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THERMODYNAMICAL, THERMOELECTRICAL AND ELECTRICAL PROPERTIES OF THE NARROW-GAP Ag_4SSe SEMICONDUCTOR

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Temperature dependencies of the basic thermoelectrical and electrical properties such as Seebeck coefficient, electroconductivity, Hall constant and thermoconductivity were investigated in the case of n-type semiconducting Ag_4SSe compound. Thermoelectrical efficiency of this material was determined as well. On the basis of temperature dependence of electroconductivity, thermal band gap energy of this material of 0.23 ± 0.01 eV was determined. The influence of doping with Cd on all of these properties was also studied. On the basis of the reduced Fermi energy level value in the studied temperature interval, conclusions about the state of the electron gas in this semiconducting compound were derived. The phase transition β-$Ag_4SSe \leftrightarrow L$ (melting) was characterized by its basic thermodynamical parameters.

Keywords: semiconducting compounds; thermodynamics; electrical properties; thermal conductivity

1. INTRODUCTION

Ag_4SSe occurs in nature as mineral *aguilarite* [1]. Among the other interesting features of this compound, probably the most prominent one, especially in the context of its properties relevant to the potential applicability, is the reversible $\alpha \leftrightarrow \beta$ phase transition it undergoes. In a brief recent report, we have demonstrated the occurrence of this phase transition, and presented a preliminary study of the basic thermodynamical parameters characterizing it [2]. In this report, also the peculiarities in the basic temperature trends of various thermoelectrical parameters characterizing this material occurring due to this transition were detected. According to the band gap value, Ag_4SSe belongs to the group of narrow-gap semiconductors, with electrons as predominant charge carriers (*i.e.* it is an n-type semiconductor). On the basis of its electrical and thermoelectrical properties, this compound can be used for a variety of different purposes. Some of these include the application in construction of thermoelectrical generators, the Hall sensors, superlattices, etc. [3, 4]. Besides on its own, this compound is also interesting with respect to its alloying properties. Recently, the phase equilibria in the Ag_4SSe-ZnTe and Ag_4SSe-InSb systems have been studied, and the formation of solid solutions and intermediate phases has been specified [5, 6].

Since, from the aspect of the potential field of applicability of this material, its thermoelectrical properties are of notable importance, it is of certain interest to perform a more detailed study of these properties, particularly of their temperature dependence. In the present paper, some basic thermodynamical, thermoelectrical and electrical properties of Ag_4SSe are studied as functions of temperature. The thermoelectrical efficiency of this material is also determined. Besides that, the influence of Cd-doped impurity (0.013 – 0.333 mass %) on these parameters is specified. Also, particular attention is paid to the β-$Ag_4SSe \leftrightarrow L$

(melting) phase transition, and its basic thermodynamical parameters are determined.

2. EXPERIMENTAL

Ag_4SSe was prepared by direct synthesis from Ag_2S and Ag_2Se (purity 5N for Ag, S, and Se) at 1000 °C inside sealed quartz ampoules [7] (Ag_2S and Ag_2Se were produced by the method described elsewhere [8]). Homogenization annealing at 353 K (240 h) for both sample types, undoped and Cd-doped, was performed.

The phase transition temperature $T_{\alpha\leftrightarrow\beta}$ was studied by differential thermal analysis (DTA) at heating rates of 2.5, 5.8, 9.4, 13.5, 16.4 and 17.8 °C min^{-1} to an accuracy of ±2 °C (Al_2O_3 was used as a reference).

The thermoelectrical and electrical properties were investigated in vacuum of 10^{-3} Pa by the following procedures: the Seebeck coefficient (α) and the thermoconductivity (λ) – at temperature gradients up to 10 K with direct and absolute stationary methods, respectively, electroconductivity (σ) – at current densities of less than 10^3 A m^{-2} by a two-point probe technique, reversing the electric field for each measurement in order to avoid the picking up a Peltier component, the Hall effect (R) – conventional d.c. method, reversing the magnetic and electrical field. The error margin for α measurement was estimated to be ±1 %, and for σ and λ it is ±3 %. The thermoelectrical efficiency (z) was calculated from the relation $z = \alpha^2\sigma/\lambda$.

3. RESULTS AND DISCUSSION

As already mentioned in the Introduction, having in mind the significance of various semiconducting properties of the studied material in the sense of its potential applicability, we investigated the basic thermoelectrical and electrical properties of this compound and their temperature dependencies. A special emphasis was put on the influence of doping with Cd on the measured parameters. Fig. 1 shows the temperature dependence of the Seebeck coefficient (α) for an undoped Ag_4SSe sample, as well as for a series of samples containing various amounts of Cd as dopant. This parameter is characterized by negative values, which leads to a conclusion that Ag_4SSe is an *n*-type semiconductor (*i.e.* the predominant type of charge carriers are electrons). Two maxima in the temperature dependence of this quantity (or, more precisely, its absolute value) are observed – the first one appearing at 310 K, while the second one at 368 K. The first of these maxima is connected with the intrinsic conductivity, while the second appears due to the $\alpha\leftrightarrow\beta$ phase transition. In fact, the second maximum is a rather weak one, and becomes more prominent upon increasing Cd-content from 0.013 to 0.067 mass %.

