Synthesis of $LnFeAsO_{1-y}$ superconductors ($Ln = \text{La and Nd}$) using the high-pressure technique

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**Abstract.** The high-pressure synthesis technique is utilized for synthesizing a series of oxygen (O)-deficient $LnFeAsO$ ($Ln = \text{La and Nd}$) polycrystalline samples ranging from the undoped parent compound to the highest $T_c$ superconductor. Introduction of the O vacancy causes a decrease of lattice parameters, and superconductivity appears when the $a$- and $c$-axis lattice parameters shrink by 0.1% compared with the undoped compounds. The maximum $T_c$, 28 K for $Ln = \text{La}$ and 54 K for $Ln = \text{Nd}$, is achieved when the $a$-axis lattice parameter is shrunk by 0.2%. Upon further introduction of O-deficiency, $T_c$ goes down to less than 20 K for $Ln = \text{La}$, while the maximum $T_c$ value is sustained for $Ln = \text{Nd}$. The difference indicates that the superconducting region is much narrower for $Ln = \text{La}$ than for $Ln = \text{Nd}$.

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1. Introduction

The discovery of the 28 K superconductivity in LaFeAsO$_{1-x}$F$_x$ by Kamihara et al and the immediate enhancement of $T_c$ in related materials have demonstrated that cuprate superconductors are not the only systems that exhibit high transition temperature (high-$T_c$) superconductivity [1]–[6]. Since the above discovery, extensive efforts have been made to sort out the superconducting mechanism and to discover new superconducting materials.

Similar to the case of cuprate superconductors, it is now established that chemical substitution dramatically changes the physical properties, including $T_c$’s, of Fe-based superconductors. For $Ln$FeAsO based superconductors (where $Ln$ is lanthanide), superconductivity is induced when one introduces F-substitution [1]–[4] or O-deficiency [5, 6]. For BaFe$_2$As$_2$, superconductivity with the highest $T_c = 38$ K shows up by replacing Ba by K [7]. Moreover, it is known that the $T_c$ of $Ln$FeAsO-based superconductors depends on the $Ln$ elements. The $T_c$ goes up to 55 K when one replaces La by smaller $Ln$’s, such as Nd and Sm [3]–[6]. Recently, it was reported that a high $T_c$ exceeding 50 K is sustained for those containing much smaller $Ln$’s, such as Tb and Dy [8].

Chemical substitution results in (i) the doping of carriers into the system, by introducing heterovalent ions, and (ii) deformation of the crystal structures, caused by the ionic radius mismatch of the guest elements. F- and K-substitution and O-deficiency are considered to play both roles, namely, to supply electron/hole carriers and to suppress the crystal structural transition occurring in the parent compounds. As for the case of $Ln$ substitution, smaller $Ln$ atoms result in the shrinkage of the lattice parameters and modify the bond length/angles of the crystal structure. Based on the structural analysis of the $Ln$FeAsO systems, a correlation between $T_c$ and the bond angle of the FeAs$_4$ tetrahedron is proposed [9, 10].

In order to understand the role of chemical substitution, it is necessary to prepare a series of samples with controlled stoichiometry and to characterize their physical properties in a systematic way. In this study, we have tried to establish a method for preparing O-deficient $Ln$FeAsO$_{1-x}$ samples with $Ln =$ La and Nd by employing the high-pressure (HP) synthesis technique. In particular, we have successfully extended the doping range from the undoped ‘parent’ compound to the highest $T_c$ superconductors.

In section 2, we describe our method for sample synthesis and characterization. The results and discussions are presented in section 3. A summary is given in section 4.
2. Sample synthesis and characterization

A typical flowchart of the HP synthesis procedure is presented in figure 1. The starting materials are: grained \( Ln \) metal soaked in oil (rare metallic, Soekawa Chem, Furuuchi Chem, 99.9%, 20 mesh), As-chips with particle diameter 1–4 mm (High Quality Chem, 6N), Fe powder (Furuuchi Chem, 99.9%, 100 mesh) and \( \alpha \)-Fe\(_2\)O\(_3\) powder (rare metallic, 99.9%).

Before the HP synthesis, we synthesized \( Ln \)As precursors by making \( Ln \) and As react with each other. Compared with \( Ln \) ingots, reacted \( Ln \)As is relatively brittle and is thus useful for mixing the starting elements homogeneously, which is responsible for the purity of the phase.

