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THEORETICAL MODELS OF ORDERED ALLOYS OF THERMOELECTRIC MATERIALS BASED ON *Bi-Sb-Te*

Theoretical models of ordered alloys of promising thermoelectric materials of Bi-Sb-Te ternary systems have been developed. Diagrams of distribution of phase regions in such systems have been constructed using binary state diagrams of the initial components (Bi-Sb, Bi-Te, Sb-Te). Calculations of electron density redistribution, dissociation energy, and effective radii of chemical bonds forming the crystal structure of Bi-Sb-Te depending on interatomic distances are given.

Key words: theoretical models, chemical bond, effective radii, dissociation energy, state diagrams, non-equivalent hybrid orbitals (NHO).

Introduction

Antimony compounds and tellurium compounds are considered to be promising thermoelectric materials among binary compounds [1]. Depending on the mode of heat treatment and the method of cooling, antimony and tellurium alloys can crystallize in accordance with stable and metastable state diagrams [2]. The nature of the chemical bond in such alloys can vary from metallic to ionic, covalent and intermediate.

Considering also that the search for new thermoelectric materials is increasingly reduced to the need of studying multicomponent systems, the research of ternary systems based on *Bi-Sb-Te* is becoming especially relevant both from the standpoint of chemical bond and from the standpoint of phase diagrams. The need to conduct such studies is due to the fact that ternary systems are complex, nonlinear, and known theoretical approaches to problems of phase transformations of simple systems no longer detect the conditions for the appearance of the desired properties with the prospect of changing them in the desired direction. There is no consistent theory of phase transformations from the standpoint of chemical bond yet. This, in turn, raises the question of the relationship between physics and chemistry in technological research.

Physics plays a major role in modern natural science. Not only quantum mechanics, but much earlier thermodynamics and the science of electricity gave rise to new directions of chemical and physico-chemical research. The emergence of quantum chemistry has changed traditional ideas about the relationship between these two scientific disciplines.

There is a point of view that scientific knowledge develops intensively and extensively. Intensive development means a significant deepening of knowledge, which leads to a new view of nature. Along this path, quantum mechanics arose. Then these ideas and concepts, which arose on the way of intensive development, are added to new facts and used to solve new problems. Along this path, quantum chemistry arose.

In each area of knowledge, one fundamental theory can be distinguished. But the theory does not consist of just the foundation. Non-fundamental theoretical constructions (they are called theories of medium generality) model reality in their own way and solve scientific problems in their own way. They can be considered as "models of reality", then fundamental theories can be called "models of models".

Principles of quantum mechanics are the foundation of the modern theory of the structure of matter. In the course of reduction, which means reducing a complex process to a simpler one by complicating the original model, quantum mechanics is overgrown with approximate methods, hypothetical and model representations and “goes over“ into quantum chemistry [3].

At the same time, the original model of quantum mechanics changed somewhat (the model of the hydrogen atom to the model of the hydrogen molecule) and the basis of the theory is no longer a one-center, but a two-center problem. In this regard, quantum chemistry is often called chemical bond theory. Now quantum chemistry explains and implies various properties of crystals based on the electronic structure of molecules.

In reality, the structure of scientific knowledge is even more complicated. Each theoretical construction of an average degree of generality contains within itself another concept of an average degree of generality, and that is even narrower, and so on until the "degeneration" of theoretical knowledge into some concepts of "common sense" occurs.

It is this approach that has made it possible to unite the multilayer structure of theoretical knowledge in different fields. In this case, the structural element of the system under consideration is no longer the hydrogen atom, as the original model for solving the Schrödinger equation in quantum mechanics, but a two-center formation – a model of the hydrogen molecule. This unification became possible due to interdisciplinary synthesis. The basis of such synthesis, according to [4], is the unification of the electronic, oscillatory and configurational components of the energy of the "molecule" as a single whole, as a general measure of different types of interaction. In this case, energy is considered both from the position of its organizational structure and from the position of the state function. This made it possible to calculate the ordering processes in alloys by statistical methods; regularities of the formation of the short-range order of the chemical bond in melts – by quantum-chemical methods; redistribution of electron density and dissociation energy of non-equivalent chemical bonds in ternary systems – by methods of microscopic theory using solutions of inverse problems and molecular models [5].

