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Cooperative transformations in REE-containing nitrate precurso systems during preliminary processes of perovskite-like oxide material property modification

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Using a complex of physicochemical methods the nature and features of chemical interaction, as well as heterogeneous equilibria of structural components in water-salt systems of neodymium and magnesium nitrates, calcium, strontium and barium in the temperature range of9 25–65°C, were studied. A number of features and patterns in their joint behavior were revealed. Current competing reactions are the strong technological factor that significantly affects the change in the activity of structural forms of Ln^{3+}. The obtained new empirical data expand the knowledge about possible directions for modifying the properties of modern multifunctional layered perovskite-like oxide materials by means of "chemical design" involving the studied class of nitrate-containing rare earth element precursors. The possibilities of such applications and the prospects of new practical solutions are clarified.

Keywords: rare earth elements, magnesium, alkaline earth metals, nitrates, complexation, water-salt systems, properties.

Кооперативні перетворення в РЗЕ-вмісних системах нітратних прекурсорів у підготовчих процесах модифікування властивостей перовскітоподібних оксидних матеріалів. *О.Г. Дрючко, В.В. Соловйов, О.В. Шефер, Н.В. Бунякіна, М.В. Москаленко, Р.В. Захарченко, А.В. Трет'як*

Із застосуванням комплексу фізико-хімічних методів авторами вивчено природу й особливості хімічної взаємодії, гетерогенної рівноваги структурних компонентів у водно-сольових системах нітратів неодиму і магнію, кальцію, стронцію, барію в інтервалі температур 25-65 °С. Виявлено низку особливостей та закономірностей у їхній спільній поведінці. Поточні конкуруючі реакції є сильним технологічним фактором, який суттєво впливає на зміну активності структурних форм Ln^{3+}. Одержані нові емпіричні дані розширюють відомості про можливі напрямки модифікування властивостей сучасних поліфункціональних шаруватих перовскітоподібних оксидних матеріалів методами «хімічного дизайну» за участю досліджуваного класу нітратних РЗЕ-вмісних прекурсорів. З'ясовуються можливості таких застосувань і перспективність нових практичних рішень.

1. Introduction

Currently, multicomponent oxide structural and special materials with mixed electron and oxygen conductivity and fast ion transport play an important role in systems for the mutual conversion of various types of energy: oxygen-conducting materials for natural gas conversion, fuel cells, many catalytic and magnetic systems, oxygen membranes, materials for high-temperature electrodes, heating elements, in gas sensors, etc. Among these multifunctional materials, complex oxides with the perovskite ABO_3 structure and double perovskite $AMe^{II}B_2O_{6-\delta}$ containing lanthanides in the A positions and *d*-metal atoms in the B positions are the most widely used. These compounds are absolute leaders both in terms of the scale of application and the attention of researchers [1 - 15].

Systematic studies of the structure, fundamental properties, defect structure and oxygen non-stoichiometry of perovskite-like phases with partial isomorphic substitutions in the A and B sublattices for other elements show that such modifications lead to a significant change in all target characteristics of these compounds (electrical, magnetic, catalytic and other properties).

The proposed study is the result of an analysis of information on systematic studies carried out over the past 15 years, and devoted to the study of oxygen non-stoichiometry, defect structure, processing technology and the properties caused by them in perovskite-like oxides of REE (Ln), magnesium, alkaline earth elements (Ca, Sr, Ba) and *d*-metals (Cr, Mn, Fe, Co, Ni, Cu, others).

Most studies of REE-containing complex oxides are mainly aimed at studying a wide range of physical properties; however, the production technology of these finely dispersed materials has received insufficient attention, although it plays an exceptional role in the formation of various structure-sensitive properties.

