Phasing Diagrams TlGaSe₂ - CuGaSe₂ and TlInS₂ – CuInS₂ Systems

Matiev A.Kh.
Department of general physics
Ingush State University
Magas, Russia
matiyev-akhmet@yandex.ru

Khamkhoev V.M.
Department of general physics
Ingush State University
Magas, Russia
khamkhoev1950@mail.ru

Torshhoeva Z.S.
Department of general physics
Ingush State University
Rostov, Russia
torshhoeva.zina@yandex.ru

Israilova L.I.
Department of physics
Grozny State Petroleum Technical University named after
M.D. Millionschikov
Grozny, Russia
daydov.akhemd.1997@mail.ru

Uspazhiev R.T.
Department of physics
Grozny State Petroleum Technical University named after
M.D. Millionschikov
Grozny, Russia
ruslan-chr@mail.ru

Gachaev A.M.
Department of advanced and applied mathematics
Grozny State Petroleum Technical University
named after M.D. Millionschikov
Grozny, Russia
gachaev.chr@mail.ru

Evtieva R.M.
Department of physics
Grozny State Petroleum Technical University
named after M.D. Millionschikov
Grozny, Russia
roza.efteeva@mail.ru

Umarov S.Kh.
Department of informatics and biophysics
Bukhara Medical Institute
Bukhara, Uzbekistan
salim_umarov49@mail.ru

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 TlInS₂ - CuInS₂ and TlGaSe₂ - CuGaSe₂ 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 TlGaSe₂ - CuGaSe₂ system occurs with the formation of one eutectic and one peritectic points, in the TlInS₂ system - CuInS₂ with the formation of one eutectic and two peritectic points. Eutectic at 1048 K corresponds to 18 mol. % CuGaSe₂ and at 945 K 17 - mol. % CuInS₂. Solid solutions based on CuGaSe₂, CuInS₂, 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 TlGaSe₂ and 0.5 mol. % on CuGaSe₂ in the TlGaSe₂ - CuGaSe₂ system, as well as 1.5 mol. % on TlInS₂ and 0.5 mol. % on CuInS₂ in the TlInS₂ - CuInS₂ 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; smoldius; liquidus; X-ray analysis; electrical conductivity; density.
I. INTRODUCTION

The compounds TiGaSe_2, TlInS_2, CuGaSe_2 and CuInS_2 belong to new classes of semiconductors of the type $\text{A}^{III}\text{B}^{III}\text{C}^{VI}_2$ and $\text{A}^{IV}\text{B}^{III}\text{C}^{VI}_2$ are of scientific interest for modern optoelectronics and are intensively investigated [1-11, 15].

TiGaSe_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 $\text{T}^+$ ions and a tetrahedron with $\text{Ga}^{3+}$ 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 close to 2 [1].

In this article, the authors consider the interactions in the TlInS_2 - CuInS_2 and TiGaSe_2 - CuGaSe_2 systems.

II. METHODS AND MATERIALS

In order to construct the TlInS_2 - CuInS_2 and TiGaSe_2 - CuGaSe_2 system phasing diagram, the authors synthesized ternary semiconductor compounds: TiGaSe_2, TlInS_2, CuGaSe_2 and CuInS_2. The initial materials were high purity elements: Tl-000; Ga-000; In-000; Cu-OCC-11-4; S-OCC-16-5; Se-OCC-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^-4 Pa.

The synthesis was carried out in two-section heaters at a temperature of 1100 K for TlInS_2, TiGaSe_2 and at 1300 K for CuInS_2 and CuGaSe_2, TiGaSe_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 TiGaSe_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, NaSO_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 TiGaSe_2 - CuGaSe_2 systems, created according to the data of DTA, XRA, and also based on the measurement of specific conductivity and pyrometric 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 TiGaSe_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 $\alpha$ based on TiGaSe_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 $\alpha$-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 $\beta$ - soluiton 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 $E_1$, 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 $\beta$ - phase at a peritectic temperature of 1293 K is 95.2 mol. % CuInS_2 in the TlInS_2 - CuInS_2 system. Point $E_2$ 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 $\gamma$ - phase at this temperature is 96.1 mol. % CuInS_2.
Fig. 1. System phasing diagram TlGaSe₂ - CuInS₂.

