THERMOLUMINESCENCE IN DOPED SINGLE CRYSTALS $Li_2B_4O_7$:A (A = Cu, Ag)

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On the basis of the results of studies of the thermoluminescence (TL) and absorption spectra of $Li_2B_4O_7$:Cu and $Li_2B_4O_7$:Ag single crystals, we propose a mechanism of formation of A^0-centers of TL with the participation of growth defects of the type of "strange" boron-oxygen complexes. A^0-centers play a dominant part in the accumulation of the light yield under radiation. The TL radiation is realized by means of the energy transfer to a self-trapped electron in the $Li_2B_4O_7$, crystal lattice followed by its radiative annihilation. It is established that the absorption spectra of Cu^+ ions in $Li_2B_4O_7$ single crystals are formed by the parity-forbidden $3d^{10} \to 3d^9 4s$ electron transitions between the levels split by the crystal field, while, in the case of Ag^+ ions, by the allowed $4d^{10} \to 4d^9 5p$ transitions. It is concluded that the presence of Cu and Ag impurities promotes an increase of the TL efficiency for $Li_2B_4O_7$ single crystals due to the accumulation of a higher light yield and/or a decrease of the number of nonradiative acts of annihilation of self-trapped excitons.

1. Introduction

Lithium tetraborate $Li_2B_4O_7$ (LTB) is considered to be a perspective material for TL-based radiation dosimetry due to the fact that its effective atomic number (7.3) is almost equal to that of a human body (7.4) [1]. In addition, LTB is sensitive to neutrons, and this sensitivity can be regulated by means of changing the isotope composition with respect to Li and B [2]. However, in order to provide the high parameters of dosimeters based on LTB single crystals, the latter should be doped. By now, an essential number of chemical elements has been tested for the doping of LTB single crystals, namely: Ce, Eu, and Tm [3], Cu [4,5], Cu, K, Ag, and Ga [6], Cu, Mn, and Mg [7], Ce, In, Ni, Cu, and Ti [8], etc. From the standpoint of TL dosimetry, the best results were so far obtained when doping LTB single crystals with Cu and Ag. Moreover, the promising preliminary results were obtained with Mn. However, a successful and wide practical application of LTB:Cu or LTB:Ag single crystals in TL dosimetry requires a significant increase of the TL light yield. For this purpose, it is necessary to give a deeper consideration to the mechanisms of formation of the centers responsible for TL in doped LTB single crystals and to construct models for their description.

In the present work, we carry out spectroscopic investigations of the optical properties (absorption and TL) of LTB:A single crystals (A=Cu, Ag). On the ground of the obtained results, a model describing the mechanism of formation of TL centers in these single crystals is proposed.

2. Experimental Technique and the Results of Investigations

LTB:A single crystals were grown from a melt by the direct Czochralski method in Pt-crucibles in air. The doping was carried out at the stage of synthesis of the LTB compound using Li_2CO_3 and H_3BO_3 by means of adding CuO or $AgNO_3$. In this case, CuO was chosen solely as the most available chemical, as our technological investigations had not discovered any difference in TL in LTB:Cu single crystals obtained under conditions of the adding of elementary Cu, Cu_2O, or CuO to the LTB melt. The Cu and Ag concentrations were chosen in the range 0.015—0.02 at. %, which corresponds to the optimum of the TL light yield in LTB single crystals.

