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Phase Equilibria of Melts of Thermoelectric Materials Based on Bi-Sb-Se-Te

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Theoretical models of ordered alloys of quaternary systems based on Bi-Sb-Se-Te have been developed. A scheme of distribution of phase regions of quaternary systems based on ternary systems has been constructed using phase diagrams of binary alloys of the initial components Bi-Te, Bi-Sb, Bi-Se, Te-Sb, Sb-Se, Te-Se. Isothermal cross-sections of quaternary systems at different temperatures are presented, on the basis of which conoid triangles are constructed and cases of congruent and incongruent melting are predicted for materials with programmable properties.

Keywords: chemical bond, state diagrams, dissociation energy, effective charges, effective radii, thermoelectric materials, ordered alloys.

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Introduction

Complex ternary and quaternary systems of bismuth tellurides have long attracted the attention of thermoelectricians. This is due to the fact that with a change in the concentration of the initial elements in such systems, solid phases of variable composition are formed. The chemical composition of materials affects their phase state, which in turn depends on external actions: heating, cooling, deformation. This leads to phase transformations, processes, ordering in melts and alloys that form the physicochemical properties of the resulting materials.

Traditionally, thermoelectric materials (TEMs) were obtained mainly by melt crystallization methods [1].Much attention is paid to improving the methods for obtaining TEMs based on bismuth tellurides. One of the directions of such improvement was the study of the processes of chemical bond formation and phase transition in ternary systems based on bismuth tellurides using binary phase diagrams and molecular models [2-3], which gave encouraging results and made it possible to establish the boundaries of phase equilibrium in the liquid-crystal regions and the region of existence in the equilibrium of solid solutions, as well as to predict cases of incoherent melting of chemical compounds of different compositions. It is in such systems that solid phases of variable composition are formed, within which a transition occurs both in chemical composition and in structure with corresponding changes in physical properties. The nature of the chemical bond in such systems varies widely, which is reflected in the change in the structure of the short-range order of interatomic interactions and is associated with the features of state diagrams and phase transformations both in the solid state and in melts [4-6]. This approach made it possible to describe the processes of formation of interatomic interactions at different technological levels from the standpoint of chemical bonding. Therefore, the purpose of this work was to develop scientific foundations for creating theoretical models of ordered alloys of the quaternary systems Bi-Sb-Se-Te to find optimal compositions and processing modes, alloys, compounds and solid solutions that provide the best performance characteristics of the resulting materials. This work is devoted to theoretical models of phase equilibria and state diagrams of the quaternary systems Bi-Sb-Se-Te.

The choice of starting components was not accidental. The main task was to develop methods and approaches to improve the thermoelectric parameters of Bi_2Te_3. Therefore, Sb and Se were introduced into the composition of the resulting compound. The melting point of Se in this system was the lowest, and Sb was the highest. In addition, the peculiarity was that these elements, together with Bi and Te, form continuous solid solutions. The change in the atomic sizes of the components during the formation of solid solutions is interconnected with interatomic interaction and redistribution of electron density, which affects the formation of stable and metastable phases.

Thus, the use of multicomponent systems to improve methods for obtaining TEMs from melts requires, first of all, to generalize methods for constructing theoretical models of such systems that would take into account the characteristics of each component included in the system; make it possible to evaluate interatomic interaction depending on the concentration of the initial components and temperature using isothermal sections of phase diagrams of binary alloys of compounds and solid solutions, taking into account eutectic-peritectic regularities.

I. Theoretical models of Bi-Sb-Se-Te state diagrams

When constructing theoretical models, the results of experimental studies of the physicochemical and quantum regularities of the initial components Bi; Sb; Se; Te; state diagrams of binary systems based on them Bi-Sb; Bi-Te; Bi-Se; Sb-Te; Sb-Se; Se-Te were summarized, and a diagram of the distribution of phase regions in ternary systems based on them was constructed: Bi-Sb-Te; Bi-Sb-Se; Sb-Se-Te; Bi-Se-Te. Thus, the quaternary system Bi-Sb-Se-Te was represented by triangulation methods using state diagrams of binary systems of the initial components in the form of four ternary interconnected systems, which allowed us to study the dynamics of phase transformations depending on temperature as a single system. The results obtained are shown in Fig. 1, where the following notations are introduced:

α – solid phase based on Bi;
η – solid phases based on Bi-Se;.
β – solid phase based on Te;
χ – solid phases based on Sb-Se;
γ – solid phase based on Sb;
θ – solid phases based on Bi-Sb-Se;
λ – solid phase based on Se;
μ – solid phases based on Se-Te.
δ – solid phases based on Bi-Sb;
φ – solid phases based oni Bi-Te-Se;
σ – solid phases based on Sb-Te;.
ψ – solid phases based on Sb-Te-Se.
ε – solid phases based on Bi-Te;
L – liquid.
ζ – solid phases based on Bi-Sb-Te;

Fig. 1 shows a diagram of the distribution of phase regions of the Bi-Sb-Se-Te quaternary system in the solid state. The approach developed in this work makes it possible to trace the division of the quaternary system Bi-Sb-Se-Te into four ternary Bi-Sb-Te; Bi-Sb-Se; Sb-Se-Te; Bi-Se-Te; and those, in turn, each into six ordered ternary subsystems with the formation of binary compounds, solid solutions and mechanical mixtures of

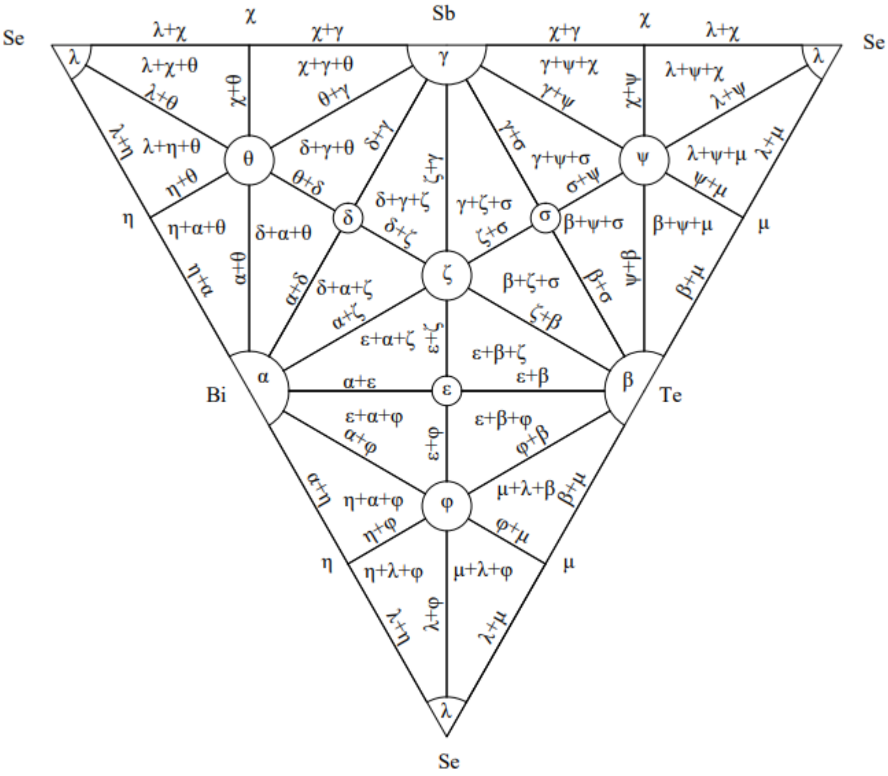

Fig. 1. Schematic of the distribution of phase regions in the solid state of Bi-Sb-Se-Te.

