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INFLUENCE OF Ag_2Te ON TRANSPORT PROPERTIES OF $(AgSbTe_2)_{0.9}(PbTe)_{0.1}$

The transport properties of $(AgSbTe_2)_{0.9}(PbTe)_{0.1}$, namely, the electrical conductivity and the Seebeck (S) and Hall (R_H) coefficients, are studied in the temperature interval 80–560 K. An endothermic peak at 410 K is found by the differential scanning calorimetry (DSC). Sharp changes in the temperature dependences of the electrical conductivity and thermoelectric power in the region near 410 K are observed. The temperature dependence of Hall coefficient passes through maximum at ∼200 K and has negative sign. It is shown that, these peculiarities are due to the presence of the Ag_2Te phase. The thermoelectric Z-factor has the maximum value of 2.7×10^{-3} K^{-1} at 400 K.

Keywords: thermoelectric material, endothermic effect, electrical conductivity, Seebeck coefficient, Hall coefficient.

1. Introduction

Thermoelectric materials are used for the conversion of thermal energy into electricity and in the solid-state cooling [1–3]. These materials are characterized by the energy conversion efficiency coefficient or Z-factor. The high value of the Z-factor corresponds to a high Seebeck coefficient, high electrical conductivity, and low thermal conductivity.

The thermoelectric properties of the lead antimony silver telluride have been investigated actively, in [3–7]. $AgPb_mSbTe_{2+m}$ is a highly effective thermoelectric material, which can be considered as a combination of $AgSbTe_2$ and PbTe in the form $(AgSbTe_2)(PbTe)_m$. PbTe is an excellent thermoelectric material used in the thermoelectric power generation [1, 3, 8]. The ternary compound $AgSbTe_2$ is also a good p-type thermoelectric material [1, 3, 9–11]. $AgSbTe_2$ and PbTe crystallize in the cubic lattice structure, which allows the production of a series of solid solutions.

To increase the thermoelectric characteristics of $AgSbTe_2$, we synthesized the composition $(AgSbTe_2)_{0.9}(PbTe)_{0.1}$. In this case, the crystal structure will not change. The defects in the structure are the scattering centers for charge carriers. This leads to a decrease in the thermal conductivity, which is very important for thermoelectric materials.

This paper presents the results of a study of the transport properties of $(AgSbTe_2)_{0.9}(PbTe)_{0.1}$ in the 80–550 K temperature interval.

2. Experimental Details

2.1. Synthesis

The investigated $(AgSbTe_2)_{0.9}(PbTe)_{0.1}$ sample was produced by the following method. The high-pu-

