

Crystal and Magnetic Structure of the Pillared Perovskite, $\text{La}_5\text{Mo}_3\text{VO}_{16}$

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The general formula for pillared perovskites can be represented as $\text{A}_2\text{B}_2\text{MM}'\text{O}_5$ where A is a large cation - usually a lanthanide ion. The M and M' cations form corner sharing octahedra that result in perovskite type layers parallel to the *ab* plane. These perovskite layers are connected through edge sharing dimers of octahedra, B_2O_{10} units. Figure 1c shows the pillared perovskite structure. It should be noted that MO_6 octahedra (grey) share only four corners (equatorial corners) with the neighboring octahedra within the layer, whereas $\text{M}'\text{O}_6$ octahedra (black) share all their six apexes. They share the four equatorial corners with MO_6 octahedra and the two axial corners with B_2O_{10} units (grey with hatching) that are responsible for connecting the adjacent perovskite layers.

Since the first pillared perovskite compound was reported [1], only a small number of pillared perovskites have been synthesized. 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 [2].

In an effort 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, a new pillared perovskite compound $\text{La}_5\text{Mo}_{2.76(4)}\text{V}_{1.25(4)}\text{O}_{16}$ [3], was synthesized by solid state chemistry method.

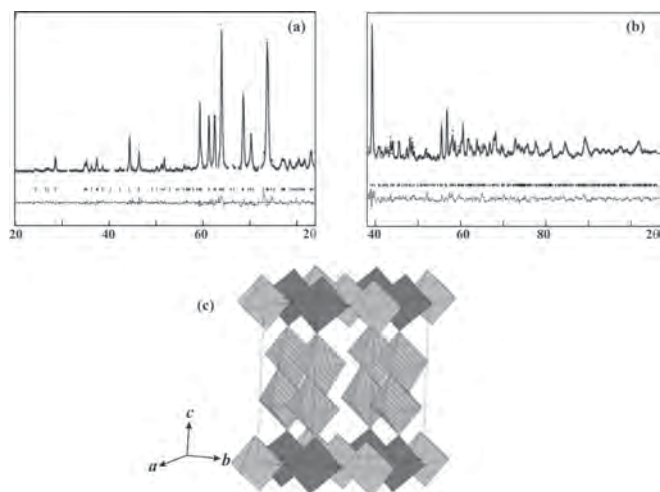


Fig 1. (a) Rietveld refinements of powder neutron diffraction data with $\lambda = 2.37150 \text{ \AA}$ at 300K (b) Rietveld refinements of neutron data with $\lambda = 1.33037 \text{ \AA}$ at 300K (c) Crystal structure of pillared perovskite $\text{La}_5\text{Mo}_{2.76(4)}\text{V}_{1.25(4)}\text{O}_{16}$.

The X-ray and neutron powder diffraction methods were employed to determine the crystal structure. The structure was refined in $\text{C2}/m$, and it was shown that there is a mixed oc-

cupancy of Mo and V in the ratio $\text{Mo}/\text{V} = 0.75/0.25$ in the M site in the perovskite layer. However, the M' site is almost fully occupied by V, resulting in the formula $\text{La}_5\text{Mo}_{2.76(4)}\text{V}_{1.25(4)}\text{O}_{16}$. The Rietveld refinement profiles for high and low wavelength neutron data are shown in Figure 1a and 1b respectively. In the dimeric pillaring unit, there is a very short Mo–Mo distance of $2.46(2) \text{ \AA}$, indicating a Mo–Mo double bond between two $\text{Mo}^{4+}(4d^2)$. Therefore the pillaring units are diamagnetic, and Mo^{4+} ions in these dimers do not contribute to the magnetic properties of the compound [3].

