Kinetics of cathodoluminescence of LiF crystals doped with uranium

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Abstract. The work presents results of a study of the pulsed cathodoluminescence uranium doped LiF crystals. Introduction of the activator (U) and the co-activator (OH) shown in occurrence of additional absorption in the range 260-320 nm. The activated crystals luminescence observed in the field of 400-530 nm when excited by pulsed electron beam with energy 250 keV. In all crystals, the main attenuation component has a value in the range of 40-70 μs. Crystals of lithium fluoride, activated by uranium, with injected coactivators can have highly efficient conversion of radiation energy into light in the visible range of the spectrum.

1. Introduction
Lithium fluoride crystals activated by uranium are promising but poorly studied scintillation materials [1-4]. In crystals, luminescence is effectively excited upon exposure to hard radiation fluxes. The position of the luminescence maximum depends on the concentration of uranium, the presence of oxygen, hydroxyl, and growing conditions as a modifier. One of the main parameters of the scintillation material is the decay time of luminescence excited by high-energy radiation. The luminescence decay time determines the sensitivity and resolution of the scintillation system, which usually operates in the photon counting mode. In this paper we present the results of an investigation of the kinetic characteristics of the luminescence of lithium fluoride crystals activated by uranium.

2. Experimental equipment and research samples
The kinetic characteristics of the damping of the luminescence of the crystals were measured by excitation with a pulse of an electron beam with an energy of 250 keV and a duration of 10 ns. The luminescence was recorded through a monochromator MDR-20, PMT "Hamamatsu" R928, oscilloscopes GDS-2204 and LeCroy 6030A. The integrated luminescence spectra were recorded with
an AvaSpec-3648 fiber optic spectrometer in the spectral range 200–1100 nm. The integration time was 100 μs.

The pure and doped lithium fluoride crystals were grown by the improved Kyropoulos method in a platinum air dish from a special purity reagent. Impurities were introduced into the charge before growing the crystal in the form of uranyl nitrate and lithium hydroxide. The amount of introduced impurity U and OH in the text is given by the concentration of UO$_2$(NO$_3$)$_2$ and LiOH in the charge. Crystals were prepared for the studies: LiF pure, grown in the Research and Technology Institute of Optical materials of Vavilov State Optical Institute: LiF+2.0 mole% OH, LiF+0.005 mole% U, LiF+0.05 mole% U, LiF+0.05 mole% U+0.5 mole% OH, LiF+0.05 mole% U+2.0 mole% OH.

The introduction of an uranium impurity leads to the appearance of absorption in the spectral region with λ<400 nm, which increases to 200 nm (figure 1). At 260 and 320 nm clear bands appear in the spectrum of uranium concentration of more than 0.005 mole% in the crystal. The introduction of OH into the crystal also leads to the appearance of absorption in the UV region of the spectrum. The combined introduction of uranium and OH impurities into the crystal results in the crystals becoming opaque in the region below 280 nm. Obviously, the introduction of uranium in the synthesis is facilitated by the presence of OH ions that enter the emerging crystal to compensate for local elastic stresses. Similar regularities in the variation of the absorption spectra in the short-wavelength region in polyvalent impurities are introduced into crystals of lithium fluorides have been described in [5–8].

Figure 1. Absorption spectra of LiF crystals: 1 – pure; 2 – LiF+2.0 mole% OH; 3 – LiF+0.005 mole% U; 4 – LiF+0.05 mole% U+0.5 mole% OH; 5 – LiF+0.05 mole% U; 6 – LiF+0.05 mole% U+2.0 mole% OH.

3. Results and discussion

The excitation of crystals by a high-energy electron beam pulse (250 keV) leads to the excitation of the luminescence of crystals with integrated spectra shown in figure 1. The positions of the bands in the 450-600 nm region correspond to those described in Ref. [9]. In pure and OH-containing crystals, a band is excited at 425 nm. In crystals containing U or co-activators of U and OH, the luminescence spectra differ substantially in structure and intensity. In the spectra of crystals containing co-activators U and OH, a luminescence band is observed in the 490 nm region. The higher its intensity, the higher the concentration of OH introduced at the same concentration of introduced uranium. We note that this band also appears in the spectrum of a crystal with a large concentration of uranium (compare curves 5 and 6 in figure 2). Obviously, this is a consequence of the fact that OH is present in uranyl, it is possible that
OH enters the crystal from the air atmosphere during synthesis. Introduction of OH as a coactivator in the synthesized LiF crystal with uranium leads to the development of a complex defect in the crystal containing OH as a structural element [10].

