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Synthesis and Structural Characterization of Reduced Ternary Tantalum Oxides in the Tetragonal Tungsten Bronze Structure

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Single crystals of $Ba_3Ta_5O_{15}$ were prepared by heating a pressed pellet of $Ba_5Ta_4O_{15}$, Ta_2O_5, and Ta powder with 10 wt % $BaCl_2$ in a sealed tantalum tube at 1640 °C for 12 h. $Ba_3Ta_5O_{15}$ crystallizes in the tetragonal tungsten bronze structure (space group *P*4/*mbm*) with $a = 12.590(1)$ Å and $c = 3.967(2)$ Å. Ba cations occupy the two largest types of cation sites in the structure. An understanding of the thermal parameters of the Ba atom in the large tricapped trigonal prismatic site requires the inclusion of four additional more distant oxygen atoms in the coordination sphere. Ba stoichiometry is observed to range from $Ba_3Ta_5O_{15}$ to the fully oxidized $Ba_{2.5}Ta_5O_{15}$ without any change in structure type. A negative deviation from Vegard's law suggests some degree of cation ordering among available sites occurs. Properties of $Ba_3Ta_5O_{15}$ clearly indicate it should be classified as a metal oxide bronze. Two additional isostructural compounds, $Sr_3Ta_5O_{15}$ ($a = 12.379(2)$, $c = 3.8796(8)$ Å) and $Eu_3Ta_5O_{15}$ ($a = 12.386(3)$, $c = 3.875(1)$ Å), have also been prepared.

Introduction

There continues to be a significant amount of interest in transition metal oxide bronzes even though the first ternary transition metal bronze, Na_xWO_3, was discovered over 170 years ago.[1] Much of this interest has resulted from the unusual electronic properties and extreme corrosion resistance observed in a large number of these compounds. Recent work has focused primarily on the study of molybdenum oxide bronzes because of their quasi-low-dimensional properties which are manifested in the presence of charge density wave induced metal-to-semiconductor transitions, sliding charge density waves, and highly anisotropic transport properties.[2–5] Although a large number of bronzes are known for W and Mo and their mixtures with other transition metals, relatively few bronzes based solely on the group VB metals have been reported. Those containing group VB metals in reduced oxidation states include $M_xV_2O_5$ (M = Li, Na, K, Cu, Ag),[6] M_xNbO_3 (M = Sr, Ba),[7,8] Sr_xTaO_3,[9] $Ba_3Nb_5O_{15}$,[10–11] and $Ba_{0.5}TaO_{3-x}$.[9,12–13] The last compound was reported to exist both in the tetragonal tungsten bronze structure with oxygen vacancies and in a partially solved hexagonal structure. Later work revealed the hexagonal phase contained adventitious Si and was actually $Ba_3Ta_6Si_4O_{23}$.[14] A number of fully oxidized Nb and Ta compounds with the tetragonal tungsten bronze structure have also been prepared and examined primarily because of their ferroelectric properties.[15,16]

We have recently undertaken an investigation of the reduced Ba–Ta–O system in search of compounds characterized by Ta–Ta bonds. Although a large number of reduced ternary metal oxides with M–M bonds have been synthesized over the past 5 years for niobium, no similar compounds have been reported for tantalum. While recognizing that the chemistry of reduced niobium and tantalum systems is often quite different with tantalum tending to be less easily reduced, precedence for the formation of reduced tantalum compounds with metal–metal bonds exists both in TaO_2[17] and the tantalum halide systems.[18] In the process of our investigation we have prepared single crystals of $Ba_3Ta_5O_{15}$ which crystallizes in the tetragonal tungsten bronze (TTB) structure. The presence of a phase with the TTB structure in the Ba–Ta–O system was previously recognized by Galasso et al. and reported as the fully oxidized compound $Ba_{0.5}TaO_3$.[9] An apparently oxygen-deficient phase, $Ba_{0.5}TaO_{2.5}$, with the same structure and cell parameters as $Ba_{0.5}TaO_3$ was also noted but was incompletely characterized. In our study of $Ba_3Ta_5O_{15}$, we confirm the TTB structure and observe a range in Ba stoichiometry that extends from $Ba_{2.5}Ta_5O_{15}$ to $Ba_3Ta_5O_{15}$. No variation in oxygen stoichiometry was detected. Two structurally isomorphous

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compounds, $Sr_3Ta_5O_{15}$ and $Eu_3Ta_5O_{15}$, were also prepared and structurally characterized by X-ray powder diffraction.

