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 5×10^{-8} Pa
- Scintag PADV diffractometer (CuKα radiation)
- Thermal Mechanical Analyzer (TMA)
- Optical microscope

Lanthanum based cobaltites

$LaCoO_3$	$La_{0.8}Ca_{0.2}CoO_3$	$La_{0.6}Ca_{0.4}CoO_3$	$La_{0.45}Ca_{0.55}CoO_3$
$T_{C\rightarrow R}$ = ~1600°C;	$T_{C\rightarrow R}$ = 950 ° C;	$T_{C\rightarrow R}$ = 700 ° C	cubic

- Grain size - 3-5 μm
- Polycrystalline ceramics prepared by Praxair Surface Technologies

High temperature

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

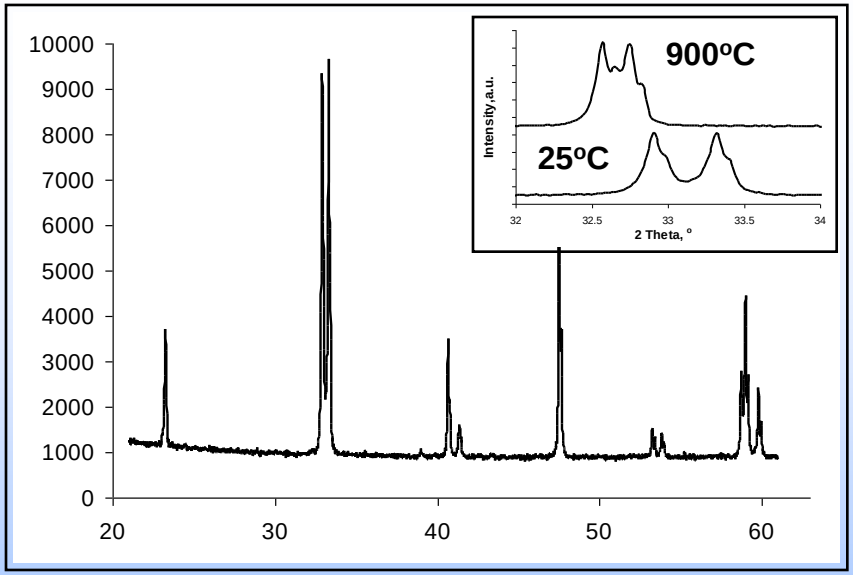
Upon cooling, $LaCoO_3$ exhibits a displacive phase transition at T_c

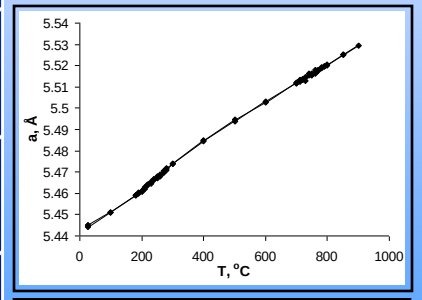
Room temperature

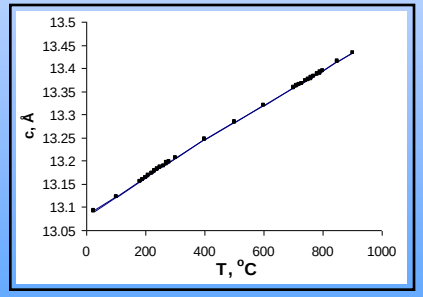
Rhombohedral structure with the space group $R\bar{3}c$

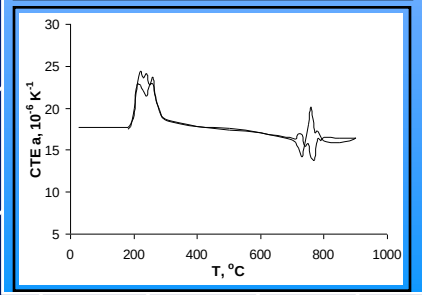
T_c is decreases with a divalent cation doping

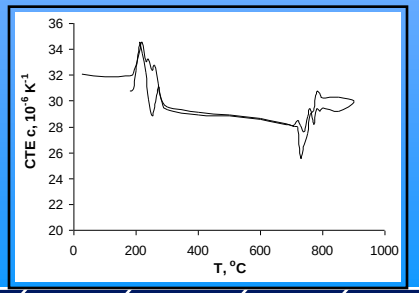
$LaCoO_3$

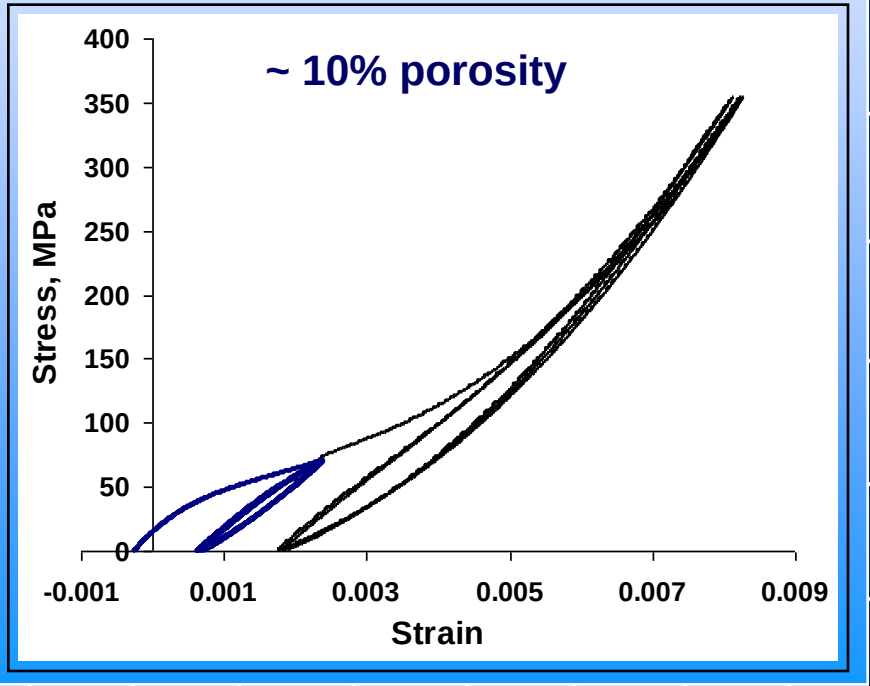

10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
20
30
40
50
60
900ºC
25ºC
Intensity,a.u.
32
32.5
33
33.5
34
2 Theta, °


a, Å
T, °C

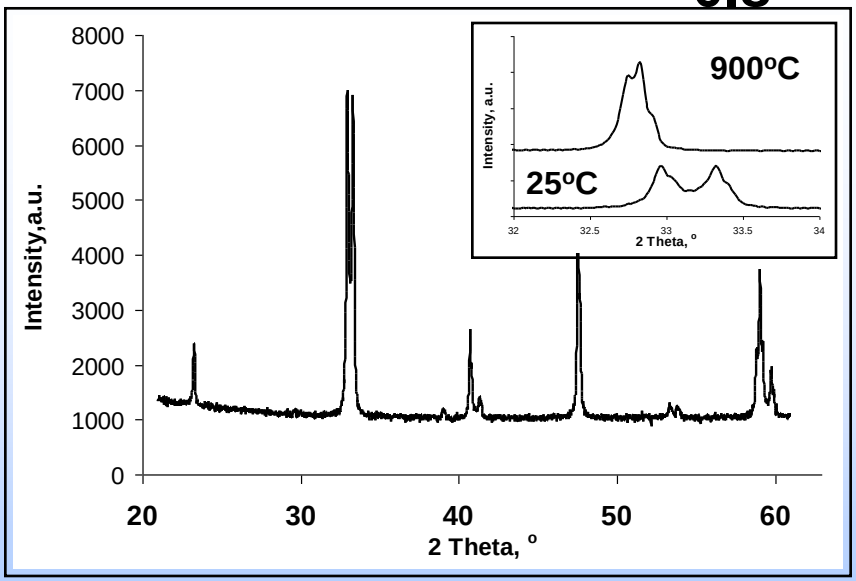

c, Å
T, °C

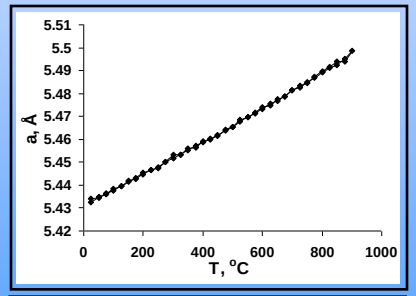

CTE a, 10⁻⁶ K⁻¹
T, °C

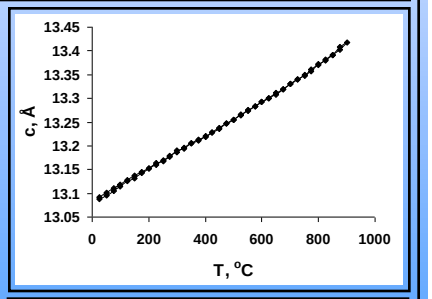

CTE c, 10⁻⁶ K⁻¹
T, °C

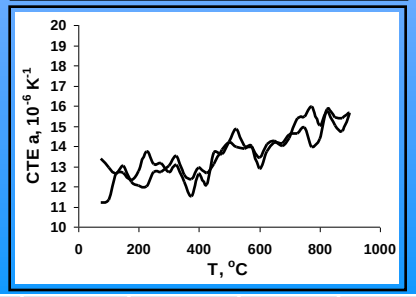

~ 10% porosity
Stress, MPa
Strain
400
350
300
250
200
150
100
50
0
-0.001
0.001
0.003
0.005
0.007
0.009