This work is a continuation of complex studies [4] and is devoted to the construction of theoretical models of ordered alloys of ternary systems of promising thermoelectric materials based on *Bi-Sb-Te*. The use of the triangulation method was new in the study of tellurides and antimonides [6]. In chemistry, this method allows for the distribution of ternary systems into simpler binary ones, taking into account the patterns of formation of compounds; the formation of solid solutions and mechanical mixtures. In this paper, the inverse problem of triangulation is solved: using the known phase diagrams of binary systems [7], taking into account the chemical interaction between the elements *Bi*; *Te*; *Sb*, a diagram of the distribution of phase regions for various isothermal sections of *Bi-Te*, *Bi-Sb*, *Sb-Te* in the *Bi-Sb-Te* system is constructed, and the parameters of phase transformations are calculated theoretically using quantum chemistry methods.

Theoretical models of *Bi-Sb-Te* state diagrams

When constructing theoretical models of *Bi-Sb-Te*, it was necessary to summarize the results of experimental studies of binary state diagrams of *Bi-Sb*, *Bi-Te* and *Sb-Te* [7]; physicochemical properties and the results of studying quantum regularities of the initial components [2]. This will make it possible to establish the boundaries of phase equilibrium in the liquid-crystal regions (melting diagrams) and predict cases of incongruent melting of metastable phases.

In this regard, the choice of bismuth as a constituent component of *Bi-Sb-Te* was not accidental. First of all, bismuth is part of Bi_2Te_3 – the most widely used material in thermoelectricity [8]. In addition, bismuth in compounds can have different oxidation states, which can take values from – 3 to + 5. Pentavalent bismuth salts are strong oxidizers. In humid air, bismuth is covered with an oxide layer. At high temperature, bismuth burns to Bi_2O_3. It does not dissolve in hydrochloric and dilute sulfuric acids. It dissolves easily in nitric acid and aqua regia.

Bismuth is extracted from concentrates by pyro- or hydrometallurgical methods. Much bismuth is extracted from copper and lead production waste. Metallic bismuth is used to make low-melting alloys as a coolant in nuclear reactors in devices for various purposes. Bismuth compounds are used in medicine as binding antiseptic and adsorption agents for the treatment of stomach and intestinal ulcers, skin and mucous diseases.

Such a wide set of physicochemical properties of Bi and the ability to change them under certain conditions allows forming the short-range order of the chemical bond in *Bi-Sb-Te* compounds and, accordingly, the physicochemical properties of the obtained material in the desired direction.

The choice of antimony as a component of the ternary *Bi-Sb-Te* system was also not accidental. Research into antimony-based semiconductor materials is currently of great value [4]. Increased attention to antimony is also due to its inherent polymorphic transformations, since each modification has a corresponding stability field of the state diagram, which leads to technological difficulties.

Antimony is known in four modifications: ordinary – crystalline and three amorphous – yellow, black and explosive. Under normal conditions, only crystalline antimony with a rhombohedral structure, $a = 0.45064$ μm, $\alpha = 57.1°$, is stable. Crystals of pure antimony consist of cells of a rhombohedral structure, the distance between atoms within which is equal to 2.87 Å, and the angles between covalent bonds are 94°. Melting antimony changes the nature of bonds from covalent to metallic. At the same time, the coordination number increases to six, and the interatomic distances increase from 2.87 Å to 2.89 Å. The type of crystal lattice also changes - from rhombohedral to hexagonal. The hexagonal cells are arranged so that the shortest distance between atoms of adjacent layers is 3.38 Å, and the lattice periods are $a = 4.307$ Å; $c = 11.127$ Å. Antimony easily forms alloys with many metals – antimonides. The most common antimonides are indium, gallium, aluminum, cobalt, zinc, tellurium, cadmium, calcium, mercury, chromium, iron, cesium, potassium and sodium.

In addition, according to the state diagram (*Bi-Sb*), both components (*Bi* and *Sb*) are infinitely soluble in liquid and solid states and do not form chemical compounds. At the same time, the state diagrams of *Bi-Te* and *Sb-Te* are diagrams with eutectics, where both compounds and solid solutions can be formed. In this regard, the task was set: to calculate the parameters of chemical bonds depending on interatomic distances and to construct phase distribution schemes in the *Bi-Sb-Te* system.

When building theoretical models, the results of experimental studies of binary systems were summarized; physicochemical properties and quantum regularities of the initial components, which made it possible to determine the quantitative ratios of congruent and incongruent melting.

