

Rapid synthesis and magnetic and electronic transport properties of FeSe_{1-x} superconductors

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Tetragonal PbO-type FeSe_{1-x} (0.04 ≤ x ≤ 0.12) compounds are synthesized by a rapid process of annealing at 673 K for 30 min after ball-milling 5h (single anneal). The superconducting transition temperature is ~7 K. However, zero-resistance is not observed in these samples because of the large distance between grains. After increase of annealing time to 20 h (double anneal), the zero resistance phenomenon was observed and the temperature is 6.0, 6.4 and 6.6 K for x = 0.04, 0.08 and 0.12, respectively. All samples exhibits Meissner effect, but the magnetization is not a negative value because of the positive magnetization contribution of ferromagnetic/ferrimagnetic impurities existing in the samples.

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1. Introduction

The discovery of superconductivity in F-doped LaFeAsO at 26 K has attracted tremendous interest [1]. Within a few years, other layered Fe compounds of four structural types were found to be superconducting, including Sr₄Sc₂O₆Fe₂P₂, Ba_{1-x}K_xFe₂As₂, LiFeAs, and FeSe_{1-x} [2-5]. The simplest compound relative to the iron phase-based superconductors is FeSe_{1-x}, which has the superconducting transition temperature T_c~8 K at atmospheric pressure and acquires a T_c of 37 K under ~7 GPa [5, 6]. Its structure comprises stacks of edge-sharing FeSe₄ tetrahedra with a packing motif essentially identical to that of the FePn (Pn = pnictogen) layers in the families of iron phase-based superconductors [5, 7]. In view of its important test ground to account for high-T_c superconductivity in the iron phase-based superconductors, FeSe_{1-x} superconductor has been investigated in detail [8-17]. However, the synthesis of the subject FeSe_{1-x} usually requires a very long time. For instance, when high-purity powders of α-iron and selenium were used as the starting materials, the sample was annealed at 973 K for 48 h, and annealed at 673 K for 36 h [5]. An effective and rapid method to synthesize FeSe_{1-x} superconductors is desired, and it is important to study the effect of synthesis conditions on their electronic transport properties. In this work, polycrystalline FeSe_{1-x} (x = 0.04, 0.08 and 0.12) superconductors have been synthesized by mechanical alloying and subsequent annealing. The structure, magnetic properties, and electronic transport properties of these compounds are investigated, and the effect of annealing time is studied also.

2. Experimental

Fe and Se powders of better than 99% purity were mixed according to the composition of FeSe_{1-x} (x = 0.04, 0.08 and 0.12). The powder mixtures of 10 g were sealed in a hardened steel vial with steel balls of 12 mm diameter under high-purity argon atmosphere. Mechanical alloying of the mixtures was performed in a high-energy ball mill, which was rotated in two dimensions perpendicular to the horizontal plane. The ball-to-alloy weight ratio was 20:1. The rotation speed of the mill was about 700 rpm and the milling time was 5 h. The as-milled powders were prepared by single anneal in a furnace that was filled with high-purity argon gas and was directly connected to a closed glove box. X-ray diffraction (XRD) analysis of the samples was performed at room temperature using Cu Kα radiation in a Rigaku D/max-2500pc diffractometer equipped with a graphite monochromator. The magnetic properties were measured by a superconducting quantum interface device (SQUID) at different temperatures at an applied magnetic field of 10 Oe. After cooling to room temperature, the samples are crisp (like biscuit). For resistivity measurement, the samples were pressed into pellets in a diameter of 20 mm by using a 200 MPa axial pressure with a steel die. The temperature dependence of resistivity of the FeSe_{1-x} compounds was studied using SQUID by the dc four-probe method. Part of the samples prepared by single anneal were ground, pressed into pellets under a pressure of 200 MPa, sealed in an evacuated quartz tube, and synthesized by double anneal.

3. Results and discussion

Fig. 1 shows the XRD patterns of the FeSe_{1-x} samples with $x = 0.04, 0.08$ and 0.12 , which were prepared by single anneal. All FeSe_{1-x} samples are found to be almost single-phase with the tetragonal PbO -type structure, but with small amounts of Fe and Fe_7Se_8 as impurity phases. With the increase of Fe content ($x > 0.04$), iron impurity phase increases; while with the increase of Se content ($x < 0.12$), Fe_7Se_8 impurity phase appears, in agreement with the results in Ref. [17]. The reflections of the FeSe_{1-x} phase are indexed in Fig. 1. The calculated lattice constants are $a = 0.3776$ nm and $c = 0.5523$ nm for $\text{FeSe}_{0.88}$, $a = 0.3775$ nm and $c = 0.5521$ nm for $\text{FeSe}_{0.92}$, and $a = 0.3773$ nm and $c = 0.5514$ nm for $\text{FeSe}_{0.96}$. With decreasing x , the lattice constant slightly shrinks in both a and c axes. This tendency is consistent with the result of Hsu et al. [5]. This lattice evolution is probably due to the deficiency of Se.

