ABSTRACT

Deep-ultraviolet (DUV) nonlinear optical (NLO) crystals that can extend the output range of coherent light below 200 nm are pivotal materials for solid-state lasers. To date, KBe$_2$BO$_3$F$_2$ (KBBF) is the only usable crystal that can generate DUV coherent light by direct second harmonic generation (SHG), but the layered growth habit and toxic ingredients limit its application. Herein, we report a new fluoroborophosphate, (NH$_4$)$_3$B$_{11}$PO$_{19}$F$_3$ (ABPF), containing four different functional units: [BO$_3$], [BO$_4$], [BO$_3$F] and [PO$_4$]. ABPF exhibits a KBBF-like structure while eliminating the limitations of KBBF crystal. The unique [B$_5$PO$_{10}$F]$_\infty$ layers enhance ABPF’s performance; for example, it has a large SHG response (1.2 \times KDP) and a sufficient birefringence (0.088 at 1064 nm) that enables the shortest phase-matching wavelength to reach the DUV region. Meanwhile, the introduction of strong B-O-P covalent bonds decreases the layered growth habit. These findings will enrich the structural chemistry of fluoroborophosphate and contribute to the discovery of more excellent DUV NLO crystals.

Keywords: deep-ultraviolet, nonlinear optical materials, KBBF-like structure, fluoroborophosphate
systems, and typical crystals include LiB₃O₅ (LBO), β-BaB₂O₄ (BBO) and KH₂PO₄ (KDP) [20–23]. Borophosphate, as a mixed-anionic system, is also a source of NLO crystals, and BPO₄ (BPO) and MBPO₅ (M = Sr, Ba) have been reported as NLO crystals with excellent properties [8,24]. Recently, we proposed a ‘fluorination strategy’ by substituting fluorine for oxygen atoms in borates to regulate the structure of NLO crystals, so as to achieve the balance of the three parameters mentioned above (i.e. $d_{tr}$, $\lambda_{\text{cutoff}}$ and $\Delta n$) [5,6,25]. Also, this strategy was further extended to the phosphate system. Consequently, [BOₓF₄₋ₓ] (x = 1, 2 and 3) and [POₓF₄₋ₓ] (x = 2, 3) units with superior microscopic properties were employed in NLO materials design, which led to the discovery of the promising NLO crystals: ABF₃OₓF (A = NH₄, Na, Rb, Cs), MBₓOₓFₓ₃ (M = Mg, Ca, Sr, Pb), (NH₄)ₓPOₓFₓ, NaNH₄POₓFₓHₓOₓ etc. [26–34]. However, fluoroborophosphate, as a system with even more functional anionic groups, has been left behind. To date, only 14 cases of fluoroborophosphates (organic–inorganic hybrids and mineral compounds are not included in the statistical data here) have been reported and deposited in the international inorganic crystal structure database (ICSD) [35–43]. As shown in Supplementary Table 1, non-$\pi$-conjugated units, including [BO₃], [BO₂F₂], [BO₄], [PO₄] and [PO₂F₂], construct the backbone of fluoroborophosphates. These compounds have large band gaps in the range of 4.34–6.45 eV, indicating their feasibility for applications in the UV or DUV region. Among them, five compounds are acenitic and exhibit a moderate SHG response of 0.3–1.1 times that of the benchmark KDP. Their birefringence (≤0.044) is not large enough to satisfy the DUV PM condition.

In this work, we attempt to introduce $\pi$-conjugated [BO₃] units into the fluoroborophosphate system to enhance the birefringence, thus regulating the PM wavelength for DUV applications. A new fluoroborophosphate, (NH₄)ₓBₓPO₄Fₓ (ABPF), with four kinds of structural units—[BO₃], [BO₂F₂], [PO₄] and [BO₄]—was successfully designed and synthesized. Fascinatingly, ABPF exhibits a new type of KBBF-like structure with unique [BₓPO₄Fₓ]∞ layers connected by shared oxygen atoms forming the final 3D framework. It inherits the excellent properties of KBBF, such as a wide transparency range, a large SHG response and a suitable birefringence to satisfy the DUV PM condition. Beyond these, ABPF has a non-layered growth habit and is chemically benign. These properties make ABPF a promising DUV NLO crystal. In addition, the contributions of multiple anionic groups to the linear and NLO properties of ABPF were confirmed by the first-principles calculations. Our results highlight the synergistic effect of multiple anionic groups on the design of DUV NLO materials and open up new possibilities for exploring DUV NLO materials in fluoroborophosphates.

