

Increase in T_c and change of crystal structure by high-pressure annealing in BiS_2 -based superconductor $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$

Joe Kajitani¹, Takafumi Hiroi¹, Atsushi Omachi¹, Osuke Miura¹, and Yoshikazu Mizuguchi^{1*}

1. Department of Electrical and Electronic Engineering, Tokyo Metropolitan University, 1-1, Minami-osawa, Hachioji, 192-0397, Japan

KEYWORDS: BiS_2 -based superconductor, $\text{CeO}_{1-x}\text{F}_x\text{BiS}_2$, crystal structure, high-pressure annealing

Abstract

Recently, several types of BiS_2 -based superconductor such as $\text{Bi}_4\text{O}_4\text{S}_3$, $\text{REO}_{1-x}\text{F}_x\text{BiS}_2$ (RE: rare earth) and $\text{Sr}_{1-x}\text{La}_x\text{FBiS}_2$ have been discovered. In this study, we have investigated the crystal structure and the superconducting properties for two kinds of polycrystalline samples (As-grown and high-pressure-annealed samples) of the BiS_2 -based superconductor $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$. We found that both the As-grown and the high-pressure-annealed $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$ samples show bulk superconductivity. A higher T_c was observed in the high-pressure-annealed sample. The T_c of $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$ increased from $T_c^{\text{zero}} = 2.7$ K to $T_c^{\text{zero}} = 3.7$ K by high-pressure annealing. The lattice constant of a and c axis did not show remarkable differences between the As-grown and the high-pressure-annealed samples. Nevertheless, the peak symmetry of the (200) peak seemed to become more symmetric while the (004) peak did not show such a difference, indicating that the crystal structure within the ab plane changed to a higher-symmetric phase, a perfect tetragonal, by high-pressure annealing in $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$.

1. Introduction

Recently, several types of BiS_2 -based superconductor such as $\text{Bi}_4\text{O}_4\text{S}_3$,¹⁾ $\text{REO}_{1-x}\text{F}_x\text{BiS}_2$ (RE: rare earth),²⁻⁶⁾ and $\text{Sr}_{1-x}\text{La}_x\text{FBiS}_2$ ^{7,8)} have been discovered. The typical parent material LaOBiS_2 has a crystal structure composed of an alternate stacking of BiS_2 conduction layers and LaO blocking layers. Electron carriers, which are essential for the appearance of superconductivity in the BiS_2 -based family, can be controlled by manipulating the structure and composition at the blocking layers. In LaOBiS_2 , electron carriers can be generated by a partial substitution of O^{2-} by F^- .^{2,9)} Electrical resistivity and magnetic susceptibility measurements under high pressure revealed that the transition temperature (T_c) of the BiS_2 -based family was sensitive to application of external pressure and can be significantly increased¹¹⁻¹³⁾ as observed in the Fe-based superconductor family.¹⁴⁻¹⁷⁾

In addition, superconducting properties of the BiS_2 -based superconductors strongly depend on the sample preparation method. Solid-state-reacted (As-grown) $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$ shows filamentary superconductivity: in other words, the superconducting volume fraction is obviously low, whereas superconducting states are evidently generated. To induce bulk superconductivity, high pressure annealing is effective.^{2,10)} Using the high-pressure technique, the onset of T_c of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ reaches a value of 11 K. It was suggested that the crystal structure obviously changed after high-pressure annealing. Recently, we revealed that uniaxial lattice contraction generated along the c axis was positively linked to the enhancement of T_c in high-pressure-annealed $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ and $\text{PrO}_{0.5}\text{F}_{0.5}\text{BiS}_2$.^{18,19)}

In this study, we focus on $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$. In the previous studies, it was reported that As-grown $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$ does not show bulk superconductivity.^{3,4)} In addition, the magnetic ordering, which was regarded as a ferromagnetic ordering, was observed. Bulk superconductivity is induced by application of high pressure¹¹⁾ or annealing the As-grown samples under high pressure (high-pressure annealing).⁴⁾ Interestingly, it was found that the magnetic ordering at the blocking layer (Ce moment) and bulk superconductivity at the BiS_2 layer could coexist. So far, the correlation between the superconducting properties and the crystal structure under high pressure in $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$ remains to be clarified. In this article, we have investigated the

correlation between the crystal structure and the superconducting properties of the As-grown and the high-pressure-annealed $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$ samples.

