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Some Physicochemical Aspects of the Preparatory Stages in the Formation of Self-cleaning Photocatalytic Active Coatings for Building Construction Materials



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Abstract A complex systematic study of the interaction of structural components in cerium subgroup lanthanide nitrate systems and representatives of the IA group (Li, Na, K) of the elements of the periodic system, precursors of modern multicomponent oxide multifunctional materials based on them, established the formation of a representative class of alkaline coordination nitrates Ln. Their composition, formation conditions, atomic-crystalline structure, forms of Ln coordination polyhedral, types of ligand coordination, a number of their properties were studied using a complex of physicochemical methods: chemical, X-ray phase, X-ray structural, IR-spectroscopic, crystal-optical, thermographic, and SHG laser radiation. The data obtained are the basis for identifying and monitoring the phase state of processing facilities in the preparatory stages when forming self-cleaning coating layers of building construction materials by using innovative technologies; using nanostructured composite systems of lanthanides and transition elements with photocatalytically active and hydrophilic properties; various combined methods of their activation; and establishing technological and functional dependencies to modify the properties of the products obtained.

Keywords Alkali coordination nitrates of lanthanides · Conditions of formation · Crystalline structure of compounds · Properties

1 Introduction

This work is aimed at finding new comprehensive solutions for the creation of a new generation of float glass for the construction industry (both external and interior), covering the designs of solar photovoltaic energy, and other specialized industries. It is known that the leading companies (Pilkington, AGC Flat Glass Europe, Saint-Gobain, and others) develop and sell lines of types of self-cleaning glass, products

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based on them with a coating of complex action with photocatalytic and hydrophilic properties by developed own technologies and using compositions of titanium dioxide. Their products are in great demand when constructing high-rise buildings, glass roof structures, for glazing facades of commercial and artistic architectural objects, parking lots, greenhouses, structures with good visibility solar photovoltaic panels, sports arenas of stadiums, outdoor premises of airports [1, 2], that is, in cases of difficult access and complicated, labor-intensive cleaning. The implementation of these simple solutions also allows you to solve the problem of improving the efficiency of converters of renewable energy forms in energy, energy conservation and sun protection simultaneously, providing a spectacular appearance of the facade of buildings and creating a comfortable microclimate for people who are indoors.

1.1 Problem Statement and Solution Methods

Self-cleaning eliminates the pollution of the environment, contains particles of photocatalytic titanium dioxide (TiO_2), and is capable of forming electron–hole pairs in electromagnetic irradiation, in particular ultraviolet (UV) close to ultraviolet light and/or visible light. Preferably, the photocatalytic titanium dioxide in the anatase modification is capable of significant photoactivity when exposed to visible light. It has been found that careful regulation of the crystalline form and size of TiO_2 particles can provide photocatalysts that is capable of removing contaminants even in low-light UV light, in particular in interior light, and which have significant initial activity, even without activation by solvent washing. The degree of crystallinity and the nature of such crystalline phases are determined by X-ray diffraction methods. The average particle size of TiO_2 for use in the compositions is 5–30 nm.

Photocatalytically active coatings are precipitated by using a variety of technologies, such as sol–gel, spray pyrolysis, by means of chemical vapor deposition or gas phase, magnetron sputtering. Regulations are currently being implemented using “solution burning” methods [3].

An interesting innovative solution is the method of preparation of sol–gel method of hydrophilic self-cleaning coating with photocatalytic activity, in which butyl titanate and ethyl orthosilicate are used as precursors for the formation of nanosol $\text{TiO}_2/\text{SiO}_2$ particles [4]. Anatase composite film is applied to the surface of the object (window or architectural glass, solar photovoltaic panel) and naturally dried at room temperature in a natural way to obtain photocatalytic activity rapidly. Pollutants, when decomposed into inorganic substances, are easily washed off with rainwater or artificial washing.

