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Some aspects of the production of multifunctional oxide REE-containing materials using nitrate systems

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The formation of a class of alkaline coordination nitrates of lanthanides was established by complex systems studies of the interaction of structural components in nitrate systems of rare earth elements and elements of groups IA and IIA of the Periodic Table - precursors of modern multicomponent oxide polyfunctional materials. All of them are synthesized in single crystal form. Their composition, atomic-crystalline structure, forms of coordination of polynuclear Ln, types of the ligand coordination and a number of their properties were studied using a set of physico-chemical methods: chemical, X-ray diffraction, IR spectroscopy, crystallo-optical, thermographic, the generation of the second harmonic of laser irradiation. Obtained new crystallo-chemical regularities of the structure of Ln compounds deepen the understanding of the chemical and physical properties, their composing ability. The obtained data can serve as the basis for detection, identifying, controlling the formed phases in innovative technologies using nitrate precursors of elements of different electronic structures.

Keywords: alkaline coordination nitrates of lanthanides, crystal structure of compounds, X-ray diffraction data, IR absorption spectra, formation conditions, properties

Деякі аспекти виготовлення багатофункціональних оксидних РЗЕ-вмісних матеріалів з використанням нітратних систем. *О.Г. Дрючко, В.В. Соловйов, Н.В. Бунякіна, А.Г. Вігдорчик, С.Г. Кислиця, М.В. Москаленко, Л.І. Леві, V.M. Galay*

Комплексним системним дослідженням взаємодії структурних компонентів у системах нітратів рідкісноземельних і елементів IA та IIA груп Періодичної системи – прекурсорів сучасних багатокомпонентних оксидних поліфункціональних матеріалів– встановлено утворення цілого класу лужних координаційних нітратів лантаноїдів. Всі вони синтезовані в монокристалічному виді. Їхній склад, атомно-кристалічну будову, форми координаційних поліедрів Ln, типи координації лігандів, ряд їхніх властивостей досліджено з використанням комплексу фізико-хімічних методів: хімічним, рентгенофазовим, рентгеноструктурним, ІЧ-спектроскопічним, кристалооптичним, термографічним, ГДГ лазерного випромінювання. З'ясовані кристалохімічні закономірності будови сполук Ln поглиблюють розуміння про хімічні і фізичні властивості, їх комплесоутворюючу здатність. Одержані дані є основою для виявлення, ідентифікації, контролю утворюваних фаз, визначення елементного складу в інноваційних технологіях з використанням нітратних прекурсорів елементів різної електронної структури і різними комбінованими способами їх активації, встановлення технологічно-функціональних залежностей, керованого модифікування властивостей продуктів синтезу.

1. Introduction

Currently, the search for new methods and complex technologies for the synthesis of REE-containing oxide materials using liquid multicomponent nitrate systems continues [1–15]. The basis of such process flow charts is the production of finely dispersed powder materials by chemical homogenization of the initial components with the joint isolation of products from the liquid phase by sequential precipitation or co-precipitation followed by heat treatment in the form of their hydroxides or other insoluble compounds, the use of ionic and molecular coordination precursors, solvent replacement, spray drying, cryochemical crystallization, sol-gel processes, etc. The synthesis of such nanocrystalline materials presents a complex scientific and technological problem.

These studies are aimed at improving the complex of structure-sensitive characteristics of the target product by optimizing the synthesis conditions; studying the features of the fractal structure of nanoparticles when isolated from solutions; the processes occurring at grain boundaries in polycrystalline systems determined by the features of the chemical interaction of the system components, the nonequilibrium of their flow; applying the 'structural design' method to control electrophysical properties; studying nanodevices in crystalline systems; developing new types of materials, etc.

The latest data on the results of such studies are not abundant, in some cases they are due to large experimental difficulties, sometimes they are contradictory and do not give a complete picture of the complexing ability of rare earth elements in such objects. A systematic study of chemical interactions, phase equilibria in water-salt systems, melts of nitrates of rare earth elements and elements of IA and IIA Groups of the Periodic Table, ammonium in full concentration ranges and in a wide temperature range, atomic-crystalline structure and properties of the compounds formed in them are of interest for:

- determination of the influence of the type of self-ordering on the properties of both nanoparticles and polycrystalline materials based on them [1];
- revealing unusual physical and chemical properties in nanoparticles caused by the so-called 'quantum-size effects'. In this case, leading (electron, ion), piezoelectric, magnetic materials are of particular interest since the differences between bulk and nanosized objects are most pronounced [2-8]. The use of nanoparticles for the synthesis of bulk samples often does not lead to the desired result. In bulk ceramics, grain boundaries, associated barrier effects, the negative influence of intermediate phases, etc., can make a significant contribution to the properties of materials [4-7];
- establishing factors influencing the shape of particles, their anisotropy [6, 7];
- obtaining and establishing crystallochemical regularities of complex REE-containing systems with garnet and perovskite structures; practical implementation of their synthesis by the method of 'structural design' [1, 9]. (Currently, such systems are actively studied with the aim of creating high-Q thermostable dielectrics for centimeter and millimeter wave ranges on their basis);
- study of textured ceramics, etc.

