

# Effect of Oxide Additions on the Polymorphism of Tantalum Pentoxide

## II. "Stabilization" of the High Temperature Structure Type

R. S. Roth, J. L. Waring, and W. S. Brower

Institute for Materials Research, National Bureau of Standards,  
Washington, D.C. 20234

(March 12, 1970)

The high temperature, apparently tetragonal, polymorph of tantalum pentoxide can be obtained at room temperature by quenching a specimen containing 2–5 mole percent of the following oxides:  $\text{SnO}_2$ ,  $\text{Ga}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Sc}_2\text{O}_3$ , or  $\text{MgO}$ . All the x-ray patterns can be indexed on a body centered tetragonal cell with  $a \approx 3.830 \text{ \AA}$ ,  $c \approx 35.68 \text{ \AA}$ . However,  $\text{P}_2\text{O}_5$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{ZrO}_2$ ,  $\text{Lu}_2\text{O}_3$ ,  $\text{NiO}$ , or  $\text{ZnO}$  do not stabilize the tetragonal form at room temperature. Single crystals of scandium "stabilized"  $\text{Ta}_2\text{O}_5$  have been grown by the Czochralski technique.

Key words: High temperature polymorph; single crystals; stabilization; tantalum oxide.

### 1. Introduction

$\text{Ta}_2\text{O}_5$  is probably the only pure metal oxide stable at high temperature in air (mp  $\sim 1890^\circ\text{C}$ ) about which little or nothing is known of the crystal structure. The reason for this is that no suitable crystals of pure  $\text{Ta}_2\text{O}_5$  have been prepared due to the peculiar polymorphic behavior of the material. The polymorphism of  $\text{Ta}_2\text{O}_5$  has been discussed by several authors [1, 2, 3]<sup>1</sup> and fully reviewed by the present authors in a previous publication [4] together with the changes which occurred in the polymorphic behavior with the addition of  $\text{TiO}_2$ .

The low-temperature form of  $\text{Ta}_2\text{O}_5$  has an, as yet, unknown structure related to the low-temperature form of  $\text{Nb}_2\text{O}_5$ , as well as to  $\alpha\text{-U}_3\text{O}_8$  and  $\alpha\text{-UO}_3$ . On heating to a temperature of about  $1360^\circ\text{C}$  [2]  $\text{Ta}_2\text{O}_5$  exhibits an enantiotropic, sluggishly reversible, phase transition to a high-temperature form. This form apparently has a unique structure unlike any other reported compound. When quenched from above the equilibrium phase transition, the apparently tetragonal high-temperature form transforms, through a monoclinic polymorph, to a third metastable polymorph which has an x-ray powder pattern which appears to be triclinic at room temperature [4]. These transformations result in a mechanical disruption of the crystals, making an accurate measurement of the intensities of the x-ray diffraction spots essentially an

impossible task. The addition of  $\text{TiO}_2$  lowers the equilibrium transition temperature from about  $1360^\circ\text{C}$  to about  $1150$  to  $1200^\circ\text{C}$  and the metastable tetragonal  $\rightleftharpoons$  monoclinic transition of the high-temperature form from about  $950^\circ\text{C}$  to as low as  $600^\circ\text{C}$  [4]. However, the quality of the room temperature single crystals is not improved by this addition.

In the present study, oxides other than  $\text{TiO}_2$ , containing cations of similar size, have been added to  $\text{Ta}_2\text{O}_5$  in an effort to obtain the high temperature tetragonal modification of  $\text{Ta}_2\text{O}_5$  at room temperature.

### 2. Materials

The general quantitative spectrochemical analyses for the  $\text{Ta}_2\text{O}_5$  used in this study has been previously reported [4]. All other oxides used were of reagent grade or better, as described in previous publications [5, 6, 7, 8, 9]. These other oxides were  $\text{P}_2\text{O}_5$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{SnO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Ga}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Sc}_2\text{O}_3$ ,  $\text{Lu}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{NiO}$ , and  $\text{ZnO}$ .

### 3. Specimen Preparation and Test Methods

One gram batches of 95 : 5 and 90 : 10 mole ratio compositions of  $\text{Ta}_2\text{O}_5$  and each of the additional oxides were weighed, mixed in a mechanical shaker for approximately 10 min, and pressed into disks at about  $10^4$  psi. The disks were placed on Pt setters and calcined in air at appropriate temperatures from  $500$  to  $1200^\circ\text{C}$  depending on the relative volatility of

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

the additive, for 6 to 12 hr. Other compositions of interest were prepared in a similar manner. After the preliminary heat treatment portions of the ground specimen were placed in sealed Pt tubes and heated in the quenching furnace at approximately 1325, 1450, and 1600 °C for various periods of time. Some specimens of particular interest were heated at other temperatures.

The sealed tubes containing specimens were quenched into ice water, opened, and examined by x-ray diffraction techniques. A high angle recording Geiger counter-diffractometer and Ni-filtered Cu radiation was used in the study. The Geiger counter traversed the specimen at 1/4 deg/min and radiation was recorded on the chart at 1 deg-2θ/in. The unit cell dimensions reported can be considered accurate to about ±2 in the last decimal place listed.

