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Note

POLYNARY URANIUM OXIDES FROM THE THERMAL DECOMPOSITION OF URANYL CARBOXYLATE COMPLEXES

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The thermal decomposition reactions of some uranyl carboxylates with alkaline-earth and transition metals have been described previously [1–4]. Some of them showed quite a similar decomposition scheme with regard to the products isolated during the thermolysis process, as well as their crystal structures. These similarities are quite remarkable in the cobalt and manganese uranyl carboxylates.

However, the formation of manganese uranium mixed oxide with fluorite type structure occurs at a considerably lower temperature than in the cobalt compound, and while the manganese f.c.c. phase is formed in an immediate endothermic reaction, cubic cobalt uranate is obtained through several-steps [3], in which the progressive reduction of uranium(VI) is detected.

Bearing in mind these similarities, quaternary uranium manganese cobalt oxides of several Co^{2+} and Mn^{2+} molar ratios were prepared. These molar ratios clearly modify the temperature of formation and the cell parameters of the new mixed uranium oxides.

EXPERIMENTAL

Several mixtures of manganese and cobalt uranyl propionates, prepared as described elsewhere [2], in molar ratios $Mn^{2+}/Co^{2+} = 0.20/0.80$, 0.50/0.50 and 0.80/0.20, were ground together and ignited at different temperatures in platinum crucibles, using a Heraeus RSK 10 furnace. The thermal assays were made on samples previously heated up to 900°C using a Mettler TA 1 apparatus. X-Ray powder diagrams were obtained with a Philips PW 1310 spectrometer and silicon powder was used as internal standard. After heating at the temperatures indicated in the thermograms, the samples were quenched by immersion in liquid nitrogen. The experimental conditions were as described previously [2].

RESULTS AND DISCUSSION

Thermal studies and X-ray diffraction data

The DTA, TG and DTG heating and cooling curves obtained on mixtures previously ignited up to 900°C are shown in Fig. 1. The compounds identified at this temperature correspond to the mixed manganese cobalt uranium triuranates and monouranates; their cell parameters are shown in Table 1.

Between 955 and 1048°C the decomposition reactions of mixed manganese cobalt uranates occur as indicated by the endothermic effects observed in this temperature range (Table 2), and the corresponding mixed manganese cobalt monouranates are isolated together with uranium oxide U_3O_8. The

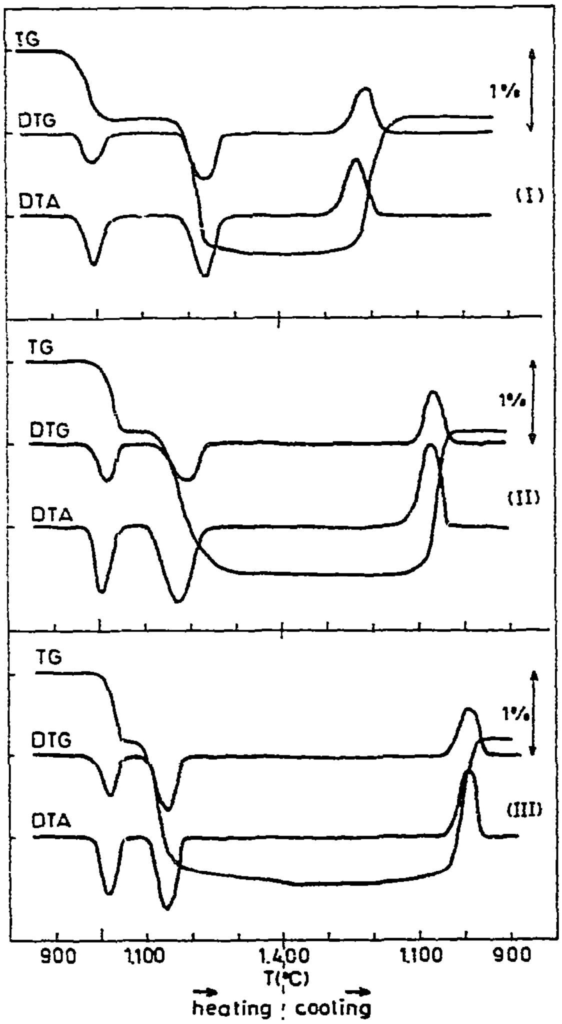

Fig. 1. DTA, TG and DTG curves of mixtures of manganese and cobalt uranyl propionates in molar ratios (I) 0.20/0.80; (II) 0.50/0.50; and (III) 0.80/0.20, previously ignited up to 900°C.