Research objective. To assess the possibility of controlling the processes of obtaining materials with given properties, it is necessary to study the nature and patterns of chemical interactions, thermal transformations (in 25–1000 °C range) in model systems of REE nitrates and elements.

The expansion of the application areas of modern oxide REE-containing polyfunctional materials, increasing requirements for their stability and reproduction of a set of functional and technological characteristics, improvement of their manufacturing technologies and hardware capabilities necessitate further research.

2. Experimental part

To clarify the nature of the chemical behavior of structural components and phase equilibria in the studied water-salt systems - precursors of multicomponent REE-containing functional materials, under isothermal conditions (at 25, 50, 65, 100 °C), in the temperature range of the existence of solutions in full concentration ratios, the solubility method and the technique described in our previous publications [16, 17] were used. Phase equilibria were achieved within 1–2 days. Hydrated and anhydrous nitrates of the above-mentioned elements of the analytical grade were used as starting salts. The choice of temperature cross-sections is determined by the intervals of existence of crystal hydrate forms of the starting components.

The chemical analysis of the liquid and solid phases ('residues') was carried out to determine the contents of Ln^{3+}, Mg^{2+}, $Ca^{2+} – Ba^{2+}$ ions and nitrogen. The content of Ln^{3+} was determined

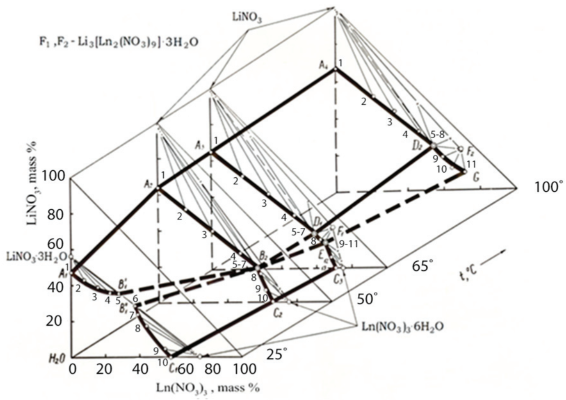

Fig. 1 Polytherm solubility of the system $LiNO_3 - Ln(NO_3)_3 - H_2O$ (Ln – La ÷ Nd)

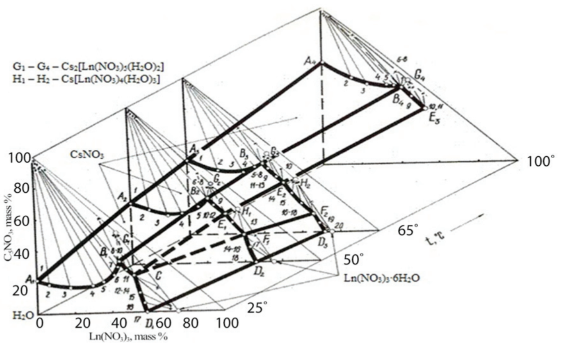

Fig. 2 Solubility polytherm of system $CsNO_3 - Ln(NO_3)_3 - H_2O$ (Ln – La – Sm)

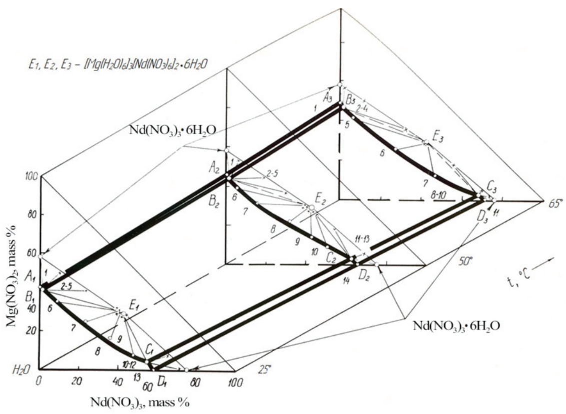

Fig. 3 Polytherm of solubility of the system $Mg(NO_3)_2 - Nd(NO_3)_3 - H_2O$ at 25-65 °C

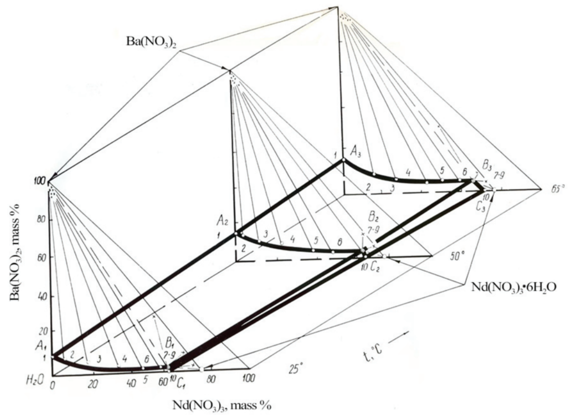

Fig. 4 Polytherm solubility of the system $Ba(NO_3)_2 - Nd(NO_3)_3 - H_2O$ at 25-65°C

