JOURNAL OF SOLID STATE CHEMISTRY **8**, 159–165 (1973)

The Crystal Structure of Triclinic β-$BiNbO_4$

E. T. KEVE* AND A. C. SKAPSKI

Chemical Crystallography Laboratory, Imperial College, London S.W.7

Received August 2, 1971, revised version February 5, 1973

The crystal structure of β-$BiNbO_4$ has been determined from three-dimensional X-ray data. The crystals are triclinic with $a = 7.61_1$ Å, $b = 5.53_6$ Å, $c = 7.91_9$ Å, $\alpha = 89.88°$, $\beta = 77.43°$, $\gamma = 87.15°$, $Z = 4$, space group $P\bar{1}$. Full-matrix least-squares refinement using isotropic temperature factors has reached $R = 0.122$ for 642 visually estimated reflections.

The structure contains unusual sheets of formula $[NbO_4]_\infty$ in which the Nb–O octahedra are joined at four vertices such that the two free ones are *cis*. Nb–O distances range from 1.80 to 2.31 Å. The bismuth atoms hold these sheets together and are coordinated to eight oxygens in the form of a very distorted square antiprism.

Structurally, β-BiNbO may be considered an antiferroelectric, ferroelastic member of the $BaMF_4$ prototype family.

Introduction

In a previous communication (*1*) we gave preliminary details of the crystal structure of triclinic $BiNbO_4$, henceforth referred to as β-$BiNbO_4$, which we investigated as part of a study of compounds in the Bi_2O_3–Nb_2O_5 binary system (*2, 3*), as well as the final part of a systematic study of some $A^{III}B^{V}O_4$ compounds (*4, 5*).

We find the structure to contain sheets of octahedra of a novel type. The unusual mode of joining of octahedra at four vertices, such that the two free ones are adjacent, was first seen in this compound, and has since been found in a number of fluorides (*6, 7*) and an oxide fluoride $NaNbO_2F_2$ (*8*).

The triclinic form of $BiNbO_4$ and the isostructural $BiTaO_4$ were first prepared by Aurivillius (*9*). Roth and Waring subsequently showed the existence of the low-temperature orthorhombic modifications (*10*).

Experimental

Crystal data: β-$BiNbO_4$, $M = 365.9$, Triclinic, $a = 7.61_1$ Å, $b = 5.53_6$ Å, $c = 7.91_9$ Å, $\alpha = 89.88°$, $\beta = 77.43°$, $\gamma = 87.15°$ [Ref. (*10*)],† $U = 324.0$ Å^3, $D_m = 7.5$ g cm^{-3} [Ref. (*9*)], $Z = 4$, $D_c = 7.3$ g cm^{-3}, $F(000) = 752$. Space group $P\bar{1}$. For Cu$K\alpha$ radiation $\mu = 1299$ cm^{-1}.

Crystals of β-$BiNbO_4$ were prepared by firing a 1 : 1 mixture of high-purity bismuth sesquioxide and niobium pentoxide, sealed in a platinum capsule, for 48 hr at 1150°C, and quenching in air. The crystals were pale-yellow prisms. Oscillation and Weissenberg photographs showed good agreement with the previously published unit cell dimensions. Crystals are normally twinned in two different ways, one of which is polysynthetic. The composition plane is *bc* in both cases. This is fully described elsewhere (*3, 11*).

A crystal was cleaved such that only twinning of the polysynthetic type remained. Due to the very small size of the fragment (0.006 × 0.002 × 0.001 cm) Cu$K\alpha$ radiation was used to collect intensity data. The crystal was rotated about the *b* axis and equi-inclination Weissenbergs were taken using the multiple-film technique. Layers *h*0*l*–*h*4*l* were recorded, and a total of 662 independent reflections were estimated visually. The five interlayer scale factors were used as parameters in isotropic least-squares refinement.

---

* Present address: Mullard Research Laboratories, Redhill, Surrey.

† The triclinic cell chosen both by Aurivillius, and Roth and Waring, is retained.

