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Thermostimulated luminescence of SrB_4O_7 single crystals and glasses

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Thermostimulated luminescence (TSL) of X-ray irradiated SrB_4O_7 single crystals and glasses has been studied for the first time and compared with polycrystalline samples. The TSL of SrB_4O_7 single crystals is due to radiative recombination of charge carriers trapped on the intrinsic defects of the crystal lattice. The X-ray luminescence of SrB_4O_7 single crystals peaked at $\lambda \approx 330$ to 340 nm is ascribed to the self-trapped exciton emission. In SrB_4O_7 glasses, the TSL seems to be connected with decomposition of *F*-like centers and O^- ones.

Впервые изучена термостимулированная люминесценция (ТСЛ) монокристаллов и стекол SrB_4O_7, облученных рентгеновскими квантами, в сравнении с поликристаллами. ТСЛ монокристаллов SrB_4O_7 обусловлена излучательной рекомбинацией носителей заряда, захваченных на собственных дефектах кристаллической решетки. Рентгенолюминесценция монокристаллов SrB_4O_7 с максимумом при $\lambda \approx 330 \div 340$ нм приписывается свечению автолокализованных экситонов. ТСЛ стекол SrB_4O_7, вероятно, связана с распадом *F*-подобных и O^- центров.

The strontium tetraborate SrB_4O_7 (SBO) crystals are well-known nonlinear optics materials [1, 2]. Recently, the SBO crystal luminophors have been shown to be of promise for individual monitoring of ionizing radiation using thermoluminescence. The polycrystalline samples show an intrinsic thermostimulated luminescence (TSL) that is comparable with that of TLD-700 ($^7LiF:Mg,Ti$) [3, 4] increasing by several orders due to introduction of rare-earth activators, such as Eu or Dy [4–6].

The thermoluminescence properties of a material are known to vary considerably depending on the material defectness extent. For example, for $Li_2B_4O_7$ single crystals, appreciable distinctions in the shape and intensity of TSL curves have been observed depending on the growth conditions and the purity grade of initial materials [7]. The study of such regularities can be used to develop and optimize the procedures for estimation of a material structure perfection [8]. At the same time, literature data on the effect of SBO defectness extent on its thermoluminescence properties are rather scarce today. In this connection, the work [5] is worth to mention where the optical properties of polycrystalline strontium tetraborate storage phosphors have been tested as functions of the manufacturing conditions. There are no similar data for undoped SBO single crystals. This work is aimed at comparative consideration of radiation-sensitive properties of SBO single crystals, polycrystals, and glasses.

The SBO single crystals were grown as described in [9]. The 3 mm thick tablets of 10 mm in diameter were produced by compacting the synthesized SBO powders under 10^8 Pa loading. The synthesis was performed by solid phase technique at 700 to

900 K in air. Strontium carbonate (special purity grade) and boric acid (analytical purity grade) were used as starting components. The phase composition of final product was checked by X-ray phase analysis (XPA). For compacting, a weighed powder sample was mixed with aqueous polyvinyl alcohol solution (3 %) and triturated thoroughly. The SBO glasses were prepared by melting the pre-synthesized SrB_4O_7 in a platinum crucible. The melt was heated up to 1100°C, hold at that temperature until the complete homogenization and removal any gas bubbles, and then poured onto a platinum plate and cooled together with the furnace.

The spectral and luminescence properties of SBO samples were studied using an SDL-2 automated setup (LOMO, Russia) under excitation with a xenon lamp (for photoluminescence) or a REIS-I X-ray tube (U = 30 kV, I = 50 μA, Cu anticathode, E = 30 keV) for X-ray luminescence. The optical absorption spectra were measured using a Specord M40 UV-VIS double-beam spectrophotometer. The TSL curves were recorded using experimental setup provided with a FEU-79 PMT. The samples were heated using a RPM-2 heat controller at a rate of 5 K/min. The samples were irradiated with X-rays at room temperature using a RUP-150/300-10-1 X-ray unit (Cu anode, U = 160 kV, I = 9 mA).

The SBO single crystals belong to orthorhombic system ($P2_1$ nm space group) and have the lattice parametres a= 4.4255(7) Å, b = 10.709(2) Å, and c = 4.2341(9) Å, Z = 2 [9]. The crystal structure of the compound consists of six-member cyclic $(B_3O_9)^{9-}$ anionic groups, each comprising three $(BO_4)^{3-}$ tetrahedrons. All boron atoms are coordinated by four oxygen ones. The oxygen atoms occupy four independent positions. The voids of the 3D boron-oxygen skeleton positioned along the a and b axes are filled with strontium atoms having the coordination number 9 [2]. The SBO single crystals are transparent within the wavelength range of 130 to 3200 nm [1]. In the glasses, the intrinsic absorption maximum is in UV region ($\lambda \approx 260$ nm).

