High-pressure effects on La(0,F)BiS₂ single crystal using diamond anvil cell with dual-probe diamond electrodes

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The high-pressure phase of La(0,F)BiS₂ exhibits the highest transition temperature among all the BiS₂-based superconductors. Various studies, such as the investigation of isotope effects, have been conducted to explain its superconducting mechanism. However, there are very few reports on the electrical transport properties and vibration modes of single-crystalline La(0,F)BiS₂ under high pressure. In this study, we developed a diamond anvil cell with dual-probe diamond electrodes to measure the electrical transport properties of La(0,F)BiS₂ single crystal and Pb as a manometer at low temperature. Using the developed system, a linear decrease in the transition temperature and phonon hardening was observed under the application of pressure on La(0,F)BiS₂ single crystal. © 2021 The Japan Society of Applied Physics

The study of high-pressure effects on the electrical transport properties of La(0,F)BiS₂ is especially important because it exhibits the highest Tc among the BiS₂-based superconductors. La(0,F)BiS₂ has a layered structure composed of conducting layers (BiS₂) and charge reservoir blocking layers [La(0,F)]. Although the parent compound LaOBiS₂ is a semiconductor with a direct band gap of 0.8–1.0 eV, electron doping by the partial substitution of O by F induces superconductivity at 2.5 K under ambient pressure. As mentioned before, Tc can be increased by applying pressure in the case of polycrystalline samples. However, there is no report on electrical transport measurements of single-crystal sample of La(0,F)BiS₂ under high pressure. In addition, the analysis of Raman vibration modes has never been conducted on La(0,F)BiS₂, which can provide important information about the structure under high pressure.

A diamond anvil cell (DAC) is typically used for the simultaneous investigation of electrical transport properties and Raman modes under high pressure because a transparent anvil facilitates in situ optical analysis. However, the precise determination of the pressure value at low temperatures is difficult in a DAC. In general, the pressure in a DAC is estimated from the shift in the fluorescence peak position of a ruby crystal in the sample chamber at room temperature. However, the pressure changes slightly at low temperatures due to the thermal shrinkage of the cell components. Moreover, the detection of slight shifts in the fluorescence peak of ruby in the low-pressure region is difficult. In the case of the piston cylinder cell, the pressure at low temperatures can be estimated from the pressure-induced Tc shift of Pb, which is located near the sample. However, the simultaneous measurement of the sample and Pb is difficult using the DAC because of the small size of the sample chamber.

In this study, we developed a DAC configuration with dual-probe electrodes composed of a boron-doped conducting diamond thin film for simultaneous electrical transport measurement of two types of samples under high pressure. Using the developed system, electrical transport measurements and Raman spectroscopic studies of La(0,F)BiS₂ single crystal were carried out.

Following the discovery of BiS₂-based superconductors, various related compounds have been developed by changing the combination of the conducting layers and charge reservoir blocking layers, as R(O,F)BiCSe₂ (R: La, Ce, Pr, Nd, Sm, Yb, Cfr: S, Se). The properties of BiS₂-based materials are still being explored widely, as evidenced by the recent discovery of superconductivity in multi-layer type La₂O₂Bi₃Ag₀.₆Sn₀.₄S₆ with a transition temperature (Tc) of 2.5 K. The pairing mechanism of BiS₂-based superconductors is a subject of broad and current interest as a theoretical prediction of nonphonon-mediated nature on LaO₀.₅F₀.₅BiS₂ and experimental observation of an unconventional isotope effect in LaO₀.₅F₀.₅Bi(S,Se)₂. In addition to superconductivity, BiS₂-based materials have been studied for their superior thermoelectric property with figure of merit ZT = 0.36 on LaOBiSe, a platform for the exploration of superconductivity on high-entropy alloy and as a candidate for topological superconductor.