The obtained results are shown in Figs. 1 – 4, where the following designations are entered:

α – solid phase based on *Bi*;

β – solid phase based on *Te*;
γ – solid phase based on *Sb*;
δ – solid phases based on *Bi-Sb*;
ρ – solid phases based on *Sb-Te*;
ε – solid phases based oni *Bi-Te*;
σ – solid phases based on *Bi-Sb-Te* intermediate compound;
L – liquid.

Fig. 1 shows the diagram of distribution of *Bi-Sb-Te* phase regions in the solid state. This approach made it possible to trace the division of the *Bi-Sb-Te* ternary system into six ordered ternary subsystems. It should also be noted that in the presence of additional experimental data, the number of ordered subsystems may be larger. This makes it possible to study in more detail the eutectic, peritectic, phase transitions of stable and metastable phases, the formation of short-range chemical bond order in ternary systems depending on the interatomic distances in a narrower range of concentrations.

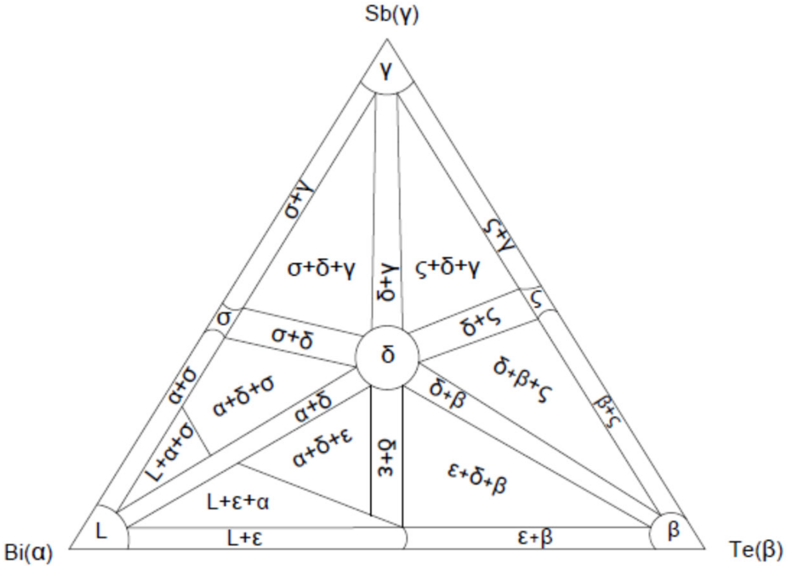

Fig. 1. Diagram of distribution of Bi-Sb-Te phase regions in the solid state.

Fig. 2 shows an isothermal section at a temperature of *t* = 300 °C. This temperature is higher than the melting point of bismuth (271.3 °C) and lower than the melting point of tellurium (450 °C) and antimony (630.5 °C). Part of the section (*Bi-Te*) and (*Bi-Sb*) is occupied by the liquid (*L*), and the two-phase equilibrium (*L*, α), (*L*, ε), (*L*, δ) is carried out by primary crystals α and crystals ε and β based on *Bi-Te* and *Bi-Sb*. In contrast to the previous case, the section contains conoid triangles with equilibrium phases (*L* + α + δ) and (*L* + α + ε), which are formed by primary crystals based on *Bi-Sb* and *Bi-Te* compounds. This division of ternary systems into separate sectors of dual state diagrams makes it possible to study the processes of formation of the short-range order of chemical bond and the fine structure of cooling and heating of individual elements depending on their environment in ternary systems.

Fig. 3 shows an isothermal section at a temperature of *t* = 425 °C, which is higher than the melting temperature of bismuth and higher than the temperatures of eutectics $Bi_{0.1}Te_{0.9}$ (*t* = 413 °C) and $Sb_{0.1}Te_{0.9}$ (*t* = 424 °C). In this case, liquid *L* occupies a larger part of the section (*Bi-Sb*) than in the previous case at *t* = 300 °C, and the equilibrium phases with conoid triangles (*L* + α + ε) and (*L* + α + δ) are replaced by phases (*L* + ε + δ).