Experimental Section

Synthesis. The compound $Ba_3Ta_5O_{15}$ was prepared by inductively heating a stoichiometric mixture of $Ba_5Ta_4O_{15}$, Ta_2O_5, and Ta powder in a sealed tantalum tube at 1500 °C for 5 h. The dark blue-gray microcrystalline powder appeared to be single phase and was obtained in greater than 95% yield as estimated by Guinier powder diffraction patterns. The diffraction patterns showed excellent agreement in both reflection intensity and position with a pattern calculated on the basis of the single crystal structural data. $Ba_3Ta_5O_{15}$ can be prepared at 1100 °C, but several regrindings are necessary and phase pure material is not obtained. $Ba_3Ta_5O_{15}$ apparently melts congruently (>1650 °C) and can be prepared by arc-melting a stoichiometric mixture of $Ba_5Ta_4O_{15}$, Ta_2O_5, and Ta under argon. The growth of single crystals from the molten $Ba_3Ta_5O_{15}$ may be possible but has not been explored in any detail because of the very high temperatures required. $Ba_5Ta_4O_{15}$ was prepared by heating stoichiometric quantities of BaO_2 (Strem) and Ta_2O_5 in air at 1100 °C for 24 h. Ta_2O_5 was made by oxidizing Ta powder (Strem, 99.9%) in air at 900 °C.

Single crystals of $Ba_3Ta_5O_{15}$ were obtained by the addition of 10 wt % $BaCl_2$ to a 1:2:2 molar mixture of $Ba_5Ta_4O_{15}$:Ta:Ta_2O_5 in a sealed Ta tube. Small dark blue rod-shaped crystals, most less than 0.2 mm in the long direction, were found growing from the pressed pellet after 12 h at 1640 °C. Reactions run under similar conditions without $BaCl_2$ have failed to produce any significant crystal growth and strongly suggest that $BaCl_2$ acts as a flux or mineralizer in this reaction. Microprobe analysis verified the metal composition and the absence of chlorine in crystals grown in the presence of $BaCl_2$.

$Ba_{3-x}Ta_5O_{15}$ samples were prepared from appropriate mixtures of $Ba_3Ta_5O_{15}$ and $Ba_{2.5}Ta_5O_{15}$. These mixtures were pressed into a pellet and heated under vacuum in Al_2O_3 crucibles at 1500 °C for 5 h. No visible attack of the crucibles was observed and microprobe analysis of samples prepared in this manner showed no detectable levels of aluminum. $Ba_{2.5}Ta_5O_{15}$ samples were obtained by direct reaction of stoichiometric quantities of $Ba_5Ta_4O_{15}$ and Ta_2O_5 in air at 1300 °C for 48 h. An open Al_2O_3 crucible was used as the reaction container.

$Sr_3Ta_5O_{15}$ and $Eu_3Ta_5O_{15}$ were prepared in microcrystalline form in sealed Ta tubes under identical conditions as those used to prepare $Ba_3Ta_5O_{15}$. $Sr_5Ta_4O_{15}$ and Eu_2O_3 were used as the Sr and Eu sources in the stoichiometric reactions, respectively. $Sr_5Ta_4O_{15}$ was prepared by heating a stoichiometric mixture of Ta_2O_5 and $SrCO_3$ in pressed pellet form in air at 1100 °C for 24 h. Eu_2O_3 was heated to 1100 °C overnight, prior to use, to decompose any carbonate present.

The $M_3Ta_5O_{15}$ (M = Ba, Sr, Eu) compounds appear to be indefinitely stable in air, water, and nonoxidizing acids, although they are very slowly attacked by HF/HNO_3 mixtures.

X-ray Powder Diffraction. Powder diffraction patterns were obtained on an Enraf-Nonius Guinier camera using Cu $K\alpha_1$ radiation. Samples were ground and mixed with a small amount of Si powder and mounted on transparent tape. Lattice parameters were calculated by least-squares fit of the Guinier powder diffraction data using the first five lines of the Si pattern as an internal standard.

