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Structural Properties of the Molybdenum–Ruthenium Telluride of Composition $Mo_{4.5}Ru_{1.5}Te_8$

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Atomic coordinates for the molybdenum–ruthenium telluride of composition $Mo_{4.5}Ru_{1.5}Te_8$ have been refined by analysis of an X-ray powder diffraction pattern using the Rietveld method. The results confirm the presence of a cluster containing both molybdenum and ruthenium atoms. The compound $Mo_5Ru_1Te_8$ has been found to undergo a phase transformation between 77 and 4 K. © 1991 Academic Press, Inc.

Introduction

The metal molybdenum chalcogenides of composition $M_xMo_6X_8$, where M can be any one of a wide range of metallic elements and X is sulfur, selenium, or tellurium, have been known for some time (*1*). Considerable interest has been shown in these materials, which are also known as the Chevrel phase compounds, because of their superconducting properties with large critical magnetic fields (*1*). The Chevrel phase compounds have structures which are closely related to those of the binary molybdenum chalcogenides of composition Mo_6X_8 (X = S, Se, Te). This Mo_6X_8 unit (Fig. 1) consists of an Mo_6 trigonal antiprism surrounded by eight chalcogens arranged in a distorted cube. The molybdenum atoms occupy positions close to, but just outside, the faces of the chalcogen cube and the Mo_6X_8 units are slightly elongated along the $\bar{3}$-axis along [001]. Each Mo_6X_8 unit has two chalcogen sites. The axial sites lie on the c-axis and are designated as $X(2)$, while the peripheral chalcogen sites are designated as $X(1)$. There are three types of molybdenum–molybdenum bonds, two are intracluster and are denoted d_1 and d_2 while the other, which is denoted as d_3, is intercluster. The stacking of the Mo_6X_8 units creates channels in which the ternary metal element in the Chevrel phase compounds is located.

The partial substitution of molybdenum in the Mo_6X_8 units by some second- or third-row transition metals has also been described although only two compounds of composition $Mo_4Ru_2Se_8$ and $Mo_{1.5}Re_{4.5}Se_8$ have been subjected to detailed structural examination (*2*). Only a few tellurium-containing analogues of the Chevrel phase and related compounds have been reported (*1*).

We have recently prepared (*3*) some molybdenum metal tellurides of the type $Mo_{6-x}M_xTe_8$, where M is ruthenium or rhodium and $0 \leq x \leq 1.5$. Attempts to prepare monophasic samples with larger ruthenium or rhodium contents were unsuccessful and gave rise to the formation of multiphasic products. In this paper we report on the

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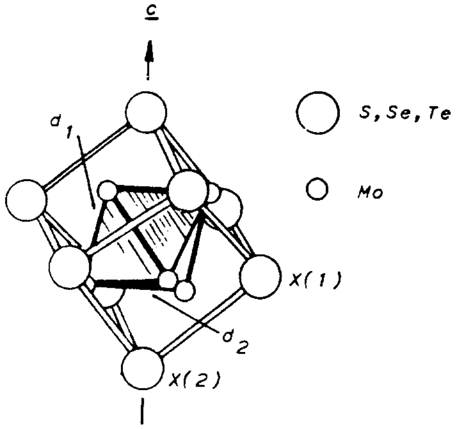

FIG. 1. The Mo_6X_8 unit (X = S, Se, Te) showing the $X(1)$ and $X(2)$ chalcogen sites and the d_1 and d_2 Mo–Mo bonds.

structural characterisation by X-ray powder diffraction of the material with the highest ruthenium content of composition $Mo_{4.5}Ru_{1.5}Te_8$. We also describe our studies at 77 and 4 K of the structural properties of the compound $Mo_5Ru_1Te_8$ in which the metal cluster may be associated with twenty-two electrons. Chevrel phase compounds such as $EuMo_6S_8$ and $BaMo_6S_8$ have been found (*4–6*) to undergo structural transformations which have been associated (*4*) with the availability of twenty-two electrons for metal cluster bonding.

Experimental

The compounds of composition $Mo_{4.5}Ru_{1.5}Te_8$ and $Mo_5Ru_1Te_8$ were prepared by heating appropriate molar ratios of the powdered high purity elements (99.9%+) in an evacuated sealed quartz ampoule at 1200°C (4 days), allowing the product to cool in the furnace, grinding, and heating again at 1200°C (45 min).

