ELECTROPHYSICAL PROPERTIES OF $TlIn_{1-x}Sm_xSe_2$ $(0 \le x \le 0,08)$ CRYSTALS

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In the present paper we outline the research results of the temperature dependence of the specific electroconductivity, the Hall coefficient and thermo e.m.f. in the temperatures ranges 300÷1100 K of $TlIn_{1-x}Sm_xSe_2$ $(0 \le x \le 0,08)$ alloys. The width of the forbidden band of indicated alloys system is determined. It was revealed, that the width of the forbidden band reduces according to the additivity law at the partial substitution of indium atoms by samarium ones in $TlSmSe_2$. By investigating the influence of the directed deformation on electron properties of $TlIn_{1-x}Sm_xSe_2$ alloys we found their dependence on temperature and deformation. These crystals have high coefficient of the strain sensitivity.

The information about the existence of $TlIn_{1-x}Sm_xSe_2$ type alloys was given in papers [1-6].

In present paper we outline research results of electrophysical properties of $TlIn_{1-x}Sm_xSe_2$ crystals. The alloys synthesis was carried out according to the methods described in [1]. As initial substances Tl-99,99 mass%; In-99,99 mass%; Se- specially pure, Sm, containing as impurities (mass%): sizes-0,05, Cu-0,01, Fe-0,01 were used. Monocrystals of $TlIn_{1-x}Sm_xSe_2$ alloys system with content up to 5mole % of $TlSmSe_2$ were obtained by the method of the zone growth from before synthesized samples. Monocrystal samples with average sizes $2 \times 4 \times 6$ mm^3 were cut out from the average part of ingots. Alloys, containing (6÷8) mole % of $TlSmSe_2$ were semicrystal. Curves of the concentration dependence of the microhardness (h), electroconductivity (σ) and thermo e.m.f. (α) were plotted to reveal boundaries of the solid solutions existence.

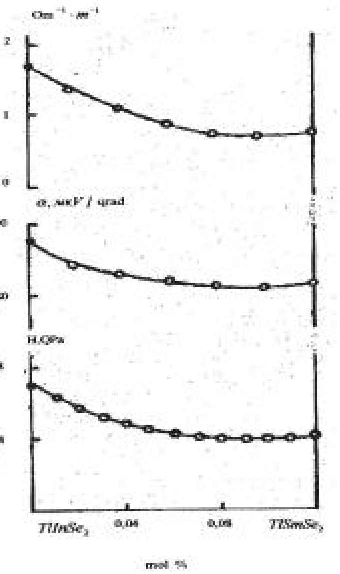

Fig. 1. Concentration dependences of microhardness (H), electroconductivity (σ) and thermo-e.m.f. (α) of system alloys $TlInSe_2$-$TlSmSe_2$ alloys system.

The microhardness was measured on the PMT-3 device. Loads of ~10H were used. Numerical values of the crystal microhardness for each alloy were obtained by the statistical treatment of 10 measurements results. The measurements results of the system $TlIn_{1-x}Sm_xSe_2$ are presented on fig 1. At the partial substitution of indium atoms by samarium ones H reduces and beginning from 8 % of $TlSmSe_2$ it remains constant. The H reduction corresponds to the homogeneity region. Such supposition is in agreement with measurements results of α and σ, in the range 0÷8 mole % of $TlSmSe_2$ thermoelectric parameters change, α and σ do not practically change across limits of the indicated concentration region. In whole, concentration dependence of H, σ and α are well correlated and allow to reveal boundaries of the solid solution homogeneity of the indicated system.

Electric properties of crystals were measured by the compensational method in the constant magnetic field at the constant current in the temperature range 300÷1100 K on four samples with identical concentration of electrons and $TlSmSe_2$ content, whose electric heterogeneity does not exceed 5 %.

Temperature dependences of the electroconductivity (σ), Hall coefficient (R) and thermo e.m.f.

(α) were investigated. The errors of measurement of α, σ and r were 4,8 and 5 %, respectively. The forbidden band width of solid solutions of the indicated system was determined from high-temperature dependences of $lg\,\sigma = f(10^3/T)$ and $lgRT^{3/2} = f(10^3/T)$. As it follows from fig.2a, the alloys electroconductivity of the $TlInSe_2$- $TlSmSe_2$ system at low temperature reduces mainly with the temperature growth, but, further, it grows with the own carriers appearance. The thermal dependence of the Hall coefficient for the indicated system alloys corresponds to the thermal dependence of the electroconductivity (fig. 2b), i.e. the free carriers concentration remains constant at low temperatures, but the Hall mobility is limited mainly by the scattering on longitudinal acoustic oscillations. Therefore, the mobility as well as the electroconductivity of these alloys fall with the temperature growth (fig. 2a).