Crystal Structure Determination. Two octants of single crystal X-ray diffraction data were collected on a well-faceted rectangular prism of $Ba_3Ta_5O_{15}$ sealed in a 0.3 mm glass capillary. Measurements were carried out at room temperature on a Rigaku AFC5S diffractometer using monochromatic Mo Kα radiation (λ = 0.710 73 Å). Initial examination of the crystal suggested a tetragonal cell with systematic absences of $0kl$, $k = 2n + 1$ consistent with previously obtained oscillation and Weissenberg photographs. The systematic extinctions suggested $P4bm$, $P\bar{4}b2$, and $P4/mbm$ as possible space groups. Intensity data were measured using a $\omega-2\theta$ scan. Six standard reflections were measured every 150 reflections during data collection. An average 8.6% decrease in the intensities of the standard reflections during data collection was observed and adjusted for by application of a linear decay correction to the data. Data reduction was done with the TEXSAN package.[19] Absorption effects were corrected empirically using ψ scans.[20] Averaging of symmetry equivalent reflections resulted in 594 unique reflections with an R_{ave} of 0.033. Details of the data collection are summarized in Table 1.

Table 1. Summary of Single-Crystal Diffraction Information for $Ba_3Ta_5O_{15}$

space group	$P4/mbm$ (No. 127)
Z	2
a, Å	12.590(1)
c, Å	3.967(2)
V, Å^3	628.8(4)
cryst size, mm	0.08 × 0.08 × 0.46
T	room temp
λ, Å	0.71073
μ, cm^{-1}	521.30
octants	$h, k, \pm l$
total reflns	1990
R_{ave}	0.033
indep reflns	594
indep reflns ($I > 1\sigma(I)$)	522
transmission factors	0.68−1.00
secondary ext coeff	$1.61(8) \times 10^{-6}$
R[a]	0.033
R_w[b]	0.042

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F) = [\sum(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$, $w = 1/\sigma^2(F_o)$.

The similarity of the cell constants, systematic extinctions and X-ray powder diffraction pattern of $Ba_3Nb_5O_{15}$[11] with those of the material being examined suggested that the two compounds were isostructural. The coordinates of the atoms in $Ba_3Nb_5O_{15}$ were used as a starting point for the least-squares refinement in $P4/mbm$. Complex neutral atom scattering factors were used.[21] The model converged to $R = 0.033$, $R_w = 0.042$ after application of a secondary extinction coefficient.[22] All atoms were refined anisotropically with the exception of O2 and O5 which were refined isotropically. Attempts to refine these two atoms anisotropically resulted in nonpositive definite thermal parameters. The Ba1 and Ba2 sites refined to full occupancy and were fixed at that level in the final cycle of refinement. The final difference electron density map contained maximum and minimum peak heights of 3.3 and −4.4 e$^-$/Å^3, respectively.

As a consequence of the problems encountered in the anisotropic refinement of O2 and O5 and the somewhat elongated thermal ellipsoid observed for Ba2, several additional models were investigated. A brief description of two of the models examined is provided below.

The elongation of the Ba2 thermal ellipsoid perpendicular to one of the mirror planes suggested that the actual Ba2 position might not lie on the mirror plane but slightly displaced from it. Movement of Ba2 off the mirror plane (in $P4/mbm$) and reduction of the occupancy to 50% to account for the doubling of the number of atomic positions, resulted in a stable model with Ba2 converging to a site ~0.16 Å off the mirror plane. No other significant differences or improvements in the refinement were noted, however, and anisotropic refinement of O2 and O5 still resulted in nonpositive definite thermal ellipsoids.

A reduction in the symmetry cell to an acentric space group was examined in our second alternate model. A number of

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Table 2. Positional and Thermal Parameters for $Ba_3Ta_5O_{15}$

atom	x	y	z	B_{eq}[a], Å^2
Ba1	0	0	0	0.76(3)
Ba2	0.17096(7)	0.67096	0	1.55(3)
Ta1	0	1/2	1/2	0.60(2)
Ta2	0.07551(4)	0.21416(4)	1/2	0.45(2)
O1	0	1/2	0	0.9(4)
O2	0.2822(8)	0.7822	1/2	0.6(2)[b]
O3	0.0774(8)	0.2107(8)	0	0.7(4)
O4	0.3434(8)	0.0065(9)	1/2	1.1(4)
O5	0.1417(7)	0.0687(7)	1/2	0.5(1)[b]

[a] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$. [b] Atoms were refined isotropically.

