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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

KINETICAL EVENTS IN COMPLEX CONDUCTOR CRYSTALS OF SYSTEM $[Ce(Sm)]_xSn_{1-x}Se$

Speciality: 2220.01 – Semiconductor Physics

Field of science: Physics

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GENERAL DESCRIPTION OF THE WORK

Relevance and development of the work. The pace of development of science and technology requires a complex study of modern electronics, new complex compounds and solid solutions that can meet the needs of technology in the face of solid state physics. These newly purchased substances must be environmentally and economically efficient. In this sense, one of the preferred fields of physics is the study of semiconductors with defective crystalline and complex electronic structure, high thermoelectric efficiency, resistant to harsh operating conditions and heavy metal atoms. The study of the physical properties of compounds with semiconducting properties, the determination of the mechanism of change of these physical properties by external influences such as temperature, pressure, radiation, is one of the main research areas of modern condensed matter physics. It is known from the results of many years of scientific research that defects in the crystal structure of semiconductor compounds have a significant impact on their physical properties. Therefore, it is very important to determine the mechanism of change in the physical properties of semiconductor compounds and their solid solutions under different conditions and by partial substitutions with atoms of elements of different ionic radius. The difference between the ionic radius of the Sm and Ce atoms is reflected in the physical properties of the $Sm_{1-x}Ce_xSnSe_2$ compounds.

Studies have shown that the replacement of Sn atoms with rare earth elements (REEs) can produce materials that can exhibit different physical properties. For example, studies of alloys $(SnSe)_{1-x-}(SmSe)_x$ synthesized by partial substitutions with the element Sm in the temperature range $77K \leq T \leq 700K$ have shown that the nature of these semiconductor properties changes as the concentration of Sm atoms in the composition increases. When x> 0.25mol%, the p-type conductivity becomes the n-type conductivity.

The object and subject of the research:

As the objects of research, the triple compounds of Ln-Sn-Se

(Ln=Ce,Sm) systems, which have not been fully studied so far, are ($SmSnSe_2$, $CeSnSe_2$) and $Ln_xSn_{1-x}Se$ (Ln=Ce,Sm) type ($Ce_xSn_{1-x}Se$, $Sm_xSn_{1-x}Se$) solid solutions.

The purpose and objectives of the study:

It consists of the study of the mechanism of action of REE on the properties of electro-thermal and galvanomagnetic properties of three-component compounds based on SnSe and their solid solutions. The practical purpose of the work is to obtain a material with high thermoelectric efficiency, which is important for application in thermoelectric converters.

In accordance with the purpose of the dissertation, the following issues were resolved:

- Selection of technology for the production of SnSe, $SmSnSe_2$, $CeSnSe_2$ compounds and solid solution crystals;
- Carrying out a comprehensive X-ray phase analysis of the synthesized compound and solid solution crystals, physical and chemical analysis of the obtained results and determination of cage parameters;
- Clarification of the type of conductivity of the obtained compounds and solid solutions and determination of the components of practical importance;
- Investigation of kinetic parameters in samples studied over a wide temperature range;

Research methods:

Single crystals of the compounds were obtained by the Bricman-Stockbarger method. Structural phase analyzes were performed by X-ray diffraction at room temperature and under normal conditions to determine the crystal structures of the obtained compounds. In accordance with the purpose of the dissertation, differential thermal analysis, X-ray structure analysis, D8 ADVANCE type diffractometer and mathematical calculation methods for multi-phase systems were used from the capabilities of Perkin Elmer STA6000 Calorimeter devices.

Defensive provisions:

The presence of two types of charge carriers (holes) in the electrical conductivity of the SnSe compound, the valence band consisting of two sub-zones.

The donor-type function of REE-additive atoms in solid solutions of Ln-Sn-Se systems.

Dependence of the scattering mechanism of carriers in the Ln-Sn-Se system on the nature and quantity of REE atoms entering the solid solution.

The role of scattering from polarized phonons as well as scattering from acoustic phonons in the electron-phonon processes occurring in Ln-Sn-Se systems.

Dependence of changes in the physical properties of $CeSnSe_2$ and $SmSnSe_2$ on changes in the valence of the metal atoms Ce and Sm.

Obtaining high thermoelectric efficiency in $(SnSe)_{1-x}$-$(CeSe)_x$ system solid solutions.

Scientific novelty of the research:

1. Compensated semiconductor crystals are obtained and the type of conductivity (p to n) varies depending on the temperature of some components.

2. A wide range of kinetic parameters of SnSe compounds, carriers based on a complex study in the concentration range, the scattering mechanism, effective mass and valence zone structure of carriers were studied.

3. Interactions of SnSe-CeSe, SnSe-SmSe systems were studied in the solid solution area, kinetic parameters were measured and analyzed.

4. $CeSnSe_2$ and $SmSnSe_2$ triple compounds with 1:1 ratio of SnSe-CeSe, SnSe-SmSe system components were obtained, their thermoelectric, galvanomagnetic properties, thermal conductivity were studied in a wide temperature range, the main kinetic parameters were determined.

5. By studying the electrophysical properties of $Ln_xSn_{1-x}Se$ (Ln=Ce,Sm) solid solutions, the concentration of carriers, the mechanism of electrical conductivity determined by the activation energy were investigated, and the scattering processes were analyzed.

6. Heat treatment in solid solutions improves the thermal conductivity of the substance, increases the density of the substance.

7. Based on the $(SnSe)_{1-x}$-$(CeSe)_x$ system, a new thermoelectric material of the order $Z \approx 2{,}7 \cdot 10^{-3} K^{-1}$ in the temperature range T = (300-700) K was obtained.

Theoretical and practical significance of the research:

These newly purchased substances must be environmentally and economically efficient. In this sense, one of the preferred fields of physics is the study of semiconductors with defective crystalline and complex electronic structure, high coefficient of thermoelectric efficiency, resistant to harsh operating conditions and heavy metal atoms.

