DOI: 10.63527/1607-8829-2025-3-29-36

D.E. Rybchakov[1,2] (https://orcid.org/0009-0002-2891-2258),
O.M. Manyk[1] (https://orcid.org/0000-0003-2525-5280),
V.V. Razinkov[2] (https://orcid.org/0009-0004-2882-5466)

[1]Yuriy Fedkovych Chernivtsi National University,
2 Kotsiubynskyi str., Chernivtsi, 58012, Ukraine;
[2]Institute of Thermoelectricity of the NAS and MES of Ukraine,
1 Nauky str., Chernivtsi, 58029, Ukraine

Corresponding author: O.M. Manyk, e-mail: *o.manyk@chnu.edu.ua*

Molecular Aspects of Mechanical Activation of Chemical Processes of Quaternary Systems of Promising Thermoelectric Materials by Halogen Solutions

Theoretical models of mechanical activation processes of powder technology for obtaining thermoelectric materials of the Bi-Sb-Se-Te quaternary systems using iodine solutions have been developed. Calculations of effective radii, redistribution of electron density and energy, dissociation of nonequivalent hybrid orbitals depending on the interatomic distances Bi-I; Sb-I; Se-I; Te-I have been performed. It *has been shown that under certain conditions the redistribution of electron density changes sign. This means that chemical bonds can be both donor and acceptor. Bibl. 8. Tabl. 5.*

Keywords: thermoelectric material, chemical bond, powder technologies, mechanochemistry, mechanoactivation methods, multicomponent systems, effective radii, electron density, donors, acceptors, nonequivalent hybrid orbitals, energy.

Introduction

Technological aspects of obtaining thermoelectric materials of ternary and quaternary systems of bismuth and antimony chalcogenides by powder metallurgy methods require further comprehensive research. This is due to the presence of a number of features in such systems:

- formation of solid phases of variable composition;
- change in chemical bond from metallic (in the original components) to covalent (in compounds) and intermediate (in solid solutions).

These features lead to phase transformations of ordering processes in solutions and alloys, which form the physicochemical properties of thermoelectric materials. There is no consistent

Citation: D.E. Rybchakov, O.M. Manyk, V.V. Razinkov (2025). Molecular Aspects of Mechanical Activation of Chemical Processes of Quaternary Systems of Promising Thermoelectric Materials by Halogen Solutions. *Journal of Thermoelectricity*, (3), 29–36. https://doi.org/10.63527/1607-8829-2025-3-29-36

theory of phase transformations from the standpoint of chemical bond [1] for such materials yet. At the same time, the main technological issues of creating extruded and pressed thermoelectric materials have to be solved experimentally [2].

For the further development of powder metallurgy technological methods for obtaining high-quality thermoelectric materials based on Bi-Te, the task of developing theoretical models that will allow generalizing the capabilities of existing methods by combining thermodynamic, statistical, quantum, and mechanical approaches taking into account chemical bond is presented.

Search is underway for new methods and approaches to solving such problems [3]. Of particular importance is the question of how general principles can be fruitfully used to solve the posed nonlinear problems? The answer to this question is connected with the multilayer structure of theoretical knowledge from various fields that deal with nonlinear systems. Their cognition is possible through interdisciplinary synthesis. The basis of such synthesis, according to [1], is the energy approach. In this case, energy, as a general measure of various types of interaction, is considered both in terms of its organizational structure and the 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 [4], the regularities of the formation of short-range order of chemical bonds in melts by quantum-chemical methods [5], the redistribution of electron density and dissociation energy of non-equivalent chemical bonds in ternary systems by methods of microscopic theory using solutions, inverse problems and molecular models [6].

This work contributes to further comprehensive research [4–6] and is devoted to the construction of theoretical models of chemical bond activation in quaternary Bi-Sb-Se-Te systems subjected to preliminary mechanical treatment using halogen solutions.

Theoretical models of mechanical activation of chemical bonds

The chemical composition of materials affects their phase state, which in turn depends on the external action (heating, cooling, deformation, irradiation) which leads to a deviation from the equilibrium state of the system. With this approach, varying degrees of deviation from the stoichiometric and equilibrium state of the system of elements united by certain chemical laws also make it possible to obtain new materials. At the same time, physical materials science - scientific disciplines that study the patterns of formation of metallic and semiconductor phases (elementary substances, solutions, alloys, compounds) in equilibrium and non-equilibrium conditions of the influence of chemical and phase composition, atomic structure and structural defects on the properties of materials, are closely intertwined and continue in mechanochemistry.

