Development of High Temperature/High Sensitivity Novel Chemical Resistive Sensor

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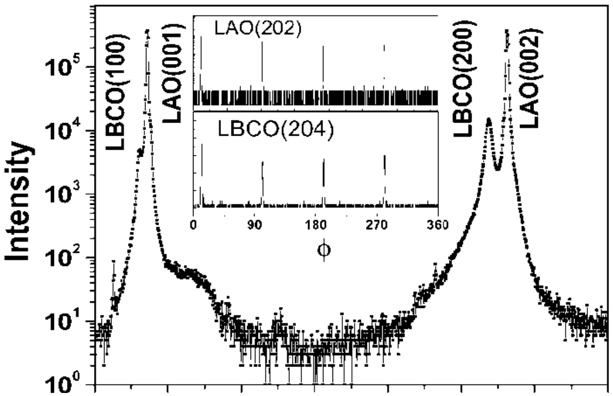
Project Manager: Dr. Susan M. Maley
Performance Period: 09/01/2010-8/31/2012

- Introduction
- Mixed Ionic/Electronic Conductive $LnBaCo_2O_{5.5}$ Oxides
- Full Scale Chemical Sensor Development
- Summary

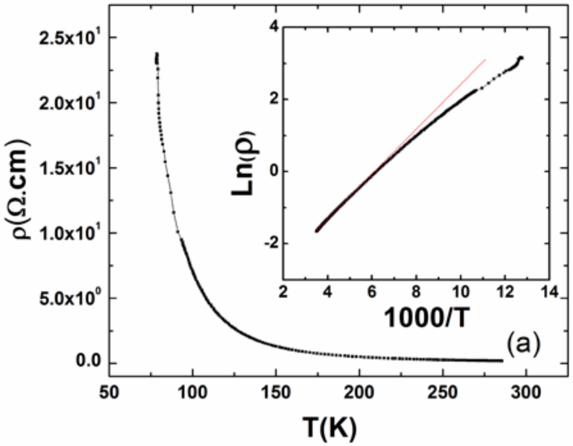
OBJECTIVES & GOALS

- **The objective of this research is:**
  - investigate and understand the mechanisms of mixed ionic electronic conductive $LaBaCo_2O_{5+\delta}$ highly epitaxial thin-films
  - establish the relationship between electrochemical properties and surface/interface microstructure of the mixed conductive thin films
  - determine the overall feasibility of the $LaBaCo_2O_{5.5+\delta}$ based novel electrochemical devices for sensing gases in high temperature applications.
- **The goals of this research are:**
  - resolving and optimizing fabrication issues of highly epitaxial $LaBaCo_2O_{5+\delta}$ single crystalline thin films
  - establishing relationship of processing—microstructure—sensing properties—stability of the $LaBaCo_2O_{5+\delta}$ thin film
  - understanding the kinetics and mechanisms of redox processes on the $LaBaCo_2O_{5.5+\delta}$ thin films
  - demonstrating the new concept high temperature, high sensitivity, and chemically stable devices for high temperature applications.

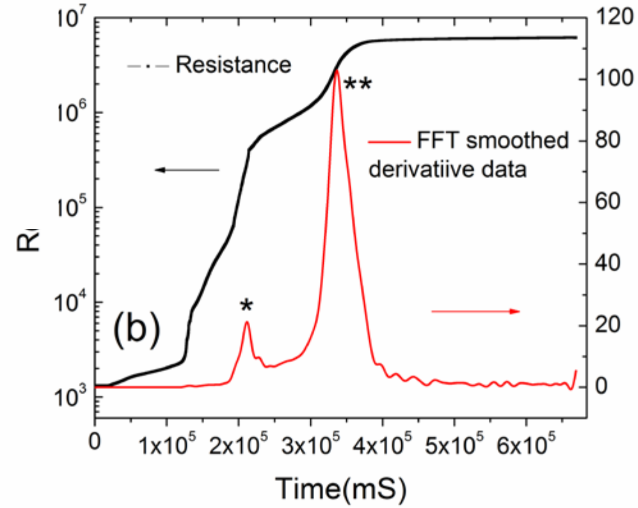
Why LBCO?



