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## Аннотации на английском языке

### Review

Review article

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#### Complex copper-based chalcogenides: a review of phase equilibria and thermodynamic properties

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#### Abstract

Complex copper-based chalcogenides are among the most important functional materials in modern engineering and technology due to their diverse physical and physicochemical properties, environmental safety and availability. The development of new similar materials and the improvement of the applied characteristics of known compounds is largely associated with the use of approaches based on the physicochemical analysis and, in particular, the “composition-structure-property” relationship.

This review summarizes the available data on phase equilibria in ternary systems Cu-Tl(B<sup>IV</sup>, B<sup>V</sup>)-X (B<sup>IV</sup>-Si, Ge, Sn; B<sup>V</sup>-As, Sb, Bi; X-S, Se, Te) and the thermodynamic properties of their intermediate phases. Similar data are also considered for more complex systems forming solid solutions of various types of substitution based on known ternary copper chalcogenides. A significant part of the presented sets of mutually consistent data on phase equilibria and thermodynamic properties of the considered systems was obtained by our group over the past 10-15 years. Although these data cover only a small part of the systems described above, they provide great possibilities for manipulation of composition and structure, including entropic engineering strategies. The authors consider it extremely important to further develop fundamental research on phase equilibria and thermodynamic properties of complex copper chalcogenides and use their results widely in selecting alloy compositions for physical measurements.

**Keywords:** Environmentally friendly materials, Complex copper chalcogenides, Phase diagram, Solid solutions, Thermodynamic properties

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Review article

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#### Functional borates and their high-pressure polymorphic modifications. Review

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#### Abstract

The article presents the results of many years of studies of the growth of a low-temperature modification of barium borate  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> (R3c) crystals in the Na, Ba, B // O, F quaternary reciprocal system. Barium borate  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> is the most important nonlinear optical crystal of the UV spectrum. The key factor determining the quality of crystals is the choice of an optimal solvent. The article presents phase diagrams and the results of the growth of  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> crystals in several subsystems of the studied quaternary reciprocal system. Using atomistic modeling, we predicted and then experimentally obtained new high-pressure modifications:  $\gamma$ -BaB<sub>2</sub>O<sub>4</sub> (P2<sub>1</sub>/n), whose structure includes edge-sharing tetrahedra, and d-BaB<sub>2</sub>O<sub>4</sub> with assumed symmetry Pa $\bar{3}$ . In our study, we also focused on a solid solution with an “antizeolite” structure, which also crystallizes in the Na, Ba, B // O, F system.

**Keywords:** Low-temperature modification of barium metaborate, Quaternary reciprocal system, High-temperature solution growth, Borates with “antizeolite” structure

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## Review article

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### Nonstoichiometry of refractory inorganic compounds with a volatile component determined by new methods of physicochemical analysis. Review

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#### Abstract

The nonstoichiometry of refractory compounds with a volatile component is based on solid-phase and heterophase processes. At the same time, measurements of the parameters of these high-temperature phase transformations are often inaccurate. The inaccuracy results from the instability of the equipment as well as the behavior of themselves samples. To overcome these limitations, we developed three new methods of physicochemical analysis, which were then used in a comprehensive approach to the study of nonstoichiometry and the chemical composition of defective phases at the macro and micro levels. We refer to are high-speed thermal analysis, static tensimetric membrane technique, and stoichiographic differential dissolution method. The methods were used to measure temperatures up to 2400 °C, pressure up to 10 atm, and the degree of nonstoichiometry up to  $10^{-4}$  mol. %.

