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High-Pressure Synthesis of $SmFeAsO_{1-x}F_x$ (x=0.2) Single Crystals

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$SmFeAsO_{1-x}F_x$ (x=0.2)의 고압 단결정 합성

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Abstract

Fluorine-doped $SmFeAsO_{1-x}F_x$ single crystals with the nominal value of x=0.2 were grown at 1350-1450 °C under the pressure of 3.3 GPa by using the self-flux method. Plate-shaped single crystals in the range of a few-150 μm in their lateral size were obtained. The detailed crystal structure was analyzed by using the x-ray diffractometry. Superconducting transition temperature, determined by the resistive transition, of a single crystal was about 49 K with a narrow resistive transition width of ~1 K. A relatively sharp transition, a low residual resistivity, and a large residual resistivity ratio compared with those reported for $REFeAsO_{1-x}F_x$ (RE=Sm, Nd) single crystals indicate the high quality of our single crystals.

Keywords : FeAs-based superconductor, F-doped Sm-1111, $SmFeAsO_{1-x}F_x$ single crystal

I. Introduction

A new class of FeAs-based superconductors, $REFeAsO_{1-x}F_x$ (RE=rare-earth element) [1], which were discovered at the beginning of the year 2008, still remain as a high focus of studies. These new superconductors, whose superconducting mechanism is not clearly understood yet, are anticipated to provide a clue to the basic mechanism of cuprate high-T_c superconductivity. In order to investigate the basic superconducting properties of the $REFeAsO_{1-x}F_x$ materials high-quality single crystals are highly demanded, although the growth of single crystals is known to be extremely difficult. For this reason, studies on FeAs-based superconductors are more shifted to $A_{1-x}K_xFe_2As_2$ (A=Ba, Sr, Ca) [2-4] single crystals, which can be grown with relative ease at the

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ambient pressure. However, the superconducting transition temperature (T_c) of the double-layered $A_{1-x}K_xFe_2As_2$ is usually below 38 K, while one-layered $REFeAsO_{1-x}F_x$ shows superconducting transition at about 55 K. Thus, in order to link the studies on FeAs-based superconductors to the mechanism of high-T_c superconductivity, a longstanding issue, investigation on the single crystalline $REFeAsO_{1-x}F_x$ is more desired.

In spite of many efforts, up to date only a few groups have reported the successful growth of single crystals out of fluorine-doped $REFeAsO_{1-x}F_x$ (RE=La, Pr, Nd, Sm, Gd) materials [5-8]. Nonetheless, even the results obtained from these single crystals are contradictory with each other on some important issues, such as pairing symmetry and gap nature. For instance, both multi-band [9-11] and single-band [12] characters were observed. Moreover, a fully gapped order parameter [10, 12, 13] was obtained, which is contrary to the theoretical expectations [14-18]. Thus, to reach the basic consensus on a number of key issues about the FeAs-based superconductors, high-quality $REFeAsO_{1-x}F_x$ single crystals are highly demanded.

In this paper, we report on a series of new steps to establish a reliable crystal-growing scheme of fluorine-doped $SmFeAsO_{1-x}F_x$ single crystals by using a high-pressure technique. To grow high-quality $SmFeAsO_{1-x}F_x$ single crystals, rapid cooling was employed right after the heat treatment. This is to prevent the single phase formed at the high reaction temperature from being separated into several different phases such as Fe_xAs_y and $Sm_xFe_yAs_z$ for slow cooling. The phase separation is confirmed by using the energy-dispersive x-ray spectroscopy after synthesis. The size of our $SmFeAsO_{1-x}F_x$ crystals is comparable with that of $REFeAsO_{1-x}F_x$ crystals grown by others. They usually use very long heat treatment along with NaCl/KCl flux to increase the crystal size. Our scheme will provide a guidance to grow high-quality $REFeAsO_{1-x}$ superconducting single crystals and will significantly contribute to promoting the in-depth and more accurate studies on these exciting materials.

