

SOLID-STATE MATERIALS CHEMISTRY

Our research seeks to understand the relationship between structure and properties in a broad spectrum of materials, in order to proceed to the rational design of new materials with controllable functionality. The work involves a blend of synthesis, structural characterisation and measurement of a range of transport and magnetic properties. A wide range of chemical systems is investigated, including chalcogenides, oxides, intermetallics and organic solids. Synthetic strategies employed range from ambient temperature routes, through structure-directed synthesis, to conventional high-temperature approaches. A variety of physical properties are measured over the temperature range 5–1300 K, using dedicated equipment available within the group. In addition, neutron diffraction underpins much of our work and we make extensive use of neutron techniques at ISIS in the UK and ILL in France. Much of our work lies at the interface with other disciplines while several projects are carried out with industrial partners.

• **Thermoelectric Materials:-** Thermoelectric materials for energy recovery represent a major interest within the group. Such materials offer unique opportunities to create devices able to harvest electrical

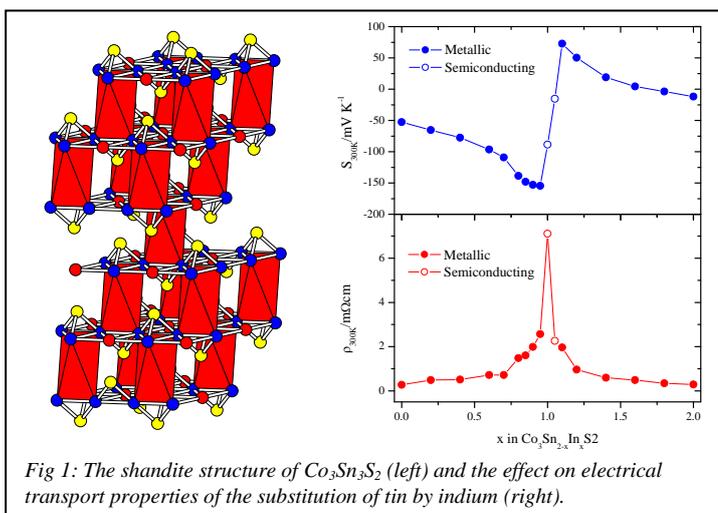


Fig 1: The shandite structure of $\text{Co}_3\text{Sn}_3\text{S}_2$ (left) and the effect on electrical transport properties of the substitution of tin by indium (right).

power from otherwise waste heat. High efficiency materials require the unusual combination of high Seebeck coefficient (S) and low thermal conductivity (κ) – characteristics associated with non-metals – together with a high electrical conductivity (σ) typically found in metals. The interdependence of these three quantities prevents them being independently optimised to maximise the figure-of-merit ($ZT = S^2\sigma T/\kappa$), on which the efficiency depends.

The presence of low-dimensional structural units in a solid, leads to a more highly structured electronic density of states (DOS). Since the Seebeck coefficient is dependent on the derivative of the DOS at the Fermi level, S may be maximised by tuning the charge carrier concentration in the region of E_F . For example, substitution of tin by indium in the shandite phase $\text{Co}_3\text{Sn}_{2-x}\text{In}_x\text{S}_2$ (Figure 1) progressively depopulates narrow bands of predominantly Co- d character. This leads, with increasing indium content, to a double metal-semiconductor-metal transition, characterised by discontinuities in the transport properties (Figure 1). Compositions just prior to the onset of semiconducting behaviour at $x=1$, show marked increases in the thermoelectric response, leading to $ZT \approx 0.3$ at 350K.

