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Chapter 5

Physicochemical Analysis and Synthesis of Nonstoichiometric Solids

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/54815

1. Introduction

Technological progress is intimately associated with creation of new materials, such as composites, piezoelectrics, ferroelectrics, semiconductors, superconductors and nanomaterials with preset functional properties. For the synthesis of these materials, it is necessary to study the chemical processes that lead to the composition, structure, and accordingly desired properties. Investigation of the interrelation between the composition, structure and properties of matter and determination of synthetic conditions for obtaining substances with preset composition and structure are the major problems of physicochemical analysis. Although significant progress has been made in understanding several challenges remain for further advancements. These challenges and new approaches include some definitions – stoichiometry, nonstoichiometry, deviation from stoichiometry, substance, phase, component as well as the use of phase diagrams in selecting conditions for the synthesis of nonstoichiometric solids. Since nonstoichiometry is associated with defects, attention is also paid to their classification and formation. Synthesys of solid involves control over phase transformations. For this reason some features of the *P–T–x* phase diagrams are discussed. The following inportant features of *P–T–x* phase diagrams will be considered: highest maximal melting point $T_{m,AB}^{\max}$ of the solid compound S_{AB}, noncoincidence of the solid, liquid and vapor compositions ($x^L \neq x^S \neq x^V$) at this temperature, factors determining the value of the homogeneity range, some features of the terms congruent and incongruent phases and phase processes. Criteria for evaluating the homogeneity of nonstoichiometric solids are also considered.

The term *Physicochemical analysis* was introduced in [1] and defined as the field of chemistry dealing with the interrelation between the composition and properties of matter [1]. The foundations of physicochemical analysis were in [1-6].

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It has been realized that it is necessary to study the thermodynamic properties of solids and the phase diagrams of the systems in which these solids occur. Because the properties of solids depend significantly on their composition, great attention has been focused on the physicochemical analysis and foundations of the directed synthesis.

2. The essence of physicochemical analysis — Some definitions

Investigation of the interrelation between the composition, structure, and properties as well as determination of synthetic conditions for obtaining solids with preset composition and structure are the the basic problems of physicochemical analysis.

The subject of chemistry is the conversions of substances. What is a substance, and what is its conversion? A substance is a multitude of interacting particles possessing certain characteristics: composition, particle size, structure, and the nature of chemical bonding. It is these characteristics that determine the properties of the substance (Figure 1).

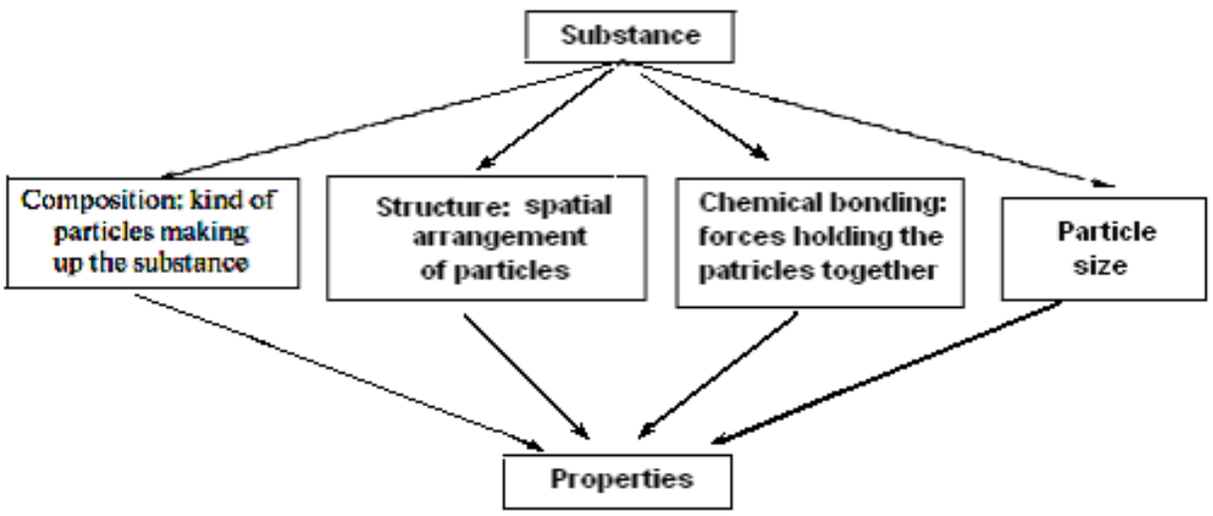

Figure 1. Interrelation between the basic characteristics and properties of a substance.

Composition is defined as the kinds of particles constituting the substance. For example, a sodium chloride crystal is built of sodium and chloride ions occupying cationic sites (Na^{+}_{Na}) and anionic sites (Cl^{+}_{Na}), respectively. The constituent particles can be not only atoms or ions, but also molecules (e.g., I_2 molecules in iodine crystals and water molecules in ice), coordination polyhedra (e.g., SO_4^{2-} tetrahedra in potassium sulfate), and other entities.

Structure is some ordered arrangement of the above particles in space.

The properties of a crystal, such as the lattice energy and electrical, optical, and chemical properties, are determined by the composition and structure of the crystal. Different spatial arrangements of the same particles, such as carbon atoms in diamond and graphite, are

characterized by different lattice energies and, accordingly, different properties, including melting and boiling points and hardness.

The chemical bond is understood as the forces binding the particles together. These forces arise from the the Coulomb interaction of electrons and nuclei. Depending on the electron distribution among nuclei, there can be ionic, covalent, and metallic bonds.

The particle interaction energy depends on the particle size. At the nanometer level (1–100 nm), it changes markedly, making possible the formation of new physical and chemical properties of the substance. This is explicable in terms of surface physics and chemistry (dependence of the surface energy on the particle size).

A conversion of a substance is a change in one or several characteristics of the substance (Figure1). This process is accompanied by a change in energy (dU) in the form of heat transfer (δQ) or work execution (δA):

$$dU = \delta Q - \delta A. \tag{1}$$

The main purpose of directed synthesis is to obtain substances with the preset composition, structure, and, hence, properties.

The direct synthesis of solids includes control of phase transitions. Therefore, thermodynamic data characterizing phases and their transitions are necessary to estimate the optimum synthetic conditions.

Now let us consider some specific features of the concepts of a phase and a component.

2.1. Phase and component

A substance is made up of particles or their interacting sets with a certain structure and chemical bonding. Energy is an equivalent or measure of these interactions. In thermodynamics, the state of a system is defined using a set of variables, or coordinates, such as pressure P, temperature T, and volume V. For a thermodynamic state of a system characterized by a set of coordinates (intensive thermodynamic properties), Gibbs suggested the term *phase of matter* [7, 8]. This definition emphasizes that the phase of matter is size- and shape-independent. Later, the word combination *phase of matter* gave way to the term "*phase.*"

The equation of state of a phase in terms of pressure (P), temperature (T), and composition (x) is written as (2)

$$dG = -SdT + VdP + \sum_{i=1}^{k} \left(\frac{\partial G}{\partial x_i} \right)_{P,T,x_j} dx_i, \tag{2}$$

where G, S, and V are the molar Gibbs energy, molar entropy, and molar volume of the phase, espectively; x_i is the mole fraction of the i-th component k; x_j means the constancy of the mole

fractions of all components but not the *i*-th component. The phases can be individual solid, liquid, gaseous compounds, or solid solutions, including nonstoichiometric compounds, whose thermodynamic properties are described by equations of state like Eq. (2) and are continuous functions of P, T, and x.

Note the following specific features of the concept of a phase. Firstly, existing phases should be distinguished from coexisting phases. The properties (Gibbs energy G, enthalpy, etc.) of an existing phase, such as a solution containing different concentrations of the same substance, are continuous functions of composition. By contrast, the properties of coexisting phases (i.e., phases that are in equilibrium) are equal in all parts of the system. The second specific feature is associated with the definition of a phase as the homogeneous part of a heterogeneous system. This definition is inexact because it does not specify whether homogeneous parts of a heterogeneous system are one phase or different phases. Thirdly, the concept of a phase is broader than the concept of a physical state (gas, solid or liquid). Finally, the fourth specific feature of the concept of a phase is associated with the issue of the minimum set of particles describable in terms of one equation of state like Eq. (2). From the standpoint of kinetic molecular theory, this set should be sufficiently large to allow regular particle energy distribution. Estimates demonstrate that the number of particles must be at least several tens. The properties of such a phase will be affected by surface tension [9].

