Carrier-Doping Dependence of Critical Current Density in $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ Single Crystals and Superconducting Wires

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Abstract. The carrier-doping dependence of $J_c$ in $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ single crystals and superconducting wires were investigated. $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ single crystals ($0.24 < x < 0.4$) are synthesized by commonly used FeAs self-flux method, while $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ wires are fabricated by powder-in-tube (PIT) method and hot isostatic pressing (HIP) technique, using polycrystalline $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ ($0.25 < x < 0.4$) prepared by solid state reaction and silver and copper tubes. Their magnetic $J_c$ was characterized by magnetization measurements. We found that the $x$-dependence of $J_c$ in single crystals shows the peak in under-doped region around $x \sim 0.28$ similar to previous study. In the HIP wire, although significant peak is not observed, $J_c$ shows a broad plateau in a wide doping region of $0.3 < x < 0.4$. These results indicate that $J_c$ in the under-doped $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ HIP wire is controlled by intergranular $J_c$.

1. Introduction
Iron-based superconductors (IBSs) are promising candidates for high-field applications of superconductors because they exhibit high critical temperature $T_c$, large upper critical field $H_{c2}$, and relatively low anisotropy compared with cuprate superconductors. Among them, $A_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ ($A = \text{Ba}$, $\text{Sr}$) compounds (122-type) are considered to be most attractive candidates. They have small anisotropies of 2-3, moderate $T_c$’s, large $H_{c2}$’s, and large $J_c$’s [1-2]. Actually high critical current density is realized in superconducting wires or tapes using $A_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ [3-10]. In these report, K content $x$ in the staring materials for superconducting wires and tapes are fixed to 0.4, where $T_c$ is optimized [11,12]. Recently, however, Song et al. reported distinct doping dependence of $J_c$ and $T_c$ in $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ single crystals, which were synthesized by KAs self-flux method [13]. The $x$-dependence of $J_c$ is characterized by a peak at $x = 0.3$, which corresponds to the under-doped region. The origin of the characteristic doping dependence of $J_c$ may be connected with the pinning forces related to the orthorhombic phase domain boundary or to the chemical inhomogeneity introduced by the dopant substitutions [13]. This result implies that higher $J_c$ may also be achieved not at the optimal-doping level of $x \sim 0.4$ for $T_c$ but at under-doped region in 122-type superconducting wires and tapes. However, to our knowledge, there have been no systematic studies on the $x$-dependence of $J_c$ in $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ wires and tapes. Furthermore, we were also interested in the investigation of $x$-dependence of $J_c$ in $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ single crystals synthesized by commonly used FeAs self-flux method, since the process of crystal growth should affect chemical homogeneities which generate pinning forces.

In this work, we focused on carrier-doping dependence of $J_c$ in $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ single crystals and superconducting wires. Single crystals are synthesized by FeAs flux method. And superconducting wires were fabricated by powder-in-tube (PIT) method using well characterized $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$
polycrystalline powders. $J_c$ and $T_c$ in prepared samples were evaluated from magnetization measurements.

2. Experiment

Single crystals of (Ba,K)Fe$_2$As$_2$ were synthesized by self-flux method using FeAs flux. We used Ba pieces, K ingots and FeAs powder as starting materials. FeAs was prepared by placing stoichiometric amounts of As pieces and Fe powder in an evacuated quartz tube and reacting them at 700°C for 40 h after heating them at 500°C for 10 h. A mixture with a ratio of Ba:K:FeAs = 1-x:1.1x:4 was placed in an alumina crucible and sealed in a stainless steel containers [14] in a nitrogen-filled glove box. In order to compensate the loss of elements, 10% excess K was added. They were heated for 1 h at 1200–1250°C followed by cooling down to 900°C at a rate of 5°C/h. Obtained single crystals were separated from flux and cut into rectangular shape as shown in fig.1(a). In order to characterize the compositions of pieces of single crystals, a scanning electron microscope equipped with an energy-dispersive x-ray spectroscopy (SEM-EDX) was used (S-4300, Hitachi High-Technologies equipped with EMAX x.act, HORIBA). Bulk magnetization was measured by a superconducting quantum interference device (SQUID) magnetometer (MPMS-5XL, Quantum Design).

