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Growth, structure and optical properties of nonlinear optical crystal $BaZnBO_3F$

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ABSTRACT

Nonlinear optical (NLO) crystal $BaZnBO_3F$ (BZBF) with the size of about $20 \times 20 \times 0.5$ mm^3 is obtained from BaF_2–NaF flux, and single crystal X-ray diffraction reveals that it belongs to space group $P\bar{6}$ with cell parameters of $a=5.1045(6)$ Å, $c=4.3116(10)$ Å and $Z=1$. In the structure of BZBF, the BO_3 planar triangles are interconnected through O atoms from ZnO_3F_2 trigonal bipyramid to form $(Zn_3B_3O_6F_6)$ twelve-membered rings (12-MRs), then the layers which are built with condensation from 12-MRs at *ab* plane, are further linked by the apical F from ZnO_3F_2 to form three dimensional framework along the *c* direction. The title crystal exhibits high transmittance in the range of 300–3000 nm with a UV transmission cutoff at 223 nm according to transmission spectra. Powder SHG tests indicate that the effective NLO coefficient of BZBF crystal is about 2.8 times that of KH_2PO_4 (KDP) crystal due to perfect alignment of the BO_3 groups.

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1. Introduction

Since the advent of β-BaB_2O_4 (BBO) crystal, borate crystals play an important role in the nonlinear optical (NLO) fields because of their excellent physical and chemical properties, e.g: wide transmission range, high damage threshold and rich chemistry types [1–3]. It was known that the elimination of the dangling bonds of B–O groups or partial oxygen substitution by fluorine atoms can push the UV cut-off blue shift, thus fluoroborate compounds have been intensively investigated due to their wide band gaps (short UV cut-off) [4]. Among them the famous $KBe_2BO_3F_2$ (KBBF) family NLO crystals including KBBF, $RbBe_2BO_3F_2$ (RBBF), and $CsBe_2BO_3F_2$ (CBBF) were found [5–7]. Until now, KBBF and RBBF crystals are the only two NLO materials capable to produce deep UV (below 200 nm) laser output through a simple second harmonic generation (SHG) process. Important applications of those crystals included recent developed scientific instruments equipped with the deep UV laser sources, such as angle-resolved photoemission spectroscopy (ARPES) and photoemission electron microscopy (PEEM) [8,9]. Other related fluoroborate NLO crystals have been subsequently discovered, such as $BaAlBO_3F_2$ (BABF) [10], $Ca_5(BO_3)_3F$ [11], $BaMBO_3F$ (M=Ca, Mg) [12], $M_3B_6O_{11}F_2$ (M=Ba, Sr) [13], and so on.

$BaZnBO_3F$ (BZBF) compound was firstly synthesized by our group and its crystal structure was solved by powder X-ray diffraction method [12c]. It was very difficult to synthesize pure BZBF samples. BaF_2 is always present as the main impurity. In this paper, single crystal of BZBF was successfully grown by high temperature solution method, and its single crystal structure was solved with more accurate crystallographic parameters. Besides, optical characterization of the crystalline samples including transmission spectra and SHG tests was investigated.

2. Experimental section

2.1. Crystal growth

Analytical pure chemicals from Sinopharm Chemical Reagent Co., Ltd. of $BaCO_3$ (157.87 g, 0.8 mol), ZnO (65.11 g, 0.8 mol), H_3BO_3 (49.46 g, 0.8 mol), BaF_2 (70.13 g, 0.4 mol) and NaF (10.07 g, 0.24 mol) in molar ratios of 1:1:1:0.5:0.3 were mixed in an Φ 50×50 cm^3 platinum crucible. Then the mixtures were heated to 850 °C and held for 12 h to homogenize the melt. After determining the saturation point, a crack-free seed which was chosen from spontaneous crystallization in several crystal growth runs was dipped into the melt, then the crucible temperature was decreased at a cooling rate of 0.2 °C/h. Finally, the crystal was pulled from the melt and cooled down to room temperature at a rate of 20 °C/h.

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Table 1
Crystal data and structure refinement for $BaZnBO_3F$.

Empirical formula	$BaZnBO_3F$
Formula weight	280.52
Wavelength (Å)	0.71073
Crystal system	Hexagonal
Space group	$P\bar{6}$
Cell parameters (Å)	$a=5.1045(6)$ $c=4.3116(10)$
Volume (Å^3)	97.29(3)
Z	1
Density (g/cm^3)	4.788
μ (mm^{-1})	16.102
F(000)	124
Crystal size (mm^3)	$0.08 \times 0.03 \times 0.03$
GOF on F^2	1.230
R indices [$I > 2\sigma(I)$][a]	R1=0.0222, wR2=0.0490
R indices (all data)[a]	R1=0.0222, wR2=0.0490
Flack factor	0.00(9)
Extinction coefficient	0.89(7)

[a] $R1 = \frac{\sum ||F_O| - |F_C||}{\sum |F_O|}$; $wR2 = \{\frac{\sum [w(F_O^2 - F_C^2)^2]}{\sum [w(F_O^2)^2]}\}^{\frac{1}{2}}$

2.2. Single crystal X-ray diffraction

The crystal data were collected on a Bruker Smart APEX II diffractometer equipped with Mo Kα radiation ($\lambda=0.71073$ Å) at room temperature. The crystal structure was solved by SHELXS-97 and refined by full matrix least squares on F^2 by SHELXL-97 programs [14]. The structure was checked for missing symmetry elements using the PLATON program [15]. The detailed crystallographic data for BZBF are given in Table 1. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 2. The selected bond lengths are presented in Table 3.

