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Topochemical Synthesis of Europium Molybdenum Oxynitride Pyrochlores

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Materials based on stoichiometric mixed metal oxynitrides show many important properties,[1] for example, $CaTaO_2N$-$LaTaON_2$ red-yellow pigments,[2] the lithium battery material $Li_{7.9}MnN_{3.2}O_{1.6}$,[3] $BaTaO_2N$, which has a high dielectric constant[4] and photocatalytic activity,[5] and the CMR (colossal magnetoresistance) materials $EuNbO_2N$[6] and $EuWON_2$.[7,8] Such phases can be difficult to synthesize, as the high temperatures required to activate cation diffusion also lead to nitrogen loss. This can be overcome through the use of high pressure, for example, to synthesize $RZrO_2N$ perovskites (R = Pr, Nd and Sm) directly from R_2O_3 and Zr_2ON_2,[9] but a more common strategy is to heat an oxide precursor containing the metals in the desired ratio under a flow of ammonia gas (ammonolysis). This has been used to prepare many mixed metal oxynitrides and is usually accompanied by structural rearrangement, for example, $La_2Zr_2O_7$ pyrochlore to $LaZrO_2N$ perovskite,[10] scheelite types $RTaO_4$ to $R_2Ta_2O_5N_2$ pyrochlores for R = Nd, Sm, Gd, Dy,[11] and $EuMO_4$ scheelites to $EuMO_2N$ perovskites for M = Nb and Ta.[6] $R_2W_2O_9$ are ammonolyzed to RWO_3N scheelites for R = Pr, Nd, Sm, Gd, Dy,[12] but $Eu_2W_2O_9$ undergoes two structural rearrangements to form the perovskite $EuWON_2$ via the scheelite $EuWO_4$.[8] Reported transformations of $R_2Mo_2O_7$ pyrochlores (R = Sm and Y) to isostructural $Sm_2Mo_2O_{3.83}N_{3.17}$[13] and $Y_2Mo_2O_{4.5}N_{2.5}$,[14] are thus a rare example of structure retention, but the necessity of structural control and the ranges of anion content were not explored. Following discoveries of CMR in $EuNbO_2N$ and $EuWON_2$,[6−8] we have explored the synthesis of possible $EuMo(O,N)_3$ perovskites through ammonolysis of two precusors with different structures and oxidation state distributions, $Eu^{3+}{}_2Mo^{4+}{}_2O_7$ and $Eu^{2+}\ Mo^{6+}O_4$.[15] This has led to the discovery of unambiguous structural control in mixed metal oxynitride synthesis, as we show that anion-deficient pyrochlores based on $Eu_2Mo_2O_5N_2$ are obtained from ammonolysis of the pyrochlore $Eu_2Mo_2O_7$, but not from the scheelite precursor $EuMoO_4$ under identical conditions. $R_2Mo_2O_5N_2$ pyochlores could be excellent materials to explore the ground states of highly frustrated $S = 1/2$ magnets.

