

PHYSICOCHEMICAL AND SOME ELECTROPHYSICAL PROPERTIES OF IN₂TE₃-NI₃TE₄ SYSTEM ALLOYS

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Abstract- The In₂Te₃-Ni₃Te₄ system was investigated by complex physical and chemical analysis methods and its phase diagram was plotted. The system is quasi-binary with limited regions of solid solutions based on both initial components, whose boundaries at 300 K reach ~10 mol% In₂Te₃ and ~5 mol% Ni₃Te₄. The temperature dependences of the total thermal conductivity and the Hall mobility of charge carriers was plotted and it was found that the main role in heat transfer in (In₂Te₃)_{1-x}(Ni₃Te₄)_x belongs to the single-phonon mechanism. At low temperatures electrons are scattering going on ionized impurity atoms, at high temperatures - on thermal lattice vibrations.

Keywords: Quasi-Binary System, Solid Solution, Crystal Structure, Lattice Parameters, Thermal Conductivity, Hall Mobility, Pycnometric Density, Thermogram, Phase Diagram.

I. INTRODUCTION

Indium and nickel tellurides are promising materials for solid-state electronics devices [1-3]. Obtaining new complex homogeneous phases on their basis can expand the fields of application of these compounds, as well as enrich scientific information in the field of inorganic materials science [4].

In₂Te₃ melt congruently at ~940 K and has polymorphous conversion at 890 K [5]. The reports on crystal structure of this compound are contradictory. In particular, the authors [6] indicate that In₂Te₃ crystallizes in cubic syngony with ZnS structure and lattice parameter $a=18.480$ Å. The recent investigation in this direction has been carried out in [7], according to results of which a parameter of crystal lattice is $a=18.486$ Å. However, there exist publications, where one and a half indium telluride crystallizes in a Bi₂Te₃-type structure [8].

Synthesized by us and used in the present work as the initial component of the In₂Te₃-Ni₃Te₄ system one and a half indium telluride, according to the results of X-ray phase analysis, has a cubic crystal lattice with $a=6.165$ Å. Density of In₂Te₃ equals to 5.78 g/cm³ and microhardness is $H_{\mu}=1660$ MPa. Electric conductivity is in the range $\sigma=10^{-5}$ - 10^{-6} Om⁻¹·cm⁻¹, total thermal conductivity is $\alpha_{tot}=3.68 \times 10^{-3}$ kcal·m⁻¹·sec⁻¹·deg⁻¹ and the band gap is $\Delta E_g=1.0$ eV [9].

The information on the existence and properties of the Ni₃Te₄ compound is different. For example, in [10] it was shown that there are two stable congruently melting compounds Ni₃Te₄ and Ni₃Te₂ in the Ni-Te binary system. Such a homogeneous phase as NiTe and NiTe₂ does not reflect on the phase diagram presented by these authors.

In [10], there is information about the high-temperature modification β' of the Ni₃Te₄ compound, which below 1065 K passes into the low-temperature β -phase. However, neither in our investigations [11], nor in works of other authors [12] this phase was not detected. Although the authors of [12], investigating the thermodynamic parameters of Ni₃Te₄ in the temperature dependence of the heat capacity, found some weakly-expressed extremes that, according to the authors, are associated with the presence of vacancies in the crystal structure of this compound.

In [13] the Ni₃Te₄ compound is designated as the δ -phase, which crystallizes in the hexagonal closest packing with parameters $a=3.968$ Å, $c=5.362$ Å, pycnometric density ~7.79 g/cm³ and exhibits a metallic conductivity.

II. EXPERIMENTAL PART

The alloys of the In₂Te₃-Ni₃Te₄ system were obtained by direct synthesis from the In₂Te₃ and Ni₃Te₄ components in quartz ampoules evacuated to 10⁻³ mmHg. Depending on the composition of the alloys, synthesis was carried out in 1100-1250 K temperature range. Homogenizing annealing of all alloys was implemented at ~873 K within 240 h.