2. Experimental detail

Polycrystalline samples of $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$ were prepared by a solid-state reaction using powders of Bi_2O_3 (99.9 %), BiF_3 (99.9 %), Bi_2S_3 , Ce_2S_3 (99.9 %), and grains of Bi (99.99 %). The Bi_2S_3 powder was prepared by reacting Bi (99.99 %) and S (99.99 %) grains in an evacuated quartz tube. Other chemicals used in this study were purchased from Kojundo-Kagaku Laboratory. The starting materials with a nominal composition of $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$ were mixed-well, pressed in pellets, sealed in an evacuated quartz tube and heated at 700 °C for 10 h. The obtained products were ground, sealed into an evacuated quartz tube and heated again under the same heating condition to obtain a homogenized sample; in this article, we call this sample *As-grown* sample. The obtained sample was annealed at about 600 °C under a high pressure of about 3 GPa for 1 h using a cubic-anvil high-pressure synthesis instrument; in this article, we call this material *HP* sample. All the obtained samples were characterized by X-ray diffraction using the θ - 2θ method with a $\text{CuK}\alpha$ radiation. The temperature dependence of electrical resistivity was measured using the four-terminal method. The temperature dependence of magnetization was measured using a superconducting quantum interface device (SQUID) magnetometer with an applied field of 5 Oe after both zero-field cooling (ZFC) and field cooling (FC).

3. Results and discussion

Figure 1(a) shows the X-ray diffraction patterns of the As-grown and the HP samples of $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$. Almost all of the obtained X-ray peaks were explained using the tetragonal $P4/nmm$ space group. The numbers displayed in the profile indicate Miller indices. The obtained X-ray profiles are quite similar, but the peaks of the HP sample are slightly broadened. To discuss the change of the lattice constants in detail, the enlarged X-ray profiles around the (004) peaks and the (200) peaks are shown in Figs.

1(b) and 1(c), respectively. To clarify the changes in X-ray peaks, the peak intensities of (102) in Fig. 1(b) and (200) in Fig. 1(c) were normalized to 1, respectively. The (004) and (200) peak position does not show a remarkable differences between the As-grown and the HP samples. The lattice constants estimated from the peak positions are $a = 4.0477 \text{ \AA}$ and $c = 13.429 \text{ \AA}$ for the As-grown sample, and $a = 4.0477 \text{ \AA}$ and $c = 13.429 \text{ \AA}$ for the HP sample. The calculated lattice constants for the As-grown and the HP samples are the same within the resolution of our Laboratory level X-ray diffraction instrument.

Nevertheless, it can be noted that the shape of the (200) peak of the As-grown sample is relatively asymmetric. The (200) peak has a small hump around $2\theta = 45^\circ$, which indicates that the *ab*-plane could be strained, and the crystal structure symmetry would be not a perfect tetragonal for the As-grown sample. In contrast, the hump structure disappears in the (200) peak of the HP sample. These facts indicate that the crystal structure changes to a higher-symmetric phase (more perfect tetragonal) by high-pressure annealing in $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$. In addition, the (004) peaks for both samples are almost symmetric, which indicates that there is no change in the structure symmetry and/or lattice strain along the *c* axis.

Figure 2 shows the temperature dependences of electrical resistivity for the As-grown and the HP samples of $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$ below 15 K. The As-grown sample shows zero-resistivity states below $T_c^{\text{zero}} = 2.7 \text{ K}$. The HP sample shows zero-resistivity states below $T_c^{\text{zero}} = 3.7 \text{ K}$. It is hard to define the onset of T_c in the resistivity measurements because the resistivity for both samples gradually begins to decrease below $\sim 8 \text{ K}$. The broad transition is caused by the sensitivity of the superconducting properties to the change in the local crystal structures or strain.

