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CONCENTRATION AND TEMPERATURE DEPENDENCE OF LUMINESCENCE FOR THE COPPER-DOPED LITHIUM TETRABORATE SINGLE CRYSTALS

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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 various amount of copper. There was found the optimal dopant concentration (19.1×10^{-3} wt. % Cu) at which the maximum TSL intensity of the high-temperature maximum occurs. Further increase of copper concentration results in the decrease of the TSL intensity due to the concentrational damping of luminescence. For the $Li_2B_4O_7$ single crystals with optimal Cu dopant concentration within the temperature range under study TSL is primarily due to the carriers released from two local trapping levels with E_{t1}= 0.90±0.03 eV, E_{t2}=1.72±0.07 eV energies and frequency factors of $4\times10^{10}s^{-1}$ and $5\times10^{16}s^{-1}$, respectively. The occurrence of these local levels has a considerable influence on the temperature dependence of X-ray luminescence. Above 215°C the temperature damping of luminescence is observed. This damping is well described by the Mott's formula with the activation energy E_A=0.65±0.05 eV.

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1. Introduction

The copper-doped lithium tetraborate ($Li_2B_4O_7$:Cu or LTB: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 single crystal samples exhibit thermostimulated luminescence (TSL) intensity higher than that of the polycrystalline ones, as well as lower hygroscopicity. The aim of the present work is to study the effect of the copper concentration on the luminescent properties of the $Li_2B_4O_7$:Cu single crystals, to determine the local trapping level parameters stipulating the TSL and to investigate the temperature influence on the recombination processes.

2. Single crystal production

The LTB:Cu single crystals were grown by 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 in normal atmosphere. The single crystals with various dopant

concentration were produced by sequential growth 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 single crystals was controlled by means of the photometric and atomic absorption analysis. Two series of single crystals were produced with reproducible luminescent properties (the positions of the maxima on the temperature scale varied under ± 3°C, while their intensities varied up to ± 30%). One of the faces of every sample was polished. Samples of size 5×5×0.5 mm were prepared for measuring.

3. Experimental methods

The TSL measurements were carried out by means of an automated PC-based set-up, whose hardware and software provision were described elsewhere [7]. The samples were preliminarily excited by the radiation of an X-ray tube provided with copper anticathode, working at 20 mA current and 20 kV voltage. The irradiation dose was determined by irradiating in the same conditions the LiF:Mg, Ti samples of a certified dosimetric DTU-01 apparatus. The temperature range 35 - 450°C was scanned at linear heating rates of β=1.15 or 2.90 deg/s. The integral luminescence intensity was detected by the photon counting 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 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_o) was determined by substituting the temperatures for maxima (T_m) and local trapping level energies (E_t) into the relation [8]:

$$E_t / k T_m^2 = W_0 \exp(-E_t / k T_m) / \beta, \quad (1)$$

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 one (at the fixed heating rate) and the static one (at the fixed temperatures). In the first case the program used was similar to that applied when measuring TSL. 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 other program allowing for the stabilization of any temperature within the 35-350°C range with the accuracy of ±0.1°C and for recording the XL intensity at given temperatures. The mode of scanning (from lower temperatures to the higher ones) and the scanning step were preset prior to measuring. The exciting radiation intensity was varied within the range 0.03-10 Gy/s.

4. Results and discussions

4.1. TSL dependence on concentration

The TSL studies were performed on pure and copper-doped ((0.9–38.1)×10^{-3} wt. % Cu) LTB single crystals. For the nominally pure single crystals, unlike the results shown in [10], no TSL was observed in our experiments even at the 1000 Gy irradiation doses. TSL was not found in the non-irradiated doped single crystals, too. After irradiating the doped samples by X-rays (by the dose of 30 Gy) 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 (β=2.90 deg/s). The first maximum is asymmetrical and exhibit a large half-width. This maximum results, probably, from the superposition of some local trapping levels or a quasicontinuous distribution of levels. 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 maximum does not depend on the copper concentration and is almost stable when one passes from polycrystalline material to single crystal one [11,12].

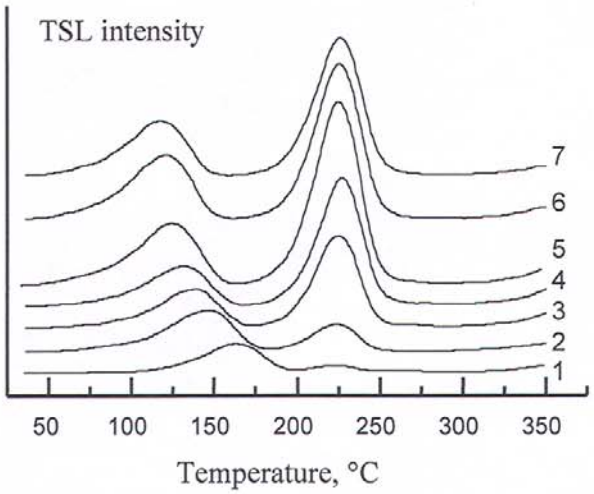

Fig. 1 TSL curves for the LTB:Cu single crystals with various copper concentrations: 0.9 (1); 4.5 (2); 9.4 (3); 15.5 (4); 19.4 (5); 28.2 (6); 381 (7) (×10^{-3} wt.% Cu).

