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PAPER

Crystal growth and optical properties of a noncentrosymmetric haloid borate, $K_3B_6O_{10}Br$†

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A high quality single crystal of $K_3B_6O_{10}Br$ has been grown with sizes up to $14 \times 12 \times 7$ mm^3 by the top-seeded solution growth method. It crystallizes in a noncentrosymetric trigonal system, space group $R3m$ with cell parameters $a = 10.1153(8)$ Å, $c = 8.8592(14)$ Å, $Z = 3$, $V = 785.02(15)$ Å^3. $K_3B_6O_{10}Br$ has a three-dimensional network consisting of B_6O_{13} units, which are surrounded by a K–Br framework. A transmission spectrum of the $K_3B_6O_{10}Br$ crystal was reported. Its refractive indices were measured by a minimum deviation technique and fit to Sellmeier equations. Nonlinear optical measurements demonstrate that the material has second harmonic generation properties, with efficiency approximately three times that of KH_2PO_4.

1. Introduction

Currently, considerable interest has focused on the nonlinear optical (NLO) crystals, especially borate crystals, due to their important application in second harmonic generation (SHG).[1–16] The alkaline metal borates combined with wide transparency and a sufficiently large NLO coefficient are perspective materials for efficient harmonic generation from infrared to ultraviolet spectral ranges.[17,18] A series of alkaline metal borates, such as LiB_3O_5 (LBO),[18] CsB_3O_5 (CBO),[19,20] $CsLiB_6O_{10}$ (CLBO),[21] are useful NLO materials for efficient SHG of Nd:YAG lasers. Since crystal structures directly affect the NLO properties of crystals, many strategies were employed to synthesize promising compounds with excellent NLO efficiency.[22–29] A number of haloid borates with prominent SHG property, such as $KBe_2BO_3F_2$ (KBBF),[30] $Ca_5(BO_3)_3F$[31] and $BaCaBO_3F$[32] were achieved. Considering the excellent properties of alkaline metal borates and haloid borates, the combination of the alkaline metal and halogen with borate in the same crystal is anticipated to produce a new class of NLO materials. Extensive efforts in the ternary alkaline metal–borate–halogen system led to a new NLO crystal of $K_3B_6O_{10}Br$ (KBB).

KBB was first reported by Al-Ama *et al.*,[33] where the small-sized crystals used for determining crystal structures were synthesized under hydrothermal conditions. To the best of our knowledge, the growth of a sizable single crystal large enough for measurement of NLO properties has not been reported in the literature. In this work, the growth, structure and optical properties of KBB crystal are presented.

2. Experimental section

Compound synthesis and crystal growth

Polycrystalline samples of KBB were synthesized *via* high temperature solid state reaction. A stoichiometric mixture of K_2CO_3 (Tianjin Damao Chemical Reagent Co., Ltd., 99.0%), KBr (Tianjin Hengxing Chemical Reagent Co., Ltd., 99.8%) and H_3BO_3 (Beijing Chemical Industry Co., Ltd., 99.5%) was ground thoroughly. The mixture was packed into a Pt crucible, heated up to 500 °C, held for 10 h and ground again. Then the compound was gradually heated up to 700 °C and kept at this temperature for 48 h with several intermediate grinding and mixing steps. As a result, a single-phase powder of KBB was obtained.

Single crystals of KBB were grown by the top-seeded solution growth (TSSG) method in a KF–PbO flux system. H_3BO_3, KBr, $KF \cdot 2H_2O$ (Tianjin Hengxing Chemical Reagent Co., Ltd., 99.0%) and PbO (Tianjin Baishi Chemical Reagent Co., Ltd., 99.0%) in the molar ratio of 6 : 1.5 : 2 : 2 were precalcined at 200 °C and 400 °C for 4 h, respectively, to decompose the boron acid and crystallization water. The mixture was ground carefully and placed in the center of a vertical, programmable temperature furnace with a Pt crucible container. The mixture was heated to 700 °C and kept at that temperature for 10 h to ensure that the

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† Electronic supplementary information (ESI) available: X-ray crystallographic file (CIF); experimental and calculated XRD patterns; the coordinations and bond lengths of Br atoms and K atoms; atomic coordinates and equivalent isotropic displacement parameters; selected bond distances; bond valence analysis. CCDC reference number 796881. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0ce00725k

powder melted into solution completely and mixed homogeneously. After that the mixture was cooled to 613 °C and the seed crystal was introduced into the liquid surface for 20 min to dissolve the outer surface. Then it was quickly cooled down to 593 °C and followed by a slow cooling at a rate of 0.2 °C per day until the desired size was obtained.