In the spectra shown in figure 2, we can distinguish a group of bands with maxima in the region of 508, 521 nm. The relationship between the bands depends on the concentration of the introduced uranium.

The main band is at 508 nm in crystals with a large impurity concentration U, whereas in a crystal with a lower concentration, it is at 521 nm.

![Figure 2. The cathodoluminescence spectra of crystals 1 – LiF, 2 – LiF+2.0 mole% OH, 3 – LiF+0.05 mole% U+2.0 mole% OH, 4 – LiF+0.05 mole% U+0.5 mole% OH, 5 – LiF+0.05 mole% U, 6 – LiF+0.005% U.](image)

Figure 2. The cathodoluminescence spectra of crystals 1 – LiF, 2 – LiF+2.0 mole% OH, 3 – LiF+0.05 mole% U+2.0 mole% OH, 4 – LiF+0.05 mole% U+0.5 mole% OH, 5 – LiF+0.05 mole% U, 6 – LiF+0.005% U. Figure 3 shows, for example, the kinetic curve of the luminescence decay in the region of 415 nm after the excitation pulse by an electron beam in LiF and LiF+2.0 mole% OH crystals. The results of analysis of kinetic curves of damping are given in table 1.

![Figure 3. Luminescence kinetic decay curves at 415-nm after the excitation pulse by an electron beam in 1 – LiF, 2 – LiF+0.05 mole% U+0.5 mole% OH, 3 – LiF+0.005 mole% U, 4 – LiF+0.05 mole% U, 5 – LiF+0.05 mole% U+2.0 mole% OH, 6 – LiF+2.0 mole% OH.](image)

Figure 3. Luminescence kinetic decay curves at 415-nm after the excitation pulse by an electron beam in 1 – LiF, 2 – LiF+0.05 mole% U+0.5 mole% OH, 3 – LiF+0.005 mole% U, 4 – LiF+0.05 mole% U, 5 – LiF+0.05 mole% U+2.0 mole% OH, 6 – LiF+2.0 mole% OH.

The kinetics of the luminescence decay in all the studied crystals is multicomponent. In all crystals, with the exception of LiF+0.05 mole% U+0.5 mole% OH, there is a short-term component with a characteristic attenuation time of about 4 μs and an amplitude of A1, which is almost two times higher than that of the remaining components. The short-term component provides the main contribution to the luminous sum of light. In the LiF+0.05 mole% U+0.5 mole% OH crystal of the short-term component
has a much larger value of the characteristic decay time, the contribution of this component is smaller. The probable reason for this deviation is the strong overlap of all the bands of the spectrum in this crystal.

Table 1. Characteristics of the kinetic curves of the PCL attenuation in the region of 415 nm:
1 – LiF, 2 – LiF+2.0 mole% OH, 3 – LiF+0.05 mole% U+0.5 mole% OH, 4 – LiF+0.05 mole% U+2.0 mole% OH, 5 – LiF+0.05 mole% U, 6 – LiF+0.005 mole% U.

| №  | \( A_1 \) | \( A_2 \) | \( A_3 \) | \( A_1/A_2/A_3, \text{100\%} \) | \( \tau_1 (\mu\text{s}) \) | \( \tau_2 (\mu\text{s}) \) | \( \tau_3 (\mu\text{s}) \) |
|----|-----|-----|-----|-----------------|----------------|----------------|----------------|
| 1  | 1.43 | 0.36 | 0.115 | 75/19/6         | 4.24           | 25.36          | 140.57         |
| 2  | 1.53 | 0.02 | 98/1.2 | 3.84           | 64.69          |
| 3  | 0.46 | 0.34 | 0.033 | 55/41/0.04     | 11.67          | 24.72          | 102            |
| 4  | 1.63 | 0.03 | 98/1.2 | 4              | 67.4           |
| 5  | 2.26 | 0.04 | 98/1.7 | 4.38           | 86.5           |
| 6  | 0.944 | 0.19 | 0.041 | 80/16.6/3.4   | 4.55           | 21.5           | 155            |

Figure 4 shows, for example, the kinetic curves of the luminescence decay in the region 488±521 nm after the excitation pulse by the electron beam in crystals LiF+0.05 mole% U+0.5 mole% OH, LiF+0.005 mole% U and LiF+0.05 mole% U+2.0 mole% OH. The results of analysis of the kinetic curves of attenuation are given in table 2.

