Improved transport critical current in Ag and Pb co-doped Ba$_x$K$_{1-x}$Fe$_2$As$_2$ superconducting tapes

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Abstract

Fe-clad Ba$_x$K$_{1-x}$Fe$_2$As$_2$ superconducting tapes were fabricated by the ex situ powder-in-tube method combined with a short high-temperature annealing technique. The effects of annealing time and different dopants on the transport properties of Ba$_x$K$_{1-x}$Fe$_2$As$_2$ tapes were systematically studied. By co-doping with Ag and Pb, the transport critical current densities $J_c$ of Ba$_x$K$_{1-x}$Fe$_2$As$_2$ tapes were significantly improved in the whole field region and the highest transport $J_c$ was up to 1.4 × 10$^4$ A cm$^{-2}$ ($I_c$ = 100 A) at 4.2 K in self-field. It is proposed that the superior $J_c$ values in the co-doped samples are due to the combined effects of Pb doping at low fields and Ag doping at high fields.

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

1. Introduction

The discovery of superconductivity in LaFeAsO$_{1-x}$F$_x$ [1] in 2008 has led to an enormous amount of research on the iron-based superconductors. With high critical temperature [2–5] and upper critical field [6–8], the iron-based superconductors are very promising for high-field applications [9, 10]. As an important aspect for practical applications, high-performance superconducting wires and tapes, which can be used in cables and magnets, need to be developed. Therefore, soon after the discovery of iron-based superconductors, (La, Sm) FeAsO$_{1-x}$F$_x$ (1111 type) [11–13], Sr$_x$K$_{1-x}$Fe$_2$As$_2$ (122 type) [14] and Fe(Se, Te) (11 type) [15] superconducting wires were fabricated using the powder-in-tube (PIT) method. At the same time, some efforts such as sheath optimization and dopant addition were made to attain and improve their transport current density $J_c$ [16]. However, in the polycrystalline iron-based superconductors, the misorientation of grains, inclusions at grain boundaries and other crystal defects strongly limit the transport current [17–19]. In order to improve the current carrying property, it is very important to obtain a superconducting core with good grain connectivity, uniform composition, high density and low impurity content in iron-based superconducting wires and tapes.

At present, the optimal candidate for applications in the iron-based superconductor family is the 122 type, which has a relatively low anisotropy of 1–3, a high pinning potential of 10$^4$ K, a moderate transition temperature, and a high critical field and critical current density [20]. In order to improve the transport $J_c$ of 122-type superconducting wires and tapes, Ag or Pb doped Sr$_x$K$_{1-x}$Fe$_2$As$_2$ wires and tapes were fabricated by our group [21, 22]. The results show that the Pb doping can increase the transport $J_c$ in low field, but give no help in the high-field region. On the other hand, the Ag doping can effectively improve the transport $J_c$ in the high-field region. The $J_c$ enhancement by Ag doping was also proved by the recent report [23], which improved the $I_c$ of Ag doped...
Ba$_{1-x}$Fe$_2$As$_2$ tape up to 60.7 A using a melting process at 1100$^\circ$C to prepare the precursor.

Based on the previous work, this study aims to investigate the co-doping effects of Ag and Pb on the superconducting properties of Ba$_{1-x}$Fe$_2$As$_2$ tapes. It is expected that by combining the advantages of the doping effects of Ag and Pb, the $I_c$ performance can be improved in the whole field region. For comparison, Ag and Pb doped Ba$_{1-x}$Fe$_2$As$_2$ tapes were also fabricated following the same process. It was found that the transport $I_c$ of Ba$_{1-x}$Fe$_2$As$_2$ tape at 4.2 K in self-field was further increased to 100 A by being co-doped with Ag and Pb, and its high-field performance was also improved compared to the case of single doping. The microstructure and superconducting properties of Ba$_{1-x}$Fe$_2$As$_2$ tapes with single doping and co-doping were comparatively investigated.