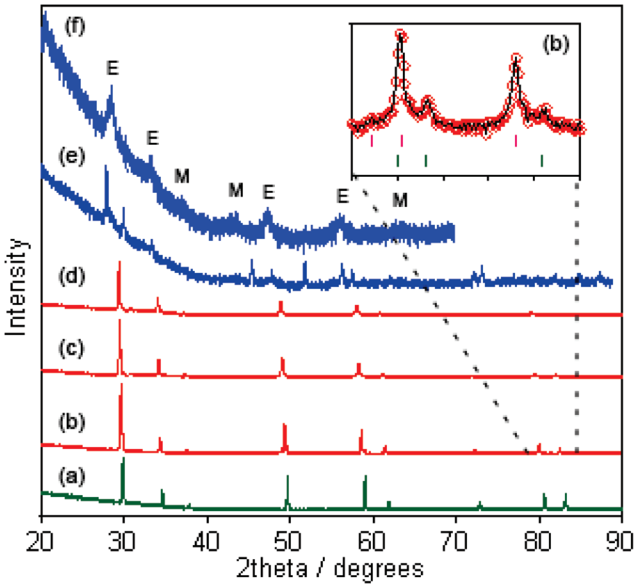

Figure 1. Powder X-ray diffraction patterns of $Eu_2Mo_2O_7$, (a) as-synthesized and after ammonolysis for 12 h at (b) 500, (c) 600, and (d) 630 °C. $EuMoO_4$ ammonolyzed at 600 °C (e) shows slight decomposition after 3 h, and (f) is fully decomposed to a mixture of poorly crystalline Eu_2O_3 (E) and γ-Mo_2N (M) after 24 h. The inset expansion of (b) for 2θ = 79−84° shows the fitted peaks from $Eu_2Mo_2O_7$ (lower markers) and $Eu_2Mo_2O_5N_2$ (upper markers) pyrochlore phases.

Ammonolysis of pyrochlore type $Eu_2Mo_2O_7$ at 500−630 °C[16] resulted in the formation of a pyrochlore type oxynitride, as shown in Figure 1 and Table 1, although prolonged treatment resulted in decomposition to Eu_2O_3 and γ-Mo_2N. The cubic cell parameter and nitrogen

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(1) Fuertes, A. *Dalton Trans.* **2010**, *39*, 5942–5948.
(2) Jansen, M.; Letschert, H. P. *Nature* **2000**, *404*, 980–982.
(3) Cabana, J.; Rousse, G.; Fuertes, A.; Palacín, M. R. *J. Mater. Chem.* **2003**, *13*, 2402–2404.
(4) Kim, Y.; Woodward, P. M.; Baba-Kishi, K. Z.; Tai, C. W. *Chem. Mater.* **2004**, *16*, 1267–1276.
(5) Highashi, M.; Abe, R.; Takata, T.; Domen, K. *Chem. Mater.* **2009**, *21*, 1543–1549.
(6) Jorge, A. B.; Oró-Solé, J.; Bea, A. M.; Mufti, N.; Palstra, T. T. M.; Rodgers, J. A.; Attfield, J. P.; Fuertes, A. *J. Am. Chem. Soc.* **2008**, *130*, 12572–12573.
(7) Kusmartseva, A.; Yang, M.; Oró-Solé, J.; Jorge, A. B.; Fuertes, A.; Attfield, J. P. *Appl. Phys. Lett.* **2009**, *95*, 022110.
(8) Yang, M.; Oró-Solé, J.; Kusmartseva, A.; Fuertes, A.; Attfield, J. P. *J. Am. Chem. Soc.* **2010**, *132*, 4822–4829.
(9) Yang, M.; Rodgers, J. A.; Middler, L. C.; Oró-Solé, J.; Jorge, A. B.; Fuertes, A.; Attfield, J. P. *Inorg. Chem.* **2009**, *48*, 11498–11500.
(10) Clarke, S. J.; Guinot, B. P.; Michie, C. W.; Calmont, M. J. C.; Rosseinsky, M. J. *Chem. Mater.* **2002**, *14*, 288–294.
(11) Maillard, P.; Tessier, F.; Orhan, E.; Cheviré, F.; Marchand, R. *Chem. Mater.* **2005**, *17*, 152–156.
(12) Antoine, P.; Marchand, R.; Laurent, Y. *Rev. Int. Hautes Temp. Refract. Fr.* **1987**, *24*, 43–46. Cheviré, F.; Tessier, F.; Marchand, R. *Mater. Res. Bull.* **2004**, *39*, 1091–1101.
(13) Veith, G. M.; Greenblatt, M.; Croft, M.; Goodenough, J. B. *Mater. Res. Bull.* **2001**, *36*, 1521–1530.
(14) Martinez-Lope, M. J.; Casais, M. T.; Alonso, J. A. *Z. Naturforsch.* **2006**, *61B*, 164–169.
(15) McCarthy, G. J. *Mater. Res. Bull.* **1971**, *6*, 31–39.

