

Superconductivity in BiS₂-Based Layered Compounds

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Abstract

Crystal structure and physical properties of the novel BiS₂-based layered superconductors are briefly reviewed. Superconductivity in the BiS₂-based layered compounds is induced by electron doping into the BiS₂ conduction layers. The superconducting properties seem to correlate with the crystal structure. Possible strategies for increasing transition temperature in this family are discussed.

Introduction

Since the discovery of the cuprate layered superconductors, materials possessing a layered crystal structure have been one of the mostly-studied systems on exploration of new superconductors [1]. The discovery of the Fe-based superconductors in 2008 has also accelerated studies on new layered materials [2]. One of the reasons for the tremendous amount of attentions in the layered superconductors is the observation of unconventional paring mechanisms due to low-dimensional characteristics of conductive electrons. Another merit of layered materials in exploring for new superconductors is the variation of crystal structure. In general, the layered superconductors possess a crystal structure composed of an alternate stacking of a common superconducting layer and a blocking (spacer) layer. In the Fe-based family, the Fe₂An₂ layers (An = P, As, S, Se or Te) could act as a common superconducting layer, and a lot of Fe-based superconductors have been discovered by changing the blocking layer structure [2-4]. Namely, if we discover a new type of superconducting layers, we can design a lot of layered superconductors. In 2012, the novel layered superconductors with a BiS₂-based superconducting layer have been discovered [5,6]. So far, 11 superconductors have been discovered, and some notable characteristics have been observed in this family [7-11]. Here, the crystal structure and physical properties of the BiS₂-based superconductors are briefly reviewed.

Crystal structure and superconducting properties

Figure 1(a) and (b) show the schematic images of the crystal structure of typical BiS₂-based superconductor LaOBiS₂ and Bi₄O₄S₃, respectively. Both materials are composed of an alternate stacking of the BiS₂ double layers and the blocking layer. Electron carriers, which are essential for the appearance of superconductivity in the BiS₂-based family, can be generated (controlled) by modifying the structure and the composition at the blocking layers. In the REOBiS₂ system (RE = Rare earth), electron carriers can be generated upon a partial substitution of O²⁻ by F⁻ [6], which is an electron-doping strategy used in the FeAs-based superconductors. In the Bi₄O₄S₃ superconductor, partial defects at the (SO₄)²⁻ site can provide electron carriers into the BiS₂ layers [5].

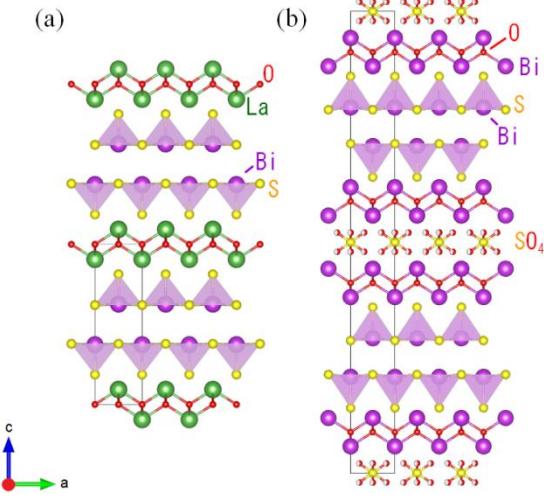


Fig. 1. (a) Crystal structure of LaOBiS_2 . (b) Crystal structure of $\text{Bi}_4\text{O}_4\text{S}_3$. In this figure, the structure is depicted with full site occupancy: Namely, the elemental composition of the shown structure is $\text{Bi}_6\text{O}_8\text{S}_5$. In real, there would be $\sim 50\%$ defects at the $(\text{SO}_4)^{2-}$ site, which corresponds to the composition of $\text{Bi}_4\text{O}_4\text{S}_3$.