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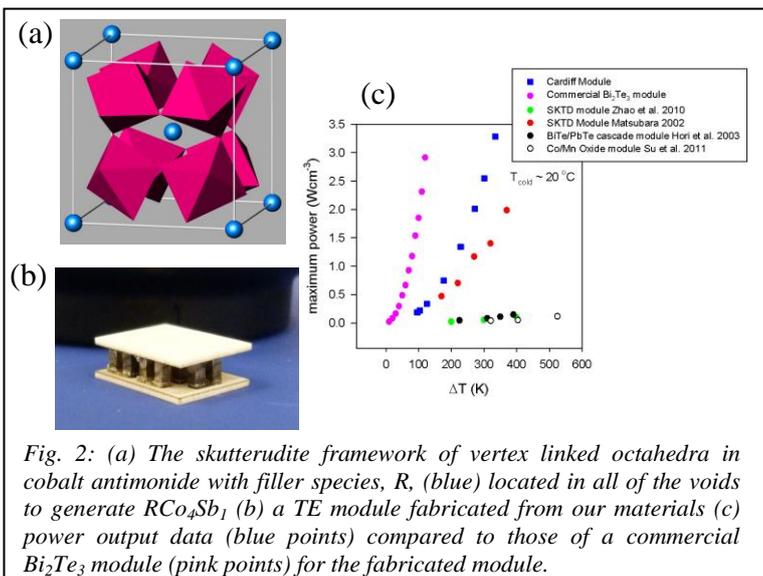
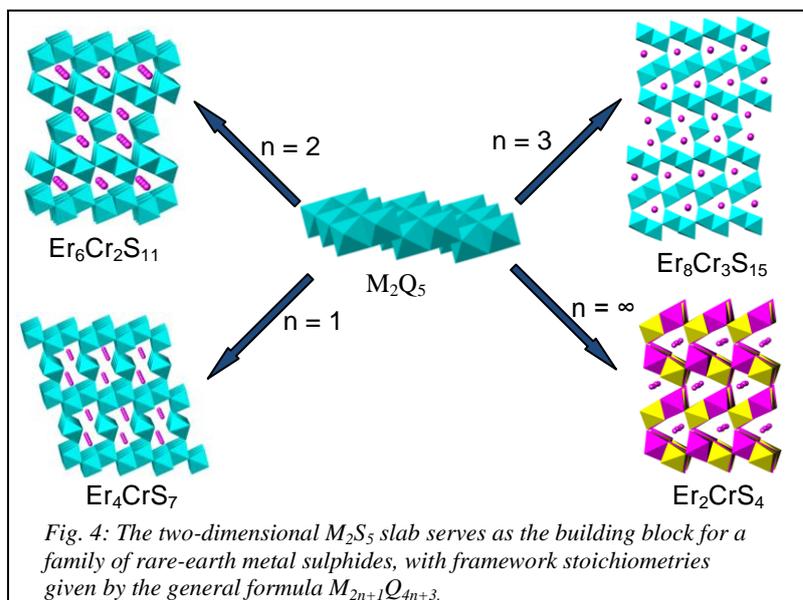
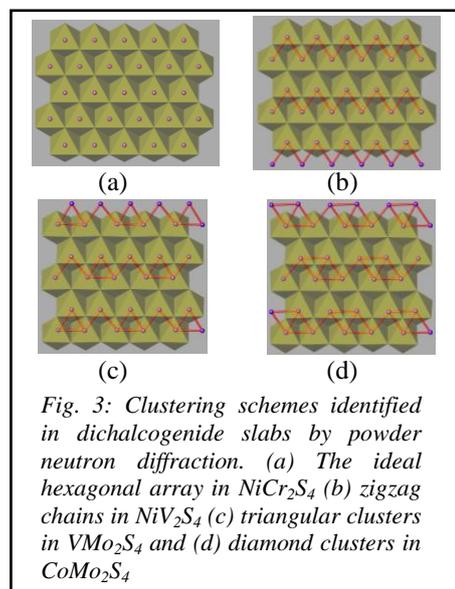


Fig. 2: (a) The skutterudite framework of vertex linked octahedra in cobalt antimonide with filler species, R , (blue) located in all of the voids to generate RCo_4Sb_3 (b) a TE module fabricated from our materials (c) power output data (blue points) compared to those of a commercial Bi_2Te_3 module (pink points) for the fabricated module.

We are also investigating materials based on the skutterudite structure (Figure 2(a)) in which vertex linking of MSb_6 octahedra creates a network of stoichiometry MSb_3 . The structure contains large cavities into which guest species such as rare-earth ions may be introduced. The localised vibrations of the guest species serve to scatter phonons, thereby reducing the thermal conductivity. In a joint project with Loughborough and Cardiff Universities, we are investigating the potential of skutterudite materials for use in automotive waste-heat recovery applications. A skutterudite thermoelectric module (Figure 2(b)) constructed during this project exhibits a performance (Figure 2(c))

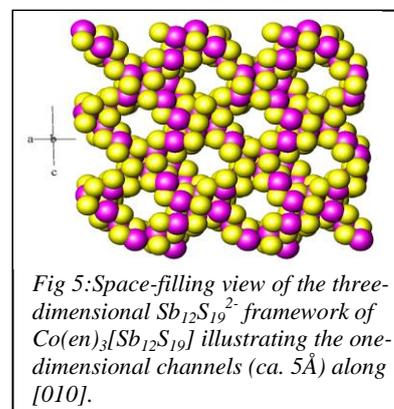
comparable with that of the current commercial material, Bi_2Te_3 but at a significantly higher temperature.

