ESRF	**Experiment title:** Determination of tilting and deformation of MnO_6 octahedra in epitaxial $La_{0.7}Sr_{0.3}MnO_3$ ultrathin perovskite films on cubic $SrTiO_3$(100) substrates induced by misfit strain	**Experiment number**: SI 2378
Beamline:	**Date of experiment**: from: 7 september 2011 to: 12 september 2011	**Date of report**: 1/03/2012
Shifts:	**Local contact(s)**: Pilar Ferrer, BM25, SpLine	*Received at ESRF:*

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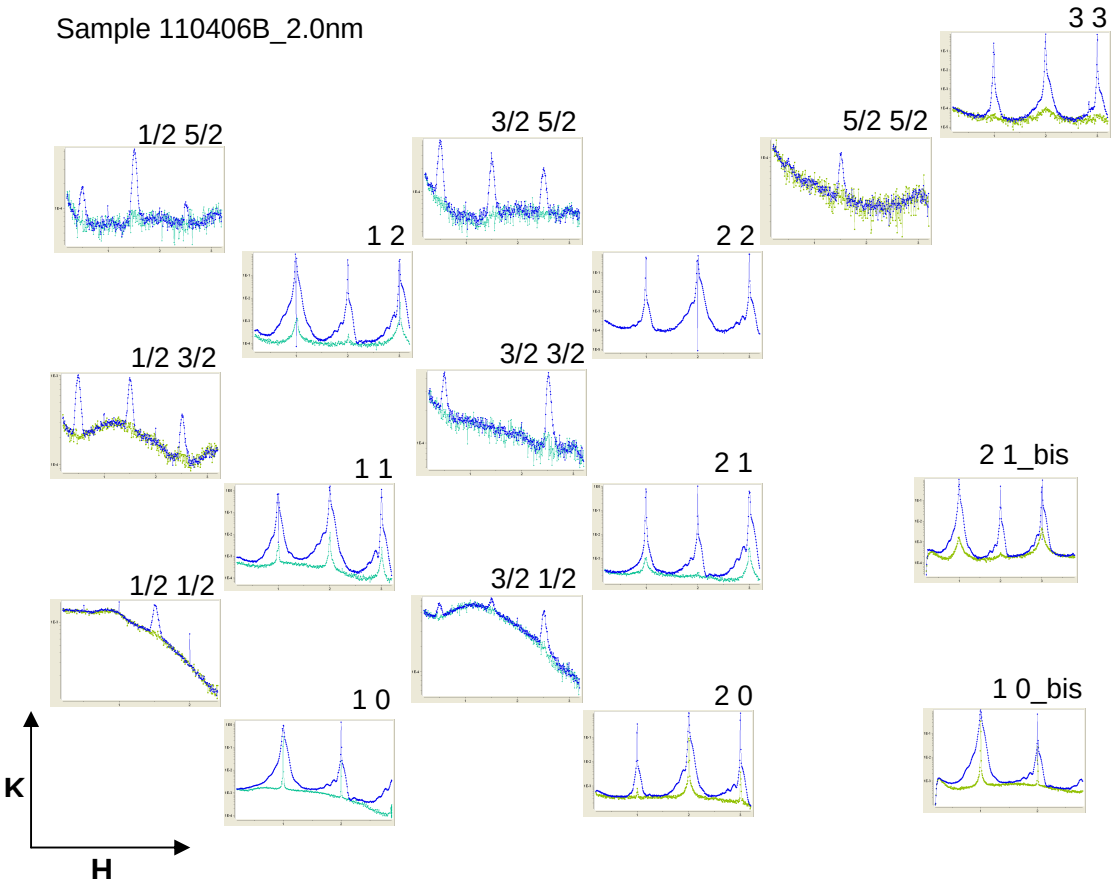
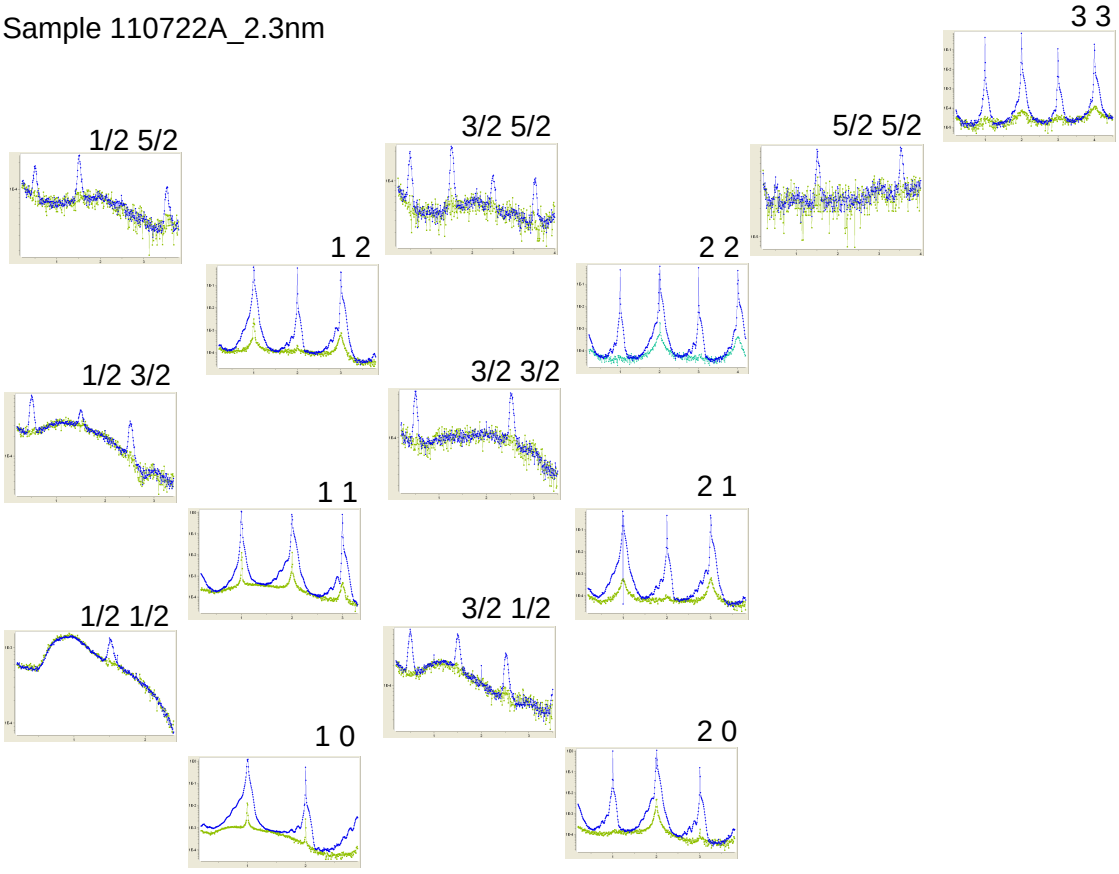
Report:

In this experiment we used kappa-geometry XRD goniometer at BM25B, at beam energy *E*=14.5KeV (λ=0.85 Å) always at grazing incidence. We measured at ambient conditions four different $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) epitaxial films on $SrTiO_3$(001) substrates of (5x5.0.5mm^3) with thicknesses: 1.8, 2.0. 2.3 and 3.5 nm. For the purpose of the experiment we explored mainly *L*-scans at different *HK* positions. Since bulk LSMO presents rhombohedral *R*-3C structure it should show reflections at different H/2 K/2 L/2 which do not overlap with cubic substrate The following table lists the measurements performed (the table indicates the name of the corresponding .spec file):

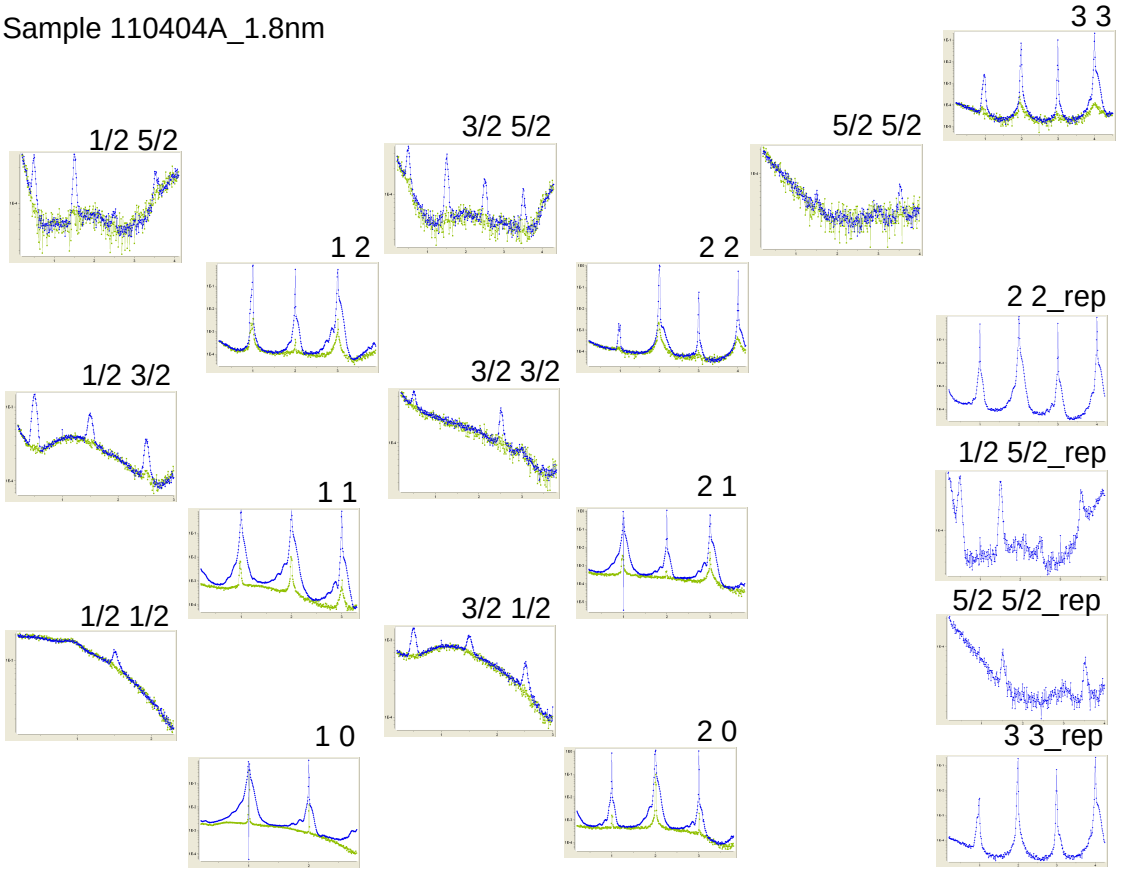
	110406B_2.0nm	110722A_2.3nm	110404A_1.8nm	101222_3.5nm
1 0 L	_2 / 3 (4) _4 / 3 (4) rep	_3 / 2 (3)	_3 / 3 (4)	_3 / 3 (4)
1 1 L	_2 / 5 (6)	_3 / 4 (5)	_3 / 5 (6)	_3 / 5 (6)
2 1 L	_2 / 7(8) _4 / 5 (6) rep	_3 / 6(7)	_3 / 7(8)	_3 / 7(8)
1 2 L	_2 / 9(10)	_3 / 8(9)	_3 / 9(10)	_3 / 9(10)
2 2 L	_2 / 11(_4 / 7)	_3 / 10(37)	_3 / 11(12) _4 / 3	_3 / 11(12)
2 0 L	_2 / 13(14)	_3 / 12(13)	_3 / 13(14)	_3 / 13(14)
0.5 0.5 L	_2 / 15(16)	_3 / 14(15)	_3 / 15(16)	_3 / 15(16)
1.5 0.5 L	_2 / 17(18)	_3 / 16(17)	_3 / 17(18)	_3 / 17(18)
0.5 1.5 L	_2 / 19(20)	_3 / 18(19)	_3 / 19(20)	_3 / 19(20)
1.5 1.5 L	_2 / 21(22)	_3 / 20(21)	_3 / 21(22)	_3 / 21(22)
0.5 2.5 L	_2 / 23(24)	_3 / 22(23)	_3 / 23(24) _4 / 4	_3 / 23(24)
1.5 2.5 L	_2 / 25(26)	_3 / 24(25)	_3 / 25(26)	_3 / 25(26)
2.5 2.5 L	_2 / 27(28)	_3 / 26(27)	_3 / 27(28) _4 / 7	_3 / 27(28)
3 3 L	_2 / 29(30)	_3 / 28(29)	_3 / 29(30) _4 / 8	_3 / 29(30)
-1.5 1.5 L	_2 / 31(32)	_3 / 30(31)	_3 / 31(32)	_3 / 31(32)
1.5 -1.5 L	_2 / 33(34)	_3 / 32(33)	_3 / 33(34)	_3 / 33(34)
-1.5 -1.5 L	_2 / 35(36)	_3 / 36(35)	_3 / 35(36)	_3 / 35(36)
XRR	_ / 19(21,22)	_3 / 48	_ / 43	_ / 48
Hscan	_2 / 246	_3 / 57	_4 / 27	_2 / 3