The alloys were compact, had a black and gray color, were resistant to air humidity, water, organic solvents, they dissolve only in mineral acids. The physicochemical analysis was performed similarly to the procedure given in [14]. The electrophysical properties were measured on polycrystalline samples of the parallelepiped shape according to the method [15].

III. RESULTS AND DISCUSSION

Based on the results of complex methods, a phase diagram of the In₂Te₃-Ni₃Te₄ system has been plotted (Figure 1). It was found that the system is quasi-binary. The phase transformations typical for In₂Te₃ compound are also reflected in phase diagram of system under study.

Under the influence of Ni_3Te_4 , the $\alpha \rightarrow \beta$ phase transition characteristic to In_2Te_3 has a peritectic nature. A stable α -phase transition into an unstable β -phase is observed on thermograms of alloys enriched in one and a half indium telluride. In general, three series of isothermal effects were found on alloys thermograms. The first effects correspond to the temperature ~ 973 K and reflect the reaction $\beta + \alpha \leftrightarrow \alpha + \gamma$. On the basis of this reaction, the majority of the compositions (except for solid solutions based on both initial components) complete the crystallization in the two phase mixture form.

The second series of thermal effects (at ~ 1073 K) reflects the equilibrium state β and γ modifications of the initial tellurides and is characterized by reaction $L + \gamma \leftrightarrow \beta + \gamma$. The third series of thermal effects reflect the melting points of individual compositions of In_2Te_3 - Ni_3Te_4 system alloys.

On the basis of both initial components, regions of solid solutions were found, which boundaries at 300 K reach on the In_2Te_3 side to ~ 10 mol%, and on the Ni_3Te_4 side to ~ 5 mol.%.

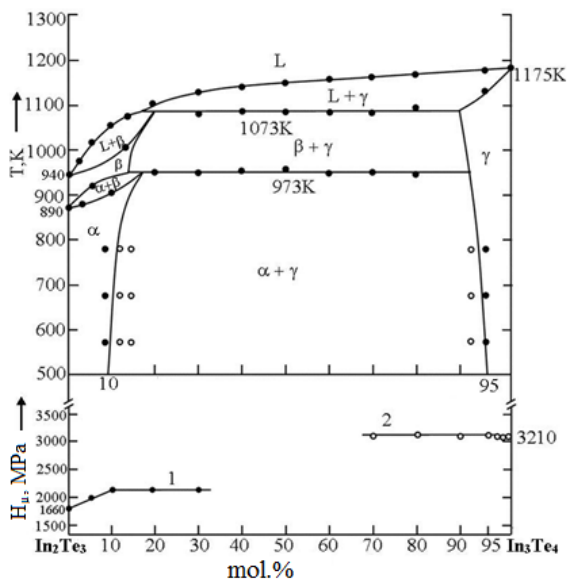


Figure 1. Phase diagram of the In_2Te_3 - Ni_3Te_4 system and microhardness values changing depending on the composition of the alloys (graph at the bottom)

Somewhat wide homogeneous region on the basis of one and a half indium telluride seems to be the result of the observation of defectiveness (such as vacancies) of the structure [16]. As can be seen from the phase diagram, the addition of Ni_3Te_4 in In_2Te_3 raises the temperature of the phase transitions and they assume a peritectoid character. Upon cooling solid solutions based on In_2Te_3 , crystallization centers are formed, the speed of which may be either decelerating or accelerating. If the speed of such centers is decelerating, then the phase transition temperature will increase, as it happens in the In_2Te_3 - Ni_3Te_4 system under investigation. The main role in this phenomenon belongs to the process of heat exchange between the phases of interacting substances.

In a lower part of Figure 1 the dependence of microhardness values on the alloys composition of the system under investigation are presented. An increase in the value of H_μ in the detected solid solutions indicates the formation of substitutional solid solutions. The X-ray diffraction pattern of the initial In_2Te_3 and solid solution of composition 95 mol% In_2Te_3 +5 mol% Ni_3Te_4 was illustrated in Figure 2. As can be seen, the intensity of In_2Te_3 X-ray lines is preserved in the solid solutions obtained on its basis.

