

Pb₂BO₃Cl: A Tailor-Made Polar Lead Borate Chloride with Very Strong Second Harmonic Generation

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Abstract: A meticulously designed, polar, non-centrosymmetric lead borate chloride, Pb₂BO₃Cl, was synthesized using KBe₂BO₃F₂ (KBBF) as a model. Single-crystal X-ray diffraction revealed that the structure of Pb₂BO₃Cl consists of cationic [Pb₂(BO₃)]⁺ honeycomb layers and Cl[−] anions. Powder second harmonic generation (SHG) measurements on graded polycrystalline Pb₂BO₃Cl indicated that the title compound is phase-matchable (type I) and exhibits a remarkably strong SHG response, which is approximately nine times stronger than that of potassium dihydrogen phosphate, and the largest efficiency observed in materials with structures similar to KBBF. Further characterization suggested that the compound melts congruently at high temperature and has a wide transparency window from the near-UV to the mid-IR region.

Nonlinear optical (NLO) materials,^[1] the key components of solid-state lasers producing coherent light through a cascaded frequency conversion, have received extensive commercial and academic interest owing to their versatile scientific and technological applications. Over the past several decades, many efforts have been devoted to elucidating the relationship of the structures, compositions, and NLO properties of crystalline compounds; however, it still remains challenging to efficiently design novel NLO materials with excellent overall properties, including large second harmonic generation (SHG) coefficients, moderate birefringence for the phase-matching condition, wide transparency windows for a high damage threshold, good chemical stability, and facile crystal growth.

A few strategies for creating new NLO materials employ non-centrosymmetric (NCS) chromophores, such as anions in π -delocalized systems,^[1b,2] second-order Jahn–Teller (SOJT) distorted cations (d⁰ cations exhibiting intra-octahedral distortion and cations with stereochemically active lone pairs),^[2f,3] and d¹⁰ metal cations with polar displacement,^[4] as building units during the syntheses. Metal borates have

been intensively investigated as ultraviolet (UV) or deep-UV NLO materials. Developing NLO crystals based on borate systems has been particularly successful on the basis of anionic group theory,^[5] where the overall crystal non-linearity is the geometrical superposition of the microscopic second-order susceptibility of the NLO-active anionic groups.^[6] Thus far, a variety of important UV NLO crystals, including β -BaB₂O₄ (BBO),^[7] LiB₃O₅ (LBO),^[8] CsB₃O₅ (CBO),^[9] CsLiB₆O₁₀ (CLBO),^[10] and YCa₄O(BO₃)₃ (YCOB),^[11] have been discovered. The discovery of KBe₂BO₃F₂ (KBBF) was a breakthrough in the area of deep-UV NLO crystals^[12] as it is the only material that can generate coherent light at wavelengths below 200 nm by direct SHG. The excellent NLO properties of KBBF, such as moderate SHG coefficients, a wide transparency window, and proper birefringence, certainly arise from its distinct crystal structure. The [Be₂BO₃F₂]_∞ layers made up from tetrahedral [BeO₃F] units and the trigonal-planar [BO₃] units within the chiral structure adopt a coplanar configuration to promote SHG and birefringence. The firm linkages between the three terminal oxygen atoms of the BO₃ groups and the Be atoms prevent the formation of dangling bonds in the BO₃ groups, which results in a very short absorption edge in the UV region.

Owing to the structure-based superior NLO properties of KBBF, many researchers have made long-lasting endeavors to develop similarly excellent new NLO crystals. A few representative compounds belonging to the KBBF family are ABe₂B₃O₇ (A = K or Rb),^[13] Na₂CsBe₆B₅O₁₅,^[14] NaSr₃Be₃B₃O₉F₄,^[15] NaCaBe₂B₂O₆F,^[16] and Cs₃Zn₆B₉O₂₁.^[17] In spite of their distinguished characteristics, it is very difficult to grow large crystals of the KBBF family owing to their layered structures. With these ideas in mind, we utilized a tailored molecular design approach by selectively modifying the KBBF structure to develop an excellent UV NLO material based on Pb, B, O, and Cl. First, replacement of the alkaline-earth-metal cation, Be²⁺, in the [Be₂BO₃F₂]_∞ layers by the lone-pair cation Pb²⁺ was expected to lead to large birefringence and an enhanced SHG response owing to the strong electronic polarizability as well as the stereoactive lone pair.^[18] Second, the F atom in the tetrahedral [PbO₃F] unit was removed to make room between the layers so that the lone pairs in the [PbO₃] units remain stereoactive. Third, a light halide, Cl[−], was introduced for charge balance as well as to cause an effective blue shift of the UV absorption edge. Guided by these ideas, we were able to synthesize a novel congruently melting NLO material, Pb₂BO₃Cl, which consists of the targeted [Pb₂BO₃]_∞ layers and Cl[−] anions. Powder NLO measurements indicate that Pb₂BO₃Cl exhibits the largest SHG response in the KBBF family, which is approx-

