Semiconductor Physics, Quantum Electronics & Optoelectronics. 2000. V. 3, N 2. P. 227-232.

PACS: 78.60.Kn, Ya, 07.77.Ka

Thermostimulated luminescence and the temperature dependence of X-ray luminescence of the $Li_2B_4O_7$ single crystals

B.M.Hunda, P.P.Puga, A.M.Solomon, V.M.Holovey

Institute of Electron Physics, NAS of Ukraine, 88016, Uzhgorod, Universitetska Str. 21, tel/fax (03122) 4-37-72, e-mail: iep@iep.uzhgorod.ua

Abstract. The copper-doped lithium tetraborate ($Li_2B_4O_7$:Cu) is one of the famous tissue-equivalent materials for the thermoluminescent dosimetry, being characterized by a high radiation resistivity, a linear dose dependence, a wide operation dose range and a weak dependence of the dose on the ionizing radiation energy. We have performed the thermostimulated luminescence (TSL) studies of the lithium tetraborate single crystals doped with different copper concentrations. The optimal dopant concentration ($1.91 \cdot 10^{-3}$ weight % Cu) at which the maximum TSL intensity of the high-temperature maximum is revealed has been found. It has been elucidated that the further copper concentration increase results in the TSL intensity decrease due to the concentrational damping luminescence. It has been found that for the $Li_2B_4O_7$ single crystals with the optimal Cu dopant concentration within the temperature range under study TSL is primarily due to the carriers deliverance from two local trapping levels with the $E_{t1} = 0.90 \pm 0.03$ eV, $E_{t2} = 1.72 \pm 0.07$ eV energies and the frequency factors of $4 \cdot 10^{10}$ s^{-1} and $5 \cdot 10^{16}$ s^{-1}, respectively. The occurrence of these local levels affects considerably the temperature dependence of X-ray luminescence. Above 215°C the temperature damping of luminescence is observed being well described by the Mott formula with the $E_A = 0.65 \pm 0.05$ eV activation energy.

Keywords: thermostimulated luminescence, dosimetry, $Li_2B_4O_7$, X-ray luminescence

Paper received 07.10.99; revised manuscript received 26.11.99; accepted for publication 21.03.00.

1. Introduction

The copper-doped lithium tetraborate ($Li_2B_4O_7$:Cu) is one of the famous tissue-equivalent materials for the thermoluminescent dosimetry [1,2], being characterized by a high radiation resistivity [3], a linear dose dependence, a wide operation dose range [4] and a weak dependence of the dose on the ionizing radiation energy [5]. However, due to a lower sensitivity as compared with that for the LiF-based materials, this material has gained no wide spread. It is known [6] that the monocrystalline samples possess the thermostimulated luminescence (TSL) intensity higher than that of the polycrystalline ones, as well as the lower hygroscopicity. In this relation, the objective of the present work was to study the effect of the copper concentration on the luminescent properties of the $Li_2B_4O_7$:Cu single crystals, to determine parameters of the local trapping level associated with the TSL and to investigate the temperature influence on the recombination processes.

2. Single crystal production

The LTB:Cu single crystals were grown by the Czochralski method along the [100] direction at the 3 mm/day drawing rate and 4.4 rpm rotation velocity. The initial burden ($Li_2B_4O_7$) was synthesized from the pure reactives B_2O_3 and Li_2CO_3 (with at least 99.999% basic component content) in the platinum crucible at the air. The single crystals differing by the dopant concentration were produced by sequential growing processes, the burden mass left in the crucible was determined at the beginning of each process and, as a result of calculations, the required CuO amount was added. The copper concentration in the produced single crystals was controlled by means of the photometric and atomic absorption analysis. Using this

method, two series of single crystals were produced with well reproducible luminescent properties (the temperature positions of maxima differed by not larger than ± 3°C, while their intensities - by ± 30%). One of the faces of the 5×5×0.5 mm^3 samples was polished.

