Substitutional doping of trirutiline transition metal antimonates, MSb_2O_6

S. Patel[1,2], H.B. Kang[1], H. Maynard-Casely[3], T. Söhnel[1,2]

[1]School of Chemical Sciences, University of Auckland, 23 Symonds Street, Auckland 1010, New Zealand, [2]Macdiarmid Institute for Advanced Materials and Nanotechnology, Victoria University of Wellington, Wellington 6140, New Zealand [3]Australian Centre for Neutron Scattering, Australian Nuclear Science and Technology Organisation, New Illawarra Road, Lucas Heights, NSW 2234, Australia

spt796@aucklanduni.ac.nz

In the Cu-Sb-O ternary system, $CuSb_2O_6$ is the most intensively studied compound, owing to its unusual structural and magnetic behaviour. Jahn-Teller distortions from the Cu^{2+} cause an axial elongation of the Cu-O octahedra to give rise to a monoclinic structure (s.g. $P2_1/n$)[1,2]. At high temperatures, this material undergoes a second-order phase transition to the tetragonal phase (s.g. $P4_2/mnm$), isostructural to room temperature structures of $CoSb_2O6$ and $NiSb_2O_6$[3]. This modification may only be possible through an intermediate orthorhombic modification in P*nmm* as defined through systematic symmetry reduction [4]. Through the doping of $CuSb_2O_6$ with Co and Ni, this structural transition can be investigated.

Neutron, lab X-ray and synchrotron single crystal and powder diffraction have been used to study phase transitions in both solid state solutions. In the $Cu_{1-x}Co_xSb_2O_6$ system, it was found that two phases exist between compositions x = 0.2 and 0.5, with a Cu-rich monoclinic phase and a Co-rich tetragonal phase [4]. By contrast, the $Cu_{1-x}Ni_xSb_2O_6$ system exhibits a single-phase region from x = 0.4, where only the tetragonal phase remains. A phase transition can be observed in the solid solution where the monoclinic phase becomes tetragonal at high temperature. The orthorhombic intermediate structure can only be observed through Synchrotron powder diffraction.

X-ray absorption spectroscopy indicates that there has been a partial reduction of Cu^{2+} to Cu^{1+} in the higher doping concentrations of $Cu_{1-x}Ni_xSb_2O_6$; neutron powder diffraction on these materials confirm a net oxygen deficiency in the materials. Compounds with similar structures have also been investigated, including $NiSb_{2-x}Sn_xO_6$ and $ZnSb_{2-x}Sn_xO_6$, which also show a net oxygen deficiency in the structure. At higher temperatures, these materials also indicate a mixed occupation of Ni and Sb on the 2a and 4f sites, that suggests the material is undergoing a high temperature phase transition to the rutile phase.

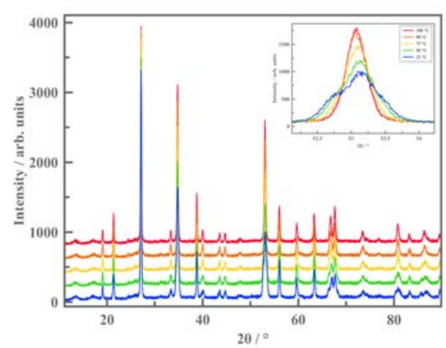

Figure 1. High-temperature XRD of $Cu_{0.8}Ni_{0.2}Sb_2O_6$ with inset showing phase transition of monoclinic to tetragonal at the (123) and (213) peaks.

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