Raman Diagnostics of Temperature and Stress Induced Structural Modifications in $LaCoO_3$ based Perovskites

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"Ferroelasticity and Hysteresis in Mixed Conducting Perovskites"

Objectives

- Study lattice vibrations and optical phonons in rhombohedral $LaCoO_3$ perovskite
- Analyze the experimental Raman spectra as a function of a laser power
- Use Stocks/anti-Stocks band ratio to determine the temperature of the perovskite surface under laser heating
- Determine stress-induced changed in Raman spectra of $LaCoO_3$ perovskites using indentation technique

Material

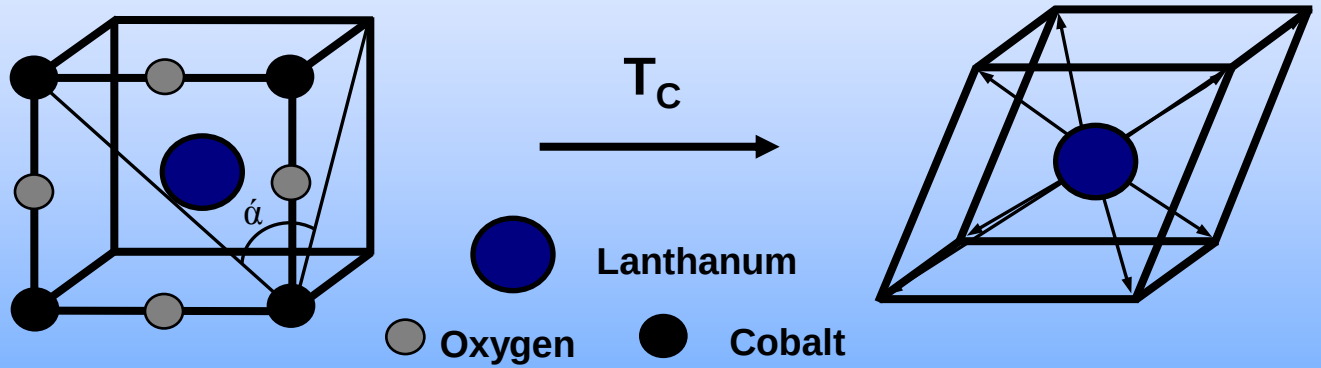
$LaCoO_3$ $T_{C\rightarrow R}$ = ~1600°C; Grain size - 3-5 μm

High temperature - Cubic structure with the space group $Pm\bar{3}m$

Room temperature - Rhombohedral structure with the space group $R\bar{3}c$

Semiconductor to metallic conduction crossover exists at 230°C

Ferroelastic Phase Transition



$T_{C\rightarrow R}$ = $LaCoO_3$ at ~1600°C; $La_{0.8}Ca_{0.2}CoO_3$ at 950 ° C; $La_{0.6}Ca_{0.4}CoO_3$ at 700 ° C

High Temperature	Low Temperature
High symmetry prototypic phase	Low symmetry phase
a = b = c; α = β = γ = 90°	a = b = c; α = β = γ ≠ 90°
ά = 60°	ά = 60.78°
Cubic	Rhombohedral

Classification of the ☝-point phonons

The space group $Pm\bar{3}m$

At perfect perovskite cubic structure all lattice sites have inversion symmetry and first order Raman scattering is forbidden

The space group $R\bar{3}c$

- La atoms occupy the 2*a* (¼, ¼, ¼) positions and participate in four ☝-point phonons modes ($A_{2g} + A_{2u} + E_g + E_u$).

- Co atoms occupy the 2*b* (0,0,0) positions and also participate in four ☝-point phonons modes ($A_{1u} + A_{2u} + 2E_u$).

- Oxygen atoms occupy the 6e (x ,$\bar{x}$ + ½, ¼) positions and take part in twelve modes ($A_{1g} + A_{1u} + 2A_{2g} + 2A_{2u} + 3E_g + 3E_u$).