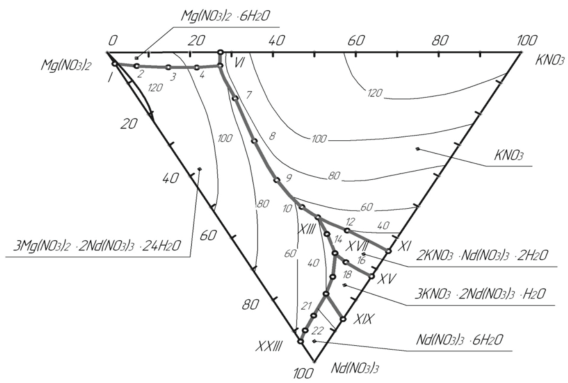

Fig. 5 Horizontal projections of the system solubility isotherms $KNO_3 - Mg(NO_3)_2 - Nd(NO_3)_3 - H_2O$ in 50 °C

trilonometrically in the presence of a xylenol orange indicator (acetate buffer solution, pH=5÷6) [18]; Mg^{2+} – by a volumetric method; $Ca^{2+} - Ba^{2+}$ – by complexometric titration of the substituent in the filtrate freed from Ln^{3+} with an ammonia buffer; nitrogen – by distillation [19], Me^{+} ions – by calculation of the difference based on the total nitrate content and partially on the dry residue.

The obtained data for individual ions were transferred to the salt content and, according to the principle of correspondence, plotted on the solubility diagram. Graphic display of the composition of solid phases formed in the system was carried out according to the Schreinemaker method [20]. Their individuality was confirmed by chemical, crystal optical, X-ray diffraction, IR spectroscopic, SHG laser radiation, thermographic and other methods of analysis.

Crystallographic determinations of the compounds were performed by the immersion method using a MIN-8 microscope. Phase analysis was performed on a DRON-3M diffractometer (Cu Kα radiation, Ni filter) using the 'powder' method. The diffraction patterns were deciphered using the JCPDS PDF file. Determination of symmetry, unit cell parameters, and measurements of the intensity of diffraction reflections from single crystals were performed on an automatic CAD-4F 'Enraf-Nonius' single-crystal X-ray diffractometer (Mo Kα radiation, graphite monochromator; ω/2θ method). All calculations for determining and refining atomic structures were performed using the SHELX, XTL-SM, and AREN crystallographic software

Table 1 – Conditions for the formation and compositions of compounds crystallizing in the water-salt systems of yttrium nitrate, rare earth elements and alkali metals (25 – 100 °C)

<table>
<tr><th>M/ REE</th><th>La</th><th>Ce</th><th>Pr</th><th>Nd</th><th>Pm</th><th>Sm</th><th>Eu</th><th>Gd</th><th>Tb</th><th>Dy</th><th>Ho</th><th>Er</th><th>Tm</th><th>Yb</th><th>Lu</th><th>Y</th></tr>
<tr><td rowspan="2">Li</td><td colspan="4">$Li_3[Ln_2(NO_3)_9]\cdot 3H_2O$
cubic.; $P2_13$</td><td rowspan="2"></td><td>euth.</td><td rowspan="2"></td><td colspan="10" rowspan="2">euth.
25–100 °C</td></tr>
<tr><td>100 °C</td><td>100 °C</td><td>100 °C</td><td>65–100 °C</td><td>25–100 °C</td></tr>
<tr><td rowspan="2">Na</td><td colspan="6">$Na_2[Ln(NO_3)_5]\cdot H_2O$
monocl.; $P2_1/a$</td><td rowspan="2"></td><td colspan="10" rowspan="2">euth.
25–100 °C</td></tr>
<tr><td colspan="2">25–100 °C</td><td colspan="2">50–100 °C</td><td></td><td>100 °C</td></tr>
<tr><td rowspan="4">K</td><td colspan="4">$K_2[Ln(NO_3)_5(H_2O)_2]$
rhombic.; Fdd2</td><td colspan="3" rowspan="2"></td><td colspan="10" rowspan="4">$K[Ln(NO_3)_4(H_2O)_2]$
rhombic.; $P2_1cn$
50–100 °C</td></tr>
<tr><td colspan="4">25-50 °C</td></tr>
<tr><td colspan="6">$K_3[Ln_2(NO_3)_9]\cdot H_2O$
cubic.; $P4_332$</td><td rowspan="2"></td></tr>
<tr><td colspan="2">100 °C</td><td colspan="4">50–100 °C</td></tr>
<tr><td rowspan="4">Rb</td><td colspan="2">$Rb_2[Ln(NO_3)_5(H_2O)_2]$
monocl.; Cc</td><td colspan="4">$Rb_5[Ln_2(NO_3)_{11}]\cdot H_2O$
monocl.; C2/c</td><td rowspan="4"></td><td colspan="10" rowspan="4">$Rb[Ln(NO_3)_4(H_2O)_2]\cdot H_2O$
monocl.; $P2_1/n$
25-50 °C</td></tr>
<tr><td colspan="2">25–100 °C</td><td colspan="2">25-50 °C</td><td></td><td>50–100 °C</td></tr>
<tr><td colspan="6">$Rb_3[Ln_2(NO_3)_9]\cdot H_2O$
cubic.; $P4_332$</td></tr>
<tr><td colspan="6">50–100 °C</td></tr>
<tr><td rowspan="4">Cs</td><td colspan="4">$Cs_2[Ln(NO_3)_5(H_2O)_2]$
monocl.; C2/c</td><td colspan="2" rowspan="2"></td><td rowspan="4"></td><td colspan="10" rowspan="4">$Cs[Ln(NO_3)_4(H_2O)_2]\cdot H_2O$
monocl.; $P2_1/n$
25-50 °C</td></tr>
<tr><td colspan="3">25-50 °C</td><td>25–100 °C</td></tr>
<tr><td colspan="2" rowspan="2"></td><td colspan="4">$Cs[Ln(NO_3)_4(H_2O)_3]$
tricl.; $P\bar{1}$</td></tr>
<tr><td>50 °C</td><td colspan="3">50-65 °C</td></tr>
</table>