The term “mechanochemistry” was introduced by W. Ostwald in a textbook on general chemistry [7], in which he, in particular, considered various types of stimulation of chemical processes. This term refers to chemical reactions with reagents in all states of aggregation [8].

However, it is most often used in the study of solid-phase reaction processes previously subjected to mechanical treatment, which usually represents a combination of pressure and

shear, therefore it is important to identify the role of each of these components in changing the physicochemical properties of substances subjected to mechanical treatment.

It should also be noted that the influence of pressure on the course of chemical reactions in solids has been studied to a much lesser extent than the influence of temperature. The reason for this is the difficulties associated with the experimental technique and the complexity of observing the course of the process at high pressures. The following main areas can be distinguished where high pressure exerts an influence on the course of chemical reactions in the solid phase:

- influence on intergranular interactions in mixtures of solids that enter into a solid-phase reaction by increasing the contact area of reacting particles and improving the conditions for diffusion along interfacial surfaces;

- changes inside the particles of solids are associated with changes in their real structure, concentration of defects, changes in interatomic distances. As a result, this leads to a decrease in the band gap and the dielectric begins to exhibit semiconductor properties.

At present, such a classification cannot be considered complete, since it does not cover all the accumulated material. However, it can be taken as a basis when considering, in a first approximation, uniform, distributed pressure in all directions (hydrostatic pressure) and expanding the range of phenomena devoted to the influence of pressure on the physicochemical properties of anisotropic solids, molecular crystals, and intermolecular interactions of biological objects. Thus, the study of the behavior of solids under pressure is not only necessary for understanding the mechanisms of mechanochemical processes, but also promising as a method for studying structural and intermolecular interactions. This approach makes it possible to solve a number of problems in physics, chemistry, and mathematics, which combine analytical and topological approaches with calculations of the energy of interaction of components in different phases and increase the role of theoretical calculations in solving complex nonlinear problems. As an example of solving such problems, this work presents the results of calculations of the influence of halogens on the formation of chemical bonds in powder materials of quaternary systems. Bi-Sb-Se-Te was chosen as a representative of quaternary systems, and iodine solution was chosen from halogens. Calculations of the dissociation energies of Bi-I; Sb-I; Se-I; and Te-I were performed.

Theoretical analysis of empirical dependencies of crystallization processes is associated with a revision of views on the problems of interatomic interaction. For example, the distribution of electron density around an isolated atom has spherical symmetry, and the formation of a chemical bond is accompanied by a restructuring of the valence shells of interacting atoms and a redistribution of electron density along chemical bonds. Generalization of empirical information on the properties of atoms and ions based on the crystal chemical approach led to the appearance of effective charges Δq_i, effective ionic radii R_u, and dissociation energies D_i of individual chemical bonds [6].

The most effective in searching for the form of a graphical solution to the problem of the relationship between R_u and the number of electrons in the outer shell of atoms n were numerical values of electronegativity. The relationship between $\mathrm{tg}\alpha = \frac{\Delta \lg R_u}{\Delta n}$ and electronegativity makes

it possible to fix the position of the appearance of these dependences in the coordinates $\lg R_u = f(n)$. Good agreement between the complex of studied data on various physicochemical properties of atoms and their ions with R_u and tgα is given by the postulated dependence

$$\lg R_{UA}^{x} = \lg R_{UA}^{(0)} - x\mathrm{tg}\alpha, \quad (1)$$

where $R_U^{(0)}$ is radius of atoms in the unexcited state, x is valence.

Since equation (1) describes changes in Ru of atoms *A* and *B* with a change in the number of electrons in the orbitals of each, then, assuming the equality of the absolute values of the charges of the interacting atoms, dependence (1) takes the form of a system of equations [5–6]:

$$\lg R_{UA}^{+x} = \lg R_{UA}^{(0)} - x\mathrm{tg}\alpha_A, \quad (2)$$

$$\lg R_{UB}^{-x} = \lg R_{UB}^{(0)} + x\mathrm{tg}\alpha_B, \quad (3)$$

$$d_{min} = R_{UA}^{+x} + R_{UB}^{-x}, \quad (4)$$

where d_{min} is the smallest interatomic distance between interacting atoms.