Raman active - $A_{1g} + 4E_g$ Infrared active - $3A_{2u} + 5E_u$

M. Abrashev, A. Litvinchuk, M. Iliev, R. Meng, V. Popov, V. Ivanov, R. Chakalov, C. Thomsen, *Phys. Rev. B*, 59, 6, 4146-4153, 1999

Experimental difficulties of Raman spectra collection in the rhombohedral $LaCoO_3$ perovskite

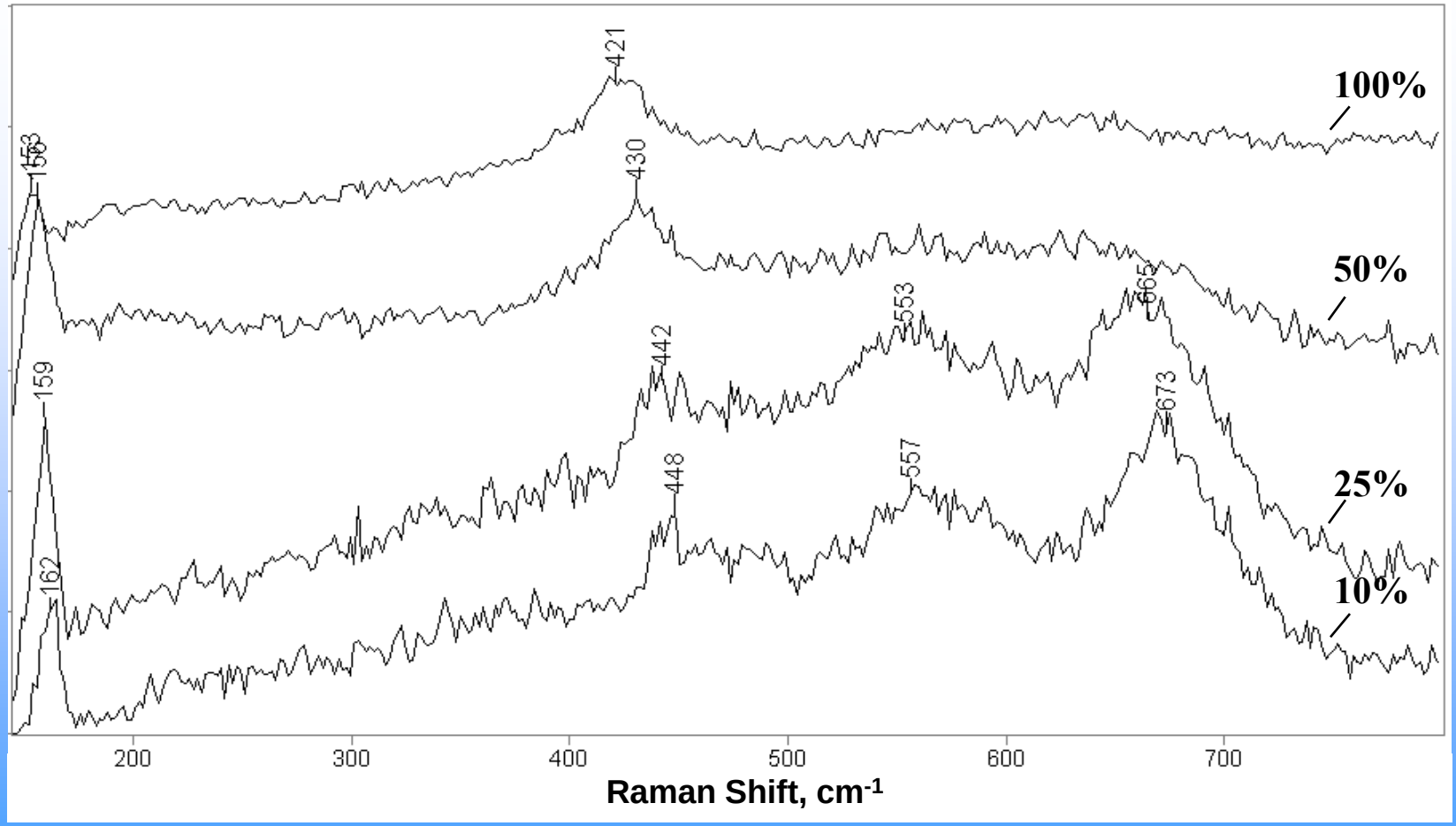
- Extremely low intensity of Raman lines and, therefore, a need for a long time of spectra collections. The average time of collection varied from 200 to 500 s per point.

