High-pressure effects on superconducting properties and crystal structure of Bi-based layered superconductor \( \text{La}_2\text{O}_2\text{Bi}_3\text{Ag}_{0.6}\text{Sn}_{0.4}\text{S}_6 \)

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Abstract
The effects of pressure on the superconducting properties of a Bi-based layered superconductor \( \text{La}_2\text{O}_2\text{Bi}_3\text{Ag}_{0.6}\text{Sn}_{0.4}\text{S}_6 \), which possesses a four-layer-type conducting layer, have been studied through the electrical resistance and magnetic susceptibility measurements. The crystal structure under pressure was examined using synchrotron x-ray diffraction at SPring-8. In the low-pressure regime, bulk superconductivity with a transition temperature \( T_c \) of \( \sim 4.5 \) K was induced by pressure, which was achieved by in-plane chemical pressure effect owing to the compression of the tetragonal structure. In the high-pressure regime above 6.4 GPa, a structural symmetry lowering was observed, and superconducting transitions with a \( T_c \) \( \sim 8 \) K were observed. Our results suggest the possible commonality on the factor essential for \( T_c \) in Bi-based superconductors with two-layer-type and four-layer-type conducting layers.

Keywords: pressure effect, structural phase transition, Bi-based superconductor, layered superconductor, diamond anvil cell, synchrotron XRD

Supplementary material for this article is available online (Some figures may appear in colour only in the online journal)

1. Introduction
Since the discovery of BiS\(_2\)-based layered superconductors, \( \text{Bi}_2\text{O}_3\text{S}_2 \) and \( \text{La(O,F)BiS}_2 \), in 2012 [1, 2], many superconductors having BiS\(_2\)-type superconducting layers have been synthesized [3]. The typical BiS\(_2\)-based superconductor system is RE(O,F)BiS\(_2\) (RE: rare earth), whose RE site is occupied by La, Ce, Pr, Nd, Sm, Yb, and Bi [2–9]. The crystal structure of RE(O,F)BiS\(_2\) is composed of alternate stacks of a superconducting BiS\(_2\) bilayer (Bi\(_2\)S\(_4\) layer) and an insulating RE\(_2\)O\(_2\) layer. In RE(O,F)BiS\(_2\), electron carriers generated through the partial substitution of F for the O site are needed for the emergence of superconductivity because the pristine phase, REOBiS\(_2\) with no carrier doping, is a semiconductor with a band gap [10, 11]. One of the notable features of La(O,F)BiS\(_2\)
Figure 1. Schematic images of crystal structure of REOBiS$_2$ and La$_2$O$_2$Bi$_2$M$_2$S$_6$ with M = Bi$_{0.5}$Ag$_{0.3}$Sn$_{0.2}$.

Figure 2. (a) Schematic image of the configuration of our DAC. (b) Optical image of the diamond anvil with boron-doped diamond electrodes.

Figure 3. Temperature dependence of electrical resistance for La$_2$O$_2$Bi$_3$Ag$_{0.6}$Sn$_{0.4}$S$_6$. The inset shows low-temperature data near the superconducting transition.

(RE = La) is the observation of filamentary superconductivity, in which a superconducting volume fraction is significantly low as compared to a bulk superconductor [2]. To induce bulk superconductivity in La(O,F)BiS$_2$, two pressure effects are applicable. One route to induce bulk superconductivity is application of external pressures. The transition temperature ($T_c$) of LaO$_{0.5}$F$_{0.5}$BiS$_2$ increases from 2 K to 10–11 K by the effect of external pressures, and the superconductivity of the high-pressure phase of LaO$_{0.5}$F$_{0.5}$BiS$_2$ is bulk in nature [2, 12–15]. The dramatic improvement of the superconducting properties can be explained by a structural transition from tetragonal ($P4/nmm$) to monoclinic ($P2_1/m$), which takes place at quite low pressure of ~1 GPa [15]. In addition, the structural transition largely affects electronic structure and the bonding nature in the crystal structure [15, 16]. Another route to induce bulk superconductivity in the RE(O,F)BiS$_2$ system is application of chemical pressures. The chemical pressure effect can be
generated through isovalent substitutions. For example, partial substitutions of La by a smaller RE element induce bulk superconductivity. $T_c$ increases up to 5–6 K by the substitution with Nd or Sm in RE(O,F)BiS$_2$ [9]. Furthermore, the partial substitutions of S at the conducting layer by larger Se are also effective to induce bulk superconductivity [17]. Those chemical pressure effects do not induce a structural transition but compresses the tetragonal lattice. The compression of the Bi-Ch (Ch: S, Se) square network suppresses intrinsic structural disorder [18–20], which is present due to the presence of Bi lone pairs, in RE(O,F)BiS$_2$ [21].

