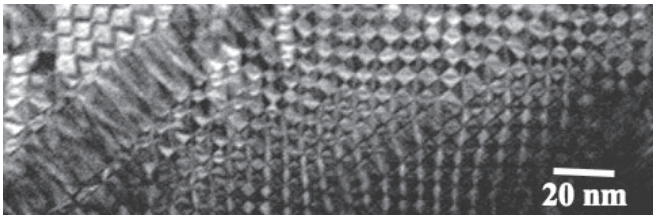

Fig.1. Low mag image of an x = 0.1, $Li_{3x}Nd_{2/3-x}TiO_3$, *A*-site ordered, 'defect' perovskite exhibiting complex ordering on multiple length scales.

The sensitivity of electron diffraction to weak, subtle features of reciprocal space (such as weak additional satellite reflections and/or structured diffuse intensity distributions) coupled with the capacity to also image over a wide range of length scales makes the Transmission Electron Microscope (TEM) an extremely well-adapted instrument for the structural characterization of 'modulated' materials of this type.

In this contribution, the results obtained from several such systems will be described including inherently Pb-free polar functional materials, relaxor ferroelectric systems and the $Li_{3x}Ln_{2/3-x}TiO_3$, $0.047 < x < 0.147$, family of Li ion conductors. The local crystal chemical 'rules' underlying the inherent structural flexibility of such materials will be highlighted along with the characteristic diffraction signatures of such behaviour.

[1] R.L.Withers *Advances in Imaging and Electron Physics* **2008**, *152*, 303-337.

Keywords: modulated, disordered, electron_diffraction

MS.79.3

Acta Cryst. (2011) A**67,** C175

Bonding charge density in $srtio_3$ under an electric field measured by electron diffraction

Andrew W S Johnson, [a] Philip N H Nakashima,[b,c,d] Terry J Frankcombe,[e] *[a]Centre for Microscopy, Characterisation & Microanalysis and School of Physics, University of Western Australia, 35 Stirling Hwy., Crawley, WA 6009, (Australia). [b]Monash Centre for Electron Microscopy, [c]ARC Centre of Excellence for Design in Light Metals and [d]Department of Materials Engineering, Monash University, Victoria 3800, (Australia). [e]Research School of Chemistry, Australian National University, ACT 0200 (Australia).* E-mail: bill@physics.uwa.edu.au

The precise measurement of charge density when influenced by an electric field is clearly of interest in the understanding of the electrical properties of dielectrics. Considerable practical difficulties have prevented the production of experimental results that could test theoretical calculations of such distortion of charge density. This comment applies to both X-ray and electron diffraction charge density measurements. With X-rays, due to the requirement to use a perfect crystal when an electric field is applied, severe extinction prevents access to the charge density sensitive, low order region of reciprocal space. With electron diffraction, the application of a sufficiently strong electric field while simultaneously cooling the sample is a combination not available in commercial specimen holders. In the present work, modification of an old design of the Gatan 636 double tilting cooling holder has overcome this limitation.

The near zone axis technique of Quantitative Convergent Beam Electron Diffraction, QCBED, as detailed in [1], was used to measure the low order structure factors of $SrTiO_3$ with zero field applied. Some 150 diffraction patterns were recorded over a range of zone axes, accelerating voltages and temperatures between -144C and room temperature. The experiment is planned to repeated with a field of 1 to 4 V/micron applied in the 001 direction, limiting patterns to orientations near the 100 zone axis. The zero field data is a reference against which the field data may be measured as a perturbation. Also, two prior measurements of charge density at zero field, which differ substantially from each other, [2] [3] were available for comparison.

Upon the application of a field in the 001 direction, the 010 mirror line of symmetry in $SrTiO_3$, available in CBED patterns near the 100 zone, should disappear, the crystal symmetry being lowered from Pm3m to P4mm.

Calculated CBED patterns for the above geometry and with an applied electric field are being prepared, using the JEMS program with theoretical Fourier coefficients of the potential. The Fourier coefficients were obtained from the Discrete Fourier Transform of the total electrostatic potential derived from DFT calculations. These were performed with the Abinit program using the projector augmented wave density functional theory method (PAW-DFT), with a PBE density functional. A finite electric field was applied using the Berry phase approach.

Experimentally, samples to which an electric field can be applied are being prepared and the results will be reported at the conference.

