	Experiment title: Structural study of ferroelectric / relaxor multilayers of the (1-x) PbMg$_{1/3}$Nb$_{2/3}$O$_3$ – x PbTiO$_3$ family	**Experiment number**: 02.02.642
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Introduction

The complex oxide ferroelectric materials (1-x) Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ - x PbTiO$_3$ [(1-x)PMN – xPT] have generated a great deal of interest for certain compositions due to their exceptional electromechanical coupling in single crystal form. The fabrication of such compounds as thin films is an important challenge for practical applications. Since the microscopic origin of these exceptional piezoelectric properties seems to be directly linked to the complex nanostructure of the material, it is fundamental to understand the influence of strain in these materials, when they are in the form of films and heterostructures.

In order to investigate the effect of strains and interactions between the relaxor PMN and the ferroelectric PT, we grew a series of [PMN$_{(1-x)\Lambda}$/PT$_{x\Lambda}$]$_{10}$ superlattices [1] on substrates of buffered MgO for which x varies from 0.2 to 0.9 and the modulation period Λ is nominally 150Å. Here we report on measurements performed on two of these samples: a PT rich superlattice (x = 0.8) and a PMN rich superlattice (x = 0.2). The aim of this experiment is to investigate both the out-of-plane and the in-plane structure of PMN and PT layers under different strain states, produced by two superlattices composed of significantly different thicknesses of the constituent layers.

Experimental set-up

The experimental set-up allows us to record the diffraction profiles over several orders (from L = 1 to L = 8) and the fine details of the diffraction curves can be examined. By comparing the measured curves with the simulated (00L) diffraction profiles, we can extract relevant information about the superlattice structure along the growth direction. For these measurements, the energy was fixed at 16 keV (0.77578 Å).

In order to investigate the in-plane structure, a reciprocal space mapping was performed around the (H0L) and (0KL) nodes. The experiments were carried out in asymmetric reflection geometry and the energy was fixed at 9.865 keV (1.2568 Å). We measured the (204) and (024) reflections by determining the orientation matrix of each sample in the frame of the substrate and then used the hkl scan routines of SPEC.

Results

Preliminary results on the (00L) lines show that PT layers are a-axis oriented which means that the polarization axis is in the film plane. This result agrees with our laboratory X-ray investigations of these

superlattices. The experimental data are now being further analysed using a modeling program developed specifically for superlattices [2], in order to evaluate structural features along the direction growth, such as thickness fluctuations or atomic inter-mixing, which can take place at the PMN/PT interfaces.

We present in Fig. 1 contour maps in reciprocal space of a section of the HL plane, recorded around the (204) reflection for both samples. Clearly the in-plane structures for the two superlattices are quite different. For the PMN rich sample in Fig.1a, the contour map shows two series of equidistant peaks along the L direction, one centered about L = 4.32 corresponding to diffraction from the PT sub-layers, and the other centered about 4.15 corresponding to the PMN sub-layers. The equidistant peaks are indicative of a modulated structure along the growth direction with the periodicity determined by the spacing of two adjacent peaks. The separation between these two series of peaks can be explained by the difference of lattice parameters of PMN and PT. Moreover the peak alignment along the L direction means that PT and PMN layers have the same in-plane parameter of 4.04Å. The comparison with the (024) map (not shown here) allows us to conclude that both constituents are tetragonal. As shown in Fig. 1b, the modulation structure of the PT-rich superlattice is not as readily visible compared to the PMN-rich sample. Since the scattering from the PMN layers is less intense than that from PT, the overall contribution of PMN is very weak due to the small volume of PMN in the superlattice. The most striking feature here is the splitting (at L=4.3) of the PT(204) node along the H direction. This is due to the presence of two types of PT a-domains: a_1 and a_2 for which the c-polarization-axis is respectively along the [100] and the [010] direction . From the (204) and (024) (not shown here) maps we have determined the same in-plane structure for these two types of domains: 4.025 Å for the polarisation axis and 3.90 Å for the non polar axis.
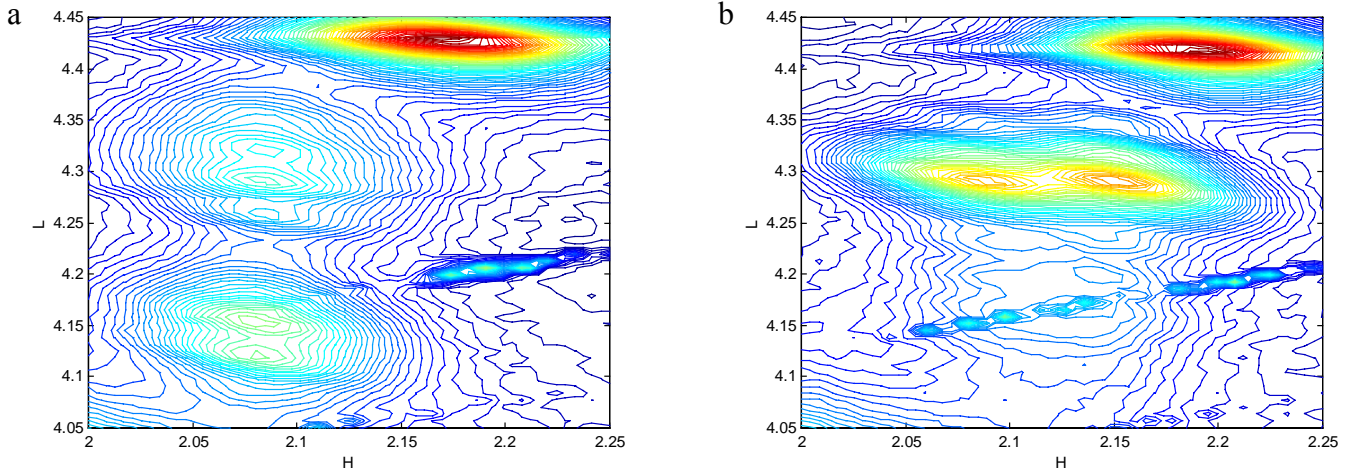
Figure 1 : *Two-dimensional contour maps, in logarithmic scale, of reciprocal space of section of the HL-plane around the (204) reflection for a :*
(a) 0.8 PMN – 0.2 PT superlattice (layer thickness : around 100 Å for PMN and 25 Å for PT)
(b) 0.2 PMN – 0.8 PT superlattice (layer thickness : around 25 Å for PMN and 125 Å for PT)
The intense peak near L = 4.4 is the contribution from the $La_{1/2}Sr_{1/2}CoO_3$ buffer layer.
The streaks crossing the map diagonally are induced by the substrate.

The presence of a_1 and a_2 domains is expected since this type of domain structure is usually observed in PT thin films. These polydomain patterns result from the strain relaxation at the substrate/ferroelectric film interface and is thickness dependent [3]. **But to our knowledge, it is the first time that this domain structure is observed in superlattices.** The absence of these two types of domains in the low PT content superlattice as well as the significantly different values of the in-plane parameters for the 2 superlattices suggests a critical thickness for the PT layers. Below this critical thickness they form a partially coherent structure with the PMN layers while above it, the strains are likely to partially relax via the formation of differently oriented micro-domains.

References

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