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Pb_4VBO_8: Synthesis, Crystal Structure, and Properties

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The first compound Pb_4VBO_8 in the $PbO–V_2O_5–B_2O_3$ ternary system has been synthesized. Its structure was solved by single-crystal X-ray diffraction analysis. It crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $a = 10.4047(5)$ Å, $b = 7.0906(4)$ Å, $c = 12.8968(7)$ Å, $\beta = 113.128(3)°$, $Z = 4$, $R_1 = 0.0261$, and $wR_2 = 0.0628$. The new structure contains an infinite three-dimensional matrix that is built from BO_3, VO_4, and PbO_n ($n = 4$ and 5) polyhedra.

In searching for noncentrosymmetric (NCS) oxides, much attention has been paid to combine boron–oxygen units with other NCS as a binary building unit in the syntheses of nonlinear optical (NLO) materials. Mostly researched NCS chromophores are oxides containing second-order Jahn–Teller (SOJT) distorted cations such as d^0 transition-metal ions (V^{5+}, Ti^{4+}, Nb^{5+}, W^{6+}, etc.) and cations with a lone pair electrons of ns^2 (Pb^{2+}, Sn^{2+}, Se^{4+}, Te^{4+}, Bi^{3+}, etc.).[1–6] In recent decades, some significant investigations have been carried out on d^{10} cations (Cd^{2+}, Zn^{2+}, etc.), whose polar displacement is likely to lead to an asymmetric bonding configuration.[7–9] Borates are of considerable interest because of their rich structural chemistry and potential applications, such as nonlinear optics. The success of the borates can be attributed to the ability to bind to either three or four oxygen atoms to form a BO_3 triangle or a BO_4 tetrahedron. And these BO_3 triangles and BO_4 tetrahedra can further link together via common oxygen atoms to form isolated rings and cages or polymerize into infinite chains, sheets, and networks.[10–13]

We have, therefore, started investigating $PbO–V_2O_5–B_2O_3$ systems because there has been no report on the mixed borates in the $PbO–V_2O_5–B_2O_3$ systems until now. Extensive efforts in the ternary $PbO–V_2O_5–B_2O_3$ systems led to a new phase, Pb_4VBO_8. Here we report its synthesis, growth, crystal structure, and optical properties.

A polycrystalline sample of Pb_4VBO_8 was prepared by standard solid-state reaction using PbO (99.0%), V_2O_5 (99.0%), and B_2O_3 (99.5%) as the starting components in the molar ratio 8:1:1. The reagents were mixed and ground in an agate mortar. The mixture was heated to 600 °C in air for 24 h (with occasional grinding) and then sintered at 600 °C for an additional 48 h. The resultant yellow powder was found to be pure by powder X-ray diffraction (XRD) analysis.

Single crystals of Pb_4VBO_8 were grown from high-temperature solution. The solution was prepared in a platinum crucible by melting a mixture of PbO, V_2O_5, and B_2O_3 with a molar ratio of 10:1:1. A 50-g portion of polycrystalline sample was melted in a platinum crucible at 750 °C and kept at this temperature for 10 h. The furnace was slowly cooled to 600 °C at a rate of 1 °C h^{-1} and then cooled to room temperature at a rate of 20–30 °C h^{-1}. Yellow plate crystals were separated from the crucible and selected under an optical microscope for the structure determination. The measured powder XRD pattern matches the one simulated from single-crystal XRD studies (Figure S1 in the Supporting Information; SI[27]). A yellow plate crystal of Pb_4VBO_8 with dimensions 0.038 mm × 0.053 mm × 0.142 mm was chosen for the structure determination. Details of crystal parameters, data collection, structure refinements are given in Table S1, and the atomic coordinates and the equivalent isotropic displacement parameters are summarized in Table S2, bond lengths are listed in Table S3, and the bond angles are listed in Table S4 (SI[27]).

The XRD pattern shows that the Pb_4VBO_8 crystallizes in a monoclinic space group $P2_1/c$. In the asymmetric unit, there are four Pb atoms, one unique B atom, one V atom, and eight O atoms. All the Pb atoms (Figure S2; SI[27]) connected by O atoms form two-dimensional layers. The BO_3 triangles fill in the intralayer. The V atoms are located between these layers to balance charge and also to hold the layers together through coordination with oxygen atoms (Figure 1). The adjacent VO_4 and BO_3 groups are in isolated distribution in a parallel formation from the opposite direction. There are four types of Pb atoms which possess different coordination environments. Three Pb atoms are bonded to four O atoms, and one Pb atom is bonded to five O atoms. The bond distances of Pb–O (Table S3; SI[27]) are between 2.319(6) and 2.728(6) Å. They are all closely comparable to 2.24(2)–2.99(2) Å in $Pb_2Bi(V_{0.84}P_{0.16})O_6$,[14] 2.171(4)–2.729(11) Å in $Pb_6B_2WO_{12}$,[15] 2.395(5)–2.894(4) Å in $Pb_2CuB_2O_6$,[16] 2.374(6)–2.800(7) Å in $Pb_2Cu_3B_4O_{11}$[17] reported previously.

