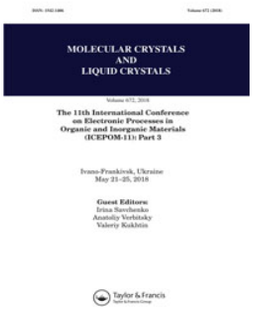

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Features of transformations in REE-containing systems of nitrate precursors in preparatory processes of formation of multifunctional oxide materials

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ABSTRACT

The complex study provides a reliable idea of the trends in the joint behavior of structural components in the water-salt systems of nitrate precursors of REE, alkaline, alkaline earth metals in the preparatory stages of the processes of forming multicomponent oxide polyfunctional materials on their basis with thermal activation. Stages of such transformations are revealed; The regularities of complex and phase formation in systems and factors influencing them are determined; A number of physicochemical properties of the intermediate phases formed - coordination lanthanides nitrates: their composition, types of compounds, atomic-crystalline structure, regularities of transformations during heat treatment were studied.

KEYWORDS

Rare earth elements; alkaline metals; alkaline earth metals; nitrates; complex formation; water-salt systems

Introduction

The research is aimed at solving the fundamental problems of creating new and improving existing technologies for obtaining perfect oxide materials of transitional and rare earth elements with a structure of defective perovskite, garnet with reproducible properties by low-temperature methods of "soft chemistry" and using nitrate precursors. They have a complex structure and in scientific and technological terms are complex objects that are intensively investigated [1–10].

The general principles concerning the distribution of cations according to the crystallographic locations of their structure are now formulated and the great possibilities of isomorphous substitutions have been revealed. Methods of managing the parameters of functional materials on their basis are found out by the choice of composition, conditions of synthesis and subsequent processing. The processes for obtaining the target product pass through a series of stages and is accompanied by the formation of intermediate phases. Knowledge about their composition, conditions of formation and existence, properties, features and regularities of transformation give an opportunity to manage these processes and conduct its directed synthesis.

In the processes of formation of oxide polyfunctional materials using nitrate REE-containing precursors at the stages of preparation, conduction, control, with the improvement of technological schemes there are difficulties associated with the lack of

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generalized, systemic information about the complexing ability of rare-earth elements. This limits the possibility of objective understanding, interpretation of the relevant mechanisms of chemical transformation.

The purpose and tasks of the study

To evaluate the possibility of controlling these processes and obtaining materials with given properties using a set of physico-chemical methods to study the nature and regularities of chemical interaction, thermal transformations (25–1000 °C) in modeling systems of rare-earth metals and elements of IA, IIA groups of the periodic system, ammonium, which are now widely used in the synthesis of multifunctional oxide materials of various applications.

New knowledge about the nature and mechanisms of the investigated phenomena, trends in the development of technical means, expansion of the scope of use of modern oxide-based REE-containing polyfunctional materials, increase of requirements for their stability and reproduction of a complex of functional and technological characteristics, search for ways to improve the technologies of their production and the capabilities of hardware supply have been accumulated. Continuation of our research on this topic.

Experiment Methodology

Systems research is carried out isotermically (at 25, 50, 65, 100 °C) by the method of additives using the method described in [11, 12]. Phase equilibrium was achieved within 1–2 days. Hydrated and anhydrous nitrates of these elements of the brand "ch.d.a." were used as starting salts. The choice of temperature cross sections is due to the existence of crystalline hydrated forms of the initial components.

The chemical analysis of liquid and solid phases, "residues" was carried out on the ion content Ln^{3+}, Mg^{2+}, Ca^{2+}–Ba^{2+}, nitrogen [13]. The content of Ln^{3+} was determined trilonometrically in the presence of xylenol orange as an indicator (acetate buffer solution, pH = 5–6) [14]; Mg^{2+} – volumetric method [15]; Ca^{2+}–Ba^{2+} – complexometric titration of the substituent in the filtrate liberated from Ln^{3+} by the ammonia buffer ($NH_3 \cdot H_2O + NH_4Cl$) [15]; nitrogen – the method of distillation; Me^{+}, NH_4^{+} ions – based on the difference, based on the total content of nitrates and partly on the dry residue.

The obtained data for individual ions were transferred to the salt content and, according to the principle of conformity, were applied to the solubility diagram. The graphic representation of the solid phase composition formed in the system was carried out by the Skreinemakers [12]. Their individuality was confirmed by chemical, crystalloptic, X-ray diffraction, X-ray structural, IR spectroscopic, GDG laser radiation, thermographic and other methods of analysis.

Crystal-optical determinations of compounds were performed using an imestion method using a MIN-8 microscope. Phase analysis was performed on the DRON–3M diffractometer (Cu K_α – radiation, Ni – filter) by the powder method. The diffractograms were decoded using the JCPDS PDF file. The determination of the symmetry, the parameters of the elementary cells and the measurement of the intensity of the

diffraction reflections from the single crystals were carried out on an automatic X-ray crystal diffractometer CAD–4F «Enraf-Nonius» (Mo K_α – radiation, a graphite monochromator, $\omega/2\theta$ method). All calculations for the determination and refinement of atomic structures were performed using the complexes of the crystallographic programs SHELX, XTL-SM, AREN. Infrared absorption spectra of synthesized compounds in the range 400–4000 cm^{-1} were recorded on a UR-20 spectrophotometer using a standard suspension method in petroleum jelly. Thermogravimetric analysis was carried out on a derivative digitizer Q-1500 D at temperatures from 293 K to 1273 K in an air medium at a heating rate of 10 deg./min and developed device for DTA.

