a pulsed electron gun at accelerated electron energy of 36 keV, the average electron penetration depth in the sample was $\approx$ 4 μm. The current of the electron beam in a pulse varied in the range from 0.01 to 0.2 A, the beam diameter was 8 mm, the average generation rate of electron-hole pairs in the excited layer in this case was $10^{24}$ - $10^{26}$ pairs cm$^{-3}$ s$^{-1}$. The duration of the excitation pulse was 250 ns (non-annealed samples) and 800 ns (annealed samples). Electron irradiation and CL were observed at an angle of 45 degrees to the sample surface. The CL radiation was coupled out of the chamber through a CaF$_2$ window and focused on the input slit of an MS2004 (SOL Instruments Ltd) monochromator. As a detector, we used a PD42NB (IoffeLED Ltd) diode with a spectral sensitivity within the range 3.15 – 4.75 mm. The time resolution of detection system (photodiode and amplifier) was about 50-100 ns. A signal from the detection system was sent to the input of a digital oscilloscope directly.

The CL kinetics were approximated by the exponent function:

$$y = A_1 e^{\left(\frac{-x}{t_1}\right)} + A_2 e^{\left(\frac{-x}{t_2}\right)},$$

where $A_1$ and $A_2$ are amplitudes, $t_1$ and $t_2$ are lifetimes. The intensity of the CL was determined by the maximum signal.

3. Experimental results and discussion

Figures 1(a, b) and 2(a, b) show the kinetics of the pulses of non-annealed and annealed samples at 77 and 300 K temperatures. The kinetics of CL at 300 K temperature was almost same of the non-annealed and annealed samples, was quite independent of the Fe concentration and was approximated by a single exponential with the lifetime in the range of 220 - 380 ns. The rise time varied in the range of 100 -150 ns and was close to the time constant of the detection system.

The CL kinetics of non-annealed sample with Fe concentration of 0.01 wt.% observed at 77 K (fig. 1(a)) was approximated by two exponentials with lifetimes of 3.5 μs and 20 μs; the 0.05 wt.% sample – 750 ns and 3.8 μs; the CL of 0.1 wt.% sample approximate by single exponential with lifetime of 630 ns. The rise time for 0.01 wt.% sample was about 450 ns, and 300-350 nm for 0.05 and 0.1 wt.% samples. The CL kinetics of the samples with concentration higher than 0.5 wt.% observed at 77 K temperature were similar to CL kinetics observed at 300 K (fig. 1(b)).
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Slightly different results of CL kinetics of annealed samples were observed at 77 K temperature (fig. 2(a)). The CL lifetimes of samples with 1 wt.% and higher were about 350-380 ns.

The rise time of the CL was 100 – 150 ns and was less than the duration of the exciting pulse. Kinetics of the crystal with an iron concentration of 0.05 wt. % was close to that of the non-annealed samples with an iron concentration of 0.01 wt. %. The CL kinetics was approximated by two exponents with lifetimes of 2.8 µs and 19.5 µs. The rise time was about 3 µs. The CL kinetics of samples with an iron concentration in the range of the 0.05 wt. % and 1.5 wt. % were approximated by two exponents with lifetimes of 380 - 400 ns and 3.5-1.3 µs. The rise time of the luminescence intensity decreased from 600 ns to regular 100–150 ns with increasing iron concentration.

Therefore the rate of transition of carriers from the $^5T_2$ level to the $^5E$ level of Fe$^{2+}$ ions at 77 K temperature strongly depends on the concentration of iron. Apparently, the interaction between iron ions significantly increases the transfer probability of carriers from those levels. The mechanism of this effect is unclear and requires further research. This effect in ZnSe:Fe crystals was observed for the first time in present paper. Consequently, the samples with non-homogenous distribution of iron ions in crystal volume (e.g. thermal diffusion based doping) had areas with different transition times from $^5T_2$ to $^5E$ at 77 K temperature. The observed decrease in the rise time of the luminescence intensity
with increasing iron concentration at a temperature of 77 K can be associated with a change in the mechanism of excitation of iron ions. At low iron concentrations, the observed luminescence is the result of the recombination of non-equilibrium carriers generated by the electron flow through Fe$^{2+}$ ions. The known mechanisms of such a process consist of several stages including the initial capture of an electron by a shallow donor and the subsequent transfer of excitation to the Fe$^{2+}$ ion [9-11]. These processes can lead to extension of the rise time of the CL kinetics and that becomes longer than the duration of the excitation pulse. The iron concentration increasing leads to increase of the impact ionization probability of Fe$^{2+}$ ions by “hot” electrons (including “primary” electrons). These processes are faster and stop after the end of the exciting pulse and after the “thermolization” of hot electrons. We suggest that at concentrations higher than 0.5 wt. % the mechanism of Fe$^{2+}$ ions excitation by hot electrons impact ionization was dominated.

It should be noted that the results of CL kinetics excited with electron beam at 77 K were significantly differ from luminescence obtained with optical excitation into the absorption band of Fe$^{2+}$ ions [6, 8]. The results obtained at 300 K (fig. 2(b)) temperature are similar. The kinetics of the luminescence with optical excitation of ZnSe:Fe samples with the maximum Fe concentration of 3$\times$10$^{19}$ and 8$\times$10$^{19}$ cm$^{-3}$ at 77 K temperature was non-approximated by the exponent, and the lifetime decreasing was observed with iron concentration increasing.

The difference is that lifetime with optical pumping, obtained by the exponential part of the luminescence pulse, is much longer (about 40 μs) than the lifetime with electron pumping is 20 μs at samples with iron concentrations of 5$\times$10$^{18}$cm$^{-3}$. Perhaps this trend associated with different experimental conditions. In case of electron excitation a lot of non-equilibrium carriers are generated. In the case of optical excitation of ions in their absorption band, the non-equilibrium carriers are not generated. The different rise time of CL in cases of non-annealed and annealed samples can be explained by changing of defective-impurity composition of the samples.

4. Conclusion
The results obtained in this paper allow us to draw the following conclusions:

The relaxation time of current carriers from level $^5T_2$ to level $^5E$ of iron ions at liquid nitrogen temperature strongly depends on the concentration of iron

The processes of excitation and relaxation of iron ions may be influenced by the impurity-defect composition and concentration of current carriers in ZnSe:Fe crystals.

At concentrations greater than 0.5 wt. % may be the change of the mechanism of iron ion excitation from recombination of non-equilibrium current carriers through them to impact ionization by hot electrons.

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