It is known that the SnSe compound crystallizes in an orthorhombic symmetrical crystal structure and maintains its stable crystal structure over a wide temperature range up to T ~ 800K. Therefore, it is a very important material for the production of various converters that can operate in a variety of extreme operating conditions, including partially in high temperature region.

Approbation and application of the research:

The main research results obtained in the dissertation were discussed at national and international conferences:

• At the VIII Republican Conference "Modern Problems of Physics" dedicated to the 95th anniversary of BSU (Baku-2014).

• Materials of the Republican Scientific Conference "Actual Problems of Physics" of BSU (Baku-2015).

• III International Scientific Conference of Young Researchers dedicated to the 92nd birthday of national leader Heydar Aliyev at BEU (Qafqaz University) (Baku-2015).

• III International Scientific Conference of Young Researchers (Baku-2019) dedicated to the 96th anniversary of national leader Heydar Aliyev at BEU (Qafqaz University).

• Kabardino-Balkaria State University, Micro and nanotechnology in electronics, Proceedings of the XI International Scientific and Technical Conference (Nalchik-2019)

Publications**:** The main results reflecting the essence of the dissertation were published in 11 articles (4 of them in the journal with an impact factor included in the list of SCI) and 5 conference proceedings.

Name of the organization where the dissertation work is carried out:

The dissertation work was performed in the laboratory of "Physics of Bionanostructures" of the Institute of Physics named after academician H.M.Abdullayev of the Ministry of Science and Education of Azerbaijan

The structure and scope of the study:

The dissertation consists of an introduction, four chapters, main results, and a list of 120 references, commented on 171 pages. There are 18 tables and 61 figures in the dissertation. Except for tables and references, the introduction consists of 11692, chapter I 22985, chapter II 37252, chapter III 70984, chapter IV 85788, result 1760, abbreviations and symbols 477 characters. The total volume of the dissertation consists of 231412 characters.

CONTENT OF THE WORK

The introduction describes the general characteristics of the dissertation, the relevance and prospects of the topic, the purpose of the work, the main issues to be addressed, innovations based on the results of research on the dissertation, approbation and publication, the main provisions, their theoretical and practical significance.

In the first chapter, the literature on the crystal structures of compounds formed in SnSe-LnSe (Ln=Sm,Ce) systems and their

temperature-dependent structural changes are analyzed from a physicochemical point of view and the relevance of the topic is substantiated.

The second chapter provides information on the solid solutions of the Ce-Sn-Se and Sm-Sn-Se systems we have studied and the technology for obtaining triple compounds based on them, physical and chemical analysis and methods for determining the kinetic parameters. Along with the description of the existing technological methods for the acquisition of facilities, information was provided on the rules of conducting experiments on samples and errors. This chapter also explains in detail the analysis of system case diagrams and information about cage parameters.

In the third chapter, the study of the electrophysical properties of SnSe and $CeSnSe_2$, $SmSnSe_2$ triple compounds based on it, the calculation of the basic parameters, the results obtained, as well as a detailed explanation of some related crystallochemical issues are given. The study of kinetic effects in semiconductor materials allows to obtain information about the thermal parameters of the band gap, the calculation of key parameters such as the concentration, mobility, effective mass of carriers, the structure of the energy spectrum of carriers, as well as their scattering mechanism. The studies were performed in the temperature range 77K <T <800K. It can be said that the results of experimental studies and their analysis form the basis of this chapter.

The temperature dependence of the thermo e.d.f. of the SnSe compound has been investigated and determined. As the concentration of the carriers increases, the value of the thermo e.d.f. in the 77-320K temperature range increases. In a low-concentration sample (Sample №1 $p_{77} = 0{,}52 \cdot 10^{18}$ cm^{-3}), the value of thermo e.d.f. increases monotonically with increasing temperature, in the remaining samples (Sample №2 $p_{77} = 0{,}64 \cdot 10^{18}$ cm^{-3}, Sample №3 $p_{77} = 1{,}32 \cdot 10^{18} cm^{-3}$, Sample №4 $p_{77} = 2{,}1 \cdot 10^{18} cm^{-3}$) and the rate of increase of thermo e.d.f. does not correspond to the increase in temperature, as in the sample of 1 №. In the average value of the temperature range, the 2 № sample has a minimum, and in the 3 and

4 № samples, this minimum changes its position towards the high temperature range, and then rises again (increases) depending on the temperature.

The temperature dependence of the Hall effect has a number of features. In samples one (p_{77} = $0.52 \cdot 10^{18} cm^{-3}$) and two ($p_{77}$ = $0.64 \cdot 10^{18} cm^{-3}$), as the temperature increases from 110K to 150K, the Hall coefficient initially rises to 14.8 and 18 cm^3/Kl. increases, then decreases to 9.6 and 8.0 cm^3/Kl, respectively. In samples 3 and 4 №, whose concentrations are lower than in samples one and two, the Hall constant varies very little depending on the temperature. The hall coefficient increases with temperature up to 200K and then decreases regularly, but in the specified temperature range this coefficient does not change the conductivity sign. The change in the Hall coefficient with temperature corresponds to the change in thermo e.d.f. with temperature.

The Hall effect is analogous to the change in the Hall coefficient with temperature. In low-concentration samples of current carriers (Samples 1 and 2) there is a monotonous decrease in Hall conductivity depending on temperature, in samples 3 and 4 (U(T)) in the temperature range (160-210) K passes through a very small extremum.

