

High-Purity FeSe_{1-x} Superconductors Prepared by Solid-State Synthesis and Liquid Phase Processing

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 $FeSe_{1-x}$ samples have been prepared by a solid-state reaction in the Ar+3% H₂ gas flow. The samples sintered at 410°C were of the tetragonal PbO structure (β-phase), showing little trace of δ-phase (hexagonal). However, the samples sintered at higher temperatures contained a fair amount of δ -phase, which was unable to be eliminated completely by subsequent annealing at \leq 450°C for a prolonged period. Both *M*-*T* and *R*-*T* measurements showed that sintered samples of β-phase were superconducting with an onset T_c above 8.1 K. Thick films of $FeSe_{1-x}$ were grown on LaAlO₃ substrates by liquid phase processing with SeSn as the flux. In contrast to the sintering, the films grown around 910°C from the Sn-containing liquid had a pure β-phase. Although the phase diagram showed some solid solubility of Sn in FeSe, energy-dispersive X-ray spectroscopy failed to find Sn trace in the crystallized films, which showed a steeper superconducting transition at lower T_c of 6.0 K. To clarify whether the possible Sn contamination caused the drop of T_c , $FeSe_{1-x}$:5% Sn samples were sintered, which showed little change of T_c from the pure β -FeSe_{1-x}. The cause for the T_c reduction of thick films remains unclear.

I. Introduction

RECENT discovery of superconductivity in the compounds containing a magnetic element of iron has brought about a new wave of interest in this field.^{1–5} Intensive researches worldwide have now driven the superconducting transition temperature to as high as 56 K.³ Of great interest to the research community is that these iron-based compounds neither resemble the conventional superconductors nor behave in the same way as the high- T_c cuprates,⁴ and therefore provide a new opportunity for the better understanding of unconventional superconductivity. In this family, FeSe has the simplest composition and structure, but yet possesses all the electronic, magnetic, and structural effects relevant to the superconductivity in the complex iron pnictides.⁵ Therefore, it will play an important role for the research into this new class of superconductors.

There are several compounds of the composition around the stoichiometric ratio 1:1 in the Fe–Se binary system, as indicated in the phase diagram.⁶ The superconductivity is only found for the Se-deficient phase FeSe_{1-x} ,² which has the tetragonal PbO structure with the space group *P4/nmm* and is termed as the β -phase. The second phase (δ -phase) is a Se-rich phase, FeSe_{1+x} , having the hexagonal *P*6₃/*mmc* lattice isostructural to NiAs.⁶ The third phase is actually a stoichiometric compound, Fe₇Se₈, whose struc-

ture is very similar to δ and can be regarded as the defect ordered phase of δ .⁷ Efforts to prepare samples of pure β -phase have not been very successful so far. Most samples shown in recent publications contained some amounts of δ -phase and/or Fe₇Se₈, as well as the traces of metallic α -Fe and iron oxides (Fe₃O₄).^{2,8-12} The samples in these publications were usually prepared by sintering at over 700°C, followed by annealing at about 400°C.^{2,8-12} This is not the best route suggested by the Fe–Se phase diagram,⁶ which shows a peritectoid reaction at 457°C that will unavoidably result in certain amount of δ -phase and/or Fe₇Se₈.

In this paper, we report on the low-temperature synthesis of high-purity β -FeSe_{1-x} in the flowing Ar+3% H₂ atmosphere by a solid-state reaction. In addition, liquid phase processing was also used to grow thick films of β -FeSe_{1-x} on the LaAlO₃ (LAO) single crystal substrates with SeSn as the flux. Other than for the pure β -phase samples, the use of this method, which was a process similar to single crystal growth, had another purpose that was to grow high-purity Sn-doped FeSe. As shown in the FeSe–SeSn phase diagram,¹³ there exists a solid solution region for Fe_{1-x}SeSn_x, which means that the single crystals or polycrystalline solids precipitated from the liquid will have the samples with Sn truly doped in the FeSe lattice, rather than presented as the aggregates of Sn-enriched phases, as it is often seen in many doped powder samples.

