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Cubic ReO_3-type $W_{1-x}Ta_xO_{3-x/2}$ and $W_{1-x}Nb_xO_{3-x/2}$

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New types of compounds in the systems $W_{1-x}Ta_xO_{3-x/2}$ and $W_{1-x}Nb_xO_{3-x/2}$ were obtained from thermal decomposition of Ta- (or Nb-) doped peroxo-polytungstic acids at 750–900°C in air. The compounds were cubic with the ReO_3-type structure when $x \geq 0.2$ for the Ta system and $x \geq 0.26$ for the Nb system. However they were tetragonal at $x \sim 0.1$. Observed densities and X-ray intensities indicated that these compounds had oxygen vacancies. © 1988 Academic Press, Inc.

A number of studies have been performed on the W–Ta–O and W–Nb–O systems, especially regarding their phase equilibria and crystallographic shear structures (*1–6*). Sleight and Magneli (*3*) reported that these systems have tetragonal tungsten bronze (K_xWO_3)-type phases in the composition range $0.2MO_{2.5}0.8WO_3$–$0.5MO_{2.5}$ $0.5WO_3$ (M = Nb or Ta) at 1400°C. According to a W–Nb–O phase diagram established by Roth and Waring (*4*), there are 12 stable phases in the fully oxidized WO_3–$NbO_{2.5}$ system over 1250°C.

In this paper, we report previously unreported cubic ReO_3-type and related tetragonal phases in the fully oxidized $(1 - x)$ WO_3–$x$$TaO_{2.5}$ and $(1 - x)WO_3$–$x$$NbO_{2.5}$ systems obtained from thermal decomposition of mixed peroxo-polyacids based on W and Ta (or Nb). These peroxo-polyacids were developed by the present authors as an inorganic resist material for microlithography (*7, 8*).

Synthesis procedures for Nb-doped peroxo-polyacids denoted by xNb–IPA (where x = Nb/(W + Nb) atomic ratio) were similar to those previously reported for nondoped acids (*9, 10*), of which empirical formula is typically, $m$$CO_2$$12WO_3$ $7H_2O_2$$n$$H_2O$, where m = 0–4 and n = 20–25. An appropriately weighed powder mixture of metallic tungsten (8–9 μm particle size) and niobium carbide (5.4 μm) was dissolved in 15% H_2O_2, yielding a pale yellow acidic solution. A small amount of insoluble impurities was removed using a 0.2-μm filter paper and excess H_2O_2 was catalytically decomposed with platinized Pt nets. The solution was then dried at room temperature. Yellow amorphous glassy matter (xNb–IPA) was thus obtained.

The above procedures were not applicable to the synthesis of Ta-doped peroxo-polyacids (xTa–IPA), because neither metallic Ta nor TaC was soluble in H_2O_2.

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Therefore, they were synthesized from metallic W, $Ta(OC_2H_5)_5$, and H_2O_2. Ethanol-diluted $Ta(OC_2H_5)_5$ was slowly added to a $H_2O_2/C_2H_5OH/H_2O$ solution. White matter precipitated, but it quickly dissolved, giving an almost clear solution. Ethanol was evaporated at room temperature. The solution was then transferred to a separatory funnel together with diethyl ether to remove organic compounds produced during the reaction. The residual ether was evaporated, and excess H_2O_2 and insoluble particles were removed from the solution, yielding a clear peroxo-polytantalic acid (Ta–IPA) solution. This solution was added to a nondoped peroxo-polytungstic acid solution and left at room temperature for 24 hr or more. It was then dried at room temperature, yielding a noncrystalline Ta-doped peroxo-polytantalic acid (*x*Ta–IPA). Raman spectra indicated that *x*Ta–IPA was not a mixture of Ta- and W-based polyacids, but a compound based on a polyanion consisting of W and Ta. This was also the case for *x*Nb–IPA.

