Growth and characterization of CaFe$_{1-x}$Co$_x$AsF single crystals by CaAs flux method

Yonghui Ma$^{a,b}$, Kangkang Hu$^{b,c}$, Qiucheng Ji$^{b}$, Bo Gao$^{b}$, Hui Zhang$^d$, Gang Mu$^{b, *}$, Fuqiang Huang$^d$, Xiaoming Xie$^{a,b}$

$^a$School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China
$^b$State Key Laboratory of Functional Materials for Informatics and Shanghai Center for Superconductivity, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai 200050, China
$^c$College of Sciences, Shanghai University, Shanghai 200444, China
$^d$CAS Key Laboratory of Materials for Energy Conversion, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

Abstract

Millimeter sized single crystals of CaFe$_{1-x}$Co$_x$AsF were grown using a self-flux method. It is found that high-quality single crystals can be grown from three approaches with different initial raw materials. The chemical compositions and crystal structure were characterized carefully. The c-axis lattice constant is suppressed by the Co substitution. Superconductivity with the critical transition $T_c$ as high as 21 K was confirmed by both the resistivity and magnetic susceptibility measurements in the sample with $x = 0.12$. Moreover, it is found that $T_c$ can be enhanced for about 1 K under the very small hydrostatic pressure of 0.22 GPa, which is more quickly than that reported in the polycrystalline samples. Our results is a promotion for the physical investigations of 1111 phase iron-pnictide superconductors.

Keywords: A1. Doping, A2. Single crystal growth, B2. Superconducting materials

*Corresponding author. Tel.: 86-21-62511070.
Email address: mugang@mail.sim.ac.cn (Gang Mu)
1. Introduction

Investigations on the physical properties of 1111 phase of the iron-pnictide superconductors are restricted remarkably, compared with the 122 phase and 11 phase, due to the difficulties in obtaining high-quality and sizable single crystals. NaCl and KCl were first used as the flux and small single crystals with small sizes of 20-70 \( \mu m \) can be obtained because of the low solubility of NaCl/KCl flux. Then the high pressure method was developed and the crystal size was enhanced to several hundred micrometers. After that, a new flux NaAs used under ambient pressure was reported to improve the crystal size, but the crystal quality is not sufficient for the physical investigations possibly due to the extrinsic contaminants induced by the flux. A noteworthy progress in this field was made by our group by using the CaAs flux, where millimeter sized single crystals of CaFeAsF with high quality was grown successfully. It is the parent compound of the fluorine-based 1111 phase of the iron-pnictide superconductors, whose \( T_c \) can be increased to above 50 K by doping rare-earth elements to the sites of the alkaline-earth elements and to above 20 K by doping transition-metal elements to the sites of Fe.

To grow the doped single crystals with superconductivity was found to be more difficult than we expected. After many trials, single crystals of Co-doped CaFeAsF were demonstrated to be the breakthrough and grown successfully. In this paper, we report the technical approaches to grow the CaFe\(_{1-x}\)Co\(_x\)AsF single crystals with a high quality and large size. The compositions and structure of the crystals were determined. The superconducting properties were confirmed by the low-temperature resistivity and magnetization measurements. We also checked the influence of the pressure on the superconductivity.

2. Experiment

The CaFe\(_{1-x}\)Co\(_x\)AsF single crystals were grown on the basis of the successful growth of the parent phase CaFeAsF, where a CaAs self-flux method was developed. It was found that the CaFeAsF single crystals can been grown
successfully with different initial raw materials as the following formulas (1) and (2) describe.

\[ \text{CaAs} + 0.5\text{FeF}_2 + 0.5\text{Fe} + 4\text{CaAs(Flux)} \Rightarrow \text{CaFeAsF} + 4\text{CaAs(Flux)} \] (1)

\[ \text{CaAs} + \text{CaF}_2 + \text{Fe}_2\text{As} + 8\text{CaAs(Flux)} \Rightarrow 2\text{CaFeAsF} + 8\text{CaAs(Flux)} \] (2)

Based on the formula (1), two approaches (see formula (3) and (4)) was tried to substitute Co to the site of Fe and both were found to be successful in growing the single crystals.

