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THEORETICAL MODELS OF ORDERED ALLOYS OF TERNARY SYSTEMS OF THERMOELECTRIC MATERIALS 3. CHEMICAL BOND AND STATE DIAGRAMS OF *Cd-Zn-Sb*

A diagram of the distribution of phase regions in the Cd-Zn-Sb system was constructed based on the isothermal sections of intermediate binary compounds Cd-Zn, Cd-Sb, and Zn-Sb. The results of calculations of effective radii, electron density redistribution and dissociation energy of non-equivalent chemical bonds depending on interatomic distances in the Cd-Zn-Sb ternary system are presented. Bibl. 7, Fig. 4, Tabl. 6.

Key words: theoretical models, chemical bond, state diagrams, effective radii, dissociation energies, interatomic interaction.

Introduction

This work is a continuation of studies begun in [1] on ordered alloys of cadmium antimonides using statistical and thermodynamic methods and is devoted to the construction of theoretical models of ordered alloys of ternary systems and state diagrams of *Cd-Zn-S*b from the standpoint of chemical bond.

The need to conduct such studies is due to the fact that the nature of chemical bond in such systems varies from metallic to ionic, covalent, and intermediate in layered sublattices.

In turn, a change in the chemical bond is reflected in a change in the structure of the short-range order of interatomic interaction, which, in turn, is associated with the features of state diagrams and phase transformations both in the solid state and in melts.

However, it should be noted that there is no consistent theory of phase transformations yet. That is why in this work the task was set to obtain theoretical schemes of state diagrams of ternary *Cd-Zn-Sb* systems and to calculate the parameters of chemical bonds using microscopic theory methods.

This approach allows us to generalize experimental data for binary state diagrams (*Cd-Zn*, *Cd-Sb*, *Zn-Sb*) to the case of ternary systems (*Cd-Zn-Sb*), and calculations of chemical bond parameters can be used to correct physicochemical properties of the resulting materials.

The availability of such information makes it possible to get closer to the solutions of the problems of melting and crystallization processes of ternary systems.

State diagrams

To solve the problem, it was necessary to summarize the results of experimental studies of binary state diagrams of *Cd-Zn*, *Cd-Sb*, *Zn-Sb* [2], physicochemical properties, and theoretical studies of quantum regularities of the original components [3, 4].

The results of state diagram studies were summarized by constructing isothermal sections (*Cd-Zn*, *Cd-Sb*, *Zn-Sb*) and solving the inverse problem. Its essence is that, unlike the direct problem, when the study of a complex system is carried out by breaking it down into simpler ones, according to established rules and patterns, in the case of the inverse problem, the elements *Cd*, *Zn*, *Sb* and state diagrams of binary systems *Cd-Zn*, *Cd-Sb*, *Zn-Sb* were chosen as the initial data. Next, based on the analyzed patterns, the components of the *Cd-Zn-Sb* ternary system were constructed. What was new in the study of ternary systems of cadmium and zinc antimonides was that to solve the problem, a triangulation method was used, based on the geometric properties of a triangle [5].

This mathematical approach makes it possible to solve a number of problems in physics, chemistry, and mathematics. In particular, in chemistry, when studying state diagrams of ternary systems, this approach allows for the distribution of such systems taking into account the chemical interaction between the elements *Cd*, *Zn*, *Sb*, located at the vertices of the triangle (solubility; substitution; exchange; formation of compounds; formation of solid solutions and mechanical mixtures), and the parameters of phase transformations can be found by means of theoretical calculations using the methods of quantum chemistry.

When constructing the theoretical model of *Cd-Zn-Sb*, first the analysis of binary state diagrams was given and isothermal sections were constructed at different temperatures. Further, by constructing conode triangles, the quantitative ratios of coexisting phases were determined and the limits of phase equilibrium in ternary systems 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 Fig. 1-4, where the following designations are entered:

α – solid phase based on *Cd*; β – solid phase based on *Zn*; γ – solid phase based on *Sb*; ε – solid phase based on *Cd-Zn* binary systems; ρ – solid phase based on *Zn-Sb* binary systems; δ – solid phase based on *Cd-Sb* binary systems; σ – solid phase based on *Cd-Zn-Sb* ternary system; *L* – liquid phase.