Currently, methods for controlling the technical parameters of such materials by selecting the composition, synthesis conditions and subsequent processing are being studied. The wide range of functional tasks, principles and methods for their solution, as well as the lack of materials that fully satisfy the entire range of technical and technological requirements, determine the absence of universal methods for their solution. To obtain such advanced materials, nanoparticles of substances are used as components of technological mixtures; this, in turn, increases interest in low-temperature methods of their synthesis by "chemical methods" using liquid multicomponent nitrate systems.

Existing methods for obtaining perovskites are complex and laborious, and often yield products with low specific surface areas and properties that do not meet the requirements of many potential applications. Currently, traditional ceramic technology, co-precipitation methods, sol-gel, ester polymer precursors (Pechini method, synthesis of ceramic powders), glycine-nitrate, mechanochemical, plasma-chemical and others are used to obtain the perovskites. The use of a microwave treatment stage of precursors in the synthesis process is one of the new promising approaches.

It should also be noted that the combined use of the 'soft chemistry' methods for the synthesis of multicomponent oxides in modern implementation allows us to simultaneously solve a number of important problems and find effective ways to solve them fundamentally and technologically. This method provides:

– production of finely dispersed components in multicomponent systems;
– promoting efficient homogenization of reaction mixtures;
– direct interaction of structural components in a given reaction environment;
– flexibility in selecting compositions and process conditions;
– the ability to perform transformations at high speed, including chain mechanisms;
– the energy efficiency of process flow charts due to the low activation energy of the reactants;
– straightforward implementation using simple equipment;
– changes in technical and technological parameters of synthesis and changes in target properties that affect the structural perfection of products.

Therefore, the acquired new knowledge and technical capabilities make it possible to raise the perfection, reproducibility and predictability of the characteristics of synthesized products to a higher level and open up new prospects for their practical application.

The presented methods are based on the isolation of target products with different dispersion of nanosized particles (20–60 nm), which cannot be achieved by conventional ceramic technology (typically ≥100 nm) due to various chemical interactions between the structural

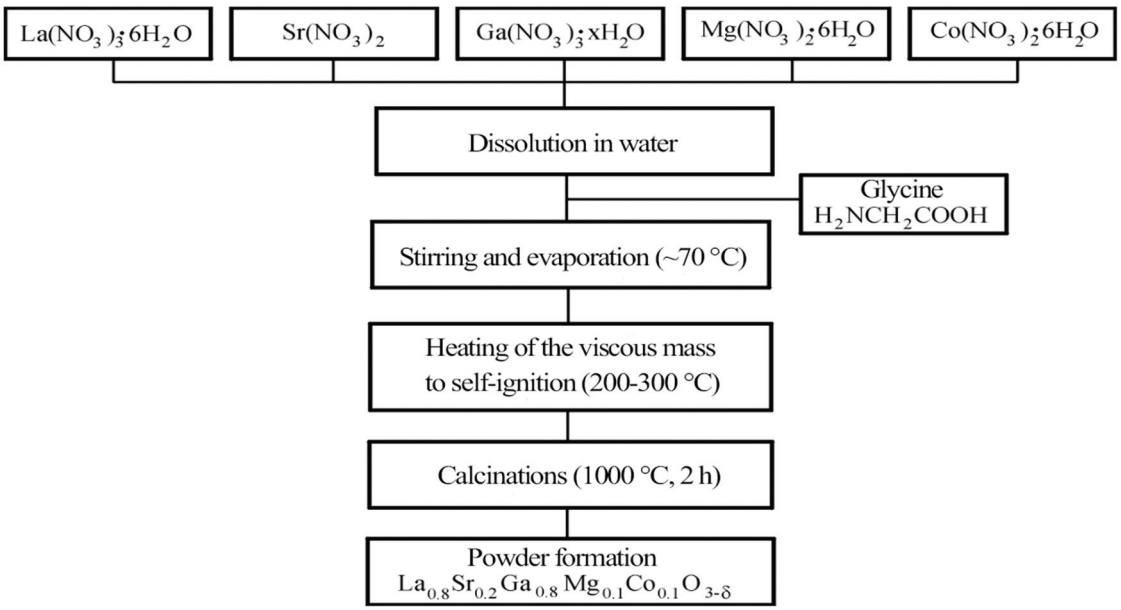

Fig. 1 – Sequence of operations for the formation of perovskite-like oxide phases $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.1}Co_{0.1}O_{3-\delta}$ by the glycine–nitrate method [15]

