CHEMISTRY OF MATERIALS

VOLUME 20, NUMBER 23 DECEMBER 9, 2008

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Communications

Synthesis of a New Member in Iron-Based Layered Superconductor: $Nd_{0.8}Th_{0.2}OFeAs$ with $T_c = 38$ K

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Received July 18, 2008
Revised Manuscript Received October 13, 2008

Recently superconductivity with high superconducting transition temperatures (T_c) up to 55 K has been discovered in the iron−pnictide compounds with the ZrCuSiAs-type structure.[1] This is the second class of systems besides cuprates that has the superconducting T_c beyond the theoretical limit of the conventional BCS theory and thus is of great importance for application and understanding of high temperature superconducivitivity.[2]

This family of compounds consists of stacked FeAs layers and LnO (Ln = La, Ce, Pr, Nd, Sm, and Gd) layers, which act as superconducting layers and carrier reservoirs, respectively.[3] Usually, the superconductivity is enhanced with the increased carrier density by the substitution of oxygen with fluorine within the LnO layers. In this paper we report the synthesis of a new superconductor: $Nd_{0.8}Th_{0.2}OFeAs$ in which the doping is tuned by the substitution of Nd^{3+} with Th^{4+}.[4] This cation substitution process adds electrons into the system as well, just like the anion replacement, and the superconducting T_c reaches 38 K.

The polycrystalline samples of $Nd_{0.8}Th_{0.2}OFeAs$ were synthesized by solid state reaction in the evacuated quartz tube by taking NdAs, ThO_2, FeAs, Fe, and Fe_2O_3 as starting materials. Fe_2O_3 was chosen to offer oxygen other than Nd_2O_3, for it is more reactive.[4] First, NdAs was prepared by sintering Nd flakes and As powder at 850 °C for 10 h, and the mixture was then ground and annealed at 850 °C for another 10 h. FeAs was prepared in a similar way, but the reacting temperature was 750 °C. Furthermore, a 5% excess of pnictide was introduced to compensate for its evaporation loss during the reaction. The powders of NdAs, ThO_2, FeAs, Fe, and Fe_2O_3 with high purity (>99.9%) have been dehydrated and weighed according to the stoichiometric ratio of $Nd_{0.8}Th_{0.2}OFeAs$. The weighed powders were fully mixed by grinding and pressed into pellets under the pressure of 15 MPa. The pressed pellets were wrapped with Ta foil and sealed in an evacuated quartz tube. The sealed tube was heated up to 940 °C, held for 10 h, and then sintered at 1150 °C for another 48 h, before it was cooled down to room temperature.

Powder X-ray diffraction (XRD) was performed at room temperature with BRUKER/AXS D8 Advance using Cu Kα radiation from 20° to 70° with a step of 0.01°. The energy dispersive X-ray microanalysis (EDX) measurements were conducted with an JSM-7000F from JEOL. The magnetic susceptibility, resisitivity, and Hall coefficient measurements were performed with a Quantum Design Physical Property

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10.1021/cm801964h CCC: $40.75 © 2008 American Chemical Society
Published on Web 11/07/2008

