Study of the structural, superconducting and electrochemical corrosion properties of F and Se co-doped LaOBiS$_2$ materials

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This study was conducted to successfully synthesize LaOBiS$_2$, F-doped LaOBiS$_2$, Se-doped LaOBiS$_2$, and F and Se codoped LaOBiS$_2$ by the standard solid state reaction route, and study the structural, superconductivity, and electrochemical corrosion properties. The layered nature of the pure and doped LaOBiS$_2$ samples’ crystals and their growth along the c-axis were revealed by structural investigations. Results revealed that Fe and Se doping caused expansion along the c-axis, respectively, confirming the effectiveness of the doping method. Studies on the relationship between resistance and temperature revealed a rapid superconducting transition for the F-doped LaOBiS$_2$ system with a $T_c$ of 3.18 K, and F-ion substitution can increase the superconductivity. The results demonstrated that Se substitution could be the cause of the elevated carrier mobility by successfully suppressing local distortion. Results showed that F and Se doping increased the density of electron carriers. The temperature dependence of the ZFC and FC DC magnetic susceptibilities was studied, and the results revealed that the higher $T_c$ of the F and Se-codoped LaOBiS$_2$ led to a diamagnetic transition into the superconducting state at $T_c$~3.8 K. According to electrochemical corrosion investigations, F and Se codoped LaOBiS$_2$ had a higher charge transfer resistance than other electrodes, showing a synergistic effect of F and Se on enhancing corrosion resistance.

Keywords: Superconductivity; LaOBiS$_2$; Se doping; Fe doping; Solid state reaction method; Electrochemical corrosion

1. INTRODUCTION

A superconductor is a perfect conductor of electric charge [1, 2]. It experiences no resistance and an electric current in a superconductor can persist indefinitely. It does not allow magnetic fields to penetrate [3, 4]. So, in addition to being incredibly effective, superconductive materials also have the added advantage of being able to float. When chilled below a specific temperature, certain materials have the ability to carry direct current electricity without losing energy (referred to as $T_c$) [5-7].
Superconducting wire can carry immense electrical currents with no heating, which allows it to generate large magnetic fields [8, 9]. An electromagnet with non-superconducting copper windings would melt with the same current [10, 11].

The world could change thanks to superconductors. A superconductor operating at ambient temperature would change technology [12, 13]. Since energy is not lost through resistance in a superconducting power grid, it would consume significantly less energy than current technologies. Applications of superconductivity include levitating trains, extremely precise magnetoencephalograms, and smaller and lighter engines, generators, and transformers [14]. Cellular phone towers now use high-temperature superconductors as electronic filters to separate radio signals from different phone calls. Conventional filters lose some of the signal due to electrical resistance, and the sharper the filter, the more of the signal it loses. Nuclear magnetic resonance (NMR) and electromagnetic resonance imaging (NMR) In order to create the large-volume, steady, and high-intensity magnetic fields required for MRI and NMR, superconductivity is most commonly used [15, 16]. Railguns, coilguns, cell phone base stations, quick digital circuits, and particle detectors are all powered by superconductors [17, 18].

Though there has been clear progress in research and innovation, superconductors are not a novel technology, and there is still much space for advancement. Aluminium, niobium, magnesium diboride, cuprates such as yttrium barium copper oxide and iron pnictides, as well as chemical substances with layered crystal structures, are prominent examples of superconductors [19, 20]. Superconductors face a serious problem when it comes to other practical applications: they operate at incredibly low temperatures [21, 22]. It is impossible to find superconductors at room temperature. Superconducting materials only really superconduct when kept below the transition temperature, which is a specified temperature. For known practical superconductors, the temperature is significantly lower than 77 K, the temperature of liquid nitrogen [23-25].

