

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.

The authors are grateful for financial assistance for this work provided by the National Science Foundation through grants GP-5934 and GP8481 and to the National Aeronautics and Space Administration for a predoctoral fellowship (to J.S.). Computations were carried out in the Computer Center of the University of Connecticut, which is supported in part by grant GJ-9 of the National Science Foundation.

References

- BUSING, W. R., MARTIN, K. D. & LEVY, H. A. (1962). *A Fortran Crystallographic Least-Squares Program*. ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge Tennessee, as modified by W. C. Hamilton, Brookhaven National Laboratory, Upton, New York.
- BUSING, W. R., MARTIN, K. D. & LEVY, H. A. (1964). *A Fortran Crystallographic Function and Error Program*. ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- CROMER, D. T. (1965). *Acta Cryst.* **18**, 17.
- GALASSO, F. S. & KATZ, L. (1961). *Acta Cryst.* **14**, 647.
- GALASSO, F. S., BARRANTE, J. R. & KATZ, L. (1961). *J. Amer. Chem. Soc.* **83**, 2830.
- HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *A Fortran Thermal-Ellipsoid Plot Program for Crystal Illustrations*. ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. p. 547. Cornell Univ. Press.
- PREWITT, C. T. (1965). *ACACA*. E. I. Dupont de Nemours & Co., Wilmington, Delaware.
- PREWITT, C. T. & SLEIGHT, A. W. (1968). *Inorg. Chem.* **7**, 1090.
- SLEIGHT, A. W., LONGO, J. M. & WARD, R. (1962). *Inorg. Chem.* **1**, 245.
- THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 239.
- ZACHARIASEN, W. H. (1963a). *Acta Cryst.* **16**, 1139.
- ZACHARIASEN, W. H. (1963b). *Acta Cryst.* **16**, 385.

Acta Cryst. (1970). B**26**, 105

The Structure of Barium Silicon Niobium Oxide, $\text{Ba}_3\text{Si}_4\text{Nb}_6\text{O}_{26}$: A Compound with Linear Silicon–Oxygen–Silicon Groups

BY JOSEPH SHANNON AND LEWIS KATZ

*Department of Chemistry and Institute of Materials Science,
University of Connecticut, Storrs, Connecticut 06268 U.S.A.*

(Received 31 March 1969)

Barium silicon niobium oxide, $\text{Ba}_3\text{Si}_4\text{Nb}_6\text{O}_{26}$, has basically the same structure as $\text{Ba}_3\text{Si}_4\text{Ta}_6\text{O}_{26}$. The symmetry is hexagonal, space group $P\bar{6}2m$, with $a=9.00\pm 0.01$, $c=7.89\pm 0.01$ 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 1.599 ± 0.006 Å; other Si–O distances are 1.629 ± 0.007 Å. In the octahedral environment around niobium, Nb–O distances range from 1.918 ± 0.004 to 2.056 ± 0.003 Å. The environment for barium is a distorted pentagonal prism in which Ba–O distances range from 2.867 ± 0.010 to 2.989 ± 0.007 Å. Three additional oxygen ions are within 3.332 ± 0.015 Å of each barium ion.

Introduction

The determination of the structure of $\text{Ba}_3\text{Si}_4\text{Ta}_6\text{O}_{23}$ (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 $\text{Ba}_3\text{Si}_4\text{Ta}_6\text{O}_{23}$ 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,

$\text{Ba}_3\text{Si}_4\text{Nb}_6\text{O}_{26}$, so the possible existence of square pyramidal coordination for niobium (IV) could not be checked in this study.

Experimental

Samples were prepared by mixing $5\text{BaO} + 4\text{Nb}_2\text{O}_5 + 2\text{Nb}$ with 1% BaF_2 and heating in sealed, evacuated silica capsules. The best crystals were obtained at 1100°C . Above 1200°C melting occurred. The black crystals were mostly of poor quality; twinning and cracking were common. However, a single crystal was found and mounted with the c axis parallel to the fiber axis. The shape of the crystal could be described by twelve bounding planes: $X=0.032$, $-X=0.032$, $Y=0.044$, $-Y=0.044$, $Z=0.024$, $-Z=0.024$, $-X-Y=0.070$, $X-Y=0.070$, $X+Y=0.070$, $-X+0.35Y=0.030$, $-X+0.35Y-Z=0.030$, $X+Z=0.032$ mm. The Laue group, $6/mmm$ was checked by measuring the intensities of several sets of six symmetry related reflections with the scintillation counter, correcting for absorption, and comparing each value with the mean for its set of six. The conventional R value for 288 measurements was 1.7%.