3. Experimental methods and conditions

The experimental TSL curves measurements were carried out by means of an automated PC-based set-up, the hardware and software provision of which were described elsewhere [7]. The samples were preliminarily excited by a solid emission of the X-ray tube with the copper anticathode at 20 mA current and 20 kV voltage. The dose capacity was determined by irradiating the LiF:Mg, Ti samples of the certified dosimetric DTU-01 apparatus at the same conditions and was varied within the 35 to 450°C range at the $\beta = 1.15$ (or 2.90 deg/s) linear heating rates. The integral luminescence intensity was detected by the photon count method using the FEU-106 photomultiplier.

To determine the depth of the trapping levels (E_t) from the experimental TSL curves we have used different heating rates and TSL initial rise methods [2, 8]. The more detailed studies of the energy positions of the local trapping levels were carried out by the partial thermal cleaning method [9], which increases considerably the reliability of the local level energy determination. The frequency factor (W_0) was determined by substituting the maximum temperatures (T_m) and local trapping level energies (E_t) into the relation [8]:

$$E_t/kT_m^2 = W_0 \exp(-E_t/kT_m)/b, \quad (1)$$

as well as by the computer simulation of the TSL curves in the first-order luminescence kinetics approximation.

The temperature dependence of the X-ray luminescence (XL) was studied in two regimes – the dynamic (at the fixed heating rate) and the static (at the fixed temperatures) ones. In the first case the program used was similar to that applied when measuring TSL, however, the X-ray tube window was not shut down during heating. The temperature dependence of XL in the static regime was investigated by using an another program allowing one to stabilize any temperature within the 35-350°C range with the accuracy of ±0.1°C and measure the XL intensity at given temperatures. The temperature range scanning mode (from lower temperatures to the higher ones) and the scanning step were preset prior to measuring. The exciting radiation intensity was varied within the 0.03–10 Gy/s range.

4. Results and discussions

4.1. TSL concentrational dependence.

The TSL studies were performed for the nominally pure and copper-doped (at the $(0.9\text{-}38.1)\cdot10^{-3}$ weight % Cu concentrations) LTB single crystals. For the nominally pure single crystals, unlike [10], no TSL was observed in our experiments even at the 1000 Gy irradiation doses. In the non-irradiated doped single crystals, no TSL was also found. After the irradiating the doped samples by the X-rays (at the 30 Gy dose) two intense maxima (Fig. 1) were revealed in the curves – the low-temperature maximum within the 100-160°C region and the higher-temperature one at 228°C ($\beta = 2.90$ deg/s). The first maximum is non-symmetric and has quite large half-width, which testifies to its complicated nature. Probably, this maximum results from the superposition of some local trapping levels or their quasicontinuous distribution. With the increasing copper concentration in the single crystals under study, the displacement of the first maximum towards the lower temperatures is observed (Fig. 1, curves 1-7). Contrary to the low-temperature maximum, the position of the second maxsimum does not depend on the copper concentration and is almost stable when transiting from the polycrystals to the single crystals [11,12].

The dependence of the TSL maxima intensities on the copper dopant concentration is shown in Fig. 2. At low concentrations (i.e. $(0.9\text{-}4.5)\cdot10^{-3}$ weight % Cu) the first TSL maximum intensity is slightly increased, while, at the same time, that of the second maximum increases by several times. The further rise in the copper concentration results in the decrease of both TSL maxima intensities.

Such concentrational dependence of the TSL intensity may result from the concentrational luminescence damping. Evidently, due to the step-by-step interaction between the luminescence centres in LTB, the emitted energy is, finally, transferred to the luminescence damping centres. Since the probability of the step-by-step energy transfer is proportional to r^{-6}, it increases abruptly with decreasing distance (r) between the interacting centres [13]. Therefore the phenomena related to the step-by-step energy transfer are sharply enhanced with luminescent centre concentration, resulting, thus, in the TSL intensity reduction.

