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The Preparation and Properties of the Rutile Phase $VTaO_4$

E. J. FELTEN, D. E. FORNWALT, AND A. V. KARG

Advanced Materials Research and Development Laboratory, Pratt and Whitney Aircraft, Division of United Aircraft Corporation, Middletown, Connecticut 06547

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A new mixed oxide $V^{+3}Ta^{+5}O_4$ has been prepared by reacting V_2O_3 with Ta_2O_5 in a reducing atmosphere between 1400 and 1600°C. $VTaO_4$ crystallizes in the rutile structure, with $a = 4.68_4$ and $c = 3.04_5$Å. Reactions between Ti_2O_3 and Ta_2O_5 under the same conditions result in the formation of $Ti_{0.6}Ta_{0.4}O_2$, a solid solution between $TiTaO_4$ and TiO_2. Solid solutions of $VTaO_4$ with $AlTaO_4$ and $CrTaO_4$ have been prepared. A linear relationship was observed between the ionic radii of the trivalent ion in the tantalates having the rutile structure and their lattice parameter.

Introduction

A number of ternary metal oxides crystallize in the rutile structure or distorted variations of this structure. Titanium dioxide (TiO_2) is the model for this type of structure. In addition to a number of simple oxides, this structure is also assumed by more complex oxides. Brandt (*1*) synthesized a number of ABO_4-type compounds where A can be assumed to have a valence of +3 and the B ion has a valence of +5. The A and B cations, which are nearly equivalent in size to Ti^{4+} are distributed uniformly over the Ti^{4+} sites in the structure. Complex oxides of this type were prepared in which the +3 ion is aluminum, chromium, iron, gallium, and rhodium, and the +5 ion is niobium, tantalum, antimony, and vanadium. All of these ABO_4-type compounds belong to the space group $P\ 4/mnm$. The cations are octahedrally coordinated to the oxygen ions in the structure, and the octahedra are joined together by the sharing of corners.

Except for the compounds prepared by Brandt (*1*) very few new ternary oxides with this structure have been added to the list. Vernon and Milligan (*2*) have prepared $RhVO_4$, $SbVO_4$, and $TiVO_4$ which crystallize in the rutile structures. In these oxides it is assumed that vanadium is in the +5 state. A number of AB_2O_6-type oxides in which the A ion assumes a valence of +2 and the B ion has a valence of +5 crystallize with the rutile structure, but only at elevated temperatures. Thus, Goldschmidt (*3*) observed that $CoNb_2O_6$, $NiNb_2O_6$ and $MgNb_2O_6$ crystallized in the columbite structure at low temperatures. In this type structure the cations assume an ordered arrangement. At elevated temperatures the cations become disordered and the rutile structure is assumed in these compounds. The transformations of $CoNb_2O_6$ and $NiNb_2O_6$ were confirmed by Felten et al. (*4, 5*). Compounds of the AB_2O_6-type more often assume the trirutile structure. This structure is related to the rutile structure, except that the cations assume ordered positions resulting in a tripling of the c axis.

The work described in this paper is concerned primarily with the formation of $VTaO_4$ and to a limited extent the formation of a titanium tantalum oxide. The experimental work was suggested by the work of Bernier and Poix (*6, 7*) who have prepared the trirutile phase VTa_2O_6 ($a = 4.578$, $c = 9.159$, $c/3 = 3.053$ Å). The preparation of $VTaO_4$ was the precursor to an anticipated investigation of possible order–disorder across the $VTaO_4$–VTa_2O_6 pseudobinary join. At the present time the authors have been unable to prepare VTa_2O_6.

Experimental Techniques

The mixed oxide phases described in this report were prepared by the reaction of either V_2O_3 or Ti_2O_3 with Ta_2O_5 in a hydrogen atmosphere in the temperature range 1200–1600°C. The $AlTaO_4$ and $CrTaO_4$ preparations used to form solid solution with $VTaO_4$ were prepared under similar conditions from Al_2O_3 or Cr_2O_3 and Ta_2O_5. The powders were blended in a high-speed blender, pressed into pellets and heated for extended periods of time at the temperatures indicated below. After the initial firing the pellets were crushed, reblended and pelletized, and refired.

X-ray diffraction patterns of all materials were obtained with monochromatic CuKα radiation. Intensity measurements were obtained by integrating each peak and subtracting the average background which was obtained by counting background level immediately before and after the peak. Each peak was scanned at $\frac{1}{8}$°/min.

Results

In order to determine the stability of the starting materials, V_2O_3, Ti_2O_3, and Ta_2O_5 were heated for 64 hr at 1400°C in hydrogen. No changes were observed in the V_2O_3 and Ta_2O_5, but the oxidation potential of the furnace atmosphere was sufficiently high to transform the Ti_2O_3 to Ti_3O_5 ($Ti_2O_3 \cdot TiO_2$). Thus while the valence of the vanadium in the oxide remained in the +3 state, the valence of the titanium was a mixture of the +3 and +4 states.

