Materials Science and Engineering B 130 (2006) 206–209

MATERIALS SCIENCE & ENGINEERING B

www.elsevier.com/locate/mseb

Thermal conductivity of $BaWO_4$ single crystal

Donggang Ran [a,*], Hairui Xia [a,b], Shangqian Sun [a], Zongcheng Ling [a], Wenwei Ge [b,c], Huaijin Zhang [b,c]

[a] School of Physics and Microelectronics, Shandong University, Shandong, Jinan 250100, PR China
[b] State Key Laboratory of Crystal Materials, Shandong University, Shandong, Jinan 250100, PR China
[c] Institute of Crystal Materials, Shandong University, Shandong, Jinan 250100, PR China

Received 5 December 2005; received in revised form 14 March 2006; accepted 15 March 2006

Abstract

Barium tungstate ($BaWO_4$) single crystal has been grown using Czochralski technique. It belongs to the scheelite structure, forming the space group $I4_1/a$ at room temperature and the primitive cell contains two formular units. The thermal expansion, specific heat and thermal diffusivity were measured, and then the thermal conductivity was calculated. These results show that $BaWO_4$ possesses large anisotropic thermal expansion and its thermal expansion coefficients are $\alpha_a = 1.10 \times 10^{-5}$/K, $\alpha_b = 1.08 \times 10^{-5}$/K, and $\alpha_c = 3.51 \times 10^{-5}$/K in the temperature range from 303 to 1423 K. However, its thermal conductivity shows small anisotropic in the temperature range from 297 to 563 K and even displays isotropic at about 428 K. The calculated thermal conductivities are 2.59 and 2.73 W m^{-1} K^{-1} at room temperature, along [1 0 0] and [0 0 1] directions, respectively.

Keywords: $BaWO_4$ crystal; Thermal properties

1. Introduction

In recent years, much attention has been paid to the research of all-solid-state Raman lasers based on stimulated Raman scattering (SRS) in crystals [1–7]. Applications of such lasers include lidar and ladar measurements, medical treatment, laser guide stars or up-conversion fiber lasers, spectroscopy and so on. SRS allows shifting laser radiation frequency with a certain energy shift that is determined by the crystal structure of Raman materials. At present, the most commonly used Raman-active crystals are $Ba(NO_3)_2$ and $KGd(WO_4)_2$ [8–12]. Among the tungstate crystals, $BaWO_4$ is proposed to be a universal Raman-active crystal for its high gain in both nano- and pico-second pumping regimes [7,8,13,14]. Among the thermal properties, thermal expansion, specific heat, thermal diffusivity and thermal conductivity have great influence on crystal growth, processing and applications in all-solid-state Raman lasers. During the Raman lasers working, the Raman-active crystal absorbs energy from the pump source and deposit as heat due to the inelastic nature of the SRS process, which is called thermal loading. The thermal loading must be taken into account in Raman lasers designs, especially for scaling devices to higher average powers [15], because the thermal loading would cause a temperature gradient in the crystal and lead to thermal expansion, and the thermal expansion would cause thermal lensing and thermal-optic effects. Otherwise, if the crystal possesses excellent thermal properties, the crystal would be stable and high quality laser beams would be obtained.

In this paper, the thermal expansion, specific heat, thermal diffusivity and thermal conductivity of $BaWO_4$ were investigated.

2. Experiments

2.1. Crystal growth

Polycrystalline $BaWO_4$ was synthesized through a solid-state reaction with high-purity (99.9%) $BaCO_3$ and WO_3 in a platinum crucible. A $BaWO_4$ single crystal up to 22 mm diameter × 80 mm length was grown using the Czochralski method with an iridium crucible, which was heated by a 2-kHz intermediate frequency furnace [16].

2.2. Thermal expansion measurements

In order to investigate cracking problem of the crystal, thermal expansion measurements were planned by using a thermal

* Corresponding author. Tel.: +86 531 8837 8422; fax: +86 531 8837 7031.
E-mail address: rdg@mail.sdu.edu.cn (D. Ran).

0921-5107/$ – see front matter
doi:10.1016/j.mseb.2006.03.018

dilatometer (NETZSCH DIL 402C) in the temperature range from 303 to 1423 K and thermal expansion ratio versus temperature curves along *a*, *b*, and *c* crystallographic directions were measured. Sample for the measurement was carefully cut into a rectangular piece of 7.80 mm × 6.14 mm × 4.32 mm ($a \times b \times c$) then the sample was annealed. During the measurements, the sample was heated at a constant rate of 10 K/min.

2.3. Specific heat measurement

Specific heat was measured by the method of differential scanning calorimeter (DSC) using a simultaneous thermal analyzer (NETZSCH DSC 204 F1) made by NETZSCH Company. A small piece of $BaWO_4$ crystal weighting 42.09 mg was used for the measurement. First, two empty Pt–Rh crucibles were heated together to carry out the baseline measurement. Second, a sapphire calibration sample weighing 42.05 mg was kept in one of the two Pt–Rh crucibles and the $BaWO_4$ sample was placed in another Pt–Rh crucible and third, the temperature of two crucibles was raised from 336 to 573 K at a constant rate of 10 K/min. Finally, the specific heat of $BaWO_4$ crystal was calculated by a comparison method using the C_p software package provided by the NETZSCH Company.

