



日本物理学会論文賞

Outstanding Paper Award of the Physical Society of Japan

Title of Article

*Superconductivity in Novel BiS₂-Based
Layered Superconductor LaO_{1-x}F_xBiS₂*

Journal

J. Phys. Soc. Jpn. 81, 114725 (2012)

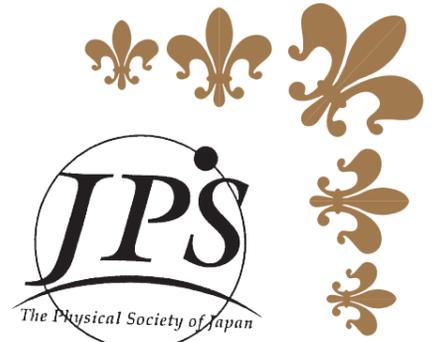
Authors

Yoshikazu Mizuguchi Satoshi Demura

Keita Deguchi Yoshihiko Takano

Hiroshi Fujihisa Yoshito Gotoh

Hiroki Izawa Osuke Miura



This is to certify that your article has been selected
for the 22nd Outstanding Paper Award from

Journal of the Physical Society of Japan

Progress of Theoretical and Experimental Physics

Progress of Theoretical Physics

JPS Conference Proceedings

published by the Physical Society of Japan.

March 19, 2017

一般社団法人日本物理学会

会長 藤井保彦



Yasuhiko Fujii

President, The Physical Society of Japan



Superconductivity in Novel BiS₂-Based Layered Superconductor LaO_{1-x}F_xBiS₂

Yoshikazu MIZUGUCHI^{1,2*}, Satoshi DEMURA², Keita DEGUCHI², Yoshihiko TAKANO²,
Hiroshi FUJIIHISA³, Yoshito GOTOH³, Hiroki IZAWA¹, and Osuke MIURA¹

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

²National Institute for Materials Science, Tsukuba, Ibaraki 305-0047, Japan

³National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan

(Received September 8, 2012; accepted October 2, 2012; published online November 1, 2012)

Layered superconductors have provided some interesting fields in condensed matter physics owing to the low dimensionality of their electronic states. For example, the high- T_c (high transition temperature) cuprates and the Fe-based superconductors possess a layered crystal structure composed of a stacking of spacer (blocking) layers and conduction (superconducting) layers, CuO₂ planes or Fe-Anion layers. The spacer layers provide carriers to the conduction layers and induce exotic superconductivity. Recently, we have reported superconductivity in the novel BiS₂-based layered compound Bi₄O₄S₃. It was found that superconductivity of Bi₄O₄S₃ originates from the BiS₂ layers. The crystal structure is composed of a stacking of BiS₂ superconducting layers and the spacer layers, which resembles those of high- T_c cuprate and the Fe-based superconductors. Here we report a discovery of a new type of BiS₂-based layered superconductor LaO_{1-x}F_xBiS₂, with a T_c as high as 10.6 K.

KEYWORDS: BiS₂-based superconductor, layered material, high pressure synthesis, superconducting properties, structural analysis

1. Introduction

Layered crystal structures are an exotic stage to explore superconductors with a high transition temperature (T_c) and to discuss the mechanisms of exotic superconductivity, as have the high- T_c cuprates¹⁻⁴⁾ and the Fe-based superconductors.⁵⁻¹³⁾ The discovery of basic superconducting layers, such as the CuO₂ plane and Fe₂An₂ (An = P, As, S, Se, Te) layers, have opened new fields in physics and chemistry of low-dimensional superconductors, because many analogous superconductors can be designed by changing the structure of the spacer layers. Recently, we reported superconductivity in the novel BiS₂-based superconductor Bi₄O₄S₃.¹⁴⁾ The crystal structure analysis indicated that Bi₄O₄S₃ had a layered crystal structure with space group of *I4/mmm*. The structure is composed of a stacking of rock-salt-type BiS₂ layers and Bi₄O₄(SO₄)_{1-x} layers (blocks), where x indicates the defects of SO₄²⁻ ions at the interlayer sites. Thus, the parent phase ($x = 0$) is Bi₆O₈S₅, and Bi₄O₄S₃ is expected to have about 50% defects of the SO₄²⁻ site ($x = 0.5$). The band calculations indicated that Bi₄O₄S₃ ($x = 0.5$) was metallic while the parent phase of Bi₆O₈S₅ ($x = 0$) was found to be a band insulator with Bi³⁺. In Bi₄O₄S₃, the Fermi level lies within the bands which mainly originate from the Bi 6p orbitals. In particular, the Fermi level is just on the peak position of the partial density of states of the Bi 6p orbital within the BiS₂ layer. With respect to the fact that the BiS₂ layers mainly contribute to the superconductivity of Bi₄O₄S₃, we expected that the BiS₂ layer would be a basic structure for a new class of an exotic superconducting family. Therefore we investigated the electron doping effects in an analogous BiS₂-based layered compound LaOBiS₂.¹⁵⁾ The parent phase of LaOBiS₂ is a band insulator, and possesses a layered structure composed of BiS₂ layers and La₂O₂ layers like Bi₆O₈S₅. Here we report the evolution of superconductivity in the BiS₂-based layered

