

## The effect of many-component compound $\text{CuZn}_2\text{InTe}_4$ on the physico-chemical and thermophysical properties of $\text{In}_2\text{Te}_3$

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*The system  $\text{In}_2\text{Te}_3\text{-CuZn}_2\text{InTe}_4$  has been investigated by the complex methods of analysis, as well measurement of microhardness, pycnometric density and some thermophysical parameters. The plotted state diagram showed quasibinarity of these both initial components, the boundaries of at 300K reach: on side of  $\text{CuZn}_2\text{InTe}_4$  till ~5 mol.% of  $\text{In}_2\text{Te}_3$ ,  $\text{In}_2\text{Te}_3$  till ~3 mol.%  $\text{CuZn}_2\text{InTe}_4$ , while on side of  $\text{Cu}_2\text{Zn}_2\text{InTe}_4$  till ~5 mol.%  $\text{In}_2\text{Te}_3$ . the effect of slight substitutions of  $\text{CuZn}_2\text{InTe}_4$  on thermophysical properties of  $\text{In}_2\text{Te}_3$  has been defined and the mechanisms of dispersing electrons and phonons in solid solutions  $(\text{In}_2\text{Te}_3)_{1-x}(\text{CuZn}_2\text{InTe}_4)_x$  determined.*

**Keywords:** *phase diagram, solid solutions, peritectic transition, dispersion mechanism, heat resistance*

**Introduction.** Chalcogenides of indium and copper, as well the complex homogeneous phases on their basis are referred to the perspective materials for making switching solid structures, for transformers of alternative energy, as well as magnetic elements of memory [1-3].

Therefore obtaining and research of the properties of the complex homogeneous phases on their basis is a vital task and demands fundamental searches. From this point of view it would be interesting of observe the influence of many-component chalcogenide compound  $\text{CuZn}_2\text{InTe}_4$  on the physico-chemical and thermophysical properties of  $\text{In}_2\text{Te}_3$ .

The goal of the present work is a study of the character of chemical interaction in the system, exposing the mechanism of dispersion on electrons and phonons in the homogeneous phases of this system.

One of the initial components  $\text{In}_2\text{Te}_3$  has congruent melting at  $\sim 900$  K, crystallizes in cubic syngony with the parameters of crystalline lattice  $a=18,480\text{\AA}$  (spatial group  $F43m - T_d^2$ ).

Picknometric density  $d=5,78$  g/cm<sup>3</sup>, micro hardness.  $H_y=1660$  MPa. At has a polymorphous transformation. It is semiconductor with «n»-type on conductivity and width of prohibited zone 0,96 eV [4].

The compound  $\text{CuZn}_2\text{InTe}_4$  also melts congruently at  $a=6,130\text{\AA}$ , crystallizes in a cubic syngony with a parameter  $a=6,130\text{\AA}$  (spatial group  $P_{63}mc$ ).

The density  $d= 5,96$  g/cm<sup>3</sup>, microhardness  $H_y=2650$  MPa. It has low values of mobility of current carriers ( $U_n=3,31$  cm<sup>3</sup>/V·sec.) and electric conductivity ( $\sigma=2.6\text{ohm}^{-1}\cdot\text{cm}^{-1}$ ), and the coefficient of thermo-e.m.f. is equal to  $a=-153$  mV/grad [5].

**Experimental part.** At synthesis of the alloys of the system  $\text{In}_2\text{Te}_3$  of metallic mark  $\text{CuZn}_2\text{InTe}_3$  there were used the initial materials: indium of metallic mark In-000, copper 99,998 and Te of B-4 mark and zinc OSCh. The triple alloys were directly synthesized by melting the components  $\text{In}_2\text{Te}_3$  and  $\text{CuZn}_2\text{InTe}_4$  by ampule method in the range of 1073-1423 K with the subsequent cooling under mode of switched off furnace. For the purpose of achieving the balanced state the samples were annealed at 873 K within 140 h.

