### References

Cruickshank, D. W. J. (1965). *Computing Methods in Crystallography*, edited by J. S. Rollett, p. 107. Oxford: Pergamon Press.

De Ranter, C. J. & Van Dijck, M. (1971). *Z. Kristallogr.* **134**, 97–106.

*International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 99–100. Birmingham: Kynoch Press.

Jennison, D. R. & Barry Kunz, A. (1976). *Phys. Rev. B*, **13**, 5597–5602.

Linkoaho, M. (1968). *Ann. Acad. Sci. Fenn. Ser. A*6, No. 284.

Linkoaho, M. V. (1972). *Phys. Scr.* **5**, 271–272.

Linkoaho, M., Rantavuori, E., Korhonen, U., Kurki-Suonio, K. & Ruuskanen, A. (1972). *Acta Cryst.* A**28**, 260–264.

Nagel, S., Maschke, K. & Baldereschi, A. (1976). *Phys. Status Solidi B*, **76**, 629–632.

Schoknecht, G. (1957). *Z. Naturforsch. Teil A*, **12**, 983–996.

---

*Acta Cryst.* (1979). A**35**, 142–145

# New Layered Structure of $Bi_2W_2O_9$ Determined by 1 MV High-Resolution Electron Microscopy

By Y. Bando, A. Watanabe, Y. Sekikawa, M. Goto and S. Horiuchi

*National Institute for Researches in Inorganic Materials, Sakura-mura, Niihari-gun, Ibaraki, Japan* 300–31

(*Received* 6 *June* 1978; *accepted* 26 *July* 1978)

## Abstract

The crystal structure of bismuth tungstate, $Bi_2W_2O_9$, has been examined by 1 MV high-resolution electron microscopy. The symmetry is orthorhombic with lattice parameters $a = 5.43$, $b = 5.41$ and $c = 23.7$ Å and space group $Pna2_1$. The point group is determined directly from the images in which each cation site is resolved. The structure is similar to that of conventional layered Bi compounds with respect to the $Bi_2O_2$ sheets normal to the $c$ axis; however, the layer between the sheets is of a deformed $ReO_3$ type. The strong chemical bonds between the Bi ions and the apex O atoms cause the rotation of the $WO_6$ octahedron about the $c$ axis. W ions are displaced antiparallel in the $WO_3$ layer.

## Introduction

Since the discovery of layered Bi compounds by Aurivillius (1949) more than sixty ferroelectrics belonging to this family have been found. The family is represented by the general chemical formula $Bi_2M_{n-1}R_nO_{3n+3}$, where $M$ = Bi, Pb, Na, K, Sr, Ca, Ba and several rare-earth ions, and $R$ = Ti, Nb, Ta, Fe, Ga, W and Cr. The structure consists of $M_{n-1}R_nO_{3n+1}$ perovskite-like layers interleaved with $Bi_2O_2$ sheets, where $n$ = 1, 2, 3, 4 and 5 (Newnham, Wolfe & Dorrian, 1971).

The phase relations in the $Bi_2O_3$–$WO_3$ system have been widely investigated. The compounds $Bi_2WO_6$ and $Bi_2W_2O_9$ were prepared first by Hey, Bannister & Russell (1938) and later by Gal'perin, Erman, Kolchin, Belova & Chernyshev (1966). They are both orthorhombic with lattice parameters $a = 5.45$, $b = 5.46$, $c = 16.4$ and $a = 5.42$, $b = 5.41$, $c = 23.7$ Å respectively (Hoda & Chang, 1974). X-ray and neutron powder diffraction have revealed that $Bi_2WO_6$ has the same structure as that of the family mentioned above (Wolfe, Newnham & Kay, 1969). The X-ray powder pattern suggested that $Bi_2W_2O_9$ has a layer structure; however, the structure analysis has never been carried out.

The high-voltage electron microscope (Hitachi – 1250 kV) constructed in our institute has a resolving power near 2·0 Å at an accelerating voltage of 1 MV with axial illumination and a goniometer stage (Horiuchi, Matsui & Bando, 1976). Such a high resolving power enables us to take structure images even from crystals with a relatively small unit cell. This was first demonstrated for a mixed-layer bismuth titanate, $Bi_7Ti_4NbO_{21}$, and the crystal structure was determined on the basis of direct imaging of atoms from more than two directions (Horiuchi, Kikuchi & Goto, 1977).

