Mechanical Properties of $LaGaO_3$ Single Crystals by Indentation

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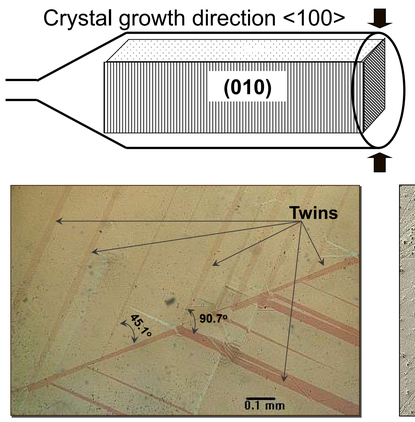
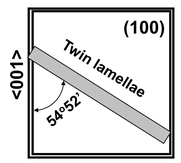
1. Introduction

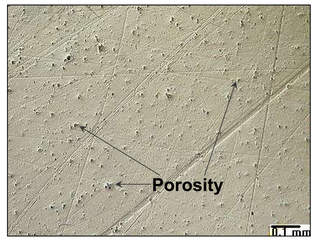
- Doped $LaGaO_3$ is the most recent material for use as a superior thin film electrolyte in intermediate temperature (650-800°C) SOFCs
- Mechanical properties of these ceramics are still largely unexplored for long-term endurance.
- Why single crystals?
  - Investigation of single crystals could detect anisotropies of physical properties in different crystallographic directions.
  - $LaGaO_3$ single crystals themselves have considerable potential as an electronic substrate material for epitaxic layers of high-temperature superconductors (HTSC)

2. $LaGaO_3$ Single Crystals





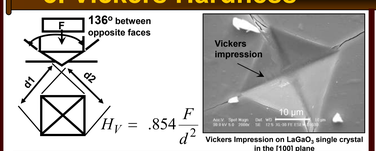
$LaGaO_3$ single crystal in the [100] plane



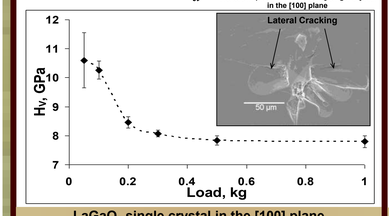
$LaGaO_3$ single crystal in the [001] plane

- Single-crystals of $LaGaO_3$ were grown by Czochralski technique.
- Crystals up to 2.5cm diameter and 10cm length can be grown in the [100] and [001] direction.
- Crystal Structure = Orthorhombic *Pbnm* space group at 25°C and Rhombohedral $R\bar{3}c$ at >145°C
- Molecular Weight=256.63 gm mol^{-1}
- Density@25°C = 7.23 gm/cc
- Melting point 1800°C

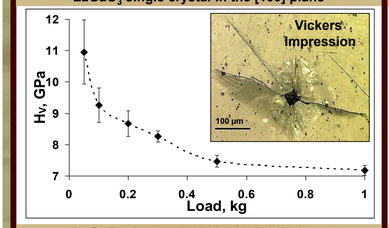
3. Vickers Hardness



Vickers Impression on $LaGaO_3$ single crystal in the [100] plane

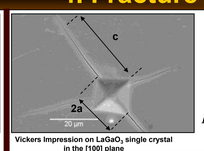


$LaGaO_3$ single crystal in the [100] plane

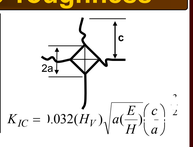


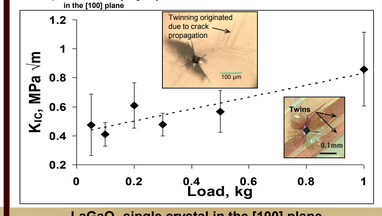
$LaGaO_3$ single crystal in the [001] plane

