Homogeneity range of ternary 11-type chalcogenides Fe$_{1+y}$Te$_{1-x}$Se$_x$

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The 11-type Fe-chalcogenides belong to the family of Fe-based superconductors. In these compounds, the interstitial Fe is known to strongly influence the magnetic and superconducting properties. Here we present the chemical homogeneity range of ternary compounds Fe$_{1+y}$Te$_{1-x}$Se$_x$ based on powder x-ray diffraction, energy dispersive x-ray analysis and magnetization measurements. Our investigations show that the maximum amount of excess Fe in homogeneous Fe$_{1+y}$Te$_{1-x}$Se$_x$ decreases with increase in Se substitution for Te. Using our synthesis procedure, single-phase Fe$_{1+y}$Te$_{1-x}$Se$_x$, with $0.5 \leq x < 1$ could not be formed for any amount of excess Fe. Further, the superconducting volume fraction in the material is found to be strongly suppressed by excess Fe.

INTRODUCTION

The 11-type Fe-chalcogenides (Fe-Ch) are considered as representative members of the family of Fe-based superconductors because their crystal structure comprises only of the basic tetrahedral building blocks of edge-sharing Fe(Ch)$_4$ units which are similar to the Fe(As)$_4$ units of the Fe-arsenides (Fe-As). The composition of single-phase material of Fe$_{1+y}$Se with $0 \leq y \leq 0.01$ is very close to stoichiometry [1, 2]. The superconducting properties of FeSe were found to be extremely sensitive to the amount of excess Fe present in the sample. The superconducting transition temperature $T_c$ decreases drastically with increasing Fe [1]. In contrast, the isostuctural phase of the heavier homologue tellurium, Fe$_{1+y}$Te, occurs only in the presence of excess Fe $0.06 \leq y \leq 0.15$ [3–6]. The excess Fe is situated in the interstitial 2$c$ crystallographic site within the tellurium planes [7]. Bulk Fe$_{1+y}$Te does not show a superconducting transition, but its magnetic and structural properties can be tuned by changing the amount of excess Fe in the sample [3–7]. Substitution of Se for Te in Fe$_{1+y}$Te induces superconductivity with a maximum $T_c \approx 15$ K observed for $\approx 50$ % Se substitution [8–12]. Also for the substituted materials, the superconducting as well as the normal state properties of Fe$_{1+y}$Te$_{1-x}$Se$_x$ are found to be influenced by excess Fe. In the normal state, a charge carrier localization in the electrical transport has been observed in Fe$_{1+y}$Te$_{0.5}$Se$_{0.5}$ for higher Fe concentrations [10, 11]. Since the concentrations of excess Fe in single phase materials of Fe$_{1+y}$Te [5] and Fe$_{1+y}$Se [2] are substantially different, a composition gradient of Fe can be expected in the substitution series of Fe$_{1+y}$Te$_{1-x}$Se$_x$. To our knowledge, a careful investigation of the chemical homogeneity range of Fe$_{1+y}$Te$_{1-x}$Se$_x$ is still lacking even though the knowledge of the chemical homogeneity range of these materials is of utmost importance for a proper interpretation of more complex phenomena such as the coexistence of magnetism and superconductivity. Therefore, we synthesized a series of polycrystalline Fe$_{1+y}$Te$_{1-x}$Se$_x$ and investigated the properties by powder x-ray diffraction (PXRD), energy dispersive x-ray spectroscopy (EDX), and magnetization measurements to establish the homogeneity range of the ternary phase.

EXPERIMENTAL

Polycrystalline samples of Fe$_{1+y}$Te$_{1-x}$Se$_x$ were synthesized by solid-state reaction. More than sixty compounds with different compositions in the range $0 \leq y \leq 0.15$ and $0 \leq x \leq 1$ were synthesized by taking appropriate mixtures of nominal amounts of Fe, Se and Te. Starting materials were heated up to 973 K with a rate of 100 K/h and kept at this temperature for 24 hours before increasing the temperature to 1193 K. The dwelling at 1193 K for 24 h was followed by cooling to 973 K with a rate of 100 K/h, and further annealing for 12 hours. Finally, samples were cooled to room temperature at a rate of 100 K/h. In specific cases, the samples were annealed at 973 K for 48 h to enhance the homogeneity. For the nominal compositions with $x \geq 0.5$, a lower annealing temperature (673 K) was used. All synthesized materials were characterized by PXRD and EDX analysis. The lattice parameters were determined using the diffraction lines of LaB$_6$ as an internal standard.