It is known from the solid state theory of semiconducting materials that the Seebeck coefficient can be expressed by [9]:

$$\alpha = \pm\frac{k}{e}\left[\frac{(5/2-s)}{(3/2-s)}\frac{F_{3/2-s}(\eta)}{F_{1/2-s}(\eta)} - \eta\right] \qquad (1)$$

In the last equation, $F_i(\eta)$ are Fermi-Dirac integrals, defined with:

$$F_i(\eta) = \frac{1}{\Gamma(i+1)}\int_0^\infty \frac{t^i}{\exp(t-\eta)+1}\mathrm{d}t \qquad (2)$$

where $\Gamma(x)$ denotes Euler's Γ-function. η, on the other hand, is the reduced Fermi energy level, while s is the coefficient characterizing the scattering mechanism of charge carriers. On the basis of eqs. (1) and (2), using the experimental data for temperature dependence of α, the following conclusions were derived for the studied system. In the temperature interval from 80 to 400 K, the value of η is larger than 2 ($\eta > 2$). According to [10], this implies that the electron gas in this semiconducting compound is in degenerate state.

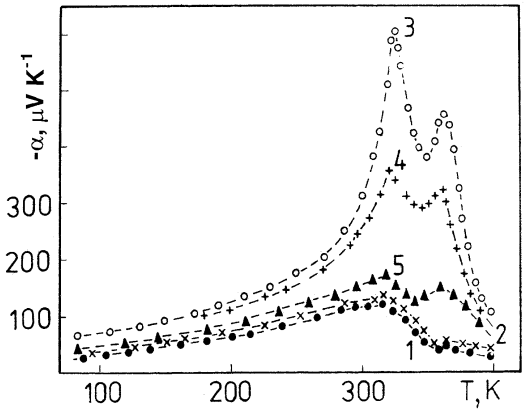

Fig. 1. Temperature dependences of α
1) undoped; 2) 0.013 mass % Cd; 3) 0.067 mass % Cd;
4) 0.150 mass % Cd; 5) 0.333 mass % Cd

The measured temperature dependence of electrical conductivity for both pure Ag_4SSe sample, as well as for several samples doped with various contents of Cd is shown on Fig. 2. The variation of σ with T exhibits the following regions of electroconductivity. First region (from 80 to ~280 K) corresponds to extrinsic conductivity mechanism, *i.e.* the conductivity changes in this region are basically governed by impurity energy levels (located in the forbidden band). The second region corresponds to the intrinsic mechanism of charge carrier generation (*i.e.* due to the interband electronic transitions, leading to formation of pairs of charge carriers – electrons and holes). This region, which is in fact the most important for the present study, starts from about 310 K and is actually limited from the higher temperature side at $T = T_{\alpha\leftrightarrow\beta}$ (at which the phase transition occurs; $T_{\alpha\leftrightarrow\beta}$ = 368 K). At temperatures higher than $T_{\alpha\leftrightarrow\beta}$, the conduction becomes metallic, as can be seen from Fig. 2. A narrow range, in which both extrinsic and intrinsic mechanisms introduce important contributions to the electroconductivity, exists around 300 K, where σ reaches its minimum value. In the region of predominance of the intrinsic conduction mechanism, the temperature dependence of the conductivity is given by:

$$\sigma = \sigma_0 \cdot \exp\left(-\frac{E_g}{2kT}\right) \qquad (3)$$

where σ_0 is constant, E_g is the band gap energy of the semiconductor, while all other symbols have their standard meanings. Taking the natural logarithm on both sides of the last equation and successively differentiating with respect to $1/T$, it follows that:

$$E_g = -2k\frac{\mathrm{d}\ln(\sigma(T))}{d\left(\frac{1}{T}\right)} \qquad (4)$$

On the basis of the previously outlined arguments, the thermal energy gap of this semiconducting material was determined from the constructed $\ln\sigma = f(1/T)$ dependence. This was done on the basis of least-squares linear interpolation of the experimental data in the region of intrinsic electroconductivity. The calculated value using equation (4) for the pure (undoped) Ag_4SSe sample is 0.23 ± 0.01 eV.

As can be seen from Fig. 2, the electroconductivity decreases upon Cd-doping at up to 0.067 mass %, and further increases upon dopant content increase up to 0.333 mass % Cd.