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 reflections: $a=9.00 \pm 0.01$, $c=7.89 \pm 0.01$ Å. Intensities were measured with Nb 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 2.67° scan. Intensities were collected for all reciprocal lattice points for which $k \geq 0$, $h \geq k$, $0 \leq l < 10$, and $2\theta < 90^\circ$ and for the Friedel related $\bar{h}\bar{k}l$ reflections. ($\bar{h}\bar{k}l$ reflections are not equivalent to hkl reflections unless $k=0$) Part of the tenth level was also collected. The total of 1133 independent reflections were corrected for absorption with Prewitt's (1965) program *ACACA* ($8 \times 8 \times 8$ grid). The linear absorption coefficient was 87.1 cm^{-1} , substantially lower than that for

isomorphous tantalum compounds. Standard deviations of observed structure factors were computed using a weighting scheme suggested by Prewitt (Prewitt & Sleight, 1968). Of the 1133 independent reflections, $|F|$ was greater than $2\sigma_F$ for 847 reflections and greater than $3\sigma_F$ for 724 reflections.

Refinement was begun using parameters from $\text{Ba}_3\text{Si}_4\text{Ta}_6\text{O}_{23}$ (space group $P\bar{6}2m$) with reflections for which $|F| \geq 3\sigma_F$. Convergence was obtained after four cycles of isotropic refinement to a conventional $R = \Sigma ||F_o| - k|F_c|| / \Sigma |F_o| = 0.09$, a disappointingly high value. A difference Fourier synthesis with barium, tantalum, and silicon only in the calculated structure factors showed, in addition to the expected oxygen peaks, a peak of oxygen density at $0.225, 0, \frac{1}{2}$. (Smaller peaks indicating anisotropic thermal motion for tantalum and barium were also present.) Inclusion of oxygen at $0.225, 0, \frac{1}{2}$ lowered R to 0.071. Refinement with anisotropic thermal motion allowed for barium and niobium lowered R to 0.042 and the weighted $R = [\Sigma \omega(|F_o| - k|F_c|)^2 / \Sigma \omega |F_o|^2]^{1/2} = 0.050$. An attempt to refine with all atoms anisotropic was unsuccessful, since some of the oxygen thermal parameters became physically unrealistic. Similar refinements with all $|F_{\text{obs}}| \geq 2\sigma_F$ gave $R=0.046$ (weighted $R=0.050$); with all data included, $R=0.075$ (weighted $R=0.058$). Atomic parameters for all three refinements were in good agreement. A final difference Fourier synthesis revealed a hole of $2e \cdot \text{Å}^{-3}$ at the barium position, possibly because the scattering factors for the neutral atoms were used, but no other fluctuations greater than $0.5e \cdot \text{Å}^{-3}$ were observed.

The scattering factors for neutral barium and niobium were taken from the compilation of Thomas & Umeda (1957) and for neutral silicon and oxygen from *International Tables for X-ray Crystallography* (1962). Anomalous dispersion corrections were obtained from Cromer (1965).

The results reported are based on the refinement with data for which $|F_{\text{obs}}| \geq 2\sigma_F$. Atomic parameters are listed in Table 1, selected distances and angles are

Table 1. Atomic parameters for $\text{Ba}_3\text{Si}_4\text{Nb}_6\text{O}_{26}$
Space group $P\bar{6}2m$ (No. 189).

	Position	x	y	z	B ($\times 10^2$)	
Ba	3(g)	0.59334 (12)	0	$\frac{1}{2}$	—	
Nb	6(i)	0.23809 (12)	0	0.23939 (21)	—	
Si	4(h)	$\frac{1}{2}$	$\frac{3}{4}$	0.20309 (60)	25 (7)	
O(1)	2(c)	$\frac{1}{2}$	$\frac{3}{4}$	0	61 (28)	
O(2)	3(f)	0.2734 (15)	0	0	69 (24)	
O(3)	6(i)	0.8188 (11)	0	0.2358 (14)	74 (15)	
O(4)	12(l)	0.4888 (9)	0.1830 (8)	0.2841 (8)	48 (10)	
O(5)	3(g)	0.2269 (14)	0	$\frac{1}{2}$	68 (20)	
Anisotropic thermal parameters* ($\times 10^5$)						
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ba	109 (6)	228 (16)	237 (16)	114 (8)	0	0
Nb	69 (6)	82 (16)	860 (27)	41 (8)	-120 (16)	0

* Temperature factor in form $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

listed in Table 2, and observed and calculated structure factors are listed in Table 3. The programs used were those of Busing, Martin & Levy (1962, 1964) and Trotter (1966).

