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Research paper



Peculiarities of Chemical Interaction and Phase Setting in Water-Salt Systems of Nitrates of Cesium, Strontium and Neodymium

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Abstract

The complex study provides a reliable idea of the trends in the joint behavior of structural components in water and salt systems of nitrate precursors of neodymium, cesium, strontium in the preparatory stages of technological regulations for the concentration and immobilization of liquid radioactive waste of the nuclear power industry complex using schemes of porous and layered matrix fixators of ^{137}Cs, ^{90}Sr radionuclides and 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 - the coordination neodymium nitrates: 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 were studied. It is established that in the conditions of existence of solutions, the system $CsNO_3 – Nd(NO_3)_3 – H_2O$ is characterized by the formation of 2 anionic complex compounds Ln^{3+}, $Sr(NO_3)_2 – Nd(NO_3)_3 – H_2O$ - eutonic type. Leaking competing reactions are a powerful technological factor that significantly affects the activity of the structural forms of Ln^{3+}. The systematized information allows us to find out the mechanisms, the kinetics of transformations of structural components in similar objects, and enable us to transfer the acquired knowledge system to the plane of promising technological solutions for the solidification of liquid radioactive waste.

Keywords: *cesium; complex formation; neodymium; nitrates; properties; strontium; water-salt systems.*

1. Introduction

Expansion of knowledge about the mutual behavior of structural components in water-salt systems of REE nitrates and IA, IIA elements of the periodic system in full concentration ratios and a wide range of temperatures, phases formed in them, conditions of their existence and properties; thermal transformations; available information on the state and possible ways to improve the technology of forming complex oxide materials of transition elements, methods of activating processes, existing requirements for their reproducibility and stability initiated this study and open new areas of their practical use in creating frame materials for immobilizing liquid radioactive waste from the nuclear power industry (porous and layered types), as well as in the processes of modeling and experiment to substantiate the possibility of using certain engineering forms of sorbents and mineral-like man-made phases-fixers of radionuclides ^{137}Cs, ^{90}Sr.

1.1. Problem statement and solution methods

In view of the diversity of sources of origin of radioactive waste, there is a wide variety of compositions and physicochemical properties. The greatest danger to the biosphere is liquid highly active waste containing radionuclides ^{137}Cs and ^{90}Sr high heat generation, and often in combination with long-lived ($T_{1/2} \geq 10^5$ years) α-emitting actinides. The highly active waste of complex composition includes a number of categories of liquid radioactive waste of wide radioisotope and chemical composition, such as accidental waste of nuclear power plants, lanthanoid-actinoid fraction of high-level waste from reprocessing in nuclear fuel cycles, unfractionated high-level waste from temporary storage tanks, which contain rare-earth and transuranic metals , radionuclides of cesium and strontium, transition metals, and often against the background of high concentrations of salts and high acidity.

The multicomponent composition of high-level liquid waste and the combined presence of transuranium elements and fission products with a high content of ^{137}Cs and ^{90}Sr in their composition complicates their further processing, therefore, with the development of extraction separation methods, high-level waste is further fractionated with different groups of radionuclides released according to their chemical properties and half-life [1-12].

In [13], the content of actinoids and lanthanides in the actinoid-lanthanoid fraction of high-level wastes that had been converted to waste after 5 years of spent nuclear fuel was estimated to show that the bulk of this fraction is lanthanides, and the content of uranium and transuranium elements is about 4 % by weight of lanthanides. Of the lanthanides, the absolute majority consists

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of the elements of the cerium subgroup (Ce-Sm), with the most high content of neodymium (36.5%). It should be noted that, despite the progress achieved in the fractionation of high-level waste by extraction processing, the concentrate of rare-earth and transplutonium elements may contain several units of percent of cesium and strontium radionuclides [14]. These available information and determined the object and directions of research in this work.

The international strategy for the safe management of all types of radioactive waste is to minimize them and is aimed at reducing the amount of waste by concentrating and retaining radionuclides inside stable solid materials. At the same time, the most dangerous components of high-level wastes are supposed to be included in mineral-like matrices with their subsequent safe multi-barrier burial in stable geological formations of the earth's crust.

One of the promising technological solutions for curing liquid radioactive waste is the use of inorganic sorbents, which, after saturation with radionuclides in the form of nitrate soluble structural components, are in fact precursors of the final form of radioactive waste. Further structural reorganization of the precursor with the inclusion of radionuclides in the target phase is carried out in the process of solid-phase crystallization when heated.

