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Syntheses, crystal structures, and optical properties of $Pb_6B_3O_{10}X$ (X=F, Cl, Br)

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ABSTRACT

A series of lead-containing halogen oxyborates, $Pb_6B_3O_{10}X$ (X=F, Cl, Br), have been grown by high-temperature solution method and their crystal structures were determined by single-crystal X-ray diffraction. They are isostructural and crystallize in the space group *Pbcm* of the orthorhombic crystal system. The crystal structures are dominated by one-dimensional $_{\infty}[(Pb_4O)(BO_3)_3]$ "*Zig-Zag*"-chains, while the remaining Pb atoms and X (X=F, Cl, Br) atoms are filled to balance the charge. Compared with the previously reported compound $Pb_4O(BO_3)_2$ (the molecular formula $Pb_4O(BO_3)_2$ can be regarded as $Pb_6B_3O_{10.5}$) with the space group *Aba*2, the structures of $Pb_6B_3O_{10}X$ (X=F, Cl, Br) are completely different from that of $Pb_4O(BO_3)_2$. IR spectroscopy, UV–vis-NIR diffuse reflectance spectroscopy, thermal analysis, and theoretical calculations were also performed on the reported materials.

1. Introduction

Borate compounds have attracted extensive attention in the past decades because of the various anionic groups. Two bonding types between B and O atoms, the BO_3 triangle and the BO_4 tetrahedron in the borate class [1,2], may be further linked via corner-sharing [3,4] or edge-sharing [5,6] to form isolated rings and cages or condense into infinite chains, layers and networks [7–11]. Owing to the stereochemically active lone-pair effect in Pb^{2+} [12–18], extensive efforts are concentrated in the syntheses and characterizations of lead-containing borate materials, which have led to the discoveries of many new compounds with intriguing structures, such as PbB_4O_7 [19], $Pb_4O(BO_3)_2$ [20], $Pb_5B_3O_8(OH)_3H_2O$ [21], $Pb_6B_{11}O_{18}(OH)_9$ [22], $Pb_3B_9O_{16}(OH)B(OH)_3$ [23], $Pb_2B_5O_9(OH)H_2O$ [24], and $PbB_8O_{11}(OH)_4$ [25]. Metal halogen borates are of special interest because these materials have tunable electronic structures and diverse structural chemistry [26,27]. However, in the PbO–B_2O_3-PbX_2 (X=F, Cl, Br, I) system, to the best of our knowledge, only several lead-containing fluoride borates, Pb_2BO_3F [13], Pb_3OBO_3F [15], $Pb_8B_9O_{21}F$ [17], $Pb_4O[Pb_2(BO_3)_3Cl]$ [28] and the series of $Pb_2B_5O_9X$ (X=Cl, Br, I) compounds have been reported [29–32], which show attractive properties. Based on these results, the X (X=F, Cl, Br) atoms are expected to introduce into the $Pb_4O(BO_3)_2$ compound. Through the introduction of the X (X=F, Cl, Br) atoms as the partial substitutions of the O atoms into $Pb_4O(BO_3)_2$, a family of lead-containing halogen oxyborates, $Pb_6B_3O_{10}X$ (X=F, Cl, Br), has been synthesized successfully.

Here, we report a family of lead-containing halogen oxyborates, $Pb_6B_3O_{10}X$ (X=F, Cl, Br), in which isolated Pb_4O tetrahedra and BO_3 triangles are connected to form one-dimensional $_{\infty}[(Pb_4O)(BO_3)_3]$ "*Zig-Zag*"-chains and the remaining Pb and X (X=F, Cl, Br) atoms are filled to balance the charge. Because of the introduction of the X (X=F, Cl, Br) atoms as the partial substitutions of the O atoms in $Pb_4O(BO_3)_2$ (the molecular formula $Pb_4O(BO_3)_2$ can be regarded as $Pb_6B_3O_{10.5}$), the structures of $Pb_6B_3O_{10}X$ (X=F, Cl, Br) are completely different. $Pb_4O(BO_3)_2$ crystallizes in the space group *Aba*2, but $Pb_6B_3O_{10}X$ (X=F, Cl, Br) crystallize in the space group *Pbcm*. It should be noted that $Pb_6B_3O_{10}Cl$ was first synthesized by Behm [28], however, only crystal structure and IR spectrum were reported. In this paper, the syntheses, structures, and properties of $Pb_6B_3O_{10}X$ (X=F, Cl, Br) compounds are described in detail.

