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Effect of Local Structure Distortion on Superconductivity in Mg- and F-Codoped $LaOBiS_2$

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Supporting Information

ABSTRACT: $La_{1-x}Mg_xO_{1-2x}F_{2x}BiS_2$ (x = 0.1−0.35) were synthesized, and their superconductive properties were investigated. The superconducting transition temperature (T_c) increased below the codoping level ($x \leq 0.25$). $La_{1-x}Mg_xOBiS_2$ (x = 0−0.2) and $La_{1-x}Mg_xO_{0.6}F_{0.4}BiS_2$ (x = 0.1−0.3) were further prepared to explore the effect of Mg^{2+}. We found that the introduction of Mg^{2+} and F^- leads to local structure distortion. Larger distortion is beneficial for superconductivity in $LaOBiS_2$, which was further confirmed by the results in $La_{1-x}Ca_xO_{1-2x}F_{2x}BiS_2$ (x = 0.2, 0.3).

The BiS_2-based superconductors have motivated considerable attention since the discovery of superconductivity (T_c^{onset} = 8.6 K) in $Bi_4O_4S_3$, which is constructed by superconducting $[BiS_2]^-$ layers and blocking $[Bi_4O_4(SO_4)_{1-\delta}]^+$ layers.[1] Recently, new BiS_2-based superconducting compounds were found in doped $LnOBiS_2$ (Ln = La, Ce, Pr, Nd).[2−9] These compounds possess layered structures and doping mechanisms similar to Fe- and Cu-based superconductors.[10−13] The $[BiS_2]^-$ layer plays a role similar to those of the $[FePn]^-$ (Pn = P, As) layer in Fe-based superconductors and the $[CuO_2]^{2-}$ layer in Cu-based ones. For better superconductivity, it is necessary to preserve the integrity of the conducting constituents, which have been demonstrated in both the Fe- and Cu-based superconductors. Herein, it can be expected that the superconductivity may be improved by modifying the $[LnO]^+$ layers in the BiS_2-based superconductors, such as F^- doping in the O site[2] and tetravalent ion doping in the Ln site.[7]

In Fe-based superconductors, doping in the $[LnO]^+$ layers generates more carrier density and local structure distortion, as a result of the diverse valences and radii between the different ions.[14] It has also been demonstrated that higher carrier (electron) density is beneficial for superconductivity in BiS_2-based superconductors.[7] Furthermore, external high-pressure preparation methods have also been carried out to prepare the BiS_2-based superconductors, and a higher transition temperature (T_c) was also obtained.[15−17] However, the effect of local structure distortion, which is different from that of the external high pressure, needs to be explored. In our former research, we investigated the effect of lattice distortion on the superconductivity by codoping Mg^{2+}/F^- and Sc^{3+}/F^- into SmFeAsO.[18−20] Considering the similar layered structures between LaFeAsO and $LaOBiS_2$, Mg^{2+} and F^- were codoped into $LaOBiS_2$ and their superconductivity was fully investigated. Polycrystalline $La_{1-x}Mg_xO_{1-2x}F_{2x}BiS_2$ (x = 0.1−0.35) were synthesized. $La_{1-x}Mg_xOBiS_2$ (x = 0−0.2), $La_{1-x}Mg_xO_{0.6}F_{0.4}BiS_2$ (x = 0.1−0.3), and $La_{1-x}Ca_xO_{1-2x}F_{2x}BiS_2$ (x = 0.2, 0.3) were prepared to understand the role of local structure distortion in $LaOBiS_2$.

The crystal structures of $LaOBiS_2$ and LaFeAsO are shown in Figure 1a. Both of them are crystallized in a layered structure with

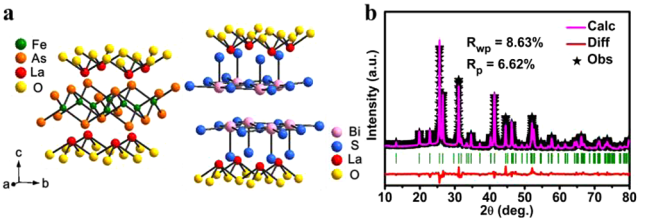

Figure 1. (a) Comparison of the crystal structures between $LaOBiS_2$ and LaFeAsO. (b) Fitted profiles of $La_{0.8}Mg_{0.2}O_{0.6}F_{0.4}BiS_2$ calculated by the Rietveld method.

