

## Peculiarities of yellow luminescence decay kinetics in LiF–UO<sub>2</sub> crystals

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A fast component, on the order 387 ns (300 K), has been detected in the decay kinetics of the yellow luminescence (563 nm) in LiF-UO<sub>2</sub> crystals. It is shown that the emitting centers are anisotropic formations oriented in the crystal lattice along the second-order symmetry axes (C<sub>2</sub>) using the method of azimuthal dependence of the luminescence polarization. A model of the radiating centre is proposed and the position of the oxygen defect excited level is determined, from which the transition of an electron to the conduction band occurs. The luminescence (387 ns) from of the U<sup>5+</sup> ion is observed as a result of electron transfer from oxygen ion to the excited U<sup>6+</sup> level. The subsequent hole localization on U<sup>5+</sup> in the ground state is accompanied by the reduction of the U<sup>6+</sup> ion, that luminescence is observed in the green region of the spectrum (523 nm) with time decay 100 microsecond.

**Keyword:** decay kinetics of luminescence, polarization, LiF-UO<sub>2</sub> crystals.

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### Introduction

Currently, the three main ion activators Ce<sup>3+</sup>, Eu<sup>3+</sup> and Mn<sup>4+</sup> are used most often in typical LED phosphors. The quantum efficiency of these phosphors often exceeds 90% over the entire spectrum of the visible range when excited by blue LEDs. However, the peak wavelengths and line widths of their emission, as well as their stability, are still factors that can be improved. When developing „white“ light sources, blue LEDs and phosphors are used, converting this radiation into white light. A phosphor based on the crystal Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> is used to convert to the yellow-green region of the spectrum: Ce [1–3]. The phosphor should have high radiation efficiency, be resistant to degradation over a long service life and be cost-effective. Measuring the efficiency of converting blue LED radiation into the green region of the spectrum in a LiF-UO<sub>2</sub> crystal showed its high value — about 0.9 [4]. It should be noted that the crystal does not lose its quantum efficiency during a long storage period (for more than 40 years). Comparing the simple crystallographic structure of LiF-UO<sub>2</sub> with its analog based on YAG-Ce<sup>3+</sup>, we come to the conclusion that the studied phosphor can compete in a number of parameters. The crystallographic structure is not of the last importance, since in order to achieve a high quantum yield, it is necessary to preserve certain crystallographic parameters.

Earlier [4] we detected a fast luminescence decay component ( $\tau = 210$  ns,  $T = 300$  K) in the green region of the spectrum when excited in the charge transfer band of the crystal LiF-UO<sub>2</sub>. Along with the green glow, luminescence is observed (also with high efficiency) in the yellow region of the spectrum. In this regard, the task was to establish

the nature of the radiative centers responsible for the glow with a maximum of 563 nm in LiF-UO<sub>2</sub> crystals with the prospect of using these results in the development of white light sources.

It should be noted that, despite the large number of publications on the luminescence of uranium centers, there are few papers devoted to the kinetics of fluorescence of fluoride crystals with an admixture of uranium. The pioneers in this field are the authors of the paper [5], in which an abnormal luminescence decay with  $\tau = 20\text{--}30\mu\text{s}$  at 527.8 nm in LiF-UO<sub>3</sub> crystals under high-intensity excitation was recorded. With low-intensity excitation, the luminescence decay time reached a value of the order of 900,  $\mu\text{s}$ . Luminescence excitation was carried out by a standard xenon lamp at the temperature of liquid nitrogen. We note, that we also observe these glow components at a crystal temperature of 78 K with excitation by nitrogen laser radiation. One of the few papers — paper [6], which provides data for other spectral regions: 327 nm (components with  $\tau = 23$  and 111  $\mu\text{s}$ ), 376 nm (2.2 and 8.2 ns) and 522 nm (1.6 and 4.5 ns) at an excitation energy exceeding the band gap width. In the cited paper, the luminescence, excitation and reflection spectra of a LiF-U,Cu crystal were studied using synchrotron radiation with an energy of 2–40 eV at a temperature of 10–295 K). The dominant role of the electron-hole mechanism in charge transfer to impurity ions U<sup>6+</sup> is shown. The authors note, that with such an excitation, a component with a duration of 40 ns appears for radiation in the green region of the spectrum. The same component was observed in the paper [7] when excited by nitrogen laser pulses. It should be noted, that the measured