- The small penetration depth of the excitation radiation also results in a decrease of the scattering intensity.

- The micro-inhomogeneous areas exist at the perovskite surface.

- Undesired/desired laser induced heating of the cobaltite surface occurs. To avoid overheating one needs to limit of the power of the laser excitation. To induce heating one needs to use a maximum of the laser power. The maximum power was 25mW with a possibility to reduce by 50, 75, 90, and 99%.

Raman spectra of $LaCoO_3$



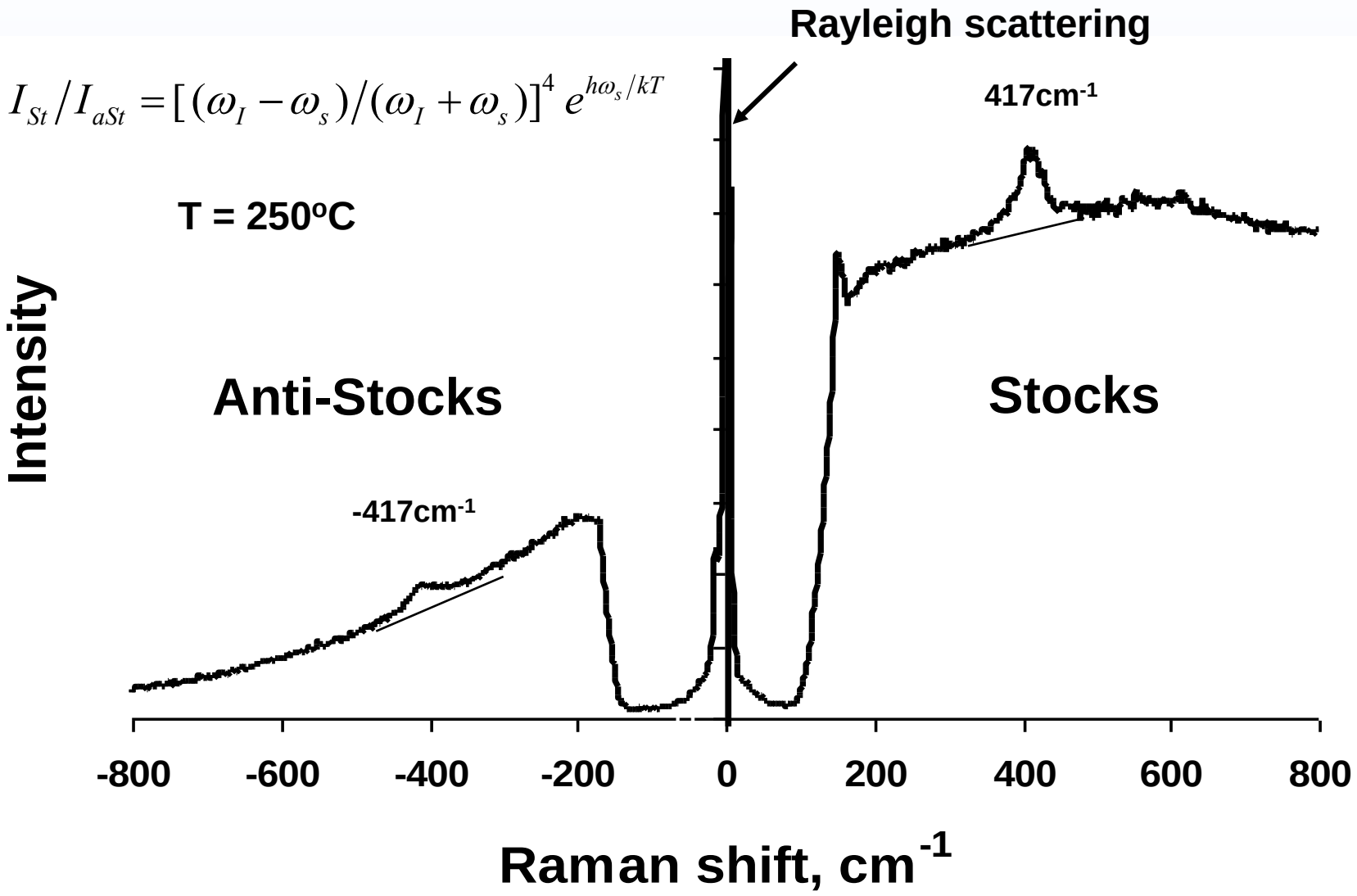
~ 155 cm^{-1} – rare earth internal vibration mode

