

Topotactic synthesis of a new BiS₂-based superconductor Bi₂(O,F)S₂

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A new BiS₂-based superconductor Bi₂(O,F)S₂ was discovered. This is a layered compound consisting of alternate stacking structure of rock-salt-type BiS₂ superconducting layer and fluorite-type Bi(O,F) blocking layer. Bi₂(O,F)S₂ was obtained as the main phase by topotactic fluorination of undoped Bi₂OS₂ using XeF₂, which is the first topotactic synthesis of an electron-doped superconductor via reductive fluorination. With increasing F-content, *a*- and *c*-axis length increased and decreased, respectively, and *T_c* increased up to 5.1 K.

Since the discovery of superconductivity in LaFeAs(O,F) with superconducting transition temperature (T_c) of 26 K¹⁾, superconductivity in novel layered compounds have attracted intense attention. Consequently, several new layered superconductors with Ti₂O plane (ex. Ba₂Ti₂Sb₂O with T_c = 1.2 K²⁾), and BiS₂ layer (ex. Bi₄O₄S₃ with T_c = 8.3 K³⁾) are recently discovered. Some of these newly discovered superconductors, such as iron-based superconductors REFeAs(O,F)¹ and BiS₂-based superconductors RE(O,F)BiS₂ (RE = La⁴, Ce⁵, Pr⁶ and Nd⁷), contains fluorite-type RE(O,F) blocking layers. In these cases, undoped REFeAsO and REOBiS₂ does not show superconductivity and partial substitution of F⁻ for the O²⁻ site causes electron-doped superconductivity in the FeAs and BiS₂ layer.

Not only rare earth metals, but also Bi forms fluorite-type BiO layer. Among the BiS₂-based superconductors reported to date, Bi₄O₄S₃³⁾ and Bi₃O₂S₃^{8,9)} contains fluorite-type BiO layer in the blocking layer. In addition, Bi₂OS₂ (i.e. BiOBiS₂) is isostructural with REOBiS₂, consisting of rock-salt-type BiS₂ layer and fluorite-type BiO layer, as shown in **Fig.1**. This compound was synthesized first by Phelan *et al.* in 2013 and reported to be a non-superconductor⁸⁾. However, no further investigation on physical properties of this compound has been reported, while partial substitution of F⁻ for the O²⁻ site of fluorite-type BiO layer might lead to superconductivity.

In general, conventional solid-state reaction has been usually adopted for introduction of fluorine to oxides, where metal fluorides and other raw or precursor materials are mixed at the stoichiometric composition of the objective substance and reacted at high temperatures. On the other hand, various topotactic fluorination reactions have also been reported to date, mainly on transition metal oxides having perovskite-type structures, where precursor oxides reacts on fluorinating agents, such as F₂ gas¹⁰⁾, XeF₂^{11),12)}, NH₄F¹³⁾, MF₂ (M = Ni, Cu, Zn, Ag)¹⁴⁾, poly (vinylidene fluoride) (PVDF)¹⁵⁾, and polytetrafluoroethylene (PTFE)¹⁶⁾. When F⁻ is inserted to the interstitial site of the transition metal oxide, oxidation state of the transition metal increases. This type of reaction; topotactic oxidative fluorination, is sometimes adopted to prepare hole-doped high- T_c cuprates, such as Sr₂CuO₂F_{2+δ}^{10), 12)-14)}. On the contrary, when F⁻ is partially substituted for the O²⁻ site, the oxidation state of transition metal decreases. Synthesis of several oxyfluorides, such as CrOF₃¹¹⁾, RbLaNb₂O₆F¹⁶⁾ and Sr₃Fe₂(O,F)₇¹⁷⁾, were reported via this route, *i.e.* topotactic reductive fluorination, but any superconductors have never been discovered through this method.

