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Subnanosecond luminescence of molecular clusters in LiF crystals implanted with silver ions

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Parameters of luminescent layers formed in samples of lithium fluoride crystals as a result of irradiation with a beam of high-energy (~ 100 keV) silver ions have been studied. Three components were detected in the luminescence spectra, two of which correspond to the emission of radiation-induced aggregate color centers of the F_3^+ and F_2 types. The third, thermally stable component associated with the spectral maximum at the wavelength of 440 nm, corresponds to the luminescence of molecular silver clusters formed in the irradiated surface layers of lithium fluoride. In the kinetic luminescence decay curves, four components are distinguished; two slow components correspond to aggregate centers, and two intense fast components with decay times of 1.3 and 0.2 ns correspond to molecular silver clusters.

Keywords: subnanosecond luminescence, molecular clusters, LiF crystals, implantation of silver ions.

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Composite optical media containing subnanoscale luminescent metal clusters remain the subject of active research for a number of years. This is because of a great number of applications of such composite materials in photonics and optoelectronics [1]. The most extensive research is being performed for the case of an amorphous matrix based on various types of glasses where nanoclusters get formed from atoms of metal impurities as a result of appropriate treatment of the matrix (irradiation, annealing, etc.) [2]. At the same time, promising optical properties are exhibited by similar composite materials in which submicrometer-thick layers containing metal clusters are formed by implanting into the matrix beams of high-energy metal ions [3].

Notice also that a relatively small number of papers are devoted to studying the emission of crystal-based composite materials, e.g. Al_2O_3 [4] or LiF [5]. The study of the latter is of interest also because ion implantation creates in LiF crystals aggregate luminescence centers; those centers are of independent interest and are widely used in optics [6]. In this work, we have studied spectral and kinetic parameters of luminescence of LiF crystals containing thin layers of (sub)nanosized silver clusters synthesized by irradiation with a beam of high-energy Ag ions. On the one hand, these parameters are important to demonstrate possible applications of such composite materials; on the other hand, they are important for elucidating physical mechanisms of nanocluster luminescence.

Irradiation of samples of lithium fluoride crystals was performed on Ion Implanter MEVVA [5]. The samples were placed in a vacuum chamber with the residual gas pressure of $\sim 10^{-2}$ Pa and were irradiated with a pulsed Ag-ion beam with the duration of 200 μs and current density of about 5 mA/cm^2 at the accelerating voltage of 50 kV; for the Ag^{2+} ions which make up the main part of the ion beam [7], this value corresponds to the energy of 100 keV.

Spectral and kinetic characteristics of the irradiated samples luminescence were studied by using a MicroTime 200 confocal scanning fluorescence microscope (PicoQuant GmbH Company). To excite photoluminescence, a highly stable laser with the wavelength of 405.0 ± 0.7 nm was used; the laser was operated in the pulsed mode with the pulse repetition rate of 10 MHz and pulse width of about 50 ps. Photoluminescence spectra were recorded with an Ocean Optics 6500 spectrometer combined with a MicroTime 200 microscope. To cut off the exciting radiation scattered by the sample, interference filter HQ430LP (Chroma Technology Corp.) was used; the transmission spectrum cutoff wavelength was 430 nm (optical density $\mathrm{OD} = 6$). The photoluminescence decay curves were processed with specialized program code SymPho Time included in the MicroTime 200 microscope infoware. The processing algorithm is based on analyzing histograms measured by the method of time-correlated single photon counting, which provides time resolution $\Delta t \approx 16$ ps.

The luminescence spectrum of the irradiated sample shown in Fig. 1, *a* can be approximated with sufficient accuracy by three Gaussian contours with maxima at wavelengths of 440, 540 and 665 nm. It is natural to relate the last two contours to aggregate color centers F_3^+ and F_2, respectively, whose luminescence band maxima are quite close to the obtained values [8]. These radiation-induced centers got formed in the LiF matrix as a result of irradiation with a beam of high-energy silver ions.

