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Crystal Growth, Structure, and Magnetic Properties of $H_{0.23}Li_{1.68}Mo_{1.05}O_3$

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Electrolysis of fused Li_2MoO_4 at 850°C resulted in the growth of large crystals of $H_{0.23}Li_{1.68}Mo_{1.05}O_3$ at the anode. The composition of the crystals was determined by chemical analysis, thermogravimetry, and X-ray diffraction. Single crystal X-ray structure analysis was carried out and confirmed that the crystals have the trigonal α-$NaFeO_2$ structure type previously reported for Li_2MoO_3, but with evidence for a displacive superstructure. Magnetic susceptibility measurements down to 4.2 K show weak Curie–Weiss paramagnetism with $\mu_{eff} = 0.35\ \mu_B$. This contrasts with the almost total absence of paramagnetism in stoichiometric Li_2MoO_3 prepared by hydrogen reduction of Li_2MoO_4.

Introduction

Oxides containing molybdenum (IV) crystallize with a variety of interesting structures. The common feature is the tendency of Mo(IV) to form localized Mo–Mo bonds with its two unpaired electrons rather than forming broad, delocalized bands as in the tungsten bronzes. Examples of localized Mo–Mo bonding include MoO_2, in which formation of Mo–Mo pairs between Mo(IV) ions in adjacent, edge-sharing octahedra leads to a doubling of the c-axis of the rutile structure (*1*), and $La_2Mo_2O_7$, which also contains Mo_2 pairs (*2*). More complex Mo–Mo bonding is observed in the isostructural series $M_2Mo_3O_8$ (M = Zn, Mg, Mn, Fe, Co, No, Cd) (*3, 4*), in which all the molybdenum is present as triangular Mo_3O_{13} clusters, and in the spinel-like compound $Ga_{0.5}Mo_2S_4$, which contains paramagnetic, tetrahedral Mo_4 clusters (*5*). More generally, Burdett and Hughbanks have carried out extended Huckel calculations on MoO_2^{n-} close-packed layers; they predict the formation of clusters or chains of Mo atoms for all cases where $-1 < n < 1$ (*6*). This prediction is supported by the structure of $Na_{0.85}MoO_2$, which contains infinite zig-zag chains of Mo atoms (*7*).

Until recently it was thought that Li_2MoO_3 was an exception to this general tendency of Mo(IV) compounds to form localized Mo–Mo bonds. On the basis of X-ray powder diffraction data, both Lang (*8*) and Reau *et al.* (*9*) assigned to it the monoclinic β-Li_2SnO_3 structure, which consists of a cubic-close-packed oxide-ion lattice with basal planes of octahedral cation sites filled with Li^+ alternating with basal planes of octahedral sites containing a mixture of $\frac{1}{3}Li^+ : \frac{2}{3}Sn^{4+}$; the Sn^{4+} ions in these layers

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are further ordered into an infinite, planar hexagonal network. However, not only is this structure unexpected for Li_2MoO_3 on the basis of the known crystal chemistry of Mo(IV) oxides, but it is also inconsistent with the X-ray diffraction data: although the powder diffraction pattern of Li_2MoO_3 can be indexed to the β-Li_2SnO_3 unit cell ($C2/c$, $a = 4.97$ Å, $b = 8.61$ Å, $c = 10.10$ Å, $\beta = 99.5°$), a number of peaks that are predicted to be intense for this structure and that are clearly visible in the X-ray diffraction pattern of β-Li_2SnO_3 itself are not observed for Li_2MoO_3. In a recent paper (*10*), one of us suggested that the true structure of Li_2MoO_3 is a novel, disordered type similar to that of α-$NaFeO_2$ but with no ordering of Mo and Li in the mixed ⅓Li : ⅔Mo layers. The Mo(IV) ions themselves were assumed to be present as randomly distributed Mo_3O_{13} clusters within these layers. The resulting unit cell is trigonal ($R\bar{3}m$, $a = 2.884$ Å, $b = 14.834$ Å); the structure is very similar to that of α-$NaFeO_2$ ($R\bar{3}m$, $a = 3.025$ Å, $b = 16.094$ Å), which consists of a cubic-close-packed oxide-ion lattice in which basal planes of octahedral cation sites filled with Na^+ alternate with basal plans of octahedral sites filled with Fe^{3+} ions. The same structure is adopted by Li CoO_2 and $LiNiO_2$. This model provided a good fit to neutron powder diffraction data on a sample of Li_2MoO_3 prepared by hydrogen reduction of Li_2MoO_4; the trigonal lattice parameters given above were obtained from this refinement. The presence of Mo(IV) as Mo_3O_{13} clusters was deduced from the extremely low electronic conductivity of the material and its observed diamagnetism at room temperature (Mo_3O_{13} clusters are diamagnetic). However, the lack of good magnetic susceptibility data and the rather poor quality of the neutron diffraction data which made refinement of individual atomic temperature factors impossible in this earlier study made further research into this system desirable. In this paper we report the preparation, by electrolysis of fused Li_2MoO_4, of crystals of $H_xLi_yMo_zO_3$ having the Li_2MoO_3 structure with partial substitution of H^+ for Li^+. Analysis, thermogravimetry, and single-crystal X-ray structure determination show that the composition of these crystals is $H_{0.23}Li_{1.68}Mo_{1.05}O_3$. The structure is the same trigonal α-$NaFeO_2$-type previously reported for Li_2MoO_3, but there is some evidence from single-crystal X-ray diffraction data for the formation of a displacive superstructure.