The review demonstrates the effectiveness of the proposed methodology applied to refractory compounds  $\text{LnS}$ ,  $\text{Ln}_2\text{S}_3$  ( $\text{Ln} = \text{P3M}$ ),  $\text{Yb}(\text{Ln})_{14}\text{MnSb}_{11}$ ,  $\text{ZrGeO}_4$ ,  $\text{Zr}_3\text{GeO}_8$ ,  $\text{MgO}$ , and  $\text{Mg}(\text{Ru})\text{O}$ , as well as highly volatile REM polychalcogenides and  $\text{ZnMo}(\text{W})\text{O}_4$ , presented in the form of powders, large crystals, ceramics, and films. For each of the studied substances, fundamental knowledge was gained regarding their spatial-temporal evolution responsible for the occurrence and the degree of nonstoichiometry. The data was obtained by studying  $T$ - $x$  and  $p$ - $T$  diagrams and by using of the stoichiographic method to determine the phase purity, microstructural inclusions, and spatial chemical inhomogeneity of individual phases at a micro level.

The obtained new quantitative thermodynamic and physicochemical data regarding the nonstoichiometry of the studied compounds was used as a basis for the choice of the composition and the design of the crystallization process, sintering and chemical deposition of thin films to realize a directed synthesis of materials with the desired properties. The review was initiated by Professor Magomed Babanly, DSc in Chemistry, Associate Member of the Russian Academy of Sciences, and editor of the special issue of the journal *Condensed Matter and Interphases* dedicated to physicochemical analysis in material science.

**Keywords:** Refractory chemically unstable compounds, Physicochemical analysis, Phase diagrams, nonstoichiometry

**Funding:** The research was carried out with the financial support of the Ministry of Science and Higher Education of the Russian Federation under the Government Order by Nikolaev Institute of Inorganic Chemistry of the Siberian Branch of the Russian Academy of Sciences (agreement No. 21031700315-2).

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## Review article

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### Phases with layered (AB) and “defective” ( $\text{A}_2\text{B}_3$ ) structures in $\text{A}^{\text{III}}\text{--B}^{\text{VI}}$ systems Part 1. Structural uniqueness and properties of bulk samples and films. Review

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#### Abstract

The review analyses and, where possible, reconciles data on two large groups of inorganic substances that are very unusual in terms of structure and properties, designated as  $\text{A}^{\text{III}}\text{B}^{\text{VI}}$  compounds. The structures and properties of typical compounds of these systems:  $\text{A}_1^{\text{III}}\text{B}_1^{\text{VI}}$  and  $\text{A}_2^{\text{III}}\text{B}_3^{\text{VI}}$  were considered. The relationship between the structure and the nature of the chemical bond and the organization of stoichiometric vacancies in crystal lattices is described in detail. The genesis of structures was analyzed for various modifications of  $\text{A}_2^{\text{III}}\text{B}_3^{\text{VI}}$  sesqui-chalcogenides. The transformations of these compounds into each other were also considered in relation with the ordering/disordering processes of stoichiometric vacancies. The possibilities of forming nanolayer structures, tubulenes, and intercalates were demonstrated for  $\text{A}_1^{\text{III}}\text{B}_1^{\text{VI}}$  layered compounds. The prospects for the application of both nanolayer coatings and bulk single crystals of  $\text{A}_1^{\text{III}}\text{B}_1^{\text{VI}}$  and  $\text{A}_2^{\text{III}}\text{B}_3^{\text{VI}}$  phases were analyzed. The presented review is based on the analysis of both literary data and the results of the studies of the authors and some other researchers of Voronezh State University.

**Keywords:** Gallium chalcogenides, Indium chalcogenides, Stoichiometric vacancies, Polymorphism, Vacancy ordering, Epitaxy, Layered structure

**For citation:** Zavrazhnev A. Y., Brezhnev N. Y., Nekrylov I. N., Kosyakov A. V., Kostryukov V. F. Phases with layered (AB) and “defective” ( $\text{A}_2\text{B}_3$ ) structures in AIII–BVI systems. Part 1. Structural uniqueness and properties of bulk samples and films. Review. *Condensed Matter and Interphases*. 2024;26(4): 646–665. <https://doi.org/10.17308/kcmf.2024.26/12398>

## Review article

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### Phase transformations in systems formed by titanium, silicon, aluminum, and zirconium oxides: Phase diagrams prediction and modeling. Review

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#### Abstract

This paper provides a review of variants of phase diagrams of binary and ternary systems constituting the  $\text{TiO}_2\text{--Al}_2\text{O}_3\text{--SiO}_2\text{--ZrO}_2$  four-component system.

