The development of the superconducting tetragonal PbO-type FeSe and related compounds

M. K. Wu\textsuperscript{1,2}, K. W. Yeh\textsuperscript{1}, H. C. Hsu\textsuperscript{3}, T. W. Huang\textsuperscript{1}, T. K. Chen\textsuperscript{1}, J. Y. Luo\textsuperscript{1}, M. J. Wang\textsuperscript{1}, H. H. Chang\textsuperscript{4}, C.T. Ke\textsuperscript{1}, M. H. Moh\textsuperscript{1}, and S. M. D. Rao\textsuperscript{1}

\textsuperscript{1}Institute of Physics, Academia Sinica, Nankang, Taipei, Taiwan
\textsuperscript{2}Department of Physics, National Tsing Hua University, Hsinchu, Taiwan
\textsuperscript{3}Institute of Astronomy and Astrophysics, Academia Sinica, Taipei, Taiwan
\textsuperscript{4}Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan

Received 16 September 2009, revised 28 January 2010, accepted 29 January 2010
Published online 23 February 2010

PACS 74.62.Bf, 74.70.Ad, 74.78.Db

*Corresponding author: e-mail mkwu@phys.sinica.edu.tw, Phone: +886-2-27896716, Fax: +886-2-27898347

An overview of the recent development of the superconducting FeSe\textsubscript{1-x} and related compounds is presented. Methods to synthesize high purity poly-crystalline samples, single crystals, and thin films with preferred orientation are described. It was found that the effects of chemical doping to the Se-site or Fe-site are rather different. Ionic size of the doping is found to play critical role on the occurrence of superconductivity. We also review the physical properties, including transport, magnetic, and thermal properties. There exist interesting transport anomalies in the resistivity and Hall coefficient at low temperature; and it was found that a structural distortion at low temperature is critical to the occurrence of superconductivity in these materials. However, the exact origin of these observed anomalies are not clear, and the exact pairing symmetry in FeSe-based superconductors is also still in question.

\textbf{1 Introduction} Right after the discovery of superconductivity [1] in the Fe-based quaternary oxypnictides, it was soon realized that the Fe–As tetrahedron is the key component responsible for superconductivity in this novel material system. This picture led us to the discovery of superconductivity in the binary tetragonal PbO-type FeSe compound with $T_{c} \approx 8$ K [2]. A detailed investigation of crystal structure at low temperature showed that tetragonal PbO-type FeSe undergoes a structural transition from $P4/mnm$ to $P112/n$ space group symmetry at $\sim 105$ K [2]. The planar sub-lattice is stretched with the $a, b$ lattice parameters unchanged while the $c$ axis shrinks and so that the $\gamma$ angle increases from $90^\circ$ to $90.3^\circ$. A subsequent study of Te-doping, FeSe\textsubscript{1-x}Te\textsubscript{x}, showed that the small amount of Te-addition favors monoclinic symmetry even at room temperature, and the sample with larger $\gamma$ angle corresponded to higher achievable $T_c$, with maximum onset $T_{c}$ of 15.2 K for $x = 0.5$ [3]. On the other hand, addition of sulfur component was found to be detrimental to superconductivity.

In order to better understand these observations it is necessary to develop the method to prepare better quality samples including single crystals or high quality thin film for more detailed physical properties characterizations. In this paper, we present our recent effort on the preparations of crystals and thin films. We shall also present some detailed crystal structure information at low temperature. It is unambiguously shown that the low temperature structural distortion is essential for superconductivity.

\textbf{2 FeSe single crystal growth} FeSe is known to melt congruently around 1075 °C from the phase diagram reported in the literature [4, 5]. However, the high vapor pressure of Se at this temperature would impede the growth of the tetragonal PbO-type FeSe phase deficient in Se by the melt growth techniques [6]. It is therefore more viable to grow the crystals by low temperature methods such as hydrothermal, vapor transport, and solution growth. The efforts to grow crystals by the high temperature solution
growth technique yielded good results, using KCl or KBr as a solvent. Stable tetragonal PbO-type FeSe crystals with hexagonal plate like morphology were obtained with both solvents.

Crystals were grown in a homemade vertical wire wound tube furnace. To grow crystals from high temperature solutions, pre-reacted powders of FeSe_{0.88} (nominal composition) were loaded into quartz crucibles along with KCl. A KCl to FeSe ratio of 10:1 was maintained. The solubility of FeSe in KCl was obtained by melting KCl mixed with different amounts of FeSe in evacuated quartz crucibles and rapidly cooling them.

