

Article

Discovery of BiS₂-Based Superconductor and Material Design Concept

Yoshikazu Mizuguchi

Department of Electrical and Electronic Engineering, Tokyo Metropolitan University, 1-1 Minami-osawa, Hachioji 192-0397, Japan; mizugu@tmu.ac.jp

Academic Editor: Antonio Bianconi

Received: 25 November 2016; Accepted: 26 January 2017; Published: date

Abstract: In 2012, we discovered new layered superconductors whose superconducting states emerge in the BiS₂ layers. Since their crystal structure, composed of alternate stacks of BiS₂ conduction layers and electrically insulating (blocking) layers, is similar to those of cuprate and Fe-based superconductors, many researchers have explored new BiS₂-based superconductors and have studied the physical and chemical properties of the BiS₂-based superconductors. In this paper, we present the histories of the discovery of the first BiS₂-based superconductor, Bi₄O₄S₃, and the second one, LaO_{1-x}F_xBiS₂. The structural variation of the BiS₂-based superconductor family is briefly introduced. Then, we show the material design concept for the emergence of bulk superconductivity in BiS₂-based compounds. At the end, a possible strategy for the enhancement of the transition temperature in the BiS₂-based superconductors is proposed.

Keywords: new superconductor; layered superconductor; BiS₂-based superconductor; pressure effect; chemical pressure effect

1. Discovery of BiS₂-Based Superconductor Family

1.1. Layered Superconductors

Since the discovery of the Fe-based superconductor in 2008 [1], many researchers have explored new Fe-based superconductors [2]. During the Fe age, I studied physics, chemistry, and the application of the Fe-chalcogenide superconductors and obtained a Ph.D. in 2010. Then, in 2011, I launched new research group at Tokyo Metropolitan University and started exploring new layered superconductors such as Fe-based or cuprate superconductors [3]. Those layered superconductors have a layered structure composed of alternate stacks of conducting (superconducting) and insulating (blocking) layers. The FeAs layer and CuO₂ plane are the essential structures for the emergence of superconductivity in Fe-based and cuprate superconductors, respectively. Namely, by utilizing the structural flexibility, new superconductors with various stacking structures could be designed by changing the blocking layer and/or the thickness of the superconducting planes. Therefore, I aimed to discover a new layered superconductor with a new type of superconducting layer other than the FeAs layer and CuO₂ plane.

To discover new layered superconductors, experience in the material design of the Fe-based superconductor family is very useful. A typical crystal structure of the Fe-based superconductor is the ZrSiCuAs-type (*P4/nmm*) structure, for example LaOFeAs [1]. As shown in Figure 1a, the crystal structure of LaOFeAs is composed of the FeAs superconducting layer and the LaO blocking layer. Among layered compounds, the ZrSiCuAs-type structure is one of the typical structures. For example, BiOCuSe, whose structure is composed of a CuSe conducting layer and a BiO blocking layer, is a famous thermoelectric material [4]. When substituting the CuSe layer of BiOCuSe with a CuS layer, we obtain BiOCuS with the ZrSiCuAs-type structure.

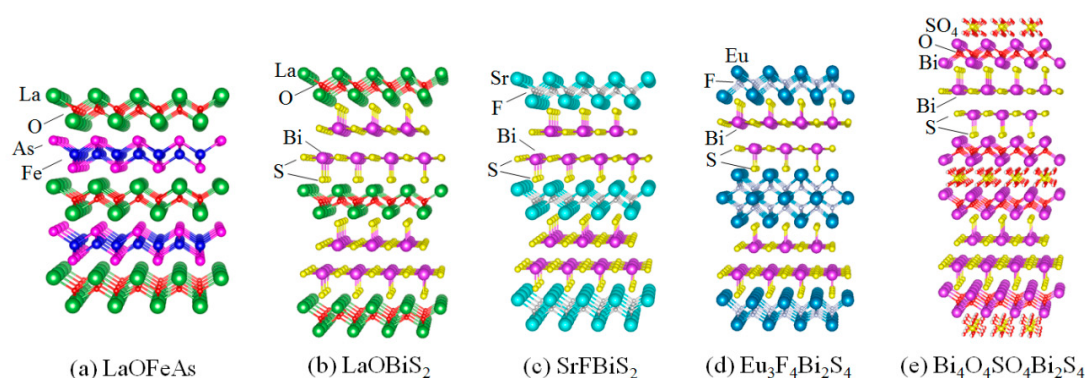


Figure 1. (a) Schematic images of crystal structure of Fe-based LaOFeAs. (b–e) Schematic images of crystal structures of BiS₂-based (b) LaOBiS₂, (c) SrFBiS₂, (d) Eu₃F₄Bi₂S₄, and (e) Bi₄O₄SO₄Bi₂S₄. The crystal structure images in this article were drawn using VESTA (Version 3.3.1) [5].

1.2. Discovery of the Bi–O–S Superconductor

In the beginning, we explored new superconductors near the BiOCuS system because a superconductivity signal was detected for Cu-deficient BiOCu_{1-x}S [6]. Although Reference [6] reported superconductivity, the shielding volume fraction of the sample was not high, indicating that the superconductivity was not bulk in nature. In addition, the other research group also examined the BiOCu_{1-x}S and its Pb-doped samples [7]; superconductivity, however, was not discovered in those samples. Therefore, we modified the composition of Bi–O–Bi–S and finally synthesized Cu-free Bi₂O₂S, which is a layered compound, according to the material database [8]. Surprisingly, the Bi₂O₂S sample prepared at 500 °C showed a superconducting signal at *T* of ~5 K in the temperature dependence of magnetization. The X-ray diffraction (XRD) pattern of the sample was not what was expected from the Bi₂O₂S structure and indicated that the sample was not a single phase. This suggests the presence of a Bi–O–S superconducting phase stable at around 500 °C. Then, we explored the optimal composition of the unknown Bi–O–S superconducting phase. After synthesizing and evaluating over 100 samples of Bi_xO_yS_z (with various synthesis temperatures), we obtained the optimal composition of Bi₄O₄S₃, in which the superconducting volume fraction is the highest, and the XRD pattern seemed to be a single phase.

