

Cite this: *Chem. Sci.*, 2021, 12, 13897

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## Ba<sub>4</sub>Ca(B<sub>2</sub>O<sub>5</sub>)<sub>2</sub>F<sub>2</sub>: $\pi$ -conjugation of B<sub>2</sub>O<sub>5</sub> in the planar pentagonal layer achieving large second harmonic generation of *pyro*-borate†

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The nonlinear optical (NLO) crystals that can expand the wavelength of the laser to the deep-ultraviolet (DUV) region by the cascaded second harmonic generation (SHG) are of current research interest. It is well known that borates are the most ideal material class for the design of new DUV NLO crystals owing to the presence of good NLO genes, e.g., BO<sub>3</sub> or B<sub>3</sub>O<sub>6</sub> groups. However, the NLO *pyro*-borates with the B<sub>2</sub>O<sub>5</sub> dimers as the sole basic building units are still rarely reported owing to their small SHG responses. In this communication, by constructing a planar pentagonal [Ca(B<sub>2</sub>O<sub>5</sub>)<sub>∞</sub>] layer, the NLO *pyro*-borate Ba<sub>4</sub>Ca(B<sub>2</sub>O<sub>5</sub>)<sub>2</sub>F<sub>2</sub> with a large SHG response (~2.2 × KDP, or ~7 ×  $\alpha$ -Li<sub>4</sub>B<sub>2</sub>O<sub>5</sub>) and a DUV transparent window has been designed and synthesized. The first-principles calculations show that the large SHG response of Ba<sub>4</sub>Ca(B<sub>2</sub>O<sub>5</sub>)<sub>2</sub>F<sub>2</sub> mainly originates from the better  $\pi$ -conjugation of the coplanar B<sub>2</sub>O<sub>5</sub> dimers in the [Ca(B<sub>2</sub>O<sub>5</sub>)<sub>∞</sub>] layer. In addition, the planar pentagonal pattern in the [Ca(B<sub>2</sub>O<sub>5</sub>)<sub>∞</sub>] layer provides an ideal template for designing the new DUV NLO crystals, apart from those in known DUV borates, e.g., the [Be<sub>2</sub>BO<sub>3</sub>F<sub>2</sub>]<sub>∞</sub> layer in KBe<sub>2</sub>BO<sub>3</sub>F<sub>2</sub> (KBBF).

Received 6th September 2021  
Accepted 22nd September 2021

DOI: 10.1039/d1sc04913e

rsc.li/chemical-science

Deep-ultraviolet (DUV,  $\lambda < 200$  nm) coherent lights with high photon energy, high spatial resolution, and a small heat-affected zone are of significance for applications in photolithography, high-resolution spectroscopy, laser cooling, and scientific equipment.<sup>1–4</sup> However, it is difficult or well-nigh impossible for solid-state lasers to directly radiate the DUV coherent lights. In contrast, relying on the process of second harmonic generation (SHG) of nonlinear optical (NLO) crystals is a more effective way to generate the DUV coherent lights and causes much attention.<sup>5,6</sup> Therefore, the NLO crystal has become an important material basis of solid-state lasers, which seriously affects the development of all-solid-state laser technology. However, it is still a great challenge to rationally design and synthesize DUV NLO crystals because of the extremely rigorous requirements of structural symmetry and properties.<sup>7–10</sup> Structurally, the DUV NLO crystals must crystallize in the noncentrosymmetric (NCS) space groups which are the prerequisite for the materials to exhibit SHG responses.

