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 \( \text{LaCoO}_3 \) 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 changes in Raman spectra of \( \text{LaCoO}_3 \) perovskites using indentation technique
Material

LaCoO₃  $T_{C \rightarrow R} = \sim 1600^\circ C$; 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

$T_{C \rightarrow R} = \text{LaCoO}_3$ at $\sim 1600^\circ C$; $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ at 950 °C; $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ at 700 °C

High Temperature
High symmetry prototypic phase

- $a = b = c$; $\alpha = \beta = \gamma = 90^\circ$
- $\hat{\alpha} = 60^\circ$
- Cubic

Low Temperature
Low symmetry phase

- $a = b = c$; $\alpha = \beta = \gamma \neq 90^\circ$
- $\hat{\alpha} = 60.78^\circ$
- Rhombohedral
Classification of the $\Gamma$-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 $2a$ ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) positions and participate in four $\Gamma$-point phonons modes ($A_{2g} + A_{2u} + E_g + E_u$).

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

- Oxygen atoms occupy the $6e$ ($\chi + \chi + \frac{1}{2}, \frac{1}{4}$) 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 - $3A_{2u} + 5E_u$

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$_3$

- $\sim 155 \text{ cm}^{-1}$ – rare earth internal vibration mode
- $\sim 430 \text{ cm}^{-1}$ – O-O octahedra rotation; $\sim 557 \text{ cm}^{-1}$ – Co-O bending vibration
- $\sim 650 \text{ cm}^{-1}$ – Co-O stretching vibration

Raman spectra taken at the different laser intensity, 25mW, 514.5 nm Ar Ion
Temperature determination using Raman scattering

Rayleigh scattering

\[ \frac{I_{St}}{I_{aSt}} = \left[ \frac{(\omega_I - \omega_s)}{(\omega_I + \omega_s)} \right]^4 e^{\hbar \omega_s / kT} \]

T = 250°C

\(-417\text{cm}^{-1}\)

\(417\text{cm}^{-1}\)

Stocks

Anti-Stocks
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 $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ 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.
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.
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.