Unabridged phase diagram for single-phased FeSe$_x$Te$_{1-x}$ thin films

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A complete phase diagram and its corresponding physical properties are essential prerequisites to understand the underlying mechanism of iron-based superconductivity. For the structurally simplest 11 (FeSeTe) system, earlier attempts using bulk samples have not been able to do so due to the fabrication difficulties. Here, thin FeSe$_x$Te$_{1-x}$ films with the Se content covering the full range (0 ≤ $x$ ≤ 1) were fabricated by using pulsed laser deposition method. Crystal structure analysis shows that all films retain the tetragonal structure in room temperature. Significantly, the highest superconducting transition temperature ($T_C = 20$ K) occurs in the newly discovered domain, i.e., 0.6 ≤ $x$ ≤ 0.8. The single-phased superconducting dome for the full Se doping range is the first of its kind in iron chalcogenide superconductors. Our results present a new avenue to explore novel physics as well as to optimize superconductors.

 Shortly after the discovery of iron-based superconductors, in the form of LaFeAsO$_{1-x}$F$_x$, with a critical transition temperature ($T_C$) of 26 K$^1$, superconductivity was observed in PbO type iron chalcogenides (11 system)$^2$. Due to its simple crystal structure, composed of a stack of superconducting Fe$_x$Ch$_2$ (Ch = Se, Te) layers along the c-axis, as well as its rich phase diagram$^3$, the 11 system has attracted tremendous interest in exploring the mechanism of high temperature superconductivity. Although the $T_C$ of FeSe is as low as 8 K, it can be substantially enhanced up to 15 K with partial substitution of Te for Se at $x = 0.5$ for both polycrystalline$^4$ and single crystal samples$^5$, or to 37 K under high pressure$^6$. Moreover, under the influence of strain effects induced by the lattice mismatch between the film and substrate$^7$, or by Fe vacancies$^8$, a maximum $T_C$ of 21 K can be obtained in FeSe$_{0.5}$Te$_{0.5}$ films. The recent discovery of a record high $T_C$ of 65 K in monolayer FeSe films$^9$,10 led to the exciting perspective that its $T_C$ can be as high as the liquid nitrogen boiling temperature. Nevertheless, a detailed phase diagram for the 11 system is yet to be established$^{11,12}$; in particular, the physical properties of samples with high Se content, 0.6 ≤ $x$ ≤ 0.8, are still unclear. One of the major reasons for such uncertainty is the lack of samples with the right stoichiometric ratios. Polycrystalline samples with Se concentrations in the range of 0.6 ≤ $x$ ≤ 0.8 are found to have multiple-phases$^4$, while pure single crystal samples have never been fabricated. As a result, the FeSe$_{0.5}$Te$_{0.5}$ ($x = 0.5$) sample is regarded to have the maximum $T_C$ so far, based on the incomplete phase diagram, which might be misleading. Here, we have overcome the phase separation issues and successfully fabricated single-phased 11 films for 0.6 ≤ $x$ ≤ 0.8 via the pulsed laser deposition (PLD) method. By characterizing the structural and superconducting properties for the full range of FeSe$_x$Te$_{1-x}$ thin films, for the first time, we were able to construct the complete phase diagram. In particular, we uncovered a higher $T_C$ phase can be obtained in $x = 0.6–0.8$ samples, in contrast to the previous assumption of $x = 0.5$. Also interestingly, the $x = 0.6$ sample exhibits the maximum upper critical magnetic field ($H_{c2}$) compared to the other samples. This new phase diagram would now be strikingly critical for potential superconductor application and a better understanding of the superconducting mechanism.

Results

As reference systems, we first start with bulk samples. Figure 1(a) shows the XRD patterns for the targets (bulk) with different Se concentrations, where all the XRD peaks were normalized by the values of the intensity of the respective (101) peaks for direct comparison. From the XRD analysis, all samples seem to be well-developed single