Although we obtained the single-phase sample of Bi₄O₄S₃, the crystal structure was unknown, and no similar XRD pattern could be found in the database [8]. The XRD pattern was analyzed by Fujihisa and Gotoh of AIST (National Institute of Advanced Industry Science and Technology), who are specialists in crystal structure determination. From the XRD pattern, the framework of Bi and S was determined. Since the XRD pattern was collected with a powder sample, the determination of the O site was difficult. Therefore, we determined the final structure model with the combination of calculation and Rietveld refinement. Finally, we concluded that Bi₄O₄S₃ had a layered structure as depicted in Figure 1e. In addition, we analyzed the band structure with the support of Kuroki's group (Osaka University). The crystal structure of Bi₄O₄S₃ is composed of alternate stacking of the BiS₂ bilayer, which is electrically conducting, and the Bi₄O₄(SO₄)_x blocking layer. The parent phase (*x* = 0) was expected to be a band insulator, but the present phase, Bi₄O₄S₃, corresponded to *x* = 0.5. Namely, there are 50% SO₄ defects in the blocking layer, and, hence, electrons are doped to the BiS₂ layers, resulting in metallic conductivity and superconductivity [9]. Interestingly, the stable phase (composition) contains defects at the SO₄ site, and the control of the doping level is very difficult in this Bi₄O₄SO₄Bi₂S₄ structure. Motivated by this difficulty, we tried to synthesize other BiS₂-based superconductors with a simpler structure.

1.3. 1112-Type BiS₂-Based Superconductors

After the discovery of the Bi₄O₄S₃ superconductor, we studied LaOBiS₂, the crystal structure of which is composed of a La₂O₂ blocking layer and a BiS₂ bilayer (Figure 1b). Although this material was already known [10], the physical properties and the carrier doping effects had not been examined

in detail. Thus, on the basis of the analogies on the crystal structure and electronic structure between $\text{Bi}_4\text{O}_4\text{S}_3$ and LaOBiS_2 , we synthesized *electron-doped* LaOBiS_2 , $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$. The partial substitution of F^- for O^{2-} generates electron carriers in the BiS_2 layer [11,12], which will be explained in Section 2.1. The $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$ superconductor shows a T_c of ~ 3 K with $x = 0.5$, but the superconductivity is not in bulk, according to the results of the magnetic susceptibility measurements. Bulk superconductivity in $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ can be induced by the pressure effect [13–16]. Under a pressure above 1 GPa, the T_c reaches 10 K and the superconducting volume fraction is largely enhanced, which indicates the emergence of bulk superconductivity. In addition, high-pressure synthesis also produces the bulk superconductivity phase of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ [10,17,18]. In order to induce bulk superconductivity in $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$, the chemical pressure effect is also effective. By replacing La with smaller rare-earth ions, Ce, Pr, Nd, or Sm, bulk superconductivity can be induced [19–24]. Namely, $\text{REO}_{1-x}\text{F}_x\text{BiS}_2$ with RE = La, Ce, Pr, Nd, or Sm is basically superconductive, and has a crystal structure as shown in Figure 1b. The detailed explanations on the external and chemical pressure effects will appear in Sections 2.2 and 2.3.

The R_2O_2 layer can be replaced by the Sr_2F_2 or Eu_2F_2 layer, as depicted in Figure 1c [25–28]. The SrFBiS_2 compound is a band insulator and superconductivity can be induced by electron doping as well as LaOBiS_2 . In this series, the R^{3+} substitution for the Sr (or Eu) site can generate electron carriers in the BiS_2 layer, and superconductivity is induced [26]. EuFBiS_2 shows a superconducting transition at 0.3 K without chemical doping because the valence of Eu is not 2+ but about 2.2+, which results in self-doped electron carriers [27]. Since the lattice constants of SrFBiS_2 -type compounds are similar to those of LaOBiS_2 -type ones, the physical properties of those two systems are quite similar. Namely, the strategies of carrier doping and the pressure effects can be applied similarly.

1.4. Other Bi-Chalcogenide Layered Compounds

Figure 1d shows the crystal structure of $\text{Eu}_3\text{F}_4\text{Bi}_2\text{S}_4$, which is composed of alternate stacks of the Eu_3F_4 blocking layer and the BiS_2 bilayer [29,30]. This compound also exhibits the mixed-valence state of Eu, and shows superconductivity at low temperatures ($T_c \sim 1$ K). The T_c can be enhanced by 3.35 K with Se substitution [31].

Recently, a new Bi-S layered compound with a thicker conducting layer was discovered. LaOBiPbS_3 has a La_2O_2 blocking similar to LaOBiS_2 , but its conducting layer is $\text{Bi}_2\text{Pb}_2\text{S}_6$, which is the four-layer-type conducting layer [32]. Although LaOBiPbS_3 is not metallic, carrier doping may induce superconductivity and will open a new playground of Bi-chalcogenide superconductors.

I would like to briefly introduce the existence of the sister phases of $\text{Bi}_4\text{O}_4\text{S}_3$. In $\text{Bi}_3\text{O}_2\text{S}_3$, the SO_4 site of $\text{Bi}_4\text{O}_4\text{S}_3$ is replaced by the S_2 dimer, and superconductivity is observed without substitution [33]. The Bi–O–S series possess quite characteristic structures, and thus, the design of new superconductors in the Bi–O–S series may be one of the strategies for enhancing T_c in the BiS_2 -based systems.

2. Emergence of Superconductivity in BiS_2 -Based Compounds

2.1. Carrier Doping

As mentioned above, the parent phases of the BiS_2 -based compounds, such as LaOBiS_2 or SrFBiS_2 , are generally an insulator with a band gap. Figure 2a shows the band structure of LaOBiS_2 . The bands just above the Fermi energy are composed of Bi-6p orbitals (p_x and p_y) [12]. Therefore, it is expected that the BiS_2 layer becomes metallic by electron doping. There are several ways to induce metallicity and superconductivity in the BiS_2 layer. In the REOBiS_2 -type structure, the most typical way of electron doping is the partial substitution of F^- for O^{2-} [11,19,21–23]. Figure 2b shows the temperature dependences of electrical resistivity for LaOBiS_2 and $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$. By F substitution, the electrical resistivity decreases and the superconducting transition is observed at 2.5 K. Figure 2c shows the temperature dependence of the magnetic susceptibility for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$. Diamagnetic signals corresponding to the emergence of superconductivity are observed. However, the magnitude of the superconductivity signal, $4\pi\chi$, is very small as a bulk superconductor. As shown in the inset of Figure

2c, the optimal F concentration, at which the T_c is the highest, is $x = 0.5$ [11,17,34]. Therefore, the weak superconductivity signal observed in the magnetic susceptibility measurement is caused not by the insufficiency of the carrier concentration but by another factor. To induce bulk superconductivity in $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$, external and chemical pressure effects are essential.

