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Structural investigation of doped quaternary antimonates

Copper containing oxides hold a widespread research interest in inorganic fields due to the fascinating electronic and magnetic properties the compounds exhibit. In the Cu-Sb-O ternary system, CuSb₂O₆ is the most intensively studied compound [1], owing to its unusual structural and magnetic behaviour. Jahn-Teller distortions from the Cu²⁺ cause an axial elongation of the Cu-O octahedra to give rise to a monoclinic structure (s.g. P2₁/n) [2]. At high temperatures, this material undergoes a second order phase transition to the tetragonal phase (s.g. P4₂/mmn), isostructural to room temperature structures of CoSb₂O₆ and NiSb₂O₆ [3]. This modification may only be possible through an intermediate orthorhombic modification in Pnma as defined through systematic symmetry reduction[4]. Through the doping of CuSb₂O₆ 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}CoxSb₂O₆ 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. The magnetic susceptibility for all compounds match closely to CoSb₂O₆, even at low doping levels. This indicates a change from the 1D magnetic behaviour of CuSb₂O₆ to 2D. By contrast, the Cu_{1-x}NixSb₂O₆ system exhibits a single phase region from $x = 0.4$, where only the tetragonal phase remains. This has been attributed to a reduction of Cu²⁺ due to the high temperatures used in synthesising these compounds.

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Topic

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