## 4. Results and Discussion

The experimental data is shown in table 1 and is interpreted diagrammatically as phase equilibria data in figures 1-4. Sufficient data has not been collected to establish the exact nature of the phase equilibria diagrams. Therefore, the system, Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> (redrawn in fig. 1), has been used as a model and the other systems have been drawn in accordance with Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>, with the appropriate modifications necessary to fit the limited experimental data. No attempt has been made to delineate the metastable equilibrium relations of the H-Ta<sub>2</sub>O<sub>5</sub> solid solution phase transitions as was previously done for Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> [4].

From the results reported for the system Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> [4], it can be concluded that any specimen containing some form of H-Ta<sub>2</sub>O<sub>5</sub> solid solution was

TABLE 1. Experimental data

System	Composition mol percent	Heat treatment				X-ray diffraction analyses <sup>c</sup>			
		Initial <sup>a</sup>		Final <sup>b</sup>					
		Temp. °C	Time hr	Temp. °C	Time hr				
Ta <sub>2</sub> O <sub>5</sub> -P <sub>2</sub> O <sub>5</sub>	95 : 5	300	1			<sup>0</sup> 5 <sub>19</sub> O <sub>25</sub> (ss) + L-Ta <sub>2</sub> O <sub>5</sub> phase(s) PTa <sub>9</sub> O <sub>25</sub> (ss) + H <sub>tri</sub> -Ta <sub>2</sub> O <sub>5</sub> PTa <sub>9</sub> O <sub>25</sub> (ss) + H <sub>tri</sub> -Ta <sub>2</sub> O <sub>5</sub>			
		500	1						
		<sup>a</sup> 1000	10	1331	16				
	90 : 10	300	1						
		500	1						
		<sup>a</sup> 1000	10	1331	16				
Ta <sub>2</sub> O <sub>5</sub> -V <sub>2</sub> O <sub>5</sub>	95 : 5	1000	10	1333	19	VTa <sub>9</sub> O <sub>25</sub> (ss) + L-Ta <sub>2</sub> O <sub>5</sub> phase(s) VTa <sub>9</sub> O <sub>25</sub> (ss) + H-Ta <sub>2</sub> O <sub>5</sub> (ss) H <sub>tri</sub> -Ta <sub>2</sub> O <sub>5</sub> + H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5</sub> VTa <sub>9</sub> O <sub>25</sub> + unknown phase VTa <sub>9</sub> O <sub>25</sub> VTa <sub>9</sub> O <sub>25</sub> + L-Ta <sub>2</sub> O <sub>5</sub> phase(s) <sup>e</sup> VTa <sub>9</sub> O <sub>25</sub> + L-Ta <sub>2</sub> O <sub>5</sub> phase(s) <sup>e</sup> H <sub>tri</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + liquid H <sub>tri</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + liquid			
				1444	65				
				1587	5				
	90 : 10	500	16						
		1000	16						
				1247	6				
	Ta <sub>2</sub> O <sub>5</sub> -Nb <sub>2</sub> O <sub>5</sub>	95 : 5	1000	10	1333		19	L-Ta <sub>2</sub> O <sub>5</sub> phase(s) H <sub>tri</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + L-Ta <sub>2</sub> O <sub>5</sub> phase(s) (trace)	
					1444		65		
		90 : 10	1000	10	1331		16		L-Ta <sub>2</sub> O <sub>5</sub> phase(s) H <sub>tri</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + L-Ta <sub>2</sub> O <sub>5</sub> phase(s) (trace)
					1444		65		
Ta <sub>2</sub> O <sub>5</sub> -SnO <sub>2</sub>	99 : 1	1200	10	1445	16	H <sub>tri</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + L-Ta <sub>2</sub> O <sub>5</sub> phase(s) (trace) H <sub>tri</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) H <sub>tri</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) H <sub>tri</sub> -Ta <sub>2</sub> O <sub>5</sub> + H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) H <sub>tri</sub> -Ta <sub>2</sub> O <sub>5</sub> + H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss); a = 3.830, c = 35.68 H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss); a = 3.830, c = 35.68 H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + H <sub>tri</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) <sup>f</sup> H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + H <sub>tri</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) <sup>f</sup> H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + H <sub>tri</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) <sup>f</sup>			
							1571	4	
							1446	16	
	98 : 2	1200	10						
							1446	16	
							1446	16	
	97 : 3	1200	10						
							1446	16	
							1571	4	
95 : 5	1000	10	1325	16					
			1448	16					
			1660	2					
			1769	17					
			1463	65					

