

CONDENSED-MATTER
SPECTROSCOPY

Impurity Cathodoluminescence of Oxygen-Containing LiF Crystals

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Abstract—Cathodoluminescence of oxygen-containing LiF crystals (LiF–O, LiF–O,OH, LiF–WO₃) is studied by pulsed spectrometry with nanosecond resolution upon excitation of crystals by a single electron-beam pulse at 15 K.

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INTRODUCTION

In recent years, crystals with complex oxygen-containing anions, such as MeWO₄ (where Me = Zn, Mg, Ca, Cd, and Pb [1, 2]) and Li₂WO₄ [3], have been extensively used as scintillation detectors of ionizing radiation. The high luminescence energy yield, high radiation stability, low radiation background, and high density of materials allow recording of their emission in comparatively small volumes and make them promising for the application in high-energy physics and medicine. It is assumed that an emitting center in the above-listed materials is the oxyanion complex and that the luminescence observed is intrinsic [3–5]. However, available data are insufficient to draw a conclusion on the nature of luminescence centers and, moreover, to predict the luminescence characteristics of these new systems.

In this work, we study oxygen-containing LiF crystals with impurities in the form of OH[−] and O^{2−} ions and tungsten oxide complexes. This study is focused on the spectral–kinetic characteristics of impurity cathodoluminescence in these crystals at 15 K.

OBJECTS AND METHODS OF INVESTIGATION

We studied three types of crystals, i.e., LiF–O, LiF–O,OH, and LiF–WO₃. The LiF–WO₃ crystal was grown by the Kyropoulos method at the Institute of Scintillation Materials of the National Academy of Sciences of Ukraine. An impurity was introduced into the melt in the form of tungsten oxide. The concentration of the oxide in the crystal was chemically determined to be 0.2 mol %.

The LiF–O and LiF–OH crystals were grown by the Stockbarger method at the State Optical Institute (St. Petersburg, Russia). The concentration of oxygen in the LiF–O and LiF–O,OH crystals was determined by the proton-activation method to be 2×10^{-4} and 10^{-3} wt %, respectively.

The initial purity of crystals was determined by the optical absorption spectra. Nonactivated pure LiF crystals were transparent in the region $0.4 \leq E \leq 13.6$ eV. In the VUV region, the absorption spectra of all the impurity LiF crystals under study contained bands at 10.6, 9.05, 7.29, and 6.2 eV, which point to the presence of oxygen in the form of O^{2−} in the crystal lattice. The IR absorption spectra of the LiF–O,OH and LiF–WO₃ crystals contained additional bands at 0.43–0.46 eV, which were caused by bound and free hydroxyl ions [6, 7]. A distinguishing feature of LiF–O crystals is their transparency in the region of 0.43–0.46 eV.

The pulsed cathodoluminescence (PCL) in crystals at 15 K in the spectral range of 3.7–2.1 eV was excited by an electron-beam pulse with a duration of 10 ns, an average electron energy of 250 keV, and an electron fluence of 10^{11} cm^{−2} per pulse. We studied the PCL of both unirradiated crystals and crystals preliminarily irradiated at 15 K by a series of electron-beam pulses with integral absorbed doses of (D) $\leq 10^5$ Gy.

The luminescence intensity was measured using an MDR-206 monochromator and an FEU-97 photomultiplier. The PCL kinetic curves at a chosen wavelength were recorded on a LeGroy-WP-6030a oscilloscope within a time interval of 10^{-8} – 10^{-3} s after the end of the electron beam pulse.

