Structural Studies of the $A_3CoNb_2O_9$ "1:2" Ordered Perovskites ($A = Ca^{2+}, Sr^{2+}, Ba^{2+}$)

Valeska Peesiew Ting[a], Y.Liu[a], L. Norén[a], R.L.Withers[a], D.J. Goosens[a], C.Ferraris[b] [a]*Australian National University, Australia.* [b]*Nanyang Technological University, Singapore.* E-mail: vting@rsc.anu.edu.au

A TEM, XRD and bond valence sum study of the $A_3CoNb_2O_9$ (A = Ca^{2+}, Sr^{2+}, Ba^{2+}) "1:2" perovskite compounds found P-3m1 (**a** = $\mathbf{b}_p$-$\mathbf{c}_p$, **b** = -$\mathbf{a}_p$+$\mathbf{c}_p$, **c** = $\mathbf{a}_p$+$\mathbf{b}_p$+$\mathbf{c}_p$) symmetry for the A = Ba compound and $P12_1/c1$ (**a** = $\mathbf{a}_p$+$\mathbf{b}_p$+**2**$\mathbf{c}_p$, **b** = $\mathbf{a}_p$-$\mathbf{b}_p$, **c** = 3($\mathbf{a}_p$+$\mathbf{b}_p$), subscript p for the perovskite parent sub-structure) symmetry for the A = Sr and Ca compounds. All three compounds exhibit B-site Co/Nb ordering in layers along a $[111]_p$ direction. The Sr and Ca compounds exhibit octahedral tilting as well as minor octahedral distortion. A constrained modulation wave approach to Rietveld refinement of neutron powder diffraction data was used to determine their crystal structures.

$Ba_3CoNb_2O_9$ exhibited fine scale twinning and translational stacking faulting (apparent in HREM images and in powder diffraction data as systematic discrepancies between predicted and observed intensities of satellite reflections). The effect of such stacking faulting was modelled by refining the amount of two stacking faulted variants (offset by displacive shifts of ±**R**) in addition to the main variant.

The Sr and Ca compounds, each with 42 refinable atomic fractional coordinates, showed rather less fine scale faulting and refined normally - these being amongst the first reported successful neutron powder refinements of tilted 1:2 perovskites.

Keywords: perovskite oxides, structural characterisation, neutron diffraction