II. Experiments

For the synthesis of single crystalline $SmFeAsO_{1-x}F_x$, starting compounds of SmAs, FeAs, Fe_2O_3, Fe, and SmF_3 were finely ground to the nominal composition of x=0.2 and were pressed into a pellet. Then, the pellet sealed with a boron-nitride container was placed in a cubic pyrophyllite cell equipped with a carbon heater. These processes were done in a glove box for safety against toxic arsenic and in an argon-gas atmosphere to protect the compounds from the impurity contamination. A 14-mm cubic multi-anvil-type press was used to pressurize the whole assembly. Pressure was kept constant at 3.3 GPa during the heat treatment for 8-10 h at 1350-1450 °C, which was then followed by rapid cooling to room temperature. After the pressure was released, the final bulk was mechanically crushed to separate the single crystals from the flux.

The shape and the surface morphology of the crystals were examined using the optical microscopy and the field-emission scanning electron microscopy, respectively. The crystal structure was investigated by using the x-ray diffractometry (XRD). Superconducting properties of the bulk was analyzed by measuring the magnetization using superconducting quantum interference device (SQUID) magnetometer. The temperature dependence of the resistivity of $SmFeAsO_{1-x}F_x$ single crystals was measured using a standard four-probe technique.

III. Results and discussion

Figure 1 shows the x-ray diffraction (XRD) pattern for the polycrystalline sample of the final bulk after the synthesis procedure described above. The resulting product mostly consisted of irregular plate-shaped small single crystals. Optical microscopic images of the $SmFeAsO_{1-x}F_x$ single crystals with nominal composition of x=0.2 selected from the bulk are shown in the inset of Fig. 1. The grown crystals were in the range of 5-150 μm in lateral size and 0.5-20 μm in thickness. The main peaks of the XRD pattern are well indexed to the tetragonal ZrCuSiAs-type structure with a=3.933 Å and c=8.487 Å. The lattice constants for our sample are consistent with those reported earlier for polycrystalline $SmFeAsO_{1-x}F_x$ with nominal composition of x=0.2 [19-20] but are slightly smaller than those for F-free SmFeAsO (a=3.938 Å and c=8.511 Å) [20].

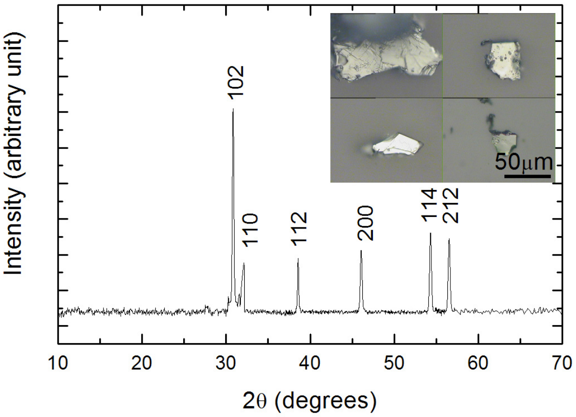

Fig. 1. XRD pattern of the $SmFeAsO_{1-x}F_x$ (x=0.2) polycrystalline sample, which contains many plate-like crystal pieces with lateral sizes of 5-150 μm. The inset shows the optical microscopy image of $SmFeAsO_{1-x}F_x$ (x=0.2) single crystals selected from the bulk grown by the self-flux method under high pressure.

Figure 2 shows the temperature dependence of zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves, at a field of 10 G, of the final bulk containing single crystals. The onset of superconducting transition takes place at about 50 K. The transition width is relatively broad, which is caused by the distribution of T_c among crystals in the bulk. It results from the differences in the F content of crystals. This is consistent with the case of $SmFeAsO_{1-x}F_x$ single crystals grown by others [5].

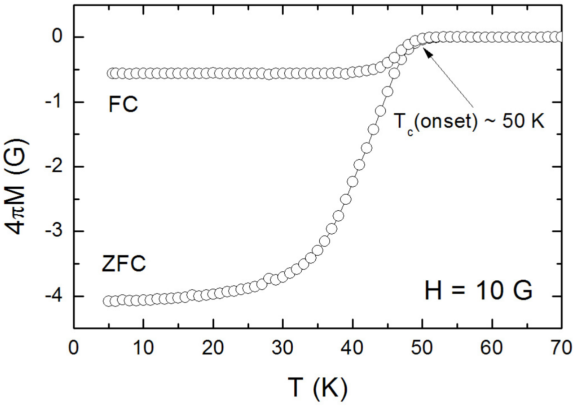

Fig. 2. Temperature dependence of low-field magnetization, 4πM, of the $SmFeAsO_{1-x}F_x$ (x=0.2) polycrystalline sample measured at a field of 10 G. The onset of superconducting transition occurs at about 50 K.