Results of the research and their discussion

The experimental data on the study of the features and patterns of the mutual behavior of structural components, heterogeneous equilibria

(25–100 °C) in the water-salt systems of nitrate precursors of lanthanides, yttrium and elements of IA, IIA groups of the periodic system, and ammonia are generalized in the form of their spatial polythermal solubility diagrams (see Figures 1–5) and summarized in Table 1 and 2. On their basis, the presence of the chemical interaction between the constituent elements in the research objects was established; the number, composition, the nature of solubility, the temperature and concentration limits of the formation of the starting substances and new phases, the composition of the euthonic and transition points, the positions of the lines of equilibrium equations are determined in the regions of coexistence of the phases; the optimum conditions of formation are

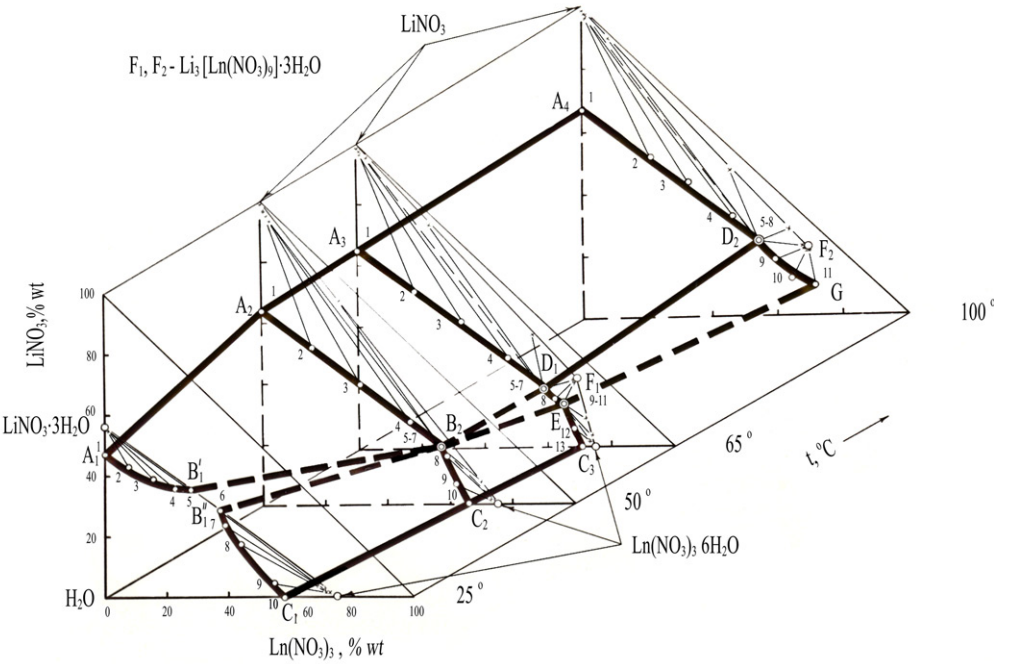


Figure 1. Polytherm solubility of the system $LiNO_3$ – $Ln(NO_3)_3$ – H_2O (Ln – La–Nd)

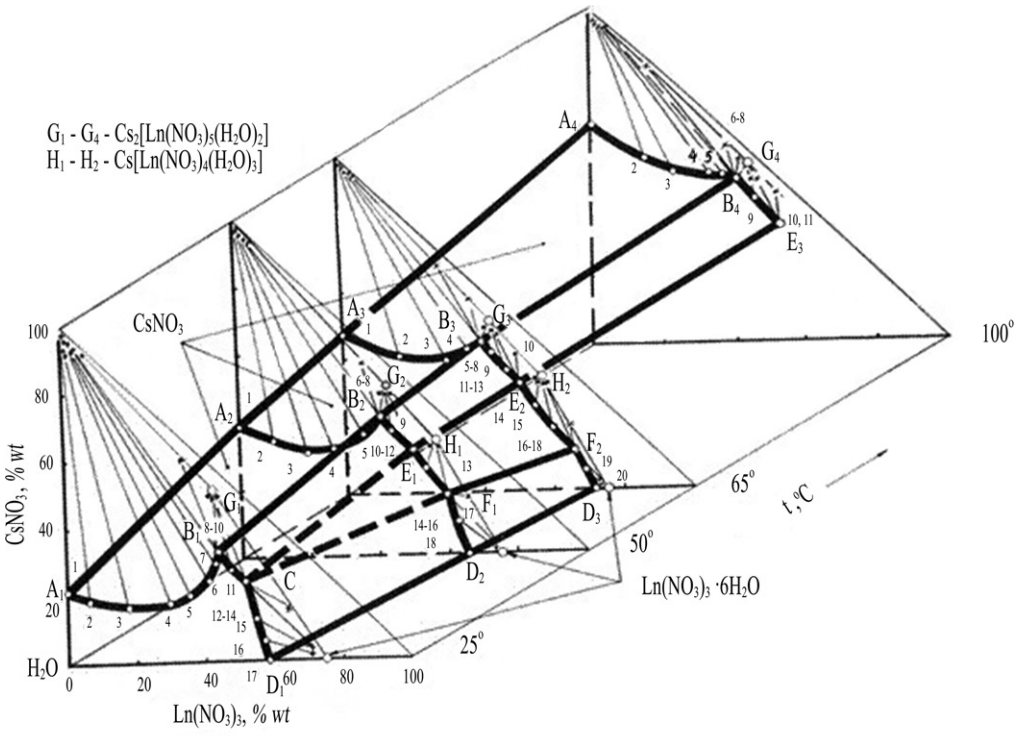


Figure 2. Solubility polytherm of system $CsNO_3$ – $Ln(NO_3)_3$ – H_2O (Ln – La–Sm)

