Synthesis and characterization of the oxynitride pyrochlore - Sm$_2$Mo$_2$O$_{3.83}$N$_{3.17}$

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Abstract

Sm$_2$Mo$_2$O$_{3.83}$N$_{3.17}$, the first molybdenum oxynitride pyrochlore, was synthesized by heating the Sm$_2$Mo$_2$O$_7$ pyrochlore in flowing ammonia at 625°C for 24 hours. Sm$_2$Mo$_2$O$_{3.83}$N$_{3.17}$ forms with the cubic pyrochlore structure, space group $Fdar{3}m$ ($a = 10.4975$ Å). The sample is semiconducting and the temperature-dependent magnetic susceptibility follows Curie-Weiss behavior. X-ray absorption near-edge spectroscopy measurements indicate that in the oxynitride, molybdenum has a formal oxidation state significantly larger than $+4$. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Since the reports of colossal magnetoresistance in Tl$_2$Mn$_2$O$_7$, there has been a great deal of interest in pyrochlore-type compounds [1]. The pyrochlores, A$_2$B$_2$O$_6$O’, contain a 3D network of corner-sharing BO$_6$ octahedra with a B-O-B bond angle $\sim 135^\circ$ interconnected with a network of A$_2$O’ chains where the A cation is coordinated to eight oxygen positions (6-O and 2-O’). The pyrochlore Sm$_2$Mo$_2$O$_7$ was first synthesized in 1971 by McCarthy [2]. Subramanian et al. [3] reported a semi-metallic behavior from room temperature to low
temperatures with a ferromagnetic ordering at 77 K [3,4]. Recently Taguchi et al. reported that polycrystalline and single crystals of Sm$_2$Mo$_2$O$_7$ exhibit a large negative magnetoresistance around 77 K [5].

The pyrochlore structure tolerates a large variety of chemical substitutions. In fact, the mineral pyrochlore, (NaCa)(NbTa)O$_6$F/(OH), contains O$^{2-}$, F$^-$ and hydroxide anions [6]. There are several reports of anionic substitutions in pyrochlore-type materials: Pannetier et al. [7] reported that some of the oxygen atoms can be replaced by S$^{2-}$ in Cd$_2$Nb$_2$O$_7$, producing a phase that exhibits ferroelectricity at high temperatures [8]. There have also been reports of the formation of tantalum oxynitride [9,10] and titanium oxynitride pyrochlores [11].

Our objective in this work was to induce mixed Mo valancies in the Sm$_2$Mo$_2$O$_7$ pyrochlore by substitution of N$^{3-}$ for O$^{2-}$ and to investigate the effects of the substitutions on the physical properties. A common synthetic method for the synthesis of oxynitrides is the heating of the parent oxide in flowing gaseous ammonia at elevated temperatures [12–14]. Under favorable conditions, partial substitution of oxygen by nitrogen yields an oxynitride with properties that differ from those of the parent oxide. In this paper we report on the synthesis and properties of Sm$_2$Mo$_2$O$_{3.83}$$N_{3.17}$ prepared by ammonolysis of Sm$_2$Mo$_2$O$_7$.

2. Experimental

Stoichiometric amounts of MoO$_3$ (99%, Alfa) and Sm$_2$O$_3$ (99.99% Alfa) were thoroughly ground in an agate mortar, sealed in a quartz tube under vacuum ($\sim$10$^{-5}$ torr) and sintered at 1250°C for 24 hours to obtain Sm$_2$Mo$_2$O$_7$. The oxygen content of MoO$_3$ was verified by thermally oxidizing a sample to MoO$_3$ under O$_2$ in a TA Instrument 2050 thermal analyzer. The Sm$_2$O$_3$ was heated to 1000 °C for 24 hours prior to use. For the synthesis of the oxynitride, Sm$_2$Mo$_2$O$_7$ in an alumina boat was placed in a quartz tube and annealed under flowing ammonia (Tanner Industries) at 625°C for 24 hours followed by furnace cooling to room temperature.

Powder X-ray diffraction (PXD) data were collected with a Scintag PAD V diffractometer with Ni-filtered CuK$_\alpha$ radiation and a Li-drifted germanium detector. Data were collected over a range of 10° $\leq$ 2$\theta$ $\leq$ 110° with a step size of 0.02°. Silicon was used as an internal standard. Lattice parameters were calculated by Rietveld refinement with the program GSAS [15].