The components of a system are the types of particles constituting this system. They are called constituents, and their number is designated n. If the concentrations of the n constituents are related by m independent equations, then $k = n - m$ is the number of independent constituents, or, simply, the number of components. For example, the system $NH_3(g) + HCl(g) = NH_4Cl(s)$, which consists of three substances ($n = 3$), whose concentrations are related by one equation ($m = 1$), is two-component since $k = n–m = 3–1= 2$.

The components are subject to the following constraints:

1. their concentrations must be independent of one another;
2. they should completely describe the concentration dependence of the properties of the system;
3. their number should satisfy the electroneutrality principle.

2.2. Stoichiometry, nonstoichiometry, deviation from stoichiometry

The properties of a substance depend on its composition. The great focus of materials sience are the concepts of stoichiometry, nonstoichiometry, and deviation from stoichiometry.

The proportions in which substances react are governed by stoichiometric laws (stoichiometry). These laws, which characterize the composition of chemical compounds, were discovered by systematizing experimental data. The fundamental laws of stoichiometry include the law of constant composition and the law of multiple proportions.

The law of constant composition, established in the 19th century by the French chemist Joseph Louis Proust, states that the chemical composition of a compound is independent of the way

in which this compound was obtained. The law of multiple proportions, formulated by the English chemist John Dalton in 1807, states that, when two elements combine with each other to form more than one compound, the mass fractions of the elements in these compounds are in a ratio of prime numbers. Both laws follow from atomistic theory and suggest that the saturation of the chemical bonds is necessary for the formation of a molecule from atoms. Any change in the number of atoms or their nature or arrangement indeed means the formation of a new molecule with new properties.

Are the law of constant composition and the law of multiple proportions always obeyed? They are valid only for the substances constituted by molecules. In fact, the composition of a substance can vary significantly, depending on the preparation conditions. It was long believed that only those chemical substances exist whose composition obeys the law of multiple proportions. They are stoichiometric and are called daltonides in honor of John Dalton. However, as methods of investigation were making progress, it turned out that the properties of solid inorganic substances, such as vapor pressure, electric conductivity, and diffusion coefficients, are composition dependence. In some composition range, the structure, i.e. the arrangement of the components in space remains invariable, while the component concentrations vary continuously. This range is called the homogeneity range or the nonstoichiometry range. These substances are referred to as nonstoichiometric or variable-composition compounds. Earlier, they were called berthollides in honor of Claude Louis Berthollet, Proust's compatriot. A nonstoichiometric compound can be treated as a solid solution of its components, such as cadmium and tellurium in the compound CdTe.

The homogeneity range is characterized by the corresponding deviation from stoichiometry. The stoichiometric composition of a solid compound, e.g., AnBm, where n and m are prime numbers, is the composition that obeys the law of multiple proportions. The deviation from stoichiometry or, briefly, nonstoichiometry (Δ) is defined as the difference between the ratio of the number of nonmetal atoms B to the number of metal atoms A in the real $A_nB_{m+\delta}$ crystal ($\delta \neq 0$) and the same ratio in the stoichiometric crystal A_nB_m [10]:

$$\Delta = \frac{m+\delta}{n} - \frac{m}{n} = \frac{\delta}{n}. \tag{3}$$

For the three-component system A–B–C, the composition of the solid phase $(A_{1-x}B_x)_{1-y}C_y$ is conveniently expressed in terms of the mole fraction of the binary compound (x) and nonstoichiometry (Δ).

In this case, the nonstoichiometry Δ can be viewed as the difference between the ratio of the equivalent numbers of nonmetal and metal atoms in the real crystal and the same ratio in the stoichiometric crystal. For example, for $(Pb_{1-x}Ge_x)_{1-y}Te_y$ crystals with a NaCl structure,

$$\Delta = y/(1-y) - 1/1 = (2y-1)/(1-y). \tag{4}$$

The mole fraction (molarity) of the binary compound determines the fundamental properties of nonstoichiometric crystals, including the band gap and heat capacity. The concentration of carriers—electrons and holes—and, accordingly, the galvanomagnetic and optical properties of nonstoichiometric crystals are also associated with nonstoichiometry.

3. Directed synthesis of nonstoichiometric solids

The strategy of directed synthesis of substances with the preset nonstoichiometry, structure, and properties is based on physicochemical analysis and includes the steps presented in Figure 2.

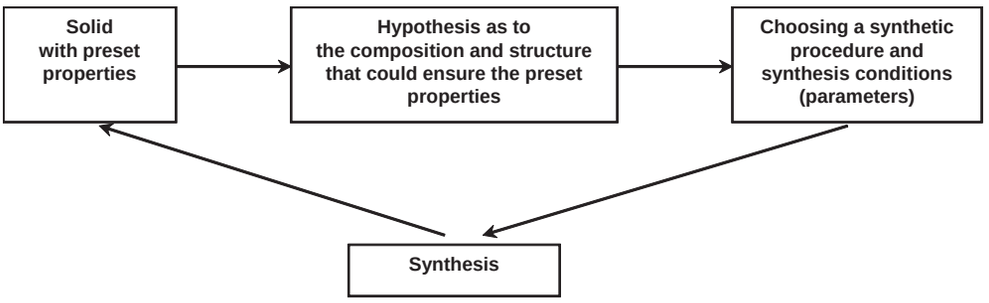

Figure 2. Steps of the directed synthesis of nonstoichiometric solids.

Synthesis is the consequence of processes involved in the conversion of the starting compounds into products. It includes selection and preparation of the starting chemicals (precursors), homogenization of the growth medium (melt, vapor, etc,), the nucleation of the desired phase, nucleus development (growth), and cooling (heating) of the product from the synthesis temperature to room temperature.

Each synthesis step depends on certain conditions or operating parameters. These include the chemical nature and composition of the growth medium, temperature, pressure, diffusion coefficients, heat and mass transfer, and the driving forces of chemical reactions (such as concentration, temperature, pressure, and chemical potential gradients). Figure 3 presents the most important operating parameters of the synthesis.

Provided that the analytical relationship between the rate of solid synthesis (growth) and the operating parameters is known, this process can be carried out under computer control. This problem has been solved for the Czochralski growth of silicon and germanium crystals and for the Bridgman growth of transition metal oxide crystals [10-14].

Solid synthesis involves phase transitions. For this reason, synthesis conditions are selected using phase diagrams (see section 4). The phase diagram of a system indicates the number of compounds forming in this system and the regions of their stability, specifically, the temperature, pressure, and composition intervals. Thus, using the phase diagram, it is possible to choose the medium (melt, vapor, etc.) for the synthesis of the desired solid, the synthesis conditions (temperature, pressure, and growth medium composition), and the way of carrying out the necessary conversions.

