# Growth and characterization of $A_{1-x}K_xFe_2As_2$ (A = Ba, Sr) single crystals with $x = 0–0.4$

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**Abstract**
Single crystals of $A_{1-x}K_xFe_2As_2$ (A = Ba, Sr) with high quality have been grown successfully by an FeAs self-flux method. The samples have sizes up to 4 mm with flat and shiny surfaces. The x-ray diffraction patterns suggest that they have high crystalline quality and $c$-axis orientation. The non-superconducting crystals show a spin-density-wave (SDW) instability at about 173 and 135 K for the Sr-based and Ba-based compound, respectively. After doping K as the hole dopant into the $BaFe_2As_2$ system, the SDW transition is smeared, and superconducting samples of the compound $Ba_{1-x}K_xFe_2As_2$ ($0 < x \leqslant 0.4$) are obtained. The superconductors, characterized by AC susceptibility and resistivity measurements, exhibit very sharp superconducting transitions at about 36, 32, 27 and 23 K for $x = 0.40, 0.28, 0.25$ and 0.23, respectively.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

The newly discovered superconductivity in iron oxypnictide superconductors has stimulated intensive research on high-temperature superconductivity outside the cuprate system. In just a few months, the superconducting transition temperature ($T_c$) was increased to 55 K in the electron-doped system [1–6], as well as 25 K in hole-doped $La_{1-x}Sr_xOFeAs$ compound [7]. Because of the layered structure, the doping behavior and many other properties of the iron-based system are very similar to those of the copper oxides, and it has been thus expected that higher $T_c$ values may be found in multi-layer systems. Soon after, single crystals of $LnFeAs(O_{1-x}F_x)$ (Ln = Pr, Nd, Sm) were grown successfully by the NaCl/KCl flux method [8–10], though the sub-millimeter sizes limit the experimental studies on them [11, 12]. Therefore, FeAs-based single crystals with high crystalline quality, homogeneity and large sizes are highly desired for precise measurements of the properties.

Very recently, the $BaFe_2As_2$ compound in a tetragonal $ThCr_2Si_2$-type structure with infinite Fe–As layers was reported [13]. By replacing the alkaline earth elements (Ba and Sr) with alkali elements (Na, K, and Cs), superconductivity

up to 38 K was discovered both in hole-doped and electron-doped samples [14–17]. $T_c$ varies from 2.7 K in $CsFe_2As_2$ to 38 K in $A_{1-x}K_xFe_2As_2$ (A = Ba, Sr) [14, 18]. Meanwhile, superconductivity could also be induced in the parent phase by high pressure [19, 20] or by replacing some of the Fe by Co [21, 22]. More excitingly, large single crystals could be obtained by the Sn flux method in this family to study the rather low melting temperature and the intermetallic characteristics [23–25]. However, single crystals with high homogeneity and low contamination are still hard to obtain by this method [26]. To avoid these problems, the FeAs self-flux method may be more appropriate.

Here we report the successful growth of $A_{1-x}K_xFe_2As_2$ (A = Ba, Sr) single crystals by a self-flux method using FeAs as the flux; both non-superconducting parent phase $AFe_2As_2$ (A = Ba, Sr) and superconducting $Ba_{1-x}K_xFe_2As_2$ crystals are obtained. X-ray diffraction (XRD) measurements indicate high crystalline quality in both kinds of sample, and the AC susceptibility results show sharp superconducting transitions in the superconducting samples. The resistivity measurements on the non-superconducting phase suggest a clear resistivity anomaly which is induced by the formation of the spin-density-wave (SDW) and structure transition [13, 27–29]. The
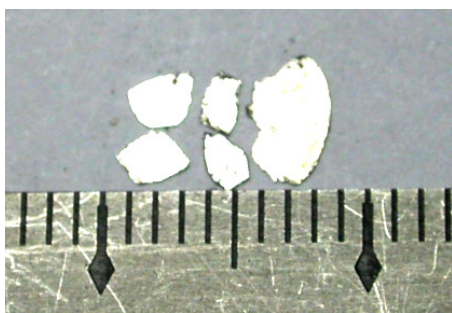
**Figure 1.** Photograph of the $A_{1-x}K_xFe_2As_2$ (A = Ba, Sr) crystals cleaved from the as-grown bulk. The crystals have rather shiny surfaces with sizes up to 4 mm.