Temperature-dependent magnetic-susceptibility, $\chi$, measurements were made with a Quantum Design MPMS-XL SQUID magnetometer. The susceptibility data were collected after cooling the sample from 5 to 400 K in the absence (ZFC) and in an applied magnetic field (FC) of 1000 G, respectively. Temperature-dependent resistivity, $\rho$, was measured with conventional four-point probe techniques at two magnetic fields, 0 and 5 T, in the SQUID.

The Mo L-edge X-ray absorption near-edge spectroscopy (XANES) measurements were performed on beam line X-19A at the Brookhaven National Synchrotron Light Source using a double crystal Si [111] monochromator. Fluorescence and electron-yield measurements were made and checked for consistency. The relative energies between various spectra were established by comparison with standard spectra. In general, the relative accuracy of the
energy is about ±0.1 eV. All spectra were normalized to unity step in the absorption coefficient from well below to well above the edge.

Nitrogen analysis was performed by Quantitative Technologies Inc., Whitehouse, NJ. The nitrogen content of the oxynitride was 7.34 ± 0.3%, which is consistent with the formation of Sm$_2$Mo$_2$O$_{3.83}$N$_{3.17}$.

3. Results and Discussion

The synthesis of the Sm$_2$Mo$_2$O$_7$ pyrochlore has been reported before [3,4]. The structural, magnetic (Fig. 1), and electrical properties (Fig. 2) of Sm$_2$Mo$_2$O$_7$ prepared here are consistent with previously reported results [2–4,16].

The ammonolysis of Sm$_2$Mo$_2$O$_7$ yields Sm$_2$Mo$_2$O$_{3.83}$N$_{3.17}$ reproducibly. The PXD data (Fig. 3) show a single-phase pyrochlore; no impurities are observed. Further, the absence of a superconducting transition in the susceptibility at ~12 K also rules out any trace of a MoN impurity in the sample [17]. The broad, poorly defined higher angle reflections are presumably due to the relatively poor crystallinity of Sm$_2$Mo$_2$O$_{3.83}$N$_{3.17}$. The slightly
larger lattice parameters for the oxynitride Sm$_2$Mo$_2$O$_{3.83}$N$_{3.17}$ (a = 10.4975 Å) compared to that of the parent Sm$_2$Mo$_2$O$_7$ (a = 10.398 Å) reflect the competing effects of the enlargement of the volume due to the larger N$^{3-}$, $r_{\text{eff}} = 1.32$ Å [18,19] replacing the smaller O$^{2-}$ anion, $r_{\text{eff}} = 1.24$ Å [18,19] and the decrease of the volume due to the oxidation of Mo$^{4+}$, $r_{\text{eff}} = 0.79$ Å [18,19] to Mo$^{5+}$, $r_{\text{eff}} = 0.75$ Å [18,19].

Rietveld refinement was carried out in the space group $F3d m$. The background was modeled by a Chebyschev polynomial of the first kind and the peak shape was described by a pseudo-Voigt function. There are two sites in the pyrochlore $Fd3m$ structure over which the O/N can be distributed: 48f and 8b [6]. Using as constraints the total amount of O and N in the sample based on the elemental analysis, assuming unit occupancy at each site, taking O/N [1] and O/N [2] ratios at 0.55:0.45 on each site and allowing the atomic positions to refine over the two sites gave the structural parameters of Table 1. These considerations were based on previously reported neutron-diffraction results in oxynitride perovskites where there was no anion ordering observed [20,21]; moreover, the similar X-ray scattering factors of N$^{3-}$ and O$^{2-}$ rule out the possibility of differentiating N and O by PXD. The isotropic thermal parameters were constrained to refine together for O/N [1] and O/N [2] (Table 1). The X-ray diffraction pattern including the raw data, the fitted profile and the difference plot are shown.

Fig. 2. Temperature-dependent resistivity data for Sm$_2$Mo$_2$O$_{3.83}$N$_{3.17}$ at 0 and 5 T. (Inset Temperature-dependent resistivity data for Sm$_2$Mo$_2$O$_7$).
in Fig. 3. Neutron-diffraction studies are needed to determine whether there is any anion ordering in the structure.