compound LaO_{1-x}F_xBiS₂ by electron doping via F substitution at the O site. The appearance of superconductivity upon electron doping is corresponding to the case of Bi₄O₄S₃.

2. Experimental Details

Polycrystalline samples of LaO_{1-x}F_xBiS₂ were prepared using three different methods, AP1, AP2, and HP, where AP and HP stand for the second annealing at “ambient pressure” and “high pressure”, respectively. All the chemicals used in this study were purchased from Kojundo Chemical Lab. For the method AP1, we prepared the polycrystalline samples using powders of La₂O₃ (99.9%), LaF₃ (99.9%), La₂S₃ (99.9%), Bi₂S₃ and Bi (99.99%) grains. The Bi₂S₃ powders were prepared by reacting Bi and S (99.9%) grains at 500 °C in an evacuated quartz tube. The starting materials with a nominal composition of LaO_{1-x}F_xBiS₂ were well-mixed, pressed into pellets, sealed into an evacuated quartz tube, and heated at 800 °C for 10 h. The product was ground, mixed for homogenization, pressed into pellets and annealed again in an evacuated quartz tube at 800 °C for 10 h. For the method AP2, we prepared the polycrystalline samples using powders of Bi₂O₃ (99.9%), BiF₃ (99.9%), La₂S₃, Bi₂S₃, and Bi grains. The sample preparation process is almost the same as AP1, except for the heating temperature. Using this method, we could obtain single-phase samples with heating at 700 °C. For the method HP, we prepared precursor powders of LaO_{1-x}F_xBiS₂ by first annealing with the process in AP2, and performed a second annealing at 600 °C under a high pressure of 2 GPa using a cubic-anvil high pressure synthesis instrument with 180 ton press.

X-ray diffraction (XRD) patterns were collected by a Rigaku x-ray diffractometer with Cu K α radiation using the 2θ - θ method. Lattice parameters were calculated using the peak positions by least-square calculations. Rietveld refinements were performed using RIETAN2000 program.¹⁶⁾ In the refinement, the small impurity peaks near 27.5 and 43.5° were excluded. The schematic image of the crystal structure was depicted using VESTA.¹⁷⁾