The electrophysical properties of the $CeSnSe_2$ compound (σ (T), R(T), $\Delta\rho/\rho_0$, μ(T)) have been studied over a wide temperature range (T = 77-780 K). In the $CeSnSe_2$ sample, the hall coefficient and electrical conductivity were measured in the temperature range T=300-800K. It was found that the Hall coefficient varies in a complex form, which indicates that the energy zone structure of the $CeSnSe_2$ compound is complex. The temperature dependence of electrical conductivity (σ(T)) can be roughly divided into three temperature regions: 1st region T=300-445K temperature The value of σ in the interval increases weakly, monotonously. This area is called the additive conductivity area. The activation energy of carriers in this region is $\Delta E_{g1} \approx 0{,}14$eV; Temperature range 2 covers the temperature range T=385-588K. The activation energy of carriers in this region is $\Delta E_{g2} \approx 0{,}44$eV; Area 3 covers the temperature range

T≥588K. The activation energy of carriers in this region is ΔE_{g3}≈0,5eV. Note that at a temperature of T=400-410K, the electrical conductivity increases sharply, exceeding the minimum.

The presence of two types of carriers (light and heavy) in the sample, as well as acceptor holes (light and heavy) causes a magnetic resistance $\frac{\Delta\rho}{\rho_0}$. The value of magnetic resistance varies depending on the concentration of the second type of carrier. In practice, the dependence of the change of $\frac{\Delta\rho}{\rho}$-resistance of the $CeSnSe_2$ compound on the magnetic field was considered at different temperature values. It was found that the magnetic field increases at a value of H=11000Er and at a temperature of T = 305K $\frac{\Delta\rho}{\rho}$= 0.084 = 8.4%. In other words, the value of the electrical conductivity of the sample decreases by ~8.4% in the magnetic field. As can be seen from Figure (1), the value of $\frac{\Delta\rho}{\rho}$ decreases partially at relatively high temperatures. The applied magnetic field is a weak magnetic field ($\mu^2H^2<<1$) and $\frac{\Delta\rho}{\rho}$ -values for the $CeSnSe_2$-sample, do not saturate themselves in a given magnetic field. This change in the sign of the magnetic resistance indicates that there are different types of charge carriers in the sample, and that the scattering mechanism of the charge carriers changes twice in the temperature range (T=300-600K) we studied.

In practice, it is possible to estimate the concentration of the additive, the degree of compensation and the degree of degradation by determining the Hall coefficient. Theorists show that REEs have a high concentration (~10^{22} cm^{-3}) in terms of the number of free electrons, regardless of their composition, and that the R(T) dependence should remain constant over a wide temperature range. However, as can be seen in practice, T= 300-830K, which we studied, varies twice over the maximum in the temperature range. The inverse of the Hall coefficient gives us the concentration of carriers in the material. The value of the Hall coefficient of the $CeSnSe_2$ compound in the temperature range T = 77-700 K was

determined by measuring and based on it the temperature dependence of the free carriers n(T), μ_H(T)-Holl effect and the nature

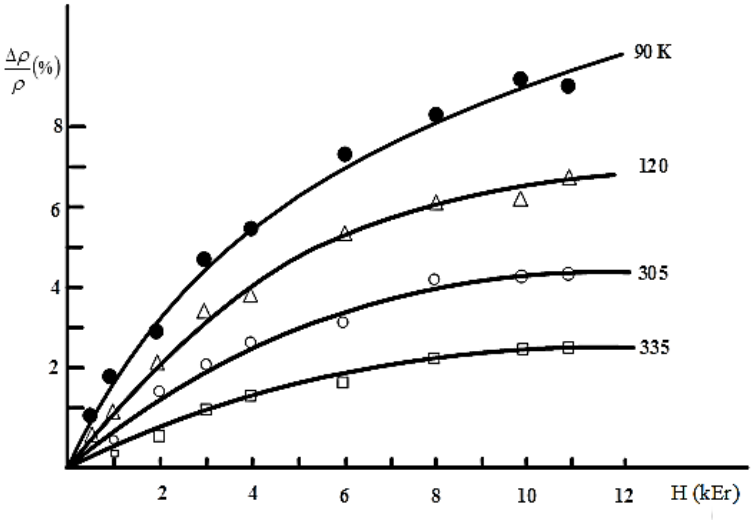

Figure 1. The dependence of the magnetic resistance on the field intensity on the $CeSnSe_2$ crystal

of the scattering mechanism r(T) were studied.

One of the parameters that is sensitive to the degree of purity and crystalline structure of the material in semiconductor materials, as well as the defects in it, is the Hall yield of the carriers.

Experiments show that the Hall's mobility (μ_H) is inversely proportional to temperature ($\mu_H \sim T^{-1}$). This, in turn, characterizes the mechanism of scattering of carriers.

Using the values $\mu_H = \bar{R}\sigma_0$ for the $CeSnSe_2$ compound, the μ_H (T) dependence of the μ_H – Hall's mobility in the temperature range T=77-700K was constructed and analyzed. Figure 2 shows the temperature dependence (μ_H (T)) of the Hall's mobility. As can be seen from the figure, the value of the μ_H coefficient partially increases with increasing temperature, and at T temperature 560K this increase partially intensifies. T=300-550 K varies with the law $\mu_H \sim T^{2,25}$ in the

temperature range and with the law $\mu_H \sim T^{3/2}$ at the temperature T≥560K. This is partly due to the presence of a leap conduction

