ISSN 1027-5495. Functional Materials, 33, No.1 (2026), p. 5-14
doi:http://dx.doi.org/10.15407/fm33.01.5

Peculiarities of the compatible behavior of structural components in nitrate systems of cesium, strontium and neodymium precursors: some applied aspects of their use

O.G. Dryuchko*[1]* V.V. Soloviev*[2]*, O.V. Shefer*[1]*, N.V. Bunyakina*[1]*,
***M.V. Moskalenko*[1]*, N.V. Yermilova*[1]*, V.M. Galay*[1]*, B.R. Boriak*[1]**

[1] National University “Yuri Kondratyuk Poltava Polytechnic”,
24 Vitalii Hrytsayenko Avenue, 36011, Poltava, Ukraine
[2] Poltava V.G. Korolenko National Pedagogical University,
2 Ostrohradskyi Street, 36003, Poltava, Ukraine;
* dog.chemistry@gmail.com

Received September 9, 2025, approved October 30, 2025

The comprehensive study provides a reliable understanding of the trends in the joint behavior of structural components in water-salt systems of nitrate precursors of neodymium, cesium, strontium in the preparatory stages of technological regulations for both concentration and immobilization of liquid radioactive waste of the nuclear energy industrial complex ^{137}Cs, ^{90}Sr and thermal activation. The stages of such transformations have been revealed; the patterns of complex and phase formation in the systems and the factors influencing them have been clarified. Various physicochemical properties of the resulting intermediate phases of neodymium coordination nitrates were studied: their composition, types of compounds, atomic crystal structure, shapes of Ln coordination polyhedra, types of ligand coordination, features and patterns of behavior in heat treatment processes. It has been established that under the conditions of the 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+}, the system $Sr(NO_3)_2 – Nd(NO_3)_3 – H_2O$ – is of the eutonic type. The ongoing competing reactions are a powerful technological factor that has a significant impact on changes in the activity of structural forms of Ln^{3+}. Systematized information enables to elucidate the mechanisms and kinetics of transformations of structural components in similar objects. Also, it enables to transfer the resulting system of knowledge to the promising technological solutions for the solidification of liquid radioactive wastes.

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

Особливості сумісної поведінки структурних компонентів у нітратних системах прекурсорів цезію, стронцію і неодиму: деякі прикладні аспекти їх використання.
О.Г. Дрючко, В.В. Соловйов, О.В. Шефер, Н.В. Бунякіна, М.В. Москаленко, Н.В. Єрмілова, В.М. Галай, Б.Р. Боряк

Комплексне дослідження дає достовірне уявлення про тенденції у спільній поведінці структурних компонентів у водно-сольових системах нітратних прекурсорів неодиму, цезію, стронцію у підготовчих стадіях технологічних регламентів концентрування й іммобілізації рідких радіоактивних відходів ядерного енергопромислового комплексу за схемами з використанням пористих і шаруватих матричних фіксаторів радіонуклідів ^{137}Cs, ^{90}Sr і тепловою активацією. Виявлено стадійність таких перетворень; з'ясовано закономірності комплексо- і фазоутворення в системах та фактори впливу на них; вивчений ряд фізико-хімічних властивостей утворюваних проміжних фаз - координаційних нітратів неодиму: їхній склад, види сполук, атомно-кристалічну будову, форми координаційних поліедрів Ln, типи координації лігандів, особливості і закономірності поведінки в процесах термооброблення. Встановлено, що в умовах існування розчинів система $CsNO_3 – Nd(NO_3)_3 – H_2O$ характеризується утворенням 2 аніонних комплексних сполук Ln^{3+}+, система $Sr(NO_3)_2 – Nd(NO_3)_3 – H_2O$ – евтонічного типу. Протікаючі конкуруючі реакції є сильнодіючим технологічним фактором, що суттєво впливає на зміну активності структурних форм Ln^{3+}. Систематизовані відомості дозволяють з'ясовувати механізми, кінетику перетворень структурних компонентів в аналогічних об'єктах та дають можливість перенести одержану систему знань у площину перспективних технологічних рішень отверднення рідких радіоактивних відходів.