The target phase of this study is La$_2$O$_2$Bi$_3$Ag$_{0.6}$Sn$_{0.4}$S$_6$, whose basic crystal structure can be regarded as the stacking of La$_2$O$_2$Bi$_2$S$_4$ and M$_2$S$_2$ (M = Bi$_{0.5}$Ag$_{0.3}$Sn$_{0.2}$) layers [22]. In the La$_2$O$_2$Bi$_2$M$_2$S$_6$-type structure, the rock-salt-type M$_2$S$_2$ layer is inserted into the van-der-Waals gap of LaOBiS$_2$ [23–25]. Regarding the superconducting layer of RE(O,F)BiS$_2$ as two-layer-type, we can classify that of La$_2$O$_2$Bi$_3$AgS$_6$ as four-layer-type (see figure 1). The first La$_2$O$_2$Bi$_2$M$_2$S$_6$-type compound was obtained with M = Pb and was reported as a thermoelectric material [23]. In 2018, we observed superconductivity in La$_2$O$_2$Bi$_3$AgS$_6$ (M = Bi$_{0.5}$Ag$_{0.5}$) below 0.5 K [26]. The low $T_c$ in La$_2$O$_2$Bi$_3$AgS$_6$ was found to be related to the charge-density-wave-like transition. The partial substitution of Sn for the Ag site was found to be effective to suppress the transition and improved superconducting properties in La$_2$O$_2$Bi$_3$Ag$_{0.6}$Sn$_{0.4}$S$_6$, in which $T_c$ reaches 2.5 K [22]. Furthermore, application of chemical pressures in La$_2$O$_2$Bi$_3$Ag$_{0.6}$Sn$_{0.4}$S$_6$ further improved $T_c$ up to 4 K in Eu-substituted La$_2$O$_2$Eu$_{0.5}$Bi$_3$Ag$_{0.6}$Sn$_{0.4}$S$_6$ and similar phases with various RE [27–29]. On the basis of the knowledge on the dramatic external pressure effects in the two-layer-type BiS$_2$-based systems, we expected further increase in $T_c$ by external pressures in La$_2$O$_2$Bi$_3$Ag$_{0.6}$Sn$_{0.4}$S$_6$. Therefore, in this study, we have investigated the superconducting properties and crystal structure of La$_2$O$_2$Bi$_3$Ag$_{0.6}$Sn$_{0.4}$S$_6$ under high pressures.

2. Experimental details

A polycrystalline sample of La$_2$O$_2$Bi$_3$Ag$_{0.6}$Sn$_{0.4}$S$_6$ was prepared by solid-state reaction. Powders of La$_2$S$_3$ (99.9%), Bi$_2$O$_3$ (99.999%), Ag$_2$O (99% up), Bi (99.999%), Sn (99.9%),
Figure 5. Temperature dependences of resistance at (a) 0.25 GPa and (b) 11.2 GPa under magnetic fields.

Figure 6. (a) Temperature dependences of magnetic susceptibility for La$_2$O$_2$Bi$_3$Ag$_{0.6}$Sn$_{0.4}$S$_6$ under pressures up to 1.22 GPa. (b) Pressure dependence of $T_{cmag}$ for La$_2$O$_2$Bi$_3$Ag$_{0.6}$Sn$_{0.4}$S$_6$.

and S (99.9999%) with a nominal composition were mixed by mortar and pestle in air, pressed into a pellet, sealed in an evacuated quartz tube, and heated at 720 °C for 15 h. The obtained sample was ground, mixed, pelletized, and annealed under the same condition as the first sintering. The sample quality was comparable to that reported in reference [22], which was confirmed by laboratory powder x-ray diffraction (XRD) and energy dispersive x-ray spectroscopy.