Characterization techniques

The thermal behavior of KBB was investigated using a NETZSCH STA 449C simultaneous thermal analyzer. The sample and reference Al_2O_3 were placed in a Pt crucible and heated at a rate of 10 °C min^{-1} in the range 25–900 °C under flowing of nitrogen gas. As-synthesized KBB powder was identified using a Bruker D8 ADVANCE X-ray diffractometer. Experimental and calculated XRD patterns of the KBB are shown in Fig. S1 in the ESI.† Single-crystal XRD data were collected on a Rigaku R-axis Spider IP diffractometer at 293(2) K using Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) and integrated with a SAINT-Plus program.[34] All calculations were performed with programs from the SHELXTL crystallographic software package.[35] Final least-squares refinement on F_o^2 with data having $F_o^2 \geq 2\sigma(F_o^2)$ includes anisotropic displacement parameters for all atoms. The final difference Fourier synthesis map showed the maximum and minimum peaks at 0.485 and −0.664 e $Å^{-3}$, respectively. The structure was checked for missing symmetry elements with PLATON.[36] Crystal data and structure refinement information are summarized in Table 1. The final refined atomic positions and isotropic thermal parameters are given in Table S1 in the ESI.† The main interatomic distances and angles are listed in Table S2 in the ESI.†

Table 1 Crystal data and structure refinement for the KBB crystal

Empirical formula	$K_3B_6O_{10}Br$
FW	422.07
Temperature (K)	293(2)
Crystal system	Trigonal
Space group	*R*3m
Unit cell dimensions	$a = 10.1153(8)$ Å $c = 8.8592(14)$ Å
Volume ($Å^3$)	785.02(15)
Z	3
Density (calcd) (g/cm^3)	2.678
Abs coeff (mm^{-1})	5.165
F(000)	606
Crystal size (mm^3)	0.340 × 0.240 × 0.200
θ range for data collection (°)	3.27 to 24.93
Limiting indices	$-12 \leq h \leq 11$, $-12 \leq k \leq 12$, $-10 \leq l \leq 8$
Reflections collected	1915/332 [R(int) = 0.0499]
Completeness to $\theta = 24.93°$(%)	99.5
data/restraints/parameters	332/1/26
GOF on F^2	1.157
Final *R* indices [$F_o^2 > 2\sigma(F_o^2)$][a]	$R1 = 0.0273$, $wR2 = 0.0637$
R indices (all data)[a]	$R1 = 0.0275$, $wR2 = 0.0639$
Extinction coefficient	0.296(16)
Largest diff peak and hole (e $Å^{-3}$)	0.535 and −0.682

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$ and $w^{-1} = \sigma^2(F_o^2) + (0.0154P)^2 + 0.92P$ where $P = (F_o^2 + 2F_c^2)/3$.

The powder SHG test was carried out on the KBB sample by the Kurtz–Perry method.[37] About 100 mg of the powder that was ground from the KBB single crystal was hand-pressed into a 1 cm diameter round box with two glass windows, which was irradiated with a pulsed infrared beam (1064 nm, 10 ns, 15 kHz) produced by a Q-switched Nd:YAG laser. A 532 nm filter was placed between the crystal and energy meter to block the fundamental light and a digital oscilloscope was used to view the SHG signal. Since the SHG efficiency of powders has been shown to depend strongly on particle size,[37,38] a KBB crystal was ground and sieved into distinct particle size ranges, <20, 20–38, 38–55, 55–88, 88–105, 105–150, and 150–200 μm. For comparison, well known SHG materials, crystalline SiO_2 and KH_2PO_4 (KDP) samples, were used as references.

