



Cathodoluminescence of monoclinic Li_3AlF_6 crystals in the spectral region of 150–600 nm



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HIGHLIGHTS

- The pulsed and steady-state cathodoluminescence of monoclinic Li_3AlF_6 crystals was studied in the 150–600 nm spectral range.
- Thermal quenching of dominant self-trapped exciton emission band at 350 nm obeys the Mott law ($E = 0.072$ eV and $\omega = 750$).
- The VUV cathodoluminescence bands at 172 and 208–212 nm have more complex temperature dependence.

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ABSTRACT

Cathodoluminescence (CL) of monoclinic LiAF crystals was studied in the spectral (150–600 nm) and temperature (78–302 K) ranges using both the steady-state CL and pulse CL (PCL) techniques. Three CL emission bands were found in the spectral range of 150–600 nm. The dominant complex CL band at 350 nm obeys the Mott law ($E = 0.072$ eV and $\omega = 750$). On heating, the 172 and 208–212 nm CL bands vary in intensity non-monotonically. At $T = 78$ K, the CL decay kinetics comprises three components: a dominant fast exponential component with a lifetime of 750 ns, and two low-intensity components with the lifetimes of 20 and 240 μs . The last two components were fitted by a second order hyperbolic law. Time-resolved PCL spectra were recorded using time-windows corresponding to the PCL decay components. Paper discusses the reasonable interpretation of the CL emission bands.

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1. Introduction

Lithium Hexafluoroaluminate Li_3AlF_6 (LiAF) crystals are practically unknown as optical material. We are aware of only one work by photoluminescence (PL) spectroscopy of LiAF crystals. Pustovarov et al. (2015) have identified PL emission and PL excitation (PLE) bands of LiAF and gave estimates of the electronic structure parameters at $T = 7.2$ K: bandgap $E_g \approx 12.5$ eV, energy threshold for creation of unrelaxed excitons 11.8 eV $< E_n < 12.5$ eV. From (Pustovarov et al., 2015) it follows that LiAF shows broad emission band at 350 nm, comprising an intensive fast decay component with a lifetime of several tens of nanoseconds, and the PL emission bands in the VUV spectral range. Combined with a large bandgap E_g , it creates favorable conditions for the application

of LiAF crystals as an optical material for radiation detectors and VUV-emitters. However, studies of LiAF luminescence upon excitation by ionizing radiation has not yet been carried out.

β -LiAF modification possesses monoclinic $C2/c$ symmetry with $a = 14.201(1)$, $b = 8.387(1)$, $c = 9.860(1)$ Å, and $\beta = 94.07(1)^\circ$ Tyagi and Köhler (1997). Only a few research works have been devoted to the study of β -LiAF: among them, thermodynamic analysis of lithium cryolite in the $\text{LiAF}-\text{AF}_2$ ($A = \text{Ca}, \text{Ba}, \text{Sr}$) systems (Koštenská et al., 1973); study of the heat capacity of β -LiAF in the temperature range from 15 to 380 K (Furukawa et al., 1970); electrical conductivity of low melting baths for aluminum electrolysis: the system Na_3AlF_6 -LiAF- AlF_3 (Fellner et al., 1993); Li^+ -ion conductivity of LiAF (Miyazaki and Maekawa, 2012). Pustovarov et al. (2015) recently held a Rietveld refinement of the LiAF crystal structure.

The aim of this research work is to study luminescence properties of undoped LiAF crystals. The research work was carried out in the spectral (150–600 nm) and temperature (78–302 K) ranges using the methods of both the steady-state cathodoluminescence

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(CL) and pulse cathodoluminescence (PCL) techniques.

2. Experimental details

Monoclinic β - Li_3AlF_6 crystals suitable for optical studies were grown using Bridgman technique at Institute of Geology and Mineralogy of Siberian Branch of Russian Academy of Sciences (Novosibirsk, Russia). Pustovarov et al. (2015) have previously described in considerable detail the crystal growing process and crystallographic structure of LiAF.

All cathodoluminescence studies were performed using the laboratory setups in the University of Tartu (Estonia).

The steady-state cathodoluminescence spectra and their temperature dependences in the temperature range of 78–302 K were performed using continuous electron gun (Kimball Physics EGG-3101, $E_e = 10$ keV, $I_e = 1.5$ μA) as an excitation source. As the registration system an ARC Spectra Pro 2300i monochromator was used for the UV–visible range, and a home-designed 0.5 m double grating vacuum monochromator for the VUV range. For the study of the decay kinetics in microsecond range the gun is equipped with beam blanker. In the current experiment the pulse width was 100 ns. The Becker&Hickl MSA-300 Multiscaler card was used for decay curve recording. The 20 nm platinum coating was applied to the sample preventing the accumulation of electric charge during the measurements.

The study of the time-resolved pulse cathodoluminescence (PCL) spectra were done using the electron gun based on RADAN-303A high voltage (HV) generator (designed at the Institute of Electrophysics of the Ural Branch of Russian Academy of Sciences, Yekaterinburg). The gun is equipped with SLICER pulse compressor for achieving excitation pulse width of 300 ps and peak electron current density at the sample in the order of 40 A/cm². The time-resolved spectra were recorded using Andor Shamrock 303i spectrograph with an iStar gated iCCD camera, and decay kinetics in the nanosecond time range by Hamamatsu R3809U-50 microchannel plate photomultiplier with LeCroy WavePro760Zi-A oscilloscope. The detailed description of the setup is given in (Pustovarov et al., 2015).

