Effects of the sintering atmosphere on the superconductivity of SmFeAsO$_{1-x}$F$_x$ compounds

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Abstract

A series of SmFeAsO$_{1-x}$F$_x$ samples were prepared in quartz tubes filled with air of different pressures. The effects of the sintering atmosphere on the superconductivity were systematically investigated. The SmFeAsO$_{1-x}$F$_x$ system maintains a transition temperature ($T_c$) near 50 K until the concentration of oxygen in the quartz tubes increases to a certain threshold, after which $T_c$ decreases dramatically. Fluorine losses, whether due to vaporisation, reactions with starting materials or reactions with oxygen, proved to be detrimental to the superconductivity of this material. The deleterious effects of the oxygen in the sintering atmosphere were also discussed in detail.

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

1. Introduction

The discovery of superconductivity at 26 K in the iron oxypnictide LaFeAs(O, F) by Hosono et al [1] in 2008 soon afterwards led to the development of iron-based superconductor families with different crystal structures, generally referred to as ‘1111’ for REFeAs(O, F), ‘122’ for AEF$_2$As$_2$ [2] and AEF$_2$Se$_2$ [3], ‘111’ for LiFeAs [4] and ‘11’ for (Fe(Se, Te)) [5]. Here RE denotes rare earth and AE denotes alkali earth. The REFeAs(O, F) superconductors, in which $T_c$ is over 50 K when La is replaced by Sm [6], Gd [7] or Tb [8], show very high upper critical fields $H_{c2}$ of about 300 T [9] and high intragrain critical current densities ($J_c$) over 10$^6$ A cm$^{-2}$ (5 K, 0 T) [10]. However, the REFeAs(O, F) superconductors do share several properties with cuprates, such as layered structures, short coherence length [11], low carrier density [12, 13], significant evidence for granularity and low intergranular $J_c$ [14–17]. The superconducting properties of the polycrystalline REFeAs(O, F) materials need to be greatly improved by optimising preparation conditions. Recently, many efforts were devoted to enhance the sample quality through special techniques such as the hot isostatic pressing (HIP) method [15], mechanical alloying [18] and low-temperature synthesis [19]. The phase formation of the LaFeAs(O, F) compound was studied in detail [20].

Since the REFeAs(O, F) superconductors contain elements that can be easily oxidised, ultrahigh vacuum and the presence of protective inert gases seem mandatory during preparation. The understanding of the detrimental effects of air on the formation and properties of REFeAs(O, F) systems is important in understanding the superconducting mechanisms and with regards to applications. However, no related investigations were yet reported. In this paper, we present detailed studies on a series of SmFeAsO$_{1-x}$F$_x$ samples sintered in quartz tubes filled with air of different pressures. The effects of the sintering atmosphere on the phase formation and superconductivity were investigated by means of x-ray powder diffraction measurements and resistivity measurements.

2. Experimental details

The SmFeAsO$_{1-x}$F$_x$ samples were prepared by the two-step solid-state reaction method. The precursor SmAs was first synthesised by reacting Sm and As chips (both 99.99%) in a quartz tube under vacuum (0.001 Pa) at 500°C for 10 h and then 750°C for 10 h. The mixture of starting materials SmAs, Fe, Fe$_2$O$_3$ and FeF$_2$ powders with the nominal stoichiometric ratio of SmFeAsO$_{0.8}$F$_{0.2}$ were ground thoroughly and pressed...
into a pellet weighing about 1 g, then loaded in a alumina crucible to avoid contact with the quartz tube. After filling air in the quartz tube, the sealed tube of 20 ml volume was sintered at 1160°C for 45 h. The temperature ramping rate is 1°C min⁻¹ for all heat treatments. After the heat treatments, the precursor SmAs and the SmFeAsO₀.₈F₀.₂ samples were furnace-cooled to room temperature. Along this method several samples were prepared under different air pressure, \( P_{\text{air}} \) (\( P_{\text{air}} = 0.001 \text{ Pa–95 kPa} \)), which was controlled by a ZDF-5227-type vacuum gauge.

To investigate the reaction of the starting materials with the oxygen in the sintering atmosphere, and the reactions among the starting materials, two additional samples were prepared. SmAs and FeF₂ powders were mixed in the ratio of 10:1 and pressed into a pellet, then sealed in a quartz tube with \( P_{\text{air}} = 100 \text{ kPa} \). SmAs, Fe₂O₃ and FeF₂ powders were mixed in the ratio of 6:3:2 and pressed into a pellet, then sealed in a quartz tube. After filling air in the quartz tube, the sealed tube of 20 ml volume was sintered at 1100°C for 20 h. The tube volumes (20 ml), the ramping rate and the cooling were the same as those used to prepare the SmFeAsO₀.₈F₀.₂ samples.