RESULTS AND DISCUSSION

The PXRD patterns and back scattered electron (BSE) images of Fe$_{1+y}$Te$_{0.75}$Se$_{0.25}$ for $0 \leq y \leq 0.12$ are presented in Fig. 1. For samples with $y \geq 0.12$, the EDX analysis confirms the presence of unreacted Fe. The BSE image of the sample $x = 0.25$, $y = 0.12$ is presented in Fig. 1(b), in which the elemental Fe is indicated by an arrow. In the case of PXRD, the reflection corresponding to unreacted α-Fe overlaps with the main phase and hence, could not be detected. For low Fe contents ($y \leq 0.02$), a second phase with EDX composition Fe$_{0.69(1)}$Te$_{0.79(1)}$Se$_{0.21(1)}$ is observed, see Fig. 1(c). The peak positions of this second phase suggest...
that the impurity phase is related to the structure motif of hexagonal Fe$_{0.67}$Te ($P6_3/mmc$) [13]. The refined lattice parameters of the second phase are $a = 3.7779(2)$ Å and $c = 5.6668(5)$ Å. These lattice parameters are larger than the reported values for NiAs-type Fe$_{0.685}$Te$_{0.8}$Se$_{0.2}$ ($a = 3.771$ Å and $c = 5.660$ Å) [14]. Single phase Fe$_{1+y}$Te$_{0.75}$Se$_{0.25}$ samples can be obtained for $0.02 < y < 0.12$. Lattice parameters and unit cell volumes as a function of the Fe content are given in Fig. 2. With increasing amount of Fe, lattice parameters and volume decrease within the homogeneity range. The compositions obtained from the EDX analysis are presented in Table I. The EDX results are in agreement with the PXRD analysis.

The compositions of the two phases are listed in Table II. However, after annealing the samples at 973 K for 2 days, chemically homogeneous samples could be obtained. The compositions of the annealed samples are also listed in Table II while their PXRD patterns are presented in Fig. 3, top panel. Impurities were observed only for samples with $y = 0$ and $y = 0.1$. The bottom panel of Fig. 3 displays back-scattered and secondary electron images of samples with nominal compositions Fe$_{1.06}$Te$_{0.55}$Se$_{0.45}$ and Fe$_{1.04}$Te$_{0.55}$Se$_{0.45}$. These images

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**TABLE I. Compositions according to EDX measurements of polycrystalline samples Fe$_{1+y}$Te$_{0.75}$Se$_{0.25}$ after annealing at 973 K for 2 days.**

| $y$ | Phase 1 | Phase 2 |
|-----|---------|---------|
| 0.00 | Fe$_{0.99(2)}$Te$_{0.71(2)}$Se$_{0.29(2)}$ | * |
| 0.04 | Fe$_{0.98(1)}$Te$_{0.70(1)}$Se$_{0.30(1)}$ | |
| 0.06 | Fe$_{1.03(1)}$Te$_{0.75(2)}$Se$_{0.25(2)}$ | |
| 0.08 | Fe$_{1.06(2)}$Te$_{0.77(2)}$Se$_{0.23(2)}$ | |
| 0.10 | Fe$_{1.10(5)}$Te$_{0.77(3)}$Se$_{0.23(1)}$ | |
| 0.12 | Fe$_{1.07(1)}$Te$_{0.72(1)}$Se$_{0.28(1)}$ | Fe |
TABLE II. Compositions obtained from the EDX analysis of as-grown as well as annealed polycrystalline samples Fe$_{1+y}$Te$_{0.55}$Se$_{0.45}$. The as-grown samples phase-separated into Phase 1 and Phase 2. After annealing the samples at 973 K for 2 days, single phase materials could be obtained.

