Influence of isovalent doping on the cathodoluminescence of $Li_2B_4O_7$:A (A = K, Cu, Ag) single crystals

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The study results of cathodoluminescence (CL) of isovalently doped $Li_2B_4O_7$:A single crystals (A = K, Cu, Ag) are reported. The main CL emission mechanism of undoped $Li_2B_4O_7$ is the annihilation of self-trapped excitons (STE). The Cu and Ag impurities have their intrinsic emission bands in CL spectra which are overlaid onto $Li_2B_4O_7$ STE band about 3.65 eV. The models of CL centers and mechanisms in $Li_2B_4O_7$:A single crystals are proposed.

Представлены результаты исследований катодолюминесценции (КЛ) изовалентно замещенных монокристаллов $Li_2B_4O_7$:A (A = K, Cu, Ag). Основным механизмом КЛ свечения нелегированного $Li_2B_4O_7$ является аннигиляция автолокализированных экситонов (АЛЭ). Примеси Cu и Ag имеют свои полосы излучения в спектрах КЛ, которые накладываются на полосу АЛЭ нелегированного $Li_2B_4O_7$ около 3,65 эВ. Предложены модели центров и механизмы КЛ свечения в монокристаллах $Li_2B_4O_7$:A.

Anhydrous borates, lithium tetraborate in particular, are considered to be a materials of good prospects for radiation detecting [1, 2] and dosimetry based on thermo-stimulated luminescence (TL) [3, 4]. The additional advantage of lithium borates is the sensitivity thereof to thermal neutrons that can be regulated changing the isotopic composition in Li and B [5]. However, it is necessary to make the most extensive studies concerning the luminescence characteristics of anhydrous borates single crystals to use those successfully and widely in the field of nuclear technique. A special attention should be paid to the influence of doping on the luminescence properties.

Nowadays, the most attention is paid to TL investigations of $Li_2B_4O_7$ single crystals doped with various chemical elements, such as Ce, Eu, and Tm [6], Cu [7, 8], Cu, K, Ag and Ga [9], Cu, Mn and Mg [10], Ce, In, Ni, Cu and Ti [11], etc. As to TL dosimetry, the best results have been got when doping $Li_2B_4O_7$ single crystals with Cu and Ag while promising preliminary results have been got when doping with Mn. However, there is almost no information about the doping effect on scintillation parameters of borates. The work is done to study this problem and is dedicated to spectroscopic investigations of cathodoluminescence (CL) of $Li_2B_4O_7$ single crystals doped with K, Cu and Ag elements (1st group of Periodic System) substituting Li. That is an actual question, since the CL excitation due mainly to

the impact mechanism, which is inherent in scintillators.

The $Li_2B_4O_7$ single crystals were grown from stoichiometric melt using the Czochralski method from Pt crucibles in air. The doping was done by adding K_2CO_3, CuO or $AgNO_3$ to the melt during solid-phase synthesis of $Li_2B_4O_7$ using Li_2CO_3 and H_3BO_3. Samples of $5\times5\times1$ mm^3 were made from the grown crystals oriented perpendicular to the Z crystallographic axis. Since $Li_2B_4O_7$ single crystals have no surfaces of easy cleaving, the sample surface cut out using a diamond saw was worked up thoroughly to minimize the thickness of broken surface layer. To that end, a set of abrasive powders with decreasing grain size was used during the machining operations (grinding and polishing). In the last process stage, the mechanochemical polishing using elplaz with grain size not more than 0.05 μm was used. This allows us to assert that the the near-surface broken layer depth did not exceed 50 nm. This is important to emphasize, since the surface states may influence heavily the observed CL spectra under a little accelerating voltage. To avoid it, the incident electron beam should have enough energy to penetrate through the "dead" layer created by surface states and to generate CL luminescence from the crystal volume. In such a case, the CL intensity can be described as $I_{CL} = f(I_e, d, T)(U - U_0)^m$, where U is the accelerating voltage; U_0, the "dead voltage"; T, temperature; d, the electron beam diameter; $1 \le m \le 2$.