3. Results and discussion

Steady-state CL spectra. Fig. 1 shows steady-state CL spectra of

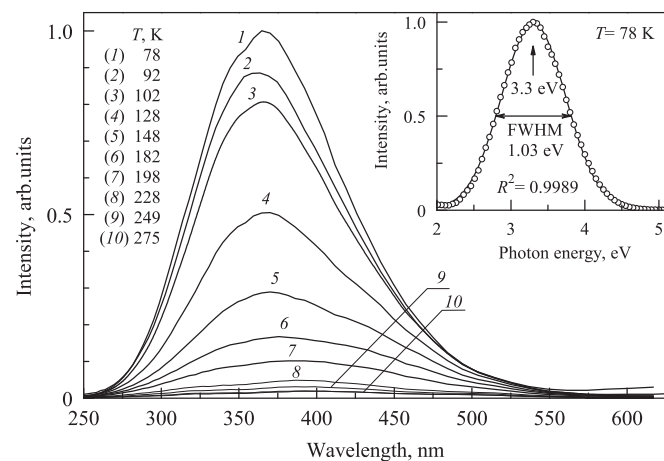


Fig. 1. Steady-state CL spectra of LiAF crystals recorded at different temperatures T between 78 and 275 K. The inset shows Gauss-decomposition of a dominant CL-emission band recorded at 78 K, and presented in electron-volts scale: open circles are the experimental data and the solid line represents Gauss-approximation.

LiAF crystal recorded at different temperatures between 78 and 275 K. At $T = 78$ K, CL-spectrum comprises a wide emission band extending from 250 to 600 nm and peaked at 365 nm. Its FWHM is about 111.5 nm (1.03 eV). Upon heating, CL-intensity decreases fairly uniformly over the spectrum. However, a large spectral width can testify to its complex origin. To verify this, we performed a Gauss-decomposition of the dominant CL-emission band, Fig. 1. From this result it follows that the dominant CL-emission band can be considered as a single band. Even if there are more spectral bands, the contribution of the dominant band is absolutely superior at $T = 78$ –90 K.

Fig. 2 shows steady-state CL spectra in the VUV spectral range recorded for LiAF crystal at different temperatures between 78 and 302 K.

When heated from $T = 78$ K, two CL-emission bands behave differently. The 172 nm-emission band varies in intensity, but the spectral location of its maximum is apparently unchanged. The temperature behavior of UV-band is somewhat different. When heated from 78 to 150 K intensity of the 212 nm-band gradually decreases, and at 182 K, there is a two-humped profile (208 and 212 nm). When heated from 180 to 230 K, the intensity of the 208 nm band increases while further heating to room temperature decreases its intensity. Note that the total light yield in the range 160–240 nm stands fairly independent on the temperature in the studied range.

These two CL emission bands are well comparable with two intense PL emission bands at 170 and 208 nm, revealed in (Pustovarov et al., 2015) and interpreted as a defect emission. Pustovarov et al. (2015) attributed these two PL emission bands to interconfigurational 5d–4f radiative transitions in unintentionally introduced Er^{3+} or Tm^{3+} impurity ions in LiAF. It is important that CL-emissions at 172 and 212 nm, recorded for LiAF crystals at 302 K, have substantially identical characteristics. This opens up the possibility of using VUV CL emission of LiAF crystals in scintillators for radiation detectors, which employ photosensitive gases or photocathodes sensitive mostly to VUV photons.

Temperature dependence of CL intensity. Fig. 3 shows temperature dependence of steady-state CL-intensity recorded for LiAF crystal in the temperature range from 78 to 302 K monitoring emission at 365 nm. It should be noted that the measurement of the temperature dependence $I(T)$ were performed using a slow heating rate in the temperature range from 78 to 302 K with temperature stabilization at intermediate points. Unfortunately, due to technical

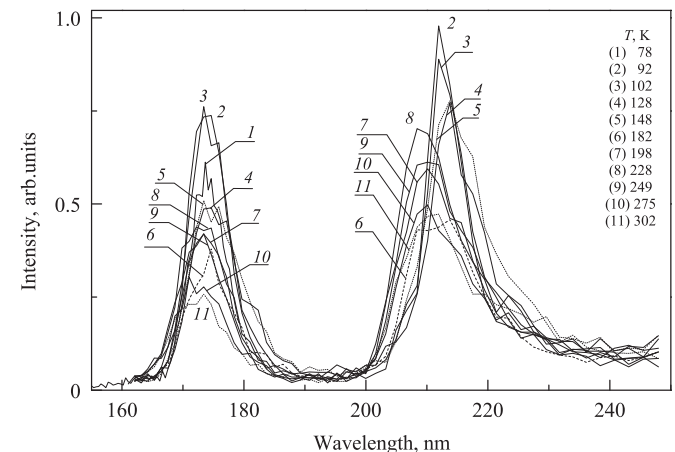


Fig. 2. Steady-state CL spectra in the VUV spectral range recorded for LiAF crystal at different temperatures T between 78 and 302 K. At $T = 78$ K there are two relatively narrow (FWHM of about 20 nm) CL-bands at 172 and 212 nm.

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