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ALKALINE-EARTH URANATES FROM THERMAL DECOMPOSITION OF URANYL CARBOXYLATES

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ABSTRACT

The thermal behaviour of some alkaline-earth uranyl carboxylates with U/M ratios = 2:1 (M = Ca, Sr, Ba) and U/M = 3:1 (M = Mg, Ca, Sr, Ba) have been studied. The phases isolated in the heating process were identified, and the temperature of formation of the cubic ternary oxides was considered as a function of the values of the ionic radii of the alkaline-earth metals.

INTRODUCTION

The solubility of the oxides MO (M = Mg, Ca, Sr, Ba) in hyperstoichiometric uranium dioxide UO_{2+x} markedly increases on the formation of fluorite phases. A substitutional mechanism for the replacement of uranium ions by divalent cations has been considered[1].

The fluorite type compounds can be isolated in the system UO_{2+x}/MO, or may be also obtained by mixing the divalent uranates MUO_4 with uranium dioxide and heating the mixture in vacuum sealed ampoules[2, 3, 18]. These ternary oxides are easily formed by calcination of uranyl carboxylates, in which the desired U/M ratio exists.

EXPERIMENTAL

Synthesis

Two series of uranyl compounds with U/M ratio 2:1 and 3:1 were obtained. The 2:1 compounds were prepared by reacting an aqueous solution of uranyl propionate and the divalent metal carbonate previously dissolved in propionic acid. A similar procedure was employed for the synthesis of ammonium and alkaline-earth metal uranyl propionates but the stoichiometric quantity of ammonium propionate was added to the resulting solution.

Both types of compounds can be isolated as well formed crystals, and their general formulae correspond to $M[UO_2(C_2H_5COO)_3]_2 \cdot nH_2O$ and $NH_4M[UO_2(C_2H_5COO)_3]_3 \cdot nH_2O$, where n = 3–8.

The results of the quantitative analysis of the samples are given below.

Calc. for $MgNH_4[UO_2(C_2H_5COO)_3]_3 \cdot 8H_2O$(%): C, 19.59; H, 3.93; N, 0.84; U, 43.18; Mg, 1.47. Found(%): C, 19.56; H, 3.85; N, 0.85; U, 43.28; Mg, 1.42.

Calc. for $Ca[UO_2(C_2H_5COO)_3]_2 \cdot 6H_2O$(%): C, 19.18; H, 3.73; U, 42.27; Ca, 3.55. Found(%): C, 19.22; H, 3.70; U, 42.55; Ca, 3.57.

Calc. for $CaNH_4[UO_2(C_2H_5COO)_3]_3 \cdot 6H_2O$(%): C, 19.84; H, 3.73; N, 0.85; U, 43.72; Ca, 2.45. Found(%): C, 19.79; H, 3.68; N, 0.87; U, 43.69; Ca, 2.45.

Calc. for $Sr[UO_2(C_2H_5COO)_3]_2 \cdot 4H_2O$(%): C, 18.98; H, 3.34; U, 41.87; Sr, 7.70. Found(%): C, 19.04; H, 3.33; U, 41.88; Sr, 7.71.

Calc. for $SrNH_4[UO_2(C_2H_5COO)_3]_3 \cdot 4H_2O$(%): C, 19.67; H, 3.46; N, 0.85; U, 43.36; Sr, 5.32. Found(%): C, 19.29; H, 3.42; N, 0.85; U, 43.56; Sr, 5.34.

Calc. for $Ba[UO_2(C_2H_5COO)_3]_2 \cdot 3H_2O$(%): C, 18.47; H, 3.07; U, 40.70; Ba, 11.74. Found(%): C, 18.10; H, 2.99; U, 40.71; Ba, 11.75.

Calc. for $BaNH_4[UO_2(C_2H_5COO)_3]_3 \cdot 3H_2O$(%): C, 19.32; H, 2.92; N, 0.83; U, 42.59; Ba, 8.19. Found(%): C, 18.90; H, 2.87; N, 0.80; U, 42.60; Ba, 8.06.