To date, the optimal strategy for immobilizing such wastes within the sorption-mineralogical approach can be the use of a sorbent whose composition is focused on extracting a wide range of elements and forming polyphase ceramics based on the compositions of phase concentrators of alkaline and alkaline-earth elements (^{137}Cs, ^{90}Sr), on the one hand , and the lanthanoid-actinoid fraction in combination with other metals, on the other hand.

When choosing a matrix material for immobilization of actinides, the radiation resistance of their crystal structure to the effects of β-radiation is among the defining properties.

The group of such radiation-resistant phases - potential matrix materials fall into the framework of REE zirconomolybdates of composition $Ln_2Zr_3(MoO_4)_9$, Ln – La ÷ Tb, (for example neodymium, see fig. 1) [15].

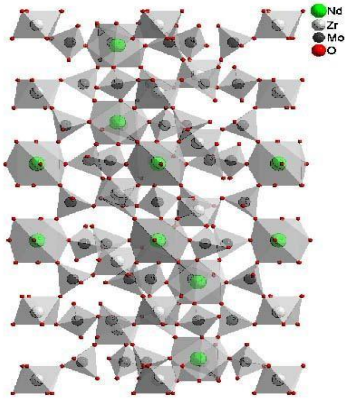


Fig. 1: Frame structure $Nd_2Zr_3(MoO_4)_9$ (triangular sinongion, spatial group R3c, Z=6)

For practical implementation of these projects for the development and improvement of the above-described composite sorption-active systems and technologies for the purification and immobilization of high-salt radioactive waste of complex composition based on them, data on the chemical interaction processes of structural components, phase formation in water-salt systems of neodymium, cesium nitrate are of interest and strontium in the range of 25 – 100°C, the properties of the phases they form.

1.2. The purpose and tasks of the study

For the systematic study of cooperative processes in the considered technological objects and the clarification of the possibility of controlling them requires using a set of physico-chemical methods:

a) to study the nature and mechanisms of chemical interaction, phase equilibria in model water-salt systems $CsNO_3$ – $Nd(NO_3)_3$ – H_2O, $Sr(NO_3)_2$ – $Nd(NO_3)_3$ – H_2O at 25 – 100°C;

b) to construct polythermal diagrams of solubility of systems; determine the concentration and temperature limits of the crystallization of the starting materials and the detected new phases;

c) to find out the optimal conditions of growth and to synthesize the coordination neodymium nitrates (as a representative of the natural number of rare earth elements, which is most likely to undergo changes in the composition and structure of the compounds formed), to study their properties and to confirm the individuality;

d) to establish the regularities of the dependence of the number, composition, properties of coordination nitrates, which are formed in the systems under study, on the nature of the ion Ln^{3+}-complex form, the conditions of formation.

2. Experimental part

2.1. Experiment Methodology

Systems research is carried out isotermically (at 25, 50, 65, 100 °C) by the method of additives using the method described in [16, 17]. 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 Nd^{3+}, Sr^{2+}, nitrogen. The content of Ln^{3+} was determined trilonometrically in the presence of xylenol orange as an indicator (acetate buffer solution, pH=5–6); Sr^{2+} – complexometric titration of the substituent in the filtrate liberated from Ln^{3+} by the ammonia buffer ($NH_3 \cdot H_2O$ + NH_4Cl); nitrogen – the method of distillation; Cs^+ 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 [17]. 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.

2.2. Results of the research and their discussion

Experimental data are obtained for the study of the features and patterns of mutual behavior of structural components, heterogeneous equilibria (25-100 ℃) in water-salt systems of neodymium and cesium nitrates, and strontium are summarized in Table 1 and 2, and generalized in the form of their spatial polythermal solubility diagrams (see Fig. 2, 3). On their basis, the presence of chemical interaction between the constituent elements in the objects of research; quantity, composition, nature of solubility, temperature and concentration limits of the formation of starting substances and new phases, composition of electron and transition points; The optimal conditions of formation were determined and synthesis of cesium double neodymium nitrates

Table 1: Data on the study of phase equilibria in the system $CsNO_3$ – $Nd(NO_3)_3$ – H_2O at 25-100°C