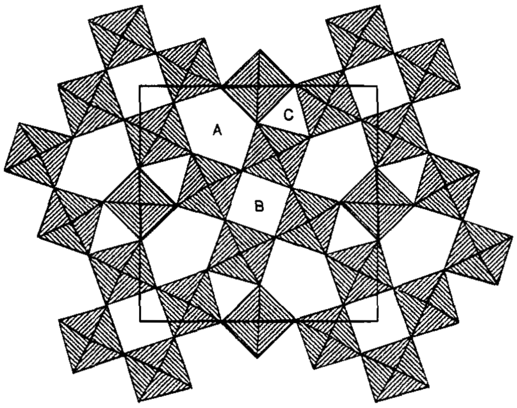

Figure 1. Projection of the tetragonal tungsten bronze structure emphasizing the cation sites A, B, and C formed by linkage of the shaded MO_6 octahedra through vertices. A, B, and C are the large tricapped trigonal prismatic, cuboctahedral, and small tricapped trigonal prismatic sites, respectively.

fully oxidized compounds with the tetragonal tungsten bronze structure exhibit ferroelectric properties[15,16] and hence have noncentrosymmetric structures. Refinement of the model was carried out in $P\bar{4}b2$ by placing Ta2, O3, O4, and O5 in general positions and all other atoms in appropriate special positions. The mirror plane perpendicular to the direction of elongation of the Ba2 thermal ellipsoid is removed in this space group. The Ba2 position is now located on a 2-fold axis. Although the acentric model did converge, it failed to provide any improvement in the structure over the refinement in the centric space group $P4/mbm$. In most cases the atomic positions converged to within 3σ of the values in $P4/mbm$. Anisotropic refinement of O2 and O5 once again produced nonpositive definite thermal ellipsoids. Further reductions in space group symmetry to an orthorhombic cell were considered unlikely in light of the very reasonable R_{ave}.

Results and Discussion

Structure. Final positional parameters and relevant interatomic distances for $Ba_3Ta_5O_{15}$ are tabulated in Tables 2 and 3, respectively. Thermal parameter and structure factor data are available as supplementary material.

$Ba_3Ta_5O_{15}$ crystallizes in the well-known tetragonal tungsten bronze structure.[23] In the TTB structure, MO_6 octahedra share vertices to form a three-dimensional structure containing three distinct types of holes or potential cation sites. A projection of the structure emphasizing the MO_6 framework is shown in Figure 1. The three cation sites from largest to smallest are a large tricapped trigonal prism (A), a slightly distorted cuboctahedron (B), and a small tricapped trigonal prism (C). The large tricapped trigonal prismatic site when viewed down the *c* axis appears to be a pentagonal prism. An examination of the cation-to-oxygen distances suggests that the tricapped trigonal prismatic description is probably an appropriate description of the localized bonding. However, the pentagonal prismatic description appears to be more appropriate and in fact necessary to understand the behavior of cations occupying the site (see below). Each cation site shares a face perpendicular to the *c* axis with an equivalent type of site above and below to form a set of continuous tunnels that run parallel to the *c* axis. Occupation of sites A, B, and C is primarily a function of the number of cations and their size. The smallest site (C) is typically occupied only by very small cations such as Li.

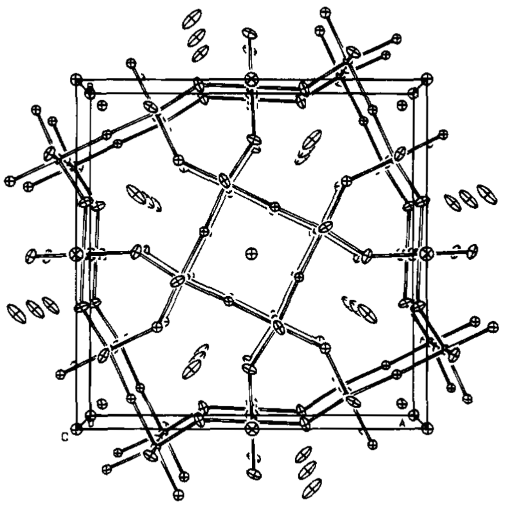

Figure 2. Crystal structure of $Ba_3Ta_5O_{15}$ viewed down the *c* axis. Ta–O bonds are shown.

