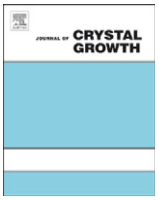
Journal of Crystal Growth 364 (2013) 46–50

Contents lists available at SciVerse ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro



Growth, thermophysical and dielectric properties of the nonlinear optical crystal CsB_3O_5

Shanshan Liu [a,b], Guochun Zhang [a,*], Kai Feng [a,b], Yicheng Wu [a]

[a] Beijing Center for Crystal Research and Development, Key Laboratory of Functional Crystals and Laser Technology, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China

[b] Graduate University of Chinese Academy of Sciences, Beijing 100049, PR China

A R T I C L E I N F O

Article history:
Received 7 September 2012
Received in revised form
10 November 2012
Accepted 27 November 2012
Communicated by: R.S. Feigelson
Available online 5 December 2012

Keywords:
A1. CsB_3O_5 (CBO)
A2. Top-seeded solution growth
B1. Borate
B2. Nonlinear optic materials

A B S T R A C T

CsB_3O_5 (CBO) single crystal, up to $47 \times 45 \times 41$ mm^3 in size and 221 g in weight, has been grown by the top-seeded solution growth (TSSG) method from Cs_2O–B_2O_3–MoO_3 system. Thermophysical properties including the specific heat, thermal diffusion, thermal conductivity, and thermal expansion were systematically investigated for the first time. The specific heat was measured to be 0.512–0.796 J g^{-1} K^{-1} in the temperature range from 25 to 300 °C. According to the measured thermal diffusion coefficients, the thermal conductivities along the *a*-, *b*-, and *c*-axis at 30 °C were calculated to be $\kappa_a = 1.43$ W m^{-1} K^{-1}, $\kappa_b = 2.50$ W m^{-1} K^{-1}, and $\kappa_c = 1.51$ W m^{-1} K^{-1}, respectively. CBO exhibits strongly anisotropic thermal expansion behavior, and the mean thermal expansion coefficients in the temperature range from 25 to 500 °C are $\alpha_a = 46.77 \times 10^{-6}$/°C, $\alpha_b = 18.39 \times 10^{-6}$/°C, and $\alpha_c = -3.80 \times 10^{-6}$/°C. The measured dielectric constants, ε_a, ε_b, and ε_c, are 8.41, 8.31, and 8.13, respectively.

1. Introduction

CsB_3O_5 (CBO) crystal possesses a relatively large effective nonlinear optical coefficient, a high laser damage threshold (26 GW/cm^2 for 1.0 ns pulses at 1053 nm), and a wide optical transparency range (167–3400 nm) [1,2]. For the generation of high power 355 nm laser by third harmonic generation (THG) of Nd:YAG laser radiation, CBO crystal is expected to be more efficient than the commercially available LiB_3O_5 (LBO) crystal [3–5]. However, the thermophysical properties of CBO crystal have not been investigated until now. In fact, the thermophysical properties of crystal play an important role in its growth and applications. If a crystal has low specific heat and thermal conductivity, and high anisotropic thermal expansion, the laser absorption will cause high thermal gradient in the crystal, which could lead to variation of refractive index, phase mismatching of the incident laser beam, and even fracture of the crystal. The specific heat is also one of the important factors that influences the damage threshold of crystals. Meanwhile, the thermal expansion should also be considered in the growth of large size and high quality crystals because the thermal stress in different crystallophysical directions can induce dislocations, striations or cracks during growing and cooling.

In the past few years, the as-grown CBO crystals usually had scattering centers, which are harmful to thermal diffusion. Recently, large CBO crystals without scattering centers have successfully been grown by the top-seeded solution growth (TSSG) method from Cs_2O–B_2O_3–MoO_3 system. In the present work, the thermophysical properties of the CBO crystals, such as the specific heat, thermal expansion coefficient, and thermal conductivity, have been measured for the first time. The relationship between the thermal expansion and crystal structure has also been discussed. In addition, the dielectric constants of CBO crystal have been reported.