Figure 3 shows the temperature dependence of magnetization for (a) the As-grown and (b) the HP samples of $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$. For both samples, magnetic ordering was observed below a magnetic transition temperature of 7.5 K as reported in the previous studies.^{3,4)} The magnetic transition temperature does not change by high-pressure annealing. The As-grown sample shows the superconducting T_c^{mag} of 2.7 K, while the

HP sample shows the superconducting T_c^{mag} of 3.5 K. These results almost correspond to the T_c^{zero} observed in the resistivity measurements for the As-grown and the HP samples. A large shielding volume fraction is observed in the ZFC data at 2 K for both samples, indicating both samples show bulk superconductivity.

The fact that the As-grown sample shows bulk superconductivity seems to be inconsistent with the previous works.^{3,4)} We consider the difference in the observed properties of $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$ between this study and the previous studies was due to the difference of the sample synthesis conditions. In fact, the annealing temperature is different. As shown in the X-ray diffraction part, the changes in the crystal structure after high-pressure annealing are not obvious as compared to the case of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$, in which a large uniaxial contraction along the c axis is observed for the HP sample.¹⁸⁾ Therefore, a slight change in the crystal structure could induce bulk superconductivity in $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$. Then, bulk superconducting states are realized in the As-grown sample by optimizing the synthesis temperature.

To understand the increase in T_c by high-pressure annealing in $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$, we suggest two possibilities. The first scenario is the slight change in the lattice symmetry within the ab plane. As shown in Fig. 1(c), the shape of the (200) peak of the As-grown sample is relatively asymmetric, and the (200) peak becomes symmetric by high-pressure annealing. A higher symmetry within the ab plane may be important for raising T_c in $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$. The other possibility is that the atoms locally moved without any changes in lattice constants by high-pressure annealing. For example, the z coordinate of the interlayer S site could easily move or fluctuate because the S^{2-} is combined with not only Bi in the superconducting layer but also Ce in the blocking layer. If this scenario is real, the electronic states which enhance superconducting properties could be modified without any change in lattice constants.

4. Conclusion

We investigated the crystal structure and superconducting properties of the As-grown and HP samples of $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$. We found that both As-grown and HP samples show bulk superconductivity. The lattice constant of a and c axis does not show a remarkable differences between the As-grown and HP samples. Nevertheless, the peak symmetry of the (200) peak seems to become more symmetric by

high-pressure annealing while the (004) peak does not show such a difference, indicating that the crystal structure within the *ab* plane changed to a higher-symmetric phase, more perfect tetragonal, by high-pressure annealing in $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$. The T_c of $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$ increased from $T_c^{\text{zero}} = 2.7$ K to $T_c^{\text{zero}} = 3.7$ K by high-pressure annealing. We assume that the increase in T_c could be explained by a change in the crystal structure symmetry within the *ab* plane or optimization of the local atomic coordinates without any changes in lattice constants.

Acknowledgements

This work was partly supported by JSPS KAKENHI Grant Numbers 25707031, 26600077.