In our opinion, the above character of the TSL curves variation (Figs 1,2) can be explained by the peculiarities of the LTB crystalline stucture [14, 15]. The boron atom has three electrons. Being in the tetrahedral coordination, it attaches one extra electron of the cation modifying the anion network, which is involved into the LTB composition at the account of the alkali metal oxide (Li_2O). Thus, the tetrahedron complex becomes a negatively charged point defect provided it is isolated from the intermediate cation compensating the charge. Such negative effects may act as the hole traps, while the oxygen vacancies in the structure form the positively charged point defects, which can trap electrons. In some cases the electron and hole traps can be associated with the bridge-like and non-bridge-like oxygen bounds. Due to the mobility of the intermediate cathions prior to, during and after the irradiation, the cation clusters may be produced resulting in the production of extremely efficient electron centres-traps comprising several cations [13,15]. Therefore, both the electron and hole traps result, primarily, from the defects related to the basic structural units

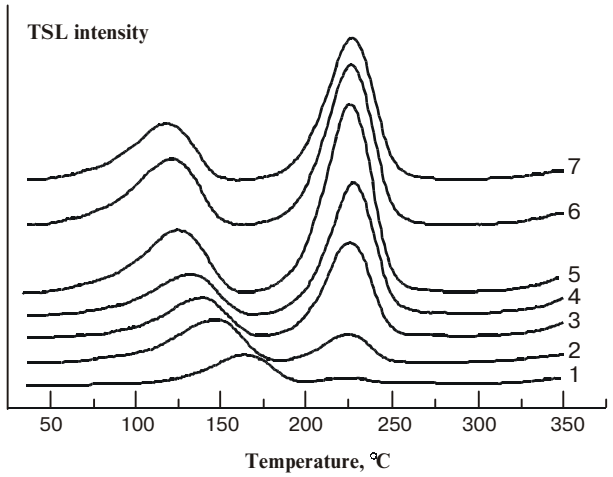

Fig. 1. TSL curves for the LTB:Cu single crystalls at different copper concentrations.

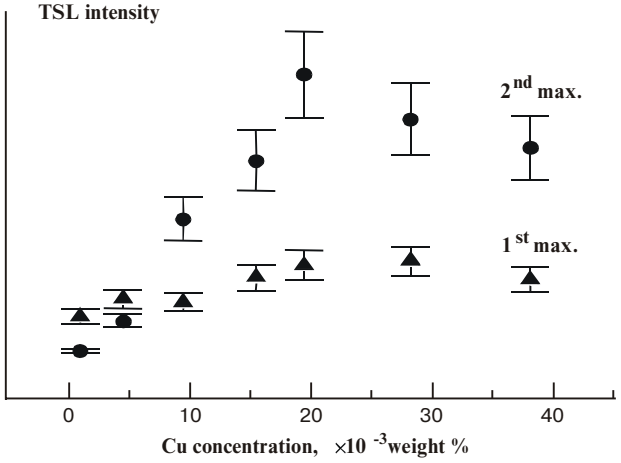

Fig. 2. Concentrational dependences of the TSL maxima.

of the lattice. Copper, involved into the crystal as the dopant, may exist in a form of the Cu^0, Cu^+ and Cu^{2+} ions. Taking into account that the atomic-ionic radius for copper (1.35 A) is less than that for lithium (1.45 A) [16], it is obvious that a certain part of the copper atoms at $Li_2B_4O_7$ doping may occupy the lithium atoms positions whereas the rest of them will be placed at the internodal sites. The copper ions also form the positively charged complexes with oxygen atom vacancies and other structural defects, therefore the carrier capture cross section increases resulting in the appearance of the maxima in the curves (Fig. 1). The emission spectrum for the $Li_2B_4O_7$:Cu crystals during TSL has a maximum near 365 nm and is due to the Cu^+ ion emission [6,15], therefore, one may assume that the TSL process in $Li_2B_4O_7$:Cu takes place by the following scheme:

$$Cu^+ \text{ irradiate} \rightarrow Cu^{2+} + e^- \text{ heat} \rightarrow$$
$$\rightarrow (Cu^+)^* \rightarrow Cu^+ + h\nu \ (3.4\,\text{eV})$$