The magnetic susceptibility of the oxynitride as a function of temperature is shown in Fig. 4. There was no appreciable difference between the FC and ZFC susceptibilities, nor was there any FM ordering similar to that observed for Sm$_2$Mo$_2$O$_7$, Fig. 1. The observed magnetic data were analyzed with the equation:

$$\chi(T) = \chi_{\text{dia}} + \chi_0 + C/(T - \theta)$$

where $\chi_{\text{dia}}$ is the contribution to the total susceptibility from the core diamagnetic ions. $\chi_{\text{dia}}$ was determined to be negligible and excluded from the calculation. By considering the

![X-ray diffraction data for Sm$_2$Mo$_2$O$_7$ and O/N ratio](image)

Fig. 3. Observed (+), calculated (solid line) and allowed reflections (tic) X-ray diffraction data for Sm$_2$Mo$_2$O$_{3.83}$N$_{3.17}$. Difference plot is at the bottom.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
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<th>y</th>
<th>z</th>
<th>U$_{iso}$(Å$^2$)</th>
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<tr>
<td>Sm</td>
<td>16d</td>
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<td>0.500</td>
<td>0.500</td>
<td>0.00442</td>
</tr>
<tr>
<td>Mo</td>
<td>16c</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.00265</td>
</tr>
<tr>
<td>O/N(1)$^a$</td>
<td>48f</td>
<td>0.323(5)</td>
<td>0.125</td>
<td>0.125</td>
<td>0.01387</td>
</tr>
<tr>
<td>O/N(2)$^a$</td>
<td>8b</td>
<td>0.375</td>
<td>0.375</td>
<td>0.375</td>
<td>0.08559</td>
</tr>
</tbody>
</table>

$^a$ = O/N ratio 0.55/0.45. $a = 10.4975(5)$ Å. $\chi^2 = 1.773$. wRp = 0.0561. Rp = 0.0438.
derivative of the susceptibility with respect to temperature we can eliminate $x_o$, the temperature independent Pauli term. Specifically, by plotting $[d\chi/dT]^{-1/2}$ versus $T$ [100–350 K] the Curie constant, $C$, and Weiss constant, $\theta$, were estimated to be 0.23 (K emu/mole) and $-26$ K, respectively. The negative Weiss constant indicates that the exchange interactions are antiferromagnetic, but no long-range order was observed down to 5 K. In contrast, $C$ and $\theta$ for Sm$_2$Mo$_2$O$_7$ were estimated to be 1.74 (K emu/mole) and 114 K, respectively, which are close to those previously reported [4]. The $x_o$ portion of the oxynitride was estimated to be $2.04 \times 10^{-3}$ emu/mole. The calculated $\mu_{\text{eff}}$ (0.65 $\mu_B$) is in good agreement with the theoretical full $\mu_{\text{eff}}$ (0.84 $\mu_B$) for Sm$^{3+}$ especially in view of the fact that a crystal-field Sm$^{3+}$ moment reduction in this temperature range can be expected. The results suggest that the Curie-Weiss portion of the magnetic data is due solely to the Sm$^{3+}$ ions and the temperature-independent portion, $x_o$, is due to electrons on the Mo ions. The magnitude of the Weiss temperature for the oxynitride coincides with the temperature where the magnetization decreases in Sm$_2$Mo$_2$O$_7$ (Fig. 1). Ali et al. [4] suggested that this decrease in susceptibility below 25 K may be due to antiferromagnetic Mo(IV)-Sm(III) coupling. Recently, Yasui et al confirmed

Fig. 4. Temperature-dependent magnetic susceptibility data for Sm$_2$Mo$_2$O$_{3.83}$N$_{3.17}$. (Inset inverse susceptibility vs. temperature for Sm$_2$Mo$_2$O$_{3.83}$N$_{3.17}$).
by neutron diffraction study of Nd\textsubscript{2}Mo\textsubscript{2}O\textsubscript{7} that the spontaneous order of the Nd moments at low temperature partially cancels that of the Mo moments, because the net magnetization of the Mo and Nd moments are anti parallel [22]. In the oxynitride, Sm-Sm interactions are more likely to be responsible for antiferromagnetic coupling at low temperature. In the oxynitride, loss of conduction electrons, disorder on the anion site, and covalency effects appear to destroy the FM order of the parent compound. Moreover, in the oxynitride, strong Mo-N covalent bonding result in a delocalization of the Mo-4d electrons in spin-paired Mo-N:pπ-Mo interactions.