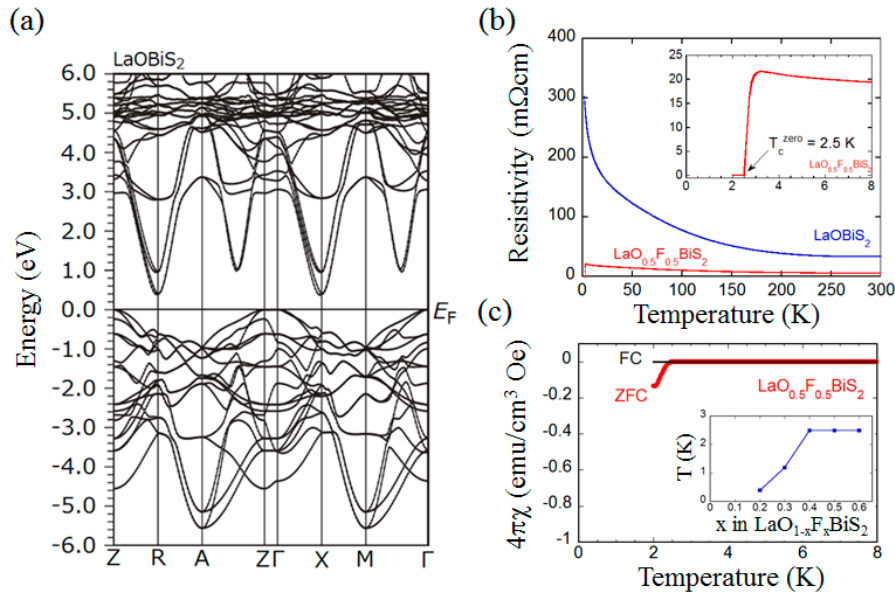


Figure 2. (a) Band structure of LaOBiS_2 . (b) Temperature dependences of electrical resistivity for LaOBiS_2 and $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$. The inset shows the enlargement of the low-temperature data of the resistivity. (c) Temperature dependences of magnetic susceptibility (measured after zero-field cooling and field cooling) for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$. The inset shows the F concentration (x) dependence of T_c of $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$.

2.2. External Pressure Effect

The superconducting properties of $\text{REO}_{1-x}\text{F}_x\text{BiS}_2$ are very sensitive to the external pressure [35]. The first example is the high-pressure synthesis effect. As shown in Figure 2c, the superconductivity in $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ is not perfect (not bulk in nature) on the basis of the shielding fraction observed in the magnetic susceptibility measurement. Surprisingly, the superconducting properties of the $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ sample dramatically change when the sample is prepared under the high pressure of 2 GPa [11,17,18]. Figure 3a shows the temperature dependence of the magnetic susceptibility for two different samples of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$: one was synthesized in an evacuated quartz tube (low pressure) and the other was synthesized at a high pressure of 2 GPa (high pressure). The high-pressure (high-P) phase shows a large shielding fraction, which indicates the emergence of bulk superconductivity, and a higher T_c of ~8 K. Please note that the susceptibility measurements were performed in vacuum (not under high pressure), but the low-P and high-P samples show different properties. Therefore, high-pressure synthesis can modify the crystal structure. Importantly, we can obtain intermediate phases with $T_c = 2.5\text{--}8$ K by modifying the annealing temperature and pressure. Indeed, for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$, there are at least two stable structures which can be transformed by temperature and/or pressure.

The high-P phase can be obtained by applying external pressure during low-temperature measurements. Figure 3b shows the pressure dependences of T_c for $\text{REO}_{1-x}\text{F}_x\text{BiS}_2$ with an optimal F doping ($\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$, $\text{CeO}_{0.3}\text{F}_{0.7}\text{BiS}_2$, $\text{PrO}_{0.5}\text{F}_{0.5}\text{BiS}_2$, and $\text{NdO}_{0.5}\text{F}_{0.5}\text{BiS}_2$) [13–16,35]. All the $\text{REO}_{1-x}\text{F}_x\text{BiS}_2$ superconductors show an increase in T_c by applying external pressure. Interestingly, the pressure dependences of T_c show a transition-like increase at different pressures, which is 0.5–1 GPa for RE = La and about 2 GPa for RE = Nd. The critical pressure seems to be related to the lattice constant of the a -axis of $\text{REO}_{1-x}\text{F}_x\text{BiS}_2$. This can be understood with the crystal structure transition from tetragonal ($P4/nmm$) to monoclinic ($P2_1/m$) in $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$ [13] under high pressure, as depicted in

Figure 3c,d. This structural transition associated with the formation of the Bi-S zigzag chain is shown in Figure 3d. It can be easily assumed that the formation of the zigzag chain takes place when the Bi-S square lattice in the tetragonal structure is not constrained and has some space to distort. In fact, recent crystal structure analysis using synchrotron X-ray showed that the crystal structure of LaOBiS_2 is the monoclinic structure at room temperature [36]. In addition, different three-dimensional stacking sequences of the BiS_2 layers were theoretically proposed [37]. On the basis of these results, the crystal structure of the $\text{REO}_{1-x}\text{F}_x\text{BiS}_2$ system can be easily transformed between tetragonal and monoclinic by tuning the lattice volume, and the systematic investigations of the crystal structure are very important for understanding the mechanisms of the emerging superconductivity.

