Jülich Centre for Neutron Science

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JÜLICH Forschungszentrum

Tuning Physical Properties of $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ via Oxygen Off-Stoichiometry Using Thermal Annealing and Ionic Liquid Gating

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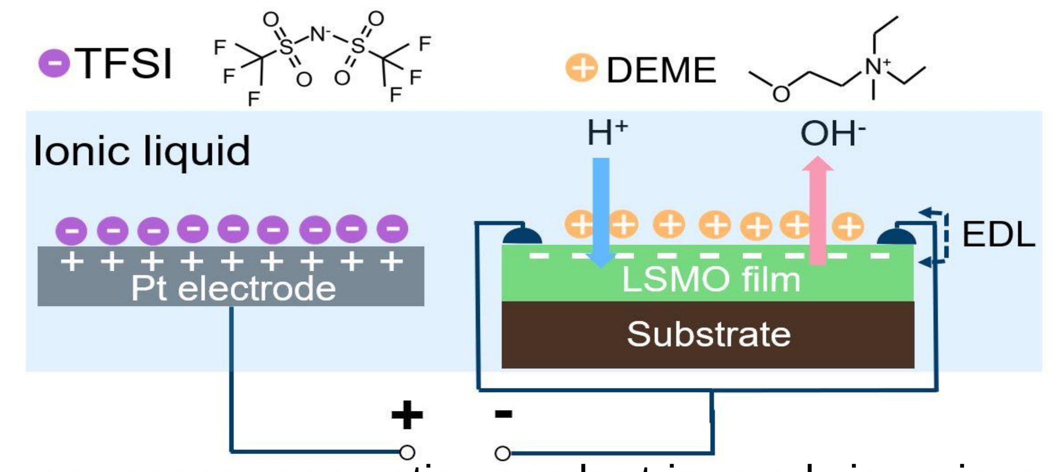
Motivation/Introduction

- $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ (LSMO) exhibits oxygen sponge like behavior.
- Oxygen vacancies induce a topotactic phase transition from the perovskite (PV) to a layer vacancy ordered Brownmillerite (BM).
- Ferromagnetic to antiferromagnetic, metallic to insulating.