In the present Letter, synthesis and properties of F-doped Bi₂OS₂ are reported. Bi₂(O,F)S₂ was successfully synthesized by topotactic reaction between undoped Bi₂OS₂ and XeF₂, and showed superconductivity with T_c = 5.1 K. This is the first topotactic

reductive fluorination resulting in an electron-doped superconductor.

Undoped Bi_2OS_2 was synthesized by the solid-state reaction. Bi_2O_3 (Furuuchi Chemical, 99.9%) and Bi_2S_3 (ALDRICH, 99%) powders were weighed at the stoichiometric composition of Bi_2OS_2 , mixed, pelletized, sealed in an evacuated quartz ampoule and heated at 300~600°C with several times of regrinding process. $\text{Bi}_2(\text{O},\text{F})\text{S}_2$ was prepared by two different methods. The first procedure is simple solid-state reaction. Powders of Bi_2O_3 , Bi_2S_3 , BiF_3 (Kojundo Chemical Laboratory, 99.9%) and Bi (Furuuchi Chemical, 99.9%) were mixed at the nominal compositions of $\text{Bi}_2(\text{O}_{1-x}\text{F}_x)\text{S}_2$ and heated at 300 ~ 500°C for 12 ~ 100 h with intermediate grindings. The second procedure is the topotactic reaction between undoped Bi_2OS_2 and XeF_2 . Undoped Bi_2OS_2 synthesized by solid-state reaction and XeF_2 (Matrix Scientific, 99%) powder were weighed, mixed, pelletized, sealed in an evacuated quartz ampoule and heated at 100 ~ 450°C for 24 ~ 72 h to form $\text{Bi}_2(\text{O},\text{F})\text{S}_2$. Note that during the mixing and pelletizing process, the mixture easily causes explosion thus careful treatment under Ar-filled glove box was mandatory.

The constituent phases of the samples were analyzed by X-ray diffraction (XRD) measurement (RIGAKU Ultima-IV) with $\text{Cu}-K\alpha$ radiation generated at 40 kV and 40 mA. Silicon powder was used as the internal standard to determine the lattice parameters. Measurements of magnetization and resistivity were performed by a SQUID magnetometer (Quantum Design MPMS-XL5s) and by the AC four-probe method using the Quantum Design PPMS, respectively. The thermoelectric power was measured by the steady-state method.

Undoped Bi_2OS_2 polycrystalline bulks with almost single phase were obtained by sintering at 300°C for ~100 h with two or three times of intermediate grindings as shown in **Fig. 2**. The diffraction peaks were well indexed to the space group $P4/nmm$, and the lattice constants were calculated to be $a = 3.961 \text{ \AA}$ and $c = 13.808 \text{ \AA}$. Small amount of impurity phases, such as Bi_2S_3 and Bi, always remained in this study.

$\text{Bi}_2(\text{O}_{1-x}\text{F}_x)\text{S}_2$ was at first synthesized by the conventional solid-state reaction using BiF_3 as a fluorine source. For a sample with $x = 0.3$, $\text{Bi}_2(\text{O},\text{F})\text{S}_2$ formed with a lot of impurity phase of BiOF , Bi_2S_3 and Bi as shown in **Fig. 2**. Lattice constants were calculated to be $a = 3.969 \text{ \AA}$ and $c = 13.769 \text{ \AA}$, which are different from those of undoped Bi_2OS_2 , suggesting partial substitution of F^- for the O^{2-} site. This sample showed large diamagnetic signal below ~4 K in the zero-field-cooled (ZFC) magnetization measurement under 1 Oe. When x is increased to 0.5, the sample contained only BiOF , Bi_2S_3 and Bi. This sample and undoped Bi_2OS_2 sample did not show large diamagnetism above 2 K, while very small diamagnetism without temperature

dependence was observed possibly due to the diamagnetism of Bi, which is not related to superconductivity.

