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THE USAGE OF SPECIFIC STATE OF STRUCTURAL COMPONENTS OF RARE EARTH ELEMENTS CONTAINING WATERSALT SYSTEMS IN PREPARATION PROCESSES OF THE FORMING MULTICOMPONENT OXIDE FUNCTIONAL MATERIALS

The preparatory processes phases of synthesis of REE multicomponent constructional and functional ceramic materials with rare earth elements (REE) with the use of salt systems of elements and with different electronic structures by chemical mixing of initial components with general product extraction from liquid phase with consecutive or joint deposition and next thermal processing occur through formation of a number of intermediate phases.

The system investigation of chemical interaction of heterogeneous equilibriums in model systems there were found complex processes of interaction between their structural components as for formation of an integral class of anionic complexes Ln^{3+} . The effective concurrent reactions are drastic processing factors essentially affecting activity of structural forms Ln^{3+} .

Keywords: *alkaline metals, chlorides, neodymium, nitrates, sulfates, water-salt systems.*

Introduction. To obtain nanodispersed inorganic materials based on transition of oxides and rare earth elements the promising is the use of "soft chemistry" methods based on synthesis of aqueous (or non-aqueous) solutions at relatively low temperatures. Their key advantages are: the possibility of obtaining products with controlled composition and micromorphology, economically and ecologically rationally, etc. The mechanism of nanoparticles formation in such conditions is rather complicated from physical and chemical point of view and may result in parallel processes of hydration (solvation), association, aggregates formation, as well as formation and transformation of heterophases. The process regularities of it had not been studied enough. Therefore main tasks are the fundamental study of mechanisms and dynamics of processes happened in formation of nanoparticles that requires systematic study of composition, structure, properties and micromorphology of intermediates which in most cases determine the microstructure and structure of sensitive characteristics of finite functional nanomaterials.

Today, the search is being carried out in the field of new methods and technologies for synthesizing specific functional oxide rare earth compounds (REC) using multi-component water-salt systems [1 – 9]. The available information on the status and potential ways of improving the technologies of these materials obtaining by the existing requirements to their stability and properties reproducibility, expansion of their application spheres [3 – 9] initiated our further research on this subject matter.

Selection of neodymium based systems as objects of study is determined by the existing statistic data on most probable changes of composition or structure of compounds formed by neodymium in the course of transition from lanthanum to lutetium by natural way.

Problem. To estimate the possibility of above processes monitoring and to obtain materials with the desired properties using a number of physical and chemical methods it is necessary:

a) to study the chemical interaction and heterogeneous balances in model water salt systems $M_2SO_4 - Nd_2(SO_4)_3 - H_2O$, $MNO_3 - Nd(NO_3)_3 - H_2O$, $MCl - NdCl_3 - H_2O$

($M - Li^+, Na^+, K^+, Rb^+, Cs^+$) in interval 25 – 100°C;

b) to build polythermal diagrams of systems solubility to determine the concentration and temperature limits of the ultimate substance crystallization and detected double salts;

c) to clarify the best growth conditions and to synthesize double sulfates, nitrates, chlorides of neodymium and the IA group elements of the periodic system to study their properties and to verify their identity;

d) to establish the correlation patterns of number, composition and properties of double salts formed in the studied systems depending on the radius of alkaline metal cation, on the anion's nature and temperature.

Experimental part. To clarify the nature of the structural components and phase balances chemical behavior in the studied water-salt systems, which are precursors of multi-component REE containing functional materials, we used the solubility method, isothermally, in the temperature range of solutions existence in full concentration ratios. The methodology was described in our previous publication [10].

Chemical analysis of liquid and solid phases were performed to determine contents of Nd^{3+} , SO_4^{2-} , Cl^- ions and nitrogen. The amount of neodymium was determined by trilonometric methods in the presence of xylenol orange in acetate buffer sulfate-ion was determined by method of gravimetric analysis; chloride-ion was detected by Mohr's method, nitrogen by fume method. The content of alkaline metal salts was calculated by the difference, according to the total content of sulfates, nitrates or chlorides. The obtained results were recalculated for separate parts of analysis as for salts compositions and then they were applied to the solubility diagram.

