

# The Activator Luminescence of LiF Crystals

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**Abstract – The results of the comparative analysis of spectral kinetic parameters of activator pulse cathodoluminescence and photoluminescence excited at 300 K in oxygen-containing crystals LiF are presented in the research.**

## 1. Introduction

Owing to tissue-equivalence activated LiF crystals are widely used in radiobiology and medicine as thermoluminescence dosimeters. However, the search of the optimum coactivators for sensitization of activated luminescence is still actual.

Oxygen – containing crystals LiF grown by Stockbarger method and uranyl LiF crystals grown in air by Kiropulos method were investigated in the present research. Cation activator was put into charge in the form of nitrate uranyl (uranium concentration in the charge 0.01 mol. %). On the basis of optical absorption spectra in the range of 120...3000 nm the initial level of crystal defects has been monitored.

The crystals of two types were studied: transparent in IR region up to 3300 nm (type 1) and crystals type 11 with a number of bands in IR region referring to hydroxyl ions, or complexes – metal – hydroxyl ions (Fig. 1, an insert). 10.3, 9.2, 7.3 and 6.2 eV bands were observed in VUV region of the nonactivated oxygen-containing crystal. Uranyl crystals being studied were non transparent in VUV region and in UV region the spectrum containede 5.1 and 3.1eV. According to [1] in the VUV spectrum region of the uranyl crystals there are the same oxygen bands as those presented in oxygen-containing crystals spectrum (Fig. 1).

Different oxygen-containing dope ratio in the form of  $O^{2-}$  and  $OH^-$  ions is the basis for the division of the crystal into two types. I type crystals (transparent in IR region) contain a small number of  $OH^-$  ions as compared with  $O^{2-}$  ions, whereas in II type crystals (non-transparent in IR region) the concentration of  $OH^-$  ions was larger by a factor of 100.

The results of the comparative analysis of spectral kinetic parameters of pulse cathodoluminescence (PCL) and pulse photoluminescence (PPL), excited at 300 K in I and II type crystals containing identical concentration of uranium (0.01 mol. %), and not containing purposely introduced cation activators are presented in the research.

The PPL was excited in crystals by the nanosecond pulse of the nitric laser, its radiation wave length of 337 nm getting into the activation absorption band at 4 eV,

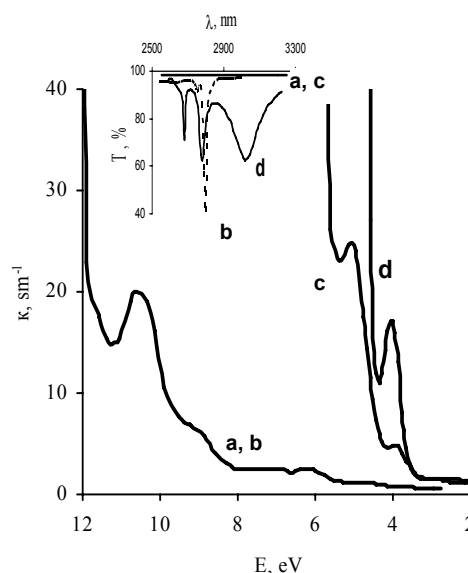


Fig. 1. Optical absorption spectra of nonirradiated LiF crystals (a, b) and LiF (U) (c, d) of type 1 (a, c) and type 11 (b, d) (see the text).

which can be observed in non irradiated uranyl crystals spectra of both types. The PCL was excited by the nanosecond electron pulse (EP) with the energy of 400 keV and volumetric density of energy per pulse –  $0.001 \text{ J/cm}^3$ .

Kinetic luminescence parameters were studied in the range of  $10^{-9} \dots 10^{-1} \text{ s}$  after the termination of the exciting pulse. Spectral region of luminescence research – 4...2 eV.

## 2. Results of research

The results of the experimental research can be presented as follow.

1. There is a luminescence of identical spectral structure, consisting of two well resolved wide bands with the maxima at 3.8 and 3.1 eV (Fig. 2) under EP in oxygen-containing LiF crystals of both types in the blue spectrum region ( $> 2.8 \text{ eV}$ ). The bands have different values of kinetic decay parameters that cause the change of spectrum of luminescence in the time after excited pulse (Fig. 2). The short-wave band (3.8 eV) is short-time life, it decays according to the monoexponential law with  $\tau = 1 \mu\text{s}$ . The long-wave band decay is described by the two exponents with  $\tau_1 = 7 \mu\text{s}$  and  $\tau_2 = 350 \mu\text{s}$  in I type crystals.

The long time life luminescence in the region 3.1 eV according to [2] can be optically excited in each of the absorption bands in VUV region: 10.3, 9.2, 7.3 and 6.2 eV, in the spectrum of nonirradiated oxygenic LiF crystals of 1 and 11 type (Fig. 1).

