Article

Single crystal growth and superconducting properties of Antimony Substituted $NdO_{0.7}F_{0.3}BiS_2$

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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 $Bi_4O_4S_3$ 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

$NdO_{0.7}F_{0.3}Bi_{1-x}Sb_xS_2$($x$=0.01-0.10) single crystals were synthesized using a CsCl/KCl flux method in an evacuated quartz tubes [19, 20]. Powders of Nd_2S_3, Bi_2O_3, Bi_2S_3, Sb_2S_3 and BiF_3 with Bi grains were used as a starting material. The Bi_2S_3 powders were prepared by reacting Bi and S grains in an evacuated quartz tube at 500 ˚C for 10 hours. The mixture of staring 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

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measurements were prepared by grinding single crystals. Lattice constants along the *a* and *c* axis are determined by using θ-2θ 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 $NdO_{0.7}F_{0.3}Bi_{1-x}Sb_xS_2$ (x=0.01-0.10). All the peaks correspond to the (00*l*) peaks of $CeOBiS_2$ type structure with the space group *P*4/*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 $NdO_{0.7}F_{0.3}BiS_2$ 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.

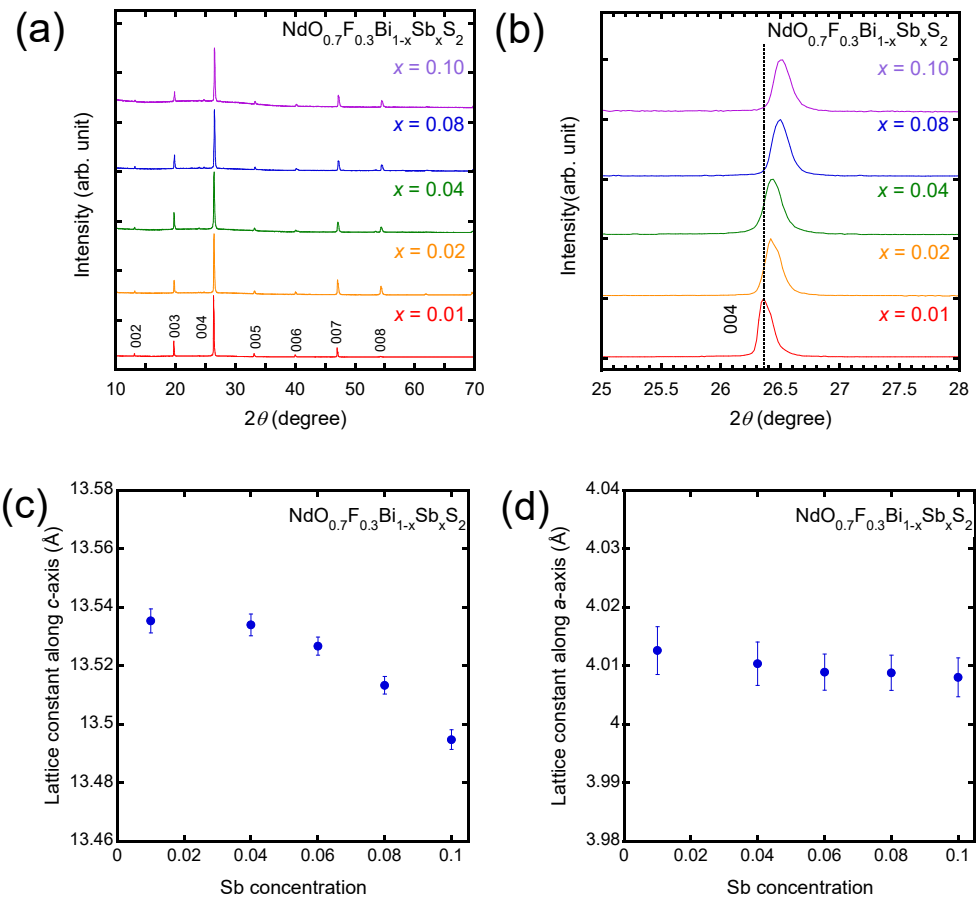

Figure 1. XRD patterns and lattice parameters of $NdO_{0.7}F_{0.3}Bi_{1-x}Sb_xS_2$ single crystals. (**a**) XRD patterns from x=0.01 to 0.10 on the $NdO_{0.7}F_{0.3}Bi_{1-x}Sb_xS_2$. (**b**) Magnified figure near (004) peak in Fig. 1(a). (**c, d**) Lattice constants along the *c* and *a* axis for $NdO_{0.7}F_{0.3}Bi_{1-x}Sb_xS_2$.