**RESULTS AND DISCUSSION**

Polycrystalline samples of ABPF were synthesized via the high-temperature solution method in a closed system, and the photograph of ABPF crystals is shown in Supplementary Fig. 1. Crystallographic data are contained in CCDC 2153289 in crystallographic information file format. The purity of the phase was checked by powder X-ray diffraction (XRD; see Supplementary Fig. 2). The results of thermogravimetric analysis-differential scanning calorimetry (TG-DSC) curves and powder XRD patterns show that ABPF begins to decompose after 180°C, and BPO₄ was found in decomposition products (see Supplementary Figs 2 and 3). The constituent elements and the anion units are further confirmed by elemental analysis and infrared (IR) spectroscopy (see Supplementary Figs 4 and 5).

ABPF crystallizes in the trigonal space group R3 (see Supplementary Table 2), and the basic structure is shown in Fig. 1. Five crystallographically independent boron atoms exhibit three types of coordination environments, i.e. [BO₃] triangle, [BO₄] and [BO₂F₂] tetrahedra, while one crystallographically independent phosphorus atom exhibits the coordination environment of [PO₄] tetrahedron. The bond lengths, bond angles and bond valences are all in the reasonable range (see Supplementary Tables 3–8). The fundamental building block (FBB) is unique [BₓPO₄Fₓ] which is composed of the [BₓOₓFₓ] ring and three branches: [PO₄] tetrahedron, [BO₂F₂] tetrahedron and [BO₄] triangle (Fig. 1a). Three FBBs are closed to form a large 18-membered ring (MR), and further polymerized to unprecedented 2D $[BₓPO₄Fₓ]_\infty$ layers extending in the $ab$-plane (Fig. 1b). Amazingly, similar layers with 18-MRs were also found in NH₄BₓO₆F (ABF), and play important roles in its excellent NLO properties [26] (see Supplementary Fig. 6). Different from the 2D $[BₓOₓFₓ]_\infty$ layers in the structure of ABF, the layers in ABPF are further connected by shared oxygen atoms of [BO₄] and [PO₄] tetrahedra, stacking along the $c$-direction to form a 3D framework. Also, the interlayer spacing of ABPF is 3.97 Å, less than that of KBBF (6.25 Å), and NH₄⁺ cations are filled in the interlayer (Fig. 1c and d). Viewed along the $a$-axis, the $[BₓBO₂F₃]_\infty$ layers of KBBF are substituted by the $[BₓPO₄Fₓ]_\infty$ layers for non-toxicity and K⁺ cations are substituted by NH₄⁺ cations.
Moreover, the SHG capabilities of ABPF were measured by the Kurtz-Perry method [46] under incident laser 1064 and 532 nm, respectively. Two standard NLO crystals, KDP and BBO, were used as the references. The output SHG response of ABPF is 1.2 × KDP at 1064 nm and 0.2 × BBO at 532 nm in the 200~250 μm particle size range, respectively (Fig. 2c and d).

To further explore the structure–property relationship of ABPF, electronic structures and optical proprieties were calculated by the first-principles calculations based on density functional theory (DFT). The direct band gap of ABPF under a generalized gradient approximation (GGA) framework is 5.96 eV (see Supplementary Fig. 8), which is slightly smaller than the experimental value of 6.78 eV due to the discontinuity of exchange-correlation energy functional. To keep the band gap consistent with the realistic condition, a scissors operation (0.82 eV) was utilized when performing the optical properties calculations. From the partial densities of states (PDOS), the top of valence bands (VBs) and the bottom of conduction bands (CBs) are essentially dominated by O-2p and B-2p states, respectively (Fig. 3a). According to the Kleinman approximation of point group 3, there are four non-zero NLO coefficients for ABPF. The calculated values are $d_{11} = 1.19$ pm V$^{-1}$, $d_{32} = -0.91$ pm V$^{-1}$, $d_{31} = 0.08$ pm V$^{-1}$ and $d_{33} = 0.06$ pm V$^{-1}$, of which $d_{11}$, $d_{32}$ and $d_{31}$ are in the effective NLO coefficient ($d_{eff}$) expressions [47,48]. The largest tensor, $d_{11}$, was analyzed by the SHG-density method to understand the contribution of NLO-active electron states and units. It shows that the virtual electron (VE) process is dominant in the SHG process, and the contributions of occupied states are mainly determined by the non-bonding O-2p and F-2p, while unoccupied states are mainly determined by the orbitals of B-2p, N-2p, O-2p and F-2p (Fig. 3c and d). In fact, the orbitals of non-centrosymmetric sublattices near the top of valence bands from [BO$_3$] are mainly responsible for the SHG effect [49]. Meanwhile, the contribution origins of the SHG response were analyzed by the real-space atom-cutting method [48], and the result indicates that [BO$_3$] units contribute most to the SHG response, while other units contribute relatively little (see Supplementary Table 9).