The transmission spectrum of the KBB crystal was measured at room temperature using a Shimadzu SolidSpec-3700DUV UV-VIS-NIR Spectrophotometer with the measurement range extended from 165 to 2300 nm under a flow of nitrogen gas. For optical measurements, crystal sample plates of 2 mm in thickness were obtained by cutting the as-grown crystal and polishing with diamond-impregnated laps on both sides.

The refractive indices dispersion of KBB was determined by the minimum-deviation method at 9 different wavelengths between 404.7 and 694.3 nm at room temperature. Because KBB is a uniaxial crystal with the *R*3m space group, it is enough to measure both the ordinary and extraordinary light, n_o and n_e, using one prism cut with the edge at the apex parallel to the crystallographic *c*-axis and the (100) face as the incident surface.

3. Results and discussion

The DTA curve of a ground KBB crystal is shown in Fig. 1, which presents one remarkable endothermic peak at 775 °C and one weak endothermic peak at 815 °C on the heating curve, suggesting that KBB melts incongruently. Hence, appropriate fluxes should be introduced to decrease the crystal growth temperature. After a mass of attempts, the KF–PbO flux system was adopted to grow a large crystal. A colorless and transparent KBB crystal with dimensions 14 × 12 × 7 mm^3 was grown by the TSSG method, shown in Fig. 2. The crystal exhibits fairly distinguishable facets. Moreover, the KBB crystal is stable in an environment of air and moisture, and the hardness is about 4–5 on the Mohs scale, so during the cutting, and polishing processes, it does not crack.

KBB crystallizes in a noncentrosymmetric trigonal space group *R*3m. The crystal structure of KBB is schematically shown in Fig. 3 (the bonds of K atoms with O atoms are removed for clarity). Br(1) and O(3) atoms occupy the site 3*a*, while K(1), B(1), B(2) and O(2) atoms occupy the 9*b* position, and O(1) atoms occupy the site 18*c* (Table S1†). K atoms bind with Br atoms to form a three-dimensional network. Meanwhile, three BO_4 units are joined together through corner-sharing of an O atom; three BO_4 units are connected with three BO_3 units to form a compact hexa-borate unit B_6O_{13}, which inserts into a K-Br network. Connectivities between the B_6O_{13} units occur only through vertex sharing. The Br atoms are coordinated by six K atoms; K atoms have got six O atoms and two Br atoms in the coordination sphere. The coordinations of Br atoms and K atoms are shown in Fig. S2(a) and S2(b)†, respectively.

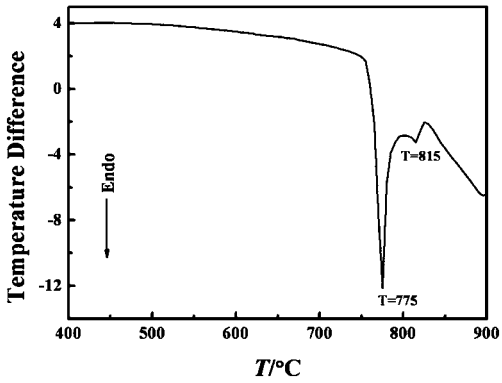

Fig. 1 DTA curve of KBB.

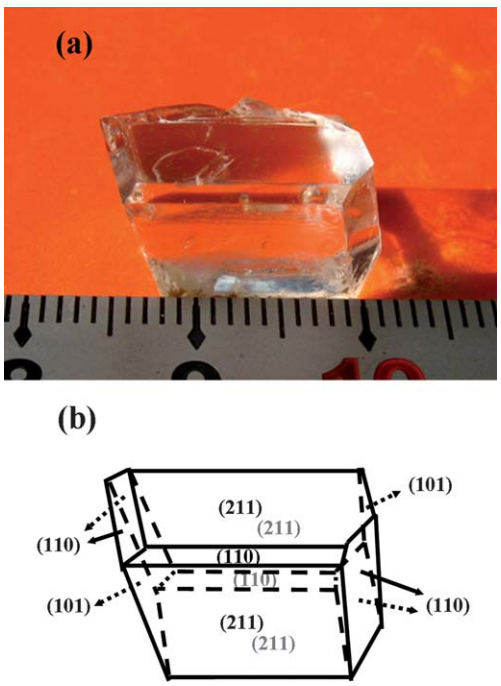

Fig. 2 Photograph (a) and morphology (b) of a KBB crystal. (The minimum scale of the ruler is one millimetre).