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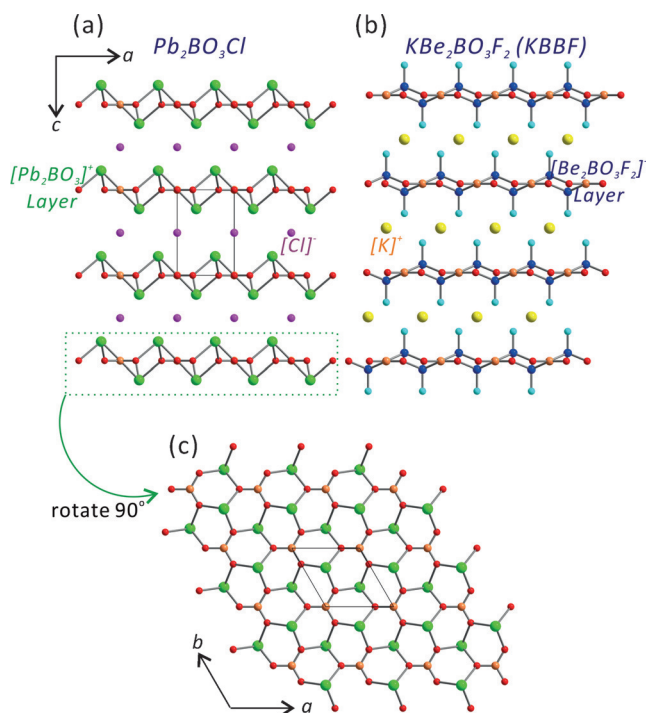


Figure 1. Ball-and-stick models of a) $\text{Pb}_2\text{BO}_3\text{Cl}$ and b) $\text{KBe}_2\text{BO}_3\text{F}_2$ (KBBF) in the ac plane. B orange, Be blue, Cl purple, F cyan, K yellow, O red, Pb green. c) Each BO_3 planar triangle shares its corners with six PbO_3 trigonal pyramids and forms a honeycomb-like cationic $[\text{Pb}_2\text{BO}_3]^+$ layer in the ab plane of $\text{Pb}_2\text{BO}_3\text{Cl}$.

imately nine times stronger than that of potassium dihydrogen phosphate (KDP).

$\text{Pb}_2\text{BO}_3\text{Cl}$ crystallizes in the trigonal polar NCS space group $P321$ (No. 150). As shown in Figure 1a, the structure of $\text{Pb}_2\text{BO}_3\text{Cl}$ is composed of cationic $[\text{Pb}_2\text{BO}_3]^+$ layers made from BO_3 triangular units and PbO_3 trigonal pyramids with Cl^- anions residing in the interlayer space. As a new member of the KBBF family, $\text{Pb}_2\text{BO}_3\text{Cl}$ can also be written as $[\text{Cl}]^-[\text{Pb}_2\text{BO}_3]^+$, with a structure comparable to that of $[\text{K}]^+[\text{Be}_2\text{BO}_3\text{F}_2]^-$ (see Figure 1b). Specifically, the $[\text{Cl}]^-$ anions occupy the positions of the $[\text{K}]^+$ cations in the interlayer space of KBBF for charge balance. The lone pairs on the Pb^{2+} cations in the cationic $[\text{Pb}_2\text{BO}_3]^+$ layer can somehow be considered as taking the place of the F^- anions in the anionic $[\text{Be}_2\text{BO}_3\text{F}_2]^-$ layer of KBBF. Within the cationic $[\text{Pb}_2\text{BO}_3]^+$ layer of $\text{Pb}_2\text{BO}_3\text{Cl}$, a unique B^{3+} cation is coordinated to three O atoms in the BO_3 planar-triangular geometry with B–O bond lengths of 1.370(17) Å. The Pb^{2+} cation lying on the site of $3m$ symmetry is also bonded to three O atoms in a trigonal-pyramidal coordination environment with Pb–O bond lengths of 2.297(8) Å. As seen in Figure 1c, each BO_3 planar triangle shares its corners with six PbO_3 trigonal pyramids and forms a honeycomb-like cationic $[\text{Pb}_2\text{BO}_3]^+$ layer in the ab plane. As we will discuss in more detail later, the cooperative interactions of the polarizable lone pairs in the PbO_3 trigonal pyramids and all the parallel triangular BO_3 groups oriented in the same direction within the layer may be mainly responsible for the large macroscopic SHG effect. The three dangling bonds of the BO_3 groups are

successfully eliminated by robust bonding between the three terminal O atoms of the BO_3 group and Pb, which should broaden its transparency window. The bond valence sums^[19] for Pb^{2+} and B^{3+} in $\text{Pb}_2\text{BO}_3\text{Cl}$ were calculated to be 2.15 and 3.00, respectively.