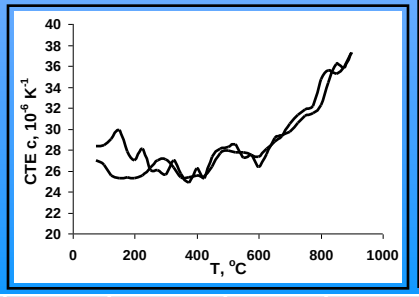
$La_{0.8}Ca_{0.2}CoO_3$

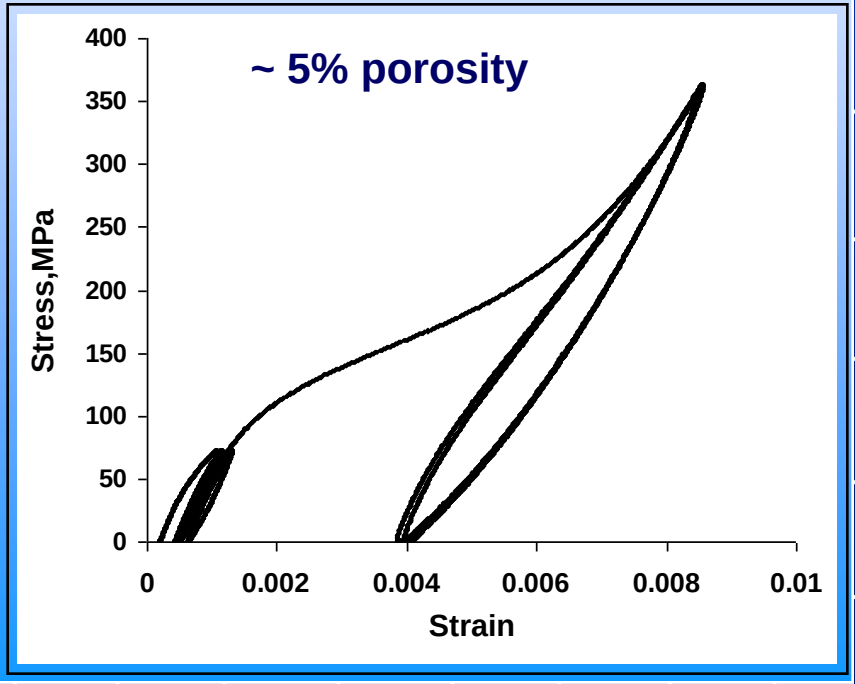




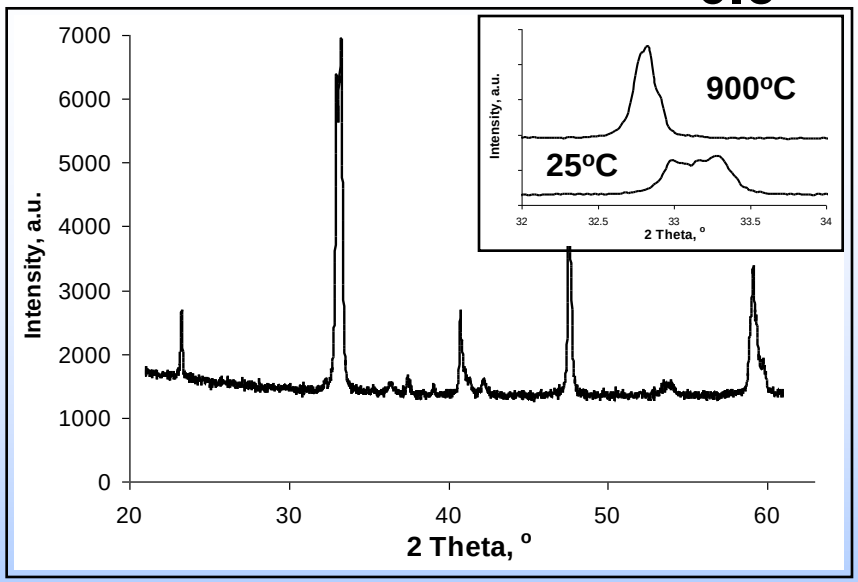


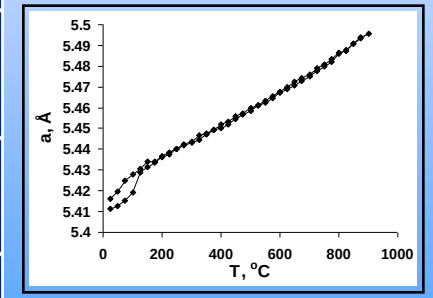


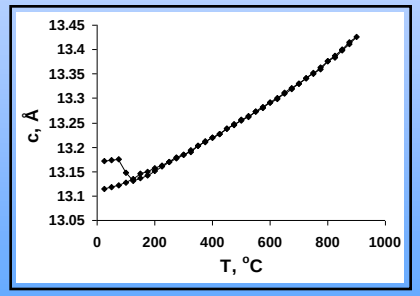


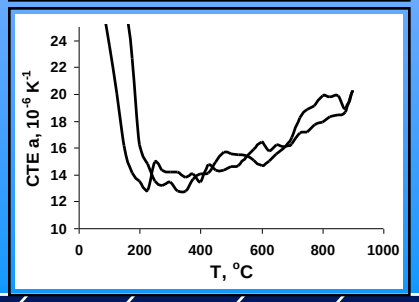


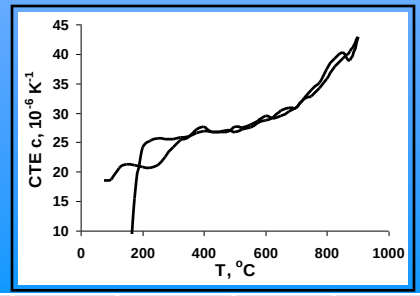
$La_{0.6}Ca_{0.4}CoO_3$

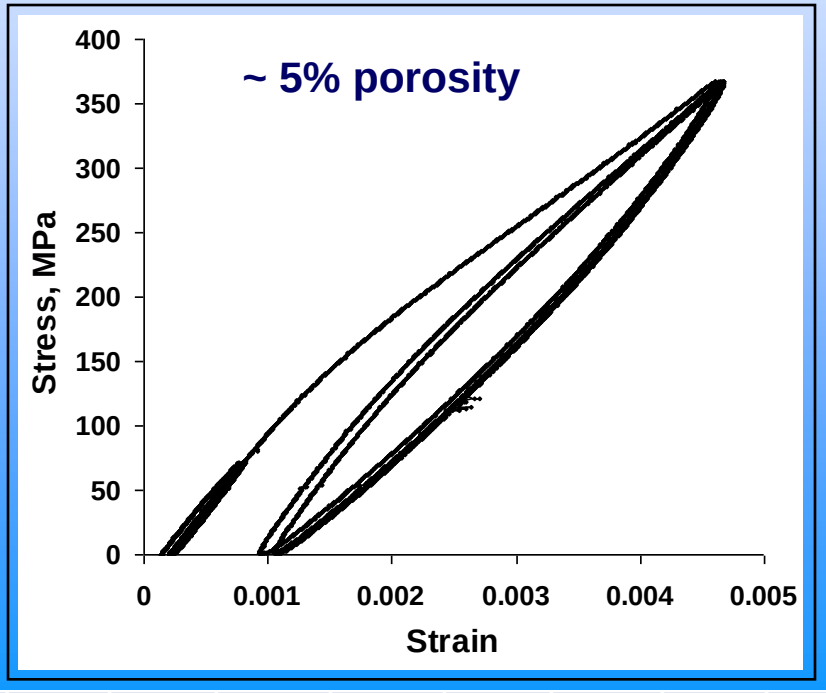




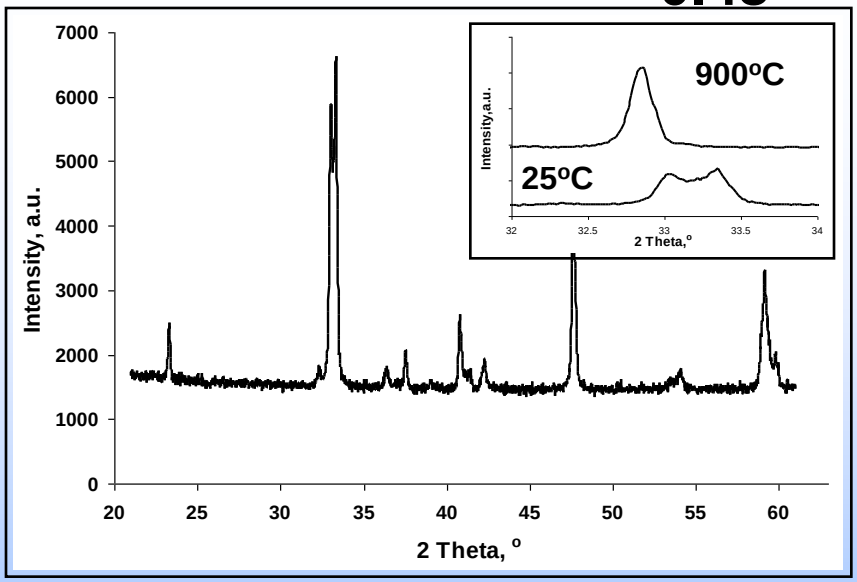


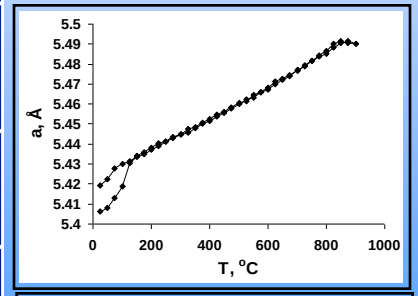


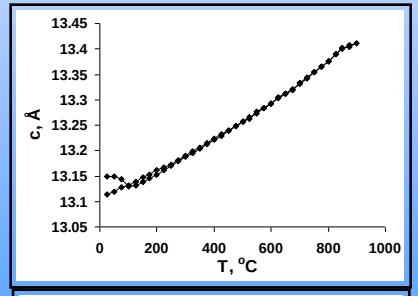


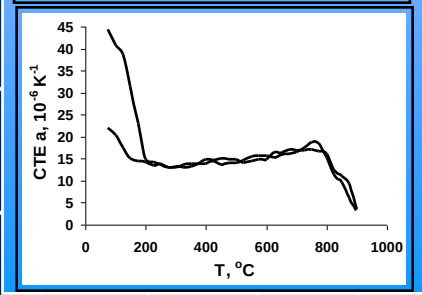


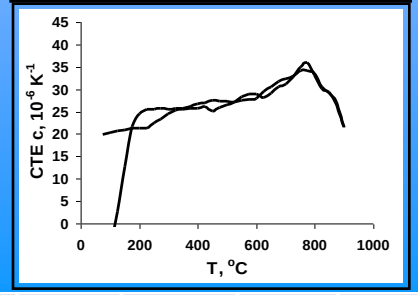
$La_{0.45}Ca_{0.55}CoO_3$

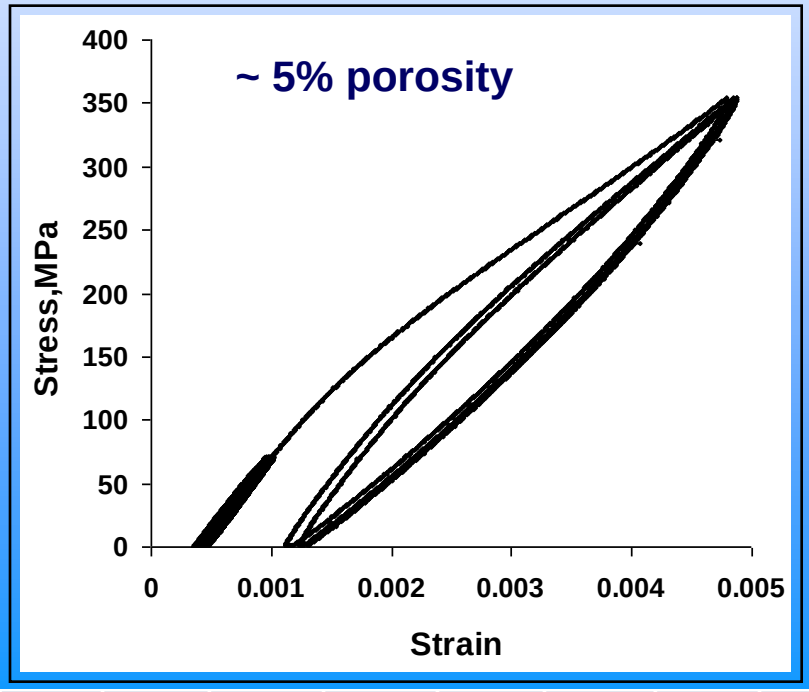




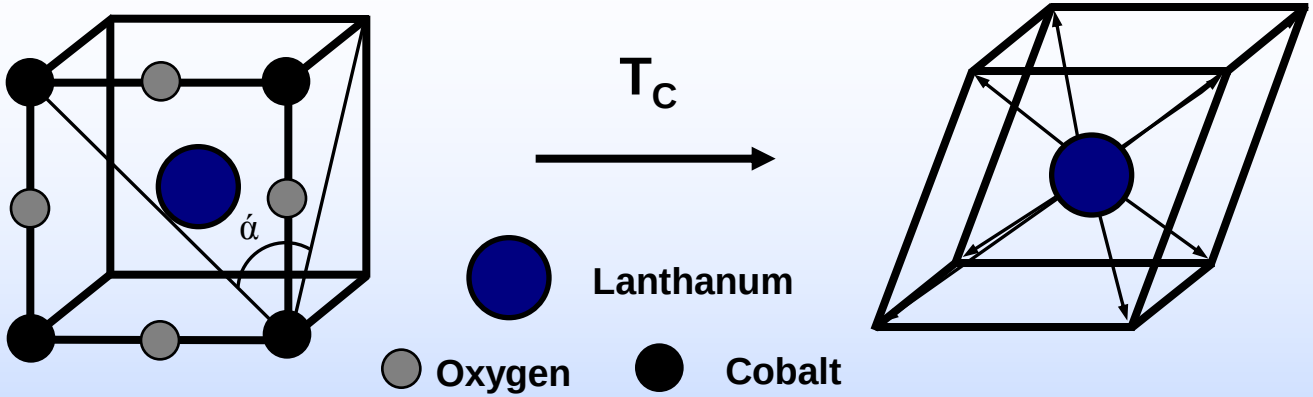






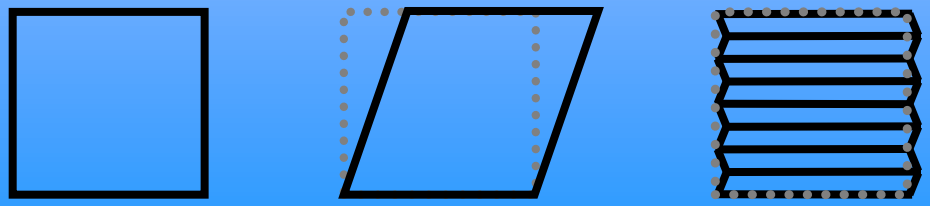


Ferroelastic Phase Transition

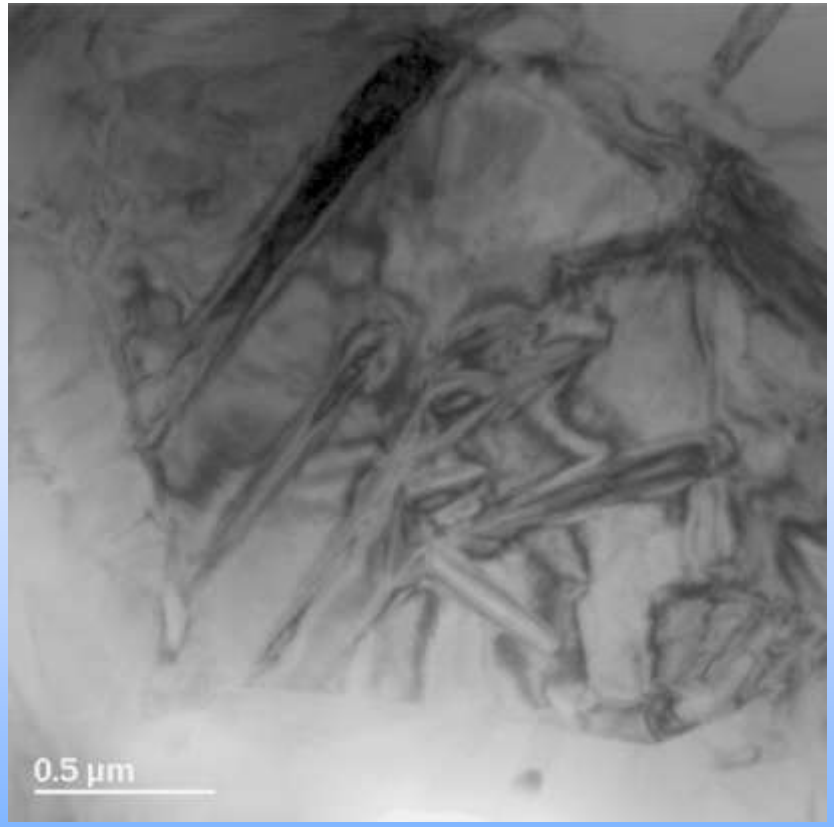


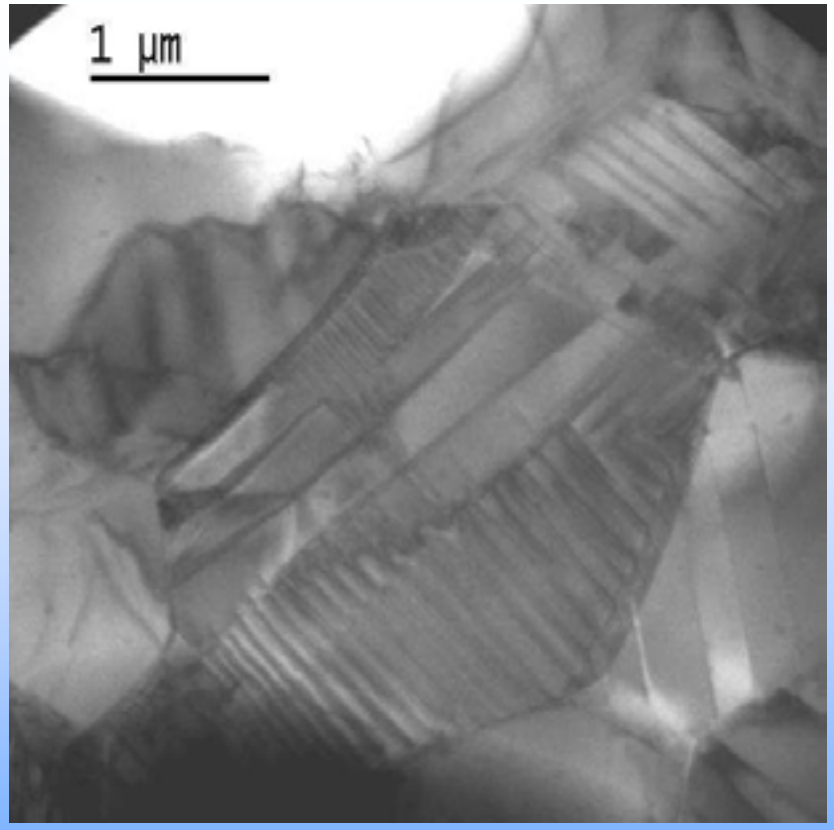