complexes. IR absorption spectra of the synthesized compounds in the 400–4000 cm^{-1} range were recorded on a UR–20 spectrophotometer using the standard suspension method in vaseline oil. Thermogravimetric analysis was performed on a Q–1500 D derivatograph at temperatures from 293 °C to 1273 °C in air with a heating rate of 10 °C/min and a developed device for DTA.

3. Results and their discussion

Experimental data on the features and regularities of the mutual behavior of structural components, heterogeneous equilibria (25–100 °C) in water-salt systems of nitrate precursors of lanthanides, yttrium and elements of IA, IIA groups of the periodic table, ammonium, are summarized in the form of their spatial polythermal solubility diagrams (see Fig. 1–5) and are presented in Tables 1, 2. On their basis, the presence of chemical interaction between the constituent elements was established; the quantity, composition, nature of solubility, temperature and concentration limits of the formation of starting substances and new phases, the composition of eutonic and transition points, the positions of divariant equilibrium lines in the regions of phase coexistence were determined; the optimal conditions for the formation were clarified and the synthesis of double nitrates was carried out, the growth forms of their crystals and a number of their inherent properties were investigated.

Tabular and diagrammatic presentations of the obtained results are the most accessible, informative and useful for the develop-

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

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

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

Newly formed compounds	Ratio										
	$\gamma\ H_2O$	$\nu_4(A_1)(C_{2v}, O_2NO)$	$\nu_4(B_2)(C_{2v}, O_2NO)$	$\nu_2(B_1)(C_{2v}, O_2NO)$	$\nu_1(A_1)(C_{2v}, O_2NO)$	$\nu_3(A_1)(C_{2v}, O_2NO)$	$\nu_3(B_2)(C_{2v}, O_2NO)$	$\delta\ H_2O$	$\nu_1(A_1') + \nu_4(E')$ (D_{3h}, NO_3^-)	$\nu\ H_2O$	$\Delta\nu_3 = \nu_3(B_2) - \nu_3(A_1)$
$Li_3[Nd_2(NO_3)_9]\cdot 3H_2O$	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
$Cs[Nd(NO_3)_4(H_2O)_3]$	–	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

ment of innovative projects, the data permit to predict the cause-and-effect fundamental patterns of behavior of structural components in similar production processes, to choose cor-

