

**Enhancement of Tc in BiS₂ based superconductors NdO_{0.7}F_{0.3}BiS₂ by substitution
of Pb for Bi**

S. Demura^{1,2}, Y. Fujisawa¹, S. Otsuki¹, R. Ishio¹, Y. Takano² and H. Sakata¹

¹Tokyo University of Science, Department of Physics, Shinjuku-ku, Tokyo 162-8601, Japan

²National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

E-mail : demura@rs.tus.ac.jp

Abstract

We succeed in enhancement of a superconducting transition temperature (T_c) for $\text{NdO}_{0.7}\text{F}_{0.3}\text{BiS}_2$ single crystal by partial substitution of Pb for Bi. The T_c increases with increasing Pb concentration until 6%. The maximum T_c^{zero} is 5.6 K, which is the highest value among BiS_2 based superconductors synthesized under an ambient pressure. Pb substitution for Bi induces lattice shrinkage along the c axis. These results reflect that superconductivity in this system is responsive to the lattice strain.

Key word : A. Superconductivity, A. BiS_2 -superconductor, E. Transport properties, E. Magnetism, E. Scanning tunneling spectroscopy(STM)

Introduction

High temperature superconductivity is the one of the most interesting phenomena in solid state physics. This phenomenon has been achieved in cuprates and iron-based superconductors [1-13]. One of the common features in these materials is the layered structure composed of block layers and conduction layers. This structure leads to two dimensional conduction, which is intrinsic to unconventional superconducting mechanism. This structure also contribute to the carrier doping which is needed to realize superconductivity: the block layers supply carriers into the conduction layers without introducing structural disorder of the conduction layers.

Recently, BiS_2 based superconductors has been discovered [14,15]. These superconductors have the similar layered structure to cuprates and iron-based superconductors. So, this material is possible candidate for another high temperature superconductor. Up to now, many members of BiS_2 superconductors have been reported [16-26]. Among them, NdOBiS_2 shows superconductivity when a part of O^{2-} ions are partly substituted F^- ions [16]. The T_c changes by the control of the F concentration and becomes the maximum value of 5.2K at the F concentration of 40 %. This T_c is the highest value among BiS_2 based superconductors synthesized in an ambient pressure. Interestingly, the T_c increases up to around 6.5 K when the samples are measured under a high pressure [27]. This increase of T_c is common properties in BiS_2 compounds with the block layers of LnO ($\text{Ln}=\text{La, Pr, Ce, Nd}$) [28-36].

Furthermore, a theoretical study for La(O,F)BiS₂ using a first principle band calculation indicated that the distance between La and S outside of the BiS₂ layer significantly affects the electronic structure [37]. These results may imply that the properties of BiS₂ superconductors are quite sensitive for a lattice strain. Considering these facts, it is interesting to induce the lattice strain into the compounds by a partial substitution of atoms to investigate the relation between T_c and the lattice strain.

In this study, we report an increase of T_c for NdO_{0.7}F_{0.3}BiS₂ single crystals by partial substitution of Pb for Bi. The ionic radius of Pb ion is larger than that of Bi ion. Therefore, a strain can be introduced to the crystal structure in an ambient pressure when Pb ions are substituted for Bi ions. These single crystals were synthesized by a flux method in quarts tubes. A c axis significantly decreases with increasing Pb concentration up to 6% while a a axis gradually increases. The T_c of these crystals increases with increasing Pb concentration until 6 %. A maximum value of T_c^{zero} is 5.6 K, which is the highest value among those of BiS₂ superconductors synthesized in an ambient pressure. These facts suggest that superconducting properties are responsible to the lattice strain.

Experimental

Single crystal samples of NdO_{0.7}F_{0.3}Bi_{1-x}Pb_xS₂ ($x=0.01-0.1$) were prepared by a CsCl flux method in vacuumed quarts tubes [38,39]. Mixtures of Bi (Mituswa Chemicals Co. Ltd.,

