European Synchrotron Radiation Facility
Experimental Report

	Experiment title: Domain structure engineering in free surface LSMO perovskites	**Experiment number:** 01-02-986
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Shifts: 9	**Local contact(s):** Dmitry Chernyshov	Received at ESRF:

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Report

The main objective of the experiment reported here was to investigate the possibility of using lattice defects, such as vacancies, to influence and control domain formation and pinning in free-standing single crystals of $La_{1-x}Sr_xMnO_3$ (LSMO), one of the archetype ferroelastic and ferromagnetic perovskites [1].

Sintering in atmospheres with different partial pressure P_{O_2} have been demonstrated to have pronounced effect on the formation of oxygen vacancies in the LSMO lattice [2], and as the vacancies can be associated with local strains they could potentially affect the formation and pinning of domain walls [3]. The idea subjected to testing was: i) whether a post-sintering annealing of samples at $T > T_C$ and in different P_{O_2} atmospheres could yield similar equilibrium concentrations of vacancies, and ii) if subsequent rapid quenching to $T < T_C$ of materials with high vacancy concentrations could influence the domain size, possibly by a lock-in of nano-sized domain structures, due to vacancy-induced wall pinning and stress relaxation effects.

Samples from four different combinations of quenching/cooling rate and atmospheric annealing conditions were investigated by XRD/diffuse X-ray scattering, i.e. fast quench (> 100 K/s) and slow cooling (< 5 K/min), for samples annealed in N_2 atmosphere and air, respectively. After treatment the samples were cooled down to room temperature, and mounted on a goniometer equipped with a motorized translation in the horizontal direction, orthogonal to the incident beam. Prior to the heat treatment the samples had been grinded down to a wedge shape so that the thin edge ~ 150 µm, corresponding to a few grains. The incident X-ray beam was slitted down to about 50×50 µm, and accordingly with the motorized goniometer translation, we could scan along the thin edge trying to locate a region with one or a few large grains in its center.

The scattering measurements were carried out with the PILATUS 2M/Huber Kappa setup at BM01A, as one of the first user experiments scheduled on the new setup. Despite still being in a somewhat provisoric state with respect to experimental user software control and protocols, the new setup worked extremely well and produced high quality data with an impressive data collection efficiency. In fact, we hardly experienced any problems with the setup, apart from some limitations caused by SPEC when scan velocities were set very slow in order to collect high resolution 3D data from weak/diffuse scattering objects.

Results

Unfortunately, it turned out that the sample response to annealing and subsequent quenching/cooling had pronounced effects on the sintered coarse-grained materials besides those intended with respect to domain-wall pinning. In both materials treated in N_2 it is clearly evident that the coarse grains break up into distinct subgrains with slight differences in orientation, evidenced by several separable reflections along the azimuth, cf. figs. 1a to 1d, and in some scans more than the two expected pseudo-cubic twins, cf. fig. 1d. Also, in the air-treated samples the general reflection widths indicate a substantial amount of crystal mosaicity which may result from residual strain and subgrain formation, cf. figs. 1e and 1f. Presumably, the annealing/quenching in N_2 causes some of the mosaic blocks to separate into distinct crystallites.

Even though some diffuse scattering can be identified and ascribed to the pseudo-cubic twin formation [4], it will be very difficult if not impossible to analyze the scattering from these samples in a systematic approach due to the presence of multiple subgrains with closely similar but still distinctive differences in orientations and compositions/lattice parameters.