Table 3. Selected Interatomic Distances (Å) in $Ba_3Ta_5O_{15}$

Ba1–O3	2.83(1)	Ta1–O1	1.9835(9)
Ba1–O5	2.804(6)	Ta1–O4	1.97(1)
Ba2–O1	3.0441(7)	Ta2–O2	1.986(9)
Ba2–O2	2.802(5)	Ta2–O3	1.9841(9)
Ba2–O3	3.21(1)	Ta2–O4	1.93(1)
Ba2–O4	2.873(8)	Ta2–O5	2.013(9)
Ba2–O5	3.340(7)	Ta2–O5	2.031(9)

The three-dimensional structure of $Ba_3Ta_5O_{15}$ viewed down the *c* axis is shown in Figure 2. The two largest cation sites, A and B, are completely occupied by Ba atoms while site C is empty. The cuboctahedral site (B), illustrated in Figure 3, is occupied by Ba1 and shows a slight compression along the *c* axis. Ba–O distances are 2.80–2.83 Å and are approximately 0.15–0.20 Å smaller than the sum of the Ba and O crystal radii (2.99 Å).[24] Similarly short distances are observed in the isostructural compound $Ba_3Nb_5O_{15}$[11] and in $Ba_3Ta_6Si_4O_{23}$.[14] Short Ba–O distances are also observed in a number of other compounds including the cubic form of $BaTiO_3$ (2.84 Å) where Ba occupies a cuboctahedral site.[25]

Ba2 resides in the large tricapped trigonal prismatic site (A) with the nine neighboring oxygen atoms at distances of 2.80–3.21 Å. Seven of the nine neighbors, those at the vertices of the triangular prism and one of the face-capping atoms, lie at distances of 2.804–2.873 Å.

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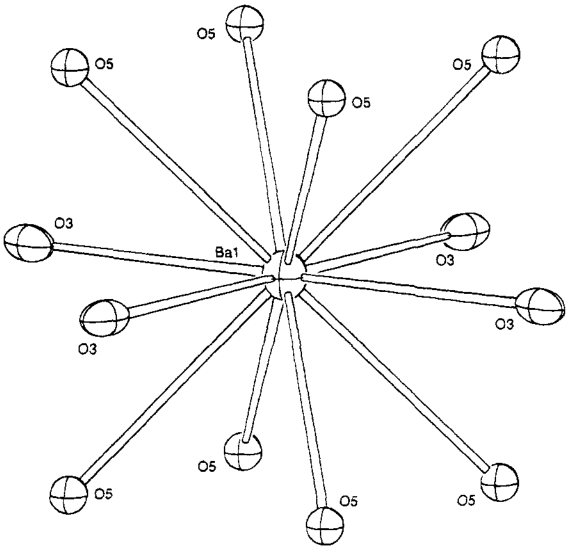

Figure 3. Bal site (B) in $Ba_3Ta_5O_{15}$. A 4-fold axis runs vertically through Bal and perpendicular to the mirror plane that passes through the O3 atoms (80% ellipsoids).

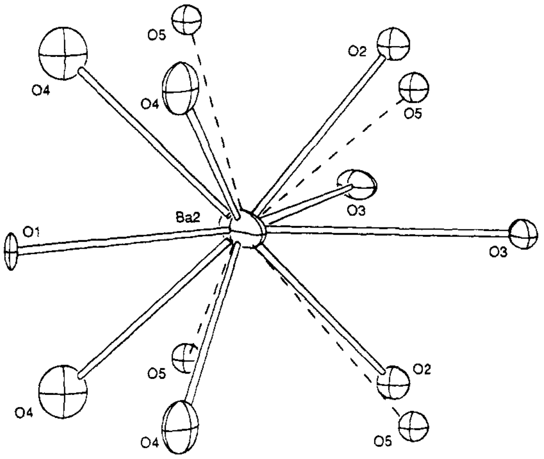

Figure 4. Ba2 site (A) in $Ba_3Ta_5O_{15}$. The Ba atom lies at the intersection of two perpendicular mirror planes. One mirror plane runs approximately in the page and passes through atoms O1 and Ba2. The other passes through O1, Ba2, and the two O3 atoms, roughly perpendicular to the page. Solid bonds are drawn to the oxygen atoms making up the tricapped trigonal prism. The four O5 neighbors connected by dashed bonds are at 3.34 Å and complete a distorted tricapped pentagonal prism around Ba2 (80% ellipsoids).