High-pressure experiments play an important role in the early stages of development of BiS₂-based materials. Bi₁O₁S₃, the first BiS₂-based superconductor shows a gradual decrease in Tc with application of high pressure. On the other hand, the second one, La(O,F)BiS₂ exhibits a discrete enhancement in Tc from 2.5 to 10.7 K with a structural phase transition from tetragonal to monoclinic. Interestingly, the enhanced Tc of the high-pressure phase can be quenched by high-pressure synthesis or annealing at 600 °C–700 °C and 2 GPa. Similar high-pressure effects with the structure change have been observed in various BiS₂-based superconductors, such as EuFBiS₂ and Ce(O,F)BiS₂, suggesting a common mechanism for Tc enhancement. According to an investigation of isotope effects, the high-pressure phase of (Sr,La)FBiS₂ with a monoclinic crystal structure exhibits conventional-type Tc shifts by substituting ³²S and ³⁴S, unlike the unconventional isotope effects observed in La(O,F)Bi(S,Se)₂ and Bi₁O₁S₃ with tetragonal structures. The high-pressure approach is also beneficial for inducing superconductivity in BiS₂-based compounds, such as NdO₁.₀₈F₀.₂Sb₁.₄Bi₄Se₂ (x = 0 to 0.8) and EuFBiS₂.
The diamond electrodes were designed by a nanofabrication technique using electron beam lithography and chemical vapor deposition, as described in the literature. Figure 1 presents the schematic images of the DAC with dual-probe diamond electrodes. High pressure is generated by squeezing the diamond anvils. One side of the diamond anvil is equipped with boron-doped diamond electrodes for electrical transport measurement of the samples. An optical microscope image of the fabricated anvil is shown in Fig. 1(c). The electrodes can be used repeatedly until the anvil is broken because the boron-doped diamond is mechanically and chemically stable and epitaxially grown from the anvil. The carrier concentration is of the order of $10^{21}$ cm$^{-3}$, indicating metallic nature with Fermi surface. The other side of the diamond anvil has a culet with a diameter of 1 mm to induce high pressure. The sample chamber consists of a metal gasket made of stainless steel (316 L) with a hole 600 μm in diameter. As a pressure-transmitting medium, cubic boron nitride powder was added to the gasket hole. A Raman microscope image of the fabricated anvil is shown in Fig. 1(c). The electrodes were electrically insulated from the metal gasket using cubic boron nitride powder.

Single crystals of La(O,F)BiS$_2$ were grown using an alkali metal flux with a nominal composition of LaO$_{0.5}$F$_{0.5}$BiS$_2$ according to a previously reported method. The chemical composition of the products was determined by scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDX) using a JSM-6010LA (JEOL) instrument and single-crystal X-ray diffraction (XRD) using an XtaLAB mini (Rigaku) with Mo-Kα radiation ($\alpha = 0.71072$ Å). The temperature dependence of the resistance of La(O,F)BiS$_2$ in the range of 300–0.2 K at ambient pressure was measured by a four-probe method using an adiabatic demagnetization refrigerator option on a physical property measurement system (Quantum Design). The high-pressure generation and in situ transport measurements were performed using a DAC with dual-probe diamond electrodes. The Raman spectrum of the sample and the fluorescence spectrum of ruby were acquired using an inVia Raman microscope (Renishaw).

Figure 2(a) shows the typical SEM image of the obtained crystal exhibiting a well-developed plate-like shape. The compositional ratio was determined to be La:Bi:S = 1:0.99:1.72, by normalizing La = 1 in the EDX analysis, which is consistent with the cation composition of La(O,F)BiS$_2$. The single-crystal XRD analysis revealed that the compound crystallizes with a tetragonal structure, with typical lattice constants of $a = 4.0541(15)$ Å and $c = 13.4826(52)$ Å. The EDX and XRD analyses establish that the obtained products are La(O,F)BiS$_2$ single crystals. The actual F concentration $x$ of the obtained LaO$_{1-x}$F$_x$BiS$_2$ is estimated to be $x = 0.2$–0.3 from the known relationship between $x$ and the lattice constant of the $c$ axis. The crystal cleaved by scotch tape was located on one side of the dual probe of the diamond anvil, as shown in Fig. 2(b). Figure 2(c) shows the enlarged image of the sample space. On the other side of the probe, a 130 nm thick Pb film was prepared by resistive heating vapor deposition. By measuring the $T_c$ of Pb, the applied pressure at low temperature was estimated using the relationship $P (\text{GPa}) = (T_c^{\text{ambient}} - T_c)/0.361$. Figure 3(a) shows the temperature dependence of the normalized resistance of Pb under various pressures. The $T_c$ of Pb gradually decreases with an increase in pressure. The pressures estimated at low temperature from the $T_c$ of Pb are labeled in the figure. Here, the onset $T_c$ and zero-resistance $T_c$ of Pb mean the lowest pressure and highest pressure, respectively. The labeled pressures are the average value of the lowest and highest pressures. The superconducting transition becomes broader with an increase in pressure, indicating an increase in pressure distribution. The temperature dependences of the normalized resistance of La(O,F)BiS$_2$ single crystals under different pressures are presented in Fig. 3(b). The sample at ambient pressure exhibits an onset $T_c$ of 2.2 K. According to a previously reported relationship between $T_c$ and the amount of F ($x$) in the LaO$_{1-x}$F$_x$BiS$_2$ single crystal, the value of $x$ of the obtained crystal is estimated to be 0.2–0.3, which is consistent with the estimation from the lattice constant. By applying pressure, the onset $T_c$ is drastically enhanced to 8.9 K at 0.9 GPa. The transition width of superconductivity is broad because of the pressure distribution in the sample space. Above 0.9 GPa, the $T_c$ gradually decreases with an increase in pressure up to 2.2 GPa. In contrast, the zero-resistance $T_c$ is increased above 0.9 GPa, indicating an enhancement of the volume fraction of higher $T_c$ phase.
dependence of Tc of the La(O,F)BiS2 single crystal. The rhombus symbols of Tc,M and Tc,on indicate the Tc determined by magnetization and resistivity measurements, respectively, using a polycrystalline sample from a previous study. A discrete enhancement in the Tc is observed at 0.9 GPa. The Tc values at pressures above 0.9 GPa of a single-crystal sample are slightly lower than those of a polycrystalline sample. According to the literature, La(O,F)BiS2 synthesized with a lower content of F by high-pressure annealing exhibits a lower Tc compared with that of an optimally doped sample. Hence, the amount of F in our sample is believed to be lower than the optimum doping amount, which may result in a lower Tc value. The discrete enhancement in Tc at pressures above 0.9 GPa is followed by a linear suppression at the rate of dTc/dP = −0.71 K GPa−1 up to 2.2 GPa, where P is the applied pressure. Here, we used the single-crystal sample and hard pressure-transmitting medium of cubic boron nitride. This configuration generally induces pseudo-uniaxial pressure. An investigation into the difference in the distortion rate of the lattice constant and bonding angle on single crystal under pseudo-uniaxial pressure is impressive and will be the subject of a future work.