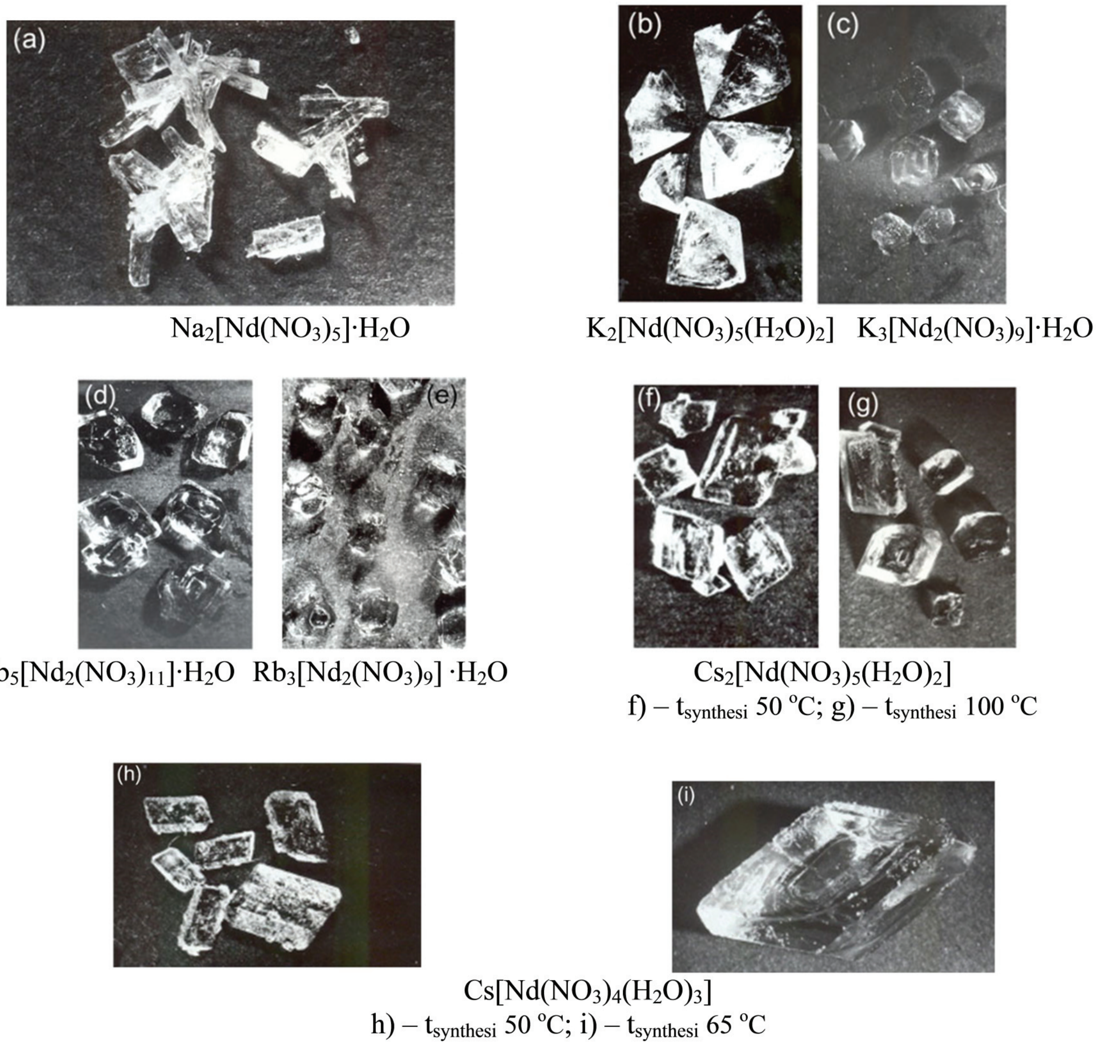

Fig. 6 – Micrographs of single crystals of coordination nitrates Nd

rectly the modes, stages, methods of formation and obtaining target products with reproducible structure-sensitive characteristics. The obtained objective information makes it possible to model the preparatory stages of formation of multicomponent oxide polyfunctional materials based on them using liquid nitrate precursors.

Most of the studied solution systems are characterized by the formation of new REE coordination nitrate compounds. The concentration limits of saturated solutions, from which complex nitrates are isolated, correspond to the compositions of nonvariant points of the corresponding solubility isotherms. The obtained data can be used for phase identification, quantitative calculations of the process parameters of evaporation and crystallization for similar objects.

All newly discovered phases were synthesized in single-crystal form (Fig. 6). Most of them have an isometric shape and size of 4–30 mm. Chemical analysis of the isolated compounds confirms the ratio of the masses of elements in the formulas proposed above. The composition of the synthesized compounds and their fixation in the coordination form were clarified based on the data of their comprehensive study by the above-mentioned methods and conducting a low-temperature X-ray experiment in the process of studying their atomic-crystal structure.

Table 3 presents the wave numbers of the absorption bands of the new solid phases and their assignment. For comparison, the absorption bands of $Nd(NO_3)_3\cdot 6H_2O$ are also given there. The compounds include coordinated nitrate groups, since the spectra contain high-intensity bands of fully symmetrical vibrations v_1 and the sufficiently large splitting of the bands corresponding to degenerate valence v_3

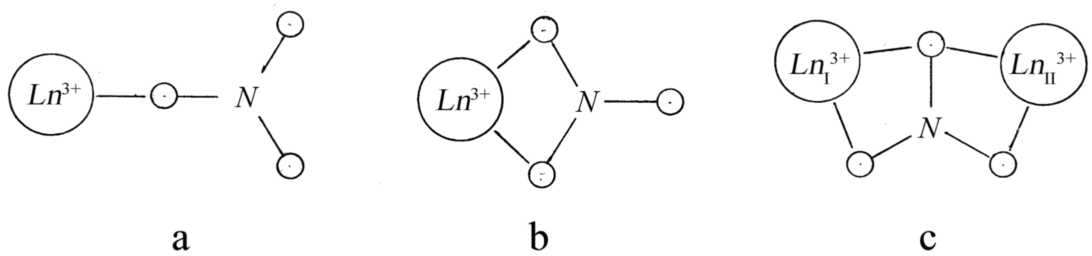

Fig. 7 – Three types of coordinating by nitrate groups lanthanides in coordination nitrates structure: a) monodentate; b) symmetrical bidentate; c) symmetrical bridge bidentate

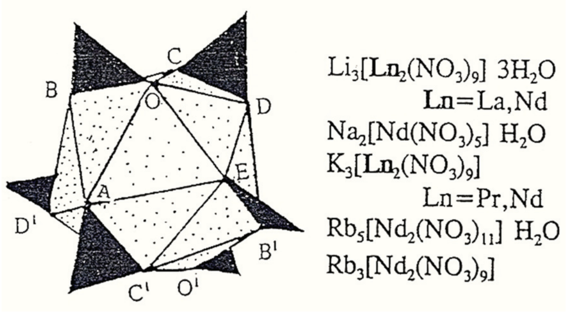

Fig. 8 Schematic image and general view of Ln-icosahedra, found in the structures of coordination nitrates of REE of cerium subgroup and elements of IA groups of periodic system