Experimental

The crystals of $H_xLi_yMo_zO_3$ were grown by electrolysis of fused Li_2MoO_4. The Li_2MoO_4 was prepared from stoichiometric amounts of MoO_3 and Li_2CO_3 mixed and heated in air at 600°C for 6 hr with intermittent grinding. Approximately 20 g of this material was placed in a zirconia crucible inside a vertically mounted tube furnace. The furnace was continuously flushed with dry N_2, but otherwise no attempt was made to exclude air or moisture. The Li_2MoO_4 (mp 650°C) was heated to 840°C and electrolyzed with 2 cm^2 Pt foil electrodes at a current density of 10 mA cm^{-2} for 60 hr. The measured voltage across the cell was a constant 1.4 V throughout the electrolysis. Crystals of $H_xLi_yMo_zO_3$ formed rapidly at the negative electrode; after growing to a certain size they dropped off the electrode and accumulated at the bottom of the flux. The crystals were recovered by dissolving away the remaining Li_2MoO_4 with cold water, brief washing with 2 M HCl to remove traces of MoO_3, and washing with water and acetone. The electrolysis carried out as described yielded 1.7 g of black, shiny crystals with well-developed hexagonal habits and typical dimensions 0.2 × 0.2 × 0.02 mm. The surface of the crystals appears to degrade slowly on standing in air for a period of days. Single-crystal X-ray diffraction data were collected from two crystals prepared in separate electrolysis runs; they were examined on an ENRAF-NONIUS CAD4 single-crystal diffractometer. Details of the data collection are given in Table II. All subsequent calculations were carried out with the NRCVAX structure package (*12*) on an Alliant IX/80 computer.

A powder sample of Li_2MoO_3 was also prepared by the method of Gleitzer (*11*): Li_2MoO_4 was reduced with H_2 at 650°C for 48 hr with intermittent grinding. Both this material and a sample of the electrochemically grown $H_xLi_yMo_zO_3$ crystals were submitted to the Schwartzkopf microanalytical laboratory for analysis by atomic absorption spectrophotometry. The magnetic susceptibilities of both materials were measured in the temperature range 5–300 K by means of a Faraday balance and thermogravimetric data were collected with a Du-Pont Instruments 951 thermogravimetric analyzer.

Results and Discussion

The results of the chemical analyses carried out on samples of ceramic Li_2MoO_3 prepared by hydrogen reduction of Li_2MoO_4 and on electrochemically grown $H_xLi_yMo_zO_3$ crystals are given in Table I, together with the expected Li and Mo contents for stoichiometric Li_2MoO_3. The ceramic is clearly very close to the stoichiometric composition. However, the electrochemically grown crystals are slightly molybdenum rich and substantially lithium deficient; the Li : Mo ratio in the crystals calculated from this analysis is 1.60 : 1. Such lithium deficiency in the Li_2MoO_3 system is familiar; two previous studies (*10, 13*) have shown that partial topotactic extraction of Li from Li_2MoO_3 is possible with mild oxidizing reagents such as dilute I_2 in acetonitrile. The resulting $Li_{2-x}MoO_3$ has Li vacancies concentrated in the mixed Li : Mo cation layers. It was also shown that substantial amounts of H^+ could be ion-exchanged for Li^+ by stirring the Li_2MoO_3 powder in dilute acid overnight. In the case of the electrochemically grown crystals the thermogravimetry and X-ray diffraction data point to partial substitution of H^+ for Li^+, rather than vacancies on the Li sites, as the reason for the low lithium content. Such substitution could take place if the molten Li_2MoO_4 from which the crystals are grown is sufficiently hygroscopic to retain some dissolved H_2O at 840°C. Figure 1 shows thermogravimetry data for the electrochemically grown crystals in N_2. There is a weight loss near 600°C in N_2 arising from loss of H_2O due to the presence of H^+ in the material. From the magnitude of this weight loss (1.27%), we arrive at an H^+ content of 0.225 H^+ per Li_2MoO_3 formula unit in the crystals. Taking this together with the analytical data we can deduce that the compo-