Discussion

The structural analysis revealed that the black crystal was largely oxidized. This was disappointing, since a crystal of the reduced phase might have allowed us to study a coordination polyhedron novel for niobium. (The environment for tantalum in the corresponding reduced tantalum compound is square pyramidal.)

The barium environment is a distorted pentagonal prism. Ba–O distances are similar to each other, and to other reported values, for the nearest neighbor oxygen atoms. Three other oxygen atoms are somewhat further away, at 3.13–3.33 Å. The octahedron of oxygen ions around niobium is also distorted, but in a way which is electrostatically predictable. For example, Nb–O(4) is a longer than average bond because O(4) is part of the tightly bound (relatively) tetrahedron around silicon. The belt of oxygen atoms in the octahedron around niobium defined by O(3) and O(4) atoms is tilted 17° from a constant-z plane.

The Si–O(1) and Si–O(4) bond lengths of 1.599 ± 0.006 and 1.629 ± 0.007 Å are in good agreement with the values of 1.607 ± 0.007 and 1.626 ± 0.012 Å found for 'inner' and 'outer' bonds in the very similar thortveitite structure (Cruickshank, Lynton & Barclay, 1962). An explanation for these values has been given by Cruickshank (1961). In general, Si–O bond lengths tend to exhibit a very narrow spread around 1.63 Å; the 1.60 Å value is on the short end of the observed range.

As expected, oxygen–oxygen bond distances within the NbO₆ octahedron are longer than those within the SiO₄ tetrahedron, although one of the octahedral edges is short.

The linearity of the Si–O(1)–Si groups is of particular interest. Liebau (1961) argues that Si–O–Si angles of 180° do not exist and has shown that some previous assertions to the contrary were based on incorrect space group assignments. Cruickshank (1961) and Cruickshank, Lynton & Barclay (1952) argue in favor of the existence of linear Si–O–Si groups in some instances. Other authors, for example Zoltai & Buerger (1959) have reported linear Si–O–Si groups without making a special issue of it. In the case of Ba₃Si₄Ta₆O_{23–26}, Shannon & Katz (1968) have claimed that linear Si–O–Si groups are present. They admit that the evidence cannot be completely conclusive, but no contrary evidence was found from optical or X-ray data. In the present case, the area of doubt in the X-ray evidence is reduced, since the substitution of niobium (atomic No. 41) for tantalum (atomic No. 73) makes the lighter atoms more accurately determinable and reduces, though it does not eliminate, the possibly complicating effects of absorption. It should be noted that the thermal motion for O(1) is of about the same magnitude as that of the other oxygen atoms, so there is no reason to postulate statistical threefold symmetry for this atom, which would have the effect of allowing non-linear Si–O–Si groups. Rather it appears that, measuring angles in the usual way from the average positions of the individual atoms involved, the Si–O(1)–Si angle is 180°.

The structure of Ba₃Si₄Nb₆O₂₆ is shown in Fig. 1. This stereo view, drawn with Johnson's (1965) *ORTEP* program, is the same as for Ba₃Si₄Ta₆O₂₆. The rings of three corner-linked NbO₆ octahedra linked again to form continuous chains, the chains in turn held together by Si₂O₇ groups, are clearly visible. The barium ions fit into pentagonal prismatic sites and help to hold the structure together in the z direction. In the reduced phase, Ba₃Si₄Ta₆O₂₃ layers instead of chains are formed, and the barium ions are solely responsible

Table 2. *Interatomic distance and angles Ba₃Si₄Nb₆O₂₆*

		Distances	
Ba–O(3)	2.867 (10) Å	O(1)–O(4)	2.671 (7) Å
Ba–O(4)	2.873 (7); 2.989 (7)	O(2)–O(3)	2.865 (11)
Ba–O(5)	3.132 (4); 3.332 (15)	O(2)–O(4)	2.870 (9)
Nb–O(2)	1.918 (4)	O(3)–O(3)	2.815 (17)
Nb–O(3)	1.937 (4) (two/Nb)	O(3)–O(4)	2.781 (9)
Nb–O(4)	2.044 (7) (two/Nb)	O(3)–O(5)	2.802 (11)
Nb–O(5)	2.056 (3)	O(4)–O(4)	2.597 (11); 2.846 (12)
Si–O(1)	1.599 (6)	O(4)–O(5)	2.685 (10)
Si–O(4)	1.629 (7)		
Nb–Nb	3.712 (5); 3.781 (5); 4.11 (6)		
		Angles	
	O(1)–Si–O(4)	113.0 (3)°	
	O(4)–Si–O(4)	105.7 (3)	
	O(2)–Nb–O(3)	96.0 (4)	
	O(2)–Nb–O(4)	92.8 (4)	
	O(3)–Nb–O(3)	93.2 (6)	
	O(3)–Nb–O(4)	88.7 (3)	
	O(4)–Nb–O(4)	88.2 (4)	
	Si–O(1)–Si	180	

for holding these layers together. Whether a similar result will be obtained with niobium is yet to be determined.

