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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

THERMOELECTRIC PROPERTIES OF $(AgSbSe_2)_x(PbTe)_{1-x}$ SOLID SOLUTIONS

Speciality: 2220.01- Semiconductor physics

Field of science: Physics

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GENERAL DESCRIPTION OF WORK

Relevance of the research topic. The development of modern equipment and technology always requires the development and improvement of more efficient power sources. Recently, one of the main requirements for power sources is that they are not only highly efficient, but also environmentally friendly. The energy produced must be recoverable and must not adversely affect the environment. A promising direction of development is the use of thermoelectric processing in industry due to the widespread use of thermoelectric generators based on the Zeebek effect and the direct conversion of heat into electrical energy. An important disadvantage of modern thermoelectric generators is that the coefficient of conversion of heat into electrical energy is small, i.e. does not exceed 8%, and is limited by the properties of a thermoelectric material- semiconductor used in thermoelectric generators, which also has high electrical conductivity, thermoelectric power and low thermal conductivity. These properties of a semiconductor determine the search and development of new scientific and technological approaches to enhance its thermoelectric figure of merit ZT.

For this purpose, recently, both from changing structure of materials and optimization of the composition and thermoelectric properties with the doping of various elements or the synthesis of new solid solutions and chemical compounds based on starting materials have been used. In this case, it is possible to control the electrical conductivity by changing the concentration of the charge carriers and to create a special defective structure for thermal conductivity.

The ternary semiconductor compounds belonging to the $A^{I}B^{V}C^{VI}$ group are very interesting due to their thermoelectric properties, especially very low thermal conductivity. The lower thermal conductivity of compounds of this group $AgSbTe_2$ and $AgSbSe_2$ in comparison with other thermoelectric materials makes them more attractive material from the point of view of application.

It should be noted that both thermoelectric and galvanomagnetic properties of GeTe- and PbTe- based solid

solutions of $AgSbTe_2$, belonging to groups $A^IB^VC^{VI}$, have been well studied over a wide temperature range.

The investigations of $AgSbSe_2$ basically were carrying out above room temperature in order to study thermoelectric properties. In addition, the kinetic properties of $AgSbSe_2$ have not been practically studied at low temperatures. The solid solutions based on this compound have practically not been investigated. The nature of structural inhomogeneities in $AgSbSe_2$ compound and its solid solutions, their electronic structure and their influence on the mechanisms of electric charge and heat transfers, and other issues has been insufficiently investigated.

Object and subject of research:

The object of research is $AgSbSe_2$ and $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85; 0,825; 0,8) solid solution crystals and the subject is the study of thermoelectric and galvanomagnetic properties in these crystals.

Research aims and objectives:

The determination of the mechanisms of electric charge and heat transfer in $AgSbSe_2$ and $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85; 0,825; 0,8) solid solutions and to determine the applicability of the obtained results in thermoelectric converters.

To achieve this goal, there were determineted following tasks:

- Synthesis of $AgSbSe_2$ crystal.
- Synthesis of $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85; 0,825; 0,8) solid solution crystals.
- Differential scanning calorimetry and X-ray structural analysis of the investigated composition.
- Investigation of kinetic phenomena in a wide temperature ranges (80-600K) in $AgSbSe_2$ and solid solutions of $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85; 0,825; 0,8).
- Revealing the possibility of using the studied crystals of the solid solutions in thermoelectric converters.

Research methods:

To determine the structure and phase analysis were used X-ray diffractometry and differential scanning colorimetry methods. To

determine thermoelectric and galvanomagnetic properties were used Van der Pauw and four-probe potentiometric methods.

The main provisions for the defense:

1. Observation of endothermic effects at T=363,5K, T=412,8K and T=498,6K temperatures.
2. The electrical conductivity of $AgSbSe_2$ and $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85**)** solid solutions have a hopping mechanism in the temperature range 80-235K.
3. Change in the type of conductivity (n→p) of $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,9; 0,85; 0,825; 0,8) solid solution crystals and a shift in the temperature of the change of sign towards higher temperatures with increasing the amount of PbTe.
4. The very low value of lattice thermal conductivity of $AgSbSe_2$ and $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85; 0,825; 0,8) solid solutions.
5. In $(AgSbSe_2)_{0,9}(PbTe)_{0,1}$ solid solution was observed a sharp decrease of specific resistivity from 17550 Om·cm up to zero likely superconducting transition in the range 110-66K with the temperature decreases.
6. Determination of the components that obtain maximum values for thermoelectric figure of merit and thermoelectric sensitivity.

Scientific novelty of the research:

1. In the thermogram of $AgSbSe_2$ endothermic effects were observed at temperatures T=363,5K, T=412,8K and T=498,6K, as a result of silver ions leave from their position and their arrangement in more ordered and energetically favorable states.
2. For the first time, the mechanism of electrical conductivity of $(AgSbSe_2)_x(PbTe)_{1-x}$ solid solutions was determined.
3. Change in the type of conductivity of $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,9; 0,85; 0,825; 0,8) solid solutions were observed.
4. A sharp decrease of specific resistivity of the $(AgSbSe_2)_{0,9}(PbTe)_{0,1}$ solid solution were observed at temperatures below T≈110K.
5. It was shown that a number of factors, such as inhomogenety of crystal lattice, scattering by point defects and structural components, caused low lattice thermal conductivity in $AgSbSe_2$

and $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85; 0,825; 0,8) solid solution.

