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Properties of FeSe-type superconductors with ternary mixture of chalcogens

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ABSTRACT

A series of $Fe_{1.02}Te_{0.5}Se_{0.5-x}S_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5) samples has been synthesized by solid state reaction. Keeping the tellurium content unchanged the influence of the substitution of sulfur for selenium on the crystal structure and superconducting properties of synthesized samples has been studied by means of X-ray diffraction, electrical resistivity and magnetic susceptibility measurements. It has been found that the unit cell volume of the superconducting phase increases with increasing S concentration despite the lower ionic radius of sulfur in comparison with selenium. Together with expansion of the lattice the S for Se substitution is observed to reduce the T_c value in $Fe_{1.02}(Te_{0.5}Se_{0.5})$.

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1. Introduction

Iron-based layered compounds like iron oxypnictides [1,2] and iron chalcogenides [3–7] exhibit unusual high-temperature super-conductivity. Among these materials iron selenide has a simplest crystal structure, as compared with pnictides. This circumstance favors experimental and theoretical studies of FeSe chemical sub-stitutions and high pressure effects that could lead to a better understanding of a superconductivity mechanism in iron-contain-ing compounds. It was found that the critical temperature may be increased by partial substitution of Se atoms by S or Te [6,8–11]. Such a chalcogen substitution can be considered as a chemical pres-sure and an effective T_c changer because the S, Se and Te atoms have the same valence but the different ionic radii. As reported in litera-ture [6–10], the non-homogeneities and strains in the lattice caused by substitution affect the superconducting properties of these materials. The mechanical pressure was observed to lead to the non-monotonous change of the critical temperature in FeSe-based superconductors with a maximal value up to 37 K [11–18]. The T_c value in iron-oxypnictide and iron-chalcogenide superconductors is found to correlate well with the structural parameters such as the distance between the anions and the Fe plane (anion height) and angles between Fe-anion bonds [19–23]. However, as sug-gested in [23], the correlation between structural parameters and superconducting properties may not be universal for all of the iron-based superconductors; the optimal structural parameters in chalcogenide and pnictide systems may be slightly different. More-over, in the substituted iron chalcogenide compounds, the presence of anions with different ionic radii may result in the disorder of the anion height and affect the superconducting properties [21].

In previous studies [6–11], the substitution effects on the crystal structure and properties of iron chalcogenide superconductors were investigated in the compounds with different binary mixtures of chalcogens (Se–Te, Se–S, Te–S). The aim of the present work is to study how the presence of all three chalcogens will affect the crys-tal structure and superconducting properties of FeSe-type com-pounds bearing in mind that the chalcogen ions have not only different radii but also different electronegativities and polarizabil-ities and, therefore, may form chemical bonds with different covalency/ionicity ratio and varying strength. We chosen the $Fe_{1.02}(Te_{0.5}Se_{0.5})$ compound with a highest value of T_c as a starting material and attempted to synthesize a series of $Fe_{1.02}Te_{0.5}Se_{0.5-x}S_x$ samples with the substitution of sulfur for selenium at a fixed tellu-rium content suggesting that the large tellurium ions bonded with iron will form the skeleton of the superconducting phase.

2. Experimental

Polycrystalline samples with nominal compositions $Fe_{1.02}Te_{0.5}Se_{0.5-x}S_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$) were prepared by

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a solid state reaction method. The starting materials: iron powder (99.98%), tellurium (99.99%), selenium (99.99%) and sulfur (99.99%) were sealed into evacuated quartz tubes and heat treated at 700 °C for 24 h at the start of samples preparation. The resulting samples were ground, pressed into pellets and re-sealed in evacuated quartz tubes. In order to reach homogeneity we used the prolongated annealing processes: the first annealing at 500 °C for 10 h, then at 700 °C for 38 h and additional annealing at 700 °C for 120 h. Structure and phase purity of the samples were examined at room temperature by powder X-ray diffraction using a Bruker D8 Advance diffractometer with Cu Kα radiation. The electrical resistivity was measured by a four-probe dc method in the temperature range from 8 up to 300 K with using a closed-cycle refrigerator. Temperature dependence of the magnetization was measured by means of a SQUID magnetometer MPMS XL-7 EC.