[1] P N H Nakashima et al, *Science* **2011**, *331*, 1583. [2] J Friis et al, Acta Cryst., **2004**, *A60*, 402. [3] W Jauch & M Reehuis, Acta Cryst., **2005**, *A61*, 411.

Keywords: charge-density, electric-field, CBED

MS.79.4

Acta Cryst. (2011) A**67,** C175-C176

Automated quantitative 3d electron diffraction rotation tomography

Peter Oleynikov,[ab] Sven Hovmöller,[b] Xiaodong Zou,[a,b] *[a]Berzelii Centre EXSELENT on Porous Materials, Stockholm University, Stockholm, (Sweden).* [b]*Department of Materials and Environmental Chemistry, Stockholm University, 106 91 Stockholm, (Sweden).* E-mail: peter.oleynikov@mmk.su.se

A new method of three-dimensional reciprocal space scanning using automated 3D electron diffraction rotation tomography is developed [1]. Sweeping reciprocal space is implemented by using the electron beam tilt within a given angular range and a small step. The beam tilt is combined with the mechanical crystal tilt in order to cover the full range of tilt angles available for the accessible transmission electron microscope (TEM) goniometer.

The automatic data collection procedure is split into two parts. Firstly, the mechanical tilt is used in order to reach different low-index crystallographic axes. Secondly, the deflection coils of the electron microscope are used for tilting the beam electronically around some axis, thereby sampling and scanning reciprocal space with desired precision. The smallest beam tilt step depends on the TEM machine but can be as small as ~0.0005°.

At present, this method allows the collection of 3D data by sweeping reciprocal space in the range from –43° to +43° (these values are the actual limits for our JEOL 2100 double tilt TEM sample holder) covering ~86° of reciprocal space or from –75° to +75° using the single ultra-high tilt holder. The complete data set contains 36 individual subsets for single tilt holder. Each subset covers 4° and has 80 individual frames, recorded by tilting the beam with 0.05° steps between frames. Every data subset was recorded after physically tilting the sample at an interval of 3.5° introducing some overlap between data subsets. This automated electron diffraction rotation tomography which we have developed allows collecting 2880 individual frames within 90 min (~1 frame per second, ~60 minutes for 2000 frames including crystal tracking). Scanning reciprocal space using rotation tomography allows registering not only the reflections, but also the 3D

diffuse scattering intensity around and between diffraction spots.

The collected data of high quality can be used for further determination of a 3D crystal structure. For example, it was possible to identify all oxygen atoms in the calculated three-dimensional potential map after the crystal structure analysis of the experimental 3D data, collected using the rotation diffraction tomography method applied to $K_2Nb_{14}O_{36}$ sample (space group *P4/mbm*, unit cell is $a = b = 27.5$ Å, $c = 3.94$ Å). This is the first time for the given structure when the oxygen atoms have been localized and identified in the 3D potential map using electron microscopy.

The use of cryo-TEM specimen holder allowed us to collect a data set and perform a partial reconstruction of a small part of reciprocal space for a *sucrose* sample. It was possible to maintain the data collection for ~12 min covering 16.5° in reciprocal space using 3D tomography.

[1] D. Zhang, P. Oleynikov, S. Hovmöller and X.D. Zou. *Z. Kristallogr*., **2010**, *225*, 94–102.

Keywords: Electron_diffraction, Tomography, Reciprocal_Space

MS.79.5

Acta Cryst. (2011) A**67,** C176

Electrostatic potential analysis of the rhombohedral phase of ferroelectric $BaTiO_3$ using CBED

Kenji Tsuda, Rikiya Sano, Michiyoshi Tanaka, *IMRAM, Tohoku University, Sendai (Japan).* E-mail: k_tsuda@tagen.tohoku.ac.jp

A CBED structure analysis method using convergent-beam electron diffraction developed by Tsuda and Tanaka [1, 2] enables accurate determination of crystal structural parameters such as atom positions, atomic displacement parameters (ADPs) and low-order structure factors from nanometer-sized specimen areas. From the refined parameters, electrostatic potential and electron density distributions are reconstructed. Recently, the method was successfully applied to the electrostatic potential analyses of silicon [3] and the orbital ordered phase of spinel oxide $FeCr_2O_4$ [4].

The method is particularly advantageous for the analysis of ferroelectric materials: (1) Reliable diffraction intensity data are obtained from a single ferroelectric-domain area of specimens containing minute ferroelectric domains. (2) The direction of ferroelectric polarization can be readily identified from the symmetries of CBED patterns through strong dynamical diffraction effect. (3) Electric polarization can be evaluated from the electrostatic potential distribution directly determined by the CBED analysis.

