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THE OCCURRENCE OF DEFECTS IN HARD ALLOYS $Tb_xSn_{1-x}Se$ WITHIN THE γ-IRRADIATION

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Abstract: Herein, the results of studies on the influence of γ - irradiation on electrophysical properties of terbium-doped alloys $Tb_xSn_{1-x}Se$ have been presented. It is assumed that terbium atoms are located in vacant places between the nodes of the crystal lattice within the irradiation of samples, and there occurs self-compensation with the occurrence of the Frenkel defect. This leads to a decrease in the concentration of charge carriers, however, the activation energy does not change.

Keywords: chalcogenides, solid solutions, electrical conductivity, Hall coefficient, Hall mobility.

1. Introduction

The active development of electronic technology requires the creation and study of new semiconductor materials with improved properties compared to traditional semiconductors. Such materials include rare-earth semiconductors, whose properties are associated with the uniqueness of the electronic structure. A feature of the electronic structure of rare-earth elements is the filling of the 4f-shell with an unfilled d-shell [1,2].

In the compound *SnSe*, *Sn* atoms behave as divalent. REE atoms have a stable electronic configuration $4f$ - orbitals ($4f^0, 4f^7, 4f^{14}$) and also, the $4f$ - orbital is not directly involved in chemical bonds. Participation in a chemical bond is carried out as a result of a $f \to d$ transition in the form of $4f^n \to 4f^{n-1}5d^1$ and electrons to determine their valence [1]. In an isolated state, *Tb* atoms have two types of the electronic spectrum: $4f^8 5d^1 6s^2$ and $4f^9 5d^0 6s^2$. A variable valence (3 or 4) is observed within the transition of *Tb* atom to a condensed state [3].

The introduction of REM into tin monoselenide leads to the formation of several physical features associated with the nature of defect formation and with the interaction of defects. Therefore, the study of the interaction between *SnSe* and *TbSe* chalcogenides, as well as a comprehensive study of charge transfer processes in the formed solid solutions, is of scientific and practical interest for the creation of some electric energy converters, various kinds of thermistors that are resistant to radiation, pressure, and humidity. The influence of irradiation on solid solutions with the participation of REE and, in particular, *Tb* doped tin selenide, has been little studied. Single crystals of $Tb_xSn_{1-x}Se$ solid solutions obtained by the directional crystallization method and the influence of γ - radiation on their conductivity have been studied. The paper presents the results of the temperature dependence of the electrical conductivity, the Hall coefficient and the Hall mobility of charge carriers, as well as the dependence of these parameters on the terbium concentration in the $Tb_xSn_{1-x}Se$ solid solution.

$Tb_xSn_{1-x}Se$ hard alloys were synthesized by direct alloying from individual components. Samples were subjected to prolonged annealing. The obtained alloys were investigated in terms of phase equilibrium using physicochemical analysis. Single crystals $Tb_{0.01}Sn_{0.99}Se$ and $Tb_{0.05}Sn_{0.95}Se$ were obtained by directional zone melting. Some electrophysical properties of the

$Tb_xSn_{1-x}Se$ alloy system, before and after irradiation, were investigated in the wide temperature range (250-520 K), and the influence of γ-irradiation on these properties was analyzed. The samples were irradiated with γ-rays with an energy of 1.25 MeV $\left({}^{60}Co\right)$, doses of D = 65 Mrad. Then, the role of γ- irradiation in the mechanism of scattering and the occurrence of defects in $Tb_xSn_{1-x}Se$ hard alloys was revealed.

2. Experimental technique

The alloys of the *SnSe-TbSe* system were synthesized using the initial components of the tin of the "B4-000" brand, selenium of "OC417-4" brand and chemically pure terbium (99.98%). The synthesis was carried out in evacuated quartz ampoules at a pressure of 0.1333 Pa by the direct melt of components in two stages. Samples of the $(SnSe)_{1-x}$-$(TbSe)_x$ solid solution with the composition of x_1=0.01 and x_2=0.05 were synthesized. At the initial stage, the ampoule together with the substance was heated up to the melting temperature of selenium at a speed of 4-5 degrees/minute and kept at this temperature for 3-4 hours, then the temperature was gradually increased depending on the composition up to 950-1000^{0}C, and kept for 8-9 hours.