Figure 4(b) shows the Raman spectra of the La(O,F)BiS2 single crystal at various pressures. At ambient pressure, two peaks are observed at 70 and 123 cm−1, which correspond to the Raman active A1g symmetric mode originating from the in-plane vibrations of Bi and S atoms. According to the Raman investigation of Nd(O,F)BiS2, an electron–phonon coupling constant λ ≈ 0.16 driven from the A1g mode is not sufficient to explain their Tc, suggesting an unconventional pairing mechanism at ambient pressure. The pattern of the vibration modes is completely changed at 0.9 GPa, indicating a pressure-induced structural phase transition. This is the first reported observation of the Raman modes of the higher Tc phase of La(O,F)BiS2 single crystal. Almost all the observed modes are gradually shifted to higher wavenumbers with an increase in pressure up to 2.2 GPa. The Raman spectrum of the sample showed the initial Raman modes after the pressure was released. Thus, it is evident that the pressure-induced phase transition and phonon hardening are reversible. After the experiment, the diamond electrodes showed no degradation and the same anvil was used repeatedly.

A linear decrease in Tc with the application of pressure is typically observed in conventional BCS-type superconductors such as MgB2. According to the BCS theory, the pressure effect on Tc can be described by dlnTc/dP = dlnN(0)/dP + 1.02[λ(1−μ*2)−μ*2]/(dμ*/dP), where P is the applied pressure, ω is the phonon frequency, μ* is the Coulomb repulsion and λ is the electron–phonon coupling constant. Here, λ = N(0) × ⟨F⟩/M(ω2), where N(0) is the density of states at the Fermi energy, ⟨F⟩ is the averaged square of the electronic matrix element, M is the atomic mass and ⟨ω2⟩ is the averaged square of the phonon frequency. The applied pressure is expected to reduce N(0) and enhance ω because of bandwidth broadening and phonon hardening, respectively. Although the enhancement of ω gives a positive effect for the first term dlnN(0)/dP, the decrease in N(0) and increase in ⟨ω2⟩ induce a drastic decrease in λ, namely a negative effect for the second term dμ*/dP, possibly resulting in Tc reduction. The linear decrease in Tc and the
phonon hardening feature from the Raman spectra of the high-pressure phase of La(O,F)BiS₂ support the phonon-mediated pairing mechanism of superconductivity, as observed in the conventional isotope effect.19)

In conclusion, we successfully demonstrated simultaneous measurements of the electrical transport properties of La(O,F)BiS₂ single crystal and Pb as a manometer at low temperature by using the developed DAC with dual-probe diamond electrodes. The transport measurements and Raman studies under high pressures revealed that the discrete enhancement in $T_c$ originated from the structural phase transition. A linear reduction in $T_c$ and phonon hardening were observed with an increase in the applied pressure on the high-pressure phase of the La(O,F)BiS₂ single crystal. The developed DAC with dual-probe electrodes is extremely useful for high-pressure research because two samples can be measured simultaneously with in situ optical analysis.

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