THERMOSTIMULATED LUMINESCENCE AND X-RAY LUMINESCENCE IN UNDOPED $Li_2B_4O_7$ SINGLE CRYSTALS

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The luminescent studies of more than 20 technological batches of undoped $Li_2B_4O_7$ single crystals grown in different laboratories with different drawing and rotation rates, from different raw materials have been carried out to cover a wide range of possible structural imperfections. It has been shown that all the $Li_2B_4O_7$ single crystals contain a certain defect concentration, while the thermostimulated luminescence intensity at the isodose irradiation may serve as a criterion of crystal defectness. It has also been found that above the 20 °C the temperature luminescence damping is revealed with the Ea=0.32±0.01 eV activation energy.

Lithium tetraborate ($Li_2B_4O_7$, LTB) single crystals possess a complex of significant physical properties and due to that have found a wide application in different areas of science and technology. For instance, they are promising in the production of piezoelectric transducers, surface-active wave filters, acousto-optical modulators and high-efficiency generators of 2 to 5 harmonics [1-4]. Besides, the Mn and Cu-doped $Li_2B_4O_7$ poly- and single crystals are being widely used as the thermoluminescent dosimeters of ionizing radiation [5-7]. High radiation-optical resistance, wide transparency band and mechanical rigidity are the principal benefits of $Li_2B_4O_7$ single crystals [8-10].

Up to date, the basic crystallographic parameters of the $Li_2B_4O_7$ structures (i.e. their symmetry, lattice period) are well-studied by the X-ray, NMR and Raman-spectroscopy methods, however, some experimental data are available proving the existence of an incommensurate phase in LTB [11-12].

In our opinion, the anomalous temperature behavior of parameters found in [11,12] should be related to the crystalline structure defects. It is known that one of the most sensitive methods of studying the crystalline structure defects is the thermostimulated luminescence (TSL) [13]. Thus, we have carried out the luminescent studies of undoped LTB single crystals of more than 20 technological batches grown in different laboratories with different drawing and rotation rates, from different raw materials have been carried out to cover a wide range of possible structural imperfections.

The technology of the production of $Li_2B_4O_7$ single crystals is described in detail elsewhere [14]. The samples were produced both of the most high-quality top are of the crystal and of the middle and bottom areas. It should be noted that the bottom samples contained macroscopic defects (i.e. blocks, cracks).

The TSL in nominally pure $Li_2B_4O_7$ single crystals is insignificant and almost three orders lower than that in the dosimetric LiF-based samples and copper-doped LTB single crystals. In our first experiments, it was comparable with the background [15]. We have succeeded to detect it only after the increase of the X-ray radiation dose up to 1000 Gy and an additional improvement of the signal-to-noise ratio of our apparatus. The TSL curves for different areas of undoped $Li_2B_4O_7$ single crystal of one of the technological batches (A) are shown in Fig. 1(a). As follows from dependences shown, the TSL curve for the most perfect single crystal area reveals small but clear maxima at 103, 124, 140 та 160 °C (β=2.8 deg/s). For the middle-area samples TSL is almost two times higher, the maxima at the same temperatures are stronger overlapped, and two new maxima at 54 and 180 °C arise. The bottom-area samples have much higher TSL intensity and reveal slight maxima at 300 and 314 °C. Figure 1(b) illustrates the results of the similar studies for the single crystal of the B batch. It is seen that in this case the top-area samples have the lowest TSL intensity, and the maxima are revealed at 61, 89, 116, 137, 167 and 185 °C. For the middle single crystal area the TSL intensity at 116 °C is 2.5 times higher and some changes in the high-temperature region are noticed (the decrease in the intensity of the maximum at 167°C and the appearance of the maxima at 200 and 266°C). The bottom area is characterized by a complex structure in the TSL curve (up to 15 maxima).