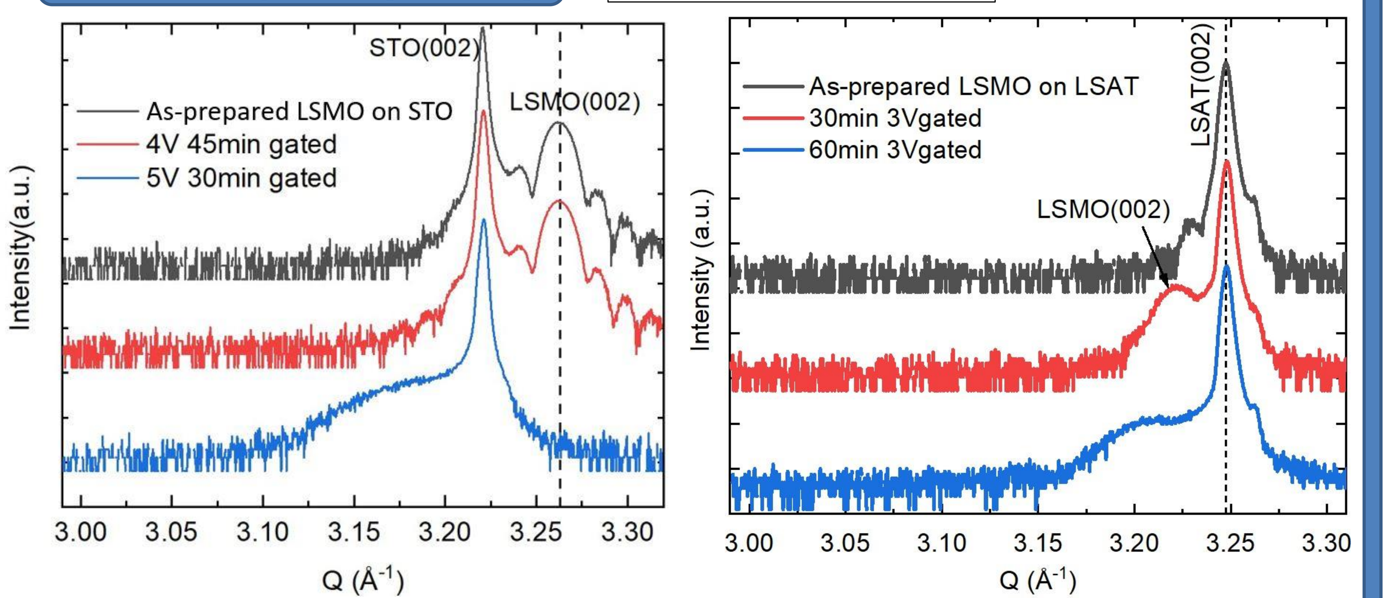


- Oxygen vacancy generation can be triggered via various methods, e.g. thermal vacuum annealing and ionic liquid gating (ILG).
- Via ILG: dual-ionic transfer, i.e. oxygen vacancy generation and hydrogen generation.

Cao, L., et al., Advanced Materials, 2019.31(7): p.1-7.
Lu, N., et al., Nature, 2017.546(7656): p.124-128.