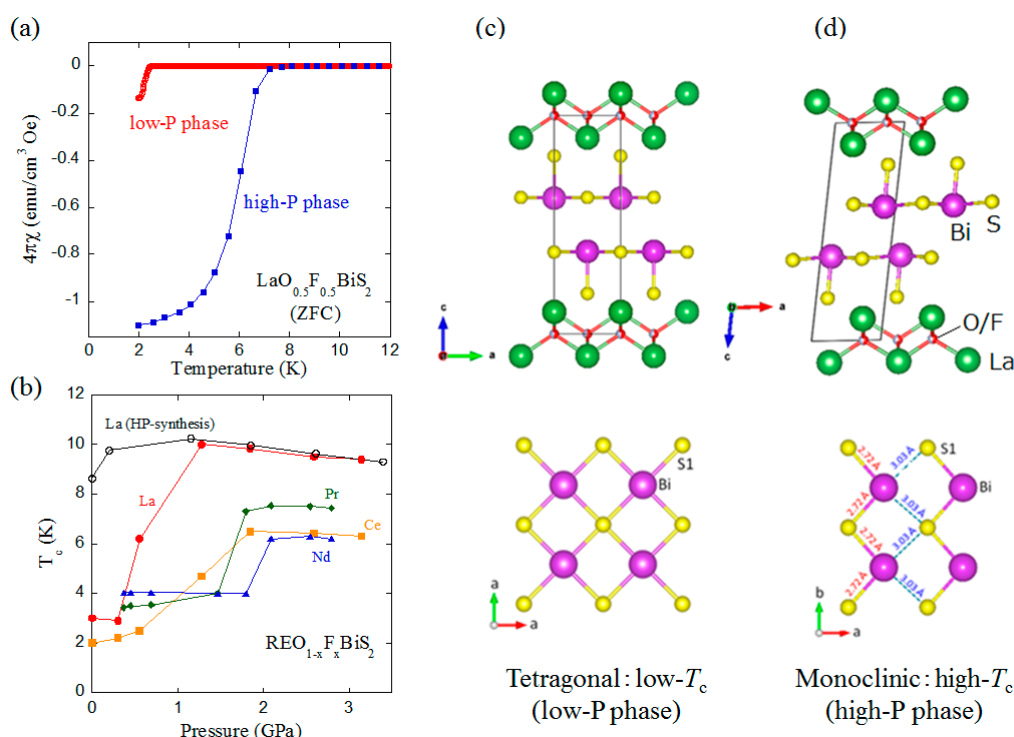


Figure 3. (a) Temperature dependences of magnetic susceptibility for two different $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ samples, low-pressure phase (low-P phase) and high-pressure phase (high-P phase). (b) Pressure dependences of T_c for $\text{REO}_{1-x}\text{F}_x\text{BiS}_2$ with an optimal F concentration. (c,d) Schematic images of crystal structure of tetragonal (low-P) phase and monoclinic (high-P) phase of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$.

2.3. Chemical Pressure Effect

Another method to induce the bulk superconductivity of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ is the chemical pressure effect. Generally, the chemical pressure can be applied by substitutions of an isovalent element with a different ionic radius. In the case of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$, there are two methods of applying chemical pressure. The first method is the substitution of La^{3+} by the smaller RE^{3+} ions, such as Ce^{3+} , Pr^{3+} , Nd^{3+} , or Sm^{3+} . In $\text{REO}_{0.5}\text{F}_{0.5}\text{BiS}_2$, bulk superconductivity (at above 2 K) is induced at $\text{RE} = \text{Ce}_{0.6}\text{Nd}_{0.4}$. The T_c increases with decreasing the mean RE^{3+} ionic radius. The lattice volume basically decreases with decreasing the mean RE^{3+} ionic radius, as shown in Figure 4c. Therefore, the shrinkage of the BiS_2 layer should be related to the emergence of bulk superconductivity in $\text{REO}_{0.5}\text{F}_{0.5}\text{BiS}_2$. These results seem to be consistent with the external pressure effects, while the crystal structure remains tetragonal up to $\text{RE} = \text{Sm}$ [23,24]. Then, please note that the filamentary (non-bulk) superconductivity observed in $\text{RE} = \text{La}$ is suppressed by Ce substitution. Although the reason for this strange behavior is unclear, this should be related to the structural fluctuation between tetragonal and monoclinic on a local scale.

The other method to apply chemical pressure is the substitution of S^{2-} by Se^{2-} . This is a direct chemical pressure to the superconducting BiS_2 layer. Since the ionic radius of Se^{2-} is larger than S^{2-} , the lattice volume increases with the increasing Se concentration, as shown in Figure 4c. Therefore,

the chemical pressure effect by the Se substitution seems to be the opposite to that by the substitution of the smaller RE^{3+} . However, the obtained superconductivity phase diagram for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_{2-x}\text{Se}_x$ (Figure 4b) is quite similar to that for $\text{REO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ (Figure 4a). The filamentary superconductivity is suppressed by the small doping of Se, and bulk superconductivity is induced at $x \geq 0.4$. T_c increases with the increasing Se concentration [38].