*E-mail: mizugu@tmu.ac.jp

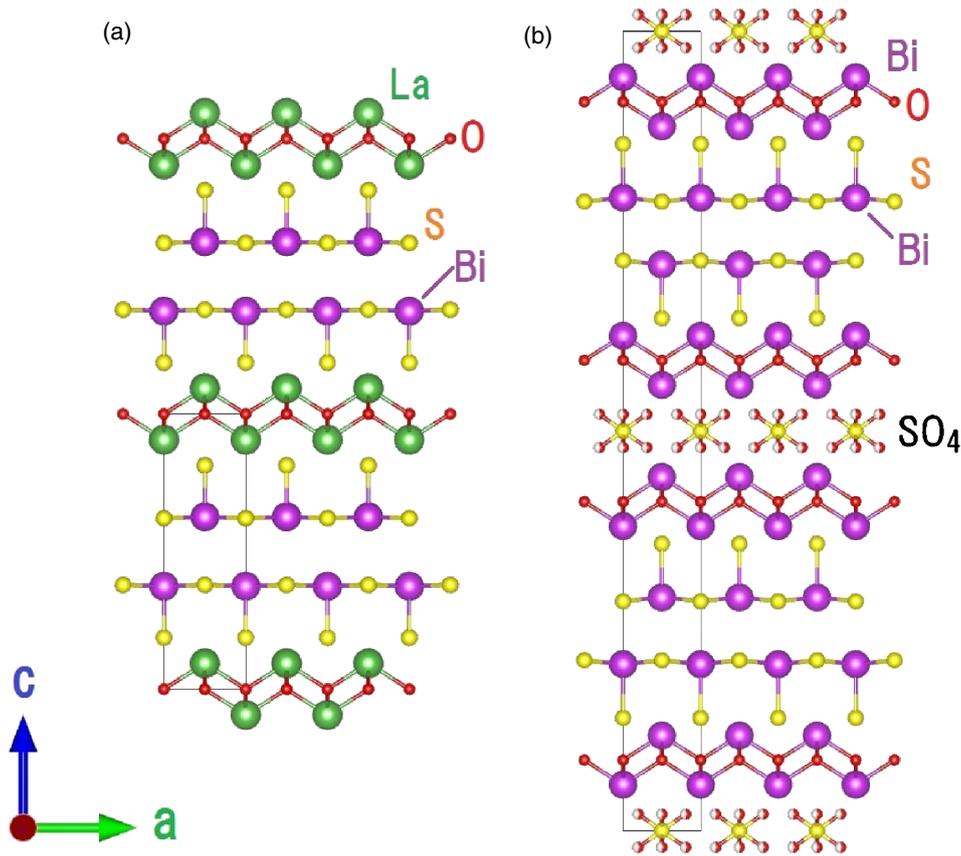


Fig. 1. (Color online) Crystal structure of (a) LaOBiS_2 and (b) $\text{Bi}_4\text{O}_4\text{S}_3$. The solid line indicates the unit cell.

Temperature dependence of magnetic susceptibility from 15 to 2 K after both zero-field cooling (ZFC) and field cooling (FC) was measured using a superconducting quantum interference device (SQUID) magnetometer with a magnetic properties measurement system (Quantum Design). Temperature dependence of resistivity from 300 to 2 K was measured using the four terminals method with a physical properties measurement system (Quantum Design).

3. Results

3.1 Structural analysis of $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$

LaOBiS_2 has a layered crystal structure with a space group of $P4/nmm$. Figure 1(a) displays a schematic image of the crystal structure of LaOBiS_2 . The structure is composed of a stacking of La_2O_2 layers and Bi_2S_4 layers (two BiS_2 layers in the unit cell), which is analogous to the $\text{Bi}_4\text{O}_4\text{S}_3$ superconductor [see Fig. 1(b)]. To dope electrons into the BiS_2 conduction layers, we substituted O^{2-} by F^- with a range of $x = 0-0.7$ in $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$. Figure 2(a) shows the XRD patterns for $x = 0$ and 0.5 synthesized using three methods of AP1, AP2, and HP (see §2). Almost all of the observed peaks are well indexed to the space group of $P4/nmm$ [Fig. 2(b)], except for a few peaks relating to impurity phases of BiF_3 or LaF_3 near 27.5° and 43.5° . For $x \geq 0.4$, impurity peaks appear, indicating the existence of a solubility limit of O/F near $x = 0.4-0.5$. It is found that the XRD profiles for the $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ samples prepared using two different methods of AP1 and AP2. For the $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ sample prepared by HP, the broadening of the

Table I. Atomic coordinates for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ (AP2).

Site	x	y	z	Occupancy
La1	0.5	0	0.1015	1
Bi1	0.5	0	0.6231	1
S1	0.5	0	0.3657	1
S2	0.5	0	0.8198	1
O/F	0	0	0	0.5/0.5 (fixed)

peaks is observed, which implies that LaOBiS_2 system is not stable at high pressures. To confirm the crystal structure of the F-substituted system, we performed Rietveld refinement. Figure 2(b) shows the result of Rietveld refinement for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ (AP2). The obtained lattice parameters and reliability factor are $a = 4.0527 \text{ \AA}$, $c = 13.3237 \text{ \AA}$, $R_{\text{wp}} = 13.12\%$. The obtained atomic coordinates are summarized in Table I. Figures 2(c)–2(e) display the nominal x dependence of the calculated lattice parameters of a , c , and V for $x = 0-0.7$ (AP1) and $x = 0.5$ (AP2). The a lattice parameter does not exhibit a remarkable F concentration dependence. The c lattice parameter and volume (V) obviously decrease with increasing F concentration up to $x = 0.5$. For $x > 0.5$, the changes in lattice constants are saturated, which indicates that the O/F solubility limit is near $x = 0.5$.