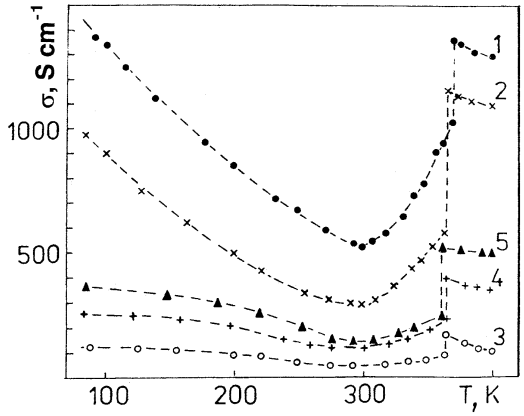

Fig. 2. Temperature dependence of σ
(the numbers correspond to those in Fig. 1)

The temperature dependence of the Hall constant for undoped and a series of doped Ag_4SSe samples is given in Fig. 3. A most prominent feature observed in Fig. 3 is the jump in the temperature dependence of the Hall constant (R) at T=368 K. The negative values of R in the whole temperature region explored further confirm the fact that Ag_4SSe is an *n*-type semiconductor. The variation of R (*i.e.* its absolute value) with Cd-content goes through minimum at 0.067 mass % Cd, *i.e.* the concentration of electrons increases up to this content and decreases above it. A most probable reason for this experimental observation is the substitution of Ag atoms in the crystal lattice of Ag_4SSe by Cd up to the above-mentioned Cd content, and separation of a new phase above it.

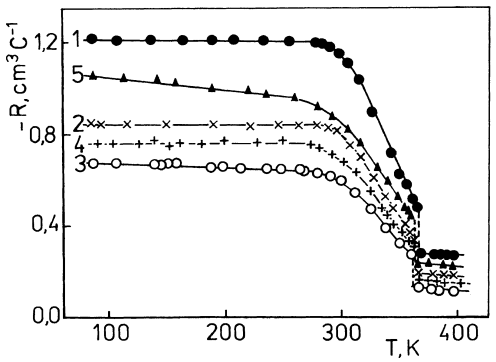

Fig. 3. Temperature dependence of R
(the numbers correspond to those in Fig. 1)

Regarding the changes of the thermoconductivity of studied samples upon temperature increase, as can be seen from Fig. 4, they are gener-

ally much more significant (rapid) in the range corresponding to intrinsic conductivity mechanism, *i.e.* in the temperature region above 310 K. In other words:

$$\left(\left|\frac{d\lambda(T)}{dT}\right|\right)_{intrinsic} > \left(\left|\frac{d\lambda(T)}{dT}\right|\right)_{extrinsic} \quad (5)$$

This is connected mainly with the increase of the electron component of λ. In other words, since the concentration of dopant Cd-atoms is rather lower than that of Ag-atoms, the lattice component is negligible [7]. The values of λ are minimal at dopant content of 0.067 mass % Cd.

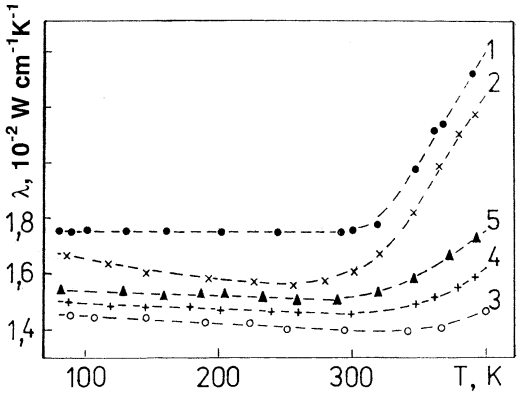

Fig. 4. Temperature dependence of λ (the numbers correspond to those in Fig. 1)

Temperature dependence of thermoelectrical efficiency (z) of the studied material is presented in Fig. 5, where only data for an undoped sample and for a sample containing 0.065 mass % of Cd are shown. Thermoelectrical efficiency is one of the basic parameters from a practical point of view. In the present case it was found that convenient doping leads to an increase of its values. In particular, a significant increase of z for Ag_4SSe in the range of 300–400 K at doping level of 0.067 mass % Cd is observed (Fig. 5). The dependence $z = f(T)$ basically follows that of the Seebeck coefficient because of its dominant contribution to this quantity.

We have further proceeded with characterization of thermodynamical parameters of the β-$Ag_4SSe \leftrightarrow$L (melting) transition on the basis of detailed and reliable measurements. One of the aims of this work was to get a definite reliable value of the temperature at which this transition occurs, as well as the corresponding entropy and specific heat (*i.e.* enthalpy).

