Crystal and magnetic structures of the brownmillerites $Ca_2Fe_{1.5}Mn_{0.5}O_5$ and $Ca_2Fe_{1.33}Mn_{0.67}O_5$

J. E. Greedan[1] and F. Ramezanipour[1]

[1] McMaster University, Hamilton, ON, Canada L8S 4M1

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. Introducing an ordered array of oxygen vacancies to the perovskite structure results in formation of brownmillerite structure. This family of compounds has a general formula $A_2MM'O_5$, where M and M′ are octahedral and tetrahedral site cations respectively, and A is a large cation residing in the spaces between the layers. The structure consists of alternating layers of octahedra and tetrahedra. All connections between the polyhedra are corner sharing.

The crystal and magnetic structures of the brownmillerite Ca_2FeMnO_5 have been reported recently [1]. This study has been extended to materials with 2:1 and 3:1 ratios of Fe:Mn, $Ca_2Fe_{1.33}Mn_{0.67}O_5$ and $Ca_2Fe_{1.5}Mn_{0.5}O_5$, respectively.

Neutron diffraction study (3.9 - 299K) showed both of these materials crystallize in an orthorhombic system with space group *Pnma*. A very high contrast between manganese and iron, due to a very large difference between their scattering lengths: 9.45(2) fm for Fe and – 3.75(2) fm for Mn, makes neutron an ideal probe for this study, especially to determine site occupancies, and ordering of Mn^{3+} and Fe^{3+} ions in the octahedral and tetrahedral sites.

The magnetic susceptibility data within the temperature range of 5 - 300 K are similar in two compounds, and show a decrease in susceptibility as temperature increases to ~100 K, and then an upturn begins and continues up to 300 K. This is a different trend compared to the one observed for a brownmillerite compound with 1:1 ratio of Mn:Fe studied before by our group. However, the transition temperatures could not be found using the magnetic susceptibility data, and are needed to be determined using variable temperature powder neutron diffraction, at temperatures higher than room temperature.

The magnetic structures of these materials were determined by neutron diffraction. Rietveld refinement result of neutron diffraction data (λ = 2.37150 Å) at 300 K showing both crystal and magnetic structures for $Ca_2Fe_{1.5}Mn_{0.5}O_5$ is shown in Figure 1. The magnetic structure was found to be G-type, described by k = (0 0 0). Each spin in the octahedral layer is coupled antiferromagnetically to all nearest neighbors within that layer. The tetrahedral layer has a similar coupling of spins within the layer. In addition, there is an antiparallel coupling between the octahedral and tetrahedral layers. Therefore all intra and inter-layer spin interactions are antiferromagnetic.

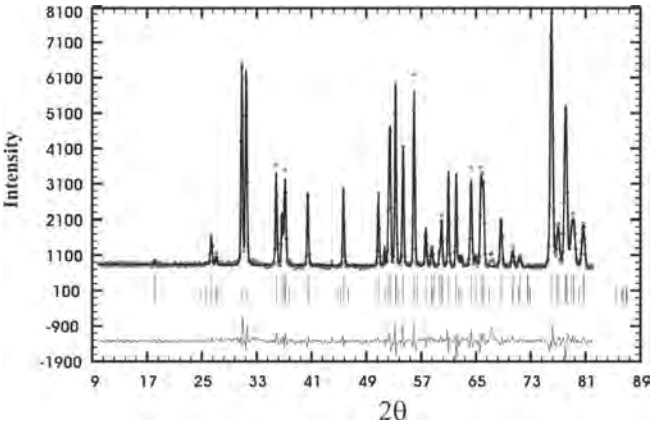

Fig 1. Rietveld refinement of neutron diffraction data with λ = 2.37150 Å (at 300 K) for brownmillerite $Ca_2Fe_{1.5}Mn_{0.5}O_5$. The upper vertical bars show the crystal and lower vertical lines show the magnetic structure.

References

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