Electronic transitions and oxygen vacancies in $Ba_2LnSn_xSb_{1-x}O_{6-\delta}$

Paul J. Saines and Brendan J. Kennedy

School of Chemistry, The University of Sydney, Sydney, New South Wales, 2006, Australia

Double perovskites are of interest due to the interesting physical and magnetic properties these materials possess. Perovskites in which either electronic valence fluctuations or oxygen deficiencies can be induced by changes in stoichiometry are of particular interest due to their electronic and ionic conductivities. Understanding the structures of these materials and in particular how any oxygen vacancies are distributed pose interesting crystallographic challenges and have significant impact on the application of these compounds. In particular the potential for oxygen vacancies to concentrate on one site in these materials is of specific interest as it could lead to the development of anisotropic ionic conductivity and hence more efficient electrolytes.

In the series $Ba_2LnSn_xSb_{1-x}O_{6-\delta}$ (Ln = Nd or Pr) substitution of Sb^{5+} by Sn^{4+} can lead to the formation of oxygen vacancies. However while lanthanides are usually found to occur in the trivalent state some ions such as praseodymium have variable oxidation state similar to that found in transition metals. Therefore it is possible that oxidation of Pr^{3+} to Pr^{4+} as x increases may be favoured over the formation of oxygen vacancies.. Apart from electronic features Pr^{3+} and Nd^{3+} have very similar properties and therefore a comparison between these series could potentially provide an insight into the effect of substitution in different electronic environments and the relatively stability of oxygen vacancies in the perovskite structure.

Therefore these two series have been structurally characterized using a combination of powder neutron and synchrotron X-ray diffraction. Neodymium containing compounds were found to feature a phase transition from rhombohedral to monoclinic symmetry with increasing values of x allowing the possibility of ordering of oxygen vacancies. This has been confirmed using neutron diffraction over a range of 800 °C with oxygen vacancies in $Ba_2NdSnO_{5.5}$ being found to concentrate on the equatorial sites at ambient conditions but relocate to the axial sites at higher temperatures. This rearrangement can be explained using crystal chemistry. By comparison the praseodymium compounds undergo a series of phase transition from rhombohedral to monoclinic to a pseudo-cubic tetragonal symmetry. Those compounds adopting tetragonal symmetry do not feature B-site ordering. A large two phase region of the monoclinic and tetragonal symmetry has been found to form at high tin concentrations. Thermal-gravimetric and spectroscopic analysis of $Ba_2PrSn_xSb_{1-x}O_{6-\delta}$ suggest that increasing the tin content of the compounds results in oxidation of Pr^{3+} to Pr^{4+} in preference to an increase in oxygen vacancies and it is believed this change of oxidation state leads to loss the B-site order and the formation of the two phase region at higher Pr^{4+} concentrations.