Apparatus

Both the equipment used and the experimental conditions were those indicated in an earlier paper[4]. The thermal assays were carried out on the initial compounds and using samples previously calcined at 700°C.

Thermal studies and X-ray diffraction data

The thermal behaviour of magnesium uranyl carboxylate has been described[5]. Calcium, strontium and barium uranyl propionate dehydrate between 50–150°C, and a similar behaviour occurs in the ammonium salts. All of them decompose and burn; the residue obtained at 800°C was identified.

When magnesium ammonium uranyl propionate decomposes, it leaves as residue a mixture of magnesium triuranate and a small amount of magnesium monouranate and U_3O_8. Magnesium triuranate decomposes at 1050°C to $MgUO_4$ and U_3O_8 (refs. 6, 18), but some significant thermal effects were present in the DTA and TG curves obtained on ammonium magnesium uranyl propionate calcined up to 700°C. Two very close endothermic peaks appear on the DTA curve in the temperature range 1051–1093°C, which correspond with two successive steps on the TG curve. Both the second endothermic peak and step, but not the first one, are caused by a reversible reaction. These facts suggest that the second reaction could be the formation of an oxygen-deficient magnesium uranate[17], and the overall reaction scheme could be

$$3\,MgU_3O_{10} + MgUO_4 + 2/3\,U_3O_8 \xrightarrow{1051-1066\,^\circ C} 2\,MgU_3O_{10} + 2\,MgUO_4 +$$

$$+ 4/3\,U_3O_8 \xrightarrow{1066-1093\,^\circ C} 4\,MgUO_{3.95} + 8/3\,U_3O_8 \qquad (1)$$

Finally, the fluorite type phase is formed between 1186–1208°C.

