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<th>Title</th>
<th>Structural Difference in Superconductive and Nonsuperconductive Bi–S Planes within Bi$_4$O$_4$Bi$_2$S$_4$ Blocks</th>
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<td>Author(s)</td>
<td>Miura, Akira; Mizuguchi, Yoshikazu; Sugawara, Tsuyoshi; Wang, Yongming; Takei, Takahiro; Kumada, Nobuhiro; Magome, Eisuke; Moriyoshi, Chikako; Kuroiwa, Yoshihiro; Miura, Osuke; Tadanaga, Kiyoharu</td>
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ABSTRACT: The relationship between the structure and superconductivity of Bi$_4$O$_3$S$_3$ powders synthesized by heating under ambient and high pressures was investigated using synchrotron X-ray diffraction, Raman spectroscopy and TEM observation. The Bi$_4$O$_3$S$_3$ powders synthesized under ambient pressure exhibited a strong superconductivity (diamagnetic) signal and zero resistivity below ~4.5 K, while the Bi$_4$O$_3$S$_3$ powder synthesized by the high-pressure method exhibited a low intensity signal down to 2 K. Further annealing of the latter Bi$_4$O$_3$S$_3$ powder under ambient pressure led to the development of a strong signal and zero resistivity. The crystal structures of all Bi$_4$O$_3$S$_3$ phases consisted of Bi$_2$O$_2$BiS$_3$ blocks including Bi–S layer and anion(s) sandwiched between Bi$_2$O$_2$BiS$_3$ blocks, but minor structural differences were detected. Comparison of the structure of the superconductive and non-superconductive Bi$_4$O$_3$S$_3$ samples suggested that the superconductive Bi$_4$O$_3$S$_3$ phases had slightly smaller lattice parameters. The average structures of the superconductive Bi$_4$O$_3$S$_3$ phases were characterized by a slightly shorter and less bent Bi–S plane. Raman spectrum detected vibration of S–O bonds, which can be attributed to sandwiched anion(s) such as SO$_2$. TEM observation showed stacking faults in the superconductive Bi$_4$O$_3$S$_3$ phases, which indicated local fluctuation of the average structures. The observed superconductivity of Bi$_4$O$_3$S$_3$ was discussed based on impurity phases, enhanced hybridization of the p$_x$ and p$_y$ orbitals of the Bi–S plane within Bi$_2$O$_2$BiS$_3$ blocks, local fluctuation of the average structures, compositional deviation related to suspicious anion(s) sandwiched between Bi$_2$O$_2$BiS$_3$ blocks, and the possibility of the suppression of the charge-density-wave state by enriched carrier concentrations.

Introduction

Superconductive materials are widely used in various areas such as medical diagnostics and energy transport. Superconductors require a large energy input for cooling to temperatures below the transition temperature. Thus, the development of new superconductors and understanding their mechanism of operation have remained challenging issues since the discovery of superconductivity. In 1986, copper-based layered oxides were found to be superconductors, and in 2008, iron-based layered pnictides were discovered as superconductors. In 2012, Bi$_2$O$_3$S$_3$ was reported as a new layered superconductor with $T_c$ ~ 5 K. Thereafter, a number of structurally-related layered Bi$_2$S$_3$ superconductors were reported, such as Bi$_2$(O,F)BiS$_3$, Ln(O,F)BiS$_3$ (Ln=La)FBiS$_3$, Ln(O,F)BiSe$_3$, and Eu$_2$Bi$_2$Se$_4$. These Bi$_2$S$_3$ compounds have been recognized as a new class of layered Bi$_2$S$_3$ superconductors with $T_c$ values of up to ~10 K. The compositional and structural diversity demonstrates the potential to further increase the transition temperature of Bi$_2$S superconductors and also provides a key for understanding the mechanism underlying superconductivity.