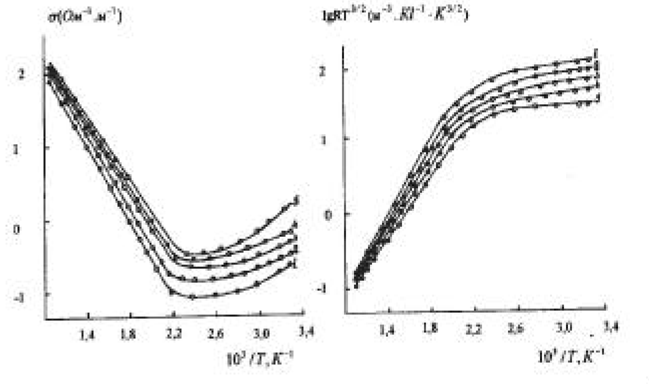

Fig.2. Temperature dependences of electroconductivity (a) and Hall coefficient (b) of $TlIn_{1-x}Sm_xSe_2$ alloys system, where *1-x=0; 2-x=0,02; 3-x=0; 4-x=0,06; 5-x=0,08*.

The dependence of thermo-e.m.f. on the temperature for alloys $TlInSe_2$-$TlSmSe_2$ is presented on fig. 3. In the impurity region the thermo-e.m.f. increases with the temperature growth, reaching maximum in the biased region and it reduces with the own conductivity receipt, what is typical for all investigated phases.

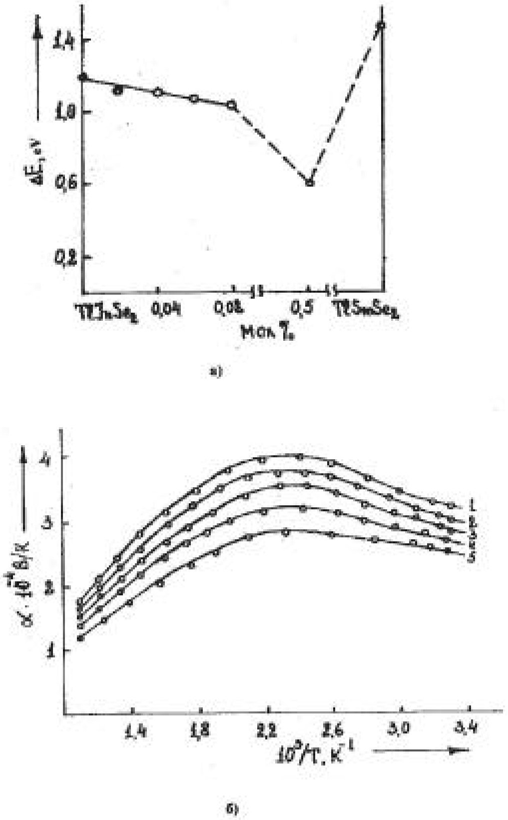

Fig.3. Concentration dependence of the forbidden band width (a) and the temperature dependence of thermo-e.m.f. (b) of $TlIn_{1-x}Sm_xSe_2$ alloys system

The concentration dependence of the forbidden band width, determined by high-temperature slope of curves lg σ~10^3/T and lg $RT^{3/2}$~10^3/T of $TlIn_{1-x}Sm_xSe_2$ alloys is presented on fig. 4. These data show, that the width of the forbidden band reduces according to the additivity law at the partial substitution of indium atoms by samarium ones in the $TlInSe_2$ lattice. Obviously, it is connected with the fact, that in $TlInSe_2$ the valent band is mainly formed by fissionable 4r-levels of selenium ions and partial by 5r5s-levels of indium ions, but the conductivity band is formed by 5r5s levels of indium ions and 6r-levels of tallium ions. D-states of samarium atoms, which are energetically placed upper, are hit in the conductivity band at the partial substitution of indium atoms by samarium ones. In the $TlInSe_2$-$TlSmSe_2$ system at the samarium concentration growth their valent electrons transfer into the itinerant state, which causes the strong electron interaction and the lattice "distension". In this regard in the $TlInSe_2$-$TlSmSe_2$ system at the transition from the $TlInSe_2$ to the solid solutions on its base the width of the forbidden band reduces.

As it is well known [7] $TlInSe_2$ is crystallized by the tetragonal syngony. The growth of the samarium concentration in $TlInSe_2$ does not lead to the compound structure breakdown. It means, that in the case given the samarium atoms reveal the trivalence, approved by semiconductive properties. However, it is possible to form the trivalence state with spare, mobile electrons, weakly connected with f-orbit and providing in solid solutions the growth of velocity of electrons, weakly connected with f-orbit, what, in its turn, leads to the change of the forbidden band width.

