Abstract

The temperature dependence of thermal conductivity and the temperature and magnetic field dependence of electrical resistivity have been measured for FeTe$_{1-x}$S$_x$ polycrystalline samples. The samples were prepared by solid state reaction with a three-step procedure. For FeTe$_{0.8}$S$_{0.2}$ and FeTe$_{0.7}$S$_{0.3}$, zero resistivity due to the superconducting transition was observed not only in oxygen post-annealed samples but also in as-grown ones. These samples include the certain amount of impurities FeTe$_2$ and Fe$_3$O$_4$. The formation of these ion compounds reduces the excess Fe atoms leading to the appearance of the zero resistivity in as-grown samples. Positive magnetoresistivity and/or negative magnetoresistivity, which were extremely small, were observed for FeTe and S-doped samples. The magnetoresistivity curves show B$^2$ dependence. It was observed that the thermal conductivity $\kappa$ of FeTe exhibits a hump structure below 72 K which corresponds to the crystal structural and magnetic transitions. The enhancement of $\kappa$ due to the superconducting transition could not be detected for as-grown FeTe$_{0.8}$S$_{0.2}$ and FeTe$_{0.7}$S$_{0.3}$ because of the absence of the bulk superconductivity in the as-grown samples and the extremely small ratio of the electronic contribution to $\kappa$.

1. Introduction

It is known that in synthesizing FeTe$_{1-x}$S$_x$ compounds, excess Fe atoms cannot be avoided, and these excess Fe atoms suppress the superconducting transition. Moreover, several iron oxides may be formed during the sinter at...
high temperature. In order to investigate the influence of impurities, electrical resistivity and thermal conductivity are measured for as-grown and post-annealed samples of Fe-11 type which has the simplest crystal structure.

2. Experimental

Polycrystalline samples of FeTe$_{1-x}$S$_x$ with $x = 0.0, 0.1, 0.2, 0.3$ were synthesized by a solid state reaction technique with a three-step procedure. The starting materials are Fe (99 %, 75 μm), Te (99 %, 75 μm) and S (99.99 %, 75 μm). At first, the TeS powder was prepared to avoid evaporation of S during the sinter at high temperature. A mixture of Te and S powders with a nominal composition of Te:S = 1:1 was encapsulated in an evacuated quartz tube and heated 450 °C for 10 hours. The powders of Fe, Te and TeS were mixed with a stoichiometric ratio of FeTe$_{1-x}$S$_x$, and were pelletized, sealed into an evacuated quartz tube and heated at 600 °C for 12 hours. The sintered pellet was reground, pressed into pellet again, sealed into an evacuated quartz tube and heated at 750 °C for 12 hours. Some of obtained samples were further annealed under the oxygen atmosphere at 200 °C for 2 hours. The crystal structure was characterized by X-ray diffraction (XRD). The electrical resistivity measurement was carried out with a Physical Properties Measurement System (Quantum Design). The thermal conductivity was measured by a steady state method in a temperature range 4 - 140 K. One strain gauge KFG-1-350-C1-11 (Kyowa Electronic Instruments Co.) and two chromel/Au-7at%Fe thermocouples were attached to a sample. The Strain gauge was used as a heater to generate a temperature gradient in the sample. Two thermocouples were used to measure the temperature gradient. The temperature of a sample stage was controlled with a GM-refrigerator and a heating system with a PID controller.

3. Results and discussion

The room temperature XRD patterns for as-grown and post-annealed samples of FeTe$_{1-x}$S$_x$ ($x = 0.0, 0.1, 0.2$ and 0.3) are presented in Fig. 1. It can be seen that all crystals have a tetragonal basic structure with the space group of $P4/nmm$. In addition, impurity phases of FeTe$_2$ and Fe$_3$O$_4$ are clearly observed. The intensity of reflections of FeTe$_2$ phase is especially strong. The amounts of FeTe$_2$ and Fe$_3$O$_4$ hardly change by post-annealing. The volume of unit cell and lattice parameters “$a$” and “$c$” were deduced from XRD by using a unit cell parameter refinement program CellCalc. The obtained values are listed in Table 1. For as-grown samples, both “$a$” and “$c$” decrease monotonically with increasing nominal S content due to substitution of S at Te site. After annealing, the lattice parameter “$a$” slightly decreases.