6. For the first time, the maximum value of thermoelectric sensitivity $\delta=12{,}2\cdot10^{-4}$ V·m/W was obtained for $(AgSbSe_2)_{0,85}(PbTe)_{0,15}$ solid solution at a temperature of T≈300K with the aim of using it in thermoelectric converters.

Theoretical and practical significance of the research:

The results obtained in the dissertation work have been applied in the interpretation of kinetic phenomena in solid solutions and complex semiconductors;

The results of complex analysis of thermal and electrical phenomena of $AgSbSe_2$ and $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85; 0,825; 0,8) solid solutions may be used in the manufacture of various thermoelectric converters and devices;

$AgSbSe_2$ and $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85; 0,825; 0,8) solid solution crystals may be used as a sensitive element of the p-branch in various thermoelectric converters due to the very low value of the thermal conductivity. These materials also may be used as a promising material to prevent overheating of chips in electronics and for apply in thermoelectric generators.

Approbation and application:

The results of the dissertation were presented at the following conferences:

- VIII Republican conference "Modern problems of physics" dedicated to the 95th anniversary of BSU (Azerbaijan, Baku, 2014);
- XI international seminar "Magnetic phase transitions" dedicated to the 80th birthday of corresponding member of the Russian Academy of Sciences Kamilov Ibragimkhan Kamilovich (Russia, Makhachkala, 2015);
- VIII republic scientific conference "Actual problems of physics" (Azerbaijan, Baku, 2015);
- "IV international scientific conference of young researchers" dedicated to the 93rd anniversary of the national leader of Azerbaijan Heydar Aliyev (Azerbaijan, Qafqaz University, 2016);

- VIII international scientific and technical conference “Micro- and nanotechnology in electronics” (Russia, Nalchik, 2016).

On the topic of the dissertation work, 12 original articles and 5 reports in conference proceedings were published in the republican and foreign publications, a total of 17 scientific works.

The name of the organization where the dissertation work was perfomed:

The dissertation work was carried out at the Institute of Physics of the National Academy of Sciences of Azerbaijan.

The structure and scope of the dissertation:

The dissertation work consists of an introduction, 4 chapters, main results, a list of cited references. The work is presented on 155 page contains 38 figures, 4 tables and a list of cited references contains 133 works. Excluding figures, tables, and a list of cited references, the introduction consists of 19350, Chapter I 49979, Chapter II 16810, Chapter III 37493, Chapter IV 43144, the results 1582, abbreviations and conditional symbols 868 characters. The total volume of the dissertation consists of 173046 characters.

MAIN CONTENT OF THE DISSERTATION

In the **Introduction** was substantiates the relevance of the topic of dissertation, the aim and objectives of research, research methods, the main provisions for the defense, the scientific novelity of the research, theoretical and practical significance of the research. Also information of degree of approbation, publication was provided and a brief explanation of the main content of the chapters.

In the **First Chapter** of the dissertation was collected and analyzed the literature on the crystalline structure of the ternary compound $AgSbSe_2$, which belongs to the group $A^IB^VC^{VI}$ and thermoelectric properties of solid solutions obtained on its basis and their application areas. Simultaneously special attention was paid to publications in which the influence of various impurities on the thermoelectric properties of $AgSbSe_2$ was considered.

Analysis of the results of structural studies makes it possible to say unambiguously that the $AgSbSe_2$ has a NaCl type face-centered

cubic structure. The differences in the values of the lattice parameters are due to the effect of synthesis regimes and impurities.

An analysis of the literature has shown that $AgSbSe_2$ has been investigated at temperatures above room temperature mainly for the study of thermoelectric properties.

In addition, the kinetic properties of $AgSbSe_2$ have not been studied at temperatures below room temperature. The study of solid solutions based on this compound is almost very rare. Also, the nature of structural disordered in the $AgSbSe_2$ and its solid solutions, their electronic structure and their influence on the mechanisms of electrical charge and heat transfer have not been sufficiently studied.

In the dissertation work, in order to eliminate the above disadvantages, as well as stabilize the crystal structure, improve the thermoelectric properties, and to carry out more detailed studies in these areas, solid solutions based on $AgSbSe_2$ with various PbTe contents were obtained and their kinetic properties were studied in a wide temperature range (80-600K). It should be noted that $AgSbSe_2$ and PbTe have the same crystal structure, which allows to obtain a number of solid solutions based on them.

In the **Second Chapter** of the dissertation was presented the method of obtaining crystals of $AgSbSe_2$ and $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85; 0,825; 0,8) solid solutions. The studied crystals were obtained by direct melting method of the initial components (Ag, Sb, Se, Te, Pb) and elements with a purity of 99,99% were used during the synthesis.

Further, the methods of making electrical and thermal contacts on the studied samples, the measurement methods, the schemes of devices used to study the thermoelectric properties, and the principles of their operation were explaned.

Pristine $AgSbSe_2$ and some of the studied crystals of solid solutions have a relatively high resistance. Therefore, their specific resistance and Hall coefficient were investigated by the Van der Pauw method on the HL5500PC Hall Effect Measurement System. In this case, silver and graphite pastes were used to make the measuring contacts.

The thermoelectric properties of $(AgSbSe_2)_x(PbTe)_{1-x}$ solid solutions were studied by direct current, four-probe potentiometric method.

This chapter also presents working formulas, formulas for calculating the experimental error and the value of allowed errors during the measurement are given.

In the **Third Chapter** of the dissertation, the results of the structural investigations, also results of experimental investigation of the galvanomagnetic and thermoelectric properties of $AgSbSe_2$ were explained and the mechanism of electrical conductivity was presented.