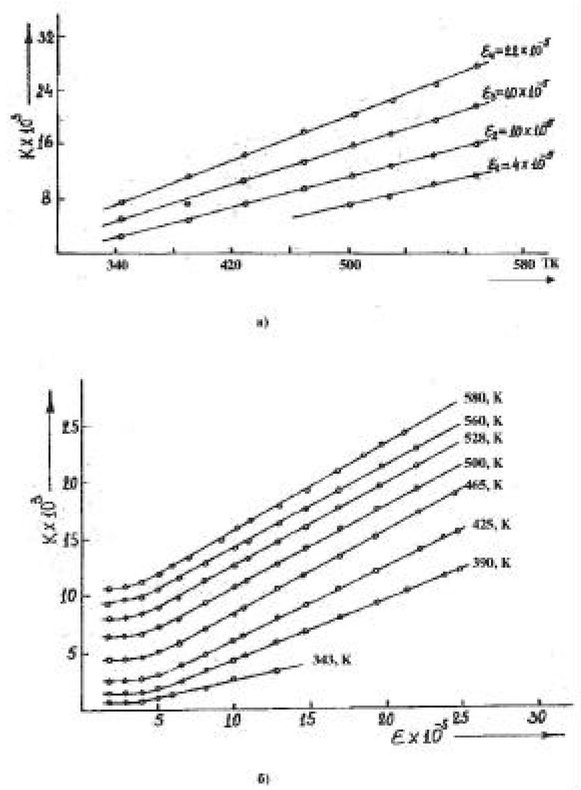

Fig. 4. The dependence of strain sensitivity on the temperature at various deformations (a), and the dependence of the strain sensitivity on the deformation at various temperatures (b) of alloys $TlIn_{1-x}Sm_xSe_2$ where *1-õ=0*; *2-õ=0,03*.

The influence of the directed deformation on the electron process in $TlIn_{1-x}Sm_xSe_2$ crystals was investigated. Ohmic contacts were formed by the indium melting in the gas flow with the following soldering of copper wires (*d*=0.01 mm) on obtained needle crystal billets with mirror faces without additional treatment.

Plates from 45 steel with the thickness of 0,5 mm and the length 50 mm were tared beams for pasted sensors. The substrate surface according to the treatment range corresponded to the 7 class. Before the sublayer application substrates were treated by the ethyl spirit. On the cleaned substrates the sublayer of the epoxy-cresol varnish (EP-96), presented as the solution of the epoxide resin (E-40 is the modification of same acids with the addition of butanomodified pesol (PB) and the resin K-421-02) was applied.

The sublayer thickness was 10 mk. The uniform (with respect to the thickness) covering was provided in the process of the sublayer application.

After an hour heating (keeping) at the room temperature the substrate was carried in the drying cabinet for the high-temperature polymerization.

The slow temperature increase up to 480 K and the heating during 1 hour at this temperature provide the full polymerization and exclude the air bubbles appearance. The second layer of the varnish, a bit exceeding the strain resistor sizes, was applied on the prepared substrate.

$TlIn_{1-x}Sm_xSe_2$ crystals with soldered tapings were placed on the varnish layer and slightly pressed, the crystal surface was fully covered by the varnish. The crystal was simultaneously set in the necessary position in the substrate plane. The sensor drying was being carried out at 318÷323 K during an hour with the following annealing, at 490 K during 2 hours. The indicated drying mode showed to be the most optimal one and the devices showed the maximal sensitivity.

The strain sensitivity coefficient, being the main characteristic of the strain resistor, was determined by the formula $K = \frac{\Delta R}{R_o \varepsilon}$ where $\varepsilon = \frac{\Delta l}{l}$ is the relative change of the samples length or the relative deformation, $\Delta R/R_o$ is a relative change of the resistance, $\Delta R = R - R_o$ is the resistance change, where R_o is the sample resistance before deformation, and R is the sample resistance after deformation, l is the samples length, Δl is its change.

The temperature dependence of $TlIn_{1-x}Sm_xSe_2$ crystals strain sensitivity (K) was carried out in the temperature range 300-560 K.

As a particular case, K dependences on the temperature at the constant deformation are presented on fig. 5, but K dependences on the deformation at various temperatures are presented on fig. 6 for $TlInSe_2$.

From conducted research it follows, that for $TlInSe_2$ the dependence of the strain sensitivity coefficient on the deformation is linear at various temperatures, beginning from room up to 580 K.

CONCLUSIONS

By our research of electrophysical properties of $TlIn_{1-x}Sm_xSe_2$ alloys system depending the content and temperature it was established that the width of the forbidden band reduces in the solubility region $(0 \le x \le 0,08)$ at the partial substitution of indium atoms by samarium ones in $TlInSe_2$. It was found, that $TlIn_{1-x}Sm_xSe_2$ $(0 \le x \le 0,03)$ crystals have high coefficient of the strain sensitivity.

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