Growth and characterization of millimeter-sized single crystals of CaFeAsF

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Abstract
High-quality and sizable single crystals are crucial for studying the intrinsic properties of unconventional superconductors, which are lacking in the 1111 phase of Fe-based superconductors. Here we report the successful growth of CaFeAsF single crystals with sizes of 1–2 mm using the self-flux method. Owing to the availability of the high-quality single crystals, the structure and transport properties were investigated with a high reliability. The structure was refined by using single-crystal x-ray diffraction data, which confirms earlier reports on the basis of powder data. A clear anomaly associated with the structural transition was observed at 121 K from the resistivity, magnetoresistance, and magnetic susceptibility measurements. Another kink-feature at 110 K, most likely an indication of antiferromagnetic transition, was also detected in the resistivity data. Our results supply a basis from which to propel physical investigations of the 1111 phase of Fe-based superconductors.

Keywords: CaFeAsF, single crystals, Fe-based superconductors

(Some figures may appear in colour only in the online journal)

1. Introduction

The F-doped LnFeAsO (Ln = rare-earth elements), which has been abbreviated as the 1111 phase, is the first reported family with the highest critical transition temperature $T_c$ in bulk in the Fe-based superconductors (FeSCs) [1]. However, investigations on the physical properties of the 1111-type FeSCs are restricted remarkably, compared with the 122 phase and 11 phase, due to the difficulties in obtaining sizable single crystals. As we know, it is essential to have high-quality single crystals when carrying out many experiments, including measurements of electrical transport, inelastic neutron diffraction, angle-resolved photoemission spectroscopy, and so on. Over the past several years, many efforts have been made to improve the quality and size of the single crystals. NaCl and KCl were first used as the flux and small single crystals with sizes of 20–70 μm were obtained [2]. Then more attempts, including the high-pressure method and the NaAs-flux method [3, 4], were made to further improve the growth processes. Up to now, the two goals, large size and high quality, have still not been achieved commendably. Recently, single crystals with a size of several millimeters were reported to be accessible in F-vacant and Na-doped CaFeAsF [5, 6], which is another type of 1111 phase without oxygen [7, 8], possibly due to the decrease of melting point in this fluorine-based system. As we know, a rather high $T_c$ above 50 K can also be achieved by doping in this fluorine-based 1111 system [9–12]. More important
information can be obtained owing to the availability of the sizable single crystals. To our knowledge, investigations on the single crystals of the parent phase CaFeAsF are still lacking. Here we present the growth, structure, and transport measurements of the high-quality CaFeAsF single crystals with sizes of 1–2 mm. The single crystals were grown by the self-flux method. The structure details were obtained from the refinement of the single-crystal x-ray diffraction data. The structural transition at 121 K was confirmed by the resistivity, magnetoresistance, and magnetic susceptibility measurements. A feature coming from the antiferromagnetic transition was also observed in the resistivity data.

2. Experimental details

High-quality CaFeAsF single crystals were grown using the self-flux method with CaAs as the flux. First, the starting materials Ca granules (purity 99.5%, Alfa Aesar) and As grains (purity 99.995%, Alfa Aesar) were mixed in 1:1 ratio. Then the mixture was sealed in an evacuated quartz tube and followed by a heating process at 700 °C for 10 h to get the CaAs precursor. CaAs, FeF2 powder (purity 99%, Alfa Aesar) and Fe powder (purity 99+%, Alfa Aesar) were mixed together in the stoichiometric ratio 10:1:1, and the mixture was placed in an alumina crucible. Finally, the crucible was sealed in a quartz tube with a vacuum. All the weighing and mixing procedures were carried out in a glove box with a protective argon atmosphere. 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 20 h. Finally it was cooled down to 900 °C at a rate of 2 °C h⁻¹ followed by a quick cooling down to room temperature.