The samples synthesized for complex physicochemical analysis and electrophysical studies were annealed for 100-140 hours, depending on the composition: the annealing period increased with increasing terbium content. Homogenizing annealing of the obtained single-phase samples was carried out in spectrally pure argon at 800 K. Single crystals were grown by the Bridgman method.

The structure, phase and elemental composition of the obtained ingots and the surface state along the plane of the natural layers of the studied samples were determined by conducting complex X-ray diffraction, radiographic, thermographic and microscopic analyses.

To determine the thermal effects of the obtained samples and phase transitions, was performed on a Perkin Elmer Simultaneous Thermal Analyzer instrument, STA 6000 (USA). Nitrogen with a feed rate of 20 ml/s was used as the working gas; the sample is heated until melting at a heating rate of 5°C/min.

X-ray diffraction analysis was carried out on a Miniflex X-ray diffractometer ("Rigaku Corporation"), at a mode of 30kV, 10 mA, CuK_α radiation (λ = 1.5406Å). Diffraction reflections were observed at a step of 0.01° and a displacement angle of 2θ in the range of 0–80°. To study the morphology and microstructure of the surface of the sample, a Japanese-made JEOL JSM6610-LV scanner electron microscope was used.

After annealing, $2\times4\times18$ mm^3 samples were cut from crystal ingots in an electro spark installation. The electrical conductivity and the Hall coefficient were measured at a constant current and a constant magnetic field of an electromagnet [4]. The thermal electromotive force was measured by the stationary method according to the method described in [5]. The measurements were carried out in the temperature range of 80÷600 K. The experimental error did not exceed 4.2%

However, with partial replacement of atoms *Sn* by atoms *Tb*, it partially enhances hybridization, being introduced into the *p*-orbital of *Sn* atom (the hybridization property is characteristic of *sp*-elements). Due to the covalent component, the ion-covalent bond is enhanced, and the electrons pass to local levels. This causes both a change in the type of conductivity (p → n) and a decrease in the concentration of charge carriers. As a result of our studies, upon the transition from a compound *SnSe* with the participation of *Tb* in alloys $Tb_xSn_{1-x}Se$ (x = 0.01; 0.05), there is observed a change in the type of conductivity, a decrease in the concentration of charge carriers and the bandgap, that are shown in Table 1.

Table. Kinetic parameters of $Sn_{1-x}Tb_xSe$ alloys at the temperature of T = 300K.

Content	*R*, Cm^3/Kl	*P(n)*, $10^{16}\,cm^{-3}$	σ $Om^{-1}cm^{-1}$	μ $cm^2/V\cdot s$	α $\mu V/K$	χ ,10^{-3} $W/cm\cdot s$
SnSe	+8.6	72	*18*	*156*	*+420*	20
$Tb_{0.01}SeSn_{0.99}$	- 75	8.3	0.0063	6.5	-242	17.5
$Tb_{0.05}SeSn_{0.95}$	- 41.6	15	0.047	2.96	-210	14.5

Figure 1. shows the temperature dependences of the electrical conductivity of the initial and irradiated samples; the temperature dependences of the electrical conductivity before and after irradiation for both crystals $\sigma(T)$ have the same course (although in the irradiated sample the value of σ decreases in the low-temperature region at $T < 400K$) and the activation energy of charge carriers for samples No. 1 and 2 at the impurity level of $\Delta E_1 \approx 0.02\,\text{eV}$ (after irradiation became $\Delta E_1^{/} \approx 0.03\,\text{eV}$), i.e. the order of the activation energy of charge carriers from the impurity level is almost the same before and after irradiation for both samples. In both samples, at higher temperatures $T \geq 400K$, the electrical conductivity noticeably increases with increasing T, and the activation energy of charge carriers is the same and equal to $\Delta E = 0.45\,\text{eV}$.