In order to obtain $\text{Bi}_2(\text{O},\text{F})\text{S}_2$ with higher purity and evaluate more intrinsic superconducting properties, we employed different synthesis route; topotactic reaction between undoped Bi_2OS_2 and XeF_2 . We expected that reductive fluorination occurs in the present case according to the following chemical reaction:



Fig. 2 shows the XRD patterns of the samples synthesized via the topotactic reaction at 400°C for 72 h. $\text{Bi}_2(\text{O},\text{F})\text{S}_2$ is obtained as the main phase and amounts of co-existing impurity phases were largely reduced compared to the samples synthesized via conventional solid-state reaction. With an increase in nominal XeF_2 content up to ~30 mol% ($x/2 = 0.3$) of the Bi_2OS_2 , the a -axis length slightly increased while the c -axis length largely decreased. This systematic change of lattice parameter indicates that the fluorine content is successfully varied by changing the nominal XeF_2 content, though investigation of actual fluorine content is difficult due to small difference in X-ray scattering factors between O and F. The actual fluorine concentrations in the samples are considered to be lower than the nominal x , because part of XeF_2 is considered to decompose into gases of Xe and F_2 before reacting with Bi_2OS_2 . Nevertheless, we are sure that partial substitution of F^- for the O^{2-} site occurred in this case, following the reaction equation (1), and oxidation state of Bi is reduced by this reaction. One reason is the systematic changes of lattice parameters as described above. Both topotactic fluorination and fluorine doping via conventional solid-state reaction caused similar change of lattice parameters: expansion of a -axis and contraction of c -axis lengths. Large contraction of c -axis length by F⁻ doping is consistent with the case of other $RE(\text{O},\text{F})\text{BiS}_2$ electron-doped superconductors⁴⁻⁷⁾, suggesting that electron doping is successfully achieved in Bi_2OS_2 by topotactic fluorination. The results of thermoelectric power measurement shown in **Fig. 3** strongly support this idea. Seebeck coefficient of both undoped and topotactically fluorinated Bi_2OS_2 are negative in the temperature range of 4.2 to 300 K and the absolute value of the thermoelectric power significantly decreased in $\text{Bi}_2(\text{O},\text{F})\text{S}_2$. At 300 K, Seebeck coefficient of undoped Bi_2OS_2 is ~70 μVK^{-1} , while that of $\text{Bi}_2(\text{O},\text{F})\text{S}_2$ fluorinated by XeF_2 with 50 mol% of Bi_2OS_2 is ~30 μVK^{-1} , indicating increase of electron type charge carriers.

Fig. 4(a) shows ZFC and field-cooled (FC) magnetization curves of $\text{Bi}_2(\text{O},\text{F})\text{S}_2$ samples with $x/2 = 0.1$ and 0.3 prepared by topotactic fluorination. Since both samples

exhibited very sharp transition and perfect diamagnetism, $\text{Bi}_2(\text{O},\text{F})\text{S}_2$ is concluded to be the bulk superconductor. T_c increases up to 5.1 K as increasing nominal XeF_2 content up to ~ 30 mol% of the undoped Bi_2OS_2 . **Fig. 4(b)** shows the temperature dependence of resistivity measured for a sample with $x/2 = 0.3$. Very sharp superconducting transition within 0.4 K and zero resistivity at 4.8 K is observed under 0 T, while superconductivity is rapidly suppressed in magnetic fields and resistivity drop were not observed above 2 K under 3 T. The behavior of normal state resistivity seems metallic, contrary to the semiconducting behavior observed in polycrystalline samples of $RE(\text{O},\text{F})\text{BiS}_2^{4-7}$. However, our sample contains small impurity of Bi metal, which might affect the normal state resistivity. Therefore, intrinsic behavior of normal state transport of this compound remains unrevealed.