2. Experimental details

The starting materials for preparing Ba$_{0.66}$K$_{0.48}$Fe$_2$As$_2$ precursor are small Ba pieces, K bulks and fine FeAs powder. They were mixed and then put in an Al$_2$O$_3$ crucible, which was immediately sealed in a stainless steel pipe by argon arc welding. Then the pipe was put into a tubular furnace maintained at a temperature at 1100$^\circ$C for 10 min and cooled to room temperature by switching off the furnace. This heating temperature is higher than the melting point of FeAs compound, which can improve the mixing of constituent elements [23]. The precursor was ground into powder in an agate mortar and packed in an Nb tube, which was sealed in a stainless steel pipe and heat treated at 900$^\circ$C for 20 h. Then the sintered product was ground into fine powder and doped with Ag and Pb, following the stoichiometries Ba$_{0.66}$K$_{0.48}$Fe$_2$As$_2$ + Ag$_{0.5}$, Ba$_{0.66}$K$_{0.48}$Fe$_2$As$_2$ + Pb$_{0.2}$ and Ba$_{0.66}$K$_{0.48}$Fe$_2$As$_2$ + Ag$_{0.5}$ + Pb$_{0.2}$ respectively. Finally, the mixture was filled into Fe tubes with 8 mm outer and 5 mm inner diameter. These tubes were sequentially rotary swaged, drawn to wires, and rolled into tapes 0.7 mm thick. In order to avoid reaction between the Fe sheath and the superconducting core, a short high-temperature annealing technique [24] was used in the heat treatment of the tapes. The tapes were cut into short samples 6 cm long, which were sealed into Fe tubes and sintered at 1100$^\circ$C for 5, 10 and 15 min respectively. In the rest of this paper, these samples are given their own code names for short, and their process parameters are summarized in table 1.

The phases of the superconducting core were studied by the x-ray diffraction (XRD) on a Rigaku D/MAX 2500 diffractometer. The microstructure of crushed superconducting core was analyzed with a Hitachi S4800 scanning electron microscope (SEM). The element distribution on the tape section was examined with energy dispersive x-ray spectroscopy (EDX) mapping and line scanning. The resistance measurements were carried out on a Quantum Design physical property measurement system (PPMS) using the four-probe method. The transport critical current $I_c$ was measured at 4.2 K using short tape samples of 3 cm in length with the standard four-probe method and evaluated by the criterion of 1 $\mu$V cm$^{-1}$, then the critical current was divided by the cross section area of the superconducting core to get the critical current density $J_c$. The applied fields in transport $I_c$ measurement were parallel to the tape surface.

3. Results and discussion

Figure 1(a) shows a typical SEM image of the cross section of Ba$_{1-x}$Fe$_2$As$_2$ tape prepared following the process mentioned above. We can see a clear boundary between the superconducting core and the Fe sheath, indicating that there is no obvious reaction at the inner surface of the sheath during the heat treatment. This is essential for the transport $I_c$ measurement of the tapes [12, 25]. To further investigate the element distribution, an EDX line-scan was performed on the cross section of undoped Ba$_{1-x}$Fe$_2$As$_2$ tape. As shown in figure 1(b), most of the Ba, K and Fe elements are successfully restricted within the Fe sheath. For each element, the content has a dramatic change at the boundary of the superconducting core. In figure 2, the EDX element mapping shows a similar result in Ag and Pb co-doped tape. Therefore, using the ex situ PIT method combined with a short high-temperature annealing technique, reaction between the superconducting core and the Fe sheath can be avoided. In addition, the EDX mapping in figure 1(b) shows that the elements of the parent compounds are homogeneously dispersed in the superconducting core.

Compared to the previously reported bimetallic Ag/Fe sheath, using the Fe sheath can reduce the fabrication cost and simplify the structure of the tapes, which is favorable for comparing the co-doping effects of Ag and Pb on the superconducting core.
for practical applications. More importantly, without the Ag inner sheath, the temperature of heat treatment can exceed the melting point of Ag (961.78 °C), and the deformation pressure during cold working can be applied more effectively on the superconducting core, which will promote its deformation and improve its density. As can be seen in figure 1, the superconducting core of the tapes in this work looks denser than that in Ag/Fe-clad tape [21], which will be beneficial to the current carrying property of the tapes.

