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Synthesis and Study of Polyuranates $M^{III}U_3O_{10.5}\cdot 6H_2O$ (M^{III} = La, Ce, Pr, Nd, Sm)

N. G. Chernorukov, O. V. Nipruk, M. I. Arova, and D. V. Blazhenova

Lobachevskii Nizhnii Novgorod State University, pr. Gagarina 23, Nizhnii Novgorod, 603950 Russia
e-mail: nchernorukov@yandex.ru

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Abstract—Previously unknown individual crystalline compounds $M^{III}U_3O_{10.5}\cdot 6H_2O$ were obtained by the reaction of synthetic schoepite $UO_3\cdot 2.25H_2O$ with aqueous solutions of La, Ce, Pr, Nd, and Sm nitrates in hydrothermal conditions at 200°C. Their composition and structure were determined, and the processes of dehydration and thermal decomposition were studied by the methods of chemical analysis, X-ray diffraction, IR spectroscopy, and scanning calorimetry.

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The information on chemical and structural compatibility of uranium(VI) and elements of the rare earth series is necessary for the fulfilment of various schemes of separation in the radioactive waste reprocessing. The information about uranium(VI) compounds with rare earth elements is important for understanding chemical processes of formation and subsequent conversion of natural uranium compounds to secondary mineral formations, as such processes proceed presently because of large-scale utilization of uranium raw material in the modern nuclear technology.

In this work we present the procedure of the synthesis of polyuranates of some rare earth elements $M^{III}O_{10.5}\cdot 6H_2O$ (M^{III} = La, Ce, Pr, Nd, Sm) by reaction (1).

$$2M^{III}(NO_3)_3 + 9UO_3\cdot 2.25H_2O + nH_2O \xrightarrow{t,\,p} 2M^{III}U_3O_{10.5}\cdot 6H_2O + 3UO_2(NO_3)_2 + (n + 8.25)H_2O. \quad (1)$$

All compounds were obtained in the form of individual crystal phases. We have studied the chemical and functional composition of the compounds and determined their crystallographic characteristics, the state and role of H_2O in the structure formation, and the boundaries of dimensional parameters [$r(M^{3+})$] of rare earth atoms, within which polyuranates with the composition and structure under study can be obtained. The choice of the elements La, Ce, Pr, Nd, and Sm is caused by the fact that we have synthesized and investigated a uniform set of polyuranates of analogous composition and structure beginning with lanthanum polyuranate and ending with samarium polyuranate. The use of the following rare earth elements in the reactions yields a set of polyuranates of a different structure.

At present there is no available information on the formation processes, composition, structure, and properties of uranium(VI) compounds with rare earth elements in aqueous solutions.

The data of the chemical analysis of samples of polyuranates arranged in decreasing order of ionic M(III) radii are given in Table 1. This table also contains ratios of ionic radii $r(M^{3+})/r(O^{2-})$ for $r(O^{2-})$ 1.36 Å used for the estimation of the most probable form of M(III) coordination polyhedra in the structure of polyuranates. The chemical analyses show that all synthesized polyuranates have similar formulas. They are characterized by a rather narrow range of ratios of ionic radii from 0.76 for La up to 0.71 for Sm, which corresponds to the septenary coordination and allows the formation of M(III) coordination polyhedra of equal shape. Samarium is the last element in the rare earth series, which forms a polyuranate belonging to the uniform set of crystallographic analogs. Polyuranates of the rare earth elements following Sm, namely Eu, Gd, Tb, and other including Lu, form a different set of structurally equivalent compounds, and the information on them will be presented in another publication.

Table 1. Chemical analysis data on $M^{III}U_3O_{10.5}\cdot 6H_2O$ polyuranates

M^{III}	$M_2^{III}O_3$, wt %		UO_3, wt %		H_2O, wt %		$r(M^{3+})$[a], Å	$r(M^{3+})/r(O^{2-})$
	found	calculated	found	calculated	found	calculated		
La	14.31	14.43	75.89	76.00	9.51	9.57	1.04	0.76
Ce	14.43	14.52	75.86	75.92	9.48	9.56	1.02	0.75
Pr	14.49	14.58	75.79	75.87	9.47	9.55	1.00	0.74
Nd	14.47	14.83	75.58	75.65	9.44	9.52	0.99	0.73
Sm	15.19	15.29	75.13	75.24	9.38	9.47	0.97	0.71

[a] Ionic radii after Belov and Bokii [1].

