Synthesis of Metal Molybdenum Tellurides of Composition $Mo_{6-x}M_xTe_8$ (M = Ru or Rh)†

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Monophasic compounds of compositions $Mo_{6-x}Ru_xTe_8$ (x = 0.5, 1.0 or 1.5) and $Mo_{5.5}Rh_{0.5}Te_8$ have been synthesised. The preparation of the pure compounds depends critically on the thermal treatments used. The maximum value of x in compounds of the type $Mo_{6-x}Ru_xTe_8$ is *ca.* 1.75. The compounds have been characterised by X-ray powder diffraction and the lattice parameters shown to vary with ruthenium content.

Metal molybdenum chalcogenides of composition $Mo_6M_xX_8$, where M represents a wide variety of metallic elements and X is sulphur, selenium or tellurium have been known for some time to adopt structures containing the Mo_6X_8 unit[1] (Fig. 1). In these materials, which are commonly known as the Chevrel phase compounds, the ternary metal occupies positions in channels created by stacking of the Mo_6X_8 units.[2–7] Since the ternary molybdenum chalcogenides were first reported the number of characterised Chevrel phase sulphides and selenides has grown rapidly with alkali-, alkaline earth-, p block-, transition- and lanthanide-metals all being reported as ternary elements.[1] Pseudo-ternary compounds containing two chalcogenides such as $Mo_6PbS_{8-x}Se_x$ ($0 < x < 8$) or two ternary metals such as $Mo_6Sn_{1-x}Zn_xS_8$ (x = 0.2 or 0.4) have also been synthesised and characterised.[8,9] The partial substitution of molybdenum atoms by selected second- or third-row transition metals has also been described although only two compounds, $Mo_4Ru_2Se_8$ and $Mo_{1.5}Re_{4.5}Se_8$, have been the subject of detailed structural examination.[10] In contrast, the number of tellurium-containing analogues of the Chevrel phase compounds is sparse. The lattice parameters of compounds described as $Mo_6M_xTe_8$ (M = Fe, Ni or Cu, $0 < x < 4$; M = Co, $0 < x < 0.66$) have been reported[11] and a compound of composition $Mo_6Ni_{0.85}Te_8$ described.[12] The detailed preparation and characterisation of compounds of the type $Mo_{6-x}M_xTe_8$ has not been described.[13,14]

The considerable interest in the Chevral phase compounds prior to the discovery of high-temperature oxide superconductors derives[1] from their superconducting properties (T_c *ca.* 13 K) with large critical magnetic fields [B_c *ca.* 650 kG (0.065 T) at 2 K]. Some of the compounds have been found to be both superconducting and antiferromagnetically ordered[15] and some have been evaluated as components in solid-state batteries.[16]

In this paper we report on the preparation of metal molybdenum tellurides of the type $Mo_{6-x}M_xTe_8$ (M = Ru or Rh) and their characterisation by X-ray powder diffraction.

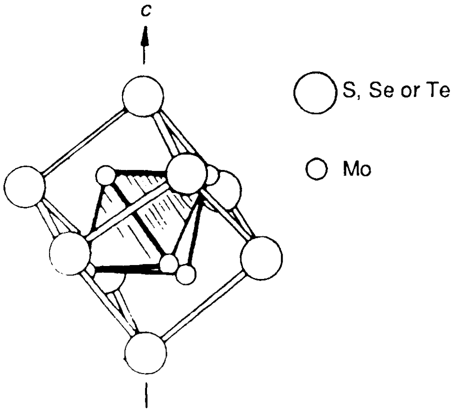

Fig. 1 The Mo_6X_8 (X = S or Se) unit

Table 1 Conditions required for the preparation of monophasic compounds of compositions Mo_6Te_8 and $Mo_{6-x}M_xTe_8$ (M = Ru or Rh)

Compound	Conditions
Mo_6Te_8	1150 °C (2 d)
$Mo_{5.5}Ru_{0.5}Te_8$	1200 °C (1 d)
Mo_5RuTe_8	1150 °C (4 d)
$Mo_{4.5}Ru_{1.5}Te_8$	1200 °C (4 d), furnace cooled, ground, 1200 °C (45 min)
$Mo_{5.5}Rh_{0.5}Te_8$	1150 °C (2 d)

Experimental

Compounds of the type $Mo_{6-x}M_xTe_8$ (M = Ru or Rh) were prepared by heating mixtures of the appropriate molar ratios of the high purity elements (99.9%+) in evacuated sealed quartz ampoules according to the conditions described in Table 1. It should be noted that the times of heating include *ca.* 15 min during which the furnace was heating up to the selected temperature.

