Pb₇O(OH)₃(CO₃)₃(BO₃): First Mixed Borate and Carbonate Nonlinear Optical Material Exhibiting Large Second-Harmonic Generation Response

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Ⓢ *Supporting Information*

ABSTRACT: The first borate carbonate UV nonlinear optical material Pb₇O(OH)₃(CO₃)₃(BO₃) was hydrothermally synthesized, which features a (3,9)-connected IrSi₃-like structure constructed by Pb₇O(OH)₃(BO₃) units and carbonates. This compound exhibits a large second-harmonic generation (SHG) response about 4.5 times that of KH₂PO₄ (KDP), attributed to synergistic interactions between the stereoeffect of the Pb(II) cations and coparallel BO₃ and CO₃ triangles groups.
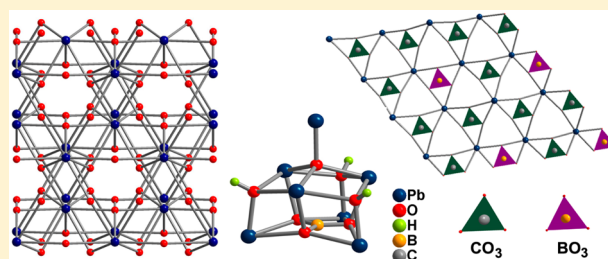
INTRODUCTION

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.[1−14] 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 BO₃ and CO₃ groups and have them co-aligned;[15−19] (ii) to use second-order Jahn−Teller distorted cations such as high valence d⁰ transition metals,[2a,8a,20] lone pair effect cations,[9a,21] or polar chalcogenide units (e.g., [AsS₃]³⁻, [SbS₃]³⁻, and [TeS₃]²⁻);[3] (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 BO₃ 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 BO₃ unit, the famous borate UV and deep UV NLO materials such as BBO,[22] LBO,[23] and KBBF[24] have been synthesized. It should be particularly noted that the excellent deep UV NLO properties of KBBF come from the conjugated [Be₂BO₃F₂]∞ layers. Analogous to the BO₃ structural unit, the CO₃ 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 MNCO₃F (M = K, Rb, Cs; N = Ca, Sr, Ba),[16] CsPbCO₃F,[17] RbPbCO₃F,[18] and K₂.₇₀Pb₅.₁₅(CO₃)₅F₃[19] have been synthesized and revealed to have moderate to large

second-harmonic generation (SHG) coefficients. It is also found that coparallel alignment of CO₃ groups may produce higher bulk NLO coefficients.[17]

One may expect that the incorporation of BO₃ and CO₃ into one acentric 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 Ba₂(BO₃)₁₋ₓ(CO₃)ₓCI₁₊ₓ[25] Ca₄Mn₃O₃(BO₃)₃CO₃,[26a,b] Pb₇.₁Mg₄.₅(Si₄.₈Al₀.₂O₁₄)(BO₃)(CO₃)[(BO₃)₀.₇(SiO₄)₀.₃]-(OH,F)₆.₇,[26c] etc., synthesized. However, all these mixed borate and carbonate compounds crystallize in centrosymmetric space groups. Only Sr₂CuO₂(CO₃)₀.₈₅(BO₃)₀.₁₅[27a] and Ca₄(Ca₀.₇Na₀.₃)₃(Na₀.₇)Li₅[B₁₂B₁₀O₃₆(O,OH)₆](CO₃)(OH)·(OH,H₂O)[27b] 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 Pb²⁺ ions as cations because they may synergistically interact with BO₃ and CO₃ structural units to enhance the NLO coefficient. Herein we present the first borate−carbonate UV NLO material Pb₇O(OH)₃-(CO₃)₃(BO₃) (**1**), which features (3,9)-connected IrSi₃-like structure with layered [Pb₄(CO₃)₃(BO₃)]∞ 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 $Pb(NO_3)_2$, H_3BO_3, Cs_2CO_3, 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 = 0.710 73 Å) and integrated with the SAINT program.[28] The structure was determined by the direct methods and refined by full-matrix least-squares fitting on F^2. 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

