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Abstract

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ON THE INVESTIGATION OF DOUBLE OXIDES CONTAINING TUNGSTEN, TANTALUM, OR NIOBIUM

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There is a large amount of data in the literature on compounds of the oxides of tungsten, tantalum, and niobium with basic oxides, i.e., on tungstates, niobates, and tantalates. Double oxides have been less studied (somewhat better than others—the compounds with niobium pentoxide ([1])). The present investigation to some extent fills this gap.

We investigated the reactions of thorium, cerium, and uranium dioxides with tantalum and niobium pentoxides, and of tantalum pentoxide with tungsten trioxide; new data were also obtained on oxygen compounds of uranium and tungsten. Mixtures of oxides were sintered in air, in nitrogen, or in evacuated quartz ampoules. Phase analysis of the sintering products was carried out in a Guinier camera. The results are given in Table 1.

Table 1*

Results of X-ray phase analysis of calcination products

Composition of starting preparation	Treatment	Observed phases	Composition of starting preparation	Treatment	Observed phases
$UO_2 + 2Ta_2O_5$	N_2, 1800°	$U(TaO_3)_4$	$UO_2WO_4 + 3WO_3$	1200°	$(U, W)O_3 + WO_2$
$UO_2 + 2Nb_2O_5$	Vacuum, 1200°	$U(NbO_3)_4$	$UO_2 + 6WO_3$	1200°	$U_{1/8}WO_3$
$UO_2 + Ta_2O_5$	N_2, 1800°	$UO_2 + U(TaO_3)_4$	$UO_2 + 10WO_3$	1200°	$U_{1/12}WO_3$
$CeO_2 + 2Nb_2O_5$	1100°	$Ce(NbO_3)_4$	$3WO_3 + Ta_2O_5$	1100–1150°	$3WO_3 \cdot Ta_2O_5$
$ThO_2 + 2Ta_2O_5$	N_2, 1750°	$Th(TaO_3)_4$	$4WO_3 + 3Ta_2O_5$	1100–1150°	$4WO_3 \cdot Ta_2O_5$
$ThO_2 + 2Nb_2O_5$	1200°	$Th(NbO_3)_4$	$3WO_3 + Nb_2O_5$	1100–1150°	$3WO_3 \cdot Nb_2O_5$

* The WO_3—Ta_2O_5 system was investigated completely (at intervals of 10 at. %). Only the compounds indicated in the table were found.

Uranium, thorium, and cerium dioxides form with niobium and tantalum pentoxides a group of compounds of the same type, Me($O_3)_4$. The structures of these compounds are very close to perovskite, but on the X-ray patterns a considerable number of superstructure lines are observed, and the true cells are tetragonal. It is interesting to note that niobates and tantalates have different superstructures: in the case of tantalates all lines of the X-ray patterns are indexed with a period a twice as large as that of the perovskite cell, while the period c does not change; in niobates the period c is doubled, and the period a does not increase. Table 2 gives the results of indexing the X-ray patterns of thorium niobate and tantalate.

Cerium niobate crystallizes in a rhombic cell, but the deviation from tetragonal symmetry is small. The intensity of the lines indicates displacement of tantalum and niobium atoms from the corners of the perovskite cell. The superstructure in the tantalates corresponds to a completely ordered arrangement of the atoms of the tetravalent elements over 1/4 of the cuboctahedra.

In niobates, layers of empty cuboctahedra alternate along the c axis with filled layers. In the filled layers, statistically, half of the cuboctahedra are occupied.

In this connection it was of interest to check whether the phase $(U, W)O_3$, which we had found earlier ([2]), is not the lower limit of the phases U_xWO_3, and to determine whether the phase $U(WO_3)_4$ has a superstructure. The specimen $U(WO_3)_4$ proved to be two-phase (a mixture of the perovskite phase and WO_2). On the X-ray patterns of $U_{1/8}WO_3$ and $U_{1/12}WO_3$ only lines of the perovskite phase were present, without superstructure lines. The periods of the cubic lattices are 3.813 kX for $U_{1/8}WO_3$ and 3.804 ± 0.001 kX for $U_{1/12}WO_3$. The lattice parameter of the phase $(U, W)O_3$ corresponds to the composition $U_{1/12}WO_3$.