Printed in Great Britain

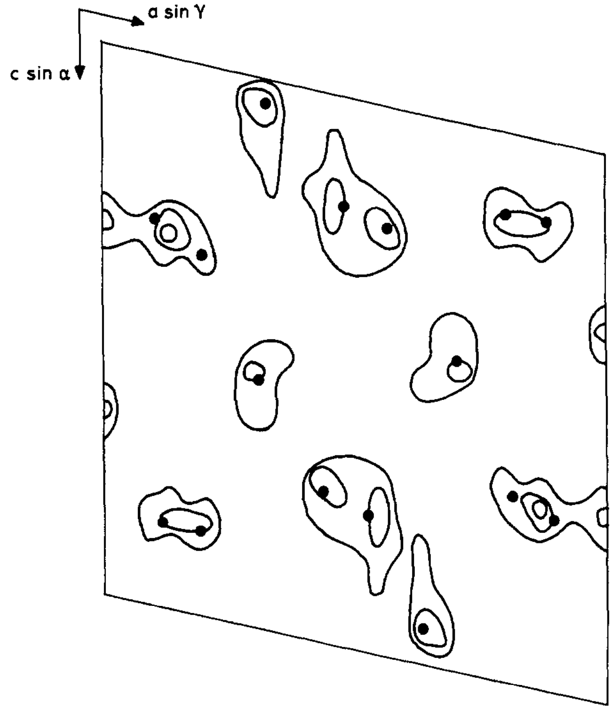

FIG. 1. β-BiNbO$_4$: [010] difference Fourier, $F_o - F_{c(\mathrm{Bi+Nb})}$; ● indicates final oxygen positions.

Calculations were carried out on the Imperial College IBM 7090 computer, using the X-Ray-63 system of crystallographic computer programs (*12*). The function minimized in full-matrix least-squares refinement was $\sum\omega(|F_o| - |F_c|)^2$, and R is defined as $\sum||F_o| - |F_c||/\sum|F_o|$, where the symbols have their usual meaning. Atomic scattering factors for Bi$^+$ were obtained by interpolating between neutral Bi and Bi^{3+} (*13*), for Nb^{3+} by adding the differences between Nb^{3+} and Nb given by Thomas and Umeda (*14*) to the values for Nb by Cromer and Waber (*13*), while scattering factors for O$^-$ were taken from the "International Tables for X-Ray Crystallography" (*15*). These ionization states were used as a compromise between a purely ionic and purely covalent model. The real part of the anomalous dispersion correction was applied for bismuth and niobium.

Solution and Refinement of the Structure

The structure was solved by projection from *h*0*l* data while the higher layers were photographed. Space group $P1$ was assumed at first, and trial and error methods were adopted to determine the bismuth and niobium positions consistent with the Patterson synthesis. The eight positions which emerged as correct corresponded to a centrosymmetric projection. A two-dimensional difference Fourier synthesis, $F_o - F_{c(\mathrm{Bi+Nb})}$, showed all the oxygen positions. This map is shown in Fig. 1 with the final, refined, positions of the oxygen atoms also shown. The peak on the *c* axis disappeared after least-squares refinement.

The three-dimensional structure was postulated with the aid of a model. Assuming an octahedral arrangement of oxygens about each niobium, there was only one satisfactory way of arranging the atoms due to the relatively short repeat in the *b* direction. This involved placing the heavy atoms at heights of about $\frac{1}{4}$ and $\frac{3}{4}$, and joining octahedra by corners. A centre of symmetry was now assumed.

The total complement of atoms was then refined by full-matrix least squares. A weighting scheme of the type recommended by Hughes (*16*) was used, where $w = 1$ for $F < F^*$, $\sqrt{w} = F^*/F$ for $F \geqslant F^*$, with $F^* = 60$. Twenty of the strongest reflections were removed from refinement because of suspected extinction, and

TABLE I

β-BiNbO$_4$: FRACTIONAL COORDINATES x, y, z AND ISOTROPIC TEMPERATURE FACTORS (B) WITH ESTIMATED STANDARD DEVIATIONS: ORTHOGONAL COORDINATES X, Y', Z', IN Å[a]