$T_{C\rightarrow R}$ = $LaCoO_3$ at ~1600°C; $La_{0.8}Ca_{0.2}CoO_3$ at 950 ° C; $La_{0.6}Ca_{0.4}CoO_3$ at 700 ° C

High Temperature	Low Temperature
High symmetry prototypic phase	Low symmetry phase
a = b = c; $\alpha = \beta = \gamma = 90°$	a = b = c; $\alpha = \beta = \gamma \neq 90°$
$\acute{\alpha} = 60°$	$\acute{\alpha} = 60.78°$
Cubic	Rhombohedral

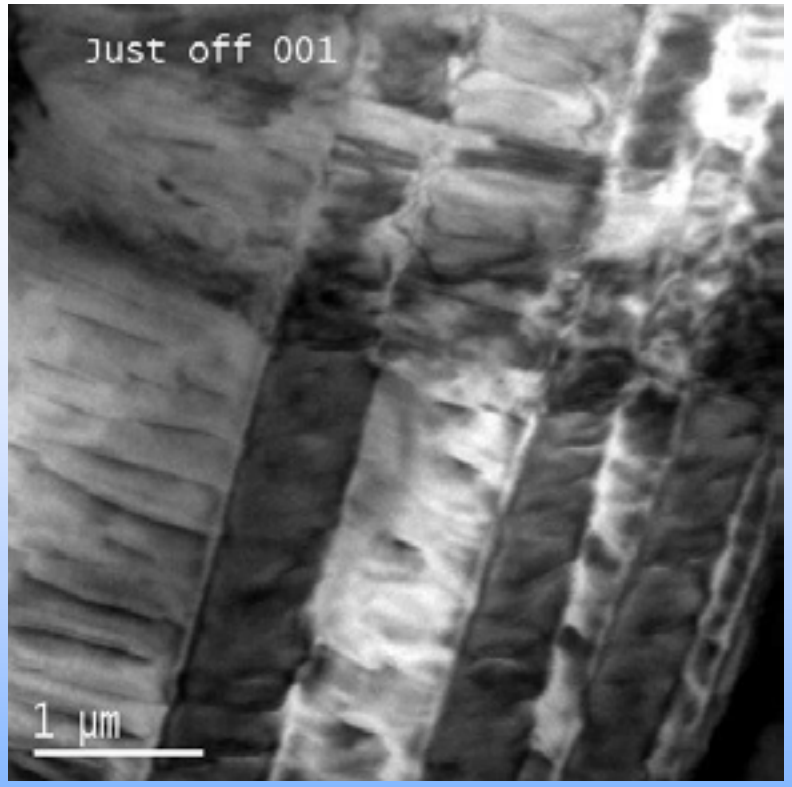


Stress relaxation by twinning

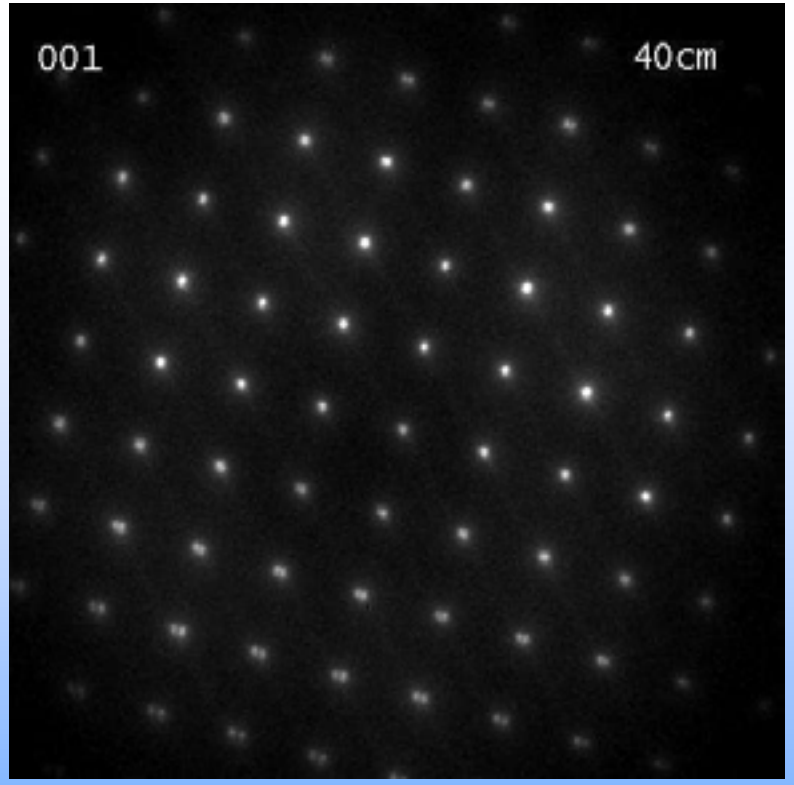




TEM micrographs of $La_{0.6}Ca_{0.4}CoO_3$ perovskite grains showing a complex configuration of twins

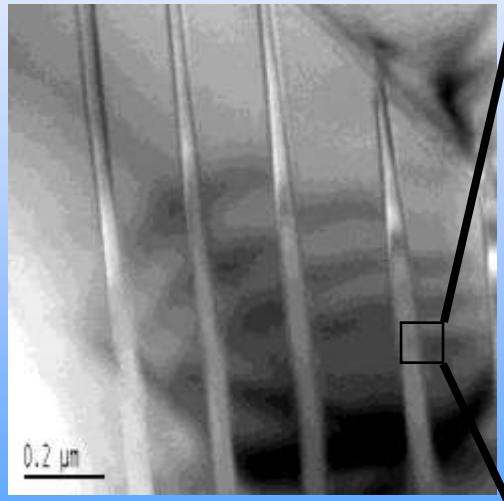


TEM micrograph showing a configuration of twins in $LaCoO_3$

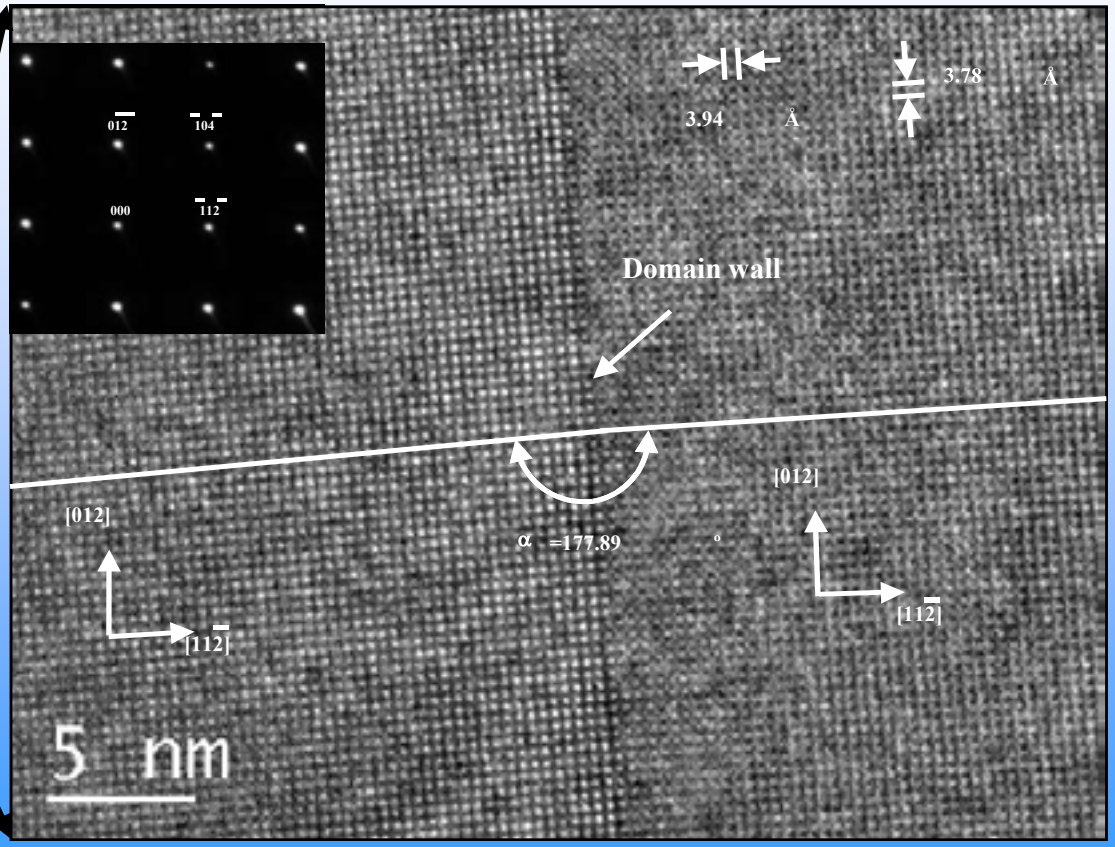


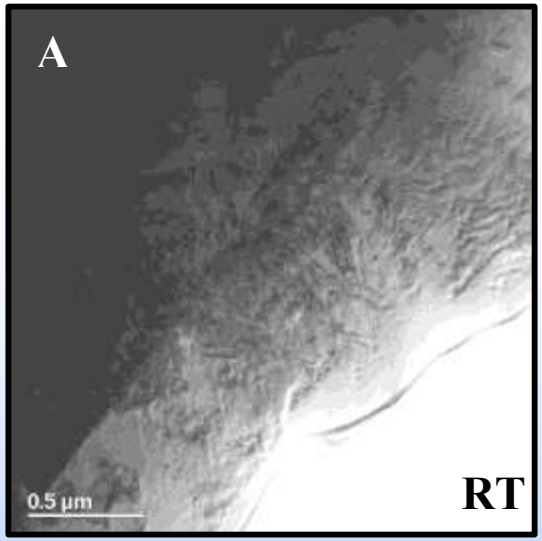
Electron diffraction pattern exhibits splitting of the spots. The magnitude of the splitting increases with the distance from the center of the pattern

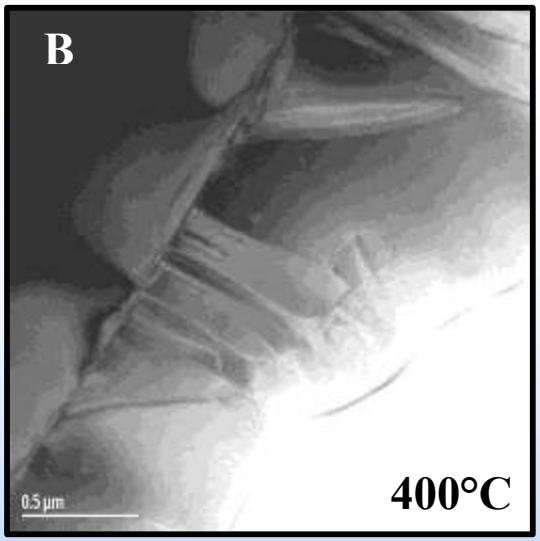
Domain wall in $LaCoO_3$.