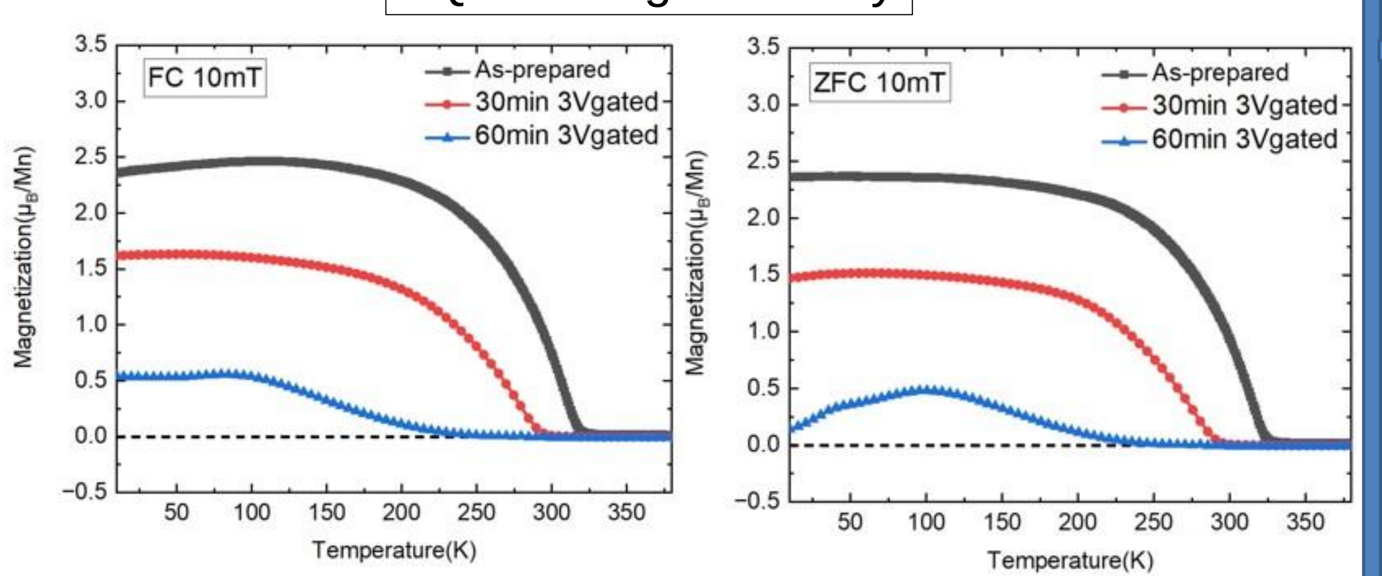
Ionic liquid gating

X-ray Diffraction



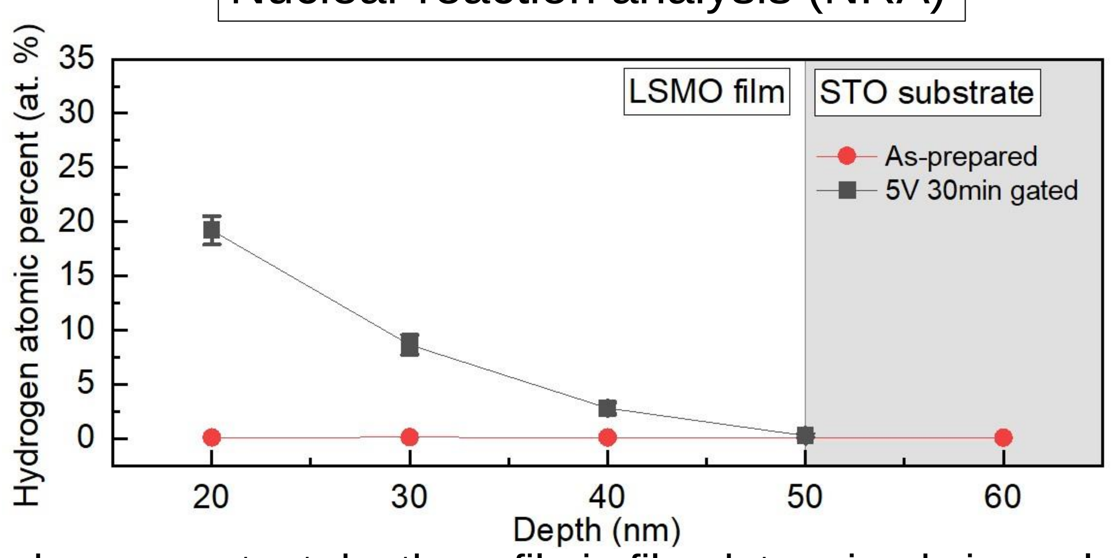
- LSMO thin films grown via sputtering on STO and LSAT substrates.
- ILG induced lattice expansion.

SQUID-magnetometry



- FM to AFM magnetic transition via ILG.

