2846 *Chem. Mater.* **2009,** *21,* 2846–2850
DOI:10.1021/cm900560x

CHEMISTRY OF MATERIALS
Article

Growth, Structure, and Optical Properties of a Congruent Melting Oxyborate, $Bi_2ZnOB_2O_6$

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Received February 25, 2009. Revised Manuscript Received May 4, 2009

A single crystal of $Bi_2ZnOB_2O_6$ has been grown with sizes up to $18 \times 13 \times 6$ mm^3 by the top-seeded growth method for the first time with high quality. It crystallizes in the orthorhombic system, space group *Pba*2 with unit-cell parameters $a = 10.8200(7)$ Å, $b = 11.0014(7)$ Å, $c = 4.8896(3)$ Å, $Z = 4$, $V = 582.03(6)$ Å^3. $Bi_2ZnOB_2O_6$ has a three-dimensional network consisting of $ZnB_2O_7^{6-}$ layers alternating with six-coordinated Bi^{3+} cations along the *c* axis. Transmission spectrum of $Bi_2ZnOB_2O_6$ crystal was reported. The refractive indices of the crystal were measured by the minimum deviation technique and fitted to the Sellmeier equations. The powder second-harmonic generation (SHG) properties measured by the Kurtz−Perry method indicate that $Bi_2ZnOB_2O_6$ is phase-matchable.

Introduction

In recent years, there has been considerable progress in the development of coherent sources based on nonlinear optical (NLO) crystals, especially borate crystals.[1−16] The success of these crystals can be attributed to the unique structural characteristics of boron−oxygen groups.[17] A number of borate crystals such as β-BaB_2O_4 (BBO),[18] LiB_3O_5 (LBO),[19] CsB_3O_5 (CBO),[20] and $CsLiB_6O_{10}$ (CLBO)[21] are useful NLO materials for efficient second harmonic generation (SHG) of Nd:YAG lasers. BiB_3O_6 (BIBO) is a relatively new NLO material that has attracted more attention recently for its large SHG effect.[22] Theoretical studies have shown that the BO_3 and BiO_4 anionic groups in BIBO are the main contribution to the linear and nonlinear properties.[23,24] Considering these excellent properties of BO_3 and BiO_4 group, we expect that the combination of the bismuth cation and another metal cation in borate crystal may generate a whole new class of NLO materials. A broad search for new NLO materials in the ternary $Bi_2O_3-MO-B_2O_3$ system led to a new NLO crystal $Bi_2ZnOB_2O_6$ (BZB).

The $Bi_2ZnB_2O_7$ compound was first reported by J. Barbier et al.; its sructure has been determined by powder X-ray diffraction (XRD) and refined by the Rietveld method using powder neutron diffraction data.[25] M. Li et al. prepared $Bi_2ZnB_2O_7$ by solid-state reactions and got the crystal with size $0.4 \times 0.4 \times 0.5$ mm^3.[26] The growth of crystals large enough for the measurements of linear and NLO properties has not been

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 Published on Web 05/21/2009

reported in the literature. On study of the Bi_2O_3−ZnO−B_2O_3 system, we found that $Bi_2ZnB_2O_7$ may be formulated as $Bi_2ZnOB_2O_6$, and it melts congruently; thus BZB crystal could be grown from a stoichiometric melt. Its lower melt point (no more than 700 °C), nonviscous properties, as well as the congruent melting in nature make it easy to grow sizable BZB single crystals. In this work, we present the crystal growth, crystal structure, and linear and nonlinear optical properties of BZB.

Experimental Section

Compound Synthesis. Polycrystalline samples of BZB were synthesized via solid-state reactions from powder mixtures of Bi_2O_3 (99.0%, Tianjin Benchmark Chemical Reagent Co., Ltd.), ZnO (99.5%, Tianjin Benchmark Chemical Reagent Co., Ltd.), and H_3BO_3 (99.5%, Tianjin Baishi Chemical Co., Ltd.). The stoichiometric mixture of Bi_2O_3 (46.596 g, 0.1 mol), ZnO (8.141 g, 0.1 mol), and H_3BO_3 (12.367 g, 0.2 mol) was ground thoroughly. The sample was heated to 630 °C slowly and hold at this temperature for 48 h with several intermediate grindings and mixings. The purity of the sample was checked by XRD diffraction shown in Figure S1 (see the Supporting Information). BZB compounds were performed at room temperature on a Bruker D8 ADVANCE X-ray diffractometer with graphite monochromatized Cu $K\alpha$ radiation. The diffraction patterns were taken from 10 to 70° (2θ) with a scan step width of 0.02° and a fixed counting time of 1 s/step. The experimental XRD pattern of BZB is in agreement with the calculated one based on its single-crystal data, suggesting that the synthesized phase is pure (see Figure S1 in the Supporting Information).