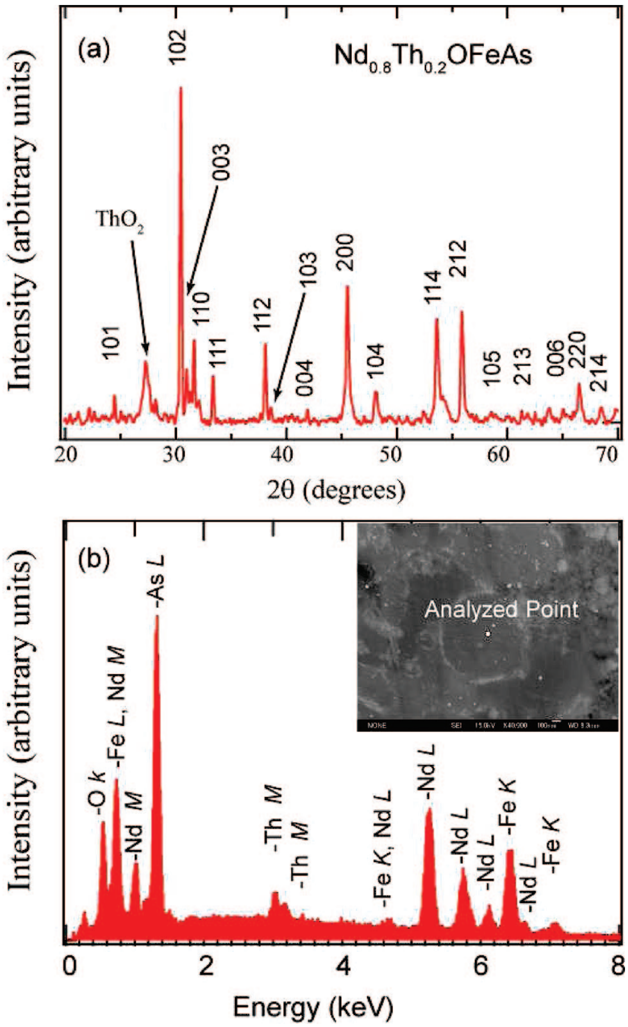

Figure 1. Powder XRD (a) and EDX data (b) of $Nd_{0.8}Th_{0.2}OFeAs$. The inset in panel b shows the scanning electron microscope picture. The white spot shows where the EDX data were taken.

Measurements System (PPMS-9T). The electrical resistivity and Hall measurements were measured with the standard four-probe and five-probe methods, respectively.

Figure 1a shows the powder XRD pattern of the $Nd_{0.8}Th_{0.2}OFeAs$ sample, which resembles that of its parent compound LaOFeAs.[5] The main impurity phase is ThO_2 which also indcates the doping level is less than nominal. All the other peaks could be well indexed on the basis of ZrCuSiAs-type structure. The least-squares fit of these peaks gives the ambient temperature lattice parameters: $a = b =$ 3.9802(3)Å and $c =$ 8.6124(5) Å. Comparing with the undoped case, we find Th substitution expands the crystal in the *a* and *b* directions and squeezes it in the *c* direction.[5−7]

In Figure 1b, we present EDX spectrum with an acceleration voltage of 15 kV. The intensity analysis gives the atomic ratio Th:Nd:O:Fe:As = 5.5:22:24:26.1:22.4. It is slightly off the nominal stoichiometric value, which indicates there are

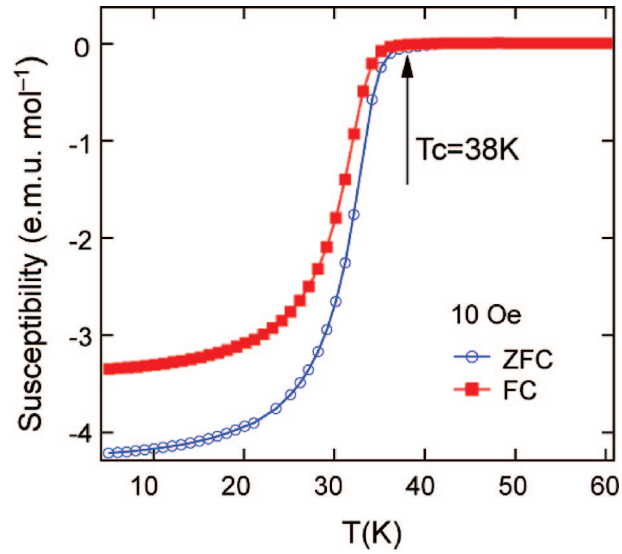

Figure 2. Temperature dependence of the magnetic susceptibility of $Nd_{0.8}Th_{0.2}OFeAs$ under 10 Oe in zero-field cooling and field cooling process.

a few percents of impurity phases. However, it shows that significant amount of Th has been doped into the system. There might be some oxygen deficiency that will also induce electron doping. However, for the oxygen deficient compound, the lattice constants were shown to decrease at all directions,[8,9] which is different from our case. Therefore, the Th doping is the dominant factor for the carrier concentration and structural changes. It is thus safe to conclude that the sample is indeed doped by Th and the doping level is close to the nominal value of 0.2.

To probe the magnetic property across the superconducting transition T_c, DC magnetic susceptibility measurements were performed on the $Nd_{0.8}Th_{0.2}OFeAs$ polycrystalline sample with and without exteral field. The supercondcutivity induced the Messner effect and is illustrated in Figure 2, where the onset temperature is about 38 K. The transition width defined from the 10%−90% is around 10 K, which is comparable with that of the best anion substituted $LnO_{1-x}F_xFeAs$ polycrystalline samples. The superconducting volume fraction is estimated to be about 15%.

