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Cation Coordination Control of Anionic Group Alignment to Maximize SHG Effects in the $BaMBO_3F$ (M = Zn, Mg) Series

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Two new noncentrosymmtric fluoroborates, $BaZnBO_3F$ and $BaMgBO_3F$, have been synthesized and characterized. It is found that $BaZnBO_3F$ possesses a $P\bar{6}$ space group with cell parameters of $a = 5.0657(1)$ Å, $c = 4.2800(1)$ Å, and $Z = 1$. The structure is built up by five coordinated trigonal bipyramidal ZnO_3F_2 polyhedra and triangular BO_3 groups. The ZnO_3F_2 bipyramid shares its three equatorial oxygen atoms with three separate BO_3 groups to form a $ZnO_3{-}BO_3$ layer, and the layers are linked by the apical fluorine atoms in the third dimension. Owing to its special coordination, ZnO_3F_2 forces its three neighboring BO_3 groups to arrange into a perfect parallel alignment in the plane to give maximum contribution to the nonlinear optical (NLO) effect. Both calculation and powder second harmonic generation tests show that its effective NLO coefficient is on about the same order as that of LiB_3O_5. In contrast, in $BaMgBO_3F$, which crystallizes in space group *Cc* with $a = 17.614(3)$ Å, $b = 30.546(6)$ Å, $c = 8.060(2)$ Å, and $\beta = 90.008(2)°$, Mg coordinates to four oxygen and two fluorine atoms to form a severely distorted MgO_4F_2 octahedron. It also uses four equatorial oxygen atoms, sharing with three BO_3 groups to form a $MgO_4{-}BO_3$ layer, and again the layers are linked by the apical F atoms. Every Mg atom links with one edge-sharing and two corner-sharing BO_3 groups, leaving the BO_3 group misaligned and resulting in most of their contributions to NLO effects being canceled.

Introduction

Nonlinear optical (NLO) crystals play important roles in modern solid-state laser technology, owing to the inherent property that laser host materials often lase in discrete wavelengths. When second harmonic generation (SHG), sum frequency generation (SFG), and optical parameter generation (OPG) are combined, NLO crystals can extend laser frequencies covering from the deep UV to far-infrared regions.[1,2] One vital prerequisite for a material showing NLO properties is that the crystal must be acentric—noncentrosymmetric (NCS).[3] Traditionally, new NLO materials, such as KDP (KH_2PO_4),[4] KTP ($KTiOPO_4$),[5] BBO (BaB_2O_4),[6] and LBO (LiB_3O_5),[7] have been found when searching for NCS compounds in known structures[8] or by trials of synthesizing new compounds and testing their NLO abilities using the Kurtz and Perry powder SHG test method.[9]

Since the first calculation of the nonlinear optical property of the BBO crystal,[10] the idea of anionic groups being the main contributors to the nonlinear optical effect has been proven successfully in the development of many new nonlinear optical crystals in the borate series.[11] According to the anionic group theory,[12] the contributions of cations to the macroscopic NLO effect are neglected, and the macroscopic SHG coefficients are calculated by summing up the second-order polarizabilities ($\chi^{(2)}$) of the constituent anionic groups. On the basis of these ideas, the complex borate structures can be classified into several simple anionic $[B_nO_m]$ groups, and their contributions to the NLO effect can be fairly accurately calculated.[13] Though this idea has led to the findings of several important NLO crystals (e.g., LBO,[7] CBO,[7] and KBBF[14]), which have already found wide applications in

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(1) Dmitriev, V. G.; Gurzadyan, G. G.; Nikogosyan, D. N. *Handbook of Nonlinear Optical Crystals*; Springer-Verlag: Berlin, Germany, 1999.

(2) Sutherland, R. L.; McLean, D. G.; Kirkpatrick, S. *Handbook of Nonlinear Optical Crystals*; Marcel Dekker, Inc.: New York, 2003.