The dependence of the TSL maxima intensities on the copper dopant concentration is shown in Fig. 2. At low concentrations (i.e. (0.9-4.5)×10^{-3} wt. % Cu) the first TSL maximum intensity is slightly increased, while, that of the second maximum increases several times. The further rise in copper concentration results in the decrease in intensity of both TSL maxima.

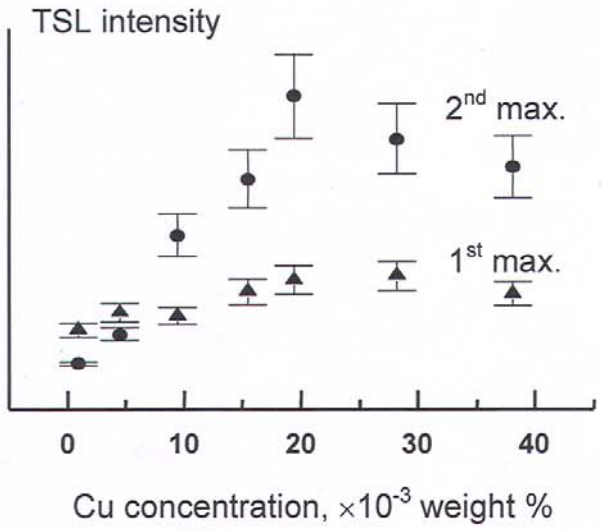

Fig. 2 Concentrational dependences of the TSL maxima.

Such dependence on concentration of the TSL intensity may result from the damping of luminescence as a function of concentraction. Obviously, 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}, then this transfer 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 when the concentration of the luminescent centres increases and this results in the decrease of the TSL intensity.

In our opinion, the particular behaviour of the TSL curves (Figs. 1, 2) can be explained by the peculiarities of the LTB crystalline stucture [14,15]. The boron atom has three electrons. In tetrahedral coordination it attaches one extra electron of the cation and modifies 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 which compensates the charge. Such negative defects 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 cations 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 of the lattice. Copper, involved into the crystal as dopant, may exist as Cu^0, Cu^+ and Cu^{2+} ions. Taking into account that the atomic-ionic radius for copper (1.35 Å) is less than that of lithium (1.45 Å) [16], it is obvious that a certain part of the copper atoms introduced in $Li_2B_4O_7$ 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 exhibits 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:

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

From the above discussion one may assume the following explication of the variation of the shape of the TSL curve 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 which occupy the Li^+ locations. Obviously, such complexes will be more stable as compared to those produced around the Cu^+ ions in the internodal sites, and, respectively, they will be destroyed at higher temperatures. At low dopant concentration the number of such replacements will be insignificant and, consequently, 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 rise of the high-temperature maximum intensity (Fig. 1, curves 2-5). If one relates the low-temperature maximum to the complexes created by the Cu^+ ions in the internodal sites, the displacement of the first maximum towards the low-temperature region with the increasing dopant concentration can be understood. 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 quasi-continuous distribution). The increase of the copper concentration results, in this case, in the dominant formation of certain types of complexes or in the enhancement of their interaction.

For the $Li_2B_4O_7$ single crystals with 19.4×10^{-3} wt. % Cu concentration (at which the largest intensity of the high temperature TSL maximum is observed) the local trapping level parameters have been defined 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, the TSL curves have been measured at different heating rates. Using the temperature values corresponding to the maxima of TSL curves (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 maximum, 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±0.03 eV E_t=1.72±0.07 eV). Substituting the temperature and energy values of the maxima into (1) we obtained for the parameter W_o the value of 4×10^{10} s^{-1} for the low-temperature and 5×10^{16} s^{-1} for the high-temperature maxima, respectively. The computer modeling 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 experimental 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 defined local trapping level parameters, proving 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 release of carriers from two local trapping levels with relevant energies and frequency factors (Fig. 5), and not from a single trapping level and three frequency factors [18] or from a 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], and this speaks in favour of the similar character of trapping centres in the polycrystalline and single crystal LTB:Cu samples.