The sample CL was excited at room temperature or at liquid nitrogen temperature in a pulsed mode (the pulse duration 3 μs with the repetition rate 20 Hz). The electron beam energy was 9.5 keV, the beam current 200 μA, the electron beam diameter at the sample 1 mm, the angle of incidence 30°. The electron penetration depth was calculated using an empirical formula [12]

$$R = \frac{2.76 \cdot 10^{-2} A U^{5/3}}{\rho Z^{8/9}} \cos 30 \ (\mu m), \quad (1)$$

where Z is the effective atomic number; A, the effective atomic mass corresponding to the effective Z; U, accelerating voltage; ρ, density. In our scase, the calculation for $Li_2B_4O_7$ crystals (with $Z = 7.3$, $A = 12$, $\rho = 2.44$ g/cm^3) has shown that the penetration depth R of exciting electrons under the accelerating voltage 9.5 kV and at the angle of incidence 30° did not exceed 0.85 μm, and the number
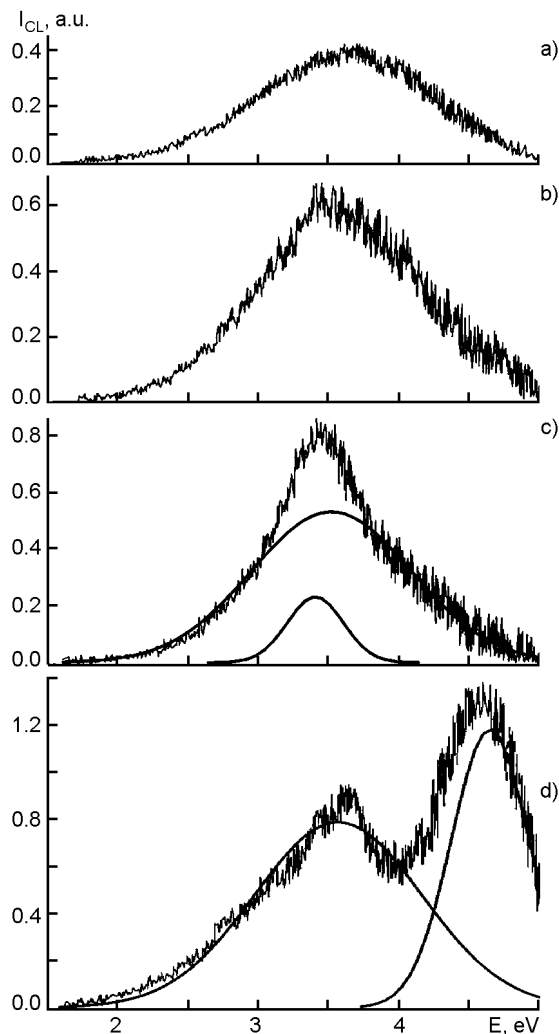

Fig. 1. CL spectra at 295 K of $Li_2B_4O_7$ single crystals undoped (a) and doped with K (b), Cu (c) and Ag (d).

of electron-hole pairs (*e-h* pairs) for one incident electron is at least 100. We can consider that the fixed CL emission referred to the crystal volume, while the surface contribution can be neglected. The luminescence light was passed through the double prism monochromator (MDR-4), registered photomultiplier (PMT-106) within the spectral range 1.5–5.0 eV, and corresponding spectra were recorded using a computer system.