Moreover, it should possess a broad transparency window, a largely effective NLO coefficient ( $d_{\text{eff}} \geq 0.39$  pm V<sup>-1</sup>), and a moderate birefringence (0.05–0.10@1064 nm) to achieve the phase-matching (PM) conditions in the DUV region.<sup>10</sup> Based on these requirements, borates have been considered as the ideal material class for DUV NLO crystals because of their special structure and properties' virtues, including the rich acentric structural types, large band gaps, and stable physical and chemical properties.<sup>8</sup> To date, the commercialized borate-based UV NLO crystals consist of  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> (BBO), LiB<sub>3</sub>O<sub>5</sub> (LBO), CsLiB<sub>6</sub>O<sub>10</sub> (CLBO),<sup>9,10</sup> and the practical DUV NLO crystal KBe<sub>2</sub>BO<sub>3</sub>F<sub>2</sub> (KBBF). Especially for KBBF, it has become the sole material that can generate DUV coherent laser light (177.3 nm) by a direct SHG method.<sup>7</sup> Other excellent borate-based UV NLO crystals also consist of K<sub>3</sub>B<sub>6</sub>O<sub>10</sub>Cl,<sup>11</sup> SrB<sub>5</sub>O<sub>7</sub>F<sub>3</sub>,<sup>12</sup> Li<sub>2</sub>B<sub>6</sub>O<sub>9</sub>F<sub>2</sub>,<sup>5</sup> CsAlB<sub>3</sub>O<sub>6</sub>F,<sup>13</sup> M<sub>2</sub>B<sub>10</sub>O<sub>14</sub>F<sub>6</sub> (M = Ca, Sr),<sup>14</sup> NH<sub>4</sub>B<sub>4</sub>O<sub>6</sub>F,<sup>15</sup> NaSr<sub>3</sub>-Be<sub>3</sub>B<sub>3</sub>O<sub>9</sub>F<sub>4</sub>,<sup>16</sup> AB<sub>4</sub>O<sub>6</sub>F (A = K, Rb, and Cs),<sup>17</sup> etc.

The above borate-based materials have achieved great success as UV and DUV NLO crystals, which are mainly attributed to the ability of boron atoms to coordinate with three or four oxygen anions forming trigonal-planar or tetrahedral building blocks.<sup>18,19</sup> For example, the first borate-based NLO crystal, KB<sub>5</sub>O<sub>8</sub>·4H<sub>2</sub>O (KB<sub>5</sub>), has the basic building units (BBUs) of [B<sub>5</sub>O<sub>10</sub>], while the BBUs of  $\beta$ -BBO, LBO, and KBBF are [B<sub>3</sub>O<sub>6</sub>], [B<sub>3</sub>O<sub>7</sub>], and isolated [BO<sub>3</sub>], respectively.<sup>7,8</sup> Remarkably, although various borate crystals with different types of borate groups have been explored during the past decades, the *pyro*-borate

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† Electronic supplementary information (ESI) available. CCDC 2095000. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1sc04913e

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NLO crystals with  $B_2O_5$  groups as the sole BBUs are rarely reported owing to their weak SHG responses.<sup>20–23</sup> For example, the SHG response of the DUV transparent  $\alpha$ - $Li_4B_2O_5$  (ref. 23) is only  $\sim 0.3 \times$  KDP, which is far smaller than the expected value ( $0.39 \text{ pm V}^{-1}$ ,  $1 \times$  KDP).

Actually, the flexible  $B_2O_5$  groups which are composed of two  $\pi$ -conjugated  $BO_3$  units through corner-sharing may also be capable of generating excellent optical performance if they have benign arrangements. In recent research, Pan's group has indicated that the  $B_2O_5$  dimers are perfect for the design of DUV birefringent crystals. By the synergistic combination, they have successfully designed a potential *pyro*-borate birefringent crystal,  $Li_2Na_2B_2O_5$ , with a short UV cut-off edge (181 nm) and large birefringence ( $0.095@532 \text{ nm}$ ).<sup>21</sup> And they have also grown  $Ca(BO_2)_2$  crystals exhibiting a short UV cut-off edge and larger birefringence (169 nm;  $0.2471@193 \text{ nm}$ ). Based on the analysis of the structure–property relationship of  $Ca(BO_2)_2$ , they stated that the polymerized planar  $B_nO_{2n+1}$  groups, *e.g.*,  $B_2O_5$ , could generate a larger anisotropy than isolated  $BO_3$ .<sup>22</sup> However, their opposite arrangements of B–O groups make them crystallize in the centrosymmetric (CS) space groups, which limit their further development as NLO compounds. Thus, it is clear that *pyro*-borates exhibiting a large birefringence and a short UV cut-off edge would also be promising DUV NLO crystals if their SHG responses can be enhanced.

