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Phasing Diagrams $TlGaSe_2$ - $CuGaSe_2$ and $TlInS_2$ – $CuInS_2$ Systems

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***Abstract* – According to the data of differential thermal, X-ray phase analyzes, as well as measurements of conductivity and pycnometric density, phase equilibriums were studied and phasing diagrams of $TlInS_2$ - $CuInS_2$ and $TlGaSe_2$ - $CuGaSe_2$ systems were created in the entire concentration range. The studied systems are quasi-binary with limited mutual solubility of the components in the solid state. The interaction in the $TlGaSe_2$ - $CuGaSe_2$ system occurs with the formation of one eutectic and one peritectic points, in the $TlInS_2$ system - $CuInS_2$ with the formation of one eutectic and two peritectic points. Eutectic at 1048 K corresponds to 18 mol. % $CuGaSe_2$ and at 945 K 17 - mol. % $CuInS_2$. Solid solutions based on $CuGaSe_2$, $CuInS_2$, like the initial compounds themselves, undergo phase transformations. It is found that in these systems limited solid solutions are formed, which make up 1.5 mol. % at indoor temperature on $TlGaSe_2$ and 0.5 mol. % on $CuGaSe_2$ in the $TlGaSe_2$ - $CuGaSe_2$ system, as well as 1.5 mol. % on $TlInS_2$ and 0.5 mol. % on $CuInS_2$ in the $TlInS_2$ - $CuInS_2$ system. The nature of the interactions of the components makes it possible to assign the presented phasing diagrams to type VI according to Rooseboom.**

Keywords – diagram; solid solution; smolidus; liquidus; X-ray analysis; electrical conductivity; density.

I. INTRODUCTION

The compounds $TlGaSe_2$, $TlInS_2$, $CuGaSe_2$ and $CuInS_2$ belong to new classes of semiconductors of the type $A^{III}B^{III}C_2^{VI}$ and $A^{I}B^{III}C_2^{VI}$ are of scientific interest for modern optoelectronics and are intensively investigated [1-11, 15].

$TlGaSe_2$ and $TlInS_2$ - are typical representatives of recently discovered non-polyvalent semiconductor compounds with a specific structure of crystal lattices consisting of two independent structural lattices - octahedra with T^{l+} ions and a tetrahedron with Ga^{3+} ions [1]. The $CuGaSe_2$ and $CuInS_2$ compounds crystallize in chalcopyrite structures, in which the cations form ordered sublattices. Unit cells containing 8 atoms each (2Cu, 2In, 2Ga, 4Se, 4S) are characterized with *c/a*, close to 2 [1].

In this article, the authors consider the interactions in the $TlInS_2$ - $CuInS_2$ and TlGaSe2 - $CuGaSe_2$ systems.

II. METHODS AND MATERIALS

In order to construct the $TlInS_2$ - $CuInS_2$ and $TlGaSe_2$ - $CuGaSe_2$ system phasing diagram, the authors synthesized ternary semiconductor compounds: $TlGaSe_2$, $TlInS_2$, $CuGaSe_2$ and $CuInS_2$. The initial materials were high purity elements: Tl-000; Ga-000; In-000; Cu-OCCH-11-4; S-OCCH-16-5; Se-OCH-17-4. The oxide film and other contaminants were removed from the copper surface by etching in a 5% HNO_3 solution for 8–10 minutes, followed by washing in running distilled water, and thallium was subjected to vacuum distillation.

Synthesis ampoules made of thick-walled quartz with an internal diameter of 25 mm were first etched with 40% HF solution for 5 minutes, washed intensively with distilled water, and then annealed in a vacuum oven at a temperature of 1300K. In order to prevent the melting contact with the surface of quartz, the inner part of the ampoules was covered with a layer of graphite. The starting compounds were obtained by direct fusion of the components taken in a stoichiometric ratio in the vacuum quartz ampoules evacuated to a residual pressure of 1.10^{-3} Pa.