TABLE 1. Experimental data—Continued

System	Composition mol percent	Heat treatment				X-ray diffraction analyses <sup>c</sup>
		Initial <sup>a</sup>		Final <sup>b</sup>		
		Temp. °C	Time hr	Temp. °C	Time hr	
Ta <sub>2</sub> O <sub>5</sub> -ZrO <sub>2</sub>	90 : 10	1000	10	1325 1448	16 16	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + SnO <sub>2</sub> (ss) H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + SnO <sub>2</sub> (ss)
	95 : 5	1000	10	1326	19	L-Ta <sub>2</sub> O <sub>5</sub> phase(s)
				1449	19	H <sub>tri</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss)
				1586	4	H <sub>tri</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss)
90 : 10	1000	10	1327	19	L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + H-Ta <sub>2</sub> O <sub>5</sub> (ss)	
			1449	19	H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss)	
			1592	4.5	H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss)	
					L-Ta <sub>2</sub> O <sub>5</sub> phases(s)	
Ta <sub>2</sub> O <sub>5</sub> -Ga <sub>2</sub> O <sub>3</sub>	75 : 25	1225	168			
	95 : 5	1000	10	1523	16	H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + Ta <sub>2</sub> O <sub>5</sub> · 6ZrO <sub>2</sub>
		1000	10			
Ta <sub>2</sub> O <sub>5</sub> -Cr <sub>2</sub> O <sub>3</sub>	90 : 10	1000	10	1300	16	L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + H-Ta <sub>2</sub> O <sub>5</sub> (ss) + GaTaO <sub>4</sub> -wolframite type <sup>g</sup>
				1444	64	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + GaTaO <sub>4</sub> -ixiolite type
				1586	4	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + GaTaO <sub>4</sub> -rutile type
	95 : 5	300 <sup>d</sup> 1000	1 10	1602	20	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) <sup>f</sup>
				1300	16	L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + GaTaO <sub>4</sub> -wolframite type
				1444	64	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + GaTaO <sub>4</sub> -ixiolite type
			1602	4	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + GaTaO <sub>4</sub> -rutile type	
Ta <sub>2</sub> O <sub>5</sub> -Fe <sub>2</sub> O <sub>3</sub>	90 : 10	300 <sup>d</sup> 1000	1 10	1320	16	H-Ta <sub>2</sub> O <sub>5</sub> (ss) + L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + CrTaO <sub>4</sub> -rutile type <sup>g</sup>
				1444	16	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + H <sub>mon</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + CrTaO <sub>4</sub> -rutile type <sup>g</sup>
				1591	44	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + CrTaO <sub>4</sub> -rutile type (trace) <sup>f</sup>
	99 : 1	1200	10	1602	4	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + CrTaO <sub>4</sub> -rutile type
				1320	16	L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + H-Ta <sub>2</sub> O <sub>5</sub> (ss) + CrTaO <sub>4</sub> -rutile type <sup>g</sup>
				1448	16	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + CrTaO <sub>4</sub> -rutile type
			1597	4	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + CrTaO <sub>4</sub> -rutile type	
Ta <sub>2</sub> O <sub>5</sub> -Sc <sub>2</sub> O <sub>3</sub>	98 : 2	1200	10	1457	16	H <sub>tri</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss)
				1585	4	H <sub>tri</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss)
				1445	16	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss)
	97 : 3	1200	10	1468	65	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss)
				1650	67	H <sub>tri</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) <sup>f</sup>
				1725	0.5	L-Ta <sub>2</sub> O <sub>5</sub> phase(s)
				<sup>h</sup> 1000	1	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + L-Ta <sub>2</sub> O <sub>5</sub> phase(s)
				<sup>h</sup> 1000	16	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + L-Ta <sub>2</sub> O <sub>5</sub> phase(s)
				<sup>h</sup> 1100	16	L-Ta <sub>2</sub> O <sub>5</sub> phase(s)
	97 : 3	1200	10	<sup>h</sup> 1200	60	L-Ta <sub>2</sub> O <sub>5</sub> phase(s)
				<sup>h</sup> 1250	10	L-Ta <sub>2</sub> O <sub>5</sub> phase(s)
				<sup>h</sup> 1300	10	L-Ta <sub>2</sub> O <sub>5</sub> phase(s)
95 : 5	1000	10	1641	2	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss)	
			1445	16	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + FeTaO <sub>4</sub> -rutile type	
			1581	4	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + FeTaO <sub>4</sub> -rutile type	
90 : 10	1000	10	1327	16	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + FeTaO <sub>4</sub> -rutile type <sup>g</sup>	
			1442	16	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + FeTaO <sub>4</sub> -rutile type	
			1619	19	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + FeTaO <sub>4</sub> -rutile type	
			1327	16	L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + FeTaO <sub>4</sub> -rutile type <sup>g</sup>	
			1442	16	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + FeTaO <sub>4</sub> -rutile type	
			1650	72	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss)	
98 : 2	1200	10	1734	19	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss)	
			1737	2	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss)	
			1737	0.5	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss)	
95 : 5	1000	10	1327	16	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + L-Ta <sub>2</sub> O <sub>5</sub> (ss) + ScTaO <sub>4</sub> -AlNbO <sub>4</sub> type <sup>g</sup>	
			1448	16	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + ScTaO <sub>4</sub> -AlNbO <sub>4</sub> type	
			1606	4	H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + ScTaO <sub>4</sub> -AlNbO <sub>4</sub> type	

