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THEORETICAL MODELS OF ORDERED ALLOYS OF TERNARY SYSTEMS OF THERMOELECTRIC MATERIALS.
2. CHEMICAL BOND AND STATE DIAGRAMS OF *Bi-Pb-Te*

A comprehensive approach has been developed for the construction of theoretical models of ordered alloys of ternary systems of promising thermoelectric materials. Calculations of effective radii, redistribution of electron density and dissociation energy of non-equivalent hybrid orbitals (NHO) in the Bi-Pb-Te system depending on interatomic distances are presented. Triangulation methods were used to construct the distribution scheme of phase areas and isothermal sections in the Bi-Pb-Te system based on intermediate binary compounds Pb-Te; Bi-Te; Pb-Bi. Bibl. 15, Fig. 4, Table 7.

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

Introduction

Bismuth telluride is considered to be the most studied thermoelectric material. It has high thermoelectric parameters [1, 2].

However, despite many years of research into its physicochemical properties, many important questions remain unanswered. The question of chemical bonds remains open, and the theoretical understanding of many empirical relationships is associated with a revision of views on the problem of interatomic interactions [3].

In this connection, the study of the problems of synthesis of new materials based on tellurides with programmable properties remain an urgent issue. At the same time, the search for new promising thermoelectric materials is increasingly reduced to the need to study multicomponent systems. The reason is that solid phases of variable composition are formed in such systems, within which a transition is made in both chemical composition and structure with corresponding changes in physical properties [4, 5].

However, it should be noted that when studying complex systems, the classical scheme of dividing them into the sum of one-sided experiments no longer reveals the conditions for the appearance of the desired properties with the prospect of their change in the desired direction, since such systems are nonlinear, and there is still no consistent theory of phase transformations from the standpoint of chemical bond [7].

There is a search for new ways and approaches to solving such problems. The question of how general principles can be fruitfully use d to solve the set nonlinear problems acquires special relevance and significance. The answer to this question is related to the multi-layer structure of theoretical knowledge in various areas dealing with nonlinear systems. Knowledge of them is possible on the paths of interdisciplinary synthesis. The basis of this synthesis, according to [7], is the energy approach. In so doing, energy, as a general measure of various types of interaction, is considered both in terms of its organizational structure and state function. The combination of electronic, vibrational and configurational components of energy made it possible to calculate the ordering processes in alloys by statistical methods [8]; regularities of the formation of short-range order of chemical bonds in melts – by quantum chemical methods [9]; 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 10].

This work contributes to further comprehensive research [3 – 10] and is devoted to the construction of theoretical models of ordered alloys of the *Bi-Pb-Te* ternary systems. What was new in the study of tellurides was that a method based the geometrical properties of a triangle was used to solve the given problem [11]. This mathematical approach - the method of triangulation - makes it possible to solve a number of problems of physics, chemistry, mathematics. In particular, in chemistry, when studying state diagrams of ternary systems, this approach allows you to divide them into simpler binaries with regard to the laws of chemical interaction (solubility; substitution; exchange; formation of compounds; formation of solid solutions and mechanical mixtures).

This work solves the inverse problem of triangulation: based on the experimentally established and given in [12] state diagrams of binary alloys with regard to chemical interaction between the elements *Bi*, *Pb, Te*, located at the vertices of the triangle, a diagram of the distribution of phase regions for different isothermal sections is constructed in the *Bi-Pb-Te* system, and the parameters of phase transformations were calculated theoretically by the methods of quantum chemistry [7].

The availability of such information makes it possible to theoretically describe the processes of melting and crystallization in ternary systems *Bi-Pb-Te* and to optimize the synthesis of new materials based on them with programmable properties.

Theoretical models of state diagrams

When constructing the theoretical model of *Bi-Pb-Te*, it was necessary to summarize the results of experimental studies of binary state diagrams of *Pb-Te*; *Bi-Te*; *Pb-Bi* [12]; physicochemical properties and results of studies of quantum regularities of the initial components [9,10]. First, an analysis of binary state diagrams was given and isothermal sections at different temperatures were constructed. Then, by constructing the corresponding conoid triangles, the quantitative ratios of the coexisting phases were determined and the limits of phase equilibrium in the liquid-crystal regions were established. This made it possible to predict cases 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 *Pb*;
ε – solid phase based on intermediate *Bi-Te* binary compounds;
ς – solid phase based on intermediate *Pb-Te* binary compounds;
σ – solid phase based on intermediate *Pb-Bi* binary compounds;
δ – solid phase based on intermediate *Bi-Pb-Te* ternary compound;
L – liquid.

