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## A family of rare earth molybdenum bronzes: Oxides consisting of periodic arrays of interacting magnetic units

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## ABSTRACT

The family of rare earth molybdenum bronzes, reduced ternary molybdates of composition  $LnMo_{16}O_{44}$ , was synthesized and a detailed structural study carried out. Bond valence sum (BVS) calculations clearly show that the molybdenum ions in tetrahedral coordination are hexavalent while the electron count in the primitive unit cell is odd. Yet, measurements show that the phases are semiconductors. The temperature dependence of the magnetic susceptibility of samples containing several different rare earth elements was measured. These measurements verified the presence of a 6.5 K magnetic phase transition not arising from the rare earth constituent, but likely associated with the unique isolated  $ReO_3$ -type  $Mo_8O_{36}$  structural subunits in this phase. To better understand the behavior of these materials, electronic structure calculations were performed within density functional theory. Results suggest a magnetic state in which these structural moieties have an internal ferromagnetic arrangement, with small  $\sim 1/8 \mu_B$  moments on each Mo. We suggest that the  $Mo_8O_{36}$  units behave like pseudoatoms with spin 1/2 derived from a single hole distributed over the eight Mo atoms that are strongly hybridized with the O atoms of the subunit. Interestingly, while the compound is antiferromagnetic, our calculations suggest that a field-stabilized ferromagnetic state, if achievable, will be a narrow band half-metal.

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## 1. Introduction

Reduced ternary molybdenum oxides, known as bronzes, possess a rich and varied structural chemistry [1]. Additionally, a wide variety of interesting physical phenomena occur in the reduced ternary tungsten and molybdenum oxides including superconductivity [2,3], low dimensional metal physics [4–7], charge density waves and incommensurate structures [8–15]. These basic electronic features arise from the combination of strong hybridization of the 4d states of high-valent Mo with O *p*-orbitals, leading to a tendency towards itinerancy and reduced dimensionality arising from ordered O vacancies. Indeed, it may be argued that these materials were foundational to the study of the chemistry of inorganic materials. Here we describe the synthesis, structural and computational investigations of a family of lanthanoid, or rare earth, molybdenum bronzes of composition  $Ln_{0.25}Mo_4O_{11}$  ( $Ln$ =Lanthanoid), or  $LnMo_{16}O_{44}$ , isostructural to the previously studied  $GdMo_{16}O_{44}$  [16]. These phases have also been reported as

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$Ln_{0.08}MoO_3$  [17,18]. Crystalline samples are prepared by electrolytic reductions of eutectic melts and by direct reaction of stoichiometric mixtures in sealed evacuated fused silica ampoules. Crystallographic changes as a function of lanthanoid size and of temperature are discussed. The temperature dependence of the magnetic susceptibility has been measured for the La, Ce, Pr, and Gd analogs and the samples display paramagnetic behavior with weak antiferromagnetic interactions between the lanthanoids. More interestingly, though, the *d*-orbital occupation in a unique  $Mo_8O_{36}$   $ReO_3$ -type structural subunit leads to a magnetic transition observed in the magnetic susceptibility measurements at temperatures around 6.5 K.

## 2. Experimental

## 2.1. Direct reactions

A 1–2 g charge consisting of stoichiometric mixtures of high purity  $Ln_2O_3$ , Mo, and  $MoO_3$  that had been ground together in agate mortars and pestles were placed in fused silica tubes and sealed under vacuum. The ampoules were heated in a horizontal

tube furnace at a rate of 100 °C/h to 700 °C. The samples were kept at that temperature for at least 5 days and then furnace-cooled. The products had a greenish bronze luster and crystalline facets were often visible under a low power optical microscope. Direct reactions yield large amounts of crystalline product that are often essentially single phase by powder diffraction, with Mo<sub>4</sub>O<sub>11</sub> as the main impurity phase present. Unfortunately, these crystals also suffer from significant amounts of merohedral twinning as discussed later in this paper.

## 2.2. Electrochemical growth

The apparatus used for the electrochemical crystal growth has been described previously [19]. A typical charge of approximately 15 g of MoO<sub>3</sub> and rare earth oxide (Cerac) was vacuum dried before melting. The melt was contained in a new high purity recrystallized alumina crucible (Coors) which was seated in a graphite support. This assembly was contained under inert atmosphere within a quartz vessel itself inside a crucible furnace. In all runs, a Pt foil electrode served as the anode and a 1 mm Pt wire as the cathode. Electrolyses were carried out under galvanostatic control using a Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat equipped with a Model 179 digital coulometer. Following deposition, traces of the melt were removed by gently heating the crystalline product in 12 M HCl.

