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Facile Assembly of an Unusual Lead Borate with Different Cluster Building Units via a Hydrothermal Process

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S *Supporting Information*

ABSTRACT: $Pb(BO_2)_2 \cdot H_2O$ as sources of B and Pb via a simple hydrothermal process provided the first binodal 5,9-connected lead borate, $Pb_6B_4O_{11}(OH)_2$ (**1**). Compound **1** crystallizes in the orthorhombic space group *Pnma*. The crystal structure is composed of different cluster building units of B_4O_9 and Pb_6O_4. Compound **1** has an optical band gap of 3.24 eV.

Metal borates are of current interest because of their rich structural chemistry and diverse applications in mineralogy, catalysis, ion exchange, and nonlinear-optical (NLO) materials.[1−3] Up to now, main-group borates, transition-metal borates, and lanthanide borates have been successfully synthesized through different synthetic approaches.[4−12] For example, Mao and co-workers successfully obtained a series of germanium borates with second-order NLO properties via high-temperature solid-state reaction;[4] Lin and co-workers systematically investigated the aluminoborates (denoted as PKU-*n*) and prepared a porous PKU-2 with extra-large pores of 24-ring channels using the boric acid flux method.[2a,7] A family of open-framework aluminoborates and germanium borates have been synthesized by Yang and co-workers under mild hydrothermal/solvothermal conditions using different alkali-metal cations or organic amine cations as templates.[10]

Recently, some open-framework inorganic solids have been obtained by incorporating different cluster building units into the same framework, which cause much more diversity of the structures.[13,14] B atoms can be three- and four-coordinated to O atoms to form different polyborate anions such as $[B_3O_3(OH)_4]^-$, $[B_4O_5(OH)_4]^{2-}$, $[B_6O_{11}(OH)_2]^{6-}$, $[B_7O_9(OH)_5]^{2-}$, $[B_8O_{10}(OH)_6]^{2-}$, $[B_{11}O_{22}]^{11-}$, and $[B_{14}O_{20}(OH)_6]^{4-}$.[15−17] Therefore, it should be possible to combine rich structural motifs of oxo boron clusters with metal clusters to produce novel metal borates. Compared with a large number of 3D metal borates assembled by single metal ions with different oxo borate clusters, only a few examples of 3D metal borates containing both large metal clusters and oxo boron clusters are reported to date.[6b,7a,9a]

Lead borates are known to act as good candidates for NLO materials because of the stereochemically active lone pairs and high polarizability of the Pb^{2+} ion.[9,18] The Pb^{2+} ion exhibits variable coordination numbers ($2 \leq CN \leq 8$) and easy-to-form diversity of lead oxo/hydroxo clusters.[19] $Pb(BO_2)_2 \cdot H_2O$ is a commercial product and finds various industrial use. It is known that different metastable kinetic phases can be obtained under the hydrothermal process.[10b] $Pb(BO_2)_2 \cdot H_2O$ contains both Pb and B; if a hydrothermal process is introduced, a new lead borate may be formed that contains Pb and B units different from $Pb(BO_2)_2 \cdot H_2O$, which would be helpful in understanding the formation mechanism of lead borate.

Accordingly, our aim is to synthesize 3D lead borate frameworks using different building units via a simple hydrothermal treatment of $Pb(BO_2)_2 \cdot H_2O$. Here, we report the synthesis, structure, and UV−vis spectra of a novel 3D lead borate, $Pb_6B_4O_{11}(OH)_2$ (**1**), which contains B_4O_9 and Pb_6O_4 clusters with an unusual 5,9-connected binodal network.

Colorless lamellar crystals of **1** were obtained by hydrothermal reactions of $Pb(BO_2)_2 \cdot H_2O$ (0.5 mmol, 0.155 g) in water (8 mL) at 170 °C for 6 days. The crystals were obtained in a yield of about 33% based on Pb. Its purity was confirmed by powder X-ray diffraction (PXRD) studies (Figure S1 in the Supporting Information, SI). Energy-dispersive spectrometry shows that Pb is a major component in compound **1**. Compound **1** could not be obtained when $Pb(BO_2)_2 \cdot H_2O$ was replaced with PbO and other B sources (B_2O_3, H_3BO_3, or $K_2B_4O_7 \cdot 4H_2O$).