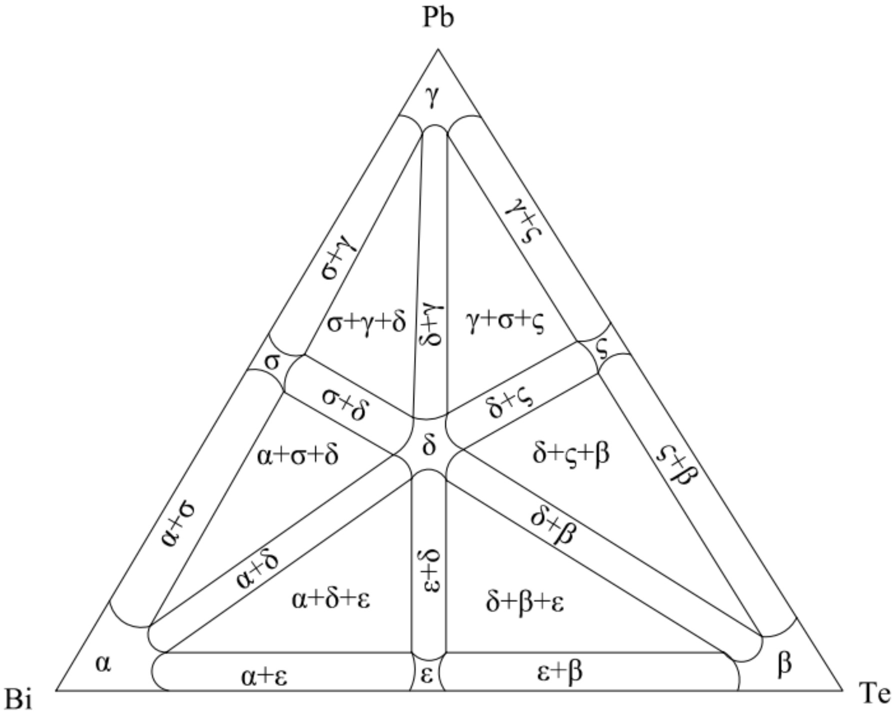

Fig. 1. A diagram of the distribution of
Bi-Pb-Te phase regions for
equilibrium in the solid state

Fig. 1 shows a diagram of the distribution of *Bi-Pb-Te* phase regions in the solid state. The division of the *Bi-Pb-Te* ternary system into six ordered ternary subsystems is clearly observed. This makes it possible to consider the issue of interatomic interaction both from the standpoint of state diagrams and chemical bond. It should be also noted that with the availability of additional experimental data, the number of ordered ternary systems may be larger.