Recently, studies have shown that superconductivity was discovered in the BiS$_2$-based layered compounds such as Bi$_2$O$_2$S$_3$, Bi$_2$O$_2$S$_3$, Sr$_{1-x}$La$_x$FBiS$_2$, SrFBiS$_2$ and LnO$_1$-$x$F$_x$BiS$_2$ (Ln = La, Ce, Pr, Nd and Yb) [26, 27]. The crystal structure composed of an alternate stacking of the BiS$_2$ superconducting layers and blocking layers is quite similar to those of the Cu-oxide and Fe-based superconductors [28-30]. Thus, the BiS$_2$-based materials have been demonstrated to become superconducting upon electron doping into the Bi-6p orbitals within the BiS$_2$ layers [27, 31]. To the best of our knowledge, the electrochemical corrosion studies of superconductors based on BiS2 are not successfully carried out. LaOBiS$_2$, F-doped LaOBiS$_2$, Se-doped LaOBiS$_2$, and F and Se-codoped LaOBiS$_2$ were effectively synthesized in this study, and its structural, superconducting, and electrochemical corrosion properties were investigated.

2. EXPERIMENT

2.1. Synthesis of superconductor

LaOBiS$_2$ was prepared using the standard solid state reaction route via vacuum encapsulation [32]. The powders of La (99%, Sigma-Aldrich), Bi (99%, Merck Millipore, Germany), S (97%, Merck
Millipore, Germany), LaF₃ (99%, Sigma-Aldrich), and La₂O₃ (99%, Sigma-Aldrich) and either F (≥99.5%, Sigma-Aldrich) and Se (99.99%, Sigma-Aldrich) were weighed in a stoichiometric ratio of LaO₀.₅F₀.₅BiS₂ as perfect superposition of F-doped LaOBiS₂ which was confirmed in many studies [33-35]. The ground and homogenously mixed thoroughly in a very clean glove box which filled with a high purity argon atmosphere. Then, the mixed powder was pelleted in a quartz tube under 10⁻³ Pa which heated in a tube furnace at 850°C for 8 hours with a heating rate of 5 C°/min.

2.2. Characterizations of instruments

The crystal structure of the starting material was examined by X-ray diffraction (XRD; MiniFlex-600, Rigaku Corporation, Tokyo, Japan). Scanning electron microscopy (SEM) experiments were performed on an environmental scanning electron microscope (FEI Model Quanta 450 FEG, Hillsboro, OR, USA). The temperature dependence of resistivity was recorded with a four-probe set-up in a Physical Property Measurement System (PPMS-9, Quantum Design Inc., USA). A Quantum Design PPMS-AG system (Quantum Design Inc., USA) was used for the measurement of temperature dependence of DC magnetization for the samples under 10 Oe in both zero fields cooled (ZFC) and field cooled (FC) modes. Electrochemical impedance spectroscopy (EIS) experiments were carried out using an electrochemistry workstation (CS1005, Zhengzhou CY Scientific Instrument Co., Ltd., China) equipped with a conventional three-electrode system containing a superconductor disc as the working electrode, platinum mesh as counter electrode, and a saturated calomel electrode as a reference electrode. EIS experiments were performed in 0.1 M Na₂SO₄ (≥99.0%, Sigma-Aldrich) at frequency range of 10²–10⁵ Hz with ±10 mV amplitude.

3. RESULTS AND DISCUSSION

3.1. Structural analyses

Figure 1 shows the XRD patterns of LaOBiS₂, Se-doped LaOBiS₂, F-doped LaOBiS₂ and F and Se-codoped LaOBiS₂. As seen for all XRD patterns, there are the main diffraction peaks, which corresponded to the reported tetragonal crystal phase of CeOBiS₂ with the space group P4/nmm [36]. For F-doped LaOBiS₂ and F and Se-codoped samples, small amounts of Bi₂O₃ and Bi₂Se₃ impurity phases are observed as indicated by an asterisk in the XRD patterns. By substituting the F atoms at the oxygen site, these impurity phases can be created because their synthesis temperature is relatively low and can break the chemical stoichiometry [37], similar to the F doping in the crystal structures of superconducting LaO₁₋ₓFxBiS₂ [38, 39]. The pure LaOBiS₂ indicates to refined lattice parameters of ‘a’ and ‘c’ which are lower than those of Se-doped LaOBiS₂ samples, illustrating to lattice expansion because the atomic radius of Se is bigger than that of S [40-42]. For studying the influence of F and Se doping, codoping, and structure modulation on LaOBiS₂, the refined lattice parameters of LaOBiS₂, F-doped LaOBiS₂, Se-doped LaOBiS₂, and F and Se-codoped LaOBiS₂ from the XRD data are depicted in Figure 2. It is observed that for F and Se-codoped LaOBiS₂, the crystal structure shows a lattice shrinkage along the c-axis, while the a-axis remains almost unchanged. The Se substitution on S sites
may expand the lattice, and it is observed that there is separation between the (102) and (004) peaks which relates to a characteristic feature for F-doped LaOBiS\textsubscript{2} superconductors [43-45]. The (004) peak slightly shifts to higher angles after F doping at the O-site, indicating that the c axis decreases [43], while the position of the (110) peak (a-axis) remains almost unchanged attributed to the unchanged tetragonal crystal structure of LaOBiS\textsubscript{2} [46, 47].

