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Influence of reducing annealing on the luminescent properties of $Li_2B_4O_7$:Cu single crystals

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Abstract

$Li_2B_4O_7$:Cu single-crystal annealing in the reducing environment results in a sharp drop of intensity of thermoluminescence (TSL) and X-ray luminescence (XL) peaks. It was suggested that during annealing in the reducing environment, an oxygen vacancy is produced in the LTB structure at the bridging oxygen atom site. Oxygen vacancy charge compensation takes place at the expense of reduction of the doping Cu^+ ion to the Cu^0 state. In this case the A^0-type thermoluminescence center formation mechanism due to irradiation becomes impossible.

Keywords: $Li_2B_4O_7$:Cu; Single crystal; Reducing annealing; Thermoluminescence; X-ray luminescence

1. Introduction

$Li_2B_4O_7$:Cu (LTB:Cu) thermoluminophore has found application in the personal ionizing radiation dosimetry due to advantages such as linearity of characteristics in a wide operating range and insufficient energy dependence within the 10–100 keV energy range [1–4]. The luminescent properties of the single-crystal LTB:Cu are under investigation now by many researchers and groups [5–8]. It has been found that copper addition is involved in the LTB structure at the lithium ion site [5,6]. One has to take into account that the proper genetic defects also occur in the LTB single crystals, in particular, lithium and oxygen vacancies as well as clusters related to the violation of the relation between the boron–oxygen triangles and tetrahedrons [5,9].

It is known that annealing in the reducing environment induces changes of the defect structure of oxide compounds (including doped ones). They include the oxygen vacancies formation in the anionic sublattice and the change of the charge state of ions in the cationic sublattice, in particular, the doping ones. As a rule, such reconstruction induces a certain distortion of the crystalline lattice related to displacement of a part of atoms from their previous sites, however, with conservation of their symmetry. In certain cases, the above changes become irreducible, i.e. the repeated annealing of the samples in oxidizing environment does not result in complete recovery of their structure-sensitive properties, in particular, the luminescent ones. Therefore, the goal of the present study was to find the effect of reduction and repeated oxidizing annealing on luminescent properties of LTB:Cu single crystals, in particular, due to the oxygen vacancies formation.

2. Experimental

The initial charge for LTB:Cu single-crystal production was prepared by melting preliminarily dehydrated high-purity B_2O_3, Li_2CO_3 and CuO. It contained up to 0.3 mol% of the B_2O_3 excess to compensate incongruent LTB melt evaporation losses [10]. Single crystals were grown by using the Czochralski method from the platinum

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crucibles in the ambient atmosphere towards the [1 0 0] direction at pulling and rotating velocities 3 mm/day and 5 rpm, respectively.

The specimens under study had a form of plane parallel polished 0.5 mm thick plates (5 mm OD). All the specimens did not contain gaseous and/or solid-state inclusions. Copper content in the specimens was determined using the atomic absorption analysis and reached 1.2×10^{-3} wt%. In each series of measurements of thermo-stimulated luminescence (TSL) and spectral dependence of X-ray luminescence (XL), the same "as-grown" specimen annealed in the reducing environment and repeatedly annealed in the oxidizing environment was used. Reducing annealing was carried out in the 10^{-4} Torr vacuum at 1025 ± 5 K during 48 h, while oxidizing annealing in the ambient atmosphere in the identical temperature–time regime.

TSL measurements were carried out using an automated setup with an FEU-136 photomultiplier operating in the photon-counting mode. Prior to each measurement, the specimens were thermally cleaned at 625 K for 100 s ensuring complete erasure of preliminary dosimetric information. Then the specimens were exposed to X-ray radiation produced by a copper-anticathode tube at voltage 20 kV and current 10 mA. Accumulated dose was 1.7 Gy at 0.03 Gy/s dose capacity. To prevent low-temperature peak relaxation, the TSL curves were recorded immediately after irradiating. Specimen heating rate was 0.5 K/s, and this allowed to minimize the TSL glow curve displacement to the high-temperature region due to the temperature lag [2]. Five single-crystal specimens cut from one part of a single crystal were used in our experiments. Experimental data were averaged, and the measurement uncertainty was determined in accordance with the standard procedure.