In the range 200—900 nm, the transmission spectra of LTB:A single crystals were registered at temperatures of 290 and 77 K (using a cryostat) with the help of a UV-VIS "Specord — M40" spectrophotometer, while the measurements were carried out at 290 K in the range 220—140 nm by means of a "McPherson VUV 2000" spectrophotometer using a purified nitrogen atmosphere. After the irradiation of the samples with X-quanta, the absorption spectra were registered at 290 K with the help of an MDR-6 device. The spectral distribution of TL radiation was detected in the temperature range 300—
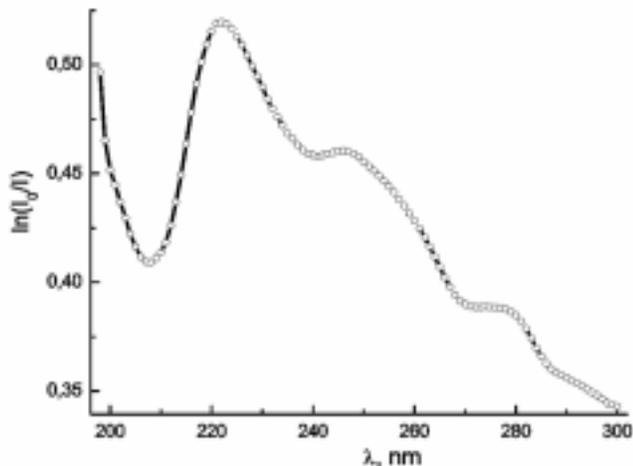
Fig. 1. Absorption spectrum of a $Li_2B_4O_7$:Cu^+ single crystal at a temperature of 77 K
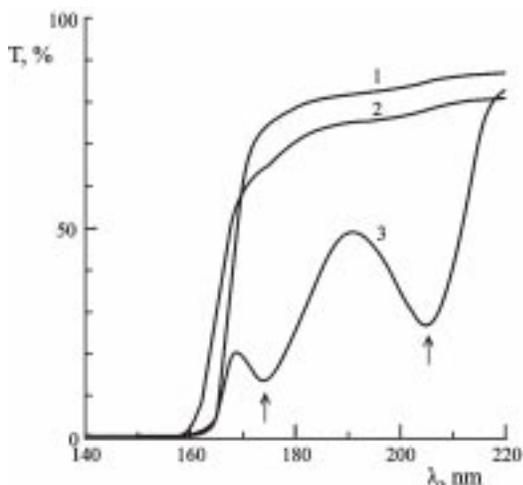
Fig. 2. Transmission spectra of $Li_2B_4O_7$:A single crystals at a temperature of 290 K: 1 –– an undoped single crystal, 2 — A=Cu, 3 — A=Ag

500 K corresponding to the basic TL peaks at the heating rate of 20°C/min. using a DMR-4 device. The samples used for measurements had a cross section of 10×10 mm^2 and thicknesses of 0.25, 1, and 20 mm.

For LTB:Cu samples, the absorption spectra obtained with the help of a "Specord — M40" at a temperature of 290 K include a wide low-intensity band in the UV region with a weakly developed structure. At a temperature of 77 K, it turns out that this band consists of three components with maxima located at $\sim$220, 247, and 280 nm (Fig. 1). In the transmission spectra obtained with the use of a "McPherson VUV 2000" spectrophotometer, no additional absorption bands that
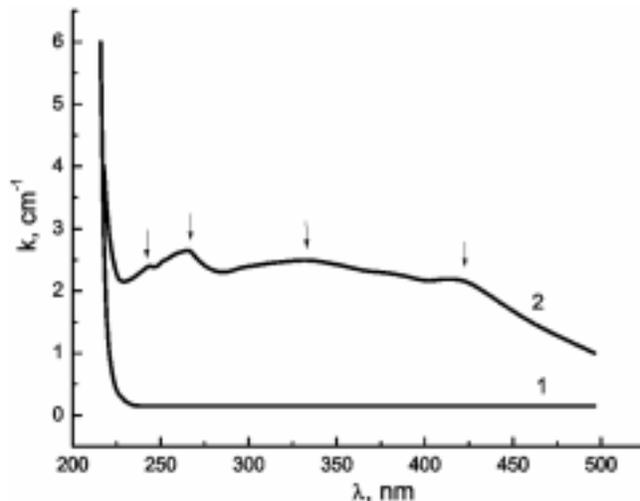
Fig. 3. Absorption spectra of a $Li_2B_4O_7$:Ag^+ single crystal of 20 mm in thickness at a temperature of 290 K: 1 — before the irradiation, 2 –– after the hour-long irradiation with X-quanta

could be associated with the Cu impurity were observed up to the edge of the characteristic absorption of LTB single crystals lying near 165 nm [9] (Fig. 2, curve 1). Thus, the presence of three absorption bands in LTB:Cu single crystal agrees well with the absorption of Cu^+ centers in $CuLaO_2$ crystals [10].

