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Model of TSL-centers in $Li_2B_4O_7$:A (A = Cu, Ag) single crystals

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Basing on spectral studies of the transmission and thermostimulated luminescence of LTB:A single crystals (A = Cu, Ag), a new mechanism has been proposed to explain the formation of TSL centers therein, so-called A^0 centers, involving the growth defects of the foreign boron-oxygen complexes. The TSL emission occurs via the energy transfer to a self-localized exciton followed by emissive annihilation thereof.

По результатам спектральных исследований пропускания и термостимулированной люминесценции монокристаллов ТБЛ:А (где A = Cu, Ag) предложен новый механизм формирования в них ТСЛ-центров, так называемых A^0-центров, с участием ростовых дефектов типа "чужих" борокислородных комплексов. ТСЛ излучение происходит через механизм передачи энергии автолокализированному экситону с его последующей аннигиляцией с излучением.

Lithium tetraborate $Li_2B_4O_7$ (TBL) is considered to be a promising material for the thermoluminescence (TL) dosimetry because its effective atomic number (7.3) is almost the same as for the human body (7.4) [1]. Its sensitivity to neutrons controllable by varying of isotope composition of Li and B, is an additional advantage of TBL [2]. However, doping is necessary to provide high parameters for TL dosimeters on the basis of TBL single crystals. To date, numerous chemical elements for doping of TBL single crystals have been studied by various authors, but the best results were obtained only for TBL single crystals doped with Cu and Ag [3–5]. Nevertheless, the absence of model for centers responsible for TL in TBL:Cu, Ag single crystals, hinders the optimization of parameters of individual dosimeters on the basis of those crystals. In this work, we propose a model and new mechanism of the TL centers formation in TBL:Cu, Ag single crystals basing on results of spectral investigations.

The TBL:Cu, Ag single crystals were grown from the melt by direct Czochralsky technique in Pt crucibles in air atmosphere. The doping was performed at the synthesis (using Li_2CO_3 and H_3BO_3) of TBL compound by adding of CuO or $AgNO_3$. The optimum Cu and Ag concentrations for the TL light yield were chosen to be within the limits of 0.015 to 0.02 % (at). The transmission spectra of TBL:Cu, Ag single crystals were registered in the 200–900 nm range at 290 and 77 K using an UV-VIS spectrophotometer Specord-M40. The absorption spectrum of TBL:Ag after X-quanta irradiation at 290 K was registered using a of MDR-6. Spectral distribution of TL radiation was registered using a DPS in temperature regions of main TL peaks (300–500 K) at heating rate 20°C/min. The samples for investigations had the cross-section size of 10×10 mm^2 and thickness 1 and 20 mm.

In absorption spectrum for TBL:Cu samples obtained on Specord-M40 at 290 K, a wide absorption band of low intensity was observed in UV region with weakly defined structure. At 77 K, this band was found to comprise three components peaked at about 220, 247, and 280 nm (Fig. 1). In the trans-

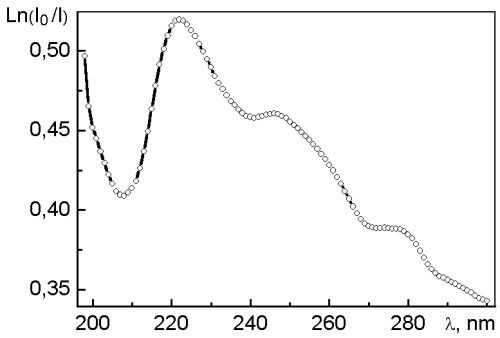

Fig. 1. Absorption spectrum of TBL:Cu single crystal at 77 K.

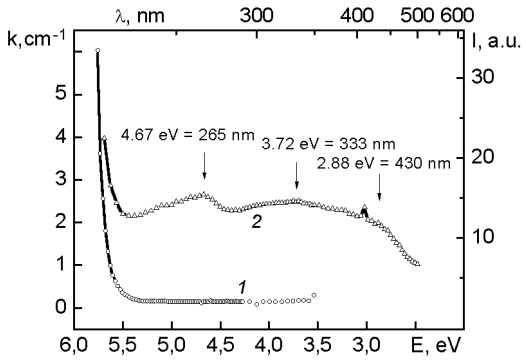

Fig. 2. Absorption spectrum of TBL:Ag single crystal: *1* — absorption of non-irradiated sample; *2* — absorption after irradiated.