Bi$_2$O$_3$S$_3$ is the first-discovered Bi$_2$S$_3$ superconductor, and its superconductivity is considered to be related to the hybridized p$_x$ and p$_y$ orbitals between Bi and S. Bi$_2$O$_3$S$_3$ can also be described as Bi$_2$O$_2$BiS$_3$(SO$_4$)$_2$ (x = 0.5), in which sulfate anions are sandwiched by Bi$_2$O$_2$BiS$_3$ blocks (Fig. 1). Different groups confirmed the superconductivity of this material via transport, magnetic, specific heat, and muon-spin-spectroscopy measurements. However, the impurities and structure of Bi$_2$O$_3$S$_3$ remain controversial. The reported X-ray diffraction patterns of Bi$_2$O$_3$S$_3$ powder samples invariably show impurity peaks, and single crystals of Bi$_2$O$_3$S$_3$ have not been successfully synthesized. Similar compounds, such as Bi$_2$O$_3$S$_3$ and Bi$_2$O$_3$S$_3$, were recently reported; these are possibly coexisting impurity phases of Bi$_2$O$_3$S$_3$. Phelan et al. suggested that the stacking faults of Bi$_2$O$_3$S$_3$ could lead to more complicated compounds: Bi$_2$O$_2$BiS$_3$(SO$_4$)$_2$ (x = 0.5). Sathish et al. characterized Bi$_2$O$_3$S$_3$ samples synthesized through ambient-pressure and high-pressure methods by analysis of the X-Ray diffraction, magnetic, and transport properties. They reported that the superconductivity of Bi$_2$O$_3$S$_3$ samples was plausibly attributed to an impurity phase(s), though they found minor structural difference between the Bi$_2$O$_3$S$_3$ phases synthesized under ambient and high pressure. Thus, the question of which crystal structures or impurities induce the superconductivity of Bi$_2$O$_3$S$_3$ samples remains open. Although structural analysis based on laboratory XRD have been performed, synchrotron X-ray diffraction is a powerful tool for
addressing this question since this technique can detect small amounts of impurity phase(s) and provides more reliable structural information. Further, TEM observation furnishes information about the local structure, such as stacking faults in layered structures, and Raman spectroscopy revealed the information of sandwiched anion(s).

In this paper, we examine the structures and impurities in Bi$_2$O$_3$S$_3$ samples synthesized via ambient- and high-pressure methods in order to reveal the correlation between crystal structure and superconductive properties of the first-discovered BiS$_2$ superconductor. Synchrotron X-ray diffraction, TEM and Raman analyses provide detailed information about the structure and impurities of Bi$_2$O$_3$S$_3$, and reveal that minor structural changes in the Bi–S layer within Bi$_2$O$_3$BiS$_2$ blocks are correlated to the superconductive properties.

**Experimental**

Three approaches were employed for synthesis of Bi$_2$O$_3$S$_3$ from BiS$_3$, Bi$_2$O$_3$, and S powders using the stoichiometric ratio. The first synthesis was performed in an evacuated quartz tube under ambient pressure at 510 °C, as described in a previous report; the sample thus-obtained is denoted AP Bi$_2$O$_3$S$_3$. The second was a high-pressure method using a cubic-anvil high-pressure apparatus with a 180 ton press operated at 700 °C/3 GPa for 1 h (sample HP Bi$_2$O$_3$S$_3$). The third method involved further annealing of HP Bi$_2$O$_3$S$_3$ in an evacuated quartz tube under ambient pressure at 510 °C (sample HP-AP Bi$_2$O$_3$S$_3$). Synchrotron X-ray powder diffraction measurements were performed at room temperature at the BL02B2 experimental station of SPring-8 (JASRI; Proposal Nos. 2014B1003, 2014B1071, and 2015A1441). The wavelength of the radiation beam was 0.49542(8) Å. Structural refinement was performed using RIETAN-FP and Dysnomia, and crystal structures were drawn with VESTA. Vibration of the S-O bonds was evaluated via Raman microscopy. The local structure was examined via transmission electron microscopy (TEM). The temperature dependence of resistivity was measured by four-terminal method. The magnetic susceptibility was measured by using a superconducting quantum interference device (SQUID) magnetometer with a magnetic field of ~ 4.5 Oe after zero-field cooling.

