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A Refinement of the Structure of Barium Tantalum Oxide, Ba5Ta4O15

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The five-layer structure previously reported for $Ba_5Ta_4O_{15}$ has been confirmed. An isotropic structure refinement was carried out with 253 counter-recorded reflections larger than 2σ for their background to a conventional R value of 5·7%. Anomalous dispersion, absorption, and secondary extinction corrections were made. The space group is $P\bar{3}m1$; cell dimensions are $a=5·776\pm0·005$, $c=11·82\pm0·01$ Å, and there is one formula unit per cell. The octahedral environments of the tantalum atoms are distorted in a manner consistent with the requirements of local charge balance. The shortest Ta–O distances in the octahedra are $1·86\pm0·02$ Å, the longest are $2·22\pm0·03$ Å. The shortest Ba–O distance is $2·64\pm0·03$ Å.

Introduction

The preparation and structure of $Ba_5Ta_4O_{15}$ and the related compounds $Sr_5Ta_4O_{15}$, $Ba_5Nb_4O_{15}$ and the oxygen deficient compounds $Ba_5Ta_4O_{13}$ and $Ba_5Nb_4O_{13}$ were reported by Galasso & Katz (1961). The structure determination was based on data for $Ba_5Ta_4O_{15}$, but since even the longest exposure – a 30° precession photograph which ran for 22 days – showed less than half of the possible $h0l$ reflections, it was considered impractical then to collect more than the 88 observed reflections recorded. As a result, oxygen positions had to be inferred, though there seemed to be no doubt as to the essential correctness of the proposed structure. Since the time it was first reported, the structure has been shown to be quite stable. Under certain conditions the compound $Ba_3SrTa_3O_9$ undergoes chemical change producing $(Ba,Sr)_5Ta_4O_{15}$ as one of the products (Galasso, Barrante & Katz, 1961). Also some of the compounds containing rhenium with ordered perovskite structures reported by Sleight, Longo & Ward (1962) were found to be unstable when heated in air at 1000 °C; the products obtained in many instances have a structure of the $Ba_5Ta_4O_{15}$ type. A refinement of this structure has now been carried out which permits a more detailed description than was possible before, even though it was still not possible to collect a large set of data.

Experimental

The preparation $5BaCO_3 + 2Ta_2O_5 \rightarrow Ba_5Ta_4O_{15} + 5CO_2$ yielded a tan-colored product when carried out in air at 1100 °C. This tan compound produced a powder pattern identical to that reported by Galasso for $Ba_5Ta_4O_{15}$. Well formed platy crystals were then grown from a lead(II) oxide flux.

The best crystal available for study was a thin hexagonal plate, 0·014 mm thick and 0·106 mm between opposite faces of the hexagonal prism. The crystal was mounted with the a^* axis parallel to the fiber axis. Precession photographs confirmed the previously reported Laue group $\bar{3}m$ and were consistent with the assigned space group $P\bar{3}m1$.

Cell dimensions and intensities were measured on a General Electric XRD-5 diffractometer equipped with a single-crystal orienter. Lattice constants were determined by averaging results from high order $h00$ and $h0l$ reflections and were found to be $a=5·776\pm0·005$, $c=11·82\pm0·01$ Å. Intensities were measured on the orienter with Zr-filtered Mo radiation, pulse height selection, and a scintillation counter by the moving-crystal moving-counter method. Background was determined from 20 second counts on both sides of the 80 second 2·66° scan. A standard reflection monitored daily showed an overall variation of less than 2%. Intensities were collected for all $h \geq 0$, $k \geq 0$, $0 \leq l \leq 6$

and $l=9$ for which $2\theta \le 90°$. The $hk0$ and $kh0$ reflections are related by a twofold axis of symmetry, but the collected reflections are otherwise independent. Of the 501 independent observations, 253 reflections were larger than 2σ for the background. This set was used in the refinement.

Refinement

In order to correct for absorption (Prewitt, 1965) a rectangular parallelepiped $0.0014 \times 0.0124 \times 0.0106$ cm was divided into $10 \times 10 \times 10$ grid points, 760 of which were inside the crystal. The value of μ_L was 500 cm^{-1}, and the transmittances calculated by the program ranged from 0.496 to 0.052. After correction, refinement was begun in space group $P\bar{3}m1$ with the parameters reported in the earlier study of Galasso & Katz (1961). (Positional parameters were inadvertently interchanged in Table 1 of that paper, though the drawing is correct.) Least-squares refinement was carried out with a modification of $ORFLS$ (Busing, Martin, & Levy, 1962) provided by Dr W.C. Hamilton. Scattering factors for Ba$^+$ and Ta^{2+} were obtained from the compilation of Thomas & Umeda (1957) and for O$^-$ from *International Tables for X-ray Crystallography* (1962). Anomalous dispersion corrections were obtained from Cromer (1965). After four cycles of isotropic refinement using the weighting scheme of Prewitt & Sleight (1968) and varying all parameters, convergence was obtained with $R=\Sigma||F_o|-k|F_c||/\Sigma|F_o|=0.06$.

