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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, CuSb_2O_6 is the most intensively studied compound [1], 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. $P2_1/n$) [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_2O_6 and NiSb_2O_6 [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 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 $\text{Cu}_{1-x}\text{Co}_x\text{Sb}_2\text{O}_6$ 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. The magnetic susceptibility for all compounds match closely to CoSb_2O_6 , even at low doping levels. This indicates a change from the 1D magnetic behaviour of CuSb_2O_6 to 2D. By contrast, the $\text{Cu}_{1-x}\text{Ni}_x\text{Sb}_2\text{O}_6$ system exhibits a single phase region from $x = 0.4$, where only the tetragonal phase remains. This has been attributed to a reduction of Cu^{2+} due to the high temperatures used in synthesising these compounds.

[1] Gieré O -E, Brahim A, Deiseroth H J and Reinen D (1997) *J. Solid State Chem.* 131, 263

[2] Prokofiev A V, Ritter F, Assmus W, Gibson B J and Kremer R K (2003) *J. Cryst. Growth.* 247, 457

[3] Nikulin, AY, Zvereva EA, Nalbandyan VB, et al., *Dalton Trans* (2017), 46, 6059

[4] Bärnighausen H 1980 *MATCH, Commun. Math. Chem.* 9, 139

Topic

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