In the present paper, we try to determine the crystal structure of $Bi_2W_2O_9$ on the basis of super-high-resolution structure images. It is shown that the point group of the crystal is evident directly from the images.

0567-7394/79/010142-04$01.00

## Experimental procedure

Powders of pure bismuth oxide and tungsten oxide were mixed with a composition of $Bi_2O_3.2WO_3$. The mixture was heated in a Pt crucible at a rate of 200 °C $h^{-1}$ and kept at 950 °C for 10 h. The melt was cooled to 850 °C at a rate of 2 °C $h^{-1}$ and then quenched to room temperature. As the compound $Bi_2W_2O_9$ melts incongruently, the products obtained contained a small amount of $Bi_2WO_6$ and $WO_3$.

Greenish-white polycrystals were selected from the aggregates and crushed in an agate mortar to fragments of several microns in size. They were set on a holey C supporting film and observed in the high-voltage electron microscope operated at 1 MV. The objective aperture size corresponded to about 0·5 $Å^{-1}$ in reciprocal space. The astigmatism of the objective lens was corrected by observing a granular structure image of the C supporting film. The contrast of the images obtained at underfocus between 500 and 1000 Å could be interpreted intuitively. The direct magnification was $2{\cdot}5 \times 10^5$. Details of the adjustment and operation of the microscope have been given elsewhere (Horiuchi, Matsui, Bando, Katsuta & Matsui, 1978).

## Results and interpretation

Many electron diffraction patterns corresponding to various reciprocal-lattice sections were taken from $Bi_2W_2O_9$ crystal fragments. The results show that the crystal has orthorhombic symmetry with lattice parameters $a = 5{\cdot}43$, $b = 5{\cdot}41$ and $c = 23{\cdot}7$ Å; these are in good agreement with the results of X-ray powder diffraction (Watanabe & Goto, 1978). The systematic absences are $k + l = 2n + 1$ for $0kl$ and $h = 2n + 1$ for $h0l$. The possible space groups are therefore $Pna2_1$ (noncentrosymmetric) or *Pnam* (centrosymmetric).

Fig. 1 shows a structure image taken with the incident electron beam parallel to the [110] direction. Zigzag chains with dark contrast run normal to the *c* axis at intervals of about 12 Å. When compared with previous observations (Horiuchi *et al.*, 1977), they can be attributed to the $Bi_2O_2$ sheets. Layers interleaved with the sheets seem to be composed of the $ReO_3$-type structure (from the relatively simple array of the contrast). Dark dots in the layers are then tungsten ions. The structure model obtained from the image contrast is represented in the same figure.

Images taken from the incident electron beam along the [010] and [100] directions are shown in Fig. 2(*a*) and (*b*) respectively. It should also be noted from these photographs that the crystal consists of $WO_3$ layers interleaved with $Bi_2O_2$ sheets. Each tungsten ion site is resolved with dark contrast, while the cubo-octahedral site is bright. The structure models projected onto the (010) and (100) planes are illustrated in the figures.

It should be noticed in Fig. 1 that the tungsten ions in the $WO_3$ layer are slightly shifted from the positions corresponding to those in the ideal $ReO_3$-type structure. The direction connecting two adjoining dark dots makes an angle of 10° with the *c* axis in the projected plane. On the other hand, the direction connecting two adjoining tungsten ions in Fig. 2(*a*) is tilted by 14°, while that in Fig. 2(*b*) is almost parallel to the *c* axis in the (100) projection.

It is important to note in Fig. 1 and Fig. 2(*a*) that the mirror symmetry element perpendicular to the *c* axis is absent. The space group of the crystal can therefore be selected as $Pna2_1$. The arrangement of oxygen octahedra in the $WO_3$ layer can then be designated. The crystal structure model projected onto the (010) plane is shown in Fig. 3. The crystallographic non-equivalent positions are indicated. The unit cell contains four molecular units in a volume of 696·2 $Å^3$. The calculated density is 8·83 Mg $m^{-3}$, which is in good agreement with the observed value of 8·80 Mg $m^{-3}$ (Speranskaya, 1970). The structure is different from