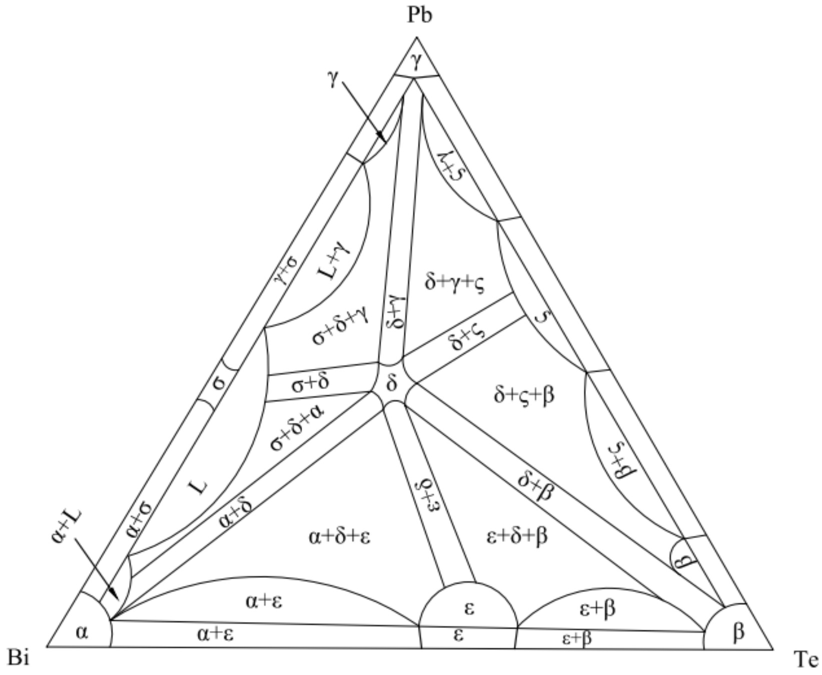

Fig. 2. Bi-Pb-Te isothermal section at t = 200°C

Fig. 2 shows an isothermal section at a temperature of $t = 200$°C, which is lower than the melting temperature of *Bi*, *Pb*, *Te* components and at the same time higher than the temperature of the first eutectic of the *Pb-Bi* system. Most of the *Pb-Bi* section is occupied by liquid L. Two-phase equilibrium (L+α), (L+γ), (L+σ) is realized by primary crystals α and γ, as well as σ- crystals (based on Bi_nPb_m compounds) and liquid.

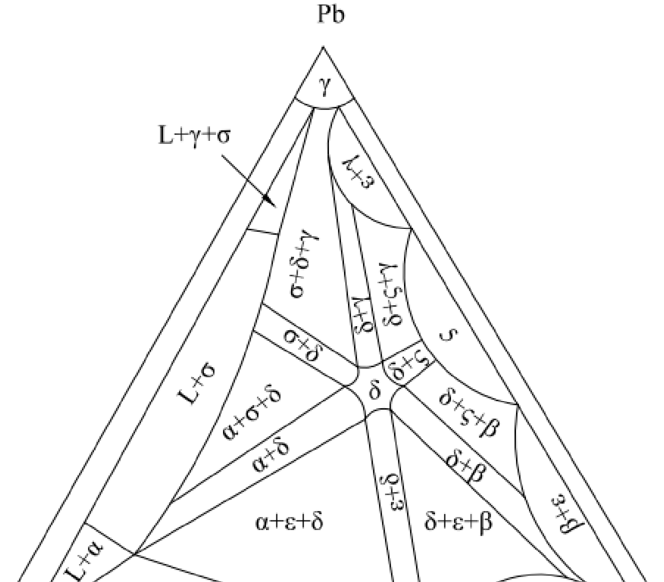

Fig. 3. Bi-Pb-Te isothermal section at t = 300°C

Fig. 3 shows an isothermal section at a temperature of 300°C, which is slightly lower than the melting temperature of *Pb* and *Te* components. As in the previous case, most of the *Pb*-*Bi* section is occupied by liquid *L*, but unlike the previous case, the cross-section contains conoid triangles with equilibrium phases (L+α+ε) and (L+γ+σ), which are formed by primary crystals α and γ, as well as ε and σ crystals (based on Bi_nTe_m and Bi_ePb_k) and liquid *L*. Exactly this division of ternary systems into separate sectors of dual state diagrams makes it possible to study the fine structure of cooling and heating of individual elements depending on their environment and the processes of forming the short-range order of chemical bonding.

