Crystal Structures of Two Tin–Tungsten Oxides

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A compound of approximate composition $\mathrm{Sn_{0\cdot2}WO_3}$ has an orthorhombic structure, space-group *Pmma*, with $a = 7{\cdot}415 \pm 0{\cdot}002$, $b = 3{\cdot}787 \pm 0{\cdot}005$, $c = 20{\cdot}40 \pm 0{\cdot}02$ Å, and a superstructure containing 12 of these units. The structure of the basic unit, was determined from photographic data by Patterson techniques and refined by least-squares methods to R 0·13 for 395 reflections. It is formed by corner-sharing octahedra, both the tungsten and tin ions occupying the octahedra. A similar structure of composition $\mathrm{Sn_{0\cdot3}WO_3}$ was also determined and refined to R 0·15 for 295 reflections. The basic unit has space-group *Cmmm* and unit-cell dimensions $a = 7{\cdot}12 \pm 0{\cdot}03$, $b = 33{\cdot}24 \pm 0{\cdot}04$, $c = 3{\cdot}795 \pm 0{\cdot}004$ Å; the superstructure contains 14 of the basic units.

In the series of compounds $\mathrm{Sn}_x\mathrm{WO_3}$ ($x = 0{\cdot}01$—$0{\cdot}4$) three structural regions are found. At the upper end of the series ($x = 0{\cdot}3$—$0{\cdot}4$) the tetragonal bronze structure [1,2] occurs, and at the lower end ($x = 0{\cdot}01$—$0{\cdot}15$) a family of orthorhombic structures has been reported.[3] The present paper reports two related structures in the intermediate range ($x = 0{\cdot}2$—$0{\cdot}3$), both of which possess large superstructures and also show some disorder.

EXPERIMENTAL

Crystals were prepared by means of reaction (1), the reactants being heated for 170 h at 1100 °C in sealed silica

$$x\mathrm{SnO_2} + \frac{(3-2x)}{3}\mathrm{WO_3} + \frac{2x}{3}\mathrm{W} \longrightarrow \mathrm{Sn}_x\mathrm{WO_3} \quad (1)$$

tubes under 5×10^{-4} torr. The preparation $\mathrm{Sn_{0\cdot2}WO_3}$ was a mass of dark purple crystals in the form of rods and plates, all with the '6-type' structures described later. The $\mathrm{Sn_{0\cdot3}WO_3}$ contained '5-type' crystals and crystals with the tetragonal bronze structure.

The insolubility of these, and all other, reduced tin–tungsten oxides prevented precise analysis, but an estimate of the tin–tungsten ratio carried out by electron-probe microanalysis confirmed that it is approximately that calculated from the quantities of materials used in the preparation. Heating these compounds in air at 1000 °C oxidises them to a light yellowish-green powder, and the resulting gain in weight after heating $\mathrm{Sn_{0\cdot3}WO_3}$ was 88% of the gain expected from reaction (2). The crystals

$$\mathrm{Sn}_x\mathrm{WO_3} + x\mathrm{O_2} \longrightarrow x\mathrm{SnO_2} + \mathrm{WO_3} \quad (2)$$

are semiconductors, and measurements carried out on

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[1] A. Magneli, *Arkiv Kemi*, 1949, **1**, 24, 213.

[2] A. S. Ribnick, B. Post, and E. Banks, 'Advances in Chemistry,' Series No. **39**, Amer. Chem. Soc., 1963.

[3] R. Steadman, R. J. D. Tilley, and I. J. McColm, *J. Solid State Chem.*, 1972, **4**, 199.

sintered compacts gave values of specific resistivity in the range $3\cdot0$—$4\cdot5 \times 10^{-2}$ ohm cm at room temperature.[4]

Crystal Data.—(i) ' 6-type ', approximate cell contents $Sn_2W_{10}O_{30}$, Orthorhombic, $a = 7\cdot415 \pm 0\cdot002$, $b = 3\cdot787 \pm 0\cdot005$, $c = 20\cdot40 \pm 0\cdot02$ Å, $U = 572\cdot8$ Å^3, $F(000) = 1080$, Cu-K_α radiation, $\lambda = 1\cdot5418$ Å; μ(Cu-K_α) = 1029 cm^{-1}. Space-group *Pmma*. Superstructure orthorhombic $A = a$, $B = 12b$, $C = c$.

(ii) ' 5-type ', approximate cell contents $Sn_{4\cdot8}W_{16}O_{48}$, Orthorhombic, $a = 7\cdot12 \pm 0\cdot03$, $b = 33\cdot24 \pm 0\cdot04$, $c = 3\cdot795 \pm 0\cdot004$ Å, $U = 898\cdot0$ Å^3, $F(000) = 1808$. Space-group *Cmmm*. Superstructure orthorhombic, $A = a$, $B = b$, $C = 14c$.

RESULTS

The structures, as patterns of corner-sharing octahedra, are shown in Figure 1. The terms ' 6-type ' and ' 5-type ' refer to the marked periodic intensity variation seen on rows of spots on diffraction photographs and which is determined by the number of octahedra in the long edge of the unit cell. At this stage of the work, only reflections with h even were used in the structure determination; Weissenberg photographs of layers with h odd could only be indexed in terms of the unit cell of the superlattice. The spots on these layers were almost all extremely faint, and many were streaked because of the structural disorder, as shown in Figure 2.

Intensities of 395 reflections for the 6-type and 295 for the 5-type were obtained from microdensitometer measurements of integrated Weissenberg photographs. Least-squares refinement[5] gave R 0·13 for the 6-type and 0.15 for the 5-type structure, and the atomic co-ordinates, isotropic temperature factors and a comparison of F_o and F_c together with an account of the crystallographic reasoning are given in Supplementary Publication No. 20382 (13 pp., 1 microfiche).*

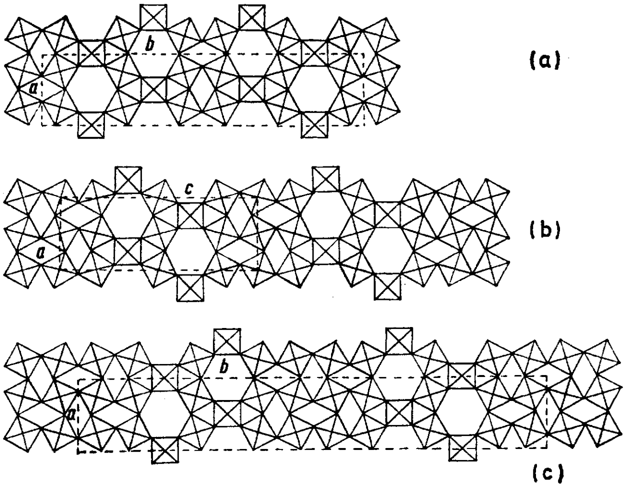

FIGURE 1 (a) Arrangement of (W, Sn)–O octahedra in the 5-type structure. The heavy atoms are at the centres of the octahedra and the oxygens are at the corners linking pairs of octahedra. Layers of octahedra identical to the one shown are stacked together in the direction perpendicular to the page and are linked by sharing oxygens. (b) 6-Type structure. (c) A possible 7-type structure

DISCUSSION

No sites in the structures shown in Figure 2 are occupied exclusively by tin; the evidence at this stage is that tin, like the tungsten, occupies the octahedral sites, and the structure refinement has been carried to this point with both metals randomly occupying the octahedra. Attempts to put the tin in the large hexagonal tunnels which penetrate the structures and which appear to be the obvious sites resulted in a large increase in R.

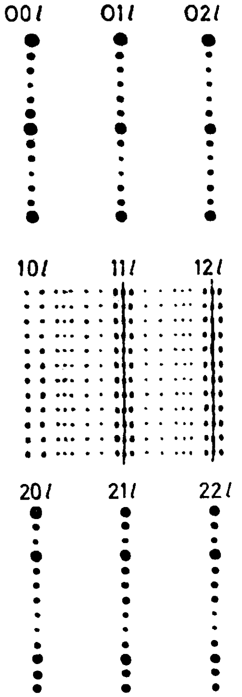

FIGURE 2 Weighted reciprocal lattice nets of the 6-type structure. The indices shown refer to the unit cell of the basic structure and do not take account of the superstructure spots shown on the 1*kl* layer. The 1*kl* spots are much more diffuse and faint than indicated here

Hexagonal structures similar to those described here are well known among compounds derived from WO_3. Hexagonal tungsten bronzes of rubidium, caesium, and potassium have been described,[6] the large alkali-metal ions being situated in the wide hexagonal tunnels, and a hexagonal WO_6 framework forms the basis of the orthorhombic forms of $MoW_{11}O_{36}$ and $MoW_{14}O_{45}$,[7] in which the molybdenum is in octahedral co-ordination, leaving the tunnels vacant. The molybdenum in these structures forms a regular pattern (destroying the hexagonal symmetry), rather than occupying random sites, and it is possible that, while the structures derived for the tin–tungsten oxides give very satisfactory agreement with observed diffraction data, when the superstructure is taken into account the tin too will be found to form an extended regular pattern.

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[4] I. J. McColm, personal communication.

[5] *X*-Ray system of programmes of July 1970, updated May 1971, edited by J. M. Stewart and F. A. Kundell, University of Maryland, and J. C. Baldwin, S.R.C. Atlas Laboratory, England.

[6] A. Magneli, *Acta Chem. Scand.*, 1959, **7**, 2, 315.

[7] J. Graham and A. D. Wadsley, *Acta Cryst.*, 1961, **14**, 379.

It has already been mentioned that at low tin concentrations another series of structures has been found, and it is possible that our 6-type and 5-type are themselves only two members of a series. Indeed, a crystal with composition $Sn_{0\cdot05}Eu_{0\cdot05}WO_3$ has been found which appears from its Weissenberg photograph to have a 7-type structure, and Figure 1(c) shows how a possible 7-type structure is related to the other two. The number of posible structures of a given n-type increases with n, and the 7-type of Figure 1(c) is merely that which seems most closely related to the 5- and 6-types. A structure of this kind should be found with a tin content less than $Sn_{0\cdot2}WO_3$; the lower the tin content, the lower is the proportion of hexagonal linking within the structure until, at about $Sn_{0\cdot15}WO_3$, we encounter the other series of orthorhombic structures which contain no hexagonal part.

The loose term ' bronze ' is applied to many ternary oxides of tungsten, and there is a question of whether it may be applied to these compounds. In terms of structure alone they do not fall into the bronze category, since their structures cannot be described in terms of a host lattice of WO_6 octahedra with tin as guest ions in interstitial sites. But, as has been pointed out,[8] the classification ' bronze ' is difficult to justify in terms of structure alone and is perhaps better defined by physical properties, particularly the colour of the crystals, their conductivity, the range of composition, and resistance to chemical attack by oxidising acids. In all these respects the tin–tungsten oxides can be regarded as bronzes, although in respect of composition the range for each structure is not wide and is not achieved by a continuous variation in the number of interstitial ions.

[1/1008 *Received*, 18*th June*, 1971]

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[8] S. Andersson and A. D. Wadsley, *Acta Cryst.*, 1962, **15**, 201.