Crystal structure, site selectivity, and electronic structure of layered chalcogenide LaOBiPbS$_3$

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Abstract – We have investigated the crystal structure of LaOBiPbS$_3$ using neutron diffraction and synchrotron X-ray diffraction. From structural refinements, we found that the two metal sites, occupied by Bi and Pb, were differently surrounded by the sulfur atoms. Calculated bond valence sum suggested that one metal site was nearly trivalent and the other was nearly divalent. Neutron diffraction also revealed site selectivity of Bi and Pb in the LaOBiPbS$_3$ structure. These results suggested that the crystal structure of LaOBiPbS$_3$ can be regarded as alternate stacks of the rock-salt–type Pb-rich sulfide layers and the LaOBiS$_2$-type Bi-rich layers. From band calculations for an ideal (LaOBiS$_2$)(PbS) system, we found that the S bands of the PbS layer were hybridized with the Bi bands of the BiS plane at around the Fermi energy, which resulted in the electronic characteristics different from that of LaOBiS$_2$. Stacking the rock-salt type sulfide (chalcogenide) layers and the BiS$_2$-based layered structure could be a new strategy to exploration of new BiS$_2$-based layered compounds, exotic two-dimensional electronic states, or novel functionality.

Designing a new layered structure is one of the strategies for creating functional materials because low-dimensional electronic states could be generated, and the electronic states could be easily tuned by altering stacking layer types. Among them, BiS$_2$-based compounds, whose crystal structure is composed of alternate stacks of an electrically conducting BiS$_2$ bilayer and various kinds of insulating layers (blocking layers), have recently drawn much attention as superconductors [1–11] and thermoelectric materials [12–16]. As for the Cu-oxide and Fe-based high-transition-temperature (high-$T_c$) superconductors [17,18], the superconducting properties and the thermoelectric performance of the BiS$_2$-based compounds, such as RE(O,F)BiS$_2$ (RE: rare earth), can be enhanced by replacing the elements at the blocking layer [19,20] and/or the conducting BiS$_2$ layers [21–24], which modifies the electronic states and local crystal structure [25–30]. As to the strategies for designing new BiS$_2$-based compounds, explorations of new blocking layer structure or new types of conducting layers have been used, so far. Since the BiS$_2$-based compounds have a layered structure with van der Waals gap, making a stacking structure with ions or molecule layers, like intercalation, should be another strategy for creating new compounds with notable functions, such as FeSe-based compounds, TNCI-based compounds ($T$ = Hf, Zr), and Bi$_2$Se$_3$ [31–35].

In this study, we have focused on a layered chalcogenide LaOBiPbS$_3$, which was firstly reported by Sun et al. in 2014 [15]. According to the previous report, the conducting layer is composed of rock-salt–type M$_4$S$_6$ layers with $M$ = Bi and Pb; the M sites are randomly occupied by Bi and Pb. However, with synchrotron X-ray diffraction
Fig. 1: (Colour online) Schematic images of the relationship of the crystal structure between PbS (rock-salt–type cubic), REOBiS$_2$ (tetragonal), and LaOBiPbS$_3$.

Fig. 2: (Colour online) Neutron diffraction pattern and refinement results for the LaOBiPbS$_3$ sample.

data, we noted that the bond lengths of M1-S and M2-S are apparently different in LaOBiPbS$_3$ (see fig. 1 for the definitions of the M1 and M2 sites), which would indicate that the crystal structure of the M$_4$S$_6$ layer is not simple as described in ref. [15]. Therefore, we have analyzed the crystal structure of LaOBiPbS$_3$ using neutron diffraction and synchrotron X-ray diffraction because neutron diffraction is more sensitive to the Bi and Pb occupancy. The structural refinements revealed site selectivity of Bi and Pb in the LaOBiPbS$_3$ structure. The Bi and Pb atoms preferably occupy the M1 and M2 sites, respectively. These results suggest that the crystal structure of LaOBiPbS$_3$ can be regarded as the alternate stacks of the rock-salt–type PbS-type layers and the LaOBiS$_2$-type layers, as shown in fig. 1. Insertion of rock-salt–type chalcogenide layers into the van der Waals gap of LaOBiS$_2$ could be a new strategy for the exploration of new BiS$_2$-based layered materials, exotic electronic states, or novel functionality.

