Thermophysical parameters of the LBO crystal

S.G. Grechin, A.V. Zuev, A.E. Kokh, N.V. Moiseev, P.A. Popov, A.A. Sidorov, A.S. Fokin

Abstract. **The thermophysical parameters (linear thermal expansion coefficients, thermal conductivities, and heat capacity) of the lithium triborate (LBO) crystal are measured and compared with previously published data.**

1. Introduction

The lithium triborate crystal (LiB_3O_5, LBO) finds wide application in various problems of nonlinear optics due to a good combination of physical properties, including a large transparency range; a high effective nonlinearity coefficient; wide angular, spectral, and temperature phase matching ranges; a high level of threshold damage; etc. The use of diode pumping for solid-state lasers allowed one to design sources with high average power densities. The recent advances in the growth of large-aperture LBO crystals make it possible to use them for frequency conversion in high-energy lasers. However, to solve the problem of creating nonlinear optical frequency converters for lasers with high energies and average powers, one should study the thermophysical properties of these crystals.

As a whole, the LBO crystal properties (first of all, physical) are rather well studied and the calculated phase-matching angles, as well as the calculated spectral and angular tuning characteristics, well agree with the available experimental data. The results of the first measurements of linear thermal expansion coefficients (TECs) published in [1] showed that LBO crystals have high and anisotropic TECs, which are positive along the x and z axes and negative along

S.G. Grechin Scientific-Research Institute of Radioelectronics and Laser Technology, N.E. Bauman Moscow State Technical University, ul. Vtoraya Baumanskaya 5, 105005 Moscow, Russia; e-mail: gera@bmstu.ru;
A.V. Zuev, A.S. Fokin All-Russian Scientific Research Institute of Aviation Materials, ul. Radio 17, 105005 Moscow, Russia; e-mail: zuev.andrey@list.ru;
A.E. Kokh V.S. Sobolev Institute of Geology and Mineralogy, Siberian Branch, Russian Academy of Sciences, prosp. Akad. Koptyuga 3, 630090 Novosibirsk, Russia; e-mail: kokh@mail.ru;
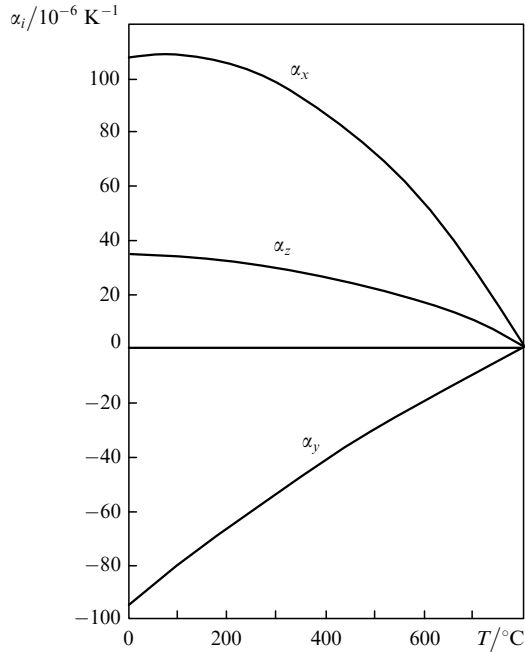**N.V. Moiseev, P.A. Popov, A.A. Sidorov** I.G. Petrovskii Bryansk State University, ul. Bezhitskaya 14, 241036 Bryansk, Russia; e-mail: nvmoiseev@mail.ru

the y axis. In conventional frequency conversion problems, the conversion efficiency is determined by the mismatch in the wave vectors and does not directly depend on the temperature expansion coefficients. However, in the case of the most general orientation of the crystal cut, the anisotropy of TECs leads to thermal deformations of the crystal faces, because of which all phase-matching ranges (angular, spectral, and temperature) can differ at different methods of crystal mounting [2].

Temperature-noncritical generation of the third harmonic of Nd^{3+} lasers and temperature-noncritical birefringence in the LBO crystal were realised in [3] and [4], respectively. The authors of [3] and [4] found that the experimental data significantly differed from the calculation results for thermal deformation variations (thermal strains), which was explained by imperfect data on the TECs of LBO crystals published in different papers. Therefore, it is necessary to perform independent measurements of the temperature expansion coefficients, as well of the thermal conductivity and heat capacity coefficients for LBO crystals.

