

MS16-P10 Electron tomography and HAADF-STEM imaging to solve the collapsed structure $\text{Pb}_4\text{Sr}_{13}\text{Fe}_{24}\text{O}_{53}$

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The strontium ferrites and cobaltites $(\text{Sr}_{4-x}\text{Ca}_x)(\text{Fe}_{6-y}\text{Co}_y)\text{O}_{13+\delta}$ exhibit mixed-conducting behaviour [1], [2] and thermoelectric power [3], which are governed by the oxygen non-stoichiometry. The refinement in 4D formalism, from single crystal X-ray diffraction data [4] of the incommensurate modulated structure of $\text{Sr}_4\text{Fe}_6\text{O}_{13+\delta}$, allowed its accurate description. The structure is described in an orthorhombic system and consists basically of an intergrowth of one perovskite-type layer $[\text{SrFeO}_3]$ with a complex $[\text{SrFe}_2\text{O}_{3.5\pm\delta/2}]$ layer, related to a rock salt-type block, where Fe can be found in three different environments : tetrahedron, trigonal bipyramids and tetragonal pyramid. To create distortions in $\text{Sr}_4\text{Fe}_6\text{O}_{13+\delta}$ as shearing mechanisms, we decided to substitute Sr^{2+} by the isovalent cation Pb^{2+} , and investigate the $\text{Sr}_{4-x}\text{Pb}_x\text{Fe}_6\text{O}_{13+\delta}$ system. Although its ionic radius is very close to the one of Sr^{2+} , distortions can easily be induced by the presence of the $6s^2$ lone pair. For $x > 0.7$, a new phase has then been isolated with a chemical formula $\text{Pb}_4\text{Sr}_3\text{Fe}_{24}\text{O}_{53}$ [5], and its complex structure has been solved using a combination of electron diffraction tomography with HAADF-STEM imaging. Selected area electron diffraction revealed a commensurately modulated structure, with the supercell parameters : $a = 3.5$ nm, $b = 0.56$ nm, $c = 2.57$ nm and $\beta = 98^\circ$. Due to the low symmetry of the crystal system and the big unit cell, a huge number of independent reflections needed to be recorded to solve this structure, that is why electron diffraction tomography was perfectly suitable for this work. The data collection was carried out by tilting the sample holder from -50° to $+50^\circ$, and to obtain the reflections of the missing cone and improve the completeness, a new collection was realized after having rotated the support grid of 90° . HAADF-STEM imaging was very complementary since it allowed the accurate determination of Pb positions. Finally the structure consists of a terrace structure derived from $\text{Sr}_4\text{Fe}_6\text{O}_{13+\delta}$ with a collapse of the layers $[\text{SrFeO}_3]_\infty$ and $[\text{SrFe}_2\text{O}_{3.5\pm\delta/2}]_\infty$.

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Keywords: structure resolution, electron diffraction tomography, collapsed structure

MS17. In situ and in operando crystallography

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MS17-P1 *In-situ* determination of the evolution of the crystallite size distributions of GH-bearing sediments using two-dimensional X-ray diffraction

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Natural gas hydrates are found worldwide in marine sediments and permafrost regions. The detection and quantification of GH present in marine sediments is crucial for safe oil and gas extraction, seafloor stability assessments and for quantifying the impact of GH in climatic change. Hence, there is a considerable interest in studying the microstructure of GH-bearing sediments. Although a large amount of research on GH has been carried out over the years, the micro-structural aspects of GH growth and the crystallite sizes of hydrate in sediments are still poorly known and understood.

The present study was undertaken to determine for the first time the evolution of the crystallite sizes of GH-bearing sediments in order to better understand the formation process of GH in porous media and its impact on the resulting aggregates. For that, a custom-build pressure cell operating up to several MPa was used to form *in-situ* xenon hydrate at 276 K in undersaturated sediments made of natural quartz sand. The evolution of GH CSD's was studied using synchrotron X-ray diffraction at the ID15B beamline (ESRF - France). The evolution of the crystallite sizes was investigated with a time resolution from seconds to several days in order to follow the initial growth and coarsening processes of GH. The size of crystallites was directly determined from the diffracted intensities using our newly developed method called "*fast diffraction CSD analysis*" [1] here applied for the first time to *in-situ* work.