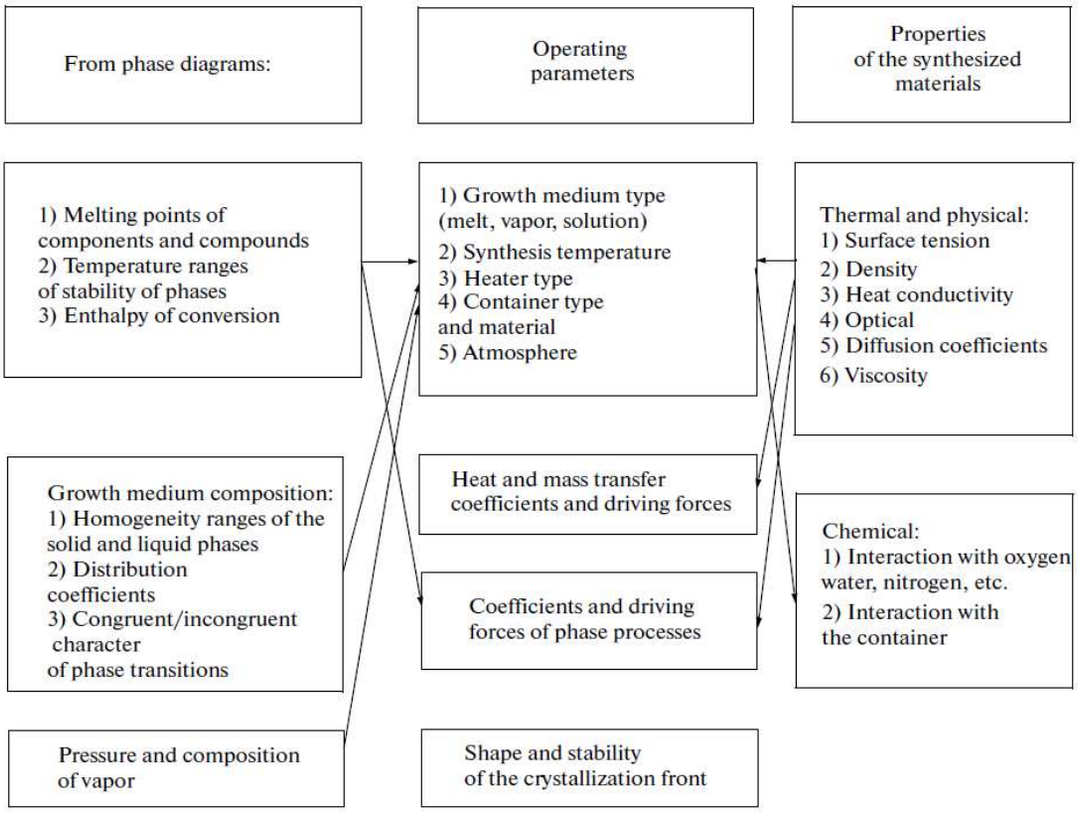

Figure 3. Operating parameters of solid synthesis.

The thermophysical and chemical properties of the starting substances, final synthesis products, and the growth medium to be used (melt, vapor, other solid phases) should be known along with thermodynamic data.

The conversion of a synthesis medium into a solid phase (crystallization) includes the nucleation and development of crystallization centers. Accordingly, it is related with heat and mass transfer and interfacial reaction kinetics. The general problem of analytically describing the crystallization process has not been solved. Furthermore, it is not always possible to evaluate the skill and equipment factors or to establish an unambiguous correlation between the properties of a nonstoichiometric phase and its molecular composition. In this sense, directed synthesis is regarded as being an art [13, 14].

4. Phase diagrams as a key to selecting conditions for synthesis of solid with well-defined nonstoichiometry

The synthetic conditions for nonstoichiometric solids (S_{AB}) coexisting with a vapor (V) and a melt (L) can be estimated using P–T–x diagrams or their T–x projections [15-17]. Let us consider the following features of the T–x diagrams: the highest (maximal) melting point $T_{m,AB}^{\max}$ of the solid S_{AB}; the compositions of the phases at this point; some fea-

tures of the solidus, liquidus, and vapor lines; the nonvariant points of congruent melting (T_m^c), sublimation (T_S^c), and evaporation (T_e^c); and, finally, congruent and incongruent phases and phase processes.

4.1. Maximal melting point $T_{m,AB}^{max}$ of a nonstoichiomertic solid S_{AB}

The Gibbs energy of a phase in a two-component system A–B is given by Eq. (2), so the phase equilibria in this case are represented graphically in a four-dimensional space. This space is explored as four three-dimensional projections: *G–P–T*, *G–P–x*, *P–T–x*, and *G–T–x*.

To clarify the features of the *T–x* diagram let us consider the derivation of part of the *T–x* projection from the *G–T–x* diagram. For this purpose, it should be considered the relative positions of the *G*-surfaces of the solid phase S, liquid phase L, and vapor V. In order to determine the arrangement of these three surfaces, we will traverse them with isothermal planes. The projections of the sections of the *G*-surface on the *G–x* plane will appear as G^S, G^L, and G^V curves representing the dependence (5) of the Gibbs energy (per gram-atom) on composition at a constant temperature (Figure 4):

$$\left.\begin{aligned} G^S_{A_{1-x}B_x} &= (1-x_B^S)\mu_A^S + x_B^S\mu_B^S \\ G^L_{A_{1-x}B_x} &= (1-x_B^L)\mu_A^L + x_B^L\mu_B^L \\ G^V_{A_{1-x}B_x} &= (1-x_B^V)\mu_A^V + x_B^V\mu_B^V \end{aligned}\right\} \tag{5}$$

where μ_A^S and μ_B^S are the chemical potentials of the components A and B in the solid phase, μ_A^L and μ_B^L are those of A and B in the liquid phase, μ_A^V and μ_B^V are those of A and B in the vapor phase, and x_B is the mole fraction of the component B.

Let us consider the effect of temperature variation on the relative positions of the *G–x* curves. At $T_1 > T_{m,AB}^{max}$ (Figure 4a), the solid phase S_{AB} is metastable and the two-phase system *L* + *V* is stable because a common tangent line can be drawn for the corresponding *G* curves, indicating the equality of the chemical potentials of the components in the equilibrium phases.

As the temperature is decreased, the arrangement of the *G* curves changes. Since the temperature dependence of the Gibbs energy is determined by the entropy $\left(\frac{\partial G}{\partial T}\right)_{P,x} = -S$ and the entropies of the vapor and melt are higher than the entropy of the solid phase, $S^V > S^L > S^S$, the *G* curves shift upwards upon cooling and the G^V and G^L curves do so more rapidly than the G^S curve. As a consequence, a common tangent for the G^S, G^L, and G^V curves can appear at some temperature $T_2 = T_{m,AB}^{max}$ (Figure 4b). This temperature $T_{m,AB}^{max}$ is referred as the highest maximal melting point of the solid S_{AB}.

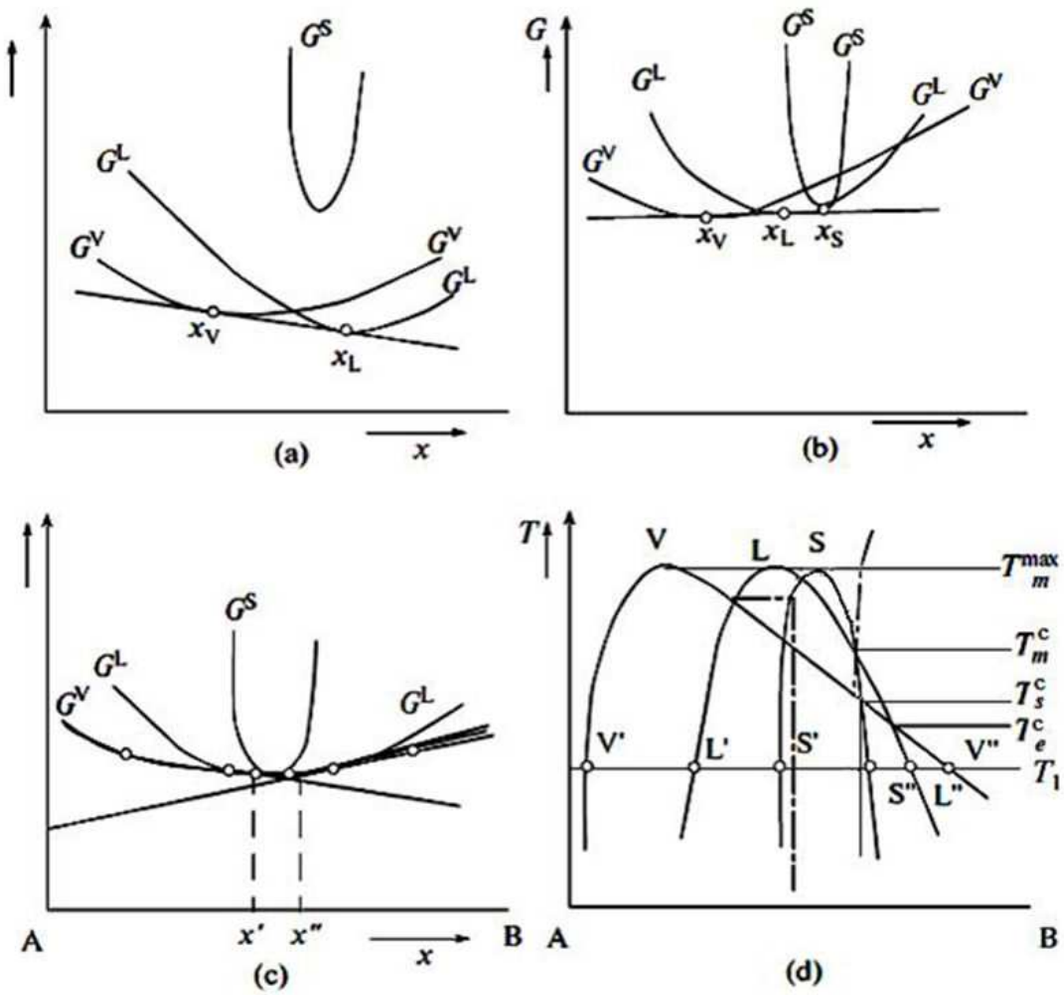

Figure 4. (*G–x*) sections of the *G–T–x* diagram: (a) $T_1 > T_{m,AB}^{max}$; (b) $T_2 = T_{m,AB}^{max}$; (c) $T_3 < T_{m,AB}^{max}$;(d) part of the *T–x* projection near $T_{m,AB}^{max}$.