• **Electronic and Magnetic Properties of Low-Dimensional Chalcogenides:-** We have a long-standing interest in materials containing low-dimensional building blocks. Much of the focus has been directed at materials constructed from the two-dimensional transition-metal disulphide unit (Figure 3). Linkage of disulphide slabs through additional cations generates a variety of three-dimensional binary sulphides, M_yMS_2 ($y < 1$) in which vacancy ordering leads to two-dimensional superstructures. Chemical substitution induces structural changes within the disulphide slabs. We have identified novel clustering schemes (Figure 3) and established that the formation of zigzag cation chains is an essential pre-requisite for metallic behaviour.



We recently extended this work to rare-earth-transition-metal sulphides (Figure 4) and identified a homologous series constructed from a two-dimensional M_2S_5 slab. These materials consist of anionic frameworks of general formula $M_{2n+1}S_{4n+3}$ in which M_2S_5 -derived slabs of varying thickness are linked through chains of edge-linked octahedra. We have prepared members of this series corresponding to $n = 1, 2, 3$ and ∞ , thereby considerably extending the number of sulphides containing the Jahn-Teller active Cr^{2+} ion beyond the few known well-characterised examples such as CrS and $CrMo_2S_4$. Moreover, using powder neutron diffraction, we have identified a correlation between the presence of long-range magnetic order at low temperatures and the degree of ordering of chromium and rare-earth cations over octahedral sites within the $M_{2n+1}S_{4n+3}$ framework.

• **Structure-Directed Synthesis:-** Structure-directed synthesis offers tremendous scope for the discovery of new materials with novel architectures and potentially unique properties. In collaboration with Drs A.M. Chippindale and P. Vaqueiro, we have applied the methodology to main-group sulphides, particularly those of antimony and transition-metal sulphates. This work has led to the synthesis of novel three-dimensional sulphide frameworks (Figure 5). The combination of a porous chalcogenide framework and semiconducting properties offers the potential to design selective chemical sensors. During the course of this work, we have identified a correlation between the optical band-gap and the structural features of the main-group sulphide matrix (Figure 6), in particular the density of main-group atom centres, which suggests the electrical transport properties may be manipulated through structural control.



Recently, we have demonstrated that it is possible to combine structural building blocks with different geometrical preferences to generate materials with new structures. The anionic layers of $[Ge(C_2N_2H_8)_3][GeSb_2S_6]$ (Figure 7) for example, are constructed from SbS_n ($n = 3, 4$) and GeS_4 units. This material is also unusual in containing germanium in both the +2 and +4 oxidation states.

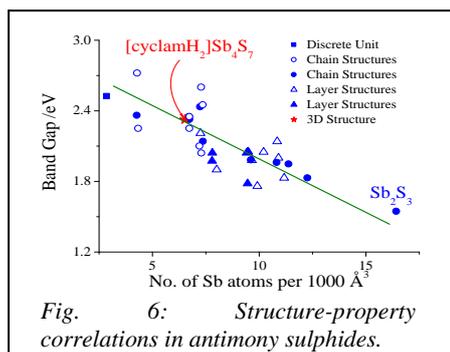


Fig. 6: Structure-property correlations in antimony sulphides.

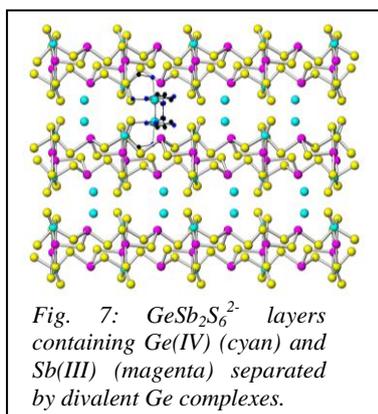


Fig. 7: $GeSb_2S_6^{2-}$ layers containing Ge(IV) (cyan) and Sb(III) (magenta) separated by divalent Ge complexes.