The reaction between V_2O_3 and Ta_2O_5 was sluggish at 1200°C. Even after 64 hr, a considerable amount of the unreacted oxides remained, along with a small amount of the rutile phase. Reheating of the mixture for 16 hr at 1400°C resulted in a complete reaction. The Ti_2O_3–Ta_2O_5 preparations had to be heated to 1600°C in order to attain a maximum amount of the reaction products. The products of both reactions were dark brown in color. The preparative details of the reactions run during this investigation are presented in Table I.

The $VTaO_4$ prepared above was heated with equimolar amounts of either $AlTaO_4$ or $CrTaO_4$ to obtain solid solutions of the mixed oxides. The reaction to prepare $V_{0.5}Cr_{0.5}TaO_4$ proceeded smoothly at 1400°C. A solid solution of $V_{0.5}Al_{0.5}TaO_4$ was obtained by the same heat treatment but the diffraction peaks were somewhat broad, indicating incomplete reaction. Reheating the mixture to 1600°C produced a more normal diffraction pattern. The lattice parameters of the materials prepared in this laboratory along with those for $AlTaO_4$ (*8*), $GaTaO_4$ (*9*), $CrTaO_4$ (*1*), $FeTaO_4$ (*1*) and $RhTaO_4$ (*1*) are plotted against the ionic radii of the +3 cation in Fig. 1. As can be seen in the figure, there is a direct correlation between the ionic radii of the trivalent cations and the lattice parameters of the rutile phase formed. Furthermore, the parameters for the $Al_{0.5}V_{0.5}TaO_4$ and $Cr_{0.5}V_{0.5}TaO_4$ phases are the average expected for the cations employed.

Portions of the $VTaO_4$ and $Ti_{0.6}Ta_{0.4}O_2$

TABLE I

SURVEY OF EXPERIMENTAL RESULTS

Starting Material	Time (hr)	Temp. (°C) in H_2	Products
$V_2O_3 + Ta_2O_5$	64	1200	Ta_2O_5, V_2O_3 and a Rutile Phase
$V_2O_3 + Ta_2O_5$	64 16	1200 1400	Rutile ($a = 4.69_1$, $c = 3.05_2$ Å)
$V_2O_3 + Ta_2O_5$	20 64	1200 1400	Rutile ($a = 4.68_2$, $c = 3.04_4$ Å)
$V_2O_3 + Ta_2O_5$	88 2	1400 1600	Rutile ($a = 4.68_6$, $c = 3.04_6$ Å)
$Ti_2O_3 + Ta_2O_5$	16	1400	Rutile ($a = 4.71_6$, $c = 3.06_8$ Å), Ta_2O_5
$Ti_2O_3 + Ta_2O_5$	16 20	1400 1600	Rutile, Ta_2O_5
$Al_2O_3 + V_2O_3 + 2Ta_2O_5$	64	1400	Rutile ($a = 4.63_8$, $c = 3.00_7$ Å)
$Al_2O_3 + V_2O_3 + 2Ta_2O_5$	88 2	1400 1600	Rutile ($a = 4.65_7$, $c = 3.01_5$ Å)
$Cr_2O_3 + V_2O_3 + 2Ta_2O_5$	64	1400	Rutile ($a = 4.66_2$, $c = 3.02_5$ Å)

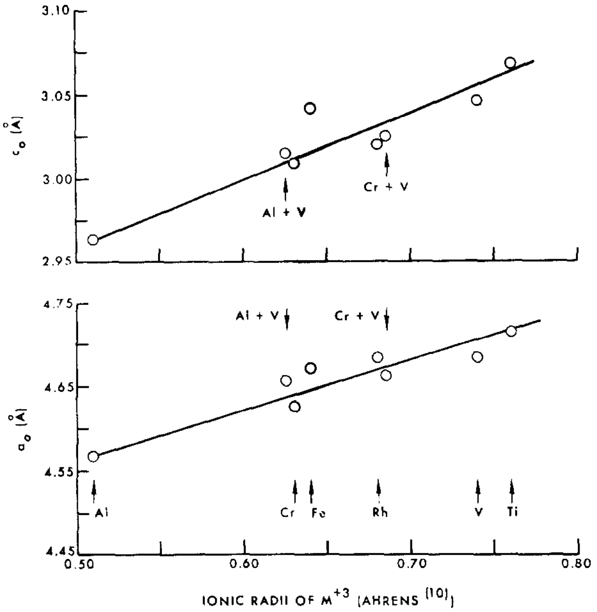

FIG. 1. Linear increase of lattice parameters for $MTaO_4$ oxides exhibiting the rutile structure.

