Structure refinement of strained LaVO$_3$ thin film.


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Introduction: epitaxial thin film structure determination

- Very difficult to characterize precisely due to:
  - Reduced amount of material
  - Substrate signal
  - Textured material
  - Residual stress

- Induced problem
  - Weak reflection
  - Overlapping of the substrate and the film

- Experimental methodology:
  - Local measurement using transmission electron microscopy (microstructure resolution)
  - Average measurement using High Resolution X-Ray Diffraction analysis (structure refinement)
Introduction: perovskites and distortion mechanisms

✓ Oxide perovskites: Very interesting compounds for physical properties (CMR, superconductivity, insulator-to-metal transition, ..):

- Perovskite type compound ABO$_3$
  - Space group $Pm-3m$ (aristotype)

- Distortion
  - Jahn-Teller effect
  - Octahedral tilting
  - Cation displacements

- Effect on physical properties
  - Orbital overlapping

In bulk compounds: cation size
In thin film: epitaxial strain (metastable phases)

Structural characterization

Figure adapted from Rondinelli et al., MRS bull., 37, 261 (2012).
Bulk LaVO$_3$ crystallographic structure @ room T (Mott insulator, AFM $T_N = 143K$):$^1$

- **Orthorhombic (Pnma)**
  - Lattice parameters: $a=5.5529(2)$ Å, $b=7.8447(3)$ Å and $c=5.5529(3)$ Å ($a_p \approx 3.92$ Å)
  - Atomic positions:

- Phase transition at about 140K toward a monoclinic structure

$^1$Bordet et al., JSSC, 106, 253 (1993).

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<thead>
<tr>
<th></th>
<th>La</th>
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<th>V2</th>
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LaVO3 thin film grown on SrTiO3 (001) oriented substrate by pulsed laser deposition.

Under biaxial stress (-3.6(1) GPa along (10-1)), we have to consider a lower symmetry!

Monoclinic

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Introduction on LaVO$_3$

✓ LaVO$_3$ thin film grown on SrTiO$_3$ (001) oriented substrate by pulsed laser deposition.

Under stress, we have to consider a lower symmetry!

10 atomic positions to refine

Rotella et al, PRB, **85**, 184101 (2012).

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Experimental measurement

Electron microscopy measurement

Cross-section observation:

- Main reflection: perovskite subcell
- Extra reflections coming from octahedral tilting

Presence of oriented domains

Bulk like structure (Pnma or lower symmetry)

Contribution of the domains in the X-ray analysis.
High resolution X-ray diffraction (HRXRD) method (P. ROUSSEL, UCCS, Lille):

High resolution configuration of a Rigaku diffractometer:

4-circles configuration:
Experimental set-up

High resolution X-ray diffraction (HRXRD) method (P. ROUSSEL, UCCS, Lille):
- High resolution configuration of a Rigaku diffractometer:

Symmetric and coplanar configuration:
Experimental set-up

✓ High resolution X-ray diffraction (HRXRD) method (P. ROUSSE, UCCS, Lille):
   - High resolution configuration of a Rigaku diffractometer:

Non-symmetric and coplanar configuration:

$I_{\text{incident}}$  \[ \chi \]  \[ \omega \]  \[ \phi \]  \[ 2\theta \]

Beam imprint
Experimental set-up

High resolution X-ray diffraction (HRXRD) method (P. ROUSSEL, UCCS, Lille):
- High resolution configuration of a Rigaku diffractometer:

Non-symmetric and non-coplanar configuration:

Beam imprint

Detector
Experimental measurement

High resolution X-Ray diffraction measurement (HRXRD):
- Reciprocal space map in coplanar configuration

Reciprocal space map with labels for (003)STO / (303)LVO and (421)LVO reflections.
High resolution X-Ray diffraction measurement (HRXRD): Reciprocal space map in coplanar configuration

