Evaluation of Bi defect concentration in LnO$_{1-x}$F$_x$BiCh$_2$ by scanning tunneling microscopy

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Abstract. We examined a concentration of Bi defects in layered BiCh$_2$ based superconductors LnO$_{1-x}$F$_x$BiCh$_2$ (Ln = La, Ce, Nd, Ch = S, Se). These materials show superconductivity by electron carrier doping into BiCh$_2$ layer. Since Bi defects affect the carrier concentration directly, an examination of the concentration is important to evaluate an actual carrier concentration. In this paper, the concentration of Bi defects on the BiCh$_2$ layers in BiCh$_2$ based superconductors was evaluated by scanning tunneling microscopy measurements in real space. We found the samples with BiSe$_2$ layers have less Bi defects than those with BiS$_2$ layers. Furthermore, the concentration of Bi defects was found to be almost constant regardless of F concentration and Ln ion.

1. Introduction

Recently discovered BiS$_2$-based superconductors are attractive materials because they have a similar layered structure to cuprates and iron-based superconductors [1-12]. Among them, LnO$_x$BiS$_2$ (Ln = La, Pr, Ce, Nd, Yb, Bi) shows superconductivity by electron carrier doping by a partial substitution of F ions for O$_2^-$ ions. The superconducting transition temperature ($T_c$) varies with the F concentration. The F concentration is often analysed by an energy dispersive X-ray spectrometry (EDS) or electron probe micro analyser (EPMA). On the other hand, the carrier concentration induced by the substitution of F ions is estimated from a size of Fermi surface observed by an angle resolved photoemission spectroscopy (ARPES) measurement. In LaO$_{1-x}$F$_x$BiS$_2$ and LaO$_{1-x}$F$_x$BiSe$_2$, the carrier concentration estimated from a size of Fermi surface is consistent with those obtained from EDS or EPMA measurements [13, 14]. However, in NdO$_{1-x}$F$_x$BiS$_2$ these values are inconsistent with each other [15, 16]. A suggested reason about this inconsistency is an existence of Bi defects. Indeed, the existence of Bi defects was confirmed by an analysis of the crystal structure and by the scanning tunneling microscopy/spectroscopy (STM/STS) observations [17-19]. However, the density of Bi defects obtained by both techniques was approximately 3%, while the expected concentration from previous EDS report was 15% [15].

Thus, it is important for understanding electronic properties in LnO$_{1-x}$F$_x$BiCh$_2$ to evaluate the concentration of Bi defects. Although, the Bi defect concentration has been evaluated in real space in some samples, a systematic evaluation of the concentration of Bi defects has not been done [18, 19]. The samples that have BiSe$_2$ plane should also be investigated. In this paper, F dependence of Bi defects concentration in NdO$_{1-x}$F$_x$BiS$_2$ was examined. In addition, we examined the concentration of Bi defects in LaO$_{1-x}$F$_x$BiSe$_2$ in real space. We found the samples with BiSe$_2$ layers have less Bi defects than those with BiS$_2$ layers. Furthermore, the concentration of Bi defects was found to be almost constant regardless of F concentration.
2. Experimental

Single crystals of NdO$_{0.1}$F$_{0.9}$BiS$_2$ were synthesized by a CsCl and KCl flux method in vacuumed quartz tubes using Nd$_2$S$_3$, Bi$_2$S$_3$, Bi$_2$O$_3$, BiF$_3$, and Bi as starting materials [21]. A detail of this synthesis procedure is described in reference 21.

Single crystals of LaO$_{0.5}$F$_{0.5}$BiSe$_2$ were synthesized by a CsCl flux method in vacuumed quartz tubes [22-24]. Mixtures of Bi (Mituswa Chemicals Co. Ltd., 99.9%), Se (Kojyundo Chemical Laboratory Co. Ltd., 99.99%), Bi$_2$O$_3$ (Kojyundo Chemical Laboratory Co. Ltd., 99.99%), and BiF$_3$ (Stella Chemifa Co. Ltd., 99%) were ground with nominal compositions of LaO$_{0.5}$F$_{0.5}$BiSe$_2$ except La. After grind, La grains (Rare Metallic Co. Ltd., 99.9 %) were put into this mixture. 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 °C/h. After this thermal process, the sintered materials were washed by distilled water to remove the flux.

The surface structure of single crystals was observed by a laboratory-build scanning tunneling microscope (STM) in the He gas at 4 K. The clean surface was prepared by cleaving the single crystal at 4 K in situ. A bias voltage was applied to the sample in all measurements.

3. Result

Figure 1 shows a typical STM image on a surface of LaO$_{0.5}$F$_{0.5}$BiSe$_2$ single crystal. The observed surface is a BiSe$_2$ plane because of the existence of the cleavage plane between two BiSe$_2$ planes [18, 19]. The observed atoms on the surface are Bi atoms, which form a square lattice with a lattice constant of approximately 0.5 nm. This value almost corresponds to a previous report [22-24].

Bi defects are imaged as black spots as shown in Fig. 1. As in the case of NdO$_{1-x}$F$_x$BiS$_2$ or CeO$_{1-x}$F$_x$BiS$_2$, streaks run along the diagonal directions of Bi square lattice from the defect sites [18, 19]. The observed concentration of Bi defects was approximately 1.0 %. This value is smaller than that observed in BiS$_2$ based superconductors [18, 19]. This result is consistent with the report that BiSe$_2$ based samples have better crystalline than BiS$_2$ based ones [14].