In the range 900—210 nm, the transmission spectra of LTB:Ag samples do not include any absorption bands. Instead, two intensive absorption bands associated with the Ag impurity can be observed closely to the edge of the LTB characteristic absorption, namely at 205 and 174 nm (Fig. 2, curve 2).

After the intense hour-long X-irradiation of a single-crystal LTB:Ag sample of 20 mm in thickness, a wide weakly structured band was observed in its absorption spectrum in the range 500—200 nm (Fig.3).

The TL spectrum of LTB:Ag single crystals is presented in Fig. 4. The same spectra were registered for LTB single crystals doped with other impurities, in particular with Cu and Mn. The spectral maximum of the radiation coincides with the TL maximum of an undoped LTB single crystal estimated with the help of light filters. Thus, the TL spectrum depicted in Fig. 4 can be considered typical of LTB single crystals and independent of doping.

3. Discussion of the Results

The first questions arising when doping LTB single crystals with the Cu and Ag admixtures are those

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concerning the valence of the admixture and its position in the crystal lattice, especially taking into account a rather essential difference between the ion radii of the activating agents ($r_{\text{Cu+}} = 0.96$ Å and $r_{\text{Ag+}} = 1.13$ Å) and those of the matrix cations ($r_{\text{Li+}} = 0.68$ Å and $r_{\text{B3+}} = 0.16$ Å). A^+ ions cannot replace B^{3+} because of both a too large difference between the ion radii and different valences. The analysis of the not numerous publications devoted to the doping of oxide compounds with copper has demonstrated that, in glasses of oxide compounds, the copper admixture can exist both in the form of Cu^+ (for example, in aluminum boron silicate [11] and calcium metaphosphate [12] glasses) and in the form of Cu^{++} (as in copper-doped glass $ARbB_4O_7$ (A = Na, K) [13]). Information concerning the doping of oxide compounds with Ag is practically absent. Instead, there exists a lot of publications dealing with the investigations of alkali halide crystals doped with these admixtures (see, for example, [14, 15]). In all these papers, it is stressed that, in alkali halide crystals, both admixtures are usually univalent (that is, Cu^+ or Ag^+)) and take up the positions of cations.

As regards LTB:Cu single crystals, the authors of publications [4—8] agree that the copper admixture is also present in the crystal lattice in the form of Cu^+. However, in order to get rid of any doubts about the valent state of copper in LTB single crystals, we performed the special investigations of the ESR spectra of single-crystal LTB:Cu samples. Our measurements have not discovered any paramagnetic Cu^{++} ions, which allows us to state that, even if there are any Cu^{++} ions in LTB:Cu single crystals, their concentration does not exceed the limits of the sensitivity of ESR to paramagnetic centers, i.e. it equals to at most 10^{12} cm^{-3}. As the density of admixture ions in LTB:Cu single crystals at the optimal concentration of 0.015 at.%

T a b l e 1. Excitation energies of the levels of free Cu^0, Ag^0 atoms and Cu^+, Ag^+ ions

