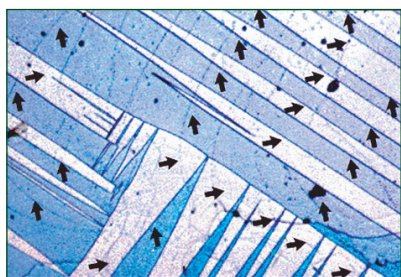




# SOLID STATE INORGANIC CHEMISTRY

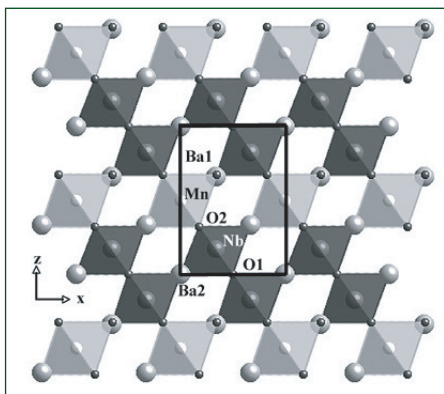
PROFESSOR RAY WITHERS

We aim to understand and exploit the factors that determine structure and function in the crystalline solid state. A major interest is in the balance between local crystal chemistry and longer-range order in a wide range of flexible crystalline phases. The principal experimental research tools used include a wide range of solid state synthesis techniques, transmission and scanning electron microscopy in combination with powder and single crystal diffraction as well as physical properties measurements including resistivity as well as dielectric properties. 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.



## A Structure, Phase Analysis and Dielectric Properties Investigation of Some Complex Perovskites

The "1:1"  $A_2\text{In}^{3+}\text{Nb}^{5+}\text{O}_6$  double perovskites have been the subject of recent interest due to their potential as visible light driven photocatalysts as well as for their microwave dielectric properties in the case of the  $A = \text{Ba}$  and  $\text{Sr}$  compounds. Likewise the 1:2  $\text{Ba}_3\text{Mn}^{2+}\text{Nb}^{5+}_2\text{O}_9$  triple perovskite is of interest for its dielectric properties. A careful investigation has therefore been carried out into the room temperature crystal structures of these complex perovskite materials as well as their



temperature-dependent dielectric properties. In the case of the nominally "1:1"  $A = \text{Ca}$  compound, an extensive  $\text{Ca}_2[(\text{Ca}_{2x/3}\text{In}_{1-x}\text{Nb}_{x/3})\text{Nb}]\text{O}_6$  'solid solution' field spanning compositions virtually the whole way from  $\text{Ca}_4\text{Nb}_2\text{O}_9$  to  $\text{Ca}_2\text{InNbO}_6$  in the  $\text{CaO}-\text{InO}_{3/2}-\text{NbO}_{5/2}$  ternary phase diagram has been shown to exist. In terms of the optimisation of physical properties, the existence of  $B$ -site variable solid solutions fields such as this is of considerable interest as it raises the possibility of being able to continuously tune desired physical characteristics. In the case of the 1:2  $\text{Ba}_3\text{Mn}^{2+}\text{Nb}^{5+}_2\text{O}_9$  triple perovskite, stacking fault disorder appears to play a strong role in the dielectric loss properties of the material. (With Y Liu, L Norén, V Ting, and J Fitz Gerald [RSES, ANU], M James [Bragg Institute, ANSTO])

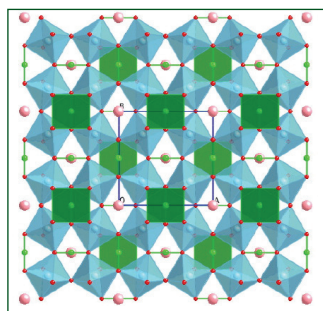
## Precise Diffraction Studies of Temperature-dependent as well as Composition-induced Structural Phase Transitions in the $\text{Ca}_{1-x}\text{Sr}_x\text{TiO}_3$ System