References

- 1) Mizuguchi, Y., Fujihisa, H., Gotoh, Y., Suzuki, K., Usui, H., Kuroki, K., Demura, S., Takano, Y., Izawa, H., Miura, O.: BiS₂-based layered superconductor Bi₄O₄S₃. Phys. Rev. B. 86, 220510(1-5) (2012)
- 2) Mizuguchi, Y., Demura, S., Deguchi, K., Takano, Y., Fujihisa, H., Gotoh, Y., Izawa, H., Miura, O.: Superconductivity in Novel BiS₂-Based Layered Superconductor LaO_{1-x}F_xBiS₂. J. Phys. Soc. Jpn. 81, 114725(1-5) (2012).
- 3) Xing, J., Li, S., Ding, X., Yang, H., Wen, H.H.: Superconductivity appears in the vicinity of semiconducting-like behavior in CeO_{1-x}F_xBiS₂. Phys. Rev. B. 86, 214518(1-5) (2012).
- 4) Demura, S., Deguchi, K., Mizuguchi, Y., Sato, K., Honjyo, R., Yamashita, A., Yamaki, T., Hara, H., Watanabe, T., Denholme, S.J., Fujioka, M., Okazaki, H., Ozaki, T., Miura, O., Yamaguchi, T., Takeya, H., Takano, Y.: Coexistence of bulk superconductivity and ferromagnetism in CeO_{1-x}F_xBiS₂. arXiv:1311.4267.
- 5) Jha, R., Kumar, A., Singh, S. K., Awana, V. P. S.: Synthesis and superconductivity of new BiS₂ based superconductor PrO_{0.5}F_{0.5}BiS₂. J. Sup. Novel Mag. 26, 499-502 (2013).
- 6) Demura, S., Mizuguchi, Y., Deguchi, K., Okazaki, H., Hara, H., Watanabe, T., Denholme, S. J., Fujioka, M., Ozaki, T., Fujihisa, H., Gotoh, Y., Miura, O., Yamaguchi, T., Takeya, H., Takano, Y.: New Member of BiS₂-Based Superconductor NdO_{1-x}F_xBiS₂. J. Phys. Soc. Jpn. 82, 033708(1-3) (2013).
- 7) Lin, X., Ni, X., Chen, B., Xu, X., Yang, X., Dai, J., Li, Y., Yang, X., Luo, Y., Tao, Q., Cao, G., Xu, Z.: Superconductivity induced by La doping in Sr_{1-x}La_xFBiS₂. Phys. Rev. B 87, 020504(1-4) (2013).
- 8) Sakai, H., Kotajima, D., Saito, K., Wadati, H., Wakisaka, Y., Mizumaki, M., Nitta, K., Tokura, Y., Ishiwata, S.: Insulator-to-Superconductor Transition upon Electron Doping in a BiS₂-Based Superconductor Sr_{1-x}La_xFBiS₂. J. Phys. Soc. Jpn. 83, 014709(1-7) (2014).

- 9) Usui, H., Suzuki, K., Kuroki, K.: Minimal electronic models for superconducting BiS₂ layers. Phys. Rev. B 86, 220501(1-5) (2012).
- 10) Deguchi, K., Mizuguchi, Y., Demura, S., Hara, H., Watanabe, T., Denholme, S. J., Fujioka, M., Okazaki, H., Ozaki, T., Takeya, H., Yamaguchi, T., Miura, O., Takano, Y.: Evolution of superconductivity in LaO_{1-x}F_xBiS₂ prepared by high pressure technique. EPL 101, 17004(1-5) (2013).
- 11) Wolowiec, C. T., White, B. D., Jeon, I., Yazici, D., Huang, K., Maple, M. B.: Enhancement of superconductivity near the pressure-induced semiconductor– metal transition in the BiS₂-based superconductors LnO_{0.5}F_{0.5}BiS₂ (Ln = La, Ce, Pr, Nd). J. Phys.: Condens. Matter 25, 422201(1-6) (2013).
- 12) Kotegawa, H., Tomita, Y., Tou, H., Izawa, H., Mizuguchi, Y., Miura, O., Demura, S., Deguchi, K., Takano, Y.: Pressure Study of BiS₂-Based Superconductors Bi₄O₄S₃ and La(O,F)BiS₂. J. Phys. Soc. Jpn, 81, 103702(1-4) (2012).
- 13) Tomita, T., Ebata, M., Soeda, H., Takahashi, H., Fujihisa, H., Gotoh, Y., Mizuguchi, Y., Izawa, H., Miura, O., Demura, S., Deguchi, K., Takano, Y.: Pressure-induced Enhancement of Superconductivity in BiS₂-layered LaO_{1-x}F_xBiS₂. arXiv:1309.4250.
- 14) Takahashi, H., Igawa, K., Arii, K., Kamihara, Y., Hirano, M., Hosono, H.: Superconductivity at 43 K in an iron-based layered compound LaO_{1-x}F_xFeAs. Nature 453, 376-378 (2008).
- 15) Mizuguchi, Y., Tomioka, F., Tsuda, S., Yamaguchi, T., Takano, Y.: Superconductivity at 27K in tetragonal FeSe under high pressure. Appl. Phys. Lett. 93 152505(1-3) (2008).
- 16) Margadonna, S., Takabayashi, Y., Ohishi, Y., Mizuguchi, Y., Takano, Y., Kagayama, T., Nakagawa, T., Takata, M., Prassides, K.: Pressure evolution of the low-temperature crystal structure and bonding of the superconductor FeSe ($T_c=37$ K). Phys. Rev. B **80** 064506(1-6) (2009).
- 17) Medvedev, S., McQueen, T. M., Troyan, I. A., Palasyuk, T., Eremets, M. I., Cava, R. J., Naghavi, S., Casper, F., Ksenofontov, V., Wortmann G., Felser, C.: Electronic and magnetic phase diagram of bold italic beta-Fe_{1.01}Se with superconductivity at 36.7 K under pressure. Nat. Mater. **8** 630-633 (2009).
- 18) Kajitani, J., Deguchi, K., Omachi, A., Hiroi, T., Takano, Y., Takatsu, H., Kadowaki, H., Miura, O., Mizuguchi, Y.: Correlation between crystal structure and

