## Electronic properties of undoped LiBaAlF<sub>6</sub> single crystals: far-ultraviolet optical, luminescence, and x-ray photoelectron spectroscopy studies

Vladimir A. Pustovarov,<sup>1</sup> Igor N. Ogorodnikov,<sup>1</sup> Sergey I. Omelkov,<sup>2</sup>\* Dmitry A. Spassky,<sup>2</sup> and Ludmila I. Isaenko<sup>3</sup>

<sup>1</sup>Experimental Physics Department, Ural Federal University, Mira Street 19, 620002 Yekaterinburg, Russia <sup>2</sup>Institute of Physics, University of Tartu, Riia 142, 51014 Tartu, Estonia

<sup>3</sup>Institute of Geology and Mineralogy SB RAS, Russkaya Street 43, 630058 Novosibirsk, Russia

\*Corresponding author: omelkovs@gmail.com

Received March 21, 2014; revised June 22, 2014; accepted June 22, 2014; posted June 26, 2014 (Doc. ID 208652); published July 23, 2014

The electronic structure properties of undoped single crystals of LiBaAlF<sub>6</sub> (LBAF) were determined using low-temperature (T = 10 K) time-resolved far-ultraviolet (3.7–40 eV) synchrotron radiation spectroscopy, calculations for the spectra of optical functions, and x-ray photoelectron spectroscopy. The bandgap of the investigated compound was found at  $E_g = 12.3$  eV, the energy threshold for creation of the unrelaxed excitons at  $E_{n=1} = 11.6$  eV, and the low-energy fundamental absorption edge at 11.0 eV. The subnanosecond photoluminescence emission band at 6.6 eV in LBAF single crystal is due to radiative valence-core transitions  $2p \text{ F}^- \rightarrow 5p \text{ Ba}^{2+}$ . © 2014 Optical Society of America

OCIS codes: (160.3380) Laser materials; (160.3220) Ionic crystals; (300.6280) Spectroscopy, fluorescence and luminescence; (300.6500) Spectroscopy, time-resolved. http://dx.doi.org/10.1364/JOSAB.31.001926

## 1. INTRODUCTION

Fluoride crystals with the general formula Li M AlF<sub>6</sub> (M = Ca, Sr, Ba) are traditionally used as optical laser materials operating in the ultraviolet (UV) and vacuum ultraviolet (VUV) spectral ranges [1,2]. Among them, the LiCaAlF<sub>6</sub> and LiSrAlF<sub>6</sub> crystalline systems have been studied in sufficient detail. These crystals doped with Ce<sup>3+</sup> ions are promising optical materials for near-infrared tunable lasers [1,3-5]. The LiCaAlF<sub>6</sub>: $Eu^{2+}$  and LiCaAlF<sub>6</sub>: $Ce^{3+}$  crystals are promising optical materials for thermoluminescent detectors [6] and scintillators [7]. In this regard, the  $LiCaAlF_6:Eu^{2+}$  luminescence has been studied in detail in [6]; the electron paramagnetic resonance of ferric ions in LiSrAlF<sub>6</sub> crystals has been studied in [8]; the energy transfer processes in  $LiCaAlF_6:Ce^{3+}$  have been studied in [7]; the energy transfer processes in undoped and Ce-doped LiCaAlF<sub>6</sub> and LiSrAlF<sub>6</sub> crystals have been studied in [9]; VUV spectroscopy of undoped  $LiCaAlF_6$  crystals has been performed in [10]; the 5d–4f luminescence of  $Ce^{3+}$ ,  $Gd^{3+}$ , and  $Lu^{3+}$  ions in  $LiCaAlF_6$  has been investigated in [11]; and the refractive indices of LiCaAlF<sub>6</sub> crystals for the visible spectral region were reported in [12,13].

At the same time, the LiBaAlF<sub>6</sub> (LBAF) system has been paid much less attention. We are aware of only a few research works on this system. Luminescent properties and selftrapped excitons (STEs) in undoped LBAF crystals have been studied in [14]. From the luminescence optical spectroscopy data it follows that the experimental estimation of the LBAF energy bandgap is  $E_{\rm g}{\approx}12.1$  eV [14]. Luminescence of  $\rm Pr^{3+}$  ions in LBAF crystals has been studied in [15]. Crystallographic data for the real LBAF crystals were presented in [16]. At the same time, we are not aware of the research work on the LBAF electronic structure. However, any practical application of LBAF as a functional material in quantum optics requires knowledge of the electronic structure not only for the rare-earth and transition dopants, but also for the host crystal.

In this paper, we focus on the experimental study of the electronic structure properties of LBAF single crystals by means of several spectroscopic methods, because any detailed study of the electronic structure should be based on the experimental spectra of solids. First, we studied the low-temperature reflection spectra in the wide energy range including the low-energy tail of the host absorption. The calculations of the spectra of the LBAF optical functions were performed on the basis of the far-ultraviolet low-temperature reflection spectra. These spectra provide information on the location of the fundamental absorption edge, excitonic states, and the width  $E_g$  of the bandgap in LBAF crystal. Second, we used x-ray photoelectron spectroscopy (XPS) methods to study both the core states and the valence band spectra. The valence band structure and specificity of the quasi-core levels Ba 5p were discussed. Third, the low-temperature (T = 10 K) luminescence VUV spectroscopy with a time resolution upon selective excitation with synchrotron radiation (SR) in the 4-40 eV energy range was used to study the radiative valence-core transitions  $F^-2p \rightarrow Ba^{2+}5p$ .