Table 1. Crystal Data and Structural Refinement for $Pb_7O(OH)_3(CO_3)_3(BO_3)$

empirical formula	$Pb_7O(OH)_3(CO_3)_3(BO_3)$
fw	1756.19
T (K)	298(2)
wavelength (Å)	0.710 73
cryst syst	hexagonal
space group, Z	$P6_3mc$, 2
unit cell dimensions	a = 10.519(16) Å
	b = 10.519(16) Å
	c = 8.900(13) Å
	γ = 120°
V (Å^3)	852.8(18)
density (calcd) (mg/m^3)	6.839
abs coeff (mm^{-1})	68.919
$F(000)$	1456
cryst size	0.08 mm × 0.08 mm × 0.05 mm
θ range for data collection (deg)	2.24–26.99
limiting indices	$-13 \leq h \leq 13$, $-12 \leq k \leq 13$, $-11 \leq l \leq 6$
no. reflns collected/ no. unique reflns	4865/592 [$R(\text{int})$ = 0.0687]
completeness to θ = 26.99° (%)	100.0
refinement method	full-matrix least-squares on F^2
GOF on F^2	1.097
final R indices [$F_o{}^2 > 2\sigma(F_o{}^2)$]^a	R1 = 0.0378, wR2 = 0.0958
R indices (all data)^a	R1 = 0.0421, wR2 = 0.0982
extinction coeff	0.000 053(4)
largest difference peak and hole	6.650 and −1.860 e/Å^3

^{a}R1 = $\sum||F_o| - |F_c||/\sum|F_o|$, and wR2 = $[\sum w(F_o{}^2 - F_c{}^2)^2/\sum wF_o{}^4]^{1/2}$ for $F_o{}^2 > 2\sigma(F_o{}^2)$.

displacement parameters are summarized in Supporting Information Table S1. The selected interatomic distances and angles are listed in Tables S2 and S3 in the Supporting Information.

Powder X-ray Diffraction. The powder X-ray diffraction (PXRD) pattern of $Pb_7O(OH)_3(CO_3)_3(BO_3)$ was collected on a Bruker D8 ADVANCE X-ray diffractometer using Cu Kα radiation (λ = 1.5418 Å) in the 2θ angular range 15–60°.

Infrared Spectroscopy. Infrared spectra of samples were recorded on a Shimadzu IR Affinity-1 Fourier transform infrared spectrometer in the range from 400 to 4000 cm^{-1} at room temperature. The sample was mixed thoroughly with dried KBr (5 mg of the sample and 500 mg of KBr).

TG Analysis. The TG analysis was carried out with NETZSCH STA 449F3 simultaneous thermal analyzer instrument. The sample and reference (Al_2O_3) 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]

Calculation Details. The DFT calculation was performed using the CASTEP module. The generalized gradient approximation (GGA) with the Ceperley and Perdew–Burke–Ernzerh (PBE) functional was adopted.[32] The interactions between the ionic cores and the electrons were described by the ultrasoft-pseudopotential. The plane-wave basis set energy cutoff was set at 340.0 eV. The total energy tolerance was 1 × 10^{-6} eV/atom. The k-point grid sampling in the Monkhorst–Pack scheme was set at 2 × 2 × 2 for the Brillouin zone.

Second-Order NLO Measurements. The fundamental wavelength is 1064 nm generated by a Q-switched Nd:YAG laser. Polycrystalline $Pb_7O(OH)_3(CO_3)_3(BO_3)$ was ground and sieved into distinct particle size ranges: <20, 20–38, 38–55, 55–88, 88–105, 105–150, and 150–200 μm. To make relevant comparisons with known SHG materials, polycrystalline KDP was ground and sieved into the same particle size ranges.

