Thermoelectric properties of Zn-Sb compound semiconductor

Lutfiddin Olimov and Utkirbek Akhmadaliev
1Andijan Machine Building Institute, Andijan, Uzbekistan

Abstract. The article discusses the results obtained in the study of the thermoelectric properties of the semiconducting Zn-Sb polycrystalline structure obtained by powder technology. Studies show that thermal processing stages and temperature changes significantly affect its thermoelectric properties. At the initial stages of heat treatment, with an increase in temperature, the Seebeck coefficient ($\alpha$), thermal conductivity ($\lambda$) and thermoelectric index (ZT) first decrease, then increase, and decrease again with an increase in temperature. From the fourth stage of heat treatment, all parameters increase with temperature. The research results were explained on the basis of the formation of intergranular boundary areas and its physical properties. The first stage of thermal treatment is the initial stage of ZnSb particle fusion, and the supplied thermal energy Q is not enough for ZnSb particle fusion. In the next stage of heat treatment, the atoms of the crystal lattice, which consists of a broken bond or defect between the pressed particles, are forced together or condensed. As the temperature increases, the phases of the crystal lattice atoms change and their reactivity increases. This leads to the formation of a ZnSb semiconductor with a polycrystalline structure. As the temperature increases, the localized traps with $E_{\text{in}}$ energy level are ionized and electron-hole pairs are formed in the two adjoining boundary areas. Charges created in area A move to area V, which has a relatively low temperature, along the $E_{\text{in}}$ energy levels. As a result, the total $\lambda$ increases at the same time as the thermal conductivity of these two adjacent areas.

1 Introduction

In recent years, there has been an increased interest in the preparation of semiconducting Zn-Sb compounds and the study of their electro physical and thermoelectric properties [1-12]. Research shows that its structure, electro physical or thermoelectric properties depend on the physical processes occurring in the stages of Zn-Sb compound preparation. In particular, it has been shown that the processes of preparation and pressing of ZnSb powders significantly affect the formation and growth of grains, as well as their electro physical and thermoelectric properties. In connection with these, recently, we studied the preparation of polycrystalline semiconductor Zn-Sb compound and some of its electrophysical properties. This method consists of heat treatment stages, and at each stage, grain growth and formation of inter-grain
boundary areas have been determined. It is proved that charge transfer processes also depend on thermal treatment stages and intergranular boundary areas. For example, at the initial stage of thermal treatment, electrical conductivity ($\sigma$), concentration of charge carriers ($n$) suddenly decreases with temperature increase, and such a process is not observed at later stages. Mobility of charge carriers ($\mu$) decreases at all stages of heat treatment. It was determined that the residence time of charge carriers in the crystal lattice varies between $\tau \sim 1.52 \pm 1.1 \cdot 10^{-12}$ sec. In connection with these, it is interesting to study the effect of thermal treatment steps and temperature, as well as the processes of grain growth and formation of inter-grain boundary areas at each step, on the thermoelectric properties of the semiconducting Zn-Sb compound. The solution of such scientific and technical issues may allow the preparation of new types of energy converters based on the semiconducting Zn-Sb compound.

2 Materials and methods

Semiconductor ZnSb compound and Egor and Disselkhorsta method [1] were chosen for studying thermoelectric phenomena. Granular ZnSb is obtained by powdering from an intermetallic compound synthesized in equal amounts of spirit and antimony, and the particle size is $10 \div 50$ μm. The thermoelectric properties of the sample were measured at the temperature of $T = 300 \div 700$ K based on the Egor and Disselkhorsta method [1, 2].

Figure 1 shows a simplified scheme of sampling using the Egor and Disselkhorsta method. ZnSb particles (1) are placed in a tube-shaped dielectric (2). Both sides of the particles (A and B) are pressed with copper contacts (MA and MB) as shown in Figure 1. The pressure force is $P \sim 30 \div 50$ kilograms [1, 2]. In this case, the sample takes the form of Stergen.

