The Crystal Structure of $Ca_{16.5}Mo_{13.5}O_{40}$, an Intermediate Phase in the Ternary System CaO–Mo–O

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The crystal structure of $Ca_{16.5}Mo_{13.5}O_{40}$ was determined from X-ray single crystal data at 298 K. Anisotropic refinement in the space group *I4/m* gave $R = 0.028$ for 1132 unique reflections. Cell parameters: $a = 8.560(1)$, $c = 11.852(3)$ Å and $V = 868.4(3)$ Å^3. A complex Mo_6O_{18} unit is linked through oxygen bridges to $(Mo,Ca)O_6$ octahedra. These octahedra consist of Mo atoms, partially exchanged by Ca, octahedrally coordinated to six O atoms. The connections between the units are further strengthened by O–Ca–O linkages. Within the Mo_6O_{18} unit the Mo–Mo distances are in accordance with the distance in metallic Mo, indicating the occurrence of a Mo_6 cluster.

Compounds in the ternary system CaO–Mo–O are the subject of a detailed study at our department.[1,2] The purpose is to determine the thermodynamic stability of intermediate phases at high temperature by measurements of the equilibrium oxygen partial pressures, using the solid state emf method. In these studies a "new" intermediate phase $Ca_{16.5}Mo_{13.5}O_{40}$, was identified.

In parallel with this structure determination, the thermodynamic stability of the phase $Ca_{16.5}Mo_{13.5}O_{40}$ has been studied by Lindblom[1] (the phase was then denoted $Ca_{1.24}Mo_{1.01}O_3$). The phase was analyzed by X-ray powder diffraction, and the following tetragonal unit cell parameters were obtained: $a = 8.5575(5)$ and $c = 11.850(1)$ Å. To be able to calculate the Gibbs free energy of formation for this phase, the exact composition had to be established. The aim of this work was therefore to determine the crystal structure, and thus the composition, by means of X-ray diffraction.

Experimental

Materials. The starting materials, Mo (Aldrich, analytical grade), MoO_2 (Pfalz & Bauer) and $CaCO_3$ (Riedel-De Haën *p.a.*), were used without further purification.

The oxide, CaO, was prepared by heating $CaCO_3$ in air at 1300 K for 24 h, while the intermediate phase, $CaMoO_4$, was prepared by heating equimolar amounts of CaO and Mo at 1270 K for 24 h in air.

Preparation and analysis of $Ca_{16.5}Mo_{13.5}O_{40}$. Single crystals of the phase $Ca_{16.5}Mo_{13.5}O_{40}$ were obtained by mixing and grinding CaO, Mo and MoO_2 in amounts corresponding to a total composition of $Ca_{1.25}MoO_3$. This powder mixture was then heated at 1473 K for 4 d in a 600 mm long, closed-end Al_2O_3 tube, which was evacuated and sealed through a glass tube glued on the top of the Al_2O_3 tube before heating. Some black, almost spherical crystals with a diameter of about 0.1 mm were found in the resultant powder.

To prepare a pure sample for analysis of the phase, the solid buffer technique described by Lindblom and Rosén[3] was used. A mixture of CaO and Mo was placed at the bottom of an ampoule to provide an oxygen partial pressure buffer. An Al_2O_3 crucible was filled with $CaMoO_4$ and CaO in a molar ratio of 1:3, and placed on top of the CaO-Mo mixture. The ampoule was then evacuated, sealed and heated at 1370 K for 24 h and then lifted out of the furnace. After the heat treatment, the buffer mixture at the bottom of the tube consisted of CaO, Mo and $Ca_{16.5}Mo_{13.5}O_{40}$. The grey sample mixture in the crucible was composed of CaO and $Ca_{16.5}Mo_{13.5}O_{40}$. Excess CaO was removed by washing first with a 0.1 M solution of HCl and then with distilled water. Finally, the remaining black powder was dried at 450 K for 1 d.

The amounts of Ca and Mo in the sample obtained above were determined by the X-ray fluorescence technique (Analytica AB, Täby, Sweden). The sample was found to contain 25.2 mass-% Ca and 48.1 mass-% Mo, with an accuracy of approx. ±2 mass-%.

X-Ray measurements. X-Ray intensity data were collected with a Nicolet R3 automatic four-circle diffractometer using graphite-monochromated Mo$K\bar{\alpha}$ radiation. Cell parameters were initially obtained by least-squares refinement of 25 automatically centered reflections with $17 < 2\Theta < 25°$. A total of 1409 reflections were measured in the 2Θ range $3.0 \leq 2\Theta \leq 80.0°$ ($0 \leq h \leq 16$, $0 \leq k \leq 16$, $0 \leq l \leq 22$). Background was measured at each side of the peak for a total

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Table 1. Summary of crystal data and experimental details.