2. Linear thermal expansion coefficients of LBO crystals

The linear thermal expansion coefficients have attracted the most attention among the whole group of thermophysical parameters. The first measurements of TECs performed in 1990 [1] were based on the measurements of a change observed in the X-ray diffraction upon heating a sample uniformly pressed in a platinum holder. The authors measured the TECs in a wide temperature range, which was necessary to optimise the crystal growth process. The temperature dependences of TECs were found based on the measured temperature dependences of lattice parameters along the main axes (Fig. 1). The approximation expressions for the temperature range $0 - 800\,°C$ are [1]*

$$\alpha_x = \left(107.1 + 32.04 \times 10^{-3}T\right.$$

$$\left. -206.3 \times 10^{-6}T^2\right) \times 10^{-6}\ (K^{-1}), \tag{1}$$

$$\alpha_y = -\left(95.35 + 148.1 \times 10^{-3}T\right.$$

$$\left. +38.49 \times 10^{-6}T^2\right) \times 10^{-6}\ (K^{-1}), \tag{2}$$

---

*In this study, the TECs are given in the crystallo-optic coordinate system (taking into account the $acb \to xyz$ relation between the coordinate systems in the LBO crystal).

Figure 1. Dependences of TECs in the temperature range $0-800\,°C$ according to [1].

$$\alpha_z = \big(33.74 + 0.34 \times 10^{-3}T$$
$$-50.67 \times 10^{-6}T^2\big) \times 10^{-6}\,(\mathrm{K}^{-1}). \tag{3}$$

A distinguishing feature of the obtained results is that all the TECs monotonically tend to zero with increasing temperature and reach zero in the region of $800\,°C$. At the temperature $T = 0\,°C$, the coefficients are: $\alpha_x = 107.1 \times 10^{-6}$ K^{-1}, $\alpha_y = -95.4 \times 10^{-6}$ K^{-1}, and $\alpha_z = 33.7 \times 10^{-6}$ K^{-1} (Table 1). Almost the same values are given in the supplemental information provided by Fujian Institute (China), Cleveland Crystals (USA), and other companies: $\alpha_x = 108.2 \times 10^{-6}$ K^{-1}, $\alpha_y = -88 \times 10^{-6}$ K^{-1}, and $\alpha_z = 33.6 \times 10^{-6}$ K^{-1}.

The data of [1] on the crystal deformations along the x and z axes were used in [5], the author of which performed a more accurate approximation of the experimental data for the temperature-induced changes in the lattice parameters and obtained the following temperature dependences of TECs:

$$\alpha_x = \big(62.6 + 332.12 \times 10^{-3}T$$
$$-584.49 \times 10^{-6}T^2\big) \times 10^{-6}\,(\mathrm{K}^{-1}), \tag{4}$$

$$\alpha_z = \big(29.859 + 28.308 \times 10^{-3}T$$
$$-88.008 \times 10^{-6}T^2\big) \times 10^{-6}\,(\mathrm{K}^{-1}). \tag{5}$$

The TECs obtained in [5] at $T = 0\,°C$ are given in Table 1. These data were used to process the measured temperature changes in the optical path and to determine the temperature derivatives of refractive indices. The results well agreed with the experimentally measured temperature tuning characteristics for different frequency conversion processes.

Table 1. TECs of LBO crystal.

$T(\Delta T)/°C$	$\alpha_x/10^{-6}\,\mathrm{K}^{-1}$	$\alpha_y/10^{-6}\,\mathrm{K}^{-1}$	$\alpha_z/10^{-6}\,\mathrm{K}^{-1}$	Literature
0	107.1	−95.4	33.7	[1]
0	62.6	–	29.86	[5]
25–150	66.4	−52.8	27.3	[6]
25–600	65.77	−62.51	29.08	[7]
25–783	57.96	−47.72	28.42	[7]
25–250	86.355	−64.477	34.741	[8]
20–530	101	−71	31	[9]
0	51.5	−43.5	22.6	This paper

The authors of a subsequent paper [6] measured the temperature expansion coefficients by a dilatometer. Although the measurements were performed in the temperature range $20-500\,°C$ and the temperature dependences of the crystal deformations were plotted (with an error not exceeding $3\,\%$), the authors published the average TECs only for the temperature region $25-150\,°C$ (Table 1). In [7], the TECs were measured by X-ray diffraction for a sample $100\,\mu m$ in size in the temperature region $25-783\,°C$ (the results for two temperature regions are given in Table 1).