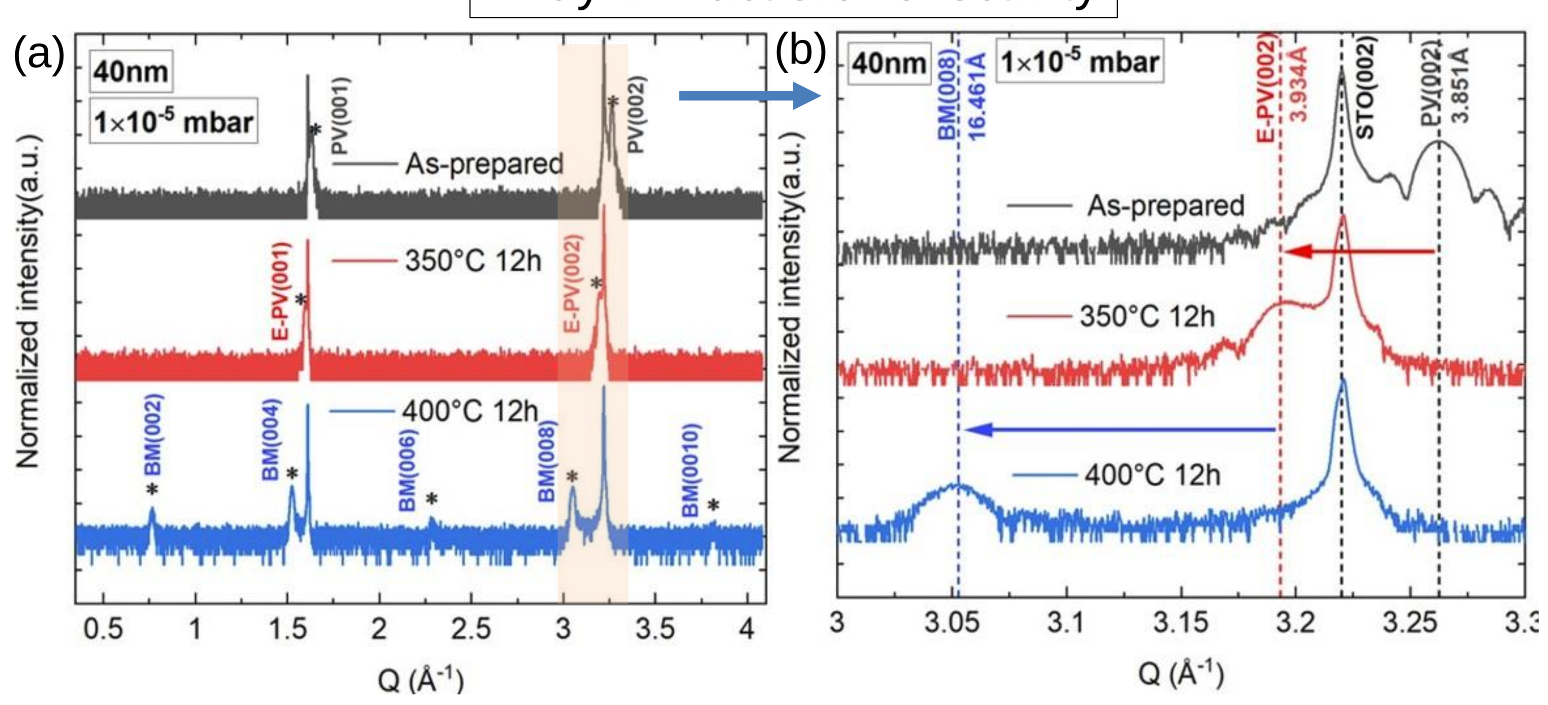
Nuclear reaction analysis (NRA)



- Hydrogen content depth profile in film determined via nuclear reaction analysis .
- Ca. 20% atomic percent hydrogen found near sample surface.

Thermal Annealing, Thin Film

X-ray Diffraction/Reflectivity



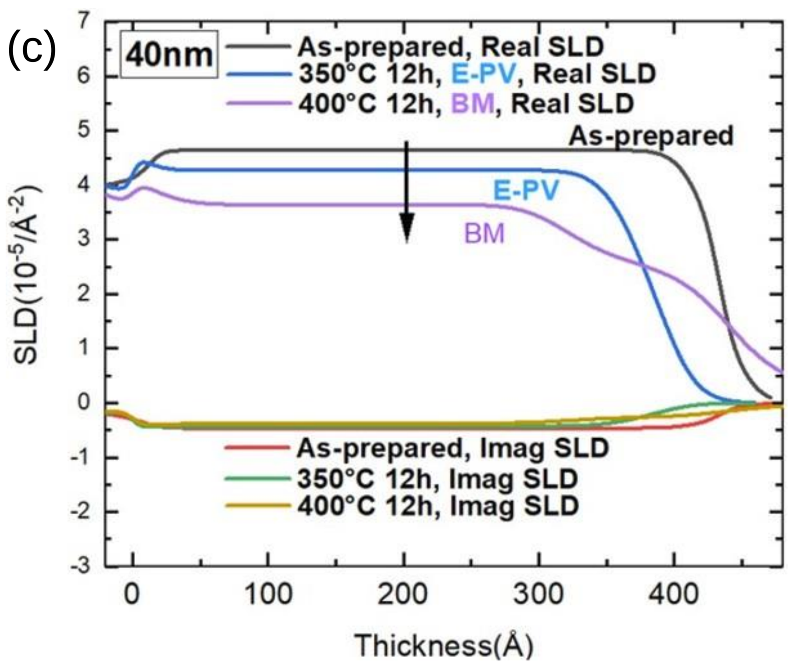


Fig. (a, b)XRD of the as-prepared and annealed LSMO films (40nm). (c) Corresponding SLD fitted from XRR.

