

KINETIC PARAMETERS OF THE URANIUM LUMINESCENCE IN LiF CRYSTALS

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The results of researches with nanosecond time resolution of kinetic characteristics of luminescence buildup and decay in crystals LiF(U)-O at 300 K under action of both laser pulse with energy 3,68 eV and electron pulse with energy 300 keV have been presented. Influence of excite method on kinetic characteristics of uranium luminescence buildup and influence of uranium on kinetic characteristics of oxygen luminescence in crystal were established.

1. Introduction

Owing to tissue-equivalence activated crystals LiF are widely used for dosimetry in radiobiology and medicine. Crystals LiF activated by uranium having high quantum yield of luminescence are of obvious interest.

In spite of the fact that uranium luminescence has been studied more than 150 years either nature of uranium luminescence centers (ULC) in various matrices or the mechanism of uranium luminescence and a part of oxygen in the process of its excitation are not still clear. ULC according to [1–4] represent a complex $(\text{UO}_5\text{F})^0$ high efficiency of developing which is stipulated by its charge neutrality. It is supposed that discrete structure of luminescence spectrum is stipulated by radiative transitions of different multipolarity to a general system of vibrational levels of the main state [1, 3–5].

The alternative point of view [6–8] consists in supposition about simultaneous presence in luminescence spectra of radiative transitions carried out in ULC of different composition: $(\text{UO}_2\text{F}_4)^{3+}$, $(\text{UO}_5\text{F})^0$, $(\text{UO}_4\text{F}_2)^{1+}$, $(\text{UO}_6)^{1-}$ differ in oxygen ion quantity substituting ions F^- in equatorial plane of linear uranium complex $(\text{UO}_2)^{2+}$. Quantity and charge of ULC are determined relative to the charge of substituted group LiF_6 .

At the whole variety of research techniques of uranium-containing crystals using spectroscopy with high time resolution allows measuring and correlating excited radiative transitions by kinetic parameters both at the stage of luminescence buildup and at the stage of its decay. Presence of such information allows carrying out comparative analysis of numerous radiative transitions according to kinetic parameters of luminescence process.

Pulse cathode luminescence (PCL) and pulse photoluminescence (PPL) of crystals LiF-O and LiF(U)-O in spectral range 4,0...2,0 eV and time range $3 \cdot 10^{-8}$... 10^{-1} s after the end of the pulse action at 300 K at time resolution 30 ns were studied in this paper. PCL was excited by a pulse of electrons (PE) with energy 300 keV and fluence in the pulse (P) in the range 10^{11} ... 10^{13} cm $^{-2}$. PE duration was 20 ns. The thickness of studied crystals did not exceed 0,3 mm, penetration depth of electrons into crystal LiF was 0,26 mm. Crystal area was about 10 mm 2 .

PPL was excited by a pulse of nitrogen laser, radiation of which (3,68 eV) occurs into one of activator absorption bands of uranium-containing crystals. Excitation pulse duration was 20 ns. Power was about 10 mW, beam cross-section was about 1 cm 2 .

Crystals LiF-O and LiF(U)-O – oxygen-containing crystals LiF non-activated and activated with uranium were studied. Uranium batch concentration – 0,01 wt. %. Luminescence was excited both in unirradiated crystals and in crystals radiated preliminarily by a series of pulses of electrons at 300 K ($\leq 10^5$ Gy).

Oxygen in the form of Li_2O was introduced into batch at growth process, uranium – in the form of nitroacid uranyl. Crystals were grown in the Institute of physics of Kyrgyzstan NAS.

The original imperfection of unirradiated crystals was controlled by optical absorption spectra in the range of 12,0...0,35 eV. In IR area of the spectrum crystals LiF-O and LiF(U)-O were transparent. In VUV and UV areas of spectra there is a number of bands (Table 1) positions of which coincide with other authors' data. It is supposed that VUV bands of spectrum of crystal LiF-O are stipulated by oxygen in the form of O^{2-} and in the form of OH^- [12, 13]. Bands in the range of 250...410 nm in spectrum of crystals LiF(U)-O are stipulated by uranium centers as such bands are absent in spectrum of crystals LiF-O non-activated with uranium. Presence of bands at 170 and 200 nm in spectra of crystals of both types indicates obviously their belonging to oxygen imperfections not connected with uranium ions.

