doi:10.1246/cl.2012.812

Synthesis, Crystal Structure, and Properties of a New Lead Barium Borate, $Pb_{1.13}Ba_{7.87}B_{18}O_{36}$

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A new compound, $Pb_{1.13}Ba_{7.87}B_{18}O_{36}$, has been synthesized by a solid-state reaction, and its structure was determined by single-crystal X-ray diffraction. It crystallizes in the noncentrosymmetric space group *R*32. The fundamental building units of $Pb_{1.13}Ba_{7.87}B_{18}O_{36}$ are the hexagonal B_3O_6 rings, which are parallel to the (001) plane and stack along the *c* axis. $Pb_{1.13}Ba_{7.87}B_{18}O_{36}$ exhibits a short-wavelength absorption onset at 210 nm. Functional groups present in the sample were identified by Fourier transform infrared spectrum.

The design and synthesis of nonlinear optical (NLO) materials[1–5] is one of the most interesting and challenging goals of the chemistry and materials science field. Borate crystals[6,7] are considered as perspective sources of NLO materials due to their excellent performance such as a wide transparency region, high laser damage tolerance, good thermal stability, and other useful properties for technical applications.[8–11]

To tune the final structure and increase the probability of NLO, some structure units are considered. For example, compounds with BO_3^{3-}, $B_3O_6^{3-}$, and $B_3O_7^{5-}$ groups are viewed as the most promising NLO materials for ultraviolet generation.[12] The d^0 transition metals (Ti^{4+}, Nb^{5+}, Mo^{6+}, and W^{6+}) and cations with stereoactive lone pairs (Se^{4+}, Pb^{2+}, and Te^{4+}), which are susceptible to second-order Jahn–Teller (SOJT) distortions, favor the large NLO response.[12–15]

We, therefore, turn our attention to the PbO–BaO–B_2O_3 ternary system. Ba and Pb have a close ion radius. This means that some materials can be obtained by the substitution of Ba atoms by Pb atoms in β-BaB_2O_4. Specifically, the Pb^{2+} cations with lone pairs promote the formation of noncentrosymmetric (NCS) structural motifs. In doing so, we have synthesized a new NCS compound, $Pb_{1.13}Ba_{7.87}B_{18}O_{36}$ and report its synthesis and structural and functional properties.

Polycrystalline samples of $Pb_{1.13}Ba_{7.87}B_{18}O_{36}$ were synthesized by traditional solid-state reaction technique with a stoichiometric mixture of PbO, $BaCO_3$, and H_3BO_3 powders. The mixtures were heated in air to 500 °C for 12 h. Afterwards, the sample was heated to 800 °C for 12 h with some intermittent regrindings, followed by allowing to cool to room temperature by switching off heating. The purity of sample was checked by powder X-ray diffraction (PXRD) (Figure S1 in the Supporting Information).[24] The experimental powder pattern tallies well with the theoretical patterns of the compound, simulated from single-crystal data.

Single crystals of $Pb_{1.13}Ba_{7.87}B_{18}O_{36}$ were grown by melting a mixture of BaF_2, PbO, and H_3BO_3 with 1:1:4 molar ratios at 850 °C in a platinum crucible. The crucible, which was placed in the center of a vertical temperature-programmable furnace, was heated to 850 °C in 2 h and held at this temperature for 20 h. The melt was cooled down to the initial crystallization temperature in 30 min, a platinum wire with a diameter of 0.5 mm was promptly dipped into the melt, then the platinum wire was pulled out from the melt when the temperature was decreased to 750 °C at a rate of $5\,°C\,h^{-1}$, and then allowed to cool to room temperature at a rate of $30\,°C\,h^{-1}$. The colorless and water-resistant crystal platelets of $Pb_{1.13}Ba_{7.87}B_{18}O_{36}$ were obtained. The crystal data and structure refinement for $Pb_{1.13}Ba_{7.87}B_{18}O_{36}$ are presented in Table S1 in the Supporting Information.[24] The final atomic coordinates with equivalent isotropic displacements for $Pb_{1.13}Ba_{7.87}B_{18}O_{36}$ are shown in Table S2 in the Supporting Information.[24] The structure disorder was observed for the Ba2 disordered with Pb in the structure. Selected bond distances and angles are illustrated in Table S3 in the Supporting Information.[24]

The single-crystal $Pb_{1.13}Ba_{7.87}B_{18}O_{36}$ belongs to the *R*32 space group. The structure is built up of BaO_9, Ba/PbO_6, and isolated B_3O_6 rings. The $(Ba2,Pb)O_6$ sites consist of about 62.3% Ba2 and 33.7% Pb. The plane hexagonal ring B_3O_6 sheets stack along the [001] direction, BaO_9 and $(Ba,Pb)O_6$ polyhedra alternately situate between the B_3O_6 sheets (Figure 1). The fundamental building unit, B_3O_6 rings consist of three BO_3 triangles. The B–O bond lengths vary from 1.272(19) to 1.486(18) Å, and the O–B–O angles are between 111.3(16) and 131(2)°. These values are normal in a BO_3 plane triangle.

In the structure, the bond distances are identical (2.601 Å) in the $(Ba2,Pb)O_6$ octahedron. For the Ba1 site, the Ba atoms are surrounded by nine O atoms (Figure S2 in the Supporting Information),[24] bond lengths range from 2.734(11) to 3.062(19) Å, and the average bond distance of Ba1–O is 2.860 Å.