TABLE I

POWDER X-RAY DIFFRACTION DATA FOR 800°C-TREATED *x*Ta-IPA($W_{1-x}Ta_xO_{3-x/2}$, $x = 0.3$)

(cubic, 0^1 – *Pm*3*m*, $a = 3.819(2)$ Å) *h k l*	*d*(obs)	*d*(calc)	*I*(obs)	*I*(calc-1)	*I*(calc-2)
1 0 0	3.822	3.819	100	100	100
1 1 0	2.698	2.700	45	56	68
1 1 1	2.202	2.205	12	14	13
2 0 0	1.909	1.910	17	15	18
2 1 0	1.707	1.708	28	31	31
2 1 1	1.558	1.559	15	16	20
2 2 0	1.350	1.350	4	7	9

Note. *d*(obs), *d*(calc): observed and calculated *d*-spacing. *I*(obs), observed intensity. *I*(calc-1), *I*(calc-2), intensities calculated assuming two different site occupations (see text). $R = \Sigma|I(\text{obs}) - I(\text{calc})|/\Sigma|I(\text{obs})| = 0.10$ for calc-1 and 0.17 for calc-2.

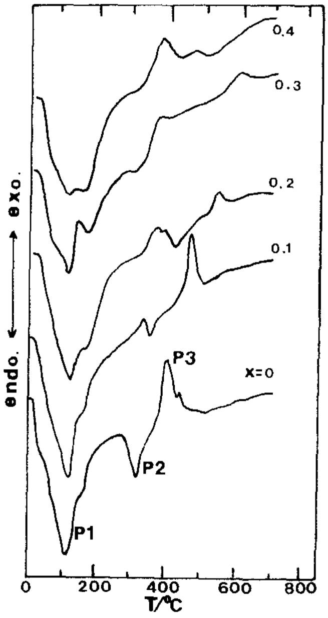

FIG. 1. Differential thermal analysis curves for *x*Ta–IPA ($x = 0$–0.4). Sample weight, about 40 mg; heating rate, 30°C/min; atmosphere, air.

Differential thermal analysis results recorded for *x*Ta–IPA are shown in Fig. 1. The strong endothermic peak (P1) in the 100–200°C region for every *x*Ta–IPA corresponds to the release of zeolitic water and peroxo-oxygen. The second endothermic peak (P2), which shifts to the high-temperature side and becomes vaguer as *x* increases, corresponds to the decomposition of the polyanion structure. This peak was accompanied by a slight weight loss probably due to the release of the structural water of polyanion. It is reasonable to assume that an amorphous framework consisting of WO_6 and TaO_6 octahedra is completed at the temperature for P2. The exothermic peak (P3) with no accompanying weight change is due to crystallization heat. The greater the Ta content *x*, the higher the crystallization temperature and the vaguer the peak shape. X-ray diffraction showed that crystallization of *x*Ta–IPA ($x = 0.4$) was not complete at 700°C, because every diffraction peak was broad and there was a significantly intense halo peaking nearly at $d \div 3.7$ Å. Even at 900°C, a weak halo peak was still observable, indicating presence of amorphous networks. These facts indicate that the thermal stability of the (W,Ta)O_6 amorphous framework increases remarkably with increasing x. The thermal decomposition of xNb-IPA was basically similar to the above.

Crystalline phases derived from xTa–IPA by heating them at 750–900°C were cubic if $x > 0.2$. Observed d-spacings and powder X-ray diffraction intensities for 800°C-treated xTa–IPA ($x = 0.3$) are compared with calculated values in Table I. Intensities were calculated assuming the space group of $Pm\bar{3}m$ with the following site occupancies, where the metal site(s) were statistically occupied by W and Ta:

Atoms	Sites	Site occupancies calc-1	 calc-2
W, Ta	1a	1.0	1.0
W, Ta	1b	0.0	$x/(6 - x)$
O	3d	$1 - x/6$	1.0

Observed and calculated intensities agree satisfactorily. The agreement of calc-1 is better than calc-2, indicating the oxygen vacancy scheme (R indices for calc-1 and -2 are 0.10 and 0.17, respectively). This scheme is also confirmed by comparing observed and calculated densities (Fig. 2). Therefore, this compound may have an ReO$_3$-type structure with oxide ion vacancies, and can be described as $W_{1-x}Ta_xO_{3-x/2}$ ($x = 0.3$).

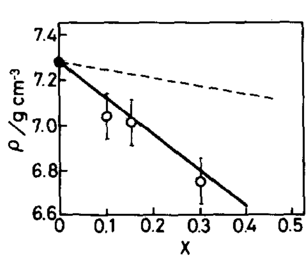

FIG. 2. Comparison of observed and calculated densities of $(1 - x)WO_3$–xTa$O_{2.5}$ derived from xTa–IPA. Solid circle at $x = 0$, usually accepted density of WO_3; open circles, observed densities; solid line, density calculated assuming oxide ion vacancy scheme; dashed line, density assuming full occupation of anion lattice points. (See text.)

