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Determination of band gap of $(AgSbTe_2)_{0.8}(PbTe)_{0.2}$ from electrophysical and optical properties

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Abstract

It was investigated the temperature dependence of the specific resistivity and thermoelectric power of $(AgSbTe_2)_{0.8}(PbTe)_{0.2}$ in the 80-550 K temperature range and the spectroscopic ellipsometric optical measurements at 300K. The band gap of $(AgSbTe_2)_{0.8}(PbTe)_{0.2}$ was estimated according to experimental data on electrical conductivity (E_g=0.13eV), thermal power (E_g=0.18eV) and using Vegard's rule (E_g=0.214 eV). The value E_g=0.2eV for band gap of $(AgSbTe_2)_{0.8}(PbTe)_{0.2}$) was obtained according to optical measurements.

Keywords*: thermal power, specific resistivity, band gap, optical measurement*
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1. Introduction

Thermoelectric materials are used to convert thermal energy into electrical energy, as well as in solid-state cooling [1-3]. The main task in this case is to increase the efficiency of energy conversion of the thermoelectric material. These materials are mainly semimetals or semiconductors with a band gap Eg= 0−1 eV.

$AgSbTe_2$ and PbTe are narrow gap semiconductors and are good thermoelectric materials. $AgSbTe_2$ has been studied by many authors as a promising p-type thermoelectric material [4-8]. Based on this thermoelectric material, various thermoelectric compositions have been created. Based on the compounds $AgSbTe_2$ and PbTe the

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system is called LAST and can be represented as $(AgSbTe_2)_X(PbTe)_{1-X}$. Note that both $AgSbTe_2$ and PbTe crystallize in a cubic lattice structure. At different values of the components, it is possible to obtain a series of solid solutions. The creation of solid solutions leads to a change in several fundamental characteristics of the material, in particular, the width of the band gap, the effective mass of carriers, etc.

Manipulation of the band structures is a key strategy for improving the thermoelectric properties of materials. By this way can achieve to obtain a high value of thermal power and electrical conductivity coefficients.

The experimental determination of the band gap of $AgSbTe_2$ based solid solutions has still not been sufficiently studied. The optical studies of solid solutions, which make it possible to determine the band gap, as well as studies of optical absorption spectra, and the type of optical transitions are very valuable.

In this work are presented the results of the band gap value, estimated from temperature dependencies of electro physical and optical properties of $(AgSbTe_2)_{0.8}(PbTe)_{0.2}$.

2. Experimental results and their discussion

The studied $(AgSbTe_2)_{0.8}(PbTe)_{0.2}$ sample was obtained by slow cooling method. The initial components firstly were fused in sealed quartz ampoules with an exposure of 10 hours to 100 K above the melting point. Then it was slowly cooled at a rate of 1 K/min. to room temperature.

X-ray diffraction analysis was performed on a BRUCKER-D2 PHASER diffractometer. According to the results of X-ray structural analysis $(AgSbTe_2)_{0.8}(PbTe)_{0.2}$ has a face-centered cubic lattice. The lattice constant a=6.1390Å, and corresponds to the Fm3m space group.

The electro physical experiments were carried out by the four-probe method in the 80-550 K temperature range. Electrical conductivity and Seebeck coefficient are determined only by the electronic properties of the material. By changing the composition, it is possible to vary the parameters of band structure of materials. This is very important for optimizing their thermoelectric properties.

The temperature dependence of the electrical conductivity is presented in fig. 1. As is seen the electrical conductivity passes through a maximum in the region of 200 K. Further, in the temperature range 200-400 K, the value of electrical conductivity decreases.

The temperature dependence of the Seebek coefficient is presented in fig. 2. The sign of the Seebek coefficient was positive, which indicates a hole conduction mechanism.

Thermal band gap is one of the main fundamental characteristics of a semiconductor. It is usually determined from resistivity measurements. The activation energy was determined from the temperature dependence of electrical conductivity [9].