The temperature dependence of the resistivity in different external fields is shown in Figure 3a. During the zero field cooling process, the onset transition and midpoint temperatures are 47 K and 43 K, respectively, which suggests the possibility for further improving the T_c. The 90−10% transition width is about 5 K. We note that the transition width in the resistivity measurement is very sensitive to the external field. And it is boardened by 1 K, 5 K, and 7 K in 0.1 Telsa, 2.5 Telsa, and 5 Telsa, respectively. On the other hand, the onset transition temperature is quite insensitive to the external field. These behaviors have been widely observed in the iron-pnictide superconductors and indicated that the

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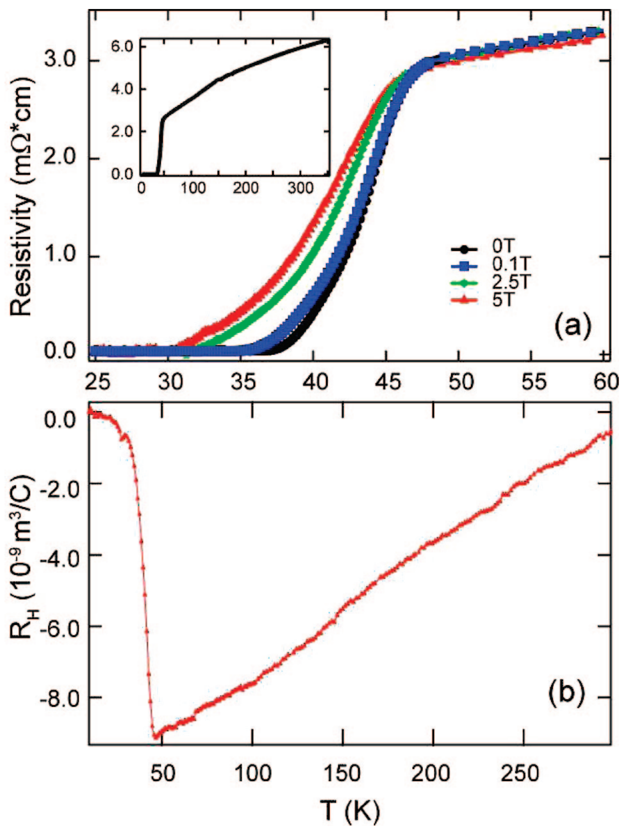

Figure 3. Temperature dependence of (a) the resistivity of polycrystal $Nd_{0.8}Th_{0.2}OFeAs$ sample under external field and (b) Hall coefficient under an external field of 1 T.

upper critical field is very high.[10] In the inset of Figure 3, resistivity in zero filled is shown from 10 K to 350 K. A change of slope could be observed near 150 K, similar to the case of $GdO_{1-x}F_xFeAs$,[11] which is possibly related to the fluctuations of the spin density wave instabilities.

The negative Hall coefficient under an external field of 1 T indicates that the charge carriers in this compound are electrons [Figure 3b]. R_H is very small at ambient temperatures and decreases with decreasing temperature. It reeaches the minimum at around 50 K and then increases again to zero as the sample enters the superconducting state. This behavior is very similar to those observed in other iron pnictides with electron type charge carriers, such as the Co-doped $BaFe_2As_2$.[12]

In summary, we reported the synthesis of a new iron−pnictide superconductor in which the charge carrier concentration was tuned by replaceing Nd^{3+} ions with Th^{4+} ions. Previously, such substitution was only found to be possible in systems with rare earth ions of relatively small radii such as Gd^{3+} and Tb^{3+}.[4,13] It illustrates that the doping could be tuned by Th^{4+} ions other than by the fluorin substitution in a wide range of iron−pnictide compounds.

Acknowledgment. We would like to thank Professor Zhu-An Xu and Professor Guang-Han Cao for their generous sharing of the starting material ThO_2, and we appreciate Prof. Ming-Wei Chen and Dr. Fujita for their great help in the EDX measurements. This work is supported by the Nature Science Foundation of China, the Ministy of Science and Technology of China (National Basic Research Program No. 2006CB921300), and STCSM of China.

CM801964H

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