Most of the scans were taken in the H, K>0 quadrant. Snapshots of the L-scans are shown in the following pages arranged along their respective HK values:

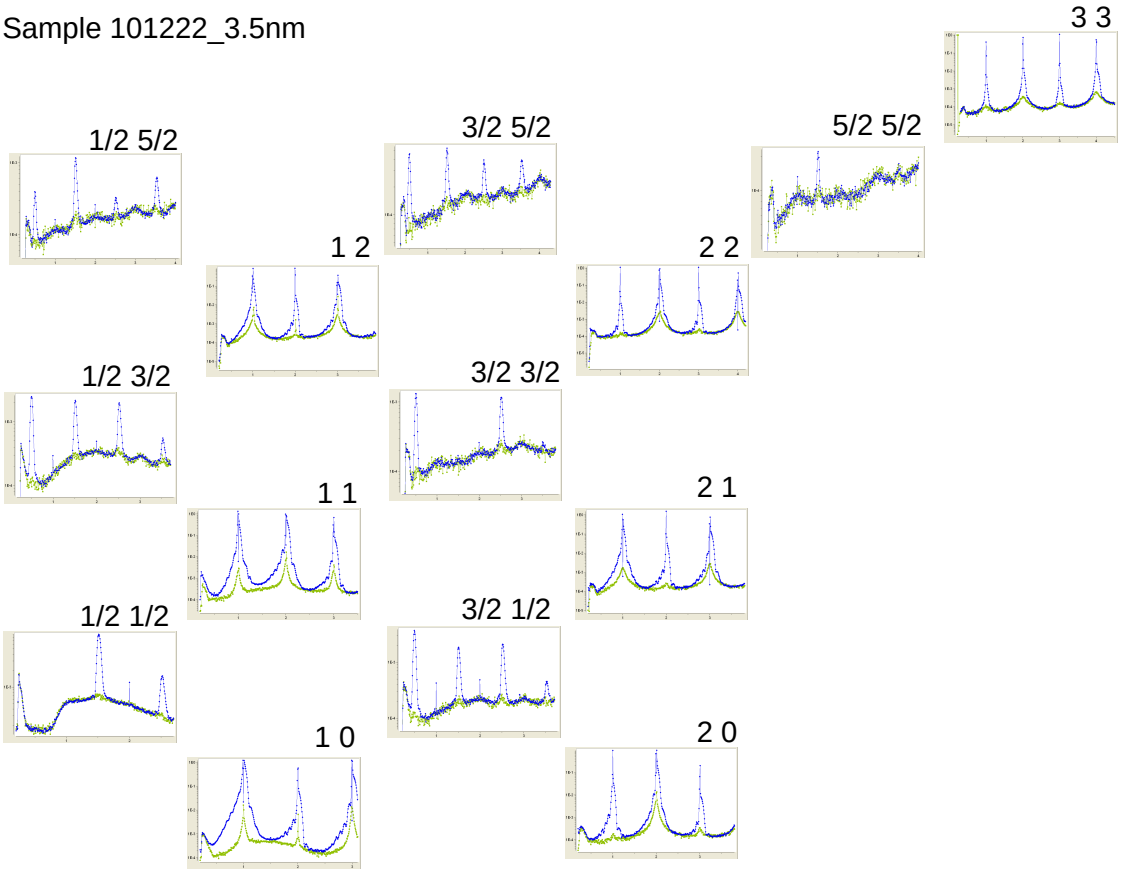




Sample 110404A_1.8nm



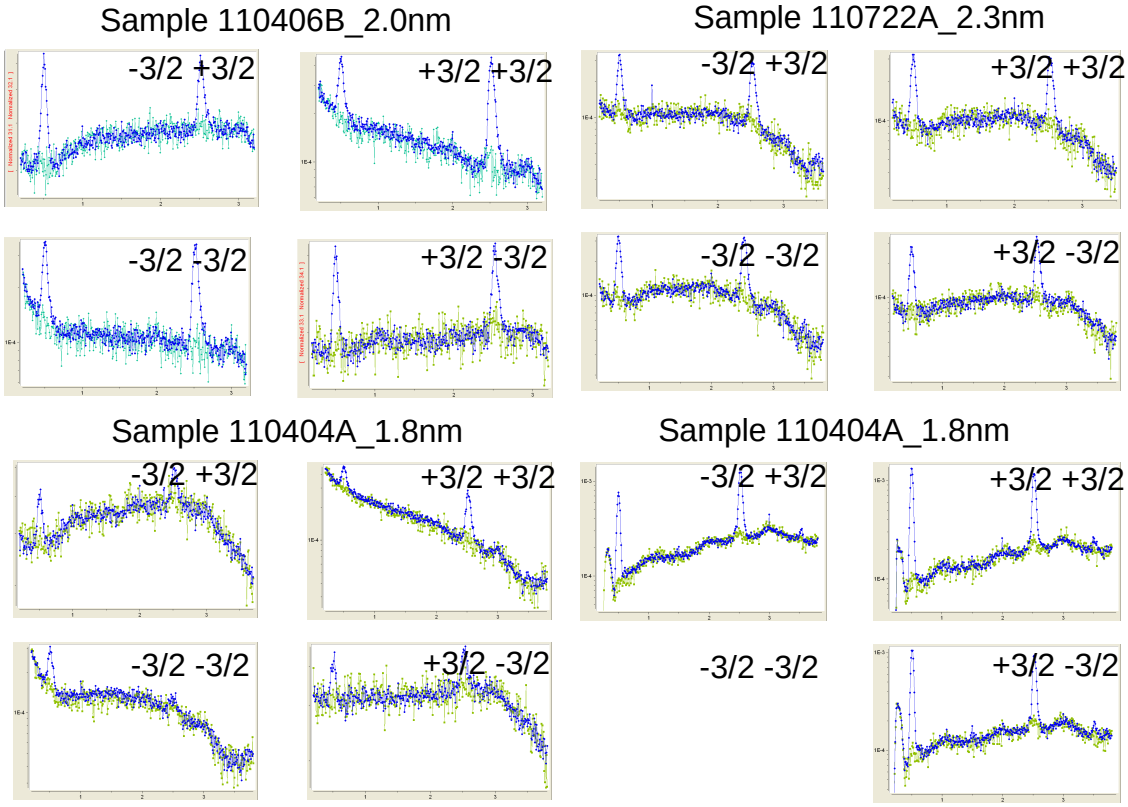
Sample 101222_3.5nm



The scans were taken along the central axis (optimized H1K1-H2K2 trajectory at low and high L values for each L-scan) as well as H+ΔH, K+ΔK slightly shifted from the central rod positions to serve as reference for background subtraction (also depicted in graph with green symbols).

