the protons in the silyl group decreases. This effect is just the opposite of that predicted from simple electronegativity considerations and parallels the variations in chemical shifts of the CH_3 group in ethyl halides[14] and of the SiH_3 group in disilanyl halides.[15] The increase in shielding on going from the SiH_3 group to the SiH group is explicable in terms of the reduced electronegativity of silicon compared with hydrogen.

The H–H and ^{29}Si–H coupling constants are given in Table II. They are of the same order of magnitude as those reported by Abedini, *et al.*[15] Although the mechanism of the spin–spin interaction is not clearly understood, it is logical to expect that if this interaction is through the bonds it should decrease with an increase in the number of interposed bonds. The value of 3.5 to 4 c.p.s. for the coupling constant of vicinal protons in the higher silanes and the value of 2.75 c.p.s. of geminal protons in silane reported by Ebsworth and Turner[16] indicate that something other than mere "through-bond" interaction is involved. In the case of saturated hydrocarbons, vicinal proton coupling constants lie in the range of 5–8 c.p.s., and the geminal proton coupling constant in methane is 12.4 c.p.s.[17]

TABLE I

CHEMICAL SHIFTS IN P.P.M. (±0.02) TO LOW FIELD OF TMS

Compound	$-SiH_3$	$-SiH_2-$	$>SiH$
Si_2H_6	3.26		
Si_3H_8	3.36	3.18	
n-Si_4H_{10}	3.36	3.26	
i-Si_4H_{10}	3.42		2.93

TABLE II

COUPLING CONSTANTS IN C.P.S.

Compound	$H_3Si{-}SiH_n$ ±0.2	$^{29}Si{-}H_3$ ±1.0	$^{29}Si{-}H_2$ ±1.0
Si_2H_6	3.5	199	
Si_3H_8	4.0	199	194
n-Si_4H_{10}	3.7	199	197
i-Si_4H_{10}	4.0	192 ± 5	

Acknowledgment.—This research was supported by the U. S. Atomic Energy Commission.

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[14] B. P. Dailey and J. N. Shoolery, *J. Am. Chem. Soc.*, **77**, 3977 (1955).

[15] M. Abedini, C. H. Van Dyke, and A. G. MacDiarmid, unpublished data.

[16] E. A. V. Ebsworth and J. J. Turner, *J. Chem. Phys.*, **36**, 2631 (1962).

[17] Reference 13, pp. 193, 236.

CONTRIBUTION FROM THE GENERAL ELECTRIC COMPANY,
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Crystal Chemistry of the Rhombohedral $MO_3 \cdot 3R_2O_3$ Compounds[1]

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Two new rhombohedral phases were found in the UO_2–UO_3–Y_2O_3 ternary system. Both of these phases exist at a fixed oxygen-to-metal atom ratio, one of which (designated rhomb 1) can be expressed by the formula $U_mY_{7-m}O_{12}$ where m = 1 to 3.4. For values of m greater than 2.8, low temperature oxidation produces the second rhombohedral structure (designated rhomb 2) of composition $U_nY_{8-n}O_{15}$ where n = 2 to 3.9. The rhombohedral 1 crystal structure is characteristic of a large family of new compounds formed between rare earth oxides and UO_3, WO_3, or MoO_3. Crystallographic data on these isostructural compounds are presented. The influence of ionic size and valence upon the formation and stability of this structure are discussed.

Introduction

Many generic families of mixed oxide compounds are well-known. Some of these are the group II–III spinels, II–IV perovskites, and III–IV pyrochlores. However, little or no information has been published on compound formation between III–VI oxides. In 1962, Chase[2a] revealed the existence of a rhombohedral phase in the U–Y–O system at the composition $UO_3 \cdot 3Y_2O_3$. Since then, a paper by Borchardt[2b] on yttrium–tungsten oxides gave data on the isostructural compound $WO_3 \cdot 3Y_2O_3$.

During a study of the phase relations in the system UO_2–UO_3–Y_2O_3,[3] it was found that a rhombohedral phase persisted over a wide range of compositions. Since the nature and behavior of the III–VI mixed oxides are unknown, this investigation was undertaken to study the crystal chemistry of this new family of compounds.

Experimental

Sample Preparation.—The metal oxides of greater than 99% purity were blended in a Mix-R-Mill (Spex Industries). To vary oxygen concentration, reactions were carried out in dry air, in hydrogen (~−46° dew point), and in a mixture of 10 parts CO_2 to 1 part CO at temperatures between 1000 and 1700°. Platinum or yttria-stabilized zirconia crucibles were used in the

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[1] (a) This paper originated from work sponsored by the Fuels and Materials Development Branch, Division of Reactor Development, U. S. Atomic Energy Commission, under Contract AT(40-1)-2847; (b) presented in part at the Basic Science Division Meeting, American Ceramic Society, Washington, D. C., Oct. 7–8, 1963.