![XRD patterns of LaOBiS\textsubscript{2}, Se-doped LaOBiS\textsubscript{2}, F-doped LaOBiS\textsubscript{2} and F and Se-codoped LaOBiS\textsubscript{2}.](image)

**Figure 1.** XRD patterns of LaOBiS\textsubscript{2}, Se-doped LaOBiS\textsubscript{2}, F-doped LaOBiS\textsubscript{2} and F and Se-codoped LaOBiS\textsubscript{2}.

![Refined lattice parameters of LaOBiS\textsubscript{2}, F-doped LaOBiS\textsubscript{2}, Se-doped LaOBiS\textsubscript{2}, and F and Se-codoped LaOBiS from the XRD data (a) ‘a’ and (b) ‘c’.](image)

**Figure 2.** The refined lattice parameters of LaOBiS\textsubscript{2}, F-doped LaOBiS\textsubscript{2}, Se-doped LaOBiS\textsubscript{2}, and F and Se-codoped LaOBiS from the XRD data (a) ‘a’ and (b) ‘c’.

Figure 3 exhibits the SEM images of F-doped LaOBiS\textsubscript{2}, Se-doped LaOBiS\textsubscript{2}, and F and Se-codoped LaOBiS\textsubscript{2}. As seen, almost all of the samples are synthesized in crystal structure with slice-
shaped crystals in the main phase which mix with a few slice-shaped ones, illustrating the nature of the layered structure of LaOBiS\textsubscript{2} samples. The F and Se-codoped LaOBiS\textsubscript{2} sample shows a larger surface area and more porosity. However, the SEM image of Se-doped LaOBiS\textsubscript{2} displays a slice-shaped crystal that grew along the c-axis, indicating that the F doping leads to a remarkable shrinkage along the c-axis that is in agreement with the XRD results.

**Figure 3.** The SEM images of F-doped LaOBiS\textsubscript{2}, Se-doped LaOBiS\textsubscript{2}, and F and Se-codoped LaOBiS\textsubscript{2}.

