Superconducting properties of BiSe$_2$-based LaO$_{1-x}$F$_x$BiSe$_2$ single crystals

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Published online 1 August 2014

PACS 74.70.Dd – Ternary, quaternary, and multinary compounds (including Chevrel phases, borocarbides, etc.)
PACS 74.25.F – Transport properties
PACS 74.20.Mn – Nonconventional mechanisms

Abstract – F-doped LaOBiSe$_2$ superconducting single crystals with typical size of $2 \times 4 \times 0.2$ mm$^3$ are successfully grown by flux method and the superconducting properties are studied. Both the superconducting transition temperature and the shielding volume fraction are effectively improved with fluorine doping. The LaO$_{0.48}$F$_{0.52}$BiSe$_2$ sample exhibits zero-resistivity at 3.7 K, which is higher than that of the LaO$_{0.5}$F$_{0.5}$BiSe$_2$ polycrystalline sample (2.4 K). Bulk superconductivity is confirmed by a clear specific-heat jump at the associated temperature. The samples exhibit strong anisotropy and the anisotropy parameter is about 30, as estimated by the upper critical field and effective mass model.

Materials with layered structure have been intensively studied as a promising approach to the exploration of new high-transition-temperature superconductors, since the discovery of cuprate superconductors [1]. This scheme has been accelerated and became much more fruitful by the discovery of the iron-based superconductors [2] and the importance since it represents a novel BiSe$_2$-based superconducting system. However, due to the lack of single crystal, the superconducting properties remain to be investigated. In this paper, we report the successful growth of LaO$_{1-x}$F$_x$BiSe$_2$ single crystal samples by flux method. The superconducting parameters are determined based on the high-quality single crystals.

The LaO$_{1-x}$F$_x$BiSe$_2$ single crystals were grown by flux method using a mixture of CsCl and KCl as the flux (the molar ratio of CsCl : KCl is 5 : 3) [18–21]. The starting materials of high-purity Bi$_2$O$_3$, BiF$_3$, bismuth, lanthanum and selenium were weighed with nominal concentrations of LaO$_{1-x}$F$_x$BiSe$_2$ and thoroughly ground in an agate mortar. Then the flux of CsCl and KCl were added, with the mass ratio of CsCl/KCl to raw materials of 1 : 8. The total mixture was thoroughly ground and then sealed in an evacuated quartz tube. It was slowly heated to 800°C and kept for 48 h and then cooled down at a rate of 2 K/h.

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to 560 °C before the furnace was shut down. After cooling down to the room temperature, the product was removed from the quartz tube and washed by distilled water to get the single crystal samples.

The real compositions of the obtained single crystals were determined by an energy dispersive x-ray spectroscopy (EDX) analysis, which was performed using an Oxford SWIFT3000 spectroscope equipped with a Si detector. The EDX measurement were done on several pieces of single crystals randomly selected from each sample. For each piece, at least six different points were randomly selected in the EDX measurements and the average was defined as the actual composition. The structure of the obtained crystal was characterized by powder and single crystal x-ray diffraction with Cu-Kα at room temperature. The temperature dependence of resistivity from 2 K to 300 K was measured by a standard four-probe method in a commercial Quantum Design physical-property measurement system (PPMS-14 T). The magnetic properties were measured using a superconducting quantum interference device magnetometer. The specific heat measured by a thermal relaxation method from 2 K down to 1.9 K was measured using a superconducting quantum interferometry (SQUID) magnetometer. The specific heat measured by a standard four-probe method in a commercial Quantum Design physical-property measurement system (PPMS-14 T). The magnetic properties were measured using a superconducting quantum interference device magnetometer. The specific heat measured by a thermal relaxation method from 2 K down to 1.9 K was also studied on PPMS-14 T system.

Figure 1 shows the scanning electron microscopy photograph of the La0.59F0.41BiSe1.92 sample. The obtained single crystal samples have typical dimensions of 2 × 12 mm. In order to determine the actual compositions of the samples, we perform an energy-dispersive x-ray spectrometry (EDX) analysis on the as-grown single crystals. The results are given in table 1. The obtained values are normalized by La = 1, and the oxygen content is defined as 1 − x (x is the content of F), considering the inaccuracy of oxygen by the EDX measurement. No Cs, K, and Cl elements are detected in the samples. For La, Bi and Se elements, the relative ratio agrees well with the stoichiometric ratio except for a little deficiency of Se, which is similar to the deficiency of S in NdO1−xF2BiS2 single crystals [22]. It can be seen that the actual F concentration increases with increasing nominal F content. However, the actual F content saturates at about 0.5 (for example, the actual F content is x = 0.52 in the sample with nominal content of x = 0.9). Another noticeable fact is that for the samples with nominal contents x = 0.1 and x = 0.2, actual F contents are about 0.37 and 0.38, which are significantly higher than the nominal contents. These results indicate that in the La0.1xF2BiSe2 single crystals, the preferred F content is in the x = 0.3–0.6 region. Similar results have also been discovered in La0.1xF2BiS2 single crystals [23].