Table 1. Spectral position of optical absorption bands of unirradiated activated crystals LiF

Crystal	Information source	Wave length, λ , nm							
*LiF-O		117		137	170	200			
LiF-O	[9]	117		137	170	200			
*LiF(U)-O		–	–	–	–	–	250	305	410
LiF(U)-O	[10]		127		165	200	244	305	405
LiF(U)-O	[11]	–	–	–	–	–	250	310	

*Data of the given paper, – unmeasured spectrum region

2. Results of investigations

2.1. Luminescence of crystal LiF(U)-O in the range of 2,63...2,1 eV

PPL spectrum of crystal LiF(U)-O measured at 300 K in 50 ns after the end of laser pulse action is given in Fig. 1, curve *a*. Spectrum general view and position of largest bands in it (2,28, 2,38 and 2,46 eV) coincide with data [11].

Front of luminescence buildup in each band of spectrum is described by the function:

$$I(t) = I_{\max}(1 - \exp(-t/\tau_1)), \quad (1)$$

where $I_{\max}$ is the amplitude value of intensity, t is the time from the moment of excitation pulse start, τ_1 is the characteristic time of the process equal to 40 ns and exceeding time resolution of measuring track (30 ns).

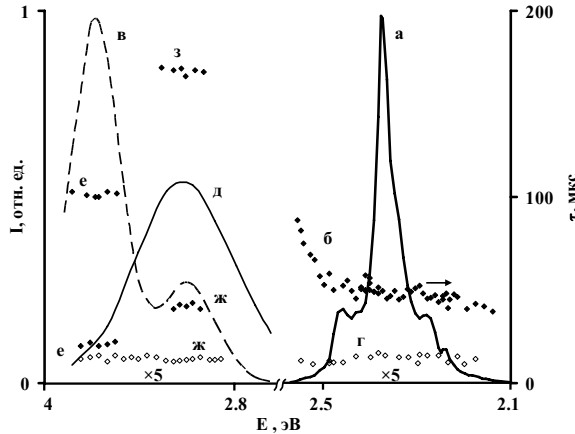


Fig. 1. Luminescence spectra measured in 50 ns (a, b), 300 ms (d) after beginning of pulse excitation action at 300 K and dispersion of decay time (b, e-z), inertial component of PCL buildup (r) in crystal LiF(U)-O (a-r, e, z) and LiF-O (b, d-z).

In Fig. 2, curve a, the kinetics of luminescence buildup (KLI) in the band 2,38 eV at crystal optical excitation is presented as an example.

As a spectrum of green luminescence represents a set of overlapping narrow bands the kinetics of luminescence decay (KLD) was studied in the range of 2,63...2,1 eV with a step equal 2 nm. It was stated that KLD in the given range is described by monoexponential law. Dispersion of characteristic decay time is presented in Fig. 1, curve b and indicates the monotone increase of decay time from 50 ms per 2,1 eV to 90 ms at 2,6 eV.

Spectrum of PCL of crystal LiF(U)-O excited by PE consists of a group of bands of uranium green luminescence (curve a) described before and luminescence in blue region 4,0...2,65 eV (curve e) (Fig. 1). Description of blue luminescence is given below in section 2.2.

It was stated that spectral composition of crystal green luminescence and the character of dispersion of its decay time do not depend on a manner of excitation and they are the same at electron and optical excitation.

However at the same duration of optical pulse and pulse of electrons the manner of luminescence excitation turned out to influence the kinetic characteristics of buildup process. So, in comparison with (1) the PCL increase process in each band of green luminescence spectrum is described by a set of two exponents [14]:

$$I_j(t) = \sum I_{j\max}(1 - \exp(-t/\tau_j)), \quad (2)$$

where $\tau_1=40$ ns and coincide with the value of characteristic time of PPL increase (Fig. 2, curves a, b) and $\tau_2=2,5$ ms. Value τ_2 does not depend on wave length and it is the same in the whole spectral area of green luminescence (Fig. 1, curve e).