![Figure 1](image-url)
In order to investigate F dependence of the Bi defect concentration in BiS\(_2\) compounds, we examined NdO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\), and obtained the concentration of about 2.5%. Compared with the result in NdO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) [18], the concentration of Bi defects was almost same. This indicates that the concentration of Bi defect is almost independent of F concentration.

In Table 1, we summarized the observed and reported concentration of Bi defects observed by STM measurements. Regardless of Ln, Ch or F concentration, the concentration of Bi defects in LnO\(_1\)\(_x\)F\(_x\)BiCh\(_2\) is in a range between 1 – 3%. The large deviation from this range such as 15% was not observed [15]. Since the defect concentration is almost independent of F concentration, this result certifies that F concentration is proportional to the carrier concentration.

STM measurements examine the Bi defects on the outer most layer that prepared by the cleavage. Because the cleavage may induce the Bi defects on the top most layer, the observed concentration of Bi defects is possibly the upper most one. However, because the cleavage was performed at low temperature of 4.2K, we believe the observed concentration is bulk one, which correspond to the value observed by EDS or EPMA.

Table 1. The summary of the concentration of Bi defects for LnO\(_1\)\(_x\)F\(_x\)BiCh\(_2\).

| F\(_{\text{nominal}}\) | S   | Se  |
|---------------------|-----|-----|
| La      | 0.5 | -   | 1.0 % |
| Ce      | 0.5 | 2.0 % [19] | - |
| Nd      | 0.7 | 3.0 % [19] | - |
|         | 0.3 | 3.0 % [18] | - |
|         | 0.9 | 2.5 % | - |

4. Summary

We examined concentration of Bi defects in layered BiCh\(_2\) based superconductors LnO\(_1\)\(_x\)F\(_x\)BiCh\(_2\) (Ln = La, Ce, Nd Ch = S, Se) by STM measurements in real space. We found the sample with BiSe\(_2\) layer has less Bi defects than that with BiS\(_2\) layers. Furthermore, the concentration of Bi defects was found to be almost constant regardless of F concentration and Ln ion.

Acknowledgements

We are grateful to Dr. T. Machida and Dr. M. Nagao. 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] Mizuguchi Y et al 2012 Phys. Rev. B 86 220510
[2] Mizuguchi Y, Demura S, Deguchi K, Takano Y, Fujihisa H, Gotoh Y, Izawa H and Miura O 2012 J. Phys. Soc. Jpn. 81 114725
[3] Demura S et al 2013 J. Phys. Soc. Jpn. 82 033708
[4] Lei H, Wang K, Abeykoon M, Bozin E S and Petrovic C 2013 Inorg. Chem. 52 10685
[5] Xing J, Li S, Ding X, Yang H and Wen H H 2012 Phys. Rev. B 86 214518
[6] Jha R, Kumar A, Singh S K and Awana V P S 2013 J. Sup. and Novel Mag. 26 499
[7] Yazici D, Huang K, White B D, Chang A H, Friedman A J, Maple M B 2012 Philosophical Magazine 93 673
[8] Yazici D et al Phys. Rev. B 87 174512
[9] Lin X et al 2013 Phys. Rev. B 87 020504
[10] Zhai H F et al Phys. Rev. B 90 064518
[11] Krzton-Maziopa A et al 2014 J. Phys.: Condens. Matter 26 215702
[12] Thakur G S, Selvan G K, Haque Z, Gupta L C, Samal S L, Arumugam S and Ganguli A K 2015 Inorg. Chem. 54 1076
[13] Terashima K et al 2014 Phys. Rev. B 90 220512
[14] Saini N L et al 2014 Phys. Rev. B 90 214517
[15] Ye Z R et al 2014 Phys. Rev. B 90 045116
[16] Zeng L K et al 2014 Phys. Rev. B 90 054512
[17] Miura A, Nagao M, Takei T, Watauchi S, Tanaka I and Kumada N 2014 J. Solid State Chem. 212 213
[18] Machida T, Fujisawa Y, Nagao M, Demura S, Deguchi K, Mizuguchi Y, Takano Y and Sakata H 2014 J. Phys. Soc. Jpn 83 113701
[19] Demura S, Y.Fujisawa Y, Machida T, Nagao M, Takano Y and Sakata H 2016 Phys. Proc. 81 49
[20] Nagao M, Demura S, Deguchi K, Miura A, Watauchi S, Takei T, Takano Y, Kumada N and Tanaka I 2012 J. Phys. Soc. Jpn. 81 103702
[21] Nagao M, Miura A, Demura S, Deguchi K, Watauchi S, Takei T, Takano Y, Kumada N and Tanaka I 2014 Solid. State. Commun. 178 33
[22] Nagao M, Tanaka M, Watauchi S, Tanaka I and Takano Y 2014 J. Phys. Soc. Jpn. 83 114709
[23] Tanaka M, Nagao M, Matsushita Y, Fujioka M, Denholme S J, Yamaguchi T, Takeya H, and Takano Y 2014 J. Solid State Chem. 219 168
[24] Shao J, Liu Z, Yao X, Zhang L, Pi L, Tan S, Zhang C and Zhang Y 2014 Europhysics Lett. 107 37006