One-step atmospheric pressure synthesis of the ground state of Fe based LaFeAsO$_{1-\delta}$ superconductor

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Abstract

We report an easy and versatile one-step route of synthesis for newly discovered Fe based superconductor LaFeAsO$_{1-\delta}$ with $0.0 \leq \delta \leq 0.15$. Instead of widely used high-pressure-high-temperature (HPHT) synthesis, we applied the normal atmosphere solid-state reaction route. The stoichiometric mixtures of Fe, La$_2$O$_3$, La and As in ratio LaFeAsO$_{1-\delta}$ with $0.0 \leq \delta \leq 0.15$ are sealed in an evacuated quartz tube and further heated at 500, 850 and 1100 °C in Ar for 12, 12 and 33 hours respectively in a single step. The resulting compounds are single phase LaFeAsO crystallized in tetragonal $P4/nmm$ structure. These samples showed the ground state spin density wave (SDW) like metallic behavior below around 150 K. In conclusion the ground state of newly discovered Fe based superconductor is synthesized via an easy one-step solid-state reaction route.

Introduction

The search for new superconducting materials got a boost after the invention of high $T_c$ superconductivity in 1987 by Muller and Bednorz [1]. Soon after various Cu based high $T_c$ superconducting (HTSc) compounds were invented with their critical transition temperatures ranging from 20 to 134 K [2-4]. However this search remained strictly confined to cuprates until the invention of superconductivity in MgB$_2$ at 40 K in year 2001 [5]. Later the superconductivity was observed at around 5 K in oxy-cobalt hydrate (Na$_x$CoO:H$_2$O) [6]. Another important
compound outside the popular cuprates family was $\text{Sr}_2\text{RuO}_4$ with triplet pairing [7]. As far as the pairing mechanisms are concerned though the $\text{MgB}_2$ still seems to follow the strong electron phonon coupling, the others; in particular the $\text{HTSc}$ cuprates, are still a scientific mystery for the theoreticians [8]. In this direction very recent reports on superconductivity of up to 55 K in REFeAsO (RE = La, Pr, Sm, Nd, Gd) had renewed the interest of scientific community to search for high $T_c$ superconductors outside the cuprates family [9-24].

The recent compound i.e. REFeAsO is the only known superconductor yet having its $T_c$ outside the so-called strong BCS (Bardeen Cooper and Schreifer) limit i.e. 40 K. Further the normal state resistivity behavior and with some other features of the REFeAsO are very similar to that of $\text{HTSc}$ cuprates [18-21]. The Fe based compound provides an opportunity to the theoreticians to think outside the cuprate families in search for the mechanism of high $T_c$ superconductivity [22-24]. The newly discovered Fe based superconducting material is mainly synthesized by the high pressure high temperature ($\text{HPHT}$) process with pressure as high as 6 Gpa at 1150 $^0\text{C}$ [9-12]. Few scant reports are for the normal pressure synthesis as well, but with complicated two or three step reaction routes [13-17]. In the current short rapid communication, we report an easy and versatile single step route for the synthesis of the ground state of the Fe based superconductor $\text{LaFeAsO}_{1-\delta}$ with $0.0 \leq \delta \leq 0.15$.

**Experimental**

Stoichiometric amounts of better than 3 N purity of As, Fe, La metal and $\text{La}_2\text{O}_3$ were weighed and mixed thoroughly in formula ratio $\text{LaFeAsO}_{1-\delta}$ with $0.0 \leq \delta \leq 0.15$. For example in case of $\text{LaAsFeO}_{0.9}$ the stoichiometric amounts used are: Fe+As+0.3$\text{La}_2\text{O}_3$+0.4La. The weighed and mixed powders are sealed in evacuated (better than $10^{-4}$ Torr) quartz tubes. The sealed quartz tubes containing various respective samples are heated at 500, 850 and 1100 $^0\text{C}$ in Ar for 12, 12 and 33 hours respectively in a single step. The x-ray diffraction patterns of these compounds are taken on Rigaku mini-flex diffractometer. The resistivity measurements are carried out by four-probe method on a close cycle refrigerator in temperature range of 12 to 300 K.
Results and Discussion

