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

Xiao-Li Shen*

Huazhong University of Science and Technology Wenhua College, Wuhan 430074, China

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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.

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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

*Corresponding author. *Email address:* xlshen369@gmail.com (X. L. Shen)

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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

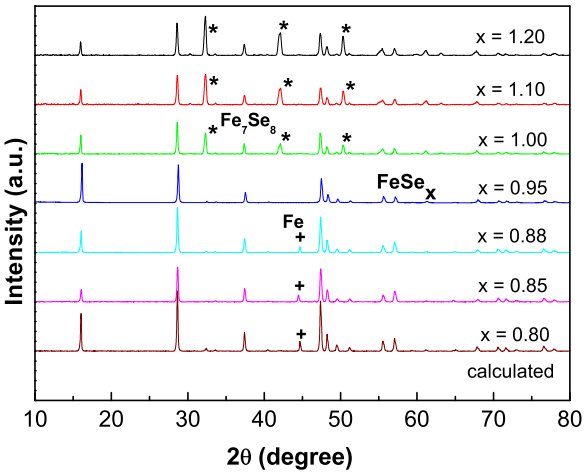

Figure 1: X-ray diffraction patterns at room temperature for the nominal $FeSe_x$ samples; the vertical bars at the bottom correspond to the calculated diffraction patterns; impurity phases of Fe and Fe_7Se_8 are marked with '+' and '*' symbols.

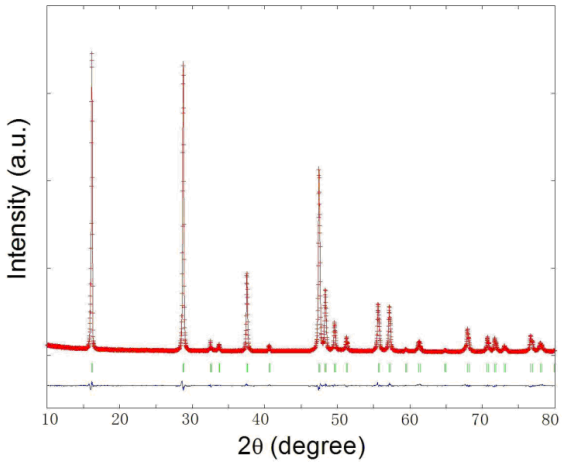

Figure 2: Rietveld refinement for the XRD pattern of the $FeSe_{0.95}$ sample. The symbol '+' represents the experimental data, the solid curve is the calculated pattern, and the difference between experimental and calculated intensities is shown at the bottom and the markers in the middle correspond to the calculated peak positions.

S.G. P4/nmm; and the occupation factor for Se is 0.951 (denoted as 1 for Fe), with the reliability factors of $R_{wp}=6.12\%$ and $R_p=2.36\%$, and the "goodness-of-fit" indicator $S=1.52$. The refinement result is shown in Fig. 2. These results indicate the near single phase of $FeSe_{0.95}$ sample and the existence of Se vacancies.

The DC electrical resistivity measurement for all $FeSe_x$ samples was performed by the standard four-probe method from room temperature down to 4.5 K with bar-shaped samples, with the electrical contacts made by indium-press. Fig. 3 shows the temperature dependence of resistivity for all the synthesized FeSex samples, with the magnified curve around 10 K at the right panel. At the normal state, all the resistivity shows a broad bump at about 240 K and exhibits metallic characteristics. A clear anomalous downturn in resistivity around 100 K can be observed for samples with $x<1$ (same as previously reported [8,9]), while it disappears in samples when $x>1$. All samples show superconducting resistivity drop at low temperature, while zero resistivity can only be observed in samples with nominal Se content $x<1$, with the highest $T_c(\text{zero})=9.0$ K for $x=0.88$. The absence of zero resistivity when $x>1$ indicates the importance of Se vacancy for the occurrence of superconductivity, and the superconductivity could be suppressed if the Se vacancy content decreases. The anomaly around 100 K was supposed to be connected with a structural phase transition around 70–100 K (from the tetragonal phase to a low temperature orthorhombic phase), and may correlate with the origin of superconductivity [8,9]. Here our results indicate clearly that with the decrease of Se vacancy concentration, this anomaly disappears (whether the structural transition disappears need further checking), and superconductivity is also quickly suppressed. Interestingly, in spite of the minor phase, the samples with $x=1.10$ and 1.20 show higher onset resistivity drop near 15 K. This indicates the existence of a small amount of superconducting phase with higher T_c, and the possibility to further increase T_c in $FeSe_x$ compound.