## 2. EXPERIMENTAL DETAILS

All the examined LBAF crystals of high optical quality were grown from the melt of the corresponding fluorides (99.99%) at the Institute of Geology and Mineralogy SB RAS (Novosibirsk, Russia) utilizing the Bridgman technique. The crystal growth method was described in detail in [16]. A brief description of the crystal growth process is as follows. The initial LiBaAlF<sub>6</sub> powder mixture melts congruently in the temperature range from 1113 to 1133 K. The partial pressure of AlF<sub>3</sub> at this temperature is about  $10^5$  Pa (1 bar). The 2 wt. % excess of AlF<sub>3</sub> was added to the initial composition to compensate for the higher volatility of this component. The crystal growing process was carried out in a graphite container placed inside a quartz ampoule. All manipulations were carried out in a dry argon box at overpressure of ca. 0.1 bar to avoid contamination by oxygen impurities. To prevent decomposition, CF4 was added to the reactor. The axial temperature gradient in a growth region was 10-20 K/cm, and the pulling speed of the ampoule was varied from 0.5 to 5 mm per day. The crystal composition was analyzed by the energy dispersive x-ray spectroscopy (EDS) method using a microprobe to 0.5% match the stoichiometric composition. The LBAF samples studied were in the form of optically transparent plane-parallel plates (ca.  $7 \text{ mm} \times 7 \text{ mm} \times 1 \text{ mm}$ ) with the large surface polished to laser-grade quality. The orientation of the crystallographic axes of LBAF samples was arbitrary with respect to the polarization vector of the SR.

The real crystal structure of LBAF was studied in [16]. These crystals belong to the monoclinic system (space group  $P2_1/c$ ) with lattice parameters, nm: a = 0.53372(10), b = 1.0150(2), c = 0.8535(2), and the angle  $\beta = 90.34(3)^{\circ}$ ; the crystallographic unit cell contains four formula units (Z = 4) and has a volume of 0.46235(17) nm<sup>3</sup>.

Photoluminescence (PL) spectra in the energy range of 1.2-6.2 eV, photoluminescence excitation (PLE) spectra, reflection spectra at incidence angle of 17° (3.7-20 eV), and PL decay kinetics were measured at the SUPERLUMI experimental station of HASYLAB [17] upon selective photoexcitation with SR. The primary 2 m vacuum monochromator equipped with two in situ interchangeable gratings, Al and Pt coated, had a typical resolution of 0.32 nm. The PLE spectra were corrected to an equal number of incident photons using sodium salicylate-a luminophore with energy-independent quantum yield over the studied spectral range. The 0.3 m ARC Spectra Pro-300i monochromator equipped with an R6358P (Hamamatsu) photomultiplier was used as a registration system. The measurements were performed at a temperature of 10 K using a continuous-flow liquid helium cryostat mounted in the ultrahigh vacuum chamber with a pressure of residual gases lower than  $1 \times 10^{-8}$  Pa.

The PL emission spectra excited with 22 eV photons (2.5– 8.0 eV, Fig. <u>6</u>), reflection spectra, and PLE spectra (15–40 eV) were recorded using the mobile luminescence setup [<u>18</u>] attached to the branch-line FINEST of the I3 beamline at MAX-lab, Lund [<u>19</u>]. PL emission spectra were measured by the means of a 0.4 m vacuum monochromator (Seya–Namioka scheme) equipped with a microchannel plate photomultiplier (MCP 1645, Hamamatsu).

The time-resolved PL emission spectra (2.5–8.0 eV) and decay curves of PL excited with the 120 eV photons were recorded using the mobile luminescence setup [18] attached

to the BW3 beamline of the DORIS storage ring (Hamburg, Germany). At DORIS the full width at half-maximum (FWHM) of SR pulses was 130 ps with a repetition period of 190 ns (five-bunch mode). Such pulses of excitation enable the recording of spectra within a time window (TW) correlated with the arrival of SR pulses. In the present experiments we recorded time-resolved spectra in two independent TWs. The first one (TW1) was set for detection of the luminescence signal within the 0–17 ns range relative to the beginning of the SR pulse, and the second (TW2) was within the 54–139 ns range. TW parameters were chosen based on the PL decay kinetics. Time-integrated (TI) spectra were recorded within the full time range available between two sequential excitation pulses, i.e., 190 ns. The convolution method was used to analyze fast components of the PL decay kinetics.

The XPS spectra of LBAF crystals were measured at the Institute of Solid States Chemistry of Ural Branch of RAS (Yekaterinburg, Russia) by means of an ESCALAB MK II x-ray photoelectron spectrometer equipped with nonmonochromatic Mg K $\alpha_{1,2}$  (1253.6 eV) and Al K $\alpha_{1,2}$  (1486.6 eV) sources, the ion-pumped chamber having a base pressure less than  $1 \times 10^{-8}$  Pa, a three-channel hemispherical energy analyzer (150°, 12 in), and an AG-21 inert gas ion gun for sample cleaning with Ar<sup>+</sup>-ions (E = 2–10 keV). The energy scale of the spectrometer was calibrated by setting the measured Au  $4f_{7/2}$  binding energy to 84.0 eV [20], with regard to the Fermi energy,  $E_{\rm F}$ . The binding energy was determined with an accuracy of  $\pm 0.1$  eV. The electrical charging of the sample surfaces was estimated from the C 1*s* line (284.6 eV).

The satellites arising due to the nonmonochromatic x-ray source were subtracted using the special supplement for LabView. The further experimental XPS spectra treatment was carried out using special computer program XPSPEAK 4.0. The Shirley algorithm was used to remove a nonlinear background.

It is known [21] that the XPS method is very sensitive to the quality of the sample surfaces. Therefore, special attention in our investigation was paid to the preparation of the crystal surface, which was subject to electrochemical polishing. Just before placing a crystal into the vacuum chamber of the spectrometer, the surface of each sample was mechanically processed with the ethanol solution of Al<sub>2</sub>O<sub>3</sub> powder with dispersity of 0.3 µm, and then the sample was ethanol washed. Afterward it was mounted on the sample holder using a double-sided conductive carbon tape and placed into the preparation vacuum chamber of the spectrometer. In this chamber the sample was warmed up by an incandescent lamp at 400 K for 1 h. On the further stage the sample was transferred into the analyzer chamber, where an additional cleaning of the crystal surfaces was performed by 5 min bombardment with the Ar<sup>+</sup>-ion beam (angle of incidence  $= 30^{\circ}$ , E = 3 keV,  $I = 15 \,\mu\text{A/cm}^2$ ). The total Ar<sup>+</sup> flux was approximately  $5 \times 10^{16}$  ions/cm<sup>2</sup>.

