COMPORTAMENTO E NATUREZA DA DESINTEGRAÇÃO DE
SOLUÇÕES SÓLIDAS BASEADAS EM SULFATOS DE SÓDIO E CÁLCIO
EM SISTEMAS DE SULFATO TERNÁRIO

BEHAVIOUR AND NATURE OF DISINTEGRATION OF SLID
SOLUTIONS BASED ON SODIUM AND CALCIUM SULPHATES IN
TERNARY SULPHATE SYSTEMS

ПОВЕДЕНИЕ И ХАРАКТЕР РАСПАДА ТВЕРДЫХ РАСТВОРОВ НА ОСНОВЕ
СУЛЬФАТОВ НАТРИЯ И КАЛЬЦИЯ В ТРОЙНЫХ СУЛЬФАТНЫХ СИСТЕМАХ

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RESUMO

Informação sobre a formação de fases em sistemas físico-químicos complexos é a base para a síntese de novas fases e, portanto, de base lógico-informacional para o desenvolvimento de novos materiais polifuncionais. Foi estudado pela primeira vez um conjunto de sistemas ternários contendo sulfato utilizando um sistema de métodos para análise física e química, tais como análise térmica diferencial (DTA), análise visual-politérmica (VPA). Identificou-se a natureza de soluções sólidas à base de $\text{Na}_2\text{SO}_4\text{--CaSO}_4$; Os valores dos campos de força foram calculados pela fórmula de Goldschmidt. Determinou-se a influência do terceiro componente (M_2SO_4 (M-Li, K, Rb, Cs, Tl(I))) sobre o comportamento e desintegração dessas soluções sólidas.

Palavras-chave: Sistema, diagrama, equilíbrio de fase, solução sólida, desintegração de soluções sólidas, sulfatos, campos de força, raio iônico..

ABSTRACT

Information on phase formation in complex physical-chemical systems is the basis for the synthesis of new phases and thus informational-logical basis for the developing of new polyfunctional materials. For the first time set of sulfate-containing ternary systems was studied using a complex of methods for physical and chemical analysis, such as differential thermal analysis (DTA), visual-polythermal analysis (VPA). The nature of solid solutions based on $\text{Na}_2\text{SO}_4\text{--CaSO}_4$ was identified; the values of force fields were calculated by Goldschmidt's formula. The influence of the third component (M_2SO_4 (M-Li, K, Rb, Cs, Tl(I))) on the behavior and disintegration of these solid solutions was determined.

Keywords: System, diagram, phase equilibrium, solid solution, disintegration of solid solutions, sulphates, force fields, ionic radius.

Аннотация

Впервые с применением комплекса методов физико-химического анализа, в частности дифференциального термического (ДТА), визуально-поли термического (ВПА) анализов изучен ряд сульфатсодержащих тройных систем. Выявлен характер твердых растворов на основе $\text{Na}_2\text{SO}_4\text{--CaSO}_4$, вычислены значения силовых полей по формуле Гольдшмидта. Определено влияние третьего компонента ($(\text{M}_2\text{SO}_4 (\text{M-Li,K,Rb,Cs,Tl(I)}))$) на поведение и распад этих твердых растворов.

Ключевые слова: система, схема, фаза равновесия, твердый раствор, распад твердых растворов, сульфатов, силовых полей, ионный радиус.

INTRODUCTION

The tendency to complex formation, more precisely, to the formation of double salt type compounds when crystallizing from the melts in dual systems with a common anion, increases, as a rule, with the increase in charge and decrease in the radius of a single cation, and thus, with the decrease in charge and increase in the radius of the other cation (Reshetnikov 1964).

As a rule, the interaction in the ternary and more complex systems depends largely on the nature of interaction in their limiting elements (dual systems) (Bazarov *et al.*, 2006; Bergman *et al.*, 2013). One might list a large number of multicomponent systems, which double sides are eutectic, and, as a consequence, the emergence of eutectic inside multicomponent systems is a normal event (Gasanaliev *et al.*, 2016; Akhmedova & Gamataeva 2012). However, a series of works performed by A.G. Bergman's school of physical-chemical analysis showed that multicomponent sulphate systems were often far more complex than one might expect based on the nature of interaction of dual system phase diagrams (Gasanaliev *et al.*, 2015; Gasanaliev *et al.*, 2016; Gasanaliev 1970).

In particular, when analyzing $\text{Na,Ca//SO}_4\text{,PO}_3$ ternary reciprocal system, the crystallization fields of new phases, which were the products of disintegration of solid solutions based on sodium and calcium sulfates under the influence of a third component, in this case, sodium metaphosphate, were detected on the state diagram.

