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Ba$_3$Mg$_3$(BO$_3$)$_3$F$_3$ polymorphs with reversible phase transition and high performances as ultraviolet nonlinear optical materials

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Nonlinear optical (NLO) materials are the vital components of future photoelectric technologies as they can broaden the tunable wavelength range supplied by common laser sources. However, the necessary prerequisites for a practical NLO material are rather strict. Accordingly, considerable efforts have been focused on finding potential NLO materials. Here we report two asymmetric beryllium-free borates $Pna2_1$ and $P62m$-Ba$_3$Mg$_3$(BO$_3$)$_3$F$_3$ featuring NLO-favorable $2\infty[Mg_3O_2F_5(BO_3)_{2}]$ layered structures. The reversible phase transition among two polymorphs was demonstrated by multiple experimental tests. The optical measurements reveal that $Pna2_1$-Ba$_3$Mg$_3$(BO$_3$)$_3$F$_3$ possesses the optical properties required for ultraviolet NLO applications. Remarkably, $Pna2_1$-Ba$_3$Mg$_3$(BO$_3$)$_3$F$_3$ has a large laser damage threshold, a deep-ultraviolet cutoff edge, a favorable anisotropic thermal expansion as well as the capacity of insolubility in water. These optical properties can be comparable or superior to that of commercial NLO material $\beta$-BaB$_2$O$_4$, which make $Pna2_1$-Ba$_3$Mg$_3$(BO$_3$)$_3$F$_3$ a promising ultraviolet NLO material.

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Online optical (NLO) materials applied from ultraviolet (UV) to infrared spectral ranges are the vital components of future photovoltaic technologies. Accordingly, considerable and sustained efforts have been focused on designing and synthesizing new potential NLO materials. Generally speaking, a practical UV NLO material should simultaneously satisfy the following criteria: a noncentrosymmetric structure; a broad transparent spectral range down to the UV region ($\lambda < 400$ nm); a relatively large second-order nonlinear coefficient ($d_{ij} > 0.39$ pm/V); a moderate birefringence to satisfy the phase-matching condition, chemical stability (non-deliquescent), and resistance to laser (large laser damage threshold, large LDT); and ease of growth of large single crystals with high optical quality. Targeting above conditions, until now, the borate system plays a dominant role in UV NLO materials because borates possess wide optical transparency windows, varied acentric structure types, high LDTs, and large polarizabilities. Therefore, we attempted to substitute and synthesizing new potential NLO materials. Considering and developing NLO materials with presupposed structures and properties is critically important. The following ideas were considered for designing the target molecules: (1) introducing anion ($\pi$-conjugated) fluorine-containing units into the structural framing of borate system based on the classic NLO materials with the goal of enhancing the interlayer interaction. Based on the top designing molecule structures, large-size single crystals of Pna21-BMBF were also grown through finding the suitable flux system. The optical measurements based on the crystal reveal that Pna21-BMBF possesses the NLO properties required for the UV NLO applications, which indicates that Pna21-BMBF is a potential UV NLO material.

### Results

The reversible phase transition between two polymorphs. Single crystal X-ray diffraction reveals that two new borates crystallize into the asymmetric space group of Pna21 (No. 33) and $P6_2m$ (No. 189), respectively (Table 1 and Supplementary Table 1). Interestingly, the molecular formula of both phases was determined as $\text{Ba}_3\text{Mg}_3(\text{BO}_3)_3\text{F}_3$ through structure solutions, which have the same simplest molecular formula with $\text{BaMg}_2\text{OF}_5$ (monoclinic, $Cc$) reported by Li et al. And the relatively low temperature factors and residual factors verify the correctness of those two crystal models, which also indicates the existence of two polymorphs. Furthermore, the BMBF polymorphs and phase transitions are further confirmed by high-temperature in situ powder X-ray diffraction and thermal expansion coefficients experiment based on the results of thermal gravimetric and differential scanning calorimetry analysis (Fig. 1a), we make circular heating and cooling the Pna21-BMBF samples in the region of 100–650°C. When the temperature rises to 500°C, the Pna21-BMBF phase start to transfer into $P6_2m$-BMBF phase, and $P6_2m$-BMBF is stable up to 650°C. When the temperature begins to decrease, $P6_2m$-BMBF phase can also transfer into Pna21-BMBF, indicating the reversibility of this phase transition behavior. More intuitively, the disappearance and appearance of X-ray diffraction peaks at about $2\theta = 23.690, 26.994$, and 27.686° in BMBF series can help us to judge this phase transition (Fig. 1b, c). The measured average thermal expansion coefficients based on the three as-polished (100), (010), and (001) wafers occur sudden change at about 450°C, which is caused by the phase transitions of BMBF series (Fig. 1d).

