

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 1493 K. 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.

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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 $\text{BaFe}_{2-x}\text{Co}_x\text{As}_2$ single samples using excess $\text{Fe}(\text{Co})\text{As}$ 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 Letter 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 samples have typical dimensions of $4\times 3\times 0.5\text{mm}^3$ 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.

Single crystal samples were grown using prefired $\text{BaFe}_{2-x}\text{Co}_x\text{As}_2$ polycrystalline samples as the starting materials. The polycrystalline samples with nominal composition $\text{BaFe}_{2-x}\text{Co}_x\text{As}_2$ 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 $0.5\times 0.5\text{ mm}^2$). 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 1220°C at a rate of 60°C per hour. After holding at 1220°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, despite of small amount of adhesive on the inner surface of the tube. When we break the quartz tube and pick out the sample, slides of samples with shining surfaces can be easily cleaved.

The inset of Fig. 1 shows a picture of a single crystal sample which has dimensions of about $4 \times 3 \times 0.5 \text{ mm}^3$. In order to judge the quality of the samples, we perform x-ray diffraction (XRD) measurement on the as-grown samples. Figure 1 gives the typical XRD patterns of the $\text{BaFe}_{2-x}\text{Co}_x\text{As}_2$ ($x=0, 0.06, 0.12, 0.18, 0.25, \text{ and } 0.35$) samples. Only the $(00l)$ 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. It can be seen that the $(00l)$ peaks slightly shift to higher angle with increasing Co content, meaning that the c -axis constant decreases monotonously as the Co content is increased.

The superconducting properties of the $\text{BaFe}_{2-x}\text{Co}_x\text{As}_2$ single crystals are given in Fig. 2. The superconductivity emerges in the $x \geq 0.06$ 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 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 bulk magnetic susceptibility at $T > T_c$ is almost temperature independent. In fact, the bulk susceptibility is almost undetectable within the accuracy limit of

the *Quantum Design* MPMS magnetometer (about 10^{-8} emu), indicating that both the Fe and Co lose their magnetism. The argument that both Fe and Co lose their magnetism in $\text{CaFe}_{1.80}\text{Co}_{0.20}\text{As}_2$ can also be concluded from the experimental data of the magnetization as the function of external magnetic field at different temperatures, which are shown in Fig. 3(b)-(f). The $M\sim H$ curve at 4 K shown in Fig. 3(b) exhibits typical superconducting behavior. From Fig. 3(c)-(f) one can see that the $M\sim H$ curves at $T>T_c$ exhibit only very weak paramagnetic signal. More importantly, the absolute value of magnetization does not exhibit any increase with decreasing temperature, indicating that the magnetic state of the $\text{BaFe}_{1.80}\text{Co}_{0.20}\text{As}_2$ 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 $\text{BaFe}_{1.80}\text{Co}_{0.20}\text{As}_2$ system. The predominant Pauli-paramagnetic state in the Co-doped sample suggest that the sample can nearly be treated as free electron system. From these results one can draw a conclusion that in $\text{BaFe}_{1.80}\text{Co}_{0.20}\text{As}_2$, the conducting-electrons are all itinerant, and all the Fe and Co ions have no magnetic interactions.

Figure 4(a) shows magnetic hysteresis loops at various temperatures below T_c calculated by applying the magnetic field up to 6 T. The $M\sim H$ 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] 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 $J_c = 20\Delta M/a(1 - a/3b)$, [11] where a and b are the width and length of the sample, respectively ($a < b$), and ΔM is the difference between the upper and the lower branches in the $M\sim H$ loops. It is found from Fig. 4(b) that the critical current density J_c of the sample reaches to 1.2×10^6 A/cm² without external magnetic field. We notice that this J_c value is higher than previous reported J_c value of $\text{BaFe}_{2-x}\text{Co}_x\text{As}_2$ single crystal samples, either grown using self-flux method or using flux method.[8, 12–14] For example, the J_c values of recent grown Co-doped BaFe_2As_2 single crystal thin films are within the range of 60-100 kA/cm² at 12 K (without external magnetic field), [8] which is less than the value of 280 kA/cm² in present sample. The J_c value of a $\text{BaFe}_{1.80}\text{Co}_{0.20}\text{As}_2$ sample grown by self-flux method is about 6×10^5 A/cm² at 5 K.[12] For a $\text{BaFe}_{1.852}\text{Co}_{0.148}\text{As}_2$ single crystal grown using Sn flux, the J_c value at 16 K under 6 Tesla is about 5 kA/cm², [13] which is also less

than the value of 26 kA/cm² 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/cm² in Co-Doped BaFe₂As₂ epitaxial films which was recently grown on (La,Sr)(Al,Ta)O₃ substrates.[15] 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_xAs₂ 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 (≤ 20 K), the trend of J_c decay is similar to that of conventional high- T_c cuprates.[16] 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.[17]

In summary, we have grown large-size Co-doped BaFe₂As₂ single crystals without using any fluxing agent. The magnetization measurement results of the BaFe_{1.80}Co_{0.20}As₂ sample suggest that there is no magnetic interaction in the Fe and Co sublattice and that the conduction electrons are nearly free electrons. We also find that the as-grown samples have very large current carrying ability comparing to those grown with the aid of fluxing agent, indicating promising industrial applications.

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FIGURE CAPTION

FIG. 1 X-ray diffraction pattern at room temperature for the $\text{BaFe}_{2-x}\text{Co}_x\text{As}_2$ single crystals. The inset shows the typical topography of the as-grown sample.

FIG. 2 (color online) Temperature dependence of in-plane resistivity for the $\text{BaFe}_{2-x}\text{Co}_x\text{As}_2$ samples.

FIG. 3 (a) Temperature dependence of magnetic susceptibility for the $x=0.20$ sample both under zero-field cooling condition and under field-cooling condition at 10 Oe. (b)-(f)

The magnetization as the function of external magnetic field at different temperatures.

FIG. 4 (a) The magnetization as the function of external magnetic field below T_c for the $x=0.20$ sample. (b) The critical current density as the function of magnetic field for the $x=0.20$ sample at different temperatures. (c) The temperature dependence of critical current density for the $x=0.20$ sample under zero-field and under external magnetic field.