Superconductivity in some heavy rare-earth iron arsenide $\text{REFeAsO}_{1-\delta}$ ($\text{RE} \equiv \text{Ho, Y, Dy and Tb}$) compounds

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*New Journal of Physics* **11** (2008) 025005 (5pp)
Received 23 September 2008
Published 27 February 2009
Online at [http://www.njp.org/](http://www.njp.org/)
doi:10.1088/1367-2630/11/2/025005

**Abstract.** Here, we report some new iron arsenide superconductors of $\text{REFeAsO}_{1-\delta}$ ($\text{RE} \equiv \text{Ho, Y, Dy and Tb}$) that were successfully synthesized by a high-pressure synthesis method with a special rapid quenching process, with the onset superconducting critical temperatures at 50.3, 46.5, 52.2 and 48.5 K for $\text{RE} \equiv \text{Ho, Y, Dy and Tb}$, respectively, as determined from the resistivity measurements.

Recently, new superconductivity was discovered in some iron arsenide $\text{REFeAsO}_{1-x}F_x$ ($\text{RE} \equiv \text{rare earth elements}$) compounds by fluorine doping, with the highest critical temperature ($T_c$) at 55 K [1]–[6]. In these compounds, the FeAs layer was found to be responsible for the occurrence of unconventional superconductivity upon electron doping induced by fluorine, and meanwhile, F-free and oxygen-deficient $\text{REFeAsO}_{1-\delta}$ compounds were also found to be superconducting at similar temperatures [7]. These quaternary superconductors form in a layered tetragonal $\text{ZrCuSiAs}$-type structure with space group $\text{P4/nmm}$ (denoted as 1111 phase), and can be described by the alternating stacking of $[\text{Fe}_2\text{As}_2]^{2-}$ layers and $[\text{RE}_2\text{O}_2]^{2+}$ layers. Besides, some different structural type iron arsenide superconductors were discovered later, such as $\text{AFe}_2\text{As}_2$ ($\text{A} \equiv \text{Ba, Sr, Ca, Eu, etc}$) by carrier doping or under pressure, $\text{Li}_x\text{FeAs}$ and $\text{FeSe}$, which

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superconducts at lower temperatures [8]–[14]. So far the electron pairing mechanism is still unclear in these superconducting materials, while all these iron arsenide superconductors have made up the second high-$T_c$ family after cuprates.

After the discovery of F-free REFeAsO$_{1-x}$ superconductors with RE = La, Ce, Pr, Nd and Sm [7], we have also investigated these quaternary compounds of all other heavy rare earth (RE) elements by a high-pressure (HP) synthesis method, and clear superconducting signals have been observed in some multi-phase samples with the $T_c$ around 50 K when RE = Gd, Tb, Dy, Ho and Y. However, a 1111 superconducting phase cannot be distinguished by x-ray diffraction (XRD) analysis except for RE = Gd [15]. It is speculated that the unobservable of 1111 phase by XRD was probably due to the line broadening effect of the tiny crystal grains and the shielding of abundant impurity phases. One possible explanation is that the 1111 phases with these heavy RE elements are metastable and easy to decompose. Independently, by synthesizing under a ultra-high pressure of about 12 GPa, F-doped 1111 phase of TbFeAs(O,F) and DyFeAs(O,F) were reported to be superconducting around 46 K [16].

Here, we report the high-$T_c$ superconductivity in some oxygen-deficient REFeAsO$_{1-x}$ (RE = Ho, Y, Dy and Tb) compounds, which were successfully synthesized and stabilized by a revised HP method with a rapid quenching approach.

The starting chemicals of Ho, Y, Dy and Tb chips and As, Fe and Fe$_2$O$_3$ powders are all with a purity better than 99.99%. At the first step, REAs powder was obtained by reacting RE pieces and As powders at 650 °C for 12 h and 1180 °C for 40 h, and then thoroughly ground into a fine powder after cooling. For the HP synthesis, appropriate amounts of REAs, Fe and Fe$_2$O$_3$ powders were mixed together according to a nominal chemical formula REFeAsO$_{0.8}$ and then ground thoroughly and pressed into small pellets. The pellet was sealed in boron nitride crucibles and then mounted on a six-anvil high-pressure synthesis apparatus. After applying a high pressure of 5 GPa, the temperature was increased to 1000 °C by electrical heating, and sintering for 1 h while keeping the pressure constant. Here, a special rapid cooling process was adopted. After switching off the power, the sample was quickly quenched to room temperature by water cooling within about 1 min and then the pressure was released (HP method). The rapid quenching process was supposed to keep the metastable phase that formed under high temperature and high pressure. The synthesized samples are dense and hard with black color. For comparison, we have also synthesized the above mentioned REFeAsO undoped compounds in a sealed evacuated quartz tube at 1180 °C for 60 h (AP method).

