

Amorphous FeAs-free $\text{SmFeAsO}_{1-x}\text{F}_x$ using low temperature sintering with slow cooling

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Abstract. We obtained the highest superconducting transition temperature of $\text{SmFeAsO}_{1-x}\text{F}_x$ at 58.1 K by using low temperature synthesis with slow cooling. We found that the low temperature sintering suppresses the formation of amorphous FeAs, and the slow cooling introduces a high level of fluorine into oxygen site. By using this method, impurity phases are not formed up to $x = 0.16$, and they gradually increase above $x = 0.16$. However, the resistivity of the normal state continues to decrease and T_c onset gradually increases with increasing fluorine concentration even when $x > 0.16$. Therefore, it is suggested that the fluorine is gradually introduced into oxygen site above $x = 0.16$.

1. Introduction

The first report of $\text{SmFeAsO}_{1-x}\text{F}_x$ was published in 2008 by Chen *et al* [1]. The superconducting transition temperature (T_c) was reported at only 43 K. Afterward, T_c was immediately improved to around 55 K [2]. Through the various researches, it is found that introduction of a high level of fluorine into oxygen site is effective to obtain the superconductivity with a high T_c . However, up to the present time, overdoped $\text{SmFeAsO}_{1-x}\text{F}_x$ has not still been reported. Therefore, how to effectively introduce fluorine is important in this system. Table 1 shows the various

Table 1. Synthesis conditions for $\text{SmFeAsO}_{1-x}\text{F}_x$

$\text{SmFeAsO}_{1-x}\text{F}_x$	Sintering temperature (°C)	T_c (K)	Reference
$x = 0.15$	1160	43	[1]
$x = 0.35$	1160-1180	52	[3]
$x = 0.20$	1160	54	[4]
$x = 0.2 + \delta$ ($\delta = 0.4$)	1100	55	[5]
$x = 0.20$	1000	56.1	[6]
$x = 0.25$	900	57.8	[7]



reports for synthesis of $\text{SmFeAsO}_{1-x}\text{F}_x$. In this table, fluorine concentrations, sintering temperatures and T_c are presented. Interestingly, T_c seems to relate with the sintering temperature. It gradually increases with decreasing sintering temperature. To obtain $\text{SmFeAsO}_{1-x}\text{F}_x$ with a high superconducting transition temperature, it is necessary to reveal the effect on a low temperature sintering.

2. Low temperature sintering with slow cooling

Figure 1 (a) and (b) show the polished surface of $\text{SmFeAsO}_{0.9}\text{F}_{0.1}$ sintered at 1200 °C and 980 °C respectively. Although a high temperature synthesis of 1200 °C produces an amorphous FeAs impurity phase, a low temperature synthesis 980 °C does not form this impurity phase. Amorphous FeAs prevents the current from flowing, because it is formed between superconducting grains. Therefore, to enhance the superconducting properties, how to remove this impurity from between superconducting grains should be considered. We found that a low temperature sintering is one of the effective methods to avoid the formation of this impurity phase. Actually, any impurities phases cannot be observed in the sample sintered at 980 °C as shown in figure 1 (b).

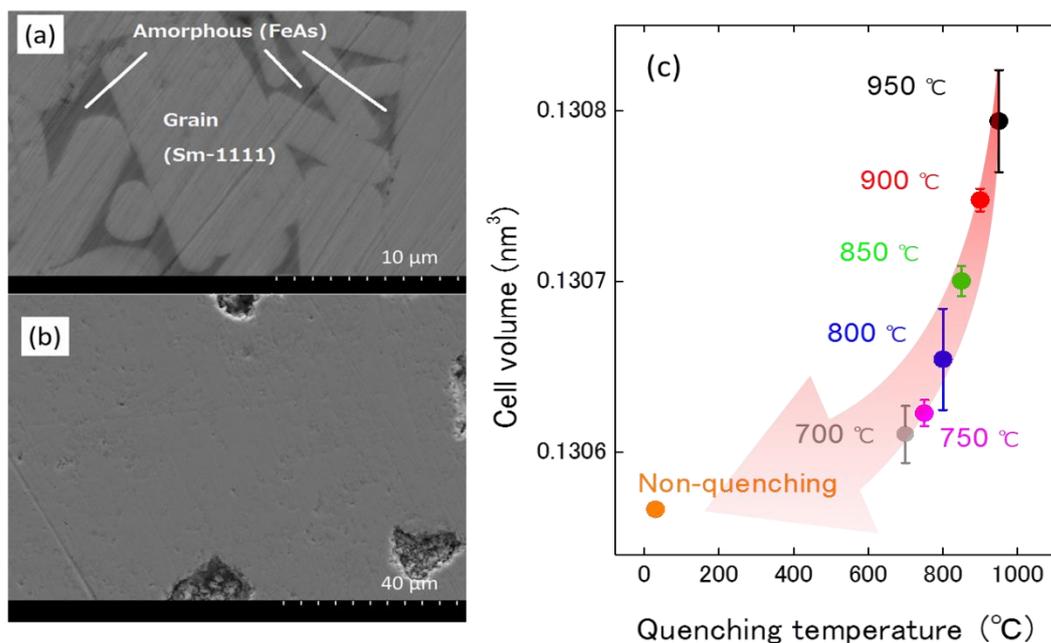


Figure 1. (a): SEM image of the polished surface of $\text{SmFeAsO}_{0.9}\text{F}_{0.1}$ sintered at 980 °C. (b): SEM image of the polished surface of $\text{SmFeAsO}_{0.9}\text{F}_{0.1}$ sintered at 1200 °C. (c): Cell volume versus quenching temperature.

