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Growth of single crystal $PrFeAsO_{1-y}$ and its characterization

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ABSTRACT

We have successfully grown single crystals of oxygen deficient oxypnictide superconductor $PrFeAsO_{1-y}$ using high pressure synthesis technique. Typical crystal size is about $600 \times 800 \times 30\ \mu m^3$, with its $T_c = 44$ K. Their resistivity measurements under magnetic field yield the anisotropic factor $\Gamma \sim 5$, consistent with previous results on smaller single crystals.

1. Introduction

The research of high-T_c superconductivity has been one of the main subjects in condensed matter physics. So far, the highest-T_c superconductivity is known to occur in the materials containing two-dimensional copper oxide planes. Recently, Kamihara et al. discovered the 26 K superconductivity in iron-based oxypnictide LaFeAs(O, F) [1]. Soon T_c raises to above 50 K with the replacement of La by other Lanthanoid (*Ln*) such as Nd, Sm, and Gd [2], which makes this material to be the second highest-T_c superconductor next to cuprates. Intense studies have been done on this material. Unfortunately, many studies have been done on polycrystalline samples due to the lack of sizable single crystals. Studies using single crystals have the advantages on precise physical property measurements such as STM/STS and ARPES, including estimation of the anisotropy. As for the $BaFe_2As_2$ (Ba122) based materials, several groups have reported the successful growth of large size (mm size) single crystals. On the other hand, in *Ln*FeAs(O, F) (*Ln*1111) system, there are only three papers about single crystal growth [3–5]. And the crystal size is at most few hundreds micron size, much smaller than the Ba122 system. Since small single crystal size limits the variation of the physical property measurements, we need big single crystals. For example, resistivity (without using FIB technique), STM/STS and ARPES measurements usually require 0.5 mm size crystal, while optical measurement may need 1.5 mm size. In the case of neutron scattering, 1 cm size would be necessary. Because *Ln*1111 system is the highest T_c material among the Fe-based pnictide superconductors, it is important to study this material to elucidate the mechanism of high-T_c superconductivity. Therefore we have tried to grow big Pr1111 single crystals. In this study, we have succeeded to grow Pr1111 single crystals and characterized them.

2. Experimental method

High-pressure technique has been applied to grow the single crystals, which have few advantages, (a) safety (free from arsenic evaporation), (b) speedy synthesis, and (c) experience in synthesizing polycrystalline samples. In addition, oxygen deficient $LnFeAsO_{1-y}$ can be synthesized only in using high-pressure technique so far. Single crystals of $PrFeAsO_{1-y}$ have been grown by high-pressure method using belt-type-anvil apparatus. Powders of PrAs, Fe, and Fe_2O_3 were used as the starting materials. PrAs was obtained by reacting Pr chips and As pieces at 500 °C for 10 h and then 850 °C for 5 h in an evacuated quartz tube. The starting materials with their nominal compositions of $PrFeAsO_{0.7}$ were mixed with flux, and then ground by an agate mortar in a glove box filled with dry nitrogen gas and pressed into pellets. The samples were grown by heating the mixtures in BN crucibles under a pressure of about 2 GPa at 1300–1400 °C for 2 h. We have tried the following flux candidates, (a) no flux (stoichiometric), (b) As, (c) FeAs, (d) Fluorine: PrFeAs(O, F).

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3. Results and discussion

Table 1 summarizes the present results of the single crystal size for several fluxes. Without any flux, crystals grew up to about 200–300 μm as grain growth. When we add arsenic as a flux, crystals grow to about 500–800 μm. In case of FeAs, only FeAs single crystals have been grown. This result suggests that there is a eutectic point between PrFeAsO and FeAs compositions below 40at% in FeAs. In the fluorine-doped stoichiometric case, PrFeAs(O, F), single crystals were successfully grown. The obtained crystal sizes are of the same order as the oxygen-deficient ones. Note that our crystals grow to one order larger than the previous reports [3–5]. Fig. 1 shows photographs of a grown single crystal with arsenic flux, which has shiny ab-plane surface. The crystal size is about $500 \times 200 \times 30\ \mu m^3$. Laue photograph shows fourfold symmetry pattern, confirming that the sample is a single crystal. Sharp (0 0 *l*) peaks in the X-ray diffraction pattern leads to *c*-axis lattice length of 8.5668 Å.

Table 1
Grown single crystal sizes for several fluxes.