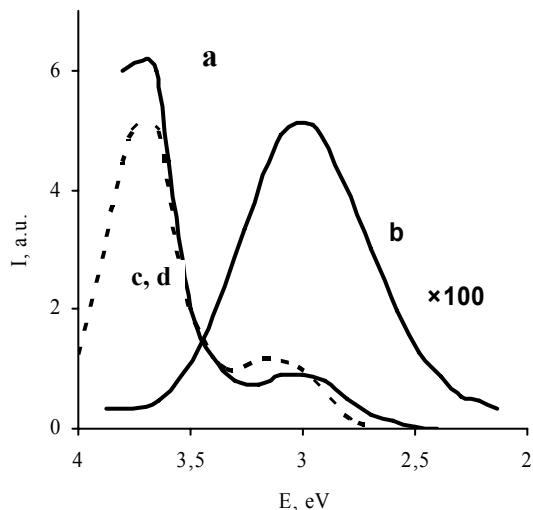


Fig. 2 PCL spectra excited by electron pulse in LiF crystal (a, b) and LiF (U) (c, d) at 300 K, measured in 50 ns (a, c, d) and 100  $\mu$ s (b) after EP influence termination. Crystals of type 1 (a – c), type 11 – (d). (Curves c, d normalized).

2. The blue luminescence spectrum of uranyl crystals at 300 K has the same spectral structure, as oxygen-containing LiF crystals, and represents two wide bands at 3.1 and 3.7 eV with half width values 0.4 and 0.33 eV respectively. In 1 type crystal of luminescence decay in each band is presented by the sum of two exponents with characteristic time decay values 3 and 20  $\mu$ s (at band 3.7 eV) and 3 and 50  $\mu$ s – at band 3.1 eV with the contribution of short time component decay (60 %) in each band. In 11 type crystal the blue luminescence in both bands decays according to the monoexponential law with the identical characteristic time value equal to 3  $\mu$ s (Fig. 2).

While comparing the data presented in Fig. 2, it can be concluded that neither uranium nor the oxygen in the form of  $O^{2-}$  or  $OH^-$  does not influence on the spectrum of the blue luminescence. However kinetic parameters of luminescence decay are determined by the sample prehistory. In the uranyl crystals and in non uranyl crystals the decay process in band at 3.1 eV is accelerated. If the uranium concentration is constant  $OH^-$  ions accelerate the decay process.

3. The nitric laser can excite the blue luminescence neither in uranyl crystals nor in nonactivated by uranium.

4. Except for a blue doublet in PCL spectrum of uranyl LiF crystals there is a group of narrow bands in green region 2...2.6 eV (Fig. 3). The luminescence spectrum consists of eight narrow bands 2.55, 2.51, 2.46, 2.43, 2.38, 2.34, 2.28, 2.18 eV with practically constant distance value between the adjacent bands

(0.05 eV). In all the bands the luminescence decay is describes by the monoexponential law, its characteristic time values being equal to 100  $\mu$ s in short-wave spectrum region and 50  $\mu$ s – in long-wave one (Fig. 3).

The green luminescence is excited by both the electron and laser pulses. The spectral structure and kinetic decay parameters of the green luminescence do not depend on the way it is excited. Within the limits of the investigated irradiation dozes (<  $10^5$  Gy) the bands ratio in the spectrum does not depend on the doze of a preliminary irradiation of a crystal by electrons.

In contrast to 1 type crystals (LiF(U)-O), the bands ratio in spectrum PPL of the uranyl 11 type crystal (LiF(U)-OH) as it was proved, depends on the doze of preliminary irradiation of crystal by electrons (Fig. 4).

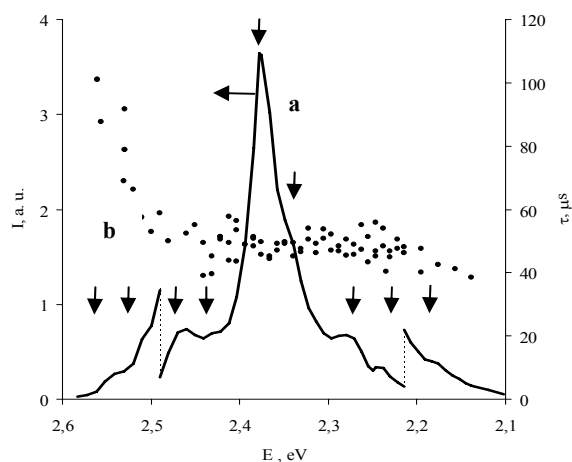


Fig. 3. Green luminescence spectrum of LiF(U) crystal, type 1 (a) and spectral dispersion decay time at 300 K – (b).

