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The Futures of the Physic-Chemical and Thermoelectric Properties of the InTe-Cu_2ZnSnS_2 System Alloys

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----------ABSTRACT----------
By the methods of the physic-chemical analysis as well the measurements of microhadness and picknomentric density the semiconducting system InTe-Cu_2ZnSnS_4 has been investigated and its state diagram has been plotted. Guazibinarity of the system with restricted homogeneous fields has established on the basis of both initial components. The boundaries of solid solutions at 300K reach on side of InTe ~ 2mol% and on side of Cu_2ZnSnS_4 ~ 13mol%. The coordinates of the system eutectic correspond to the composition ~23mol% Cu_2ZnSnS_4 and temperature ~813K. A study of thermoelectric and galvanomagnetic parameters of solid solutions $(InTe)_{1-x}(Cu_2ZnSnS_4)x$ showed dispersion of electrons from the ionized admixture at low temperatures, and at higher temperatures from thermal vibrations of crystalline lattice. Heat transfer takes place according to one-phonon mechanism. The alloy of solid solution $(InTe)_{0,98}(Cu_2ZnSnS_4)_{0,02}$ possesses a high value of thermoelectric efficiency.

Keywords: *phase diagram, quaribinary system, dispersion of electros and phonons, thermoelectric efficiency.*

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I. INTRODUCTION

The complex chalcogenides of copper and indium proved the cusclves as the perspective materials with ionic and super ionic conductivity, as well a high value of thermoelectric quality coefficient [1, 2]. Besides, Cu_2ZnSnS_4 enters a family of the semiconductors applied the mechanisms of solar energetics [3, 4]. Therefore on studying the character of physic-chemical interaction between the compounds InTe and Cu_2ZnSnS_4 it is possible to reveal the new complex composition phases with improved applied parameters.

The compound InTe possesses the congruent character of melting at ~969K, it crystallires in a tetragonal structure with the parameters a=8,437; c=7,139Å; z=8. Picknometric density is 6,29 g/cm^3, the value of microhardness ~960MPa. Electric conductivity ~101 $ohm^{-1}cm^{-1}$, thermo-e.m.p. coefficient. Within 80-100 mcv/d. possesses anisotropy of properties [5].

Cu_2ZnSnS_4 has also tetragonal structure with the parameters a=5,427; c=10848Å. Picknometric density is 4,5 g/cm. According to [6] melting point of this compound is ~ 1265 K, and Debye temperature – 320 K. The width of the banned zone at 300K is equal to ~1,5eV with decrease in temperature increases and at ~ 25 K reaches – 1,64 eV. The coefficient of optical absorption is rather high and has a value > 104 cm^{-1}.

II. METHODS OF EXPERIMENTS

The alloys of the InTe-Cu_2ZnSnS_4 system are synthesized by the direct method from the received beforehand components InTe and Cu2ZnSnS4 in quarter ampules evacuated till ~0,33 Pa at ~1073-1523 K. All the alloys were undergoes homogenizing annealing at ~973 K within 240 hours. The differential-thermic analysis (DTA) was made on the low frequency pyrometer of HTP-73 mark using $^{Pt}/_{Pt-Rh}$ thermocouple. In this case the rate of temperature increase was ~10 d./min. The x-ray phase (RPh.A) analysis was made on x-ray diffractometer D2 Phase with the use of CuK_2 radiation with nicked fitter. At malcing the microstructural analysis (MSA) they used the microscope MUM-8, and the inverstigations were carried out on the grinding and polishing surfaces. As the etchants there were used NHO_3 diluted till ~20%. The measurements of microhardness were carried out using the microscope PMT-3, while the density was determined by picknometric way, where toluene served as liquid.

The thermoelectric properties were studied by the samples of solid solutions on a base of InTe of parallelepiped form in analogy with methods cited in [7].

III. RESULTS AND THEIR DISCUSSION

Synthesized bars were dense of grey color with metallic glitter. They were resistant against air moisture and water, but could not bear actions of such mineral acids as, for instance, H2SO4 and HNO3. They observed two endothermic effects on thermograms. The microstructural analysis indicated to the existence of homogeneous fields on a base of bots initial components. For the purpose of exposing the character of physic-chemical interaction in the InTe-Cu_2ZnSnS_4 there were registered x-ray diffractograms of the initial components and alloys of composition 40 and 60 mol% Cu_2ZnSnS_4. As it turned out from diffractograms (Fig.1) both shown compositions include the lines of intensities of x-ray grams of the initial InTe and Cu_2ZnSnS_4 that testifies to two-phase nature of the examined alloys as well quasibinarity of the system on a whole.