Based on the above-mentioned ideas, a systematical investigation has been performed on DUV *pyro*borates. And finally, we successfully synthesized a new NCS *pyro*-borate,  $Ba_4Ca(B_2O_5)_2F_2$ , which can exhibit not only a large SHG response ( $\sim 2.2 \times$  KDP and  $\sim 7 \times \alpha$ - $Li_4B_2O_5$ ) but also a short UV cut-off edge ( $<190 \text{ nm}$ ). Analyzing its structure, one can find that its excellent NLO properties mainly originate from the unique planar pentagonal  $[Ca(B_2O_5)]_\infty$  layer, where the  $B_2O_5$  groups adopt the almost coplanar configurations that favor the structure to generate large SHG response and birefringence,<sup>21</sup> meanwhile the terminal O atoms of  $B_2O_5$  groups are also linked by the  $Ca^{2+}$  cations, which eliminate the dangling bonds of  $B_2O_5$  groups and further blue-shift the UV cut-off edge. More importantly, the adjacent  $[Ca(B_2O_5)]_\infty$  layers in  $Ba_4Ca(B_2O_5)_2F_2$  are linked by other  $B_2O_5$  groups to form a 3D framework, which will be favorable for the material to avoid the layer habit that KBBF suffers from. In this sense, the planar pentagonal  $[Ca(B_2O_5)]_\infty$  layer is similar to the  $[Be_2BO_3F_2]_\infty$  layer in KBBF, and it can be seen as a new structure template for the design of new DUV NLO crystals, especially for the DUV *pyro*-borates. Herein, we will describe the synthesis, experimental and computational characterization as well as the functional properties of the new DUV NLO material,  $Ba_4Ca(B_2O_5)_2F_2$ .

A polycrystalline sample of  $Ba_4Ca(B_2O_5)_2F_2$  was synthesized by the conventional solid-state reaction and the purity was confirmed by powder X-ray diffraction (XRD) (Fig. S1†). With the polycrystalline sample, the thermal behavior of  $Ba_4Ca(B_2O_5)_2F_2$  was studied by the thermogravimetric (TG) and differential scanning calorimetry (DSC) measurements. The heating DSC curve shows a sharp endothermic peak at  $815 \text{ }^\circ\text{C}$  with no obvious weight loss in the TG curve (Fig. S2†), suggesting that  $Ba_4Ca(B_2O_5)_2F_2$  has good thermal stability. To further

investigate the thermal behavior of  $Ba_4Ca(B_2O_5)_2F_2$ , the polycrystalline sample was calcined at  $840 \text{ }^\circ\text{C}$  and the XRD analysis showed that the calcined sample was  $Ba_4Ca(B_2O_5)_2F_2$ ,  $Ba_2Ca(BO_3)_2$  (PDF #01-085-2268),  $Ba_2CaB_6O_{12}$  (PDF #01-075-1401) and other unknown phases (Fig. S3†). These results illustrate that  $Ba_4Ca(B_2O_5)_2F_2$  melts incongruently and the suitable flux is necessary for the crystal growth.