All the powders were stored in dry boxes to prevent oxidation. KCl and KBr powders were heated to 450 °C before filling into the quartz crucibles to remove traces of moisture that might be present. Three to four crucibles of 8 mm inner diameter were placed together in an alumina crucible filled with alumina powder to provide temperature stability. The temperature of the crucibles was monitored using a separate thermocouple placed in the alumina powder. The temperature of the furnace was raised to 840 °C and held for 30 h to homogenize the solution. It was cooled to 820 °C within 1 h to provide the necessary supersaturation for nucleation. Further cooling was programmed at 0.3–0.5 °C/h from 820 to 770 °C. Then the furnace was rapidly cooled to 400 °C and held for 24 h to help stabilize the tetragonal PbO-type FeSe phase [7]. This was followed by cooling to room temperature in 2–3 h. After the furnace cooled to room temperature, the crucible was taken out of the furnace and cut to recover the KCl crystalline mass with the tetragonal PbO-type FeSe crystals embedded in it.

The tetragonal PbO-type FeSe crystals were rinsed three to four times in acetone to remove water and moisture sticking to the surface of the crystals. The rinsed crystals were dried in an oven at 80–90 °C before they were stored in evacuated desiccators and used subsequently for investigations. Washing the crystals in water did not produce any visible damage to the crystal surface even though slow attack could not be ruled out.

Figure 1 shows the single crystal X-ray scans at different temperatures with respect to the (220) orientation in comparison with the Cu (220) peak. Figure 1(a) displays the variation of the FeSe (220) peak with temperature. A clear splitting of the peak was observed at low temperature confirming the distortion from tetragonal symmetry to monoclinic symmetry. Figure 1(b) gives the temperature trace of the peak splitting. The results suggest the transition appears below ~90 K.

The temperature dependence of resistance of FeSe_{0.88} is shown in Fig. 2(a). The data for FeSe_{0.88} exhibit metallic behavior in the normal state and show zero resistance at 7.5 K with an onset transition at ~11 K. The result is very much similar to that of polycrystalline samples [2], suggesting the anisotropy in β-FeSe is rather small. A broad resistive bump is observed at a temperature close to 250 K. In addition, a small dip in resistance appears at ~100 K, which is close to the structural distortion temperature as determined by low temperature X-ray diffraction.

Figure 2(b) displays the zero field cooled (ZFC) and field cooled (FC) magnetic susceptibility for FeSe_{0.88} crystal. The data were measured with crystal c-axis oriented either perpendicular or parallel to the magnetic field. A clear superconducting transition appears at an onset temperature around 11 K. It is interesting to note that the susceptibility at normal state behaves differently with different field orientation. An anomalous bump is observed in the field along ab-plane data, but not in the other orientation. The temperature where this bump appears is similar to the resistive bump observed, as shown in Fig. 1(a). The origin of this observed anomaly is currently unknown. One possible source is related to the presence of strong spin–orbital coupling of the sample. On the other hand, the susceptibility appears to flatten out at around 100 K where the structural distortion occurs. This is consistent with the observations made in polycrystalline samples.

### 3 FeSe_{1-x}Te_{x} crystals grown by zone-melting

High purity powder materials of Fe, Se, and Te with desired stoichiometry (FeSe_{x}Te_{1−x} of x = 0 ~ 1.0) were mixed in a ball mill for at least 4 h [8]. The well-mixed powders were cold-pressed into disks under 400 kg/cm² uniaxial pressure, and then sealed in an evacuated quartz tube with a pressure of 1x10^{-5} Pa.
Figure 2 (online colour at: www.pss-b.com) Resistivity (a) and magnetic susceptibility (b) of FeSe0.88 single crystal grown by using KCl high temperature solution. The crystal axes marked in the figures refer to the direction perpendicular (∥c-axis) or parallel (∥ab-plane) to the crystal surface.

less than 10^{-4} torr and heat treated at 600°C for 20 h. The reacted bulk sample weighing about 5–8 g was reground into fine powders and loaded into double quartz ampoule. The ampoule was then loaded into an optical floating-zone furnace with 2 × 1500 W halogen lamps as infrared radiation sources. The ampoule was rotated at a rate of 20 rpm and moved at a translation rate of 1–2 mm/h. To anneal the product, as-grown crystals were heated at a rate of 100 °C/h up to 700–800 °C, held at this temperature for 48 h, cooled at the same rate down to 420 °C and held for another 30 h, then finally furnace-cooled to room temperature. The grown crystals were stored in a desiccator to avoid decomposition.