luminescence decay duration corresponds to the duration of the exciting laser pulse  $\approx 40$  ns, i.e. the shape of the activator luminescence pulse repeats the shape of the exciting pulse. In the previous paper [4] we showed that the luminescence decay time of centers comprising the ion  $U^{5+}$ , surrounded by oxygen ions located on the axis of symmetry  $C_4$  [cite8,9], is on the order of 210 ns and is accompanied by photoluminescence in the green region of the spectrum. As for the anisotropic glow centers with an axis of symmetry  $C_2$ , the models of which are considered in [10,11], the maximum of their luminescence is in the blue and green regions of the spectrum. We have not found experimental data on the kinetics of luminescence in the yellow spectral region with a maximum at 563 nm.

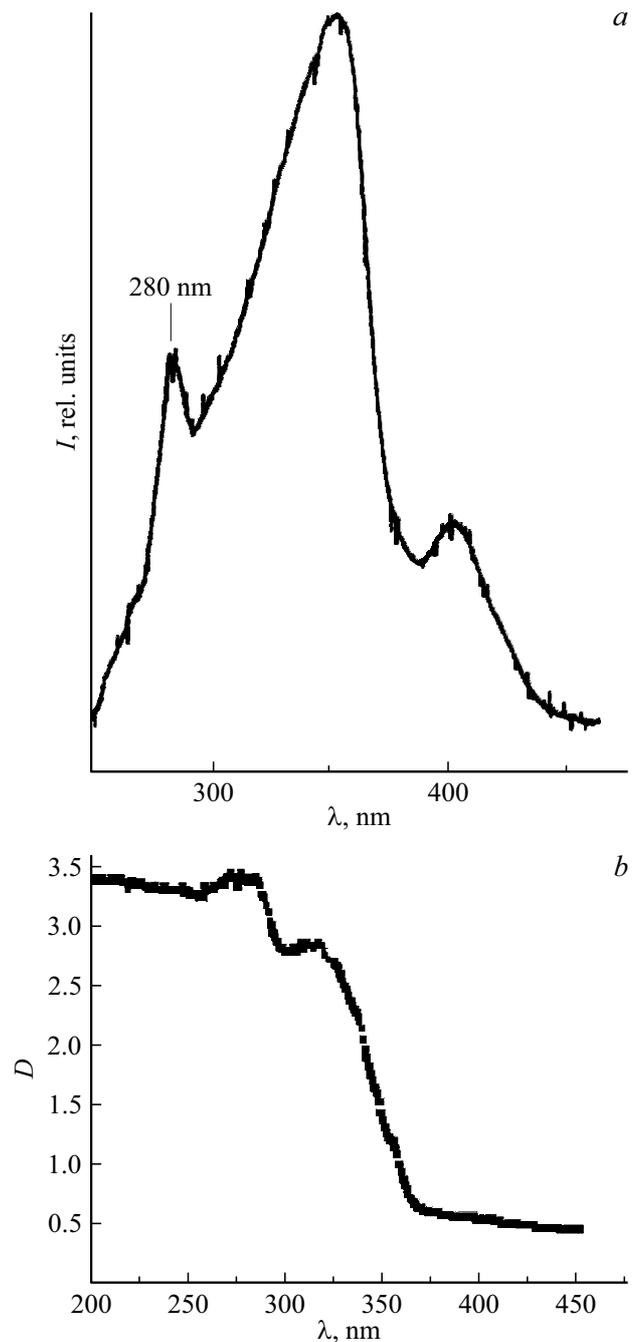
## Research targets and methods

In this paper, samples of single crystals of LiF activated by  $UO_2$  were studied. The absorption coefficient at the maximum of the activator band (312 nm) was about  $37 \text{ cm}^{-1}$ . Luminescence excitation was carried out using an LGI-21 nitrogen laser with  $\lambda_m = 337$  nm and a pulse duration of 40 ns, and the time characteristics of the glow were recorded using a silicon photodiode FD-24K and an AKIP-4122/4 oscilloscope. Measurements were carried out both at liquid nitrogen temperature (78 K) and at room temperature (300 K). The luminescence