

SYNTHESIS AND PROPERTIES OF THE METALLIC MOLYBDATE(IV) CaMoO_3

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Polycrystalline CaMoO_3 was prepared by a new method making use of the oxygen stability range, and revealed to have an orthorhombic lattice ($a=5.448\text{Å}$, $b=7.776\text{Å}$, $c=5.582\text{Å}$), metallic conduction and Pauli paramagnetism. The results indicate that $4d^2$ electrons of Mo^{4+} are delocalized in CaMoO_3 as same as those in BaMoO_3 and SrMoO_3 .

INTRODUCTION The perovskite-type compounds containing $\text{Mo}^{4+}(4d^2)$, i.e., BaMoO_3 and SrMoO_3 ^{1,2)}, show metallic and Pauli paramagnetic properties similar to that of ReO_3 ³⁾. While the crystallographic, electrical and magnetic properties of BaMoO_3 and SrMoO_3 are well studied^{1,2)}, no detailed reports for CaMoO_3 have been presented. Ward et al. reported only the crystallographic property of CaMoO_3 (monoclinic, $a=c=7.80\pm 0.01\text{Å}$, $b=7.77\pm 0.01\text{Å}$, $\beta=91^\circ 23' \pm 6'$)⁴⁾. But, these lattice constants appear to be suspicious judging from the crystallographic investigation of other perovskites containing Ca^{2+} as A-cation in $\text{A}^{2+}\text{B}^{4+}\text{O}_3$. The scarcity of reliable data on CaMoO_3 might come from the difficulty of preparing stoichiometric CaMoO_3 . In the present work, we show a new method of synthesis making use of the oxygen stability range, and provide the crystallographic, electrical and magnetic properties for polycrystalline CaMoO_3 .

EXPERIMENTAL Equimolar mixtures of reagent grade CaCO_3 and MoO_3 were pressed and heated at 800°C for 20hr in order to obtain the molybdate(VI) CaMoO_4 . The oxygen stability range for CaMoO_3 was determined by thermogravimetric method in $\text{H}_2\text{-CO}_2$ mixture gas atmosphere originally designed by Darken and Gurry⁵⁾. Ground and loosely pressed CaMoO_4 was suspended from a digital balance by 40%Rh60%Pt wire in a vertical furnace kept at 1200°C and at a desired oxygen partial pressure. Figure 1 shows the oxygen stability range of CaMoO_3 ranging from $\log P_{\text{O}_2} = -12.45$ to $\log P_{\text{O}_2} = -13.20$. The oxygen partial pressure in this procedure was measured by using a stabilized zirconia cell.

The pellet of CaMoO_3 was quenched by moving quickly from the hot part maintained at 1200°C and $\log P_{\text{O}_2} = -12.62$ to the cold part of the furnace. This sample, 4.31g/cc as the apparent density, was ascertained to be almost free from microcracks using a microscope (about 40 diameters). X-ray powder diffraction patterns were taken at room temperature by $\text{CuK}\alpha$ radiation. The chemical analysis gave calcium 21.61% and molybdenum 52.29% corresponding to the chemical formula of $\text{Ca}_{0.99}\text{Mo}_{1.00}\text{O}_{2.99}$. The d.c. conductivity of the ceramic sample was measured over a temperature range from 80 to 300K by four-probe method in vacuo. The magnetic measurement was performed using a magnetobalance in the same temperature range as the electrical measurement.

RESULTS AND DISCUSSION

As shown in Figure 1, it is a noted result that a distinct presence of the oxygen stability range in complex oxides is experimentally proved just as done in monoxides⁶⁾. The narrow width of the oxygen stability range suggests the difficulty of obtaining CaMoO_3 by ordinary methods^{1,4)}.