[2] (a) G. A. Chase, *Acta Cryst.*, **15**, 91 (1962); (b) H. J. Borchardt, *Inorg. Chem.*, **2**, 170 (1963).

[3] S. F. Bartram, E. F. Juenke, and E. A. Aitken, *J. Am. Ceram. Soc.*, **47**, 171 (1964).

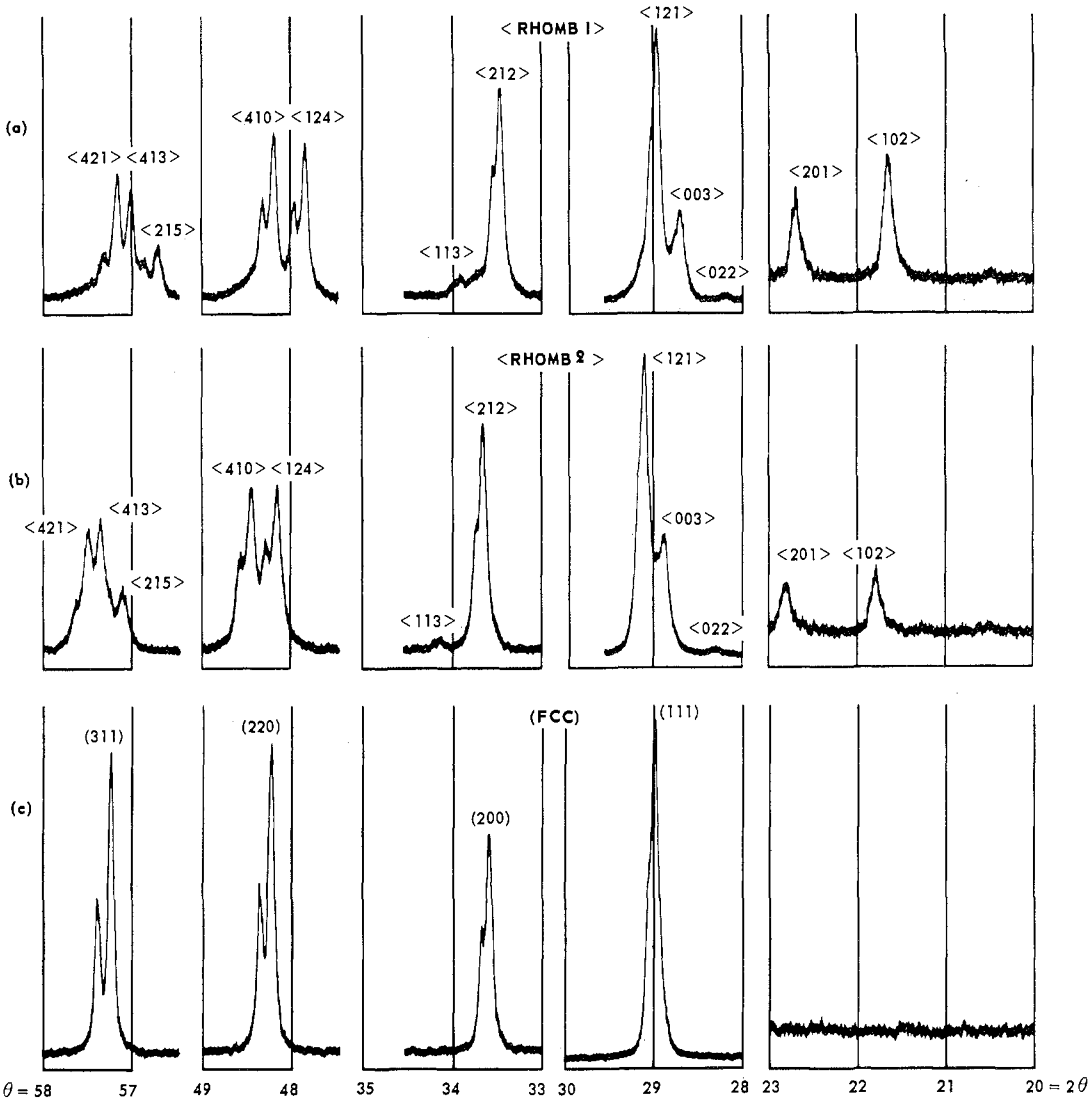

Fig. 1.—Phase changes in $2UO_{2+x}\cdot 3Y_2O_3$: (a) reduced at 1540° in H_2; (b) oxidized at 340° in O_2; (c) oxidized at 1950° in air.

preparation of the mixed oxide phases in air and CO_2–CO atmospheres. Molybdenum boats were used for reactions in hydrogen. Reaction times were from 4 to 24 hr.