1. Introduction

This study was initiated by expanding our knowledge of the mutual behavior of structural components in water-salt systems of rare-earth element nitrates and IA and IIA elements of the Periodic Table in complete concentration ratios and a wide temperature range, as well as the formation conditions and properties of the phases formed in them. Further comprehensive study was aimed at systematizing data on the status and potential methods for improving production technologies for complex oxide materials of transition elements. Its goal was to clarify the features of thermal transformations of such objects, the stages, temperature ranges, process activation methods, and existing requirements for their reproducibility and stability. The obtained results open up new applications in the creation of framework materials for the immobilization of liquid radioactive waste from nuclear power (porous and layered types), as well as in the modeling and experimental justification of the use of specific engineering forms of sorbents and mineral-like technogenic phases-fixators of ^{137}Cs, ^{90}Sr radionuclides.

Due to the diversity of sources of origin, radioactive wastes have a wide variety of compositions and physicochemical properties. The greatest danger to the biosphere is represented by liquid high-level waste containing radionuclides ^{137}Cs and ^{90}Sr with high heat release, often in combination with long-lived ($T_{1/2} \geq 10^5$ years) α-emitting actinides. High-level waste of complex composition includes a number of categories of liquid radioactive wastes with a wide radioisotope and chemical compositions, such as emergency waste from nuclear power plants, the lanthanide-actinide fraction of high-level waste from processing in nuclear fuel cycles, unfractionated high-level waste from temporary storage tanks that contain rare earth and transuranium metals, radionuclides of cesium and strontium, transition metals, and often against the background of high concentrations of salts and increased acidity.

The multicomponent composition of liquid high-level waste and the joint presence in their composition of transuranium elements and fission products with a high content of ^{137}Cs and ^{90}Sr complicate their further processing; therefore, with the development of extraction separation methods, further fractionation of high-level waste is carried out with the separation of different groups of radionuclides in accordance with their chemical properties and half-life time [1-11].

In [12], the content of actinides and lanthanides in the actinide-lanthanide fraction of high-level waste after a 5-year soaking of spent nuclear fuel shows that the bulk of this fraction is represented by lanthanides, and the content of uranium and transuranic elements is approximately 4% by weight of the lanthanides. The absolute majority of the lanthanides is represented by elements of the cerium subgroup (Ce-Sm), with the highest neodymium content (36.5%). It should also 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 percent of cesium and strontium radionuclides. This available information determines both the object and the direction of the research..

The international strategy for the safe management of all types of radioactive waste is aimed at their minimization and reduce the amount of waste by concentrating and retaining radionuclides within stable solid materials. In this case, the most dangerous components of high-level waste are supposed to be enclosed in mineral-like matrices, followed by safe multibarrier disposal in stable geological formations of the Earth's crust.

One of the promising technological solutions for solidifying liquid radioactive waste is the use of inorganic sorbents, which, after saturation with radionuclides in the form of nitrate soluble structural components, are actually precursors to the final form of radioactive waste. Further structural rearrangement of the precursor with the inclusion of radionuclides into the target phases is carried out in the process of solid-phase crystallization upon heating. At present, the optimal strategy for the immobilization of such waste within the framework of the sorption-mineralogical approach may be the use of a sorbent, the composition of which is focused on the extraction of a wide range of elements and the formation of polyphase ceramics based on compositions of phase concentrators of alkali and alkaline earth elements (^{137}Cs, ^{90}Sr), on the one hand, and the lanthanide-actinide fraction in combination with other metals, on the other hand.

When choosing matrix materials for the immobilization of actinides, one of the determining properties is the radiation resistance of their crystal structure to the β-irradiation. The group of such radiation-stable phases – potential matrix materials – includes REE framework zirconomolybdates of the composition $Ln_2Zr_3(MoO_4)_9$, Ln – La ÷ Tb, (for example, neodymium, see Fig. 1) [13]. To implement the above-mentioned projects, data are required on the processes of chemical interaction of structural components, phase formation in water-salt systems of neodymium, cesium and strontium nitrates in the temperature range of 25–100 °C, as well as the properties of the resulting phases.

