ESRF	**Experiment title:** X-ray resonant diffraction study of thin films of the magnetoelectric $GaFeO_3$	**Experiment number**: **02-02-795**
Beamline: BM02	**Date of experiment**: from: 25 November 2011 (08:00) to: 29 November 2011 (08:00)	**Date of report**: 29 August 2014
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Report:

Objective

$Ga_{2-x}Fe_xO_3$ (GFO) is a room temperature magnetoelectric, and possibly ferroelectric, material. The origin of these properties is still controversial, and certainly requires the determination of the Fe and Ga cationic positions in the 4 available sites of its structure. The technological use of the room temperature magnetoelectric properties of GFO necessitates its fabrication in thin films. We have reported the epitaxial growth of GFO thin films but the determination of the cationic distribution in these thin films was not possible via neutron diffraction because of a lack of matter, nor by using laboratory X-rays due to the small contrast between Ga and Fe.

The aim of the proposal was to determine the cationic distribution in GFO thin films by X-ray resonant diffraction. This technique is the best suited for this aim, if not the only available one, for it necessitates small amounts of matter and allows discrimination between the Fe^{3+} and Ga^{3+} cations.

Experimental

Diffraction Anomalous Near-Edge Structure (DANES) experiments were performed on the BM02 beam line. Spectra were acquired on GFO thin films of three different Ga/Fe ratios, $Ga_{1.2}Fe_{0.8}O_3$, $GaFeO_3$ and $Ga_{0.6}Fe_{1.4}O_3$, and one Mg doped sample $Ga_{0.6}Fe_{1.4}O_3$:Mg2%. Between 30 and 60 reflections were measured at both the Ga (10.337 - 10.397 keV) and Fe (7.065 - 7.185 keV) edges for each of the 4 samples. (Only the reflections not impacted by superimpositions occuring due to the existence of 3 in plane variants in the films are considered.) The data obtained for the (122) reflection at both the Fe and Ga edges is shown on Figure 1 as a representatve example of the acquired data.

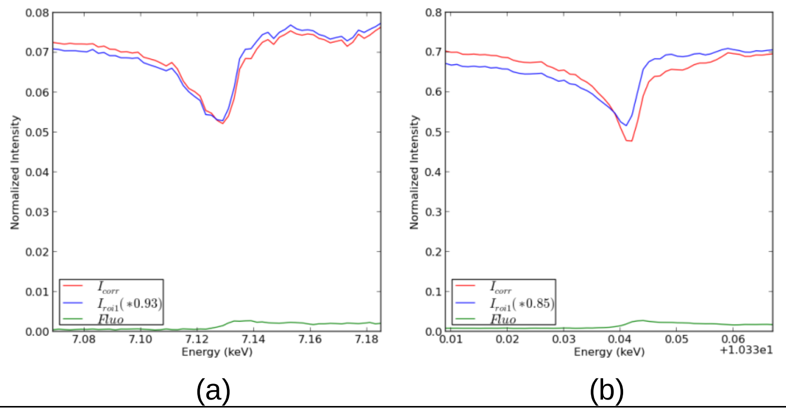

Figure 1 : Diffracted intensities measured for the the $Ga_{0.6}Fe_{1.4}O_3$ sample at the (a) Fe and (b) Ga edges for the (122) reflection

Results

The diffracted intensities of the reflections are systematically refined using as input parameters:
- the Fe occupancies of the 4 cationic sites through a (Fe1,Fe2,Ga1,Ga2) quadruplet (the occupancies in Ga will be taken as the complement)
- an 'orientation' parameter η, wich takes into consideration the fact that the cells can have grown in the + or -b direction (η = 1 if all cells are oriented along the +b direction, 0 if all the cells are oriented along the –b direction, and 0.5 if there is an exact mixture of both orientations)

A fully automatic refinement procedure has been programmed in the Python programming language. It systematically simulates the spectra awaited for all possible sites occupancies and orientation parameters (with adjustable steps) and compares them to the experimental data using a least squares method. This poweful sofware allows an efficient processing of the high amount of experimental data and allows obtaining relevant results with no ambiguities. The refined spectra obtained for the (122) reflection for both the Fa and Ga edges are shown on Figure 2 as representative of the refinement process.

