

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 Ta<sub>6</sub>Br<sub>12</sub> bound to lysozyme for powder experiments will also be described. Overall, such *multi heavy atom cluster compounds* like K<sub>2</sub>PtBr<sub>6</sub> and Ta<sub>6</sub>Br<sub>12</sub> offer a way forward to solve de novo protein structures by powder diffraction.

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**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<sup>a</sup>, Semen Gorfman<sup>b</sup>, Petra Becker<sup>c</sup>, Ladislav Bohatý<sup>c</sup>, Ullrich Pietsch<sup>a</sup>. <sup>a</sup>Department of Physics, University of Siegen., <sup>b</sup>Department of Physics, University of Warwick, <sup>c</sup>Institute of Crystallography, University of Cologne.

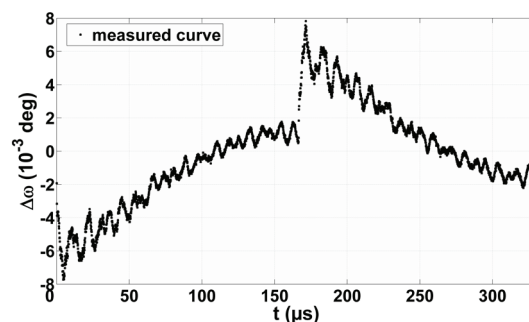
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Interaction of a crystal with a permanent external electric field is well known in the form of the macroscopic phenomena such as dielectric polarization and converse piezoelectric effect. Deeper insights into the nature of the corresponding physical 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 Li<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O and BiB<sub>3</sub>O<sub>6</sub> 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 BiB<sub>3</sub>O<sub>6</sub> crystal exhibits a maximum longitudinal piezoelectric effect that is about 17 times higher than that of  $\alpha$ -quartz and 2 times higher than that of Li<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O. 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  $\omega$ -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,  $\Delta\omega(t, HV(t))$ , of single reflections, recorded as a function of time and the respective HV state, see figure below. Both the jumps in  $\Delta\omega$  at 0  $\mu$ s and 167  $\mu$ s correspond to HV changes from  $U_+$  to  $U_-$  or vice versa. The observed oscillation behavior of  $\Delta\omega$  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 TiO<sub>2</sub> Thin Films and Powders.** Lea Nichtová<sup>a</sup>, Radomir Kužel<sup>a</sup>, Zdenek Matěj<sup>a</sup>. <sup>a</sup>Department 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

by the Avrami equation [1] (modified by the introduction of initial time of crystallization, without this the fits are not very good). The evolution of the integrated intensities  $I$  of diffraction lines of anatase phase is then described as,  $I = 1 - \exp[-b(t-t_0)^n]$ , where the initial time of crystallization  $t_0$  is related to the first appearance of any diffracted intensity above the background level at the peak position. It increases abruptly with decreasing thickness. The rate of crystallization  $b$  grows quickly with the thickness. Low values of  $n$  ( $\sim 2$ ) indicate two-dimensional character of the crystallite growth.

Evolution of preferred orientation and stress generation during the crystallization were observed. At the beginning, the crystallites with the (001) orientation were developed but after complete crystallization, the texture was weak except the very thin films (below 100 nm). Tensile residual stresses were developed slowly during the crystallization and confirmed later by detailed measurements at room temperature. Line broadening was constant and relatively small from the very beginning of observable crystallization. This is probably due to the rapid growth of a few crystallites.

Above 600 °C the transformation of anatase into rutile proceeds. This was studied mainly for nanocrystalline powders and it seems that the transition is faster for powders with originally smaller crystallites.

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**Keywords: titanium dioxide; crystallization; in-situ measurements**