J Supercond Nov Magn (2011) 24:2041–2045
DOI 10.1007/s10948-011-1163-z

ORIGINAL PAPER

Single-Crystal Growth of $BaFe_{2-x}Co_xAs_2$ Without Fluxing Agent

Changjin Zhang · Lei Zhang · Chuanying Xi · Langsheng Ling · Wei Tong · Shun Tan · Yuheng Zhang

Received: 24 February 2011 / Accepted: 20 March 2011 / Published online: 8 April 2011

Abstract We report a simple, reliable method to grow high-quality $BaFe_{2-x}Co_xAs_2$ 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 $4 \times 3 \times 0.5$ 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

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 nonnegligible. For example, if we grow $BaFe_{2-x}Co_xAs_2$ single samples using excess Fe(Co)As mixture as fluxing agent, the actual Fe/Co ratio cannot be accurately controlled in the growth procedure. If one uses Sn as fluxing agent, the problem is that one cannot remove the Sn from the surface of the sample easily [5]. In this paper we report a simple, reliable method to grow high-quality $BaFe_{2-x}Co_xAs_2$ 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 is 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 $BaFe_{2-x}Co_xAs_2$ polycrystalline samples as the starting ma-

C. Zhang (✉) · L. Zhang · C. Xi · L. Ling · W. Tong · Y. Zhang
High Magnetic Field Laboratory, Chinese Academy of Sciences, Hefei 230031, People's Republic of China
e-mail: zhangcj@hmfl.ac.cn

S. Tan · Y. Zhang
Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei 230026, People's Republic of China

terials. The polycrystalline samples with nominal composition $BaFe_{2-x}Co_xAs_2$ 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 0.5×0.5 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 $4.5 \times 3 \times 0.5$ mm^3. 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,

Table 1 The comparison between nominal and real compositions and the c-axis lattice parameters of the $BaFe_{2-x}Co_xAs_2$ samples

Nominal composition	Real composition	c (Å)
$BaFe_2As_2$	$BaFe_2As_2$	13.018(4)
$BaFe_{1.9}Co_{0.1}As_2$	$BaFe_{1.9}Co_{0.1}As_2$	13.004(4)
$BaFe_{1.8}Co_{0.2}As_2$	$BaFe_{1.81}Co_{0.19}As_2$	12.983(2)
$BaFe_{1.7}Co_{0.3}As_2$	$BaFe_{1.71}Co_{0.29}As_2$	12.956(5)

we perform X-ray diffraction (XRD) measurement on the as-grown samples. Figure 1(b) gives the typical XRD patterns of the $BaFe_{2-x}Co_xAs_2$ ($x = 0$, 0.06, 0.12, 0.18, 0.25, 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. 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-Kα_1 radiation and the one at higher angle is the reflection of the Cu-Kα_2 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 $BaFe_{2-x}Co_xAs_2$ 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 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 behavior above T_c, indicating that the magnetic state of the $BaFe_{1.80}Co_{0.20}As_2$ system cannot 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

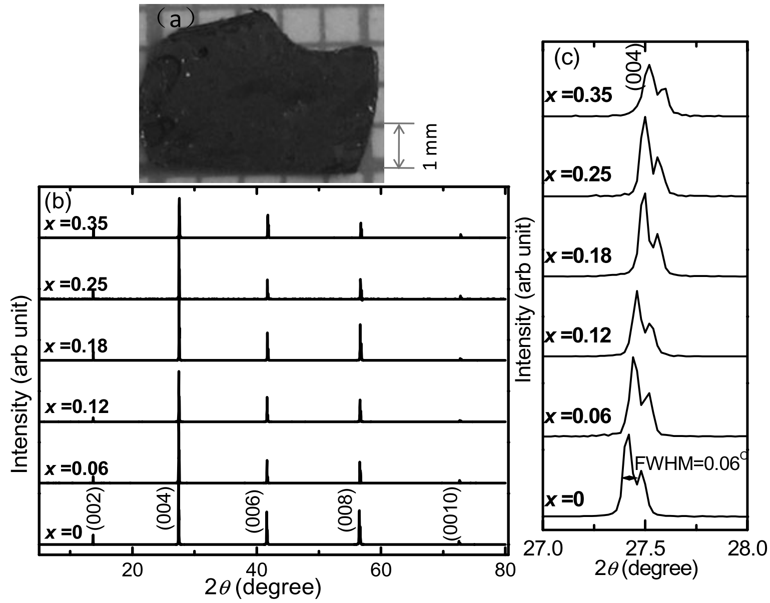

Fig. 1 (**a**) Photograph of an as-grown $BaFe_2As_2$ single crystal. (**b**) X-ray diffraction pattern at room temperature for the $BaFe_{2-x}Co_xAs_2$ single crystals. (**c**) An enlarge view of the (004) reflection