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 Oxford Instruments device. The crystals were first checked using a DX-2700 type powder x-ray diffractometer. The detailed structure was characterized and analyzed by single-crystal x-ray diffraction measurements on a Bruker D8 Quest diffractometer equipped with the graphite-monochromatized Mo Kα radiation. The magnetic susceptibility measurement was carried out on the magnetic property measurement system (Quantum Design, MPMS 3). The electrical resistivity and magnetoresistance (MR) were measured using a four-probe technique on the physical property measurement system (Quantum Design, PPMS) with magnetic field up to 9 T. For the MR measurements, the magnetic field was oriented parallel to the c-axis of the samples and the data were measured for both positive and negative field orientations to eliminate the effect of the Hall signals.
3. Results and discussions

The typical dimension of the single crystals is 1.2 × 1.0 × 0.1 mm$^3$. The morphology was examined by the scanning electron microscopy. An SEM picture for the CaFeAsF single crystal can be seen in figure 1(a), which shows a flat surface and some terrace-like features. An enlarged view of this picture can be seen in figure 1(b). The composition of the crystals was characterized by energy-dispersive x-ray spectroscopy (EDS) measurements. We measured the EDS at different positions of the sample. Here we show a typical result in figure 1(c) and table 1, which revealed that the ratio of Ca:Fe:As is close to the stoichiometric ratio. The content of the light element F is difficult to determine precisely based on EDS measurements. The structure of the crystals was first checked by a powder x-ray diffractometer, where the x-ray was incident on the $ab$-plane of the crystal. The diffraction pattern is shown in figure 2. All the diffraction peaks can be indexed to the tetragonal ZrCuSiAs-type structure (see the inset of figure 2). Only sharp peaks along the (00l) orientation can be observed, suggesting a high $c$-axis orientation. The full width at half maximum (FWHM) of the diffraction peaks is only about 0.10° after deducting the $K_{\alpha2}$ contribution, indicating a rather fine crystalline quality. The $c$-axis lattice constant was determined to be 8.584 Å by analyzing the diffraction data.

We used high-resolution single-crystal x-ray diffraction to study the structural details of our sample. The diffraction data were collected at room temperature by the $ω$- and $ϕ$-scan method. The crystal structure was solved by SHELXS-2014 [13]. The parameters for the data collection and structure refinement are listed in table 2. The values of $R_1$ and $wR_2$ are much smaller than the previously reported polycrystalline results [10], and also small compared to the Na-doped single crystalline system [6], indicating the high-quality of our sample and the reliability of our refinement. As shown in table 3, the final cell constants are determined to be $a = b = 3.8774(4)$ Å, $c = 8.5855(10)$ Å. It is clear that the $c$-axis lattice constants are very close to that obtained from the data in figure 2. In addition, the $a$- and $c$-axis lattice constants determined from our experiment are consistent with the polycrystalline samples reported previously [9, 10]. Compared to the Na-doped single crystalline samples, the $a$-axis lattice constant is similar while the $c$-axis constant is clearly smaller [6].

### Table 1. Compositions of the crystal characterized by EDS measurements.

| Element | Weight (%) | Atomic (%) |
|---------|------------|------------|
| F       | 14.90      | 34.52      |
| Ca      | 19.58      | 21.50      |
| Fe      | 27.31      | 21.52      |
| As      | 38.22      | 22.46      |

### Figure 2. X-ray diffraction pattern measured on the CaFeAsF single crystal with the x-ray incident on the $ab$-plane. The inset is the schematic of the crystal structure of CaFeAsF.

