Synthesis and physical property characterization of LaOBiSe$_2$ and LaO$_{0.5}$F$_{0.5}$BiSe$_2$ superconductor

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Abstract

Bulk polycrystalline samples of La$_{(1-y)}$F$_y$BiSe$_2$ ($x$ ranges from 0 to 0.5) with nominal composition have been successfully synthesized by solid state reaction. Detailed structural analysis shows that LaOBiSe$_2$ crystallizes in a tetragonal structure (P4/nmm) with lattice parameters of $a=4.1565(1)$ Å and $c=14.1074(3)$ Å. Experimental results of electrical transport demonstrate that LaOBiSe$_2$ is a bad metal with an evident anomaly at about 120 K, while the magnetic susceptibility exhibits an evident anomaly around 120 K, suggesting a possible charge density wave (CDW) transition around this temperature. Furthermore, superconductivity is observed in LaO$_{0.5}$F$_{0.5}$BiSe$_2$ sample with nominal composition at 3.1 K from magnetic and transport measurements.

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1. Introduction

Since the discovery of superconductivity with $T_c$ around 8.6 K in layered bismuth oxyxulfide Bi$_4$O$_7$S$_2$ [1], superconductivity in the structurally related materials has been extensively investigated. A series of LnOBiSe$_2$ with Ln=$\text{La}$ [2], Nd [3], Ce [4], Pr [5], and Yb [6] materials have been found to be superconducting at low temperatures with currently the highest $T_c$ at about 10.8 K in LaO$_{0.5}$F$_{0.5}$BiSe$_2$ sample under high pressure [2]. Instead of substituting F for O, electron doped materials by substitution of tetravalent Th$^{4+}$, Hf$^{4+}$, Zr$^{4+}$, and Ti$^{4+}$ for trivalent La$^{3+}$ have showed superconductivity up to 2.85 K in LaOBiSe$_2$ [7]. A new compound SrFBiSe$_2$ has also been reported to show superconductivity at 2.8 K by La doping [8]. Furthermore, it was reported that the replacement of sulfur by isovalent selenium leads to the isostructural superconductor LaO$_{0.5}$F$_{0.5}$BiSe$_2$ with $T_c=2.6$ K in polycrystalline form [9]. Very recently, single crystals of LaO$_{0.5}$F$_{0.5}$BiSe$_2$ have been successfully synthesized by the flux method and the bulk superconductivity were further confirmed to occur with slightly different $T_c$ ($T_c=3.7$ K [10], 3.6 K [11], and 3.5 K [12]).

These materials have a layered crystal structure composed of a charge reservoir layer (LnO, where Ln is a lanthanoid) or SrF layer alternating with BiS(Se)$_2$ functional planes that play the same role as CuO$_2$ planes in cuprates or the FeAs and Fe(Se,Te) planes in iron-based superconductors. Despite the similar structural configuration, BiS(Se)$_2$-based layered superconductors exhibit some important differences comparing with Fe-pnictide superconductors, and the superconducting mechanism remains unclear. Theoretical calculation suggests that LaO$_{0.5}$F$_{0.5}$BiSe$_2$ and LaO$_{0.5}$F$_{0.5}$BiSe$_2$ belong to conventional electron-phonon coupling induced superconductors [13–16]; g-wave [17] and s-wave [18–20] pairing symmetries have been proposed by different groups. Physical measurement shows that the parent compound LnOBiSe$_2$ is a bad metal without detectable antiferromagnetic transition or structure phase transition, implying that magnetism is of less importance to superconductivity in Bi$_2$Se$_2$-based systems [7], and the superconductivity appears in close proximity to an insulating normal state for the optimal superconducting samples, in sharp contrast to the iron-based superconductors where superconductivity grows from a metallic state [21,22]. Ren reported enhanced superconductivity in F-doped LaO$_{1-x}$F$_x$Bi$_2$Se$_3$ [23]. Recently, Demura reported the coexistence of bulk superconductivity and ferromagnetism in CeO$_{1-x}$F$_x$Bi$_2$Se$_3$ [24] and, Cao [25] observed a CDW-like transition occurs at 280 K in EuBi$_2$F$_4$ below which superconductivity emerges at 0.3 K, without any extrinsic doping. So far, there is no detailed work has been carried out on the investigation of the parent compound LnOBiSe$_2$ in literature.