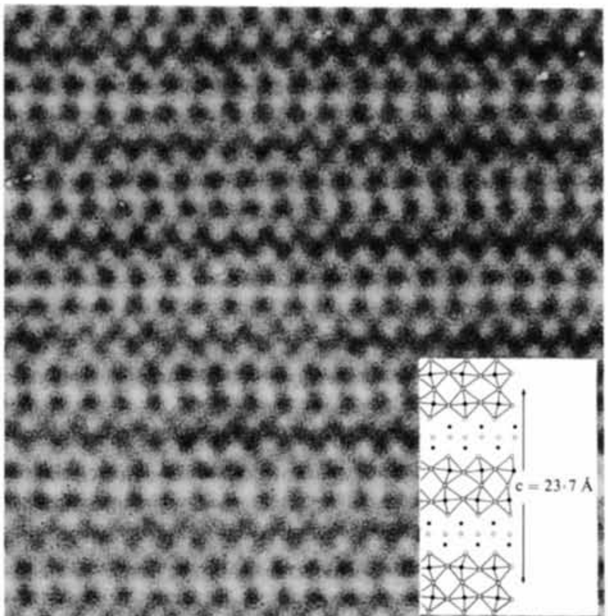


Fig. 1. A structure image of $Bi_2W_2O_9$ taken with the incident electron beam parallel to the [110] direction. The structure model is shown. Dark circles indicate Bi and W ions and open circles oxygen ions.

that of conventional layered bismuth compounds; that is, the layers interleaved with the $Bi_2O_2$ sheets have the structure not of the perovskite type but of the $ReO_3$ type. The vectors of O(3)–O(3), O(4)–O(4), O(6)–O(6) and O(7)–O(7) are in the planes normal to the [001] direction, while those of O(3)–O(4) and O(6)–O(7) are slightly tilted with respect to the $b$ axis, resulting in a primitive Bravais lattice.

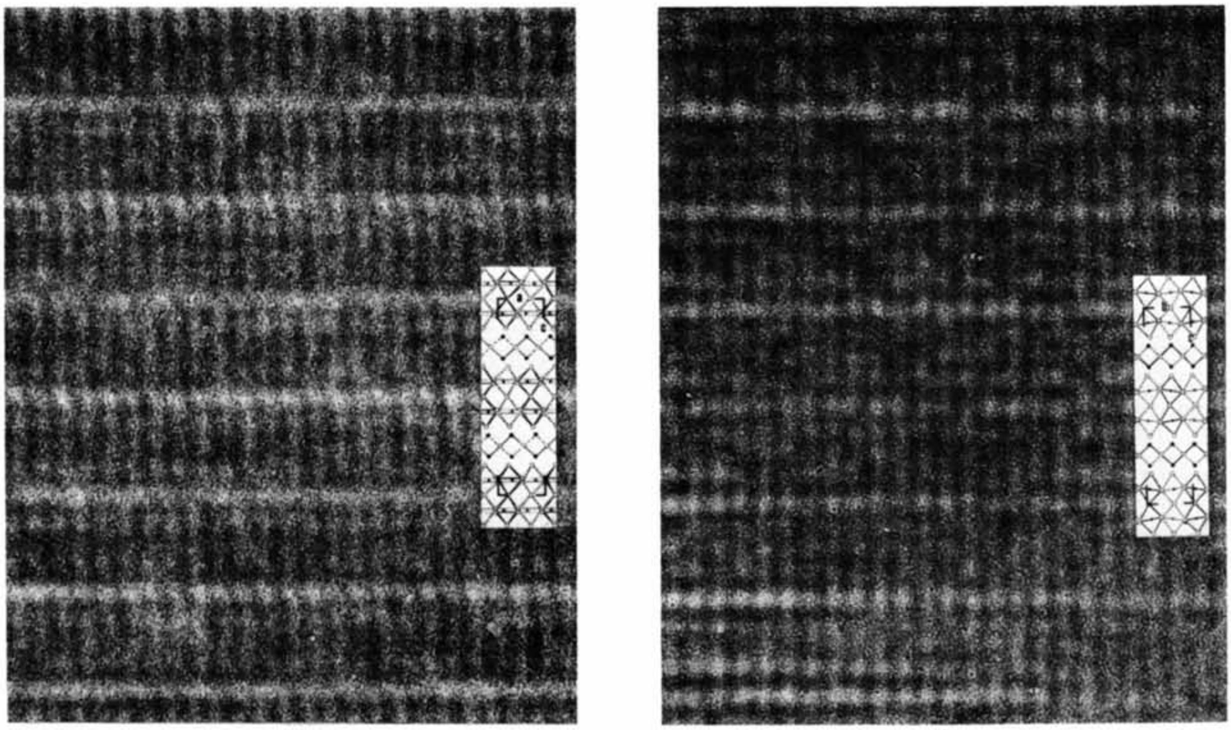

(a) (b)