TABLE 1. *Experimental data*—Continued

System	Composition mol percent	Heat treatment				X-ray diffraction analyses <sup>c</sup>
		Initial <sup>a</sup>		Final <sup>b</sup>		
		Temp. °C	Time hr	Temp. °C	Time hr	
Ta <sub>2</sub> O <sub>5</sub> -Lu <sub>2</sub> O <sub>3</sub>	90 : 10	1000	10	1327	16	L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + ScTaO <sub>4</sub> -AlNbO <sub>4</sub> type <sup>g</sup> H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + ScTaO <sub>4</sub> -AlNbO <sub>4</sub> type H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + ScTaO <sub>4</sub> -AlNbO <sub>4</sub> type
				1448	16	
				1608	4.5	
Ta <sub>2</sub> O <sub>5</sub> -MgO	95 : 5	1200	10	1640	20	H <sub>tri</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + LuTaO <sub>4</sub> H <sub>tri</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + LuTaO <sub>4</sub>
				1640	19	
				1327	16	
Ta <sub>2</sub> O <sub>5</sub> -NiO	95 : 5	1000	10	1445	16	L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + MgTa <sub>2</sub> O <sub>6</sub> -trirutile type H“30:1”-Ta <sub>2</sub> O <sub>5</sub> (ss) + MgTa <sub>2</sub> O <sub>6</sub> -trirutile type H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + MgTa <sub>2</sub> O <sub>6</sub> -trirutile type (trace)
				1608	4.5	
				1327	16	
Ta <sub>2</sub> O <sub>5</sub> -ZnO	90 : 10	1000	10	1445	16	L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + MgTa <sub>2</sub> O <sub>6</sub> -trirutile type H“30:1”-Ta <sub>2</sub> O <sub>5</sub> (ss) + MgTa <sub>2</sub> O <sub>6</sub> -trirutile type H <sub>tet</sub> -Ta <sub>2</sub> O <sub>5</sub> (ss) + MgTa <sub>2</sub> O <sub>6</sub> -trirutile type L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + NiTa <sub>2</sub> O <sub>6</sub> -trirutile type L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + H-Ta <sub>2</sub> O <sub>5</sub> (ss) + NiTa <sub>2</sub> O <sub>6</sub> -trirutile type <sup>g</sup> H“30:1”-Ta <sub>2</sub> O <sub>5</sub> (ss) + L-Ta <sub>2</sub> O <sub>5</sub> phase(s) <sup>f</sup> H“30:1”-Ta <sub>2</sub> O <sub>5</sub> (ss) + L-Ta <sub>2</sub> O <sub>5</sub> phase(s)
				1597	4.5	
				1331	65	
				1444	16	
				1559	16	
				1570	16	
	95 : 5	1000	10	1590	4	L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + NiTa <sub>2</sub> O <sub>6</sub> -trirutile type L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + H-Ta <sub>2</sub> O <sub>5</sub> (ss) + NiTa <sub>2</sub> O <sub>6</sub> -trirutile type <sup>g</sup> H-Ta <sub>2</sub> O <sub>5</sub> (ss) + L-Ta <sub>2</sub> O <sub>5</sub> (ss) + NiTa <sub>2</sub> O <sub>6</sub> -trirutile type <sup>g</sup> H-Ta <sub>2</sub> O <sub>5</sub> (ss) + L-Ta <sub>2</sub> O <sub>5</sub> (ss) + NiTa <sub>2</sub> O <sub>6</sub> -trirutile type <sup>g</sup> L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + ZnTa <sub>2</sub> O <sub>6</sub> -columbite type L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + H-Ta <sub>2</sub> O <sub>5</sub> (ss) + ZnTa <sub>2</sub> O <sub>6</sub> -columbite type <sup>g</sup> H“30:1”-Ta <sub>2</sub> O <sub>5</sub> (ss) + ZnTa <sub>2</sub> O <sub>6</sub> -rutile type L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + ZnTa <sub>2</sub> O <sub>6</sub> -columbite type L-Ta <sub>2</sub> O <sub>5</sub> phase(s) + H-Ta <sub>2</sub> O <sub>5</sub> (ss) + ZnTa <sub>2</sub> O <sub>6</sub> -columbite type <sup>g</sup> H“30:1”-Ta <sub>2</sub> O <sub>5</sub> (ss) + ZnTa <sub>2</sub> O <sub>6</sub> -rutile type
				1331	65	
				1444	16	
				1590	4	
				1333	19	
				1444	16	

<sup>a</sup> (Initial Heat Treatment)—All specimens were calcined as pressed disks on Pt foil at the indicated heat treatment with heating and cooling rates of approximately 4°C/min unless otherwise specified.

<sup>b</sup> (Final Heat Treatment)—All specimens were quenched in sealed Pt tubes from the indicated temperature, unless otherwise specified.

<sup>c</sup> The phases identified are given in the order of amount present at room temperature (greatest amount first). The phases are not necessarily those present at the temperature to which the specimen was heated.

L-Ta<sub>2</sub>O<sub>5</sub> phase(s)—One or more phases with an x-ray powder diffraction pattern similar to the low-temperature form of Ta<sub>2</sub>O<sub>5</sub>.

H<sub>tri</sub>-Ta<sub>2</sub>O<sub>5</sub> —Triclinic metastable distortion of the high-temperature form.