![Fig. 1. The XRD patterns of as-grown samples (upper panel), and annealed samples (lower panel) of FeTe$_{1-x}$S$_x$ ($x = 0.0, 0.1, 0.2$ and 0.3).](image-url)
The temperature dependence of electrical resistivity $\rho$ is represented in Fig. 2 for FeTe$_{1-x}$S$_x$ ($x = 0.0, 0.1, 0.2$ and $0.3$). It can be seen that FeTe is not superconducting, and takes a remarkable maximum near 85 K, which corresponds to the structural and magnetic transitions [1]. The S-substituted samples exhibit the negative temperature dependence of $\rho$ above 10 K, below which the onset of the superconducting transition appears. An anomaly is observed in $\rho$ ($T$) curve at $\sim 120$ K for all samples, namely, the slope of resistivity $d\rho/dT$ changes abruptly. In the XRD patterns, reflect peaks of impurity phase Fe$_3$O$_4$ are found. Fe$_3$O$_4$ is known to exhibit the Verwey metal-nonmetal transition at 120 K, below which the conductivity sharply drops [2]. Therefore, this resistivity anomaly can be attributed to the Verwey transition on account of Fe$_3$O$_4$ impurity. An enlargement of the temperature range below 15 K is shown in Fig. 2 (b) for as-grown samples and in Fig. 2 (d) for post-annealed samples. The zero resistivity due to the superconductivity is observed not only in post-annealed samples but also in as-grown ones. The zero resistivity temperatures $T_c$ are estimated to be 3.4 K and 3.8 K for as-grown FeTe$_{0.8}$S$_{0.2}$ and FeTe$_{0.7}$S$_{0.3}$. It is known that in synthesizing these compounds, excess Fe atoms cannot be avoided, and these excess Fe atoms suppress the superconducting transition. The result of XRD indicates that the samples made by our method include considerable amounts of FeTe$_2$ and Fe$_3$O$_4$. The formation of these iron compounds leads to a depletion of Fe concentration and hence leads to the enhancement of superconductivity. After annealing, the $T_c$ increases to 5.2 K for FeTe$_{0.8}$S$_{0.2}$ and to 6.5 K for FeTe$_{0.7}$S$_{0.3}$.

Table 1 Lattice parameters estimated from XRD analysis for the as-grown and the post-annealed samples of FeTe$_{1-x}$S$_x$.

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<th>$x$</th>
<th>$a$ (nm)</th>
<th>$c$ (nm)</th>
<th>$V$ (nm$^3$)</th>
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<th>$c$ (nm)</th>
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Fig. 2. Resistivity versus temperature curves of FeTe$_{1-x}$S$_x$. (a) and (b) for as-grown samples, (c) and (d) for post-annealed samples. (e): Temperature dependence of magnetoresistivity $\Delta \rho/\rho(0) = (\rho(B) - \rho(0))/\rho(0)$ at $B = 7$ T for as-grown FeTe and post-annealed FeTe$_{0.8}$S$_{0.2}$.
Other notable phenomena of electrical resistivity are the very week minimum appeared in FeTe and a negative magnetoresistivity observed in S-substituted samples. As shown in the inserted figures, the resistivity of FeTe takes a minimum around 4.0 K and increases with logarithmic temperature dependence with decreasing temperature. In Fig. 2 (e), the normal state magnetoresistivity $\Delta \rho(0)$ at $H = 7$ T is plotted as a function of the temperature for FeTe and post-annealed FeTe$_{0.8}$S$_{0.2}$. For FeTe, a relatively large positive magnetoresistivity is observed around 70 K. Similar behaviour has been reported for Se-substituted FeTe compound [3]. FeTe$_{0.8}$S$_{0.2}$ exhibits a negative magnetoresistivity with extremely small magnitude, namely below 0.3%. The critical magnetic fields $H_{c2}(T)$ and $H_{irr}(T)$ were estimated using two criterions of $H_{c2} = H$ at which $\rho = 90 \% \rho_n$ or 10 $\% \rho_n$, respectively, where $\rho_n$ is the normal state resistivity. The values of $H_{c2}(T)$ and $H_{irr}(T)$ were calculated according to the WHH theory. The values of $H_{c2}(0)$ and $H_{irr}(0)$ estimated for FeTe$_{0.7}$S$_{0.3}$ are 125 T and 75 T, respectively.

Fig. 3 shows the temperature dependence of thermal conductivity $\kappa$ for as-grown samples. The magnitude of $\kappa$ of FeTe is almost the same as that reported by M. Tropeano et. al.[3]. The FeTe has the highest $\kappa$ within the series in Fig. 3. In this sample, no disorder related to S-substitution is present. The $\kappa$ decreases with increasing the ratio of S-substitution due to an increase in substitutional disorder. The $\kappa$ for FeTe exhibits a hump structure below 73 K which corresponds to the resistivity anomaly caused by the structural and magnetic transitions. This means that below this temperature a phonon scattering is suppressed by the structural and magnetic orderings. On the other hand, it is hard to find the reflection of the Verway transition of impurity Fe$_3$O$_4$ in the $\kappa$ within the measurement accuracy. The expected enhancements of $\kappa$ at the respective superconducting transition temperatures cannot be recognized for both FeTe$_{0.8}$S$_{0.2}$ and FeTe$_{0.7}$S$_{0.3}$, which is considered to be caused by the absence of the bulk superconductivity and the extremely small contribution of electrons to the thermal conductivity. The electronic thermal conductivities evaluated by the Wiedeman-Franz law are 2.5 mW/cm K at 300 K and 0.027 mW/cm K at 10 K for FeTe$_{0.8}$S$_{0.2}$. These values are negligibly small.

4. Summary

The FeTe$_{1-x}$S$_x$ samples were made by the three-step solid-state reaction method. The as-grown samples with $x = 0.2$ and 0.3 exhibit the zero resistivity below 3.4 K and 3.8 K, respectively, which is considered to be caused by the reduction of the excess Fe due to the formation of FeTe$_2$ and Fe$_3$O$_4$ impurity phases. The $\kappa$ of FeTe exhibits a hump around 73 K corresponding to the structural and magnetic transitions. The extremely small negative and positive magnetoresistivities are observed. The $H_{c2}(0)$ and $H_{irr}(0)$ were estimated according to the WHH theory.

References