**Figure 2.** A typical EDX spectrum for one single crystal. The inset is the SEM photograph of this crystal, which shows a very flat surface morphology and a layered structure.

doping dependence of the *c*-axis lattice constant and $T_c$ are very consistent with the reported results from polycrystalline samples [30, 31].

## 2. Experimental details

The $A_{1-x}K_xFe_2As_2$ (A = Ba, Sr) single crystals were grown by the FeAs self-flux method. The FeAs precursor was synthesized by the reaction of Fe powder (Alfa Aesar, 99.99% in purity) and As chips (99.999%) at 500 °C for 10 h and then 700 °C for 20 h in a sealed silica tube. The starting materials of FeAs, and high purity Ba or Sr (Alfa Aesar, 99.2% in purity) were mixed in the ratio 4:$(1 - x)$, then a soft bulk of the proper amount of K was added to cover the powder. The whole procedure was performed in a glove box with a protective argon atmosphere in which the concentrations of both $O_2$ and $H_2O$ were less than 1 ppm. The mixture was placed in an alumina oxide crucible with dimensions of diameter 15 mm × 35 mm, and sealed under vacuum in a silica tube with dimensions of diameter 18 mm × 90 mm. Because the silica tube would break due to the gas pressure of potassium at a temperature around 1000 °C, the superconducting samples could only be obtained by using a limited amount of potassium and a thick enough silica tube ($t > 3$ mm). For example, if the total mass of staring material was supposed to be 2.0 g with the ratio of Ba:K:Fe:As = 0.6:0.4:4.0:4.0, the mass for each materials was $m$(Ba) = 0.265 g, $m$(K) = 0.050 g and $m$(FeAs) = 1.684 g, respectively. Considering the loss of K during the growth (about 0.12 g in most cases), the total amount of K should be 0.170 g. It should be noted that the safe amount of K is less than 0.25 g under our conditions to prevent explosion of the silica tube. The actual contents of K in the as-grown crystals were determined by quantitative analysis in later measurements. The sealed silica tube was placed in a muffle furnace and heated up to a high temperature (about 1000–1150 °C) to melt completely. Then it was cooled down to a temperature below 800 °C at a very slow speed (less than 10 °C h$^{-1}$). The melting temperature and cooling down speed depended on the ratio of Ba:K in the starting material. Finally, the muffle furnace was powered off. After it was cooled down to room temperature, the tube was fetched out and broken. The crystals were obtained by cleaving the as-grown bulks. Then they were selected and shaped under a microscope.
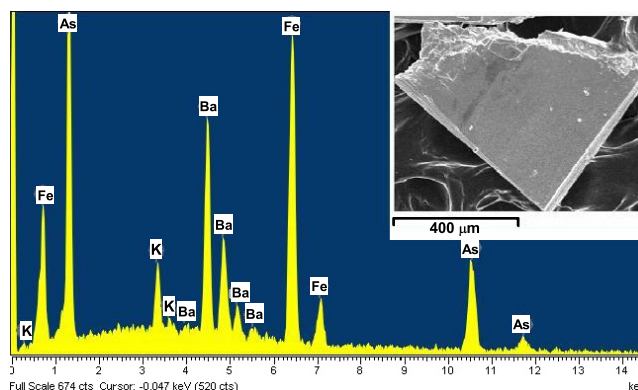
Various techniques were used to characterize our samples. The crystal surface morphology and composition were examined by scanning electron microscopy (SEM, Hitachi S-4200) and energy dispersive x-ray (EDX, Oxford-6566, installed in the S-4200 apparatus) analysis, and x-ray diffraction of the crystals was carried out with Mac-Science MXP18A-HF equipment with a $\theta$–$2\theta$ scan to examine the crystalline quality of the samples. K$\alpha$ radiation from a Cu target was used, and the continuous scanning range of $2\theta$ was from 10° to 80°. The raw XRD data were analyzed by PowderX software; the zero shift, K$\alpha$2 elimination, and other factors were taken into account [32]. The AC susceptibility was measured on an Oxford cryogenic system (Maglab-EXA-12). An alternating magnetic field ($H = 1$ Oe) was applied perpendicular to the *ab*-plane at a frequency $f = 333$ Hz when the AC susceptibility measurement was undertaken. The $T_c$ value was derived from the AC susceptibility curve by the point at which the real part of the susceptibility becomes flat. The resistivity measurements were carried out on a Quantum Design physical property measurement system (PPMS) using a standard four-probe method with a low contact resistance (<1 Ω).