İn this chapter presented the diffractogram obtained by X-ray structure analysis of $AgSbSe_2$ (figure 1).

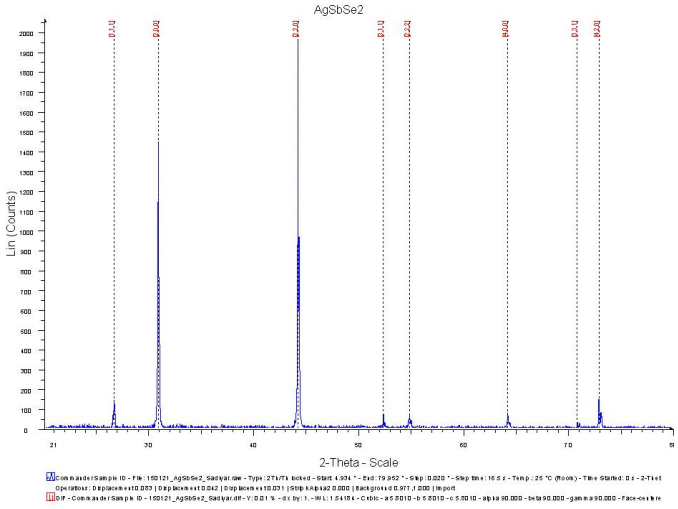

Figure 1. The X-ray diffraction pattern of $AgSbSe_2$

The results of X-ray analysis showed that the $AgSbSe_2$ crystal has a structure of sodium chloride with the space group Fm3m. The lattice constant is a=5,762Å and the volume of unit cells is $V=191,355Å^3$. To determine whether phase transitions occur in $AgSbSe_2$ crystal in the studied temperature range, its X-ray structural

analysis was performed at different temperatures (-180°C to 300°C) too. The X-ray diffraction patterns obtained at different temperatures confirmed that the $AgSbSe_2$ was single phase and no additional phases were observed. The presence of diffraction peaks showed that the compound was polycrystalline properties.

Differential thermal analysis (DTA) of $AgSbSe_2$ was carried out at a temperature up to T=900ºC (1173K), it was shown that incongruent melting began at T=636ºC (909K) and compound are happen separates into Ag_2Se and Sb_2Se_3 phases. The separation process started at 420-430ºC (693-703K) and ended at 730-740ºC (1003-1013K). During cooling, crystallization observed with a diffuse exothermic effect at T=670ºC (T=943K). A weak endothermic effect was also observed around T=110ºC (T=383K).

In order to complete the results of X-ray structural analysis, a more detailed differential scanning calorimetric analysis (DSC) of $AgSbSe_2$ was performed in the temperature range from -100°C to 300°C (from 173 to 573K). As a result of DSC analysis of $AgSbSe_2$ were observed three endoeffects in the 323-393K (T_{max}=63,5K), 398-423K (T_{max}=412,8K) and 483-523K (T_{max}=498,6K) temperature ranges (figure 2)[1].

As is known, $AgSbSe_2$ has a face-centered cubic NaCl- type structure. In this structure, Se atoms form a periodic sublattice and Ag and Sb atoms occupy the Na site at random. As a result of such a distribution, both the Ag^+ and Sb^{3+} ions can occupy neighboring energetically unfavorable sites. In addition, silver and stibium ions can be situated in energetically favorable Ag^+-Sb^{3+} states. Thus, there may be exist energetically favorable and unfavorable regions of Ag^+ and Sb^{3+} ions in the Ag-Sb sublattice. On the other hand, with the increase in temperature, the process of migration of Ag ions to more energetically favorable states is possible. These types of processes require a certain of energy. This, as a result, leads to the endothermic maximum observed in the DSC curve[1].

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[1]Ragimov, S.S. Hopping conduction in $AgSbSe_2$ and $(AgSbSe_2)_{0.9}(PbTe)_{0.1}$ / S.S. Ragimov, A.A. Saddinova, A.I. Alieva [et al.] // Inorganic materials, – 2020. 56(8), – p. 779-784.

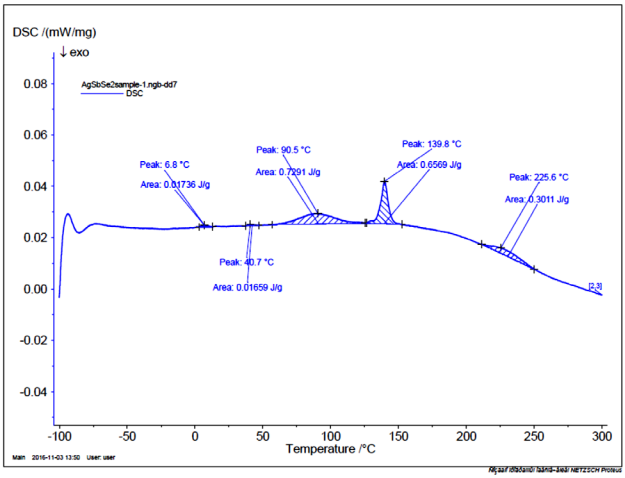

Figure 2. DSC curve of $AgSbSe_2$ in the temperature range of -100-300ºC

The endothermic effects which were observed in the DSC analysis results of $AgSbSe_2$ in the temperature range 323-523K are due to the fact that, with increasing temperature, the silver ions leave their sites and thereby enhance the more energetically favorable state of crystal lattice (Ag^{+}-Sb^{3+}). It should be noted that the stoichiometric composition of $AgSbSe_2$ remains stable until melting temperature and does not decompose. All these endoeffects, which were observed in DSC analysis results are clearly manifested in the temperature dependence of both electrical conductivity and thermoelectric power.