\( Ln \) and As at a molar ratio of 1 : 1 are taken and sealed into a quartz ampoule. The ampoule is heated to 500 °C at a rate of 50 °C h\(^{-1}\) and maintained at that temperature for 15 h, and then the temperature is increased to 850–950 °C at a rate of 50 °C h\(^{-1}\), and the ampoule is maintained at that temperature for 10 h, followed by a furnace cooling. Since the resultant \( Ln \)As is susceptible to oxidation and releases toxic arsine (AsH\(_3\)) gas upon reaction with moisture, precaution is required in handling. In our case, all the processes were carried out within a dry, oxygen-free glove box.

\( Ln \)As, Fe and Fe\(_2\)O\(_3\) powders were taken at the molar ratio \( Ln : Fe : As : O = 1 : 1 : 1 : 1 - y \). The amount of the nominal oxygen content was controlled by changing the ratio of Fe and Fe\(_2\)O\(_3\). We obtained optimal superconductivity at the nominal oxygen content.
Figure 2. Schematic illustration of the sample cell assembly used in the HP synthesis technique.

$1 - y = 0.6 - 0.7$. However, subsequent neutron diffraction studies of the NdFeAsO$_{1-y}$ samples showed the real oxygen content to be larger than the nominal one [9]. The discrepancy arises from oxidation either of the starting materials ($Ln$As and Fe) or during HP synthesis. In this paper, we use the nominal value for $y$, due to a lack of information on the oxygen content of LaFeAsO$_{1-y}$.

A wedge-type cubic-anvil high pressure apparatus was used for the HP synthesis. The powders were encapsulated into closed containers made up of a boron nitride (BN) sleeve, and then embedded into solid media (pyrophyllite [Al$_2$Si$_4$O$_{10}$(OH)$_2$]), which transmit the pressure (typically 2 GPa) from the surrounding anvils (figure 2(a)). The samples were heated at 1050–1150°C in situ using an electrical heater that surrounds the sample container (BN sleeve), also embedded into the pressure media. The configuration of the sample cell is shown in figure 2(b).

To compare the effects of O-deficiency and F-substitution, as well as the dependence on the synthesis method, we also synthesized the F-substituted $Ln$FeAsO ($Ln = La$ and Nd) by the conventional solid-state reaction method. We used FeF$_2$ as a source of F. The detail of the sample synthesis is described in [11].
Figure 3. Powder XRD patterns for $LnFeAsO_{1-y}$ samples. (a) The results for $Ln = \text{La}$. (c) The results for $Ln = \text{Nd}$. (b, d) Enlarged view of (a) and (c) around the $(2, 1, 2)$ peaks, respectively.

Powder x-ray diffraction (XRD) patterns were measured using CuK$_\alpha$ radiation (Rigaku Ultima IV). The dc magnetic susceptibility was measured using a SQUID magnetometer (Quantum Design MPMS). The resistivity was measured by a standard four-probe method.

3. Results and discussions

In figures 3(a) and (c), we show the powder XRD patterns of $LaFeAsO_{1-y}$ and $NdFeAsO_{1-y}$, which cover from the parent non-SC (top) to the most heavily O-deficient (bottom) samples,
respectively. Nearly all the peaks can be indexed on the basis of the tetragonal ZrCuSiAs-type crystal structure with P4/nmm symmetry, as expected for LnFeAsO as well as its O-deficient form.

In figures 3(b) and (d), we represent the magnified 212 peaks from figures 3(a) and (c), which distinctly shift to higher angles with an increase in y. The shift of the peaks to higher angles indicates the shrinkage of the lattice parameters. Shrinkage of the lattice parameters with y is reasonable, considering the charge distribution between LnO layers and FeAs layers. Stoichiometric LnFeAsO is composed of an alternating stack of (LnO)$^{1+}$ and (FeAs)$^{-1}$ layers. O depletion changes the charge distribution into (NdO$_{1-\delta}$)$^{1+23}$ and (FeAs)$^{1-28}$. As a result, the
Coulomb potential between the two layers increases, which causes the displacement of these layers closer to each other, thus resulting in shrinkage along the $c$-axis. This tendency explains why HP is effective in synthesizing O-deficient $Ln$FeAsO, since pressure modifies the phase diagrams of matter towards the direction that favors smaller volume.

