The Redetermination of the Crystal Structure of a Sodium Molybdenum Oxide Bronze: $Na_{0\cdot9}Mo_6O_{17}$

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Summary The single-crystal *X*-ray structure determination of the sodium molybdenum oxide bronze, $Na_{0\cdot9}Mo_6O_{17}$ shows the existence of localized MoO_4 tetrahedra closely associated with the sodium atoms in a structure which otherwise comprises ReO_3-type corner-sharing MoO_6 octahedral slabs.

UNTWINNED crystals of the reported composition $Na_{0\cdot9}Mo_6O_{17}$ were prepared by melt electroslysis and characterized by Wold *et al.*[1] The crystal structure of this bronze in the twinned form was partially solved by Stephenson.[2]

We have prepared single crystals of composition *ca.* $Na_{0\cdot9}Mo_6O_{17}$ by treating sodium hydride with an excess of molybdenum trioxide in open Pythagoras furnace-ware and extracting with ammonia solution. The crystals are monoclinic, space group $C2/m$, $C2$ or Cm with $z = 2$; $a = 9\cdot55$, $b = 5\cdot52$, $c = 12\cdot98$ Å, $\beta = 90\cdot1°$. Slight but significant variation is observed in these unit cell dimensions for different crystals. Intensity data collected initially using Cu-K_α radiation with the multiple-film Weissenberg technique was used to solve the structure by the conventional Patterson methods, but was not adequate for the determination of some of the partial occupancies observed. Subsequently data were collected from two other crystals using Mo-K_α radiation with a Picker four-angle diffractometer and the structural models from both sets of data, although not yet fully refined, are essentially identical at an agreement factor of $R = 0\cdot081$.

The structure consists basically of ReO_3-type slabs of corner-shared MoO_6 octahedra perpendicular to the c-axis, with the molybdenum atoms at the surfaces of these slabs in tetrahedral co-ordination to oxygen atoms. The slabs are weakly held together by sodium ions as indicated in the Figure; the planes containing sodium ions correspond to the pronounced cleavage plane observed for these crystals.

There is evidence, in small areas of the crystal, for the existence of MoO_6 octahedra, which replace MoO_4 tetrahedra near the $z = \frac{1}{2}$ plane, thus extending the ReO_3-type slabs and crosslinking the $z = \frac{1}{2}$ plane by corner-sharing octahedra. The sodium site is about 80% occupied in the provisional model. When tetrahedral groups are present the sodium co-ordination is distorted cube octahedral, but when octahedra groups crosslink the $z = \frac{1}{2}$ plane, the sodium co-ordination is nearly regular cube octahedral.

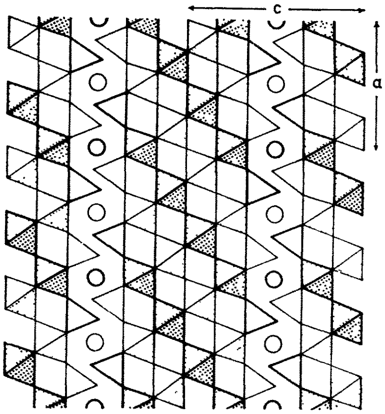

FIGURE. *An* 010 *projection of part of the structure of* $Na_{0\cdot9}Mo_6O_{17}$ *represented as* MoO_6 *octahedra,* MoO_4 *tetrahedra, and sodium atoms. Heavy lines represent species at* $y = 0, 1$, *lighter ones represent those at* $y = \frac{1}{2}$.

This structure accounts for features not readily explained by Stephenson's model; in particular, the localization of sodium atoms in the $z = \frac{1}{2}$ plane and the reported formula $Na_xMo_6O_{17}$ (x *ca.* $0\cdot9$), which is realized if the tetrahedral sites are fully occupied. Many similarities are seen to the higher molybdenum oxides, in particular to the monoclinic form of Mo_4O_{11}.[3]

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