~ 430 cm^{-1} – O-O octahedra rotation; ~ 557 cm^{-1} – Co-O bending vibration

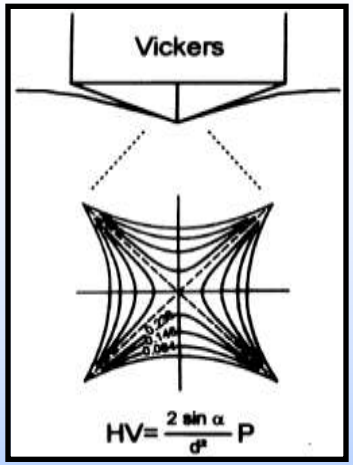
~ 650 cm^{-1} – Co-O stretching vibration

Raman spectra taken at the different laser intensity, 25mW, 514,5 nm Ar Ion

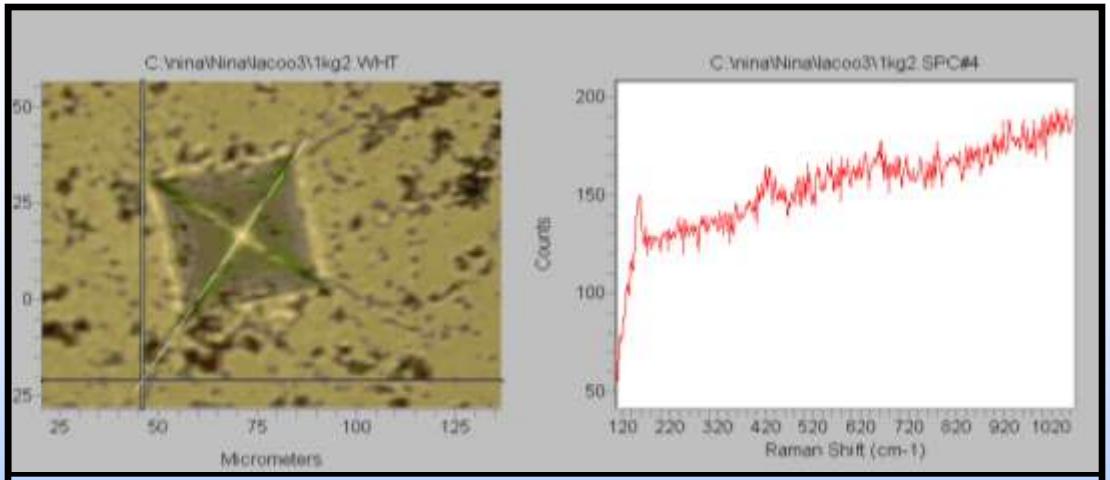
Temperature determination using Raman scattering