Fig. 1 presents the X-ray luminescence spectra of SBO crystals. The luminescence spectrum forms a broad band peaked at λ = 330 to 340 nm with about 1.69 eV half-width. The 330–340 luminescence band is excited in the interband transition region and it can be ascribed either to the radiative recombination of the self-trapped excitons, or to emission of excitons localized on insignificant lattice distortions, similar to that in $Li_2B_4O_7$, LiB_3O_5 and other oxide crystals [10, 11]. This supposition is confirmed by the large Stokes shift, the large emission peak half-width and the absence of excitation bands in the crystal transparency region. In [5], the photoluminescence of undoped SBO powders was observed to be different in the spectral composition from the X-ray one presented in Fig. 1. That photoluminescence is due most likely to the presence of uncontrollable impurities.

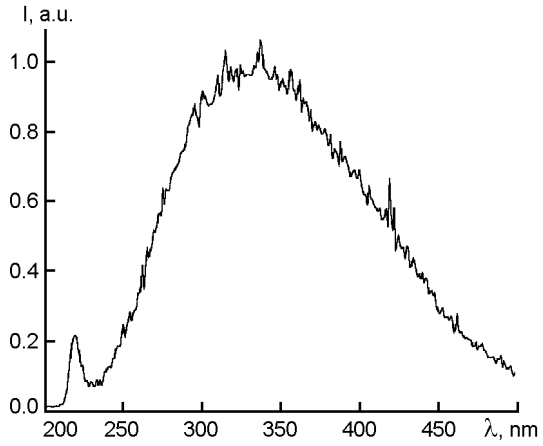

Fig. 1. X-ray luminescence spectrum of SBO single crystals.

The irradiation with X-rays or ^{60}Co quanta at doses up to 10^3 Gy does not result in any induced optical absorption of the SBO single crystals. The glasses irradiated at $9 \cdot 10^3$ R dose took the induced optical absorption in a wide spectral range. In Fig. 2, shown is the differential absorption spectrum of unirradiated and irradiated SBO glass. The differential curve is approximated well by three Gaussians peaked at 308, 367, and 510 nm (dashed lines in Fig. 2). This evidences the generation of at least three color center types in the SBO glasses due to X-ray irradiation. Consideration of literature data allowed us to ascribe the 308 nm band to the absorption of the F^+ color centers [12, 13]. The induced optical absorption in the long-wavelength spectral region may be associated with F centers [14] (the band at λ = 367 nm was ascribed to O^- centers absorption). The induced optical absorption in a close spectral region was found in glasses [14] and single crystals of LiB_3O_5 (λ = 360 nm) [15] and $Li_6Gd(BO_3)_3:Eu^{3+}$ ($\lambda \approx 365$ nm) [16]. At the same time, the borate glasses are known to contain high-temperature boron-oxygen color centers being a hole trapped at the oxygen bridge

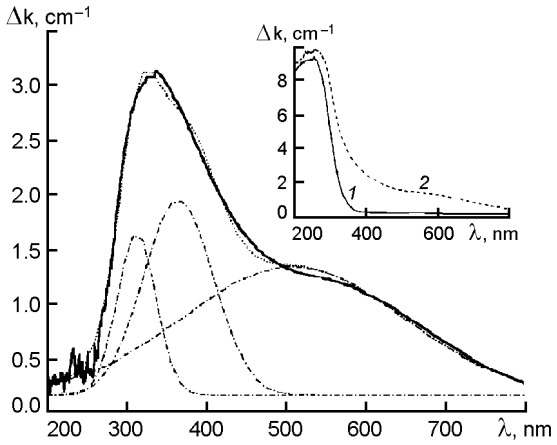

Fig. 2. Differential absorption spectrum of unirradiated and irradiated (X-quanta, 9000 R dose) SBO glass. The dashed lines show the expansion into Gaussians. Inset: absorption spectra of the glass prior to (*1*) and after (*2*) irradiation.

