Discovery of BiS₂-Based Superconductor and Material Design Concept

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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, LaO₁₋ₓFₓBiS₂. 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.
was determined. Since the XRD pattern was collected with a powder sample, the determination of which is a layered compound, according to the material database [8]. Surprisingly, the Bi$_2$O$_2$S sample was expected to be a band insulator, but the present phase, Bi$_4$O$_4$S$_3$, corresponded to a layered 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 $^\circ$C. Although we obtained the single-phase sample of Bi$_4$O$_4$S$_3$, 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 Bi$_4$O$_4$S$_3$ 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 Bi$_4$O$_4$S$_3$ is composed of alternate stacking of the BiS$_2$ bilayer, which is electrically conducting, and the Bi$_4$O$_4$(SO$_4$)$_2$ blocking layer. The parent phase ($x = 0$) was expected to be a band insulator, but the present phase, Bi$_4$O$_4$S$_3$, corresponded to $x = 0.5$. Namely, there are 50% SO$_4$ defects in the blocking layer, and, hence, electrons are doped to the BiS$_2$ layers, resulting in metallic conductivity and superconductivity [9]. Interestingly, the stable phase (composition) contains defects at the SO$_4$ site, and the control of the doping level is very difficult in this Bi$_4$O$_4$SO$_4$Bi$_2$S$_3$ structure. Motivated by this difficulty, we tried to synthesize other BiS$_2$-based superconductors with a simpler structure.

Figure 1. (a) Schematic images of crystal structure of Fe-based LaOFeAs; (b–e) Schematic images of crystal structures of BiS$_2$-based (b) LaOBiS$_2$, (c) SrFBiS$_2$, (d) Eu$_3$F$_4$Bi$_2$S$_4$, and (e) Bi$_4$O$_4$SO$_4$Bi$_2$S$_4$. 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-Bu-S and finally synthesized Cu-free Bi$_2$O$_2$S, which is a layered compound, according to the material database [8]. Surprisingly, the Bi$_2$O$_2$S sample prepared at 500 $^\circ$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 Bi$_2$O$_2$S 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 $^\circ$C. Then, we explored the optimal composition of the unknown Bi–O–S superconducting phase. After synthesizing and evaluating over 100 samples of Bi$_4$O$_4$S$_3$ (with various synthesis temperatures), we obtained the optimal composition of Bi$_4$O$_4$S$_3$, 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 Bi$_4$O$_4$S$_3$, 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 Bi$_4$O$_4$S$_3$ 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 Bi$_4$O$_4$S$_3$ is composed of alternate stacking of the BiS$_2$ bilayer, which is electrically conducting, and the Bi$_4$O$_4$(SO$_4$)$_2$ blocking layer. The parent phase ($x = 0$) was expected to be a band insulator, but the present phase, Bi$_4$O$_4$S$_3$, corresponded to $x = 0.5$. Namely, there are 50% SO$_4$ defects in the blocking layer, and, hence, electrons are doped to the BiS$_2$ layers, resulting in metallic conductivity and superconductivity [9]. Interestingly, the stable phase (composition) contains defects at the SO$_4$ site, and the control of the doping level is very difficult in this Bi$_4$O$_4$SO$_4$Bi$_2$S$_3$ structure. Motivated by this difficulty, we tried to synthesize other BiS$_2$-based superconductors with a simpler structure.
1.3. 1112-Type BiS$_2$-Based Superconductors

After the discovery of the Bi$_4$O$_4$S$_3$ superconductor, we studied LaOBiS$_2$, the crystal structure of which is composed of a La$_2$O$_2$ blocking layer and a BiS$_2$ 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 Bi$_4$O$_4$S$_3$ and LaOBiS$_2$, we synthesized electron-doped LaOBiS$_2$, LaO$_{1-x}$F$_x$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 LaO$_{1-x}$F$_x$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 LaO$_{0.5}$F$_{0.5}$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 LaO$_{0.5}$F$_{0.5}$BiS$_2$ [10,17,18]. In order to induce bulk superconductivity in LaO$_{0.5}$F$_{0.5}$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, REO$_{1-x}$F$_x$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$_2$O$_2$ layer can be replaced by the Sr$_2$F$_2$ or Eu$_2$F$_2$ 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 Eu$_4$F$_3$Bi$_2$S$_4$, which is composed of alternate stacks of the Eu$_4$F$_3$ 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 ($T_c$ ~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$_2$O$_2$ blocking similar to LaOBiS$_2$, but its conducting layer is Bi$_2$Pb$_2$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 Bi$_4$O$_4$S$_3$. In Bi$_3$O$_2$S$_3$, the SO$_4$ site of Bi$_4$O$_4$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 LaO$_{0.5}$F$_{0.5}$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 LaO$_{0.5}$F$_{0.5}$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 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 LaO$_{1-x}$F$_x$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 LaO$_{0.5}$F$_{0.5}$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 LaO$_{0.5}$F$_{0.5}$BiS$_2$. The inset shows the F concentration ($x$) dependence of $T_c$ of LaO$_{1-x}$F$_x$BiS$_2$.](image)

