ELSEVIER

Journal of Alloys and Compounds 317–318 (2001) 132–135

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

$GaMgMo_4O_7$ and $Fe_2Mo_4O_7$ — two low-valent molybdenum oxides with a fully ordered $Sc_{0.75}Zn_{1.25}Mo_4O_7$ type structure

M. Hainz, H. Boller*

Institut für Chemie, Allgemeine und Anorganische Chemie, Johannes-Kepler-Universität Linz A-4040 Linz, Austria

---

Abstract

The title compounds have been prepared by sintering at 1200°C. Their crystal structures have been determined from single crystal diffractometer data: space group Imma, with a=6.016(3), b=5.712(1), c=16.606(4) Å ($GaMgMo_4O_7$) and a=6.018(1), b=5.782(1), c=16.901(5) Å ($Fe_2Mo_4O_7$), Z=4. The structure is interpreted as a substitutional derivative of a cubic closed-packing of oxygen ions with the molybdenum cluster atoms occupying octahedral holes. While gallium is in tetrahedral and magnesium in octahedral oxygen coordination, bond valences suggest that iron(II) is in the tetrahedral and iron(III) in the octahedral sites.

Keywords: Molybdenum oxides; Metal clusters; Crystal structure; Bond valences

---

1. Introduction

On the occasion of syntheses of $NaMo_4O_6$ in steel crucibles sometimes small needles of an iron containing minority phase were observed. A single crystal X-ray investigation revealed isotypy with $Fe_{1.89}Mo_{4.11}O_7$ [1,2]. However, the composition of the crystal appeared to be very close to the ideal formula $Fe_2Mo_4O_7$. Since $Fe_{1.89}Mo_{4.11}O_7$ as well as all the other phases isotypic with $Sc_{0.75}Zn_{1.25}Mo_4O_7$ [2–4] are reported to be disordered with respect to the metal positions, a direct synthesis of stoichiometric $Fe_2Mo_4O_7$ and other fully ordered isotypic compounds at not too high temperatures was undertaken resulting in the discovery of $GaMgMo_4O_7$.

2. Sample preparation

The very well mixed powders (Fe, Mo and dried MoO_3 for $Fe_2Mo_4O_7$, and Mo, $MgMoO_4$ and freshly prepared Ga_2O_3) were heated in evacuated sealed silica tubes (heating program: 100°C h^{-1} up to 1200°C, 7 days at this temperature and then rapidly cooled to room temperature). The resulting products were composed of strongly intergrown needle-like crystals with metallic lustre. Crystals of $GaMgMo_4O_7$ have a faint violet shine. Guinier photographs revealed that the products were almost pure $Fe_2Mo_4O_7$ and isotypic $MgGaMo_4O_7$ with traces of Fe and MoO_2 or Ga_2O_3 and MoO_2 respectively.

Experiments to synthesize the following phases were not successful: $InMgMo_4O_7$, $GaVMo_4O_7$, $GaCoMo_4O_7$, $GaNiMo_4O_7$, $GaCuMo_4O_7$, $GaZnMo_4O_7$, $Mn_2Mo_4O_7$, $Co_2Mo_4O_7$, $Ni_2Mo_4O_7$, $FeMnMo_4O_7$, $FeCoMo_4O_7$, $FeZnMo_4O_7$.

3. Crystal structure analyses

Preliminary examinations by precession photographs revealed an orthorhombic body centered lattice with ($h0l$) and ($hk0$) only with $h = 2n$, indicating the space groups Ima2 or Imma. Data collection of two needle-like crystals of the two compounds were performed on a CAD4 diffractometer (Enraf Nonius) operated with graphite monochromated MoKα-radiation (λ=0.7107 Å). For both crystals intensity data were collected at 21(1)°C over one quadrant of reciprocal space ($2\vartheta \leq 54°$) using the $\omega - 2\vartheta$ scan mode. The scan width was adjusted according to $0.85° + 0.35° \tan \vartheta$ for $Fe_2Mo_4O_7$ and $1.20° + 35° \tan \vartheta$ for $GaMgMo_4O_7$. Lattice constants were refined on the basis of 24 reflections ($30° \leq 2\vartheta \leq 40°$). Absorption was accounted for by an empirial method (DIFFABS) [5]. All

---

*Corresponding author. Tel.: +43-732-2468-805; fax: +43-732-24689681.