preparations were heated to constant weight in air to determine the compositions of the rutile phases. The $VTaO_4$ preparation was heated to constant weight in air at 650°C, assuming the following reaction:

$$V_2O_3 \cdot Ta_2O_5(2VTaO_4) + O_2 \rightarrow V_2O_5 \cdot Ta_2O_5. \quad (1)$$

A weight gain of 5.41 % is expected for this reaction, a weight gain of 5.56 % was observed. In addition the black $VTaO_4$ became yellow-brown as the result of oxidation. For the titanium preparation the material was heated to constant weight in air at 1200°C. Two reactions were considered:

$$Ti_2O_3 \cdot Ta_2O_5(2TiTaO_4) + 1/2O_2 \rightarrow Ti_2O_4 \cdot Ta_2O_5 \quad (2)$$

and

$$Ti_3O_5 \cdot Ta_2O_5(5Ti_{0.6}Ta_{0.4}O_2) + \tfrac{1}{2}Ta_2O_5 + 1/2O_2 \rightarrow Ti_3O_6 \cdot Ta_2O_5 + \tfrac{1}{2}Ta_2O_5. \quad (3)$$

For reaction (2) a weight gain of 2.73 % would be expected, compared to 1.81 % for reaction (3). The

TABLE II

X-RAY DIFFRACTION DATA FOR $VTaO_4$

hkl	$\sin^2\theta \times 10^4$ (obsd)	$\sin^2\theta \times 10^4$ (calcd)	I/I_0 (calcd)	I/I_0 (obsd)	I/I_0 (calcd for VTa_2O_6)
110	540	540	100	100	100
101	912	909	72.5	73.9	75.5
200	1083	1080	20.6	23.6	22
111	1183	1179	4.3	6.4	3.3
211	1994	1989	59.0	59.7	61
220	2162	2160	14.8	15.5	14.6
002	2556	2557	6.3	7.4	5.9
310	2704	2700	12.7	13.2	13.7
301	3072	3069	16.6	16.1	16.5
112	3100	3097	12.0	11.3	15.7
202	3644	3637	5.8	6.2	6.0
321	4152	4149	9.8	10.4	11.4
400	4323	4320	3.3	3.9	3.7
222	4719	4717	6.7	6.2	7.2
330	4862	4860	3.3	3.2	3.5
411	5232	5229	9.0	8.9	9.4
312	5258	5257	8.2	8.2	9.8
420	5399	5400	4.2	4.2	4.9
103	6026	6024	3.6	3.4	4.0
402	6876	6877	4.1	4.2	4.3
510	7019	7020	4.4	4.3	4.3
213	7105	7104	8.6	8.5	8.5
501	7386	7389	2.8	2.8	12.0
422	7956	7957	8.3	8.5	7.4
303	8183	8184	6.0	5.9	4.5
521	8463	8469	12.6	12.4	10.0

observed weight gain was 1.95%, indicating that the material prepared by the method described above is $Ti_{0.6}Ta_{0.4}O_2$ or is very close to that composition.

The X-ray diffraction and intensity data obtained from a representative specimen of $VTaO_4$ appear in Table II. Excellent agreement was obtained between the theoretical and measured intensities. The intensities of the primary diffraction peaks for VTa_2O_6 (*7*) have also been added for comparison purposes. No superlattice lines, as are obtained for VTa_2O_6, were observed in the phase described in Table II. Their presence should have been detected if ordering had occurred.

Discussion and Conclusions

The experiments described above concern the formation of two new and interesting rutile phases. The synthesis of the materials was possible because of the excellent stability of Ta_2O_5 in a reducing atmosphere. In ternary oxides of the $A^{+3}B^{+5}O_4$-type crystallizing in the rutile structure, V^{+3} and Ti^{+3} are significantly larger than any previously used A^{+3} ion. It is assumed that the $Ti_{0.6}Ta_{0.4}O_2$ formed in the experiments described here consists of a solid solution between $TiTaO_4$ and TiO_2.

The successful synthesis of $VTaO_4$ and its solid solutions with $AlTaO_4$ and $CrTaO_4$ can be attributed to the stability of V_2O_3, Al_2O_3, Cr_2O_3, and Ta_2O_5 in dry hydrogen. Under the conditions employed Ti_3O_5 is the stable oxide of titanium. This synthesis cannot be employed to form $VNbO_4$, because NbO_2 is the thermodynamically stable phase in hydrogen at elevated temperatures.

Both $VTaO_4$ and $Ti_{0.6}Ta_{0.4}O_2$ should prove of considerable interest because of their electrical properties. Both materials are semiconductors, exhibiting a large but finite resistance at room temperature. By contrast, the parent compound, TiO_2, and the other ternary rutile phases are insulators.

Note added in proof. Since this manuscript was written it has come to the attention of the authors that $VTaO_4$ has been prepared by an alternate method (*11*). The lattice parameters reported for this preparation were $a = 4.667$ and $c = 3.043$, in good agreement with those obtained in the present work.

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