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X-ray and thermal studies on $KLnU(C_2O_4)_4 \cdot 8H_2O$ (Ln = La, Ce, Pr, Nd and Tb)

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Abstract

The solid compounds $KLnU(C_2O_4)_4 \cdot 8H_2O$, where Ln = La, Ce, Pr, Nd and Tb have been synthesised and characterised by chemical, X-ray diffraction, infrared and thermogravimetric methods. The X-ray powder data for all five oxalate compounds were indexed on orthorhombic cells. While thermal decomposition in air leads to the formation of $K_2U_2O_7$ and (Ln,U) mixed oxide phases, that in helium results in the mixed oxide phase only. The lattice parameters of the (Ln,U) mixed oxides have been derived.

INTRODUCTION

The thermal decomposition of $K_4U(C_2O_4)_4$ results in the well-known tetragonal potassium monouranate(VI) K_2UO_4. When the K^+ ions in potassium uranium(IV) tetraoxalate are replaced partially by bivalent Ca^{2+} or Cd^{2+} ions, the thermal decomposition of the resultant oxalates leads to the formation of new cubic uranate phases [1]. While all the uranium atoms are present as uranium(VI), X-ray studies showed that these cubic phases have structures similar to that of KUO_3, a uranate of uranium(V). Recently, similar cubic phases have been reported to be formed by the incorporation of small amounts of bivalent alkaline earth metal ions (Ca^{2+}, Sr^{2+} or Ba^{2+}) in tetragonal Rb_2UO_4, also by solid state reactions [2]. The structure derived for these phases shows a limiting composition of $M^{I}_{8}M^{II}_{2}U_6O_{24}$ with the unit cell parameters being double that of MUO_3 where M^{I} = K or Rb and M^{II} = Ca, Sr or Ba. It is therefore related to the $M^{I}U^{V}O_3$ structure in which the positions of a quarter of the U(V) atoms are occupied by M(II) ions and all other uranium atoms are converted to U(VI) [33]. Chemically these compounds can be considered to be formed by replacing a third of the M(I) ions in M_2UO_4 with half that number of M(II) ions, so that all the uranium atoms are present as U(VI). Thus the presence of small amounts of bivalent ions stabilises the cubic phases. In order to determine whether such stabilisation could be effected by incorporating trivalent ions also, mixed metal oxalates, $KLnU(C_2O_4)_4 \cdot 8H_2O$, were synthesised by the replacement of three-quarters of the K^+ ions with Ln^{3+} ions, where Ln = La, Ce, Pr, Nd and Tb; these mixed oxalates were then decomposed to study the nature of the products formed. The results of the X-ray and thermal studies on the oxalates and their decomposition products are discussed in this paper.

EXPERIMENTAL

The compounds $KLnU(C_2O_4)_4 \cdot 8H_2O$ were prepared following the method described for the preparation of lanthanum and cerium derivatives [4]. Dilute aqueous solutions of the respective rare earth nitrates and $K_4U(C_2O_4)_4$ were mixed in stoichiometric ratio to precipitate the mixed metal oxalates. The solid compounds were filtered, washed with water, alcohol and, finally, with ether and then dried in air.

The compounds were analysed chemically for the rare earths, uranium, potassium, carbon and hydrogen. The rare earth elements were determined after decomposing the oxalates by heating them at 600°C and separating the uranium by extraction with tri-isooctylamine in 6N HCl. The rare earths in aqueous phase were precipitated as oxalates, heated to 800°C and weighed as oxides. The uranium extracted into the organic phase was back-extracted with dilute HCl and was precipitated as ammonium diuranate which was heated to 900°C and weighed as U_3O_8.

The potassium content of the compounds was determined by electrothermal atomisation–atomic absorption spectrometry (ETA/AAS) on a Varian Tectron Unit equipped with a CRA-63 atomiser.

The oxalate contents were determined by estimating the carbon contents by oxidation to CO_2 at 1200°C and measuring the thermal conductivity in a LECO WR12 carbon analyser.

The number of water molecules was calculated by estimating the hydrogen content in the compounds by the inert gas fusion technique, employing a LECO RH1EN hydrogen determinator.

The thermograms were recorded in a Mettler TA1 thermoanalyser in a flowing stream of dry air or helium gas. About 50 mg of sample were heated up to 900°C at the rate of 8°C min^{-1} using preheated alumina as a reference material for the DTA measurements. X-ray powder patterns were taken on a Siemen's diffractometer using Cu $K\alpha$ radiation. The infrared spectra of the compounds were recorded on samples pressed in KBr pellets using a Perkin–Elmer IR Spectrophotometer Model 577 in the range 4000–400 cm^{-1}.