The temperature dependences of the specific electrical conductivity (σ), total thermal conductivity (α_{tot}), Hall charge carrier mobility (U_x) and phonon thermal resistance (W_f) on $(\text{In}_2\text{Te}_3)_{0.95}(\text{Ni}_3\text{Te}_4)_{0.05}$ and $(\text{In}_2\text{Te}_3)_{0.90}(\text{Ni}_3\text{Te}_4)_{0.10}$ polycrystalline samples were investigated in the 300-850 K range.

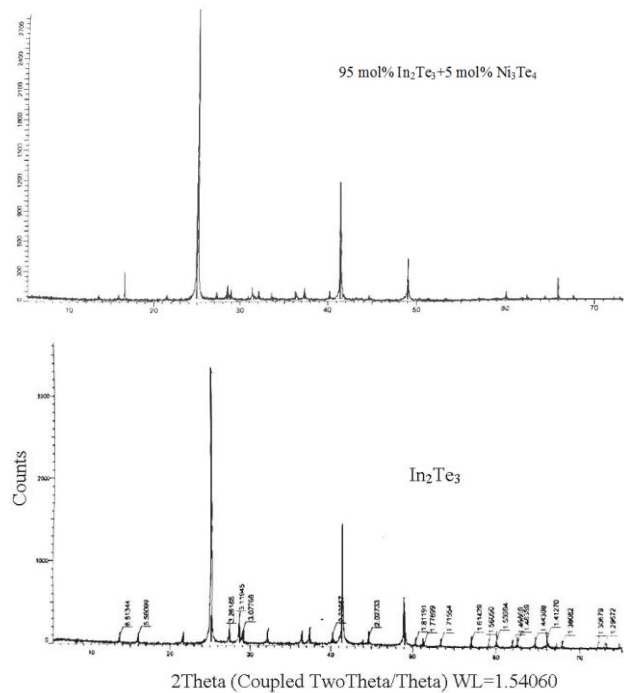


Figure 2. X-ray patterns of an initial In_2Te_3 (1) and solid solution of composition 95 mol% In_2Te_3 +5 mol% Ni_3Te_4 (2)

Figure 3 shows the temperature dependences of the specific electrical conductivity of solid solutions of these compositions. As can be seen, the $\log \sigma \sim f(10^3/T, K)$ dependence has semiconductor nature with a wide range of impurity conductivity. From 573 K, a sharp increase in electrical conductivity is observed, due, apparently, to the beginning of its own conductivity region. According to the change tangent of the angle of the graphs in this area, the values of the width of the band gaps were calculated for both compositions $(\text{In}_2\text{Te}_3)_{0.95}(\text{Ni}_3\text{Te}_4)_{0.05}$ and $(\text{In}_2\text{Te}_3)_{0.90}(\text{Ni}_3\text{Te}_4)_{0.10}$.

Inset in Figure 3 shows the graphs of the change in the band gap values as a function of composition of solid solutions $(\text{In}_2\text{Te}_3)_{1-x}(\text{Ni}_3\text{Te}_4)_x$. The addition of Ni_3Te_4 is accompanied by decreasing in band gap of In_2Te_3 . Decreasing in ΔE_g in solid solutions $(\text{In}_2\text{Te}_3)_{1-x}(\text{Ni}_3\text{Te}_4)_x$ may be due to the fact that the three-dimensional heteropolar chemical bond shows a leading character with formation of solid solutions based on In_2Te_3 .

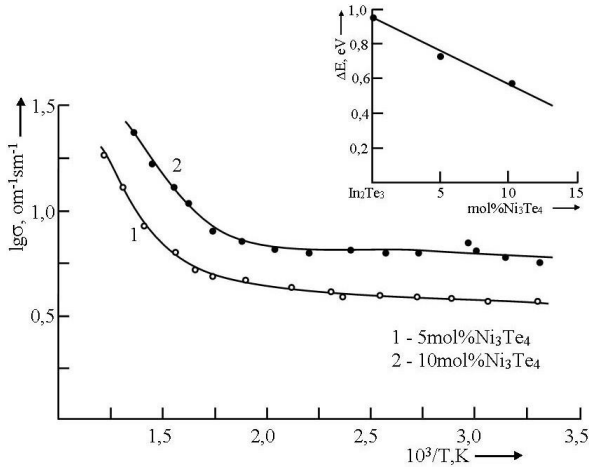


Figure 3. Electrical conductivity of the alloys of the $(\text{In}_2\text{Te}_3)_{1-x}(\text{Ni}_3\text{Te}_4)_x$ solid solutions vs temperature and dependence of values of thermal width of the band gap on composition of solid solutions (in the inset)

