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Iron-Based Layered Superconductor: LaOFeP

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Since the discovery of high transition temperature (T_c) superconductivity in layered copper-based oxides,[1,2] extensive efforts have been devoted to the exploration of new material systems containing transition metal ions other than copper in a hope to realize higher transition temperatures because it is widely believed that the high T_c values of the copper oxides are related to the strong electron correlation associated with the transition metal ions. Further, researchers have focused mostly on layered structures due to a freedom to control the carrier density in the transition metal oxide layer. These efforts have led to the discoveries of several novel superconductors, such as Sr_2RuO_4,[3] KOs_2O_6,[4] $Na_xCoO_2/1.3H_2O$,[5] and $LnFe_4P_{12}$ (Ln = Y, La).[6,7] Although their T_c's are much lower than those of the copper oxides, the discoveries of superconductivity in the new material systems provide valuable knowledge for understanding physics underlying the oxide superconductors as well as for finding an approach to a novel high T_c superconductor. Here we report a new class of superconductor, an iron-based layered oxy-pnictide LaOFeP. LaOFeP is composed of an alternate stack of lanthanum oxide ($La^{3+}O^{2-}$) and iron pnictide ($Fe^{2+}P^{3-}$) layers (Figure 1a).[8] It is thought that carriers flow in the two-dimensional ($Fe^{2+}P^{3-}$) layers, while impurity doping to the ($La^{3+}O^{2-}$) layer transfers the carriers generated in the ($La^{3+}O^{2-}$) layer to the ($Fe^{2+}P^{3-}$) layers, which works as "natural modulation doping", similar to the high T_c superconductors[9] and transparent P-type semiconductor copper-based oxychalcogenides.[10,11] The first synthesis and the crystal structure analysis of LaOFeP were performed by Zimmer et al.,[8] although electronic and magnetic properties have not been reported.

We employed a different synthesis process from the one reported by Zimmer et al. in this study. First, LaP, FeP, and Fe_2P were prepared by heating stoichiometric mixtures of La (Shinetsu Chemical, purity 99.5%), Fe (Kojundo Chemical, 99.9%+), and P (Rare Metallic Chemical, 99.999%) at 700 °C for 10 h in evacuated silica tubes. On the other hand, La_2O_3 was prepared by dehydrating commercial La_2O_3 powder (Kojundo Chemical, 99.99%) at 600 °C for 10 h in air. Then, nominally pure and F-doped LaOFeP [$La(O_{0.94}F_{0.06})FeP$] were synthesized by heating stoichiometric mixtures of LaP, FeP, Fe_2P, La, LaF_3 (Morita Chemical 99%), and La_2O_3 powders in silica tubes at 1200 °C for 40 h. The silica tubes were filled with atmospheric pressure of high purity Ar gas at room temperature to prevent implosion of the silica tubes. The crystal structure of the resulting powder was examined by powder X-ray diffraction (XRD; Rigaku RINT) using Cu Kα radiation and refined by the Rietveld method using the code RIETAN2000.[12] DC electrical resistivity measurement was performed by a dc four-probe technique employing silver paste as electrodes. Thermoelectric power was measured with a Cu probing to determine the charge type for the majority carrier.

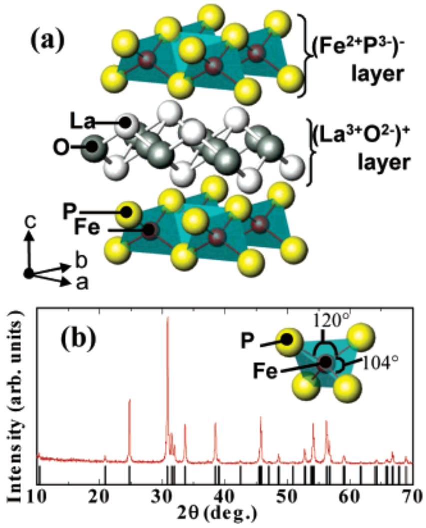

Figure 1. (a) Crystal structure of LaOFeP. The green polyhedra indicate the FeP_4 tetrahedra. (b) Observed XRD pattern for LaOFeP. The vertical bars at the bottom show the calculated positions of Bragg diffractions. Inset shows the structure of a FeP_4 tetrahedron with P−Fe−P bonding angles analyzed by the Rietveld method.

The magnetic measurements were made by a vibrating sample magnetometer (VSM; Quantum Design). The magnetic susceptibility (χ) was obtained from the magnetization in a magnetic field at <10 Oe after zero-field cooling.

Synthesized powders show dark brown color with a metallic luster, and they are stable in air. Figure 1b shows the powder XRD pattern of the obtained sample with a calculated diffraction pattern. The diffraction angles shown were calculated from the lattice parameters obtained by the least-squares fitting method ($a = b = 0.3964(1)$, $c = 0.8512(3)$ nm). All the diffractions were indexed to this crystal structure, showing the sample was single phase. The refined structure shows that the FeP_4 tetrahedron is distorted with two different P−Fe−P bonding angles of 104.39(4) and 120.18(8)° (Figure 1b). Figure 2 shows the $\rho - T$ curves for pure and F-doped LaOFeP at a magnetic field (H) of 0 Oe. It is evident that both the data exhibit metallic behavior in the electrical conductivity at temperatures >10 K. At temperatures below 5 K, a sharp drop in ρ is observed, and the resistivity vanishes at 3.2 K (Figure 3a), implying transition to a superconductivity phase. The transition temperature shifts to lower temperatures with increasing H, indicating that the magnetic field breaks the superconductivity state. The superconducting transition temperature was significantly raised by F-doping as seen in Figure 3b. The magnetic susceptibilities

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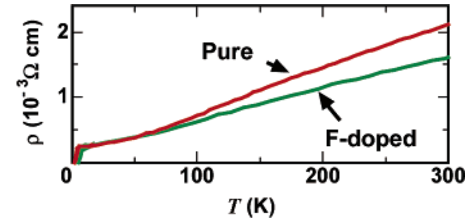

Figure 2. Electrical resistivity (ρ) versus temperature (T) for pure and F-doped LaOFeP.