State of the admixture	Transition	Excitation energy, eV	Reference
Cu^+	$3d^{10} \rightarrow 3d^9 4s$	3.2	[14]
	$3d^{10} \rightarrow 3d^9 4p$	9.12	
Cu^0	$3d^{10} 4s^1 \rightarrow 3d^{10} 4p^1 \, (^2P_{1/2})$	3.79	[17]
	$3d^{10} 4s^1 \rightarrow 3d^{10} 4p^1 \, (^2P_{3/2})$	3.82	
	$3d^9 4s^2 \rightarrow 3d^{10} 4s^1 4p^1 \, (^2P_{3/2})$	1.39	
	$3d^9 4s^2 \rightarrow 3d^{10} 4s^1 4p^1 \, (^2P_{5/2})$	1.64	
Ag^+	$4d^{10} \rightarrow 4d^9 5s$	5.67	[14]
	$4d^{10} \rightarrow 4d^9 5p$	11.10	
Ag^0	$4d^{10} 5s^1 \rightarrow 4d^{10} 5p^1 \, (^2P_{1/2})$	3.67	[17]
	$4d^{10} 5s^1 \rightarrow 4d^{10} 5p^1 \, (^2P_{3/2})$	3.78	
	$4d^9 5s^2 \rightarrow 4d^{10} 5s^1 5p^1 \, (^2P_{3/2})$	3.75	
	$4d^9 5s^2 \rightarrow 4d^{10} 5s^1 5p^1 \, (^2P_{5/2})$	4.30	
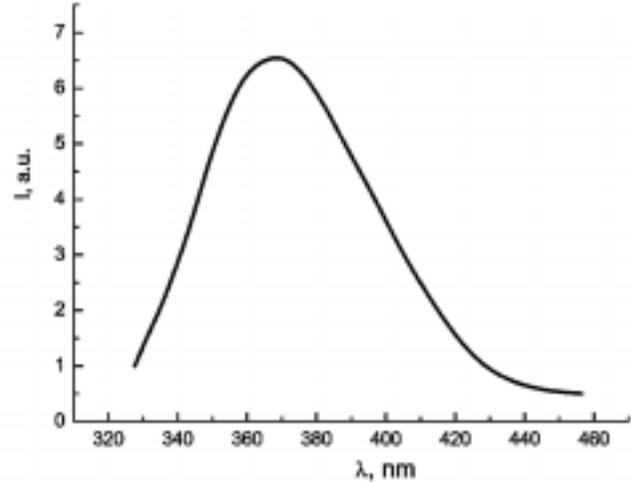
Fig. 4. TL spectrum of $Li_2B_4O_7$:Ag^+ single crystals after the X-irradiation obtained for the 150-K peak

amounts to 2.55×10^{18} cm^{-3}, one can undoubtedly regard Cu^+ ions as the defining ones.

In the neutral state (Cu^0 and Ag^0), Cu and Ag atoms used as admixtures belong to the elements with the external electron configuration $(n-1)d^{10}ns^1$ or $(n-1)d^9ns^2$ [16]. For example, for Cu^0, this configuration has a form $3d^{10}4s^1$ or $3d^94s^2$, for Ag^0 – $4d^{10}5s^1$ or $4d^95s^2$. Losing one s-electron due to ionization, Cu^+ and Ag^+ ions possess the outer electron shells of $3d^{10}$ and $4d^{10}$ configurations, respectively. That's why, in order to analyze the obtained spectra of LTB:A single crystals, it is logical to make use of some theoretical conclusions and results of investigations of the spectra of ions of $(n-1)d^{10}$ configuration in various crystals [17]. The data on the excitation energies of free atoms Cu^0 and Ag^0 and ions Cu^+ and Ag^+ are given in Table 1.

All investigators of various copper-doped single crystals agree that the absorption bands of Cu^+ ions in various matrices lying near 5 eV correspond to the $3d^{10} \rightarrow 3d^94s$ electron transitions ($4d^{10} \rightarrow 4d^95s$ for Ag^+ ions, respectively) and depend on the splitting of these levels by the crystal field. In free ions Cu^+ and Ag^+, these transitions are parity-forbidden, but they can take place in crystals at the expense of the attenuation of forbidenness due to odd vibrations of the crystal lattice. At higher energies, the allowed transitions $3d^{10} \rightarrow 3d^94p$ for Cu^+ ions and $4d^{10} \rightarrow 4d^95p$ for Ag^+ ions can occur.

The positions of three weak absorption bands (Fig.1) that we separated in LTB:Cu single crystals agree well with those of the absorption bands of Cu^+ ions in oxide compounds, in particular, in calcium metaphosphate glass [12]. The authors of that paper convincingly

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demonstrated that the absorption bands of Cu^+ ions observed by them were conditioned by the environment of the distorted oxide octahedron. Hence, according to the conclusions of those authors, the absorption bands observed in our researches must correspond to the parity-forbidden $3d^{10} \to 3d^9 4s$ electron transitions, namely: the band at 221 nm — to $^1A_g \to {}^1A_1$, the band at 247 nm – to $^1A_g \to {}^1E_1$, and the band at 279 nm – to the $^1A_g \to {}^1E_g$ transition in a Cu^+ ion surrounded by the distorted oxide octahedron in the LTB crystal lattice.

