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Single crystal growth of $\text{BaFe}_{2-x}\text{Co}_x\text{As}_2$ without fluxing agent

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Abstract We report a simple, reliable method to grow high quality $\text{BaFe}_{2-x}\text{Co}_x\text{As}_2$ single crystal samples without using any fluxing agent. The starting materials for the single crystal growth come from well-crystallized polycrystalline samples and the highest growing temperature can be 1230°C. The as-grown crystals have typical dimensions of $4 \times 3 \times 0.5 \text{ mm}^3$ with $c$-axis perpendicular to the shining surface. We find that the samples have very large current carrying ability, indicating that the samples have good potential technological applications.

Keywords Single crystal growth · magnetism · critical current density

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1 Introduction

The discovery of superconductivity in iron-pnictide systems has attracted tremendous interests not only due to its scientific value but also its potential industrial applications [1]. The relatively high transition temperature, highly flexibility, very high upper-critical magnetic field and other physical qualities make the iron-pnictide systems very useful in industry [2-4]. The existing challenges, such as optimizing synthesis methods for technological applications and clarifying the ambiguity in the superconducting mechanism,
will keep iron-pnictide systems on the frontiers of research for a long time, in parallel to high-$T_c$ cuprates [4].

In order to determine the application parameters which are important to commercial use, great efforts have been made to grow high-quality single crystals of iron-pnictide superconductors [5-8]. A lot of physical properties, such as the transition temperature, the upper critical field, the vortex structure, etc., have been determined using single crystal samples. However, due to the relatively high melting temperature of the iron-pnictide samples, the single crystals of iron-pnictides are generally grown by using self-flux method or flux method where excess FeAs mixture or Sn is used as the fluxing agent. The advantage of these methods is that the melting temperature can be significantly decreased comparing to the melting point of the crystal itself. While the disadvantage of these methods is unnegligible. For example, if we grow BaFe$_{2-x}$Co$_x$As$_2$ single samples using excess Fe(Co)As mixture as fluxing agent, the actual Fe/Co ratio can not be accurately controlled in the growth procedure. If one uses Sn as fluxing agent, the problem is that one can not remove the Sn from the surface of the sample easily [5]. In this paper we report a simple, reliable method to grow high quality BaFe$_{2-x}$Co$_x$As$_2$ single crystal samples without using any fluxing agent. The samples have typical dimensions of $4 \times 3 \times 0.5$ mm$^3$ with $c$-axis perpendicular to the shining surface. The critical current density of the samples are also determined. The critical current density without external magnetic field is quite high, meaning large current carrying ability of the samples, which points to optimistic applications.

2 Experimental detail

Single crystal samples were grown using well-crystalized BaFe$_{2-x}$Co$_x$As$_2$ polycrystalline samples as the starting materials. The polycrystalline samples with nominal composition BaFe$_{2-x}$Co$_x$As$_2$ were prepared by conventional solid-state reaction method using high-purity Ba (crystalline dendritic solid, 99.9%, Alfa-Aesar), Fe (powder, 99.9%, Alfa-Aesar), Co (powder, 99.9%, Alfa-Aesar), and As (powder, 99%, Alfa-Aesar) as starting materials. The crystalline dendritic solid Ba was pressed into thin pellet using an agate mortar and was cut into very small size (typically less than $0.5 \times 0.5$ mm$^2$). The raw materials were mixed and wrapped up by Ta foil and sealed in an evacuated quartz tube. They were pre-heated at 600°C for 12 hours and cooled down slowly to room temperature. The mixture was then ground and pressed into pellets and heated at 900°C for 24 hours. When the furnace was cooled down, the pellets were taken out and placed in an argon-filled glove box. We performed powder x-ray diffraction measurements on these samples and found that the samples were all in single phase.

The polycrystalline powder was pressed into pellets and placed in a quartz tube in an Argon-filled glove box. The quartz tube was sealed after it was evacuated by a molecular pump. Then the quartz tube was placed into a box furnace. The furnace was heated to 1230°C at a rate of 60°C per hour. After holding at 1230°C for 12 hours, it was cooled to 850°C at 2°C per hour followed by furnace cooling to room temperature. The quartz tube was
found almost intact after the whole procedure. When we break the quartz tube and pick out the sample, slides of samples with shining surfaces can be easily cleaved. It should be noted that we have tried to melt the samples at even higher temperature using a double-wall quartz tube. However, we find that the samples begin to decompose at temperature higher than 1240°C.

