Pb$_7$O(OH)$_3$(CO$_3$)$_3$(BO$_3$): First Mixed Borate and Carbonate Nonlinear Optical Material Exhibiting Large Second-Harmonic Generation Response

Maierhaba Abudoureheman,† Li Wang,*† Xianming Zhang,‡ Hongwei Yu,*§ Zhihua Yang,*§ Chen Lei,*§ Jian Han,*§ and Shilie Pan*§

†College of Chemistry & Chemical Engineering, Xinjiang Normal University, Urumqi 830054, P. R. China
‡School of Chemistry & Material Science, Shanxi Normal University, Linfen 041004, P. R. China
§Key Laboratory of Functional Materials and Devices for Special Environments of CAS, Xinjiang Technical Institute of Physics & Chemistry of CAS, No. 40-1, Beijing South Road, Urumqi 830011, P. R. China

Supporting Information

ABSTRACT: The first borate carbonate UV nonlinear optical material Pb$_7$O(OH)$_3$(CO$_3$)$_3$(BO$_3$) was hydrothermally synthesized, which features a (3,9)-connected IrSi$_3$-like structure constructed by Pb$_7$O(OH)$_3$(BO$_3$) units and carbonates. This compound exhibits a large second-harmonic generation (SHG) response about 4.5 times that of KH$_2$PO$_4$ (KDP), attributed to synergistic interactions between the steroefect of the Pb(II) cations and coparallel BO$_3$ and CO$_3$ triangles groups.

INTRODUCTION

Nonlinear optical (NLO) crystals have attracted considerable attention due to their important applications in laser frequency conversion, optical parameter oscillator, and other optical and photonic devices. Understanding the relationship between structure and NLO behavior is very important for the design of new NLO crystals. Generally, three effective strategies or their combinations have been used to guide NLO crystals: (i) to choose favorable structural units like coplanar π-conjugated BO$_3$ and CO$_3$ groups and have them co-aligned; (ii) to use second-order Jahn–Teller distorted cations such as high valence d$^0$ transition metals, lone pair e$^-$fect cations, or polar chalcogenide units (e.g., [AsS$_3$]$^{3-}$, [SbS$_3$]$^{3-}$, and [TeS$_3$]$^{2-}$); (iii) to increase the density of the active asymmetric NLO structural units. From a structural unit point of view, it is well-known that the planar BO$_3$ group possesses a relatively large microscopic second-order susceptibility and moderate birefringence, suitable for UV and deep-UV light generation. On the basis of the BO$_3$ unit, the famous borate UV and deep UV NLO materials such BBO, LBO, and KBBF have been synthesized. It should be particularly noted that the excellent deep UV NLO properties of KBBF come from the conjugated [Be$_2$BO$_3$F$_2$]$_{n}$ layers. Analogous to the BO$_3$ structural unit, the CO$_3$ groups possess a similar planar triangle with a π-conjugated molecular orbital, which can produce a moderate birefringence. Thus, carbonate UV NLO crystals have recently attracted much attention, and several materials including MnCO$_3$F (M = K, Rb, Cs; N = Ca, Sr, Ba), CsPbCO$_3$F, RbPbCO$_3$F, and K$_{2-2x}$Pb$_{15}$[(CO$_3$)$_{3-2x}$]$_x$F$_{15}$ have been synthesized and revealed to have moderate to large second-harmonic generation (SHG) coefficients. It is also found that coparallel alignment of CO$_3$ groups may produce higher bulk NLO coefficients.