components of systems from aqueous solutions of salts containing cations of different metals in the required ratio. For example, Fig. 1 illustrates the sequence of the advanced operations for the preparation of perovskite-like oxide phases of REE and 3d-elements of catalytic, as implemented by the leading Korean companies [15]. According to this regulation, the absence of grinding operations during the preparation of the initial charge ensures high purity of the final products.

The purpose of the present study is to investigate the cooperative interactions between structural components during the formation of perovskite-like oxide phases of rare-earth and transition elements in the preparatory stages. This was achieved by using nitrates of elements with different electronic structures and determination of possible approaches to influencing liquid- and solid-phase systems based on the thermal activation of the reagents. The goal is to reproduce their structure-dependent properties.

Together with the literature data, the obtained results indicate the possibility of controlling the physical properties of REE-containing multicomponent perovskite-like phases by varying particle size, both through the choice of formation methods and by adjusting temperature and other technological factors during synthesis. Such studies enable a better understanding of the features and potential of specific protocols for forming structure-sensitive physical properties of perovskite-like oxide solid solutions, which are promising for practical applications. Furthermore, determining the dependence of the most significant properties of these materials on the particle size provides guidance on whether it is necessary to obtain the nano-dispersed structures and how to modify the composition, content or formation methods to achieve meaningful changes in their structure, morphology and properties.

The most recent data on the results of similar studies are inconsistent; significant experimental difficulties often lead to contradictory results and do not allow a full understanding of the ability of rare earth elements to form complexes in such systems. The unambiguous interpretation of the above-mentioned processes is often complicated by the incongruent solubility (melting) of the intermediate phases, the simultaneous coexistence of several metastable thermolysis products, the formation of heterophases, and the dependence of their state on the history of the process itself (possible amorphous or poorly crystalline state of the precursors [14]). Additionally, the complexity of processes occurring at grain boundaries in polycrystalline systems due to the specifics of chemical interactions between the components of the system, the non-equilibrium nature of the transformations and the presence of limiting stages further complicates the analysis.

Therefore, the available information regarding the state and potential directions for

Table 1 – Data on phase equilibria in the $Mg(NO_3)_2$ – $Nd(NO_3)_3$ – H_2O system at 25 – 65 °C

