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Effect of an electron beam irradiation on optical and luminescence properties of $LiBaAlF_6$ single crystals

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ABSTRACT

Paper reports the effect of a 10 keV, 110 keV and 10 MeV electron beam irradiation on optical and luminescence properties of $LiBaAlF_6$ (LBAF) single crystals at 10, 90, and 293 K. Five absorption bands at 2.0, 3.2, 4.3, 4.9 and 5.5 eV were revealed in irradiated crystals in the energy range of 1.2–9.5 eV. Several PL emission bands (1.7–1.8, 2.2 and 2.5–3.5 eV) related to defects were found in the luminescence spectra at room temperature, while only one luminescence band at $E = 2.2$ eV appears at $T = 90$ K in LBAF crystals after a 10 MeV electron bombardment. The PL excitation spectra and time-response for these emission bands were studied at 10, 90, and 293 K. Thermoluminescence (TL) of irradiated crystals was studied in the temperature range of 90–740 K. New TL glow peaks at 166, 530 and 670 K were revealed and their parameters were determined. Temperature dependence of relative photoluminescence yield recorded monitoring emission at the 1.87 and 2.23 eV in the temperature range from 130 to 450 K, were fitted using five quenching processes related to TL glow peaks revealed in our research. Significant similarity in the manifestation of radiation-induced defects for LBAF and previously studied $LiBaF_3$ single crystals is noted. The effect of an electron beam irradiation on optical and luminescence properties of LBAF single crystals and possible origin of the radiation defects were discussed.

1. Introduction

Optical materials on the basis of complex fluorides and double fluorine salts have many useful applications [1]. Among them, Li–Ba compounds are of particular interest for radiation detection because the ^{6}Li-isotope has advantages in interaction with thermal neutrons. There are two more crucial reasons. First, the Ba^{2+} ion is responsible for core-valence transitions F^- $2p \rightarrow Ba^{2+}$ $5p$ (so called 'cross-luminescence'), which features subnanosecond decay times. Second, a fluorine compound as a whole exhibits self-trapped exciton luminescence, which is not manifested under thermal-neutron irradiation. As both emissions give a response under gamma-ray excitation, this offer a unique opportunity for thermal neutron – gamma discrimination [2]. Some important impurities were tested as luminescence centers for $LiBaF_3$, for example Eu^{2+} [3] and Pb^+ [4,5].

Among the complex fluorides triple fluorine salts with common formula Li *Me* AlF_6 (*Me* = Ca, Sr, Ba) are distinguished. These optical crystals are used in laser technology for the far-ultraviolet spectral range. $LiCaAlF_6$ (LCAF) and $LiSrAlF_6$ (LSAF) crystals have been studied in sufficient detail, but $LiBaAlF_6$ (LBAF) crystals have attracted less attention. Luminescence and optical properties of undoped LBAF single crystals are reported in Refs. [6,7]. The band gap E_g was estimated as 12.1 eV in Ref. [6] and updated to more precise value of 12.3 eV in Ref. [8]. Both the cross-luminescence and intra-band luminescence of LBAF were reported in Refs. [6,7]. Because of partial overlapping between first core level and valence band of LBAF, their intensities and decay profiles are comparable. In a certain sense, the cross-luminescence in LBAF could be considered as a hole intra-band luminescence, as it is caused by radiative transitions of holes inside the 'complex' valence band. The luminescence spectroscopy of Pr^{3+}-doped LBAF crystals was previously reported in Ref. [9].

In this paper, we focus on the experimental study of the optical, luminescence and thermoluminescence properties of radiation defects in LBAF single crystals after electron beam irradiation at 10, 110 keV and 10 MeV. Despite the fact that the experimental technique used does not allow us to identify the origin of the created radiation defects, the spectroscopic 'portraits' of the defects

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identified in this paper provide us with relevant information for future practical applications of this compound. We would like to emphasize also that our experimental research work does not intend to perform any quantum-chemical simulation of electronic structure of these defects.

2. Experimental details

All the examined LBAF crystals of high optical quality were grown from the melt of the corresponding fluorides (99.99%) utilizing the Bridgman technique at Institute of Geology and Mineralogy, Siberian Branch of Russian Academy of Sciences (Novosibirsk, Russia). The crystal growth technique was described in sufficient detail in Refs. [8,10]. The LBAF samples studied were in the form of optically transparent plane-parallel plates with the large surface polished to laser-grade quality, Fig. 1. Thickness of each sample is 1.8 mm. The orientation of the crystallographic axes of LBAF samples was arbitrary with respect to the polarization vector of the synchrotron radiation.

Photoluminescence (PL) excitation spectra in the ultraviolet (UV) and vacuum ultraviolet (VUV) energy regions (3.7–20 eV) were recorded at the SUPERLUMI experimental station of HASYLAB [11] upon selective photoexcitation with synchrotron radiation. 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 PL excitation (PLE) spectra were corrected to an equal number of incident photons using sodium salicylate — a luminophore with the energy-independent quantum yield over the studied spectral range. The 0.3 m ARC Spectra Pro-300i monochromator equipped with an R6358P (Hamamatsu) photomultiplier were used as a registration system. The measurements were performed at temperature of 10 K using a continuous-flow liquid helium cryostat mounted in the ultra-high vacuum chamber with a pressure of residual gases lower than 1×10^{-8} Pa.