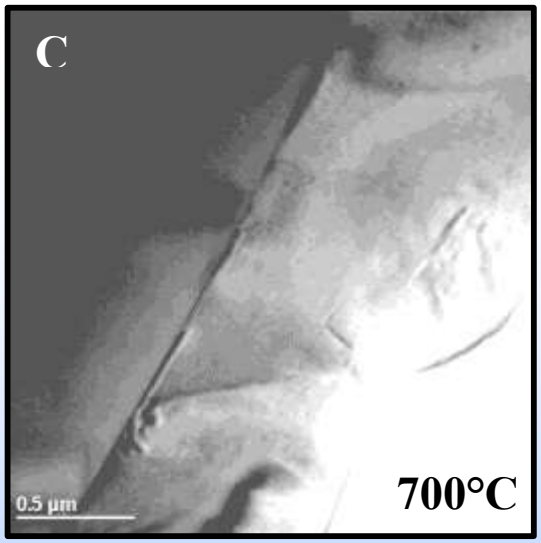


No splitting of diffraction spots in the SAD pattern has been observed

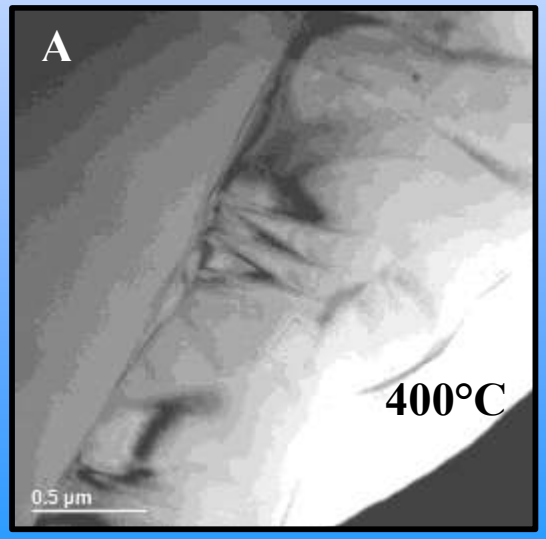


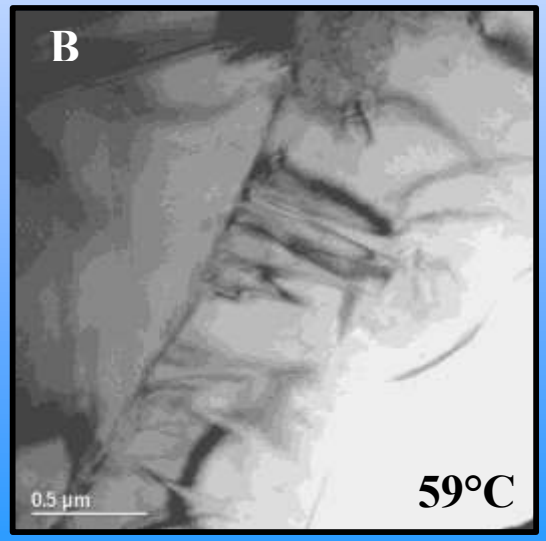


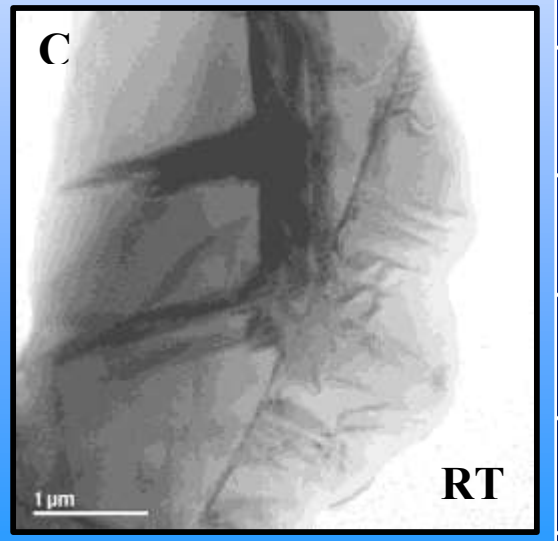




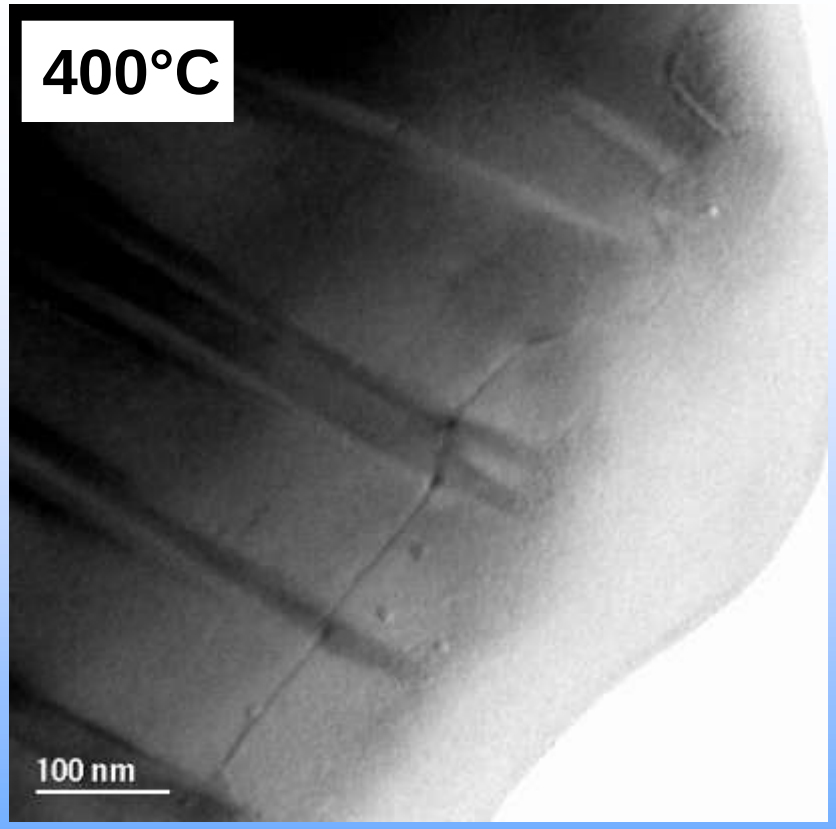
The micrographs showing detwinning upon heating in $La_{0.6}Ca_{0.4}CoO_3$

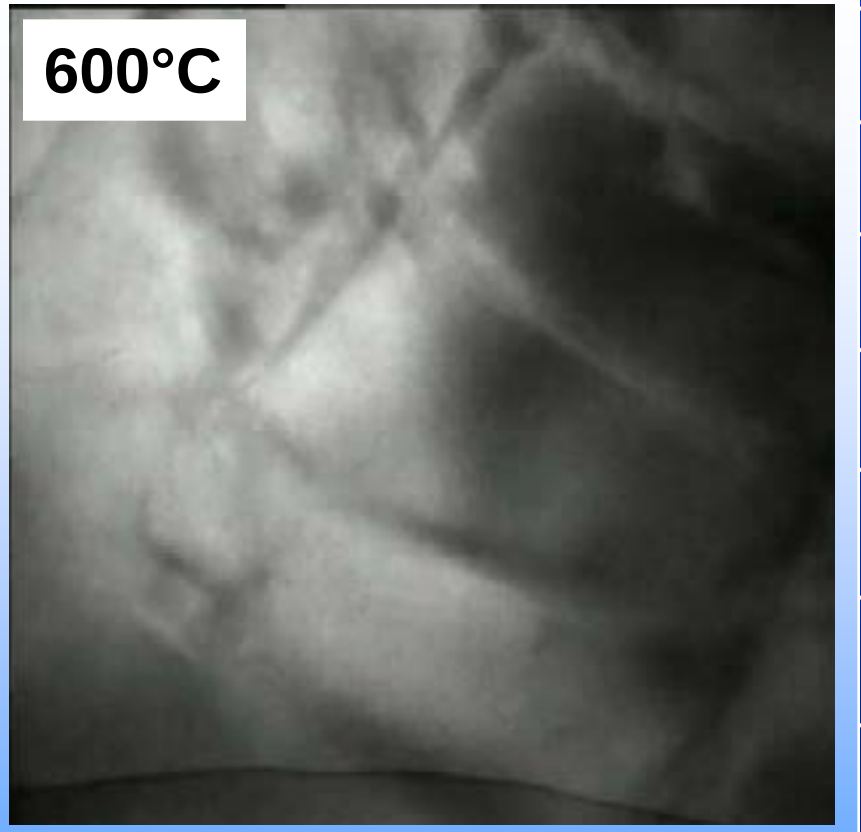




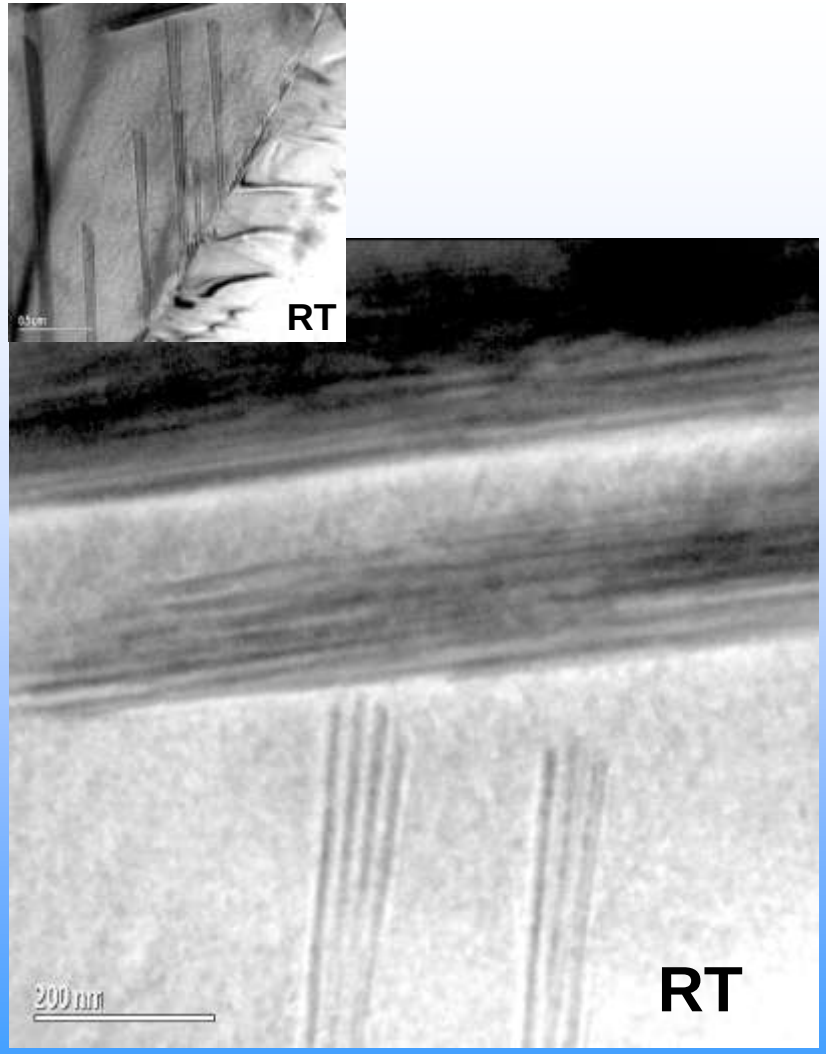


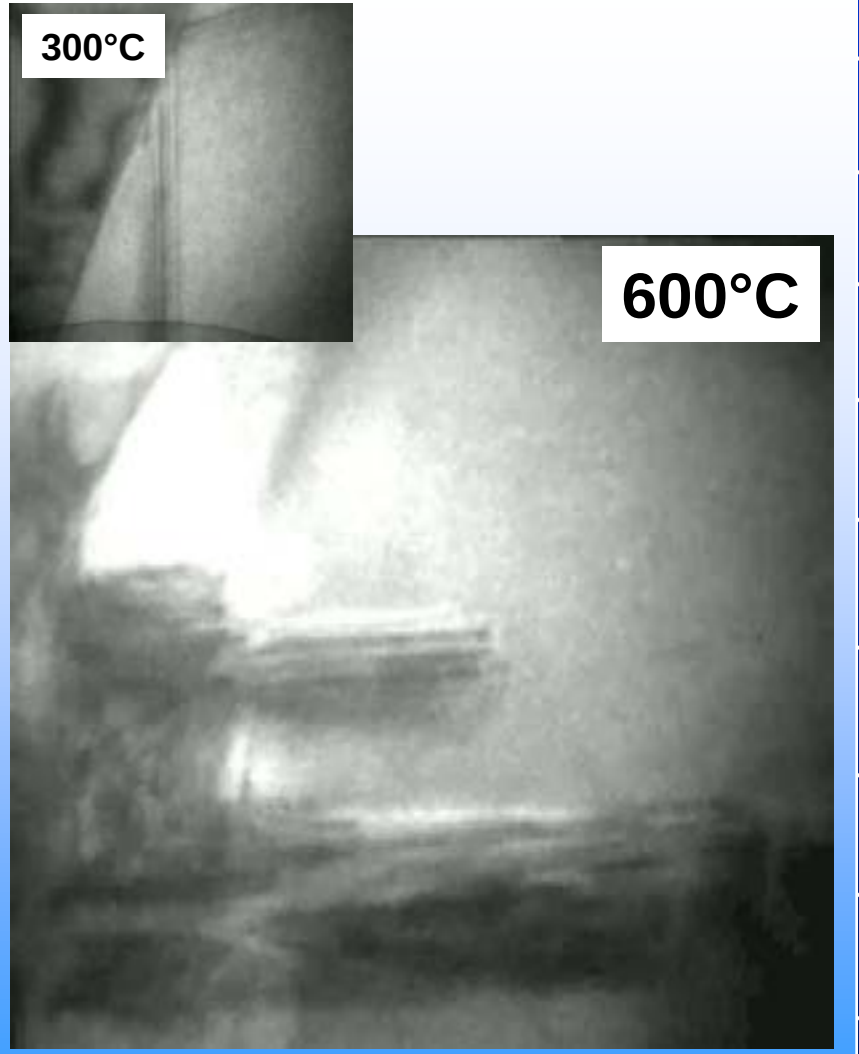
The micrographs showing reappearance of twins during cooling