**Results**

Figure 2 shows the synchrotron XRD profiles of the three Bi$_2$O$_3$S$_3$ powders: AP, HP, and HP-AP. Table 1 exhibits the summary of the analysis. For all samples, the main phases were indexed as tetragonal phases with long c-axes. The large lattice parameters were indcited by the peaks around 1.38 Å (d ~ 20.7 Å), which were indexed as the 002 peak of the tetragonal Bi$_2$O$_3$S$_3$ phase (Figure S1). The calculated mass fractions of the Bi$_2$O$_3$S$_3$ phase were 82.6, 89.6, and 93.1 % for AP, HP, and AP-HP Bi$_2$O$_3$S$_3$, respectively (Table 1). Bi and Bi$_2$S$_3$ impurities were also found. Approximately 3 mass% of the Bi$_2$O$_3$S$_3$ phase appeared only in Bi$_2$O$_3$S$_3$ (AP); a weak peak appeared at 2.06 Å (d ~ 13.8 Å) and was indexed as the 001 peak of the Bi$_2$O$_3$S$_3$ phase (Figure S1). The lattice parameters of the AP Bi$_2$O$_3$S$_3$ and HP-AP Bi$_2$O$_3$S$_3$ phases were slightly shorter than that found in HP Bi$_2$O$_3$S$_3$ (AP: a = 3.96398(5) Å, c = 41.2907(7) Å, HP: a = 3.99610(8) Å, c = 41.5046(11) Å, HP-AP: a = 3.96228(3) Å, c = 41.26192(4) Å).

**Table 1. Summary of Rietveld refinements of AP Bi$_2$O$_3$S$_3$, HP Bi$_2$O$_3$S$_3$, and HP-AP Bi$_2$O$_3$S$_3$ powders**

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**FIGURE 1. Crystal structure of Bi$_2$O$_3$S$_3$.** Right schemes are structures of BiS$_2$ layers in Bi$_2$O$_3$S$_3$: AP: synthesized in a quartz tube at 510 °C; HP: at 700 °C/3 GPa, and HP-AP: with subsequent annealing at 510 °C. Unit cell is marked by dotted lines.
As mentioned, Bi$_4$O$_2$S$_3$ can be described as Bi$_4$O$_2$Bi$_2$S$_3$ blocks with sandwiched (SO)$_2$; the value of r is 0.5 for Bi$_4$O$_2$S$_3$. The Rietveld refinements for the Bi$_4$O$_2$Bi$_2$S$_3$ blocks were straightforward and robust. No or small amounts of vacancies were found in the Bi$_4$O$_2$Bi$_2$S$_3$ blocks for all samples; thus, further refinements were performed with full occupations. We focus on the coordination of Bi(2) and the S(2) plane, which is considered as a superconductivity plane. The Bi(2)–S(2) bond found in AP and HP-AP is slightly shorter than that in HP (AP: 2.8121(8) Å, HP: 2.8240(10) Å, HP-AP: 2.8096(7) Å) and the S(2)–Bi(2)–S(2) angle in AP and HP-AP is less acute (AP: 170.77(19)°, HP: 166.5(3)°, HP-AP: 171.41(18)°). Though trials with different sandwiched species (SO$^2_2$, S$^2_2$, S$^2_3$) affected the fitting parameters, the coordination of the Bi(2)–S(2) plane was not significantly changed (Table S5-6). Anion(s) sandwiched between Bi$_4$O$_2$Bi$_2$S$_3$ blocks were examined by Raman spectroscopy. The Raman shift at ~970 cm$^{-1}$ was detected in the spectra of all three samples (Figure 3), which can be attributed to SO$_4$ tetrahedrons. This Raman signal was stable during a few ten minutes, thus the laser-induced decomposition of the Bi$_4$O$_2$S$_3$ samples was unlikely. Nonetheless, these results cannot rule out the possible coexistence of other S-O/S$^2_2$/S$^2_3$ species. Final refinements were performed by the assumption that SO$_4$ tetragonal with half occupancy was sandwiched between Bi$_4$O$_2$Bi$_2$S$_3$ blocks. Trials with freely-refined S and O suggested the existence of multiple positions along the 00z within the interlayered space. We proposed a model comprising upward as well as downward SO$_4$ tetrahedrons rotating along the c-axis (Figure 1), thereby achieving low refinement parameters (AP: $R_{wp} = 5.24 \%$, HP: $R_{wp} = 3.34 \%$, HP-AP: $R_{wp} = 3.35 \%$) with reasonable bonding distances around the SO$_4$ tetrahedron (Table S4) and electron density without remarkable ghost spots (Figure S2).