Electrical resistance measurements were performed at ambient pressure and high pressures using a standard four-probe method on a physical property measurement system (Quantum Design: PPMS). A diamond anvil cell (DAC) with boron-doped diamond electrodes (see figure 2(a) for the cell configuration) was used for the high-pressure measurements [30, 31]. One side of diamond anvil equipped the electrodes and the polycrystalline sample was mounted on the center part of anvil, as shown in figure 2(b). The opposite anvil was culet-type with a diameter of 400 μm. A stainless-steel (SUS316) and a mixture of cubic boron nitride and ruby powders were used as a sample chamber and a pressure-transmitting medium, respectively. The applied pressure was estimated from the relationship between the pressure and wavelength of the ruby fluorescence [32] measured by an inVia Raman microscope (RENISHAW). The temperature dependence of magnetic susceptibility was measured using a superconducting quantum interference device magnetometer (MPMS-3, Quantum Design) under pressures from ambient pressure to ∼1.2 GPa. To apply pressures, a piston cylinder cell for MPMS-3 was used. A pressure medium was Daphne 7373, and Pb was used as a manometer. A magnetic field used for the magnetization experiment was 10 Oe. The applied pressure was estimated from a superconducting transition ($T_c$) of Pb.

The crystal structure investigation was performed using powder synchrotron x-ray diffraction (SXRD) at the beamline BL10XU of SPring-8 under the proposal (No: 2020A2051). The powder sample was loaded into a sample hole drilled in an SUS gasket together with a pressure medium, He gas. The samples were compressed to the pressures of interest using single crystal diamond anvils with 600 and 400 μm culet. Pressure was determined by the wavelength shift of the ruby
Figure 7. (a) Powder SXRD patterns (Run-2) for La$_2$O$_2$Bi$_3$Ag$_{0.6}$Sn$_{0.4}$S$_6$. (b) Evolution of the 200 (tetragonal) peak under high pressure. The dashed lines are eye-guide and showing the peak splitting at a pressure between 6.4 and 7.9 GPa. (c), (d) Pressure dependence of the lattice constant $a$ and $c$ obtained through Run-1 and Run-2.

R1 fluorescence line [33]. The wavelength was 0.413102 Å (Run-1) and 0.41315 Å (Run-2). The experiments Run-1 and Run-2 were performed using different powders. The obtained powder XRD patterns were refined by the Rietveld refinement using RIETAN-FP [34]. Crystal structure images were depicted using VESTA [35]. As shown in figure 1(b), we regarded that the outer metal site (in the BiS$_2$ layer) is occupied by Bi only according to the site selectivity found in previous structural analyses [22, 24, 25]. Instead, the inner metal site (the M site of the MS layer) was regarded as the solution of Bi, Ag, and Sn. In the refinements, the isotropic displacement parameters ($B$) for the La, O, and S sites were fixed to 1.

3. Results and discussion

3.1. Electrical resistance

To investigate the pressure evolution of $T_c$, the electrical resistance was measured on DAC. Figure 3 shows the temperature dependence of the electrical resistance of La$_2$O$_2$Bi$_3$Ag$_{0.6}$Sn$_{0.4}$S$_6$ at ambient pressure. The $T_c$ onset was $\sim$2.5 K, which is consistent with that reported in reference [22]. Figure 4(a) shows the temperature dependences of the resistance under pressures up to 11.2 GPa. The low-temperature resistance data near the superconducting transition is plotted in figure 4(b), and the temperature dependences of normalized resistance $R(T)/R(T = 8 K)$ under pressures up to 20.5 GPa are plotted in figure 4(c). At 4.6 GPa, a jump of $T_c$ onset was seen, and the $T_c$ onset reached 8 K at 11.2 GPa. To confirm that the resistance drops observed under high pressures were a superconducting transition, the temperature dependences of the resistance under magnetic fields were measured. As shown in figure 5, the $T_c$ onset for the data at 0.25 and 11.2 GPa clearly decreases with increasing magnetic field. Through the magnetoresistance measurements, we confirmed that the resistance drops are a superconducting transition.