		Saturated solution		«Residue» composition, wt.%					Saturated solution		«Residue» composition, wt.%		
		Composition, wt. %							Composition, wt. %				
t, °C	Composition points	$CsNO_3$	$Nd(NO_3)_3$	$CsNO_3$	$Nd(NO_3)_3$	Solid pha-ses*	t, °C	Composition points	$CsNO_3$	$Nd(NO_3)_3$	$CsNO_3$	$Nd(NO_3)_3$	Solid pha-ses*
1	2	3	4	5	6	7	1	2	3	4	5	6	7
25	1 A_1	20,96	0,00	99,64	0,00	K	65	1 A_3	47,16	0,00	99,69	0,00	K
	2	18,59	5,91	99,58	0,00	Same		2	40,50	16,72	98,77	0,71	Same
	3	16,58	18,51	99,14	0,67	-‖-		3	39,32	29,61	97,58	1,69	-‖-
	4	17,95	30,07	97,84	1,43	-‖-		4	43,24	35,86	95,48	3,12	-‖-
	5	20,67	35,68	97,76	1,60	-‖-		5			94,61	4,08	-‖-
	6	23,92	41,17	96,90	2,34	-‖-		6	44,92	40,11	67,95	27,47	K+M
	7			95,45	3,10	-‖-		7 B_3			57,37	36,91	Same
	8 B_1	31,82	43,88	60,03	34,62	K+M		8			51,89	42,34	M
	9			51,08	42,15	M		9	42,61	41,13	50,96	43,23	Same
	10	27,02	48,08	50,00	43,09	Same		10	37,02	47,33	49,67	42,89	-‖-
	11			4992	43,16	-‖-		11			48,63	43,81	-‖-
	12 C	23,07	52,04	15,28	65,36	M+L		12 E_2	32,11	50,75	42,12	49,50	M+O
	13			2,67	72,66	L		13			34,64	56,10	O
	14	12,47	55,04	1,98	72,79	Same		14	24,51	54,79	33,76	56,77	Same
	15	6,00	57,67	1,60	72,88	-‖-		15	18,25	59,84	33,32	56,69	-‖-
	16D_1	0,00	58,49	0,00	75,25	-‖-		16			30,92	57,81	-‖-
50	1 A_2	39,17	0,00	99,72	0,00	K		17 F_2	11,99	66,26	15,77	66,42	O+L
	2	34,72	9,93	98,63	0,57	Same		18			4,44	72,70	L
	3	31,10	20,53	98,37	1,08	-‖-		19	6,25	68,91	1,86	73,23	Same
	4	32,71	27,63	97,82	1,52	-‖-		20D_3	0,00	71,58	0,00	75,26	-‖-
	5	36,99	36,68	96,54	2,47	-‖-	100	1 A_4	64,36	0,00	99,87	0,00	K
	6			94,47	3,86	-‖-		2	54,44	14,95	98,76	0,83	Same
	7 B_2	40,98	40,84	59,34	35,74	K+L		3	50,32	22,89	97,71	0,95	-‖-
	8			50,90	43,03	L		4	49,51	33,23	96,69	2,16	-‖-
	9	36,54	44,23	49,48	43,12	Same		5	49,05	36,69	94,72	3,86	-‖-
	10			49,64	43,26	-‖-		6			81,74	16,14	K+N
	11 E_1	30,94	50,38	39,06	52,20	M+O		7 B_4	47,56	41,28	57,48	37,98	Same
	12			33,64	56,35	O		8			52,89	41,93	-‖-
	13	25,84	53,72	32,87	56,43	Same		9	41,62	46,07	50,34	43,30	N
	14			32,86	56,97	-‖-		10 E_3	33,80	52,92	51,71	44,41	Same
	15 F_1	17,52	59,98	17,54	64,69	O+L							
	16			4,61	71,90	L							
	17	9,77	62,91	2,81	72,12	Same							
	18D_2	0,00	66,16	0,00	75,28	-‖-							

*K – $CsNO_3$, L – $Nd(NO_3)_3 \cdot 6H_2O$, M - $2CsNO_3 \cdot Nd(NO_3)_3 \cdot 3H_2O$, N – $2CsNO_3 \cdot Nd(NO_3)_3 \cdot 2H_2O$, O – $CsNO_3 \cdot Nd(NO_3)_3 \cdot 3H_2O$