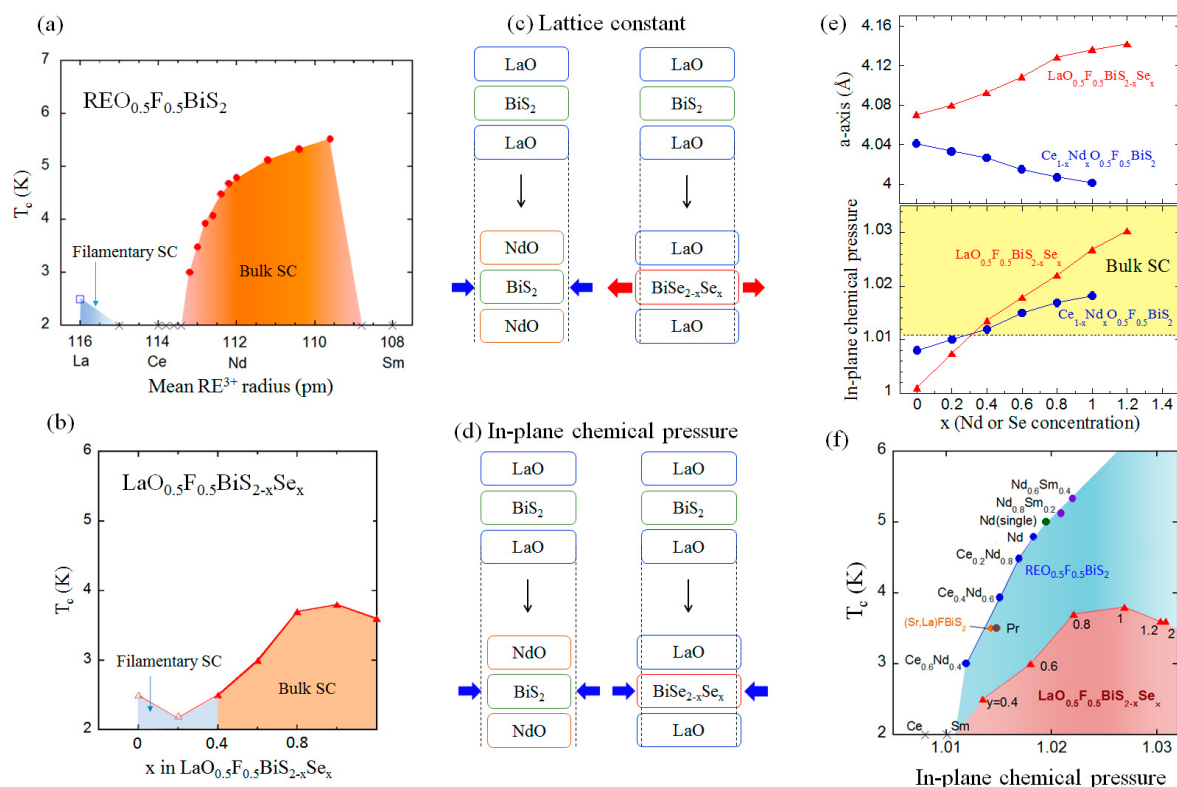


Figure 4. (a) Superconductivity phase diagram of $\text{REO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ plotted as a function of mean RE^{3+} ionic radius. (b) Superconductivity phase diagram of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_{2-x}\text{Se}_x$ plotted as a function of Se concentration (x). (c,d) Schematic images of the evolutions of lattice constant and in-plane chemical pressure. (e) Evolutions of lattice constant of a and in-plane chemical pressure by the Nd or Se substitutions. (f) Relationship between T_c and in-plane chemical pressure in the $\text{REO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ -type structure.

2.4. Importance of In-Plane Chemical Pressure

On the basis of the experimental facts on $\text{REO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ and $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_{2-x}\text{Se}_x$, we explored a factor essential for the evolution of bulk superconductivity in this family. To address it, the crystal structures of $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{0.5}\text{F}_{0.5}\text{BiS}_2$ and $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_{2-x}\text{Se}_x$, which exhibit a crossover region between non-superconductivity and bulk superconductivity, were examined using synchrotron X-ray [39]. Since the changes in the lattice volume are opposite between these two systems, as shown in Figure 4c, almost all the structural parameters show opposite doping dependences. Therefore, we have introduced the concept of *in-plane chemical pressure*. The magnitude of in-plane chemical pressure was calculated by the equation of $(R_{\text{Bi}} + R_{\text{Ch}})/(\text{in-plane Bi-Ch distance})$ where R_{Bi} and R_{Ch} are the ionic radii of Bi and the mean ionic radius of the chalcogen (Ch) site [39]. The estimated in-plane chemical pressure is plotted as a function of the Nd or Se concentration (x) in Figure 4e. Surprisingly, the x dependences of the in-plane chemical pressure for the two systems showed the same tendency, and the bulk superconductivity appeared at above the same threshold. The x dependences of the lattice constant of a are also plotted in Figure 4e. It is clear that the lattice constant exhibits opposite x dependences. With the concept of in-plane chemical pressure, we finally obtained the factor correlating to the emergence of superconductivity in the $\text{REO}_{0.5}\text{F}_{0.5}\text{BiCh}_2$ structure.

Figure 4f shows the in-plane chemical pressure dependences of T_c for the $\text{REO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ -type and $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_{2-x}\text{Se}_x$ superconductors. There is a trend that T_c increases with the increasing in-plane chemical pressure [39]. Indeed, the magnitude of the in-plane chemical pressure becomes the scale for T_c in the tetragonal phase of $\text{REO}_{0.5}\text{F}_{0.5}\text{BiS}_2$.

3. Material Design Strategies for the BiS_2 -Based Superconductor

In the Section 2, the requirements for the emergence of superconductivity in the BiS_2 -based compounds were reviewed. *Electron carrier doping* to the BiS_2 layer is needed to induce superconductivity. However, the carrier doping is not the sole factor related to the emergence of superconductivity in this system. *In-plane chemical pressure* should be optimized as well. According to these two requirements (the recipe of BiS_2 -based superconductivity), new superconductors can be easily designed as demonstrated in $\text{Eu}_{0.5}\text{La}_{0.5}\text{FBiS}_{2-x}\text{Se}_x$ [40].

Then, what is the strategy for enhancing T_c in this system? One idea comes when considering the large enhancement of T_c in $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ by the external pressure effect. The crystal structure of the high-P phase is monoclinic, and the Bi-S zigzag chains are formed in the BiS plane (Figure 2d). To link the monoclinic structure to the tetragonal structure, the concept of in-plane chemical pressure can be modified as quasi-one-dimensional (quasi-1D) chemical pressure. Since we have already obtained the trend that T_c increases when higher chemical pressure is created, we consider the shorter Bi-S distance (in-chain Bi-S distance) of the high-P phase of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ as the origin of the high T_c . As plotted in Figure 5, the calculated quasi-1D chemical pressure for the high-P phase of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ locates on the extrapolated line of the T_c in-plane chemical pressure relation. This may suggest that a higher T_c can be obtained in a monoclinic structure with an extremely distorted Bi-S chain. In addition, according to the results on the external pressure studies, BiS_2 -based compounds with a larger a -axis should be candidates for the extremely distorted phase with a high T_c .

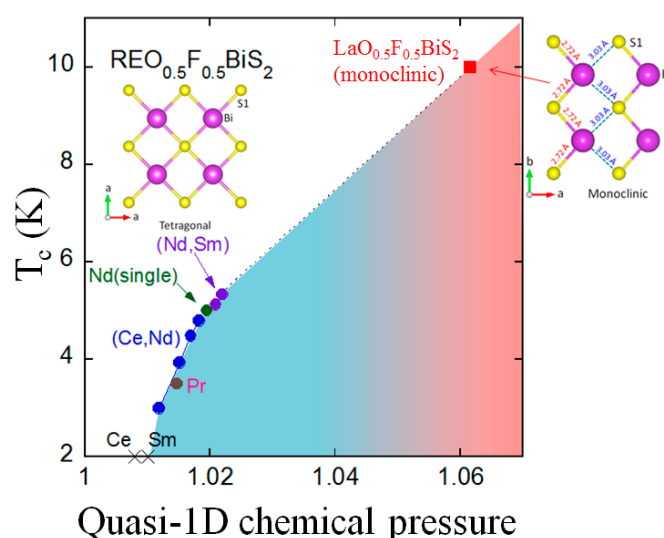


Figure 5. Possible superconductivity phase diagram plotted as a function of quasi-1D (one dimensional) chemical pressure of the $\text{REO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ -type structures with the tetragonal or monoclinic space group.