■ RESULTS AND DISCUSSIONS

Crystal Structure. X-ray single crystal diffraction reveals that compound **1** features (3,9)-connected polar network
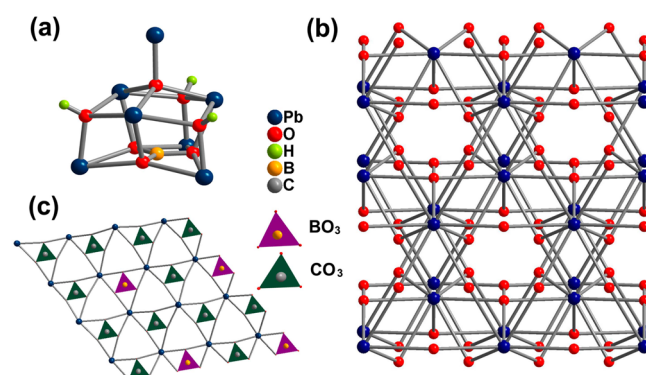

Figure 1. (a) Side view of the $Pb_7O(OH)_3(BO_3)$ unit constructed by tent-shaped $Pb_7O(OH)_3$ and basal BO_3 group showing capped octahedral arrangement of the Pb atoms. (b) Schematic view of the (3,9)-connected net. Blue and red balls represent $Pb_7O(OH)_3(BO_3)$ and $(CO_3)_3$, respectively. (c) View of the planar $Pb_4(CO_3)_3(BO_3)$ layer.

constructed by the $Pb_7O(OH)_3(BO_3)$ units and CO_3 groups. It crystallizes in the hexagonal system with polar space group $P6_3mc$, and the asymmetric unit consists of three crystallographically independent Pb(II), one μ_4-oxo, one μ_3-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 (Wykoff letter 2b), coordinated by three equivalent oxygen atoms with B(1)–O(3) distance of 1.39(2) Å. The C(1) atom of carbonate has symmetry of mirror plane (Wykoff letter 6c), coordinated by two O(5) and one O(4) atom with C(1)–O distance 1.28(3)–1.35(4) Å, characteristic of carbonates.[16−19] The Pb(1) atom shows a hexagonal pyramidal geometry, coordinated by six oxygen atoms from
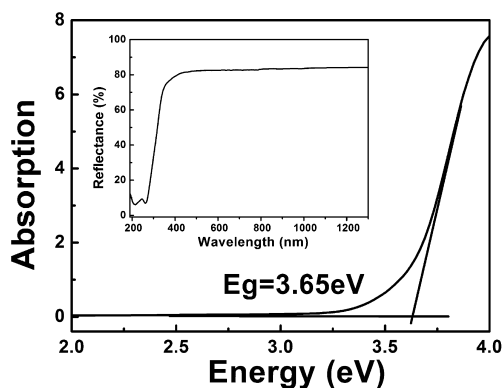
Figure 2. Plot of transformed Kubelka−Munk function versus the energy of the light adsorbed. Insert: The reflectance spectrum of $Pb_7O(OH)_3(CO_3)_3(BO_3)$.

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 μ_4-oxo and three μ_3-hydroxides into a $Pb_7O(OH)_3$ unit with an internal void which is occupied by one borate to obtain $Pb_7O(OH)_3(BO_3)$ unit. Within the $Pb_7O(OH)_3(BO_3)$ 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 $Pb_7O(OH)_3(BO_3)$ units are linked by μ_3-η^2:η^2:η^2-carbonates into three-dimensional polar network. Topologically, the network can be simplified as (3,9)-connected IrSi$_3$ net with Schläfli symbol of $\{4^2.6\}_3\{4^6.6^{24}.8^6\}$, in which the $Pb_7O(OH)_3(BO_3)$ units and carbonates act as nine and three connected nodes, respectively. Alternately, the structure of **1** may be viewed as hexagonal packing of $Pb_7O(OH)_3(BO_3)$ units with trigonal interstitial voids filled by carbonates.

One of the important features of **1** is that there are trigonal planar $Pb_4(CO_3)_3(BO_3)$ layers within *ab* plane. Within a
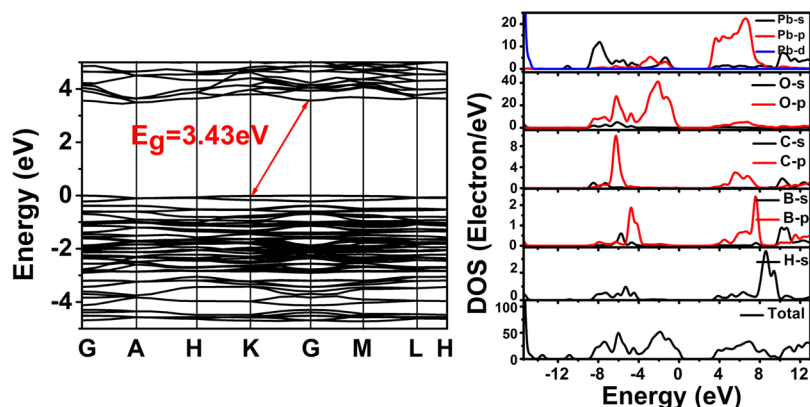