The investigation of the alloys  $\text{In}_2\text{Te}_3\text{-CuZn}_2\text{InTe}_4$  was carried out by the complex methods of physico-chemical analysis, i.e., differential-thermic (DTA), X-ray phase (XPhA), microstructural (MSA) analyses, as well determination of density and measurement of micro hardness. Thermograms were taken on low frequency thermoregister LTR-73 with heating rate in 9 grad./min. The diffractograms were taken on the plant D<sub>2</sub>PHASER ( $\text{CuK}_\alpha$  - radiation). Microhardness was measured on microhardometer PMT-3 under loads, chosen as a result of radiation of phase microhardness. They studied microstructure of the alloys on the microscope MIM-8. For etching the polishing alloys there was used solution of

composition 10 ml  $\text{HNO}_3$  conc. +  $\text{H}_2\text{O}_2 = 1:2$ , time of etching made up 20-25 sec. The density was determined by the pycnometric method. As working liquid toluene was used. Electro physical properties were studied on the samples of parallelepiped form by methods [6].

## Results and Discussions

The alloys of the  $\text{In}_2\text{Te}_3\text{-CuZn}_2\text{InT}_4$  are got in compact form of black-grey colour. The alloys are proof to atmospheric air and water. The concentrated mineral acids ( $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ) and alkali disintegrate them on the whole. The results of DTA showed that all the fixed thermic effects on the curves of heating and cooling are reversible. On thermograms of the system alloys there were revealed two endo thermal effects corresponding to liquidus and solidus of the system.

Microstructures of the alloys of the system  $\text{In}_2\text{Te}_3\text{-CuZn}_2\text{InT}_4$  were studied after annealing. MAS showed that dissolubility of the components in solid state on basis of  $\text{InTe}_3$  makes up 3 mol.%  $\text{CuZn}_2\text{InTe}_4$ , while on basis of  $\text{CuZn}_2\text{InT}_4 \sim 1$  mol.%  $\text{In}_2\text{Te}_3$ . In the break of the concentrations 3-95 mol.%  $\text{CuZn}_2\text{InT}_4$  all alloys are two-phase. Microhardness of polished samples was measured under loads for  $\alpha$ - and  $\gamma$ - solid. Solutions made up 0,20 and 0,25 respectively.

For molded samples there has been considerable scattering the values of microhardness, which after 240 hours of annealing was stabilized.

In the Table 1 there are cited the results of the basic physico-chemical properties of the alloys of the  $\text{In}_2\text{Te}_3\text{-CuZn}_2\text{InT}_4$  system.

*Table 1.*

Compositions, results of DTA, measurements of microhardness and determination of density of the alloys of the  $\text{In}_2\text{Te}_3\text{-CuZn}_2\text{InT}_4$