The results of studies of the temperature dependence of the Hall mobility of charge carriers $(\text{In}_2\text{Te}_3)_{1-x}(\text{Ni}_3\text{Te}_4)_x$ solid solutions are shown in Figure 4. Up to ~ 353 K, in both compositions based on In_2Te_3 , an increase in the mobility of charge carriers is observed.

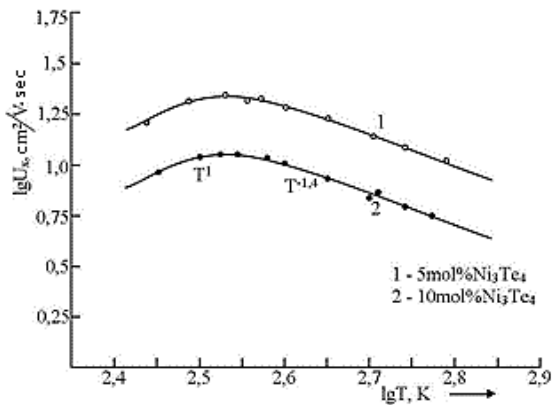


Figure 4. Dependence of Hall mobility of charge carriers of alloys of $(\text{In}_2\text{Te}_3)_{1-x}(\text{Ni}_3\text{Te}_4)_x$ solid solutions on temperature

The change in mobility in this region obeys the law $\sim T^{1.0}$, which indicates the scattering of charge carriers from ionized impurity centers. Passing through a gentle maximum, the mobility curves then show a noticeable decrease in temperature. The $\sim T^{-1.4}$ law prevails in this region, which indicates the scattering of electrons from thermal vibrations of the crystal lattice. The numerical value of the degree of temperature does not exclude the action of optical phonons in the process of scattering of charge carriers. Moreover, a flat maximum in the curves of $\log U_H \sim f(\log T)$ indicates to scattering of current carriers from polarized optical vibrations of the crystal lattice.

In Figure 5 the temperature dependences of the total thermal conductivity of alloys of $(\text{In}_2\text{Te}_3)_{1-x}(\text{Ni}_3\text{Te}_4)_x$ solid solutions is shown. The change in thermal conductivity with temperature occurs according to a negative power law, which indicates the presence of normal phonon processes in the samples under study [17]. However, it is known that in chalcogenide

compounds heat transfer can be realized by several mechanisms [18]. To clarify this issue using the Wiedemann-Franz formulas ($\alpha_{elec} = L\sigma T$, where L is Lorenz number, σ is electrical conductivity, T is temperature, at which thermal conductivity measurements were taken), the electronic component of thermal conductivity of the $(\text{In}_2\text{Te}_3)_{1-x}(\text{Ni}_3\text{Te}_4)_x$ alloys was determined and then using the difference $\alpha_{phonon} = \alpha_{tot} - \alpha_{elec}$ value of phonon component was found.

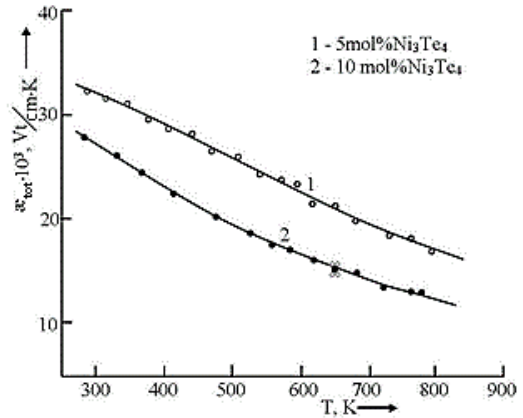


Figure 5. Total thermal conductivity of the alloys of solid solutions $(\text{In}_2\text{Te}_3)_{1-x}(\text{Ni}_3\text{Te}_4)_x$ vs temperature

