BiS$_2$ - based superconductivity in F-substituted NdOBiS$_2$

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Abstract

We have successfully synthesized a new BiS$_2$-based superconductor NdOBiS$_2$ with F-doping. This compound is composed of superconducting BiS$_2$ layers and blocking NdO layers, which indicates that the BiS$_2$ layer is the one of the common superconducting layers like the CuO$_2$ layer of cuprates or Fe-As layer of Fe-based superconductors. We can obtain
NdO$_{1-x}$F$_x$BiS$_2$ with bulk superconductivity by a solid-state reaction under ambient pressure. Therefore, NdO$_{1-x}$F$_x$BiS$_2$ should be the suitable material to elucidate the mechanism of superconductivity in the BiS$_2$-layer.
Quite recently, Y. Mizuguchi et al. reported superconductivity in the novel BiS$_2$-based superconductor Bi$_4$O$_4$S$_3$ with a superconducting transition temperature ($T_c$) of 8.6 K [1]. This material has a layered structure composed of superconducting BiS$_2$ layers and blocking layers of Bi$_4$O$_4$(SO$_4$)$_{1-x}$, where $x$ indicates the defects of SO$_4^{2-}$ ions at the interlayer sites. The stacking structure of the superconducting and blocking layer is analogous to those of high-$T_c$ cuprates [2-5] and Fe-based superconductors [6-14]. In both systems, their $T_c$ can be enhanced by changing the blocking layers. In order to enhance the $T_c$ of the BiS$_2$-based superconductor, the investigation of exchanging the blocking layer will be of great interest.

Soon after the discovery of Bi$_4$O$_4$S$_3$, a new BiS$_2$-based superconductor LaO$_{1-x}$F$_x$BiS$_2$ was reported [15]. This compound consists of the same superconducting layer but with different blocking layers compared to that of Bi$_4$O$_4$S$_3$. Furthermore, the superconductivity shows a relatively high $T_c$ of 10.6 K. This fact suggests that the BiS$_2$ layer is the common superconducting layer, and the blocking layer contributes to the enhancement of the $T_c$ in this system. LaO$_{1-x}$F$_x$BiS$_2$ shows a small superconducting volume fraction for ambient pressure but achieves bulk superconductivity under high pressure. This result suggests that high pressure would promote F substitution. Therefore, chemical pressure for the exchange of La by Nd possibly induces the promotion of F substitution. Here, we report that a new BiS$_2$-based superconductor NdO$_{1-x}$F$_x$BiS$_2$ ($x = 0.1 - 0.7$) can be obtained by a solid-state reaction under ambient pressure.
The polycrystalline samples of NdO$_{1-x}$F$_x$BiS$_2$ ($x = 0.1\text{-}0.7$) were prepared by a solid-state reaction. Mixtures of Bi grains, Bi$_2$S$_3$ grains, Nd$_2$O$_3$ powders, Nd$_2$S$_3$ powders, and NdF$_3$ powders with nominal compositions of NdO$_{1-x}$F$_x$BiS$_2$ ($x = 0.1\text{-}0.7$) were ground, pelletized, and sealed into an evacuated quartz tube. The tube was heated at 800 °C for 10 h. The obtained samples were characterized by X-ray diffraction with Cu-K$\alpha$ radiation using the $\theta$-2$\theta$ method. The temperature dependence of magnetization was measured by a superconducting quantum interface device (SQUID) magnetometer with an applied field of 1 Oe. The resistivity measurements were performed using the four-terminal method from 300 to 2 K. In order to investigate an upper critical field of NdO$_{1-x}$F$_x$BiS$_2$, the temperature dependence of resistivity between 10 and 2 K was measured under a magnetic field of up to 7 T.

Figure 1(a) shows the X-ray diffraction profile for the powdered samples of NdO$_{1-x}$F$_x$BiS$_2$ ($x = 0.1\text{-}0.7$). With the exception of a few minor peaks relating to impurity phases, all of the peaks can be characterized to space group $P4/nmm$. The nominal $x$ dependence of the lattice constants $a$ and $c$ is summarized in Fig. 1(b) and (c). These lattice constants were estimated from 2$\theta$ values and Miller indices. The $a$ lattice constant exhibits little change with increasing $x$ while the $c$ lattice constant dramatically decreases. The decrease of the lattice parameter $c$ indicates that F substitutes O since the ionic radius of F is smaller than that of O.
Figure 2(a) shows the temperature dependence of magnetic susceptibility for NdO$_{1-x}$F$_x$BiS$_2$ ($x = 0.1 - 0.7$). A superconducting transition is observed for all samples. These samples with $x = 0.1 - 0.6$ exhibit a high shielding volume fraction exceeding 90 % (2 K, ZFC), indicating the appearance of bulk superconductivity in those samples. The $x$ dependence of $T_c$ is plotted in Fig. 2(b). The $T_c$ varies like a bell curve with increasing $x$. The NdO$_{0.7}$F$_{0.3}$BiS$_2$ sample exhibits the optimal $T_c$ of all samples.