3.2 Magnetic susceptibility measurements for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$

In this article, we show the physical property data for $x = 0.5$ because a superconducting transition was not

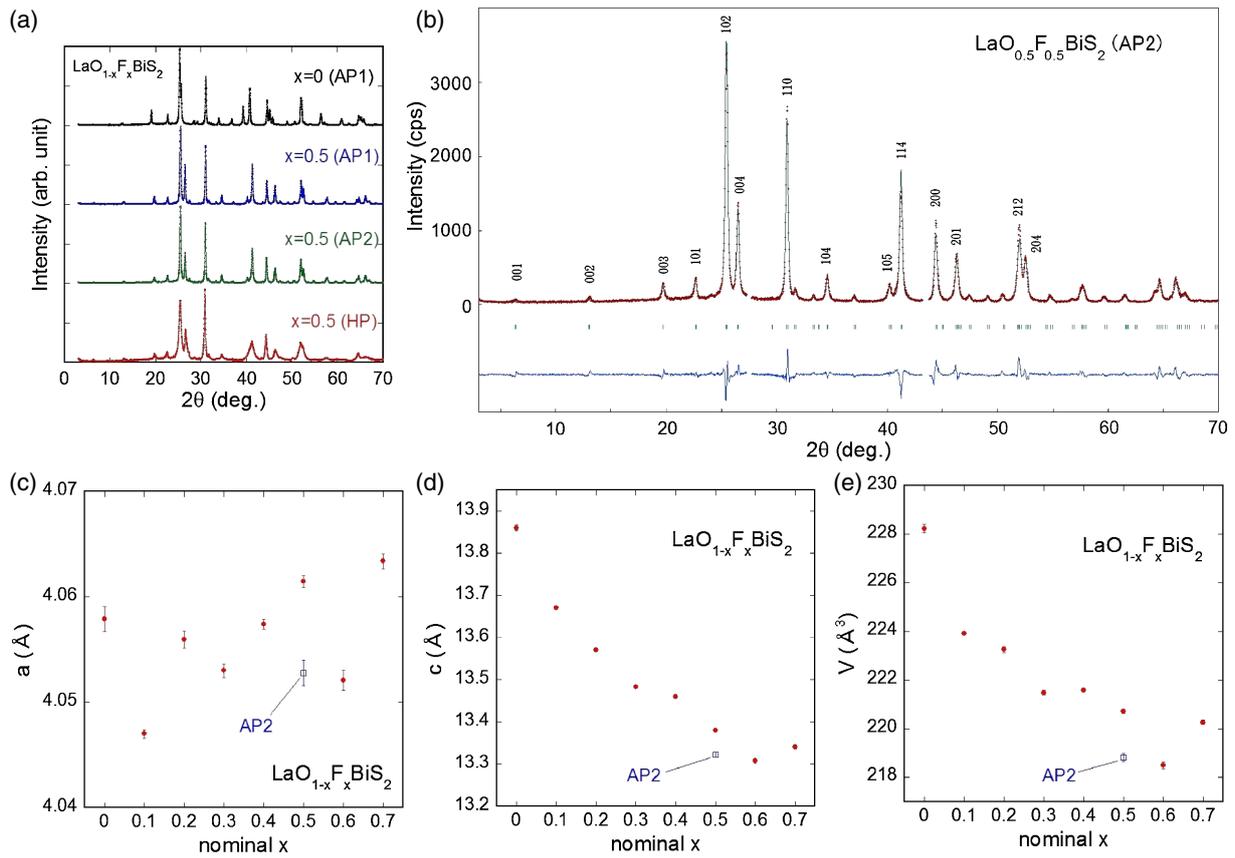


Fig. 2. (Color online) XRD patterns and Crystal structural analysis of $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$. (a) XRD pattern for $x = 0$ and 0.5 synthesized by three different methods of AP1, AP2, and HP. (b) XRD pattern and the result of Rietveld refinement for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ (AP2). The numbers are the Miller indices. (c-e) Lattice parameters of a , c , and V for $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$ (AP1) (red circles) and $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ (AP2) (blue squares).

