Growth of large single crystals of BaFe$_{1.87}$Co$_{0.13}$As$_2$ using a nucleation pole

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Abstract

Co-doped iron arsenic single crystals of BaFe$_{1.87}$Co$_{0.13}$As$_2$ with dimensions up to $20 \times 10 \times 2$ mm$^3$ were grown using a nucleation pole: an alumina stick served as a nucleation center during growth. The high quality of the crystals was illustrated using measured neutron rocking curves and x-ray diffraction patterns. A very sharp superconducting transition temperature of $T_c \sim 25$ K was revealed by both resistivity and susceptibility measurements. A nearly 100% shielding fraction and the bulk nature of the superconductivity for the single crystals were confirmed using magnetic susceptibility data.

1. Introduction

The newly discovered iron–arsenic superconductors [1] have stimulated great interest in the study of their structural, transport and magnetic properties. The parent compounds show a spin-density-wave (SDW) ground state. On introducing charge carriers by electron or hole doping, the SDW transition is suppressed while a superconducting transition takes place, which is reminiscent of the situation for high $T_c$ cuprate superconductors. For instance, the compounds RO$_{1-x}$F$_x$FeAs ($R$ = La, Pr, Sm, Ce, Nd, and Gd) have shown a superconducting transition with fluorine substitution for oxygen, resulting in the highest $T_c$ at 56 K [1–7], upon electron doping. In the case of hole doping, La$_{1-x}$Sr$_x$OFeAs shows a relatively low $T_c$. For the oxygen-free compounds, $T_c$ reaches 38 K for hole-doped A$_{1-x}$K$_x$Fe$_2$As$_2$ (A = Ba, Sr, Ca) and 22 K for electron-doped AF$_{2-x}$M$_x$As$_2$ (M = Co or Ni) [8–15]. The superconductivity is suggested to compete with the SDW order, and spin fluctuations could play a role in forming the Cooper pairs. In addition, the compounds display anisotropic behavior owing to the layered structure when measuring upper critical field [16], coherence length and penetration depth [17] in the plane and along the $c$ axis. Therefore, investigations of spin dynamics are highly attractive for exploring the superconducting mechanism of iron–arsenic superconductors. High quality and large single crystals are urgently required for various experiments, particularly as regards neutron scattering measurements.

A flux method could be used to grow single crystals of iron–arsenic superconductors [2, 10–15]. Several groups reported the growth of AFe$_2$As$_2$ single crystals using KCl/NaCl, Sn or the self-flux technique, obtaining sizes as large as $12 \times 8 \times 1$ mm [18]. However, the crystals are contaminated with Sn at about 1–2 at.% [10]. It has been proved that the Sn is incorporated into the Fe sites, as detected by atomic spectroscopy, and this leads to a decrease of the SDW transition temperature [11]. Therefore, the self-flux method is preferred for the growth to prevent contamination of the crystal [12–15]. In this work, we present the growth of BaFe$_{2-x}$Co$_x$As$_2$ single crystals using an alumina stick as a nucleation center in the melt during growth. Large crystal disks sized up to $\geq 40 \times 5$ mm were obtained. Structure characterizations with neutron rocking curves and x-ray diffraction illustrate the high quality of the samples. The measurements of the resistivity and magnetic susceptibility show a sharp superconducting transition temperature at $\sim 25$ K.

2. Experimental details

The starting materials in the formula BaFe$_{5-x}$Co$_x$As$_5$ (all elements are from Alfa Aesar, 4–5N in purity) with $x = 0.5$ were used for the self-flux growth. Usually $\sim 20$ g of the mixtures were well ground and then loaded into a
ZrO₂ crucible covered with a lid to minimize the arsenic volatilization. An Al₂O₃ stick of $\geq 2$ mm $\times$ 70 mm is inserted in a hole drilled through the lid and dips into the mixtures to serve as a nucleation pole. All preparation procedures were carried out in a glove box containing Ar. The loaded crucible was then sealed in a quartz ampoule filled with 250 mbar argon atmosphere. The ampoule was placed in a furnace and heated up to 1190 °C for 10 h. The temperature of the melt was then lowered to 1090 °C at a rate of $\sim 2$ °C h$^{-1}$, and this was followed by decanting of the residual flux. Finally the furnace was cooled down to room temperature at 100 °C h$^{-1}$. The whole procedure of crystal growth was carried out in a sealed system with a specially designed apparatus, as shown in figure 1.