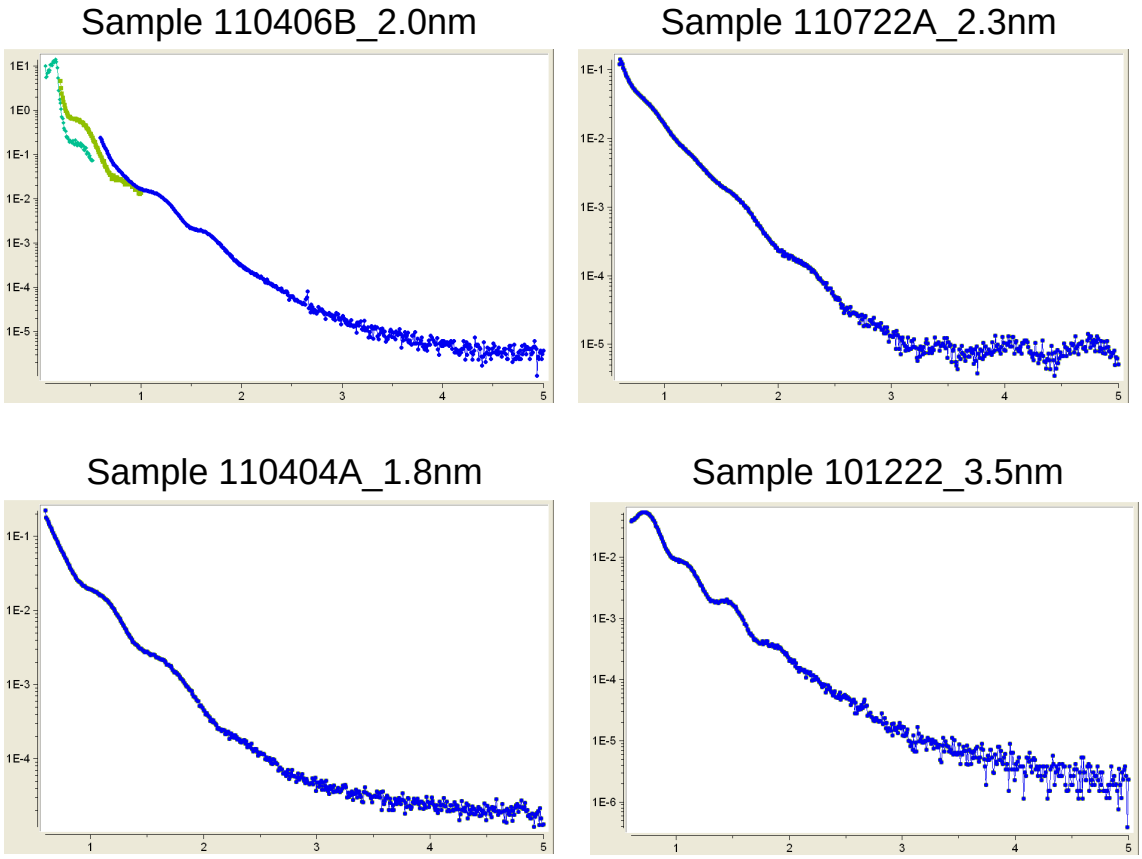
L-scans at integer HK values show intense peaks (at integer L values) corresponding to the $SrTiO_3$ (STO) substrate (taken as reference for the HKL units). They also show broad tails with clear Kiessig fringes corresponding to the overlapped film contribution with crystal coherence length of the full film thickness for each sample (proving the high crystal quality of the epitaxial films).
L-scans at H/2 K/2 values do not show any overlap with the substrate and consist mostly of the expected L/2 reflections compatible with either *R*-3c rhombohedral or *C*2/c monoclinic structures (extinction conditions are fulfilled only for H/2=K/2=L/2 for all the samples). Only slight differences in their relative intensities were observed, which have to be analysed in detail in order to distinguish between rhombohedral and monoclinic structures.
Some scans they also show a very narrow contribution at some L integer which is probably related to a 2nd order substrate contribution.