The other two face-capping oxygen atoms are found at a significantly longer distance of 3.21 Å. The Ba2 position, shown in Figure 4, lies at the intersection of two mirror planes. One mirror plane runs vertically through the tricapped trigonal prism cutting through O1, O2, and Ba2 positions and the other runs horizontally through the O1, O3, and Ba2 positions. Ba2 exhibits a somewhat elongated thermal ellipsoid (~2.4 times longer than wide) with the long axis directed perpendicular to the vertical mirror plane in Figure 4. A small expansion of the distances used to construct the coordination polyhedron of Ba2 shows four additional oxygen atoms (O5) at 3.340 Å located in approximately the direction of the Ba2 ellipsoid elongation. The four additional oxygen atoms complete the pentagonal prism around the Ba2 position that is evident in views of the structure along the *c* axis of the cell as seen in Figures 1 and 2. Ba2 can actually be refined in a pair of related positions located ~0.16 Å off the position on the mirror plane, although no overall improvement of the structure is observed (see Crystal Structure Determination). No evidence of long range ordering of Ba2 in the two mirror related sites in the form of superstructure reflections was observed in either oscillation or Weissenberg photographs. The expanded coordination sphere plays a fundamental role in understanding the behavior of Ba2 by providing a more accurate representation the size and shape of the cation cavity formed by the nearest-neighbor oxygen atoms than that provided by the tricapped trigonal prismatic description. The elongated ellipsoid, therefore, probably represents some disorder of the cation over at least two energy-equivalent sites within the expanded coordination polyhedron. As noted above, attempts to reduce the symmetry of space group and the Ba2 position did not result in any improvement in the overall refinement. Refinement of the Bal and Ba2 occupancies showed no statistically significant deviation from full occupancy.

Two crystallographically different TaO_6 octahedra exist in the structure. The octahedra containing Ta2, i.e., those that form the cuboctahedral cation site, show a sizable distortion from octahedral symmetry. Ta2–O distances range from 1.93 to 2.03 Å. The distortion appears to be a necessary structural consequence of the way the TaO_6 octahedra are linked in the *ab* plane. The structural arrangement parallel to the *ab* plane can be achieved only with octahedra having edges of different lengths. A similar distortion from octahedral symmetry was noted in $Ba_3Nb_5O_{15}$.[11] The octahedron containing Tal is centered at the intersection of three mirror planes. Within experimental error, the site has octahedral symmetry with Ta–O distances of 1.97(1) and 1.984(1) Å perpendicular and parallel to the *c* axis, respectively.

As noted on a number of occasions above, the structural details of $Ba_3Ta_5O_{15}$ and the $Ba_3Nb_5O_{15}$[11] are very similar. M–O and Ba–O distances in the two structures typically differ by less than 0.01 Å, consistent with the fact that the crystal radii of Nb and Ta are identical.[24] Although the anisotropic thermal parameters of Ba2 were not discussed in the structural description of $Ba_3Nb_5O_{15}$, the reported attempts to refine the structure in acentric space groups suggest that problems similar to those observed in the refinement of $Ba_3Ta_5O_{15}$ were encountered.[11]

Nonstoichiometry. The existence of $Ba_{0.5}TaO_3$ in the same structure type as $Ba_3Ta_5O_{15}$ suggested that it was probably possible to vary the Ba content of the structure in a continuous manner from $Ba_{2.5}Ta_5O_{15}$ ($Ba_{0.5}TaO_3$) to $Ba_3Ta_5O_{15}$. Three samples of intermediate composition were prepared using the appropriate mixtures of the two end members of the series ($x = 2.5$ and 3.0). Sample homogeneity for the entire series was verified X-ray powder diffraction. A plot of unit cell parameters for the series as a function of the Ba content (Table 4) is shown in Figure 5. The plot shows a gradual increase in the cell parameters with increasing Ba content, consistent with solid solution formation and a range of Ba stoichiometry. The slight negative deviation from Vegard's law observed is not unreasonable because Ba sites of two different sizes can be involved. Although the actual Ba distribution among cation sites in $Ba_{2.5}Ta_5O_{15}$ has not been investigated, a partial ordering of Ba in the A and B sites on the basis of site size would

