

Double Oxides Containing Niobium or Tantalum. V. Systems Containing a Group III Element

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In the course of an investigation of mixed oxides containing niobium or tantalum, the binary systems Nb_2O_5 and Ta_2O_5 with Al_2O_3 , Ga_2O_3 , In_2O_3 and Tl_2O have been studied, together with their reduction products. The following new phases were obtained: $\text{Al}_2\text{Nb}_2\text{O}_7$, $\text{Ga}_2\text{Nb}_2\text{O}_7$, $\text{Ga}_2\text{Nb}_2\text{O}_{7.25}$, $\text{In}_3\text{Ta}_2\text{O}_7$, TlNbO_3 and $\text{Tl}_2\text{Nb}_{16}\text{O}_{41}$ (approximately). Except for TlNbO_3 , unit-cell data for all these compounds and for the previously reported phases ABO_4 ($A = \text{Al, Ga or In}$; $B = \text{Nb or Ta}$) are presented. AlTaO_4 and GaTaO_4 are dimorphic.

Introduction

The few studies on mixed oxides of Nb or Ta with the metals of Group III b which have been reported are mainly confined to the aluminium compounds. Brandt (1943), seeking compounds of rutile structure, prepared AlNbO_4 and AlTaO_4 but found neither of them to be of this type. Goldschmidt (1960) and Müller & Nicholson (1962) studied the system Al_2O_3 – Nb_2O_5 and found AlNbO_4 to be the only intermediate compound. Pedersen (1962) has fully determined the structure of this compound. Goldschmidt reported AlTaO_4 to differ in structure from its niobium analogue, and Sarazin (1959) found it to form a rutile phase at high temperatures. In a study of the Al_2O_3 – Ta_2O_5 system, King, Schuetz, Durkin & Duckworth (1956) found a single solid-solution phase which existed from 50 to 75 mol% alumina. Its powder pattern did not correspond to that of the mineral simpsonite $\text{Al}_6\text{Ta}_4\text{O}_{10}$ (Kerr & Holmes, 1945).

Coates & Kay (1958) reported some electrical properties of 'compounds' AlNb_3O_9 and AlTa_3O_9 . No evidence that either of their products was a single phase was advanced however. Neither Goldschmidt nor Müller & Nicholson, who specifically sought it, found any sign of AlNb_3O_9 .

Roy (1954) reported GaTaO_4 to exhibit the rutile structure on the basis of its powder pattern and optical properties, but gave no details of its preparation. A structure analysis was reported by Morosin & Rosenzweig (1965).

InNbO_4 was synthesized by Hulme (1953) in connection with low-temperature dielectric studies. Keller (1962) found this compound and its tantalum analogue to have the wolframite structure.

Experimental

The mixed oxides were prepared by solid-state reactions between the appropriate pure oxides (except in the case of thallium compounds for which thallos carbonate was used) on a 100 mg scale. The niobium and tantalum oxides were spectrographically standardized material of about 99.95% purity. The other starting materials were of analytical-reagent quality. Niobium dioxide was prepared by the reduction of the pentoxide in hydrogen.

In each binary system studied, mixtures of various compositions were first fired and examined by X-ray powder diffraction, in order to identify the intermediate phases formed. The products were not analysed chemically because of the impossibility of achieving complete solution, but they were weighed after firing to check for possible changes in composition by volatilization of one component.

Electric resistance furnaces (850 to 1500°C) were used for the majority of the firings, but a few were carried out in an oxyacetylene furnace (*ca* 1800°C) and some in an arc image furnace reaching about 3000°C for short periods of time.

Single crystals of the products were grown by melting the mixed oxide in platinum or iridium boats and slow cooling. Powder patterns from the single-crystal material were used to check the composition against that previously determined from the powder work. Although some uncertainties (say $\pm 5\%$) attach to the compositions so determined, we are confident that our results, except where serious volatilization is noted below, are not grossly in error.

Reduction of the products was attempted by heating in a stream of hydrogen which had been passed through (i) finely divided copper supported on asbestos at 200°C, (ii) a molecular sieve (type 4a), and (iii) concentrated sulphuric acid.

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X-ray data were obtained with Ni-filtered Cu K radiation using Debye-Scherrer and Weissenberg cameras.

Wavelengths were taken to be $K\alpha_1$ 1.54051, $K\alpha_2$ 1.54432, and $K\alpha_m$ 1.54178 Å. Cell constants were obtained wherever possible from powder data by a Nelson-Riley extrapolation procedure using the least-squares computer program of Wait (1961). Otherwise they were determined from Weissenberg patterns by measurement of α_1/α_2 spot separations using the method of Main & Woolfson (1963). Lattice dimensions are given in ångströms and are considered accurate to ± 0.005 Å, except where other limits are quoted. For fuller experimental details see Whiston & Smith (1965) or Whiston (1963).