X-ray diffraction (XRD) was carried out by a Rigaku-D/max−gA diffractometer using high-intensity Cu-Kα radiation to screen for the presence of an impurity phase and the changes in structure. The homogeneity and chemical compositions of the samples were examined using an energy dispersive x-ray spectrometer (EDXS). The resistivity was measured using a standard four-probe method in a closed-cycle helium cryostat. The magnetic susceptibility and the magnetic hysteresis loops of the samples were determined by a SQUID magnetometer (Quantum Design, MPMS).

3 Results and discussion

Figure 1(a) shows a picture of a single crystal sample which has dimensions of about 4.5×3×0.5mm³. We select several pieces of crystal and perform EDXS measurement and find that the Co-contents in all pieces are close to the nominal compositions, indicating that the samples having shining surface are chemically homogeneous. The nominal and measured compositions of the selected samples are summarized in table 1. In order to judge the orientation of the samples, we perform x-ray diffraction (XRD) measurement on the as-grown samples. Figure 1(b) gives the typical XRD patterns of the BaFe₂₋ₓCoₓAs₂ (x=0, 0.06, 0.12, 0.18, 0.25, and 0.35) samples. Only the
(00\ l) diffraction peaks with even \ l\ are observed, confirming that the crystallographic c-axis is perpendicular to the shining surface. For all the diffraction peaks, the full width at half maximum (FWHM) is less than 0.06°, indicating the excellent quality of the single crystals. In order to see the shift of the peaks clearly, we plot in Fig. 1(c) the enlarged view of the (004) reflection. One can see that all the reflections are splitted into two shoulder peaks. The shoulder peak at lower angle is the reflection of the Cu-Kα1 radiation and the one at higher angle is the reflection of the Cu-Kα2 radiation. It can be seen that the (004) peak slightly shifts to higher angle with increasing Co content, meaning that the c-axis constant decreases monotonously as the Co content is increased. The calculated c-axis lattice contents for the samples are given in Table 1.

The superconducting properties of the BaFe\(_{2-x}\)Co\(_x\)As\(_2\) single crystals are given in Fig. 2. The superconductivity emerges in the \(x\geq0.06\) samples. And the maximum critical transition temperature \(T_{c,\rho=0}\) reaches to 23.3 K at the optimal doping concentration \(x=0.15\). With further increasing Co doping content, \(T_c\) decreases monotonously. The superconductivity disappears when \(x>0.35\).

Figure 3(a) gives the temperature dependence of magnetic susceptibility below \(T_c\) for the \(x=0.20\) sample both under zero-field cooling condition and under field-cooling condition at 10 Oe. It is found that the superconducting transition occurs at 23.1 K, consistent with the resistivity results. For the magnetic susceptibility at \(T>T_c\), the susceptibility signal is almost undetectable within the accuracy limit of the Quantum Design MPMS magnetometer (about \(10^{-8}\) emu). In order to know the magnetic state at the normal state, we measure the temperature dependence of magnetic susceptibility under 1 Tesla. The result is shown in Fig. 3(b). From Fig. 3(b) we notice that the magnetic susceptibility exhibits almost temperature-independent behav-
ior above $T_c$, indicating that the magnetic state of the BaFe$_{1.80}$Co$_{0.20}$As$_2$ system can not be the Curie paramagnetism. The fact that the magnetization is very weak and temperature-independent suggest that the paramagnetic state is a Pauli-paramagnetic state, which is consistent with the metallic behavior of the BaFe$_{1.80}$Co$_{0.20}$As$_2$ system. The predominant Pauli-paramagnetic state in the Co-doped sample suggest that the magnetic moment of the electrons near the Fermi surface should be delocalized. Previous neutron scattering experiments on CaFe$_2$As$_2$ have suggested that the magnetism is neither purely local nor purely itinerant and that it is a complicated mix of the two [9]. Here the predominant Pauli-paramagnetic state in the Co-doped sample suggest that the itinerant moments might be dominate in the superconducting sample.