Setting objectives. For a systematic study of cooperative processes in the technological objects under consideration and for the determination of the possibility to control them, it is necessary to use a complex of physical and chemical methods:

a) studying the chemical interaction nature and mechanisms, 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 a temperature 25 – 100°C;

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

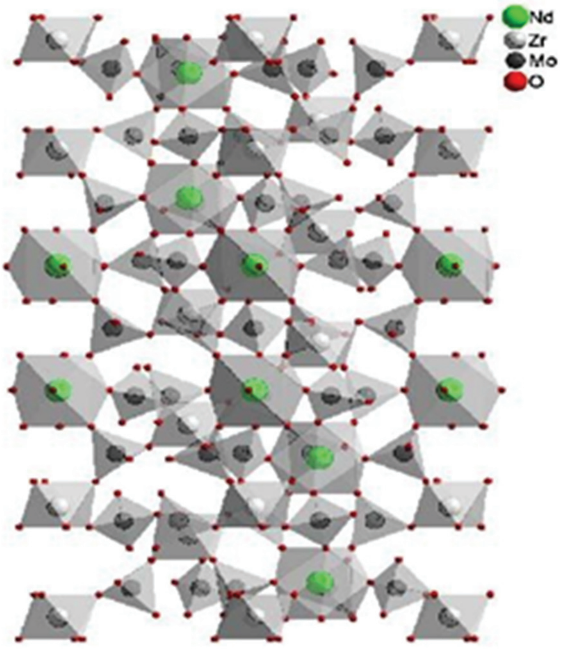

Fig. 1 - Frame structure $Nd_2Zr_3(MoO_4)_9$ (trigonal space group R3c, Z=6), [13]

c) determination of optimal growth conditions and the synthesis of neodymium coordination nitrates (as a representative of the natural series of rare earth elements, where changes both in the composition and structure of compounds occur with the highest probability) to study their properties and confirm their individuality;

d) establishing patterns of dependence of the number, composition, properties of coordination nitrates formed in the systems, on the nature of the Ln^{3+} complex-forming ion and conditions of their formation.

2. The experimental methods

The solubility method and the technique described in [14, 15] were used to clarify the chemical behavior of structural components and phase equilibria in the studied water-salt systems isothermally, in the temperature range of existence of the solutions in full concentration ratios. Phase equilibrium was achieved within 1–2 days. Hydrated and anhydrous nitrates of the indicated grade elements were used as the starting reagents for analysis.

Chemical analysis of liquid and solid phases and residues was carried out for the content of Nd^{3+}, Sr^{2+} ions. The Ln^{3+} content was determined by the trilonometric method; Sr^{2+} was determined by complexometric titration of the substituent in the filtrate, where Ln^{3+} was re-

