

# Importance of uniaxial compression for the appearance of superconductivity in $\text{NdO}_{1-x}\text{F}_x\text{BiS}_2$

Omachi A, Hiroi T, Kajitani J, Miura O and Mizuguchi Y

Tokyo Metropolitan University, 1-1, Minami-osawa, Hachioji, 192-0397, Japan

mizugu@tmu.ac.jp

**Abstract.** We have investigated the crystal structure and superconducting properties of the new layered superconductor  $\text{NdO}_{1-x}\text{F}_x\text{BiS}_2$ . Bulk superconductivity with a  $T_c$  above 4.5 K was observed. It was found that the  $T_c$  depended on both F concentration and crystal structure. Uniaxial compression along the  $c$  axis upon F substitution seemed to be linked with the appearance of bulk superconductivity. Furthermore, we considered that a higher  $T_c$  can be achieved when the  $c/a$  parameter was optimized in the  $\text{NdO}_{1-x}\text{F}_x\text{BiS}_2$  system.

## 1. Introduction

Layered materials have been actively studied in the field of superconductivity because superconductors with unconventional pairing mechanisms and/or high transition temperature ( $T_c$ ) had been discovered in layered crystal structures. Recently, we have reported superconductivity in several layered materials possessing a  $\text{BiS}_2$ -type superconducting layer [1,2]. The crystal structure composed of an alternate stacking of the  $\text{BiS}_2$  superconducting layers and blocking layers is quite similar to those of the Cu-oxide and Fe-based superconductors. So far, three structure types of  $\text{BiS}_2$ -based materials,  $\text{Bi}_4\text{O}_4\text{S}_3$ , REOBiS<sub>2</sub> family (RE = La, Ce, Pr, Nd, Yb) and SrFBiS<sub>2</sub>, have found to become superconducting upon electron doping into the Bi-6*p* orbitals within the  $\text{BiS}_2$  layers [1-9]. Electrical resistivity measurements under high pressure revealed that the  $T_c$  of  $\text{BiS}_2$ -based family was sensitive to application of pressure and can be largely enhanced [10-12] as observed in the Fe-based family [13]. Furthermore, the superconducting properties of  $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$  strongly depended on the sample preparation method; polycrystalline samples prepared with post-annealing at high pressure showed a  $T_c$  above 10 K while the sample prepared solid-state reaction in an evacuated quartz tube showed lower  $T_c$  of 2.5 K and low shielding volume fraction [14]. These facts indicate that the appearance of a higher  $T_c$  requires optimization of local crystal structure in the  $\text{BiS}_2$ -based superconductors. In this article, we have investigated the crystal structure and superconducting properties of  $\text{NdO}_{1-x}\text{F}_x\text{BiS}_2$  synthesized with two preparation temperatures of 700 and 800 °C to clarify crystal structure parameters correlating with the superconducting properties in the  $\text{BiS}_2$ -based superconductors. We found that uniaxial compression along the  $c$  axis is essential for the appearance of bulk superconductivity with a higher  $T_c$  in the  $\text{NdO}_{1-x}\text{F}_x\text{BiS}_2$  system.

## 2. Experimental details

The polycrystalline samples of  $\text{NdO}_{1-x}\text{F}_x\text{BiS}_2$  ( $x = 0.1\sim 0.7$ ) were prepared by a solid-state reaction method. Bi grains,  $\text{Nd}_2\text{O}_3$  powders,  $\text{Nd}_2\text{S}_3$  powders,  $\text{BiF}_3$  powders and  $\text{Bi}_2\text{S}_3$  powders were used as the starting materials. The  $\text{Bi}_2\text{S}_3$  powder was synthesized by a direct reaction of Bi grains and