	x	y	z	B (Å^2)	X	Y'	Z'
Bi(1)	0.1215(4)	0.7644(6)	0.6272(4)	−0.01(8)	2.302	4.221	4.787
Bi(2)	0.8335(4)	0.2820(7)	0.8745(4)	0.04(8)	7.966	1.557	6.736
Nb(1)	0.6556(9)	0.775(2)	0.6784(8)	0.34(12)	6.460	4.281	5.182
Nb(2)	0.3243(9)	0.247(2)	0.8228(8)	0.06(12)	3.988	1.364	6.339
O(1)	0.325(4)	0.292(7)	0.047(4)	−2.2(5)	2.665	1.612	0.341
O(2)	0.106(7)	0.988(11)	0.319(6)	−0.2(8)	1.740	5.457	2.394
O(3)	0.167(8)	0.464(13)	0.360(8)	0.8(1.1)	2.074	2.562	2.743
O(4)	0.312(6)	0.167(9)	0.551(5)	−0.9(7)	3.392	0.922	4.241
O(5)	0.108(9)	0.439(14)	0.822(8)	1.0(1.1)	2.415	2.424	6.321
O(6)	0.168(7)	0.972(11)	0.863(6)	−0.2 (8)	3.150	5.373	6.591
O(7)	0.448(7)	0.918(11)	0.226(6)	−0.3(8)	4.147	5.070	1.673
O(8)	0.540(9)	0.449(14)	0.278(8)	1.4(1.3)	4.761	2.479	2.113

[a] X is paralled to a, Y' is perpendicular to a in the plane of a and c, Z' is perpendicular to both.

R fell to 0.122. An analysis of the weighting scheme indicated that the value of F^* should be raised. $F^* = 90$ was found to be optimum and gave lower standard deviations. although R was not reduced further. Refinement was continued until parameter shifts had become negligible. Refinement with anisotropic temperature factors was not justified in view of possible errors caused by lack of an absorption correction in such a twinned crystal. A final difference Fourier showed no unusual features.

Refinement was also tried in the noncentrosymmetric space group $P1$ but gave negligible improvement in R factor and the atomic positions were not significantly different from those in $P\bar{1}$. Subsequently crystals of β-BiNbO$_4$ were Czochralski grown by K. Nassau of Bell Laboratories. Second harmonic generation tests by the Kurtz and Perry method (*17*) on powders of this material were negative, confirming our choice of $P\bar{1}$ as the correct space group.

Table I shows the final positional parameters and temperature factors with their standard deviations, and also the orthogonalized coordinates. The negative "temperature factors" are an effect of the neglected absorption errors. Table I lists the observed structure amplitudes and calculated structure factors. Structure factors were also calculated for reflections too weak to be observed.

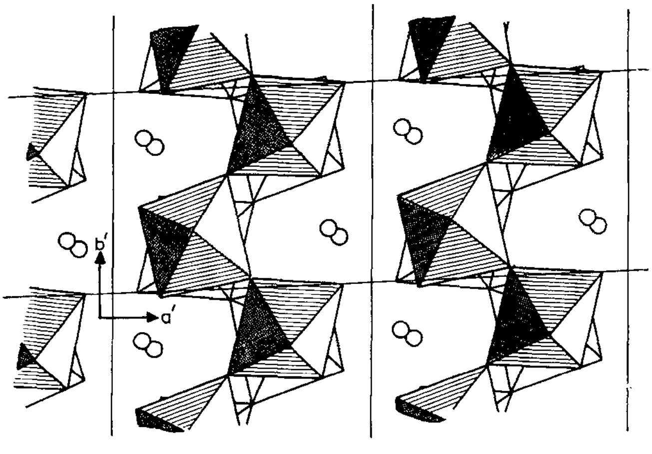

FIG. 2. β-BiNbO$_4$: [001] view of the structure showing puckered $[NbO_4]_\infty$ sheets and bismuth atoms.

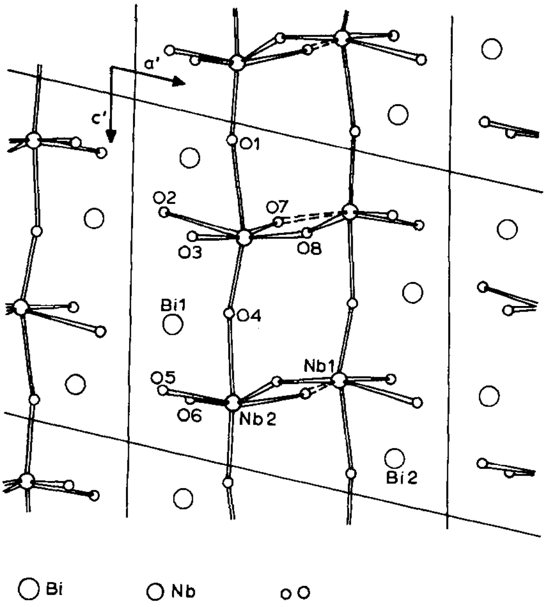

FIG. 3. β-$BiNbO_4$: [010] projection. Dashed lines indicate bonds between Nb and O atoms in the cell above.