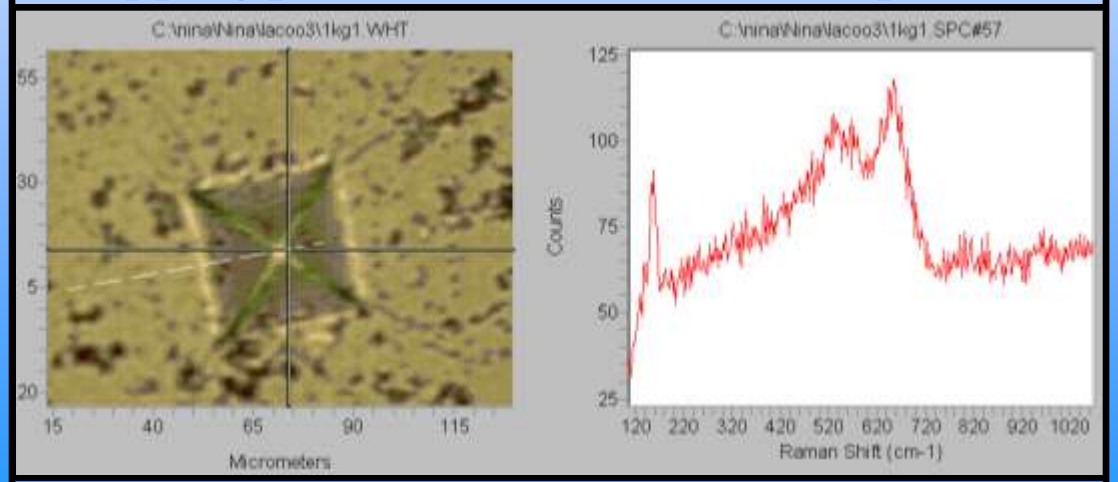
Optical Micrographs and Raman Spectra of Vickers Impression of $LaCoO_3$ Ceramics



Sketch of Vickers indentations showing contact stresses, that arise at the interface between the indenter and material.
The maximum contact stresses occur in the center of indentation zone and decrease according to the stress isobars

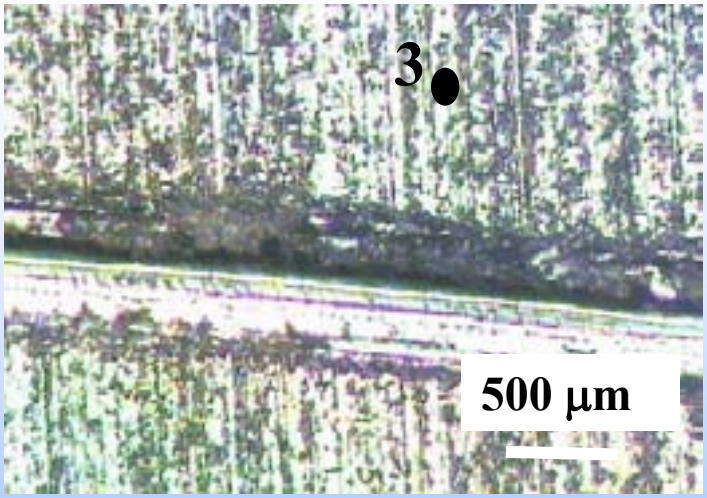


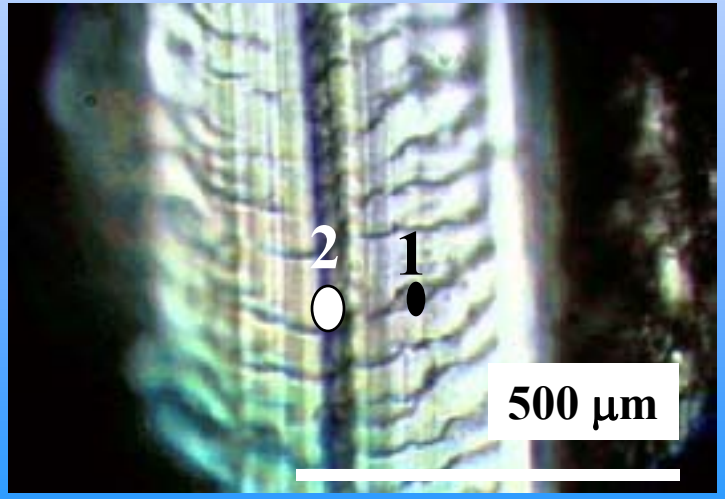
Mapping point outside of Vickers impression