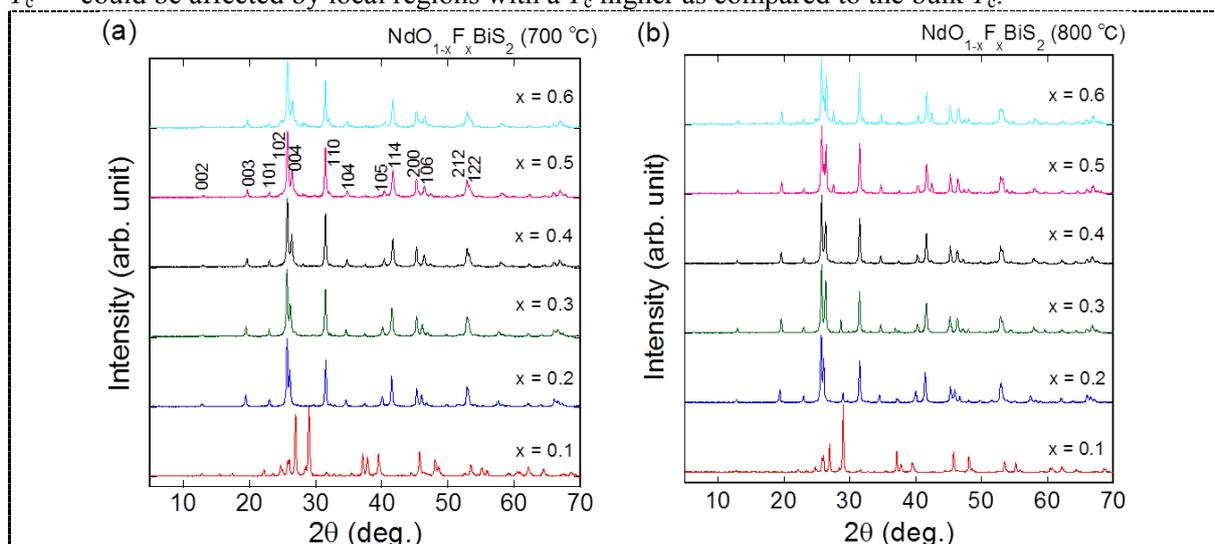


S grains at 500 °C in an evacuated quartz tube. Other chemicals were purchased from Kojundo-Kagaku laboratory. The mixture of the starting materials with nominal compositions of  $\text{NdO}_{1-x}\text{F}_x\text{BiS}_2$  ( $x = 0.1\sim 0.7$ ) was well-mixed, pelletized and sealed into an evacuated quartz tube. The  $\text{NdO}_{1-x}\text{F}_x\text{BiS}_2$  pellets were heated at 700 and 800 °C for 15h. The obtained products were ground, sealed into an evacuated quartz tube and heated again with the same heating conditions to homogenize the samples. The obtained samples were characterized by X-ray diffraction using the  $\theta$ - $2\theta$  method. Lattice constants were calculated using the peak positions of the X-ray profile by the least-square method. The temperature dependence of magnetization was measured by a superconducting quantum interface device (SQUID) magnetometer with an applied field of 5 Oe after both zero-field cooling (ZFC) and field cooling (FC).