The main disadvantage of this approach is that in many cases the internuclear distances *A–B* in molecular and crystalline compounds and alloys *d* are less than d_{min} and the difficulties can be overcome only by abandoning the attempt to interpret the solution of system (2–4) from the position of the crystal chemical approach. Additional criteria are necessary that allow the crystal chemical system (2–4) to be translated into the language of quantum chemistry. It is necessary to take into account that the formation of chemical bonds *A–B* is accompanied by the transition of electrons to other directions of interatomic interaction and this bond becomes donor. This condition is met, if the separation (+Δe) of electrons, or their localization (-Δe) in a given direction, equally change the values of the charges that this pair has at $d < d_{min}$ i.e. $z_{\mathrm{e}f}A(B) = z_{min}A(B) - \left(\frac{\Delta e}{z}\right)$. The thus calculated $z_{\mathrm{e}f}A(B)$ and R_u characterize the conditions for preserving the continuity of the wave function in the zone of interacting atoms for an arbitrary d_i and these conditions are described by a system of equations:

$$d_i = R_{UA}^{zx} + R_{UB}^{zx}, \quad (5)$$

$$\lg R_{UA}^{zA} = \lg R_{UA}^{(0)} - (z_{minA} + \frac{\Delta e}{z})\mathrm{tg}\alpha_A, \quad (6)$$

$$\lg R_{UB}^{zB} = \lg R_{UB}^{(0)} + (z_{minA} + \frac{\Delta e}{z})\mathrm{tg}\alpha_B, \quad (7)$$

Externally, equations (2)–(4) and (5)–(7) are similar, but in reality, replacing x with $(z_{minA} + \frac{\Delta e}{z})$changes their physical meaning. The function $d = f(z_{\mathrm{e}f})$ is calculated in accordance with the crystal chemical approach for ($Z_A = -Z_B$), which is correct from a quantum molecular point of view only at $d = d_{min}$, but this turned out to be sufficient for the system (5)–(7) to be solved for known *d*. With this approach, system (5)–(7) allows not only to reconcile the theoretical part with the experimental one, but also to make a prediction when the corresponding bonds can become donor, acceptor and change physical properties. Thus, as a

result of taking into account the quantum interpretation of the empirical material, the expression for the energy of chemical bonds takes the form:

$$D_{A-B}^{(i)} = \frac{c_i(R_{UA}^{(0)}+R_{UB}^{(0)})}{\mathrm{tg}\alpha_A+\mathrm{tg}\alpha_B}\left[\frac{c_2 d_i}{d_i^2-R_{UA}R_{UB}}-\frac{1}{d_i}\right], \quad (8)$$

where $R_{UA(B)}^{(0)}$ and $\mathrm{tg}\alpha_{A(B)}$ are the coefficients of equations (2)–(4) for atoms *A* and *B*, R_{UA} and R_{UB} are the effective radii of ions in bonds *A* and *B*, length d_i, *i* is the number of non-equivalent distances in the compounds under consideration; C_1 is the coefficient reflecting the relationship between the dimensional and energy characteristics of the interatomic interaction (measured in electron volts); C_2 is the coefficient depending on the type of crystal structure and chemical bond and is chosen to be dimensionless.

The given equations were used in calculations of effective charges, effective radii and dissociation energies of nonequivalent chemical bonds included in the quaternary system. The results of calculations of the coefficients of equations (2)–(4) $R_U^{(0)}$ and tgα of the initial components are given in Table 1.

Table 1

Coefficients of equations of the original components.

Z	Element	$R_U^{(0)}(A)$	tgα
34	Se	1.35 *A*	0.088
51	Sb	1.45 *A*	0.074
52	Te	1.57 *A*	0.076
54	I	1.815 *A*	0.078
88	Bi	1.63*A*	0.068

Table 2

Effective charges Δq_i, effective radii R_{Ui} and dissociation energies of chemical bonds φ_i for nearest neighbours at the nonequivalent distances d_i of I-Bi structural varieties

φi	φ1	φ2	φ3	φ4	φ5	φ6	φ7	φ8	φ9	φ10	φ11	φ12
$d_i(A)$	2.5	2.6	2.7	2.8	2.9	3.0	3.1	3.2	3.3	3.4	3.445	3.5
$R_U^I(A)$	1.317	1.370	1.423	1.475	1.528	1.581	1.633	1.686	1.739	1.791	1.815	1.844
$R_U^{Bi}(A)$	1.183	1.230	1.271	1.325	1.372	1.419	1.467	1.514	1.561	1.609	1.63	1.656
$\Delta q(\varphi_i)$	1.916	1.682	1.456	1.239	1.029	0.827	0.631	0.441	0.257	0.078	0	–0.095
$D_i(ev)$	3.134	3.014	2.903	2.798	2.718	2.613	2.551	2.448	2.374	2.304	2.28	2.27

Table 3

Effective charges Δq_i, effective radii R_{Ui} and dissociation energies of chemical bonds φ_i for nearest neighbours at the nonequivalent distances d_i of I-Se structural varieties