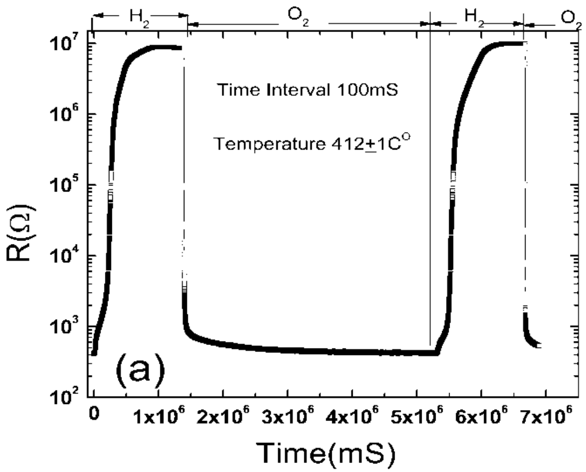
Intensity
LBCO(100)
LAO(001)
LBCO(200)
LAO(002)
LAO(202)
LBCO(204)
ϕ



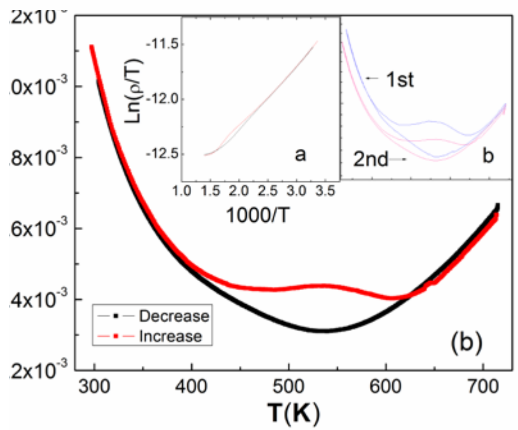
ρ(Ω.cm)
Ln(ρ)
1000/T
T(K)
(a)



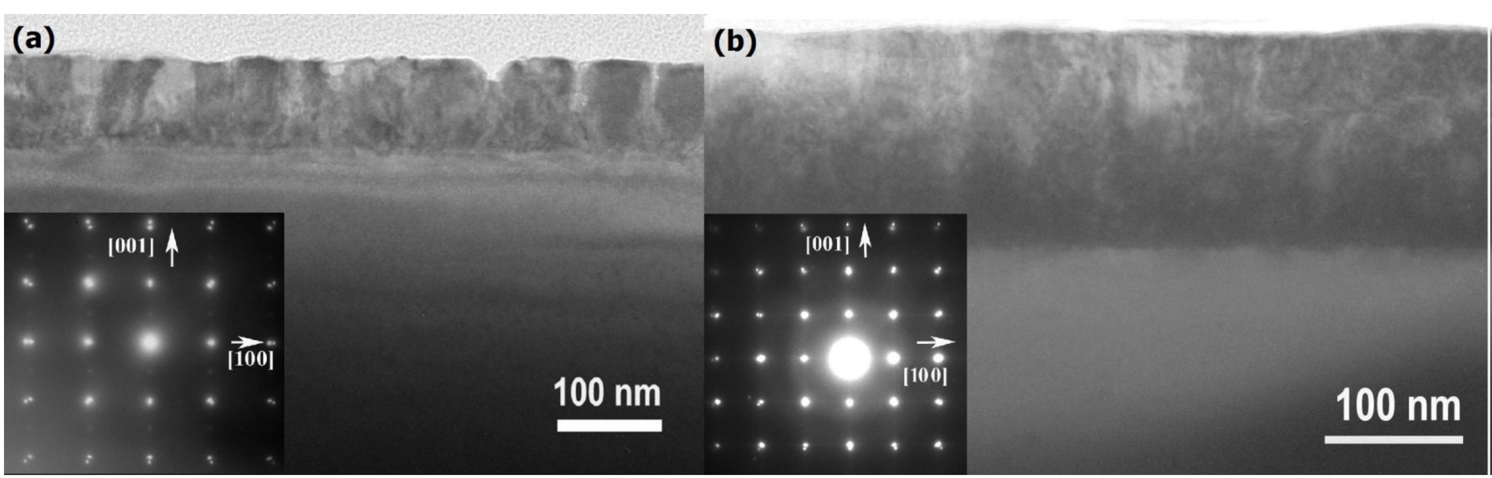
Resistance
FFT smoothed
derivatiive data
Time(mS)
(b)



