The physical and magnetic properties of FeSe-11 superconductor

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Abstract. In this study, polycrystalline of FeSe$_{0.98}$ and FeSe$_{1.2}$ samples were synthesized by a solid-state reaction method to investigate the microstructural and magnetic properties in these systems. Different heating cycles were applied and the best synthesis cycle has been established by optimization. Samples were characterized regarding structure, composition and superconducting properties. The microstructural investigations showed that structural formation of the samples was not strictly depending on the heating cycles. Transition temperature is obtained as 10 K from Zero Field Cooled magnetization measurement.

1. Introduction

During the past seven years, a new type of Fe-based superconductor, tetragonal FeSe with a superconducting transition temperature $T_c$ of 8K, was reported [1]. As observed in the cuprates, the Fe-based superconductors exhibit interplay between magnetism and superconductivity suggesting the possible occurrence of unconventional superconducting states. Other general properties of these superconductors are the layered structure and the low carrier density. Among the Fe-based superconductors, FeSe has the simplest structure with layers in which Fe cations are tetrahedrally coordinated by Se anions [2].

The report describing the superconductivity in the tetragonal FeSe suggests that superconductivity is observed in samples prepared with significant selenium deficiency. The stoichiometry of the superconducting phase is reported to be between FeSe$_{0.82}$ and FeSe$_{0.88}$ [3]. The first powder neutron diffraction experiment also argue that selenium vacancies are present, proposing a stoichiometry of FeSe$_{0.92}$ in that particular sample [4]. Theoretical treatments of this phase have either assumed the stoichiometry to be FeSe [1,5], without accounting for the critical differences in electron count of 0.16-0.3 Se/Fe that would be present for selenium-deficient materials, or have specifically address the importance of the vacancies in giving rise to the superconductivity [6,7]. Many measurements have been reported on samples that have been prepared with the assumption that iron selenide is deficient in Se [8-12]. Many preparation techniques can be used for the synthesis of FeSe samples. These techniques are solid-state reactions, high pressure synthesis, flux growth and Bridgman methods [13]. In generally the first and second methods are used to prepare polycrystalline samples while the latters are used for the growth of FeSe single crystals.

As we have mentioned above, the superconductivity in $\beta$-FeSe is very sensitive to composition and disorder, since the nonstoichiometry and intrinsically Se deficient nature plays crucial role in the matrix. A reproducible sample fabrication procedure and prevention from the oxidation are needed.
during the preparation process. Therefore, in this study, polycrystalline of FeSe\textsubscript{0.98} and FeSe\textsubscript{1.2} samples were synthesized by solid-state reaction method to study the microstructural, superconducting properties in these systems. Different heating cycles were applied and the best synthesis cycle has been established by optimization. We emphasize here that almost single phase of FeSe can only be obtained at near a perfect 1:1 ratio of Fe to Se.

2. Experimental

Polycrystalline FeSe\textsubscript{1.2} and FeSe\textsubscript{0.98} samples were prepared by solid-state reaction method in sealed quartz tubes using high purity powders of the iron (99.999 % Alfa Aesar) and selenium (99.999 % Alfa Aesar) with appropriate stoichiometries of Fe/Se: 1/1.2 and 1:0.98, respectively. Initially well homogenized raw powders were placed into quartz tube and sealed in the glove box. For synthesis of FeSe\textsubscript{1.2} a quartz tube containing the elements in the corresponding ratio was heated up to 700°C with 3 different durations, namely 12, 24 and 36 hours. For each heating cycles, constant heating and cooling ramps of 20°C/min were used. In each step, intermediate grinding were applied in glove box under Ar atmosphere and then sealed into an evacuated quartz tubes. For the last heating stage samples were pulverized again and pressed isostatically in to a pellet of 8 mm diameter by applying an 80 kN pressure in the glove box.

For synthesis of FeSe\textsubscript{0.98}, the mixture of the elements in the corresponding ratio was heated up to 780°C with a heating ramp of 10°C/min where it was kept for 48 h. This high temperature step is required for scrubbing oxygen from the system and obtaining homogeneous product. The furnace was cooled down to room temperature with a cooling ramp of 5°C/min. Then the powder was ground and pressed again isostatically in to a pellet of 8 mm diameter by applying an 80 kN pressure in the glove box and put again in the furnace. The sample was heated up to 430°C with a heating ramp of 20°C/h where it was kept 96 h. This step is needed to avoid the low temperature decomposition of superconducting phase. Finally, the sample was taken out after the furnace cooling to room temperature.