The Hall effect was studied to determine the charge carrier concentration and simultaneously the mobility of charge carriers of $AgSbSe_2$. On the temperature dependence of Hall coefficient of $AgSbSe_2$ was observed a maximum at T=150K. This maximum was stipulated by moves most of the electrons to the top subzone by the temperature increases and therefore the effective concentration of electrons involved in the conduction decreases. Then, by temperature increases the Fermi level is change and the vast majority of electrons are involved in conduction. Therefore the value of the Hall coefficient decreases again by expense of electrons with high

mobility. The experimental studies showed that the $AgSbSe_2$ compound has p-type conductivity and in the room temperature value of the charge carriers consentration is $p=5,6\cdot10^{17}cm^{-3}$.

In addition, the temperature dependence of Hall mobility u(T) was determined based on the temperature dependence of the Hall coefficient and electrical conductivity. Based on this dependence the scattering mechanism of charge carriers was determined. It was shown that, in the temperature range 77-175K the scattering mechanism of charge carriers are correspond to the scattering by impurity ions (r=2) and in the temperature range 175-300K the scattering by acoustic phonons (r=0) one.

This chapter also presents the results of the study of the thermoelectric power of $AgSbSe_2$ in the 80-600K temperature range. It was showed that the temperature dependence of thermoelectric power increases almost linearly by temperature in the 80-400K range and decreases above T≈400K. It was shown that these properties, which are observed near T≈400K in the temperature dependence of thermoelectric power of $AgSbSe_2$, to be caused by the very small amount of Ag_2Se phase existing in the composition. This is really confirmed by the result of DTA which obtained for the $AgSbSe_2$. The value of thermoelectric power of $AgSbSe_2$ had demonstrated p-type conductivity in the entire investigated temperature range and thermoelectric power value was S=350 μV/K at room temperature.

In addition, the value of the effective mass of the charge carriers of $AgSbSe_2$ was calculated based on the parabolic zone model, using the value of thermoelectric power and the concentration of the charge carriers. As a result of the calculations, it was obtained that the effective mass of the charge carriers is $m_p^*=0,12m_0$.

The band gap of $AgSbSe_2$ was optically estimated on the base of spectroscopic ellipsometry data and the value $E_g=0,32eV$ was obtained[2].

[2]Рагимов, С.С. О ширине запрещенной зоны $AgSbSe_2$ / С.С. Рагимов, А.И. Алиева, В.Э. Багиев [и др.], Физика и Техника Полупроводников, – 2021, т.55, №4, – с. 291-298.

The thermal conductivity k of $AgSbSe_2$ was investigated in the temperature range 80-350K. It was observed that the value of the thermal conductivity increased slightly[3]. The results of the study showed that in the studied temperature range the value of the thermal conductivity of $AgSbSe_2$ is very small and obtained the value k=0,85W/m·K.

The low thermal conductivity of $AgSbSe_2$ may be caused by several factors: disordering, point defects and structural components. The presence of regions with orderly and disorderly distribution of Ag and Sb atoms in $AgSbSe_2$, high anharmonicity of the Sb-Se bond, displacement of atoms and deformation of crystal lattice reduce to the formation of phonon scattering centers in the crystal lattice. This leads to decrease of the thermal conductivity value stipulated by phonon scattering. Silver chalcogenides are known to have high ionic conductivity. As the temperature increases, the silver ions leave of their places, intensifying the reconstruction of the crystal lattice. All this leads to the distortion of the crystal lattice and as a result, to a very small value of the thermal conductivity, which is characteristic of amorphous substances. The thermal conductivity of $AgSbSe_2$ is low due to the combination of the above mechanisms.

In this chapter was given the temperature dependence of electrical conductivity of $AgSbSe_2$ in the temperature range 80-600K. The main purpose of studying the temperature dependence of electrical conductivity was to study the mechanism of conductivity of $AgSbSe_2$ and its solid solutions. As a result of investigation it was determined that the electrical conductivity value is sufficiently low compared to other thermoelectric materials of this type. The temperature dependence of the electrical conductivity is divided into several intervals. In these temperature ranges, the exponential dependence is satisfied at temperatures above T≈200K, but at temperatures below T≈200K, this dependence is not satisfied. Then the results obtained at temperatures below T≈200K were to verify in

[3]Ragimov, S.S., Saddinova, A.A., Aliyeva, A.I. Mechanism of electrical conductivity and thermal conductivity in $AgSbSe_2$ // Russian Physics Journal, –2019. 62 (6), – p.1077-1081.

Mott coordinates. To see more clearly the mechanism of conductivity the temperature dependence of the specific resistivity of $AgSbSe_2$ was given in Mott coordinates in the temperature range 80-350K and it is showed that the experimental results correspond to the linear dependence (figure 3).

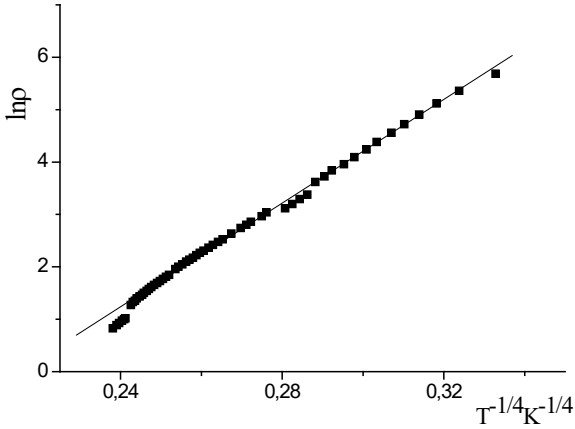

Figure 3. Temperature dependence of the specific resistivity of $AgSbSe_2$ in Mott coordinates

These results showed that in the $AgSbSe_2$, the charge transfer occurs by the hopping conduction of charge carriers over localized states lying in a narrow energy region near the Fermi level[1,3].