Calcium uranyl propionate left as a residue calcium diuranate but small

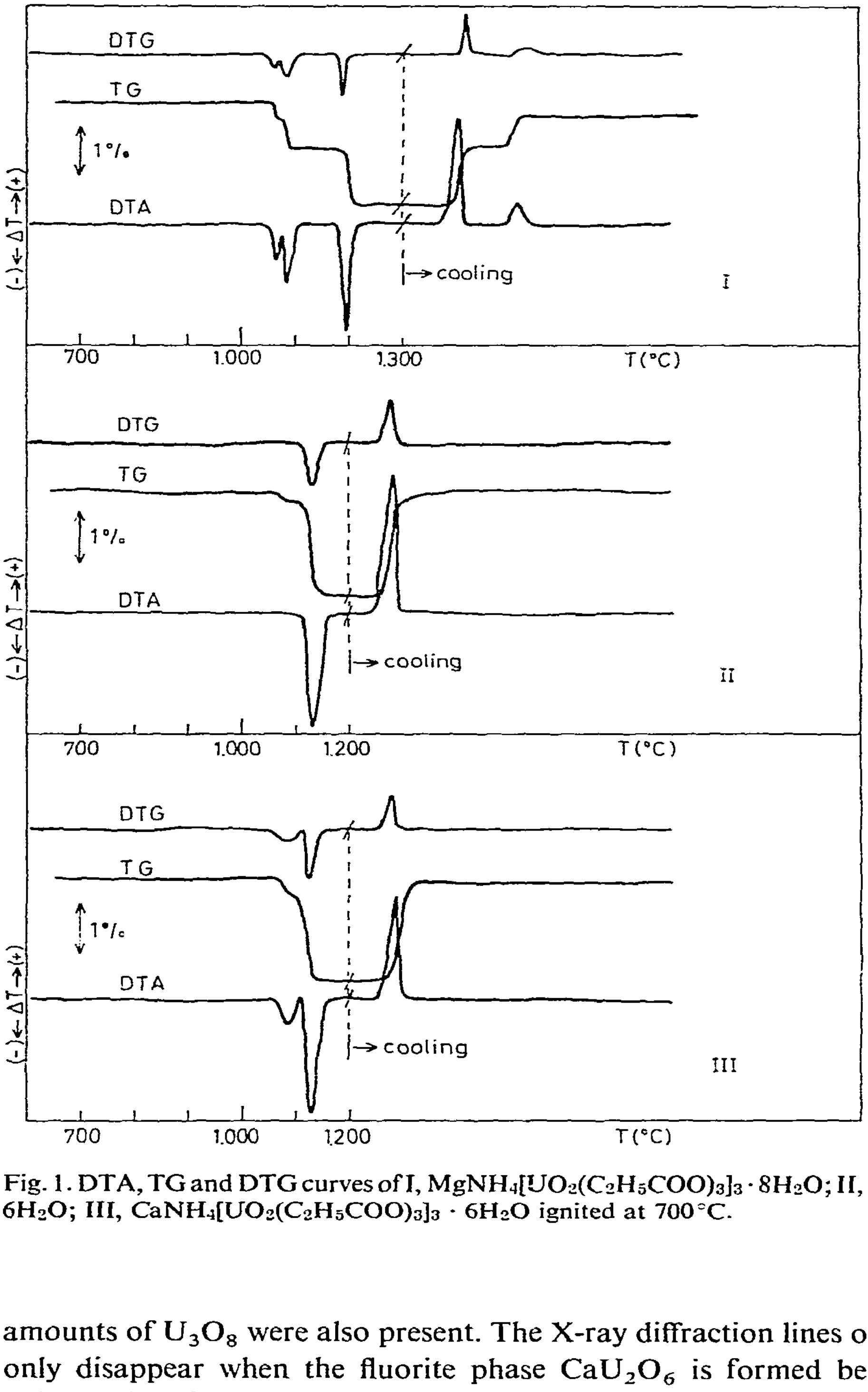

Fig. 1. DTA, TG and DTG curves of I, $MgNH_4[UO_2(C_2H_5COO)_3]_3 \cdot 8H_2O$; II, $Ca[UO_2(C_2H_5COO)_3]_2 \cdot 6H_2O$; III, $CaNH_4[UO_2(C_2H_5COO)_3]_3 \cdot 6H_2O$ ignited at 700 °C.

amounts of U_3O_8 were also present. The X-ray diffraction lines of this uranium oxide only disappear when the fluorite phase CaU_2O_6 is formed between 1151–1138 °C (Fig. 1, II). If the cubic phase, after quenching, is heated again up to 900–1000 °C, the U_3O_8 X-ray diffraction maxima are observed, together with the CaU_2O_7 lines[8-10].

The weight losses calculated from the TG curve (Table 1) can be justified assuming the reactions

TABLE 1

DECOMPOSITION REACTIONS AND WEIGHT LOSSES CALCULATED FROM THE TG CURVES OF ALKALINE-EARTH URANYL PROPIONATES IGNITED AT 700°C

Compounds	*Accumulative weight loss*	
	Found	*Calc.*
$3\ CaU_2O_7 + 2/3\ U_3O_8 + CaO$		
↓ 1062–115°C	0.182	0.191
$3\ CaU_2O_{6.9} + 2/3\ U_3O_8 + CaO$		
↓ 1115–1138°C	2.11	2.132
$4\ CaU_2O_6$		
$2\ Sr_2U_3O_{11} + SrU_4O_{13}$		
↓ 1100–1130°C	0.393	0.394
$5/2\ Sr_2U_3O_{11} + 5/6\ U_3O_8$		
↓ 1300–1350°C	2.37	2.368
$5\ SrU_2O_6$		
$1/3\ Ba_2U_3O_{11} + Ba_3U_7O_{24} + 1/3\ BaO$		
↓ 942–978°C	0.365	0.367
$2\ Ba_2U_3O_{11} + 2/3\ U_3O_8$		
↓ 1400–1500°C	2.82	2.823
$4\ BaU_2O_{5.72}$		

$$3\ CaU_2O_7 + 2/3\ U_3O_8 + CaO \xrightarrow{1062\text{–}1115\,°C} 3\ CaU_2O_{6.9} + 2/3\ U_3O_8 + \\ + CaO \xrightarrow{1115\text{–}1138\,°C} 4\ CaU_2O_6 \qquad (2)$$

The formation of $CaU_2O_{6.9}$ causes the small step observed between 1062–1115°C, without any modification in the X-ray diffraction pattern since this composition is included in the homogeneity range for CaU_2O_{7-x}, its lower limit at 1100°C being $CaU_2O_{6.75}$ (ref. 7).