- superconductivity in $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$. Solid State Commun. 181, 1-4 (2014).
- 19) Kajitani, J., Deguchi, K., Hiroi, T., Omachi, A., Demura, S., Takano, Y., Miura, O., Mizuguchi, Y.: Enhancement of T_c by uniaxial lattice contraction in BiS_2 -based superconductor $\text{PrO}_{0.5}\text{F}_{0.5}\text{BiS}_2$. J. Phys. Soc. Jpn., in printing (arXiv: 1401.7506).

Figure captions

Fig. 1. X-ray diffraction profiles of the As-grown and the HP samples of $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$.

- (b) Enlarged X-ray profiles around the (004) peaks of the As-grown and the HP samples.
- (c) Enlarged X-ray profiles around the (200) peaks of the As-grown and the HP samples.

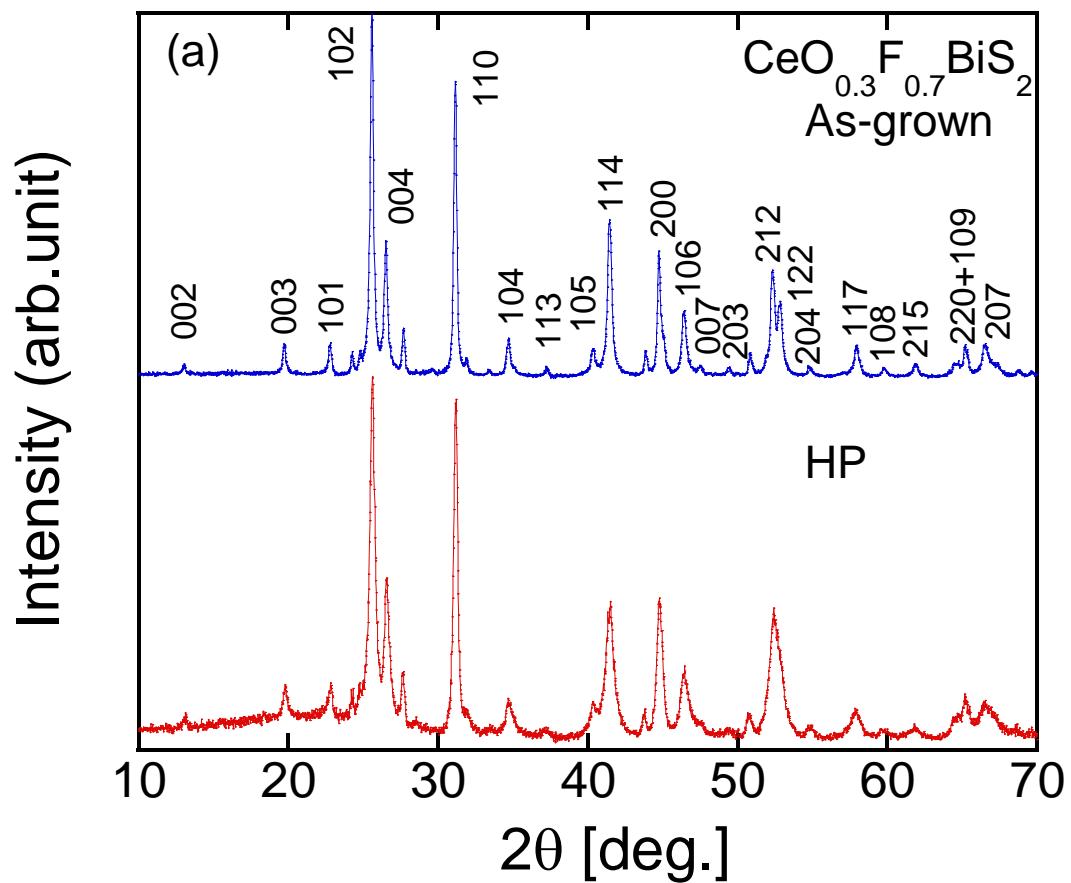
Fig. 2. Temperature dependences of electrical resistivity for the As-grown and the HP