It was determined that the hopping conductivity of $AgSbSe_2$ corresponds to the 105K<T<230K temperature range. As a result of the calculations, for the density of localized states near the Fermi level was obtained the value $g(\mu)=4{,}3\cdot10^{16}eV^{-1}cm^{-3}$.

The value of the total conductivity increase with temperature due to the predominance of holes conductivity in the band at the T≈235K. At the higher temperatures, only the band conductivity prevails.

It was taken into account that the specific electrical conductivity of $AgSbSe_2$ is exponentially dependence in the

temperature. Therefore the value of the activation energy E_a of charge carriers of $AgSbSe_2$ was calculated based on the values in the linear region at the coordinates $\ln\sigma \sim \frac{1}{T}$ in the temperature range 200-550K. As a result of the calculations, for the activation energy of charge carriers of $AgSbSe_2$ in the different temperature ranges were obtained the values of ΔE=78meV (200-300K), ΔE=211meV (300-400K) and ΔE=130meV (400-500K), respectively. As can be seen from the results obtained, the activation energy takes different values in different temperature ranges, due to the presence of different impurity levels in the impurity band.

In the **Fourth chapter** of the dissertation, were studied the structural and thermoelectric properties of $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85; 0,825; 0,8) solid solutions which were obtained by adding different amounts of PbTe to $AgSbSe_2$. The results were interpreted in comparison with the results obtained for $AgSbSe_2$. The mechanism of electrical conductivity was given in the temperature range 80-350K. The activation energy, thermoelectric figure of merit and thermoelectric sensitivity were calculated for each sample.

The results of X-ray structure analysis of $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85; 0,825; 0,8) solid solution crystals were presented as a diffractograms form. The results showed that the studied crystals were single-phase, had a structure of the NaCl type with the Fm3m space group. It was shown that the lattice constants of $(AgSbSe_2)_x(PbTe)_{1-x}$ solid solution crystals increase linearly depending with the PbTe content (figure 4). This shows the formation of solid solution crystals in the investigated system at a given interval.

The thermoelectric power of $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85; 0,825; 0,8) solid solutions were studied in the temperature range 80-600K.

According the studies on the temperature dependence of thermoelectric power of $(AgSbSe_2)_{0,95}(PbTe)_{0,05}$ solid solution were observed three maximum in the temperature ranges 100-350K, 350-450K and 450-550K.

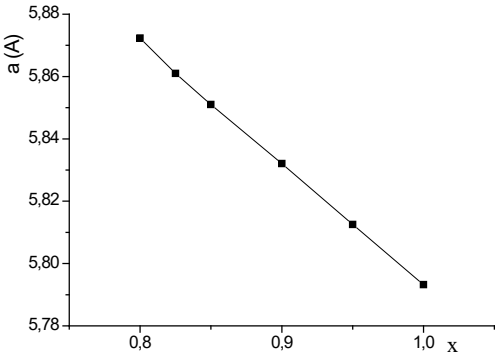

Figure 4. Dependence of lattice constants of $(AgSbSe_2)_x(PbTe)_{1-x}$ solid solutions from PbTe content

As stated above, as a result of DSC analysis of $AgSbSe_2$ were observed three endoeffects in the temperature ranges 328-393K, 398-423K and 483-523K (figure 2). Also, the addition of PbTe to the $AgSbSe_2$ causes Pb atoms to enter the crystal lattice and, as a result, the lattice was deformed. In other words, a solid solution of $AgSbSe_2$ which obtained by adding 5% PbTe to $AgSbSe_2$ decreases the stability of the crystal lattice, but in general the value of the lattice parameters increase while maintaining the cubic structure. On the other hand, silver chalcogenides are substances with ionic conductivity, and therefore, as the temperature increases, the silver ions leave their sites and to influence the reconstruction of the crystal lattice. All these peculiarity are reflected in the temperature dependence of thermoelectric power.

The sign of the thermoelectric power of $(AgSbSe_2)_x(PbTe)_x$ (x=0,9; 0,85; 0,825; 0,8) solid solutions was negative at temperatures below T≈110K, T≈108K, T≈190K, respectively[1] (figure 5).

The thermoelectric power of $(AgSbSe_2)_{0,8}(PbTe)_{0,2}$ solid solution changes sign after T≈430K. Then, as the temperature increases the thermoelectric power becomes positive by changing the

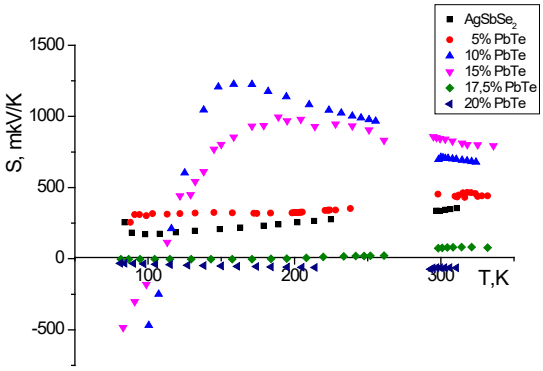

Figure 5. Temperature dependences of thermoelectric power of $(AgSbSe_2)_x(PbTe)_{1-x}$ solid solutions

sign after a given transition temperature[4].