Figure 1 depicts the X-ray diffraction (XRD) patterns of fitted and observed LaFeAsO$_{0.9}$. The XRD patterns of the compound is fitted on the basis of tetragonal, $P4/nmm$ space group. Besides the main phase (tetragonal $P4/nmm$) some very small intensity un-reacted lines arising from either FeAS, or LaAs are also seen in the XRD pattern. Worth mentioning is the fact that quality of our one-step atmospheric pressure synthesized material is as good as the HPHT or the complicated multi-step route [9-21,25]. The Lattice parameters are: $a = 4.03421(23)\,\text{Å}$ and $c = 8.73545(74)\,\text{Å}$ for LaFeAsO$_{0.9}$. The co-ordinates positions and the quality of fitting parameters are given in Table 1. The XRD fitting of other samples of LaFeAsO$_{1-\delta}$ with $0.0 \leq \delta \leq 0.15$ is same to that as observed in Fig. 1 for LaFeAsO$_{0.9}$. The lattice parameters for all the studied samples are tabulated in Table 2. With increase in oxygen vacancies the $a$ and $c$ lattice parameters and unit cell volume decrease continuously. This is in agreement with a recent report on LaFeAsO$_{1-\delta}$ [25].

The Resistance versus temperature ($R$-$T$) plot for the LaFeAsO$_{0.85}$ sample is shown in Figure 2. The resistance behaviour is metallic from room temperature down to 250 K and later is semiconductor like till 150 K, below 150 K a shallow metallic step is seen down to 90 K and than again semiconducting down to 12 K. The 150 K shallow metallic step is clear indication of the spin density wave (SDW) transition of the system [9,13, 16, 19]. It is known that the ground state of this newly discovered Fe based superconductor is magnetic with SDW character [9-19, 22-24]. With induction of electron or hole carriers either by F doping [9-21,24] or aliovalent substitutions [16,25,27], the superconductivity can be introduced with $T_c$ of up to 26 K. For our sample the SDW character is reminiscent in conductivity measurements as a metallic shallow step below 150 K. Though for sack of brevity the R-T plot of only LaFeAsO$_{0.85}$ sample is shown in Fig.2, but the SDW characteristic metallic step is seen in all LaFeAsO$_{1-\delta}$ samples with $0.0 \leq \delta \leq 0.15$. Further all these samples are crystallised in single phase. Our results demonstrate that the SDW ground state of LaFeAsO$_{1-\delta}$ is versatile and stable over a wide range of oxygen content. The method of synthesis applied by us is easy and versatile and could be tailored for F doped superconducting REFeAsO$_{1-\delta}$ (RE = La, Pr, Sm, Nd, Gd) compounds.
In summary, the ground state of newly discovered LaFeAsO superconductor was synthesized via an easy and versatile one step route over a wide range of oxygen content. The method applied by us is unique and versatile and hence can be tailored easily for the F doped or substituted LaFeAsO superconductor.

Table 1. Reitveld refined parameters for LaFeAsO$_{0.90}$.

| Atom | Site | x  | y  | z       |
|------|------|----|----|---------|
| La   | 2c   | 0.25 | 0.25 | 0.1398(4) |
| Fe   | 2b   | 0.75 | 0.25 | 0.5     |
| As   | 2c   | 0.25 | 0.25 | 0.6508(6) |
| O    | 2a   | 0.75 | 0.25 | 0       |

$R_p$: 5.54\%, $R_{wp}$: 7.37\%, $R_{exp}$: 3.32\%, $\chi^2$: 4.92

Table 2. Lattice parameters and cell volume of LaFeAsO$_{1-\delta}$ ($\delta=0.0 - 0.15$).

| Sample          | $a$(Å)     | $c$(Å)     | $V$(Å$^3$) |
|-----------------|------------|------------|------------|
| LaFeAsO         | 4.0363(3)  | 8.7356(7)  | 142.322(11)|
| LaFeAsO$_{0.90}$| 4.0342(2)  | 8.7354(7)  | 142.168(17)|
| LaFeAsO$_{0.85}$| 4.0321(7)  | 8.7353(24) | 142.023(54)|

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Figure Captions

Fig. 1: Figure 1: Fitted and observed X-ray diffraction patterns of LaFeAsO$_{0.9}$.

Fig. 2: R(T) of the LaFeAsO$_{0.85}$, the SDW transition at around 150K is marked.
Fig. 1

LaFeAsO$_{0.91}$, P4/nmm

$a$ = 4.03421(23) Å
$c$ = 8.73545(74) Å

Fig. 2

LaFeAsO$_{0.85}$

$T_{SDW}$

500°C - 12 hrs
850°C - 12 hrs
1100°C - 33 hrs
Vacuum sealed & Ar flow