2. Experimental

2.1. Crystal growth

2.1.1. Caution

Hydrofluoric acid is toxic and corrosive and must be handled with extreme caution and the appropriate protective gear!

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If contact with the liquid or vapor occurs, proper treatment procedures should be followed immediately [33–36].

Single crystals of $Pb_6B_3O_{10}X$ (X=F, Cl, Br) were obtained by high temperature solution method.

2.1.2. $Pb_6B_3O_{10}F$

Reaction mixtures of 2.232 g of PbO (Tianjin Damao Chemical Industry Co., Ltd., 99.5%), 0.100 g of aqueous hydrofluoric acid (Tianjin Fuyu Chemical Industry Co., Ltd., 40% HF by weight), and 0.494 g of H_3BO_3 (Tianjin Hongyan Chemical Reagent Co., Ltd., 99.5%) (the $PbO/HF/H_3BO_3$ molar ratio is 5:1:4) were thoroughly ground in an agate mortar, and then transferred to a platinum crucible, which was placed in computer-controlled furnace under air. The furnace was gradually heated to 630 °C for 3 h, left for 12 h to ensure that the solution melt completely and homogeneously, cooled to 580 °C rapidly, and further to 540 °C at 1 °C/h, and followed by cooling to room temperature at a rate of 20 °C/h.

2.1.3. $Pb_6B_3O_{10}Cl$

Reaction mixtures of 2.455 g of PbO (Tianjin Damao Chemical Industry Co., Ltd., 99.5%), 0.278 g of $PbCl_2$ (Tianjin Shuangchuan Chemical Industry Co., Ltd., 99.5%), and 0.371 g of H_3BO_3 (Tianjin Hongyan Chemical Reagent Co., Ltd., 99.5%) (the $PbO/PbCl_2/H_3BO_3$ molar ratio is 11:1:6) were thoroughly ground in an agate mortar, and then transferred to a platinum crucible, which was placed in computer-controlled furnace under air. The furnace was gradually heated to 610 °C, where it was kept for 12 h, then cooled down to 570 °C rapidly, further to 530 °C at 1 °C/h and finally cooled to room temperature at a rate of 20 °C/h.

2.1.4. $Pb_6B_3O_{10}Br$

Reaction mixtures of 2.232 g of PbO (Tianjin Damao Chemical Industry Co., Ltd., 99.5%), 0.372 g of $PbBr_2$ (Aladdin Chemical Industry Co., Ltd., 99.0%), and 0.494 g of H_3BO_3 (Tianjin Hongyan Chemical Reagent Co., Ltd., 99.5%) (the $PbO/PbBr_2/H_3BO_3$ molar ratio is 10:1:8) were ground carefully to homogeneity in an agate mortar, and then transferred to a platinum crucible. The platinum crucible was put into a computer-controlled furnace under air, and then the furnace was heated up to 550 °C and kept at this temperature for 6 h. After then, the furnace was cooled rapidly down to 490 °C, and then slowly down to 430 °C at a rate of 1 °C/h, kept at a constant temperature, and then cooled down to room temperature at a rate of about 20 °C/h.

The crystals were manually selected for structural characterization and later determined as $Pb_6B_3O_{10}X$ (X=F, Cl, Br).

2.2. Solid-state synthesis

Polycrystalline samples of $Pb_6B_3O_{10}X$ (X=Cl, Br) were synthesized by solid-state reaction techniques. Stoichiometric mixture of PbO, $PbCl_2$, and H_3BO_3 were mixed thoroughly and then calcined at 475 °C with several intermediate grindings until a single-phase powder was obtained. The polycrystalline samples of $Pb_6B_3O_{10}Br$ were synthesized using stoichiometric mixture of PbO, $PbBr_2$, and H_3BO_3, which were mixed thoroughly and then calcined at 430 °C with several intermediate grindings until a single-phase powder was obtained. We failed to synthesize the $Pb_6B_3O_{10}F$ phase by solid-state reaction techniques owing to the stable phase of $Pb_4O(BO_3)_2$ although we tried to synthesize it by using excess H_3BO_3 or heating the sample for a longer time.