One may expect that the incorporation of BO$_3$ and CO$_3$ into one anetric structure will result in new borate–carbonate UV NLO materials. A literature search reveals that there are indeed some mixed borate and carbonate compounds including natural mineral Ba$_2$(BO$_3$)$_{1-x}$(CO$_3$)$_x$Cl$_{1+x}$, Ca$_4$Mn$_3$O$_3$(BO$_3$)$_3$CO$_3$, Pb$_7$Mg$_{4.5}$(Si$_{4.8}$Al$_{0.2}$O$_{14}$)(BO$_3$)(CO$_3$)[$(BO_3)_0.7$(SiO$_4$)$_0.3$]·(OH,F)$_{6.7}$, Sr$_2$CuO$_2$(CO$_3$)$_{0.85}$(BO$_3$)$_{0.15}$, and Ca$_4$(Ca$_{0.7}$Na$_{0.3}$)$_3$(Na$_{0.7}$)Li$_5$[B$_{12}$B$_{10}$O$_{36}$(O,OH)$_6$](CO$_3$)(OH)·(OH,H$_2$O) and Pb$_{7.1}$Mg$_{4.5}$(Si$_{4.8}$Al$_{0.2}$O$_{14}$)(BO$_3$)(CO$_3$)[$(BO_3)_0.7$(SiO$_4$)$_0.3$]·(OH,F)$_{6.7}$ are synthesized. However, all these mixed borate and carbonate compounds crystallize in centrosymmetric space groups. Only Sr$_2$CuO$_2$(CO$_3$)$_{0.85}$(BO$_3$)$_{0.15}$ and Ca$_4$(Ca$_{0.7}$Na$_{0.3}$)$_3$(Na$_{0.7}$)Li$_5$[B$_{12}$B$_{10}$O$_{36}$(O,OH)$_6$](CO$_3$)(OH)·(OH,H$_2$O) crystallize in noncentrosymmetric space groups.

To date, a mixed borate and carbonate UV NLO material has not been documented.

During our search on missed borate and carbonate UV NLO material, we chose lone pair effect Pb$^{2+}$ ions as cations because they may synergistically interact with BO$_3$ and CO$_3$ structural units to enhance the NLO coefficient. Herein we present the first borate–carbonate UV NLO material Pb$_7$O(OH)$_3$(CO$_3$)$_3$(BO$_3$) (1), which features (3,9)-connected IrSi$_3$-like structure with layered [Pb$_7$(CO$_3$)$_3$(BO$_3$)$_3$]$_{n}$ structural motifs and exhibits a large SHG response about 4.5 times that of KDP.
**EXPERIMENTAL SECTION**

**Synthesis.** Compound 1 was hydrothermally synthesized by treatment of Pb(NO₃)₂, H₂BO₃, Cs₂CO₃, and KOH in the molar ratio 1:4:1:10 in a 23 mL autoclave at 180 °C for 12 h in 75% yield, based on Pb. The bulk phase purity was confirmed by powder X-ray diffraction (PXRD) pattern.

**Single Crystal X-ray Diffraction.** Single crystal X-ray diffraction data were collected at 298(2) K on an APEX II CCD diffractometer using monochromatic Mo Kα radiation (λ = 0.71073 Å) and integrated with the SAINT program.³⁰ The structure was determined by the direct methods and refined by full-matrix least-squares fitting on F². All the calculations were performed with programs from the SHELXTL crystallographic software package.²⁹ All non-hydrogen atoms were refined with anisotropic thermal parameters. The structure was checked with PLATON for missing symmetry elements.³⁰ Crystal data, details of data collection, and structure refinement information are given in Table 1. Atomic coordinates and equivalent isotropic displacement parameters are summarized in Supporting Information Tables S2 and S3 in the Supporting Information.

**TG Analysis.** The TG analysis was carried out with NETZSCH STA 449F3 simultaneous thermal analyzer instrument. The sample and reference (Al₂O₃) were enclosed in Pt crucibles, and heated from 25 to 900 °C at a heating rate of 10 °C/min under a nitrogen atmosphere.

**UV–Vis–NIR Diffuse Reflectance Spectrum.** The Shimadzu SolidSpec-3700DUV spectrophotometer is used to measure the spectra of powder sample over a 190–2600 nm wavelength range. Reflectance spectra are converted to absorbance with the Kubelka–Munk function.³¹