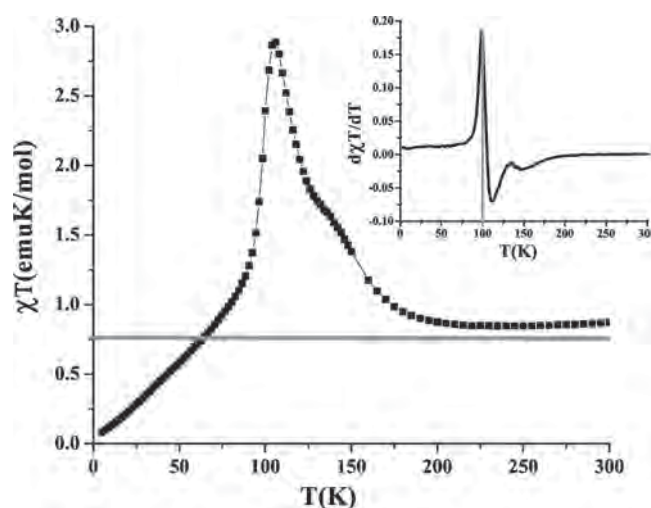


Fig 2. χT as a function of temperature. The horizontal line shows the calculated spin only Curie constant. The inset shows the Fisher heat capacity [4] in which the transition temperature is marked by a vertical line.

The bulk magnetic susceptibility (χ) measurements showed that a magnetic transition happens below 100 K. The diagram of χT vs T is shown in Figure 2. The horizontal line marks the calculated spin-only Curie constant, 0.75 emu/mol K , for two $S = \frac{1}{2}$ ions, appropriate for both Mo^{5+} and V^{4+} , per formula unit. As can be seen, the data approach this value as T approaches 300 K. The χT product exceeds the spin only, paramagnetic value below about 175K and reaches a maximum value at 110 K. This is taken as evidence for short range ferrimagnetic correlations within the perovskite planes. Note also the shoulder near 150 K which might signal short-range intraplanar AF correlations. The sharp drop in χT below the maximum normally signals long-range AF coupling of ferrimagnetic layers. The critical temperature can be estimated from a plot of the so called Fisher heat capacity, $d(\chi T)/dT$ vs. T shown in the inset which gives $T_c = 100 \text{ K}$. Isothermal field sweeps give evidence for a metamagnetic critical field of $\sim 1.7 \text{ T}$ at 5 K [3].

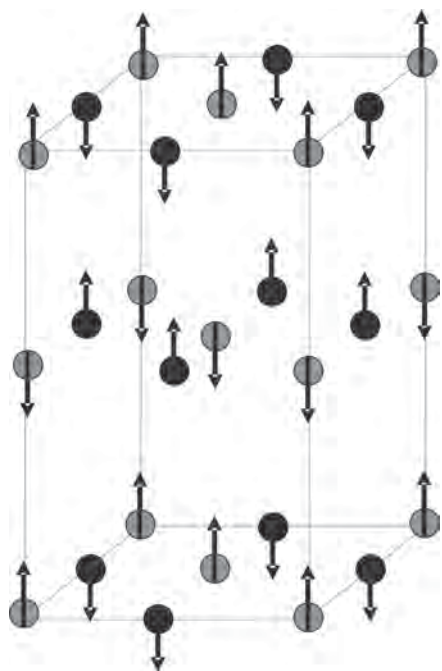


Fig 3. The magnetic structure of $\text{La}_5\text{Mo}_{2.76(4)}\text{V}_{1.25(4)}\text{O}_{16}$. The gray and black circles represent M and M' sites, respectively. The diamagnetic dimer sites are not shown.

The application of neutron diffraction helped to determine the magnetic structure of this compound for the first time for any Mo-based pillared perovskite. The magnetic moments on M and M' ions within the perovskite layer are ordered ferrimagnetically which is also consistent with a theoretical study of spin interactions within the perovskite-type layers that was performed using extended Hückel, spin dimer analysis. These perovskite layers are then coupled antiferromagnetically with respect to each other, which is consistent with the ordering wave vector $\mathbf{k} = (0\ 0\ \frac{1}{2})$ that was found based on the magnetic peak indexing [3].

References

- [1] McCarroll, W. H.; Darling, C.; Jakubicki, G. J. *Solid State Chem.* 48 (1983) 189.
- [2] Ramanujachary, K.V.; Lofland, S.E.; McCarroll, W.H.; Emge, T.J.; Greenblatt, M. J. *Solid State Chem.* 164 (2002) 70.
- [3] Ramezanipour, F.; Derakhshan, S.; Greedan, J. E.; Cranswick, L. M. D. J. *Solid State Chem.* 181 (2008) 3366.
- [4] M.E. Fisher, *Philos. Mag.* 7 (1962) 1731.