E-mail address: herbert.boller@jk.uni-linz.ac.at (H. Boller).

0925-8388/01/$ – see front matter
PII: S0925-8388(00)01331-1

Table 1
Crystallographic data for $GaMgMo_4O_7$ and $Fe_2Mo_4O_7$

	$GaMgMo_4O_7$	$Fe_2Mo_4O_7$
Pearson Symbol:	oI52	
a (Å)	6.016 (3)	6.018(1)
b (Å)	5.712(1)	5.782(1)
c (Å)	16.606(4)	16.901(5)
Space group:	Imma (No.74)	
Z		2
V (Å^3)	570.7	588.1
d_x (gcm^{-3})	6.864	6.860
M_r	589.8	594.29
μ (MoK_α) (cm^{-1})	131	129
Structure refinement:		
Unique reflections	377	387
Observed reflections	224	317
Cutoff	$3\sigma(F_o)^2$	
Variables	33	
$R = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma \lvert F_o\rvert$	0.032	0.026
$R_w = [\Sigma\, w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \Sigma\, w\lvert F_o\rvert^2]^{1/2}$	0.030	0.029
$w = [\sigma(F_o^2)^2 + (0.005F_o^2)^2]^{-1/2}$		
Residual electron density (eÅ^{-3})	1.867	0.652

computations were performed on a VAX 3520 work station using the MOLEN crystallographic software package [6].

The crystal structures were solved by direct methods (Multan 88) and subsequent difference Fourier syntheses. In the least-squares refinements anisotropic thermal parameters were used except for the oxygen atoms, which were refined isotropically. The crystallographic data and details of the measuring conditions and the structure refinement of the two compounds are given in Table 1. The atomic positions and isotropic thermal parameters are presented in Table 2.

Table 2
Positional parameters and equivalent isotropic temperature factors for $GaMgMo_4O_7$ and $Fe_2Mo_4O_7$

Atom	x	y	z	B_{eq} [a]
$GaMgMo_4O_7$				
Ga	0	0.25	0.3063(2)	0.41(6)
Mg	0.25	0.25	0.75	0.4(1)
Mo(1)	0	0.0197(3)	0.11337(7)	0.29(2)
Mo(2)	0.2305(3)	0.25	0.99597(8)	0.34(2)
O(1)	0	0	0.5	0.7(3)
O(2)	0.263(3)	0.25	0.1207(5)	0.1(2)
O(3)	0.272(3)	0.25	0.6251(6)	0.5(2)
O(4)	0	0.506(2)	0.2421(6)	05(2)
$Fe_2Mo_4O_7$				
Fe(1)	0	0.25	0.3074(2)	0.93(4)
Fe(2)	0.25	0.25	0.75	0.74(4)
Mo(1)	0	0.0052(3)	0.11108(2)	0.71(2)
Mo(2)	0.2312(2)	0.25	0.99726(6)	0.38(1)
O(1)	0	0	0.5	0.5(2)
O(2)	0.243(2)	0.25	0.1179(4)	0.7(1)
O(3)	0.244(1)	0.25	0.8746(5)	0.6(1)
O(4)	0	0.521(2)	0.2359(4)	0.7(1)

[a] $B_{eq} = \frac{8\pi^2}{3} \Sigma_i \Sigma_j U_{ij}\, a_i^* \, a_j^* \mathbf{a}_i \mathbf{a}_j$.

4. Magnetic properties of $Fe_2Mo_4O_7$

The magnetic susceptibilities of $Fe_2Mo_4O_7$ were measured by means of a pendulum Faraday magnetometer in the temperature range from 100 K to 220 K. Below 200 K a field dependence of the susceptibility is observed indicating ferrimagnetism due to different magnetic moments of the iron atoms in the two crystallographically district positions.

5. Calculation of bond valences and Madelung Energies

Bond valences (v_{ij}), as presented in Table 3 together with the interatomic distances (d_{ij}), were calculated using the formula:

$$\nu_{ij} = \exp[(Ro_{ij} - d_{ij})/b_{ij}],$$

with the following pairs of constants Ro_{ij}/b_{ij}:

Mo–O: 1.89/0.30; Ga–O: 1.73/0.37; Mg–O: 1.69/0.37; Fe–O: 1.75/0.37;

Mo–Mo: 2.59/0.26 (adapted to the formula from Pauling's values [7]).