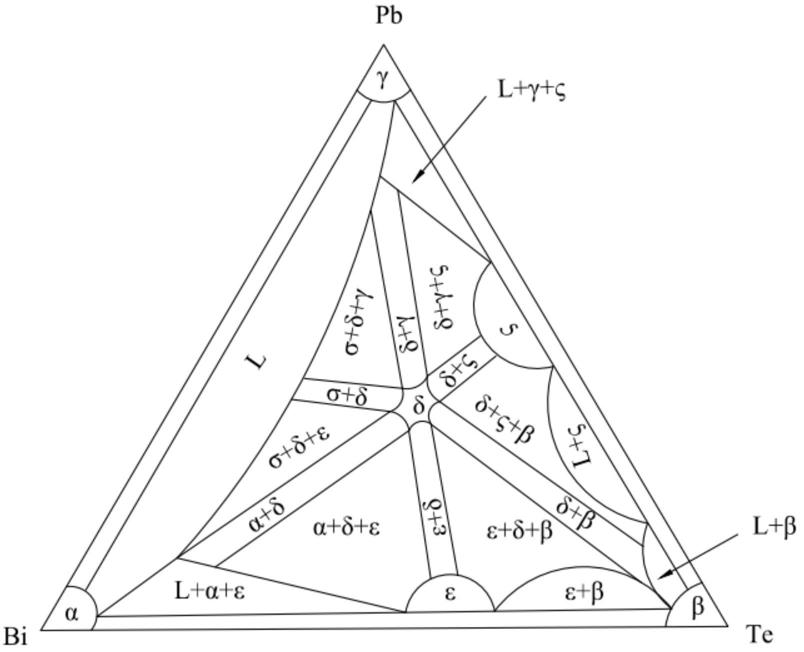

Fig. 4. Bi-Pb-Te isothermal section at t = 400°C.

Fig. 4 shows the isothermal section at t = 400°C, which is higher than the melting temperature of *Bi* and *Pb*. The entire *Bi*-*Pb* section is occupied by liquid, and in the *Bi*-*Te* and *Pb*-*Te* diagrams three-phase equilibria are represented by conoid triangles with phases (L+α+ε) and (L+γ+ς). Alloys of *Bi*-*Pb*-*Te* triangle are in a solid state at this temperature. Thus, the given isothermal sections make it possible to:

1. Determine quantitative ratios of coexisting phases and their concentrations.
2. Establish the limits of phase equilibrium in the liquid-crystal regions and transformations in the solid state.
3. Distinguish state diagrams corresponding to chemical compounds and solid solutions of different concentrations and mechanical mixtures.
4. Separate the boundaries of eutectic and peritectic state diagrams.
5. Predict cases of incongruent melting of chemical compounds, the composition of which differs from the composition of the original compound.

However, it should be also noted that isothermal sections alone do not yet indicate the temperature points of phase transitions of multicomponent systems. In such cases, additional methods are used that combine analytical and topological approaches with calculations of the interaction energy in both phases and increase the role of theoretical calculations in the construction of the state diagram of ternary systems.

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

The theoretical analysis of empirical dependences of crystallization processes is related to the revision of views on the problem of interatomic interaction and the emergence of new ideas which are not always the result of the development of existing theories, but mostly deny some of them.

Analytical relations reflecting the quantum patterns of interatomic interaction in tellurium were given in [9, 10]. However, there is still no single quantitative method for calculating the electronic structure of tellurium compounds and alloys based on both the quantum mechanical and empirical approaches.

Thus, for instance, the calculation of electron density distribution between interacting atoms by the methods of quantum mechanics does not take into consideration the fact that different types of their hybrid orbitals affect the strength of the electron-nucleus bond, and the electron density distribution around an isolated atom (ion), according to the calculation method, has spherical symmetry. This contradicts the fact that the formation of a chemical bond is accompanied by a rearrangement of the valence electron shells of the interacting atoms, and a redistribution of the electron density along the chemical bonds.

On the other hand, allowance for statistical regularities made it possible to obtain the dependence of electrons n on the outer shell of an atom on the Fermi radius r_F. Establishing the relationship between r_F and n can be considered the beginning of a quantitative theory of chemical bonding [13].

Empirical information on the properties of atoms and ions based on the experience and traditions of the crystal-chemical approach can be combined by introducing the concept of unpolarized $R_{ин}$ ionic radii [13]. Since both the functions that include the Fermi radii $r_F = f(n)$ and the equations that include $R_{ин}$ determine the electronic configurations of the interacting atoms depending on the length and number of bonds formed by them, all this gives reason to consider the concepts of the Fermi radius and unpolarized radius identical and denote by one symbol R_u – effective ionic radii.

Despite the imperfection, from a theoretical point of view, of the concepts of the crystal chemical radius of ions, electronegativity, polarizability and other empirical criteria, 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 numerical values of these criteria are determined on the basis of the generalization of experimental data in combination with their interpretation from the standpoint of quantum mechanics, which contain important information about the nature of interatomic interactions.