X-Ray powder diffraction patterns were recorded with a Philips PW1050/70 diffractometer using Cu-Kα radiation.

Results and Discussion

Monophasic compounds of compositions Mo_6Te_8 and $Mo_{6-x}M_xTe_8$ (M = Ru or Rh) were prepared according to the conditions described in Table 1. Conditions other than those presented in Table 1 were found by X-ray powder diffraction to give multiphasic products. The X-ray powder diffraction pattern recorded from Mo_6Te_8 compared well with that reported previously.[17,18] The X-ray powder diffraction patterns recorded from the new compounds were indexed by comparison with Mo_6Te_8.

Attempts to prepare Mo_6Te_8 under conditions different from

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† *Supplementary data available* (No. SUP 56802, 5 pp.): X-ray powder diffraction data for $Mo_{6-x}Ru_xTe_8$ (x = 0.5, 1.0 or 1.5). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 2 Lattice parameters and unit-cell volumes, with estimated standard deviations in parentheses, of compounds of the type $Mo_{6-x}M_xTe_8$ (x = 0, 0.5, 1.0 or 1.5) and the $Mo_{6-x}Ru_xTe_8$-type phases corresponding to nominal compositions $Mo_4Ru_2Te_8$ and $Mo_3Ru_3Te_8$

Compound	a_{hex}/Å	c_{hex}/Å	a_{rhom}/Å	α_{rhom}/°	U_{hex}/Å^3
Mo_6Te_8	10.195(3)	11.663(5)	7.054(2)	92.54(3)	1049.8(1.1)
$Mo_{5.5}Ru_{0.5}Te_8$	10.221(6)	11.615(8)	7.058(5)	92.79(5)	1050.8(2.0)
$Mo_{5.5}Rh_{0.5}Te_8$	10.229(5)	11.563(6)	7.052(4)	92.98(4)	1047.8(1.2)
Mo_5RuTe_8	10.234(5)	11.488(7)	7.041(4)	93.23(4)	1042.0(1.6)
$Mo_{4.5}Ru_{1.5}Te_8$	10.259(6)	11.391(7)	7.036(4)	93.62(4)	1038.3(1.8)
$Mo_{6-x}Ru_xTe_8$-type (nominally $Mo_4Ru_2Te_8$)	10.274(3)	11.355(3)	7.036(2)	93.78(2)	1038.3(5)
$Mo_{6-x}Ru_xTe_8$-type (nominally $Mo_3Ru_3Te_8$)	10.275(6)	11.351(6)	7.036(4)	93.80(4)	1037.8(1.8)

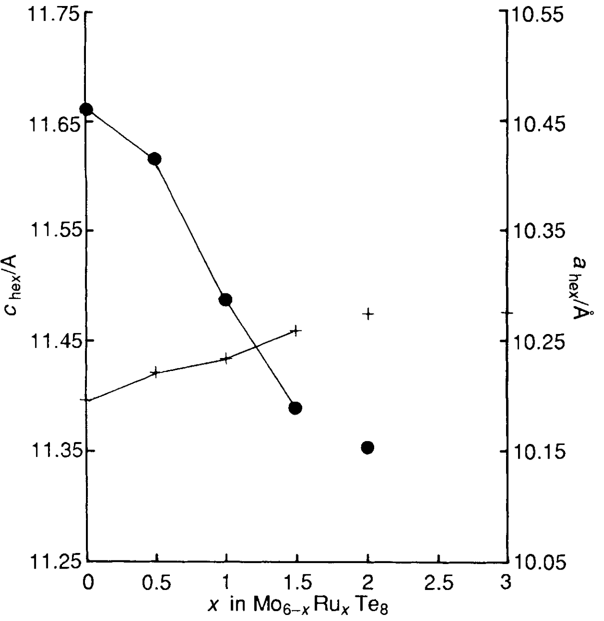

Fig. 2 Variation of hexagonal (hex) lattice parameters for compounds of the type $Mo_{6-x}Ru_xTe_8$ as a function of x: a, +; c, ●