# 3. EXPERIMENTAL RESULTS AND DISCUSSION

#### A. Far-Ultraviolet Optical Spectroscopy

Reflection spectra were analyzed using two different methods: the oscillator model for the analysis of the fundamental absorption edge in the energy range of 8–15 eV and the Kramers–Krönig transform for analysis in the energy range from 8 to 40 eV.

Figure <u>1</u> displays the reflection spectrum recorded at T = 10 K in the energy range of the low-energy tail of the fundamental absorption of LBAF crystal. The reflection spectrum was initially measured in arbitrary units. The normalization procedure performed to calculate the absolute values of the reflection coefficient used the refractive index spectra for the transparency region of the crystal. The refractive index of LBAF single crystal was measured at room temperature in the UV spectral region, using the same sample from which the reflection spectra were recorded. The refractive index of LBAF single crystal at E = 4.13 eV was evaluated as n(E) = 1.4475 [22]. In the framework of the oscillator model [23,24], the contribution of each oscillator, labeled as j, into the complex dielectric constant of the optical material is given by

$$\delta \hat{\varepsilon}_j = \frac{M_j}{E_j^2 - E^2 - \mathrm{i}\Gamma_j E},\tag{1}$$

where i is the imaginary unit; E is the excitation energy; and  $E_j$ ,  $\Gamma_j$ , and  $M_j$  are the spectral parameters of the oscillator the maximum position, the FWHM, and the amplitude, respectively. The total contribution of the electronic transitions outside of the measured spectrum is accounted for by two additional oscillators with indices j = r (red) for the lowenergy region and j = b (blue) for the high-energy region:

$$\hat{\varepsilon}(E) = \varepsilon_{\infty} + \frac{M_r}{E_r^2 - E^2 - i\Gamma_r E} + \frac{M_b}{E_b^2 - E^2 - i\Gamma_b E} + \sum_j \frac{M_j}{E_j^2 - E^2 - i\Gamma_j E},$$
(2)

where the summation over j = 1-7 takes into account the contribution of the seven electronic transitions found in our measurements;  $\varepsilon_{\infty}$  is the high-frequency dielectric constant.

Complex refractive index  $\hat{n}$  is associated with the dielectric function through the relation  $\hat{\varepsilon} = \hat{n}^2$ . Here,  $\hat{n} = n + ik$ , where n and k are indices of refraction and absorption, respectively. For a given incidence angle  $\theta$ , the reflection coefficient for



Fig. 1. Reflection spectrum of LBAF single crystal recorded at 10 K. The points correspond to the experimental data, and the solid lines are the results of the approximation. The vertical arrow indicates the calculated value of  $E_{\rm g}$ .

the s-polarized light in a vacuum can be calculated by the formula [25]

$$R(E) = \left| \frac{\cos \theta - \hat{n} \cos \hat{\theta}}{\cos \theta + \hat{n} \cos \hat{\theta}} \right|^2.$$
(3)

The complex refraction angle  $\hat{\theta}$  is given by Snell's law, sin  $\theta = \hat{n} \sin \hat{\theta}$ . The quality of the experimental data approximation was evaluated by the formula

$$D = \frac{1}{N} \sum_{l=1}^{N} \frac{|R_l^{(m)} - R_l^{(c)}|}{R_l^{(m)}},$$
(4)

where  $R_l^{(m)}$  and  $R_l^{(c)}$  are measured (m) and calculated (c) reflection spectra; N is the number of experimental points. The results of the best fit, which are presented in Table 1 and Fig. 1, correspond to D = 0.022. The specified approximation quality had a required minimal set of seven oscillators (Table 1). The oscillators should be compared with prospective electronic transitions, which are manifested in our measurements. Let us discuss a possible interpretation of the electronic transitions j = 1-7.

From Fig. 1 it follows that the characteristic "excitonic" decline between the extrema at 11.76-12.06 eV in the reflection spectrum is due to electronic transition  $E_4$ . This suggests that the electronic transition  $E_4$  can be ascribed to the excitation of unrelaxed excitons in LBAF crystal. The energy threshold  $(E_{n=1})$  for the creation of such excitons in LBAF at 10 K is 11.61 eV. The next higher-energy transition  $E_5$  at 12.31 eV should be attributed to the beginning of the interband transitions, and a reasonable assessment of the bandgap will be  $E_{\rm g} = 12.3$  eV. It should be noted that the calculated value of  $E_{\rm g}$  is consistent with earlier qualitative assessment of 12.1 eV [14]. The  $E_6$  and  $E_7$  electronic transitions (Table 1), which exceed the energy  $E_{g}$ , should be attributed to interband transitions, and their reasonable interpretation requires quantum-chemical calculation of the LBAF electronic structure. Interpretation of low-energy electronic transitions  $E_1 - E_3$  does not look unambiguous. It is worth noting that in our measurements the samples were mounted without monitoring the

Table 1. Parameters of Approximation for Reflection Spectra Recorded in the Energy Range of the Low-Energy Tail of the Host Absorption: Ordinal Number of a Transition (j), Transition Energy  $(E_j)$ , Full Width at Half-Maximum  $(\Gamma_i)$ , and Amplitude  $(M_i)^a$ 

Oscillator	$E_{j}$	$M_{j}$	$\Gamma_j$
1	10.50	5.000	0.47
2	10.95	15.000	0.56
3	11.29	15.000	0.44
4	11.61	8.000	0.43
5	12.31	4.307	0.51
6	12.72	12.000	0.99
7	13.46	12.000	1.49
r	10.00	5.000	0.77
b	14.41	7.929	1.50
$\varepsilon_{\infty}$		1.402	

<sup>*a*</sup>Parameters  $E_j$  and  $\Gamma_j$  are given in electron-volts.

orientation of the crystallographic axes with respect to the polarization vector of the exciting radiation, so the reflection spectra can exhibit electronic transitions with different polarizations. From the crystallographic structure of LBAF it follows that we can also expect a disordering of one of the cationic sublattices, which may lead to broadening and shifting of the band corresponding to excitonic states.

