Synthesis and Study of Uranates of Rare-Earth Elements of Compositions $LnU_3O_{10.5} \cdot 6H_2O$ (Ln = La, Ce, Pr, Nd, Sm), $LnU_6O_{19.5} \cdot 10H_2O$ (Ln = Nd, Sm, Eu, Gd, Tb, Dy), and $LnU_2O_{7.5}$ (Ln = Dy, Ho, Er, Tm, Yb, Lu)

N. G. Chernorukov[a], O. V. Nipruk[a,*], K. A. Klin'shova[a], G. N. Chernorukov[a], and O. N. Tumaeva[a]

[a] Lobachevsky Nizhny Novgorod State University, Nizhny Novgorod, 603950 Russia
*e-mail: nipruk@yandex.ru

Abstract—The interaction of synthetic skupite $UO_3 \cdot 2.25H_2O$ with aqueous solutions of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu nitrates under hydrothermal conditions at a temperature of 200°C and varied acidity of the reaction medium yielded 17 previously unknown crystalline compounds of compositions $LnU_3O_{10.5} \cdot 6H_2O$ (Ln = La, Ce, Pr, Nd, Sm), $LnU_6O_{19.5} \cdot 10H_2O$ (Ln = Nd, Sm, Eu, Gd, Tb, Dy), $LnU_2O_{7.5}$ (Ln = Dy, Ho, Er, Tm, Yb, Lu). The methods of chemical analysis, X-ray diffraction analysis, IR spectroscopy, and thermography were used to determine their composition and structure, and their dehydration and thermal decomposition processes were examined. It was shown that the radii and the electronic structure of the atoms affect the composition and structure of the compounds obtained.

Keywords: uranates, rare-earth elements, synthesis, X-ray diffraction analysis, IR spectroscopy, thermography

DOI: 10.1134/S1066362221020028

INTRODUCTION

Uranates of rare-earth elements constitute a good experimental base for determining the factors that are responsible for the possibility of synthesizing compounds with prescribed composition and structure. It is possible to distinguish among factors of this kind the size parameters of atoms of rare-earth elements in the form of their radii and also the type of valence electrons ($6s^25d^14f^n$) and vacant electron orbitals of the $6p^65d^n$ type. To estimate the contributions of these factors to the formation of individual compounds, uranates of alkali elements, from lithium to cesium, have been previously synthesized under hydrothermal-synthesis conditions [1–5]. It was found that, at a full similarity of the types of valence s electrons and vacant electronic p and d orbitals of alkali elements, the uranates synthesize have different compositions and structures. It was concluded that the most probable reason for the observed differences s the rather wide range of ionic radii (systems of other radii can be considered), which vary from $r_{ion} = 0.68$ Å for

Li to $r_{ion} = 1.65$ Å for Cs and thereby determine the different shapes of the coordination polyhedra M(I).

At the same time, it has been shown [6–8] for the example of uranates of $3d$ transition elements Mn, Co, Ni, Cu, Zn in the oxidation state +2 that the close values of ionic radii, which fall within the range 0.74–0.91 Å corresponding to the octahedral coordination, are the main reason why there is a full similarity in composition and structure between uranates of three transition elements. Also known are other studies [9–11] in which it was shown that the factor responsible for the similarity in composition and structure between the uranates are the geometric dimensions of the atoms of structure-forming elements, with the similarity in their electronic structure being of secondary importance.

An identically directed action of the similarity factor of their outer valence $6s^25d^1$ electrons and the closeness of the size parameters ($r_{Ln^{3+}}$) determining the shape of the coordination polyhedra of REEs is characteristic of rare-earth elements, including La and Ln. However, the effect of the lanthanide contraction results in that

the ionic radii decrease from 1.03 Å for La to 0.84 Å for Lu. The difference in radii between the first and the last lanthanides reaches a value of 22%, and this may be manifested in the composition and structure of the uranates under study. REE uranates can be attributed to compounds of high practical importance. A considerable part of rare earths are uranium-fission products and are contained in substantial amounts in radioactive wastes, products of the nuclear fuel cycle. Wastes of this kind can serve as a source for industrial production of REEs. Information about REE uranates is necessary for implementation of various separation schemes in processing of uranium-containing radioactive wastes. Data on uranium(VI) and REE compounds are important for understanding the chemistry of process in which natural uranium compounds are formed and subsequently transformed into mineral formation of secondary origin because processes of this kind also occur in the present because a considerable amount of uranium raw materials is used in modern nuclear technologies. Despite the high scientific and practical importance of this issue, only a limited number of publications, including those concerned with synthesis and examination of the crystallographic and thermal properties of anhydrous compounds of composition Ln_6UO_{12} (Ln = La, Nd, Sm, Eu, Gd) have been devoted to uranates of rare-earth elements [12–19]. There has been no published information about crystal hydrates of uranates of rare-earth elements before our present study. Below, we describe procedures for synthesis of REE (from La to Lu) uranates, results obtained in examining their composition and structure and analyzing the state and role of H_2O in the formation of the structure, and determine the range of size parameters of REE atoms ($r_{Ln^{3+}}/r_{O^{2-}}$) that restrict the possibility of obtaining uranates of prescribed composition and structure.

EXPERIMENTAL

The compounds $LnU_3O_{10.5} \cdot 6H_2O$ (Ln = La, Ce, Pr, Nd, Sm), $LnU_6O_{19.5} \cdot 10H_2O$ (Ln = Nd, Sm, Eu, Gd, Tb), and $LnU_2O_{7.5}$ (Ln = Dy, Ho, Er, Tm, Yb, Lu) were synthesized by using similar sets of reagents, which include a synthetic analog of the skupite mineral $UO_3 \cdot 2.25H_2O$ [20] and nitrates of rare-earth elements. Triuranates were synthesized at pH < 3, hexauranates, at pH 3–6, and diuranates ,at pH > 6.5. For this purpose, A Teflon ampule was charged with 500 mg of $UO_3 \cdot 2.25H_2O$ and its contents were poured over with

100 mL of a 0.5 M of a Ln(III) solution. The acidity of the reaction mixture was controlled by the method used to prepare the solution of a rare-earth element. The value pH ≈ 3 was created by dissolving $Ln(NO_3)_3$ (chemically pure) in water. To create pH > 3, the oxide Ln_2O_3 was poured over with an equivalent amount of nitric acid, the mixture was kept for several hours until the required pH value was attained, and then the resulting solution was separated from the undissolved precipitate by filtration. The reaction mixture was transferred into a Teflon ampule, and this ampule was placed in a steel autoclave and kept there at 200°C for 10 h. The resulting precipitate was filtered off, washed with distilled water, and dried in air.