The study involved building spatial (three-dimensional (3D)) computer models of the isobaric phase diagrams for four ternary oxide systems (and their variants, in case of contradicting initial data obtained by different researchers) constituting this quaternary system.

The geometric structure of its phase diagram was also predicted. For this purpose, phase diagram models were constructed as geometric objects in three-dimensional (3D) or four-dimensional (4D) space in the “concentration-temperature” coordinates by assembling (hyper) surfaces (unruled and ruled) and/or phase regions.

As a result:

- For the  $\text{TiO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$  system, it was considered possible variants of the structure of liquidus surfaces. These variations were due to availability of different theories describing the formation of compounds in the  $\text{TiO}_2\text{-Al}_2\text{O}_3$  binary system ( $\text{Al}_2\text{TiO}_5$  can melt congruently or incongruently and either possesses or does not possess the property of polymorphism).
- For the  $\text{TiO}_2\text{-Al}_2\text{O}_3\text{-ZrO}_2$  and  $\text{TiO}_2\text{-SiO}_2\text{-ZrO}_2$  systems, 3D-models of phase diagrams were developed at temperatures above 1,280 and 1,400 °C, respectively. The temperature limits were due to the lack of definitive description of the structure of subsolidus regions in the  $\text{TiO}_2\text{-ZrO}_2$  binary bounding system.
- Since the main contradictions in the  $\text{ZrO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$  system are associated with the type of phase reaction related to zircon formation (peritectic or peritectoid), the 3D model of the phase diagram was built according to the second variant, which involved the formation of the internal field of liquidus corresponding to the primary crystallization of  $\text{ZrSiO}_4$ .

The structure of the phase diagrams in the subsolidus was deduced for all four systems. It was also shown that in these systems at decreasing of temperature triangulation had a place twice.

For the  $\text{TiO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2\text{-ZrO}_2$  quaternary system, a scheme of phase reactions with the participation of the melt was deduced. This scheme includes six five-phase invariant reactions: two peritectic, two eutectic, and two quasi-peritectic reactions.

**Keywords:** Phase diagrams, Computer modeling, Four-dimensional visualization, Titanium, aluminum, Silicon, and Zirconium oxides

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Review article

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**Sodium fluoride and rare earth trifluorides systems. Review**

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**Abstract**

$\text{NaF-RF}_3$  systems, which are composed of sodium fluorides and rare earth trifluorides, are sources of many functional materials. Data on phase formation and phase equilibria in these systems were analyzed. The polymorphism and morphotropy of rare earth fluorides were considered taking into account the influence of pyrohydrolysis. A summary series of  $\text{NaF-RF}_3$  phase diagrams are presented and the coordinates of invariant equilibria are tabulated. The data of research by Thoma et al., performed in the sixties of the twentieth century, are now only of historical interest. In these systems,  $\alpha\text{-Na}_{0.5-x}\text{R}_{0.5+x}\text{F}_{2+2x}$  (cubic,  $R = \text{Pr-Lu, Y}$ ) and  $\beta\text{-Na}_{3x}\text{R}_{2-x}\text{F}_6$  (hexagonal,  $R = \text{La-Lu, Y}$ ) phases of variable composition with fluorite and gagarinite structures, respectively, are formed. In addition, solid solutions based on rare earth trifluorides with the  $\text{LaF}_3\text{-tysonite}$  ( $R = \text{La-Gd}$ ) structure and the berthollide phase of such a structure in the system with  $\text{TbF}_3$  were identified. Data was presented on the concentration dependence of the lattice parameters of fluorite phases. High temperature  $\alpha$ -phases with maxima on the melting curves allow growing single crystals from the melt. A complex pattern of ordering of these phases with decreasing temperature was observed. Low-temperature syntheses of intermediate phases in these systems led, in accordance with the Ostwald's step rule, to the initial formation of nonequilibrium phases of a fluorite structure, usually designated as “ $\alpha\text{-NaRF}_4$ ”, which were then replaced by equilibrium low-temperature hexagonal phases of “ $\beta\text{-NaRF}_4$ ”. The hexagonal phase in the  $\text{NaF-YF}_3$  system, doped with ytterbium and erbium (“ $\beta\text{-NaYF}_4\text{:Yb,Er}$ ”), is one of the most well-known, efficient up-conversion phosphors.