The octahedral oxide environment testifies to the fact that Cu^+ ions are obviously located at specific positions of the LTB crystal lattice different from those of Li^+ ions. Indeed, in the case of the direct replacement of Li^+ ions (that is, if Cu and Ag were ordinary substitutional impurities), the oxide environment of Cu^+ ions would have a form of a distorted tetrahedron, which really takes place for Li^+ ions in the LTB crystal lattice [18].

A somewhat different explanation should be given to the results of investigation of the absorption spectra of an LTB:Ag single crystal not exposed to radiation, for which we observed a considerable absorption with maxima at 174 and 205 nm (Fig. 2), whereas the absorption in this region is weak for LTB:Cu. This can testify to the fact that, in LTB:Ag, we deal most probably with the allowed $4d^{10} \to 4d^9 5p$ transitions in Ag^+ ions located in the same oxide environment as Cu^+ ions in LTB:Cu, but the influences of the crystal field and the electron-phonon interaction for Ag^+ and Cu^+ are different.

In order to explain the nature of the octahedral oxide environment of A^+ impurities in the LTB crystal lattice, one can assume that it is associated with some real growth defects. The clarification of their origin requires a more detailed consideration of the process of formation of the LTB crystal lattice. As is known from [18], the basis of the crystal lattice is formed with the so-called tetraborate boron-oxygen anion complexes $[B_4O_9]^{6-}$ that consist of two boron atoms in the triangular (Δ) oxide environment (elementary $[BO_3]$ complexes) and two boron atoms in the tetrahedral ($\square$) one (elementary $[BO_4]$ complexes), so that the whole tetraborate complex can be described as $(2\Delta + 2\square)$. However, taking into account the established existence of a great variety of compound boron-oxygen complexes constructed from the elementary blocks Δ and $\square$ [19], it is natural to suppose that some complexes in molten LTB can differ from tetraborate ones (for example, "distorted" tetraborate complexes $(3\Delta + \square)$ or open complexes 4Δ)). This is confirmed by the results [20]

demonstrating that, with increase in the temperature of melts of lithium borates, the ratio of the numbers of elementary complexes $\Delta/\square$ in the melt varies towards an increase of the number of Δ. In other words, the overheating of the melt, which occurs necessarily in the crucible volume while growing an LTB single crystal by the Czochralski method, results in the prevalence of the elementary Δ complexes. This implies that, during the growing of an LTB single crystal, "strange" boron-oxygen complexes (an open anion complex 4Δ or $(3\Delta + \square)$) inevitably get into its crystal lattice. Perhaps, these complexes penetrate into the LTB crystal lattice simultaneously; in this case, it is easy to understand the presence of two basic temperature TL peaks in LTB:A single crystals. The mentioned "strange" boron-oxygen compounds are absolutely analogous to the tetraborate anion complex $[B_4O_9]^{6-}$, where all boron atoms are connected to oxygen with a strong covalent bond. Moreover, the case of 4Δ additionally provides for the deficiency of one oxygen atom but, due to the closure of this complex conditioned by covalent B—O bonds, the shortage of oxygen should not result in the formation of the V_A^+ vacancy typical of these cases.

Hence, the ingress of $(3\Delta + \square)$ or 4Δ complexes into the LTB single crystal instead of tetraborate $(2\Delta + 2\square)$ ones, results in the appearance of a growth defect with a somewhat changed arrangement of oxygen atoms that can certainly form a distorted oxygen octahedron. As is known from [21], growth defects essentially facilitate the penetration of admixture atoms into the crystal lattice in the course of growing a single crystal, especially under conditions of a substantial difference between the ion radii, as in the case of LTB:A. Thus, one can explain why the spectra obtained in our investigations for LTB:Cu single crystals completely correspond to the electron levels of Cu^+ ion in the crystal field of a strongly distorted oxide octahedron.