Numerical values of electronegativity turned out to be most useful when searching for the form of a graphical solution to the problem of the connection of R_u to n. The relationship between

$\tan\alpha = \dfrac{\Delta \log R_u}{\Delta n}$ and electronegativity does not make it possible to change the compared values arbitrarily, fixing the position of the lines in the coordinates $\log R_u = f(n)$. A good agreement of the complex of experimental data on various physicochemical properties of atoms and their ions with the values of R_u and $\tan\alpha$ gives the postulated dependence

$$\log R_{uA}^{x} = \log R_{uA}^{0} - x\tan\alpha, \qquad (1)$$

Where R_{uA}^{0} is the radius of the atoms in the unexcited state, and x is the valence which allows us to state that the derivation of equations for ionic radii is based on the generalization of the main empirical material of physics and chemistry, and their usefulness is determined by the extent to which their use allows overcoming the difficulties of the modern theory of chemical bonding and obtaining quite accurate and physically justified result of interatomic interaction.

As already noted, the formation of a chemical bond is accompanied by a rearrangement of valence electron shells of interacting atoms. The possibility of using the system of ionic radii for their description follows from the basic principles of quantum mechanics. Since the equations of the system of ionic radii describe the change in R_u of atoms A and B when the number of electrons in the orbitals changes, assuming the equality of the absolute values of the charges of interacting atoms, dependence (1) takes the form of a system of equations [13]:

$$\lg R_{uA}^{+x} = \lg R_{uA}^{o} - x\tan\alpha_A, \qquad (2)$$

$$\lg R_{uB}^{-x} = \lg R_{uB}^{o} + x\tan\alpha_B, \qquad (3)$$

$$d_1^0 = \log R_{uA}^{+x} + \log R_{uB}^{-1}, \qquad (4)$$

The presence of d_{min} and two possible values of $z_{еф}$ for $d_1 > d_{min}$ from the standpoint of crystal chemical approach is justified by the increase in the internuclear distance with a change in the ionicity and covalency between the same partners.

The main drawback of this approach is that in many cases the internuclear distances A-B in molecular and crystalline compounds are smaller than the $d_{\min}$ value, and it is impossible to calculate the charge of ions using $z_{еф} = f(d)$ diagrams. Therefore, difficulties can be overcome only by abandoning the attempt to interpret the solution of system (2)-(4) in terms of crystal-chemical approach. The reason is that in the system (2)-(4) the ideas of the theory of polarization and the concept of electronegativity (EN) are combined, as it describes the mutual change of the polarization of anion and cation depending on tan α. From the standpoint of a quantum mechanical approach to solving the problem of chemical bonding, system (2)-(4) formally considers the geometrical conditions of contact of spherical electron shells with different density at the boundary. In this case, the single quantum system is replaced by an arithmetic sum of parts that retain their individuality, and the complex process of rebuilding the electronic shells of interacting atoms comes down to a simple transfer of electrons from the orbitals of one to the orbitals of the other. Thus, additional criteria are necessary to translate the crystal chemical system (2)-(4) into the language of quantum chemistry. It should be taken into consideration that in the zone of binding localized orbitals, the spherical symmetry of the electron density is broken and for $d_1 > d_{min}$, the formation of *A*-*B* bonds is accompanied by the transition of electrons to other directions of interatomic interaction, and this bond becomes a donor.

Thus, at $d_1 \neq d_{min}$, the change in the values of $z_{eф}$ of atoms should be such as to ensure the equality of the density of states at the boundary of the corresponding ions. This condition is fulfilled if the extraction ($+\Delta e$) of electrons or their localization ($-\Delta e$), in the given bond direction equally change the value of charges that this pair has at $d_1 = d_{min}$, i.e. $z_{eф}A(B) = z_{min}\,A(B) + (\Delta e/z)$. The thus calculated $z_{eф}$ and R_u characterize for arbitrary d_1 the conditions for preserving the continuity of the wave function in the zone of interacting atoms. These conditions are described by a system of equations:

$$d_1 = R_{uA}^{zA} + R_{uB}^{zB} \tag{5}$$

$$\log R_{uA}^{zA} = \log R_{uA}^{0} - \left(z_{\min A} + \frac{\Delta e}{r} \right) \tan \alpha, \tag{6}$$

$$\log R_{uB}^{zB} = \log R_{uB}^{0} - \left(z_{\min B} + \frac{\Delta e}{r} \right) \tan \beta, \tag{7}$$

