STATE DIAGRAM OF $TlInS_2 - TlCrS_2$, $TlGaSe_2 - TlCrSe_2$ SYSTEM AND ELECTRIC PROPERTIES OF LAYERED COMPOUNDS $TlCrS_2$, $TlCrSe_2$

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State diagram of $TlInS_2 - TlCrS_2$ and $TlGaSe_2 - TlCrSe_2$ systems has been investigated. It is established that the limited solid solutions form on the base of initial compounds. It is supposed that the existence of polar (dipole) and magnetic (spin) orderings is possible in the forming solid solutions. The electric properties of $TlCrS_2$ and $TlCrSe_2$, which reveal that these compounds are semiconductors of *p*-type, are investigated in temperature interval 80-400K.

The search of semiconductor ferroelectromagneto-active layered crystals is the actual task of solid-state physics, i.e. physicotechnical parameters of such crystals are varied in wide range in the result of the fact that the dependence of physical properties of traditionally regulated factors such as temperature, electric and magnetic fields on main crystallographic directions is added to them [1,2].

The layered compounds $TlInS_2$, $TlGaSe_2$ at high temperatures have semiconductor properties [3,4], and at low temperatures they have ferroelectric ones [5-8].

In work [9] the compounds $TlCrS_2$, $TlCrSe_2$ had been synthesized firstly and X-ray-, neuron-graphic and magnetic investigations had been carried out. The authors conclude that given compounds crystallize in hexagonal structure with big enough relation *c/a (~6)* and are ferromagnetics. However, electric properties of layered ferromagnetics $TlCrS_2$, $TlCrSe_2$ haven't been investigated; correspondingly, it isn't clear what type of conduction they have.

Taking into consideration above mentioned, $TlCrS_2$, $TlCrSe_2$ are investigated by us from chemical elements, suspended in stoichiometric relation. Previously the chromium is rendered in powdered state with the help of ball mill. The compounds are put into quartz ampoules, which are evacuated up to residual pressure $\sim 10^{-3}$ Pa. The synthesis is carried out in the electric furnace at temperature ~1150K during 120 hours, further the reaction product is thoroughly crushed and synthesis repeats. Further the given compositions are rendered in powdered state, pressed and treated by homogenizing in evacuated quartz ampoules at temperature ~600K during 480 hours.

X-ray analysis of $TlCrS_2$, $TlCrSe_2$ is carried out at room temperature (~300K) on diffractometer DRON-3M in CuK_α-radiation. The angular resolution of the shooting is $\sim 0{,}1^0$. The diffraction patterns are recorded constantly and diffraction angles are defined by measurement method on intensity maximum. The calculation error of diffraction patterns show that synthesized compositions indicate on the base of parameters of hexagonal lattice: a=3,538Å; c=21,962Å; c/a~6,207; z=3;sp.gr. R3m; ρ_x=6,705г/см^3 for $TlCrS_2$ and a=3,6999Å; c=22,6901Å; $c/a \approx 6{,}133$; z=3; sp.gr. R3m; ρ_x=6,209 г/см^3 for $TlCrSe_2$.

Note, X-ray investigations, carried out by us well agreed with [9].

The electric properties of compounds $TlCrS_2$ and $TlCrSe_2$ are investigated in temperature interval 80-400K. The electron conduction (σ) and thermo-e.m.f. coefficient (α) of $TlCrS_2$, $TlCrSe_2$ are measured by four-probe compensation method.

The temperature dependencies of electric conduction and thermo-e.m.f. coefficient of $TlCrS_2$ compound are presented on the fig.1. As it is seen from the figure, the temperature dependence of electric conduction has the semiconductor motion and behavior of thermo-e.m.f. coefficient on temperature evidences about charge transition by carriers of *p*-type. Moreover, the anomaly on *a(T)* $TlCrS_2$ dependence (~340K) which is connected with umklapp process of *p*-type carriers in conduction band of $TlCrS_2$ semiconductor is observed.

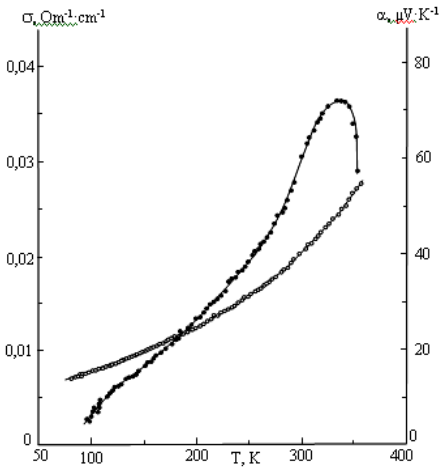

Fig.1. The temperature dependence of electrical conduction (●) and thermo-e.m.f. coefficient (○) of $TlCrS_2$.

