Luminescence of LiF crystals doped with uranium

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Abstract. The work presents the results of the study of the luminescence of uranium doped LiF crystals. Introduction of the dopant (U) and the co-dopant (OH) shows the occurrence of additional absorption in the range of 260–320 nm. The IR spectrum in crystals containing OH has distinguished characteristic absorption bands at 3725 cm⁻¹. In crystals doped with (U), the bands 3550–3580 cm⁻¹ are observed, which are responsible for OH ions. The doped crystals with co-dopant contain an additional band at 3342 cm⁻¹. The luminescence is observed in the 470–520 nm spectral range excited by ionizing and UV radiation.

1. Introduction
Lithium fluoride crystals activated by multivalent ions are effective converters of hard radiation flow energy into emission of visible range. The crystals have a potential for using as scintillation materials in medicine, since their density is close to the body tissue density. On the other hand, LiF crystals can be used as model crystals with complex defects [1]. The paper provides spectral and kinetic performance of lithium fluoride crystal luminescence doped with uranium and hydroxyl ions entered along with it to compensate for the difference between charge states and elastic stresses.

2. Research methodology
The luminescence and excitation spectra were measured using a spectrofluorimeter Agilent Cary Eclipse, and a xenon flash lamp was used as a light source. The transmittance spectra of samples in the area of 4000–2000 cm⁻¹ were measured using a Jasco FT/IR-4700 spectrometer. Optical absorption spectra in a range of 195–1200 nm were measured with spectrophotometers SF-256 and SPECORD 250 PLUS. Luminescence decay kinetics of crystal after excitation by ns electron pulses was measured. Luminescence was recorded using a monochromator MDR-204 photoelectric multiplier Hamamatsu R928, GDS-2204 and LeCroy 6030A oscillographs.

The integrated luminescence spectra of crystals were also measured under excitation by UV radiation of the xenon lamp and pulsed electron flow with energy of 250 keV with λ exct=340 nm. Integrated luminescence spectra were recorded using a fiber-optic spectrometer AvaSpec-3648 in the spectral range of 200–1100 nm. Integration time was 100 ms.
3. Research samples

Pure and doped crystals of lithium fluoride were grown according to the improved Kyropoulos method in a platinum dish in the air from a chemical agent of extra pure grade. Dopants were added in the load before crystal growing in the form of uranyl nitrate and caustic lithium. Uranium content in samples was determined using spectral analysis. The presence of OH dopant was controlled within the absorption line of 3720 cm$^{-1}$. The amount of OH dopant added is indicated in the text by the concentration of LiOH in the load.

The following crystals were prepared for the study: LiF pure grown in the Research and Technology Institute of Optical Materials of Vavilov State Optical Institute: LiF+2.0 mol% OH, LiF+0.005 mol% U, LiF+0.05 mol% U, LiF+0.05 mol% U+0.5 mol% OH, and LiF+0.05 mol% U+2.0 mol% OH.

Doping gives rise to absorption bands in the spectral range with $\lambda<400$ nm (Fig.1). The pure LiF crystal is transparent in the examined spectral range from 195 to 1000 nm.

![Figure 1. Absorption spectra of LiF crystals: pure (1); LiF + 2.0 mol% OH (2); LiF + 0.005 mol% U (3); LiF + 0.05% U + 0.5 mol% OH (4); LiF + 0.05 mol% U (5); LiF + 0.05 mol% U + 2.0 mol% OH (6).](image)

Uranium doping gives rise to absorption in the spectral range with $\lambda<400$ nm, which grows up to 200 nm. When uranium concentration in the crystal is over 0.005 %, 260 and 320 nm, distinct bands appear in the spectrum. Doping the crystal with OH leads to absorption in the ultraviolet spectrum. Simultaneous adding uranium and OH groups results in crystal non-transparency in the region below 280 nm. Obviously, adding uranium in a forming crystal, when synthesizing, compensates for local elastic stresses of OH ions. These regularities of absorption spectra changes in the short-wave region, when adding multivalent dopants to lithium fluoride crystals, were described in [2-5].