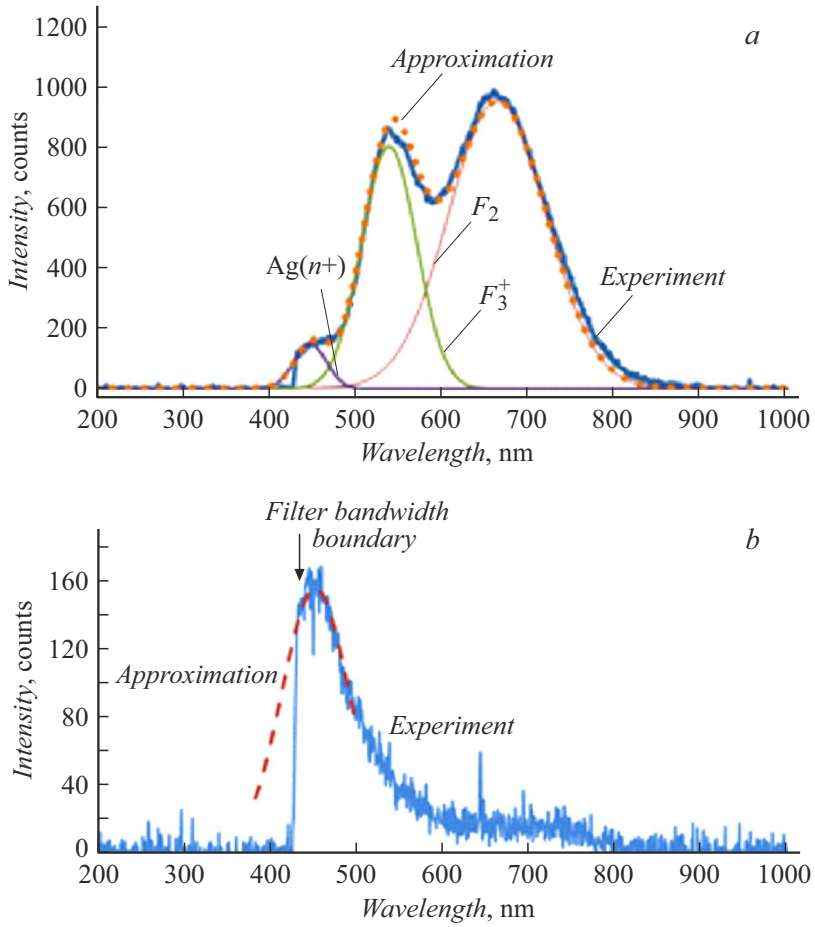

Figure 1. *a* — luminescence spectra of a LiF crystal after irradiation with silver ions with the fluence of $5 \cdot 10^{15}$ ion/cm^2 ($\lambda_{exc} = 405$ nm). Thin solid lines represent Gaussian contours approximating the spectral components, dotted line is the general contour, and thick solid line is the experimental contour. *b* — luminescence spectrum of the same crystal after annealing. The dashed line is the Gaussian contour approximating the Ag(n+) cluster luminescence spectrum.

The band with a maximum at 440 nm may be assumed to be related with (sub)nanosized silver clusters formed as a result of coalescence of silver ions (atoms) implanted into the LiF crystal. This assumption is supported by the fact that the amplitude of this band remains almost unchanged after annealing the sample for 30 min at 633 K (Fig. 1, *b*).

In the kinetic luminescence decay curves (Fig. 2, *a*), four components with decay constants of ~ 0.27, 1.29, 5.20 and 13.5 ns can be distinguished. The last two values are quite close to the luminescence decay constants of centers F_3^+ and F_2, respectively [8]. Two fast components correspond to luminescence of Ag clusters, and intensities of these components significantly exceed intensities of the F_3^+ and F_2 center bands.

After annealing under the above-mentioned conditions, the amplitude of the component corresponding to luminescence of the F_2 centers fell below the detection threshold, amplitude of the component corresponding to luminescence of the F_3^+ centers decreased by more than 60 times, while amplitude of the fast component with the decay constant of ~ 0.2 ns decreased by less than 4 times (Fig. 2, *b*). This result confirms the assumption that the fast components correspond to luminescence of thermally stable silver clusters.

Fig. 3 presenting the luminescence intensities of various temporal components in a wide range of doses of implanted Ag ions shows that, at the dose of about $5 \cdot 10^{14}$ ion/cm^2, intensity saturation is observed for all the components; further increase in the dose leads to a decrease in the radiation intensity.

Previously it was established that the minimum decay time of broadband (450–700 nm) luminescence of silver clusters formed in oxyfluoride glass under excitation by picosecond radiation with the wavelength of 406 nm was 0.5 and 2.4 ns for the observed two temporal components of the 450 nm radiation [9]. The character of luminescence kinetics similar to what we discovered evidences similar mechanisms of this process; in our case, however, a narrower luminescence spectrum and significantly shorter emission time are indicative of the influence of the matrix and/or luminescent layer characteristics.