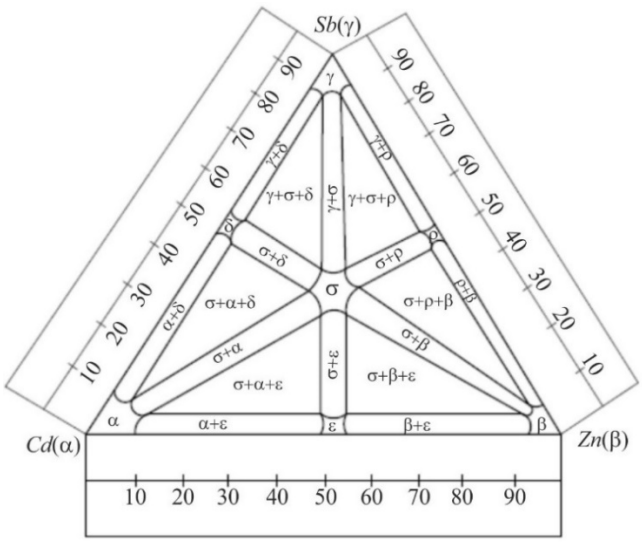

Fig. 1. A diagram of the distribution of Cd-Zn-Sb equilibrium phase regions in the solid state

Fig. 1 shows a diagram of the distribution of *Cd-Zn-Sb* phase regions in the solid state. The *Cd-Zn-Sb* ternary system was divided into six ordered ternary subsystems. This made it possible to consider interatomic interaction in a specific subsystem both from the standpoint of state diagrams and chemical bonds.

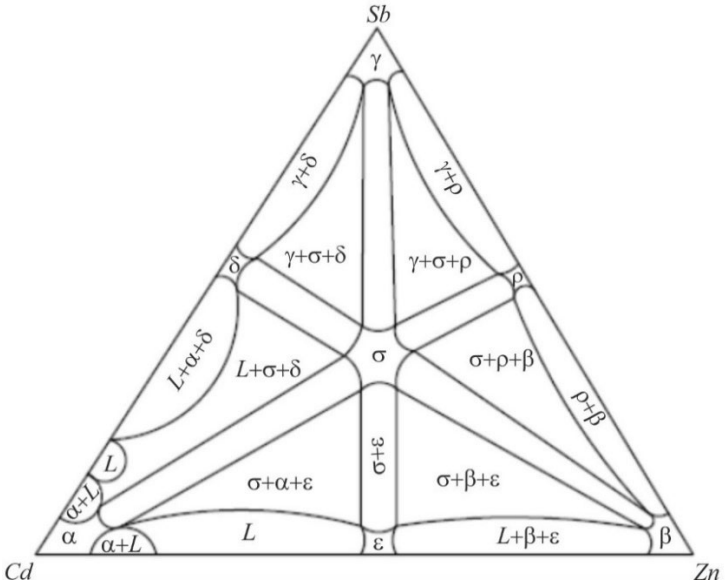

Fig. 2. Cd-Zn-Sb isothermal section at t=300°C

Fig. 2 shows an isothermal section at a temperature t = 300 °C, which is lower than the melting point of the *Cd*, *Zn*, *Sb* components and at the same time higher than the temperature of the first eutectic of the *Cd-Zn* system. Part of the cross section (35 %) of *Cd-Zn* is occupied by liquid *L*. Two-phase equilibrium (*L*+α), (*L*+ε), is carried out by primary crystals α and crystals ε (based on Cd_n Zn_m compounds) and liquid. Three-phase equilibrium (*L*+ε+β) is carried out by primary β crystals, ε crystals and liquid.