t, °C	Composition points	Saturated solution				Composition of the "residue", mass.%		Solid phases*
		Composition, mass.%		Properties				
		$Mg(NO_3)_2$	$Nd(NO_3)_3$	d x 10^3, кг/м^3	n	$Mg(NO_3)_2$	$Nd(NO_3)_3$	
1	2	3	4	5	6	7	8	9
25	1 A_1	41.69	0.00	1.389	1.4100	57.61	0.00	F
	2					56.60	0.89	the same
	3					49.50	9.26	F+E
	4 B_1	41.16	1.21	1.394	1.4104	40.93	23.74	the same
	5					31.27	39.05	E
	6	34.99	8.87	1.192	1.4073	30.02	40.86	the same
	7	24.83	23.55	1.469	1.4166	31.06	41.74	« - »
	8	16.26	35.81	1.698	1.4342	29.37	41.00	« - »
	9	7.44	48.33	1.739	1.4417	27.97	42.49	« - »
	10					27.8	42.81	« - »
	11 C_1	4.18	55.29	1.982	1.4532	7.81	66.30	E+G
	12					1.17	72.02	G
	13 D_1	0.00	58.49	1.887	1.4551	0.00	75.25	G
50	1 A_2	45.35	0.00	1.383	1.4129	57.80	0.00	F
	2					56.62	0.00	the same
	3					53.84	6.95	F+E
	4 B_2	43.64	1.96	1.467	1.4144	44.10	18.78	the same
	5					37.32	27.83	« - »
	6	38.75	5.42	1.417	1.4112	30.61	39.61	E
	7	30.88	16.06	1.460	1.4141	29.86	40.09	the same
	8	21.70	32.39	1.561	1.4253	28.18	41.03	« - »
	9	13,68	43.35	1.718	1.4382	27.16	42.67	« - »
	10	8.67	51.20	1.727	1.4472	26.62	44.23	« - »
	11					26.23	45.14	« - »
	12 C_2	2.73	62.90	1.900	1.4659	17.50	54.83	E+G
	13					3.93	68.04	the same
	14 D_2	0.00	66.16	1.974	1.4667	0.00	75.28	G
65	1 A_3	48.52	0.00			57.45	0.00	F
	2					56.39	2.64	F+E
	3 B_3	45.94	1.99			48.68	11.48	F+E
	4					34.50	32.86	the same
	5	40.67	6.63			29.35	39.33	E
	6	24.96	27.58			26.96	41.40	the same
	7	11.16	47.11			27.83	42.87	« - »
	8					19.39	54.99	E+G
	9 C_3	2.29	68.27			5.19	68.97	the same
	10					0.84	73.30	« - »
	11 D_3					0.00	75.26	G

* F – $Mg(NO_3)_2 \cdot 6H_20$; G – $Nd(NO_3)_3 \cdot 6H_2O$; E – $[Mg(H_2O)_6]_3[Ln(NO_3)_6]_2 \cdot 6H_2O$

improving technologies for the production of multifunctional REE-containing oxide materials, as well as existing requirements for their stability and reproducibility, served as motivation for our study.

Table 2 – Data on phase equilibria in the $Sr(NO_3)_2$ – $Nd(NO_3)_3$ – H_2O system at 25 – 65 °C

Fig. 1 – Se-	Composition points	Saturated solution				Composition of the "residue", mass.%		Solid phases*
		Composition, mass.%		Properties				
		$Sr(NO_3)_2$	$Nd(NO_3)_3$	d x 10^3, кг/м^3	*n*	$Sr(NO_3)_2$	$Nd(NO_3)_3$	
1	2	3	4	5	6	7	8	9
25	1 A	44.6	0.00	1.539	1.4068	99.87	0.00	D
	2	41.66	5.12	1.541	1.4084	99.32	0.00	"-"
	3	30.71	17.66	1.547	1.4129	97.56	0.79	"-"
	4	20.86	29.99	1.550	1.4164	95.87	1.52	"-"
	5	12.58	41.84	1.569	1.4299	95.60	1.69	"-"
	6					95.72	2.80	"-"
	7 B	5.94	56.97	1.873	1.4548	52.50	34.84	D+E
	8					19.05	59.51	"-"
	9						70.62	"-"
	10 C	0.00	58.49	1.887	1.4551	0.00	75.25	E
50	1 A	48.03	0.00	1.487	1.4055	99.91	0.00	D
	2	39.75	10.75	1.544	1.4079	99.23	0.57	"-"
	3	29.35	20.28	1.589	1.4184	97.57	1.39	"-"
	4	14.38	43.08	1.623	1.4298	96.45	1.87	"-"
	5					94.90	3.40	"-"
	6 B_2	3.88	65.34	1.850	1.4691	13.73	64.75	D+E
	7					7.26	9.76	"-"
	8 C_2	0.00	66.16	1.974	1.4667	0.00	75.28	E
65	1 A_3	48,60	0,00			99,92	0,00	D
	2	33,85	13,40			98,23	0,69	"-"
	3	25.84	23.91			98.11	0.85	"-"
	4	10.93	40.17			97.50	1.38	"-"
	5	4.97	53.11			95.85	1.69	"-"
	6	2.35	61.72			95.30	2.18	"-"
	7					94.89	2.23	"-"
	8 B_3	2.52	68.39			10.39	67.78	D+E
	9					3,64	72,88	"-"
	10 C_3	0,00	71,58			0,00	72,26	E

* D – $Sr(NO_3)_2$; E – $Nd(NO_3)_3 \cdot 6H_2O$.