Externally, Eqs. (2)-(4) and (5)-(7) are similar, but in reality, replacing *x* with $\left(z_{\min} + \frac{\Delta e}{r} \right)$ changes their physical content. The function $d_1 = f(z_{eф})$ is calculated in accordance with the traditions of the crystal chemical approach ($Z_A = -Z_B$), is correct from the quantum molecular point of view only at $d = d_{min}$, but this turns out to be sufficient for system (5)-(7) to be solved for known d_1. With this approach, the system (5)-(7) allows to reconcile the theoretical part with the experimental one and was solved for all possible values of d_i in the considered compounds. Thus, as a result of taking into consideration quantum interpretation of empirical material, the expression for the energy of chemical bonds acquires the form:

$$D_{A-B}^{(i)} = \frac{c_1 \left(R_{uA}^{\mathrm{o}} + R_{uB}^{\mathrm{o}} \right)}{\left(\tan \alpha_A + \tan \alpha_B \right)} \left(\frac{c_2 d_i}{d_1^2 - R_{uA} R_{uB}} - \frac{1}{d_i} \right) \tag{8}$$

where $R_{uA(B)}^{\mathrm{o}}$ and $\tan \alpha_{A(B)}$ are coefficients of equations (2)-(4) for atoms *A* and *B*, and R_{UA} and R_{UB} are the effective radii of their ions, in *A*-*B* bonds of length d_i, i is the number of non-equivalent interatomic distances in the considered compounds; C_1 is a coefficient reflecting the relationship between dimensional and energy characteristics of interatomic interaction (measured in electric volts);

C_2 is a coefficient which depends on the type of crystal structure and chemical bond and is chosen dimensionless.

The given 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-Pb-Te*. The result of calculating the coefficients of equations (2)-(4) $R_u^{(0)}$ and $\tan\alpha$ of initial components are given in Table 1.

Table 1

Coefficients of equations of initial components

Z	Element	$R_u^{(0)}(A)$	$\tan\alpha$
52	*Te*	1.57	0.076
82	*Pb*	1.53	0.0675
83	*Bi*	1.63	0.068

Effective charges Δq_i, effective radii R_{ui} and dissociation energies for nearest neighbours at different interatomic distances d_i ($1 \le i \le 8$) of structural modifications of bismuth are given in Table 2.

Table 2

Effective charges Δq_i, effective radii R_{ui}, dissociation energies D_i of chemical bonds φ_i for nearest neighbours at different interatomic distances d_i of various structural modifications of bismuth.

Parameters	*Bi*							
	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8
$d_i^{екс}(A)$	2.8	2.9	3.0	3.1	3.3	3.5	3.7	4.7
$d_i^{теор}(A)$	2.805	2.9033	3.009	3.1008	3.3036	3.5034	3.7008	4.7024
$R_u(A)$	1.4025	1.45165	1.5045	1.5504	1.651	1.7517	1.8504	2.3512
Δq_i	0.13	0.10064	0.06936	0.0435	-0.111	-0.0625	-0.11	-0.318
$D_i(ev)$	2.8536	2.75524	2.6634	2.577	2.421	2.2829	2.1595	1.700

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

Table 3

Effective charges Δq_i, effective radii R_{ui}, dissociation energies D_i of chemical bonds φ_i for nearest neighbours at different interatomic distances d_i of various structural modifications of tellurium.

Parameters	*Te*							
	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8
$d_i^{екс}(A)$	2.8	2.9	3.0	3.1	3.3	3.5	3.7	4.7
$d_i^{теор}(A)$	2.024	2.9046	3.00558	3.1018	3.30056	3.4998	3.7014	4.7042
$R_u(A)$	1.4012	1.4523	1.50279	1.5509	1.65028	1.7499	1.8507	2.3521
Δq_i	0.0988	0.06764	0.038	0.01064	-0.04332	-0.09424	-0.143	-0.35112
$D_i(ev)$	2.45927	2.37447	2.29533	2.2213	2.0866	1.9674	1.86107	1.465097

Table 4

Effective charges Δq_i, effective radii R_{ui}, dissociation energies D_i of chemical bonds φ_i for nearest neighbours at different interatomic distances d_i of various structural modifications of Pb.