With the use of a dilatometer, the authors of [8] measured TECs for a crystal defined by them as $\mathrm{Li_2O(B_2O_3)_3}$ (LOBO), which is structurally completely equivalent to the LBO crystal. The obtained TECs for the region $20-250\,°C$ are also presented in Table 1. Table 1 also contains the TECs in the region $20-530\,°C$ determined in [9] by X-ray diffraction.

Comparing the TECs measured by different methods, one can see that these coefficients differ by two and more times. This made it necessary to perform independent measurements.

## 3. Measurements of linear thermal expansion coefficients

In this study, we measured the TECs of LBO crystal by two methods: by measuring the sample size with a DIL-402 (All-Russian Scientific Research Institute of Aviation Materials) low-temperature dilatometer and by measuring the temperature-induced changes in the position of the X-ray diffraction maximum (Bryansk State University). We studied the samples of LBO crystals grown in the Institute of Geology and Metrology SB RAS under change of the heat field symmetry and its rotation [10], which had a high optical quality and a rather low optical absorption (~ 10 ppm cm^{-1} at a wavelength of 1064 nm).

The measurements in the region of $143-473$ K were performed with a DIL-402 dilatometer equipped with a cryostat. Prior to the experiment, the setup was calibrated by standard corundum and quartz samples with a heating rate of 60 K h^{-1}. The samples had a cubic shape with an edge length of 10 mm and the faces oriented perpendicular to the principal crystal axes with an error of $\pm 30'$.

For measurements in the region $55-305$ K, we used a modified DRON-3 X-ray diffractometer with a special low-temperature chamber [11]. The Bragg reflections from the crystallographic planes (001) were recorded in the Co α emission line ($\lambda = 1.78892$ Å), and the reflections from the (010) and (100) planes were measured in the Co β emission line ($\lambda = 1.62075$ Å) with an average temperature step of about 3 K. The diffraction maxima for the (001), (010) and (100) planes were observed at the angles $2\Theta \approx 152°$, $2\Theta \approx 140°$, and $2\Theta \approx 148°$, respectively. The error in the

interplane distance calculated from the Wulf–Bragg equation did not exceed $\pm 6 \times 10^{-5}$ Å. The samples of LBO crystals were $4 \times 12.5 \times 1.5$ mm in size and were heated with a rate of 60 K h^{-1}.

The measurements performed by different methods well agree with each other in both the values and the temperature dependence behaviour of TECs. The TECs measured in the temperature range 55–473 K are shown in Fig. 2. An important difference between these results and the data given in [1] (see Fig. 1) is that, in our case, the moduli of all the temperature coefficients increase with increasing temperature.
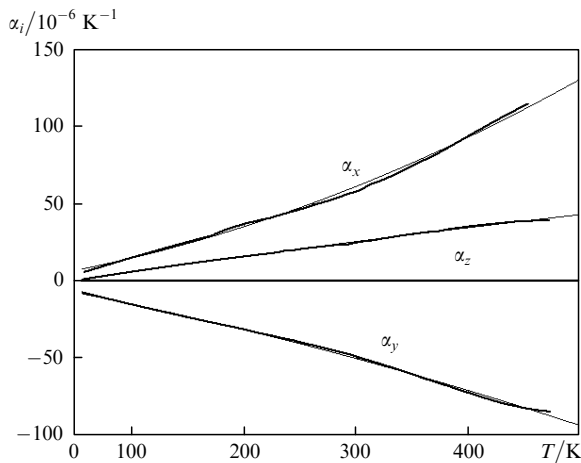
Figure 2. Dependences of TECs of LBO crystal in the temperature range 50–480 °C.