4.3. The temperature dependence of the X-ray luminescence

The temperature dependence of XL measured at the β=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 and this point out to the temperature damping of the luminescence. The analysis of the high-temperature area of curve 2 with the use of the Mott's formula [8]:

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

gives E_A=0.62±0.03 eV. Here I 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 Boltzman's constant.

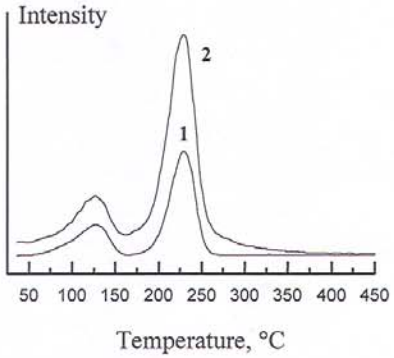

Fig. 3 TSL curve (1) and temperature dependence of the dynamical X-ray luminescence (2) at the 2.90 deg/s heating rate.

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 further temperature increase results firstly in a rapid and then in a 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.

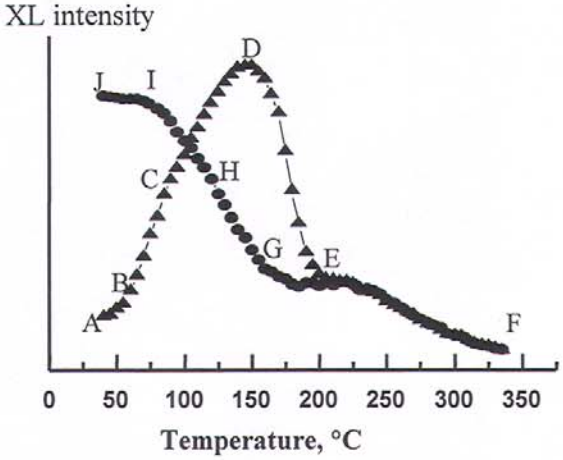

Fig. 4 Temperature dependence of the statical X-ray luminescence in the heating (ABCDEF) and cooling (FEGHIJ) regimes.

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 recombinate with the emission of a quantum of light (processes 6, 7) or without light 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 increasing 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 the number of carriers which recombine via the transitions 6, 7, i.e. in the XL intensity increase. In the CD area, the similar capture (4) and release of accumulated carriers (5) from the high-temperature level E_{t2} occur. 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 amount becomes significant, the number of

releasd carriers from this level (process 5) increases with the temperature. Simirarly, in the HI area the processes 2 and 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.

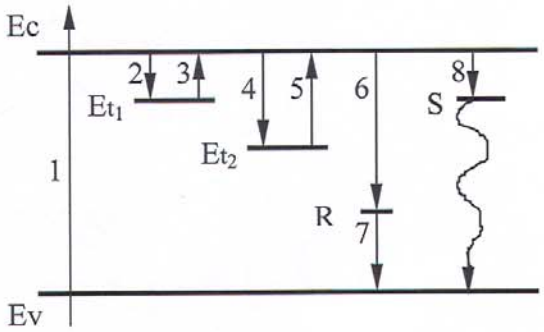

Fig. 5 Energy level and electron process diagram for the LTB:Cu single crystal.

The analysis of the curves obtained with Mott's formula (Fig. 4) indicates that in the 215-340°C temperature interval occurs the temperature damping of XL which is characterized by the activation energy 0.65±0.05 eV. Since the formula (2) describes the damping of both the inner-central and recombination luminescence, it is difficult to conclude about the mechanism of the temperature damping of 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 not detected in our experiments takes place. However, 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 that the non-radiative transitions take place instead of the radiative ones.

5. Conclusions

We have performed the TSL studies of the LTB single crystals doped with various copper concentrations. There was found the optimal dopant concentration (19.1×10^{-3} weight % Cu) at which the maximum TSL intensity of the high-temperature maximum occurs. It has been established that further copper concentration increase results in the TSL intensity decrease due to the concentrational damping of luminescence. The dopant concentration variation within the 0.9×10^{-3}-38.1×10^{-3} wt. % Cu range results in no change of the position on the temperature scale for the high-temperature maximum, its intensity is though considerably affected. For the low-temperature maxima, the intensity almost does not vary when the concentration of Cu increases, but a shift towards 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 release 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 $4\times10^{10}s^{-1}$ and $5\times10^{16}s^{-1}$, respectively. The occurrence of these local levels influences considerably the temperature dependence of X-ray luminescence. Above 215°C the temperature damping of luminescence is observed and is well described by the 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 orders of magnitude larger than that in polycrystals [11,12], while the intensity of the dosimetric (high-temperature) maximum is by nearly 40 times higher in single crystals than in polycrystals. The enhanced sensitivity of the LTB:Cu single crystal samples with respect to the polycrystalline ones makes them more promising for the thermoluminescent dosimetry.

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