Table 2. X-ray characteristics of $M^{III}U_3O_{10.5}\cdot 6H_2O$ polyuranates (M^{III} = La, Ce, Pr, Nd, Sm)

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	–	–	2.155	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

The X-ray data shown in Table 2 confirm the crystallographic similarity of the polyuranates under study. The reflection maxima close in positions and relative intensities correspond to each of presented sets of interplanar distances that allows us regarding all polyuranates under study as complete crystallographic analogs. As an example of the crystallographic similarity we refer to the X-ray patterns of $LaU_3O_{10.5}\cdot 6H_2O$ and $SmU_3O_{10.5}\cdot 6H_2O$ shown in Fig. 1. In each of the presented patterns in the region of small 2θ angles there are fairly intensive reflection maxima indicative of the layered structure. According to the IR spectroscopy and thermography data, the $[(UO_2)_3O_{4.5}]^{\delta-}_{2\infty}$ or $[U_3O_{10.5}\cdot 6H_2O]^{\delta-}_{2\infty}$ layers containing only uranium polyhedra and uranyl groups in their composition are joined in a three-dimensional lattice by interlayer atoms of rare earth elements in the coordination environment of molecular H_2O. Numerous examples are uranyl phosphates, arsenates, vanadates, schoepite, etc. [2–5].

Table 3. Assignment of bands (cm^{-1}) in IR spectra of $M^{III}U_3O_{10.5}\cdot 6H_2O$ compounds

M^{III}	ν(H_2O)	ν(H–O)M^{III}	δ(H_2O)	ν(UO_2^{2+})
La	3388	3206	1615	865
Ce	3379	3227	1616	874
Pr	3378	3207	1614	864
Nd	3376	3215	1617	870
Sm	3380	3229	1612	868

To estimate the functional composition of polyuranates under study and the state of water in them, we

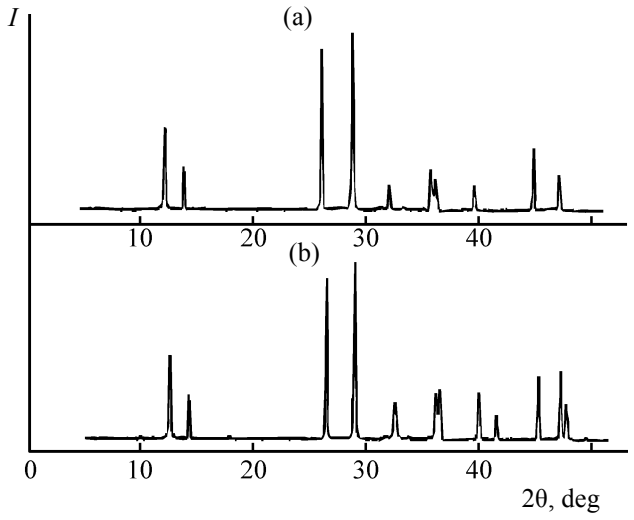
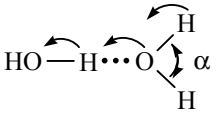


Fig. 1. X-ray data of polyuranates (a) $LaU_3O_{10.5}\cdot 6H_2O$ and (b) $SmU_3O_{10.5}\cdot 6H_2O$.

have carried out an IR-spectroscopic investigation. All the spectral data presented in Table 3 are simple enough and characteristic. They contain three groups of vibration frequencies: of molecular H_2O, of $[M^{III}\frown OH_2]$ groups, and of uranyl bonds. The band of bending vibrations at 1595 cm^{-1} is characteristic of H_2O molecules in the gas phase [6] free from involvement in the formation of any bonds. This band is a distinctive indicator of H_2O molecular individuality. Its participation in the formation of H-bonds [Eq. (2)] causes the increase in the valence angle α and the displacement of the band of H_2O bending vibrations to the short-wave range of 1612–1617 cm^{-1}.



(2)

The bands of stretching vibrations of such molecular H_2O are not split into ν_s and ν_{as} appearing in the spectra as summarized bands in the region of 3380–3488 cm^{-1}. Table 3 contains data on the bands of medium intensity in the form of a shoulder at 3200 cm^{-1}, which can be assigned to the ($M^{III}O$–H) stretching vibrations in the $[M^{III}\frown OH_2]$ coordination complex. Bands of the $\nu(M^{III}$–O) stretching vibrations corresponding to this complex are absent from the spectra, as they are located outside of the spectrometer operating range. In the region of the stretching vibrations of the uranyl group all the spectra contain only one intensive band ν_{as} in the range of 868–872 cm^{-1}, which can be a consequence of the linearity and equal-arm character of the uranyl group. As an example the spectrum of $LaU_3O_{10.5}\cdot 6H_2O$ is shown in Fig. 2.

