

1T-MoS₂, a New Metallic Modification of Molybdenum Disulfide

Fernando Wypych and Robert Schöllhorn*

Technische Universität Berlin, Institut für Anorganische und Analytische Chemie, Strasse des 17. Juni 135, D-1000 Berlin 12, Germany

Hydration and subsequent electrochemical or chemical oxidation of potassium thiomolybdate(III) KMoS₂ yields a new metastable and metallic modification of molybdenum disulfide with distorted layers and octahedral coordination to Mo atoms.

The structural chemistry and polytype formation of layered transition metal dichalcogenides of groups 4–6 have been the subject of intensive investigation in the last two decades. For the group 6 chalcogenides MoS₂ and WS₂, both of which are major components of important heterogeneous catalyst systems, one stable 2H structure type has been observed which is characterized by neutral MS₂ layers formed by trigonal prismatic MX₆ units sharing edges; both phases are semicon-

ductors.¹ Recently the formation of an orthorhombic metastable polytype o-WS₂ has been reported, whose detailed structure is unknown so far.² We report here on the preparation and characterization of a new metastable metallic MoS₂ polytype with a distorted layer structure and octahedral coordination of the metal atoms.

The synthesis started from the ternary phase potassium thiomolybdate(III) KMoS₂ which has been described earlier.³

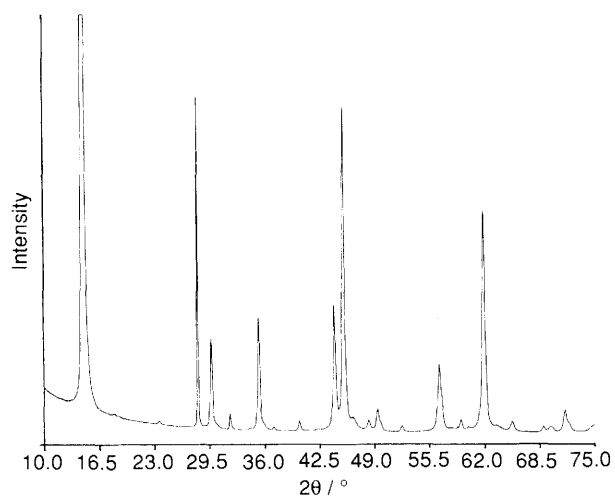


Fig. 1 Powder X-ray diffraction pattern of 1T-MoS₂; the line at $2\theta = 28.4^\circ$ belongs to the Si standard; minor lines or shoulders at $2\theta = 35.8$, 46.5 and 63.5° have not been indexed; (hkl) and experimental d values: (001) 5.999, (100) 4.850, (101) 3.776, (002) 2.998, (110) 2.799, (111) 2.537, (200) 2.423, (201) 2.246, (112) 2.045, (003) 1.998, (202) 1.884, (210) 1.832, (211) 1.753, (300) 1.616, (212) 1.561, (301) 1.561, (004) 1.498, (220) 1.399, (221) 1.363, (310) 1.343, (311) 1.311, (222) 1.267

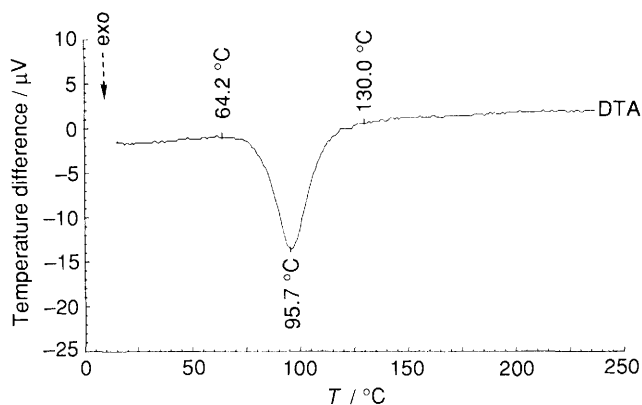
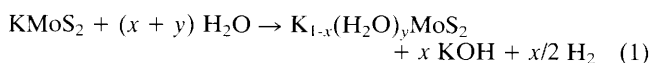