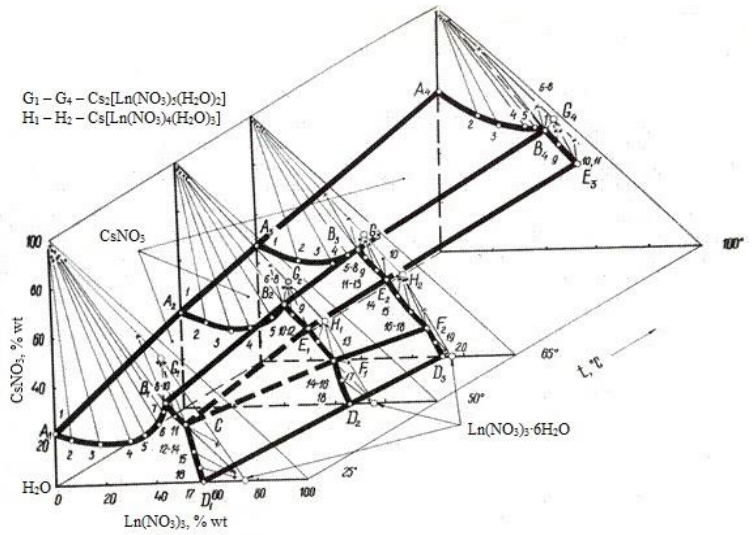


Fig. 2: Solubility polytherm of system $CsNO_3 – Ln(NO_3)_3 – H_2O$ (Ln – Nd)

Table 2: Data on the study of phase equilibria in the system $Sr(NO_3)_2 – Nd(NO_3)_3 – H_2O$ at 25 – 65 ºC

t,ºC	Composition points	Saturated solution				Composition „remainder", wt, %		Solid phase*
		Composition,wt, %		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_1	44,60	0,00	1,539	1,4068	99,87	0,00	K
	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_1	5,94	56,97	1,873	1,4548	52,50	34,84	K+L
	8					19,05	59,51	"-"
	9					2,89	70,62	"-"
	10 C_1	0,00	58,49	1,887	1,4551	0,00	75,25	L
50	1 A_2	48,03	0,00	1,487	1,4055	99,91	0,00	K
	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	"-"
	7					7,26	9,76	"-"
	8 C_2	0,00	66,16	1,974	1,4667	0,00	75,28	L
65	1 A_3	48,60	0,00	–	–	99,92	0,00	K
	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	K+L
	9					3,64	72,88	"-"
	10 C_3	0,00	71,58	–	–	0,00	72,26	L

* K – $Sr(NO_3)_2$; L – $Nd(NO_3)_3 \cdot 6H_2O$

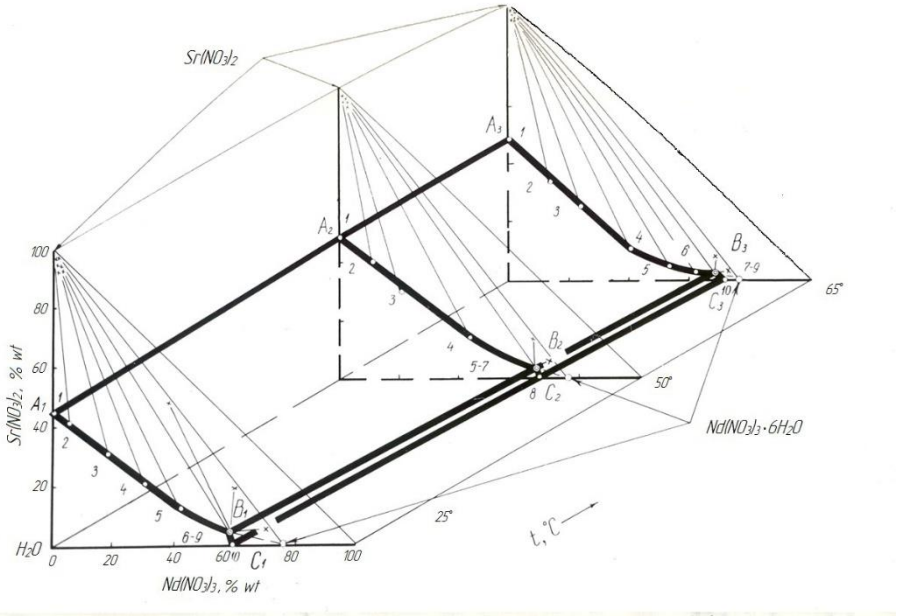


Fig. 3: Polytherm solubility of the system $Sr(NO_3)_2 – Nd(NO_3)_3 – H_2O$ at 25-65 ºC

was carried out, forms of growth of their crystals and a number of their inherent properties were investigated.