The XRD patterns of several samples are given in figure 3. Except for some minor impurity peaks, the diffraction patterns show strong peaks of Ba-122 phase, indicating that the main phase of all the samples is \( \text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2 \) phase. The Ag or Pb peak could be respectively detected in the single doped tapes, and both of them were simultaneously observed in the XRD pattern of the co-doped sample. The Fe impurity detected in all the samples was introduced by the Fe sheath of the tapes. On the other hand, it should be noted that the XRD patterns of BaKFeAs–AgPb-5 and BaKFeAs–AgPb-15 are almost the same, suggesting that the time of high-temperature annealing has no significant effect on the phases of the samples.

Figure 1. (a) SEM image of the cross section of \( \text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2 \) tape. The superconducting core and the Fe sheath are indicated by arrows. (b) EDX line-scan on the cross section of undoped tape. The scanning direction is indicated by the white solid line. From top to bottom, the color curves crossing the white dashed line represent the intensities of Fe, Ba, K, O and As elements respectively.

Figure 2. EDX mapping images on the cross section of Ag and Pb co-doped tape.

Figure 4 gives the temperature dependence of the resistivity normalized by the resistivity at 300 K for samples with various dopants and annealing times. The onset superconducting critical temperatures \( T_c \) of BaKFeAs–Ag-5, BaKFeAs–Pb-5 and BaKFeAs–AgPb-5 tape are 33.8 K, 31.4 K and 33.7 K, respectively. The \( T_c \) of Ag doped samples is higher than the others, meaning that Ag has a positive effect on the \( T_c \) of the samples. On the other hand, we can see that the superconducting transitions of BaKFeAs–AgPb-10 and BaKFeAs–AgPb-15 are a little sharper than that of BaKFeAs–AgPb-5. This indicates that a longer annealing time can improve the crystallinity of the superconducting core, but its influence on \( T_c \) is weaker than chemical addition.

In order to further understand the co-doping effect of Ag and Pb on the superconducting property, the temperature dependent resistivities of BaKFeAs–Pb-5 and
BaKFeAs–AgPb-5 in various magnetic fields ($B = 0, 1, 3, 5, 7$ and $9$ T) were studied. With the increase of magnetic field, the superconducting transitions of these two samples shift towards lower temperature, and become less steep. Their upper critical fields $H_{c2}$ and irreversibility fields $H_{irr}$, which are estimated with the criteria of 90% and 10% of resistivity at normal state respectively, are shown in figure 5. The upper critical field at zero-temperature $H_{c2}(0)$ was calculated using the Werthamer–Helfand–Hohenberg (WHH) formula: $H_{c2}(0) = -0.693 T_c (dH_{c2}/dT)$. For the BaKFeAs–Pb-5 and BaKFeAs–AgPb-5 samples, taking $T_c = 28.5$ and $31.5$ K, the values of $H_{c2}(0)$ are $124$ and $129$ T. In practical application, $H_{irr}$ is an important parameter which has a strong relationship with the critical current density $J_c$. In figure 5, it can be seen that the $H_{irr}$ of BaKFeAs–AgPb-5 is much higher than that of BaKFeAs–Pb-5 at the same temperature, indicating that, compared to the Pb doping, the Ag + Pb co-doping can further improve the superconducting property of Ba$_x$K$_{1-x}$Fe$_2$As$_2$ tapes when applying external magnetic field.

The transport critical $I_c$ of tapes with various dopants and annealing times in self-field at 4.2 K are summarized in table 1. In general, the $I_c$ decreases with increasing annealing time, and the $I_c$ of co-doped tapes is about twice as much as that of the Pb doped samples with the same annealing time. Therefore, Ag+Pb co-doping can enhance the transport property in self-field. Meanwhile, we can see that the $I_c$ of Ag doped tapes is much lower than those of the Pb doped and Ag+Pb co-doped tapes. This is different from a previous report, where $J_c$ was improved effectively by Ag doping only [21–23]. In their work, the tapes and wires were sintered at 850–900 °C, whereas the tapes in this work were heated at 1100 °C after cold working. Hence the Ag dopant in Ba$_x$K$_{1-x}$Fe$_2$As$_2$ tapes may be sensitive to this change of the heat treatment condition.