Figure 2 shows a low-temperature reflection spectrum recorded in the energy range of 8-40 eV for LBAF single crystal at 10 K, and the optical functions spectra calculated on the basis of the experimental data using the Kramers-Krönig transform [26]. Let us compare the experimental and calculated data on the refractive indices of LBAF single crystal obtained in this work with literature data for some related crystals. The refractive index for LiCaAlF<sub>6</sub> crystal at E =6.2 eV is 1.4383 [12], which is somewhat lower than that for LBAF single crystal in the present work. It is worth noting that the refractive indices for the simple binary compounds at room temperature are 1.4758 for CaF<sub>2</sub> at  $\lambda = 230$  nm (5.39 eV) [27] and 1.5103 for BaF<sub>2</sub> at  $\lambda = 270$  nm (4.59 eV) [13]. The lowest-energy peak in the k(E) spectrum at 11.6 eV has excitonic origin, and it is caused by the electronic transition  $E_4$ . Increase in intensity in the k(E) and  $\varepsilon_2(E)$  spectra in the energy region from 12.1 to 12.9 eV is due to the start of interband transition  $E_5$ , which was attributed to  $E_g$  (Table 1). With further increase in the energy range from  $E_{\rm g}$  to ca. 20 eV,



Fig. 2. Spectra of LBAF single crystal: (a) reflection spectrum recorded at T = 10 K, (b),(c) spectra of the optical functions calculated by Kramers–Krönig transform. The vertical arrows indicate the calculated value of  $E_g$  and the possible interpretations of the electronic transitions.

the profiles of all of the spectra are determined by specificity of the interband transitions in LBAF single crystal. Their reasonable interpretation requires quantum-chemical calculations of the LBAF electronic structure. Electronic transitions in the energy range of 20–22 eV occur involving core Ba 5*p* electrons. We tentatively assign the structure at 20–22 eV to excitation of the Ba 5*p* cationic excitons. A broad peak in the reflection spectrum at 22–23 eV corresponds to the most intense peak in the  $-\text{Im} \hat{\epsilon}^{-1}$  and  $-\text{Im} (1 + \hat{\epsilon})^{-1}$  spectra. It is known [28] that the energy position of the dominant peaks in these spectra coincides with the energies of the bulk  $(E_{\rm pv})$  and surface  $(E_{\rm ps})$  plasmons. According to our calculations, LBAF crystal has  $E_{\rm pv} = 25.2$  and  $E_{\rm ps} = 22.2$  eV.

#### **B. X-Ray Photoelectron Spectroscopy**

Figure 3 shows the overview x-ray photoelectron spectrum of LBAF single crystal registered at room temperature in the range of binding energies from 0 to 1200 eV in increments of 0.5 eV. The energy range from 0 to 500 eV is shown in enlarged scale. The spectrum (Fig. 3) comprises photoelectron emission lines from Ba, Al, F, C, and O. Besides them, there are the Auger electron emission lines from F, O, and C. The Auger lines were labeled as F(KLL), O(KVV), and C(KLL). The main attention was paid to the analysis of chemical forms of crystal elements-barium, aluminum, fluorine, and oxygenas well as the XPS spectrum of the valence band. A formula composition of the compound was assessed using closely spaced lines F 2s, Li 1s, Al 2p, and Ba 4d (Fig. 3). The concentration ratio of the four elements Li, Ba, Al, and F was 15.0: 14.1: 9.2: 61.3. This ratio is very close to the formular composition of LBAF single crystal. The fairly high content of lithium and barium on the surface as compared to aluminum can be explained by the activity of these elements with respect to oxygen and other oxidizing agents present in the air. The overview spectrum contains a weak line from oxygen, indicating the existence of metal oxide forms on the surface of the fluoride crystal. We suggest that a more detailed analysis of the 1s carbon line will show the presence of the  $(CO_3)^{-2}$ -carbonate groups on the surface, which are also preferentially associated with barium and lithium. In general, the above quantitative estimations show that the LBAF crystal surface has a chemical composition similar to the bulk composition and



Fig. 3. Overview of x-ray photoelectron spectrum of LBAF single crystal. The energy range from 0 to 500 eV is shown on an enlarged scale.



Fig. 4. X-ray photoelectron spectra registered for LBAF single crystal in the energy range of quasi-core electronic levels: (a) Li 1s, (b) Al 2p, (c) C 1s, (d) O 1s, (e) F 1s, and (f) Ba 3d. Line intensities are normalized to the maximum for better viewing.

corresponds to the chemical formula of the LBAF compound. Figure 4 shows the XPS spectra of the core levels of all these elements, taking into account the charging of the samples. It should be noted that the barium XPS spectra show only the lines corresponding to one of the barium chemical states. The same conclusion can also be derived for fluorine and oxygen. The XPS spectrum of aluminum Al 2p differs from the previous spectra. In addition to the states of a given element in fluoride, at the binding energy of 75.4 eV there has been an increase from the low binding energies, which we can attribute to Al<sub>2</sub>O<sub>3</sub> oxide. The spectral line of the oxygen  $(O \ 1s)$  at 531.2 eV can correspond either to this oxide or to some other oxide comprising aluminum and barium. The intensity of the Li 1s level is extremely low due to the low photoionization cross section. So it is fairly difficult to say something regarding the chemical form of lithium. The overview spectrum shows the Li 1s line; a fragment of the spectrum with the Li 1s line is shown in Fig. 4. The binding energy of 56.4 eV corresponds to the chemical bonding in lithium fluoride. The XPS spectra of the carbon C 1s include only one band at 284.5 eV. We have attributed this band to unintentional hydrocarbon contaminants adsorbed on the surface.