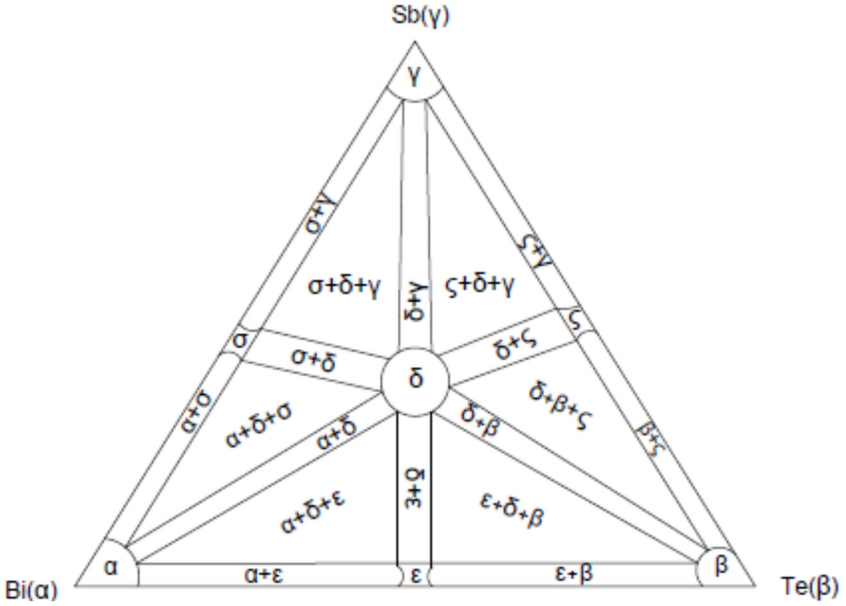

Fig. 2. Bi-Sb-Te isothermal section at t = 300 °C.

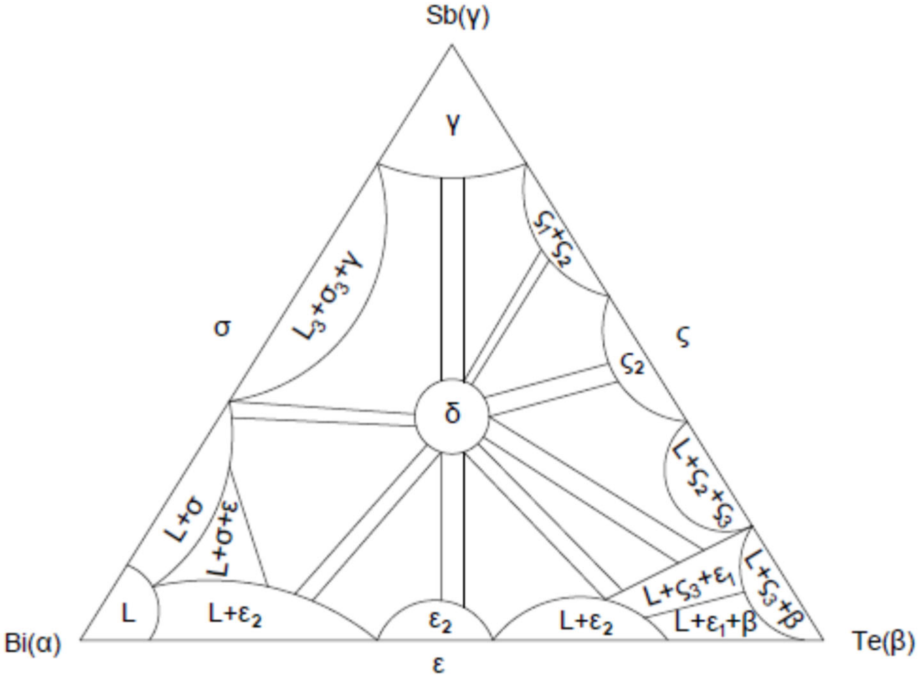

Fig. 3. Bi-Sb-Te isothermal section at t = 425 °C.

On the section (*Te-Sb*), the equilibrium phases ρ_1 ($Sb_{0.72}Te_{0.28}$); ρ_2 ($Sb_{0.4}Te_{0.6}$); ρ_3 ($Sb_{0.1}Te_{0.9}$) are clearly delineated. In this case, the compositions of phases ρ_1 and ρ_2 at this temperature remain stable and the concentration of components γ and ρ corresponds to the state diagram (*Te-Sb*), and does not change upon cooling. At the same time, in the area of tellurium concentrations from 60 % to 89 %, with a decrease in temperature from 622 °C to the eutectic of 425 °C, crystals of composition ρ_2 are released and the composition of the liquid changes towards increasing the component ρ_3. At the same time, the equilibrium phases ($L + \delta + \rho$) are replaced by intermediate phases ($L + \rho_3 + \sigma$) and ($L + \sigma + \rho_2$). This makes it possible to study the fine structure of the formation of intermediate compounds in ternary systems depending on the concentration of the initial components.