**Keywords:** Sodium fluoride, Rare earth fluorides, Phase diagrams, Fluorite, Gagarinite, Morphotropy

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## Original articles

Research article

<https://doi.org/10.17308/kcmf.2024.26/12428>

**Phase transformations of ternary copper iron sulfide  $\text{Cu}_{1.1}\text{Fe}_{1.9}\text{S}_{3.0}$  under temperature variations: thermodynamic and kinetic aspects**

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**Abstract**

The article considers ternary sulfide  $\text{Cu}_{1.1}\text{Fe}_{1.9}\text{S}_3$  with a metal/sulfur ratio corresponding to the complete stoichiometry of cubanite  $\text{CuFe}_2\text{S}_3$  as an intermediate phase of a solid solution with chemically disordered Cu and Fe cations in the ordered anionic framework. A new approach to determining the nature of the solid solution, its stability and behavior during cooled over a wide temperature and time range is suggested. To synthesize the sample, we used controlled directional solidification of a homogeneous melt with the  $\text{Cu}_{1.1}\text{Fe}_{1.9}\text{S}_3$  composition under quasi-equilibrium conditions and obtained a solidified zoned ingot, where the distribution of Cu, Fe, and S elements along its length was quantitatively determined. To detect small-scale structural and chemical changes, we used optical and electron microscopy methods, electron-probe X-ray spectral microanalysis, full-profile X-ray diffraction analysis, and the differential dissolution method, which allowed

to determine the phase and chemical states of the samples both at the macro level and with a high spatial resolution. With this approach, we established the following:  $\text{Cu}_{1.1}\text{Fe}_{1.9}\text{S}_3$  is an intermediate phase of a system with end-members of cubanite  $\text{CuFe}_2\text{S}_3$  and chalcopyrite  $\text{CuFeS}_2$ ; a homogeneous solid solution of chalcopyrite with 5 mol. % of cubanite exists near 930 °C with a chaotic distribution of Cu and Fe between the existing crystallographic positions; a solid solution of chalcopyrite with 6 mol. % of cubanite at 900 °C facilitates lattice strain relaxation through the formation of a block nanostructure; there is a solid solution of cubanite with 30 mol. % of chalcopyrite at 900–720 °C, with small-size clusters with a chalcopyrite stoichiometry evenly distributed inside the  $\text{Cu}_{0.94}\text{Fe}_2\text{S}_3$  matrix. The factors determining the evolution and stability of solid solutions are discussed taking into account the polymorphism of chalcopyrite phase. The newly obtained data is important for the synthesis of magnetic nanosized Cu-Fe sulfide materials and can also be used in the processing of sulfide ores rich in copper.

**Keywords:** System Cu-Fe-S, Directional Crystallization, Solid Solutions, Ordering

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Research article

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#### Physicochemical study of the processes of $\beta$ -cyclodextrin hydrates dehydration

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#### Abstract

The research involved synthesizing  $\beta$ -cyclodextrin hydrates of the  $\beta\text{-CD}\cdot n\text{H}_2\text{O}$  ( $n = 11.9\text{--}0.9$ ) composition.

