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Letter

Electrical and magnetic properties of La deficient superconductor $La_{1-x}OFeP$

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ABSTRACT

We have succeeded to prepare $La_{1-x}OFeP$ ($0 \le x \le 0.2$) by sintering La, FeO and P powders in a vacuum at 1373 K for 192 h. This is a first report of hole doped superconductivity without introducing fifth elements in the LnOFePn (Ln: rare earths; Pn: pnictogen elements). The lattice constants a and c are 0.3961 and 0.8506 nm, respectively for $x = 0$, and they are almost independent of x. However, the superconducting transition temperature T_c increases with x and has a maximum value of 7 K at $x = 0.10$ and then decreases. This indicates that the hole concentration is optimum for $x = 0.10$ and becomes over doping above $x = 0.10$. The lower and upper critical magnetic fields H_{c1} and H_{c2} are 2×10^2 and 1.7×10^4 Oe, respectively, for $x = 0.10$, which are larger than those of LaOFeP and $LaO_{1-x}F_xFeP$.

1. Introduction

Zimmer et al. firstly prepared the layered oxypnictides LnOMP (Ln: rare earths; M: Fe, Co, Ru) and investigated their crystal structure in 1995 [1]. Layered oxypnictide LnOMP has the ZrCuSiAs type crystal structure with the space group $P4/nmm$. LaO and FeP layers are stacked along the c-axis, and Fe and O atoms are surrounded tetrahedrally by P and La atoms in FeP and LaO layers, respectively (Fig. 1).

In 2005, Takano et al. succeeded to prepare almost single phase samples of LnOZnPn (Ln: La, Ce, Pr, Nd; Pn: P, As, Sb) and investigated their magnetic properties [2]. They found that LaOZnPn showed a diamagnetism and other LnOZnPn showed a paramagnetism [3]. The effective magnetic moments the latter compounds were well explained by the trivalent rare earth free ions.

On the other hand, Hosono and coworkers reported that LaOFeP was a superconductor with the superconducting transition temperature T_c of ~ 4 K [4]. Their study was followed by the development of homologous hole doped high T_c superconductors. T_c of $LaO_{1-x}F_xFeAs$ is ~ 26 K [5] and that of $LnO_{1-x}F_xFeAs$ (Ln: Pr, Nd, Sm, Gd) exceeds 50 K [6–9].

Baumbach et al. reported that the LaOFeP showed a superconductivity at $T_c = 6.6$ K in 2008 [10]. However, McQueen et al. denied the superconductivity of LaOFeP [11]. Thus, the electric properties of LaOFeP are still controversial. The stoichiometry of the sample is considered to be very important to determine the electrical properties.

Then, we have prepared the La deficient $La_{1-x}OFeP$ in order to investigate the effect of the stoichiometry. Holes are expected to be doped into FeP layers to keep the charge balance between LaO and FeP layers. This is a first report of hole doped superconductivity without introducing fifth elements in the LnOFePn compounds. In this study, we report the preparation method and their electrical and magnetic properties.

2. Experimental

Samples were prepared by the solid state reaction. Stoichiometric amounts of La (99.9%), FeO (99.9%) and P (99.9%) powders were thoroughly mixed and pressed in to bars at ~ 1 GPa in Ar atmosphere [12]. They were sealed in an evacuated quartz tube of $\sim 10^{-3}$ Pa. They were heated under the following two conditions with an intermediate grinding (Fig. 2). In the first process, they were heated at 773 K for 12 h, at 1123 K for 24 h, at 1373 K for 96 h, and finally at 973 K for 24 h. In the second process, the finally heat treatment at 973 K was omitted and the temperature was decreased from 1373 to 300 K for 12 h.

The powder X-ray diffraction (XRD) measurement was carried out by Rigaku RINT 1100. The electrical resistivity, magnetization and Hall effect measurements were carried out by Quantum Design PPMS system.