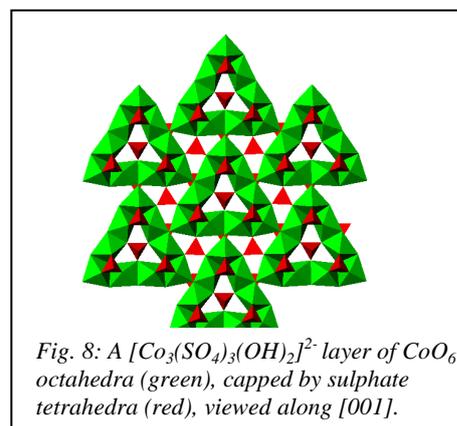


Fig. 8: A $[Co_3(SO_4)_3(OH)_2]^{2-}$ layer of CoO_6 octahedra (green), capped by sulphate tetrahedra (red), viewed along [001].

In related work, we have investigated the use of sulphuric acid as a reaction medium, leading to a variety of novel transition-metal sulphates, including $Co_3(SO_4)_3(OH)_2[enH_2]$, in which triangular Co_9O_{36} clusters produce a Kagome-like structure (Figure 8), characteristic of a magnetically frustrated system.

• **Co-Crystals of Pharmaceuticals:-** Co-crystallisation in which non-covalent interactions between donor and acceptor functional groups on different molecules leads to the crystallisation of a new organic solid, offers considerable attractions in the search for new Active Pharmaceutical Ingredient (API) formulations. In particular, co-crystallisation of an API with pharmaceutically acceptable guest components into a single crystal lattice is becoming an attractive method of targeting a solid dosage form of an API that is stable, bio-available, soluble and non-hygroscopic. However, the method of selecting which components to use is still poorly understood. Working closely with Solid Form Solutions Ltd, we have begun to investigate the factors that influence the co-crystallisation of APIs. By exploiting a combination of crystal design principles and database screening, we have adopted a targeted approach to co-crystal formation. An early success of this approach is the formation of a series of new co-crystals of the API paracetamol with diamine co-crystal formers (Figure 9).

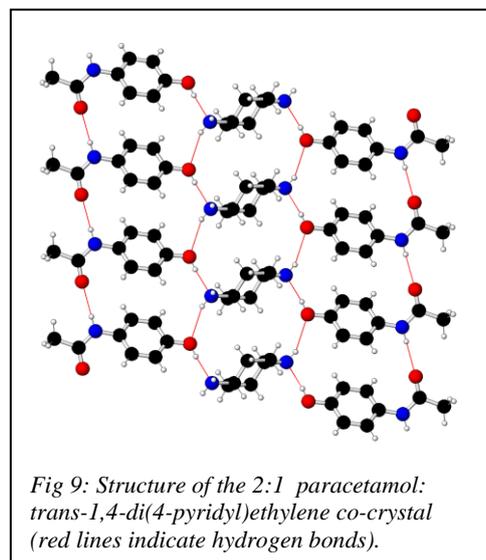


Fig 9: Structure of the 2:1 paracetamol: *trans*-1,4-di(4-pyridyl)ethylene co-crystal (red lines indicate hydrogen bonds).

Selected Recent Publications

$Co_3M_2S_2$ (M = Sn, In) Shandites as Tellurium-Free Thermoelectrics, J. Corps, P. Vaqueiro and A.V. Powell, *J. Mater. Chem. A*, **1**, 6553, (2013).

Fabrication and Evaluation of a Skutterudite-Based Thermoelectric Module for High Temperature Applications, J. García-Cañadas, A.V. Powell, A. Kaltzoglou, P. Vaqueiro and G. Min, *J. Electron. Mater.*, **42**, 1369, (2013).

Crystal Design Approaches to the Synthesis of Co-Crystals of Paracetamol, V.K Srirambhatla, A. Kraft, S. Watt and A.V. Powell, *Crystal Growth & Design*, **12**, 4870, (2012).

Structural Effects on the Electronic Properties of $TiCu_{7-8}S_4$ Investigated by Diffraction-Resistance Measurements, T.E. Engin, S. Hull and A.V. Powell, *Z. Anorg. Allg. Chem.*, **638**, 2565, (2012).

Solvothermal Synthesis of a Bimetallic Thiometallate Containing Germanium in Two Oxidation States. A.V. Powell and R. Mackay, *J. Solid State Chem.*, **184**, 3144, (2011)

Recent Developments in Nanostructured Materials for High-Performance Thermoelectrics; P. Vaqueiro and A.V. Powell, *J. Mater. Chem.*, **20**, 9577, (2010).

Ternary Erbium Chromium Sulfides: Structural Relationships and Magnetic Properties; P. Vaqueiro, I. Szkoda, R. Sanchez and A.V. Powell, *Inorg. Chem.*, **48**, 1284, (2009).