## 2.3. X-ray analysis

X-ray powder diffraction patterns of the samples were acquired using a Huber Guiner G670 image foil camera with CuK $\alpha_1$  radiation and a cold stage system for a temperature range of 12–300 K. The temperature stability of the cold stage is 0.2 K. The X-ray patterns were analyzed using the Winprep program [20], and unit cell parameters were refined via a full pattern fit. Single crystals were measured on an Oxford Diffraction Xcalibur 2 CCD diffractometer, using graphite-monochromated MoK $\alpha$  radiation. The data frames were analyzed using the CrysAlis suite of programs to produce absorption corrected integrated intensities. The structures were subsequently refined with the CRYSTALS program [21], applying twin laws to account for merohedral twinning where necessary, with the twin law based on a 180° rotation around the *a*-axis. Twin ratios of 0.5/0.5 were common, and the largest ratio was 0.8/0.2. The quality of the crystals from various preparations was sufficient for single crystal X-ray structure refinements in the case of the phases with Ce, Pr, Nd, Tb, Dy and Ho only. These phases span a reasonable range of lanthanoid radii, with the Ce radius of 1.043 Å and the Ho radius of 0.893 Å [22]. However, even in these cases, severe reflection overlap from twinning and from residual flux was observed, and extraction of integrated intensities was hampered and correspondingly, the completeness of the reflection data was reduced. Structure refinements were carried out for data sets with completeness above 0.5 and a minimum of 19 observations per refined parameter (PrMo<sub>16</sub>O<sub>44</sub>). Further details of the crystal structure investigations may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, [http://www.fiz-karlsruhe.de/request\\_for\\_deposited\\_data.html](http://www.fiz-karlsruhe.de/request_for_deposited_data.html)) on quoting the deposition numbers CSD-428592 (CeMo<sub>16</sub>O<sub>44</sub>), -428593 (PrMo<sub>16</sub>O<sub>44</sub>), -428594 (NdMo<sub>16</sub>O<sub>44</sub>), -428595 (TbMo<sub>16</sub>O<sub>44</sub>), -428596 (DyMo<sub>16</sub>O<sub>44</sub>) and -428597 (HoMo<sub>16</sub>O<sub>44</sub>).

## 2.4. First principles calculations

Electronic structure calculations were performed within density functional theory using the linearized augmented plane wave (LAPW) method [23], as implemented in the WIEN2k code [24] and the Perdew–Burke–Ernzerhof (PBE) [25] generalized gradient

approximation (GGA). Using LaMo<sub>16</sub>O<sub>44</sub> as a starting point, we employed LAPW spheres of 2.38 Bohr for La, 1.81 Bohr for Mo, and 1.46 Bohr for O, respectively. The cut-off parameter for the plane wave cutoff,  $K_{\max}$  was determined by the choice  $R_{\min}K_{\max}=7$ , where  $R_{\min}$  is the smallest sphere radius, i.e. 1.46 Bohr. We used a  $3 \times 3 \times 3$  *k*-point mesh during the self-consistent iterations. The calculations reported here are based on the experimental lattice parameters with the internal atomic coordinates determined by energy minimization.

## 2.5. Magnetic susceptibility measurements

The magnetic susceptibilities of powder samples of various rare earth-containing phases were measured between 2 and 300 K in a Quantum Design SQUID magnetometer and an applied field of 0.1 T. Samples were contained in gelatin capsules.

## 3. Results

The reduced lanthanoid molybdenum bronzes all crystallize in a rhombohedral unit cell with space group  $R\bar{3}$ . Crystals investigated often showed merohedral twinning, and an apparent higher symmetry of  $R\bar{3}2$  or  $R\bar{3}m$ . Products obtained from the direct reaction, in particular, did not yield crystals of sufficient size and quality for a single crystal investigation. Furthermore, these samples often contained traces of additional phases, hampering the unit cell determination using powder diffraction methods due to extensive overlap of reflections. The refined lattice parameters for LnMo<sub>16</sub>O<sub>44</sub> samples with a minimum of 60% majority phase are given in Table 1. Unfortunately, it was not possible to extract reliable unit cell data for the Sm and Eu molybdenum bronzes due to excessive amounts of Mo<sub>4</sub>O<sub>11</sub>.

The lanthanide contraction is clearly observed in the *c*-axis parameter, whereas the *a*-axis shows virtually no lanthanide size effect, as is shown in Fig. 1. Since the structure contains only a small fraction of lanthanoid atoms, the Mo<sub>16</sub>O<sub>44</sub> framework is anticipated to dominate the unit cell volume, with only small changes attributed to the radii of the different lanthanide ions. However, the contraction of the *c*-axis is pronounced despite the modest lanthanoid concentration in the unit cell. We examined the linear thermal expansion of GdMo<sub>16</sub>O<sub>44</sub> in the temperature range of 200–300 K in steps of 10 K for potential anomalous behavior, motivated in part by the fact that the *a*-axis is almost constant for different Ln atoms. A positive thermal expansion coefficient of  $6.5(3) \times 10^{-5}$  Å/K along the *a*-axis is observed, while

**Table 1**  
Unit cell parameters of Ln<sub>0.25</sub>Mo<sub>4</sub>O<sub>11</sub> phases.

Ln	Radius [Å]	<i>a</i> [Å]	<i>c</i> [Å]	Volume [Å <sup>3</sup> ]
La	1.071	10.7832(2)	27.6514(6)	2784.5(3)
Ce	1.034	10.7867(2)	27.6168(6)	2782.8(3)
Pr	1.013	10.7732(2)	27.5414(8)	2768.3(3)
Nd	0.995	10.7881(3)	27.5338(9)	2775.2(4)
Sm	0.964			
Eu	0.95			
Gd	0.938	10.7860(3)	27.4778(9)	2768.4(4)
Tb	0.923	10.7724(2)	27.4449(8)	2758.1(4)
Dy	0.908	10.7782(2)	27.4308(7)	2759.7(3)
Ho	0.894	10.7808(2)	27.4364(6)	2761.6(3)
Er	0.881	10.7867(3)	27.4357(9)	2764.5(4)
Tm	0.869	10.7839(5)	27.3701(9)	2756.5(4)
Yb	0.858	10.7842(3)	27.3942(9)	2759.1(4)
Lu	0.848	10.7815(3)	27.3744(9)	2755.7(4)
Y	0.905	10.7827(3)	27.4567(9)	2764.6(4)

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