A New KBBF-Family Nonlinear Optical Material with Strong Interlayer Bonding

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Supporting Information

ABSTRACT: A new beryllium-free borate Rb₃Ba₃Li₂Al₄B₆O₂₀F features a layered structure analogous to that of the solely available deep-ultraviolet nonlinear optical (NLO) material KBe₂BO₃F₂ (KBBF), and thus preserves its outstanding linear and nonlinear optical properties to a great extent. Furthermore, the interlayer bonding in Rb₃Ba₃Li₂Al₄B₆O₂₀F is significantly reinforced, with a magnitude of more than 15.6 times that of KBBF. As a result, a bulk Rb₃Ba₃Li₂Al₄B₆O₂₀F crystal is successfully grown in the preliminary experiments. The result demonstrates that the Rb₃Ba₃Li₂Al₄B₆O₂₀F crystal may have no (or only a tiny) layering growth habit, which severely hinders the practical applications of KBBF. Notably, Rb₃Ba₃Li₂Al₄B₆O₂₀F overcomes the structural instability problem present in the notable KBBF-family member Sr₂Be₂B₂O₇. These results make Rb₃Ba₃Li₂Al₄B₆O₂₀F a promising candidate for the next generation of deep-ultraviolet NLO materials. First-principles calculations are performed to elucidate the optical properties and structural stability.

INTRODUCTION

Deep-ultraviolet (deep-UV, wavelengths below 200 nm) nonlinear optical (NLO) materials, which can double the frequency of incident light to the deep-UV region, are essential for a number of advanced scientific instruments.1–6 Such materials should be of high second-harmonic generation (SHG) efficiency, wide transparent window down to the deep-UV region, and moderate birefringence to achieve phase-matching, etc.7,8 Limited by these fundamental requirements, to date, only one NLO material KBe₂BO₃F₂ (KBBF)9 is able to directly generate deep-UV coherent light in practice. The required optical properties in KBBF are mainly ascribed to the layered structural units (namely, [Be₂BO₃F₂]∞ single-layers perpendicular to the crystallographic c axis), which provide the NLO-active [BO₃]³⁻ units in a perfectly coplanar and aligned arrangement. However, it is still challenging to obtain thick KBBF crystals because KBBF suffers from a severe layering growth habit arising from a very weak interlayer bonding (dominated by K−F ionic bonds) along the c direction. Consequently, the thicknesses of as-grown KBBF crystals are limited to 3.7 mm so far.10 Moreover, the high toxicity of beryllium in KBBF makes it urgent to develop new beryllium-free candidates for KBBF.11–16

In order to inherit the brilliant optical advantages while overcoming the layering growth habit of KBBF, many attempts have been made to develop the KBBF-family NLO materials with reinforced interlayer bonding.4,8,11,12,17–19 Especially, Sr₂Be₂B₂O₇ (SBBO) was considered to be one of the most attractive substitutes of KBBF.8 Its structure features [Be₂B₂O₇]∞ double layers that are interconnected by Sr−O bonds, which enhance the interlayer bonding to about 4.9 times that of KBBF. Nevertheless, SBBO suffers from a structural instability problem, and as a result, its crystal structure has not been well solved yet.16,20

The structural instability problem of SBBO may be resolved through enlarging the space inside the double layers. In 2011, Huang et al. developed a new NLO material NaCaBe₂B₂O₆F with [Be₃B₃O₆F₃]∞ double layers perpendicular to the crystallographic c axis), which provide the NLO-active [BO₃]³⁻ units in a perfectly coplanar and aligned arrangement. However, it is still challenging to obtain thick KBBF crystals because KBBF suffers from a severe layering growth habit arising from a very weak interlayer bonding (dominated by K−F ionic bonds) along the c direction. Consequently, the thicknesses of as-grown KBBF crystals are limited to 3.7 mm so far.10 Moreover, the high toxicity of beryllium in KBBF makes it urgent to develop new beryllium-free candidates for KBBF.11–16

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$3 \times KH_2PO_4$ (KDP). Recently, by substituting relatively longer Al–O and Li–F bonds for the bridging Be–O bonds of SBBO, our group successfully developed a new beryllium-free borate $K_3Ba_3Li_2Al_4B_6O_{20}F$. This borate consisting of double layers with an enlarged in-layer space has no structural instability problem and shows brilliant NLO properties. Nevertheless, its interlayer bonding is just up to $4.4 \times$ KBBF.