II. Experimental Procedure

The FeSe samples were prepared from the powders of metallic Fe (99.9% 1–9 µm, Stern Chemicals, Newburyport, MA) and Se (99.5% +200 mesh, Acros, Fair Lawn, NJ). The powders were weighed according to the ratio Fe:Se = 1:1-x (x = 0-0.20) and then mixed by grinding in an agate mortar. For a better mixing and also avoiding absorption of ambient moisture, water-insoluble toluene was added to the mixture during the grinding. The dried powder mixture was then pressed into the disks of thickness of 2 mm and diameter of 10 mm. The sintering was carried out in an air-tight quartz tube furnace, which was preevacuated to 0.1 atm and flushed with the Ar+3% H₂ gas for several times. To ensure extremely low oxygen partial pressure (p_{O_2}) inside the quartz tube, the furnace was kept at 100°C for 4 h with the Ar+3% H₂ flowing at the rate of 60 sccm. The exit gas from the quartz tube was checked using a zirconia oxygen trace analyzer (Rapidox 2100, Cambridge Sensotec Ltd., St. Ives, Cambs, U.K.), which showed that the p_{O_2} was approaching the detecting limit of the unit (10⁻²⁰ ppm). The temperature was then raised slowly from 100° to 300°C (50°C/h) and dwelled for 2 h. This was intended to avoid preferential loss of Se before any chemical reaction occurred, because element selenium has a very high vapor pressure above its melting point of 221°C. The temperature was finally raised to the desired sintering temperatures $(\geq 410^{\circ}C)$ for the chemical reaction to complete. The last step was repeated at least once after the samples were crushed and ground again.

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Liquid-phase processing was carried out using SeSn as the flux, which was prepared from the metallic powders of Se and Sn (99.80% 325 mesh, Acros) in the same way as described above. The final sintering temperature for SeSn was 700°C and the SeSn powders obtained were checked by X-ray diffraction (XRD) to be pure, whose diffraction patterns matched almost exactly with a known SeSn phase in the database (PDF #75-1843).¹⁴ A well-mixed FeSe+SeSn pellet with the weight of about 2 g and composition of 10 at.% SeSn was placed on top of a (001) LAO substrate measuring 5 mm \times 5 mm, which was placed in the lower end of a tilted alumina (Al₂O₃) boat. The boat was then loaded into the quartz tube and heated up to 910°C, at which the pellet was melted to form a liquid according to the FeSe-SeSn phase diagram.¹³ After being kept at 910°C for 15 h, the furnace was cooled down slowly at 2°C/h to 800°C and then quickly to room temperature at 600°C/h. When taken out from the furnace, the LAO substrate was covered with a thick film precipitated/crystallized from the Fe-Se-Sn high-temperature solution, which also wet a large area of the Al₂O₃ boat. Finally, the LAO substrate was cleaved off from the boat by a sharp blade.

The structure, composition, morphology, and superconducting properties of the samples obtained were characterized by a range of techniques including powder XRD, differential scanning calorimetry (DSC), energy-dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), SQUID magnetometry, and four-point electric transport measurements. XRD patterns were taken using a Rigaku MultiFlex diffractometer (Tokyo, Japan). DSC was performed using a TA Q2000 calorimeter (TA Instruments, New Castle, DE). SEM, EDX, and EBSD were carried out using a JEOL JSM-7001F microscope (Tokyo, Japan). SQUID magnetometry was carried with the Quantum Design MPMS SQUID-VSM system (San Diego, CA). Four-point transport measurements were performed with a home-made unit.

III. Results and Discussion

(1) Preparation by Solid-State Reaction

Figure 1 shows the XRD θ -2 θ scans of the samples sintered at various temperatures. The samples of the nominal composition FeSe_{0.85} and sintered at 750°C for 24 h contained a fair amount of Fe₇Se₈ (PDF #72-1356) and α -Fe (PDF #87-0721) after cooling down to room temperature, as shown in Fig. 1(a). Prolonged annealing at 400°C up to 72 h was unable to get rid of Fe₇Se₈.



Fig. 1. X-ray diffraction θ -2 θ scans of various samples: (a) powders sintered at 750°C for 24 h and then followed by annealing at 400°C for up to 72 h, (b) powders sintered at 410°C for 24 h, (c) large grains grown on an alumina boat from liquid at 910°-800°C. The indexed peaks belong to the superconducting β -FeSe_{1-x}.