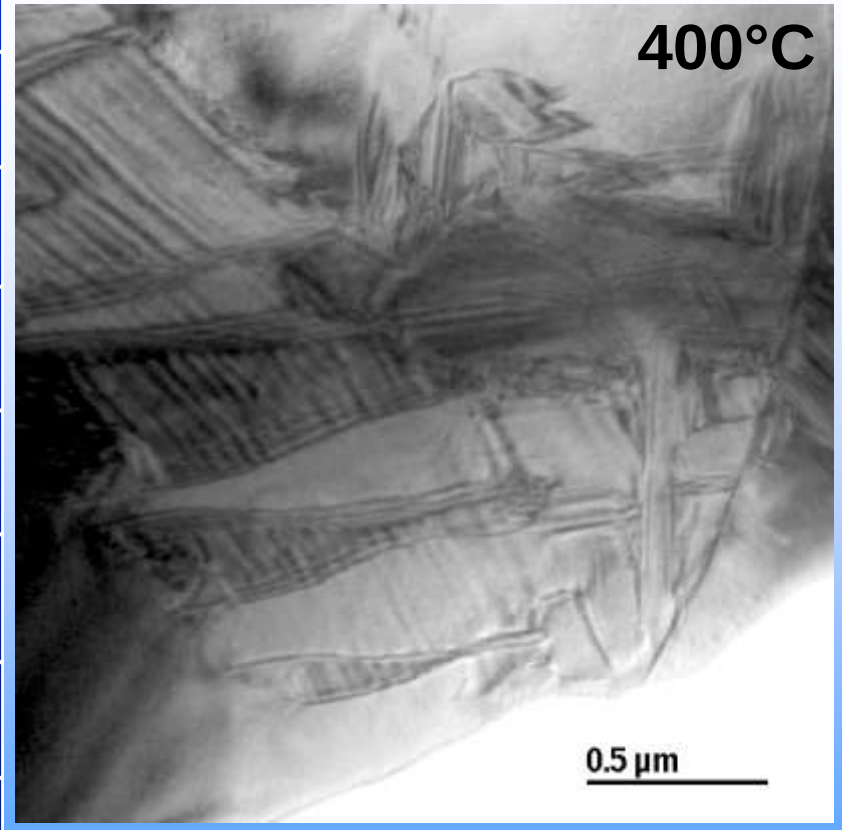


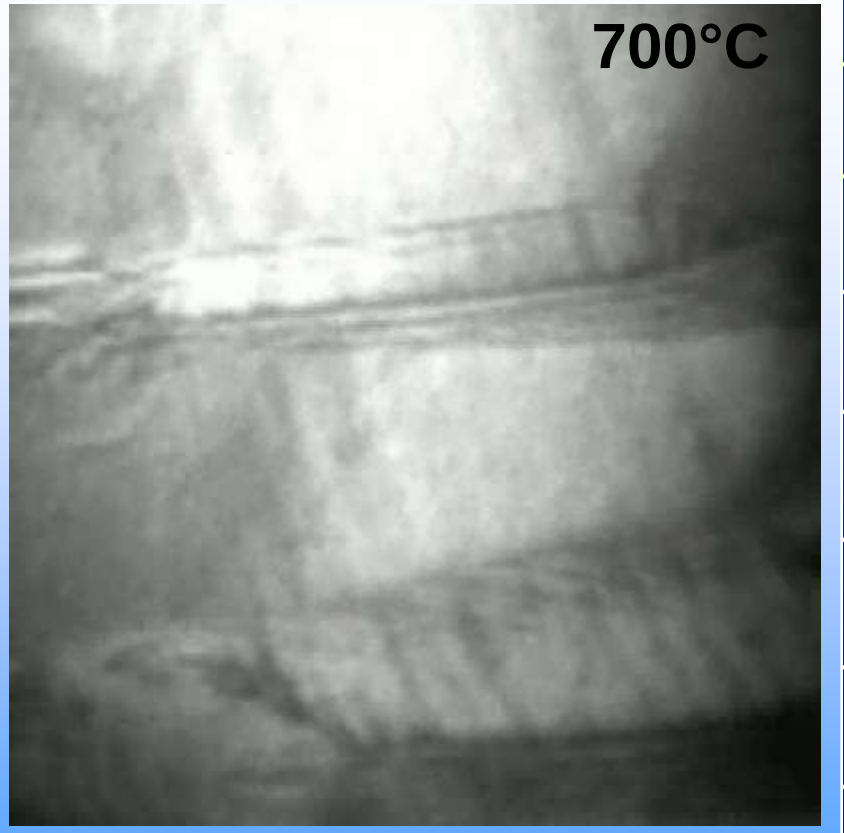
Twins in $La_{0.6}Ca_{0.4}CoO_3$ perovskite at 400°C.
A dislocation is observed near the twins' tips.
The dislocation serves as a strong pinning point delaying disappearance of the twins during heating.





Stacking faults in $La_{0.6}Ca_{0.4}CoO_3$ perovskite





Detwinning process during heating of $La_{0.6}Ca_{0.4}CoO_3$

$LaCoO_{2.5}$ structure

$LaCoO_3$ perovskite undergoes topotactic reduction to vacancy-ordered phase at high temperatures in reducing atmosphere

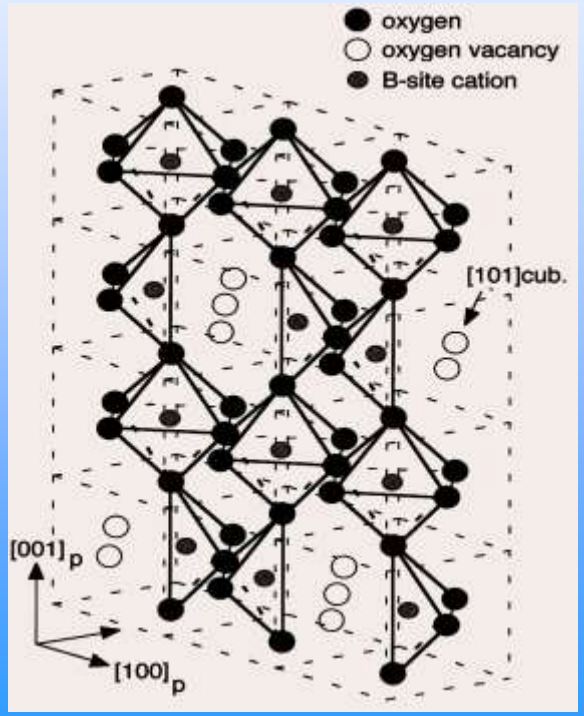
$$2\ LaCoO_3(s) \rightarrow La_2Co_2O_5(s) + \tfrac{1}{2}\ O_2(g)$$

Orthorhombic brownmillerite structure

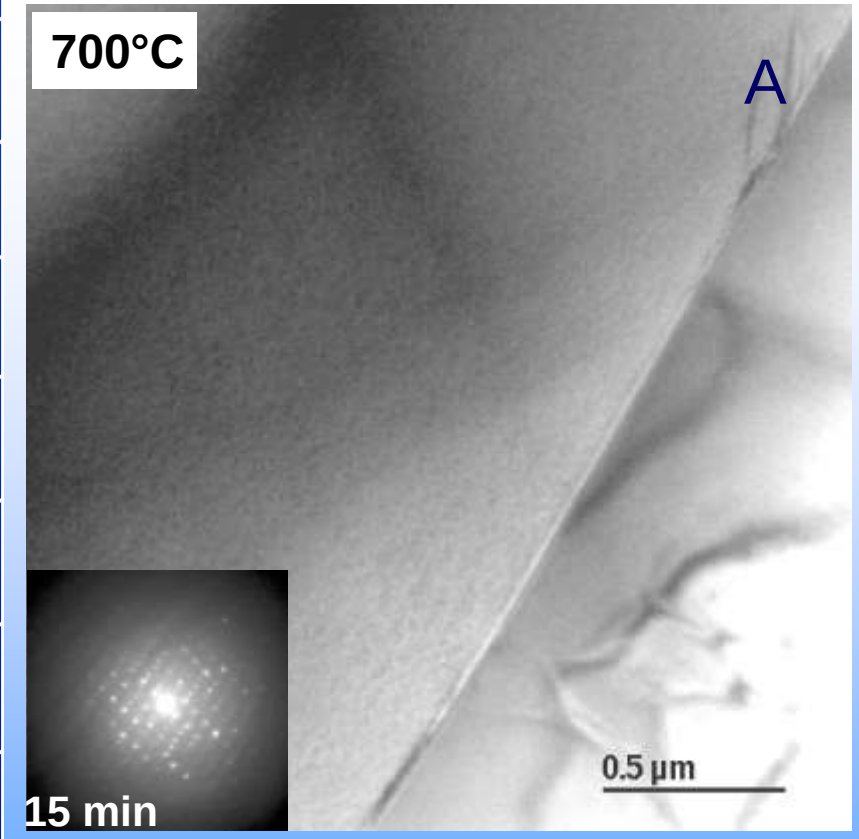
Perovskite type structure

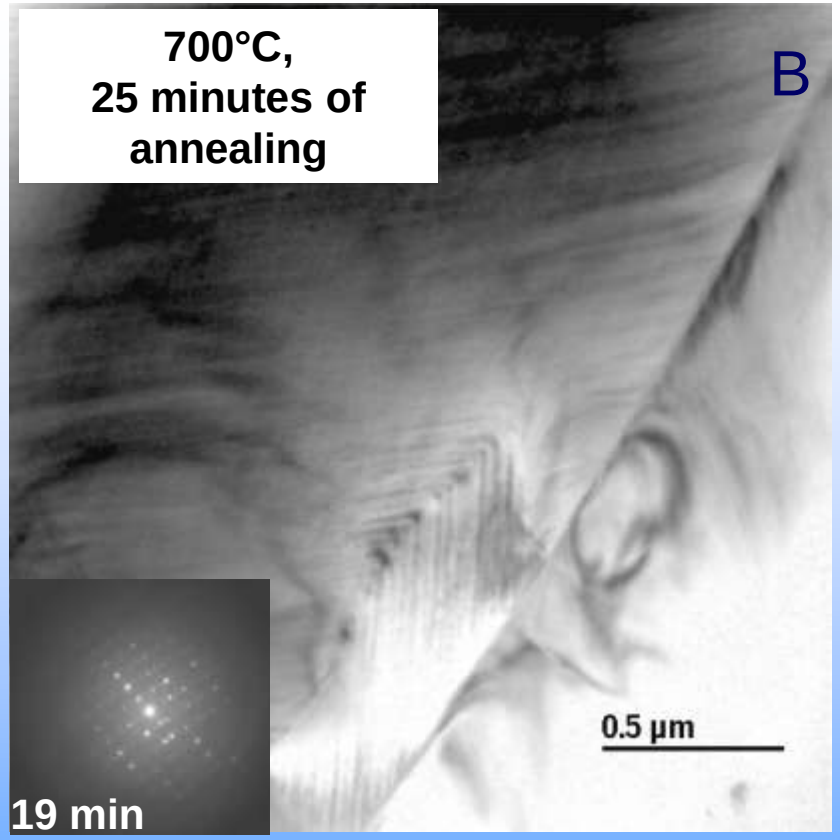
Alternate layers of Co in octahedral and tetrahedral sites

