The Structure of Triclinic $BiNbO_4$ and $BiTaO_4$

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THE group of ABO_4 compounds shown in the Table falls into three structure types, all of which are unique to this system. Previous studies[1,2] have shown the monoclinic and orthorhombic forms to be related in a very simple manner. We have now determined the crystal structure of triclinic $BiNbO_4$, a representative of the third type, and find it to have unusual features.

The triclinic forms of $BiNbO_4$ and $BiTaO_4$ were first prepared by Aurivillius[3] who showed them to be isomorphous. Subsequently Roth and Waring[4,5] found them to be the high-temperature forms and prepared the low-temperature orthorhombic modifications of these compounds. Triclinic $BiNbO_4$ forms pale yellow elongated prisms. The crystals are normally twinned on the *bc* plane in two different ways, one of them being polysynthetic. The unit-cell dimensions[4] are: $a = 7{\cdot}611$, $b = 5{\cdot}536$, $c = 7{\cdot}919$ Å, $\alpha = 89°\ 54'$, $\beta = 77°\ 28'$; $\gamma = 87°\ 9'$, U = 325·2 Å.[3] The unit-cell content is $4(Bi^{III}Nb^{V}O_4)$.

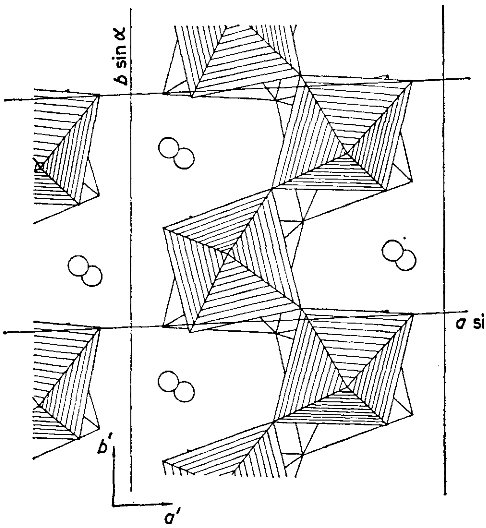

FIGURE 1a. [001] *Projection of triclinic* $BiNbO_4$.

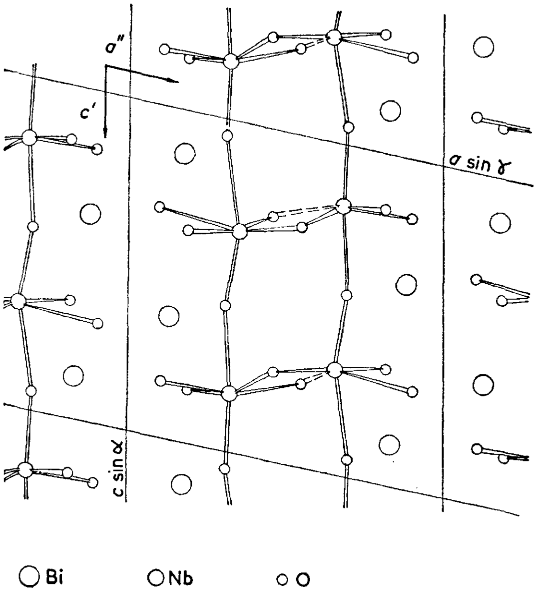

FIGURE 1b. [010] *Projection of triclinic* $BiNbO_4$. (*Dashed lines indicate bonds between niobium and oxygens in the cell above. The octahedra are joined at corners, not edges*).

TABLE

	Nb^{V}	Sb^{V}	Ta^{V}
Sb^{III}	$SbNbO_4$ (o-rh.)	α-Sb_2O_4 (o-rh.)	$SbTaO_4$ (o-rh.)
	—	β-Sb_2O_4 (mon.)	—
Bi^{III}	$BiNbO_4$ (o-rh.)	—	$BiTaO_4$ (o-rh.)
	$BiNbO_4$ (tric.)	$BiSbO_4$ (mon.)	$BiTaO_4$ (tric.)

One form of twinning could be removed by splitting a crystal, but because of the very small size of the resulting fragment Cu-K_α radiation was used to collect the visually estimated data. The structure was solved by standard methods and all the oxygen atoms were observed in a difference Fourier. Least-squares refinement on 642 independent reflections, assuming space group $P\bar{1}$, has reached $R = 0{\cdot}122$. No absorption correction could be applied because of the polysynthetic twinning.

Figures (1a) and (1b) show that the structure contains puckered sheets in the *bc* plane consisting of Nb–O octahedra joined by corners only. It can be derived by slicing an ReO_3-type structure diagonally [parallel to (110) of the ReO_3 unit cell], separating the sheets of octahedra so formed, and sidestepping them to permit more economical packing (Figure 1b). The voids in this framework (Figure 1a) are then filled by the bismuth atoms.

The type of sheet found in this structure is novel in having octahedra joined at four vertices so that the two free ones are adjacent. The other way of joining octahedra at four vertices to form a sheet of the composition $(AX_4)_n$ is found, among others, in β-Sb_2O_4[1] and $SbNbO_4$.[2] This type of sheet, however, together with those, two-octahedra thick, found in $Sr_3Ti_2O_7$[6] and Bi_3NbTiO_9[7] (as perovskite units) are analogous to slices parallel to (100) of the ReO_3 structure.

The octahedra are distorted and the Nb–O distances are within the normal range. The co-ordination of the bismuth atoms is one-sided and very irregular. Each of the two crystallographically independent bismuth atoms has eight oxygen neighbours in the range 2·10—3·00 Å; there are other oxygens at distances greater than 3·48 Å. The standard deviations are 0·04—0·08 Å.

There are no unusually short oxygen–oxygen contacts.

Both the nature and frequency of the two modes of twinning can be explained in terms of alternative ways of stacking adjacent sheets.

(*Received, October 25th,* 1966; *Com.* 824.)

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