Our results show that the sizes of GH crystallites increase with time (see Figure): the evolution of crystallite sizes is rapid at the beginning of the formation than slows down with time which suggests diffusion limited reaction and a decrease of the rate of formation by depletion of one GH constituent (water in this case). A coarsening process converting hydrate crystals into larger masses takes place and continues to time-scales beyond our study. Our findings are in good agreement with visual observations using X-ray tomography [2].

[1] S. H. Neher et al., A new fast method to derive Crystallite Size Distributions (CSD) from 2D X-ray

diffraction data, this conference.

[2] A.Falenty et al., Stop-and-go *in-situ* tomography of dynamic processes –gas hydrate formation in sedimentary matrices, this conference

[3] Klapp et al. (2010), *Earth Planet. Sci. Lett.*, 299(1-2), 207-217, doi: 10.1016/j.epsl.2010.09.001.

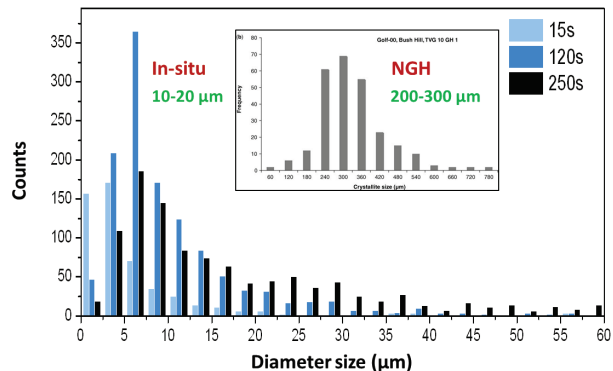


Figure 1. CSD of growing xenon hydrates after 15, 120 and 150 s. Insert shows the considerably larger CSD of a natural GH from Gulf of Mexico [3] indicative of appreciable coarsening of natural samples.

Keywords: In-situ, Crystallite Size Distribution, X-ray Dffraction, Gas Hydrates

MS17-P2 In-situ single crystal XRD study of absorption and desorption of CO₂ in zeolite Y

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X-ray diffraction methods in general allow only a limited chemical selectivity. Structural information on a subset of atoms is here obtained by modulating the stimulus supplied in situ on a crystal thus extracting structural information from the changing part of the scattering density within the overall crystal structure. Single crystal XRD data were collected in situ on a zeolite Y, in which CO₂, acting as active species, is desorbed upon heating. After out gassing the single crystal sample, anchored in a capillary, CO₂ was introduced in the capillary and the temperature modulated to obtain adsorption and desorption of the CO₂. In this way it has been possible to determine the sites where CO₂ is absorbed, its variations in occupancy and the motions between the sites. The cell parameter of the zeolite was found to decrease while increasing the temperature as CO₂ was desorbing, leaving the channels. It was then possible to determine the overall diminution in the occupancy of CO₂ while increasing the temperature and the shift of CO₂ moieties between the sites upon absorption and desorption.

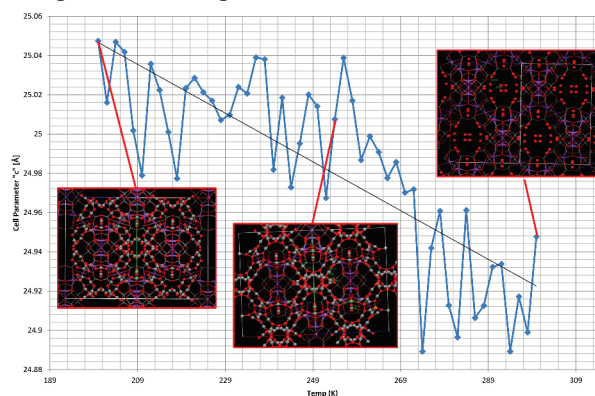


Figure 1. Cell parameter of Zeolite Y versus temperature and structures at selected temperatures.

Keywords: X-ray Single Crystal Diffraction, Chemical Selectivity, Substructure refinement, Modulation Enhanced Techniques, Fourier Filtering, Zeolites, Gas Adsorption.