The stability analysis of solid solutions was performed on the basis of calculating the ratio of sodium and calcium cation force fields (E), which

is equal to 0.53 that was calculated by Goldschmidt's formula (Smith 1961):

$$(E_{\text{eq}} = mE_{\text{M1}} + (1 - m) E_{\text{M2}},$$

where: m –fraction of one of the components, M_i – cation.

This circumstance implies the presence of solid solutions in the system that corresponds to reality, but the proximity of this value to the boundary one (i.e., to the value of 0.5) suggests possible inversion of properties in the system. This may occur both in the solidus range in case of temperature decrease and on the liquidus curve in the ternary system under the influence of a third component when the influence of two factors such as lowering of temperature, as well as the ratio of the force fields of the third component ions, potassium sulfates, rubidium, cesium and univalent thallium occur simultaneously. All of this necessitated systematic study of the influence of the third component properties on the interaction nature in the ternary sulfate systems.

EXPERIMENTAL PROCEDURE

The study of Na,Ca,M//SO_4 (M-Li,K,Rb,Cs) ternary system phase diagrams was carried out using the methods of visual-polythermal analysis (VPA), differential thermal analysis (DTA), thermogravimetric analysis (TGA) and derivatography.

Pt-Pt/Rh-thermocouple served as a temperature sensor on VPA plant, its thermal electromotive force was measured by a millivoltmeter with M1109 mirror reflector. The cold junctions of thermocouples were *thermostated* at 0°C in Dewar's vessel with a melting ice.

DTA curves were recorded at the plant assembled on the basis of KСП-4 electronic automatic potentiometer with an amplifier of the thermal electromotive force of differential thermocouple using Φ -116/7 optoelectronic amplifier. The samples were placed in the platinum microbowls of 1ml capacity, Pt-Pt/Rh-thermocouples served as a temperature gauge, and freshly incinerated Al_2O_3 of "analytical-reagent grade" qualification was used as an inert substance. All measurements were performed in the argon atmosphere.

Thermogravimetric analysis was performed by STA 409 PC derivatography (NETZSCH company, Germany).

RESULTS AND DISCUSSION

Ternary sulphate systems were studied in order to clarify the stability behavior of solid solutions based on Na_2SO_4 - CaSO_4 . Alkali-metal sulfates were used as a third component.

Li,Na,Ca// SO_4 ternary system

The system liquidus surface was studied by the above-mentioned methods of physical-chemical analysis. 18 internal cuts that made it possible to outline the system liquids surface were studied to outline the surface. The liquidus surface consisted of 5 crystallization fields belonging to three primary components and two binary compounds (Fig. 1). Characteristics of nonvariant points are presented in Table 1. The experimental data showed that solid solutions based on sodium and calcium sulphates do not disintegrate within the ternary system with the addition of lithium sulphate.

Na,K,Ca// SO_4 ternary system

To outline the liquidus surface, 15 internal cuts were experimentally studied. The above-mentioned cuts allowed to outline the liquidus surface of the ternary system, which consists of two congruently melting compounds of $\text{K}_2\text{SO}_4 \cdot 2\text{CaSO}_4$ and $2\text{K}_2\text{SO}_4 \cdot 3\text{CaSO}_4$ as well as the field of primary components. X-ray phase analysis of the resulting compounds showed that the compounds had a particular nature for each compound. The solid solutions maintain their stability in this system and they do not decompose while adding a third component.

System meltability diagram is shown in Fig. 2. The characteristics of nonvariant points are presented in Table 1.

Na_2SO_4 - Rb_2SO_4 - CaSO_4 ternary system

Due to the complexes of physical-chemical analysis methods it was possible to study this system. The system is characterized by formation of new compounds. The system liquidus surface consists of seven crystallization fields of primary components and binary compounds (Fig.3). The emergence of new compounds is of special interest. On the one hand, this can be explained by the formation of limited solid solutions based on disintegration of solid sodium and calcium solutions under the influence of a third component, in particular, rubidium calcium sulfate compound. On the other hand, this can be explained by $\text{Rb}_2\text{SO}_4 \cdot 2\text{CaSO}_4$ polymorphic differences.

The results of X-ray phase analysis showed the individuality of the identified compounds. The characteristics of the system nonvariant points are presented in Table 1.