With the  $Na_2O$ – $PbF_2$ – $B_2O_3$  as the flux, millimeter-sized block crystals of  $Ba_4Ca(B_2O_5)_2F_2$  were grown for the single-crystal XRD structure determination.  $Ba_4Ca(B_2O_5)_2F_2$  crystallizes in the NCS and polar space group,  $P2_1$  (Table S1†). In the asymmetric unit, there are four unique Ba, one Ca, four B, ten O, and two F atom(s), which all fully occupy the  $2a$  Wyckoff positions (Table S2†). All B atoms are coordinated to three oxygen atoms to form the  $BO_3$  triangles with the B–O distances ranging from  $1.312(17)$  to  $1.460(16) \text{ \AA}$  and O–B–O angles varying from  $108.0(13)$  to  $130.2(15)^\circ$ . The  $BO_3$  triangles are further connected to form two types of  $B_2O_5$  dimers, *i.e.* plane  $B(1,3)_2O_5$  and twisted  $B(2,4)_2O_5$ , which are the BBUs of  $Ba_4Ca(B_2O_5)_2F_2$ . The Ca atoms are coordinated to six oxygen atoms to form  $CaO_6$  octahedra with the Ca–O distances ranging from  $2.285(9)$  to  $2.325(13) \text{ \AA}$ . For the  $Ba^{2+}$  cations, they exhibit three different coordination environments,  $Ba(1,2)O_6F_2$ ,  $Ba(3)O_8F_2$ , and  $Ba(4)O_7F_2$  (Fig. S4†) with the Ba–O distances ranging from  $2.585(9)$  to  $3.250(11) \text{ \AA}$  and the Ba–F bond lengths ranging from  $2.635(8)$  to  $2.736(8) \text{ \AA}$ . Remarkably, for the  $F^-$  anions, each unique fluorine atom serves as a common vertex for four Ba atoms to form the  $FBa_4$  polyhedra (Fig. S5a†), which could be treated as fluorine-centered secondary building units (SBUs). The Ba–F–Ba angles vary from  $99.0(2)$  to  $120.2(3)^\circ$ . The bond valence sum (BVS) calculations show the values of  $1.67$ – $1.97$ ,  $2.45$ ,  $2.88$ – $3.10$ ,  $1.78$ – $2.13$ , and  $0.95$ – $1.09$ , for  $Ba^{2+}$ ,  $Ca^{2+}$ ,  $B^{3+}$ ,  $O^{2-}$ , and  $F^-$ , respectively (Table S2†). The BVSs of atoms are consistent with their expected oxidation states except the one from the  $Ca^{2+}$  cations. The larger BVSs of  $Ca^{2+}$  cations can be attributed to six shorter Ca–O bond lengths, which are also observed in other  $Ca^{2+}$ -containing borates, such as  $YCa_3(VO)_3(BO_3)_4$  (2.44),<sup>24</sup>  $Rb_2Ca_3B_{16}O_{28}$  (2.29), and  $Cs_2Ca_3B_{16}O_{28}$  (2.30).<sup>25</sup>

The structure of  $Ba_4Ca(B_2O_5)_2F_2$  is shown in Fig. 1. In the structure, the plane  $B(1,3)_2O_5$  dimer is first connected with four  $CaO_6$  octahedra, meanwhile, each  $CaO_6$  octahedron is also linked by four  $B(1,3)_2O_5$  dimers through sharing their four equatorial O atoms to form a unique planar pentagonal  $[Ca(B_2O_5)]_\infty$  layer in the  $b$ – $c$  plane (Fig. 1a, b). Then, these  $[Ca(B_2O_5)]_\infty$  layers are further linked by the twisted  $B(2,4)_2O_5$  dimers to construct a 3D framework with  $Ba^{2+}$  cations maintaining the charge balance (Fig. 1c). Remarkably, for the arrangements of the  $Ba^{2+}$  cations and the  $F^-$  anions, the fluorine-centered SBU  $FBa_4$  polyhedra are linked to construct the 2D  $[F_2Ba_4]$  infinite layer (Fig. S5b†) with the same orientation, which further fills the apertures in the  $[Ca(B_2O_5)_2]$  framework (Fig. S5c†). The existence of fluorine-centered SBUs would certainly have a strong influence on the local coordinate environments, and finally on the whole structure.<sup>26</sup>

It is very interesting that  $Ba_4Ca(B_2O_5)_2F_2$  contains a planar pentagonal  $[Ca(B_2O_5)]_\infty$  layer, which is similar to the  $[Be_2BO_3F_2]_\infty$  layer in KBBF. The structural evolution from KBBF to