In this work, a simple element substitution based on $K_3Ba_3Li_2Al_4B_6O_{20}F$ leads to a new beryllium-free KBBF-family borate, $Rb_3Ba_3Li_2Al_4B_6O_{20}F$ (hereafter named I). Remarkably, I exhibits a greatly reinforced interlayer bonding of more than 15.6 times that of KBBF. As a result, a bulk I crystal has been grown in our preliminary experiments, indicating that the layering growth habit present in KBBF may be overcome. In addition, the synthesis, thermal behavior, structure, the NLO properties, and the first-principles calculations on I are also reported in this article.

**EXPERIMENTAL SECTION**

Reagents. $Rb_2CO_3$, $BaCO_3$, $Li_2CO_3$, LiOH·H$_2$O, $Al_2O_3$, H$_2$BO$_3$, LiF, and BaF$_2$ were purchased from Aladdin and used as received. The aforementioned reactants were $\cdot$H$_2$O (0.168 g, 0.004 mol), $Al_2O_3$ (0.816 g, 0.008 mol), $H_3BO_3$ (1.386 g, 0.006 mol), $BaCO_3$ (3.368 g, 0.012 mol), $LiOH\cdot H_2O$ (0.104 g, 0.004 mol), and LiF (0.168 g, 0.004 mol). First, the reactants before being cooled down to room temperature. Second, the mixture was gradually heated to $500 \, ^\circ C$ in 18 h, and subsequently held at $500 \, ^\circ C$ for no less than 24 h to adequately decompose the reactants before being cooled down to room temperature. The products were finely ground and sintered at $650 \, ^\circ C$ for 150 h before being cooled to ambient temperature. Several intermediate grindings were performed during the sintering process. As a result, polycrystalline I can be obtained.

The phase purity of the products was verified by powder X-ray diffraction (XRD) analysis. The parameters of a scanning step width of 0.02 $^\circ$ and a scanning rate of 0.14 $^\circ$ min$^{-1}$ in the $2θ$ range of 7–70 $^\circ$ were set for collecting the powder XRD patterns. This data collection was performed on a Rigaku MiniFlex II diffractometer (Cu K$_\alpha$ radiation) at ambient temperature. The result shows good consistency with that deduced from single-crystal XRD analysis (see Table S1 in the Supporting Information).

Crystal Growth. Bulk single crystals of I were successfully prepared through the top-seeded solution growth method with the Li$_2$O/BaF$_2$/Bi$_2$O$_3$ self-flux system. A mixture (110 g) of polycrystalline I, LiOH·H$_2$O, BaF$_2$, and H$_2$BO$_3$ (at a molar ratio of 1:8:1:6) was finely ground, and then transfused to a $Φ$ 45 mm $\times$ 45 mm platinum crucible in batches and to be melted at 850 $^\circ C$ in a furnace. Afterward, the platinum was moved to a temperature-programmable electric furnace for crystal growth. It was quickly heated to 800 $^\circ C$ and held at this temperature for 48 h to fully melt the mixture. Subsequently, a platinum wire tied to a copper rod was descended slowly until immersing into the surface of the melt. The melt was cooled to 720 $^\circ C$ at once and subsequently cooled at 2 $^\circ C$ h$^{-1}$ until I crystals crystallized on the platinum wire. The platinum wire was then lifted out of the melt surface before being cooled to ambient temperature in 72 h. The crystals separated from the platinum wire were used as seed crystals to grow bulk single crystals.

First, the saturation temperature ($\sim$690 $^\circ C$) was detected using a tentative seed crystal method. Second, a seed crystal was fixed to a copper rod with the aid of platinum wire, which was slowly immersed into the melt at 705 $^\circ C$ and then held at this temperature for 2 h to dissolve the uneven surfaces of the seed crystal. Subsequently, the temperature was decreased quickly to 690 $^\circ C$ over 5 min before being cooled at 0.3–1.0 $^\circ C$ per day. After ~20 days of crystal growth, the crystal was lifted out of the melt and the temperature was slowly lowered to ambient temperature. A transparent crystal which was cut from the as-grown crystal is as large as 7 mm $\times$ 5 mm $\times$ 4 mm (Figure 1). The (001) face was indexed and indicated. The thickness along the $c$ axis is about 4 mm, which is comparable to that of the thickest KBBF crystal to date (3.7 mm along the $c$ axis). Clearly, the crystal has a block shape and does not show an evident layered growth habit. In comparison, the KBBF crystals are always lamellar with a small thickness along the $c$ axis, showing a severe layered growth habit.