The phase purity and structural identification were characterized by powder XRD analysis on an MXP18A-HF-type diffractometer with Cu-K$_\alpha$ radiation from 20° to 80° with a step of 0.01°. The XRD results indicate that for the 1111 REFeAsO phase of the AP samples, only TbFeAsO compound was obtained, with the lattice parameters $a = 3.898(1)$ Å and $c = 8.404(2)$ Å, while other rare earth elements cannot form the parent 1111 phase by the AP method. The XRD pattern of the AP TbFeAsO sample was plotted in figure 1, together with a calculated pattern for identification of the 1111 phase. For the HP samples, besides the reported 1111 phases for RE = Dy and Tb, the same phases for RE = Ho and Y were successfully prepared here. The XRD patterns for HoFeAsO$_{1-x}$ and YFeAsO$_{1-x}$ were also plotted in figure 1, and the main diffraction peaks for the 1111 phase were pointed out by arrows. For all these samples with heavy RE metals, impurities always exist in the synthesized samples, and the main impurity phases were identified to be RE$_2$O$_3$, REAs and FeAs, which are all not superconducting in the measuring temperature, these impurities were identified in the case of YFeAsO$_{1-x}$ in figure 1. These REFeAsO$_{1-x}$ phases were speculated to be metastable and decomposed at a
Table 1. The lattice parameters and superconducting critical temperature for some REFeAsO$_{1-\delta}$ compounds (RE = Ho, Y, Dy and Tb).

| REFeAsO$_{1-\delta}$ | a (Å)   | c (Å)   | Vol. (Å$^3$) | $T_c$ (onset-R) (K) |
|----------------------|---------|---------|--------------|---------------------|
| HoFeAsO$_{1-\delta}$| 3.846(2)| 8.295(3)| 122.7        | 50.3                |
| YFeAsO$_{1-\delta}$ | 3.842(3)| 8.303(5)| 122.6        | 46.5                |
| DyFeAsO$_{1-\delta}$| 3.859(1)| 8.341(4)| 124.2        | 52.2                |
| TbFeAsO$_{1-\delta}$| 3.878(2)| 8.354(3)| 125.7        | 48.5                |
| TbFeAsO              | 3.898(1)| 8.404(2)| 127.7        | –                   |

Figure 1. Typical XRD patterns for the synthesized undoped TbFeAsO (AP), superconducting YFeAsO$_{1-\delta}$ and HoFeAsO$_{1-\delta}$ (HP) compounds; the vertical bars indicate the calculated diffraction peaks for the TbFeAsO. All patterns contain impurities of RE$_2$O$_3$, REAs and FeAs, which are due to the metastability of these 1111 phases with heavy RE elements, and the impurities in the YFeAsO$_{1-\delta}$ were identified.

lower temperature. To check this point, these HP samples were annealed in a vacuum quartz tube at various temperatures in the range of 600–1200 °C. All 1111 phases quickly disappeared with annealing except for RE = Tb (here, we note that for all O-deficient 1111 superconductors, the superconductivity would be destroyed by annealing, and the 1111 phase becomes undoped with the appearance of impurities). This explains why the quenching process worked to preserve the 1111 phase. The lattice parameters of all these synthesized 1111 phases were summarized in table 1. Clearly, with the increase of ionic size of the RE elements (Ho \( \leqslant \) Y < Dy < Tb), the lattice parameters monotonically increase; and oxygen vacancy causes the decrease of lattice parameters as we have reported in [7].

The temperature dependence of resistivity for all samples was measured by a standard four-probe method from 5 to 300 K. The AP samples were not superconducting while all HP samples exhibit superconducting zero resistance at low temperatures above 40 K (as shown in figure 2), with nearly linear resistivity versus temperature behavior above the superconducting transition,
Figure 2. The temperature dependence of resistivity for the REFeAsO$_{1-\delta}$ (RE = Ho, Y, Dy and Tb) superconductors synthesized by the HP method.