Some additional equivalent scans were taken in different quadrants (H,K<0) to account for possible anisotropies in the sample.

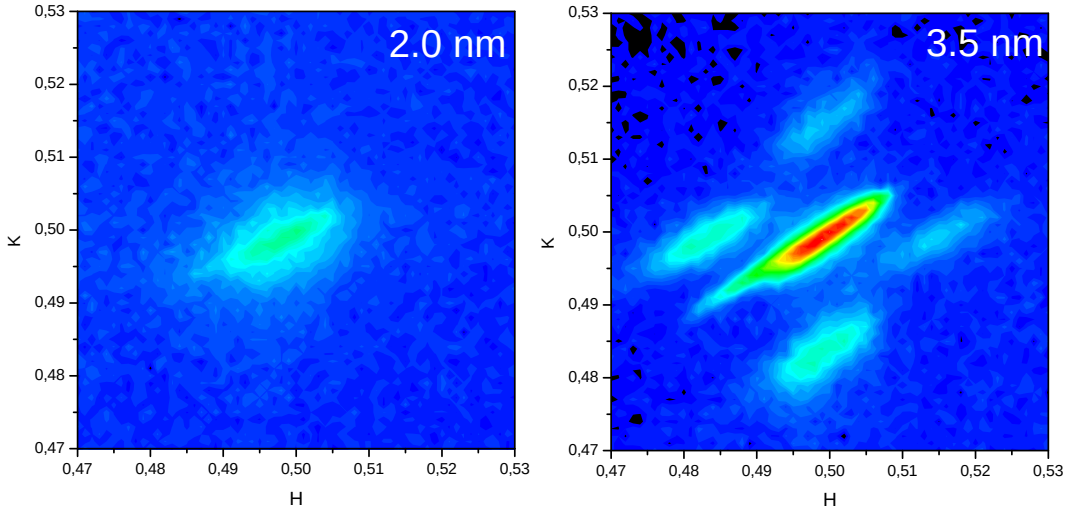


No particular differences were observed although the relative intensities of equivalent reflections are not preserved. This was one of the main problems to successfully apply the truncated rod method. The intensities for the separate reflections may be influenced by the experimental conditions so structure factor extraction is compromised.
Further experiments are needed on symmetric conditions in order to continue with truncation rod method.

These graphs show X-ray reflectivity curves for the analysed samples which correspond to their expected film thicknesses



For a selection of two samples of thickness 2.0 and 3.5 we performed longer HK maps at a fixed L position around the film ½ ½ 3/2 reflection.



In the thickest film first order satellite peaks along [100] and [010] appear clearly as a result of the periodicity of (100) and (010) twin planes. The satellite separation is consistent with the Λ= 26 nm observed by SEM in this film (the different intensity of the satellites is not yet fully understood). However, in the

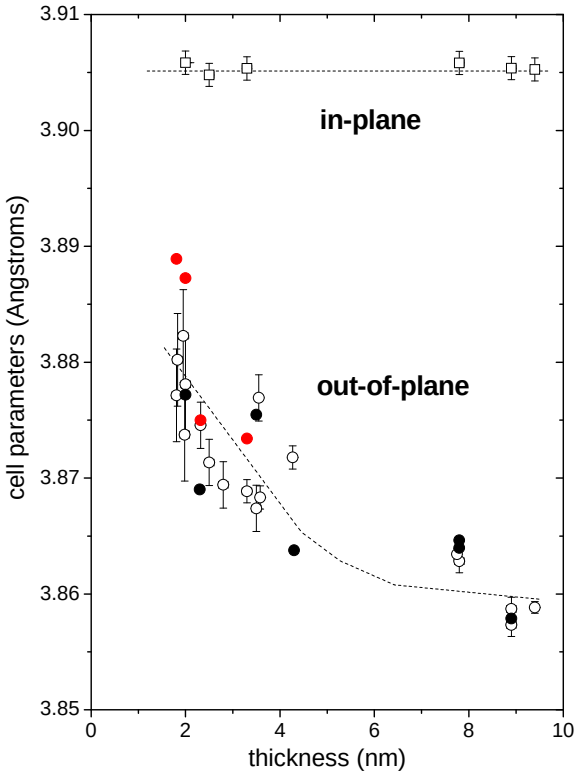
films of 2.0 nm no satellites are observed around the ½ ½ 3/2 reflection. This may indicate that below a critical thickness the twinned structure does not develop a substantial long-range periodic arrangement (in relation to the coherence length of the incoming beam).