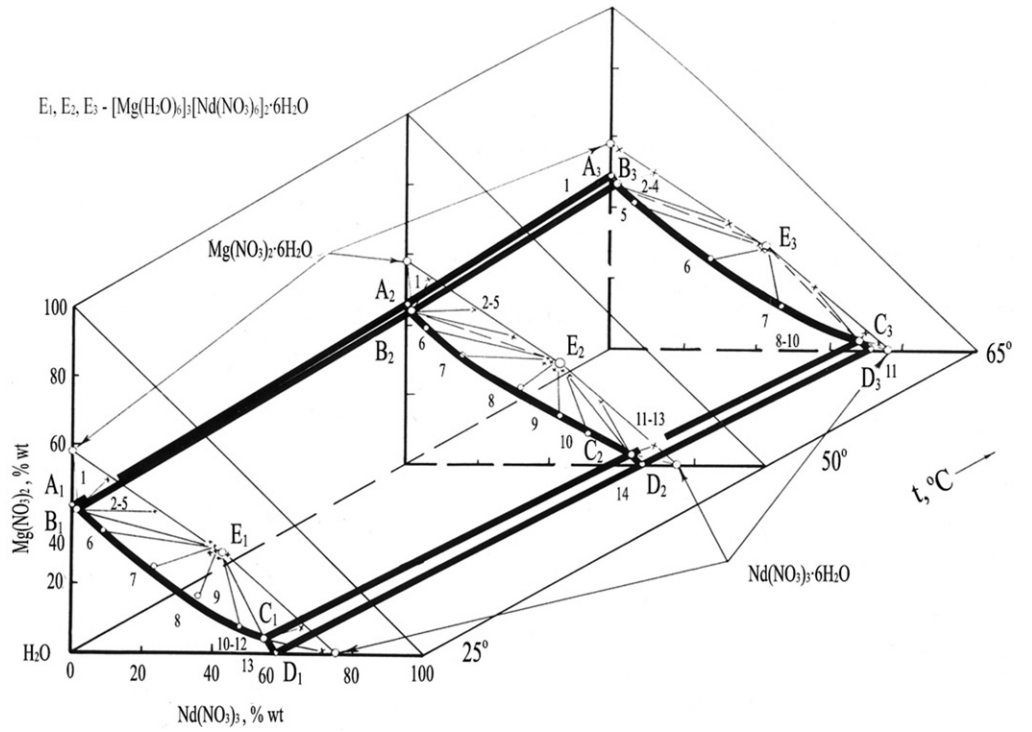


Figure 3. Polytherm of solubility of the system $Mg(NO_3)_2$ – $Nd(NO_3)_3$ – H_2O at 25–65°C

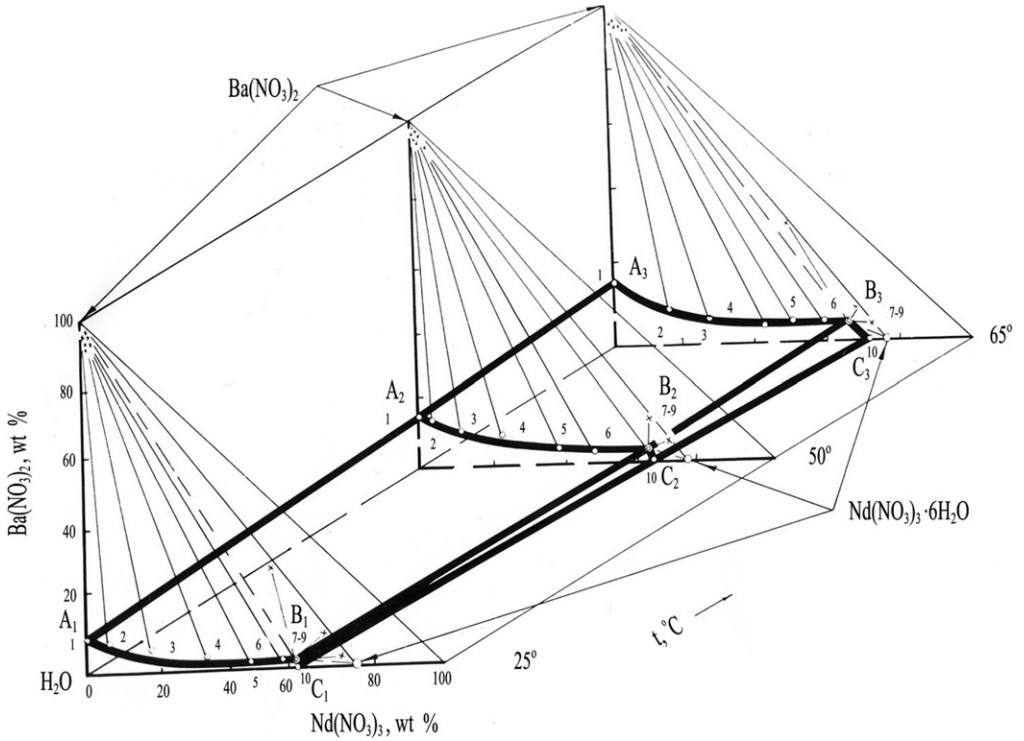


Figure 4. Polytherm solubility of the system $Ba(NO_3)_2$ – $Nd(NO_3)_3$ – H_2O at 25–65 °C

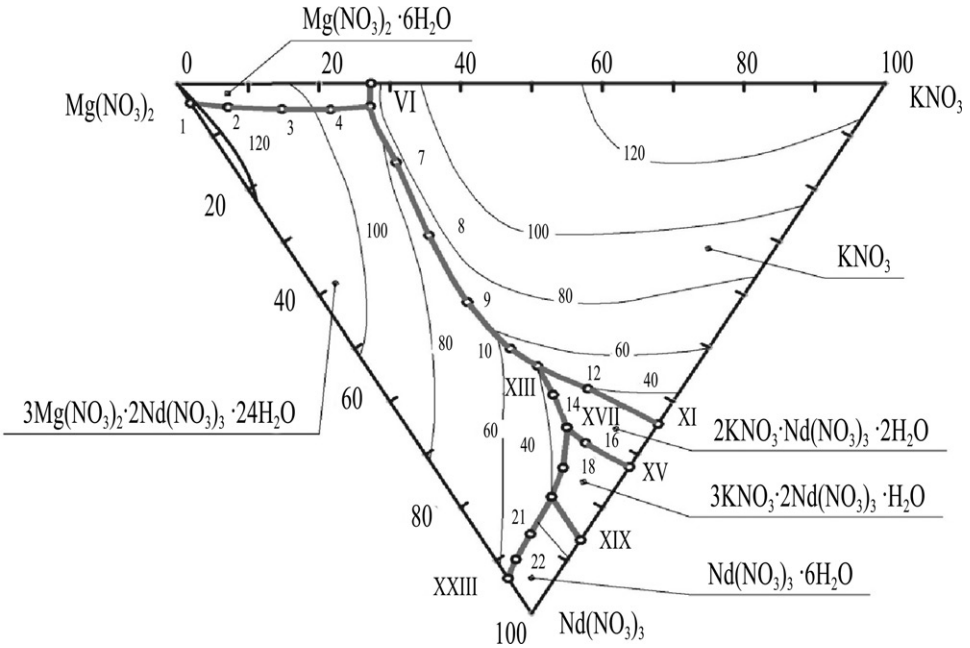


Figure 5. Horizontal projections of the system solubility isotherms KNO_3 – $Mg(NO_3)_2$ – $Nd(NO_3)_3$ – H_2O in 50 °C