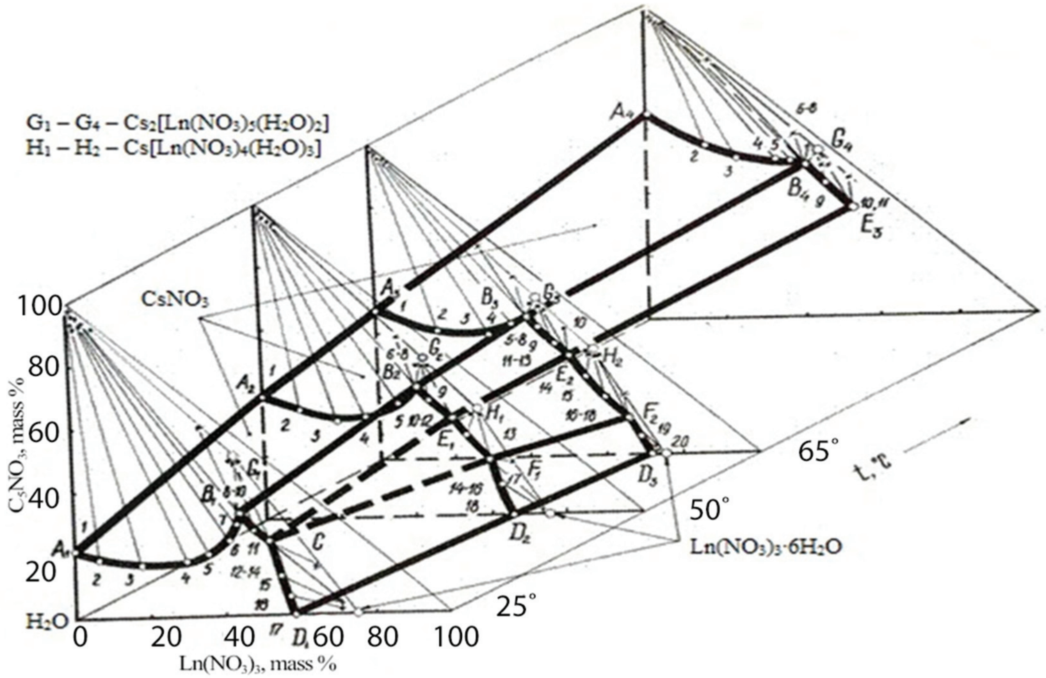

Fig. 2 - Solubility polytherm of system $CsNO_3 – Ln(NO_3)_3 – H_2O$ (Ln – Nd)

moved with an ammonia buffer. The experimental data obtained from the studied systems for individual ions were listed for salt content, summarized in Tables 1, 2 and, according to the principle of correspondence, plotted on polythermal solubility diagrams of the systems (Fig. 2, 3). Graphical display of the composition of hard phases formed in the systems was carried out according to the Schreinemaker method [14, 15]. Chemical analysis of double nitrates isolated isolated as single crystals confirms the ratio of the masses of the elements in the formulas given above. Their individuality was also confirmed by crystal optical, X-ray diffraction, X-ray structural, thermographic, IR spectrometric and other methods of analysis.

Crystallographic optical characteristics of compounds were determined by the immersion method using a MIN−8 microscope. Phase analysis was performed on a DRON–3M diffractometer (Cu-K_α radiation, Ni filter) using the powder method. The diffraction patterns were interpreted using the JCPDS PDF file. Determination of symmetry, parameters of unit cells, as well as measurements of the intensity of diffraction reflections from single crystals were carried out on an automatic X-ray single-crystal diffractometer CAD - 4F “Enraf - Nonius” (Mo K_α- radiation, graphite monochromator; ω / 2θ - method). To determine and refine atomic structures, all calculations were carried out using the crystallographic software packages SHELX, XTL–SM, AREN. IR absorption spectra of the synthesized compounds in the range of 400 – 4000 cm^{-1} were recorded on a UR-20 spectrophotometer using the standard method of suspension in petroleum jelly. Thermogravimetric analysis was carried out on a Q1500 D derivatograph at temperatures from 293 K to 1273 K in air with a heating rate of 10 degrees/min, as well as on a developed DTA device.

3. Results and discussion

Experimental data were obtained on the features and patterns of interaction of structural components, as well as heterogeneous equilibria (25–100 °C) in water-salt systems of neodymium, cesium, and strontium nitrates. They are summarized in Tables 1, 2 and generalized in the form of spatial polythermal solubility diagrams (see Fig. 2, 3). On their basis, the presence of chemical interaction between the constituent elements in the objects under study was established, as well as the quantity, composition, nature of solubility, temperature and concentration limits of the formation of the initial substances and new phases, and the composition of eutonic and transition points were determined. Optimal formation conditions were determined and the synthesis of double neodymium-cesium nitrates was accomplished. Their crystal growth patterns and a number of their inherent properties were studied.

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

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

*K – $CsNO_3$, L – $Nd(NO_3)_3·6H_2O$, G – $2CsNO_3·Nd(NO_3)_3·2H_2O$, H – $CsNO_3·Nd(NO_3)_3·3H_2O$

The choice of the proposed tabular and diagrammatic forms of presentation of the obtained results is the most visual, informative and useful in the development of effective technological regulations for the solidification of liquid radioactive wastes. It enables to predict the behavior of structural components, correctly select modes, stages, methods of forming and obtaining target products with given reproducible characteristics in similar multicomponent production processes using liquid nitrate precursors.