The recorded CL spectra for undoped and doped $Li_2B_4O_7$:A (A = K, Cu, Ag) single crystals at 295 K are shown in Fig. 1, those at 80 K, in Fig. 2, and for those for a $LiKB_4O_7$ single crystal, in Fig. 3. To consider the CL spectra, it is reasonable to compare them with luminescence spectra of similar samples due to other exciting mechanisms, espe-
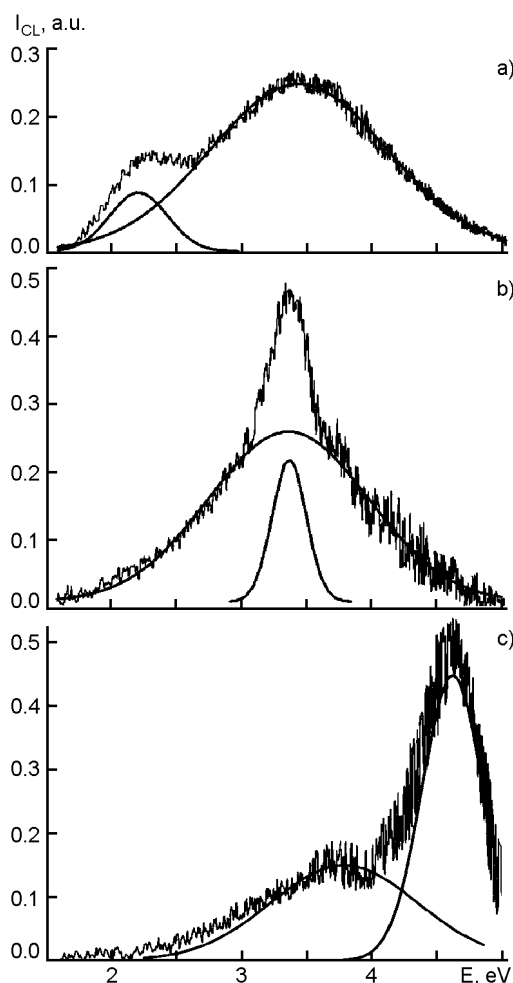
Fig. 2. CL spectra at 80 K of $Li_2B_4O_7$ single crystals undoped (a) and doped with Cu (b) and Ag (c).

cially TL, X-ray luminescence (XL), photoluminescence (PL) and radioluminescence (RL).

As is seen in Fig. 1a, the CL spectrum of undoped $Li_2B_4O_7$ single crystal at 295 K looks like gaussian with the main maximum at 3.65 eV (340 nm), but the curve is a bit asymmetric at the low-energy side. This asymmetry may be caused by the emission band at 2.2 eV (564 nm) clearly seen at 80 K (Fig. 2a). The maximum position of the main band shifts to 3.43 eV (362 nm) as the temperature decreases down to 80 K. As these CL spectra are compared with luminescence spectra under other excitations, it is seen that those are almost identical to RL [1], XL spectra at 293 K [13], as well as to TL spectrum with the main temperature band approximately 430 K [9].

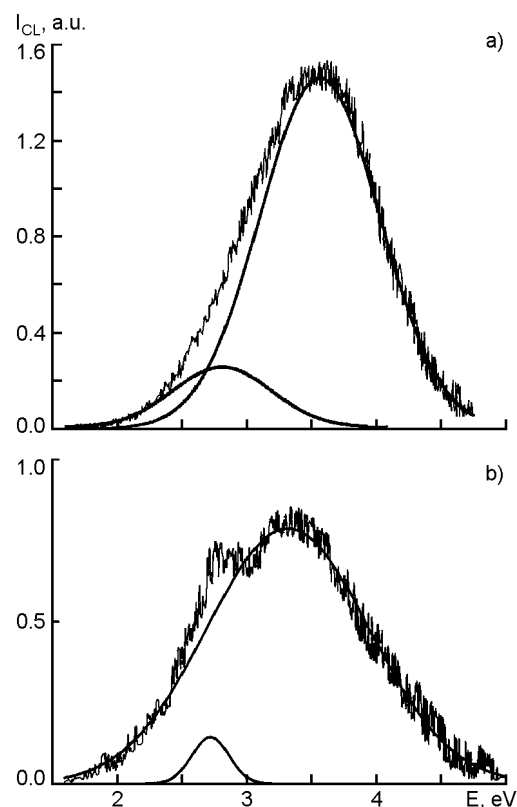The CL spectrum of $Li_2B_4O_7$:K crystal (1.0 at.% K) at 295 K differs from the CL spectrum of undoped $Li_2B_4O_7$ by a slight

Fig. 3. CL spectra of $LiKB_4O_7$ single crystals at 295 K (a) and 80 K (b).

rise of luminescence intensity (Fig. 1b). When the concentration K reaches 50 at.%, we deal with a new chemical compound $LiKB_4O_7$ [14] and the CL spectrum of its single crystal at 295 K is very different from that shown in the Fig. 1b, first of all by a significant increase of luminescence intensity. In the spectrum of $LiKB_4O_7$ crystal, another luminescence band appears at 2.84 eV (437 nm), similar to undoped $Li_2B_4O_7$ crystal at 80 K, and also the main band maximum shifts towards low-energy side to 3.30 eV (376 nm). If these CL spectra are compared with luminescence spectra under other excitations, those are seen to be almost identical to TL spectrum with the main temperature band approximately 112 K as well as to XL spectra (3.32 eV) at 293 K [15]. The luminescence band 2.84 eV appears also in XL spectra below 190 K.