those described in Table 1 gave materials which were shown by X-ray powder diffraction to contain Mo_6Te_8 and β-$MoTe_2$. Attempts to prepare compounds of the type $Mo_{6-x}Ru_xTe_8$ (x = 0.5, 1.0 or 1.5) were frequently found to give products containing $Mo_{6-x}Ru_xTe_8$ with either a β-$MoTe_2$ or $RuTe_2$ impurity phase depending on the reaction conditions. Reactions performed for longer periods of time than those specified in Table 1 tended to give the β-$MoTe_2$ impurity whilst reactions performed at lower temperatures and/or for shorter periods of time tended to give $RuTe_2$. Presumably the impure products also contained small amounts of elemental molybdenum and ruthenium which were below the limits of detection by X-ray powder diffraction.

Attempts to prepare $Mo_4Ru_2Te_8$ were unsuccessful. X-ray powder diffraction showed the products to contain a $Mo_{6-x}Ru_xTe_8$-type phase together with $RuTe_2$ impurity. The attempted preparation of $Mo_3Ru_3Te_8$ gave a $Mo_{6-x}Ru_xTe_8$-type phase together with $RuTe_2$ and elemental ruthenium according to the reaction $3Mo + 3Ru + 8Te \longrightarrow aMo_{6-x}Ru_xTe_8 + bRuTe_2 + cRu$ in which x is less than three. The results, taken together, suggest that an upper limit exists beyond which ruthenium cannot be accommodated in the Mo_6Te_8 phase.

The refined lattice parameters for Mo_6Te_8, the pure compounds $Mo_{6-x}Ru_xTe_8$ (x = 0.5, 1.0 or 1.5) and the $Mo_{6-x}Ru_xTe_8$-type phases corresponding to the nominal compositions $Mo_4Ru_2Te_8$ and $Mo_3Ru_3Te_8$ are presented in Table 2 and the trends described diagramatically in Fig. 2.

The lattice parameters of Mo_6Te_8 agree well with those reported previously[12] (a_{rhom} = 7.050 Å, α_{rhom} = 92.54°). The lattice parameters of the pure compounds $Mo_{6-x}Ru_xTe_8$ (x = 0–1.5) show steady trends with composition as might be expected for a solid solution. The greatest variation involves the decrease in c_{hex} with increasing ruthenium content. The similarity between the lattice parameters of the $Mo_{6-x}Ru_xTe_8$-type phases of nominal compositions $Mo_4Ru_2Te_8$ and $Mo_3Ru_3Te_8$ suggests the presence of a comparable ruthenium content in both compounds. It also appears that the ruthenium content in these $Mo_{6-x}Ru_xTe_8$-type compounds is less than the nominal value since the c_{hex} lattice parameters are smaller than would be expected by extrapolation of the lattice parameters of the pure compounds of composition $Mo_{6-x}Ru_xTe_8$ (x = 0.5, 1.0 or 1.5). The result is consistent with the detection by X-ray powder diffraction of both ruthenium ditelluride and elemental ruthenium in the reaction products of the attempted preparation of $Mo_3Ru_3Te_8$. The ruthenium content in $Mo_{6-x}Ru_xTe_8$-type phases of nominal compositions $Mo_4Ru_2Te_8$ and $Mo_3Ru_3Te_8$ was estimated by extrapolating their c_{hex} lattice parameters to the approximately straight line connecting the c_{hex} lattice parameters of the three pure $Mo_{6-x}Ru_xTe_8$ compounds. The procedure gives a maximum value of x of *ca.* 1.75, corresponding to the formulation $Mo_{4.25}Ru_{1.75}Te_8$. Hence the value of x in $Mo_{6-x}Ru_xTe_8$ appears to vary from 0 to 1.75 and corresponds to a maximum of 3.5 additional electrons that can be introduced into the Mo_6Te_8-type structure by the incorporation of ruthenium atoms. This is less than the 4.6 additional electrons which are reportedly[10,19] accommodated into the Mo_6Se_8-type structure when compounds of the types $Mo_{1.5}Re_{4.5}Se_8$ and $Mo_{3.7}Ru_{2.3}Se_8$ are prepared.