Flux	Content (at%)	Crystal size (μm)
No flux		200–300
As	0.2–0.4	~800
FeAs	0.4	No crystal
F-dope		~800

Fig. 1. Photograph of single crystal $PrFeAsO_{0.7}$ grown by high-pressure method. Length scale is presented in the arrow.

Fig. 2a shows the magnetic susceptibility as a function of temperature, indicating $T_c = 44$ K (see the inset). External magnetic field 5 Oe is applied along *c*-axis direction. We measured resistivity by conventional four-probe method without using FIB technique. Fig. 2b shows in-plane resistivity data of two samples grown in the same batch. Sharp superconducting transition is observed at 42 K for sample 1, and slightly broad transition at 44 K for sample 2. Slight different superconducting transition temperatures may reflect the inhomogeneous growth condition in our cell under high pressure. And the downward convex behavior is seen in both samples. Resistivity value and behavior are similar to those measured by FIB technique [6].

Fig. 3 shows the in-plane resistivity under magnetic field ($H = 1$ T ~ 7 T) for the magnetic field perpendicular to the *ab*-plane ($H \perp ab$), parallel to the *ab*-plane (and current parallel $H \| ab \| I$ or perpendicular $H \| ab,\ H \perp I$) direction. The effect of magnetic field is prominent for $H \perp ab$, in which the resistivity transition broadens rather than parallel shift.

This is the typical behavior of vortex flow region below upper critical field H_{c2}. However, we obtained H_{c2} as effective values at various positions of the resistivity drop from normal resistivity just above T_c which we defined cut percentage as shown in Fig. 4. Both $H \| ab \| I$ and $H \| ab,\ H \perp I$, change is smaller than $H \perp ab$. The results are consistent with the notion that the supercurrents flow along FeAs planes.

We estimated the anisotropic factor (Γ from the magnetoresistance. Γ is defined by $\Gamma = (H^{ab}_{c2}/H^{c}_{c2})$. Here, (H^{ab}_{c2}/H^{c}_{c2}) is the upper critical field(H_{c2}) along *ab*-plane (*c*-axis). Fig. 4 shows the temperature dependences of the upper critical field (H_{c2}) plot for (a) $H \perp ab$ and (b) $H \| ab \| I$ defined by the drop of the resistivity compared to the normal state value. Γ value is estimated from the slope of the line (dH_{c2}/dT). Fig. 5 is the cut percentage dependence of Γ. Within the error bar, Γ is about 5. In comparison to our value, Ying Jia et al. estimated $\Gamma \sim 4.9$–4.34 from the resistivity measurement using FIB technique [5]. And L. Balicas et al. reported $\Gamma \sim 9$ from torque magnetometry [7]. Thus, the estimated $\Gamma \sim 5$ is comparable to other group's value.

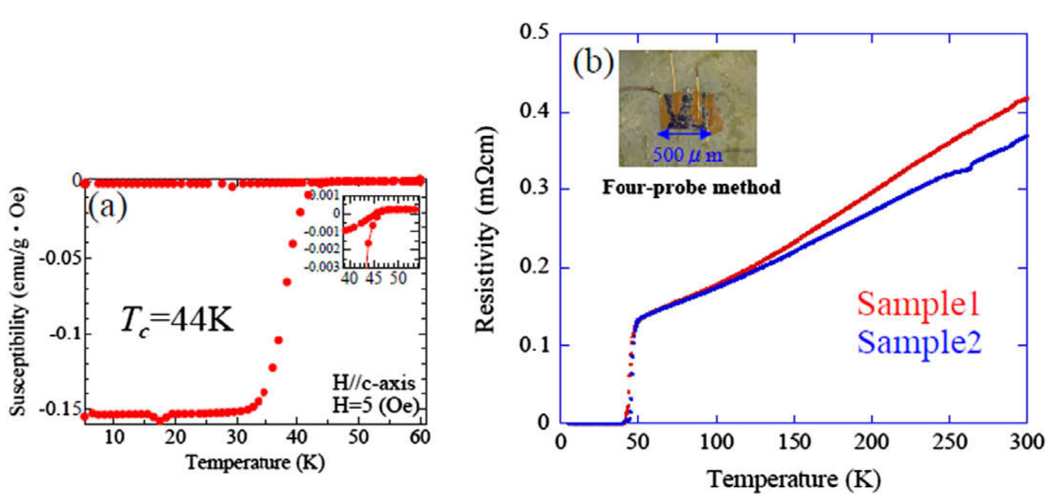

Fig. 2. Temperature dependences of (a) magnetic susceptibility and (b) in-plane resistivity data of single crystal $PrFeAsO_{0.7}$.