### Crystal structures of Pna21- and $P6_2m$-BMBF

The structural evolution among SBO, Pna21-, and $P6_2m$-BMBF are shown in Fig. 2, which verifies the validity of structure-oriented design strategy. As shown in Fig. 2a, b, e, BMBF series possess a similar

| Table 1 Crystallographic data for Pna21- and $P6_2m$-Ba3Mg3(BO3)3F3 |
|----------------|----------------|
| Empirical formula | $\text{Ba}_3\text{Mg}_3(\text{BO}_3)_3\text{F}_3$ |
| Formula weight | 718.38 |
| Crystal system | Orthorhombic |
| Space group | Pna21 (No. 33) |
| a (Å) | 8.0740(3) |
| b (Å) | 15.3072(7) |
| c (Å) | 8.8218(4) |
| Z | 4 |
| Volume (Å³) | 1090.29(8) |
| Refins collected/unique | 11,605/2377 |
| Goodnes of fit on F² | 1.233 |
| wR | 0.0118 |
| Fl | 0.0249 |
| wR | 0.0394 |
| wR (all data) | 0.0395 |

R = 2|w|(|F| - |F|)/|F| and w = (2w|F|² / |F|²)²/2 for w|F|² > 2σ(w|F|²)²/2.
Fig. 1 Basic physicochemical properties of Ba₃Mg₃(BO₃)₃F₃. a Thermal gravimetric and differential scanning calorimetry (DSC) curves. Endo means the endothermic direction. There are two remarkable endothermic peaks (741.8 and 1108.9 °C) on the heating curve and two exothermic peaks (634.1 and 1035.1 °C) on the cooling curve, respectively. b, c High-temperature in situ powder X-ray diffraction data circularly collected in the region of 100–650 °C. The experimental and calculated powder X-ray diffraction patterns of Pna2₁-Ba₃Mg₃(BO₃)₃F₃ (blue lines) and P62/m-Ba₃Mg₃(BO₃)₃F₃ (red lines). The enlarged version of c in the 2θ region from 22.3 to 28.2° is shown in b to better understand the phase transition behavior between two polymorphs. d Thermal expansion measurements tested by (100), (010), and (001) Pna2₁-Ba₃Mg₃(BO₃)₃F₃ crystal plates. d₀ and L₀ mean the change in crystal plates length and initial length of crystal plates, respectively. e Solubility experiments of Pna2₁-Ba₃Mg₃(BO₃)₃F₃, α- and β-BaB₂O₄