Based on the mentioned above one may assume the following nature of the TSL curve shape variation with the copper concentration. Since the temperature position of the high-temperature maximum does not depend on the dopant concentration, it seems most reasonably to relate it to the complexes arising around the Cu^+ ions occupying the Li^+ locations. Evidently, such complexes will be more stable as compared with those produced around the Cu^+ ions in the internodal sites, and, respectively, they will be destroyed at higher temperatures. At low dopant concentrations the number of such replacements will be insignificant and, respectively, the intensity of the high-temperature TSL maximum will be very low (Fig. 1, curve 1). The rise of the copper concentration results in more effective replacement of the lithium atoms, and, correspondingly, in the formation of a larger number of high-temperature trapping centres and the rise of the high-temperature maximum intensity (Fig. 1, curves 2-5). If one relates the low-temperature maximum to the complexes produced due to the Cu^+ ions in the internodal sites, the displacement of the first maximum towards the low-temperature region with the increasing dopant concentration becomes clear. Since the LTB crystalline structure is very complicated [14, 15, 17], the internodal copper atoms will occupy certain non-equivalent positions, the number of which may by either small (about 2–3) or very large (the quasicontinuous distribution). The rise of the copper concentration results in this case in the dominant formation of certain complex types or in the enhancement of intercomplex interaction.

For the single crystals $Li_2B_4O_7$ with $19.4 \cdot 10^{-3}$ weight % Cu concentration (at which the largest intensity of the high temperature TSL maximum is observed) the local trapping level parameters have been determined and the temperature dependence of the X-ray luminescence has been studied.

4.2. Trapping level parametrization.

In order to determine the energy depth of the local trapping levels locations, the TSL curves have been obtained at different heating rates. Using the temperature values corresponding to the TSL curves maxima (115 and 217°C at β=1.15 deg/s and, respectively, 128 and 228°C at β=2.90 deg/s), the energy positions of the local trapping levels (0.7 and 1.4 eV for the first and second maxima, respectively) have been determined. Those values found by the initial TSL rise method are 0.9 eV and 1.7 eV, respectively. The use of the partial thermal cleaning method allows one to correct these values ($E_t = 0.90 \pm 0.03$ eV, $E_t = 1.72 \pm 0.07$ eV). Substituting the temperature and energy values of the maxima into (1) we obtained the parameters W_0 of $4 \cdot 10^{10}$ s^{-1} for the low-temperature and $5 \cdot 10^{16}$ s^{-1} for the high-temperature maxima, respectively. The computer modelling of the TSL curves within the first-order luminescence kinetics approximation provides the energy and frequency factor values for the high-temperature maximum, which agree well with the experimen-

tal temperature luminescence curves at different heating rates. For the low-temperature maximum a considerably larger difference between the initial areas of calculated and experimental curves is observed at the determined local trapping level parameters, testifying to the occurrence of an additional, lower-temperature maximum that decays fast at the room temperature. It follows from the studies of the local trapping level parameters that TSL in the LTB:Cu single crystals in the temperature range under study is mainly due to the deliverance of carriers from two local trapping levels with relevant energies and frequency factors (Fig. 5), not single trapping level and three frequency factors [18] or the quasicontinuous local level distribution [15] as in the case of polycrystals. At the same time the numerical values of E_t obtained in the present work agree fairly well with those found in [15], testifying to the similar character of trapping centres in the polycrystalline and monocrystalline LTB:Cu samples.

4.3. The temperature dependence of X-ray luminescence.

The temperature dependence of XL measured at the $\beta = 2.90$ deg/s heating rate is shown in Fig. 3 (curve 2). A comparison with the TSL curve for the same heating rate (Fig. 3, curve 1) shows that irradiation results in much higher intensity of luminescence within the TSL temperature range as well as above 275°C (before the XL appearance), where almost no TSL occurs. The XL intensity decreases with increasing temperature indicating the temperature damping the luminescence. The analysis of the high-temperature area of curve 2 using Mott's formula [8]:

$$I = I_0 / (1 + \exp(-E_A/kT)), \quad (2)$$

gives $E_A = 0.62 \pm 0.03$ eV. Here is the XL intensity at the temperature T, I_0 is that in the region where no damping takes place, E_A is the damping activation energy, k is the Boltzmann's constant.

