European Synchrotron Radiation Facility
Experimental Report

	Experiment title: Bragg and Diffuse Scattering from Relaxor Thin Films	**Experiment number:** HC-1055
Beamline: BM01A	**Date of experiment:** 23 Oct 2013 - 26 Oct 2013	**Date of report:** January 30, 2015
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Introduction

Relaxor ferroelectrics were discovered more than 50 years ago, but the nature of the relaxor response is still debated [1–3]. While the average structure of relaxors is simple, the local structure is complex due to disorder phenomena, e.g. polar nanoregions, phonon induced displacements, etc. Lead magnesium niobate based perovskites (PMN) are known to display relaxor properties at ambient conditions, which manifests as butterfly-shaped diffuse scattering around the Bragg peaks. Moreover, the PMN relaxor state can be suppressed completely under compressive stress [4].

The goal of the current experiment was to investigate diffuse scattering from PMN thin films as a function of film thickness and substrate mismatch strain at ambient temperature.

Samples and experiment strategy

Thin film samples were sputtered from two $0.94\mathrm{Pb}(\mathrm{Mg}_{1/3},\mathrm{Nb}_{2/3})\mathrm{O}_3 - 0.06\mathrm{PbTiO}_3$ (PMN-PTO) targets, one with 10% excess Pb and one with 10% excess Pb and 2% excess Mg. The films were grown on two different substrates, SrTiO_3 (STO, perovskite, Pm3m, $a = 3.905$ Å) and $\mathrm{MgAl}_2\mathrm{O}_4$ (MAO, spinel, Fd3m, $a = 8.080$ Å). A total of 20 samples were screened

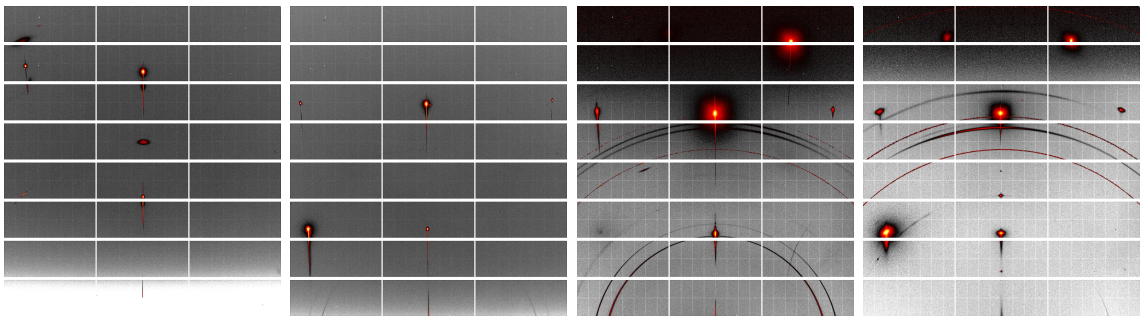

Figure 1: Data from four of the 20 PMN films that were screened. The images show the maximum intensity for each pixel position for scans of the 00l axis. **(a)**, 12 nm, STO substrate. The elongated feature in the middle is a 004 pyrochlore peak. Above are the 002 film and substrate peaks, the latter to the top and brightest. **(b)**, 42 nm, STO substrate. Despite it's thickness, this film shows very little thin film signal. **(c)** and **(d)**, 15 nm and 42 nm, respectively. MAO substrate. The strong peaks originate from the MAO substrate, and the powder rings come from perovskite PMN.

in diffraction experiments, and a subset of these were selected for further investigation. The experimental strategy was essentially the same as reported in [5], and the data was processed with the help of the newly developed software Nebula [6]. In the remainder of the text, PMN-PTO is referred to as PMN.

Results and discussion

During screening the 00l axis was mapped for each sample to give a general impression of the scattering characteristics. All the MAO based films showed powder features and strong substrate reflections, cf. fig. 1. The powder features correspond to a PMN perovskite unit cell, and there was little sign of any preferred orientation.

Only single crystalline phases were observed in the STO based samples, but there was no characteristic diffuse scattering in the PMN reflections as seen previously in bulk PMN samples. Evidently, the relaxor state has not been achieved or the substrate induced mismatch strain is suppressing the relaxor behavior.