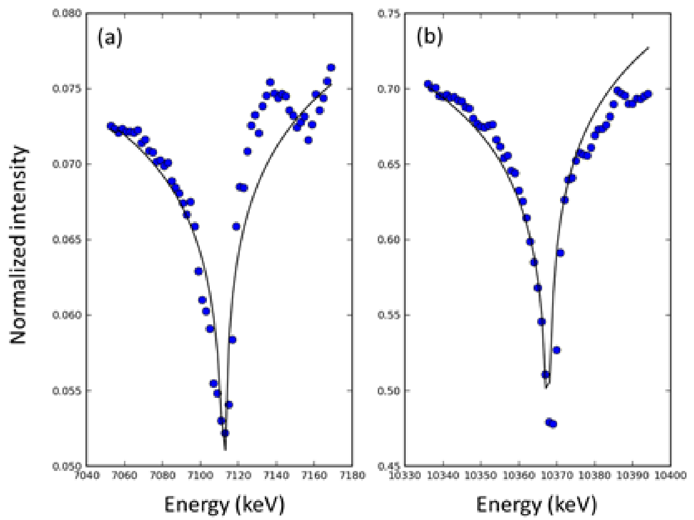

Figure 2 : Refined spectra (solid line) of the intensity experimentally measured (blue dots) for the (122) reflection of the $Ga_{0.6}Fe_{1.4}O_3$ sample at the (a) Fe and (b) Ga edges

The first important result obtained is that the orientation parameter is 0.50 ± 0.01. It means that the films are composed of head to tails cells (Figure 3).

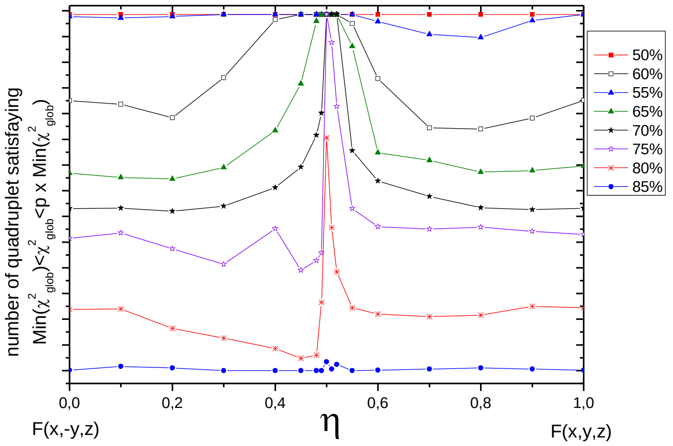

Figure 3 : Number of Fe occupancies quadruplets satisfying the imposed criterion of goodness (with different criteria of goodness *p* between 50 and 85 %) for varying inversion parameters. A maximum is clearly visible for $\eta = 0.5$.

The sites occupancies are also determined through these refinements (Figure 4). They are close to what is observed in bulk for all compositions with a very low amount of Fe in the Ga1 site. However they also show an important quantity of Fe in the usually Ga filled site Ga2. They unambiguously indicate that when the samples are doped with Mg, the Mg cations occupy the Ga2 sites. The calculations performed with those sites occupancies still lead to values of the polarization very close to the 25 µC/cm² already calculated for the bulk. Therefore, the sites occupancies cannot account for the low measured polarization.

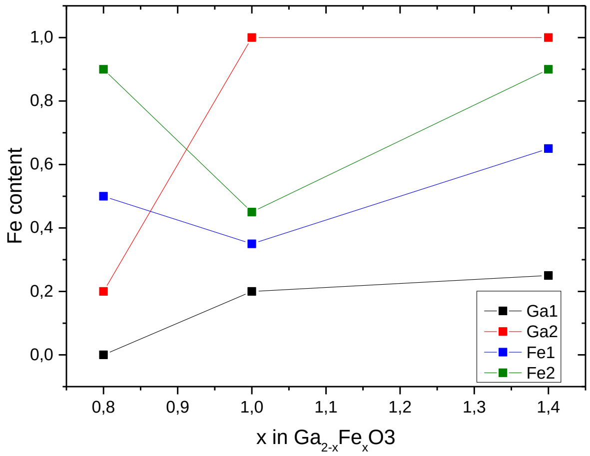

Figure 4 : Cationic site occupancies for the studied samples of different Ga/Fe ratios

Conclusions

These DANES experiments have been a real experimental success with more than 200 acquired spectra. We have put efforts on the programmation of a Python tool able to fully analyse all data systematically. The results are beyond what was expected. Not only did we determine unambigously the cationic sites occupations, as expected in the proposal, but we also unveiled the fact that the films were made of head to tails cells. This observation may be at the origin of the poor polarization measured for the thin films.

These results are in the process of being submitted for publication in Journal of Physical Chemistry C. New experimental conditions are being set-up in order to favor the deposition of thin films having only one orientation of the cells.

A new proposal will be made in order to analyse those films through the same DANES experiments. The key to the inderstanding of the room temperature ferroelectricity in this material certainly lies in those experiments.