Fig. 2. Structure images of $Bi_2W_2O_9$ taken with the incident electron beam parallel to (a) the [010] and (b) the [100] directions. The structure models are shown. Dark circles indicate Bi and W ions and open circles O ions. The octahedron and $Bi_2O_2$ sheet centered at $x = 0$ or $y = 0$ are shown by solid lines, those at $x = \frac{1}{2}$ or $y = \frac{1}{2}$ by dotted lines. The unit cell is outlined ($a = 5{\cdot}43$, $b = 5{\cdot}41$ and $c = 23{\cdot}7$ Å).

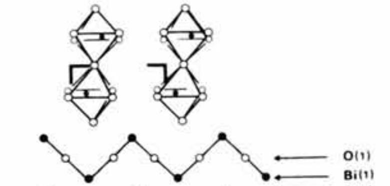
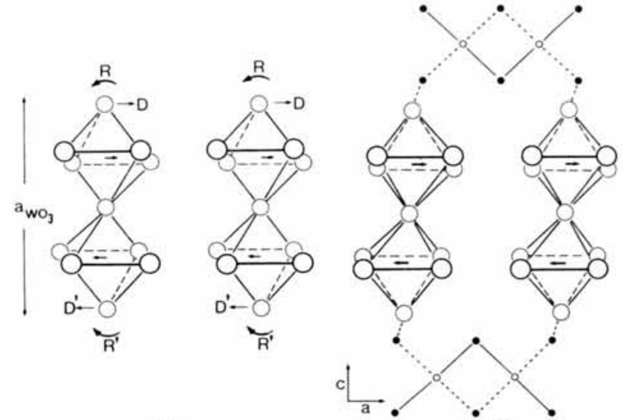


Fig. 3. A crystal structure model of $Bi_2W_2O_9$ projected onto the (010) plane. The symbols are as in Fig. 2. The octahedron and $Bi_2O_2$ sheet centered at $y = \frac{1}{2}$ are abbreviated.



(a) (b)

Fig. 4. A schematic representation of the rotation of the $WO_6$ octahedron induced by the strong chemical bonds between the Bi ions and the apex O atoms in the $WO_3$ layer. (a) The structure of part of the monoclinic $WO_3$; (b) the $WO_3$ layer in $Bi_2W_2O_9$. The octahedron centered at $y = \frac{1}{2}$ is abbreviated. The direction of the rotation is shown by the arrows $R$ and $R'$.

## Discussion

Tungsten trioxide, $WO_3$, has a monoclinic symmetry with lattice parameters $a = 7{\cdot}306$, $b = 7{\cdot}540$, $c = 7{\cdot}692$ Å and $\beta = 90{\cdot}88°$ at room temperature (Loopstra & Boldrini, 1966; Loopstra & Rietveld, 1969). The crystal has a deformed $ReO_3$-type structure. The corner-linked $WO_6$ octahedra are rotated by 8° about the *a* axis as shown in Fig. 4(*a*). The rotational direction is reversed in neighbouring octahedra in the **a** direction. Tungsten ions are displaced from the center of the octahedron toward the octahedral edge as shown by arrows. The direction of the displacement is antiparallel with respect to the center of inversion. Accordingly, the crystal is antiferroelectric (Zheludev, 1971).

The compound $Bi_2W_2O_9$ examined in the present study does not belong to any of the conventional families of layered compounds. Because of strong chemical bonds with the Bi ions, the apex O atoms of the $WO_3$ layers are shifted in the direction of the arrows *D* and *D'*; this shift causes the slight tilting of the octahedron with respect to the *a* axis. The rotation about the *c* axis then occurs in order to suppress the strain of the octahedron as much as possible. The rotational direction is shown by the arrows *R* and *R'*, which are mutually reversed. Thus the rotation that originally existed in the monoclinic $WO_3$ crystal is almost cancelled. Fig. 4(*b*) shows the structure after these changes. The amount of the antiparallel displacement of the octahedral tungsten ions remains unchanged after the tilting and rotation of the octahedron. It is likely that $Bi_2W_2O_9$ is antiferroelectric at room temperature.

