

method to determine the surface crystallography of single crystal gold nanorods grown in the presence of Ag and found that, contrary to the current consensus, the surface facets are sparsely packed atomic planes [2]. This result has profound implications for understanding nanocrystal growth and morphology and forces a reconsideration of established theoretical models of nanoparticle growth.

[1] H. Katz-Boon, C.J. Rossouw, J. Etheridge, submitted to *Ultramicroscopy*

[2] H. Katz-Boon, C. . Rossouw, M. Weyland, A.M. Funston, P. Mulvaney, J. Etheridge, *Nanoletters* **2011**, *11*, 273-278.

Keywords: quantitative scanning transmission electron microscopy, thickness profile determination, gold nanorods morphology.

MS44.P03

Acta Cryst. (2011) **A67**, C519

Real space charge density mapping by quantitative convergent beam electron diffraction (QCBED)

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Quantitative energy-filtered convergent beam electron diffraction (QCBED) can be used to measure the low order structure factor amplitudes and phases of microcrystals of known structure very accurately. This TEM-based technique uses a small electron probe of nanometer dimensions, so that a perfect crystal region can be selected for electron diffraction. It refines structure factors, absorption and specimen thickness using multiple scattering calculations, and measures the structure factors on absolute scale. Thus, extinction corrections, absorption corrections and scaling problems are avoided in electron diffraction. For non-centrosymmetric crystals, the refinement of charge density maps requires highly accurate measurements of structure factor phases, which can now also be measured using the QCBED method [1-3]. Electron diffraction is much more sensitive to ionicity at low scattering angles than X-ray diffraction [3], making it more suitable for charge-density mapping and the imaging of bonds. The accuracy is equivalent to that of the X-ray Pendulösung method [4-5], allowing the covalent and ionic contributions to be separately visualised.

Accurate structure factors of Cu, GaN and AlN have been measured by QCBED. The measurement standard deviations are normally less than 0.2% for both amplitudes and phases of low order structure factors. Accurate charge density maps have been obtained and the bonding character has been studied. Multipole refinement on Cu supports a free electron model [5]. Polar covalent bonds in Ga-N and Al-N are observed in experimental charge density maps, using multipole refinement of combined measurements of structure factor magnitudes and phases [1-2].

Supported by DOE award DE-FG03-02ER45996

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Keywords: quantitative convergent beam electron diffraction (QCBED), real space charge density, bonding

MS44.P04

Acta Cryst. (2011) **A67**, C519

Direct measurements of lattice distortion and mapping of point defects

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Recent advances in transmission electron microscopes (TEM) have enabled detection of light atoms, even the lightest hydrogen atomic columns, which have scattering strength too weak to be detected by non-aberration corrected TEM.[1] The detection limit of the state-of-the-art TEM/scanning TEM (STEM) has been tested in diverse systems; for example, identifying single light atom such as nitrogen and boron, and probing charge redistribution by chemical bonding [2-3]. Image simulations in those reports were essential to verify the experimental results. In fact, low signal to noise ratio in extreme measurements often requires substantial data processing as well as significant amount of experimental data.

Here, we present image and diffraction simulations to access the feasibility of detecting structural defects in a crystal such as point defects and static displacements. It is well known that local strain fields by structural defects enhance contrast in images. We exploited first-principles calculations to find relaxed structures of a crystal with point vacancies as well as a crystal with a structural distortion caused by strain in complex oxides. The multislice method was employed to simulate STEM images and convergent beam electron diffraction patterns of both the relaxed structures and non-relaxed structures. Adjusted parameters include convergence angles, focal depths, and scattering angles. Furthermore, the contribution of bonding charges to the images was examined by comparing simulation results using projected potentials from the first-principles calculations and using conventionally used atomic potentials.

Image simulations on strained oxide materials with tetragonal distortion, such as NdNiO₃, were applied for structural analysis. We used an aberration corrected microscope for atomic-resolution STEM images, and performed quantitative analysis of the image to extract structural parameters. The results were compared with the first-principles calculations, which indicated reliability of this approach.

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Keywords: aberration correction, atomic resolution imaging, multislice simulations

MS45.P01

Acta Cryst. (2011) **A67**, C519-C520

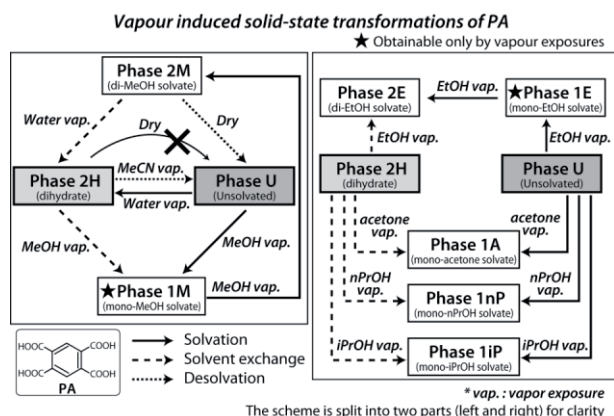
Vapour induced transformations investigated by powder diffraction analysis

