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On the existence of a compound in the system yttrium-uranium-oxygen.

By GEORGE A. CHASE, *General Electric Company, Aircraft Nuclear Propulsion Department, Cincinnati 15, Ohio, U.S.A.*

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In early 1956, during the initial studies of the phase relationships exhibited by various air-reacted mixtures of uranium dioxide and yttrium sesquioxide, a new compound was observed. Since then, studies of the rate and mechanism of the formation of this compound and thermogravimetric analyses have been made by Felten & Juenke (1960). The optical data was obtained on single crystals of the compound by McVay (1960) and a structure analysis is being made. The fully oxidized compound has the ideal formula $UO_3.3Y_2O_3$ (weight gain data gave $UO_{2.90}$) and has been found to exist over the range 70·0–71·5 wt.% Y_2O_3 at 1800–1850 °C. It is formed very rapidly at 1800 °C. in air and is stable to at least 1950 °C.

The true cell of the compound is rhombohedral with the following lattice parameters (70·0 wt.% Y_2O_3).

$$a_0 = 6{\cdot}5297 \text{ Å}, \quad \alpha = 99° 3'.$$

The corresponding hexagonal cell constants are:

$$a_0 = 9{\cdot}934 \pm 0{\cdot}001, \quad c_0 = 9{\cdot}364 \pm 0{\cdot}001 \text{ Å}.$$

The above values give a calculated density of 6·00 g.cm.$^{-3}$. The pycnometric density is 5·91 g.cm.$^{-3}$. Petrographic analyses show the material to be uniaxial negative with $N_0 = 2{\cdot}06$ and $N_e = 2{\cdot}02$.

The powder diffraction pattern in Table 1 was obtained using Nickel-filtered Cu $K\alpha$ radiation on a General Electric diffractometer scanning at 0·1° (2θ) per minute. Hexagonal indices are listed. Lattice parameters were computed on an IBM 7090 according to the method of Mueller, Heaton & Miller (1960) using 1·54050 and 1·54434 Å for Cu $K\alpha_1$ and $K\alpha_2$ wavelengths respectively.

That the rhombohedral phase has an extended range of homogeneity is indicated by the fact that an isostructural phase has been prepared at a nominal composition of 55 wt.% yttria upon reacting in hydrogen for two hours at 1510 °C. Its hexagonal cell constants are

$$a = 9{\cdot}999, \quad c = 9{\cdot}358 \text{ Å}.$$

Unpublished work by E.F.Juenke has also established the existence of isomorphous phases in air-reacted compositions of UO_2 with the rare earths Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. Although the lattice constants have not been measured, the effect of the lanthanide contraction is clearly evident on the films.

Since submitting this paper for publication, the author has become aware of the work of Baenziger, Eick, Schuldt & Eyring (1961) on the rhombohedral phases Tb_7O_{12} and Pr_7O_{12}, which appear to be isostructural with the UY_6O_{12} reported above. It is interesting to note that with two different metal atoms almost all of Baenziger's calculated values of $1/d^2$ are observed.

References

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Table 1. *X-ray data*

d	Rel. int.	*hkl*	*d*	Rel. int.	*hkl*	*d*	Rel. int.	*hkl*	*d*	Rel. int.	*hkl*
6·35	14	011	1·509	3	234	1·072	2	542	0·8978	*	561, 911
4·97	1	110	1·489	3	116	1·070	3	713	0·8903		267, 636
4·12	20	102	1·474	3	135	1·056	2	507, 606	0·8856		192, 652
3·92	16	201	1·468	4	512	1·051	3	138	0·8807		339
3·17	5	022	1·413	3	405	1·045	2	721	0·8698		831
3·12	40	003	1·371	3	306	1·033	3	526	0·8597		735
3·08	100	121	1·359	3	325	1·028	5	355, 705	0·8569		0,10,1
2·869	6	300	1·335	6	424	1·024	4	633	0·8502		457
2·673	30	212	1·322	2	226	1·018	2	119	0·8476		358
2·644	7	113	1·300	2	611	1·011	2	157	0·8462		10,0,2
2·313	3	311	1·290	2	154	1·007	*	328	0·8421		609
2·125	7	132	1·277	2	207	0·9976		454	0·8416		564, 914
2·111	9	303	1·260	2	523	0·9850		812	0·8356		628
2·056	5	204	1·242	2	440	0·9719		347	0·8302		529
1·943	3	223	1·237	4	127	0·9627		371	0·8183		834
1·931	3	231	1·228	4	245	0·9589		724	0·8150		906
1·900	30	124	1·219	7	531, 071	0·9498		248	0·8126		655, 195
1·877	25	410	1·211	2	344	0·9479		732	0·8101		481
1·830	4	105	1·200	6	416	0·9387		820	0·8076		0,10,4
1·819	6	322	1·192	2	515	0·9367		617	0·8044		826, 187
1·671	3	314	1·189	6	352, 702	0·9203		716	0·8022		548
1·623	8	215	1·160	3	108	0·9167		275	0·8009		1,5,10; 842
1·609	20	413	1·154	3	443	0·9143		903	0·7954		930
1·602	12	421	1·107	2	237	0·9100		419	0·7916		4,0,11; 385
1·561	3	006	1·101	3	218	0·9093		644	0·7841		377
1·536	10	242	1·088	6	534, 074	0·9040		537, 077			
1·524	4	151	1·084	4	630	0·8990		823			

* Intensities not measured but in range 2–4.