The electrical resistivity behavior of this oxynitride (Fig. 2) is very different from that of the parent pyrochlore (Fig. 2, Inset). The oxynitride exhibits polaronic (or variable-range hopping) behavior with a room-temperature resistivity $\rho_{RT} \sim 0.6$ ($\Omega$-cm) whereas Sm\textsubscript{2}Mo\textsubscript{2}O\textsubscript{7} exhibits metallic conduction with a room-temperature resistivity of $1 \times 10^{-3}$ ($\Omega$-cm) $[3]$. The activation energy of conduction, $E_a$, was estimated from the $\ln \rho$ ($\Omega$-cm) vs. $1/T$ [K] plot in the temperature range 120 to 300 K; it was determined to be $\sim 0.078$ eV. This

Fig. 5. Mo-$L_2$ edge XANES data.
value is considerably larger than what has been reported for other Mo pyrochlores [3]. These larger values of $\rho_{RT}$ and $E_a$ are attributed to a strong perturbation of the periodic potential on the Mo$_2$O$_{6-x}$N$_x$ array. No magnetic field dependence of the resistivity was observed.

The Mo-L$_{2,3}$ edges involve transitions into empty 4d final states and are consequently very useful probes of both the 4d state occupancy and energy distribution. The Mo-L$_2$(L$_3$) edges in Fig. 5 [6] are dominated by an intense “white line” (WL) 4d-feature. In the octahedral-coordination oxide spectra, a distinct bimodal A-B feature structure is seen with the A (B) feature being associated with t$_{2g}$ (e$_g$) hole states. Both the A/B intensity ratio and the center of spectral mass (chemical shift) of the WL (i.e. A+B) feature, are Mo-valence-state indicators.

The oxide WL features in Fig. 5 and 6 are dramatically shifted to higher energy relative to elemental Mo, consistent with their valence in the 4–5.5 range. The WL-feature centrums
for the oxynitride spectra are much lower in energy than the SrCr_{0.6}Mo_{0.4}O_3, Mo^{5.5+}. Moreover, in the N-substituted compound, the WL-feature manifests a clear upward shift in energy relative to the pure O-pyrochlore. Thus the chemical shift evidence clearly supports an increase in Mo-valence with N substitution.

Turning to the relative A-B feature spectral weight, we first note that the SrCr_{0.6}Mo_{0.4}O_3 standard provides an example of this ratio for nearly empty 4d-orbitals (a t_{2g}:e_g hole ratio of 5.5:4). The relative A (t_{2g}) intensities of the pyrochlore compounds are dramatically smaller, consistent with their smaller t_{2g} hole count. Importantly we note that the A (t_{2g}) feature is markedly enhanced (relative to the B-feature) upon N-substitution into the pyrochlore compounds, consistent with the introduction of t_{2g} holes. Thus the WL-feature structure also unambiguously indicates that N for O substitution in the oxynitride leads to the transfer of charge out of nearly all the Mo-d orbitals.

Assuming full O/N occupancy, the oxynitride material should have a formal Mo-valence of 5.6. It is clear from the much smaller relative A-feature intensity (relative to that of the SrCr_{0.6}Mo_{5.5+}O_{0.4}O_3 standard) that the Mo-valence in the oxynitride material is substantially less than 5.5+. As noted above, this observation is also supported by the WL chemical shift results. Given the chemical analysis of our compound, it would appear that the nitrogens on the Mo_2O_{6-x}N_x array are not fully reduced to N^{3-} as a result of overlap of the N-2p states and the Mo(VI)/Mo(V) redox energy.

Finally it should also be noted that the A-feature in the pure-O-pyrochlore spectrum lies at a particularly low energy, which contributes to the A-B splitting in the pure-O compound being about 2.5 eV as opposed to about 1.7 eV in the N-substituted compound. The splitting between t_{2g} and e_g orbitals is due to differences in π-bond and σ-bond covalent mixing. Stronger π bonding with nitrogen near neighbors raises the t_{2g} levels relative to the e_g for near-neighbor oxygen atoms.

4. Conclusion

We have successfully prepared the first reported molybdenum oxynitride pyrochlore, Sm_2Mo_2O_{3.83}N_{3.17}. The oxynitride has dramatically different physical properties than that of the parent compound, Sm_2Mo_2O_7. This difference is attributed to several factors including a random distribution of anions on the Mo_2O_{6-x}N_x array, which introduces a strong perturbation of the periodic potential that traps electrons in Anderson-localized states, and strong Mo-N-Mo interactions that delocalize the Mo-4d electrons.

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