In addition, to design new BiS_2 -based superconductors, we have to consider the local-scale crystal structure and physical properties. Tuning the internal strain sometimes results in local phase separation, and the coexistence of local phase separation and superconductivity has been observed in several layered superconductors [41–45]. Thus, understanding the crystal structure and superconducting (electronic) states on the local scale is very important for developing new layered superconductors and increasing T_c . In the BiS_2 -based compounds, such a phase separation could occur because the chemical pressure effects, proposed as key strategies for the emergence of

superconductivity in this system, yield a poor fit between the conducting layers and blocking layers. In addition, as an experimental fact, local structure instability on the Bi-S plane has been revealed in BiS₂-based compounds under external and chemical pressures [36,46–49]. Beyond controlling local-scale structures, we will be able to create new BiS₂-based superconductors with a high T_c .

4. Summary

In this review article, we introduced the history of the discovery of new BiS₂-based superconductors, Bi₄O₄S₃ and REO_{1-x}F_xBiS₂. Although the understanding of the mechanisms of superconductivity has advanced, the precise prediction of the emergence of superconductivity in unknown compounds is very difficult. For this reason, it is very important to stack the experiences of the material design of new superconductors. We are happy if the review on the discovery of the BiS₂-based superconductor is useful for the exploration of new superconductors.

We summarized the effects of electron carrier doping, external pressure, and chemical pressure on the emergence of superconductivity in the BiS₂-based compounds. To induce superconductivity, optimizations of both the electron carrier doping and in-plane chemical pressure are needed. Since we have already obtained some strategies for designing new BiS₂-based superconductors and increasing T_c , we expect that the field of BiS₂-based superconductivity will be a breakthrough for the discovery of new kinds of high- T_c superconductors.

Acknowledgments: The works on Bi-chalcogenide superconductors have been supported by Grant-in-Aid for Scientific Research (No. 25707031, 26600077, 15H05886, and 16H04493).

Conflicts of Interest: The author declares no conflict of interest.

References

1. Kamihara, Y.; Watanabe, T.; Hirano, M.; Hosono, H. Iron-Based Layered Superconductor La[O_{1-x}F_x]FeAs ($x = 0.05$ – 0.12) with $T_c = 26$ K. *J. Am. Chem. Soc.* **2008**, *130*, 3296–3297.
2. Ishida, K.; Nakai, Y.; Hosono, H. To What Extent Iron-Pnictide New Superconductors Have Been Clarified: A Progress Report. *J. Phys. Soc. Jpn.* **2009**, *78*, 062001.
3. Bednorz, J.G.; Müller, K.A. Possible high T_c superconductivity in the Ba-La-Cu-O system. *Z. Phys. B Condens. Matter* **1986**, *64*, 189–193.
4. Liu, Y.; Zhao, L.D.; Liu, Y.; Lan, J.; Xu, W.; Li, F.; Zhang, B.P.; Berardan, D.; Dragoe, N.; Lin, Y.H.; et al. Remarkable Enhancement in Thermoelectric Performance of BiCuSeO by Cu Deficiencies. *J. Am. Chem. Soc.* **2011**, *133*, 20112–20115.
5. Momma, K.; Izumi, F. VESTA: A three-dimensional visualization system for electronic and structural analysis. *J. Appl. Crystallogr.* **2008**, *41*, 653–658.
6. Ubaldini, A.; Giannini, E.; Senatore, C.; van der Marel, D. BiOCuS: A new superconducting compound with oxypnictide-related structure. *Physica C* **2010**, *470*, S356–S357.
7. Pal, A.; Kishan, H.; Awana, V.P.S. Synthesis and Structural Details of BiOCu_{1-x}S: Possible New Entrant in a Series of Exotic Superconductors? *J. Supercond. Nov. Magn.* **2010**, *23*, 301–304.
8. Mat Navi. Available online: <http://mits.nims.go.jp/> (accessed on 26 January 2017).
9. Mizuguchi, Y.; Fujihisa, H.; Gotoh, Y.; Suzuki, K.; Usui, H.; Kuroki, K.; Demura, S.; Takano, Y.; Izawa, H.; Miura, O. BiS₂-based layered superconductor Bi₄O₄S₃. *Phys. Rev. B* **2012**, *86*, 220510.
10. Tanryverdiev, V.S.; Aliev, O.M.; Aliev, I.I. Synthesis and physicochemical properties of LnBiOS₂. *Inorg. Mater.* **1995**, *31*, 1497–1498.
11. Mizuguchi, Y.; Demura, S.; Deguchi, K.; Takano, Y.; Fujihisa, H.; Gotoh, Y.; Izawa, H.; Miura, O. Superconductivity in Novel BiS₂-Based Layered Superconductor LaO_{1-x}F_xBiS₂. *J. Phys. Soc. Jpn.* **2012**, *81*, 114725.
12. Usui, H.; Suzuki, K.; Kuroki, K. Minimal electronic models for superconducting BiS₂ layers. *Phys. Rev. B* **2012**, *86*, 220501.
13. Tomita, T.; Ebata, M.; Soeda, H.; Takahashi, H.; Fujihisa, H.; Gotoh, Y.; Mizuguchi, Y.; Izawa, H.; Miura, O.; Demura, S.; Deguchi, K.; Takano, Y. Pressure-induced Enhancement of Superconductivity in BiS₂-layered LaO_{1-x}F_xBiS₂. *J. Phys. Soc. Jpn.* **2014**, *83*, 063704.