CaMoO_3 was found to have an orthorhombic unit cell with $a=5.448\text{\AA}$, $b=7.776\text{\AA}$ and $c=5.582\text{\AA}$ similar to that of GdFeO_3 ⁷⁾ made of four monoclinic perovskite unit cells. These values are more compatible than that of Ward's in comparison with the unit cell volumes of other calcium perovskites as seen in Figure 2. The major lines in the X-ray powder diffraction pattern showed multiple splittings as in Figure 3 indicating the line profiles of $\{220\}$ and $\{222\}$ reflections from the perovskite cell. These give sufficient conditions for the perovskite cell to be the monoclinic unit cell with $a' > c' > b'$ and $\beta > 90^\circ$. The lattice constants of the monoclinic perovskite cell were calculated as $a' = c' = 3.900 \pm 0.001\text{\AA}$, $b = 3.889 \pm 0.001\text{\AA}$ and $\beta = 91^\circ 24' \pm 1'$ from those of the orthorhombic cell by the same treatment discussed in the previous papers^{8,9)}. Table 1 shows X-ray diffraction data of CaMoO_3 ; an orthorhombic lattice and a monoclinic lattice were indexed by HKL and hkl, respectively.

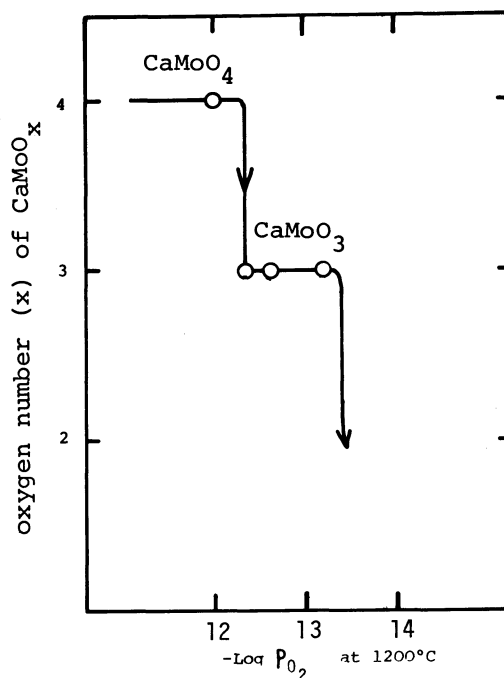


Fig. 1. Oxygen stability range of CaMoO_3 .

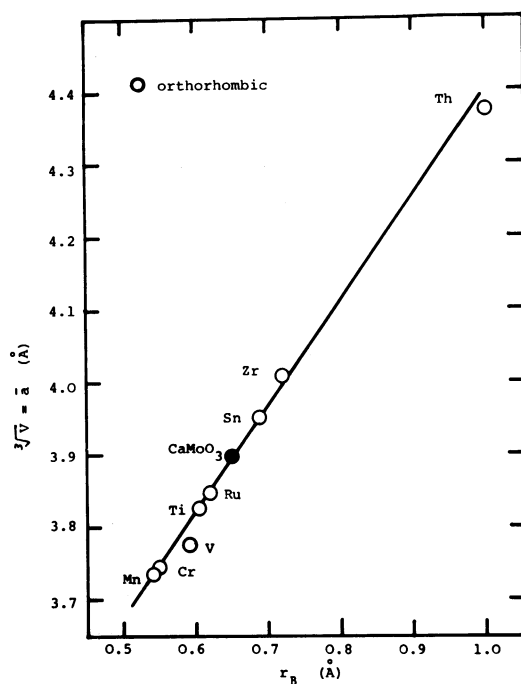


Fig.2 The linear relation between cubic root of cell volume vs. ionic radius of B^{4+} ion for perovskites $CaB^{4+}O_3$: The cell volume of $CaMoO_3$ was calculated from our result.

