

Crystal and magnetic structures of the brownmillerites $\text{Ca}_2\text{Fe}_{1.5}\text{Mn}_{0.5}\text{O}_5$ and $\text{Ca}_2\text{Fe}_{1.33}\text{Mn}_{0.67}\text{O}_5$

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Perovskite is a very versatile structure found in many transition metal oxides. Their interesting physical properties such as high-temperature superconductivity, giant magnetoresistance, and spin glass behaviour make these materials very attractive. There has been considerable interest in materials with oxygen-deficient perovskite-related structures in recent years. Fuel cells and dense membranes for the partial oxidation of hydrocarbons are some of the areas of possible applications for these materials.

A structural family derived from perovskite is brownmillerite which forms by introducing an ordered array of oxygen vacancies to the perovskite structure. If the perovskite structure is described as $\text{ABO}_3(\text{A}_2\text{B}_2\text{O}_6)$, where B is an octahedral site cation and A is a divalent cation, brownmillerite is then, $\text{A}_2\text{BB}'\text{O}_5$, where B is an octahedral site cation and B' a tetrahedral site cation. The structure consists of layers of corner sharing octahedra that are separated by chains of corner sharing tetrahedra running parallel to the a-c plane. Therefore, alternating layers of octahedra and tetrahedra form along the b-axis. The brownmillerite “super cell” is related to the parent perovskite as $a_{\text{bm}} \sim b_{\text{bm}} \sim (2)^{1/2}a_{\text{p}}$ and $c_{\text{bm}} \sim 4a_{\text{p}}$. However, the brownmillerite structure is less common than perovskite and in most cases the latter is a more thermodynamically favourable product. Consequently, the diversity of the brownmillerite family is much smaller than that of perovskite.

We have previously studied $\text{Ca}_2\text{FeMnO}_5$ [1] that belongs to the brownmillerite family. In continuation of that work we also studied the role of the B-site cation on magnetic and structural properties. Two materials with 2:1 and 3:1 ratios of Fe:Mn, $\text{Ca}_2\text{Fe}_{1.33}\text{Mn}_{0.67}\text{O}_5$ and $\text{Ca}_2\text{Fe}_{1.5}\text{Mn}_{0.5}\text{O}_5$, were therefore synthesized and their crystal and magnetic properties were studied.

Our initial experiment on these compounds helped determine the crystal structure in great detail including the exact Fe and Mn contents, and their site occupancies. Such information could not be obtained using powder x-ray diffraction, while the high contrast between neutron scattering lengths of Fe and Mn makes it possible to obtain such details. The crystal structure was found to be orthorhombic, Pnma, for both materials.

The magnetic structures for these compounds were also determined. They both have a G-type magnetic structure with $k = (0\ 0\ 0)$. Each spin is ordered antiferromagnetically relative to the nearest neighbor spins. The G-type magnetic structure of these materials is shown in Figure 1.

We collected neutron data at different temperatures, monitoring the changes in structural and magnetic peaks as function of temperature up to 300K. As a result we could obtain an estimation of the transition temperatures of these materials by extrapolation. The transition temperature seems to be above 400K for both materials. However, high temperature data will be required to obtain the exact transition points.

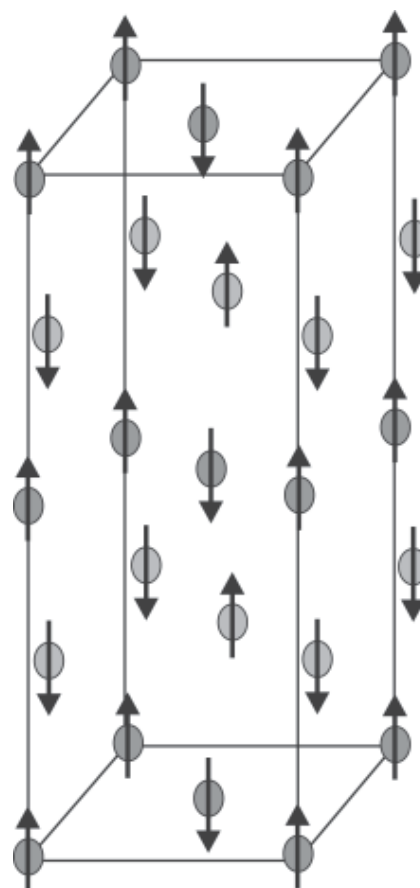


Fig. 1 The G-type magnetic structure. The octahedral and tetrahedral sites are shown by different colors. Each site couples antiferromagnetically with all nearest neighbors within the same layer and in the adjacent layers.

References

- [1] F. Ramezanipour, B. Cowie, S. Derakhshan, J.E. Greedan and L.M.D. Cranswick, *J. Solid State Chem.* 182 (2009) 153-159.