and excitation spectra were measured on a diffraction spectrometer SDL1-600 (slit 0.2 nm) and on MUR2-1200 (slit 0.5 nm) at temperatures of 85 and 300 K. The absorption spectra were measured on a Perkin-Elmer-Lambda 950 spectrophotometer at a temperature of 300 K.

When measuring the azimuthal dependence of the degree of the luminescence polarization ( $P$ ) in the yellow region of the spectrum, the yellow glow was isolated using interference light filters with a transmission of  $\lambda = 565$  nm (28%) and  $\lambda = 523$  nm (0%). The LGI-21 laser radiation was linearly polarized, and by rotating the crystal plate under study around the excitation direction, the dependences of the observed degree of luminescence polarization on the angle — the so-called azimuthal dependences of the degree of polarization were measured. The plate was cut in the plane (100). The azimuth ( $\alpha$ ) is calculated from the direction of the electric vector of the exciting light. The glow polarization was measured in relative units.

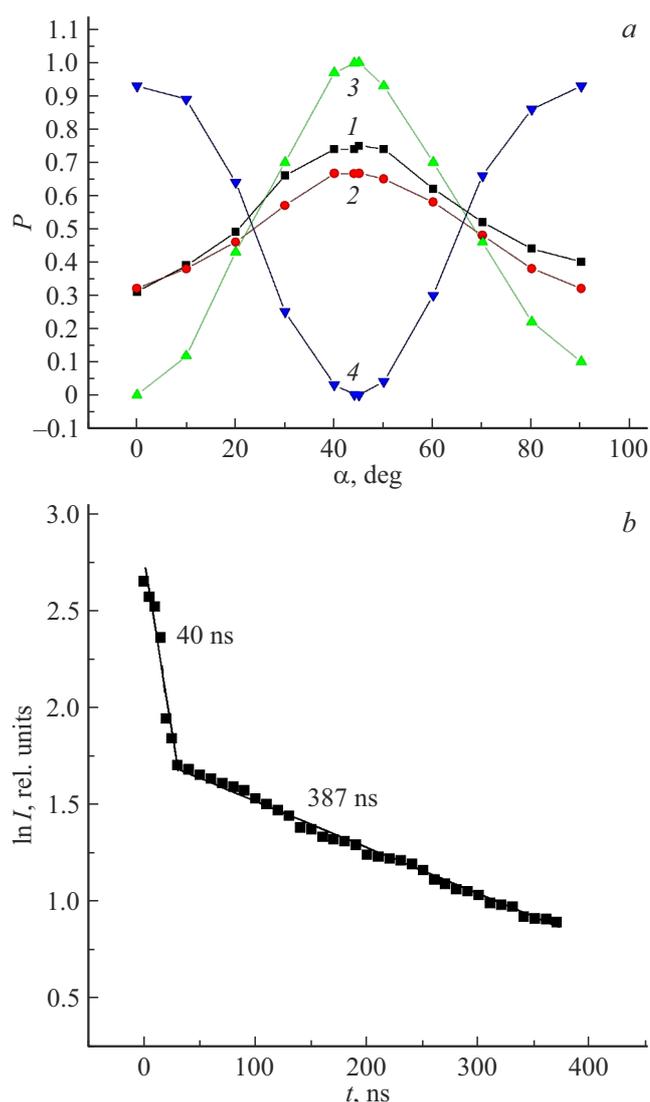
## Results and discussion

Fig. 1, *a* shows the luminescence excitation spectrum for 563 nm. In contrast to the green glow, the yellow glow is excited not only in the bands 350 and 400 nm, but also in the band with a maximum of 280 nm. It should be noted, that the same band is recorded in the absorption spectrum of the crystal under study (Fig. 1, *b*) and is caused