The structure was solved by direct methods and refined by full-matrix least squares on F^2 with the *SHELXTL-97* program.[20−22] The asymmetric unit of **1** contains 15 independent non-H atoms, including four Pb, three B, and eight O atoms. Pb1 and Pb3 atoms are six- and five-coordinated, respectively, while Pb2 and Pb4 atoms are four-coordinated all of the Pb^{2+} ions show stereochemically active lone pairs (Figure S2 in the SI). The Pb−O distances range from 2.217(18) to 2.991(0) Å. The Pb^{2+} ions are linked by O atoms to give a $[Pb_6O_4]^{4+}$ $\{Pb_6\}$ cluster (Figure 1a). The B atoms adopt two kinds of coordination models, with B−O bond distances varying from 1.35(3) to 1.38(3) Å for the BO_3 triangles (B1) and from 1.43(4) to 1.52(2) Å for the BO_4 tetrahedra (B2 and B3) (Table S1 in the SI). Two BO_3 triangles and two BO_4 tetrahedra are linked via bridging O atoms to give a B_4O_9 $\{B_4\}$ unit containing two B_3O_3 rings (Figure 1a). Bond-valence-sum calculations gave total bond valences of 1.07 for O8, indicating that O8 is an OH group; other O, Pb, and B atoms are in oxidation states of 2−, 2+, and 3+, respectively (Table S1 in the SI).

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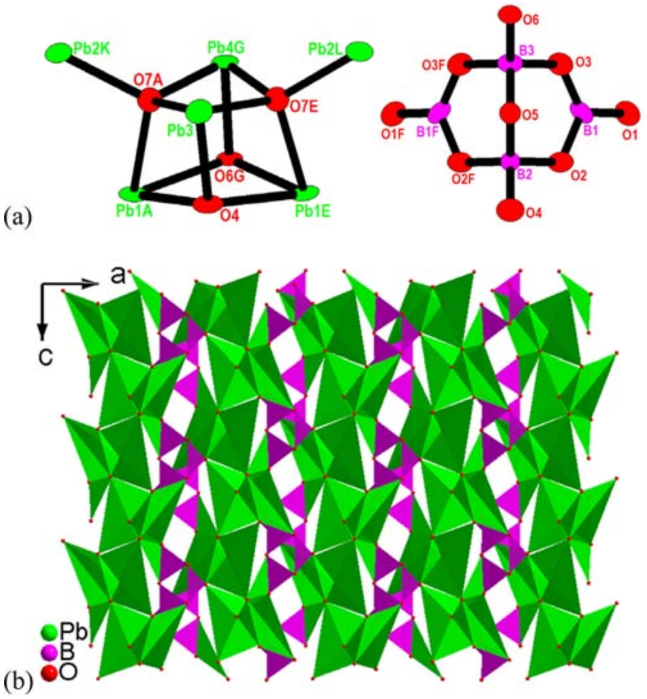

Figure 1. (a) Pb_6O_4 (left) and B_4O_9 (right) clusters in **1**. Symmetry codes: (A) $-x, -y, -z$; (E) $-x, y + {}^1/_2, -z$; (F) $x, -y + {}^1/_2, z$; (G) $x, y, z - 1$; (K) $x - 0.5, y, -z - 0.5$; (L) $x - 0.5, -y + 0.5, -z - 0.5$. (b) Polyhedral view the framework of **1** along the *b* axis.

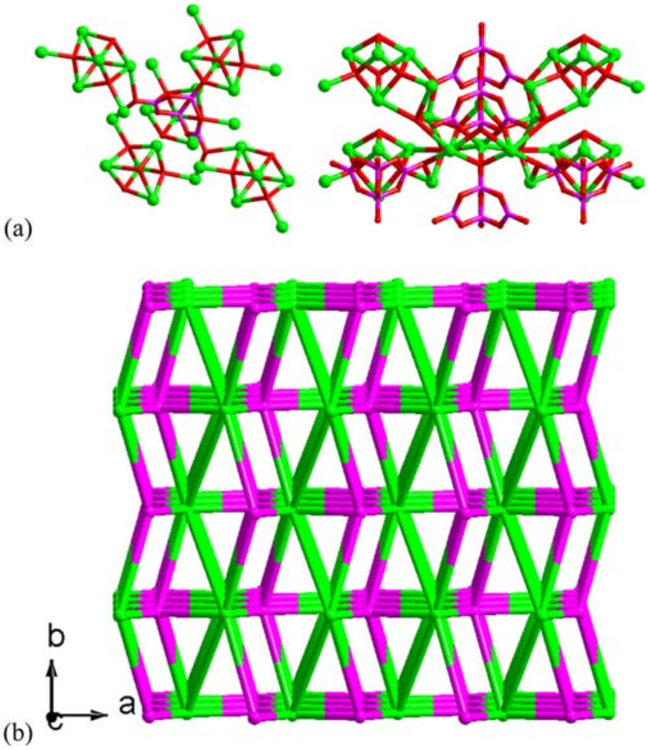

Figure 2. (a) Coordination environments of $\{B_4\}$ (left) and $\{Pb_6\}$ (right) clusters in **1**. (b) Schematic representation of the connection between $\{B_4\}$ and $\{Pb_6\}$ clusters. Color code: purple, $\{B_4\}$ cluster; green, $\{Pb_6\}$ cluster.