The LaOBiPbS$_3$ polycrystalline samples were prepared by the solid-state reaction method. The La$_2$O$_3$ (99.9%), La$_2$S$_3$ (99.9%), Bi$_2$S$_3$, and PbS (99.9%) powders were mixed, pelletedized, sealed into an evacuated quartz tube, and heated at 940 K for 25 hours. The obtained sample was ground, mixed to homogenize, pelletedized, and heated at 1020 K for 25 hours. The phase purity of the prepared pellets was examined using laboratory X-ray diffraction (XRD) with Cu-$\text{K}_\alpha$ radiation. The neutron diffraction experiment was performed at room temperature using a time-of-flight–type super-high-resolution powder diffractometer (SuperHRPD) [36–38] of the Japan Proton Accelerator Research Complex (J-PARC). The powder sample was installed into a vanadium-nickel cell. We used the Z-Rietveld software [38] to perform the Rietveld analysis. Synchrotron X-ray diffraction (SXRD) was performed at BL02B2 of SPring-8 with energy of 25 keV (project No. 2016B0074). The synchrotron XRD experiments were performed with a sample rotator system at room temperature, and the diffraction data were collected using a high-resolution one-dimensional semiconductor detector MYTHEN [39] with a step of 2$\theta = 0.006^\circ$. The crystal structure parameters were refined using the Rietveld method with RIETAN-FP [40]. Schematic images of the crystal structure were drawn using VESTA [41].
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Fig. 3: (Colour online) SXRD pattern and the result of the Rietveld analysis for the LaOBiPbS₃ sample. The Rietveld analysis was performed by multi-phase refinement with the La₂O₂S and PbS impurity phases. The inset shows an enlarged profile at higher angles.

Table 1: Crystal structure parameters for LaOBiPbS₃ obtained from neutron diffraction and synchrotron X-ray diffraction (SXRD).

| Site | Occupancy (neutron) | x  | y  | z (neutron) | z(SXRD) | U (neutron) (Å²) | U (SXRD) (Å²) |
|------|---------------------|----|----|-------------|---------|------------------|----------------|
| La   | 1                   | 0  | 0.5| 0.06184(3)  | 0.06184(9)| 0.0014(2)       | 0.0029(5)     |
| O    | 1                   | 0  | 0  | 0           | 0       | 0.0083(2)       | 0.013(3)      |
| M1   | Bi₀.89(2)Pb₀.11(2)  | 0.5| 0  | 0.57638(3)  | 0.57681(7)| 0.0104(2)       | 0.0115(4)     |
| M2   | Bi₀.11(3)Pb₀.89(3)  | 0.5| 0  | 0.25805(4)  | 0.25784(8)| 0.0077(2)       | 0.0126(4)     |
| S1   | 1                   | 0.5| 0  | 0.72980(9)  | 0.7293(4)| 0.0093(5)       | 0.010(2)      |
| S2   | 1                   | 0.5| 0  | 0.4290(1)   | 0.4281(4)| 0.0059(5)       | 0.012(2)      |
| S3   | 1                   | 0.5| 0  | 0.1342(1)   | 0.1349(4)| 0.0067(4)       | 0.017(2)      |

Figure 2 displays the neutron diffraction pattern and the Rietveld refinement results for the LaOBiPbS₃ sample. The obtained pattern could be refined using the structural model with the tetragonal P4/nmm space group (No. 129) with small impurities of La₂O₂S and PbS. The refined lattice constants were \( a = 4.09676(1) \) Å and \( c = 19.7996(6) \) Å. Assuming that the concentrations of Bi and Pb in LaOBiPbS₃ are the same, the refined occupancies of Bi for M1 and M2 were converged with 0.89 and 0.11, respectively: Bi:Pb = 89(2) : 11(2) for M1 and Bi:Pb = 11(3) : 89(3) for M2 are obtained. The final reliability factor \( R_{wp} \) was 5.16%. The refinement with the random model, in which the M1 and M2 sites had a fixed occupancy of Bi:Pb = 50 : 50, resulted in slightly higher reliability factor: \( R_{wp} = 5.19\% \). Indeed, the M1 site is selectively occupied by Bi, while the M2 site is selectively occupied by Pb in LaOBiPbS₃.