The obtained compounds were studied by powder X-ray diffraction (XRD), which revealed the transition from a monoclinic unit cell to an orthorhombic one with a decrease in the water content in the samples. The pressure of saturated vapor of the water in the  $\beta\text{-CD}\cdot n\text{H}_2\text{O}$  ( $n = 10.6\text{--}7.0$ ) hydrates was measured by static tensimetry with membrane null-manometer over a wide temperature range (293–384 K) under conditions of a quasi-constant hydrate composition. The measured vapor pressure increases in proportion to the increase in the water content of the hydrate samples.

The experimental data reduced to a single composition of  $\beta\text{-CD}\cdot 1\text{H}_2\text{O}$  were approximated by the  $\ln p(1/T)$  equation, from which the thermodynamic parameters ( $\Delta_{\text{pr}}H^\circ$  and  $\Delta_{\text{pr}}S^\circ$ ) of the process of  $\beta$ -cyclodextrin hydrate dehydration were calculated. This information was used to estimate the binding energies of the water molecules to the  $\beta\text{-CD}$  framework.

**Keywords:**  $\beta$ -cyclodextrin hydrates, PXRD, Static tensimetry, Saturated vapor pressure, Dehydration enthalpy and entropy

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Research article

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#### The solid-phase equilibria in the $\text{GeBi}_2\text{Te}_4\text{-SnBi}_2\text{Te}_4\text{-Bi}_2\text{Te}_3$ system at 300 K and the characterization of tetradymite-type layered solid solutions

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#### Abstract

The  $\text{GeTe-SnTe-Bi}_2\text{Te}_3$  system is of great interest due to the potential formation of a series of cation-substituted solid solutions based on ternary layered compounds with a tetradymite-type structure, which have significant potential as valuable thermoelectric materials and topological insulators. This study presents the results of investigating this system in the composition range of  $\text{GeBi}_2\text{Te}_4\text{-SnBi}_2\text{Te}_4\text{-Bi}_2\text{Te}_3$  using powder X-ray diffraction analysis. Particular attention is given to obtaining equilibrium alloys.

An isothermal section of the phase diagram at 300 K has been constructed, consisting of four single-phase regions separated by three two-phase regions. The X-ray diffraction patterns of the equilibrium alloys were refined using the Rietveld method. The obtained diffraction results clearly indicate the presence of continuous series of solid solutions along the sections  $\text{GeBi}_2\text{Te}_4\text{-SnBi}_2\text{Te}_4$ ,  $\text{GeBi}_4\text{Te}_7\text{-SnBi}_4\text{Te}_7$ , and  $\text{GeBi}_6\text{Te}_{10}\text{-SnBi}_6\text{Te}_{10}$ . The lattice parameters for all the solid solution series were determined, showing a linear increase with the rise in Sn concentration.

**Keywords:** Solid solutions, Germanium bismuth tellurides, Tin bismuth tellurides, Topological insulators, Isothermal section, XRD

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## Research article

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**The effect of the aging time of the  $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$  coagel: features of its phase formation and the evolution of its adsorption properties**

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**Abstract**

To date, researchers have failed to provide a physicochemical explanation of the crystallization of low-soluble X-ray amorphous  $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$  caused by its aging in contact with the mother liquor. Data obtained in previous studies may be erroneous due to the unpredictable effect of  $\text{Si}^{4+}$ ,  $\text{Na}^+$  and  $\text{K}^+$  impurity ions. This study is aimed at establishing the regularities and features of the phase formation, as well as changes in the adsorption properties of  $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$  and the functional composition of the  $\text{ZrO}_2$  surface depending on the aging time of the  $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$  coagel in contact with the mother solution and in absence of impurity ions. The research was carried out on  $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$  obtained by direct precipitation at pH = 10 followed by aging for 6–406 h in a fluoroplastic reactor and on  $\text{ZrO}_2$  obtained by heat treatment of the corresponding  $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$  at 500 °C.

The properties of  $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$  and  $\text{ZrO}_2$  were studied by methods of synchronous thermal analysis, X-ray diffraction, scanning electron microscopy, low-temperature  $\text{N}_2$  sorption, vacuum infrared spectroscopy, infrared spectroscopy, and temperature programmed desorption of molecular probes. It was shown that there is an extremum of the phase composition and adsorption properties of  $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$  and  $\text{ZrO}_2$  after 24–96 h of aging.