In Fig. 2 (curves a-e) kinetics of PPL and PCL buildup in the band 2,38 eV are given for comparison.

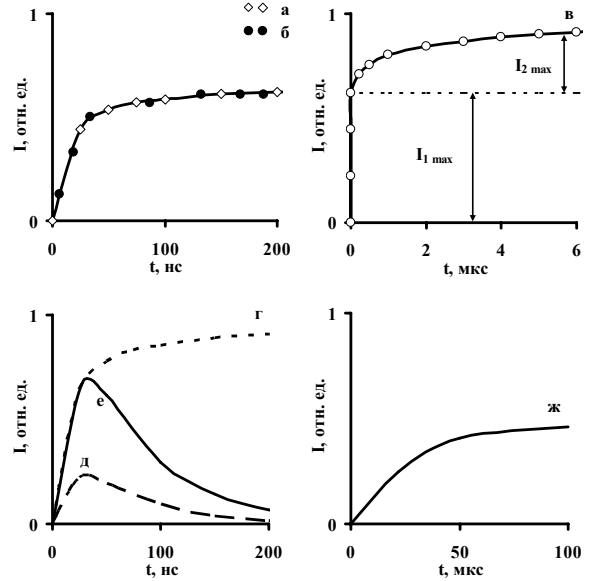


Fig. 2. Kinetic curves of luminescence at 2,38 (a-b), 3,7 (r, e), 3,1 (d) and 3,0 eV (z) in spectrum of crystal LiF(U)-O (a-r, d) and LiF-O (d-z) excited by laser pulse (a) and pulse of electrons (b-z) at 300 K.

The coincidence of spectral composition of nanosecond and microsecond intensity components of PPL and PCL measured as dependence $I_{1\max}=f(\lambda)$ and $I_{2\max}=f(\lambda)$, respectively was stated.

The influence of: fluence of electrons at a pulse (P) and value D – integral dose absorbed by crystal (at $P=\text{const}$) on excitation efficiency green luminescence at 300 K and on values of intensity of nanosecond and microsecond components $I_{1\max}$ and $I_{2\max}$ in each band of spectrum was studied.

In Fig. 3 (curves a, b) dependences $I_{1\max}=f(D)$ and $I_{2\max}=f(D)$ in a maximal spectrum band 2,38 eV are given as an example. As it follows from the given results the value $I_{1\max}$ measured in 200 ns from the moment of pulse action with growth D increases, achieves maximal value at $D=1,7\cdot 10^4$ Gy and then decreases at further growth of the absorbed dose.

Dose dependence of microsecond- intensity component has another character: value $I_{2\max}$, measured in 8 ms from the moment of the end of PE action is maximal at influence of the first PE on crystal and then in the region $D\leq 10^5$ Gy decreases slowly at dose increase (Fig. 3).

In the range of fluence value (P) of electrons in excitation pulse $10^{11}...10^{13}$ cm $^{-2}$ the existence of linear dependence between value $I_{2\max}$ and P was stated.

The value of characteristic time of green luminescence buildup τ_2 does not depend on D .

The laws of changing nanosecond and microsecond intensity components of luminescence in the band at 2,38 eV at changing values P and D described above are completely identical for nanosecond and microsecond intensity components of two other spectrum allowed bands of 2,28 and 2,46 eV. Therefore, spectrum of uranium luminescence given in Fig. 1, curve a, belongs to

one type of ULC and coincidence of kinetic characteristics of luminescence buildup in the whole spectral interval 2,63... 2,10 eV points to it.