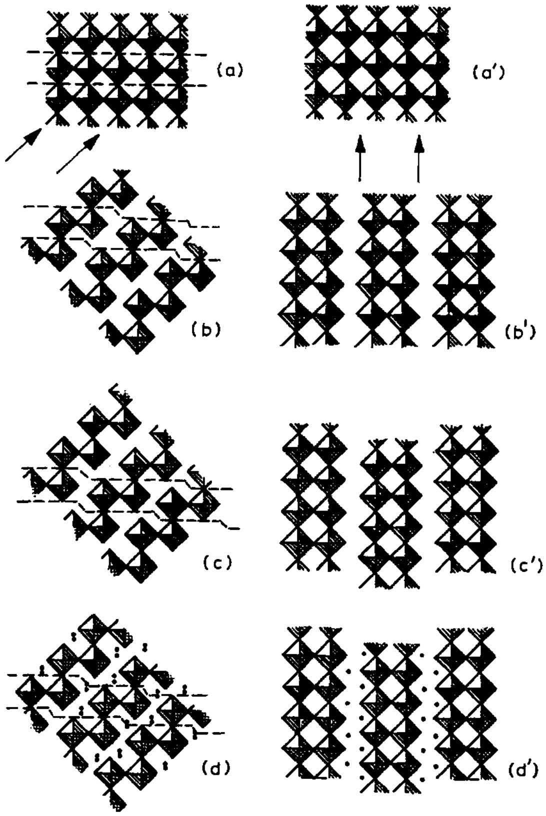

FIG. 4. Derivation of the β-$BiNbO_4$-type structure from ReO_3. Fig. 4a and a′ show [001] and [100] views of the ReO_3 structure, of which diagonal slices parallel to (110) are taken. Such sheets are stacked as shown in b and b′, and side-stepped along (001) to permit more economical packing (c and c′). The voids in the framework are then filled with bismuth atoms (d and d′). a′ is the projection of the part of the structure shown between dotted lines in a. Similarly for b′ and b etc.

Description of the Structure

Figures 2 and 3 show that the structure of β-$BiNbO_4$ contains puckered sheets of Nb-O octahedra parallel to the *bc* plane. Each octahedron is joined by corners to four others and the sheets are held together by bismuth atoms. Each sheet corresponds to a diagonal slice through an ReO_3-type structure (paralled to (110) of the ReO_3 unit cell). The full relationship to the ReO_3 structure is shown in Fig. 4.

This type of octahedral sheet, in which the two free vertices on each octahedron are adjacent (*cis*), was first reported in β-$BiNbO_4$(1). Similar sheets are found in monoclinic $NaNbO_2F_2$(8), orthorhombic $BaMnF_4$ and $BaCoF_4$(6), $BaZnF_4$(7), and $BaNiF_4$(18). In $CaNb_2O_7$(19) the sheets of composition $[Nb_4O_{14}]_\infty$ are similar, but are expanded to four octahedral edges in thickness. The structure of $BaMnF_4$ closely approximates to that of β-$BiNbO_4$ if the sense of the polar axis in $BaMnF_4$ is considered to alternate in neighbouring unit cells along its *c*-axis.

The lowering of crystal class from that of orthorhombic $BaMnF_4$ is associated with the potential ferroelasticity of the β-$BiNbO_4$ structure. Consideration of Table I shows that pseudosymmetry relationships exist between independent sets of atoms at x_1, y_1, z_1, and x_2, y_2, z_2 such that

$$x_1, y_1, z_1 = (1 - x_2, \tfrac{1}{2} + y_2, \tfrac{1}{2} - z_2) + \underset{\sim}{\Delta}$$

corresponding to a pseudo-screw axis parallel to (010) and passing through ($\frac{1}{2}$, 0, $\frac{1}{4}$). The average values of $\underset{\sim}{\Delta}$ are comparable to other ferroelastic materials, the maximum being less than 0.4 Å for Bi. The effect of postulated motions along the $\underset{\sim}{\Delta}$ would be manifested in the realignment of the spontaneous strains associated with the α and β angles deviating from 90°. This pseudosymmetry relationship is also intimately related to the polysynthetic twinning of the structure.

