Evolution of superconductivity in LaO$_{1-x}$F$_x$BiS$_2$ prepared by high-pressure technique

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received 1 October 2012; accepted in final form 19 December 2012
published online 17 January 2013

PACS 74.70.Dd – Ternary, quaternary, and multinary compounds (including Chevrel phases, borocarbides, etc.)
PACS 74.62.Bf – Effects of material synthesis, crystal structure, and chemical composition
PACS 74.25.Dw – Superconductivity phase diagrams

Abstract – Novel BiS$_2$-based superconductors LaO$_{1-x}$F$_x$BiS$_2$ prepared by a high-pressure synthesis technique were systematically studied. It was found that the high-pressure annealing strongly shrunk the lattice as compared to the LaO$_{1-x}$F$_x$BiS$_2$ samples prepared by conventional solid-state reaction at ambient pressure. Bulk superconductivity was observed within a wide F concentration range of $x = 0.2$–0.7. On the basis of those results, we have established a phase diagram of LaO$_{1-x}$F$_x$BiS$_2$.

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Introduction. – Recently, several BiS$_2$-based superconductors, commonly having the Bi-S square lattice planes, have been discovered [1–15]. Due to the layered crystal structure and some exotic physical properties similar to cuprate [16–19] and Fe-based superconductors [20–31], the BiS$_2$-based compounds are expected to provide us with the next stage to explore new superconductors and discuss the exotic superconductivity mechanisms. The Bi$_4$O$_4$S$_3$ superconductor exhibits metallic transport behavior and show a zero-resistivity state below 4.5 K [1]. The crystal structure is composed of a stacking of the Bi$_4$O$_4$(SO$_4$)$_2$ blocking layers and the Bi$_2$S$_4$ superconducting layers (two BiS$_2$ layers). Thus, the parent phase is Bi$_6$O$_6$S$_6$ and it is expected to be insulator on the basis of the band calculations. The Bi$_4$O$_4$S$_3$ phase has partial defects at the SO$_4$ site, which provide electron carriers into the BiS$_2$ superconducting layers. Another BiS$_2$-based system is ReO$_{1-x}$F$_x$BiS$_2$ (Re = rare earth). So far, LaO$_{1-x}$F$_x$BiS$_2$, CeO$_{1-x}$F$_x$BiS$_2$, PrO$_{1-x}$F$_x$BiS$_2$ and NdO$_{1-x}$F$_x$BiS$_2$ were found to be superconducting with transition temperatures ($T_c$) of 10.6 [2], 3.0 [14], 5.5 [15], 5.6 K [11], respectively. In both systems, optimal superconducting properties are obtained near the boundary between insulating and superconducting states. In fact, the electronic-specific-heat coefficient of the Bi$_4$O$_4$S$_3$ superconducting sample was found to be very small [32]. This property resembles the layered nitride family [33,34]. By theoretical studies, possible paring mechanisms relating to the charge-density-wave instability and nature of strong coupling were predicted [9]. Although the superconductivity mechanisms of the BiS$_2$-based family are unclear, we can expect a higher $T_c$ in this system, because of some exotic physical and structural properties. In fact, an enhancement of $T_c$ under high pressure was observed in the LaO$_{1-x}$F$_x$BiS$_2$ system [35]. Therefore, systematic studies of both structural and superconducting properties are important. In this article we report systematic studies on LaO$_{1-x}$F$_x$BiS$_2$ superconductors prepared using a high-pressure synthesis technique.

Experimental methods. – The polycrystalline samples of LaO$_{1-x}$F$_x$BiS$_2$ were prepared by the two-step process of the solid-state reaction and high-pressure annealing using a Cubic-Anvil-type high-pressure synthesis machine with a 180 ton press. The starting materials Bi$_2$O$_3$ (98% powder), BiF$_3$ (99.9% powder), La$_2$S$_3$ (99.9% powder), Bi (99.9% grains) were used in this study. The Bi$_2$S$_3$ powder was prepared using Bi grains and S (99.999%) grains. The starting powders with a nominal ratio of LaO$_{1-x}$F$_x$BiS$_2$ with $0 \leq x \leq 0.7$ were...
well mixed and pressed into pellets. The pellets were sealed into an evacuated quartz tube and heated at 700°C for 10h. The obtained pellets were ground and annealed at 600°C for 1h under a hydrostatic pressure of 2GPa. The obtained samples were characterized by X-ray diffraction with Cu-Kα radiation using the 2θ-θ method. Lattice parameters were calculated using the least-square calculations. The electrical resistivity was measured using the four-terminal method from 300 to 2K. The magnetic-susceptibility measurements were performed using a superconducting quantum interference device SQUID magnetometer from 12K to 2K. The magnetic-susceptibility measurements were performed after both zero-field-cooling (ZFC) and field-cooling (FC) with an applied field of 10Oe. In this article, we classify synthesis methods “HP” and “AP”, which stand for high-pressure–annealed and ambient-pressure–annealed samples, respectively.