H<sub>mon</sub>-Ta<sub>2</sub>O<sub>5</sub> —Monoclinic metastable distortion of the high-temperature form related to the triclinic form by  $\sim a\sqrt{2}$  and  $\sim b\sqrt{2}$ .

H<sub>tet</sub>-Ta<sub>2</sub>O<sub>5</sub> —The tetragonal high-temperature form of Ta<sub>2</sub>O<sub>5</sub>.

H“30:1”-Ta<sub>2</sub>O<sub>5</sub> —A metastable monoclinic form of Ta<sub>2</sub>O<sub>5</sub> solid solution similar to that reported as “30:1” in the Ta<sub>2</sub>O<sub>5</sub> : TiO<sub>2</sub> system [4].

H-Ta<sub>2</sub>O<sub>5</sub> —The high-temperature form of Ta<sub>2</sub>O<sub>5</sub> in such poor crystallinity or insufficient amounts that the exact symmetry could not be determined.

ss —Solid solution.

<sup>d</sup> Specimen was sealed in a large Pt tube to minimize possible loss of more volatile component.

<sup>e</sup> Probably a result of reduction of the addition oxide.

<sup>f</sup> Probably due to change of specimen composition by the addition oxide reacting with Pt tube.

<sup>g</sup> Presence of three phases indicates non-equilibrium.

<sup>h</sup> Specimen powder was prepared for x-ray diffraction on a Pt bar, heated, and subjected to x-ray examination without further disturbance of the specimen. Each succeeding heat treatment had also had the previous treatments.

probably of tetragonal symmetry at the temperature from which the specimen was quenched. Just as in the Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> system, this tetragonal phase could not be quenched to room temperature in the systems involving P<sub>2</sub>O<sub>5</sub>, V<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5</sub>, ZrO<sub>2</sub>, Lu<sub>2</sub>O<sub>3</sub>, NiO, or ZnO. However, very good apparently tetragonal x-ray diffraction powder patterns could be obtained from systems involving SnO<sub>2</sub>, Ga<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Sc<sub>2</sub>O<sub>3</sub>, and MgO added to Ta<sub>2</sub>O<sub>5</sub> in amounts less than 5 mol percent

The heat treatment of the single phase apparently tetragonal specimen containing 2 mol percent Fe<sub>2</sub>O<sub>3</sub> (table 1)  $a = 3.830$ ,  $c = 35.68\text{\AA}$  indicates that this phase is not stable below about 1300°C where it reverts to

the low temperature polymorph. Nevertheless, it was assumed that single crystals of a size sufficient for structure analyses could be made in any of the second group of materials by annealing a specimen at high temperatures for a long period of time in a sealed platinum tube and subsequently quenching to room temperature. As can be seen from table 1 (footnote f) this cannot be done for systems involving SnO<sub>2</sub>, Ga<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, or Fe<sub>2</sub>O<sub>3</sub>, since the latter components apparently react with the Pt container over a period of time. The specimen becomes enriched in Ta<sub>2</sub>O<sub>5</sub> and “destabilized.”

Therefore only Sc<sub>2</sub>O<sub>3</sub> and MgO can be used to synthesize crystals of tetragonal H-Ta<sub>2</sub>O<sub>5</sub> solid solu-

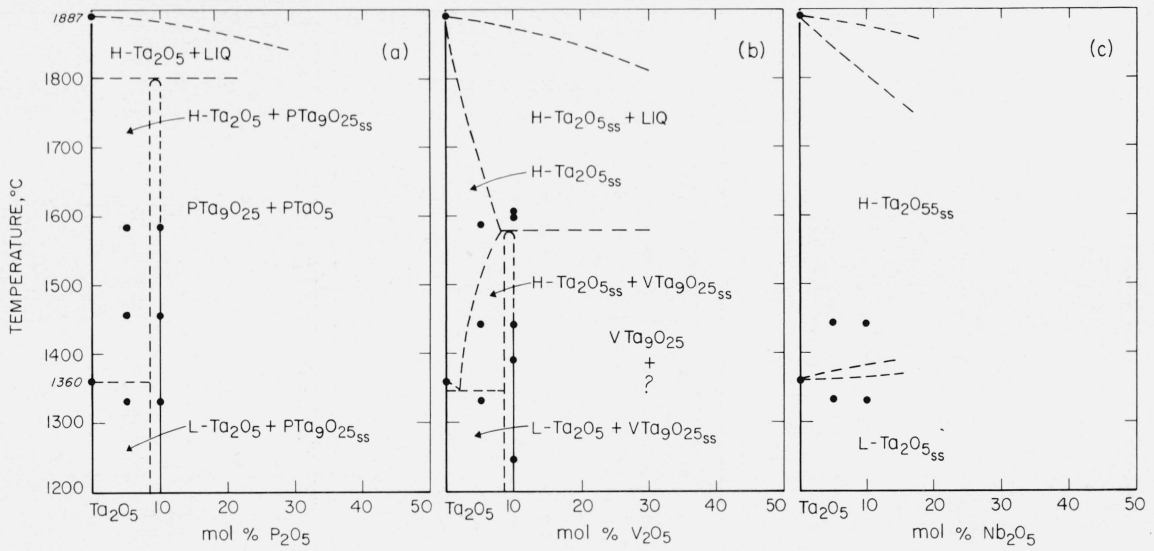


FIGURE 1.  $Ta_2O_5$ -rich region of  $Ta_2O_5$ - $Me_2O_5$  systems, as deduced from limited quenching and x-ray diffraction data.