Table 1. Conditions of the formation and composition* of compounds crystallizing in the water-salt systems of nitrate Yttrium, REE and alkali metals (25–100 °C)

M/REE	Y	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Li	eut. 25-100	3:2:4 100	3:2:4 100	3:2:4 100	3:2:4 65-100	_	eut. 25-100	_	eut. 25-100	eut. 25-100	eut. 25-100	eut. 25-100	eut. 25-100	eut. 25-100	eut. 25-100	eut. 25-100
Na	eut. 25-50	2:1:1 25-100	2:1:1 25-100	2:1:1 50-100	2:1:1 50-100	_	2:1:1 100	_	eut. 25-100	eut. 25-100	eut. 25-100	eut. 25-100	eut. 25-100	eut. 25-100	eut. 25-100	eut. 25-100
K	1:1:2 50-100	2:1:2 25-50 3:2:1 100	2:1:2 25-50 3:2:1 100	2:1:2 25-50 3:2:1 50-100	2:1:2 25-50 3:2:1 50-100	_	3:2:1 50-100	_	1:1:2 50-100	1:1:2 50-100	1:1:2 50-100	1:1:2 50-100	1:1:2 50-100	1:1:2 50-100	1:1:2 50-100	1:1:2 50-100
Rb	1:1:3 25-50	2:1:4 25-100 3:2:1 50-100	2:1:4 25-100 3:2:1 50-100	5:2:1 25-50 3:2:1 50-100	5:2:1 25-50 3:2:1 50-100	_	5:2:1 50-100 3:2:1 50-100	_	1:1:3 25-50	1:1:3 25-50	1:1:3 25-50	1:1:3 25-50	1:1:3 25-50	1:1:3 25-50	1:1:3 25-50	1:1:3 25-50
Cs	1:1:3 25-50	2:1:2 25-50	2:1:2 25-50	2:1:2 25-100 1:1:3 50-65	2:1:2 25-100 1:1:3 50-65	_	1:1:3 50-65	_	1:1:3 25-50	1:1:3 25-50	1:1:3 25-50	1:1:3 25-50	1:1:3 25-50	1:1:3 25-50	1:1:3 25-50	1:1:3 25-50

Note: *In the graph of the ratio of components, the first digit indicates the number of molecules of alkali metal nitrate; second – rare-earth nitrate, Y; the third – water.

Table 2. Conditions of formation and composition of compounds formed in water-salt systems of rare-earth metals of cerium subgroup and IIA elements of periodic system (25–65 °C)

e^2Me^{2+} \ Ln^{3+}	La	Ce	Pr	Nd	Pm	Sm	Eu
Mg	3 : 2 : 24 25–65	3 3 : 2 : 24 25–65	3 : 2 : 24 25–65	33 : 2 : 24 25–65	–	33 : 2 : 24 25–65	–
Ca	eut. < 42; >42 metastable state	eut. < 42; >42 metastable state	eut. < 42; >42 metastable state	eut. < 42; >42 metastable state	–	eut. < 42; >42 metastable state	–
Sr	eut. 25–65	eut. 25–65	eut. 25–65	eut. 25–65	–	eut. 25–65	–
Ba	eut. 25–65	eut. 25–65	eut. 25–65	eut. 25–65	–	eut. 25–65	–

Note: * In the graph of the ratio of components, the first digit indicates the number of molecules of magnesium nitrate; second – rare-earth nitrate; the third – water.

determined and synthesis of double nitrates is carried out, the forms of growth of their crystals and a number of their inherent properties are investigated.

The choice of the proposed table and chart forms of presentation of the results is the most visible and informative and useful in the development of innovative projects can predict the causal and consequential fundamental patterns of behavior of structural components in similar production processes, choose the right regimes, stages, methods for the formation and receipt of target products with reproducible structures-sensitive characteristics. Obtained objective information allows us to model the preparatory stages of the formation of multicomponent oxide polyfunctional materials on their basis using liquid nitrate precursors.

Most of the systems studied under the conditions of the existence of solutions are characterized by the formation of new coordination nitrate compounds of REE. Concentration limits of saturated solutions, from which the total nitrates are released, correspond to the composition of non-invariant points of the corresponding isotherms of solubility. The obtained data allow to identify the phases, make quantitative calculations in the processes of evaporation, crystallization for similar objects.

All new detected phases are synthesized in monocrystalline form (Fig. 6). Most of them have an isometric shape, a size of 4–30 mm. The chemical analysis of the isolated compounds confirms the ratio of the masses of the elements in the formulas proposed above. Clarification of the composition of synthesized compounds and their recording in the coordination form was carried out based on the data of their complex study by the above methods and the conduct of low-temperature X-ray experiments in the process of studying their atomic-crystalline structure.

In tabl. 3 shows the wave numbers of absorption bands of new solid phases and their attribution. For comparison, the absorption bands $Nd(NO_3)_3{\cdot}6H_2O$ are given there. The composition of the compounds includes coordinated nitrate groups, since spectra exhibit high intensity of the band of full-symmetric vibration ν_1 and there is a sufficiently large splitting of the bands corresponding to degenerate valence ν_3 and deformation ν_4 oscillations. In the IR spectra, there are no absorption bands of 1390 cm^{-1} nitrate ions and in the region of 830–840 cm^{-1}, characteristic of ionic nitrates of alkali metals. The specificity of flat ligands does not allow, based only on the analysis of fundamental frequencies, to uniquely determine the type of their coordination. To resolve this issue, an X-ray diffraction study of new detected compounds was performed (see