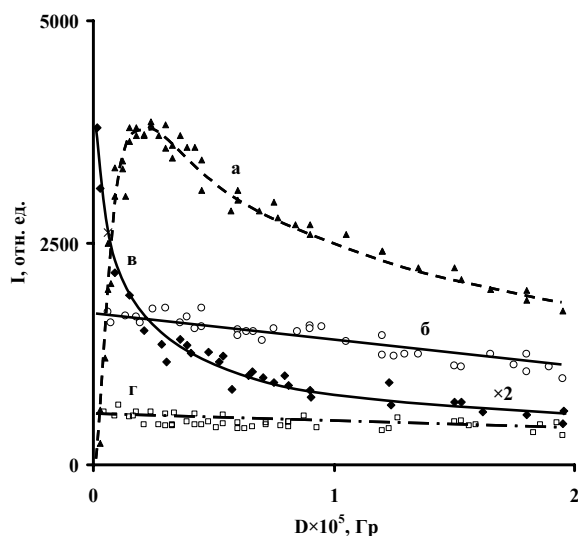


Fig. 3. Dependence of PCL intensity in the band 2,38 eV (ns-component $I_{\max}$ (a) and microsecond-component $I_{\max}$ (b)), 3,7 (b), 3,1 eV (r) on dose of preliminary radiation of crystal LiF(U)-O by electrons. Intensity is measured in 30 ns (r), 200 ns (a, b) and 8 ms (b) from the moment of excitation pulse start at 300 K

2.2. Luminescence of crystal LiF(U)-O in the range 4,0...2,65 eV

As it was described before PCL spectrum of crystal LiF(U)-O excited by PE consists of a group of bands of green luminescence in spectral interval (2,63...2,1 eV) and a group of bands of blue luminescence in spectral interval (4,0...2,65 eV). Spectrum of blue luminescence measured in 50 ns after the end of PE action consists of two wide bands of 3,1 and 3,7 eV (Fig. 1, curve *б*) with the similar value of half-width equal 0,4 eV.

In Fig. 2, curves *з*, *д* KLI are presented in bands 3,7 and 3,1 eV respectively. As it follows from the given results front of luminescence buildup in the band 3,7 eV coincides with ns-component of green luminescence buildup and described by mono-exponential function (1) with value τ_1 equal to 40 ns (Fig. 2, curves *б*, *з*). Front of luminescence buildup in the band 3,1 eV can be compared with time resolution of measured track (30 ns).

Luminescence decay in the band 3,7 eV is described by a set of two exponents with values of characteristic times 2,5 and 20 ms (Fig. 1) and in the band *в* положе 3,1 eV – by a set of three exponents with values of characteristic times 40 ns (Fig. 2, curve *д*), 2,5 and 50 ms (Fig. 1).

Studying the influence of preliminary radiation dose on spectral-kinetic characteristics of blue luminescence the following thing was stated. At growth of integral dose value (at $P=\text{const}$) radiation luminescence quenching in the band 3,7 eV (Fig. 3, curve *б*) is observed while luminescence intensity in the band 3,1 eV does not practically depend on D in the region $\leq 10^5$ Gy (Fig. 3, curve *з*). In this case contribution of ns-component of luminescence decay in the band 3,1 eV

(~50 % of amplitude value) does not depend on D as well.

It was revealed that dose dependences of amplitude value of microsecond-component of green luminescence buildup ($I_{2\max}$) and luminescence intensity in the band 3,1 eV are similar (Fig. 3, curves *б*, *з*).

Linear dependence of amplitude value of intensities of bands 3,7 and 3,1 eV of the value of electron fluence in the pulse in the range of $10^{11}...10^{13}$ cm $^{-2}$ followed at any value of integral dose absorbed by a crystal in the range $\leq 10^5$ Gy was revealed.

2.3. Luminescence of crystal LiF-O in the region 4,0...2,65 eV

PCL spectrum of crystal LiF-O depends on time of its measuring relative to the moment of PE end of the action. Spectrum measured in 50 ns consists of bands of 3,7 and 3,1 eV with similar half-width values equal 0,4 eV and coincides with spectrum of blue luminescence of crystal LiF(U)-O showed in Fig. 1, curve *а*.

Spectrum measured in 300 ms after the end of PE effect consists of wide (half-width equals 0,7 eV) band with maximum of 3,0 eV (Fig. 1, curve *д*).

Front of luminescence buildup in the band 3,1 eV in spectrum of the crystal LiF-O is described by the parameter comparable with time resolution of measuring track and KLI has the same form as in the band 3,1 eV in spectrum of crystal LiF(U)-O (Fig. 2, curve *д*).