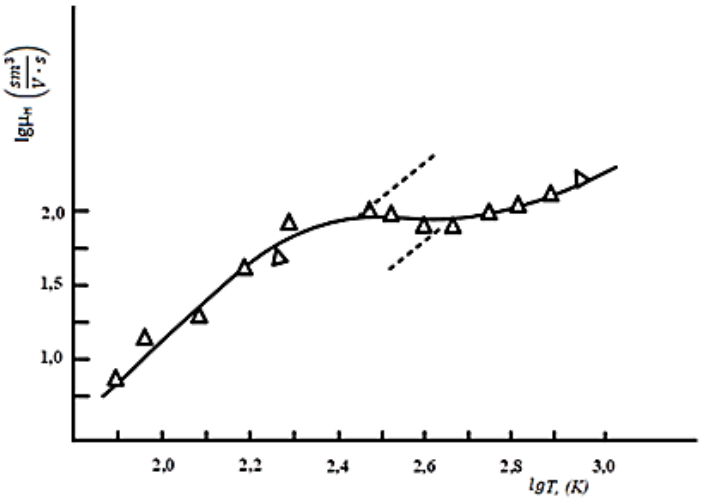

Figure 2. Temperature dependence of Hall's mobility on the $CeSnSe_2$ crystal

mechanism in the conduction. This, in turn, indicates the presence of covalent-ion bonds in the $CeSnSe_2$ compound, the degree of ionization, as well as the presence of mixed-type conductivity.Electrophysical parameters of $SmSnSe_2$ were studied in the temperature range T=300–600K. The temperature dependences of the electrical conductivity of the $SmSnSe_2$ compound σ(T) and the Hall coefficient R(T) are complex. The temperature dependence of electrical conductivity exceeds the minimum in the temperature range T=456–560K and increases with subsequent temperature values. In the region of additive conductivity (T=300–420K), the value of σ increases monotonically and the activation energy of the carriers is ΔE_1 = 0.24eV. In this temperature range, the value of the Hall coefficient decreases from the maximum. At T=300–420K, the activation energy of the carriers is ΔEg_1 = 0.24eV, and the condition

n <N_{d1} is satisfied in this temperature range. In the 2nd temperature range T=500–625K ΔEg_2=0.53eV and in this range the condition n <N_{d2} is satisfied. In the third temperature range, the activation energy of T> 630K carriers is ΔEg_2 = 0.75eV, which characterizes the value of the thermally restricted zone (n ≈ p).

Hall's mobility rate (μ_H) increases in proportion to the increase in temperature. (μ_H) dependence T=300–380K by the law $\mu_H \sim T^{2.0}$ in the temperature range; At T=380-460K varies with the law $\mu_H \sim T^{0,2}$. Intensive increase in T=460–480K is observed with the law of $\mu_H \sim T^{3.5}$. A similar repetition is observed with the subsequent increase in temperature: $\mu_H \sim T^{1.8}$. Thus, it was found that in the $SmSnSe_2$ combination, the Hall mobility of the carriers changes in a complex form. This is primarily due to the fact that the atoms of the element Sm have a variable valence (Sm^{2+}, Sm^{3+}) and a qualitative change in the degree of ionization of the sample. Thus, in the temperature range we studied, it was determined that the charge carriers were scattered from ionized and neutral atomic centers.

By studying the temperature dependences of the total thermal conductivity, lattice thermal conductivity and thermal resistance of the triple compound $SmSnSe_2$, the effect of the defects formed on the compound on the thermal conductivity of the lattice was determined. As a result of the measurements, it was determined that the total heat transfer coefficient decreases with increasing temperature. An anomalous change in temperatur (T) dependence is observed in the temperature range T=520-540K. According to Wiedemann-France law, the electronic thermal conductivity at temperature T=300K is 1.1% of the total thermal conductivity. With increasing temperature, a slight increase in the value of χ_e is observed, and at T = 600K, $\chi_e \approx 1{,}57\%$. In the temperature range (T=300-620K) we studied, the value of the total heat transfer coefficient is mainly the lattice and electronic heat transfer ($\chi_{total}=\chi_q+\chi_{el}$). The inverse value of the thermal conductivity of the cage - the thermal resistance was calculated and it was determined that a linear change in the temperature range T=300-490K is observed. Deviations from the linear dependence were recorded at T> 500K. The triple combination

of $SmSnSe_2$ $\chi_q(T)$ varies with the law $\chi_q \sim T^{-1,1}$ in the temperature range T = 300-480 K and $\chi_q \sim T^{-0,67}$ in T> 540K. As can be seen from the measurements, the value of χ is small and a monotonous decrease is observed with increasing temperature, except for the temperature range T = 490-500K. It is assumed that the low value of χ is due to the role of Sm atoms in the compound. Table 1 shows the experimental values of some physical parameters of the parent substance (SnSe) and triple compounds at room temperature.

Table 1: Some kinetic parameters of SnSe, $CeSnSe_2$ $SmSnSe_2$ compds (T=300K)

Samples	**σ $Om^{-1}cm^{-1}$**	**R cm^3/ Kl**	**p, (n) cm^{-3}**	**μ cm^2/ V·S**	**S mkV/ K**	**$\chi \cdot 10^{-3}$ Vt/ cm·K**	**Micro Hardness MPa**
SnSe	8,21	7,8	$0,8 \cdot 10^{18}$	64	510	18,7	
$CeSnSe_2$	3,03	-3,8	$-1,64 \cdot 10^{18}$	11,5	-375	22,4	2100
$SmSnSe_2$	3,31	13,83	$0,45 \cdot 10^{18}$	46	670	21,6	2520

The fourth chapter is devoted to a comprehensive analysis of the results of extensive research, which is almost consistent with both the purpose of the study and the direction of the research. According to the requirements of the analysis, we have divided this chapter into two parts: Part 1 is the study of electrophysical and thermoelectric properties of the studied solutions: Part 2 is a brief summary of the causes of defects in the studied components and their effects on thermal conductivity.

SnSe binary compound is considered a thermoelectric material. At the same time, the relatively large thermal band gap ($E_g \approx 0.92$eV) leads to the presence of intermediate properties in these materials with thermoelectric and optical properties, which allows to vary the concentration of current carriers in a wide range from 10^{16} to 10^{20} cm^{-3}. One possible way to increase thermoelectric efficiency is to add these materials to various heavy element atoms. It is possible to achieve a certain increase in thermal conductivity and at the same time reduce the cost of thermal conductivity by scattering phonons

from defects. Taking into account the above, the concentration dependence of the electrophysical properties of $Ce_xSn_{1-x}Se$ compounds was studied in the temperature range (77–400K).