X-ray powder diffraction patterns were recorded using $CuK\alpha_1$ radiation with a Picker X-ray diffractometer in step-scan mode by counting for 28 sec for each step of 0.02° of 2Θ over a range of 10 to 90° of 2Θ. The sample was prepared by mixing with acetone, grinding in a micronizer (30 min), and drying in air. Structural parameters were refined by the Rietveld method using a program similar to that previously described (*7*). Low temperature X-ray powder diffraction patterns were recorded using a low temperature high vacuum horizontal X-ray diffractometer attachment Model X-869C made by Materials Research Corp. Elemental silicon was mixed with the sample and used as an internal standard.

Results and Discussion

The atomic coordinates of $Mo_{4.5}Ru_{1.5}Te_8$ were refined using the space group $R\bar{3}$ and initial atomic coordinates previously reported (*1*) for the compound Mo_6Te_8. A pseudo-Voigt peak shape function was adopted and 26 parameters were refined including atomic coordinates (seven parameters), a parameter allowing for prefered orientation, and a parameter allowing for asymmetry of low angle peaks.

The observed and calculated X-ray powder diffraction patterns for $Mo_{4.5}Ru_{1.5}Te_8$ are shown in Fig. 2 and refined structural parameters are presented in Table I. We would mention that the similar X-ray scattering factors of molybdenum and ruthenium precluded an examination of order in the arrangement of molybdenum and ruthenium atoms in $Mo_{4.5}Ru_{1.5}Te_8$. Given that no evidence for order was observed in the single crystal X-ray diffraction study (*2*) of $Mo_{1.5}Re_{4.5}Se_8$, where molybdenum and rhenium atoms have different scattering factors, we assume that molybdenum and ruthenium are randomly distributed over the metal sites in the $Mo_{4.5}Ru_{1.5}Te_8$ cluster. The values of the R-factors of the refinement were 6.12% (R_I), 9.15% (R_p), 12.93% (R_{wp}) and 2.91% (R_{exp}). The low Bragg R-factor, R_I, suggests that the structural model involving the presence of a mixed molybde-

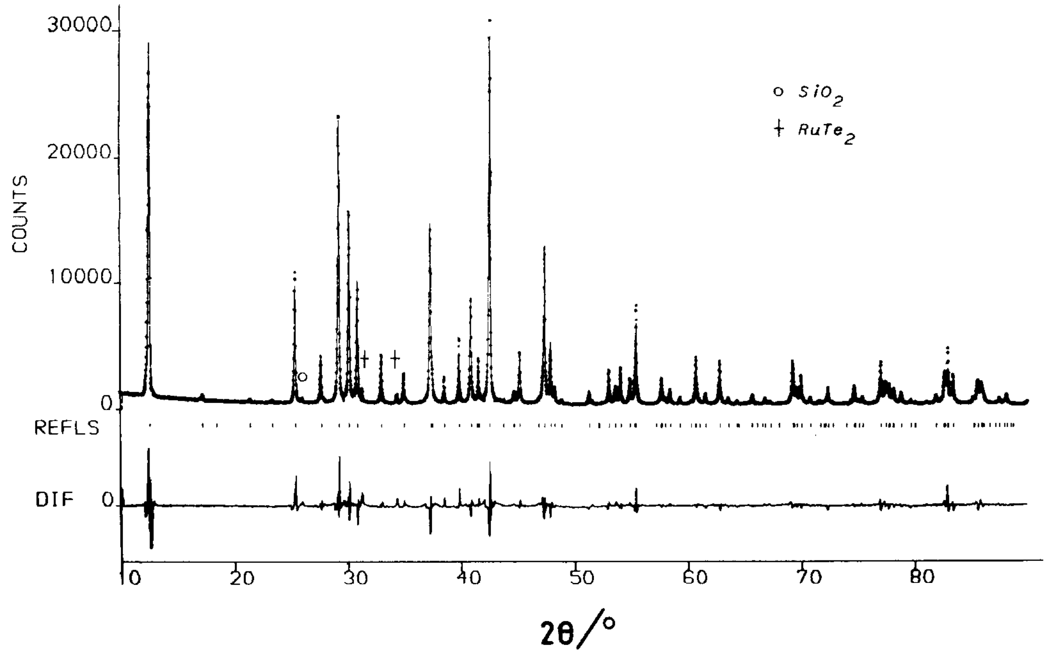

FIG. 2. Observed (dots) and calculated (continuous line) powder X-ray diffraction pattern recorded from $Mo_{4.5}Ru_{1.5}Te_8$.

num–ruthenium six atom cluster is good. The oscillation of the difference plot about zero for the more intense low angle reflections may be associated with asymmetric peaks resulting from axial divergence of the X-ray beam. Some preferred parallel orientation of the hexagonal *c*-axis to the plane of the sample holder was evident but was corrected during refinement by the preferred orientation parameter.