In the X-ray diffraction pattern of calcium ammonium uranyl propionate, the reflections corresponding to calcium diuranate can be observed as well as those of uranium oxide U_3O_8; nevertheless the latter are much more intense than could be expected if the residue consisted of a mixture of composition $CaU_2O_7 + 1/3\ U_3O_8$. Some other lines of weak intensity appear at 17.02 and 19° 2θ Bragg angles; the same diffraction lines are present in the X-ray powder pattern obtained on a mixture $UO_2(NO_3)_2 \cdot 6H_2O/CaO = 4:1$ ignited at 950°C for 3 h.

It can be concluded that the residue obtained after calcination of calcium ammonium uranyl propionate consists of a mixture of CaU_2O_7, U_3O_8 and CaU_4O_{13}, which decomposes at 1050°C to calcium diuranate and U_3O_8 (Table 2).

It is interesting to notice that no thermal effect appears in the DTA curve obtained with the U/Ca = 2:1 compound, indicating that the formation of CaU_2O_{7-x} is a gradual process. An appreciable endothermic peak occurs in the DTA curve of

TABLE 2

DECOMPOSITION REACTIONS AND WEIGHT LOSSES CALCULATED FROM THE TG CURVES OF AMMONIUM ALKALINE-EARTH URANYL PROPIONATES IGNITED AT 700 °C

Compounds	*Accumulative weight loss*	
	Found	*Calc.*
3 MgU_3O_{10} + $MgUO_4$ + 2/3 U_3O_8		
↓ 1051–1066 °C	0.299	0.297
2 MgU_3O_{10} + 2 $MgUO_4$ + 4/3 U_3O_8		
↓ 1066–1093 °C	0.972	0.982
4 $MgUO_{3.95}$ + 8/3 U_3O_8		
↓ 1186–1208 °C	2.09	2.084
4 MgU_2O_6 + 4/3 U_3O_8		
2 CaU_2O_7 + CaU_4O_{13} + 1/3 U_3O_8		
↓ 1050–1108 °C	0.386	0.389
3 CaU_2O_7 + U_3O_8		
↓ 1108–1142 °C	2.13	2.143
3 CaU_2O_6 + U_3O_8		
3 SrU_4O_{13} + $Sr_2U_3O_{11}$		
↓ 1092–1120 °C	0.821	0.831
5/2 $Sr_2U_3O_{11}$ + 15/6 U_3O_8		
↓ 1350–1383 °C	2.22	2.218
5 SrU_2O_6 + 5/3 U_3O_8		
$Ba_3U_7O_{24}$ + 2/3 U_3O_8		
↓ 942–972 °C	0.445	0.441
3/2 $Ba_2U_3O_{11}$ + 3/2 U_3O_8		
↓ 1400–1500 °C	1.53	1.53
3 $BaU_2O_{6.15}$ + U_3O_8		

calcium ammonium uranyl propionate between 1050–1108 °C as a consequence of the decomposition reaction

$$CaU_4O_{13} \rightarrow CaU_2O_7 + 2/3\ U_3O_8 + 1/3\ O_2 \qquad (3)$$

When strontium uranyl propionate decomposes, $Sr_2U_3O_{11}$ and SrU_4O_{13} are formed; the latter compound decomposes between 1100–1130 °C to a mixture of $Sr_2U_3O_{11}$ and U_3O_8. An endothermic effect is observed in the DTA curve at 1300–1350 °C, which must be due to the formation of cubic strontium diuranate SrU_2O_6, as indicated by the weight loss calculated from the TG curve. All attempts to isolate this phase were unsuccessful. Nevertheless, cubic strontium diuranate has been isolated and the parameter of the cubic lattice has been calculated[7, 12, 13], as well as its non-stoichiometric range[11].

The strontium ammonium uranyl propionate exhibits an analogous thermal behaviour and its decomposition reactions are summarized in Table 2.