The thermal behavior of $\text{Pb}_2\text{BO}_3\text{Cl}$ was investigated by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and powder X-ray diffraction (PXRD). Whereas no substantial weight loss was observed up to 640 °C in the TGA curve, an endothermic peak was located at about 630 °C in the DSC curve, which is attributable to the melting of $\text{Pb}_2\text{BO}_3\text{Cl}$ (Figure 2a). The slight weight loss observed in

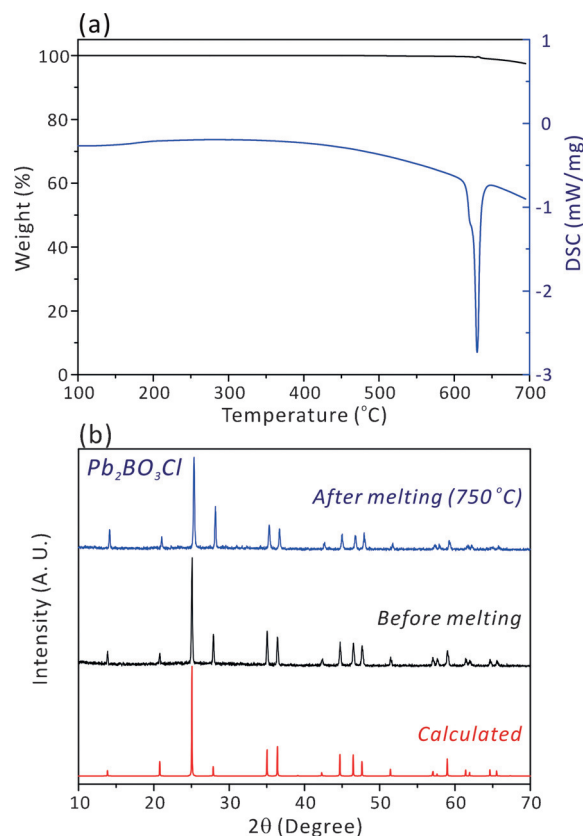


Figure 2. a) TGA and DSC analysis and b) calculated and experimental PXRD patterns for $\text{Pb}_2\text{BO}_3\text{Cl}$. Whereas no substantial weight loss was observed up to 640 °C in the TGA curve, an endothermic peak occurred at about 630 °C in the DSC curve, attributable to the melting of $\text{Pb}_2\text{BO}_3\text{Cl}$. The PXRD patterns for polycrystalline $\text{Pb}_2\text{BO}_3\text{Cl}$ at room temperature and a sample heated to 750 °C were identical.

the TGA curve is possibly due to the volatility of $\text{Pb}_2\text{BO}_3\text{Cl}$ at higher temperatures upon melting. In fact, the powder XRD patterns for polycrystalline $\text{Pb}_2\text{BO}_3\text{Cl}$ measured at room temperature and a sample heated to 750 °C revealed identical patterns, which strongly suggests that $\text{Pb}_2\text{BO}_3\text{Cl}$ melts congruently without any phase transitions (see Figure 2b). Thus large high-quality single crystals of $\text{Pb}_2\text{BO}_3\text{Cl}$ could be grown by various crystal-growth methods.

The IR spectrum of $\text{Pb}_2\text{BO}_3\text{Cl}$ revealed B–O and Pb–O vibrations. The broad bands observed at 1197 cm^{-1} were assigned to the B–O stretching vibrations. The strong bands at

742, 728, and 625 cm^{-1} were attributed to both the bending modes of the triangular BO_3 groups and the Pb–O stretching vibrations. The assignments are in agreement with other oxides containing B and Pb.^[18c,20] The IR spectrum of $\text{Pb}_2\text{BO}_3\text{Cl}$ is included in the Supporting Information.