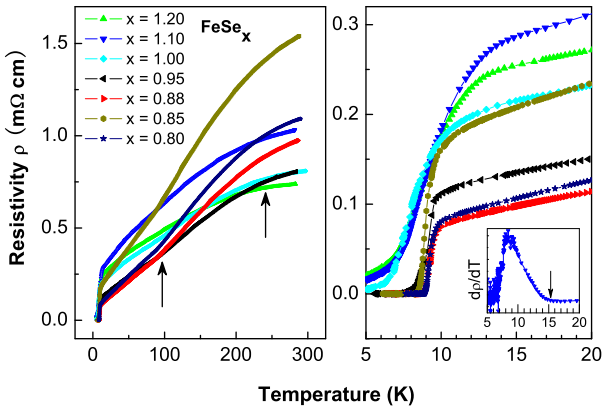

Figure 3: The temperature dependence of resistivity for the nominal composition of all $FeSe_x$ samples, with the enlarged curve at low temperature in the right panel (the inset for the differential resistivity curve of $FeSe_{1.10}$ indicates an onset of resistivity drop happens near 15 K). The arrows in the left panel indicate an anomalous hump and downturn around 240 K and 100 K respectively.

The low field DC magnetization measurement was performed on a Quantum Design MPMS XL-1 system, and all data were collected during a warming cycle under an applied field of 1 Oe after zero field cooling (ZFC) or field cooling (FC) process respectively. The temperature dependence of magnetization for all FeSex samples is shown in Fig. 4. These data indicate

that good superconductivity can only be achieved with highly Se-deficient samples. For $FeSe_x$ samples with nominal $x \leq 0.88$, the onset diamagnetic superconducting critical temperature is similar close to 8.6 K, and the sample with $x = 0.88$ has the best superconducting properties. While with the increase of Se content when $x \geq 0.95$, the superconducting volume fraction quickly decreases, and for samples with $x > 1$, only very tiny diamagnetic signal can be observed (less than 1% volume fraction). These results are consistent with the resistivity measurements, and indicate that the Se vacancy concentration is crucial for bulk superconductivity in $FeSe_x$ compound.

To reveal the relationship between the structure parameters, superconductivity and Se vacancy content in the binary $FeSe_x$ system, the lattice parameters a and c, and the T_c (onset)

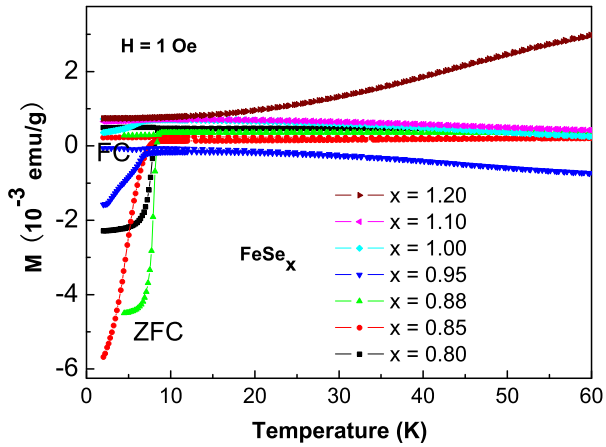

Figure 4: The temperature dependence of DC magnetic susceptibility for all $FeSe_x$ samples under zero-field-cooling (ZFC) and field-cooling (FC) process with the magnetic field of 1 Oe.

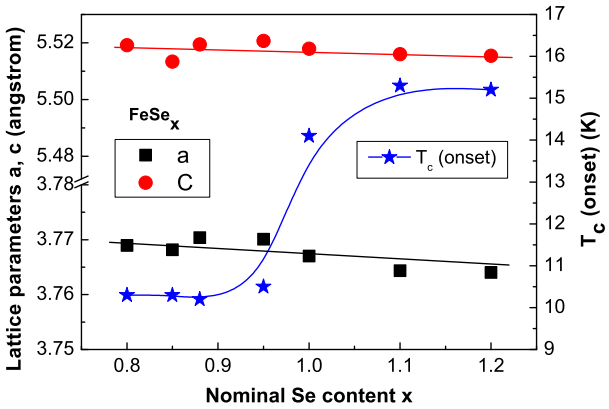

Figure 5: The relationship between the lattice parameters 'a' and 'c', the T_c(onset) and the nominal selenium content x for all $FeSe_x$ samples, with the solid lines plotted for guiding.

determined from resistivity curve were plotted upon the nominal Se content x of $FeSe_x$ compound. Only very slight decrease of a and c is observed with the increase of Se content, this indicate the crystal lattice expands a little with the increase of Se vacancy content. The T_c (onset) keeps near 10 K when $x<0.95$, while it increases to above 15 K when $x\geq 1.1$. This higher T_c phase is a minor phase as revealed from the magnetization results, and is not clear from the current results.

4 Conclusion

In conclusion, we have studied the structure phases and superconductivity for the non-stoichiometric $FeSe_x$ system. The single phase of PbO-type $FeSe_x$ compound was observed to exist near the composition of $FeSe_{0.95}$. Bulk superconductivity was observed to exist in the highly Se-deficient phase, with the highest $T_c(\text{zero})\sim 9$ K. With the increase of Se content x, this superconducting phase can be quickly suppressed, and this may correlate with the disappearance of the resistivity anomaly around 100 K that was reported to be from a structural phase transition.

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