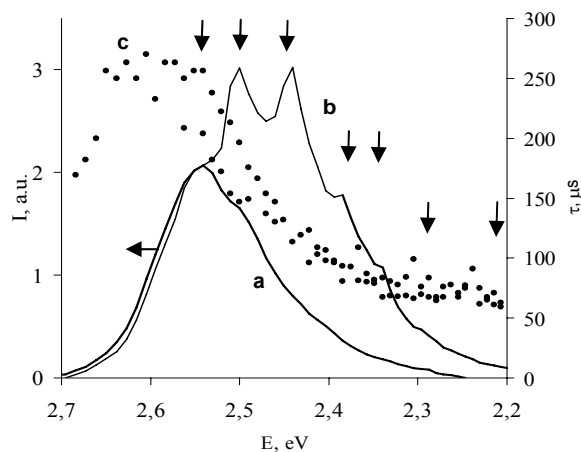


Fig. 4. Green luminescence spectra of LiF(U) crystal, type 11 (a, b) and spectral dispersion decay time at 300 K – (c). (a) – nonirradiated crystal, (b) – the crystal is irradiated by electrons  $10^5$  Gy.

The results obtained present that the PPL spectrum of the non irradiated crystal represents not resolved wide band in short-wave spectrum region (2.55 and 2.51 eV). The preliminary crystal irradiation by elec-

tron pulses resulted in bands growth in long-wave spectrum region  $< 2.5$  eV. Different speed of radiating intensity growth of various bands made the spectrum less amorphous, well resolved bands 2.55, 2.51, 2.46, 2.43, 2.38, 2.34, 2.28, 2.21 eV appeared. In all the bands the luminescence decay according to the mono-exponential law, its characteristic time values being equal to  $250 \mu\text{s}$  in short-wave spectrum region (2.5 eV) and to  $50 \mu\text{s}$  – in a long-wave one (Fig. 4).

While comparing the data presented in Figures 3 and 4, it can be concluded that PPL structure in uranyl crystals of both types is identical. The difference is that in 1 type crystal a multiband spectrum and its band ratio do not depend on the dose but is formed during the crystal growth. In 11 type crystals the ratio between bands, formed during crystal growth can be changed by irradiation, and the bands created by radiation were found to be dominant in long-wave region.

5. In the research of the luminescence excitation kinetics in oxygen-containing crystals it has been obtained.

At 300 K in oxygen-containing crystals in the blue spectrum region the two stages of luminescence increase are observed: noninertial (comparable with EP duration) and inertial – in a microsecond time interval after the termination of the exciting pulse. The noninertial component spectrum consists of the bands at 3.8 and 3.1 eV, the spectrum of the inertial component consists of the band with a maximum at 3.1 eV. The inertial component in crystals of both types is observed, i.e. both in crystals with the prevailing percentage of oxygen in the form of  $\text{O}^{2-}$ , and in crystals with the prevailing percentage of oxygen in the form of  $\text{OH}^-$ . Characteristic time of the increase of the luminescence after the termination of the exciting pulse is about  $7 \mu\text{s}$  in crystals of different types (Fig. 5, c).

6. The excitation method influence on kinetic parameters of excitation process of the green luminescence in uranyl crystals has been found. Under optical and electron excitation the luminescence in all the bands presented in Figures 3 and 4, is initiated in a noninertial way in relation to the exciting pulse. However, the inertial process is observed in addition to the noninertial one at electronic pulse excitation. The characteristic time decay value at 300 K depends on the crystal and is equal to  $3 \dots 0.5 \mu\text{s}$ . Luminescence excitation kinetics in the band at 2.42 eV (one of the 11 type crystal green luminescence bands) under laser pulse (a) and the electron pulse (b) is presented in Fig. 5. (Laser pulse and an electron pulse were of the same duration equal to 10 ns).

The spectra of the luminescence at each of the each kinetics stages under EP influence have been measured:  $\Delta I_1 = f(\lambda)$  and  $\Delta I_2 = f(\lambda)$ , where  $\Delta I_1$ ,  $\Delta I_2$  – amplitude of luminescence excitation intensity in 50 ns and  $5 \mu\text{s}$  after the termination of the exciting pulse respectively (Fig. 5). The spectral structure of the green lu-

minescence excited both at noninertial, and inertial stages was found to be identical.