A secondary extinction correction was applied in a form given by Zachariasen (1963a), $F_{corr}=KF_{obs}$ $(1+\beta_{2\theta}CJ_{obs})$, where F_{corr} is taken as F_{calc} and C is an empirical parameter. The correction resulted in substantially better agreement for the more intense reflections, for which the observed structure factors had previously been low. Agreement was improved to a conventional $R=0.057$ and a weighted $R=[\Sigma w(|F_o|-k|F_c|)^2/\Sigma w|F_o|^2]^{1/2}=0.107$.

Refinement allowing anisotropic thermal motion for

barium and tantalum was unsuccessful when all parameters were varied simultaneously. This was due to high correlation between, in particular, z positional parameters and β_{33} for barium and tantalum. These high correlations are partly attributable to the rather limited data in the z direction. It was possible to obtain convergence by refining iteratively with two blocks of parameters in which highly correlated parameters were separated and refined alternately while the bulk of the parameters were varied in every cycle. After six cycles, the conventional R index was reduced to 0.053, the weighted R to 0.102, and physically possible thermal parameters were obtained. Hamilton's (1965) significance test on the ratio of R factors applied to the hypothesis that all atoms vibrate isotropically (as opposed to the heavy atoms vibrating anisotropically) showed that the hypothesis can be rejected at the 97.5% confidence level. Despite the high-sounding value of this number, current sentiment seems to be that this is not high enough to reject the hypothesis. Since the inability to vary all parameters simultaneously in the anisotropic refinement makes it difficult to obtain trustworthy standard errors, parameters listed in Table 1 and bond distances and angles listed in Table 2 are based on the isotropic refinement. However, parame-

Table 1. *Atomic coordinates for atoms in* Ba$_5$Ta$_4$O$_{15}$

Space group $P\bar{3}m1$ (No. 164).

	Position	x	z	B ($\times 10^2$)
Ba(1)	1(a)	0	0	55 (7)
Ba(2)	2(d)	$\frac{1}{3}$	0.8837 (5)	59 (5)
Ba(3)	2(d)	$\frac{1}{3}$	0.4282 (5)	83 (6)
Ta(1)	2(c)	0	0.6873 (3)	26 (4)
Ta(2)	2(d)	$\frac{1}{3}$	0.1035 (3)	36 (4)
O(1)	3(e)	$\frac{1}{2}$	0	77 (52)
O(2)	6(i)	0.1695 (23)	0.1916 (26)	143 (47)
O(3)	6(i)	0.1632 (18)	0.6136 (24)	47 (32)

Position 1(a): 0,0,0. Position 2(c): $0,0,z$; $0,0,\bar{z}$. Position 2(d): $\frac{1}{3},\frac{2}{3},z$; $\frac{2}{3},\frac{1}{3},\bar{z}$. Position 3($e$): $\frac{1}{2},0,0$; $0,\frac{1}{2},0$; $\frac{1}{2},\frac{1}{2},0$. Position 6($i$): $x,\bar{x},z$; $x,2x,z$; $2\bar{x},\bar{x},z$; $\bar{x},x,\bar{z}$; $\bar{x},2\bar{x},\bar{z}$; $2x,x,\bar{z}$.

Table 2. *Bond distances and angles in* Ba$_5$Ta$_4$O$_{15}$

Bond distances

Ba(1)—O(1)	2.8880 (5) Å	O(1)—O(1)	2.8880 (5) Å
Ba(1)—O(2)	2.829 (26)	O(1)—O(2)	2.804 (27)
Ba(2)—O(1)	3.052 (45)	O(2)^1–O(2)^3	2.839 (40)
Ba(2)—O(2)	2.9028 (34)	O(2)^1–O(2)^2	2.937 (40)
Ba(2)—O(3)	2.643 (25)	O(2)^1–O(3)	2.851 (36)
Ba(3)—O(2)	3.241 (29)	O(3)^1–O(3)^6	3.122 (49)
Ba(3)^1–O(3)^{4*}	2.928 (49)	O(3)^1–O(3)^3	2.947 (33)
Ba(3)^1–O(3)^2	2.765 (26)	O(3)^1–O(3)^2	2.829 (33)
Ta(1)—O(3)	1.856 (22)	Ta(2)–O(1)	2.065 (21)
Ta(1)—O(2)	2.219 (28)	Ta(2)–O(2)	1.943 (27)

Angles

O(3)–Ta(1)–O(3)	99.2 (1.0)°
O(3)–Ta(1)–O(2)	88.3 (0.7)
O(2)–Ta(1)–O(2)	82.9 (1.0)
O(3)–Ta(2)–O(3)	88.6 (0.1)
O(2)–Ta(2)–O(1)	88.7 (0.6)
O(2)–Ta(2)–O(2)	93.9 (1.1)

* Superscripts refer to sites in the order listed for the positions at the bottom of Table 1.

ters for the isotropic refinement and for the refinement with heavy atoms vibrating anisotropically are well within two standard errors of each other. The bond distances, angles, and standard errors were calculated with the program ORFFE of Busing, Martin & Levy (1964). Observed and calculated structure factors are listed in Table 3.

