

We aim to understand and exploit the factors (strain, composition, band structure *etc.*) that determine structure and function in the crystalline solid state. Our interest is in the balance between local crystal chemistry, strain and longer range order in a wide range of compositionally and/or displacively flexible crystalline solids. The principal experimental research tools used are solid state synthesis, transmission and scanning electron microscopy in combination with powder and single crystal diffraction. On the theoretical side, group theory, lattice dynamical calculations and bond valence sum analysis are the principal techniques employed. Crystalline systems investigated include a wide range of non-stoichiometric solid solutions, displacively flexible framework structures, ferroic phases, solid electrolytes, dielectric materials and incommensurately modulated structures. Achievements over recent years include (i) the first coherent view of the crystal chemistry underlying the phenomenon of ferroelectricity within the Aurivillius family of displacive ferroelectrics, (ii) the use of compositely modulated structure formalism to understand “infinitely adaptive”, non-stoichiometric solid solutions, and (iii) the discovery and subsequent modelling of displacive flexibility and its consequences in the silica polymorphs and various zeotypic microporous molecular sieve materials.



Local Crystal Chemistry, Induced Strain and Short Range Order in the Cubic Pyrochlore $(\text{Bi}_{1.5-\alpha}\text{Zn}_{0.5-\beta})(\text{Zn}_{0.5-\gamma}\text{Nb}_{1.5-\delta})\text{O}_{(7-1.5\alpha-\beta-\gamma-2.5\delta)}$ (BZN)

As part of an ongoing ARC funded project into the effects of substitutional strain on local crystal chemistry, a combined electron diffraction, neutron powder diffraction and Monte Carlo simulation study of short range order in the cubic pyrochlore $(\text{Bi}_{1.5-a}\text{Zn}_{0.5-b})(\text{Zn}_{0.5-g}\text{Nb}_{1.5-d})\text{O}_{(7-1.5a-b-g-2.5d)}$ (BZN) has been carried out. BZN is attractive as a resonator and decoupling capacitor in microwave circuits as a result of its high dielectric constant (ϵ), low dielectric loss and compositionally tuneable temperature coefficient of capacitance (t_c). Clear evidence (in the form of structured diffuse scattering) was found for short range ordering of metal ions and associated induced structural relaxation in two members of the cubic BZN solid solution. A detailed bond valence sum analysis has been used to suggest possible local cation ordering schemes along with the induced displacive relaxation that is likely to accompany such local cation ordering. The observed diffuse distribution was qualitatively interpreted via Monte Carlo modelling. (*with F. Brink, A-K. Larsson, Y. Liu, L. Norén, T.R. Welberry, and N. Ishizawa [Tokyo Inst. Tech., Japan], A. Pring [S. Australian Museum], H. Rundlof [U. Uppsala, Sweden]*)

Flexible Framework Structures

Displacively flexible, corner-connected polyhedral framework structures represent a large, technologically important and ever-growing family of crystalline phases (*eg.* zeotypic, microporous molecular sieve materials, nanoporous molecular framework structures, the silica polymorphs, fresnoites *etc.*) of fundamental importance to solid state chemistry, mineralogy and materials science. They exhibit a wide range of technologically important physico-chemical properties including low or even negative thermal expansion, selective adsorption and/or diffusion of gas molecules through the channels of the framework, shape selective catalysis, piezoelectricity, pyroelectricity *etc.* Their inherent flexibility arises as a result of numerous essentially zero frequency Rigid Unit Modes (RUM's) involving rotations but not distortions of the constituent polyhedral units. We have systematically investigated a range of flexible, microporous framework structures in order to identify the appropriate RUM modes (via temperature-dependent

electron diffraction), to analyze the displacive structural phase transitions therein, and to understand the physical properties associated with this inherent displacive flexibility. Attention has recently focussed on the microporous aluminophosphate materials AlPO_4-5 and -11 , on stuffed tridymites found in industrial waste ash and on the incommensurately modulated fresnoite $\text{Ba}_2\text{VSi}_2\text{O}_8$. (with Y. Liu, L. Norén, and T. Höche [U. Leipzig, Germany], T.J. White, L. Ying, [Inst. Environmental Science & Engineering, Nanyang Technological U. Singapore])

Electron Diffraction and Bond Valence Sum Studies of the Structures of Photocatalytic 1:1 Double and 1:2 Triple Perovskites

A careful investigation has been carried out into the space group symmetries, structures and crystal chemistries of the photocatalytic, B-site ordered, 1:1 double perovskites A_2InNbO_6 and 1:2 triple perovskites $\text{A}_3\text{CoNb}_2\text{O}_9$ ($\text{A} = \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}$) using a combination of bond valence sum calculations, powder XRD and electron diffraction. Recent investigations of these compounds reported a random distribution of $\text{In}^{3+}/\text{Co}^{2+}$ and Nb^{5+} ions onto the perovskite B-site positions. Careful diffraction investigations, however, have shown that B site ordering occurs in both families of compounds. Bond valence sum calculations are used to explain why this should be so as well as to provide a useful first order approximation to the structures of each of the compounds. (with Y. Liu, L. Norén, V. Ting, and T.J. White, L. Ying, [Inst. Environmental Science and Engineering, Nanyang Technological U., Singapore])

A Low Temperature Electron Diffraction Study of Structural Disorder and Its Relationship to the Kondo Effect in ThAsSe

A low temperature electron diffraction study has been carried out on ThAsSe to search for evidence of structural disorder responsible for the unusual low temperature transport properties of this material. A highly structured and extremely complex characteristic diffuse intensity distribution has been observed at low temperature and interpreted in terms of a gradual charge density wave type phase transition upon lowering of temperature involving disordered As-As dimerization within (001) planes. Plausible models of the proposed gradual As-As dimerization and its consequences for transport properties have been obtained using a group theoretical approach. (with J. Schoenes [Technical U. Braunschweig, Germany], R. Vincent [U. Bristol, UK])

A Low Temperature Phase Transition that Leads to Problems in Space Group Determination and Refinement

A low temperature X-ray diffraction study of bis(2,6-bis(pyrazol-3-yl)pyridine) iron(II) nitroprusside revealed a very interesting interpretation problem. A high spin-low spin transition changed the P4/ncc room temperature structure to a twinned orthorhombic structure which was studied at 100 K. The diffraction pattern had $4/mmm$ diffraction symmetry and the structure could be described as a commensurate modulation of the parent structure. The use of the theory of irreducible representations for space groups allowed the identification of two possibilities, either a Pnca/Pcnb twin or a Pcna/Pncb twin. Using systematic absences to distinguish between these space group options was impossible because of the twinning. However the different site symmetries for the two options and the subsequently allowed displacements identified the appropriate solution as the Pnca/Pncb option. This allowed a z-displacement of the cation to initiate refinement as a displacement from the P4/ncc structure. (A.D. Rae, with D.C. Craig, H.A Goodwin, [U. NSW])

<http://rsc.anu.edu.au/research/withers.php>