Effect of starting materials on the superconducting properties of SmFeAsO$_{1-x}F_x$ tapes

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Abstract

SmFeAsO$_{1-x}F_x$ tapes were prepared using three kinds of starting materials. This showed that the starting materials have an obvious effect on the impurity phases in the final superconducting tapes. Compared with the other samples, the samples fabricated with SmAs, FeO, Fe$_2$As, and SmF$_3$ have the smallest arsenide impurity phases and voids. As a result, these samples possess much denser structures and better grain connectivities. Moreover, among the three kinds of sample fabricated in this work, this kind of sample has the highest zero resistivity temperature, $\sim 40$ K, and the largest critical current density, $\sim 4600$ A cm$^{-2}$, in self-field at 4.2 K. This is the highest $J_c$ value reported so far for SmFeAsO$_{1-x}F_x$ wires and tapes.

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

1. Introduction

The discovery of superconductivity in SmFeAsO$_{1-x}F_x$ with an onset transition temperature of $T_c \sim 56$ K has attracted great interest due to its highest value of $T_c$ in iron-based superconductors and potential applications in high field [1–8]. Compared with the ‘122’ superconductors, the ‘1111’ superconductors have more complex crystal structures and higher sintering temperatures [8–10]. Moreover, the F element in the ‘1111’ superconductors is very sensitive to the sintering temperature. A high sintering temperature usually causes serious F$^-$ losses, which will depress the superconducting properties of the SmFeAsO$_{1-x}F_x$ [7].

At a low sintering temperature (\sim 900°C), SmFeAs O$_{1-x}F_x$ bulks with a good superconductivity were prepared by our group [7]. Using one-step PIT methods, SmFeAsO$_{1-x}F_x$ superconducting wires and tapes were also successfully synthesized at about 900°C, achieving transport $J_c$ values of 1.3 kA cm$^{-2}$ and 2.7 kA cm$^{-2}$ at 4.2 K, respectively [11, 12]. More recently, Fujioka et al have reported an ex situ technology to produce SmFeAsO$_{1-x}F_x$ wire. In order to compensate for the F losses, a binder with stoichiometric Sm, Fe, As, and F was added during the secondary sintering processing, and a $J_c$ of about 4 kA cm$^{-2}$ at 4.2 K was obtained in their work [13]. Generally, samples fabricated by the above methods have a lot of impurity phases, such as FeAs, SmAs, and SmOF. These impurity phases, especially for arsenide, usually form current-blocking networks and reduce the critical current density.

It is well known that Fe is more prone to reacting with As to form a stable covalent compound, while Sm tends to form a stable ionic compound with the O element. As a result, the reaction between the two stable compounds (FeAs and Sm$_2$O$_3$) becomes very difficult [14]. Therefore, there are always Sm$_2$O$_3$ and FeAs impurities in the SmFeAsO$_{1-x}F_x$ compound. However, the impurity phase can be reduced by
changing the starting materials. In this work, the influences of different starting materials on the superconducting properties of SmFeAsO$_1-x$F$_x$ tapes were systematically compared for the first time.

2. Experimental details

Fluorine-doped SmFeAsO$_1-x$F$_x$ tapes were prepared by three different methods. Sm filings, Fe powder, Fe$_2$O$_3$ powder, As pieces and SmF$_3$ powder were taken as raw materials. Firstly, we synthesized the starting compounds of SmAs, Fe$_2$As, FeO and Sm$_3$As$_2$Fe$_{1+2x}$ at about 700°C for 20 h from the stoichiometric reaction of (Sm + As), (2Fe + As), (Fe$_2$O$_3$ + Fe) and ((1 + 2x)Fe + (3 − x)Sm + 3As, where x is determined by the F-doping level), respectively. Then, Sm$_3$As$_2$Fe$_{1+2x}$, Fe$_2$O$_3$ and SmF$_3$ were mixed together in a certain ratio (named Sm1111-1), and certain masses of SmAs, FeO, Fe$_2$As and SmF$_3$ were blended as the second batch (named Sm1111-2). In order to compare with the two kinds of sample mentioned above, a simple one-step PIT method was also adopted (named Sm1111-3), following the preparation process in [15]. These three mixtures were all thoroughly ground. The final powder was packed into silver tubes with outer- and inner-diameters of about 8 mm and 6.2 mm, respectively. Then the silver tubes were put into iron tubes with outer- and inner-diameters of about 11.6 mm and 8.2 mm, respectively. Subsequently, the composite tubes were swaged and drawn down to a wire of ∼1.9–2.0 mm in diameter. Finally, the wires were rolled as tapes with a thickness of ∼0.6–0.8 mm. Short samples were cut from the as-rolled tapes for sintering. The short tapes were sintered at 500°C for 10 h, and then heated at 900°C for 30–40 h.