(3) Yariv A. *Quantum Electronics*, 2nd ed.; John-Wiley & Sons, Inc.: New York, 1975; Chapter 16.

(4) Giordmaine, J. A. *Phys. Rev. Lett.* **1962**, *8*, 19–20.

(5) Zumsteg, F. C.; Bierlein, J. D.; Gier, T. E. *J. Appl. Phys.* **1976**, *47*, 4980–4985.

(6) Chen, C. T.; Wu, B. C.; Jiang, A. D.; You, G. M. *Sci. Sin., Ser. B* **1985**, *28*, 235−243.

(7) Chen, C. T.; Wu, Y. C.; Jiang, A. D.; Wu, B. C.; You, G. M.; Li, R. K.; Lin, S. J. *J. Opt. Soc. Am. B* **1989**, *6*, 616−621.

(8) Halasyamani, P. S.; Poeppelmeier, K. R. *Chem. Mater.* **1998**, *10*, 2753–2769.

(9) Kurtz, S. K.; Perry, T. T. *J. Appl. Phys.* **1968**, *39*, 3798–3813.

(10) Li, R. K.; Chen, C. T. *Acta Phys. Sin.* **1985**, *34*, 823−827 (in Chinese).

(11) Chen, C. T.; Bai, L.; Wang, Z. Z.; Li, R. K. *J. Cryst. Growth* **2006**, *292*, 169–178.

(12) Chen, C. T.; Wu, Y. C.; Li, R. K. *Int. Rev. Phys. Chem.* **1989**, *8*, 65–91.

(13) Chen, C. T.; Wu, Y. C.; Li, R. K. *J. Cryst. Growth.* **1990**, *99*, 790–798.

(14) Chen, C. T.; Wang, Y. B.; Xia, Y. N.; Wu, B. C.; Tang, D. Y.; Wu, K. C.; Zeng, W. R.; Yu, L. H.; Mei, L. F. *J. Appl. Phys.* **1995**, *77*, 2268–2272.

solid-state laser systems, fewer and fewer new crystals can be found in known structures.

Though one can choose BO_3 groups with a large $\chi^{(2)}$ (about 4 times larger than that of BO_4) to construct new structures, we do not have a tool to arrange them in a crystal to let them work in concert to give maximum contribution rather than canceling out with each other as in centrosymmetric crystals. Parallel to our anionic group approach, many new NCS materials have been synthesized by incorporating asymmetric anion units with Jahn–Teller distorted ions or ions with electron lone pairs.[15] However, starting with an asymmetric unit only increases the chance to find NCS compounds; one still faces the same difficulty in aligning the asymmetric unit to maximize nonlinear effects. Different approaches have been proposed to overcome the alignment problem: Marvel et al. proposed that cation–anion interaction in a fluoroniobate is important for obtaining acentric polar structures.[16] They chose acentric anions $NbOF_5$ to interact with Na, K, or Cs and found that a slight off-centering K ion due to stronger K–O interaction causes $KNaNbOF_5$ to crystallize in an acentric structure. Although perfect alignment of the $NbOF_5$ group was not achieved, the individual dipoles partially aligned in an additive manner; as a result, a SHG effect (0.6 × KDP) was observed for the compound. More recently, Chang et al. found that compact octahedral coordination of LiO_6 and NaO_6 in $A_2Ti(IO_3)_6$ (A = Li, Na) forces the lone pairs in the IO_3 groups to point in the same direction, resulting in polar structures with large SHG effects.[15]

As the microscopic mechanism of the nonlinear optical effect is well-known, and there have been over 20 new borate nonlinear optical crystals reported so far, one may expect to apply crystal chemistry to the rational design of NLO crystals in the borate series, as is being done on new high-Tc layered cuprates.[17] From known NLO borates, we knew that MO_4 or other MO_n coordination groups with three basal or equatorial bonds could align BO_3 groups parallelly in one layer, while among layers, large cations (Ba, Sr, Rb, K) tended to arrange them acentrically.[18−20] In this work, we chose MO_3F_2 and Ba and found, as expected, a perfectly aligned BO_3 in $BaZnBO_3F$, which shows a relatively large SHG signal on the order of LBO ($d_{eff} \approx 3\ d_{eff}$ KDP). In comparison, with a higher coordination number of MgO_4F_2, the BO_3 groups in $BaMgBO_3F$ arrange in a misaligned fashion, which results in a small SHG signal of this crystal (one-tenth that of KDP).