The temperature dependencies of electric conduction and thermo-e.m.f. coefficient of $TlCrSe_2$ compound are given on the fig.2. As it seen from the figure, the temperature dependence of electric conduction of $TlCrSe_2$ has the semiconductor character in whole. However, beginning from temperature $T \approx 125$K the fracture with temperature duration ~110K appears on dependence *σ(T)* $TlCrSe_2$. Probably, the fracture on dependence *σ(T)* $TlCrSe_2$ is connected with scattering of charge p-carriers on spin fluctuation heterogeneities [10], appearing at transition of spin system of layered ferromagnetic $TlCrSe_2$ from three-D magnetic ordering into paramagnetic state. The behavior of thermo-e.m.f. coefficient on $TlCrSe_2$ temperature evidences about charge transition by *p*-type carriers, i.e. the positive numerical *a* values increase in the investigated temperature interval.

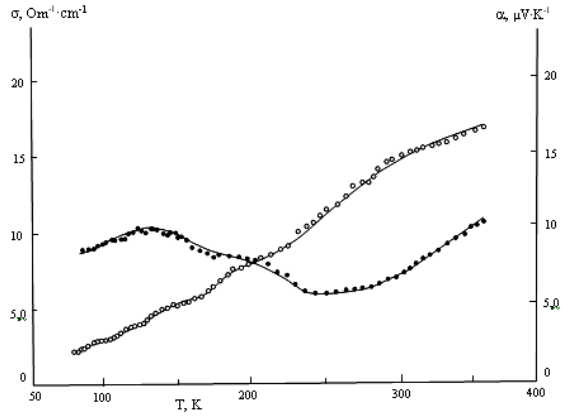

Fig.2. The temperature dependence of electrical conduction (●) and thermo-e.m.f. coefficient (○) of $TlCrSe_2$.

18 samples are prepared for study of interaction of $TlInS_2$ with $TlCrS_2$. The initial compounds $TlInS_2$ and $TlCrS_2$ are synthesized from chemical elements, suspended in stoichiometric relation in quartz ampoules, evacuated up to residual pressure ~10^{-3} Pa. The mode of alloy synthesis is chosen on the base of melting point of initial compounds: 1050K for $TlInS_2$, 1455K for $TlCrS_2$. Each alloy is heated higher melting point of initial compounds and endured at this temperature during 7-9 hours, further the temperature in furnace is decreased up to room one with velocity 100K in hour. The synthesized alloys for homogenization are annealed during 480 hours at ~700K in the case of alloys, containing $TlInS_2$ and during 570 hours at ~970K in the case of alloys, containing $TlCrS_2$.

The annealed samples in evacuated quartz ampoules with the end, concave inside, are investigated by the method of differential-thermal analysis (DTA). DTA is carried out on installation HTP-64, allowing fixing the phase transformation temperature with delicacy ±10K. The heating rate is 2-4K/min. The temperature of the ampoules with annealed compositions is controlled by thermocouple *Pt-Pt/Rh*. Previously, the thermocouple is graduated on standard substances in interval 430-1560K.

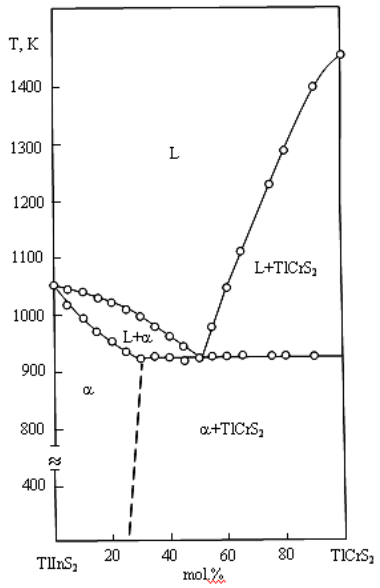

Fig.3. State diagram of $TlInS_2$ –$TlCrS_2$ system.

State diagram of $TlInS_2$ - $TlCrS_2$ system, constructed on the results of differential-thermal analysis is presented on the figure 3. This system is quazi-binary one of eutectic type with wide regions of solid solutions on the base of $TlInS_2$, achieving at 300K up to 25 мol.% $TlCrS_2$. The eutectic forms at component relation 1:1. The eutectic melts at 925K and has the composition $(TlInS_2)_{0,5}$ $(TlCrS_2)_{0,5}$.

Thus the existence of polar (dipole) and magnetic (spin) orderings is possible in $TlInS_2$ - $TlCrS_2$ system from the side of $TlInS_2$ (up to 25 мol.% - $TlCrS_2$). Moreover, homogeneous phases will have the semiconductor motion of conduction, i.e. initial compounds $TlInS_2$ and $TlCrS_2$ are semiconductors.