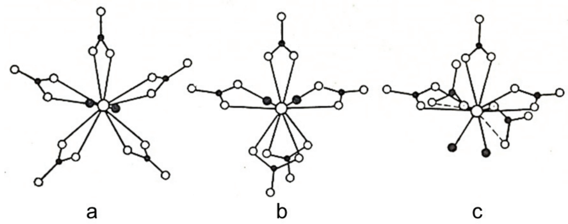

Fig. 9 Schematic representation of the coordination environment of atoms of rare-earth elements in structures $(NH_4)_2[La(NO_3)_5(H_2O)_2]H_2O$ (a), $K_2[La(NO_3)_5(H_2O)_2]$ (b), $Cs_2[Nd(NO_3)_5(H_2O)_2]$ (c). Black circles - oxygen atoms of water molecules. Dashed lines on rice in Fig c - unrealized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

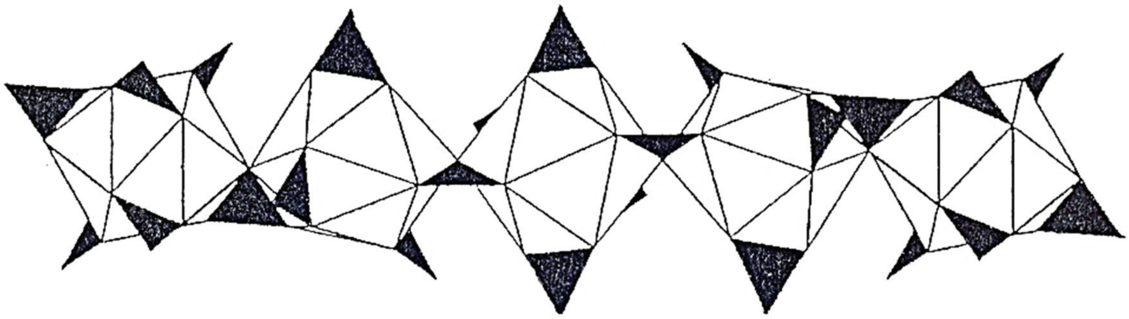

Fig. 10 A chain of neodymium polyhedrons in the structure $Na_2[Nd(NO_3)_5]H_2O$

and deformation v_4 vibrations is observed. The IR spectra do not contain absorption bands of the nitrate ion at 1390 cm^{-1} and in the 830–840 cm^{-1} range, proper to alkali metal nitrates. The specificity of planar ligands does not allow one to unambiguously determine the type of their coordination based only on the analysis of the fundamental frequencies. To solve this issue, an X-ray structural study of the newly discovered compounds was performed (see Table 4). The absorption spectrum of the obtained compounds exhibits bands corresponding to stretching, deformation, and liberational vibrations of water molecules; their occurrence/shape, depending on the context (appearance or type), is associated with the coordination of water molecules.

Using X-ray structural analysis, the atomic structure of single crystals of identified coordination nitrates of lanthanides and alkali metals [21–33], the types of ligand coordination (Fig. 7), the shapes of Ln coordination polyhedra (Fig. 8) were studied; possible variants of the coordination environment of Ln atoms (Fig. 9), the spatial arrangement of polyhedra (Fig. 10) in the construction of compounds with aqua-containing and anhydrous complex anions and the general crystallochemical patterns of the structure of this type of compounds were established. More detailed information and analysis of the features of the construction of this class of compounds are given in the abovementioned original publications of the authors. The obtained experimental data are consistent with the previously obtained results of X-ray diffraction of potassium-lanthanum nitrate $K_2[La(NO_3)_5(H_2O)_2]$ [34], potassium-praseodymium nitrate $K_2[Pr(NO_3)_5(H_2O)_2]$ [35] and neutron diffraction of lanthanum-magnesium nitrate $[Mg(H_2O)_6]_3[La(NO_3)_6]_2{\cdot}6H_2O$ [36].

The conducted studies made it possible to systematize information on the nature and regularities of chemical interactions of structural components; heterogeneous equilibria in water-salt systems of nitrates of lanthanides, yttrium and elements of IA, IIA Groups of the Periodic Table and ammonium; existing types of compounds, conditions of their formation; to present their formulas in complex form; to establish the limits of their isostoichiometricity and the transition schemes of composition and structure along the natural series of ions Y^{3+}, La^{3+}–Lu^{3+}; Li^+–Cs^+, NH_4^+; Mg^{2+}–Ba^{2+}; to determine the role of the complex-forming ability of the central Ln atom in similar technological objects; non-monotonicity of changes in the properties of Ln in complex formation processes.

The largest number of compounds are formed by elements of the 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, elements of yttrium subgroup form compounds only with KNO_3, $RbNO_3$, $CsNO_3$, NH_4NO_3 – $K[Ln(NO_3)_4(H_2O)_2]$ (Ln = Y, Gd – Lu), $M[Ln(NO_3)_4(H_2O)_2]{\cdot}H_2O$ (Me = Rb, Cs, NH_4^+, Ln = Y, Gd – Lu.

Statistical data indicate that the greatest probability of changes in composition and structure under corresponding equal conditions is observed for Nd compounds. In the study, binary alkaline-neodymium nitrates are also represented by the most numerous group of compounds (see Table 1). At the same time, an increase in temperature and an increase in the radii of monovalent cations in the studied nitrate systems result in the increase of complexing ability of Nd (in systems with the participation of Li^+ i Na^+, one type of compounds is formed; with the participation of K^+, NH_4^+, Rb^+, Cs^+ – two types each).