The XL temperature dependence for the LTB:Cu single crystal obtained in the stationary mode at the sequential temperature rise is presented in Fig. 4 (curve ABCDEF). With increasing temperature the XL intensity first rises sharply, while above 85°C the rise is somehow reduced. At 150°C the maximum XL intensity is observed, and the further temperature increase results first in a rapid and then in the slower decrease of the luminescence intensity. The XL dependence at the step-by-step temperature decrease is shown in Fig. 4 (curve FEGHIJ). Within the 340-215°C temperature range, it is almost similar to the previous curve, but its further behaviour is considerably different. Within the 215–180°C temperature range, the XL intensity is almost constant, whereas at 175-70°C a sharp intensity increase is observed. The further temperature decrease reveals no XL intensity variation.

The exciting emission intensity variation as well as that of heating rate and temperature step do not modify the shapes of the above XL temperature dependences, but affect their intensity. The displacement of the dynamical XL maximum towards the higher temperatures with respect to the static XL maximum is due to the known TSL dependence on the heating rate [8].

It seems reasonable to explain the above XL behaviour by means of the energy level and electron process diagram shown in Fig. 5. At the LTB:Cu excitation by the X-ray radiation (process 1), the charge carriers are produced, which can be captured to the local trapping levels E_{t1} and E_{t2} (processes 2, 4), and recombine with the emission of a light quantum (processes 6, 7) or with no emission (process 8). Two maxima in the TSL curve are due to the temperature deliverance of the carriers from the trapping levels (processes 6, 7). At low temperatures the probability of non-radiative transitions (8) is low. The XL intensity in the AB area corresponds to a certain stationary state established between the processes 1-8 when the local levels E_{t1}, E_{t2} population is low. With in-

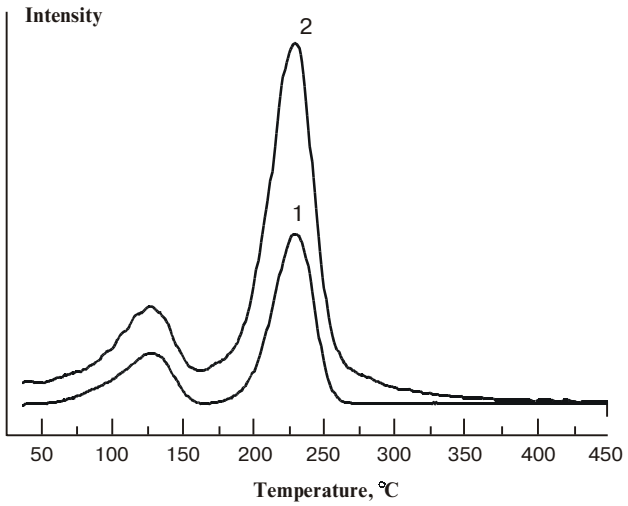

Fig. 3. TSL curve (1) and temperature dependence of the dynamical X-ray luminescence (2) at the 2.90 deg/s heating rate.

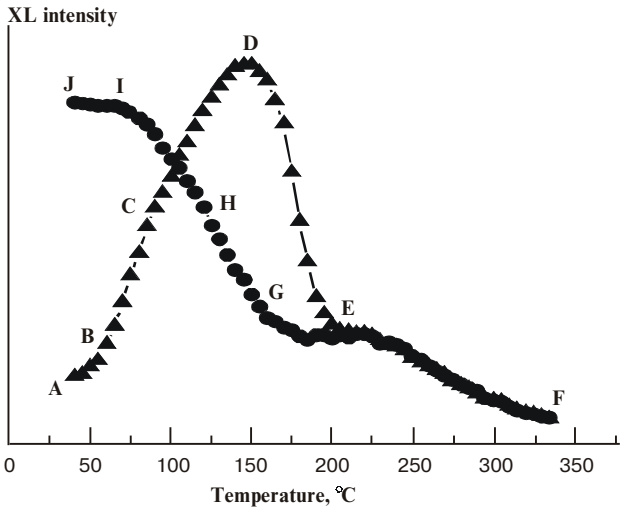

Fig. 4. Temperature dependence of the statical X-ray luminescence in the heating (ABCDEF) and cooling (FEGHIJ) modes.