Experimental Section

Materials. Fresh BaF_2 (99%, Sinopharm Chemical Reagent Co., Ltd.) and all other starting materials (analytically pure), ZnO, MgF_2, $Mg_5(OH)_3CO_3$, and H_3BO_3, were used as received, except $BaCO_3$, which was preheated at 1000 °C for 10 h to remove absorbed moisture.

$BaZnBO_3F$. $BaCO_3$, ZnO, and borate acid were allowed to react at 750 °C for 24 h in a platinum crucible. After they cooled down to room temperature, an appropriate amount of BaF_2 was added. With thorough grinding, the content was repeatedly sintered between 700 and 800 °C until the sample did not show variations in X-ray diffraction patterns. Single-crystal growing trials of $BaZnBO_3F$ with different fluxes have not been successful; ZnO crystals were obtained for most runs.

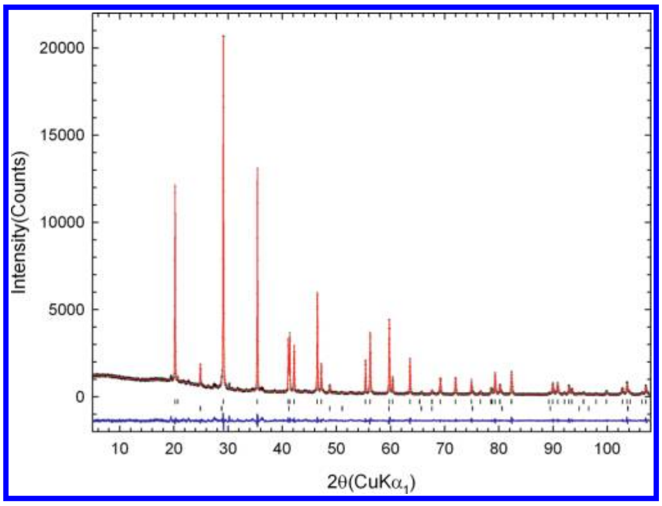

Figure 1. The calculated (line) and observed (dots) XRD patterns of $BaZnBO_3F$. The vertical bars are the diffraction peak positions of the main phase $BaZnBO_3F$ [upper, 96.3(1) wt %] and impurity phase BaF_2 [lower, 3.7(1) wt %].

$BaMgBO_3F$. Powder samples of $BaMgBO_3F$ can be synthesized similarly to $BaZnBO_3F$, by using MgF_2 as the fluorine source instead of using BaF_2. Care must be taken that the sintering temperature should be kept below 850 °C, since examinations of the samples by XRD powder diffraction showed that the compound started to decompose to $Ba_2Mg_2B_2O_6$ at 870 °C. Flux crystal growth on $BaMgBO_3F$ was therefore attempted. Needle crystals of sizes up to 1 × 1 × 5 mm^3 were obtained by slow cooling (at 0.1−0.5 °C/day) the content of $BaMgBO_3F$ in a LiF–$LiBO_2$ flux (1:0.5:0.5 ratio) from 855 °C.