It should be noted that, the addition of PbTe to $AgSbSe_2$, which has a p-type conductivity, leads to the formation of impurity levels that play the role of donor centers when in content PbTe increases ($x \leq 0,9$). This leads to the presence of electrons in the conductivity, which mobility is higher than the mobility of holes. As a result, the thermoelectric power of $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,9; 0,85; 0,825; 0,8) solid solutions have a negative sign below the transition temperatures. Then thermoelectric power changing the sign becomes positive by the temperature increases.

In addition, the values of thermoelectric power of solid solutions $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,825; 0,8) at T=300K (S=78μV/K and S=-63μV/K, respectively) is more smaller than the value of thermoelectric power of $AgSbSe_2$ at that temperature (S= 350μV/K). This decrease is stipulated by an increase in the concentration and a decrease in the mobility of carriers in the samples doped with PbTe.

[4]Rəhimov, S.S., Səddinova, A.A., Bağırov, T.T. $(AgSbSe_2)_{0,8}(PbTe)_{0,2}$ bərk məhlulunun termoelektrik xassələri // Fizika, – 2020. c. XXVI, №2, section: Az, – s. 16-19.

The analysis of the results obtained from the study of the thermal conductivity of $AgSbSe_2$ and $(AgSbSe_2)_x(PbTe)_{1-x}$ solid solutions are given in the 80-350K temperature range (figure 6).

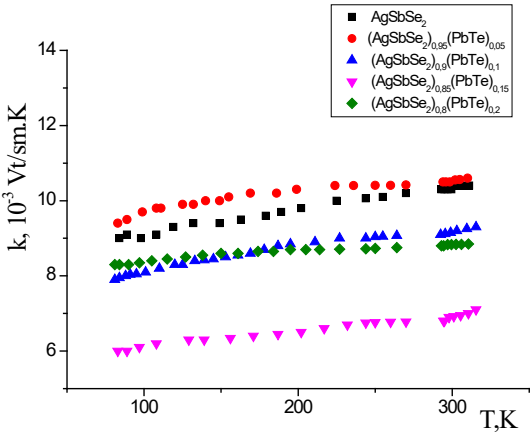

Figure 6. Temperature dependences of thermal conductivity of $(AgSbSe_2)_x(PbTe)_{1-x}$ solid solutions

The main purpose of the study of thermal conductivity was to determine a mechanism for heat transfer. As can be seen from the figure, the thermal conductivity of all the investigated solid solution samples increases slightly depending on the temperature.

As mentioned above, $AgSbSe_2$ crystallized in a face-centered cubic disordered NaCl type structure. The random distribution of non-chalcogenide atoms in such a stucture causes Ag^+ and Sb^{3+} ions to be stiuated in energetically favorable (Ag^+- Sb^{3+}) and unfavorable (Ag^+- Ag^+ and Sb^{3+}- Sb^{3+}) states. As a result, in the Ag-Sb sublattice may be exist energetically favorable and unfavorable regions of Ag^+ and Sb^{3+} ions. On the other hand, as the temperature rises, the Ag^+ ions leave of their places, intensifying the more energetically favorable state of the crystal lattice. This leads to relatively reduction of defects in the structure, an increase in ordered and as a result, a decrease scattering of phonons. This leads to the thermal conductivity increases slightly with temperature.

High anharmonicity of the octahedral coordination, disordered of the crystal lattice, scattering from point defects which exists in the crystal lattice stipulated by the small value of the thermal conductivity of $AgSbSe_2$ and $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85; 0,8) solid solutions. An increase of PbTe amount in the composition lead to a decrease of the value of thermal conductivity.

In addition, an analysis the values obtained by different authors at T=300K of the thermal conductivity of $AgSbSe_2$ are given. As a result of the analyzes, it was shown that there are some discrepancies between the values of the thermal conductivity of $AgSbSe_2$. Analysis of the obtained results shows that these discrepancies are related to the method of estimating the thermal conductivity and the different synthesis regimes of the samples. It should be noted that the synthesis regime has a strong influence on the disordered of the crystal structure and the value of thermal conductivity

In this chapter, the temperature dependences of the electrical conductivity of $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85; 0,825; 0,8) solid solution samples were analyzed comparatively with the $AgSbSe_2$ in the 80-350K temperature range. At temperatures below T=300K, the electrical conductivity of the samples is relatively small and does not change much. The value of electrical conductivity in other compositions except for $(AgSbSe_2)_{0,8}(PbTe)_{0,2}$, with the temperature rise begins to increase. Due to the high content of PbTe in the $(AgSbSe_2)_{0,8}(PbTe)_{0,2}$, in its temperature dependence of electrical conductivity was observed the metallic character.

The temperature dependences of the resistivity of $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85) solid solution samples was shown in Mott coordinates in comparison with $AgSbSe_2$ (figure 7). Correspondence of the experimental points to the linear dependence in Mott coordinates, as in $AgSbSe_2$, also in $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85) solid solutions the charge transfer occurs by the hopping conductivity of charge carriers over localized states lying in a narrow energy region near the Fermi level.

