Phase diagram and superconductivity at 58.1 K in α-FeAs-free SmFeAsO$_{1-x}$F$_x$

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Abstract

The phase diagram of SmFeAsO$_{1-x}$F$_x$ in terms of $x$ is exhibited in this study. Specimens of SmFeAsO$_{1-x}$F$_x$ from $x = 0$ to $x = 0.3$ were prepared by low-temperature sintering with slow cooling. The low-temperature sintering suppresses the formation of the amorphous FeAs, which is inevitably produced as an impurity when using high-temperature sintering. Moreover, slow cooling is effective in obtaining a high fluorine concentration. The compositional change from feedstock composition is quite small after this synthesis. We can reproducibly observe a record superconducting transition for an iron-based superconductor at 58.1 K. This achievement of a high superconducting transition is due to the success in substituting a large amount of fluorine. A shrinking of the $a$ lattice parameter caused by fluorine substitution is observed and the substitutional rate of fluorine changes at $x = 0.16$.

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

1. Introduction

The first report on SmFeAsO$_{1-x}$F$_x$ was published in 2008 by Chen et al [1]. The superconducting transition temperature ($T_c$) was 43 K. Afterwards, $T_c$ was immediately improved to around 55 K by several groups [2–6]. Although these groups adopted a high-temperature sintering of around 1200°C, some research into a low-temperature sintering process had also been reported. For example, Chen et al synthesized polycrystalline SmFeAsO$_{1-x}$F$_x$ with a $T_c = 55$ K by low-temperature sintering at 1100°C [7]. Wang et al obtained superconductivity at 56.1 K when the heating temperature was 1000°C [8] and Singh et al also reported superconductivity at 57.8 K when the heating temperature was 900°C [9]. Therefore, low-temperature sintering is very effective in obtaining samples with a high transition temperature. Moreover, it was found that SmFeAsO$_{1-x}$F$_x$ has a quite large upper critical magnetic field of over 100 T [10]. Due to these advantages, iron-based superconductors have been widely studied as a promising material for applications as superconducting wires and films [11–14]. Ueda et al obtained a SmFeAsO$_{1-x}$F$_x$ film with $T_c = 57.8$ K by using molecular beam epitaxy [15]. They used the diffusion from an overlayer of SmF$_3$ to introduce fluorine into the thin film.

The most important point for the synthesis of SmFeAsO$_{1-x}$F$_x$ is how to substitute fluorine at the oxygen sites. In our previous study, it was found that fluorine is substituted not only at the maximum heating temperature but also during the cooling process. In particular, slow cooling is very effective in introducing a considerable amount of fluorine [16]. In this study, our samples are processed and it is found that low-temperature sintering, below the melting point of FeAs, does not form the amorphous FeAs impurity phase which is inevitably produced by high-temperature sintering of around 1200°C in polycrystalline SmFeAsO$_{1-x}$F$_x$. Due to this impurity located between the superconducting grains of SmFeAsO$_{1-x}$F$_x$, the superconducting current has difficulty flowing over the grain boundaries. Therefore, low-temperature sintering with slow cooling is very useful in...
obtaining amorphous FeAs-free SmFeAsO$_{1-x}$F$_x$ with a high fluorine concentration [16].

In this study, we show a record high $T_c^{\text{onset}}$ (58.1 K) obtained by using this method. Moreover, we obtained a high solid solubility limit of fluorine and produced a phase diagram of SmFeAsO$_{1-x}$F$_x$ in terms of $x$. While the phase diagram of SmFeAsO$_{1-x}$F$_x$ has been already reported by other two groups [2, 6], they prepared samples by using high-temperature sintering. This is the first report of a phase diagram for SmFeAsO$_{1-x}$F$_x$ obtained using low-temperature sintering with slow cooling.

2. Experiment

Specimens of SmFeAsO$_{1-x}$F$_x$ from $x = 0$ to $x = 0.3$ were prepared using low-temperature sintering with slow cooling, where $x$ shows the nominal amount of fluorine concentration in this report. First, two precursors namely 133 and 233 powder were obtained by sintering a mixture of Sm, Fe and As metal powders at 850 °C for 10 h [13, 17]. Stoichiometric Sm$_2$O$_3$, SmF$_3$, 133 and 233 powders were mixed in a mortar and compressed into pellets. They were sintered at 980 °C for 40 h in evacuated quartz tubes, then cooled down at a rate of $-5$ °C h$^{-1}$ to 600 °C.

