smectites as a function of time, location and temperature. As the reusability of the moulding sand is critically related to the hydration and dehydration of smectite, we designed experiments to investigate of the dehydration kinetics in-situ. At the neutron radiography beamline ANTARES (FRM II, Germany) we simulated a casting process by dropping a special casting mould filled with moulding sand (12 wt% bentonite) on a hot copper plate (Figure 1). The design ensured an ideal heat transfer corresponding to the thermal shock-like heat induction during the real casting process. With this experimental set up, we were successful to in-situ visualize water fluxes within the moulding sand quantitatively with high temporal and spatial resolution. Thermocouples placed within the moulding sand simultaneously provided information on the temporal temperature gradients.

The experiments revealed a progressive movement of water in the sand and resolved a broad transitional zone from the pristine hydration state of the sand to a fully dehydrated state. At this transitional zone positions can be determined which on the one hand relate to the onset of pore water dehydration and on the other hand relate to the completion of interlayer dehydration. Thus, the experiments allowed us to successfully simulate the shock-heating of the mould material in a industrial casting process. The consequence of the shock-heating is a strongly non-linear temperature-time-position relation convoluted with the diffusion processes. A quantitative evaluation of the simulation data will be presented.
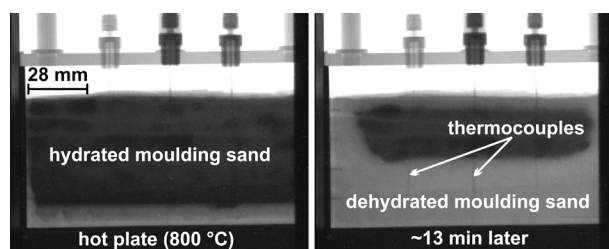

Fig.1. Two neutron radiographs showing the dehydration of the moulding sand. The process initiates at the hot bottom. The transitional zone between the pristine hydration state (top) and the fully dehydrated state (bottom) can be seen.

Keywords: smectites, interface processes, neutron radiography

FA5-MS39-P08

Surface and embedded 2-dim structures: a direct space approach to modelling. Armin Kirfel[a], Karl F. Fischer[b], [a]*Steinmann Institute, University Bonn, Germany,* [b]*Technical Physics, University of Saarland, Germany*
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In the parameter space concept developed for the determination of 1-dimensional structures or structure projections without Fourier inversion, an arrangement of m equal scatterers is represented by a vector $\mathbf{t}(x_1, x_2, ... x_m)$ defined in space $\mathbf{P}^m$ [1,2]. Given a suitable number $n \geq m$ of observed intensities of reflections h, the principal objective of this approach is to find those test vectors $\mathbf{t}_t$ for which the best overall agreements between the observed $e(h)_{obs}$ and the model $e(h)_{calc}$ are obtained. The $e(h)$ are normalized structure amplitudes on absolute scale according to $e(h)^2 = n \cdot I(h)/\Sigma\, I(k)$,

$k = 1,...n$ [3], and the $\mathbf{t}_t$ proposed are fit to start a refinement procedure. Thus, it should be noted that (i) neither structure metrics nor any structure factor phases are needed, (ii) high spatial resolution is obtained from rather few experimental data, and (iii) homometric and quasi-homometric structures are automatically included. - The 1-dimensional approach was successfully tested in numerous examples with equal or nearly equal scatterers up to $m = 20$. In addition, we have shown that it is possible to reconstruct a 3-dimensional structure from the solutions obtained from up to 13 structure projections reflected in the central reciprocal lattice rows with low indices, *e.g. h*00, 0*k*0, 00*l*, *hh*0,…*hhh etc* [3]. - Encouraged by our experiences with the 1-dimensional structures we have started to apply the approach to simple acentric 2-dimensional structures or structure projections of symmetry *p*1 with emphasis on exploring (a) the number(s) of scatterers m that can be handled in feasible PC computing times and (b) the numbers and kinds of reflections needed for finding test vectors $\mathbf{t}_t(x_1,y_1;\ ...x_m,y_m)$. - In *p*1, one scatterer (preferably the strongest) in (0,0) fixes the origin so that the problem is reduced to (m-1). In principle, there are two ways to generate $\mathbf{t}_t$'s, namely the systematic one by employing grid techniques (with the problem of finding the optimal spacing) and a random one (which is not necessarily inferior). Confining the discussion to the first technique we consider four basic strategies, *i.e.* the (i) exclusive use of a 2-dimensional grid and of general reflections *hk,* (ii) use of 1-dimensional *x*- or *y*-projection results based on reflections *h*0 or 0*k,* respectively, with subsequent inspection of the corresponding rods at the proposed x_i or y_i to find the missing information from *hk* reflections, (iii) use of *x*- and *y*-projection results from *h*0 and 0*k* reflections, respectively, followed by finding correct (x,y) combinations from *hk* reflections, and finally, (iv) as (iii) but finding the correct (x,y) combinations with the aid of results obtained from reflections *hh* and -*h,h*, *i.e.* additional projections onto the directions [11] and [-1,1]. - Advantages and shortcomings of the different approaches with respect to structure sizes and computing times are compared, and including data errors examples of structure determinations are presented. Also addressed are possible extensions and applications, for instance in electron diffraction.

[1] Fischer K.F., Kirfel A., Zimmermann H., *Z. Krist.* 2005, 220, 643.
[2] Zimmermann H., Fischer K.F., *Acta Cryst.,* 2009, A65, 443. [3] Kirfel A., Fischer K.F., *Z. Krist.* 2009, 224, 325.