Also, changing the nominal composition in the range x = 0 - 0.2did not have a notable result on reducing the amount of Fe₇Se₈, but it was found that the amount of α -Fe could be substantially reduced when the Se content was increased up to FeSe_{0.97}. However, efforts to eliminate the α -Fe trace completely by fine tuning of the composition were unsuccessful. It was suspected that the trace of α -Fe might result from the trace of some Fe₃O₄ in the starting iron powder, which was reduced back to α -Fe in the extremely low p_{O_2} atmosphere at a later stage of the sintering. Indeed, Fe₃O₄s were found as a tiny trace in the samples sintered at lower temperatures. Figure 1(b) is a typical XRD pattern for the samples of the composition FeSe_{0.97}, which were sintered at 410°C for 24 h. Except for the trace of Fe₃O₄ (PDF #75-0033), the samples had a nearly pure β -phase (PDF #85-0735) with barely observable Fe₇Se₈. Longer sintering time at 410°C appeared not to be necessary because XRD did not show any significant change in the samples sintered for up to 7 days, apart from that the trace of oxide was reduced to α -Fe.

The results agreed well with the Fe–Se phase diagram.⁶ At 750°C, the FeSe_{1-x} (x = 0-0.2) samples were in the α –Fe+ δ two phase region. Upon cooling through 457°C, although the majority of δ -phase undertook a peritectoid reaction with α -Fe to form the β -phase, i.e. α –Fe+ $\delta \leftrightarrow \beta$, some δ and/or α -Fe remained even for those samples of the composition within the β single phase range (1–x = 0.961-0.976),⁶ due to segregation or incomplete diffusion. Therefore, annealing at about 400°C for the samples sintered at 750°C would not be able to get rid of the δ -phase.

The structure of the δ -phase was very similar to that of Fe₇Se₈ and it was very difficult to distinguish the powder XRD patterns of δ (PDF #75-0608) and Fe₇Se₈ (PDF #72-1356). However, DSC analysis on the samples, which showed the trace of δ (or Fe₇Se₈) in XRD, agreed with the Fe–Se phase diagram that



Fig. 2. The differential scanning calorimetry graphs for the samples: (a) with and (b) without the trace of Fe_7Se_8 on X-ray diffraction.

there was an eutectoid reaction: ${}^{6}\delta \leftrightarrow \beta + Fe_7Se_8$, at $340^{\circ}-350^{\circ}C$ as shown in Fig. 2(a). The heating/cooling rate for DSC was $5^{\circ}C/\text{min}$, indicating this eutectoid reaction could occur quickly. Therefore, we tend to think that the minor phase present in the room temperature XRD, Fig. 1(a), was Fe_7Se_8 rather than δ . Also observed in DSC was the peritectoid reaction: $\alpha - Fe + \delta \leftrightarrow \beta$, at about 460°C, very close to the 457°C given in the Fe–Se phase diagram.⁶ For the samples whose XRD did not show the trace of Fe_7Se_8 , only one peak corresponding to this peritectoid reaction was observed, as shown in Fig. 2(b).

(2) Liquid-Phase Processing

Figure 3(a) is a low-magnification SEM image, showing a typical overall surface morphology of the thick films grown on (001) LAO. An area rich of the features are highlighted in Fig. 3(b), in which the places where the EDX analyses have been performed are also indicated. The EDX results, Fig. 3(c), showed that the thick films had the Se:Fe atomic ratio approximately equal to 1 within the experimental error. Both EBSD structural analyses and the superconducting measurements, which will be discussed later, verified the films being β -phase. Figure 4 shows the Al₂O₃ boat surface, which was also wetted by the liquid during the growth over the temperature range of 910°–800°C. The grains grown from the liquid on the rough Al₂O₃ surface were large with a diameter 100-200 µm, compared with about 100 nm for the sintered powders. EDX showed these large grains having the same composition as the thick films on LAO. XRD of the samples, Fig. 1(c), matched well with the tetragonal P4/nmm structure (PDF #85-0735), except for those lines from the Al₂O₃ (PDF #78-2427), confirming that they were pure β -phase.