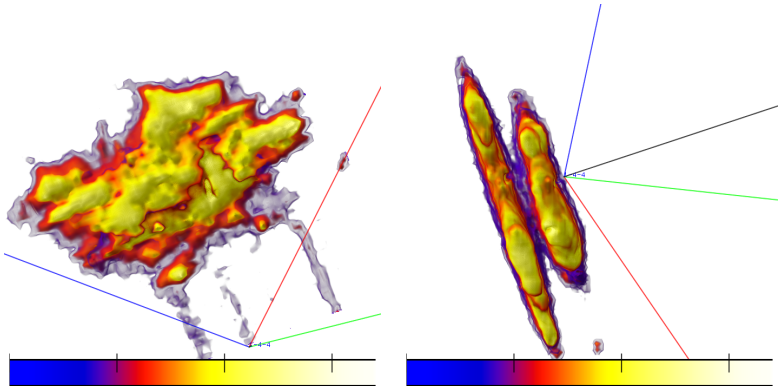
References

[1] J. Hemberger, *et al.*, *Phys. Rev. B* **66**, 094410 (2002). 1

[2] X. Ren, *Nature Materials* **3**, 91 (2004). 1

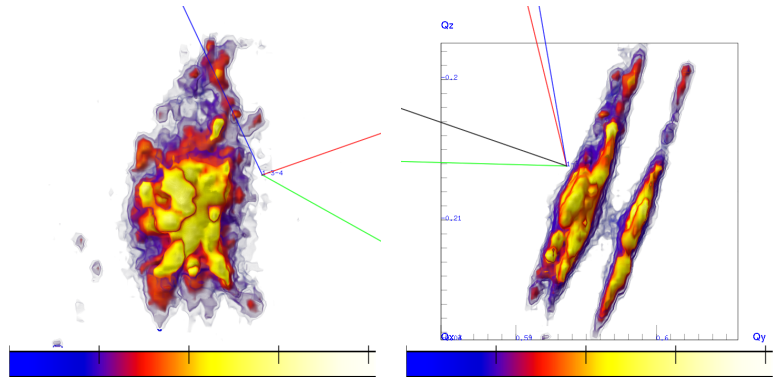
[3] T. Grande, J. R. Tolchard, S. M. Selbach, *Chemistry of Materials* **24**, 338 (2012). 1

[4] P. Vullum, H. Lein, M.-A. Einarsrud, T. Grande, R. Holmestad, *Philosophical Magazine* **88**, 1187 (2008). 2



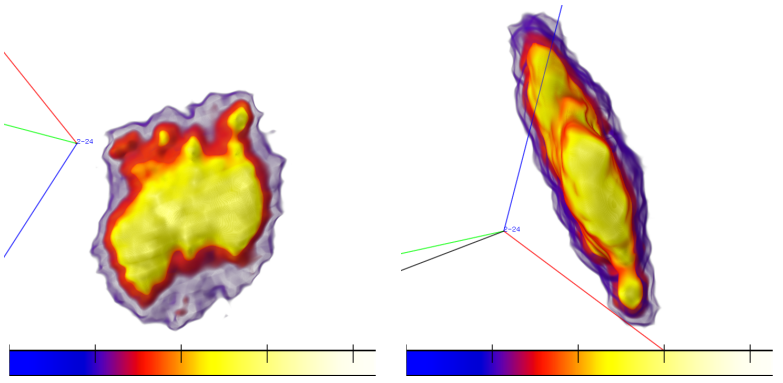
(a) Fast N_2 treatment, $(hkl) = (1\bar{4}\bar{4})$, along scattering vector.

(b) Fast N_2 treatment, $(hkl) = (1\bar{4}\bar{4})$, normal to scattering vector.



(c) Slow N_2 treatment, $(hkl) = (13\bar{4})$, along scattering vector.

(d) Slow N_2 treatment, $(hkl) = (13\bar{4})$, normal to scattering vector.



(e) Slow O_2 treatment, $(hkl) = (2\bar{2}4)$, along scattering vector.

(f) Slow O_2 treatment, $(hkl) = (2\bar{2}4)$, normal to scattering vector.

Figure 1: Examples of reflections from two samples. One had been cooled quickly in N_2, and the other slowly in air. The red, green, and blue lines correspond to the reciprocal h, k, and l directions, respectively. The black line is the scattering vector (from (000) to (hkl)). Note that for (c) and (d), the sample had been subject to a fast quench before the slow one.