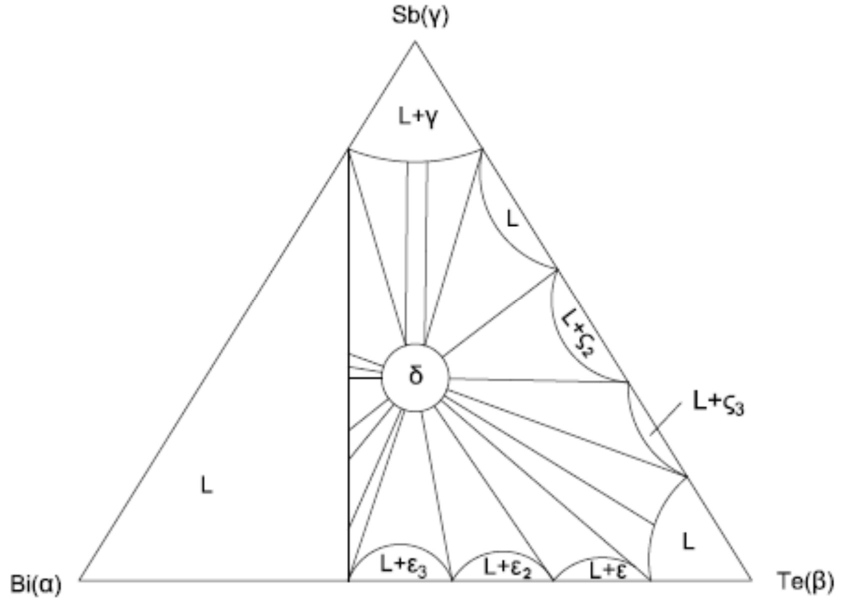

Fig. 4. Bi-Sb-Te isothermal section at t = 550 °C.

Fig. 4 shows an isothermal section at a temperature of t = 550 °C. In this case, a liquid phase is observed on the *Bi-Sb* diagram in the segment up to 75 % *Sb*. Both the solid phase of antimony and solid solutions based on *Sb-Bi* are observed in the segment 75 – 10 % *Sb*. A similar situation is observed in the *Sb-Te* diagram. Further, 25 – 35 % *Te* – a liquid phase is observed. In the 35 – 75 % segment, polymorphic transformations occur with the formation of Sb_2Te_3, and then – a liquid phase. As for the *Bi-Te* state diagram, in the segment from 30 to 50 %, polymorphic transformations occur with the formation of Bi_2Te_3, and in the other two – a liquid.

Thus, the above isothermal sections made it possible:

1. To establish the limits of phase equilibrium, their dynamics of change in the liquid-crystal regions and the region of existence in equilibrium of solid solutions.
2. To separate the boundaries of eutectic and peritectic state diagrams.
3. To predict cases of incongruent melting of chemical compounds of different composition.

However, it should be noted that isothermal sections alone do not provide the values of the phase transition parameters of multicomponent systems. Methods are needed that combine experimental approaches with calculations of the interaction energy in both phases when constructing phase diagrams of ternary systems. This will allow combining empirical information on the properties of atoms based on the experience and traditions of the crystal-chemical approach with analytical relationships reflecting the quantum laws of interatomic interaction; statistical laws – with the electron configurations of interacting atoms and the formation of a chemical bond between them.

Theoretical models of chemical bonding of ordered *Bi-Sb-Te* alloys

The theoretical analysis of empirical dependences of crystallization processes is connected with the revision of views on the problem of interatomic interaction. At the same time, there is still no single quantitative method for calculating the electronic structure of compounds and alloys based on both the quantum mechanical and empirical approaches.

On the other hand, taking into account statistical regularities made it possible to obtain the dependence of the number of electrons n on the outer shell of an atom on the Fermi radius r_F, and empirical information on the properties of atoms and ions can be combined on the basis of a crystal chemical approach, introducing the concept of unpolarized ionic radii R_{Un} [9]. Since the functions that include the Fermi radii $r_F = f(n)$ and the equations that include $R_{Un}^{1}1$ determine the electronic configurations of the interacting atoms depending on the length and number of bonds they form, all this gives reason to consider r_F and R_{Un} identical and denote by one symbol R_U – effective ionic radii.