Satellite reflections along [100] and [010] directions are consistently observed in most of the HKL reflections of the 3.5 nm thick sample (*this twin domain structure added some difficulties to apply the "truncation rod method" since part of the reflection intensities is split into lateral peaks, so simple scans along optimized central HK positions do not contain all the information from the structure factor of the HKL reflections*)

Cell parameter determination

One of the objectives of the present experiment was to accurately determine the out-of-plane cell parameter of the Films, since the measurements by using conventional Cu tube x-ray source in our home laboratory indicated an unexpected expansion of the c-axis parameter for ultrathin films below 8nm.

We planed to use the different L-scans to determine the cell parameter. However, when we analysed a simple L-scan we observed inconsistent c-axis parameters for different L values. This was reproduced in different HK positions. *The spread of the extracted c-axis values was much larger than the foreseen variations between samples*. When we analysed in detail the deviations of the fit c-axes parameters for each HKL reflection from an average c-axis value we noticed that it was arranged in a particular pattern for most of the analysed samples. Depending on HK values the shift alternates between consecutive reflections. This unexpected result made us think about the possible coexistence of two overlapped domains, *which has to be further investigated in next experimental run*.
Still we could extract average c-axis parameter values, which were consistent with previous observations in our home X-ray laboratory.



The synchrotron source values are depicted in the following graph in red symbols (along with previously measured values by other sources). Bulk R-3c LSMO cell parameter values of the primitive pseudocubic cell are a=3.878 Å. Since in-plane parameter is fully strained to match the substrate (a=3.905 Å) the expected elastic response of the LSMO would be to reduce its c-axis parameter to 3.85 Å (taking the Poisson ratio as standard values as for other perovskites of ν~0.33). These are the values attained for our LMSO films at thickness of about 10nm. However, thinner films show increasing c-axis values, which are not compatible with a mere elastic response. This behaviour was supposed to be related either with additional structure constraints induced by the rotational octahedral pattern imposed by substrate matching at the interface, or by nanoscale/substrate-induced variations in the Mn^{3+}/Mn^{4+} electronic configuration balance, thus causing additional Jahn-Teller distortion affecting the overall LSMO cell volume. *This was the main objective of determining the oxygen sublattice positions by the truncated rod method, still to be further analysed in continuation of this experiment at BM25B.*

Part of these results have been included in two papers:

- F. Sandiumenge, J. Santiso, Ll. Balcells, Z. Konstantinovic, J. Roqueta, A. Pomar, J. P. Espinós, and B. Martínez, Competing misfit relaxation mechanisms in epitaxial correlated oxides, *Phys. Rev. Lett* (2013) accepted for publication, in press (included as a separate file)

- J. Santiso, Ll. Balcells, Z. Konstantinovic, J. Roqueta, P. Ferrer, A. Pomar, B. Martínez, and F. Sandiumenge, Thickness evolution of the twin structure and shear strain in LSMO films , *Cryst. Eng. Comm*. (2013) accepted for publication (icluded as a separate file)

Those results were also presented at MRS Spring meeting in San Francisco, Symposium HH, oral presentation HH5.4 and posters HH6.8, HH 6.9.