2. Experimental

To assess the possibility of controlling the above-mentioned processes and obtaining materials with predetermined properties we chose $Me(NO_3)_2$ – $Ln(NO_3)_3$ – H_2O (Me – Mg, Ca, Sr, Ba; Ln – Nd) as model systems (see Tables 1, 2; Figures 2, 3). The components of these systems determine the technical characteristics of the synthesized products or modify their physical properties. The choice of neodymium nitrate (as a representative of the cerium subgroup of REEs) was determined by available statistical data indicating the highest probability of changes in the composition or structure of neodymium compounds in the natural series from lanthanum to lutetium. The choice of temperature cross-section values of 25, 50 and 65°C for studying the solubility isotherms of systems is due to the instability of neodymium nitrate

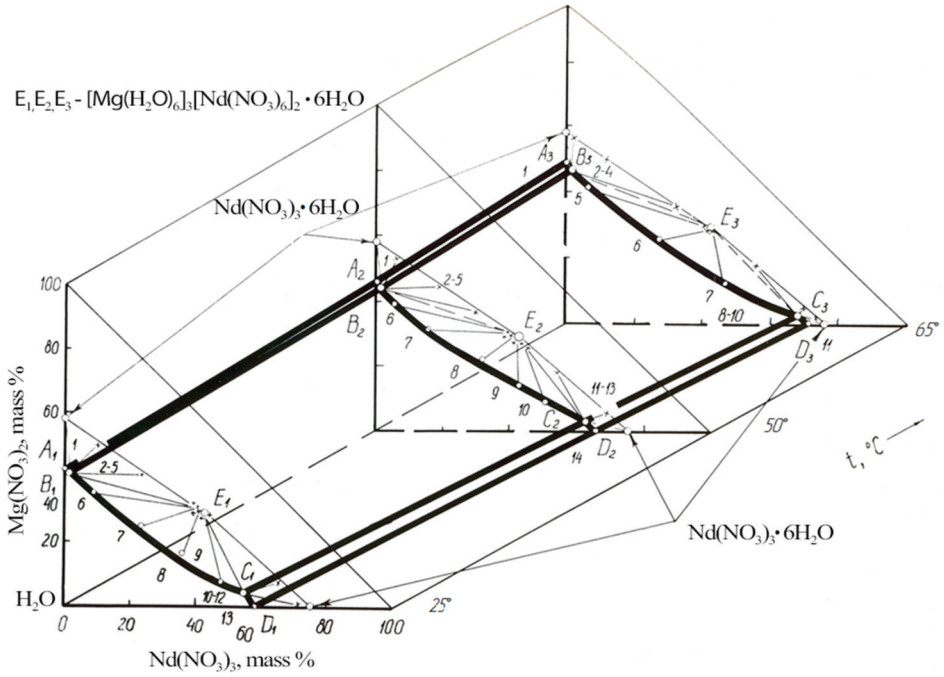

Fig. 2 – Polythermal solubility diagram of the $Mg(NO_3)_2$ – $Nd(NO_3)_3$ – H_2O system at 25–65 °C

hexahydrate and the onset of its melting in crystallization water at 68°C, above which it exists in a liquid, highly viscous, metastable state.

To clarify the nature of chemical interactions and phase equilibria in the aqueous–salt systems of the studied nitrates (precursors of multicomponent oxide multifunctional materials) over the full range of concentration ratios within the temperature range of solution stability, an additional doping method described in [16] was used. This method is based on the study of solubility as one of the properties most sensitive for detecting phase transformations in these systems; it simultaneously serves as a parameter of their state and can be measured using simple, readily available experimental methods. The method allows us to find the limits of self-development to which an isolated system of a given composition tends under certain conditions in an equilibrium state. To enhance the reliability of the obtained data, a simultaneous comprehensive investigation of the solubility of the system components, solution density, and relative refractive index was conducted. A good consistency of the results was observed.