φi	φ1	φ2	φ3	φ4	φ5	φ6	φ7	φ8	φ9	φ10	φ11	φ12
$d_i(A)$	2.5	2.6	2.7	2.8	2.9	3.0	3.1	3.165	3.2	3.3	3.4	3.5
$R_U^I(A)$	1.434	1.491	1.538	1.606	1.663	1.72	1.778	1.815	1.835	1.892	1.95	2.007
$R_U^{Se}(A)$	1.066	1.109	1.162	1.194	1.237	1.28	1.322	1.35	1.365	1.408	1.45	1.493
$\Delta q(\varphi_i)$	1.239	1.033	0.834	0.643	0.459	0.281	0.109	0	–0058	–0.219	–0.376	–0.528
$D_i(ev)$	2.469	2.375	2.293	2.205	2.142	2.059	2.01	1.95	1.93	1.87	1.816	1.764

Table 4

Effective charges Δq_i, effective radii R_{Ui} and dissociation energies of chemical bonds φ_i for nearest neighbours at the nonequivalent distances d_i of I-Sb structural varieties

φi	φ1	φ2	φ3	φ4	φ5	φ6	φ7	φ8	φ9	φ10	φ11	φ12
$d_i(A)$	2.5	2.6	2.7	2.8	2.9	3.0	3.1	3.2	3.265	3.3	3.4	3.5
$R_U^I(A)$	1.39	1.445	1.50	1.557	1.612	1.668	1.723	1.779	1.815	1.834	1.89	1.946
$R_U^{Sb}(A)$	1.11	1.155	1.20	1.243	1.288	1.332	1.377	1.421	1.45	1.466	1.51	1.554
$\Delta q(\varphi_i)$	1.527	1.302	1.087	0.879	0.678	0.485	0.297	0.23	0	–0.23	–0.238	–0.397
$D_i(ev)$	2.816	2.709	2.608	2.515	2.444	2.348	2.294	2.20	2.157	2.134	2.071	2.012

Table 5

Effective charges Δq_i, effective radii R_{Ui} and dissociation energies of chemical bonds φ_i for nearest neighbours at the nonequivalent distances d_i of I-Te structural varieties

φi	φ1	φ2	φ3	φ4	φ5	φ6	φ7	φ8	φ9	φ10	φ11	φ12
$d_i(A)$	2.5	2.6	2.7	2.8	2.9	3.0	3.1	3.2	3.3	3.385	3.4	3.5
$R_U^I(A)$	1.33	1.394	1.448	1.501	1.555	1.609	1.662	1.71	1.769	1.815	1.823	1.877
$R_U^{Te}(A)$	1.17	1.206	1.252	1.299	1.345	1.391	1.438	1.49	1.531	1.57	1.577	1.623
$\Delta q(\varphi_i)$	1.71	1.488	1.275	1.07	0.872	0.681	0.496	0.317	0.143	0	–0.025	–0.188
$D_i(ev)$	2.859	2.745	2.643	2.549	2.461	2.379	2.323	2.323	2.163	2.108	2.099	2.039

Tables (2)–(5) show the results of calculations of the effect of iodine solutions on the formation of chemical bonds of the initial components. It is taken into consideration that obtaining new materials by pressing and extrusion leads to a change in interatomic distances. These changes can occur both due to changes in pressure and temperature. In doing so, in order to assess the contribution of each factor, an inverse problem was solved in this work, the essence of which is that when solving the direct problem from the position of the crystal chemical approach (system (2)–(4)) the function $d = f(z_{ef})$ is correct only at $d = d_{min}$ and this is a disadvantage of this system when the internuclear distances are less than d_{mi}, but this is enough

for system (5)–(7) to be solved at a known d_i and the effective radii R_u, the redistribution of the electron density and the dissociation energy were found. In this work, the internuclear distance was set every 0.1 A in the interval $2.5 \leq d_i \leq 3.5$(A) for each non-equivalent hybrid orbital of the chemical bond Bi-I; Sb-I; Se-I; Te-I.

Conclusions

Analysis of the obtained results, given in tables (1)–(5) allows us to describe the processes of formation of interatomic interaction at different technological levels from the position of chemical bond. This is, first of all, the formation of a crystal structure based on the initial elements [5], where information about the physicochemical properties and chemical bond of the initial elements of binary compounds was taken into consideration. What was new in this work was that the influence of iodine solutions on the formation of the structure and properties of the obtained materials was carried out by calculating the effective radii, redistribution of electron density, dissociation energy of binary compounds of the initial components and iodine, for different interatomic distances in the interval $2.5 \leq d_i \leq 3.5$A. Comparison of the results obtained in this work showed that the change in the sign of the redistribution of electron density on Bi-Bi bonds occurs in the interval 2.7–2.8 A and the bond energy is $D_{Bi-Bi}^{d_i=2.7\text{A}}$ while on the bond Bi-I the change in sign occurs in the interval 3.4–3.5 A and the bond energy $D_{Bi-I}^{d_i=2.7A} = 2.903$ eV decreases somewhat.