The uranium concentration in the samples obtained was determined photometrically by the reaction with Arsenazo III (λ_{max} = 650 nm, pH 3) after their dissolution in sulfuric acid [21]. Rare-earth elements in aqueous solutions were determined photometrically via titration with a 10^{-3} M solution of Trilon B in the presence of a Xylenol Orange. The equivalence point was determined graphically from the intersection of the linear portions of the photometric-titration curves [22]. The optical density was measured with a UV-1650 spectrophotometer (Shimadzu). The mass fraction of H_2O was determined in all the samples by the weighing method upon their calcination at 600°C for 2 h. The X-ray diffraction characteristics of the samples were measured with an XRD-6000 diffractometer (Shimadzu). The functional composition ofvthe uranates was determined with a FTIR-8400s IR spectrometer (Shimadzu). The thermal stability was examined by the method of differential scanning calorimetry on a Labsis instrument (Setaram).

RESULTS AND DISCUSSION

Table 1 presents the results of a chemical analysis of REE uranates. The same table presents the ionic radii of REEs according to Belov and Bokii for the coordination number of 6 and also the ratios $r_{Ln^{3+}}/r_{O^{2-}}$, which can be used to roughly estimate the most probable form of metal-oxygen coordination polyhedra in the uranates under study.

It would be expected, in accordance with the results presented in Table 1, that three groups of REE uranates can be obtained. To the first of these can be attributed the formula analogs of composition $LnU_3O_{10.5} \cdot 6H_2O$.

Table 1. Results of a chemical analysis of uranates f rare-earth elements

Compound	Ln$_2$O$_3$, wt %		UO$_3$, wt %		H$_2$O, wt %		$r_{Ln^{3+}}$, Å	$r_{Ln^{3+}}/r_{O^{2-}}$
	calculated	found	calculated	found	calculated	found		
LaU$_3$O$_{10.5}$·6H$_2$O	14.4	14.3	76.0	75.9	9.6	9.5	1.04	0.76
CeU$_3$O$_{10.5}$·6H$_2$O	14.5	14.4	75.9	75.9	9.6	9.5	1.02	0.75
PrU$_3$O$_{10.5}$·6H$_2$O	14.6	14.5	75.9	75.8	9.6	9.5	1.00	0.74
NdU$_3$O$_{10.5}$·6H$_2$O	14.8	14.5	75.7	75.6	9.5	9.4	0.99	0.73
NdU$_6$O$_{19.5}$·10H$_2$O	8.2	8.1	83.1	83.0	8.7	8.7		
SmU$_3$O$_{10.5}$·6H$_2$O	15.3	15.2	75.2	75.1	9.5	9.4	0.97	0.71
SmU$_6$O$_{19.5}$·10H$_2$O	8.4	8.4	82.9	82.8	8.7	8.7		
EuU$_6$O$_{19.5}$·10H$_2$O	8.5	8.4	82.8	82.7	8.7	8.6	0.95	0.70
GdU$_6$O$_{19.5}$·10H$_2$O	8.7	8.7	82.6	82.5	8.7	8.6	0.94	0.69
TbU$_6$O$_{19.5}$·10H$_2$O	8.8	8.7	82.5	82.5	8.7	8.5	0.89	0.65
DyU$_6$O$_{19.5}$·10H$_2$O	9.0	8.9	82.4	82.3	8.7	8.6	0.88	0.64
DyU$_2$O$_{7.5}$	24.6	24.5	75.4	75.3	–	–		
HoU$_2$O$_{7.5}$	24.8	24.7	75.2	75.1	–	–	0.86	0.63
ErU$_2$O$_{7.5}$	25.1	25.0	74.9	74.8	–	–	0.85	0.62
TmU$_2$O$_{7.5}$	25.2	25.1	74.8	74.7	–	–	0.85	0.62
YbU$_2$O$_{7.5}$	25.6	25.6	74.4	74.3	–	–	0.81	0.60
LuU$_2$O$_{7.5}$	25.8	25.7	74.2	74.1	–	–	0.80	0.59

This group includes uranates of lanthanum to samarium. No representatives of this group could be obtained for REEs situated in the Periodic table after samarium. The most probable reason for the formula analogy among La, Ce, Pr, Nd, Sm uranates should be considered the closeness of ionic radii of La, Ce, Pr, Nd, Sm within the range from 1.03 Å for La to 0.97 Å for Sm, which is characteristic of the septenary and stronger coordination [23] in the structure of the oxygen polyhedra of REEs.

The second group of uranates has the LnU$_6$O$_{19.5}$·10H$_2$O composition and includes derivatives of Nd, Sm, Eu, Gd, Tb, Dy and partly overlaps with the first group. The overlapping of the first and second groups of uranates may be due to the nearly coinciding ranges of $r_{Ln^{3+}}/r_{O^{2-}}$, which combine their coordination opportunities. Compounds of the second group can be only synthesized in weakly acid solutions at pH 3–6.5. In more acid media (pH < 3), uranates belonging to the first group are formed.

The third group of REE uranates of composition LnU$_2$O$_{7.5}$ combines derivatives of Dy, Ho, Er, Tm, Yb, Lu. It can be synthesized at pH > 6.5 and, as regards the given set of REEs, it cannot be obtained as compounds of some other composition and structure.