Without uranium KLI in the band 3,7 eV in crystal LiF-O has the form given in Fig. 2, curve *е* and differs from KLI in the band 3,7 eV in spectrum of crystal LiF(U)-O in presence of ns-component of decay (Fig. 2, curves *з*, *е*).

Thus, in spectrum of crystal LiF-O both bands of blue luminescence are described by similar increase parameter comparable with time resolution of the path.

Kinetics of luminescence decay in each band are described by two exponents with similar set of values of characteristic times: 40 ns and 2,5 ms. Contribution of ns-component of decay in each band depends on a value of integral absorbed dose and amounts to 90 % of amplitude value of intensity in the range $D \leq 10^2$ Gy and 50 % – in the range $\geq 1 \cdot 10^4$ Gy.

Characters of longtime relaxation of luminescence in the range 3,7 and 3,0 eV are different. In the band 3,7 eV luminescence decay is observed; it is described by a value of characteristic time equal 100 ms. In the range of 3,0 eV two processes are overlapped: luminescence decay in the band 3,1 eV and buildup in the band of 3,0 eV that does not allow extracting longtime decay component in the band 3,1 eV.

Kinetics of luminescence buildup spectrum of which represents a band with maximum of 3,0 eV (Fig. 1, curve *д*) is presented in Fig. 2, curve *ж*. Characteristic buildup time equals 20 ms and does not depend on oxygen concentration in crystal. Luminescence decay is of mono-exponential character. As it was stated the value of characteristic decay time depends on oxygen concentration in crystal and equals 400 and 100 ms in crystals LiF containing oxygen in the amount $2 \cdot 10^{-4}$

and $3 \cdot 10^{-3}$ wt. %, respectively by the data of neutron activation analysis. In crystals LiF containing oxygen impurity of less than 10^{-5} wt. % luminescence buildup in the band 3,0 eV is not observed.

Dependences of excitation efficiency at 300 K of blue luminescence in crystals LiF-O on parameters of radiation P and D were studied. Amplitude values of intensity of both bands 3,7 and 3,1 eV were measured in 30 ns from the moment of PE action. It was stated that in crystal LiF-O as well as in crystal LiF(U)-O with growth of integral dose the radiation luminescence quenching in the band 3,7 eV and linear dependence of intensity value on P are observed and as it turned out, uranium presence in crystal does not influence the rate of radiation quenching.

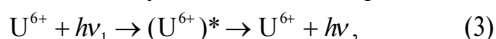
Luminescence intensity in the band 3,1 eV in crystal LiF-O does not practically depend on the value of integral dose as well as intensity of band 3,1 eV in spectrum of crystal LiF(U)-O. And luminescence intensity in the band 3,1 eV depends linearly on P as well as in crystal LiF(U)-O.

3. Discussion of results and conclusions

To determine interaction between centers conditioning blue and green luminescence spectral-kinetic parameters of luminescence of unirradiated crystals LiF-O both with and without uranium and crystals subjected to preliminary radiation of PE in the interval of absorbed doses $\leq 10^5$ Gy were studied.

The whole set of obtained results may be stated in the form of the following statements:

1. In crystal LiF(U)-O green uranium luminescence of similar spectral composition occurs both at optical excitation with quantum energy 3,68 eV and at electron excitation with energy $3 \cdot 10^5$ eV. Therefore, population of radiative states is implemented both without free charge carriers and at occurrence of electron-hole pairs in crystal.
2. At constant spectral composition of uranium luminescence the way of its excitation determines kinetics of buildup process. The microsecond-component appears at electron excitation additionally to ns-component of buildup the value of characteristic time of which (40 ns) is the same both at optical and electron excitation. Its characteristic time value (2,5 ms) is the same for all wave lengths in the region of green luminescence.
3. Ns-component of PPL of hexavalent uranium activated by laser radiation with quantum energy 3,68 eV is obviously the result of direct process:



where $h\nu_1$ is the quantum energy of excitation.