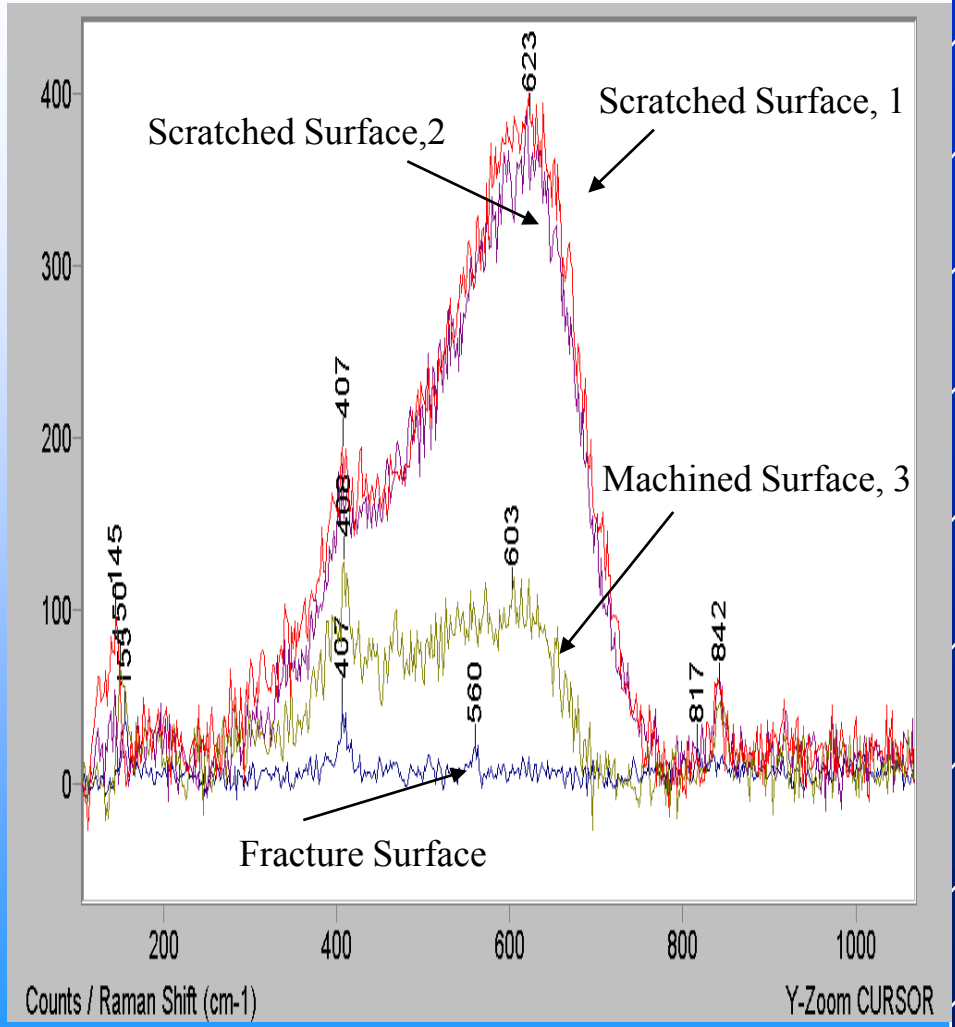
Mapping point inside of Vickers impression

Raman Spectra of $La_{0.8}Sr_{0.2}CoO_3$ ceramics from fracture, machined and scratched surfaces