Phase identification was characterized by powder x-ray diffraction (XRD) analysis with Cu Kα radiation from 20° to 70°. Resistivity measurements were carried out by the standard four-probe method using a PPMS system. The microstructures were determined by scanning electron microscopy (SEM) after peeling away the sheaths. The transport critical currents $I_c$ at 4.2 K and their magnetic dependences were evaluated at the High Field Laboratory for Superconducting Materials (HFLSM) in Sendai, Japan, by a standard four-probe resistive method, with a criterion of 1 $\mu$V cm$^{-1}$. To check the reproducibility, we measured 2–3 specimens for every batch.

3. Results and discussion

The x-ray diffraction patterns of the three kinds of SmFeAsO$_1-x$F$_x$ tape after heat-treatment are shown in figure 1. Clearly, SmFeAsO$_1-x$F$_x$ with ZrCuSiAs structure is the main phase for all kinds of sample. Because it is very difficult to completely clear away the Ag from the surface of the SmFeAsO$_1-x$F$_x$ core, a tiny quantity of Ag reflecting peaks are also observed in the XRD patterns in figure 1. As fluorine evaporation during the heat-treatment process is unavoidable, especially for these very thin tapes, the final F-doping level will be less than the nominal F-doping level of $x = 0.2$ in the present study. According to figure 1, the main impurity phases for these tapes are SmAs, Sm$_2$O$_3$ and SmOF, and some FeAs phase is also found. However, the relative intensities of the impurity phases were obviously different among these samples using different starting materials. For the Sm1111-3 samples, all the reflection peaks of the three impurities were very strong and a slight FeAs impurity was also found, indicating much more impurity in this kind of sample. This is consistent with other results from samples fabricated by the same method [5, 6, 11]. For the Sm1111-1 samples, the impurities of Sm$_2$O$_3$ and FeO were decreased and the main impurity phases were SmAs and FeAs. However, the reflection peaks of SmAs and FeAs nearly disappeared for the Sm1111-2 samples. The decrease of arsenide is favorable for good grain linkages, because the arsenide usually exists at the grain boundary of the Sm1111, blocking the superconducting current [16].

The main differences in starting materials for Sm1111-1 and Sm1111-2 samples are Fe$_2$O$_3$ and FeO. It is obvious that FeO is more active than Fe$_2$O$_3$. Thus, it is much easier for SmAs to react with FeO (to generate Sm$_2$O$_3$) than with Fe$_2$O$_3$. As a result, there are many more Sm$_2$O$_3$ impurity phases left in Sm1111-2. However, the reaction between SmAs and Fe$_2$O$_3$ becomes difficult, therefore some SmAs impurity phases are found in Sm1111-1 samples. For the Sm1111-3 samples, Sm is a higher electropositive element than Fe. Thus Sm can reduce Fe$_2$O$_3$ to produce Sm$_2$O$_3$. At the same time, Sm can also react with As to produce SmAs. As a result, the reaction among SmAs, Sm$_2$O$_3$ and other materials in the Sm1111-3 samples becomes very difficult. So there are both Sm$_2$O$_3$ and SmAs impurity phases left in the Sm1111-3 samples. Briefly, compared with the Sm1111-3 samples, the Sm1111-2 and Sm1111-1 samples are prepared from the metastable compounds, which can effectively decrease the reaction difficulty. Thus the impurities are obviously reduced.

Figure 2 displays the normalized resistivity versus temperature of the three specimens of SmFeAsO$_1-x$F$_x$ tape. In agreement with other reports, all the specimens show a
metallic characteristic before the superconducting transition. The onset superconducting transition temperature and zero resistivity temperature for the Sm1111-1, Sm1111-2 and Sm1111-3 samples are about 46 K and 32 K, 47 K and 40 K, and 46 K and 37 K, respectively. It is well known that the $T_c$ for a SmFeAsO$_{1-x}$F$_x$ sample is sensitive to the final F-doping level in the crystal, and the obvious $T_c$ suppression is an indication of the F$^-$ loss. In fact, the loss of F$^-$ is one of the main challenges in preparing SmFeAsO$_{1-x}$F$_x$ wires and tapes. For example, Wang et al prepared SmFeAsO$_{1-x}$F$_x$ wire with a zero resistivity $T_c$ of only about 31 K [11], and Masaya et al recently reported an ex situ technology to fabricate SmFeAsO$_{1-x}$F$_x$ wire with a zero resistivity $T_c$ of only about 36 K [13]. The residual resistivity ratios (RRRs), $R(300)/R(T_c)$ for the Sm1111-1, Sm1111-2 and Sm1111-3 samples are 3.70, 4.47 and 3.57, respectively. The high RRR in the Sm1111-2 samples indicates that the impurity scattering level is low, consistent with the XRD results.