The synthesis was carried out in two-section heaters at a temperature of 1100 K for $TlInS_2$, $TlGaSe_2$ and at 1300 K for $CuInS_2$ and $CuGaSe_2$. $TlGaSe_2$, $TlInS_2$, $CuGaSe_2$ and $CuInS_2$ melts were exposed to these temperatures for 5 hours, subjecting to intensive mixing, and then the temperature was slowly lowered to 900K and 1000K, respectively. To bring the alloys to an equilibrium state, homogenizing annealing was used at the indicated temperatures for 240 hours. The single phase and homogeneity of the obtained polycrystals of the compounds $TlGaSe_2$ (dark cherry color), $TlInS_2$ (light yellow color), $CuGaSe_2$ and $CuInS_2$ (gray colors) were controlled by the methods of differential thermal (DTA), X-ray phase (XRA).

Using the above mentioned method 6 g four-component samples were prepared from the obtained compounds.

DTA was performed using a software device for increase and decrease of temperature [12], a two-coordinate recorder H-306 and a highly sensitive two-stage amplifier. DTA curves of alloys were recorded at a heating rate of 10 ° C / min using Pt-Pt / Rh thermocouples PR-30/6, graduated from the melting points of the following substances: Bi, Pb, Se, Te, Sb, KCl, NaCl, Na_2SO_4, Ag and Cu. The error in the determination of the temperature was 50 ° C. One-gram samples of the compositions were evacuated in Stepanov quartz vessels with an internal diameter of 5 mm, and annealed alumina was used as a reference.

The resistance was measured using universal voltmeters Shch-31, B7-30. The measurement error did not exceed 0.05% in the first case and 5% in the second. The substance in the form of a fine mass was pressed into quartz capillaries with a length of 10 mm and a diameter of 2.7 mm. The frontal parts of the capillaries were covered with indium, into which copper electrodes were introduced.

X-ray phase analysis of the system was performed on a Dron-3 installation, in *CuKα* radiation (Ni-filter, 40 kV, 20 mA, the moving speed of a counter was 10 / min). The ground sample was rotated during the survey.

III. RESULTS

T-X sections of phasing diagrams of $TlInS_2$ - $CuInS_2$ and $TlGaSe_2$ - $CuGaSe_2$ systems, created according to the data of DTA, XRA, and also based on the measurement of specific conductivity and pycnometric density, are presented in Figure 1, 2. The studied systems are quasi-binary with limited mutual solubility of the components in the solid state. The interaction in the $TlGaSe_2$ - $CuGaSe_2$ system occurs with the formation of one eutectic and one peritectic points, in the $TlInS_2$ - $CuInS_2$ system with the formation of one eutectic and two peritectic points.

Solid solutions α based on $TlGaSe_2$ and $TlInS_2$ do not undergo any transformations, their range of existence narrows with decreasing temperature. Eutectic point at 1048K corresponds to 18 mol. % $CuGaSe_2$ and at 945 K 17 - mol. % $CuInS_2$. The limiting concentration of the α-solution at the eutectic temperature is 3% $CuGaSe_2$. Solid solutions based on $CuGaSe_2$, as well as the starting compound itself, possess deformism and undergo transformations from the chalcopyrite structure to the sphalerite structure.

Peritectic is characterized by the composition of 86 mol. % $CuGaSe_2$ and a temperature of 1328K. The limiting concentration of the β - solution at a peritectic temperature is 98.1 mol. % $CuGaSe_2$. The $CuInS_2$-based solid solutions, as well as the starting compound itself, have phase transformations (cation-cation and cation-anion disordering) at temperatures of 1263, 1313 and 1363K. Point E_2, characterized by the composition of 86 mol. % $CuGaSe_2$ (72 mol. % $CuInS_2$ in the $TlInS_2$ - $CuInS_2$ system) corresponds to the onset of the transformation that occurs according to the peritectic scheme.