Transport measurements were carried out on several $SmFeAsO_{1-x}F_x$ single crystals, which were selected from the same batch as used in XRD and the magnetization measurements, with nominal value of x=0.2 by using a standard DC four-probe technique. Contact leads were patterned on the flat and clean surfaces of the single crystals by using the photolithography. The representative image of four-probe-patterned single crystals with the size of 70×50×20 μm^3 is shown in the upper inset of Fig. 3. The main panel presents the in-plane resistivity (ρ) of the $SmFeAsO_{1-x}F_x$ single crystal. As shown in the lower inset of Fig. 3, the onset of the superconducting transition [$T_{c(onset)}$] is about 49 K with a narrow transition width of ΔT_c~1 K by adopting the criterion of 10-90% of the normal-state ρ. The transition width ΔT_c of our $SmFeAsO_{1-x}F_x$ single crystal is smaller than the value of 2.5 K for $SmFeAsO_{0.7}F_{0.25}$ single crystals [8] and 2-4 K for $NdFeAsO_{0.82}F_{0.18}$ single crystals [7, 9] determined by the resistive transition. The residual resistivity (ρ_0) at

T_c of our single crystal is about 0.15 mΩcm, which is also smaller than $\rho_0(T_c)$=0.18 mΩcm for $SmFeAsO_{0.7}F_{0.25}$ single crystals [8] and $\rho_0(T_c)$=0.28 mΩcm for $NdFeAsO_{0.82}F_{0.18}$ single crystals [7, 9]. The residual resistivity ratio, RRR≡ρ(300 K)/ρ_0 ($T_{c(\mathrm{onset})}$)≈4, of our crystal turns out to be significantly larger than the value of 2.5 for $NdFeAsO_{0.82}F_{0.18}$ single crystals [7, 9]. The values of T_c of single crystals from the same batch vary between 40 K and 50 K as shown in Fig. 3. The relatively narrow transition width, the low residual resistivity (ρ_0), and the large residual resistivity ratio (RRR) of a unit piece of single crystal confirm that crystals grown by our high-pressure scheme is of superior quality.

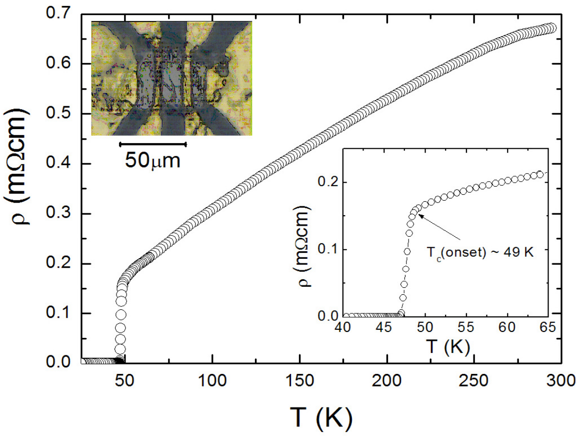

Fig. 3. Temperature dependence of the resistivity in zero magnetic field for the $SmFeAsO_{1-x}F_x$ (x=0.2) single crystal selected from the same batch for the crystal used in Figs. 1 and 2. The upper inset shows the optical microscopy image of the four-probe-patterned crystal. The lower inset shows a magnified view of $\rho(T)$ near the superconducting transition.

IV. Conclusion

We report the successful growth of $SmFeAsO_{1-x}F_x$ single crystals with the nominal composition of x=0.2 under high pressure. The XRD peaks indicate a well-defined tetragonal ZrCuSiAs-type structure of our single crystals. Superconducting properties of $SmFeAsO_{1-x}F_x$ were investigated by measuring the magnetization and the resistance. The magnetization of a collection of small $SmFeAsO_{1-x}F_x$ single crystals and remnant flux reveals a wide variation of T_c, which indicates the varying F contents among crystals. However, various transport properties of a unit piece of single crystal indicate the superior quality of our crystals. Our scheme will provide a good guidance to the growth of high-quality F-doped single crystals of Fe-based superconductors.

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