The Madelung energies were calculated by means of the program EUTAX1 [8]. The bond valences were calculated either by EUTAX1 or DISTV [9].

6. Results and discussion

The interatomic distances of the two compounds are compiled in Table 3. The crystal structure of $\mathrm{GaMgMo_4O_7}$ is shown in Fig. 1. The central structural elements are $[\mathrm{Mo_4}]_\infty$ rods formed by trans-edge-sharing molybdenum octahedra to form linear $[\mathrm{Mo_4O_8}]_\infty$ pseudo-cluster chains aligned along the *b*-axis. They are linked together by the apical oxygens to form $[\mathrm{Mo_4O_6O_{2/2}}]_\infty$ sheets perpendicular to the [1] direction. These sheets are held together by the cations in tetrahedral (Ga, Fe1) and in octahedral (Mg, Fe2) oxygen coordination. There are three different kinds of oxygen atoms with regard to the pseudo-cluster chains (Fig. 2): apical oxygens (O4) are terminal, equatorial (O1) oxygens are cross-linking the $[\mathrm{Mo_4O_6O_{2/2}}]$ units, and lateral ones (O2 and O3) are each bonded to one equatorial Mo2 and two apical Mo1 atoms. The apical Mo1 atoms have bonding contacts to 4 equatorial Mo2 atoms and a short distance to one neighbouring Mo1 atom in $\mathrm{GaMgMo_4O_7}$. Thus a definite pair formation by alternating short (2.63 Å) and long (3.08 Å) Mo1–Mo1 distances is observed, whereas in $\mathrm{Fe_2Mo_4O_7}$ almost equal, but longer Mo1–Mo1 distances (2.83 and 2.95 Å) exist. A similar observation was reported and discussed in terms of cluster electron counts by McCarley [4] in the case of $\mathrm{Sc_{0.75}Zn_{1.25}Mo_4O_7}$ and $\mathrm{Ti_{0.5}Zn_{1.5}Mo_4O_7}$. Indeed, the mean bond valences of the Mo–Mo bonds are 0.49 for $\mathrm{GaMgMo_4O_7}$ and 0.44 for $\mathrm{Fe_2Mo_4O_7}$.

Table 3
Interatomic distances (Å) and bond valences in $\mathrm{GaMgMo_4O_7}$ and $\mathrm{Fe_2Mo_4O_7}$

		Distance		Bond valence
Ga/Fe(1)	O(4)	1.810(5)/1980(5)	2×	0.81/0.54
	O(2)	1.872(6)/1994(7)	2×	0.68/0.52
				2.98/2.12
Mg/Fe(2)	O(4)	2.055(6)/2.018(5)	4×	0.38/0.49
	O(3)	2.078(5)/2.106(5)	2×	0.35/0.38
				2.21/2.72
Mo(1)	O(2)	2.061(5)/2.040(6)	2×	0.57/0.61
	O(3)	2.072(5)/2.095(5)	2×	0.55/0.50
	O(4)	2.143(6)/2.115(6)		0.43/0.47
				2.67/2.70
	Mo(1)	2.631(1)/2.831(2)		0.85/0.40
	Mo(2)	2.730(2)/2.732(2)	2×	0.58/0.58
	Mo(2)	2.756(2)/2.764(2)	2×	0.53/0.51
	Mo(1)	3.081(2)/2.951(2)		0.15/0.25
				3.22/2.83
Mo(2)	O(3)	2.011(7)/2.075(6)		0.67/0.54
	O(2)	2.080(6)/2.040(6)		0.53/0.61
	O(1)	2.162(2)/2.170(1)	2×	0.41/0.39
				2.02/1.93
	Mo(2)	2.774(2)/2.783(2)		0.49/0.48
		2.859(3)/2.893(3)	2×	0.36/0.31
				3.43/3.28[a]
O(1)	Mo(2)	2.162(2)/2.170(1)	4×	0.41/0.39
				1.64/1.56
O(2)	Ga/Fe(1)	1.872(6)/1.994(7)		0.68/0.52
	Mo(1)	2.061(5)/2.040(6)	2×	0.57/0.61
	Mo(2)	2.080(6)/2.040(6)		0.53/0.61
				1.67/2.35
O(3)	Mo(2)	2.011(7)/2.075(6)		0.67/0.54
	Mo(1)	2.072(5)/2.095(5)	2×	0.59/0.51
	Mg/Fe(2)	2.078(5)/2.106(5)		0.35/0.38
				2.12/1.93
O(4)	Ga/Fe(1)	1.810(5)/1.980(5)		0.81/0.54
	Mg/Fe(2)	2.055(6)/2.018(5)	2×	0.38/0.49
	Mo(1)	2.143(6)/2.115(6)		0.43/0.47
				2.00/1.99