X-ray diffraction (XRD) measurements of single crystals were carried out with an x-ray diffractometer (Philips PW 3710) using Cu Kα radiation and with a scanning rate of 0.02° min$^{-1}$. The lattice parameters were derived from the powder XRD using TOPAS v2.1, which is general profile and structure analysis software for powder diffraction data analysis (Karlsruhe, Germany, 2002). Energy dispersive x-ray spectroscopy (EDX) analyses were employed to determine the crystal composition. The error of the analysis is within 1 at.%. Neutron data were collected using the thermal triple-axis spectrometer PUMA at the research reactor FRM-II, Garching, Germany. The initial neutron wavelength was fixed at 2.66 Å and a flat PG (002) monochromator was used. The resistivity was measured using a physical property measurement system (PPMS™, Quantum Design). The DC susceptibility was obtained using a SQUID (VSM, Quantum Design) magnetometer.

### 3. Results and discussion

A nucleation center is crucial for the growth of a large and high quality single crystal. In our growth experiment, we used an alumina stick which served as a ‘seed’ to play a role of a nucleation pole in the melt during growth. The alumina stick was positioned at the bottom of the crucible. This allows heat convection transport from the hotter melt $T_1$ to the colder end $T_2$ of the stick, creating a temperature gradient of $\sim 8$–3 °C cm$^{-1}$ when the heating temperature ranges between 1190 and 1090 °C. A schematic drawing of the experimental setup is shown in figure 1. By the use of this ‘seeding’ method together with the low cooling rate of $\sim 2$ °C h$^{-1}$ applied, spontaneous and numerous nuclei can be minimized during growth. The process of crystallization takes place around the ‘seed’, which is the colder pole of the stick. With cooling, the crystals gradually grow, resulting in a large crystal together with some small crystals being formed around the big one. We demonstrate that the biggest crystal can be grown as large as $\geq 40$ mm $\times$ 5 mm where thickness depends on the amount of source materials. Figure 2(a) shows the ‘seed’ rod located in the center of the crystal disk and a broken part of the crystal measuring up $20 \times 10 \times 2$ mm$^3$, whose size is one third of the disk size. This is the largest crystal of iron–arsenic superconductor ever reported [2, 10–15]. It is noticed that to obtain crystal mostly free from flux a temperature of $\geq 40$ °C had to be maintained for $\sim 2$ h after decanting and then cooling to room temperature. This allows the residual flux flowing out to completely leave free-standing crystals inside of the crucible. It is emphasized that the decanting device is specially designed with a movable nickel wire for tilting the crucible and 1090 °C. Finally the crucible was cooled down to room temperature at 100 °C h$^{-1}$. The whole procedure of crystal growth was carried out in a sealed system with a specially designed apparatus, as shown in figure 1.

Figure 1. A schematic drawing of the apparatus used to grow single crystals of BaFe$_{1-x}$Co$_{0.13}$As$_2$. The inset shows a temperature gradient of 8–3 °C cm$^{-1}$ distributed from the bottom to the upper part of the solution.

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![Decanting wire](image-url)
Figure 2. (a) Parts of BaFe$_{1.87}$Co$_{0.13}$As$_2$ crystals with a mass of $\sim 2$ g and the alumina ‘seed’ located in the center of the crystal disk. (b) The related Laue pattern showing the (00$l$) face and (c) the neutron rocking curve of the crystals (a). The weaker diffraction peaks were obtained from the misorientated small crystals which adhered on the sides of the big one during decanting.

Figure 3. X-ray diffraction patterns of BaFe$_{1.87}$Co$_{0.13}$As$_2$; (a) the cleaved plane of a crystal and (b) the powders of a ground crystal.

Figure 4. Temperature dependence of the resistivity for single crystals of BaFe$_2$As$_2$ obtained by the self-flux method [11] and BaFe$_{1.87}$Co$_{0.13}$As$_2$.