The resultant powder samples were analyzed by the powder X-ray diffraction technique which was performed at room temperature in the 2θ range from 10° to 70° with a scan step width of 0.02° and a fixed counting time of 1 s/step using a Bruker D2 PHASER diffractometer. Fig. S1 in the Supporting Information presents the calculated single-crystal data of $Pb_6B_3O_{10}X$ (X=F, Cl, Br), from which we can know that the peak positions are shifted to the lower angles from $Pb_6B_3O_{10}F$ to $Pb_6B_3O_{10}Br$. Fig. 1 presents the powder X-ray diffraction patterns of the polycrystalline samples, which are in good agreement with the calculated ones derived from the single-crystal data.

2.3. Structural determinations

The single-crystal X-ray diffraction measurements were performed on a Bruker Smart APEX II 4 K CCD diffractometer using monochromatic Mo-$K\alpha$ radiation (λ=0.71073 Å) at 296 (2) K and integrated with the *SAINT-Plus* program [37]. All refinements were completed with programs from the *SHELXTL-97* crystallographic software package [38]. The crystal structures of $Pb_6B_3O_{10}X$ (X=F, Cl, Br) were solved in space group *Pbcm* (No. 57) with initial heavy-atom positions, Pb and Br atoms, located by direct methods. The Cl, F, O, and B atoms were located by subsequent cycles of refinements and Fourier difference maps. The final full-matrix least-squares refinement was on F_o^2 with data having $F_o^2 \geq 2\sigma(F_o^2)$ and included anisotropic thermal parameters for all atoms. The structures were checked for missing symmetry elements with *PLATON* [39].

The crystal data and structure refinements for $Pb_6B_3O_{10}X$ (X=F, Cl, Br) are presented in Table 1. The final atomic coordinates with equivalent isotropic displacements and bond valence analysis for $Pb_6B_3O_{10}X$ (X=F, Cl, Br) are given in Table S1 and selected bond distances are in Table S2 in the Supporting Information [40,41].

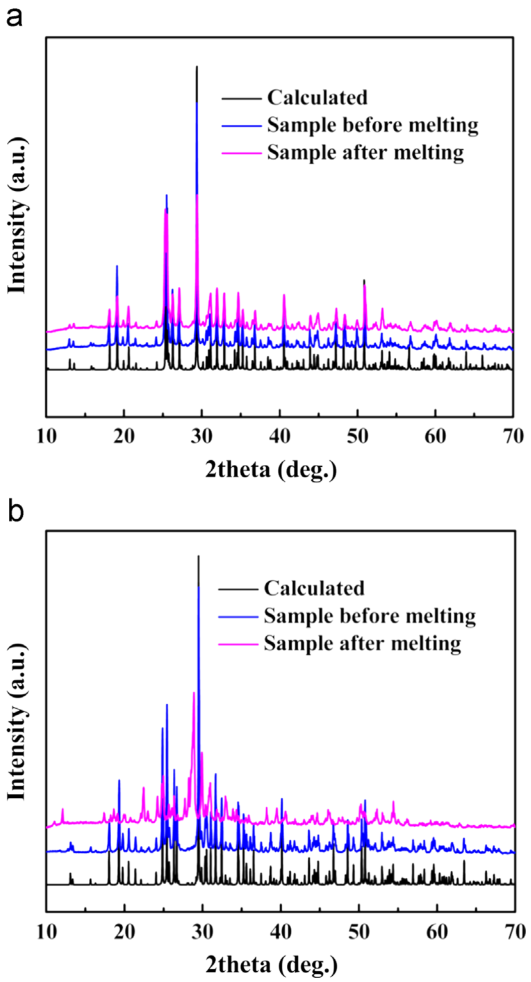

Fig. 1. X-ray diffraction patterns of (a) $Pb_6B_3O_{10}Cl$; and (b) $Pb_6B_3O_{10}Br$.