**Single-Crystal Structure Determination.** Diffraction data collection for a single crystal was collected on an Agilent SuperNova Dual diffractometer (Mo K$_\alpha$ radiation, $λ = 0.71073$ Å). The data collection and reduction were performed by virtue of the program CrystAlisPro. The structure was determined by the direct method using SHELXS and refined using the full-matrix least-squares program SHELXL. Anisotropic parameters were also applied for the refinements of all atoms. The structure was checked through the ADDSYM algorithm from PLATON, and no higher symmetries were found. Table 1 summarizes the relevant crystallographic data. Additional information is included in the Supporting Information (Tables S1–S3).

**Thermal Stability.** Differential thermal analysis of I was carried out using a NETZSCH STA 449C simultaneous analyzer. The crystal

![Figure 1. (a) Photograph of a I crystal. (b) Schematic representation of the I crystal with the (001) face being indicated.](image-url)
sample (22.2 mg) placed in an Al2O3 crucible was heated to 1100 °C from ambient temperature at 20 °C min⁻¹, followed by being cooled to ambient temperature at the same rate under flowing nitrogen gas.

**UV Transmittance Spectrum.** The UV optical transmittance spectrum of I was measured at room temperature using a UV/visible/near-infrared spectrophotometer (Lambda950, PerkinElmer) in the wavelength range of 190–800 nm. A piece of single crystal with a thickness of about 1 mm, which was cut from the bulk I crystal (Figure 1), was used for the measurement.

**Second-Harmonic Generation Measurements.** According to the Kurz—Perry method, powder second-harmonic generation of I was tested. A Q-switched Nd:YAG laser (1064 nm) served as the fundamental laser. The finely ground crystals were sieved into different mesh ranges (60–270 meshes). The sieved samples with different particle sizes were held using two glass cover slides, and then put into aluminum holders with an 8 mm diameter hole, which were further irradiated by the fundamental laser. The intensity of output light was recorded on an oscilloscope by virtue of a photomultiplier tube with a filter (535 ± 10 nm). Under the same conditions, sieved KDP crystals were used as the reference.

**First-Principles Computational Methods.** We calculated the electronic structure of I using CASTEP software on the basis of density functional theory (DFT). The Perdew–Burke–Ernzerhof functional with the generalized gradient approximation form was selected to describe the exchange-correlation energy. To model the effective interaction between atom cores and valence electrons, the optimized norm-conserving pseudopotentials in the Kleinman–Bylander form were adopted. Meanwhile, very high kinetic energy cutoffs (900 eV) and dense Monkhorst–Pack k-point meshes (finer than 0.04 Å⁻³ in the Brillouin zones) were used. Our tests found that the computational setups adopted above are accurate enough for our purposes.

Generally, the standard DFT method gives smaller calculated energy band gaps as compared to the experimental values. Thus, the scissor operators were used to shift the conduction band to match the calculated band gap with the measured value. The imaginary part of the calculated dielectric function was figured out on the basis of the Kramers–Kronig transform, and then the refractive indices were determined. The SHG coefficients were obtained according to the formula proposed by Lin et al. In order to study the structure stability, we calculated the phonons dispersion spectrum for the title compound based on the linear response method. This method is an effective way to calculate the second derivative of the total energy under a perturbing effect. Thus, the lattice dynamics (or the characterization of atomic interaction) in a concerned crystal structure can be deducted.

# RESULTS AND DISCUSSION

**Thermal Behavior.** For I, only one sharp endothermic peak appears in the vicinity of 860 °C on the DTA curves (Figure S2) with negligible weight loss, indicating that I melts incongruently. Thus, its large crystals should be grown through the flux method below 860 °C.

**Crystal Structure.** I crystallizes into a noncentrosymmetric hexagonal space group of P62c (No. 190). Its structure is composed of alveolate [LiAl4B8O24F]₉⁺ single layers bridged via Al−O and Li−F bonds or Al−O bonds in the direction of the crystallographic c axis, resulting in a three-dimensional framework (Figure 2). Rb⁺ and Ba²⁺ cations are located in the cavities of the framework to keep charge balance. Within a [LiAl4B8O24F]₉⁺ single layer, each B atom is three-fold coordinated to form a [BO₃]³⁻ triangle with B−O bond distances ranging from 1.342(6) to 1.391(7) Å and O−B−O bond angles from 119.5(5)° to 124.2(4)°, suggesting that the [BO₃]³⁻ group is nearly coplanar (Figure 2b). The Al/Li atoms are four-fold coordinated to form AlO₄/LiO₂F tetrahedra, and the bond parameters are normal. Notably, the F atoms of LiO₂F tetrahedra all point to the same side of the [LiAl₂B₄O₁₀F]₉⁺ layer to connect one adjacent single layer, while the apical oxygen atoms of AlO₄ tetrahedra alternately point upward and downward of the [LiAl₂B₄O₁₀F]₉⁺ layer to further bridge two adjacent single layers (Figure 2c). The spatial orientations of [BO₃]³⁻ groups are similar to that of K₃Ba₃Li₂Al₄B₆O₂₀F, which is beneficial to generate a large SHG response. The results of bond valence calculations for I are summarized in Table S1, indicating that the derived oxidation states of Rb, Ba, Li, Al, B, O, and F atoms show good agreement with their expected chemical valence.