A UV/Vis diffuse reflectance spectrum was also recorded for $\text{Pb}_2\text{BO}_3\text{Cl}$, and the absorption (K/S) data were calculated from the Kubelka–Munk function (Figure 3a).^[21] As shown in Figure 3a, the UV absorption spectrum of $\text{Pb}_2\text{BO}_3\text{Cl}$ exhibits

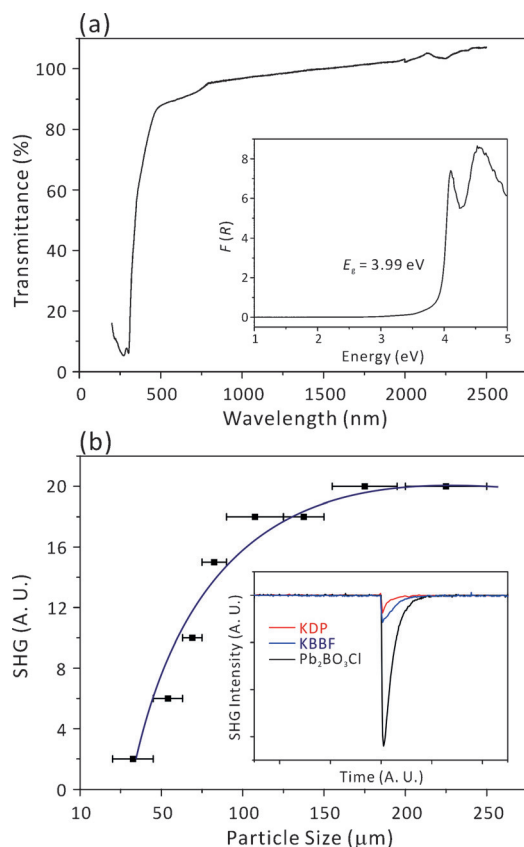


Figure 3. a) UV/Vis/NIR transmittance spectrum and b) phase-matching curve for $\text{Pb}_2\text{BO}_3\text{Cl}$. The curve is drawn as a guide to the eye and not a fit to the data. The insets in (a) and (b) are an optical diffuse reflectance spectrum and an oscilloscope trace showing the SHG intensity, respectively, for $\text{Pb}_2\text{BO}_3\text{Cl}$. The SHG intensities for KDP and KBBF are also plotted for comparison.

no absorption from 300 to 2500 nm, suggesting that the material has a wide transparency region ranging from the near-UV to the mid-IR. The observed UV absorption edge for $\text{Pb}_2\text{BO}_3\text{Cl}$ is at a substantially shorter wavelength than those of other lead borates, which might be due to the light halide ion, Cl^- , that was introduced, which can effectively blue-shift the absorption edge. The diffuse reflectance spectrum also indicates that $\text{Pb}_2\text{BO}_3\text{Cl}$ has a wide optical band gap of 3.99 eV.

$\text{Pb}_2\text{BO}_3\text{Cl}$ exhibited a very large SHG response that was about nine times stronger than that of KDP and almost six times stronger than that of KBBF (see Figure 3b). Furthermore, the curve obtained by plotting the SHG signals as

a function of the particle size determined for ground crystals of $\text{Pb}_2\text{BO}_3\text{Cl}$ indicated that the material is type I phase-matchable (Figure 3b, inset).^[1c,22]

To gain further insight into the band structure and optical properties of $\text{Pb}_2\text{BO}_3\text{Cl}$, density functional theory (DFT) calculations were performed by using the TB-LMTO-ASA method. The band-structure calculations predict a band gap of 2.32 eV for $\text{Pb}_2\text{BO}_3\text{Cl}$, which is considerably smaller than the experimental value (see Figure 4). It is well documented

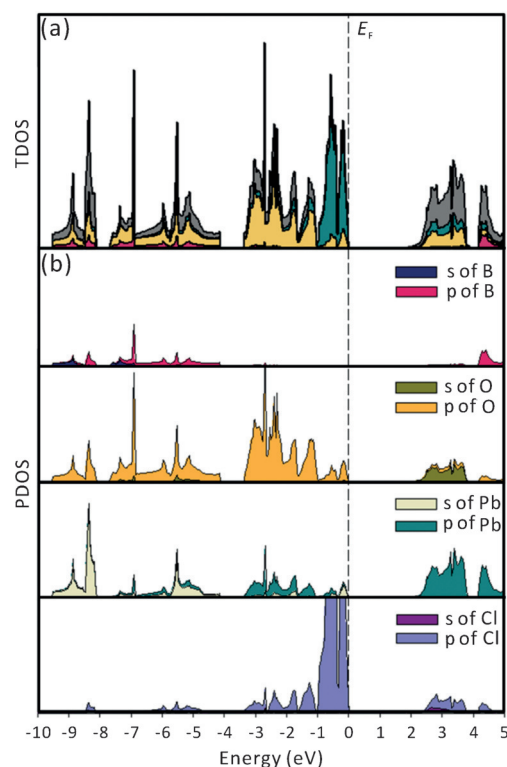


Figure 4. a) Total and b) partial DOS curves for $\text{Pb}_2\text{BO}_3\text{Cl}$. Individual PDOS curves of selected orbitals for B, O, Pb, and Cl are also shown. The E_F is displayed as a dashed vertical line and was used as a reference for all energy values (0 eV).