X-Ray Analysis.—X-Ray diffraction analyses were made with a Norelco high-angle diffractometer using nickel-filtered copper $K\alpha$ radiation. Relative amounts of phases present were determined from comparisons of the strongest peak intensities. The limit of detection with this method was about 5 vol. % for most preparations, increasing to 10 vol. % for those compositions in which the reflections were nearly superimposed. Powder diffraction patterns recorded on a strip chart over the 2θ range from 100 to 160° were used for lattice parameter determinations. Lattice constants were calculated using the IBM 7090 computer according to the method of Mueller, Heaton, and Miller.[4]

Single crystal rotation and Weissenberg photographs were made to determine reflection intensities and the crystal symmetry of the rhombohedral $UO_3\cdot 3Y_2O_3$ compound. With this information the powder diffractometer patterns were successfully indexed.

Chemical Analyses.—Chemical compositions of the uranium compounds were determined by analysis. Tetravalent uranium was determined by dissolution in phosphoric acid under nitrogen and titration with a standard ceric sulfate solution. Total uranium was determined by the standard lead reductor–ceric titration method with ferroin indicator. Hexavalent uranium was obtained by difference. The praseodymium compound, $UO_3\cdot 3Pr_2O_3$, was analyzed for Pr since this element exhibits multivalency. The results indicated the praseodymium to be present almost exclusively in the trivalent state.

Transpiration Studies.—Transpiration measurements were conducted to determine the vapor pressure of UO_3 gas over the $UO_3\cdot 3R_2O_3$ compounds in the temperature range from 1100 to 1700° in dry air at 1 atm. pressure. The flow rates were varied to ensure that saturation of the carrier gas was achieved. The sample was contained in a rhodium boat enclosed in a high density alumina tube furnace. The volatile component was collected on a platinum collector tube inserted into the furnace. The uranium oxide deposits were removed from the collector by repeated internal elutions with hot concentrated nitric acid, and the solutions were analyzed for uranium by the fluorometric method. The partial pressure of the volatile component (UO_3) was calculated assuming Dalton's law of partial pressures and the ideal gas law.

Results

Characterization of the Rhombohedral Phases.—X-Ray powder patterns of these new compounds are quite complex and could not at first be unequivocally indexed. However, the fortuitous discovery of small

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[4] M. H. Mueller, L. Heaton, and K. T. Miller, *Acta Cryst.*, **13**, 828 (1960).

