

FA3-MS04-O1

Opportunities for Observing Functional Materials in Operation Using Time-/Space-Resolved Diffraction. Paul Barnes. *Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K; and School of Crystallography, Birkbeck College, Malet Street, London WC1E 7HX, UK.*

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A full understanding of the working of functional materials requires the use of intense radiation sources to explore structure resolved in both time and space and within a working environment. The practical limits of measurement range in space from Å (atomic structure) to mm (real working systems) and in time from seconds (bulk solid state processes) upwards. *In situ X-ray diffraction* has emerged as a powerful technique for observing functional materials during both the synthesis stage and subsequently during their in-service performance. The revolution of the last two decades has been the realization of these goals using the unrivalled X-ray photon power made available through X-ray-dedicated synchrotrons. In this lecture I will give a personal account of this adventure, giving examples of “fast” *in situ* diffraction to follow rapid phase transformations or solid state reactions in response to changes in sample temperature, gas composition and pressure. This leads onto the use of energy-dispersive diffraction and the related *TEDDI* (Tomographic Energy-Dispersive Diffraction Imaging) technique for imaging of materials in action, such as catalysts, cements and functional oxides, and for exploring materials processes such as crystallization, transport and zonation. However the fuller objective, of imaging functional materials in *real time*, will require major advances in X-ray detection, and so a glimpse will be provided into current developments to make this happen.

Keywords: functional materials; space-resolved; synchrotron

FA3-MS04-O2

Kinetics of Solid State Reactions/Transitions Investigated by Real Time Neutron Spectroscopy. Kludia Hradil^a, Jeannis Leist^a, Friedrich Güthoff^a, Holger Gibhardt^a, Götz Eckold^a. *“Institut für Physiologische Chemie, Universität Göttingen, D-37077 Göttingen, Germany.*

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Inelastic neutron scattering technique provides information about the microscopic dynamics of solids. Investigations on a real time scale within external fields (temperature, pressure, magnetic/electrical fields) would yield the microscopic information of relaxation processes (phase transitions, domain order/disorder processes, decomposition processes).

Conventional inelastic neutron scattering technique is due to the low intensity of the investigated excitations and

therefore the relatively long measuring times beyond the scope for real-time experiments in timescales which are of interest. Eckold [1] introduced a method to combine real time resolution together with inelastic neutron scattering by a stroboscopic measuring technique. By cycling of the sample in an external field, the scattered intensity is not only detected as a function of momentum and energy transfer but also sorted within time channels. The reversibility of the processes is a necessary condition for the application of the technique. This technique was recently implemented within the spectrometer electronics of the triple axis spectrometer PUMA at FRM II and can provide the possibility to analyze excitations within relaxation processes on a timescale down to microseconds. Beside introducing the technique and possibilities for performing experiments first experiments applying electrical fields for the study of ferroelectrics or cycling of temperature to follow decomposition processes will be introduced.

[1] G. Eckold, *Nucl.Instr.&Methods*, **1990**, A289, 221.

Keywords: inelastic neutron scattering; in-situ experiments; time-resolved structural studies

FA3-MS04-O3

Time-resolved Binding of K_2PtBr_6 to Lysozyme by Protein Powder and Single Crystal X-ray. John Richard Helliwell^a, Tony A. Bell^b, Pat Bryant^c, Stu Fisher^{a,d}, George J. Habash^a, Madeleine Helliwell^a, Rena I. Margiolaki^e, Kaenket Surasak^a, Yves Watier^e, Jon Wright^e, Sampath Yalamanchilli^a. *“School of Chemistry, University of Manchester, UK. ^bSTFC Daresbury Laboratory, UK. ^cLife Sciences, University of Manchester, UK. ^dInstitut Laue Langevin, Grenoble, France. ^eESRF, Grenoble, France.*

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Protein powder diffraction continues to excite strong international interest; there are a variety of applications, including industrial protein characterization, such as polymorphs of insulin as well as extending structure determination to yet smaller crystal samples, which would otherwise be outside the range of synchrotron X-ray data collection from a protein microcrystal [1,2,3,4]. Furthermore there are the upcoming X-ray Laser Facilities, with possibilities for protein nanocluster-crystallites diffraction and de novo structure determination, as well as the MWatt spallation neutron sources for new neutron powder diffraction opportunities with neutrons as a neutral probe, for specific protein structural studies free of X-ray damage effects. Using ESRF ID31 we have recorded high quality protein powder diffractograms from K_2PtBr_6 bound to lysozyme at 80K to protect against X-radiation damage as much as possible and also to trap ie fix the K_2PtBr_6 heavy atom compound bound state. With multiple powder pattern analysis we have then extracted individual reflection intensities and thus been able to show the presence of $PtBr_6^{2-}$ bound in lysozyme in (Fo-Fc) Fourier omit maps at two binding sites. The wavelength dispersive

difference Patterson for the ID31 data at two wavelengths around the Br K edge and also the Pt LIII edge shows up binding site 1 clearly in one of the six samples tested. In order to investigate the detailed binding behaviour we have conducted single crystal analyses with time-resolved freeze quenching after lysozyme single crystal soak times of 10, 90 and 170 minutes. Whilst the quick soaking of 10 minutes, used in our first experiments at ESRF ID31 above, shows clear binding there is a steady progression of increasing binding strength with increasing soak time. Thus, these time-resolved analytical chemistry results show that further heavy atom signal optimizations, and reproducible behaviour, are possible. Prospects for extending our approach to the yet larger isomorphous and wavelength dispersive signal case of Ta₆Br₁₂ bound to lysozyme for powder experiments will also be described. Overall, such *multi heavy atom cluster compounds* like K₂PtBr₆ and Ta₆Br₁₂ offer a way forward to solve de novo protein structures by powder diffraction.