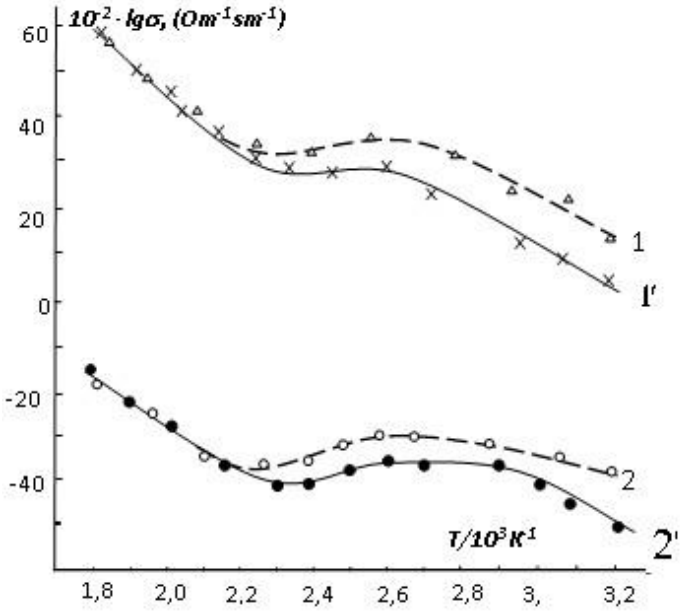

Fig. 1. Temperature dependence of electrica conductivity $Tb_xSn_{1-x}Se$. 1,1′ - x=0,01 after irradiation (1′), before irradiation (1), 2,2′ - x=0,05 after irradiation (2′), before irradiation (2)

Figure 2 shows the temperature dependences of the Hall coefficient. It can be seen from the figure that after irradiation the Hall coefficient noticeably increased in both samples. This is especially observed in samples No. 1 in the temperature range of 77–200K. At 80K in samples No. 1, the concentration of charge carriers was $n \approx 8.3 \cdot 10^{16}$ before irradiation, and it became $n \approx 6.9 \cdot 10^{16}\,\text{cm}^{-3}$ after irradiation, i.e. the concentration decreased by 17% and this is apparently due to the fact that, under irradiation with γ - quanta, terbium impurities are located between the nodes of the crystal lattice and self-compensation occurs with the occurrence of a Frenkel defect, as a result of which the impurity concentration of carriers decreases.

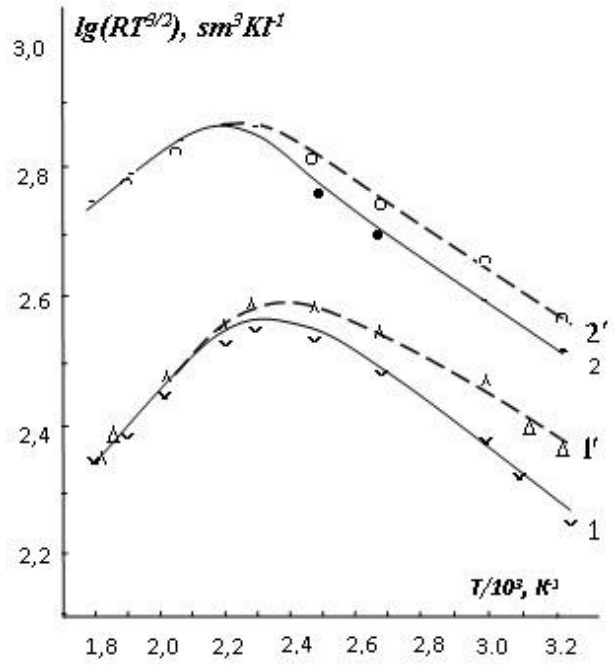

Fig. 2. Temperature dependences of the Hall coefficient $Tb_xSn_{1-x}Se$. 1,1′ - x=0,01 after irradiation (1′), before irradiation (1), 2,2′ - x=0,05. after irradiation (2′), before irradiation (2)

Figure 3 shows the temperature dependences of the Hall mobility of charge carriers. The analysis of temperature dependences of Hall mobility of charge carriers shows that, in the $Tb_{0,01}Sn_{0,99}$ sample, the mobility of charge carriers before irradiation increases with the temperature increase according to the law $\mu \propto T^{1.5}$, and after irradiation - $\mu \propto T^{2.0}$, in the studied temperature range. This means that the main scattering mechanism of charge carriers is scattering by charged impurity centers; scattering is enhanced after irradiation. In the $Tb_{0,05}Sn_{0,95}Se$ sample, where the terbium content increases, the dependences $\mu(T)$ before and after irradiation are the same and change according to the $\mu \propto T^{0.8}$ law, which corresponds to scattering by weakly charged impurity centers, and their influence weakens with increasing temperature and neutral impurities begin to play a major role with the strengthening of Frenkel defects.