The CL spectrum of $Li_2B_4O_7$:Cu single crystal (0.015 at.% Cu) differs slightly from luminescence spectra under other excitation mechanisms. The emission maximum position difference is insignificant, for example, CL maximum at 295 K (Fig. 1c) is seen at 3.50 eV (355 nm), while at all the rest excitations it is at 3.35 eV (370 nm)

[2, 9, 14, 16, 17]; but the forms of the curves differ considerably. In our case, the superposition of some luminescence bands in CL spectra can be clearly seen. The CL spectra were analyzed using the "LabPlot 1.6.0" program. Two Gaussian like bands can be obtained when decomposing this spectrum. The maxima positions are 3.40 eV (365 nm) and 3.55 eV (350 nm) (Fig. 1c). The intensity redistribution in the luminescence bands is noticeable at 80 K (Fig. 2b) and the maxima positions substantially coincide at 3.36 eV (369 nm).

The CL spectrum of $Li_2B_4O_7$:Ag crystal (0.02 at. % Ag) is different in that two luminescence bands with maxima at 3.56 eV (370 nm) and 4.62 eV (269 nm) appear even at 295 K (Fig. 1d). At 80 K (Fig. 2c), the maximum position at 4.62 eV remains practically the same but the total CL light yield is reduced significantly. This makes it impossible to determine the position of the first maximum although its presence in the spectrum is indubitable (Fig. 2c). A similar high-energy luminescence band with maximum at 4.56 eV (272 nm) was observed in $Li_2B_4O_7$:Ag single crystals [14] in the PL spectra under excitation from the 205 nm band. But in TL spectra $Li_2B_4O_7$:Ag, only one luminescence band peaked at 3.56 eV (370 nm) was always observed [15].

The comparative analysis of all the CL spectra proves the presence of the luminescence band that is connected with self-trapped excitons (STE) near crystal defects [13, 18, 19]. Basing of our research, the CL mechanism is somewhat different from the TL mechanism but it is close to the PL or XL ones. The difference is that in cases of CL, PL or XL, the *e-h* pairs formation in the samples proceeds simultaneously with the emission that can cause the luminescence of the impurity itself. It is especially noticeable in the CL spectra of $Li_2B_4O_7$ single crystals doped with Cu and Ag (Figs. 1c and 1d) where it may occur in this way. At CL excitation of Cu- and Ag- doped $Li_2B_4O_7$ single crystal samples by 9.5 keV electrons, a certain amount of hot *e-h* pairs is formed. Quickly losing the excess energy due to non-elastic collisions with atoms of crystal lattice, these secondary charge carriers, *e* and *h*, run different distances before being captured, depending on their mobility. The ions A^+ ($A^+ = Cu^+$, Ag^+, etc.) capture quickly most of these secondary electrons and form so-called A^0 centers [17, 19]. As the concentration of holes, which go on being generated by the exciting electrons, exceeds the number of hole traps, an enough number is left for taking part in above-mentioned mechanism of luminescence through STE.

In the colliding process of a large number of hot *e* and *h* carriers, the Cu^+ and Ag^+ impurities become excited as well and go again to the ground state with photon emission. Thus, the CL luminescence band of $Li_2B_4O_7$ at 3.40 eV (Fig. 1.c) can be ascribed to $3d^94s \rightarrow 3d^{10}$ electron transitions in Cu^+ ions. In free Cu^+ ions, these transitions are prohibited by pair rule but in crystals they may occur as a result of weakening prohibition due to non-paired oscillations of crystal lattice [17]. The intense CL emission band in $Li_2B_4O_7$:Ag crystals at 4.62 eV can logically be ascribed to allowed $4d^95p \rightarrow 4d^{10}$ transitions in Ag^+ ions. The difference can be explained by the fact that the value of electron-phonon interaction parameter for Ag^+ impurities in the $Li_2B_4O_7$:Ag crystal differs from that for Cu^+ impurities in the $Li_2B_4O_7$:Cu crystal. However, in the case of $Li_2B_4O_7$:Ag, we cannot refuse the mechanism proposed in [20] to explain the luminescence band at 4.30 eV for RbCl:Ag single crystals. According to this mechanism, the holes ionize Ag^+ centers transferring them to the Ag^{2+} state with the subsequent recombination of electrons with Ag^{2+}. As a result, the so-called A-luminescence of Ag^+ centers appears.