Table 1. Cell Parameters, Analyzed Compositions, and Average Mo Oxidation States $+n$ for $Eu_2Mo_2O_{5-x}N_{2+x-\delta}$ Samples Prepared by Ammonolysis of Various Masses of $Eu_2Mo_2O_7$[a] for 12 h at 500−630 °C with a Flow Rate of 250 cm^3/min

T (°C)	mass (mg)	a (Å)	x	δ	δ/x	n
500[b]	200	10.3859(1)				4
		10.4479(2)	0.08			5.04
550	200	10.4532(1)	0.40	0.08	0.20	5.08
550	85	10.4917(1)	1.21	0.11	0.09	5.44
600	200	10.4979(2)	1.13	0.21	0.19	5.25
615	200	10.5070(2)	1.25	0.19	0.15	5.35
630	100	10.5386(4)	1.74	0.29	0.17	5.43

[a] The $Eu_2Mo_2O_7$ precursor has a = 10.3832(1) Å. [b] Fitting of X-ray diffraction data (Figure 1b) shows that this sample is a mixture of 20(1)% $Eu_2Mo_2O_7$ (upper row) and 80% $Eu_2Mo_2O_{5-x}N_{2+x-\delta}$, (lower row) pyrochlores. The N excess of the latter phase x is estimated from the bulk analyzed content of 1.66 N atoms/formula unit, assuming $\delta = 0$ and that the $Eu_2Mo_2O_7$ phase has negligible nitrogen content.

content[17] of the oxynitride phase increase with ammonolysis temperature and surface area. The $Fd\bar{3}m$ pyrochlore superstructure of the fluorite structural arrangement is confirmed by observation of the (331) X-ray peak at $2\theta \approx 37°$ (Figure 1) and by electron diffraction (see the Supporting Information). Two pyrochlore phases were observed in the sample ammonolyzed at 500 °C (see Figure 1b). One has a lattice parameter that is very close to that of $Eu_2Mo_2O_7$, although the small shift indicates that a very limited nitrogen substitution may occur. The other pyrochlore has a composition close to $Eu_2Mo_2O_5N_2$, demonstrating that $Eu_2Mo_2O_7$ is initially converted to a distinct phase that is analogous to $R_2Ta_2O_5N_2$ phases.[11] There is no miscibility (solid solution) between the pyrochlores $Eu_2Mo_2O_7$ and $Eu_2Mo_2O_5N_2$ although they are isostructural (Figure 2a), showing that nitride only stabilizes high Mo oxidation states ($\geq +5$) in this structure type.

The single-phase oxynitride pyrochlores have nitrogen contents of 2.3−3.5 atoms per formula unit showing that further nitridation of $Eu_2Mo_2O_5N_2$ occurs. Two facile compensation mechanisms are available; oxidation of Mo^{5+} to Mo^{6+} and the formation of anion vacancies. Hence these phases are formulated $Eu_2Mo_2O_{5-x}N_{2+x-\delta}$ and the substitutional (x) and anion deficiency (δ) variables shown in Table 1 were determined by performing nitrogen and thermo-gravimetric analyses. The possible range of anion deficiency is $0 < \delta < x/3$, where $\delta = 0$ corresponds to maximum oxidation, i.e., $Eu_2Mo^{(5+x/2)+}{}_2O_{5-x}N_{2+x}$ up a limit of $x = 2$ for Mo^{6+}, whereas $\delta = x/3$ describes vacancy formation at a constant oxidation state, i.e., $Eu_2Mo^{5+}{}_2O_{5-x}N_{2+2x/3}$. Four of the analyzed samples are halfway between these limits, with $\delta/x = 0.15-0.20$, and their lattice parameters show a linear correlation with nitrogen content (Figure 2a). A high-surface-area sample ammonolyzed at low temperature (550 °C) has a significantly lower $\delta/x = 0.09$, and the lattice parameter does not follow the trend of the others. This shows that Mo oxidation state and anion vacancy formation can be varied independently in the $Eu_2Mo_2O_{5-x}N_{2+x-\delta}$ pyrochlores. Reduction of Eu^{3+} to Eu^{2+} is also possible under ammonolysis conditions, but comparison of the refined Eu−O/N distance of 2.40 Å in the crystal structure of $Eu_2Mo_2O_{3.87}N_{2.92}$ (see the Supporting Information) to the predicted values of 2.46 and 2.65 Å from the respective ionic radii of Eu^{3+} and Eu^{2+} shows that no substantial reduction of Eu^{3+} occurs. Furthermore, these phases have a very similar structure and composition to $Y_2Mo_2O_{4.5}N_{2.5}$, where no reduction of yttrium is likely.