Table 2

Results of indexing the X-ray patterns of $Th(NbO_3)_4$ **and** $Th(TaO_3)_4$

I	d	$1/d^2 \cdot 10^4$, observed	$1/d^2 \cdot 10^4$, calculated	hkl	I	d	$1/d^2 \cdot 10^4$, observed	$1/d^2 \cdot 10^4$, calculated	hkl
			$Th(NbO_3)_4$					$Th(TaO_3)_4$	
5	7,822	163,4	163,2	001	5	7,8079	164	165,6	100
2	3,9162	652	653,6	002	1	5,4892	332	331	110
4	3,8789	665	665	100	9	3,8891	661	662, 657,5	200, 001
5	3,4723	830	829	101	5	3,4750	828	828, 823	210, 101
10	2,7487	1323	1330, 1319	110, 102	10	2,7487	1323	1325, 1329	220, 201

I	d	$1/d^2 \cdot 10^4$, observed	$1/d^2 \cdot 10^4$, calculated	hkl	I	d	$1/d^2 \cdot 10^4$, observed	$1/d^2 \cdot 10^4$, calculated	hkl
1	2,6068	1471	1469	003	2	2,5992	1488	1490, 1485	300, 211
2	2,5864	1495	1493	111	3	2,2454	1984	1982	211
1	2,1647	2133	2136	103	1/2	2,1577	2147	2153, 2148	320, 301
3	1,9553	2616	2614	004	1/2	1,9497	2630	2630	002
6	1,9387	2660	2660	200	8	1,9426	2649	2650	400
2	1,8891	2802	2799	113	2	1,8870	2808	2815, 2870	410, 321
1/2	1,8818	2823	2823	201	7	1,7386	3307	3312, 3307	240, 401
1/2	1,7448	3284	3279	104	1	1,6938	3485	3473	411
1	1,7355	3322	3325	210	8	1,5866	3971	3969	241
2	1,6926	3489	3488	211	1/2	1,5548	4136	4140	500
2	1,5916	3946	3944	114					
6	1,5856	3976	3979	212					
1	1,5567	4125	4131	203					

Thus, the tantalates and niobates of uranium, cerium, and thorium are, structurally, rather close to the meta-tantalates and niobates of the alkali and alkaline-earth metals. Apparently, this is explained by the sufficiently large radii of the thorium, cerium, and uranium ions. It is characteristic that their dioxides are isostructural (fluorite type) and form continuous series of solid solutions.

Table 3

Lattice parameters (Å) of niobates and tantalates of U, Th, and Cl

Compound	a	b	c	c/a
$U(TaO_3)_4$	$7,720 \pm 0,003$	–	$3,860 \pm 0,002$	1/2
$Th(TaO_3)_4$	$7,773 \pm 0,003$		$3,900 \pm 0,001$	0,502
$U(NbO_3)_4$	$3,855 \pm 0,003$		$7,783 \pm 0,003$	2,019
$Th(NbO_3)_4$	$3,878 \pm 0,002$		$7,820 \pm 0,003$	2,016
$Ce(NbO_3)_4$	$3,881 \pm 0,002$	$3,897 \pm 0,002$	$7,843 \pm 0,002$	$c/a = 2,021 c/b = 2,013$

It would be of undoubted interest to obtain analogous compounds with dioxides

of the rutile type, if such compounds are in fact formed (the available data are contradictory).

