

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  $a = b = 27.5 \text{ \AA}$ ,  $c = 3.94 \text{ \AA}$ ). 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  $16.5^\circ$  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) A67, C176

### Electrostatic potential analysis of the rhombohedral phase of ferroelectric BaTiO<sub>3</sub> 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<sub>3</sub>. CBED analysis of the tetragonal phase of ferroelectric BaTiO<sub>3</sub> 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) A67, 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  $180^\circ$  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) A67, C176-C177

### Structural Studies on Photoactivated Transition Metal Complexes

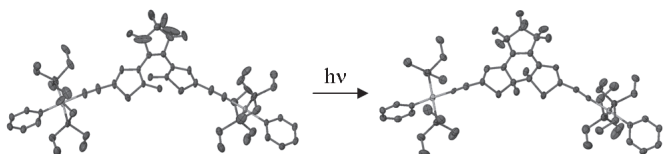
Paul R. Raithby,<sup>a</sup> Simon K. Brayshaw,<sup>a</sup> Sara Fuertes,<sup>a</sup> Lauren E. Hatcher,<sup>a</sup> Stefanie Schiffrers,<sup>a</sup> Anna J. Stevenson,<sup>a</sup> Mark R. Warren,<sup>a</sup> Christopher H. Woodall,<sup>a</sup> David R. Allan,<sup>b</sup> Simon J. Teat,<sup>c</sup> <sup>a</sup>*Department of Chemistry, University of Bath, Bath (UK)*. <sup>b</sup>*Diamond Light Source Ltd, Diamond House, Harwell Science and Innovation Campus, Didcot, Oxfordshire (UK)*. <sup>c</sup>*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

activation, the activated species returns to its original state or, (ii) irreversible processes where a new species is obtained. We have been investigating both types of process.

A series of octahedral nickel(II) nitro complexes display high levels of conversion from the nitro linkage isomer to the nitrito linkage isomer when photoactivated with blue or UV light, at low temperatures, in the single crystal. The nitrito isomers are metastable, and if the temperature is raised above 200 K, the structures revert to the nitro isomer. Examples of systems that display this phenomenon include  $[\text{Ni}(\text{dppe})(\text{Cl})(\text{NO}_2)]$  [1] and  $[\text{Ni}(\text{Et}_4\text{dien})(\text{NO}_2)_2]$  ( $\text{Et}_4\text{dien} = N,N,N',N'$ -tetraethyldiethylenetriamine) [2].

In our studies of irreversible processes, we have established that high conversions of the open form to the closed form of dithienylethene (DTE) ligands in platinum and gold diyne complexes. The ring closing photoconversion in a single crystal of  $[\text{Pt}(\text{PEt}_3)_2(\text{C}\equiv\text{C})(\text{DTE})(\text{C}\equiv\text{C})\text{Pt}(\text{PEt}_3)_2\text{Ph}]$  occurs with the extremely high yield of 80% [3].



[1] M.R. Warren, S.K. Brayshaw, A.L. Johnson, S. Schiffers, P.R. Raithby, T.L. Easun, M.W. George, J.E. Warren, S.J. Teat, *Angew. Chem.-Int. Edit.* **2009**, *48*, 5711-5714. [2] L.E. Hatcher, M.R. Warren, D.R. Allan, S.K. Brayshaw, A.L. Johnson, S. Fuertes, S. Schiffers, A.J. Stevenson, S.J. Teat, C.H. Woodall, P.R. Raithby, *Angew. Chem.-Int. Edit.* **2011**, in press. [3] S.K. Brayshaw, S. Schiffers, A.J. Stevenson, S.J. Teat, M.R. Warren, R.D. Bennett, I.V. Sazanovich, A.R. Buckley, J.A. Weinstein, P.R. Raithby, *Chem. Eur. J.* **2011**, *17*, 4385-4395.

**Keywords:** photochemistry, metastable, isomerism

### MS.80.3

*Acta Cryst.* (2011) A67, C177

#### Real Time Dynamics of Solid Molecular Switches and "Machines" Investigated with Ultrafast Pulsed X-ray Radiation

Mirko Scholz, IFG Structural Dynamics of (Bio)Chemical Systems, Max Planck Institute for Biophysical Chemistry, Göttingen (Germany). E-mail: mirko.scholz@mpibpc.mpg.de

Common for all our time-resolved x-ray experiments is the applied pump/probe scheme, where an optical pump-laser initiates a reaction whose structural time evolution is then investigated by x-ray probe pulses at various time delays. In the present contribution we will refer to our work in time-resolved x-ray diffraction of organic solids. We will reflect capabilities and limitations of state-of-the-art time resolved x-ray diffraction for the investigation of different kind of molecular switches and motors in the crystalline phase. Besides our time-resolved Laue and diffuse scattering work, we will discuss our current status in reaching this goal (proof-of-principle experiments) with free electron laser radiation and how the investigation of chemical reactions benefits from pulsed synchrotron radiation and free electron laser science as they have been performed at the FLASH facility and at LCLS.