In this article, we report the successful synthesis and the detailed characterization of LaO$_{(1-y)}$F$_y$BiSe$_2$ ($x=0$–0.5) samples. The parent compound LaOBiSe$_2$ exhibits an evident metallic behavior with
a small semiconducting hump at about 117 K. For sample with \( x = 0.5 \), the resistivity at normal state still shows the metallic behavior but the anomaly is evidently suppressed, followed by a sharp superconducting transition below \( 3.1 \) K. The strong diamagnetic signal provides compelling evidence of bulk superconductivity in \( \text{LaO}_{0.5}\text{F}_{0.5}\text{BiSe}_2 \) compound with nominal composition.

2. Experimental

Polycrystalline samples of \( \text{LaO}_{1-x}\text{F}_x\text{BiSe}_2 \) (\( x \) ranges from 0 to 0.5) were obtained via solid state reaction. Mixture of high purity pieces of La and Bi, powders of \( \text{La}_2\text{O}_3, \text{LaF}_3 \) and Se with designed composition was pressed into pellets; three pellets with 0.8 g mass were placed in three \( \text{Al}_2\text{O}_3 \) crucibles, which then further sealed in an evacuated quartz tube of 20 ml. The tubes were placed in a furnace at room temperature. The temperature slowly ramped up to \( 300 \) °C and held there for 5 h, then heated to \( 870 \) °C and held for 12 h. Additional regrinding and sintering following similar procedure were performed to promote phase homogeneity.

The temperature dependence of resistivity was measured by a standard four-probe method. Microstructure analysis was performed on a Hitachi model S-4800 field emission scanning electron microscope (SEM) and a FEI Tecnai-F20 transmission electron microscope (TEM) with double-tilt heating holder. X-ray diffraction (XRD) is performed on a Bruker AXS D8 Advanced diffractometer equipped with Cu K\(_\alpha\) radiation at 40 kV and 40 mA. XRD spectrum of powder \( \text{LaOBiSe}_2 \) used for refinement was acquired at room temperature with 2\( \theta \) ranging from \( 5\)° to \( 120\)°, a step width of 0.02°, and a counting time of 5 s/step. A Rietveld method was applied on XRD data by means of General Structure Analysis System (GSAS) to resolve the crystal structure, in which the Pseudo-Voigt function of Toraya was used as a profile function, and the isotropic atomic displacement parameters \( B_{iso} \), the isotropic Debye–Waller factor, were assigned to all atomic sites. Magnetization measurements

### Table 1
Structure parameters of \( \text{LaOBiSe}_2 \) at 293 K.\(^a\)

<table>
<thead>
<tr>
<th>Site</th>
<th>Wyckoff position</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>( B_{iso} ) (Å(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>2c</td>
<td>1/4</td>
<td>1/4</td>
<td>0.0918(1)</td>
<td>1.12(3)</td>
</tr>
<tr>
<td>Bi</td>
<td>2c</td>
<td>1/4</td>
<td>1/4</td>
<td>0.6233(1)</td>
<td>1.03(1)</td>
</tr>
<tr>
<td>Se1</td>
<td>2c</td>
<td>1/4</td>
<td>1/4</td>
<td>0.8133(1)</td>
<td>1.25(4)</td>
</tr>
<tr>
<td>Se2</td>
<td>2c</td>
<td>1/4</td>
<td>1/4</td>
<td>0.3849(1)</td>
<td>1.25(4)</td>
</tr>
<tr>
<td>O</td>
<td>2a</td>
<td>3/4</td>
<td>1/4</td>
<td>0</td>
<td>2.3(2)</td>
</tr>
</tbody>
</table>

\( d(\text{La–O}) = 2.4486(7) \) Å (\( \times 4 \)), \( d(\text{Bi–Se}) = 2.9414(1) \) Å (\( \times 4 \)), 2.681(2) Å, and 3.363(2) Å.