Figure 5 shows the temperature dependence of the magnetic susceptibility of BaFe$_2$As$_2$ and BaFe$_{1.87}$Co$_{0.13}$As$_2$ crystals at 2 T field and for the temperature range of 2–300 K. A kink associated with the SDW transition is observed for BaFe$_2$As$_2$ crystal [10, 11], consistent with the result of the resistivity measurement. For BaFe$_{1.87}$Co$_{0.13}$As$_2$, the SDW transition is entirely suppressed with the occurrence of the superconducting transition. There is no sign of a SDW transition with an application of 2 T magnetic field. A sharp transition occurs at $T_c \sim 25$ K for the BaFe$_{1.87}$Co$_{0.13}$As$_2$ crystal, as shown in the inset of figure 5. The shielding fraction close to 1 demonstrates the bulk nature of the superconductivity. The onset transition temperature $T_c \sim 25$ K is defined as where the magnetic susceptibility in the normal state decreases by 10%; it is the highest one ever reported.

a higher doping content in solution results in a lower one in the crystals. The in-plane and out-of-plane crystallizations of the whole bulk BaFe$_{1.87}$Co$_{0.13}$As$_2$ crystals were revealed by the neutron rocking curve, as shown in figure 2(c). The (200) reflection is pronounced and symmetrical. The FWHM is around 1.01° (in-plane case) and 1.083° (out-of-plane case). Both peaks are very sharp and clearly formed within the limited instrumental resolution. Therefore the real peak width (for the mosaic of the samples) could be even narrower. This is indicative of an excellent quality for the whole crystal.

The structure of the BaFe$_{1.87}$Co$_{0.13}$As$_2$ single crystal was identified using XRD measurements. The XRD diffraction patterns were obtained using ground powders of as-grown crystals. Figure 3(a) shows the (00$l$) reflections obtained from the naturally cleaved surface, indicating a good crystallization along the $c$ axis of the crystal. The powder XRD pattern can be well indexed with the space group $I4/mmm$, as shown in figure 3(b). The lattice parameters $a = 3.9633(8)$ Å and $c = 12.991(2)$ Å were derived from the program using TOPAS 2.1. Compared to the undoped BaFe$_2$As$_2$ with $a = 3.9635(5)$ Å, $c = 13.022(2)$ Å [14], BaFe$_{1.87}$Co$_{0.13}$As$_2$ has a $c$ lattice parameter which is slightly shrunk, by 0.24%, while $a$ is almost unchanged. This is owing to the ionic radius relation $R_{Co}^{3+}$ (0.61 Å) $< R_{Fe}^{2+}$ (0.78 Å), since the Co$^{3+}$ ions partially substitute for Fe$^{2+}$ in the basal plane of BaFe$_{1.87}$Co$_{0.13}$As$_2$. Our results are consistent with the reported data [14].

The temperature dependence of the resistivity for BaFe$_2$As$_2$ and BaFe$_{1.87}$Co$_{0.13}$As$_2$ single crystals in the temperature range of 2–300 K is shown in figure 4. For the pure BaFe$_2$As$_2$, the resistivity shows a rapid decrease below $T_s \sim 138$ K, corresponding to SDW transition. In the case of BaFe$_{1.87}$Co$_{0.13}$As$_2$ crystal, a very sharp superconducting transition occurs at $T_c \sim 25$ K, while the resistivity kink of the SDW disappears for the Co-doped sample.
The superconducting transition width is 0.5 K with $\Delta T_c = T_c(10\%) - T_c(90\%)$, which is close to the reported 0.6 K ($T_c = 22$ K) for BaFe$_{1.87}$Co$_{0.13}$As$_2$ [14], and much smaller than the 2.3 K ($T_c = 14.3$ K) for LaFe$_{0.92}$Co$_{0.08}$AsO [19], 2.5 K ($T_c = 36.3$ K) for Ba$_{0.8}$K$_{0.2}$Fe$_2$As$_2$ [12] and 4.5 K ($T_c = 28.2$ K) for LaFeAsO$_{0.89}$F$_{0.11}$ [20].

4. Conclusions

In summary, large and high quality BaFe$_{1.87}$Co$_{0.13}$As$_2$ single crystals have been grown successfully by the 'seeding' method. The neutron rocking curve and x-ray diffraction patterns show good crystallization of the sample. The resistivity and susceptibility results show sharp superconducting transitions at 25 K and nearly 100% shielding fraction, which confirms the bulk nature of the superconductivity and the high quality of the single crystal.

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