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Ternary tantalate compositions

The purpose of this communication is to present refined powder X-ray diffraction data and some properties of tantalates selected for a previous study [1] of possible low thermal expansion oxides. Four ternary* $A^{3+}B^{4+}C^{5+}O_6$ compounds were prepared, $AlTiTaO_6$, $AlHfTaO_6$, $YTiTaO_6$, and $YHfTaO_6$. Of these, $AlTiTaO_6$ and $YTiTaO_6$ had been previously studied [2, 3], but no powder X-ray diffraction data were available for them.

These oxides were prepared by co-hydrolysis to the mixed metal hydroxides from solutions of the respective metal alkoxides, using starting materials nominally of ⩾99% purity. Co-precipitated products were vacuum-dried and calcined for 40 h at 800 to 1000° C in air. Calcined powders were isostatically pressed into rods and sintered at a temperature ~20 to 30% below the melting point in argon.

Specimens were analysed chemically (X-ray fluorescence), their densities were measured by mercury intrusion porosimetry, and their melting points were determined by differential thermal analyses. Electrical resistivities were obtained with a digital multimeter or megohmmeter, and thermal expansion was determined with a fused silica pushrod dilatometer. Preparation of samples and property determinations have been discussed in more detail elsewhere [1].

The powder X-ray diffraction (XRD) patterns were obtained from a 114.6 mm Debye–Scherrer camera (with Cu$K\alpha$ radiation) and were corrected for film shrinkage. A densitometer† scan was made of each film, and integrated intensities recorded with a digitiser‡. Lattice constants were refined by a least squares fit to the Nelson–Riley extrapolation function [4]. Theoretical densities were calculated from refined lattice parameters. The structure types were determined by comparison of observed diffraction data with reported data for analogous structures. The structure types and

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*With respect to cations or systems (i.e. $A_2O_3 \cdot 2BO_2 \cdot C_2O_5$).
†GAF Model 652.
‡Hewlett-Packard 9821A Calculator with Model 20 Digitizer Pac.

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TABLE I Characterization of four $ABCO_6$ tantalates

Compound	Structure type*	Melting point (° C)	Average coefficient of linear thermal expansion ($\bar{\alpha} \times 10^6$) in the range 25 to 1000° C	Electrical resistivity (Ω cm)	Chemical analyses			Bulk density† (g cm^{-3})
					Oxide component	Theoretical (%)	Measured (%)	
$AlTiTaO_6$	Cassiterite (Vol. 1, p. 250), SnO_2, space group $P4_2/mmm$ (136)	1698	7.09	3.7×10^4	Al_2O_3	14.5	14.22	4.51
					TiO_2	22.7	22.47	
					Ta_2O_5	62.8	63.37	
$AlHfTaO_6$	Alpha lead oxide (Vol. 1, p. 259) $\alpha - PbO_2$, space group *Pbcn* (60)	2160	4.43		Al_2O_3	10.6	10.83	5.78
					HfO_2	43.6	44.96	
					Ta_2O_5	45.8	44.72	
$YTiTaO_6$	Columbite (Vol. 3, p. 362), $Nb_2(Fe, Mn)O_6$, space group *Pbcn* (60)	1750	7.49	1.1×10^8	Y_2O_3	27.2	27.13	4.51
					TiO_2	19.4	19.40	
					Ta_2O_5	53.4	53.85	
$YHfTaO_6$	Type A: unknown	1910	6.56	3.6×10^7	Y_2O_3	20.7	20.78	7.09
					HfO_2	38.7	37.03	
					Ta_2O_5	40.6	41.70	
$YHfTaO_6$	Type B: fluorite (Vol. 1, p. 239), CaF_2, space group *Fm*3*m* (225)							

*Volume and page number refer to [7].

†Of sintered specimens used for resistivity and expansion tests.