From the definition of a phase as the totality of the parts of the system whose properties are described by the same equation of state, it follows that the properties of the system are homogeneous functions of composition, pressure, and temperature. Therefore, upon further cooling, for example, to $T_3 < T_{m,AB}^{max}$, it will be possible to draw two tangent lines for each of the G_{AB}^S , G^L, and G^V curves (Figure 4c). The coordinates of the equilibrium phases are designated as *V*, *L*, and *S* in Figure 4d. The subscripts (') and ('') are given to the phase compositions to the left and right, respectively, of the composition corresponding to $T < T_{m,AB}^{max}$.

As the temperature changes, the G^V-, G^L- and G^S-curves, shifting upwards and to the sides, describe three surfaces: $G^V = G^V(T, x)$, $G^L = G^L(T, x)$ and $G^S = G^S(T, x)$ – and the projections of the tangency points on the *T–x* plane draw the solidus line S'–S'', the liquidus line *L'–L''*, and the vapor line *V'–V''* (Figure 4d). Thus, Figure 4d shows part of the *T–x* projection of the *P–T–x* diagram near the highest melting point of the S_{AB} compound. The points *V'*, *L'*, and S' and

the points *V*'', *L*'', and *S*'', as examples, represent the compositions of the vapor *V*, solid phase S, and liquid phase *L* that are in equilibrium at the temperature $T = T_1$ and are called conjugate points. The lines *VV*'', *LL*'', and *SS*'' and the lines *VV*', *LL*', *SS*', as examples, formed by series of these points, are called conjugate lines. The lines connecting conjugate points, such as *V'L'S*' and *V*''*L*''*S*'', are called tie lines. Note that, among the various intersection points between the vapor, liquidus, and solidus lines (Figure 4d), only the intersections points of the conjugate lines (*VV''*, *LL*'', *SS''*, *V V '*, *LL '*, *SS '*) have a physical meaning, as distinct from those of the lines *LL '* и *VV''*, etc.

4.2. Specific features of the solids, liquidus and vapor lines

Here, let us consider the continuity of the solidus, liquidus, and vapor lines; the factors determining the homogeneity range; the issue of whether this range must include the stoichiometric composition; the causes of the retrograde character of the solidus line; and the concepts of a pseudocomponent and psevdobinary section in multicomponent systems.

The *T*–*x* and *P*–*T* projections of the *P*–*T*–*x* diagram of a two-component system having a compound *AB* [10, 15] are shown in Figure 5. The Gibbs energy of any phase is a homogeneous function of composition, so the solidus line *S*'*S*'', the liquidus line *L*'*L*'', and the vapor line *V 'V''*, which represent the temperature dependence of the compositions of the equilibrium phases, are continuous lines having no inflection points.

The homogeneity range of a solid compound is bounded by the solidus line. It is determined by the coordinates of the tangency points of the common tangent line for the *G* curves of the equilibrium phases (Figure 4), i.e., by the equality of the chemical potentials of the components. Therefore, in the general case the homogeneity range (Δ in Eq. (3)) is determined by the relative positions of the G^S, G^L and G^V curves (Figure 4) (i.e., the properties of all coexisting phases) and by the shape of the $(G–x)_{P,T}$ curves. Thus the nonstoichiometry value depends not only the specific features of the nonstoichiometric solid, namely the radius value, electronic configuration and electronegativity of the constituents species, but on the properties of all coexisting phases.

In the case of the compound *AB* formed from solid components *A* and *B*,

$$A_S + B_S = AB_S;\ \Delta_f G^0 \tag{6}$$

the homogeneity range can be estimated using the following relationship [17]:

$$f(\delta' / k) - f(\delta''/k) = -\Delta_f G^{\hat{i}}, \tag{7}$$

where $\Delta_f G°$ is the standard Gibbs energy of reaction (6), *f* is the monotonic function of composition *δ*, the subscripts ' and '' refer to the left and right sides of the homogeneity range, and *k* is a temperature dependent parameter. It follows from Eq. (7) that, the more negative the Gibbs energy $\Delta_f G°$, the larger the difference $f(\delta'/k) - f(\delta''/k)$ and, accordingly, the broader

http://dx.doi.org/10.5772/54815

the homogeneity range $\delta'' - \delta'$. For crystals dominated by covalent bonding, such as those of the $A^{III} B^{V}$ compounds *GaAs*, *InP*, etc., $\delta'' - \delta'$ is on the order of thousandths of an atomic percent. For crystal with polar bonds (*CdTe*, *PbSe*, *SnTe*), the homogeneity range is between a few tenths of an atomic percent and several atomic percent.

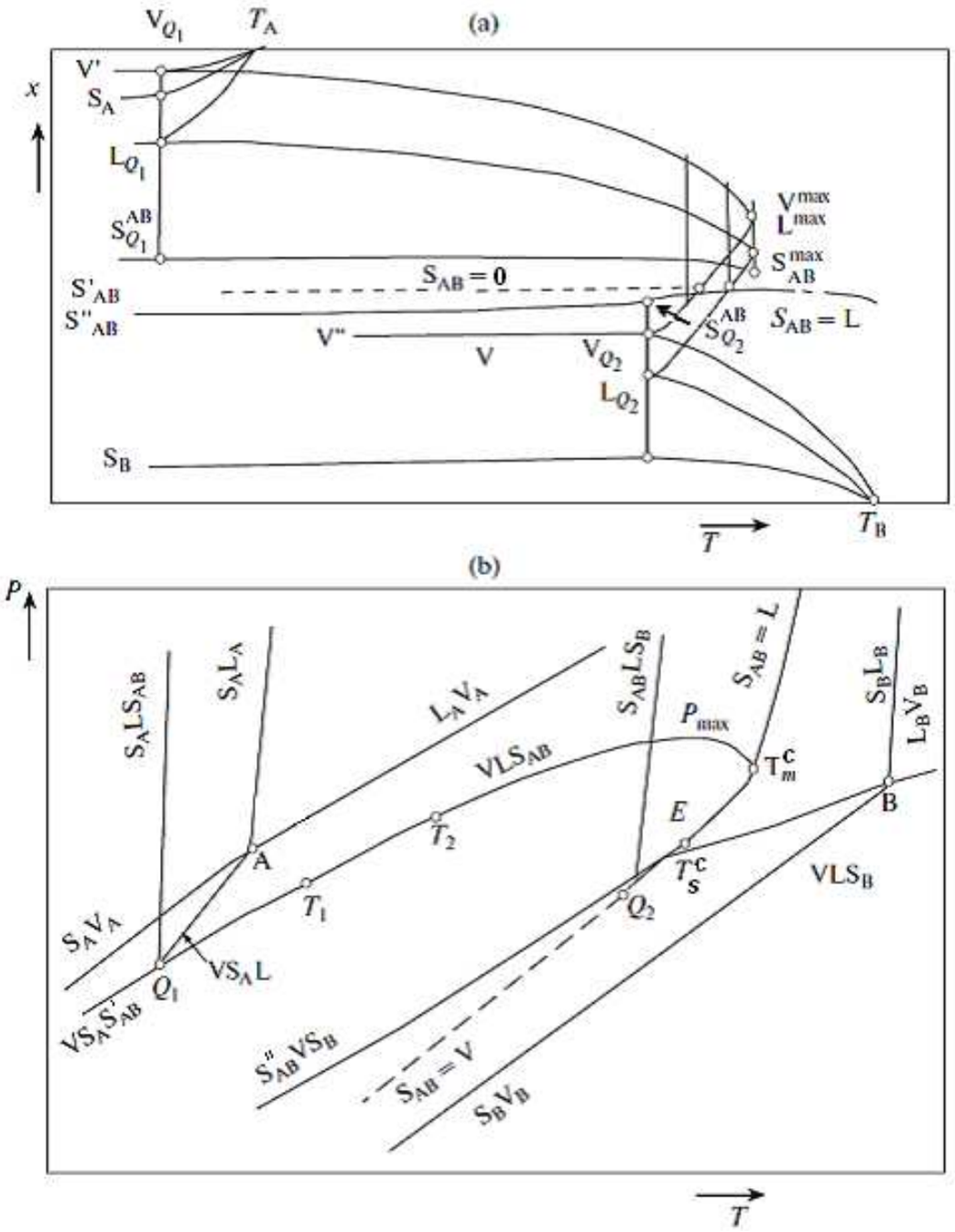

Figure 5. (a) *T–x* and (b) *P–T*- projections of the *P–T–x* diagram of a two-component system with a congruently melting compound (S_{AB}).