| Samples | AP Bi$_4$O$_2$S$_3$ | HP Bi$_4$O$_2$S$_3$ | HP-AP Bi$_4$O$_2$S$_3$
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<td>3</td>
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<td>Phase</td>
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<td>Mass fraction (%)</td>
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<td>93.1, 6.9</td>
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<td>$I4/mmm$, Pnma, R-3m</td>
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FIGURE 2 Rietveld profile of synchrotron X-ray diffraction of (a) AP Bi$_4$O$_2$S$_3$, (b) HP Bi$_4$O$_2$S$_3$, and (c) HP-AP Bi$_4$O$_2$S$_3$. Red dots and black lines indicate experimental and calculated points. Residuals are indicated by blue lines. Red, blue, green, and black bars show allowed diffractions of Bi$_4$O$_2$S$_3$, Bi$_2$OS$_2$, Bi$_2$S$_3$, and Bi, respectively.
FIGURE 3 Raman spectra of (a) AP Bi$_4$O$_4$S$_3$, (b) HP Bi$_4$O$_4$S$_3$, (c) HP-AP Bi$_4$O$_4$S$_3$ and (d) sapphire substrate.

FIGURE 4 High-resolution TEM images (×300,000) and corresponding electron diffraction of (a, b) AP Bi$_4$O$_4$S$_3$, (c, d) HP Bi$_4$O$_4$S$_3$, and (e, f) HP-AP Bi$_4$O$_4$S$_3$.

Figure 4 presented typical high-resolution TEM images showing lattice fringes and corresponding electron diffraction; lower magnification images are shown in Fig. S3. The fringes of 2.0 nm corresponds to the approximate distance between the anion layers sandwiched between Bi$_4$O$_4$S$_3$ blocks. The TEM and electron diffraction images of AP Bi$_4$O$_4$S$_3$ show significant amounts of stacking faults with diffused diffraction streaks along the c-axis (Fig. 4(a, b)). On the other hand, fewer stacking faults were observed for HP and HP-AP Bi$_4$O$_4$S$_3$ with relatively clear diffraction spots (Fig. 4 (c-f)).

FIGURE 5 Temperature dependence of electronic resistivity down to 2 K of (a) AP Bi$_4$O$_4$S$_3$, (b) HP Bi$_4$O$_4$S$_3$, and (c) HP-AP Bi$_4$O$_4$S$_3$.

FIGURE 6 Temperature dependence of magnetization between 2-10 K of (a) AP Bi$_4$O$_4$S$_3$, (b) HP Bi$_4$O$_4$S$_3$, and (c) HP-AP Bi$_4$O$_4$S$_3$.