The bond valence sums of each atom in KBB are calculated[39,40] and listed in Table S3 in the ESI.† These charges, based on the bond lengths determined by the X-ray structure analysis, are in agreement with the expected oxidation states.

The curve of SHG signal *versus* particle size of samples that are ground from the KBB crystal is shown in Fig. 4. Obviously, the SHG intensity increases as the particle size of KBB increases, and the maximum intensity is attained when the particle size reaches about 130 μm, then the intensity is independent of particle size. It is consistent with the phase-matching behavior based on the rules proposed by Kurtz and Perry.[37] Our study shows that KBB has a powder SHG effect about three times as large as that of KDP standard of a similar grain size (105–150 μm). According to the literature reports,[3,4] the trigonal BO_3 anionic group possessing a conjugated π orbital is one of the most active NLO clusters in borate crystals. The unit cell of KBB contains BO_3 triangles, BO_4 tetrahedra and KO_6Br_2 polyhedra, the major SHG effect of KBB

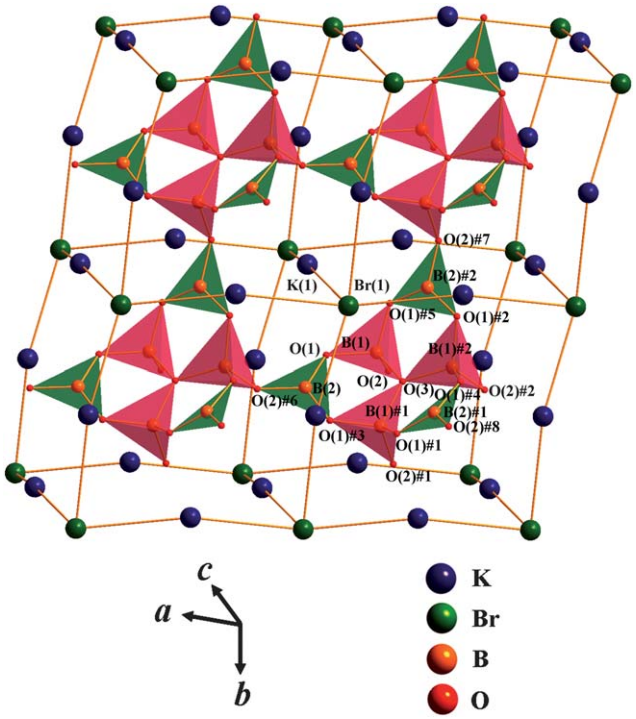

Fig. 3 Drawing of the structure of KBB. BO_4 tetrahedra and BO_3 triangles are shaded in red and green, respectively. Symmetry transformations used to generate equivalent atoms: (#1) $1-y, x-y, z$; (#2) $1-x+y, 1-x, z$; (#3) $x, x-y, z$; (#4) $1-x+y, y, z$; (#5) $1-y, 1-x, z$; (#6) $5/3-x+y, 4/3-x, 1/3+z$; (#7) $2/3-y, -2/3+x-y, 1/3+z$; (#8) $-1/3+x, 1/3+y, 1/3+z$.

comes from the BO_3 triangles, whereas KO_6Br_2 polyhedra and BO_4 tetrahedra contribute less.[31]

Fig. 5 shows the transmittance spectrum of the KBB crystal at room temperature. The transmission intensity from 288 nm to 2300 nm is about 90%; and the transmission intensity sharply decreases below 288 nm; the spectrum clearly has an absorption peak at 233 nm between 280 and 184 nm. The distinct absorption peak at 233 nm is possibly due to the impurity introduced by reagents. A similar situation is also presented in the growth of a $K_2Al_2B_2O_7$ crystal reported by Liu *et al.*[41,42]