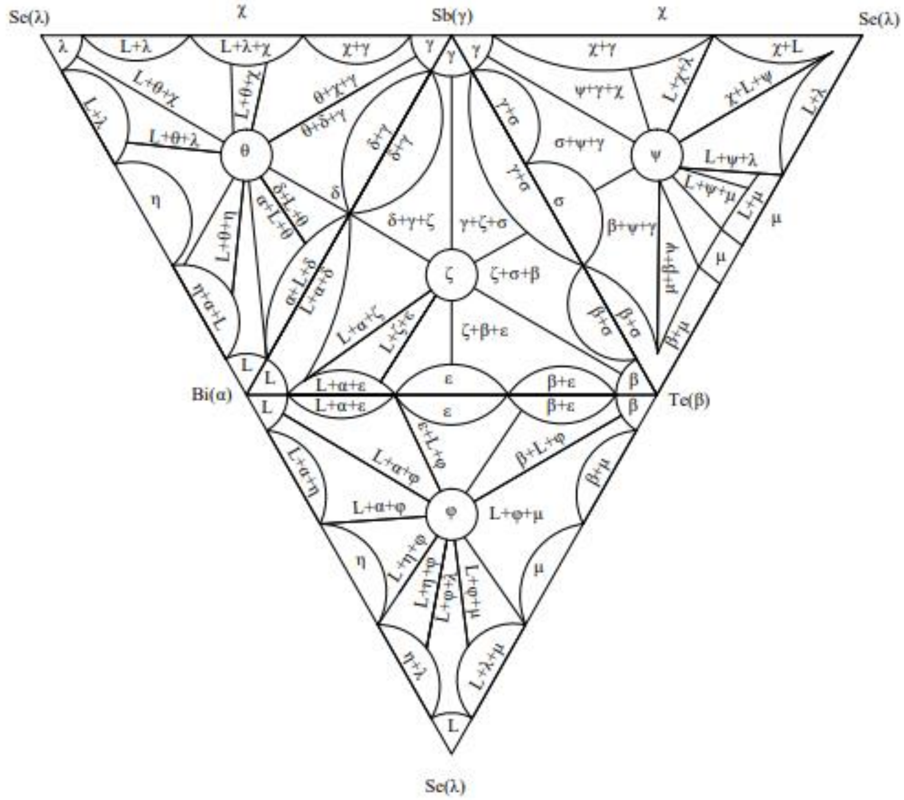

Fig. 2. Isothermal cross-section of Bi-Sb-Se-Te at 300°C.

the initial components in the subsystems under consideration. All this allows us to track in more detail the conditions for the formation of binary, ternary and quaternary compounds, the formation of solid solutions and mechanical mixtures; to investigate the conditions for the formation of phase transitions, the fields of eutectics and peritectics, depending on the concept and interatomic distances of the initial components from the position of the chemical bond.

Fig. 2 shows the isothermal cross section of Bi-Sb-Se-Te at a temperature of t = 300°C. This temperature is higher than the melting points of bismuth (271.3°C). This led to the fact that part of the Bi-Te; Bi-Sb; Sb-Se; Se-Te; cross-section is occupied by liquid (L), and two-phase equilibria (L, α), (L, ε), (L, δ), (L, λ), (L, χ), (L, μ) are realized by primary crystals α and λ and crystals ε and δ based on Bi-Te and Bi-Sb, as well as crystals χ and μ based on Se-Te and Sb-Se. In addition, on the sections of the quaternary system there are conoid triangles with equilibrium phases (L, α, δ), (L, α, ε), (L, α, ζ), (L, δ, ζ), (L, ε, ψ) та (L, λ, μ), (L, λ, χ), (L, λ, η), (L, λ, ψ), (L, λ, θ).

It is this division of quaternary systems into ternaries, and those in turn into separate sectors of binary phase diagrams, using the available empirical material, that makes it possible to investigate the processes of formation of short-range chemical bond order and the fine structure of cooling and heating of individual elements depending on their environment in quaternary systems.

Fig. 3 shows the isothermal cross section of Bi-Sb-Se-Te at a temperature of t = 400°C, which, as in the previous case, is higher than the melting point of bismuth and selenium and close to the temperature of the eutectic $Bi_{0.1}Te_{0.9}$ (t = 413°C) and Sb0.1Te0.9 (t = 424°C). In this case, liquid L occupies a larger part of the Bi-Sb cross section 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). A similar situation is observed for the other three ternary components of the quaternary system: Bi-Sb-Se; Sb-Se-Te; Bi-Se-Te. A similar situation is observed for the other three ternary components of the quaternary system: Bi-Sb-Se; Sb-Se-Te; Bi-Se-Te. In this case, the equilibrium phases (L + λ + χ), (L + λ + μ), (L + λ + η) are replaced by the phases (L + χ + μ), (L + μ + φ). This makes it possible to study the fine structure of the formation of intermediate compounds in quaternary systems depending on the concentration of the initial components.