### 3.2. Superconductivity analyses

Figure 4 depicts the in situ temperature dependence of the resistance of LaOBiS\textsubscript{2}, F-doped LaOBiS\textsubscript{2}, Se-doped LaOBiS\textsubscript{2}, and F and Se-codoped LaOBiS\textsubscript{2} measured at different temperatures from 2 K to 300 K. It is observed, the resistivity profiles of LaOBiS\textsubscript{2}, F-doped LaOBiS\textsubscript{2} samples exhibit semiconducting-like characteristics in normal state in the temperatures range from 2 K to 300 K, the resistivity increases with decreasing temperature, and the F-doped LaOBiS\textsubscript{2} indicates a sharp superconducting transition with T\textsubscript{c} of 3.18 K, which is sizably higher than that of reported data for LaOBiS\textsubscript{2} (2.6 K) [48], which can be attributed to the main factors at F doping that included the increase of the charge transfer between adjacent blocks [LnO]→[BiS\textsubscript{2}] (Ln=La) related to metallization of superconducting blocks [BiS\textsubscript{2}]; and the reconstruction of the 2D-like Fermi surface associated with the nesting effect [49, 50]. It should be noted that the effect of chemical pressure on the superconductivity of doped LaOBiS\textsubscript{2} with F-ion substitution can enhance the superconductivity in the F-doped LaOBiS\textsubscript{2} system [51]. Moreover, studies have shown that an effective method for doping electrons into the BiS\textsubscript{2} conduction layer is the partial substitution of the O site at the blocking layer by F, and because of the difference in the valency between O\textsuperscript{2-} and F, electron doping into the BiS\textsubscript{2} layers is expected [52, 53]. As seen, the resistivity for doped and codoped samples is obviously smaller than that of undoped LaOBiS\textsubscript{2}, indicating that electron carrier density was enhanced by F and Se doping [52, 54]. Results show that the resistivity profiles of Se-doped LaOBiS\textsubscript{2} exhibit similar semiconducting behavior but the resistivity profiles of F and Se-codoped LaOBiS\textsubscript{2} demonstrate metallic behavior at normal state. The resistivity of F and Se-codoped LaOBiS\textsubscript{2} samples shows a linear temperature dependence as the temperature varied from 50 K to 300 K with superconducting phase transitions at low temperatures which is clearly different from the LaOBiS\textsubscript{2}, F-doped LaOBiS\textsubscript{2} samples, implying that Se substitution effectively suppresses local distortion and can be responsible for the increased carrier mobility together with a change in the Fermi level electronic structure [55, 56].
Figure 4. The temperature dependence of resistance of LaOBiS\textsubscript{2}, F-doped LaOBiS\textsubscript{2}, Se-doped LaOBiS\textsubscript{2}, and F and Se-codoped LaOBiS\textsubscript{2} measured at different temperatures from 2 K to 300 K.

Figure 5a depicts the in situ temperature dependence of the zero-field cooled (ZFC) and field cooled (FC) DC magnetic susceptibility of F-doped LaOBiS\textsubscript{2}, Se-doped LaOBiS\textsubscript{2}, and F and Se-codoped LaOBiS\textsubscript{2} at temperatures ranging from 2 K to 6 K under a magnetic field of 10 Oe. It is indicated by a diamagnetic transition into the superconducting state in the low-temperature DC-susceptibility data (less than T\textsubscript{c}~3.8 K), and the F and Se-codoped LaOBiS\textsubscript{2} sample shows an enhanced T\textsubscript{c}. The T\textsubscript{c} determined from resistivity of samples are presented in Figure 5b, indicating to the maximum T\textsubscript{c} is determined for and F and Se-codoped LaOBiS\textsubscript{2} sample which in agreement with XRD results.

Figure 5. (a) The temperature-dependence of the zero-field cooled (ZFC) and field cooled (FC) DC magnetic susceptibility of F-doped LaOBiS\textsubscript{2}, Se-doped LaOBiS\textsubscript{2}, and F and Se-codoped LaOBiS\textsubscript{2} at temperatures range from 2 K to 6 K under a magnetic field of 10 Oe; (b) The T\textsubscript{c} determined from resistivity of samples.
3.2. Electrochemical corrosion analyses

Figure 6 shows the Nyquist impedance responses of F-doped LaOBiS$_2$, Se-doped LaOBiS$_2$, and F and Se-codoped LaOBiS$_2$ electrodes in 0.1 M Na$_2$SO$_4$. A small incomplete capacitive semicircle is observed in the high frequency region, followed by a straight line with an angle close to 45° in the low frequency region that is attributed to the Warburg impedance [57]. The interfacial charge transfer resistance (Rct) between electrode and electrolyte is responsible for the generation of the incomplete semicircle [58, 59]. The diffusion straight lines in the low frequency region indicated a faster ion diffusion rate on the F and Se-codoped LaOBiS$_2$ than other superconductor electrodes. The enhanced ion diffusion rate can be related to the larger effective surface area of the electrode which provides more surface area to be in contact with the electrolyte and forms shortcuts for ion diffusion between the electrode and the electrolyte [60]. It can be implied to highly capacitive behavior of the codoped electrode [61, 62]. The EIS data of F-doped LaOBiS$_2$, Se-doped LaOBiS$_2$, and F and Se-codoped LaOBiS$_2$ were commonly analyzed by fitting to an equivalent electrical circuit model which is presented in Figures 7a, 7b and 7c, respectively. These models are represented by a series and parallel resistor and capacitor, and Warburg impedance (W) [63], where Rs is solution resistance, CPE reflects the constant phase element, and Rct is charge transfer resistance inversely proportional to corrosion rate. The fitting results are summarized in Table 1. As seen, F and Se-codoped LaOBiS$_2$ shows the higher charge transfer resistance than other electrodes, indicating to synergetic effect of the F and Se on enhancement of corrosion resistance. The drop in the non-ideal double layer capacitances ($Q_1$ and $Q_2$) can corroborate the enhancement of corrosion resistance in the F and Se-codoped LaOBiS$_2$ sample due to the generation of a film of corrosion products on the electrode surface [64]. It can be related to thickness of the protective part of the film is inversely proportional to its surface capacity [65]. Thus, the drop in $Q_1$ and $Q_2$ indicates an increase in the thickness of the protective film.