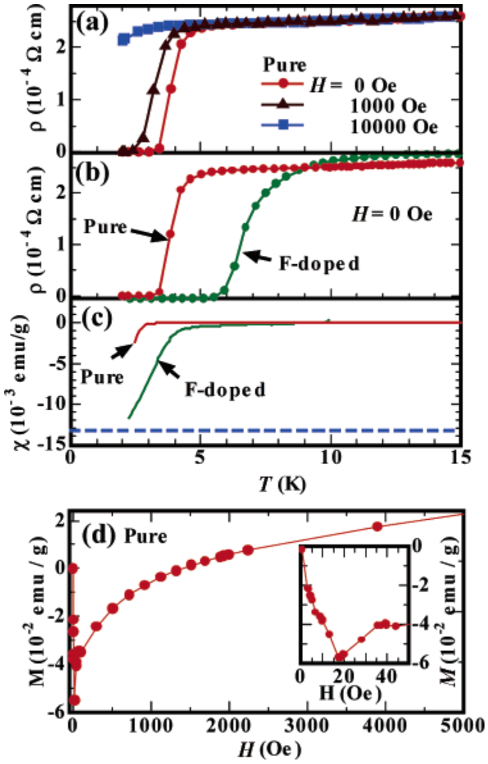

Figure 3. Superconducting properties of pure and F-doped LaOFeP. (a) Electrical resistivity (ρ) versus temperature (T) for pure LaOFeP at various magnetic fields (H). (b) ρ versus T for F-doped LaOFeP in comparison with pure LaOFeP. (c) Magnetic susceptibility (χ) versus T for pure and F-doped LaOFeP. The dashed line indicates the χ value of the perfect diamagnetism (-1.32×10^{-2} emu/g). (d) Magnetization (M) versus H for pure LaOFeP. Inset shows the expanded $M-T$ curve near H_{c1}.

(χ) measured in zero-field cooling processes (Figure 3c) reach -2.4×10^{-3} and -1.2×10^{-2} emu/g at 2.3 K for pure and F-doped LaOFeP, respectively. These values correspond to the volume fraction of the superconductivity phase of 18 and 91% (estimated from the χ value of the perfect diamagnetism). These observations, zero resistivity and perfect diamagnetism, verify the occurrence of the superconducting transition in LaOFeP at ~4 K. Figure 3d shows a magnetization ($M-H$) curve for pure LaOFeP at ~2 K. This $M-H$ curve shows a typical profile for type-two superconductor-like layered copper-based oxides, and the lower superconducting critical magnetic field (H_{c1}) is observed at around 17 Oe and the upper superconducting critical magnetic field (H_{c2}) at >1000 Oe (deduced from Figure 3a). The Seebeck coefficients of all the samples were negative in the normal state, indicating the electron carriers are responsible for the conduction. Fe-based superconductors so far discovered, $LnFe_4P_{12}$ (Ln = La, Y)[6,7,13] in the Skutterudite family and the present LaOFeP, commonly contain Fe^{2+} ions coordinated by P anions. However, there are two major differences in the crystal structure between them: (1) $LnFe_4P_{12}$ has a three-dimensional structure, while LaOFeP has a two-dimensional layered structure; (2) the coordination around Fe^{2+} is octahedral for $LnFe_4P_{12}$ but tetrahedral for LaOFeP. Similar to the layered copper-based oxide high T_c superconductors, the aliovalent ion doping to LaOFeP caused the significant difference in the superconducting transition temperature. LaOFeP has a layered structure and contains a transition metal ion different from Cu and, therefore, constitutes a new alternative material system to the layered copper-based oxides.

However, there is a marked difference in the coordination structure in LaOFeP compared with the layered copper-based superconductors reported so far; that is, a Cu^{2+} occupies a planar 4-fold square site while Fe^{2+} in LaOFeP occupies a *tetrahedral* site coordinated with four P^{3-} ions, and the tetrahedrons are linked with each other by edge-sharing to form the ($Fe^{2+}P^{3-}$) layer. As a consequence, the electrons at the Fermi level occupy Cu^{2+} $3d_{x^2-y^2}$ orbitals in the layered copper-based superconductors, while either Fe^{2+} $3d_{xy}$ or $3d_{yz}/3d_{zx}$ orbitals form the Fermi level for LaOFeP. Therefore, we like to note that LaOFeP has an importance for superconductivity physics and material exploration: the finding of the iron-based new superconductor with a different type of a layered structure will provide an opportunity for studying the mechanism of high T_c superconductivity in layered crystals. It would be informative that electronic transport at 2 K in LaO*M*P (M: +2 charge state transition metal cation) is drastically changed by varying M from Mn ($3d^5$) to Co ($3d^7$): semiconductor for Mn, superconductor for Fe, and metal for Co were observed.[14] A variety of derivatives can be synthesized by replacing the La, M, and/or P sites, which allows for the systematic study on superconductivity.

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Supporting Information Available: Crystal structure data of LaOFeP at room temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

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