As $Pb_{1.13}Ba_{7.87}B_{18}O_{36}$ crystallizes in NCS space group, powder second-harmonic generation (SHG) response was measured using the Kurtz–Perry experimental method.[16] We determined that $Pb_{1.13}Ba_{7.87}B_{18}O_{36}$ has a weak SHG response about 0.3 times of KH_2PO_4 (KDP).

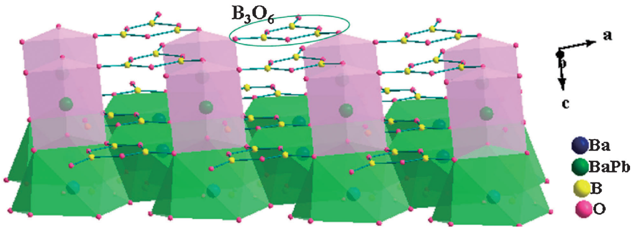

Figure 1. Structure of $Pb_{1.13}Ba_{7.87}B_{18}O_{36}$ along the [010] direction. The fundamental building unit B_3O_6 is indicated. $(Ba,Pb)O_6$ polyhedra are pink and BaO_9 polyhedra are green.

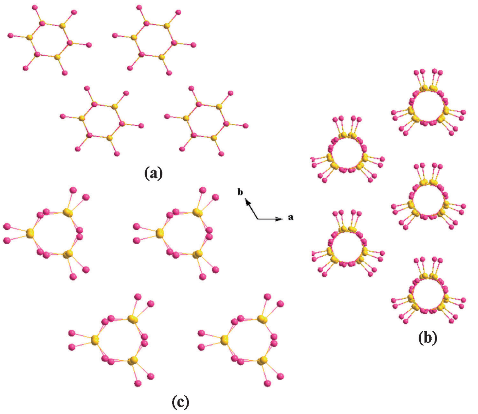

Figure 2. The arrangement of B_3O_6 groups along the [001] direction (yellow, B; pink, O). (a) In α-BaB_2O_4, (b) in β-BaB_2O_4, and (c) in $Pb_{1.13}Ba_{7.87}B_{18}O_{36}$.

Comparing the structures $Pb_{1.13}Ba_{7.87}B_{18}O_{36}$ with α-BaB_2O_4[17] and β-BaB_2O_4,[18] we found that the three compounds all stack in a three-dimensional layer-like structure along the [001] direction with basic units of plane B_3O_6 groups. According to the previous study, B_3O_6 group can yield large SHG response,[19] but the arrangement of B_3O_6 groups in the compounds leads to different SHG effect. In α-BaB_2O_4, there is one type of B atom. The planar B_3O_6 rings are parallel to each other, and the rings in the neighborhood layers point in exactly opposite directions (Figure 2a). In β-BaB_2O_4, there are four types of B atoms. All the B_3O_6 rings are parallel to the (001) plane, and in different layers the B_3O_6 rings rotate a little (Figure 2b), which contributes to large SHG effect. In $Pb_{1.13}Ba_{7.87}B_{18}O_{36}$, the (Ba2,Pb) is bonded with six O atoms to form the octahedron, the bond distances within the octahedron are identical (2.601 Å), which are shorter than that of α-BaB_2O_4 (2.671 Å). The coordination behaviors of the counter cations can affect the alignment of the basic unit B_3O_6.[20] So, in $Pb_{1.13}Ba_{7.87}B_{18}O_{36}$, the B_3O_6 rings in two neighborhood layers are chiral fold (Figure 2c). The arrangement leads to the weak SHG effect.

The IR absorption spectrum was recorded to confirm the coordination of boron in the $Pb_{1.13}Ba_{7.87}B_{18}O_{36}$ structure (Figure S3 in the Supporting Information).[24] According to previous work,[21,22] the peaks at 1409, 1240, and 954 cm^{-1} can be attributed to stretching vibrations of BO_3 groups. The band at 729 cm^{-1} is due to bending of B–O–B linkage in the borate network, and the band observed at 630 cm^{-1} is due to bending of O–B–O linkage,[23] which suggest that boroxol B_3O_6 ring exists. The band at 480 cm^{-1} characterizes the bending modes of triangular BO_3 groups, which is consistent with the results obtained from the single-crystal X-ray structural analyses.

The UV–vis–NIR diffuse reflectance spectrum is shown in Figure 3. Clearly, a wide transmission range is observed with UV cutoff edge at about 210 nm. No obvious absorption peak in the range of 400–2600 nm was observed, indicating that the crystal may have potential use in the UV region.

A new borate compound, $Pb_{1.13}Ba_{7.87}B_{18}O_{36}$ containing B_3O_6 building blocks was synthesized by conventional solid-state reaction. The crystal was obtained by high-temperature-solution method using PbO–BaF_2 flux system. The three-dimensional network consists of isolated B_3O_6 blocks connected by (Ba,Pb)O_6 and BaO_9 polyhedra. The structural disorder is observed for the Ba2 atoms which are disordered with Pb atoms. The UV–vis–NIR diffuse reflectance spectroscopy indicates that it has a wide transparent region with the short-wavelength cutoff edge about 210 nm.

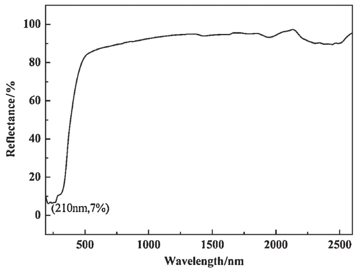

Figure 3. UV–vis–NIR diffuse reflectance spectrum of $Pb_{1.13}Ba_{7.87}B_{18}O_{36}$.

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