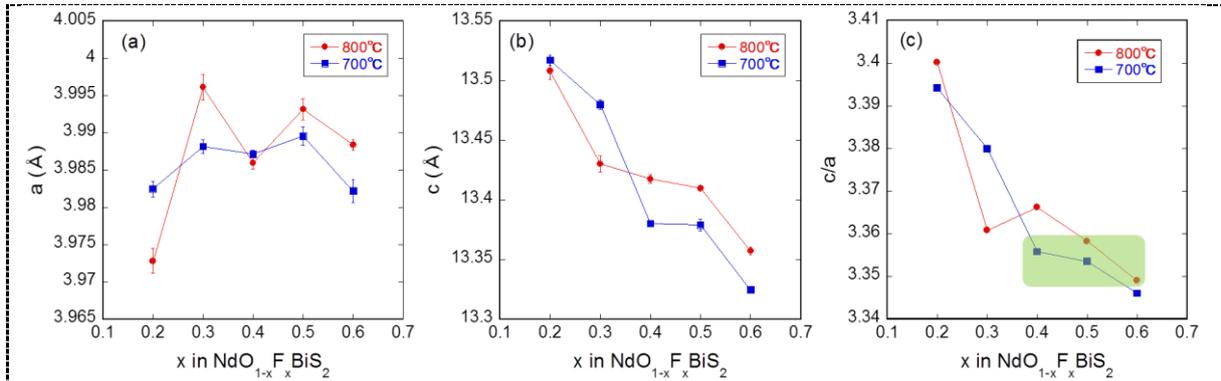
### 3. Results and discussion

Figure 1 (a) and (b) show the X-ray diffraction patterns for the  $\text{NdO}_{1-x}\text{F}_x\text{BiS}_2$  samples prepared at 700 and 800 °C, respectively. The profiles for the 700 and 800 °C samples exhibit quite similar tendency upon F substitution except for the slight differences in peak shifts corresponding to the changes in lattice constants. For  $x = 0.2\sim 0.6$  the peaks are characterized using the tetragonal space group of  $P4/nmm$  as indexed with the Miller indices in Fig. 1(a). Almost no impurity peaks are observed for  $x = 0.2 - 0.5$ . For  $x \geq 0.6$ , impurity peaks appear, indicating that the solubility limit of F in the REOBiS<sub>2</sub>-type structure is near  $x = 0.5$  for this system. Interestingly, the REOBiS<sub>2</sub>-type structure does not form for  $x \leq 0.1$ . The estimated lattice constants are plotted in Fig. 2. The  $a$  axis does not show a remarkable dependence on F concentration, while the  $c$  axis largely decreases with increasing F concentration. Figure 2(c) shows the  $c/a$  ratio. It is clear that the uniaxial compression along the  $c$  axis is generated upon F substitution.

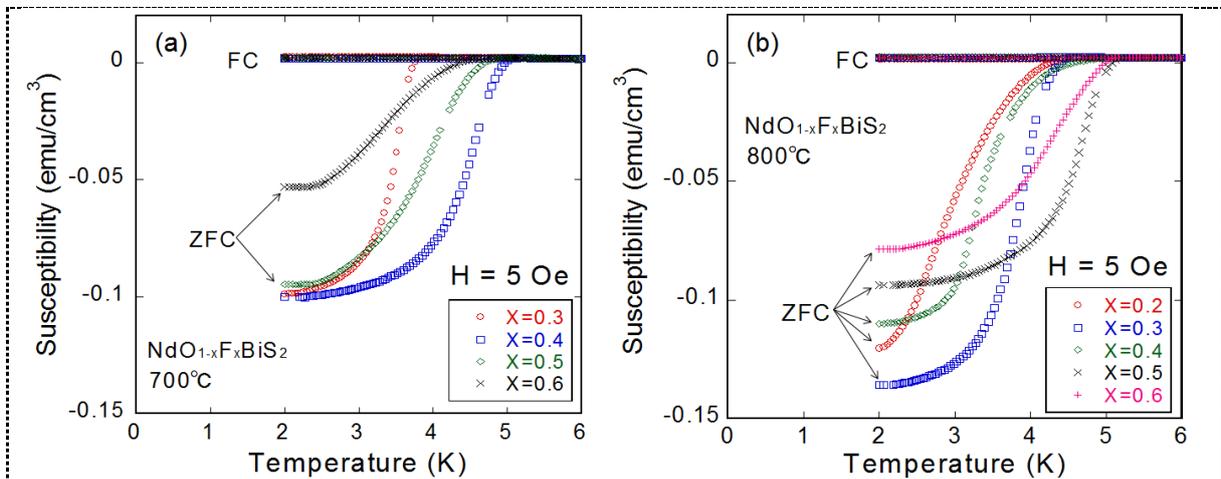
Figure 3(a) and (b) show the temperature dependence of magnetic susceptibility for  $\text{NdO}_{1-x}\text{F}_x\text{BiS}_2$  prepared at (a) 700 and (b) 800 °C, respectively. For the 700 °C samples, superconductivity is observed for  $x \geq 0.3$ . For the 800 °C samples, superconductivity is observed for  $x \geq 0.2$ . We estimate two types of transition temperatures,  $T_c^{\text{onset}}$  and  $T_c^{10\%}$ , to investigate the bulk nature of the samples. The  $T_c^{\text{onset}}$  is defined as a temperature at which the magnetic susceptibility begins to decrease. The  $T_c^{10\%}$  is defined as a temperature at which the value of the ZFC diamagnetic signal corresponds to 10 % of the value at 2 K. This value should represent the bulk properties of the sample because the  $T_c^{\text{onset}}$  could be affected by local regions with a  $T_c$  higher as compared to the bulk  $T_c$ .