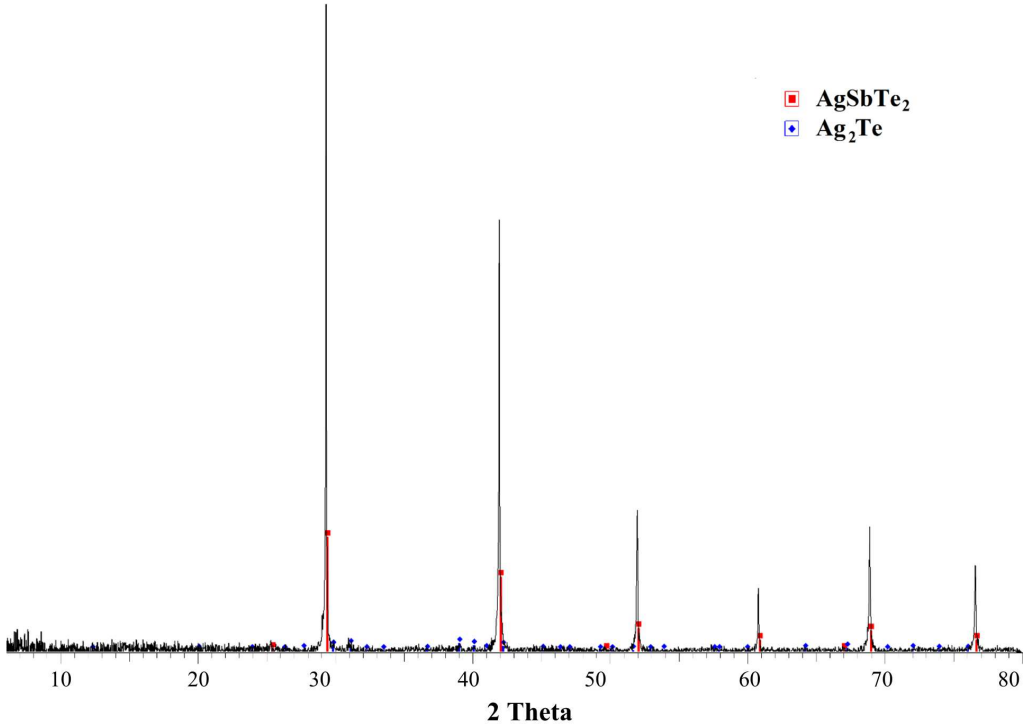

Fig. 1. XRD pattern of $(AgSbTe_2)_{0.9}(PbTe)_{0.1}$

rity starting materials, namely, Ag (99.9%), Sb (99.999%), Te (99.999%), and Pb (99.99%) were weighed according to the nominal composition of $(AgSbTe_2)_{0.9}(PbTe)_{0.1}$ and then sealed in an evacuated quartz tube (10^{-2}Pa). The synthesis was carried out in a furnace at the 3 degree/cm temperature gradient. The quartz tube was kept for 15 h above the melting temperature (at 1123 K). Then it was slowly cooled at a rate of $\backsim$1 deg./min to room temperature.

The synthesized compound was controlled by the DSC analysis and the powder X-ray diffraction technique (PXRD).

The DSC analysis of $(AgSbTe_2)_{0.9}(PbTe)_{0.1}$ was carried out in the temperature interval from 173 K to 573 K using a DSC 204F1 Phoenix setup of NETZSCH-Geratebau GmbH (Germany). The NETZSCH Proteus software was used to carry out a measurement and to evaluate the data.

The analysis of X-ray diffraction spectra of the studied $(AgSbTe_2)_{0.9}(PbTe)_{0.1}$ was conducted for phase identifications by using a powder X-ray diffractometer "D2 Phaser" with CuK1 radiation ($5° \leqslant \leqslant 2\theta \leqslant 120°$). The TOPAS-4.2 software (Bruker) was used.

2.2. Transport properties

The electrical conductivity, Hall effect, and thermal power of the obtained material were studied in the temperature interval 80–560 K. The sample for measurements was made in the form of a rectangular bar with dimensions of $2.5 \times 5 \times 12$ mm^3. The measurements were carried out with a direct current of 20 mA, the 6-point method (2-current; 4- for measurements), and the 0–1.5 T magnetic field.

3. Results and Discussion

Figure 1 shows the X-ray diffraction pattern of $(AgSbTe_2)_{0.9}(PbTe)_{0.1}$. The X-ray diffraction analysis showed that this composition has a face-centered cubic lattice (space group Fm3m) with the lattice constant $a = 6.206$ Å.

On the X-ray diffraction pattern, in addition to the main phase, some lines corresponding to Ag_2Te phase are also observed. The results of the DSC analysis of $(AgSbTe_2)_{0.9}(PbTe)_{0.1}$ are shown in Fig. 2. Above room temperature, a sharp endothermic peak is observed in the $\sim$423 K region. This endothermic process begins at 420.9 K and ends at 426.6 K. This peak corresponds to a phase transition in Ag_2Te.

The authors of works [9, 12, 13] noted that the second Ag_2Te phase is present in $AgSbTe_2$. In the region near 420 K, there is a phase transition of Ag_2Te from the α-phase to the β-phase [12]. The observed endothermic effect is due to the structural phase transition in Ag_2Te.

Figure 3 shows the temperature dependence of the electrical conductivity of $(AgSbTe_2)_{0.9}(PbTe)_{0.1}$. As is seen, the value of the electrical conductivity is slowly decreased up to 430 K.

The temperature dependence reveals several features:

a) in the region 160–430 K, the electrical conductivity decreases;

b) in the region 400–420 K, the conductivity value sharply decreases

c) passing through a minimum at 440 K, it then increases with the temperature.

The corresponding changes are also observed in the temperature dependence of the Seebeck coefficient of $(AgSbTe_2)_{0.9}(PbTe)_{0.1}$ (Fig. 4). In the ∼200 K region, the growth rate for the Seebeck coefficient slows down. Then, in the interval 400–420 K, the Seebeck coefficient sharply increases. At 440 K, it passes through a maximum and then decreases, as the temperature grows.