Resolution sphere

11 reflections
High resolution X-Ray diffraction measurement (HRXRD):
- Reciprocal space map in non-coplanar configuration

11 additional reflections are observed
A total of 22 reflections
Reciprocal space map analysis

- High resolution X-Ray diffraction measurement:
  - Integrated intensity of the reciprocal lattice point related to atomic positions
  - Ellipse centre position related to cell parameters
  - Gap between centres due to misalignment and stress.
  - Reciprocal lattice point shape depending on film texture:
    - tilt, twist, coherence length (lateral and vertical)
Reciprocal space map analysis

Intensity integration (software development made by H. OUERDANE):

Numerical fit:
- Noise level
- Background
- Integrated intensity

Implementation in refinement structure software:
Atomic positions refinement

Integrated intensity of the 22 RSM
Conclusion

✓ Conclusion:

- This work is the study of a LaVO$_3$ thin film structure using High resolution X-ray diffraction
  - The experimental methodology is well established
  - RSM Integrated intensities exported.
  - Atomic positions refinement is under way!

✓ Future work (ongoing):

- Refinement of all the parameters of the thin film structure using **MAUD Program**.
THANK YOU FOR YOUR ATTENTION
The objective of this study is to characterize the structure of a LaVO$_3$ (LVO) strained thin film grown on SrTiO$_3$ (001)-oriented substrate.
Residual stress

- Generalized Hooke’s law:
  \[ \sigma_i = C_{ij} \varepsilon_j \]

- Stiffness tensor from Khan et al.: ¹
  \[
  \begin{pmatrix}
  391.3 & 158.1 & 142.7 \\
  158.1 & 399.3 & 158.1 \\
  142.7 & 158.1 & 436.5
  \end{pmatrix}
  \]

- Rotational matrix from crystalline orientation:
  \[
  \begin{pmatrix}
  \cos 45 & 0 & \sin 45 \\
  0 & 1 & 0 \\
  -\sin 45 & 0 & \cos 45
  \end{pmatrix}
  \]

\[
\begin{align*}
\sigma_1 &= \frac{(c_{11} + c_{13})}{\sqrt{2}} \varepsilon_1 + \frac{(c_{12} + c_{23})}{\sqrt{2}} \varepsilon_2 + \frac{(c_{13} + c_{33})}{\sqrt{2}} \varepsilon_3 \\
\sigma_3 &= \frac{(-c_{11} + c_{13})}{\sqrt{2}} \varepsilon_1 + \frac{(-c_{12} + c_{23})}{\sqrt{2}} \varepsilon_2 + \frac{(-c_{13} + c_{33})}{\sqrt{2}} \varepsilon_3 \\
\varepsilon_1 &= \varepsilon_2 = -3.847(8) \cdot 10^{-3} \\
\sigma_3 &= 0
\end{align*}
\]

\[\sigma_1 = -3.6(1) \text{ GPa}\]
Intensity correction

\[ I_{cor} = \frac{I_{mes}}{A} \]

\[ A^{as}_{\chi=0} = \frac{2}{\sin(\theta) \left( \frac{1}{\sin \theta} + \frac{1}{\sin(2\omega - \theta)} \right)} \frac{1 - \exp \left( -\mu T \left( \frac{1}{\sin \theta} + \frac{1}{\sin(2\omega - \theta)} \right) \right)}{1 - \exp \left( -\frac{2\mu T}{\sin \omega} \right)} \]

\[ A^{as}_{\chi \neq 0} = \frac{2}{\sin(\theta) \left( \frac{1}{\sin \theta} + \frac{1}{\sin(2\omega - \theta)} \right)} \frac{1 - \exp \left( -\frac{\mu T}{\cos \chi} \left( \frac{1}{\sin \theta} + \frac{1}{\sin(2\omega - \theta)} \right) \right)}{1 - \exp \left( -\frac{2\mu T}{\sin \omega \cos \chi} \right)} \]

\( \mu \): linear absorption coefficient
\( T \): thickness