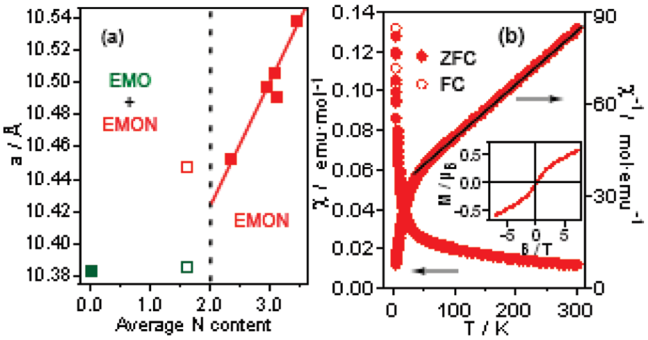

Figure 2. Results for $Eu_2Mo_2O_{5-x}N_{2+x-\delta}$. (a) Plot of cell parameters against average N content for samples in Table 1 showing the miscibility gap (two phase region) between the $Eu_2Mo_2O_7$ (EMO) and $Eu_2Mo_2O_{5-x}N_{2+x-\delta}$(EMON) pyrochlores. Both phases (open symbols) are observed in a sample with average N content of 1.66. (b) Zero-field-cooled (ZFC) and field-cooled (FC) ac magnetic susceptibilities and the inverse ZFC susceptibility of $Eu_2Mo_2O_{3.75}N_{3.06}$, using a 0.01 T magnetic field. The paramagnetic moment derived from the linear fit is 6.77 μ_B/f.u. The inset shows the magnetization-field loop at 5 K.

The $Eu_2Mo_2O_{5-x}N_{2+x-\delta}$ phases have Mo oxidation states $n = 5.0-5.5$, so 0.5−1.0 d electrons are present per Mo. Sintered pellets are semiconducting with room temperature resistivities of 1−10 Ωcm and activation energies of 60−80 meV. The high temperature Curie−Weiss behavior (Figure 2b) shows that strong antiferromagnetic interactions are present (Weiss constant $\theta = -183$ K), in contrast to $Eu_2Mo_2O_7$ which is metallic and orders ferromagnetically at 56 K.[18] Ferromagnetic correlations

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(16) $Eu_2Mo_2O_7$ and $EuMoO_4$ precursors were synthesised from Eu_2O_3, MoO_3, MoO_2, and Mo (all 99.99%, Aldrich) in stoichiometric ratios. Eu_2O_3 and MoO_3 were preheated at 800 and 350 °C, respectively. $Eu_2Mo_2O_7$: a pellet of Eu_2O_3 and MoO_2, sandwiched between two pieces of Mo foil and covered by Mo powder, was heated in an alumina boat at 1450 °C for 24 h under flowing argon. $EuMoO_4$: a pellet of Eu_2O_3, MoO_3, and Mo was sealed in an evacuated quartz tube and heated to 600 °C for 24 h and 1050 °C for 36 h. Both black, air-stable solid products were phase pure by powder X-ray diffraction; 85−300 mg of the precursors were placed in an alumina boat (sample surface area was altered by spreading different masses over the same 0.5 × 1.0 cm^2 area) within a tube furnace and heated at temperatures of 500−1000 °C for times of 3−48 h and then slow cooled to room temperature under ammonia gas (99.999%, BOC) with flow rates of 20−250 cm^3/min. Pellets for resistivity measurements were heated at 500 °C for 3 h under a 250 cm^3/min flow of ammonia.