Table 1: Comparison between the nominal and real compositions of the LaO1−xF2BiSe2 single crystals determined by EDX.

| Nominal composition | Measured chemical composition |
|---------------------|------------------------------|
| LaO0.4F0.2BiSe2     | La0.63F0.37Bi1.00Se1.92     |
| LaO0.7F0.3BiSe2     | La0.62F0.38Bi1.00Se1.92     |
| LaO0.5F0.5BiSe2     | La0.59F0.41Bi0.99Se1.92     |
| LaO0.3F0.7BiSe2     | La0.54F0.46Bi0.99Se1.93     |
| LaO0.1F0.9BiSe2     | La0.48F0.52Bi1.00Se1.93     |

Fig. 1: The SEM photograph of an as-grown LaO1−xF2BiSe2 single crystal.
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Fig. 2: (Color online) (a) Powder XRD pattern (black dots) and the Rietveld refinement (red curve) of the LaO\textsubscript{0.59}F\textsubscript{0.41}BiO\textsubscript{0.99}Se\textsubscript{1.92} sample. The inset gives the site occupancy and coordinates of each atom. (b) Schematic image of the LaO\textsubscript{0.59}F\textsubscript{0.41}BiSe\textsubscript{2} crystal structure. The orthog indicates the unit cell. (c) Single crystal x-ray diffraction patterns of the as-grown LaO\textsubscript{1–\textit{x}}F\textsubscript{\textit{x}}BiSe\textsubscript{2} samples. (d) A detailed view of the shift of the (004) diffraction peaks with different F concentration.

which are much higher than those of LaO\textsubscript{0.5}F\textsubscript{0.5}BiSe\textsubscript{2} polycrystalline samples. Both the $T_{\text{onset}}$ and $T_{\text{zero}}$ values shift toward lower temperature as the F doping content decreases, which is shown in the inset of fig. 3(a). For all samples, the superconducting transition width is less than 0.5 K, suggesting the high quality of the single crystals. In order to investigate the superconducting properties under magnetic field, we perform the resistivity vs. temperature measurements at different applied magnetic field. The results for $H∥ab$ and $H∥c$ are shown in figs. 3(b) and (c), respectively. It can be seen that the $T_{\text{onset}}$ value decreases and the superconducting transition width becomes larger with increasing applied magnetic field, indicating that the superconducting state is suppressed by applying a magnetic field. It can also be seen that the suppression effect is much faster in the $H∥c$ case than that in the $H∥ab$ case. To estimate the upper critical fields of the LaO\textsubscript{0.48}F\textsubscript{0.52}BiSe\textsubscript{1.93} sample along different directions, we plot the field dependence curves of the $T_{\text{onset}}$ and $T_{\text{zero}}$ values for the $H∥ab$ and $H∥c$ cases. The results are shown in the insets of figs. 3(b) and (c), respectively. The irreversible field $\mu_0H_{\text{irr}}(0)$ is estimated to be about 5.4 T and 0.4 T for the $H∥ab$ and $H∥c$ cases, respectively. The upper critical field at zero temperature is estimated to be 29 T and 1 T for the $H∥ab$ and $H∥c$ cases, as determined by the Werthamer-Helfand-Hohenberg (WHH) theory [24]:

$$\mu_0H_{c2}(0) = -0.69 T_c (d\mu_0 H_{c2} / dT)_{T_c}. \quad (1)$$

The anisotropy parameter is preliminary evaluated to be 33.3 using the equation

$$\gamma_s = dH_{c2}^{\parallel ab} / dT = dH_{c2}^{\parallel c} / dT. \quad (2)$$

Figure 3(d) shows the temperature dependence of the magnetic susceptibility measured under the zero-field-cooling (ZFC) and field-cooling (FC) processes for the LaO\textsubscript{1–\textit{x}}F\textsubscript{\textit{x}}BiSe\textsubscript{2} samples. The applied field is parallel to the $ab$-plane. A large diamagnetic signal is observed in all samples, confirming the occurrence of superconductivity. The diamagnetic signal is enhanced with increasing F content. We calculate the shielding volume fraction (SVF) using the formula $\text{SVF} = 4\pi \rho \rho / H$ ($\rho$ is the mass density of the sample and $H$ is the applied magnetic field). For the LaO\textsubscript{0.48}F\textsubscript{0.52}BiSe\textsubscript{1.93} sample, the estimated SVF is almost 100% at 2 K, confirming the occurrence of bulk superconductivity.
superconductivity. Table 2 gives a comparison of the lattice constants and the superconducting transitions in the polycrystalline (P) and single crystal (S) samples of LaO$_{0.5}$F$_{0.5}$BiSe$_2$ and LaO$_{0.5}$F$_{0.5}$BiS$_2$.