Figure 6. The Nyquist impedance responses of (a) F-doped LaOBiS$_2$, (b) Se-doped LaOBiS$_2$, and (c) F and Se-codoped LaOBiS$_2$ electrodes in 0.1 M Na$_2$SO$_4$. 
Figure 7. The equivalent electrical circuit model of (a) F-doped LaOBiS$_2$, (b) Se-doped LaOBiS$_2$, and (c) F and Se-codoped LaOBiS$_2$ samples used for fitting EIS data.

Table 1. The fitting results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_s$ ($\Omega$.cm$^2$)</th>
<th>$Q_1$ (µF.cm$^{-2}$)</th>
<th>$R_2$ ($\Omega$.cm$^2$)</th>
<th>$Q_2$ (µF.cm$^{-2}$)</th>
<th>$R_{ct}$ ($\Omega$.cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-doped LaOBiS$_2$</td>
<td>119</td>
<td>---</td>
<td>---</td>
<td>1792</td>
<td>155</td>
</tr>
<tr>
<td>Se-doped LaOBiS$_2$</td>
<td>89</td>
<td>2345</td>
<td>54</td>
<td>72</td>
<td>2549</td>
</tr>
<tr>
<td>F and Se-codoped</td>
<td>61</td>
<td>1741</td>
<td>1720</td>
<td>1805</td>
<td>4938</td>
</tr>
<tr>
<td>LaOBiS$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

4. CONCLUSION

In conclusion, LaOBiS$_2$, F-doped LaOBiS$_2$, Se-doped LaOBiS$_2$, and F and Se-codoped LaOBiS$_2$ were successfully synthesized by a standard solid state reaction route. Structural analyses using SEM and XRD showed superconductors were synthesized in crystal structure and slice-shaped crystals, illustrating the nature of the layered structure of pure and doped LaOBiS$_2$ samples which grew along the c-axis, and that the Se doping and Fe doping led to expansion and growth along the c-axis, respectively that confirm the successful doping process. Temperature dependence of resistance studies indicated a sharp superconducting transition with $T_c$ of 3.18 K F-doped LaOBiS$_2$ system, which can be attributed to the metallization of superconducting blocks [BiS$_2$] and F-ion substitution can enhance the superconductivity in the F-doped LaOBiS$_2$ system. Results demonstrated that Se substitution effectively suppressed local distortion and can be responsible for the increased carrier mobility together with a change in the Fermi level electronic structure. Results indicated that the resistivity for doped and codoped samples was obviously smaller than that of undoped LaOBiS$_2$, indicating that electron carrier density was enhanced by F and Se doping. Studies of the temperature dependence of the ZFC and FC DC magnetic susceptibilities showed that a diamagnetic transition into the superconducting state occurred at $T_c \sim$ 3.8 K for F and Se-codoped LaOBiS$_2$ which exhibited an
enhanced Tc. Electrochemical corrosion analyses showed that F and Se-codoped LaOBiS\textsubscript{2} displayed a higher charge transfer resistance than other electrodes, indicating a synergetic effect of F and Se on enhancement of corrosion resistance. The drop in the non-ideal double layer capacitances can corroborate the enhancement of corrosion resistance in the F and Se-codoped LaOBiS\textsubscript{2} sample due to the generation of a film of corrosion products on the electrode surface, and the drop in capacitances indicated that the thickness of the protective film had grown.

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