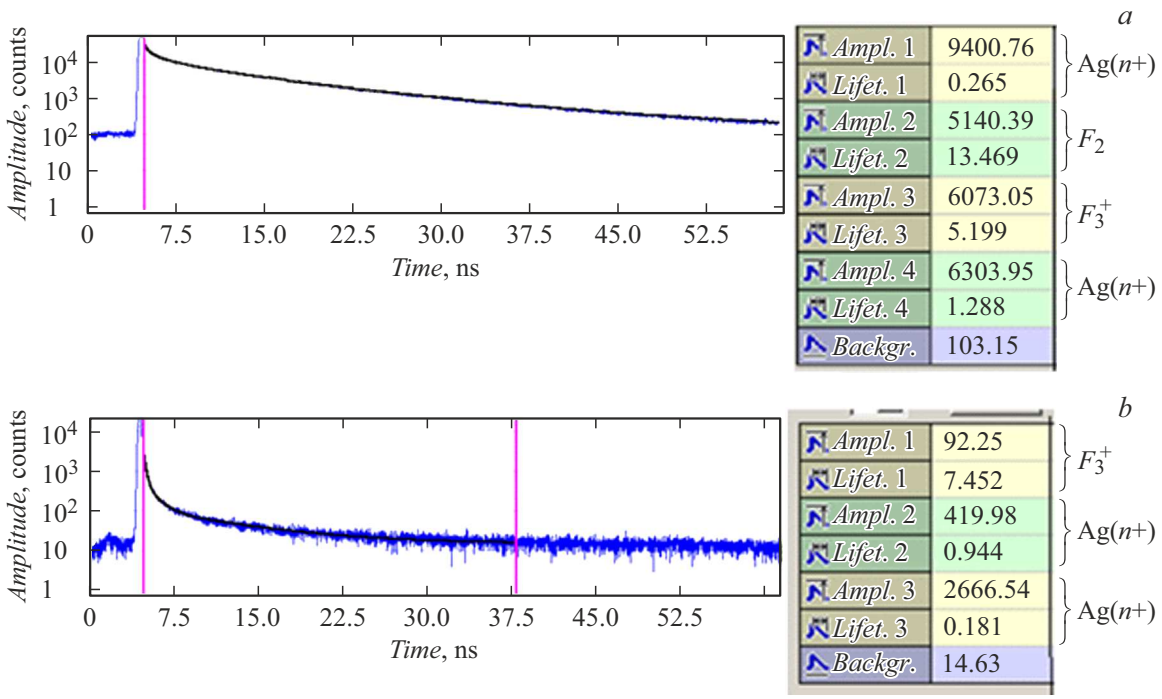

Figure 2. *a* — luminescence kinetics of color centers and silver clusters in the LiF crystal after ion implantation. *Lifet.* — decay time [ns], *Ampl.* — amplitudes of these components [a. u.], *Backgr.* — background. *b* — luminescence kinetics of the sample after annealing at 633 K for 30 min.

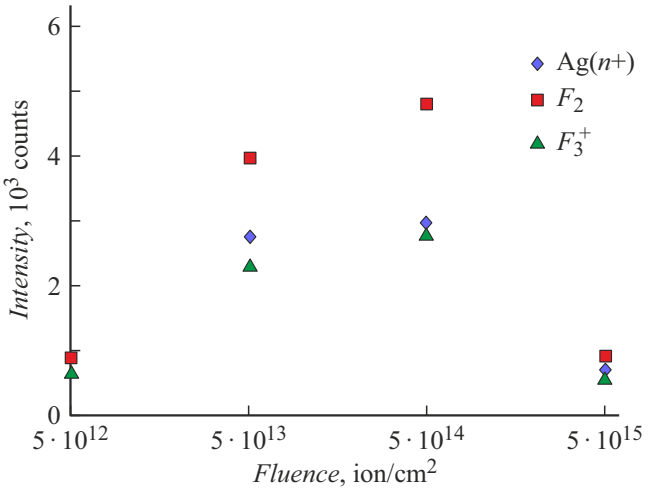

Figure 3. Luminescence intensities of various components versus the dose of implanted ions.

Thus, the paper shows that in the luminescence spectrum of layers formed in LiF crystals as a result of silver ions implantation there are two intense bands corresponding to emission of silver clusters whose decay constants (~ 0.2 and 1.3 ns) appeared to be considerably lower than relevant minimal values previously measured for a similar system in the amorphous fluoride glass matrix. This result shows the possibility of using the observed effect to create picosecond optical elements for photonics problems.

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Conflict of interests

The authors declare that they have no conflict of interests.

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