**RESULTS AND DISCUSSIONS**

**Crystal Structure.** X-ray single crystal diffraction reveals that compound 1 features (3,9)-connected polar network constructed by the Pb₂O(OH)₈(BO₄)₃ units and CO₃ groups. It crystallizes in the hexagonal system with polycrystalline Pb₆m₃c and the asymmetric unit consists of three crystallographically independent Pb(II), one μ₄-oxo, one μ₅-hydroxide, 1/2 carbonate, 1/6 borate. The assignment of carbonate and borate is based on bond lengths and structural refinement, infrared spectra (IR), TG analysis, energy dispersive spectroscopy (EDS), and elemental analysis. The B(1) atom of borate has symmetry of 3m (Wyckoff letter 2b), coordinated by three equivalent oxygen atoms with B(1)–O(3) distance of 1.39(2) Å, characteristic of carbonates. ³⁸,³⁹

![Figure 1](https://example.com/figure1.png)

**Figure 1.** (a) Side view of the Pb₂O(OH)₈(BO₄)₃ unit constructed by tent-shaped Pb₂O(OH)₈ and basal BO₃ group showing capped octahedral arrangement of the Pb atoms. (b) Schematic view of the (3,9)-connected net. Blue and red balls represent Pb₂O(OH)₈(BO₄)₃ and (CO₃)₆, respectively. (c) View of the planar Pb₂O(CO₃)(BO₄) layer.
three carbonate groups in the basal plane and one O(1) atom at the axial position. The basal Pb(1)−O(5) distances are 2.63(17) Å, and the axial Pb(1)−O(1) distance is 2.19(4) Å. The Pb(2) atom also shows hexagonal pyramidal geometry, but is coordinated by four oxygens from two carbonate groups and two oxygen atoms from a borate group in the basal plane and one hydroxide at the axial position. The basal Pb(2)−O distances are in the range 2.22(2)−2.78(2) Å, and the axial Pb(1)−O(1) distance is 2.19(4) Å. Pb(3) atom is four coordinate, bonded by one oxo, hydroxides, and one carbonate oxygen atom. The Pb(3)−O distances are in the range 2.36(13)−2.55(17) Å. Very interestingly, seven Pb atoms are linked by one μ₄-oxo and three μ₃-hydroxides into a Pb₇O(OH)₃ unit with an internal void which is occupied by one borate to obtain Pb₇O(OH)₃(BO₃) unit. Within the Pb₇O(OH)₃(BO₃) unit, seven Pb atoms adopt a capped octahedron geometry, and it is expected that the lone pair of Pb(1) projects outward of the cap. The Pb₇O(OH)₃(BO₃) units are linked by μ₃-hydroxides into three-dimensional polar network. Topologically, the network can be simplified as (3,9)-connected IrSi₃ net with Schläfli symbol of {4.6}₃{4.6}₃{4.6}₃, in which the Pb₇O(OH)₃(BO₃) units and carbonates act as nine and three connected nodes, respectively. Alternately, the structure of 1 may be viewed as hexagonal packing of Pb₇O(OH)₃(BO₃) units with trigonal interstitial voids filled by carbonates.

One of the important features of 1 is that there are trigonal planar Pb₄(CO₃)₃(BO₃) layers within ab plane. Within a Pb₄(CO₃)₃(BO₃) layer, there are two types of Pb atoms: Pb(1) is chelated by three carbonate groups, and Pb(2) is chelated by two carbonate groups and a borate. It should be noted that adjacent Pb₄(CO₃)₃(BO₃) layers in 1 are covalently linked by Pb₇O(OH)₃ units via a variety of Pb−O bonds into 3D framework, different from weak interlayer K⁺−F⁻ ionic interactions in KBBF (Figure 1 and Figure S1 in the Supporting Information). Supporting Information Figure S2 (PXRD) showed the calculated one in good agreement with that derived from the single crystal data. Infrared spectra (IR), TG analysis, energy dispersive spectroscopy (EDS), and elemental analysis are shown in Figures S3−S5 and Table S4 in the Supporting Information.