The homogeneity range may include the stoichiometric composition or not. Since the $\delta' + \delta''$ value defines the position of the center of the homogeneity range, the expression

$$f(\delta'/k) + f(\delta''/k) = [\mu_B(B) - \mu_A(A)] / RT - [\mu_B(\delta = 0) - \mu_A(\delta = 0)] / RT \tag{8}$$

describes the dependence of the position of the homogeneity range center on the difference between the Gibbs energies of the pure components (first term in (8)) relative to the isolated atoms in their ground states and on the difference between the chemical potentials of the components in the stoichiometric solid (second difference in (8). If the latter quantity is neglected in a series of crystallochemically similar compounds, the center of the homogeneity range, $(\delta' + \delta'')/2$ will shift in the direction in which the difference $\mu_B(B) - \mu_A(A)$ increases. This can easily be illustrated by examples of nontransition metal chalcogenides.

In the general case, the stoichiometric composition does not correspond to the minimum of the free energy of the solid phase and can fall outside the homogeneity range. When this is the case, the stoichiometric compound does not exist. For example, strictly stoichiometric ferrous oxide can be obtained only at high pressure.

The temperature dependence of the solidus $S'_{AB}S^{max}_{AB}S''_{AB}$ (Figure 5), which defines the boundaries of the homogeneity range of the nonstoichiometric compound S_{AB}, is described by the following equation [16, 18]:

$$\left(\frac{dx^S}{dT}\right)_P = \frac{\left(\partial S / \partial x\right)^S_{P,T} - (S^L - S^S) / (x^L - x^S)}{\left(\frac{\partial^2 G}{\partial x^2}\right)_{P,T}} \tag{9}$$

where S^L and S^S are the molar entropies and x^L and x^S are the compositions of the solid phase (S) and melt (L). The solubility of the components in the nonstoichiometric solid $A_{1-x}B_x == A_{1/2-\delta}B_{1/2+\delta}$ can be retrograde: it can initially increase with increasing temperature ($(dx^S/dT)>0$) and, on passing though a maximum, decrease ($(dx^S/dT)_P < 0$). The maximum solubility $(x^S)_{max}$ is found from the extremum condition for function (9) ($(dx^S/dT)_P = 0$) since $\left(\frac{\partial^2 G}{\partial x^2}\right)_P > 0$, according to the phase stability criterion. The retrograde solubility is due to the difference between the rates at which the entropies S^L and S^S, including their configurational components, grow with increasing temperature.

The liquidus line ($L_{Q_1}L^{max}L_{Q_2}$) and vapor line ($V_{Q_1}V^{max}V_{Q_2}$) in Figs. 4 and 5 represent the temperature dependence of the compositions of the melt (L) and vapor (V) in equilibrium with the nonstoichiometric solid S_{AB}.

4.3. Noncoincidence of the phase compositions at the maximum melting point of a nonstoichiometric solid S_{AB}

Both pressure and temperature extrema at T = const and P = const, respectively, exists in a three-phase two-component system provided that the following condition is satisfied [16]:

$$(x^L\text{-}x^S)/\left(x^V\text{-}x^S\right) = \left(S^L\text{-}S^S\right)/\left(S^V\text{-}S^S\right) = \left(V^L\text{-}V^S\right)/\left(V^V\text{-}V^S\right) \tag{10}$$

Thus, if the coexisting phases have different molar volumes V and entropies S, the composition of one of them will be a linear function of the compositions of the two others: $x^L = \beta x^S + (1 - \beta)x^V$ where β is a coefficient depending on the pressure and temperature and independent of the composition. Since $V^L \neq V^S \neq V^V$ and $S^S \neq S^L \neq S^V$ in the general case, at $T = T^{\max}_{m,AB}$ the composition of the solid phase S_{AB} does not coincide with the composition of the melt L and vapor V: $x^S \neq x^L \neq x^V$. This is in agreement with the phase rule:

$$c = k + 2 - r - \alpha, \tag{11}$$

where k is the number of components, 2 is the number of external fields (baric and thermal), r is the number of phases, and α is the number of independent constraints imposed on the intensive variables (c). Indeed, if it is assumed that, at $T = T^{\max}_{m,AB}$ $x^S = x^L = x^V$, then $\alpha = 2$ in Eq. (11) and $c = 2 + 2 - 3 - 2 = -1 < 0$, which is impossible. Unfortunately, this mistake is frequently encountered in the literature [18-21].

In the case of lead, germanium, tin, and cadmium chalcogenides, the vapor phase consists mainly of a chalcogen, so it can be accepted that $x^S - x^V = -0.5$. At $P \cong 1$ atm, $V^S - V^V \cong 10^{-3} V^S$ and $V^S - V^L \cong 5 \bullet 10^{-2} V^S$. Therefore, $x^S - x^L = 2.5 \times 10^{-5}$; that is, the compositions of the phases at the highest melting point do not coincide, even though they are very similar [14, 22, 23].

4.4. Nonvariant congruent melting, sublimation, and evaporation points of the three-phase equilibrium $S_{AB} + L + V$

Since the solid, liquid, and vapor phases are characterized by different temperature and concentration dependences of the Gibbs energy, the following intersection points of the conjugate liquidus, solidus, and vapor lines can appear on the T–x projection. The temperature of the intersection point of the conjugate liquidus and solidus lines refers to solid and liquid phases of equal compositions ($x^S = x^L$) and is called the congruent melting point T^c_m of the S_{AB} phase. The temperature of the intersection point of the solidus and vapor lines refers to a solid phase and vapor of equal compositions ($x^S = x^V$) and is called the congruent sublimation point T^c_S. The temperature of the intersection point of the conjugate liquidus and vapor lines refers to a liquid phase and vapor of equal compositions ($x^S = x^V$) and is called the congruent evaporation point T^c_e. The temperatures T^c_m, T^c_S and T^c_e do not correspond to the stoichiometric

composition ($\delta = 0$) of the solid phase $A_{1/2-\delta}B_{1/2+\delta}$, where $x = 1/2 + \delta$ and δ is the deviation from its stoichiometric composition AB. For example, congruently melting lead telluride contains $(2.8 \pm 0.3)\ 10^{-4}$ mol excess Te per mole of $PbTe$ [22, 23]. Because the formation energies of the defects responsible for the nonstoichiometries $\delta > 0$ and $\delta < 0$ are different, the G^S curve (Figure 4a, 4b, 4c) is asymmetric relative to the $\delta = 0$ composition. Accordingly, the coordinates of the common tangency points of the G curves in the general case do not coincide with the $\delta = 0$ composition.

The equality of the compositions of two phases of the three ones involved in the equilibrium means the appearance of one more relationship $\alpha = 1$ between independent variables (degrees of freedom) in the phase rule expression (11). Therefore, the equilibrium at the points T_m^c, T_S^c and T_e^c is nonvariant: $c = 2+2-3-1 = 0$. The solid S_{AB}, which has a homogeneity range at these points, can be considered a pseudocomponent whose properties are composition-independent, and the sections through ternary, quaternary, and other multicomponent systems involving the S_{AB} solid can be considered as pseudobinary.