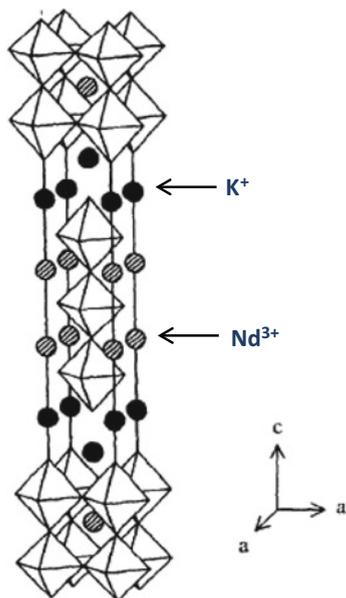
It has also been found that titanium oxide coatings deposited on the surface of sodium–calcium glass can reduce the level of photoactivity and hydrophilicity due to the migration of alkali metal ions from such glass into the TiO_2 layer and therefore introduce barrier layers of SiO_2 more often.

Nowadays, the implementation of innovative solutions is linked to:

- the development of methods of synthesis of thin films, functional coatings, and nanosized inorganic oxide fillers with chemically modified surface;
- the development of nanochemical liquid phase and pyrolytic methods for the synthesis of thin oxide films on the surface of solids;
- the study of the peculiarities of chemical modification reactions and the formation of nanoparticles in thin oxide films and composite systems;
- the creation of film structured photocatalysts; functional, special, protective, anticorrosive, and decorative coatings on the surface of inorganic materials;
- the development of a protective superhydrophobic coating on the surface of $\text{TiO}_2/\text{SiO}_2$, TiO_2/Si compositions, which facilitates dust, polar, and non-polar contaminants and also protects against the adverse effects of atmospheric factors.

One of the most promising classes of photocatalytically complex rare earth oxides and titanium oxide materials that can act as alternatives to existing developments is nanostructure-layered perovskite-like compounds and solid solutions based on them. Depending on their composition and structure, they have a wide range of physicochemical properties. The perovskite-like layered titanates presented in this paper belong to the homologous series $(\text{Me}, \text{Ln})_{n+1}\text{Ti}_n\text{O}_{3n+1}$ —of the Ruddlesden–Popper phase, where $\text{Me}=\text{H}, \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$; $\text{Ln}=\text{La}, \text{Nd}$; n —the number of nanowires of perovskite, with a thickness of about 0.5 nm; in accordance, MeLnTiO_4 contains one perovskite nanolayer in its structure, $\text{Me}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$ —contains three. As an example, a three-layer perovskite-like oxide $\text{K}_2\text{Nd}_2\text{Ti}_3\text{O}_{10}$ was obtained and researched by the authors of the following works [5–7]. Figure 1 shows his expanded elemental cell.

Fig. 1 Extended unit cell
 $\text{K}_2\text{Nd}_2\text{Ti}_3\text{O}_{10}$



Oxides $\text{K}_2\text{Nd}_2\text{Ti}_3\text{O}_{10}$ crystallize in a tetragonal structure similar to the structure $\text{Sr}_4\text{Ti}_3\text{O}_{10}$, which is one of the first synthesized phases of Ruddlesden–Popper. The space group for these compounds is defined as $I4/mmm$. The thickness of the layered oxides of this type is characterized by three titanium-oxygen octahedra $[\text{Nd}_2\text{Ti}_3\text{O}_{10}]$, alternating between themselves and separated by cations of alkali metals, in this case by potassium cations, between the layers. The lattice parameter c ($\approx 30 \text{ \AA}$) indicates the displacement of adjacent perovskite layers by $1/2$. The neodymium cation is located in the center of the perovskite lattice and is characterized by a 12-coordinated oxygen environment. The alkali metal cation is in the interlayer space and is usually 9-coordinated [8].

For innovative applications, it is important to study the stability of systems that have proven to be promising photocatalysts, in conditions close to their use in aqueous solution, in conditions simulating a flow reactor, and in moist air. In research [9] using methods of TGA, DSC and X-ray phase analysis regularities of the behavior of layered perovskite-like oxides $\text{A}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$ ($\text{A} = \text{Li}, \text{Na}, \text{K}; \text{Ln} = \text{La}, \text{Nd}$) with water for different times are established. It has been found that all alkaline forms of layered oxides are characterized by the flow of protonation processes; in the case of $\text{K}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$, this process is accompanied by the intercalation of water into the interlayer space. The dependence of the protonation process from the choice of the rare earth metal cation is revealed. For Nd-containing compounds, ion exchange for protons proceeds faster than La-containing counterparts due to the greater mobility of alkali metal cations in the interlayer space, which is associated with greater distortion of titanium-oxygen octahedra and smaller (compared to La^{3+}) radii. It has been found that $\text{K}_2\text{Nd}_2\text{Ti}_3\text{O}_{10}$ and its stable intercalated proton derivatives are not changed when interacting with atmospheric humidity, which indicates the stability of the compounds under possible operating conditions. A layered structure consisting of lamellar particles is stored for the incubation product, which is confirmed by scanning electron microscopy (see Fig. 2, [9]).