Na_2SO_4 - Cs_2SO_4 - CaSO_4 ternary system

This ternary system was studied via 13 internal cuts that made it possible to outline the liquidus surface of the system itself. Two new incongruently melting compounds were revealed inside the system. These compounds are adjacent to the double side of sodium and cesium sulfates. Double solid solutions of a dual system of sodium and calcium sulfates disintegrate when a third component, i.e., cesium sulfate, is added. The decay curve is wedging out at the point R - 588°C . These results of the experimental data are confirmed by calculations regarding ionic radii that limited solid solutions disintegrate in this system.

It seemed interesting to study the influence of specific properties of each of these cations (Li^+ , K^+ , Rb^+ , Cs^+) on the nature of solid solutions based on sodium and calcium sulfates. Moreover, the force field values of all of these cations was possible to calculate in order to determine at least a qualitative relationship between the ratio of the third component (M_2SO_4 (M-Li,K,Rb,Cs) force field and the force field ratio value of the original dual system of sodium and

calcium sulphates based on which the limited solid solutions are formed. There should be a dynamic equilibrium between like-charged cations, which are oriented and spaced apart at well-defined distances inversely proportional to the values of interaction fields of all three cations in the ternary systems with a common anion in terms of electrostatic representations. It is easy to imagine that the orientation and relative positioning will vary depending on the cation mutual concentration. For the case of ternary system, the interaction of force fields can be represented as an interaction of two charges, one of which is the component and the other one is replaced with the equivalent field of the compound under consideration. Under these circumstances, it is possible to extend the known relationship between the force field ratios of two cations and complex formation nature in the dual systems with a common anion to the ternary systems. For example, intersecting the ternary system in the usual manner, as is taken during carrying-out of thermal analysis, the equivalent of the analyzed compound force field is calculated. The value of the ratio of cations calculated force field of an intermediate compound to the third component force field value is then determined. It is possible to propose the interaction nature of substances in the area of this section based on the value of this ratio. Na,Ca,M//SO₄ (M-Li,K,Rb,Cs) ternary sulfate systems were studied as real-life objects for verification of this hypothesis.

The force field total value for 20CaSO₄ – 80Na₂SO₄ compound, which corresponds to the maximum on the curve of solid solutions in Na,Ca//SO₄ binary system, is calculated according to Goldschmidt's formula.

$E_{eqv} = (20E_{Ca} + 80E_{Na}) = 0.2 \times 0.447 + 0.8 \times 1.04 = 0.923$ of the cation force field value ($E_{Li} = 1.64$; $E_{Na} = 1.04$; $E_K = 0.565$; $E_{Rb} = 0.448$; $E_{Cs} = 0.366$; $E_{Ti} = 0.45$; we shall calculate the ratio of the equivalent value of the cation force field (E_{eqv}) of the chosen compound in Na,Ca//SO₄ system to the force field values of (E_{Mi}) cations (M-Li,K,Rb,Cs) of the third components (M₂SO₄) in Na,Ca,M//SO₄ ternary systems according to the following equation (Table 2):

$$W = E_{eqv} / E_{mi}.$$

It is difficult now to judge the versatility of this methodology, the analysis of experimental data on phase equilibria and the calculations based on ionic radii is indicative of the qualitative convergence of calculations with the experimental results.

The presented set of ternary systems obviously demonstrates the influence of a third component (different cations) on the behavior and nature of disintegration of solid solutions based on sodium and calcium sulfates.

CONCLUSIONS

When studying complex multicomponent systems, the major role is played by diagrams of double system meltability. When studying double systems from sulfates of alkaline and alkali-earth metals on the double side of Na₂SO₄-CaSO₄ limited solid solutions were found. These solid solutions maintain their stability and do not disintegrate in all triple.

Due to experimental data and calculations with the use of ionic reduce values and Goldschmidt's formulas, the character of solid solutions and their disintegration under the influence of the third component was proved for the first time. All this allows to reduce significantly the time for the study of multicomponent systems at preliminary planning of an experiment.

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Table 1. Characteristics of system nonvariant points

