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Preparation of Molybdenum Intercalated Tantalum Disulphide Mo_xTaS_2

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Molybdenum intercalated tantalum disulphides have been prepared from the elements at 1350 °C. The crystal structures of the compounds were found to be dependent on the amount of intercalated molybdenum atoms. The structures were type 1s at x=0 in Mo_xTaS_2, type 3s at x=1/9, and type 2s at x=1/5. There was no evidence of ordered distribution of molybdenum atoms in the layers.

Tantalum disulphide has received a lot of attention in the past, partly because it displays the phenomena CDW, and partly because it readily forms intercalation compounds with many organic compounds and metals, such as Ti,V, Mn, etc.[1] In the process of studying the phase diagram of Mo-Ta-S system, we found molybdenum intercalated tantalum disulphides (Mo_xTaS_2) at the composition x=1/9 and 1/5. The aim of this paper is to describe the existence of these phases which until now have never been known.

Tantalum disulphide has several polytypes, namely, 1s (1T), 2s (2Ha), 3s (3R), 4s (4H), and 6s (6R). The crystal structures of these compounds were represented in Jellinek notation. It stands for the number of the S-Ta-S slab contained in the unit cell. Another notation was also shown in parentheses for comparison.

The molybdenum intercalated tantalum disulphides Mo_xTaS_2 were prepared as follows. A calculated amount of Mo(purity 99.9%), Ta(99.9%), and S(99.9999%) were sealed in an evacuated silica tube, which was then kept at 400 °C for 3 d. After cooling to room temperature, the specimen was ground and resealed in an evacuated double walled silica tube, and heated at 1350 °C for 4 h, followed by

quenching in water.

Preparation of the compounds was attemped at compositions of x=1/20 - x=1/3 in Mo_xTaS_2. The relation of the phases and compositions are given in Table 1.

Table 1. Relation of compositions and phases

x	0	1/20	1/9	1/8	1/7	1/6	1/5	1/4	1/3
Phase	1s	1s+3s	1s(trace)+3s	3s+2s	3s+2s	2s	2s	2s	2s+X

As can be seen in the table, there are two phases in this composition range. They have been denoted as 2s and 3s in the table. Type 3s, which will be referred to as 3s-$Mo_{1/9}TaS_2$, was formed at x=1/9, although it was always contaminated by the small amount of 1s-TaS_2 or type 2s. This suggests that 3s-$Mo_{1/9}TaS_2$ has no homogeneity range at 1350 °C. Another phase, which will be referred to as 2s-$Mo_{1/5}TaS_2$, was formed at x=1/6 - x=1/4. This phase had a large homogeneity range.

The crystal structures of these specimens were examined by powder X-ray diffraction. The diffraction pattern of the 3s-$Mo_{1/9}TaS_2$ could be indexed on the basis of a type 3s with lattice constants of a=3.31 Å, c=17.94 Å in hexagonal setting. The structure is given in Fig.1. The structure of the 3s-$Mo_{1/9}TaS_2$ is essentially the same as that of 3s-TaS_2, with additional Mo atoms statistically occupying the partly filled layers. The structure is represented in space group R3m (No.160) with the following parameters.

Atomic position (0,0,0; 1/3,2/3,2/3; 2/3,1/3,1/3)+

3(a) 0,0,z

3Ta: z=1/6, 3xMo: z=0, 3S(1): $z \approx 5/12$,

3S(2): $z \approx 7/12$

The diffraction pattern of the 2s-$Mo_{1/5}TaS_2$ could be indexed on the basis of a 2s type structure with lattice constants of a=3.29 Å c=12.30 Å. The structure of the 2s-$Mo_{1/5}TaS_2$ is essentially the same as that of 2s-TaS_2, with additional Mo atoms statistically occupying the partly filled layers. The structure is described in space group $P6_3/mmc$ (No.194) with the atomic positions given below.

Ta in 2(b):(0,0,1/4) (0,0,3/4), xMo in 2(a): (0,0,0) (0,0,1/2)
S in 4(f):(1/3,2/3,z), (2/3,1/3,-z), (2/3,1/3,1/2 + z), (1/3, 2/3, 1/2 - z), with $z \approx 1/8$.

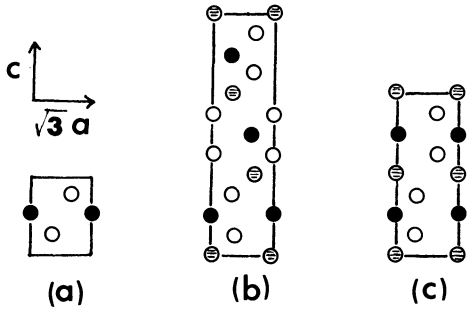
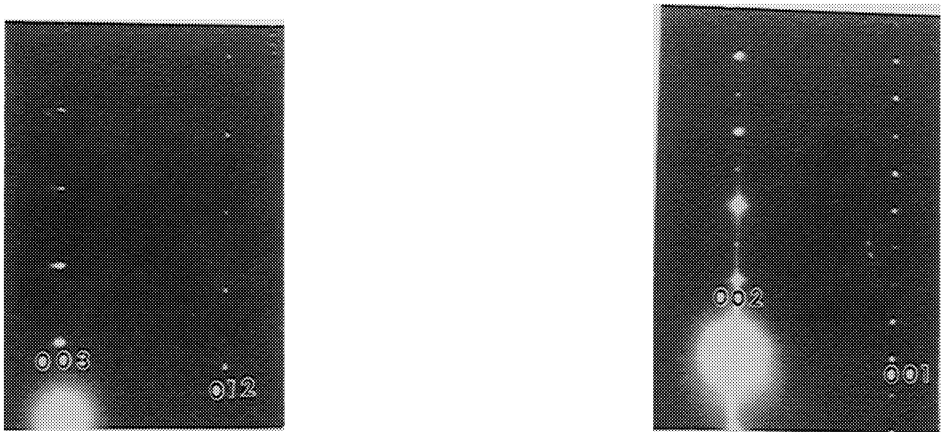


Fig.1.
Sections through the hexagonal (110) planes of the sulphides: Sulphur atoms are indicated by open circles, tantalum atoms by solid circles, and sites in layers partly filled by molybdenum atoms by hatched circles.
(a) 1s-TaS_2, (b) 3s-$Mo_{1/9}TaS_2$,
(c) 2s-$Mo_{1/5}TaS_2$

The d-values of the specimens were compared with calculated values. They agreed quite well. The peak intensities of the powder X-ray diffraction were measured to compare with the calculated ones. However, agreement in the intensities between the observed and calculated values was poor probably because of preferred orientation and the stacking faults within the specimen. From this result, therefore, we could not confirm that partly filled layers were occupied only by molybdenum atoms.



(a) 3s-$Mo_{1/9}TaS_2$, (b) 2s-$Mo_{1/5}TaS_2$

Fig.2. Electron diffraction patterns with the incident beam perpendicular to the c axis.

In order to confirm the cell dimension, electron diffraction patterns were taken on the specimens. (The diffraction patterns shown in Fig.2 were not clear because of the difficulty of obtaining diffraction patterns with an incident beam parallel to the layer). The distance of the repeating unit along the c-axis in the hexagonal setting was found to be about 18 Å for $Mo_{1/9}TaS_2$, and about 12 Å for $Mo_{1/5}TaS_2$. This result agreed with that of the powder X-ray diffraction. In the electron diffraction and powder X-ray diffraction, there was no evidence of the ordered distribution of molybdenum atoms in the layers.

Reference

1) For example, S.S.P.Parkin and R.H.Friend, Philosophical Magazine B, 41, 65 (1980).

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