The isothermal stops of this transition form, at a temperature of 293 K in the $TlInS_2$ - $CuInS_2$ system, a second connector. The limiting concentration of the β - phase at a peritectic temperature of 1293 K is 95.2 mol. % $CuInS_2$ in the $TlInS_2$ - $CuInS_2$ system. Point E_3 in Figure 5, characterized by the composition of 90 mol. % $CuInS_2$, which corresponds to the onset of peritectic decomposition, which occurs at a temperature of 1343 K. The limiting concentration of the γ - phase at this temperature is 96.1 mol. % $CuInS_2$.

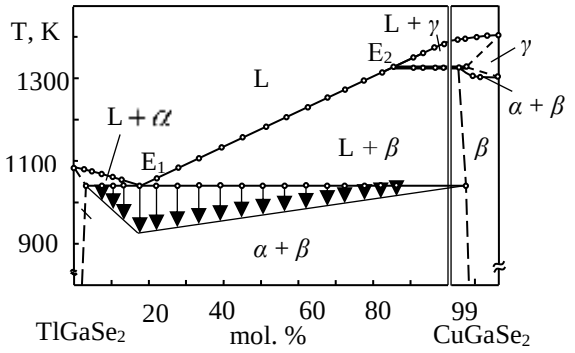

Fig. 1. System phasing diagram $TlGaSe_2$ -

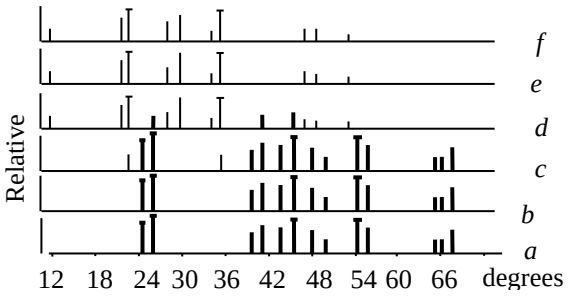

Fig. 2. System bar charts TlGaSe2-$CuGaSe_2$:
a - $CuGaSe_2$; *b* - $Tl_{0.015}Cu_{0.985}GaSe_2$; *c* - $Tl_{0.02}Cu_{0.98}GaSe_2$;
d - $Tl_{0.025}Cu_{0.975}GaSe_2$; *e* - $Tl_{0.98}Cu_{0.02}GaSe_2$; *f* - $TlGaSe_2$.

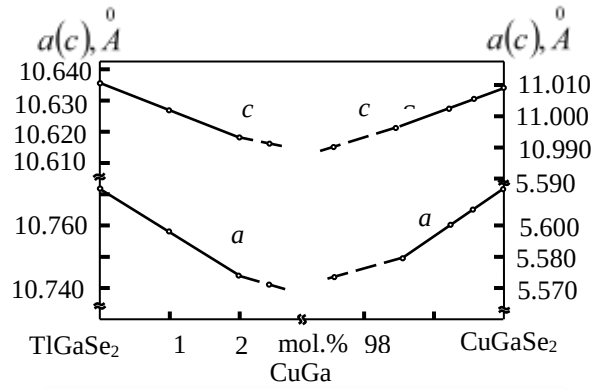

Fig.3. Dependence of changes in tetragonal parameters cells by composition in the system $TlGaSe_2$-$CuGaSe_2$.

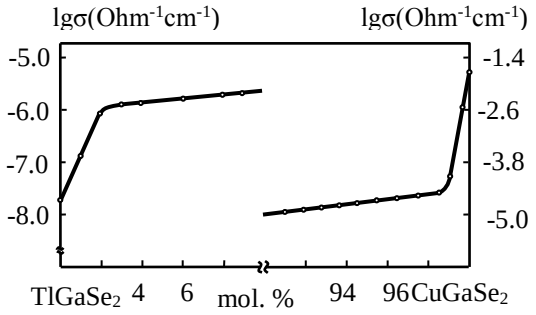

Fig.4. Dependence of specific conductivity on composition in the system $TlInSe_2$- $CuGaSe_2$.