● — experimental data points  
 H- $Ta_2O_5$ —high temperature form of  $Ta_2O_5$   
 L- $Ta_2O_5$ —low temperature form of  $Ta_2O_5$   
 ss—solid solution  
 (c) See references [13, 14] for more complete phase diagrams of  $Ta_2O_5$ - $Nb_2O_5$  system.

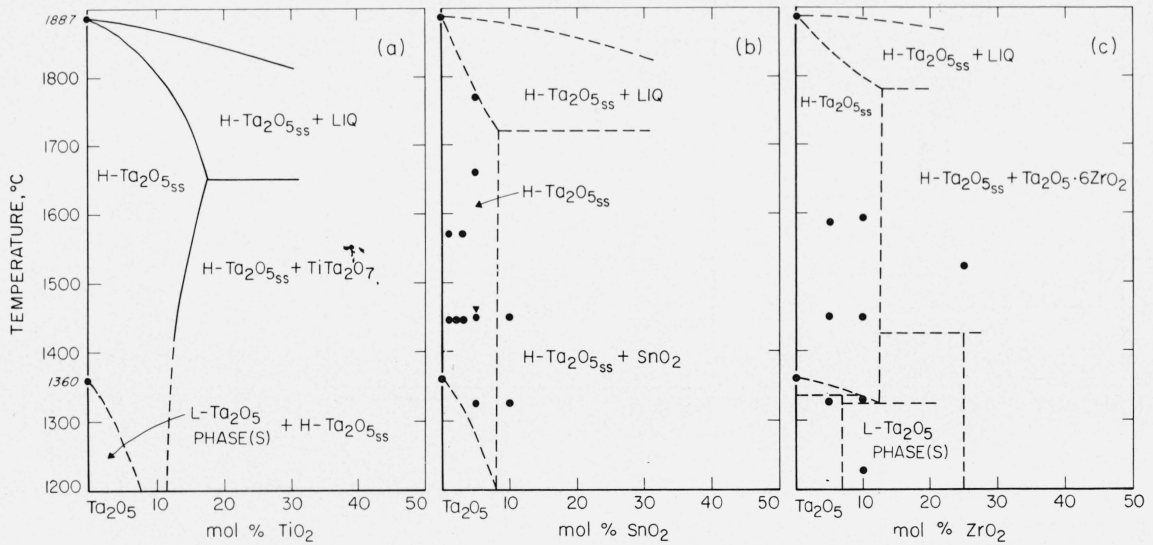


FIGURE 2.  $Ta_2O_5$ -rich regions of  $Ta_2O_5$ - $MeO_2$  systems, as deduced from limited quenching and x-ray diffraction data.

● — experimental data points  
 ▼ — specimen reheated at lower temperature than original heat treatment (see table 1)  
 H- $Ta_2O_5$ —high temperature form of  $Ta_2O_5$   
 L- $Ta_2O_5$  phase(s)—one or more phases with an x-ray powder diffraction pattern similar to the low temperature form of  $Ta_2O_5$   
 ss—solid solution  
 (a) Portion of  $Ta_2O_5$ - $TiO_2$  system redrawn from reference [4].