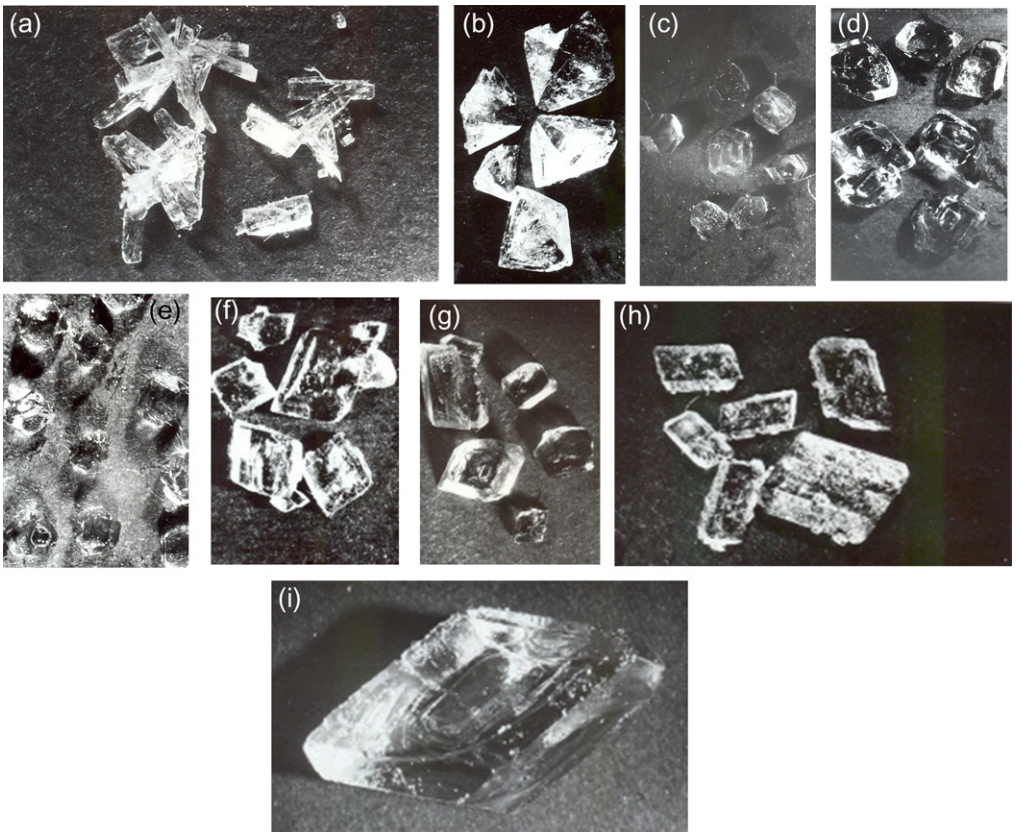


Figure 6. Microphotos of coordination nitrates crystals Ln: a) $Na_2[Nd(NO_3)_5]\cdot H_2O$; b) $K_2[Nd(NO_3)_5(H_2O)_2]$, c) $K_3[Nd_2(NO_3)_9]\cdot H_2O$; d) $Rb_5[Nd_2(NO_3)_{11}]\cdot H_2O$, e) $Rb_3[Nd_2(NO_3)_9]\cdot H_2O$; f) $Cs_2[Nd(NO_3)_5(H_2O)_2]$ ($t_{synthesi.}$ – 50 °C), g) $Cs_2[Nd(NO_3)_5(H_2O)_2]$ ($t_{synthesi.}$ – 100 °C); h) $Cs[Nd(NO_3)_4(H_2O)_3]$ ($t_{synthesi.}$ – 50 °C), i) $Cs[Nd(NO_3)_4(H_2O)_3]$ ($t_{synthesi.}$ – 65 °C)

Table 4). In absorption spectra of the obtained compounds, bands corresponding to valence, deformation, librational vibrations of water molecules, whose appearance is associated with the coordination of water molecules, are observed.

The authors analyzed the atomic structure of the single crystals of the detected coordination lanthanides and alkali metal nitrates (see [16–28]), the types of coordination of the ligands (Fig. 7), the forms of coordination polynuclears Ln (Fig. 8), the possible variants of the coordination The environment of Ln atoms (Fig. 9), the spatial arrangement of polyhedrons (Fig. 10) in the construction of compounds with aqua-containing and anhydrous complex anions, general crystallochemical patterns of the structure of this type of compounds. (More detailed information and analysis of the peculiarities of constructing such a class of compounds are given in the above-mentioned original publications of the authors). The experimental data obtained are in agreement with the results of previously studied X-ray nanoscale nitrate lanthanum [29], praseodymium [30], lanthanum-magnesium nitrate [31] – neutronographically.

The conducted research allowed to systematize information about the nature and regularities of the chemical interaction of structural components, heterogeneous

Table 3. Wave numbers (cm^{-1}) of absorption bands in IR spectra of coordination nitrates Nd

	Assignment										
Newly formed compounds	γ H_2O	$\nu_4(A_1)$ (C_{2v}, O_2NO)	$\nu_4(B_2)$ (C_{2v}, O_2NO)	$\nu_2(B_1)$ (C_{2v}, O_2NO)	$\nu_1(A_1)$ (C_{2v}, O_2NO)	$\nu_3(A_1)$ (C_{2v}, O_2NO)	$\nu_3(B_2)$ (C_{2v}, O_2NO)	δ H_2O	$\nu_1(A_1') + \nu_4(E')$ (D_{3h}, NO_3^-)	ν H_2O	$\Delta\nu_3 = \nu_3(B_2) - \nu_3(A_1)$
$Li_3[Nd_2(NO_3)_9]\cdot 3H_2O$	570-645	720	750	820	1045 1055	1320	1520	1645	1760 1800	3200-3600	200
$Na_2[Nd(NO_3)_5]\cdot H_2O$	570-650	722	750	817	1050	1325	1525	1640	1760 1795	3200-3600	200
$K_2[Nd(NO_3)_5(H_2O)_2]$	570-680	720	750	820	1045 1055	1315	1520	1665	1760 1795	3200-3600	205
$K_3[Nd_2(NO_3)_9]\cdot H_2O$	–	730	750	820	1050	1315 1335	1520	1665	1765 1800	3200-3600	205
$Rb_5[Nd_2(NO_3)_{11}]\cdot H_2O$	580-660	730	750	820	1045 1055	1315	1520	1640	1760 1800	3200-3600	205
$Rb_3[Nd_2(NO_3)_9]\cdot H_2O$	–	730	750	820	1050	1315 1335	1525	1665	1760 1800	3200-3600	210
$Cs_2[Nd(NO_3)_5(H_2O)_2]$	570-645	720	745	820	1045 1055	1310	1520	1640	1760 1800	3200-3600	210
$Cs[Nd(NO_3)_4(H_2O)_3]$	570-650	718	745	820	1045	1310	1520	1640	1760 1800	3200-3600	210
$Nd(NO_3)_3\cdot 6H_2O$	600-680	720	750	820	1045	1320	1460	1630 1665	1760 1790	3200-3600	140