Features of application of methods of “soft chemistry” during the formation of nanosystems are the possibility of synthesis of new photocatalytically active coating materials with high chemical homogeneity of multicomponent systems due to the

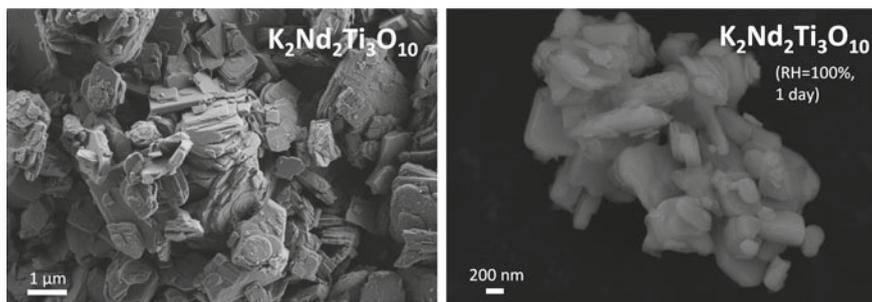


Fig. 2 Output micrographs $\text{K}_2\text{Nd}_2\text{Ti}_3\text{O}_{10}$ i $\text{K}_2\text{Nd}_2\text{Ti}_3\text{O}_{10}$ after keeping in a humid atmosphere ($\text{RH} = 100\%$, 1 day) [9]

uniform (molecular level) distribution of components in the original solution, a significant decrease in the temperature control of their properties, the target products obtained in the synthesis process, and the simplicity and accessibility of this method contribute to its application on an industrial scale. However, as for the mechanisms of formation of nanocomposites from film-forming solutions by the above technologies, the influence of the formation conditions on the structure, physicochemical and target properties, these issues are hardly covered. Therefore, the successful use of nanomaterials in mass technology requires a systematic fundamental study of these aspects.

In [10–13], the effect of non-film-forming components of colloidal solutions (salts of inorganic REE acids, oxide filler systems, metals) on the film-forming properties of such systems is investigated. It is shown that salts of inorganic acids act as the electrolyte stabilizer of colloidal solutions and significantly extend the interval of film-forming properties of solutions, and increasing the concentration of electrolyte and increasing the charge of the nucleus on a number of REE, increase the stability of the system to aggregation and coagulation of the structure and transition of the solution to the gel state.

The processes of the formation of simple and complex oxides in thin-film and dispersed state are non-equilibrium, transient flows through a series of successive stages. They include evaporation of adsorbed solvents, the formation of complex associates, hydrolysis and condensation of hydrolysis products, the emergence of amorphous or metastasis, salts and removal of gaseous products, combustion of organic residues, crystallization processes, and other physicochemical transformations. The processes that take place in the thin layer are more energy-efficient—there is a decrease in the temperature of film formation compared to powders and a decrease in the activation energy of the processes going on the substrate surface.

The influence of the dimensional factor on the structure and properties of the fine-layer coatings is determined [10], which is to stabilize the metastable and high-temperature phases in the nanosystems. The influence of the oriented action of the substrate and the conditions of forming of obtaining films with amorphous and crystalline structures are also revealed.

For effective management of the processes of the formation of self-cleaning coatings of building structural materials using compositions based on titanium dioxide and inherent valuable set of photocatalytic and hydrophilic properties requires a deep understanding of the physicochemical processes, phenomena that occur during their manufacture. Moreover, their complex research with the application of modern physicochemical methods allows us to improve our knowledge about the characteristic features of transient processes, the stage of evolution of the structure, and microstructure of technological objects.

1.2 *The Purpose and Tasks of the Study*

The aim is to carry out research of cooperative processes of interaction between structural components in systems of nitrate precursors of representatives of REE of the cerium subgroup and elements of IA subgroup of the periodic system (Li, Na, K) under conditions similar to the regulatory ones when creating hydrophilic self-cleaning coatings of building structural materials using photocatalytic active TiO_2 in order to form credible ideas and obtain objective knowledge about the peculiarities of transformations and the cumulative behavior of the constituent elements in the preparatory stages of processing of technological objects with thermal activation, necessary for the improvement and development of methodologies and regulations of modern technologies of their production.