The data will be compared to recent results collected at ultrafast pulsed table-top x-ray sources. General features of structural dynamics in solid molecular switches and motors will be presented.

**Keywords:** time-resolved diffraction, laue diffraction, free electron laser radiation

### MS.80.4

*Acta Cryst.* (2011) A67, C177

#### Time-resolved photo-crystallography of ruthenium sulfur-dioxide complexes

Jacqueline M. Cole,<sup>a,b</sup> Anthony E. Phillips,<sup>a,c</sup> <sup>a</sup>*Cavendish Laboratory, University of Cambridge, (UK)*. <sup>b</sup>*Department of Chemistry, University of New Brunswick, (Canada)*. <sup>c</sup>*Current address: Centre for Condensed Matter and Materials Physics, Queen Mary, University of London, (U.K.)*. E-mail: jmc61@cam.ac.uk

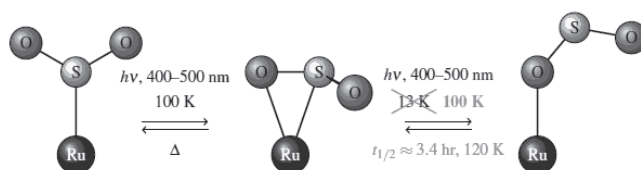
Time-resolved solid-state photo-isomerism is presented in a ruthenium (II) sulfur dioxide based complex,  $[\text{Ru}(\text{SO}_2)(\text{NH}_3)_4(\text{H}_2\text{O})][\text{C}_{10}\text{H}_{15}\text{O}_4\text{S}]_2$ , using the developing technique, photo-crystallography [1-4]. Such materials are of interest due to their potential for optical data storage applications.

Previously, single-crystal to single-crystal photo-isomerism of the  $\text{SO}_2$  ligand has been demonstrated in these complexes whereby the original ground-state,  $\eta^1\text{-SO}_2$  (Fig. 1, left) photo-converts to form metastable species: side-bound coordinated  $\eta^2\text{-SO}_2$  at 100K (Fig. 1, centre) [5] and, additionally, O-bound  $\eta^1\text{-OSO}$  when at 13K (Fig. 1, right) [6].

Here, it is shown, for the first time, that the  $\eta^1\text{-O}$ -bound OSO photo-isomer can exist above liquid nitrogen temperatures [7]. We show that this  $\eta^1\text{-O}$ SO photoisomer is not metastable at 100K; rather, it has a finite lifetime and decays to the more stable  $\eta^2\text{-S-O}$ O photoisomer, in a fashion that is consistent with first-order kinetics. While hints of  $\eta^1\text{-OSO}$  have been noted in photo-induced FTIR studies [5], our photo-crystallography studies provide the first clear evidence of its existence. The thermodynamic quantification of its decay, monitored by time-resolved photocrystallography, is the first of its kind; it has the particular merit that it grounds the topic on a thermodynamic crystallographic footing.

New paradigms to describe these 4-D (space-time) photo-induced transformations are presented as an alternative to the more conventional thermodynamic equilibria description. The need for this new schematic descriptor for time-resolved photo-crystallography is explained in the context of the subject example as well as other studies.

The paper concludes with the exposition of new computational work with aims to rationalize the distribution of the various photo-converted species and investigates possible photo-induced cooperativity mechanisms. This leads to the 'smart material' design and prediction of new ruthenium sulfur dioxide complexes with improved and more controlled photo-conversion efficiencies and wider optical applications.



[1] J.M. Cole, *Chem. Soc. Rev.* **2004**, *33*, 501-513. [2] J.M. Cole, *Analyst*, **2011**, *136*, 448-455. [3] J.M. Cole, *Acta Crystallogr. A* **2008**, *64*, 259-271. [4] J.M. Cole, *Zeit. Krist.* **2008**, *223*, 363-369. [5] A.Y. Kovalevsky, K.A. Bagley, J.M. Cole, P. Coppens, *Inorg. Chem.* **2003**, *42*, 140-147. [6] K.F. Bowes, J.M. Cole, S.L.G. Husheer, P.R. Raithby, T.A. Savarese, H.A. Sparkes, S.J. Teat, J.E. Warren, *Chem. Commun.* **2006**, 2448-2450. [7] A.E. Phillips, J.M. Cole, T. d'Almeida, K.S. Low, *J. Am. Chem. Soc.* **2011** (in preparation).

**Keywords:** photochemistry, kinetics, photostimulated