X-ray diffraction data show all diffraction peaks belong to the tetragonal phase without any second phases. Only (001) diffraction peaks found in single crystal X-ray diffraction pattern suggest that the crystallographic c axis is perpendicular to the plane of plate-like crystal. Four-fold symmetry of the (221) φ-scan on FeSe0.3Te0.7 crystal was observed, indicating the high crystalline quality of the sample. X-ray rocking curves of (010) Bragg-reflections reveal in-plane and out-of-plane mosaic structure at room temperature. The full-width half maximum (FWHM) is only 0.092° indicating excellent crystallinity.

Figure 3 (online colour at: www.pss-b.com) Resistive transitions of as grown FeSe0.3Te0.7 crystal, and after post-annealing at 700 and 800 °C. Transition becomes sharper with 800 °C annealing.

Single crystal X-ray diffraction for FeSe0.3Te0.7 crystal indicate that at room temperature, the crystal lattice already deviates from tetragonal symmetry and distorts to form the structure with space group P1121/n (a = 3.8158 Å, c = 6.2300 Å, and γ = 90.24° at 300 K). This further confirms our earlier observations on polycrystalline samples [2] that partially substituted Te atom induces a local strain in the lattice at room temperature.

The resistivity measurements on all crystals show clear superconducting transition for compositions with 0.3 < x < 0.9, with the maximum Tc at x ~ 0.6. This result is consistent with the bulk results. It is noted that the superconducting transition of crystals with all compositions are as narrow as 2–3 K. More detailed investigations suggest that the most critical step that influences the uniformity of the crystals is the post-annealing temperature. As shown in Fig. 3, sharp transition of less than 2.2 K was achieved in FeSe0.3Te0.5 and FeSe0.3Te0.7 after 800 °C post-annealing treatment. On the other hand, the crystallinity of FeSe0.3Te0.9 degraded with 780–800 °C annealing. Therefore, the temperature of post-annealing should not be higher than 750 °C for the non-superconducting x = 0.9 sample.

The results of Hall effects measurements on the crystal are consistent with those on thin films. Typical results are shown in Fig. 4 for x = 0.5 and 0.7. Noticeable temperature dependence of Hall coefficient reveals the multi-band characteristics, which is dominated by the scattering time of hole carriers. Furthermore, the R_{H,T} behavior is strongly dependent on the Te substitution level because of the modification of its Fermi surface. It is also noted that the Te-substituted crystals exhibit enhancement in upper critical field, the larger the higher Te concentration. Though it was speculated that this effect is due to the more 2-D characteristics in the Te-substitute sample, a more detailed study is needed to better understand its origin.

4 Superconducting FeSe_{1-x}Te_x thin films We have successfully made high quality superconducting
To further characterize the film quality, we have measured the in-plane \(\Phi\)-scan of some selected peaks of FeSe and FeSe\textsubscript{0.5}Te\textsubscript{0.5} films. We observed two kinds of domains with four-fold symmetry but having 45° rotation to each other. This is likely due to the large lattice mismatch (>10%) between film and substrate so that results in the 45° rotation of lattice. The calculated lattice constants for FeSe \(a = 3.787(1)\) Å, \(c = 5.528(8)\) Å, and for FeSe\textsubscript{0.5}Te\textsubscript{0.5} are \(a = 3.776(4)\) Å, \(c = 5.931(3)\) Å. Comparing with the bulk values, the \(a\)-axis lattice constant of FeSe film is expanded slightly, while it is compressed for FeSe\textsubscript{0.5}Te\textsubscript{0.5}.

Detailed resistive behavior of the as grown films has been reported. The room temperature resistivities are typically in the order of 1 mΩ cm. The temperature dependence of resistivity changes from metallic to semiconductor-like behavior as \(T\)-content increases, which is consistent with the bulk result. All films show sharp superconducting transition at low temperature, except the pure FeSe film. The undoped FeSe film is surprisingly found to be non-superconducting when deposited at relatively low temperature. A detailed study shows superconductivity can be restored either by raising the deposition temperature or increasing the film thickness. This orientation and thickness dependence of superconductivity in FeSe films was found to be closely related to the occurrence of the low temperature structural distortion.