Crystal data	
Formula	$Ca_{16.5}Mo_{13.5}O_{40}$
Mol. mass	2596.5
Crystal system	Tetragonal
Space group	*I4/m* (No. 87)
a/Å	8.560(1)
c/Å	11.852(3)
V/Å^3	868.4(3)
Z	1
d_{calc}/Mg m^{-3}	4.964
Radiation	Mo*K*$\bar{\alpha}$ ($\lambda = 0.71069$ Å)
μ(Mo*K*$\bar{\alpha}$)/mm^{-1}	7.04
Crystal size/mm	0.1×0.1×0.1
Data collection and structure refinement	
2Θ scan speed/°min^{-1}	Variable 1–3 (Θ/2Θ)
2Θ scan width/°	2.4 plus α_1-α_2 dispersion
No. of total reflection	1409
No. of unique reflections [$I_{obs} > 3\sigma(I_{obs})$]	1132
Abs. correction (empirical ψ scan)	Min. trans. factor range 0.84–0.92 (max. trans. 1.0)
No. of parameters refined	108
R	0.028
$R_w\{w=1/[\sigma^2(F_o)+(0.0075F_o)^2]\}$	0.028
Maximum residual electron density/e Å^{-3}	2.6

time equal to the scan time. The 4 standard reflections (0 0 6), (1 3 0), (2 1 3) and (3 1 0) were measured after every 50 reflections. A maximum intensity drop of 4 % was accepted. An empirical absorption correction was made from 20 reflections evenly distributed in 2Θ, each reflection being rotated around its diffraction vector in steps of 10°. The relative transmission factor was 0.850–1.000. Lorentz and polarization corrections were also made. Details of crystal data and structure refinement are given in Table 1. Tables of observed and calculated structure factors and anisotropic temperature factors are available from the authors on request.

Structure determination and refinement

The atomic positions of Mo were obtained from the Patterson map, and those for Ca and O from successive electron density calculations. Scattering factors used were neutral atom values for Mo, O and Ca, with account being taken for anomalous dispersion.[4] The refinements were carried out in space group *I4/m* using the least-squares program UPALS.[5] Anisotropic full-matrix least-squares refinement of positional and anisotropic thermal parameters was performed, minimizing $w(|F_o| - |F_c|)^2$. Final $R = 0.028$, $R_w = 0.028$ and $S = 1.565$. Atomic coordinates and equivalent isotropoic thermal parameters are given in Table 2.

Description of the structure

A complex Mo_6O_{18} unit, shown in Fig. 1, is located with its center at ½,½,½. This position, in which there is a center of symmetry, is vacant. The whole unit consists of six Mo atoms, each coordinated to five O atoms, cross-linked by Mo-O-Mo bridges involving four of the five O atoms. The fifth O atom is in common with a $(Mo,Ca)O_6$ unit, which consists of a Mo atom partially exchanged by Ca, octahedrally coordinated to six O atoms (Fig. 2). The connections between the Mo_6O_{18} and $(Mo,Ca)O_6$ groups are further strengthened by O-Ca-O linkages not shown in the

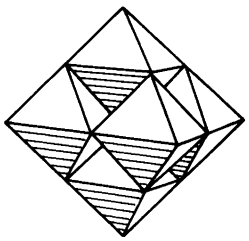

Fig. 1. A schematic drawing of the Mo_6O_{18} unit. It should be observed that the centre of the unit is unoccupied.

Table 2. Fractional coordinates (*x*,*y*,*z*), occupancy factors (*G*) and equivalent isotropic thermal parameters (B_{eq} [a]) for $Ca_{16.5}Mo_{13.5}O_{40}$.

Atom	*x*	*y*	*z*	*G*	B_{eq}/Å^2
Mo(1)	0.11778(4)	0.19640(4)	0.0	0.5	0.339(6)
Mo(2)	0.0	0.0	0.15298(4)	0.25	0.330(6)
Mo(3)	0.0	0.0	0.5	0.0962(9)	0.31(1)
Ca(1)	0.0	0.0	0.5	0.0288(9)	0.31(1)
Ca(2)	0.43158(7)	0.21000(8)	0.15246(6)	1.0	0.80(1)
O(1)	0.3473(3)	0.3192(3)	0.3336(2)	1.0	0.65(4)
O(2)	0.3292(4)	0.0577(4)	0.0	0.5	0.55(5)
O(3)	0.2137(4)	0.1153(4)	0.5	0.5	0.84(6)
O(4)	0.5	0.5	0.1697(4)	0.25	0.78(6)
O(5)	0.0	0.5	0.25	0.25	0.47(5)

[a] Isotropic equivalent of the anisotropic temperature factors.[7]