The residue isolated at 800 °C after thermal decomposition of barium uranyl

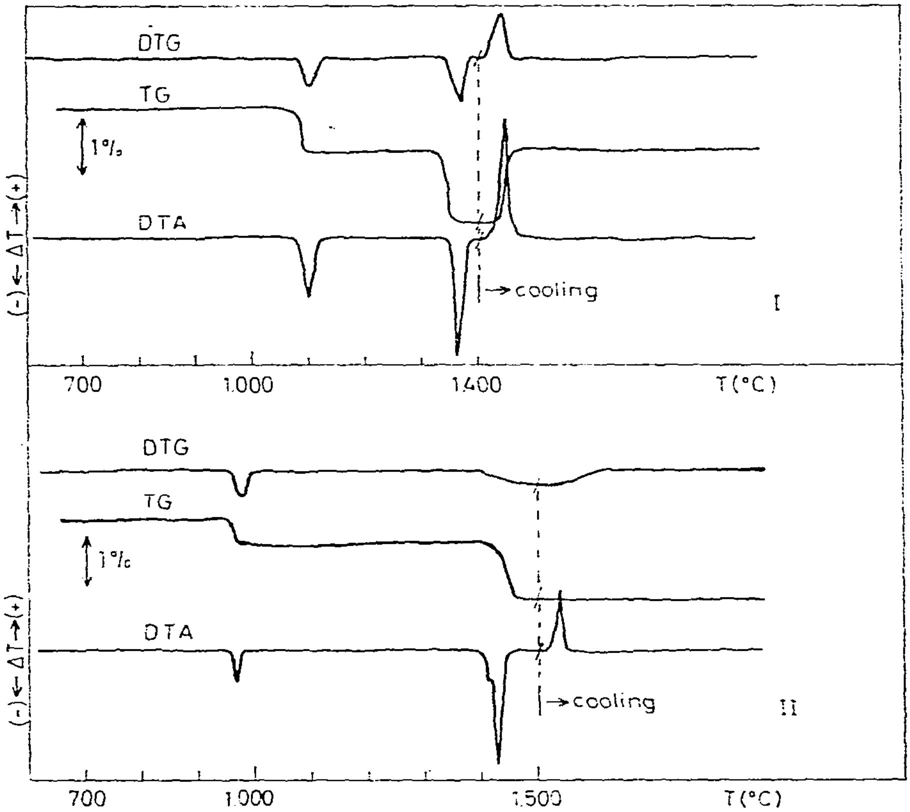

Fig. 2. DTA, TG and DTG curves of I, $SrNH_4[UO_2(C_2H_5COO)_3]_3 \cdot 4H_2O$; II, $BaNH_4[UO_2(C_2H_5COO)_3]_3 \cdot 3H_2O$ ignited at 700°C.

propionate consists of a mixture of a small amount of $Ba_2U_3O_{11}$ and BaO, the major component being a substance whose X-ray diffraction lines agree with those published for the possible new form of UO_3 described by Allpress[14], and no lines of barium diuranate were present. If several samples of barium uranyl propionate are calcined at 800 and 900°C for 1.5 h, the same mixture is formed; BaU_2O_7 is only formed, together with $Ba_2U_3O_{11}$ and U_3O_8 as minor components, when the samples are ignited at 900°C for at least 72 h.

The weight loss observed in the TG curve occurs between 942 and 978°C and the product isolated after this step consists of a mixture of $Ba_2U_3O_{11}$ and U_3O_8, as indicated by the X-ray diffraction diagrams. This temperature is far lower than that corresponding to the thermal decomposition of barium diuranate[14]. However, when barium ammonium uranyl propionate decomposes, the residue consists of a mixture of U_3O_8 and the new form of UO_3, and no lines indicating any other compounds appear in the X-ray diagrams. Bearing in mind that in this complex the U/Ba ratio is 3:1, the new form of UO_3 must be an uranium derivative: it could be the phase $BaO \cdot (2+x)UO_3$, ($x = 0.2$–0.5) described by Ippolitova et al.[15]. The x value calculated for this phase corresponds to 1/3, and the observed weight losses can be justified assuming the reactions (Table 2)