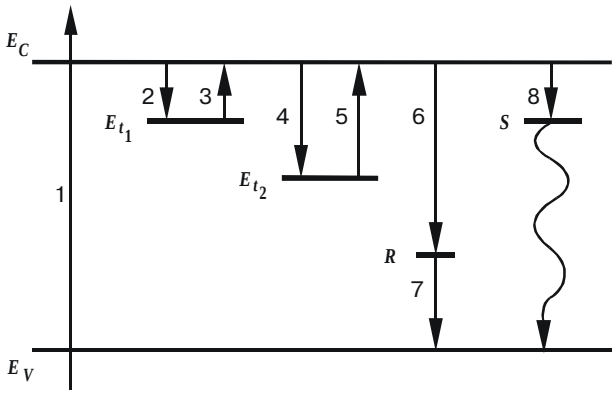

Fig. 5. Energy level and electron process diagram for the LTB:Cu single crystal.

creasing temperature the probability of accumulated carriers deliverance from the low temperature trapping level (process 3) increases, and that of the carriers capture to that level (process 2) decreases. This results in a rise of a number of carriers recombining via the transitions 6, 7, i.e. in the XL intensity increase. In the CD area, the similar capture (4) and accumulated carriers deliverance (5) from the high-temperature level E_{t2} occur, and the latter process proceeds much effectively with approaching the point D. A fast decrease of the intensity in the DE area may be due to a total depletion of levels E_{t1} and E_{t2}. During the cooling process in the E_G area the carriers are accumulated at the trapping level E_{t2}, and when their quantity becames significant, the number of carriers temperature liberated from this level (process 5) increases. Simiralry, in the HI area the processes 2, 3 occur. The XL intensity in the IJ area corresponds to a certain stationary state established between the processes 1–8, when the local levels E_{t1}, E_{t2} population is high.

The analysis of the curves obtained by Mott's formula (Fig. 4) indicates that the temperature damping XL in the 215-340°C temperature interval occurs being characterized by the activation energy 0.65 ± 0.05 eV. Since the formula (2) describes the damping of both the inner-central and recombinational luminescence, it is difficult to conclude about the mechanism of the temperature damping luminescence. Possibly, in the LTB:Cu single crystals at the temperatures above 215°C, the new non-radiative recombination levels arise (transition 8) or the IR-emission takes place, not detected in our experiments. Howerer, it seems most probable that the XL damping is due to the crossing of the potential curves of the excited and ground states of emitting center in the configuration coordinates. This results in the non-radiative transitions taking place instead of the radiative ones.

Conclusions

We have performed the TSL studies of the LTB single crystals doped with different copper concentrations. The optimal dopant concentration ($19.1 \cdot 10^{-3}$ weight % Cu) at which the maximum TSL intensity of the high-temperature maximum is revealed has been found. It has been elucidated that the further copper concentration increase results in the TSL intensity decrease due to the concentrational damping luminescence. The dopant concentration variation within the $0.9 \cdot 10^{-3}$-$38.1 \cdot 10^{-3}$ weight % Cu range results in no change of the temperature position of the high-temperature maximum, though affects considerably its intensity. For the low-temperature maxima, the intensity almost does not vary with concentration increase, but the shift towards the lower temperatures is observed.

It has been found that for the $Li_2B_4O_7$ single crystals with the optimal Cu dopant concentration within the temperature range under study TSL is primarily due to the carriers deliverance from two local trapping levels with the E_{t1} = 0.90 ± 0.03 eV, E_{t2} = 1.72 ± 0.07 eV energies and the frequency factors of $4 \cdot 10^{10} s^{-1}$ and $5 \cdot 10^{16} s^{-1}$, respectively. The occurrence of these local levels affects considerably the temperature dependence of X-ray luminescence. Above 215°C the temperature damping of luminescence is observed being well described by Mott's formula with the E_A = 0.65 ± 0.05 eV activation energy.