## 3. Results and discussion

By varying the content of potassium in the starting material, we obtained non-superconducting crystals of both Ba-based and Sr-based compounds and superconducting samples with the composition $Ba_{1-x}K_xFe_2As_2$. Figure 1 shows a photograph of some crystals cleaved from the as-grown bulks. They all have very shiny plate-like cleaved surfaces. The sizes of the largest one are about 2.5 mm × 4.0 mm × 0.2 mm, and the others have sizes up to 2 mm. In the flux method, the real amounts of each element always deviate from those of the starting material. The composition of our single crystals was determined by an energy dispersive x-ray (EDX) analysis. From each batch, 3–5 pieces of as-grown single crystal were selected carefully. Then they were cleaved under a microscope and the EDX measurements were taken immediately, before the surface degenerated in air. A typical EDX spectrum is shown in figure 2. The
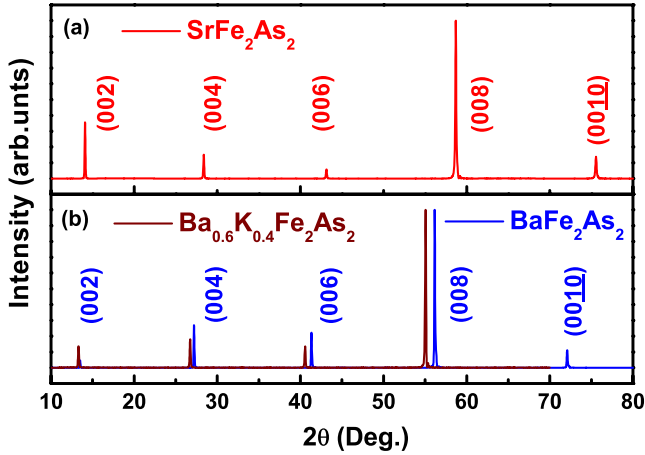
**Figure 3.** Typical XRD patterns for cleaved crystals. The FWHM of each peak is around 0.10°. A clear shift was observed after doping 40% of K in the $Ba_{1-x}K_xFe_2As_2$ system.

**Table 1.** A brief summary of the properties of $Ba_{1-x}K_xFe_2As_2$ single crystals: the actual cationic composition (Ba:K) determined by EDX, $c$-axis parameter, critical temperature, and typical size of crystals.

| No. | Ba:K | $c$ (Å) | $T_c$ (K) | Typical size (mm³) |
|---|---|---|---|---|
| 1 | 0.60:0.40 | 13.344 | 36.3 | $1 \times 1 \times 0.1$ |
| 2 | 0.72:0.28 | 13.226 | 31.8 | $4 \times 3 \times 0.2$ |
| 3 | 0.75:0.25 | 13.196 | 27.5 | $3 \times 2 \times 0.1$ |
| 4 | 0.77:0.23 | 13.189 | 23.4 | $2 \times 1 \times 0.1$ |
| 5 | 0.92:0.08 | 13.077 | 0 | $1 \times 0.5 \times 0.1$ |
| 6 | 0.94:0.06 | 13.065 | 0 | $3 \times 2 \times 0.3$ |

inset is the SEM photograph of this crystal, which shows a very flat surface morphology and a layered structure. A brief summary of the properties of $Ba_{1-x}K_xFe_2As_2$ single crystals is given in table 1. We successfully obtained four categories of superconducting sample with K doping level $x = 0.40$, 0.28, 0.25 and 0.23. The non-superconducting crystals also contain a little K, less than 10% for both Ba-based and Sr-based compounds.