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



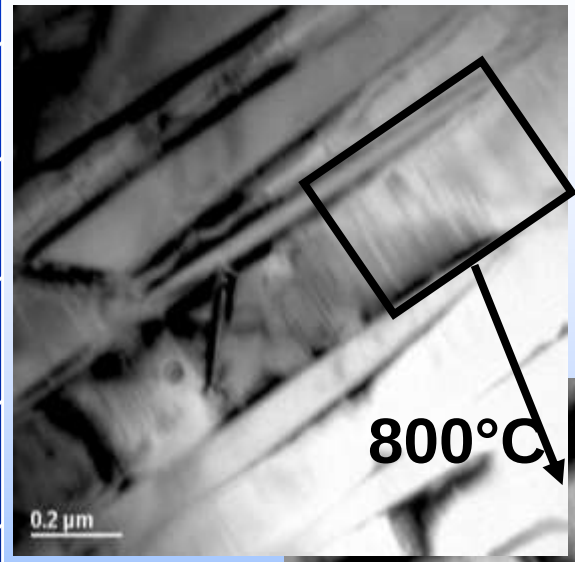


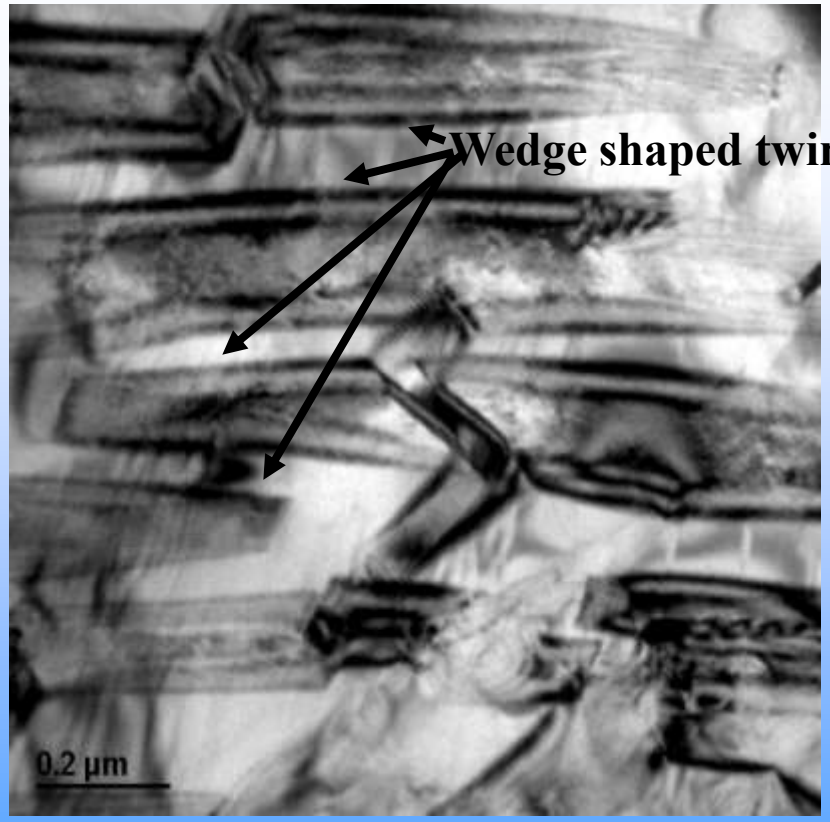
TEM micrographs of $La_{0.6}Ca_{0.4}CoO_3$ perovskite at 700°C.

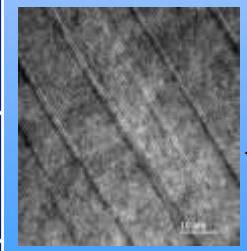
A) Micrograph taken immediately after heating. A single domain grain can be clearly seen.

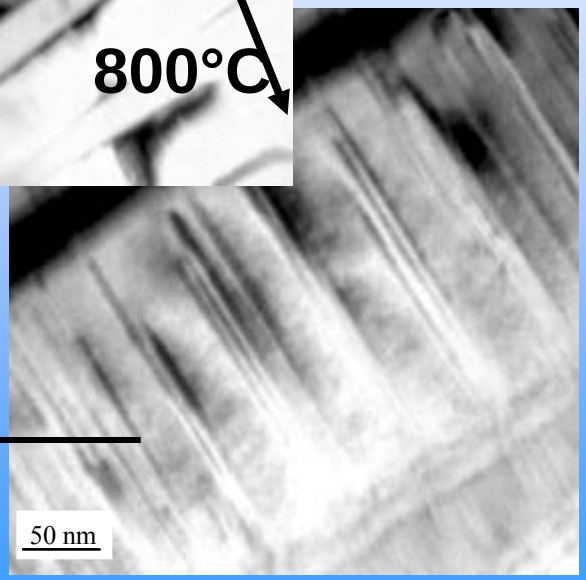
B) Micrograph taken after 25 min of annealing at 700°C

Twins in $La_{0.8}Ca_{0.2}CoO_3$

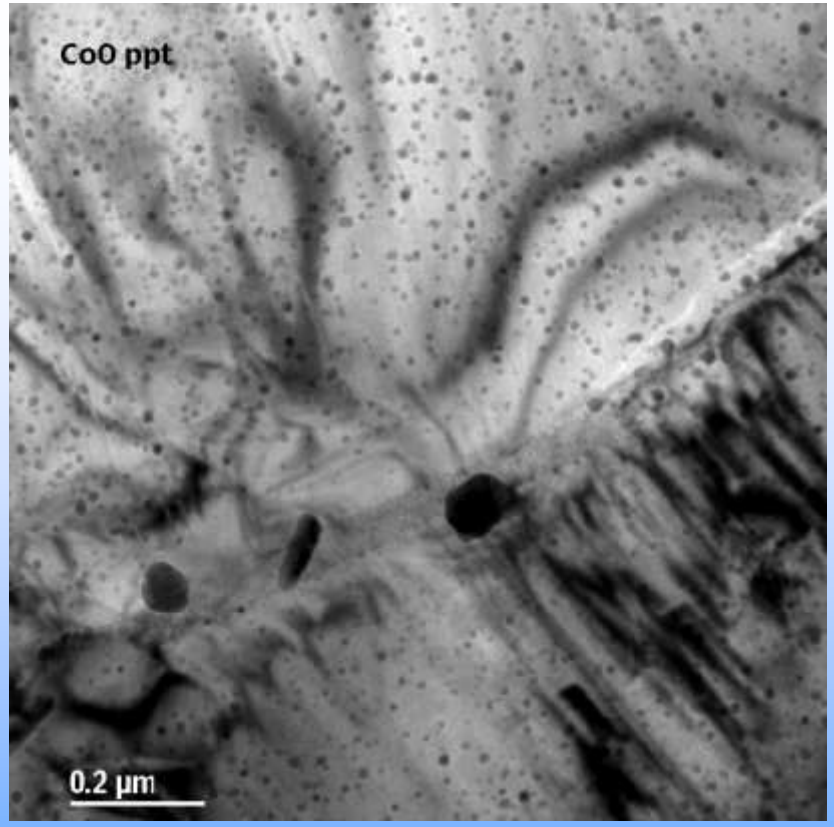


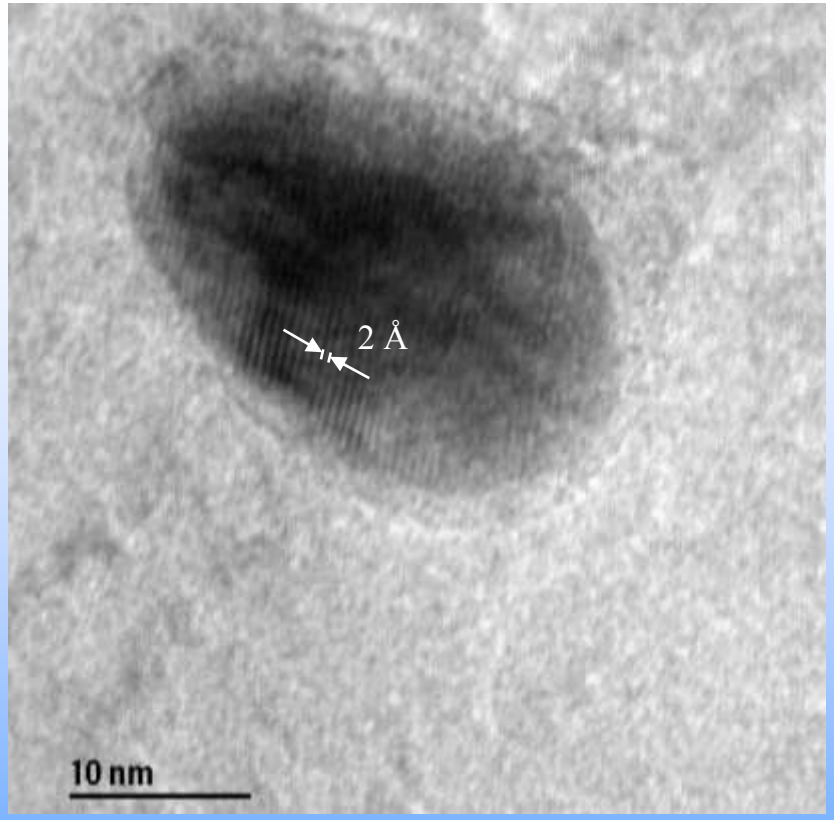




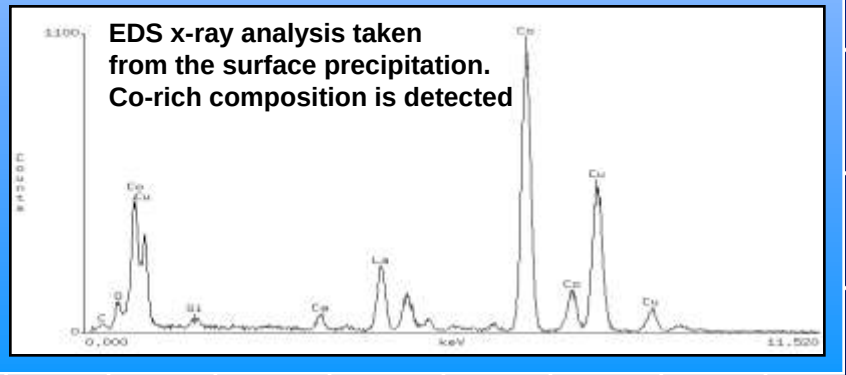


Wedge shaped twins along with short parallel to each other domains are stable up to 850°C in $La_{0.8}Ca_{0.2}CoO_3$ perovskite

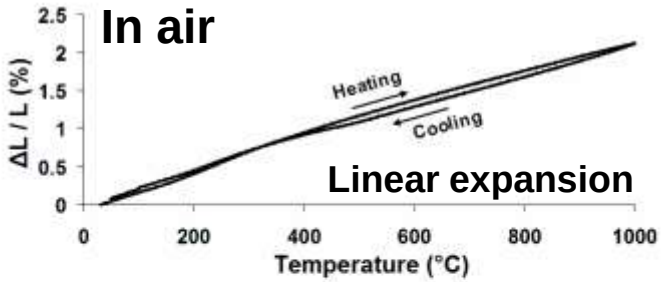


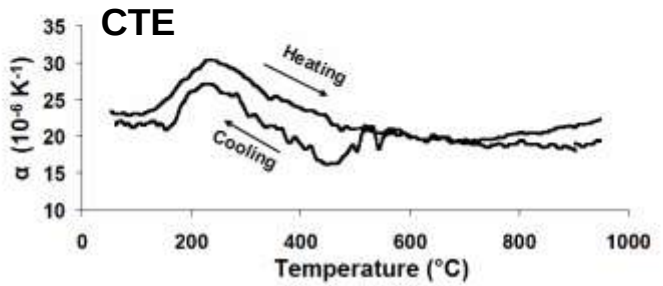


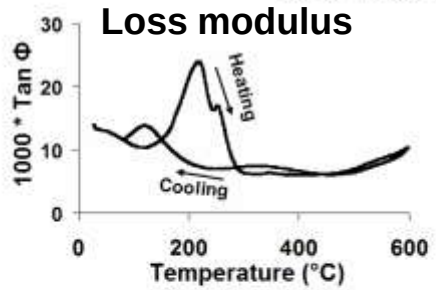
Co oxide surface precipitations during annealing of $La_{0.8}Ca_{0.2}CoO_3$ for 1.5 hours at 800°C. Precipitations are favored along the grain boundaries.

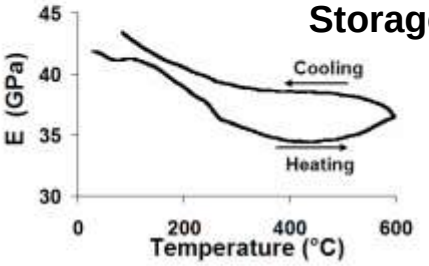


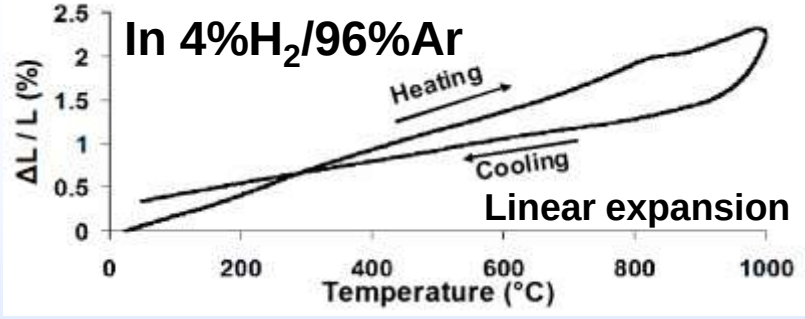
$LaCoO_3$ in oxidizing and reducing environment