Powder x-ray diffraction (XRD) was performed on a MAX-RC-type diffractometer with Cu Kα radiation from 2θ = 20°–80°. The calculations for the crystal parameters were performed on the basis of a least-squares fit using the Checkcell programs. Rietveld refinements were carried out with GSAS [21, 22]. The temperature dependence of resistivity was measured by the standard four-probe method on a Quantum Design PPMS.

### 3. Results and discussion

The phase identification was performed on the samples sintered under various \( P_{\text{air}} \). Figure 1 shows the XRD patterns normalised by the strongest peaks. The diffraction peaks can be well indexed on the basis of tetragonal ZrCuSiAs-type structure, confirming the main phases are SmFeAsO₁₋ₓFₓ. The impurities of SmOF and FeAs were detected in all the samples. The impurity SmAs, however, was only observed in samples sintered under 0.001 and 0.55 Pa. Sm₂O₃ was only observed in the sample sintered under 95 kPa.

Figure 1. X-ray powder diffraction patterns of the SmFeAsO₁₋ₓFₓ samples sintered under different air pressures. The impurities of SmOF and FeAs were detected in all the samples. SmAs was only observed in samples sintered under 0.001 and 0.55 Pa. Sm₂O₃ was only observed in the sample sintered under 95 kPa.

The transport properties of these samples were investigated. Figure 3 shows the temperature dependence of the resistivity, \( \rho \), from 5 to 60 K. The transition temperature \( T_c \) slowly decreases as \( P_{\text{air}} \) increasing from 0.001 to 100 Pa, and dramatically shifts to lower temperature when \( P_{\text{air}} \) reaches 75 kPa. This result is in agreement with the increase in \( a \) and \( c \) shown in figure 2. The inset of figure 3 shows \( \rho \) versus temperature of the samples sintered under \( P_{\text{air}} = 90 \text{ and } 95 \text{ kPa} \). The 95 kPa \( \rho(T) \) curve shows a spin-density-wave (SDW) instability at about 150 K as in the parent compound [23]. The abnormality in the \( \rho(T) \) curve of the 90 kPa sample shifts to lower temperature, indicating the SDW is suppressed by the F doping. According to the phase diagram [24], the actual F doping level in the

Figure 2. The lattice constant \( a \) and \( c \) of the samples sintered under different air pressures in semilogarithmic scale. Both \( a \) and \( c \) increase dramatically when \( P_{\text{air}} \) reaches 75 kPa. The solid and dashed lines are guides to the eyes.
The temperature dependence of the resistivity of the samples sintered under different air pressures from 5 to 60 kK. The inset shows the temperature dependence of the resistivity of the samples sintered under 90 and 95 kK from 5 to 300 K.

Figure 4. RRR, \( T_c \) and \( \Delta T_c \) versus both air pressure and \( R \) in semilogarithmic scale. Here \( R \) is the ratio of the mole fraction of oxygen in quartz tubes versus the mole fraction of oxygen vacancies in the sample and RRR = \( \rho(300\text{ K})/\rho(52\text{ K}) \). The inset shows the magnification in the range of \( R = 38\%–50\% \). \( T_c \) drops to zero when \( R \) is about 47\%. The solid and dashed lines are guides to the eyes.

90 kK sample is estimated to be less than 0.037. The mole fraction of \( \text{O}_2 \) in the quartz, \( M_{\text{O}_2} \), was calculated. \( P_{\text{air}} \) was converted to \( R \), where \( R = M_{\text{O}_2}/M_{\text{vac}} \times 100\% \). Here \( M_{\text{vac}} \) is the mole number of oxygen vacancies in the samples (0.2 in \( \text{SmFeAsO}_3\text{Fe}_2 \)). The residual resistivity ratio (RRR) was calculated as \( \rho(300\text{ K})/\rho(52\text{ K}) \). Figure 4 shows RRR versus both \( P_{\text{air}} \) and \( R \) in semilogarithmic scale. The RRR shows a shoulder with increasing \( R \) and then decreases quickly when \( R \) reaches 39\%. The decrease of RRR together with the increase of normal-state resistivity indicates the increase of impurity scattering with increasing \( R \).

The effects of sintering atmosphere on the superconducting transition were studied. The onset \( T_c \) was determined by 90\% normal-state \( \rho \). The transition width, \( \Delta T_c \), was defined as \( \Delta T_c = T(\text{onset}) - T(\rho = 0) \). \( T_c \) and \( \Delta T_c \) versus both \( P_{\text{air}} \) and \( R \) were also listed in figure 4. The inset in figure 4 shows the magnification in the range of \( R = 38\%–50\% \). The \( R \) dependence of \( T_c \) is in agreement with the RRR data and the crystal parameter results in figure 2. \( T_c \) with the highest value of 51.48 K (0.001 Pa) drops to zero when \( R \) is about 47\%. The increase of \( \Delta T_c \) from 2, 3 to 14 K indicates that the F doping becomes more inhomogeneous with increasing \( R \).