TABLE 1

Experimental and calculated cell parameters (Å) of mixed manganese cobalt uranium oxides

Compound	Experimental			Calculated		
	a		*c*	*a*		*c*
$Mn_{0.2}Co_{0.8}U_3O_{10}$	7.58_5		16.36_8	7.58		16.36_8
$Mn_{0.5}Co_{0.5}U_3O_{10}$	7.58_6		16.44_1	7.58		16.44_0
$Mn_{0.8}Co_{0.2}U_3O_{10}$	7.58_2		16.51_3	7.58		16.51_2
	a	*b*	*c*	*a*	*b*	*c*
$Mn_{0.2}Co_{0.8}UO_4$	6.52_9	6.95_4	6.54_6	6.52_7	6.95_8	6.54_7
$Mn_{0.5}Co_{0.5}UO_4$	6.57_5	6.96_4	6.62_9	6.57_2	6.96_8	6.62_3
$Mn_{0.8}Co_{0.2}UO_4$	6.61_3	6.97_9	6.69_4	6.61_7	6.97_7	6.69_9
		a			*a*	
$Mn_{0.2}Co_{0.8}U_2O_6$		5.26_7			5.26_6	
$Mn_{0.5}Co_{0.5}U_2O_{5.96}$		5.28_2			5.28_1	
$Mn_{0.8}Co_{0.2}U_2O_{5.96}$		5.29_7			5.29_6	

Ref. 5—MnU_3O_{10}: $a=7.58$ Å, $c=16.56$ Å; CoU_3O_{10}: $a=7.58$ Å, $c=16.38$ Å. Ref. 7—$MnUO_4$: $a=6.64_7$ Å, $b=6.98_4$ Å, $c=6.75$ Å. Ref. 6—$CoUO_4$: $a=6.49_7$ Å, $b=6.95_2$ Å, $c=6.49_7$ Å. Ref. 1—MnU_2O_6: $a=5.30_6$ Å. Ref. 2—CoU_2O_6: $a=5.25_7$ Å.

reaction scheme is given by

$$Mn_xCo_{1-x}U_3O_{10} + Mn_xCo_{1-x}UO_4 \rightarrow 2\ Mn_xCo_{1-x}UO_4 + 2/3\ U_3O_8$$

The decomposition temperatures increase with increase in manganese proportion in the mixed triuranates, and this can be explained if we consider the decomposition temperatures of pure manganese or cobalt monouranates, 1015 and 965°C, respectively [5].

Between 1088 and 1240°C the cubic f.c.c. are formed, but for these reversible reactions the temperature of formation of the cubic fluorite phases diminishes as the proportion of manganese in the mixture increases, as would be expected according to the temperature of formation of cubic manganese or cobalt uranates (Table 2). The stoichiometries of the mixed uranates also modify their cell parameters, as can be seen in Table 1 and Fig. 2 in which the volume of the unit cell of the mixed monouranates, the *c* parameter for the triuranates, and the cell parameter *a* for the f.c.c. cubic phases are represented versus the quantity of divalent cations present in the mixed uranates. These values are linearly related to the composition of the mixed uranates and are located between the values of the cell parameters for the single cobalt or manganese uranates.

It is interesting to note that in the mixed triuranates the cell parameter *a* does not change, and it is suggested that it is along the *c* axis where the

TABLE 2

Temperatures of the thermal effects and accumulative weight losses calculated from the DTA and TG curves for the reactions of mixed manganese cobalt uranium oxides