3.2. Magnetic susceptibility

Investigation of the temperature dependence of the magnetic susceptibility is useful to obtain information about $T_c$ and bulk nature of the superconductivity under high pressures. Figure 6(a) shows the temperature dependences of the susceptibility for La$_2$O$_2$Bi$_3$Ag$_{0.6}$Sn$_{0.4}$S$_6$ under pressures. As reported in reference [22], the superconducting states at ambient pressure is not bulk in nature,
and bulk superconductivity was induced by chemical pressure effects via a partial substitution of S by Se (or a partial substitution of La by smaller RE) [22, 27–29]. With increasing pressure, \( T_c \) of La\(_2\)O\(_2\)Bi\(_3\)Ag\(_{0.6}\)Sn\(_{0.4}\)S\(_6\) reached 4 K, and bulk superconductivity was induced at pressures above 0.48 GPa, which was evaluated through the emergence of large shielding volume fraction of magnetic susceptibility. Although the shielding fraction does not reach 100% under pressures, the bulk nature is clearly induced by the pressure effect. The shielding fraction lower than 100% would be due to the inhomogeneity of applied pressure and very low lower critical field \( (H_{c1} \sim 2.5 \text{ Oe}) \) for the sample (figure S1(b) https://stacks.iop.org/JPCM/33/225702/mmedia). The estimated magnetic \( T_c \left( T_c^{\text{mag}} \right) \) is plotted as a function of pressure in figure 6(b). See supplemental materials (figure S1(a)) for the criterion of the estimation of \( T_c^{\text{mag}} \). The \( T_c \) shows a plateau behavior at \( P = 0.48–1.22 \text{ GPa} \). The origin of the plateau was discussed with the structural evolution in the following section.

### 3.3. Powder synchrotron x-ray diffraction

To discuss the evolution of superconductivity under pressures from structural viewpoints, we have performed SXRD experiments under high pressures. Figure 7(a) shows the powder SXRD patterns (Run-2) at 2.0–9.9 GPa. The SXRD patterns for Run-1 are displayed in figure S2 (supplemental materials). The position of the peaks shifts to higher angles with increasing pressure. Figure 7(b) shows the evolution of the 200 peak (tetragonal) by pressure. Since the 200 peak does not split below 6.4 GPa, the data suggests that the tetragonal \( (P4/mnm) \) [22] was maintained up to 6.4 GPa. In figures S3 and S4 (supplemental materials), typical Rietveld refinement results \( (P = 0.2 \text{ and } 6.4 \text{ GPa}) \) analyzed with the tetragonal model are presented. For all the refinements, the reliability factor \( R_{wp} \) was less than 7%. The refined lattice constants are plotted as a function of pressure in figures 7(c) and (d). In the low-pressure regime below 0.4 GPa, lattice constants clearly decrease. At \( P = 0.4–2 \text{ GPa} \), a plateau was observed. This behavior is very similar to the trend in the \( T_c^{\text{mag}}–P \) plot (figure 6(b)). Therefore, the \( T_c^{\text{mag}} \) plateau observed in the low-pressure regime is related to the unique compression of the lattice by pressure in the low-pressure regime. These nonlinear lattice compressions would be caused by the flexible nature of the lattice to pressure in BiS\(_2\)-based layered structure [3].

In a high-pressure regime above \( 6.4 \text{ GPa} \), the splitting of the tetragonal 200 peak was clearly observed as shown in figure 7(b). The peak splitting indicates lowering of the in-plane symmetry from the tetragonal (four-fold) symmetry. Due to broadened peaks under high pressures, we could not refine the high-pressure structure from the SXRD data. From the structural analogy to two-layer-type BiS\(_2\)-based systems, a monoclinic \( (P2_1/m) \) is one of the candidate space groups [15, 36, 37]. However, there is another structural model suggested for the high-pressure phase of La\(_2\)(O,F)Bi(S,Se)\(_2\), in which a stacking faults are yielded due to a loss of long-range order along the stacking direction [38]. Therefore, to clarify the crystal structure of the high-pressure phase of La\(_2\)O\(_2\)Bi\(_3\)Ag\(_{0.6}\)Sn\(_{0.4}\)S\(_6\), single crystal structural analysis and local structure analysis are needed.