One of the three reflections not attributable to $Mo_{4.5}Ru_{1.5}Te_8$ (see Fig. 2) corresponds to an interplaning spacing of 3.43 Å, which is similar to the most intense reflection (*8*) (3.40 Å) of β-quartz and presumably arises from the introduction of β-quartz into

TABLE I

REFINED ATOMIC PARAMETERS ($R\bar{3}$ HEXAGONAL AXES), TEMPERATURE FACTORS (B), AND LATTICE PARAMETERS OF $Mo_{4.5}Ru_{1.5}Te_8$.

	Site	*x*	*y*	*z*	$B(\text{Å}^2)$
Mo/Ru	18(*b*)	0.0121(4)	0.1587(4)	0.3993(3)	1.36(7)
Te(1)	18(*b*)	0.3263(3)	0.2904(3)	0.4100(3)	0.95(5)
Te(2)	6(*c*)	0	0	0.2065(3)	0.65(12)

Note. Molybdenum, ruthenium, and tellurium(1) atoms in 18(*b*) positions, tellurium(2) atoms in 6(*c*) positions. Hexagonal lattice parameters $a = 10.2563(2)$ Å; $c = 11.3899(3)$ Å. Numbers in parentheses are estimated standard deviations.

TABLE II

SELECTED INTERATOMIC DISTANCE IN $Mo_{4.5}Ru_{1.5}Te_8$ AND Mo_6Te_8

	$Mo_{4.5}Ru_{1.5}Te_8$ (Å)	Mo_6Te_8 (Å)
M–M intracluster distance d_1	2.779(5)	2.772(5)
M–M intracluster distance d_2	2.718(3)	2.699(3)
M–M intercluster distance	3.713(4)	3.674(4)
Te(1)–*M* intracluster distances	2.806(5) 2.704(4) 2.705(4)	2.785(5) 2.707(4) 2.773(4)
Te(2)–*M* intracluster distances (×3)	2.699(5)	2.744(5)
Te(1)–*M* intercluster distance	2.782(5)	2.837(5)

Note. Numbers in parentheses are estimated standard deviations.

the reaction product during the opening of the quartz reaction tube. The other two reflections corresponding to interplanar spacings of 2.86 and 2.61 Å may be associated (*9*) with the presence of a small amount of ruthenium ditelluride. Further refinement of the X-ray diffraction data failed to give any evidence for the occurence of nonstoichiometry in the $Mo_{4.5}Ru_{1.5}Te_8$ phase. Given the lack of clear evidence for the occurence of nonstoichiometry in the Chevrel phase compounds (*2, 10–12*) and the failure of our data to show the presence of unreacted molybdenum or ruthenium we assume that the composition of the compound examined is $Mo_{4.5}Ru_{1.5}Te_8$.

Important interatomic distances in $Mo_{4.5}Ru_{1.5}Te_8$ are collected in Table II and are compared with corresponding values in Mo_6Te_8, which have been generated during the course of this work from the atomic coordinates and lattice parameters of Mo_6Te_8, a = 10.195 (3) Å, c = 11.663(5) Å, which have been reported elsewhere (*1*). The most significant difference between the lattice parameters is that c_{hex} for $Mo_{4.5}Ru_{1.5}Te_8$ is ca. 0.27 Å shorter than for Mo_6Te_8. The distance *A* which lies on the c_{hex}-axis between the Te(2) atom and the plane defined by the three nearby cluster metal atoms can be calculated for these compounds. The unit cell origin–Te(2) separation and distance *A* in $Mo_{4.5}Ru_{1.5}Te_8$ are 0.073 and 0.063 Å shorter than the corresponding distances in Mo_6Te_8. Since two of each of these distances contribute to c_{hex}, the observed decrease in the c_{hex} lattice parameter of $Mo_{4.5}Ru_{1.5}Te_8$ can be totally associated with the changes in these dimensions.