**Fig. 1.** A simplified scheme of measuring samples based on the Egor and Disselkhorsta method (a), temperature difference (b), ZnSb particle structure (a), zone diagram (d). Here, 6 – granulated ZnSb particles, 7 – heat-resistant dielectric case, 5 and 8 – interparticle boundary area, ohmic contacts and thermocouples in areas A and V, respectively, $M_A$ and $M_B$, $T_A$ and $T_B$.

Based on the method of Egor and Disselkhorsta, when Q heat is given, the charges generated in area A move to area V, and an electric force is generated due to the temperature difference in MA and MV contacts [1-4]. The temperature difference is monitored using TA and TV thermocouples. In this case, thermal conductivity can be determined as follows [4]:
\[ \lambda = \frac{U \sigma}{\Delta t}, \]  

(1)

where, \( \sigma \) is the electrical conductivity of the studied sample, \( U \) is the voltage, \( \Delta t \) is the temperature difference in the A and B areas of the sample. If the experiment is carried out by determining the current, formula (1) can be expressed as follows:

\[ \lambda = \frac{I l}{\Delta t s}, \]  

(2)

\( l \) and \( S \) are the length and cross-sectional area of the studied sample, respectively. In the stationary case, based on the expressions (1) and (2), it is required to pay attention to the uniformity of the heat transfer values. It should be noted that all studies were conducted during the processes of increasing and decreasing the temperature of heat treatment and time intervals. Between each heat treatment, the sample was cooled and then reweighed.

3 Results and discussion

Figures 2-4 show the temperature dependence of the Seebeck coefficient \( (\alpha) \), thermal conductivity \( (\lambda) \) and thermoelectric efficiency \( (ZT) \). It can be seen from the pictures that at the initial stages of heat treatment, these parameters first decrease, then increase, and decrease again with increasing temperature (line 1). From the fourth stage of heat treatment, all parameters increase with temperature (lines 2-4). Such a change in thermoelectric parameters may be due to the interconnection of ZnSb particles during the thermal treatment stages. To explain the results of the research, let's consider the structure of the granulated ZnSb compound and its simplified scheme depicted in Fig. 1.

![Fig. 2. Temperature dependence of Seebeck coefficient (\( \alpha \)), thermal conductivity (\( \lambda \)) and thermoelectric efficiency (ZT): 1, 4, 6, 7 – stages of heat treatment.](image)

We considered the ZnSb particle structure obtained by powder technology. According to it, the atomic structure of the particle consists of a surface defect and complex-shaped bumps (areas 1 and 2, Fig. 1c). The amount of crystallographic distortion increases from the particle
core to the surface. This causes the atoms of the crystal lattice to change phases. The reactivity of the surface area increases from the core to the surface [5, 6]. They are arranged sequentially and parallel to each other in a heat-resistant ceramic pipe, forming areas 5 and 8 (Fig. 1a) [1-4]. Through the metal contacts M_A and M_B, ZnSb particles are pressed together with a specified force from both sides. Studies show that thermal processing steps and temperature have a significant effect on the adhesion of ZnSb particles (Figures 2-4). In order to facilitate the explanation, we will divide the heat treatment steps into two parts. The first 1-3 stages of heat treatment are called stage 1, and stages 4-7 are called stage 2. Let's look at step 1 first.

In our opinion, stage 1 is the initial stage of ZnSb particle coalescence and depends on the interaction phenomena of atoms between two adjacent particles. At this stage, ZnSb particles do not coalesce. That is, the interconnected atoms on the surface of two neighboring particles are mechanically contacted. The supplied thermal energy Q will not be sufficient for the fusion of ZnSb particle atoms. Therefore, parameters \( \alpha \), \( \lambda \) and ZT decrease at \( T \leq 350 \) K and \( T=375-410 \) K. As the temperature increases, a temperature gradient (\( T_A \) and \( T_B \), Fig. 1a) and a potential difference appear in A and B (\( x_A \) and \( x_B \)) areas. This leads to an increase in these parameters.