Figure <u>5</u> shows the valence band spectrum of the LBAF crystal at room temperature. The XPS spectrum contains both the quasi-core levels of fluorine F 2s and barium Ba 5p, and electron density distributions of the electronic states of the valence band. The last of them is located in the 6–12 eV range



Fig. 5. X-ray photoelectron spectrum of the valence band and the upper quasi-core states registered for LBAF single crystal at room temperature. The vertical arrow indicates the estimated  $E_g/2$  value.

below the Fermi level  $E_{\rm F}$  and unambiguously characterizes the crystal as a wide gap insulator. It is advisable to note that the Fermi level is usually located in the middle of the bandgap, so the energy gap of the crystal can be estimated from these spectra as  $E_{\rm g} > 11$  eV. It is important to note that the quasicore levels of barium Ba 5p partially overlap the valence band spectrum. Unfortunately, the energy resolution of the spectrometer used does not allow us to resolve these bands in more detail. We can assume that between them there is an energy gap  $E_{\rm g2}$ . The Ba  $5p_{3/2}$  maximum was determined by us at 16.0 eV below  $E_{\rm F}$ . The pronounced maximum of the valence band states is located at 8.5 eV, and there is another weaker maximum of the valence band states at 10.5 eV.

It is still difficult to clearly determine which electronic states are responsible for these peaks. It is understood that the valence band of LBAF crystal, like of the most of the other complex fluorides (see for example [29]), was formed by 2p states of fluorine. The proximity of the quasi-core levels of barium Ba 5p to the valence band states can affect the internal electronic transitions between them. From the above XPS spectra it follows that the energy difference between the maxima of the electron density of the valence band states and the Ba 5p quasi-core states does not exceed 6–7 eV, and the crystal bandgap  $E_g \approx 12.3$  eV. In this regard, one can expect in these crystals manifestation of valence-core radiative transitions, the so-called cross luminescence. A detailed study of the PL emission spectra in the far-ultraviolet spectral range proves this conclusion.

#### C. Time-Resolved Luminescence Spectroscopy

Figure <u>6</u> shows the PL emission spectra recorded for LBAF single crystal upon photoexcitation at 22 eV. A broad emission band at 4.3 eV dominates the PL spectrum at 10 K. This PL emission band is caused by radiative annihilation of STEs. At room temperature the STE luminescence has negligible intensity. A detailed study of this luminescence was carried out earlier and presented in [14].

Figure <u>7</u> shows both the PLE spectra recorded for LBAF single crystal monitoring emission at two different PL emission bands and the dispersion of the absorption coefficient  $\mu(E)$  calculated on the basis of the extinction coefficient k (Fig. 2) using the formula



Fig. 6. PL emission spectra recorded for LBAF single crystal at T = 10 K (1,3) and 290 K (2) monitoring emission at TI mode (1,2) and at 0–0.5 ns time window upon selective photoexcitation at  $E_{\text{ex}} = 22 \text{ eV}$ . Curves (1,2) are plotted in the same scale, while curve (3) is normalized to the maximum.

$$\mu = \frac{4\pi k}{\lambda} \times 10^7,\tag{5}$$

where  $\mu$  is the absorption coefficient, cm<sup>-1</sup>, and  $\lambda$  is the wavelength, nm.

Let us first discuss the PLE spectrum recorded monitoring emission at 4.3 eV, i.e., the PLE spectrum of excitonic luminescence (Fig. 7). It is well known that many properties of such PLE spectra in the far-ultraviolet region are determined by the surface energy losses. In the framework of a simple diffusion concept [30,31], the profile of the PLE spectrum can be represented as

$$I(E) = \eta(E)(1 - R(E))\frac{1 - \exp(-\mu(E)d)}{1 + \mu(E)L},$$
(6)

where  $\eta(E)$  is the photoluminescence quantum yield in the bulk, *R* is the reflection coefficient,  $\mu$  is the absorption coefficient, *L* is the diffusion length for electronic excitations, and *d* is the crystal thickness. The profile of the PLE band at 11.2 eV (Fig. 7) is caused by two competing processes. The low-energy slope of this band is determined by the factor  $(1 - \exp(-\mu(E)d))$ , and corresponds to an increase of the



Fig. 7. Spectra of LBAF single crystal: PLE spectra recorded at T = 10 K monitoring emission at  $E_{\rm m} = 4.3$  and 6.6 eV; dispersion of the absorption coefficient  $\mu(E)$  calculated by Kramers–Krönig transform.

optical absorption up to several tens of inverse centimeters in the low-energy tail of the fundamental absorption. From the physical point of view, the PLE spectrum of the excitonic luminescence at 4.3 eV has a low energy threshold corresponding to the low-energy tail of the fundamental absorption band of the crystal. Increasing the exciting photons' energy above this threshold increases the intensity of the excitonic luminescence. In this connection, a reasonable estimation for the fundamental absorption edge should coincide with the cutoff energy for the low-energy tail of the PLE band. For LBAF single crystal it is about 11 eV (Fig. 7), which is consistent with the data on a similar LiCaAlF<sub>6</sub> crystal [2].