alternate positive and negative layers. The structure of $[BiS_2]^-$ layers (rock-salt-type) is different from that of $[FeAs]^-$ layers (PbO-type). The $[LaO]^+$ layer acts as a blocking layer in both compounds, and the $[BiS_2]^-$ layer plays a role in $LaOBiS_2$ similar to that of the $[FeAs]^-$ layer in LaFeAsO for charge transfer, which is crucial for superconductivity. In the Mg^{2+}- and F^--codoped SmFeAsO, Mg^{2+} and F^- are preferred to substitute for Sm^{3+} and O^{2-}, respectively.[19] The same occupancies can be expected in $LaOBiS_2$. The Rietveld method was used to refine the crystal structure of $La_{0.8}Mg_{0.2}O_{0.6}F_{0.4}BiS_2$ with R_{wp} = 8.63% and R_p = 6.62%, and the fitted profile is shown in Figure 1b.

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Substitution of O^{2-} by F^- leads to electron doping and La^{3+} by Mg^{2+} to hole doping. In the $La_{1-x}Mg_xO_{1-2x}F_{2x}BiS_2$ system, the introduction of Mg^{2+} generates x holes. Simultaneously, the introduction of F^- generates $2x$ electrons. The average oxidation state of Bi is $+(3-x)$ in $La_{1-x}Mg_xO_{1-2x}F_{2x}BiS_2$, and the electronic configuration of $Bi^{(3-x)+}$ becomes Bi $6s^2 6p^x$. Herein, x electrons were introduced into n-type $LaOBiS_2$. A higher electron density was realized. First-principle density functional theory (DFT) calculations were performed by using the VASP code to obtain electronic density of states (DOS) for $LaOBiS_2$ and $La_{0.75}Mg_{0.25}O_{0.5}F_{0.5}BiS_2$ (Figure 2a). Compared to $LaOBiS_2$,

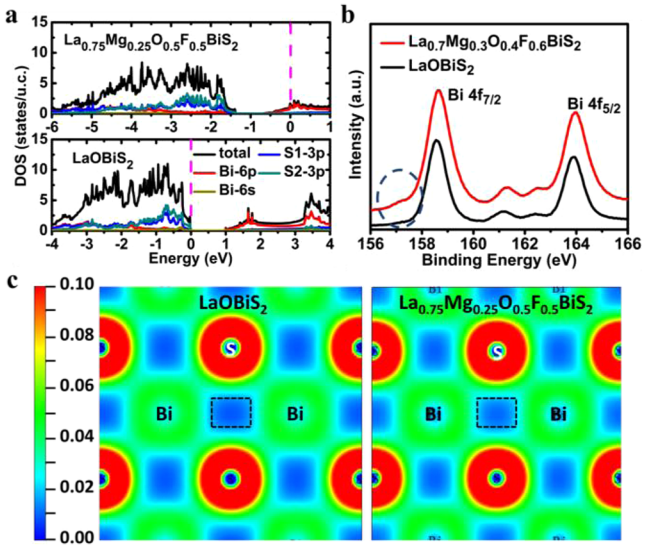

Figure 2. (a) Total and partial electronic DOS for $LaOBiS_2$ and $La_{0.75}Mg_{0.25}O_{0.5}F_{0.5}BiS_2$. (b) Bi 4f XPS spectra of the as-prepared $LaOBiS_2$ and $La_{0.7}Mg_{0.3}O_{0.4}F_{0.6}BiS_2$. (c) Charge density distribution (0.1 e/Å^3) on the Bi−S plane.

the Fermi level in $La_{0.75}Mg_{0.25}O_{0.5}F_{0.5}BiS_2$ moves upward toward the conduction band, resulting in a higher carrier density at the Fermi energy. Figure 2b shows Bi 4f X-ray photoelectron spectroscopy (XPS) spectra of the as-prepared $LaOBiS_2$ and $La_{0.7}Mg_{0.3}O_{0.4}F_{0.6}BiS_2$. The Bi $4f_{7/2}$ and Bi $4f_{5/2}$ XPS peaks centered at binding energies of 158.6 and 163.9 eV are typical for Bi−S bonds. In the marked area, the intensity of the curve in $La_{0.7}Mg_{0.3}O_{0.4}F_{0.6}BiS_2$ is stronger than that of $LaOBiS_2$, which indicates the existence of a smaller valence state of the Bi element. To further analyze the Bi−S bonds, the charge density distributions of $LaOBiS_2$ and $La_{0.75}Mg_{0.25}O_{0.5}F_{0.5}$ are given in Figure 2c. The contour lines are plotted from 0.0 to 0.1 e/Å^3. In the marked field, the area of the latter is smaller than that of the former, which indicates that the charge density near Bi atoms in $La_{0.75}Mg_{0.25}O_{0.5}F_{0.5}$ is higher than that of $LaOBiS_2$. This result is consistent with DOS analysis and XPS spectra.