\[ \text{CaAs} + 0.5\text{FeF}_2 + (0.5 - x)\text{Fe} + x\text{Co} + 4\text{CaAs(Flux)} \]

\[ \Rightarrow \text{CaFe}_{1-x}\text{Co}_x\text{AsF} + 4\text{CaAs(Flux)} \] (3)

\[ \text{CaAs} + (0.5 - x)\text{FeF}_2 + x\text{CoF}_2 + 0.5\text{Fe} + 4\text{CaAs(Flux)} \]

\[ \Rightarrow \text{CaFe}_{1-x}\text{Co}_x\text{AsF} + 4\text{CaAs(Flux)} \] (4)

Starting from formula (2), only Fe\textsubscript{2}As can be substituted by Co\textsubscript{2}As and we have the following formula to grow the single crystals of CaFe\textsubscript{1-x}Co\textsubscript{x}AsF.

\[ \text{CaAs} + \text{CaF}_2 + (1 - x)\text{Fe}_2\text{As} + x\text{Co}_2\text{As} + 8\text{CaAs(Flux)} \]

\[ \Rightarrow 2\text{CaFe}_{1-x}\text{Co}_x\text{AsF} + 8\text{CaAs(Flux)} \] (5)

In practice, the arsenide precursors CaAs, Fe\textsubscript{2}As and Co\textsubscript{2}As were first synthesized by heating a mixture of Ca granules (purity 99.5%, Alfa Aesar), Fe powder (99+%, Alfa Aesar), Co powder (99.8%, Alfa Aesar), and As grains (purity 99.995%, Alfa Aesar) at 700-800 °C for 10-15 h in an evacuated quartz tube. Then homemade precursors and other reagents was mixed according to formula (3), (4) and (5) and placed into a crucible. The purities of the reagents are FeF\textsubscript{2} (purity 99%, Alfa Aesar), CoF\textsubscript{2} (purity 98%, Alfa Aesar), and CaF\textsubscript{2} (purity 99.95%, Alfa Aesar). All the weighing and mixing procedures were carried out in a glove box with a protective argon atmosphere. Finally, the crucible was sealed in a quartz tube with vacuum. The quartz tube was heated at 950 °C for 40 h firstly, and then it was heated up to 1230 °C where it remained for
Table 1: Compositions of the crystal with $x_{\text{nominal}} = 0.15$ characterized by EDS measurements.

| Element | Weight (%) | Atomic (%) |
|---------|------------|------------|
| Ca      | 23.43      | 31.91      |
| Fe      | 27.62      | 26.99      |
| Co      | 3.90       | 3.61       |
| As      | 43.30      | 31.54      |

20 h. Finally it was cooled down to 900 °C at a rate of 2 °C/h and followed with a quick cooling down to room temperature. In the end, by exposing the resultant to air in the fume hood for a few days, the flux CaAs decomposed and the single crystals appeared. We found that all of the three methods are successful to obtain the CaFe$_{1-x}$Co$_x$AsF single crystals and the quality of the single crystals is very similar to each other with a small fluctuation of $T_c$ for about ±0.5 K, so we will not distinguish them in our paper.

The microstructure was examined by scanning electron microscopy (SEM, Zeiss Supra55). The composition of the single crystals was checked and determined by energy dispersive x-ray spectroscopy (EDS) measurements on an Bruker device with the model Quantax200. The crystal structure and lattice constants of the materials were examined by a DX-2700 type powder x-ray diffractometer using Cu K$_\alpha$ radiation. The electrical resistivity was measured using a four probe technique on the physical property measurement system (Quantum Design, PPMS). The magnetic susceptibility measurement was carried out on the magnetic property measurement system (Quantum Design, MPMS 3) with the magnetic field oriented parallel to the ab-plane of the samples. The magnetization susceptibility under different pressures was obtained using the Mcell 10 (Almax easylab).
3. Results and discussions

The morphology of the single crystals was examined by the optical microscope and the scanning electron microscopy, which are shown in figures 1(a) and (b) respectively. The crystals are black in color and show the flat surfaces. The typical crystal size was found to be as large as $1 \text{ mm} \times 0.7 \text{ mm} \times 0.06 \text{ mm}$. Some impurities on the surface of the sample are the remaining flux CaAs. The composition of the crystals was examined by the EDS analysis and one of the typical EDS spectrums for $x_{\text{nominal}} = 0.15$ is shown in figure 1 and table 1. The square frame in figure 1(b) indicates the measuring field of EDS. Note that the content of F is not precise as other elements because the EDS is not sensitive to light element. The EDS data revealed that the ratio of Ca:(Fe+Co):As is close to 1:1:1, and the actual composition of Co can be determined to be about $x_{\text{actual}} = 0.12$. Hereinafter the variable $x$ denotes the actual doping level $x_{\text{actual}}$ in this paper.