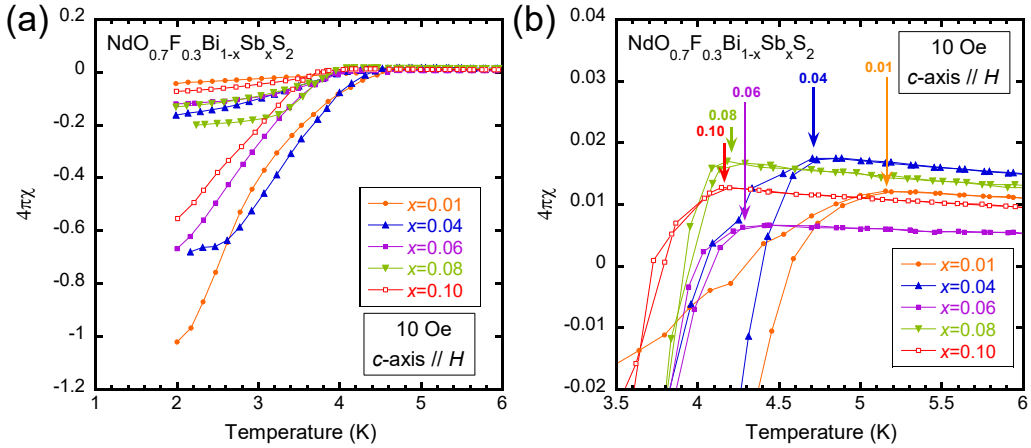

Figure 2. Magnetic susceptibility for $NdO_{0.7}F_{0.3}Bi_{1-x}Sb_xS_2$ as a function of Temperature. (**a**) Temperature dependence of magnetic susceptibility for $NdO_{0.7}F_{0.3}Bi_{1-x}Sb_xS_2$ from 1K to 6K. (**b**) The magnetic susceptibility near the superconducting transition for $NdO_{0.7}F_{0.3}Bi_{1-x}Sb_xS_2$.

Fig. 2 (a) and (b) show magnetic susceptibility as a function of temperature for $NdO_{0.7}F_{0.3}Bi_{1-x}Sb_xS_2$ (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)Bi*Ch*$_2$ (*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.

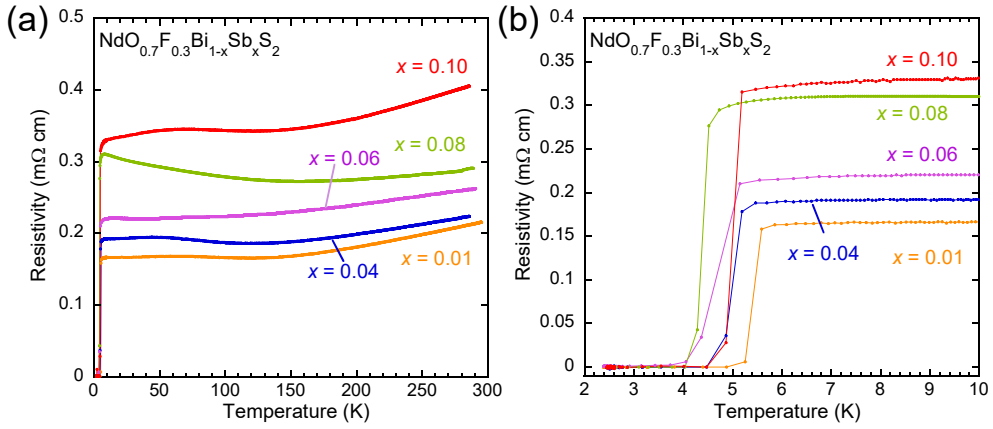

Figure 3. Temperature dependence of electrical resistivity for $NdO_{0.7}F_{0.3}Bi_{1-x}Sb_xS_2$. (a) Temperature dependence of electrical resistivity for $NdO_{0.7}F_{0.3}Bi_{1-x}Sb_xS_2$ (x=0.01-0.10) from 2K to 300K. (b) Temperature dependence of electrical resistivity for $NdO_{0.7}F_{0.3}Bi_{1-x}Sb_xS_2$ (x=0.01-0.10) from 2K to 10K.

