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TECHNICAL PHYSICS

Heat Conductivity and Thermal Expansion of Crystal Strontium Tetraborate SrB_4O_7

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Crystals of strontium tetraborate SrB_4O_7 (SBO) are a promising multipurpose material having a unique combination of physical properties. The very far edge of fundamental absorption (~120–130 nm) [1, 2], relatively high values of nonlinear optical coefficients for borates, and very high radiation resistance [2, 3] make extremely attractive the use of these single crystals for nonlinear optical conversion of radiation into the far-UV spectral region. The SBO application in nonlinear optics is restrained only by the absence of phase synchronism due to the low value of birefringence [1]. Nevertheless, the possibility of using SBO crystals for autocorrelation measurements of femtosecond pulses with ultimate nonlinear optical conversion to radiation with the wavelength of 125 nm [2] is shown. Possible schemes of wave-guide correlation of harmonics [1] are proposed. The existence of extended domain structures [4] is revealed in SBO single crystals making it possible to use them in various nonlinear optical processes [5–7]. The relatively extensive field of investigations of this compound is related to the luminescent and thermoluminescent properties of strontium tetraborate doped with various REEs. A promising trend in SBO practical use makes necessary complex investigation of its physical properties. At present, its dielectric optical, nonlinear optical, elastic, piezoelectric, and certain mechanical (crack resistance) characteristics have been investigated [1–3, 8, 9].

The purpose of this study is experimental investigation of the heat conductivity and thermal expansion of an SBO crystal in wide temperature intervals.

The single crystals used for manufacturing samples were grown by the Czochralski method from a melt with a stoichiometric ratio of components.

In this study, the crystallographic definition of SBO crystals was carried out according to [1] (the spatial symmetry group of $Pnm2_1$, the elementary cell parameters $a = 4.4255(7)$, $b = 10.709(2)$, $c = 4.2341(9)$ Å, and density $\rho = 4.011$ g/cm^3).

The blend was synthesized from "especially pure" strontium carbonate and boric acid. The components were mechanically mixed in a carbon-glass bowl with the addition of a small amount of distilled water. The mixture was heated on a sandy bath to 60–90°C and shuffled with periodic addition of small portions of water until the carbonic-gas bubbles ceased to release.

The growth of crystals was carried out on a seed oriented in the crystallographic direction b, and the extraction rate amounted to 2.4 mm/day over 6 days. A transparent colorless single crystal of ~2.5 × × 2 × 3 cm in size with a limited number of defective regions was obtained. The X-ray-phase analysis carried out on the powder of the crushed single-crystalline part confirmed the correspondence to the radiographic data [10].

From the regions of the grown single crystal containing no inclusions and twinning structures, we manufactured three oriented samples in the form of rectangular parallelepipeds of square cross section with the linear sizes of 18.240, 12.245, and 18.610 mm along the crystallographic directions a, b, and c, respectively. These samples were used when investigating the heat conductivity and thermal expansion.

The heat conductivity was determined by the absolute stationary method of the longitudinal thermal flow. The equipment and measurement technique were described in [11]. The error of determining the absolute value of heat conductivity was lower than 6%.

The thermal expansion was measured on the induction dilatometer DIL-402C NETZCH in the

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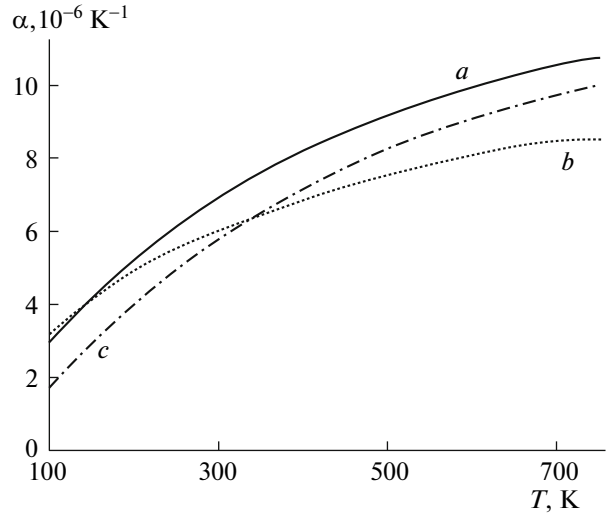

Fig. 1. Temperature dependence of linear thermal-expansion coefficients of the SrB_4O_7 crystal along the principal crystallographic directions.

range of 120–750 K in the dynamic mode with a heating rate of 3–5 K/min. For the calibration and for taking into account the expansion of the measuring system, we used standards from fused quartz. The error in determining the absolute value of thermal-expansion coefficients (TECs) was less than 5%.

The plots of the temperature dependences of the linear TECs are shown in Fig. 1. It can be seen that the TEC absolute values are typical for dielectric oxide crystals with the ionic covalent bond. We approximated the TEC temperature dependences for the three investigated directions by the 4th degree polynomial in the form

$$\alpha(T) = p_4T^4 + p_3T^3 + p_2T^2 + p_1T + p_0.$$

In the table, we listed the values of coefficients included in this polynomial.

