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ScienceDirect
Physics Procedia 58 (2014) 94 – 97
Physics Procedia

26th International Symposium on Superconductivity, ISS 2013

Superconductivity in BiS_2-Based Layered Compounds

Yoshikazu Mizuguchi*

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

Abstract

Crystal structure and physical properties of the novel BiS_2-based layered superconductors are briefly reviewed. Superconductivity in the BiS_2-based layered compounds is induced by electron doping into the BiS_2 conduction layers. The superconducting properties seem to correlate with the crystal structure. Possible strategies for increasing transition temperature in this family are discussed.

Peer-review under responsibility of the ISS 2013 Program Committee

Keywords: Layered superconductor; BiS_2-based superconductor; Crystal structure; Physical property

1. 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 Fe_2An_2 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

* Corresponding author. Tel.: +81-42-677-2748; fax: +81-42-677-2756.
E-mail address: mizugu@tmu.ac.jp

Peer-review under responsibility of the ISS 2013 Program Committee
doi:10.1016/j.phpro.2014.09.032

superconductors. In 2012, the novel layered superconductors with a BiS_2-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 BiS_2-based superconductors are briefly reviewed.

2. Crystal structure and superconducting properties

Figure 1(a) and (b) show the schematic images of the crystal structure of typical BiS_2-based superconductor $LaOBiS_2$ and $Bi_4O_4S_3$, respectively. Both materials are composed of an alternate stacking of the BiS_2 double layers and the blocking layer. Electron carriers, which are essential for the appearance of superconductivity in the BiS_2-based family, can be generated (controlled) by modifying the structure and the composition at the blocking layers. In the $REOBiS_2$ system (RE = Rare earth), electron carriers can be generated upon a partial substitution of O^{2-} by F^- [6], which is an electron-doping strategy used in the FeAs-based superconductors. In the $Bi_4O_4S_3$ superconductor, partial defects at the $(SO_4)^{2-}$ site can provide electron carriers into the BiS_2 layers [5].

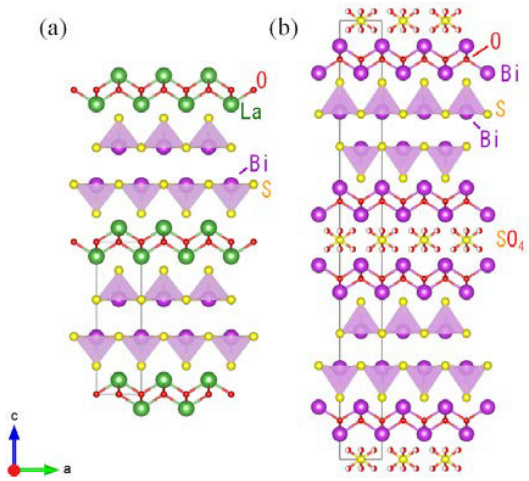

Fig. 1. (a) Crystal structure of $LaOBiS_2$. (b) Crystal structure of $Bi_4O_4S_3$. In this figure, the structure is depicted with full site occupancy: Namely, the elemental composition of the shown structure is $Bi_6O_8S_5$. In real, there would be ~50 % defects at the $(SO_4)^{2-}$ site, which corresponds to the composition of $Bi_4O_4S_3$.

The physical properties of BiS_2-based compounds are introduced with the data of the $LaO_{1-x}F_xBiS_2$ system. Figure 2(a) displays the temperature dependence of resistivity for $LaOBiS_2$ (parent phase) and $LaO_{0.5}F_{0.5}BiS_2$. 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 $LaO_{0.5}F_{0.5}BiS_2$. The superconducting properties can be enhanced by annealing the $LaO_{0.5}F_{0.5}BiS_2$ superconducting sample under high pressure (HP). Figure 2(b) shows the temperature dependence of resistivity for as-grown and HP-annealed $LaO_{0.5}F_{0.5}BiS_2$. 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 $LaO_{0.5}F_{0.5}BiS_2$. 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, $LaO_{0.5}F_{0.5}BiS_2$ (HP-annealed), $CeO_{0.3}F_{0.7}BiS_2$ (HP-annealed), $NdO_{0.7}F_{0.3}BiS_2$ (as-grown) and$Bi_4O_4S_3$ (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 $Bi_4O_4(SO_4)$. 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.