X-ray diffraction (XRD; Rigaku Rint 2500) using Cu Ka radiation was applied for the characterization of the obtained samples. The lattice parameters and cell volumes were calculated from the x-ray peak positions. Si powder (RIGAKU; RSRP-43275G) was used as an internal standard material. Their electrical resistivity was measured by the standard four-probe technique using Au electrodes. All samples were cut into almost the same size and shape using the following dimensions ($1.4 \times 0.7 \times 6.0$ mm$^3$). In this study, $T_c^{\text{onset}}$ was regarded as the crossing point of the fitting lines for resistivity in the normal state near the transition and in the drop where resistivity drastically decreases. $T_c^{\text{zero}}$ was also regarded as the crossing point of the line for zero resistivity and the $\rho$–$T$ curve. Magnetic measurements were performed with a SQUID magnetometer (Quantum Design: MPMS). The measurements were carried out under zero-field cooling (ZFC) and field cooling (FC).

3. Results and discussion

Figure 1 shows a XRD pattern of SmFeAsO$_{0.84}$F$_{0.16}$. Black bars at the bottom show the calculated Bragg diffraction positions of SmFeAs(O, F). They correspond with almost all of the obtained peaks except for the Si peaks. However, several weak peaks from SmOF, SmAs and FeAs are also detected. The inset shows the expanded view near the main peak (102) of SmFeAs(O,F). The intensities of the peaks for SmOF and SmAs gradually increase when $x > 0.18$. On the other hand, in all samples with $x < 0.16$, their intensities are quite small and almost comparable. Additionally, the gradual shift of the main peak (102) to a higher angle is observed in samples from $x = 0$ to $x = 0.16$. However, the shift is almost inhibited above $x = 0.18$. The lattice parameters and cell volume can be estimated by these peak shifts. The $a$ lattice parameter versus nominal amount of fluorine is shown in figure 2. From $x = 0$ to $x = 0.04$, it shows a gradually decreasing trend, then the slope rapidly becomes steep from $x = 0.04$ to $x = 0.16$. These decreases indicate an increase in fluorine concentration. When $x > 0.16$, although the reduction rate decreases, the $a$ lattice parameter linearly decreases with an increasing nominal amount of fluorine. This also suggests that fluorine continues to be slightly introduced into SmFeAs(O,F), when $x > 0.16$. When $x = 0.26$, the smallest value of the $a$ lattice parameter is observed. The inset shows the cell volume versus the nominal amount of fluorine. A similar behavior to the $a$ lattice parameter is observed.

Figure 3 shows the temperature dependence of resistivity for $x = 0.02, 0.06, 0.08, 0.10, 0.16$ and 0.26. The behavior of resistivity obviously changes according to the change of fluorine concentration. When $x = 0.02$, although superconductivity is not obtained, an anomalous kink is observed at around 145 K. This anomaly shifts to a lower temperature and the hump becomes smaller with increasing...
Figure 3. Resistivity versus temperature from 5 to 200 K for samples with $x = 0.02, 0.06, 0.08, 0.1, 0.16$ and $0.26$. Black and red arrows denote the anomalous kink and superconducting transition respectively.

Figure 4. Resistivity versus temperature for samples from $x = 0.12$ to $x = 0.26$. Inset shows the expanded view near $T_{c\text{onset}}$ of the sample with $x = 0.26$. Red lines are fitted lines for an estimation of $T_{c\text{onset}}$.

Figure 5. Magnetic susceptibility versus temperature for the samples with $x = 0.16$ and $x = 0.26$. Inset shows the expanded view near $T_{c\text{onset}}$ of the samples. The magnetic field is 1 Oe.

Table 1. Superconducting transition temperatures for each nominal amount of fluorine.

| $x$  | $T_{c\text{onset}}$ (K) | $T_{c\text{zero}}$ (K) | $T_{c\text{anom}}$ (K) |
|------|------------------------|------------------------|------------------------|
| 0    | —                      | 147.1                  | —                      |
| 0.02 | —                      | 145.2                  | —                      |
| 0.04 | —                      | 144.7                  | —                      |
| 0.06 | —                      | 129.5                  | —                      |
| 0.08 | 7.6                    | —                      | —                      |
| 0.1  | 39.1                   | 30.31                  | —                      |
| 0.12 | 54.4                   | 49.7                   | —                      |
| 0.14 | 55.9                   | 51.3                   | —                      |
| 0.16 | 57.4                   | 53.7                   | —                      |
| 0.18 | 57.6                   | 53.5                   | —                      |
| 0.2  | 57.7                   | 53.3                   | —                      |
| 0.22 | 57.8                   | 52.9                   | —                      |
| 0.24 | 58.4                   | 52.7                   | —                      |
| 0.26 | 58.1                   | 52.2                   | —                      |
| 0.28 | 57.7                   | 50.9                   | —                      |
| 0.3  | 57.9                   | 51.2                   | —                      |

of figure 4. On the other hand, the maximum value of $T_{c\text{zero}}$ is obtained at 53.7 K when $x = 0.16$. A decrease in $T_{c\text{zero}}$ is observed for $x > 0.16$. $T_{c\text{onset}}$, $T_{c\text{zero}}$, $T_{c\text{anom}}$ and the cell volume of each sample are listed in table 1.