The crystallochemical regularities of the structure of the newly discovered complex nitrates of lanthanides and alkali metals, elucidated by X-ray structural analysis, indicate that the basis of the structure of such com-

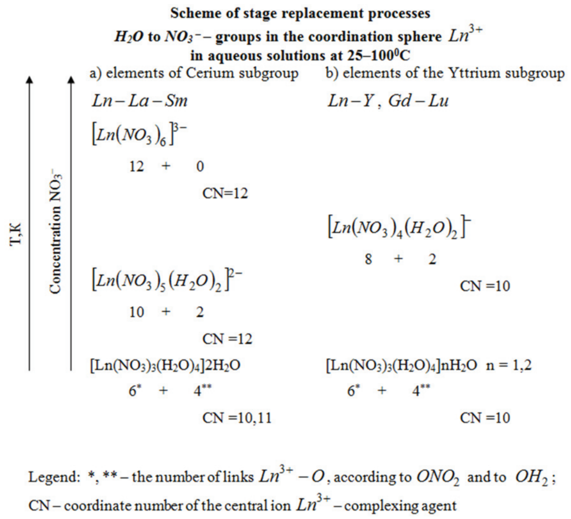

Fig. 11 Schemes of the complexation mechanism from the positions of competing substitutions of water molecules in the immediate vicinity of Ln^{3+} by the NO_3 – group

pounds is rare-earth coordination polyhedra, 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 lanthanide complexes occurs without the participation of water molecules, the nitrate group of one of the 3 independent nitrogen atoms 'serves' as two independent Ln-complexing agents, and its bridging oxygen atoms bind the $[Ln(NO_3)_6]^{3-}$ complexes into a three-dimensional framework of the $[Ln_2(NO_3)_9]^3$ composition;

– the entry of water into the coordination sphere of the Ln complexing agent prevents the polymerization of complexes due to the formation of bridging nitrate groups and is a condition for the existence of discrete Ln^{3+} complexes (the connection of complexes into a three-dimensional structure is carried out using ionic M-O bonds);

– the uniqueness of sodium nitrate systems of the REE cerium subgroup lies in the fact that Ln-polyhedra, connecting at common vertices, form chains - the basis of the crystal structure of these compounds (see Fig. 10 and [22]);

– the cesium-containing phase $Cs[Nd(NO_3)_4(H_2O)_3]$ [32] is of particular interest because it exhibits the coordination of nitrate groups by neodymium in the form of a monodentate ligand;

– cesium complex nitrate compounds of neodymium (see Fig. 9, c) and [31, 32]) of different compositions exhibit an equally organized coordination sphere, which clearly illustrates the

Table 4. Influence of the type of symmetry on the physical properties in crystals of coordination nitrates of rare earth elements [21–33]

Connections	Syngonium	Point group	Spatial group	Properties	Temperature range of location, °C	The nature of solubility	References
$Li_3[Ln_2(NO_3)_9]\cdot 3H_2O$ Ln – La ÷ Sm	cubic.	23	$P2_13$		65–100	congr.	[21]
$Na_2[Nd(NO_3)_5]\cdot H_2O$ Ln – La ÷ Sm ÷ Sm ÷ Sm	monocl.	2/m	$P2_1/a$		50–100	incongr.	[22]
$M_3[Ln_2(NO_3)_9]\cdot H_2O$ M – K, Rb, NH_4^+ Ln – La ÷ Sm	cubic.	432	$P4_332$		50–100	congr.	[23, 24]
$K_2[Ln(NO_3)_5(H_2O)_2]$ Ln – La ÷ Sm	rhombic.	mm2	Fdd2		50	incongr	[23]
$K[Ln(NO_3)_4(H_2O)_2]$ Ln – Y, Gd ÷ Lu	rhombic.	mm2	$P2_1cn$		50–100	congr.	[25]
$Rb_2[Ln(NO_3)_5(H_2O)_2]$ Ln – La, Ce	monocl.	m	Cc		25–100	incongr.	[26]
$Rb_5[Ln_2(NO_3)_{11}]\cdot H_2O$ Ln – Pr ÷ Sm	monocl.	2/m	C2/c		25-50	incongr.	[27]
$Rb[Ln(NO_3)_4(H_2O)_2]\cdot H_2O$ Ln – Y, Gd ÷ Lu	monocl.	2/m	$P2_1/n$		25-50	congr.	[28]
$Cs_2[Ln(NO_3)_5(H_2O)_2]$ Ln – Ce ÷ Nd	monocl.	2/m	C2/c		25–100	incongr.	[29-31]
$Cs[Ln(NO_3)_4(H_2O)_3]$ Ln – Pr ÷ Sm	tricl.	$\bar{1}$	$P\bar{1}$		50-60	incongr.	[32]
$Cs[Ln(NO_3)_4(H_2O)_2]\cdot H_2O$ Ln – Y, Gd ÷ Lu	monocl.	2/m	$P2_1/n$		25-50	congr.	[33]

dominant role of the Ln^{3+} ion in the structure formation of alkaline rare-earth nitrates.