The relationship $tg\alpha = \frac{\Delta lgR_U}{\Delta n}$ where α is the slope of the lines in the coordinates $lgR_U = f(n)$, turned out to be useful when searching for the dependence of R_U on n. The latter should be given special attention. Despite the imperfection, from a theoretical point of view, of empirical criteria (crystal chemical radius, electronegativity, polarizability, and others), their positive role in the systematization of experimental data and the development of ideas about the nature of interatomic interaction does not raise doubts, since the determination of the numerical values of these criteria is based on the generalization of experimental data in combination with their interpretation from the standpoint of quantum chemistry, which contains important information about the nature of interatomic interactions.

A good agreement between the complex of research data on various physical and chemical properties of atoms and their ions and the values of R_U and tgα is given by the postulated [9] dependence: and tgα is given by the postulated [9] dependence:

$$lgR_{UA}^{x} = lgR_{UA}^{0} - xtg\alpha, \tag{1}$$

where $R_{U\mathrm{A}}^{0}$ is the radius of atoms A in an unexcited state, and x is the valence, which allows us to overcome the difficulties of chemical bond theory and obtain a physically substantiated result of interatomic interaction.

The use of ionic radii to describe the processes of formation of a chemical bond by rearrangement of valence shells made it possible to write equation (1) in the form:

$$lgR_{UA}^{+x} = lgR_{UA}^{0} - xtg\alpha_{\mathrm{A}}, \tag{2}$$

$$lgR_{U\mathrm{B}}^{-x} = lgR_{U\mathrm{B}}^{0} + xtg\alpha_{\mathrm{B}}, \tag{3}$$

$$d_1 = R_{UA}^{+x} + R_{U\mathrm{B}}^{-x}, \tag{4}$$

where d_1 is the A – B internuclear distance.

From the point of view of the crystal-chemical approach, the presence of d_{min} and two possible values of effective charges r_{ef} for $d_1 > d_{min}$ is justified by the increase of the internuclear distance when the ionicity and covalency between the same partners change.

The main drawback of this approach is that in many cases the internuclear distances ($A - B$) in crystalline compounds and alloys are smaller than the d_{min} value, and it is impossible to calculate the charge of ions using the diagrams $Z_{ef} = f(d)$. Therefore, difficulties can be overcome only by abandoning the method of interpreting the solution of system (2) – (4) from the point of view of the crystal-chemical approach. Additional criteria are needed to translate system (2) – (4) into the language of quantum chemistry. It should be taken into consideration that in the zone of formation of a chemical bond, the spherical symmetry of the electron density of the initial components is broken and the formation of bonds ($A - B$) is accompanied by the transition of electrons to other directions of interatomic interaction and this bond becomes a donor. This condition is fulfilled if the extraction $(+\Delta e)$ of electrons or their localization $(-\Delta e)$, in the given direction of communication equally change the value of the charges that this pair has at $d_1 = d_{min}$, i.e. $Z_{ef}A(B) = Z_{min}A(B) + \left(\frac{\Delta l}{2}\right)$. These conditions are described by a system of equations:

$$d_1 = R_{UA}^{ZA} + R_{\text{UB}}^{ZB}, \tag{5}$$

$$lgR_{UA}^{ZA} = lgR_{UA}^{0} - (Z_{minA} + \frac{\Delta e}{2})tg\alpha_{\text{A}}, \tag{6}$$

$$lgR_{\text{UB}}^{ZB} = lgR_{\text{UB}}^{0} - (Z_{minB} + \frac{\Delta e}{2})tg\alpha_{B} \tag{7}$$

Externally, equations (2) – (4) and (5) – (7) are similar, but in reality, replacing x with $(Z_{min} + \frac{\Delta e}{2})$ changes their physical meaning: if the function $d_1 = f(Z_{ef})$ according to (2) – (4) is calculated in the approximation $(Z_A = -Z_{\text{B}})$ and is correct from a quantum point of view only when $d_1 = d_{min}$, this is enough for the system (5) – (7) to be solved when d_1 is known. Thus, taking into consideration the quantum interpretation of empirical material made it possible to obtain an expression for the energy of chemical bonds in the form:

$$D_{A-B}^{i} = \left(\frac{C_1(R_{UA}^{0} + R_{UB}^{0})}{(\text{tg}\,\alpha_A + \text{tg}\,\alpha_B)}\right)\left(\frac{C_2 d_i}{d_i^2 - R_{UA}R_{UB}} - \frac{1}{d_i}\right), \tag{8}$$

where $R_{UA(B)}^{0}$, $tg\alpha_{\text{A(B)}}$ are coefficients of equations (2) – (4) for atoms A and B; R_{UA} and, R_{UB} are effective radii of ions in bonds (A-B) with length d_i; i is the number of non-equivalent interatomic distances in the considered compounds; C_1 is a coefficient reflecting the interrelationship of dimensional characteristics of interatomic interaction (measured in electron volts); C_2 is a coefficient that depends on crystal structure and chemical bond and is chosen dimensionless.