Differential Thermal Analysis. The melting behaviors of BZB were investigated by differential thermal analysis (DTA) using a NETZSCH STA 449C simultaneous analyzer under static air. The sample and reference (Al_2O_3) were enclosed in Pt crucibles, heated from room temperature to 970 °C at a rate of 10 °C/min.

Crystal Growth. BZB single crystal was grown by the top-seeded growth method from stoichiometric composition melt. The BZB compound with 60 g was put into a platinum crucible. The growth furnace was quickly heated to 800 °C, kept at that temperature for 15 h, and then quickly cooled to 693 °C. Meanwhile, the seed crystal was introduced into liquid surface at 693 °C for 15 min to dissolve the outer surface of the seed crystal. The temperature of the furnace was lowered quickly to 690 °C, and then held at this temperature for 40 h. When the growth of crystal ended, it was lifted out of the liquid surface. The furnace was then cooled to room temperature at a rate of 20 °C/h. As a result, transparent BZB crystal, shown in Figure 1, with a size of 18 mm × 13 mm × 6 mm was obtained in 3 days.

Structure Determination. The crystal structure of BZB was investigated by single-crystal X-ray diffraction on a Bruker SMART APEX II CCD diffractometer using monochromatic Mo $K\alpha$ radiation (λ = 0.71073 Å) at 100(2) K and integrated with the SAINT program.[27] All calculations were performed with programs from the SHELXTL crystallographic software package.[28] The structure was solved by direct methods. A face-indexed absorption correction was performed using the XPREP program, followed by the SADABS program;[29] equivalent reflections were then averaged. Final least-squares refinement is on F_o^2 with data having $F_o^2 \geq 2\sigma(F_o^2)$. The final difference Fourier synthesis may have shown maximum and minimum peaks at 1.236 (0.75 Å from Bi(2)) and −0.824 e Å^{-3} (1.25 Å from O(2)), respectively. The structure was checked for missing symmetry elements with PLATON.[30] Crystal data and structure refinement information are summarized in Table S1 (see the Supporting Information). The final refined atomic positions and isotropic thermal parameters are given in Table S2 in the Supporting Information. The main interatomic distances and angles are listed in Table S3 in the Supporting Information. (Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-391477, or from the CIF file in the Supporting Information.)

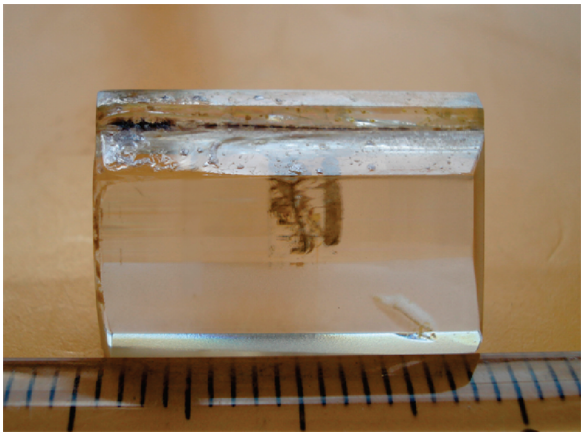

Figure 1. Photograph of BZB crystal. (The minimum scale of the ruler is one millimeter.)

Elemental Analysis. Elemental analysis of BZB single crystal was measured by using a VISTA-PRO CCD Simultaneous ICP-OES. The crystal samples were dissolved in nitric acid at the boiling point for 1 h.