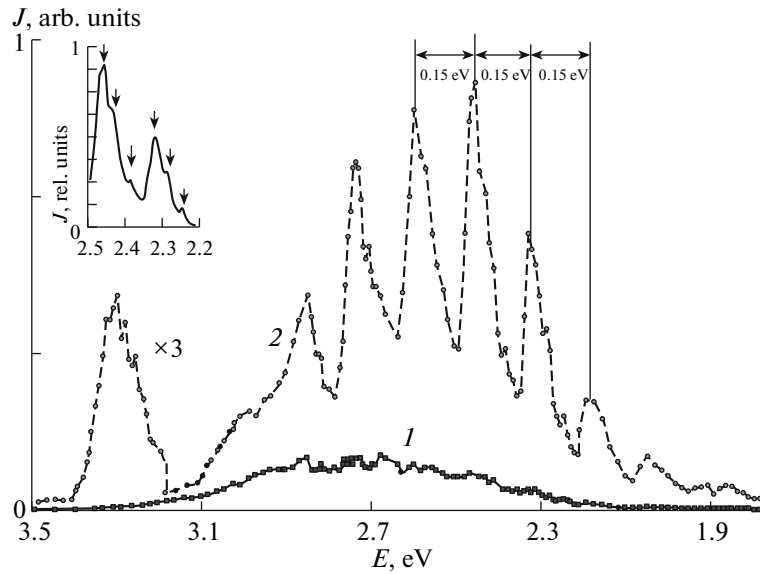


Fig. 1. Spectra of (1) microsecond and (2) nanosecond PCL decay components at 15 K for a preliminarily irradiated LiF–WO₃ crystal ($D = 10^3$ Gy). Inset shows fine structure of vibronic bands.

The PCL kinetics in a band peaked at E_j was described by the formula

$$J(E_j, t) = \sum J_{0i}(E_j) \exp(-t/\tau_i),$$

where $J_{0i}(E_j)$ and τ_i are, respectively, the intensity amplitude and the characteristic decay time of the i th PCL component. The spectrum of the first PCL decay component was measured as the dependence $J_{0i} = f(E)$.

INVESTIGATION RESULTS

Impurity PCL of LiF–WO₃ Crystal

The first electron-beam pulse incident on a LiF–WO₃ crystal immediately excites PCL, the spectrum of the long-lived component of which at 15 K consists of a single band at 2.73 eV (Fig. 1, curve 1) with a half-width of 0.6 eV. The characteristic PCL decay time is 170 μ s. The irradiation of the crystal by a series of electron-beam pulses does not change the type a of the PCL spectrum; however, the PCL decay kinetics contains not only a microsecond, but also an additional nanosecond, component, the intensity of which increases with an increasing absorbed dose (Fig. 2, inset). The spectrum of this component (dependence $J_{01} = f(E)$) consists of a 3.3-eV band with a halfwidth of 0.2 eV and a series of narrow equidistant bands spaced from each other by 0.15 eV (Fig. 1, curve 2). Each of the five central well-resolved equidistant bands has a fine structure, which indicates the splitting of the energy level into three sublevels spaced from one another by an identical distance of ~ 0.03 eV (Fig. 1, inset). All bands of the vibronic PCL spectrum decay

simultaneously by a monoexponential law. The characteristic decay time at 15 K is 70 ns.

The PCL observed is obviously impurity because the PCL spectra of nonactivated pure LiF crystals in the temperature range of 15–25 K show only an excitation band in the region of 5.8 eV [8, 9].

An increase in the dose absorbed by the crystal in the range of 10^1 – 10^4 Gy has no effect on the amplitude intensity of the long-lived PCL spectrum (the single band with a maximum at 2.73 eV; Fig. 2, curve 1), i.e., $J_{02}(E) \neq f(D)$. At the same time, the intensity of the vibronic bands increases with increasing dose absorbed by the crystal and saturates at doses of 10^3 Gy (Fig. 2, curve 2). The dependence $J_1(E_j) = f(D)$ can be described by the equation

$$J_1(E_j, D) = J_{01}(E_j)[1 - \gamma \exp(-D/k)], \quad (1)$$

where D is the dose absorbed by the crystal, $J_{01}(E_j)$ is the PCL intensity amplitude in the band with a maximum at E_j , and γ and k are coefficients.