The compound $Mo_{5.5}Rh_{0.5}Te_8$ was prepared by heating appropriate molar ratios of molybdenum, rhodium and tellurium for 2 d at 1150 °C. The lattice parameters are included in Table 2. Attempts to prepare compounds of compositions Mo_5RhTe_8 and $Mo_{4.66}Rh_{1.33}Te_8$ were unsuccessful, the products being invariably composed of mixtures of a $Mo_{6-x}Rh_xTe_8$ phase and $RhTe_2$.

Attempts to prepare compounds of the type $Mo_{6-x}M_xTe_8$ (M = Nb, Ta, W, Re, Os or Ir) gave multiphasic products which were generally dominated by the presence of the metal telluride.

In conclusion, we would emphasise that the preparation of pure compounds of the type $Mo_{6-x}M_xTe_8$ where M is ruthenium or rhodium is a non-trivial matter. Our results do not confirm those described earlier[13,14] which, without details of preparation conditions and comprehensive X-ray diffraction data, have suggested that the solubility of ruthenium in $Mo_{6-x}Ru_xTe_8$ exeeds the limit reported here. We would make clear that we have found no generality in the heating conditions required to synthesise monophasic compounds of the type $Mo_{6-x}M_xTe_8$ and that most routes to prepare these types of compounds lead to the formation of impurity metal and metal telluride phases.

Finally, we would mention that low-temperature specific heat measurements indicate that the compound of composition

Mo_5RuTe_8 shows the onset of superconductivity at 2.21 K. A detailed account of these measurements will be published elsewhere.

Acknowledgements

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References

1 K. Yvon, in *Current Topics in Materials Science*, ed. E. Kaldis, North-Holland, Amsterdam, 1979, vol. 3, p. 53.
2 R. Chevrel, J. Prigent and M. Sergent, *J. Solid State Chem.*, 1971, **3**, 515.
3 O. Bars, D. Grandjean and J. Guillevic, *J. Solid State Chem.*, 1973, **6**, 48.
4 O. Bars, D. Grandjean and J. Guillevic, *J. Solid State Chem.*, 1973, **6**, 335.
5 O. Bars, D. Grandjean and J. Guillevic, *J. Solid State Chem.*, 1973, **7**, 158.
6 E. Corenzwit, P. D. Dernier, M. Marezio, B. T. Matthias and J. P. Remeika, *Mat. Res. Bull.*, 1973, **8**, 657.
7 R. Chevrel and M. Sergent, *J. Solid State Chem.*, 1973, **6**, 433.
8 R. Chevrel, O. Fischer and M. Sergent, *Mat. Res. Bull.*, 1975, **10**, 1169.
9 J. W. Downey and F. Y. Fradin, *Mat. Res. Bull.*, 1979, **14**, 1525.
10 H. D. Flack, W. Hönle and K. Yvon, *J. Solid State Chem.*, 1983, **49**, 157.
11 R. Chevrel and M. Sergent, in *Superconductivity in Ternary Compounds*, eds. O. Fischer and M. B. Maple, Springer-Verlag, Berlin, Heidelberg, 1982, vol. 1, p. 30.
12 W. Hönle and K. Yvon, *J. Solid State Chem.*, 1987, **70**, 235.
13 O. Fischer, A. Perrin and M. Sergent, *Mat. Res. Bull.*, 1978, **13**, 259.
14 R. Chevrel, O. Fischer, A. Perrin and M. Sergent, *J. Solid State Chem.*, 1980, **33**, 43.
15 O. Fischer and M. Ishikawa, *Solid State Commun.*, 1977, **24**, 747.
16 R. Kanno, Y. Takeda, M. Ohya and O. Yamamoto, *Mat. Res. Bull.*, 1987, **22**, 1283.
17 Joint Committee on Powder Diffraction Standard (J.C.P.D.S.) Index Card No. 23–1257.
18 R. Chevrel, J. Prigent and M. Sergent, *Mat. Res. Bull.*, 1974, **9**, 1487.
19 N. V. Vante, W. Jaegermann, H. Tributsch, W. Hönle and K. Yvon, *J. Am. Chem. Soc.*, 1987, **109**, 3251.

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