The crystal structure of non-superconducting samples was examined by x-ray diffraction measurement with the incident x-ray along the $c$-axis. Typical diffraction patterns are shown in figure 3. Only sharp peaks along (00$l$) could be observed, and the full width at half maximum (FWHM) of each peak is around 0.10°. These indicate high $c$-axis orientation and crystalline quality in our samples. The raw XRD data were analyzed by PowderX software, with the zero shift, K$\alpha$2

elimination and other factors taken into account [32]. The $c$-axis parameters were calculated and they also presented in table 1. For the non-superconducting samples, the $c$-axis lattice constant is about 13.07 Å for the Ba-based compound and 12.58 Å for the Sr-based compound, respectively. The $c$-axis magnitudes are very close to results from the polycrystalline parent phase without K doping, where they were reported to be 13.02 Å [13] for the Ba-based compound and 12.40 Å [16] for the Sr-based compound. In addition, it should be noted that the EDX analysis has an uncertainty of around 10%, which will be larger especially for light elements. It is possible that the real contents of K in non-superconducting samples are less than the magnitudes shown in table 1. Thus we just denote them using the chemical formula as parent compounds $BaFe_2As_2$ and $SrFe_2As_2$. Figure 3(b) also displays the XRD pattern for the sample with $x = 0.40$. A clear shift for each peak appears, which indicates that the lattice has a small variation after doping K into the parent phase.

AC susceptibility measurements were used to characterize the superconducting $Ba_{1-x}K_xFe_2As_2$ single crystals. Figure 4 shows three typical groups of the susceptibility curves. The $T_c$ value was determined as the onset point of $\chi'$, and the transition width was defined as $\Delta T_c = T_c(90\%) - T_c(10\%)$. There is a flat diamagnetic signal in the low-temperature region
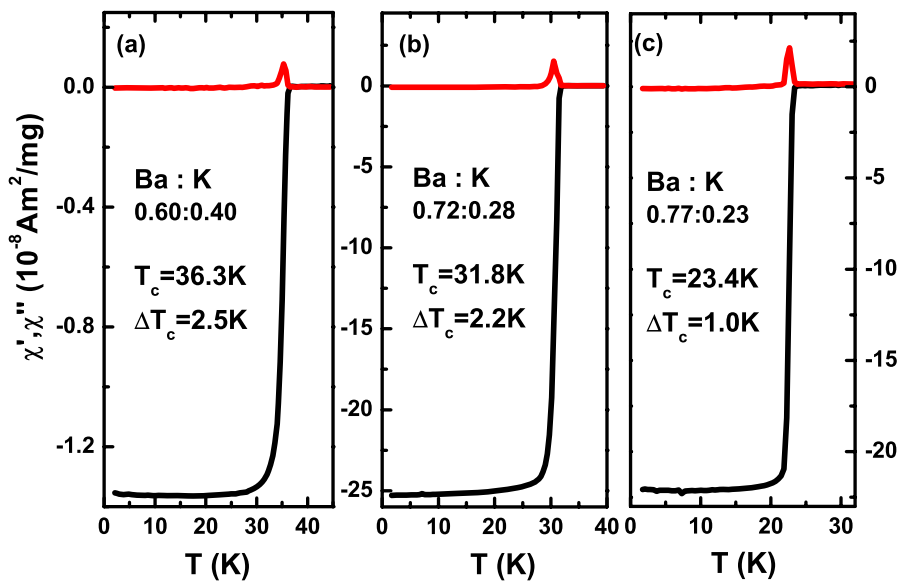


