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Tantalum Analogs of the Tetragonal Tungsten Bronzes[1]

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Phases of composition $A_{0.5}TaO_3$ and $A_{0.5}TaO_{2.5}$ where A = Sr^{+2} or Ba^{+2} were found to have the tetragonal tungsten bronze structure the ideal formula for which is $K_{0.6}WO_3$. This structure apparently may exist with both anion and cation deficiencies. Analogous phases were found in the niobium system with barium but not with strontium. Partial substitution of the alkali metals in the tetragonal and hexagonal tungsten bronzes was effected by valence compensation using tantalum(V). Measurement of the electrical conductivity of pressed pellet samples showed that the substitution of Nb(IV) for Ta(IV) leads to much higher conductivity.

Introduction

Several ternary oxide systems have been described which are related to the cubic sodium tungsten bronze. $SrMoO_3$ and $BaMoO_3$[2] have the same structure but appear to be stoichiometric. $CaMoO_3$[3,4] is also stoichiometric, but has an orthorhombic structure. $La_{1-x}TiO_3$[5] and $Sr_{0.5+x}NbO_3$,[6] on the other hand, are both non-stoichiometric cubic phases, the latter showing the variation in color from blue to red with increasing strontium content. None of the other phases exhibits this property of color change with changing composition so characteristic of the sodium–tungsten bronzes. It is strange that tantalum has not been found to form similar phases in view of the negligible difference in size of the tantalum and niobium ions. Attempts to prepare such phases led to the isolation of a hexagonal barium–tantalum oxide.[7] This phase was produced when a particular batch of tantalum pentoxide was heated with metallic tantalum and barium oxide. Tantalum pentoxide from all other sources yielded a tetragonal phase under the same conditions. The hexagonal phase may be formed from any sample of tantalum pentoxide by the use of various fluxes and the study of its composition and structure is being continued. This paper is concerned with the characterization of the tetragonal phase and related compounds.

Experimental

Reactants.—The preparations of BaO and SrO[8] and of NbO_2[6] have been described in earlier papers. The other reactants were reagent grade chemicals. In general, the preparations were effected by heating appropriate mixtures of the alkaline earth carbonates and the transition metal oxide in Leco boats at 1100°. Phases containing tantalum in a lower oxidation state were obtained by using metallic tantalum as reducing agent, those containing niobium(IV) by using NbO_2 as reactant. In these cases the mixtures were heated in evacuated sealed silica capsules. Chemical analyses were obtained only for the compound $Ba_{0.5}TaO_3$. The compositions of other phases were assumed to be given approximately by the composition of the mixtures used to prepare them. The phases were identified from X-ray powder diagrams.

Results

The compound $Ba_{0.5}TaO_3$ formed by the reaction

$$BaCO_3 + Ta_2O_5 \longrightarrow 2Ba_{0.5}TaO_3CO_2$$

at 1100° was obtained as a single crystal by heating the product with lead(II) oxide.[9] Precession photographs served to determine the tetragonal symmetry. The complex X-ray powder diagram could be indexed satisfactorily with the parameters a = 12.60 Å., and c = 3.95 Å. The dimensions suggested an analogy with the tetragonal potassium tungsten bronze structure.[10] The relative intensities of the reflections given in Table I were calculated upon the assumption that the parameters for barium and tantalum were the same as those of potassium and tungsten. The agreement between the calculated and observed values is shown to be satisfactory. Analysis of the compound gave Ba = 23.15%, Ta = 60.32%. The values calculated from $Ba_{0.5}TaO_3$ are Ba = 23.08%, Ta = 60.78%. Further evidence that the two structures are similar was obtained by the preparation of similar phases of intermediate composition exemplified by the substances listed in Table II. In contrast to the highly colored tungsten bronzes, all of these preparations are colorless. The replacement of tungsten by tantalum apparently permits all of the elements to assume the highest oxidation state.

TABLE I

COMPARISON OF OBSERVED AND CALCULATED INTENSITIES OF REFLECTIONS FOR $Ba_{0.5}TaO_3$

Plane	I_{obsd}	$I_{calcd} \times 10^{-5}$
110	W^{--}	13.8
220	W^{--}	4.8
310 001	M	250.0
320	M	246.0
201	W^{--}	7.9
211	M^{+}	358.0
400	W	33.6
410	M^{++}	552.0
330 221	W^{+}	142.0
420 311	S	968.0
321	M	269.0
510 401	W^{-}	25.7
411	W^{--}	2.4
002	M^{-}	141.1
630	W	46.9
601	W	57.0

A series of oxygen-deficient phases with the same structure was prepared corresponding to the gen-

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[1] This research was sponsored by the Office of Naval Research; reproduction in whole or in part is permitted for any purpose of the United States Government.

