

Discovery of a New Type of Layered Structure by High Resolution Electron Microscopy and Electron-induced X-Ray Microanalysis

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Combined high resolution electron microscopy, energy dispersive X-ray emission microanalysis, and computer simulation studies indicate that a layered intermediate phase exists in the Bi–Mo–W–O system, its idealized composition being $\text{Bi}_2(\text{W},\text{Mo})_{12}\text{O}_{35}$; the structure consists of Bi_2O_3 sheets interleaved with $(\text{W},\text{Mo})_2\text{O}_5$ sheets which contain crystallographic shear planes that are perpendicular to the layers.

The so-called bismuth molybdates, $\text{Bi}_2\text{Mo}_n\text{O}_{3n+3}$ ($n = 1, 2,$ and 3) are efficient selective oxidation catalysts,^{1–3} their mode of action, though not yet fully clarified,⁴ being associated with the ease of removal and replacement of structural oxygen. The $n = 1$ member of this series consists of $\text{Bi}_2\text{O}_2^{2+}$ layers separated by layers of MoO_4^{2-} . The structure of Bi_2WO_6 ⁵ is similar, WO_4^{2-} sheets made up of corner sharing WO_3 octahedra separated by sheets of $\text{Bi}_2\text{O}_2^{2+}$. But whereas in the Bi–W–O system this interleaving of $\text{Bi}_2\text{O}_2^{2+}$ sheets with $\text{W}_n\text{O}_{3n+1}^{2-}$ sheets occurs for $n = 2$ ⁶ and for $n = 3$,⁷ (metastable) in the Bi–Mo–O system this type of structure is not adopted. For $n \geq 2$, the octahedral co-ordination of Mo is abandoned in favour of a tetrahedral arrangement, the $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ structure, for example, being scheelite-related. In view of these striking differences, and also because of their current use as selective oxidation catalysts, we have examined by high resolution electron microscopy (h.r.e.m.) the structures of quaternary oxides (Bi–Mo–W–O) quenched from melts held at ca. 950 °C. The resulting materials are frequently polyphasic and almost invariably microcrystalline. X-Ray single crystal analyses are,

at present, not feasible, and even powder diffractometry, because of the coexistence of several phases, is usually inapplicable. Such materials are, however, amenable to h.r.e.m. and to electron-induced X-ray emission studies (x.r.e.).

From a melt of nominal composition $\text{Bi}_2\text{MoW}_2\text{O}_{12}$ two principal constituents were identified by x.r.e. and selected area electron diffraction (s.a.e.d.). The majority phase appeared to be related to $\text{Bi}_2\text{Mo}_3\text{O}_{12}$, with up to 30% replacement of Mo by W, and will be described fully elsewhere. The second phase, with very variable composition, but with a much lower Bi content has structural features, which to our knowledge, have not hitherto been identified.

In Figure 1, the real-space h.r.e.m. image shows layer repeats of 25 Å and other details reminiscent of the layered Bi–W–O family of compounds ($n = 1–3$ in $\text{Bi}_2\text{W}_n\text{O}_{3n+3}$). The unit cell dimensions, obtained from s.a.e.d. patterns taken down [001], [010], and [110] zone axes, are $a = 11.8$, $b = 3.8$, $c = 25.8$ Å, $\beta = 107^\circ$, and the structure is monoclinic. The observed xy unit mesh and separation of the vertical striations in the h.r.e.m. images can be reconciled with the composition

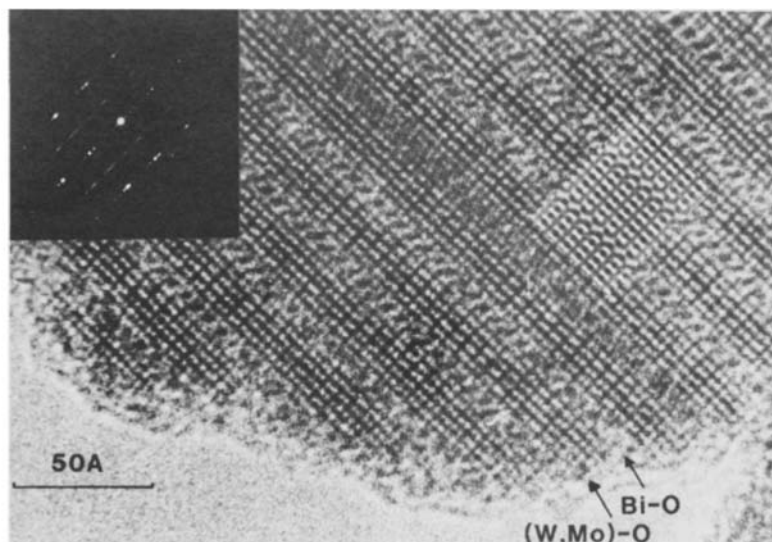


Figure 1. The h.r.e.m. image of a crystal of the new phase, with inset s.a.e.d. pattern, taken with the electron beam parallel to [010]. Suggested positions of Bi-O and (W,Mo)-O components are indicated. The computer simulated image (inset) was evaluated for a crystal thickness of 20 Å at 1200 Å defocus.

