J. At. Mol. Sci.
doi: 10.4208/jams.040311.051411a

Vol. **3**, No. 1, pp. 89-94
February 2012

The synthesis, structural characterization and superconductivity of $FeSe_x$ with $0.80 \leq x \leq 1.20$

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Received 3 April 2011; Accepted (in revised version) 14 May 2011
Published Online 28 September 2011

Abstract. We have performed a detailed study on the synthesis, the characterization of structural phases and superconductivity of the binary $FeSe_x$ system from the Fe-rich phase into the Se-rich phase with $0.80 \leq x \leq 1.20$. The results indicate that by long-time low-temperature annealing, single phase sample could be obtained near the composition of $FeSe_{0.95}$ with the tetragonal PbO-type structure, while impurities of Fe or Fe_7Se_8 would appear if Fe enriched or Se enriched in the starting composition respectively. Bulk superconductivity was found to exist in highly Se deficient phase, but not the single phase, and superconductivity is very sensitive to the Se vacancy content. The anomalous downturn of resistivity around 100 K was eliminated in Se-rich phase, along with the suppression of the main superconducting phase.

PACS: 74.70.-b, 74.70.Ad, 74.62.Bf

Key words: iron-based superconductors, FeSe, synthesis

1 Introduction

The recently discovered superconductivity in the doped iron-based quaternary REFeAsO (RE = rare earth elements) compounds has induced intense interests on experimental and theoretical studies of iron-based materials, and the superconducting critical temperature (T_c) has been quickly increased to 55 K by a high pressure synthesis technique [1–5]. Subsequently, new superconductivity was also found in some other iron-based structure types, e.g., the 38 K T_c in the $(Ba_{1-x}K_x)Fe_2As_2$ compound with a tetragonal $ThCr_2Si_2$ structure [6], the 18 K Tc in the Li_xFeAs compound with a Cu_2Sb structure [7], and the 8 K T_c in a simple PbO-tybe compound $FeSe_x$ [8]. For the simple $FeSe_x$ superconductor, similarity has been found between it and the unconventional FeAs-based superconductors, and Se vacancy was reported to be crucial for the occurrence of superconductivity, and the T_c was also observed to be very sensitive to

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physical pressure [8–11]. Here we report a detailed study on the synthesis, superconductivity and structural phases of $FeSe_x$ binary compound from the Fe-rich phase into the Se-rich phase.

2 Sample synthesis

From the updated binary phase diagram of Fe-Se in Ref. [12], it can be seen that the tetragonal PbO-type $FeSe_x$ (had been denoted as β-FeSe, S.G. P4/nmm; here we note that this phase has been referred to α-phase in some recent publications, and we adopt the original β-phase here) forms at a lower temperature, with the Se content x in a narrow range between 0.95 and 0.97; while the hexagonal NiAs-type $FeSe_x$ (had been denoted as δ-FeSe, S.G. P63/mmc) forms at a relatively higher temperature. Currently the superconductivity was reported to well exist in a nominal composition of $FeSe_{0.88}$ composition [8], which is out of the single phase area in the phase diagram [12]. To further clarify the relationship between the structure phase, superconductivity and the Se vacancy, here the $FeSe_x$ compound with nominal compositions of $x = 0.80$, 0.85, 0.88, 0.95, 1.00, 1.05, 1.15 and 1.20 were prepared and studied. The polycrystalline samples were synthesized by a solid state reaction method. High purity (better than 99.99%) powders of Fe and Se were mixed together according to the chemical ratio of $FeSe_x$, then ground thoroughly and pressed into small pellets. The pellets were sealed in evacuated quartz tubes and then sintered in a muffle furnace. The furnace was first heated to the temperature of 680 °C (for the formation of $FeSe_x$ compound) and maintained for 20 hours and then cooled down to 400 °C and maintained for 60 hours (for the formation of PbO-type β-$FeSe_x$). The samples were finally cooled down to room temperature.

3 Results and discussion

The structural phases of all samples were characterized by powder X-ray diffraction (XRD) analysis on an MXP18A-HF type diffractometer with Cu-K_α radiation from 20° to 80° with a scanning step of 0.01°. Fig. 1 shows the XRD patterns of all the $FeSe_x$ ($x = 0.80$, 0.85, 0.88, 0.95, 1.00, 1.10, 1.20) samples. For comparison, the theoretical diffraction peaks were calculated based on the PbO-type structure, and plotted with vertical bars at the bottom of Fig. 1. The results proved that long-time low-temperature annealing helped to form β-$FeSe_x$ phase. The patterns show that the near single phase of $FeSe_x$ only exist with the sample of nominal composition of $x = 0.95$. With the increase of Fe content ($x < 0.95$), iron impurity phase appears; while with the increase of Se content ($x > 1.00$), Fe_7Se_8 impurity phase appears. These results confirmed the previous reported phase diagram, in which the PbO-type $FeSe_x$ forms a Se-deficient phase, and the composition around $FeSe_{0.95}$ is optimal to produce the single phase sample. The lattice parameters of all these samples were also calculated and will discuss hereinafter.

For the single phase sample $FeSe_{0.95}$, step-scan XRD data were collected and Rietveld analysis was used for structure refinement [13]. The refined results give the lattice parameters: $a = 3.7701(1)$, $c = 5.5207(2)$, with Fe sites at (0, 0, 0), Se sites at (0.5, 0, 0.2635) within the