The maximum in the PLE spectra of LBAF recorded monitoring excitonic luminescence occurs at 11.2 eV (Fig. 7). The high-energy slope of this band and the PLE spectrum at higher energies are determined by the denominator  $(1 + \mu(E)L)$ , which describes the surface energy losses. Because of this factor, the  $\mu(E)$  function can modulate the PLE spectrum. This modulation effect explains, in particular, the presence of local extrema at 11.45 and 11.85 eV and the subsequent gradual decline in PLE spectrum (Fig. 7). From the physical point of view, with further increase of the exciting photon energy, there is an increase in the absorption coefficient and, ultimately, a reduction of the thickness of the crystal area, where the creation of unrelaxed excitons can occur. When the thickness of the area becomes comparable with the mean free path for the excitons, there is an increase of nonradiative energy losses on the crystal surface. This process determines the high-energy slope of the PLE band at 11.2 eV.

The PLE spectrum for the excitonic luminescence shows a minimum at 11.9 eV, and a further increase in the excitation energy to 20 eV leads to interband transitions from different valence band states to the conduction band. In the energy range of 20-22 eV there are electronic transitions from the quasi-core states Ba 5p onto the conduction band bottom. The PLE efficiency of the excitonic luminescence reaches a minimum at 22–25 eV. Further increase of the exciting photon energy in the investigated energy range up to 40 eV leads to a monotonic increase in the intensity of the excitonic luminescence. Since the calculated value of the absorption coefficient  $\mu$  in the energy range above  $2E_{\rm g}$  is changed only slightly (Fig. 7), this increase in luminescence intensity in the energy range from 25 to 40 eV can be reasonably correlated with the process of multiplication of electronic excitations. From the above results, it follows that the total width of the valence band of the LBAF crystal is less than the minimum energy for interband transitions, so the generation of secondary electron-hole pairs is due to the inelastic scattering of photoelectrons.

All the facts discussed above clearly indicate that the mobile electronic excitations and excitons exist in LBAF crystals. Unfortunately, any quantitative simulation of the PLE spectrum through the use of formula (6) is very difficult. Indeed, careful consideration of PLE spectrum (Fig. 7) reveals a hump at 10–11 eV in the energy range of the proposed fundamental absorption edge. In our opinion, the 10–11 eV hump in the PLE spectrum is due to the contribution from the luminescence centers originating from defects that have absorption bands in the vicinity of the low-energy tail of the fundamental absorption band of the crystal. In this connection, this component of the PLE spectrum cannot be described by the formula (6). Therefore, for the quantitative modeling of the PLE spectrum, it is necessary to carry out further detailed studies in the energy region of low-energy tail of the fundamental absorption of LBAF single crystal.

In addition to the dominant band, the PL emission spectrum shows luminescence in a wide energy range of 6-7 eV (Fig. 6). The TI spectra are recorded in the same scale, which shows that the emission intensity at 6.6 eV is the same at both studied temperatures. The spectrum recorded in a fast TW shows, that, unlike the excitonic band at 4.3 eV, the 6.6 eV emission has mostly fast (subnanosecond) decay components and is clearly manifested at T = 10 K as well as at room temperature. Figure 8 demonstrates the PL decay kinetics recorded for LBAF crystal at 10 K monitoring emission at 6.6 eV upon excitation in the energy range of 120 eV. Approximation of the experimental data was made using the technology of integral convolution of a Gaussian excitation pulse (FWHM = 0.15 ns) and two exponential components of the PL decay kinetics with lifetimes of  $\tau_1 < 0.1$  ns and  $\tau_2 = 1.8$  ns. The time resolution of the system does not allow precise measurement of  $\tau_1$ . The partial light yield of the second component  $(\tau_2)$  is less than 5% of the total.

Let us discuss the basic properties of 6.6 eV luminescence. It cannot be attributed to excitonic luminescence, because the emission keeps a stable light output over a wide temperature range from 10 K to temperatures above 290 K. Neither can this emission originate from the transitions associated with defects, because it cannot be excited with photons below 21 eV.

Figure 9 shows time-resolved (TW1 and TW2) and TI PL emission spectra recorded for LBAF single crystal at 10 K upon excitation at 120 eV. From Fig. 9 it is obvious that the PL emission spectrum recorded in a time window TW1, which is dominated by the fast component of  $\tau_1$ , is concentrated in the PL band at 6.6 eV. At the same time, the TW2 and TI spectra demonstrate insignificant PL intensity in the energy range near the 6–7 eV PL emission band.

The PLE spectrum recorded monitoring emission at 6.6 eV is fundamentally different from the spectrum recorded monitoring an excitonic luminescence (Fig. 7). First, we should note a threshold character of the PLE spectrum recorded monitoring emission at 6.6 eV. The 6.6 eV PL emission band



Fig. 8. PL decay kinetics recorded for LBAF single crystal at T = 10 K monitoring emission at 6.6 eV upon excitation at  $E_{ex} = 120$  eV.



Fig. 9. Fragments of the time-resolved (TW1, TW2) and time-integrated (TI) PL emission spectra recorded for LBAF single crystal at T = 10 K upon selective excitation at  $E_{\rm ex} = 120$  eV. All spectra are normalized to unity at the maximum at 4.3 eV.

can be excited by photons only at energies above 21 eV. At lower excitation energies, the 6.6 eV PL emission band cannot be observed, and a slight luminescence intensity, recorded in this energy range, is due to the high-energy tail of the dominant excitonic band located at 4.3 eV. Indeed, the fast component of PL emission at 3.0 eV in LBAF has a lifetime of ca. 3 ns [14], and it cannot be excluded from the PL spectra recorded in the time window TW1.

The obtained data allow us to attribute the 6.6 eV luminescence in LBAF single crystals to the valence-core radiative transitions, i.e., the so-called cross luminescence. The radiative valence-core transitions are efficient in some simple compounds, as well as bi-cation halides [32]. From [32–34] it follows that the radiative valence-core transitions are characterized by subnanosecond PL decay kinetics, and their PL emission spectra are practically unchanged when heated to 600 K. The subnanosecond PL decay component appears in the PLE spectra when the exciting photon energy exceeds the threshold value corresponding to the electronic transitions from the upper core band onto the conduction band of the crystal. In the previous section we have shown that the upper core band of LBAF single crystal is formed by predominantly Ba 5p states. From the PLE spectrum it follows that the energy gap  $\Delta E_{\rm cc}$  between the upper core band and the conduction band of the LBAF crystal is 21.5 eV. Since these transitions occur between different levels of the valence band and the core band top, the low-energy edge of the PL emission band should be associated with valence-core transitions corresponding to a gap  $E_{g2} =$ 6-7 eV between the valence band and the core band top. The width of the PL emission band in the first approximation corresponds to the width of the valence band of the crystal  $\Delta E_0$ .

