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Flux growth and thermal properties of $LiBaB_9O_{15}$ single crystal

Shujuan Han [a], Jiyang Wang [a,*], Jing Li [a], Yongjie Guo [a], Yongzheng Wang [a], Lanling Zhao [a], Yang Zhang [a], R.I. Boughton [b]

[a] State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, PR China
[b] Department of Physics and Astronomy, Bowling Green State University, Bowling Green, OH 43403, USA

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ABSTRACT

A large $LiBaB_9O_{15}$ single crystal has been grown by the top-seeded solution growth (TSSG) method using a $Li_2Mo_3O_{10}$ flux system. The crystal obtained exhibits (1 1 0), (1 1 3) and (1 0 2) faces. For the first time, thermal properties of the as-grown crystal, including thermal expansion, specific heat and thermal conductivity, have been investigated as a function of temperature. The specific heat of the $LiBaB_9O_{15}$ crystal was measured to be 0.663–1.110 J g^{-1} K^{-1} over the temperature range of 20–400 °C. The crystal exhibits thermal expansion along the *a*- and *b*-axis, coupled with thermal contraction along the *c*-axis, over the measured temperature range of 25–500 °C. The average thermal expansion coefficients along the *a*- and *c*-axis of the $LiBaB_9O_{15}$ crystal from 25 to 500 °C are calculated to be $\alpha_a = 6.56 \times 10^{-6}$ K^{-1} and $\alpha_c = -4.82 \times 10^{-6}$ K^{-1}, respectively.

1. Introduction

Borates, due to the possible 3- or 4-fold coordination of boron atoms, form a great number of compounds having diverse structures. For this reason borates have been widely studied and even now promising new borate compounds are still being discovered [1–8]. Studies of alkali metal and alkaline-earth-metal borates have produced a large family of compounds with outstanding physical properties, such as β-BaB_2O_4 [9] and LiB_3O_5 [10]. Ternary borates have also been synthesized and structurally characterized [11–14]. Recently, great interest has been directed to the investigation of new crystal systems, especially the ternary borates, which have not been widely studied in the past.

Single crystals of $LiBaB_9O_{15}$ were first synthesized by Penin et al. using a cooling process from the stoichiometric melt [15]. They reported that $LiBaB_9O_{15}$ crystallizes in the trigonal system with space group *R*3*c*. Nanoborate $LiBaB_9O_{15}$ was obtained by Pushcharovsky et al. with hydrothermal synthesis systems [16]. The structure was solved in $R\bar{3}c$ space group by them. In addition, we reported flux growth and spectroscopic studies of $LiBaB_9O_{15}$ [11]. However, up to now, there have no reports on the thermal properties of single crystal $LiBaB_9O_{15}$.

As is well known, thermal properties such as the thermal expansion, specific heat and thermal conductivity of a crystal have a significant influence on crystal growth, wafer processing and other applications [17–19]. If a crystal possesses a large anisotropy in its thermal expansion, a low specific heat and low thermal conductivity, it can easily be cracked during growth and processing if the temperature gradient is too large. The thermal properties should therefore be regarded as important parameters for assessing possible practical applications of a particular crystal.

In this paper, we report the growth and measurement of the thermal properties of single crystal $LiBaB_9O_{15}$, including thermal expansion, specific heat and thermal conductivity. In addition, the relation between the structure and thermal expansion has been discussed.

2. Experimental

2.1. Crystal growth and processing

A large $LiBaB_9O_{15}$ single crystal with dimensions up to $33 \times 31 \times 19$ mm^3 has been grown by the top-seeded solution growth (TSSG) method from a $Li_2Mo_3O_{10}$ flux system. The mass ratio between solute and solvent is 1:6. Starting materials for the preparation of the crystal consist of the oxides, Li_2CO_3, $BaCO_3$, H_3BO_3, MoO_3, with purities of 99.95%, 99.99%, 99.99% and 99.99%, respectively. The weighed materials were completely mixed and placed in a platinum crucible with dimensions of Ø70 × 80 mm^2. The platinum crucible was then covered with a lid and was placed in the center of a vertical furnace. The furnace temperature was measured by a Pt–Rh thermocouple and controlled by a FP-21 digital microprocessor temperature programmer controller. The mixture was heated up to 1060 °C and held at this temperature for

* Corresponding author. Tel.: +86 0531 88364340; fax: +86 0531 88564963.
E-mail address: jywang@sdu.edu.cn (J. Wang).

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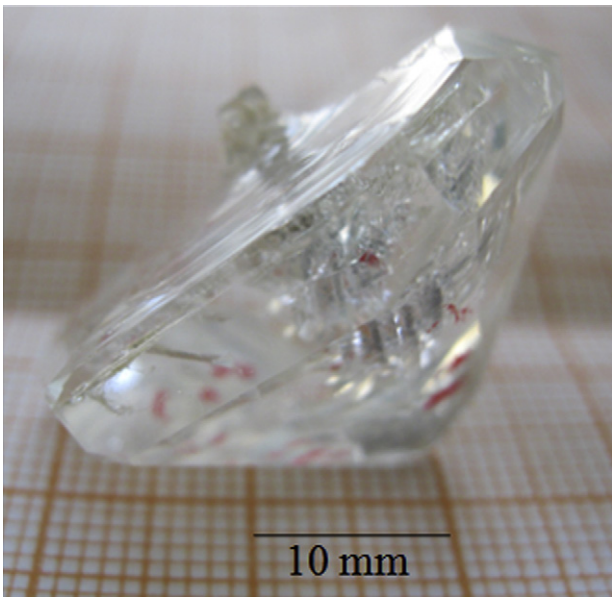

Fig. 1. Photograph of the as-grown $LiBaB_9O_{15}$ crystal.