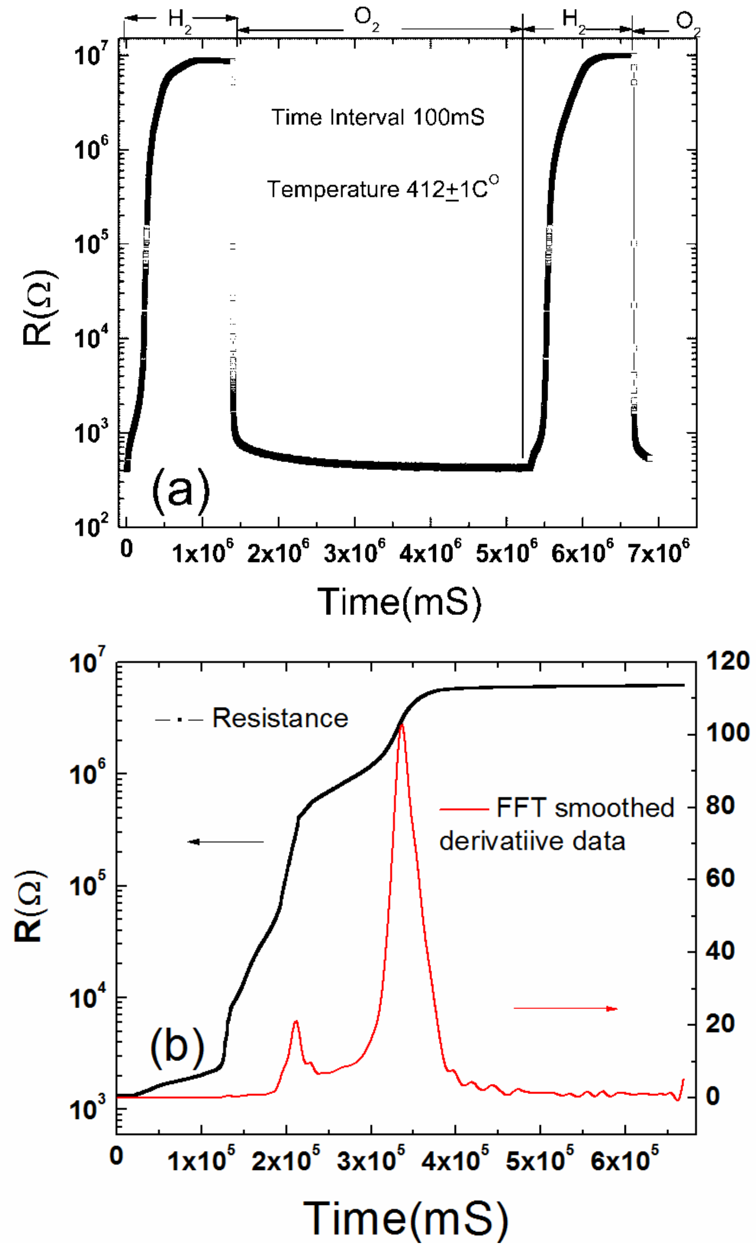
H2
O2
Time Interval 100mS
Temperature 412±1C°
R(Ω)
Time(mS)
(a)