The sign of the Seebeck coefficient was positive indicating p-type conduction in the whole investigated temperature interval.

A sharp decrease in the electrical conductivity and an increase in the Seebeck coefficient in interval 400–420 K are due to the presence of the second Ag_2Te phase.

The presence of Ag_2Te is confirmed by the fact that DSC analysis shows an endo effect in the ∼420 K region. Note that a structural phase transition also occurs in the region of 400–420 K in other silver chalcogenides [14].

The presence of the Ag_2Te phase affects the temperature dependence of the Hall coefficient of $(AgSbTe_2)_{0.9}(PbTe)_{0.1}$ differently. Figure 5 shows the temperature dependence of the Hall coefficient of the studied sample. The Hall coefficient increases in the interval 80–200 K, passes through a maximum in the region about 200 K, and then decreases, as the temperature increases. The sharp change in the Hall coefficient is observed at 410 K. Note that the sign of the Hall coefficient was negative (with a positive sign of the Seebeck coefficient). Such a difference between

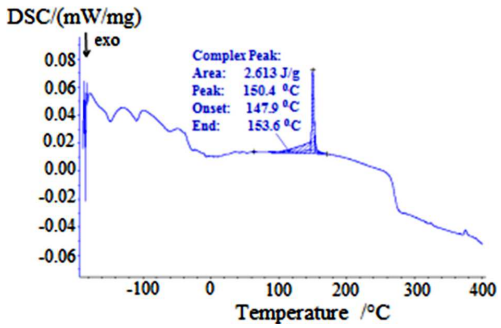

Fig. 2. DSC curve of $(AgSbTe_2)_{0.9}(PbTe)_{0.1}$

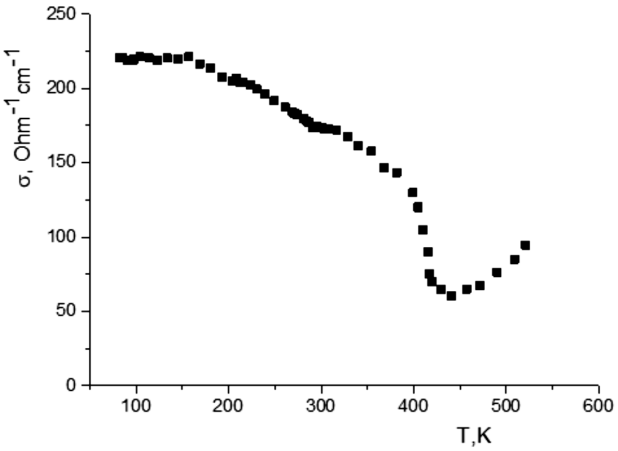

Fig. 3. Temperature dependence of the electrical conductivity of $(AgSbTe_2)_{0.9}(PbTe)_{0.1}$

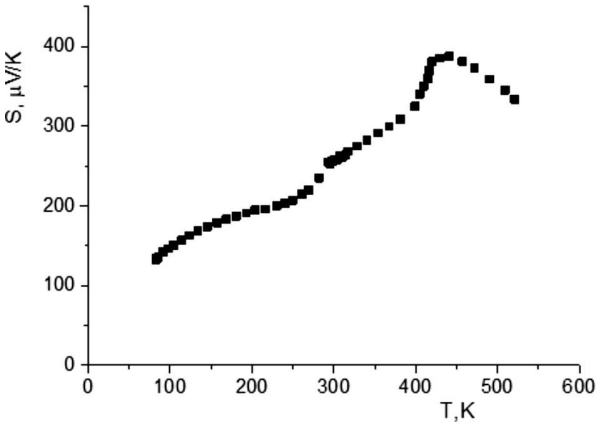

Fig. 4. Temperature dependence of the Seebeck coefficient of $(AgSbTe_2)_{0.9}(PbTe)_{0.1}$

the signs of the Hall and Seebeck coefficients was previously observed in $AgSbTe_2$ [9, 13, 15]. A similar dependence is also observed in the temperature dependences of $AgSbTe_2$. According to [9], the difference

