tions of the interesting properties of these materials can be ventured with confidence.

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¹ Fischbach, D. B., and Kotlensky, W. V., *Electrochem. Tech.*, **5**, 207 (1967).

² Green, W. V., *Carbon*, **4**, 81 (1966).

³ Green, W. V., and Zukas, E. G., *Electrochem. Tech.*, **5**, 203 (1967).

⁴ Zukas, E. G., and Green, W. V., *Nature*, **212**, 1454 (1966).

⁵ Zukas, E. G., and Green, W. V., *Paper MI 45, Eighth Conf. on Carbon*, Buffalo, New York (June 1967).

⁶ Green, W. V., Levenson, L. S., Reiswig, R. D., and Zukas, E. G., *Paper MI 44, Eighth Conf. on Carbon*, Buffalo, New York (June, 1967).

⁷ Kotlensky, W. V., *Carbon*, **4**, 209 (1966).

Structure corresponding to the Ideal Composition $3\text{Bi}_2\text{O}_3 \cdot 17\text{Nb}_2\text{O}_5$

As part of a study¹ of the structures of compounds in the $\text{Bi}_2\text{O}_3\text{--Nb}_2\text{O}_5$ binary system, we have determined the crystal structure of $3\text{Bi}_2\text{O}_3 \cdot 17\text{Nb}_2\text{O}_5$, which we believe to be the ideal formula of the compound prepared by Roth and Waring² and referred to as $\text{Bi}_2\text{O}_3 \cdot 6\text{Nb}_2\text{O}_5$.

Fig. 1. The [001] projection of the structure of $3\text{Bi}_2\text{O}_3 \cdot 17\text{Nb}_2\text{O}_5$ showing the $\text{Me}_{41}\text{O}_{94}$ matrix (shaded) and the occupancies of the bismuth sites.

The pale yellow plates of this material are orthorhombic with $a = 12.516 \pm 0.005$, $b = 37.14 \pm 0.02$, $c = 3.922 \pm 0.002$ Å, $U = 1828.3$ Å³. Using this unit cell we have been able to index fully the X-ray powder pattern published by Roth and Waring². Single crystal photographs suggested that the structure was of the tetragonal bronze type³ but with one cell edge tripled, and the intensities showed a remarkable similarity to those found by Sleight⁴ for $\text{Nb}_{16}\text{W}_{18}\text{O}_{94}$.

The structure has been determined from some 1,300 independent reflexions, obtained with Cu- $K\alpha$ radiation and visually estimated. Least-squares refinement, in space group $Pba2$, has now reached $R = 0.10$ and is being continued.

All atoms in $3\text{Bi}_2\text{O}_3 \cdot 17\text{Nb}_2\text{O}_5$ are situated near two levels approximately $c/2$ apart. The structure is based on an $\text{Me}_{41}\text{O}_{94}$ matrix in which four of the twelve pentagonal tunnels are regular (in contrast with the other eight) and contain niobium atoms in pentagonal bipyramidal co-ordination. All the other niobium atoms have an octahedral co-ordination. The remaining eight pentagonal

and six diamond-shaped tunnels, which are empty in $\text{Nb}_{16}\text{W}_{18}\text{O}_{94}$, contain all the bismuth atoms. We have found that these are statistically distributed among a number of possible sites, and have used the occupancy at each site as a parameter in the least-squares refinement. The resulting structure is shown schematically in Fig. 1.

The apparent chaos among the bismuth atoms is not unreasonable. The pentagonal and even the diamond-shaped tunnels are too large for the bismuth atom (ionic radius 0.96 Å) and, consequently, these atoms are located away from the centre of the hole. Furthermore, the bismuth atoms show a very strong tendency towards a one-sided four-fold co-ordination similar to that found, for example, in BiSbO_4 (ref. 5) and a number of other complex oxides and oxyhalides of bismuth⁶⁻⁹. This kind of co-ordination, a consequence of a lone pair of electrons, is more often associated with trivalent antimony^{10,11} and is even found for arsenic¹². The bismuth atoms could achieve this co-ordination at a number of sites. The bismuth occupancies of these sites are uneven (see Fig. 1) but add up to 5.7 ($2\sigma = 0.2$) per unit cell, whereas 6 would be expected from the formula. It seems likely that the remaining 0.3 atoms are spread out thinly among some or all of the other possible sites. If, however, the true formula is $\text{Bi}_2\text{O}_3 \cdot 6\text{Nb}_2\text{O}_5$, there would be $5\frac{1}{2}$ bismuth atoms per unit cell, but electrical neutrality would require the random removal of half an oxygen atom per unit cell.

It is difficult to reach a clear-cut decision between the two compositions, the difference between which is very slight (15.0 per cent Bi_2O_3 , 85.0 per cent Nb_2O_5 , $D_{\text{calc}} =$

5.37 g cm⁻³ for 3 : 17, and 14.3 per cent Bi_2O_3 , 85.7 per cent Nb_2O_5 , $D_{\text{calc}} = 5.30$ g cm⁻³ for 1 : 6). We consider, however, that $3\text{Bi}_2\text{O}_3 \cdot 17\text{Nb}_2\text{O}_5$ represents the ideal structural formula.

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¹ Keve, E. T., and Skapski, A. C., *Chem. Commun.*, 281 (1967).

² Roth, R. S., and Waring, J. L., *J. Res. Nat. Bur. Stand., Sect. A*, **66**, 451 (1962).

³ Magnéli, A., *Arkiv Kemi*, **1**, 213 (1949).

⁴ Sleight, A. W., *Acta Chem. Scand.*, **20**, 1102 (1966).

⁵ Aurivillius, B., *Arkiv Kemi*, **3**, 153 (1951).

⁶ Aurivillius, B., *Arkiv Kemi*, **1**, 463 (1949).

⁷ Aurivillius, B., *Arkiv Kemi*, **1**, 499 (1949).

⁸ Aurivillius, B., *Arkiv Kemi*, **2**, 519 (1950).

⁹ Aurivillius, B., *Arkiv Kemi*, **5**, 39 (1952).

¹⁰ Edstrand, M., *Scensk. Kem. Tidskr.*, **67**, 230 (1955).

¹¹ Rogers, D., and Skapski, A. C., *Proc. Chem. Soc.*, 400 (1964).

¹² Skapski, A. C., *Chem. Commun.*, 10 (1966).