Even when nominal XeF_2 content was increased up to ~ 50 mol% of Bi_2OS_2 , the result was almost the same as the case when nominal XeF_2 content was ~ 30 mol%, probably owing to solubility limit of F⁻ for the O²⁻ site. Changing reaction temperature did not lead to increase of fluorine content. The sample reacted at 200~300°C also showed superconductivity below 4 ~ 5 K. Their superconducting transitions were broader with smaller superconducting volume fraction at ~ 2 K compared to the samples reacted for 400°C, suggesting insufficient substitution of fluorine. The sample reacted at lower than 200°C did not show apparent diamagnetism due to superconductivity. On the other hand, the reaction at 450°C lead to the decomposition of Bi_2OS_2 phase.

The a -axis length of $\text{Bi}_2(\text{O},\text{F})\text{S}_2$ is shorter than other isostructural $RE(\text{O},\text{F})\text{BiS}_2^{4-7}$ and $(\text{Sr},\text{La})\text{FBiS}_2^{18}$. In $RE(\text{O},\text{F})\text{BiS}_2$, a -axis shrinks and T_c increases with increasing atomic number of RE from La to Nd⁴⁻⁷. The T_c of $\text{Bi}_2(\text{O},\text{F})\text{S}_2$ (5.1 K) is higher than those of $RE(\text{O},\text{F})\text{BiS}_2$ with $RE = \text{La} \sim \text{Pr}$ and comparable to that of $\text{Nd}(\text{O},\text{F})\text{BiS}_2$ (5.2 K)⁷. It seems that smaller a -axis length is preferable for higher T_c in $MO\text{BiS}_2$ synthesized under ambient pressure. However, $\text{La}(\text{O},\text{F})\text{BiS}_2$ shows large increase of T_c up to ~ 10 K by annealing under high-pressure⁴. In order to discuss the intrinsic relationship between lattice parameter and T_c , high-pressure studies are necessary.

Synthesis of $\text{Bi}_2(\text{O},\text{F})\text{S}_2$ using XeF_2 is the first example for topotactic synthesis of electron-doped superconductor via reductive fluorination process, while topotactic oxidative fluorination has been used to obtain hole-doped cuprates^{10), 12)-14)}. We think that topotactic reductive fluorination can also be a powerful method to explore other novel superconductors. Besides, researches on topotactic fluorination^{10), 12)-17)} and hydrogenation¹⁹⁾²⁰⁾ have been mainly focused on simple and layered perovskite-related materials, such as Ruddlesden-Popper type layered perovskite oxides, but our result indicate that topotactic reaction can also be applied on layered compounds containing

fluorite-type layer.

In summary, a new member of BiS_2 -based superconductor, $\text{Bi}_2(\text{O},\text{F})\text{S}_2$ with $T_c = 5.1$ K was discovered. Topotactic reductive fluorination using XeF_2 in the temperature range of $200 \sim 400^\circ\text{C}$ was found to be useful for obtaining $\text{Bi}_2(\text{O},\text{F})\text{S}_2$ as the main phase and the reaction at 400°C is suitable for successful control of fluorine content resulting in high quality superconductors with sharp transitions and large superconducting volume fractions. Our synthesis of $\text{Bi}_2(\text{O},\text{F})\text{S}_2$ using XeF_2 is the first topotactic reductive fluorination to obtain an electron-doped superconductor. Topotactic fluorination could be widely used for the control of physical properties in various compounds, including layered compounds with complex stacking structure, and this would be helpful for further exploration of novel superconductors.

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Note added : During editorial process J. Shao *et al.* have reported superconductivity in $\text{Bi}_2(\text{O},\text{F})\text{S}_2^{21)}$, while their sample synthesis method and T_c (3.5 K) are different from ours.

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Figure Captions

Fig.1 Crystal structure of $\text{Bi}_2(\text{O},\text{F})\text{S}_2$. The unit cell is depicted with the solid line.

Fig. 2 Powder XRD patterns of undoped and F-doped Bi_2OS_2 synthesized via solid-state reaction (the lower two lines) and $\text{Bi}_2(\text{O},\text{F})\text{S}_2$ synthesized via topotactic reaction with XeF_2 (the upper two lines).