4. Fracture Toughness

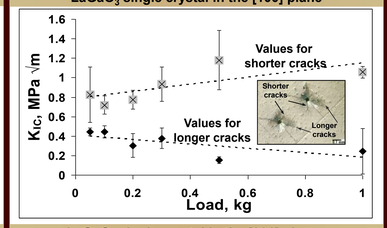


Vickers Impression on $LaGaO_3$ single crystal in the [100] plane





$LaGaO_3$ single crystal in the [100] plane



$LaGaO_3$ single crystal in the [001] plane

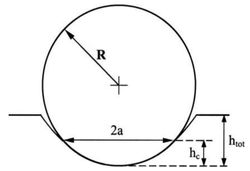
5. Nano indentation

$$h_{tot} = \left(\frac{3P}{4E^*}\right)^{\frac{2}{3}}\left(\frac{1}{R}\right)^{\frac{1}{3}}$$

$$\frac{1}{E^*} = \frac{1-\nu_s^2}{E_s} + \frac{1-\nu_i^2}{E_i}$$

Hertzian Principle

P- Applied Load
E*-Reduced Modulus
E_s- Sample Modulus
E_i- Indenter Modulus
v = Poisson's ratio



$$E^* = \frac{\sqrt{\pi}}{2}\frac{S}{\sqrt{A}}$$

$$a = \sqrt{2h_cR - h_c^2}$$

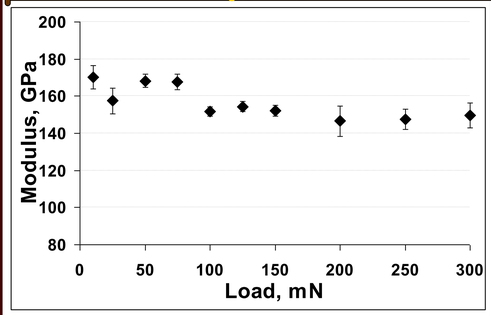
$$h_c = h_{tot} - 0.75P/S$$

S – Initial unloading slope of the load displacement curve

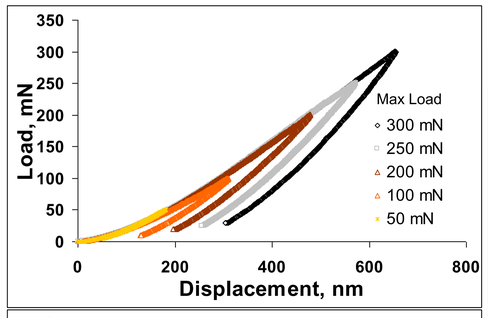
- Depth-sensing nanoindentation was used to study the deformation behavior of [100] and [001] $LaGaO_3$ single crystals using incremental loading.
- 13.5 µm spherical tipped diamond indenter was used for all experiments since the spherical indenter gives more reliable modulus values.
- Young's modulus values of both the [100] and [001] $LaGaO_3$ samples were found to vary slightly with the maximum load applied.
- Average modulus values for the [001] crystal was found to be less than the [100] crystal. The reasons for the lower modulus values could be the strong anisotropy of mechanical properties such as stiffness of the material.

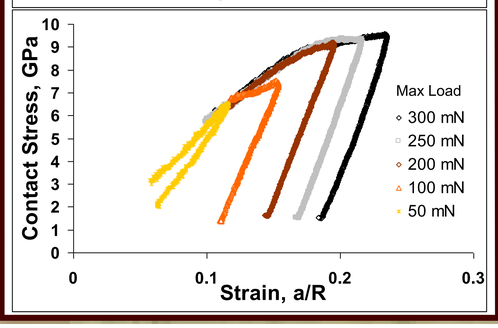
Results

$LaGaO_3$ [100]

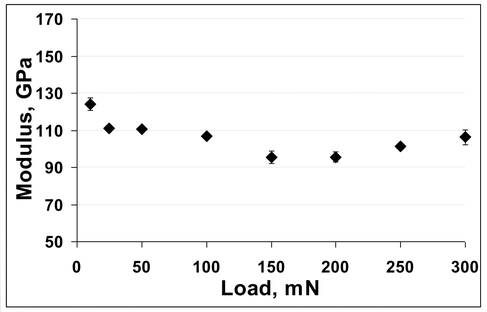


Indentation (Contact) Stress is given by $P/\pi a^2$ and Indentation Strain by a/R. where P is the applied load, a the contact circle radius, and R the indenter radius.