(17) Powder X-ray diffraction patterns were recorded using a $\theta-2\theta$ diffractometer with monochromatic CuKα1 radiation. Data were taken in the range 2θ = 10−90° at a 0.007° step size, with 3 s count times. Electron diffraction micrographs were obtained in a JEOL 1210 transmission electron microscope operating at 120 KV. Nitrogen contents were measured as N_2 gas by a combustion method using a Carlo Erba CHNS analyzer. An average from three analyses of approximately 3 mg material was taken for each sample. Thermogravimetric analysis was performed using a TG/DSC Netzsch STA 449 F1 Jupiter while heating up to 1000 °C under flowing O_2, resulting in oxidation to Eu_2O_3 and MoO_3 with loss of N_2 gas. Magnetization and four-probe resistivity measurements at 2−300 K were obtained using Quantum Design PPMS and MPMS instruments.

(18) Kézsmárki, I.; Hanasaki, N.; Watanabe, K.; Iguchi, S.; Taguchi, Y.; Miyasaka, S.; Tokura, Y. *Phys. Rev. B* **2006**, *73*, 125122. Hanasaki, N.; Watanabe, K.; Ohtsuka, T.; Kézsmárki, I.; Iguchi, S.; Miyasaka, S.; Tokura, Y. *Phys. Rev. Lett.* **2007**, *99*, 086401.

are seen at low temperatures but no long-range order is apparent down to 2 K, evidencing considerable magnetic frustration. Hence $R_2Mo_2O_5N_2$ pyochlores could be excellent materials to explore the ground states of highly frustrated $S = 1/2$ magnets.

A notable result is that ammonolysis of scheelite type $EuMoO_4$ under the same conditions results in direct decomposition (see Figure 1e, f) without a pyrochlore, perovskite, or any other oxynitride phase being formed. This is surprising, as other scheelite oxides are converted to pyrochlore or perovskite oxynitrides as noted above. This demonstrates that the $Eu_2Mo_2O_{5-x}N_{2+x-\delta}$ phases are only accessible from the $Eu_2Mo_2O_7$ precursor and hence the structural relationship is necessary, i.e., the ammonolysis reaction is topochemical. It is likely that the reaction is also topotactic, but in situ study of individual crystal transformations would be needed to confirm this. A probable explanation for the topochemistry/topotacticity is that these oxynitrides are thermodynamically unstable with respect to the formation of low-valent binary Mo nitrides such as γ-Mo_2N, and are only formed as metastable intermediates during the ammonolysis process.

In conclusion, a metastable anion-deficient pyrochlore phase $Eu_2Mo_2O_{5-x}N_{2+x-\delta}$ $(0 < x < 1.74, 0 < \delta < 0.29)$ is obtained from ammonolysis of $Eu_2Mo_2O_7$ but not from $EuMoO_4$. This demonstrates structural control of reactivity, however $Eu_2Mo_2O_7$ and $Eu_2Mo_2O_5N_2$ do not form solid solutions despite their structural relationship. This suggests that other distinct new stoichiometric oxynitrides may be discovered from ammonolysis of mixed metal oxide precursors with appropriate structures. $R_2Mo_2O_5N_2$ phases may show novel magnetic ground states resulting from frustration within a pyrochlore lattice of $S = 1/2$ spins.

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Supporting Information Available: X-ray and electron diffraction and conductivity results for $Eu_2Mo_2O_{5-x}N_{2+x-\delta}$ (PDF); refinements in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.