**Table 2. Detailed Contributions from PbOₙ Polyhedra and BO₃, CO₃ Triangles and the Total Polarization of the Whole Unit Cell**

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*Figure 2. Plot of transformed Kubelka–Munk function versus the energy of the light adsorbed. Insert: The reflectance spectrum of Pb₉O(OH)₉(CO₃)₉(BO₃).*

*Figure 3. Calculated band structure and total density of states and the corresponding partial density of orbital of Pb₉O(OH)₉(CO₃)₉(BO₃) with commercial KDP as a reference.*

*Figure 4. SHG intensities of Pb₉O(OH)₉(CO₃)₉(BO₃) with commercial KDP as a reference.*

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which clearly reveals highly asymmetric lobes on the Pb$^{2+}$ states (Figure 3). The band is mainly composed of Pb 6s, 6p states, and O 2p states. The calculated band gap being 3.43 eV. The upper region of valence band is mainly composed of Pb 6s, 6p states, and O 2p states. The bottom of conduction band is mainly composed of Pb 6p states (Figure 3).

**Second-Order NLO Measurements.** Powder second-harmonic generation test was measured using the Kurtz–Perry method,\(^8\) which indicates that SHG response of 1 was ~4.5 times that of the KDP standard with a similar grain size (Figure 4). On the basis of the anionic group theory,\(^9\) the overall SHG response of crystal is the geometrical superposition of the second-order susceptibility. Therefore, the packing of the BO$_3$ and CO$_3$ structural units and stereochemically active lone pair (SCALP) in the Pb polyhedra may also affect the macroscopic SHG coefficients. A bond-valence method\(^21,39\) has been used to calculate the direction and magnitude of the dipole moments, and the validity of this method has been confirmed in the calculation on distortion of MoO$_6$, TeO$_4$, PbO$_6$, and BaO$_6$ polyhedra.\(^21,39\) As to the PbO$_6$ polyhedra, the lone pair is given a charge of ~2 and localized 0.86 Å from the Pb$^{2+}$ cation.\(^40\) It should be emphasized here that the cooperative action of the polyhedral dipoles has been evaluated using the complete crystal symmetry, including both point and translation operations. Not only the contribution from single PbO$_6$ polyhedra, CO$_3$, and BO$_3$ groups of the asymmetric unit but also the total polarization of the whole unit cell (Z = 2) is considered. The detailed calculation results are given in Table 2. Calculated results show that the PbO$_{6}$, CO$_3$, and BO$_3$ groups yield dipole moments of 25.51, 5.85, and 6.47 D, respectively. The magnitudes of dipole moments along the bc plane are almost canceled, and their vector sum is well-enhanced along the c-axis direction (Figure 5).

To further visualize SCALPs of Pb\(^{2+}\), the electron localization function (ELF) map containing the Pb atoms has been given, which clearly reveals highly asymmetric lobes on the Pb\(^{2+}\) cations due to SCALP. Considering the direction and packing of the SCALPs, there is a superposition of electronic distribution from the lone pairs of Pb(1), Pb(2), and Pb(3) atoms. These results show that SCALPs of Pb\(^{2+}\) lead to a heterogeneous electronic distribution (Figure S6 in the Supporting Information).

**CONCLUSION**

In summary, we report a new NLO material exhibiting strong second-order effects of the lone pair of the Pb$^{2+}$ cation bound by BO$_3$ and CO$_3$ groups in the crystal structure. All of the coplanar π-conjugated BO$_3$ and CO$_3$ ionic groups are parallel aligned. It exhibits an SHG response about 4.5 times that of KDP. The calculation of the dipole moments and first principle calculations show that the SHG response of 1 mainly originates from the cooperation of the PbO$_6$ polyhedra and coparallel BO$_3$ and CO$_3$ triangles. This work indicates that combining π-conjugated species with the isostructural but nonisoelectric BO$_3$ and CO$_3$ active groups in acentric structures can produce materials with very strong NLO response.

**ASSOCIATED CONTENT**

Crystallographic data in CIF format, final coordinates, selected bond distances, bond angles, XRD, IR, TG, elemental analysis, EDS, and electron localization function map. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

Corresponding Authors

E-mail: wangliresearch@163.com.
E-mail: slpan@ms.xjb.ac.cn.

Notes

The authors declare no competing financial interest.

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**SUPPORTING INFORMATION**

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Figure 5. Direction of dipole moments of each group as well as the whole unit structure.