(Ba,K)Fe$_2$As$_2$ superconducting wires were fabricated by ex-situ PIT method. Polycrystalline powders of Ba$_{1-x}$K$_x$Fe$_2$As$_2$ were prepared by the solid-state reaction. Ba pieces, K ingots, Fe powder, and As pieces were used as starting materials. In order to compensate the loss of elements, the starting mixture contained 15% excess K and 5% excess As. They were mixed in a nitrogen atmosphere more than 10 hour using a ball-milling machine and densely packed into a niobium tube. The niobium tube was then put into a stainless steel tube and sealed in nitrogen filled glove box at 900°C for 30 h. The surface of the obtained polycrystalline ingot was polished to remove small impurities. It was then ground into powder using an agate mortar in nitrogen filled glove box. The phase identification of the sample was carried out by means of powder x-ray diffraction (XRD) with Cu-Kα radiation (Smartlab, Rigaku). Ground powders were filled in a silver tube with an outer diameter of 4.5 mm and an inner diameter 3 mm, thencold drawn into a square shape with a diagonal dimension of ~1.2 mm. After cutting it into short pieces, one of the pieces was put into 1/8 inch copper tube and redrawn down to the diagonal dimension of 1.2 mm. After that, both ends of the wires were sealed by using an arc furnace. The sealed wires were sintered using the hot isostatic pressing (HIP) technique. Wires and tapes were heated for 0.5 h at 700°C in argon atmosphere under the pressure of 9 MPa. An optical micrograph of the cross section of the HIP wire is shown in fig. 1(b). Bulk magnetization was measured by the same method and intergranular $J_c$ was evaluated using the extended Bean model.

![Figure 1](image)

**Figure 1.** Optical micrographs of typical Ba$_{1-x}$K$_x$Fe$_2$As$_2$ (a) single crystal and (b) HIP wire, respectively.

3. Results and Discussion

Before the fabrication of wires, polycrystalline powders of Ba$_{1-x}$K$_x$Fe$_2$As$_2$ were characterized by magnetization and powder x-ray diffraction measurements. Fig. 2(a) shows the temperature dependence of magnetization of several Ba$_{1-x}$K$_x$Fe$_2$As$_2$ polycrystalline powders with x from 0.25 to 0.40. All the samples show bulk superconductivity. While diamagnetism starts at ~38 K in all the
sample, the magnetization curves of under-doped samples show broad drop, especially in $x \sim 0.25$. These broadenings indicate the distribution of carrier concentration in polycrystalline powders. Considering the superconducting dome in $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ phase diagram [11], broadening of the superconducting transition caused by the distribution of carrier contents should become wider at under-doped region. It should be noted that no impurity phases are detected in the x-ray diffraction pattern of these powders. As shown in fig. 2(b), (0 0 2) powder x-ray diffraction peaks of several $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ powders shows the systematic shift. These results suggest that obtained polycrystalline powders are single phases, respectively, and carrier content of $x$ is systematically controlled. Using these powders, HIP wires were fabricated.

![Figure 2](image)

**Figure 2.** (a) Temperature dependence of magnetization of several $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ polycrystalline powders. (b) Normalized (0 0 2) powder x-ray diffraction peak of several $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ powders.

![Figure 3](image)

**Figure 3.** Typical temperature dependence of magnetizations of several $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ (a) single crystal and (b) HIP wire, respectively. K content dependence of $T_c$ in several $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ (c) single crystals and (d) HIP wires, respectively. $T_c$ is defined at the temperature where normalized magnetization reaches at -0.1 as shown in (a) and (b).
To evaluate the carrier-concentration dependence of superconducting properties, such as $T_c$ and $J_c$, K content of samples should be estimated. From SEM-EDX analyses, the chemical compositions in single crystal and the core of HIP wires were evaluated. In the case of HIP wire, nominal and analyzed carrier contents are almost identical. In the case of single crystals, analyzed K content $x$ is quite different from the nominal value in some pieces. For example, analyzed carrier content in single crystals with nominal carrier content $x \approx 0.28$ are distributed in the range of $0.20 < x < 0.30$. So we perform EDX analysis for each single crystal before evaluating its $T_c$ and $J_c$.