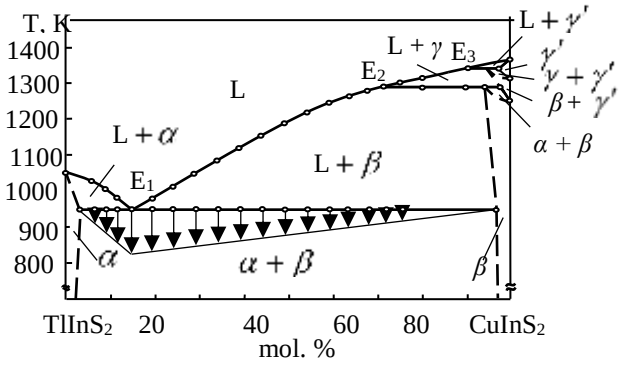

Fig. 5. System phasing diagram $TlInS_2$ – $CuInS_2$

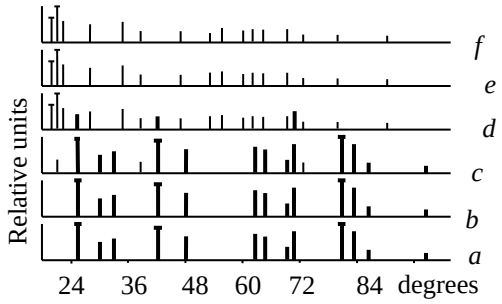

Fig. 6. System bar charts TlInS2-$CuInS_2$:
a - $CuInS_2$; *b* – $Tl_{0.005}Cu_{0.995}InS_2$; *c* - $Tl_{0.01}Cu_{0.99}InS_2$;
d - $Tl_{0.98}Cu_{0.02}InS_2$; *e* - $Tl_{0.99}Cu_{0.01}InS_2$; *f* - $TlInS_2$.

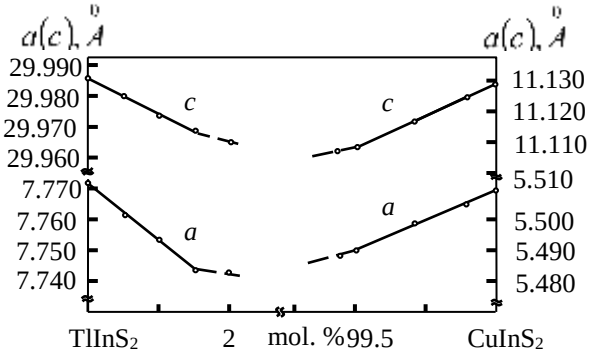

Fig.7. Dependence of changes in tetragonal parameters cells by composition in the system $TlInS_2$ - $CuInS_2$.

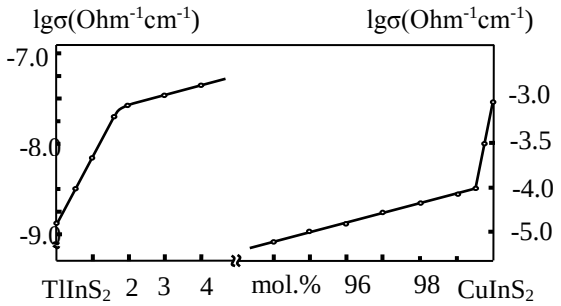

Fig.8. Dependence of specific conductivity on composition in the system $TlInS_2$-$CuInS_2$.

The nature of the interactions of the components makes it possible to assign the presented state diagrams to type VI according to Rooseboom [13].

