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First-Principles Design of a Deep-Ultraviolet Nonlinear-Optical Crystal from $\text{KBe}_2\text{BO}_3\text{F}_2$ to $\text{NH}_4\text{Be}_2\text{BO}_3\text{F}_2$ Lei Kang,^{†,‡} Siyang Luo,[†] Guang Peng,[§] Ning Ye,^{*,§} Yicheng Wu,[†] Chuangtian Chen,[†] and Zheshuai Lin^{*,†}[†]Beijing Center for Crystal R&D, Key Lab of Functional Crystals and Laser Technology of Chinese Academy of Sciences, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China[§]Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fujian 350002, P.R. China[‡]University of Chinese Academy of Sciences, Beijing 100190, P.R. China

S Supporting Information

ABSTRACT: $\text{KBe}_2\text{BO}_3\text{F}_2$ (KBBF) is so far the sole nonlinear-optical (NLO) material that can be practically applied in the deep-ultraviolet (DUV) region. For the purpose of overcoming its layering tendency in crystal growth, herein a computer-assisted material design system is employed to design a new KBBF analogue, ammonia beryllium fluoroborate ($\text{NH}_4\text{Be}_2\text{BO}_3\text{F}_2$, ABBF). The first-principles calculations demonstrate that ABBF possesses NLO properties very close to those of KBBF, thus exhibiting good DUV NLO capability. Moreover, owing to the relatively strong chemical binding between layers, ABBF would have a better growth habit compared with KBBF. Upon synthesis, ABBF would be a very promising DUV NLO material.

Nonlinear-optical (NLO) crystals, usually as a key component of all-solid-state lasers, are of great importance for many advanced scientific and technical applications.¹ So far, quite a few NLO crystals with superior performance, such as $\beta\text{-BaB}_2\text{O}_4$,² LiB_3O_5 ,³ and KTiOPO_4 ,⁴ have been discovered from the near-ultraviolet to near-infrared range (wavelength λ from ~ 0.2 to ~ 2 μm) and satisfy almost all requests in these spectral regions. As a comparison, in the deep-ultraviolet (DUV) region ($\lambda < 200$ nm), only the $\text{KBe}_2\text{BO}_3\text{F}_2$ (KBBF)⁵ family, including KBBF, $\text{RbBe}_2\text{BO}_3\text{F}_2$ (RBBF),⁶ and $\text{CsBe}_2\text{BO}_3\text{F}_2$ (CBBF),⁷ exhibits the applicable second-harmonic-generation (SHG) capability in (or near) the DUV region. In particular, KBBF is the sole NLO borate that can practically generate DUV coherent light by a direct SHG process and is prospected to almost achieve the DUV NLO limits in all known materials.⁸ However, KBBF has a strong layering tendency along the c axis in single-crystal growth processes,⁵ which heavily hinders its applications for industrial and commercial demands. Therefore, it is very desirable to search for new DUV NLO materials.⁹

In order to more effectively and efficiently search for new DUV NLO materials, after numerous efforts, a computer-assisted material design system (CAMDS) has been developed.¹⁰ Within this system, key NLO parameters, including energy band gap E_g , SHG coefficients d_{ij} , birefringence Δn , and shortest SHG output wavelength λ_{PM} of the target compounds can be accurately

determined from first-principles calculations, which have helped in the discovery of crystals with good NLO performance in experiments.¹⁰ The layering tendency of the KBBF crystal originated in the weak ionic binding of K^+ between the $(\text{Be}_2\text{BO}_3\text{F}_2)_\infty$ layers,^{5,11} and thus we propose that the introduction of some ionic groups (e.g., NH_4^+) instead of K^+ would be a suitable way to enhance the interlayer interaction. Moreover, considering the similarity of NH_4^+ and K^+ in their ionic radii and valence electronic properties, this substitution is feasible just like the case from KH_2PO_4 (KDP) to $\text{NH}_4\text{H}_2\text{PO}_4$.¹² Accordingly, in the present work, we employ the CAMDS to design a new ammonia beryllium fluoroborate ($\text{NH}_4\text{Be}_2\text{BO}_3\text{F}_2$, ABBF) analogous to the KBBF structure via A-site cationic substitution of K^+ to NH_4^+ . By selection of the same polar direction of the NH_4^+ groups, the most possible phase with $R3$ symmetry is obtained theoretically. Note that the prediction is not intended to search for all possible structures, which is made in a “constrained” structure space.