At the temperature $T = 0\,°C$, we obtained the following coefficients $\alpha_x = 51.5 \times 10^{-6}$ K^{-1}, $\alpha_y = -43.5 \times 10^{-6}$ K^{-1}, and $\alpha_z = 22.6 \times 10^{-6}$ K^{-1}, which in general agree with the results of [5–7], but considerably differ from the results of [1], [8], and [9]. At temperatures from -223 to 250 °C, the temperature dependences of TECs are approximated as follows (with an error not exceeding 2 %)*:

$$\alpha_x = (53.64 + 0.273T + 2.88 \times 10^{-4}T^2) \times 10^{-6}\ (\text{K}^{-1}), \quad (6)$$

$$\alpha_y = -(44.87 + 0.191T + 1.02 \times 10^{-4}T^2) \times 10^{-6}\ (\text{K}^{-1}), \quad (7)$$

$$\alpha_z = (23.04 + 0.094T - 0.26 \times 10^{-4}T^2) \times 10^{-6}\ (\text{K}^{-1}). \quad (8)$$

For practice, it is more convenient to use the approximation in the temperature range from -20 to 230 °C (the approximation error does not exceed 0.2 %):

$$\alpha_x = (51.37 + 0.258T + 5.51 \times 10^{-4}T^2) \times 10^{-6}\ (\text{K}^{-1}), \quad (9)$$

$$\alpha_y = -(43.256 + 0.2317T - 0.85 \times 10^{-4}T^2) \times 10^{-6}\ (\text{K}^{-1}), (10)$$

$$\alpha_z = (22.465 + 0.112T - 1.17 \times 10^{-4}T^2) \times 10^{-6}\ (\text{K}^{-1}). \quad (11)$$

4. Measurements of thermal conductivity coefficients

The thermal conductivity and its temperature dependence $k(T)$ are strongly and in a complicated manner influenced

---

*Hereinafter, all the approximation expressions are given for the temperature in Celsius degrees.

by the structural properties of the material. Therefore, *a priori* predictions of the $k(T)$ dependence are unreliable and the experimental investigations are of decisive importance. The measurements performed in [12] yielded the average thermal conductivity coefficient of 3.5 W m^{-1}K^{-1}. The thermal conductivity coefficients measured in [13] at room temperature are 3.03 ± 0.05 W m^{-1}K^{-1} along the z axis and 3.97 ± 0.05 W m^{-1}K^{-1} in the direction perpendicular to it (it was not indicated whether along the x or y axis). The websites of various companies usually give a value of 3.5 W m^{-1}K^{-1} without identification of crystallographic direction and crystal temperature.

In the present work, the thermal conductivity coefficients were measured at the Bryansk State University by the steady-state longitudinal heat flow method in the temperature range 50–300 K. The LBO crystal samples were $4 \times 4 \times 40$ mm in size, their faces being oriented along the principal axes of the crystal with an error not exceeding $30'$. The equipment and measurement technique were described in [14]; the error in determination of the thermal conductivity coefficient did not exceed 5 %. The measured dependences $k(T)$ for three optically uniform samples whose long edges were oriented along the x, y, and z crystallographic axes are given in Fig. 3 [curves (3), (2), and (1), respectively]. At $T = 50$ K, the coefficient $k(T)$ is minimum for the z axis. In contrast, in the region of $T > 100$ K, the maximum thermal conductivity is observed for the highest-order symmetry axis of the crystal lattice, which is typical for this type of crystals.
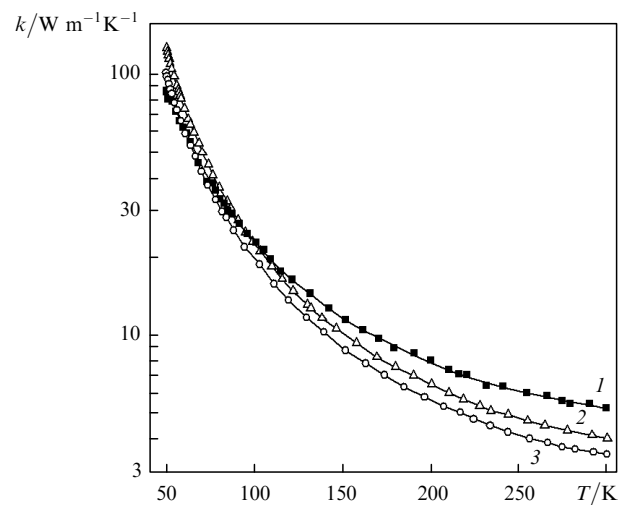
Figure 3. Dependences of the thermal conductivity coefficient of LBO crystal in the temperature range 50–300 °C.