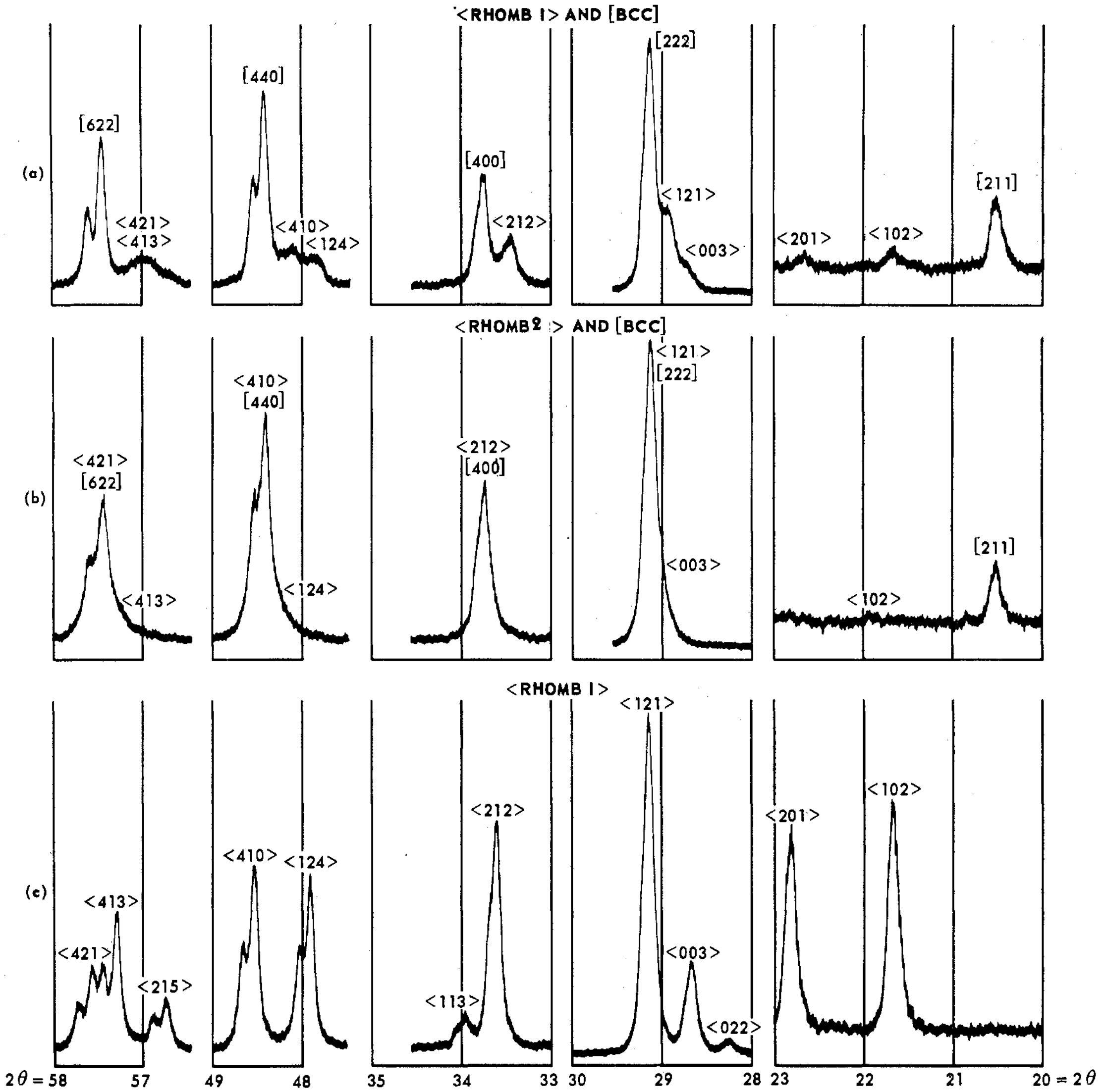

Fig. 2.—Phase changes in $1UO_{2+x} \cdot 3Y_2O_3$: (a) reduced at 1700° in H_2; (b) oxidized at 285° in air; (c) oxidized at 1370° in air.

single crystals of the $UO_3 \cdot 3Y_2O_3$ compound in one specimen permitted the determination of its crystal symmetry as rhombohedral. This structure (rhomb 1) exists at a definite oxygen-to-metal ratio of 12:7 and was observed to occur in the U–Y–O system over the composition range from about $17UO_{2.17} \cdot 18Y_2O_3$ to $UO_3 \cdot 3Y_2O_3$. The general formula for this phase can be written as $U_mY_{7-m}O_{12}$ where m varies from 1 to 3.4.

Oxidation of the above compositions with m values greater than 2.8 produces a closely related metastable phase which is also rhombohedral and has been designated rhomb 2. This phase occurs at a constant oxygen-to-metal ratio of 15:8 over the composition range from $17UO_{2.67} \cdot 18Y_2O_3$ to $2UO_3 \cdot 3Y_2O_3$. Its formula can thus be written as $U_nY_{8-n}O_{15}$ where n varies from 2 to 3.9. When heated at temperatures above 1000°, this structure rearranges to give a face-centered cubic solid solution of the fluorite type. These phase inversions for the composition $2UO_{2+x} \cdot 3Y_2O_3$ $(0 < x < 1)$ are illustrated in Fig. 1, which reproduces selected portions of their X-ray diffraction patterns. Note the marked similarity between the rhomb 1 and rhomb 2 structures; the major differences are a shrinkage of the unit cell and changes in the relative line intensities.

For comparison, Fig. 2 shows the same regions of the diffraction patterns for the composition $1UO_{2+x} \cdot 3Y_2O_3$ $(0 < x < 1)$. In this case, reduction at 1700° produces a mixture of rhomb 1 phase and a body-centered cubic phase. Low temperature oxidation has little effect upon the b.c.c. phase, but the contraction of the rhombohedral phase causes its reflections to coincide with the strong cubic peaks, making it difficult to detect. At temperatures above 1000°, rearrangement of the structure produces single phase rhomb 1 when fully oxidized to $1UO_3 \cdot 3Y_2O_3$. Representative X-ray diffraction patterns for both phases are given in Table I.

Hexagonal unit cell dimensions and volumes of the rhombohedral phases are compared in Table II, which also shows the corresponding cubic cell dimensions. It is noteworthy that the space requirements are nearly the same irrespective of structure, indicating