TABLE II Powder X-ray diffraction pattern for $AlTiTaO_6$*

Observed d-spacings (Å)	Calculated d-spacings (Å)†	Indices ($h\,k\,l$)	Relative intensities‡
3.216	3.238	1 1 0	77
2.485	2.489	1 0 1	70
2.283	2.290	2 0 0	20
2.182	2,187	1 1 1	13
2.044	2.048	2 1 0	5
1.683	1.685	2 1 1	100
1.616	1.619	2 2 0	37
1.481	1.483	0 0 2	19
1.446	1.448	3 1 0	32
1.357	1.357	3 0 1	42
1.347	1.348	1 1 2	36
1.244	1.245	2 0 2	16
1.167	1.168	3 2 1	31
1.145	1.145	4 0 0	11
1.093	1.094	2 2 2	25
1.078	1.079	3 3 0	16
1.040	1.040	4 1 1	32
1.037	1.037	3 1 2	37
1.024	1.024	4 2 0	16
0.967	0.968	4 2 1	16
0.967	0.966	1 0 3	
0.907	0.906	4 0 2	23
0.899	0.898	5 1 0	26
0.891	0.890	2 1 3	46
0.889	0.889	4 1 2	
0.875	0.875	5 0 1	82
0.875	0.875	4 3 1	
0.873	0.873	3 3 2	
0.843	0.843	4 2 2	40
0.830	0.830	3 0 3	37
0.818	0.817	5 2 1	83
0.818	0.817	3 1 3	
0.810	0.810	4 4 0	19
0.786	0.785	5 3 0	36
0.780	0.781	4 4 1	96
0.780	0.780	3 2 3	
0.780	0.779	4 3 2	

*$Z = 0.667$ (or $2MeO_2$); theoretical density = 6.26 g cm^{-3}; observed density = 6.26 g cm^{-3}.

†Based on tetragonal cell with $a = 4.5793 + 0.0003$ Å and $c = 2.9659 \pm 0.0003$ Å.

‡For Cu$K\alpha_{1,2}$ radiation, integrated; for approximately equal-valued observed d-spacings, a single value of observed intensity is given.

TABLE III Powder X-ray diffraction pattern for $AlHfTaO_6$*

Observed d-spacings (Å)	Calculated d-spacings (Å)†	Indices ($h\,k\,l$)	Relative intensities‡
3.538	3.564	1 1 0	22
2.879	2.900	1 1 1	100
2.710	2.730	0 2 0	18
2.480	2.494	0 0 2	18
2.383	2.395	0 2 1	14
2.341	2.353	2 0 0	11
2.124	2.134	1 2 1	7
2.034	2.044	1 1 2	15
1.837	1.841	0 2 2	22
1.775	1.782	2 2 0	33
1.706	1.712	2 0 2	77 br
1.691	1.697	1 3 0	
1.673	1.678	2 2 1	47
1.602	1.607	1 3 1	25
1.503	1.508	3 1 0	58
1.503	1.507	1 1 3	
1.444	1.450	2 2 2	77 br
1.439	1.443	3 1 1	
1.416	1.420	0 2 3	21
1.400	1.403	1 3 2	33
1.314	1.317	0 4 1	26
1.314	1.312	3 2 1	
1.286	1.290	3 1 2	7
1.245	1.247	0 0 4	11
1.213	1.216	2 2 3	9
1.186	1.188	3 3 0	21
1.186	1.188	1 3 3	
1.175	1.177	1 1 4	11
1.175	1.176	4 0 0	
1.149	1.156	3 3 1	39
1.149	1.149	2 4 1	
1.133	1.134	0 2 4	14
1.115	1.117	3 1 3	22
1.101	1.102	2 0 4	17

*$Z = 1.333$ (or $4MeO_2$); theoretical density = 8.33 g cm^{-3}; observed density = 8.27 g cm^{-3}.

†Based on orthorhombic cell with $a = 4.706 \pm 0.002$ Å, $b = 5.460 \pm 0.003$ Å, and $c = 4.989 \pm 0.002$ Å.