Table 4. Lattice Parameters of $M_{3-x}Ta_5O_{15}$ Compounds from Guinier Powder Diffraction Data[a]

compound	a, Å	c, Å	V, Å^3
$Ba_{2.5}Ta_5O_{15}$	12.556(3)	3.945(1)	622.0(3)
$Ba_{2.6}Ta_5O_{15}$	12.557(2)	3.9453(9)	622.1(2)
$Ba_{2.7}Ta_5O_{15}$	12.567(2)	3.9470(6)	623.1(1)
$Ba_{2.8}Ta_5O_{15}$	12.580(2)	3.9561(9)	626.1(2)
$Ba_3Ta_5O_{15}$	12.600(2)	3.9636(6)	629.3(2)
$Sr_3Ta_5O_{15}$	12.379(2)	3.8796(8)	594.5(2)
$Eu_3Ta_5O_{15}$	12.386(3)	3.875(1)	594.4(2)

[a] Cu Kα_1 radiation, internal Si standard.

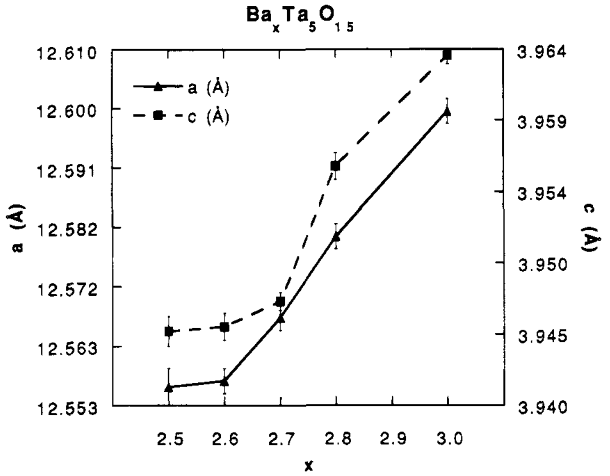

Figure 5. Plot of a and c lattice parameters the series $Ba_xTa_5O_{15}$ from $2.5 \le x \le 3.0$.

be expected. A comparison of the intensities in the observed X-ray diffraction pattern with those calculated for different cation distributions in $Ba_{2.5}Ta_5O_{15}$ suggests that the majority of the vacancies exist on the cuboctahedral site (B). The preference of Ba for the large tricapped-trigonal prismatic site (A) over the cuboctahedral site is consistent with its size and structural studies of a number of compounds in the TTB structure with mixed metal cations.[15,16] As previously noted, the Ba–O distances in the cuboctahedral site are 0.15–0.20 Å shorter than the sum of the Ba and O crystal radii. The small initial increase in cell parameters observed between $x = 2.5$ and 2.6 may result from the occupation of a small number of vacancies on the large tricapped trigonal prismatic site. Additional Ba atoms are subsequently accommodated in the smaller cuboctahedral sites resulting in the larger monotonic increase in cell parameters observed between $x = 2.6$ and 3.0. It should be noted, however, that the exact distribution and ordering of cations and hence the cell parameter variation with composition may be highly dependent on sample history.

The small increase in cell parameters between $x = 2.5$ and 2.6 can alternatively be explained by assuming the range of Ba stoichiometry only extends to 2.6, with more Ba deficient compositions being mixtures of $Ba_{2.6}Ta_{5-x}O_{15}$ and Ta_2O_5. Two observations suggest this is probably not the case. Metal framework vacancies have not been observed in a number of previous studies of fully oxidized tetragonal tungsten bronzes.[15,16] Second, detectable amounts of unreacted Ta_2O_5 should also be present in samples where the Ba content is less than 2.6. If one assumes "$Ba_{2.5}Ta_5O_{15}$" is actually $Ba_{2.6}Ta_{4.96}O_{15}$ plus Ta_2O_5, approximately 7 mol % of the sample must be Ta_2O_5 to retain the correct Ba to Ta ratio. This amount of Ta_2O_5 should be discernible in the Guinier X-ray diffraction patterns. None has been observed.