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phase and can be indexed as PbO tetragonal structure except in the 0.6 ≤ x ≤ 0.8 region. In that particular region, all the peaks split into two groups, indicating the coexistence of two structural phases, denoted as phase A and phase B, respectively, as shown in Figure 1(a). Phase A exists for 0 ≤ x ≤ 0.8, while phase B emerges in the region 0.6 ≤ x ≤ 1. Figure 1(b) displays the calculated values of the lattice parameters as a function of Se content in the bulk samples. For phase A, both the lattice parameters a and c decrease remarkably with increasing Se concentration, while for phase B, the lattice parameters change only slightly with variation of x. These results are consistent with a previous report, indicating that the structure of FeSe is different from the structure of FeTe, even though both of them have a similar tetragonal structure. In the dual phase region of 0.6 ≤ x ≤ 0.8, both a and c in the A and B phases show almost no dependence on x, indicating that either A or B possesses the same stoichiometric composition among the three samples. The only variation among these three samples (x = 0.6, 0.7, and 0.8) is the component ratio between phase A and B, which can be identified by the changes in the diffraction peak intensity in Figure 1(a). Quantitative results on the peak intensity, as shown in Supplementary Fig. S1, demonstrate the linear variation of the A or B component as a function of Se content. The variations in the lattice parameters and the linear variation of the component ratio with changing x imply that there is no single phase in the bulk samples for the 0.6 ≤ x ≤ 0.8 region.

In sharp comparison, there is no phase separation for the peak reflection of all thin films samples. Figure 1(c) displays the XRD patterns for thin films normalized by the intensity of their respective (00l) peaks, where all films are denoted by the nominal composition of their targets. Only the (00l) reflections of thin films and of substrates can be detected, implying the out-of-plane orientation of these films. Interestingly, all the peaks show a systematic shift with changing x. Figure 1(d) displays a linear relationship between lattice parameter c and the Se content x, indicating that the Se contents in the thin films are close to the nominal values and that single phase for 0.6 ≤ x ≤ 0.8 is actually formed in the thin film state. This is crucial for material characterization as well as for phase diagram construction.

Figure 2(a) shows the electronic resistivity versus temperature (R-T) curves for all film samples normalized by their respective resistance at 300 K. For the un-doped FeTe film, a kink around 70 K is observed, corresponding to the antiferromagnetic (AFM) transition accompanied by a structural transition. The kink disappears when the Se content increases up to x = 0.2, which is similar to that found in polycrystalline samples and single crystal. With further Se doping, the R-T curve in the normal state becomes more metallic.

Figure 1 | (a) XRD patterns of FeSe$_x$Te$_{1-x}$ targets. The marks A and B stand for two phases coexisting in the targets for 0.6 ≤ x ≤ 0.8. (c) XRD reflections of FeSe$_x$Te$_{1-x}$ thin films deposited on CaF$_2$ (100) substrate. "*" marks the reflections of impurity phases in the substrate, identified by ICDD card. The corresponding calculated lattice parameters of the targets and thin films are shown in (b) and (d), respectively.
and $T_C$ increases from 10 K at $x = 0.2$ up to around 20 K for $x$ in the range of 0.6 to 0.8, as shown in Figure 2(b). It should be noted that $T_C$ of the FeTe$_{0.5}$Se$_{0.5}$ film is around 16 K, consistent with the results of bulk$^4$ and single crystal samples$^3$. There are a lot of works$^7,8,12–15$ indicating that strain, caused by the mismatch between thin films and substrates, plays a critical role in the emergence of higher $T_C$ ($\sim$19 K) compared with the bulk value. Nevertheless, with all the films being prepared on same substrate (CaF$_2$) in our study and a linear relationship between lattice parameter and Se concentration, the dominant factor for the $T_C$ variation is attributed to the Se doping rather than lattice mismatch.

Measurements of electronic resistivity as a function of temperature for all films, under different magnetic fields ranging from 0 T to 13 T parallel to the $c$-direction, were also performed. Figure 3(a) displays $R$-$T$ curves for FeSe$_{0.6}$Te$_{0.4}$ film samples at temperatures from 12 K to 22 K. All the other curves are displayed in Supplementary Fig. S2. Broadening of the resistivity transition in magnetic field is direct evidence of thermal fluctuation in a vortex system$^{16}$. The width of the superconducting transition is calculated from the formula $\Delta T_C = T_{C_{\text{onset}}} - T_{C_{\text{zero}}}$, where $T_{C_{\text{onset}}}$ and $T_{C_{\text{zero}}}$ are determined by 90% and 10% of the normal state resistivity for all the films, respectively. The broadening of the transition width can be characterized by $(\Delta T_C(B) - \Delta T_C(0))$, where $\Delta T_C(B)$ is the transition width under the magnetic field. Figure 3(b) shows the broadening of the superconducting transition width as a function of magnetic field for all the superconducting films. It can be seen that samples of $0.6 \leq x \leq 0.8$ show higher slope gradient in comparison to other samples. In general, such a difference may reflect different vortex mechanism or superconducting order parameters between high $T_C$ samples and other samples. The upper critical field ($H_{c2}$) is determined by 90% of normal state resistivity for all films. Figure 3(c) shows the dependence of the upper critical field for all superconducting films on the normalized temperature (by the respective $T_C$ values). It can be seen clearly that the highest $H_{c2}$ exists in the sample with $x = 0.6$. The values of $H_{c2}$ were obtained by using the Werthamer-Helfand-Hohenberg model$^{17}$, $H_{c2}(0) = 0.67T_C dH_{c2}/dT|_{T_C}$. The estimated value of $H_{c2}(0)$ exceeds 100 T, which is expected to be useful for high-field applications.