14. Wolowiec, C.T.; Yazici, D.; White, B.D.; Huang, K.; Maple, M.B. Pressure-induced enhancement of superconductivity and suppression of semiconducting behavior in $\text{LnO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ ($\text{Ln} = \text{La}, \text{Ce}$) compounds. *Phys. Rev. B* **2013**, *88*, 064503.
15. Wolowiec, C.T.; White, B.D.; Jeon, I.; Yazici, D.; Huang, K.; Maple, M.B. Enhancement of superconductivity near the pressure-induced semiconductor-metal transition in BiS_2 -based superconductors $\text{LnO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$). *J. Phys. Condens. Matter* **2013**, *25*, 422201.
16. Kotegawa, H.; Tomita, Y.; Tou, H.; Izawa, H.; Mizuguchi, Y.; Miura, O.; Demura, S.; Deguchi, K.; Takano, Y. Pressure Study of BiS_2 -Based Superconductors $\text{Bi}_4\text{O}_4\text{S}_3$ and $\text{La}(\text{O},\text{F})\text{BiS}_2$. *J. Phys. Soc. Jpn.* **2012**, *81*, 103702.
17. Deguchi, K.; Mizuguchi, Y.; Demura, S.; Hara, H.; Watanabe, T.; Denholme, S.J.; Fujioka, M.; Okazaki, H.; Ozaki, T.; Takeya, H.; et al. Evolution of superconductivity in $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$ prepared by high pressure technique. *EPL* **2013**, *101*, 17004.
18. Kajitani, J.; Deguchi, K.; Omachi, A.; Hiroi, T.; Takano, Y.; Takatsu, H.; Kadowaki, H.; Miura, O.; Mizuguchi, Y. Correlation between crystal structure and superconductivity in $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$. *Solid State Commun.* **2014**, *181*, 1–4, doi:10.1016/j.ssc.2013.11.027.
19. Xing, J.; Li, S.; Ding, X.; Yang, H.; Wen, H.H. Superconductivity Appears in the Vicinity of an Insulating-Like Behavior in $\text{CeO}_{1-x}\text{F}_x\text{BiS}_2$. *Phys. Rev. B* **2012**, *86*, 214518.
20. Demura, S.; Deguchi, K.; Mizuguchi, Y.; Sato, K.; Honjyo, R.; Yamashita, A.; Yamaki, T.; Hara, H.; Watanabe, T.; Denholme, S.J.; et al. Coexistence of bulk superconductivity and ferromagnetism in $\text{CeO}_{1-x}\text{F}_x\text{BiS}_2$. *J. Phys. Soc. Jpn.* **2015**, *84*, 024709.
21. Jha, R.; Kumar, A.; Singh, S.K.; Awana, V.P.S. Synthesis and superconductivity of new BiS_2 based superconductor $\text{PrO}_{0.5}\text{F}_{0.5}\text{BiS}_2$. *J. Supercond. Nov. Magn.* **2012**, *26*, 499–502.
22. Demura, S.; Mizuguchi, Y.; Deguchi, K.; Okazaki, H.; Hara, H.; Watanabe, T.; Denholme, S.J.; Fujioka, M.; Ozaki, T.; Fujihisa, H.; et al. BiS_2 -based superconductivity in F-substituted NdOBiS_2 . *J. Phys. Soc. Jpn.* **2013**, *82*, 033708.
23. Kajitani, J.; Hiroi, T.; Omachi, A.; Miura, O.; Mizuguchi, Y. Chemical pressure effect on superconductivity of BiS_2 -based $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{1-y}\text{F}_y\text{BiS}_2$ and $\text{Nd}_{1-z}\text{Sm}_z\text{O}_{1-y}\text{F}_y\text{BiS}_2$. *J. Phys. Soc. Jpn.* **2015**, *84*, 044712.
24. Thakur, G.S.; Selvan, G.K.; Haque, Z.; Gupta, L.C.; Samal, S.L.; Arumugam, S.; Ganguli, A.K. Synthesis and properties of $\text{SmO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ and enhancement in T_c in $\text{La}_{1-y}\text{Sm}_y\text{O}_{0.5}\text{F}_{0.5}\text{BiS}_2$. *Inorg. Chem.* **2015**, *54*, 1076–1081.
25. Lei, H.; Wang, K.; Abeykoon, M.; Bozin, E.S.; Petrovic, C. New layered oxysulfide SrFBiS_2 . *Inorg. Chem.* **2013**, *52*, 10685.
26. Lin, X.; Ni, X.; Chen, B.; Xu, X.; Yang, X.; Dai, J.; Li, Y.; Yang, X.; Luo, Y.; Tao, Q.; et al. Superconductivity induced by La doping in $\text{Sr}_{1-x}\text{La}_x\text{FBiS}_2$. *Phys. Rev. B* **2013**, *87*, 020504.
27. Zhai, H.F.; Tang, Z.T.; Jiang, H.; Xu, K.; Zhang, K.; Zhang, P.; Bao, J.K.; Sun, Y.L.; Jiao, W.H.; Nowik, I.; et al. Possible Charge-density wave, superconductivity and f-electron valence instability in EuBiS_2F . *Phys. Rev. B* **2014**, *90*, 064518.
28. Jha, R.; Tiwari, B.; Awana, V.P.S. Appearance of bulk Superconductivity under Hydrostatic Pressure in $\text{Sr}_{0.5}\text{RE}_{0.5}\text{FBiS}_2$ ($\text{RE} = \text{Ce}, \text{Nd}, \text{Pr}$ and Sm) new compounds. *J. Appl. Phys.* **2015**, *117*, 013901.
29. Zhai, H.F.; Zhang, P.; Wu, S.Q.; He, C.Y.; Tang, Z.T.; Jiang, H.; Sun, Y.L.; Bao, J.K.; Nowik, I.; Felner, I.; et al. Anomalous Eu Valence State and Superconductivity in Undoped $\text{Eu}_3\text{Bi}_2\text{S}_4\text{F}_4$. *J. Am. Chem. Soc.* **2014**, *136*, 15386–15386.
30. Luo, Y.; Zhai, H.F.; Zhang, P.; Xu, Z.A.; Cao, G.H.; Thompson, J.D. Pressure-enhanced superconductivity in $\text{Eu}_3\text{Bi}_2\text{S}_4\text{F}_4$. *Phys. Rev. B* **2014**, *90*, 220510.
31. Zhang, P.; Zhai, H.F.; Tang, Z.J.; Li, L.; Li, Y.K.; Chen, Q.; Chen, J.; Wang, Z.; Feng, C.M.; Cao, G.H.; et al. Superconductivity enhanced by Se doping in $\text{Eu}_3\text{Bi}_2(\text{S},\text{Se})_4\text{F}_4$. *EPL* **2015**, *111*, 27002.
32. Sun, Y.L.; Ablimit, A.; Zhai, H.F.; Bao, J.K.; Tang, Z.T.; Wang, X.B.; Wang, N.L.; Feng, C.M.; Cao, G.H. Design and Synthesis of a New Layered Thermoelectric Material $\text{LaPbBiS}_3\text{O}$. *Inorg. Chem.* **2014**, *53*, 11125–11129.
33. Li, L.; Parker, D.; Babkevich, P.; Yang, L.; Ronnow, H.M.; Sefat, A.S. Superconductivity in semimetallic $\text{Bi}_3\text{O}_2\text{S}_3$. *Phys. Rev. B* **2015**, *91*, 104511.
34. Higashinaka, R.; Miyazaki, R.; Mizuguchi, Y.; Miura, O.; Aoki, Y. Low-Temperature Enhancement in the Upper Critical Field of Underdoped $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$ ($x = 0.1\text{--}0.3$). *J. Phys. Soc. Jpn.* **2014**, *83*, 075004.
35. Jha, R.; Awana, V.P.S. Effect of Hydrostatic Pressure on BiS_2 -Based Layered Superconductors: A Review. *Nov. Supercond. Mater.* **2016**, *2*, 2299–3193.