Fig. 2 Crystal structural features of Pna2₁-Ba₃Mg₃(BO₃)₃F₃. a, b The structural evolution from Sr₂Be₂B₂O₇ to Pna2₁-Ba₃Mg₃(BO₃)₃F₃. c, d The orientation of [BO₃]³⁻ groups in Pna2₁- and P62/m-Ba₃Mg₃(BO₃)₃F₃, respectively. e The layered structure of derivative P62/m-Ba₃Mg₃(BO₃)₃F₃ derived by phase transition from Pna2₁-Ba₃Mg₃(BO₃)₃F₃.
layered crystal structures, their crystal structures are both composed of $2_{-}[\text{Mg}_2\text{O}_3\text{F}_3(\text{BO}_3)_2]$ layers (Supplementary Figure 1) along the $a$-axis for $\text{Pna}_{21}$-BMBF and $c$-axis for $\text{P6}2\text{m}$-BMBF, and those single layers are further connected by the Mg–F bonds to construct a three-dimensional framework with tunnels running along the $c$ (or $a$)-axis. In the asymmetric unit of $\text{Pna}_{21}$-BMBF, the Ba, Mg, B, and F atoms occupy three crystallographically unique positions, for the O atoms there are nine unique positions. In both BMBF polymorphs, the B atoms possess only one coordination type, the \([\text{BO}_3]^{3-}\) triangles (Fig. 2c, d). The B–O bond distances and O–B–O bond angles locate in the range from 1.341 to 1.395 Å, 117.6 to 120.9 ° for $\text{Pna}_{21}$-BMBF, and 117.0 to 122.8 ° for $\text{P6}2\text{m}$-BMBF, respectively (Supplementary Tables 4 and 7). The Mg atoms in both polymorphs are six-coordinated into the MgO$_4$F$_2$ octahedra with four O and two F atoms locating in the equatorial and axial positions, respectively. Three MgO$_4$F$_2$ units share three O atoms to generate a six-membered ring cluster Mg$_3$O$_9$F$_6$ (Supplementary Figure 2), then those clusters link together via the axial Mg–F bonds to build an isolated $3_{-}[\text{Mg}_2\text{O}_3\text{F}_3]$ triangular prism (Supplementary Figure 3). Interestingly, two \([\text{BO}_3]^{3-}\) units in and out of the six-membered ring Mg$_2$O$_6$F$_6$ to form polymer and further polymerize into $2_{-}[\text{Mg}_2\text{O}_3\text{F}_3(\text{BO}_3)_2]$ infinite layers, and the connection is by bridging Mg–F bonds to form a three-dimensional multi-layered structure. All the Ba atoms are coordinated into BaO$_m$F$_m$ ($m + n = 10$ and 11) polyhedra, located between the adjacent $2_{-}[\text{Mg}_2\text{O}_3\text{F}_3(\text{BO}_3)_2]$ layers, which is quite like the arrangement of the Sr atoms in SBO$_3$.

Structurally, the triangular \([\text{BO}_3]^{3-}\) units in both $\text{Pna}_{21}$- and $\text{P6}2\text{m}$-BMBF adopt nearly coplanar configuration. This is propitious to generate large SHG response and birefringence because of the strong anisotropy resulting from their different polarizabilities in different directions, which is similar to the NLO materials containing $\pi$-planar triangular \([\text{CO}_3]^{2-}\). The F–Mg–F bonds act as bridge-linking role to connect the neighboring layers, which is similar to the $[\text{B}_2\text{O}_5]^{4-}$ dimers in LiNa$_3\text{Be}_2\text{Si}_2\text{O}_7$ $\text{F}^{5-}$ and the $[\text{B}_2\text{O}_6]^{3-}$ groups in $\text{Cs}_3\text{Zn}_6\text{B}_9\text{O}_{21}$ $\text{F}^{6-}$. Further, the electrostatics force of the interaction between layers in $\text{Pna}_{21}$- and $\text{P6}2\text{m}$-BMBF was evaluated and $|\text{F}_{\text{Mg–F}}|$ is stronger than that of $|\text{F}_{\text{K–F}}|$ in KBBF (Supplementary Table 8), indicating that the electrostatic interactions between Mg–F bonds in $\text{Pna}_{21}$- and $\text{P6}2\text{m}$-BMBF provide better linkage of neighboring layers, which is favorable to improve the layering tendency and the same results can be concluded from the ease of the growth of block-like crystals of BMBF series than that of KBBF.

**Crystal growth and optical quality of $\text{Pna}_{21}$-BMBF.** After various attempts, $\text{Pna}_{21}$-BMBF crystal with dimensions up to $16 \times 14 \times 8 \text{mm}^3$ has been grown at the optimal conditions (Fig. 3a). $\text{Pna}_{21}$-BMBF crystal has never cracked during cutting and polishing into (100), (010), and (001) wafers (Fig. 3b). The crystallization quality of the as-grown crystal was checked by the X-ray rocking curve. As shown in Fig. 3c, the full-width at half-maximum on (100) face of $\text{Pna}_{21}$-BMBF crystal was measured to be 18°, indicating high crystalline quality. The conoscopic interference pattern (Fig. 3d) shows that the as-grown $\text{Pna}_{21}$-BMBF crystal is biaxial, optical homogeneous, and does not have any strain inside. When taken together, $\text{Pna}_{21}$-BMBF crystal shows high optical quality, and the optical measurements based on this crystal are reliable.