The first-principles calculations are performed by the plane-wave pseudopotential method implemented in the CASTEP package based on density functional theory.¹³ The computational details are summarized in the Supporting Information. To verify the design accuracy, we calculate the optimized structures of KBBF, RBBF, and CBBF. As shown in Table S1 of the Supporting Information, a very good agreement with the experimental results is reached. Consequently, the crystallographic data of ABBF are theoretically obtained by optimizing the KBBF structure after NH_4^+ substitution (see Tables S1 and S2). The comparison of the unit cells between ABBF and KBBF/RBBF/CBBF is displayed in Figure 1. Clearly, the ABBF structure (Figure 1a) is analogous to that of KBBF/RBBF/CBBF (Figure 1b). In each unit cell, there are three two-dimensional $(\text{Be}_2\text{BO}_3\text{F}_2)_\infty$ layers perpendicular to the c axis composed by virtue of $(\text{BO}_3)^{3-}$ triangles and $(\text{BeO}_3\text{F})^{5-}$ polyhedra shared with O atoms. All $(\text{BO}_3)^{3-}$ groups are planar and aligned in the same orientation, in which the B–O distances are uniform and the O–B–O bond angles are exactly 120° . Each Be^{2+} cation in the $(\text{BeO}_3\text{F})^{5-}$ group links with three O^{2-} anions in the same plane and one F^- anion outside of the layer. The A-site cations, i.e., K^+ /

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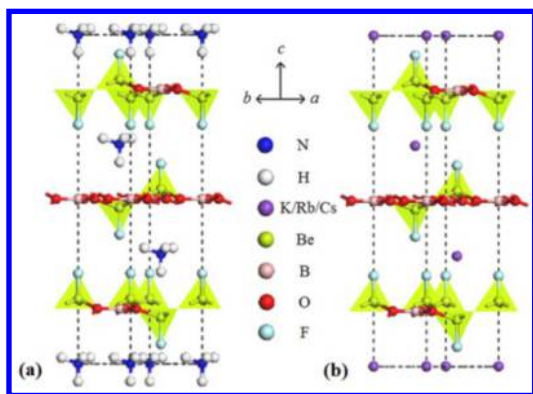


Figure 1. Structures of ABBF (a) and KBBF/RBBF/CBBF (b).

Rb^+/Cs^+ and NH_4^+ , are located between the $(\text{Be}_2\text{BO}_3\text{F}_2)_\infty$ layers in KBBF/RBBF/CBBF and ABBF, respectively. Note that in all structures the $(\text{BO}_3)^{3-}$ groups are almost kept the same size, while the $(\text{BeO}_3\text{F})^{5-}$ groups are slightly elongated along the c axis, with the A-site ion size increasing from K^+ to NH_4^+ , Rb^+ , and Cs^+ (see Table S2). The c cell parameter of ABBF is thus between those of KBBF and RBBF. Because the spatial orientation and density of the $(\text{BO}_3)^{3-}$ groups determine the optical anisotropy, whether linear and nonlinear, in the DUV borates,^{10,13} it is expected that the birefringence and SHG effects of ABBF should be slightly smaller than those of KBBF but larger than those of RBBF and CBBF.