The most noticeable feature of the electronic structure of LBAF single crystal should be associated with an energy gap  $E_{g2} = 6-7$  eV between the occupied Ba 5p states, which form the top of the core band and the valence band states, formed by 2p states of fluorine. Energy gap  $E_{g2}$  is half the bandgap  $E_g$ . Because of this, the Auger process is energetically impossible. Under these conditions the valence-core transitions with a lifetime less than 1 ns have been detected and interpreted in a binary crystal BaF<sub>2</sub> [35]. It should be noted that the decay

time of the valence-core luminescence in LBAF is significantly smaller than in binary  $BaF_2$ , where it is reported to be ~0.6 ns. Indeed, XPS data do not exclude the possibility of overlap between the upper core band and the valence band of a crystal. If such overlap exists, it allows nonradiative relaxation of upper core holes into the valence band, thus partly quenching the valence-core luminescence.

The data obtained in this study confirm that the subnanosecond PL emission band at 6.6 eV in LBAF single crystal is due to radiative valence-core transitions  $F^- 2p \rightarrow Ba^{2+} 5p$ .

### 4. CONCLUSION

This paper presents the results of a study of undoped LBAF single crystals, carried out using the low-temperature (T = 10 K) far-ultraviolet optical and luminescence spectroscopy with a time resolution. The spectroscopy is conducted upon excitation with SR in the energy range of 3.7-40 eV and supported by the XPS at room temperature. Calculations of the spectra of the optical functions were made on the basis of the low-temperature (T = 10 K) reflection spectra recorded in the energy range of 3.7-40 eV. The bandgap of the investigated compound was found at  $E_g = 12.3$  eV, the energy threshold for creation of the unrelaxed excitons at  $E_{n=1} = 11.6$  eV, and the low-energy fundamental absorption edge at 11.0 eV. The valence band of LBAF single crystal is formed by 2p states of fluorine. The second energy gap  $E_{g2} =$ 6-7 eV separates these states from the upper core states consisting of filled 5p Ba states. The subnanosecond photoluminescence emission band at 6.6 eV in LBAF single crystal is due to radiative valence-core transitions  $2p \operatorname{F} \rightarrow 5p \operatorname{Ba}^{2+}$ .

## ACKNOWLEDGMENTS

This work was partly supported by the Ministry of Education and Science of the Russian Federation (the basic part of the government mandate), Siberian Branch of the Russian Academy of Sciences (Grant No. 28), HASYLAB DESY (Project No. 20110843), the European Social Fund ("Mobilitas", MJD219 and MTT83), the Estonian Research Council (Institutional Research Funding IUT02-26), and the Baltic Science Link project coordinated by the Swedish Research Council, VR. We are grateful to Michael Kuznetsov for assistance in XPS measurements, Aarne Kasikov for help in ellipsometry measurements, and Sebastian Vielhauer for setting up the experiment at I3 beamline.

#### REFERENCES

- M. J. Weber, *Handbook of Lasers*, Laser & Optical Science & Technology (CRC Press, 2000).
- K. Shimamura, H. Sato, A. Bensalah, H. Machida, N. Sakura, and T. Fukuda, "Growth of Ce-doped colquiriite- and scheelitetype single crystals for UV laser applications," Opt. Mater. 19, 109–116 (2002).
- C. D. Marshall, S. A. Payne, J. A. Spaeth, W. F. Krupke, G. J. Quarles, V. Castillo, and B. H. T. Chai, "Ultraviolet laser emission properties of Ce<sup>3+</sup>-doped LiSrAlF<sub>6</sub> and LiCaAlF<sub>6</sub>," J. Opt. Soc. Am. B **11**, 2054–2065 (1994).
- D. J. Spence, H. L. Coutt, and D. W. Coutt, "Low-threshold miniature Ce:LiCAF lasers," Opt. Commun. 262, 238–240 (2006).
- G. Alderighi, G. Toci, M. Vannini, D. Parisi, S. Bigotta, and M. Tonelli, "High efficiency UV solid state based on Ce:LiCaAlF<sub>6</sub> crystals," Appl. Phys. B 83, 51–54 (2006).