System	Nature of nonvariant points	$t_{\text{melt}}, ^\circ\text{C}$	Equivalent compound %						Equilibrium solid phases
			Li_2SO_4	Na_2SO_4	K_2SO_4	Rb_2SO_4	Cs_2SO_4	CaSO_4	
Li,Na,Ca//SO_4	E	554	60	33	-	-	-	7	$\text{Li}_2\text{SO}_4, \text{Na}_2\text{SO}_4, \text{CaSO}_4$
	P	565	53,5	38,5	-	-	-	8	$\text{Na}_2\text{SO}_4, \text{CaSO}_4, \text{Na}_2\text{Ca}(\text{SO}_4)_2$
	R	604	51	44	-	-	-	5	$\text{Li}_2\text{SO}_4, \text{Na}_2\text{SO}_4, \text{Li}_2\text{Na}_4(\text{SO}_4)_3, \text{Na}_2\text{Ca}(\text{SO}_4)_2$
K,Na,Ca//SO_4	P_1	814	-	9	50	-	-	41	$\text{K}_2\text{SO}_4, \text{K}_4\text{Ca}_3(\text{SO}_4)_5, \text{K}_2\text{Ca}_2(\text{SO}_4)_3$
	P_2	772	-	21	39	-	-	40	$\text{K}_2\text{SO}_4, \text{K}_2\text{Ca}_2(\text{SO}_4)_3, \text{CaSO}_4$
	E	750	-	34,5	26,5	-	-	39	$\text{K}_2\text{SO}_4, \text{Na}_2\text{SO}_4, \text{CaSO}_4$
Rb,Na,Ca//SO_4	P_1	724	-	37,5	-	43	-	19,5	$\text{Rb}_2\text{SO}_4, \text{S}_1, \text{S}_3$
	P_2	690	-	46	-	29	-	25	$\text{S}_1, \text{S}_3, \text{S}_4$
	P_3	860	-	25	-	34	-	41	$\text{S}_1, \text{S}_2, \text{S}_4$
	P_4	860	-	29	-	23	-	48	$\text{CaSO}_4, \text{S}_2, \text{S}_4$
	P_5	738	-	50	-	15	-	35	$\text{CaSO}_4, \text{Na}_2\text{Ca}(\text{SO}_4)_2, \text{S}_4$
	E	670	-	55	-	27	-	18	$\text{Na}_2\text{Ca}(\text{SO}_4)_2, \text{S}_3, \text{S}_4$
Cs,Na,Ca//SO_4	P_1	626	-	27	-	-	50	23	$\text{Cs}_2\text{SO}_4, \text{CaSO}_4, \text{Na}_2\text{Ca}(\text{SO}_4)_2$
	P_2	630	-	45	-	-	49	6	$\text{Cs}_2\text{SO}_4, \text{Na}_2\text{Cs}_2(\text{SO}_4)_2, \text{Na}_2\text{Cs}_4(\text{SO}_4)_3$
	E	562	-	40	-	-	43	17	$\text{CaSO}_4, \text{Na}_2\text{Cs}_2(\text{SO}_4)_2, \text{Na}_2\text{Ca}(\text{SO}_4)_2$
	R	588	-	50	-	-	31	19	$\text{Na}_2\text{SO}_4, \text{Na}_2\text{Cs}_2(\text{SO}_4)_2, \text{Na}_2\text{Ca}(\text{SO}_4)_2$

Designations: $\text{S}_1 - \beta\text{-Rb}_2\text{SO}_4 \cdot 2\text{CaSO}_4$, $\text{S}_2 - \alpha\text{-Rb}_2\text{SO}_4 \cdot 2\text{CaSO}_4$, $\text{S}_3 - \text{Rb}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$, $\text{S}_4 - \gamma\text{-Rb}_2\text{SO}_4 \cdot 2\text{CaSO}_4$.

Table 2. The ratio of cation force field equivalent to the value of the third component force fields

Ternary system	E_{Mi}	W (E_{eqv}/E_{Mi})	Stability analysis of limited substitution solid solutions in the section $Ca_{0.2}Na_{0.8}SO_4 \rightarrow M_i$
Li,Na,Ca//SO ₄	$E_{Li} = 1.64$	0.56	Solid solutions do not disintegrate
K,Na,Ca//SO ₄	$E_K = 0.565$	1.62	The section under consideration has the nature of quasi-binary system with non-disintegrating solid solutions
Rb,Na,Ca//SO ₄	$E_{Rb} = 0.448$	2.05	There is a crystallization branch of incongruently melting compounds of rubidium and sodium sulphates in the system.
Cs,Na,Ca//SO ₄	$E_{Cs} = 0.366$	2.5	Makes it possible to assume the existence of crystallization fields of new compounds.
		2.01	Additional calculations for the section of the compound 80% Na ₂ SO ₄ +20% Cs ₂ SO ₄ per calcium sulfate. This value is indicative of disintegration that corresponds to the truth

Figure1. Li Li,Na,Ca//SO₄ system meltability diagram

Figure 2. K,Na,Ca//SO₄ system meltability diagram

Figure 3. Rb,Na,Ca//SO₄ system meltability diagram

Figure 4. Na,Cs,Ca//SO₄ system meltability diagram