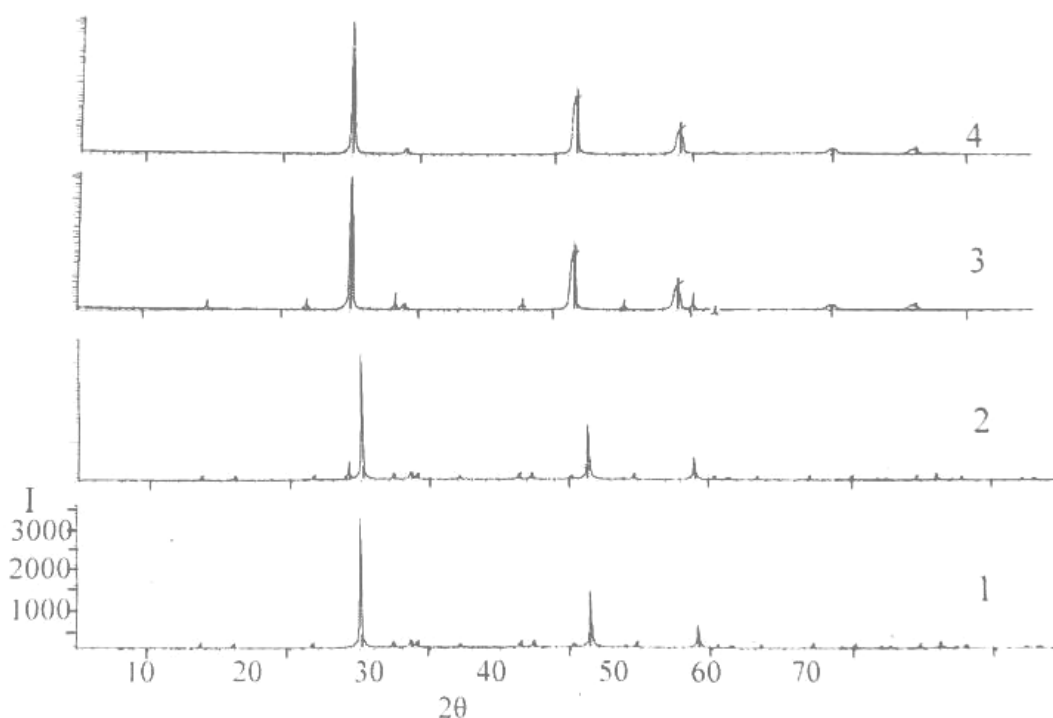
Composition, mol. %		Thermic effects of heating, K	Density, g/cm <sup>3</sup>	Microhardness of phases, MPa	
				I $\alpha$	II $\beta$
In <sub>2</sub> Te <sub>3</sub>	CuZn <sub>2</sub> InT <sub>4</sub>			R=0,15 N	R=0,20 N
100	0,0	890, 940	5,78	1660	-
97	3,0	850, 953	5,79	1690	-
95	5,0	943, 1003	5,79	1750	-
93	7,0	953, 1043	5,80	1750	-
90	10	953, 1023, 1053	5,80	1750	-
85	15	953, 1023, 1078	5,81	-	-
80	20	953, 1023, 1000	5,82	-	-
70	30	923, 1023, 1140	5,83	-	2680
60	40	923, 1023, 1153	5,84	-	2680
50	50	923, 1023, 1173	5,85	-	2680
40	60	923, 1023, 1193	5,86	-	2680
30	30	923, 1023, 1213	5,88	-	2690
20	80	923, 1023, 1243	5,90	-	2690
10	90	923, 1023, 1253	5,98	-	2690
0,0	100	1308	5,96	-	2650

At defining microhardness of the In<sub>2</sub>Te<sub>3</sub>-CuZn<sub>2</sub>InT<sub>4</sub> system alloys two rows of values were received: an a light phase (1660-1750) MPa, corresponding to a solid solutions on base of In<sub>2</sub>Te<sub>3</sub>, on grey phase 2650-2690 MPa corresponding to  $\beta$ -solid solutions on base of CuZn<sub>2</sub>InT<sub>4</sub>.

To confirm the results of DTA and MSA of the system alloys there was made X-ray analysis.

The initial compounds and intermediate alloys were compared relying on experimentally calculated of interplanc distances and intensities lines.