3. Results and discussion

Fig. 3(a) shows the XRD patterns of $La_{1-x}OFeP$. Although tiny amount of impurity phase FeP is observed in $x = 0$ samples, almost single phase samples are obtained for $0 \le x \le 0.2$. The lattice constants a and c are 0.3961 and 0.8506 nm, respectively for LaOFeP, and those are almost independent of x. The intensity ratio of the diffraction peaks with the Miller index (1 0 1) to (1 0 2), $I_{(101)}/I_{(102)}$ decreases with increasing of x. This change agrees with the numerical calculation (Fig. 3(b)). This fact indicates that La ions become properly deficient from the La sites.

The temperature dependences of the electrical resistivity of $La_{1-x}OFeP$ are shown in Fig. 4(a). All compounds show a

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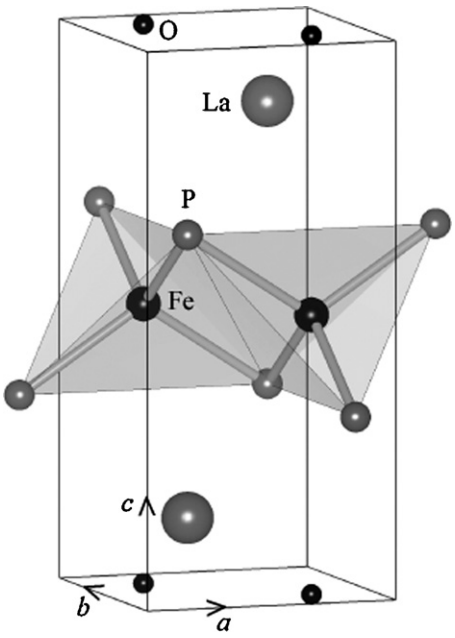

Fig. 1. Crystal structure of LaOFeP.

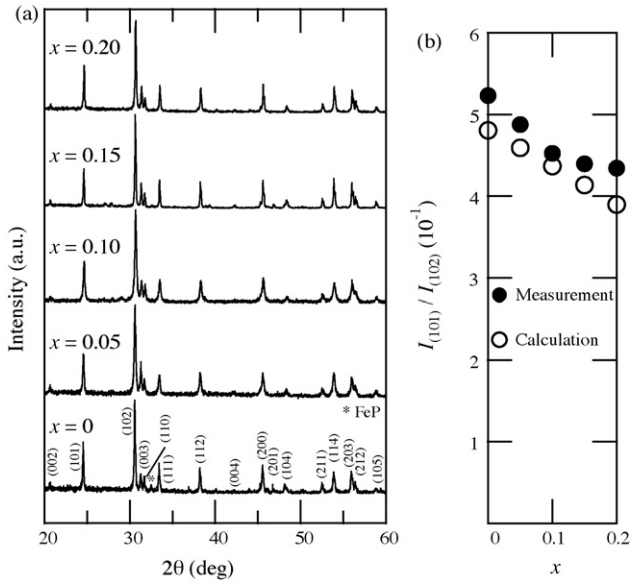

Fig. 3. (a) XRD patterns of $La_{1-x}OFeP$ and (b) the x dependences of the intensity ratios of (1 0 1) to (1 0 2), $I_{(101)}/I_{(102)}$.

superconductivity above 4 K. Fig. 4(b) shows the x dependence of the superconducting transition temperature T_c. T_c firstly increases with x and has a maximum value of 7 K at $x = 0.10$ and then decreases. This x dependence of T_c is similar to that of electron doped $LaO_{1-x}F_xFeP$ [4]. The origin of the increase and the decrease of T_c is considered to be an introduction of holes in FeP layers due to the lanthanum deficiency. Optimum hole doping is obtained at $x = 0.10$ and the range of $x > 0.10$ corresponds to the over doping region. Fig. 4(c) shows the temperature dependence of the electrical resistivity of the samples with $x = 0.10$ and 0.15 measured at 0 and 10^4 Oe. Estimated upper magnetic field H_{c2} at 0 K exceeds 10^4 Oe for both samples.