Phase equilibrium was achieved within 1-2 days. Hydrated and anhydrous nitrates of the specified elements of analytical grade of purity were used as starting salts.

The chemical analysis of the liquid and solid phases ('residues') was carried out to determine the content of Nd^{3+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} ions and nitrogen. The content of Nd^{3+} was determined by a complexometric method in the presence of a xylenol orange indicator (acetate buffer solution, pH=5÷6) [17]; Mg^{2+} – by a volumetric method; Ca^{2+}, Sr^{2+}, Ba^{2+} – by complexometric titration of the substituent in the filtrate purified from Ln^{3+} with an ammonia buffer; nitrogen – by distillation [18]. The experimental data for individual ions in the studied systems were recalculated to salt content, summarized, tabulated (Tables 1, 2), and, in accordance with the correspondence principle, were plotted on polythermal solubility diagrams of the systems (Figs. 2, 3). The graphical representation of the composition of solid phases formed in the systems was performed according to the Schreinemakers method [16]. The chemical analysis of the isolated double nitrates obtained in single-crystalline form confirmed the stoichiometric ratios in the above formulas. Their individuality was also verified by crystal-optical, X-ray phase, thermographic, IR spectrometric and other analytical methods.

3. Results and discussion

The regularities of complex formation of lanthanides in the systems were established; the number, composition, solubility characteristics and the temperature and concentration limits