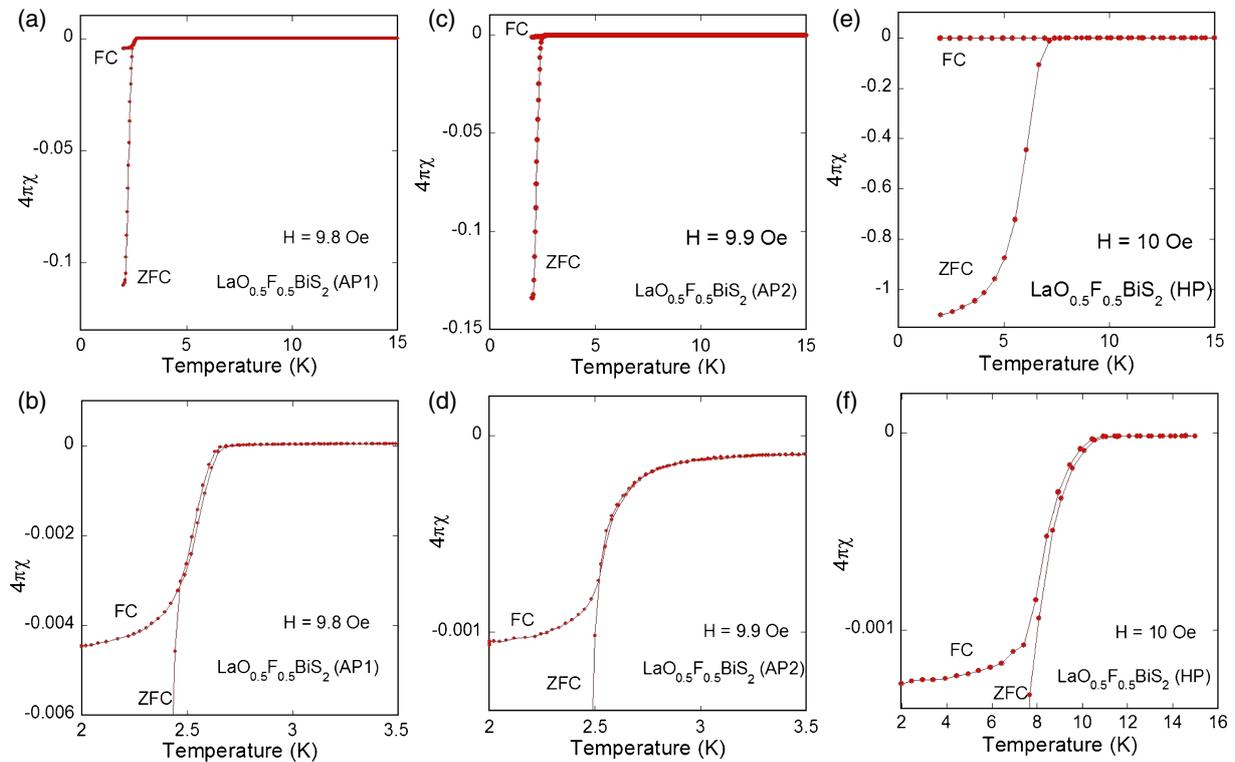


Fig. 3. (Color online) Temperature dependence of magnetic susceptibility for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ synthesized by three methods of AP1, AP2 and HP. (a, b) Temperature dependence of magnetic susceptibility for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ (AP1). (c, d) Temperature dependence of magnetic susceptibility for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ (AP2). (e, f) Temperature dependence of magnetic susceptibility for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ (HP).