| y    | Phase 1                        | Phase 2                        | after annealing (single phase) |
|------|--------------------------------|--------------------------------|-------------------------------|
| 0.00 | Fe$_{1.02(2)}$Te$_{0.56(2)}$Se$_{0.44(2)}$ | Fe$_{0.98(1)}$Te$_{0.35(2)}$Se$_{0.65(2)}$ | Fe$_{1.04(1)}$Te$_{0.57(2)}$Se$_{0.43(2)}$ |
| 0.02 | Fe$_{1.01(1)}$Te$_{0.54(5)}$Se$_{0.46(5)}$ | Fe$_{0.95(1)}$Te$_{0.22(1)}$Se$_{0.78(1)}$ | Fe$_{1.06(3)}$Te$_{0.58(1)}$Se$_{0.42(1)}$ |
| 0.04 | Fe$_{1.04(1)}$Te$_{0.54(1)}$Se$_{0.46(1)}$ | Fe$_{0.95(1)}$Te$_{0.26(6)}$Se$_{0.74(6)}$ | Fe$_{1.07(3)}$Te$_{0.58(2)}$Se$_{0.42(2)}$ |
| 0.06 | Fe$_{1.09(2)}$Te$_{0.56(2)}$Se$_{0.44(2)}$ | Fe$_{0.98(1)}$Te$_{0.37(3)}$Se$_{0.63(3)}$ | Fe$_{1.10(1)}$Te$_{0.57(1)}$Se$_{0.43(1)}$ |
| 0.08 | Fe$_{1.12(3)}$Te$_{0.56(1)}$Se$_{0.44(1)}$ | Fe$_{1.06(4)}$Te$_{0.33(1)}$Se$_{0.67(1)}$ | Fe$_{1.12(2)}$Te$_{0.57(1)}$Se$_{0.43(1)}$ |
| 0.10 | Fe$_{1.13(1)}$Te$_{0.56(1)}$Se$_{0.44(1)}$ | Fe                        | Fe$_{1.12(1)}$Te$_{0.57(2)}$Se$_{0.43(2)}$ |

FIG. 4. (a) Lattice parameters and (b) unit cell volume as a function of nominal Fe composition for annealed samples Fe$_{1+y}$Te$_{0.55}$Se$_{0.45}$ ($0.00 \leq y \leq 0.10$).

| y    | a (Å)   | c (Å)   | Volume (Å$^3$) |
|------|---------|---------|----------------|
| 0.00 | 3.975   | 6.03    | 86.7           |
| 0.02 | 3.975   | 6.03    | 86.7           |
| 0.04 | 3.975   | 6.03    | 86.7           |
| 0.06 | 3.975   | 6.03    | 86.7           |
| 0.08 | 3.975   | 6.03    | 86.7           |
| 0.10 | 3.975   | 6.03    | 86.7           |

do not display any secondary phases. Fig. 4 shows the variation of lattice parameters ($a$ and $c$) and unit cell volumes of annealed Fe$_{1+y}$Te$_{0.55}$Se$_{0.45}$ samples. Both lattice parameters and unit cell volume decrease with increasing Fe-content up to $y = 0.06$. A further increase of the Fe concentration, i.e., ($y \geq 0.08$) does not change the lattice parameters. As a summary of our PXRD, EDX, and lattice parameter analysis of this series, single phase materials Fe$_{1+y}$Te$_{0.55}$Se$_{0.45}$ can be obtained when the nominal Fe-content rises into the range $0.00 < y \leq 0.06$. For further increase in Se ($x \geq 0.5$) in Fe$_{1+y}$Te$_{1-x}$Se$_x$, a chemically homogeneous phase could not be obtained even after annealing the samples. Although it is known that long-time annealing of these ternary samples at high temperatures homogenizes the distribution of Se and Te in a crystal, removes local lattice distortions, and induces bulk superconductivity [15–17], single phase samples of Fe$_{1+y}$Te$_{1-x}$Se$_x$ for $x \geq 0.5$ are not reported in literature.