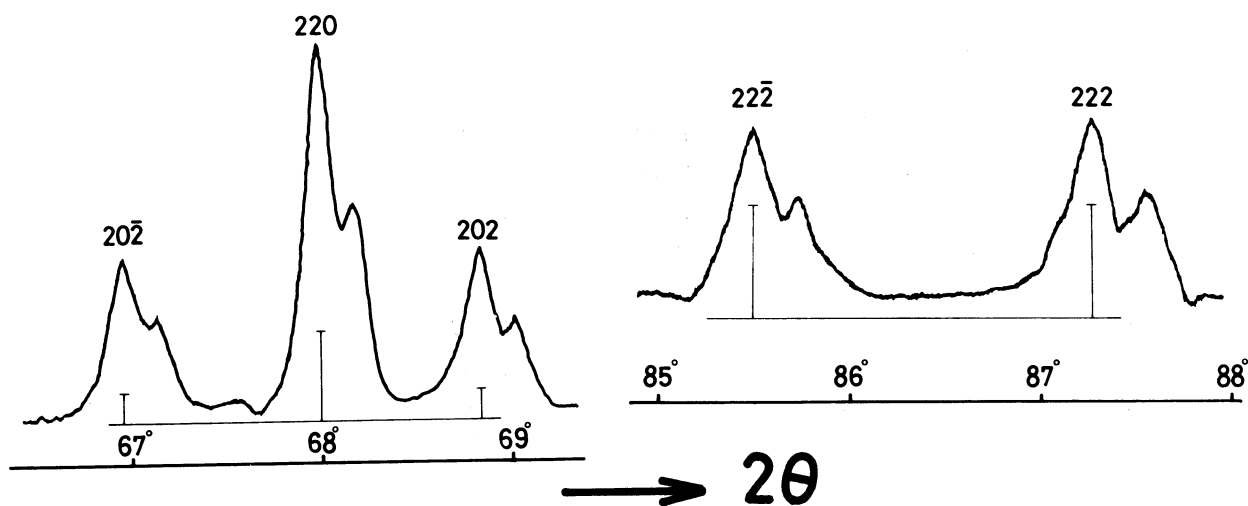


Fig.3 Line Profiles of the perovskite reflections in X-ray powder diffraction patterns. The lines due to $K\alpha_1$ are always accompanied by those due to $K\alpha_2$.

Table 1. X-ray powder diffraction data for CaMoO_3 .

$2\theta^\circ$	H K L	h k l	$d_{\text{calc.}}$	$d_{\text{obs.}}$	$(I/I_0)_{\text{obs.}}$
22.79	1 0 1	{1 0 0}	3.898	3.91	70
25.59	1 1 1		3.485	3.49	4
32.04	0 0 2	{1 1 0}	2.792	2.80	33
32.53	1 2 1		2.753	2.75	100
32.83	2 0 0		2.723	2.72	34
34.15	0 1 2		2.628	2.63	4
36.68	2 0 1		2.447	2.44	3
38.41	1 3 0		2.341	2.342	7
39.72	0 2 2	{1 1 1}	2.268	2.267	4
40.40	2 2 0		2.231	2.231	9
41.85	1 3 1		2.159	2.157	2
43.18	1 2 2		2.094	2.093	2
46.55	2 0 2	{2 0 0}	1.949	1.949	46
46.66	0 4 0		1.945	1.946	45
48.10	2 1 2		1.891	1.890	2
51.87	1 0 3	{2 1 0}	1.761	1.761	14
52.57	2 2 2/1 4 1		1.743/1.740	1.741	21
52.93	3 0 1		1.726	1.728	7
57.40	1 2 3	{2 1 1}	1.604	1.604	20
57.73	0 4 2		1.596	1.596	17
58.26	2 4 0		1.582	1.582	18
58.43	3 2 1		1.578	1.579	39
63.83	1 3 3		1.457	1.459	2
66.98	0 0 4	{2 2 0}	1.396	1.396	9
68.05	2 4 2		1.377	1.377	23
68.89	4 0 0		1.362	1.362	6
71.74	0 2 4	{2 2 1}	1.314	1.315	4
72.29	1 4 3		1.305	1.306	23
73.23	3 4 1		1.291	1.290	2
76.65	2 0 4		1.242	1.242	4
77.35	3 2 3	{3 1 0}	1.233	1.233	12
77.56	1 6 1		1.230	1.230	17
78.03	4 0 2		1.224	1.224	9

orthorhombic and monoclinic systems are indexed by HKL and hkl, respectively.