99.9%), Bi₂S₃, Bi₂O₃ (Kojyundo Chemical Laboratory Co. Ltd., 99.99%), BiF₃ (Stella Chemifa Co. Ltd., 99%), Nd₂S₃ (Kojyundo Chemical Laboratory Co. Ltd., 99%), and PbO (Kojyundo Chemical Laboratory Co. Ltd., 99.9%) were ground with nominal compositions of NdO_{0.7}F_{0.3}Bi_{1-x}Pb_xS₂ ($x=0.01\text{-}0.1$). Bi₂S₃ was obtained by sintering the mixtures of Bi and S (Kojyundo Chemical Laboratory Co. Ltd., 99.99%) in the evacuated quartz tube at 500 °C for 10 hours. The mixture of 0.8 g was mixed with CsCl powder (Kojyundo Chemical Laboratory Co. Ltd., 99.9%) of 5 g, and sealed in an evacuated quartz tube. The tube was heated at 800 °C for 10 hours and cooled down to 630 °C at a rate of 0.5 or 1.0 °C/h. After this thermal process, the sintered materials were washed by distilled water to remove the flux. The obtained single crystals were characterized by X-ray diffraction measurements with Cu-K α radiation using the $\theta\text{-}2\theta$ method. The surface structure of single crystals was observed by a laboratory-build scanning tunneling microscope (STM) at 4 K. The temperature dependence of magnetic susceptibility was measured by a superconducting quantum interface device (SQUID) magnetometer with an applied field of 10 Oe. The field was applied parallel to the *c* axis of the sample. T_c^{mag} is defined as the crossing point of fitting lines for the magnetic susceptibility in the normal state near the transition and the line in the drop area during the transition. The resistivity measurements were performed using the four-terminal method from 2 to 300 K. The T_c^{onset} is defined as a crossing point of fitting lines for resistivity in the normal state near the transition and the line in the drop area during the transition. The T_c^{zero} is defined

as the temperature where resistivity becomes zero.

Results

Figure 1(a) shows X-ray diffraction profiles for the single crystal samples of $\text{NdO}_{0.7}\text{F}_{0.3}\text{Bi}_{1-x}\text{Pb}_x\text{S}_2$ ($x=0.01-0.10$), respectively. The bottom profile shows $(00l)$ peaks of NdOBiS_2 as reference. All of the peaks are corresponded to the $(00l)$ peaks of CeOBiS_2 type structure with the space group $P4/nmm$ symmetry. Enlarged (004) peaks are shown in Fig.1(b). These peaks gradually shift to higher angle with increasing Pb concentration. Figure 2(a) exhibits c axis of Pb doped samples. The c axis significantly decreases with increasing Pb concentration until $x=0.06$, and become almost constant up to $x=0.10$. The a axis was estimated by X-ray diffraction using the powder prepared by grinding the single crystals. As shown in Fig. 2(b), the a axis gradually increases with increasing Pb concentration up to $x=0.10$. The monotonic change in the a axis guarantees the partial substitution of Pb for Bi in this x range.

We also observed the cleaved sample surface by STM technique. Figure 3 shows a STM image of $\text{NdO}_{0.7}\text{F}_{0.3}\text{Bi}_{0.96}\text{Pb}_{0.04}\text{S}_2$ single crystal. The observed surface shows a square lattice with a lattice constant of 3.9 \AA , which corresponds to the lattice constant a . No indication of Pb segregation or phase separation was observed. The observed atoms are thought to be Bi atoms on the topmost BiS_2 layer as in the case of $\text{NdO}_{0.7}\text{F}_{0.3}\text{BiS}_2$ [40]. The

number of dark spots, which indicate Bi defect, was about 4%. This concentration of the defect is the almost same as previous report in $\text{NdO}_{0.7}\text{F}_{0.3}\text{BiS}_2$ [40]. Thus, the number of defects is not affected by the Pb substitution.

Figure 4(a) exhibits temperature dependences of magnetic susceptibility for $\text{NdO}_{0.7}\text{F}_{0.3}\text{Bi}_{1-x}\text{Pb}_x\text{S}_2$ ($x=0.01-0.10$) single crystals. Large diamagnetic signal corresponds to superconductivity can be seen for all Pb doped samples. To determine these superconducting transition temperatures (T_c), the magnetic susceptibility near the T_c is shown in Fig. 4(b). The T_c increases with increasing Pb concentration until $x=0.06$, and decreases at $x=0.10$. The highest T_c^{mag} is 5.6 K.

The temperature dependence of resistivity for all Pb doped samples is presented in Fig. 5(a). All samples show the sharp superconducting transition and zero resistivity around 6K, which is correspond to superconducting transition. The resistivity near the T_c is exhibited in Fig. 5(b). The T_c^{onset} and T_c^{zero} increase with increasing Pb concentration until $x=0.06$, and decrease at $x=0.10$. The maximum T_c^{zero} is 5.6 K at $x=0.06$, which is the highest value among the BiS_2 -based superconductors synthesized under an ambient pressure.

In order to discuss the temperature dependence of resistivity, we fit the resistivity data to the formula:

$$\rho = \rho_0 + AT^n$$

where ρ_0 and A, n is fitting parameters. These fitting lines are drown as the gray lines in

the Fig. 5(a) and fitting parameters are shown in a table 1. The resistivity of samples with $x=0.02$ and 0.04 can be fitted to the formula from 300 K down to 80 K, and shows a slight upturn below 80 K. For the samples with $x=0.06$ and 0.10 , the fitting region goes down to 20 K. Namely, these sample shows the more metallic behavior than the samples with $x=0.02$ and 0.04 . This result implies that the upturn of resistivity is suppressed by Pb doping.