Results and discussion

1. Aluminium compounds

Alumina and niobium pentoxide reacted at 1300°C to form AlNbO_4 . This was the only compound formed in this system. By cooling it from temperatures above 1600°C single crystals were obtained and the dimensions of the monoclinic unit cell determined agree well with Pedersen's (1962) parameters:

	a	b	c	β
Pedersen (1962):	12.13 Å	3.726 Å	6.46 Å	107.2°
Present work:	12.163	3.715	6.456	109.

On reducing AlNbO_4 in oxygen-free hydrogen at 1300°C a blackish-grey product of composition $\text{Al}_2\text{Nb}_2\text{O}_7$ was obtained; its powder pattern indicated a rutile-type cell with dimensions slightly different from those of niobium dioxide.

	a	c
NbO_2 pseudo cell:	4.846 Å	2.993 Å
$\text{Al}_2\text{Nb}_2\text{O}_7$:	4.824	3.006.

No single crystals were obtained, nor could the compound be made by heating alumina with niobium dioxide in either hydrogen or argon at temperatures up to 1500°C.

Alumina and tantalum pentoxide reacted at 1500°C to yield a mixed oxide which appeared as a single phase extending over the range 50 to 75 mol% alumina, confirming the observation of King *et al.* (1956). The phase probably corresponds to Sarazin's (1959) low-temperature form of AlTaO_4 . Crystals of the phase were grown from a melt in oxidizing conditions at 1700°C. These were monoclinic with $a = 12.07$, $b = 3.883$, $c = 6.375$ Å, and $\beta = 108.0^\circ$. The observed density was 6.3 g cm^{-3} (calculated for $Z = 4$, 6.4 g cm^{-3}). When the melting was carried out in an argon atmosphere, a dark product was obtained which

corresponded to Sarazin's high-temperature modification of AlTaO_4 . The tetragonal parameters determined were $a = 4.569$ and $c = 2.965$ Å.

Both forms of AlTaO_4 were unchanged on firing in pure hydrogen for 12 h at 1000°C.

2. Gallium compounds

β -Gallia and niobium pentoxide reacted at 1300 to 3000°C to form GaNbO_4 . Single crystals were grown by the cooling of melts from 1450°C. The colourless crystals were monoclinic with $a = 12.44$ (1), $b = 3.783$ (1), $c = 6.596$ (2) Å, and $\beta = 107.4$ (2)°. Morosin & Rosenzweig (1965) gave $a = 12.660$ (5), $b = 3.7921$ (22), $c = 6.6147$ (28) Å, and $\beta = 107.90$ (2)°. Our cell is slightly smaller than theirs and gives a calculated density of 5.08 g cm^{-3} agreeing better than theirs with our observed density of 5.30 g cm^{-3} . The systematic absences were the same as for AlNbO_4 and AlTaO_4 and these three compounds are apparently isostructural.

GaNbO_4 was reduced by oxygen-free hydrogen at 900°C to give black $\text{Ga}_2\text{Nb}_2\text{O}_7$. On being stored in dry air this substance increased in weight by absorption of oxygen up to the limiting composition of about $\text{Ga}_2\text{Nb}_2\text{O}_{7.25}$. The absorption was accompanied by slight changes in the tetragonal lattice parameters:

	a	c	ρ_{obs}	ρ_{calc}
$\text{Ga}_2\text{Nb}_2\text{O}_7$:				
	4.838 Å	3.023 Å	5.80 g cm^{-3}	5.86 g cm^{-3}
$\text{Ga}_2\text{Nb}_2\text{O}_{7.25}$:				
	4.821	3.031	5.75	5.74.

The materials have the rutile structure with interstitial cations.

β -Gallia and tantalum pentoxide reacted at 1400°C to form GaTaO_4 , which was the only compound which could be prepared within this system. At the temperature required for its preparation, loss of gallia by vaporization was serious, and an excess of this reactant had to be used to produce the pure mixed oxide. Single crystals were formed by heating a mixture of $3\text{Ga}_2\text{O}_3 + \text{Ta}_2\text{O}_5$ in platinum for 12 h at 1530°C. They were found to be orthorhombic with $a = 4.964$, $b = 5.572$, and $c = 4.535$ Å, and to belong to one of the space groups $P2_1am$, $Pma2$ and $Pmam$. The monoclinic space group $P2_1/c$ required by the wolframite structure is obtained by the setting $a_o \rightarrow c_m$, $b_o \rightarrow b_m$, $c_o \rightarrow a_m$, $\beta \sim 90^\circ$. No departure from orthogonality was detected from single-crystal photographs. Several broad lines on the powder pattern of the material were resolved into doublets on Keller's diagram.