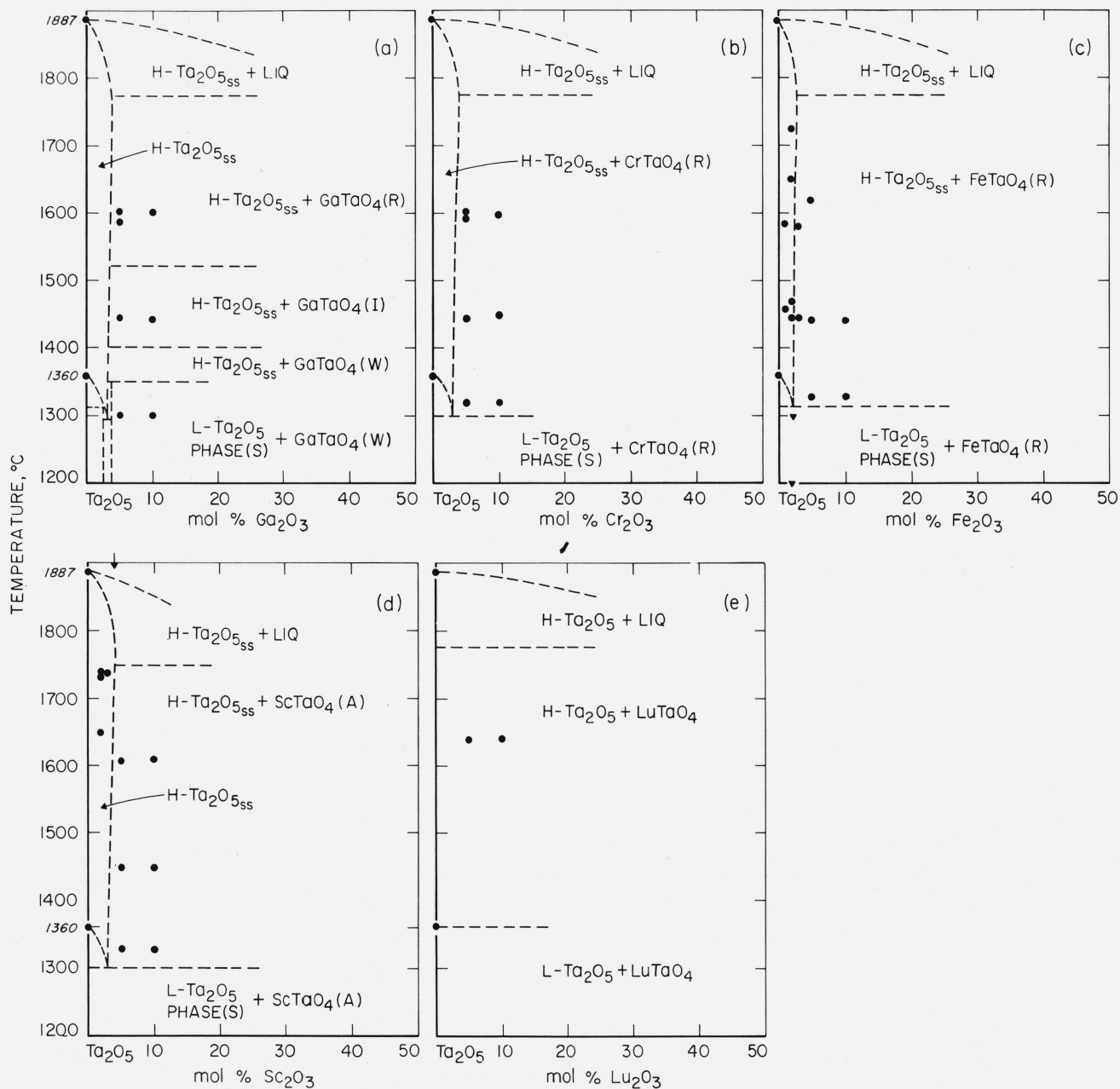


FIGURE 3.  $Ta_2O_5$ -rich regions of  $Ta_2O_5-Me_2O_3$  systems, as deduced from limited quenching and x-ray diffraction data.

- — experimental data points
- ▼ — specimens reheated at lower temperatures than original heat treatment (see table 1)
- H- $Ta_2O_5$  — high temperature form of  $Ta_2O_5$
- L- $Ta_2O_5$  phases — one or more phases with an x-ray diffraction powder pattern similar to the low temperature form of  $Ta_2O_5$
- ss — solid solution
- R — rutile-type structure
- I — ixiolite-type structure
- W — wolframite-type structure
- A —  $AlNbO_4$ -type structure.

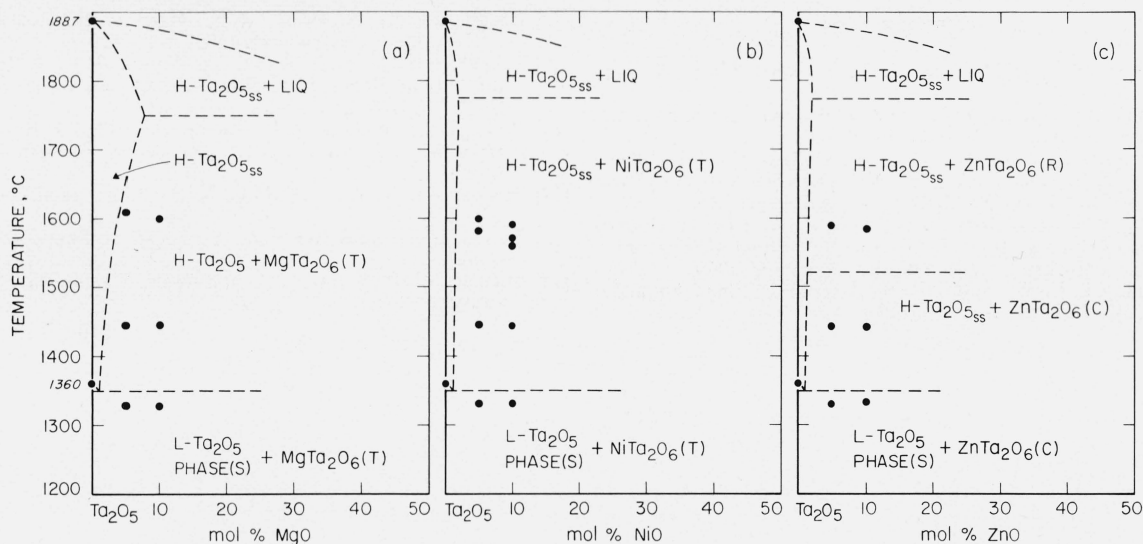


FIGURE 4.  $Ta_2O_5$ -rich regions of  $Ta_2O_5$ -MeO systems, as deduced from limited quenching and x-ray diffraction data.