The influence exerted by the acidity of the medium on the composition of the compounds being formed is a consequence of complex heterogeneous equilibria involving various ionic and molecular form of uranium(VI) in solution. Previously, it has been shown [24–27] for the example of uranophosphates, uranoarsenates, uranovanadates, uranosilicates, and uranogermanates that the chemical state of U(VI) in solutions of its salts largely depends on the acidity of the reaction medium. For example, the diagram in Fig. 1, calculated by the procedure reported in [25,26], demonstrates that nearly the whole amount of uranium(VI) in nitrate solutions at pH ≤ 3 is in the form of uranyl groups UO$_2^{\delta+}$ and the charge of all the ionic forms of uranium(VI) is positive. In less acidic media at 3 < pH < 6.5, the charge of ionic and molecular forms of U(VI) decreases to zero and even negative values. In weakly alkaline and even alkaline media, the conversion of U(VI) continues to give in solutions only anionic forms of uranium, which rule out any involvement of uranyl functional groups in the synthesis reaction.

To find factors determining the possibility of attributing REE uranates to groups of formula analogs, let us consider the specific features of their structure. The results of an an X-ray diffraction analysis, presented
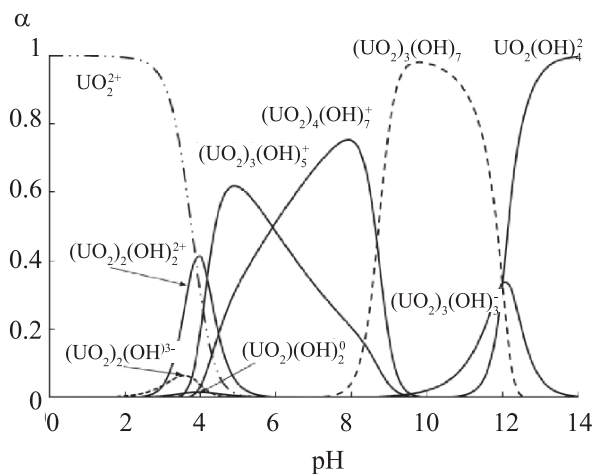
Fig. 1. State diagram of U(VI) in aqueous solutions (CU = 1 × 10^{-2} M, α is the molar fraction of the corresponding form).

Fig. 2. X-ray diffraction patterns of the compounds $LnU_3O_{10.5} \cdot 6H_2O$.

in Table 2 and Fig. 2, show that all the La, Ce, Pr, Nd, Sm uranates of composition $LnU_3O_{10.5} \cdot 6H_2O$, which belong to the first group are crystallographically similar compounds. To each of these corresponds is similar, in its position on the 2θ axis and relative intensity of reflection peaks, set of interplanar spacings with indices *hkl*. This gives reason to believe that the uranates of this group are full crystallographic analogs.

Each of the diffraction patterns in Fig. 2 have at small angles 2θ rather intensive reflection peaks that are indicative of the layered type of the structure. Below, it is shown by an analysis of the IR spectroscopic and thermographic data that layers of the type $[(UO_2)_3O_{4.5}]_{2\infty}^{\delta-}$ or $[U_3O_{10.5}]_{2\infty}^{\delta-}$ contain only polyhedra of uranium, combined into a 3D lattice by the cationic forms of interlayer $Ln^{\delta+}$ atoms in the form of the coordination polyhedra LnO_n. As numerous examples of the structure of this kind in U(VI) compounds can be considered skupite [20], phosphates [28].arsenates [29], etc. [30].

To assess the functional composition and structural specificity of the compounds $LnU_3O_{10.5} \cdot 6H_2O$, an IR spectroscopic study was carried out. All the spectral data related to the compounds $LnU_3O_{10.5} \cdot 6H_2O$, presented in Table 3, are rather simple and characteristic. They contain three groups of vibratory frequencies. Among these, vibrations of the uranyl fragment $LnU_3O_{10.5} \cdot 6H_2O$ are represented in the spectrum by only a single high-intensity band ν_{as} in the range 865–874 cm^{-1}, which may be a consequence of its linearity and equal-arm nature. The presence of $\nu_{as}(UO_2^{\delta+})$ vibrations

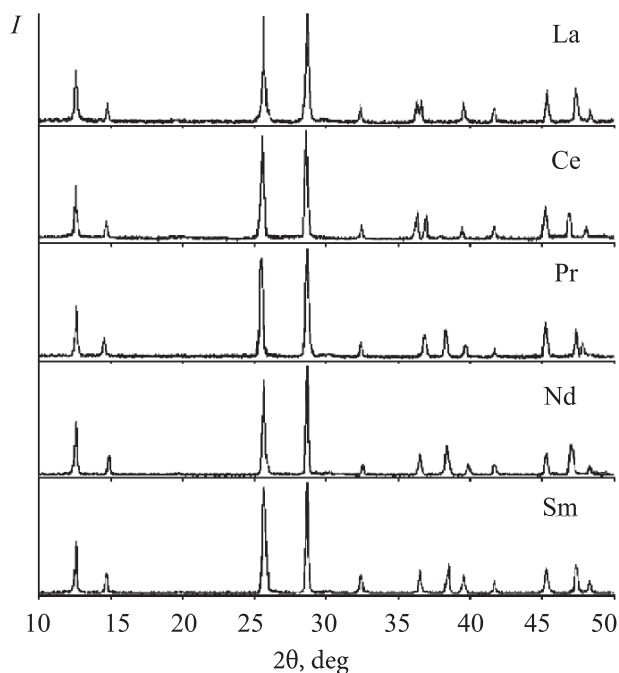confirms that uranium exhibits an oxidation state +6 in $LnU_3O_{10.5} \cdot 6H_2O$ compounds.