$$1/3\ Ba_2U_3O_{11} + 3\ BaO(2 + 1/3)UO_3 + 1/3\ BaO = 1/3\ Ba_2U_3O_{11} +$$

$$+ Ba_3U_7O_{24} + 1/3\ BaO \xrightarrow{942\text{–}978\,^{\circ}C} 2\ Ba_2U_3O_{11} + 2/3\ U_3O_8 \qquad (4)$$

$$Ba_3U_7O_{24} + 2/3\ U_3O_8 \xrightarrow{942\text{–}972\,^{\circ}C} 3/2\ Ba_2U_3O_{11} + 3/2\ U_3O_8 \qquad (5)$$

It can be concluded that barium diuranate is not formed in the dynamic heating process carried out in the thermal analysis apparatus, and a prolonged ignition at 900 °C is necessary before pure BaU_2O_7 can be obtained[16].

$Ba_2U_3O_{11}$ seems to be stable up to 1500 °C[14], but between 1400 and 1500 °C, a weight loss is observed in the TG curves of both the 2:1 and 3:1 compounds. The residues could not be isolated but if it is assumed that a cubic fluorite phase is formed, the calculated composition from the experimental weight losses would be $BaU_2O_{5.72}$ and $BaU_2O_{6.15}$, respectively.

It must be noted that whatever phases are formed, they do not gain any weight during the cooling process, but in both cases, an exothermic peak appears in the cooling DTA curve whose area is far smaller than that calculated for the corresponding exothermic heating peak.

As has been indicated, between 1000 and 1500 °C, the ternary uranium alkaline-earth oxides with fluorite-type structure seem to be formed. In both series of compounds, the temperatures at which the fluorite-type compounds are formed increase with the ionic radii of the divalent cation, with the exception of the calcium uranium oxide. The values of the unit cell parameters increase from magnesium to strontium (Fig. 3 and Table 3). If it is assumed that some U^{4+} ions are substituted by divalent cations to form the cubic uranates[1], and the coordination number of Ca^{2+} is six, both Ca^{2+} and U^{4+} have the same ionic radii values (1.00 Å)[19] and thus the cubic uranium calcium phase will be more readily formed than when the other alkaline-earth cations have to be included in the crystal cubic lattice.

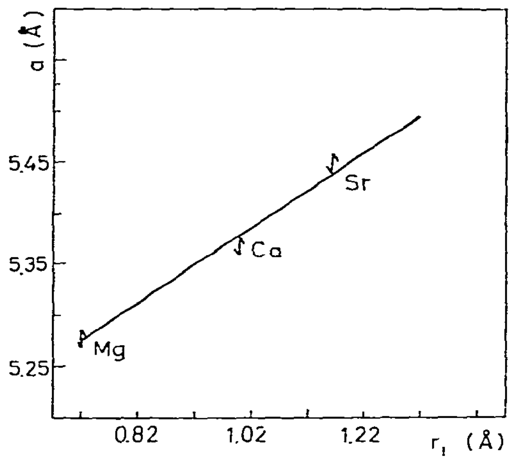

Fig. 3. Plot of the cell constants of some cubic alkaline-earth uranates vs. the ionic radii of the divalent metals.

TABLE 3

CALCULATED CELL CONSTANTS FOR SOME ALKALINE-EARTH URANATES

Compound	*a* (*Å*)	$r_{M^{2+}}$ (*Å*)[19]	*Ref.*
$MgU_2O_{6.04}$	5.281	0.72	7
$MgU_2O_{5.9}$	5.292		7
$Mg_{0.333}U_{0.667}O_{1.986}$	5.283		5
$Mg_{0.333}U_{0.667}O_2$	5.2831		3
MgU_2O_6	5.275		20
CaU_2O_6	5.379	1.00	7
CaU_2O_6	5.378		[a]
$CaU_2O_{6.24}$	5.360		9
SrU_2O_6	5.452	1.16	7
$Sr_{1-x}U_{1+x}O_{4+2x}$	5.456		21

[a] Calculated by us.

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