Parameters	*Pb*							
	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8
$d_i^{екс}(A)$	2.8	2.9	3.0	3.1	3.3	3.5	3.7	4.7
$d_i^{теор}(A)$	2.80057	2.90024	3.00345	3.1006	3.302	3.50032	3.7016	4.699
$R_u(A)$	1.400285	1.45012	1.50428	1.5503	1.651	1.75016	1.8508	2.3495
Δq_i	0.07695	0.046575	0.0162	0.011475	-0.06615	-0.1168	-0.1654	-0.3726
$D_i(ev)$	2.6984	2.5272	2.5185	2.43729	2.289562	2.15873	2.04204	1.60756

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

Table 5

Effective charges Δq_i, effective radii R_{ui}, dissociation energies D_i of chemical bonds φ_i for nearest neighbours at non-equivalent interatomic distances d_i of various structural modifications of Bi-Te.

Parameters	*Bi-Te*							
	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8
$d_i^{\text{екс}}(A)$	2.8	2.9	3.0	3.1	3.3	3.5	3.7	4.7
$d_i^{\text{теор}}(A)$	2.803	2.906	3.0048	3.106	3.303	3.502	3.702	4,707
$R_{ui}^{Bi}(A)$	1.438	1.488	1.536	1.584	1.681	1.775	1.871	2.347
$R_{ui}^{Te}(A)$	1.365	1.418	1.468	1.522	1.622	1.727	1.831	2.36
Δq_i	0.1152	0.08352	0.05472	0.02736	-0.0288	-0.0785	-0.126	-0.3355
$D_i(ev)$	2.6429	2.5664	2.4672	2.38814	2.24367	2.115826	2.00169	1.576

Table 6

Effective charges Δq_i, effective radii R_{ui}, dissociation energies D_i of chemical bonds φ_i for nearest neighbours at non-equivalent interatomic distances d_i of various structural modifications of Pb-Te.

Parameters	*Pb-Te*							
	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8
$d_i^{\text{екс}}(A)$	2.8	2.9	3.0	3.1	3.3	3.5	3.7	4.7
$d_i^{\text{теор}}(A)$	2.804	2.904	2.998	3.104	3.302	3.504	3.7062	4.7037
$R_{ui}^{Pb}(A)$	1.392	1.4378	1.4827	1.531	1.6231	1.7163	1.8096	2.2635
$R_{ui}^{Te}(A)$	1.412	1.4662	1.5153	1.573	1.6771	1.7877	1.8966	2.4402
Δq_i	0.0868	0.0574	0.0290	-	-0.05455	-0.106	-0.1549	-0.36162
$D_i(ev)$	2.5718	2.4828	2.40	2.344	2.18132	2.05638	1.945	1.5291

Table 7

Effective charges Δq_i, effective radii R_{ui}, dissociation energies D_i of chemical bonds φ_i for nearest neighbours at non-equivalent interatomic distances d_i of various structural modifications of Pb-Bi.

Parameters	*Pb-Bi*							
	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8
$d_i^{екс}(A)$	2.8	2.9	3.0	3.1	3.3	3.5	3.7	4.7
$d_i^{теор}(A)$	2.8028	2.90014	3.0014	3.11	3.306	3.5027	3.7051	4.704
$R_{ui}^{Pb}(A)$	1.3574	1.40464	1.4535	1.506	1.601	1.6952	1.7928	2.273
$R_{ui}^{Bi}(A)$	1.4454	1.4955	1.5479	1.604	1.705	1.8075	1.9123	2.451
Δq_i	0.104	0.0745	0.0447	0.01355	-0.0393	-0.0894	-0.1382	-0.3455
$D_i(ev)$	2.773	2.677	2.588	2.504	2.3528	2.2181	2.098	1.65148

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

Discussion of results

As follows from the results presented in Table 2, with increasing interatomic distances, the dissociation energy of the corresponding chemical bonds decreases, the redistribution of the electron density in the interval of interatomic distances $3.1 \leq d_i \leq 3.3$ changes its sign. This means that chemical bonds can be donors and acceptors in certain conditions. In turn, this confirms the experimentally established fact [14] that in compounds bismuth has different oxidation states, which can take values from -3 to +5 and can exhibit electronic properties in semiconductor melts as metallizing liquids, semimetallic liquids and semiconductors withy one and bilateral arrangement [15].