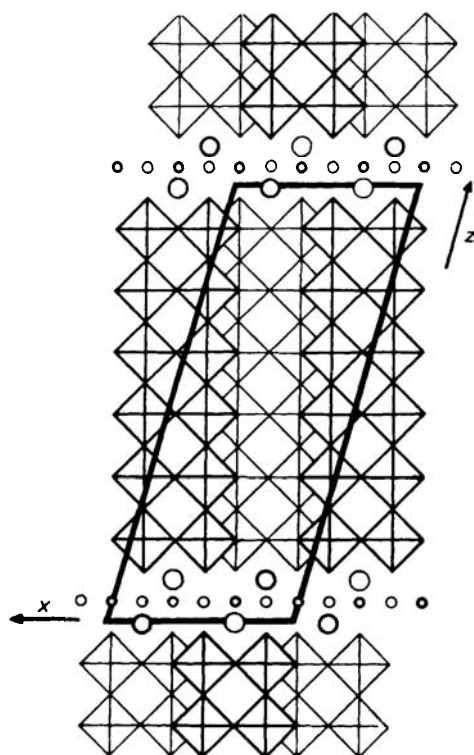


Figure 2. The structural model (idealised) used in the computer-image matching process. Projection down [010].

and known solid-state chemistry of Mo and W oxides only if these striations are taken to signify crystallographic shear where corner-sharing of octahedra [(Mo,W)O₆] has been replaced by edge-sharing, *i.e.* where the sheets separating the individual bismuth oxide sheets have a stoichiometry based on M₂O₅, rather than on MO₃ as in Bi₂WO₆ or in Bi₂MoO₆. The occurrence of the crystallographic shear planes in this new structure requires diminution in the bismuth content of the bismuth oxide sheets compared with their composition in

the ordinary layered tungstates or molybdates. Indeed, the compositions of the interleaved components of this new structure are M_{2n}O_{5n+2} (where M = Mo, W, and *n* = number of layers in this component) and Bi₂O₃.

A structural model may, therefore, be constructed and its validity tested by computing the h.r.e.m. image contrast as a function of thickness and microscope defocus. The model shown in Figure 2 satisfies all the known experimental features. It is to be noted that there are stacking offsets for successive sheets of $-a/6 + b/2$.

In this approach to structural elucidation the disposition of the atoms are determined to within approximately 0.5 Å, and the overall structural skeleton only is derived. To confirm this structure, and to locate the atoms more precisely, attempts must be made to grow somewhat larger crystallites, the maximum size so far obtainable being *ca.* 5000 Å.

An X-ray crystallographic determination using synchrotron sources could, in principle, be carried out with crystallites of 2–5 μm.

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References

- 1 A. F. Van den Elzen and G. D. Rieck, *Acta Crystallogr., Sect. B*, 1973, **29**, 2436.
- 2 A. F. Van den Elzen and G. D. Rieck, *Mater. Res. Bull.*, 1975, **10**, 1163.
- 3 A. F. Van den Elzen and G. D. Rieck, *Acta Crystallogr., Sect. B*, 1973, **29**, 2433.
- 4 R. K. Grasselli and J. D. Burrington, 'Catalysis of Organic Reactions,' eds. W. R. Moser and M. Webber, Wiley, New York, 1981, p. 17; A. W. Sleight, *Science*, 1980, **208**, 895; R. K. Grasselli, J. D. Burrington, and J. F. Brazdil, *Faraday Discuss. Chem. Soc.*, 1982, **72**, 203.
- 5 S. N. Hoda and L. L. Y. Chang, *J. Am. Ceram. Soc.*, 1974, **57**, 323.
- 6 Y. Bando, A. Watanabe, Y. Sekikawa, M. Goto, and S. Horiuchi, *Acta Crystallogr., Sect. A*, 1979, **35**, 142.
- 7 D. A. Jefferson, J. Gopalakrishnan, and A. Ramanan, *Mater. Res. Bull.*, 1982, **17**, 269.