The studies performed indicate that the LTB:Cu single crystals possess the TSL which is by order of magnitude larger than that in the polycrystals [11,12], while the intensity of the dosimetric (high-temperature) maximum increases by nearly 40 times. The enhanced sensitivity of the LTB:Cu monocrystalline samples with respect to the polycrystalline ones makes them more promising for the thermoluminescent dosimetry.

This work was supported by the STCU (grant # 576). The authors are grateful to S.M. Sukharev for chemical analysis of the samples.

References

1. Y.S.Horowitz, The theoretical and microdosimetric basis of thermoluminescence and applications to dosimetry // *Physics in Medicine & Biology* **28**(5) pp.765-824 (1981).
2. S.W.S. McKeever, M.Moscovitch and P.D.Townsend. *Thermoluminescence dosimetry materials: properties and uses.* Nuclear Technology Publishing: Ashford (1995).
3. D.Yu.Sugak, A.O.Matkovskii, N.A.Mironova et al., in: *11th Int. Conf. on Solid State Dosimetry. Abstr.*Nuclear Technology Publishing, Ashford, England (1995) p. 64.
4. S.Lorrain, J.P.David, R.Visocecas and G.Marinello, A study of new preparations of radiothermoluminescent lithium borates with various activators // *Radiat. Prot. Dosim.* **17**(1-4) pp.385-392 (1986).
5. B.Ben-Shachar, G.L.Catchen and J.M.Hoffman, Characteristics of the Panasonic UD-802 phosphors // *Radiat. Prot. Dosim.* **27**(2) pp. 121-124 (1989).
6. M.Martini, F.Meinardi, L.Kovacs and K.Polgar, in: *11th Int. Conf. on Solid State Dosimetry. Abstr.* Nuclear Technology Publishing, Ashford, England (1995) p. 37.
7. B.M.Hunda and P.P.Puga, in: Scientific works IEP'96, Uzhgorod (1996) pp. 48-52 (In Ukrainian).
8. V.V.Serduk and Yu.F. Vaxman. *Luminescence of semiconductors,* Vishcha shkola, Kiev-Odessa (1988).
9. G.P.Blinnikov, V.N.Golonzka and A.F.Gumenjuk, Energetic spectrum of traps in $CsCdCl_3$ crystals // *Optika i spektroskopiya,* **69**(5) pp. 1054-1058 (1990) (In Russian).

10. Y.Kutomi, M.H.Kharita and S.A.Durrani, in: *11th Int. Conf. on Solid State Dosimetry. Abstr.* Nuclear Technology Publishing, Ashford, England (1995) p. 36.
11. B.M.Hunda, in: *Elementary Processes in Atomic Systems(EPAS'98). Abstr.* IEP NAS Ukr., Uzhgorod (1998) pp. 58-67 (In Ukrainian).
12. B.M.Hunda, V.M.Holovey, M.I.Holovey et al., *12th Int. Conf. on Solid State Dosimetry. Abstr.* Nuclear Technology Publishing, Ashford, England (1998) p.52.
13. I.A. Parfianovich and V.N.Salomatov, *Luminescence of crystals*, Nauka, Moscow (1988) (In Russian).
14. M.Natarajan, R.Faggiani and I.D.Brown, Dilithium tetraborate, $Li_2B_4O_7$ // *Cryst. Struct. Commun.* (8) pp. 367-370 (1979).
15. J.K.Srivastava and S.J.Supe, The thermoluminescence characterization of $Li_2B_4O_7$ doped with Cu // *J. Phys. D: Appl. Phys.* **22**(6), pp. 1537-1543 (1989).
16. A.A.Chernov, E.I.Givargizov, H.S.Bagdasarov et al., *Modern Crystallography,* **3**, Nauka, Moscow (1980) (In Russian).
17. S.F.Radaev, L.A.Muradjan, L.F.Malahova et al., Atomic structure and electronic density of lithium tetraborate $Li_2B_4O_7$ // *Kristallografiya* **34**(6), pp. 1400-1407 (1989) (In Russian)