Figure 3 shows the SXRD pattern and the Rietveld refinement result for the LaOBiPbS₃ sample. The obtained pattern was refined using a structural model with the tetragonal P4/nmm space group, too. Impurity phases of La₂O₂S (11%) and PbS (7%) were detected, where the impurity ratio is the mole ratio. The refined lattice constants were \( a = 4.09717(4) \) Å and \( c = 19.7933(2) \) Å. The reliability factor \( R_{wp} \) was 7.5%. Note that the occupancies for M1 and M2 were fixed as the values obtained from neutron diffraction in the final Rietveld refinement of the SXRD pattern presented in fig. 3. The refined lattice constants and atomic positions were close to those determined by neutron diffraction. The crystal structure parameters obtained from neutron diffraction and SXRD were listed in table 1. In table 2, the typical bond lengths and the bond angles around the M1 and M2 sites are

Table 2: Typical bond lengths and angles of LaOBiPbS₃ determined from SXRD analysis.

|          | M1-S1 | M1-S2 | M1-S3 | M2-S1 | M2-S3 (in-plane) | M2-S3 (c-axis) | S1-M1-S1 angle | S3-M2-S3 angle |
|----------|-------|-------|-------|-------|------------------|----------------|----------------|----------------|
| M1-S1    | 2.9083(8) Å | 2.433(9) Å | 3.370(9) Å | 3.018(9) Å | 2.8988(3) Å     | 2.943(9) Å     | 170.0(3)°      | 176.2(3)°      |
| M1-S2    |       |       |       |       |                  |                |                |                |
| M1-S3    |       |       |       |       |                  |                |                |                |
| M2-S1    |       |       |       |       |                  |                |                |                |
| M2-S3    |       |       |       |       |                  |                |                |                |
From the refined bond lengths, we calculated the bond valence sum (BVS) for the M1 and M2 sites as 3.17 and 2.19, respectively. The BVS is calculated from
\[ \text{BVS} = \sum_{i=1}^{n} \exp\left(\frac{r_0 - r_{i0}}{a}\right), \]
where \( r_0, r_{i0}, \) and \( n \) are the parameter for the bond, the bond distance (available at the database of International Union of Crystallography), and the number of nearest bonds, respectively. These values of the bond valence sum also suggest that the M1 and M2 sites are selectively occupied by Bi\(^{3+}\) and Pb\(^{2+}\), respectively, which is consistent with what obtained from neutron diffraction.

To visualize the refined structure, the typical bond lengths and bond angles are displayed with a crystal structure image of LaOBiPbS\(_3\) in fig. 4. The M1 site is surrounded by S1 and S2, forming Bi-rich M1S\(_5\) pyramids, in which M1 and S2 locate at the bottom center and the apical position, respectively. The Bi-rich M1S\(_5\) pyramid structure is quite similar to that in LaOBiS\(_2\)\[30\]: shorter M1-S2 bonds and longer M1-S1 bonds form the pyramid. The M2-S3 bonding forms rock-salt–like layers. As shown in fig. 4, the in-plane M2-S3 bond length and the M2-S3 bond length along the c-axis direction are 2.8987 and 2.9443 Å, respectively. From the almost isotropic bonding in the M2-S3 layers, the structure can be regarded as a distorted rock-salt structure. In fact, the bond length of Pb-S in rock-salt–type PbS is 2.989 Å \[42\], which is close to the M2-S3 lengths in LaOBiPbS\(_3\). From these structural characteristics, the structure of LaOBiPbS\(_3\) can be described as Bi-rich LaOM1S\(_2\) sandwiched by a Pb-rich M2S layer. The in-plane (M1-S1) bond length in LaOBiPbS\(_3\) is slightly longer than the in-plane Bi-S1 distance in LaOBiS\(_2\), which can be explained by the misfit between Bi-rich M1-S1 and Pb-rich M2-S2.