‡For Cu$K\alpha_{1,2}$ radiation; integrated; br = broad peak; for approximately equal-valued observed d-spacings, a single value of observed relative intensity is given.

unrefined lattice constants of two of the compounds ($AlTiTaO_6$ and $YTiTaO_6$) have been reported [2, 3]. For one compound, $YHfTaO_6$, an unknown structure type was apparent; its X-ray diffraction pattern was computer-indexed [5, 6].

Table I summarizes the purity, properties, and structures determined for these tantalates. Two structures of $YHfTaO_6$ were observed. After calcining (≤ 1000° C), the cubic phase existed. On sintering at 1350° C for 18 h, the material completely transformed to an unknown structure. Later experiments showed that transformation occurs as low as 1200° C. The exact point is uncertain since thermal analysis failed to indicate the transformation. It is possible that the cubic phase occurs because of the co-precipitation technique, and is metastable at all temperatures, with its transforma-

TABLE V Powder X-ray diffraction pattern for $YHfTaO_6$ (type A)*

Observed *d*-spacings (Å)	Calculated *d*-spacings (Å)†	Indices (*h k l*)	Relative intensities‡
3.687	3.704	2 5 0	41
3.117	3.122	3 0 0	100
3.117	3.121	0 1 2	
3.068	3.072	0 2 2	81
2.957	2.964	0 9 1	80
2.957	2.961	1 1 2	
2.916	2.919	1 2 2	94
2.805	2.795	3 0 1	16
2.723	2.749	3 2 1	
2.723	2.732	2 9 0	27 br
2.723	2.726	0 10 1	
2.598	2.597	2 1 2	53
2.502	2.505	2 9 1	24
2.459	2.464	2 4 2	52
2.412	2.415	0 8 2	13
2.412	2.408	3 8 0	
2.353	2.356	2 10 1	2
2.353	2.348	3 7 1	
2.188	2.194	4 0 1	
2.188	2.190	3 2 2	8
2.188	2.188	4 1 1	
2.141	2.144	4 3 1	2
2.092	2.092	2 12 1	
2.092	2.092	0 0 3	6
2.092	2.087	0 1 3	
2.062	2.063	4 5 1	
2.062	2.060	2 9 2	8
2.062	2.059	4 7 0	
1.912	1.910	3 8 2 (2 0 3, 2 1 3)	41
1.884	1.883	0 7 3 (4 0 2, 2 3 3)	28
1.849	1.849	3 9 2 (4 10 0, 2 4 3, 1 7 3)	90 br
1.760	1.767	5 3 1	21
1.741	1.738	3 0 3	58
1.726	1.726	3 2 3 (3 1 3)	43
1.700	1.705	2 8 3	19
1.676	1.679	5 8 0 (4 8 2)	15
1.653	1.658	5 7 1	6
1.621	1.622	5 8 1 (2 10 3)	20
1.601	1.599	5 2 2 (4 10 2)	19
1.576	1.579	3 8 3 (5 9 1)	29 br
1.555	1.553	6 2 0 (6 0 2, 0 2 4, 4 0 3 6 1 0, 4 1 3, 4 2 3 0 3 4, 1 0 4, 1 1 4	26
1.533	1.532	5 6 2 (0 4 4, 1 3 4, 4 4 3)	63
1.493	1.491	6 6 0 (4 6 3, 2 0 4, 2 1 4)	78 br
1.469	1.468	6 7 0 (0 7 4, 2 3 4, 4 7 3)	34
1.445	1.445	2 5 4 (5 9 2, 0 8 4, 6 8 0, 4 8 3	17

*$Z = 16$ (or $48MeO_2$); theoretical density $= 8.13\,g\,cm^{-3}$; observed density $= 8.17\,g\,cm^{-3}$.

†Based on orthorhombic cell with $a = 9.367 \pm 0.008$ Å, $b = 30.27 \pm 0.08$ Å, and $c = 6.275 \pm 0.004$ Å; for $d < 2$ Å, calculated values are shown only for the plane with a spacing nearest the observed value; other possible contributing planes are given in parentheses.