The studied cesium system in solution is characterized by the formation of two new coordination nitrate compounds Nd^{3+} $Cs_2[Nd(NO_3)_5(H_2O)_2]$ and $Cs[Nd(NO_3)_4(H_2O)_3]$. The concentration limits of saturated solutions, from which complex nitrates are released, correspond to the compositions of invariant points of the corresponding solubility isotherms. The strontium system is of the eutonic type; no new solid phases have been found in it.

The obtained data make it possible to identify phases and carry out quantitative calculations in the processes of evaporation and crystallization of similar objects. All detected phases were synthesized in a single crystalline form (Fig. 4). Most of them have an isometric shape and range in size from 4 to 30 mm. Chemical analysis of the isolated compounds confirms the mass ratio of the elements in the proposed formulas. The clarification of the composition of the synthesized compounds and their recording in coordination form were carried out on

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

t,°C	Composition points	Saturated solution				Composition of the "residue", mass.%		Solid phases*
		Composition, mass.%		Properties				
		$Sr(NO_3)_2$	$Nd(NO_3)_3$	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	44.6	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 B_1					95.72	2.80	“-”
	7 B_1	5.94	56.97	1.873	1.4548	52.50	34.84	D+E
	8 B_1					19.05	59.51	“-”
	9 B_1						70.62	“-”
	10 C_1	0.00	58.49	1.887	1.4551	0.00	75.25	E
50	1 A_2	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 B_2					94.90	3.40	“-”
	6 B_2	3.88	65.34	1.850	1.4691	13.73	64.75	D+E
	7 B_2					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 B_3					94.89	2.23	“-”
	8 B_3	2.52	68.39			10.39	67.78	D+E
	9 B_3					3,64	72,88	“-”
	10 C_3	0,00	71,58			0,00	72,26	E

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

the basis of data from a comprehensive study using the above methods (see Tables 3, 4) and by performing a low-temperature X-ray experiment in the process of studying their atomic-crystalline structure.

The authors studied the atomic structure of single crystals Nd^{3+} $Cs_2[Nd(NO_3)_5(H_2O)_2]$, $Cs[Nd(NO_3)_4(H_2O)_3]$ by X-ray diffraction analysis methods (see [16, 17]). The types of ligand coordination, shapes of Ln coordination polyhedra, possible variants of the coordination environment of Nd atoms, the spatial arrangement of polyhedra (Fig. 5) in the construction of compounds with aqua-containing complex anions, and the general crystallochemical regularities of the structure of this type of compound were clarified. (More detailed information and analysis of the construction features of this class of