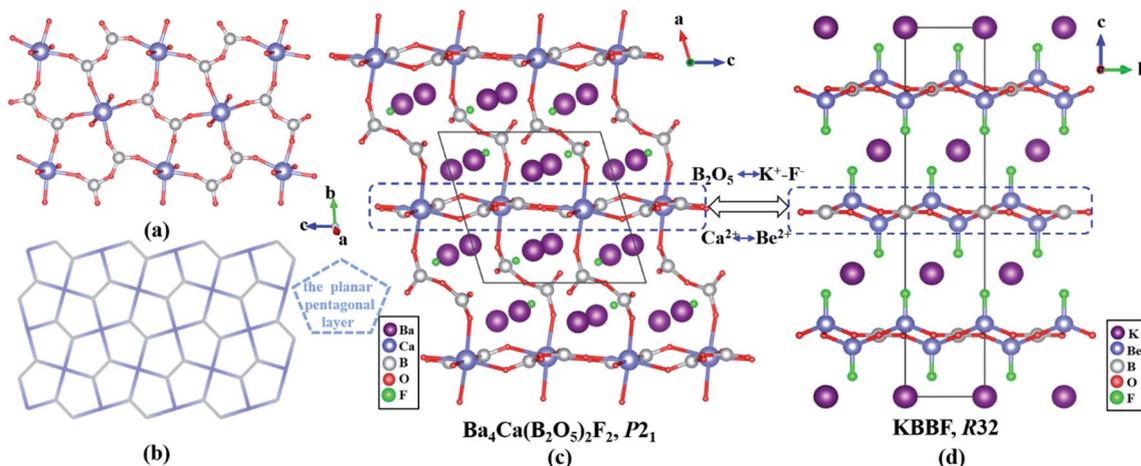


Fig. 1 (a) The  $[\text{Ca}(\text{B}_2\text{O}_5)]$  layer is composed of  $\text{B}_2\text{O}_5$  dimers and  $\text{CaO}_6$  octahedra. (b) The planar pentagonal topology layer. The comparison of structures between (c)  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  and (d) KBBF.

$\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  is also shown in Fig. 1c and d. In KBBF, the BBUs are the planar  $\text{BO}_3$  triangles, which are connected with  $\text{BeO}_3\text{F}$  in the  $a$ - $b$  plane by strong covalent bonds to form the  $[\text{Be}_2\text{BO}_3\text{F}_2]_\infty$  layers (Fig. S6c†) and the  $[\text{Be}_2\text{BO}_3\text{F}_2]_\infty$  layers have achieved excellent NLO properties of the KBBF crystal.<sup>7</sup> However in  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$ , the  $\text{BO}_3$  triangles are changed into the  $\text{B}_2\text{O}_5$  dimers, and the  $\text{BeO}_3\text{F}$  tetrahedra are substituted by the  $\text{CaO}_6$  polyhedra. These  $\text{B}_2\text{O}_5$  dimers are also connected by the  $\text{CaO}_6$  polyhedra to form the interesting planar pentagonal  $[\text{Ca}(\text{B}_2\text{O}_5)]_\infty$  layer (Fig. S6d†). More importantly, in KBBF, the adjacent  $[\text{Be}_2\text{BO}_3\text{F}_2]_\infty$  layers are connected by the weak  $\text{K}^+\text{F}^-$  ionic bonds that results in the strong layer habit of the KBBF crystals, whereas in  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$ , the  $[\text{Ca}(\text{B}_2\text{O}_5)]_\infty$  layers are bridged by the strong covalent B–O bonds to form a stable 3D framework, which will greatly overcome the layering tendency of the KBBF crystal and facilitate the crystal growth.

In addition, we also notice that the planar pentagonal  $[\text{Ca}(\text{B}_2\text{O}_5)]_\infty$  layer maybe helpful for enhancing the SHG responses of *pyro*-borates because small SHG responses of *pyro*-borates are attributed to the typical twisted configurations of the  $\text{B}_2\text{O}_5$  groups, which are unfavorable for forming the  $\pi$ -conjugation and the superposition of the microscopic SHG response. For example,  $\alpha\text{-Li}_4\text{B}_2\text{O}_5$ , a DUV transparent *pyro*-borate with sole  $\text{B}_2\text{O}_5$  units as the BBUs, has a weak SHG response, which may be derived from the twisted  $\text{B}_2\text{O}_5$  groups and non-planar arrangements (Fig. S7a†). However, in  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$ , the planar configuration of the pentagonal layers can assist the  $\text{B}_2\text{O}_5$  groups to adopt a nearly coplanar arrangement (Fig. S7b†) and effectively enhance the  $\pi$ -conjugation of  $\text{B}_2\text{O}_5$  groups. The better  $\pi$ -conjugation of the planar  $\text{B}_2\text{O}_5$  groups in the planar pentagonal  $[\text{Ca}(\text{B}_2\text{O}_5)]_\infty$  layer has also been confirmed by the electron orbital calculation based on the first-principles calculations.<sup>27</sup> The calculated result is shown in Fig. 2. Clearly, the prominent conjugated interactions are observed in the nearly coplanar  $\text{B}(1,3)_2\text{O}_5$  dimers of  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  (Fig. 2a), whereas it does little in the twisted  $\text{B}(2,4)_2\text{O}_5$  dimers of  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  (Fig. 2b) and two types of twisted  $\text{B}_2\text{O}_5$  dimers in  $\alpha\text{-Li}_4\text{B}_2\text{O}_5$  (Fig. 2c and d). It can be expected that the