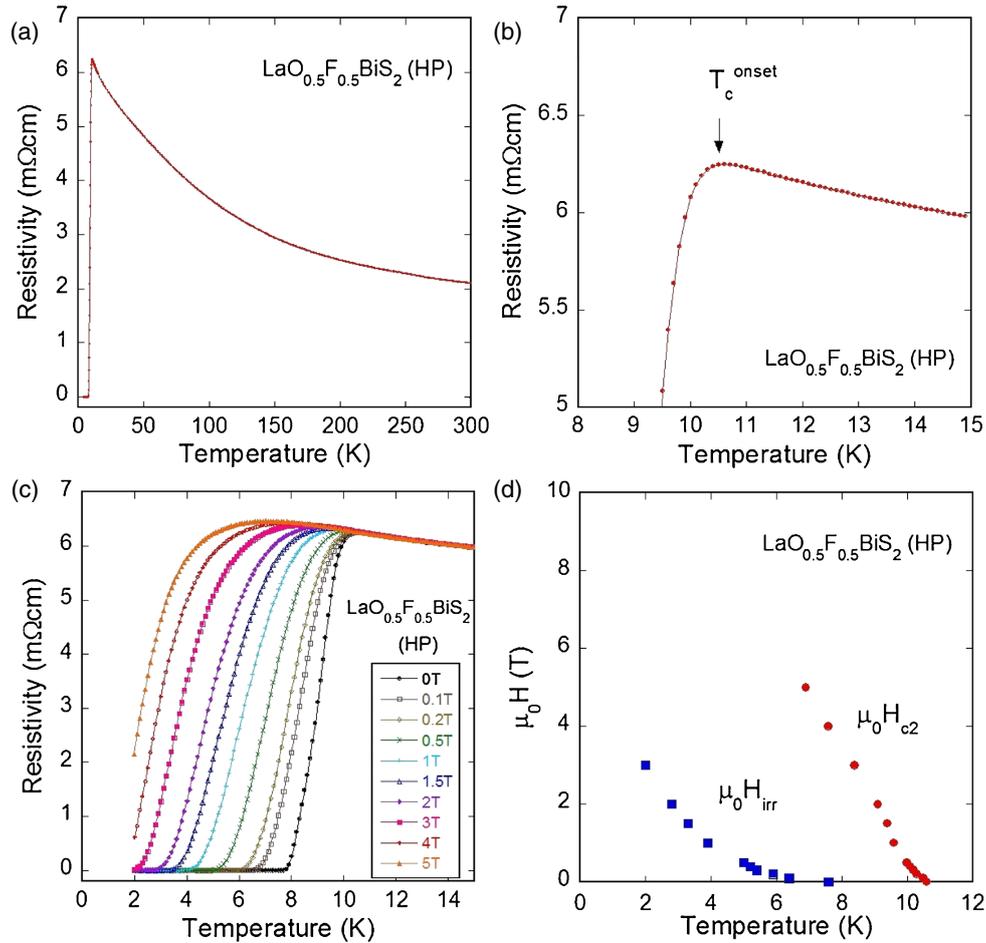


Fig. 4. (Color online) Transport properties of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ (HP). (a) Temperature dependence of resistivity for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ (HP). (b) Enlargement of superconducting transition for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ (HP) at 0 T. The onset of T_c was estimated as indicated by an arrow. (c) Temperature dependence of resistivity for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ (HP) under magnetic fields up to 5 T. (d) Magnetic field–temperature phase diagram of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ (HP).

observed for $x \leq 0.4$ and the best superconducting properties were obtained for $x = 0.5$. Figures 3(a) and 3(b) show the temperature dependence of magnetic susceptibility (χ) from 15 to 2 K and an enlargement around the onset of the superconducting transition for $x = 0.5$ (AP1). The onset of T_c is estimated to be ~ 2.7 K, and a large diamagnetic signal appears below 2.5 K. The calculated shielding volume fraction at 2 K is 11.0%. Figures 3(c) and 3(d) show the temperature dependence of magnetic susceptibility from 15 to 2 K and an enlargement around the onset transition for $x = 0.5$ (AP2). The onset of T_c is roughly estimated to be ~ 3 K, and a large diamagnetic signal appears below 2.5 K. The calculated shielding volume fraction at 2 K is 13.4%. Although superconducting signals are observed in both Figs. 2(a) and 2(c), the T_c and the shielding volume fraction were low. However, interestingly, both samples showed very slight drops at 10 K in the temperature dependence of magnetic susceptibility. Then, we expected that the maximum T_c of this system is as high as 10 K. This implies that the electron doping level is not optimal, namely underdoped, due to the O/F solubility limit near $x = 0.5$. Therefore, we performed high pressure annealing to further increase the F concentration, because the high pressure synthesis technique is generally advantageous for obtaining samples with a smaller lattice. Figures 3(e) and 3(f) show

the temperature dependence of magnetic susceptibility for $x = 0.5$ (HP). As we expected, very large shielding volume fraction as large as 100% is observed. Furthermore, a dramatic enhancement of T_c is observed. The onset of superconducting transition is above 10 K, and a large diamagnetic signal is observed below 8 K as shown in Fig. 3(f).