The choice of the proposed table and chart forms for presenting the results is the most visible and informative and useful in developing effective technological regulations for the solidification of liquid radioactive waste. It allows to predict the behavior of structural components, to choose the correct regimes, the stage, the methods of forming and obtaining target products with given reproducible characteristics in similar multi-component production processes using liquid nitrate precursors.

The studied cesium system in the presence of solutions is characterized by the formation of 2 new coordination nitrate compounds Nd^{3+} $Cs_2[Nd(NO_3)_5(H_2O)_2]$ and $Cs[Nd(NO_3)_4(H_2O)_3]$. 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. Strontsiev's system - an eutonian type, no new solid phases were found in it.

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 a monocrystalline form (Fig. 4). 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 according to the data of their complex study by the above methods (see Table 3, 4) and the conduct of low-temperature X-ray experiments in the process of studying their atomic-crystalline structure.



$Cs_2[Nd(NO_3)_5(H_2O)_2]$



$Cs[Nd(NO_3)_4(H_2O)_3]$

Fig. 4: Microphotos of coordination nitrates crystals Nd

Table 3: 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 for-mation, ºC	The nature of solubility	References
$Cs_2[Nd(NO_3)_5(H_2O)_2]$	monocl.	2/m	C2/c	* ⏐ ⏚	25–100	incongr.	[18]
$Cs[Nd(NO_3)_4(H_2O)_3]$	tricl.	$\bar{1}$	$P\bar{1}$	* ⏚	50–65	incongr.	[19]

The authors have studied the atomic structure of single crystals by X-ray diffraction analysis $Cs_2[Nd(NO_3)_5(H_2O)_2]$, $Cs[Nd(NO_3)_4(H_2O)_3]$ (see [18, 19]), types of coordination of ligands, forms of coordination polyhedra Ln, possible variants of the coordination environment of Nd atoms, spatial arrangement of polyhedrons (Fig. 5) in constructing compounds with aqua-containing complex anions, general crystallochemical patterns of 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).

Table 4: X-ray data of cesium coordination neodymium nitrates

$Cs_2[Nd(NO_3)_5(H_2O)_2]$				$Cs[Nd(NO_3)_4(H_2O)_3]$	
d, Å	I/I_0, %	d, Å	I/I_0, %	d, Å	I/I_0, %
6,799	11,5	2,2191	11	6,667	80,8
5,9375	15,5	2,1923	28,5	5,4070	19,6
5,0980	55	2,1841	26	5,2727	36,5
4,8385	51,5	2,1681	16,5	4,4489	61,9
4,3708	49,5	2,0597	16	4,2467	29,2
4,2148	10	2,03162	23	4,1409	11,9
3,6775	100	1,84121	32,5	3,9241	8,8
3,4241	18,5	–	–	3,7231	14,2
3,3334	60	–	–	3,5700	13,1
3,2995	54,5	–	–	3,4035	8,8
3,0639	27	–	–	3,3384	49,6
2,9760	8,5	–	–	3,2781	52,3
2,9024	36,5	–	–	3,2314	13,5
2,8013	11,5	–	–	2,7152	8,8
2,7427	23	–	–	2,6727	100
2,7041	10,5	–	–	2,5829	11,5
2,6573	41	–	–	2,3528	16,5
2,6048	26	–	–	2,2739	5,8
2,5758	17	–	–	2,2307	9,6
2,5293	18,5	–	–	2,1882	14,2
2,4149	16	–	–	1,91250	28,8
2,4012	16	–	–	1,62366	20,8
2,3671	22,5	–	–	1,61946	10
2,3375	27,5	–	–	–	–
2,2728	56,5	–	–	–	–

Note: d, Å - interplanar distances; I/I_0,% - are relative intensities of reflexes.

The peculiarities of processes of complex formation and crystalline-chemical structure of cesium coordination nitrates of neodymium indicate that:

- the basis of the structure of complex compounds are rare-earth coordination polyhedrons, which are somehow connected in space;
- the processes of exchange interaction between the structural components (their binding) in the studied water-salt systems occur already under normal conditions (at 25 °C, see Table 1, Fig. 2);
- the central atoms of the Nd-complexing agent in the studied conditions reveal a mono- and bidentate relationship with nitro groups, have coordinate number 10 and possibility for different composition of complex formations ($[Nd(NO_3)_5(H_2O)_2]^{2-}$ and $[Nd(NO_3)_4(H_2O)_3]^-$) o find an equally organized coordination sphere that clearly illustrates the dominant role of the Nd^{3+} ion in the formation of alkaline rare earth nitrates.
- complex formations have the opportunity to preserve the layered motif of spatial construction (see Fig. 5, [19]) from the series of atoms Nd and Cs along the alternating z axis. These rows are the faces of layers of matching polydrugging coordinates. The layers of the layers are approximately perpendicular to the plane of the pattern. It is possible to isolate packets consisting of four layers Nd – Cs – Cs – Nd, within which the coordination polyhedra contact with each other due to common ribs and hydrogen bonds. Each fourth layer with the following has no common vertices and edges, and the interaction of packets in the structure is carried out with the help of only hydrogen bonds.

