ESRF	**Experiment title: Refinement of the real structure of ferroelectric perovskites**	**Experiment number**: CH-569
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Report:

Translational periodicity results in a considerable reduction of the amount of information necessary to model the structure of solids. Any deviation from this ideal description appears as large thermal displacement parameters when this is handled within the Debye Waller approximation. The two starting hypothesis of this approximation (periodicity and harmonic lattice vibrations) are not well satisfied for ferroelectric compounds. In particular, the atoms in ferroelectric solids present random local off-site displacements (multi-well potentials ...) and are generally modeled with very large Debye-Waller factors. The object of this work is to go beyond the average structure usually obtained in conventional Rietveld refinements and to compare different approaches to better model the structural features.

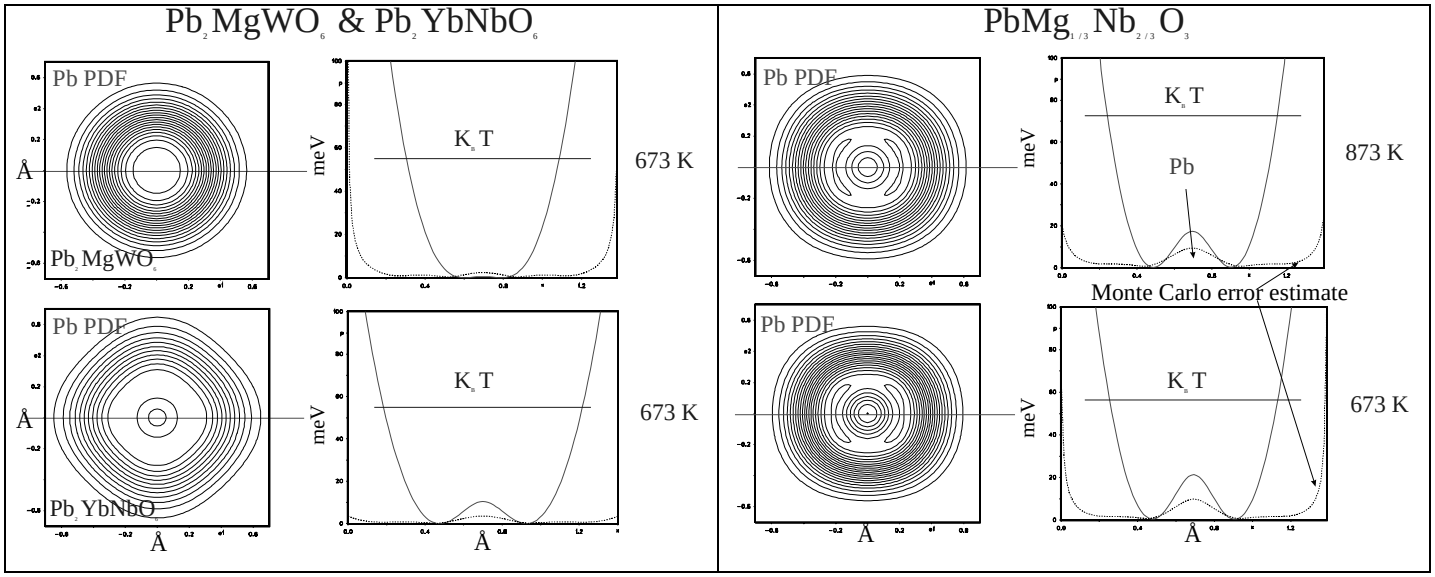
Generalized atomic displacement parameters can be used to describe the weakening of Bragg intensities via the anharmonic Debye-Waller factor and its real space counterpart, the generalized atomic probability density function (PDF). The one particle potential obtained from a structural refinement has only a limited physical significance since it does not contain the information on interatomic coupling. It respects the point group symmetry of the averaged environment of the atom. Therefore, in cubic perovskites, only a very limited number of terms are non-zero. In the Gram-Charlier formulation, the PDF calculation is straightforward:

$pdf(u)=pdf_{harm}(u)[1+(1/3!)C_{ijk}D^iD^jD^k+(1/4!)d_{ijkl}D^iD^jD^kD^l+...]$

Where $D^i=d/du_i$ and the one particle potential is given by:

$V(u)=-k_BT\{\ln[pdf(u)]-\ln[pdf(u=0)]\}$

The diffraction patterns were refined with the Rietveld program XND. Among the main advantages of collecting powder data instead of single crystal ones we can point out the faster data collection, the-easy absorption correction and the absence of extinction. The problem of peak overlap was not very important since the FWHM of our samples was slightly less than 0.015°.



Here above are shown the PDF functions of the different compound we have investigated at various temperatures above the phase transition. Below is a summary of the obtained agreement factors.

Pb_2MgWO_6 673K	Pb_2YbNbO_6 673K	$PbMg_{1/3}Nb_{2/3}O_3$ 673K	$PbMg_{1/3}Nb_{2/3}O_3$ 873K
Fm3m, 121 reflections with I/s(I)>1	Fm3m, 119 reflections with I/s(I)>1	Pm3m, 60 reflections with I/s(I)>1	Pm3m, 55 reflections with I/s(I)>1
ideal structure (7 parameters) R=4.25 Rw= 3.90	ideal structure (7 parameters) R=9.28 Rw= 2.18	ideal structure (4 parameters) R=9.49 Rw= 2.76	ideal structure (4 parameters) R=9.22 Rw= 2.42
Pb free rotator model (8 parameters) R=3.33 Rw= 3.03 r(free rotator)=0.263(3)Å	Pb free rotator model (8 parameters) R=4.62 Rw= 1.40 r(free rotator)=0.345(3)Å	Pb free rotator model (5 parameters) R=4.89 Rw= 2.07 r(free rotator)=0.309(5)Å	Pb free rotator model (5 parameters) R=5.13 Rw= 1.80 r(free rotator)=0.317(5)Å
Gram-Charlier- 4th order (10 parameters) R=3.30 Rw= 3.01	Gram-Charlier - 4th order (10 parameters) R=5.06 Rw= 1.30	Gram-Charlier - 4th order (6 parameters) R=4.50 Rw= 2.02	Gram-Charlier - 4th order (6 parameters) R=5.00 Rw= 1.73

On the other hand, both the Gram-Charlier formalism and the free rotator approach fail to provide a global answer to the $PbMg_{1/3}Nb_{2/3}O_3$ diffraction patterns at room and at lower temperatures. One of the peculiar features of these patterns is the appearance of “diffuse” scattering, resulting in a broadening of the base lineshape of a certain number of peaks. This phenomenon can be modeled introducing a correlation function to take into account the correlated displacements of Pb atoms. Some very simple models can be formulated. Among the simplest forms of correlation functions and correlation vectors, good results can be obtained via a simple square-like correlation function directed along [110]. This model is still currently improved and the actual results are very promising.