2.4. Thermal diffusivity measurements

The thermal diffusivity of $BaWO_4$ crystal was measured by the laser flash method using a flash diffusivity instrument (NETZSCH Nanoflash LFA 447) in the temperature range from 297 to 563 K. Two pieces of square wafers (8 mm × 8 mm × 1.82 mm and 8 mm × 8 mm × 2.0 mm) having polished faces perpendicular to the [1 0 0] and [0 0 1] crystallographic directions were used to carry out the measurements. In order to enhance the absorption of flash energy and the emission of IR radiation to the detector, the sample have been coated with graphite on both sides. During the experiment, a short light pulse heated the front surface of the plan-parallel $BaWO_4$ wafer and the temperature rise on the rear surface was measured versus time using an IR detector. The thermal diffusivity of the crystal was calculated using analytical software provided by the NETZSCH Company.

3. Results and discussion

3.1. Thermal expansion

As we known, the ratio of the change in volume to the change in temperature is the thermal expansion. The thermal expansion coefficient is a second rank tensor [17], for tetragonal crystal, there are only two independent principal elements of the thermal expansion tensor $\alpha_1 = \alpha_2$ and α_3. The values of α_1, α_2 and α_3 can be obtained by measuring the thermal expansion of the *a*-, *b*- and *c*-oriented crystal samples. The average linear thermal expansion can be defined as:

$$\bar{\alpha} = \frac{\Delta L}{L_0}\frac{1}{\Delta T}, \quad (1)$$

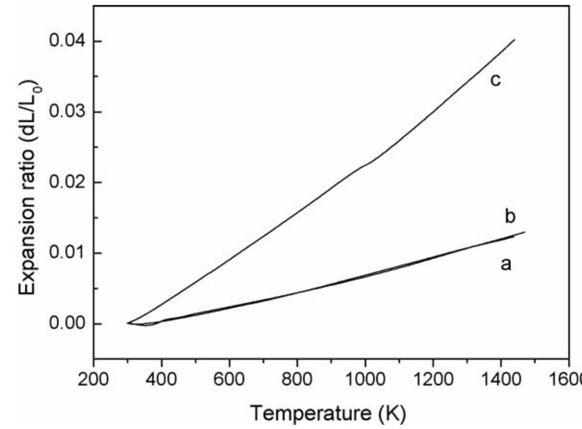

Fig. 1. The thermal-expansion ratio curves of $BaWO_4$ crystal along *a*-, *b*- and *c*-axes, respectively.

where ΔL and ΔT are the length change and temperature change, respectively. L_0 is the sample length at initial temperature.

Fig. 1 shows the thermal expansion ratio curves of $BaWO_4$ along the three crystallographic axes. In the above-mentioned temperature interval, no abrupt expansion coefficient in the three directions is observed. From Fig. 1, it can be seen that $BaWO_4$ crystal shows only thermal expansion when it was heated, which means that all the thermal expansion coefficients are positive. The average thermal expansion coefficients, which were calculated with the formula (2) from Fig. 1, are $\alpha_a = 1.10 \times 10^{-5}$/K, $\alpha_b = 1.08 \times 10^{-5}$/K, and $\alpha_c = 3.51 \times 10^{-5}$/K. The volume thermal expansion is just the sum of the linear thermal expansion of the three directions along crystalline axes. Similarly, the coefficient of volume (bulk) expansion α_v is $\alpha_a + \alpha_b + \alpha_c = 5.69 \times 10^{-5}$/K, the sum of the three linear coefficient of thermal expansion.

These small expansion coefficients of $BaWO_4$ as a Raman laser crystal are just as expected. From the results of the thermal expansion of $BaWO_4$ crystal, it can also be seen that $BaWO_4$ crystal exhibits strong anisotropic thermal expansion along the different crystallographic axes, which can explain why the $BaWO_4$ crystal is easy to cleave along the crystallographic plane of (0 0 1) in the processing of Raman laser crystal and growth.

The reason for the large anisotropic thermal expansion can be explained by the structure of this crystal. The maximum thermal expansion occurs in [0 0 1] direction, where the ions form a Ba^{2+}–Ba^{2+}–$[WO_4]^{2-}$–$[WO_4]^{2-}$ conjunction, which has lower chemical bond. When it was heated, the weaker structure makes it easily prolonged. Along [1 0 0] direction, they form a Ba^{2+}–$[WO_4]^{2-}$–Ba^{2+}–$[WO_4]^{2-}$ conjunction, which has a relatively larger chemical bond. So compared with the former, it is not changed distinctively with the temperature.

3.2. Specific heat

The ratio of the change in energy to the change in temperature is the specific heat. Specific heat also is one of important factors that affect the damage threshold of a laser crystal. Fig. 2 shows the specific heat curve of $BaWO_4$ crystal in the temperature