Impurity PCL of LiF–O,OH and LiF–O Crystals

In both crystals, the impurity PCL at 15 K is excited immediately after the action of an electron-beam pulse. The luminescence decay kinetics contains nanosecond and microsecond components, which have different spectral compositions. The spectra of the microsecond PCL component ($J_{02}(E)$) are identical for both crystals and consist of a single band at 3.1 eV with a halfwidth of 0.7 eV (Fig. 3, curve 1; Fig. 4, curve 1).

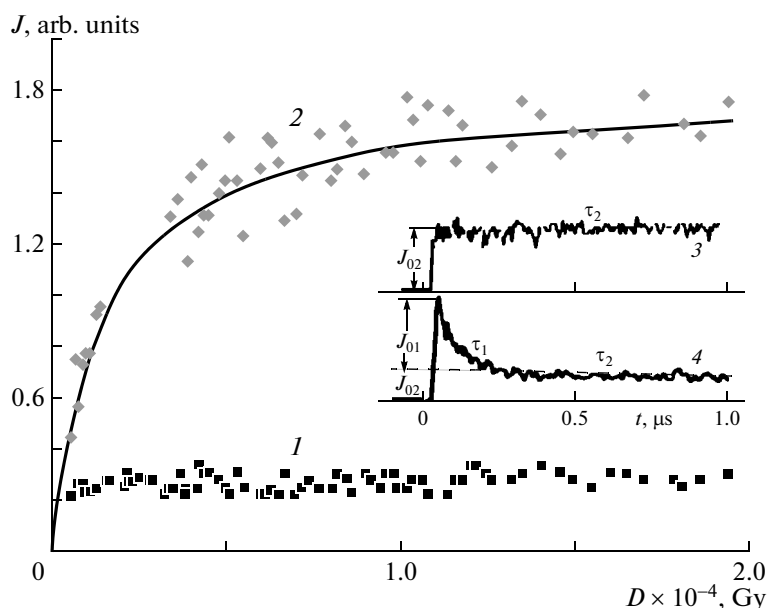


Fig. 2. Dependence of microsecond (1) and nanosecond PCL components at 2.6 eV on radiation dose absorbed by LiF–WO₃ crystal irradiated by electron pulses at 15 K. The inset shows the decay kinetics of PCL at 2.6 eV at 15K for crystals preliminarily irradiated with $D = 10^3$ Gy (3).

The spectrum of the nanosecond PCL component ($J_{01}(E)$) of the LiF–O,OH crystal contains a band at 3.3 eV with a halfwidth of 0.2 eV and a set of narrow well-resolved equidistant bands in the spectral range of 3–2.1 eV. The parameters of the vibronic PCL spectrum of the LiF–O,OH crystal, such as the spectral position and halfwidth of bands, decay time, interband spacing, and the number of fine-structure bands, coincide with the corresponding parameters for the nanosecond PCL component of the preliminarily irradiated LiF–WO₃ crystal (Figs. 1, 3).

The spectrum of the nanosecond PCL decay component of the LiF–O crystal (Fig. 4, curve 2) consists of a 3.3-eV band and a weak emission in the range of 2–3 eV. The characteristic PCL decay time is 50 ns in the entire spectral range measured (Fig. 4, curve 3). We assume that this weakly structured emission consists of a set of low-intensity vibronic radiative transitions. This assumption is evidenced by the close (70 and 50 ns) decay times of the vibronic spectra and by the coincidence of their spectral regions for all the three types of crystals, LiF–O, LiF–O,OH, and LiF–WO₃.

The impurity PCL in the LiF–O,OH and LiF–O crystals differs from the PCL in the LiF–WO₃ crystals by the following features:

(i) The vibronic spectrum can be excited by the first electron-beam pulse incident on the unirradiated crystal.

(ii) The intensity of the vibronic bands does not depend on the integral dose absorbed by the crystal in the range of 10 – 10^4 Gy.

(iii) The single-band maximum in the spectrum of the long-lived component of the impurity PCL is shifted to shorter wavelengths (3.1 eV) with respect to its position in the spectrum of the LiF–WO₃ crystal (2.73 eV).

