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The U–Ca–La–O and U–La–O Systems: a Comparative Study*

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Binary and ternary rare earth and actinide compounds crystallizing with the fluorite-type structure support large deviations from stoichiometry, due to the inherent ability of the fluorite lattice to accommodate defects.

In earlier studies on alkaline earth uranates [1], compounds having the face-centered cubic (f.c.c.) fluorite structure have been described; among them, $CaU_2O_{6\pm x}$ transforms reversibly into $CaU_2O_{7\pm x}$ in air at about 1373 K [2, 3]. Solid state studies on the U–La–O system at 1520 K have pointed out the existence of a fluorite-type solid solution, stable over a wide composition and temperature range [4].

We have undertaken a comparative study at 1673 K of the U–La–O system with the U–Ca–O system, when Ca ions are progressively substituted for La ions.

Experimental

Mixed U–Ca–La oxides (Series B) have been prepared by solid state reaction of lanthanum uranyl propionate, $CaCO_3$ and UO_3 (Table I). U–La oxides (Series P) have been prepared by mixing stoichiometric amounts of lanthanum uranyl propionate and La_2O_3 (Table II). All starting mixtures were calcined at 1673 K in air, for periods ranging from 6 to 48 h, and they were then quenched by rapidly removing the crucibles from the furnace.

Results and Discussion

X-ray powder analysis reveal that for the U–Ca–La oxides, the f.c.c. fluorite-type structure is obtained as a single phase over the whole composition range (Table I). Thermal analysis studies indicate that for samples B-1 and B-2, the single fluorite phase reversibly transforms into $CaU_2O_{7\pm x}$ or into a mixture of the cubic phase and $CaU_2O_{7\pm x}$ (Fig. 1a, b). Samples with a higher La content, B-3 to B-6, do not experience any transformation on heating and cooling (Fig. 1c), indicating that for these compounds the face-centred cubic symmetry is preserved over the whole temperature range. The presence of lanthanum ions stabilizes the fluorite structure. On the other hand, all U–La mixed oxides have the f.c.c. type structure, and they are thermally stable over the whole temperature range (Fig. 1c). The ordered rhombohedral R_{III} phase, that is reported to be formed at temperatures below 1473 K (4), has not been observed under these working conditions.

TABLE I. Starting Composition and Calculated Cell Parameter of the Fluorite Phase Obtained in the U–Ca–La–O System

Sample	Composition		Cell parameter *a* (nm)
	Starting molar ratio U:Ca:La	Formulation	
B-1	1.0:0.5:0.0	$(U_{0.67}Ca_{0.33})O_{2\pm x}$	0.5371(3)
B-2	1.0:0.4:0.1	$(U_{0.67}Ca_{0.26}La_{0.07})O_{2\pm x}$	0.5394(3)
B-3	1.0:0.3:0.2	$(U_{0.67}Ca_{0.20}La_{0.13})O_{2\pm x}$	0.5414(2)
B-4	1.0:0.2:0.3	$(U_{0.67}Ca_{0.13}La_{0.20})O_{2\pm x}$	0.5437(7)
B-5	1.0:0.1:0.4	$(U_{0.67}Ca_{0.07}La_{0.26})O_{2\pm x}$	0.5476(2)
B-6	1.0:0.0:0.5	$(U_{0.67}La_{0.33})O_{2\pm x}$	0.5480(2)

TABLE II. Starting Composition and Calculated Cell Parameters of the Fluorite Phase Obtained in the U–La–O System

Sample	Composition		Cell parameter *a* (nm)
	Starting molar ratio U:La	Formulation	
P-1	2.0:1.0	$(U_{0.67}La_{0.33})O_{2\pm x}$	0.547(8)
P-2	1.75:1.0	$(U_{0.64}La_{0.36})O_{2\pm x}$	0.548(3)
P-3	1.50:1.0	$(U_{0.60}La_{0.40})O_{2\pm x}$	0.549(2)
P-4	1.25:1.0	$(U_{0.56}La_{0.44})O_{2\pm x}$	0.550(6)
P-5	1.0:1.0	$(U_{0.50}La_{0.50})O_{2\pm x}$	0.551(1)
P-6	1.0:1.25	$(U_{0.44}La_{0.56})O_{2\pm x}$	0.551(9)
P-7	1.0:1.50	$(U_{0.40}La_{0.60})O_{2\pm x}$	0.553(4)
P-8	1.0:1.75	$(U_{0.36}La_{0.64})O_{2\pm x}$	0.554(3)
P-9	1.0:2.0	$(U_{0.33}La_{0.67})O_{2\pm x}$	0.555(4)