Fig. 4 shows the isothermal cross-section of Bi-Sb-Se-Te at a temperature of t = 500°C. In this case, a liquid phase is observed on the Bi-Sb diagram in the range up to 55% Sb. In the range of 55 – 87 % Sb, both a solid Sb phase and solid solutions based on Bi-Sb are observed. In the range of 55 – 87 % Sb, both the solid phase of Sb and solid solutions based on Bi-Sb are observed. On the Se-Te diagram, a liquid phase is observed over the entire concentration range. As for the phase diagrams of Bi-Se and Bi-Te, at this temperature a clear demarcation of the equilibrium phases is observed: Bi_3Se; Bi_7Se_3; Bi_2Se; Bi_5Se_3; Bi_4Se_3; Bi_2Se_3 and also: Bi_7Te_3; Bi_2Te; Bi_4Te_3; BiTe; Bi_6Te_7; Bi_4Te_5; Bi_2Te_3. At the same time, the highest melting point of Bi_2Te_3 is at t = 586°C, and Bi_2Se_3 at t = 705°C. This may indicate that in these compounds there is a restructuring of the crystal lattice with heat absorption. It is characteristic that Se with a melting point of t = 219°C forms the compound Bi_2Se_3 at a higher

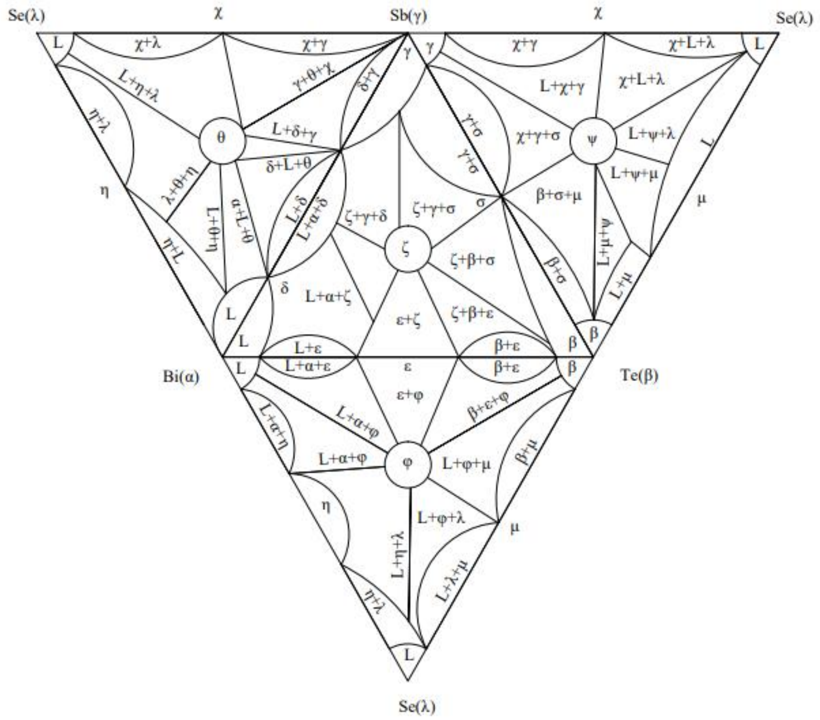

Fig. 3. Isothermal cross-section of Bi-Sb-Se-Te at 400°C.