However, reaction (3) does not describe the excitation mechanism of ns-component of PCL intensity in spite of coincidence of values of characteristic time of both buildup processes (Fig. 2) and in spite of possibility of reabsorption of oxygen luminescence of 3,7 eV being in PCL spectrum of uranium-containing crystals.

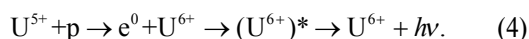
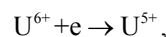
The following facts indicate in favor of this supposition. Firstly, uranium presence does not influence the rate of radiation quenching of luminescence in the band 3,7 eV. The obtained results indicate the fact that in crystals LiF-O with and without uranium these rates are the same. Secondly, the character of changing intensity of band 3,7 eV and intensity of ns-component of uranium luminescence with growth of dose do not coincide. The results given in Fig.3 indicate the fact that value $I_{1\max}$ increases by several orders at dose growth achieving maximal value in the range of $1,7 \cdot 10^4$ Gy (Fig. 3, curve *a*) and then decreases slowly at further dose increase. In the same interval of absorbed doses the luminescence intensity of 3,1 eV it decreases steadily within one order.

4. The character of the obtained dose dependence of ns-component of luminescence intensity of hexavalent uranium (Fig. 3, curve *a*) coincides with the character of dose dependence of uranium centers containing U^{5+} estimated by signal intensity of ESR founded and accumulated in crystal at X-ray irradiation [4]. The same specific character of dose dependence (by the curve with maximum) is observed for a peak of thermostimulated luminescence at 400 K of irradiated uranium-containing crystals LiF [3]. Dose range defining the position of maxima at dose dependences is of one order.

The set of results allows supposing that ns-component of luminescence intensity of hexavalent uranium in PCL spectrum occurs as a result of two stages. *The first stage* – is the stage of founding and accumulating uranium centers containing U^{5+} in crystal irradiated by electrons. A number of such centers is determined by a dose of irradiation; the character of dose dependence is described by a curve with maximum. *The second stage* – is the stage of excitation of PCL U^{6+} under the action of pulse of electrons which includes the following processes:

- a) capture of hole (p) in centers containing U^{5+} accumulated in crystal,
- b) transition of electron from U^{5+} to a hole founding near-defective exciton (e^0) and recovering uranium charge state
- b) energy transfer from exciton to hexavalent uranium with its further irradiation.

Uranium luminescence yield is determined by electron fluence in excitation pulse at any value of integral dose absorbed by crystal that is observed in the experiment. The excitation process of ns-component of luminescence buildup of hexavalent uranium may be written down in the form:



We suppose that ions O^{2-} surrounded by uranium are the places of hot hole sink.

5. Mechanisms of uranium luminescence buildup in nanosecond and microsecond time intervals are different. Different character of dose dependences of

amplitude values of nanosecond and microsecond components of uranium luminescence intensity – $I_{1\max}$ and $I_{2\max}$ respectively indicate this directly (Fig. 3). Value $I_{2\max}$ is maximal at first PE action on crystal when the value of ns-component of uranium luminescence intensity $I_{1\max}$ is minimal (Fig. 3).

Coincidence of spectra of microsecond and nanosecond intensity components indicates the fact that both intensity components are conditioned by radiative transitions at hexavalent uranium. Absence of microsecond-increase component at optical excitation indicates implementation of the second filling channel of the same radiative state only at excitation by hard radiation.

Coincidence of the character of dose dependence intensity of oxygen luminescence in the band 3,1 eV and

microsecond-uranium luminescence component (Fig. 3, *б*) as well as the coincidence of values of characteristic time of luminescence quenching of 3,1 eV (2,5 ms) and buildup time of uranium luminescence (Fig. 1) all these facts indicate oxygen participation in filling radiative state U^{6+} . Probably, transfer of electron from O^{2-} to the next ion U^{6+} occurs [15]:

and further capture of hole at U^{5+} according to (4). The efficiency of this process falls at integral dose increase owing to decrease of uranium initial concentration in hexavalent state. Experimental results indicate the decrease of intensity of microsecond-uranium and oxygen luminescence component by 3,1 eV at equal rate in the same interval of the absorbed dose.

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Received on 22.12.2006