The temperature dependence of magnetic susceptibility for the samples with $x = 0.16$ and $0.26$ is shown in figure 5 and the demagnetization factor has been taken into consideration. These samples show a sharp diamagnetic transition and a high superconducting volume fraction. The inset shows ZFC and FC close to $T_c$. Although the magnetic susceptibility of the sample with $x = 0.26$ starts to rise at a lower temperature compared with that of the sample where $x = 0.16$, a higher $T_c$ is obtained in the sample with $x = 0.26$. These transition temperatures are observed at 57.5 and 56.5 K. The $T_c$ obtained from the magnetization measurement is slightly lower than those obtained from the resistivity measurement. Moreover, the superconducting volume fractions reach 97% and 90% in these samples ($x = 0.16$ and 0.26) respectively. The decrease in the superconducting volume fraction of the sample with higher fluoride concentration. When $x = 0.08$, the first appearance of $T_{c\text{onset}}$ is observed at 7.6 K, however, the resistivity does not reach zero at 5 K. $T_{c\text{onset}}$ increases rapidly with increasing fluoride concentration, going above 55 K when $x > 0.14$. Moreover, the hump almost disappears, and the resistivity of the normal state shows linear behavior. The expanded view of the temperature dependence of resistivity near $T_c$ is shown in figure 4. Although samples with $0.12 < x < 0.26$ show the same behavior, $T_{c\text{onset}}$ gradually increases. When $x = 0.26$, the highest value of $T_{c\text{onset}}$ is observed at 58.1 K, as shown in inset of table 1.
fluorine concentration is thought to correlate with the increase in the impurity phases observed in figure 1.

Figure 6 displays the phase diagram of SmFeAsO$_{1-x}$F$_x$ in terms of $x$. The crystallographic transition from the tetragonal to the orthorhombic structure for undoped SmFeAsO is known to be at around 150 K [2, 6]. In this study, the kink of resistivity caused by this transition is observed at 147–144 K when $x < 0.06$. This transition disappears and superconductivity in SmFeAsO$_{1-x}$F$_x$ simultaneously appears between $x = 0.06$ and 0.08. $T_c$ (onset) rapidly increases above $x = 0.08$. Whereas, the slope of the $a$ lattice parameter changes at $x = 0.16$, as shown in figure 2, and the intensity of impurities starts to increase from $x = 0.16$, as shown in the inset of figure 1. This means that the nominal amount of fluorine is almost same as the actual amount of fluorine up to $x = 0.16$. Moreover, it is also found that fluorine is not so easily substituted over $x = 0.16$. However, the $a$ lattice parameter gradually decreases over a nominal amount of $x = 0.16$. The maximum value of $T_c$ (onset) is obtained at $x = 0.26$ and simultaneously this sample shows the smallest value of the $a$ lattice parameter. $T_c$ (onset) is decided by the strongest areas of superconductivity. Although the sample with $x = 0.26$ contains many impurities, it also contains a large amount of fluorine. Therefore this sample locally composes a strong superconducting area. On the other hand, $T_c$ (zero) is decided by the weakest superconducting area in the polycrystalline SmFeAsO$_{1-x}$F$_x$. Therefore, when $x > 0.16$, because the samples include the many impurities, they form weak areas of superconductivity. Actually, gradual decreases in $T_c$ (zero) are observed in samples with $x > 0.16$. In this study, we enhanced the superconductivity up to 58.1 K. We might be able to obtain a higher $T_c$, if we succeed in further fluorine substitution.

4. Conclusion

We obtained a record superconducting transition temperature for an iron-based superconductor at 58.1 K by using low-temperature sintering with slow cooling. This achievement of a high superconducting transition is due to the success in the large amount of fluorine substitution. Low-temperature sintering with slow cooling does not form the amorphous FeAs phase in SmFeAsO$_{1-x}$F$_x$ and is very effective for fluorine substitution. The substitutional rate of fluorine changes at $x = 0.16$. The impurity phases start to increase from $x = 0.16$ and the superconducting volume fraction of this sample achieves 97%. This means that, up to $x = 0.16$, $x$ is highly reliable in identifying the fluorine content in SmFeAsO$_{1-x}$F$_x$ and we are able to make a phase diagram of SmFeAsO$_{1-x}$F$_x$ with more credibility.

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