that electronic-band-structure calculations by DFT calculations tend to underestimate the energy gap.^[23] However, the calculations are very helpful in locating the crucial orbital interactions. The total density of states (TDOS) curve shows an overall orbital mixing of four elements over the entire energy range as shown in Figure 4a. The valence band region below the Fermi level (E_F) can be divided into five smaller regions based on the atomic orbital contributions. In particular, the largest orbital contributions in the valence band region are due to the trigonal-planar-shaped $[\text{BO}_3]^{3-}$ moiety: 1) The lowest-energy region between -9.5 and -8 eV includes strong contributions from the s states of the central B atom and the p_y group orbitals of the surrounding three O atoms, leading to σ interactions with some mixing of Pb s states. 2) The region between -7.8 and -7 eV mostly displays the p_x and p_y states of B and the p_y group orbitals of three O atoms, which also contributes to the σ -interactions, with some contributions from the s states of Pb as well. 3) The

region between -7 and -4 eV contains large contributions from the p_z states of both B and the group orbitals of O, eventually building up the π interactions over the $[\text{BO}_3]^{3-}$ group. 4) The region between -3.5 and -1 eV contains rather small contributions from the p_x and p_y states of B and the large p_x states from the group orbitals of O, both of which form nearly non-bonding interactions between them, with some contributions from the p states of both Pb and Cl. 5) The region between -1 eV and E_F is mostly dominated by the p states of Cl. Interestingly, according to the partial DOS (PDOS) analyses for Pb and Cl, the s states of Pb somewhat contribute to regions 1 and 2, where the B and O atoms in the $[\text{BO}_3]^{3-}$ group form the σ interactions. In addition, the p states of Pb overlap with region 3, where the p_z states of both B and O lead to π interactions on the $[\text{BO}_3]^{3-}$ group. These interatomic interactions between Pb and O can be clearly observed in the Pb–O COHP curve shown in Figure S2. In addition, the p states of Cl also somewhat contribute to region 3, implying a particular interaction with orbitals of Pb as well (see Figure S2b).

All of the interatomic interactions within the $[\text{BO}_3]^{3-}$ groups in the ab plane and among the $[\text{BO}_3]^{3-}$, Pb, and Cl units in the ab and ac planes can be clearly visualized by the electron localization function (ELF) diagrams (Figure 5a). First, to look for interatomic interactions between the $[\text{BO}_3]^{3-}$ groups and Pb along the ab plane, we plotted (001) slices with $z=0$ and $z=0.112$ (Figure 5a,b). In particular, in the (000.112) plane, which is located between 2D layers of $[\text{BO}_3]^{3-}$ and Pb, some electron density from Pb is directed towards O on the $[\text{BO}_3]^{3-}$ groups. More interestingly, these interatomic interactions between the $[\text{BO}_3]^{3-}$ groups and Pb are very nicely visualized on two other planes sliced perpendicular to the b axis. Figure 5c illustrates the plane with $y=0.137$ where two O atoms in the $[\text{BO}_3]^{3-}$ group are included. This ELF diagram clearly shows the interatomic interactions between the $[\text{BO}_3]^{3-}$ trigonal-planar groups and Pb atoms, forming the extended 2D layered structures, and, as already discussed for the PDOS curves, the nearly non-

bonding states of O and the p states of Pb contributing to region 4 in the PDOS curve were attributed to these interactions. Another slice with $y=0.274$ (Figure 5d), which is located at the midpoint between O and Pb atoms, displays comparatively weaker but still strong interatomic interactions between Pb and Cl along the c axis. Therefore, we claim that the interconnection of $[\text{BO}_3]^{3-}$ groups by Pb^{2+} cations in the ab plane results in extended 2D layers (see Figure 5c). Furthermore, considerable interactions between lone pairs on Pb^{2+} in the 2D layers and Cl^- were observed (Figure 5d). For comparison, an ELF diagram of the (1–10) slice of KBBF was also plotted after careful theoretical calculations (Figure 5e). No particular interactions between K and O were observed in the ELF diagram of KBBF, which may be due to an extended interatomic distance of $4.036 \text{ \AA}$. Despite the shorter bond lengths of Be–O ($1.636 \text{ \AA}$) and F–O ($2.596 \text{ \AA}$) in KBBF compared to those of Pb–O and Cl–O in $\text{Pb}_2\text{BO}_3\text{Cl}$, respectively, no substantial interatomic interactions were observed between Be and O or F and O. Thus the overall networking of all of the polarizable components in the crystal structure of $\text{Pb}_2\text{BO}_3\text{Cl}$ synergistically influences and produces a very strong SHG response. Whereas the spatial density for the $[\text{BO}_3]^{3-}$ groups in $\text{Pb}_2\text{BO}_3\text{Cl}$ (0.00742 per unit volume) is smaller than that of KBBF (0.00946 per unit volume), the synergistic effect of the interactions between the lone pairs on the Pb^{2+} cations and Cl^- anions, and the p – π interactions between Pb^{2+} and $[\text{BO}_3]^{3-}$ groups within the extended $[\text{Pb}_2(\text{BO}_3)]^+$ layers, resulted in a very large SHG response.