Table 4. Influence of the type of symmetry on the possibility of occurrence of physical properties in crystals of coordination nitrates of rare earth elements

Connections	Sononia	Point group	Spatial group	Properties	Temperature range of formation, °C	The nature of solubility	References
$Li_3[Ln_2(NO_3)_9 \cdot 3H_2O$ La – La–Sm	cubic	23	$P2_13$		65-100	congr.	[16]
$Na_2[Ln(NO_3)_5] \cdot H_2O$ La – La–Sm	monocl.	2/m	$P2_1/a$		50-100	incongr.	[17]
$M_3[Ln_2(NO_3)_9]$ M – K, Rb, NH_4^+ La – La–Sm	cubic	432	$P4_332$		50–100	congr.	[18, 19]
$K_2[Ln(NO_3)_5(H_2O)_2]$ La – La–Sm	rhombic	mm2	Fdd2		50	incongr.	[18]
$K[Ln(NO_3)_4(H_2O)_2]$ Ln – Y, Gd–Lu	rhombic	mm2	$P2_1cn$		50–100	congr.	[20]
$Rb_2(Ln(NO_3)_5(H_2O)_2]$ La – La, Ce	monocl.	m	Cc		25–100	incongr.	[21]
$Rb_5[Ln_2(NO_3)_{11}] \cdot H_2O$ Ln – Pr ÷ Sm	monocl.	2/m	C2/c		25–50	incongr.	[22]
$Rb[Ln(NO_3)_4(H_2O)_2] \cdot H_2O$ Ln – Y, Gd–Lu	monocl.	2/m	$P2_1/n$		25–50	congr.	[23]
$Cs_2[Ln(NO_3)_5(H_2O)_2]$ Ln – Ce–Nd	monocl.	2/m	C2/c		25–100	incongr.	[24–26]
$Cs[Ln(NO_3)_4(H_2O)_3]$ Ln – Pr–Sm	tricl.	$\bar{1}$	$P\bar{1}$		50–65	incongr.	[27]
$Cs[Ln(NO_3)_4(H_2O)_2] \cdot H_2O$ Ln – Y, Gd–Lu	monocl.	2/m	$P2_1/n$		25–50	congr.	[28]

equilibrium (25–100 °C) in the water-salt systems of nitrate lanthanides, yttrium and elements of IA, IIA groups of the periodic system, ammonium; existing types of compounds, conditions for their formation, to submit their formulas in a complex form; to establish the limits of their isosteochyometricity and the scheme of the transition of composition and structure by natural series of ions Y^{3+}, La^{3+}–Lu^{3+}; Li^+–Cs^+, NH_4^+; Mg^{2+}–Ba^{2+}; the decisive role of the complex-forming ability of the central atom Ln in similar technological objects; nonmonotonicity of the change in the properties of Ln in the processes of complex formation.

The largest number of compounds form the elements of cerium subgroup $Na_2[Ln(NO_3)_5] \cdot H_2O$ (Ln – La–Sm), $Me_2[Ln(NO_3)_5(H_2O)_2] \cdot nH_2O$ (Me – K Ln – La–Nd n = 0; Me – Rb Ln – La, Ce n = 0; Me – Cs Ln – La–Nd n = 0; Me – NH_4^+ Ln – La n = 1, 2), $Rb_5[Ln_2(NO_3)_{11}] \cdot H_2O$ (Ln – Pr–Sm), $Me_3[Ln_2(NO_3)_9] \cdot nH_2O$ (Me – Li n = 3, Me – K, Rb, NH_4^+ n = 0, 1 Ln – La–Sm) , $Cs[Ln(NO_3)_4(H_2O)_3]$ (Ln – Pr–Sm).

In the temperature range of 25–100 °C, the elements of the Yttrium subgroup form compounds with only KNO_3, $RbNO_3$, $CsNO_3$, NH_4NO_3 – $K[Ln(NO_3)_4(H_2O)_2]$ (Ln – Y, Gd–Lu), $Me[Ln(NO_3)_4(H_2O)_2] \cdot H_2O$ (Me – Rb, Cs, NH_4^+; Ln – Y, Gd–Lu.

Statistical data indicate that the greatest probability of change in composition and structure under corresponding equal conditions is observed for compounds Nd. In our

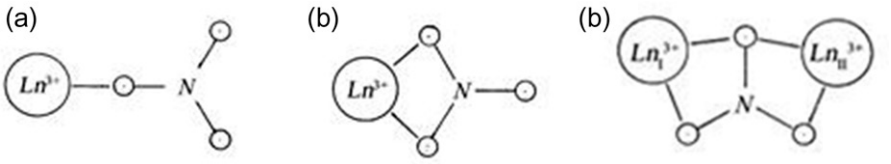


Figure 7. Three types of coordinating by nitrate groups lanthanides in coordination nitrates structures: a) monodentate; b) symmetrical bidentate; c) symmetrical bridge bidentate

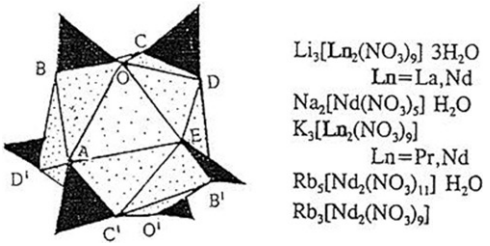


Figure 8. Schematic image and general view of Ln-icosahedra, found in the structures of coordination nitrates of REE of cerium subgroup and elements of IA groups of periodic system