TABLE I

X-RAY DIFFRACTION PATTERNS FOR RHOMBOHEDRAL PHASES

Hexagonal *hkl*	$17UO_{2.17} \cdot 18Y_2O_3$ *d*	Rel. int.[a]	$UO_3 \cdot 3Y_2O_3$ *d*	Rel. int.[a]	$2UO_3 \cdot 3Y_2O_3$ *d*	Rel. int.[a]
011	6.37	w	6.35	mw	6.30	w
110	5.02	vw	4.97	vw	4.97	vw
102	4.12	mw	4.12	m	4.09	w
201	3.94	w	3.92	mw	3.91	w
022	3.19	vw	3.17	w	3.15	vw
003	3.12	ms	3.12	ms	3.09	ms
121	3.10	vs	3.08	vs	3.07	vs
300	2.897	vw	2.869	w	2.864	vw
212	2.688	ms	2.673	ms	2.659	ms
113	2.650	mw	2.644	w	2.618	vw
311	2.334	vw	2.313	vw	...	...
132	2.143	w	2.125	w	2.111	vw
303	2.123	w	2.111	mw	2.100	vw
204	2.060	vw	2.056	w	2.039	vw
223	1.955	vw	1.943	vw	...	...
231	1.950		1.931	vw	1.930	vw
124	1.906	m	1.900	ms	1.888	ms
410	1.896	m	1.877	ms	1.874	ms
105	1.830	w	1.830	w	...	...
322	1.834		1.819	w	...	...
314	...	...	1.671	vw	...	...
215	1.627	w	1.623	w	1.611	mw
413	1.620	m	1.609	m	1.604	m
421	1.617	mw	1.602	mw	1.600	m
006	1.560	vw	1.561	vw	1.540	vw
242	1.549	w	1.536	mw	1.532	w
151	1.539	vw	1.524	w	1.532	
234	1.518	vw	1.509	vw	...	...
116	...	...	1.489	vw	...	...
135	1.479	vw	1.474	vw	...	...
512	1.480		1.468	w	...	...
405	...	...	1.413	vw	...	...
306	...	...	1.371	vw	...	...

[a] v, very; s, strong; m, medium; w, weak.

TABLE II

UNIT CELL DIMENSIONS FOR THE $UO_{2+x} \cdot Y_2O_3$ PHASES

Composition	Structure	Lattice constants, Å.	Rhombohedral vol., Å.^{3}
$1UO_{2.10} \cdot 1Y_2O_3$	F.c.c.	5.361	269.63
$17UO_{2.17} \cdot 18Y_2O_3$	Rhomb 1	$a = 10.033$, $c = 9.362$	272.36
$2UO_{2.36} \cdot 3Y_2O_3$	Rhomb 1	$a = 10.002$, $c = 9.353$	270.44
$4UO_{2.67} \cdot 9Y_2O_3$	Rhomb 1	$a = 9.967$, $c = 9.338$	268.08
$1UO_{3.0} \cdot 3Y_2O_3$	Rhomb 1	$a = 9.934$, $c = 9.364$	267.04
$1UO_{2.67} \cdot 1Y_2O_3$	F.c.c.	5.334	265.58
$17UO_{2.67} \cdot 18Y_2O_3$	Rhomb 2	Not measured	...
$2UO_{3.0} \cdot 3Y_2O_3$	Rhomb 2	$a = 9.943$, $c = 9.289$	265.38
$2UO_{2.9} \cdot 3Y_2O_3$	F.c.c.	5.337	266.03

very similar coordination oxygen polyhedra are present in both structure types.

Oxides Isostructural with Rhombohedral 1.—During the course of this work, Baenziger, Eick, Schuldt, and Eyring[5] reported a stable phase of composition $TbO_{1.715}$ which was deduced to have a rhombohedral unit cell containing seven terbium and twelve oxygen atoms. These results were part of a program of research on rare earth–oxygen systems by Ferguson, Guth, Holden, Baenziger, and Eyring[6–8] being carried out at the State University of Iowa. Tb_7O_{12} was found to be isostructural with our rhomb 1 phase by the similarity in their X-ray diffraction patterns. An analogous phase was subsequently reported by Eyring and Baenziger[9] in the Pr–O system. The only other evidence for pure oxides of composition R_7O_{12} was presented in 1955 by Bevan[10] for the cerium–oxygen system.

The isostructural relationship between the $U_mY_{7-m}O_{12}$ compounds and the rare earth R_7O_{12} oxides suggested that these examples might be members of a large family of a completely new structure type. This was proved to be the case by the preparation of the following compounds: (a) UR_6O_{12} where R = La and all rare earths from Pr to Lu; (b) WR_6O_{12} where R = Y and the rare earths from Ho to Lu; (c) MoR_6O_{12} where R = Y and the rare earths from Er to Lu. The hexagonal lattice constants and rhombohedral cell volumes of most of the compounds in these series are given in Table III.