It was established for the first time that the process of decomposition of dense aggregates of primary particles and submicron and micron aggregates and agglomerates of X-ray amorphous  $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$  accompanied by the appearance of edge OH-groups precedes its crystallization in contact with the mother solution (6–48 h). Further aging (96–406 h) revealed a gradual crystallization of  $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$  in the form of a mixture of the tetragonal and monoclinic phases of  $\text{ZrO}_2$  in a 1:1 ratio as a result of the attachment of primary particles of  $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$  with the participation of edge and bridging OH groups. Acid-base properties of the  $\text{ZrO}_2$  surface are in extreme dependence on the aging time. With prolonged aging (more than 213 hours), the acid function of the  $\text{ZrO}_2$  surface begins to prevail due to the participation of the basic edge OH groups in the attachment of the  $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$  primary particles. The observed changes are discussed from the perspective of the theory of oriented attachment of nanocrystals.

**Keywords:** Zirconium, Dioxide, Hydrated, Phase, Porosity, Morphology, Attachment, Surface, Acidity, Basicity

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## Research article

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**Phase subsolidus separation of the Ge–P–Sn ternary system**

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**Abstract**

2D materials are becoming increasingly attractive for use in modern electronic devices due to new properties that can arise from reduced dimensionality and the quantum confinement of charge carriers. Many studies are aimed at the search for materials characterized by a layered structure, which allows obtaining chemically stable atomic layers without surface broken bonds. Binary compounds of elements of IV (Si, Ge, Sn) and V (P, As) groups form layered structures in which two-dimensional layers with covalent bonds are bound by weak van der Waals forces, and from this point of view they can be considered as being promising 2D materials. However, it should be noted, that obtaining crystals of compounds of this class is associated with significant difficulties due to the high vapor pressure of phosphorus. Attempts have been made to obtain the GeP samples from tin melt solutions, which can significantly soften the synthesis conditions. The study of phase equilibria and the construction of a phase diagram of the Ge–P–Sn ternary system would allow approaching the production of both bulk and two-dimensional samples of germanium phosphide, as well as determining the possibility of alloying them with tin.

In this study, based on the investigation of several alloys of the Ge–P–Sn ternary system using the X-ray phase analysis, it was established that the phase subsolidus separation of the state diagram is carried out by the  $\text{Sn}_4\text{P}_3$ –Ge,  $\text{Sn}_4\text{P}_3$ –GeP,  $\text{Sn}_3\text{P}_4$ –GeP and  $\text{SnP}_3$ –GeP sections. The composition of the alloys corresponded to the figurative points of the intersecting sections. A scheme of phase equilibria in the Ge–P–Sn system was proposed. This scheme assumes the existence of a nonvariant peritectic equilibrium  $\text{L} + \text{Ge} \leftrightarrow \text{Sn}_4\text{P}_3 + \text{GeP}$  and eutectic processes  $\text{L} \leftrightarrow \text{Ge} + \text{Sn} + \text{Sn}_4\text{P}_3$  and  $\text{L} \leftrightarrow \text{Sn}_4\text{P}_3 + \text{GeP} + \text{SnP}_3$ .

The study of alloys using the differential thermal analysis method allowed determining the temperatures of these processes, equal to 795 K, 504 K, and 790 K, respectively. The  $T$ - $x$  diagram of the Sn–GeP polythermal cross section, which experimentally confirms the proposed scheme, was constructed.