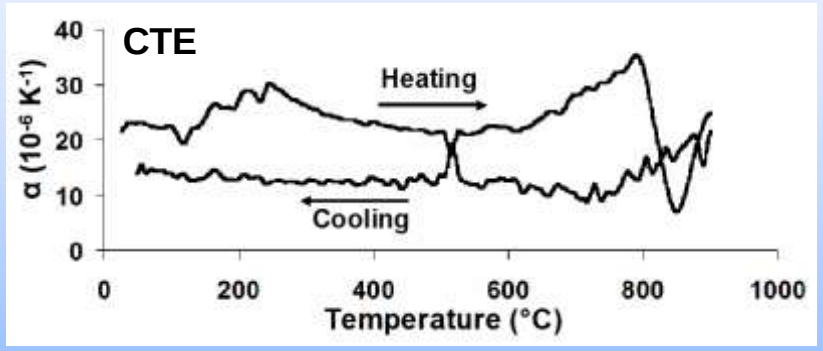


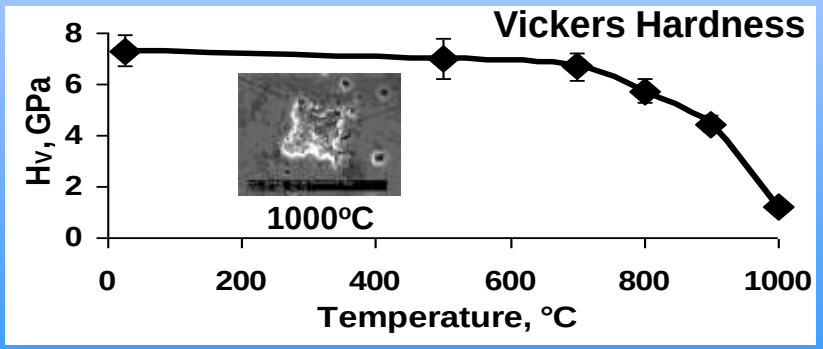






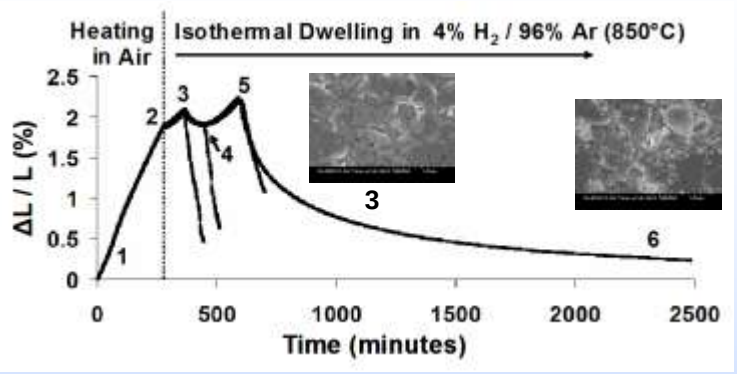






$LaCoO_3$ is not stable in reducing atmosphere with the most significant changes starting to occur at 800-900ºC

$LaCoO_3$ reduction steps



#1

$6LaCoO_3 \rightarrow 2La_3Co_3O_8 + O_2\uparrow$

$4La_3Co_3O_8 \rightarrow 6La_2Co_2O_5 + O_2\uparrow$

#2

$8LaCoO_3 \rightarrow 2La_4Co_3O_{10} + 2CoO + O_2\uparrow$

$4LaCoO_3 \rightarrow 2La_2CoO_4 + 2CoO + 3O_2\uparrow$

$La_2Co2O_5 \rightarrow La_2CoO_4 + CoO$

#3

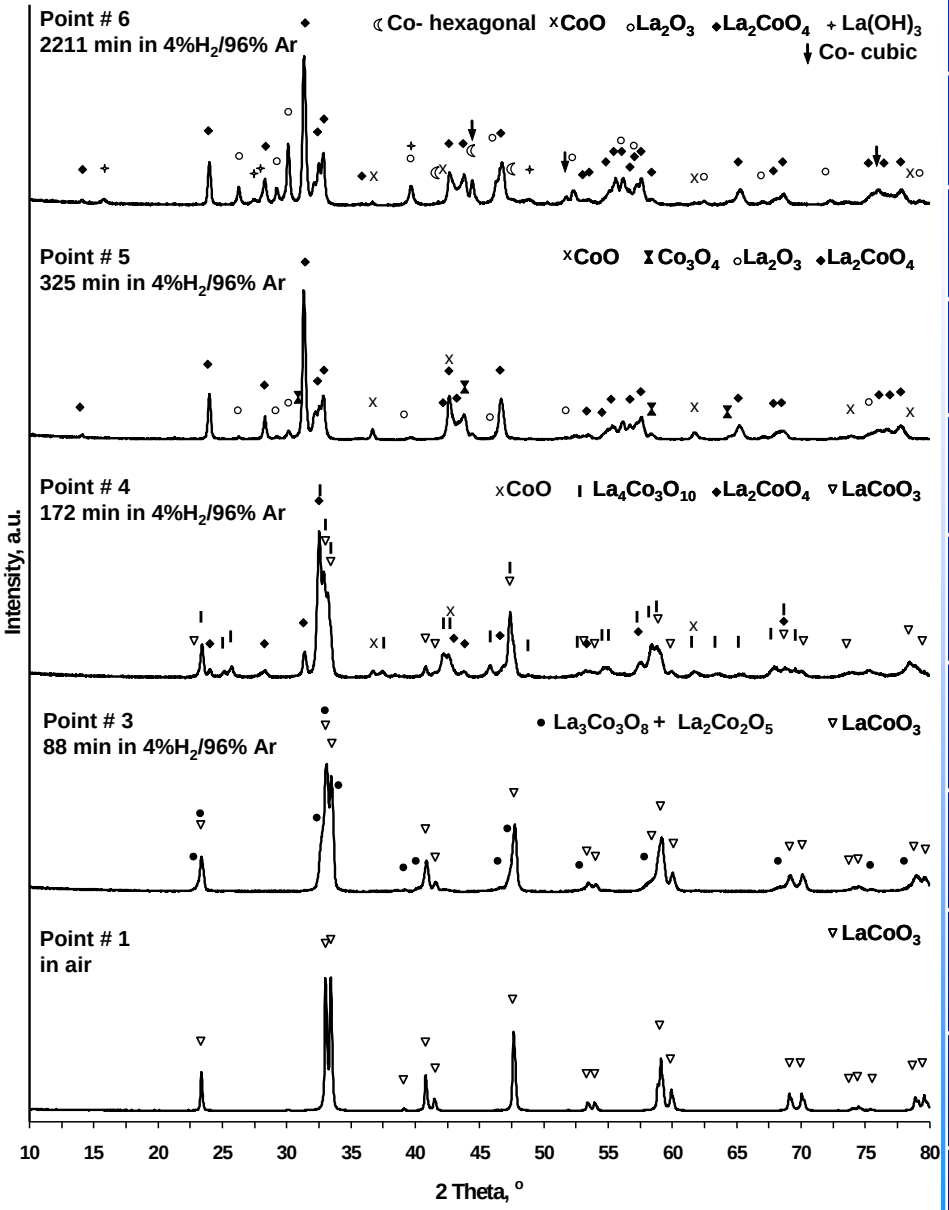
$La_4Co_3O_{10} \rightarrow 2La_2O_3 + Co_3O_4$

$La_2CoO_4 \rightarrow La_2O_3 + CoO$

#4

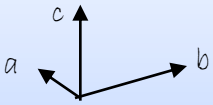
$2Co_3O_4 \rightarrow 6CoO + 3O_2\uparrow$

$2CoO \rightarrow 2Co + O_2\uparrow$

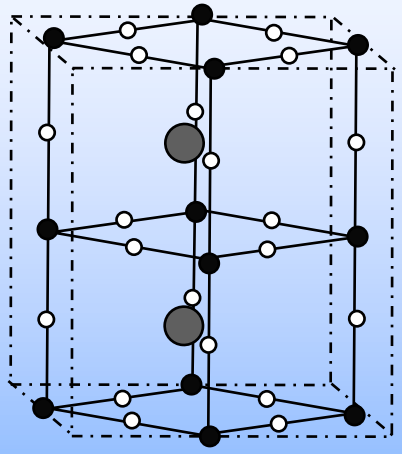


$LaGaO_3$ Crystal Structure

Orthorhombic



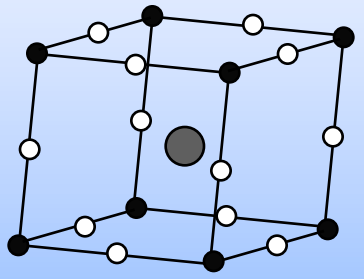
a = 5.520Å
b = 5.490Å
c = 7.770Å

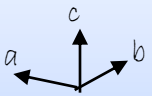


Ga
La
O

145°C ⟺

Rhombohedral





a = 3.889Å
α = 89.50°

Room temperature

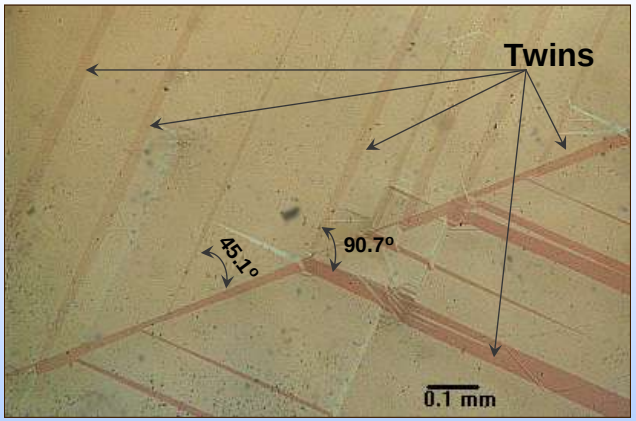
The first-order transition orthorhombic ↔ rhombohedral @ ~145°C → leads to twinning of $LaGaO_3$ crystals → change of volume [2]

(1) I.K.Bidikin, I.M.S.k., A.M. Balbashov, A.V. Kazansky, *Twinning of LaGaO3 Single Crystals.* J. Appl. Cryst., 1993. **26**: p. 71-76

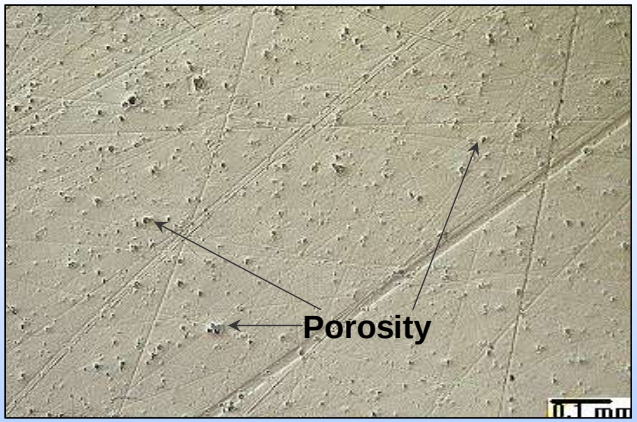
(2) A.N.Morozov, O.Y.M., N.M.Ponomarev, *Real Structure of single crystals of LaGaO3 grown by the Czochralski method. 1. X-ray diffraction and X-ray topographic methods.* Kristallografiya, 1993. **38**: p. 149-159

$LaGaO_3$ single crystals preparation

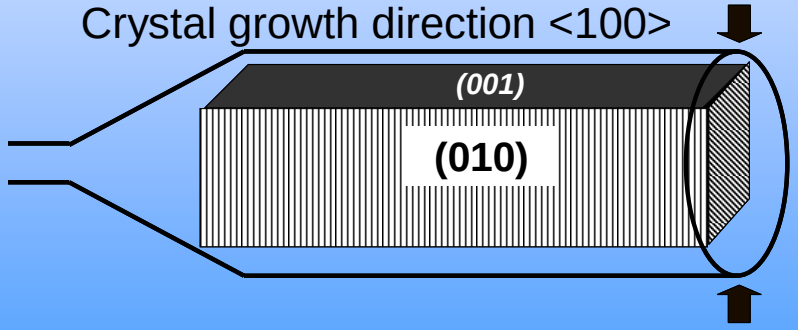
$LaGaO_3$ single crystal in the [100] plane