The dependence of the electrical conductivity on the amount of the metal element serium (Ce) (T = 300K) in the solid solutions of system $Ce_xSn_{1-x}Se$ ($x \leq 0{,}035$) has been studied. The value of electrical conductivity decreases proportionally in the range $x \leq 0.02$, depending on the amount of x, and increases to a minimum at a concentration of x = 0.02. due to a decrease in the concentration of equal carriers. With the subsequent increase in the addition of ce metal, the occurrence of anti-structural defects in the components is sharply reduced, and the electrical conductivity of the components improves.

Figure 3 shows the temperature dependence of the thermo e.d.f. (S) for different compositions. As can be seen from the figure, an increase in the amount of Ce element additive in the temperature range T=(77-200)K relatively reduces the value of S in a sample with x=0.005 (S=(300→260) mV/K); The value of the other x=0.01 and x=0.020 (№5) S increases in absolute value. As can be seen from the graph, in samples with $x \geq 0.010$, the sign of S changes from p to n at different temperatures (x=0.010: №3 and x=0.015 №4), respectively. Sample №5 (x=0.020) is an n-type conductor, and the value of S decreases with absolute value at T temperature 260K, exceeding the maximum. Figure 4 shows the temperature dependence of the Hall coefficient R(T) for samples №2, №3 and №4 in the temperature range 77–400K. In the first example (tin monoselenide without the Ce additive atom), the temperature coefficient of the Hall coefficient has a wide maximum at ~ 180K.

The small inclusion of Ce atoms in the $Ce_xSn_{1-x}Se$ system (sample №2, x=0.005) leads to a significant increase in the amplitude of R(T) and the state of temperature peaks shifts to the lower temperature (up to 120K). Note that for samples №1 and №2, the Hall coefficient does not change the sign in the entire studied temperature range (p-type conductivity).

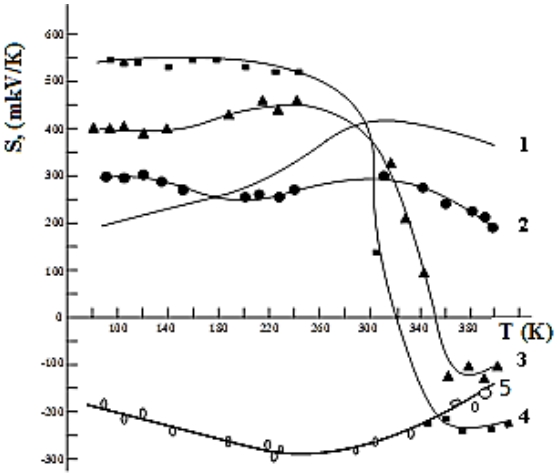

Figure 3. Temperature dependence of thermo e.d.f. of $Ce_xSn_{1-x}Se$ x= 0 (№1); x=0,005 (№2); x= 0,01 (№3) ; x=0,015 (№4); x=0,02 (№5) system alloys

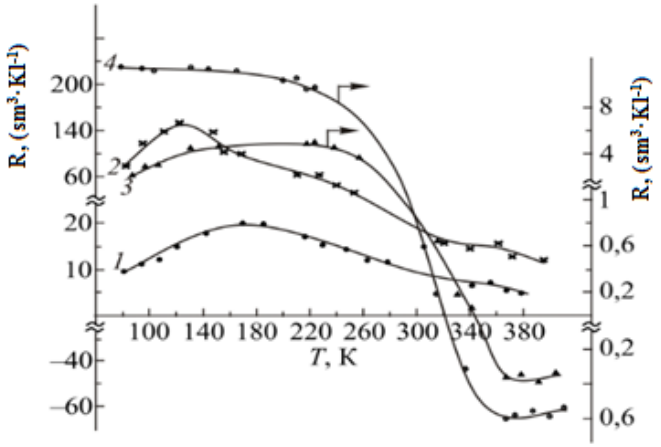

Figure 4. Temperature dependence of the Hall coefficient in $Ce_xSn_{1-x}Se$, x: 0 (№1); 0,005 (№2); 0,01 (№3) ; 0,015 (№4) systems

Unlike the above-mentioned samples, no maxima are observed in the R(T) curves of №3 and №4 samples. From low temperatures to ~ 240–260K, the temperature dependence of the Hall coefficient forms a "plateau", then the amplitude of the R(T) dependence decreases sharply with the next increase in temperature and changes the sign of the Hall coefficient in the opposite direction (for example №3 at 340 K. and at 320 K for №4 sample). For samples №3 and №4, the change in the sign of the Hall coefficient can be interpreted as a change in the type of conductivity from p-type to n-type in the system under study.

Figure 5 shows the temperature dependence graphs of the electrical conductivity 77-400K in the samples studied. As can be seen from the figure, the electrical conductivity decreases significantly during the transition from a double SnSe compound to a solid solution of $Ce_xSn_{1-x}Se$, and the σ(T) dependence differs sharply from the ($\sigma_{SnSe}(T)$) dependence. As the cerium component increases, the activation energy of the additives decreases. In the initial example (№1), the activation energy of the charge carriers is ΔE_1 = 0.67eV. In sample number two (№2) ΔE_2 = 0.53eV, in sample number three (№3) ΔE_3 = 0.06eV, and in sample number four ΔE_4 = 0.03eV. Thus, with the increase of the additive concentration in the $Ce_xSn_{1-x}Se$ system, the activation energy of the carriers decreases significantly. As can be seen from Figure 13, in samples №3 and №4 (x=0.010 and 0.015), a minimum of lgσ (1/T) is observed in the temperature range 200–320K. It can be assumed that this is due to the reduction of additive carriers. With the next increase in temperature, the cost of conductivity increases. As can be seen from the graph, in the region of additive conductivity (at temperature T = (300-460) K) the activation energy of the carriers is E_{g3}≈0,63eV, and the energy of the thermally restricted zone is E_g≈0,63eV (curve 3).