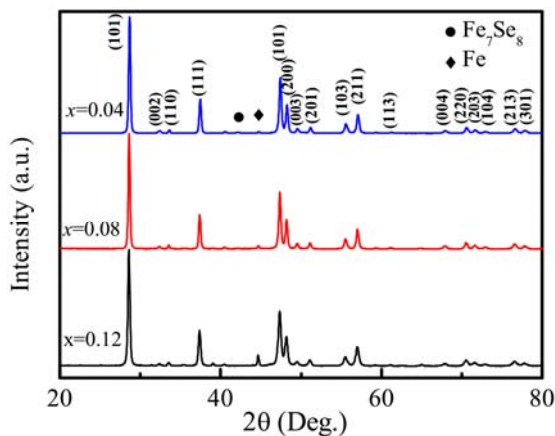


Fig. 1. XRD patterns of FeSe_{1-x} compounds.

The temperature dependence of the resistivity of the FeSe_{1-x} ($x = 0.04, 0.08$ and 0.12) compounds synthesized by single anneal is displayed in Fig. 2(a). The resistivity of the samples drops rapidly below ~ 9 K, indicating a phase transition. With decreasing x (i.e., increase the content of Se), the resistivity at a certain temperature decreases. Fig. 2(b) shows the temperature dependence of the magnetization of the FeSe_{1-x} ($x = 0.04, 0.08$ and 0.12) compounds in the temperature range from 3 to 20 K. With decreasing x , the magnetization at a same temperature decreases, since Se is non-magnetic. The magnetization of the compounds decreases as the temperature decreases and it decreases sharply when temperature further decreases below ~ 7 K. In the temperature down to 3 K, the magnetization of all compounds is still positive. We speculate that the present phase transition is superconducting transition. But because of the large distance between grains and the existence of ferromagnetic impurities, the zero-resistance and negative magnetization are not observed in these

samples.

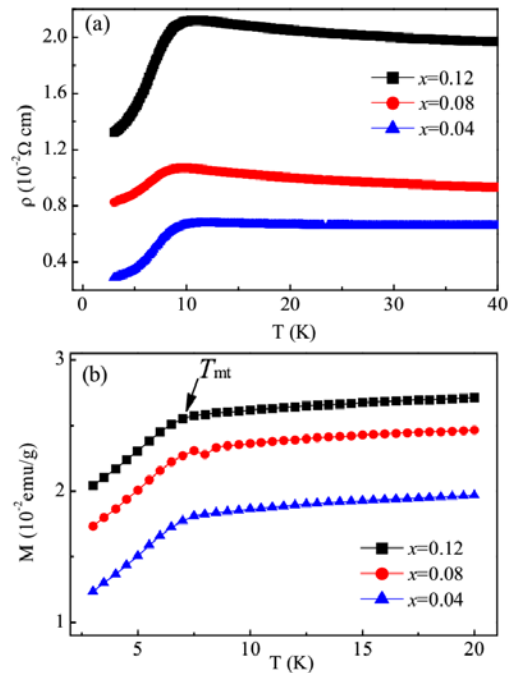


Fig. 2. (a) Temperature dependence of the resistivity of FeSe_{1-x} compounds. (b) Temperature dependence of the magnetization of FeSe_{1-x} compounds recorded at 10 Oe after zero-field cooling.

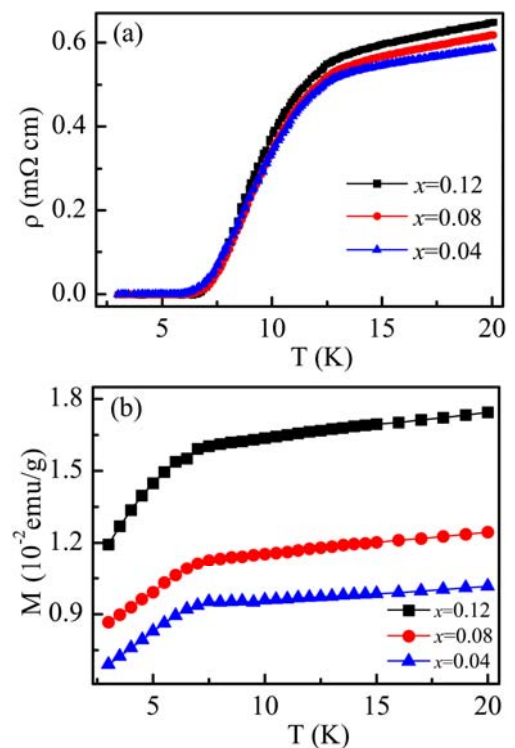


Fig. 3. (a) Temperature dependence of the resistivity of FeSe_{1-x} compounds synthesized by double anneal. (b) Temperature dependence of the magnetization of FeSe_{1-x} compounds recorded at 10 Oe after zero-field cooling.