Table 3. *Observed and calculated structure factors*

The columns are h, k, $|F_o|$ and $|F_c|$.

expected for an octahedron. An illustration of the entire structure as drawn by ORTEP program of Johnson (1965) is presented in Fig. 2. The twelvefold coordination for Ba is evident in the drawing.

Based on an idealized close packed model, the sum of electrostatic bonds to each oxygen ion from adjacent cations (Pauling, 1960) is: O(1), $2\frac{1}{3}$; O(2), $2\frac{1}{3}$; O(3), $1\frac{1}{2}$. The deviations from the ideal close packed model reduce localized charge imbalance in the following ways:

(1) The low sum of electrostatic bond strengths to O(3) is effectively increased, chiefly by the drastic shortening of the Ta(1)–O(3) bond.

(2) The resultant lengthening of the Ta(1)–O(2) bond is compensated by a shortening of the Ta(2)–O(2) bond, thus maintaining a proper degree of bonding to this oxygen atom. The distortion of the Ta(2) octahedron may be thought of as a secondary, and second order, effect.

(3) Rather short Ba–O(3) distances are found (2·64 and 2·77 Å) which also increase the sum of electrostatic bond strengths to O(3).

Zachariasen (1963b) maintains that the distortion in such cases should cause equality of the strengths of

Fig. 1. The tantalum environment in Ba₅Ta₄O₁₅.

Discussion

The refinement confirmed the general correctness of the structure reported earlier, but certain features now revealed warrant comment. Considerable distortion may be noted about the O(3) position, the position of greatest electrostatic valency imbalance. Oxygen–oxygen and barium–oxygen distances show greater variation for O(3) than for the other two oxygen ions. The greatest effect of this local charge imbalance is the distortion of the Ta(1) octahedron. Fig. 1 shows the coordination of Ta(1) and Ta(2); the greater distortion of the oxygen octahedron about Ta(1) is particularly evident from the greater departure from the 90° angles

Fig. 2. Stereoscopic illustration of the Ba₅Ta₄O₁₅ unit cell. Small open circles are Ta atoms, large open circles are O atoms, and black circles are Ba atoms.

electrostatic bonds. Unfortunately, his quantitative method for correcting the electrostatic charge distribution for variations in bond lengths requires an empirical correlation between bond order and bond length. This correlation is not available for tantalum–oxygen bonds.

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The Structure of Barium Silicon Niobium Oxide, Ba₃Si₄Nb₆O₂₆: A Compound with Linear Silicon–Oxygen–Silicon Groups

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Barium silicon niobium oxide, $Ba_3Si_4Nb_6O_{26}$, has basically the same structure as $Ba_3Si_4Ta_6O_{26}$. The symmetry is hexagonal, space group $P\bar{6}2m$, with $a=9\cdot00\pm0\cdot01$, $c=7\cdot89\pm0\cdot01$ Å. Allowing anisotropic thermal motion for barium and niobium, structure refinement was carried out with 847 counter recorded reflections for which the structure factors were greater than twice their standard deviation, to a conventional R value of 4·6%. Si–O–Si groups are required by symmetry to be linear. Si–O distances in these groups are $1\cdot599\pm0\cdot006$ Å; other Si–O distances are $1\cdot629\pm0\cdot007$ Å. In the octahedral environment around niobium, Nb–O distances range from $1\cdot918\pm0\cdot004$ to $2\cdot056\pm0\cdot003$ Å. The environment for barium is a distorted pentagonal prism in which Ba–O distances range from $2\cdot867\pm0\cdot010$ to $2\cdot989\pm0\cdot007$ Å. Three additional oxygen ions are within $3\cdot332\pm0\cdot015$ Å of each barium ion.

Introduction

The determination of the structure of $Ba_3Si_4Ta_6O_{23}$ (Shannon & Katz, 1968) uncovered two interesting structural features that warranted more detailed investigation: the square pyramidal environment for the transition element and linear Si–O–Si groups. The existence of 180° Si–O–Si angles has been a matter of dispute, so it was considered important to investigate this possibility in a structure which could yield more reliable information than had so far been obtained. The substitution of niobium, (atomic no. 41) for tantalum (atomic no. 73) allows positions of the light atoms to be determined more accurately both because of reduced scattering by the heavy atoms and because of reduced absorption. An effort was therefore made to substitute Nb for Ta in $Ba_3Si_4Ta_6O_{23}$ in order to carry out a new structure determination.

During the course of the refinement it became clear that the crystal was really of the oxidized compound,