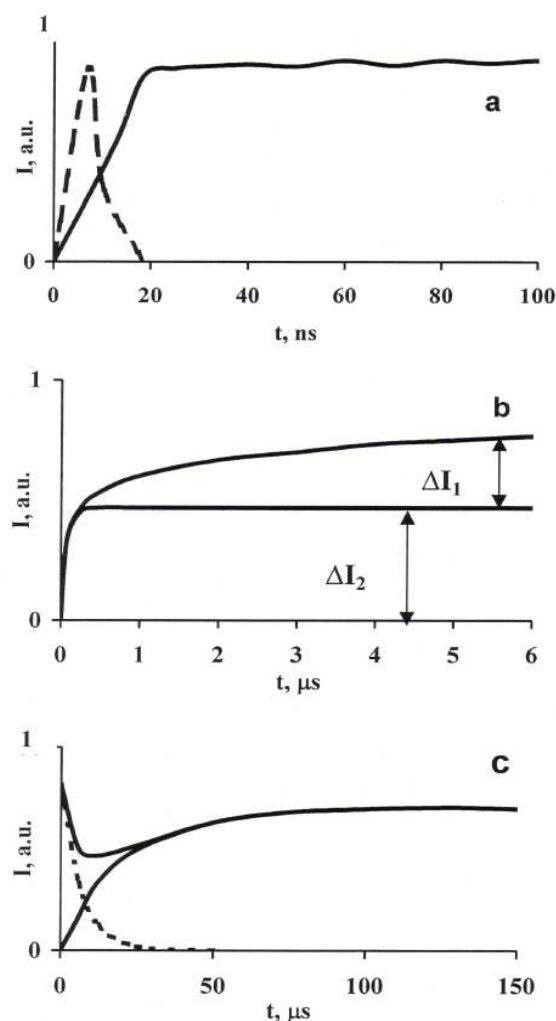


Fig. 5. Luminescence excitation kinetic curves at 2.42 (a, b) and 3.1 eV (c) in  $\text{LiF(U)}$  crystal, type 11 (a, b) and  $\text{LiF}$  crystal, type 1 (c) excited by laser pulse (a) and electron pulse (b, c). (The excitation pulse is specified by a dotted line).

### 3. Conclusion

1. Oxygen in  $\text{LiF}$  crystals in the form of  $\text{O}^{2-}$  and / or  $\text{OH}^-$  does not influence the spectral structure of the excited oxygen luminescence, however the kinetic parameters of the increase and decay processes decrease with the growth of hydroxyl ion concentration in the crystal.

2. The comparative analysis of spectral-kinetic PCL parameters of  $\text{LiF(U)OH}$  crystals testifies to the variety of hydroxyl ions influence on the characteristics of the luminescence excited in these crystals as compared to the  $\text{LiF(U)-O}$  crystal. The  $\text{OH}^-$  ions considerably change the ratio between bands being formed in the crystal grown process without any influence upon the luminescence band position. If the luminescence inten-

sity is the maximum in the 2.38 eV region in the spectrum of both the grown LiF(U)-O crystal and the irradiated one (Fig. 3). The hydroxyl ion in LiF(U)OH makes the short-wave luminescence in the nonirradiated crystal 2.55, 2.51 eV prevailing. The display of the other six bands in a long-wave spectrum region is the result of the electron radiation influence on the crystal (Fig. 4). (In [3, 4] the change of ratio between green luminescence bands in favor of long-wave bands was assigned to the uranium concentration increase in the crystal.)

It was found that irrespective of the method of the luminescence centers creation in the long-wave region (by radiation or during growth) luminescence decay kinetic parameters in this spectral region have identical values in crystals of both types (50  $\mu$ s) (compare Fig. 3 and 4).

3. The hydroxyl ions influence on the blue (oxygen) luminescence parameters leads to the significant suppression of this luminescence and to the change of decay character and to the complete suppression of the long-time decay component in LiF(U) crystals contribution.

4. Models of the luminescence centers in uranyl crystals are suggested [5 – 9], considering the isomorphic replacement of  $\text{Li}^+$  ion by  $\text{U}^{6+}$  activator ion and the principle of local compensation of the excess charge. The luminescence center  $\text{U}^{6+}$  carries the excess charge its compensation is realized in different ways. A large variety of possible luminescence centers is being discussed: a linear complex  $(\text{UO}_2)^{2+}$ ,  $(\text{UO}_5\text{F})^{5-}$ ,  $(\text{UO}_4\text{F}_2)^{4-}$ , and  $(\text{UO}_6)^{6-}$  and only one of them is neutral –  $(\text{UO}_5\text{F})^{5-}$ . The others have efficient positive and negative charge, the compensation can be carried out in different ways depending on the level of initial material defects (cation impurities, anion OH complexes,

cation and anion vacancies). In [9] it is assumed that in crystals with low initial defects level the uranium complexes of only one type –  $(\text{UO}_5\text{F})^{5-}$  can be found.

The existence of the inertial stage of luminescence increase in both the oxygen centers in LiF crystals (Fig. 5, c) and in the uranium oxygen centers in LiF(U) crystals (Fig. 5, b) found out in the present study can testify to the energy exchange between the components of excited oxygen uranium complexes and oxygen centers in lattice sites.

Selectively excited optically green luminescence of the uranium complexes has no inertial component and the blue oxygen luminescence is not to be found in the crystal spectrum.

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