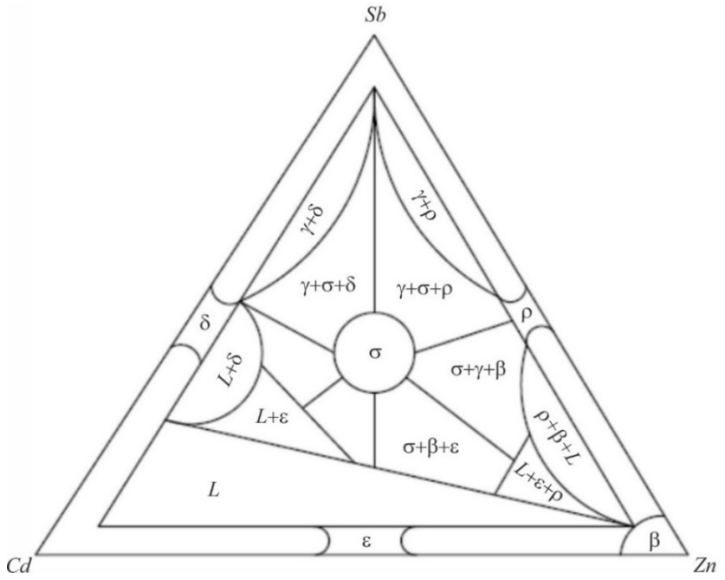

Fig. 3. Cd-Zn-Sb isothermal section at t=400°C

Fig. 3 shows an isothermal section at a temperature of 400 °C, which is lower than the melting point of *Zn* and *Sb*. But higher than the melting point of *Cd* (321°C). Most of the *Cd-Zn* cross section is occupied by liquid *L*, but unlike the previous case, the cross section contains conode triangles with equilibrium phases (*L*+ε+δ) and (*L*+ε+ρ), which are formed by crystals (ε+δ) and (ε+ρ) based on *Cd-Sb* and *Zn-Sb* compounds and liquid *L*. This division of ternary systems into separate sections of double state diagrams makes it possible to study the fine structure of cooling and heating depending on the short-range order of the chemical bond.

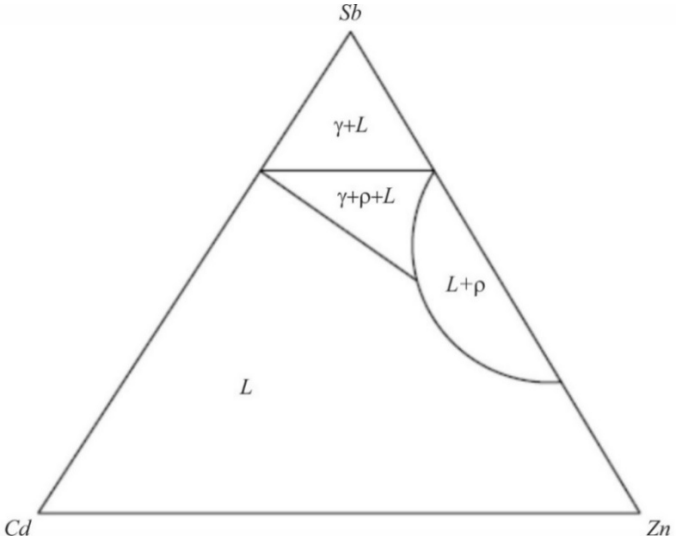

Fig. 4. Cd-Zn-Sb isothermal section at t=500°C

Fig. 4 shows the isothermal section at t = 500 °C above the melting point of *Cd* and *Zn*. The entire cross section of *Cd-Zn* is occupied by liquid, and in the *Zn-Sb* and *Cd-Sb* diagrams three-phase equilibria are represented by a conode triangle with phases (L + γ + ρ). Thus, the given isothermal sections make it possible to:

1. Find the limits of phase equilibrium in the liquid-crystal regions and between transformations in the solid state.
2. Separate phase diagrams corresponding to chemical compounds and solid solutions of different concentrations and mechanical mixtures.
3. Determine quantitative ratios of coexisting phases.
4. Determine the structure of the cooling and heating processes depending on the short-range order of the chemical bond.