The vibrations of H_2O in the spectra of the triuranates are represented by the δ(HOH) bands at 1612–1617 cm^{-1} and ν(HO–H) integral bands peaked at 3380 – 3388 cm^{-1} without separation into ν_{as} and ν_s. A certain shift of the δ(HOH) band to shorter wavelengths and the fact that there is no separation of ν(HO–H) into ν_{as} and ν_s is a consequence of the involvement of H_2O in the formation of H bonds. To find the mechanism of dehydration of REE triuranates and assess the place of H_2O in their structure, a thermographic study was carried out. Figure 3 shows a thermogram of $LaU_3O_{10.5} \cdot 6H_2O$. The thermograms of Ce, Pr, Nd, Sm triuranates differ only slightly in the dehydration temperature, which increases from La derivatives to the Sm derivative. Two H_2O molecules per formula unit of the compound are removed ina single stage in accordance with the first *endo* effect in the DTA curve at 66°C without changes in the diffraction patterns. This behavior in the dehydration, combined with IR spectroscopic data, indicates that two H_2O molecules preserve their vibratory individuality, occupy in the structure of the compounds no independent crystallographic positions, are not involved in the coordination environment of REEs, execute a function of compensation of the layer charge, and are retained in the

**Table 2.** X-ray diffraction characteristics of REE uranates

$LnU_3O_{10.5} \cdot 6H_2O$									
La		Ce		Pr		Nd		Sm	
d, Å	I, %	d, Å	I, %	d, Å	I, %	d, Å	I, %	d, Å	I, %
7.047	49	7.081	51	7.036	48	7.025	49	7.047	47
6.018	20	6.059	19	6.115	21	5.961	19	6.009	18
3.476	96	3.493	95	3.491	91	3.472	87	3.474	96
3.115	100	3.127	100	3.110	100	3.114	100	3.106	100
2.765	19	2.768	18	2.767	16	2.756	11	2.755	15
2.475	23	2.475	21	2.438	21	2.463	19	2.463	18
2.455	24	2.438	25	2.349	27	2.348	28	2.348	30
2.278	22	2.281	12	2.273	14	2.275	9	2.275	15
2.168	16	2.167	14	2.165	11	2.166	10	2.155	9
2.001	33	2.003	33	2.004	34	2.001	19	2.001	19
1.919	33	1.938	29	1.921	31	1.931	28	1.931	22
1.883	12	1.894	13	1.905	18	1.883	9	1.881	11

$LnU_6O_{19.5} \cdot 10H_2O$											
Nd		Sm		Eu		Gd		Tb		Dy	
d, Å	I, %	d, Å	I, %	d, Å	I, %	d, Å	I, %	d, Å	I, %	d, Å	I, %
7.510	60	7.492	70	7.453	83	7.439	86	7.435	70	7.431	65
6.405	3	6.323	4	6.345	3	6.329	5	6.326	4	6.335	3
6.106	5	6.125	6	6.036	3	6.044	5	6.050	5	6.057	4
5.595	8	5.618	6	5.582	8	5.571	5	5.578	7	5.575	7
4.606	10	4.595	12	4.578	10	4.567	13	4.563	10	4.559	10
4.387	9	4.364	9	4.354	7	4.350	8	4.349	8	4.352	7
3.824	5	3.834	4	3.819	4	3.818	5	3.816	5	3.811	5
3.734	25	3.719	25	3.707	29	3.707	29	3.698	27	3.693	26
3.566	10	3.552	11	3.539	13	3.534	12	3.544	12	3.531	13
3.477	85	3.476	77	3.469	75	3.467	78	3.453	85	3.469	86
3.395	32	3.395	30	3.386	29	3.386	31	3.387	32	3.388	33
3.344	4	3.353	11	3.341	13	3.336	12	3.340	11	3.341	12
3.154	100	3.150	100	3.143	100	3.141	100	3.142	100	3.143	100
2.890	6	2.877	12	2.870	13	2.867	13	2.869	14	2.873	14
2.860	15	2.848	19	2.843	19	2.842	22	2.839	20	2.838	22
2.540	29	2.534	34	2.530	28	2.527	31	2.526	31	2.525	30
2.492	14	2.484	17	2.476	14	2.475	17	2.472	17	2.471	17
2.246	19	2.246	14	2.242	15	2.241	13	2.243	16	2.243	17
2.065	6	2.062	8	2.060	6	2.058	6	2.059	9	2.060	10
1.991	45	1.989	46	1.987	36	1.986	37	1.986	45	1.986	48
1.937	18	1.936	17	1.935	14	1.933	13	1.933	20	1.933	21
1.928	19	1.922	21	1.924	14	1.912	16	1.911	18	1.907	19
1.861	18	1.859	23	1.857	15	1.856	18	1.856	25	1.857	26

Table 2. (Contd.)

| LnU$_2$O$_{7.5}$ | | | | | | | | | | | |
| Dy | | Ho | | Er | | Tm | | Yb | | Lu | |
d, Å	I, %	d, Å	I, %	d, Å	I, %	d, Å	I, %	d, Å	I, %	d, Å	I, %
4.169	36	4.156	33	4.152	33	4.133	31	4.128	39	4.099	36
3.515	6	3.537	8	3.531	6	3.529	7	3.485	8	3.489	8
3.437	100	3.437	100	3.436	100	3.432	100	3.430	100	3.429	100
3.180	19	3.184	23	3.181	21	3.188	18	3.185	19	3.183	12
2.856	6	3.845	9	2.857	8	2.855	6	2.855	8	2.860	7
2.649	59	2.650	50	2.637	51	2.635	53	2.630	58	2.629	56
2.085	6	2.077	7	2.067	8	2.063	5	2.059	8	2.057	6
1.987	12	1.984	14	1.991	14	1.981	13	1.977	12	1.971	16
1.963	9	1.934	6	1.936	6	1.931	7	1.929	7	1.929	8

structure by weak H bonds. The next four H$_2$O molecules form a coordination environment of REEs, are retained in the structure by the coordination REE–O bonds, and occupy independent crystallographic positions. Their removal cause a coordination unsaturation of REEs and, as a consequence, disintegrates the crystal lattice of the triuranates to the amorphous state. Amorphous products formed in the thermal decomposition at 600–800°C are crystallized to form full crystallographic analogs of composition LnU$_3$O$_{10.5}$.