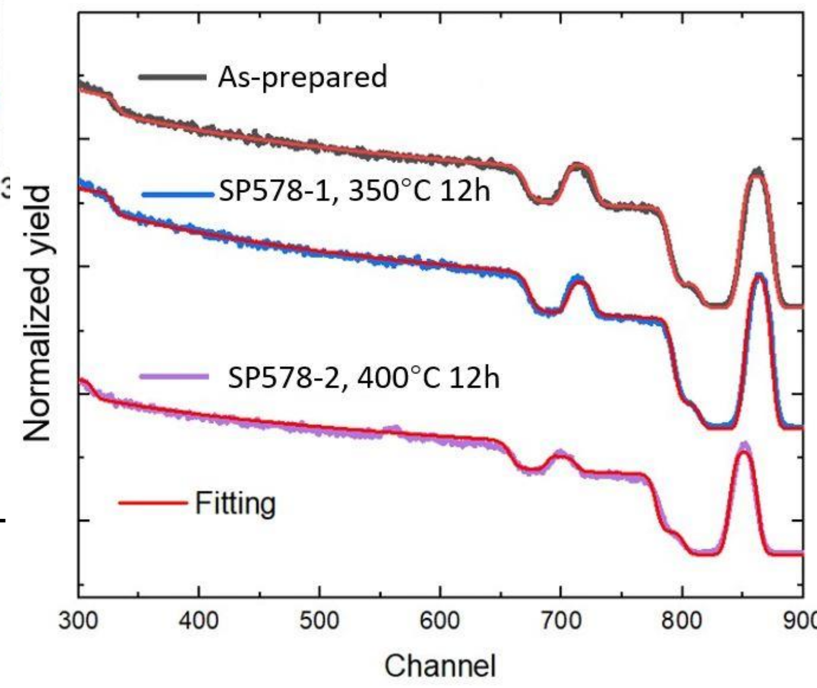
- An expanded perovskite phase (E-PV) after 350°C 12h.
- PV to BM topotactic phase transition realized after 400°C 12h.
- BM-LSMO: ΔSLD= 21.5%>10.2% (theoretic) ➡ decomposition.

Freshly polished Al-foils as oxygen getter: AL ➡ AL_2O_3

Sealed in quartz tube in vacuum range of 10^{-6}mbar.

LSMO thin film / powder.