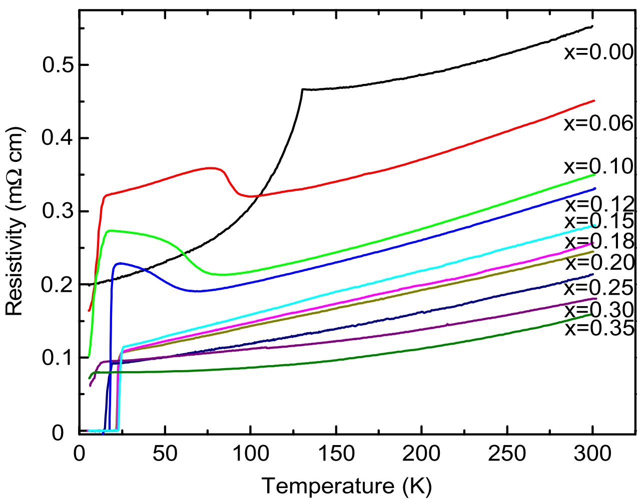

Fig. 2 (Color online) Temperature dependence of in-plane resistivity for the $BaFe_{2-x}Co_xAs_2$ samples

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 $CaFe_2As_2$ 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 $M{\sim}H$ 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, 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 $J_c = 20\Delta M/a(1 - a/3b)$ [12], 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/cm^2 without external magnetic field. We notice that this J_c value is higher than previous reported J_c value of $BaFe_{2-x}Co_xAs_2$ 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 $BaFe_2As_2$ 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 6×10^5 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 $BaFe_2As_2$ 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 $BaFe_{2-x}Co_xAs_2$ samples have upper critical field as high as 60 T, critical temperatures of above 20 K, low anisotropy,

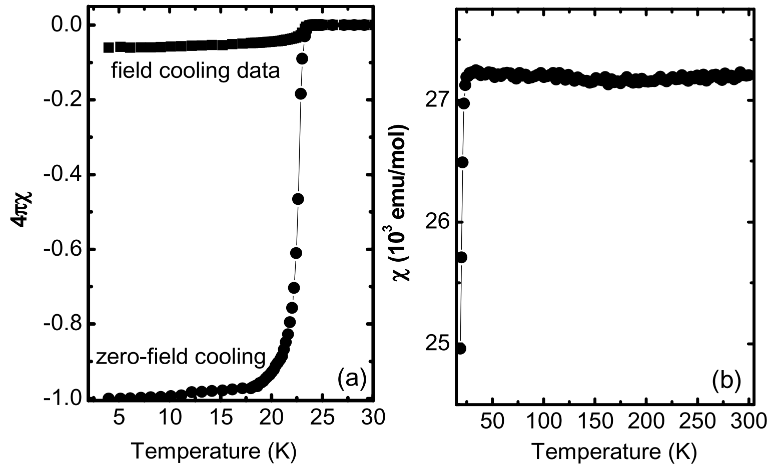

Fig. 3 (**a**) Temperature dependence of magnetic susceptibility for $BaFe_{1.80}Co_{0.20}As_2$ both under zero-field-cooling condition and under field-cooling condition at 10 Oe. (**b**) The magnetization as the function of temperature under 1 Tesla magnetic field

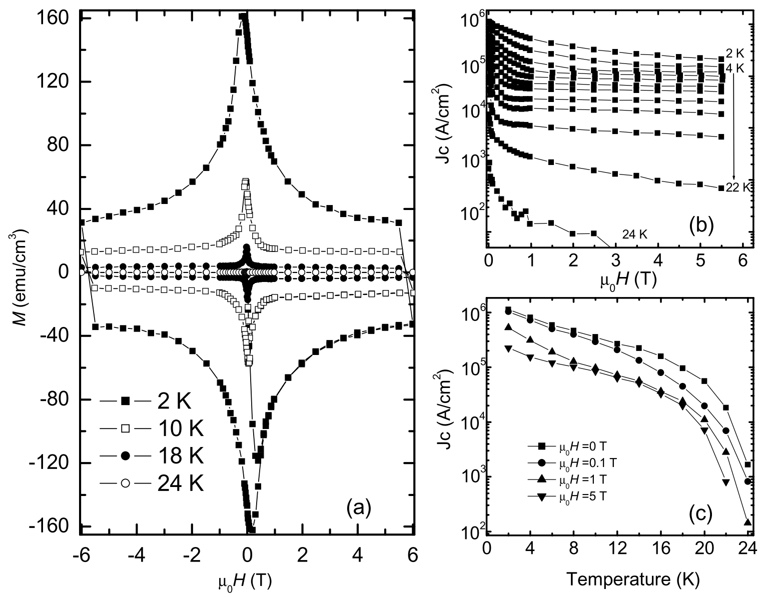

Fig. 4 (**a**) The magnetization as the function of external magnetic field below T_c for the $x = 0.20$ sample. (**b**) The critical current density as the function of magnetic field for the $x = 0.20$ sample at different temperatures. (**c**) The temperature dependence of critical current density for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

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].