TABLE I

ELEMENTAL ANALYSIS OF MATERIALS

	Li %(w/w)	Mo %(w/w)
Li_2MoO_3 (calculated)	8.79	60.80
Li_2MoO_3 (powder)	8.70	60.50
$H_{0.23}Li_{1.68}Mo_{1.05}O_3$ (crystals)	7.22	62.24

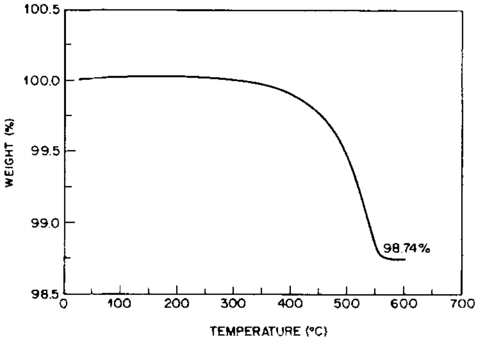

FIG. 1. Thermogravimetric data for a sample of $H_{0.23}Li_{1.68}Mo_{1.05}O_3$ heated in N_2 at 2°C/min.

TABLE II

SUMMARY OF CRYSTALLOGRAPHIC INFORMATION FOR $H_{0.23}Li_{1.68}Mo_{1.05}O_3$

Dimensions (mm)	0.15 × 0.08 × 0.02
Radiation	MoK_α, $\lambda = 0.70930$ Å
Monochromator	Graphite
Crystal system	Rhombohedral
Space group	$R\bar{3}m$ (No. 166)
Temperature	Ambient
Calculated density	4.961 g cm^{-3}
Scan mode	θ–2θ
2θ range	0 to 120°
μ (cm)	56.6
Abs. correction	Gaussian integration
Transmission factors	0.49 to 0.91
Extinction (μm)	0.11(2)
Total reflections	1313
Unique reflections	241
Observed reflections ($I > 2.5\sigma$)	194
R_f (significant reflections)	0.041
R_w (significant reflections)	0.026

sition of the crystals is $H_{0.23}Li_{1.68}Mo_{1.05}O_3$, implying that there are very few vacancies on the octahedral cation sites.

Structural parameters obtained by refinement of the single-crystal diffraction data are given in Table II. The parameters are given for only one of the two crystals studied; the structural parameters obtained from the other crystal were identical to within two standard deviations. The refinement confirms that these crystals have the disordered α-$NaFeO_2$ structure type proposed for Li_2MoO_3, with lattice parameters close to those previously determined for stoichiometric Li_2MoO_3 prepared by hydrogen reduction of Li_2MoO_4 (*10*). One feature that is clear from the refinement is excess occupancy on the molybdenum (3b) sites. Interpretation of this is complicated by the fact that these sites are also occupied by lithium and, perhaps, hydrogen atoms. Since scattering from hydrogen atoms can be ignored and the Li occupancy of these sites must be between 0 and 0.33, we arrive at a fractional Mo occupancy on the 3b sites of 0.70 ± 0.015 and an overall molybdenum : oxygen ratio of 1.05(2):3 (the oxygen site occupancy is normalized to 1.000 in the refinement), fully consistent with the analytical data. The anisotropic thermal parameters of the Mo atoms show large components in the *ab* plane; too large for thermal motions alone. This is exactly what would be expected if formation of Mo_3O_{13} clusters results in small, random in-plane displacements of the Mo atoms from the 3b sites. Indeed, small superstructure reflections with fractional indices in *h* and *k* only were observed, indicating a doubling of the unit cell parameters in the *ab* plane.