At $T = 300$ K, the coefficients k for the x, y, and z axes were found to be 3.49 ± 0.17, 4.10 ± 0.20 и 5.20 ± 0.26 W m^{-1} K^{-1}, respectively. The approximations of dependences (1)–(3) in Fig. 3 at temperatures from -60 to 27 °C have the form (the approximation error does not exceed 0.5 %)

$$k_x = 1.9843\,\frac{273.15 + T}{143.53 + T}\ (\text{W m}^{-1}\ \text{K}^{-1}), \quad (12)$$

$$k_y = 2.3964\,\frac{273.15 + T}{148.301 + T}\ (\text{W m}^{-1}\ \text{K}^{-1}), \quad (13)$$

$$k_z = 3.1166 \frac{273.15 + T}{151.8787 + T} \text{ (W m}^{-1}\text{ K}^{-1}\text{).} \qquad (14)$$

The temperature dependence $k(T)$ of the studied samples is determined by the purity of their chemical composition and by the small amount of structural point defects. The study of the thermal conductivity of two samples oriented along the y axis with different densities of so-called growth bands revealed no pronounced deviations from the characteristics of the reference crystal. The same was observed for a sample that contained a small-angle grain boundary lying perpendicular to the x axis of the sample. In all the cases, the corresponding differences did not exceed the reproducibility error of $\pm 3\,\%$, which determined the possibility of comparing the data obtained with our experimental setup for different samples.

5. Measurement of heat capacity

The heat capacity of LBO crystal was determined experimentally in [15] and by calculations in [16]. According to [15], the heat capacity in the temperature range $80-300$ K monotonically increases from 24.74 to 121.63 J mol^{-1} K^{-1}. The LBO heat capacity calculated in the temperature range from 0 to 600 K [16] well agrees with the experimental results of [15].

In this work, to measure the heat capacity $C_p(T)$, we crushed the LBO crystals that were used to measure the thermal conductivity. The measurements were performed at the Bryansk State University by adiabatic calorimetry with stepwise heating. The $C_p(T)$ measurement method is described in [17]. The error in the heat capacity determination did not exceed $1\,\%$ in the temperature range $56-302$ K. The obtained results (Fig. 4) are almost the same as the data of [15] in the overlapped temperature regions. At temperatures from -217 to $27\,°$C, the expression approximating the dependence shown in Fig. 4 has the form

$$C_p = 950.02 + 3.153T - 0.00351T^2 \text{ (J kg}^{-1}\text{K}^{-1}\text{).} \qquad (15)$$

The heat capacity $C_p(T)$ changed from 105 ($T = -217\,°$C) to 1022 J kg^{-1}K^{-1} ($T = 29.3\,°$C) or from 12.5 ($T = 56.5$ K) to 123 J kg^{-1}K^{-1} ($T = 302.4$ K). At $T = 0\,°$C, the heat capacity was $C_p = 950$ J kg^{-1}K^{-1}.
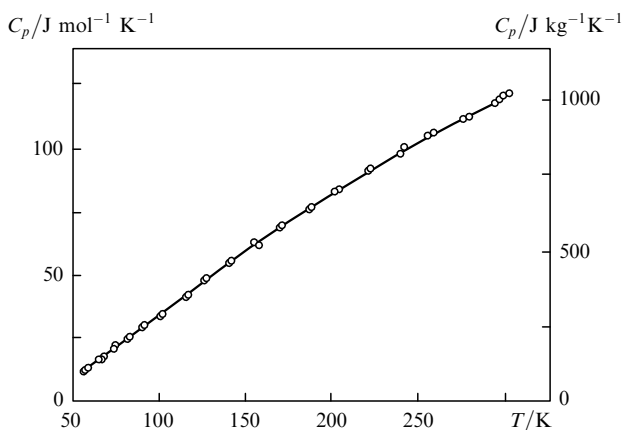
Figure 4. Dependences of the heat capacity of LBO crystal in the temperature range $50-300\,°$C.