The XL spectra within the 240–650 nm were measured by means of an automated setup on the basis of an MDR-23 monochromator using a FEU-106 photomultiplier. Specimens were irradiated by the X-rays from the molibden-anticathode tube at 34 kV voltage and 20 mA current at room temperature. The spectra obtained were corrected with the spectral sensitivity of detection system being taken into account.

3. Results and discussion

The TSL curves of "as-grown" single-crystal LTB:Cu specimen annealed in the reducing environment and repeatedly annealed in the oxidizing environment are shown in Fig. 1. They are characterized by the presence of the two well-separated maxima, which agree well with Refs. [5,6,11]. The low-temperature maximum for "as-grown" specimen was observed at 374.5 ± 2.5 K, while the high-temperature one, at 473.5 ± 2.5 K. For the specimen annealed in vacuum, the TSL intensity for both peaks decreased sharply, and the intensity ratio changed in favor of the low-temperature peak, while their maxima were slightly displaced towards the low-temperature region, up to 369.5 ± 2.5 and 471 ± 2.5 K, respectively. After the repeated annealing in the ambient atmosphere the low-temperature peak intensity was partially recovered, though the maximum did not return to the previous position and remained at $369.5 + 2.5$ K. The high-temperature peak intensity also slightly increased, and the maximum returned to the previous position at 473.5 ± 2.5 K.

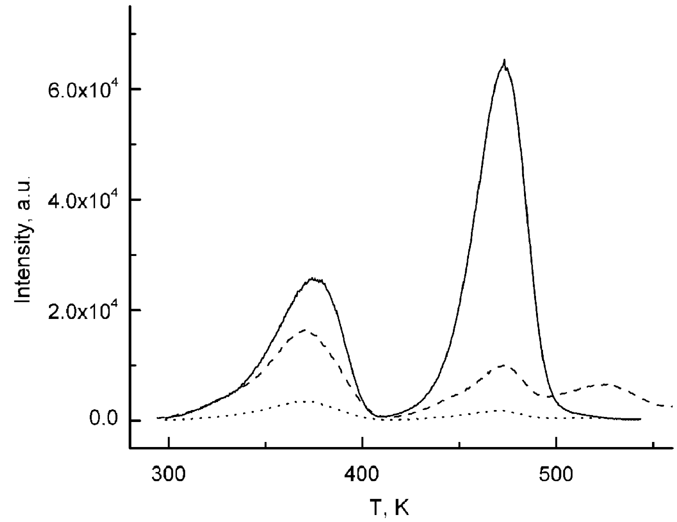

Fig. 1. SL curves for the single crystal LTB:Cu specimens: Solid line—"as-grown" specimens; dot line—vacuum-annealed; dash line—repeatedly annealed in the ambient atmosphere.

The main specific feature of the TSL curves for the specimens repeatedly annealed in the ambient atmosphere is the appearance of new high-temperature maximum at 525.5 ± 2.5 K not observed in the "as-grown" and vacuum-annealed specimens. One may assume that at more protracted annealing in the ambient atmosphere, the TSL peak intensity could be increased (for the low-temperature peak, possibly, to the initial values).

Spectral dependences of XL for "as-grown" single-crystal LTB:Cu specimens annealed in the reducing environment and repeatedly annealed in the oxidizing environment are presented in Fig. 2, and the positions of the maxima for certain peaks, in Table 1. As results from the above data, for "as-grown" specimens, besides a distinct maximum at 364 ± 2 nm, due to copper doping reported in Ref. [12] and low-intensity one at 309 ± 2 nm, another maximum was observed at 511 ± 2 mn. A complex peak in the "blue" XL spectral region (240–450 nm) could be fitted by two principal Gaussians at 298 and 364 nm (Fig. 3). Distinct maximums at 304 and 360 nm are observed in the XL spectra for non-doped LTB single crystals [9,13]. Hence, their presence should be related to the proper defects of the crystalline lattice. Vacuum annealing resulted in the decrease of intensity of both peaks in the "blue" spectral region, and underwent redistribution in favor of lower-wavelength peak. Its maximum appeared to be shifted to $318 + 2$ nm, while the