$LaGaO_3$ [001]

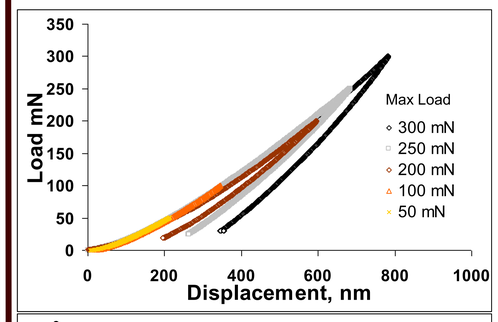


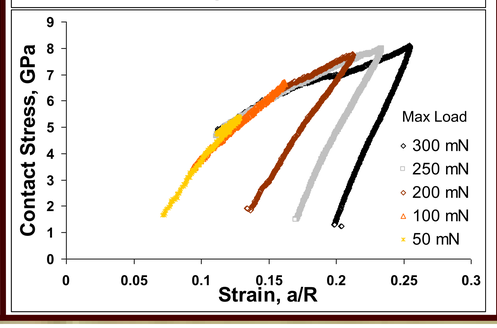
From Hertzian contact mechanics, in elasto-plastic regime

$$he = \left(\frac{3P}{4E^*}\right)^{\frac{2}{3}}R^{-\frac{1}{3}}$$

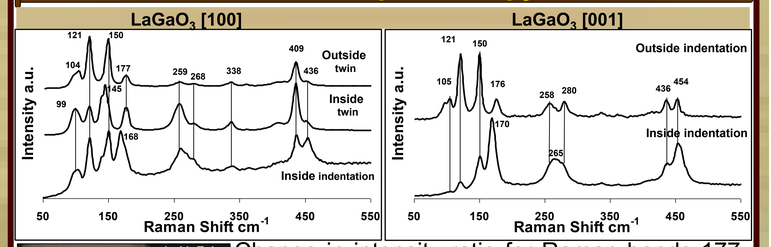
$$h_c \approx h_{tot} - h_e/2$$

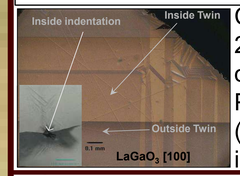
$$a = \sqrt{2h_cR - h_c^2}$$





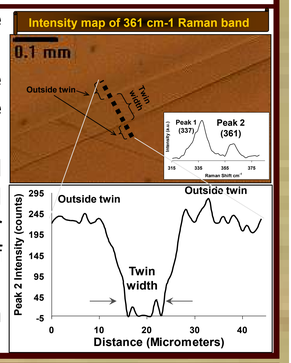
6. Raman Spectroscopy





Change in intensity ratio for Raman bands 177, 268, 436, 454 cm^{-1} for both crystals have been observed after indentation.
Possible reason : structure rearrangement (domain switching or phase transformation) induced by indentation.

- Raman mapping was performed on the [100] $LaGaO_3$ surface along the dotted line
- 337 and 361 cm^{-1} Raman bands were used to create an intensity map of the $LaGaO_3$ [100] surface across a twin.
- Significant decrease (up to full disappearance) of 361 cm^{-1} Raman band was observed inside the twin in a particular case which indicates different orientation of the crystal inside the twin.
- The position of the twin boundary and twin width can be estimated from the line map.



7. Conclusions

- Vickers hardness for [100] = 8.04±0.04 GPa
  Vickers hardness for [001] = 7.89±0.11 GPa
- Young's modulus [100] $LaGaO_3$ = 156.54±4.46 GPa
  Young's modulus [001] $LaGaO_3$ = 106.35±4.71 GPa.
  The modulus values were constant with increasing maximum load.
- Study of the deformation behavior of the $LaGaO_3$ single crystals show an elastic response of the load-displacement and stress-strain curves up to a stress of around 6 GPa.

At higher stresses both the [100] and [001] $LaGaO_3$ single crystals show increasing irreversible deformation.

- K_{1c} of [100] $LaGaO_3$ single crystals = 0.57±0.07 MPa $m^{1/2}$.
  K_{1c} of [001] $LaGaO_3$ single crystals in two perpendicular directions = 0.32±0.07 MPa $m^{1/2}$ and 0.91±0.10 MPa $m^{1/2}$
  This signifies the anisotropic behavior of [001] single crystals.
- The difference in the K_{1c} values measured from crack lengths propagated in different crystallographic directions is a result of strong anisotropy in the $LaGaO_3$ single crystal. Anisotropy and porosity of the [100] crystal also explains the lower Young's modulus values.

Similar anisotropy in coefficient of thermal expansion (CTE) was reported by L. Vasylechko et. al. (*J. Solid State Chemistry* 172 2003 pp 396-411) for Sr and Mg doped LSGM-05 and LSGM-10 single crystals.