Results and discussion. –

Crystal structure. – Figure 1 shows the powder X-ray diffraction patterns for $x = 0$–0.7 (HP). Almost all of the peaks are indexed using the space group of $P4/nmm$. For lower $x$, the pattern and peak sharpness seem to be relevant to those of AP samples. With increasing $x$, however, the peaks become broader. To compare the peak shifts, we plotted the enlarged patterns near the (102) and (004) peaks for $x = 0$ (HP), 0.2 (HP) and 0.5 (HP) with those for $x = 0$ (AP), 0.2 (AP) and 0.5 (AP) in fig. 2. For both the AP and HP samples, clear peak shifts corresponding to lattice shrinkage with increasing F concentration. Interestingly, we note an obvious deference in between the powder patterns for $x = 0$ (AP) and 0 (HP). The (102) peak position of $x = 0$ (HP) is clearly higher than that of $x = 0.5$ (AP), while the (004) peak position seems to show a slight shift. These facts indicate that the high-pressure annealing can shrink the $ab$ plane as compared to the AP synthesis. The calculated lattice constants $a$, $c$ and volume ($V$) are plotted as a function of $x$ in figs. 3(a), (b) and (c), respectively. In fig. 3(a), it is found that the $a$ parameters of HP samples are smaller than those of AP samples. The $x$ dependence of a parameter exhibits a dome-shaped dependence for the HP
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Fig. 4: (Colour on-line) (a) Temperature dependence of the resistivity from 300 to 2 K for LaO$_{1-x}$F$_x$BiS$_2$ with $x = 0–0.7$. (b) Blow-up of (a) at low temperatures near the superconducting transition.

In contrast, the c-axis and lattice volume shows a continuous decrease with increasing $x$.

Superconducting properties. Figure 4(a) shows the temperature dependence of resistivity from 300 down to 2 K for LaO$_{1-x}$F$_x$BiS$_2$ with $x = 0–0.7$. For $x = 0$, a semiconducting-like behavior is observed and superconducting transition is not detected above 2 K. An enlargement of low temperatures below 15 K is shown in fig. 4(b). With F doping, the semiconducting-like behavior is slightly suppressed and superconductivity appears in $x = 0.2$. With further F doping, the semiconducting-like behavior is enhanced again. However, the $T_c$ is enhanced and exceeds 10 K (onset) at $x = 0.5$. Then, superconductivity is gradually suppressed for $x > 0.5$ and disappears at $x = 0.7$. Correspondingly to the resistivity measurements, the evolution of bulk superconductivity is also confirmed by magnetic-susceptibility measurements. Figure 5(a) shows the temperature dependence of magnetic susceptibility below 12 K for LaO$_{1-x}$F$_x$BiS$_2$ with $x = 0–0.7$. With increasing $x$, the $T_c$ and the diamagnetic signals are strongly enhanced, and the optimal superconducting properties are obtained at $x = 0.5$. With further F doping, bulk superconductivity is suppressed.

Figure 5(b) displays an enlargement of fig. 5(a) near the superconducting transition. We defined $T_{mag}^c$ as an onset temperature and $T_{irr}^c$ as the starting temperature of bifurcation between $\chi_{ZFC}$ and $\chi_{FC}$. The $T_{irr}^c$ almost corresponds to the zero-resistivity temperature ($T_{zero}^c$) where the superconducting current appears. Both $T_{mag}^c$ and $T_{irr}^c$ are highest at $x = 0.5$, which is consistent with the resistivity measurements.

On the basis of the obtained results, we established a phase diagram of LaO$_{1-x}$F$_x$BiS$_2$ prepared using high-pressure annealing at 600 °C under 2 GPa. Figure 6 shows the established phase diagram with the determined $T_{onset}^c$, $T_{zero}^c$, $T_{mag}^c$ and $T_{irr}^c$. The optimal superconducting properties are obtained at the summit of the dome. The dome structure resembles the curvature of the a lattice constant as shown in fig. 3(a). This fact implies that the $T_c$ of LaO$_{1-x}$F$_x$BiS$_2$ correlates with the a-axis. In fact, the maximum $T_c$ observed in several BiS$_2$-based superconductors depends on blocking layer structure. When we focus only bulk BiS$_2$-based superconductors, namely Bi$_4$O$_{11}$S$_3$, NdB$_{1-x}$F$_x$BiS$_2$, PrO$_{1-x}$F$_x$BiS$_2$ and LaO$_{1-x}$F$_x$BiS$_2$, we note the tendency of higher $T_c$ to appear with larger a-axis [1,2,11,15]. Furthermore, Xing et al. indicated that the BiS$_2$-based superconductivity is realized near the
vicinity of insulating phase [14]. A larger $a$ value may enhance the insulating nature and simultaneously realize higher-$T_c$ superconductivity in this family. In this respect, exploration for new BiS$_2$-based superconductors with larger blocking layers will be important. To achieve that, the high-pressure technique will be a great challenge.

**Conclusion.**— We have synthesized novel BiS$_2$-based superconductors LaO$_{1-x}$F$_x$BiS$_2$ with $x=0-0.7$ using solid-state reaction and high-pressure post annealing. As compared to the LaO$_{1-x}$F$_x$BiS$_2$ samples prepared using only the solid-state reaction, the lattice constants of the high-pressure samples were smaller. Superconducting transition was observed for $x=0.2-0.7$, and the optimal superconducting properties were obtained for $x=0.5$ with the $T_c^{\text{onset}}$ exceeding 10 K. The phase diagram showed an $x$-dependent superconducting dome. The evolution of dome-shaped dependence resembled the $x$ dependence of the $a$-axis. This may indicate that the correlation between the $T_c$ and the $a$-axis is essential for BiS$_2$-based superconductivity.

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This work was partly supported by a Grant-in-Aid for Scientific Research (KAKENHI). This research was partly supported by Strategic International Collaborative Research Program (SICORP-EU-Japan) and Advanced Low Carbon Technology Research and Development Program (JST-ALCA), Japan Science and Technology Agency.

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