



Synthesis, crystal structure and magnetic properties of a new pillared perovskite $\text{La}_5\text{Mo}_{2.75}\text{V}_{1.25}\text{O}_{16}$

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ABSTRACT

A new pillared perovskite compound $\text{La}_5\text{Mo}_{2.76(4)}\text{V}_{1.25(4)}\text{O}_{16}$, has been synthesized by solid-state reaction and its crystal structure has been characterized using powder X-ray and neutron diffraction. The magnetic properties of this compound have been investigated using SQUID magnetometry, and the magnetic structure has been studied using neutron diffraction data. A theoretical calculation of relative strengths of spin interactions among different magnetic ions and through different pathways has been performed using extended Hückel, spin dimer analysis. The crystal structure of this material contains perovskite-type layers that are connected through edge-sharing dimeric units of octahedra. The structure is described in space group $C2/m$ with unit cell parameters $a = 7.931(2)\text{Å}$, $b = 7.913(2)\text{Å}$, $c = 10.346(5)\text{Å}$ and $\beta = 95.096(5)^\circ$. The material shows both short-range ferrimagnetic correlations from ~ 200 to 110K and long-range antiferromagnetic order below $T_c \sim 100\text{K}$. The magnetic structure was investigated by neutron diffraction and is described by $k = (0\ 0\ \frac{1}{2})$ as for other pillared perovskites. It consists of a ferrimagnetic arrangement of Mo and V within the layers that are coupled antiferromagnetically between layers. This is the first magnetic structure determination for any Mo-based pillared perovskite.

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1. Introduction

Materials with perovskite-related structures have been attracting a great deal of interest over the past decades. Observation of interesting physical properties such as superconductivity, metal–insulator transitions and colossal magnetoresistance in perovskite-type structures with possible applications in magnetic memory devices and in detection of magnetic fields has inspired a large number of studies [1–7]. Starting with the synthesis of $\text{La}_5\text{Mo}_4\text{O}_{16}$ in 1983 [8] via fused salt electrolysis and the report of its crystal structure 10 years later [9] a new family of perovskite-related materials was introduced (Fig. 1), consisting of a quasi-two-dimensional structure with perovskite-type layers separated by dimeric units of edge-sharing octahedra (hatched grey). Note that there are two types of octahedra in a corner-sharing layer: the $M(1)\text{O}_6$ octahedron (grey) shares only four equatorial corners with the other octahedra, and its apical corners are not shared. The second octahedron, $M(2)\text{O}_6$ (black), shares all six corners: the two apical corners are shared with the pillaring units located on the top and below, and the four equatorial corners are shared with

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the other octahedra within the perovskite-type layer. The two types of octahedra are arranged so that $M(1)\text{O}_6$ has only $M(2)\text{O}_6$ neighbors and vice versa. For several years this material was the unique example of this structure type, until two groups of compounds with the formulae $\text{La}_5\text{Re}_3\text{MO}_{16}$ ($M = \text{Mn, Mg, Fe, Co, Ni}$) and $\text{La}_5\text{Mo}_{4-x}\text{M}_x\text{O}_{16}$ ($M = \text{Mn, Mg, Fe, Co}$ and $x \sim 0.75$) were reported [10–12], followed by another compound, $\text{La}_5\text{Os}_3\text{MnO}_{16}$ [13]. In these cases Re^{5+} and Os^{5+} substitute for Mo^{4+} in both the dimers and the perovskite layers on the $M1$ site and divalent $3d$ transition metal ions occupy the $M2$ site. These materials exhibit interesting magnetic properties. Short metal–metal distances within the dimeric units provide evidence for multiple metal–metal bonding. Due to the long separation ($\sim 10\text{Å}$) of the perovskite layers by the pillaring, diamagnetic, dimeric units, one may expect to see a two-dimensional magnetic correlations in these materials, with only weak interaction between the layers. However, detailed magnetic studies of these compounds showed long-range magnetic order at temperatures up to 193K [10,12–18]. Neutron diffraction studies of $\text{La}_5\text{Re}_3\text{MnO}_{16}$ for example showed an antiferromagnetic coupling of ferrimagnetic layers ($\text{Re} \downarrow \text{Mn} \uparrow$) resulting in a three-dimensional magnetic structure below 162K [15].