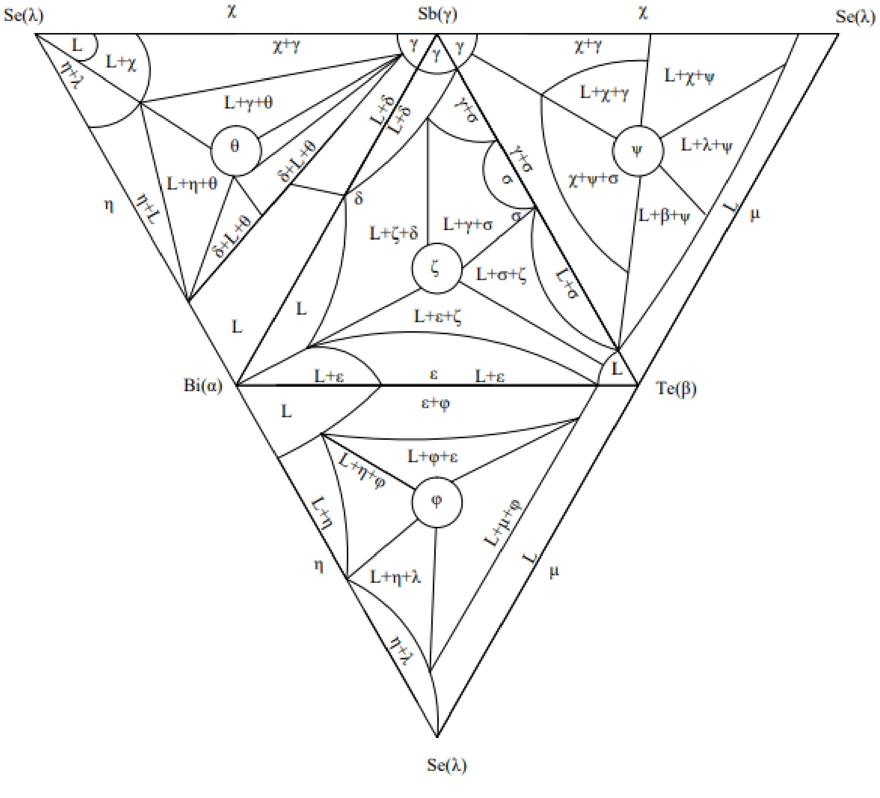

Fig. 4. Isothermal cross-section of Bi-Sb-Se-Te at 500°C.

temperature than Bi_2Te_3. This fact requires additional study from the point of view of chemical bonding.

Fig. 5 shows the isothermal cross section of Bi-Sb-Se-Te at a temperature of t = 600°C. At the same time, the liquid phase L is observed in the Se-Te and Bi-Te diagrams over the entire concentration range. The liquid phase is observed in the Bi-Se diagram in the interval up to 50 % Se, and with increasing Se concentration, a solid phase of different composition is formed. In the Bi-Sb diagram, a liquid phase is observed in the concentration range up to 90 % Sb, with an increase in the Sb concentration in the range of 90 – 97 % Sb, solid phases based on Sb (L+γ) are formed. As for the Sb-Se and Sb-Te melts, the phase diagrams are almost equally filled with liquid L.