The resistivity at the room temperature for each Pb doped sample increases with increasing Pb concentration until $x=0.06$. This change in resistivity mainly comes from the change in ρ_0 . Because Pb substitution of Bi in BiS_2 layer, which is the conduction layer, may increases the disorder of the conduction plane, residual resistivity ρ_0 seems to increase with Pb doping. However, parameter A also increases at $x=0.06$. The increase in A cannot be explained by the disorder. This indicates that the Pb doping induces not only as enhancement of the disorder but also modification of the electronic structure through the change in the lattice parameter. It is noted that the resistivity at the room temperature slightly decreases when the amount of Pb is $x=0.10$. This also shows that the effect of the Pb doping is not only the enhancement of the disorder.

Figure 6 shows a Pb concentration dependence of T_c obtained by each measurement. All T_c gradually increase with increasing Pb concentration until $x=0.06$. This result indicates that superconductivity is obviously enhanced by the Pb doping. Now, let's

consider a relation between Pb doping and the enhancement of T_c . Following two effects are expected by Pb doping. One is the change of the carrier number. A valence of Pb ion is typically Pb^{2+} . This valence is one electron fewer than that of Bi^{3+} . This means that carriers are taken from the compound by Pb doping. Thus, the enhancement of T_c may due to the change in the carrier number. However, this is not the case. In the previous study, the carrier number dependence on T_c was reported in $\text{NdO}_{1-x}\text{F}_x\text{BiS}_2$, where the carrier number was controlled by the amount of F^- concentration substituted for O^{2-} . In that study, the maximum T_c was achieved at the F concentration of $x=0.4$ [16]. Thus, to obtain the maximum T_c by carrier doping into $\text{NdO}_{0.7}\text{F}_{0.3}\text{BiS}_2$, it needs 0.1 electron per Bi ion doping into the sample. On the other hand, Pb doping introduces the hole carriers into the sample. This should decrease T_c . Therefore, the enhancement of T_c is not due to the carrier doping. Furthermore, the observed maximum T_c in Pb doped sample is higher than that of $\text{NdO}_{1-x}\text{F}_x\text{BiS}_2$. Thus, the observed enhancement of T_c cannot be explained by the change in the carrier number.

The other effect of the Pb doping is the change in the lattice constant. Ionic radius of Pb^{2+} ion is larger than that of Bi^{3+} ion. Thus, the crystal is slightly strained by doping Pb ions. As shown in Fig. 2, the lattice constant a and c changes depending on the amount of doped Pb. This effect may be related to the enhancement of T_c . Actually, many papers have revealed that T_c of BiS_2 based superconductors with LnOBiS_2 type structure increases under the high-pressure where the lattice constant decreases [27-36]. Theoretical study also

reported that the band structure of BiS_2 -based materials is sensitive to the lattice constant along the c axis [37,41,42]. Thus, it is plausible that the T_c enhancement with Pb doping is achieved by shrinkage along the c axis. In this scenario, the saturation of T_c at $x=0.1$ is consistent with the saturation of the lattice constant c as shown in Fig.2 (b).

Summary

We achieved the increase of T_c by the Pb substitution of Bi in $\text{NdO}_{0.7}\text{F}_{0.3}\text{BiS}_2$. The enhancement of T_c is attributed the change in the lattice contraction along the c axis. The T_c^{zero} increases with decreasing c axis, and becomes the maximum value around 5.6 K at the Pb concentration of 6 %, which is the highest value among BiS_2 based superconductors synthesized under the ambient pressure. These results indicate that superconductivity in this material is strongly associated with the lattice strain.

Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology (KAKENHI).

References

- [1] J. G. Bednorz and K. Müller, Z. Physik B Condensed Matter **64** (1986) 189.
- [2] M. K. Wu et al., Phys. Rev. Lett. **58** (1987) 908.
- [3] H. Maeda, Y. Tanaka 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 et al., Chinese 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 et al., Proc. Natl. Acad. Sci. U. S. A. **105** (2008) 14262.
- [11] K. W. Yeh et al., Europhys. Letter **84** (2008) 37002.
- [12] Y. Mizuguchi, F. Taomita, T. Yamaguchi and Y. Takano, Appl. Phys. Lett. **94** (2009) 012503.
- [13] J. Guo, S. Jin, G. 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, Phys. Rev. B **86** (2012) 220510(R).

[15] Y. Mizuguchi, S. Demura, K. Deguchi, Y. Takano, H. Fujihisa, Y. Gotoh, H. Izawa and O.

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

[16] S. Demura et al., J. Phys. Soc. Jpn. **82** (2013) 033708.