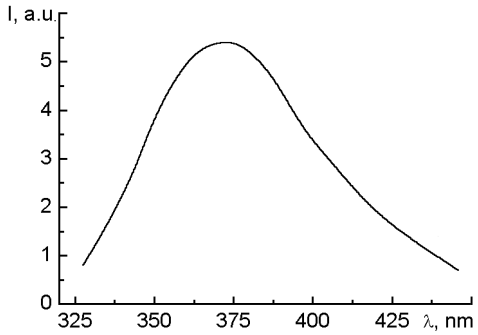

Fig. 3. TL emission spectrum of TBL:Cu single crystal.

mission spectrum of TBL:Ag samples in 210–900 nm range, no absorption bands were observed. After intense irradiation with X-quanta (during 1 hour), a wide, weakly structured absorption band appears in the 200–500 nm region (Fig. 2) in the absorption spectrum of TBL:Ag single crystal of 20 mm thickness.

A typical TL spectrum from Cu doped TBL single crystals is presented in Fig. 3 (similar TL spectra have been obtained for TBL single crystals doped with Ag and Mn). In this case, the spectral maximum of radiation coincides with that for undoped TBL single crystal, as estimated using filters.

The first questions associated with the TBL single crystal doping with Cu and Ag are connected with the dopant valence and its location in the crystal lattice, especially taking into account a rather large difference between their ionic radii: $r_{Cu^+} = 0.96$ Å and $r_{Ag^+} = 1.13$ Å, while $r_{Li^+} = 0.68$ Å and $r_{B^{3+}} = 0.16$ Å. Ions A^+ doubtless cannot pretend for positions of B^{3+} ions because of too large difference between their ionic radii, and different valence. The performed analysis of various but rather few publications about doping of the oxide compounds with copper had shown that in glasses of oxide compounds, the copper impurity may exist both in the form of Cu^+ ion, for example, in aluminum-boron-silicate [6] and in calcium metaphosphate [7] glasses, and in the form of Cu^{++}, for example, in the Cu doped $ARbB_4O_7$ (A = Na, K) glasses [8]. There is essentially no information on doping of the oxide compounds with silver. Nevertheless, there are very much publications on investigating of doping of alkali halide crystals with this impurity, for example [9, 10]. It is emphasized in all these works that both impurities exist usually in univalent state A^+ (i.e., Cu^+ or Ag^+) in alkali halide crystals and occupy the cation sites.

As to TBL:Cu single crystals, all authors agree with a fact that the copper impurity is located in the lattice also in the form of Cu^+ [3–5]. Three weak absorption bands in TBL:Cu single crystals discriminated by us (Fig. 1) agree well with positions of the absorption bands for Cu^+ ions in calcium metaphosphate glass [7]. Besides, authors of this work have proved clearly that absorption bands of Cu^+ ions, registered by them, exist due to surrounding of distorted oxygen octahedron. Therefore, by analogy with conclusions of those authors, our absorption bands for TBL:Cu single crystal can be connected with parity-forbidden $3d^{10} \rightarrow 3d^9 4s$ electron transitions: band 221 nm, with $^1A_g \rightarrow {}^1A_1$, band 247 nm, with $^1A_g \rightarrow {}^1E_1$, and band 279 nm, with $^1A_g \rightarrow {}^1E_g$ in Cu^+ ion being in the environment of distorted oxygen octahedron in the TBL crystal lattice.

Octahedral oxygen environment shows that Cu^+ ions are located certainly in specific sites of the TBL crystal lattice. Under ordinary substitution of Li^+ ions (i.e., if

copper and silver would be ordinary substitutive impurities), the oxygen environment of Cu^+ ions must be in a form of distorted tetrahedron, as it takes place in the case of Li^+ ions in TBL lattice. To explain the octahedral oxygen environment for Cu^+ (or Ag^+) impurities in the TBL lattice, the following hypothetic model can be proposed connected with possible specific growth defects. As it is known, the basis of the crystal lattice consists of so-called tetraborate boron-oxygen anion complexes $[B_4O_9]^{6-}$, which consist of two boron atoms in triangular (Δ) oxygen environment (elementary $[BO_3]$ — complexes), and two boron atoms in tetrahedral ($\square$) oxygen environment (elementary $[BO_4]$ — complexes); i.e., the tetraborate complex can be written as $(2\Delta + 2\square)$. But, due to the melt overheating which necessarily occurs in the crucible volume during the TBL single crystal growth by the Czochralsky technique, some complexes can differ from the tetraborate ones (for example, "damaged" tetraborate complexes $(3\Delta + \square)$ or open complexes 4Δ). It is fixed uniquely in [11] that under increasing melt temperature for different lithium borates, the ratio between elementary complexes $\Delta/\square$ in the melt tends to increasing Δ number. If tetraborate complexes $(2\Delta + 2\square)$ in TBL single crystal are substituted by $(3\Delta + \square)$ or 4Δ complexes, this means that a growth defect arises with somewhat changed positions of oxygen atoms which can form the distorted oxygen octahedron. Besides, as it is known, the growth defects facilitate entering of the impurity atoms into the crystal lattice in the process of the single crystal growth, especially at significant difference of ionic radii, as it is the case at TBL:A. In such a way, it is possible to explain why the registered spectra for TBL:Cu single crystals are quite within the frame of Cu^+ ion electron system in the crystal field of strongly distorted oxygen octahedron.