Thus, in the systems of REE alkaline nitrate precursors, both isolated complexes and those polymerized to varying degrees were found: dinuclear $[Nd_2(NO_3)_{11}]^{5-}$, chain $[Nd(NO_3)_5]^{2-}$_, framework $[Ln_2(NO_3)_9]^{3-}$_. Being involved in the coordination spheres of Ln and M, NO_3^- groups retain a planar shape. Water, which is a part of most alkaline rare-earth nitrates, coordination and crystallization, plays an important coordination and crystallization role, coordinatingly

Table 5. Thermal transformations of representatives of isostructural groups of coordination nitrates of rare earth elements, 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	183	–	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	–	–

saturating Ln^{3+} ions and making additional contacts in the structures through hydrogen bonds.

The individuality of Ln complexes of nitrate precursors is manifested in a limited set of Ln coordination polyhedra; in the tendency of the Ln^{3+} complexing agent ion to create a symmetrically organized coordination sphere around itself and in the fact that the same coordination polyhedra can correspond to complexes of formally different composition and stoichiometry.

Data on the nature of the interaction of the cerium subgroup elements and Mg, Ca, Sr, Ba in nitrate systems indicate that only in magnesium-containing systems congruently soluble $[Mg(H_2O)_6]_3[Ln(NO_3)_6]_2{\cdot}6H_2O$ are formed in the studied temperature range [36]. In others, new solid phases are not formed (systems of eutonic type).

In the studied water-salt systems the mechanism of complex formation can be explained from the standpoint of competing substitutions of water molecules in the immediate vicinity of Ln^{3+} by NO_3^{-} – groups (see Fig. 11). The degree of completeness of substitution depends on the nature of Ln^{3+}, the influence of the disordering action on the structure of solutions of the available singly and doubly charged cations Li^+–Cs^+, NH_4^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} on these processes, the nature of the thermal motion of structural components, the properties of electron-donating oxygen atoms and the spatial structure of ligands, the concentration of anions, and the amount of solvent. A significant influence of temperature on these processes and their stages was revealed. The specific temperature at which the solid phase separation of complex compounds begins indicates the existence of an energy barrier and the need to provide the system with some additional energy to enable such transformations.

Technologically important systematic data on the characteristics of transformation processes in systems containing rare earth elements (REEs) and nitrate precursors have been obtained over full component concentration ratios and in a wide temperature range. These data can be used in modern process regulations for the production of multicomponent, multifunctional oxide materials. The established processes of complexation in aqueous solutions of nitrates contribute to the homogenization of systems of structural components at the molecular level during complex or combined processing of similar objects.

The potential for using this type of precursor is also demonstrated by the existence of a fairly representative segment (an entire class) of coordination nitrate compounds of alkali metals and magnesium containing rare earth elements. Among them, groups of compounds have been identified that are isotypic in composition and structure to the corresponding representatives of the lanthanide series and the alkali metal series, exhibiting a range of technologically valuable 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 Li^+, Na^+, K^+, NH_4^+, Rb^+, Mg^{2+} compounds both in solutions and in the molten state; d) high activity of their reacting particles obtained by thermolysis of the solvent, which are nanosized and uniform in size and morphology [37]. In addition, there is a wide range of methods, techniques, and technical means for activating such processes. It should also be noted that combined transformation methods with special requirements and fast syntheses with combined methods of system activation and mass production are now becoming more widespread [38–40].

The analysis of the nature and stages of dehydration processes, the nature and temperature ranges of transformations in systems of nitrate precursors of rare earth elements and alkali metals, as well as phase transformations during processing with thermal activation were carried out using thermoanalytical, chemical and X-ray phase methods (Table 5). The results of the studies indicate the different nature of the transformation processes of REE compounds of the cerium and yttrium subgroups, low- and high-temperature forms of compounds of 'light lanthanides'. Thermograms of compounds of the elements of the first subgroup are characterized by the formation of anhydrous nitrates. Among compounds with the same outer-sphere cation, nitrates with higher lanthanide content are more heat-stable. The thermal properties of compounds of the yttrium subgroup are characterized by the absence of stable anhydrous forms of nitrates, low melting points, 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 corresponding alkali metal oxides. The thermolysis products of the first three types of compounds (Table 5) in addition to M_2O oxides contain $MLnO_2$. In the decomposition products of the latter compounds, only Ln_2O_3 was detected.

4. Conclusions

The presented systematic study provides a reliable idea of the trends in the combined behavior of structural components of REE nitrate precursors, alkali, alkaline earth metals in the preparatory stages of the processes of formation of cation-ordered perovskite-like phases with thermal activation. The stages of such transformations and the regularities of phase formation have been revealed, the factors of influence and their determinants have been clarified, and a number of physicochemical properties of the formed intermediate phases – coordination nitrates of lanthanides – have been studied. The systematized information allows us to clarify the mechanisms, kinetics of transformations of structural components in similar technological objects and makes it possible to transfer the obtained system of knowledge to the plane of the regulation of controlled synthesis of the latest schemes for obtaining oxide REE-containing multifunctional materials with reproducible structure-sensitive characteristics.

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