nearly coplanar  $\text{B}_2\text{O}_5$  dimers are more conducive to the large SHG response than the twisted  $\text{B}_2\text{O}_5$  dimers. Remarkably, the similar pentagonal layers are also observed in other *pyro*-phosphates, such as  $\text{Ba}_2\text{NaClP}_2\text{O}_7$ ,  $\text{K}_2\text{Sb}(\text{P}_2\text{O}_7)\text{F}$ ,  $\text{Rb}_3\text{PbBi}(\text{P}_2\text{O}_7)_2$ , and  $\text{Rb}_3\text{BaBi}(\text{P}_2\text{O}_7)_2$ . Clearly, as *pyro*-phosphates are the non- $\pi$ -conjugated systems, the planar pentagonal layers are only helpful for the orientation of anion groups.<sup>28–31</sup> However, they cannot form the better  $\pi$ -conjugation. Therefore, the better  $\pi$ -conjugation of the nearly coplanar  $\text{B}_2\text{O}_5$  groups in planar pentagonal layers of *pyro*-borate  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  would have a different contributing mechanism to the SHG effect with other non- $\pi$ -conjugated *pyro*-phosphates.

The presence of  $\text{BO}_3$  triangles in  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  is confirmed by the IR spectral measurements (Fig. S8†). The peaks at  $1362\text{ cm}^{-1}$  and  $1208\text{ cm}^{-1}$  can be attributed to the asymmetric stretching of  $\text{BO}_3$  groups.<sup>32</sup> A strong band at  $1069\text{ cm}^{-1}$  in the IR spectrum may be associated with the stretching vibration of B–O–B in  $\text{B}_2\text{O}_5$ .<sup>33,34</sup> The weak absorption bands at  $950$ , and  $810\text{ cm}^{-1}$  correspond to the symmetrical stretching vibrations of  $\text{BO}_3$  and B–O–B in  $\text{B}_2\text{O}_5$ , respectively. The peaks at  $751$  and  $615\text{ cm}^{-1}$  can be attributed to the out-of-plane bending of the  $\text{BO}_3$  groups.<sup>34</sup> Further, the UV-vis-NIR

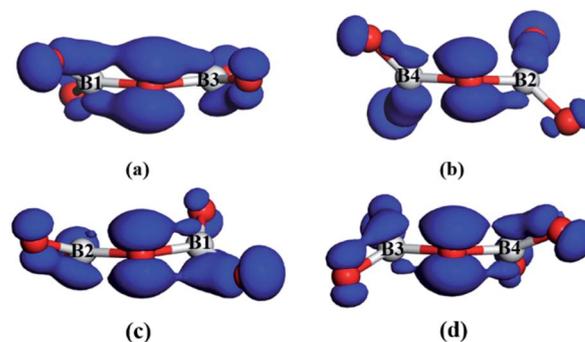


Fig. 2 The orbitals of the nearly coplanar  $\text{B}(1,3)_2\text{O}_5$  (a) and twisted  $\text{B}(2,4)_2\text{O}_5$  dimers (b) in  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$ . The orbitals of two twisted  $\text{B}_2\text{O}_5$  dimers (c and d) in  $\alpha\text{-Li}_4\text{B}_2\text{O}_5$ .



diffuse reflectance spectrum was also measured (Fig. S9†), which shows that  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  is transparent down to the DUV region with a UV cut-off edge less than 190 nm (corresponding to a large band gap of 6.2 eV), which is comparable to the newly developed NLO-active borates, such as  $\text{RbB}_3\text{O}_4\text{F}_2$  (<190 nm),  $\text{CsZn}_2\text{BO}_3\text{X}_2$  ( $\text{X}_2 = \text{F}_2, \text{Cl}_2$ , and  $\text{FCl}$ ) (<190 nm) and so on.<sup>35–38</sup> The short cut-off edge demonstrates the potential application of  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  as a DUV NLO crystal.