It is logically to connect the registered absorption bands in the TBL:Ag single crystal after intensive irradiation by X-quanta (Fig. 2) with formation of Ag^0 centers with the electron configurations $4d^{10}5s^1$ and $4d^95s^2$. The results of investigations presented in [12], where existence of the electron Li^0-centers involved in the process of interdefect tunnel recombination involving the hole centers in undoped TBL single crystals, can be a confirmation of the role of A^0-centers for the process of TL emission in the TBL single crystals.

Using the model of A^0 type TL centers in TBL:A single crystals, the following mechanism of TL emission can be proposed connected with self-trapped excitons (STE) observed in TBL single crystal [13] and confirmed by the later precise investigations [14]. This is confirmed by results of the photoluminescence investigations, TL and X-ray luminescence in TBL single crystals. As well as in the most publications of different authors, in our investigations of TL spectra, the position of the emission band (Fig. 3) is independent of the impurity type (in particular, Cu, Ag, Mn), and its maximum is always located at 365–370 nm, as in undoped TBL crystal. This band just coincides well with the STE band [13].

Therefore, the TL mechanism in TBL:A single crystals can be represented as follows. During irradiation, a pair consisting of an electron in conduction band and a hole in valence band is formed in the TBL crystal lattice. The electron, migrating in the conduction band, is captured quickly by A^+ ion with formation of so-called A^0-center. Similarly, the hole is precipitated onto the nearest boron-oxygen complex. Under heating of the crystal, the hole is released and begins to migrate near the "defect" anion. As a result of the electron tunneling from A^0-center, a polaron of small radius is formed involving the migrating hole, followed by formation of a STE in excited state. The radiative annihilation of STE just results in TL emission of the TBL:A single crystal. Therefore, the TL emission process in $Li_2B_4O_7$:A single crystals can be represented as

$$TBL \xrightarrow{\text{irradiation}} e + hole \rightarrow A^+ + e =$$
$$= A^0 \xrightarrow{\text{heating}} A^0 + hole = STE \xrightarrow{\text{annihilation}} h\nu.$$

Thus, Cu^+ and Ag^+ impurities can be concluded to favor one of two (or both simultaneously) TL processes in TBL:A single crystals: storage of larger light sum and/or decreasing number of non-radiative STE annihilation acts. That is why the doping of TBL single crystals with these impurities results in an increased TL light yield.

In conclusion, the growth defects of "foreign" boron-oxygen complexes near which the doping impurities in univalent state are deposited take essential part in the process of TL center formation in TBL:A single crystals (where A = Cu, Ag). Absorption spectra of Cu^+ ions in TBL single crystal are formed due to parity-forbidden $3d^{10} \rightarrow 3d^94s$ electron transitions between levels split by the TBL crystal field. A^0 cen-

ters, which are formed under irradiation, take the main part in the mechanism of TL light sum accumulation. TL radiation occurs according to energy transfer mechanism to self-trapped exciton followed by its radiative annihilation. Cu and Ag doping results in increasing TL yield in TBL:A single crystals due to a larger light sum accumulation and/or decreasing amount of non-radiative annihilation acts of self-trapped excitons.

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Модель ТСЛ-центрів у монокристалах $Li_2B_4O_7$:A (A = Cu, Ag)

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За результатами спектральних досліджень пропускання і термостимульованої люмінесценції монокристалів ТБЛ:А (де А = Cu, Ag) запропоновано новий механізм формування в них ТСЛ-центрів, так званих A^0-центрів, з участю ростових дефектів типу "чужих" борокисневих комплексів. ТСЛ випромінювання відбувається через механізм передачі енергії автолокалізованому екситону з його наступною анігіляцією з випромінюванням.