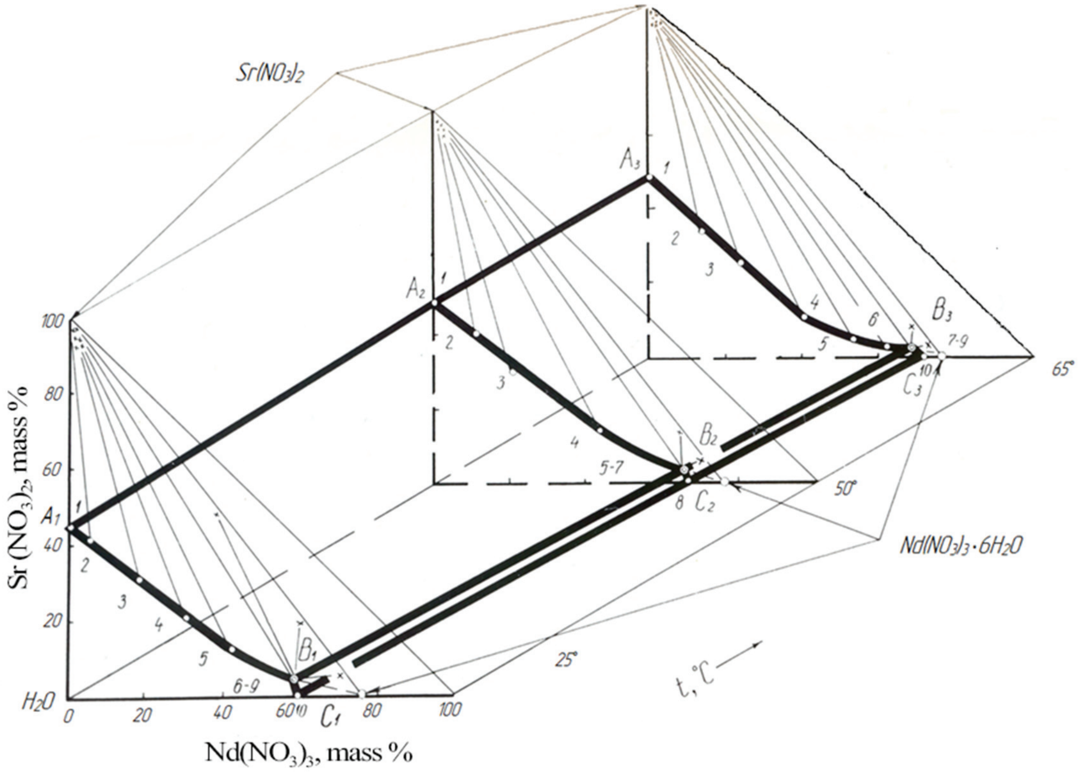

Fig. 3 - Polytherm solubility of the system $Sr(NO_3)_2 – Nd(NO_3)_3 – H_2O$ at 25 – 65 °C


a) b) c) d)

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

a) – $t_{synthesi}$ 50 °C; b) – $t_{synthesi}$ 100 °C

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

c) – $t_{synthesi}$ 50 °C; d) – $t_{synthesi}$ 65 °C

Fig. 4 - Microphotos of coordination nitrates crystals Nd

compounds are given in the above-mentioned original publications of the authors).

Features of the processes of complex formation and crystal-chemical structure of cesium coordination nitrates of neodymium indicate that:

- the structure of complex compounds is based on rare-earth coordination polyhedra, somehow connected in space;;
- processes of exchange interaction between structural components (their binding) in the studied water-salt systems occur already under normal conditions (at 25 °C, see Table 1, Fig. 2);
- under the conditions of the study, the central atoms of the Nd complexing agent exhibit a mono- and bidentate nature of the connection with NO_3^- groups having a coordination number of 10; at the same time, the possibility of forming coordination structures of different compositions ($[Nd(NO_3)_5(H_2O)_2]^{2-}$ and $[Nd(NO_3)_4(H_2O)_3]^-$) reveals an identically organized coordination sphere, clearly illustrating the dominant role of the Ln^{3+} ion in the structure formation of alkali rare earth nitrates;
- complex formations have the ability to retain a layered motif of spatial construction (see Fig. 5, [17]) from rows of alternating rows of Nd and Cs atoms along the *z*-axis. These rows are the ends of the layers of the corresponding coordination polyhedra. The planes of the layers are approximately perpendicular to the plane

Table 3 - Influence of the type of symmetry on the possible physical properties in crystals of coordination nitrates of rare earth elements

Connections	Sononia	Point group	Spatial group	Properties	Temperature range of formation, °C	The nature of solubility	References
$Cs_2[Nd(NO_3)_5(H_2O)_2]$	monocl.	2/m	C2/c	* ↕ μ	25–100	incongr.	[18]
$Cs[Nd(NO_3)_4(H_2O)_3]$	tricl.	$\bar{1}$	$P\bar{1}$	* μ	50–65	incongr.	[19]

Table 4 - X-ray data for 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	–	–	–	–
2,2939	15	–	–	–	–
2,2728	56,5	–	–	–	–

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

of the drawing. It is possible to distinguish packets consisting of four Nd – Cs – Cs – Nd layers, within which coordination polyhedra are in contact with each other due to common edges and hydrogen bonds. Every fourth layer and the next one do not have common vertices and edges, and the interaction of packages in the structure is carried out exclusively through hydrogen bonds.