For several STO based films a relatively strong reflection appears midway between the 001 and the 002 film/substrate Bragg peak doublets, cf. fig. 1a. This feature would correspond well with a doubling of the unit cell in the out-of-plane direction, and could indicate the presence of an antiferroelectric phase. Anomalous scattering was conducted for three STO based films over the Pb L3 (13035.1 eV) absorption edge to identify the lead contribution in the super reflection. Subsequent data analysis showed negligible difference in Pb sensitivity between the structure factors of the film Bragg peaks and the super reflection. However, as panoramic scans revealed more superimposed reflections, cf. fig. 2, it was possible after the experiment to conclude that they correspond to a pyrochlore phase (Spinel, Fd3m, a = 10.5988 Å [7]), with the ab-plane rotated 45° to the PMN perovskite.

Dielectric permittivity measurements on both STO and MAO based samples were carried

out concurrently, and revealed a temperature shifted relaxor phase in the MAO film.For the STO film, however, the dielectric response of the substrate easily overshadows relaxor contribution from thin films and could therefore not be used a reliable measurement.

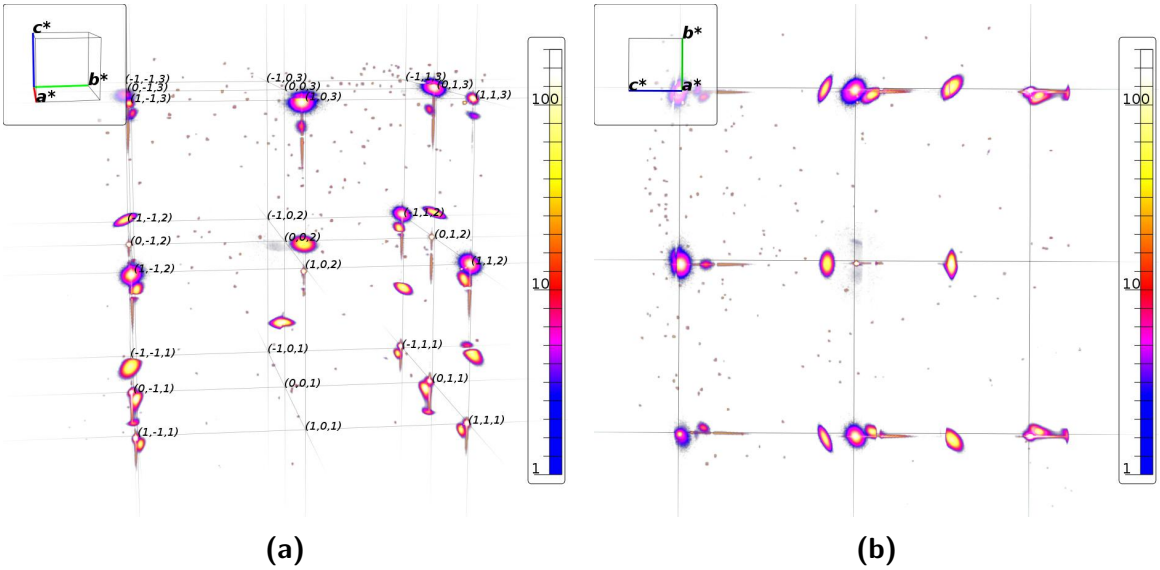

Figure 2: 3D reconstruction of a 15 nm PMN film on an STO substrate. The data was reconstructed and visualized using Nebula [6]. **(a)**, A 3D view of the reconstructed data. **(b)**, Orthonormal side view of the reciprocal lattice, with pyrochlore reflections clearly visible between the film and substrate peaks.

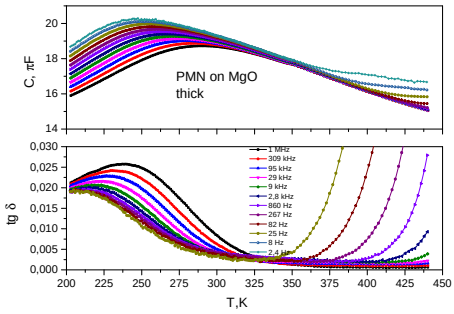

Figure 3: Dielectric response for PMN thin film grown on a $MgAl_2O_4$ substrate. It shows a broad peak in the dielectric constant below room temperature - a relaxor response.

Conclusion

We have tested the experimental strategy available at BM01-A in conjunction with Nebula, a new reciprocal space mapping software, and successfully characterized PMN thin films.

This combination of experimental technique and data processing could be further developed into an easy-to-use and effective tool for thin film characterization. Unfortunately, the PMN films grown on MAO substrates were poly crystalline and therefore unsuitable for further investigation. The films grown on STO substrates were single crystalline, but the majority of the films had significant amounts of the unwanted pyrochlore phase, and furthermore did not show the diffuse features observed in bulk PMN relaxors. Three STO based films did not show any indication of pyrochlore, and could be suitable candidates for checking for relaxor behavior at other temperatures.

References

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