### Table 2. Parameters for the data collection and structure refinement of CaFeAsF.

| Parameter                              | Value                      |
|----------------------------------------|----------------------------|
| Theta range for data collection        | 4.749 to 27.508°           |
| Index ranges                           | $-4 \leq h \leq 5$          |
|                                        | $-5 \leq k \leq 5$          |
|                                        | $-11 \leq l \leq 11$        |
| Reflections collected                  | 2035                       |
| Refinement method                      | Full-matrix least-squares  |
|                                        | on $F^2$                   |
| Refinement program                     | SHELXL-2014 (Sheldrick, 2014) |
| Data restraints /parameters            | 114 / 0 / 12               |
| Goodness-of-fit on $F^2$               | 1.224                      |
| Final $R$ indices                      | $R_1 = 0.0139$             |
|                                        | $wR_2 = 0.0318$            |
| Weighting scheme                       | $w = 1/(σ^2(F^2)+0.6368P)$ |
|                                        | where $P = (F^2 + 2F'^2)/3$ |
| Extinction coefficient                 | 0.014(3)                   |
| Largest diff. peak and hole            | 0.655 and -0.364 eÅ$^{-3}$ |
| R.M.S. deviation from mean             | 0.122 eÅ$^{-3}$            |

### Table 3. Refined lattice constants for the CaFeAsF single crystal.

| Parameter                              | Value                      |
|----------------------------------------|----------------------------|
| Chemical formula                       | CaFeAsF                   |
| Formula weight                         | 189.85 g mol$^{-1}$        |
| Temperature                            | 296(2) K                   |
| Wavelength                             | 0.71073 Å                  |
| Crystal system                         | tetragonal                 |
| Space group                            | P4/mmm (No. 129)           |
| $Z$                                    | 2                          |
| Unit cell dimensions                   | $a = b = 3.8774(4)$ Å, $\alpha = 90°$ |
|                                        | $c = 8.5855(10)$ Å, $\beta = 90°$ |
| Volume                                 | 129.076(4) Å$^3$           |
| Bond angle ($\delta_{As-Fe-As}$)       | 107.82(6)$° \times 2$     |
|                                        | 110.30(4)$° \times 4$     |
| Anion height                           | $h_{As} = 1.413$ Å         |
| Density (calculated)                   | 4.885 g/cm$^3$             |
| Absorption coefficient                 | 20.223 mm$^{-1}$           |
| F(000)                                 | 176                        |
are the transition temperatures from tetragonal to cubic phase, respectively. Our results supply a platform to understand the mechanism of high-temperature superconductivity.

Temperature dependence of the in-plane resistivity (a), magnetoresistance (b), and the magnetic susceptibility (c). The field of 1 T was applied along the c-axis of the crystal during the magnetic susceptibility measurement. The MR data were collected under the field of 9 T. The dashed lines are guides for the eyes.

Table 4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for CaFeAsF.

| Atom | x     | y     | z     | U(eq)    |
|------|-------|-------|-------|----------|
| As   | 1/4   | 1/4   | 0.16461(8) | 0.0067(3) |
| Fe   | 3/4   | 1/4   | 0     | 0.0069(3) |
| Ca   | 3/4   | 3/4   | 0.34801(16) | 0.0080(4) |
| F    | 3/4   | 1/4   | 1/2   | 0.0092(8)  |

The resistivity, MR, and magnetic susceptibility change the variation tendency at the same temperature, 121 K, on the temperature-dependent curves, as revealed in figures 3(a)–(c). This seems to be a common feature in most of the parent phase of FeSCs associated with the structural and the spin-density-wave (SDW)-type antiferromagnetic transition. This behavior should be very important to understand the mechanism of high-temperature superconductivity because it was also observed in undoped and highly underdoped cuprates [18]. In the pnictide compounds, this feature was interpreted by the antiferromagnetic fluctuations with the local SDW correlations [19].

4. Conclusions

In summary, high-quality and sizable single crystals of CaFeAsF were grown successfully by the self-flux method. The single-crystal x-ray diffraction measurements were carried out and the structure details were refined based on the data. The resistivity, magnetoresistance, and magnetic susceptibility show clear different behaviors below and above 121 K. The critical temperatures of the structure and antiferromagnetic transition were determined to be $T_{str} = 121$ K and $T_N = 110$ K, respectively. Our results supply a platform to study the intrinsic properties of the 1111 phase of FeSCs.

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