30 h to retain homogeneous convection in the high temperature solution. The seeds were cut along the *c*-axis from crystal obtained and reported elsewhere [11]. The saturation temperature was measured by using the seed-tentative method. The selected seed was immersed into the solution and rotated at 15 rpm. The temperature was reduced at a rate of 0.5–1 °C per day from the saturation temperature. The period of growth ranged from 40 to 50 days. Fig. 1 shows the as-grown $LiBaB_9O_{15}$ crystal. The crystal morphology is good. On the basis of the XRD data and interfacial angle measurements, the crystal was found to be bounded by the (1 1 0), (1 1 3), and (1 0 2) faces.

2.2. Density measurement

The room temperature density of the $LiBaB_9O_{15}$ crystal was measured by using the buoyancy method. The density is calculated by

$$\rho_{exp} = \frac{m_0 \rho_{water}}{m_0 - m_1}$$

where m_0 is the sample weight in air, m_1 is the sample weight immersed in distilled water, and ρ_{water} is the density of distilled water at room temperature. The density was determined by averaging the values obtained for the three samples fabricated in this experiment. The density can also be calculated from the crystal structure. The theoretical density was calculated using the following equation:

$$\rho_{theory} = \frac{MZ}{N_A V}$$

where M is the atomic weight of the crystal, Z is the number of molecules per unit cell, N_A is Avogadro's number and V is the volume of the unit cell.

2.3. Single-crystal X-ray diffraction

Crystals suitable for single-crystal X-ray diffraction data collection are selected and cut to the desired dimensions of $0.14 \times 0.13 \times 0.10\ mm^3$ which were mounted on glass fiber with epoxy. Data were collected in the 2θ range from 3.21° to 27.40° using a Bruker APEX2 CCD area-detector diffractometer with graphite monochromated Mo KR radiation ($\lambda = 0.71073$ Å) at 293 K. The structure was solved by the direct method and refined by full-matrix least-squares methods on F^2 using SHELXL-97 (Sheldrick, 1997).

2.4. Thermal expansion measurement

The thermal expansion of the $LiBaB_9O_{15}$ crystal was measured as a function of temperature up to 500 °C by using a thermal dilatometer (Diamond TMA made by Perkin-Elmer). The sample was cut from the as-grown crystal into a specimen with dimensions of $7 \times 6 \times 5\ mm^3$ ($a \times b \times c$). The thermal expansion was measured along the crystallographic axes by heating at 5 °C min^{-1}.

2.5. Specific heat measurement

The specific heat was measured by using a differential scanning calorimetry using a simultaneous thermal analyzer (Diamond DSC made by Perkin-Elmer) at a heating rate of 10 K min^{-1}.

2.6. Thermal diffusion coefficient measurement

The thermal diffusion coefficient of the crystal was measured along the crystallographic axis by the laser flash method using a laser flash apparatus (NETZSCH LFA 447 Nanoflash). Two wafer pieces of the same size of $4 \times 4 \times 1\ mm^3$ oriented perpendicular to the *a*- and *c*-axis were prepared for thermal diffusion coefficient measurements. Prior to measurement, both the front and back faces of the specimens were coated with graphite to prevent the direct transmission of the laser beam through the translucent specimens. During the experiment, a short light pulse is used to heat the front surface of the wafer, and the temperature rise versus time on the opposite surface is measured using an IR detector over the temperature range from 20 to 400 °C.

3. Results and discussion

3.1. Density

Using the cell parameters determined with the XRPD method, we calculated the density of the crystal to be 2.702 g cm^{-3}. By comparison, the buoyancy method measurements give an average experimental density of 2.709 g cm^{-3} (Table 1), which is in good agreement with the calculated value.

3.2. Thermal expansion and crystal structure

For a trigonal crystal like $LiBaB_9O_{15}$, the thermal expansion coefficient tensor with respect to the crystal axes in the conventional orientation is

$$\begin{pmatrix} \alpha_{11} & 0 & 0 \\ 0 & \alpha_{11} & 0 \\ 0 & 0 & \alpha_{33} \end{pmatrix}$$

There are only two independent principal thermal components, α_{11} and α_{33}. They can be obtained by measuring the thermal expansion of the *a*- and *c*-axis oriented crystal samples. Fig. 2

Table 1
Density measurement of $LiBaB_9O_{15}$ crystal.

Samples	m_0	m_1	ρ_{exp} (g cm^{-3})	ρ_{av} (g cm^{-3})	ρ_{theory} (g cm^{-3})
1	4.400	2.775	2.707		
2	4.551	2.874	2.713	2.709	2.702
3	1.004	0.633	2.706		