Since β-$BiNbO_4$ also fits the structural

TABLE II

β-BiNbO$_4$: INTERATOMIC DISTANCES AND THEIR STANDARD DEVIATIONS (Å)[a]

Nb(1)$_1$-O(3)	1.80(6)	Nb(2)-O(1)$_3$	1.80(3)
Nb(1)$_1$-O(4)	1.81(4)	Nb(2)-O(7)$_1$	1.87(5)
Nb(1)$_1$-O(7)$_2$	1.91(5)	Nb(2)-O(5)	1.90(7)
Nb(1)$_1$-O(8)	1.98(7)	Nb(2)-O(6)$_2$	1.97(6)
Nb(1)$_1$-O(1)	2.24(3)	Nb(2)-O(8)$_1$	2.10(7)
Nb(1)$_1$-O(2)$_2$	2.31(6)	Nb(2)-O(4)	2.23(4)
Mean	2.01	Mean	1.98
Bi(1)-O(2)$_5$	2.10(5)	Bi(2)$_1$-O(2)	2.10(4)
Bi(1)-O(6)	2.30(6)	Bi(2)$_1$-O(5)$_6$	2.27(7)
Bi(1)-O(5)	2.37(7)	Bi(2)$_1$-O(3)	2.33(8)
Bi(1)-O(3)$_6$	2.59(7)	Bi(2)$_1$-O(6)$_7$	2.51(5)
Bi(1)-O(3)	2.64(6)	Bi(2)$_1$-O(1)	2.59(4)
Bi(1)-O(4)$_4$	2.74(5)	Bi(2)$_1$-O(7)	2.74(6)
Bi(1)-O(2)	2.75(5)	Bi(2)$_1$-O(6)$_5$	2.96(5)
Bi(1)-O(8)$_1$	3.01(7)	Bi(2)$_1$-O(5)$_7$	2.99(7)
Bi(1)-O(4)	3.52(5)	Bi(2)$_1$-O(1)$_4$	3.48(4)

[a] The suffixes in the tables refer to the following symmetry operations: 1: $1-x$, $1-y$, $1-z$; 2: x, $y-1$, z; 3: x, y, $z+1$; 4: x, $y+1$, z; 5: $-x$, $2-y$, $1-z$; 6: $-x$, $1-y$, $1-z$; 7: x, y, $z-1$.

TABLE III

β-BiNbO$_4$: INTERATOMIC ANGLES AND THEIR STANDARD DEVIATIONS IN °

O(4)-Nb(2)-O(5)	83(2)	O(1)-Nb(1)$_1$-O(2)$_2$	83(2)
O(4)-Nb(2)-O(6)$_2$	81(2)	O(1)-Nb(1)$_1$-O(3)	81(2)
O(4)-Nb(2)-O(8)$_1$	86(2)	O(1)-Nb(1)$_1$-O(7)$_2$	82(2)
O(4)-Nb(2)-O(7)$_1$	87(2)	O(1)-Nb(1)$_1$-O(8)	86(2)
O(1)$_3$-Nb(2)-O(5)	97(2)	O(4)-Nb(1)$_1$-O(2)$_2$	88(2)
O(1)$_3$-Nb(2)-O(6)$_2$	95(2)	O(4)-Nb(1)$_1$-O(3)	92(2)
O(1)$_3$-Nb(2)-O(8)$_1$	99(2)	O(4)-Nb(1)$_1$-O(7)$_2$	101(2)
O(1)$_3$-Nb(2)-O(7)$_1$	94(2)	O(4)-Nb(1)$_1$-O(8)	103(3)
O(5)-Nb(2)-O(6)$_2$	85(3)	O(8)-Nb(1)$_1$-O(7)$_2$	107(2)
O(7)$_1$-Nb(2)-O(8)$_1$	86(3)	O(7)$_2$-Nb(1)$_1$-O(2)$_2$	74(2)
O(8)-Nb(2)-O(5)	86(3)	O(2)$_2$-Nb(1)$_1$-O(3)	83(3)
O(6)$_2$-Nb(2)-O(7)$_1$	101(2)	O(3)-Nb(1)$_1$-O(8)	94(3)
O(2)$_5$-Bi(1)-O(6)	79(2)	O(6)$_5$-Bi(2)$_1$-O(2)	64(2)
O(6)-Bi(1)-O(4)$_4$	65(2)	O(2)-Bi(2)$_1$-O(7)	62(2)
O(4)$_4$-Bi(1)-O(2)	63(2)	O(7)-Bi(2)$_1$-O(6)$_7$	97(2)
O(2)-Bi(1)-O(2)$_5$	74(2)	O(6)$_7$-Bi(2)$_1$-O(6)$_5$	65(2)
O(5)-Bi(1)-O(8)$_1$	60(2)	O(5)$_6$-Bi(2)$_1$-O(3)	76(2)
O(8)$_1$-Bi(1)-O(3)	91(2)	O(3)-Bi(2)$_1$-O(1)	65(2)
O(3)-Bi(1)-O(3)$_6$	70(2)	O(1)-Bi(2)$_1$-O(5)$_7$	59(2)
O(3)$_6$-Bi(1)-O(5)	69(2)	O(5)$_7$-Bi(2)$_1$-O(5)$_6$	68(2)
O(3)$_6$-Bi(1)-O(2)$_5$	70(2)	O(5)$_6$-Bi(2)$_1$-O(6)$_5$	58(2)
O(5)-Bi(1)-O(6)	82(2)	O(2)-Bi(2)$_1$-O(3)	83(2)
O(3)-Bi(1)-O(2)	66(2)	O(6)$_7$-Bi(2)$_1$-O(5)$_7$	67(2)
O(8)$_1$-Bi(1)-O(6)	71(2)	O(1)-Bi(2)$_1$-O(7)	97(2)
O(8)$_1$-Bi(1)-O(4)$_4$	84(2)	O(7)-Bi(2)$_1$-O(3)	85(2)