Figure 4(a) shows magnetic hysteresis loops at various temperatures below $T_c$ calculated by applying the magnetic field up to 6 T. The $M$ vs $H$ curves exhibit a central peak at zero magnetic field and the magnetization decreases continuously with increasing magnetic fields. The sharp peak around $\mu_0 H = 0$ is similarly observed in other iron-pnictide materials [8, 10-11]. Figure 4(b) shows the magnetic field dependence of the critical current density $J_c$ derived from the hysteresis loop width by Bean critical state model using the relation $J_c = 20 \Delta M / a (1 - a/b) [12]$, where $a$ and $b$ are the width and length of the sample, respectively ($a < b$), and $\Delta M$ is the difference between the upper and the lower branches in the $M$ vs $H$ loops. It is found from Fig. 4(b) that the critical current density $J_c$ of the sample reaches to $1.2 \times 10^6$ A/cm$^2$ without external magnetic field. We notice that this $J_c$ value is higher than previous reported $J_c$ value of BaFe$_{2-x}$Co$_x$As$_2$ single crystal samples, either grown using self-flux method or using flux method [8,13-15]. For example, the $J_c$ values of recent grown Co-doped BaFe$_2$As$_2$ single crystal thin films are within the range of 60-100 kA/cm$^2$ at 12 K (without external magnetic field) [8], which is less than the value of 280 kA/cm$^2$ in present sample.
The $J_c$ value of a BaFe$_{1.80}$Co$_{0.20}$As$_2$ sample grown by self-flux method is about $6\times10^5$ A/cm$^2$ at 5 K [13]. For a BaFe$_{1.852}$Co$_{0.148}$As$_2$ single crystal grown using Sn flux, the $J_c$ value at 16 K under 6 Tesla is about 5 kA/cm$^2$ [14], which is also less than the value of 26 kA/cm$^2$ in present case. Based on these facts we suggest that the samples grown without any fluxing agent may have better current carrying ability comparing to those from flux growth. But this value is slightly less than the highest critical current density of 4 MA/cm$^2$ in Co-Doped BaFe$_2$As$_2$ epitaxial films which was recently grown on (La,Sr)(Al,Ta)O$_3$ substrates [16]. The comparison between single crystals grown using different methods reveals that further improvement of critical current density is still possible. Considering that the BaFe$_{2-x}$Co$_x$As$_2$ samples have upper critical field as high as 60 T, critical temperatures of above 20 K, low anisotropy, and, as shown here, high intrinsic critical current density, these materials can be considered as good candidates for applications.

The $J_c$ value decreases both with increasing temperature and with increasing external magnetic field, as can be seen from Figs. 4(b) and (c). At low temperatures ($\leq$20 K), the trend of $J_c$ decay is similar to that of conventional high-$T_c$ cuprates [17]. At high temperature (>20 K), the flux creep effect is evident by showing relatively strong dependence of critical current density on the external magnetic field [18].
Table 1 The comparison between nominal and real compositions and the c-axis lattice parameters of the BaFe$_{2-x}$Co$_x$As$_2$ samples

| Nominal composition | real composition | c (Å)   |
|---------------------|------------------|---------|
| BaFe$_2$As$_2$      | BaFe$_2$As$_2$   | 13.018(4) |
| BaFe$_{1.9}$Co$_{0.1}$As$_2$ | BaFe$_{1.9}$Co$_{0.1}$As$_2$ | 13.004(4) |
| BaFe$_{1.8}$Co$_{0.2}$As$_2$ | BaFe$_{1.8}$Co$_{0.2}$As$_2$ | 12.983(2) |
| BaFe$_{1.7}$Co$_{0.3}$As$_2$ | BaFe$_{1.7}$Co$_{0.3}$As$_2$ | 12.956(5) |

4 Conclusions

In summary, we have grown large-size Co-doped BaFe$_2$As$_2$ single crystals without using any fluxing agent. We find that the as-grown samples have larger current carrying ability comparing to those grown with the aid of fluxing agent, indicating promising industrial applications.

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