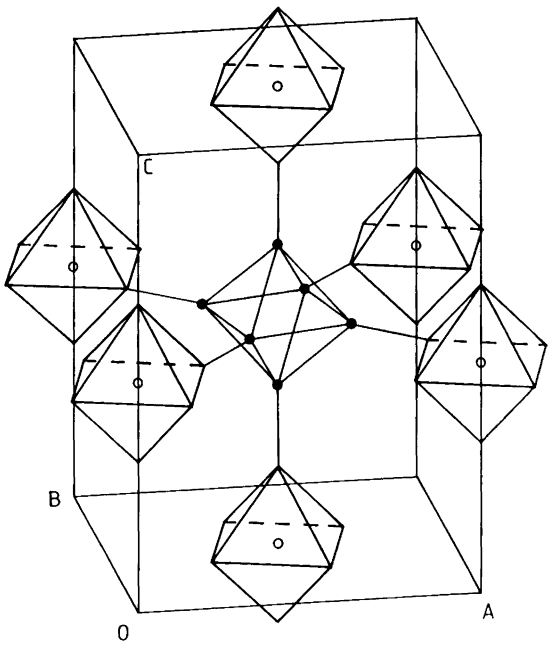

Fig. 2. A schematic drawing of the Mo-O-Mo coupling between the Mo_6O_{18} unit and the six $(Mo,Ca)O_6$ units. For clarity, most of the oxygen atoms in Mo_6O_{18} have been omitted. Filled circles: Mo sites in Mo_6O_{18}. Open circles: (Mo,Ca) sites in $(Mo,Ca)O_6$.

figure. These Ca atoms are surrounded by seven O atoms in a complex arrangement in which the Ca-O distances range from 2.22 to 2.66 Å. The symmetry of the $(Mo,Ca)O_6$ unit is $4/m$, top and bottom (Mo,Ca)-O distances being slightly shortened. In this unit, 23 % of the Mo atoms are substituted with Ca.

Table 3. Selected atomic distances (Å) and angles (°) in the structure.

The Mo_6O_{18} unit	
Distances	
Mo(1)–Mo(1^{i}) [a]	2.7723(6)
Mo(2)–Mo(1)	2.6702(6)
Mo(1)–O(1)	1.999(2)
Mo(1)–O(2)	2.164(3)
Mo(1)–O(2^{i}) [a]	1.883(3)
Mo(1)–O(3)	2.163(3)
Mo(2)–O(1)	2.032(2)
Mo(2)–O(4)	2.101(5)
Angles	
Mo(1^{i})–Mo(1)–Mo(2) [a]	58.73(1)
Mo(2^{ii})–Mo(1)–Mo(2) [a]	85.53(2)
The $(Mo,Ca)O_6$ unit	
Distances	
(Mo(3),Ca(1))–O(3)	2.078(3)
(Mo(3),Ca(1))–O(4)	2.012(5)
Angles	
O(3^{iii})–O(4)–O(3^{iv}) [a]	61.07(9)
The Ca(2)–O distances	
Ca(2)–O(1)	2.406(2)
Ca(2)–O(1^{i}) [a]	2.450(2)
Ca(2)–O(2)	2.395(2)
Ca(2)–O(3)	2.483(2)
Ca(2)–O(3^{i}) [a]	2.655(3)
Ca(2)–O(4)	2.5587(8)
Ca(2)–O(5)	2.2160(7)

[a] The subscripts refer to the following symmetry operations: (i) $y,-x,z$; (ii) $x,y,-z$; (iii) $x+½, y+½, z+½$; (iv) $y+½,-x+½,z+½$.

Discussion

Selected atomic distances are shown in Table 3. The shortest Mo-Mo distances in the Mo_6O_{18} unit range from 2.67 to 2.77 Å. These values are in accordance with the Mo-Mo distance in metallic Mo (2.73 Å), which means that within this unit there are intermetallic interactions between the Mo atoms, indicating the occurrence of a Mo_6 cluster. The Me-O distances in the $(Mo,Ca)O_6$ unit range from 2.01 to 2.08 Å. While these distances are shorter than expected for Ca-O, they are not unreasonable.[6]

In the early stages of the structure refinement, Mo fully occupied the site 0,0,½ and an R value of 0.034 was obtained. However, the difference Fourier calculations showed that there was an excess of 5.8 e Å^{-3} at this site. We tried to decrease this excess electron density by the following two methods: (1) by refining the occupancy factor of Mo. Here, the occupancy factor of Mo decreased from 0.125 to 0.1090 after convergence. This gave the unit cell content $Ca_{16.0}Mo_{13.7}O_{40}$. The R value was 0.028 and the difference Fourier calculations showed a maximum residual electron density of 2.6 e Å^{-3}; or (2) by allowing Ca to occupy this site besides Mo. Here, the occupancy factors for Ca and Mo obtained from the refinement were 0.0288 and 0.0962, respectively. This gave the unit cell content $Ca_{16.5}Mo_{13.5}O_{40}$. The R value was 0.028 and the maximum residual electron density was 2.6 e Å^{-3}.

From this we conclude that there is no way, using crystallographic data alone, of definitely determining which of the above two models is the true one. However, as stated above, the composition obtained from the X-ray fluorescence analysis was 25.2 mass-% Ca and 48.1 mass-% Mo, with an accuracy of approx. ±2 mass-%. The formula obtained in model (1), $Ca_{16.0}Mo_{13.7}O_{40}$, corresponds to a composition of 24.7 mass-% Ca and 50.7 mass-% Mo, whereas that from model (2), $Ca_{16.5}Mo_{13.5}O_{40}$, corresponds to 25.5 mass-% Ca and 49.9 mass-% Mo, the latter being within the stated uncertainty of the results of the X-ray fluorescence technique. With the support of the analytical data, we therefore propose model (2) to be the most accurate.

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