In the studied water-salt systems, the mechanism of complex formation can be explained from the standpoint of competing replacements of water molecules in the immediate environment of Ln^{3+} with NO_3^-– groups. The degree of completeness of substitution depends on the nature of Ln^{3+}, the influence on these processes of the disordering effect on the structure of solutions of the existing singly and doubly charged cations Cs^+, Sr^{2+}, the nature of the thermal movement of structural components, the properties of electron-donating oxygen atoms and the spatial structure of solvents. A significant influence of the thermal factor on these processes and their staging have been revealed.

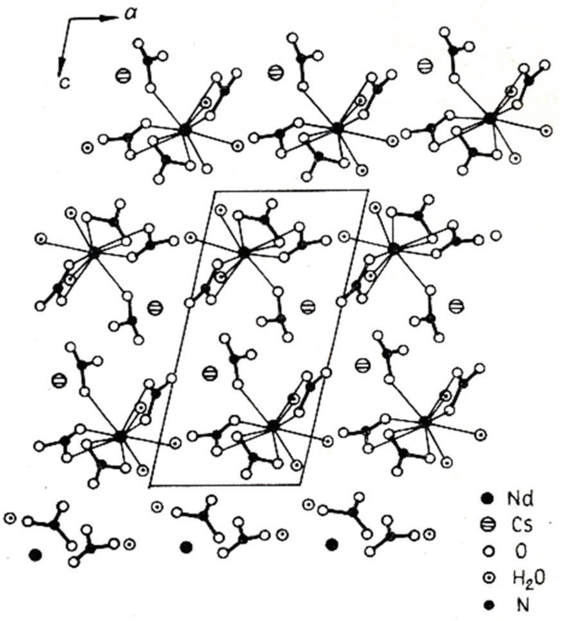

Fig. 5 - Projection of the $Cs[Nd(NO_3)_4(H_2O)_3]$ structure onto the xy plane, [17]

The certain temperatures of the beginning of the release of complex compounds into the solid phase indicates the existence of an energy barrier and the need to provide the system with some additional energy to carry out such transformations.

All this makes the objects under study a promising group of nitrate precursors in the development of compositions for liquid technological systems based on them and the implementation of technological schemes with impregnation, adsorption on radiation-resistant substrates with the possibility of thermal activation and solid-phase reactions. They have a complex of technologically valuable inherent properties: a) high solubility and compatibility with most components; b) a fairly wide temperature range for the existence of complex nitrates; c) the possibility of detecting high activity by their reacting particles obtained by thermolysis of the solvent, and also nanosized and uniform in size and morphology [18]; d) the availability of a wide range of methods and technical means for activating such processes. It should also be noted that combined methods of transformation with special requirements and fast syntheses with combined methods of system activation and mass production are currently becoming increasingly widespread [19, 20].

Using thermoanalytical, chemical and X-ray phase methods, the analyses of the nature and stages of dehydration processes, the nature and temperature intervals of transformation into $Cs_2[Nd(NO_3)_5(H_2O)_2]$, $Cs[Nd(NO_3)_4(H_2O)_3]$ (20 – 1000 ^{o}C) were performed.

On the $Cs_2[Nd(NO_3)_5(H_2O)_2]$ derivatogram, the endoeffects at 95, 122 and 156 ^{o}C correspond to the stepwise process of dehydration. The decrease in mass at 95 ^{o}C corresponds to the loss of one water molecule. At 156°C, the incongruent melting of the sample in the crystallization water occurs and leads to the formation of an anhydrous double salt which melting point is 236°C.

For $Cs[Nd(NO_3)_4(H_2O)_3]$, the dehydration process is also a three-stage process (endoeffects at 62, 90 and 162 ^{o}C). The loss of one water molecule according to the TG curve corresponds to temperature of 139 ^{o}C. The increase in temperature to 162 °C entails incogruent melting of the double nitrate dihydrate; subsequent heat treatment results in the formation of $CsNO_3 \cdot Nd(NO_3)_3$ from temperature 355 ^{o}C. The thermal decomposition products of both coordination salts at t > 920 °C contain neodymium oxide.