Let us further consider hexauranates of composition LnU$_6$O$_{19.5}$·10H$_2$O, where Ln = Nd, Sm, Eu, Gd, Tb,
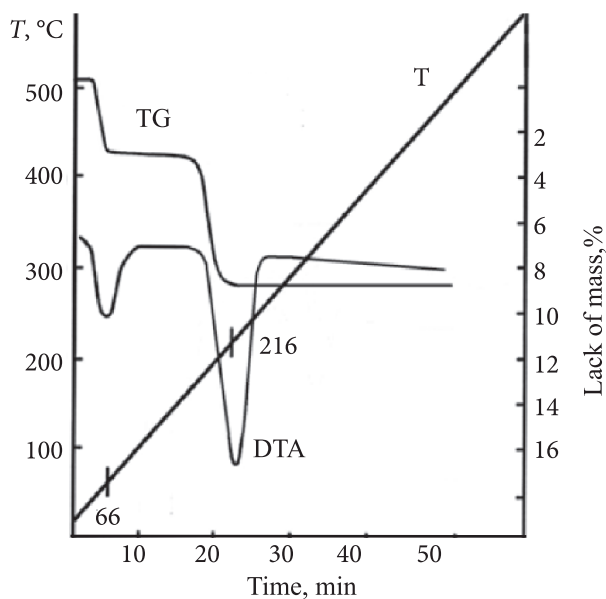
Fig. 3. Thermogram of the compound LaU$_3$O$_{10.5}$·6H$_2$O.

Dy, we attributed to the second group. It was noted above that tri- and hexauranates form two independent groups of individual crystalline compounds, with the same representatives of a number of REEs involved in the syntheses. This result was obtained due to the varied acidity of the reaction medium. All the compounds LnU$_6$O$_{19.5}$·10H$_2$O (Ln = Nd, Sm, Eu, Gd, Tb) represented in Table 1 are not only formula analogs, but also crystallographic analogs. The X-ray diffraction patterns of these compounds contain sets of reflection peaks with close values of 2θ and relative intensities (Table 2). Figure 4 presents as an illustration the diffraction patterns of all the hexauranates. The presence of high-intensity reflection peaks at small 2θ angles, characteristic of uranyl compounds, indicates that compounds with layered structure are formed.

To assess the functional composition of REE hexauranates, an IR spectroscopic study was carried out. Table 3 presents frequency assignment. Each of the spectra contains the same number absorption bands with close positions and relative intensities, which is indicative of the similar nature of distortions of the coordination U(VI) and Ln polyhedra and water molecules. Three types of absorption bands are well pronounced in the spectra. Among these are vibrations of the uranyl fragment $UO_2^{\delta+}$, vibrations of uranium-hydroxide UOH groups, and vibrations of molecular H$_2$O. The $\nu(UO_2^{\delta+})$ vibrations are separated into the components ν_{as} and ν_s and is in a good agreement with the mathematical model $\nu_s = 0.912\nu_{as} = 1.04$ (cm^{-1}), suggested in [31]. The δ(H$_2$O) band in the spectrum of each hexauranate is shifted to shorter wavelengths and falls within the range
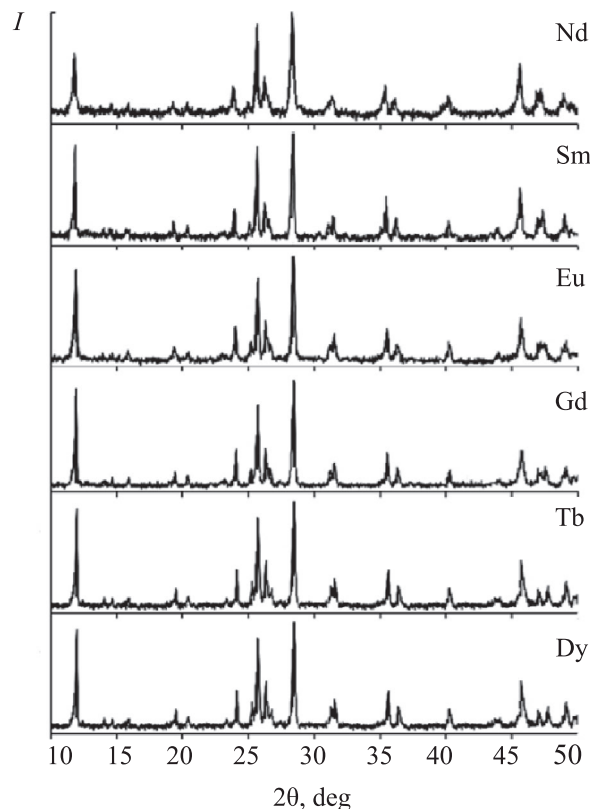
Fig. 4. X-ray diffraction patterns of the compounds $LnU_6O_{19.5} \cdot 10H_2O$.

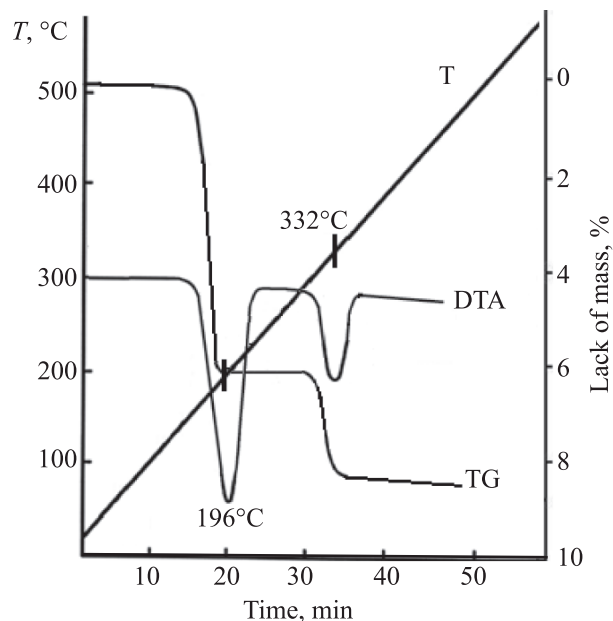**Fig. 5.** Thermogram of the compound $EuU_6O_{19.5} \cdot 10H_2O$.