2 Experimental Part

2.1 *Experiment Methodology*

To evaluate the possibility of controlling, the processes of multistage formation of complex-oxide compositions with polyfunctional properties and to substantiate the mechanisms of phase formation as model we use a complex of physicochemical methods studied water-salt systems of nitrates $\text{MeNO}_3\text{-Ln}(\text{NO}_3)_3\text{-H}_2\text{O}$ (Me—Li, Na, K; Ln—La—Sm) at 25–100 °C. The choice of the composition of the objects of study, the temperature cross sections are due to a number of factors. Among the rare earth elements, the higher complexing ability is found by the cerium subgroup; among them, the biggest changes in the composition, structure, properties of their compounds are the elements of its middle, Pr and Nd. The selected system components specify the specifications of the target product or are modifiers of its properties. In addition, the presence of large quantities for the use of potential electronic analogues (representatives of natural series of rare earths, alkaline elements) determines the considerable variability and breadth of the range of modification of their characteristics. The temperature cross sections are due to the regions of the crystalhydrate forms of the original components.

To determine the nature of the chemical interaction and phase equilibria in water-salt systems of the investigated nitrates (precursors of multicomponent oxide polyfunctional materials) in full concentration ratios in the temperature range of solutions, the additive method described in [14, 15] and based on the study was used as one of the properties of the most “sensitive” to detect phase transformations in systems, which is both a parameter of their state, and, moreover, the simplest experiment available notional methods. The method allows finding the boundaries of self-development, to which, under specific conditions, in an equilibrium state, an isolated system of a given composition goes.

Phase equilibrium was reached within 2–3 days. As starting, salts hydrated and anhydrous nitrates of these brand elements “p.f.a.” were used.

Chemical analysis of the liquid and solid phases, “residues,” was performed for the content of Ln^{3+} and nitrogen. The content of Ln^{3+} was determined trigonometrically; nitrogen—by distillation; Me^+ ions—calculated by difference based on total nitrate content and partly on dry residue.

The data obtained for the individual ions were converted to salt content and plotted according to the principle of correspondence. The graphical representation of the composition of the solid phases formed in the system was carried out by Skreemakers [14, 15], confirmation of their individuality and characterization, chemical, X-ray phase, X-ray structural, IR-spectroscopic, crystal-optic, thermographic, and other methods.

Crystal-optical determination of the compounds was performed by immersion using a microscope MIN-8. Phase analysis was performed on a DRON-3M diffractometer (Cu K_α radiation and Ni filter) using the powder method. The diffraction patterns were decoded according to the JCPDS PDF file. Determination of symmetry, parameters of elementary cells, and measurement of the intensity of diffraction reflections from single crystals were performed on an automatic X-ray single crystal diffractometer CAD-4F «Enraf-Nonius» (Mo K_α radiation, graphite monochromator; $\omega/2\theta$ —method). All calculations for the determination and refinement of atomic structures were performed using SHELX, XTL-SM, AREN crystallographic software packages. The IR absorption spectra of the synthesized compounds in the 400–4000 cm^{-1} region were recorded on a UR-20 spectrophotometer using a standard Vaseline oil suspension technique. Thermogravimetric analysis was performed on a Q-1500 D derivatograph at temperatures from 293 to 1273 K in the air with a heating rate of 10°/min and the developed device for DTA.

2.2 Results of the Studies and Their Discussion

Generalized and important for practical use of information on alkaline coordination nitrates of rare earth elements of the cerium subgroup—precursors of perspective modern multifunctional materials—regarding the conditions of their formation and existence, the nature of chemical bond, composition, structure, type of coordination of ligands, the existence of isotopic rows in the steppe structures, manifested properties systematized by the authors and in the most obvious form are given in Tables 1, 2 and 3. The choice of this form of data presentation is the most informative and useful in the development of innovative projects allows to predict the cause and effect fundamental patterns of behavior of structural components in similar production processes, to properly choose the modes, stages, methods of formation and obtaining of target products with reproducible structure-sensitive characteristics.