- — experimental data points
- H- $Ta_2O_5$ —high temperature form of  $Ta_2O_5$
- L- $Ta_2O_5$  phase(s)—one or more phases with an x-ray diffraction powder pattern similar to the low temperature form of  $Ta_2O_5$
- ss—solid solution
- T—trirutile-type structure
- R—rutile-type structure
- C—columbite-type structure.

tion. Small crystals of  $98Ta_2O_5 : 2Sc_2O_3$  were successfully grown in the solid state using sealed or open Pt tubes at about  $1735^\circ C$ . Preliminary single crystal x-ray patterns, made with the Burger precession camera and Weissenburg camera, indicated that the crystals were of sufficient size for single crystal structure determination. However, accurate measurement of intensities revealed serious inconsistencies from one crystal to the next.

It should be noted that all of the additional oxides which tend to stabilize the high-temperature form are those with cations generally occurring in octahedral coordination. Another group of oxides containing smaller cations were found to stabilize phases structurally similar to the low-temperature form of  $Ta_2O_5$ . These experiments are reported in Part III of this series [10].

## 5. Crystal Growth

Attempts to grow larger crystals of  $H_{tet}\text{-}Ta_2O_5\text{-}Fe_2O_3$  solid solution by the Czochralski method were unsuccessful as there was an apparent slow reaction with the iridium container. Therefore efforts were directed toward growing a Sc stabilized crystal. The initial crystal growth attempts were made using 2 mol percent  $Sc_2O_3$  in the melt. At this level the amount of Sc incorporated into the crystal was insufficient to stabilize the high form. The concentration of  $Sc_2O_3$  in the melt was increased to 4 mol percent and this was sufficient for the crystals to be stabilized in the high

form in the "as grown condition." The actual amount of Sc incorporated in the crystals is not known.

For all compositions there were some general problems encountered which seem noteworthy and give a general indication of the unusual nature of this material. The first problem encountered was in the preliminary melting or filling of the iridium crucibles with either partially sintered pellets or powder. As the material melted it wet the iridium and the surface tension would pull the unmelted central core up in the container until some of the contents would flow over the sides. This problem was overcome by increasing the size of the container from  $\frac{3}{4}$  in ID to  $1\frac{1}{2}$  in ID. The second problem was encountered when the  $Ta_2O_5$  remaining in the iridium container was solidified at the termination of a growth attempt. Evidently  $Ta_2O_5$  undergoes a volume expansion on freezing and this expands the container after each run, thus drastically shortening the container's useful lifetime. The third problem was one which is common to those materials which are poor thermal conductors, particularly at high temperatures. In such a material, growth across the melt surface occurs, which insulates the top of the melt. "Melt off" occurs and a hollow bowl like crystal is grown. A similar behavior has been noted for the growth of  $TiO_2$  [11]. Due to the difficulties mentioned the largest crystals obtained were of the order of  $1 \times 2$  mm long and about 1 inch in diameter. A small cleavage fragment of one of these crystals has been used to determine the structure of H- $Ta_2O_5$  and the results of this structure determination will be reported elsewhere [12].

## 6. References

- [1] Lagergren, S., and Magneli, A., *Acta Chem. Scand.* **6**, 444 (1952).
- [2] Reisman, A., Holtzberg, F., Berkenblit, M., and Berry, M., *J. Am. Chem. Soc.* **78**, 4514 (1956).
- [3] Laves, F., and Peter, W., *Helv. Phys. Acta* **37**, 617 (1964).
- [4] Waring, J. L., and Roth, R. S., *Nat. Bur. Stand. (U.S.)*, **72A** (Phys. and Chem.) No. 2, 175-186 (Mar.-Apr. 1968).
- [5] Waring, J. L., and Roth, R. S., *Acta Cryst.* **17**, 455 (1964).
- [6] Waring, J. L., and Roth, R. S., *Nat. Bur. Stand. (U.S.)*, **69A**, (Phys. and Chem.) No. 2, 119-129 (Mar.-Apr. 1965).
- [7] Coughanour, L. W., Roth, R. S., Marzullo, S., and Sennett, F. E., *J. Res. NBS* **54**, 149 (1955).
- [8] Coughanour, L. W., Roth, R. S., Marzullo, S., and Sennett, F. E., *J. Res. NBS* **54**, 191 (1955) RP2576.
- [9] Schneider, S. J., Roth, R. S., and Waring, J. L., *J. Res. Nat. Bur. Stand. (U.S.)*, **65A** (Phys. and Chem.) No. 4, 345-374 (July-Aug. 1961).
- [10] Roth, R. S., Waring, J. L., (to be published, *J. Res. NBS*).
- [11] Nassau, K., and Boyer, A. M., *J. Am. Ceram. Soc.* **45**, 474-478 (1962).
- [12] Stephenson, N. C., and Roth, R. S. (to be published, *Acta Cryst.*).
- [13] Holtzberg, F., and Reisman, A., J., *Phys. Chem.* **65**, 1192 (1961).
- [14] Mohanty, G. P., Fiegel, L. J., and Healy, J. H., *J. Phys. Chem.* **68**, 208 (1964).

(Paper 74A4-613)