Fig. 2 DTA curve for 1T-MoS₂ showing the transition to disordered 2H-MoS₂ (heating rate 2 K min⁻¹, argon atmosphere)

The preparation of the latter as a pure single phase has been achieved by the reaction of K₂MoO₄ with dry hydrogen sulfide at 320 °C for 12 h and subsequently at 470 °C for 12 h. The resulting product was reduced at 850 °C with a mixture of H₂ and N₂ (20% vol and 80% vol, respectively) for 72 h to form black KMoS₂. The latter was repeatedly washed with water until the suspension reached a pH of 7–8. The washing process is correlated with a partial oxidation of KMoS₂ under formation of hydrogen and a simultaneous hydration process [eqn. (1)].



The analytical composition of the air dried product is K_{0.33}(H₂O)_{0.6}MoS₂ (monoclinic lattice parameters are $a = 570.0 \pm 0.1$, $b = 323.8 \pm 0.1$, $c = 946.0 \pm 0.2$ pm, $\beta = 100.54 \pm 0.03^\circ$). The hydrated layered chalcogenide was thereafter oxidized by chemical means (e.g. aqueous K₂Cr₂O₇ in 0.05 mol dm⁻³ H₂SO₄; MeCN-I₂) or by galvanostatic anodic oxidation of pressed polycrystalline electrodes in aqueous K₂SO₄ electrolyte [eqn. (2)]. After washing with water and

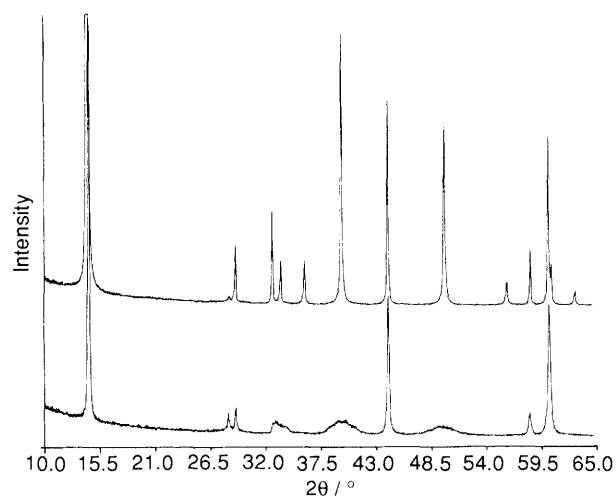
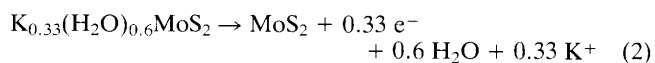


Fig. 3 Powder X-ray diffraction pattern of disordered 2H-MoS₂ obtained after the phase transition 1T → 2H (lower curve); powder diffraction pattern of crystalline 2H-MoS₂ (upper curve) obtained on extended annealing

drying at 10⁻³ Torr/300 K (1 Torr = 133.322 Pa) a bronze coloured single phase product I was obtained; analytical data confirmed the presence of a binary phase with a ratio Mo:S ca. 1:2. The powder X-ray diffraction diagram (Siemens D 500 diffractometer, Cu-Kα₁ radiation) obtained in reflection mode is given in Fig. 1; the texture effect of the layered compound results in high intensities of the basal reflections. The hexagonal lattice parameters of I were determined by Guinier photographs and correspond to $a = 559.7 \pm 0.1$, $c = 599.4 \pm 0.1$ pm. The small line width of the Bragg reflections demonstrates the high crystallinity and low defect concentration of I. According to conventional simple polytype notation I is therefore to be described as 1T-MoS₂. The relation between the unit cells of 1T-MoS₂ and 2H-MoS₂ is $a_{1T} \approx a_{2H} \sqrt{3}$ and $c_{1T} \approx 1/2 c_{2H}$. Differential thermal analysis (DTA) in argon atmosphere and X-ray data show that 1T-MoS₂ is a metastable compound that undergoes an irreversible phase transition at constant mass at 95 °C to disordered 2H-MoS₂. The thermal phase change is shown in Fig. 2. The 2H-phase obtained without annealing displays rotational disorder with sharp 00 l , 100 and 110 reflections while the mixed reflections 10 l are strongly broadened (Fig. 3: lower curve). Extended annealing at a temperature of 900 °C yields the powder pattern of well crystalline 2H-MoS₂ (Fig. 3: upper curve).