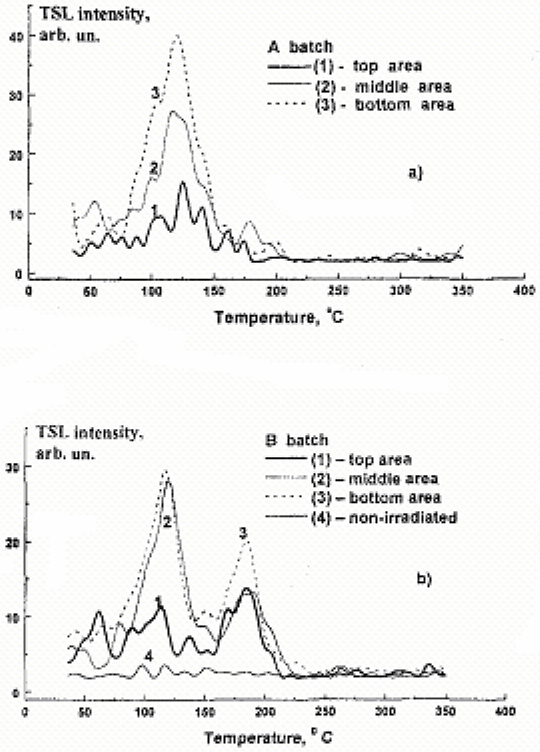

Fig. 1. The TSL curves for different undoped LTB single crystal areas.

Since the TSL curves for the single crystals under study differ, Fig. 2(a) shows the TSL results for the crystals taken from other technological batches (C, D, E), where only the most high-quality single crystal areas were used. As follows from Fig. 2(a), the TSL maxima are revealed at approximately the same temperatures, though each crystal has its own intensity distribution. To increase the reliability of the present investigation we have studied at the same conditions the TSL in the undoped LTB single crystals produced at the Institute of single crystals, Ukr. Nat. Acad. Sci. (batches F, G). The results of these studies are illustrated in Fig. 2(b). The F batch samples were produced of the optically perfect single crystal, while the G batch samples – of the lower-quality single crystal and contained a small amount of macroscopic defects (cracks) revealed in the TSL curve, since it has the highest intensity among all the undoped single crystals under study.

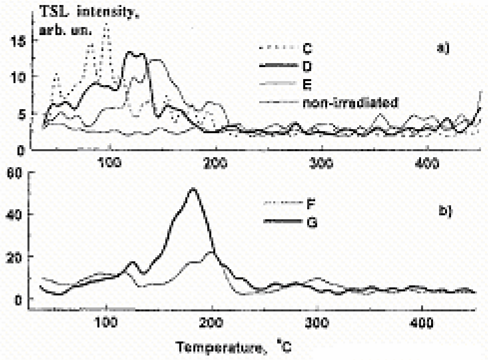

Fig. 2. TSL curves of undoped LTB single crystals of different technological batches.

Due to low TSL intensity of undoped single crystals, large number of maxima and their considerable overlapping, it is impossible to determine reliably the energy positions of local trapping levels based on the temperature luminescence curves. According to our estimates, as well as to the data [16–19], the depths of these levels lies within 0.5–1.6 eV.

One may note a good agreement between our TSL data with those taken from [16–19]. The best agreement is seen for the data [17] obtained at close heating rates (β=2 deg/s). In this paper, after the single crystal irradiation three intense TSL maxima were observed at 160, 260 and 310°C and three less pronounced maxima at 90, 120 and 210°C. The high-temperature annealing (at 880°C for 3 h) resulted in the appearance of two very intense (as compared to unannealed samples) maxima at 170 and 260°C and one low-intensity maximum at 310°C.

The TSL maxima in nominally pure single crystals revealed by us and the authors of papers [16–20] within a wide temperature range give a direct experimental evidence for our assumption on the possible relationship between a series of anomalies in physical properties with the defective structure of $Li_2B_4O_7$ single crystals grown in different technological laboratories, and, consequently, in different technological conditions.