Figure 3. The temperature dependence of the dc susceptibility (H = 1 Oe) for the REFeAsO$_{1-\delta}$ (RE = Ho, Y, Dy and Tb) superconductors synthesized by the HP method.

similar to the previously discovered 1111 superconductors with light RE elements. The onset superconducting transition temperatures ($T_c$ (onset)) for these REFeAsO$_{1-\delta}$ superconductors are 50.3, 46.5, 52.2 and 48.5 K for RE = Ho, Y, Dy and Tb, respectively, as shown in table 1.

The dc magnetization was measured using a Quantum Design MPMS XL-1 system. For an experimental cycle, the sample was cooled to 1.8 K in zero field cooling (ZFC) and data were gathered when warming in an applied field and then the sample was cooled under an applied field (FC) and data were collected again when warming up. The dc-magnetization data (measured under a magnetic field of 1 Oe) for all the HP samples of HoFeAsO$_{1-\delta}$, YFeAsO$_{1-\delta}$, DyFeAsO$_{1-\delta}$ and TbFeAsO$_{1-\delta}$ are shown in figure 3 with both the ZFC and FC results, with the onset diamagnetic transition temperature (determined from the ZFC curves) at 49.1, 45.2, 51.0 and 46.8 K, respectively. These are a little lower than the $T_c$ (onset) determined from the
resistivity measurements, which can be attributed to the poorer quality of these superconductors than those with light RE elements [7], because of the difficulty in forming these heavy RE 1111 phases. Nevertheless, the diamagnetic superconducting shielding fractions for all these superconductors are from 30 to 75%, which indicates the bulk superconducting behavior of these compounds.

In conclusion, superconductivity has been achieved in some layered quaternary REFeAsO$_{1-\delta}$ compounds (for RE = Ho, Y, Dy and Tb) by the introduction of oxygen vacancy through HP synthesis, and the 1111 phase structure was successfully stabilized by a rapid quenching process. Therefore, together with previous discovery, high-$T_c$ superconductivity has been discovered in all these REFeAsO$_{1-\delta}$ compounds for RE = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho and Y.

Acknowledgments

We thank Mrs Shun-Lian Jia for her kind help with resistivity measurements. This work was supported by the Natural Science Foundation of China (NSFC, numbers 50571111 and 10734120) and the 973 Program of China (numbers 2006CB601001 and 2007CB925002). We also acknowledge the support of the EC under the project COMEPHS TTC.

References

[1] Kamihara Y, Watanabe T, Hirano M and Hosono H 2008 J. Am. Chem. Soc. 130 3296
[2] Ren Z A, Yang J, Lu W, Yi W, Che G C, Dong X L, Sun L L and Zhao Z X 2008 Mater. Res. Innov. 12 105
[3] Ren Z A et al 2008 Europhys. Lett. 82 57002
[4] Chen X H, Wu T, Wu G, Liu R H, Chen H and Fang D F 2008 Nature 453 761
[5] Chen G F, Li Z, Wu D, Li G, Hu W Z, Dong J, Zheng P, Luo J L and Wang N L 2008 Phys. Rev. Lett. 100 247002
[6] Ren Z A et al 2008 Chin. Phys. Lett. 25 2215
[7] Ren Z A et al 2008 Europhys. Lett. 83 17002
[8] Rotter M, Tegel M and Johrendt D 2008 Phys. Rev. Lett. 101 107006
[9] Sasmal K, Lv B, Lorenz B, Guloy A M, Chen F, Xue Y Y and Chu C W 2008 Phys. Rev. Lett. 101 107007
[10] Jeevan H S, Hossain Z, Geibel C and Gegenwart P 2008 Phys. Rev. B 78 092406
[11] Torikachvili M S, Budko S L, Ni N and Canfield P C 2008 Phys. Rev. Lett. 101 057006
[12] Alireza P L, Gillet J, Chris Ko Y T, Sebastian S E and Lonzarich G G 2008 arXiv:0807.1896
[13] Wang X C, Liu Q Q, Lv Y X, Gao W B, Yang L X, Yu R C, Li F Y and Jin C Q 2008 Solid State Commun. 148 538
[14] Hsu F C et al 2008 Proc. Natl Acad. Sci. USA 105 14262
[15] Yang J et al 2008 Supercond. Sci. Technol. 21 082001
[16] Bos J-W G, Penny G B S, Rodgers J A, Sokolov D A, Huxley A D and Attfield J P 2008 Chem. Commun. 3634