**Keywords:** Phase diagrams, Germanium phosphide, Tin phosphides, Ge–P–Sn system, Subsolidus phase separation

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## Research article

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**Behavior of major and minor elements during directional crystallization of Fe-Ni-Cu-S-(Rh, Ru, Ir, Pt, Pd, Ag, Au) melt**

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**Abstract**

The Cu-Fe-Ni-S system is unique in terms of the number of crystalline phases with a variety of combinations of properties, which makes it relevant for prospective material studies. The phases of this system compose typical associations of massive zonal sulfide Cu-Ni ores, and their copper-rich zones are characterized by a high content of noble metals. Therefore, this system is among the most important of those used for the geochemistry of sulfides and for the metallurgy of copper and nickel. There is insufficient quantitative information on the equilibrium distribution coefficients of macrocomponents and the behavior of impurities upon crystallization of solid solutions in the region of the solid-melting diagram corresponding to natural ores or intermediate products of metallurgical production. Therefore, the goal of the work was to obtain new data on the phase diagram of the Cu-Fe-Ni-S system and corresponding phases of noble metals (Rh, Ru, Ir, Pt, Pd, Ag, Au) during the process of fractional crystallization of the melt simulating zonal copper-rich ores of platinum-copper-nickel sulfide deposits.

We conducted quasi-equilibrium directional crystallization of the melt with a composition of (at. %): Fe 29.20, Ni 5.85, Cu 17.60, S 47 with addition of 0.05% of Rh, Ru, Ir, Pt, Pd, Ag, and Au. The obtained sample was studied using optical and scanning electron microscopy, energy-dispersive spectrometry (SEM/EDS), and X-ray phase analysis. Differential thermal analysis (DTA) was used to determine the liquidus temperatures along the crystallization path.

The distribution of macrocomponents along the cylindrical ingot showed that it consisted of five primary zones. Primary phases and phase associations crystallized from the melt in the following sequence: mss / mss + iss / iss / iss + bnss / bnss + pnss, where mss is monosulfide solid solution  $(\text{Fe}_x\text{Ni}_{1-x})\text{S}_{1+x}$ , iss is intermediate solid solution  $(\text{Cu,Fe})\text{S}_{1-x}$ , bnss is bornite solid solution  $\text{Cu}_{5+3x}\text{Fe}_{1+x}\text{S}_{4+3x}$ , and pnss is pentlandite solid solution  $(\text{Fe}_x\text{Ni}_{1-x})\text{S}_8$ . This indicated a complex structure of the solid-melting diagram in the studied region. We determined the crystallization temperatures of mss and iss. A new type of secondary (phase) zoning was identified, formed as a result of subsolidus transformations of primary phases, which can be present in Cu-Ni sulfide ores. It was found that impurities can dissolve in the main sulfide phases, form individual microphases in the sulfide matrix, or be present in these microphases in the form of solid solutions. The main concentrators of Pd were pn and sug. Ir, Rh, and Ru were distributed between mss and pn, and Ag preferred bnss. Most impurities of noble metals formed inclusions as independent microphases:  $\text{RuS}_2$ ,  $\text{Pt}_3\text{Fe}$ , Au\* gold-based alloy, Pt-Fe-Au alloy,  $\text{CuIr}_2\text{S}_4$ , and native Ag. The results of the work showed that the behavior of macrocomponents could be described using distribution coefficients, and the behavior of microcomponents did not strictly correspond to the classical theory of fractional crystallization of multicomponent melts with impurities.

**Keywords:** Cu-Fe-Ni-S system, Phase equilibria, Noble metals, Directional crystallization, DTA

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## Research article

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**Labile states are the basis of functional materials**

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**Abstract**

The available data refute the widespread postulate of thermodynamics, according to which labile states are physically unrealizable, unobservable and, thus, devoid of practical interest, since the transition to a stable state does not require overcoming a potential barrier, and a random fluctuation leads to an accelerated shift of the system from the initial state. The cases when a system remains in a labile state for an indefinite period of time are well known. The corresponding states are not only observable, but can be used to create functional materials.