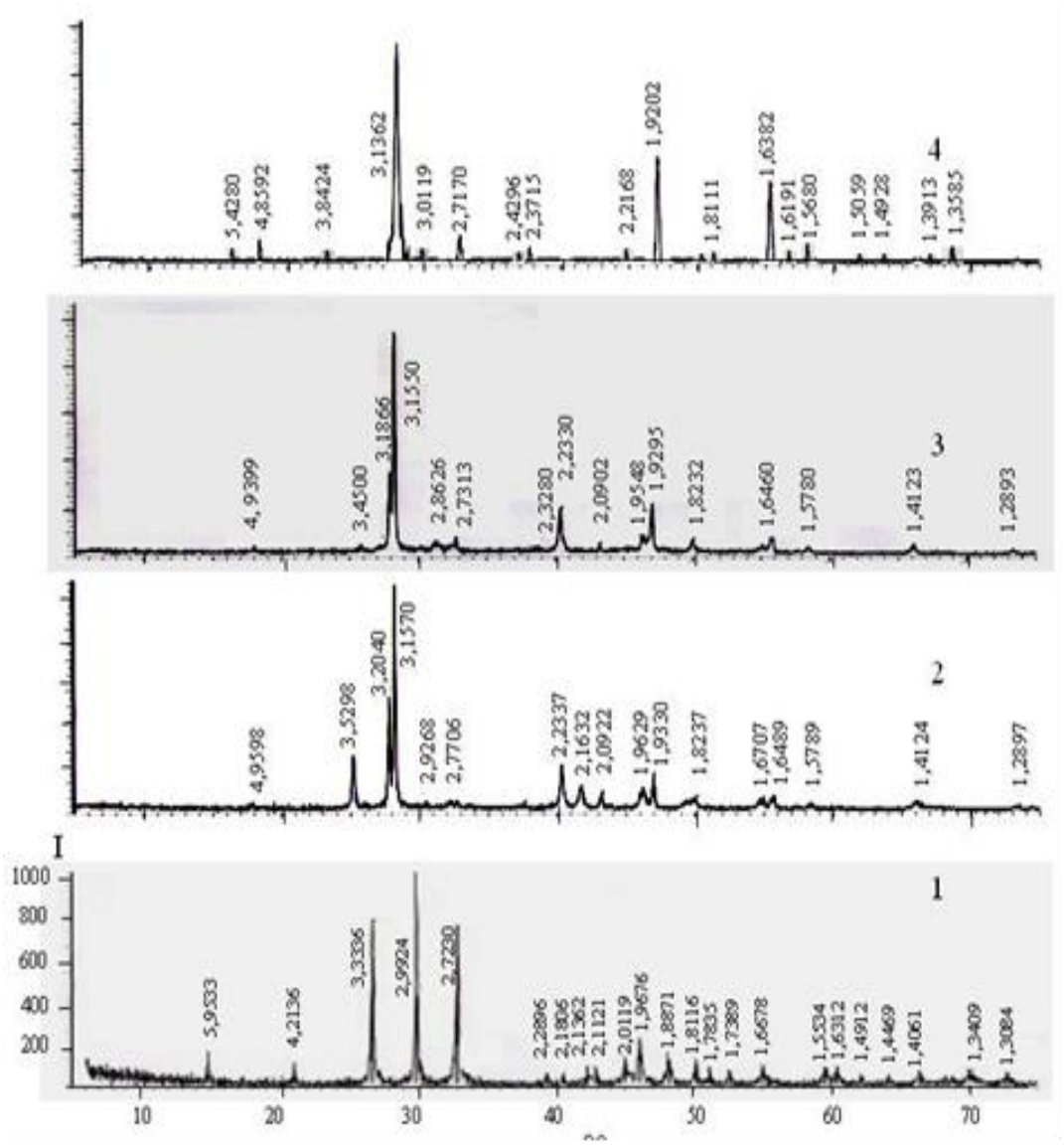

Fig.1. X-ray dffractograms of the alloys of the InTe-Cu2ZnSnS4 system
(1 – InTe; 2 – 40 mol%; 3 – 60% mol% Cu_2ZnSnS_4; 4 – Cu_2ZnSnS_4)

And the built diagram of state testifies in favour of the said. As is seen the system liquidus curves at ~ 813 K and composition in ~75 mol% InTe has common coordinates corresponding to the system eutectic. There exist the fields of solid solutions on the basis of the initial components of the InTe-Cu_2ZnSnS_4 system, the boundaries of which at 300 K reach ~ mol% Cu_2ZnSnS_4 and ~13 mol% InTe.