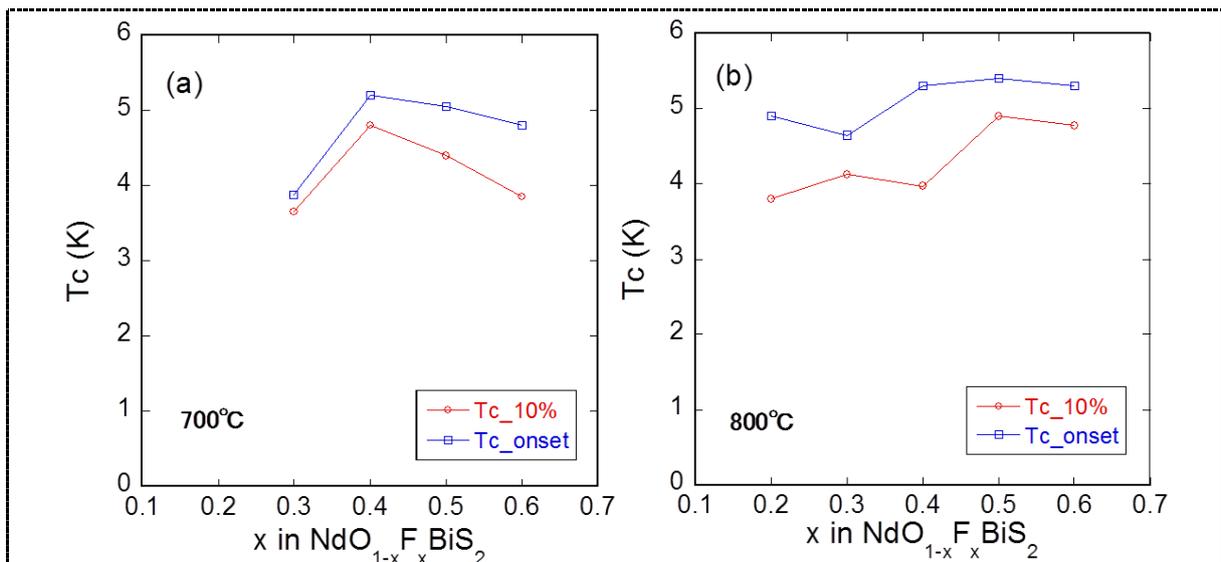
**Figure 1.** X-ray diffraction patterns for  $\text{NdO}_{1-x}\text{F}_x\text{BiS}_2$  prepared at (a) 700 °C and (b) 800 °C. The numbers indicate Miller indices.



**Figure 2.** F concentration dependence of lattice constants (a)  $a$  axis, (b)  $c$  axis and (c)  $c/a$  ratio for  $\text{NdO}_{1-x}\text{F}_x\text{BiS}_2$ . The green square indicates the data points whose  $T_c^{10\%}$  is around 4.5 K.



**Figure 3.** Temperature dependence of magnetic susceptibility for  $\text{NdO}_{1-x}\text{F}_x\text{BiS}_2$  prepared at (a) 700°C and (b) 800°C.



**Figure 4.** F concentration dependence of  $T_c^{onset}$  and  $T_c^{10\%}$  for  $\text{NdO}_{1-x}\text{F}_x\text{BiS}_2$  prepared at (a) 700°C and (b) 800°C.

On the basis of the systematic investigation on the lattice constants and the susceptibility, we find that uniaxial compression seems to be linked with the appearance of superconductivity in  $\text{NdO}_{1-x}\text{F}_x\text{BiS}_2$ . The higher  $T_c$ , with a criterion of  $T_c^{10\%} \sim 4.5$  K, is observed for  $x = 0.4$  and  $0.5$  for the  $700^\circ\text{C}$  samples and  $x = 0.5$  and  $0.6$  for the  $800^\circ\text{C}$  samples. We note that the  $c/a$  ratio of those higher- $T_c$  samples is located around  $c/a \sim 3.35$ , as indicated by a green area in Fig. 2 (c). This implies that the optimization of  $T_c$  requires the optimization of the  $c/a$  ratio in the  $\text{NdO}_{1-x}\text{F}_x\text{BiS}_2$  system. Uniaxial compression should affect the local structure parameter such as  $z$  coordinate of in-plane S and/or apical S. To analyze which is a local structure which is essential for superconductivity in  $\text{NdO}_{1-x}\text{F}_x\text{BiS}_2$ , crystal structure analysis using single crystals is required for the next step.

#### 4. Conclusion

We have systematically synthesized the  $\text{NdO}_{1-x}\text{F}_x\text{BiS}_2$  polycrystalline samples, and investigated the superconducting properties by X-ray diffraction and the susceptibility measurements. We have found that uniaxial compression should be linked with the appearance of superconductivity in  $\text{NdO}_{1-x}\text{F}_x\text{BiS}_2$ . Furthermore, it was expected that the optimization of  $T_c$  requires the optimization of the  $c/a$  parameter, which should be linked to the change (optimization) of the local crystal structure along the  $c$  axis.

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