4.5. Congruent and inconguent phases and phase processes

The concept of congruence is of great significance in the synthesis of nonstoichiometric solids because, in the case of noncoincidence between the synthetics medium (vapor, melt) and solids compositions, there are fluxes of rejected material and the corresponding kinetic instability of the crystallization front.

A phase can be congruent and incongruent in different temperature intervals. A phase obtainable from the phases that are in equilibrium with it by mixing them in appropriate proportions is called a congruent phase. A phase that cannot be obtained from the coexisting phases is called incongruent [24, 25]. As an example, let us consider the phase S_{AB} (Figure 5a) in the three-phase equilibrium $S_{AB} + L + V$ at different temperatures. Above the congruent melting point ($T_{m,\circledcirc AB}^c < T < T_{m,AB}^{\max}$) the solid phase S_{AB} is incongruent. In the temperature range $T_S^c < T < T_{m,\circledcirc AB}^c$, it is congruent with respect to the vapor and melt. In designations of three phase equilibria, a congruent phase is written in the middle. Thus, in the former case, the three-phase equilibrium is designated VLS_{AB}; in the latter case, $VS_{AB}L$.

The concepts of congruent and incongruent phases should not be confused with the concepts of congruent and incongruent phase processes.

Phase processes are changes in the state of the system such that the masses of some phases increase owing to the decrease in the masses of others without changes in the intensive parameters (temperature, pressure, phase compositions) [26]. A phase process in which one phase forms or disappears is called congruent. A phase transition in which more than one phase forms or disappears is called incongruent.

The same phase, for example, S_{AB} (Figure 5a), can be involved both in congruent and in incongruent phase processes. At a temperature or pressure corresponding to the three-phase line Q_1Q_2 in Figure 5b, the solid phase S_{AB} melts congruently, yielding a melt

and a vapor: $S_{AB} = L + V$. The compositions of the phases involved in this congruent phase process are different and are represented by the solidus, liquidus, and vapor lines in the T–x projection (Figure 5a). The melt and solid phase compositions coincide only at the congruent melting point T_m^c. At the temperatures corresponding to the eutectic nonvariant points T_{Q_1} and T_{Q_2} (Figure 5a), the S_{AB} phase is involved in the incongruent phase processes

$V + S_A = L + S_{AB}$ and $S_{AB} + L = V + S_B$.

Thus, S_{AB} phase can be said to melt congruently only in a certain temperature range.

Now let us consider the usage of the terms *congruently melting compound* and *incongruently melting compound* in the literature. Firstly, this differentiation is not strict, because the same compound (e.g., S_{AB}) can be involved in congruent and incongruent phase processes, depending on the temperature. Sometimes, a congruently melting compound is understood as a compound melting without dissociation or decomposition. However, a solid–melt phase transition is accompanied by the breaking and relaxation of chemical bonds in the crystal and by long-range disordering. Therefore, the term *melting without decomposition* is not quite correct, and it should be understood as the identity of the overall compositions of the coexisting phases. In the strict sense, the overall compositions of the phases coincide only at the congruent melting point $T_{m,\circledcirc AB}^c$, which is below the highest melting point $T_{m,AB}^{\max}$: $T_{m,\circledcirc AB}^c << T_{m,AB}^{\max}$.

An incongruently melting compound is sometimes understood as a solid compound that decomposes into a solid phase S_B and a liquid L upon melting (Figure 6). The compositions of the resulting phases differ from the composition of the parent phase. However, in some temperature range, such as $T_{Q_1} < T < T_P$, the "incongruently melting compound" is involved in the congruent melting process $S_{AB} = L + V$.

An essential feature differentiating congruently and incongruently melting compounds is that the highest melting point of a congruently melting compound is higher than the temperatures of the nearest nonvariant points: $T_{m,AB}^{\max} > T_{Q_1}$ and T_{Q_2} (Figure 5a).

The highest melting point of an incongruently melting compound is intermediate between the temperatures of the nearest nonvariant points of the system.

Supersaturation and synthesis of a nonstoichiometric solid at a fixed vapor pressure of the volatile component can be produced by cooling or, conversely, heating the three-phase system. The latter case corresponds to the temperature range $T_1 < T < T_2$ in Figure 5b. For example, cadmium telluride crystals were obtained by heating cadmium enriched melts [10]. Note that the composition of the crystals that were grown using the vapor–liquid–crystal technique always lies in the solidus line, i.e., at the boundary of the homogeneity range [15].

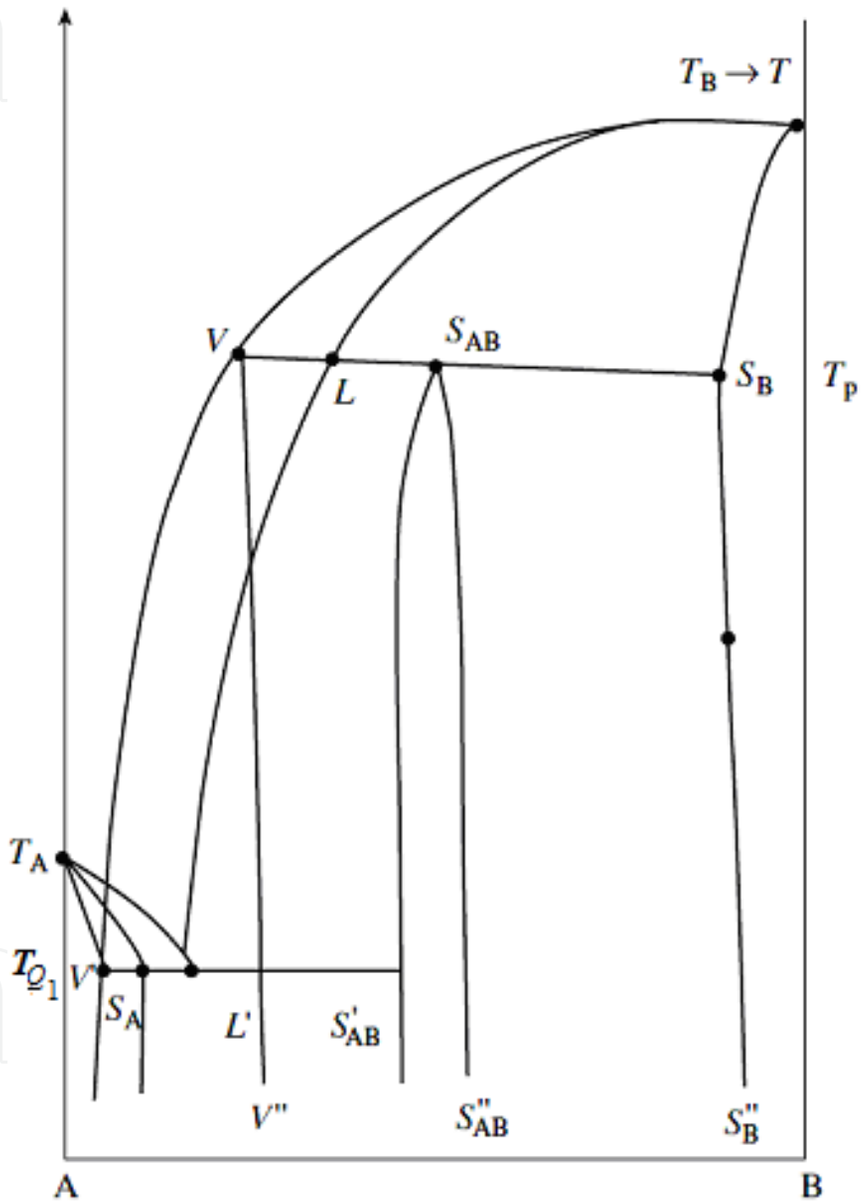

Figure 6. *T–x* projection of the *P–T–x* diagram of a two-component system with an incongruently melting compound (S_{AB}).

5. Nonstoichiometry and defects in solids

Solids like S_{AB} are grown from the vapor, melt (solution), or solid phases, which are called growth media. Crystallization can be viewed as the transfer of atoms of the components A and B from the growth medium (g.m.) to their regular sites A_A^x and B_B^x in the crystal lattice of the S_{AB} compound:

$$A^{g.m.} = A_A^x + V_B^x;\ \Delta G_1;\quad K_1 = \frac{[A_A^x][V_B^x]}{a_A} = exp(-\Delta G_1 / kT), \tag{12}$$

$$\hat{A}^{g.m.} = B_B^x + V_A^x\ ;\ \Delta G_2;\ \ K_2 = \frac{[B_B^x][V_A^x]}{a_B} = exp(-\Delta G_2 / kT) \tag{13}$$

where [ ] designates concentrations and a_A and a_B are the activities of the components in a growth media. The generation of V_B^x and V_A^x vacancies via reactions (12) and (13) is explained by the principle of conservation of the ratio of the numbers of sites characteristic of a given crystal lattice.