The authors are grateful for financial assistance for this work provided by the National Science Foundation through grants GP-5934 and GP-8481 and to the National Aeronautics and Space Administration for a predoctoral fellowship (to J.S.). Computations were carried out in the Computer Center of the University of Connecticut, which is supported in part by grant GJ-9 of the National science Foundation.

References

- BUSING, W. R., MARTIN, K. D. & LEVY, H. A. (1962). ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee, as modified by W. C. Hamilton, Brookhaven National Laboratory, Upton, New York.
- BUSING, W. R., MARTIN, K. D. & LEVY, H. A. (1964). ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- CROMER, D. T. (1965). *Acta Cryst.* **18**, 17.
- CRUICKSHANK, D. W. J. (1961). *J. Chem. Soc.* p. 5486.
- CRUICKSHANK, D. W. J., LYNTON, J. & BARCLAY, G. A. (1962). *Acta Cryst.* **15**, 491.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *A Fortran Thermal-Ellipsoid Plot Program for Crystal Illustrations*. ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- LIEBAU, F. (1961). *Acta Cryst.* **14**, 1103.
- PREWITT, C. T. (1965). *ACACA*. E. I. Dupont de Nemours & Co., Wilmington, Delaware.
- PREWITT, C. T. & SLEIGHT, A. W. (1968). *Inorg. Chem.* **7**, 1090.
- SHANNON, J. & KATZ, L. (1968). Abstracts, A.C.A. Winter Meeting, Tucson, Arizona. To be published.
- THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 239.
- TROTTER, J. (1966). *Fourier Summation Program*. Univ. of British Columbia, Vancouver, B. C.
- ZOLTAI, T. & BUERGER, M. J. (1959). *Z. Kristallogr.* **111**, 129.

Acta Cryst. (1970). **B26**, 109

The Crystal Structure of RhBe_{6.6}*

BY QUINTIN JOHNSON, GORDON S. SMITH AND OSCAR H. KRİKORIAN

Lawrence Radiation Laboratory, University of California, Livermore, California 94550, U.S.A.

AND DONALD E. SANDS

Chemistry Department, University of Kentucky, Lexington, Kentucky 40506, U.S.A.

(Received 22 January 1969)

The crystal structure of a compound in the beryllium-rich portion of the Rh-Be system has been determined. The final structure corresponds to the composition RhBe_{6.6}. The crystals are hexagonal, with probable space group *P6m2*. The structure is closely related to the *D2a* type. The non-integer formula is a result of partial occupancy of two sites. Identical powder patterns are observed in the Fe-Be, the Co-Be and the Ir-Be systems. Cell constants for these compounds are as follows:

	<i>a</i>	<i>c</i>	<i>c/a</i>
FeBe _x	4·137 ± 0·002 Å	10·720 ± 0·005 Å	2·591
CoBe _x	4·114 ± 0·006	10·66 ± 0·01	2·591
RhBe _{6.6}	4·191 ± 0·001	10·886 ± 0·003	2·597
IrBe _x	4·197 ± 0·001	10·842 ± 0·003	2·583

Compositions for the Fe-, Co- and Ir-Be compounds were not determined. In the case of FeBe_x, this unit cell and structure account for the powder pattern of 'ζ-FeBe₁₁' (*J. Metals*, **1**, 285). This suggests that a considerable compositional variation might be expected.

Introduction

The most beryllium-rich structure observed in binary compounds between the Group VIII elements and beryllium is of the type ThMn₁₂ (Florio, Rundle & Snow, 1952), so far reported for Fe, Co, Pd, and Pt with Be

(Batchelder & Raeuchle, 1957, 1958). This type of structure has not yet been found in the Ni, Os, Ru, Ir and Rh-Be systems, although size considerations alone would not appear to rule it out. A previous publication dealt with the currently most beryllium-rich phase found in the Os- and Ru-Be systems (Sands, Johnson, Krikorian & Kromholtz, 1962). This work covers the most beryllium-rich phase so far identified in the Rh- and Ir-Be systems.

* This work was performed under the auspices of the U.S. Atomic Energy Commission.