Charge carrier population is one of the major parameters that are critical to high $T_C$ in Fe-based superconductors$^{18}$. Therefore, we performed Hall measurements on three representative film samples, namely an under-doped sample (FeSe$_{0.3}$Te$_{0.7}$), an optimally-doped sample (FeSe$_{0.6}$Te$_{0.4}$), and an over-doped sample (FeSe$_{0.9}$Te$_{0.1}$). Figure 4(a–c) shows the transverse resistivity, $\rho_{xy}$, at different temperatures for $x = 0.3$, 0.6, and 0.9, respectively. All curves show linear-like behavior in the field measurement range. The Hall coefficient, $R_H = \rho_{xy}/B$, where $B$ is the magnetic flux density, is determined by the linear fitting of $\rho_{xy}$ curves. Figure 4(d) demonstrates that the $R_H$ of all three films is almost temperature independent from 80 K to room temperature. This phenomenon is similar to that in both films$^{19}$ and single crystal$^{20}$. In the low temperature regime below 80 K, $R_H$ for all three films shows an obvious diver-
The dependence of Hall coefficient for the three films. An unusual charge carrier population is developed in the high TC continuously increasing Se concentration, indicating that the n clearly show the discrete variation of RH. According to conventional valency assumption, Se doping can be considered as isovalent element doping, and no charge carriers should be induced in this case. As a result, we think that local structural variation plays a critical role in driving the emergence of the unique charge carrier population, which has stimulated the highest TC in the region of 0.6 ≤ x ≤ 0.8. The substitution of Se for Te is expected to induce a significant reduction in anion height and to alter the magnetic orders in the FeSe1−xTe system. When the anion height is reduced below a critical value, the magnetic ground state will switch from a bicollinear (π, 0) to collinear (π, π) pattern, which gives rise to superconducting pairing. The magnetic correlation is still present, which localizes the charge carriers and thus enhances |RH| at low temperature. This localization has been observed in 11 single crystals. Furthermore, it has been reported that the dimensionality of the Fermi surface is quite sensitive to local structural properties, or the anion height, in iron-based superconductors. The reduction in anion height could, in turn, affect the density of states (DOS) at the Fermi energy (Ef) and the carrier density, by tuning the overlap between the Te 5p (Se 4p) and Fe 3d orbits. It should be noted that the sign reversal from positive to negative in RH(x = 0.6) should be considered as an intrinsic property for high TC samples in the 11 system, which has been found in high-quality thin film and single crystal samples. Our results thus highlight the role of structural parameters in the determination of charge carrier behaviour because both the AFM order and the modification of the Fermi surface show a strong relationship with anion height.

Collectively, our results enable us to construct the complete electronic phase diagram for the 11 film system, as shown in Figure 5. The AFM transition temperature, TN, is determined by the position of the kink mentioned above, and TC is determined as the intersection point by extrapolation of the normal state resistivity and the superconducting transition, as shown in Figure 2. The previously reported TC values of polycrystalline and single crystal samples...
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Author contributions

W.K.Y., Z.S., S.P.R. and S.X.D. conceived and directed the research. Samples were prepared by J.Z. and X.C. XRD data was collected and analysed by X.X. and X.W. Y.D. and J.Z. contributed to superconducting and transport properties measurement. All authors discussed the results; J.Z. and W.K.Y. wrote the manuscript, with discussions mainly with X.C.

Additional information

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