The results of X-ray phase analysis (Fig. 2, 6) comply with the DTA data. On radiographs of alloys containing ≤ 2 mol. % $CuGaSe_2$ (≤ 1.5 mol. % $CuInS_2$) and> 98 mol. % $CuGaSe_2$ (≤ 99.5 mol. % $CuInS_2$) there are slight shifts of the peak displacement, indicating the formation of solid solutions. Radiographs of other alloys are a superposition of lines corresponding to the initial compounds. The refined areas of the existence of solid solutions at indoor temperature are 2 mol. % on $TlGaSe_2$ and 1.5 mol. % on $CuGaSe_2$ ($TlGaSe_2$ - $CuGaSe_2$ system) and 1.5 mol. % on $TlInS_2$ and 0.5 mol. % on $CuInS_2$ ($TlInS_2$ - $CuInS_2$ system).

Figure 3, 7 shows the concentration dependences of the parameters of tetragonal cells in the $TlInS_2$ - $CuInS_2$ and $TlGaSe_2$ - $CuGaSe_2$ systems. In the range of 98 –100 mol. % $TlGaSe_2$ and 98.5 - 100 mol. % $CuGaSe_2$ and 98.5-100 mol. % $TlInS_2$ and 99.5 - 100 mol. % $CuInS_2$, the lattice parameters are additively reduced. The concentration dependences of conductivity (Fig. 4, 8) do not contradict the presented phasing diagrams and form characteristic bends in the areas indicated above the boundaries.

TABLE I.

Density in the systems $Tl_{1-x}Cu_xGaSe_2$ and $Tl_{1-x}Cu_xInS_2$		
Compound	X-ray density, g/cm^3	Pycnometric density, g/cm^3
$TlInS_2$	5.772	5.731
$Tl_{0.995}Cu_{0.005}InS_2$	5.781	5.741
$Tl_{0.99}Cu_{0.01}InS_2$	5.792	5.753
$Tl_{0.98}Cu_{0.02}InS_2$	5.794	5.754
$TlGaSe_2$	6.475	6.440
$Tl_{0.995}Cu_{0.005}GaSe_2$	6.480	6.413
$Tl_{0.99}Cu_{0.01}GaSe_2$	6.496	6.454
$Tl_{0.98}Cu_{0.02}GaSe_2$	6.516	6.461
$Tl_{0.97}Cu_{0.03}GaSe_2$	6.517	6.452
$CuGaSe_2$	5.630	5.627
$Tl_{0.005}Cu_{0.995}GaSe_2$	5.650	5.647
$Tl_{0.01}Cu_{0.99}GaSe_2$	5.670	5.668
$Tl_{0.02}Cu_{0.98}GaSe_2$	5.675	5.673
$CuInS_2$	4.770	4.767
$Tl_{0.003}Cu_{0.997}InS_2$	4.775	4.779
$Tl_{0.005}Cu_{0.995}InS_2$	4.784	4.782
$Tl_{0.01}Cu_{0.99}InS_2$	4.785	4.781

The table presents the values of X-ray pycnometric densities of both the initial compounds and the solid solutions of the systems. The density was determined using a pycnometer. Toluene was used as a pycnometric liquid. Since the values of densities according to XRA data coincide within the error with the experimentally found ones, the studied solid solutions can be attributed to substitutional solid solutions [14]. From the analysis of tabular data it can be found that at the boundaries of mutual solubility, the value of densities reveal characteristic behavior.

IV. CONCLUSION

1. These compounds form limited solid solutions (type VI according to Rooseboom): 2 mol. % on the $TlGaSe_2$ and up to 1.5 mol. % on $CuGaSe_2$ at indoor temperature to the $TlGaSe_2$ — $CuGaSe_2$ system and 1.5 mol. % on $TlInS_2$ and 0.5 mol. % on $CuInS_2$ in the $TlInS_2$ - $CuInS_2$ system.
2. The dependences on the composition, changes in the parameters of tetragonal cells, specific electric conductivities and pycnometric densities of alloys on the composition show behavior characteristic of the formation of limited solid solutions.

References

[1] A.Kh. Matiev, Phase equilibria and electron-optical properties of T1B3C62-A1B3C62 systems (A-Cu, Ag; B-Iп, Ga; C-S, Se2), The dissertation for the competition uch. Art. Dr. Physics and Mathematics Sciences, UlSU, 2005, 399 p.