As part of an ongoing ARC-funded project involving precise diffraction studies of structural phase transitions in functional metal oxides, a coupled electron, synchrotron X-ray and neutron diffraction study of temperature-dependent as well as composition induced structural phase transitions in the  $\text{Ca}_{1-x}\text{Sr}_x\text{TiO}_3$  system is under way. The mineral perovskite itself,

$\text{CaTiO}_3$  is a major component of Synroc, a synthetic rock form designed for the immobilisation of radioactive waste. Our interest in the  $\text{Ca}_{1-x}\text{Sr}_x\text{TiO}_3$  system derives from the fact that the  $\text{CaTiO}_3$  acts as a host for fission product Sr. It is therefore of some importance to precisely characterise the polymorphic and phase transition behaviour of this archetypal perovskite system. We are concentrating on regions of the phase diagram where significant disagreements currently exist in the literature. Attention is currently focussed on the  $x = 0.70$  composition where diffraction studies have shown that the room temperature space group symmetry of  $\text{Ca}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$  is  $I4/mcm$  rather than  $Imma$  as recently claimed. Work is also currently underway on the  $x \sim 0.63$  composition where a novel anti-ferroelectric polymorphic form is being carefully investigated. (With C J Howard [ANSTO], B J Kennedy [U Sydney], M Carpenter [U Cambridge, UK])

### Structurally Frustrated Relaxor Ferroelectric Behaviour in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$

Ever since  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) was first reported in 2000 to have a giant dielectric constant at 1 kHz of  $\sim 12,000$  that was nearly constant from room temperature up to  $\sim 600\text{K}$  but which dropped rapidly to less than 100 below 100K, a huge amount of interest and work has been carried out in an attempt to understand the origin of these remarkable



and potentially very useful dielectric properties. Both extrinsic (microstructural) as well as intrinsic mechanisms for the observed dielectric properties have been proposed. Dielectric constants greater than 1000 have traditionally been associated with intrinsic ferroelectric or relaxor ferroelectric (RF) behaviour. We have recently observed a reversible ferroelectric effect in CCTO as well as found direct diffraction evidence for structurally frustrated RF behaviour in the form of 1-d correlated, off-centre displacements of Ti ions within the  $\text{TiO}_6$  octahedra of CCTO. That this incipient ferroelectric behaviour is only correlated along 1-d columns of  $\text{TiO}_6$  octahedra in the absence of an applied electric field offers a crucial insight into the underlying nature of CCTO and suggests the existence of a unique new class of

structurally frustrated, ferroelectric relaxors. As part of a newly funded ARC grant, the correlation between composition, synthesis conditions, structure (both local as well as microstructural) and dielectric properties (dielectric constant as well as dielectric loss) will be carefully investigated in CCTO and related materials. (With Y Liu, L Norén)

### Refinement of Minor Components in Twin-disordered Crystal Structures

The structure determination and refinement of crystalline materials using diffraction techniques is often complicated by the presence of minor components of the scattering density that compromise the accuracy and chemical detail obtainable. Refinement, for example, can be very pathway dependent, especially when twinning occurs. A number of strategies are being pursued to overcome these problems. An in-house program RAELS is currently being rewritten to simplify comparative refinement. Symmetrisation is the description of a structure using irreducible representation theory. Each component of the overall electron density has the true symmetry as a subgroup and is itself a subgroup of an idealised parent space group. The process becomes useful when it reveals symmetrised components which make a limited contribution to the overall intensity of a diffraction pattern. Such components are often poorly defined if standard refinement procedures are used and mechanisms for stacking faulting and twinning are not recognised. There is no correlation between symmetrised components if powder diffraction data is used. The program RAELS allows the combination of structure factors from pseudo-equivalent reflections of an ideally ordered prototype structure to simulate the diffraction pattern. Recent results have shown that robust geometrical parameters can be obtained using this approach. (A D Rae)

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