\(^a\) Space group \( P4/nmm \) (No. 129) at the origin choice 2; \( a = 4.1565(1) \) Å, \( c = 14.1074(3) \) Å, and \( V = 243.726(6) \) Å\(^3\). \( d_{\text{calc}} = 7.16 \) g/cm\(^3\), \( \chi^2 = 2.1 \), \( R_{wp} = 5.65\% \), and \( R_p = 3.97\% \). The occupation \((g)\) of all the sites is unity.

Fig. 1. (Color online) (a) Powder X-ray diffraction pattern at room temperature for \( \text{LaOBiSe}_2 \). The solid line represents the intensities calculated using the Rietveld method. The bottom curves are the differences between the experimental and calculated intensities. The vertical lines indicate the Bragg peak positions of the target compound. The inset shows the crystal structure of the tetragonal compound \( \text{LaOBiSe}_2 \). (b) A SEM image of \( \text{LaOBiSe}_2 \). (c) The EDX spectrum taken on a piece of single crystal, an SAED pattern taken from the [001] zone axis direction is shown as inset.
between 2 and 300 K were carried out on a commercial superconductor quantum interference device magnetometer.

Careful Rietveld analysis at the room-temperature XRD powder pattern indicates that the synthesized LaOBiSe$_2$ material is crystallized into ZrCuSiAs type tetragonal crystal structure with space group P4/nmm (No. 129) as shown in Fig. 1(a). Most of the Bragg peaks can be indexed and some minor peaks (noted by stars) are characterized as impurities, such as La$_2$O$_3$ and Bi$_2$O$_3$, produced during the synthesis process. The resultant lattice parameters are determined as $a=4.1565(1)$ Å and $c=14.1074(3)$ Å converging the goodness of fit of the refinement ($\chi^2$) ultimately to be 2.1 with $R_p=3.97\%$ and $R_{wp}=5.65\%$. The relatively large $\chi^2$ is due to the non-trivial extra peaks originated by impurities. Final lattice parameters, $R$ factors, fractional coordinates, $B$ parameters, and selected bond lengths are listed in Table 1. The structure of LaOBiSe$_2$ is similar to LaOBiS$_2$, which is built up by stacking the rock salt-type BiS$_2$ layer and fluorite-type LaO layer alternatively along the $c$ axis as illustrated as the inset of Fig. 1(a).

In order to understand the microstructural features of the LaOBiSe$_2$ materials, we have performed a series of investigations by means of scanning electron microscopy (SEM) and selected-area electron diffraction (SAED). Fig. 1(b) shows a SEM image illustrating the typical morphological features of LaOBiSe$_2$ crystal with clearly layered structural feature. In Fig. 1(c), we present the energy dispersive X-ray microanalysis (EDX) spectrum taken on a piece of single crystal, which confirmed the presence of the La, O, Bi and Se elements. The composition of the materials is estimated as LaOBiSe$_2$. The crystal structure of the as made samples is further tested by electron-diffraction patterns taken along the various zone axis directions, all results show that all primary diffraction spots with strong intensity in these patterns can be well indexed by a tetragonal unit cell with lattice parameters of $a=4.15$ Å and $c=14.11$ Å, and a space group of P4/nmm, which is in good agreement with the XRD data. No additional superstructure spots were detected at room temperature. A typical diffraction pattern taken from the [001] zone axis direction is shown in Fig. 1(c).

The temperature dependence of the resistivity $\rho$ ($T$) for LaOBiSe$_2$ was measured by the standard four-probe method under a zero magnetic field, and the result is displayed in Fig. 2(a). On lowering the temperature, $\rho$ decreases rather linearly and then exhibits an evident upturn between 93 and 128 K. With further cooling, $\rho$ decreases again, indicating conventional metallic behavior below and above the transition temperature. Fig. 2(b) shows experimental results of the zero-field cooled (ZFC) temperature dependent dc magnetic susceptibility of the LaOBiSe$_2$ under applied fields of 5000 Oe. It can be clearly seen that the magnetic susceptibility exhibits an evident anomaly around 120 K, suggesting a possible charge density wave (CDW) transition around this temperature.