Preliminary single crystal X-ray data of 1T-MoS₂ indicate that the compound has a distorted layer type structure; in contrast with 2H-MoS₂ where the molybdenum atoms are located in trigonal prismatic sites, the coordination of the metal atoms in 1T-MoS₂ is octahedral.⁴ The sulfur atoms appear to be displaced from their ideal positions in the (001) direction which results in a superstructure $a\sqrt{3} \times a\sqrt{3}$.

In agreement with a recent theoretical band structure calculation,⁵ we found a negative temperature coefficient for the electronic conductivity of 1T-MoS₂ and Pauli paramagnetism. In contrast with the semiconducting properties of 2H-MoS₂ the new phase is thus a metal. The structural and electronic distortions induce similarly strong consequences for the chemical reactivity: while 2H-MoS₂ (Fermi level in d band gap) does form highly unstable intercalation compounds with very low electrochemical potentials, the polytype 1T-MoS₂ (Fermi level within the d band) is easily accessible for all electron/ion transfer and exchange reactions described earlier for layered transition metal dichalcogenides MX₂ of groups 4 and 5;⁶ the compounds obtained from 1T-MoS₂ are rather stable in air at room temperature owing to the higher

electrochemical potential of the distorted $(\text{MoS}_2)^{x-}$ layer units.⁷ The intercalated phases are monoclinic with one MoS_2 layer per unit cell and show high crystallinity. It is interesting to compare these compounds with those obtained by direct intercalation of 2H- MoS_2 , e.g. solvated phases^{8,9} or Li_xMoS_2 .^{10,11} The lithium phases also show distorted structures; their properties and structural details appear, however, not to be identical with those of the phases derived from 1T- MoS_2 . Further investigations by us showed that related dichalcogenides 2M- WS_2 and 1T- $\text{Mo}_{0.5}\text{W}_{0.5}\text{S}_2$ with distorted structures can be obtained in a similar way.⁷ Since intercalation compounds with Ni and Co can be prepared from the binary phases by intercalation, it should be useful to compare their catalytic properties with those of the Ni and Co doped hydrodesulfurization catalysts derived from the stable 2H polytypes.

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References

- 1 *Crystallography and Crystal Chemistry of Materials with Layered Structures*, ed. F. Lévy, Reidel, Dordrecht-Boston, 1976; F. Jelinek, in *Inorganic Sulphur Chemistry*, ed. G. Nickless, Elsevier, Amsterdam, 1968, p. 669.
- 2 R. Schöllhorn, U. Bethel and W. Paulus, *Rev. Chim. Miner.*, 1984, **21**, 545.
- 3 M. Sergent and J. Prigent, *C.R. Acad. Sci. Paris*, 1965, **261**, 5135.
- 4 F. Wypych and R. Schöllhorn, unpublished work.
- 5 L. F. Mattheis, *Phys. Rev. B*, 1973, **8**, 3719.
- 6 G. V. Subba Rao and M. W. Shafer, in *Intercalated Layered Materials*, ed. F. Lévy, Reidel, Dordrecht, 1979, p. 99; R. Schöllhorn, *Angew. Chem.*, 1980, **92**, 1015; *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 983; R. Schöllhorn, in *Inclusion Compounds*, ed. J. L. Atwood, J. E. D. Davies and D. D. MacNicol, Academic Press, London, 1984, p. 78.
- 7 F. Wypych, K. Sollmann and R. Schöllhorn, *Mater. Res. Bull.*, 1992, **27**, 545.
- 8 R. B. Somoano, V. Hadek and A. Rembaum, *J. Chem. Phys.*, 1973, **58**, 697.
- 9 W. Rüdorff and H. Sick, *Angew. Chem.*, 1959, **71**, 127.
- 10 M. A. Py and R. R. Haering, *Can. J. Phys.*, 1983, **61**, 76.
- 11 P. J. Mulhern, *Can. J. Phys.*, 1989, **67**, 1049.