3.3 Transport properties of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$

Figure 4(a) shows the temperature dependence of resistivity for $x = 0.5$ (HP). Resistivity increases with decreasing temperature and a superconducting transition is observed at low temperatures. This behavior resembles the case of the carrier-doped band insulators, such as B-doped diamond^{18,19} and the HfNCl family.^{20–22} As shown in Fig. 4(b), the onset of the superconducting transition is observed at 10.6 K where the onset temperature (T_c^{onset}) is defined to be a temperature at which resistivity begins to decrease as indicated by the arrow. Figure 4(c) displays the temperature dependence of resistivity below 15 K under magnetic fields up to 5 T. To obtain a magnetic field–temperature phase diagram, we plotted the T_c^{onset} and the zero-resistivity temperature (T_c^{zero}) with the respective applied fields in Fig. 4(d). The upper critical field is estimated to be 10 T using the WHH theory, which gives $\mu_0 H_{c2}(0) = -0.69 T_c (d\mu_0 H_{c2}/dT)|_{T_c}$.²³

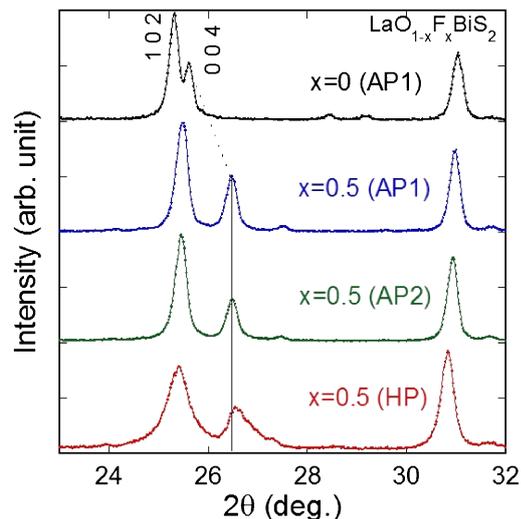


Fig. 5. (Color online) Comparison of (102) and (004) peaks between the sample preparation methods. The dashed and solid lines are the guidelines to clarify the shift of the (004) peaks.

4. Discussion

Here we discuss the requirements of the evolution of bulk superconductivity in $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$. The F-concentration dependence of structural properties indicates that the O/F solubility limit seems to be near $x = 0.5$. A superconducting transition is observed for x (nominal) ≥ 0.5 . However the shielding volume fraction in the magnetic susceptibility measurement is only 13.4% for the best sample of $x = 0.5$ (AP2), which implies that the electron doping level is in the under-doped region of this system. Therefore, we performed the high pressure annealing to achieve further doping of F. Figure 5 shows the XRD profiles near the (102) and (004) peaks. The (004) peak slightly shifts to higher angles after high pressure annealing, indicating that the c -axis decreases. This change indicates that the F concentration increased by the high pressure annealing. As described in §3.1, the $x = 0.5$ (AP2) sample contains small amount of BiF_3 and LaF_3 . The F ions would be supplied from the impurity fluorides. With the fact that bulk superconductivity can be achieved by a slight increase of F concentration from $x = 0.5$, we guess the optimal doping level is slightly above $x = 0.5$. The estimated optimal doping level is comparable to that of $\text{Bi}_4\text{O}_4\text{S}_3$. Therefore, we will be able to achieve bulk superconductivity in $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$ by optimizing the carrier doping techniques or modifying the optimal doping level (band structure) by changing the spacer layer structures.

In conclusion, we have discovered a new type of BiS_2 -based superconductor $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$ with a T_c as high as 10.6 K. This superconductor has a layered structure analogous to the BiS_2 -based $\text{Bi}_4\text{O}_4\text{S}_3$ superconductor, suggesting that the BiS_2 layer is a basic structure which provides new layered superconducting family like CuO_2 plane of cuprates and Fe_2An_2 layers of Fe-based family. Furthermore, we note that the spacer layer of LaOBiS_2 is almost the same as that

of LaOFeAs , which is the first FeAs-based system. Thus, we will be able to discover many BiS_2 -based superconductors on the basis of the analogy to FeAs-based compounds. We expect that the novel superconductors with the BiS_2 superconducting layers will open a new field in physics and chemistry of low-dimensional superconductors.

Acknowledgment

The authors would like to thank Dr. S. J. Denholme of National Institute for Materials Science (NIMS), Dr. H. Okazaki of NIMS, Dr. T. Yamaguchi of NIMS and Dr. H. Takatsu of Tokyo Metropolitan University for their experimental helps and fruitful discussion. This work was partly supported by a Grant-in-Aid for Scientific Research and JST-EU-JAPAN project on superconductivity.