We also tried to explore the superconductivity in the $F$ doped samples with this new layered system. Fig. 3a shows the X-ray diffraction data for the powdered samples of La$_{1-x}$F$_x$BiSe$_2$ ($x=0$–$0.5$) with nominal composition. The XRD pattern looks very similar to the standard LaOBiSe$_2$ with a few minor peaks of the impurity phase. The Rietveld fitting result also reveals that the lattice parameters are $a=4.156(2)$ Å and $c=14.017(9)$ Å for La$_{0.5}$F$_0.5$BiSe$_2$, which shows a the slightly decrease of the $c$-axis lattice constant similar as the $F$ doping effect observed in the LnOBiS$_2$ system [6], suggesting that $F$ has been successfully substituted to the $O$ site, as the ionic radius of $F$ is smaller than that of $O$.

In Fig. 3(b), we present the temperature dependence of resistivity for a different doped samples of La$_{0.5}$F$_{0.5}$BiSe$_2$ with $x=0.4$ and 0.5. We can also realize that the resistivity of these materials increases with the doping of the $F$ concentrations, similar as the doping effect on the LnO$_1$-F$_x$BiSe$_2$ materials. For the $F$ doped samples, we can see that the anomaly at 120 K is gradually suppressed with the increase of doping level and a superconducting transition temperature with $T_c$ (onset) at 3.1 K and $T_c$ ($\rho=0$) at 2.8 K can be clearly observed in the enlarged low temperature resistivity curves of La$_{0.5}$F$_{0.5}$BiSe$_2$ sample (Fig. 3c). Superconductivity observed in the La$_{0.5}$F$_{0.5}$BiSe$_2$ is further confirmed by the magnetization measurement. Fig. 3(d) gives a typical result of the La$_{0.5}$F$_{0.5}$BiSe$_2$ sample; the field-cooling (FC) temperature dependence of the magnetic susceptibility was measured under an applied field of 1 Oe. The ZFC curve demonstrates an evident diamagnetic transition around 3.1 K, consistent with the $T_c$ (onset) estimated from the $\rho$ ($T$) curve.

According to the density functional theory (DFT) calculations, the parent phase of this kind of material exhibits semiconducting behavior with a band gap of about 0.17 eV (not shown here) which, however, contradicts with the nature of a bad metal deduced from the physical measurements. The metallic behavior of the parent phase may be induced by the strong spin-orbital coupling, which shifts the bottom of the $p_z$ and $p_y$ bands below the Fermi energy, as observed in the CeOBiS$_2$ samples [4]. In this metallic state, the Fermi surface topology has a “hidden” quasi-one-dimensional character and a strong Fermi surface nesting which would be found along the (110) direction. In fact, the observed resistivity anomaly at about 110 K for the parent and underdoped LaOBiSe$_2$ samples supports the occurrence of the CDW formation, as shown in Fig. 3. Unlike BiS$_2$-based superconductor in which the superconductivity occurs in the vicinity of the semiconducting state under electron doping, the normal state of the superconducting compound La$_{1-x}$F$_x$BiSe$_2$ at $x=0.5$ still exhibits metallic behavior, although the electrical resistivity is relatively large in comparison with the parent compound. In LaOBiSe$_2$, the $F$ doping suppresses the CDW transition, and it is possible that the electron–phonon coupling would be enhanced by the phonon softening in the non-CDW state, since the
strong electron–phonon coupling and phonon softening were predicted. Therefore, the superconductivity would be maximized at specific k points associated with the CDW ordering vectors owing to electron–phonon coupling, as observed in other systems \[16,26,27\].

In conclusion we have synthesized a nearly single phase LaO\(_{1-x}\)F\(_x\)BiSe\(_2\) compound, which is a bad metal with a possible CDW transition at about 120 K. Superconductivity is observed in LaO\(_{0.5}\)F\(_{0.5}\)BiSe\(_2\) sample with nominal composition at 3.1 K from magnetic and transport measurements. Our data clearly demonstrate a competition between the possible CDW instability and superconductivity in this system.

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References