If we take the concentration of Cu^+ ions equal to 0.015 at.% which is optimal for TL and assume that all these ions settle on the mentioned growth defects, the number of "strange" boron-oxygen complexes in an LTB single crystal will be approximately equal to 10^{18} cm^{-3}. In other words, an LTB single crystal contains one "strange" boron-oxygen complex per 10 000 regular tetraborate ones or one per 1 000 unit cells of the LTB crystal lattice. When all defects are occupied with Cu^+ ions, the following increase of their concentration in the melt does not any more result in the growth of their concentration in the single crystal and, correspondingly, in the rise of the TL radiation intensity. This fact

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is confirmed by the existence of the A^+ admixture concentration optimal for the TL light yield.

Based on the proposed model of TL centers in LTB:A single crystals, one can reconsider the TL mechanisms in them which were suggested in [6] and associated only with A^0 centers for both the TL peaks. In order to discover such centers in LTB:A single crystals, we carried out special investigations. The very fact of the formation of an Ag^0 center with a clear absorption band at 2.9 eV in an alkali halide RbCl:Ag crystal exposed to X-radiation was established in [22]. The additional information concerning the role of A^0 centers in the TL process in LTB:A single crystals was obtained from the results of investigations performed in [23], where the existence of electron Li^0 centers in undoped LTB single crystals was established, as well as the fact of their participation in the process of interdefect tunnel recombination with hole centers involved.

Hence, it is natural to correlate the absorption bands, which we discovered for an LTB:Ag single crystal intensively irradiated with X-quanta (Fig. 3), with the formation of Ag^0 centers. For the sake of obviousness, the positions of maxima of the absorption bands in LTB:A single crystals observed before and after the irradiation by X-quanta are given in Table 2.

The attention should be paid to the fact that, in the absorption spectrum of an LTB:Ag single crystal exposed to X-radiation, one can distinguish 4 additional bands, while, for LTB:Cu single crystal, no additional absorption bands were discovered in the investigated wavelength range. Under the assumption that LTB:Cu crystals must contain Cu^0 centers, we have failed to discover them because of two possible reasons: 1) additional absorption is too weak and the thickness of the sample was insufficient; 2) the electron configuration of Cu^0 atom in the LTB crystal lattice is $3d^9 4s^2$ and, as one can see from Table 1, the electron transitions for this configuration have very low excitation energies, that's why the corresponding absorption bands lie in the IR range. The excitation energies of Ag^0 centers are almost identical for both electron configurations ($4d^{10} 5s^1$ and

T a b l e 2. Energy positions of the absorption bands of LTB:A single crystals before and after X-irradiation

Single crystal	Before irradiation, eV	After irradiation, eV
$Li_2B_4O_7$:Cu	4.45	—
	5.02	
	5.61	
$Li_2B_4O_7$:Ag	6.06	2.88
	7.14	3.72
		4.67
		5.10

$4d^9 5s^2$), and the absorption bands can be registered in the investigated spectral range.

Using the models of TL centers of the A^0 type in LTB:A single crystals, one can propose a TL mechanism related to self-trapped excitons (STE). The latter were first discovered in LTB crystals in [9], which was confirmed by the following detailed investigations [24]. One can arrive at such a conclusion analyzing the results of investigations of the photoluminescence, TL, and röntgenoluminescence spectra of LTB single crystals. The absolute majority of the investigations of TL spectra (including ours) demonstrates that the location of a radiation band (see Fig. 4) does not depend on the impurity type (Cu, Ag, or Mn) and the maximum of the band corresponds to 365—370 nm in the same way as in an undoped LTB crystal. This band coincides well with that of STE [9].

Hence, the TL process in LTB:A single crystals can be described in the following way: under the irradiation, an electron − hole pair is formed in the LTB crystal lattice.