**Structure Evolution.** It is interesting to elucidate the structural evolution in the KBBF family. As illustrated in Figure 3, the structures of the KBBF family evolve from the single-layer structure of KBBF, the double-layer structures of SBBO, and K₃Ba₃Li₂Al₄B₆O₂₀F, to the infinitely layered structure of I. All of these borates consist of layered structural units with planar [BO₃]³⁻ groups and tetrahedra (BeO₄F tetrahedra for KBBF, BeO₄F tetrahedra for SBBO, as well as AlO₄ and LiO₂F tetrahedra for K₃Ba₃Li₂Al₄B₆O₂₀F and I). As compared to KBBF with a very weak interlayer connection (K−F bonds), the interlayer connection for the rest of the aforementioned borates (dominated by Sr−O bonds for SBBO, Ba−O bonds for K₃Ba₃Li₂Al₄B₆O₂₀F, and Al−O and Li−F bonds for I, respectively) is significantly reinforced, thereby weakening the tendency of layering growth for their single crystals.

In order to evaluate the layering growth habit, we quantified the interlayer connection through computing the layered electrostatic force according to the Coulomb’s law, given that the interlayer bonds are basically ionic. This method has been adopted in our previous works and the results are well consistent with the experimental observation. The electrostatic force magnitude of one interlayer bond (bridging bond between two adjacent layers) can be calculated using the following equation

\[ |F| = \frac{k_e q_1 q_2}{r^2} \]

where \( k_e \) is the electrostatic constant (given that all the bonds submerged in the same dielectric media), \( q_1 \) and \( q_2 \) are the charge magnitude of the two bonding ions, respectively, and \( r \) is the bond distance. As shown in Table 2, due to the relatively large charge magnitude and short bond distances, the electrostatic interaction force of one Al−O bond in I reaches...
15.6 × K–F bond in KBBF, which is far larger than those of other ion bonds such as Sr–O and Ba–O. Considering that Al–O bonds are partially covalent, the interaction force of Al–O bonds should be larger than the calculated values. As we know, the interlayer connection is dominantly determined by the relatively strong bridging bonds between the adjacent layers. In I, the strong Al–O bonds rather than the weak Ba–O bonds, determine the interlayer bonding. Such a strong interlayer bonding is very beneficial to the growth of thick I crystals.

Unlike the double-layer structure of K₃Ba₃Li₂Al₄B₆O₂₀F, I possesses a different layered structure whose single layers are infinitely interconnected via Al–O or Li–F bonds along the c axis. From the viewpoint of structural stability, when the K⁺ cations are replaced by the relatively larger Rb⁺ cations, the [Li₂Al₄B₆O₂₀F]∞ double layers may be too crowded (Figure 4).

We proposed that, to maintain the structural stability, half of the Al–O bridging bonds of K₃Ba₃Li₂Al₄B₆O₂₀F are squeezed out of the double layers and further serve as new bonds to connect the adjacent double layers in the direction of the crystallographic c axis (Figure 4c,d), finally constructing the three-dimensional framework of I. On the other hand, this structural difference results in distinct interlayer bonding in both borates (4.4 × KBBF in K₃Ba₃Li₂Al₄B₆O₂₀F vs 15.6 × KBBF in I). The structural convergence factor is as small as 0.0238 (in comparison, SBBO > 0.065), indicating that I is structurally stable. In our preliminary experiments, a bulk I crystal was successfully grown (Figure 1), providing a solid evidence for its structural stability. The first-principles calculations displayed in the following section of this article also support this conclusion.