![Figure 4](image_url)

Figure 4. Luminescence kinetic decay curves at difference wavelengths after the excitation pulse by an electron beam in 1 – LiF+0.05 mole% U+2.0 mole% OH (488 nm), 2 – LiF+0.05 mole% U (508 nm), 3 – LiF+0.05 mole% U + 0.5 mole% OH (508 nm), 4 – LiF+0.005 mole% U (521 nm).

Table 2. Kinetic luminescence decay curves in the 488-521 nm region after the excitation pulse by the electron beam in crystals: 1 – LiF+0.05 mole% U+2.0 mole% OH (508 nm), 2 – LiF+0.05 mole% U+0.5 mole% OH (508 nm), 3 – LiF+0.05 mole% U (508 nm), 4 – LiF+0.005 mole% U (521 nm).

| №  | \( A_1 \) | \( A_2 \) | \( A_3 \) | \( A_1/A_2/A_3, \text{100\%} \) | \( \tau_1 (\mu\text{s}) \) | \( \tau_2 (\mu\text{s}) \) | \( \tau_3 (\mu\text{s}) \) |
|----|-----|-----|-----|-----------------|----------------|----------------|----------------|
| 1  | 0.42 | 0.12 | 78/22 | 42.9           | 217.8          |
| 2  | 1.16 | 0.57 | 0.022 | 66/32.5/1.2   | 30             | 70             | 644            |
| 3  | 0.86 | 0.07 | 92.4/7.5 | 53.83          | 226.6          |
| 4  | 100 |     |          | 60.6           |                |                |                |
The kinetics of damping in all the crystals studied in the three main luminescence bands is multicomponent. In all crystals the main attenuation component has a value in the range of 40–70 μs. The long-term component makes a small contribution to the luminescence sum of light. A certain difference in the kinetic curve of damping in a LiF+0.05 mole% U+0.5 mole% OH crystal is explained by the overlap of all bands of the spectrum in this crystal.

4. Conclusion
Crystals of lithium fluoride activated by uranium with injected coactivators can have highly efficient conversion of radiation energy into light in the visible range of the spectrum. Therefore, it seems promising to use them as scintillation ones. The results of the study of the kinetics of luminescence decay presented in this study have shown that at least three pronounced attenuation components are observed in the kinetics. Of the three components, the main contribution to the light sum is made by a component with an attenuation time in the range of 40-70 μs. Therefore, a lithium fluoride-based scintillator can be used to detect low-intensity radiation fluxes.

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References
[1] Cherepanov A N et al. 2016 (Ekaterinburg: GOU VPO USTU-UPI) 304 p
[2] Raikov et al. 2012 Proc. Int. Conf. on Radiation-optical effects in lithium and sodium fluoride crystals (Bishkek-Ekaterinburg: NAS of KR UrFU Press) p 259
[3] Pustovarov V A 2000 Optics and Spectroscopy 88 790
[4] Koroleva T S et al. 2012 Proc. Int. Conf. on Radiation-optical effects in lithium and sodium fluoride crystals (Bishkek-Ekaterinburg: NAS of KR UrFU Press) p 274
[5] Lisitsyna L A et al. 2011 Optics and spectroscopy 110 568
[6] Nepomnyaschikh A I, Radzhabov E A and Egranov A V 1984 LiF crystals color centers and luminescence (Novosibirsk: Nauka) 113 p
[7] Jain V K 1986 Journal of Physics D: Applied Physics 19 1791
[8] Rebane L A 1968 Proceedings of the Institute for the Physics of the Atmosphere of the Estonian Soviet Socialist Republic 37 14
[9] Lisitsyna L A, Oleshko V I, Putintseva S N and Lisitsyn V M 2008 Optics and Spectroscopy 105 531
[10] Lisitsyna L A and Lisitsyn V M 2013 Physics of the Solid State 55 2297