So, the availability of defects and related trapping centers can explain the anomalies in the temperature dependence of dielectric permeability [21,23]. When determining the electric conductivity activation energies (ΔH_σ) by the formula $\sigma=\sigma_0\exp(-\Delta H_\sigma/kT)/T$, the liberation of carriers from the trapping centers at heating results in the increase of σ_0 value, while their trapping to the trapping centers at cooling – to the decrease of σ_0 value. Not taking into account this fact results in the overestimated ΔH_σ values within the 60–100°C range, whereas the different defect concentration in crystals – in the discrepancies between the data [1, 21–23].

Since the considerably deep local trapping levels are produced at the defects, the electron-phonon interaction constant increases significantly [24]. With the account for that fact as well as for the influence of the high-temperature annealing on the defect redistribution [17], one may explain the changes in the Raman scattering spectra [25] and the anomalies in other physical properties related to the crystalline lattice oscillations (sound wave velocity, elastic properties, etc.).

Thus, based on our TSL studies and the literature data [16–20], one may firmly conclude the existence of certain concentration of crystalline structure defects in almost all $Li_2B_4O_7$ single crystals, which stipulate the TSL maxima between –196 and 400°C. It has been found that the TSL intensity is the lowest in the most high-quality crystal areas. The bottom areas have 2–3 times higher TSL intensity that could be explained by a considerably higher concentration of point and macroscopic defects. Obviously, the TSL intensity serves a criterion of $Li_2B_4O_7$ single crystals defectness, similarly to the Al_2O_3 single crystals studied much more extensively [26]. Since the TSL curves for the single crystals of different technological batches differ significantly, this indicates a considerable effect of a number of technological factors on the LTB single crystal quality resulting in the uncontrolled crystal defectness. To define the regularities of defect production in single $Li_2B_4O_7$ crystals one requires further technological research.

The studies of the X-ray luminescence (XL) of undoped single crystals was carried out by means of the same setup [27]. Prior to measurements the spectral sensitivity used in experimental XL spectra correction was thoroughly determined.

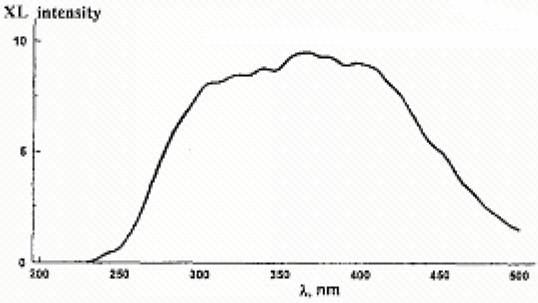

Fig. 3. XL spectrum for undoped LTB single crystals

It should be noted that almost no discrepancies were noticed in the XL spectra for single crystals of different batches. No change in the curve shape was found in defect and quality crystals, except the fact that the XL intensity in quality crystals was 20–30% lower. The sample-averaged XL spectrum has a form of a wide band (240–530 nm) with no distinct maximum (Fig.3). The XL band is asymmetric – the left-hand side rises more sharply than the right-hand one. Band FWHM is 160 nm. A large half-width and the lack of clear maximum indicate a complicated nature of the XL spectrum in $Li_2B_4O_7$ single crystals. One should note a good agreement of the obtained spectrum with that in [20], however, in our case a less pronounced luminescence within the 490–600 nm range is due to the presence of uncontrolled impurities.

Since in [20] the main attention was drawn to the low-temperature studies, the high-temperature XL damping has not been studied for LTB single crystals. Therefore, the investigation of the temperature dependence of the integral XL from room temperature to 440°C was of specific interest (see Fig. 4). Curve 1 represents the dependence of the intensity at step-by-step heating (with the 10°C step), while curve 2 – at step-by-step cooling. Each point was stabilized with the ±0.5°C accuracy.

As follows from the obtained dependences, the XL intensity decreases rapidly *with temperature, and at 200°C it is 10 times* less that that at room temperature. The further temperature increase results in a slower XL intensity reduction, but even at 440°C the luminescent emission still occurs. During cooling the XL intensity increases first slowly, and above 200°C – starts to rise rapidly. The temperature and exciting radiation intensity step variation changes only the intensity value and does not affect the character of the dependences shown.