Identified patterns in the behavior of structural components in nitrate systems of rubidium, cesium and La–Sm; in similar objects based on REE of the yttrium subgroup (Y, Gd–Lu) indicate the possibility of only limited or special use of the

Table 1 Composition of the newly formed associated forms and the conditions of their crystallization in the systems of nitrate precursors REE cerium subgroup and alkali metals—lithium, sodium, potassium (wt%)

	System	La	Ce	Pr	Nd	Sm
<i>LiNO₃–Ln(NO₃)₃–H₂O at 100 °C</i>						
E ₁	LiNO ₃	27,11	26,84	24,09	24,03	17,56
	Ln(NO ₃) ₃	53,35	54,35	54,66	54,68	67,31
Connection	Correlation components	3:2:4	3:2:4	3:2:4	3:2:4	
	Nature solubility	Congruent				
E ₂	LiNO ₃	9,92	9,76	8,73	9,68	
	Ln(NO ₃) ₃	71,03	71,45	72,20	72,51	
<i>NaNO₃–Ln(NO₃)₃–H₂O at 50 °C</i>						
E ₁	NaNO ₃	17,43	17,37	17,08	16,55	8,39
	Ln(NO ₃) ₃	50,97	51,24	51,57	51,62	60,87
Connection	Correlation components	2:1:2	2:1:2	2:1:2	2:1:2	
	Nature solubility	Incongruent				
E ₂	NaNO ₃	7,43	7,51	7,87	8,60	
	Ln(NO ₃) ₃	62,66	62,55	62,62	62,58	
<i>KNO₃–Ln(NO₃)₃–H₂O at 50 °C</i>						
E ₁	KNO ₃	28,03	27,19	25,94	27,26	23,44
	Ln(NO ₃) ₃	42,80	43,88	48,37	51,62	54,29
Connection. I	KNO ₃	35,23	35,35	35,31	35,38	29,96
	Ln(NO ₃) ₃	57,63	57,83	57,68	57,77	67,43
	Correlation components	2:1:2	2:1:2	2:1:2	2:1:2	3:2:1
	Nature solubility	Incongruent				
E ₂	KNO ₃	11,23	11,55	21,11	21,34	18,19
	Ln(NO ₃) ₃	62,66	62,72	53,86	54,91	56,08
Connection. II	KNO ₃			30,28	30,95	21,38
	Ln(NO ₃) ₃			67,47	67,41	70,68
	Correlation components			3:2:1	3:2:1	3:2:1
	Nature solubility			Incongr.	Congr.	
E ₃	KNO ₃			11,58	11,49	9,67
	Ln(NO ₃) ₃			63,17	63,31	64,22

above predecessors in the studied field. There are a number of objective and economic reasons for this. These are the features of the electronic structure of their atoms, a lower manifestation of the chemical activity and complexation ability of these Ln³⁺ compared to elements of the cerium subgroup, a weaker effect of the considered influencing factors on the processes under study. In order to find out the general laws and to construct a holistic objective picture of the behavior of such technological

Table 2 Radiographic data of neodymium lithium, sodium, potassium coordination nitrates

Li ₃ [Nd ₂ (NO ₃) ₉]·3H ₂ O			Na ₂ [Nd(NO ₃) ₅]·H ₂ O			K ₂ [Nd(NO ₃) ₅ (H ₂ O) ₂]			K ₃ [Nd ₂ (NO ₃) ₉]·H ₂ O		
d, Å	I/I ₀ , %	d, Å	I/I ₀ , %	d, Å	I/I ₀ , %	d, Å	I/I ₀ , %	d, Å	I/I ₀ , %	d, Å	I/I ₀ , %
8,36	30	2,013	19	7,84	63	5,42	66	2,056	24	9,48	85
7,64	77	1,979	19	7,54	47	5,27	90	1,993	27	7,74	92
6,68	13	1,944	28	7,07	73	4,94	45	1,947	26	7,65	32
6,00	38	1,931	26	5,18	27	4,11	72	1,777	11	5,36	39
5,75	79	1,855	15	4,23	100	3,88	15			5,27	40
5,42	98	1,778	15	3,80	57	3,80	42			4,94	30
5,26	74	1,726	28	3,15	23	3,66	12			4,76	46
4,76	51	1,708	34	3,09	67	3,53	42			4,49	87
4,64	100			3,02	86	3,35	38			4,26	27
4,35	43			2,629	20	3,18	13			4,06	100
4,19	47			2,391	17	3,05	73			3,89	40
3,94	51			2,346	17	2,873	17			3,78	22
3,90	40			2,307	8	2,843	33			3,73	39
3,56	26			2,234	13	2,783	14			3,36	19
3,32	19			2,178	27	2,750	17			3,27	26
3,22	47			1,979	13	2,724	40			3,18	55
2,978	34					2,664	14			3,07	16
2,772	19					2,639	19			3,04	17
2,617	28					2,594	100			2,844	20
2,545	43					2,463	37			2,755	12