Because of the size and energy differences, the Gibbs energies ΔG_1 and ΔG_2, the equilibrium constants of reactions (12) and (13), and, accordingly, the numbers of atoms A and B in the crystals turn out to be different: $K_1 \neq K_2$ and $[A_A^x] \neq [B_B^x]$. Thus, nonstoichiometry appears; that is, the difference between the B-to-A ratios in the real and stoichiometric crystals becomes nonzero.

Note that the properties of crystals are affected not by the nonstoichiometric atoms A_A^x and B_B^x that occupy their regular sites, but by the defects (resulting from a disordering of the ideal structure).

These defects may be the vacancies V_A^x and V_B^x or the interstitial atoms A_i^x and B_i^x

$$A^{g.m.} = A_i^x + \Delta G_3, \tag{14}$$

$$B^{\mathbf{g.m.}} = B_i^x + \Delta G_4. \tag{15}$$

This circumstance is due to the fact that the A_A^x and B_B^x species do not change the energy structure of the crystal, but complete it in a way. Near the defects (V_A^x , V_B^x , A_i^x , B_i^x), the energy field and, accordingly, the electrical, mechanical and other properties of the crystal are altered (Figure 7). Thus, defects play an important role in the description of the real structure and properties of nonstoichiometric solids.

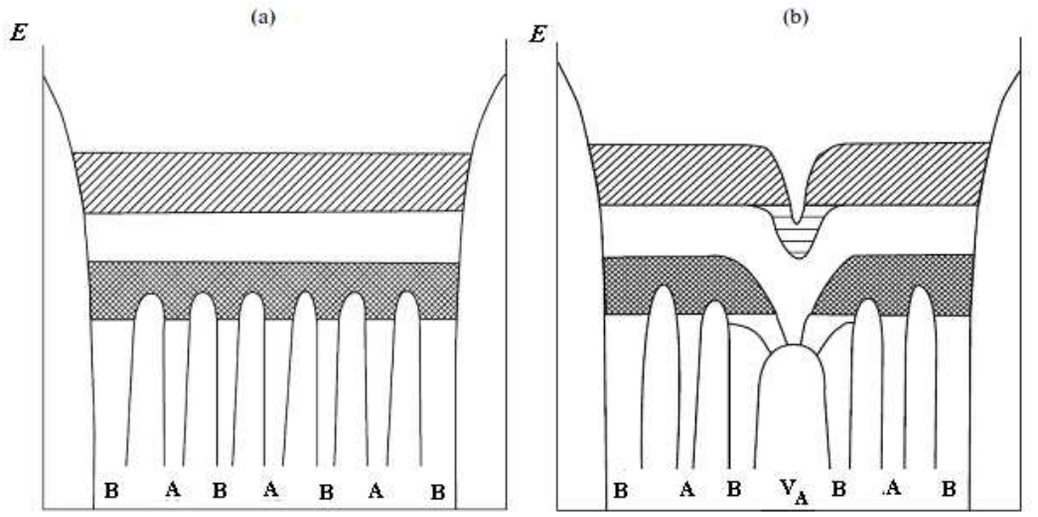

Figure 7. Model of the energy spectrum of (a) an ideal and (b) a nonstoichiometric crystal containing V_A vacancies.

6. Classification and formation of defects

Defect formation processes and defect classification are significant points in control of the defect composition of solids in their directed synthesis.

An ideal, or perfect, solid is one in which all particles making up the substance or structure elements (atoms, ions, molecules, etc.) occupy their regular sites in the lattice. Under heating, irradiation with a beam of high-energy particles, or mechanical treatment, the regular arrangement of particles over their sites undergoes disordering: some particles can leave their sites. The resulting disorder in the arrangement of particles over their normal sites is called defects [27].

In terms of geometry and size, all defects are divided into point and extended defects [27, 28] (Figure 8).

The size of point, or zero-dimensional, defects is comparable with the interatomic parameter. The zero-dimensional (OD) defects include electronic defects (holes, electrons, exitons), energy defects (phonons, polarons), and atomic point defects (APDs). The APDs in nonstoichiometric AB crystals include V_A^x and V_B^x vacancies (absence of atoms or ions in lattice sites); interstitial atoms A_i^x , B_i^x and F_i^x , where F - foreign atoms (the upper symbol x means the neutrality of the defect with respect to its environment), the lower symbol means the defect location.

The formation of an APD is an endothermic process requiring a small amount of energy: $0.5 \leq E_f \leq 3$ eV. Therefore, APDs are equilibrium defects and their concentration depends on synthesis conditions, namely, the temperature and the partial pressures of the components. The size of an APD is 0.1–0.5 nm; however, APDs polarize their environment in the crystal structure, causing slight displacements of neighborions, and largely determine the physical

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and chemical properties (diffusion, electric conductivity, etc.) of the nonstoichiometric crystal.

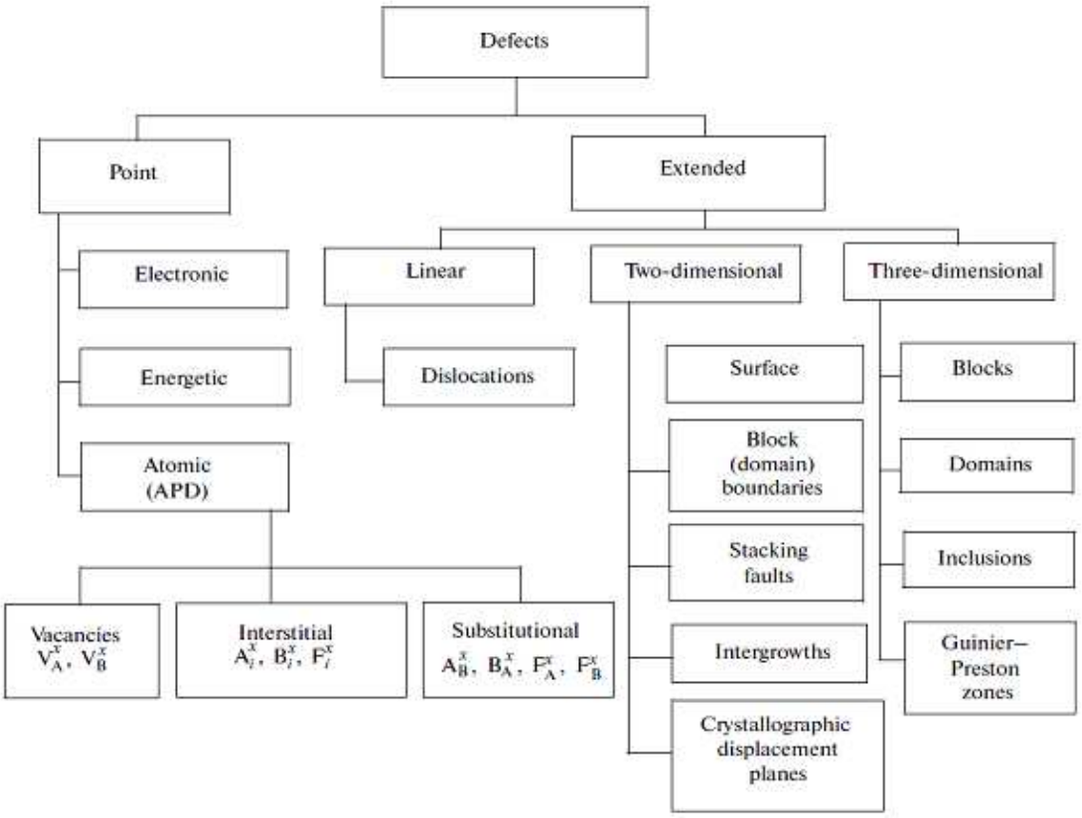

Figure 8. Classification of defects.