- G. A. Aghalte, S. K. Omanwar, and S. V. Moharil, "Luminescence characteristics of LiCaAlF<sub>6</sub>:Eu phosphor," Phys. Status Solidi (a) 204, 1561–1566 (2007).
- A. V. Gektin, N. V. Shiran, S. V. Neicheva, M. J. Weber, S. E. Derenzo, and W. W. Moses, "Energy transfer in LiCaAlF<sub>6</sub>:Ce<sup>3+</sup>," J. Lumin. **102–103**, 460–463 (2003).
- R. Y. Abdulsabirov, I. I. Antonova, S. L. Korableva, N. M. Nizamutdinov, V. G. Stepanov, and N. M. Khasanova, "EPR of trivalent iron ions in a crystal LiSrAlF<sub>6</sub>," Phys. Solid State **38**, 893–894 (1996).
- N. Shiran, A. Gektin, S. Neicheva, M. Weber, S. Derenzo, M. Kirm, M. True, I. Shpinkov, D. Spassky, K. Shimamura, and N. Ichinose, "Energy transfer in pure and Ce-doped LiCaAlF<sub>6</sub> and LiSrAlF<sub>6</sub> crystals," Nucl. Instrum. Methods Phys. Res. A 537, 266–270 (2005).
- M. Kirm, M. True, S. Vielhauer, G. Zimmerer, N. V. Shiran, I. Shpinkov, D. Spassky, K. Shimamura, and N. Ichinose, "VUV spectroscopy of pure LiCaAlF<sub>6</sub> crystals," Nucl. Instrum. Methods Phys. Res. A 537, 291–294 (2005).
- V. N. Makhov, M. Kirm, G. Stryganyuk, S. Vielhauer, G. Zimmerer, B. Z. Malkin, O. V. Solovyev, and S. L. Korableva, "5d–4f luminescence of Ce<sup>3+</sup>, Gd<sup>3+</sup> and Lu<sup>3+</sup> in LiCaAlF<sup>6</sup>," J. Lumin. **132**, 418–424 (2012).
- B. W. Woods, S. A. Payne, J. E. Marion, R. S. Hughes, and L. E. Davis, "Thermomechanical and thermooptical properties of the LiCaAlF<sub>6</sub>:Ce<sup>3+</sup> laser material," J. Opt. Soc. Am. B 8, 970–977 (1991).
- M. Bass, G. Li, and E. van Stryland, eds., Optical Properties of Materials, Nonlinear Optics, Quantum Optics, 3rd ed., Vol. 4 of Handbook of Optics (McGraw-Hill Professional, 2010).
- S. I. Omelkov, M. Kirm, E. Feldbach, V. A. Pustovarov, S. O. Cholakh, and L. I. Isaenko, "Luminescence properties of undoped LiBaAlF<sub>6</sub> single crystals," J. Phys. Condens. Matter 22, 295504 (2010).
- S. I. Omelkov, V. Kiisk, I. Sildos, M. Kirm, V. Nagirnyi, V. A. Pustovarov, L. I. Isaenko, and S. I. Lobanov, "The luminescence microspectroscopy of Pr<sup>3+</sup>-doped LiBaAlF<sub>6</sub> and Ba<sub>3</sub>Al<sub>2</sub>F<sub>12</sub> crystals," Radiat. Meas. **56**, 49–53 (2013).
- A. A. Merkulov, L. I. Isaenko, S. I. Lobanov, D. Y. Naumov, and N. V. Kuratieva, "LiBaAlF<sub>6</sub> and the crystal chemistry of Li A<sup>II</sup>B<sup>II</sup>F<sub>6</sub> phases," Acta Crystallogr. C64, i66–i68 (2008).
- G. Zimmerer, "SUPERLUMI: a unique setup for luminescence spectroscopy with synchrotron radiation," Radiat. Meas. 42, 859–864 (2007).
- 18. M. Kirm, A. Lushchik, C. Lushchik, S. Vielhauer, and G. Zimmerer, "Luminescence of pure and doped  $Al_2O_3$  and MgO single crystals under inner-shell excitation," J. Lumin. **102–103**, 307–312 (2003).
- T. Balasubramanian, B. Jensen, S. Urpelainen, B. Sommarin, U. Johansson, M. Huttula, R. Sankar, E. Nõmmiste, S. Aksela, H. Aksela, and R. Nyholm, "The normal incidence monochromator beamline I3 on MAX III," AIP Conf. Proc. **1234**, 661–664 (2010).
- J. F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bomben, Handbook of X-ray Photoelectron Spectroscopy. A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data. (Physical Electronics, 1995).
- M. Cardona and L. Ley, eds., *Photoemission in Solids. I General* Principles (Springer-Verlag, 1978).
- I. N. Ogorodnikov, S. I. Omelkov, A. Kasikov, M. Kirm, and V. A. Pustovarov, "Optical and luminescence characterization of LiBaAlF<sub>6</sub> single crystals," Opt. Mater. (submitted).
- 23. M. Weissbluth, Atoms and Molecules (Academic, 1978).
- 24. P. W. Milonni and J. H. Eberly, Laser Physics (Wiley, 2010).
- 25. M. Born and E. Wolf, Principles of Optics (Pergamon, 1980).
- V. Lucarini, J. J. Saarinen, K. E. Peiponen, and E. M. Vartiainen, Kramers-Krönig Relations in Optical Materials Research (Springer-Verlag, 2005).
- I. H. Malitson, "A redetermination of some optical properties of calcium fluoride," Appl. Opt. 2, 1103–1107 (1963).
- D. Pines, *Elementary Excitation in Solids* (W. A. Benjamin, 1963).
- H. Qiao, T. Liu, Q. Zhang, F. Cheng, and X. Zhou, "First-principles study of LiBaF<sub>3</sub> crystals containing interstitial fluoride," Curr. Appl. Phys. **10**, 1286–1289 (2010).

- A. N. Vasil'ev and V. V. Mikhailin, *Introduction in Solid State Spectroscopy* (Moscow University, 1987).
- A. Belsky and J. C. Krupa, "Luminescence excitation mechanisms of rare earth doped phosphors in the VUV range," Displays 19, 185–196 (1999).
- P. A. Rodnyi, M. A. Terekhin, and S. V. Petrov, "Radiative core-valence transitions in a RbCaF<sub>3</sub> crystal," Sov. Phys. Solid State **32**, 1844–1845 (1990).
- A. S. Voloshinovskii, V. B. Mikhailik, P. A. Rodnyi, and S. N. Pydzyrailo, "Core-valence luminescence in crystals based on CsBr," Sov. Phys. Solid State 34, 366–370 (1992).
   V. N. Makhov, "VUV spectroscopy of wide band-gap crystals,"
- V. N. Makhov, "VUV spectroscopy of wide band-gap crystals," in *Brilliant Light in Life and Material Sciences*, V. Tsakanov and H. Wiedemann, eds. (Springer, 2007), pp. 349–359.
- P. A. Rodnyi, "Core-valence luminescence in scintillators," Radiat. Meas. 38, 343–352 (2004).