**Figure 4.** Temperature dependence of AC susceptibility for superconducting $Ba_{1-x}K_xFe_2As_2$ single crystals. The $T_c$ value was derived from the point where the real part of the susceptibility becomes flat, and the transition width was defined as $\Delta T_c = T_c(90\%) - T_c(10\%)$.
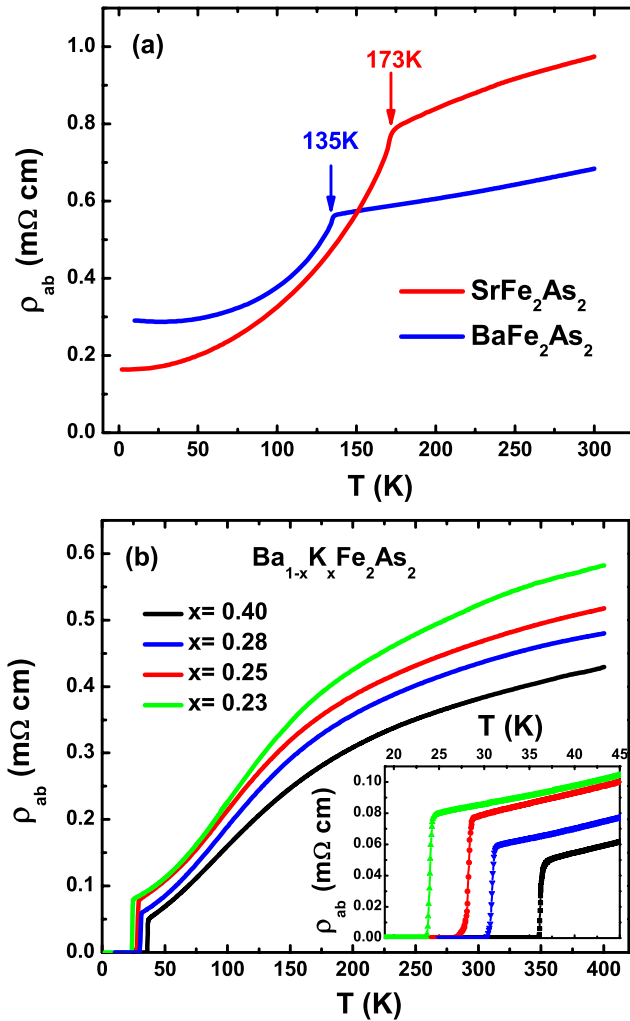
**Figure 5.** (a)Temperature dependence of the resistivity for $BaFe_2As_2$ and $SrFe_2As_2$ crystals. The SDW anomaly happens at 135 K and 173 K, respectively. (b) Temperature dependence of the resistivity for the superconducting single crystals. The inset is an enlarged graph around the superconducting transition.



**Figure 6.** Doping dependence of the *c*-axis and $T_c$ for our single crystals (blue points). The open black squares and green triangles are polycrystalline data from [30] and [31], respectively.

and there is a very sharp superconducting transition around $T_c$; the demagnetizing factor is not taken into account in these measurements. The $T_c$ value increases gradually as more and more K is doped into the samples. The superconducting transition is almost the same for single crystals cleaved from the same batch, which indicates that our samples are very homogeneous.