‡For $CuK\alpha_{1,2}$ radiation, integrated; br = broad peak; for approximately equal-valued observed *d*-spacings, a single value of observed intensity is given.

TABLE IV Powder X-ray diffraction pattern for $YTiTaO_6$*

Observed d-spacings (Å)	Calculated d-spacings (Å)†	Indices ($h\,k\,l$)	Relative intensities‡
5.213	5.195	1 1 0	4
3.639	3.663	3 1 0	16
3.345	3.368	2 1 1	16
2.978	2.994	3 1 1	100
2.767	2.779	0 2 0	16
2.620	2.632	4 1 1	7
2.584	2.597	0 0 2	12
2.584	2.587	5 1 0	
2.554	2.557	1 0 2	11
2.431	2.450	0 2 1	35 br
2.431	2.435	6 0 0	
2.185	2.189	3 2 1	8
2.112	2.119	3 1 2	8
2.029	2.035	4 2 1	8
1.973	1.978	4 1 2	6
1.936	1.941	5 0 2	12
1.893	1.898	0 2 2	20
1.875	1.882	1 2 2	9
1.826	1.833	5 1 2	28
1.826	1.832	6 2 0	
1.769	1.777	6 0 2	28
1.724	1.733	1 3 1	51
1.724	1.732	3 3 0	
1.724	1.727	6 2 1	
1.639	1.646	8 1 1	23
1.639	1.643	3 3 1	
1.639	1.643	1 1 3	
1.623	1.627	7 0 2	9
1.609	1.612	2 1 3	18
1.587	1.592	5 2 2	8
1.587	1.589	7 2 1	
1.563	1.565	3 1 3	16
1.563	1.565	5 3 0	
1.563	1.562	7 1 2	
1.502	1.506	4 1 3	17
1.502	1.500	1 3 2	
1.502	1.497	6 2 2	
1.489	1.493	9 1 1	50
1.474	1.477	2 3 2	11
1.474	1.470	0 2 3	
1.460	1.464	8 2 1	20
1.460	1.462	1 2 3	
1.438	1.443	8 1 2	20
1.438	1.441	3 3 2	
1.438	1.441	2 2 3	

*$Z = 4$ (or $12MeO_2$); theoretical density = 6.51 g cm^{-3}; observed density = 6.28 g cm^{-3}.

†Based on orthorhombic cell with $a = 14.612 \pm 0.007$ Å, $b = 5.558 \pm 0.003$ Å, and $c = 5.195 \pm 0.002$ Å.

‡For Cu$K\alpha_{1,2}$ radiation; integrated; br = broad peak; for approximately equal-valued observed d-spacings, a single value of observed relative intensity is given.

TABLE VI Powder X-ray diffraction pattern for $YHfTaO_6$ (type B)*

Observed d-spacings (Å)	Calculated d-spacings (Å)†	Indices ($h\,k\,l$)	Relative intensities‡
2.998	2.990	1 1 1	100
2.592	2.589	2 0 0	32
1.835	1.831	2 2 0	52
1.562	1.561	3 1 1	37
1.496	1.495	2 2 2	8
1.293	1.295	4 0 0	5
1.190	1.188	3 3 1	12
1.157	1.158	4 2 0	9
1.058	1.057	4 2 2	5
0.996	0.997	5 1 1	8
0.996	0.997	3 3 3	
0.917	0.915	4 4 0	6
0.876	0.875	5 3 1	17
0.864	0.863	6 0 0	11
0.864	0.863	4 4 2	

*$Z = 1.333$ (or $4MeO_2$); theoretical density = 8.68 g cm^{-3}.

†Based on cubic cell with $a = 5.178 \pm 0.002$ Å.