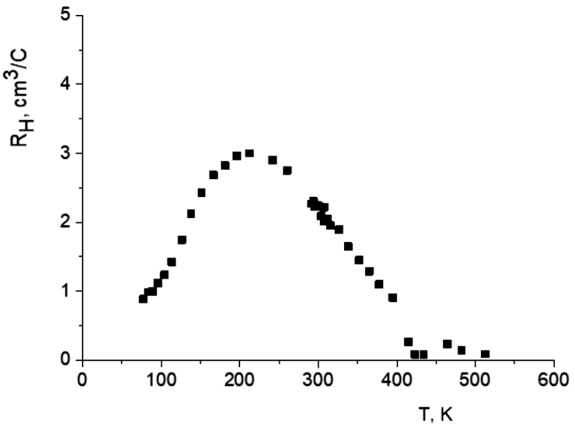

Fig. 5. Temperature dependence of the Hall coefficient of $(AgSbTe_2)_{0.9}(PbTe)_{0.1}$

between the signs of these two coefficients in $AgSbTe_2$ occurs above ∼55 K. At temperatures below ∼55 K, both these coefficients have a positive sign. The Hall coefficient in the temperature interval 4.2–40 K is independent of the temperature. Further, as the temperature increases, the Hall coefficient changes the sign from positive to negative at 55 K.

We believe that the difference in the signs of the Seebeck and Hall coefficients in $(AgSbTe_2)_{0.9}(PbTe)_{0.1}$, as in the case of $AgSbTe_2$, is due to the presence of the Ag_2Te phase.

The Seebeck coefficient in the two-carrier system is defined as:

$$S = \frac{S_e e n \mu_e + S_h p n \mu_h}{\mu_e + \mu_h}. \quad (1)$$

Here, e is the charge of the carrier; p and n are the partial carrier concentrations; μ_e and μ_h are the electron and hole mobilities; and S_e and S_h are the partial electron and hole Seebeck coefficients. As is seen from (1), the Seebeck coefficient is the sum of first-order terms of the carrier mobilities.

However, the Hall coefficient is defined as the sum of quadratic terms of the carrier mobilities:

$$R_H = \frac{-n\mu_e^2 + p\mu_h^2}{-n\mu_e + p\mu_h}. \quad (2)$$

Note that, the Seebeck coefficient is determined by the major carriers. Due to the high electron mobility, the Hall coefficient changes the sign from positive to negative.

Thus, the Hall coefficient can have a sign opposite to that of the Seebeck coefficient, when the mobility of electrons is much higher than the mobility of holes.

The energy conversion efficiency of thermoelectric materials is characterized by the Z-factor $Z = S^2\sigma/k$, where S, σ, and k are the Seebeck coefficient, electrical conductivity and thermal conductivity. As is seen, to increase the Z value, it is necessary to reduce the lattice thermal conductivity and to increase the electrical conductivity and Seebeck coefficient. On the base of experimental data, we have estimated the Z-factor at various temperatures. The calculations show that, the maximum value of $Z = 2.7 \times 10^{-3}$ K^{-1} is attained at 400 K.

4. Conclusions

The endothermic effect due to the presence of Ag_2Te is detected on the DSC curve of $(AgSbTe_2)_{0.9}(PbTe)_{0.1}$ at ∼420 K. It is shown that the detected maximum in the temperature dependence of the Hall coefficient at ∼200 K and sharp changes in the Seebeck coefficient and electrical conductivity in the interval 400–420 K are due to the presence of the Ag_2Te phase in $(AgSbTe_2)_{0.9}(PbTe)_{0.1}$.

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ВПЛИВ Ag_2Te НА ТРАНСПОРТНІ ВЛАСТИВОСТІ $(AgSbTe_2)_{0,9}(PbTe)_{0,1}$

Вивчено транспортні властивості $(AgSbTe_2)_{0,9}(PbTe)_{0,1}$, такі як електрична провідність та коефіцієнти Зеєбека (S) і Холла (R_H) в інтервалі температур 80–560 K. Із застосуванням методу диференціальної растрової калориметрії знайдено ендотермічний пік при 410 K. Спостережено різкі зміни температурних залежностей електричної провідності та термоелектричної потужності поблизу 410 K. Залежність коефіцієнта Холла від температури має максимум при ∼200 K і негативний знак. Показано, що ці особливості завдячують присутності фази Ag_2Te. Термоелектричний Z-фактор має максимальне значення $2{,}7 \cdot 10^{-3}$ K^{-1} при 400 K.

Ключові слова: термоелектричний матеріал, ендотермічний ефект, електрична провідність, коефіцієнт Зеєбека, коефіцієнт Холла.