Thus, the use of the obtained results of the electronic properties of bismuth makes it possible to predict the shape of the liquidus, and hence the type of melting of the resulting material.

As for tellurium, with increasing interatomic distances, the dissociation energy of chemical bonds decreases, and the redistribution of electron density changes sign, just like bismuth. Tellurium can also have different oxidation states +4, +6 and -2, and has semiconducting properties. In melts with bismuth and lead, it behaves as a semi-metallic liquid.

The results of calculations of effective charges, effective radii and dissociation energies obtained in this work are in good agreement with the results of thermal rearrangement of atoms, during the formation of short-range order of chemical bonds in the *Bi-Te*, *Pb-Te* and *Pb-Bi* systems, which expands the technological possibilities when considering phase transformations, which are affected by such factors as the destruction of existing connections and the formation of new ones. This makes it possible to calculate the influence of the composition on the formation of the nuclei of a new phase, the influence of the distribution of phase components on the physical properties of the obtained materials.

Conclusions

1. A method of constructing theoretical models of ordered *Pb-Bi-Te* alloys using the geometric properties of a triangle is proposed.
2. The diagram of the distribution of phase regions and isothermal sections in the *Bi-Pb-Te* ternary systems has been constructed.
3. Calculations of effective radii, effective charges, dissociation energies in the *Bi-Pb-Te* ternary systems have been carried out.
4. The results obtained are consistent with the results of calculations of chemical bond parameters by the methods of microscopic theory [3 – 5], [7] and can be used in the development of technological modes for obtaining new materials based on *Bi-Pb-Te*.

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ТЕОРЕТИЧНІ МОДЕЛІ ВПОРЯДКОВУВАНИХ СПЛАВІВ ПОТРІЙНИХ СИСТЕМ ТЕРМОЕЛЕКТРИЧНИХ МАТЕРІАЛІВ.
2. ХІМІЧНИЙ ЗВ’ЯЗОК ТА ДІАГРАМИ СТАНУ *Bi-Pb-Te*

Розроблено комплексний підхід для побудови теоретичних моделей упорядкованих сплавів потрійних систем перспективних термоелектричних матеріалів.

Представлено розрахунки ефективних радіусів, перерозподілу електронної густини та енергії дисоціації нееквівалентних гібридних орбіталей (нго) в системі Bi-Pb-Te в залежності від міжатомних віддалей.

Методами триангуляції побудовано схему розподілу фазових областей та ізотермічні перерізи в системі Bi-Pb-Te. На основі проміжних бінарних сполук Pb-Te; Bi-Te; Pb-Bi. Бібл. 15, рис.4, табл. 7.

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

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ТЕОРЕТИЧЕСКИЕ МОДЕЛИ УПРАВЛЯЕМЫХ СПЛАВОВ ТРОЙНЫХ СИСТЕМ ТЕРМОЭЛЕКТРИЧЕСКИХ МАТЕРИАЛОВ. 1. ХИМИЧЕСКАЯ СВЯЗЬ И ДИАГРАММЫ СОСТОЯНИЯ *Bi-Pb-Te*

Разработан комплексный подход для построения теоретических моделей упорядоченных сплавов тройных систем перспективных термоэлектрических материалов. Представлены расчеты эффективных радиусов, перераспределения электронной плотности и энергии диссоциации неэквивалентных гибридных орбиталей (нго) в системе Bi-Pb-Te в зависимости от межатомных расстояний. Методами триангуляции построена схема распределения фазовых областей и изотермические сечения в системе Bi-Pb-Te. На основе промежуточных бинарных соединений Pb-Te; Bi-Te; Pb-Bi. Библ. 15, рис.4, табл. 7.

Ключевые слова: теоретические модели, химическая связь, неэквивалентные гибридные орбитали, эффективные радиусы, электронная плотность, энергия диссоциации, диаграммы состояния.

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