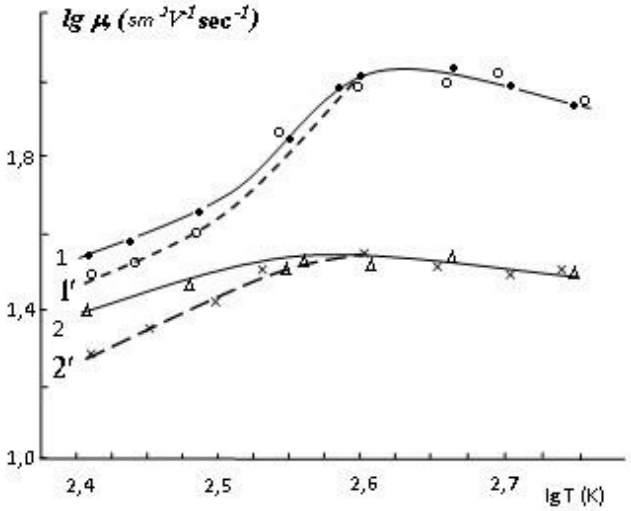

Fig. 3. Temperature dependences of the Hall mobility $Tb_xSn_{1-x}Se$. 1,1′ - x=0,01 after irradiation (1′), before irradiation (1), 2,2′ - x=0,05. after irradiation (2′), before irradiation (2)

From the obtained experimental data it follows that the electron concentration decreases under the influence of γ-irradiation, but with an increase in the terbium content in the composition, the change in the electron concentration weakens due to the strengthening of Frenkel defects. At low temperatures (77–200 K), the scattering of charge carriers mainly occurs at weakly ionized centers [6], and with an increase in the temperature up to 300 K, neutral impurities begin to play the dominant role.

3. Conclusion

When crystals $Tb_xSn_{1-x}Se$ (x=0.01; 0.05) are irradiated with γ-rays with a dose of 6.5 Mrad, two processes occur simultaneously. On the one hand, the concentration of Frenkel point defects increases in the crystal, and on the other hand, the $f \to d$ transition under the influence of γ radiation is simplified. In other words, the probability of 3 or 4 valences increases and the concentration of charge carriers in the alloy decreases, that is, localization by sp^3 increases. The statistical weight of the configuration $4f^7$ as a result of the $f \to d$ transition increases.

Under the influence of γ-radiation, which has n-type conductivity in a crystal, acceptor-type radiation defects arise that compensate for the centers of donor impurities. With increasing temperature, the Hall coefficient in the crystal $Tb_xSn_{1-x}Se$ (x=0.01; 0.05) decreases sharply, and the concentration of charge carriers increases sharply. This means that at high temperatures (high energies) the role of γ-radiation eliminates.

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ПОЯВЛЕНИЕ ДЕФЕКТОВ В ТВЕРДЫХ СПЛАВАХ $Tb_xSn_{1-x}Se$ ПРИ γ - ОБЛУЧЕНИИ

Т.А. Джафаров

Резюме: В работе представлены результаты исследований влияние γ-облучения на электрофизические свойства сплавов легированных тербием в $Tb_xSn_{1-x}Se$. Предполагается, что при облучении образцов атомы тербия располагаются в вакантных местах между узлами кристаллической решетки и локализуясь происходит самокомпенсация с появлением дефекта

Френкелю. Это приводит к уменьшению концентрации носителей зарядов, однако энергия активации не меняется.

Ключевые слова: халькогениды, твердые растворы, электропроводность, коэффицент Холла, холловской подвижности.

γ-ŞÜALANMA NƏTİCƏSİNDƏ $Tb_xSn_{1-x}Se$ BƏRK MƏHLULLARINDA DEFEKTLƏRİN ƏMƏLƏGLMƏSİ

T.A. Cəfərov

Xülasə: İşdə terbiumla aşqarlanmış $Tb_xSn_{1-x}Se$ sistem ərintilərinin elektrofiziki xassələrinə γ -şüalarının təsiri öyrənilmişdir. Şüalanma zamanı terbium atomlarının kristalda düyünlərarası vakant yerlərini tutaraq lokallaşdığı, Frenkel defektəmələgəlmə ilə öz-özünə kompensasiyanın baş verdiyi fərz olunur. Bu yükdaşıyıcıların konsentrasıyasının azalmasına səbəb olsa da, aktivləşmə enerjisi dəyişmir.

Aşar sözlər: Halkogenidlər, bərk məhlul, elektrik keçiriciliyi, Holl əmsalı, yürüklük, istilik keçiriciliyi, istilik müqaviməti.