**High performances as UV NLO materials.** $\text{Pna}_{21}$-BMBF was subjected to physicochemical property characterizations based on the single-crystal level.

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**Fig. 3** The as-grown single crystal and optical quality experiments of $\text{Pna}_{21}$-Ba$_3$Mg$_3$(BO$_3$)$_2$F$_3$. a Photograph of the as-grown crystal with dimensions up to $16 \times 14 \times 8 \text{mm}^3$ grown by the top-seeded solution growth method. b The cut and polished (100), (010), and (001) wafers with dimensions up to $4 \times 4 \times 1 \text{mm}^3$. The crystals were cut plane parallel and polished to optical quality using a Unipol-300 grinding/polishing machine. c The high-resolution X-ray diffraction rocking curve for (100) wafer. The full-width at half-maximum on (100) face of the $\text{Pna}_{21}$-Ba$_3$Mg$_3$(BO$_3$)$_2$F$_3$ crystal is about 18°, indicating high crystalline quality. d The conoscopic interference pattern of $\text{Pna}_{21}$-Ba$_3$Mg$_3$(BO$_3$)$_2$F$_3$ crystal. All the images and elements of them were created by ourselves.
Thermal expansion coefficients are vital parameters for crystal growth and application in devices. As can be seen in Fig. 1d, the average thermal expansion coefficients in the region from 100 to 450 °C are evaluated to be $a_x = a(100) = 2.17 \times 10^{-5} \text{ K}^{-1}$, $a_y = a(010) = 1.63 \times 10^{-5} \text{ K}^{-1}$, and $a_z = a(001) = 1.53 \times 10^{-5} \text{ K}^{-1}$, respectively. The value of $a_x/a_z$ is about 1.43 for Pna21-BMBF crystal, which is smaller than that of $\beta$-BaB$_2$O$_4$ ($\beta$-BBO) ($a_x/a_z = 9$)\textsuperscript{40}. Therefore, Pna21-BMBF crystal exhibits a more favorable anisotropic thermal expansion, which will effectively protect the crystals from cracking caused by thermal expansion during crystal growth and optical devices fabrication.

To study the water solubility of Pna21-BMBF, we dipped the target Pna21-BMBF (0.113 g) crystal as well as the references $\alpha$- and $\beta$-BBO crystals (0.159 and 0.105 g) into 20 mL de-ionized water at room temperature. As plotted in Fig. 1e, the weight of Pna21-BMBF did not change in the measured time ranges, while for $\alpha$- and $\beta$-BBO crystals, they were dissolved in water in 90 h. These indicate that Pna21-BMBF is chemically stable and not soluble in the water.

We carried out the SHG measurements by the Kurtz–Perry method\textsuperscript{41} with incident lasers at $\lambda = 1064\text{ nm}$. Meanwhile, the well-known NLO material KH$_2$PO$_4$ (KDP) was used as the reference. The comparison of SHG signals produced by Pna21-, and P62m-BMBF polycrystalline samples in the same particle sizes ranging from 200 to 250 μm reveals that Pna21-, and P62m-BMBF exhibit suitable SHG responses of $\sim 1.8$ and $2.0 \times$ KDP, respectively. Such SHG responses are large enough for the applications of UV NLO materials and it is also comparable to those reported borates with deep-UV cutoff edges, such as KBBF (1.26 × KDP)\textsuperscript{39}, LiNa$_5$Be$_{12}$B$_{12}$O$_{37}$ (1.4 × KDP), and Li$_4$Sr (BO$_3$)$_2$ (2 × KDP)\textsuperscript{22}. According to the results, the SHG efficiency increases with the raising particle sizes, indicating that both BMBF polymorphs exhibit type I phase-matching behavior in 1064 nm incident lasers. In addition, the effective NLO coefficients ($d_{eff}$) of Pna21- and P62m-BMBF crystal are estimated to be about 1.3 and 1.4 × KDP according to the square roots of the ratios of their corresponding SHG signal intensities. In order to verify the results, large sizes of single crystals should be grown and cut to evaluate the SHG coefficients based on the crystal level, which is discussed in detail in the following parts.