In figure 4, we plot the magnetic susceptibility of LaFeAsO$_{1-y}$ (figure 4(a)) and NdFeAsO$_{1-y}$, (figure 4(b)), respectively. For both cases, $y$ (nominal) = 0.1 corresponds to the undoped composition, LnFeAsO ($y = 0$). (The discrepancy between the nominal and real $y$ is due to the oxidation of the samples during the synthesis process.) They do not show superconductivity above $T_c = 5$ K. The resistivity data of the same samples (inset) exhibit an anomaly around 150 K, which is associated with a magnetic and/or structural phase transition, a common behavior observed among the parent compounds of iron arsenide [1, 2].

With an increase in O-deficiency, superconductivity shows up with onset $T_c = 19, 28$ and $16$ K for $y = 0.75, 0.7$ and 0.65 for $Ln = La$ and $T_c = 32, 52$ and $54$ K for $y = 0.8, 0.7$ and 0.65 for $Ln = Nd$, respectively. The highest $T_c$, 28 K for $Ln = La$ and 54 K for $Ln = Nd$, quantitatively agree with those obtained for F-substituted $Ln$FeAsO [1, 4], indicating that the role of O-deficiency and F-substitution is essentially the same.

At this moment, we cannot establish the relationship between $T_c$ and the real oxygen content, $y$, due to a lack of information on the latter parameter. Instead, we plot the relationship between $T_c$ and the $a$- and $c$-axis lattice parameters, which also captures the evolution of $T_c$ induced by the O-depletion. In figure 5, we plot 22 (35) data sets for $Ln = La$ (Nd), respectively, together with the data for F-substituted $Ln$FeAsO synthesized under ambient conditions (open symbols). For both cases, superconductivity is concomitant with the shrinkage of lattice parameters. In particular, one can find a common relationship between $T_c$ and the

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**Figure 5.** Relationship between $T_c$ and the lattice parameter $a$- (a) and $c$- (b) axis lattice parameters of the La- and Nd-based $Ln$FeAsO$_{1-y}$ samples.
$a$-axis length both in the F-substituted and O-deficient $LnFeAsO$. Superconductivity sets in when the $a$-axis length becomes shorter compared with the non-SC parent compound by about 0.005 Å, corresponding to $\Delta a/a = -0.1\%$. The $T_c$ increases steeply once the lattice parameters shorten beyond the threshold, reaching the highest values around $\Delta a/a = -0.2\%$.

While the F-doped and O-deficient samples share a common relationship between $T_c$ and the $a$-axis length, the relationship between $T_c$ and the $c$-axis length is different from each other. Figure 5(b) suggests that the $c$-axis of the F-substituted samples is longer than that of the O-deficient samples. This might be because more volume is required to incorporate F-substitution compared with O depletion, which results in thickening of $LnO$ layers.

Figure 5 indicates the distinct $T_c$ versus $a$-axis relationship between the Nd- and La-based $LnFeAsO$. For $Ln = Nd$, $T_c$ shows a monotonic increase with a decrease in the lattice parameter up to $\Delta a/a = 0.6\%$. For La, on the other hand, $T_c$ reaches its maximum value of 28 K at $\Delta a/a = 0.2\%$, followed by a gradual decrease down to 18 K upon further substitution. The difference indicates that the superconducting region is much narrower for $Ln = La$ than for $Ln = Nd$.

4. Summary

The HP synthesis technique has been utilized for synthesizing a series of O-deficient $LnFeAsO$ ($Ln = La$ and Nd) polycrystalline samples. Introduction of the O vacancy results in a decrease of lattice parameters, and superconductivity shows up when the $a$- and $c$-axis lattice parameters shrink by 0.1% compared with the undoped compounds. The maximum $T_c$, 28 K for $Ln = La$ and 54 K for $Ln = Nd$, is achieved when the $a$-axis lattice parameter is decreased by 0.2%. For $Ln = La$, further O-deficiency eventually results in a decrease of $T_c$. On the other hand, for $Ln = Nd$, the maximum $T_c$ value is robust against the introduction of O-deficiency, suggesting that the superconducting region is much narrower for $Ln = La$ than for $Ln = Nd$.

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6 In [5], Ren et al reported a dome-like phase diagram also in NdFeAsO$_{1-y}$, which apparently contradicts our results. However, it should be noted that our results quantitatively agree with theirs, within a range $3.93 \text{ Å} < a < 3.97 \text{ Å}$. It is reported that the decrease of $T_c$ starts to occur when $a$ is smaller than 3.93 Å, which cannot be reached in our study. The decrease of $T_c$ in LaFeAsO occurs much closer to the non-SC phase.
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