The structure of the crystals was examined by a powder XRD measurement,
Figure 2: Typical XRD patterns of CaFeAsF (black line) and CaFe$_{1-x}$Co$_x$AsF with $x_{\text{actual}} = 0.12$ (red line).

where the x-ray was incident on the ab-plane of the sample. The XRD spectrum for the undoped crystal CaFeAsF is displayed together with the sample with $x=0.12$ in figure 2 for a comparison. Only sharp peaks with the index $(00l)$ could be observed, suggesting a high c-axis orientation of the crystals. It is clear that the diffraction peaks for the doped sample shifts to the right sides compared with the parent compound, suggesting the shrinkage of the crystal along the c axis. The raw data of XRD was analyzed by PowderX software [12, 13], where the zero-shift, K$_\alpha$2-elimination and other factors were taken into account. The c-axis lattice parameters was calculated to be 8.584 Å and 8.547 Å for the samples with $x = 0$ and $x = 0.12$ respectively, which is consistent with the results of the polycrystalline samples [14].

Temperature dependence of resistivity in the temperature range from 0 to 300 K for the single crystal CaFe$_{1-x}$Co$_x$AsF with $x = 0.12$ is shown in figure 3(a). The $\rho - T$ curve is lowered gradually with the decrease of temperature above 100 K, and followed by a clear upwarp below 100 K, which suggests that the sample is slightly underdoped. The onset of the superconducting transition
Figure 3: (a) Temperature dependence of resistivity for the CaFe$_{1-x}$Co$_x$AsF single crystal with $x_{\text{actual}} = 0.12$ measured in a wide temperature range 0 - 300 K under zero magnetic field. (b) The normalized magnetic susceptibility measured in zero-field-cooled (ZFC) and field cooled (FC) models and the resistivity data in the low temperature range near the superconducting transition.

appears at about 22 K, whereas the zero resistivity is reached at about 20 K. The dc magnetic susceptibility for the same sample was measured under a magnetic field of 10 Oe in zero-field-cooling and field-cooling processes, which is presented in figure 3(b) with temperature between 0 and 40 K. In order to minimize the effect of the demagnetization, the magnetic field was applied parallel to the ab-plane of the crystal. The absolute value of magnetic susceptibility $\chi$ is over 95%, indicated a high superconducting volume fraction of our sample. An enlarged $\rho - T$ curve is also shown in figure 3(b) in order to be compared with susceptibility curve expediently. The superconducting transition temperature revealed by the $\rho - T$ curve is slightly higher than that by the $\chi - T$ curve, which is rather reasonable and common for the compound superconductors.

We investigated the influence of pressure on the superconductivity of our samples. The magnetization susceptibility under different pressures for the sample CaFe$_{1-x}$Co$_x$AsF with $x = 0.12$ was obtained using Mcell 10. The pressure was generated using a Be-Cu pressure cell with a Teflon cup which was filled
with the pressure-transmitting medium. The actual pressure was calibrated and determined by the shift of the superconducting transition temperature of pure Tin. The results of the $\chi - T$ data with pressure varying from 0 to 1.5 GPa are presented in figure 4. The intensity of the diamagnetic signals are variable for different pressure due the change of the orientation of the sample in the pressure cell. All of the susceptibility curves have been normalized by the dada at 10 K for the convenience of distinguishing their changes. It is clearly demonstrated that a pressure as small as 0.22 GPa can enhance $T_c$ for about 1 K, and then, with further increasing of the pressure, the change of $T_c$ becomes inconspicuous.

The inset of figure 4 shows the pressure dependence of $T_c$ for the sample. With the increasing of pressure, $T_c$ rises steeply initially and then it becomes smooth and stable around a maximum value 21.5 K. Actually, the pressure effect on the superconductivity of CaFe$_{1-x}$Co$_x$AsF has been studied on the polycrystalline samples [15]. The amplitude of the $T_c$ enhancement of our samples induced by

Figure 4: Temperature dependence of the magnetic susceptibility under hydrostatic pressures of up to 1.5 GPa for $x_{\text{actual}} = 0.12$ below 24 K. The inset presents the pressure dependence of $T_c$ for this sample. These data were obtained using Mcell 10.
pressure is comparable with that observed in the polycrystalline samples, which is much smaller than the LaFeAsO$_{1-x}$F$_x$. Moreover, it is found that our observations are more similar to the polycrystalline sample with $x = 0.1$, because $T_c$ was reported to decrease above merely 0.4 GPa for the samples with $x = 0.15$ and 0.2. However, $T_c$ increase more quickly for our single-crystalline samples.

