

## 726. *The Oxides of Uranium. Part VIII.\* The System Uranium Dioxide–Yttria.*

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The mixed-oxide system  $\text{UO}_2\text{-Y}_2\text{O}_3$  has been investigated by *X*-ray powder techniques. A range of solid solutions, with pseudo-fluorite structures, exists between 0 and 78 moles % of  $\text{YO}_{1.5}$ , whose cell constant is a non-linear function of composition. Between 78 and 96 moles % of  $\text{YO}_{1.5}$  there is an immiscibility gap. Beyond 96 moles % of  $\text{YO}_{1.5}$  a solid solution range occurs based upon the  $\text{Tl}_2\text{O}_3$  structure. Density measurements show that all these solid solutions have an anion-vacancy structure. Samples were prepared and handled *in vacuo*, as they absorb oxygen at room temperature.

THE structures of uranium dioxide and yttria are related. Uranium dioxide has a fluorite-type lattice with a cube-cell edge of  $5.457 \text{ kX}$ ; yttria has a larger cubic unit cell of the  $\text{Tl}_2\text{O}_3$  type, with an edge of  $10.585 \text{ kX}$ . The structure of yttria can be considered in terms of a fluorite pseudo-cell, with an edge of  $5.293 \text{ kX}$ , in which the tervalency of yttrium causes an ordered omission of oxygen from the anion sub-lattice. These oxides' structural and dimensional similarity makes it likely that they will form anomalous solid solutions. This possibility was therefore investigated, extending the work of Anderson *et al.* on uranium dioxide to include a related mixed oxide with a defective anion sub-lattice.

Anderson, Burden, and Johnson<sup>1</sup> showed that solid solutions with the fluorite structure could be prepared by heating the mixed oxides at  $2000^\circ \text{C}$  *in vacuo*. Anderson, Ferguson, and Roberts<sup>2</sup> showed that such preparations were oxidised rapidly in air at room temperatures. The existence of a wide range of fluorite-type solid solutions in this system was confirmed by Hund *et al.*<sup>3</sup> None of these determined the oxygen content of the preparations and it appears<sup>4,5</sup> that their samples were oxidised, and not typical of the system uranium dioxide–yttria. We prepared mixed crystals containing uranium(IV) and anion defects by an already proved method,<sup>2,5</sup> and examined them by *X*-ray diffraction. Ferguson and Roberts<sup>5</sup> have studied corresponding mixed crystals in the system U–Y–O in which the anion sub-lattice is intact and the uranium valency exceeds 4. These studies confirm and extend the results of Hund and his co-workers.

### EXPERIMENTAL

*Materials.*—Pure uranium oxide was used. Yttria, purchased from New Metals and Chemicals, Ltd., London, was shown spectroscopically to be 99.99% pure.

*Preparation.*—The rapid oxidation of samples in air at room temperature necessitated their preparation by a technique with use of a uranium getter, followed by manipulation in a vacuum. The mixed crystals were prepared by co-precipitating the hydroxides from solutions containing known amounts of yttrium and uranyl nitrates by addition of excess of carbon dioxide-free aqueous ammonia. The precipitate was decomposed at  $375^\circ \text{C}$ , partially reduced by heating it overnight at  $1400^\circ$  in a stream of carbon monoxide, then made into a pellet and heated to  $2000^\circ$  *in vacuo*. These ignitions increased the crystallite size and thus improved the final *X*-ray diffraction photographs. The product was finely ground and reduced *in vacuo* by heating it with clean, cast uranium at  $950^\circ\text{--}1050^\circ$  in a sealed, evacuated silica tube. A silica jacket around this tube was evacuated continuously to minimise diffusion of gases into the reaction vessel. After an arbitrary heating time (1–3 days) the sample was shaken into an attached ball-mill, ground, and then shaken into *X*-ray capillaries and the density holder.

\* Part VII, *J.*, 1955, 3946.

<sup>1</sup> Anderson, Burden, and Johnson, 1951, unpublished work.

<sup>2</sup> Anderson, Ferguson, and Roberts, *J. Inorg. Nuclear Chem.*, 1955, **1**, 340.

<sup>3</sup> Hund, Peetz, and Kottenhahn, *Z. anorg. Chem.*, 1955, **278**, 184.

<sup>4</sup> Ferguson, Thesis, London, 1956.