It is assumed that the sintered samples were mainly affected by the air pressures and the concentration of \( \text{O}_2 \) in the quartz tubes, because no nitride was observed in the XRD patterns, and the mole fraction of the other components, such as \( \text{CO}_2 \) and the moisture, were negligible compared to the pellets. The effects of air pressure are less pronounced since the samples sintered in vacuum underwent significant F vapourisation but still have high \( T_c \). The presence of \( \text{O}_2 \) may oxidise the starting materials, producing impurities of SmOF and \( \text{Sm}_2\text{O}_3 \), consuming F and reducing available oxygen vacancies [25]. The XRD patterns of the \( \text{SmAs} + \text{FeF}_2 \) pellet sintered under 100 kPa (sample A) is shown as the bottom curve in figure 5, with the peaks identified as \( \text{SmAs}, \text{SmOF} \) and a small amount of \( \text{FeAs}_2 \). The reaction may be described as

\[
2\text{SmAs} + 3\text{FeF}_2 + F_2O_3 \rightarrow 6\text{SmOF} + 5\text{FeAs} + \text{Fe}_2\text{As}_2
\]  

Results here show that the reactions of the starting materials with \( \text{O}_2 \) in the sintering atmosphere may reduce F that is available for doping, and consume Sm, Fe and As by forming impurities, thus increasing the relative oxygen ratio in the samples.

However, the \( R \) values of the samples with \( P_{\text{air}} = 90 \) and 95 kK are only 47\% and 50\%, respectively. After reaction (1), there should still be about 50\% of the residual vacancies and enough F to induce superconductivity. The fact that the sample...
of \( P_{atm} = 0.001 \) Pa also has impurity peaks suggests that impurities can form through the reactions between the starting materials without \( O_2 \) in the sintering atmosphere. This was confirmed by the XRD pattern of the SmAs + \( Fe_2O_3 + FeF_2 \) pellet sintered under 0.001 Pa (sample B), shown as the upper curve in figure 5, with the peaks identified as SmOF, FeAs and a small amount of Fe\( _2As \). The reaction may be described as

\[
6SmAs + 3FeF_2 + 2Fe_2O_3 \rightarrow 6SmOF + 5FeAs + Fe_2As. \tag{2}
\]

We tried to determine the ratio of the resultants after reactions (1) and (2) quantitatively by Rietveld refinement. Figures 6(a) and (b) show the GSAS fit of the XRD patterns for samples A and B, respectively. Results indicate that, for sample A, the mole ratio of SmAs:SmOF:Fe\( _2As \) is 6.6:2.0:0.5. For sample B, the mole ratio of SmOF:Fe\( _2As \):Fe\( _2As \) is 6.0:5.3:0.5. The ratios of SmAs:SmOF (6.6:2.0) in sample A and SmOF:Fe\( _2As \) (6.0:5.3) in sample B are close to the theoretical values of 8.2 and 6.5, respectively. The mole fractions of Fe\( _2As \) and Fe\( _2As \) are much smaller than the theoretical values. The possible reason is that Fe\( _2As \) and Fe\( _2As \) are poorly crystallised.

According to the results in figures 5 and 6, it is speculated that, when sintering under vacuum, F is lost due to the formation of SmOF and Fe\( _2As \) vapourisation. The latter also causes an iron deficiency, leading to the presence of extra SmAs, as observed in figure 1. According to the phase diagram [26], the residual F doping level is about 0.08–0.1 to maintain a \( T_c \) near 50 K. However, as the concentration of \( O_2 \) increases, \( O_2 \) reacts with SmAs and Fe\( F_2 \) to form SmOF, leading to an increase of impurities supported by the RRR results, and the decreased sample homogeneity, which can be seen from \( \Delta T_c \). The F was consumed to an insufficient doping level to induce superconductivity.

The impurities are easily formed because the starting materials have very disparate melting temperatures, which lead to parasitic reactions and inhomogeneous phase formation. Recent reports show that lowering the sintering temperature to 850–900 °C reduced the impurities and improved the connectivity to obtain high transport \( J_c \) [27], while a higher sintering temperature of 1000 °C is optimal for F doping to achieve high \( T_c \) [19]. Further investigations are needed to identify the accurate solubility limit of F in the system and the optimisation of the synthesis conditions to improve the sample quality.

4. Conclusions

In summary, the effects of sintering atmosphere on the SmFe\( AsO_{1-x}F_x \) compound were systematically investigated. The evolution of the superconductivity with the concentration of oxygen was observed. Results indicate that fluorine is lost due to vapourisation, reactions with starting materials and reactions with oxygen.

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