Fig. 3 Temperature dependence of Seebeck coefficient of $\text{Bi}_2(\text{O},\text{F})\text{S}_2$ synthesized via topotactic reaction with XeF_2 and undoped Bi_2OS_2 .

Fig. 4 Temperature dependence of **(a)** magnetization ($H = 1$ Oe) and **(b)** resistivity of $\text{Bi}_2(\text{O},\text{F})\text{S}_2$ synthesized via topotactic reaction with XeF_2 .

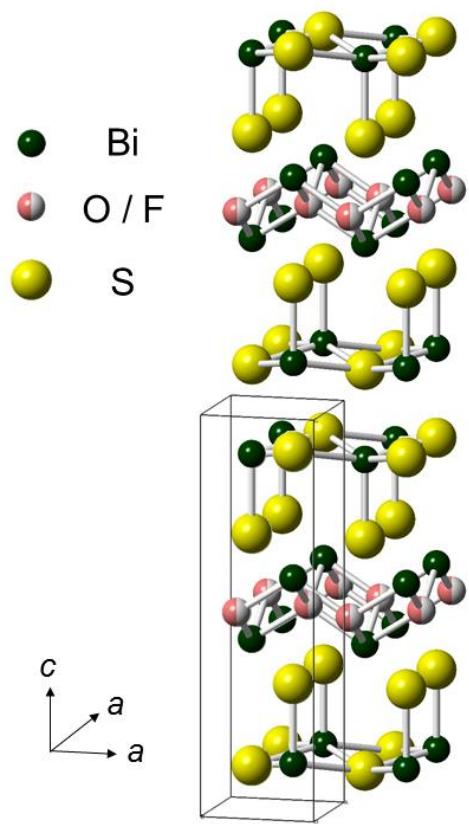


Fig. 1.