Compound	Thermal effect *T* (°C)	Accumulative wt. losses (%)	
		Exptl.	calcd.
$Mn_{0.2}Co_{0.8}U_3O_{10} + Mn_{0.2}Co_{0.8}UO_4$			
$\downarrow$	955–1026	0.825	0.825
$2\ Mn_{0.2}Co_{0.8}UO_4 + 2/3\ U_3O_8$			
$\downarrow$	1156–1240	2.477	2.476
$2\ Mn_{0.2}Co_{0.8}U_2O_6$			
$Mn_{0.5}Co_{0.5}U_3O_{10} + Mn_{0.5}Co_{0.5}UO_4$			
$\downarrow$	976–1048	0.822	0.827
$2\ Mn_{0.5}Co_{0.5}UO_4 + 2/3\ U_3O_8$			
$\downarrow$	1122–1225	2.579	2.579
$2\ Mn_{0.5}Co_{0.5}U_2O_{5.96}$			
$Mn_{0.8}Co_{0.2}U_3O_{10} + Mn_{0.8}Co_{0.2}UO_4$			
$\downarrow$	989–1048	0.842	0.844
$2\ Mn_{0.8}Co_{0.2}UO_4 + 2/3\ U_3O_8$			
$\downarrow$	1088–1165	2.571	2.569
$2\ Mn_{0.8}Co_{0.2}U_2O_{5.96}$			

Ref. 2

$CoU_3O_{10} \xrightarrow{936-1000°C} CoUO_4 + 2/3\ U_3O_8$

Ref. 4

$MnU_3O_{10} \xrightarrow{980-1020°C} MnUO_4 + 2/3\ U_3O_8$

Ref. 2

$CoUO_4 + 1/3\ U_3O_8 \xrightarrow{1260-1300°C} CoU_2O_6$

Ref. 1

$MnUO_4 + 1/3\ U_3O_8 \xrightarrow{1080-1120°C} MnU_2O_6$

divalent cations are preferably located, and replacement of the uranium atoms by divalent metal ions [5,8] probably takes place in the *c* direction. In the X-ray powder diagrams there is no indication of the existence of any type of structural order, but an electron microscopy study is under way.

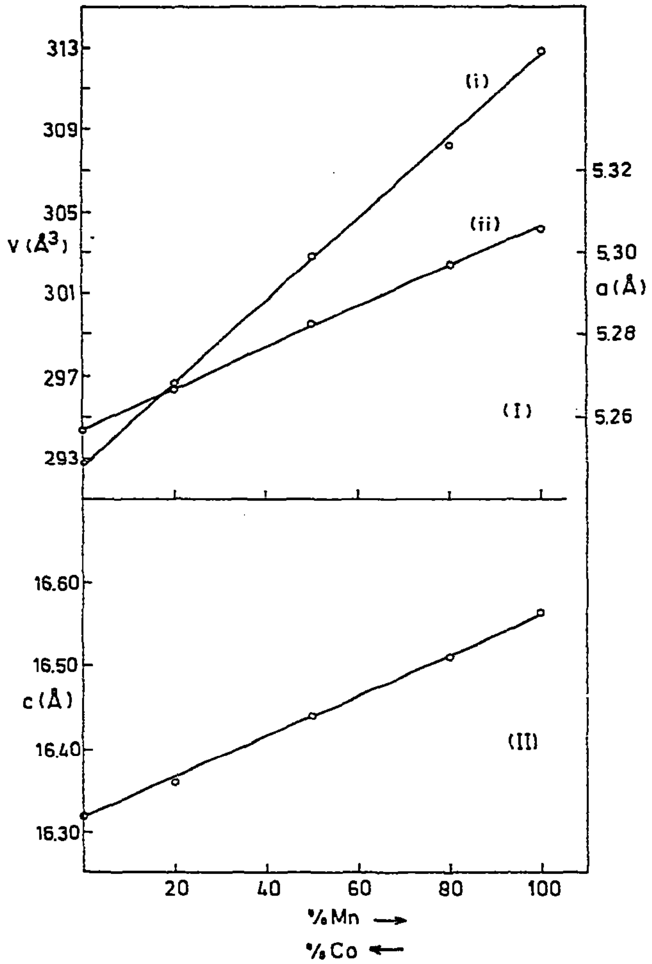

Fig. 2. Plot of I (i) volume of the unit cell of orthorhombic manganese cobalt monouranates, (ii) *a* cell parameters of cubic mixed manganese cobalt uranates; and (II) *c* cell parameters of mixed hexagonal manganese cobalt triuranates vs. the percentage of divalent cations.

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