2.3. Powder X-ray diffraction

X-ray diffraction (XRD) data were collected on a Bruker D8 Focus powder X-ray diffractometer using Cu Kα radiation at room temperature in the 2θ range of 7–70° with the step size of 0.02° and counting time of 0.1 s per step. The XRD patterns on ground crystals are well indexed and in good agreement with the calculated patterns from single crystal structure (Fig. S1).

2.4. Thermal analysis

The differential scanning calorimetric (DSC) analysis was performed on a NETZSCH TG–DTA-MS apparatus under N_2 flow with a sample heating rate of 15 °C per minute from room temperature to 960 °C.

2.5. Transmission spectroscopy

The transmittance spectrum of BZBF crystal with the thickness about 0.15 mm was performed using a Perkin-Elmer Lambda 900 UV–vis-NIR spectrometer in the range of 185–3000 nm. The interference pattern of BZBF crystal along the *c* axis was observed on an Olympus BX51TRF microscopy.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for $BaZnBO_3F$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	U_{eq}
Ba	0.3333	0.6667	0.5	0.0058(4)
Zn	0.6667	0.3333	0	0.0046(4)
O	0.7195(12)	0.7406(10)	0	0.0126(10)
F	0.6667	0.3333	0.5	0.0189(12)
B	0	0	0	0.0169(13)

Table 3
The important bond distances (Å) for $BaZnBO_3F$.

Ba–O × 6	2.816(4)	Zn–F × 2	2.1558(5)
Ba–F × 3	2.9471(4)	B–O × 3	1.381(4)
Zn–O × 3	1.958(5)		

2.6. Raman spectroscopy

Single crystal of BZBF was chosen to perform Raman spectra on a Renishaw inVia-Reflex micro-zone Raman spectrometer. The room Raman spectrum was recorded in the range from 50 to 1700 cm^{-1} under 532 nm excitation.

2.7. SHG measurement

The polycrystalline BZBF samples ground by using as-grown crystal were sieved into six different particle sizes (< 20, 20–50, 50–75, 75–105, 105–150, and 150–200 μm). The sieved KH_2PO_4 (KDP) crystals in the same size with BZBF were referred as the reference. The intensity of the second harmonic at 532 nm emitted from the samples illuminated with a Q-switched Nd:YAG 1064 nm laser was recorded by the photomultiplier tube.

3. Results and discussion

BZBF crystal with the dimensions of about $20 \times 20 \times 0.5$ mm^3 was obtained for about twenty days growth period (Fig. S2). It exhibits typical layer habit, which resembles that of KBBF family crystals. The uniaxial character of the crystal is obviously observed, confirming the single crystal structure.

3.1. Crystal structure

The crystallographic parameters of BZBF are in good agreement with that obtained by powder X-ray diffraction [12c]. In the structure, B atom coordinates to three O atoms in an ideal D3h symmetry with bond length of 1.381(4) Å, which is slightly longer than that of the powder one (1.372(7) Å) but reasonable in agreement considering the standard deviation. Zn atom is connected with three O atoms and two F atoms to form ZnO_3F_2 trigonal bipyramid (Fig. 1). The bond distances of Zn–O (1.958(5) Å) and Zn–F (2.1558(5) Å) are also in good agreement with the previous values (d(Zn–O)=1.940(11) Å and d(Zn–F)=2.140 Å). The $(ZnBO_3F)^{2-}$ layers at *ab* plane are formed by $(Zn_3B_3O_{12}F_6)$ twelve-membered rings (12-MRs) which are built from the BO_3 and ZnO_3F_2 groups with interconnection via corner O atoms. The $(Zn_3B_3O_{12}F_6)$ 12-MRs, which resemble $(Al_3B_3O_{12}F_6)$ and in BABF and $(Al_3B_3O_{15})$ in $K_2Al_2B_2O_7$ (KABO) [16], respectively, were also found in two centrosymmetric zinc-containing fluoroborates $KMZn_2(BO_3)_2F$ (M=Ca, Cd) [17]. Then the $(ZnBO_3F)^{2-}$ layers are further connected through the apical F atoms of ZnO_3F_2 bipyramids to form a three dimensional framework. The Ba atom, which is in coordination to six O atoms and three F atoms, occupies among the layers and maintains charge balance.

3.2. Thermal analysis

DSC curve exhibits one single endothermic peak in the heating curve and two exothermic peaks in the cooling curve, indicating that BZBF melts incongruently (Fig. S3). Powder XRD on residual

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