[17] H. Lei, K. Wang, M. Abeykoon, E. S. Bozin, C. Petrovic, Inorg. Chem. **52** (2013) 10685.

[18] J. Xing, S. Li, X. Ding, H. Yang, Hai-Hu Wen, Phys. Rev. B **86** (2012) 214518.

[19] R. Jha, A. Kumar, S. K. Singh, V. P. S. Awana J. Sup. and Novel Mag. **26** (2013) 499.

[20] D. Yazici, K. Huang, B. D. White, A. H. Chang, A. J. Friedman, M. B. Maple, Philosophical Magazine **93** (2012) 673.

[21] D. Yazici et al., Phys. Rev. B **87** (2013) 174512.

[22] X. Lin et al., Phys. Rev. B **87** (2013) 020504(R).

[23] H. F. Zhai et al., Phys. Rev. B **90** (2014) 064518.

[24] A. Krzton-Maziopa et al., J. Phys.: Condens. Matter **26** (2014) 215702.

[25] G. S. Thakur, G. K. Selvan, Z. Haque, L. C. Gupta, S. L. Samal, S. Arumugam and A. K. Ganguli, Inorg. Chem. **54** (2015) 1076.

[26] H. F. Zhai et al., J. American Chem. Soc. **136** (2014) 15386.

[27] C. T. Wolowiec, B. D. White, I. Jeon, D. Yazici, K. Huang, M. B. Maple, J. Phys.: Condens. Matter **25** (2013) 422201.

[28] H. Kotegawa, Y. Tomita, H. Tou, H. Izawa, Y. Mizuguchi, O. Miura, S. Demura, K.

Deguchi, Y. Takano, J. Phys. Soc. Jpn. **81** (2012) 103702.

[29] G. K. Selvan, M. Kanagaraj, S. E. Muthu, R. Jha, V. P. S. Awana, S. Arumugam, Phys. Stat. Sol. Rapid Res. Lett. (2013).

[30] C. T. Wolowiec, D. Yazici, B. D. White, K. Huang and M. B. Maple, Phys. Rev. B **88** (2013) 064503.

[31] G. K. Selvan, M. Kanagaraj, R. Jha, V. P. S. Awana, S. Arumugam, arXiv:1307.4877.

[32] T. Tomita et al., J. Phys. Soc. Jpn. **83** (2014) 063704.

[33] R. Jha, H. Kishan, V. P. S. Awana, Solid State Communications **194** (2014) 6.

[34] M. Fujioka, M. Nagao, S. J. Denholme, M. Tanaka, H. Takeya, T. Yamaguchi, Y. Takano, Appl. Phys. Lett. **105** (2014) 052601.

[35] R. Jha, V. P. S. Awana, arXiv:1502.05502.

[36] G. S. Thakur, R. Jha, Z. Haque, V. P. S. Awana, L. C. Gupta, A. K. Ganguli, arXiv:1504.08088.

[37] K. Suzuki, H. Usui and K. Kuroki, Physical Procedia **45** (2013) 21.

[38] M. Nagao, S. Demura, K. Deguchi, A. Miura, S. Watauchi, T. Takei, Y. Takano, N. Kumada and I. Tanaka, J. Phys. Soc. Jpn. **81** (2012) 103702.

[39] M. Nagao, A. Miura, S. Demura, K. Deguchi, S. Watauchi, T. Takei, Y. Takano, N. Kumada and I. Tanaka, Solid State. Commun. **178** (2014) 33.

[40] T. Machida, Y. Fujisawa, M. Nagao, S. Demura S, Deguchi K, Y. Mizuguchi, Y. Takano Y,

H. Sakata, J. Phys. Soc. Jpn **83** (2014) 113701.

[41] T. Sugimoto, B. Joseph, E. Paris, A. Iadecola, T. Mizokawa, S. Demura, Y. Mizuguchi, Y. Takano and N. L. Saini, Phys. Rev. B **89** (2014) 201117.

[42] E. Paris et al., J. Phys.: Condens. Matter **26** (2014) 435701.

Figure caption

Fig. 1 (Color online)

(a) X-ray diffraction patterns for single crystals of $\text{NdO}_{0.7}\text{F}_{0.3}\text{Bi}_{1-x}\text{Pb}_x\text{S}_2$ ($x=0.01-0.1$). The bottom black line shows the reference (00*l*) peaks of NdOBiS_2 . (b) Enlarged figure of (004) peaks for Pb doped samples.

Fig. 2 (Color online)

(a, b) Pb concentration dependence of *c* and *a* axis. These *a* axis were estimated by the powder X-ray measurements using ground single crystals.