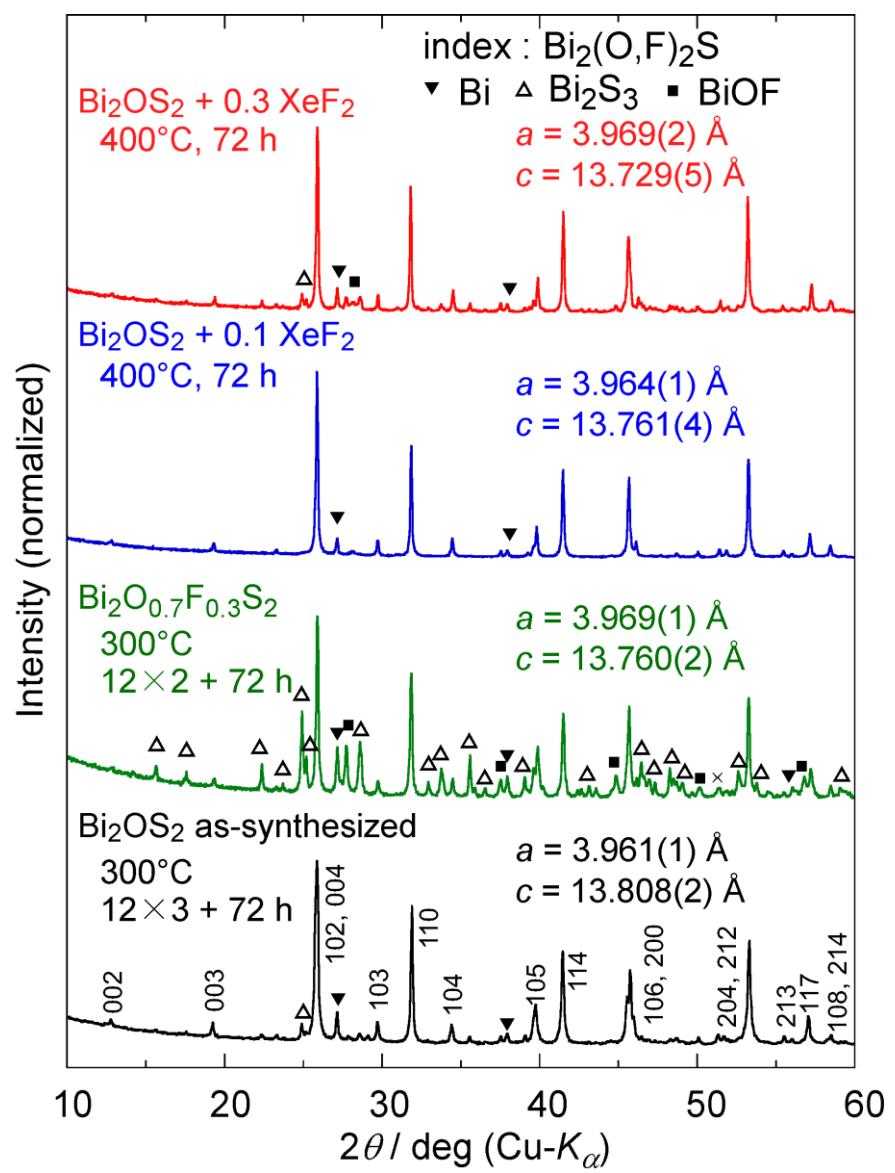


Fig. 2.

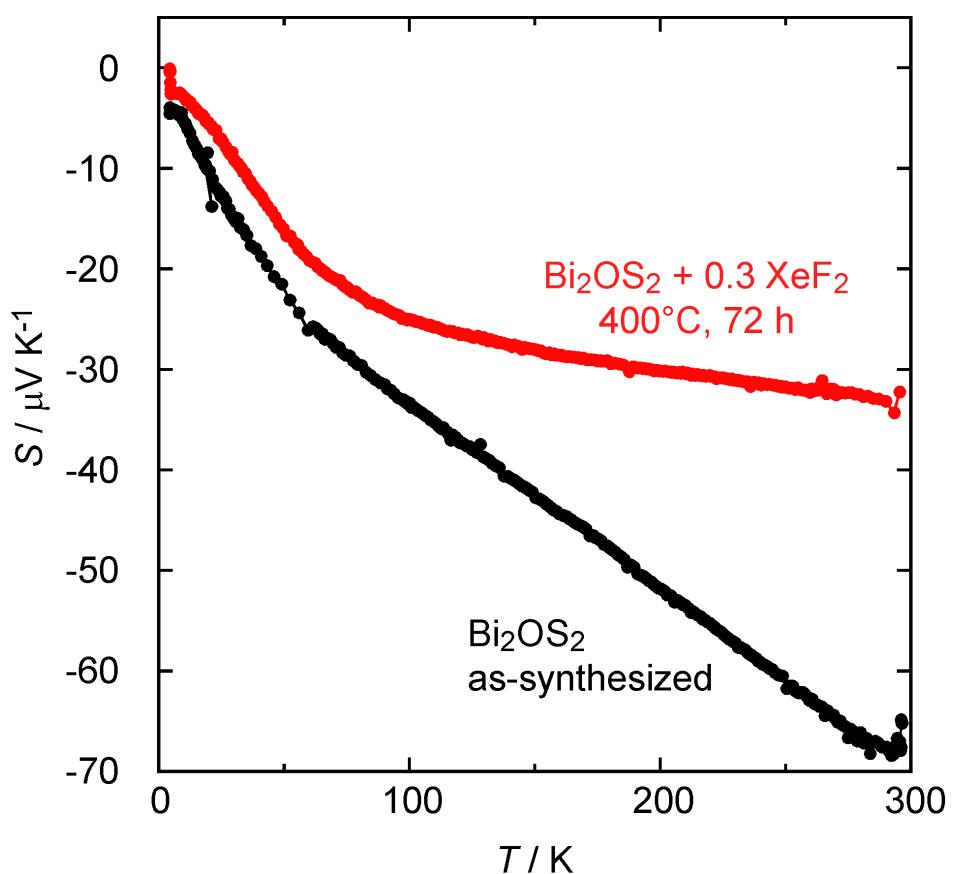


Fig. 3.