It is somewhat problematic to explain the luminescence band in CL spectra of undoped $Li_2B_4O_7$ crystals discovered at 80 K peaked at about 2.2 eV (Fig. 2a). The temperature behavior and Gaussian form of the 2.2 eV luminescence curve prompts that an *F* type center could be responsible for it. As it is known, In oxide compounds, the *F*-centers are known to be formed basing on oxygen vacancies. However, oxygen vacancies in $Li_2B_4O_7$ crystals cannot be formed due to strong covalent B–O binding in boron-oxygen complexes, which in their turn are united in strong framework forming the crystal lattice [21]. In our experiments, the electron beam energy did not exceed 10 keV that is almost two orders lower than kinetic energy necessary to displace the oxygen atoms out of their positions in oxygen compounds. Thus, the formation of oxygen vacancies in $Li_2B_4O_7$ as well as *F*-centers is impossible in our case. But if we admit that instead of tetraborate complex (2Δ +2), some other different one gets therein during the single crystal growth, then the appearance of *F*-centers is quite possible. The

complexes $(2\Delta +)$, $(3\Delta +)$ or $(4\Delta +)$ will be such differing ones [17]. For a $(4\Delta +)$ complex, for example, the total anion charges of the tetraborat complex $[B_4O_9]^{6-}$ and pentaborat ones $[B_5O_{10}]^{5-}$ differ by one unit, so such a substitution, when compensating the charge at the expense of lithium cation vacancies, may cause the appearance of a similar oxygen vacancy in $Li_2B_4O_7$ crystal lattice which can be referreed to as an "anion pseudo vacancy". The presence of such an anion pseudo vacancy, provided that electron is captured by it, is a precondition for appearing an *F*-center analogue which should be called "pseudo *F*-center". The difference of this pseudo *F*-center from classical one consists in that it is impossible to define the position of the captured electron in the "alien" complex anion complex $[B_3O_7]^{5-}$. Such pseudo *F*-centers in the $Li_2B_4O_7$ crystal lattice may exist only at low temperatures that is evidenced by the actual absence of the 2.2 eV band in the CL spectra at 295 K (Fig. 1a).

Taking into account that boron-oxygen framework of $LiKB_4O_7$ is formed by two boron-oxygen complexes $(\Delta + 2)$ and $(4\Delta +)$ [14], the strengthening of STE emission in $Li_2B_4O_7$:K single crystals (Fig. 1b) is easy to explain. The K^+ ions promote obviously entering of the $(4\Delta +)$ complexes into the $Li_2B_4O_7$ crystal lattice and thus increase the concentration of above-mentioned pseudo *F*-centers. This is especially noticeable for single crystal with a high K concentration, that is, $LiKB_4O_7$ (Fig. 3a). This is confirmed also by the appearance of another luminescence band with maximum at 2.70 eV in the CL spectrum of $LiKB_4O_7$ crystal at 80 K (Fig. 3b). This band is the full analog of that peaked at 2.2 eV (Fig. 2a) for the undoped $Li_2B_4O_7$ crystal as well as due to the same emission mechanism.

A parameter of importance for scintillation applications of single crystals is the decay time τ. Our estimations of τ parameter for slow component of decay time at CL have given results similar to those obtained by other authors [1, 6, 14, 18] using other mechanisms of luminescence excitation, namely τ > 300 ns for undoped crystals and τ > 50 μs for doped $Li_2B_4O_7$ crystals.