samples of $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$ below 15 K.

Fig. 3. (a) Temperature dependence of ZFC and FC magnetization for the As-grown $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$ sample. (b) Temperature dependence of ZFC and FC magnetization for the HP sample of $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$.

Figures

Fig. 1.



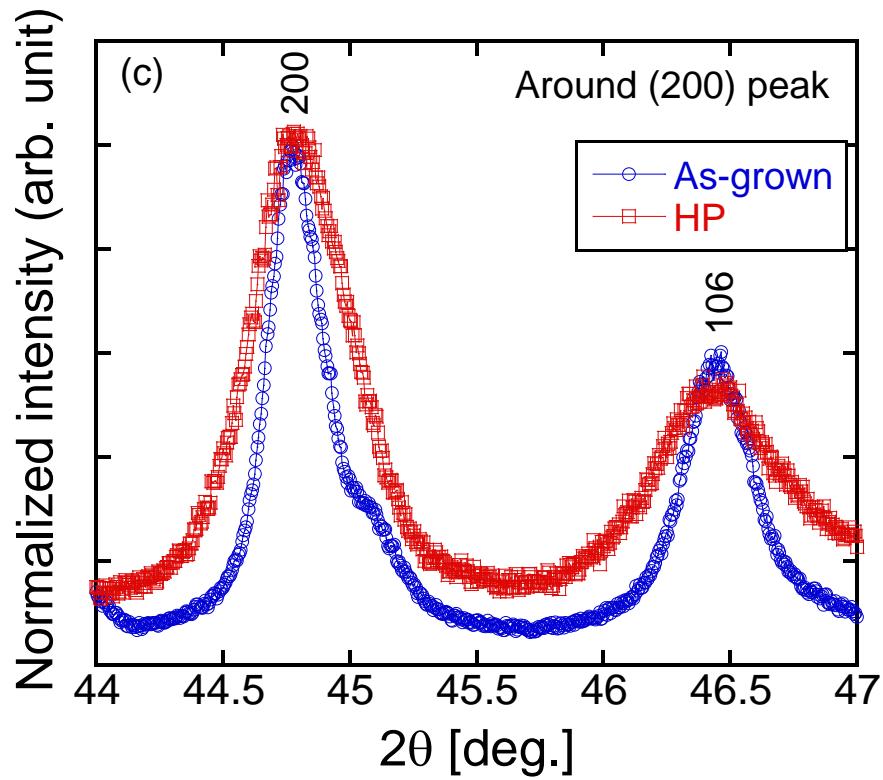
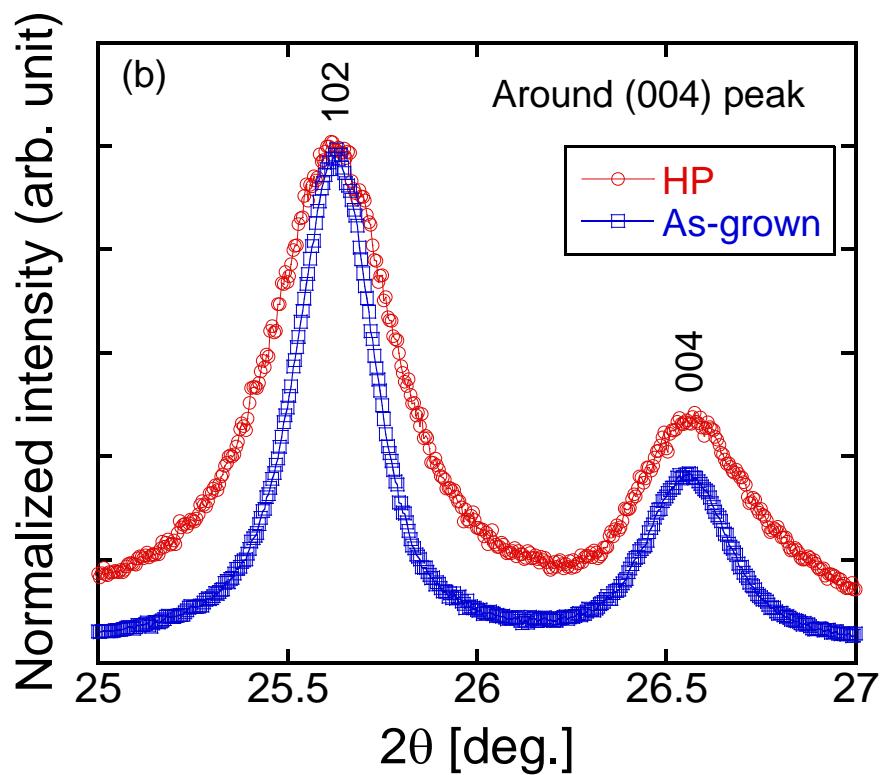