Identification of double salts found in the systems was performed due to Schreinemakers' method and by chemical and crystal optical methods of analysis. The synthesized compounds were also studied by picnometer, photomicrographic, thermographic, (infrared) IR-spectroscopic, X-ray phase and where it was possible by X-ray diffraction methods.

Results and discussion. The experimental data of systematic systems study have been generalized and summarized in Table 1 and they are used for the graphical interpretation of study results.

In the range of 25 – 100°C among the structural components the metabolic interactions forming new double salts have been found. They can be regarded as coordinative compounds of varying stability. We have studied their number (twenty-one), composition, possible types of compounds, phase crystallizing concentration limits, coexisting in certain systems, their solubility nature. The solubility phase diagrams have been built. Concentration limits of saturated solutions in which the double salts are isolated from correspond to compositions of nonvariant points of the respective solubility isotherms. They all are synthesized in the monocrystalline form. Their identity have been confirmed and a number of their properties have been systematically studied.

Polythermal systems solubility diagrams have been obtained (for example, see Fig. 1 for the system $K_2SO_4 - Nd_2(SO_4)_3 - H_2O$, Fig. 2 – $KCl - NdCl_3 - H_2O$) in the temperature range of the solutions existence we illustrate the complexity of the interaction nature between

Table 1. Phase balances and double salts in the ternary sulfate, nitrate and chloride systems of alkaline metals and neodymium at 25 – 100°C

System $M_2SO_4 - Nd_2(SO_4)_3 - H_2O$			
M – alkaline metal	Double sulfate composition	Crystallization temperature interval	Nature of the double sulfate solubility
<i>Li</i>	eutonic type system at 25 – 100°C		
<i>Na</i>	eutonic type system at 25°C		
	1–1–2	50 – 100°C	congruent

<i>K</i>	eutonic type system at 25°C		
	1-1-2	50 – 100°C	congruent
	3-2-8	50°C	incongruent
	5-1	50 – 100°C	incongruent
<i>Rb</i>	eutonic type system at 25°C		
	1-1	50 – 100°C	congruent
<i>Cs</i>	eutonic type system at 25°C		
	1-1-8	50 – 75°C	congruent
	1-1	100°C	congruent
System $MNO_3 - Nd(NO_3)_3 - H_2O$			
M – alkaline metal	Double nitrate composition	Crystallization temperature interval	Nature of the double nitrate solubility
<i>Li</i>	eutonic type system at 25 – 50°C		
	3-2-4	65°C	incongruent
		100°C	congruent
<i>Na</i>	eutonic type system at 25°C		
	2-1-2	50 – 100°C	Incongruent
<i>K</i>	eutonic type system at 25°C		
	2-1-2	50°C	incongruent
	3-2-1	50°C	incongruent
	3-2-1	65 – 100°C	congruent
<i>Rb</i>	5-2-2	25°C	incongruent
		50°C	congruent
	3-2-1	50°C	incongruent
	3-2-1	65 – 100°C	congruent
<i>Cs</i>	2-1-3	25 – 65°C	incongruent
	2-1-2	100°C	incongruent
	1-1-3	50 – 65°C	incongruent
System $MCl - NdCl_3 - H_2O$			
M – alkaline metal	Double chloride composition	Crystallization temperature interval	Nature of the double chloride solubility
<i>Li</i>	eutonic type system at 25 – 100°C		
<i>Na</i>	eutonic system at 25 – 100°C		
<i>K</i>	eutonic type system at 25 – 50°C		
	1-1-5	75 – 100°C	incongruent
<i>Rb</i>	1-1-5	25 – 100°C	congruent
	3-1-2	100°C	incongruent
<i>Cs</i>	2-1-10	25°C	congruent
	1-1-5	50 – 75°C	congruent
		100°C	incongruent
	3-1-1	75 – 100°C	congruent

* The first cypher indicates the number of alkaline metal sulfate (nitrate, chloride) molecules; the second – the number of neodymium sulfate (nitrate, chloride) molecules; the third – the number of water molecules.

the structural components in the objects of study, state nature of transformations and indicate the sufficient sensitivity and efficiency of the used set of physical and chemical methods for solving such problems.

