

**K1 Electron Density Determination under non Ambient Conditions.** Ullrich Pietsch, *Institute of Physics, University of Potsdam, Am Neuen Palais 10, D-14469 Potsdam, Germany, E-mail: upietsch@rz.uni-potsdam.de*

**Keywords: Electron Density; Electric Field; Non Ambient Conditions**

Usually the determination of the static electron density distribution in crystals is performed using x-ray diffraction techniques under ambient conditions. This includes measurements at very low temperatures in order to reduce the influence of atomic vibrations. Nowadays the accuracy of experimental electron densities is comparable with those of theoretic ab-initio calculations and allows quantitative analysis of the nature of chemical bonds in crystals. The subsequent next step consists in the investigation of electron density variations under influence of external excitation, i.e., at non-equilibrium conditions. Although the availability of synchrotron radiation sources this is an experimental challenge and the reason why the number of respective experiments is small. First pump-and-probe experiments have been performed to measure the charge density distribution of excited energy levels of molecules in crystals [1]. Also first studies of electron density variations under influence of an external magnetic field are known [2]. Measurements under influence of an external high-electric field have been performed by a few groups [3]. Here one applies a low frequent E-field to a capacitor arrangement of a high-resistant crystal material and measures the x-ray scattering intensity quasi-static with and without the electric field. For most sensitive reflections the change of intensity is in the order of one per-cent and can be determined with an accuracy of 0.1 per-cent.

Respective experiments of our group have been performed at piezoelectric materials as GaAs, ZnSe,  $\alpha$ -quartz and  $\alpha$ -GaPO<sub>4</sub>. For all these materials the experiment provides an answer of the atomic origin of the piezoelectric effect. Whereas for the zinc-blende materials the charge density response to the external electric field is simply a displacement of the cationic and anionic sublattices against each other [4], the answer for quartz-like materials consists in a rotation of charged MO<sub>4</sub> tetrahedra (M = Si, Ga, P...) lying parallel to the applied field and a subsequent deformation of neighbored tetrahedra [5]. The interpretation of experimental data required a compromise between semi-empirical modelling and ab-initio calculations caused by the break of 3D periodicity due to the applied field.

The talk will introduce into the experimental technique of electron density determination under non ambient conditions and will present new results with respect to the understanding of the electron density variations under influence of external electric fields.

- [1] Ch. Kim et al. *Acta Cryst.* (2002) A58, 133-137
- [2] V.A. Stretsov, private comm.
- [3] H.Graafsma et al. *Acta Cryst.* (1997) B53, 565
- [4] J.Stahn et al. *Phys.Rev.* (2001) B65, 165205
- [5] J.Davaasambuu et al. *Europhys.Lett.* (2003), 62, 843

**K2 Negative Thermal Expansion Materials.** John S.O. Evans, *Department of Chemistry, University of Durham, UK. E-mail: john.evans@durham.ac.uk*

**Keywords: Thermal Expansion; Oxide Materials; Powder Diffraction**

We have an on going interest in materials which show the unusual phenomenon of "Negative Thermal Expansion" and which undergo a contraction in volume on heating.[1] Such materials have a number of potential applications, the most obvious being as components of composites which could be adjusted to have controlled positive, negative or even zero coefficients of expansion. ZrW<sub>2</sub>O<sub>8</sub> is perhaps the best-known of such materials and undergoes continual, reversible and isotropic contraction as it is warmed from 2 K to 1050 K. The coefficient of contraction ( $\alpha = -9 \times 10^{-6} \text{ K}^{-1}$ ) is of comparable magnitude to the positive expansion coefficient of many "normal" materials. We have performed a number of "parametric" diffraction experiments which have provided key insight into the origin of this unusual effect in this and other framework material; selected examples from these will be discussed. We have also developed new methodologies to allow us to combine powder diffraction and solid state NMR information, which have allowed us to investigate the structure of some remarkably complex NTE-related framework inorganic materials. We have, for example, shown that compounds with apparently simple formulae such as SnP<sub>2</sub>O<sub>7</sub> and Mo<sub>2</sub>P<sub>4</sub>O<sub>15</sub> are actually amongst the most complex extended inorganic materials known, SnP<sub>2</sub>O<sub>7</sub> having over 500 crystallographically unique atoms in its asymmetric unit![2] The structural chemistry of some of these remarkable compounds, the origins of their complexity and its relevance to thermal expansion will be discussed. We have also performed a number of variable temperature/time in-situ diffraction studies which have revealed new information about the synthesis and reactivity of framework materials,[3] and given insight into the unusual phenomenon of low temperature (<200 K) oxygen migration in certain phases.[4,5,6] Selected examples will be presented.

- [1] J. S. O. Evans, *J. Chem. Soc.-Dalton Trans.*, 1999, 3317.
- [2] F. Fayon; I. J. King; R. K. Harris; R. K. B. Gover; J. S. O. Evans; D. Massiot, *Chem. Mat.*, 2003, 15, 2234.
- [3] S. Allen; N. R. Warmingham; R. K. B. Gover; J. S. O. Evans, *Chem. Mat.*, 2003, 15, 3406
- [4] S. Allen; J. S. O. Evans, *J. Mater. Chem.*, 2004, 14, 151
- [5] M. R. Hampson; P. Hodgkinson; J. S. O. Evans; R. K. Harris; I. J. King; F. Fayon, *Chem. Commun.*, 2004, 392.
- [6] S. Allen; J. S. O. Evans, *Phys. Rev. B*, 2003, 68, 134101