Based on our studies, we constructed a ternary phase diagram of the Fe-Te-Se system for homogeneous compositions of Fe$_{1+y}$Te$_{1-x}$Se$_x$, see Fig. 5. The values of the homogeneity ranges of NiAs-type $\delta$-Fe$_2$Se and Fe$_{0.67}$Te, and monoclinic Fe$_{0.75}$Te phases taken from the Pauling File Inorganic Materials Database [18] are also presented in the upper panel. It can be seen that single phases of tellurium-rich compositions can be obtained in the presence of excess Fe. For example, compounds of Fe$_{1+y}$Te$_{0.55}$Se$_{0.45}$ and Fe$_{1+y}$Te$_{0.75}$Se$_{0.25}$ can be realized without impurity phase when the nominal Fe-content falls into the range $0.00 < y \leq 0.08$ and $0.02 < y < 0.12$, respectively. Upon increasing Fe content, the feasible substitution amount of Se decreases. For $y = 0.13$, Se substitution is possible in the range $0.00 \leq x < 0.20$, whereas for $y = 0.06$ single phase samples of Fe$_{1.06}$Te$_{1-x}$Se$_x$ can be prepared with $0.00 \leq x \leq 0.45$. For low Fe content ($y \approx 0$), impurity peaks of NiAs-type Fe$_{1-y}$Te$_{1-x}$Se$_x$ are observed, whereas for Fe contents $y \geq 0.12$ in Fe$_{1+y}$Te$_{0.75}$Se$_{0.25}$, elemental Fe remains unreacted.

In order to investigate the effect of excess Fe on the superconducting properties of Fe$_{1+y}$Te$_{1-x}$Se$_x$, we performed magnetization measurements on phase-pure samples. We find that both the superconducting volume fraction as well as the $T_c$ of the materials drastically decrease when the amount of excess Fe is increased by small amounts. This can clearly be inferred from the example presented in Fig. 6 where magnetic susceptibilities $\chi(T)$ measured in the field cooled (FC) and zero field cooled (ZFC) protocols for Fe$_{1.02}$Te$_{0.55}$Se$_{0.45}$ and Fe$_{1.04}$Te$_{0.55}$Se$_{0.45}$ are compared. For Fe$_{1.02}$Te$_{0.55}$Se$_{0.45}$, the onset of the superconducting transition is $\approx 13$ K, with a large diamagnetic shielding, which appears to saturate at low temperatures. Upon a 2 % increase in excess Fe, it can be seen that both the onset of superconductivity and the superconducting shielding factor decreases drastically. A similar behavior of $\chi(T)$ was observed for samples with $y > 0.02$. These studies confirm that, even if the samples are chemically homogeneous, bulk superconductivity occurs for the samples with lowest amount of excess Fe possible.

CONCLUSIONS

We synthesized a series of ternary compounds with compositions Fe$_{1+y}$Te$_{1-x}$Se$_x$ in order to determine their chemical homogeneity range. For single-phase materials, we found that the maximum amount of excess Fe decreases with increase in Se substitution. For compounds with $x \geq 0.5$, our synthesis procedure did not yield ho-
mogeneous compositions. Based on our studies we constructed a ternary phase diagram of the Fe-Te-Se system. We also showed that even in chemically homogeneous compounds, the superconducting volume fraction as well as the transition temperature $T_c$ are rapidly suppressed by an increase in the amount of excess Fe.

FIG. 5. Upper panel: Ternary phase diagram of the Fe-Te-Se system. Blue dots indicate single phase of tetragonal Fe$_{1+y}$Te$_{1-x}$Se$_x$. The values for homogeneity ranges of NiAs-type $\beta$-Fe$_{1-y}$Se and Fe$_{0.67}$Te, and monoclinic Fe$_{0.75}$Te phases Fe$_{0.75}$Te are taken from the Pauling File Inorganic Materials Database [18]. Lower panel: Homogeneity range of Fe$_{1+y}$Te$_{1-x}$Se$_x$ given in a two-dimensional plot for clarity.

FIG. 6. Magnetic susceptibility $\chi(T)$ measured in the field cooled (FC) and zero field cooled (ZFC) protocols for Fe$_{1.02}$Te$_{0.55}$Se$_{0.45}$ and Fe$_{1.04}$Te$_{0.55}$Se$_{0.45}$.

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