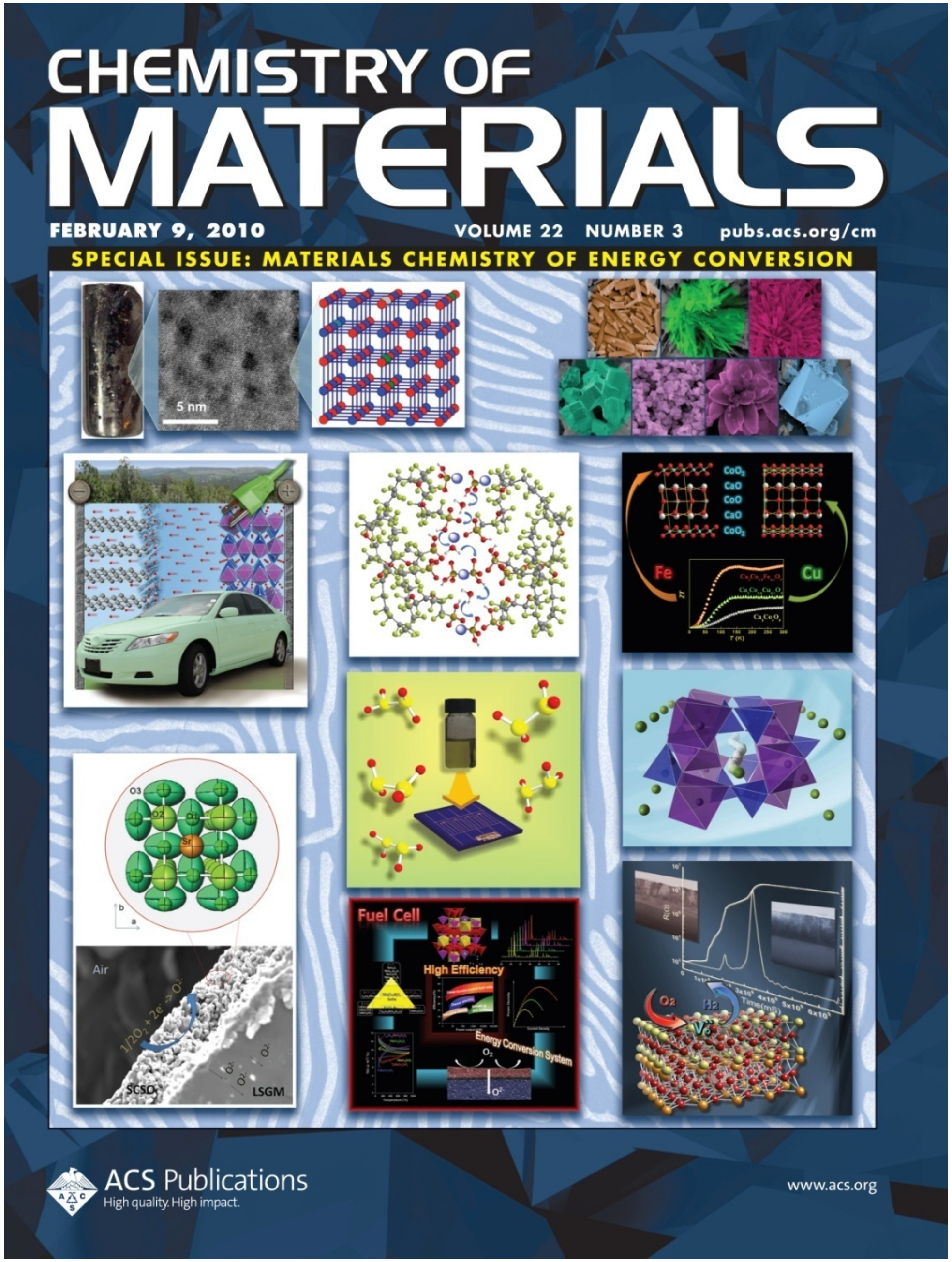


Ln(ρ/T)
1000/T
1st
2nd
Decrease
Increase
T(K)
(b)