Linear optical analysis shows that the refractive index dispersion curves display strong anisotropy and follow the order of $n_o > n_e$, indicating that $\text{Pb}_2\text{BO}_3\text{Cl}$ is a uniaxial negative crystal (see Figure S4a). The birefringence Δn is relatively large (0.12 at 1064 nm), which is favorable for phase matching in the SHG process. Compared with KBBF, the enlarged birefringence Δn , which is due to the introduction of Pb^{2+} cations, can generate strong electronic anisotropic polarizability and a large SHG response, which is also consistent with the experimental observations. As the space group of $\text{Pb}_2\text{BO}_3\text{Cl}$ belongs to class 32 under the restrictions of Kleinman symmetry, only one set of independent SHG tensor components (d_{11}) remains. The calculated frequency-dependent SHG tensor components of $\text{Pb}_2\text{BO}_3\text{Cl}$ are plotted in Figure S4b. The value of d_{11} for $\text{Pb}_2\text{BO}_3\text{Cl}$ at a wavelength of 1064 nm (1.165 eV) is 7.2 pm V^{-1} , which is slightly higher than our experimental value.

In summary, we have synthesized a new NLO material, $\text{Pb}_2\text{BO}_3\text{Cl}$, through a molecular engineering design approach. The material revealed a remarkably strong SHG response that was approximately nine times stronger than that of KDP, constituting the largest value ever reported for the KBBF family. A subtle balance was successfully achieved between large non-linear coefficients, moderate birefringence, and wide transparency, which means that $\text{Pb}_2\text{BO}_3\text{Cl}$ may have great potential as a high-performance NLO material in photonic applications. The growth of large crystals for further physical property studies is ongoing. The tailored synthetic approach based on excellent crystal structures provides an opportunity to further design other structure-driven functional materials.

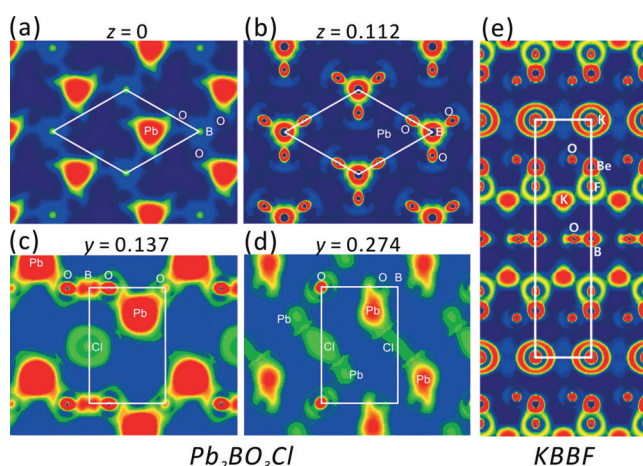


Figure 5. ELF diagrams illustrating slices along the ab plane with a) $z=0$ and b) $z=0.112$ and slices perpendicular to the b axis with c) $y=0.137$ and d) $y=0.274$ for $\text{Pb}_2\text{BO}_3\text{Cl}$. e) ELF diagram displaying a slice along the $[0-11]$ direction for KBBF.