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 [2] J.R. Helliwell, M. Helliwell and R.H. Jones, **2005**, *Acta Cryst* A61, 568-574. [3] B. Hedman, K.O. Hodgson, J.R. Helliwell, R. Liddington and M.Z. PNAS. USA, **1985**, 82, 7604-7607. [4] J.P. Wright, C. Besnard, I. Margiolaki, S. Basso, F. Camus, A. N. Fitch, G. Fox, P. Pattison, M. Schiltz, **2008**, *J. Appl. Cryst.* 41, 329-339

Keywords: proteins; heavy atom derivatives; time-resolved

FA3-MS04-O4

X-ray Diffraction Study of Piezoelectric Crystal Response on the Nanosecond Time Scale. Oleg Schmidt^a, Semen Gorfman^b, Petra Becker^c, Ladislav Bohatý^c, Ullrich Pietsch^a. ^aDepartment of Physics, University of Siegen., ^bDepartment of Physics, University of Warwick, ^cInstitute of Crystallography, University of Cologne.

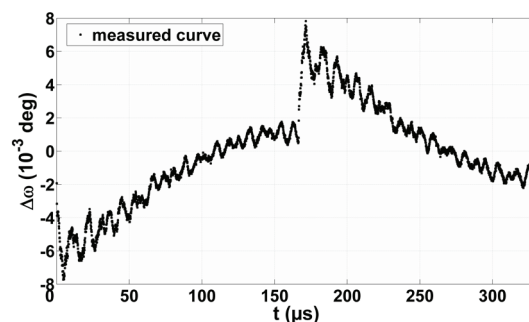
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Interaction of a crystal with a permanent external electric field is well known in the form of the macroscopic phenomena such as dielectric polarization and converse piezoelectric effect. Deeper insights into the nature of the corresponding physical properties of solids (dielectricity and piezoelectricity) may be obtained by investigating the time dependence of the various processes that are initiated in a crystal by an ultra-fast change of an external electric perturbation state.

In the present study we applied periodically to single about 0.5 mm thin piezoelectric Li₂SO₄·H₂O and BiB₃O₆ crystal plates a 2-step modulated high voltage (HV), consisting of U₊ = 1 kV and U₋ = -1 kV HV states, with a frequency up to 3 kHz. The non-ferroelectric polar BiB₃O₆ crystal exhibits a maximum longitudinal piezoelectric effect that is about 17 times higher than that of α-quartz and 2 times higher than that of Li₂SO₄·H₂O. The switching time between the both different HV states was of the order of 200 ns. The time-resolved scanning of the diffraction intensity for each single angle step of a ω-rocking curve was performed using a commercial FPGA-board. In detail, the incoming digital

signals of a scintillation counter were assigned to successive up to 20 ns short single time channels. All measurements were carried out on a single crystal diffractometer at the ESRF BM01A (Swiss-Norwegian) beamline.

In particular, the piezoelectric crystal response accompanied by a relaxation process was extracted from the shift of the Bragg peak position, Δω(t, HV(t)), of single reflections, recorded as a function of time and the respective HV state, see figure below. Both the jumps in Δω at 0 μs and 167 μs correspond to HV changes from U₊ to U₋ or vice versa. The observed oscillation behavior of Δω was associated with superimposed piezoelectric-induced elastic waves propagating in a crystal plate.



Keywords: time-resolved X-ray diffraction; piezo- and ferroelectric materials; physics of solids

FA3-MS04-O5

In-Situ Study of Time and Thickness Dependence of Crystallization of Amorphous TiO₂ Thin Films and Powders. Lea Nichtová^a, Radomir Kužel^a, Zdenek Matěj^a. ^aDepartment of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University in Prague, 121 16 Praha 2, Czech Republic.

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Titanium dioxide is a material intensively investigated not only because of its good chemical stability, mechanical hardness, high refractive index and nontoxicity but also due to its photocatalytic activity enabling a conversion of solar light into useful chemical energy.

It is known that photocatalytic activity of titanium dioxide strongly depends on crystallization and phase composition. In this work, time dependences of crystallization of amorphous thin films on Si substrates with different thickness (50–2000 nm) prepared by magnetron sputtering were studied by in-situ measurements in high-temperature chamber in laboratory X-ray diffractometer X'Pert Pro at several temperatures. They were selected below the temperature where fast crystallization appears (about 220 °C). The process is then slow and allows detailed time in-situ investigations even in laboratory conditions. For comparison, amorphous and nanocrystalline powders were measured in the chamber as well.

Strong dependence of crystallization, especially for samples with thickness lower than about 300 nm, on the film thickness was found. The process could be well described