The physical properties of BiS_2 -based compounds are introduced with the data of the $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$ system. Figure 2(a) displays the temperature dependence of resistivity for LaOBiS_2 (parent phase) and $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$. The parent phase exhibits semiconducting transport behavior. With the partial substitution of O by F, the resistivity decreases and superconducting transition is observed at ~ 3 K for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$. The superconducting properties can be enhanced by annealing the $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ superconducting sample under high pressure (HP). Figure 2(b) shows the temperature dependence of resistivity for as-grown and HP-annealed $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$. The onset of the transition temperature (T_c) is clearly enhanced from 3 to 10.6 K by the HP annealing [6,10]. It was found that the uniaxial strain (contraction) along the c axis is generated by the HP annealing [11]. These facts indicate that the optimization local structure is essential for the appearance of bulk superconductivity at a higher temperature in the BiS_2 -based superconductors. It was also reported that the application of external pressure could enhance the T_c of as-grown $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$. Furthermore, the crystal structure analysis under HP showed that the structural transition from tetragonal to monoclinic was positively linked with the enhancement of T_c under high pressure [12]. Theoretical investigations suggested that the slight changes in the local crystal structure such as the z coordinate of S at the BiS_2 layer could largely affect the band structure [13,14]. In these regards, the correlation between superconductivity and local crystal structure should be important to understand the mechanisms and to enhance the T_c in the BiS_2 -based superconductors.

Figure 3(a) shows the temperature dependence of normalized resistivity around superconducting transition for the typical BiS_2 -based superconductors, $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ (HP-annealed), $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$ (HP-annealed), $\text{NdO}_{0.7}\text{F}_{0.3}\text{BiS}_2$ (as-grown) and $\text{Bi}_4\text{O}_4\text{S}_3$ (as-grown). Here the transport data for the samples with the highest T_c in the respective systems are summarized. The midpoints of T_c are summarized in Fig. 3(b). To discuss the tendency of the T_c , the area where the superconducting properties (T_c) are optimized is highlighted with a green square. The optimized T_c in the LaOBiS_2 system is the highest. Then, the optimized T_c tends to decrease by changing the blocking layer structure in an order of La_2O_2 , Ce_2O_2 , Nd_2O_2 and $\text{Bi}_4\text{O}_4(\text{SO}_4)$. The tendency can be understood with the change in the ionic radius of the anion (La^{3+} , Ce^{3+} , Nd^{3+} and Bi^{3+}) in the blocking layer. The ionic radius of the anion directly tune the a axis length in this family. In fact, the optimized T_c in the BiS_2 -based superconductors well correlates with the length of the a axis.

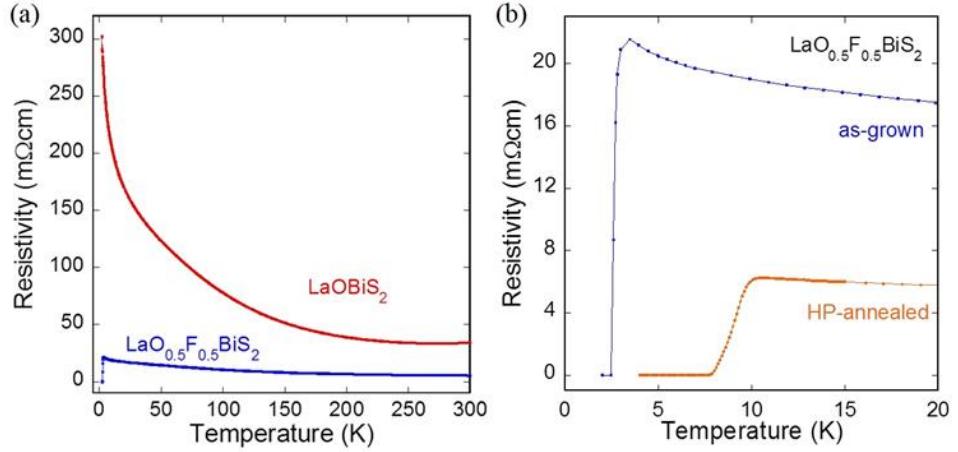


Fig. 2. (a) Temperature dependence of resistivity for LaOBiS₂ and LaO_{0.5}F_{0.5}BiS₂. (b) Temperature dependence of resistivity for as-grown and HP-annealed LaO_{0.5}F_{0.5}BiS₂.

