MS38-O4 **Vaterite structure from electron diffraction data – a definitive answer for an old question?** Iryna Andrusenko,[a] Enrico Mugnaioli,[a] Robert E. Dinnebier,[b] Martin Panthöfer,[c] Wolfgang Tremel,[c] Ute Kolb,[a] *[a]Institut für Physikalische Chemie, Johannes Gutenberg Universität, Germany, [b]Max-Planck Institut für Festkörperforschung, Germany, [c]Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg Universität ,Germany*
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Vaterite, one of the common natural $CaCO_3$ polymorphs, plays a pivotal role in weathering and biomineralization processes. Differently from calcite and aragonite, vaterite can be found only as nanosized crystals. Like for many other natural and synthetic nanocrystalline materials, the structure of vaterite is still an unsolved dilemma despite the common occurrence of this mineral, its relevance in biomineralization processes and the impressive number of published studies around this subject. In the last century X-ray powder diffraction techniques has mostly been used for deriving structural information. Still, a number of compounds are crystallographically intractable with conventional X-ray or synchrotron radiation, because they are highly disordered, with strong pseudosymmetries or available only in small amounts in polyphasic or polymorphic systems. Single nanoparticles can be visualized by high resolution transmission electron microscopy, but obtaining three-dimensional information is still a difficult task, especially for highly beam sensitive materials and crystal structures with long cell parameters. Electron diffraction provides even higher resolution data with a significant lower electron dose on the sample, but is biased by a substantial number of missing reflections and the occurrence of dynamical scattering that affects reflection intensities. Recently, a new routine for electron diffraction data acquisition and analysis based on the combination of automated diffraction tomography (ADT)[1,2] and precession electron diffraction[3] has been developed in order to overcome these drawbacks. Here we report the *ab-initio* determination of vaterite structure from electron diffraction data collected via ADT approach. For the first time complete three-dimensional diffraction data are available from a single vaterite nanocrystal.[4] Vaterite cell was recognized as monoclinic with parameters geometrically related with previously proposed hexagonal and orthorombic models. Vaterite structure was determined *ab-initio* in space group *C2/c*. It is characterized by a layer arrangement of Ca^{2+} ions alternated by $\{CO_3\}^{2-}$ groups, both with two symmetrically distinct positions. This structure is now consistent with the Raman spectra and a number of independent physical properties reported by previous authors. Vaterite nanocrystals are always characterized by stacking disorder and local modulation. Such modulation was described by a 6-layer superstructure triclinic cell, resulting in an even better fit to synchrotron powder data.

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MS38-O5 **Precession coupled orientation / phase mapping on nanomaterials with TEM Cs microscopes**
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EBSD (electron backscattering diffraction) is a well-established technique that allows orientation /phase mapping using an SEM (scanning electron microscope). Although very powerful, the technique has serious limitations related to a) spatial resolution limited to 50 nm (for SEM-FEG) and b) specimen preparation issues linked to the difficulty to obtain adequate surface states. A novel technique has been developed recently (EBSD-TEM like) allowing automatic orientation and phase mapping using template matching analysis of diffraction patterns acquired with a TEM (transmission electron microscope) [1].

Electron beam is scanned through the sample area of interest coupled with beam precession of an angle < 1°; the acquired precession electron diffraction (ED) patterns from all successive locations are compared via cross-correlation techniques with pre-calculated simulated kinematical ED templates to reveal local crystal orientation and phases. Beam precession improves substantially the quality of acquired diffraction patterns and results to precise and high resolution orientation-phase maps.

The dedicated technique (ASTAR) allows orientation/ phase maps in a region of interest up to 100μm^2, with a step size/map resolution ranging from 1 nm to 20 nm depending on the TEM setting (FEG/LaB6). The system can work successfully with latest generation Cs aberration (spherical and probe) corrected TEMs in combination with beam precession, resulting in possible sub-nanometric map resolution (Fig.1).

Application examples cover different fields of material science: metallurgy (steels and alloys), semiconductors, nanoparticles, ceramics, thin layers, minerals and also applications with beam sensitive materials.

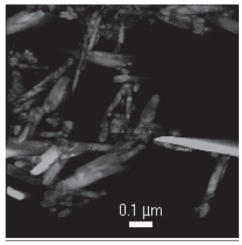

Fig.1 Nanoscale ASTAR phase map acquired with a Libra 200 FE Cs where elongated geothite α–FeO(OH) particles (in blue) can be seen together with brookite (TiO_2) particles (in red). Sample courtesy L. Andre IFP, C. Chaneac LCMCP (Paris VI)

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