The field dependent $J_c$ at 4.2 K of Pb doped and Ag+Pb co-doped tapes are given in figure 6. We can see that the $J_c$ of Pb doped tapes drops dramatically in increasing field. In contrast, the Ag+Pb co-doping can effectively enhance the $J_c$ performance in the whole field region. In this work, the $J_c$ of the BaKFeAs–AgPb-5 tape achieved $1.4 \times 10^4$ A cm$^{-2}$ in self-field. However, even in the co-doped sample, the $J_c$ still showed a drop of about one order of magnitude in a field of 0.5 T. This is similar to the $J_c$ of cobalt-doped BaFe$_2$As$_2$ bicrystal films with large misorientation angles [19], indicating a weak-link characteristic in these tape samples. The inset of figure 6 shows the $J_c$ curves of BaKFeAs–AgPb-5 tape measured in increasing and decreasing fields. The hysteretic effect of $J_c$ is relevant to the penetration of flux into strong pinning intragranular regions, and the presence of intragranular $I_c$ can enhance the intergranular $I_c$ when the field is decreasing [26]. This also suggests that there are weak-linked current paths between the grains in these tapes.

To investigate the effects of different dopants and annealing times on the tapes during the short high-temperature
Figure 6. Transport critical current density $J_c$ of Pb doped and Ag+Pb co-doped tapes at 4.2 K in increasing fields. The inset shows the $J_c$ of BaKFeAs–AgPb-5 tape measured in increasing and decreasing fields successively.

annealing of the tapes. SEM images of the superconducting cores are shown in figure 7. In figure 7(a), there are some large Ag particles (marked by arrows) embedded in the matrix in BaKFeAs–Ag-5. These inhomogeneously dispersed Ag particles may be caused by the melting and segregation of Ag at a temperature as high as 1100°C. This is the reason why the $I_c$ of the Ag doped samples are much lower than the others under this short high-temperature annealing. In figure 7(b), we can see that the Pb additions (marked by arrows) bind the Ba$_x$K$_{1-x}$FeAs matrix tightly in BaKFeAs–Pb-5, but their distribution in the parent compound is also not very homogeneous. In the BaKFeAs–AgPb-5 sample of figure 7(c), we can see that the Ba$_x$K$_{1-x}$FeAs particles and doping induced particles are finer and more uniform compared to the case of single doping, and it exhibits a better crystallinity than BaKFeAs–Pb-5 due to the Ag addition. Some very small voids (marked by circles) and a few impurity particles (marked by arrows) can be observed in this sample, but these defects are much smaller than those in BaKFeAs–Ag-5 and BaKFeAs–Pb-5. Accordingly, it seems that Pb doping can improve the particle connections, while Ag doping is helpful for grain formation. This is in accordance with the results in tapes prepared with long time final annealing [27, 28]. When comparing figures 7(c) and (d), we can see that with the increase of annealing time, the egg-shape particles gradually melt into large irregular bulks in BaKFeAs–AgPb-15, which may lead to a relatively bad crystallinity.

In a word, a homogeneous microstructure with uniformly distributed dopants is critical to achieve high superconducting properties in Ba$_x$K$_{1-x}$Fe$_2$As$_2$. Furthermore, tapes with a high-temperature annealing of less than 5 min will have a better $J_c$ performance, while the doping amount of the Ag+Pb co-doped tape still needs to be optimized. One the other hand, although the co-doping in this work can increase the $J_c$ in self-field and the $J_c$ plateau in the high-field region, it does not eliminate the rapid drop of $J_c$ in low field. Therefore, besides reducing defects such as pores, cracks, and inhomogeneous phases in Ba$_x$K$_{1-x}$Fe$_2$As$_2$ tapes, solution of the weak link problem is another important issue to further improve the critical current in future.
4. Conclusion

In summary, we have fabricated Fe-clad $Ba_xK_{1-x}Fe_2As_2$ superconducting tapes by the \textit{ex situ} powder-in-tube method combined with a short high-temperature annealing as the final heat treatment after the cold deformation. EDX mapping and line-scan showed that there was no reaction layer between the Fe sheath and the superconducting core. With Ag+Pb co-doping, the transport $J_c$ of the tape was effectively enhanced in the whole field region. It seems that Pb doping can improve the particle connections, while Ag doping is beneficial to grain growth. Compared to Ag and Pb single addition, Ag+Pb co-doping successfully combines their advantages, thus achieving a further improvement of the transport $J_c$.

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