



Solid State Inorganic Chemistry

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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 wide range non-stoichiometric solid solutions, displacively flexible framework structures, ferroic phases and phase transitions, solid electrolytes, dielectric materials and incommensurately modulated structures. Achievements over recent years include the first coherent view of the crystal chemistry underlying the phenomenon of ferroelectricity within the Aurivillius family of displacive ferroelectrics, the use of compositely modulated structure formalism to understand "infinitely adaptive", non-stoichiometric solid solutions, and the discovery and subsequent modelling of displacive flexibility and its consequences in the silica polymorphs and various zeotypic microporous molecular sieve materials.

A Combined Diffraction and Hard-mode Infrared Spectroscopy Study of Composition-induced Structural Phase Transitions in the $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ ($0 \leq x \leq 0.6$) System

As part of an ongoing ARC-funded project into the effects of substitutional strain on local crystal chemistry, a combined diffraction and hard-mode infrared (IR) powder absorption spectroscopy study of composition-induced structural phase transitions in the $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ ($0 \leq x \leq 0.6$) system has been carried out. This system is of interest as a high-temperature fast oxide ion conductor for use in a wide range of electrochemical devices including oxygen sensors, solid oxide fuel cells and oxygen separation membranes. A recently introduced autocorrelation analysis method has been used to quantify composition-induced structural phase changes *via* a careful analysis of peak positions and line broadening in IR spectra as a function of composition. An orthorhombic brownmillerite to three-dimensionally disordered cubic perovskite phase transition in this system is signalled by a drastic change in slope of both wave-number and average linewidth as a function of composition. Some evidence is found for the existence of an intermediate tetragonal phase (previously reported to exist from electron diffraction data) around $x \sim 0.2$. The new spectroscopic data have been used to compare microscopic and macroscopic strain parameters arising from variation in composition. *(With Y Liu, L Norén, T R Welberry, and S Moussa, A Pring, C Tenailleau [South Australian Museum], M Carpenter, S Tarantino, M Zhang [U Cambridge, UK])*

A Structure, Conductivity and Dielectric Properties Investigation of $\text{A}_3\text{CoNb}_2\text{O}_9$ ($\text{A} = \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}$) Triple Perovskites

There has recently been considerable interest in the structures and associated physical properties of $\text{A}_3\text{Co}^{2+}\text{Nb}^{5+}_2\text{O}_9$ ($\text{A} = \text{Ca}, \text{Sr}$ and Ba) complex 1:2 perovskites, mainly as a result of their potential photocatalytic and microwave dielectric applications. A careful investigation has therefore been carried out into their room temperature structures as well as their temperature-dependent conductivity and dielectric properties. A constrained modulation wave approach to Rietveld structure refinement is used to determine their room temperature crystal structures. Correlations between these crystal structures and their physical properties are found. All three compounds undergo insulator to semiconductor phase transitions as a function of increasing temperature. The hexagonal $\text{Ba}_3\text{CoNb}_2\text{O}_9$ compound acts as an insulator at room temperature, while the monoclinic $\text{Ca}_3\text{CoNb}_2\text{O}_9$ compound is already a semiconductor at room temperature. *(With D J Goossens, Y Liu, L Norén, V Ting, and C Ferraris, S Madhavi, T J White, [School of Materials Engineering, Nanyang Technological U, Singapore], M James [Bragg Institute, Australian Nuclear Science and Technology Organisation])*



The Pyrochlore to 'Defect Fluorite' Transition in the $Y_2(ZrTi_{1-y})_2O_7$ System and its Underlying Crystal Chemistry

As a result of its high oxide ion conductivity at moderate to high temperature as well as its low activation energy for such oxide ion conduction, 'defect fluorite' type yttrium-stabilized zirconia is currently widely used as the solid electrolyte of choice in solid oxide fuel cells (SOFCs) as well as in sensors measuring oxygen partial pressure in car exhaust systems. Such properties, however, are not the only desirable characteristics required for use in SOFCs. Another very important physical requirement is chemical stability and compatibility with adjoining electrode materials. There has been much recent interest in a monolithic fuel cell design in which cathode, electrolyte and anode are inherently compatible as a result of being made up of essentially the same $A_2(B'_yB_{1-y})_2O_7$ ($A = Y^{3+}, Gd^{3+}; B = Ti^{4+}; B' = Zr^{4+}, Sn^{4+}$) 'pyrochlore'-type (mixed oxide ion as well as electronically conducting) materials. Particular interest has focussed on the $Y_2(ZrTi_{1-y})_2O_7$ system as a result of the electronic conductivity introduced by the presence of the Ti ions as well as the "... remarkable increase in (oxide ion) conductivity of three orders of magnitude as the Ti cation is replaced by the larger Zr cation". A careful diffraction and dielectric properties investigation of the previously reported single phase, pyrochlore structure type $Y_2(ZrTi_{1-y})_2O_7$, $0 \leq y \leq 0.9$, (YZT) solid solution has therefore been carried out. (With Y Liu, L Norén)

The Systematics of Problem Pseudo Symmetric Crystal Structures

Many structures cause problems for structure determination and refinement using X-ray diffraction techniques. Often an idealised 1:1 disordered parent structure can be found that corresponds to the Fourier transform of a strongly diffracting subset of reflections. The apparent Laue symmetry of this idealised structure must be lowered to account for the extra (satellite) reflections. To a first approximation this is achieved by ordering the disorder to create intensity for the satellite reflections without altering the intensities of the parent reflections. Often this ordering is not perfect. As a consequence, stacking faults and twinning result, necessitating the use of constraints and restraints to control the refinement and obtain a respectable looking answer. Often possible structures are associated with alternative orientations or origins for the stacking of ordered columns or layers. This allows the use of structure factor algebra to combine such layers or columns in a generalised twin-disorder model using appropriate parameters. This sometimes results in alternative space groups or alternative orientations for a structure. Sometimes observed intensities cannot be described using the twinning of a simple average structure and account must be taken of the consequences of having different regions of a crystal with different twin-disorder parameters. Final refinement requires lowering the symmetry of the layers or columns because of the packing. It is often useful to maintain the twin disorder parameters previously obtained as a sensible constraint on refinement, especially a stacking fault that simply changes the scale of certain reflections. (A D Rae)

The Identification of Twin Planes in Monoclinic and Triclinic Crystals

Currently the X-ray diffraction unit is identifying and refining several twinned crystals each year. Being unaware of the twinning usually does not preclude an initial structure solution. However, satisfactory refinement is only obtained by correctly identifying the twin rule so that the indices and relative positions of partially overlapping reflections is correctly determined. We have found that for packing of molecules the correct twin plane usually has the smallest repeating area. Often twinning is associated with the packing of approximately symmetric layers in such a way as to lower this layer symmetry. The layer symmetry then provides a mechanism for twinning and for the creation of possible polymorphs. (A D Rae)

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