The temperature dependence of the resistivity for NdO$_{0.7}$F$_{0.3}$BiS$_2$ is shown in Fig. 3. Resistivity slightly decreases between 300 and 130 K. Below 130 K, resistivity gradually increases and the superconducting transition appears around 6 K. This behavior, where the resistivity increases with decreasing temperature is also observed in LaO$_{1-x}$F$_x$BiS$_2$. The onset and zero-resistivity temperatures are estimated to be $T_{c \text{onset}} = 5.6$ K and $T_{c \text{zero}} = 5.2$ K, respectively. Figure 4(a) shows the temperature dependence of the resistivity from 10 to 2 K under a magnetic field. The $T_c$ of NdO$_{0.7}$F$_{0.3}$BiS$_2$ decreases with increasing magnetic field. The upper critical field ($B_{c2}$) and the irreversibility field ($B_{irr}$) are plotted in Fig. 4(b). The $B_{c2}(0)$ was estimated to be 5.2 T with the data points at 0.4 ~ 2.0 T using the WHH theory, which gives $B_{c2}(0) = -0.69T_c(dB_{c2}/dT)|_{T_c}$ [16].

In conclusion, the BiS$_2$-based superconductor NdO$_{1-x}$F$_x$BiS$_2$ ($x = 0.1 - 0.7$) has been successfully synthesized by a solid-state reaction method. Chemical pressure promotes the F substitution, which originated from the exchange of La by Nd. As a result, NdO$_{1-x}$F$_x$BiS$_2$ with
bulk superconductivity can be obtained under ambient pressure. These results demonstrate that the BiS$_2$ layer is the common superconducting layer. Thus, if we synthesize materials with the stacking structure consisting of the BiS$_2$ layer and other blocking layers, new superconductors with the BiS$_2$-layer would be discovered.

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Figure caption

Fig. 1

(a) X-ray diffraction patterns of NdO$_{1-x}$F$_x$BiS$_2$ ($x = 0.1 - 0.7$). Filled circles indicate the peaks of the impurity phases. (b) and (c) show the nominal $x$ dependence of the lattice constants $a$ and $c$, respectively.

Fig. 2

(a) The temperature dependence of the magnetic susceptibility for NdO$_{1-x}$F$_x$BiS$_2$ ($x = 0.1 - 0.7$).

(b) The F concentration dependence of the superconducting transition temperature for NdO$_{1-x}$F$_x$BiS$_2$ ($x = 0.1 - 0.7$).

Fig. 3

The temperature dependence of resistivity for NdO$_{0.7}$F$_{0.3}$BiS$_2$ between 300 and 2 K.

Fig. 4

(a) The temperature dependence of the resistivity from 10 to 2 K under magnetic fields

(b) Magnetic field – temperature phase diagram for NdO$_{0.7}$F$_{0.3}$BiS$_2$. The dashed lines are liner fits to the data.
Fig. 1(a). S. Demura
Fig. 1(b). S. Demura

\[ \text{NdO}_{1-x} \text{F}_x \text{BiS}_2 \]

\( a \) (Å) vs. nominal \( x \)
Fig. 1(c). S. Demura
Magnetic susceptibility (emu / cm$^3$)

Temperature (K)

Fig. 2(a) S. Demura
Fig. 2(b) S.Demura
Fig. 3 S. Demura

NdO$_{0.7}$F$_{0.3}$BiS$_2$

$T_c \sim 5.6$ K

Resistivity (mΩcm)

Temperature (K)
Fig. 4 S. Demura

NdO$_{0.7}$F$_{0.3}$BiS$_2$

Resistivity (mΩcm) vs. Temperature (K) for different magnetic fields (0 T, 0.4 T, 0.8 T, 1.2 T, 1.6 T, 2.0 T, 2.5 T, 3.0 T, 4.0 T).
Fig. 4(b) S. Demura