Synthesis and superconductivity of F-free NdFeAsO$_{1-y}$

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**Abstract.** We have synthesized a series of oxygen-deficient, fluorine-free polycrystalline samples with nominal chemical formula NdFeAsO$_{1-y}$ using high-pressure technique and its phase diagram is figured, which shows the distinguishable boundary between superconducting and non-superconducting state. The $a$- and $c$-parameters were contracted with increase in the oxygen deficiency. When the $a$-parameter is reduced to 3.964 Å from that of non-superconducting sample, the superconductivity is induced with an abrupt raise of $T_c$ and the $T_c$ saturates about 53 K at $a=3.94 \sim 3.95$ Å.

1. Introduction
The recent discovery of Iron (Fe)-based oxypnictide superconductor LaFeAs(O$_{1-x}$F$_x$) with its superconducting transition temperature ($T_c$) of 26 K has motivated tremendous interest in scientific community [1]. The discovery has proposed an alternative perspective for exploring novel high-$T_c$ superconductors, besides the copper-oxide superconductors, which have been thoroughly investigated for more than twenty years. Immediately after the discovery, it was reported that the replacement of La by other lanthanide elements (Ln), such as Ce, Sm, Pr, Nd, Gd, Tb significantly improves $T_c$ exceeding 50 K [2-7]. Parent compounds LnFeAsO become superconductors through doping of electrons into FeAs layers by the partial substitution of F for O$^2$- . On the other hand, we have succeeded to synthesize oxygen-deficient NdFeAsO$_{1-y}$ with $T_c = 54$ K using high-pressure synthesis technique [8]. In this case, two electrons are doped by one oxygen defect. Ren et al. independently reported the oxygen-deficient system at the same time [9].

Crystal structure of the oxygen-deficient NdFeAsO$_{1-y}$ was analyzed by electron diffraction and electron microscopy [10]. Space group is determined to be P4/nmm (No.129) and the oxygen vacancies are concluded as the state of disorder. By using above crystal structure, Rietveld analysis of powder neutron diffraction for the series of NdFeAsO$_{1-y}$ and LaFeAsO$_{1-y}$ samples were performed [11]. The oxygen contents of the samples were estimated and the superconducting phase diagram of NdFeAsO$_{1-y}$ is established as a function of the oxygen content for the first time. Moreover, it is found that the FeAs$_4$-tetrahedrons transform toward a regular shape with increasing oxygen deficiency. The superconducting transition temperatures seem to attain maximum values for regular FeAs$_4$-tetrahedrons.

The high-pressure synthesis method has advantageous compared to the other techniques as follows. We can obtain high-purity samples safely due to a suppression of toxic As evaporation and high-
density samples due to high-pressure sintering under several GPa. The NdFeAsO\(_{1-y}\) samples were used for resistivity measurements under high-pressure [12]. As increasing pressure, the transition shows the beautiful parallel shift to lower temperatures owing to the high quality and high density of samples. Short reaction time typically 2 hours is also helpful to optimize synthesis conditions promptly. This technique also versatile for the search of new compounds and we discovered a new superconductor of (Ca,Na)Fe\(_2\)As\(_2\) by using this technique [13]. In this paper, we report the synthesis of NdFeAsO\(_{1-y}\), its physical properties and electrical phase diagram.

2. Experimentals
Polycrystalline samples were prepared by using a cubic-anvil-type high-pressure apparatus (Riken CAP-07). Powders of Fe, Fe\(_2\)O\(_3\) and a precursor of NdAs were used as starting materials. Note that there are no fluorine-containing starting materials, which significantly simplifies the sample synthesis process. The precursor of NdAs was obtained by reacting Nd and As chips at 500 °C for 15 hours and then 850 °C for 10 hours in an evacuate quarts tube. Assuming that the NdAs and Fe are free from oxygen, the starting materials were weighed to the composition ratios of NdFeAsO\(_{1-y}\). The compositions written in this paper are the intended values. We note that the actual oxygen content of the obtained NdFeAsO\(_{1-y}\) compounds estimated by neutron diffraction analysis was larger than the intended values probably due to oxidation of the NdAs and Fe powders. Oxidation of the sample during synthesis process such as the weighing, mixing also may cause as the source of oxygen gain.

The starting materials were ground with an agate mortar in a glove box filled with dry nitrogen gas. The samples were synthesized by heating the mixtures in BN crucibles under a pressure of about 2 GPa at 1200 °C for 2 hours.