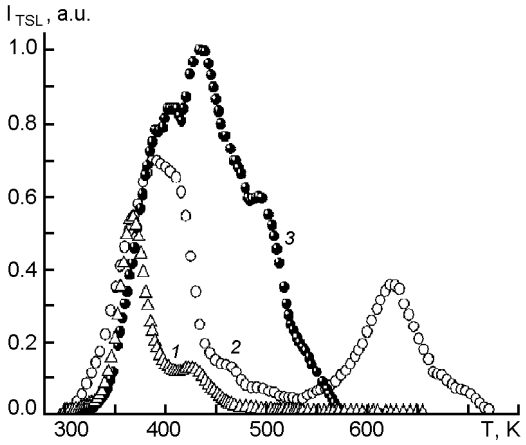

Fig. 3. TSL curves of SBO samples irradiated with X-quanta (9000 R dose): single crystal (*1*), polycrystal (*2*), glass (*3*).

connecting the tri- and tetra-coordinated boron atoms [17]. Depending on the oxygen atom local symmetry, the hole component either is localized at the oxygen atom, as in LiB_3O_5 single crystals, or belongs to the borate group as a whole, as in MgB_4O_7 crystals [18]. Thus, we suppose that the induced optical absorption of the SBO glasses may be due to the formation of *F*-like electron color centers and O^- hole ones. The glass annealed for 1 h at 600 K is completely decolored. A further investigation is necessary to correlate the induced optical absorption bands of the SBO glasses with specific color centers and TSL peaks.

The TSL of SBO samples irradiated with equal X-ray doses is shown in Fig. 3. The TSL curves of single crystals (Fig. 3, curve *1*) contain two peaks at T_1 = 367 K and T_2 = 427 K. The peak activation energy values as determined by Cheng method [19] are E_1 = 0.85 eV (first order kinetics) and E_2 = 1.22 eV (second order kinetics), respectively. For polycrystals, the TSL curve shape is the same but its intensity increases due to a higher defectness extent of the material. An additional high-temperature TSL peak at 624 K appears. The TSL peaks are obviously of the same nature in both single crystals and polycrystals. The additional 624 K TSL peak found before [4] in the latter may be associated with uncontrollable impurities in the polycrystals that are not detectable by XPA method, similar to the case of $Li_2B_4O_7$ crystals [7]. The defects at the crystalline phase boundaries may form deep trapping levels, from where the carriers are released at high temperatures [20]. We failed to estimate the activation energy of TSL peaks for SBO polycrystals, in part because the peaks are overlapping. For glasses, the TSL curves are different in shape (Fig. 3, curve *3*) and are a superposition of peaks distributed quasi-continuously in the 325 to 575 K temperature range. Three groups of peaks with maxima at 405, 430, and 490 K can be distinguished conditionally. The TSL intensity in the glasses is the highest as compared to single crystals and polycrystals, thus evidencing the presence of a large number of carrier traps, and is due to the wide variety of structure motifs realized in the glasses. Thus, in the single crystal → polycrystal → glass sequence, the TSL intensity of SBO rises with increasing defectness extent of the material.

The fact that the SBO TSL is excited with X-quanta allows to state that it is associated with the intrinsic defects of the crystal lattice. The X-quanta energy (E = 30 keV) is insufficient to create any stable radiation-induced defects according to collision mechanism, while no sub-threshold defect formation is observed in the oxides because the Frenkel couple formation energy is high as compared to AHC [21]. Thus, the X-ray luminescence of SBO single crystals peaked at 330 to 340 nm can be ascribed to emissive relaxation of self-localized excitons. The TSL intensity increase in the single crystal → polycrystal → glass sequence results from the increasing defectness extent. The SBO single crystal TSL consists of two peaks at T_1 = 367 K and T_2 = 427 K with activation energy E_1 = 0.85 eV and E_2 = 1.22 eV

and is due to the intrinsic defects of the crystal structure. The induced optical absorption of SBO glasses is like to be caused by formation of F-like electron color centers and O^- hole ones. Accordingly, the TSL of SBO glasses is due to emissive recombination of carriers released at decomposition of F, F^+, and O – centers.

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Термостимульована люмінесценція монокристалів та стекол SrB_4O_7

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Вперше вивчено термостимульовану люмінесценцію (ТСЛ) монокристалів і стекол SrB_4O_7, опромінених рентгенівськими квантами, у порівнянні з полікристалами. ТСЛ монокристалів SrB_4O_7 зумовлена випромінювальною релаксацією носіїв заряду, захоплених на власних дефектах кристалічної гратки. Рентгенолюмінесценція монокристалів SrB_4O_7 з максимумом при $\lambda \approx 330 \div 340$ нм приписується світінню автолокалізованих екситонів. ТСЛ скла SrB_4O_7, вірогідно, пов'язана з розпадом F-подібних та O^- центрів.