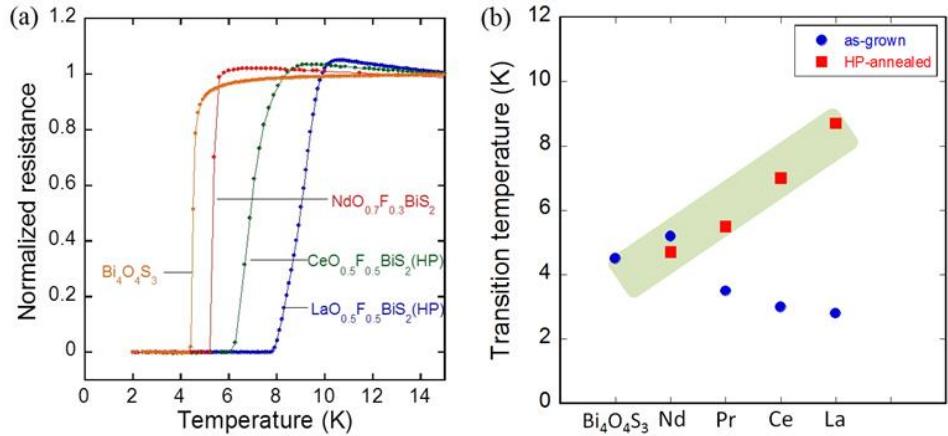


Fig. 3. (a) Temperature dependence of normalized resistivity around superconducting transition for the typical BiS₂-based superconductors, LaO_{0.5}F_{0.5}BiS₂ (HP-annealed), CeO_{0.3}F_{0.7}BiS₂ (HP-annealed), NdO_{0.7}F_{0.3}BiS₂ (as-grown) and Bi₄O₄S₃ (as-grown). (b) Transition temperatures (midpoint) are summarized.

Strategies to enhance superconducting properties

In the above, possible two structural parameters are suggested to be essential for superconductivity in the BiS₂ family. The first one is the local structure correlated with the uniaxial compression along the *a* axis, which can be optimized by applying high pressure. This should be essential for the appearance of bulk superconductivity in the respective systems. The other parameter is the length of the *a* axis, which can be tuned by changing the blocking layer. Unfortunately, the largest rare earth is La; hence, we cannot synthesize new REOBiS₂ materials with larger *a* axis. Therefore, we should discover new blocking layers. For example, the structure similar to Bi₆O₈S₅, Fig. 1(b), is a candidate. If the Bi could be substituted with rare earth, larger *a* axis could be obtained. Another strategy is to use a perovskite-oxide blocking layer, which is formed in the Fe-based superconductor Sr₄Sc₂O₆Fe₂P₂ [17].

Recently, superconductors with Bi-Se and Bi-Te conduction layers were discovered. Maziopa et al. reported that LaO_{0.5}F_{0.5}BiSe₂ with a structure similar to LaOBiS₂ showed superconductivity below 2.6 K [18,19]. Malliakas et al. reported that CsBi₄Te₆ exhibited superconductivity below 4.4 K by electron

carrier doping. The Bi-Te blocks of CsBi_4Te_6 are similar to the NaCl structure as well as the BiS_2 layers. Therefore, superconductivity observed in doped CsBi_4Te_6 could be driven with the mechanisms same as the BiS_2 -based superconductors. Hence, replacement of BiS_2 layers by Bi-Se or Bi-Te layers could be a promising strategy for enhancing T_c of Bi-based superconductors.

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