As can be seen, the width of the thermally restricted zone is significantly reduced compared to the parent material. This shows that, in contrast to the sample with x = 0.005, in the sample with x = 0.050 at% Ce, the element Ce entered the system as a component,

not as an additive.

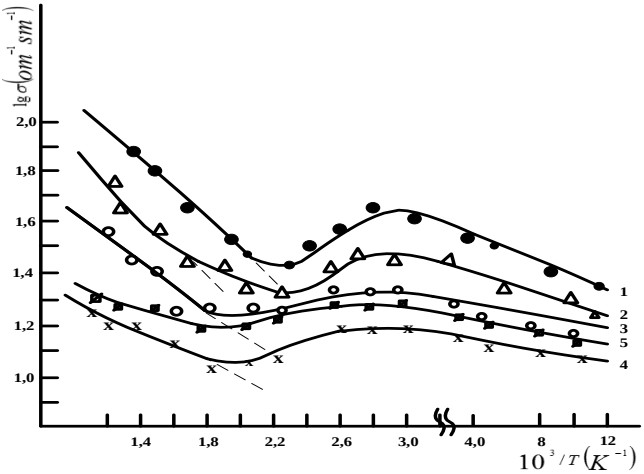

Figure 5. Temperature dependence of electrical conductivity in $Ce_xSn_{1-x}Se$ x= 0 (№1); x=0,005 (№2); x= 0,01 (№3) ; x=0,015 (№4); x=0,02 (№5) system alloys

In the studied samples, the temperature dependence of the load capacity of the carriers is investigated. It was found that the mechanism of scattering of carriers depending on the additive concentration differs significantly from each other in terms of temperature. In the second example (№2, x=0.005), the load capacity of the carriers is given by the law $\mu_H \sim T^{1.5}$ in the temperature range (77–100)K,by the law $\mu_H \sim T^{1.8}$ in the range (180–310) K, and $\mu_H \sim T^{-1,6}$ in the range T> 320K. The scattering mechanism varies from ionized centers to optical phonons depending on different temperature regions. Thus, in the temperature range (77–180)K, the charge carriers are scattered from both ionized and partially neutral atomic centers. As the temperature increases, acoustic and optical phonos (at №3 and №4) participate in scattering, and the scattering intensity of optical phonons increases.

The thermal conductivity of $Ce_xSn_{1-x}Se$ single crystals, the elastic scattering of charge carriers, the degree of decomposition of any composition and the thermal conductivity of electrons and lattice

within the parabolic zone were calculated.

The study shows that as the temperature increases, the total (χ_{total}) and lattice thermal conductivity (χ_q) decreases. We explained this decrease by the formation of additional scattering centers depending on the amount of Ce in the composition. However, thermal evaporation, on the contrary, increases the value of χ_q. At the same time, as the amount of serum element in the composition increases, the density increases.

Figure 6 shows the dependence of the thermal conductivity (χ_q) of the cage, the concentration of defects, and the density of the amount of Ce. The figure shows a graph of the change in total concentration depending on the amount of serum in the a-curve.

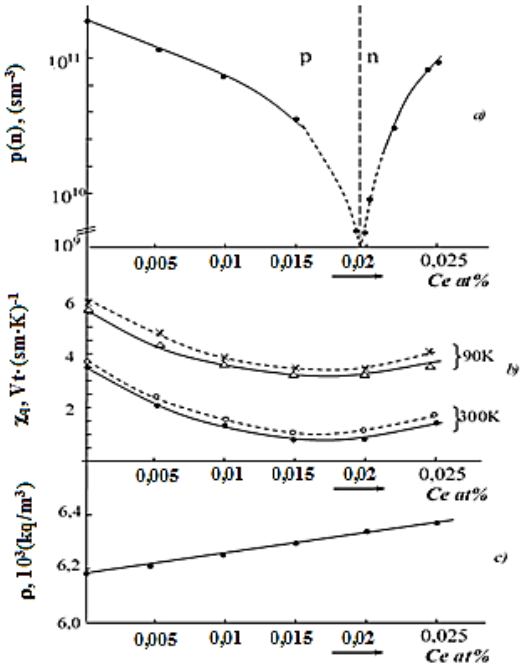

Figure 6. Dependence of the lattice thermal conductivity (χ_q) of system $Ce_xSn_{1-x}Se$ on the concentration of defects and the amount of Ce

As can be seen from the graph, in a sample with x=0.02 at% Ce, the conductivity type varies from p to n. At the same time, the concentration of the carriers around the composition, the thermal conductivity of the cage (before and after annealing dotted line) changes beyond the minimum (b-curve in the figure).

Experimental results of system alloys $(SnSe)_{1-x}$-$(SmSe)_x$ show that as the amount of SmSe component in the composition increases and the concentration of carriers decreases to $x \rightarrow 0.25$ at% SmSe. When Sm metal is introduced into the SnSe crystal by substituting SmSe form, the hole concentration decreases depending on the amount of Sm. The concentration of n-type compounds is 60% higher than the p-type concentration.

In samples with $x \geq 0.25$ at% SmSe, the type conductivity varies from p to n, the specific resistance increases, and $x \approx 0.25$ at% SmSe reaches its maximum value. There is a sharp decrease in the subsequent increase of the element Sm. This decrease is attenuated by a monotonous decrease depending on the amount of Sm in samples with $x \geq 1$at% SmSe. Experimental results show that the density of substances increases significantly depending on the amount of samarium in the composition. The increase in density is characterized by an increase in the elemental lattice of SnSe. In this case, the volume of the elemental nucleus and the number of molecules do not change.