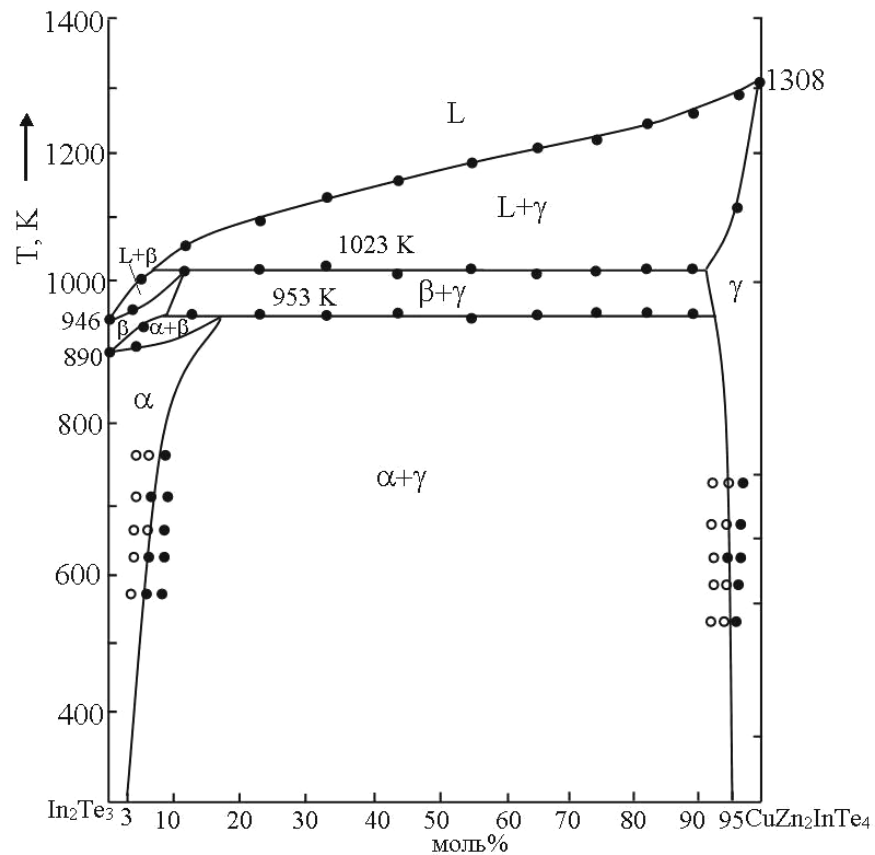
The results of XPhA in a form of diffractograms made up of X-ray patterns of the alloys, containing 40 and 80 mol. % CuZn<sub>2</sub>InT<sub>4</sub> are presented in Fig.1.



**Fig. 1.** Sahemes of the  $\text{In}_2\text{Te}_3\text{-CuZn}_2\text{InT}_4$  system alloys containing  
1-  $\text{In}_2\text{Te}_3$ , 2 – 40, 3 – 80, 4 – 100 mol.%  $\text{CuZn}_2\text{InT}_4$

An aggregate of the results DTA, MSA, XPA and the determined values of microhardness and density permitted to plot the phase diagram of state of the  $\text{In}_2\text{Te}_3\text{-CuZn}_2\text{InT}_4$  (Fig. 2).

It is established that the system is quasibinary of peritectic type. Liquids of the system consist of two branches of the corresponding to primary isolation of,  $\beta$  and  $\gamma$ -phase, formed on the basis of  $\text{In}_2\text{Te}_3$  and  $\text{In}_2\text{Te}_3\text{-CuZn}_2\text{InT}_4$ .  $\beta$ -phase characterizes high temperature modificational transition of the compound  $\text{In}_2\text{Te}_3$ . under effect of  $\text{CuZn}_2\text{InT}_4$  temperature of this transition rises from  $\sim 890$  K to  $\sim 953$  K, and then to  $\sim 1023$  K. As well it is seen from state diagram that on the basis of initial components of the system under study, there exist the regions of solid solutions, the boundaries of which at 300 K bead the sides of  $\text{In}_2\text{Te}_3$  to  $\sim 3$  mol.%  $\text{CuZn}_2\text{InT}_4$  and on side of  $\text{CuZn}_2\text{InT}_4$  to  $\sim 5$  mol.%  $\text{In}_2\text{Te}_3$ . All the compositions of the system (except  $\alpha$  and  $\gamma$ -solid solutions) complete crystallization in two-phase mixture.