Next, we evaluate $T_c$ in both single crystals and HIP wires from temperature dependence of magnetization. Typical temperature dependence of magnetization are shown in fig. 3 (a) and (b). Similar to magnetization of polycrystalline powders in fig.2, drop of magnetization tends to be broad in under-doped samples. In this study, $T_c$ is defined at the temperature where normalized magnetization reaches at -0.1 as shown in fig. 3 (a) and (b). Evaluated $T_c$ of single crystals and HIP wires are summarized in fig. 3(c) and (d), respectively. $T_c$ in single crystals is the highest at $x \sim 0.4$. This is consistent with the previous reports. $T_c$ is reduced with decreasing $x$ moderately above $x \sim 0.3$, and rapidly below $x \sim 0.3$. In the HIP wires, $x$-dependence of $T_c$ shows a broad peak.

![Figure 4. K content dependence of $J_c$ in several $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ single crystals and HIP wires. $J_c$ in self field is evaluated at 2 K and 4.2 K for single crystals and for the HIP wires, respectively.](image)

Magnetic $J_c$ in all of these single crystals and HIP wires are evaluated. Obtained results are summarized in fig.4. $J_c$ in self field is evaluated at 2 K and 4.2 K for single crystals and for the HIP wires, respectively. Maximum of $J_c$ in single crystals reaches around 5-7 MA/cm$^2$ at $x \sim 0.28$. This is relatively high value compared with the $J_c$ at $x \sim 0.4$ where $T_c$ is optimized as shown in fig. 3. In our sample grown by FeAs flux method, $J_c$ takes its maximum in the under-doped region. This result is roughly consistent with previous report by Song et al., where KAs flux was used [13], although the peak position is not $x \sim 0.30$. This difference may be caused by the difference in the starting materials for synthesis. In the case of $x$ dependence of $J_c$ in the HIP wire, significant peak is not observed at $x \sim 0.28$. However, $J_c$ shows a broad plateau in a wide doping region of $0.3 < x < 0.4$. $J_c$ is reduced only below $x \sim 0.30$. We can safely conclude that the shift of maximum of $J_c$ from optimal region to under-doped region is the common feature in 122-type single crystals and wires.

In fig. 5, K content dependences of both $T_c$ and $J_c$ in several $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ HIP wires are shown. Both dependences show broad peaks around $x \sim 0.35$. In contrast to the doping dependence of $T_c$ and $J_c$ in single crystals, maximum values are realized in almost the same doping level, although the peak is shifted to under-doped region. This fact suggests that intergranular $J_c$ is dominant compared with intragranular $J_c$ in the core of the HIP wire. Furthermore, sintering conditions for wires and tapes using
under-doped polycrystalline powders have not been well studied yet. In this sense, \( J_c \) in 122-type superconducting wires and tapes may further be enhanced by controlling the carrier content and the optimization of sintering process. Obtained results will expand the doping level of starting materials for IBS high-\( J_c \) superconducting wires and tapes.

**Figure 5.** K content dependence of both \( T_c \) and \( J_c \) in several \( \text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2 \) HIP wires.

4. Summary
The K content dependence of \( J_c \) in \( \text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2 \) single crystals and HIP wires were investigated. \( \text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2 \) single crystals are synthesized by FeAs flux method. \( \text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2 \) HIP wires are fabricated using polycrystalline \( \text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2 \). We found that the \( x \)-dependence of magnetic \( J_c \) in our single crystals shows the peak in under-doped region around \( x \approx 0.28 \). In the HIP wire, although significant peak is not observed, \( J_c \) shows a broad plateau in a wide doping region of \( 0.3 < x < 0.4 \). These results indicate that \( J_c \) in the under-doped \( \text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2 \) HIP wire is controlled by intergranular \( J_c \).

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