Thus, the systems $Li_2SO_4 - Nd_2(SO_4)_3 - H_2O$ and $Li(Na)Cl - NdCl_3 - H_2O$ at 25 – 100°C, $KCl - NdCl_3 - H_2O$ at 25 – 50°C, $LiNO_3 - Nd(NO_3)_3 - H_2O$ at 25 – 50°C, $Na(K)NO_3 - Nd(NO_3)_3 - H_2O$ at 25°C belong to the eutonic type.

In the systems: sodium (potassium, rubidium, cesium) sulfate – neodymium sulfate – water, compounds are formed of $Na_2SO_4 \cdot Nd_2(SO_4)_3 \cdot 2H_2O$ (25 – 100°C), $K_2SO_4 \cdot Nd_2(SO_4)_3 \cdot 2H_2O$ (25 – 100°C), $Rb_2SO_4 \cdot Nd_2(SO_4)_3 \cdot 8H_2O$ (25°C), $Rb_2SO_4 \cdot Nd_2(SO_4)_3$ (50 – 100°C), $Cs_2SO_4 \cdot Nd_2(SO_4)_3 \cdot 8H_2O$ (25 – 75°C), $Cs_2SO_4 \cdot Nd_2(SO_4)_3$ (100°C), $5K_2SO_4 \cdot Nd_2(SO_4)_3$ (50 – 100°C) and $3K_2SO_4 \cdot 2Nd_2(SO_4)_3 \cdot 8H_2O$ (25 – 50°C).

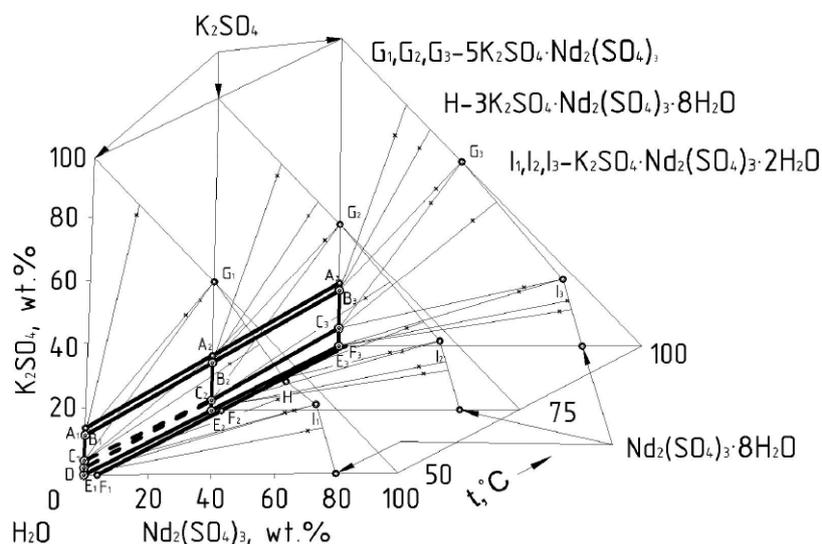


Fig. 1. Solubility polytherm of the system $K_2SO_4 - Nd_2(SO_4)_3 - H_2O$

In the systems $Li(Na, K, Rb, Cs)NO_3 - Nd(NO_3)_3 - H_2O$ the following double nitrates have been isolated: $3LiNO_3 \cdot 2Nd(NO_3)_3 \cdot 4H_2O$ (65 – 100°C), $2NaNO_3 \cdot Nd(NO_3)_3 \cdot 2H_2O$ (50 – 100°C), $2KNO_3 \cdot Nd(NO_3)_3 \cdot 2H_2O$ (50°C), $3K(Rb)NO_3 \cdot 2Nd(NO_3)_3 \cdot H_2O$ (50 – 100°C), $5RbNO_3 \cdot 2Nd(NO_3)_3 \cdot 2H_2O$ (25 – 50°C), $2CsNO_3 \cdot Nd(NO_3)_3 \cdot nH_2O$ ($n = 3$ at 25 – 65°C, $n = 2$ at 100°C), $CsNO_3 \cdot Nd(NO_3)_3 \cdot 3H_2O$ (50 – 65°C).