In order to scale the anisotropy parameter ($\gamma_s$) of the single crystal samples, we measure the angular ($\theta$) dependence of resistivity of the LaO$_{0.48}$F$_{0.52}$BiSe$_{1.93}$ sample under various applied magnetic fields at a fixed temperature of 3 K. The results are shown in fig. 4(a). Here $\theta$ is defined as the angle between the $ab$-plane and the direction of the applied magnetic field. According to the Ginzburg-Landau theory, the curves of $\rho$ vs. reduced magnetic field ($H_{\text{red}}$) under various applied magnetic fields should be fitted to one [25]. The reduced magnetic field is given by $H_{\text{red}} = H(\sin^2 \theta + \gamma_s^{-2} \cos^2 \theta)^{1/2}$. As the $H_{c2}^{\text{rc}}$ value for the LaO$_{0.48}$F$_{0.52}$BiSe$_{1.93}$ sample is about 1 T, we adopt the data taken from the 0–1 T range to make the fit for $\gamma_s$. The result is shown in fig. 4(b). The anisotropy parameter $\gamma_s$ at 3 K is about 30, which is close to the preliminary evaluated value of 33.3.

In order to confirm the occurrence of bulk superconductivity, we measure the specific heat for the LaO$_{0.54}$F$_{0.46}$BiSe$_{1.93}$ single crystal from 1.9 K to 20 K. In general, the specific heat value at low temperature is very small. Thus we select the LaO$_{0.54}$F$_{0.46}$BiSe$_{1.93}$ sample ($T_{\text{zero}} = 3.3$ K) to perform the measurement because we can get a relatively large size of LaO$_{0.54}$F$_{0.46}$BiSe$_{1.93}$ single crystals comparing to other samples. The temperature dependence of specific heat in the superconducting state ($H = 0$ T) and normal state ($H = 10$ T) is plotted in

**Table 2**: Comparison of the lattice parameters and the transition temperatures in the polycrystalline (P) and single crystal (S) samples of LaO$_{0.5}$F$_{0.5}$BiSe$_2$ and LaO$_{0.5}$F$_{0.5}$BiS$_2$.

| Compound         | $a$ (Å)   | $c$ (Å)   | $T_{\text{c,zero}}$ (K) | $T_{\text{c,susceptibility}}$ (K) |
|------------------|-----------|-----------|--------------------------|----------------------------------|
| LaO$_{0.5}$F$_{0.5}$BiSe$_2$-P | 4.15941   | 14.01567  | 2.4                      | 2.6                              |
| LaO$_{0.48}$F$_{0.52}$BiSe$_{2}$-S| 4.15663   | 14.0024   | 3.7                      | 3.7                              |
| LaO$_{0.5}$F$_{0.5}$BiSe$_2$-P | 4.0527    | 13.3237   | 2.5                      | 2.7                              |
| LaO$_{0.54}$F$_{0.46}$BiS$_{2}$-S| –         | 13.39     | 3.0                      | 3.0                              |
In summary, we report the successful growth of LaO$_{1-x}$F$_x$BiSe$_2$ superconducting single crystals for the first time. F doping can substantially enhance the superconducting transition temperature and the shielding volume fraction. The highest $T_c^{\text{zero}} \sim 3.7$ K and almost 100% shielding volume fraction are obtained in the LaO$_{0.48}$F$_{0.52}$BiSe$_{1.93}$ sample. The single crystal samples exhibit strong anisotropy and the anisotropy parameter is estimated to be about 30. The upper critical fields parallel to the $c$-axis and the $ab$-plane are evaluated to be 1 T and 29 T, respectively. We also confirm the bulk superconductivity of the LaO$_{1-x}$F$_x$BiSe$_2$ samples by specific-heat measurement.

This work was supported by the State Key Project of Fundamental Research of China (Grant Nos. 2010CB923403 and 2011CBA00111), and the Natural Science Foundation of China (Grant Nos. 11174290 and U1232142).

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