2. Experimental procedure

CBO single crystal has been grown by the TSSG method from Cs_2O–B_2O_3–MoO_3 system. The detailed growth procedures are similar to that of Ref. [6]. High-purity reagents Cs_2CO_3, H_3BO_3, and MoO_3 in an optimized molar ratio of 2:3:2.5 were accurately weighed, mixed homogeneously in an agate mortar and then melted in a platinum crucible 90 mm in diameter and 80 mm in height in several batches. The crucible was placed in a three-zone resistance-heated furnace in order to get a temperature distribution of 1 °C/6 cm in the axis direction. A Shimaden FP23 controller with an accuracy of ±0.1 °C was used to control furnace temperature and cooling rate. The mixture was heated to 750 °C, stirring with a platinum stirrer for 48 h in order to ensure that the solution melted completely and mixed homogeneously. Using the testing seed crystal method, the saturation temperature was determined to be about 611 °C. A seed oriented along [100]-direction was slowly dipped into the solution at 650 °C, and the solution was held at this temperature for half an hour

---

[*] Corresponding author. Tel./fax: +86 10 82543726.
E-mail address: gczhang@mail.ipc.ac.cn (G. Zhang).

0022-0248/$ - see front matter Crown Copyright © 2012 Published by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jcrysgro.2012.11.060

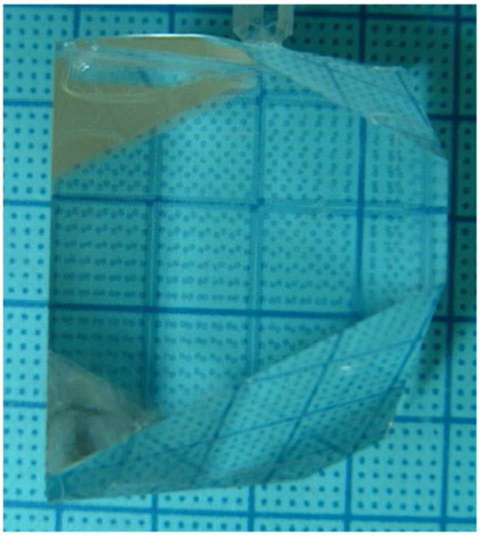


Fig. 1. As-grown CBO crystal ($47 \times 45 \times 41$ mm^3, 221 g).

to dissolve the outer surface of the seed. After that, the temperature was lowered to 611 °C at a rate of 30 °C/h, and then decreased at a rate of 0.2 °C/day until the end of the growth. The growing crystal was rotated, and the rotation rates were varied from 50 rpm at the initial growth to 20 rpm at later stage of growth. When the growth was finished after 2 months, the crystal was pulled out of the solution and cooled to room temperature at a rate of about 15 °C/h. As a result, a CBO single crystal, upto $47 \times 45 \times 41$ mm^3 in size and 221 g in weight, has been successfully grown, as shown in Fig. 1. The obtained crystal has good quality, and there are no scattering centers under 532 nm laser radiation. All the wafers used in the measurements were cut from this crystal, and then polished.

The specific heat measurement was performed on a simultaneous thermal analyzer (NETZSCH DSC 200F3) by the differential scanning calorimetry method using the 27.16 mg powder sample of CBO crystal. The measurement was made from 25 to 300 °C at a heating rate of 5 K/min. The thermal expansion was measured in the temperature range of 25–500 °C in air at the heating rate of 5 K/min using a thermal dilatometer TMA (Perkin–Elemer). The crystal samples with dimensions of $9.62 \times 4 \times 4$ $(a \times b \times c)$ mm^3, $4 \times 9.62 \times 4$ $(a \times b \times c)$ mm^3, and $4 \times 4 \times 9.60$ $(a \times b \times c)$ mm^3 were used for thermal expansion measurements. The thermal diffusion coefficient was measured by the laser flash method using a laser flash apparatus (NETZSCHLFA447 Nanoflash) in the temperature range from 30 to 290 °C. The used samples are three pieces of $10 \times 10 \times 2$ mm^3 in the directions of $(b \times c \times a)$, $(a \times c \times b)$, and $(a \times b \times c)$, respectively. The two faces perpendicular to the *a*-direction of the first sample and those perpendicular to the *c*-directions of the second one were polished and then coated with graphite to enhance the absorption of flash energy and the emission of IR radiation. The ac dielectric property was measured using complex *I–V* method based on a precision lock-in technique [7]. The samples used for dielectric property measurement were made into three thin flakes with thickness lower than 1 mm in the direction of *a*-, *b*-, and *c*-axis, respectively.