1613–1620 cm^{-1}. This, as already mentioned, is a characteristic indication of the involvement of H_2O in the formation of H bonds, with the molecular individuality of water preserved. For the same reason, the vibrations ν_{as} and ν_s are represented in the spectra by integral bands peaked at 3471–3475 cm^{-1}, together with the absorption

Table 3. Band assignment in IR spectra of REE uranates

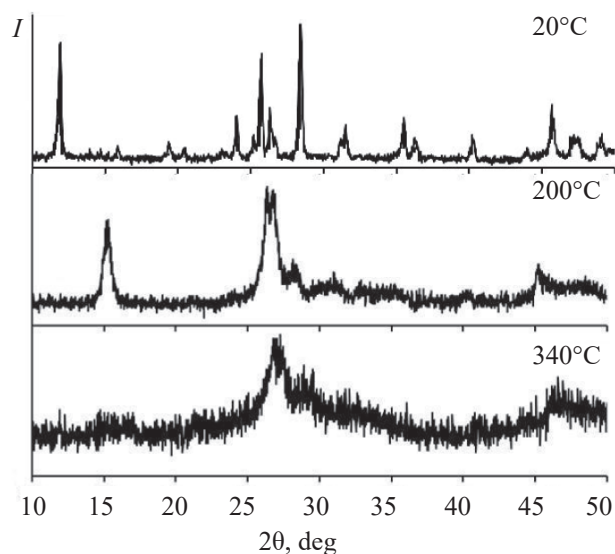| Compound	Wave number cm^{-1}					
	$\nu_{as}(UO_2^{2+})$	$\nu_s(UO_2^{2+})$	$\delta(UOH)$	$\nu(UO\text{–}H)$	$\delta(H_2O)$	$\nu(H_2O)$
$LaU_3O_{10.5} \cdot 6H_2O$	865 s	–	–	–	1615 s	3388 s
$CeU_3O_{10.5} \cdot 6H_2O$	874 s	–	–	–	1616 s	3379 s
$PrU_3O_{10.5} \cdot 6H_2O$	864 s	–	–	–	1614 s	3378 s
$NdU_3O_{10.5} \cdot 6H_2O$	870 s	–	–	–	1617 s	3376 s
$SmU_3O_{10.5} \cdot 6H_2O$	868 s	–	–	–	1612 s	3380 s
$NdU_6O_{19.5} \cdot 10H_2O$	914 s	827 med	962 w	3320 sh	1613 s	3473 s
$SmU_6O_{19.5} \cdot 10H_2O$	914 s	825 med	963 w	3319 sh	1620 s	3475 s
$EuU_6O_{19.5} \cdot 10H_2O$	909 s	824 med	962 w	3320 sh	1613 s	3475 s
$GdU_6O_{19.5} \cdot 10H_2O$	907 s	826 med	963 w	3322 sh	1615 s	3472 s
$TbU_6O_{19.5} \cdot 10H_2O$	906 s	824 med	962 w	3324 sh	1617 s	3472 s
$DyU_6O_{19.5} \cdot 10H_2O$	905 s	825 med	961 w	3326 sh	1614 s	3471 s
$DyU_2O_{7.5}$	871 s	–	–	–	–	–
$HoU_2O_{7.5}$	869 s	–	–	–	–	–
$ErU_2O_{7.5}$	871 s	–	–	–	–	–
$TmU_2O_{7.5}$	868 s	–	–	–	–	–
$YbU_2O_{7.5}$	870 s	–	–	–	–	–
$LuU_2O_{7.5}$	871 s	–	–	–	–	–

Fig. 6. X-ray diffraction patterns of $EuU_6O_{19.5} \cdot 10H_2O$.and products of its dehydration at 200 and 340°C.

Fig. 7. X-ray diffraction patterns of the compounds $LnU_2O_{7.5}$.

bands associated with $\nu(H_2O)$ in the molecular form. The IR spectra contain bands at 3319–3326 cm^{-1}, which can be attributed to valence vibrations of $\nu(UO–H)$ groups in the uranium polyhedra. The corresponding $\delta(UOH)$ bands lie at 961–963 cm^{-1}. These are rather weak, but quite probable absorption bands at a rather large reduced mass of the vibratory fragment UOH.

To assess the state and role played by H_2O in the formation of the structure of $LnU_6O_{19.5} \cdot 10H_2O$, we carried out a thermographic study, combined with an X-ray diffraction analysis and IR spectroscopy. The thermograms of Nd, Sm, Eu, Gd, Tb, and Dy hexauranates are on the whole similar and differ only in dehydration temperatures, which only slightly increase from Nd to Dy. The dehydration process occurs in two stages (TG curve, Fig. 5). The first effect in the DTA curve is observed at 190–206°C and corresponds to the removal of 7 out of 10 H_2O molecules per formula unit of hexauranate and to the formation of the $LnU_6O_{19.5} \cdot 3H_2O$ phase. The removal of water in the first dehydration stage leads to broadening of the reflection diffraction peaks and makes lower their intensity (Fig. 6). This may indicate that H2O molecules are retained in the hexauranate structure not only due to H-bonds, but also as a result of their involvement in the coordination environment of REEs. In the IR spectra of the dehydration products of composition
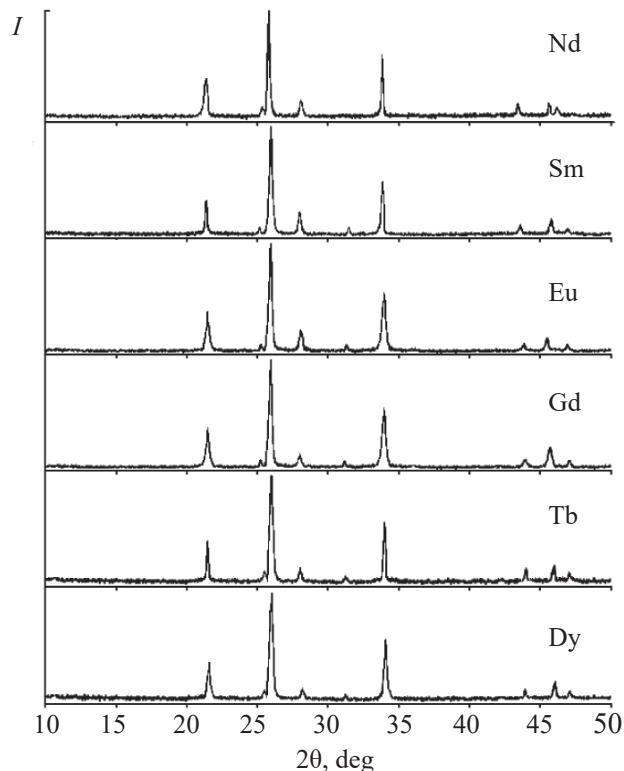
$LnU_6O_{19.5} \cdot 3H_2O$, the $\nu(H_2O)$ bands disappear in the range 3471–3475 cm^{-1} and so do the $\delta(H_2O)$ bands at 1613–1620 cm^{-1}, but the bands $\nu(UO–H)$ at 3319–3326 cm^{-1} and $\delta(UOH)$ at 961–963 cm^{-1} are preserved. The spectrum may have this form if the dehydration product would contain not three H_2O molecules, but an equivalent number of hydroxy groups in the compound $Ln[(UO_2)_6O_{4.5}(OH)_6]$. The process of a full dehydration of these compounds is complete within the temperature range 302–332°C, with the condensation of hydroxide groups and the formation of a mixture of composition $Ln_2O_3 \cdot 12UO_3$.