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- [1] a) K. M. Ok, P. S. Halasyamani, *Angew. Chem. Int. Ed.* **2004**, *43*, 5489–5491; *Angew. Chem.* **2004**, *116*, 5605–5607; b) S. Pan, J. P. Smit, B. Watkins, M. R. Marvel, C. L. Stern, K. R. Poeppelmeier, *J. Am. Chem. Soc.* **2006**, *128*, 11631–11634; c) K. M. Ok, E. O. Chi, P. S. Halasyamani, *Chem. Soc. Rev.* **2006**, *35*, 710–717; d) T. K. Bera, J.-H. Song, A. J. Freeman, J. I. Jang, J. B. Ketterson, M. G. Kanatzidis, *Angew. Chem. Int. Ed.* **2008**, *47*, 7828–7832; *Angew. Chem.* **2008**, *120*, 7946–7950; e) R. K. Li, P. Chen, *Inorg. Chem.* **2010**, *49*, 1561–1565; f) C.-F. Sun, C.-L. Hu, X. Xu, B.-P. Yang, J.-G. Mao, *J. Am. Chem. Soc.* **2011**, *133*, 5561–5572; g) P. Yu, L.-M. Wu, L.-J. Zhou, L. Chen, *J. Am. Chem. Soc.* **2014**, *136*, 480–487; h) S. Zhao, P. Gong, S. Luo, L. Bai, Z. Lin, Y. Tang, Y. Zhou, M. Hong, J. Luo, *Angew. Chem. Int. Ed.* **2015**, *54*, 4217–4221; *Angew. Chem.* **2015**, *127*, 4291–4295; i) H. Yu, W. Zhang, J. Young, J. M. Rondinelli, P. S. Halasyamani, *Adv. Mater.* **2015**, *27*, 7380–7385.
- [2] a) S. Jin, G. Cai, W. Wang, M. He, S. Wang, X. Chen, *Angew. Chem. Int. Ed.* **2010**, *49*, 4967–4970; *Angew. Chem.* **2010**, *122*, 5087–5090; b) H. P. Wu, S. L. Pan, K. R. Poeppelmeier, H. Y. Li, D. Z. Jia, Z. H. Chen, X. Y. Fan, Y. Yang, J. M. Rondinelli, H. S. Luo, *J. Am. Chem. Soc.* **2011**, *133*, 7786–7790; c) Y. Shi, S. Pan, X. Dong, Y. Wang, M. Zhang, F. Zhang, Z. Zhou, *Inorg. Chem.* **2012**, *51*, 10870–10875; d) H. Wu, H. Yu, S. Pan, Z. Huang, Z. Yang, X. Su, K. R. Poeppelmeier, *Angew. Chem. Int. Ed.* **2013**, *52*, 3406–3410; *Angew. Chem.* **2013**, *125*, 3490–3494; e) X. Xu, C.-L. Hu, F. Kong, J.-H. Zhang, J.-G. Mao, J. Sun, *Inorg. Chem.* **2013**, *52*, 5831–5837; f) G. H. Zou, L. Huang, N. Ye, C. S. Lin, W. D. Cheng, H. Huang, *J. Am. Chem. Soc.* **2013**, *135*, 18560–18566; g) X. Fan, L. Zang, M. Zhang, H. Qiu, Z. Wang, J. Yin, H. Jia, S. Pan, C. Wang, *Chem. Mater.* **2014**, *26*, 3169–3174; h) J.-L. Song, C.-L. Hu, X. Xu, F. Kong, J.-G. Mao, *Angew. Chem. Int. Ed.* **2015**, *54*, 3679–3682; *Angew. Chem.* **2015**, *127*, 3750–3753; i) T. T. Tran, J. He, J. M. Rondinelli, P. S. Halasyamani, *J. Am. Chem. Soc.* **2015**, *137*, 10504–10507.
- [3] a) R. E. Sykora, K. M. Ok, P. S. Halasyamani, T. E. Albrecht-Schmitt, *J. Am. Chem. Soc.* **2002**, *124*, 1951–1957; b) H.-S. Ra, K. M. Ok, P. S. Halasyamani, *J. Am. Chem. Soc.* **2003**, *125*, 7764–7765; c) E. O. Chi, K. M. Ok, Y. Porter, P. S. Halasyamani, *Chem. Mater.* **2006**, *18*, 2070–2074; d) C.-F. Sun, C.-L. Hu, X. Xu, J.-B. Ling, T. Hu, F. Kong, X.-F. Long, J.-G. Mao, *J. Am. Chem. Soc.* **2009**, *131*, 9486–9487; e) S. D. Nguyen, J. Yeon, S.-H. Kim, P. S. Halasyamani, *J. Am. Chem. Soc.* **2011**, *133*, 12422–12425; f) S.-J. Oh, D. W. Lee, K. M. Ok, *Inorg. Chem.* **2012**, *51*, 5393–5399; g) H. G. Kim, T. T. Tran, W. Choi, T.-S. You, P. S. Halasyamani, K. M. Ok, *Chem. Mater.* **2016**, *28*, 2424–2432.