The first-principles energy band gaps E_g , birefringence Δn , SHG coefficients d_{ij} , and shortest SHG wavelength λ_{PM} in the four crystals are shown in Table 1. As a comparison, the

Table 1. Linear and NLO Properties of ABBF^a

		E_g (eV) ^b	SHG effect (pm/V)	Δn		λ_{PM} (nm)
				400 nm	200 nm	
KBBF	exptl	8.45	$d_{22} = \pm 0.47$	0.088	0.104	161
	calcd	8.31	$d_{22} = -0.47$	0.062	0.083	176
RBBF	exptl	8.18	$d_{22} = \pm 0.45$	0.078	0.096	174
	calcd	8.08	$d_{22} = -0.45$	0.057	0.077	190
CBBF	exptl	8.23	$d_{22} = \pm 0.50$	0.064	0.086	202
	calcd	8.05	$d_{22} = -0.42$	0.054	0.071	206
ABBF	exptl	8.23	$d_{22} = \pm 0.50$	0.064	0.086	202
	calcd	8.61	$d_{22} = -0.49$ $d_{33} = 0.19$	0.058	0.076	187

^aAs a comparison, the experimental^{5–7} and calculated results of KBBF, RBBF, and CBBF are listed as well. ^bThe calcd E_g values are determined by B3LYP exchange–correlation functionals (for details, see the Supporting Information).

experimental values of KBBF, RBBF, and CBBF are shown as well, which also demonstrates the suitability of our computational methods for the present purpose. Although the calculated Δn and λ_{PM} are slightly deviated from the experimental values, their changing tendency is very consistent so that the prediction and analysis of the structure–property relationship would not be influenced. One may conclude the following: (i) the band gap E_g of ABBF is larger than those of KBBF/RBBF/CBBF, and the UV absorption edge λ_{UV} is blue-shifted to 144 nm in the former compound from about 150 nm in the latter; (ii) the four crystals

have almost the same SHG effects with $d_{22} \sim 1.2\text{KDP}$ (d_{36} of KDP = 0.39 pm/V), but for ABBF, an additional independent SHG coefficient, $d_{33} \sim 0.5\text{KDP}$, is present because of its space group $R3$; this small SHG coefficient originated from the polar NH_4^+ ionic groups; (iii) the birefringence is decreased with increases in the cell parameter c , and thus the shortest SHG output wavelength λ_{PM} red-shifts from KBBF to ABBF to RBBF to CBBF. In fact, the DUV NLO capability of ABBF is slightly better than that of RBBF, and it is very close to that of KBBF. It has been demonstrated that RBBF can achieve an applicable DUV output of 193.7 nm by direct SHG,⁶ approaching that of KBBF (~ 177.3 nm).¹⁴ The first-principles results are consistent with our understanding of the relationship between the structure and property in these crystals.

Moreover, the structural stability of ABBF is verified by the first-principles linear-response methods.¹⁵ The high similarity of the phonon spectra in ABBF and KBBF, especially in the regions close to the bottom, is evident (see Figure S1). Meanwhile, none of the imaginary phonon mode is observed in ABBF. Both strongly demonstrate that the ABBF structure is kinetically stable,¹⁶ as in the case of KBBF. Thus, ABBF synthesis seems be possible, although our prediction cannot guarantee that this compound is a thermodynamic equilibrium phase.

In order to investigate the influence of the A-site cations on the interlayer interaction along the c axis, we calculate the binding energies between NH_4^+ (or K^+) and $(\text{Be}_2\text{BO}_3\text{F}_2)_\infty$ layers for ABBF (or KBBF). It is revealed that ABBF indeed possesses a higher binding energy (3.97 eV/layer) than KBBF does (3.20 eV/layer). To understand further the interaction of A-site cations with the $(\text{Be}_2\text{BO}_3\text{F}_2)_\infty$ layered framework, the electronic density distributions are plotted for ABBF and KBBF (see Figure 2). It is

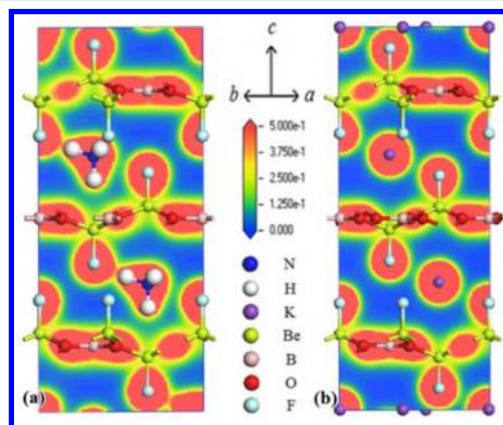


Figure 2. Electronic densities of ABBF (a) and KBBF (b).