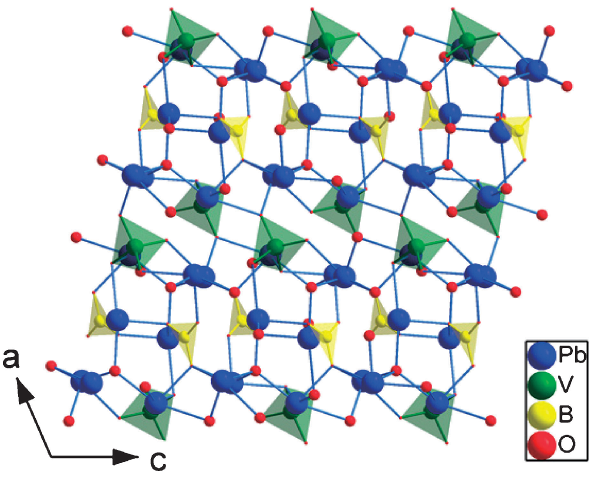

Figure 1. The three-dimensional framework in Pb_4VBO_8.

In the VO_4 polyhedra, the V–O bond lengths (Table S3; SI[27]) range from 1.689(6) to 1.726(6) Å with an average bond distance of 1.708 Å, comparable to those of $PbCo_2V_2O_8$[18] and $Na_3VO_2B_6O_{11}$,[19] which proves that the coordinations of Pb atoms are very reasonable.

The one type of B atoms is coordinated to three O atoms, the B–O bond lengths (Table S3; SI[27]) range from 1.37(11) to 1.381(11) Å and bear an average distance of 1.376 Å for B atom (Table S3; SI[27]), the O–B–O angles (Table S4; SI[27]) range from 123.1(8) to 119.9(8)° and the average of O–B–O angles equals 119.3° (BO_3 nearly planar). They are all closely comparable to those of other compounds reported previously. In the structure, isolated planar BO_3 groups are distributed in parallel along two different directions. Considering the anisotropic polarizability of planar BO_3 groups, it is likely to be a promising a birefringent crystal.[20,21] The bond valence sums of Pb, V, and B atoms have been calculated[22–24] (Table S2; SI[27]), and they are all reasonable.

Pb_4VBO_8 samples were heated to 1000 °C with a heating rate of 5 $°C\,min^{-1}$ and then cooled to room temperature at a rate of 5 $°C\,min^{-1}$. No weight loss could be observed on TG curve between room temperature and 1000 °C. It shows one endothermic peak at 637 °C on the heating curve and two exothermic peaks on the cooling curve at 573 and 643 °C, which suggests that Pb_4VBO_8 melts incongruently (Figure S3; SI[27]). In order to further verify whether Pb_4VBO_8 melts incongruently, 2 g of Pb_4VBO_8 powder was heated to 1000 °C and rapidly cooled to room temperature. Analysis of the X-ray powder diffraction pattern of the melt revealed that the peaks are very different from those of the pure phase of Pb_4VBO_8 (Figure S4; SI[27]), which demonstrates that Pb_4VBO_8 is an incongruently melting compound.

In order to specify and compare the coordination of boron in Pb_4VBO_8, the IR spectrum was measured (Figure S5; SI[27]). The band at 590 cm^{-1} mainly originates from the BO_3 bending modes, while those near 725 and 740 cm^{-1} should be assigned to BO_3 out-of-plane bending modes. The strong bands above 904 cm^{-1} are mainly attributed to the BO_3 antisymmetric stretching vibrations.[25] The IR spectrum further confirms the existence of only trigonally coordinated boron atoms, consistent with the results obtained from the single-crystal X-ray structural analyses.

The UV–vis–NIR diffuse reflectance spectrum of Pb_4VBO_8 in the region 250–2600 nm is shown in Figure S6; SI.[27] It is clear that Pb_4VBO_8 has no obvious absorption in the range from 600 to 2600 nm, and the absorption sharply decreases below 600 nm and reaches zero at about 368 nm. This means that the UV cutoff edge for the Pb_4VBO_8 crystal is around 368 nm. The band structures of Pb_4VBO_8 along the high symmetry lines in the unit cell are shown in Figure S7; SI.[27] We can see that Pb_4VBO_8 is a indirect gap crystal with the gap $E_g = 2.939$ eV by the local density approximation (LDA) calculations.[26]

The first compound Pb_4VBO_8 in the $PbO–V_2O_5–B_2O_3$ ternary system has been synthesized. Single-crystal X-ray diffraction reveals that the basic units of Pb_4VBO_8 are PbO_4, PbO_5, VO_4, and BO_3. The Pb–O polyhedra and BO_3 triangles are connected by shared O atoms to form two-dimensional layers. The layers are connected by VO_4 to form a three-dimensional framework. IR spectrum is used to verify the validity of the structure. DTA measurement proves that Pb_4VBO_8 is an incongruent melting compound. The diffuse reflectance spectrum indicates that the UV cutoff edge for the Pb_4VBO_8 crystal is about 368 nm.

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27 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.