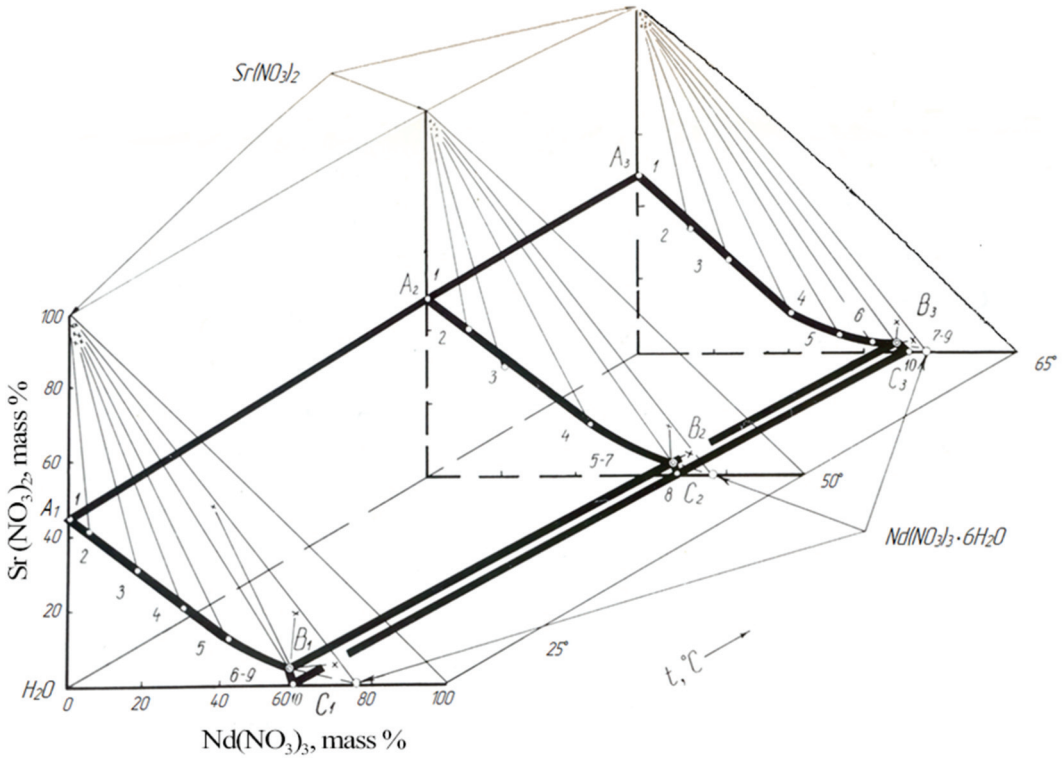

Fig. 3 – Polythermal solubility diagram of the $Sr(NO_3)_2$ – $Nd(NO_3)_3$ – H_2O system at 25 – 65°C

of phase crystallization were determined; polythermal solubility diagrams were constructed (see Figs. 2, 3). The data on the nature of the interaction of structural components in the nitrate systems of cerium subgroup elements with Mg, Ca, Sr, Ba showed that only in the magnesium systems in the temperature range of solution stability, congruently soluble compounds $[Mg(H_2O)_6]_3[Ln(NO_3)_6]_2 \cdot 6H_2O$ were formed, while in other systems new solid phases were absent (eutonic type systems).

The study of the calcium system in the temperature range of 50–65 °C at all ratios of salt concentrations turned out to be impossible, since the studied mixtures were in a pasty, not crystalline, state. In strontium and barium systems, it was found that the compositions of the eutonic and invariant solubility points of neodymium nitrate hexahydrate are close. With increasing temperature, the composition of their non-variant points changed only slightly. At the same time, a salting-out effect of neodymium nitrate with respect to strontium and barium nitrates was observed.

In ternary systems containing rare earth elements and nitrate precursors, which are integral components of more complex multicomponent systems, exchange chemical transformations began already in the liquid phase, from the moment the components dissolved in water – a highly polar solvent. The mechanism of coordination compound formation can be explained by competing processes of substitution of water molecules in the immediate environment of Ln^{3+} NO_3^-groups, the disordering of the solution structure caused by the introduction of divalent cations Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} and the influence of temperature. The degree of substitution depended on the nature of Ln^{3+}, the present Me^{2+}cations, the properties of the oxygen atoms that are electron donors, the spatial arrangement of ligands, electrolyte concentration, and temperature.

The differences were observed in the complexation ability of elements of the cerium and yttrium subgroups, as well as yttrium itself.

All identified magnesium lanthanide complex nitrates of the cerium subgroup were synthesized in a single-crystalline form (4–30 mm in size), and their optimal synthesis conditions and growth forms were studied. Their atomic-crystalline structure, coordination polyhedron geometries, types of ligand coordination, and various properties were investigated. The crystals of such compounds consisted of two types of ions $[Mg(H_2O)_6]^{2+}$ i $[Ln(NO_3)_6]^{3-}$, connected by hydrogen bonds of water molecules included in the complexes as well as uncoordinated water molecules.

4. Conclusions

Structural and functional oxide materials containing rare earth elements with nitrates of elements with different electronic structures are produced by chemically mixing the starting components and then separating the products from the liquid phase by sequential or simultaneous precipitation followed by thermal treatment; these processes proceed through the formation of a series of intermediate phases. To understand their composition, content and behavior in each specific case, preliminary systematic empirical knowledge of their mutual interactions over the entire range of concentrations and within a given temperature interval is required.

Differences were revealed in the behavior of structural components in lanthanide systems of the cerium and yttrium subgroups, in the nature of their interactions, their staging, and the features and patterns of their transformations.

The obtained knowledge provides a foundation for:

– the search for methods to increase the activity of Ln^{3+} forms;

– elucidating the nature of successive thermal transformations in nitrate-based REE-containing multicomponent systems of various aggregate states during thermal treatment, the conditions for the formation and stability of intermediate phases, their properties, influencing factors, and possible approaches for controlling the formation of the target product;

– the development of modern, advanced and low-energy technologies for synthesizing functional materials with reproducible properties.

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