In the Ta_2O_5—WO_3 system, two new phases were found: $3WO_3 \cdot Ta_2O_5$ and $3Ta_2O_5 \cdot 4WO_3$. The compound $3WO_3 \cdot Nb_2O_5$ had been described earlier ([1]). The X-ray patterns

Table 4

Results of indexing the X-ray diffraction patterns of $3WO_3 \cdot Ta_2O_5$ and $3WO_3 \cdot Nb_2O_5$

I	d	$1/d^2 \cdot 10^4$ observed	$1/d^2 \cdot 10^4$ calculated	hkl	I	d	$1/d^2 \cdot 10^4$ observed	$1/d^2 \cdot 10^4$ calculated	hkl
			$3WO_3 \cdot Ta_2O_5$						
1/2	8,7327	131,1	133,4	110	1/2	3,5769	782	784	111
3	5,4825	332,8	333,5	210	8	3,2881	925	919	201
2	4,3407	531	533,6	220	4	3,1755	992	986	211
10	3,8655	669	664,3; 667	001, 310	2	3,0455	1079	1080	400
5	3,3966	867	867	320	8	2,9522	1148	1147	410
1	3,1686	996	998	211	1	2,9020	1187	1189	221
1/2	3,0603	1068	1067	400	3	2,8656	1217	1215	330
6	2,9719	1132	1134	410	6	2,7470	1325	1325	311
2	2,8892	1198	1201, 1196	330, 221	4	2,7210	1351	1350	240
5	2,7421	1330	1334, 1332	240, 311	5	2,5604	1526	1526	321
4	2,5591	1527	1532	321	1	2,4050	1729	1729	401
$\sqrt{1/2}$	2,4062	1727	1734, 1733	510, 401	4	2,3587	1797	1796	411
4	2,3611	1794	1797	411	2	2,3165	1864	1864	311
2	2,3177	1861	1866	331	3	2,9347	2002	1999	241
3	2,2378	1997	1999	241	1	2,0863	2298	2295	530
1	2,1011	2265	2268	530	1	2,0681	2338	2336	501
3	1,9371	2657	2660	002	5	1,9634	2595	2596	002
1/2	1,9132	2733	2727	102	4	1,9231	2704	2700	620
3	1,8260	2999	3001, 2993	630, 212	1/2	1,8996	2770	2767	540
6	1,7294	3345	3335	710	4	1,8466	2931	2933	212
2	1,6856	3518	3527	322	4	1,8135	3042	3037	630
3	1,6504	3673	3663	621	1/2	1,7862	3135	3136	222

I	d	$1/d^2 \cdot 10^4$ observed	$1/d^2 \cdot 10^4$ calculated	hkl	I	d	$1/d^2 \cdot 10^4$ observed	$1/d^2 \cdot 10^4$ calculated	hkl
3	1,6257	3787	3792	412	3	1,7479	3273	3271	312
5	1,5806	4001	3994, 3996	242, 711	2	1,7276	3349	3349	621
			$3WO_3 \cdot Nb_2O_5$		4	1,7210	3376	3375	710
2	8,6136	134,8	135	110	1/2	1,7084	3428	3416	541
1	6,0745	271	270	200	3	1,6973	3472	3473	322
5	5,4351	338,5	337,5	210	4	1,6471	3686	3686, 3676	631, 402
3	4,3015	540	540	220	4	1,6331	3750	3743	412
9	3,9265	649	649	001	1/2	1,6204	3810	3811	332
8	3,8458	676	675	310	1	1,5926	3941	3946	242
1/2	3,7402	715	716	101	5	1,5761	4026	4024	711
					1	1,5582	4120	4117	650

The phases $3WO_3 \cdot Nb_2O_5$ and $3WO_3 \cdot Ta_2O_5$ are very similar and are indexed in tetragonal cells (Table 4) with the parameters: $a = 12.166 \pm 0.003$ kX, $c = 3.9265 \pm 0.0004$ kX for $3WO_3 \cdot Nb_2O_5$, and $a = 12.25 \pm 0.01$ kX, $c = 3.873 \pm 0.002$ kX for $3WO_3 \cdot Ta_2O_5$. There are two formula units $3WO_3 \cdot Me_2O_5$ per cell. The cells of these compounds may be regarded as superstructures with respect to ReO_3 (the period a of the tetragonal cell corresponds to the 310 direction of the ReO_3 cell). An analogous superstructure was found by Magnéli[3] in tetragonal tungsten bronzes, but the analogy is apparently formal, since the causes of the occurrence of the superstructure are obviously different.

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Note: Figure translations are in progress. See original paper for figures.