In the present study, the structure analysis method has been applied to the rhombohedral phase of ferroelectric $BaTiO_3$. CBED analysis of the tetragonal phase of ferroelectric $BaTiO_3$ at room temperature has not yet been successful enough. This could be attributed to the existence of partial disorder, or local fluctuations of atomic displacements which cause electric polarizations [5]. Such fluctuations are expected to be much smaller in the rhombohedral phase below 183 K.

Energy-filtered CBED patterns of the rhombohedral phase were obtained at 90K using a JEM-2010FEF energy-filter transmission electron microscope operated at an accelerating voltage of 100 kV and a liquid-nitrogen cooling specimen holder. Two dimensional intensity data of reflection disks of the energy-filtered CBED patterns were quantitatively compared with dynamical diffraction calculations based on a nonlinear least squares fitting using our analysis software MBFIT [1], [2]. Atom positions, anisotropic ADPs and some low-order structure factors were refined with a much better agreement between the experimental data and theoretical ones than that of the tetragonal phase. Detailed comparison between the result of the present analysis of the room-temperature tetragonal phase and that of the tetragonal phase will be presented.

[1] K. Tsuda, M. Tanaka, *Acta Cryst.* **1999**, *A55*, 939-954. [2] K. Tsuda, K. Takagi, Y. Ogata, T. Hashimoto, M. Tanaka, *Acta Cryst.,* **2002**, *A58*, 514-525. [3] Y. Ogata, K. Tsuda, M. Tanaka, *Acta. Cryst.*, **2008**, *A64*, 587-597. [4] K. Tsuda *et al*., *Phys. Rev.*, **2010**, *B81*, 180102-1-4. [5] R. Comes, M. Lambert, A. Guinier, *Solid State Commun.* **1968,** *6*, 715-719.

Keywords: convergent beam electron diffraction, ferroelectrics, electrostatic potential

MS.80.1

Acta Cryst. (2011) A**67,** C176

Photomechanical motion of molecular crystals

Hideko Koshima, *Department of Materials Science and Biotechnology, Graduate School of Science and Engineering, Ehime University, Matsuyama 790-8577 (Japan).* E-mail: koshima.hideko.mk@ehime-u.ac.jp

Scientific and technological communities are interested in molecules that generate mechanical motion with physical stimuli such as photon impingement. In particular, interest exists in linking the motion to macroscale mechanical work of crystals. Such machines are amenable to remote operation with external stimuli and do not require direct contact. We would like to report mechanical bending of photochromic crystals.

Azobenzenes are typical chromophores that undergo trans–cis photoisomerization. We found that platelike microcrystals of *trans*-4-(dimethylamino)azobenzene bent away from the light when irradiated at 365 nm, reaching a maximum deflection angle of 180° in half a second [1]. The crystals returned to the initial flat shape 30 seconds after stopping irradiation. The bending motion was repeatable. Trans-cis photoisomerization of azobenzene chromophores has never been observed in the crystalline state because of the large geometric changes that would be required in such densely packed crystal lattices. The molecular-level shape changes of azobenzenes near the crystal surface can be translated to the macroscale mechanical motion in crystals.

[1] H. Koshima, N. Ojima, H. Uchimoto, *J. Am. Chem. Soc.* **2009**, *131*, 6890-6891.

Keywords: mechanical bending, photochromism, crystals

MS.80.2

Acta Cryst. (2011) A**67,** C176-C177

Structural Studies on Photoactivated Transition Metal Complexes

Paul R. Raithby,[a] Simon K. Brayshaw,[a] Sara Fuertes,[a] Lauren E. Hatcher,[a] Stefanie Schiffers,[a] Anna J. Stevenson,[a] Mark R. Warren,[a] Christopher H. Woodall,[a] David R. Allan,[b] Simon J. Teat,[c] [a]*Department of Chemistry, University of Bath, Bath (UK).* [b]*Diamond Light Source Ltd, Diamond House, Harwell Science and Innovation Campus, Didcot, Oxfordshire (UK).* [c]*Advanced Light Source, Lawrence Berkeley National Lab., Berkeley California 94720 (USA).* E-mail: p.r.raithby@bath.ac.uk

Solid state photochemical processes can be placed in two general categories: (i) reversible processes where, without continued light