The above results are interesting because the thick films on LAO and also the large grains on rough alumina were grown from the Sn-containing liquid at temperatures between 910° and 800°C, well above the peritectoid temperature of 457°C, but what was obtained was the low-temperature β -phase, instead of the high-temperature δ -phase, indicating that Sn had some kind of effect on stabilizing the β -phase. However, EDX failed to find any Sn trace in the thick films or the large grains, which was in-consistent with the FeSe–SeSn phase diagram,¹³ where a solid solution region was shown with the maximum Sn solubility being about 5 at.%, for the $Fe_{1-\nu}SeSn_{\nu}$ solid solution precipitated from the liquid at the peritectoid temperature (780°C). The reason is not clear. One possibility is the significant evaporation of Sn at the growth temperatures, which decreases the actual solubility of Sn to a level beyond the sensibility of the EDX. As shown in Figs. 3(b) and 4(b), some metallic iron was observed in both the thick films and large grains. The water-drop-like shape is reminiscent that they were solidified from the liquid. But metallic iron would not melt at 910°C. The iron water-drops propose that they were solidified via the evaporation of Sn and/or Se.

EBSD was carried out to check the structure and orientation of the samples. Figure 5(a) shows the EBSD pattern from a point on the alumina sample surface, Fig. 5(b). The surface image was slightly distorted because the sample was tilted at 70° for recording the diffraction patterns, which could be indexed only according to the tetragonal P4/nmm structure, confirming again that they were indeed the superconducting β -phase. EBSD mapping over an area, Fig. 5(c), showed that the sample mainly consisted of (211) and (101) grains. This was consistent with the XRD, Fig. 1(c), where the relative intensities of these two reflections were enhanced as compared with the powder samples. To our surprise, although the thick films on (001) LAO were pure and smooth, they did not have a single orientation, as shown in the EBSD mapping in Fig. 6. The two observed orientations, (101) and (201), looked like a twin. The thickness of the film was measured using a profilometer to be about 1.5-2 μm, which was probably too thick to retain a good texture.



Fig. 3. (a) Scanning electron microscope image of the overall surface morphology for the thick films grown on LaAlO₃ (LAO). (b) A particular area rich of the features, also showing the places where energy-dispersive X-ray spectroscopy (EDX) compositional analyses were carried out. (c) A representative EDX result for the red square marked in (b), showing that the thick film had the Fe:Se ratio approximately equal to 1.

(3) Superconducting Properties

Shown in Fig. 7 are the magnetization versus temperature (M-T) curves measured by SQUID magnetometry. The samples were cooled in zero-field from room temperature to 2 K and the moment was then measured in the applied field of 10 Oe upon



Fig. 4. (a) Scanning electron microscope image of the overall surface of the alumina (Al_2O_3) boat wet by the high-temperature liquid. (b) Details of the surface and the areas where energy-dispersive X-ray spectroscopy (EDX) analyses were performed.

heating. Rapid increase of moment was observed until about 10 K. The onset T_c 's were taken at the intersection point of the two extrapolated lines, which were 8.1 and 6.0 K for the sintered powders and thick films, respectively. Four-point resistivity measurements confirmed the transitions and showed an onset T_c of 9.7 K, with zero resistance at 6.9 K, for the sintered β -FeSe_{1-x} powder, as shown in Fig. 9(a).

Magnetization versus applied-field (M-H) measurements at 4 K showed typical hysteresis loops seen in the ferromagnets for all the samples in Fig. 7, presumably due to one or more of the magnetic traces of Fe₇Se₈, α-Fe, and Fe₃O₄ observed in XRD and SEM, as discussed above. A representative of such M-Hloops is shown in Fig. 8. The influence of the magnetic impurity traces was also reflected in the M-T curves, Figs. 7(a)–(c), as the measured moments were unable to go into negative at T_{c} . Comparatively, the thick film crystallized from the high-temperature liquid appeared to have the best purity, as its moment was the most close to zero at T_c . Although the measured moments were different in Figs. 7(a)-(c) owing to the different types and/or amounts of the residual traces, the drop of the moments from the onset T_c to 2 K, i.e. $\Delta \approx M(10K) - \dot{M}(2K) \approx 9 \times 10^{-3}$ emu/g, was approximately the same, as it should be. For an easier comparison of the T_c 's, the normalized moments, [M(T)-M(10K)]/ Δ , are plotted in Fig. 7(d). The decrease of T_c for the thick film is apparent. On the other hand, its transition is steeper due to a higher purity and structural perfection. It is not very clear what exactly caused the drop of T_c . One possible cause was the small



Fig. 5. (a) A representative EBSD pattern from a point on the alumina sample surface, which is shown in (b). The pattern matched well with the structure of β phase. (c) Electron backscatter diffraction mapping on (b), showing different orientations presented (the sample was tilted at 70° for recording the diffraction patterns, and hence the images had some distortion).