Powder X-ray diffraction (XRD) patterns were measured using CuK\(_\alpha\) radiation (Rigaku RINT 1100). The dc magnetic susceptibility was measured using a SQUID magnetometer (Quantum Design MPMS) under a magnetic field of 5 Oe. The resistivity was measured by a standard four-probe method.

3. Results and discussion
Figure 1 shows the powder XRD patterns of the samples with the intended oxygen content 1-y=0.90, 0.85, 0.80, 0.75 and 0.70. The ZrCuSiAs type crystal structure, as expected for NdFeAsO (and its oxygen-deficient form), is formed as the main phase.
In the XRD pattern of $1-y=0.90$ sample, Nd$_2$O$_3$ and FeAs peaks were observed. The real oxygen content of the starting composition of $1-y=0.90$ sample would exceeded 1.0. Lattice parameters for $1-y=0.90$ and 0.85 samples were almost same, which support above possibility. The XRD pattern of $1-y=0.85$ and 0.80 samples are almost free from impurity phase, and most of the peaks can be indexed on the basis of the tetragonal structure (P4/nmm). The lattice parameters for $1-y=0.85$, 0.80, 0.75 and 0.70 samples are $a=3.9667$ and $c=8.5757$ Å, $a=3.9643$ and $c=8.5636$ Å, $a=3.9525$ and $c=8.5464$ Å, $a=3.9488$ and $c=8.5427$ Å, respectively. The $a$- and $c$-parameters were contracted with decrease in the oxygen content. With decreasing $1-y$ from 0.75, peaks assigned to NdAs were observed to increase.

The temperature dependence of the magnetic susceptibility for the $1-y=0.85$, 0.80, 0.75 and 0.70 samples are shown in Fig. 2. The $1-y=0.85$ sample did not show superconductivity above 5 K. The sharp drop of the magnetic susceptibility, corresponding to the onset of superconductivity is observed at around 50 K for $1-y=0.75$ and 0.70, both in the zero-field cooling (ZFC) and the field cooling (FC) curves. The volume fractions estimated from the magnitude of diamagnetic signal at 5 K are 93 % (ZFC) and 26 % (FC) for $1-y=0.70$, large enough as bulk superconductivity. We note that the $1-y=0.70$ sample has large magnetic moment above $T_c$, most likely due to some ferromagnetic impurities such as Fe$_2$O$_3$ and/or Fe. The $1-y=0.80$ sample that is located near the boundary between superconducting state and non-superconducting one showed the lower $T_c$ of 35 K with a larger transition width and smaller volume fraction.

**Figure 2.** Temperature dependence of the magnetic susceptibility for $1-y=0.85$, 0.80, 0.75 and 0.70 sample.

**Figure 3.** Electronic phase diagram drawn from the $a$-parameters and $T_c$ for the samples synthesized so far. The upper scale shows the oxygen content $1-y^*$ estimated by the neutron diffraction analysis.

Figure 3 shows the electronic phase diagram obtained by plotting the $a$-parameters and $T_c$ for the samples synthesized so far. The $T_c$ is determined from the onset of transition in magnetic susceptibility. The upper scale shows the oxygen content $1-y^*$ estimated using the linear fitting ($1-y^*=6.637a-25.373$)
of the data obtained by the powder neutron diffraction analysis [11]. Boundary between superconducting state and non-superconducting one is very clear. When the \( a \)-parameter is reduced from that of non-superconducting sample, superconductivity is induced with an abrupt raise of \( T_c \) at about \( a=3.964\text{Å} \) (1-\( y^*=0.94 \)) and the \( T_c \) saturates about 53 K at \( a=3.94\sim3.95\text{Å} \). Ren et al. also shows the phase diagram of NdFeAsO\(_{1-\delta} \), where the \( T_c \) decreases for further shrinkage of the \( a \)-parameter (~3.92 Å). We have not obtained such samples having lower \( T_c \) and short \( a \)-parameters. They synthesized the samples under a pressure of 6 GPa. The higher pressure might have introduced more oxygen deficiency, which results in the further shrinkage of the lattice parameters.

4. Summary
We have successfully synthesized oxygen-deficient, fluorine-free NdFeAsO\(_{1-\gamma} \) superconductors using high-pressure technique. Boundary between superconducting state and non-superconducting one is distinguished. The \( a \)- and \( c \)-parameters were contracted with decrease in the oxygen content. The superconductivity is induced with an abrupt raise of \( T_c \) when \( a \)-parameter was shrank below 3.964Å and the \( T_c \) saturates about 53 K at \( a=3.94 \sim 3.95\text{Å} \).

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