4. Conclusions

In this work, millimeter sized single crystals of CaFe$_{1-x}$Co$_x$AsF were successfully grown by CaAs self-flux method via three approaches with different initial raw materials. The chemical compositions, crystal structure, resistivity and magnetization susceptibility were investigated systematically. Both the resistivity and magnetic susceptibility show that the $T_c$ of CaFe$_{1-x}$Co$_x$AsF with $x = 0.12$ is about 21 K, which can be enhanced for about 1 K under the hydrostatic pressure of 0.22 GPa. Moreover, it is found that $T_c$ of the present single-crystalline samples increases more quickly with pressure compared with the polycrystalline samples. Our results supply a platform to study the intrinsic properties of the 1111 phase of iron-pnictide superconductors.

Acknowledgments

This work is supported by the Natural Science Foundation of China (No. 11204338), the “Strategic Priority Research Program (B)” of the Chinese Academy of Sciences (No. XDB04040300 and XDB04030000) and the Youth Innovation Promotion Association of the Chinese Academy of Sciences (No. 2015187).

References

[1] L. Fang, P. Cheng, Y. Jia, X. Zhu, H. Q. Luo, G. Mu, C. Z. Gu, and H. H. Wen, J. Cryst. Growth 311 (2009) 358.

[2] N. D. Zhigadlo, S. Weyeneth, S. Katrych, P. J. W. Moll, K. Rogacki, S. Bosma, R. Puzniak, J. Karpinski, and B. Batlogg, Phys. Rev. B 86 (2012) 214509.
[3] J. Karpinski, N. D. Zhigadlo, S. Katrych, Z. Bukowski, P. Moll, S. Weyeneth, H. Keller, R. Puznia, M. Tortello, D. Daghero, R. Gonnelli, I. Maggio-Aprioie, Y. Fasano, O. Fischer, K. Rogacki, B. Batlogg, Physica C 469 (2009) 370.

[4] Y. Q. Yan, S. Nandi, J. L. Zarestky, W. Tian, A. Kreyssig, B. Jensen, A. Kracher, K. W. Dennis, R. J. McQueeney, A. I. Goldman, R. W. McCallum and T. A. Lograsso, Appl. Phys. Lett. 95 (2009) 222504.

[5] Y. H. Ma, H. Zhang, B. Gao, K. K. Hu, Q. C. Ji, G. Mu, F. Q. Huang and X. M. Xie, Supercond. Sci. Technol. 28 (2015) 085008.

[6] F. Han, X. Zhu, G. Mu, P. Cheng, H. H. Wen, Phys. Rev. B 78, (2008) 180503(R).

[7] M. Tegel, S. Johansson, V. Weiss, I. Schellenberg, W. Hermes, R. Poettgen, D. Johrendt, Europhys. Lett. 84, (2008) 67007.

[8] P. Cheng, B. Shen, G. Mu, X. Zhu, F. Han, B. Zeng, H. H. Wen, Europhys. Lett. 85, (2009) 67003.

[9] S. Matsuishi, Y. Inoue, T. Nomura, H. Yanagi, M. Hirano, H. Hosono, J. Am. Chem. Soc. 130, (2008) 14428-14429.

[10] G. Wu, Y. L. Xie, H. Chen, M. Zhong, R. H. Liu, B. C. Shi, Q. J. Li, X. F. Wang, T. Wu, Y. J. Yan, J. J. Ying, X. H. Chen, J. Phys.: Condens. Mat. 21, (2009) 142203.

[11] X. Zhu, F. Han, P. Cheng, G. Mu, B. Shen, L. Fang, H. H. Wen, Europhys. Lett. 85, (2009) 17011.

[12] C. Dong, J. Appl. Crystallogr. 32 (1999) 838.

[13] C. Dong, H. Chen, F. Wu, J. Appl. Crystallogr. 32 (1999) 168.

[14] S. Matsuishi, Y. Inoue, T. Nomura, Y. Kamihara, M. Hirano, and H. Hosono, New Journal of Physics, 11(2), (2009) 025012.
[15] H. Okada, H. Takahashi, S. Matsuishi, M. Hirano, H. Hosono, K. Matsubayashi, Y. Uwatoko, and H. Takahashi, Phys. Rev. B 81, (2010) 054507.