Fig. 6. (a) Scanning electron microscope of the surface of a thick film grown on LaAlO₃. (b) Electron backscatter diffraction mapping on a part of (a), showing that the film did not have a single orientation.

amount of Sn doping, because the thick films were grown from the Sn-containing high-temperature liquid. However, EDX failed to detect any Sn trace in the films, indicating that the Sn contamination, if there was any, must be very low, beyond the typical EDX resolution of about 1%.

In order to see the effect of Sn doping on the FeSe_{1-x} superconductivity, β -FeSe:5% Sn powder samples were prepared by sintering at various temperatures from 410° to 750°C. All the Sn-doped samples showed little change of the T_c from the pure FeSe_{1-x} in both *M*–*T* and *R*–*T* measurements, as shown in Figs. 7 and 9. It is noted in Fig. 9(b) that the resistivity at the end of the transition for the doped sample did not go to zero. The re-



Fig. 7. Magnetization versus temperature (M-T) curves of the samples: (a) sintered powder of β -FeSe_{1-x}, (b) thick film grown from a high-temperature solution, (c) sintered powder of Sn-doped β -FeSe_{1-x} with the nominal doping concentration of 5 at.%, (d) comparison of the normalized M-T curves, showing a lower T_c for the thick film. The curves were measured in the field of 10 Oe on heating up after zero-field cooling.

maining small resistance was likely to come from the segregation of some (Se, Sn)-enriched impurity phases on the surface, which were formed during the heating because of the high vapor pressure of Se and Sn. This speculation was based on the XRD results of a number of samples sintered at high temperature for a prolonged period of time. Unknown phases were sometimes observed on the surface of such sintered pellets and a layer of a few hundred micrometers thick had to be ground off to expose the superconducting phase inside. The residuals of surface



Fig. 8. A representative magnetization versus applied field loop of the β -FeSe_{1-x} samples measured at 4 K. The observed moment and remanence were likely to come from the trace of the magnetic secondary phases (e.g., Fe₃O₄, etc.) as described in the text.





Fig. 9. R-T curves of the sintered powders of (a) pure β -FeSe_{1-x} and (b) 5% Sn-doped β -FeSe_{1-x}, showing the transitions and onset T_c 's. The nonzero resistivity at the end of transition for the doped sample might arise from the segregation of some (Se, Sn)-enriched phase on the surface of the sintered pellet.

impurity phases might cause some voltage drop across the contacts, causing nonzero resistance.

IV. Concluding Remarks

Bulk FeSe_{1-x} samples were prepared by a solid-state reaction in the Ar+3% H₂ gas flow. The samples sintered at 410° C for 24 h

had almost a pure β -phase. However, the samples sintered at higher temperatures contained some amount of δ -phase, which was unable to be eliminated completely by prolonged annealing at $\leq 450^{\circ}$ C afterward. This was due to the phase segregation above the peritectoid reaction temperature of 457° C. The measurements showed that sintered pure β -FeSe_{1-x} samples were superconducting with the onset T_c 's of 8.1 and 9.7 K determined from the M-T and R-T curves, respectively. Therefore, the optimum conditions for sintering high-purity β -FeSe_{1-x} powder samples are: temperature 400° - 450° C and composition Fe:Se = 1:0.95-0.97.

Thick films of FeSe_{1-x} were grown on (001) LAO single crystal substrates by liquid-phase processing with SeSn as the flux. In contrast to the sintering, the films grown around 910°C from the Sn-containing liquid had pure β -phase with a high crystallinity, as shown by both EBSD and XRD. Although the phase diagram showed some solid solubility of Sn in FeSe, EDX failed to find any Sn trace in the crystallized films, which were also superconducting with a steeper transition, but a lower T_c of 6.0 K determined by the magnetic measurements. In order to clarify whether the possible Sn contamination caused the drop of T_c , Sn-doped FeSe_{1-x} powder samples were synthesized, which showed little change of T_c from the pure β -FeSe_{1-x}. The cause for the slight reduction of T_c of the thick films remains unclear.

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