However, it should be borne in mind that the results of studies of isothermal sections alone are not yet sufficient to determine the temperature intervals of phase transitions in multicomponent systems. Theoretical calculations of the interatomic interaction energy in the liquid and solid phases are required, depending on the interatomic distances from the standpoint of chemical bond.

Theoretical models of chemical bonding of ordered *Cd-Zn-Sb* alloys

A joint consideration of the methods of experimental and theoretical approaches in the quantitative method of calculating the parameters of the electronic structure of matter is associated with the emergence of qualitatively new ideas, which is not the result of the development of existing theories, but also negates some of them.

Thus, the formation of a chemical bond is accompanied by a rearrangement of the valence shells of the interacting atoms and leads to the need to use a number of concepts for their description. Despite the imperfection, from a theoretical point of view, of these concepts and other empirical criteria, their positive role in the systematization of experimental data and the development of ideas about the nature of interatomic interaction is beyond doubt.

The equations given in [6] were used in the calculations of effective charges, effective radii, dissociation energies of non-equivalent chemical bonds that are part of the *Cd-Zn-Sb* ternary system.

Analytical relationships reflecting the quantum laws of interatomic interaction given in [6] made it possible to write down the expression for the energy of chemical bonds in the form:

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

where $R_{UA(B)}^{0}$ is the radius of $A(B)$ atoms in the unexcited state; $\mathrm{tg}\,\alpha$ reflects the dependence of the ionic radius R_U on the number of electrons in the orbitals of converging atoms; d_i is interatomic distance of i-chemical bond; C_1 is a coefficient that reflects the relationship between dimensional and energetic characteristics of interatomic interaction; C_2 is a coefficient depending on the type of crystal structure and chemical bond.

The results of the calculations are given in tables 1-6. The values of the coefficients C_1 and C_2 in the first approximation are chosen to be equal to unity.

Table 1

Effective charges, effective radii, dissociation energies depending on interatomic distances of Zn-Zn NHO

Zn-Zn NHO / Parameters	*Zn-Zn*					
	φ1	φ2	φ3	φ4	φ5	φ6
d_i(Å)	2.8	2.9	3.0	3.1	3.2	3.3
R_U^{Zn}(Å)	1.40	1.45	1.50	1.55	1.60	1.65
$\Delta q_i(\varphi_i)$	-0.08	-0.18	-0.3	-0.4	-0.5	-0.6
$D(\varphi_i)$ *ev*	1.268	1.166	1.128	1.091	1.057	1.025

Table 2

Effective charges, effective radii, dissociation energies depending on interatomic distances of Zn-Cd NHO

Zn-Cd NHO / Parameters	*Zn-Cd*					
	φ1	φ2	φ3	φ4	φ5	φ6
d_i(Å)	2.8	2.9	3.0	3.1	3.2	3.3
R_U^{Cd}(Å)	1.475	1.52	1.56	1.61	1.65	1.69
R_U^{Zn}(Å)	1.325	1.38	1.44	1.49	1.55	1.61

Continuation of table 2

$\Delta q_i(\varphi_i)$	0.1	-0.025	-0.15	-0.28	-0.4	-0.52
$D(\varphi_i)$ *ev*	1.471	1.422	1.376	1.332	1.291	1.253

Table 3

Effective charges, effective radii, dissociation energies depending on interatomic distances of Zn-Sb NHO

Zn-Sb NHO / Parameters	*Zn-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^{Zn}(Å)	1.36	1.42	1.485	1.55	1.615	1.68
R_U^{Sb}(Å)	1.44	1.48	1.515	1.55	1.585	1.62
$\Delta q_i(\varphi_i)$	0.25	-0.12	-0.25	-0.4	-0.52	-0.65
$D(\varphi_i)$ *ev*	1.605	1.550	1.500	1.450	1.405	1.362

Table 4

Effective charges, effective radii, dissociation energies depending on interatomic distances of Cd-Cd NHO