After heating in the arc image furnace at *ca* 3000°C GaTaO_4 was found to have changed to give a tetragonal rutile-type structure. This is the form observed by Roy (1954).

	<i>a</i>	<i>c</i>
Roy (1954):	4.64 Å	3.03 Å
Present work:	4.650 (2)	3.032 (1).

Both forms of GaTaO₄ when heated in pure hydrogen for 12 h at 1100°C were broken down into their constituent oxides.

3. Indium compounds

Indium sesquioxide and niobium pentoxide reacted at temperatures between 1000 and 1800°C to give only one compound, InNbO₄. Single crystals of this compound were obtained by heating the oxides together for 3 d in platinum at 1500°C. This treatment caused much loss of material by volatilization but the residue gave a powder pattern identical with that of InNbO₄ prepared at lower temperatures. The crystals were orthorhombic with *a* = 5.142, *b* = 5.747, *c* = 4.818 Å, and the same choice of possible space groups as for GaTaO₄.

InNbO₄, reduced in oxygen-free hydrogen at 900°C, produced niobium dioxide and indium metal.

Indium oxide and tantalum reacted at 1200 to 1700°C to form InTaO₄. Its powder pattern resembled those of GaTaO₄ and InNbO₄ but this time clearly indicated monoclinic symmetry. The parameters derived were *a* = 5.20, *b* = 5.83, *c* = 4.90 Å, and β = 91.4°. Attempts to prepare crystals of InTaO₄ were unsuccessful. Cooled melts of oxide mixtures always consisted of high-temperature tantalum.

A face-centred cubic phase with *a* = 5.1000 (5) Å was obtained by firing indium-rich mixtures at temperatures in excess of 1700°C. In most preparations it was accompanied by the monoclinic phase and the most probable composition seems to be In₃TaO₇, but the possibility cannot be ignored that it is a high-temperature fluorite form of InTaO₄.

Reduction of InTaO₄ and In₃TaO₇ in pure hydrogen at 900°C yielded Ta₂O₅ only; indium metal was presumably volatilized.

4. Thallium compounds

Thallous carbonate and niobium pentoxide reacted at temperatures from 1000 to 1400°C to form TiNbO₃.

Volatilization of Ti₂CO₃ was rather serious. No single crystals of TiNbO₃ were obtained and the powder patterns of the material were rather weak, but a new compound is definitely indicated. Above 1400°C the substance decomposed to give niobia.

Melts of initial compositions richer in thallous carbonate than 4:1 gave large rectangular crystals having the orthorhombic parameters *a* = 7.475, *b* = 12.98, *c* = 7.709 Å, and space group C222₁. Serious loss of thallous oxide took place during preparation but weight losses indicated an approximate composition of Ti₂Nb₁₆O₄₁.

Ti₂CO₃ and Ta₂O₅ did not react at temperatures below 3000°C.

References

- BRANDT, K. (1943). *Ark. Kemi Mineral. Geol.* **17A**, No. 15 (8 pp.).
- COATES, R. V. & KAY, H. F. (1958). *Philos. Mag.* **3**, 1449–1459.
- GOLDSCHMIDT, H. J. (1960). *Metallurgia*, **62**, 211–218, 241–250.
- HULME, J. K. (1953). *Phys. Rev.* **92**, 504.
- KELLER, C. (1962). *Z. Anorg. Allg. Chem.* **318**, 89–106.
- KERR, P. F. & HOLMES, R. J. (1945). *Bull. Geol. Soc. Am.* **56**, 479–504.
- KING, B. W., SCHUETZ, J. S., DURKIN, E. A. & DUCKWORTH, W. H. (1956). BMI-1106, US Atomic Energy Commission.
- MAIN, P. & WOOLFSON, M. M. (1963). *Acta Cryst.* **16**, 731–733.
- MOROSIN, B. & ROSENZWEIG, A. (1965). *Acta Cryst.* **18**, 874–879.
- MÜLLER, E. K. & NICHOLSON, B. J. (1962). *J. Am. Ceram. Soc.* **45**, 250–251.
- PEDERSEN, B. F. (1962). *Acta Chem. Scand.* **16**, 421–430.
- ROY, R. (1954). *J. Am. Ceram. Soc.* **37**, 581–588.
- SARAZIN, G. (1959). *C. R. Acad. Sci.* **248**, 815–817.
- WAIT, E. (1961). Report AERE-R3598. United Kingdom Atomic Energy Authority.
- WHISTON, C. D. (1963). PhD Thesis, Univ. of Sheffield.
- WHISTON, C. D. & SMITH, A. J. (1965). *Acta Cryst.* **19**, 169–173.