Figure 4. SHG intensities of $Pb_7O(OH)_3(CO_3)_3(BO_3)$ with commercial KDP as a reference.

Table 2. Detailed Contributions from PbO$_n$ Polyhedra and BO$_3$, CO$_3$ Triangles and the Total Polarization of the Whole Unit Cell

species	dipole moment			
	x	y	z	magnitude (D)
Pb(1)O$_7$	−0.0055	0.0055	6.1297	6.1297
Pb(2)O$_7$	−2.2755	−1.1619	−6.3575	6.6560
Pb(3)O$_4$	−1.3571	1.3879	0.0666	2.3783
Unit Cell Z = 2				
PbO$_n$	0.0484	0.0000	−25.5111	25.5112
CO$_3$	0	0	−5.8452	5.8452
BO$_3$	0.0219	0	−6.4697	6.4697
total polarization	−0.0613	0.0540	−37.8260	37.8262

$Pb_4(CO_3)_3(BO_3)$ 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 $Pb_4(CO_3)_3(BO_3)$ layers in **1** are covalently linked by $Pb_3O(OH)_3$ 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.

Figure 3. Calculated band structure and total density of states and the corresponding partial density of orbital of $Pb_7O(OH)_3(CO_3)_3(BO_3)$.
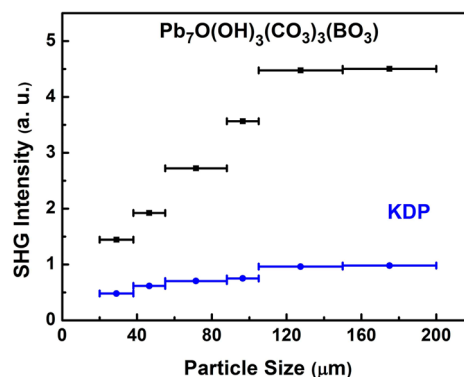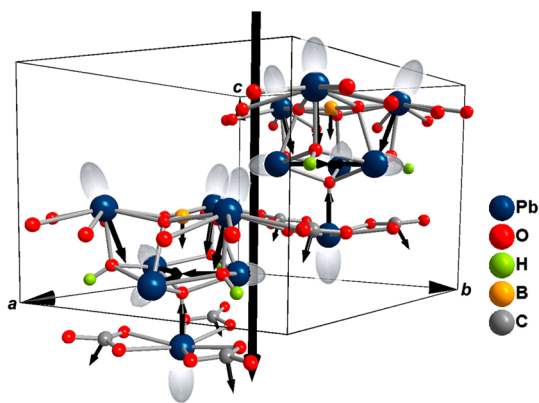
Figure 5. Direction of dipole moments of each group as well as the whole unit structure.

UV−Vis−NIR Diffuse Reflectance Spectrum. The absorption (K/S) data are calculated from Kubelka−Munk function $F(R) = (1 - R)^2/2R = K/S$. The UV cutoff edge of $Pb_7O(OH)_3(BO_3)$ is below 340 nm, corresponding to the band gap energies of 3.65 eV (Figure 2).

Calculation Details. Band structure, density of state, and the electron localization function were calculated by CA-STEP,[36] which shows that **1** is an indirect gap compound with 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,[37] 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,[38] the overall SHG response of crystal is the geometrical super-position of the second-order susceptibility. Therefore, the packing of the BO_3 and CO_3 structural units and stereochemi-cally 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_x, PbO_n, and BaO_n polyhedra.[21,39] As to the PbO_n 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_n 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_n, 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 stereoeffects 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_n 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

S Supporting Information

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.

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The authors declare no competing financial interest.

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