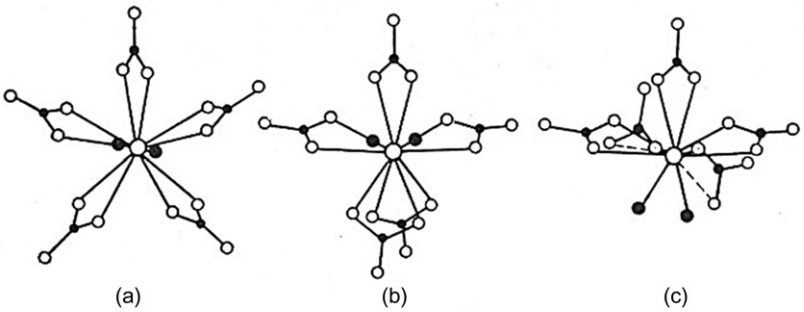


Figure 9. Schematic representation of the coordination environment of atoms of rare-earth elements in structures $(NH_4)_2[La(NO_3)_5(H2O)_2]\cdot H_2O$ (a), $K_2[La(NO_3)_5(H2O)_2]$ (b), $Cs_2[Nd(NO_3)_5(H_2O)_2]$ (c). Black circles – oxygen atoms of water molecules.Dice lines on rice in fig c – unrealized bundles O-Nd.

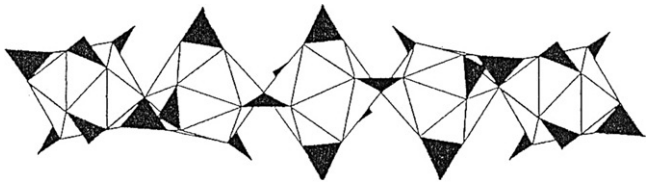


Figure 10. A chain of neodymium polyhedrons in the structure $Na_2[Nd(NO_3)_5]\cdot H_2O$

study, alkaline neodymium nitrates are also represented by the most numerous group of compounds (see Table 1). At the same time, with increasing temperature in nitrate systems studied, with the increase of the radii of monovalent cations, the complexing ability of Nd increases (in systems with Li^+ and Na^+ involved, one type of compound is formed, with K^+, NH_4^+, Rb^+, Cs^+ in two forms).

The crystallochemical patterns of the structure of new discovered complex nitrates of lanthanides and alkali metals revealed by methods of X-ray diffraction analysis indicate that the

basis of the structure of such compounds are rare earth coordination polyhedrons, which are somehow connected in space:

- in Li^+, K^+, NH_4^+, Rb^+ nitrate systems of rare-earth elements of the cerium subgroup in which the coordination saturation of the lanthanide complexes occurs without the participation of water molecules, the nitrate group of one of the three independent nitrogen atoms "serves" two independent Ln-complexing agents, and its bridged oxygen atoms bind complexes $[Ln(NO_3)_6]^{3-}$ to a three-dimensional structure of the composition $[Ln_2(NO_3)_9]^{3-}{}_{\infty\infty\infty}$;
- the occurrence of water in the coordination sphere of the Ln-complexing agent interferes with the polymerization of complexes due to the formation of bridgehead nitrate groups and is a condition for the existence of discrete $Ln3^+$ complexes (the connection of complexes to a three-dimensional construction is carried out by means of ion bonds M-O);
- the uniqueness of the sodium nitrate systems of the REE of the cerium subgroup is that the Ln polyhedrons, joined by the common vertices, form the chains - the basis of the crystalline construction of these compounds (see Figures 10 and 17)).
- The cesium phase $Cs[Nd(NO_3)_4(H_2O)_3]$ [27] is of particular interest because it co-ordinates the nitrate groups of the neodymium-type monodendental ligand;
- Cesium complex nitride compounds of the neodymium (see Figures 9, c), [26] and [27]) of different composition exhibit an equally organized coordination sphere that clearly illustrates the dominant role of the Ln^{3+} ion in the formation of alkaline rare earth nitrates.

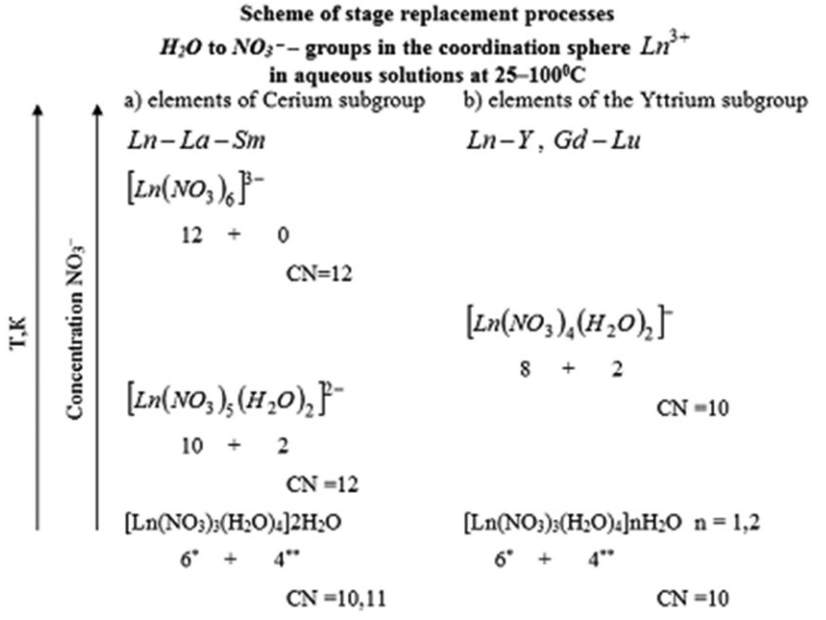
Thus, in systems of alkaline nitrate precursors REE there are both isolated systems and polymerized in varying degrees: dinuclear $[Nd_2(NO_3)_{11}]^{5-}$, stranded $[Nd(NO_3)_5]^{2-}{}_{\infty}$, frame $[Ln_2\ (NO_3)_9]^{3-}{}_{\infty\infty\infty}$. Taking part in the coordination spheres of Ln and M, the NO_3^- groups maintain a flat form. Water, which is part of most of the alkaline rare earth nitrates, coordination and crystallization, plays an important role, coordinating the Ln^{3+} ions and making additional contacts in the structures through hydrogen bonds.

The individuality of the Ln complexes of nitrate precursors is manifested: in a limited set of Ln-coordination polyhedra; in the propensity of the ion of Ln^{3+} - compactor to create a symmetrically organized coordination sphere around itself and that the identical coordination polyhedra can correspond to complexes of formally different composition and stoichiometry.