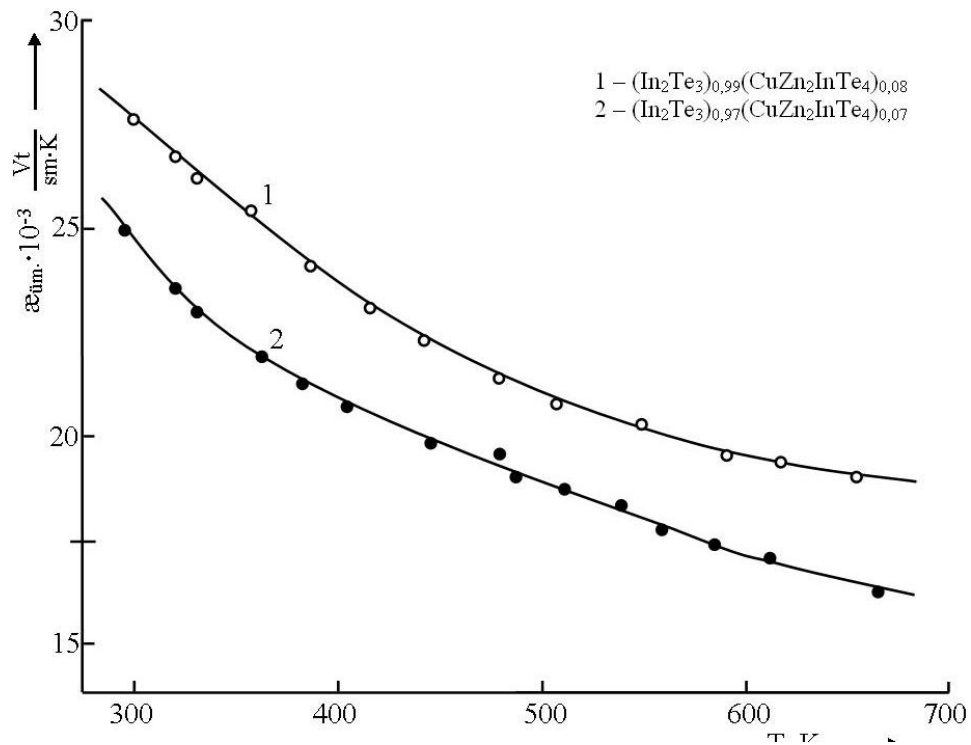


**Fig. 2.** State diagram of the  $\text{In}_2\text{Te}_3$ - $\text{CuZn}_2\text{InT}_4$  system

For the purpose of clearing up the mechanisms of electronic and phonon processes in homogeneous phases of the system  $\text{In}_2\text{Te}_3$ - $\text{CuZn}_2\text{InT}_4$  there was carried out investigation of temperature dependence of a general (common) heat conductivity and Hall's mobility of current carriers of solid solutions  $(\text{In}_2\text{Te}_3)_{1-x}(\text{CuZn}_2\text{InT}_4)_x$ . In Fig.3 the temperature dependence of common heat conductivity of two compositions of indicated solid solutions, is cited.

As is seen, common heat conductivity for both compositions of solid solutions is being changed by the negative step law. This testifies to normal phonon processes taking place in the alloys under study [7].

An effect of bipolar constituents and other conductivities on common heat conductivity is (not) obvious from then graphs.