It is interesting to compare the differences between the lattice parameters of Mo_6Te_8 and $Mo_{4.5}Ru_{1.5}Te_8$ with those recorded (*2*) from the corresponding selenides where the largest change in lattice parameters is in c_{hex}. Using the previously reported data (*2*) the changes in distance *A* and the origin–Se(2) separation account for only ca. 60% of the change in c_{hex}. The remainder of the observed decrease in c_{hex} in $Mo_4Ru_2Se_8$ can be associated with the contraction of the intracluster metal bonds, particularly the d_1 bonds, which lie approximately parallel to c_{hex}. Hence, although the differences in lattice parameters between Mo_6X_8 and $Mo_{6-x}Ru_xX_8$ (X = Se,Te) show similar trends, the behaviors of the selenides and tellurides are quite different.

Finally, we would mention that the X-ray powder diffraction patterns recorded from Mo_6Te_8 at 77 and 4 K confirmed an earlier report (*13*) that Mo_6Te_8 retains its rhombohedral structure at temperatures as low as 4 K. However, the X-ray powder diffraction pattern recorded from $Mo_5Ru_1Te_8$ at 77 and 4 K (Fig. 3) showed the material to undergo a transformation from the rhombohedral phase at 77 K to a material at 4 K in which the unit cell has lower symmetry. For example, the rhombohedral $31\bar{1}$ reflection of the high temperature structure was split at low temperature into three reflections, each of approximately one-third the intensity of the

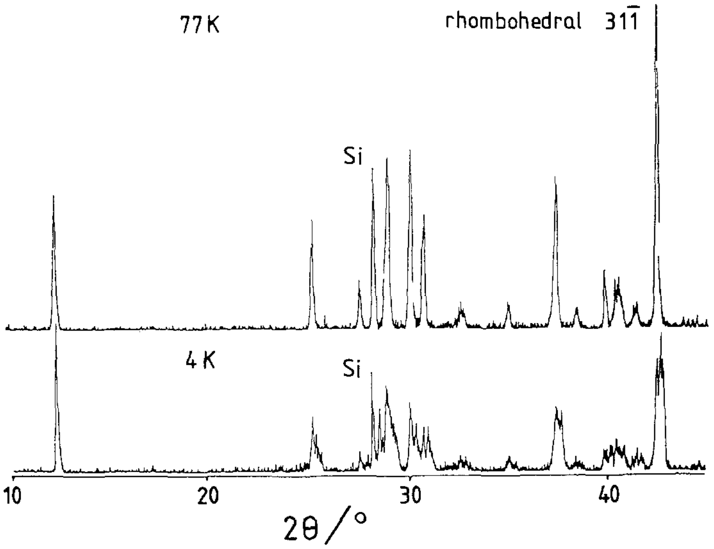

FIG. 3. X-ray powder diffraction patterns recorded from $Mo_5Ru_1Te_8$ at 77 and 4 K.

rhombohedral 31$\bar{1}$ reflection. This is consistent with orthorhombic symmetry, but lower symmetry space groups are also possible.

Although this phase transformation was found to be sensitive to experimental conditions and was not observed when the sample was rapidly cooled, it is interesting to note that the Chevrel phase compounds $EuMo_6S_8$ and $BaMo_6S_8$ have been shown (*4–6*) to undergo similar structural transformations. The phase transitions of $BaMo_6S_8$ and $EuMo_6S_8$ have been attributed (*4*) to electronic instability resulting from the availability of twenty-two electrons for metal cluster bonding. This number of electrons was associated with a half-filled energy band which in turn was considered to result in a Jahn–Teller-type distortion of the band structure and the formation of a band gap at the Fermi level. Such an explanation is consistent with a metal–semiconductor transition (*14, 15*) which is associated with the phase transformation in $EuMo_6S_8$. It may be that a similar electronic instability occurs in $Mo_5Ru_1Te_8$. Indeed, if the tellurium atoms are assigned an oxidation state of 2-, the compound $Mo_5Ru_1Te_8$ has, like $EuMo_6S_8$ and $BaMo_6S_8$, twenty-two electrons associated with the metal cluster. The absence of a similar phase transition in Mo_6Te_8 which has twenty electrons in the metal cluster is consistent with this suggestion.

Acknowledgments

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