The ratio of the light sums of the short- and long-time decay components of impurity PCL is about 1 : 1000 in LiF–OH crystals and 1 : 100 in LiF–WO₃ crystals. This is obviously one of the factors that prevents one from experimentally observing vibronic emission spectra in previous stationary investigations of oxygen-containing LiF crystals at 15 K.

DISCUSSION

It is known that, due to the growth of alkali-halide crystals in air, the heating of crystals in an oxygen atmosphere, and ionizing irradiation of oxygen-containing crystals at 300 K, their crystal lattice contains molecular O₂[−] ions [10–13], the vibronic spectrum of which lies in the range of 3–1.6 eV [14–16]. Direct EPR studies [11, 12] proved that O₂[−] ions occupy a single-site position in the lattice and their molecular axes are oriented along the $\langle 110 \rangle$ crystallographic direction.

In all studied oxygen-containing LiF crystals, at 15 K, electron-beam pulses excite PCL in the same spectral range of 2.1–3 eV with a spectrum consisting of narrow equidistant bands spaced by 0.15 eV, which is close to the energy of intrinsic vibrations of free O₂[−] molecules (0.135 eV [15]) and O₂[−] ions in the lattice of alkali-halide crystals (0.12–0.13 eV) [17, 18]. The dis-

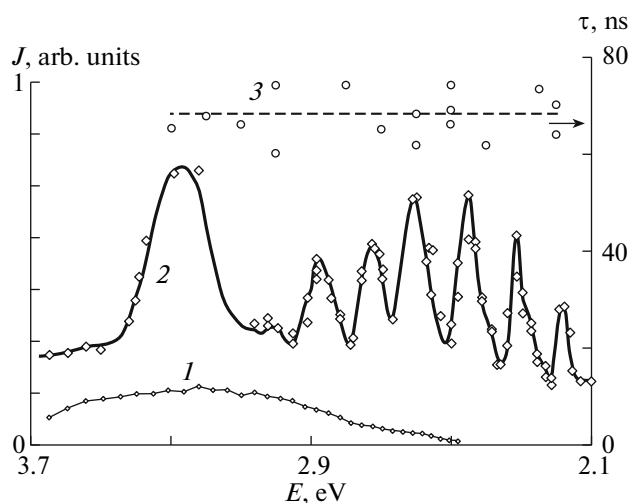


Fig. 3. Spectra of (1) millisecond and (2) nanosecond PCL components at 15 K for a LiF–O,OH crystal and (3) the characteristic decay time in different bands of short-time PCL component.

tance between the fine-structure bands is ~ 0.03 eV and is comparable to the energy of transverse optical phonons in LiF crystals [19]. A similar fine structure was observed in the luminescence spectrum of KCl– O_2^- crystals [14].

Thus, at 15 K, all the LiF crystals studied by us contain luminescence centers whose composition includes O_2^- ions. A distinguishing feature of these crystals is that, at 15 K, the concentration of O_2^- ions in the LiF–O,OH and LiF–O crystals does not depend on the absorbed dose, whereas the intensity of vibronic

bands (i.e., the concentration of O_2^- ions) in LiF– WO_3 crystals increases with increasing irradiation dose (Fig. 2).

Obviously, the reason for the observed phenomenon consists of the following. We believe that the local compensation for the excess charge of the six-valence activator occurs during the growth process due to the presence of oxygen-containing impurities in the lattice. Depending on the number, type, and position of impurity oxygen in the nearest coordination sphere of tungsten in the tungsten–oxygen complexes, they also contain cation or anion vacancies. This leads to the formation of nanodefects containing the matrix ions, activator ions, oxygen-containing ions, and intrinsic lattice defects of the lattice. The instantaneous radiative formation of molecular O_2^- ions in the region of these nanodefects can occur both upon capture of radiation-induced electronic excitations and in the process of radiation-induced charge transfer between the complex components (for example, between W^{6+} and O^{2-}). At the first stage of each of these processes, O^- ions are formed in the anionic sites of the crystal lattice, while single-site molecular O_2^- ions are formed upon dimerization at the second stage.

