Evidence of a miscibility gap in the FeTe$_{1-x}$Se$_x$ polycrystalline samples prepared with a melting process

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Abstract. The study of overdoped FeTe$_{1-x}$Se$_x$ (0.5 < x < 1) polycrystalline superconductor samples is reported. The samples were prepared using a melting technique previously developed by our group. Increasing the Se content a phase separation related to the formation of FeSe inside the Fe(Se,Te) phase happens, as demonstrated by structural analysis and magnetic characterization. The proposed phase separation picture is likely the fingerprint of a miscibility gap in the Fe(Se,Te) system.

1. Introduction

From the discovery of the chalcogenides superconductors [1], the ubiquitous character of FeTe$_{1-x}$Se$_x$ compounds to show a non homogeneous microstructure was enlightened [2,3]: a phase separation in the whole sample volume of two isostructural tetragonal phases with different Se/Te ratio was observed. The FeTe$_{1-x}$Se$_x$ phase diagram with 0 < x ≤ 0.5 has been deeply investigated, instead few studies on the compositions with 0.5 < x ≤ 1 have been performed [4]. For this reason we synthetized FeTe$_{1-x}$Se$_x$ polycrystalline samples with x = 0.5, 0.6, 0.7, 0.8, 0.9, 1 by a melting process technique [5,6] and we investigated their crystallographic, microstructural and physical properties using: Polarized Optical Microscopy (PLOM), X-Ray Powder Diffraction (XRPD), Scanning Electron Microscope (SEM) coupled with Energy Dispersive X-Ray Spectroscopy (EDS) analysis and DC magnetic susceptibility measurements.

2. Experimental

FeSe$_x$Te$_{1-x}$ samples (with x = 0.5, 0.6, 0.7, 0.8, 0.9, 1) powders were synthesized using the common solid state reaction method[3,4]. The obtained powders, once pelletized in a hydraulic press, were melted in a high frequency induction furnace in inert gas atmosphere. After the melting process a vacuum annealing treatment at 450° C for 20 days is performed. Phase identification was carried out by X-ray powder diffraction (XRPD–PHILIPSPW1830); Bragg–Brentano geometry; Cu Kα;
range $10^\circ$-$80^\circ$ 20; counting time 3 s) and the crystal structure indexing was performed using the FullProf software. Microstructure was analysed by a scanning electron microscope (SEM: CAMBRIDGE S360), coupled with an electron dispersive spectrometer for chemical analysis (EDS: Oxford AtztecEnergy X-Max) and PLOM. Magnetic measurements were performed by a dc SQUID magnetometer (MPMS by Quantum Design).

3. Results and discussions
The XRPD analysis reveals that the samples are mainly constituted of tetragonal anti PbO-type structure, with few traces of hexagonal polymorph NiAs-type phase. The diffractograms present a peak broadening of the diffraction lines, due to de-mixing of the main tetragonal phase in two isostructural phases characterized by a slightly different $|$Se$|$/$|$Te$|$ ratio. As the Se content increases a progressive peak splitting is observed (see Figure 1).

Both lower angle peak, related to the Te enriched structure, and higher angle one, related to the Se enriched structure, shift at higher angles with increasing $x$, indicating that Se enters in both the structures. The calculated volumes for the tetragonal crystal cells are reported in Figure 2. For $x$ that varies from $x = 0.5$ to $x = 1$, the percentage volume shrinking is about 8% for the Se enriched structure and about 3.5% for the Te enriched ones.

Figure 1. Magnification of the (101) Bragg’s peak of the Anti PbO-Type structure, varying the nominal Se content.

Figure 2. $x$ dependence of the unit cell volume for the Se enriched (left) and Te enriched (right) structures.
The contrast in PLOM imaging technique is related to the grains orientation; with this technique we are able to observe the grains structure in our samples. The PLOM images show an anomalous grain growth, varying the nominal Se concentration (see Figure 3). In the sample with $x = 0.5$ big oriented grains ($\sim 0.5 \text{ mm}^2$ size) are visible, while the FeSe sample ($x = 1$) presents small grains ($\sim 100 \mu\text{m}^2$ size). Increasing $x$ small grains with size close to those observed in the sample with $x = 1$ grow inside bigger ones (see Fig. 3 (b)). For all the samples no significant variations were observed after the annealing process. SEM & EDS analysis shows that the samples are constituted by three phases that differ mainly for the Se/Te ratio, Fig. 4: a light grey phase (B), a middle grey phases (D) surrounded by a dark grey phase (C).

Te is mainly concentrated in the B phase, where the Se/Te ratio varies from $\approx 0.7$ to $\approx 1.2$ and monotonically increases as $x$ increases. On the contrary, C and D are mainly constituted of Se-rich phase with a Se/Te ratio variation from $\approx 2$ up to $\approx 20$, that rapidly increases with $x$. The Fe concentration is homogeneous (around 1) in the B and C phases, while the D phase presents an iron contraction from $\approx 0.90$ to $\approx 1$ that increases with increasing $x$. All the samples present similar microstructure with different relative quantity of the above cited phases, as reported in Figure 5 for the samples with $0.5 \leq x \leq 1$.

Increasing $x$, C and D phases grow at the expense of the B one.
ZFC susceptibility measurement at low field (10⁻³ T). Are presented in Fig. 6. The x = 0.5 sample presents a sharp single step transition with Tc-onset ≈ 13.4 K and a full shielding volume fraction at 4.2 K. Double step transitions are observed in x = 0.6, 0.7 samples, with Tc-onset at 13.9 K and 12 K respectively. The sample with x = 1 presents a single step transition with Tc-onset ≈ 7.7 K as expected for FeSe samples. The onset of the second transition of the x = 0.6, 0.7 samples is ≈ 7.5 K, suggesting the presence of FeSe inclusions.

4. Conclusions
In this work we studied the Fe(SexTe1-x) overdoped region of the phase diagram. Samples with nominal Se content x = 0.5, 0.6, 0.7, 0.8, 0.9, 1 were prepared by a melting process. From the XRPD analysis we observed two isostructural anti-PbO type structures with different Se/Te ratio. This phase de-mixing increases rapidly with increasing Se content, with a clear bi-phasic behaviour for the x = 0.6, 0.7 as shown from the ZFC susceptibility. PLOM imaging shows an anomalous grain growth: small grains grow inside bigger ones with increasing x. The typical dimension of the small grains is the same as for the x = 1 sample. SEM-EDS analysis confirms a growth of a selenium enriched phase inside the tellurium enriched one. This suggest the existence of a miscibility gap in the FeSe – FeTe pseudo binary phase diagram. We observed that this phase de-mixing bring always to a worsening of the superconducting properties.

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Figure 6. Magnetic susceptibility as a function of the temperature.