The X-ray diffraction (XRD) patterns of $La_{1-x}Mg_xO_{1-2x}F_{2x}BiS_2$ (x = 0.1−0.35) are shown in Figure 3a. An impurity of Bi_2S_3 is observed in the $x \geq 0.25$ samples, which is consistent with the former report.[2] The doping limit can be determined as x = 0.25. The main peaks are well indexed into space group $P4/nmm$ with a layered structure. The magnified XRD patterns between 25.0° and 27.5° are shown in Figure S3 in the Supporting Information (SI). The two peaks transfer right with increasing x until 0.25, indicating a shrunken lattice. The calculated lattice parameters (a and c) as a function of the doping level (x) are displayed in Figure S4 in the SI. The c parameter

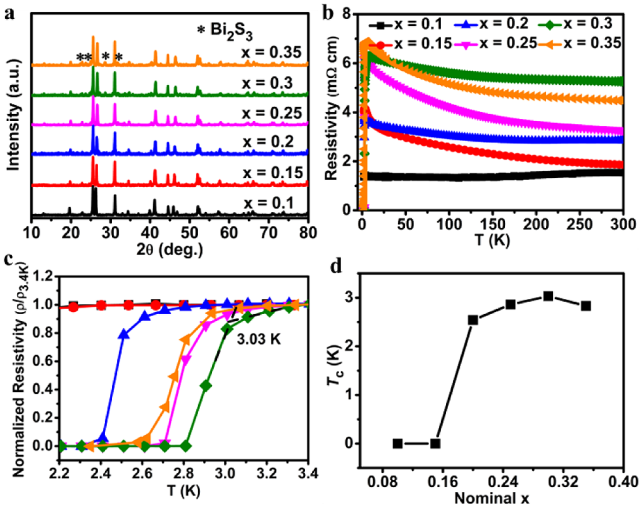

Figure 3. (a) Powder XRD patterns and (b) temperature dependence of bulk resistivity for $La_{1-x}Mg_xO_{1-2x}F_{2x}BiS_2$ (x = 0.1−0.35). (c) Magnified view near the transition temperature (T_c). (d) T_c as a function of the nominal doping (x).

decreases linearly with x below 0.25, which indicates that F^- and Mg^{2+} are successfully doped into the O and La sites, respectively. When $x \geq 0.25$, the parameters also become consistent.

Figure 3b shows the temperature dependence of resistivity for all of the samples. The resistivity increased with decreasing temperature, indicating semiconductor behavior before the superconductive transition. A magnification near the transition temperature (T_c) is presented in Figure 3c, where the resistivity is normalized. Clear superconducting resistivity transitions at low temperatures are observed with $x \geq 0.2$, as shown in Figure 3d. T_c increases with x below 0.3. As listed in Table S3 in the SI, no superconductivity is detected in $La_{0.9}Mg_{0.1}O_{0.8}F_{0.2}BiS_2$. T_c of $La_{0.7}Mg_{0.3}O_{0.4}F_{0.6}BiS_2$ (3.03 K) is higher than that of $La_{0.8}Mg_{0.2}O_{0.6}F_{0.4}BiS_2$ (2.54 K). Further doping generates smaller T_c. F^- doping can induce superconductivity in both Fe- and BiS_2-based superconductors, and more F^- in the O site leads to higher T_c.[2,10] Herein, as for $La_{1-x}Mg_xO_{1-2x}F_{2x}BiS_2$ (x = 0.1−0.35), the increase of T_c perhaps can be due to increased F^- doping. The effect of the introduction of Mg^{2+} is still uncertain.

To further evaluate the effect of partial replacement of Mg^{2+} for La^{3+}, $La_{1-x}Mg_xO_{0.6}F_{0.4}BiS_2$ (x = 0−0.3) were prepared at a fixed F^- doping level (0.4). The temperature dependence of resistivity near T_c and T_c as a function of the nominal doping (x) is shown in parts a and b of Figure 4, respectively. The introduction of Mg^{2+} suppresses T_c. As listed in Table S3 in the SI, compared to $LaO_{0.6}F_{0.4}BiS_2$ (T_c = 2.98 K), T_c (2.54 K) of $La_{0.8}Mg_{0.2}O_{0.6}F_{0.4}BiS_2$ is smaller. Substitution of divalent Mg^{2+} for trivalent La^{3+} introduces holes into the BiS_2 conduction layers, generating decreased carrier density in the n-type $LaOBiS_2$ system. Smaller Mg^{2+} (89 pm) replacing La^{3+} (116 pm) reduces lattice parameters, and results in local structure distortion.

In order to further explore the effect of local structure distortion, $La_{1-x}Ca_xO_{1-2x}F_{2x}BiS_2$ (x = 0.2, 0.3), in which divalent Ca^{2+} was introduced into the La^{3+} site, were prepared for further comparison, and the temperature dependence of resistivity is shown in Figure 4c. T_c of $La_{0.8}Ca_{0.2}O_{0.6}F_{0.4}BiS_2$ (2.07 K) is smaller than that of $La_{0.8}Mg_{0.2}O_{0.6}F_{0.4}BiS_2$ (2.54 K). Cell shrinkage of the former is smaller than that of the latter because of the smaller size difference between Ca^{2+} (112 pm) and La^{3+}

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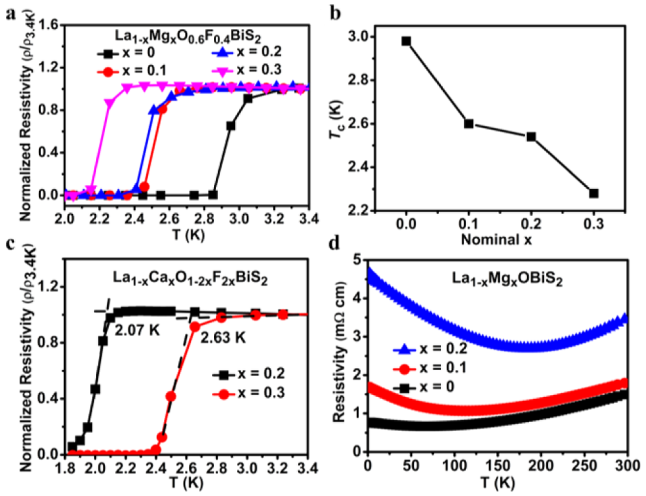

Figure 4. (a) Temperature dependence of bulk resistivity for $La_{1-x}Mg_xO_{0.6}F_{0.4}BiS_2$ (x = 0–0.3) near the transition temperature (T_c). (b) T_c as a function of the nominal doping (x). Temperature dependence of bulk resistivity for (c) $La_{1-x}Ca_xO_{1-2x}F_{2x}BiS_2$ (x = 0.2, 0.3) near the transition temperature (T_c) and (d) $La_{1-x}Mg_xOBiS_2$ (x = 0–0.2).

(116 pm), compared to that between Mg^{2+} (89 pm) and La^{3+} (116 pm). This demonstrates that larger local structure distortion is beneficial for superconductivity in $LaOBiS_2$, which can be further confirmed by a comparison of T_c between $La_{0.7}Ca_{0.3}O_{0.4}F_{0.6}BiS_2$ (2.63 K) and $La_{0.7}Mg_{0.3}O_{0.4}F_{0.6}BiS_2$ (3.03 K). In the Mg^{2+}- and F^--codoped SmFeAsO system, the introduction of Mg^{2+} to the Sm site also brought in smaller electron density, but T_c was improved, which can be attributed to the results of local structure distortion.[19] This was further confirmed in the latter Sc^{3+}- and F^--codoped SmFeAsO system.[20] In the $LaOBiS_2$ system, lower T_c was obtained. This demonstrates that the superconductivity in $LaOBiS_2$ is less sensitive to structure distortion, compared to the carrier density. This is opposite to the result in the SmFeAsO system, in which structure distortion has a stronger impact.

As shown in Figure 4d, there is no superconductivity in the $La_{1-x}Mg_xOBiS_2$ (x = 0–0.2) samples, which is accordance with the results of Sr^{2+}-doped $LaOBiS_2$.[7] Hole doping cannot introduce superconductivity in BiS_2-based superconductors. The resistivity decreased initially with temperature, reached a minimum value, and then increased with temperature. The minimum value shifts to higher temperature at the higher doping level of Mg^{2+}.

Mg^{2+} and F^- were codoped into $LaOBiS_2$ to explore the relationship between local structure distortion and superconductivity. Larger local structure distortion is beneficial for superconductivity in $LaOBiS_2$. Furthermore, the superconductivity in $LaOBiS_2$ is less sensitive to local structure distortion than carrier density, which is different in Fe-based superconductors.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, atomic positions and occupancies, microstructure, EDS spectra, magnified XRD patterns, lattice parameters, structure, upper critical field, and magnetic properties. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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