Fig. 5 shows the temperature dependences of the magnetic susceptibility measured at 10^2 Oe in zero field cooling processes. The magnetic susceptibilities are almost temperature independent above T_c. The superconducting volume fraction at 2 K are ~ 12% for $x = 0.10$ and ~ 83% for $x = 0.15$, respectively. The magnetic field dependences of the magnetization (M–H curve) at 2 K for $x = 0.10$ and 0.15 are shown in Fig. 6. The M–H curve is characteristic to the irreversible type II superconductor, where the irreversibility is not strong. The lower critical magnetic field H_{c1} is 2×10^2 and 1.5×10^2 Oe for $x = 0.10$ and 0.15, respectively. The obtained H_{c1} and H_{c2} of $La_{1-x}OFeP$ are larger than those of LaOFeP.

Temperature dependences of Hall coefficient for $x = 0$, 0.15 and 0.33 at 7×10^4 Oe are shown in Fig. 7. The hole coefficient values for $x = 0$ are minus in 30–300 K, and that seems to show almost no temperature dependence below ~240 K. The curve for $x = 0.15$ and 0.33 is drawn on plus side in 90–210 and 30–300 K, respectively. They seem to depend weakly on the temperature for the Hall coefficient of both samples. Results of Hall effect convince us that the La deficient samples are hole doped certainly.

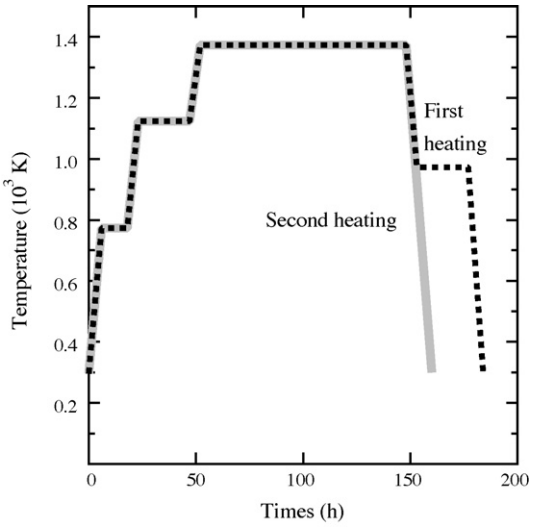

Fig. 2. Heating profile of samples; the solid line for the first heating and the dotted line for the second heating.

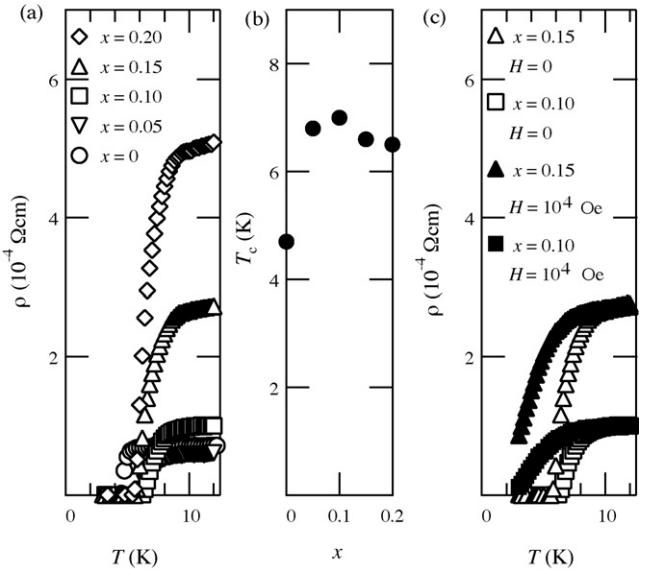

Fig. 4. (a) Temperature dependences of the electrical resistivity of $La_{1-x}OFeP$ in 0 field, (b) the x dependence of T_c and (c) temperature dependences of the electrical resistivity of $La_{1-x}OFeP$ for $x = 0.10$ and 0.15 in 0 and 10^4 Oe.