![Fig. 4: (Colour online) Schematic image of LaOBiPbS\(_3\) with the typical bond lengths and angles determined from the structural refinements. M1 is a Bi-rich site, while M2 is a Pb-rich one.](image)

On the basis of the refined crystal structure of LaOBiPbS\(_3\), we proposed that the crystal structure of LaOBiPbS\(_3\) could be regarded as the alternate stacks of PbS-type (rock-salt–type) and LaOBiS\(_2\)-type layers, as shown in fig. 1. Insertion of rock-salt–type sulfide layers into the BiS\(_2\)-type layered structures, should be a concept useful for designing new BiS\(_2\)-based superconductors, thermoelectric materials, and functional materials. Since there are many kinds of BiS\(_2\)-based compounds with various types of blocking layers, the material design concept presented here will expand the playground of chemistry and physics of BiS\(_2\)-based functional materials.

To understand the effects of the insertion of PbS-type layers into the LaOBiS\(_2\)-type layers on the electronic states, we have calculated the band structure of the ideal LaOBiPbS\(_3\) structure with 100% occupancy (complete site selectivity) of Pb at the M2 site, such as (LaOBiS\(_2\))(PbS).

Figure 5 presents the first-principles band structure and the (partial) density of states calculated with the WIEN2k code \[43\] using the Perdew-Burke-Ernzerhof parametrization of the generalized gradient approximation (GGA-PBE) \[44\]. We found that the S bands of the PbS layers are hybridized with the Bi bands of the BiS plane around the Fermi energy. The band edge of the Pb bands and the S bands of the BiS plane near the \( X \)-point are located at around 1.2 eV above and 1 eV below the Fermi energy, respectively. The calculated electronic structure with density of states at the Fermi energy looks quite different from LaOBiS\(_2\), although it is not decisive whether LaOBiPbS\(_3\) (with 100% occupancy of Pb at the M2 site) is metallic since the GGA-PBE approximation is known to underestimate the band gap. We expect, however, a tunable band structure by the insertion of various kinds of chalcogenide layers, like PbS into the van der Waals gap of the BiS\(_2\)-based compounds. Thus, stacking the rock-salt–type sulfide (chalcogenide) layers and the BiS\(_2\)-based layered structure should be a new strategy of band engineering for designing new BiS\(_2\)-based layered superconductors, thermoelectric materials, or novel functional materials.

![Fig. 5: (Colour online) (a) Band structure and (b) partial density of states for LaOBiPbS\(_3\) with the ideal structure (M1 = Bi, M2 = Pb).](image)
To induce superconductivity or high thermoelectric performance, the introduction of a carrier is expected. Based on the introduction of superconductivity in Bi$_2$S$_3$-based systems, electron doping into the conduction band seems to be needed [20]. In addition, Se substitution for the S site will be useful to enhance the carrier mobility, which is needed to enhance the thermoelectric performance in the Bi$_2$S$_3$-based systems [45]. Based on these backgrounds, we have synthesized some samples with F substitution for the O site, Se substitution for the S site, or RE substitution (RE = Ce, Pr, Nd) for the La site of LaOBiPbS$_3$. However, only solubility limits for these partial substitutions were found to be less than 10%, on the basis of our investigation so far. Therefore, another technique or replacement of blocking or conduction layers should be needed to effectively manipulate carrier concentration or carrier mobility by element substitutions.

In conclusion, the crystal structure of LaOBiPbS$_3$ has been examined using neutron powder diffraction and powder synchrotron X-ray diffraction. The structural refinements revealed that two metal sites, the M1 and M2 sites, were differently surrounded by sulfur atoms. Furthermore, we found the site selectivity of Bi and Pb in the LaOBiPbS$_3$ structure. The structural characteristics around the M1 and the M2 sites are close to those of the bi site of LaOBiS$_2$ and those of the M2 site are close to those of the Pb site of rock-salt-type PbS, respectively. These results suggested that the crystal structure of LaOBiPbS$_3$ can be regarded as alternate stacks of the Pb-rich PbS-type layers and the Bi-rich LaOBiS$_2$-type layers. From band calculations for an ideal (LaOBiS$_2$)(PbS) system, we found that the S bands of the PbS layer are hybridized with the Bi bands of the BiS plane at around the Fermi energy, which results in the electronic characteristics different from those of LaOBiS$_2$. Thus, stacking the rock-salt-type sulfide (chalcogenide) layers and the Bi$_2$S$_3$-based layered structure can largely modify the electronic structure and should be a new strategy of band engineering for designing new Bi$_2$S$_3$-based layered superconductors, thermoelectric materials, or novel functional materials.

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