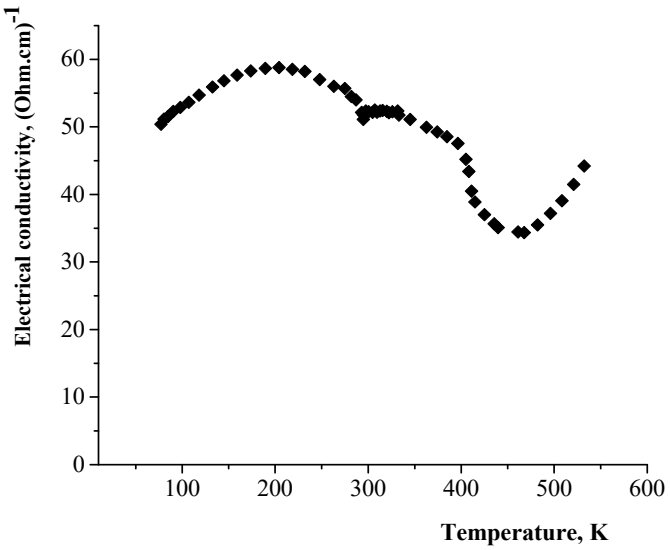

Fig. 1. The temperature dependence of the electrical conductivity of $(AgSbTe_2)_{0.8}(PbTe)_{0.2}$

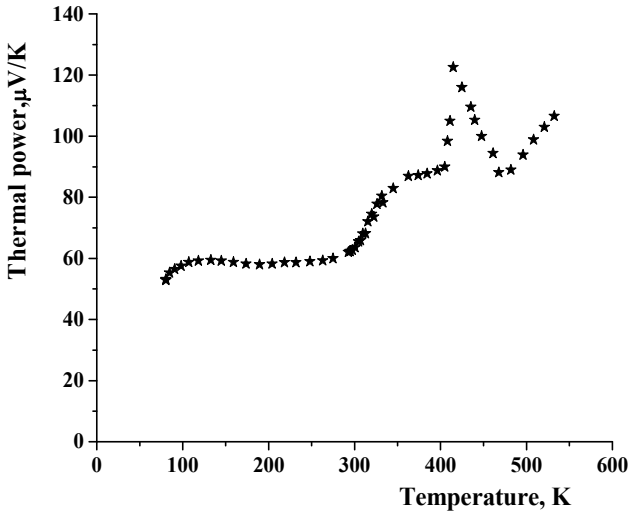

Fig. 2. The temperature dependence of the Seebek coefficient of $(AgSbTe_2)_{0.8}(PbTe)_{0.2}$

$$\Delta E = \frac{2k_B ln\,\sigma_1/\sigma_2}{T_1 - T_2} \cdot T_1 \cdot T_2. \quad (1)$$

According to experimental results of electrical conductivity the estimated activation energy of $(AgSbTe_2)_{0.8}(PbTe)_{0.2}$ was (E_g=0.13 эВ).

The bandgap width may be determined by the method based on thermopower

measurements. The Seebeck coefficient has a maximum value close to $E_g/2eT_{max}$ [10]. This approximation can be used to determine the energy gap of a thermoelectric material. The energy gap is determined in this case as

$$E_g = 2e|S_{max}|T_{max} \quad (2)$$

Using the Goldsmith–Sharpe expression (2), it was estimated the value of the energy gap E_g= 0.18 eV.

The band gap of the studied composition was also estimated using Vegard's rule. According to [5]:

$$E_g = \frac{mEA_g + nEB_g}{m+n}. \quad (3)$$

Considering the literature data on PbTe (E_g=0.31 eV) and $AgSbTe_2$ (determined from ellipsometric measurements E_g=0.19 eV), the estimated activation energy of $(AgSbTe_2)_{0.8}(PbTe)_{0.2}$ was E_g=0.214 eV.