TABLE III

HEXAGONAL CELL CONSTANTS FOR THE RHOMBOHEDRAL I $MO_3 \cdot 3R_2O_3$ COMPOUNDS

Compound	*a*, Å.	*c*, Å.	Rhombohedral vol., Å.^{3}
$UO_3 \cdot 3La_2O_3$	10.473	9.984	316.13
$UO_3 \cdot 3Pr_2O_3$	10.301	9.800	300.16
$UO_3 \cdot 3Nd_2O_3$	10.254	9.748	295.86
$UO_3 \cdot 3Sm_2O_3$	10.148	9.630	286.31
$UO_3 \cdot 3Gd_2O_3$	10.076	9.529	279.26
$UO_3 \cdot 3Tb_2O_3$	10.013	9.465	273.92
$UO_3 \cdot 3Ho_2O_3$	9.935	9.368	266.93
$UO_3 \cdot 3Y_2O_3$	9.934	9.364	266.71
$UO_3 \cdot 3Tm_2O_3$	9.853	9.283	260.17
$UO_3 \cdot 3Yb_2O_3$	9.826	9.248	257.74
$UO_3 \cdot 3Lu_2O_3$	9.797	9.204	255.04
$WO_3 \cdot 3Y_2O_3$	9.757	9.317	256.01
$WO_3 \cdot 3Tm_2O_3$	9.679	9.230	249.60
$WO_3 \cdot 3Yb_2O_3$	9.640	9.188	246.49
$WO_3 \cdot 3Lu_2O_3$	9.618	9.145	244.21
$MoO_3 \cdot 3Tm_2O_3$	9.671	9.229	249.15
$MoO_3 \cdot 3Yb_2O_3$	9.633	9.192	246.23
$MoO_3 \cdot 3Lu_2O_3$	9.609	9.147	243.84

Rhombohedral 1 structures were not obtained for CrO_3 with Y_2O_3, UO_3 with Sc_2O_3, nor for molybdenum and tungsten trioxides with rare earths of lower atomic number than dysprosium. In view of the fact that this phase was stable for compositions $U_mY_{7-m}O_{12}$ over a range of *m* values from 1 to 3.4, it was thought that this structure type might be still broader in scope and encompass such compositions as $(M + R)_7O_{12}$ where M = tetravalent and pentavalent metal ions. Attempts to prepare these compounds at the following compositions met with no success: (a) $5M_2O_5 \cdot 18Y_2O_3$ or $M_{1.52}Y_{5.48}O_{12}$ where M = Ta, V, or Nb; (b) $3TiO_2 \cdot 2Y_2O_3$ or $Ti_3Y_4O_{12}$.

Transpiration Measurements.—As a means of determining the thermal stability of rhomb 1 compounds,

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[5] N. C. Baenziger, H. A. Eick, H. S. Schuldt, and L. Eyring, *J. Am. Chem. Soc.*, **83**, 2219 (1961).

[6] R. E. Ferguson, E. D. Guth, and L. Eyring, *ibid.*, **76**, 3890 (1954).

[7] E. D. Guth, J. R. Holden, N. C. Baenziger, and L. Eyring, *ibid.*, **76**, 5239 (1954).

[8] E. D. Guth and L. Eyring, *ibid.*, **76**, 5242 (1954).

[9] L. Eyring and N. C. Baenziger, *J. Appl. Phys.*, **33**, 428 (1962).

[10] D. J. M. Bevan, *J. Inorg. Nucl. Chem.*, **1**, 49 (1955).

TABLE IV

VAPOR PRESSURE AND APPARENT VOLUME OF UO_3

Compound	Vapor press. (atm.) at 1800°K.	Ionic radius R^{3+}, Å.	Volume $3R_2O_3$, Å.^{3}	Volume rhomb 1, Å.^{3}	Apparent vol. UO_3, Å.^{3}
UO_3	6.4×10^{-3} (calcd.)	. . .	. . .	. . .	$\alpha = 56.91$[a] $\gamma = 57.88$[b]
$UO_3 \cdot 3La_2O_3$	2.2×10^{-8}	1.061	272.00 (extr.)	316.13	44.13
$UO_3 \cdot 3Nd_2O_3$	4.0×10^{-8}	0.995	253.00 (extr.)	295.86	42.86
$UO_3 \cdot 3Gd_2O_3$	5.4×10^{-8}	0.938	237.00	279.26	42.26
$UO_3 \cdot 3Y_2O_3$	9.0×10^{-8}	0.890	223.57	266.71	43.14
$UO_3 \cdot 3Ho_2O_3$	5.4×10^{-8}	0.894	223.73	266.93	43.20
$UO_3 \cdot 3Lu_2O_3$	2.8×10^{-7}	0.846	210.35	255.04	44.69

[a] W. H. Zachariasen, *Acta Cryst.*, **1**, 268 (1948). [b] D. E. Connolly, *ibid.*, **12**, 949 (1959).

transpiration measurements were made at 1800°K. on several members of the $UO_3 \cdot 3R_2O_3$ family. In most cases, vapor pressure and X-ray diffraction data were obtained from the same sample preparation. Results are compared in Table IV with the vapor pressure of UO_3 at the same temperature. The value given for UO_3 was calculated by extrapolation of reported free energy data for the solid given by Belle[11] and the expression for gaseous UO_3 tabulated by Burke.[12]

It is noteworthy that the vapor pressure of UO_3 in the rhomb 1 compounds is reduced by several orders of magnitude. This drastic reduction is obviously much larger than the sevenfold decrease which would be expected by Raoult's law. A similar situation has been observed by Wilson[13] and Hill[14] for the volatility of UO_3 in urania–lanthana and urania–yttria solid solutions of the fluorite type.