- 1) J. G. Bednorz and K. Müller: *Z. Phys. B* **64** (1986) 189.
- 2) M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu: *Phys. Rev. Lett.* **58** (1987) 908.
- 3) H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano: *Jpn. J. Appl. Phys.* **27** (1988) L209.
- 4) A. Schilling, M. Cantoni, J. D. Guo, and H. R. Ott: *Nature* **363** (1993) 56.
- 5) Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono: *J. Am. Chem. Soc.* **130** (2008) 3296.
- 6) X. H. Chen, T. Wu, G. Wu, R. H. Liu, H. Chen, and D. F. Fang: *Nature* **453** (2008) 761.
- 7) Z. A. Ren, W. Lu, J. Yang, W. Yi, X. L. Shen, Z. C. Li, G. C. Che, X. L. Dong, L. L. Sun, F. Zhou, and Z. X. Zhao: *Chin. Phys. Lett.* **25** (2008) 2215.
- 8) M. Rotter, M. Tegel, and D. Johrendt: *Phys. Rev. Lett.* **101** (2008) 107006.
- 9) X. C. Wang, Q. Q. Liu, Y. X. Lv, W. B. Gao, L. X. Yang, R. C. Yu, F. Y. Li, and C. Q. Jin: *Solid State Commun.* **148** (2008) 538.
- 10) F. C. Hsu, J. Y. Luo, K. W. Yeh, T. K. Chen, T. W. Huang, P. M. Wu, Y. C. Lee, Y. L. Huang, Y. Y. Chu, D. C. Yan, and M. K. Wu: *Proc. Natl. Acad. Sci. U.S.A.* **105** (2008) 14262.
- 11) K. W. Yeh, T. W. Huang, Y. I. Huang, T. K. Chen, F. C. Hsu, P. M. Wu, Y. C. Lee, Y. Y. Chu, C. L. Chen, J. Y. Luo, D. C. Yan, and M. K. Wu: *EPL* **84** (2008) 37002.
- 12) Y. Mizuguchi, F. Tomioka, S. Tsuda, T. Yamaguchi, and Y. Takano: *Appl. Phys. Lett.* **94** (2009) 012503.
- 13) J. Guo, S. Jin, G. Wang, S. Wang, K. Zhu, T. Zhou, M. He, and X. Chen: *Phys. Rev. B* **82** (2010) 180520.
- 14) Y. Mizuguchi, H. Fujihisa, Y. Gotoh, K. Suzuki, H. Usui, K. Kuroki, S. Demura, Y. Takano, H. Izawa, and O. Miura: arXiv:1207.3145.
- 15) V. S. Tanryverdiev, O. M. Aliev, and I. I. Aliev: *Inorg. Mater.* **31** (1995) 1497.
- 16) F. Izumi and T. Ikeda: *Mater. Sci. Forum* **321–324** (2000) 198.
- 17) K. Momma and F. Izumi: *J. Appl. Crystallogr.* **41** (2008) 653.
- 18) E. A. Ekimov, V. A. Sidorov, E. D. Bauer, N. N. Mel'nik, N. J. Curro, J. D. Thompson, and S. M. Stishov: *Nature* **428** (2004) 542.
- 19) Y. Takano, M. Nagao, I. Sakaguchi, M. Tachiki, T. Hatano, K. Kobayashi, H. Umezawa, and H. Kawarada: *Appl. Phys. Lett.* **85** (2004) 2851.
- 20) S. Yamanaka, K. Hotehama, and H. Kawaji: *Nature* **392** (1998) 580.
- 21) H. Kawaji, K. Hotehama, and S. Yamanaka: *Chem. Mater.* **9** (1997) 2127.
- 22) T. Ito, Y. Fudamoto, A. Fukaya, I. M. Gat-Malureanu, M. I. Larkin, P. L. Russo, A. Savici, Y. J. Uemura, K. Groves, R. Breslow, K. Hotehama, S. Yamanaka, P. Kyriakou, M. Rovers, G. M. Luke, and K. M. Kojima: *Phys. Rev. B* **69** (2004) 134522.
- 23) N. R. Werthamer, E. Helfand, and P. C. Hohenberg: *Phys. Rev.* **147** (1966) 295.