It should be noticed that only the positions of metal atoms were determined directly from the image. Their accuracy is rather high, since each is imaged as a dark dot. On the other hand, the positions of the O atoms were speculated from crystal-chemical considerations, because they do not show any clear contrast even for a thin crystal. Their accuracy is therefore low. We think, however, that the present technique is very suitable for determining the framework of the structure.

With a higher electron-beam intensity the crystals suffer from irradiation damage especially in the very thin edge region. An example is shown in Fig. 5. The contrast of the zigzag chains becomes weak. This means that Bi ions volatilize preferentially in the form of $Bi_2O_3$. Residual $WO_3$ layers mutually coagulate to form microdomains. The crystal orientation between $WO_3$ and $B_2W_2O_9$ is $[010]_{WO_3}\|[110]_{Bi_2W_2O_9}$.

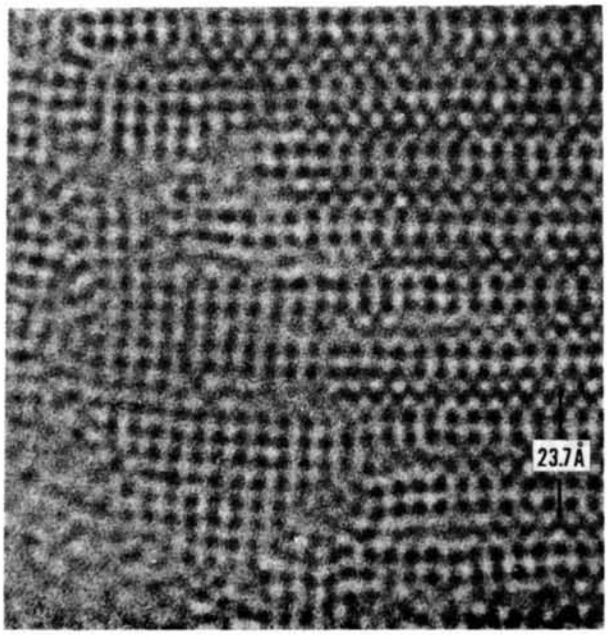


Fig. 5. Microdomains of $WO_3$ formed on irradiation by an electron beam of high intensity. The crystal orientation between $WO_3$ and $Bi_2W_2O_9$ is $[010]_{WO_3}\|[110]_{Bi_2W_2O_9}$.

The authors wish to express their deep gratitude to Mr K. Muramatsu and Mr Y. Matsui for valuable discussions.

### References

Aurivillius, B. (1949). *Ark. Kemi*, **1**, 463.

Gal'perin, E. L., Erman, L. Ya., Kolchin, I. K., Belova, M. A. & Chernyshev, K. S. (1966). *Russ. J. Inorg. Chem.* **11**, 1137–1143.

Hey, M. H., Bannister, F. A. & Russell, A. (1938). *Mineral. Mag.* **25**, 41–55.

Hoda, S. N. & Chang, L. L. Y. (1974). *J. Am. Ceram. Soc.* **57**, 323–326.

Horiuchi, S., Kikuchi, T. & Goto, M. (1977). *Acta Cryst.* A**33**, 701–703.

Horiuchi, S., Matsui, Y. & Bando, Y. (1976). *Jpn. J. Appl. Phys.* **15**, 2483–2484.

Horiuchi, S., Matsui, Y., Bando, Y., Katsuta, T. & Matsui, I. (1978). *J. Electron Microsc.* **27**, 39–48.

Loopstra, B. O. & Boldrini, P. (1966). *Acta Cryst.* **21**, 158–163.

Loopstra, B. O. & Rietveld, H. M. (1969). *Acta Cryst.* B**25**, 1420–1421.

Newnham, R. E., Wolfe, R. W. & Dorrian, J. F. (1971). *Mater. Res. Bull.* **6**, 1029–1040.

Speranskaya, E. I. (1970). *Inorg. Mater.* (*USSR*), **6**, 127–129.

Watanabe, A. & Goto, M. (1978). *J. Less-Common Met.* **61**, 265–272.

Wolfe, R. W., Newnham, R. E. & Kay, M. I. (1969). *Solid State Commun.* **7**, 1797–1801.

Zheludev, I. S. (1971). *Physics of Crystalline Dielectrics*. Vol. 1, p. 84. New York: Plenum.