Article

Single crystal growth and superconducting properties of Antimony Substituted NdO$_{0.7}$F$_{0.3}$BiS$_2$

Satshi Demura*, Satoshi Otsuki, Yuita Fujisawa and Hideaki Sakata

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

Correspondence: demura@rs.tus.ac.jp; Tel:+81-3-3260-4271(2223)

Abstract: Antimony (Sb) Substitution less than 10 % is examined on a single crystal of a layered superconductor NdO$_{0.7}$F$_{0.3}$BiS$_2$. Superconducting transition temperature of the substituted samples decreases with increasing Sb concentration. A lattice constant along the c axis showed a large decrease compared with that along the a axis. Since in-plane chemical pressure monotonically decreases with increasing Sb concentration, the suppression of the superconductivity is well described in terms of the decrease in in-plane chemical pressure.

Keywords: BiS$_2$-based superconductor; Flux growth; Layered structure; Superconducting Properties; Magnetic susceptibility measurement; Electrical resistivity measurement

1. Introduction

New layered BiS$_2$-based superconductors BiO$_x$S$_y$ and Ln(O,F)BiS$_2$ (Ln=La, Ce, Pr, Nd, Sm, Yb and Bi) have been reported [1-9]. Although a superconducting transition temperature ($T_c$) of Ln(O,F)BiS$_2$ is around 4 K, $T_c$ is increased by introduction of a lattice strain. One of the ways to introduce the lattice strain is a partial element substitution with a different ionic radius into Ln, Bi or S site [12-17]. The strain introduced by the partial element substitution in these crystals is called as chemical pressure. For instance, when Selenium (Se) is partially substituted with Sulfur (S) in the superconducting layer in La(O,F)BiS$_2$, $T_c$ and a superconducting volume fraction increase [10-11]. The substitution into Ln site in the block layer for smaller lanthanide ion also increases $T_c$ [12-14]. The increase in $T_c$ by the element substitution is correlated with in-plane chemical pressure defined by Mizuguchi: $T_c$ increases with increasing in-plane chemical pressure [18]. The change in $T_c$ by the element substitution of Ln or S sites is described by the increase of in-plane chemical pressure. On the other hand, it is not known whether the change in $T_c$ is understood by in-plane chemical pressure when an element is partially substituted into Bi site.

Here, we report on an examination of a substitution of Antimony (Sb) ion less than 10 % into NdO$_{0.7}$F$_{0.3}$BiS$_2$. Since the Sb ion has a same valence as that of Bi ion, an effect of the chemical pressure can be investigated without the effect of the carrier concentration. We found that the lattice constant along the c and a axis of Sb substituted samples decreased. On the other hand, superconductivity was suppressed by the Sb substitution. This suppression by the Sb substitution can be explained by the change of the in-plane chemical pressure.

2. Experiment

NdO$_{0.7}$F$_{0.3}$Bi$_{1-x}$S$_x$(x=0.01-0.10) single crystals were synthesized using a CsCl/KCl flux method in an evacuated quartz tubes [19, 20]. Powders of NdS$_3$, BiO$_x$, BiS$_x$, SbS$_x$ and BiF$_3$ with Bi grains were used as a starting material. The BiS$_x$ powders were prepared by reacting Bi and S grains in an evacuated quartz tube at 500 °C for 10 hours. The mixture of starting materials of 0.8 g and CsCl/KCl powder of 8 g was sealed in the evacuated quartz tube. The tube was heated at 800°C for 10 hours and kept it at 800°C for 10 hours and cooled down to 630°C at the rate of 0.3°C/h or 1°C/h. After this thermal process, the obtained material was washed by distilled water to remove the flux. X-ray diffraction (XRD) patterns using single crystal and powder samples were collected by a Rigaku X-ray diffractometer with Cu Kα radiation using θ-2θ method. These powder samples used in XRD
measurements were prepared by grinding single crystals. Lattice constants along the \( a \) and \( c \) axis are determined by using \( \theta-2\theta \) technique. Temperature dependence of the magnetic susceptibility down to 2 K was measured with MPMS (Magnetic Property Measurement System). Temperature dependence of the electrical resistivity was measured down to 2.5K with four terminals method.