4 Conclusions

In summary, we have grown large-size Co-doped $BaFe_2As_2$ 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.

Acknowledgements This work was supported by the State Key Project of Fundamental Research of China through Grant 2010CB923403 and 2011CBA00111, and the Hundred Talents Program of the Chinese Academy of Sciences.

References

1. Kamihara, Y., Watanabe, T., Hirano, M., Hosono, H.: J. Am. Chem. Soc. **130**, 3296 (2008)
2. Hunte, F., Jaroszynski, J., Gurevich, A., Larbalestier, D.C., Jin, R., Sefat, A.S., McGuire, M.A., Sales, B.C., Christen, D.K., Mandrus, D.: Nature **453**, 903 (2008)
3. Ishida, K., Nakai, Y., Hosono, H.: J. Phys. Soc. Jpn. **78**, 062001 (2009)
4. Aswathy, P.M., Anooja, J.B., Sarun, P.M., Syamaprasad, U.: Supercond. Sci. Technol. **23**, 073001 (2010)
5. Ni, N., Bud'ko, S.L., Kreyssig, A., Nandi, S., Rustan, G.E., Goldman, A.I., Gupta, S., Corbett, J.D., Kracher, A., Canfield, P.C.: Phys. Rev. B **78**, 014507 (2008)
6. Hardy, F., Adelmann, P., Wolf, T., v. Lohneysen, H., Meingast, C.: Phys. Rev. Lett. **102**, 187004 (2009)

7. Kim, J.S., Kim, E.G., Stewart, G.R.: J. Phys., Condens. Matter **21**, 252201 (2009)
8. Tarantini, C., Lee, S., Zhang, Y., Jiang, J., Bark, C.W., Weiss, J.D., Polyanskii, A., Nelson, C.T., Jang, H.W., Folkman, C.M., Baek, S.H., Pan, X.Q., Gurevich, A., Hellstrom, E.E., Eom, C.B., Larbalestier, D.C.: Appl. Phys. Lett. **96**, 142510 (2010)
9. Zhao, J., Adroja, D.T., Yao, D.-X., Bewley, R., Li, S.L., Wang, X.F., Wu, G., Chen, X.H., Hu, J.P., Dai, P.C.: Nat. Phys. **5**, 555 (2009)
10. Prozorov, R., Tanatar, M.A., Ni, N., Kreyssig, A., Nandi, S., Bud'ko, S.L., Goldman, A.I., Canfield, P.C.: Phys. Rev. B **80**, 174517 (2009)
11. Kametani, F., Li, P., Abraimov, D., Polyanskii, A.A., Yamamoto, A., Jiang, J., Hellstrom, E.E., Gurevich, A., Larbalestier, D.C., Ren, Z.A., Yang, J., Dong, X.L., Lu, W., Zhao, Z.X.: Appl. Phys. Lett. **95**, 142502 (2009)
12. Bean, C.P.: Rev. Mod. Phys. **36**, 31 (1964)
13. Nakajima, Y., Taen, T., Tamegai, T.: J. Phys. Soc. Jpn. **78**, 023702 (2009)
14. Tanatar, M.A., Ni, N., Bud'ko, S.L., Canfield, P.C., Prozorov, R.: Supercond. Sci. Technol. **23**, 054002 (2010)
15. Prozorov, R., Tanatar, M.A., Ni, N., Kreyssig, A., Nandi, S., Bud'ko, S.L., Goldman, A.I., Canfield, P.C.: Phys. Rev. B **80**, 174517 (2009)
16. Katase, T., Hiramatsu, H., Kamiya, T., Hosono, H.: Appl. Phys. Express **3**, 063101 (2010)
17. Cai, C., Holzapfel, B., Hänisch, J., Fernández, L., Schultz, L.: Phys. Rev. B **69**, 104531 (2004)
18. Matsushita, T., Fujiyoshi, T., Toko, K., Yamafuji, K.: Appl. Phys. Lett. **56**, 2039 (1990)