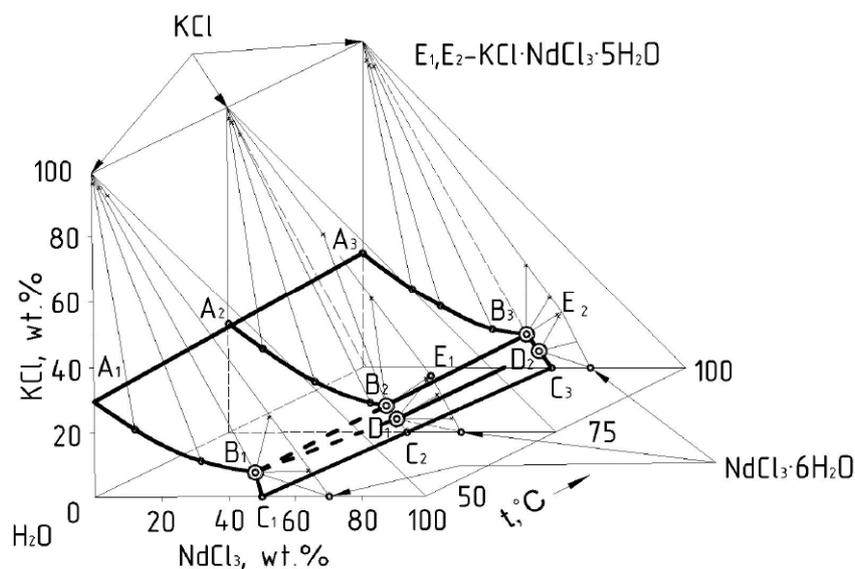


Fig. 2. Solubility polytherm of the system $KCl - NdCl_3 - H_2O$

In the system $KCl - NdCl_3 - H_2O$ at 75 – 100°C a double salt of $KCl \cdot NdCl_3 \cdot 5H_2O$ has been revealed, and in the system of rubidium chloride – neodymium chloride – water, double

chlorides $RbCl \cdot NdCl_3 \cdot 5H_2O$ (25 – 100°C) and $3RbCl \cdot NdCl_3 \cdot 2H_2O$ (100°C) are crystallized. In the system $CsCl - NdCl_3 - H_2O$ the double chlorides are formed at 25°C $2CsCl \cdot NdCl_3 \cdot 10H_2O$, at 50 – 100°C $CsCl \cdot NdCl_3 \cdot 5H_2O$, and at 75 – 100°C $3CsCl \cdot NdCl_3 \cdot H_2O$.

The double sulfates $5K_2SO_4 \cdot Nd_2(SO_4)_3$, $Rb_2SO_4 \cdot Nd_2(SO_4)_3$, $Cs_2SO_4 \cdot Nd_2(SO_4)_3$ and all double nitrates, neodymium and alkaline metals chlorides have been first isolated by the present study authors.

Conclusions. The study results testify to the following: with the radius increase of the $Na^+ \rightarrow Cs^+$ cation, at activation of the heating processes, there is an increase in the number of double compounds formed in systems of neodymium sulfates, nitrates and chlorides. The ability of neodymium to form compound salts reduces in the series $NO_3^- > SO_4^{2-} > Cl^-$. With heating, lability of water – anion substitutions in Nd^{3+} surrounding is increasing; stability of the new coordination forms and the new phases formed by them increase. The latest achievements in this field show the possibilities of wide utilization of investigated systems and serve as reliable physical and chemical base of preparatory processes in the production of REM containing functional materials for modern electronic devices.

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