[2] S.N. Mustafaeva, M.M. Asadov, A.I. Jabbarov, "Dielectric properties and charge transfer in TlInSe2) 0.1 (TlGaTe2) 0.9 at direct and alternating current", Solid State Physics, vol. 56. iss. 6. pp. 1055–1059. 2014.

[3] Sh. Hosokawa, J.R. Stellhorn, H. Ikemoto, K. Mimura, K. Wakita, N. Mamedjv. "Lattice Distortions in $TlInSe_2$ Thermoelectric Material Studied X-ray Absorption Fine Structure", Phys. Status Solidi A., pp. 215, 2018.

[4] A.U. Sheleg, V.V. Shevtsova, V.G. Gurtovoy, S.N. Mustafayev, E.M. Kerimov, "Low-temperature X-ray studies of TlInS2, TlGaS2 and TlGaSe2 single crystals. Surface", X-ray, synchrotron and neutron Research, no. 11. pp. 39–42, 2013.

[5] H. Haloui, K.Touafek, M. Zaabat, H. Ben cheikh el hocinem, A. Khelifa, "The Copper Indium Selenium ($CuInSe_2$) thin films solar cells for Hybrid Photovoltaic Thermal Collectors", Energy Procedia, vol. 74, pp. 1213–1219, August 2015.

[6] A.D.P, Leach, J.E. Vacdonald, "Optoelectronic Properties of $CuInS_2$ Nanocrystals and Their Origin", J. Phys. Chem. Lett., no. 7 (3), pp. 572–583, 2016.

[7] S.L. Castro, Sh.G. Bailey, Ry.P. Raffaella, K.K. Banger, A.F. Hepp, "Synthesis and Characterization of Colloidal $CuInS_2$ Nanoparticles from a Molecular Single-Source Precursor", J. Phys. Chem. B, no. 108 (33), pp. 12429–12435, 2004.

[8] D. Deng, L.Ou, Yu. Gu, "Near-infraed broadly emissive $AgInSe_2$/ZnS quantum dots biomedical optical imaging", J. Of Materials Chemistry C, vol. 2, no. 34, pp. 7077–7085, 2014.

[9] N. Karunagaran, P. Ramasamy. «Synthesis, growth and characterization of single crystals». Materials Science in Semiconductor Processing Volume 40, December 2015, pp. 591-595.

[10] G.V. Makhnovets, G.L. Myronchuk, L.V. Piskach, B.V. Vidrynskyi, A.H. Kevshyn, "Study of optical absorption in $TlGaSe_2:Zn^{2+}$ single crystals", Ukr. J. Phys. Opt., vol. 19, iss. 1, pp. 49–59, 2018.

[11] A.T. Nagat, S.E. Al Garni, F.S. Bahabri, G. Attia, S.R. Al Harbi, A.A. Ghamdi, "Electrical and Thermal Transport Properties of $TlGaSe_2$ Single Crystals", JKAU: Sci., vol. 21, no. 1, pp. 13–26, 2009.

[12] V.A. Gavrish, L.F. Illicheva, M.A. Karavanova, A.V. Radkevich, P.E. Stadnik, "Software device to thermostats", Instruments and equipment of the experiment, no. 6, pp. 149–150, 1979.

[13] V.Ya. Anosov, S.A., Pogodin Basic principles of physical and chemical analysis. Moscow; Leningrad: Publisher AN. THE USSR, 1947.

[14] A.A. Bochvar, Metal Science. Moscow: Metallurgizdat, 1956.

[15] A.Kh. Matiyev, A.V. Yanarsaev, R.T. Uspazhiev, R. M. Efteyeva, "*T–x* Phase Diagram of the $TlGaSe_2$-$AgGaSe_2$ System». Bulletin of the Russian Academy of Sciences", Physics, Inorganic Materials, vol. 51, no. 7, pp. 665–667, 2015.