In the absence of a polyvalent activator (complex creator), the distribution of oxygen-containing impurities in the crystal volume is more uniform. Irradiation of such crystals (LiF–O and LiF–O,OH) is also accompanied by radiation-induced transformation of the oxygen-containing impurity with creation of O^- ions in anionic sites [20, 21]. Indeed, in the LiF–O,OH crystals studied, the intensity of absorption band at 0.46 eV, which is caused by OH^- ions, decreases with increasing absorption dose at 15 K. However, in the case of uniform distribution of the

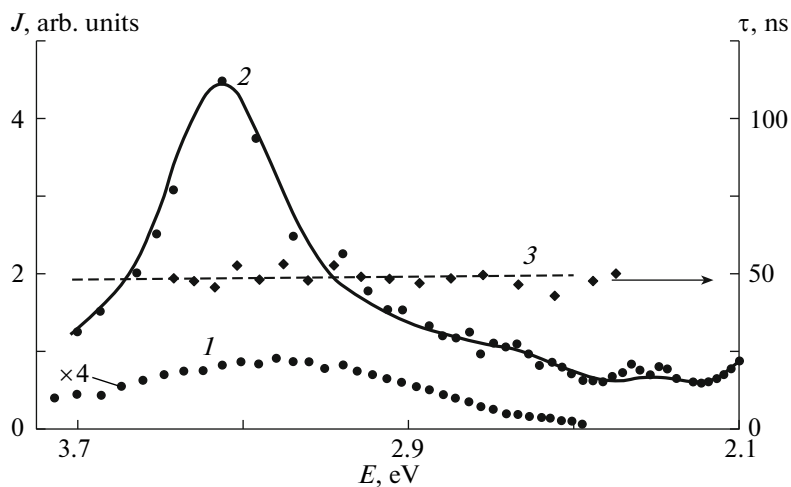
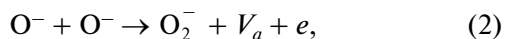


Fig. 4. Spectra of (1) millisecond and (2) nanosecond PCL components at 15 K for a LiF–O crystal and (3) the characteristic decay time in different bands of short-time PCL component.

oxygen-containing impurity over the crystal volume, the molecular O_2^- ions can only form in the process of thermally impurity diffusion [22] as follows:



where V_a is an anionic vacancy and e is an electron.

It is absolutely clear that reaction (2) cannot occur at 15 K. That is why the intensity of vibronic bands does not increase with increasing absorbed dose in LiF–O, OH crystals at 15 K despite the formation of O^- ions due to hydrate decomposition.

CONCLUSIONS

Using time-resolved spectroscopy, it was shown for the first time that the action of electron-beam pulses on oxygen-containing LiF crystals (LiF–O, LiF–O, OH, LiF–WO₃) at 15 K excites vibronic transitions in O_2^- ions, whose intensity is determined by the absorbed irradiation dose and by the oxidation–reduction conditions of the crystal growth.

The immediate formation of O_2^- luminescence centers in LiF–WO₃ crystals at 15 K does not involve diffusion processes due to the radiation-induced transformation of tungsten–oxygen complexes with a high local concentration of oxygen and lattice defects. In LiF–O and LiF–O, OH crystals, the radiation-induced transformation of the oxygen-containing impurity, which is uniformly distributed in the volume, does not lead to the formation of O_2^- luminescence centers due to the impossibility of the thermally impurity diffusion of O^- ions at 15 K.

The impurity PCL excited in crystals by electron-beam pulses decays with time. The luminescence in the vibronic band decays for a microsecond, after which the spectrum consists of a single wide long-lived band with a maximum whose position depends on the crystal imperfection before irradiation and lies at 2.73 eV for LiF–WO₃ crystals and 3.1 eV for LiF–O, OH and LiF–O crystals. The identification of this radiative transition requires further investigations.

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