‡For Cu$K\alpha_{1,2}$ radiation; integrated; for approximately equal-valued observed d-spacings, a single value of observed intensity is given.

tion kinetically inhibited (until $>$ 1000° C). The two phases are designated type A (unknown) and type B (cubic) $YHfTaO_6$.

Powder X-ray diffraction data are given for $AlTiTaO_6$ (Table II), $AlHfTaO_6$ (Table III), $YTiTaO_6$ (Table IV), $YHfTaO_6$, type A (Table V), and $YHfTaO_6$, type B (Table VI). For each of these phases, d-spacings were determined to as low a value as thought necessary for adequate identification. Refined lattice parameters, number of formula units per unit cell (Z), theoretical and observed (apparent specific gravity) densities are shown in the tables.

The X-ray diffraction pattern of $YHfTaO_6$ (type A) appears to represent a new structural type for $ABCO_6$ oxides. Initial indexing attempts (cubic, tetragonal, or hexagonal) were not sucessful, and a rather large orthorhombic cell was necessary to account for the observed reflections. This cell could be a supercell of one of the other types (cassiterite, alpha lead oxide, or columbite), or it could be mathematical coincidence. Whenever a cell with large parameters (i.e. 30 Å) is required for indexing, single-crystal data are necessary for substantiation.

The question of whether specific $ABCO_6$ phases are actually compounds was considered by Blasse [2]. As regards the four tantalate compositions studied here, three immediately qualify as ternary oxide compounds since the individual oxide components to not exhibit similar structures – $AlHfTaO_6$, $YTiTaO_6$, and $YHfTaO_6$. Since $AlTiTaO_6$ has the cassiterite structure, it could be considered as a solid solution because TiO_2 (rutile) and TaO_2 have the same tetragonal structure; thus, Al^{3+} could be considered as substituting into this structure.

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A new method for the preparation of high modulus thermoplastic films

In the last decade much effort has been made to obtain fibrous crystals of polymers with ultrahigh tensile strength and tensile modulus [1–9]. Also, a great deal of work has been done to understand the morphology and the crystallization mechanisms of fibres prepared by strain induced crystallization [10–14]. Theoretical considerations [15–19] have shown that longitudinal flow gradients of solutions or melts are the most important factors involved in extending the polymer molecules during flow processes. Therefore, most of the methods for crystallization of fibres are necessarily based on this principle. In industrial methods longitudinal flow gradients are usually achieved by high spinning rates. It is the intention of this paper to report a method which yields an extremely high longitudinal flow gradient ($\epsilon = 4 \times 10^4\ \text{sec}^{-1}$) by relatively low take up speed ($V_1 = 4\ \text{cm sec}^{-1}$) and high quenching rate in a small flow region during the preparation process. It will be shown that the flow gradient obtained by our method is sufficient to induce fibrous crystallization to a large volume fraction. The method reported here is of general applicability to semicrystalline polymers and offers easy means for the preparation of polymeric materials with high tensile modulus and strength.

For preparing the films, polymer solutions (~ 0.3 to 1%) are prepared in suitable solvents. A glass slide having a smooth surface is placed on a heating plate and allowed to attain the particular preparation temperature. For polyethylene (Lupolen 5261 Z, MW = 3×10^5) the solvent used is xylene, and the preparation temperature ranges from 122° C to 130° C. Usually, the chosen temperature for the film preparation is just above the highest crystallization temperature of the relaxed undercooled melt. In order to avoid temperature fluctuations, the heating plate is placed in a specially prepared small cabinet. The solution is dispersed uniformly over the glass slide, and the solvent is allowed to evaporate. The resulting thin molten polymer film (thickness about $\leqslant 1\ \mu$m) is taken off from one end of the glass slide with the help of a glass rod coated with the respective polymer and simultaneously wound onto a glass slide for supporting the thin oriented film (Fig. 1).

For transmission electron microscopic (TEM) investigations, the oriented film is cut into pieces and mounted onto copper grids. The microscope used is a JEOL JEM 200A operated at 100 kV.

The deformation ratio is assessed using the gold

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