Cd-Cd NHO / Parameters	*Cd-Cd*					
	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^{Cd}(Å)	1.4	1.45	1.5	1.55	1.6	1.65
$\Delta q_i(\varphi_i)$	0.33	0.18	0.025	-0.05	-0.27	-0.4
$D(\varphi_i)$ *ev*	1.853	1.789	1.730	1.674	1.622	1.572

Table 5

Effective charges, effective radii, dissociation energies depending on interatomic distances of Sb-Sb NHO

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^{Sb}(Å)	1.4	1.45	1.5	1.55	1.6	1.65
$\Delta q_i(\varphi_i)$	0.2	0	-0.2	-0.39	-0.6	-0.75
$D(\varphi_i)$ *ev*	2.332	2.252	2.177	2.107	2.041	1.980

Table 6

Effective charges, effective radii, dissociation energies depending on interatomic distances of Cd-Sb NHO

Cd-Sb NHO / Parameters	*Cd-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^{Cd}(Å)	1.42	1.48	1.53	1.6	1.65	1.71
R_U^{Sb}(Å)	1.38	1.42	1.47	1.5	1.55	1.59
$\Delta q_i(\varphi_i)$	0.27	0.1	-0.06	-0.22	-0.4	-0.55
$D(\varphi_i)$ *ev*	2.061	1.989	1.922	1.859	1.800	1.746

Discussion of the results

As follows from the results presented in tables 1-2, with the growth of interatomic distances, the dissociation energy of the corresponding chemical bonds decreases, and the redistribution of electron density in different intervals of interatomic distances changes differently: in *Cd-Cd* structural variants, the redistribution of electron density changes sign in the interval $3 \le d_i \le 3.1$ Å; (*Zn-Zn*) for all distances $2.8 \le d_i \le 3.3$ Å; (*Cd-Zn*) changes sign in the interval $2.8 \le d_i \le 2.9$ Å; (*Zn-Sb*) changes sign in the interval $2.8 \le d_i \le 2.9$ Å; (*Cd-Sb*) changes sign in the interval $2.9 \le d_i \le 3$ Å.

In addition, the obtained results confirm the fact that the overall diagram of *Cd-Zn-Sb* consists of three partial equilibrium stability diagrams of *CdSb-ZnSb* (*Cd*, *Sb*, *Zn*), three metastable Cd_4Sb_3-Zn_4Sb_3 (*Cd*, *Zn*, *Sb*) and three metastable Cd_3Sb_2-Zn_3Sb_2 (*Cd*, *Zn*, *Sb*) [7]. In this system, different structural states of melts can form. Therefore, solving problems of technology and optimization of materials based on *Cd-Zn-Sb* must be carried out taking into consideration the characteristics of the chemical bond of both the initial components (*Cd*, *Zn*, *Sb*) and intermediate systems (*Cd-Sb*, *Zn-Sb*, *Cd-Zn*).

Conclusions

1. A methodology has been proposed and theoretical models of short-range order of melts have been constructed using triangulation methods and isothermal sections in *Cd-Zn-Sb* ternary systems.
2. Calculations of chemical bond parameters in *Cd-Zn-Sb* systems depending on interatomic distances and atomic characteristics of the initial components are given.
3. It was shown for the first time that the redistribution of electron density leads to the formation of donor and acceptor chemical bonds in melts.
4. The results obtained are consistent with the results of calculations of chemical bond parameters using microscopic theory methods and optimize the technological capabilities of the synthesis of metastable phases based on *Cd-Zn-Sb* with predicted parameters.

References

1. Manik O. M., Manik T. O., Bilynskyi-Slotylo V. R. (2017.). Crystalline structure and chemical bond of *Cd- Sb-Zn*. *J. Thermoelectricity*, 5. P. 32 – 38.
2. Hansen M., Anderko K. (1958). *Constitution of Binary Alloys*, *2nd Ed*. New York: McGraw-Hill, p. 118.