Fig. 2

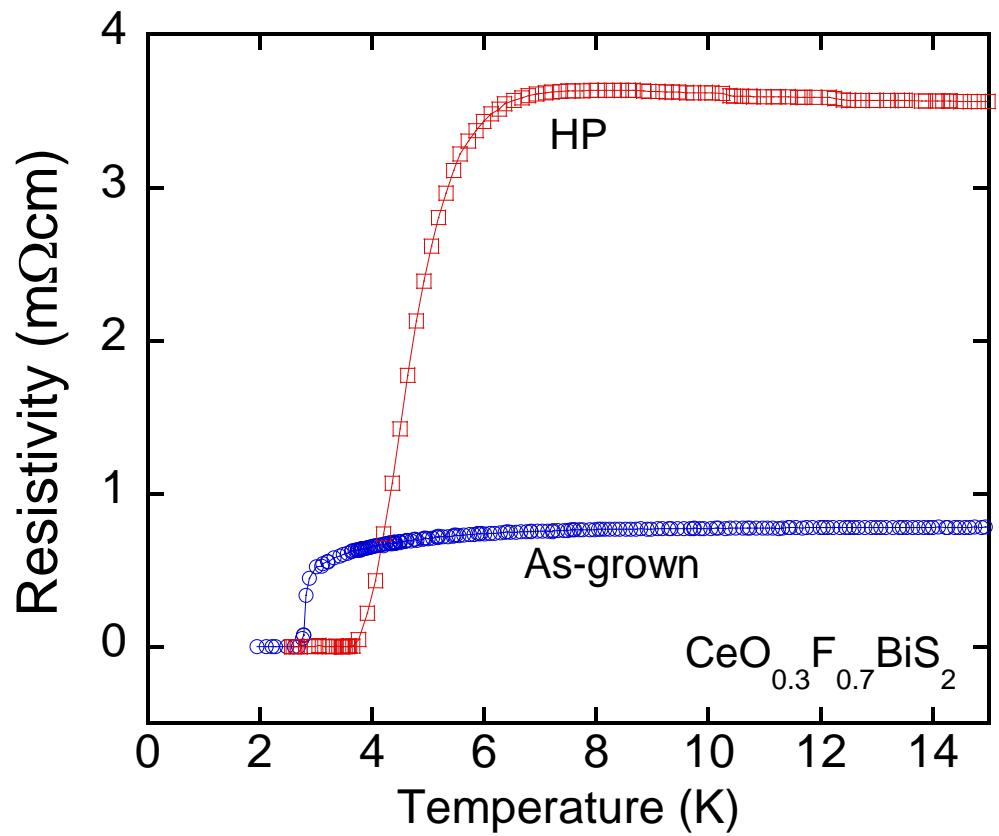


Fig. 3