ZnSb particles coalesce slowly during the 2nd stage of heat treatment. This is due to two factors. That is, the thermal treatment given in step 1 depends on the energy and the force of pressing the particles with the metal contacts M_A and M_B. They complement each other during the joining of ZnSb particles. That is, when the particles are pressed by the metal contacts M_A and M_B, the atoms of the crystal lattice consisting of a broken bond or defect in the interparticle boundary area (areas 5 and 8, Fig. 1a) are pressed together or condensed. As the heat treatment temperature increases, the phases of the crystal lattice atoms change and their reactivity increases. The research results show that the continuation of these processes in 2 stages leads to the joining of ZnSb particles and the formation of a polycrystalline structure.

Under the influence of temperature, a large number of localized traps are ionized in two adjoining boundary areas (areas 5 and 8, Fig. 1a) located in area A of the sample [1,2, 5-8]. The potential difference increases with the capture of charges in ionized traps, and a temperature gradient occurs due to the absorption of phonons in localized traps. This process may be causing an increase in \( \alpha \) (lines 2-4, Figure 2).

The considered mechanism is also valid for parameters \( \lambda \) and ZT. However, \( \lambda \) is mainly explained by crystal lattice conductivity and phonon migration. For example, a thermoelectric material with a polycrystalline structure leads to a decrease in \( \lambda \) due to phonon migration in the intergranular boundary regions and a decrease in the conductivity of the crystal lattice. However, in our case, if we ignore step 1, no decrease in \( \lambda \) was observed.

In our opinion, the increase of \( \lambda \) with temperature may depend on the physical properties of the intergrain boundary regions (areas 5 and 8, Fig. 1a) of the ZnSb semiconductor with a polycrystalline structure. That is, with an increase in temperature, localized traps with \( E_m \) energy level ionize in the areas of two contiguous boundaries (areas 5 and 8, Fig. 1a) (Fig. 1b) [1, 2, 5-12]. With the formation of electron-hole pairs in them, thermovoltaic effects appear. The formation of electron-hole pairs confirms the formation of localized traps with \( E_m \) energy level in the areas of two adjacent boundaries (areas 5 and 8, Fig. 1a), and the results of current and voltage measurements confirm the manifestation of thermovoltaic effects. As the temperature increases, the charges that appear in the area A move to the area V with a lower temperature along the \( E_m \) energy levels. As a result, the total \( \lambda \) increases at the same time as the thermal conductivity of the two adjacent areas.
Fig. 3. Temperature dependence of thermal conductivity ($\lambda$): 1, 4, 6, 7 – stages of heat treatment.

Fig. 4. Temperature dependence of thermoelectric efficiency (ZT): 1, 4, 6, 7 – stages of heat treatment.

It was observed that the physical processes that increase with temperature in the areas of the two contiguous boundaries (areas 5 and 8, Fig. 1a) also significantly affect ZT (Fig. 4).

It is known that the best (ZT) index in high-temperature thermoelectric materials today belongs to the high quantum dot lattice, and its value has been determined to be close to 3.5. American experts have shown that the ZT index is greater than 2 in the solid substance obtained on the basis of nanostructures. The ZT index of ZnSb type thermoelectric materials can be from ~0.2 to 0.9. This is much less than our research results. In our case, the increase
of the ZT index to ≤5 may be due to the physical processes manifested in the areas of two adjacent boundaries (areas 5 and 8, Fig. 1a) in the ZnSb semiconductor with a polycrystalline structure.

4 Conclusions

Thus, the thermoelectric properties of the Zn-Sb compound with a polycrystalline structure obtained by powder technology depend on the characteristics of the heterogeneous environment consisting of intergranular boundary areas. Powder technology can make it possible to prepare new types of energy converters based on Zn-Sb compound with polycrystalline structure.

The results of the research and the considerations given to explain it can be of great importance in obtaining granular materials and explaining the kinetic phenomena in them.

References