3. Result

Fig. 1(a) shows X-ray diffraction patterns for NdO\(_{0.7}\)F\(_{0.3}\)Bi\(_{1-x}\)Sb\(_x\)S\(_2\) \((x=0.01-0.10)\). All the peaks correspond to the (00l) peaks of CeOBiS\(_2\) type structure with the space group \( P4/nmm \) symmetry. The (004) peaks of these samples are magnified in Fig. 1(b). The peaks are gradually shifted to high angle side with increasing the Sb concentration. This is indicative of success in Sb substitution into NdO\(_{0.7}\)F\(_{0.3}\)Bi\(_{1-x}\)Sb\(_x\)S\(_2\) up to \( x=0.10 \). Fig. 1(c) shows a Sb concentration dependence of the lattice constant along the \( c \) axis. The lattice constant is almost constant up to \( x=0.04 \) and decreases above \( x=0.04 \). The lattice constant along the \( a \) axis shows almost constant until \( x=0.10 \) as depicted in Fig. 1(d). The lattice shrinkage in both axes by the Sb substitution was caused by the difference of ionic radius between Bi and Sb ion as we expected. Next, superconducting properties of these samples were evaluated to investigate an effect of the Sb substitution to the superconductivity.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** XRD patterns and lattice parameters of NdO\(_{0.7}\)F\(_{0.3}\)Bi\(_{1-x}\)Sb\(_x\)S\(_2\) single crystals. (a) XRD patterns from \( x=0.01 \) to 0.10 on the NdO\(_{0.7}\)F\(_{0.3}\)Bi\(_{1-x}\)Sb\(_x\)S\(_2\). (b) Magnified figure near (004) peak in Fig. 1(a). (c, d) Lattice constants along the \( c \) and \( a \) axis for NdO\(_{0.7}\)F\(_{0.3}\)Bi\(_{1-x}\)Sb\(_x\)S\(_2\).
whereas Figure 2 shows the magnetic susceptibility as a function of temperature for NdO$_{0.7}$F$_{0.3}$Bi$_{1-x}$SbxS$_2$ (x=0.01-0.10) at magnetic field of 10 Oe. All samples show diamagnetic signal due to an appearance of superconductivity. A magnitude of $4\pi\chi$ decreases from 1 at x=0.01 to 0.2 at x=0.08, and increase again to 0.6 at x=0.10. In the contrast to the magnitude of $4\pi\chi$, the superconducting transition temperature ($T_c$) monotonously decreases with increasing Sb concentration as shown in Fig. 2(b). In the zero field cooling process, all samples show a broad superconducting transition. This broad transition is often observed in the other Ln(O,F)BiCh$_x$ (Ln=La, Ce, Pr, Nd, Ch=S, Se) [21-25]. Although the reason why the transition is broadened has not been known yet, the broad transition is seemed to be common feature in these materials.

Fig. 3 (b) shows the electrical resistivity near $T_c$ as a function of temperature. Steep drop due to an appearance of superconductivity is observed at around 5.2 K at the sample with x=0.01. The transition temperature decreases with increasing the Sb concentration. At x=0.10, $T_c$ slightly recovers to 5 K. Resistivity at room temperature (RT) continuously increases by Sb substitution as shown in Fig. 3(a). This is because the Sb ion is substituted for Bi ion located in the conduction layers. This increase in resistivity at RT is also observed in Pb substituted Ln(O,F)BiS$_2$ (Ln=La, Nd) [15,16], whereas Pb substitution induced an enhancement of $T_c$. Therefore, an effect of the substitution on superconductivity does not correlate to the strength of the scattering by the substituted atoms.
Fig. 4(a) shows a summary of the observed $T_c$. Here, $T_c^{\text{zero}}$ is defined as a temperature at which magnetic susceptibility begins to decrease. $T_c^{\text{onset}}$ and $T_c^{\text{zero}}$ are defined as a temperature at which resistivity begins to decrease and the temperature where resistivity becomes zero. All $T_c$ monotonically decrease with an increase of the Sb concentration except for $x=0.1$.

Mizuguchi et al. reported that $T_c$ of BiCh$_2$ superconductors is correlated with in-plane chemical pressure [18]. To compare the result in Sb substituted samples with the previous report, we estimated in-plane chemical pressure for NdO$_{0.7}$F$_{0.3}$Bi$_{1-x}$Sb$_x$S$_2$. In-plane chemical pressure is defined by the ionic radius of Bi and chalcogenide ion, and a distance between Bi and chalcogenide ion located in BiCh$_2$ plane. In the case of Sb substitution, this in-plane chemical pressure is defined as following:

$$\text{In-plane chemical pressure} = \left((1-x)R_{\text{Bi}^+} + xR_{\text{Sb}^+} + R_{\text{Ch}^2}\right) / \text{Bi–Ch1(in-plane) distance}$$