As  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  crystallizes in the NCS space group  $P2_1$ , it possesses the SHG response, which was measured by the Kurtz-Perry method with the well-known NLO material  $\text{KH}_2\text{PO}_4$  (KDP) as a reference.<sup>39</sup> As shown in Fig. 3, the SHG intensities of  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  increase with the increase of particle sizes, indicating that  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  is type-I phase-matchable. The SHG intensity of  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  at the particle size of 150–212  $\mu\text{m}$  is about 2.2 times that of KDP, and is larger than that of KBBF ( $1.2 \times \text{KDP}$ ) or comparable with those newly reported UV NLO crystals, *i.e.*  $\gamma\text{-Be}_2\text{BO}_3\text{F}$  ( $2.3 \times \text{KDP}$ ),<sup>6</sup>  $\beta\text{-Rb}_2\text{Al}_2\text{B}_2\text{O}_7$  ( $2 \times \text{KDP}$ ),<sup>40</sup>  $\text{Li}_4\text{Sr}(\text{BO}_3)_2$  ( $2 \times \text{KDP}$ ),<sup>41</sup>  $\text{CsB}_4\text{O}_6\text{F}$  ( $\sim 1.9 \times \text{KDP}$ ).<sup>2</sup> In addition, as we know, the SHG response of  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  is the largest among all the known DUV transparent borates with  $\text{B}_2\text{O}_5$  units (Table S4†). Its SHG response ( $2.2 \times \text{KDP}$ ) is about seven times larger than that of  $\alpha\text{-Li}_4\text{B}_2\text{O}_5$  ( $0.3 \times \text{KDP}$ ), another DUV transparent *pyro*-borate with sole  $\text{B}_2\text{O}_5$  units.

To understand the origin of the excellent optical properties of  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$ , we also carried out the first-principles calculations.<sup>27</sup> It shows that  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  has an indirect band gap of 6.34 eV (Figures S10a†), which is in accordance with the experimental results. The valence band maximum (VBM) of  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  is mainly composed of the orbitals in Ba, and O atoms, while the conduction band minimum (CBM) is dominantly composed of the orbitals in Ba, B, and O atoms. Therefore, the band gap of  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  is mainly determined by Ba atoms and  $\text{B}_2\text{O}_5$  groups. Based on the calculated electron structure, the NLO coefficients of  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  are also calculated. The largest NLO coefficient of  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  is  $d_{22} = -0.524 \text{ pm V}^{-1}$ , which is about 5 times lower than that of  $\alpha\text{-Li}_4\text{B}_2\text{O}_5$  ( $d_{24} = -0.102 \text{ pm V}^{-1}$ ) (Table S5a†), which is matched with the experimental one. Further, the SHG-weighted density maps of  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  are shown in Fig. 4. These reveal that  $\text{B}_2\text{O}_5$  dimers make the dominant contribution (72.7%) to the total SHG effect (Table S5b†). The band-resolved SHG analysis

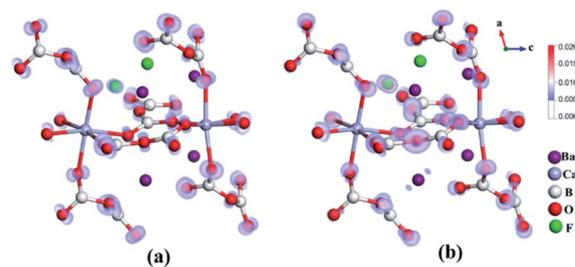


Fig. 4 The SHG-weighted density maps of the virtual electron process (a) and virtual hole process (b) of  $d_{22}$  for  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$ .