Fig. 2. System bar charts TlGaSe₂-CuGaSe₂:
- CuGaSe₂; b - Tl₀.₀₂₅Cu₀.₉₇₅GaSe₂; c - Tl₀.₀₂₅Cu₀.₉₇₅GaSe₂;
d - Tl₀.₀₂₅Cu₀.₉₇₅GaSe₂; e - Tl₀.₉₈Cu₀.₀₂GaSe₂; f - TlGaSe₂.

Fig. 3. Dependence of changes in tetragonal parameters cells by composition in the system TlGaSe₂-CuGaSe₂.

Fig. 4. Dependence of specific conductivity on composition in the system TlInS₂ - CuGaSe₂.

Fig. 5. System phasing diagram TlInS₂ - CuInS₂.

Fig. 6. System bar charts TlInS₂-CuInS₂:
- CuInS₂; b - Tl₀.₀₁₅Cu₀.₉₈₅InS₂; c - Tl₀.₀₁₅Cu₀.₹₈₅InS₂;
d - Tl₀.₉₈₅Cu₀.₀₁₅InS₂; e - Tl₀.₉₈₅Cu₀.₀₁₅InS₂; f - TlInS₂.

Fig. 7. Dependence of changes in tetragonal parameters cells by composition in the system TlInS₂ - CuInS₂.

Fig. 8. Dependence of specific conductivity on composition in the system TlInS₂ - CuInS₂.
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 1 to 2 mol. % CuGaSe₂ (≤ 1.5 mol. % CuInS₂) and 98 mol. % CuGaSe₂ (≤ 99.5 mol. % CuInS₂) 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 TlGaSe₂ and 1.5 mol. % on CuGaSe₂ (TlGaSe₂ - CuGaSe₂ system) and 1.5 mol. % on TlInS₂ and 0.5 mol. % on CuInS₂ (TlInS₂ - CuInS₂ system).

Figure 3, 7 shows the concentration dependences of the parameters of tetragonal cells in the TlInS₂ - CuInS₂ and TlGaSe₂ - CuGaSe₂ systems. In the range of 98 - 100 mol. % TlGaSe₂ and 98.5 - 100 mol. % CuGaSe₂ and 98.5 - 100 mol. % TlInS₂ and 99.5 - 100 mol. % CuInS₂, the lattice parameters are additionally 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

<table>
<thead>
<tr>
<th>Compound</th>
<th>X-ray density, g/cm³</th>
<th>Pycnometric density, g/cm³</th>
</tr>
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<tbody>
<tr>
<td>TlInS₂</td>
<td>5.772</td>
<td>5.731</td>
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<tr>
<td>Tl₀.₀₉₉Cu₀.₀₀₃In₀.₉₉₇S₂</td>
<td>5.781</td>
<td>5.741</td>
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<td>5.792</td>
<td>5.753</td>
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<tr>
<td>Tl₀.₀₉₉Cu₀.₀₂₁In₀.₉₈₉S₂</td>
<td>5.794</td>
<td>5.754</td>
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<tr>
<td>TlGaSe₂</td>
<td>6.475</td>
<td>6.440</td>
</tr>
<tr>
<td>Tl₀.₀₉₉Cu₀.₀₀₇Ga₀.₉₉₃Se₂</td>
<td>6.480</td>
<td>6.413</td>
</tr>
<tr>
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<td>6.496</td>
<td>6.454</td>
</tr>
<tr>
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<td>6.516</td>
<td>6.461</td>
</tr>
<tr>
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<td>6.517</td>
<td>6.452</td>
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<td>CuGaSe₂</td>
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<td>5.673</td>
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<td>CuInS₂</td>
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<td>4.775</td>
<td>4.779</td>
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<td>4.784</td>
<td>4.782</td>
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<tr>
<td>Tl₀.₀₉₉Cu₀.₀₀₇In₀.₉₉₇S₂</td>
<td>4.785</td>
<td>4.781</td>
</tr>
</tbody>
</table>

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 TiGaSe₂ and up to 1.5 mol. % on CuGaSe₂ at indoor temperature to the TiGaSe₂ — CuGaSe₂ system and 1.5 mol. % on TlInS₂ and 0.5 mol. % on CuInS₂ in the TlInS₂ - CuInS₂ 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