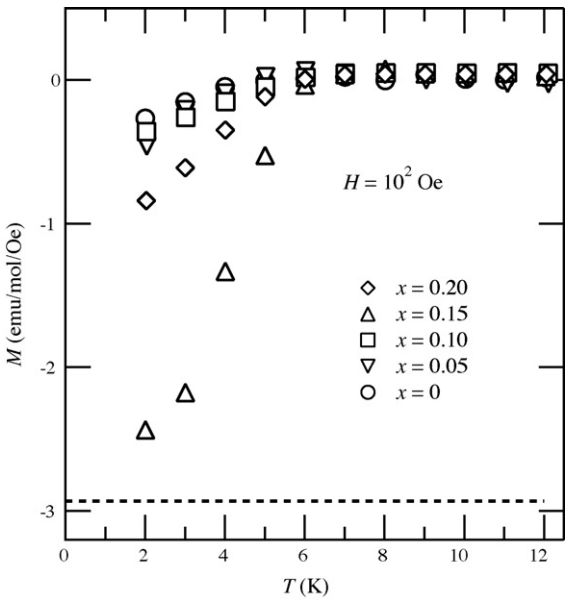

Fig. 5. Temperature dependences of the magnetic susceptibility of La_{1-x}OFeP measured at 10^2 Oe.

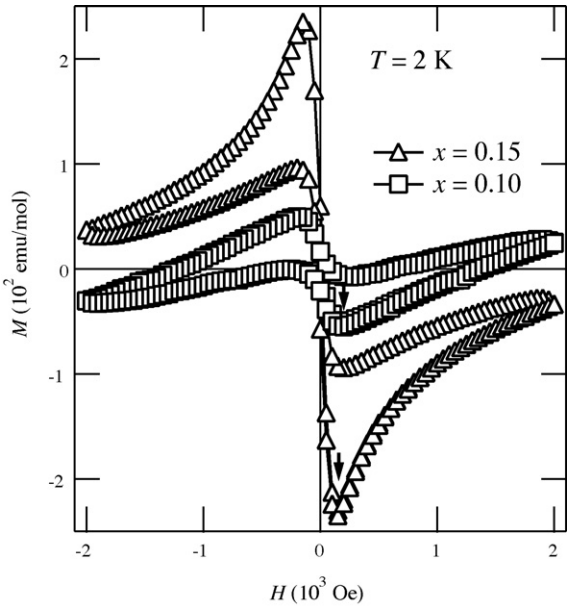

Fig. 6. Magnetic field dependences of the magnetization of La_{1-x}OFeP for $x = 0.10$ and 0.15 at 2 K. Arrows indicate the lower critical magnetic fields.

This study indicates that both types of carriers are well introduced in LaOFeP. The behavior of holes is similar to that of electrons. This is different from the cases of Cu based high T_c superconductors and carrier doped LnOFeAs.

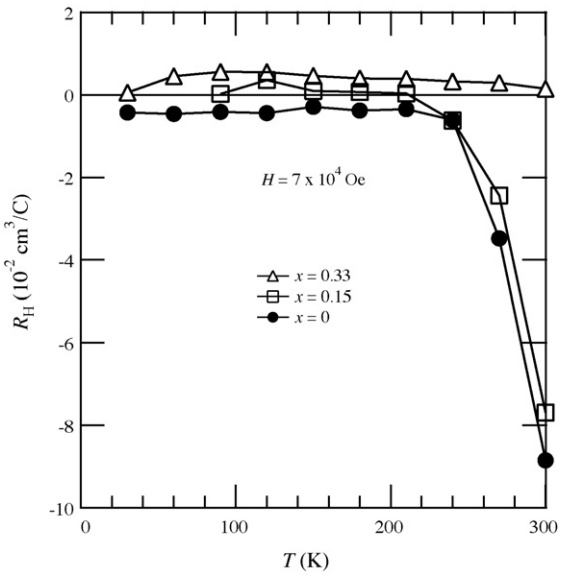

Fig. 7. Temperature dependences of Hall coefficient of La_{1-x}OFeP for $x = 0$, 0.15 and 0.33 at 7×10^4 Oe.

4. Conclusion

We have succeeded to prepare almost single phase of La_{1-x}OFeP ($0 \leq x \leq 0.2$). The x dependence of T_c is similar to that of electron doped $LaO_{1-x}F_xFeP$. The lower and upper critical magnetic fields of La_{1-x}OFeP are higher than those of reported LaOFeP and $LaO_{1-x}F_xFeP$.

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