[a] Sum taken with inclusion of Mo(2)−Mo(1) bonds.

The structure can also be interpreted as a substitutional derivative of a cubic closed packing of the oxygen atoms(ions): In pseudo-hexagonal (102) oxygen layers every eighth row of atoms running in (010) direction is substituted by an octahedral $[\mathrm{Mo_4}]$ chain in a manner that the centers of the octahedra take the place of the missing oxygen atoms, while the molybdenum atoms are situated in the incomplete octahedral holes of the packing. Thus the apical molybdenum atoms are coordinated by five and the equatorial ones by only four oxygen atoms (Fig. 3).

Although the bond valence sums for molybdenum resulting from the Mo–O bonds, as well as the bond valence sums for the oxygen atoms differ individually from the expected values (2.25 for Mo calculated from the ideal formula and normal valences, and 2 for oxygen) their mean values come close to the expected ones (Table 3). The bond valences of the iron atoms suggest that the tetrahedral positions are occupied by two-valent iron, while the octahedral site should at least predominantly be occupied by three-valent iron.

In order to estimate the impact of the different possible site occupations of the cations on the electrostatic part of the lattice energy, Madelung energies were calculated assuming the formal charge of +2.25 for molybdenum. The respective Madelung energies have their lower value for the experimentally observed site occupancy in each of the two compounds indeed (Table 4).

Table 4
Madelung energies of different site occupations (T: tetrahedral, O: octahedral coordination)

	M.E./$\mathrm{kJmol^{1-}}$
$\mathrm{GaMgMo_4O_7}$	
$\mathrm{Ga_T^{3+}}$, $\mathrm{Mg_O^{2+}}$ (observed)	−30 836
$\mathrm{Ga_O^{3+}}$, $\mathrm{Mg_T^{2+}}$ (hypoth.)	−30 698
$\mathrm{Fe_2Mo_4O_7}$	
$\mathrm{Fe_T^{2+}}$, $\mathrm{Fe_O^{3+}}$ (observed)	−30 516
$\mathrm{Fe_O^{2+}}$, $\mathrm{Fe_T^{3+}}$ (hypoth.)	−30 189

