Phase Transitions in LaCoO$_3$ and LaGaO$_3$ based perovskites

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Objectives

- Characterize the defect structure of LaCoO$_3$ based rhombohedral perovskites
- Demonstrate a ferroelastic to paraelastic phase transition in La$_{0.6}$Ca$_{0.4}$CoO$_3$ by *in-situ* high temperature TEM
- Investigate *in-situ* microstructural changes during heating, annealing and cooling in the microscope column
- Study the structural stability of LaCoO$_3$ in reducing environment by XRD
- Demonstrate the temperature induced orthorhombic to rhombohedral LaGaO$_3$ phase transition
Experimental

• JEOL JEM-3010 TEM

• Gatan Model 652 double tilt heating stage was used to heat perovskite foils up to 850°C at a controlled heating rate of 10°C or 20°C per minute.

• Oxygen partial pressure in the microscope column is about $5 \times 10^{-8}$ Pa

• Scintag PADV diffractometer (CuK$_\alpha$ radiation)

• Thermal Mechanical Analyzer (TMA)

• Optical microscope
Lanthanum based cobaltites

LaCoO$_3$  La$_{0.8}$Ca$_{0.2}$CoO$_3$  La$_{0.6}$Ca$_{0.4}$CoO$_3$  La$_{0.45}$Ca$_{0.55}$CoO$_3$

$T_{C\rightarrow R} = \sim 1600^\circ C$;  $T_{C\rightarrow R} = 950^\circ C$;  $T_{C\rightarrow R} = 700^\circ C$

cubic

- Grain size - 3-5 $\mu$m
- Polycrystalline ceramics prepared by Praxair Surface Technologies

High temperature

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

Upon cooling, LaCoO$_3$ exhibits a displacive phase transition at $T_c$

Room temperature

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

$T_c$ is decreases with a divalent cation doping
LaCoO$_3$

~ 10% porosity
$\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$

~ 5% porosity
La$_{0.6}$Ca$_{0.4}$CoO$_3$

~ 5% porosity
La$_{0.45}$Ca$_{0.55}$CoO$_3$

$\sim 5\%$ porosity
Ferroelastic Phase Transition

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

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

Stress relaxation by twinning
TEM micrographs of La$_{0.6}$Ca$_{0.4}$CoO$_3$ perovskite grains showing a complex configuration of twins
TEM micrograph showing a configuration of twins in LaCoO$_3$

Electron diffraction pattern exhibits splitting of the spots. The magnitude of the splitting increases with the distance from the center of the pattern.
Domain wall in LaCoO$_3$. 

No splitting of diffraction spots in the SAD pattern has been observed.
The micrographs showing detwinning upon heating in $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$

The micrographs showing reappearance of twins during cooling
Twins in La$_{0.6}$Ca$_{0.4}$CoO$_3$ perovskite at 400°C. A dislocation is observed near the twins’ tips. The dislocation serves as a strong pinning point delaying disappearance of the twins during heating.
Stacking faults in La$_{0.6}$Ca$_{0.4}$CoO$_3$ perovskite
Detwinnning process during heating of $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$
LaCoO$_{2.5}$ structure

LaCoO$_3$ perovskite undergoes topotactic reduction to vacancy-ordered phase at high temperatures in reducing atmosphere

$$2 \text{LaCoO}_3(s) \rightarrow \text{La}_2\text{Co}_2\text{O}_5(s) + \frac{1}{2} \text{O}_2(g)$$

Orthorhombic brownmillerite structure

Perovskite type structure

Alternate layers of Co in octahedral and tetrahedral sites

Every second row of oxygen atoms is removed from alternate planes

Stemmer, S., Sane, A., Browning, N.D., Mazanec, T. 
*Solid State Ionics*, 130, 71-80, 2000
TEM micrographs of La$_{0.6}$Ca$_{0.4}$CoO$_3$ perovskite at 700°C.
A) Micrograph taken immediately after heating. A single domain grain can be clearly seen.
B) Micrograph taken after 25 min of annealing at 700°C
Wedge shaped twins along with short parallel to each other domains are stable up to 850°C in La$_{0.8}$Ca$_{0.2}$CoO$_3$ perovskite.
Co oxide surface precipitations during annealing of La$_{0.8}$Ca$_{0.2}$CoO$_3$ for 1.5 hours at 800°C. Precipitations are favored along the grain boundaries.
LaCoO$_3$ in oxidizing and reducing environment