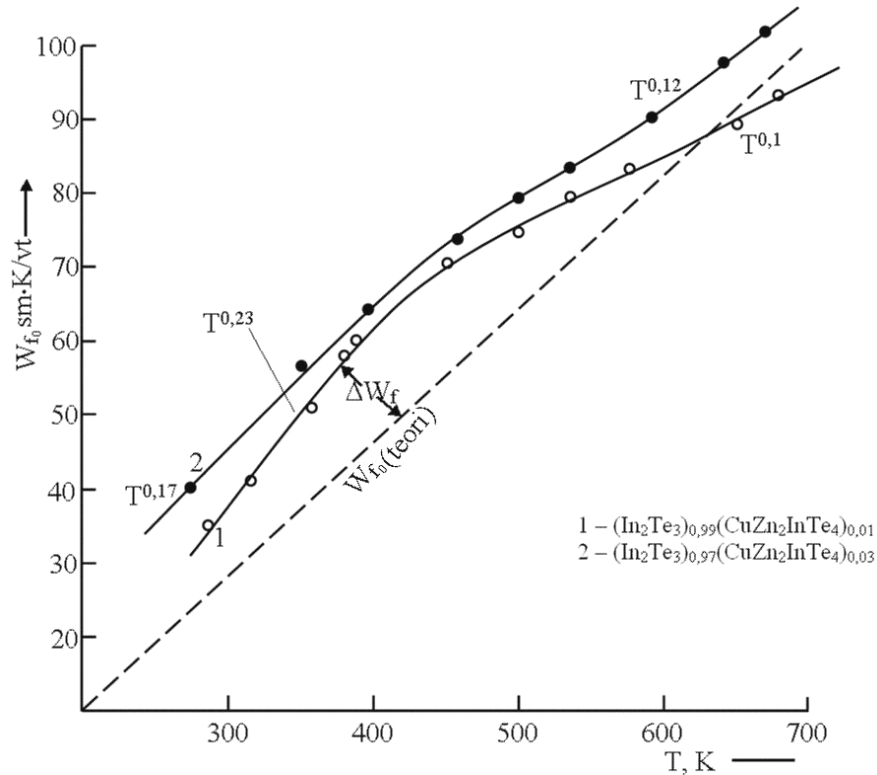


**Fig. 3.** Temperature dependence of overall thermal conductivity of solid solutions  $(\text{In}_2\text{Te}_3)_{1-x}(\text{CuZn}_2\text{InTe}_4)_x$

However, it is known that [8] in chalcogenide compounds heat transfer can be realized by several mechanisms. To make exact the give question we have determined electronic and phonon share of heat conductivity by Wiedemann-Franz law) and plotted their temperature dependences. According to the temperature development of lattice heat conductivity ( $\kappa_{\text{lat.}}$ ) there were defined the reversible values of this parameter for determining temperatures and so plotted temperature dependence of phonon heat resistance ( $W_1$ ) for two compositions of solid solutions  $(\text{In}_2\text{Te}_3)_{1-x}(\text{CuZn}_2\text{InTe}_4)_x$  (Fig. 4).

With increase in temperature for both compositions the rise of phonon heat resistance is observed. However, change of  $W_1$  by temperature for both compositions of solid solutions is not expected. In particular in the composition  $(\text{In}_2\text{Te}_3)_{0.99}(\text{CuZn}_2\text{InTe}_4)_{0.01}$  at temperature slightly more than room's one there

appears additional heat resistance ( $\Delta W_f$ ) of crystalline lattice. It is possible to determine qualitatively its value as  $\Delta W_f = W_{f(ex)} - W_{f(theor)}$ .



**Fig.4.** Temperature dependence of phonon heat resistance of solid solutions  $(\text{In}_2\text{Te}_3)_{1-x}(\text{CuZn}_2\text{InTe}_4)_x$

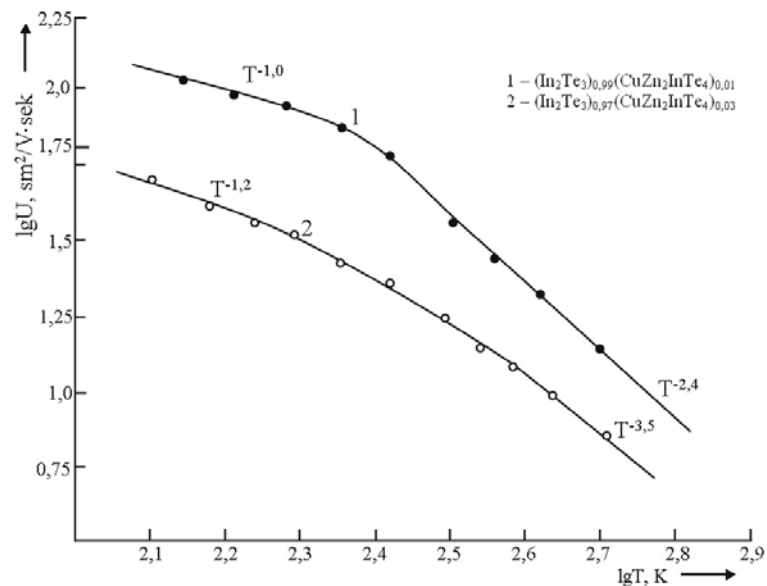
On the graph of dependence  $W_f \sim f(T)$  of the composition is approximately analogical to change  $W_f$  by temperature.