Keywords: two-dimensional structures, phase problem eliminated, high resolution

FA5-MS39-P09

Dopant Effect on Surface Electronic State of TiO$_2$ estimated by First Principles Calculation. Dong-Yoon Lee, Seung-Il Cha, Sun-Hee Seo, *Nanohybrid & Energy Materials Research Center, Korea Electrotechnology Research Institute, R. of Korea*
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The surface electronic states of TiO$_2$ doped with various metallic elements on Ti site were estimated by the discrete variation X$_\alpha$ (DV-X$_\alpha$) method, which is a sort of the first-principles molecular orbital method and uses the Hatre-Fock-Slater approximation.[1] The energy levels, the partial density of state and the charge densities were calculated by using cluster models for bulk and surface.

Doping effect of nano TiO_2 has been the main concern of material scientists in the field of photocatalyst and dye-sensitized solar cell (DSC). The electronic states of doped surface and interface, without regard to the sort of interface including solid/solid and solid/liquid, are very different from the bulk states. For example, Si doping on TiO_2 bulk almost brings minor changes of the main energy level structure near conduction band and valence band. However, when Si is doped on the surface, new doping levels appear in middle position between the conduction band edge and valence band edge. This means that the surface doping of Si will seriously change the electric and optical properties of TiO_2 having high surface area such as nano particle and mesoporous film, although the bulk doping doesn't show any effect.

The doping elements in this calculation involved a series of transient metals, IV family group and some light metals. Here, main discussion will be concentrated on the electric properties in association with DSC.

[1] H. Adachi, M. Tsukada and C. Satoko: J. Phys. Soc. Jpn., 1978, 45, 875

Keywords: Electronic state, first principles calculation, Surface doping

FA5-MS39-P10

Evolution of Formation of Interblock Boundaries in Nanothin Selenium Crystals. <u>Malkov Vyacheslav</u>[a], Strekalovsky Victor[a], Malkov Andrey[b], Malkov Oleg[b], Puchin Vladimir[c], *[a]Institute of High-Temperature Electrochemistry, Ural Division RAS, [b]"ROSNA" Scientific and Production Center, [c]Institute of Metal Physics, UD RAS, Ekaterinburg, Russia*
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Transmission electron microscopy methods were used to study the evolution of formation of interblock boundaries in nanothin (80÷100 nm) crystals of hexagonal selenium growing in amorphous films at crystallization temperatures of 180÷120 °C.

The nanothin selenium crystals growing in amorphous films at crystallization temperatures of 180÷160°C were found to form rotational interblock boundaries with the modulus and the sign of the misorientation vector ω varying along the boundary (Fig.1a).

It was found that as the crystallization temperature decreased to 150°C, the nanothin selenium crystals formed boundaries, along which not only the modulus and the sign of the misorientation vector ω changed [1], but also a variable appeared, in addition to the rotational component, along the boundary of the slope component. (Fig.1b).

Distorted interblock boundaries appeared in the nanothin selenium crystals at a crystallization temperature of 140÷120°C. Along with the aforementioned crystal geometry parameters, the direction of the vector of the normal to the boundary surface changed at the distorted interblock boundaries. The sign of the distortion of the interblock boundary surface always matched the sign of the azimuthal distortion of the lattice in the nanothin selenium crystals (Fig.1c,d). The lattice of the nanothin selenium crystals underwent a rotational distortion generally around three mutually perpendicular directions. A decrease in the crystallization temperature from 180 to 120°C caused an increase in the density of interblock boundaries with variable crystal geometry parameters, which were formed in the nanothin selenium crystals.
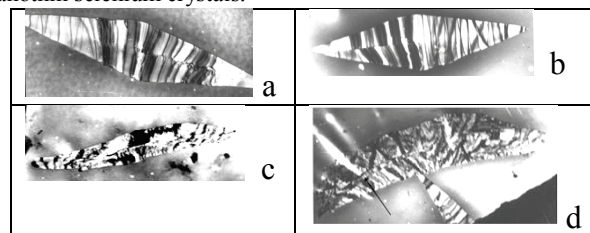

Fig. 1. Broken boundary with varying modulus ω (a); boundary with varying parameters of torsion and inclination (b); distorted boundaries and ensembles of boundaries in nanothin selenium crystals (c, d), ×10 000

It has been proposed to develop a model describing the formation of interblock boundaries with variable crystal geometry parameters in nanothin selenium crystals on the basis of concepts underlying relaxation of a nonuniform elastic rotational distortion of the lattice in a nanothin crystal of hexagonal selenium around [001].

[1] Malkov V.B. et al. Acta Cryst A. (2009). A.65. s340-s341

Keywords: selenium-1, crystals-2, boundaries-3

FA5-MS39-P11

High Brilliance microfocus beam delivery systems with scatterless collimation for SAXS. <u>Vincent Roger</u>[a], Pierre Panine, Blandine Lantz, Peter HOGHOJ
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Small Angle X-ray Scattering applications require sample illumination with a high brilliance x-ray beam having a well controlled spatial and angular distribution. Indeed high intensity at the sample is required with small beam expansion towards the detector to achieve low values of wave vector. We have developed a X-ray beam delivery system (the GeniX) made of a low power microfocus source and incorporating a unique combination of multilayer optics with innovative scatterless collimation for high performance SAXS in the lab.

The coupling of microfocus source with efficient aspheric multilayer optics (the FOX 3D optics) provides an intense x-ray beam with a well controlled beam propagation. Advantages in term of brightness preservation and range of wave vector reachable in SAXS, both for compact and for long-collimated setups will be reviewed. We will also present the new and innovative scatterless collimation integrated in the GeniX reducing parasitic slit scattering and providing simplified design. Advantages in terms of flux and resolution improvement compared to standard collimation will be detailed.

We will present SAXS data measurements acquired on high Z colloids, and polymer samples with different set-ups (radiation, detectors) illustrating the benefits of the new GeniX configuration.

Keywords: SAXS, High brilliance source, scatterless collimation