The above equations were used in the calculations of effective charges, effective radii and dissociation energies of non-equivalent chemical bonds of compounds and alloys that are part of the ternary system *Bi-Sb-Te.*

The results of calculations of the coefficients of equations (2) – (4) R_U^0 and $tg\alpha$ of the initial components are given in Table 1.

Table 1

Coefficients of equations of the initial components.

Z	Element	R_U^0(Å)	$tg\alpha$
83	*Bi*	1.63	0.068
52	*Te*	1.57	0.076
51	*Sb*	1.45	0.074

Effective charges Δq_{i}, effective radii $R_{U\text{i}}$ and dissociation energies for the nearest neighbours at different interatomic distances $d_{\text{i}}(1 \le i \le 6)$ of the structural modifications of bismuth are given in Table 2.

Table 2

Effective charges (Δq_i), effective radii (R_{Ui}) and dissociation energies $D(\varphi_i)$ depending on interatomic distances d_i of Bi-Bi.

Bi-Bi NHO Parameters	*Bi-Bi*					
	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
d_i (Å)	2.8	2.9	3.0	3.1	3.2	3.3
$R_{U_i}^{Bi}$ (Å)	1.40	1.45	1.50	1.55	1.60	1.65
Δq_i (φ_i)	+ 0.85	+ 0.70	+ 0.50	+ 0.30	+ 0.10	– 0.10
$D(\varphi_i)$ (eV)	2.8540	2.76	2.66	2.58	2.50	2.42

Results of calculations for antimony and tellurium are given in Tables 3 and 4.

Table 3

Effective charges (Δq_i), effective radii (R_{Ui}) and dissociation energies $D(\varphi_i)$ depending on interatomic distances d_i of Sb-Sb.

Sb-Sb NHO Parameters	*Sb-Sb*					
	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
d_i (Å)	2.8	2.9	3.0	3.1	3.2	3.3
$R_{U_i}^{Sb}$ (Å)	1.40	1.45	1.50	1.55	1.60	1.65
Δq_i (φ_i)	0.2	0	– 0.2	– 0.39	– 0.6	– 0.75
$D(\varphi_i)$ (eV)	2.33	2.25	2.18	2.11	2.04	1.98

Table 4

Effective charges (Δq_i), effective radii (R_{Ui}) and dissociation energies $D(\varphi_i)$ depending on interatomic distances d_i of Te-Te.

Te-Te NHO Parameters	*Te-Te*					
	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
d_i (Å)	2.8	2.9	3.0	3.1	3.2	3.3
$R_{U_i}^{Te}$ (Å)	1.40	1.45	1.50	1.55	1.60	1.65
Δq_i (φ_i)	0.65	0.45	0.26	– 0.01	– 0.11	– 0.28
$D(\varphi_i)$ (eV)	2.46	2.37	2.30	2.22	2.15	2.09

As regards the above parameters for *Sb-Te*, *Bi-Te* and *Bi-Sb* compounds, they are given in Tables 5, 6, 7.

Table 5

Effective charges (Δq_i), effective radii (R_{Ui}) and dissociation energies $D(\varphi_i)$ depending on interatomic distances d_i of Sb-Te.

Sb-Te NHO Parameters	*Sb-Te*					
	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
d_i (Å)	2.8	2.9	3.0	3.1	3.2	3.3
$R_{U_i}^{Sb}$ (Å)	1.345	1.444	1.46	1.48	1.53	1.58
$R_{U_i}^{Te}$ (Å)	1.445	1.456	1.54	1.62	1.67	1.72
Δq_i (φ_i)	0.43	0.23	0.03	– 0.16	– 0.32	– 0.52
$D(\varphi_i)$ (eV)	2.39	2.31	2.24	2.16	2.09	2.03

Table 6

Effective charges (Δq_i), effective radii (R_{Ui}) and dissociation energies $D(\varphi_i)$ depending on interatomic distances d_i of Bi-Te.