The study of the temperature dependence of thermo e.d.f. (S(T)) in the selected samples shows that the thermo e.d.f. varies qualitatively differently in p-type substances than in n-type substances. Thus, the S(T) dependence of p-type samples decreases weakly in the temperature range T=77-400K, and after the minimum, a weak extremum is observed at T=420-530K, and decreases again with subsequent increase in T. Depending on the amount of observed minimum Sm, it slides towards a lower temperature. On the other hand, as can be seen from the graphs, the concentration of holes in p-type samples x= 0.05 at% and at T = 300K decreased by 48%, and in the x=0.10 at% sample approximately one order of magnitude decreased. The decrease in the hole concentration continues until the

x=0.25 at% sample. In the n-type samples, on the other hand, a very weak increase in the interval T=77-400K is observed in the sample x=1.00 at% in relation to S(T) with increasing temperature, and the growth rate partially increases beyond the minimum (T = 400-455 K). In the x = 3at% sample, the rate of increase of S (T) in the temperature range T=77-500K was partially weak ($\upsilon_s \sim T^{0.1}$), and in the subsequent temperature range it was r $\upsilon_s \sim T^{0.92}$ law varies with. This unusual change is thought to be due to the intensification of the resonance state in the $(SnSe)_{97.00}$-$(SmSe)_{3.00}$ composition due to the Sm-metal.

The temperature dependence of the Hall coefficient also varies in different ways. In Example №2, the presence of R(S) ≈const at T=77-440K indicates the stability of the hole concentration. In the subsequent increase in temperature, a weak increase in T≥420K is observed, exceeding the minimum. At high temperatures (T≥500K), the value of R partially increases in a sample with x = 0.10at%. At T = 77-400K, a slight decrease is observed, which corresponds to the partial stability of the hole concentration. A relatively similar situation is observed in the x=1.00mol% n-type sample. However, the decrease in R(T) dependence here is due to the increase in electron concentration. Concentration stability is observed at T=300-500K. At a temperature of 400K, R(T) increases weakly and monotonously. This increase occurs due to the growth of the r-scattering mechanism due to the activation of the SmSe component and the activation of the resonance event. In the upper temperature range (T ≥ 420 K) x=3 at%, the property shown in the example is more pronounced.

The electrical conductivity of the samples is T=300-450K, the stability of the concentration (except x = 0.05 at% of the sample) is observed. In the x=0.05 at% sample, this interval covers the temperature T=300-400K. With the subsequent increase in temperature, the electrical conductivity of the samples increases due to the activation of the carriers. In the low temperature range, the activation energy of T≤400K carriers increases to a minimum. minimum (T) is associated with a decrease in the Hall load of the

minimum load carriers. The transition from the minimum in the σ (T) dependence of the sample at x=1.00 at% is very weak and occurs at relatively high temperatures (T=530-600 K). At T≥530K, the σ (T) dependence intensifies and shifts to the specific conductivity region. The width of the thermally restricted zone in this temperature range is E_g≈0.8eV. The σ (T) dependence of the x=3mol% sample is not saturated with conductivity and exhibits a ruptured semiconductor property. n-type samples are inherently different from p-type samples. Due to the high content of Sm metal in n-type samples, there is an interaction between additional Sm-Sm atoms in the composition. As a result, on the one hand, the deformation potential increases, on the other hand, the capture of various types of defects and vacancy centers increases the density of the substance.

The fact that the electron configuration of the metal atoms $4f^6 5d^0 6s^2$ is variable valence: two and three (Sm^{2+}, Sm^{3+}) valence. The samarium Sm^{3+} state has a metallic property, and the Sm^{2+} state has a semiconductor property. This variable valence varies depending on the type of defects in the crystal and the nature of the components. In both cases, the samarium metal atoms exhibit a donor-type property in the form of SmSe. On the other hand, the vacancy centers in the $4f^6$ coating of the samarium act as acceptors for electrons, and as the amount of Sm in the composition increases, they become stronger in the area created by the ion potential and cause redistribution of electron density.

Temperature dependences of thermoelectric parameters of samples containing $Ce_{0.05}Sn_{0.95}Se$ and $Sm_{0.05}Sn_{0.95}Se$ were studied.

Thermo e.d.f. is stable in the temperature range T = 300–560K, and decreases monotonically with further increase in temperature from S = 360mkV / K to S = 205mkV / K at T = 800K.

Electrical conductivity increases monotonously in the temperature range T = 300–560K, and a relatively weak increase is observed in the subsequent increase in T (in the range T=680–780K). Accordingly, the total heat transfer coefficient was calculated by measuring in the temperature range we studied, and according to the preliminary results obtained, the Z-thermoelectric efficiency of the

sample was calculated according to the criterion $Z = S^2\sigma/\chi$. As can be seen from the graph, T = 500–700 K varies between the values of $Z = (2.45\text{-}2.72) \cdot 10^{-3}T^{-1}$ in the temperature range. In other words, at relatively high temperatures, the effectiveness of the composition Z partially improves.

The thermo e.d.f. of the sample $Sm_{0.05}Sn_{0.95}Se$ increases monotonically at a temperature T = 480K and reaches a maximum value of S = 360 mV / K. A further increase in T is followed by a monotonous decrease and decreases to S = 180 mV / K at T = 800K.

Table 2: Some kinetic parameters of samples at T=300K temperature

Ln	x, at%	P(n), (cm^{-3})	σ ($Om^{-1}cm^{-1}$)	U $cm^2/V\cdot s$	S mkV/K	10^{-3}, χ Vt/cm·K	10^{-3} Z K^{-1}
O	0	$3{,}76\cdot10^{18}$	97	163	430	18,7	0,96
Ce	0,005	$3{,}4\cdot10^{18}$	62	114	441	17,2	0,72
Ce	0,025	$-1{,}1\cdot10^{19}$	186	105	-382	15,4	1,76
Ce	0,050	$-1{,}48\cdot10^{19}$	217	98	-364	12,7	2,26
Sm	0,005	-	-	-	-	-	-
Sm	0,250	$-1{,}4\cdot10^{19}$	328	146	-268	15,9	1,48
Sm	0,050	$-1{,}0\cdot10^{19}$	162	98	-225	14,7	0,71

Temperature dependences of the thermal conductivity (χ) and thermoelectric efficiency (Z) of the $Sm_{0.05}Sn_{0.95}Se$ sample were also determined. The aim is to determine whether the ingredients studied are of practical importance. Note that the temperature dependence of the thermoelectric properties of a sample containing $Sm_{0.05}Sn_{0.95}Se$ varies in different ways depending on the temperature. Most likely, this is due to the presence of different types of dislocations. The Z-thermoelectric efficiency of this composition was determined using the values of thermoelectric parameters.