The apparent volume occupied by UO_3 in this rhombohedral structure can be obtained by subtracting the known volume for three R_2O_3 units from the rhombohedral cell volume. This is valid because there is no marked discontinuity between body-centered cubic solid solutions and rhombohedral cell volumes containing equal numbers of atoms. When this is done for the rare earth oxides which crystallize in the b.c.c. (C-type) structure, the apparent UO_3 volume is nearly constant, as would be expected for an isostructural series, and is considerably smaller than the UO_3 volume of either the α or γ form of UO_3. If the ionic radii of the rare earth series are plotted against $3R_2O_3$ volumes for b.c.c. (C-type) structures, an effective volume of $3R_2O_3$ units for La_2O_3 and Nd_2O_3 can be obtained by extrapolation. This approach was checked for the lanthanum compound from data by Hill[15] which showed that the f.c.c. solid solutions of UO_{2+x} with 67 mole % La_2O_3 were roughly equivalent in volume to the rhombohedral 1 phase. The extrapolated $3R_2O_3$ volumes for lanthanum and neodymium also give UO_3 volumes in the rhombohedral cell which are in substantial agreement with the values obtained from other members of the series. The nearly constant volume for UO_3 in the rhombohedral cell of about 43 Å.^{3} indicates that stronger bonding exists in compounds of UO_3 with a rare earth oxide.

Although no transpiration measurements were made on the compounds containing WO_3 or MoO_3, qualitative tests indicated that these compounds also demonstrate high thermal stability. After 2 hr. at 1750° in air, pellets of the pure oxides had completely volatilized while both of the rhomb 1 yttria compounds showed only a small loss (0.1–0.3%) in weight.

Discussion

The formation of a complete isostructural series of rhombohedral compounds between UO_3 and all the rare earth oxides is rather unusual. The difference in ionic size between lanthanum and lutetium often is sufficient to produce a radical change in the structure of complex oxides containing these elements. For example, in the rare earth tantalates of $RTaO_4$ composition a structure change occurs between Ce and La. Another interesting feature of this new isotypic series is the substitution of WO_3 or MoO_3 for UO_3. This is a most uncommon occurrence; Na_2UO_4 is not isostructural with Na_2WO_4, and $CaUO_4$ does not have the scheelite $CaWO_4$ structure.

By analogy with the stable ordered rare earth oxide phases which exist in the Pr–O, Tb–O, and Ce–O systems[5–10] at the composition M_7O_{12}, the rhombohedral $1MO_3 \cdot 3R_2O_3$ family of compounds also have an ordered arrangement which is closely related to the face-centered cubic fluorite structure. This postulation is corroborated by the fact that fast neutron irradiation at 400° to 10^{20} neutrons/cm.^{2} produced a phase change from rhomb 1 to f.c.c.

The rhombohedral 1 compounds become increasingly difficult to prepare as the rare earth ionic size increases. In the case of MoO_3, a face-centered cubic solid solution is formed with Ho_2O_3 with a lattice parameter of 5.297 Å. With WO_3, the rhomb 1 structure may form at least to Dy_2O_3, but with Gd_2O_3 only a f.c.c. compound exists. Further investigation is required with terbium, holmium, and erbium oxides to delineate this region more accurately; complicated X-ray diffraction patterns have been obtained which indicate other intermediate phases or phase inversions.

The limited existence of these rhombohedral compounds indicates that their formation is dependent

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(11) J. Belle, "UO_2: Properties and Nuclear Applications," USAEC, U. S. Govt. Printing Office, Washington, D. C., p. 259.

(12) J. E. Burke, *Progr. Ceram. Sci.*, **1**, 84 (1960).

(13) W. E. Wilson, C. A. Alexander, and A. F. Gerds, *J. Inorg. Nucl. Chem.*, **20**, 242 (1961).

(14) D. C. Hill, *J. Am. Ceram. Soc.*, **45**, 143 (1962).

(15) D. C. Hill, *ibid.*, **45**, 258 (1962).

