	Experiment title: Anharmonic treatment of the thermal motion in perovskites– comparison between lead and barium containing compounds	Experiment number: CH944
Beamline: BM16	**Date of experiment**: from: 18/9/00 to:24/9/00	**Date of report**:
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Report:

Over the past years the purely displacive character of the transitions occurring in perovskites has been under discussion in favour of a more complicated description involving the presence of some order-disorder. From the crystallographic point of view this disorder effect has been mostly modelled within the standard approach : the atomic species, whose anomalously large thermal parameters are indicative of a structural disorder, are located on split sites. This has brought to the widespread acceptance of models for the average structures in which the term "disorder" is even too much used. However, more sophisticated models go beyond the Gaussian approximation for the atomic probability density functions (PFD) and hence are based on anharmonic one-particle potentials. The interest of such an approach is to get a better description of those crystals which undergo strictly structural phase transitions, related to the lattice dynamics.

The aim of our project is to analyse in the anharmonic approximation the atomic displacement parameters in complex perovskites containing either Pb or Ba. Since the atomic PDFs are obtained by Fourier synthesis of the structure factors in diffraction measurements, intensities must be collected up to a high value of $\sin\theta/\lambda$ if fine details in real space are desired. For this, we have recorded the diffraction patterns at BM16 with a wavelength of 0.35 Å. We examined two lead-based perovskites (one ordered Pb_2YTaO_6 and one disordered $PbFe_{0.5}Ta_{0.5}O_3$), as well as $BaTiO_3$-$BaZrO_3$ with 2 compositions. For synthesis problems the lead-based ordered perovskite was replaced by a solid solution $Pb_{1-x}Bi_x(Mg_{(1+x)/3}Nb_{(2-x)/3})O_3$, which presents an interesting dependence of the dielectric properties on the Bi content.

BaTiO$_3$-BaZrO$_3$: The phase diagram of this system is described in ref. 1.We chose a composition with a diffuse ferroelectric transition and another composition which shows a relaxor behaviour. Six diffraction patterns were recorded for subsequent standard refinement. The BaTi$_{0.80}$Zr$_{0.20}$O$_3$ compound shows a well-defined phase transition. In addition to the rhomboedral distortion, a strong broadening of the reflections is observed at low temperature. This phase is rhomboedral with ferroelectric micro-domains. For the BaTi$_{0.65}$Zr$_{0.35}$O$_3$ compound, neither reflection splitting nor extra lines appear at low temperature, as one expects with the cubic symmetry of the structure. However a weak broadening of all the reflections is observed at 100 and 10 K. This broadening does not present any preferential direction and cannot be associated with any symmetry break. In a second step, the Gram-Charlier expansions of the thermal parameters were introduced. Considering the symmetry of the atomic sites, there are one harmonic component (u_{iso}) and two fourth-order components (D_{1111} and D_{1122}) for Ba and Ti/Zr. The oxygen atoms have two harmonic components (u_{11} and u_{33}) and three fourth-order components (D_{1111}, D_{2222} and D_{1122}). In view of the scattering amplitudes of the different atoms, only the harmonic contribution was taken into account for oxygen. For any temperature, no significant improvement of the R-factors was obtained. The correlation between the parameters is weak and the refinements converge for very small values of the fourth order components [2]. All atoms show an harmonic behaviour.

PbFe$_{0.5}$Ta$_{0.5}$O$_3$: One diffraction pattern was recorded in the cubic phase at 350K. The refinement is still in progress. However, it is clear that Pb shows strong anharmonicity as in PbSc$_{0.5}$Nb$_{0.5}$O$_3$ structure [3].

Pb$_{0.8}$Bi$_{0.2}$(Mg$_{0.4}$Nb$_{0.6}$)O$_3$: Two diffraction patterns were recorded at 100K and 370K. No transition phase was observed. The structure is cubic (Pm3m) at all temperatures. Electronic microscopy studies showed that the local order between Mg and Nb is higher than in Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$. Moreover the correspondent superstructure reflections are not observable in our patterns. Compared to Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$, the diffuse scattering observed at the bases of some peaks is weaker. The refinements converge for significative values of the fourth-order components (D_{1111} and D_{1122}) for Pb atoms. Pb shows a strong anharmonicity.

Combining our results with those of reference 3, we find out that in complex perovskites, the atomic displacement of Pb is strongly anharmonic whereas Ba has an harmonic behaviour. Even in the relaxor composition the atomic displacement of Ba is harmonic. There is no direct relation between the relaxor behaviour and the anharmonicity of the A-cation of the perovskite structure.

References
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