To determine the mechanism of dehydration of rare earth elements polyuranates and to estimate the H_2O position in their structure, we have carried out a thermographic study. The thermogram of $LaU_3O_{10.5}\cdot 6H_2O$ recorded at the rate of 10 deg min^{-1} is given in Fig. 3. Thermograms of Ce, Pr, Nd, and Sm poly-

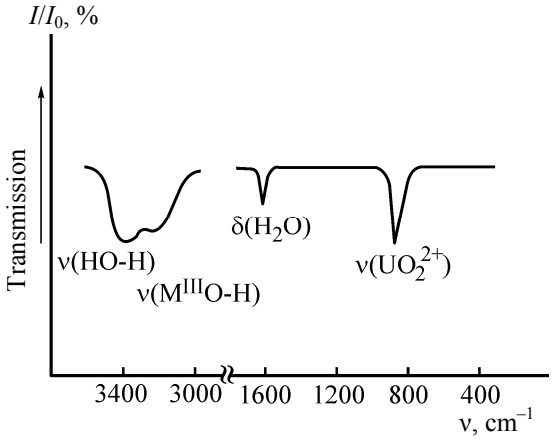


Fig. 2. IR spectra of the compound $LaU_3O_{10.5}\cdot 6H_2O$.

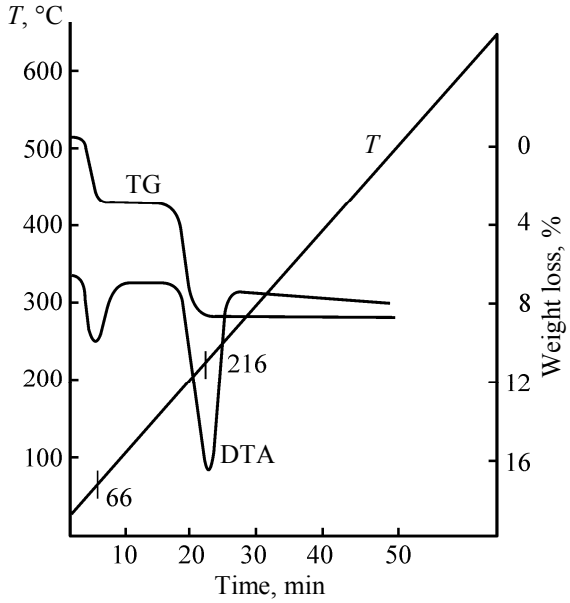


Fig. 3. A thermogram of the compound $LaU_3O_{10.5}\cdot 6H_2O$.

uranates slightly differ from each other only by temperature ranges of dehydration. The removal of two H_2O molecules from the $LaU_3O_{10.5}\cdot 6H_2O$ complex proceeds in a single stage in accordance with the first endothermic effect in the DTA curve at 66°C, the X-ray data remaining unchanged. The subsequent removal of four H_2O molecules at 216°C proceeds in a single stage and is accompanied by the destruction of the crystal lattice up to an amorphous state. Dehydration products in the form of amorphous UO_3 and Ln_2O_3 oxides react to give new crystalline compounds $LnU_3O_{10.5}\cdot 6H_2O$ (Ln = La, Ce, Pr, Nd, and Sm) in the temperature range of 600–800°C. Polyuranates of the specified lanthanides are complete crystallographic analogs.

EXPERIMENTAL

Optical density was measured on a UV-1650 Shimadzu spectrophotometer. Phase individuality and X-ray characteristics of samples were determined on an XRD-6000 Shimadzu diffractometer. The functional composition of polyuranates was determined using an FTIR-8400 Shimadzu IR spectrometer. Thermal stability was studied by the method of differential scanning calorimetry on a Labsys Seteram instrument.

To synthesize $M^{III}U_3O_{10.5}\cdot 6H_2O$ compounds, we used the synthetic analog of the mineral schoepite $UO_3\cdot 2.25H_2O$ [2], which includes basic uranium(VI) oxygen polyhedra necessary for obtaining polyuranates. The procedure of the schoepite preparation is described in [7]. A weighted sample of schoepite (500 mg) was placed in 100 ml of 0.5 M solution of nitrate of a rare-earth element. The synthesis was carried out in a steel autoclave at 200°C within 5-10 h. The resulting precipitate was filtered, washed by distilled water at 20°C, and dried in air. In hydrothermal conditions schoepite dissolves, and the new phase $M^{III}U_3O_{10.5}\cdot 6H_2O$ crystallizes from the solution in parallel.

Uranium concentration in the obtained samples was determined by the reaction with arsenazo III (λ_{max} 650 nm, pH 3) after their dissolution in sulfuric acid [8]. Rare earth elements in aqueous solutions were determined by the titration with 10^{-3} M solution of Trilonum B in presence of xylenol orange. Equivalence points were found graphically from crossings of linear sections of photometric titration curves [9, 10]. To determine weight fractions of H_2O gravimetrically, all samples were calcinated at 600°C within 2 h.

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