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TABLE II

PHASES WITH THE TETRAGONAL BRONZE STRUCTURE

Formula	Unit cell parameters (Å.) a	c
$K_{0.5}(W_{0.5}Ta_{0.5})O_3$	12.36	3.90
$K_{0.4}Ba_{0.1}(W_{0.4}Ta_{0.6})O_3$	12.41	3.92
$Ba_{0.5}TaO_3$	12.60	3.95
$Na_{0.4}Sr_{0.1}(W_{0.4}Ta_{0.6})O_3$	12.33	3.87
$Sr_{0.5}TaO_3$	12.41	3.90

eral formula $A_{0.5}TaO_{2.5}$ where A = Ba, Sr. Partial and complete substitution of niobium for tantalum could be made without change in structure when the A cation was barium but this substitution could not be effected in the presence of strontium without change in structure.

All of these phases have a deep blue color which becomes darker with increasing niobium content. The resistivities of some of the preparations were compared by use of cylindrical pellets 0.45 cm. diam., 0.1 cm. long prepared by sintering compressed samples at 1200°. The contacts were made through platinum discs held against the ends by a spring. By heating these compounds at 1100° in air, oxidation to the colorless compounds occurred without change in structure. The gain in weight was close to that expected for oxidation from M^{+4} to M^{+5}. The lattice constants and resistivities of the oxygen deficient phases are given in Table III.

TABLE III

OXYGEN-DEFICIENT PHASES OF TANTALUM AND NIOBIUM WITH THE TETRAGONAL BRONZE STRUCTURE

Formula	Unit cell parameters (Å.) a	c	Resistivity (ohm cm.)
$Ba_{0.5}NbO_{2.5}$	12.60	3.95	
$Ba_{0.5}(Ta_{0.5}Nb_{0.5})O_{2.5}$	12.59	3.95	3.5
$Ba_{0.5}TaO_{2.5}$	12.60	3.95	21.2
$Sr_{0.25}Ba_{0.25}TaO_{2.5}$	12.52	3.93	2500
$Sr_{0.5}TaO_{2.5}$	12.41	3.93	200,000

Some preliminary experiments on substitution of tungsten by tantalum in other structures indicate that the phenomenon is fairly general. Mixtures of potassium, rubidium and cesium carbonates with tantalum(V) oxide and tungsten(VI) oxide gave colorless phases such as $K_{0.3}(W_{0.7}Ta_{0.3})O_3$, which seemed to be similar in structure to the hexagonal rubidium–tungsten bronze.[11]

Discussion

Not all of the phases were obtained as homogeneous products. $Ba_{0.5}NbO_{2.5}$ for example was always contaminated with other phases. The entire X-ray powder pattern of these preparations, however, could be accounted for by reflections due to the phases $Ba_6Nb_4O_{13}$, a cubic phase with lattice constant of about 4 Å. and the phase with the tetragonal bronze type of structure. The identification of the phase was thus possible although the sample was not pure enough to use for resistance measurements.

It should be observed that the barium–tantalum oxide $Ba_{0.5}TaO_3$ is cation-deficient only with respect to the number of equivalent A-cation sites available in the structure. The full complement of six A cations to ten B cations has not been obtained in this system. Magneli's preparations of the potassium–tungsten bronze also fell short of the maximum amount of potassium. Some variation in potassium content was reported, but in the barium–tantalum system no variation in lattice constant such as would be expected with changes in barium content was ever observed. It is interesting to note that in this system the phases containing tantalum in an oxidation state lower than +5 were arrived at by oxygen deficiencies, whereas in the strontium–niobium system the lower oxidation states of niobium were secured by the introduction of additional strontium ions.

The evidence for oxygen deficiencies in the structure is not yet complete. Direct chemical determination of the oxidation state of the tantalum in the reduced phases is difficult because of their unreactive nature. The deep blue color assumed by all of those phases, their relatively high conductivity, their oxidation to colorless phases at high temperatures by air to give the expected gain in weight, and the correspondence of the X-ray diagrams of the oxidized phases to that of the analyzed phase ($Ba_{0.5}TaO_3$) all suggest that we are dealing with oxygen deficient phases. The lattice constants are the same as the oxidized phases within the limits of our measurements. This is a common phenomenon in systems of this type.

The mixed systems such as $K_{0.4}Ba_{0.1}(W_{0.4}Ta_{0.6})O_3$ all contain tungsten and tantalum in their highest oxidation state only. It would seem reasonable to suppose that such phases could be formed containing tungsten in a lower oxidation state, but none has been obtained so far.

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