Detailed results can be found in a recent publication. With higher \(T\)-concentration, the \(T\)\textsubscript{c} of films recover to the bulk result gradually. The transition width of films are rather narrow than the bulk data, indicating good quality of films. It was reported that in bulk Te-substitute samples the crystal structure at high temperature is already slightly distorted to exhibit \((P\overline{1}12n)\) symmetry. Further distortion to increase \(y\)-angle was also observed at low temperature. To confirm whether such effect also exists in thin films we studied the detailed structure of FeSe\textsubscript{1-x}Te\textsubscript{x} at low temperature. Figure 6

![Figure 5](image)

Figure 5 (online colour at: www.pss-b.com) X-ray diffraction patterns of FeSe\textsubscript{1-x}Te\textsubscript{x} thin films with \(x = 0-0.9\). The insert shows the shift of (001) peak with the change of Te content. Larger \(x\) gives lower peak position.
displays the observed result. FWHM of Bragg peak (221) 2θ is found to increase as temperature decreases to lower than 100 K, suggesting the occurrence of the structural distortion.

5 Structural distortion and superconductivity

It is now well established that there exists a structural transition at temperature \( T_c \) much higher than the superconducting transition point \( T_c \) in FeSe system. At \( T_c \) the tetragonal lattice \( P4/nmm \) distorts into a lower symmetry monoclinic lattice \( P112/n \) [2, 3, 8–10].

We have carried out intensive studies on the effects of substituting partially the Fe element by other transition metal elements [9, 11]. An interesting observation was that by substitution up to about 30% of Fe by the neighboring Mn element the superconducting properties were very little affected. On the other hand, it was a real surprise to observe that as small as 3% of Cu-doping completely suppressed superconductivity of FeSe. Figure 7 shows the X-ray data of the 10% Cu- and Mn doped sample measured at room temperature and low temperature.

No splitting could be identified for any peak in \( \text{Cu}_{0.1}\text{Fe}_{0.9}\text{Se}_{0.85} \) sample from 140 to 10 K, indicating the absence of any structural distortion in the 10 at. % Cu-doping samples. On the other hand, in the \( \text{Mn}_{0.6}\text{Fe}_{0.4}\text{Se}_{0.85} \) bulk sample, Fig. 3, peak splitting is observed in (220), (221), and (114) reflections at ~85 K indicating the onset of structural phase transition. This phase transition could be described by a structural distortion from tetragonal lattice \( P4/nmm \) to monoclinic \( P112/n \), which is much the same as observed in the FeSe and FeSe\(_{0.3}\text{Te}_{0.7} \) at temperatures below ~100 K.

In summary, we have successfully grown FeSe single crystals using high temperature solution method. The resistive measurements indicate that the sample is isotropic with 3D-like transport. A small anisotropy was found in magnetic susceptibility at high temperature. The origin of this anomalous behavior is currently unknown. High quality \( \text{Fe(Se}_{1-x}\text{Te}_{x})_2 \) single crystals with \( x > 0.3 \) can be synthesized using floating zone melting technique.

Uniform Te-substitution in the crystal can be achieved with high temperature (800 C°) post-annealing in vacuum. \( \text{Fe(Se}_{1-x}\text{Te}_{x})_2 \) superconducting films on MgO substrate were successfully prepared by PLD technique. The films reveal highly c-axis orientated characteristic. Comparing to the bulk samples, the deposited films have lower superconducting transition temperature, except of the sample with high Te concentration. The suppression of superconductivity in \( \text{Fe(Se}_{1-x}\text{Te}_{x})_2 \) films might be attributed to the suppression of lattice deformation in \( ab \)-plane originates from the strain effect between thin film and MgO substrate. We also report here the strong suppression of superconductivity by Cu substitution in the FeSe system. In contrast to the Mn substitution to Fe-site, which does not affect superconductivity up to almost 30%, we found only 3% Cu-substitution completely destroyed superconductivity.

Detailed structural studies of the crystals, thin films, and transition-metal doped FeSe polycrystalline samples all revealed that the low temperature structural distortion is essential to the occurrence of superconductivity in the FeSe superconducting system. Superconductivity only exists in those samples that exhibit low temperature distortion from \( P4/nmm \) symmetry to \( P112/n \) symmetry. It is thus a very intriguing question to find out whether similar distortion exists in other Fe-based superconductors. On the other hand, whether other important features, such as the presence of spin fluctuation or Fermi surface nesting, are closely associated with this distortion are important questions to explore. Clearly, there is still much to learn from this class of materials. Aside from the interesting and fundamental question of what role the Fe magnetism plays in these superconductors, one might also expect potential applications could result from these materials.

Acknowledgements

We wish to thank the National Science Council of Taiwan and the US AFOSR/DOARD for their generous financial support and the National Synchrotron Search Centre for experimental support in this work.

References


© 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim