radiographs. One of us (J.M.R.) wishes to acknowledge the award of a Research Fellowship by the Governors of the Portsmouth College of Technology.

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Hydrothermal Synthesis of Iron Molybdates

The crystal structures of the transition metal molybdates and tungstates are of interest because the structures of these complex oxides reveal a surprisingly large number of changes going along the series increasing the number of 3d or 4f electrons. The marked changes in volume per formula weight found in going from one member of the series to another also suggests that there might be interesting and correlated changes in the structure of a single species at different pressures. The crystal structures of some of the transition metal molybdates have been studied by Abrahams [1] and others [2]. A study of trivalent molybdates [3] has shown that $Fe_2(MoO_4)_3$ is isomorphous with scandium molybdate, which has the same orthorhombic structure as scandium tungstate [4]. However, Pliasova *et al* [5] have reported that $Fe_2(MoO_4)_3$, when crystallised hydrothermally [6], has a monoclinic structure. It was therefore of interest to investigate whether $Fe_2(MoO_4)_3$ can exist in different, pressure-dependent polymorphs.

The dry oxides Fe_2O_3 and MoO_3 were mixed together in the molar ratios of 1:3 and sealed into platinum capsules with a solution of $FeCl_3$. Two sizes of platinum capsule were used, with internal capacities of $\frac{3}{4}$ and $\frac{1}{5}$ cm^3. The charges of solid oxides were 50 and 30 mg respectively. Solutions of $FeCl_3$ which were 5 and 12 wt % both gave the same results. The platinum capsules were pressurised and heated in a standard "Tem-Pres" hydrothermal apparatus for periods between 4 to 12 days, and then quenched and opened.

It was found that, at pressures below about 400 bars (1 bar = 750 torr), the product was $Fe_2(MoO_4)_3$. After 4 days at 460° C, the crystals were only a few tenths of a millimetre in size, and the product contained unreacted Fe_2O_3 and MoO_3. After 12 days at 475 to 485° C, the reaction was complete. Single crystals of $Fe_2(MoO_4)_3$ grew as greenish-yellow, thick plates up to 1 mm in size. These monoclinic crystals were examined by X-ray diffraction using a precession camera, and the lattice constants were found to be [7]

$$\begin{aligned} a &= 15.55 \pm 0.05\ \text{Å} \\ b &= 9.27 \pm 0.04\ \text{Å} \\ c &= 18.08 \pm 0.07\ \text{Å} \\ \beta &= 124.8 \pm 0.2^\circ \end{aligned}$$

These are in good agreement with those determined by Pliasova, which were

$$\begin{aligned} a &= 15.52\ \text{Å} \\ b &= 9.21\ \text{Å} \\ c &= 18.10\ \text{Å} \\ \beta &= 125^\circ \end{aligned}$$

In the absence of good single-crystal measurements for orthorhombic $Fe_2(MoO_4)_3$, it is not possible to determine with certainty which form has the smaller volume per unit formula weight. Approximate calculations from powder patterns suggest that the X-ray density of the orthorhombic form is slightly the smaller, and so it might be expected to form at the lower pressures. The lowest pressure investigated was 170 bars and, at this pressure, the product was still monoclinic $Fe_2(MoO_4)_3$. The transition point between the monoclinic and orthorhombic polymorphs must therefore lie between 170 bars and ambient pressure.

At pressures greater than about 650 bars, the same reactants, at 480° C, produced deep-blue acicular crystals up to a few millimetres in length, but very thin. The crystals commonly grew as rosettes of radiating clusters, and the reaction appeared to be complete within 4 days. This product was identified as the high-pressure form of $FeMoO_4$, having the wolframite structure [7]. It is interesting to note that Young and Schwartz [8] synthesised this compound in powder form by heating FeO and MoO_3 together at 900° C and 60 kbars; whereas, in this work, it has been produced hydrothermally as good single crystals at 480° C between 650 and 750 bars. It is quite possible therefore that some of the other high-pressure phases reported in that paper [8] may also form under much milder conditions, particularly by the use of hydrothermal methods. Indeed, this has probably been done already in the case of $ZnMoO_4$ [9].

The parameters of the monoclinic unit cell of the hydrothermally grown $FeMoO_4$ were determined from precession films [7] as

$$\begin{aligned} a &= 4.69 \pm 0.03\ \text{Å} \\ b &= 5.69 \pm 0.03\ \text{Å} \\ c &= 4.94 \pm 0.03\ \text{Å} \\ \beta &= 90^\circ\ 15' \pm 10' \end{aligned}$$

in reasonable agreement with the results of Young and Schwartz.

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The Growth of Gallium Arsenide onto Single-Crystal Metallic Substrates

The attempts to deposit epitaxial layers of semiconductors onto single-crystal metallic substrates have been, in the main, limited to a study of the elemental semiconductors [1-4]. Amick [5, 6] has given details of an investigation to extend the study to compound semiconductors and has reported the growth of gallium arsenide onto single-crystal molybdenum and tungsten substrates. A conventional open-tube system, employing gallium, arsenic, and gallium trichloride as source materials, produced polycrystalline layers on molybdenum and highly oriented, but easily removable, deposits on tungsten. Two open-tube systems have been used in the present investigation [7]. The first system is similar to that of Amick, and the second system, using gallium and arsenic trichloride as source materials, is similar to that described by Knight [8] and Effer [9]. The furnace used in the second system is controlled by programmed cam-driven regulators which allow accurate control of temperature up to a maximum duration of 36 h. Both systems have been used to study the deposition of gallium arsenide onto electropolished (111) planes of molybdenum, tungsten, tantalum, and niobium.

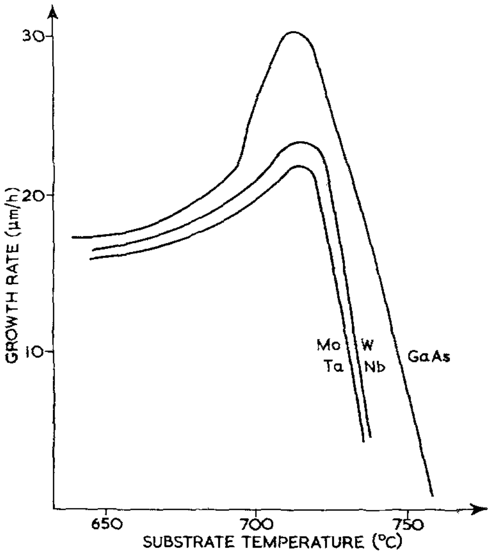

Figure 1 Rates of growth of GaAs on various substrates.