Fig. 3 (Color online)

STM image of the $\text{NdO}_{0.7}\text{F}_{0.3}\text{Bi}_{0.96}\text{Pb}_{0.04}\text{S}_2$ single crystal on a $130 \times 130 \text{ \AA}^2$ field of view taken at $V = +1400 \text{ mV}$ and $I = 500 \text{ pA}$. The inset show a Fourier transform image. The red arrows indicate the direction an atom period corresponded to cell parameter of *a* axis.

Fig. 4 (Color online)

(a) The temperature dependence of the magnetic susceptibility for single crystals of $\text{NdO}_{0.7}\text{F}_{0.3}\text{Bi}_{1-x}\text{Pb}_x\text{S}_2$ ($x=0.01-0.1$). (b) The enlarged figure of magnetic susceptibility near the

superconducting transition.

Fig. 5 (Color online)

(a) The temperature dependence of resistivity for single crystals of $\text{NdO}_{0.7}\text{F}_{0.3}\text{Bi}_{1-x}\text{Pb}_x\text{S}_2$ ($x=0.01-0.1$) between 300 and 2 K. (b) The enlarged picture of resistivity between 10 and 2 K.

Fig. 6 (Color online)

The nominal F concentration x - superconducting transition temperature phase diagram for single crystals of $\text{NdO}_{0.7}\text{F}_{0.3}\text{Bi}_{1-x}\text{Pb}_x\text{S}_2$ ($x=0.01-0.1$).

Table 1

Fitting parameters of resistivity for single crystals of $\text{NdO}_{0.7}\text{F}_{0.3}\text{Bi}_{1-x}\text{Pb}_x\text{S}_2$ ($x=0.02-0.1$).

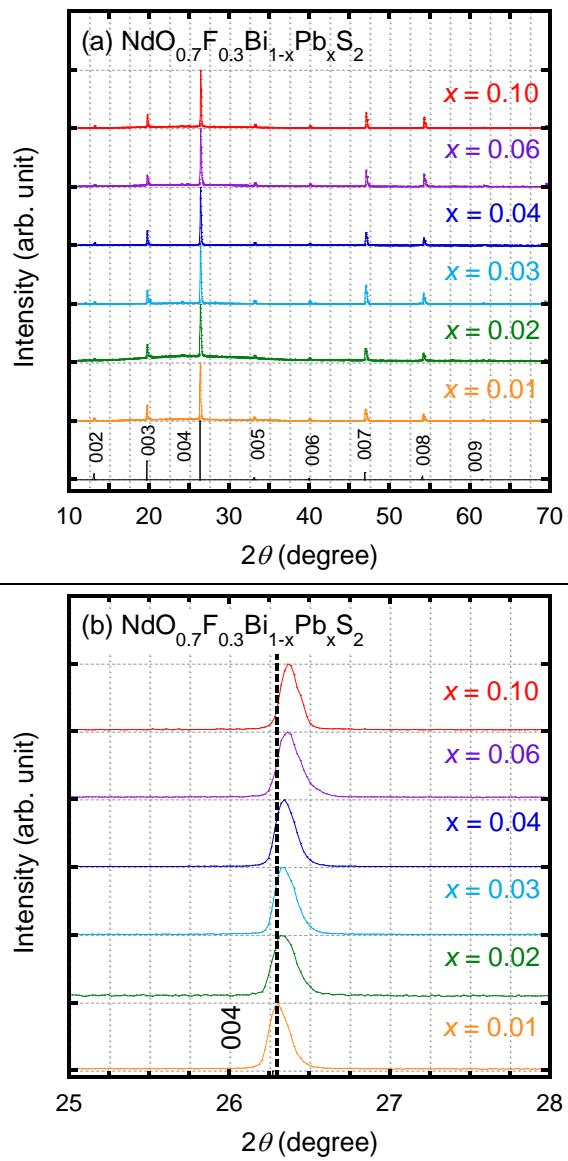


Fig. 1(a, b)