Structure Determination. Powder X-ray diffraction data of $BaZnBO_3F$ were collected with a Siemens D5000 diffractometer equipped with a monochromated Cu $K\alpha_1$ radiation source at 1.54056 Å. Structure determination of $BaZnBO_3F$ from the powder XRD data started with indexing the XRD pattern with the CRYSFIRE program,[21] which gave a simple hexagonal unit cell. Then, the data were imported to the GSAS program.[22] Since the unit cell is so small, we guessed that only one molecule can be hosted in the unit cell. Then, the structure determination was straightforward by setting Ba at the origin, and all of the other atoms were found by difference Fourier synthesis. Toward the end of refinement, peaks at $2\theta = 24.9°$ and 48.7° were found to correspond to BaF_2 (at the 3.65 wt % level), which were then included in a multiphase refinement. Final refinement with 68 parameters gave excellent agreement indices of $R_{wp} = 0.0674$ and $\chi^2 = 2.458$ (Figure 1, Table 1).

Single-crystal X-ray diffraction data for the $BaMgBO_3F$ crystal (0.267 × 0.200 × 0.167 mm^3) were collected in flowing low-temperature nitrogen gas at 93 K with a Rigaku AFC10 diffractometer equipped with a Saturn CCD detector and Mo Kα radiation. Numerical absorption corrections were applied to the data, and then the structure of $BaMgBO_3F$ was solved with the SHELX97 program.[23] Though an orthorhombic cell was assigned by the data collection program, satisfactory solution

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(15) Chang, H. Y.; Kim, S. H.; Ok, K. M.; Halasyamani, P. S. *J. Am. Chem. Soc.* **2009**, *131*, 6865−6873 and references therein.

(16) Marvel, M. R.; Lesage, J.; Baek, J.; Halasyamani, P. S.; Stern, C. L.; Poeppelmeier, K. R. *J. Am. Chem. Soc.* **2007**, *129*, 13963–13969.

(17) Tokura, Y.; Arima, T. *Jpn. J. Appl. Phys.* **1990**, *29*, 2388–2402.

(18) Hu, Z. G.; MaramatsuI, K.; Kanehisa, N.; Yoshimura, M.; Mori, Y.; Sasaki, T.; Kai, Y. *Z. Kristallogr. NCS* **2003**, *218*, 1–2.

(19) Chen, C. T.; Wang, Y. B.; Wu, B. C.; Wu, K. C.; Zeng, W. R.; Yu, L. H. *Nature* **1995**, *373*, 322–324.

(20) McMillen, C. D.; Kolis, J. W. *J. Cryst. Growth* **2008**, *310*, 2033–2038.

(21) Shirley, R. CRYSFIRE Suite, The CRYSFIRE System for Automatic Powder Indexing, **2004**.

(22) Larson, A. C.; Von Dreele, R. B. *General Structure Analysis System* (*GSAS*); Los Alamos National Laboratory Report LAUR 86-748; Los Alamos, NM, 2004.

(23) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

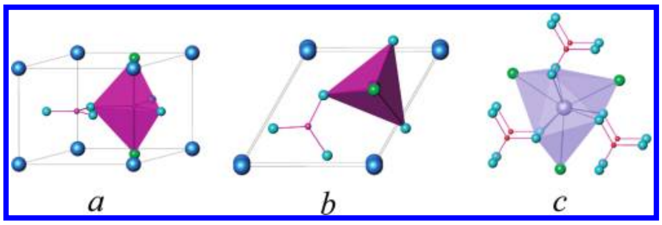

Figure 2. Perspective view (*a*) and *c* view (*b*) of $BaZnBO_3F$ and the Ba coordination environment (*c*). The large spheres represent Ba. Purple polyhedra represent the ZnO_3F_2 trigonal bipyramids. The smallest spheres are B atoms. Green and cyan medium spheres are the fluorine and oxygen atoms.