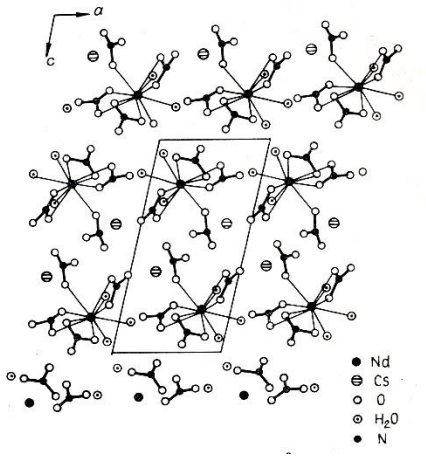


Fig. 5: Design of the structure $Cs[Nd(NO_3)_4(H_2O)_3]$ on the plane xy

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-charge cations Cs^+, Sr^{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.

All of this distinguishes the investigated objects into a perspective group of nitrate precursors in the development of the formulation of liquid process systems on their basis and the implementation of schemes of recycling with polluting adsorption on radiation-resistant substrates with the possibility of thermal activation and solid phase reactions. They possess a complex of technologically valuable properties inherent to them: a) high solubility and compatibility with most components; b) a sufficiently wide temperature range of the existence of complex nitrates; c) the detection of high activity by their reacting particles obtained by the thermolysis of the solvent, and, moreover, the nanosized and homogeneous in size and morphology [20]; d) the existence of a wide range of methods, methods, and technical means for the activation of such processes [21]. It should be noted that the combined methods of conversion with special requirements and fast-moving syntheses with combined methods of activation of systems and mass production acquire more and more now [22, 23]. Using thermoanalytic, chemical, X-ray diffraction methods, an analysis of the nature and stage of the processes of dehydration, nature and temperature intervals of transformations in $Cs_2[Nd(NO_3)_5(H_2O)_2]$, $Cs[Nd(NO_3)_4(H_2O)_3]$ (20 – 1000 °C).

On the derivogram $Cs_2[Nd(NO_3)_5(H_2O)_2]$ endoeffects 95, 122, 156 °C correspond to the stepwise process of dehydration. Зменшення The mass at 95 °C corresponds to the loss of one molecule of water. At 156 °C, an incongruous melting of the sample occurs in crystallization water, followed by the formation of anhydrous double salt, the melting point of which is 236 °C.

For $Cs[Nd(NO_3)_4(H_2O)_3]$ the process of dehydration is also three stepped (endoeffects 62, 90, 162 °C). The loss of one molecule of water in the TD curve corresponds to a temperature of 139 °C. An increase in temperature to 162 °C causes incubator melting of double nitrate dihydrate; Subsequent heat treatment - formation of $CsNO_3 \cdot Nd(NO_3)_3$ with $t_{melt.}$=355 °C. Products of thermal decomposition of both coordination salts at t> 920 °C contain neodymium oxide.

3. Conclusions

The complex study provides a reliable idea of the trends in the joint behavior of structural components in water and salt systems of nitrate precursors of neodymium, cesium, strontium in the preparatory stages of technological regulations for the concentration and immobilization of liquid radioactive waste of the nuclear power industry complex using schemes of porous and layered matrix fixators of ^{137}Cs, ^{90}Sr radionuclides and 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 - the coordination neodymium nitrates: 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 were studied. It is established that in the conditions of existence of solutions, the system $CsNO_3$ – $Nd(NO_3)_3$ – H_2O is characterized by the formation of 2 anionic complex compounds Ln^{3+}, $Sr(NO_3)_2$ – $Nd(NO_3)_3$ – H_2O - eutonic type. Leaking competing reactions are a powerful technological factor that significantly affects the activity of the structural forms of Ln^{3+}. The systematized information allows us to find out the mechanisms, the kinetics of transformations of structural components in similar objects, and enable us to transfer the acquired knowledge system to the plane of promising technological solutions for the solidification of liquid radioactive waste.