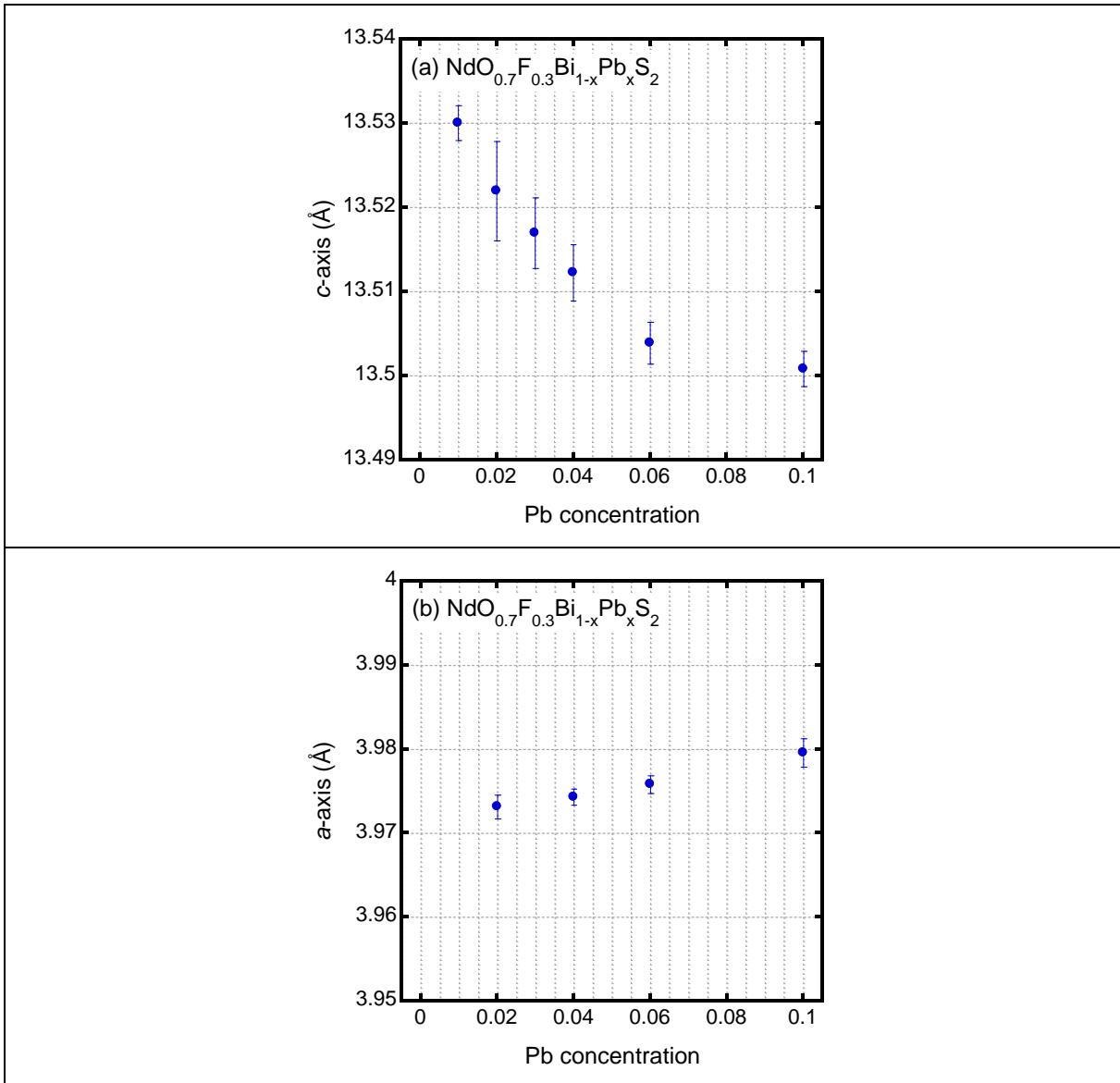


Fig. 2(a,b)