The calculations showed that in the composition  $(\text{In}_2\text{Te}_3)_{0,99}(\text{CuZn}_2\text{InTe}_4)_{0,01}$  heat conductivity changes according to the law  $T^{-(0,10 \div 0,23)}$ , while for the composition  $(\text{In}_2\text{Te}_3)_{0,97}(\text{CuZn}_2\text{InTe}_4)_{0,03}$  the law  $T^{-(0,12-0,17)}$  dominates. This testifies to that heat transfer in the examined materials is realized by one-phonon mechanism. An appearance of the additional phonon heat resistance in a solid solution of the composition  $(\text{In}_2\text{Te}_3)_{0,99}(\text{CuZn}_2\text{InTe}_4)_{0,01}$  indicates to dispersing (phonons from defects vacancy) of crystalline lattice. Such assumption is quite probable as it is known that one third of (of basic material of crystalline lattice)  $[\text{In}_2\text{Te}_3]$  consists of empty places, i.e. cation vacancies [9]. With increasing the



composition of solid solution  $(\text{In}_2\text{Te}_3)_{1-x}(\text{CuZn}_2\text{InTe}_4)_x$  a quantity of the second component, i.e. compound  $\text{CuZn}_2\text{InTe}_4$  these vacancies can be partially filled, i.e. there occurs restoration of crystalline lattice of  $\text{In}_2\text{Te}_3$ . Such supposition is acceptable as a half of the second composition (i.e. compound  $\text{CuZn}_2\text{InTe}_4$ ) consists of there elements, like those in the compound  $\text{In}_2\text{Te}_3$ . the process of filling the empty places also continues in the composition  $(\text{In}_2\text{Te}_3)_{0,97}(\text{CuZn}_2\text{InTe}_4)_{0,03}$ , however with a weak intensity. The quantitative agreement of the temperature change  $W_f$  of this composition with temperature dependence  $W_{f_0}$  testifies in favour of the stated. The law negative values of dependence degree  $W_f \sim f(T)$  testifies to existence of one more mechanism of phonon dispersion-from defects of dislocation type [10].

Temperature dependence of Hall's mobility of the carriers of (electrons), current of the alloys of solid solutions  $(\text{In}_2\text{Te}_3)_{1-x}(\text{CuZn}_2\text{InTe}_4)_x$  is cited on Fig. 5.



**Fig.5.** Temperature dependence of Hall's mobility of the carriers of current of solid solutions  $(\text{In}_2\text{Te}_3)_{1-x}(\text{CuZn}_2\text{InTe}_4)_x$

As is seen, with increasing temperature – dependence curves  $\lg U_n \sim f(\lg T)$  mainly display a tendency to decrease. It has been brought to light that temperature

dependence of Hall's mobility of investigated compositions of solid solutions subjects to the  $T=(2,4\div 3,5)$ . This testifies to that dispersion of the carriers of charge (of electrons) occurs from heat fluctuations of crystalline lattice.

Thus, it is possible to note the following aspects of the influence of the quaternary compound  $\text{CuZn}_2\text{InT}_4$  on the properties of  $\text{In}_2\text{Te}_3$ . It is obvious from the physico-chemical properties that under effect of  $\text{CuZn}_2\text{InT}_4$  the temperature of phase transition rises. As well, the values of microhardness of  $\text{In}_2\text{Te}_3$ , interaction of initial components increase and the character of phase formation is relation is relatively simple. In a field of thermophysical properties there was observed monotony of the mechanisms of dispersing electrons and phonons, whereas there would be expected more complicated mechanisms in the events of transfer of charge and heat. Under effect of  $\text{CuZn}_2\text{InT}_4$  in crystalline lattice of  $\text{In}_2\text{Te}_3$  there takes place filling the empty knots (vacancies).

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