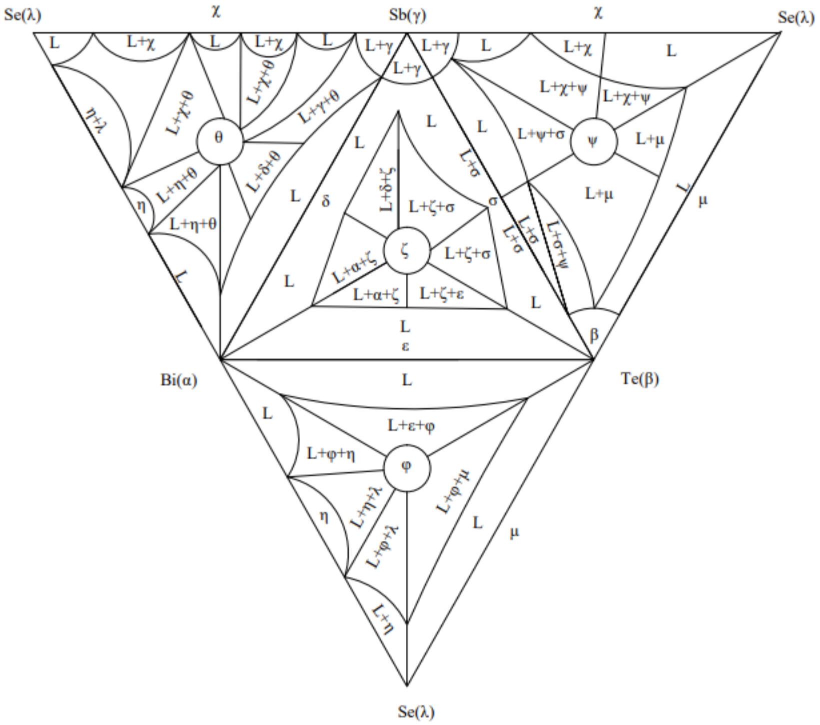

Fig. 5. Isothermal cross-section of Bi-Sb-Se-Te at 600°C.

Comparing the state diagrams of Bi-Se; Bi-Te; and Sb-Se; Sb-Te; the melting point of Bi_2-Se_3 was 705°C anda Bi_2Te_3 $t_{melt} = 586$°C, then in the case of selenium and tellurium the situation is the opposite: the melting point of Sb_2Te_3 $t_{melt} = 617$°C, and Sb_2Se_3 $t_{melt} = 590$°C, which can be, as in the previous case, associated with the rearrangement of the crystal lattice and requires additional research.

Conclusions

The use of an integrated approach to solving technological problems made it possible to construct theoretical models that combine generalized experimental information based on the analysis of isothermal sections of binary state diagrams of Bi-Sb; Bi-Te; Bi-Se; Sb-Te; Sb-Se; Se-Te; at different temperatures and theoretical methods and approaches to solving technological problems from the standpoint of chemical bonding.

The presented results expand the technological possibilities of obtaining new materials by taking into account the features of chemical bond formation, its fine structure of binary, ternary and quaternary systems and the construction of their phase diagrams, as well as eutectic-peritectic and exothermic and endothermic reactions during the formation of short-range order in Bi-Sb-Se-Te melts.

The proposed scheme of distribution of phase regions of equilibrium of quaternary systems in the solid state and the refinements made by constructing isothermal cross sections with regard to the thermodynamic features of binary and ternary systems of the initial components are in good agreement with the results of studies of thermal rearrangement of atoms during the formation of short-range chemical bond order, which is responsible for the appearance of stable and metastable phases in melts of binary and ternary systems of the initial components, which are part of Bi-Sb-Se-Te [5-6].

What was new in the study of quaternary compounds Bi-Sb-Se-Te was that when constructing the distribution diagram of the equilibrium phase regions, the inverse triangulation method was applied using the physicochemical properties of the initial components, binary compounds, and phase diagrams of binary alloys based on them. This made it possible to construct conoid triangles, determine the quantitative ratios of phases at different temperatures, and in the liquid-crystal regions, separate the boundaries of eutectic and peritectic diagrams to solve technological problems of forming stable and metastable phases, and predict cases of congruent and incongruent melting in the quaternary Bi-Sb-Se-Te systems when obtaining promising thermoelectric materials with programmable properties.

This allows us to establish the patterns of formation of compounds in systems and to reject unsuccessful ways of synthesizing new thermoelectric materials when the state diagram is unknown. In addition, in the absence of a strict microscopic theory of disordered systems, the results obtained expand the empirical basis for new theoretical developments.

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Фазові рівноваги розплавів термоелектричних матеріалів на основі Bi-Sb-Se-Te

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Розроблено теоретичні моделі впорядковуваних сплавів четвірних систем на основі Bi-Sb-Se-Te. Побудовано схему розподілу фазових областей четвірних систем на основі потрійних з використанням діаграм стану подвійних сплавів вихідних компонентів Bi-Te, Bi-Sb, Bi-Se, Te-Sb, Sb-Se, Te-Se. Приведено ізотермічні перерізи четвірних систем при різних температурах, на основі яких побудовано конодні трикутники та передбачено випадки конгруетного та інкогруентного плавлення для матеріалів з програмованими властивостями.

Ключові слова: хімічний зв’язок, діаграми стану, енергія дисоціації, ефективні заряди, ефективні радіуси, термоелектричні матеріали, упорядковувані сплави.