Vacancies, interstitial and antistructure (A_B^x , B_A^x) defects are classified as intrinsic defects of a crystal. The concentration (c_j) of these defects takes on a thermodynamically equilibrium value at any $T > 0$ K: $c_j \approx \exp(-W_j/kT)$, where Wj is the defect formation energy, $0 < W_j < 3$ eV. The higher the temperature, the higher the APD concentration c_j. As the crystal is cooled to room temperature, part of the APDs can annihilate via various mechanisms. However, many APDs persist even at exceptionally low reactions (12)–(15), but also from the irradiation of the crystal with high-energy (>1 MeV) electrons at very low temperatures.

Oppositely charged APDs can be attracted to one another to yield new APDs as electroneutral association species, such as ($V_A^- V_B^+$), ($V_A^- F_A^+$), (V_A^x)n. Dipole–dipole interaction leads to the formation of APD clusters, which can serve as nuclei of other phase in the nonstoichiometric crystal.

Extended defects include linear (1D), or one-dimensional, and two (2D)- and three-dimensional (3D) defects [29, 30] (Figure 8). Let us consider some specific features of these defects.

Linear defects, or dislocations, are similar to point and two-dimensional defects in the sense that their size is comparable with the unit cell parameter. In the third dimension, the dislocations are fairly long or even infinite. The simplest kind of dislocation is the edge dislocation.

The most important two-dimensional (2D) defects include solid surface, block (domain) boundaries, stadling faults and crystallographic displacement planes, which are surfaces in which coordination polyhedra of two contacting ideal are rearranged.

An example of periodic intergrowths is provided by the family of tungsten bronzes, A_xWO_3 (A = alkali metal). In these compounds, WO_3 layers are intergrown with hexagonal bronze bands. The formation of intergrown bronzes is likely favored by the synthesis conditions. The boundaries of intergrowths can be periodic (ordered) or nonperiodic (disordered).

Note the following specific features of two-dimensional defects. Firstly, their formation energy is fairly high (>3 eV) and they are kinetically stabilized nonequilibrium defects. The "frozen" state of these defects is responsible for their "memory" for preparation history. Secondly, these defects do not change the stoichiometry of the substance. Thirdly, planar defects result from APD interaction and exert a significant effect on on the reactivity and physical properties of nonstoichiometric solids.

The size of three-dimentional defects (Figure 8) exceeds the lattice constant in all three directions. These defects are, in essence, macroscopic imperfections of the crystal structure and are formed during crystal growth and subsequent processing. Three-dimentional defects include separate blocks; mosaics (totality of a large number of small- and large-angle boundaries); inclusions (microdeposits) resulting from phase transitions, such as the decomposition of a solid solution; magnetic domains (crystal zones with the same orientation of spins or electric dipoles); Guinier–Preston zones (parallel platelike formations as thick as a few unit cells, separated by different distances and having the same composition as the crystal); cavities; and cracks. Three-dimentional defects can be viewed as resulting from defect association and ordering. For example, pores can be considered to result from the association of a large number of vacancies. Bulk defects also include elastic tensile and compressive stresses.

Deviations from stoichiomrtry may be so large that defect interactions become significant leading to direct ordering, clustering, superstructure formation, long-range ordering, and the formation of new nonstoichiometric phases differing in symmetry, energy and other aspects from the parent phase. In such systems defects are intrinsic components of the crystal structure rather than being statistically distributed imperfections. The crystal-chemical and thermodynamic aspects of nonstoichiometric compounds with narrow and broad homogeneity range as well the approaches for controlling the nonstoichiometry and considered in [31].

7. Substance homogeneity criterion in physicochemical analysis

The Gibbs energy (G) of a crystal is a statistical quantity related to the distribution function. The mean G value determines the most likely distribution of zero-, one-, two-, and three-dimensional defects. Fluctuations around the mean value are possible, and, in a closed system (solid substance with a constant net composition at a fixed temperature), the configurational fluctuation can manifest itself as a change in composition within a small region as a consequence of a random motion of particles inside some volume element or to its surface. This

brings up the question of what substance can be called homogeneous. The degree of heterogeneity of a solid phase is characterized by the statistical distribution of structure elements from which the crystal is built. These structure elements are the atoms of the components of the system in their regular sites, as well as various zero-, one-, two-, and three-dimensional defects in their regular positions (Figure 8).

A quantitative estimate of the degree of heterogeneity can be based on the following three types of distributions:

1. distribution of structure elements in some measurable volume,
2. distribution of these volumes in the crystal, and
3. distribution of measurement data and properties of the solid phase.

Let σ be the confidence interval and c_i be the concentration of structure elements in the *i*th microvolume. If

$$\left| c_i - 1/N \sum_{i=1}^{N} c_i \right| \leq \sigma \tag{16}$$

the solid substance can be called homogeneous. If there is an *i* value at which this inequality is invalid, the solid phase should be considered to be heterogeneous. For practical use of a material, of significance are such deviations of the property in a given object from the weighted average value for the entire system that go beyond the confidence interval. In this sense, heterogeneity can be understood as the totality of property values, measured in all microvolumes, that fall outside the confidence interval. An analysis of generalized heterogeneity criteria in terms of an autocorrelation function was carried out by Nikitina et al. [32]. A thermodynamic analysis of defect ordering and an interpretation of the concentration dependences of physical properties taking into account short- and long- range order parameters were made using a model based on the above stricture elements or cluster components [33].

Some features of homogeneity criteria, physicochemical analysis, thermodynamics in materials science and inorganic crystal engineering are discussed in [34-37].

8. Conclusion

Technological progress is intimately associated with creation of new materials, such as composites, piezoelectrics, ferroelectrics, semiconductors, superconductors and nanomaterials with preset functional properties. For the synthesis of these materials, it is necessary to study the chemical processes that lead to the desired properties

Physicochemical analysis is the field of chemistry dealing with these processes, the interrelation between the composition, structure and properties of matter and determination of synthetic conditions for obtaining such substances. Several challenges and new approaches

have been discussed. They include the concepts of a substance, phase, component, directed synthesis strategy as well as some definitions. Attention was paid to nonstoichiometry, classification and formation of defects.

Synthesis of nonstoichiometric solid involves control over phase transformations. The P–T–x phase diagram is a key to selecting conditions for synthesis of solid with well-defined nonstoichiometry. For this reason the following features of *P–T–x* phase diagrams were considered: highest melting point of a nonstoichiometric compound ($T^{max}_{m,AB}$), noncoincidence between the solid-, liquid-, and vapor-phase compositions ($x^{L} \neq x^{S} \neq x^{V}$) at this temperature, factors determining the nonstoichiometry range, the terms congruent and incongruent phases and phase processes. Criteria for evaluating the degree of heterogeneity of nonstoichiometric solids were also considered.

Glossary of Abbreviations

$T^{max}_{m,AB}$ maximal melting point of a nonstoichiometric compound AB

(Na^{+}_{Na}) cationic sites

(Cl^{-}_{Cl}) anionic sites

U internal energy

Q heat

A work execution

δ nonstoichiometry

T^{c}_{m} nonvariant point of congruent melting

T^{c}_{S} nonvariant point of congruent sublimation

T^{c}_{e} nonvariant point of congruent evaporation

S solid phase

L liquid phase

V vapor

μ^{S}_{A} chemical potential of the component A in solid phase

μ^{S}_{B} chemical potential of the component B in solid phase

μ^{L}_{A} chemical potential of the component A in liquid phase

μ^{L}_{B} chemical potential of the component B in liquid phase

μ_A^V chemical potential of the component A in vapor phase

μ_B^V chemical potential of the component B in vapor phase

x_B mole fraction of the component B

S^V entropy of vapor

S^L entropy of melt

S^S entropy of solid

G^V Gibbs energy of vapor

G^L Gibbs energy of liquid

G^S Gibbs energy of solid

$\Delta_f G°$ standard formation Gibbs energy

k number of components

r number of phases

α number of independent constraints imposed on the intensive variables (c)

A_A^x regular sites of atom A in crystal lattice of the S_{AB}

B_B^x regular sites of atom B in crystal lattice of the S_{AB}

K_1 equilibrium constant

K_2 equilibrium constant

V_B^x and V_A^x vacancies

A_i^x and B_i^x interstitial atoms

c_j concentration

W_j defect formation energy

σ confidence interval

$(V_A^- V_B^+)$ electroneutral association species

$(V_A^- F_A^+)$ electroneutral association species

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