Discussion

$Ba_3Ta_5O_{15}$ represents the first structurally characterized ternary tantalum oxide containing Ta in a reduced oxidation state. To our knowledge, the only other reduced Ta oxide phase to have been characterized by single crystal X-ray diffraction is $Ba_3Ta_6Si_4O_{23}$.[14]

The preparation of reduced Ta oxides has proven to be considerably more difficult than those of Nb. In fact, the mere existence of reduced Ta oxides has been questioned.[26] Our experience suggests that considerably more vigorous conditions are required to obtain reasonable rates of reaction in the synthesis of reduced Ta compounds than are needed for similar Nb compounds. $Ba_3Ta_5O_{15}$ requires reaction temperatures 200–300 °C higher than those required for the preparation of $Ba_3Nb_5O_{15}$.

Two isostructural compounds, $Sr_3Ta_5O_{15}$ and $Eu_3Ta_5O_{15}$, were also prepared to examine the impact of cation size on the stability of the structure. The two compounds have nearly identical lattice parameters (Table 4) and show a contraction in both the a and c parameters with respect to $Ba_3Ta_5O_{15}$. Further reduction of cation size apparently destabilizes the structure. A reaction to prepare "$Ca_3Ta_5O_{15}$" did not produce a compound with the TTB structure type but resulted instead in a cubic perovskite. The large Ca–O distances that would exist in the large tricapped trigonal prismatic sites of the TTB structure probably make that structure less stable than the perovskite where the Ca ions occupy only cuboctahedral sites. Several attempts were made to fill the smaller tricapped trigonal prismatic sites in $Ba_3Ta_5O_{15}$ with Li (site C in Figure 1). No detectable amounts of Li were found in $Ba_3Ta_5O_{15}$ after reaction with BuLi at room temperature or Li vapor at higher temperatures.

Preliminary work indicates that several other reduced ternary Ta oxides exist in the Ba–Ta–O and K–Ta–O systems and intercalated versions of $LaTa_3O_9$ can also be prepared.[27]

The observation that $Ba_3Ta_5O_{15}$ was isostructural with a variety of other compounds that crystallize in the TTB structure led us to investigate whether it might have the additional characteristics needed to classify it as a metal oxide bronze. Metal oxide bronzes are typically characterized by an intense color or metallic luster, a range of a composition, resistance to attack by nonoxidizing acids and metallic or semiconducting behavior. $Ba_3Ta_5O_{15}$ has a dark blue color, a range of Ba stoichiometry and excellent resistance to nonoxidizing acids. Preliminary four-point resistivity measurements[27] on a sintered pellet of $Ba_3Ta_5O_{15}$ indicate that it exhibits semiconducting behavior. Clearly $Ba_3Ta_5O_{15}$ fits the criteria for classification as a bronze.

Conclusions

Single crystals of $Ba_3Ta_5O_{15}$ were grown for the first time by high-temperature reaction using a $BaCl_2$ flux.

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(26) Studer, F.; Fayolle, J. P.; Raveau, B. *Mater. Res. Bull.* **1976**, *11*, 1125.

(27) Feger, C. R.; Ziebarth, R. P., unpublished results.

X-ray diffraction measurements show that $Ba_3Ta_5O_{15}$ adopts the tetragonal tungsten bronze structure with complete occupation of the large tricapped trigonal prismatic and cuboctahedral cation sites. To understand the observed thermal parameters of Ba2 in the large tricapped trigonal prismatic site, it is necessary to expand its coordination sphere to include four additional oxygen neighbors at longer distances. These atoms help define the cation site boundaries in the direction of thermal ellipsoid elongation and suggest it may be appropriate to think of the site as a tricapped pentagonal prism rather than the more traditional tricapped trigonal prism. A range of Ba stoichiometry was noted for $Ba_xTa_5O_{15}$ from $x = 2.5$ to 3.0 with changes in cell parameters suggesting some preferential cation ordering among sites at low values of x. The dark blue color, range of stoichiometry, resistance to attack by nonoxidizing acids, and its semiconducting behavior classify $Ba_3Ta_5O_{15}$ as a metal oxide bronze. Isostructural compounds were also prepared with Sr and Eu cations in place of Ba. Evidence for additional reduced tantalum oxides containing alkali and alkaline earth metal cations has been obtained.

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Supplementary Material Available: Tables of anisotropic thermal parameters and interatomic distances (5 pages); table of observed and calculated structure factor tables (2 pages) for $Ba_3Ta_5O_{15}$. Ordering information is given on any current masthead page.

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