TABLE V

DETERMINATION OF THE CATION RADIUS RATIO (M/R) FOR THE RHOMBOHEDRAL 1 COMPOUNDS

Compound	Radius of M^{+6}, Å.	Radius of R^{+3}, Å.	Radius ratio M/R
$UO_3 \cdot 3La_2O_3$	0.80	1.06	0.75
$CrO_3 \cdot 3Y_2O_3$[a]	0.52	0.89	0.58
$WO_3 \cdot 3Dy_2O_3$	0.62	0.91	0.68
$WO_3 \cdot 3Gd_2O_3$[a]	0.62	0.94	0.66
$MoO_3 \cdot 3Er_2O_3$	0.615	0.88	0.70
$MoO_3 \cdot 3Y_2O_3$	0.615	0.89	0.68
$MoO_3 \cdot 3Ho_2O_3$[a]	0.615	0.89	0.68

[a] These hypothetical compounds do not form the rhombohedral 1 structure.

upon a critical ion size ratio. Using average cation radii values, the results given in Table V were obtained. It can be seen from these data that the rhomb 1 structure does not occur below a cation size ratio M/R of about 0.67.

By using the above criterion, it should be possible to predict the existence of other rhombohedral compounds of this type. For example, ReO_3 might be expected to yield rhomb 1 structures with Y_2O_3 and the rare earth oxides. This expectation has been realized recently with the preparation of $ReO_3 \cdot 3Y_2O_3$ by Grossman.[16] Other hexavalent metal oxides are somewhat rare, thereby limiting the further extension of this family.

Although there are many members of the rhomb 1 structure type, the compound $2UO_3 \cdot 3Y_2O_3$ is the only known example of the rhomb 2 structure having an oxygen-to-metal ratio of 15:8. In spite of the many ordered phases which have been found in the Pr–O, Tb–O, and Ce–O systems, no stable $RO_{1.875}$ composition has been reported. Furthermore, the metastable $2WO_3 \cdot 3Y_2O_3$ phase reported by Borchardt[2b] does not have the rhomb 2 structure.

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[16] L. N. Grossman and J. G. Wilson, Technical Summary Report, GEST-2021, General Electric Company, Vallecitos Atomic Laboratory, Pleasanton, Calif., Aug. 30, 1963.

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A Calorimetric Study of the Lead(II) Oxide–Vanadium(V) Oxide System at 680°

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Calorimetric measurements have been carried out on the heat effects associated with solution of solid lead oxide in liquid vanadium pentoxide at 680°. Over the whole liquid range, which extends to a mole fraction of lead oxide $X_{PbO} > 0.6$, the molar heat of mixing may be represented by the expression $\Delta H^M = -18.42(\pm 0.33) X_{PbO}$ kcal./mole. The significance of this result is discussed. Also measured were the heats of solution of the three solid lead vanadates in liquid vanadium pentoxide. By combination of these results with the corresponding heat of solution data for pure lead oxide, we derived the following values for the heat of formation of these compounds at 680°

$$2PbO(s) + V_2O_5(l) = Pb_2V_2O_7; \quad \Delta H = -46.65 \text{ kcal.}$$

$$3PbO(s) + V_2O_5(l) = Pb_3(VO_4)_2; \quad \Delta H = -53.51 \text{ kcal.}$$

$$8PbO(s) + V_2O_5(l) = 8PbO \cdot V_2O_5; \quad \Delta H = -54.48 \text{ kcal.}$$

Finally, a direct method for the measurement of the heat of formation of $Pb_3(VO_4)_2$ from the solid oxides was explored. In this method a powdered mixture of lead oxide and vanadium pentoxide was dropped from room temperature into the calorimeter at 680°. In these experiments we obtained a value of -39.37 kcal./mole for the heat of formation of the lead vanadate at room temperature.

Introduction

Thermodynamic and structural studies of oxidic melts are of very considerable scientific and technological interest. However, due to the high temperatures involved there have been many restrictions on the methods of measurements which have been applied. For example, we are unaware of any attempts so far at the study of oxidic melts by means of high-temperature reaction calorimetry. The only enthalpy of mixing data relating to mixed oxidic melts which may be found in the literature have been derived from the temperature dependence of the thermodynamic activity, as measured by equilibrium methods. The significance which can be attributed to these enthalpy (and the related entropy) data leaves much to be desired.

In the present communication we describe a series of calorimetric measurements involving lead oxide and vanadium pentoxide carried out at 680°. At this temperature vanadium pentoxide is liquid (m.p. 672°) while lead oxide is solid (m.p. 890°). The liquid range at 680° extends from $X_{PbO} = 0$ to $X_{PbO} \gtrsim 0.6$.

In addition to our study of the formation of these melts from the two components, we have also measured the heats of solution in liquid vanadium pentoxide of