The basic physic-chemical properties and compositions of synthesized alloys are cited in Table 1.

For microhardness olf the alloys two series of values are received. The values 960-970 MPa refer to the phases enriched in the composition InTe, and values 2720-2780 MPa to the phases enriched in the composition by the component Cu_2ZnSnS_4.

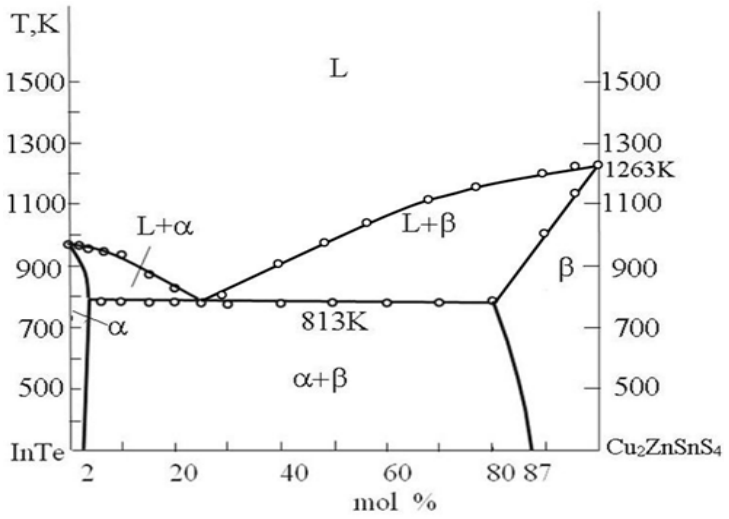

Fig.2. State diagram of the InTe-Cu_2ZnSnS_4

The investigations of thermoelectric properties of the alloys of solid solutions $(InTe)_{1-x}(Cu_2ZnSnS_4)_x$ showed to semiconducting course heat conductivity with a wide field of admixture conductivity (Fig.3).

Table 1. The Compositions and some physic-chemical properties of the InTe-Cu_2ZnSnS_4 system alloys

Compositions, mol%		Thermal effects	Picknometric density	Microhardness MPa	
InTe	Cu_2ZnSnS_4	K	g/cm^3	InTe p=0,15 N	Cu_2ZnSnS_4 p=0,20 N
100	0,0	969	6,29	960	-
98	2,0	963	6,28	960	
97	3,0	953	6,28	965	-
95	5,0	813, 948	6,25	770	-
93	7,0	813, 923	6,22	779	-
90	10	813, 903	6,20	970	-
80	20	813, 783	6,05	-	-
75	25	813	5,82	Эвтектика	Эвтектика
70	30	813, 863	5,71	-	-
60	40	813, 1053	5,60	-	2800
50	50	813, 1063	5,45	-	2800
40	60	813, 1073	5,35	-	2800
30	70	813, 1103	5,05	-	2800
20	80	813, 1243	4,82	-	2800
10	90	1253	4,65	-	2790
0,0	100	1263	4,55	-	2720