In addition, slow cooling is also effective to obtain the homogeneous $\text{SmFeAsO}_{1-x}\text{F}_x$ with a high fluorine concentration. To investigate the change of fluorine concentration during slow cooling, the following experiment was performed. For the preparation of $\text{SmFeAsO}_{1-x}\text{F}_x$, stoichiometric Sm_2O_3 , SmF_3 and two precursors, composed of compounds made of Sm, Fe, and As, were ground in a mortar and compressed into pellets. The obtained pellets were heated at 980 °C for 40 h in an evacuated quartz tube. After that, from a maximum heating temperature, samples were slowly cooled at the rate of 5 °C / h down to 600 °C. During slow cooling, samples were taken out one by one from an

electronic furnace and quenched by water at the following temperatures (950, 900, 850, 800, 750, and 700 °C). A subsection Figure 1 (c) shows the cell volume versus the temperature at which the samples were quenched during the slow cooling process. The gradual decrease in cell volume can be observed at a lower quenching temperature. When the fluorine is substituted for the oxygen site, the cell volume is supposed to decrease, because the ion size of fluorine is smaller than that of the oxygen. It is found that fluorine is introduced into the oxygen site not only at the maximum temperature but also during the cooling process. Even if the same nominal amount of fluorine is mixed in synthesizing, it is demonstrated that using low temperature sintering with slow cooling makes it possible to introduce a large amount of fluorine.

Therefore, the samples with various fluorine concentration from $x = 0$ to 0.30 were prepared by a low temperature sintering with slow cooling. Figure 2 shows the XRD pattern for these samples. Impurity phases start to increase from $x = 0.16$. The intensities of the peaks for SmOF and SmAs gradually increase when $x > 0.16$. On the other hand, in all samples where $x < 0.16$, their intensities are quite small and almost comparable. This means the solid solubility limit is near $x = 0.16$. However, the resistivity of the normal state continues to decrease and T_c onset also continues to increase with increasing x as shown in figure 3. As a result, maximum T_c is observed at 58.1 K [8]. This suggests that fluorine continues to be gradually introduced into $\text{SmFeAsO}_{1-x}\text{F}_x$ above $x = 0.16$. Moreover, the a lattice parameter estimated from XRD pattern also shows the gradual decrease. This result also suggests the gradual introduction of fluorine above $x = 0.16$ [9].

In this study, we found that a low temperature sintering suppresses the formation of amorphous FeAs and a slow cooling introduces a high level of fluorine into oxygen site. By using this method, the record T_c of 58.1 K is obtained in the sample where $x = 0.26$.

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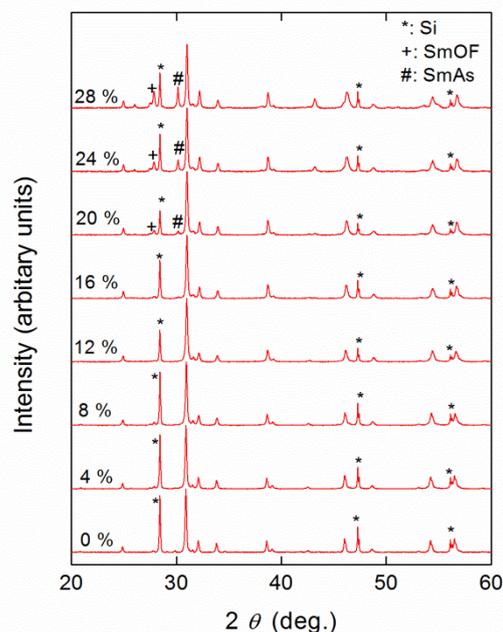


Figure 2. XRD patterns of $\text{SmFeAsO}_{1-x}\text{F}_x$ ($x = 0, 0.04, 0.08, 0.12, 0.16, 0.2, 0.24, 0.28$).

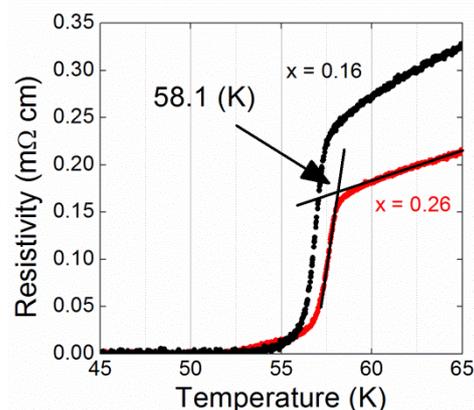


Figure 3. Temperature dependence of resistivity for $\text{SmFeAsO}_{1-x}\text{F}_x$ ($x = 0.16, 0.26$).

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