Second-Harmonic Generation Measurement. The Kurtz-Perry method[31] is a simple and quick experimental technique that requires only the material in powder form to estimate its NLO effect and phase-matching properties before the effort is made to grow large single crystals. The powder SHG test was carried out on the BZB sample by the Kurtz−Perry method. The BZB compound was powdered to approximate spherical shape and graded by standard sieves to obtain distinct particle size (in diameter) ranges, <20, 20−38, 38−55, 55−88, 88−105, 105−150, and 150−200 μm. The samples were then placed in a 0.2 mm thick quartz cell and irradiated by a Q-switched Nd:YAG solid-state laser (1064 nm, 10 kHz, 10 ns). We measured the intensity of the frequency-doubled output emitted from the sample using a photomultiplier tube. The second harmonic efficiency of the BZB sample was compared with that of a standard powder sample of KDP (KH_2PO_4). A digital oscilloscope was used to view the SHG signal and $I^{2\omega}/I^{2\omega}_{(KDP)}$ was taken for a particle size range from 55 to 88 μm.

Optical Transmission Characteristics. The UV−vis−NIR transmittance spectrum was recorded at room temperature using a Perkin-Elmer Lambda 900 UV/vis/NIR spectrophotometer in the wavelength range from 200 to 3000 nm. The plate sample used was 2 mm thick and polished on both sides.

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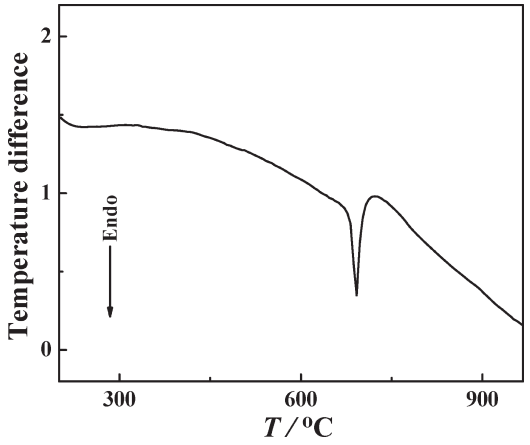

Figure 2. DTA curve of BZB.

Refractive-Index Dispersion Measurements. The refractive indices of BZB were measured by the minimum-deviation method between 400 and 1068 nm at room temperature. Because BZB belongs to orthorhombic crystal system and has a space group of *Pba*2, two prisms are needed to measure all of its refractive indices.

Results and Discussion

The DTA curve of BZB is shown in Figure 2. It shows one endothermic peak at 692 °C on the heating curve, which tentatively suggests that BZB melts congruently at 692 °C. To verify that BZB melts congruently, BZB compound powder (5 g) was put into a platinum crucible and heated to 900 °C, then slowly cooled to room temperature. Analysis of the powder XRD pattern of the solidified melt revealed that the solid product exhibited a diffraction pattern identical to that of the initial BZB powder, shown in Figure S2 (see the Supporting Information), further demonstrating that BZB is a congruently melting compound. Therefore, large crystals of BZB may be grown from stoichiometric melt, which was also verified by the following crystal growth experiments.

BZB crystallizes in the noncentrosymmetric orthorhombic space group *Pba*2. The structure is shown in Figure 3. Two unique bismuth atoms, one unique zinc atom, two boron atoms, and eight oxygen atoms are in the asymmetric unit. It has a three-dimensional network consisting of $ZnB_2O_7^{6-}$ layers alternating with six-coordinated Bi^{3+} cations along *c* axis. Except for the O(2) atom (see Figure 3), all the others are borate oxygens. As a result, the BZB compound is an oxyborate which can be formulated as $Bi_2ZnOB_2O_6$.

The bond valence sums of each atom in BZB were calculated and are listed in Table S4 in the Supporting Information. These valence sums agree with the expected oxidation states.

The ratio of the elements of a BZB crystal from the ICP elemental analysis was Bi:Zn:B = 1.959:1:2.001. It corresponded to the proportion of the result determined by crystal structure, thus it was reasonable to define the chemical formula of as-grown crystal as $Bi_2ZnOB_2O_6$.