Suitable birefringence ($\Delta n$) and mild dispersion are essential for realizing the PM conditions that foster a practical DUV laser output. The birefringence and PM wavelength were calculated by first-principles calculations based on DFT. To the best of our knowledge, ABPF has the largest birefringence of 0.088 at 1064 nm among all fluoroborophosphates reported so far (Table S1). And the calculation result of the bonding electron density
Fig. 2. Experimental results. (a) Interference pattern of polarized light. (b) Transmittance spectra. Powder second harmonic generation (SHG) measurements at (c) 1064 nm and (d) 532 nm with benchmark KH₂PO₄ (KDP) and β-BaB₂O₄ (BBO) used as references.

Figure 3. Calculation results. (a) Partial density of states (PDOS) of (NH₄)₃B₁₁PO₁₉F₃. (b) Calculated type I phase-matching (PM) SHG limit. SHG density maps of the (c) occupied and (d) unoccupied orbitals in the virtual electron process of d₁₁.

CONCLUSION

In conclusion, a new type of KBBF-like compound, ABPF, with four different units, has been successfully obtained, and the synergistic effect of π-conjugated units and non-π-conjugated units means it exhibits excellent optical properties, namely, the highest NLO coefficients, the largest birefringence and the shortest PM SHG limit among all fluoroborophosphates. Owing to a beryllium-free, no-layered growth habit, and excellent optical properties, ABPF has a promising future as DUV NLO crystal. Moreover, we propose that the introduction of strong covalent bonds between layers can enhance the interlayer interaction force while simultaneously maintaining the large optical anisotropy of layered structures. More importantly, the emergence of ABPF once again proves the advancement of the ‘fluorination strategy’ in the DUV NLO field. These findings will facilitate the discovery of more DUV NLO materials with optimal and practical performance.

METHODS

Synthesis

Crystals were obtained via the high-temperature solution method in a closed system. NH₄PF₆ (95%, Aladdin), NH₄HCO₃ (AR, Aladdin) and B₂O₃ (98%, Kelong). All chemicals above were used without further purification. A mixture of NH₄PF₆ (0.502 g, 3.077 mmol), NH₄HCO₃ (0.608 g, 7.692 mmol) and B₂O₃ (1.285 g, 18.462 mmol) was loaded into a quartz tube (the inner diameter is 35 mm, and the length is 175 mm), and the tube was flame sealed under 10⁻³ Pa. The tube was heated to 400°C for 24 h, held at this temperature for 96 h, cooled to 300°C for 150 h and cooled to room temperature with a rate of 2°C h⁻¹. Colorless crystals can be observed at the bottom of the tube, covered with a thin layer of amorphous sticky substance. After mechanical
Characterizations

Powder XRD data were collected using a Bruker D2 PHASER diffractometer at room temperature. The single-crystal XRD data were collected using a Bruker D8 Venture diffractometer and the crystal structure was solved using Olex2. The interference pattern of polarized light was measured using a polarizing microscope (ZEISS Axioscope 5). TG-DSC were measured on a simultaneous NETZSCH STA 449 F3 thermal analyzer instrument under a flowing N2 atmosphere. The sample was placed in a Pt crucible and heated from 40 to 800°C at a rate of 5°C min⁻¹. Elemental analysis was analyzed on the single crystal surface by a field emission scanning electron microscope (SEM, SUPRA 55VP) equipped with an energy dispersive X-ray spectroscopy (EDX, BRUKER X-flash-sdd-5010). IR spectroscopy was measured by Shimadzu IR Affinity-1 Fourier transform infrared spectrometer. The transmittance measurement of a transparent crystal was measured by Shimadzu SolidSpec-3700DUV spectrophotometer under a flowing N2 atmosphere. Powder SHG intensity was measured via the Kurtz-Perry method using a Q-switched Nd: YVO₄ solid-state laser (Cinlaser, DPS-1064-Q) at 1064 nm and 532 nm, for visible and UV SHG, respectively. Polycrystalline samples were ground and sieved into the following particle size ranges: 38–55, 55–88, 88–105, 105–150, 150–200 and 200–250 μm. The samples were loaded into a 1-mm-thick aluminum holder with an 8-mm-diameter hole. The sieved KDP and β-BBO samples were used as references.

SUPPLEMENTARY DATA

Supplementary data are available at NSR online.

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AUTHOR CONTRIBUTIONS

B.C. and Z.L. performed the experiments and wrote the paper. Y.C. and A.T. performed the first-principles calculations. M.M. performed the optical experiments. Z.Y. supervised the first-principles calculations. F.Z. and S.P. designed and supervised the study. All the authors discussed the results and commented on the manuscript.

Conflict of interest statement. None declared.

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