Figure 5 shows the temperature dependence of the resistivity under zero field. The applied current is 5 mA, and it flows in the *ab*-plane during the measurements. For $BaFe_2As_2$ and $SrFe_2As_2$, a strong anomaly shows up at $T_s = 135$ K and 173 K, respectively (figure 5(a)). The resistivity has a nearly $T$-linear dependence above this temperature, and sharply drops down below this temperature. This resistivity anomaly could be attributed to the SDW instability and structure transition, which was also observed in other systems [16, 27–29]. However, the characteristic temperatures found in our samples are lower than those in other reports, for both $BaFe_2As_2$ ($T_s = 140$ K) [13, 29] and $SrFe_2As_2$ ($T_s = 195$ K) [16]. It may
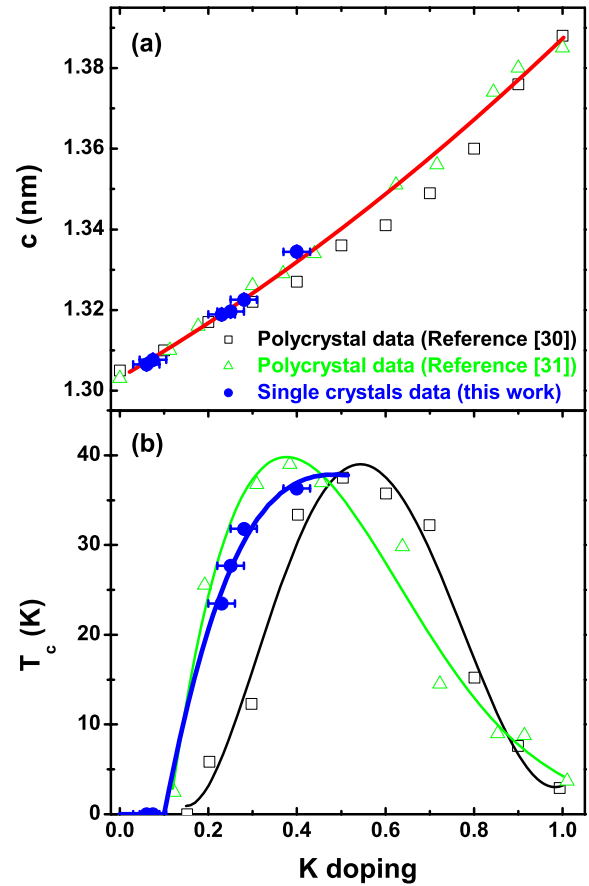
be induced by doping a small amount of potassium into the parent compounds. Increasing the hole doping further will suppress the SDW transition, and superconductivity eventually emerges [30]. Therefore, the superconducting $Ba_{1-x}K_xFe_2As_2$ samples were obtained by adding more K into the starting material. Figure 5(b) shows the temperature dependence of the resistivity for the superconducting single crystals. The SDW anomaly is smeared in the normal state, and a superconducting transition emerges at lower temperatures. The $T_c$ (onset) values for different levels of doping are about 36.6, 31.4, 28.7, and 24.5 K. The resistivity data also indicate a sharp transition in our samples, with $\Delta T_c = 0.44, 0.49, 0.71$, and 0.40 K (90%–10% of normal state resistivity). Furthermore, if we extrapolate the data just above the superconducting transition by a straight line, it could be roughly estimated that the residual resistivity is almost close to zero for the sample with $T_c = 36$ K. This indicates that our samples are rather clean.

When preparing this paper, we became aware that two papers reporting studies on $Ba_{1-x}K_xFe_2As_2$ polycrystalline samples with a series of doping levels were posted on arXiv [30, 31]. Thus we made a comparison of the doping dependence of the *c*-axis length and $T_c$ value between the polycrystalline samples and our single crystals. The result is shown in figure 6. Our data are very consistent with the data in [31], while a small deviation is found for the data in [30].

However, the general behavior is almost the same between the polycrystalline samples and single crystals. The $c$-axis length expands almost linearly on increasing the K content, while the $T_c$ value increases quickly as a little K is doped into the parent compound, then it grows slowly between $x = 0.3$ and 0.4. It seems that the maximal $T_c$ value is achieved between $x = 0.4$ and 0.5. Therefore, our samples with $x = 0$–0.4 reside in the 'underdoped' regime. Growth of 'overdoped' single crystals is underway.

## 4. Summary

In summary, we have successfully grown single crystals of $A_{1-x}K_xFe_2As_2$ (A = Ba, Sr) with high quality by using FeAs as the self-flux. By varying the K content during the growth, we obtained non-superconducting $Ba(Sr)Fe_2As_2$ single crystals and superconducting $Ba_{1-x}K_xFe_2As_2$ single crystals with $x = 0.23$, 0.25, 0.28 and 0.40. The samples have sizes up to 4 mm with flat and shiny cleaved surfaces. The x-ray diffraction patterns with only $(00l)$ peaks suggest that they have high crystalline quality. The superconductivity is characterized by AC susceptibility and resistivity measurements, which exhibit very sharp superconducting transitions. The temperature dependence of the resistivity for the non-superconducting crystals shows that the SDW instability and structure transition occur at about 173 K and 135 K for the Sr-based and Ba-based compounds, respectively. The doping dependence of the $c$-axis parameter and $T_c$ are consistent with previous data from polycrystalline samples [30, 31], which indicates the effects of different levels of potassium doping.

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