Optical absorption spectra at 293 K were recorded at the laboratory of Solid State Physics of Ural Federal University by the means of a Heλios Alpha 9423UVA1002E spectrophotometer ($\lambda = 190–1000$ nm) equipped with the Vision 32 software. The deep-UV range (250–150 nm) was covered by the special setup in the Institute of Physics, University of Tartu, where a hollow cathode H_2 lamp and a VMR-2 spectrophotometer are used. The optical absorption coefficient k was calculated using the formula $k = -\ln(T)/l$, where T is the experimental optical transmittance and l is the thickness of the sample.

The PL characteristics under excitation in the UV energy region from 3.0 to 6.0 eV were recorded in the temperature range from 90 to 293 K at the laboratory of Solid State Physics of Ural Federal University. The 400 W deuterium discharge lamp with a continuous UV emission spectrum and the primary DMR-4 monochromator were used as an excitation source. The secondary DMR-4 monochromator and the R-6358-10 (Hamamatsu) photomultiplier tube were used as registration system. The PL excitation spectra were normalized to an equal number of photons incident on the sample using yellow lumogen with the energy-independent quantum yield over the studied spectral range.

Thermoluminescence (TL) glow curves were recorded using two different experimental setups.

The low-temperature (80–500 K) TL glow curves were recorded using a digital temperature controller providing a constant heating rate of 0.3 K/s. The samples were pre-irradiated by the radiation source based on BSW-2-type X-ray tube (Cu-anode, $U_a = 40$ kV, $I_a = 15$ mA). The TL glow curves were recorded in the spectral-integrated regime (2–6.2 eV) by FEU-39 photomultiplier tube. The sample was mounted in a vacuum cryostat with quartz windows and quick thermal response.

The high-temperature (293–750 K) TL glow curves were recorded in N_2 atmosphere at linear heating rate of 2 K/s using a System 310 TLD Reader after 10 keV electron beam exposure at 10 and 293 K. This procedure has also annealed the sample.

The irradiation with keV-range electrons was performed in the Institute of Physics, University of Tartu. The 10 keV electron beam excitation source has a continuous beam current which can be varied in the range from 50 nA to 1 μA. A typical beam spot area was about 0.5 mm^2. The 110 keV excitation source is the pulsed electron gun based on RADAN-303A type high voltage generator (designed at the Institute of Electrophysics of the Ural Branch of Russian Academy of Sciences, Yekaterinburg). The peak current density on the sample holder in our experiment was approximately ~60 A/cm^2 and the pulse FWHM was 800 ps. The high voltage generator provides pulse rate up to 5 pps. We used the beam with maximum electron energy of 110 keV to measure the pulse cathodoluminescence (PCL) data published in Ref. [7], which consequently irradiated the sample.

To study radiation defects created by relatively high-energy electrons we used microtron accelerator (M-20 type) at Ural Federal University. A 10 MeV electron beam was applied to the sample at room temperature, providing fluence of 5×10^{15} cm^{-2}.

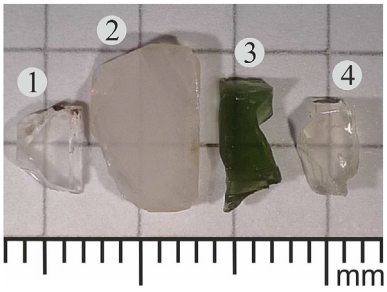

Fig. 1. Samples of LBAF crystals used in research work: pristine (1), irradiated by 110 keV electrons and then annealed in Ar at 600 °C for 2 h (2), irradiated by 10 MeV electrons (3), irradiated by 10 MeV electrons, then slowly heated to 700 K and immediately slowly cooled (10 K/min) (4). Thickness of each sample is 1.8 mm.

3. Experimental results

3.1. Optical absorption spectroscopy of defects

Fig. 2 shows the optical absorption spectra in the visible–UV energy range recorded for LBAF crystal at room temperature. Prior to electron bombardment, pristine crystal (Fig. 2, *a*, see also sample 1) was optically transparent in the investigated energy region of 1.5–6.0 eV, featuring no selective absorption bands. The effect of 10 keV electron irradiation on the optical absorption spectra of LBAF was already reported in Ref. [6] and proved to be insignificant. On the contrary, 110 keV beam (Fig. 2, *a*, curve *1*) led to a threefold increase in the absorption coefficient and induced light green coloration. We can clearly allocate at least five absorption bands at 2.0 (*A*), 3.2 (*B*), 4.3 (*C*), 4.9 (*D*) and 5.5 eV (*E*), which seemingly do not exhaust all the absorption bands in LBAF crystal. A subsequent annealing at 600 °C in argon atmosphere for two hours removed all coloration and selective absorption bands but rendered the crystal milky and poorly transparent (see sample 2). A 10 MeV electron bombardment led to even more significant increase in the absorption coefficient (Fig. 2, *b*, see also sample 3). In the energy region of 1.5–4.0 eV, we can observe the same absorption bands *A* and *B*, while above 4 eV the induced optical density is above the detection limit of our spectrometer (curve *3*). After slow heating to 700 K and immediate slow cooling in an argon atmosphere,