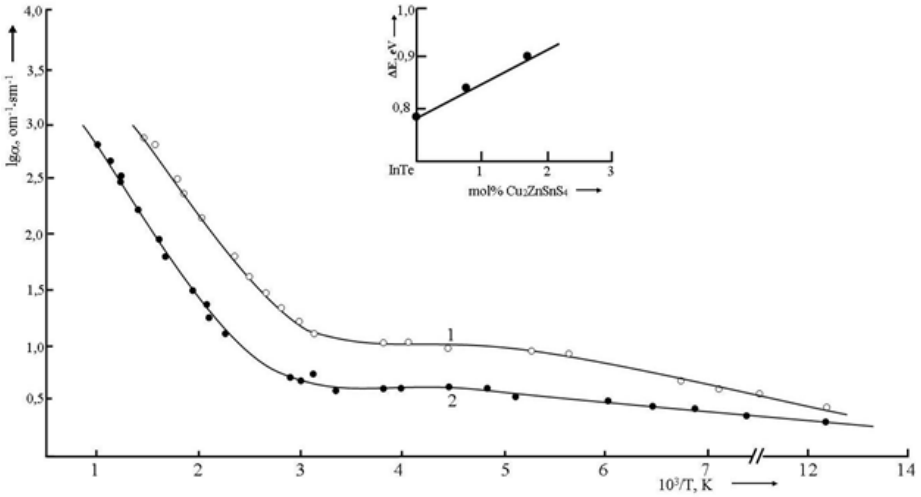

Fig.3. Temperature dependence of electric conductivity of the alloys of solid solutions $(InTe)_{1-x}(Cu_2ZnSnS_4)_x$ and change of the values of thermal width of the banned zone from the composition of solid solutions on base of InTe (1 – 99 mol% Cu_2ZnSnS_4; 2 – 99 mol% Cu_2ZnSnS_4)

Probably, conductivity in this field proceeds in analogy with compensated semiconductor by admixture subzones and admixture centers [3].

The calculations and analysis of the curves in low-temperature field showed that in the process of charge transfer the admixture center plays the basic role. However, at T>300 K the admixture subzones make the decisive contribution into the processes of phenomenon of transfer. Above 400 K electroconductivity sharply increases what is probably connected with coming the field of own conductivity. In this field the values of thermal width of the banned are calculated according to tangents of angle $\lg\sigma \sim f\left(10^3/T.K\right)$. In turned out that addition of Cu_2ZnSnS_2 leads to increasing the values of width of the banned zone. In the insertion of Fig.3. The dependence of the width of the banned zone on the composition of solid solutions $(InTe)_{1-x}(Cu_2ZnSnS_4)x$ is shown. Increase of $\Delta\varepsilon$ is probably connected with three-dimensional heteropolar chemical bond tests the lagging character with the formation of solid solutions on the base of InTe an addition of small amounts of Cu_2ZnSnS_4 in monotelluride of indium also leads to the increase in thermo-e.m.p. coefficient. In Fig.4 temperature dependences of the coefficient of solid solutions thermo-e.m.p. $(InTe)_{1-x}(Cu_2ZnSnS_4)x$ are cited. As is seen at relatively low temperatures (80-400 K) thermo-e.m.p. in analogy with semiconductors with the complex zone structure [90] increases in straight line. Passing throng maximum thermo-e.m.p coefficient manifests then tendency to decrease. Increase of a by temperature and composition leads to the increase in thermoelectric power ($a^2\sigma$) that is an important factor for solution of the applied issues of the studied solid solutions. In a whole temperature range both compositions of the alloys had electronic type of conductivity. The measurements of Holl's effect showed [10] that at low temperatures dispersion of electrons takes place from ionized admixture centers (atoms), and at highs temperatures from thermal vibrations of a crystalline lattice. However, at high temperatures the existence of the mechanisms of dispersion of current carriers from polar vibrations is not excluded as the curves of dependence LgUn ~ f(LgT) have a sloping maximum.