(continued)

Table 2 (continued)

Li ₃ [Nd ₂ (NO ₃) ₉]·3H ₂ O			Na ₂ [Nd(NO ₃) ₅]·H ₂ O			K ₂ [Nd(NO ₃) ₅ (H ₂ O) ₂]			K ₃ [Nd ₂ (NO ₃) ₉]·H ₂ O		
<i>d</i> , Å	<i>I</i> / <i>I</i> ₀ , %	<i>d</i> , Å	<i>I</i> / <i>I</i> ₀ , %	<i>d</i> , Å	<i>I</i> / <i>I</i> ₀ , %	<i>d</i> , Å	<i>I</i> / <i>I</i> ₀ , %	<i>d</i> , Å	<i>I</i> / <i>I</i> ₀ , %	<i>d</i> , Å	<i>I</i> / <i>I</i> ₀ , %
2,385	21			2,392	19			2,730	18		
2,328	17			2,374	44			2,647	55		
2,305	23			2,314	15			2,592	16		
2,226	19			2,235	25			2,508	87		
2,135	49			2,188	10			2,468	78		
2,111	43			2,099	21			2,349	32		

Note *d*, Å—interplanar distances; *I*/*I*₀, %—the relative intensities of the reflexes

Table 3 Temperature values of the detected effects during the heat treatment of the representatives of the established groups of alkali coordination nitrates REE

Compounds; spatial group of crystals	Representatives	Temperature interval of formation, °C	The nature of solubility	Dehydration	Melting in crystallization water	Polymorphic transitions	Melting anhydrous form	The composition of the products of conversion at 980°C
$\text{Li}_3[\text{Ln}_2(\text{NO}_3)_9] \cdot 3\text{H}_2\text{O}$ cubic.; $P2_13$	La-Sm	65-100	Congr.	65 183 216	183	-	274	LiLnO_2
$\text{Na}_2[\text{Ln}(\text{NO}_3)_5] \cdot \text{H}_2\text{O}$ monocl.; $P2_1/a$	La-Sm	50-100	Congr.	81 148 236	-	271	328	NaLnO_2
$\text{K}_2[\text{Ln}(\text{NO}_3)_5(\text{H}_2\text{O})_2]$ rhomb.; $Fdd2$	La-Nd	50-100	Incongr.	95, 111	95	219	314	KLnO_2 , Ln_2O_3
$\text{K}_3[\text{Ln}_2(\text{NO}_3)_9] \cdot \text{H}_2\text{O}$ cubic.; $P4_332$	La-Sm	50	Congr.	126	-	-	347	Ln_2O_3
$\text{K}[\text{Ln}(\text{NO}_3)_4(\text{H}_2\text{O})_2]$ prim. rhomb.; $P2_1cn$	Y, Gd-Lu	50-100	Congr.	138, 172	138	-	-	Ln_2O_3

precursors, the authors investigated systems by natural series Y, La–Lu, Li–Cs. The analysis of the results of the study is published in the previous works of the authors [16–23].

In ternary REE-containing systems of nitrate precursors, which are integral components of more complex multicomponent systems, exchange transformations begin from the moment of dissolution of the constituents in water. It was found that the Ln^{3+} cerium subgroup under active conditions is active complexing agents, forming anionic coordination compounds of Me^+ of all alkali metals, and their stability and complex of inherent properties are found to be powerful technological factors that significantly affect the nature of the transformations, and the results of the processes as a whole.

The obtained data allow us to model the behavior of structural components at the preparatory stages of formation of self-cleaning photocatalytically active coatings of building structural materials according to innovative technological regulations using nitrate precursors.