shown that the spherical K^+ has little electronic overlap with neighboring F^- anions in KBBF, whereas the conical NH_4^+ has quite large electronic overlap with F^- anions in ABBF, indicating stronger chemical bond interaction in the latter crystal. This conclusion can also be deduced from analysis of the partial density of states (PDOS); the overlap between the electronic states of H and F/O at an energy of about -5 eV demonstrates the production of a relatively strong chemical bond interaction between NH_4^+ groups and $(\text{Be}_2\text{BO}_3\text{F}_2)_\infty$ layers (see Figure S2). The stronger interlayer interaction means that ABBF might have a better crystal growth habit along the c axis^{9e} compared to that of KBBF. Moreover, according to energy band theory, the stronger chemical bond interaction also results in a larger energy band gap in ABBF than in KBBF. In addition, the calculated bulk and

Young moduli (see Table S3) reveal that ABBF would possess higher mechanical robustness, especially along the *c* axis, than KBBF does.¹⁷

We also consider another possible phase of ABBF, in which the NH_4^+ groups are in the opposite polar direction alternately along the *c* axis (see Figure S3). This phase has a doubled unit cell size because the cell parameter *c* is doubled, but it has almost the same linear and NLO properties. The detailed calculated results are listed in Tables S4 and S5.

In fact, one may expect that the interlayer interaction in the KBBF family structure can be further enhanced by the removal of A-site cations. Namely, the F^- anions may act as bridge ions to directly connect the adjacent $(\text{Be}_2\text{BO}_3\text{F}_2)_\infty$ layers rather than as dangling ions in the KBBF family structure. The resulting compound $\text{Be}_2\text{BO}_3\text{F}$ can be derived from the KBBF structure by removing the KF molecule from the KBBF unit. Because of the very large electronegativity of the F^- ion, the fluorine bridge would significantly enhance the rather weak ionic interaction along the *c* axis in the KBBF structure and thus improve the crystal growth behavior. Meanwhile, because the spatial density of the $(\text{BO}_3)^{3-}$ groups along the *c* axis increased, the NLO performance will be improved as well; as estimated in this new compound, the birefringence and SHG effects are about 0.10 at 400 nm and 1.5 times of KBBF, respectively. It should be noted that another phase (point group C_2) of $\text{Be}_2\text{BO}_3\text{F}$ has been reported.¹⁸ However, because of the nonparallel arrangement of the $(\text{BO}_3)^{3-}$ groups, the SHG effect in this compound is very small, only about $1/5$ times of KBBF. Synthesis experiments for the new $\text{Be}_2\text{BO}_3\text{F}$ phase with parallel $(\text{BO}_3)^{3-}$ groups are in process.

In summary, ABBF, a new member in the KBBF family, is designed in a “constrained” structure space using the first-principles calculations in the CAMDS. The calculated results demonstrate that ABBF possesses a DUV SHG capability very close to those in KBBF and RBBF. Moreover, because of the relatively strong chemical binding between NH_4^+ groups and $(\text{Be}_2\text{BO}_3\text{F}_2)_\infty$ layers, ABBF would exhibit better crystal growth behavior along the *c* axis compared to KBBF and RBBF. More importantly, the ABBF structure is predicted to be kinetically stable; hence, this compound is very likely to be synthesized in experiments. However, because of decomposition of the ammonium compounds at high temperature, one may conclude that ABBF cannot be obtained from the high-temperature flux method, which is commonly used to synthesize and grow borates. Instead, the hydrothermal method might be a suitable way because of the lower reaction temperature and hermetic condition (the formation enthalpy of ABBF is predicted to be approximately 6127 kJ/mol at 0 K). It is convincing that synthesis of ABBF in experiments would significantly prompt the discovery of new DUV NLO borates and have great implications on the search for new functional NLO materials.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01991.

Computational methods, crystallographic data of ABBF, phonon spectra, PDOS analysis, bulk and Young moduli of ABBF and KBBF, and crystallographic data, structures, and linear and NLO properties of another phase of ABBF (PDF)

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Notes

The authors declare no competing financial interest.

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