Table 1. Crystallographic Data for $BaZnBO_3F$ and $BaMgBO_3F$

formula	$BaZnBO_3F$	$BaMgBO_3F$
fw	280.52	239.44
space group	$P\bar{6}$	*Cc*
a (Å)	5.0658(1)	17.614(3)
b (Å)	5.0658(1)	30.546(6)
c (Å)	4.2800(1)	8.060(2)
α (deg)	90	90
β (deg)	90	90.008(2)
γ (deg)	120	90
V (Å^3)	95.119	4336.9
Z	1	48
T (K)	295(2)K	93(2)K
λ (Å)	1.54056	0.71073
ρ (g/cm^3)	4.897	4.401
μ (mm^{-1})		11.04
flack parameter		0.06(3)
Rwp, χ^2 (GSAS)	0.0674, 2.458	
R1, wR2 (SHELX97)		0.0623, 0.1149

could not be obtained with orthorhombic space groups. When the symmetry was lowered to monoclinic, a solution in the space group *Cc* was obtained with acceptable agreement indices of wR_2 = 0.1149, R_1 = 0.0623 ($F_o > 4\sigma$), and R_1 = 0.0701 (all reflections, Table 1).

Results and Discussion

Structure Description. Perspective and *c* direction views of the $BaZnBO_3F$ structure are shown in Figure 2a and b. In the structure, only three-coordinated boron is found as a planar BO_3 group, Zn^{2+} is found to coordinate to three oxygen and two fluorine atoms to form a trigonal bipyramid, and Ba^{2+} is found to coordinate to three fluorine and six oxygen atoms. Boron in the BO_3 group is slightly offset (0.09 Å) from the O3 plane with B−O bond lengths of 1.372(7) Å and a bond valence sum (BVS)[24] of 2.991. Bond lengths of Zn−O and Zn−F are 1.940(11) and 2.140 Å, respectively, with a BVS of 2.018 for Zn^{2+}. Ba−O and Ba−F bond lengths in the BaO_6F_3 polyhedron are 2.796(6) and 2.925 Å, respectively, which results in a BVS of 1.917 for Ba^{2+}. Both the bond lengths and BVSs for the Ba, Zn, and B coordinations show that they are close to the ideal values, indicating not only the validity of the structure but also the nonexistence of large strain in the structure. The ZnO_3F_2 bipyramid shares its three equatorial oxygen atoms with three BO_3 groups to form a flat layer and uses its apical F atoms connecting adjacent layers in the *c* direction. Within a single ZnO_3-BO_3 layer, all BO_3 groups are perfectly aligned in the *ab* plane through the cooperative trigonal ZnO_3 and triangular BO_3 connection. Among different layers, the alignment of BO_3 groups is governed by the BaO_6F_3 coordination: the nine coordinated atoms to Ba can be divided into three layers, and the steric force of the three central F atoms forces the three above- and three lower-layer O atoms to orient in an eclipse style, hence parallelly aligning the BO_3 groups in neighboring layers. This two-stage alignment of the BO_3 groups produces cooperative contribution to a large macroscopic SHG effect (see the next subsection).

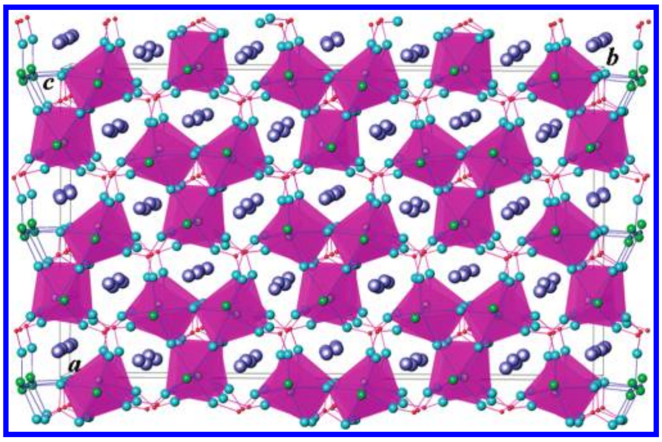

Figure 3. Structure of $BaMgBO_3F$ along the *c* axis, with large dark spheres representing Ba, purple polyhedra representing the MgO_4F_2 octahedra, small red spheres representing B atoms, and green and cyan medium spheres representing the fluorine and oxygen atoms, respectively.