TABLE IV

	Sb(III)			Bi(III)		
	Nb(V)	Sb(V)	Ta(V)	Nb(V)	Sb(V)	Ta(V)
α-type phases	$SbNbO_4$ orthorhombic $V = 324.4$ Å^3 Refs. (*5*, *10*)	α-Sb_2O_4 orthorhombic $V = 307.5$ Å^3 Ref. (*5*)	$SbTaO_4$ orthorhombic $V = 321.0$ Å^3 Refs. (*5*, *10*)	α-$BiNbO_4$ orthorhombic $V = 330.9$ Å^3 Ref. (*10*)		α-$BiTaO_4$ orthorhombic $V = 328.5$ Å^3 Ref. (*10*)
β-type phases		β-Sb_2O_4 monoclinic $V = 303.7$ Å^3 Ref. (*4*)		β-$BiNbO_4$ triclinic $V = 324.0$ Å^3 Refs. (*1*, *9*, *10*)	$BiSbO_4$ monoclinic $V = 309.6$ Å^3 Ref. (*9*)	β-$BiTaO_4$ triclinic $V = 323.1$ Å^3 Refs. (*9*, *10*)

definition (*6*) of an antiferroelectric material with the same prototype as $BaCoF_4$, it is an antiferroelectric, ferroelastic member of the $BaMF_4$ prototype family. The representation (*20*) of this family is therefore:

$$\begin{tikzcd}[column sep=small] & \mathrm{AFP}(\bar{1}) & \beta\text{-}BiNbO_4 \\ \text{Prototype } \mathrm{PPP}(mmm) \arrow[ur, dash] \arrow[r, dash] \arrow[dr, dash] & \mathrm{FPP}(mm2) & BaCoF_4 \\ & \mathrm{AAP}(2/m) & NaNbO_2F_2. \end{tikzcd}$$

The only other way of joining octahedra at four vertices to form a sheet of composition $(AX_4)_\infty$ makes the two free vertices *trans*, and is found in many compounds, e.g., β-Sb_2O_4 (*4*), $SbNbO_4$ (*5*) etc.

The interatomic distances and angles and their standard deviations are given in Tables II and III, respectively. The Nb–O octahedra are distorted with metal–oxygen distances of 1.80–2.23 Å in one case, and 1.80–2.31 Å in the other, to give mean values of 1.98 and 2.00 Å, respectively, which are normal. Four of the distances are distinctly shorter than the other two in each case, thus the niobium atoms can be pictured as being displaced towards one edge of the octahedra.

The bismuth coordination is very irregular. In each case the nearest eight oxygens about each bismuch form a very distorted square antiprism. The ninth oxygen atom in each case is about 0.5 Å further from the bismuth than the eighth. The shortest distances are ca 2.10 Å.

All the oxygen atoms are associated with the sheets of Nb–O octahedra. Their closest approach is 2.50 Å, which is unremarkable. If the volume of the unit cell is divided by the number of oxygen atoms contained within, the quotient for β-$BiNbO_4$ is 20.33 Å^3 compared to 20.68 Å^3 for α-$BiNbO_4$ and 19.45 Å for $Bi_3Nb_{17}O_{47}$ (*2*).