Figure 2 shows an example of the results of the studied crystal transmission spectra measurements in the infrared region. Pure crystals are transparent in the spectral region from 4000 to 2000 cm$^{-1}$. Introduction of uranium and OH dopants into crystals gives rise to bands in the range of 3800–3200 cm$^{-1}$. The location of the revealed bands in the crystals spectra is shown in Table 1.

As presented in the table of research results, the spectra in the short-wave region are different for crystals containing OH and those free of OH. All OH doped crystals have a band with a peak at 3735 cm$^{-1}$, apparently, due to these radicals [6]. The spectra of crystals activated by uranium feature a band in the region of 3575 cm$^{-1}$, the position of the band shifts to 3562 cm$^{-1}$ in the presence of the codopant (OH). The spectra of LiF crystals with U and OH co-dopants have a band in the region of 3342 cm$^{-1}$, the intensity of which increases at increased OH concentration. Apparently, the bands are due to complex defects incorporating OH in the area of U. [7, 8]. Moreover, there is an intensive band
for 3680 cm$^{-1}$ in the spectrum of LiF crystal + 0.05% U + 2.0 mol% OH, the nature of which is not clear.

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

**Table 1.** Absorption band location in activated lithium fluoride crystals

| Crystal                  | Band location, cm$^{-1}$ |
|--------------------------|--------------------------|
| LiF + 2.0 mol% OH        | 3725                     |
| LiF + 0.005 mol% U       | 3575                     |
| LiF + 0.05 mol% U        | 3575                     |
| LiF + 0.05 mol% U + 0.5 mol% OH | 3725 3562 3342       |
| LiF + 0.05 mol% U + 2.0 mol% OH | 3725 3680 3562 3342   |

4. Experimental results

Fig. 3 shows the excitation spectra of the uranium doped LiF crystals in the crests of luminescence bands. The excitation spectrum depends on the uranium content in the crystal. There is a complex band at 250 nm (with distinct maxima at 230 and 270 nm) in the LiF crystal excitation spectrum with uranium concentration of 0.005 mol%. There are three bands with maxima at 220, 270 and 341 nm in the LiF crystal excitation spectrum with uranium concentration of 0.05 mol%. Apparently, the excitation band at 320 nm is related to the presence of OH in the dopant.
Figure 3. The excitation spectra of the uranium doped LiF crystals at the luminescence bands maxima: LiF + 0.05 mol% U + 0.5 mol% OH (λ=508 nm) (1); LiF + 0.05 mol% U (λ=520 nm) (2); LiF + 0.005 mol% U (λ=520 nm) (3); LiF + 0.05 mol% U + 2.0 mol% OH (λ=489 nm) (4).

Introduction of OH as a co-dopant leads to spectrum smoothing. Only the band at 330 nm is clearly observed in the excitation spectrum of LiF + 0.05% U + 2% OH crystal. Luminescence is not excited in the pure crystal.

Typical photoluminescence spectra of activated LiF crystals are shown in Figures 4 and 5. As shown in Figure 4, a group of spectra bands with maxima at 487, 508, 521 and 583 nm can be distinguished. The ratio between the bands depends on the concentration of uranium added and does not depend on the wavelength of exciting radiation. In crystals with a high concentration of U dopants, the base band falls at 508 nm, whereas in the crystal with a lower concentration, it falls at 521 nm.

Figure 4. The luminescence spectra of crystals doped with uranium at different excitation wavelengths LiF + 0.05% U excited at λ=278 and 220 nm (1,2); LiF + 0.005% U excited at λ=259 and 220 nm (3,4)
Figure 5. The luminescence spectra of LiF + 0.05% U + 2.0 mol% OH ($\lambda_{em}=300$ nm) (1), LiF + 0.05 mol% U ($\lambda_{em}=222$ nm) (2), LiF + 0.05% U + 0.5 mol% OH ($\lambda_{em}=200$ nm) crystals (3).

A broad band in the region from 320 to 600 nm with a maximum at about 425 nm can be observed in the luminescence spectrum of LiF + 0.5 mol% OH crystals. The spectrum does not depend on the excitation wavelength. In the spectral range of 480–550 nm, luminescence is not observed.