### 2.2. External Pressure Effect

The superconducting properties of REO$_{1-x}$F$_x$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 LaO$_{0.5}$F$_{0.5}$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 LaO$_{0.5}$F$_{0.5}$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 LaO$_{0.5}$F$_{0.5}$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 $T_c = 2.5-8$ K by modifying the annealing temperature and pressure. Indeed, for LaO$_{0.5}$F$_{0.5}$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 REO$_{1-x}$F$_x$BiS$_2$ with an optimal F doping (LaO$_{0.5}$F$_{0.5}$BiS$_2$, CeO$_{0.3}$F$_{0.7}$BiS$_2$, PrO$_{0.5}$F$_{0.5}$BiS$_2$, and NdO$_{0.3}$F$_{0.7}$BiS$_2$) [13–16,35]. All the...
REO$_{1-x}$F$_x$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 REO$_{1-x}$F$_x$BiS$_2$. This can be understood with the crystal structure transition from tetragonal ($P4/mmm$) to monoclinic ($P2_1/m$) in LaO$_{1-x}$F$_x$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 REO$_{1-x}$F$_x$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](image_url)

**Figure 3.** (a) Temperature dependences of magnetic susceptibility for two different LaO$_{0.5}$F$_{0.5}$BiS$_2$ samples, low-pressure phase (low-P phase) and high-pressure phase (high-P phase); (b) Pressure dependences of $T_c$ for REO$_{1-x}$F$_x$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 LaO$_{0.5}$F$_{0.5}$BiS$_2$.

2.3. Chemical Pressure Effect

Another method to induce the bulk superconductivity of LaO$_{0.5}$F$_{0.5}$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 LaO$_{0.5}$F$_{0.5}$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 REO$_{0.5}$F$_{0.5}$BiS$_2$, bulk superconductivity (at above 2 K) is induced at RE = Ce$_{0.6}$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 REO$_{0.5}$F$_{0.5}$BiS$_2$. These results seem to be consistent with the external pressure effects, while the crystal structure remains tetragonal.
up to RE = Sm [23,24]. Then, please note that the filamentary (non-bulk) superconductivity observed in RE = 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 LaO$_{0.5}$F$_{0.5}$BiS$_{2−x}$Se$_x$ (Figure 4b) is quite similar to that for REO$_{0.5}$F$_{0.5}$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](image-url)

Figure 4. (a) Superconductivity phase diagram of REO$_{0.5}$F$_{0.5}$BiS$_2$ plotted as a function of mean RE$^{3+}$ ionic radius; (b) Superconductivity phase diagram of LaO$_{0.5}$F$_{0.5}$BiS$_{2−x}$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 REO$_{0.5}$F$_{0.5}$BiS$_2$-type structure.

2.4. Importance of In-Plane Chemical Pressure

On the basis of the experimental facts on REO$_{0.5}$F$_{0.5}$BiS$_2$ and LaO$_{0.5}$F$_{0.5}$BiS$_{2−x}$Se$_x$, we explored a factor essential for the evolution of bulk superconductivity in this family. To address it, the crystal structures of Ce$_{1−x}$Nd$_x$O$_{0.5}$F$_{0.5}$BiS$_2$ and LaO$_{0.5}$F$_{0.5}$BiS$_{2−x}$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 $R_{\text{Bi}}$ and $R_{\text{Ch}}$ 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 REO0.5F0.5BiCh2 structure.

Figure 4f shows the in-plane chemical pressure dependences of Tc for the REO0.5F0.5BiS2-type and LaO0.5F0.5BiS2-0.5Se0.5 superconductors. There is a trend that Tc increases with the increasing in-plane chemical pressure [39]. Indeed, the magnitude of the in-plane chemical pressure becomes the scale for Tc in the tetragonal phase of REO0.5F0.5BiCh2.

3. Material Design Strategies for the BiS2-Based Superconductor

In the Section 2, the requirements for the emergence of superconductivity in the BiS2-based compounds were reviewed. Electron carrier doping to the BiS2 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 BiS2-based superconductivity), new superconductors can be easily designed as demonstrated in Eu0.5La0.5FBiS2-0.5Se0.5 [40].

Then, what is the strategy for enhancing Tc in this system? One idea comes when considering the large enhancement of Tc in LaO0.5F0.5BiS2 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 Tc 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 LaO0.5F0.5BiS2 as the origin of the high Tc. As plotted in Figure 5, the calculated quasi-1D chemical pressure for the high-P phase of LaO0.5F0.5BiS2 locates on the extrapolated line of the Tc in-plane chemical pressure relation. This may suggest that a higher Tc 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, BiS2-based compounds with a larger a-axis should be candidates for the extremely distorted phase with a high Tc.

![Figure 5](image_url)
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 BiS$_2$-based compounds under external and chemical pressures [36,46–49]. Beyond controlling local-scale structures, we will be able to create new BiS$_2$-based superconductors with a high $T_c$.

4. Summary

In this review article, we introduced the history of the discovery of new BiS$_2$-based superconductors, Bi$_4$O$_3$S$_3$ and REO$_{1-x}$F$_x$BiS$_2$. 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 BiS$_2$-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 BiS$_2$-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 BiS$_2$-based superconductors and increasing $T_c$, we expect that the field of BiS$_2$-based superconductivity will be a breakthrough for the discovery of new kinds of high-$T_c$ superconductors.

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