- **In air**
  - Linear expansion
  - CTE
  - Loss modulus
  - Storage modulus

- **In 4%H$_2$/96%Ar**
  - Linear expansion
  - CTE

LaCoO$_3$ is not stable in reducing atmosphere with the most significant changes starting to occur at 800-900°C.
LaCoO₃ reduction steps

1. 
6LaCoO₃ → 2La₃Co₃O₈ + O₂↑
4La₃Co₃O₈ → 6La₂Co₂O₅ + O₂↑

2. 
8LaCoO₃ → 2La₄Co₃O₁₀ + 2CoO + O₂↑
4LaCoO₃ → 2La₂CoO₄ + 2CoO + 3O₂↑
La₂Co₂O₅ → La₂CoO₄ + CoO

3. 
La₄Co₃O₁₀ → 2La₂O₃ + Co₃O₄
La₂CoO₄ → La₂O₃ + CoO

4. 
2Co₃O₄ → 6CoO + 3O₂↑
2CoO → 2Co + O₂↑
LaGaO$_3$ Crystal Structure

The first-order transition orthorhombic $\leftrightarrow$ rhombohedral @ $\sim$145$^\circ$C leads to twinning of LaGaO$_3$ crystals $\rightarrow$ change of volume (2)


LaGaO$_3$ single crystals preparation

- Single-crystals of LaGaO$_3$ were grown by Czochralski technique
- LaGaO$_3$ (001) subjected to detwinning
- C. Klementz, University of Central Florida produced the crystals
LaGaO$_3$: Volume Change during Phase transition

**LaGaO$_3$ (100)**

- **Shrinkage on heating**
- **Expansion on cooling**

**LaGaO$_3$ (001)**

- **Expansion on heating**
- **Shrinkage on cooling**

**Overall volume change in the phase transition < 0.01%**
Optical microscopy: Heating of (100) LaGaO$_3$

Raman spectroscopy allows distinguishing the two phases. There are 24 allowed Raman modes in orthorhombic LaGaO$_3$ and 5 Raman modes in rhombohedral LaGaO$_3$. 

Heating 143-143.5°C

Cooling ~144°C
Raman spectra of (100) LaGaO$_3$

Intensity map of 361cm$^{-1}$ Raman band

LaGaO$_3$, 100, outside twin, RT

LaGaO$_3$, 100, inside Vickers impression, RT

LaGaO$_3$, 100, outside twin, RT

LaGaO$_3$, 100, inside Vickers impression, RT

Outside twin

Twin

Peak 1 (337)

Peak 2 (361)

Peaks

Raman Shift cm$^{-1}$

Intensity, a.u.

Outside twin

Twin

Peak 2 Intensity (counts)

Distance (Micrometers)
Conclusions

- Twins, domain walls, stacking faults and dislocations were observed in LaCoO$_3$ based perovskites.
- The mobility of domains was recorded \textit{in-situ} by high temperature TEM in the La$_{0.6}$Ca$_{0.4}$CoO$_3$ perovskite.
- The detwinning process during the heating and reappearance of domains during cooling were observed as a result of a ferroelastic phase transition.
- Annealing of the LaCoO$_3$ based specimens at high temperatures in vacuum leads to progressive transitions accompanied by nucleation and movement of new stacking faults. This can be explained by the formation of oxygen deficient brownmillerite-type LaCoO$_{2.5}$ structure.
- LaCoO$_3$ is not stable and reducing environment and can be easily reduced up to metallic cobalt.
- The orthorhombic to rhombohedral phase transition in LaGaO$_3$ occurs at $\sim$145$^\circ$C. The significant thermal expansion/contraction occurs in the material during heating/cooling cycles.