Figure 6 shows typical luminescence spectra of crystals doped with uranium (0.05 mol% U) and U + OH. Notes to Figure 6 show the wavelengths of monochromatic emission used for excitation. Luminescence spectrum type does not depend on the excitation wavelength. The type of all luminescence spectra with a dopant concentration of 0.05 mol% U does not depend on the presence of OH. This indicates that the crystal should be doped with uranium for OH entering for compensation. Introduction of uranium with a high concentration of OH dramatically changes the appearance of the luminescence spectrum. A band at 489 nm becomes the dominant band in the spectrum. It should be noted that there is low-intensity luminescence in crystals with a concentration of 0.5 mol% OH in the same area.

Figure 6. The luminescence spectra excited at $\lambda_{em}=250$ nm of LiF + 0.05 mol% U + 0.5 mol% OH (1), LiF + 0.05 mol% U + 2.0 mol% OH (2), LiF + 0.05 mol% U (3), LiF + 0.005 mol% U crystals (4).

The excitation of crystals with a pulse of high-energy electrons (250 keV) results in the excitation of luminescence of crystals with integral spectra, qualitatively similar to those measured under photoexcitation (Figure 7). A band at 425 nm is excited in pure and OH-doped crystals. Crystals containing U, or U and OH co-dopants quantitatively differ from the crystals measured under
photoexcitation. A luminescence band at 490 nm is observed in the spectra of all crystals containing U and OH co-dopants. Its intensity is higher, the higher the concentration of introduced OH. It should be noted that the band also appears in the spectrum of the crystal with a high concentration of uranium. Obviously, this is a consequence of OH entering the crystal during synthesis.

Low-intensity luminescence in the region of 350–500 nm with a maximum at 425 nm is excited with a pulse of electron flow in pure crystals and crystals containing OH.

Figure 7. The cathodoluminescence spectra of LiF (1), LiF + 2.0 mol% OH (2), LiF + 0.05% U + 2.0 mol% OH (3), LiF + 0.05 mol% U + 0.5 mol% OH (4), LiF + 0.05 mol% U (5), LiF + 0.005 mol% U crystals (6).

Figure 8 shows the results of the study of the kinetic curves of cathodoluminescence decay for doped LiF crystals. From these results, it follows that there is a sharp contrast in the kinetic characteristics of the luminescence of LiF + 0.05 mol% U + 2.0 mol% OH crystal and those free of OH or containing a small concentration of uranium. Luminescence decays in LiF + 0.05 mol% U + 2.0 mol% OH crystal predominantly within a characteristic time of 230 μs. In LiF + 0.05 mol% U + 0.5 mol% OH, LiF + 0.05 mol% U and LiF + 0.005 mol% U crystals luminescence decays mainly 10–15 times with a characteristic time of 30–60 μs. All crystals has a component with a characteristic decay time of ~220 μs.

Figure 8. LiF + 0.05 mol% U + 2.0 mol% OH (1), LiF + 0.05 mol% U (2), LiF + 0.005 mol% U (3), LiF + 0.05 mol% U + 0.5 mol% OH (4) crystals cathodoluminescence decay kinetics
4. Conclusion
Introduction of OH as a co-dopant into the synthesized LiF crystal with uranium results in a complex defect in the crystal containing OH as a structural element. The presence of OH in the area of the introduced uranium ion is proved with the following results of the experimental studies.
1. The OH-containing uranium doped crystals have additional absorption bands in the spectral region of 3575, 3562 and 3342 cm\(^{-1}\) that can be apparently attributed to OH near the uranium ions.
2. The excitation band at 320 nm is observed only in crystals containing uranium and OH as a co-dopant.
3. The presence of OH co-dopant in uranium-doped crystals leads to occurrence of the luminescence spectrum at 490 nm. This band is also found in crystals, which were not intentionally doped with OH. Obviously, OH enters the crystal during growth to compensate for stresses in the dopant.
4. The type of all luminescence spectra with a dopant concentration of 0.05% U does not depend on the presence of OH. This indicates that the crystal should be doped with uranium for OH entering for compensation.

Acknowledgments
This work was performed with the financial support of the Ministry of Education and Science of Republic of Kazakhstan, contract #316 dated May 13, 2016

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