<sup>5</sup> Ferguson and Roberts, unpublished work.

*X-Ray Measurements.*—Samples, contained in evacuated, 0.3 mm. diameter, thin-walled, Pyrex capillaries, were examined in 19 cm. Unicam Debye-Scherrer cameras. Nickel-filtered Cu- $K_{\alpha}$  radiation was used;  $\lambda_{\alpha_1}$  was assumed to be 1.537396  $kX$ , and  $\lambda_{\alpha_2}$  1.541232  $kX$ . Cell constants were obtained by extrapolation to  $\theta = 90^\circ$  by use of Nelson and Riley's method.<sup>6</sup> The accuracy of measurement of the cube cell edge depends upon the degree of crystallinity of the sample, and errors are quoted as recommended by Henry, Lipson, and Wooster.<sup>7</sup>

*Density.*—Sample volumes were determined by measuring the displacement of a known volume of helium. This method<sup>8</sup> does not expose samples to the air; the sample is contained in a tube sealed by a waxed-in plunger, which is opened by softening the wax with a low helium pressure on the outside. The measured densities were consistent to about 0.05 g./c.c.

## RESULTS AND DISCUSSION

Under our conditions of preparation, the system uranium dioxide-yttria contains two solid solution ranges separated by an immiscibility gap. One solid solution range extends from 0 to 65 moles % of  $YO_{1.5}$  and is based upon the fluorite lattice, the other extends from 96 to 100 moles % of  $YO_{1.5}$  and is based upon a  $Tl_2O_3$ -type lattice. The measured cell edges of samples are given in Table I.

The properties of the solid solutions with pseudo-fluorite lattices vary continuously with composition. It is however convenient to consider different composition ranges separately. From 0 to 25 moles % of  $YO_{1.5}$  there is a nearly linear relation between the cell edge and composition of samples. Brauer and Gradinger<sup>9</sup> suggested that this relation may be extrapolated to 100%  $YO_{1.5}$  to give a value corresponding to an unknown modification of yttria with a pseudo-fluorite structure. From a series of extrapolations in related mixed-oxide systems these workers have suggested the relation:

$$a_f = 0.78705 (a_o/2) + 1.226 \text{ (in } kX\text{)}$$

where  $a_o$  is the observed cell edge of an oxide with the  $Tl_2O_3$  structure, and  $a_f$  is the extrapolated value corresponding to its hypothetical pseudo-fluorite form. We find an extrapolated value of 5.398  $kX$ , which agrees well with the value 5.391  $kX$  calculated from the above formula. A similar value of 5.393  $kX$  is obtained from the system ceria-yttria.<sup>10</sup>

Beyond 25 moles % of  $YO_{1.5}$  the relation between cube cell edge and composition departs from linearity, but the slope of the curve is continuous and not as suggested earlier.<sup>2</sup> X-Ray powder photographs of compositions between 0 and 50 moles % of  $YO_{1.5}$  show that these solid solutions have pseudo-fluorite structures. However, beyond 50 moles % of  $YO_{1.5}$  additional faint reflexions appear which correspond to a transition from a pseudo-fluorite to a  $Tl_2O_3$  structure. This transition is not, however, continuous and an immiscibility gap appears between 78 and 96 moles % of  $YO_{1.5}$ . From 96 to 100 moles % of  $YO_{1.5}$  there is a narrow solid-solution range based upon the  $Tl_2O_3$  structure.

At 76.3 moles % of  $YO_{1.5}$  an unidentified phase was prepared, but no attempts were made to determine the composition range over which it is stable.

Formation of solid solution between these oxides may involve one of two mechanisms. To maintain a charge balance in the crystal, either vacancies must appear on the anion sub-lattice or excess of cations must be accommodated on interstitial positions. A comparison of the measured densities (Table 2) with those calculated on the basis of the above models indicates that these solid solutions contain vacancies on the anion sub-lattice. The measured densities are about 0.2 g./c.c. lower than those calculated; similar discrepancies have been discussed by others.<sup>11</sup>

<sup>6</sup> Nelson and Riley, *Proc. Phys. Soc.*, 1945, **57**, 160.

<sup>7</sup> Henry, Lipson, and Wooster, "The Interpretation of X-Ray Diffraction Photographs," Macmillan and Co., London, 1951, p. 191.

<sup>8</sup> Anderson, Harper, Moorbath, and Roberts, 1952, A.E.R.E. Report C/R 886.