Existing identified trends of phase formation in model investigated systems are thermodynamically the most probable limits of transformations in technological objects under conditions of formation and receipt of target products. In addition, the possible real deviations in such systems are due to the heterogeneity of the reaction medium in composition, the content of the reacting components, the conditions of their finding, the finiteness of the rate of transformations, diffusion peculiarities, heat capacity, viscosity, the nature of transformations at the boundaries of the formed heterophase modes, activation, and other specific factors. The revealed processes of complexation in aqueous solutions of nitrates contribute to the homogenization of systems of structural components at the molecular level in complex or combined processing.

The analysis of the obtained data indicates that systems in the immediate environment of the Ln^{3+} -complexing agent of competing processes of substitution of water molecules with nitrate ions occur in the systems. The degree of completeness of substitution depends on the nature of Ln^{3+} present in Me^+ , the properties of electron-donor oxygen atoms and the spatial structure of the ligands, the concentration of anions, and the amount of solvent. Significant influence on these processes of temperature factor is revealed. Differences in the complexing ability of the elements of cerium and yttrium subgroups, Y, and among REEs in the middle of the first subgroup are observed. The obtained results indicate the stage of complex formation processes. The presence of certain values of the temperature of the beginning of the release into the solid phase of complex compounds—the existence of an energy barrier and the need for some activation energy to effect such transformations.

The formation of nitrate complexes largely fulfills the requirements of symmetry, and planar small-sized ligand NO_3^- is “convenient” for the formation of a highly symmetric environment of the Ln^{3+} ion. Lanthanides are characterized by a tendency to form a limited number of coordination polyhedron species (see Fig. 3) and three types of coordination NO_3^- -ligands. This leads to the formation of both isolated complexes and their polymerization into dual nuclei, chains, and frames. The coordination numbers of the Ln^{3+} cerium subgroup—12 detected in low-temperature associated forms

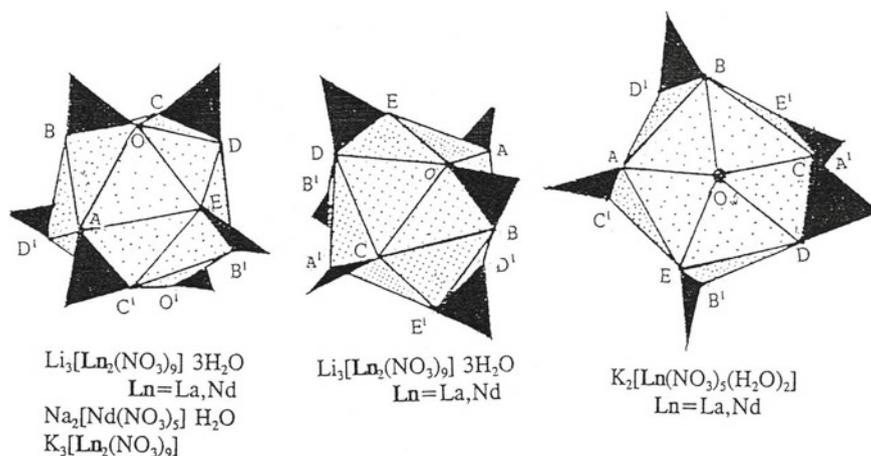


Fig. 3 Schematic representation and general view of Ln-icosahedrons found in the structures of the REEs of the cerium subgroup and lithium, sodium, and potassium

and remain unchanged until the formation of stable high-temperature multicomponent oxide phases of MeLnO_2 , $\text{Me}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$, the influence of the nature of Me^+ , on the shape of the coordination polyhedral Ln, the method of packing complexes in the spatial structure, and a number of properties of compounds.

