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Effects of oxide precursors on superconducting properties of polycrystalline $SmFeAsO_{1-x}F_x$

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ABSTRACT

A series of polycrystalline $SmFeAsO_{1-x}F_x$ samples were synthesized by one-step and two-step method at ambient pressure using different oxide precursors, namely As_2O_3, Fe_2O_3 and nano-Fe_2O_3 powder, as the source of element O. Results of X-ray diffraction and magnetic measurements manifest that starting oxides affected the phase formation and superconducting properties of $SmFeAsO_{1-x}F_x$. As_2O_3 as oxide precursor contributes to the fast formation of superconducting phase for a short period of sintering time. And samples prepared using As_2O_3 show higher superconducting transition temperature T_c and more stable fluorine doping level. Compared with Fe_2O_3, nano-Fe_2O_3 promotes fluorine doping into the O site. While using Fe_2O_3 leads to higher level of Fe and SmOF impurities. The critical current density J_{cm} were derived from magnetic hysteresis loops. Sample prepared using As_2O_3 shows higher J_{cm} in low temperature and high magnetic fields.

1. Introduction

The recent discovery of superconductivity at 26 K in the iron oxypnictide LaFeAs(O, F) leads to the emergence of novel iron-based superconductor families with different crystal structures: 1111 (REFeAs(O, F)) [1], 122 ((Ba, K)Fe_2As_2) [2], 111 (LiFeAs) [3] and 11 (Fe(Se, Te)) [4]. Among abovementioned superconducting systems, the REFeAs(O, F) superconductors have the highest T_c of over 50 K when La is replaced by Sm [5], Gd [6] or Tb [7], very high upper critical fields [8] and high intragranular critical current densities J_c [9]. However, the practical applications of REFeAs(O, F) materials are impeded by several issues such as grain boundary [10,11], which is related to doping and impurities. Many efforts have been devoted to enhance the sample quality by improving doping [12,13] and applying special techniques [14–16]. And reports suggest that the superconducting properties of the polycrystalline REFeAs(O, F) materials can be affected by the preparation processes including sintering time, temperature, atmosphere and pelletization pressure [17–21]. It is reported that the element Fe is more inclined to react with As to form FeAs. Meanwhile, the element Sm tends to react with O to form a stable compound Sm_2O_3. Nevertheless, the reaction between these compounds will be difficult [14]. Thus starting materials affect the phase formation and superconducting properties. Recently, Wang et al. reported that the starting materials have an obvious effect on the impurity phases and voids in the final superconducting $SmFeAsO_{1-x}F_x$ tapes [22]. The samples fabricated with SmAs, FeO, Fe_2As, and SmF_3 have the fewest arsenide impurities and voids, and show much denser structure and better grain connectivity. On the other hand, Yang et al. suggested that oxygen vacancies are mandatory for F doping [23], which implies that oxide precursors may affect the superconducting properties of $SmFeAsO_{1-x}F_x$. In this paper, a group of polycrystalline $SmFeAsO_{1-x}F_x$ samples were prepared using various oxides, namely Fe_2O_3 powder, Fe_2O_3 nano-powder and As_2O_3 powder, which has not been reported as far as we know. The influence of oxides precursors on the phase formation and superconducting properties were investigated by powder X-ray diffraction and magnetic measurements.

2. Experimental

The $SmFeAsO_{1-x}F_x$ samples were prepared by one-step or two-step methods. For one-step method, the starting materials are Sm filings, Fe powder, As piece, SmF_3 powder and oxides, including Fe_2O_3 powder, Fe_2O_3 nano-powder (hereinafter referred to as nano-Fe_2O_3) and As_2O_3 powder. For two-step methods, the starting materials are SmAs powder, Fe powder, SmF_3 powder and oxides.

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SmAs were synthesized by Sm filings and As piece at 900 °C for 15 h. All starting materials were thoroughly ground with a mortar and pestle, wrapped in Nb foil, and then pressed into pellets. All processes except the pelletization were carried out in a glove box filled with high purity argon atmosphere. Then pellets were sealed in the evacuated quartz tubes, sintered at 1000 °C with various sintering time. All polycrystalline $SmFeAsO_{1-x}F_x$ bulk samples were listed in Table 1. The first digit on each label refers to one step (1) or two step (2) method. A, F and N represent As_2O_3, Fe_2O_3 and nano-Fe_2O_3, respectively. Succeeding number 03 or 025 denote doping level. The number after the dash denotes sintering time, namely 24 h or 72 h.

Phase identification was performed by powder X-ray diffraction (XRD) with Cu Kα radiation from 20° to 60°. DC magnetization measurements and the magnetic hysteresis loops (MHLs) were performed using the vibrating sample magnetometer (VSM) option of a Quantum Design PPMS.

3. Results and discussion

Fig. 1(a) shows powder XRD patterns of nominal composition $SmFeAsO_{0.7}F_{0.3}$ samples after peeling off the sheath materials. The intensity data were normalized by the strongest peaks (102). The diffraction peaks can be well indexed on the basis of tetragonal ZrCuSiAs-type structure, confirming the main phases are $SmFeAsO_{1-x}F_x$. The peaks of SmOF impurity was detected in all the samples, indicating that the level of fluorine in samples are less than the nominal composition. It is noted that the relative intensity of the impurity phase is different among samples prepared by different starting oxides. Results suggest that impurity level is highest in sample 1F03-24 and lower in 1A03-24 and 1N03-24. Moreover, the impurity of SmAs was observed in sample 1A03-24 and 2N03-24. Strong reflection peak of impurity Fe was only observed in sample 1F03-24. The reason for different impurity level will be discussed later. The FeAs impurity was not detected in Fig. 1(a), which may be due to minimal amount or poor crystallization of FeAs. The lattice constants calculated from the XRD pattern using Jade program are shown in Fig. 1(b). The lattice constants vary among samples prepared by different starting oxides, implying that the choice of oxide precursor affects fluorine doping level.