Thus, the following conclusion was drawn from the experiment. From p-SnSe solid solutions alloyed with Ce metal: a new n-type semiconductor thermoelectric material is obtained, which is resistant

to moisture, radiation and can operate in a wide temperature range. Ce = 0.05 at%, $Ce_{0.05}Sn_{0.95}Se$ sample has high thermoelectric efficiency ($Z = 2.7 \cdot 10^{-3}\ K^{-1}$) and can be used in the manufacture of thermogenerators as a thermoelectric material.

Results

1. The interaction effects of SnSe-CeSe and SnSe-SmSe systems were studied, complex physico-chemical analyzes of the samples were conducted, solubility regions were determined, as the REM (rare earth metals) concentration in the solid solution region increases, microhardness, density, and elemental lattice constants increase slightly in the alloys. In this system, ternary compounds $CeSnSe_2$ (*a=8.94, b=8.97, c=6,90 Å*) and $SmSnSe_2$ (*a=8.83, b=8.90, c=6,80 Å*) crystallized in rhombic syngonia in a 1:1 ratio of components were obtained, and the crystals were grown in a special technological regime.

2. The temperature dependence of electrical conductivity of compound $CeSnSe_2$ with n-type conductivity is divided into three regions: in the additive conductivity region (T=300-445K) the activation energy of charge carriers is $\Delta\varepsilon_{g1} \approx 0{,}14$ eV; activation energy $\Delta\varepsilon_{g2} \approx 0{,}44$ eV in the temperature range T=385-588 K; The activation energy of charge carriers in the T≥588K range is $\Delta\varepsilon_{g3} \approx 0{,}5$ eV. The value of electrical conductivity decreases by ~8.4% in the magnetic field, and the value of $\frac{\Delta\rho}{\rho}$ partially decreases at relatively high temperatures. The value of $\frac{\Delta\rho}{\rho_0}$ is positive in the temperature interval T=300-420K, and its sign changes from positive to negative at the temperature T=430K.

3. In the region of additive conductivity (T=300 – 420K), the conductivity value of compound $SmSnSe_2$ increases monotonically, and the activation energy of charge carriers is $\Delta\varepsilon_1$=0,24eV, in the temperature interval T=500–625K $\Delta\varepsilon_{g2}$ = 0,53 eV, and the energy levels located deeper in this region, relatively due to the participation of heavy electrons in the conductivity, the electrical conductivity of

the substance intensifies, the width of the thermally forbidden zone in the region of T>630K is $\Delta\varepsilon_{g3}$=0.75eV. Scattering from ionic and neutral atomic centers dominates.

4. Tin monoselenide crystals doped with cerium atoms have p-type conductivity in the temperature range of 77-300 K. With increasing temperature, the Hall coefficient decreases past the maximum, and in x>0.01 samples at temperature T>320K, the conductivity changes from p-type to n-type. Due to the excess amount of cerium in $Ce_xSn_{1-x}Se$ alloys, due to the formation and redistribution of Frenkel defects, the concentration and mobility of charge carriers, the activation energy in the additive region decreases, the density increases, the inversion of the sign of the Hall coefficient shifts to the low temperature region.

5. Depending on the concentration of additives, the scattering mechanism of charge carriers in $Ce_xSn_{1-x}Se$ crystals changes. In the temperature range of T=77-100 K, the conductivity is according to the $\mu_H \sim T^{1,5}$ law, in the T=180-310 K region, the law of $\mu_H \sim T^{-1,8}$, and in the T>320 K region, $\mu_H \sim T^{-1,6}$ changes according to the law, that is, in the low temperature range, scattering from ionized dopant and neutral atomic centers dominates, and in the upper temperature range, it is replaced by scattering from acoustic and optical phonons.

6. Heat transport in $Ce_xSn_{1-x}Se$ crystals is dominated by lattice thermal conductivity, thermal resistance is due to phonon-phonon scattering, and the increase in thermal resistance with an increase in the amount of cerium in the composition is due to the scattering of phonons from point defects. As the amount of Ce in the solid solution increases, partial "cleaning" occurs and is accompanied by a slight increase in density and a decrease in thermal conductivity in the cerium-containing composition. Long-term thermal processing leads to the adjustment of the crystal structure, as a result of which the thermal conductivity of the samples increases by 12-20%, but the nature of the temperature dependence of the thermal conductivity remains unchanged.

7. In the p-type samples subjected to low-dose irradiation (D_γ=20 kGy), a partial increase in the value of electrical conductivity

is observed after irradiation, while in the n-type sample, a decrease is observed. The σ dependence of the p-type sample exposed to relatively higher radiation (D_γ=35 kGy) increases by 22% (T=77K), while it decreases by 14% in the n-type sample.

8. Thermoelectric properties vary depending on the amount of Ce and Sm element atoms in the compositions and their specific properties. It was determined that the thermoelectric efficiency of the sample containing $Ce_{0,05}Sn_{0,95}Se$ is $Z=2.26\cdot10^{-3}K^{-1}$ at room temperature, and $Z=2.7\cdot10^{-3}K^{-1}$ at T=450-600K with increasing T is in the composition. This composition can be presented as a thermoelectric generator material that can work at relatively high temperatures.

The main results of the dissertation are published in the following articles and theses.

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