3. Manik O. M., Manik T. O., Bilynskyi-Slotylo V.R. (2018). Theoretical models of ordered alloys of cadmium antimonide. *J. Thermoelectricity,* 4, 4 – 30.
4. Ashcheulov A. A., Manik O. N., Manik T. O., Bilynskyi-Slotylo V. R. (2011). Structural-energetic representations of chemical bond between cadmium and zinc. *Metal Physics and Advanced Technologies,* 33(7), 959 – 967.
5. Barchiy I. E., Peresh E. Yu., Rizak V. M., Khudolii V. O. (2003). *Heterogenni rivnovahy. [Heterogeneous equilibria]. Uzhhorod*: Zakarrpattia Publ. [in Ukrainian].
6. Manik O. M., Manik T. O., Bilynskyi-Slotylo V. R. (2021). Theoretical models of ordered alloys of ternary systems of thermoelectric materials. 1. Chemical bond and diagrams of state of *In-Cd-Sb*. *J. Thermoelectricity*. 2, 32 – 42.
7. Dremliuzhenko S. G. (2002). *Sistemy na osnove CdSb. Diagrammy sostoianiia, polucheniie i svoistva splavov. [Systems on the basis of CdSb. Diagrams of state, fabrication and properties of alloys]*. Chernivtsi: Ruta [in Russian].

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ТЕОРЕТИЧНІ МОДЕЛІ ВПОРЯДКОВУВАНИХ СПЛАВІВ ПОТРІЙНИХ СИСТЕМ ТЕРМОЕЛЕКТРИЧНИХ МАТЕРІАЛІВ. 3. ХІМІЧНИЙ ЗВ'ЯЗОК ТА ДІАГРАМИ СТАНУ *Cd-Zn-Sb*

Побудовано схему розподілу фазових областей в системі Cd-Zn-Sb на основі ізотермічних перерізів проміжних бінарних сполук Cd-Zn, Cd-Sb, Zn-Sb. Представлено результати розрахунків ефективних радіусів, перерозподілу електронної густини та енергії дисоціації нееквівалентних хімічних зв'язків в залежності від міжатомних віддалей в потрійній системі Cd-Zn-Sb. Бібл. 7, рис. 4, табл. 6.

Ключові слова: теоретичні моделі, хімічний зв'язок, діаграми стану, ефективні радіуси, енергії дисоціації, міжатомна взаємодія.

References

1. Manik O. M., Manik T. O., Bilynskyi-Slotylo V. R. (2017). Crystalline structure and chemical bond of *Cd- Sb-Zn*. *J. Thermoelectricity*, 5, 32 - 38.
2. Hansen M., Anderko K. (1958). *Constitution of Binary Alloys*, *2nd Ed*. New York: McGraw-Hill, p. 118.
3. Manik O. M., Manik T. O., Bilynskyi-Slotylo V.R. (2018). Theoretical models of ordered alloys of cadmium antimonide. *J. Thermoelectricity,* 4, 4 - 30.
4. Ashcheulov A. A., Manik O. N., Manik T. O., Bilynskyi-Slotylo V. R. (2011). Structural-energetic representations of chemical bond between cadmium and zinc. *Metal Physics and Advanced Technologies,* 33(7), 959-967.
5. Barchiy I. E., Peresh E. Yu., Rizak V. M., Khudolii V. O. (2003). *Heterogenni rivnovahy. [Heterogeneous equilibria]. Uzhhorod*: Zakarrpattia Publ. [in Ukrainian].
6. Manik O. M., Manik T. O., Bilynskyi-Slotylo V. R. (2021). Theoretical models of ordered alloys of ternary systems of thermoelectric materials. 1. Chemical bond and diagrams of state of *In-Cd-Sb*. *J.Thermoelectricity*, 2, 32 - 42.
7. Dremliuzhenko S. G. (2002). *Sistemy na osnove CdSb. Diagrammy sostoianiia, polucheniie i svoistva splavov. [Systems on the basis of CdSb. Diagrams of state, fabrication and properties of alloys]*. Chernivtsi: Ruta [in Russian].

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