Fig. 3(a) shows the temperature dependence of the resistivity in the temperature range from 3 to 20 K of the FeSe_{1-x} ($x = 0.04, 0.08$ and 0.12) compounds synthesized by double anneal. The zero-resistance transition temperatures (T_c) were observed to be 6.0, 6.4 and 6.6 K for $x = 0.04, 0.08$ and 0.12 , respectively. It may be described to that the longer annealing is helpful for close contact between grains. The temperature dependence of the magnetization of these compounds measured in a magnetic field of 10 Oe under zero-field-cooling conditions is shown in Fig. 3(b). The magnetization of all compounds is positive in temperature from 3 to 20 K. The magnetic transition temperature (T_{mt}) is ~ 7 K, marked as T_{mt} in Fig. 2(b). T_{mt} coincides roughly with T_c , which is consistent with previous results on RFeAsO_{1-x}F_x [18]. The magnetic transition at T_{mt} corresponds to the superconducting transition, although negative magnetization is still not observed in these samples because of the ferromagnetic impurities. In some of the recent papers, researchers have shown that the superconducting β -FeSe samples have a stoichiometric Fe:Se ratio of 1:1 (± 0.02) [15, 16]. The nominal composition of the sample in this work shows a Se deficiency larger than the tolerance given in Ref. [15, 16]. Yet, superconductivity is found. The reason may be that the formula of the main β -FeSe phase in this work is also within $\sim 2\%$ of stoichiometry. The iron surplus in the crystal exists in the form of α -iron and Fe₇Se₈ (Fig. 1).

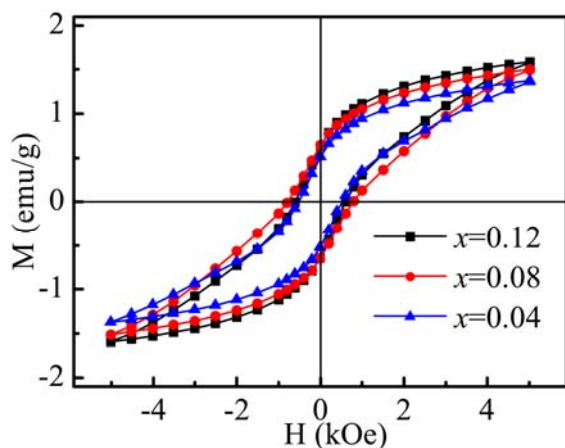


Fig. 4. Magnetization curves at 295 K for FeSe_{1-x} compounds.

The isothermal magnetization loop of the FeSe_{1-x} at 295 K is shown in Fig. 4. This plot indicates the samples include ferromagnetic/ferrimagnetic phases at 295 K. The coercive field is about 1000 Oe. As is well known, the coercive field of α -iron is not more than 100 Oe at room temperature. At room temperature, ferrimagnetic Fe₇Se₈ exhibits complex magnetism [19]. Therefore, the main contributor to the large coercive field may be Fe₇Se₈. At temperature below T_{mt} , the magnitude of ferromagnetic(α -iron)/ferrimagnetic(Fe₇Se₈) signal suppresses that of perfect diamagnetism in these samples.

This explains the fact that the negative-magnetization was not observed in Fig. 2(b) and Fig. 3(b).

4. Conclusions

In conclusion, FeSe_{1-x} superconductors with $x = 0.04, 0.08$, and 0.12 are rapidly synthesized by single anneal. The superconducting transition temperature is ~ 7 K. The zero-resistance and negative-magnetization are not observed in these samples because of the large distance between grains and the ferromagnetic/ferrimagnetic impurities. The zero-resistance temperature T_c of FeSe_{1-x} superconductors fabricated by double anneal are 6.0, 6.4 and 6.6 K for $x = 0.04, 0.08$ and 0.12 , respectively. Meissner effect is obvious but negative-magnetization does not appear in these samples because of the existence of the ferromagnetic/ferrimagnetic impurities.

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