**Figure 1.** Excitation spectrum (*a*) for luminescence 563 nm in a crystal  $LiF-UO_2$  and the absorption spectrum (*b*). The measurement temperature is 300 K.

by absorption by oxygen centers in the form of dipoles  $O^{2-}-V_a^+$  [12]. Presumably, these centers are involved in the electron transfer from the oxygen ligand to the ion  $U^{6+}$ . Fig. 2, *a* shows the azimuthal dependence of the degree of polarization of the luminescence centers 563 nm in the crystal  $LiF-UO_2$  (curve 1) and the calculated curves for the oscillator with the axis of symmetry  $C_2$  (curve 2),  $C_3$  (curve 3) and  $C_4$  (curve 4) [8]. The analysis of the curves shows that the nature of the azimuthal dependence



**Figure 2.** Azimuthal dependence of the degree of polarization of luminescence centers 563 nm in LiF-UO crystals<sub>2</sub> (1) and calculated curves for an oscillator with an axis of symmetry  $C_2$  (2),  $C_3$  (3) and  $C_4$  (4) [8] (a); fast components in the decay kinetics of luminescence when excited by a nitrogen laser,  $T = 300$  K (b).

of the degree of polarization ( $P$ ) of the luminescence of the studied centers corresponds to a greater extent to the calculated curve for an oscillator with the axis of symmetry  $C_2$ , which is described by the dependence

$$P = 1/3[1 + \sin^2(2\alpha)].$$

The obtained dependences indicate that the core of the luminescent centers can be  $U^{6+}$  surrounded by oxygen ions oriented along the second-order axis located in the third coordination sphere. At the same time, the distance between the ion activator  $U^{6+}$  and the oxygen ion is 1.73 times greater compared to the case when oxygen ions are located in the first coordination sphere, i.e. on the axis of symmetry  $C_4$ , forming centers with a green glow (523 nm). At the

same time, the decay time of yellow luminescence (387 ns) is also slightly greater, than that of green (210 ns). The decay kinetics curve of yellow glow at room temperature is shown in Fig. 2, b. Exponential luminescence decay with  $\tau = 40$  and 387 ns is observed on the curve. It should be noted that lowering the measurement temperature to 78 K leads to the absence of the component 387 ns in the decay kinetics of luminescence. This means that at a low temperature there is no electron transfer from the excited level of the oxygen center to the conduction band. Consequently, the excited level of the oxygen center can be below the bottom of the conduction band by an amount of the order of  $kT$  in multistage excitation processes.

## Conclusion

Previously unidentified glow centers were found in LiF-UO<sub>2</sub> crystals, emitting in the yellow region of the spectrum with a band maximum at 563 nm. Along with numerous emission lines of uranium centers, the observed luminescence is characterized by a relatively short decay time of 387 ns and exhibits the glow anisotropy corresponding to the orientation of the dipole along the axis of symmetry of the second order ( $C_2$ ) in the crystal LiF-UO<sub>2</sub>. The short decay time of luminescence, the inherent glow anisotropy, indicate a charge transfer process involving oxygen ions located in the nearest coordination spheres in the form of dipoles  $O_2-V_a^+$ . The presence of intense stable yellow luminescence with a short decay time along with the glow in the blue-green spectral region makes LiF-UO<sub>2</sub> crystals promising for use as LED phosphor converters.

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## Conflict of interest

The authors declare that they have no conflict of interest.

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