RESULTS AND DISCUSSION

The results of the chemical analyses for the rare earth elements, uranium, potassium, carbon and hydrogen given in Table 1 are in agreement

TABLE 1

Chemical analysis of $KLnU(C_2O_4)_4 \cdot 8H_2O$

Ln	% K		% Ln		% U		% C_2O_4		% H_2O	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
La	3.40	4.29	14.01	15.23	25.74	26.09	39.01	38.60	15.31	15.79
Ce	3.55	4.28	15.00	15.34	25.10	26.06	38.95	38.55	15.54	15.77
Pr	3.35	4.28	16.13	15.42	25.55	26.04	37.14	38.51	16.24	15.75
Nd	3.10	4.26	15.21	15.72	25.33	25.95	38.13	38.37	15.88	15.70
Tb	3.10	4.19	16.85	17.05	24.95	25.54	37.49	37.77	16.18	15.45

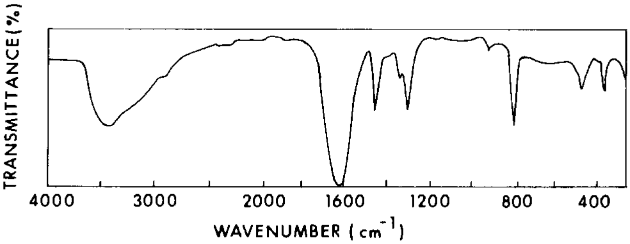

Fig. 1. IR spectrum of $KTbU(C_2O_4)_4 \cdot 8H_2O$.

with the percentages calculated for the composition $KLnU(C_2O_4)_4 \cdot 8H_2O$, where Ln = La, Ce, Pr, Nd and Tb.

The infrared absorption spectra of all the compounds were nearly identical and have absorption bands ascribable to oxalate and water molecules [5]. The IR spectrum of $KTbU(C_2O_4)_4 \cdot 8H_2O$ is shown in Fig. 1 as a representative spectrum.

The X-ray powder diffraction patterns of the lanthanum and cerium derivatives were similar suggesting that these two compounds are isostructural. Likewise, the X-ray powder patterns for praseodymium, neodymium and terbium were also similar but different from those of the other two compounds. The X-ray data of all five compounds could be indexed on orthorhombic cells. The cell parameters of these compounds were refined by the least-squares method using the program LATPAR [6]. These parameters are given in Table 2. The indexed patterns of La and Tb compounds are given in Table 3. The density of the crystals was determined pyknometrically using xylene, from which the number of molecules in the unit cell was calculated.

The thermograms recorded by heating the compounds up to 900°C in a flowing stream of dry air are shown in Figs. 2–6. The compounds lose all their water molecules below 300°C, followed immediately by the decomposition of the oxalate groups. The loss of water molecules in the lanthanum

TABLE 2

Cell parameters of $KLnU(C_2O_4)_4 \cdot 8H_2O$ [a]

Ln	Crystal system	a (Å)	b (Å)	c (Å)	d_{obs}	d_{calc}	Z
					(g cm^{-3})		
La	Orthorhombic	13.870(6)	9.781(2)	8.748(3)	2.52	2.55	2
Ce	Orthorhombic	13.762(13)	9.750(7)	8.728(9)	2.53	2.59	2
Pr	Orthorhombic	8.873(6)	17.583(16)	15.844(14)	2.37	2.46	4
Nd	Orthorhombic	8.847(5)	17.581(12)	15.835(12)	2.37	2.47	4
Tb	Orthorhombic	8.763(3)	17.462(6)	15.805(5)	2.45	2.56	4

[a] Estimated standard deviations are given in parentheses.