Figure 4 gives the curves of SHG signal as a function of particle size from the measurements made on ground

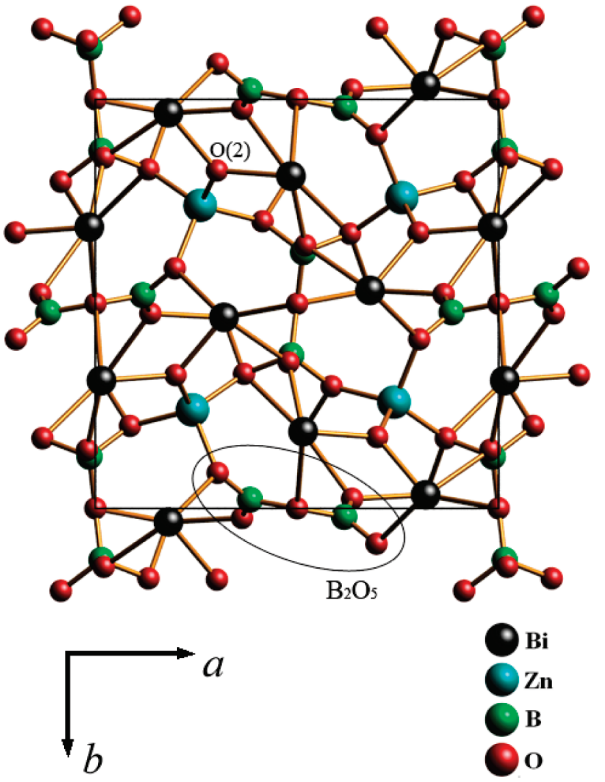

Figure 3. Drawing of the structure of BZB viewed down the *c* axis.

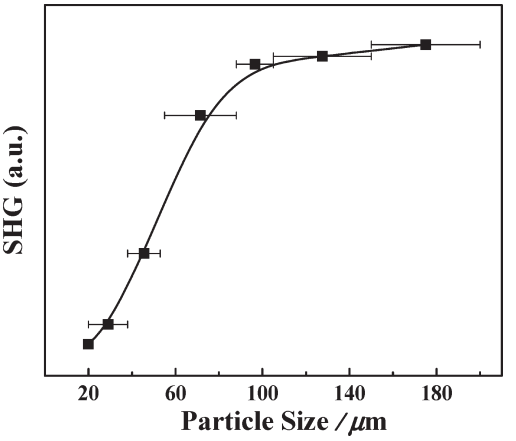

Figure 4. Phase-matching curve, i.e., particle size vs SHG intensity, for BZB. The solid curve drawn is to guide the eye and is not a fit to the data.

BZB crystals. As the particle size of BZB becomes significantly larger than the coherence length of the material, the SHG intensity is independent of particle sizes. It was consistent with the phase-matching behavior according to the rule proposed by Kurtz and Perry,[31] and BZB was found to have a powder SHG effect about 3−4 times as large as that of KDP standard of similar grain size. According to the anionic group theory of NLO effect,[32] the contribution of the borate groups to the SHG effect can be predicted qualitatively. Though the BO_3 trigonal planar ionic groups in B_2O_5 dimers seem to opposite to each other, they remain a certain angle actually, which is

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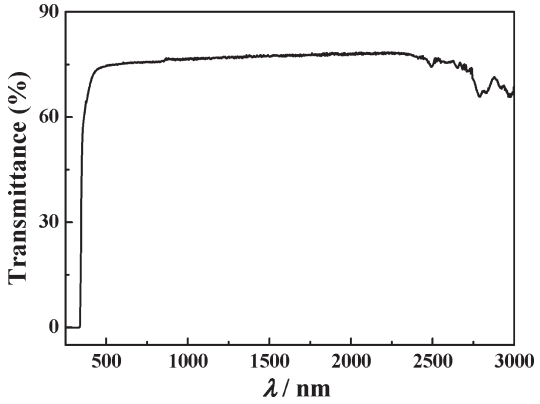

Figure 5. Transmission spectrum of BZB crystal.

responsible for the large SHG effects. Moreover, like other noncentrosymmetric oxides,[33−35] the polarizable Bi^{3+} cations that contain lone-pair electrons in BiO_6 polyhedra also make a great contribution to the SHG effect.[36,37]