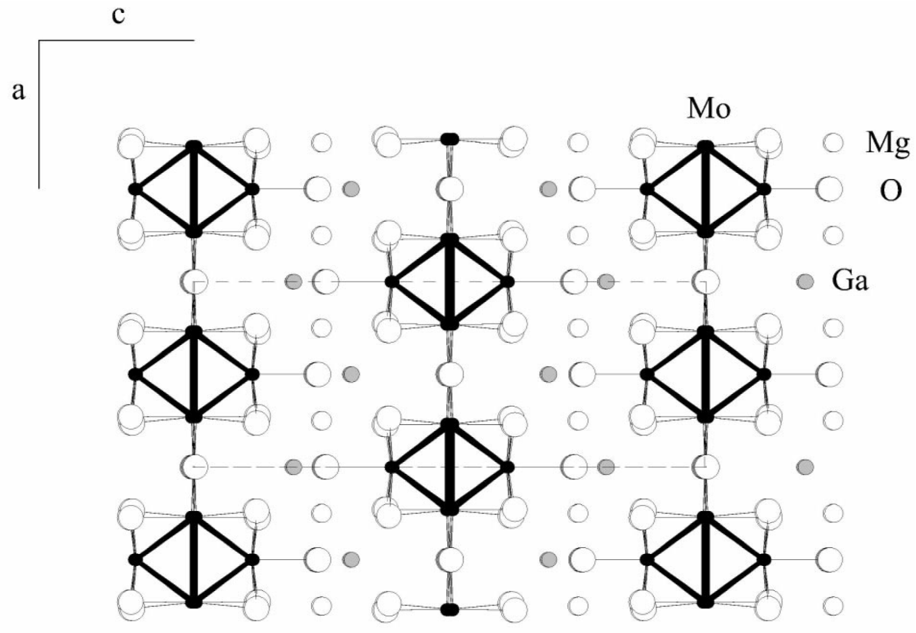

Fig. 1. The crystal structure of $GaMgMo_4O_7$.

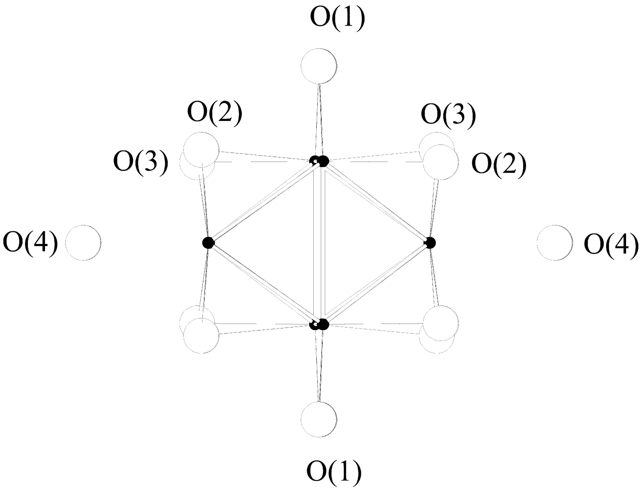

Fig. 2. The oxygen coordination of an octahedral pseudo-cluster.

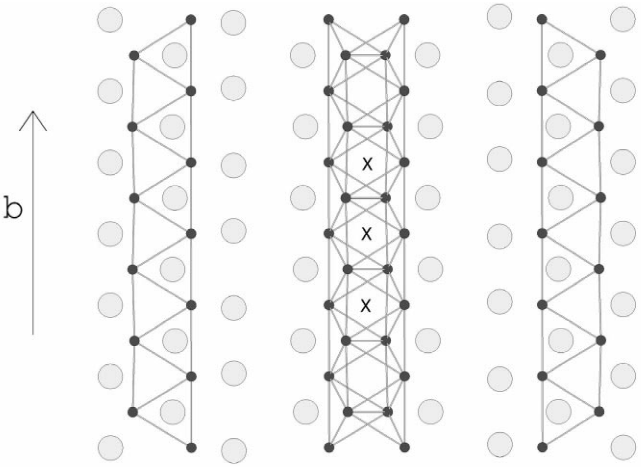

Fig. 3. Close packed pseudo-hexagonal (102) plain (some missing oxygen atoms are marked by crosses).

Acknowledgements

We thank the Österreichische Nationalbank for financial support (Project No. 4465) and Prof. K.O.Klepp for help with the crystal structure determination.

References

[1] K.-H. Lii, PhD Thesis, Iowa State University, Ames Iowa (USA), 1985.
[2] G.L. Schimek, R.E. McCarley, L.Sc. Chumbley, J. Mater. Res. 9 (1994) 891.
[3] R.E. McCarley, K.-H. Lii, P.A. Edwards, L.F. Brough, J. Solid State Chem. 57 (1985) 17.
[4] R.E. McCarley, Philos. Trans. R. Soc. London Ser. A 308 (1982) 141.
[5] N. Walker, D. Stuart, Acta Crystallogr. A 39 (1983) 158.
[6] C.K. Fair, MOLEN, An Interactive Intelligent System For Crystal Structure Analysis, User Manual, Enraf-Nonius, 1990.
[7] L. Pauling, The Nature of the Chemical Bond, 3rd Edition, eighth printing, Cornell University Press, 1973, p. 403.
[8] M. O'Keefe, N.E. Brese, Acta Cryst. B 48 (1992) 152.
[9] H. Boller, in: DISTV, A Computer Program For Calculating Interatomic Distances, Angles, And Bond Valences, 1999, unpublished.