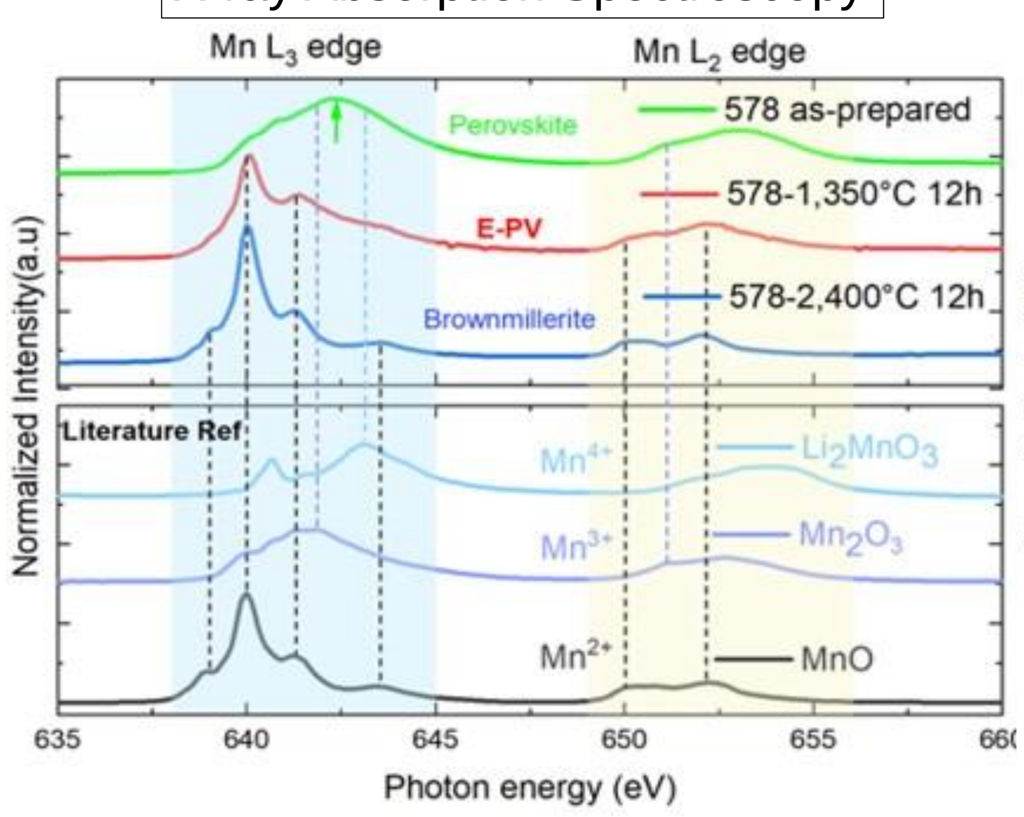
Rutherford Backscattering Spectrometry (RBS)



Sample ID	Sample state	La : Sr : Mn
SP578	As-prepared	0.71 : 0.29 : 0.95
SP578-1	E-PV	0.73 : 0.27 : 0.75
SP578-2	BM	0.69 : 0.31 : 0.55

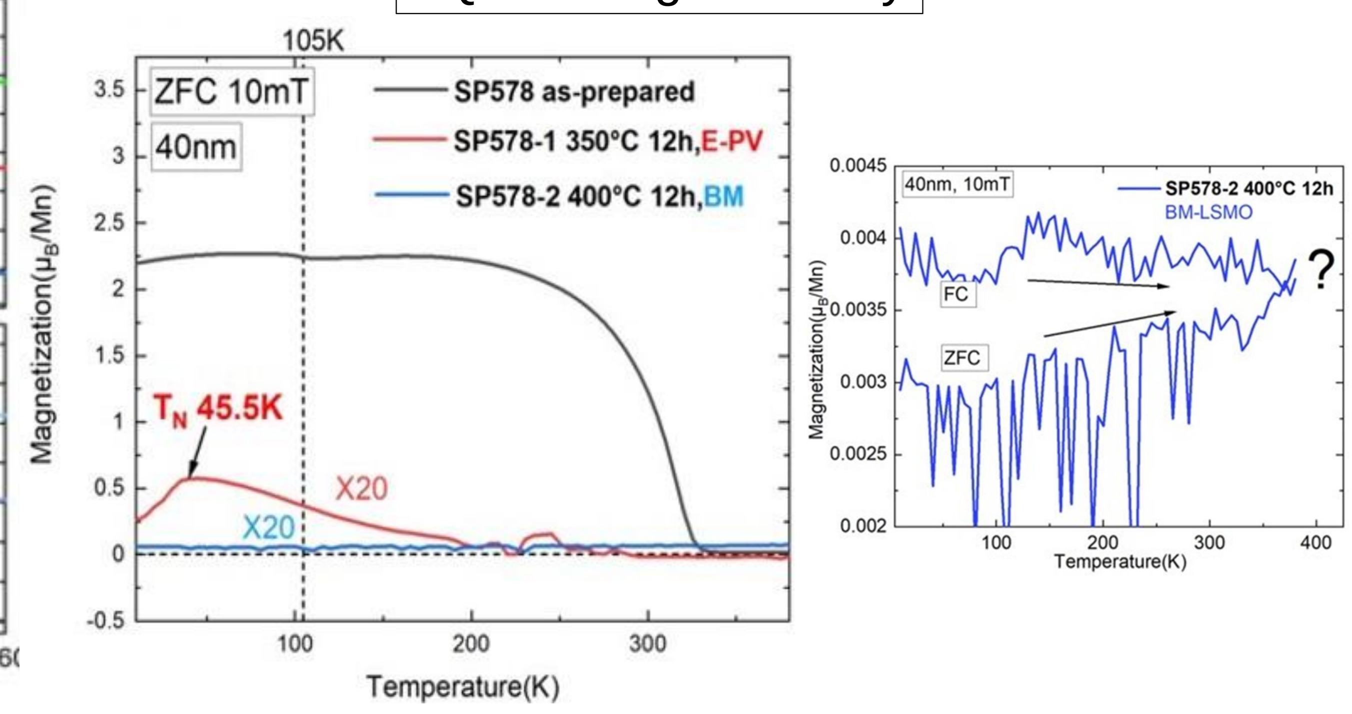
- Mn-content shows a clear reduction.
- Indicating SrO/La_2O_3 segregation.