As for the d.c. conductivity of CaMoO_3 represented by Fig.4, the negative curvature with increasing temperature and high conductivity ($\approx 10 \Omega^{-1}\text{cm}^{-1}$) indicate metallic conduction. Previous report reveals that metallic BaMoO_3 ($1.89 \times 10^4 \Omega^{-1}\text{cm}^{-1}$) has a higher conductivity than that of metallic SrMoO_3 ($1.27 \times 10^4 \Omega^{-1}\text{cm}^{-1}$). This Brixner's result is considerably reliable in spite of ceramic samples. Hence, taking experimental errors into consideration, these conductivities of molybdenum(IV) perovskites lead to an interesting relation of A-cation size to the conductivity, i.e., $\sigma_{\text{BaMoO}_3} > \sigma_{\text{SrMoO}_3} > \sigma_{\text{CaMoO}_3}$. This evidence is compatible with our discussions on the ionic potentials¹⁰⁾ that is, A-cation with a lower ionic potential (Z/r) [Z : valence number, r : ionic radius] brings about wider conduction bands and consequently, a higher conductivity.

At 300K, the net paramagnetic susceptibility (in cgs unit per mole) for CaMoO_3 is 250×10^{-6} , and appears to be independent of temperature as shown in Figure 5. This behavior similar to those of BaMoO_3 and SrMoO_3 should correspond to that of a Pauli-type electron gas, which is in gratifying agreement with the prediction of Goodenough¹¹⁾.

Some properties of the polycrystalline CaMoO_3 are summarized in Table 2.

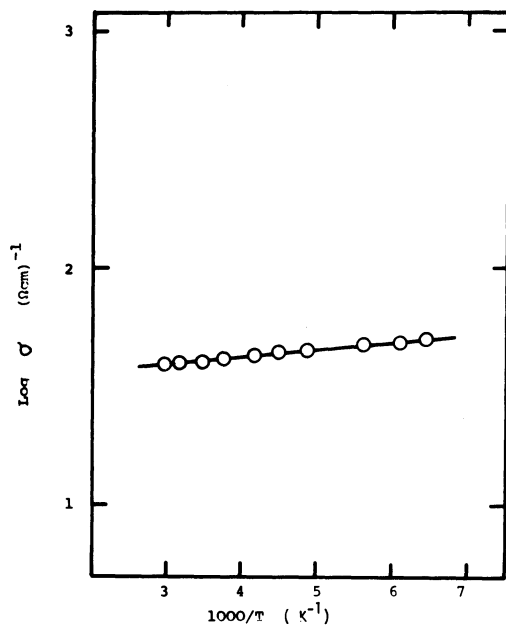


Fig. 4. Electrical conductivity vs. temperature of CaMoO_3 .

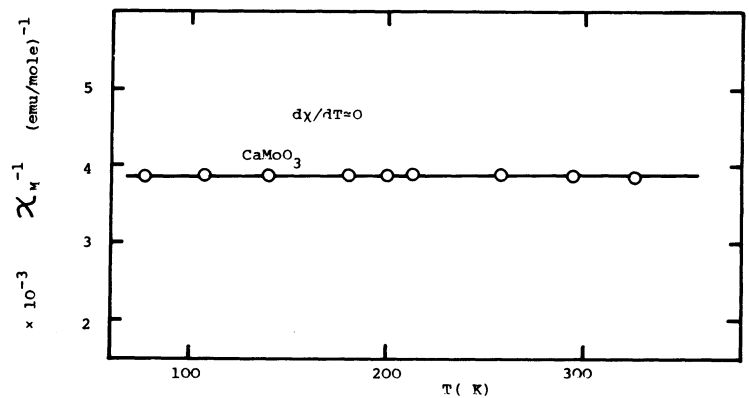


Fig. 5. Reciprocal susceptibility vs. temperature of CaMoO_3 .

Table 2. The physical properties of polycrystalline CaMoO_3 .

Compound	Color	Symmetry	lattice constant (\AA)	Electrical property (Ωcm) ⁻¹	Magnetic property	X-ray density (g/cc)
CaMoO_3	dark purple	ortho- rhombohedral	a=5.448 \pm 0.001 b=7.776 \pm 0.001 c=5.582 \pm 0.001	metallic $\sigma_{r.t} \approx 4.02$ $\times 10$	Pauli para- magnetism	5.17

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