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.

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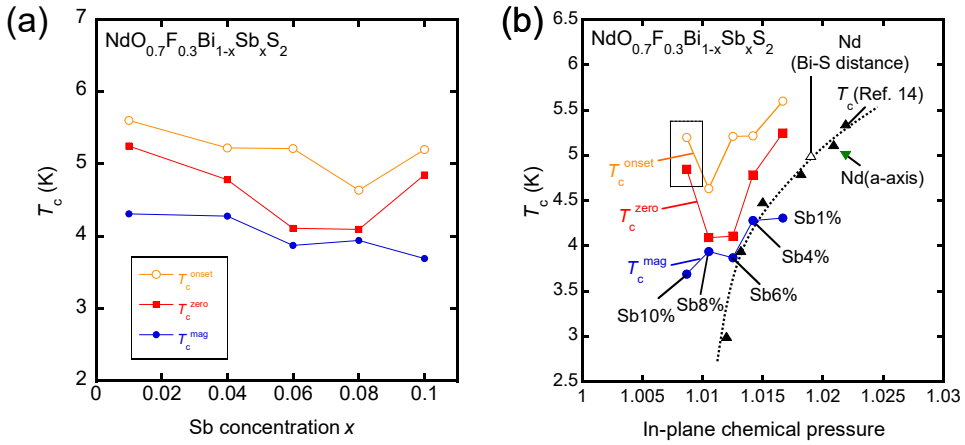

Figure 4. (a) Sb concentration x dependence of T_c for $NdO_{0.7}F_{0.3}Bi_{1-x}Sb_xS_2$. (b) Estimated in-plane chemical pressure dependence of T_c for $NdO_{0.7}F_{0.3}Bi_{1-x}Sb_xS_2$. T_c of $(Ce,Nd)O_{0.5}F_{0.5}BiS_2$ and $(Nd,Sm)O_{0.5}F_{0.5}BiS_2$ is plotted as the triangles, which is fitted by hand as shown in the dot-line [14].

Fig. 4(a) shows a summary of the observed T_c. Here, T_c^{mag} is defined as a temperature at which magnetic susceptibility begins to decrease. T_c^{onset} and T_c^{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 $NdO_{0.7}F_{0.3}Bi_{1-x}Sb_xS_2$. 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:

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

where R_{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 $LaO_{0.77}F_{0.23}BiS_2$ single crystal [26]. Thus, the value of R_{Bi} was 104.75 pm, which is the almost same value as that in the previous report [18]. R_{Sb} and R_{Ch} are ionic radiuses of Sb^{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 $1/\sqrt{2}$ 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^{onset}, T_c^{mag} and T_c^{zero}, shown in squares, filled circles and open circles, respectively. Except for T_c^{onset} and T_c^{zero} in x=0.10 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 $Ce_yNd_{1-y}O_{0.5}F_{0.5}BiS_2$ and $Nd_ySm_{1-y}O_{0.5}F_{0.5}BiS_2$ in Ref. 14, T_c of $Ce_yNd_{1-y}O_{0.5}F_{0.5}BiS_2$ and $Nd_ySm_{1-y}O_{0.5}F_{0.5}BiS_2$ 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 platted as the inversed 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_c^{onset} and T_c^{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 $NdO_{0.7}F_{0.3}BiS_2$ 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 $Bi^{+2.7}$ 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_{Bi}+R_{Pb} is around 103.8 pm which is almost same value of the ionic radius of $Bi^{2.7+}$ 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 $NdO_{0.7}F_{0.3}BiS_2$. 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 BiCh_2 superconductor.

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