We present below:

- in Table 2, Fig. 4—installed X-ray diffraction characteristic parameters of the newly formed phases for the possibility of their identification and detection during processing;

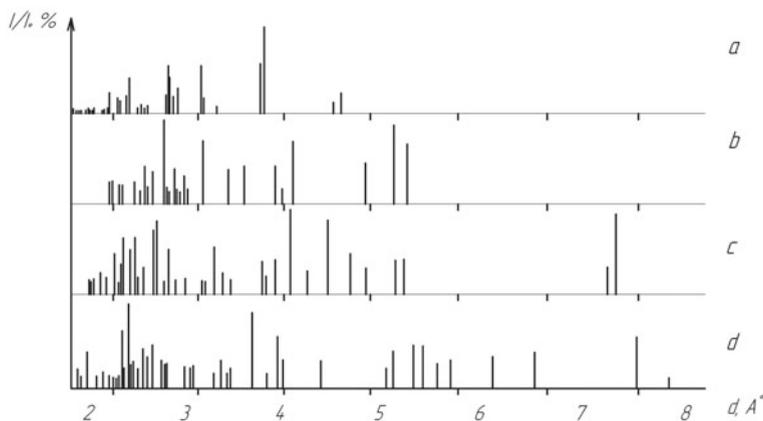


Fig. 4 Bar graphs of the starting salts of nitrates **a** potassium, **d** neodymium and identified coordination compounds **b** $\text{K}_2[\text{Nd}(\text{NO}_3)_5(\text{H}_2\text{O})_2]$, **c** $\text{K}_3[\text{Nd}_2(\text{NO}_3)_9] \cdot \text{H}_2\text{O}$

- in Table 3—we explain the nature and patterns of thermal transformations of compounds in the temperature range 25–1000 °C to find out their thermal stability and model the behavior of process objects under similar conditions. For comparison and analysis, information about the low stability and thermal stability of potassium coordination nitrates Y, Gd–Lu of the composition $K[\text{Ln}(\text{NO}_3)_4(\text{H}_2\text{O})_2]$ is provided, which causes restrictions in the use of this type of precursors in technological transformations in order to modify the properties target products.

2.3 *Scientific Novelty*

A complex systematic study of the interaction of structural components in rare earth nitrates and IA group of elements of the periodic system—precursors of modern multicomponent oxide functional materials based on them—revealed the formation of a wide class of alkali coordinate nitrates of lanthanides.

Identified objective laws have a fundamental and applied value, deepen understanding of:

- chemical and physical properties of Ln and their complexing ability,
- possibility of formation and existence in the associated systems of associated new phases, their atomic-crystalline structure, stability, and stability,
- the influence of the nature of lanthanides and alkali metals on the structure of complex anions and compounds in general,
- the individuality of the Ln complexes,
- the existence of isotopic groups in the composition and structure of groups of compounds by the natural series of lanthanides and alkali metals,
- the role of NO_3^- -groups in the stereochemistry of this class of nitrates,
- the role of water in the formation of the closest environment of Ln^{3+} ions-complexing agents.

2.4 *Practical Importance*

The obtained system of knowledge about transformation processes in systems of REE-containing nitrate precursors and crystal-chemical properties of samples of coordinate nitrates Ln is of particular value in the formation of nanostructure-layered perovskite-like compounds of lanthanides and transitional elements (including titanium); solid solutions based on them; in establishing the technological and functional dependencies between the method of preparation; the variability of the method of activation of technological systems; the methodology of production of the target product and its phase composition, lattice parameters, the specific surface area, the

morphology of the constituent particles, the activity of layers of self-purifying compositions with hydrophilic structures and special structural elements; in the practical implementation of innovative projects of decomposition of water for the purposes of hydrogen production (as an alternative fuel), decomposition of toxic organic substances in solutions and air, incomplete oxidation of carbohydrates; upon receipt of other perovskite-like phases by ion-exchange reactions and in other fields.

3 Conclusions

1. The results of the study show that the processes of obtaining oxide REE-containing structural and functional materials of various purposes using nitrates of elements of the different electronic structure are performed by chemical mixing of the initial components in the joint separation of products from the liquid phase by sequential or compatible deposition with subsequent heat treatment. Data on their composition, content, and behavior in each case require prior systematic empirical knowledge in full concentration ratios at a given temperature interval.
2. The differences in the behavior of structural components in the systems of lanthanides of cerium and yttrium subgroups, in their nature of interaction, stage, features, and regularities of flow are revealed.
3. The new knowledge obtained forms the basis for:
 - finding ways to increase the activity of Ln forms;
 - to find out the nature of sequential thermal transformations in nitrate REE-containing multicomponent systems of different aggregate states during their heat treatment; conditions of formation and existence, properties of intermediate phases; influencing factors; possible ways to control how your target product is obtained;
 - in case of the creation of modern advanced low-cost technologies of formation of functional materials of various purposes with reproducible properties.

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