Similarly, for Se-Se bonds, the redistribution of electron density occurs in the interval 2.7–2.8 A, and the bond energy is $D_{Se-Se}^{d_i=2.7\text{A}}$, and for Se-I bonds, the sign change occurs in the interval 3.1–3.2 A, and the bond energy increases to $D_{Se-I}^{d_i=2.7A} = 2.293$ eV.

The bonds Sb-Sb and Sb-I and Te-Te and Te-I behave in a completely similar way.

The results obtained are consistent with the thermal rearrangement of atoms during the formation of short-range chemical bond order in the Bi-Sb-Se-Te system, and expand technological possibilities when considering phase transformations: the effect of pressure on phase transformation temperatures and the formation of physical properties by pressing and extrusion methods.

Authors' information

Denys Rybchakov – Postgraduate.
Orest Manyk – Candidate of Physical and Mathematical Sciences, Associated Professor (Docent) at the Department of Thermoelectricity and Medical Physics.
Valeriy Razinkov – Candidate of Physical and Mathematical Sciences, Deputy Director for Science.

References

1. Manyk O.M. (1999). *Multi-factor approach in theoretical material science*. Ukraine, Chernivtsi: Prut.
2. Keshavarz M.K., Vasileskiy D., Masut R.A., Turenne S. *P*-type bismuth telluride -based

composite thermoelectric materials produced by mechanical alloying and hot extrusion. *Journal Electronical Materials*. doi:10.1007/s11664-012-2284-2.
3. Barchii I.E., Peresh E.Yu., Rizak V.M., Khudolii V.O. (2003). Heterogeneous equilibria. Uzhhorod: Zakarpattia.
4. Manyk O.M., Manyk T.O., Bilynskyi-Slotylo V.R. (2017). Crystalline structure and chemical bond of Cd-Zn-Sb. *J. Thermoelectricity*, 5, 32–38.
5. Manyk O.M., Manyk T.O., Bilynskyi-Slotylo V.R (2023). Theoretical models of ordered alloys of thermoelectric materials based on Bi-Sb-Te. *J. Thermoelectricity*, 4, 5–16.
6. Manyk O.M., Manyk T.O., Bilynskyi-Slotylo V.R (2023). Theoretical models of ordered alloys of ternary systems of thermoelectric materials. 5. Chemical bond and state diagrams of *Cd-Sb-Te*. *J. Thermoelectricity*, 3, 5–18.
7. Ostwald W. (1891). *Lehrbuch der allgemeinen Chemie. Bd.2. Stochiometrie*. Leipzig: Engelmann.
8. Hihara G., Satoh M., Uchida T., Ohtsuki T., Miyama K. (2004). *Solid State Ionics, 172, 221.*

Submitted: 14.08.2025

Рибчаков Д.Є.[1,2] (https://orcid.org/0009-0002-2891-2258),
Маник О.М.[1] (https://orcid.org/0000-0003-2525-5280),
Разіньков В.В.[2] (https://orcid.org/0009-0004-2882-5466)

[1]Чернівецький національний університет імені Юрія Федьковича,
вул. Коцюбинського 2, Чернівці, 58012, Україна;
[2]Інститут термоелектрики НАН і МОН України,
вул. Науки, 1, Чернівці, 58029, Україна

Молекулярні аспекти механічної активації хімічних процесів четверних систем перспективних термоелектричних матеріалів розчинами галогенів

Розроблено теоретичні моделі механоактиваційних процесів порошкової технології отримання термоелектричних матеріалів четверних систем Bi-Sb-Se-Te з використанням розчинів йоду. Проведено розрахунки ефективних радіусів, перерозподілу електроної густини та енергії, дисоціації нееквівалентних гібридних орбіталей в залежності від міжатомних відстаней Bi-I; Sb-I; Se-I; Te-I. Показано, що за певних умов перерозподіл електронної густини міняє знак. Це означає, що хімічні зв'язки можуть бути як донорними, так і акцепторними Бібл. 8. Табл. 5.

Ключові слова: термоелектричний матеріал, хімічний зв’язок, порошкові технології, механохімія, механоактиваційні методи, багатокомпонентні системи, ефективні радіуси, електронна густина, донори, акцептори, нееквівалентні гібридні орбіталі, енергія дисоціації.

Надійшла до редакції 14.08.2025