Thus, the results of our research made it possible to determine that the main mechanism of CL luminescence in $Li_2B_4O_7$ single crystals is STE annihilation with emission independent of the impurity type. A certain type of growing defects connected with "alien" boron and acid complexes provides the STE localization. Some impurities, such as Cu and Ag, are added to the main band of STE luminescence while other, in particular K, only increase light yield in the main band of luminescence. Thus, our research has evidenced the good prospects of a purposeful influence on some luminescence parameters such as intensity and decay time of lithium borate single crystals by the proper selection of doping impurities or changing defectness extent by technological conditions of single crystal growing.

References

1. E.L.Vinograd, Yu.T.Vydai, L.B. Zagarii et al., *Functional Materials*, **1**, 152 (1994).
2. V.N.Baumer, V.V.Chernikov, M.F.Dubovik et al., *Functional Materials*, **8**, 736 (2001).
3. K.Hubner, K.Prokert, *Kernenergie*, **26**, 118 (1983).
4. Y.Kutomi, N.Takeuchi, *J. Mat. Sci. Lett.*, **5**, 51 (1986).
5. Ya.V.Burak, B.V.Padlyak, V.M.Shevel, *Radiat. Eff. & Defects in Solids*, **157**, 1101 (2002).
6. M.F.Dubovik, E.F.Dolzhenkova, V.N.Baumer et al., *Functional Materials*, **7**, 153 (2000).
7. B.M.Hunda, P.P.Puga, A.M.Solomon et al., *Ukr. Fiz.Zh.*, **45**, 127 (2000).
8. M.Ishii, Y.Kuvano, T.Asai et al., *J. Crys. Growth*, **257**, 169 (2003).
9. O.T.Antonyak, V.T.Adamiv, Ya.V.Burak et al., *Functional Materials*, **9**, 452 (2002).
10. Kang-Soo Park, J.K.Ahn, D.J.Kim et al., *J. Cryst. Growth*, **249**, 483 (2003).
11. N.Senguttuvan, M.Ishii, M.Shimoyama at al., *Nucl. Inst. Meth. Phys. Res.*, **A486**, 264 (2002).
12. K.Kanaya, S.Okayama, *J. Phys. D:Appl. Phys.*, **5**, 43 (1972).
13. O.T.Antonyak., Ya.V.Burak, I.T.Lyseiko et al., *Optika i Spectr.*, **61**, 550 (1986).
14. M.Ignatovich, V.Holovey, T.Vidoczy et al., *Functional Materials*, **12**, 313 (2005).
15. V.T.Adamiv, O.T.Antonyak, Ya.V.Burak at al., *J. Luminescence*, **128**, 549 (2008).
16. V.T.Adamiv, O.T.Antonyak., Ya.V.Burak et al., *Functional Materials*, **12**, 278 (2005).
17. Ya.V.Burak, V.T.Adamiv, O.T.Antonyak et al., *Ukr. Fiz.Zh.*, **50**, 1153 (2005).
18. I.N.Ogorodnikov, V.A.Pustovarov, A.V.Kruzhalov et al., *Phys. Solid State*, **42**, 464 (2000).
19. I.N.Ogorodnikov, V.Yu.Yakovlev, A.V.Kruzhalov et al., *Phys. Solid State*, **44**, 1085 (2002).
20. E.A.Vasil'chenko, I.A.Kudryavceva, A.Ch.Lushchik et al., *Phys. Solid State*, **40**, 1228 (1998).
21. S.F.Radaev, L.A.Muradyan, L.F.Malakhova et al., *Sov. Phys. Crystallogr.*, **34**, 842 (1989).

Вплив ізовалентного заміщення
на катодолюмінесценцію монокристалів
Li$_2$B$_4$O$_7$:A (A = K, Cu, Ag)

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Представлено результати досліджень катодолюмінесценції (КЛ) ізовалентно заміщених монокристалів Li$_2$B$_4$O$_7$:A (A = K, Cu, Ag). Основним механізмом КЛ свічення нелегованих Li$_2$B$_4$O$_7$ є анігіляція автолокалізованих екситонів (АЛЕ). Домішки Cu і Ag мають свої смуги випромінювання у спектрах КЛ, які накладаються на смугу АЛЕ нелегованого Li$_2$B$_4$O$_7$ біля 3,65 еВ. Запропоновано моделі центрів і механізми КЛ висвічування у монокристалах Li$_2$B$_4$O$_7$:A.