The article analyses low-temperature phase equilibria and spinodal behavior in a number of binary systems containing solid solutions with a fluorite structure, such as  $\text{CaF}_2$ - $\text{SrF}_2$ ,  $\text{CaF}_2$ - $\text{BaF}_2$ ,  $\text{BaF}_2$ - $\text{RF}_3$  ( $\text{R} = \text{La, Nd}$ ),  $\text{SrF}_2$ - $\text{LaF}_3$ ,  $\text{ZrO}_2$ - $\text{Y}_2\text{O}_3$ . The investigation of low temperature phase formation in the  $\text{BaF}_2$ - $\text{LaF}_3$  system allowed to reveal the decomposition of the solid solution  $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$  with a binodal curve. In the  $\text{SrF}_2$ - $\text{LaF}_3$  system the equilibrium solubility curve of lanthanum fluoride in strontium fluoride is expressed at the inflection point on the solvus curve with a practically horizontal tangent, which corresponds to the bifurcation point – the practical coincidence of the critical point of the nonequilibrium binodal/spinodal with the solvus curve. The  $\text{Ba}_{1-x}\text{Ca}_x\text{F}_2$  continuous solid solution obtained by the mechanochemical method and possessing high fluorine-ion conductivity, remains in a labile state for an indefinitely long period of time. Upon heating, it disintegrates with an exothermic effect at 420–450 °C. In all other fluoride systems, single crystals grown from the melt retain the functional characteristics of photonics materials for years and have no signs of degradation.

Obviously, the technological stability of crystalline samples of the listed solid solutions is determined by the extremely low values of the cation diffusion coefficients. The systems are “falling”, but too slowly to detect it. The fine architecture of materials in a labile state is of considerable interest.

**Keywords:** Phase diagrams, Stability, Spinodal, Architecture of spinodal decomposition

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## Short communications

Short communication

<https://doi.org/10.17308/kcmf.2024.26/12453>**Evaluation of the thermodynamic stability of  $\text{REMgAl}_{11}\text{O}_{19}$  (RE = La, Pr, Nd, Sm) hexaaluminates with a magnetoplumbite structure in the high temperature region****K. S. Gavrichiev, V. N. Guskov, P. G. Gagarin, A. V. Guskov***Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, 31 Leninsky pr., Moscow 119991, Russian Federation***Abstract**

This study is important due to the lack of reliable data about the properties of high temperature materials for energy production and aerospace engineering. The purpose of this article was to evaluate the thermodynamic stability of RE magnesium hexaaluminates  $\text{REMgAl}_{11}\text{O}_{19}$  (RE = La, Pr, Nd, Sm) with a magnetoplumbite structure, which are promising components for thermal barrier coatings. For this, we calculated the values of the Gibbs energy of the decomposition reactions of RE magnesium hexaaluminates into simple oxides and aluminum-magnesium spinel  $\text{MgAl}_2\text{O}_4$  and  $\text{REAlO}_3$  phases in the temperature range of 298–1,800 K. For calculations, we used data on the thermodynamic properties of hexaaluminates calculated from the values of heat capacity measured by differential scanning calorimetry in the range of 300–1,800 K and from values of thermodynamic properties of simple oxides,  $\text{MgAl}_2\text{O}_4$ , and  $\text{REAlO}_3$  provided in previous research. There is hardly any information about the thermodynamic properties of RE magnesium hexaaluminates, which are promising thermal barrier materials. The purpose of the article is to provide a thermodynamic evaluation of the probability of decomposition reactions of hexaaluminates in the high temperature region.

Previously published data on the high temperature heat capacity of compounds with the composition of  $\text{REMgAl}_{11}\text{O}_{19}$  (RE = La, Pr, Nd, Sm) were used to calculate temperature dependences of entropy and changes in enthalpy, which were used to evaluate the Gibbs energy of the decomposition reactions of hexaaluminates into constituent oxides.

The temperature dependences of the Gibbs energy of the four possible decomposition reactions of hexaaluminates allowed drawing conclusions about thermodynamic stability in the high temperature region.

**Keywords:** Hexaaluminates, Magnetoplumbite, RE, Thermodynamics, Thermal barrier coatings

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