- [4] a) W.-L. Zhang, W.-D. Cheng, H. Zhang, L. Geng, C.-S. Lin, Z.-Z. He, *J. Am. Chem. Soc.* **2010**, *132*, 1508–1509; b) G. H. Zou, Z. J. Ma, K. C. Wu, N. Ye, *J. Mater. Chem.* **2012**, *22*, 19911–19918; c) H. Jo, K. M. Ok, *Inorg. Chem.* **2016**, *55*, 6286–6293.
- [5] C. Chen, Y. Wu, R. Li, *Int. Rev. Phys. Chem.* **1989**, *8*, 65–91.
- [6] a) P. Becker, *Adv. Mater.* **1998**, *10*, 979–992; b) S. Zhao, P. Gong, L. Bai, X. Xu, S. Zhang, Z. Sun, Z. Lin, M. Hong, C. Chen, J. Luo, *Nat. Commun.* **2014**, *5*, 4019; c) Y. Wang, S. Pan, *Coord. Chem. Rev.* **2016**, DOI: 10.1016/j.ccr.2015.12.008.
- [7] C. T. Chen, B. C. Wu, A. D. Jiang, *Sci. Sin. Ser. B (Engl. Ed.)* **1985**, *28*, 235–243.
- [8] C. Chen, Y. Wu, A. Jiang, B. Wu, G. You, R. Li, S. Lin, *J. Opt. Soc. Am. B* **1989**, *6*, 616–621.
- [9] Y. Wu, T. Sasaki, S. Nakai, A. Yokotani, H. Tang, C. Chen, *Appl. Phys. Lett.* **1993**, *62*, 2614–2615.
- [10] a) J.-M. Tu, D. A. Keszler, *Mater. Res. Bull.* **1995**, *30*, 209–215; b) Y. Mori, I. Kuroda, S. Nakajima, T. Sasaki, S. Nakai, *Appl. Phys. Lett.* **1995**, *67*, 1818–1820.
- [11] M. Iwai, T. Kobayashi, H. Furuya, Y. Mori, T. Sasaki, *Jpn. J. Appl. Phys.* **1997**, *36*, L276.
- [12] a) L. Mei, Y. Wang, C. Chen, B. Wu, *J. Appl. Phys.* **1993**, *74*, 7014–7015; b) D. Cyranoski, *Nature* **2009**, *457*, 953–955.
- [13] S. C. Wang, N. Ye, W. Li, D. Zhao, *J. Am. Chem. Soc.* **2010**, *132*, 8779–8786.
- [14] S. C. Wang, N. Ye, *J. Am. Chem. Soc.* **2011**, *133*, 11458–11461.
- [15] H. Huang, J. Yao, Z. Lin, X. Wang, R. He, W. Yao, N. Zhai, C. Chen, *Angew. Chem. Int. Ed.* **2011**, *50*, 9141–9144; *Angew. Chem.* **2011**, *123*, 9307–9310.
- [16] H. Huang, J. Yao, Z. Lin, X. Wang, R. He, W. Yao, N. Zhai, C. Chen, *Chem. Mater.* **2011**, *23*, 5457–5463.
- [17] H. W. Yu, H. P. Wu, S. L. Pan, Z. H. Yang, X. L. Hou, X. Su, Q. Jing, K. R. Poeppelmeier, J. M. Rondinelli, *J. Am. Chem. Soc.* **2014**, *136*, 1264–1267.
- [18] a) Y.-Z. Huang, L.-M. Wu, X.-T. Wu, L.-H. Li, L. Chen, Y.-F. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 12788–12789; b) X. Dong, Q. Jing, Y. Shi, Z. Yang, S. Pan, K. R. Poeppelmeier, J. Young, J. M. Rondinelli, *J. Am. Chem. Soc.* **2015**, *137*, 9417–9422; c) L. Liu, B. Zhang, F. Zhang, S. Pan, F. Zhang, X. Zhang, X. Dong, Z. Yang, *Dalton Trans.* **2015**, *44*, 7041–7047.
- [19] a) I. D. Brown, D. Altermatt, *Acta Crystallogr. Sect. B* **1985**, *41*, 244–247; b) N. E. Brese, M. O'Keeffe, *Acta Crystallogr. Sect. B* **1991**, *47*, 192–197.
- [20] a) W. Zhao, S. Pan, J. Han, J. Yao, Y. Yang, J. Li, M. Zhang, L. H. Zhang, Y. Hang, *J. Solid State Chem.* **2011**, *184*, 2849–2853; b) M. S. Refat, K. M. Elsabay, *Bull. Mater. Sci.* **2011**, *34*, 873–881; c) T. T. Tran, P. S. Halasyamani, J. M. Rondinelli, *Inorg. Chem.* **2014**, *53*, 6241–6251.
- [21] a) P. Kubelka, F. Munk, *Z. Tech. Phys.* **1931**, *12*, 593–601; b) J. Tauc, *Mater. Res. Bull.* **1970**, *5*, 721–729.
- [22] S. Kurtz, T. Perry, *J. Appl. Phys.* **1968**, *39*, 3798–3813.
- [23] a) H. Mizoguchi, H. W. Eng, P. Woodward, *Inorg. Chem.* **2004**, *43*, 1667–1680; b) H. Mizoguchi, P. Woodward, *Chem. Mater.* **2004**, *16*, 5233–5248.

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