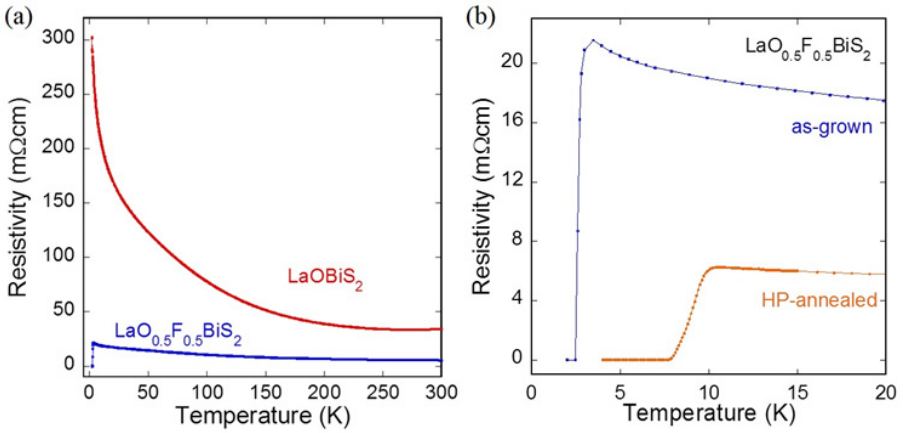

Fig. 2. (a) Temperature dependence of resistivity for $LaOBiS_2$ and $LaO_{0.5}F0_{0.5}BiS_2$. (b) Temperature dependence of resistivity for as-grown and HP-annealed $LaO_{0.5}F0_{0.5}BiS_2$.

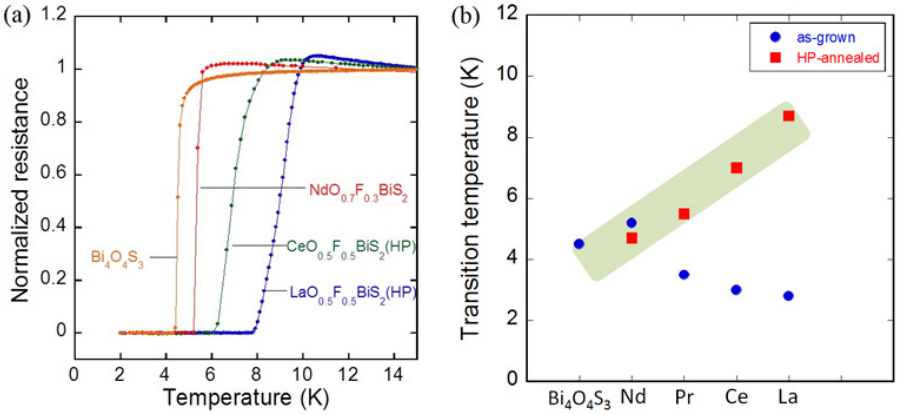

Fig. 3. (a) Temperature dependence of normalized resistivity around superconducting transition for the typical BiS_2-based superconductors, $LaO_{0.5}F_{0.5}BiS_2$ (HP-annealed), $CeO_{0.3}F_{0.7}BiS_2$ (HP-annealed), $NdO_{0.7}F_{0.3}BiS_2$ (as-grown) and$Bi_4O_4S_3$ (as-grown). (b) Transition temperatures (midpoint) are summarized.

3. Strategies to enhance superconducting properties

In the above, possible two structural parameters are suggested to be essential for superconductivity in the BiS_2 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 $REOBiS_2$ materials with larger *a* axis. Therefore, we should discover new blocking layers. For example, the structure similar to $Bi_6O_8S_5$, 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 $Sr_4Sc_2O_6Fe_2P_2$ [17].

Recently, superconductors with Bi-Se and Bi-Te conduction layers were discovered. Maziopa et al. reported that $LaO_{0.5}F_{0.5}BiSe_2$ with a structure similar to $LaOBiS_2$ showed superconductivity below 2.6 K [18]. Malliakas et al. reported that $CsBi_4Te_6$ exhibited superconductivity below 4.4 K by hole-carrier doping [19]. 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.

Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research for young scientists (A).

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