The as-grown crystals were cut and optically polished to 1 mm thickness for the spectrum measurement. As presented in Fig. 4b, the Pna21-BMBF crystal exhibits a broad transmission of 184–3780 nm, indicating that the application of Pna21-BMBF crystal can cover a spectral range from UV to near-infrared. Obviously, the UV cutoff edge of Pna21-BMBF is about 184 nm, which is 5 nm shorter than that of $\beta$-BBO (189 nm) in the same measured condition. And also the high transmittance of Pna21-BMBF in the UV spectral range makes it possible to be applied as a UV NLO material. The short cutoff edge is beneficial to obtain high LDT, therefore, LDT measurements were carried out using a pulsed nanosecond laser (1064 nm, 10 ns, and 10 Hz). A well-polished high-quality (001) wafer of Pna21-BMBF has a LDT of

Fig. 4 Optical properties of Pna21-Ba$_3$Mg$_5$(BO$_3$)$_2$F$_3$. a Powder second-harmonic generation data for Ba$_3$Mg$_5$(BO$_3$)$_2$F$_3$ polymorphs at 1064 nm laser radiation. The well-known NLO material KH$_2$PO$_4$ (KDP) was used as the reference. The curves are drawn to guide the eyes, and are not fit to the data. The error bars from left to right correspond to sieved crystal particle size ranges: 20–38; 38–55; 55–88; 88–105; 105–150; 150–200; and 200–250 μm. b Transmission spectrum of Pna21-Ba$_3$Mg$_5$(BO$_3$)$_2$F$_3$ crystal. Transmittance curve (magenta line) between 180 and 2500 nm was collected by a Shimadzu Solid Spec-3700DUV Spectrophotometer. Transmittance curve (black line) between 2500 and 4000 nm was collected by a Shimadzu IRAfinity-1 spectrometer. Inset gives transmittance curves between 170 and 400 nm for Pna21-Ba$_3$Mg$_5$(BO$_3$)$_2$F$_3$ (red line) and $\beta$-BaB$_2$O$_4$ (blue line). The ultraviolet cutoff edge of Pna21-Ba$_3$Mg$_5$(BO$_3$)$_2$F$_3$ is about 184 nm, which is 5 nm shorter than that of $\beta$-BBO (189 nm). c The refractive index dispersion curves for the Pna21-Ba$_3$Mg$_5$(BO$_3$)$_2$F$_3$ crystal. d The refractive index dispersion curves for fundamental (blue lines) and the second-harmonic (red lines) light. Based on the Sellmeier equations, when considering the type I phase-matching condition, $n(\omega) = n(2\omega)$, the shortest type I phase-matching wavelengths in the $xz$ and $xy$ plane are evaluated to be 310 and 322 nm.
the shortest type I phase-matching wavelengths in the beam diameter of 1.0 mm.

The refractive indices of Pna$_2$-BMBF were measured using prism coupling method. As it follows the inequality $n_x - n_y < n_x - n_z$, which depicts that Pna$_2$-BMBF is a negative biaxial crystal with the birefringence ($\Delta n = n_x - n_z$) ranging from 0.044@1064 nm to 0.045@532 nm and the values are comparable with those of the commercial UV NLO materials LiB$_3$O$_5$ and CsLiB$_6$O$_{10}$ ($\Delta n = 0.045$ and 0.049@1064 nm)$^{10}$. A least-square method was used to fit the dispersion parameters of the refractive indices, $n_i$, using the Sellmeier Eq. (1):

$$n_i^2 = A + \frac{B}{\lambda^2 - C} - D\lambda^2 \quad (1)$$

where $\lambda$ represents the wavelength in units of $\mu$m, and $A$, $B$, $C$, and $D$ are the Sellmeier parameters. The Sellmeier Eq. (1) deduced by the least-square fitting of all the measured refractive indices have been fitted as:

$$n_x^2 = 2.58654 + \frac{0.01672}{\lambda^2 - 0.00904} - 0.00987\lambda^2$$
$$n_y^2 = 2.71284 + \frac{0.02264}{\lambda^2 - 0.01829} - 0.00486\lambda^2$$
$$n_z^2 = 2.72604 + \frac{0.01908}{\lambda^2 - 0.01344} - 0.00819\lambda^2 \quad (2)$$