The $A^{III}B^{V}O_4$ Family of Compounds

Table IV shows the relationships of all known compounds of the type $A^{III}B^{V}O_4$ where $A = Sb$ or Bi, and $B = Nb$, Sb or Ta. Three structure types have been found in this group i.e. the orthorhombic $SbNbO_4$ type, the monoclinic β-Sb_2O_4 type, and the triclinic β-$BiNbO_4$ type. It has been pointed out (*5*) that the $SbNbO_4$ type and β-Sb_2O_4 type structures are simply related to one another. The β-$BiNbO_4$ type is found to be unrelated to the other two.

Where two phases are shown in the Table for the same compound it is found (*4*, *10*) that the β-structure, which is always centrosymmetric, is the stable one, has lower crystal class symmetry, and is more efficiently packed (density greater by a factor of ca 1.5%). Once the β-phase has been formed it cannot be converted to the α-phase by heating.

Ferroelectric behaviour has been reported recently in the mineral stibiotantalite Sb(Ta, Nb)O_4 by Gavrilova et al. (*21*), and in synthetic $SbNbO_4$ by Lobachev et al. (*22*) with Curie temperature of ca 400° in both cases. If the orthorhombic α-phases are all isostructural then they will also presumably be ferroelectric.

Acknowledgments

We are grateful to Professor D. Rogers and Dr. S. C. Abrahams for discussion and comments, and wish to thank the Science Research Council for an equipment grant, and financial support (E.T.K.).

References

1. E. T. KEVE AND A. C. SKAPSKI, *Chem. Comm.* 281 (1967).
2. E. T. KEVE AND A. C. SKAPSKI, *Nature (London)* **217**, 841 (1968); *J. Chem. Soc. (A)*, 1280 (1971).
3. E. T. KEVE, Ph.D. Thesis, London (1968).
4. D. ROGERS AND A. C. SKAPSKI, *Proc. Chem. Soc.* 400 (1964).
5. A. C. SKAPSKI AND D. ROGERS, *Chem. Comm.* 611 (1965); A. C. Skapski, *Acta Chem. Scand.* in press.
6. E. T. KEVE, S. C. ABRAHAMS, AND J. L. BERNSTEIN, *J. Chem. Phys.* **51**, 4928, (1969); **53**, 3279 (1970).
7. H. G. VON SCHNERING AND P. BLACKMANN, *Naturwiss.* **55**, 342 (1968).
8. S. ANDERSSON AND J. GALY, *Acta Cryst.* **B25**, 847 (1969).
9. B. AURIVILLIUS, *Arkiv. Kemi* **3**, 153 (1951).
10. R. S. ROTH AND J. L. WARING, *J. Res. Nat. Bur. Stand., Sect. A* **66**, 451. (1962); *Amer. Mineralogist* **48**, 1348 (1963).
11. E. T. KEVE AND A. C. SKAPSKI, to be published.
12. J. M. STEWART, Crystal Structure Calculations System X-Ray 63, Univ. of Maryland Report TR-64-6, 1965.
13. D. T. CROMER AND J. R. WABER, *Acta Crystallogr.* **18**, 104 (1965).
14. L. H. THOMAS AND K. UMEDA, *J. Chem. Phys.* **26**, 293 (1957).
15. "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham (1962).
16. E. W. HUGHES, *J. Amer. Chem. Soc.* **63**, 1737 (1941).
17. S. K. KURTZ AND T. T. PERRY, *J. Appl. Phys.* **39**, 3798 (1968).
18. D. E. COX, M. EIBSCHÜTZ, H. J. GUGGENHEIM, AND L. HOLMES, *J. Appl. Phys.* **41**, 943 (1970).
19. J. K. BRANDON AND H. D. MEGAW, *Phil. Mag.* **21**, 189 (1970).
20. E. T. KEVE AND S. C. ABRAHAMS, *Ferroelectrics* **1**, 243 (1970).
21. N. D. GAVRILOVA, N. F. KARYAKINA, V. A. KOPTSIK, AND V. K. NOVIK, *Soviet Phys. Doklady* **15**, 1075 (1971).
22. A. N. LOBACHEV, V. F. PESKIN, V. I. POPOLITOV, L. N. SYRKIN, AND N. N. FEOKTISOVA, *Soviet Phys. Solid State* **14**, 509 (1972).