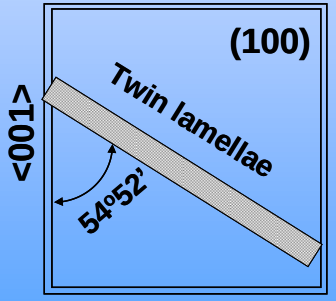


$LaGaO_3$ single crystal in the [001] plane



Crystal growth direction <100>

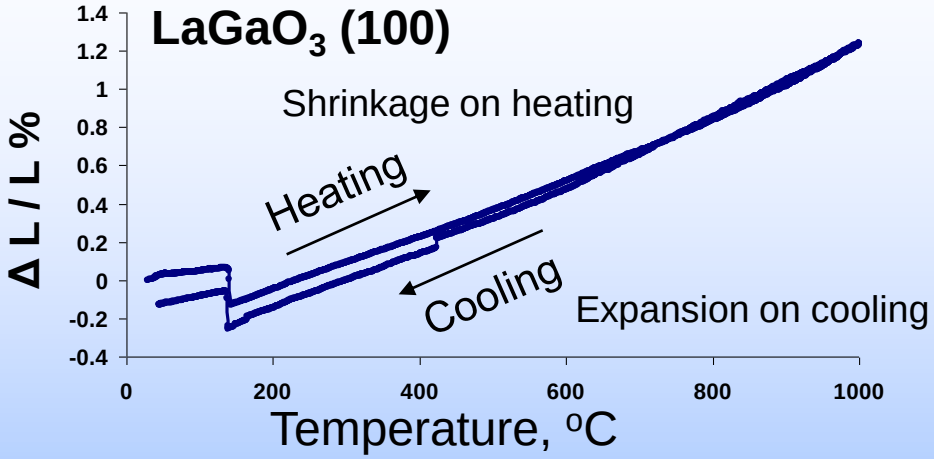


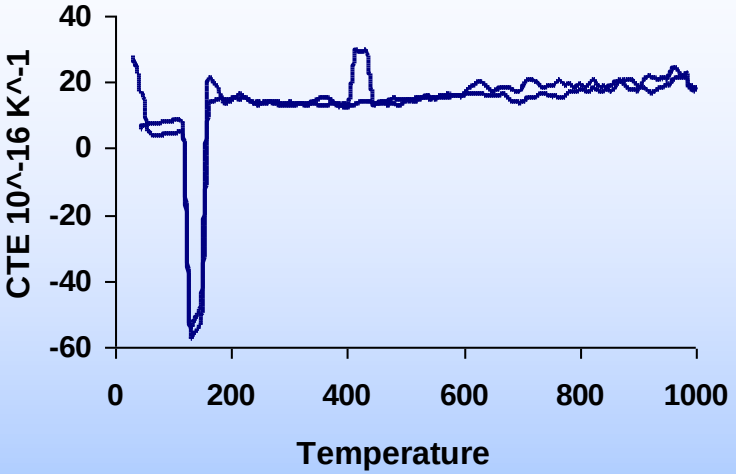


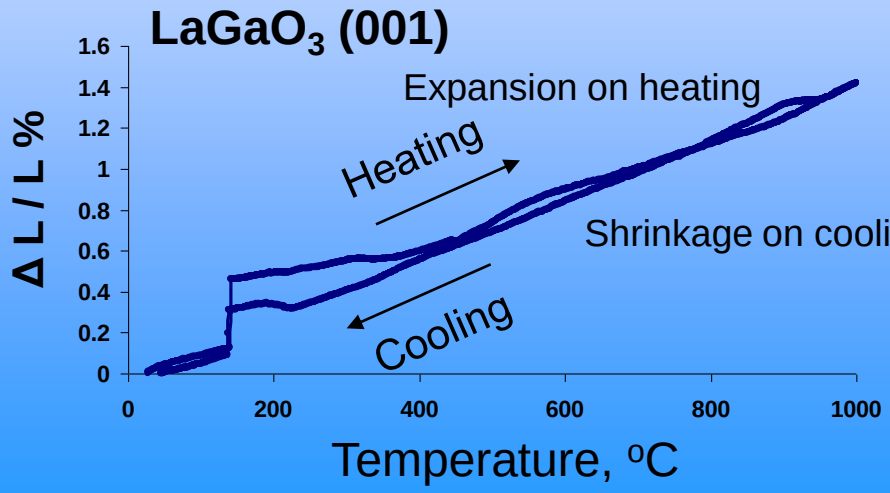
- Single-crystals of $LaGaO_3$ were grown by Czochralski technique
- $LaGaO_3$ (001) subjected to detwinning
- C. Klementz, University of Central Florida produced the crystals

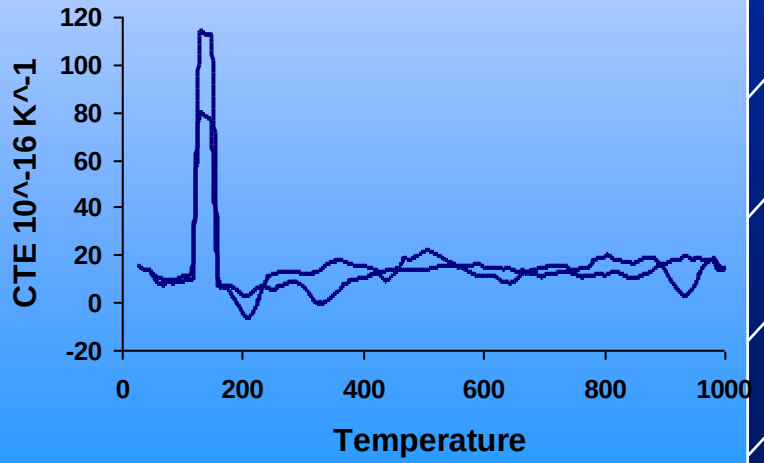
Single crystals of $LaGaO_3$ were grown at University of Central Florida by Prof. C Klementz

$LaGaO_3$: Volume Change during Phase transition



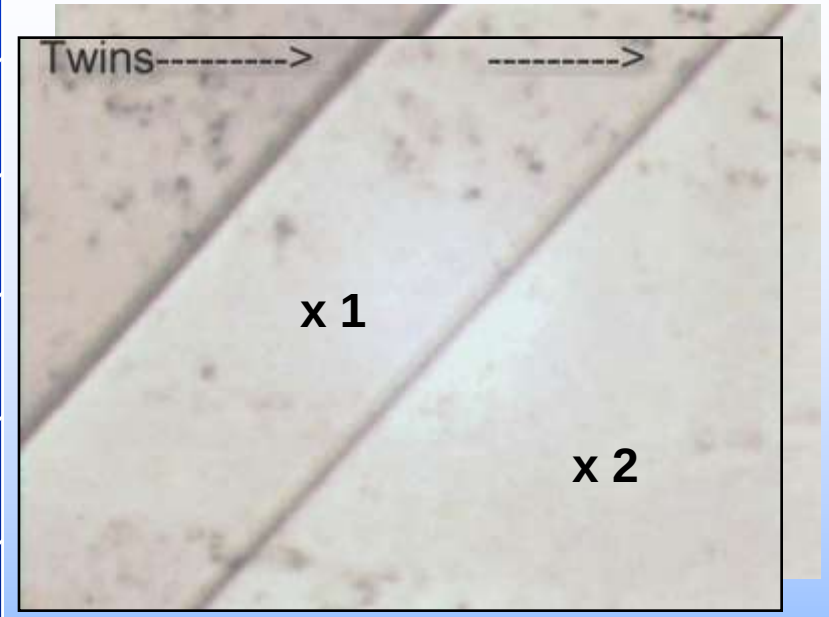






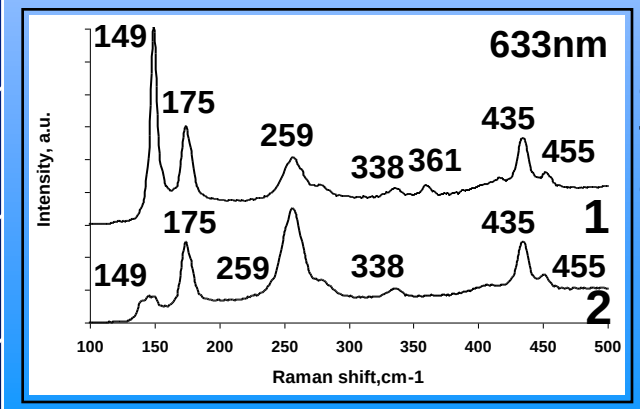
Overall volume change in the phase transition < 0.01%

Optical microscopy: Heating of (100) $LaGaO_3$

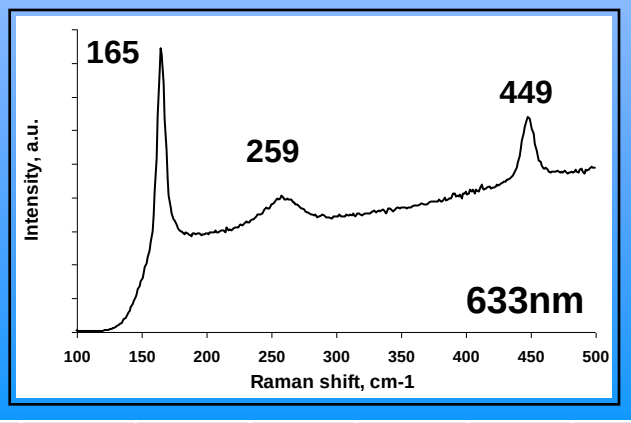


Heating 143-143.5°C

Cooling ~144°C

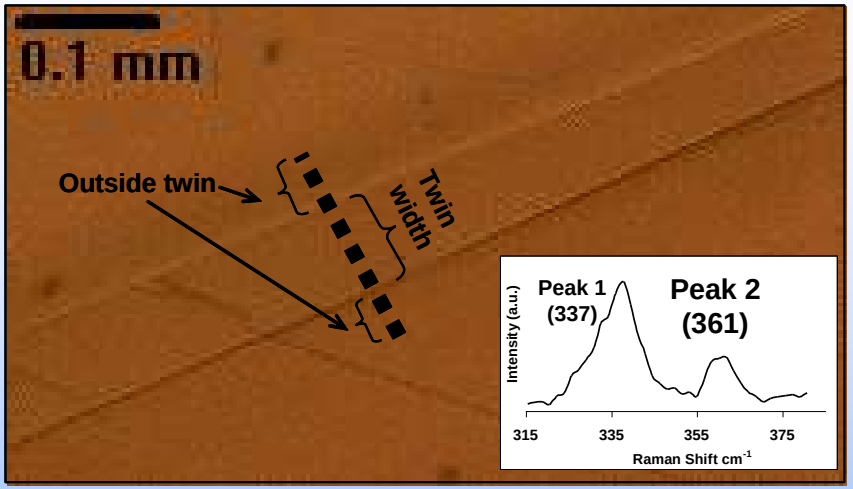


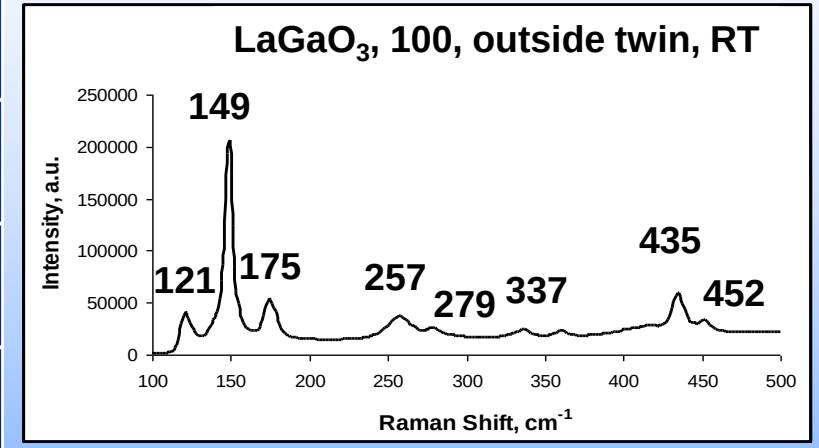
Raman spectroscopy allows distinguishing the two phases. There are 24 allowed Raman modes in orthorhombic LaGaO3 and 5 Raman modes in rhombohedral LaGaO3.

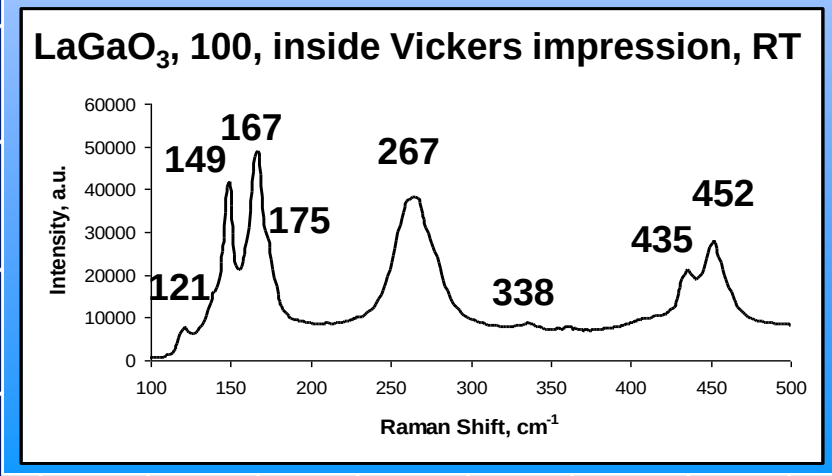


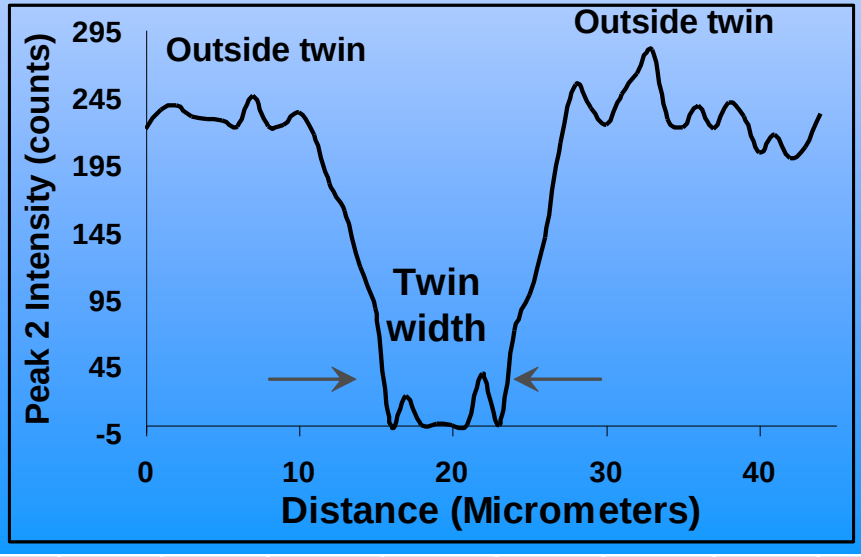
Raman spectra of (100) $LaGaO_3$

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









Conclusions

- Twins, domain walls, stacking faults and dislocations were observed in $LaCoO_3$ based perovskites.
- The mobility of domains was recorded *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 ~145^{o}C. The significant thermal expansion/contraction occurs in the material during heating/cooling cycles.