where $R_{\text{Bi}}$ is an ionic radius of Bi ion. In this study, the ionic radius of Bi ion was obtained from the structural data of the LaO$_{0.7}$F$_{0.3}$Bi$_2$ single crystal [26]. Thus, the value of $R_{\text{Bi}}$ was 104.75 pm, which is the almost same value as that in the previous report [18]. $R_{\text{Sb}}$ and $R_{\text{Ch}}$ are ionic radii of Sb$^{\text{3+}}$ and Ch$^2$ ions, respectively. These values were determined as 76 and 184 pm from a reference [27]. The Bi-Ch1 distance was estimated by the lattice constant along the a axis in this study. Since the lattice constant along the a axis corresponds to the length of a side of the Bi square lattice, we use $\sqrt{2}$ times of the lattice constant along the a axis as the Bi-Ch1 distance. Fig. 4(b) shows the estimated in-plane chemical pressure dependence of $T_c^{\text{onset}}$, $T_c^{\text{mag}}$ and $T_c^{\text{zero}}$, shown in squares, filled circles and open circles, respectively. Except for $T_c^{\text{onset}}$ and $T_c^{\text{zero}}$ in $x=0.1$ sample, $T_c$ of all samples decreases with the decrease in in-plane chemical pressure. From this result, $T_c$ in the Sb substituted materials are positively correlated to in-plane chemical pressure. To compare this result and the results in Ce$_2$Nd$_{1-x}$O$_{0.5}$F$_{0.5}$BiS$_2$ and Nd$_2$Sm$_{1-x}$O$_{0.5}$F$_{0.5}$BiS$_2$ in Ref. 14, $T_c$ of Ce$_2$Nd$_{1-x}$O$_{0.5}$F$_{0.5}$BiS$_2$ and Nd$_2$Sm$_{1-x}$O$_{0.5}$F$_{0.5}$BiS$_2$ were superimposed in Fig. 4(b), which are shown in triangles. $T_c$ in these materials shows almost close change against in-plane chemical pressure. Thus, our result is qualitatively consistent with the previous results in Ref. 14. In addition, these results suggest the concept of in-plane chemical pressure is valid in the case of substitution not only at Ln site in the blocking layer, but also at Bi site in the conduction layer.

In this study, the in-plane chemical pressure is estimated by the lattice constant along a axis. On the other hand, the in-plane chemical pressure in Ref. 14 is estimated by the Bi-Ch1 distance obtained by the data of the single crystal analysis. To compare the difference of these estimated in-plane chemical pressure, both value is estimated by using the data of the single crystal analysis the Ref. 28. The in-plane chemical pressure estimated by the Bi-Ch1 distance is plotted as open triangle, while that estimated by the a axis is plotted as the reversed triangle in Fig. 4(b). The later one slightly has the higher value in comparison with the former one. However, since this value is located at the
extrapolated line of the Tc of Sb-substituted samples, this estimation is reasonable to estimate the
in-plane chemical pressure qualitatively.

$T_{\text{onset}}$ and $T_{\text{zero}}$ in in x=0.10 sample determined by electric resistivity measurements deviate
from the $T_c$ vs. in-plane chemical pressure relation in other samples. One possible reason of this result
is the distribution of the Sb concentration. An electrical resistivity measurement is sensitive to high
conductivity pass showing the highest $T_c$ even though such a region is quite small. In this study, $T_c$
decreases with increasing the Sb concentration. Therefore, the miner region with the low Sb
concentration is expected to coexist with the major region with the high Sb concentration. To reveal
this deviation and the expectation, the further spatial composition analysis is needed.

Finally, we compare this effect of the Sb substitution with the effect of the Pb substitution in
NdO$_{1-x}$F$_x$Bi$_2$S: because this Pb ion is expected to be substituted into Bi site. The Sb substation
suppresses the superconductivity. This suppression is understood by the decrease of the in-plane
chemical pressure described by this paper. On the other hand, Pb substitution increases $T_c$ up to 6 K.

The in-plane chemical pressure of Pb substituted samples is almost constant because an ionic radius
of Pb$^{2+}$ ion is almost same as that of Bi$^{2+}$ ion calculated by the single crystal analysis. The ionic radius
of Pb$^{2+}$ ion is 100 pm [29]. If Pb ion is substituted until x=0.10, $R_{\text{Bi+}}$ is around 103.8 pm which is
almost same value of the ionic radius of Bi$^{2+}$ ion of 104.75 pm. This indicates $T_c$ of Pb substituted
samples is independent with the value of the in-plane chemical pressure.

4. Summary

The examination of Sb substitution less than 10 % is performed on NdO$_{1-x}$F$_x$Bi$_2$S. The Sb
substitution caused the decrease in lattice constants along the a and the c axis, and the decrease in $T_c$
and superconducting volume fraction. The deterioration by these superconducting properties by the
partial Sb substitution into Bi site is explained in terms of the decrease of the in-plane chemical
pressure, indicating of the usefulness of in-plane chemical pressure in BiCl$_2$ superconductor.

Acknowledgements: This work was partly supported by a Grant-in-Aid for Young Scientists (B) No. 15K17710
and the Nanotech Career-up Alliance (Nanotech CUPAL).

References

   (2012).
4. V. P. S. Awana, Anuj Kumar, Rajveer Jha, Shiva Kumar Singh, Anand Pal, Shruti, J. Saha, S. Patnaik, Solid
   033708.
   40-44.
163 16  S. Demura et al, in preparation