It is of interest to extend the crystal chemistry of this new perovskite-related family to include other $3d$ series transition elements, especially the so-called “early” $3d$ elements.

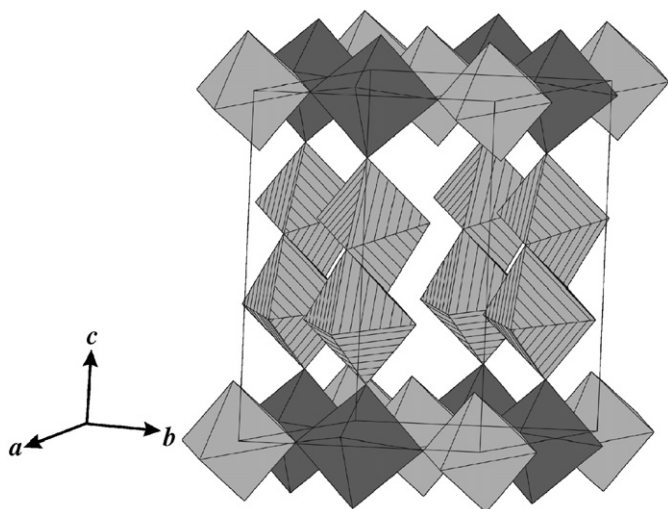


Fig. 1. Crystal structure of a pillared perovskite. The octahedral environments of distinct atomic positions are shown with different shadings. The perovskite layers contain two octahedral sites, M1 (grey) and M2 (black), which are pillared through corner sharing at M2 by edge-sharing dimeric units shown in grey with hatching.

Major synthetic difficulties are associated with these materials, especially the original molybdenum-based series. For example $\text{La}_5\text{Mo}_4\text{O}_{16}$ has been prepared only by molten salt electrolysis. Some members of the $\text{La}_5\text{Mo}_{4-x}\text{M}_x\text{O}_{16}$ series can be synthesized by standard solid-state methods but generally not as single-phase products [11]. Here the synthesis, crystal structure and magnetic properties of a new molybdenum-based pillared perovskite containing V^{4+} with the formula $\text{La}_5\text{Mo}_{2.76(4)}\text{V}_{1.25(4)}\text{O}_{16}$ is reported using standard solid-state methods. Sufficient material was produced in this manner to permit a neutron diffraction study of the magnetic structure for the first time for any Mo-based pillared perovskite.

2. Experimental section

2.1. Synthesis

A large variety of different synthetic conditions were examined, and a compound, which later proved to be $\text{La}_5\text{Mo}_{2.76(4)}\text{V}_{1.25(4)}\text{O}_{16}$ was finally prepared using La_2O_3 (99.99% Alfa Aesar), MoO_2 (99.9% CERAC), V_2O_5 (99.6% Aldrich) and V_2O_3 (prepared in the lab by reduction of VO_2 99.5% CERAC) as starting materials. La_2O_3 was pre-fired at 1000°C over night before being used in the experiment. Stoichiometric amounts of the reactant powders were weighed, ground together, pressed into a pellet, wrapped in a platinum sheet and sealed in a silica tube under the vacuum ($\sim 10^{-3}$ Pa). The reaction was completed in 24 h at a temperature of 950°C .