Heating under ambient pressure significantly affected the conductive and magnetic properties of Bi$_4$O$_4$S$_3$. Figure 5 shows the electronic resistivity of three Bi$_4$O$_4$S$_3$. All the samples exhibited metallic behavior in the normal region. AP Bi$_4$O$_4$S$_3$ showed zero resistivity at 4.4 K. Contrastingly, HP-Bi$_4$O$_4$S$_3$ displayed the possible onset of superconductive transition at ~ 2.3 K, but zero resistivity was not observed. The hump of resistivity at around 150 K was seen. Further annealed HP-AP Bi$_4$O$_4$S$_3$ exhibited zero resistivity. HP-AP Bi$_4$O$_4$S$_3$ showed zero resistivity at 4.8 K.

Figure 6 shows the magnetic properties of Bi$_4$O$_4$S$_3$. AP Bi$_4$O$_4$S$_3$ showed a strong diamagnetic signal ($T_c$~4.5 K). In contrast, HP-Bi$_4$O$_4$S$_3$ exhibited a low intensity diamagnetic signal. Further annealed HP-AP Bi$_4$O$_4$S$_3$ exhibited an intense diamagnetic signal. Thus, ambient pressure annealing is important for activating superconductivity.

Discussion

Zero resistivity of AP and HP-AP Bi$_4$O$_4$S$_3$ powders suggests that AP and HP-AP Bi$_4$O$_4$S$_3$ powders contain a superconductive phase. Large signals of magnetic susceptibility in AP and HP-AP Bi$_4$O$_4$S$_3$ powders can be attributed to either bulk superconductivity of Bi$_4$O$_4$S$_3$ phase or another superconductive phase.
covering on non-superconductive particles. Specific heat jump of AP-Bi$_2$O$_3$S$_3$ sample has been reported at 4.4 K, which is an evidence of the bulk superconductivity of Bi$_2$O$_3$S$_3$ phase. The relatively small specific heat jump, which has been also reported on many other BiS$_3$ superconductors, can be explained by a small electronic specific heat coefficient. However, it has been argued that this small specific heat jump can be attributed to a superconductive impurity.

Synchrotron X-ray diffraction detected 82.6 and 93.1 % of Bi$_2$O$_3$S$_3$ phases in AP and HP-AP Bi$_2$O$_3$S$_3$ powders, respectively. AP Bi$_2$O$_3$S$_3$ powders showed Bi$_2$S$_3$ and Bi$_2$O$_3$ as impurities while HP-AP Bi$_2$O$_3$S$_3$ powder included Bi$_2$S$_3$ as an impurity. These impurities show no superconducting transition (Figure S4). Thus, comparable intensities with its volume fraction above unity of the diamagnetic signals found in AP and HP-AP Bi$_2$O$_3$S$_3$ can be attributed to superconductive Bi$_2$O$_3$S$_3$ phases. Superconductivity of Bi$_2$S$_3$, which is a common impurity in superconductive AP and HP-AP Bi$_2$O$_3$S$_3$ powders, is unlikely since it is also found in non-superconductive HP Bi$_2$O$_3$S$_3$ powder. Moreover, TEM observation showed clean surface layers on superconductive AP and HP-AP Bi$_2$O$_3$S$_3$ phases; no obvious impurity phases were observed on their surfaces. Therefore, our results of synchrotron X-ray diffraction and TEM observation support the bulk superconductivity of AP and HP-AP Bi$_2$O$_3$S$_3$ phases.