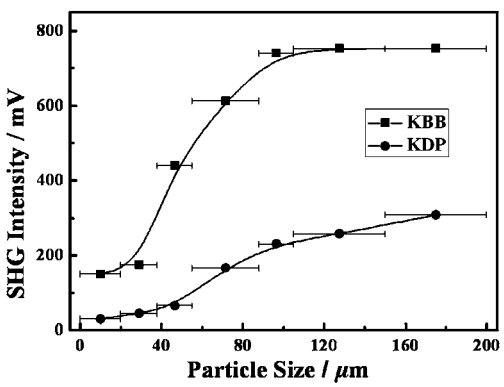

Fig. 4 Phase-matching curves, *i.e.*, particle size *vs.* SHG intensity, for KBB and KDP. The solid curve drawn is to guide the eye and is not a fit to the data.

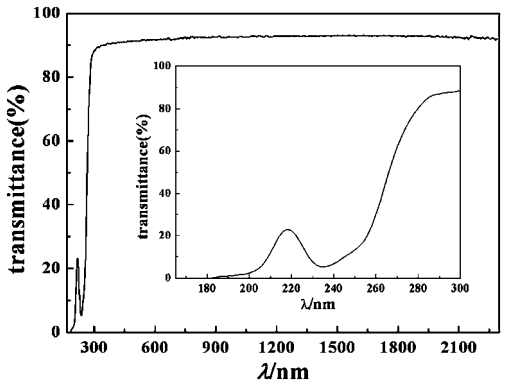

Fig. 5 Transmission spectrum of a KBB crystal. Inset gives the transmittance *versus* λ curve between 165 and 300 nm.

It is necessary to determine the dispersion curves of the nonlinear optical crystals for its application of the frequency conversion, which can predict the shortest SHG wavelength and the phase-matching (PM) direction. The measured and fit refractive index data for n_o and n_e, are shown in Fig. 6, which proved that KBB is a negative uniaxial optical crystal. The Sellmeier equations, which are fit with the measured refractive indices by the least-square-fit method, are as follows:

$$n_o^2 = 2.46155 + 0.01809027/(\lambda^2 + 0.002478024)$$

$$n_e^2 = 2.31952 + 0.01663273/(\lambda^2 + 0.009882779)$$

where λ is the wavelength expressed in micrometres. The calculated values are consistent with experimental ones to the third decimal place, which indicates that the fit Sellmeier equations are reliable. Its birefringence value is about 0.046 to 0.049 between 404.7 nm and 694.3 nm. On the basis of the Sellmeier equations, the phase-matching (PM) curves for SHG can be calculated with the shortest SHG wavelength for KBB to be about 290 nm for type I phase matching. Therefore, SHG of Nd:YAG laser (1064 nm) are possible for type-I PM. The calculated phase matching angle for type I SHG of 1064 nm calculated based on refractive-index data is 34.0°.

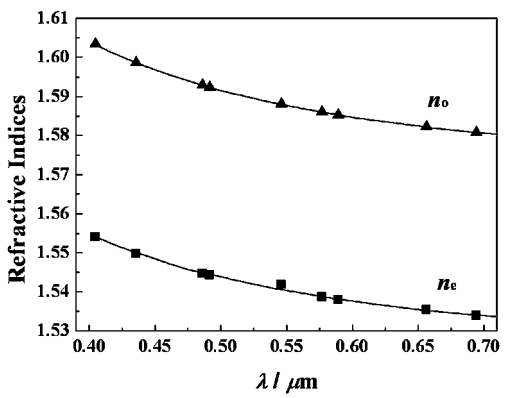

Fig. 6 Refractive index dispersion curves of a KBB crystal. The points are experimental values; curves are the fits given by the Sellmeier equations.

4. Conclusion

A transparent KBB single crystal has been successfully grown by the TSSG growth method using KF-PbO as the flux system. It is composed of a three-dimensional K-Br framework and B_6O_{13} network. KBB exhibits an SHG efficiency of about three times that of KDP. The KBB crystal is found to be transparent from 230 to 2300 nm, the absorption edge was about 230 nm. The type-I PM angles for SHG of Nd:YAG laser (1064 nm) is 34.0°. These properties, together with the characteristic of growing readily large crystals, make KBB crystal attractive for continuing research and development as a new NLO material.

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