3. Results and discussion

3.1. Specific heat

Specific heat is one of the important factors that influences the laser damage threshold. The higher the specific heat, the higher is the damage threshold of the crystal during pulse laser operation [8,9]. Fig. 2 shows the dependence of the specific heat (Cp) of the crystal on the temperature.

From the curve, it can be seen that the specific heat of CBO crystal increases slowly from 0.512 to 0.796 J g^{-1} K^{-1} in the measured temperature range of 25–300 °C. The values are lower than that of LBO and $CsLiB_6O_{10}$ (CLBO) crystals and slightly larger than that of β-BaB_2O_4 (BBO) crystal [10]. By a least-square method, the dependence of specific heat of CBO crystal on the temperature is expressed as

$$Cp = 0.4993 + 7.681 \times 10^{-4} \times T + 2.293 \times 10^{-7} \times T^2 \tag{1}$$

where T is temperature from 25 to 300 °C.

3.2. Thermal diffusion and thermal conductivity

The thermal conductivity of crystal is of great importance from both fundamental and applied perspective. The service life of crystal and the output beam quality of lasers could be greatly influenced by the thermal conductivity of the crystal. The crystal morphology, size, and growth period are also directly related to the thermal conductivity of the crystal [11]. In our experiment, the thermal diffusion coefficients of the CBO crystal along the *a*-, *b*-, and *c*-axis were measured directly in the temperature range of 30–290 °C. The results are shown in Fig. 3. It can be seen that the thermal diffusivity of CBO decrease with increasing temperature, and the thermal diffusion coefficients are anisotropic. Thermal diffusion coefficient along the *a* direction is 0.83 mm^2 s^{-1} at 30 °C and 0.46 mm^2 s^{-1} at 290 °C, along the *b* direction, 1.46 mm^2 s^{-1} at 30 °C and 0.82 mm^2 s^{-1} at 290 °C, and along the *c* direction, 0.84 mm^2 s^{-1} at 30 °C and 0.52 mm^2 s^{-1} at 290 °C, respectively.

The correlations between thermal diffusion coefficient (λ) and temperature are fitted by a least-square method. The equations are expressed as

$$\lambda_a = 0.9180 - 0.0028 \times T + 4.3357 \times 10^{-6} \times T^2 - 2.3996 \times 10^{-10} \times T^3 \tag{2}$$

$$\lambda_b = 1.6015 - 0.0053 \times T + 1.1013 \times 10^{-5} \times T^2 - 7.3722 \times 10^{-9} \times T^3 \tag{3}$$

$$\lambda_c = 0.9673 - 0.0032 \times T + 7.5584 \times 10^{-6} \times T^2 - 7.1794 \times 10^{-9} \times T^3 \tag{4}$$

where T is temperature from 30 to 290 °C.

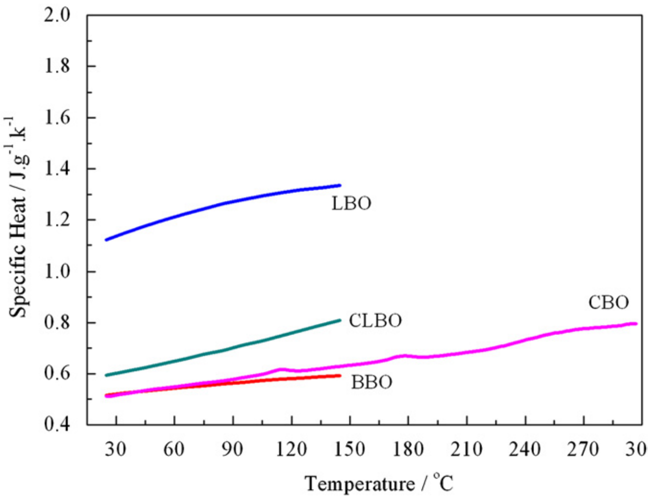


Fig. 2. Specific heat of CBO crystal.