Initially, a Mo:V ratio of 3:1 (in the form of MoO_2 and V_2O_5) was used in the expectation that the low melting point of V_2O_5 would facilitate the solid-state reaction at relatively low temperatures and that the redox couple, $\text{Mo}^{4+}/\text{V}^{5+} = \text{Mo}^{5+}/\text{V}^{4+}$ might be operative. The molar ratio of $\text{La}_2\text{O}_3:\text{MoO}_2:\text{V}_2\text{O}_5$ used for the experiment was 2.5:3:0.5. However, a large amount of a side product, identified as $\text{La}_{2.4}\text{Mo}_{1.6}\text{O}_8$ [19] with a disordered fluorite structure and Mo oxidation state of +5.5 always appeared along with a majority phase with the pillared perovskite structure. Thus, additional vanadium oxide in the form of V_2O_3 was added to reduce molybdenum to the desired oxidation states (4+ and 5+), and to form the target V-containing material instead of a purely

Mo-containing phase. Different trial amounts of excess V, in form of V_2O_3 (and by keeping the above-mentioned ratio for the other reactants), were added and finally 50% excess by mole of vanadium resulted in the desired pillared perovskite compound along with a small amount of an unidentified side product. Structural analysis of the obtained pillared perovskite compound, to be discussed later, showed the actual formula to be $\text{La}_5\text{Mo}_{2.76(4)}\text{V}_{1.25(4)}\text{O}_{16}$. Therefore, another experiment was tried using a Mo:V ratio of 2.76(4):1.25(4), that still resulted in formation of a large amount of the side product $\text{La}_{2.4}\text{Mo}_{1.6}\text{O}_8$ along with the pillared perovskite compound. Accordingly, the aforementioned procedure with excess of V (V_2O_3) seems to be the best reaction condition.

2.2. X-ray and neutron diffraction

X-ray powder diffraction data was obtained using a PANalytical X'Pert Pro MPD diffractometer with a linear X'Celerator detector. $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$) in the 2θ range of $10\text{--}110^\circ$ with a 2θ step interval of 0.0084° was used for data collection. Powder neutron diffraction measurements were performed on the C2 diffractometer at the Canadian Neutron Beam Centre at Chalk River, Ontario. The data were collected at three different temperatures, 3.8, 110.2 and 300 K. Two different wavelengths were used at 3.8 and 300 K with the same step size of 0.100° . The wavelength 1.33037 \AA was used to collect data within the 2θ range of $35\text{--}115^\circ$, and the wavelength 2.37150 \AA was applied to obtain data in the 2θ range of $5\text{--}85^\circ$. The number of Bragg reflections and profile points contained in the short wavelength dataset was 689/673 and 69/582 for the long wavelength dataset.

2.3. Magnetic property measurements

Magnetic data were collected on a Quantum Design MPMS SQUID magnetometer. The zero-field cooled and field cooled (ZFC/FC) magnetic susceptibility from 5 to 300 K and isothermal magnetization data from 0 to 5.5 T were obtained on a powder sample in a gelatin capsule. Diamagnetic corrections of 20×10^{-6} (La^{3+}), 17×10^{-6} (Mo^{4+}), 12×10^{-6} (Mo^{5+}), 7×10^{-6} (V^{4+}) and 12×10^{-6} emu/mol (O^{2-}) were made to the susceptibility data [20].

2.4. Theoretical calculations: spin dimer analyses

A computational estimation of relative strengths of spin interactions among different magnetic ions and through different pathways was obtained using extended Hückel, spin dimer analysis [21]. The strengths of spin interaction manifested in the exchange constant J are related to the hopping energies among different magnetic sites, Δe , as well as the electron correlation energy, U , resulting from accommodation of two electrons within the same orbital. These quantities are related through the formula

$$J = -2 \frac{(\Delta e)^2}{U} \quad (1)$$

when comparing J values of different interaction pathways, the correlation energy U is constant and therefore the difference in the Δe value determines the significance of a particular spin interaction relative to the other possible pathways.

In these computations different interaction pathways among two M1 sites (Mo-rich sites), two M2 sites (V-rich sites), as well as an M1 and an M2 site within a perovskite-type layer were examined, and the values of the intersite hopping energy, Δe , were acquired by employing the CAESAR package [22]. Fig. 2 shows a

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