The formula $H_{0.23}Li_{1.68}Mo_{1.05}O_3$ determined for the electrochemically grown crystals implies that the average Mo oxidation state in the crystals is only +3.90. Such reduction of the molybdenum can be accommodated by a structure containing Mo_3O_{13} clusters because, according to the calculations by Cotton (*14*), the lowest-energy empty orbital in these clusters is approximately nonbonding. However, the presence of additional, unpaired electrons on the Mo_3O_{13} clusters would be expected to give rise to a magnetic susceptibility. Figure 2 shows plots of inverse magnetic susceptibility versus temperature for the ceramic Li_2MoO_3 prepared by hydrogen reduction of Li_2MoO_4 and for the $H_{0.23}Li_{1.68}Mo_{1.05}O_3$ crystals. Both materials ex-

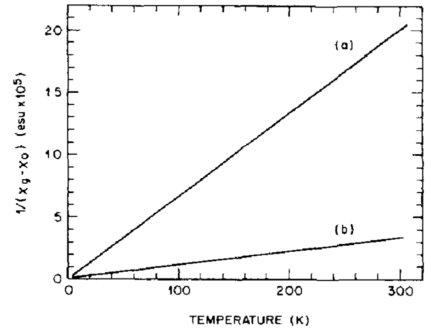

FIG. 2. Inverse magnetic susceptibility $1/(\chi_g - \chi_0)$ versus temperature for (a) ceramic Li_2MoO_3 prepared by hydrogen reduction of Li_2MoO_4; (b) $H_{0.23}Li_{1.68}Mo_{1.05}O_3$crystals.

TABLE III

CRYSTALLOGRAPHIC DATA OF $H_{0.23}Li_{1.68}Mo_{1.05}O_3$ RHOMBOHEDRAL CELL, SPACE GROUP $R\bar{3}m$ (NO. 166), $Z = 1$, $a = 2.8684(3)$ Å, $c = 15.1166(6)$ Å.

Atom	Position	x	y	z	B_{iso}(Å^2)	Occ.	$u_{11} = u_{22}$	u_{33}	u_{12}
Mo	3b	0	0	$\frac{1}{2}$	1.390(19)	0.716(12)	2.36(3)	0.552(19)	1.182
O	6c	0	0	0.2454(3)	1.34(8)		1.38(8)	2.33(15)	0.689
Li	3a	0	0	0	1.6(4)		1.2(3)	3.8(8)	0.579

Note. $u_{13} = u_{23} = 0$. The u_{ij} values are given in Å^2 × 100.

hibit weak Curie–Weiss paramagnetism; fitting the data to an expression of the form

$$\chi_g = \frac{C_g}{T - \Theta} + \chi_0$$

over the temperature range 20–300 K gives $C_g = 91.6 \times 10^{-6}$ emu K g^{-1}, $\chi_0 = 5 \times 10^{-9}$ emu g^{-1}, and $\Theta = 12$ K for the electrochemically grown crystals, and $C_g = 15.1 \times 10^{-6}$ emu K g^{-1}, $\chi_0 = 4 \times 10^{-8}$ emu g^{-1}, and $\Theta = 1$ K for the ceramic. Making the assumptions that this is a localized, magnetically dilute system with $S = \frac{1}{2}$ and no orbital contribution to the susceptibility, the observed Curie constants correspond to an effective magnetic moment of 0.35 Bohr magnetons, or one unpaired electron spin for every 25 Mo atoms in the electrochemically grown $H_{0.23}Li_{1.68}Mo_{1.05}O_3$ crystals. The corresponding values for the powdered Li_2MoO_3 prepared by hydrogen reduction of Li_2MoO_4 are $\mu_{eff} = 0.14\ \mu_B$, or one unpaired electron per 150 molybdenum atoms.

In summary, we have prepared crystalline $H_{0.23}Li_{1.68}Mo_{1.05}O_3$ by electrolysis of fused Li_2MoO_4. The composition of the crystals was determined by chemical analysis and thermogravimetry and confirmed by single-crystal X-ray diffraction. The structure of the crystals was determined; it is of the α-$NaFeO_2$ type with layers containing randomly distributed Mo, probably in the form of Mo_3O_{13} clusters. The crystals exhibit weak Curie–Weiss paramagnetism.

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