(a)
[001]
[100]
100 nm
(b)
[001]
[100]
100 nm





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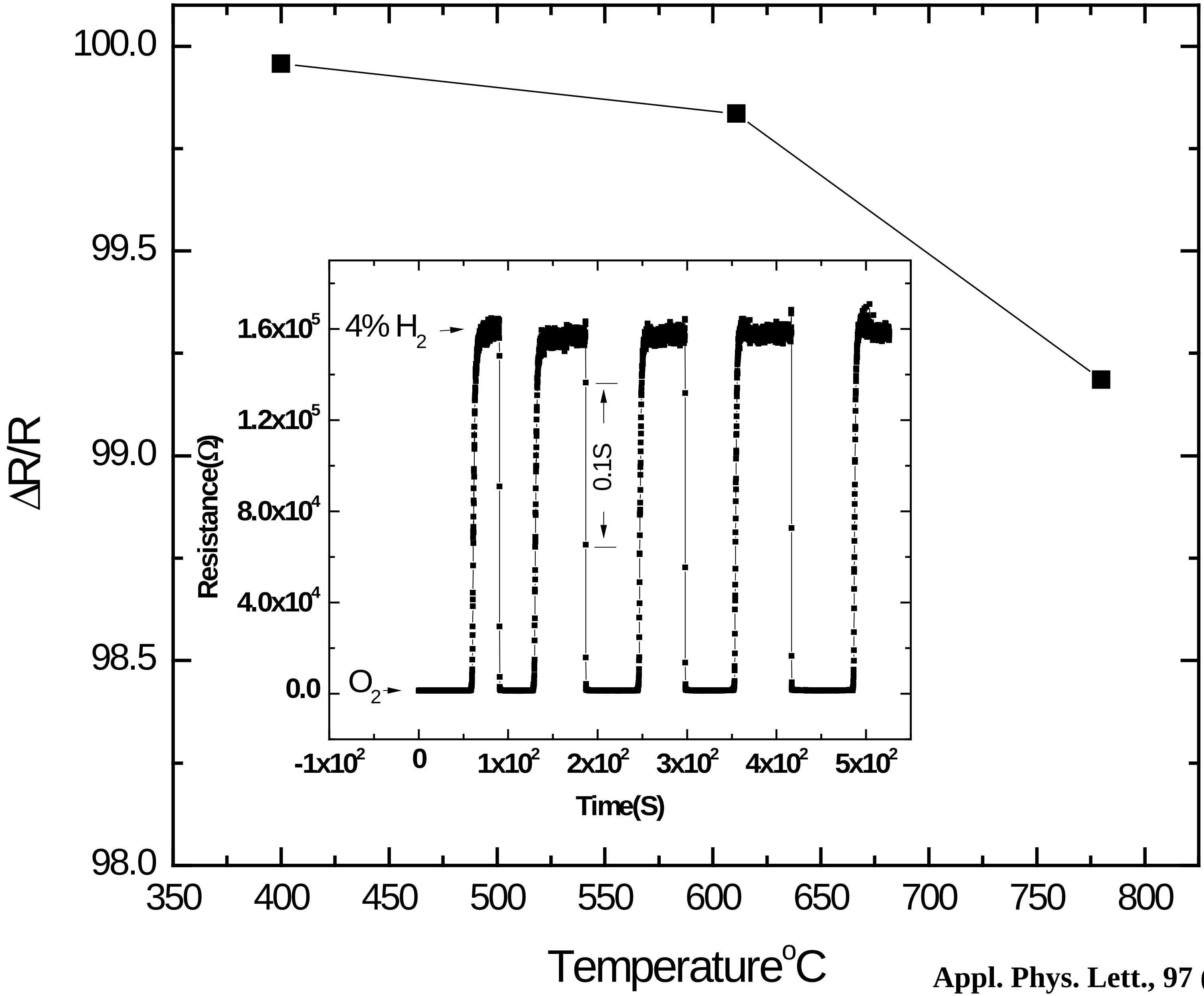
Nanoscale ordered cobaltite $LaBaCo_2O_6$ thin films