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Solvent vapour exposure on the organic crystalline materials often induces pseudo-polymorphic transformations (solvation, solvent exchange and desolvation). Such transformations have potential to improve and/or control the solid-state properties of the target materials and are important phenomena in the field of material science. However, such transformations have not been completely understood because of

the difficulty to obtain the structural information of the resulted phase, which is mainly caused by the disintegration of the single crystalline form of the parent phase during the transformations. In such cases, the crystal structure determination from the powder X-ray diffraction data is clearly most powerful technique. Herein, we report several examples of the vapour induced crystalline transformations of organic materials investigated using *ab initio* powder diffraction analysis [1]- [3].

One of the examples is the vapour induced transformations of pyromellitic acid (PA : benzene-1,2,4,5-tetracarboxylic acid). As shown in the scheme (see below), PA exhibits a wide variety of the vapour induced transformations. Eight solvates and one unsolvated phase were found by vapour induced transformations. Single crystals of some solvates could be obtained by alternative crystallise pathway, however, some of the solvates (phase U, 1M, 1E and 1iP) could only be obtained by the vapour induced transformations. Thus, the crystal structures of these phases were determined from the powder X-ray diffraction data. The structural analyses revealed that phase 1M and 1E are the mono-methanol and mono-ethanol phases, respectively. Further vapour exposures on the mono-solvate phases gave di-solvate phases (2M and 2E) and these di-solvate phases were also obtained by recrystallisation from the solutions or from the slurry of PA in these solvents. Therefore, phase 1M and 1E are the metastable phases under the existence of the solvent vapour. These mono-solvate phases are obtainable only by the vapour exposure and it clearly shows that solvent vapour exposures are very useful technique to control pseudo-polymorphs.



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Keywords: *ab-initio* powder structure determination, solid-state transformation, pseudo-polymorphism

MS45.P02

Acta Cryst. (2011) **A67**, C520

Time-resolved structure analysis of photo-induced molecular dynamics in TTF-CA

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Recent progress of the time-resolved X-ray diffraction technique

enables to elucidate photo-induced dynamics in some crystals [1,2]. But diffraction intensities' change was mainly discussed and three-dimensional geometrical change have not been clarified in detail. In this study, we reveal the photo-induced molecular dynamics in a crystal with subnanosecond time resolution by single crystal X-ray structure analysis.

Time-resolved X-ray diffraction experiment was performed at PF-AR NW14A in KEK [3]. The co-crystal of tetrathiafulvalene and *p*-chloranil (TTF-CA; Figure), which shows neutral to ionic phase transition by laser irradiation at 90 K, [4] was selected as a target sample. Diffraction data sets were collected at 150, 500, 800, 1000 ps after laser excitation.

In photo-induced phase transition of TTF-CA, intensity reconstruction of symmetrically forbidden Bragg spots should be observed [2]. But in this study, significant intensity of these spots were not observed in all data sets. This indicated that phase transition was not fully progressed and recovered to the initial phase within the time-resolution of X-ray (pulse width = 150 ps) due to a weak excitation condition to minimize the damage by laser irradiation for prolonged data collection time. However, gradual movement of Cl and O in CA was observed by crystal structure and precise electron density analyses. These movements are assigned as thermal relaxation from the photo-induced ionic phase. Moreover, shortening of C=O in CA, which corresponds to enhancement of the neutral character of CA, was observed. These molecular dynamics indicates thermal relaxation from photo-induced ionic phase to initial phase go through the novel phase which has more strong neutral character than the initial phase. That novel phase was not generated by heating, so to speak, 'hidden' in the thermal process [1,5].

In sum, we succeeded to clarify the photo-induced dynamics of TTF-CA by time-resolved crystal structure analysis. In our excitation condition, the photo-induced 'hidden' phase was generated in subnanosecond time scale. This result will lead the progress of study about non-equilibrium dynamics in condensed matters.

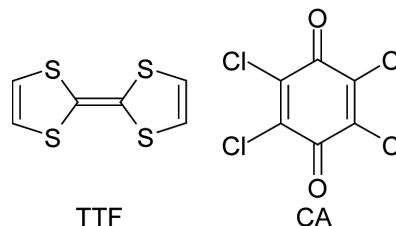


Figure. TTF and CA

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Keywords: time-resolved crystallography, photocystallography, non-equilibrium dynamics

MS45.P03

Acta Cryst. (2011) **A67**, C520-C521

Reorientation of hydrogen bonds in clathrates of Dianin's compound and hydroquinone

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