TABLE II

POWDER X-RAY DIFFRACTION DATA FOR $W_{1-x}Ta_xO_{3-x/2}$ ($x = 0.1$)

(tetragonal, $a = 5.318(14)$ Å, $c = 3.812(11)$ Å)

$h\ k\ l$	d(obs)	d(calc)	I(obs)	I(calc)
0 0 1	3.81	3.812	47	46
1 1 0	3.76	3.760	100	100
1 0 1	3.10	3.098	15	12
1 1 1 2 0 0	2.67	2.677 2.659	80	49 28
2 0 1	2.179	2.181	19	17
2 1 1	2.017	2.018	5	5
0 0 2	1.908	1.906	5	5
2 2 0	1.879	1.880	15	15
1 0 2	1.796	1.794	11	9
1 1 2	1.705	1.700	10	9
2 2 1	1.694	1.686	10	13
3 1 0	1.685	1.682	20	15
3 0 1	1.606	1.607	1	1
2 0 2	1.550	1.549	6	4
3 1 1	1.539	1.539	12	14
2 1 2	1.485	1.487	5	9
3 2 1	—	1.376	<1	1

Note. d(obs), d(calc), observed and calculated d-spacing. I(obs), I(calc), observed and calculated intensity. $R = \Sigma|I(\text{obs}) - I(\text{calc})|/\Sigma|I(\text{obs})| = 0.025$.

Powder X-ray diffraction results for a compound obtained by heat-treating xTa–IPA ($x = 0.1$) at 750°C in air are shown in Table II. Its d-spacings can be indexed in the tetragonal system with $a = 5.318(14)$ Å and $c = 3.812(11)$ Å. Observed intensities agree well with those calculated ($R = 0.025$) assuming the space group of $P4/nmm$ and the following atomic positions and occupancies:

Atoms	Sites	Occupancy
W, Ta	2c(1)	1.0
O(1)	2c(2)	$1 - x/6$
O(2)	4d	$1 - x/6$

This indicates that the compound has a dis-

TABLE III

STRUCTURE AND CELL DIMENSIONS OF MIXED OXIDES DERIVED FROM THERMAL DECOMPOSITION OF Ta_x–IPA AND Nb_x–IPA

x	Ta_x–IPA	Nb_x–IPA
0	Monoclinic $a = 7.30$, $b = 7.53$, $c = 7.68$ Å, $\beta = 90.54°$, $z = 4$ $v/4 = 52.8$ Å^3	
0.1 (0.07 for Nb)	Tetragonal $a = 5.318$, $c = 3.812$ Å, $z = 2$ $v/2 = 53.9$ Å^3	Tetragonal $a = 5.29$, $c = 3.83$ Å, $z = 2$ $v/2 = 53.6$ Å^3
0.2 (0.17 for Nb)	Cubic $a = 3.80$ Å^3, $z = 1$ $v = 54.9$ Å^3	Tetragonal $a = 5.34$, $c = 3.84$ Å, $z = 2$ $v/2 = 54.7$ Å^3
0.25 (0.26 for Nb)	Cubic $a = 3.808$ Å, $z = 1$ $v = 55.2$ Å^3	Cubic $a = 3.82$ Å, $z = 1$ $v = 55.7$ Å^3
0.3	Cubic $a = 3.819$ Å, $z = 1$ $v = 55.7$ Å^3	
0.4	Cubic $a = 3.845$ Å, $z = 1$ $v = 56.8$ Å^3	

Note. Monoclinic, $P2_1/m$; tetragonal, $P4/nmm$; cubic, $Pm3m$. v, unit cell volume.

torted $\mathrm{ReO_3}$-type structure with oxide ion vacancies.

Compounds derived from xNb–IPA yielded almost the same results. However, the tetragonal-cubic boundary for $\mathrm{W}_{1-x}\mathrm{Nb}_x\mathrm{O}_{3-x/2}$ was between $x = 0.17$ and 0.26.

Crystal structure and lattice parameters of $\mathrm{W}_{1-x}\mathrm{Ta}_x\mathrm{O}_{3-x/2}$ and $\mathrm{W}_{1-x}\mathrm{Nb}_x\mathrm{O}_{3-x/2}$ are summarized in Table III. For both systems, the average unit cell dimension, (cell volume)$^{1/3}$, increases almost linearly as Ta or Nb content x increases.

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