The calculated and experimental values of the refractive indices at five different wavelengths are summarized in Supplementary Table 9. The calculated values are consistent with experimental ones to the fourth decimal place, which indicates that the fitted Sellmeier equations based on the current data are reliable (Fig. 4c). Based on above fitted Sellmeier equations, when considering the type I phase-matching condition, $n(\omega) = n(2\omega)$, the shortest type I phase-matching wavelengths in the $xz$ and $xy$ plane are evaluated to be 310 and 322 nm (Fig. 4d), respectively.

Therefore, the Pna$_2$-BMBF crystal can generate 532 and 355 nm light by direct second and third harmonic generation from a 1064 nm laser.

In order to determine the individual NLO coefficients of Pna$_2$-BMBF, Maker fringe measurements were carried out. The schematic of the Maker fringe measurement system is shown in Fig. 5. For the SHG coefficient measurements, the orientation of the crystals and the relationships of $P_w$ and $P_{2w}$ are shown in Fig. 6a, c. The (001)-cut and (100)-cut plane-parallel uncoated plates of Pna$_2$-BMBF crystals (4 mm × 4 mm × 1 mm) were used to measure the related NLO coefficients. And also a (110)-cut plate (5 mm × 5 mm × 2 mm) of the KDP crystal was used to measure the $d_{36}$ (KDP) NLO coefficient as the reference. By fitting the calculated Maker fringes based on the current measurements and calculations, the NLO coefficient of the Pna$_2$-BMBF crystal relative to $d_{36}$ (KDP) has been determined as $d_{33} = 1.3 \times d_{36}$ (KDP) (Fig. 6b, d). However, the Maker fringe for $d_{31}$ is too weak to be observed. As $d_{36}$ coefficient of KDP is 0.39 pm/V, the absolute NLO coefficients of Pna$_2$-BMBF crystal based on the measurements and calculations are evaluated to be $d_{33} = 0.51$ pm/V.

**Discussion**

In order to achieve a deep investigation about the structure-property relationship, theoretical calculations based on density functional theory methods were performed$^{42-44}$. The total and partial density of states projected on the constitutional atoms of Pna$_2$-BMBF crystal are given in Fig. 7a. Clearly, the energy bands can be divided into several regions. The uppermost part of valence bands from $-7.5$ to $0$ eV is essentially dominated by O 2$p$ states and an appreciable contribution of F 2$p$ orbitals with a small amount of B 2$p$ states. The obvious narrow band with sharp peak locates at about $-10.7$ eV entirely dominated by Ba 5$d$, O 2$s$, O 2$p$, and B 2$s$, B 2$p$, indicating strong $sp$ hybridization of the B and O orbitals in the [BO$_3$]$_{3^-}$ groups. While the bottom of the conduction band is essentially composed of Ba 5$d$, Ba 5$s$, B 2$p$, and O 2$p$ orbitals. In principle, the optical properties are mainly...
determined by the electronic transitions among the states near Fermi level, which are mainly occupied by the O 2\( p\) nonbonding orbitals, B–O hybridization states and Ba 5\( d\) states in \(Pna_{21}\)-BMBF. Besides, the interatomic interactions within the BO\(_3\) units and MgO\(_4\)F\(_2\) octahedra can be clearly visualized by the electron localization function diagrams. Results show the ionic character of Mg–O and Mg–F bonds in the MgO\(_4\)F\(_2\) octahedra as well as the covalent nature of B–O bonds in the [BO\(_3\)]\(^{3–}\) units (Fig. 7b). Through the Mulliken population analysis, the same conclusions can also be substantiated by the calculated overlap populations for Mg–F, Mg–O and B–O, which are 0.12–0.21, 0.21–0.55, and 0.85–0.97, respectively (higher populations reflect stronger covalence).