Though the ion radius (0.74 Å) is slightly smaller than that of Zn^{2+} (0.76 Å), Mg^{2+} is found to prefer six-coordination with four oxygen and two fluorine atoms in the $BaMgBO_3F$ structure. This apparent violation of Pauling's rules can be attributed to Zn^{2+} ion (as well as Cd^{2+} and Hg^{2+}) having a stronger covalency than Mg^{2+}.[25] Similar to the situation in its Zn analog, all of the B atoms are three-coordinated to O in the forms of BO_3 planar groups. Every Mg atom uses its four equatorial oxygen atoms, sharing with three planar BO_3 groups to form the MgO_4-BO_3 layer with two of the BO_3 groups nearly parallel to the *ab* plane and one with an angle of about 30° inclined to the *ab* plane. Again, the layers are connected by apical F atoms on MgO_4F_2 in the *c* direction, forming a three-dimensional net with Ba atoms occupying the voids. A notable feature of the structure is that three MgO_4F_2 polyhedra enclose one single BO_3 group by edge-sharing to form a very compact $[Mg_3BO_3O_{6/2}F_{6/2}]$ column, which probably prompts the Mg ions to be overbonded, with a BVS of 2.134−2.301 (av. 2.210). It is also worth mentioning that the unit cell dimension is very close to that of a hexagonal cell. From the *c* direction view of the structure (Figure 3), we can deduce a hexagonal subcell of a_s = 8.812 Å and c_s = 4.025 Å with relations $a_s \approx a/2 \approx b/2\sqrt{3}$ and $c_s = c/2$ and with each subcell hosting only one $[Mg_3BO_3O_{6/2}F_{6/2}]$ unit. The enlarged unit cell is caused by twisting of the $[Mg_3BO_3O_{6/2}F_{6/2}]$ columns and a small offsetting of the Ba atoms. Unlike in the case of $BaZnBO_3F$, here each Mg atom coordinates to four oxygen atoms from three BO_3 groups, forming a severely distorted equatorial plane, which force the three BO_3 groups to arrange in a fashion

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(24) Brown, I. D.; Altermatt, D. *Acta Crystallogr., Sect. B* **1985**, *41*, 244−247.

(25) Buchanan, R. C.; Park, T. *Materials Crystal Chemistry*; Marcel Dekker, Inc.: New York, 1997.

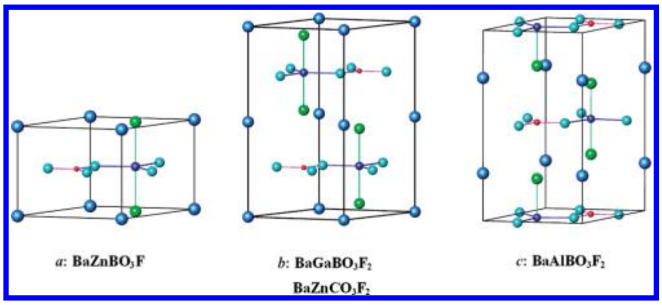

Figure 4. Structure relationship of $BaZnBO_3F$ with its double fluorine counterparts $BaMBO_3F_2$ (M = Al, Ga) and $BaZnCO_3F_2$.

of two parallel and one antiparallel. With this structure characteristic, the contributions to the SHG coefficients from two of the three BO_3 groups are canceled, leaving only one making a contribution.

Calculation of SHG Coefficients. As mentioned previously, the macroscopic SHG coefficients d_{IL} can be calculated by summing up the second-order polarizabilities ($\chi^{(2)}$) of the anionic groups BO_3.[12-14] Refractive indices, especially birefringence, are also important parameters in determining the phase matching conditions in actually generating the SHG laser output. On the basis of an estimation scheme proposed by Shannon and Fischer,[26] we have recently extended it to calculate the refractive indices for anisotropic crystallographic systems with MO_3 groups.[27] Adopting this scheme, we can estimate the refractive indices for the two compounds as

$$BaZnBO_3F : n_o = 1.7342, n_e = 1.6631$$

$$BaMgBO_3F : n_x = 1.6900, n_y = 1.6914, n_z = 1.6330$$

Using those refractive indices, the major SHG tensor elements of the title compounds can be calculated as

$$BaZnBO_3F : d_{11} = -1.24 \text{ pm/V}, d_{22} = 0.25 \text{ pm/V}$$

$$BaMgBO_3F : d_{11} = 0.04 \text{ pm/V}, d_{12} = -0.11 \text{ pm/V}, \\ d_{13} = 0.06 \text{ pm/V}$$