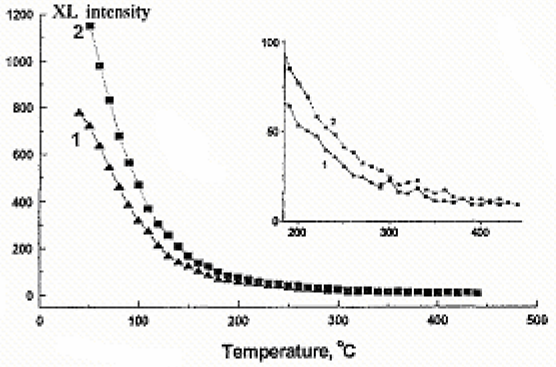

Fig. 4. XL temperature dependence for undoped LTB single crystals at step-be-step heating (1) and cooling (2)

It appears so, that the discrepancy in curves at heating and cooling has quite valid explanation. One has to take into account the fact that almost all single crystals have a certain concentration of defects, which play a role of charge carrier trapping centers. If before the measurement all the centers are not filled yet, then it is obvious that at the sample excitation a part of carriers will recombine radiatively, and the other part will be trapped to each group of local trapping levels, reducing the number of recombination acts. When measuring XL in a step-by-step cooling mode, the similar processes occur, with the difference that the part of the trapping centers lying energetically higher appear to be filled and, consequently, a larger number of charge carriers are involved into the recombination channel.

Analyzing the dependences by using Mott formula, we have found the temperature damping parameters (Table 1). As follows from table, both at heating and cooling the curves are described by the same activation energy (E_a) values and the probability ratios for non-radiative and radiative transitions (*Wo* and *Wв*, respectively). The difference is observed only in the Io value, i.e., the XL intensity at the absence of damping, that is well correlated with the mentioned above.

Table 1. Temperature damping parameters for undoped LTB single crystal at step-be-step heating (1) and cooling (2)

	Io, a.u.	*Wo/Wв*	E_a,eV
1	1051±23	56600±8500	0.32±0.01
2	2071±46	57400±5700	0.32±0.01

It is interesting to compare the obtained results with the available experimental data on the LTB single crystal electric conductivity [1, 22–23]. According to these data, within the 20–400°C temperature range the activation energy is 0.33 eV [1], while the conductivity along the z-axis is due to the lithium ions or vacancies [22, 23]. A good agreement in the activation energy values for conductivity and luminescence damping allows one to assume that the temperature increase leads to the larger lithium atom (or vacancy) mobility resulting, thus, in the increasing probability of relevant luminescence centers destroying. On the other hand, one may suppose that the luminescence damping in the LTB single crystals has an intracenter character, i.e. it is due to the intersection of the configuration coordinates of the ground and excited states of emitting centers. However, since the processes of intracenter and recombination damping are described by the similar formulae [28], one fails to conclude unambiguously from the obtained results which of these mechanisms is realized in our case.

Thus, it has been found in the studies performed that all the LTB single crystals under study contain a certain defect concentration, while the TSL intensity at the isodose irradiation can serve a crystal defectness criterion. It has been found that above the room temperature the temperature damping of luminescence is observed with the activation energy of Ea=0.32±0.01 eV. The availability of the trapping levels results in the discrepancy of XL temperature dependence obtained at step-by-step heating and cooling.

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ТЕРМОСТИМУЛЬОВАНА ЛЮМІНЕСЦЕНЦІЯ І РЕНТГЕНОЛЮМІНЕСЦЕНЦІЯ НЕЛЕГОВАНИХ МОНОКРИСТАЛІВ $Li_2B_4O_7$

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Проведено люмінесцентні дослідження більше 20 технологічних партій нелегованих монокристалів $Li_2B_4O_7$. Встановлено, що всі досліджувані монокристали містять певну концентрацію дефектів, а інтенсивність термостимульованої люмінесценції при ізодозному опроміненні може служити критерієм дефектності монокристалу. Виявлено, що при температурах, вищих за кімнатну, спостерігається температурне гасіння люмінесценції з енергією активації Ea=0,32±0,01 еВ.