TABLE 3

X-ray data of $KLaU(C_2O_4)_4 \cdot 8H_2O$ and $KTbU(C_2O_4)_4 \cdot 8H_2O$ ($\lambda = 1.54178$ Å)

$KLaU(C_2O_4)_4 \cdot 8H_2O$				$KTbU(C_2O_4)_4 \cdot 8H_2O$			
I/I_0	hkl	d_{obs}	d_{calc}	I/I_0	hkl	d_{obs}	d_{calc}
25	010	9.78	9.78	5	020	8.73	8.73
40	011	6.50	6.52	100	002	7.91	7.90
100	210	5.64	5.65	35	120	6.18	6.18
20	201	5.43	5.43	15	102	5.86	5.87
20	020	4.90	4.89		022		5.86
25	021	4.26	4.27	40	122	4.88	4.87
30	202	3.700	3.699	10	040	4.36	4.36
45	030	3.260	3.260	35	004	3.953	3.951
15	401	3.220	3.223	5	202	3.831	3.832
10	003	2.919	2.916	15	104	3.604	3.602
15	402	2.715	2.717	15	222	3.508	3.509
10	213	2.591	2.592	10	124	3.332	3.330
15	023	2.506	2.504	10	240	3.098	3.093
10	232	2.447	2.446	5	115	2.930	2.931
	040		2.445		044		2.929
10	431	2.292	2.292	15	301	2.871	2.872
25	042	2.133	2.134	15	320	2.769	2.770
20	522	2.114	2.113	5	322	2.613	2.614
	530		2.113		330		2.611
10	204	2.085	2.086	10	026	2.522	2.522
25	423	2.028	2.030	5	126	2.423	2.423
10	441	1.949	1.948		260		2.423
10	043	1.874	1.874	10	342	2.320	2.321
				10	164	2.262	2.264
				30	080	2.183	2.183
				5	236	2.105	2.105
				15	353	2.063	2.062
				20	354	1.948	1.949
				15	363	1.921	1.920
				10	370	1.897	1.897
				15	185	1.759	1.760
				5	356	1.707	1.707

and cerium compounds takes place in a single continuous step while in the other three compounds it occurs in two stages. As a result, in place of a single wide endothermic DTA peak for the former, there are two distinct endothermic DTA peaks for the latter compounds, one in the 80–110°C range and the other in the 250–290°C range. This observation is in line with the conclusion derived from X-ray studies that the lanthanum and cerium compounds have a structure different from that of the other three compounds. The percentage weight loss calculated from the thermograms also agrees with the presence of 8 water molecules in all the compounds. In the first step for praseodymium, neodymium and terbium compounds, six

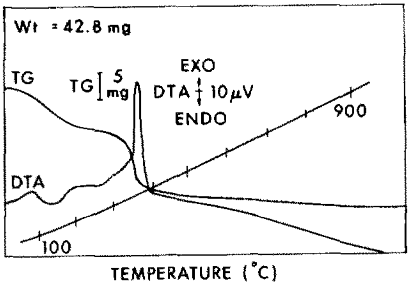

Fig. 2. TG and DTA curves for $KLaU(C_2O_4)_4 \cdot 8H_2O$.

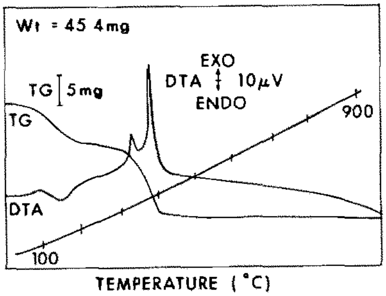

Fig. 3. TG and DTA curves for $KCeU(C_2O_4)_4 \cdot 8H_2O$.

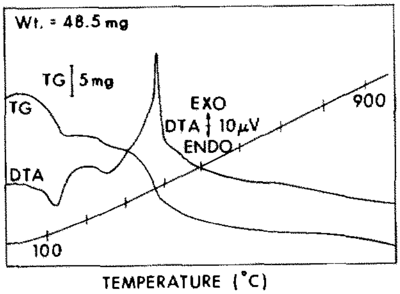

Fig. 4. TG and DTA curves for $KPrU(C_2O_4)_4 \cdot 8H_2O$.

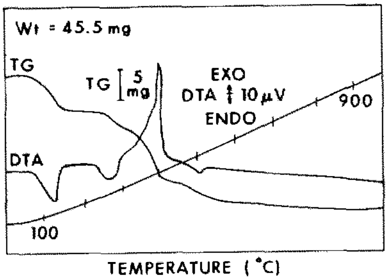

Fig. 5. TG and DTA curves for $KNdU(C_2O_4)_4 \cdot 8H_2O$.