36. Sagayama, R.; Sagayama, H.; Kumai, R.; Murakami, Y.; Asano, T.; Kajitani, J.; Higashinaka, R.; Matsuda, T.D.; Aoki, Y. Symmetry Lowering in LaOBiS₂: A Mother Material for BiS₂-Based Layered Superconductors. *J. Phys. Soc. Jpn.* **2015**, *84*, 123703.
37. Liu, Q.; Zhang, X.; Zunger, A. Polytypism in LaOBiS₂-type compounds based on different three-dimensional stacking sequences of two-dimensional BiS₂ layers. *Phys. Rev. B* **2016**, *93*, 174119.
38. Hiroi, T.; Kajitani, J.; Omachi, A.; Miura, O.; Mizuguchi, Y. Evolution of superconductivity in BiS₂-based superconductor LaO_{0.5}F_{0.5}Bi(Si_{1-x}Se_x)₂. *J. Phys. Soc. Jpn.* **2015**, *84*, 024723.
39. Mizuguchi, Y.; Miura, A.; Kajitani, J.; Hiroi, T.; Miura, O.; Tadanaga, K.; Kumada, N.; Magome, E.; Moriyoshi, C.; Kuroiwa, Y. In-plane chemical pressure essential for superconductivity in BiCh₂-based (Ch: S, Se) layered structure. *Sci. Rep.* **2015**, *5*, 14968.
40. Jinno, G.; Jha, R.; Yamada, A.; Higashinaka, R.; Matsuda, T.D.; Aoki, Y.; Nagao, M.; Miura, O.; Mizuguchi, Y. Bulk Superconductivity Induced by In-plane Chemical Pressure Effect in Eu_{0.5}La_{0.5}FBiS_{2-x}Se_x. *J. Phys. Soc. Jpn.* **2016**, *85*, 124708.
41. Ricci, A.; Poccia, N.; Joseph, B.; Arrighetti, G.; Barba, L.; Plaisier, J.; Campi, G.; Mizuguchi, Y.; Takeya, H.; Takano, Y.; Saini, N.L.; Bianconi, A. Intrinsic phase separation in superconducting K_{0.8}Fe_{1.6}Se₂ (T_c = 31.8 K) single crystals. *Supercond. Sci. Technol.* **2011**, *24*, 082002.
42. Kugel, K.I.; Rakhmanov, A.L.; Sboychakov, A.O.; Kusmartsev, F.V.; Poccia, N.; Bianconi, A. A two-band model for the phase separation induced by the chemical mismatch pressure in different cuprate superconductors. *Supercond. Sci. Technol.* **2009**, *22*, 014007.
43. Poccia, N.; Ricci, A.; Bianconi, A. Misfit Strain in Superlattices Controlling the Electron-Lattice Interaction via Microstrain in Active Layers. *Adv. Condens. Matter Phys.* **2010**, *2010*, 261849.
44. Bianconi, A.; Di Castro, D.; Bianconi, G.; Pifferi, A.; Saini, N.L.; Chou, F.C.; Johnston, D.C.; Colapietro, M. Coexistence of stripes and superconductivity: T_c amplification in a superlattice of superconducting stripes. *Physica C* **2000**, *341–348*, 1719–1722.
45. Bendele, M.; Barinov, A.; Joseph, B.; Innocenti, D.; Iadecola, A.; Bianconi, A.; Takeya, H.; Mizuguchi, Y.; Takano, Y.; Noji, T.; et al. Spectromicroscopy of electronic phase separation in K_xFe_{2-y}Se₂ superconductor. *Sci. Rep.* **2014**, *4*, 5592, doi:10.1038/srep05592.
46. Athauda, A.; Yang, J.; Lee, S.; Mizuguchi, Y.; Deguchi, K.; Takano, Y.; Miura, O.; Louca, D. In-plane Charge Fluctuations in Bismuth Sulfide Superconductors. *Phys. Rev. B* **2014**, *91*, 144112.
47. Mizuguchi, Y.; Paris, E.; Sugimoto, T.; Iadecola, A.; Kajitani, J.; Miura, O.; Mizokawa, T.; Saini, N.L. The effect of RE substitution in layered REO_{0.5}F_{0.5}BiS₂: Chemical pressure, local disorder and superconductivity. *Phys. Chem. Chem. Phys.* **2015**, *17*, 22090–22096.
48. Paris, E.; Joseph, B.; Iadecola, A.; Sugimoto, T.; Olivi, L.; Demura, S.; Mizuguchi, Y.; Takano, Y.; Mizokawa, T.; Saini, N.L. Determination of local atomic displacements in CeO_{1-x}F_xBiS₂ system. *J. Phys. Condens. Matter* **2014**, *26*, 435701.
49. Mizuguchi, Y.; Miura, A.; Nishida, A.; Miura, O.; Tadanaga, K.; Kumada, N.; Lee, C.H.; Magome, E.; Moriyoshi, C.; Kuroiwa, Y. Compositional and temperature evolution of crystal structure of new thermoelectric compound LaOBiS_{2-x}Se_x. *J. Appl. Phys.* **2016**, *119*, 155103.