The data on the nature of the interaction of nitrite elements in the cerium subgroup and Mg, Ca, Sr, Ba indicate that only congruent soluble $[Mg(H_2O)_6]_3[Ln(NO_3)_6]_2{\cdot}6H_2O$ is formed in magnesium systems in the range of investigated temperatures [31]. In others, new solid phases are not formed (euthonic – type systems).

In the studied water-salt systems, the mechanism of complex formation can be explained from the positions of competing substitutions of water molecules in the immediate environment of Ln^{3+} on NO_3^- groups. The degree of completeness of substitution depends on the nature of Ln^{3+}, the effect on these processes of disordering effect

on the structure of solutions of available single-, double-charged cations Li^+–Cs^+, NH_4^+; Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, the nature of the thermal motion of structural components, the properties of electron donor oxygen atoms and the spatial structure of the ligands, the concentration of anions, and the amount of solvent. The significant influence on these processes of the thermal factor and their stage is revealed. The presence of certain values of the temperature of the beginning of isolation in the solid phase of complex compounds indicates the existence of an energy barrier and the need to provide the system with some additional energy for the possibility of such transformations.



Legend: *, ** – the number of links $Ln^{3+} - O$, according to ONO_2 and to OH_2;
CN – coordinate number of the central ion Ln^{3+} – complexing agent

The paper presents important in the technological aspect generalized system information about the peculiarities of the transformation processes in RE-containing systems of nitrate precursors at full concentration ratios of components and a wide temperature range that can serve as factors of influence and to be used in modern technological regulations for the manufacture of multicomponent oxide polyfunctional materials on their basis.

The established processes of complexation in aqueous solutions of nitrates contribute to the homogenization of systems of structural components at the molecular level in the complex or combined transformation of similar objects.

The promise of the use of this kind of precursors is also indicated by the existence of a sufficiently representative segment (the whole class) of coordination REE-containing nitrate compounds of alkali metals and magnesium, revealing among them isotypic composition and structure of the groups of compounds of the corresponding representatives of a number of lanthanides, a number of alkali metals, the manifestation of a

Table 5. Thermal transformations of representatives of isostructural groups of coordination nitrates REE, Y

Connections	Representatives	Dehydration	Melting in crystallization water	Polymorphic transitions	Melting anhydrous form
$Li_3[Ln_2(NO_3)_9]3H_2O$	La – Nd*	65, 183, 216	–	–	274
$Na_2[Ln(NO_3)_5]H_2O$	La – Nd*	148	–	271	328
$K_2[Ln(NO_3)_5(H_2O)_2]$	La – Nd*	95, 111	95	219	314
$K_3[Ln_2(NO_3)_9]H_2O$	La – Sm*	126	–	–	347
$K[Ln(NO_3)_4(H_2O)_2]$	Y, Gd – Lu**	138, 172	138	–	–
$Rb[Ln(NO_3)_4(H_2O)_2]H_2O$	Y, Gd – Lu***	77, 190, 256	77	–	–
$Cs[Ln(NO_3)_4(H_2O)_2]H_2O$	Y, Gd – Lu***	93,170, 240	93	–	–

Note: *data for representatives of the cerium subgroup – (coordination compounds Nd); **, ***data for the representatives of the Yttrium subgroup – (respectively, coordination compounds Gd, Yb).

complex of valuable technological attitude to their inherent properties: a) high solubility and compatibility with most components; b) a sufficiently wide temperature range of the existence of complex nitrates; c) the congruent nature of the transformations of most compounds Li^+, Na^+, K^+, NH_4^+, Rb^+, Mg^{2+} in both solutions and in the molten state; d) the detection of high activity by their reacting particles obtained by the thermolysis of the solvent, and in addition, nanosized and homogeneous in size and morphology [32]; e) existence of a wide range of methods, methods, technical means for the activation of such processes [7]. It should also be noted that the combined methods of conversion with special requirements and fast-moving synthesis with combined methods of activation of systems and mass production are now becoming more widely used [8–10].

The analysis of the nature and stage of the processes of dehydration, the nature and temperature intervals of transformations in the systems of nitrate precursors of rare-earth metals and alkali metals, phase changes during the process of transformation with thermal activation was carried out using thermoanalytic, chemical, and X-ray diffraction methods (Table 5).

The results of the studies indicate the different nature of the processes of conversion of REE compounds of cerium and Yttrium subgroups, low-and high-temperature forms of "light lanthanide" compounds. Termograms of compounds of elements of the first subgroup are characterized by the formation of anhydrous nitrates. From compounds with the same foreign sphere cation more heat-resistant nitrates with high content of lanthanum.

Temperature properties of compounds of the Yttrium subgroup are characterized by the absence of stable anhydrous forms of nitrates, low values of melting temperatures, and dehydration from the molten state.

The composition of the products of thermal transformation (about 980 °C) depends on the composition of the initial nitrates, the degree of volatility of the oxides of the corresponding alkali metals. In the products of thermolysis of the first three types of compounds (Table 4), in addition to the oxides of Me_2O, they also contain their dioxolantanoid $MeLnO_2$. In the decomposition products of the last compounds, only Ln_2O_3 has been detected.

Conclusions

The complex study provides a reliable idea of the trends in the joint behavior of structural components in the water-salt systems of nitrate precursors of REE, alkaline,

alkaline earth metals in the preparatory stages of the processes of forming multicomponent oxide polyfunctional materials on their basis with thermal activation. Stages of such transformations are revealed; The regularities of complex and phase formation in systems and factors influencing them are determined; A number of physicochemical properties of the intermediate phases formed - coordination nitrates of lanthanides: their composition, types of compounds, atomic-crystalline structure, forms of coordination polynuclears Ln, types of coordination of ligands, features and regularities of behavior in the processes of heat treatment have been studied. The systematized information allows us to find out the mechanisms, the kinetics of transformations of structural components in similar technological objects, and enable to transfer the received knowledge system to the plane of the regulation of controlled synthesis of the newest schemes for the preparation of lanthanide-containing functional materials of various applications with reproducible structural-sensitive characteristics.

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