As a result of the experiments, it was established that the hopping conductivity for $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85)

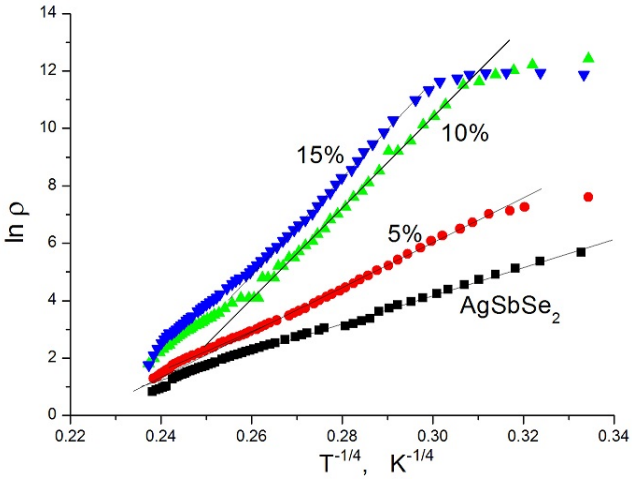

Figure 7. Temperature dependences of the specific resistivity of $AgSbSe_2$ and $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85) solid solutions in Mott coordinates

solid solutions occurs in 113K<T<215K, 118K<T<220K and 127K<T<233K temperature ranges, respectively. As a result of the calculations, for the density of localized states near the Fermi level in $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85) solid solutions were obtained the values $g(\mu)=6{,}9\cdot10^{15}eV^{-1}cm^{-3}$, $g(\mu)=3{,}4\cdot10^{14}eV^{-1}cm^{-3}$ and $g(\mu)=3{,}7\cdot10^{14}eV^{-1}cm^{-3}$, respectively.

Thus, as a result of the calculations, it was determined that in $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85) solid solutions, as in $AgSbSe_2$, the conductivity has a hopping mechanism in the temperature range 80-235K. At higher temperatures, the value of band conductivity increases, and as a result, the value of conductivity increases by the temperature rises.

The values of the E_a of charge carriers of $(AgSbSe_2)_x(PbTe)_{1-x}$ (0,95; 0,9; 0,85) solid solutions were calculated based on the values in the linear region at the coordinates $\ln\sigma\sim\frac{1}{T}$ in the temperature range 200-550K. As a result of the calculations, it was established that as the amount of PbTe in the composition increases, the value of

the activation energy increases compared to the value of the $AgSbSe_2$.

In addition, this chapter shown that an interesting result is observed in the temperature dependence of the specific resistivity of $(AgSbSe_2)_{0,9}(PbTe)_{0,1}$ solid solution[5]. The specific resistivity exceeds the maximum at T≈110K and then decreases to zero at T≈66K. It should be noted that the X-ray structure analysis of $(AgSbSe_2)_{0,9}(PbTe)_{0,1}$ at room temperature was performed and it was shown that it has the face centered cubic structure with a lattice constant a=5,8322Å. At the same time, in order to study the stability of the phase structure in the studied temperature range, X-ray structure analyzes were performed at temperatures from -180ºC to 400ºC. The results showed that the crystal structure remained stable throughout the studies temperature range and no phase transition occurred. For detailed study $(AgSbSe_2)_{0,9}(PbTe)_{0,1}$ solid solution was performed DSC analysis in the temperature range from -100ºC to 300ºC (173-573K). In the obtained DSC curve was observed an endothermic effect (T_{max}=406K). In order to determine more exact this situation and confirm the obtained result the measurements was carry out a second time in the temperature range 40-280K. The temperature dependence of the specific resistivity was measured four times - during both cooling and heating processes. It was observed that the maximum was repeated in all states and stabilized sliding from the initial T≈120K to T≈110K. The values of resistivity at maximum (T≈110K) and at room temperature were 234 kOhm and 97 Ohm, respectively.

This chapter also presents the results of the study of temperature dependence of electrical conductivity, thermoelectric power and thermal conductivity of $AgSbSe_2$ and its $(AgSbSe_2)_x(PbTe)_{1-x}$ solid solutions in the 300-600K temperature range. It was shown that the electrical conductivity of $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85; 0,825; 0,8) solid solutions,

[5]Ragimov, S. S., Saddinova, A. A. Transport properties of $(AgSbSe_2)_{0,9}(PbTe)_{0,1}$ // Fizika, – 2016. v. XXII, №4, section: En, – p.13-15.

except for $(AgSbSe_2)_{0,8}(PbTe)_{0,2}$ solid solution, increases with temperature in the temperature range 300-600K.

The σ of $(AgSbSe_2)_{0,8}(PbTe)_{0,2}$ decreases up to T≈400K and begins to increase as the temperature after T≈400K. Such a sharp change the value of conductivity depending on the temperature falls on in the temperature range of the endoeffect, which is observed in the temperature range 335-435K in the DSK curve of this solid solution and has a maximum at T=376,2K. This endoeffect manifests itself on the temperature dependences of both electrical conductivity and thermoelectric power[4].

The thermoelectric power of $AgSbSe_2$ and $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,9; 0,85; 0,825) solid solutions slowly decreases with increasing temperature in the temperature range of 300-600K.

$(AgSbSe_2)_{0,8}(PbTe)_{0,2}$ solid solution has n-type conductivity up to temperature T≈430K. After T≈430K, the sign inversion of thermoelectric power occurs and solid solution exhibits p-type conductivity. The type change in the temperature dependence of the thermoelectric power of $(AgSbSe_2)_{0,8}(PbTe)_{0,2}$ solid solution shows the presence of both electrons and holes in the conductivity.