Figure 3 shows the SEM images of the SmFeAsO$_{1-x}$F$_x$ tapes, displaying the change of microstructure with different starting materials. It can be seen that there is no obvious difference in the grain size and the average grain size is 5–10 $\mu$m. The main difference in the three kinds of specimen is that there are a large number of pores in the samples of Sm1111-1 and Sm1111-3. The pore is one of the defects which will reduce the critical current density. In addition, the grain boundary for the Sm1111-2 samples seems much cleaner and denser than those of the others, which is consistent with the XRD results. The reduced impurity phases and voids in the Sm1111-2 samples can effectively reduce the non-superconducting layer and improve the grain connectivity, resulting in a decrease of the current-blocking network. Compared to the other samples, the fewer voids and arsenide impurity phases may be the key factors that make the Sm1111-2 specimens have larger critical current density.

The transport critical currents ($I_c$) of the three kinds of SmFeAsO$_{1-x}$F$_x$ tape were evaluated by the standard four-probe method in fields up to 5 T. The zero resistive currents of the Sm1111-1, Sm1111-2 and Sm1111-3 samples in self-field were about 12 A, 20 A and 10 A, respectively. The transport critical current density $J_c$ as a function of field for the three kinds of tape is illustrated in figure 4. The largest transport $J_c$, as high as $\sim$4600 A cm$^{-2}$ at 4.2 K in self-field, was found in the Sm1111-2 samples, and the transport $J_c$ values for the Sm1111-1 and Sm1111-3 specimens were about 3050 A cm$^{-2}$ and 2200 A cm$^{-2}$, respectively. According to the XRD results, the main impurity phase is Sm$_2$O$_3$ for the Sm1111-2 samples, while there are many more arsenide impurity phases for the Sm1111-1 and Sm1111-3 samples. As
reported in the literature, the Sm$_2$O$_3$ phase usually appears in the center of the SmFeAsO$_{1−x}$F$_x$ grain, whereas the arsenide phases favor segregation at the grain boundaries and form a grain boundary wetting phase [16]. Therefore, the impurity phase of Sm$_2$O$_3$ is not as harmful as that of arsenide. However, the insulating Sm$_2$O$_3$ grains together with other defects usually force the current to cross the grain boundary and restrict the current passage regions [16]. As a result, the lowest $J_c$ is found in the Sm1111-3 sample. In addition, the Sm1111-2 samples are much denser and should have better grain connectivity than those in the Sm1111-1 and Sm1111-3 samples. All these factors are thought to have contributed to the improvement of $J_c$ in the Sm1111-2 samples. However, similarly to the YBCO superconductor, the $J_c$ shows strong field dependence in the low field region for the Sm1111 superconductor, exhibiting an intrinsic weak-link behavior. In the high field region, the transport $J_c$ is nearly field-independent with a highest value of $\sim$300 A cm$^{-2}$. So ways to overcome the weak-link problem and produce textured or quasi-textured SmFeAsO$_{1−x}$F$_x$ tapes are necessary studies for practical applications.

The phase purity improvement of polycrystalline SmFeAsO$_{1−x}$F$_x$ tapes is a very important work [19]. The Sm1111-2 fabrication process can effectively reduce the arsenide phases and voids, thereby lessening the SNS connections between the grains and densifying the samples. As a result, a $J_c$ value of about 4600 A cm$^{-2}$ was found. This is the highest value reported for SmFeAsO$_{1−x}$F$_x$ wires and tapes. However, the $J_c$–$B$ performance indicates that the weak-link behavior between grains, which is mainly caused by the high-angle misorientation of grains, has no obvious improvement. More recently, our group has achieved progress in the c-axis aligned Sm$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ superconductor; in particular, for Sn-doped samples, the transport $J_c$ is as large as $\sim$25 000 A cm$^{-2}$ [17, 18]. Thus, the methods of texturing and element-doping should be considered in the following works on the SmFeAsO$_{1−x}$F$_x$ superconductor.

4. Conclusions

The influence of starting materials on the microstructure, impurity phases and transport current density of SmFeAsO$_{1−x}$F$_x$ tapes was investigated. XRD and SEM analysis shows that the impurity phases and voids are sensitive to the starting materials. The highest $T_c$ ($\sim$40 K) and RRR ($\sim$4.47) were obtained in the sample using SmAs, FeO, Fe$_2$As and SmF$_3$ as starting materials, indicating a low impurity scattering level. This is in agreement with the XRD and SEM results. As a result, a high transport $J_c$ of about 4600 A cm$^{-2}$ in self-field was found in these specimens. On the other hand, the transport $J_c$ is very sensitive to the applied field and only about 400 A cm$^{-2}$ is left in a 0.4 T applied field, showing a weak-link behavior.

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