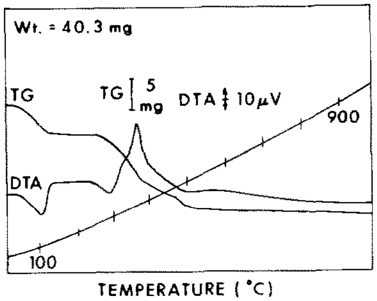

Fig. 6. TG and DTA curves for $KTbU(C_2O_4)_4 \cdot 8H_2O$.

of these water molecules are lost at around 100°C. The remaining water molecules are lost only above 250°C, indicating that these are bonded strongly.

The anhydrous oxalates decompose in the temperature range 300–450°C. Except in the case of the cerium compound, this decomposition step is accompanied by the expected exothermic DTA peak. For the cerium compound, there is an additional exothermic DTA peak at 340°C, which is caused most probably by the oxidation of Ce^{3+} to Ce^{4+}. The weight losses up to 900°C in air, shown in Table 4, are in agreement with those calculated for the loss of $8H_2O$, $4CO_2$ and 4CO from each formula unit. The products isolated after heating up to 900°C were analysed from their X-ray diffraction patterns and the results are included in Table 4. The products in all cases were identified as $K_2U_2O_7$ and a (Ln,U) mixed oxide of fluorite structure. On prolonged heating for more than 20 h, except in the case of the cerium compound, the presence of weak lines corresponding to a cubic phase similar to that of $M^{I}_{8}M^{II}_{2}U_6O_{24}$ [3] could also be detected. In order to isolate any intermediate product in the decomposition, the starting compounds were heated for 4–5 h at fixed temperatures of 400 and 500°C, but the resultant products gave only X-ray lines corresponding to the $(Ln,U)O_{2\pm x}$ phase. It is not clear whether the other

TABLE 4

Decomposition products in air and helium at 900°C

Ln	Air		Helium	
	% Loss	Products identified [a]	% Loss	Products identified [a]
La	46.36	F.P. + $K_2U_2O_7$ + C.P.	46.55	F.P.
Ce	44.45	F.P. + $K_2U_2O_7$	45.55	F.P.
Pr	48.34	F.P. + $K_2U_2O_7$ + C.P.	46.67	F.P.
Nd	47.01	F.P. + $K_2U_2O_7$ + C.P.	46.55	F.P.
Tb	45.16	F.P. + $K_2U_2O_7$ + C.P.	46.56	F.P.

[a] F.P., fluorite phase $(Ln,U)O_{2\pm x}$; C.P., cubic phase (obtained only on prolonged heating).

TABLE 5

Lattice parameters (Å) of $(Ln,U)O_{2\pm x}$ obtained by heating $KLnU(C_2O_4)_4 \cdot 8H_2O$

Ln	This study		Literature values	
	Air (900°C)	Helium (800°C)	Air	Helium
La	5.644	5.534	5.620 [7]	–
Ce	5.421	5.453	5.423 [8]	–
Pr	5.501	5.479	5.465 [9]	5.465 [9]
Nd	5.490	5.450	5.448 [10]	–
Tb	5.363	5.362	–	–

phases detected at 900°C are formed at the decomposition step or on heating above 500°C.

The thermograms recorded using a constant flow of helium gas showed that the TG curves were similar to those obtained in the experiments in air. However, the exothermic DTA peaks for the oxalate decomposition step are replaced by endothermic DTA peaks around 400°C, and the additional DTA peak present for the cerium compound in air is not present. X-ray diffraction patterns of the heated products in helium atmosphere above 800°C showed the presence of fluorite phase only (Table 4). The diuranate phases formed in experiments in air could not be detected.

The lattice parameters of the $(Ln,U)O_{2\pm x}$ phases obtained by heating the oxalates in air and helium atmospheres at 900°C are given in Table 5. In general, the cell parameters decrease with decreasing ionic radii of the rare earth ions. However, for the $(U,Ce)O_{2\pm x}$ phase, the value is much lower than expected [8]. These values are compared with some of the values reported in the literature [7–10]. The published values are for a composition $(Ln_{0.5}U_{0.5})O_{2\pm x}$ where the samples were heated to temperatures higher than the 900°C used here. It is known that the cell parameters of $(Ln,U)O_{2\pm x}$ depend on the relative compositions of Ln and U and O/M, which depends on the temperature and atmosphere of the experiment. In our experiments, the exact composition of the mixed oxide phase could not be estimated because it is formed as one of the components in a mixture. Without this information, a thorough comparison of the cell parameters observed in our work with those reported earlier is not possible. However, the marginal increase in almost all cases indicates the possibility of different relative compositions of Ln and U, and of O/M, due to the interaction of potassium ions with uranium.

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