Figure 5 shows the transmittance spectrum of the BZB crystal at room temperature. As shown in Figure 5, a wide transmission range from 330 to 3000 nm is observed in the UV-vis-IR region. The ultraviolet cutoff edge is about 330 nm, which is more accurate than the results obtained from powder diffuse reflectance (absorption edge at about 360 nm).[26]

The values of room-temperature refractive indices indicate that BZB crystal is positive biaxial optical crystal. The Sellmeier equations, which are fitted with the measured refractive indices, are as follows:

$$n_x^2 = 4.05894 + 0.07743336/(\lambda^2 - 0.05031004) - 0.01020891\lambda^2$$

$$n_y^2 = 4.21015 + 0.08095297/(\lambda^2 - 0.04688094) - 0.02019926\lambda^2$$

$$n_z^2 = 4.37721 + 0.09408252/(\lambda^2 - 0.05175977) - 0.01752041\lambda^2$$

where the wavelength, λ, is in micrometers. The values calculated from them are exactly consistent with experimental ones to the third decimal place, and there is only a small error even to the fourth decimal place. Figure 6 shows the measured and fitted refractive index data for n_x, n_y, and n_z. The Sellmeier equations predict that the phase matching range of fundamental wavelength is from 981 to 4533 nm. Phase matching angles for type I SHG of 1064 nm in the XY plane and YZ plane calculated from the Sellmeier equations are $\theta = 90°$, $\varphi = 53°$ and $\theta = 57°$, $\varphi = 90°$, respectively.

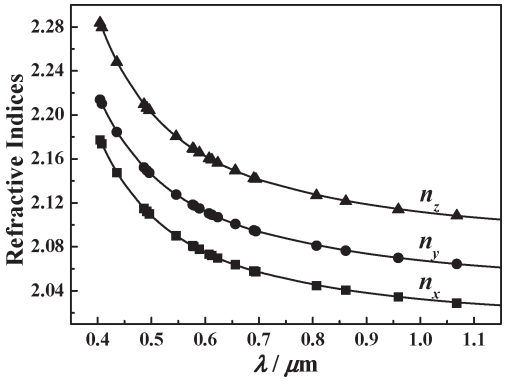

Figure 6. Refractive index dispersion curves of BZB crystal. The points are experimental values; curves are the fits given by the Sellmeier equations.

A BZB crystal with weight of 0.523 g was soaked in water for one week at room temperature, and the weight of this crystal did not change when it was taken out. Again, the weight was maintained at 0.523 g when it was put into boiling water for 1 day. Moreover, the crystal faces of this sample were lucent and transparent as its original state. Obviously, the BZB crystal is nonhygroscopic, very deliquescence-resistant, and of course, not soluble in water. The measured hardness of the BZB crystal is approximately 4−5 Mohs, close to that of BBO. During the growth, cutting and polishing, BZB crystal has never been cracked or split. The chemical stability and the good mechanical properties make it easy to cut, polish, and coat by normal processing.

Conclusion

In summary, a large and transparent BZB single crystal has been successfully grown by the top-seeded growth method from stoichiometric composition melt. It is easy to grow a large single crystal because of its congruent melting characteristic, nonviscosity melts, and lower melting point. It consists of $ZnB_2O_7^{6-}$ layers alternating with six-coordinated Bi^{3+} cations and exhibits a SHG effect about 3−4 times that of KDP. It is a positive biaxial optical crystal with large birefringence and has a wide SHG phase matching range. Moreover, it has very good deliquescence resistance, excellent cracking resistance, and moderate hardness. These advantages make it attractive for continued research and development as a NLO material.

Acknowledgment. The authors thank Professor Yadong Li for his valuable discussions. This work is supported by the National Natural Science Foundation of China (Grant 50802110), the Natural Science Foundation of Xinjiang Uygur Autonomous Region of China (Grant 200821159), the "High Technology Research and Development Program" of Xinjiang Uygur Autonomous Region of China (Grant 200816120), the Excellent "One Hundred Talented

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People" of The Chinese Academy of Sciences, and the West Light Foundation of The Chinese Academy of Sciences.

Supporting Information Available: X-ray crystallographic file (CIF); crystal data and structure refinement; atomic coordinates and equivalent isotropic displacement parameters; selected bond distances and angles; bond valence analysis; X-ray diffraction pattern data of BZB compounds (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.