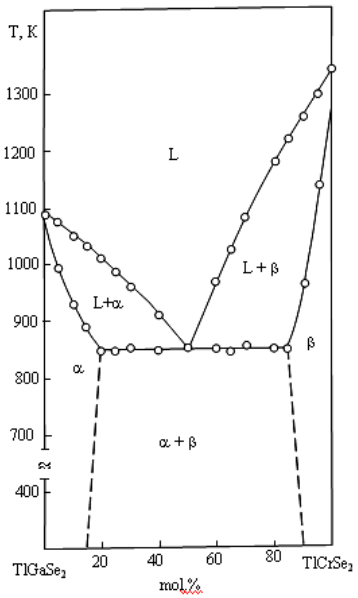

Fig.4. State diagram of $TlGaSe_2$-$TlCrSe_2$ system.

17 samples are prepared of study of interaction of $TlGaSe_2$ c $TlCrSe_2$. The initial compounds $TlGaSe_2$ and $TlCrSe_2$ are synthesized from chemical elements, suspended in stoichiometric relation in quartz ampoules, evacuated up to residual pressure ~10^{-3} Pa. The mode of alloy synthesis is chosen on the base of temperature of their melting points: 1085K for $TlGaSe_2$ and 1340K for $TlCrSe_2$. Each alloy is heated higher melting point of initial compounds and endured at this temperature during 6-8 hours, further the temperature in furnace is decreased up to room one with velocity 100K in hour. The synthesized alloys for homogenization are annealed during 480 hours at ~700K in the case of alloys, containing $TlInS_2$ and during 570 hours in the case of alloys, containing *$TlCrS_2$*. The synthesized alloys for homogenization are annealed during 410 hours at ~720K in the case of alloys, containing $TlGaSe_2$ and during 480 hours at ~890K in the case of alloys, containing $TlCrS_2$. The annealed samples in evacuated quartz ampoules with the end, concave inside, are investigated by the method of differential-thermal analysis (DTA). DTA is carried out on installation HTP-64, allowing fixing the phase transformation temperature with delicacy ±10K. The heating rate is 2-4K/min. The temperature is controlled by thermocouple *Pt-Pt/Rh*, on the head of which the ampoules with annealed compositions are get on in turn.

State diagram of $TlGaSe_2$ - $TlCrS_2$ system, constructed on the results of differential-thermal analysis is presented on the figure 4. This system is quazi-binary one of eutectic type

with limited regions of solid solutions on the base of $TlGaSe_2$, achieving up to 15 мol.% $TlCrSe_2$, on base of $TlCrSe_2$, achieving up to 10 mol% $TlGaSe_2$ at room temperature (~300K). The eutectic forms at component relation 1:1. The eutectic melts at 850K and has the composition $(TlGaS_2)_{0,5}$ $(TlCrS_2)_{0,5}$.

Thus the existence of polar (dipole) and magnetic (spin) orderings is possible in $TlGaS_2$ - $TlCrS_2$ system from both $TlGaSe_2$ (up to 15mol% $TlCrSe_2$) and $TlCrSe_2$ (up to 10 mol% $TlGaSe_2$), moreover, homogeneous phases will have the semiconductor motion of conduction, i.e. initial compounds $TlGaSe_2$ and $TlCrSe_2$ are semiconductors.

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$TlInS_2 - TlCrS_2$, $TlGaSe_2 - TlCrSe_2$ SİSTEMLƏRİNİN HAL DİAQRAMLARI VƏ LAYLI $TlCrS_2$, $TlCrSe_2$ BİRLƏŞMƏLƏRİNİN ELEKTRİK XASSƏLƏRİ

$TlInS_2 - TlCrS_2$ və $TlGaSe_2 - TlCrSe_2$ sistemlərinin hal diaqrammaları öyrənilmişdir. Müəyyən edilmişdir ki, başlanğıc birləşmələrin əsasında məhdud bərk məhlullar əmələ gəlir. Ehtimal olunur ki, əmələ gələn bərk məhlullarda dipol və spin nizamlanması mövcud ola bilər. $TlCrS_2$, $TlCrSe_2$ birləşmələrinin 80÷400K intervalında elektrik xassələri tədqiq olunmuşdur və aşkar olunmuşdur ki, göstərilən birləşmələr *p*-tipli yarımkeçirici xarakterə malik olurlar.

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ДИАГРАММА СОСТОЯНИЯ СИСТЕМ $TlInS_2 - TlCrS_2$, $TlGaSe_2 - TlCrSe_2$ И ЭЛЕКТРИЧЕСКИЕ СВОЙСТВА СЛОИСТЫХ СОЕДИНЕНИЙ $TlCrS_2$, $TlCrSe_2$

Исследована диаграмма состояния систем $TlInS_2 - TlCrS_2$ и $TlGaSe_2 - TlCrSe_2$. Установлено, что на основе исходных соединений образуются ограниченные твердые растворы. Предполагается, что в образующихся твердых растворах возможно сосуществование полярного (дипольного) и магнитного (спинового) упорядочений. В интервале температур 80÷400К исследованы электрические свойства $TlCrS_2$и $TlCrSe_2$, которые выявили, что эти соединения являются полупроводниками *p*-типа.

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