average structure reveals the distribution of the ions as described by the probability density function, which can be obtained either by Fourier transformation of the Debye Waller factor (including anharmonic terms [1]) or by Fourier methods. The former is more appropriate for interstitial diffusion processes, i.e. when the migration of the ions proceeds directly to adjacent vacant sites. In this case a continuous density is found directly representing the diffusion pathway. Moreover, by applying Boltzmann statistics effective single particle potentials can be derived containing the potential barriers to migration which can be compared with otherwise measured activation energies. On the other hand, if interstitialcy (exchange) processes prevail, it is more meaningful to analyse difference Fourier maps and/or to introduce additional (metastable) positions. All this will be illustrated by various examples.
For fluorite like ZrO_2 doped with cations and anions (e.g. Sc and N [2]) one generally finds anion diffusion pathways directly through an edge of the surrounding cation tetrahedron along <100> to a neighbouring site. Derived activation energies agree with those obtained from conductivity measurements showing that no additional energy is needed for the creation of defects. By comparing samples with and without N it is possible to derive separate activation energies for O and N. In perovskite like $LaGaO_3$ doped with Mg and Sr the pathways are curved. These and the corresponding potentials are significantly altered when measured under electric fields [3] or microwave irradiation [4]. An example of interstitialcy diffusion is provided by mayenite ($Ca_{12}Al_{14}O_{33}$) [5]. Its structure may be described as a calciumaluminate framework containing 32 of the 33 O atoms, while the remaining "free" oxygen statistically occupies 1/6 of larger cages in the structure. In spite of the presence of vacancies and rather large openings between adjacent cages no continuous density was found, therewith ruling out interstitial diffusion (probably because of too long jump distances). On the other hand, difference Fourier maps revealed various other weakly occupied positions which can be related to an exchange process with particular framework O. Moreover, each jump process is connected with a relaxation of Ca, i.e. there is considerable interaction with the framework. Interestingly, the mechanism is different when the "free" O is replaced by N, i.e. nitrogen shows the interstitial type of diffusion within the same framework.

[1] Boysen H. *Z. Kristallogr.* 2003, 218, 123.
[2] Lerch M., Boysen H., Rödel T.C., Kaiser-Bischoff I., Hoelzel M., Senyshyn A. *Z. Kristallogr.* 2007, in press.
[3] Guenter M.M., Boysen H., Corte C., Lerch M., Suard E. *Z. Kristallogr.* 2005, 220, 218.
[4] Guenter M.M., Korte C., Brunauer G., Boysen H., Lerch M., Suard, E. *Z. anorg. allg. Chemie* 2005, 631, 1277. [5] Boysen H., Lerch M., Stys A., Senyshyn A. *Acta Cryst.* B, submitted.
Acknowledgement: This work is supported by the DFG (BO 1199).

MS31 O5

Remarkable microstructure evolution in biogenic crystals upon mild annealing Emil Zolotoyabko[a], Boaz Pokroy[a], Andy Fitch[b], [a]*Department of Materials Engineering, Technion-Israel Institute of Technology, Haifa, Israel.* [b]*ESRF, Grenoble, France.*
E-mail: zloto@tx.technion.ac.il

Keywords: Biomineralization, Microstructure, Powder Diffraction

By using high-resolution X-ray powder diffraction at a dedicated synchrotron beam line ID-31 at ESRF (Grenoble, France) we studied structural and microstructural modifications in biogenic calcium carbonate crystals, calcite and aragonite, obtained from different mollusk shells and subjected to heat treatments at elevated temperatures. The usage of the advanced analyzing optics on the diffraction beam resulted in diffraction spectra of superior quality and above all in narrow diffraction peaks with an instrumental contribution to the peak widths not exceeding 0.004^0. The measured X-ray powder diffraction profiles were treated with the aid of the Rietveld refinement within the GSAS program and the EXPGUI interface. As a result, the structural parameters were extracted with the highest possible precision (about 10 ppm for lattice parameters). All investigated shells revealed anisotropic lattice distortions of the unit cell [1] as compared to geological aragonite [2]. In both biogenic calcite and aragonite the maximal distortions reached about 0.2% along the *c*-axis. Analysis of the complete set of experimental findings allowed us to unequivocally attribute the discovered lattice distortions to intra-crystalline biomacromolecules confined within individual crystallites. Strong support for this conclusion is given by the results of structural measurements in samples subjected to mild short-period annealing at temperatures of 150-200 ^{0}C. At these temperatures, pronounced lattice relaxation due to the heat-induced degradation of organic macromolecules occurs [3]. Analysis of diffraction peak shapes fitted to Voigt functions allowed us to separate the contributions to peak widths caused by the finite crystallite size and microstrain fluctuations. This analysis revealed that at room temperature the crystallite sizes are highly anisotropic. Upon annealing, a drastic reduction of the crystallite sizes occurs that causes substantial broadening of the X-ray diffraction peaks clearly resolved by a naked eye. The peak broadening is well correlated with the lattice relaxation mentioned. The reduction of crystallite size is also correlated with the growth of averaged microstrain fluctuations due to increasing number of inter-crystalline boundaries. These findings allowed us to suggest a model of the biogenic crystal development as a result of the amorphous/crystalline phase transformation within the network of oriented biomacromolecules.

[1] Pokroy B., Quintana J.P., Caspi E.N., Berner A., Zolotoyabko E., *Nature Mater.* 2004, 3, 900.
[2] Caspi E.N., Pokroy B., Lee P., Quintana J.P., Zolotoyabko E. *Acta Cryst. B* 2005, 61, 129.
[3] Pokroy B., Fitch A.N., Zolotoyabko E. *Adv. Mater.*, 2006, 18, 2363.