After the heat treatment cycles, structural properties of the materials obtained were examined by X-Ray Powder diffraction. A Rigaku RadBD MaxII diffractometer and Jade 5+ refinement program was used to analyze structure. Structural parameters were calculated by using Rietveld refinement based on the Jade 6+ crystal refinement program. The microstructures of samples were investigated by using Scanning Electron Microscopy (SEM; Leo EVO 40VPX) and Energy Dispersive X-ray spectroscopy (EDX; Bruker 125 eV). The superconducting properties of the FeSe polycrystalline samples were carried out using Physical Properties Measurement Systems, (Quantum Design; PPMS-9T). Up to 9 Tesla were applied during the magnetization measurements.

3. Results and discussions

The XRD patterns of both samples are given in Fig. 1. The broad halo around 15°≤2θ≤30° in the XRD pattern of the FeSe\textsubscript{0.98} sample is caused by a sample holder with a plastic dome. We realized significant difference between the patterns of the samples. The peak intensities of FeSe\textsubscript{1.2} are sharper than FeSe\textsubscript{0.98} indicating much higher crystallinity. While FeSe\textsubscript{1.2} sample has no different phase, FeSe\textsubscript{0.98} sample contains an impurity arising un-reacted Fe ions remains in the compound during the formation of FeSe. This may be related to the difference of melting temperature between the Fe (1521°C) and Se (221°C) [14]. Even their peak intensities are different; they have exhibited same crystallization behavior. The crystal symmetry was found to be tetragonal with the space group of P4/mmm and crystal parameters were calculated to be a= 3.77361(6) and c=5.52582(5). These results are in agreement with the results obtained by various research groups [15-17].

Fig. 2 shows the surface micrographs of samples. Randomly oriented granular formation with an average grain size of 3-4 μm is observed for two samples. This is general characteristic of Fe-based superconductors. FeSe\textsubscript{0.98} and FeSe\textsubscript{1.2} samples have similar microstructural formation, indicating that there is no significant effect of preparation process and thermal treatment on the morphological evolution.
Large scale EDX dot mapping result of FeSe$_{0.98}$ sample is given in Fig. 3. As can be seen in Fig. 3, distributions of the FeSe phase on the surface of the sample are almost homogenous. In addition, any deficient distribution of Fe and Se atoms and/or non superconducting phases on the surface of the sample has not been observed. According to EDX analysis, atomic concentration of the samples was found very close to their nominal composition. Fig. 4 shows the magnetization versus temperature ($M$-$T$) curves of samples measured at 50 Oe where $H$ applied parallel to the $c$- axis of the samples. Both samples exhibit Pauli paramagnetic type behavior up to ~125 K and then decrease very slowly down to ~10 K. Then, a very sharp transition to diamagnetic phase was observed at $T_c$. In addition, it is concluded that abnormal behavior (kink) around 125 K may be related to the structural transformation. In addition, it is observed that the field magnetization increases at low temperatures. This phenomenon indicates the presence of magnetic impurities found by XRD and SEM.

Figure 1. XRD results of the samples

Figure 2. SEM micrographs of samples
Figure 3. SEM micrographs of FeSe$_{0.98}$ sample. Inserts show elemental distribution of Fe (red dots) and Se (yellow dots).

By looking at the magnetization results, it is observed that the superconducting fractions of samples are small exhibiting no full diamagnetic shielding. The magnetization versus magnetic field ($M$-$H$) loops of samples was given in Fig.5 for different temperatures. We have observed a similar shape of the $M$-$H$ loops while temperature changed. It is seen that a narrow and ferromagnetic type $M$-$H$ curves are formed. This suggests that the co-existence of both magnetism and superconductivity in our samples due to some impurity phase. The big difference on the magnetization scale is found, i.e. the magnetization value of FeSe$_{1.2}$ is about 5 times larger than those of FeSe$_{0.98}$. It is argued that the ferromagnetic components in FeSe$_{1.2}$ are dominant in the matrix and reveal an increasing at the magnetization values with increasing magnetic field.

Figure 4. Magnetization versus temperature (M-T) curves of samples measured at 50 Oe, where $H$ applied parallel to the $c$-axis of the samples.
4. Conclusions
The FeSe$_{0.98}$ and FeSe$_{1.2}$ bulk polycrystalline superconductors have been prepared by solid-state reaction method. Structural and magnetic properties were investigated. The XRD and SEM-EDX results exhibited that microstructural evolution of the samples was not strictly depending on the sample preparation process. However, in contrary, magnetic hysteresis measurements have shown some differences for the sample of FeSe$_{1.2}$. We have found that the ferromagnetic structure in FeSe$_{1.2}$ sample is dominant down to the low temperatures.

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Figure 5. Magnetization versus magnetic field (M-H) loops of samples