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Report:

Preliminary studies

The background for this experiment consists of three previous works: i) the structural X-ray determination of the high-pressure phase of $Ca(OH)_2$ [$Ca(OH)_2$-II] by M. Kunz *et al* (High Pressure Res. **14**, 311, 1996) who determined the space group to be P 2_1/c and located Ca and O within the unit cell, ii) a subsequent TOF-neutron experiment by K. Leinenweber *et al* (J. Solid State Chem. **132**, 267, 1997) to locate the protons D in a deuterated sample in the same phase at low temperature at ambient pressure who found two non-disordered D positions, and iii) simulations by R.J. Papoular (Acta Cryst. **A55** suppl, 127, 1999 *and* unpublished) who showed that about 30 non-overlapped Bragg reflections should be available from the XRP diffraction pattern in order to recover the protons H reliably from a MaxEntropic Difference Fourier map. It was further shown that the latter approach would be superior to a full-fledged MaxEntropic Fourier electron density reconstruction using the already known CaO_2 as a non-

uniform density prior. About 30 non-overlapped Bragg peaks corresponds to an average FWHM of about .04 degrees under usual experimental conditions. In spite of experimental differences [deuteration, different P and T], the neutron information was thought at this stage to be the yardstick against which the success of our forthcoming ESRF experiment would be ranked.

The ID09 experiment

A wide-opening diamond anvil cell was used, together with a ruby chip for pressure calibration using the luminescence method. After a couple of unsuccessful preliminary loadings, our sample was eventually set in a Re-gasket and no pressure medium was added. Two series of high-P high-T in-situ runs were carried out at λ=0.38 Å and λ=0.50 Å respectively, at various pressures and temperatures up to about 300 ºC and 10 Gpa to and fro the $Ca(OH)_2$-II high-pressure phase. Our best shot was taken using λ=0.50 Å , P = 9.13 Gpa and T= 323 K. Additional calibration using Si [at both wavelengths] and Al_2O_3 [λ = 0.38 Å only] showed that the minimal FHWM we could achieve was around 0.06º, somewhat higher than the anticipated FWHM 0.04º required from our preliminary simulations. Subsequent Rietveld analyses of our sample data evidenced a FWHM increasing from 0.06º to 0.12º for the first series of runs, and from 0.07º to 0.13º for those carried out using λ = 0.50 Å.

Results and discussion

The program FullProf was used to Rietveld-analyze our data, as well as to provide the sets of structure factors required for a Maximum Entropy analysis. Only 21 isolated Bragg peaks could be obtained from our best data set due to the coarser than expected angular resolution. Prior to inserting the protons in the refinement, we found a) no a posteriori justification for asymmetric Bragg peaks in our data, b) a substantial Preferred Orientation along 2 0 1 , and c) an appreciable Anistropic Linewidth Broadening with which we coped using the PW Stephens' approach. Our first H-refinement used the published neutron positions from the work mentioned above as starting values and produced the "neutron" solution. The resulting quality factors consequently dropped from R_p = 2.08% , R_B = 8.8% and χ^2 = 1.62 to R_p=1.66%, R_B=5.8% and χ^2 = 0.908. But a second even better solution, at least in terms of these indicators as well as a Bond-Valence Sum analysis [as incorporated in FullProf], could be

found using another non-Fourier based approach to be detailed elsewhere and yielding the following values: R_p=1.55%, R_B=5.3% and χ^2 = 0.820. Finally, isotropic B values could be refined independently for Ca and O atoms yielding B_{Ca} = 1.70 $Å^2$ and B_O = 0.87 $Å^2$, B_H being kept fixed to 2.00 $Å^2$. Our best fits involving the CaO_2 framework only and the complete $Ca(OH)_2$ are shown below. Our best Lebail fit [not shown] yielded R_p=0.94% and χ^2 = 0.287. Our current solution (the "X-ray" solution) differs from the "neutron" one by essentially one number: $O_1(z)$. Even if it turns out to be to good to be true, it is darn close !