An electron diffraction study has been carried out on both series. Selected area diffraction patterns corresponding to Series B in the zone axis [110] (Fig. 2a, b, c) show that, in addition to the diffraction spots corresponding to the fluorite cell, some diffuse maxima are present in the areas in between. These additional spots always occur along the ⟨111⟩ direction and suggest the presence of short-range interactions [5]. Shape, size and number of diffuse

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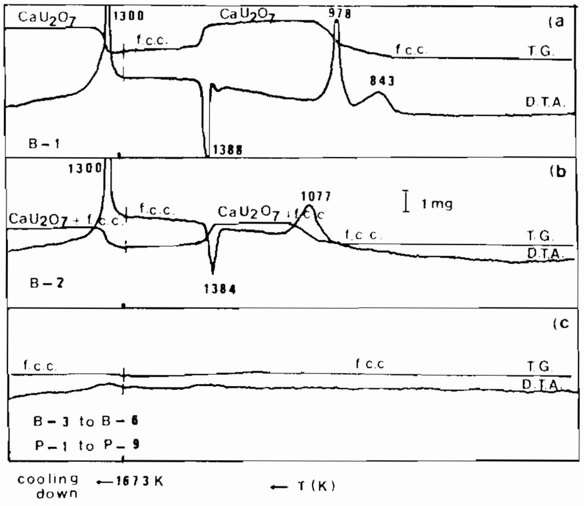

Fig. 1. Differential Thermal Analysis (DTA) and Thermogravimetric (TG) curves obtained for samples: (a) B-1, (b) B-2, (c) B-3 to B-6 and P-1 to P-9. (Heating rate: 10 deg min^{-1}, air flow: 50 ml min^{-1}. About 65 mg sample were used for each run. f.c.c. refers to face-centred cubic fluorite structure.

maxima vary with the composition of the samples. For samples belonging to Series P, similar patterns are obtained (Fig. 2c, d, e). However, it is worth stressing that sample P-5 does not present any diffuse maxima around the spots corresponding to the fluorite cell, indicating the absence of an appreciable concentration of ordered defects. Although Keller [4] has shown that the stoichiometric composition $(U, La)O_{2.0}$ ranges from 0 to 66.7 mol% $LaO_{1.5}$, electron diffraction data suggest that the only stoichiometric composition corresponds to $(U_{0.5}La_{0.5})O_2$ (sample P-5).

A likely explanation of the role of lanthanum in stabilizing the fluorite phase is the formation of clusters containing the rare earth ions [6]; such clusters should then be responsible for the observed diffuse maxima.

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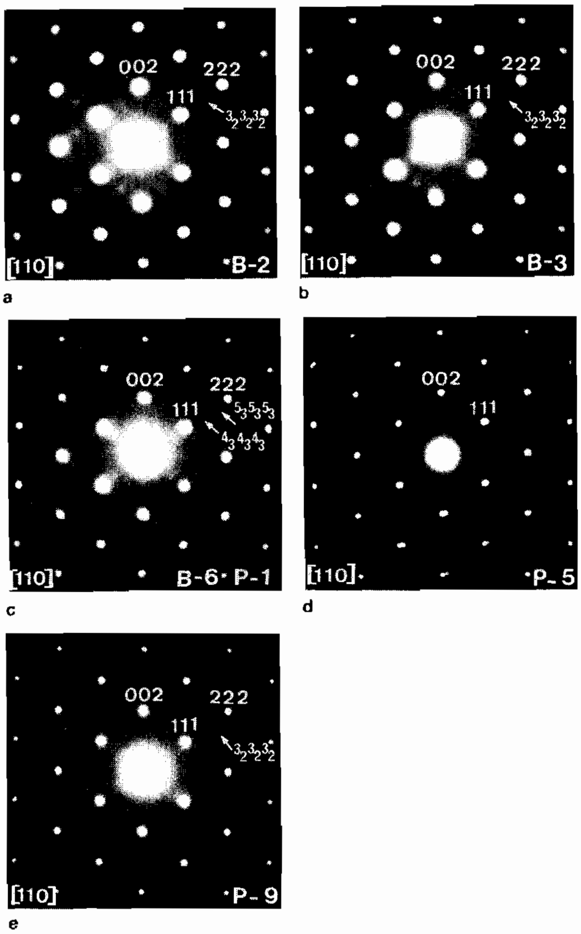

Fig. 2. Electron diffraction patterns in the zone axis [110], for samples: (a) B-2, (b) B-3, (c) B-6 and P-1, (d) P-5 and (e) P-9.

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