**Nonlinear Optical Property and UV Transmittance Spectrum.** Since I has similar layered structural units similar to that of KBBF, it is expected to possess similar SHG response. We measured the powder SHG intensity based on the Kurtz–Perry method. As illustrated in Figure 5a, the powder SHG intensities for the titled compound reach approximately saturated values with increasing particle sizes, indicating that I is phase-matching at the fundamental laser of 1064 nm based on the rule proposed by Kurtz and Perry. The SHG efficiency in the particle size range of 180–250 μm is about 1.4 times that of KDP. Obviously, the SHG response is close to that of KBBF (~1.21 × KDP) and is much larger than that of NaCaBe₂B₂O₆F (1/3 × KDP) without a structural instability problem. In order to ascertain the cutoff edge, a thin I crystal with a
thickness of about 1 mm was used to carry out the measurement of the transmittance spectrum. As shown in Figure 5b, its absorption edge is located at about 195 nm. The combination of deep-UV transparent performance and moderately phase-matching SHG efficiency makes I satisfy the fundamental optical requirements as a promising deep-UV NLO candidate.

First-Principles Calculations. In order to explain the origins of the NLO property and structural stability, we performed the first-principles calculations on density of states (DOS), NLO coefficients, birefringence, and phonon dispersion spectrum. The electronic band structure of I crystal is shown in Figure 6a, exhibiting the calculated energy band gap of 3.875 eV. The DOS and partial DOS for I are plotted in Figure 6b, from which one may obtain the following electronic characteristics: (i) The upper part of the valence band predominantly consists of the p orbitals of O (2p) and B (2p). (ii) The bottom part of the conduction band is constituted by orbitals of all atoms. Because the optical properties of a material are dominated by the electronic transitions from the valence band to the conduction band near the band gap, the [BO3]3− building units have a predominant contribution to the optical properties in I and the contributions of other ions (Li+, Rb+, Ba2+, Al3+, F−) are negligibly small.

On the basis of the calculated electronic structure, the derived birefringence value for I at the wavelength of 532 nm is \( \Delta n = 0.044 \) (Figure S3). Such a birefringence value is moderate as compared to those of KBBF and \( \text{K}_2\text{Ba}_3\text{Li}_2\text{Al}_4\text{B}_6\text{O}_{20}\text{F} \) and is favorable to achieve phase-matching, as proved by the powder SHG tests. Meanwhile, under the restriction of Kleinman’s symmetry, I has only one nonzero independent SHG coefficient. The calculated SHG coefficient for I is \( d_{32} = -0.47 \text{ pm V}^{-1} \), which shows good consistence with the result of powder SHG measurement (given \( d_{32} \) (KDP) = 0.39 pm V−1). The structural stability of I is also confirmed by the calculated phonon dispersion spectrum, which is well established to intrinsically characterize the interatomic interaction. If a crystal structure is kinetically unstable, the imaginary phonon modes (or negative phonon eigenvalues) would occur because of the repulsive forces between atoms at certain lattice points of reciprocal space. Our previous calculations on the phonon modes for SBBO, \( \text{NaCaBe}_2\text{B}_2\text{O}_5 \), and \( \text{K}_2\text{Ba}_3\text{Li}_2\text{Al}_4\text{B}_6\text{O}_{20}\text{F} \) are consistent with their structural stability. As shown in Figure 7, there are no negative phonon modes in the phonon dispersion spectrum, confirming that I overcomes the structurally dynamical instability theoretically.

CONCLUSION

In summary, a new beryllium-free KBBF-family NLO material \( \text{Rb}_3\text{Ba}_3\text{Li}_2\text{Al}_4\text{B}_6\text{O}_{20}\text{F} \) has been successfully developed. It features a layered structure similar to that of KBBF and thus exhibits NLO properties comparable to that of KBBF. Remarkably, because of the effect of counterpart cations, it exhibits a greatly reinforced interlayer bonding with a magnitude of \( \geq 15.6 \times \text{KBBF} \), being greatly stronger than those of most KBBF-family materials. Consequently, we have successfully grown a bulk \( \text{Rb}_3\text{Ba}_3\text{Li}_2\text{Al}_4\text{B}_6\text{O}_{20}\text{F} \) crystal without an evident layering growth habit. In addition, the title compound overcomes the structural instability problem that exists in the notable KBBF-family member SBBO. These findings indicate that \( \text{Rb}_3\text{Ba}_3\text{Li}_2\text{Al}_4\text{B}_6\text{O}_{20}\text{F} \) is a promising candidate for next-generation deep-UV NLO materials. Our future work will be devoted to growing large \( \text{Rb}_3\text{Ba}_3\text{Li}_2\text{Al}_4\text{B}_6\text{O}_{20}\text{F} \) crystals with high quality for practical applications. The modulation of interlayer bonding in layered materials may shed helpful highlights on the controllable design and synthesis of new deep-UV NLO materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.7b00726.

Accession Codes

CCDC 1519543 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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