What is the crystallographic difference in superconductive and non-superconductive Bi$_2$O$_3$S$_3$ phases? Although impurity phases make difficult to derive accurate structural data by Rietveld analysis even using synchrotron X-ray radiation, their good fitting with impurity phases would ensure the atomic positions of Bi$_2$O$_3$Bi$_2$S$_3$ blocks above a fair degree of accuracy. Comparison of the crystal structures of Bi$_2$O$_3$S$_3$ shows that slightly shorter and less bent Bi(2)–S(2) bonds in Bi$_2$O$_3$Bi$_2$S$_3$ blocks occur in the superconductive AP and HP-AP Bi$_2$O$_3$S$_3$ phases. This suggests a correlation between enhanced overlap of the p$_x$ and p$_y$ orbitals of Bi(2) and S(2) and the superconductive activity of the Bi$_2$O$_3$S$_3$ phases, similar to Ln(O,F)BiS$_3$ superconductors; Ln = La–Sm. The observed stacking faults in all evaluated Bi$_2$O$_3$S$_3$ phases should produce local fluctuations of the average structures. However, the similarity of the superconductivity despite different amounts of stacking faults in AP and HP-AP Bi$_2$O$_3$S$_3$ suggests that more stacking faults (i.e. local fluctuations) do not significantly affect the superconductivity.

The exact compositions and structures of Bi$_2$O$_3$S$_3$ are still suspicious because of the anion(s) sandwiched by Bi$_2$O$_3$Bi$_2$S$_3$ blocks. Raman spectroscopy detected S–O vibrations in all the Bi$_2$O$_3$S$_3$ powders, thus SO$_2$ was a candidate as the anion. However, Raman spectroscopy did not deny the presence of other species S$^2$–, S$^2$– or other S–O species. The shorter lattice parameters of superconductive AP- and HP-AP Bi$_2$O$_3$S$_3$ phases were detected, which could be attributed to less sandwiched atoms. Stacking faults can be caused by inhomogeneous anion(s) between Bi$_2$O$_3$Bi$_2$S$_3$ blocks. The pressure in the vacuum glass capillary increased after annealing HP Bi$_2$O$_3$S$_3$ powder, as confirmed by the inflated headspace of the capillary after heating using a burner. Thus, the compositional difference among Bi$_2$O$_3$S$_3$ phases are most likely, which can affect the lattice parameters, stacking faults, and superconductivity. Further investigation, such as neutron diffraction or single-crystal analysis, might clarify their exact chemical formula and lattice parameters as well as more precise structural information.

A possible explanation for the observed superconductivity is a change in a charge-density-wave state and carrier concentrations. Higher carrier concentrations are likely in the superconductive AP and HP-AP Bi$_2$O$_3$S$_3$ phases; this is indicated by the less-bent Bi(2)–S(2) plane according to a previous study of the relationship between the carrier concentration and Bi–S plane in Ln(O,F)BiS$_3$. A charge-density wave state was implicated by the electronic resistivity hump at around 150 K, observed only for non-superconductive HP Bi$_2$O$_3$S$_3$; this feature was not found in superconductive AP and HP-AP Bi$_2$O$_3$S$_3$. A similar hump was observed for EuBi$_2$F$_6$, which was explained by a possible charge-density-wave transition. Thus, superconductivity can be induced by suppression of the charge-density-wave states, which may be related to enriched carrier concentrations.

Conclusion

Synchrotron X-ray diffraction analysis demonstrated the presence of more than 80 mass % of the superconductive Bi$_2$O$_3$S$_3$ phase consisting of Bi$_2$O$_3$Bi$_2$S$_3$ blocks and sandwiched anion(s). Heating in a vacuum tube was an important process for activating the superconductivity. Heating induced slight shrinkage of the lattice parameters and shorter and less bent Bi(2)–S(2) bond together with the appearance of superconductivity. Stacking faults in the superconductive phases did not significantly affect the superconductivity. Although Raman spectroscopy detected the vibration of S–O bonding, the correlation between the appearance of superconductivity and the species/amounts of sandwiched anion(s) remains as a further challenge. Suppression of the charge-density-state with enriched carrier concentrations may explain the appearance of the superconductivity.

ASSOCIATED CONTENT

Supporting Information
Details of crystal structures and Raman spectra of Bi$_2$O$_3$S$_3$ are provided in Supporting Information.

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Notes

The authors declare no competing financial interest.

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Superconductive Bi$_4$O$_2$S$_3$ phases contain shorter and less bent Bi–S planes.