Crystal & Magnetic Structure of the Brownmillerite Ca_2FeMnO_5

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

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

Brownmillerites are a family of oxygen deficient compounds that form when a series of vacancies are introduced to the perovskite structure in an ordered manner. The result of the presence of these ordered arrays of vacancies is a structure involving alternating layers of octahedra and tetrahedra. The general formula for brownmillerites is $A_2MM'O_5$, 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 crystal structure involves both octahedral and tetrahedral layers alternating along the b–axis (Figure 1c). The octahedra share four equatorial corners with other octahedra within the layers. These layers are separated by chains of tetrahedra that run parallel to the *a–c* plane. The chains of tetrahedra are connected to the apical corners of octahedra from the layers above and below.

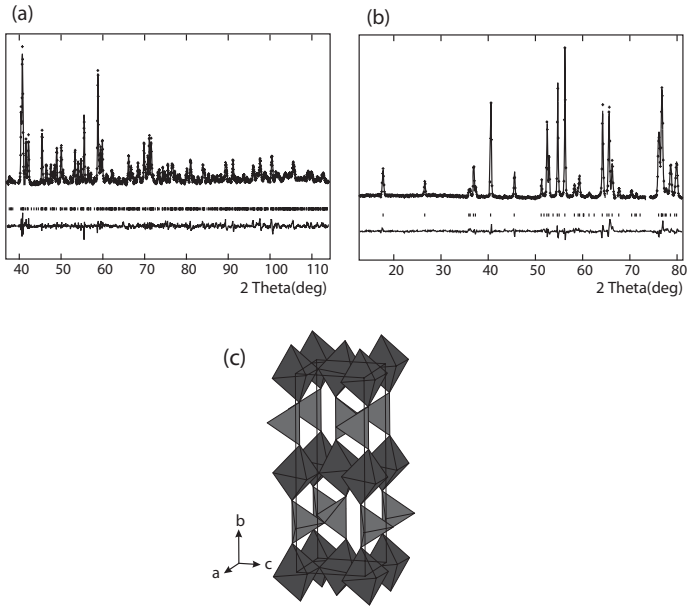

Fig 1. *(a) Rietveld refinement of fine collimation neutron diffraction data with λ = 1.33037 Å, (at 550 K) (b) Rietveld refinement of neutron data with λ = 2.37150 Å (at 550 K) (c) Crystal structure of brownmillerite* $Ca_2Fe_{1.039(8)}Mn_{0.962(8)}O_5$.

The compound Ca_2FeMnO_5 is a brownmillerite phase with 3+ ions in both B and B′ sites. The crystal and magnetic structure of this compound were studied using X-ray and neutron powder diffraction methods. Neutron diffraction has significant advantages here, as unlike for X–ray diffraction, there exists a strong contrast between Mn and Fe due to a very large difference between their scattering lengths: 9.45(2) fm for Fe and – 3.75(2) fm for Mn.

The crystal structure was refined (Figure 1a and b) in *Pnma* space group. The structure of this compound was previously assumed to contain only Mn on the octahedral site (M site) and Fe on the tetrahedral site (M′ site) [1]. However, the neutron diffraction study showed mixed occupancy of Mn and Fe on both sites, ~ 9% Mn on the M' site and 13% Fe on the M site, and a slightly higher, ~ 4%, Fe content overall, resulting in the formula $Ca_2Fe_{1.039(8)}Mn_{0.962(8)}O_5$ [2].

The magnetic structure of this compound was determined using neutron diffraction data. A G–type magnetic structure model with anti–parallel coupling between spins of nearest neighbors was verified. In the magnetic structure of this compound (Figure 2) the spins on each M (octahedral) site are coupled antiferromagnetically with the nearest M sites within the octahedral layer. The same situation applies to M′ (tetrahedral) sites that couple antiparallel to each other within the tetrahedral layer. In addition the coupling between octahedral and tetrahedral layers is antiferromagnetic as well. The spins on each site are oriented along the *b*–direction [2].

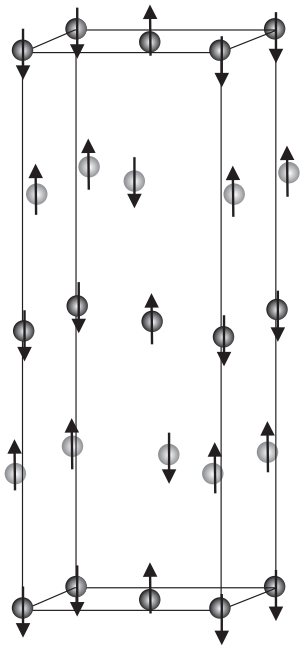

Fig 2. *The G–type magnetic structure of* $Ca_2Fe_{1.039(8)}Mn_{0.962(8)}O_5$. *The octahedral and tetrahedral sites are shown by different colors. Each site couples antiferromagnetically with all nearest neighbors within the same layer and in the adjacent layers.*

By following the temperature dependence of the magnetic peak intensities, the critical temperature for long range order can be determined. The magnetic reflections disappear between 405 K and 410 K. Plotting the refined magnetic moments of the M (mostly Mn^{3+}) and M' (mostly Fe^{3+}) sites as a function of temperature indicates T_c = 407(2) K (Figure 3) [2].

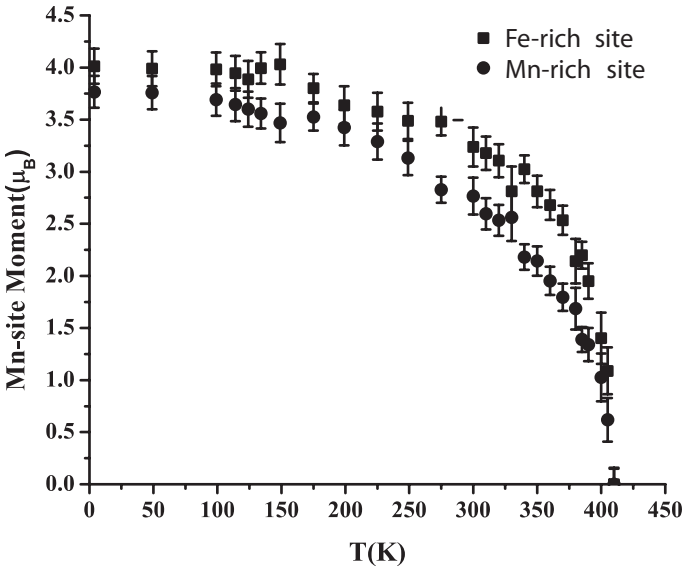

Fig 2. *Magnetic moments of Mn and Fe sites as functions of temperature. Note that the moments approach zero at about 407 K, indicating the magnetic transition temperature.*

References

[1] Nakahara, Y.; Kato, S.; Sugai, M.; Ohshima, Y.; Makino, K. Mater. Lett. 30 (1997) 163

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