My research aims are to prepare new solid-state materials with interesting structural, chemical and physical properties. My main area of interest is the preparation and structural characterisation of ‘open-framework’ materials – materials with framework structures containing regular arrays of pores or channels of suitable size to accommodate small molecules – with the idea of performing chemical reactions inside the pores. A number of these types of material occur in Nature, including a class of aluminosilicate minerals called zeolites, which, by virtue of their open structures, have a range of uses from water softeners in washing powders to catalysts in petrochemical refining. I am exploring open-framework metal phosphates, sulphides and cyanides, which are synthetic materials that can mimic, and in some cases, outperform the natural zeolites.

Solvothermal techniques are used for the synthesis of most metal phosphates, cyanides and sulphides. A gel precursor, containing sources of the framework building elements (M, P, ‘CN’ or S), a solvent (aqueous or non-aqueous) and a structure-directing agent or ‘template’ (most commonly an organic amine or alkali-metal cation), is heated in an autoclave at low temperature (<473 K). As the gel is heated, the metal and phosphate, cyanide or sulphur components assemble around the ‘templating’ species to form an open inorganic framework containing amine- or alkali-metal- filled pores. Thermodynamically metastable compounds can be formed by this approach and these are not accessible through conventional solution or solid-state synthesis techniques. A recent synthetic highlight has been the preparation of TiGaPO-1 (Fig. 1), the first example of a titanium gallophosphate with a 3-D framework structure, which undergoes topotactic oxidation at low temperatures in a single-crystal-to-single-crystal transformation.

Fig 1: TiGaPO-1. Ti^{III}O_4(H_2O)_2 (pink), Ti^{IV}O_6 (red), GaO_4 (yellow) and PO_4 (magenta) units link to form a 3-D octahedral-tetrahedral hybrid framework containing a 1-D pore network in which pyridinium cations reside.

Organically templated antimony sulphides have also been prepared by solvothermal methods in collaboration with Prof. AV Powell, Heriot Watt University. Antimony sulphides commonly exhibit low-dimensional structures and contain structural motifs based on SbS$_3$ pyramidal units linked into chains or layers. We have recently prepared and characterised the first examples of truly three-dimensional structures. One material, [M(en)$_3$][Sb$_{12}$S$_{19}$] (M = Co, Ni) (Fig. 2), represents the first sulphide-based zeolite-like structure. This remarkable framework contains one-dimensional circular channels with a cross-section of ca. 5Å, a distance comparable with the dimensions of the channels in the commercially important zeolite, ZSM-5.

A further area of great current interest is transition-metal cyanide chemistry. Work in this field is carried out in collaboration with Dr Simon Hibble.

Recent Publications

- **A.M. Chippindale**, Poly(2,2'-bipyridine-κ\textsuperscript{2} N,N')( \( \mu_2 \)-hydrogen phosphate( \( \mu_2 \)-dihydrogen phosphate)-aluminium(III)), Al(2,2'-bipy)(HPO$_4$)(H$_2$PO$_4$), a layered inorganic-organic hybrid material, *Acta Cryst.*, C62, 2006, m372-m374.

• Chippindale, A.M. Poly(2,2'-bipyridine-κ$_2$ N,N')(μ$_2$-hydrogen phosphato)(μ$_2$-dihydrogen phosphato)-aluminium(III), Al(2,2'-bipy)(HPO$_4$)(H$_2$PO$_4$), a layered inorganic-organic hybrid material. *Acta Cryst.*, C62, 2006, m372-m374.