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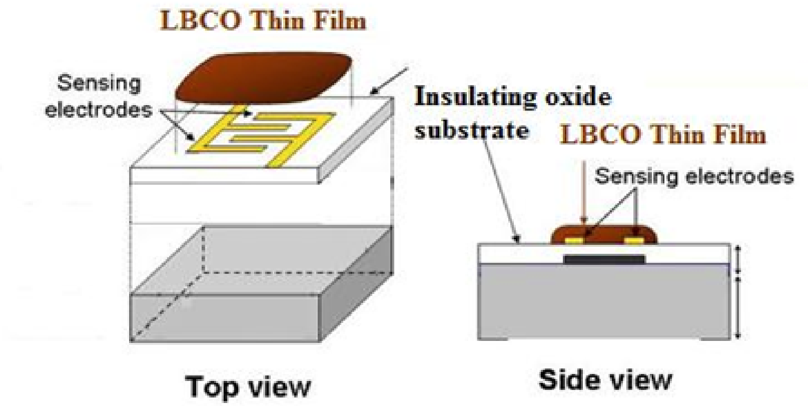
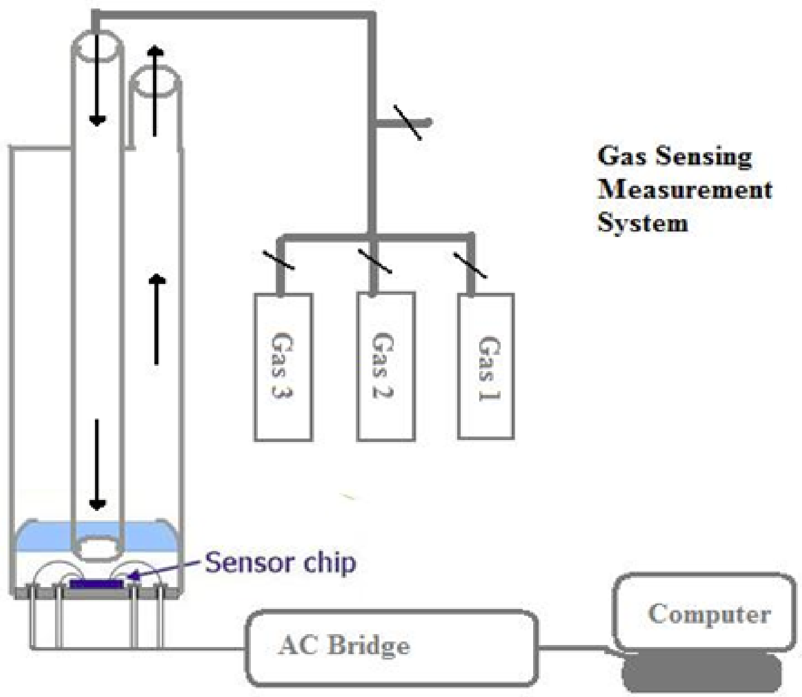
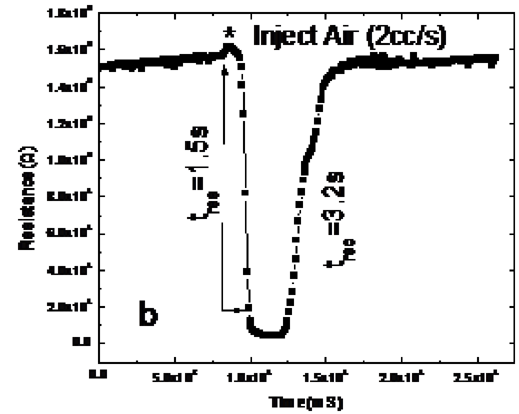
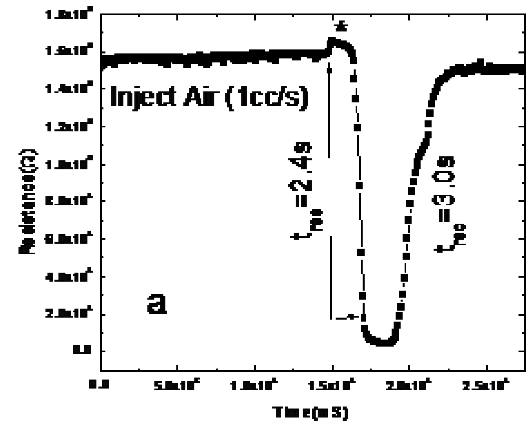
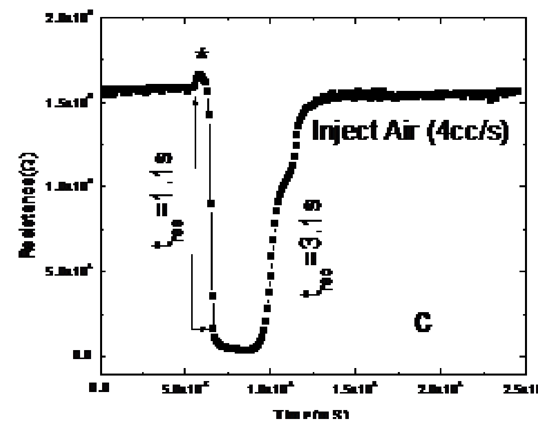
Sensor Structures