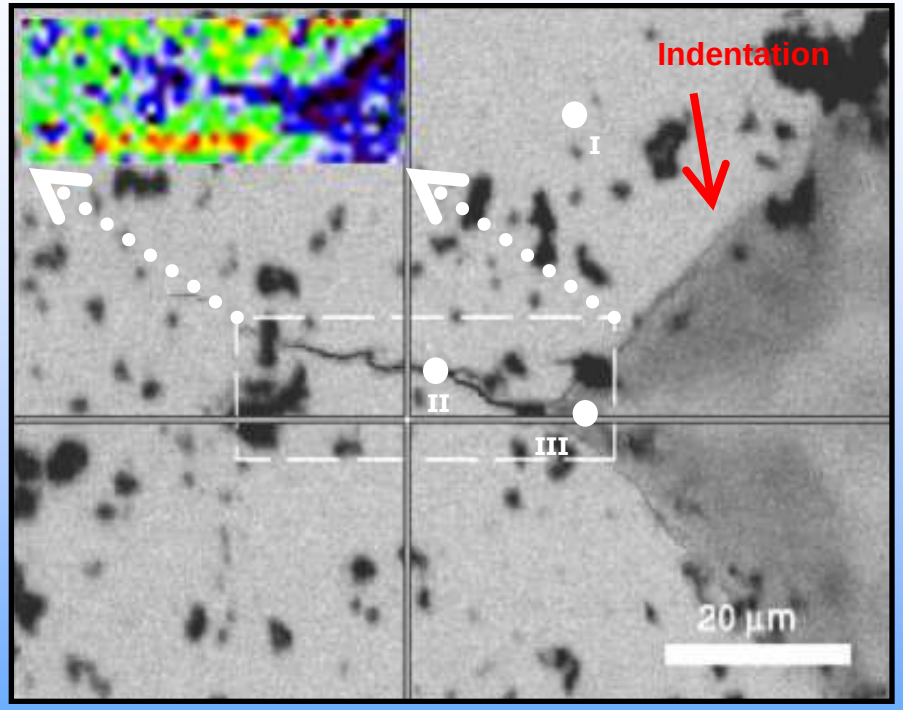


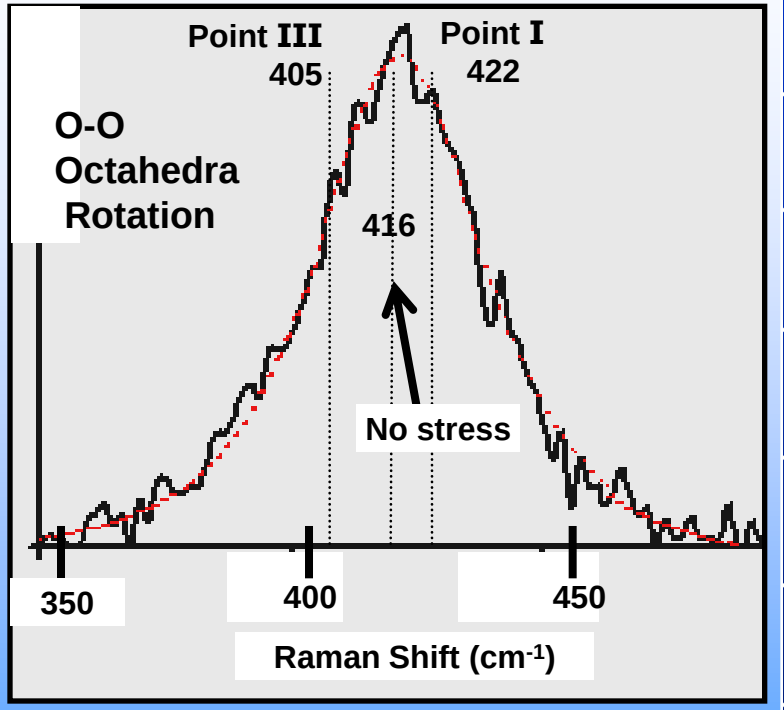


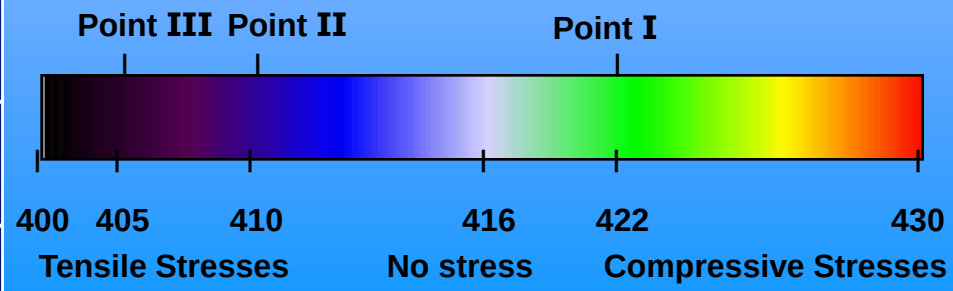
Scratch on a machined surface



2-D Raman map of a crack from Vickers indentation



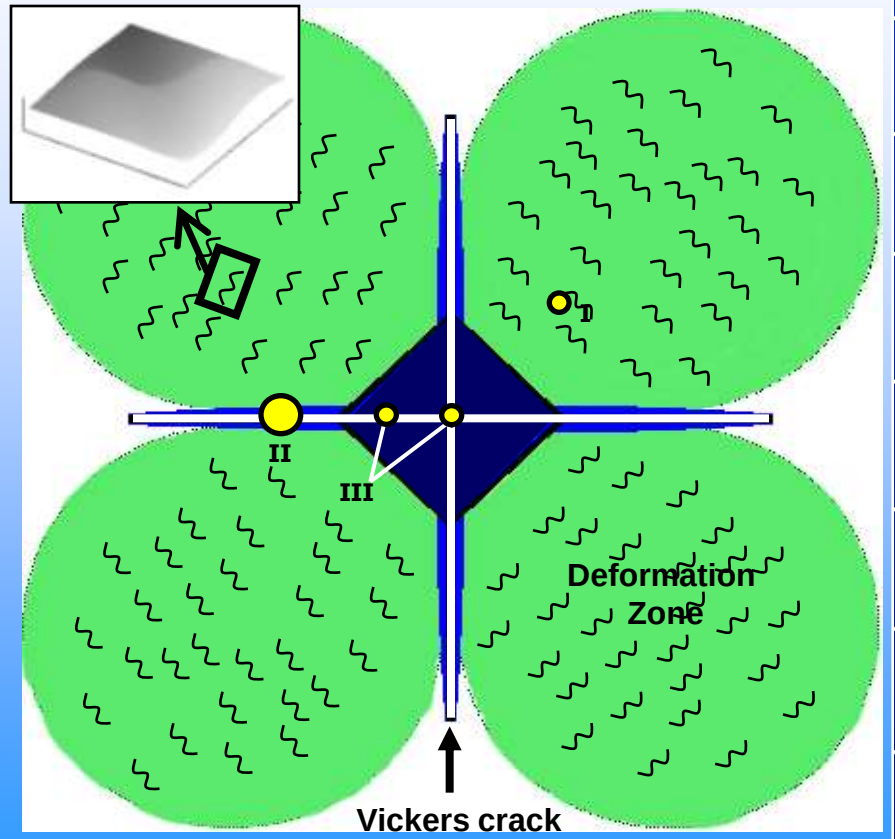




2-D position map was created using the 416 cm^{-1} O-O octahedra rotation band.

Scheme of Indentation Induced Deformation Zone Around Vickers Impression

The large deformation zones of compressive stresses around Vickers impression can be detected by Raman mapping and atomic force microscopy (AFM). Tensile stresses exist along the cracks, originating from the corners of the impression.



Upshifted Raman Peak (compressive stress)

Downshifted Raman Peak (due to tensile stress or bond stretching lattice deformation)

Conclusions

- Rhombohedral $LaCoO_3$ perovskite is Raman active material and can be studied by Raman spectroscopy.

- The semiconductor/metal transition along with a decrease in rhombohedral distortion of the $LaCoO_3$ could be driven by laser overheating during a collection of Raman signal.

- There are significant stress-induced changes in Raman spectrum of $LaCoO_3$ after indentation. The significant growth of two 557 and 670cm^{-1} bands could be possibly explained by the reversible semiconductor-metal-semiconductor transition upon loading and further unloading of the perovskite.

- 416cm^{-1} band of $LaCoO_3$ is a stress sensitive and, therefore, can be used for mapping residual stresses induced in the material after indentation.