The anisotropy of the SBO thermal expansion is well pronounced. The curves $\alpha(T)$ for the directions *a* and *c* are considerably removed from each other and have a character that is almost symbatic. In the investigated temperature interval, they are intersected by the $\alpha(T)$ plot corresponding to the direction *b*.

The results of measurements of the heat conductivity are shown in Fig. 2 as plots of the temperature dependence $k(T)$. The following features should be noted. In the low-temperature region, the highest value of the heat conductivity is shown by the sample with the long-axis direction along the crystallographic axis *a* ($k_{50\,K} = 315 \pm 19$ W/(m K)). In the temperature interval of 100–300 K, the values of $k(T)$ for the samples of the directions *a* and *c* are almost identical ($k_{300\,K} = 16.3 \pm 1.0$ W/(m K)). In the entire temperature range investigated, the lowest heat conductivity (from $k_{50\,K} = 238 \pm 14$ to $k_{300\,K} = 13.2 \pm 0.8$ W/(m K)) was found along the axis *b*. The last fact is apparently explained as follows: when moving along the axis *b*, the phonons should intersect the layers formed by rare boron–oxygen–boron covalent bonds and by the

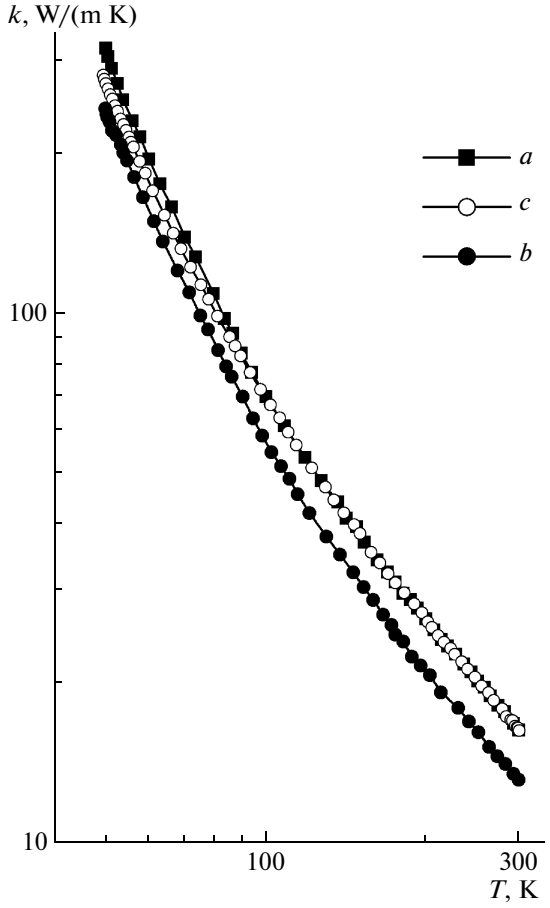

Fig. 2. Temperature dependence of heat conductivity of single-crystalline SrB_4O_7 samples along the principal crystallographic directions.

Values of coefficients p_i in the polynomial

Axis	p_4, 10^{-17} K^{-5}	p_3, 10^{-14} K^{-4}	p_2, 10^{-11} K^{-3}	p_1, 10^{-8} K^{-2}	p_0, 10^{-7} K^{-1}
a	−1.4621	4.0403	−4.9485	3.5115	−1.4314
b	−6.3089	11.889	−8.7844	3.6637	2.4346
c	−0.7534	2.4793	−3.7902	3.2593	−11.994

ionic bonds of boron–oxygen layers through the strontium ions [9].

The high degree of temperature dependence of the heat conductivity attracts attention. In all three cases, the dependence $k(T)$ is stronger than T^{-1} in the region of $T = 300$ K. Usually, such a circumstance correlates with a high fusion temperature T_{fus} of the crystal; however, in the SBO case, the value of T_{fus} is relatively low and amounts to 1273 K [1]. The extrapolation of $k(T)$ into the region of this temperature for the c direction gives a value of k exceeding 4 W/(m K). It should be noted that the extrapolation from the temperatures below room temperature determines the lattice (phonon) component of the heat conductivity, and, when approaching the melting point, it usually decreases to a value characteristic of vitreous materials (1–2 W/(m K)). For clarifying this SBO feature, we planned the calorimetric investigations for it.

The high steepness of the $k(T)$ curves in the region of $T = 50$ K and the absence of attributes of the exit onto a low-temperature maximum indicate the high degree of perfection of the structure of the single crystals grown.

As for the absolute value of the heat conductivity, it is relatively significant, especially in comparison with that for nonlinear optical crystals of other borates—LiB_3O_5 (LBO) [12] and BaB_2O_4 (BBO) [13]. The excellent elastic characteristics of SBO [8] correlate with the high value of one of the principal coefficients determining the value of heat conductivity—the average velocity of propagation of phonons (sound). When using various methods of averaging in the case of the SBO crystal, it amounts to more than 6 km/s for various crystallographic directions. The high strength qualities of an SBO crystal also correlate with the high heat conductivity [9].

It is possible to conclude that the results obtained indicate the promising use of the SBO crystal matrix as a multifunctional optical material.

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