The NLO properties of \(Pna_{21}\)-BMBF were also calculated using a theoretical technique under the static limit within the length gauge. The calculated SHG tensors are evaluated to be \(d_{33} = 0.47\), \(d_{32} = −0.39\), and \(d_{31} = 0.09\) pm/V, respectively. These values are well consistent with experimental values presented above (\(d_{33} = \ldots\))
The SHG density analysis can be used to intuitively and accurately display the SHG-contributed orbitals for an NLO crystal. Furthermore, we investigated the SHG origin of Pna21-BMBF from the perspective of orbital analysis using SHG density analysis. And the SHG process is denoted by two virtual transition processes, namely virtual electron (VE) and virtual hole processes. The SHG process is denoted by two virtual transition processes, namely virtual electron (VE) and virtual hole processes. And the SHG process is denoted by two virtual transition processes, namely virtual electron (VE) and virtual hole processes. To sum up, the large SHG response of Pna21-BMBF can be regarded as the synergistic effects of the planar [BO3]3− and distorted MgO2F2 octahedra. In summary, by starting from the SBBO structure, we designed and synthesized two beryllium-free SBBO-like borates through chemical cosubstitution strategy. A high-quality Pna21-BMBF crystal with dimensions up to 16 × 14 × 8 mm3 has been grown by the top-seeded solution growth method with a BaF2-H3BO3-LiF flux system. Linear and nonlinear optical measurements reveal a sufficiently large SHG coefficient (d33 = 0.51 pm/V), suitable birefringence (0.045@532 nm), type I phase-matching, and chemical stability. Remarkably, Pna21-BMBF has a large LDT (~6.2 GW/cm2), a deep-UV cutoff edge (λ ~ 184 nm), a weak anisotropic thermal expansion as well as the capacity of insolvability in water, these optical properties could be comparable or superior to that of commercial NLO materials β-BBO (Supplementary Table 10). Thus, these merits on optical properties make Pna21-BMBF a promising UV NLO material.

Methods

Synthesis and crystal growth. Polycrystalline samples of targeted Pna21-BMBF were synthesized through solid-state reaction method by mixing the raw materials BaF2, BaCO3, MgO, and H3BO3 according to the molar ratio of 2:0.5:3. A mixture of Pna21-BMBF polycrystalline samples, BaF2, H3BO3, and LiF were placed into a flux 30 × 30 mm platinum crucible and melted at 750 °C in a temperature-programmable electric furnace. The solution was held at 750 °C for 24 h to form a homogeneous solution. After that, cooled to 715 °C and dipped the Pna21-BMBF seed crystal into the solution and held for 2 h that allowed the seed surface to melt. The solution was slowly cooled to the saturation temperature at 712 °C. Then the Pna21-BMBF crystal was grown by cooling the solution growth procedure finished. When the growth procedure finished, the Pna21-BMBF crystal was drawn out of the solution and cooled down to room temperature at a rate of 20 °C/h. While for P62m-BMBF single crystals, the loaded compositions are Ba(NO3)2 (0.5227 g, 2 mmol), BaF2 (0.3507 g, 2 mmol), MgO (0.0403 g, 1 mmol) and H3BO3 (0.4328 g, 7 mmol). All the reagents were mixed homogenously and transferred to a platinum crucible. The samples were heated to 800 °C in 24 h and held at this temperature for 72 h and then cooled to 700 °C at a rate of 1.0 °C/h, after that, cooled to room temperature at a rate of 15 °C/h. During the process of crystallization, colorless and transparent P62m-BMBF crystals were formed in the platinum crucible.