4. Conclusions

The conducted comprehensive study provides a reliable idea of the trends in the general behavior of structural components in water-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 according to the schemes using porous and layered matrix fixators of radionuclides ^{137}Cs, ^{90}Sr and thermal activation. The stages of such transformations were revealed, the patterns of complex and phase formation in systems and the factors influencing them were clarified; a number of physicochemical properties of the resulting intermediate phases – coordination neodymium nitrates – have been studied: their composition, types of compounds, atomic crystal structure, shapes of Ln coordination polyhedra, types of coordination of ligands, features and patterns of behavior in heat treatment processes were determined. It has been established that under the conditions of the existence of the solutions, the system $CsNO_3 – Nd(NO_3)_3 – H_2O$ is characterized by the formation of 2 anionic complex compounds of Ln^{3+}, and the system $Sr(NO_3)_2 – Nd(NO_3)_3 – H_2O$ is eutonic. The ongoing competing reactions are a powerful technological factor that has a significant impact on changes in the activity of structural forms of Ln^{3+}. Systematized information makes it possible to elucidate the mechanisms and kinetics of transformations of structural components in similar objects and allows us to transfer the resulting system of knowledge to the plane of promising technological solutions for the solidification of liquid radioactive waste.

References

1. Babain V. A., Smirnov I.V., Alyapyshev M.Yu. et al. Radiation safety issues. 3, 3 (2006).
2. Logunov M. V., Dzekun E.G., Skobtsov A.S. et al. Radiation safety issues. 4, 3 (2008).
3. V.M. Ishchuk, V.L. Cherginets, O.V. Demirskaya et al., Ferroelectrics. 298, 135 (2004).
4. Salvatores M., Palmiotti G. Prog. Part. Nucl. Phys. 66 (1), 144 (2011).
5. Zilberman B.Ya., Fedorov Yu.S., Schmidt O.V. et al. J. Radioanal. Nucl. Ch. 279 (1), 193 (2009).
6. Nishihara K., Nakayama S., Morita Y. et al. J. Nucl. Sci. Technol. 45 (1), 84 (2008).
7. Forsberg C. W. Nucl. Technol. 131 (2), 252 (2000).
8. Mathur J. M., Murali M.S., Nash K.L. Solvent Extr. Ion Exc. 19 (3), 357 (2001).
9. Paiva A. P., Malik P. J. Radioanal. Nucl. Ch. 261 (2), 485 (2004).
10. Romanovsky V. N., Shadrin A.Yu., Zilberman B.Ya. et al. Radiation safety issues. 1, 3 (2004).
11. Romanovsky V. N., Shadrin A.Yu., Zilberman B.Ya. et al. Radiation safety issues. 2, 5 (2004).
12. Milyutin V.V., Gelis V.M., Nekrasova N.A., Kononenko O.A. et al. Radiochemistry. 54 (1), 71 (2012).
13. Trachenko K. J. Phys.- Condens. Mat. 16, 1491 (2004).
14. Thompson L. Fundamentals of analytical chemistry and quantitative chemical analysis. Auris Reference Limited. ISBN 13: 9781781543313 (2014).
15. Rudneva S.I., Sakhnenko M.D., Dzhenyuk A.V. Heterogeneous equilibria in chemical engineering: textbook. Kharkiv: NTU “KhPI”, – 116 p. (2020).
16. Vigdorchik A.G., Malinovskiy Yu.A., Dryuchko A.G. Crystallography. 34 (2), 292 (1989).
17. Vigdorchik A.G., Malinovskiy Yu.A., Dryuchko A.G. Journal of structural chemistry. 30 (5), 175 (1989).
18. Kudrenko E.O., Shmyt’ko Y.M., Strukova H.K. Fyzyka tverdoho tela. 50 (5), 924 (2008).
19. Varma A., Mukasyan A.S., Rogachev A.S. et al. American Chemical Society. Chem. Rev. 116, 14493 (2016).
20. Schaak R.E., Mallouk T.E. Chemistry of Materials. 14 (4), 1455 (2002).