3. Results and discussion

The X-ray diffraction patterns for $Fe_{1.02}Te_{0.5}Se_{0.5-x}S_x$ for $x = 0$ and $x = 0.4$ are shown in Fig. 1. The main phase in the samples is a tetragonal phase of the PbO-type, while impurity phases (hexagonal phase with NiAs structure and iron oxide Fe_3O_4 with cubic structure) were detected as well. As it turned out, the substitution of smaller sulfur ions for selenium ions expands the crystal lattice of the superconducting phase. It is clear seen from the inset in Fig. 1 which demonstrates the shift of the (1 0 1) peak belonging to the tetragonal phase, and from Fig. 2 which shows the concentration dependences of a and c lattice parameters of the tetragonal phase. The lattice parameters $a = 3.789$ Å and $c = 5.984$ Å obtained for our initial compound $Fe_{1.02}Te_{0.5}Se_{0.5}$ are consistent with
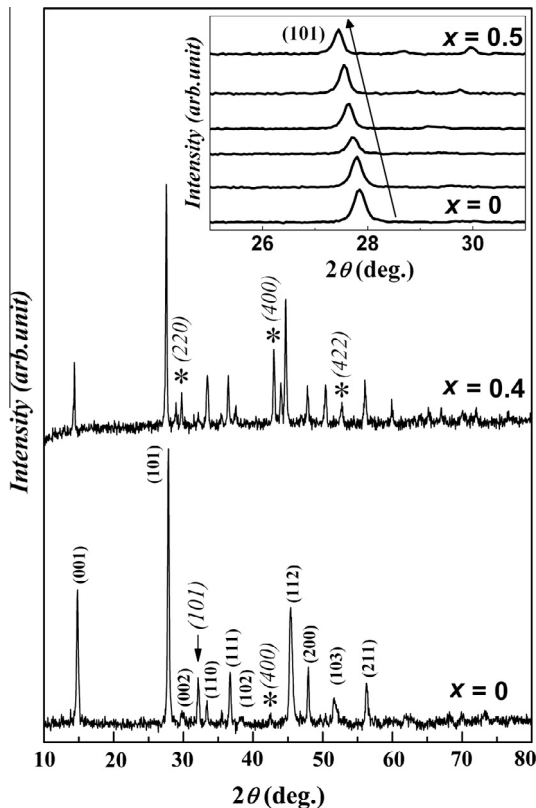
Fig. 1. X-ray diffraction patterns for samples $Fe_{1.02}Te_{0.5}Se_{0.5-x}S_x$ with $x = 0$ and $x = 0.4$. Inset shows the shift of (1 0 1) peak belonging to the PbO-type tetragonal phase with increasing S content. The peaks associated with hexagonal impurity phase are marked with arrows and the peaks associated with oxide impurity phase are marked with asterisks.
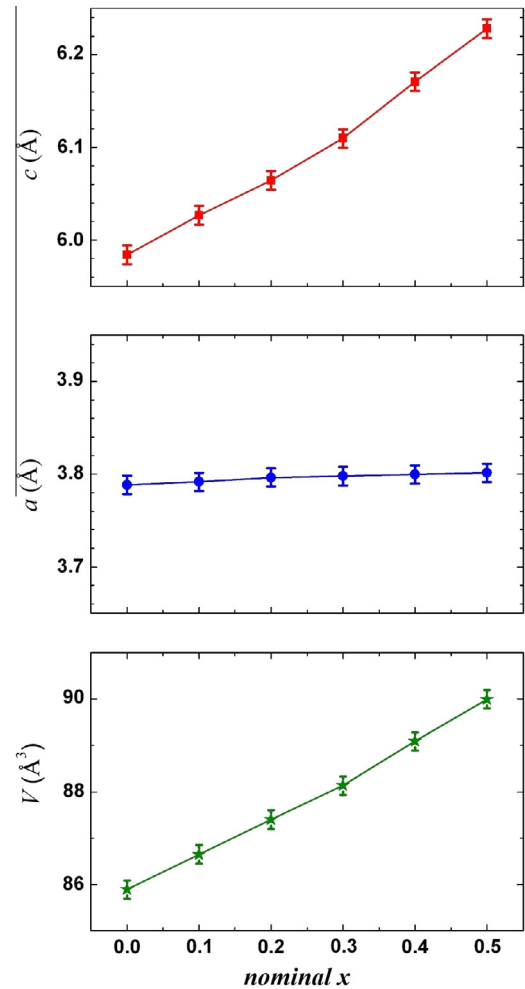
Fig. 2. Values of the lattice parameters and the unit cell volume of the tetragonal phase for the $Fe_{1.02}Te_{0.5}Se_{0.5-x}S_x$ samples as a function of the nominal sulfur concentration.

published data [10]. The simultaneous growth of both the a and c parameters with the substitution of S for Se in $Fe_{1.02}Te_{0.5}Se_{0.5-x}S_x$ seems to be an unusual result. In the compounds $Fe(Se_{1-x}S_x)$ and $Fe(Se_{1-x}Te_x)$ with the binary chalcogen mixture, a quite expected change in the crystal lattice with increasing x is observed: the contraction of the unit cell in the first system and expansion in the second one in accordance with the ratio of S, Se and Te ionic radii [10]. As follows from Fig. 2, more appreciable lattice expansion with increasing sulfur content in $Fe_{1.02}Te_{0.5}Se_{0.5-x}S_x$ occurs in the c direction. At $x = 0.5$, the growth of the c parameter reaches ∼3.9%, while the $\Delta a/a$ value is estimated to be about one order smaller (∼0.34%). This anisotropy in the lattice expansion correlates with anisotropic compressibility of FeSe evidenced by high-pressure experiments and implies softness of interlayer chalcogen–chalcogen interactions [12]. These interlayer interactions are of the van der Waals-type in contrast to the covalent/ionic bonding between iron and chalcogen atoms and thus they are weaker.

The expansion of the lattice in the $Fe_{1.02}Te_{0.5}Se_{0.5-x}S_x$ system with S for Se substitution at the permanent tellurium concentration can be caused by the difference in the iconicity/covalency ratio of chemical bonds Fe-S, Fe-Se and Fe-Te. Because of a higher electronegativity value of sulfur in comparison with selenium the Fe–S bonds exhibit a higher ionicity than Fe–Se bonds. The rough estimation of the ionicity of a single bond in Fe–X (X = S, Se, Te) can be made by using the empirical expression