Characterization. The selected single crystals with dimensions up to 0.12 × 0.10 × 0.01 mm3 for Pna21-BMBF and 0.16 × 0.07 × 0.06 mm3 for P62m-BMBF were glued on glass fibers for structure determination by single-crystal X-ray diffractometer. An APEX II CCD diffractometer equipped with monochromatic Mo Kα radiation was used for the single-crystal data collection. The Bruker SADABS software package was used to reduce the collected data. The absorption corrections were carried out with the SADABS program and integrated with the SAINT program. The original structures were established by the direct method and refined by the full-matrix least-squares program on SHELX. The PLATON program was used for checking the possible missing symmetry elements, but no higher symmetries were found. Investigation of the thermal behavior of Pna21-BMBF crystal was performed using a NETZSCH STA 449 C simultaneous thermal analyzer. The sample of 6.5 mg was enclosed in a platinum crucible and heated from 40 to 1200 °C at a rate of 5 °C/min. The measurements were carried out in an atmosphere of flowing N2. The powder X-ray diffraction data of Pna21-BMBF were collected at room temperature using an automated Bruker D2 X-ray diffractometer (Supplementary Figure 4). The transmittance spectra of Pna21-BMBF were collected by a Solid Spec-3700D UV spectrophotometer for the range of 180–2500 nm in an atmosphere of flowing N2 and by a Shimadzu IRAfinity-1 Fourier spectrometer for the range extended from 2500 to 4000 nm (Supplementary Figure 5). The powder SHG measurements for targeted Pna21- and P62m-BMBF were carried out on the basis of the Kurtz–Perry method. Polycrystalline samples of Pna21- and P62m-BMBF were grown and sieved into the following particle sizes: 20–38; 38–55; 55–88; 88–105; 105–150; 150–200; and 200–250 μm. During the measurement, Pna21- and P62m-BMBF samples were irradiated with a Q-switched Nd:YAG laser with light wavelength of 1064 nm. The intensity of the mode-locked laser was ~180 nm, a weak anisotropic thermal expansion as well as the capacity of insolvability in water, these optical properties could be comparable or superior to that of commercial NLO materials β-BBO (Supplementary Table 10). Thus, these merits on optical properties make Pna21-BMBF a promising UV NLO material.
The harmonic power $P_{2\omega}$ is expressed as the following Eq.(3):

$$P_{2\omega}(\theta) = \frac{512n_2^2}{C_{\text{FW}}^2} \overline{P_0^2} f(n, \theta) \sin \Psi$$

$$f(n, \theta) = \frac{1}{n_n^2 - n_2^2} \sqrt{\frac{n_n^2 \cos^2 \theta - n_2^2 \cos^2 \phi}{n_2^2 \cos^2 \phi}}$$

where $c$ is the speed of light in vacuum, $n_\lambda$ is the radius of light, $n_n$ and $n_2$ are the refractive indices under the fundamental and harmonic wave length, $d$ is the NLO coefficient, $P_0$ is the beam power, \( \Psi = 2\pi n_2 \cos \theta \), and $\sin \Psi$ determines the minima oscillating position, $t_\lambda$ and $t_{2\lambda}$ are the transmission coefficients of fundamental wave and harmonic wave, $\rho(\theta)$ is the projection factor, $\rho(\theta)$ is the incident multiple-reflection constant, and $\rho(\theta)$ is the beam size correction. The $f(n, \theta)$ part depicts the envelope of the Maker fringe by fitting the calculated and measured Maker fringe, a constant, $C = 512n_2/\overline{P_0^2}(\text{c wavelength})$ can be obtained. The magnitude of NLO coefficients of Pna2Z-Ba2Mg(BO3)F3 can be determined relatively to $d_{\text{KDP}}$ of KDP crystal, and the coefficient equation can be expressed as:

$$d_{\text{sample}} \approx \sqrt{\frac{C_{\text{sample}}}{C_{\text{KDP}}}} d_{\text{KDP}}$$

**Computational methods.** First-principles calculations of Pna2Z-BMF based on density functional theory were performed by a plane-wave pseudopotential calculation package CASTEP.\(^{38}\) The exchange and correlation effects were treated by Perdew–Burke–Ernzerhof in the generalized gradient approximation.\(^{39}\) The interactions between the ionic cores and electrons were described by norm-conserving pseudopotentials.\(^{50}\) The cutoff energy for the planewave basis was 990 eV. The Brillouin zone was sampled by $4 \times 2 \times 3$ Monkhorst-Pack k-point.

**Data availability.** The authors declare that the data supporting the findings of this study are available within the article and Supplementary Information files, or from the corresponding authors upon reasonable request.

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Author contributions

M.M. and M.Z. grew the single crystals and performed the experiments, data analysis, and paper writing. H.W. supervised the optical experiments. Z.Y. developed the theoretical calculations. Y.S. performed the crystal data collection. J.S. and S.P. designed and supervised the experiments. All the authors discussed the results and commented on the manuscript.

Additional information

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