The critical transition temperature T_c was estimated using the peak value in differential of zero field-cool (ZFC) curves. The T_c and superconducting volume fraction V_{sc} values of all specimens are summarized in Table 1. The fact that the T_c and V_{sc} values of samples are lower than the result of [24–26] can be attributed to the difference of preparation process. Fig. 2 shows the ZFC and field-cool (FC) $\chi(T)$ curves of $SmFeAsO_{0.7}F_{0.3}$ samples from 5 K to 60 K under 5 mT. Sample 1A03-24 has the highest T_c of 53.2 K and superconducting volume fraction V_{sc} of around 14%. Sample 2F03-24 prepared by two-step method using Fe_2O_3 powder has the lowest T_c and V_{sc} compared with sample 1A03-24, 1N03-24 and 2N03-24. Sample 1F03-24 prepared by one-step method using Fe_2O_3 powder is not superconducting. The possible reason is that the low reactivity of Fe_2O_3 leads to slowing the formation of FeAs compound starting at about 450 °C [27], hence increasing the possibility of As evaporating from the pellet-Nb composite in high temperature, which hinders the formation of superconducting phase and results in Fe excess and the appearance of Fe impurity peaks in XRD in Fig. 1(a). It is worth mentioning that Ma et al. reported preparation of superconducting $SmFeAsO_{1-x}F_x$ samples by one-step method using Fe_2O_3 powder [16,28–30]. The synthesis

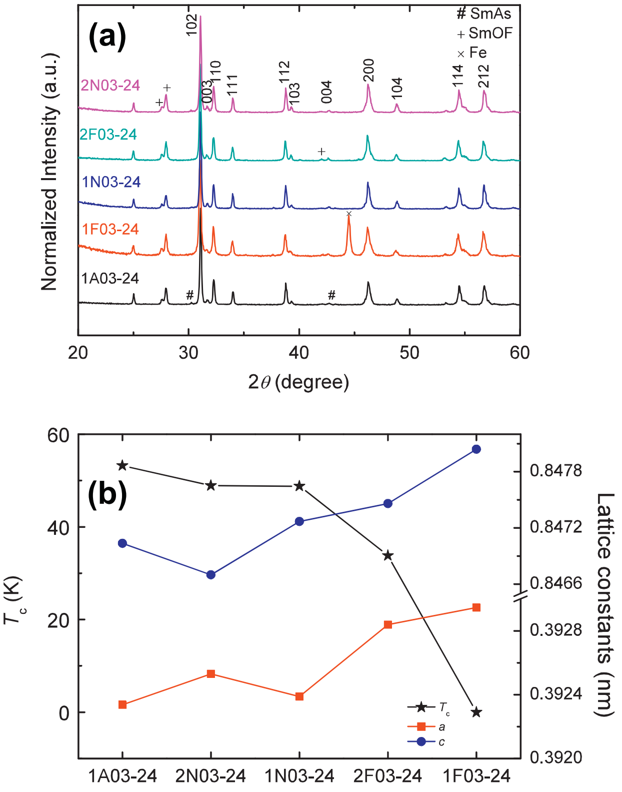

Fig. 1. (a) X-ray powder diffraction patterns of the $SmFeAsO_{0.7}F_{0.3}$ samples prepared by different oxide precursors. (b) Lattice constants and T_c dependence of the starting oxides of $SmFeAsO_{0.7}F_{0.3}$ samples.

Table 1
Starting materials and superconductivity of samples.

Nominal composition	Sintering time (h)	Sample	Starting materials	T_c (K)	V_{sc} (%)
$SmFeAsO_{0.7}F_{0.3}$	24	1A03-24	$As_2O_3 + Sm + Fe + As + SmF_3$	53.2	14
		1F03-24	$Fe_2O_3 + Sm + Fe + As + SmF_3$	0	
		1N03-24	Nano-$Fe_2O_3 + Sm + Fe + As + SmF_3$	48.8	9.8
		2F03-24	$Fe_2O_3 + SmAs + Fe + As + SmF_3$	33.8	4.9
		2N03-24	Nano-$Fe_2O_3 + SmAs + Fe + As + SmF_3$	48.9	13.3
$SmFeAsO_{0.75}F_{0.25}$	24	1A025-24	$As_2O_3 + Sm + Fe + As + SmF_3$	51.3	13.3
		1F025-24	$Fe_2O_3 + Sm + Fe + As + SmF_3$	0	
		1N025-24	Nano-$Fe_2O_3 + Sm + Fe + As + SmF_3$	40.8	9.2
		2F025-24	$Fe_2O_3 + SmAs + Fe + As + SmF_3$	35	13.4
		2N025-24	Nano-$Fe_2O_3 + SmAs + Fe + As + SmF_3$	46	7.2
$SmFeAsO_{0.75}F_{0.25}$	72	1A025-72	$As_2O_3 + Sm + Fe + As + SmF_3$	50.1	9.1
		1F025-72	$Fe_2O_3 + Sm + Fe + As + SmF_3$	0	
		1N025-72	Nano-$Fe_2O_3 + Sm + Fe + As + SmF_3$	38	8.9
		2F025-72	$Fe_2O_3 + SmAs + Fe + As + SmF_3$	30.5	7.3
		2N025-72	Nano-$Fe_2O_3 + SmAs + Fe + As + SmF_3$	45.2	11.3