Let us further consider the compounds we attributed to the third group of derivatives of U(VI) and REEs from Dy to Lu. A characteristic feature of this group of compounds is the closeness of the ionic radii (Table 1) of REEs , which fall within the range from 0.88 to 0.8 Å. The corresponding r_{Ln3+}/r_{O2-} ratio is within the narrow range 0.64–0.59, characteristic of the six-fold coordination,. One additional important specific feature of the third-group compounds should be noted. When synthesis is performed under hydrothermal conditions, the resulting compounds are anhydrous phases. This is

possible if U(VI) and Ln in a compound are coordination-saturated and there is no need for H_2O molecules as a compensator of the coordination capacity.

According to the results of a chemical analysis, presented in Table 1, all the compounds have a composition $LnU_2O_{7.5}$ and are formula analogs. Repeated syntheses of all the compounds of this group are easily reproducible, and each has characteristically close values of interplanar spacings and comparable intensities of the diffraction peaks represented in Table 2. Figure 7 shows a diffraction pattern of holmium diuranate, typical of all the REE diuranates. At the same time, the IR spectrum of each compound of this group has a single absorption band at 868–871 cm^{-1}, associated with the asymmetric valence vibration ν_{as} of the $[O{\cdots}U{\cdots}O]^{\delta+}$ group (Table 3). In accordance with published data [32], the $\nu_{as}(UO_2^{\delta+})$ band in the uranium-oxygen polyhedron with a six-fold coordination of U(VI) lies at 935–940 cm^{-1}. The seven-fold coordination results in the lengthening of U–O bonds in the uranyl group and the wave number decreases to 900–915 cm^{-1} [32]. The values of $\nu_{as}(UO_2^{\delta+})$ we observed at 868–871 cm^{-1} in the spectrum of the diuranates $LnU_2O_{7.5}$ are also a consequence of the lengthening of the U$\cdots$O bonds. This makes weaker the role played by the uranyl group in the formation of a layered type of the structure. It should be considered on the basis of the aforesaid that a skeleton, rather than layers type of structure occurs in the $LnU_2O_{7.5}$ compounds. To confirm this type of structure of $LnU_2O_{7.5}$, we made high-temperature X-ray measurements in a wide temperature range 20–1000°C with a step of 50°C. It was found that each of the compounds under study is highly thermally stable, and their X-ray diffraction patterns contain nearly identical set of diffraction reflection peaks up to 900°C inclusive. At temperatures higher than 900–950°C, $LnU_2O_{7.5}$ undergoes a thermal decomposition into Ln_2O_3 and U_3O_8 crystalline phases.

CONCLUSIONS

Thus, 17 previously unknown compounds of U(VI) and rare-earth elements were studied. The interaction of uranium(VI) with REEs ranging from La to Lu yields three groups of individual crystalline compounds with different compositions and structures. In each group of compounds of compositions $LnU_3O_{10.5}{\cdot}6H_2O$ (Ln = La, Ce, Pr, Nd, Sm), $LnU_6O_{19.5}{\cdot}10H_2O$ (Ln = Nd, Sm,

Eu, Gd, Tb), and $LnU_2O_{7.5}$ (Ln = Dy, Ho, Er, Tm, Yb, Lu) are full crystallographic and functional formula analogs. The intragroup similarity and the intergroup differences in composition and structure between REE uranates is an example of the influence exerted on the structure of the compounds by the so-called dimensional factor ($r_{Ln^{3+}}/r_{O^{2-}}$), manifested in REEs as the lanthanide contraction. REE uranates can be used as forms of the chemical binding of uranium in the natural medium and in various technological processes as individual crystalline compounds.

CONFLICT OF INTEREST

The authors state that they have no conflict of interest.

REFERENCES

1. Chernorukov, N.G., Nipruk, O.V., and Arova, M.I., *Russ. J. Inorg. Chem.,* 2013, vol. 58, no. 6, pp. 621–623. https://doi.org/10.1134/S0036023613060077

2. Nipruk, O.V., Chernorukov, G.N., Abrazheev, R.V., and Kostrova, E.L., *Neorg. Mater.,* 2017, vol. 53, no. 8, pp. 829–833.

3. Nipruk, O.V., Chernorukov, N.G., Kostrova, E.L., and Chernorukov, G.N., *Radiochemistry,* 2015, vol. 57, no. 6, pp. 580–583. https://doi.org/10.1134/S106636221506003X

4. Chernorukov, N.G., Nipruk, O.V., Chernorukov, G.N., Kostrova, E.L., and Chaplieva, K.A., *Radiochemistry,* 2015, vol. 57, no. 5, pp. 488–491. https://doi.org/10.1134/S1066362215050069

5. Chernorukov, N.G., Nipruk, O.V., and Kostrova, E.L., *Russ. J. Inorg. Chem.,* 2015, vol. 60, no. 11, pp. 1452–1456.

6. Nipruk, O.V., Chernorukov, N.G., Chaplieva, K.A., and Chernorukov, G.N., *Neorg. Mater.,* 2016, vol. 52, no. 5, pp. 551–556.