References

[1] Babain, V. A. Ispol'zovanie UNEX-processa dlya pererabotki othodov s visokim soderzhaniem redkozemel'nyh ehlementov [Use of the UNEX-process for recycling waste with a high content of rare-earth elements] / V. A. Babain, I. V. Smirnov, M. Yu. Alyapyshev [et al.] // *Radiation safety issues* , (2006), No. 3, pp. 3–12.

[2] Logunov, M. V. Razrabotka i opytno-tekhnologicheskie ispytaniya kompleksnoj ehkstrakcionno-osaditel'noj tekhnologii frakcionirovaniya zhidkih vysokoaktivnyh othodov na FGUP «PO «Mayak» [Development and experimental-technological tests of complex extraction-precipitation technology of fractionation of liquid high-level waste at the FSUE "PA Mayak"] / M. V. Logunov, E. G. Dzekun, A. S. Skobtsov [et al.] // *Radiation safety issues*. (2008), No. 4, pp. 3–15.

[3] Salvatores, M. Radioactive waste partitioning and transmutation within advanced fuel cycles: Achievements and challenges / M. Salvatores, G. Palmiotti // *Prog. Part. Nucl. Phys.* , (2011), Vol. 66, No.1, pp. 144–166.

[4] Zilberman, B.Ya. Dibutyl phosphoric acid and its acidic zirconium salt as an extractant for the separation of transplutonium elements and rare earths and for their partitioning / B. Ya. Zilberman, Yu. S. Fedorov, O. V. Schmidt [et al.] // *J. Radioanal. Nucl. Ch.*, (2009), Vol. 279, No. 1, pp. 193–208.

[5] Nishihara, K. Impact of partitioning and transmutation on LWR high-level waste disposal / K. Nishihara, S. Nakayama, Y. Morita [et al.] // *J. Nucl. Sci. Technol.* (2008), Vol. 45, No. 1, pp. 84–97.

[6] Forsberg, C. W. Rethinking high-level waste disposal: Separate disposal of high-heat radionuclides / C. W. Forsberg // *Nucl. Technol.* (2000), Vol. 131, No. 2, pp. 252–268.

[7] Del Cul, G. D. Citrate-based ―talspeak‖ actinide-lanthanide process / G. D. Del Cul, L.M. Toth, W. D. Bond [et al.] // *Separ. Sci. Technol.* (1997), Vol. 32, No. 1–4, pp. 431– 446.

[8] Mathur, J. M. Actinides partitioning – a review / J. M. Mathur, M. S. Murali, K. L. Nash // *Solvent Extr. Ion Exc.* (2001), Vol. 19, No. 3, pp. 357–390.

[9] Paiva, A. P. Recent advances on the chemistry of solvent extraction applied to the reprocessing of spent nuclear fuels and radioactive wastes / A. P. Paiva, P. Malik // *J. Radioanal. Nucl. Ch.* (2004), Vol. 261, No. 2, pp. 485–496.

[10] Romanovsky, V.N. EHkstrakcionnoe vydelenie dolgozhivushchih radionuklidov iz VAO. CH. I [Extraction isolation of long-lived radionuclides from HLW. Part I] / V.N. Romanovsky, A. Yu. Shadrin, B. Ya. Zilberman [et al.] // *Radiation safety issues*, (2004), Vol. 33, No. 1, pp. 3–19.

[11] Romanovsky V.N. Extraction isolation of long-lived radionuclides from HLW. Part II [Extraction isolation of long-lived radionuclides from HLW. Part II] / V.N. Romanovsky, A.Yu. Shadrin, B.Ya. Zilberman [and others] // *Radiation safety issues*, (2004), Vol. 34, No. 2, pp. 5–14.

[12] Pat. 2165110 Russian Federation, IPC G 21 F 9/04, G 21 F 9/16, C04B38 / 00. Keramicheskaya gubka dlya koncentrirovaniya i otverzhdeniya zhidkih osoboopasnyh othodov i sposob ee polucheniya [Ceramic sponge for the concentration and solidification of liquid highly hazardous waste and the method of its production] / Anshits A.G., Vereshchagina T.A., Pavlov V.F. [et al.]; applicant and patentee Anshits A.G. - № 99109609/06; declare 04/28/1999; publ. 10.04.2001, *Byul.*, No. 10, 8 p.