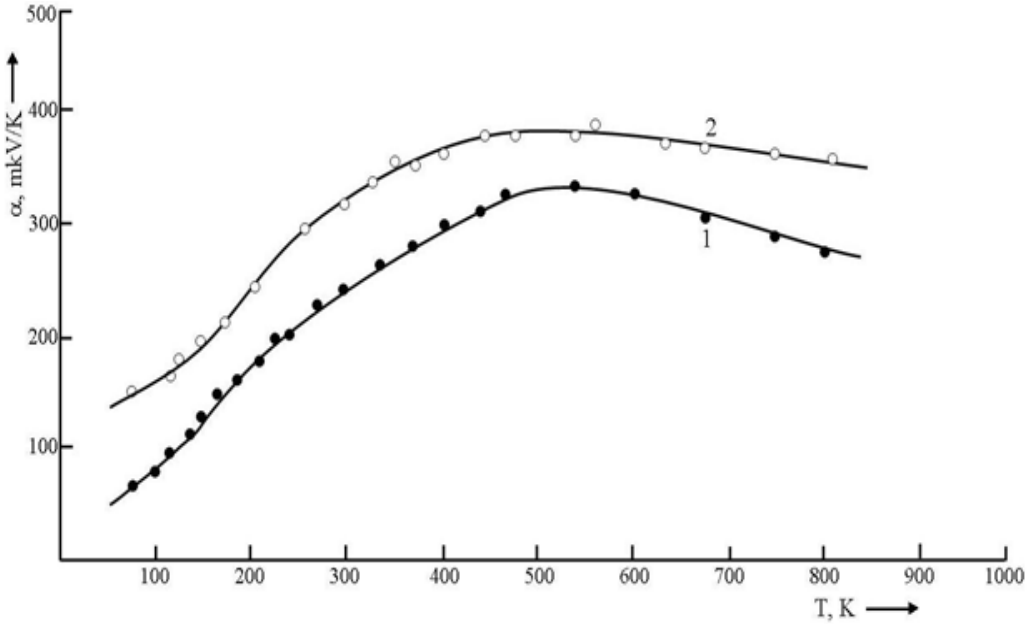

Fig.4. Temperature dependence of the coefficient of the alloys thermo-e.m.p. of solid solutions $(InTe)_{1-x}(Cu_2ZnSnS_4)_x$ (1 – 99% Cu_2ZnSnS_4; 2 – 98 mol.% Cu_2ZnSnS_4)

Temperature dependence of general heat conductivity ($æ_{gen}$) of the alloys of solid solutions $(InTe)_{1-x}(Cu_2ZnSnS_4)_x$ is cited in Fig.5. As is seen, with the increase in temperature the heat conductivity of both compositions of solid solutions monotonously decreases, i.e. heat transfer in these samples takes place according to the law $\sim T^{-1}$. This testifies to one-phonon mechanism of heat transfer. By using the values of electric conductivity (γ), thermo-e.m.p. coefficient (a) and general heat conductivity ($æ_{gen}$) by known formula $Z = \frac{a^2\sigma}{æ_{gen}}$ the values of thermoelectric efficiency of solid solutions $(InTe)_{0,88}(Cu_2ZnSnS_4)_{0,02}$ have been calculated.

As is seen from Fig.5 (curve Z) despite relatively low values of Z till temperature ~700 K later on, i.e. beginning from ~800 K thermoelectric efficiency increases and has a value $\sim 1{,}5\cdot 10^{-3}$ deg. $^{-1}$.

Taking into account this value of Z it is possible to conclude that investigated composition of solid solution can be used at making the average temperature thermoelectric transformers of energy.

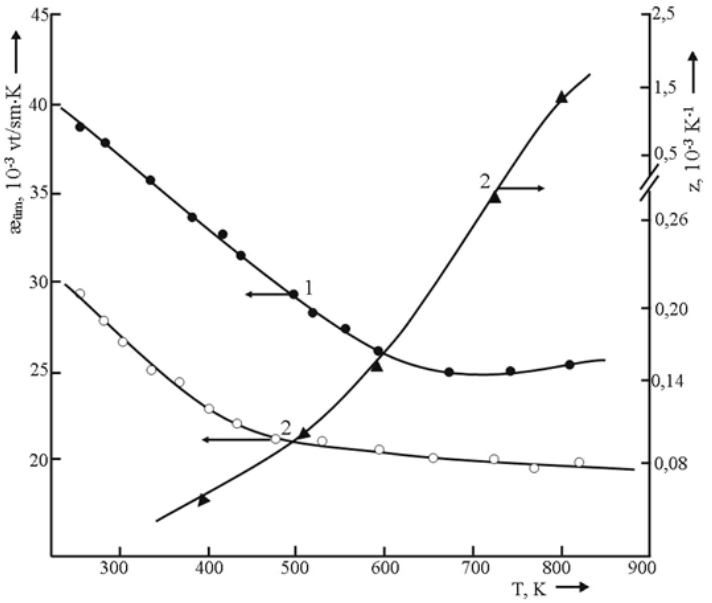

Fig.5. Temperature dependence of general heat conductivity ($æ_{gen}$) and the coefficient of thermoelectric efficiency (Z) of the alloys of solutions $(InTe)_{1-x}(Cu_2ZnSnS_4)_x$
(1 – 99 mol% Cu_2ZnSnS_4; 2 – 98 mol% Cu_2ZnSnS_4)

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