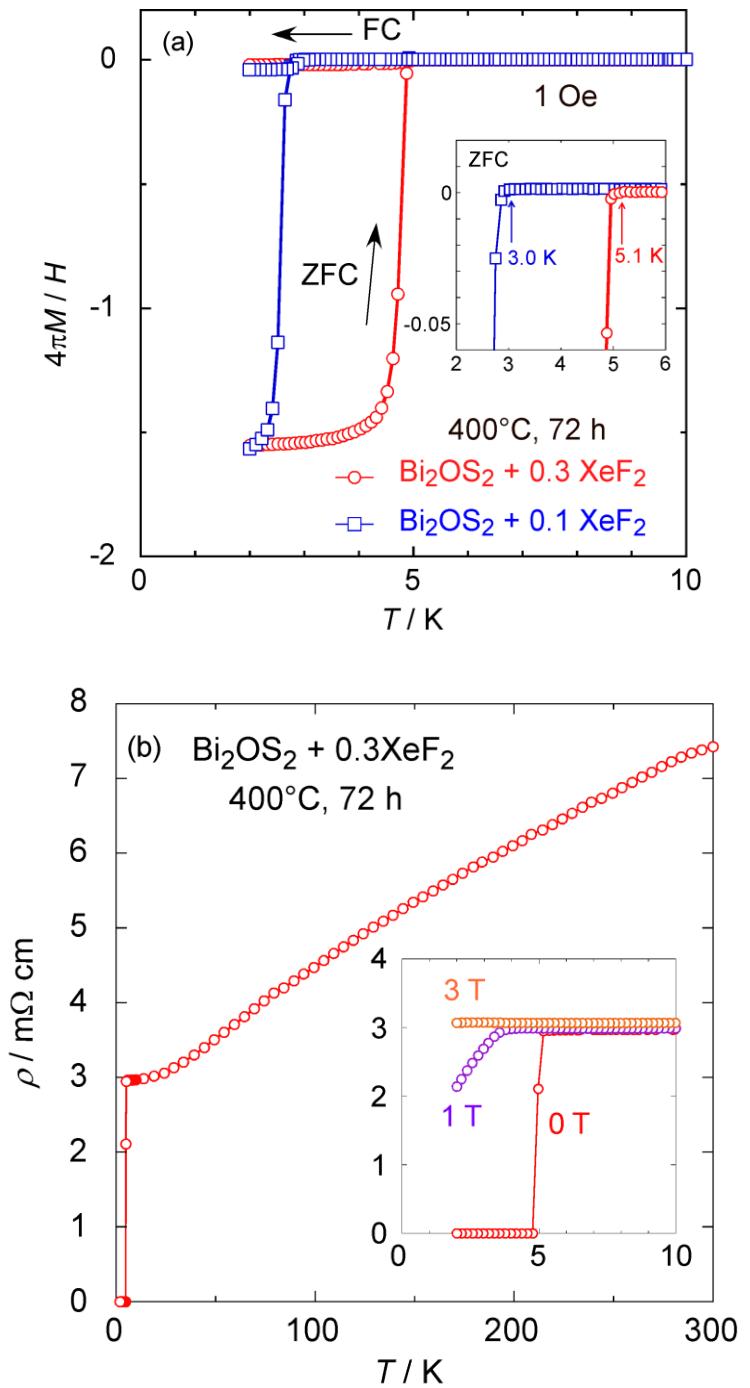


Fig. 4.