![Figure 8. Atomic distances of La\(_2\)O\(_2\)Bi\(_3\)Ag\(_{0.6}\)Sn\(_{0.4}\)S\(_6\) as a function of pressure. M-S3 (in) and M-S3 (out) denote the atomic distances along the in-plane direction and the c-axis direction, respectively.](image)

### 3.4. Phase diagram

The \( T_c^{\text{onset}} \)’s estimated through resistance measurements are plotted as a function of pressure in figure 9 with the data of...
the lattice constant $a$. In the low-pressure regime, bulk superconductivity is induced in the tetragonal phase by the application of pressure. The states are similar to that achieved by in-plane chemical pressure effects owing to the compression of the tetragonal structure, as described in the section 3.3. In the high-pressure regime above 6.4 GPa, a possible structural transition from tetragonal to a lower-symmetric phase was found, and the $T_c$ reaches 8 K at 11.2 GPa. The jump behavior in the $T_c$–$P$ is quite similar to that observed in RE(O,F)BiS$_2$ [13–15] and related BiS$_2$-based systems such as EuFBiS$_2$ and $(Sr,La)$FBiS$_2$, which show a structural transition from tetragonal to monoclinic [36, 37]. With increasing pressure above 12 GPa, $T_c$ tends to decrease slightly. The high-pressure behavior also resembles that observed in the monoclinic phase of LaO$_{0.5}$F$_{0.5}$BiS$_2$ [15]. As reported in references [24, 40] the band structure, particularly band dispersion near the Fermi energy, is clearly different between two-layer-type (BiS$_2$-based) systems like RE(O,F)BiS$_2$ and four-layer-type La$_2$O$_2$Bi$_2$M$_2$S$_6$. However, the observed $T_c$–$P$ phase diagrams exhibit clear similarity: the jump in $T_c$ is observed where a structural transition is observed. Although we need to further investigate the high-pressure structure for La$_2$O$_2$Bi$_3$Ag$_{0.6}$Sn$_{0.4}$S$_6$ and other La$_2$O$_2$Bi$_2$M$_2$S$_6$-type materials to conclude on the commonality between two-layer-type and four-layer-type systems, the present results imply that there is a commonality on the factor essential for $T_c$ in Bi-based layered superconductors with the two-layer-type and four-layer-type conducting layers.

We briefly mention possible scenario of the increase in $T_c$ under high pressure in La$_2$O$_2$Bi$_3$Ag$_{0.6}$Sn$_{0.4}$S$_6$. Recently, possible pairing symmetry switching driven by structural symmetry breaking was proposed in two-layer-type (BiS$_2$-based) systems through isotope effects [41]. In two-layer-type systems, unconventional isotope effect was observed in tetragonal phases of La(O,F)BiSSe and Bi$_2$O$_3$S$_3$ [42, 43], whereas a conventional isotope effect was observed for a monoclinic phase of (Sr,La)FBiS$_2$ [41]. Since the pressure phase diagram of $T_c$ for La$_2$O$_2$Bi$_3$Ag$_{0.6}$Sn$_{0.4}$S$_6$ resembles that of two-layer-type systems, we assume that pairing mechanisms would be switching in La$_2$O$_2$Bi$_3$Ag$_{0.6}$Sn$_{0.4}$S$_6$ by the pressure effect, and $T_c$ may have increased in the lower-symmetric phase under high pressures. To obtain information about pairing mechanisms, further theoretical and experimental studies are needed for four-layer-type La$_2$O$_2$Bi$_3$M$_2$S$_6$ with a parameter of pressure.

4. Conclusion

In this study, we investigated the effects of external pressure on the superconducting properties of a polycrystalline sample of La$_2$O$_2$Bi$_3$Ag$_{0.6}$Sn$_{0.4}$S$_6$ through the electrical resistance measurements on a DAC and the magnetic susceptibility measurements on a piston cylinder cell. The crystal structure under pressure was examined using SXRD and Rietveld refinement for the tetragonal phase. In the low-pressure regime below 2.4 GPa, bulk superconductivity with a $T_c$ of $\sim$4.5 K was induced by pressure, which was achieved by compression of the tetragonal structure. In the high-pressure regime above 6.4 GPa, a structural symmetry lowering was observed. In the high-pressure regime, superconducting transitions with a $T_c$ $\sim$ 8 K were observed. Through structural refinements, we found that the in-plane compression is essential for the improvement of the superconducting properties in the tetragonal phase. Furthermore, even in the tetragonal phase, both BiS$_2$ and MS layers show dramatic structural change under pressures. The jump of $T_c$ accompanied with a structural phase transition by applying pressure is similar to that observed in two-layer-type BiS$_2$-based systems. Therefore, there should be a commonality on the factor essential for $T_c$ in Bi-based (two-layer-type and four-layer-type) superconductors.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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