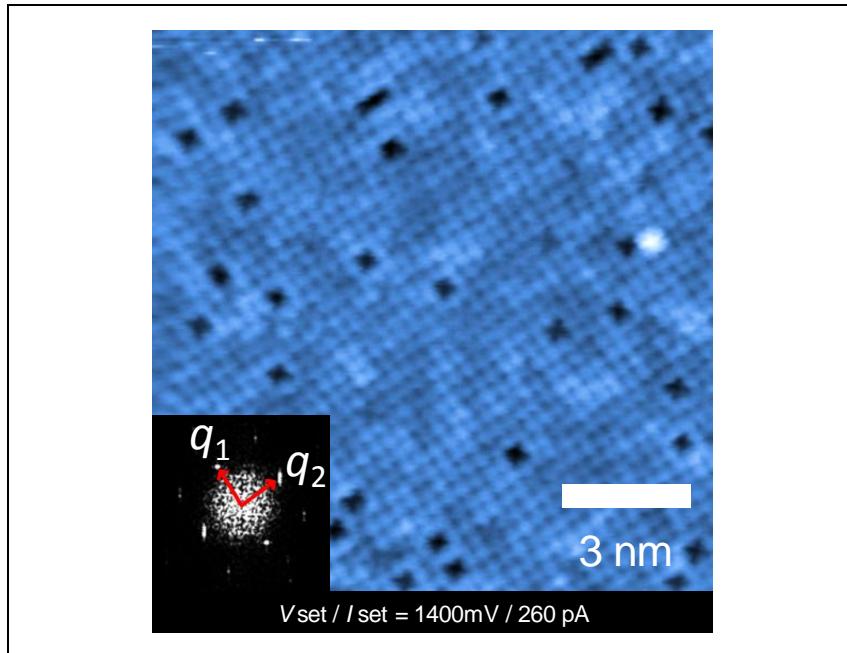


Fig. 3

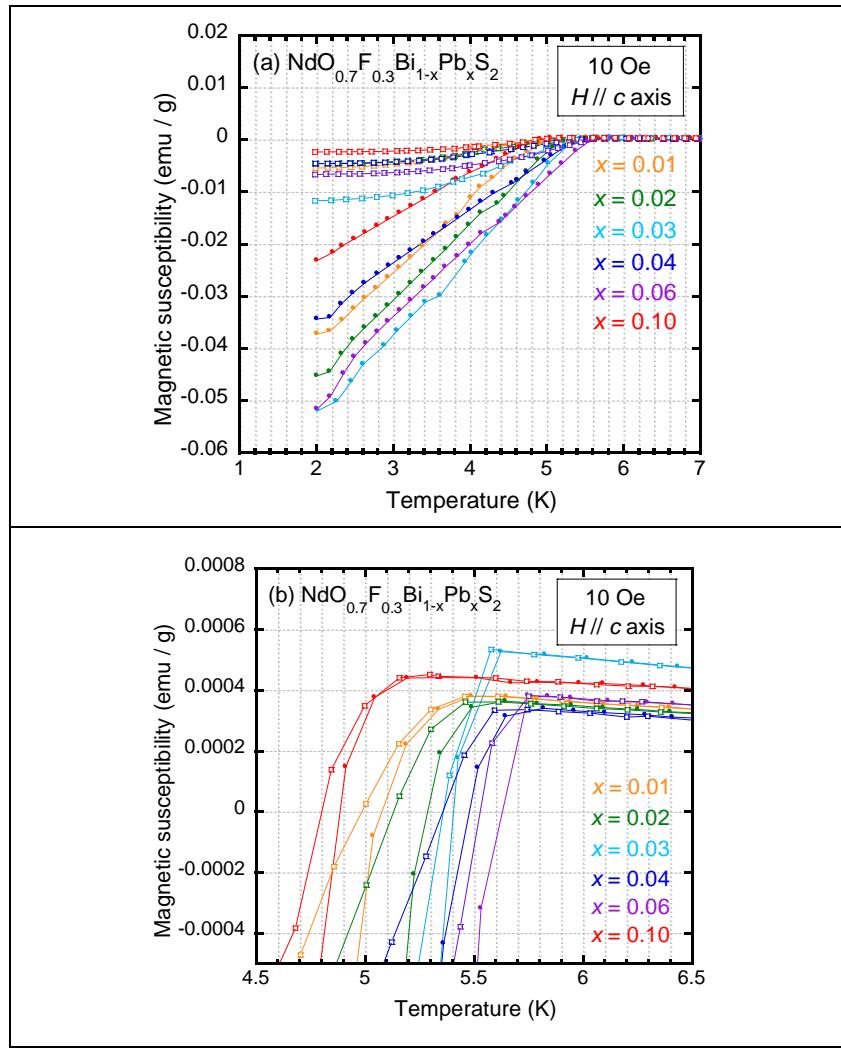


Fig. 4(a,b)