6. Conclusions

The results taken from the literature and obtained in this study on the linear thermal expansion, thermal conductivity, and heat capacity coefficients for the LBO crystal are presented for a wide temperature range. The TECs, whose values given in different papers are noticeably different, have been measured in this study by two different methods and approximated by appropriate expressions. It is shown that the moduli of all the TECs increase with increasing temperature, which is qualitatively different from the previous results. The measured thermal conductivity and heat capacity coefficients are presented. At the temperature $T = 0\,°$C, the TECs are found to be $\alpha_x = 51.5 \times 10^{-6}$ K^{-1}, $\alpha_y = -43.5 \times 10^{-6}$ K^{-1}, and $\alpha_z = 22.6 \times 10^{-6}$ K^{-1}. The thermal conductivity coefficients at $T = 27\,°$C along the x, y, and z axes are 3.49 ± 0.1, 4.00 ± 0.20, and 5.20 ± 0.26 W m^{-1} K^{-1}, respectively. The heat capacity $C_p(T)$ changes from 105 J kg^{-1} K^{-1} at $T = -217\,°$C to 1022 J kg^{-1} K^{-1} at $T = 29.3\,°$C; the heat capacity is $C_p = 950$ J kg^{-1} K^{-1} at $T = 0\,°$C.

Since the temperature derivatives of the refractive indices have been measured, as a rule, using the previously published data on TECs, it is necessary to measure them more precisely.

References

1. Lin W., Dai G., Huang Q., Zhen A., Liang J. *J. Phys. D*, **23**, 1073 (1990).
2. Grechin S.G., Dmitriev V.G., D'yakov V.A., Pryalkin V.I. *Izv. Ross. Akad. Nauk, Ser. Fiz.*, **66**, 1103 (2002).
3. Grechin S.G., Dmitriev V.G., D'yakov V.A., Pryalkin V.I. *Kvantovaya Elektron.*, **34** (6), 565 (2004) [*Quantum Electron.*, **34** (6), 565 (2004)].
4. Grechin S.G., Dmitriev V.G., D'yakov V.A., Pryalkin V.I. *Kvantovaya Elektron.*, **30** (4), 285 (2000) [*Quantum Electron.*, **30** (4), 285 (2000)].
5. Tang Y., Cui Y., Dunn M.H. *J. Opt. Soc. Am.*, **12**, 638 (1995).
6. Guo R., Markgraf S.A., Furukawa Y., Sato M., Bhalla A.S. *J. Appl. Phys.*, **78**, 7234 (1995).
7. M.D.Mathews, A.K.Tyagi, P.N.Moorthy. *Thermochim. Acta*, **319**, 113 (1998).
8. Xia H.R., Dong S.M., Lu Q.M., Ma C.Q., Liu W.L., Li L.X., Yang Z.H. *J. Raman Spectrosc.*, **35**, 148 (2004).
9. Shepelev Yu.F., Bubnova R.S., Filatov S.K., Sennova N.A., Pilneva N.A. *J. Solid State Chem.*, **178**, 2987 (2005).
10. Kokh A., Kononova N., Mennerat G., et al. *J. Crystal Growth*, **312**, 1774 (2010).
11. Sidorov A.A. *Avtoref. kand. diss.* (Bryansk: Bryanskii GPI, 1978).
12. Beasley J.D. *Appl. Opt.*, **33**, 1000 (1994).
13. Antsygin V.D. *Avtometriya*, **1**, 2 (1998).
14. Sirota N.N., Popov P.A., Ivanov I.A. *Cryst. Res. Technol.*, **27**, 535 (1992).
15. Sheleg A.U., Dekola T.I., Tekhanovich N.P., Luginets A.M. *Fiz. Tv. Tela*, **39**, 624 (1997).
16. Maslyuk V.V., Bredow T., Pfnur H. *Europ. Phys. J. B*, **42**, 461 (2004).
17. Sirota N.N., Antyukhov A.M., Novikov V.V., Fedorov V.A. *Dokl. Akad. Nauk SSSR*, **259**, 362 (1981).