Structure, Chemical Bonding and Thermoelectric Performance of Zn_4Sb_3

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Thermoelectricity is due to play an important role in today's energy challenges. The ideal thermoelectric material is a *phonon glass and electron crystal*, i.e. has a low thermal conductivity combined with high electrical conductivity and Seebeck coefficent. Zinc-antimonide, with formal stoichiometry Zn_4Sb_3, nicely fulfills these requirements, but to explain its unusual combination of properties was not possible because its detailed structure remained for a long time unknown. Now, a crystal structure consistent with the observed mass density has been proposed for the first time by structurally refining single-crystal XRD data, and by analysing powder-synchrotron-radiation diffraction data with a Rietveld-MEM technique.[1,2] Zn_4Sb_3 has a regular Sb lattice, while Zn is distributed over several non-equivalent sites with fractional occupancy. To deconvolute the space-time average inherent to XRD we carried out an extensive computational investigation, and we identified the atomistic arrangements through which the system evolves.[2] In this poster, the bonding and atomic properties of these structures are investigated within the formalism of the Quantum Theory of Atoms In Molecules, and contrasted to the proposed Zintl-phase description of Zn_4Sb_3.[1,2] Furthermore, band-structure calculations of the electronic transport properties are performed to unravel how the atomic structure relates to the material's thermoelectric performance.

[1] Snyder G.J., Christensen M., Nishibori E., Caillat T., Iversen B.B., *Nature Mater.*, 2004, **3**, 458. [2] Cargnoni F., Nishibori E., Rabiller P., Bertini L., Snyder G.J., Christensen M., Gatti C., Iversen B.B., *Chem. Eur. J.*, 2004, **10**, 3861.

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