As can be seen, there are some discrepancies in the values of the band gap determined by different methods. The expression (2) is widely used by specialists, even though in several cases, it gives an error in estimating E_g [11, 12]. This is stipulated by fact that expression (2) is valid for non-degenerate semiconductors. On the other hand, as the degree of degeneracy, the mobility ratio of carriers can also result in some deviations to the Goldsmid-Sharp band gap.

The value of band gap estimated by optical method is more correct. From this point of view, it was carried out the spectroscopic ellipsometric optical measurements of $(AgSbTe_2)_{0.8}(PbTe)_{0.2}$.

The optical properties were studied using J.A. WOOLLAM M-2000 DI and IR-Vase (J.A.WoollamCo, Inc., USA) spectroscopic ellipsometers. The spectra of the ellipsometry parameters were recorded in the photon energy range 0.038–6.5 eV with a step of 2 meV.

The refractive index n(E) and the absorption index k(E) obtained for $(AgSbTe_2)_{0.8}(PbTe)_{0.2}$ from ellipsometry measurements at 300 K in the photon energy range E = 0.07– 6.4 eV are presented in fig. 3. It was measured the spectra of the real $\varepsilon_r(E)$ and imaginary $\varepsilon_i(E)$ parts of the permittivity also.

In order to clarify the character of optical transitions forming the absorption edge and to determine the band gap, we analyzed the spectra replotted in the form of $(\alpha E)^n$ as a function of E, where the values of n = 1/2, 2, 2/3, and 1/3 should correspond to indirect allowed, direct allowed, indirect forbidden, and direct forbidden optical transitions, respectively. Such dependences are used in analyzing the absorption edge in semiconductor single crystals. According to analysis it was established, that the most extended portion of the absorption edge spectrum (0.6–1.3 eV) corresponds to the dependence with the power 1/2. Such dependence is characteristic for indirect allowed transitions in crystalline semiconductors.

According to experimental results of optical measurements it was estimated the

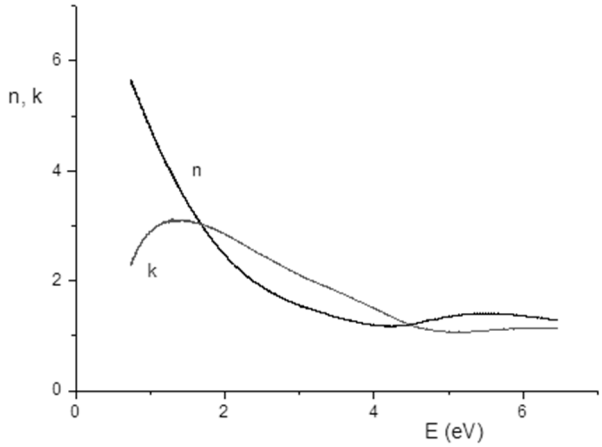

Fig. 3. Spectra of the absorption index and refraction index of $(AgSbTe_2)_{0.8}(PbTe)_{0.2}$

value of band gap width also (E_g=0.2eV).

As is mentioned in [13] the valence band of $AgSbTe_2$ is formed mainly by the p orbitals of Te and their hybridization with the d orbitals of Ag and the p orbitals of Sb atoms. At the same time the conduction band is formed mainly by the p orbitals of Sb with some contribution of the s orbitals of Ag and the p orbitals of Te atoms.

3. Conclusions

The band gap of $(AgSbTe_2)_{0.8}(PbTe)_{0.2}$ was estimated according to experimental data on electrical conductivity (E_g=0.13eV), thermal power (E_g=0.18eV) and using Vegard's rule (E_g=0.214 eV). It was observed that, there are some discrepancies in the values of the band gap determined by different methods. This is stipulated by the degree of degeneracy and mobility ratio of carriers. The more correct band gap of $(AgSbTe_2)_{0.8}(PbTe)_{0.2}$ (E_g=0.2eV) was determined according to optical measurements.

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