X-ray Absorption Spectroscopy



- Mn^{3+} and Mn^{+4} coexist in the as-prepared film. Only Mn^{2+} observed in BM-LSMO (400°C 12h).

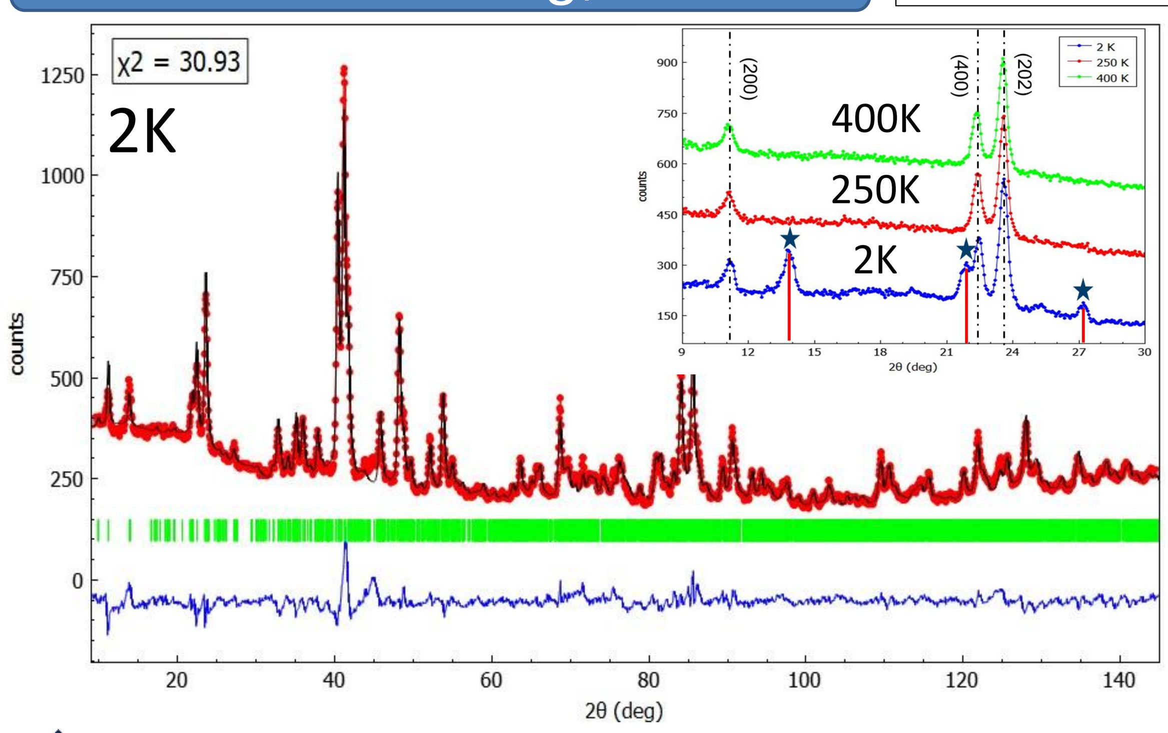
SQUID-magnetometry



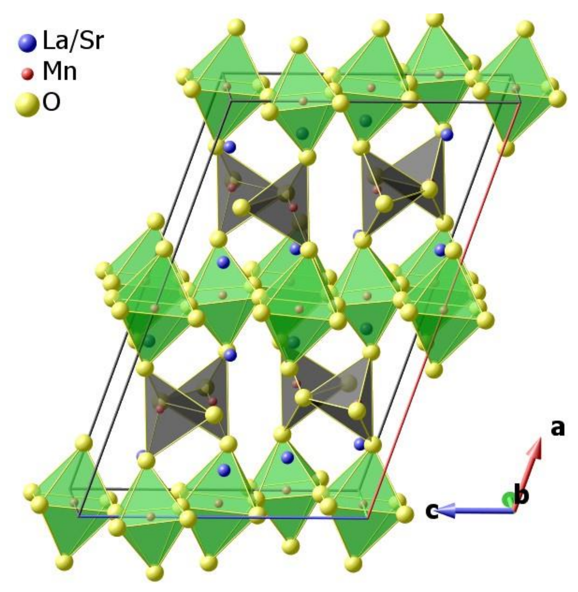
- FM for as-prepared state, AFM arose in E-PV phase, weak signal in BM phase.

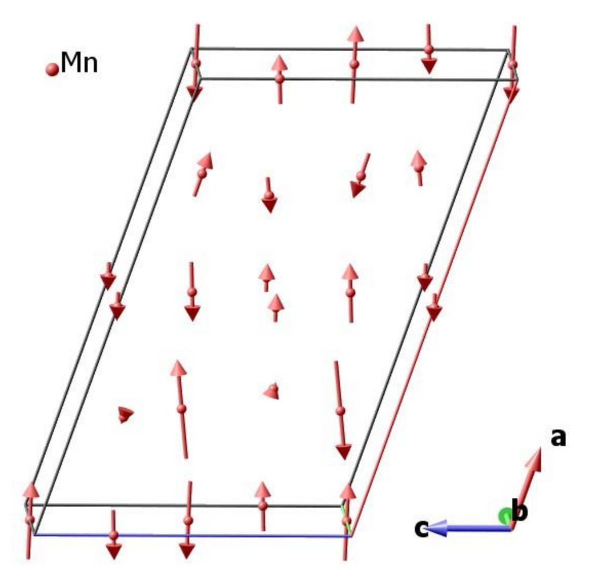
Thermal Annealing, Powder

Neutron diffraction, $La_{0.7}Sr_{0.3}MnO_{2.5-\delta}$



- As-prepared LSMO powder from a sputtering target, then applying Al-assisted thermal vacuum annealing.





- Refined lattice structure: clear octahedron tetrahedron alternating layers. With oxygen vacancy in [110].
- Refined magnetic structure: antiferromagnetic spin structure with propagation vector (0.5, 0 ,0).

Conclusions and outlooks

- PV to BM topotactic phase transition of thin film LSMO can be triggered by Al-assisted vacuum annealing at more optimal conditions, i.e. only 400ºC 12h.
- With a lower Mn oxidation state, thin film exhibits new magnetic properties. RBS results indicate a cation diffusion.
- The spin structure of $La_{0.7}Sr_{0.3}MnO_{2.5-\delta}$ powder sample is determined via neutron diffraction.
- Lattice structure variation can be triggered via ILG, with a FM to AFM magnetic transition. The hydrogen insertion is verified via NRA. The oxygen stoichiometry will be characterized combining polarized neutron reflectometry.

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