According to the temperature dependence of lattice (phonon) thermal conductivity, the inverse values of α_{lat} (i.e. thermal resistance ΔW_f) are determined and Figure 6 was plotted. As can be seen, in both compositions of $(\text{In}_2\text{Te}_3)_{1-x}(\text{Ni}_3\text{Te}_4)_x$ solid solutions a straight-line increase of phonon thermal resistance is observed, i.e. there is no additional phonon thermal resistance.

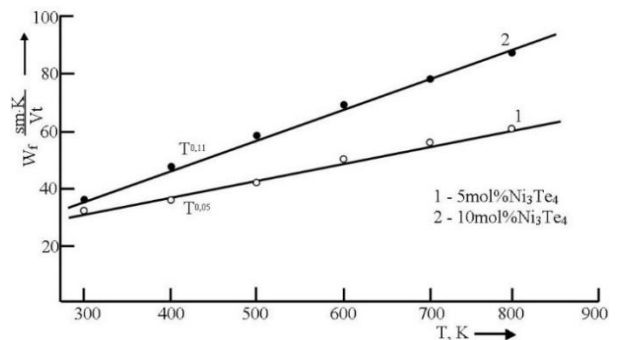


Figure 6. Phonon heat resistance of the alloys of $(\text{In}_2\text{Te}_3)_{1-x}(\text{Ni}_3\text{Te}_4)_x$ solid solutions vs temperature

It can be assumed that due to the closeness of the atomic radii of indium and nickel in the solid solutions under investigation, there is an intensive filling of vacancies in the crystal lattice takes place, which is why, like other compositions of solid solutions based on In_2Te_3 [19], the appearance of an additional phonon thermal resistance in $(\text{In}_2\text{Te}_3)_{1-x}(\text{Ni}_3\text{Te}_4)_x$ alloys is absent.

From the temperature dependence of W_f , it was determined that the thermal conductivity obeys the law $T^{-(0.05-0.11)}$, which indicates a single-phonon mechanism of heat transfer in solid solutions $(\text{In}_2\text{Te}_3)_{1-x}(\text{Ni}_3\text{Te}_4)_x$.

IV. CONCLUSIONS

The study of the physicochemical properties of the alloys showed the quasi-binary nature of the $\text{In}_2\text{Te}_3\text{-Ni}_3\text{Te}_4$ system with limited areas of solid solutions based on both initial components. It was established that under the influence of Ni_3Te_4 the phase transition temperature inherent in In_2Te_3 increases.

In the electrophysical properties of $(\text{In}_2\text{Te}_3)_{1-x}(\text{Ni}_3\text{Te}_4)_x$ solid solutions, the simple nature of the mechanisms of scattering of electrons and phonons is observed. The closeness of the atomic radii of In and Ni leads to an intense filling of vacancies of the of the defective crystal lattice In_2Te_3 .

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BIOGRAPHIES



Chingiz Ildirim Abilov was born in Shusha, Azerbaijan in 1945. He defended his thesis on specialty "Technology of semiconductors and electronic materials" and received the Ph.D. degree in Technics in 1980. He defended his doctoral thesis on the specialty "Technology of semiconductors and electronic materials" and received the Doctor of Technical Sciences in 1994 and was awarded the Associate Professor in 1996. He is currently a Professor at Electronics Department of Azerbaijan Technical University, Baku, Azerbaijan. He is the author of 265 publications, including 10 copyright certificates, 1 handbook, 2 monographs, and 5 textbooks. He has been awarded "Progress" medal in 2011. His scientific areas include $A^{III}B^{VI}$, $A_2^VB_3^{VI}$ and $A^{IV}B^{VI}$ type compounds and solid solutions based on them, the study of their physicochemical, electrophysical properties, the development of technology of thermo- and photovoltaic converters.



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