These results agree well with the observation that $BaZnBO_3F$ shows an LBO level signal and $BaMgBO_3F$ shows a much weaker signal than that of KDP according to powder SHG tests.

Structure Relationship and Design of NCS Crystals. In the compounds containing planar MO_3 groups, there are several reported structures related to the present ones. As in $BaZnBO_3F$, the same ZnO_3F_2 trigonal bipyramidal coordination has been observed in $BaZnCO_3F_2$[28] (Figure 4b). Al and Ga in $BaGaBO_3F_2$ (Figure 4b)[29] and $BaAlBO_3F_2$ (Figure 4c)[18,29] were found behaving similarly as Zn in $BaZnBO_3F$. However, all of these related compounds have one more F in their chemical formula and two more F layers in the unit cell. The additional F layer not only breaks the M−F−M bonds but also shifts two adjacent MO_3-BO_3 layers, hence doubling the unit cell along the *c* direction. The doubled unit cell leaves room for twisting between two adjacent MO_3-BO_3 layers, forming the centrosymmetric structure as $BaGaBO_3F_2$ and $BaZnCO_3F_2$ or the NCS structure as $BaAlBO_3F_2$,[18] with subtle energy differences. It is also worth noting that, from the structural point of view, the relationship of the $BaZnBO_3F$ structure with removal of the F layers from the counterpart structures is very similar to the relationship of the perovskite structure with removal of the LaO rock salt layers of the parent high-Tc compound La_2CuO_4.[30] Such a relationship is also observed in the NLO compounds of Be_2BO_3F[31] and $KBe_2BO_3F_2$.[32]

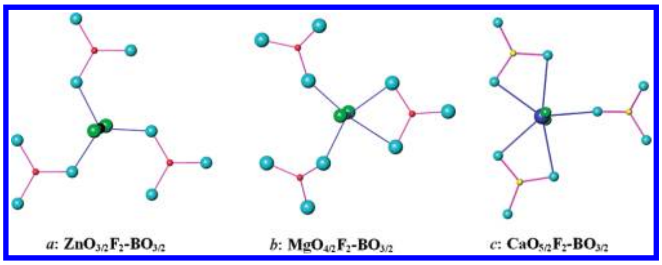

Figure 5. Alignments of BO_3 groups by the MO_nF_2 polyhedra in $BaMBO_3F$ structures (*a*, M = Zn; *b*, M = Mg; *c*, M = Ca).

From the composition point of view, the present compounds are also related to $BaCaBO_3F$, which was reported as a self-frequency doubling NLO crystal when doped with rare earth elements.[33,34] Though the three compounds have different structures, the main structure units MO_nF_2 are still strongly correlated, as shown in Figure 5. Common to all three units, two F atoms always situate at the apical positions. However, on going from Zn or Mg to Ca, the main cation−oxygen (MO_n) coordination number *n* increases from 3 to 5 at the equatorial positions. These coordination environments strongly affect the structural arrangement of the closest neighboring BO_3 groups in a crystal. In the case of $n = 3$, the three M−O bonds pointing to three different BO_3 groups force them to align in the same orientation (as shown in Figure 5a) to give a large NLO contribution, whereas when $n = 4$ or 5, two of the BO_3 groups are nearly antiparallel, hence canceling out their contributions to the NLO effect (Figure 5b,c).

