

emphasis upon their reduced tendency to exhibit polymorphism.

[1] Almarsson Ö., Zaworotko M.J., *Chem. Commun.*, 2004, 1889-1896.

Keywords: solid-state chemistry, crystal engineering, co-crystals

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An Exploration of Polymorphism in Molecular Crystals Using High Pressure

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The application of high pressure to simple molecular compounds is proving to be a powerful method for exploring the polymorphic behaviour of these compounds [1]. Direct compression of either single crystals or powders, and crystal growth from the melt are two methods that have been used to prepare new polymorphs of compounds that have been structurally characterised by X-ray and neutron diffraction. Recent examples include sulfuric acid monohydrate, thiourea dioxide, and acetamide. The development of methods for *in situ* high-pressure growth of single crystals from solution has allowed a much wider range of compounds to be studied including pharmaceuticals (e.g. paracetamol, piracetam), and has enabled us to prepare new solvates [2]. We have also demonstrated how metastable polymorphs and solvates can be prepared under pressure with subsequent recovery of bulk quantities at ambient pressure, and how pressure can be used to screen compounds for polymorphism and solvate formation.

[1] Fabbiani F. P. A., Allan D. R., Dawson A., David W. I. F., McGregor P. A., Oswald I. D. H., Parsons S., Pulham C. R., *Chem. Commun.*, 2003, 3004. [2] Fabbiani F. P. A., Allan D. R., David W.I.F., Moggach S.A., Parsons S., Pulham C. R., *CrystEngComm*, 2004, **6**, 504.

Keywords: pharmaceuticals, high pressure, polymorphs

MS05 STRUCTURAL PHASE TRANSITIONS

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Structural Transitions in Perovskites: Successes of a Group Theoretical Approach

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The author has made extensive use of group theory, as implemented in computer program ISOTROPY (<http://physics1.byu.edu/~stokesh/isotropy.html>), to underpin the study of structural variation and structural phase transitions in perovskites. A review of the work appears in the literature [1].

The approach will be illustrated for the double perovskites, $A_2BB'X_6$, where alternation of *B*-site cations is coupled with the ubiquitous BX_6 octahedral tilting. The symmetries of the cation ordering, in-phase and out-of-phase tilting are identified, respectively, with irreducible representation R_1^+ , M_3^+ , R_4^+ of the parent space group $Pm\bar{3}m$. Program ISOTROPY is used to enumerate the structures and possible phase transitions [1]. The results have guided recent structure determinations of Sr_2YNbO_6 and Sr_2YTbO_6 [2], as well as detailed studies of temperature-induced transitions in $BaBiO_3$ and Ba_2BiSbO_6 .

In another development [3], we used ISOTROPY to assist in constructing the free energy expansion for a combination of Jahn-Teller distortion (Γ_3^+) and octahedral tilting (R_4^+) in $PrAlO_3$. We proposed a mechanism for the coupling of J-T distortion to the octahedral tilting via a common tetragonal strain - such a mechanism can account for the three phase transitions observed.

[1] Howard C.J., Stokes H.T., *Acta Cryst.*, 2005, A61, 93. [2] Howard C.J., Barnes P.W., Kennedy B.J., Woodward P.M., *Acta Cryst. B*, submitted. [3]

Carpenter M.A., Howard C.J., Kennedy B.J., Knight K.S., *Phys. Rev. B*, submitted.

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Phase Transitions in Relaxor Ferroelectric Based Solid Solutions

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The phase diagrams of solid solutions of lead based complex perovskite relaxors with $PbTiO_3$ contain a morphotropic phase boundary (MPB) similar to that observed in the well known $Pb(Zr_xTi_{1-x})O_3$ (PZT) ceramics. This talk focuses on our recent work on the structural changes as a function of composition and temperature in one such system i.e., $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_{3-x}PbTiO_3$ (PMN-xPT). Our results show [1, 2] that unlike the PZT system, the MPB composition range ($0.26 < x < 0.35$) in the PMN-xPT contains two monoclinic phase regions with Cm and Pm space groups, giving rise to two peaks in the variation of the physical properties with composition. Temperature dependent dielectric, piezoelectric resonance frequency, polarization and powder diffraction studies reveal several other interesting features: (i) relaxor nature of the transitions from the rhombohedral and the two monoclinic phases to the cubic phase, (ii) non-relaxor nature of the tetragonal to cubic transition, (iii) a transition from the tetragonal to the monoclinic Pm phase below room temperature, (iv) the monoclinic to cubic transition via an intermediate tetragonal phase above room temperature and (v) elastic instability associated with transitions between two ferroelectric phases. The role of polarization rotation and elastic matching at various phase boundaries will be discussed in relation to the high piezoelectric response of PMN-xPT in the MPB regions.

[1] Singh A.K., Pandey D., *Phys. Rev. B*, 2003, **67**, 064102. [2] Singh A.K., Pandey D., Zaharko O., *Phys. Rev. B*, 2003, **68**, 172103.

Keywords: relaxor ferroelectrics, monoclinic phases of PMN-xPT, MPB

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The Phase Diagram of $Ca_{2-x}Sr_xRuO_4$: Crystal Structure and Physical Properties

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The phase-diagram of $Ca_{2-x}Sr_xRuO_4$ has been studied by several diffraction techniques and by analysis of thermodynamic properties as function of concentration, temperature, pressure and magnetic field. The substitution of Sr through the smaller Ca induces a series of structural phase transitions with a strong impact on the physical properties. The spin triplet superconductor Sr_2RuO_4 exhibits an undistorted crystal structure, and the Mott-insulator Ca_2RuO_4 shows strong structural distortions characterized by tilting, rotating and flattening of the RuO_6 -octahedra. For intermediate structural distortions samples stay metallic but with outstanding physical properties. Throughout the phase diagram we find a close coupling between the crystal structure on one side and magnetic and electronic behavior on the other side.

[1] Braden M., et al., *Phys. Rev. B*, 1998, **58**, 847. [2] Friedt O., et al., *Phys. Rev. B*, 2001, **63**, 174432. [3] Kriener M., et al., *cond-mat/0408015*, [4] Steffens P., et al., *cond-mat/0502332*.

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