7. Chernorukov, N.G., Nipruk, O.V., Knyazev, A.V., Arova, M.I., and Chaplieva, K.A., *Russ. J. Inorg. Chem.,* 2013, vol. 58, no. 1, pp. 9–13. https://doi.org/10.1134/S0036023613010051

8. Nipruk, O.V., Chernorukov, N.G., Chaplieva, K.A., and Chernorukov, G.N., *Radiochemistry,* 2015, vol. 57, no. 6, pp. 575–579.

https://doi.org/10.1134/S1066362215060028

9. Chernorukov, N.G., Nipruk, O.V., Chernorukov, G.N., and Sedelkina, O.S., *Radiochemistry,* 2015, vol. 57, no. 4, pp. 378–380.
https://doi.org/10.1134/S1066362215040062

10. Zhang, Y., Aughterson, R., Karatchevtseva, I., Kong, L., Tran, T.T., Čejka, Y., Aharonovich, I., and Lumpkin, G.R., *New J. Chem.,* 2018, vol. 42, no. 15, pp. 12386–12393.

11. Chernorukov, N.G., Nipruk, O.V., Chernorukov, G.N., Abrazheev, R.V., and Chaplieva, K.A., *Russ. J. Gen. Chem.,* 2019, vol. 89, no. 1, pp. 81–86.
https://doi.org/10.1134/S1070363219010134

12. Hrudananda, Jena, Asuvathraman, R., and Govindan Kutty, K.V., *J. Nucl. Mater.,* 2000, vol. 280, pp. 312–317.

13. Krishnaiah, M.V., Seenivasan, G., Srirama Murti, P., and Mathews, C.K., *J. Nucl. Mater.,* 2002, vol. 306, pp. 10–14.

14. Venkata Krishnan, R., Manikandan, P., Hrudananda, Jena, and Nagarajan, K., *Thermochim. Acta,* 2008, vol. 472, pp. 95–98.

15. Manjulata, Sahu, Krishnan, K., Saxena, M.K., and Ramakumar, K.L., *J. Alloys Compd.,* 2009, vol. 482, pp. 141–146.

16. Tang, M., Holliday, K.S., Jiang, C., Valdez, J.A., Uberuaga, B.P., Dickerson, P.O., Dickerson, R.M., Wang, Y., Czerwinski, K.R., and Sickafus, K.E., *J. Solid State Chem.,* 2010, vol. 183, no. 4, pp. 844–848.

17. Venkata Krishnan, R., Jena, H., Govindan Kutty, K.V., and Nagarajan, K., *J. Therm. Anal. Calorim.,* 2010, vol. 101, no. 1, pp. 371–377.

18. Krishnan, R.V., Babu, R., Panneerselvam, G., Ananthasivan, K., Antony, M.P., and Nagarajan, K., *Ceram. Int.,* 2012, vol. 38, no. 6, pp. 5277–5280.

19. Shukla, B., Sanjay Kumar, N.R., Sekar, M., Chandra Shekar, N.V., Jena, H., and Asuvathraman, R., *J. Alloys Compd.*, 2016, vol. 672, pp. 393–396.

20. Nipruk, O.V., Knyazev, A.V., Chernorukov, G.N., and Pykhova, Yu.P., *Radiochemistry,* 2011, vol. 53, no. 2, pp. 146–150.
https://doi.org/10.1134/S1066362211020044

21. Markov, V.K., Vernyi, E.A., Vinogradov, A.V., et al., *Uran. Metody ego opredeleniya* (Uranim. Methods for Its Determination), Moscow: Atomizdat, 1964.

22. Ryabchikov, D.I., Ryabukhin, V.A., *Analiticheskaya khimiya redkozemel'nykh elementov i ittriya* (Analytical Chemistry of Rare Earth Elements and Yttrium), Moscow: Nauka, 1966.

23. Urusov, V.S., *Teoreticheskaya kristallokhimiya* (Theoretical Crystal Chemistry), Moscow: Moscow Gos. Univ., 1987.

24. Nipruk, O.V., Chernorukov, N.G., and Zakharycheva, N.S., *Geokhimiya,* 2018, vol. 56, no. 8, pp. 798–811.

25. Nipruk, O.V., Chernorukov, N.G., Zakharycheva, N.S., and Kostrova, E.L., *J. Radioanal. Nucl. Chem.,* 2017, vol. 311, no. 1, pp. 519–529.

26. Nipruk, O.V., Chernorukov, N.G., Eremina, A.A., Kostrova, E.L., and Chaplieva, K.A., *Radiochemistry,* 2014, vol. 56, no. 4, pp. 392–399.
https://doi.org/10.1134/S1066362214040067

27. Nipruk, O.V., Chernorukov, N.G., Pykhova, Yu.P., Godovanova, N.S., and Eremina, A.A., *Radiochemistry,* 2011, vol. 53, no. 5, p. 483.
https://doi.org/10.1134/S1066362211050067

28. Locock, A.J. and Burn, P.C., *Amer. Mineral.,* 2003, vol. 88, pp. 240–244.

29. Locock, A.J., Burns, P.C., *J. Solid State Chem.,* 2003, vol. 176, pp. 18-26.

30. Krivovichev, S., Burns, P., and Tananaev, I., *Structural Chemistry of Inorganic Actinide Compounds,* Amsterdam: Elsevier, 2007.

31. Bagnall, K.W. and Wakerley, M.W., *J. Inorg. Nucl. Chem.,* 1975, vol. 37, pp. 329–330.

32. Volod'ko, L.V., Komyak, A.I., and Umreiko, D.S., *Uranilovye Soediniya* (Uranyl Compounds), Minsk: Bel. Gos. Univ., 1981.