Bi-Te NHO Parameters	*Bi-Te*					
	φ1	φ2	φ3	φ4	φ5	φ6
d_i (Å)	2.8	2.9	3.0	3.1	3.2	3.3
$R_{U_i}^{Bi}$ (Å)	1.435	1.485	1.536	1.584	1.653	1.681
$R_{U_i}^{Te}$ (Å)	1.365	1.415	1.464	1.516	1.547	1.619
$\Delta q_i\ (\varphi_i)$	0.12	0.08	0.05	0.03	– 0.001	– 0.03
$D(\varphi_i)$ (eV)	2.64	2.57	2.47	2.40	2.31	2.24

Table 7

Effective charges (Δq_i), effective radii (R_{Ui}) and dissociation energies $D(\varphi_i)$ depending on interatomic distances d_i of Bi-Sb.

Bi-Sb NHO Parameters	*Bi-Sb*					
	φ1	φ2	φ3	φ4	φ5	φ6
d_i (Å)	2.8	2.9	3.0	3.1	3.2	3.3
$R_{U_i}^{Bi}$ (Å)	1.852	1.542	1.583	1.642	1.688	1.742
$R_{U_i}^{Sb}$ (Å)	1.315	1.358	1.417	1.458	1.512	1.558
$\Delta q_i\ (\varphi_i)$	0.57	0.35	0.2	– 0.05	– 0.25	– 0.45
$D(\varphi_i)$ (eV)	2.57	2.48	2.40	2.32	2.25	2.18

In the tables, the values of coefficients C_1 and C_2 in the calculations in the first approximation are chosen to be equal to unity.

Discussion of the results

As follows from the obtained results presented in Figs.(1) – (4) and in Tables (1) – (7), the application of a complex approach to technological problems made it possible to build theoretical models combining generalized experimental information based on the analysis of isothermal sections of binary state diagrams of *Bi-Sb*, *Bi-Te* and *Sb-Te* at different temperatures, which allows describing phase transitions; processes of chemical bond formation in ternary systems *Bi-Sb-Te*.

This approach made it possible to describe the processes of formation of interatomic interaction at different technological levels by summarizing versatile theoretical studies from the standpoint of chemical bond. This is, first of all, the formation of a crystal structure based on the initial components (*Bi*, *Sb*, *Te*), where information on the physicochemical properties and chemical relationship of the initial elements (Tables 1 – 4), binary compounds based on a combination of the initial elements (*Bi-Sb*, *Bi-Te*, *Sb-Te*) – (Tables 5 – 7) was taken into account. What was new was that the work included calculations of the dependence of the parameters of the chemical bonds under consideration on interatomic distances (effective radii, redistribution of electron density on the corresponding chemical bonds and the dissociation energy of the bonds that form the crystal structure). This made it possible to establish the boundaries when the same chemical bond, depending on the crystal structure and interatomic distances, can be both donor and acceptor.

What was new in the study of ternary *Bi-Sb-Te* systems was that the method of inverse triangulation was used to construct the diagram of distribution of phase equilibrium regions using information on binary compounds of the initial components and their state diagrams. This made it possible to determine the quantitative relationships between the phases and, in the liquid-crystal regions, to separate the boundaries of the eutectic and peritectic type diagrams to solve problems of stable and metastable phases, and to foresee cases of congruent and incongruent melting.

The obtained results can be used in the development of technological modes of obtaining new *Bi-Sb-Te* materials.

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ТЕОРЕТИЧНІ МОДЕЛІ ВПОРЯДКОВУВАНИХ СПЛАВІВ ТЕРМОЕЛЕКТРИЧНИХ МАТЕРІАЛІВ НА ОСНОВІ *Bi-Sb-Te*

Розроблено теоретичні моделі впорядковуваних сплавів перспективних термоелектричних матеріалів потрійних систем Bi-Sb-Te. Побудовано схеми розподілу фазових областей в таких системах з використанням бінарних діаграм стану вихідних компонентів (Bi-Sb, Bi-Te, Sb-Te). Приведено розрахунки перерозподілу електронної густини, енергії дисоціації та ефективних радіусів хімічних зв'язків, що формують кристалічну структуру Bi-Sb-Te в залежності від міжатомних віддалей.

Ключові слова: теоретичні моделі, хімічний зв'язок, ефективні радіуси, енергія дисоціації, діаграми стану, нееквівалентні гібридні орбіталі (НГО).

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