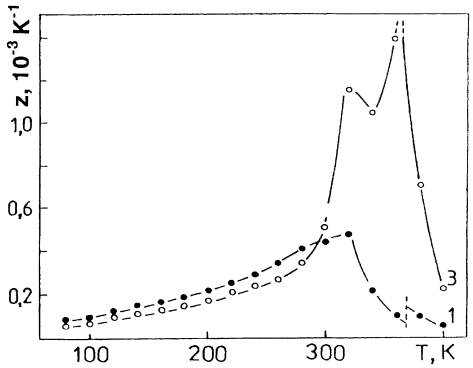

Fig. 5. Temperature dependence of z (1 – undoped; 3 – 0.067 mass % Cd)

Ag_2S was used as a standard substance (A) for determination of the enthalpy of melting for Ag_4SSe (B) because of their close parameters such as $T_m^{Ag_2S}$ = 838 °C [10] for A and 815 °C for B. The enthalpy of solid – liquid transition for A (*i.e.* for the process β-$Ag_2S \leftrightarrow$L) is 14.04 kJ mol^{-1} [11].

The enthalpy of β-$Ag_4SSe \leftrightarrow$L transition ΔH_B was calculated by the formula [12]:

$$\frac{\Delta H_A}{\Delta H_B} = X \frac{P_B}{P_A} \frac{M_A F_A}{M_B F_B} \quad (6)$$

where X is a correlation coefficient, X = 1 + 0.00058 ($T_A - T_B$) (index A corresponds to the substance with higher temperature of phase transition), P – weight, M – molecular mass, F – area of the endothermal DTA-peak.

Further, the entropy of melting was calculated by the relation:

$$\Delta S_B = \Delta H_B / T_m^{Ag_4SSe} \quad (7)$$

It was found that for Ag_4SSe, ΔH = 49.8 kJ mol^{-1} and ΔS = 45.8 J mol^{-1}K^{-1}.

4. CONCLUSIONS

(i) Ag_4SSe is a narrow-gap semiconductor. Its thermal energy gap is 0.24 eV, as determined from the temperature dependence of electrical conductivity in the intrinsic region. The Seebeck coeffi-

cient α and the Hall constant R have negative values for this material, confirming that it is an *n*-type semiconductor;

(ii) The Seebeck coefficient, electroconductivity and thermoconductivity at 300 K are 120 μV K^{-1}, 500 S cm^{-1}, and $1.75.10^{-2}$ W $cm^{-1}K^{-1}$, respectively. A jump in the change of σ, R and a minimum in the case of α (*i.e.* its absolute value) are observed at $T_{\alpha\leftrightarrow\beta}$ = 368 K, corresponding to the $\alpha\leftrightarrow\beta$ phase transition in this system;

(iii) Doping up to 0.067 mass % Cd causes an increase of the absolute values of α and a decrease of those of σ, R and λ. An improvement of the thermoelectrical efficiency at 0.067 mass % Cd-doped Ag_4SSe is established.

(iv) The temperature interval from 80 to 400 K, corresponds to the value of reduced Fermi energy level η larger than 2, which implies that the electron gas in this semiconducting compound is in degenerate state.

(v) The β-$Ag_4SSe\leftrightarrow$L phase transition in Ag_4SSe occurs at 815 °C. The specific heat and entropy of this process are 49.8 kJ mol^{-1} and 45.8 J $mol^{-1}K^{-1}$, respectively;

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Р е з и м е

ТЕРМОДИНАМИЧКИ, ТЕРМОЕЛЕКТРИЧНИ И ЕЛЕКТРИЧНИ СВОЈСТВА НА Ag_4SSe-ПОЛУСПРОВОДНИК СО МАЛА ЕНЕРГЕТСКА ШИРИНА НА ЗАБРАНЕТАТА ЗОНА

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Клучни зборови: полуспроводливи соединенија; термодинамика; електрични својства; термичка спроводливост

Кај соединението Ag_4SSe – полуспроводник од *n*-тип, се испитувани температурните зависности на основните термоелектрични и електрични својства како што се: Зибековиот коефициент, електроспроводливоста, Холовата константа и термоспроводливоста. Определена е и термоелектричната ефикасност на овој материјал. Врз основа на измерената температурна зависност на електричната спроводливост, определена е термичката ширина на забранетата зона кај овој систем, која изнесува 0,23 ± 0,01 eV. Испитувано е влијанието на допингот со Cd врз сите претходно наброени својства. Врз основа на големината на редуцираното Фермиево ниво во испитуваниот температурен интервал, изведени се заклучоци за состојбата на електронскиот гас кај овој полуспроводник. Исто така, фазната трансформација β-$Ag_4SSe \leftrightarrow L$ кај овој систем е карактеризирана од аспект на нејзините основни термодинамички параметри.