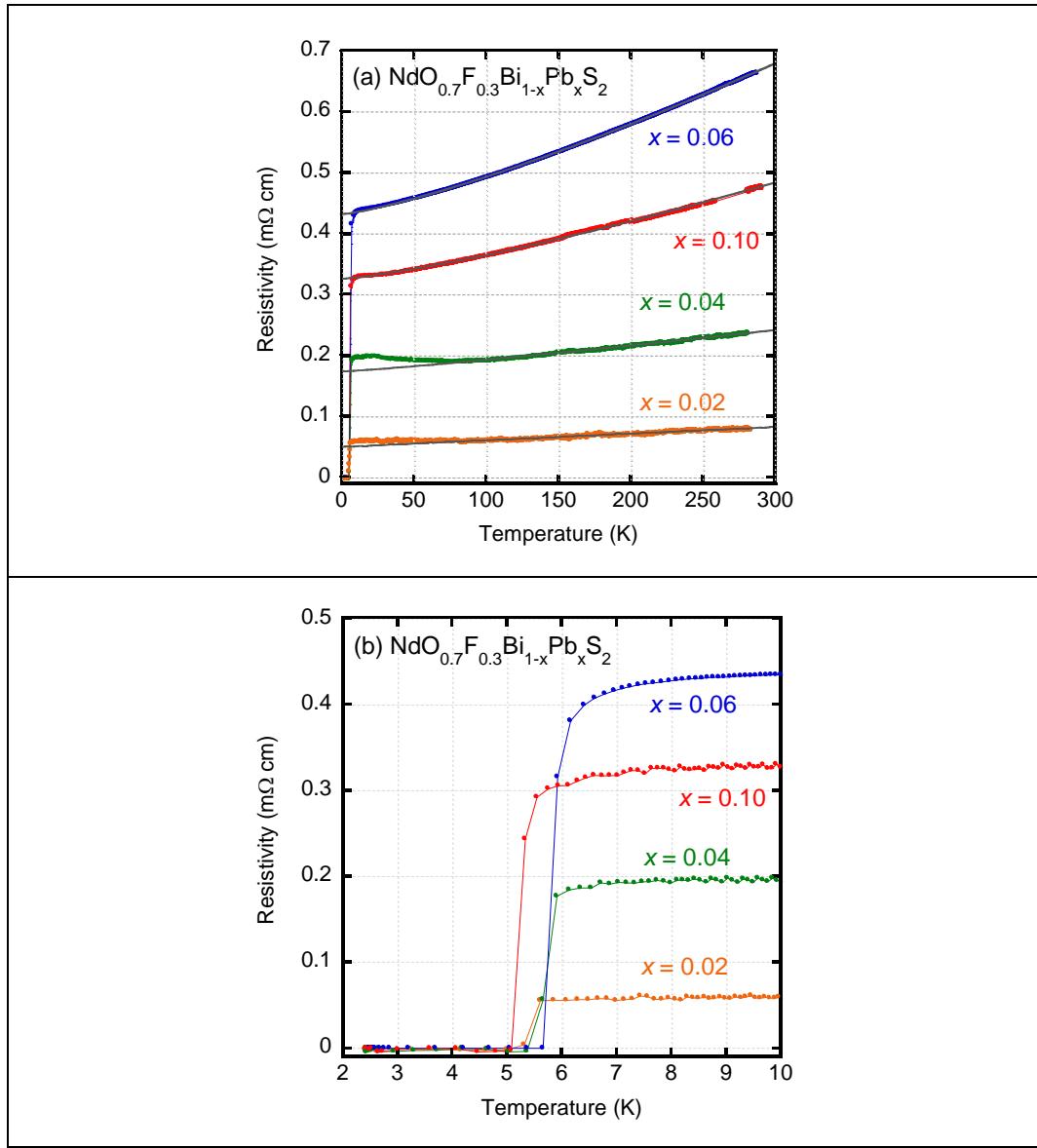


Fig. 5(a, b)

F concentration	0.02	0.04	0.06	0.1
$\rho_{\circ} (\times 10^{-1} \text{ W cm})$	0.49	1.73	4.31	3.25
$A (\times 10^{-4})$	1.20	0.94	1.76	1.08
n	0.98	1.15	1.27	1.28

Table 1

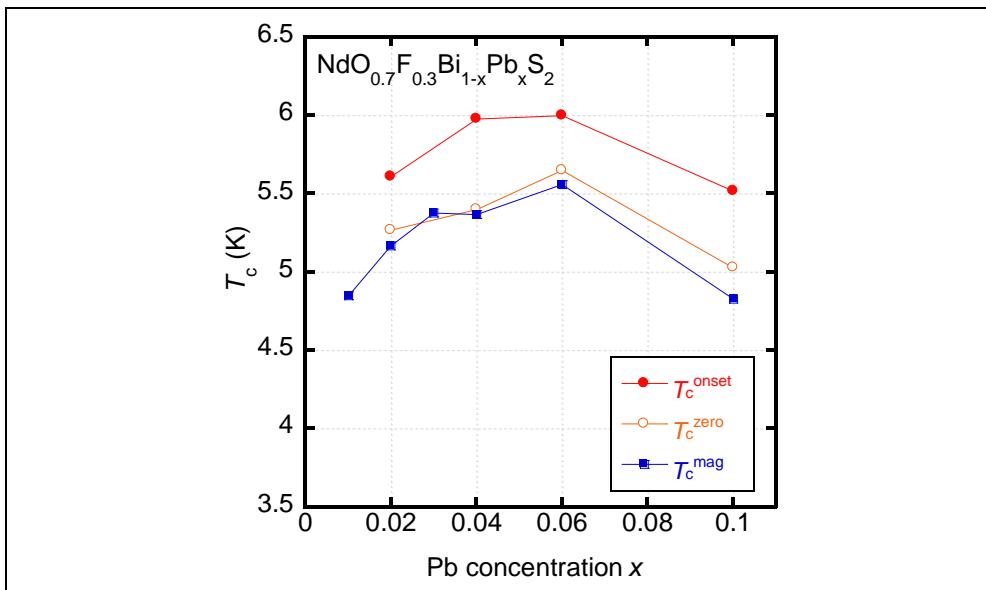


Fig. 6