[13] Merkushkin, AO. Poluchenie himicheski ustojchivyh matric dlya immobilizacii aktinoidnoj frakcii VAO [Preparation of chemically stable matrices for immobilization of the HLA actinoid fraction]: dis. ... Cand. chemical Sciences: 05.17.02 / Merkushkin Aleksey Olegovich. - M., (2003), 198 p.

[14] Pat. 2355057 Russian Federation, IPC G 21 F 9/04 (2006.1). Sposob ehkstrakcionnoj pererabotki vysokoaktivnyh othodov (VAO) s frakcionirovaniem radionuklidov [Method of extraction processing of high level waste (HLW) with fractionation of radionuclides] / Gavrilov PM, Revenko Yu. M., Bondin V.V. [et al.]; applicant and patent holder Federal State Unitary Enterprise "Mining and Chemical Combine". - № 2007134202/06; declare September 13, 2007; publ. 05/10/2009, *Byul.*, No. 13.

[15] Trachenko, K. Topical Review. Understanding resistance to amorphization by radiation damage / K. Trachenko // *J. Phys.- Condens. Mat*., (2004), Vol. 16, pp. 1491–1515.

[16] Anosov V.Ya. Osnovy fiziko-khimicheskogo analiza [Basics of Physical and Chemical Analysis] / V.Ya. Anosov, M.I. Ozerova, Yu.Ya .Fialkov. – *M.: Nauka*, Publisher, (1976), 503 p.

[17] Goroshchenko *Ya. G.* Fiziko-khimicheskiy analiz gomogennykh I geterogennykh system [Physical and Chemical Analysis of homogenous and heterogenous systems] / Ya. G. Goroshchenko. – *K.:Naukova dumka*, Publisher,(1978), 490 p.

[18] Vigdorchik A.G., Malinovskij Ju.A., Drjuchko A.G. Poluchenie i kristallicheskaja struktura $Cs_2[Nd(NO_3)_5(H_2O)_2]$ [Preparation and crystalline structure of $Cs_2[Nd(NO_3)_5(H_2O)_2]$]. *Crystallography*. (1989), Vol. 34, No. 2, pp. 292-296.

[19] Vigdorchik A.G., Malinovskij Ju.A., Drjuchko A.G. Poluchenie i kristallicheskaja struktura $Cs[Nd(NO_3)_4(H_2O)_3]$ [Preparation and crystalline structure of $Cs[Nd(NO_3)_4(H_2O)_3]$]. *Journal of structural chemistry*. (1989), Vol. 30, No. 5, pp. 175-179.

[20] Kudrenko E.O., Shmyt'ko Y.M., Strukova H.K. Struktura prekursorov slozhnykh oksydov RZƏ, poluchennykh metodom termolyza rastvorytelya [Structure of the precursors of the complex oxides rare-earth elements, obtained by the method of the thermolysis of the solvent]. *Fyzyka tverdoho tela*. (2008), Vol. 50, No. 5, pp. 924–930**.**

[21] Pat. 2440292 S 2 RU, C 01 B 3/18 Sposob poluchenija perovskitov [Method for obtaining perovskites]. Yakovleva I.S., Isupova L.A. (RU); application 2009149781/05; claimed. 31.12.2009; publ. 20.01.2012. *Bul*., No. 2, 19 p.

[22] Varma A., Mukasyan A.S., Rogachev A.S. et al. Solution Combustion Synthesis of Nanoscale Materials. *American Chemical Society. Chem. Rev.* (2016), Vol. 116, pp. 14493-14586.

[23] Schaak R.E., Mallouk T.E. Perovskites by Design: A Toolbox of Solid-State Reactions. *Chemistry of Materials*. (2002), Vol. 14, No. 4, pp. 1455-1471.

[24] Loburets, A. T., Naumovets, A. G., Senenko, N. B., & Vedula, Y. S. (1997). Surface diffusion and phase transitions in strontium overlayers on W(112). *Zeitschrift Fur Physikalische Chemie*, *202*(1-2), 75-85.

[25] Popova, A. V., Kremenetsky, V. G., Solov'ev, V. V., Chernenko, L. A., Kremenetskaya, O. V., Fofanov, A. D., & Kuznetsov, S. A. (2010). Standard rate constants of charge transfer for nb(V)/Nb(IV) redox couple in chloride-fluoride melts: Experimental and calculation methods. Russian Journal of Electrochemistry, 46(6), 671-679. https://doi.org/10.1134/S1023193510060121