As is known, both $AgSbSe_2$ and PbTe are good thermoelectric materials that used at medium temperatures (400-800K). The main requirement for such thermoelectric materials is their high thermoelectric figure of merit. For this purpose, the fourth chapter also presented the results obtained at different temperatures for the thermoelectric figure of merit and thermoelectric sensitivity of $AgSbSe_2$ and $(AgSbSe_2)_x(PbTe)_{1-x}$ (x= 0,95; 0,9; 0,85; 0,825; 0,8) solid solutions.

As is well known, thermoelectricity is of great scientific and technical interest due to its wide range of applications, from pure energy production to photon detection devices. Thermoelectric technology can be used in electricity generation, heating and cooling systems. Thermoelectricity is also considered a promising energy conversion technology due to its capability to convert heat directly into electricity. The thermoelectric generators due to their high reliability and simplicity, have been widely used in areas such as space energy in recent years.

The main quantity which determines the thermoelectric properties of thermoelectric converters is the thermoelectric figure of merit of the semiconductor materials which they are made. As is known, to increase the thermoelectric figure of merit Z ($Z = \frac{\sigma S^2}{k}$) is needed obtain materials with large thermoelectric power (S), electrical conductivity (σ) and small thermal conductivity (k), or both factors.

For this purpose, based on the values of the electrical conductivity, thermoelectric power and thermal conductivity of $AgSbSe_2$ and $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85; 0,825) solid solutions their thermoelectric figure of merit was calculated in the temperature range 300-600K.

The results of the investigations showed that the values of the thermoelectric figure of merit of $AgSbSe_2$ and $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85; 0,825) solid solutions is increases with temperature rises. The high values for the Z was obtained above T≈450K temperatures. This result was expected, because both composition are thermoelectric materials used in the medium temperature range[6].

The maximum $Z=0,16\cdot10^{-3}K^{-1}$ value for the thermoelectric figure of merit was obtained in $(AgSbSe_2)_{0,825}(PbTe)_{0,175}$ solid solution at temperature T=520K.

As is known, the Z of materials plays more important role in the materials which used in thermoelectric generators and refrigerators, usually. However, in the materials used in thermoelectric converters, the quantity determined by the ratio of their thermoelectric power to the thermal conductivity,
that is the thermoelectric sensitivity δ (δ=S/k), plays important role.

For this purpose, in dissertation work based on the values of the thermoelectric power and thermal conductivity of $AgSbSe_2$ and $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85; 0,825) solid solutions their thermoelectric sensitivity was calculated in the temperature range of 300-600K. The results of the calculations showed that the value of

[6]Səddinova, A.A. $(AgSbSe_2)_{0,825}(PbTe)_{0,175}$ bərk məhlulunun termoelektrik effektivliyi // Energetikanın problemləri, 2019. №3, – s. 76-80.

thermoelectric sensitivity of $AgSbSe_2$ and $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85; 0,825; 0,8) solid solutions at first increases depending on the amount of PbTe. Then the value of thermoelectric sensitivity begins is decrease exceeding the maximum at the value of x=0,85.

As a result of calculations, it was shown that the maximum value for the thermoelectric sensitivity $\delta=12{,}2\cdot10^{-4}$V·m/W is obtained near room temperature. This is one of the main requirements for sensitive elements used in thermoelectric converters.

Thus, it should be noted that between $AgSbSe_2$ and $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85; 0,825; 0,8) solid solutions the $(AgSbSe_2)_{0,825}(PbTe)_{0,175}$ and $(AgSbSe_2)_{0,85}(PbTe)_{0,15}$ are more useful for practical application which have maximum value of thermoelectric figure of merit and thermoelectric sensitivity.

MAIN RESULTS

1. For the first time, it was shown the electrical conductivity of $AgSbSe_2$ and $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85**)** solid solution crystals to have a hopping mechanism in the temperature range 80-235K.
2. For the first time, in $(AgSbSe_2)_{0,9}(PbTe)_{0,1}$ solid solution was observed a sharp decrease of specific resistivity from ρ=17550 Om·cm up to zero likely superconducting transition in the range 110-66K with the temperature decreases.
3. It was observed changing the type of conductivity (n→p) of $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,9; 0,85; 0,825; 0,8) solid solutions due to the presence of electrons which mobility is higher than the mobility of holes and with increasing amount of PbTe the inversion temperature shifts to higher temperatures.
4. In the thermogram of $AgSbSe_2$ at the T_{max}=363,5K, T_{max}=412,8 K and T_{max}=498,6K temperatures were observed endothermic effects. It was showed that these endoeffects occurs due to of silver ions leave their sites with increasing temperature and

thereby enhance the more energetically favorable state of crystal lattice (Ag^{+}-Sb^{3+}).

5. It was shown that a number of factors, such as, the high anharmonicity of the octahedral coordination in the crystal lattice, the disordered of the crystal lattice, scattering from point defects and structural components of $AgSbSe_2$ and $(AgSbSe_2)_x(PbTe)_{1-x}$ (x=0,95; 0,9; 0,85; 0,825; 0,8) solid solutions leads to a very small value of thermal conductivity, and the value of thermal conductivity decreases with increasing the amount of PbTe in composition.
6. It was established that the maximum value of thermoelectric figure of merit $Z=0{,}16\cdot10^{-3}K^{-1}$ was obtained at T=520K for $(AgSbSe_2)_{0,825}(PbTe)_{0,175}$ solid solution. The maximum value of thermoelectric sensitivity $\delta=12{,}2\cdot10^{-4}$ V·m/W was observed in $(AgSbSe_2)_{0,85}(PbTe)_{0,15}$ solid solution at T=300K.

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