Synthesis and Characterization of the Oxynitride $Y_2Mo_2O_{4.5}N_{2.5}$ Pyrochlore: A Neutron Diffraction and Magnetic Study

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A new molybdenum oxynitride $Y_2Mo_2O_{4.5}N_{2.5}$ with cubic pyrochlore structure (a = 10.3350(2) Å, space group $Fd3m$, $Z = 8$) has been synthesized by heating the parent $Y_2Mo_2O_7$ oxide in flowing ammonia at 898 K. The polycrystalline sample has been characterized by thermal analysis, X-ray and neutron diffraction (NPD), and magnetic susceptibility measurements. The analysis of high resolution NPD data, based on the contrast existing between the scattering lengths of O and N, shows that both atoms are distributed at random at the anion substructure; the refined crystallographic formula implies an oxidation state of +5.25 for Mo cations. The thermogravimetric curve shows a weight gain of 7.5% at 1000 K in air, corresponding to the complete elimination of N_2 and oxidation to Mo(VI) oxide, in good agreement with the proposed composition. The magnetic susceptibility exhibits a Pauli-like, temperature-independent term which derives from the partial delocalization of Mo electrons on Mo-(O,N) bands with a broader bandwidth, as a consequence of the significant opening of the Mo-(O,N)-Mo angle and strengthening of the Mo-(O,N) interactions with respect to the parent $Y_2Mo_2O_7$ oxide. As in this oxide, a reminiscent spin-glass behaviour is observed at low temperature.

Key words: Oxynitride, Pyrochlore Structure, Neutron Diffraction, Ammonolysis, Pauli Susceptibility