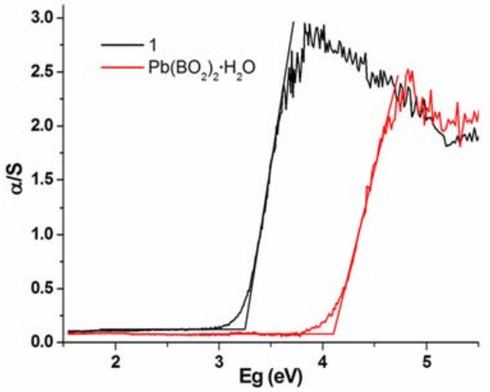

Figure 3. Optical absorption spectra for solid samples of **1** and $Pb(BO_2)_2{\cdot}H_2O$.

Each $\{Pb_6\}$ unit is bridged by μ_4-OH^- to give 2D layers in the *bc* plane (Figure S3 in the SI); these Pb cluster layers are further pillared by a $\{B_4\}$ unit into the 3D network (Figure 1b). As shown in Figure 2a, each $\{B_4\}$ unit is linked to five $\{Pb_6\}$ clusters, while each $\{Pb_6\}$ cluster is linked to the five nearest $\{B_4\}$ units and four $\{Pb_6\}$ units. From a topological point of view, the framework can be rationalized as a 5,9-connected network with the Schläfli symbol of $(3^2\cdot4^6\cdot5^2)(3^4\cdot4^{14}\cdot5^{10}\cdot6^8)$ (Figure 2b). To the best of our knowledge, the framework reported herein defines a new topology for 5,9-connected networks. To date, high-connected binodal networks are extremely rare in inorganic solids;[14a,23] the reported 5,9-connected network here is a good example of using different cluster building units to construct high-connected binodal lead borate frameworks.

The solid-state UV–visible absorption for compound **1** has been measured by the diffuse-reflectance spectra at room temperature (Figure 3). It reveals the presence of an optical band gap at 3.24 eV; the band gap is smaller than that of the starting material $Pb(BO_2)_2{\cdot}H_2O$ (4.12 eV). Thus, a much larger fraction of visible light is absorbed by compound **1**.

The thermal behavior of **1** was examined by thermogravimetric analysis (TGA) in a dry air atmosphere from 30 to 800 °C. Compound **1** undergoes one step of weight loss. Above a temperature of 320 °C, the weight loss is due to decomposition and collapse of the whole framework (calcd/found, 1.2/0.9%; Figure S4 in the SI). In the IR spectra of **1**, the strong and broad absorption bands in the range of 3000–3700 cm^{-1} are assigned as characteristic peaks of OH vibration. The characteristic band around 1270 cm^{-1} is due to the B–O asymmetric stretching of BO_3 units. The band around 1000 cm^{-1} is associated with BO_4 units (Figure S5 in the SI).

In summary, a new lead borate constructed of different cluster building units of $\{B_4\}$ and $\{Pb_6\}$ has been obtained via a simple hydrothermal process using $Pb(BO_2)_2{\cdot}H_2O$ as the starting material. The linkage between $\{Pb_6\}$ and $\{B_4\}$ gives the first 5,9-connected lead borate. The successful isolation of this compound gives a good example of an easy synthesis of lead borate under hydrothermal conditions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic files in CIF format for structure **1**, PXRD, TGA, and IR. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(20) Crystal data for $Pb_6B_4O_{11}(OH)_2$: $M = 1496.40$; orthorhombic; $Pnma$; $a = 13.3931(15)$ Å, $b = 13.0149(16)$ Å, $c = 7.8019(10)$ Å; $V = 1359.9(3)$ Å^3; $Z = 4$; $D_c = 7.309$ g cm^{-3}, $S = 1.032$. The final least-squares refinements converged at R1 (wR2) = 0.0679 (0.1613) and for 1063 reflections with $I > 2\sigma(I)$. The final difference Fourier map showed the maximum peaks at 4.576 e Å^{-3} (0.90 Å from Pb1). Relatively high residual electron densities have been observed in lead borates previously.[18c] CSD 425647.

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