Migrating in the conduction band, the electron is quickly captured by an A^+ ion forming the so-called A^0 center. That is, this ion represents a deep electron trap in the LTB crystal lattice. At the same time, the hole is rapidly localized on the nearest boron-oxygen complex. When the crystal is heated, the hole releases and starts to migrate near the activating "defect" anion. Due to the tunneling transfer of an electron from the A^0 center, a small-radius polaron is formed with the participation of the migrating hole, which is followed by the formation of an excited STE [23]. The subsequent radiative annihilation of STE gives rise to TL in LTB:A single crystals. Thus, the TL scheme in $Li_2B_4O_7$:A single crystals can be represented as follows:

$$LTB : A^{+ \text{ irradiated with X−rays}} \rightarrow LTB :(A^0 + h)^{\text{heat}} \rightarrow$$

$$\rightarrow LTB : (A^+ + STE)^{\text{annihilation}} \rightarrow$$

$$^{\text{annihilation}} \rightarrow LTB : A^+ + h\nu.$$
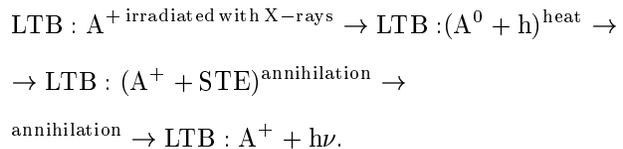
Hence, the Cu^+ and Ag^+ admixtures promote one of two TL processes in LTB:A single crystals or both of them simultaneously: the accumulation of a great light yield and/or the decrease of the number of nonradiative acts of the STE annihilation. That's why these impurities lead to an increase of the TL light yield of LTB single crystals.

The proposed mechanism of formation of TL centers while growing LTB:A single crystals is validated by experimental results, though its direct confirmation is

not easy. However, if the mechanism and the model are correct, this means that, in order to increase the TL light yield in LTB:A single crystals, it is necessary to learn to vary purposefully the number of "strange" boron-oxygen complexes in order to find their optimal concentration.

4.   Conclusions

1. A certain role in the process of formation of TL centers in LTB:A (A=Cu, Ag) single crystals is played by growth defects of the type of "strange" boron-oxygen complexes with the doping univalent admixtures settled near them.

2. The absorption spectra of Cu^+ ions in LTB single crystals are formed by the parity-forbidden $3d^{10} \rightarrow 3d^9 4s$ electron transitions between the LTB levels split by the crystal field, while those of Ag^+ ions — by the allowed $4d^{10} \rightarrow 4d^9 5p$ transitions.

3. The dominant role in accumulating the TL light yield is played by A^0 centers formed under the action of radiation.

4. TL is realized by means of the energy transfer to a self-trapped exciton followed by its subsequent radiative annihilation.

5. The Cu and Ag admixtures cause an increase of the TL light yield in LTB:A single crystals due to the accumulation of a great light yield and/or the decrease of the number of nonradiative acts of STE annihilation.

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ТЕРМОСТИМУЛЬОВАНА ЛЮМІНЕСЦЕНЦІЯ
ЛЕГОВАНИХ МОНОКРИСТАЛІВ $Li_2B_4O_7$:A (A = Cu, Ag)

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Р е з ю м е

За результатами спектроскопічних досліджень термостиму-льованої люмінесценції (ТСЛ) і поглинання монокристалів $Li_2B_4O_7$:Cu і $Li_2B_4O_7$:Ag запропоновано механізм формування в них A^0-центрів ТСЛ за участю ростових дефектів типу "чу-жих" борокисневих комплексів. A^0-центри відіграють основ-ну роль у накопиченні світлосуми під дією радіації. Висвічу-вання ТСЛ відбувається через механізм передавання енергії автолокалізованому екситону в кристалічній гратці $Li_2B_4O_7$ з його наступною випромінювальною анігіляцією. Встановле-но, що спектри поглинання іонів Cu^+ в монокристалі $Li_2B_4O_7$ формуються забороненими за парністю електронними пере-ходами $3d^{10} \rightarrow 3d^9 4s$ між розщепленими кристалічним по-лем рівнями, а у випадку іонів Ag^+ — дозволеними перехо-дами $4d^{10} \rightarrow 4d^9 5p$. Зроблено висновок, що наявність домішки Cu і Ag сприяє збільшенню світловиходу ТСЛ монокристалів $Li_2B_4O_7$ завдяки накопиченню більшої світлосуми і/або змен-шенню безвипромінювальних актів анігіляції автолокалізова-них екситонів.