Following the successful synthesizing of the two title compounds, we can work out a principle to design new NCS borates with large nonlinearity: One needs first to choose a basic structure unit that has a large nonlinearity, that is, a flat BO_3 group. Second, select a cation that forces the BO_3 groups to parallel alignment and connect the BO_3 groups to form a two-dimensional layer, that is, a MO_4 tetrahedron or MO_3F_2 trigonal bipyramid. Third, use another large cation with steric force to arrange the BO_3 groups from adjacent MO_n-BO_3 layers into an eclipse style, that is, BaO_6F_3 (Figure 2c). In practice, the controllabilities of the above rules of thumb follow a

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(26) Shannon, R. D.; Fischer, R. X. *Phys. Rev. B* **2006**, *73*, 235111.

(27) Qin, F. L.; Li, R. K. *J. Synth. Cryst.* **2009**, *38*, 26–32.

(28) Ben Ali, A.; Maisonneuve, V.; Smiri, L. S.; Leblanc, M. *Solid State Sci.* **2002**, *4*, 891–894.

(29) Park, H.; Barbier, J. *J. Solid State Chem.* **2000**, *155*, 354–358.

(30) Longo, J. M.; Raccah, P. H. *J. Solid State Chem.* **1973**, *6*, 526–531.

(31) Baidina, I. A.; Bakakin, V. V.; Podberezskaya, N. V.; Alekseev, V. I.; Batsanova, L. R.; Pavlyuchenko, V. S. *Zh. Strukt. Khim.* **1978**, *19*, 125–129.

(32) Solov'eva, L. P.; Bakakin, V. V. *Kristallografiya* **1970**, *15*, 922–925.

(33) Keszler, D. A.; Akella, A.; Schaffers, K. I.; Alekel, T., III *Mater. Res. Soc. Symp. Proc.* **1994**, *329*, 15–22.

(34) Xu, K.; Loiseau, P.; Aka, G. *J. Cryst. Growth* **2009**, *311*, 2508–2512.

descending order, with the third one being the most difficult to realize. This strategy can also be compared to that proposed in the case of $A_2Ti(IO_3)_6$ (A = Li, Na),[15] where IO_3 is the basic unit analog to BO_3 in our case. Six-fold coordinated $Ti(IO_3)_6$ first arranges the lone pairs parallelly; then, six-coordinated LiO_6 and NaO_6 keep the parallel fashion. Detailed calculation based on the anionic group approximation can reveal that the difference between the two cases is that, owing to the nonzero tensor elements $\chi_{311}^{(2)} = \chi_{322}^{(2)}$ of the IO_3 group, it is not necessary to fully align the I−O bonds in the *ab* plane to produce large SHG effect. Actually, the $\chi_{111}^{(2)}$ element is canceled in $A_2Ti(IO_3)_6$; it would give zero SHG contribution if the group were a flat BO_3 there.

Conclusion

In our previous development of NLO materials in the borate series, we mainly paid attention to the anionic groups (BO_3, BO_4, B_3O_6, etc.) and using the structural database to find new NLO crystals. The contribution from the counterions (cations) was neglected, and less attention has been paid to its role in structure formation. From the structure relationship among the title compounds $BaMBO_3F$ (M = Zn, Mg) and similar compounds and related structures, it is found that, in order to design new NCS borates with large nonlinearity, the first cation coordination sphere of the BO_3 group plays a vital role. Only those cations with a trigonal basal (in MO_4, M = Be, Al, Zn, Ga) or equatorial plane (in MO_3F_2, M = Zn, Al, Ga) can parallelly align the BO_3 groups to maximize their contribution to the SHG effect. The second cation coordination sphere to BO_3, though less controllable, also plays a role in the final NCS structures. Generally, larger cations in the second coordination sphere tend to align the BO_3 into perfect alignment, and smaller cations tend to distort BO_3 alignment to give a smaller contribution to the SHG effect.

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Supporting Information Available: A crystallographic information file is provided. This material is available free of charge via the Internet at http://pubs.acs.org.