<sup>9</sup> Brauer and Gradinger, *Naturwiss.*, 1951, **24**, 559.

<sup>10</sup> Martin, personal communication.

<sup>11</sup> Anderson, Edgington, Roberts, and Wait, *J.*, 1954, 3324.

TABLE 1. *Composition, cube cell edge and lattice type of preparations.*

(All cube cell edges are quoted in terms of a fluorite cell, or sub-cell.)

Composition (moles % of YO <sub>1.5</sub> )	Cube cell edge ( <i>kX</i> )	Lattice type	Composition (moles % of YO <sub>1.5</sub> )	Cube cell edge ( <i>kX</i> )	Lattice type
0.00	5.457 ± 0.001	Fluorite	70.0	5.365 ± 0.005	Fluorite
10.1	5.451 ± 0.001	"	70.1	5.349 ± 0.002	"
15.0	5.449 ± 0.003	"	71.2	5.352 ± 0.005	"
20.7	5.441 ± 0.001	"	75.0	{ 5.366 ± 0.005 5.332 ± 0.005 }	See †
29.4	5.437 ± 0.005	"	76.3	—	Unknown phase
30.0	5.436 ± 0.005	"	79.5	5.335 ± 0.002	Fluorite
33.8	5.4250 ± 0.0005	"	81.1	5.35 ± 0.01	" *
38.6	5.422 ± 0.002	"	87.0	{ 5.338 ± 0.002 5.294 ± 0.002 }	Fluorite } 2 phase
40.0	5.417 ± 0.002	"	90.0	{ 5.341 ± 0.005 5.303 ± 0.002 }	Fluorite } 2 phase
47.4	5.405 ± 0.005	"	93.8	5.301 ± 0.002	Tl <sub>2</sub> O <sub>3</sub>
50.0	5.400 ± 0.002	" *	95.9	5.301 ± 0.001	"
55.0	5.391 ± 0.003	"	98.2	5.2950 ± 0.0005	"
59.6	5.384 ± 0.005	"	100.0	5.2925 ± 0.0005	"
60.9	5.375 ± 0.003	"			
63.8	5.37 ± 0.05	"			
65.0	5.367 ± 0.005	"			

\* The X-ray film exhibits a background of faint Tl<sub>2</sub>O<sub>3</sub>-type reflexions.

† Two coexisting fluorite phases. The sample was prepared in duplicate.

TABLE 2. *Comparison of calculated and observed densities.*

Composition (moles % of YO <sub>1.5</sub> )	Cube cell edge ( <i>kX</i> )	Theor. density (g./c.c.) on the basis of		Measured (g./c.c.)
		Anion vacancies	Interstitial cations	
10.1	5.451 ± 0.001	10.36	10.63	10.01 ± 0.07
20.7	5.441 ± 0.001	9.74	10.27	9.46 ± 0.05
47.4	5.405 ± 0.005	8.18	9.28	8.09 ± 0.04
59.6	5.384 ± 0.005	7.46	8.77	7.57 ± 0.07
70.1	5.349 ± 0.002	6.83	8.36	6.85 ± 0.05
79.5	5.335 ± 0.002	6.31	7.87	6.01 ± 0.02
90.0	5.303 ± 0.002	5.69 *	7.35 *	5.39 ± 0.05

\* Calc. on the basis of the Tl<sub>2</sub>O<sub>3</sub> phase.

We could not determine whether our preparations are thermodynamically stable at room temperature. The cation distribution in samples may be characteristic of temperatures as high as 2000°, but the distribution of the more mobile anions is probably typical of temperatures below 1000°. Slight variations in preparative conditions may alter the distribution of ions in samples and explain the confusion in the measured cell constants between 65 and 78 moles % of YO<sub>1.5</sub>. We have been unable to decide whether the latter region represents an extension of the pseudo-fluorite solid solution range or not.

Preparations containing less than about 55 moles % of YO<sub>1.5</sub> are oxidised rapidly in air at room temperature, changing abruptly from brown to black, and the unit cell of the crystal contracts as the uranium valency rises above four. The oxidation probably involves a rapid diffusion of oxygen anions through the anion sub-lattice. A similar diffusion must accompany the reduction of samples by uranium. The mobility of oxygen in the fluorite lattice has already been noted in uranium dioxide, but there the oxygen enters interstitial positions.

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