can also conclude that B–O orbitals in  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  contribute more to the SHG response than those in  $\alpha\text{-Li}_4\text{B}_2\text{O}_5$  (Fig. S10b, S10c†), indicating that the arrangements of  $\text{B}_2\text{O}_5$  dimers in  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  is more beneficial for the large SHG response. And different from  $\alpha\text{-Li}_4\text{B}_2\text{O}_5$ , F-centered secondary building units (SBUs) exist in the structure of  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$ , and they are further linked to construct 2D  $[\text{F}_2\text{Ba}_4]_\infty$  infinite layers, which could help  $\text{B}_2\text{O}_5$  groups arrange in a planar pattern (Fig. S5†).<sup>26</sup> So, based on the above analysis, we can conclude that the nearly coplanar  $\text{B}_2\text{O}_5$  dimers in the planar pentagonal layer and the SBU  $\text{FBa}_4$  tetrahedra make a significant contribution to the SHG response of  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$ .

## Conclusions

In summary, a new *pyro*-borate  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  with a DUV absorption edge (<190 nm) has been successfully designed and synthesized. Its structure consists of interesting  $[\text{Ca}(\text{B}_2\text{O}_5)]_\infty$  layers, which is similar to the  $[\text{Be}_2\text{BO}_3\text{F}_2]_\infty$  layers in KBBF. What's more, the  $[\text{Ca}(\text{B}_2\text{O}_5)]_\infty$  layers are bridged by the strong covalent B–O bonds to form a stable 3D framework, which would greatly overcome the layering tendency of the KBBF crystal. Based on the electron orbital calculation, better  $\pi$ -conjugated interactions of the  $\text{B}_2\text{O}_5$  dimers have been confirmed owing to the coplanar requirement of the planar pentagonal layers, which is apparently different from the similar pentagonal layers reported in the *pyro*-phosphates. Further, performance measurements indicate that  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  can exhibit the largest SHG response ( $2.2 \times \text{KDP}$ ) in the DUV transparent borates with  $\text{B}_2\text{O}_5$  units, and its SHG response is about seven times larger than that of  $\alpha\text{-Li}_4\text{B}_2\text{O}_5$ . The first-principles calculations and the structure–property relationship analysis indicate that the large SHG response of  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  mainly derives from the synergistic effects of the  $\pi$ -conjugated interactions of  $\text{B}_2\text{O}_5$  dimers in the planar pentagonal layers and the fluorine-centered SBUs. These results suggest that  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  would be a promising UV or DUV NLO crystal. Further research for the large size crystal growth of  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  is also on the way.

## Data availability

Supporting data for this article is presented in the ESI.†

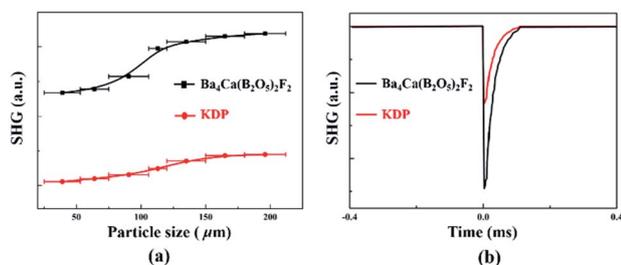


Fig. 3 (a) Phase-matching curve, *i.e.*, particle size vs. SHG intensity, data for  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  and  $\text{KH}_2\text{PO}_4$  (KDP) as reference. The solid curve is a guide for the eye, not a fit to the data. (b) Oscilloscope traces showing SHG intensities for  $\text{Ba}_4\text{Ca}(\text{B}_2\text{O}_5)_2\text{F}_2$  and KDP.



## Author contributions

Conceptualization and supervision: H. W. Yu and H. P. Wu; synthesis and characterization (single-crystal XRD, powder XRD, TG-DSC, IR, UV-vis-NIR and SHG measurements): S. S. Li; theoretical calculations: X. M. Liu, and Z. S. Lin. All authors proof-read, provided comments, and approved the final version of this manuscript.

## Conflicts of interest

The authors declare no conflict of interest.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant Nos. 22071179, 51972230, 51890864, 51802217, 61835014, and 51890865), Natural Science Foundation of Tianjin (Grant Nos. 20JCJJC00060 and 19JCZDJC38200), and the National Key R&D Program (Grant No. 2016YFB0402103) for this work.

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