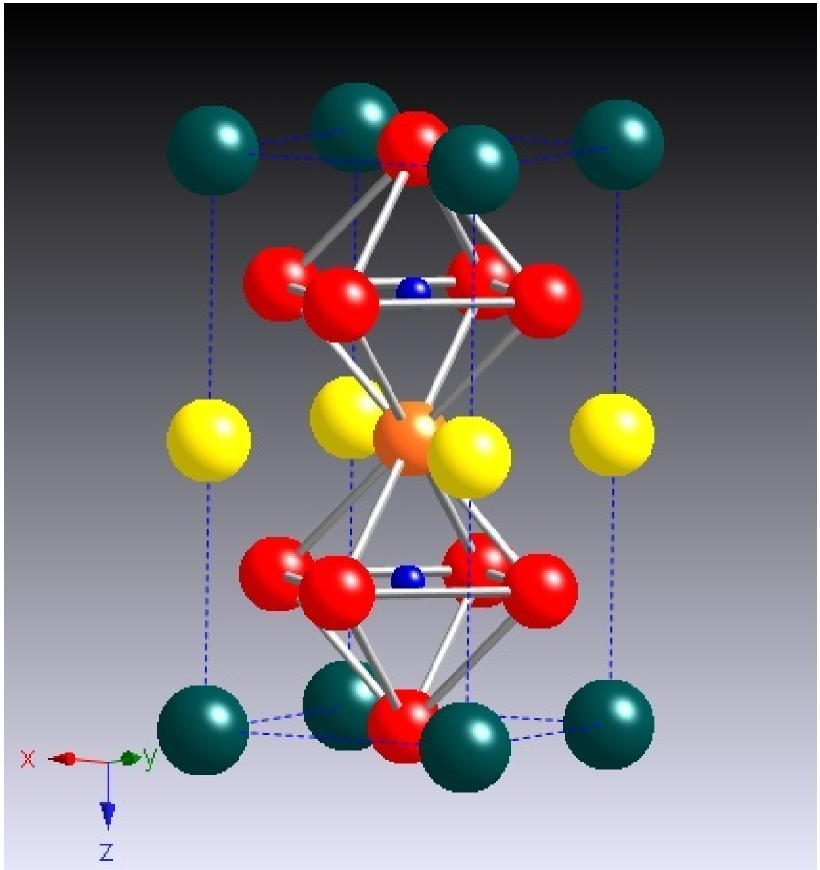




Oxygen Deficient Double Perovskite $(LnBa)Co_2O_{5+\delta}$ (Ln=Lanthanide)

Structure of $LnBaCo_2O_{5+\delta}$

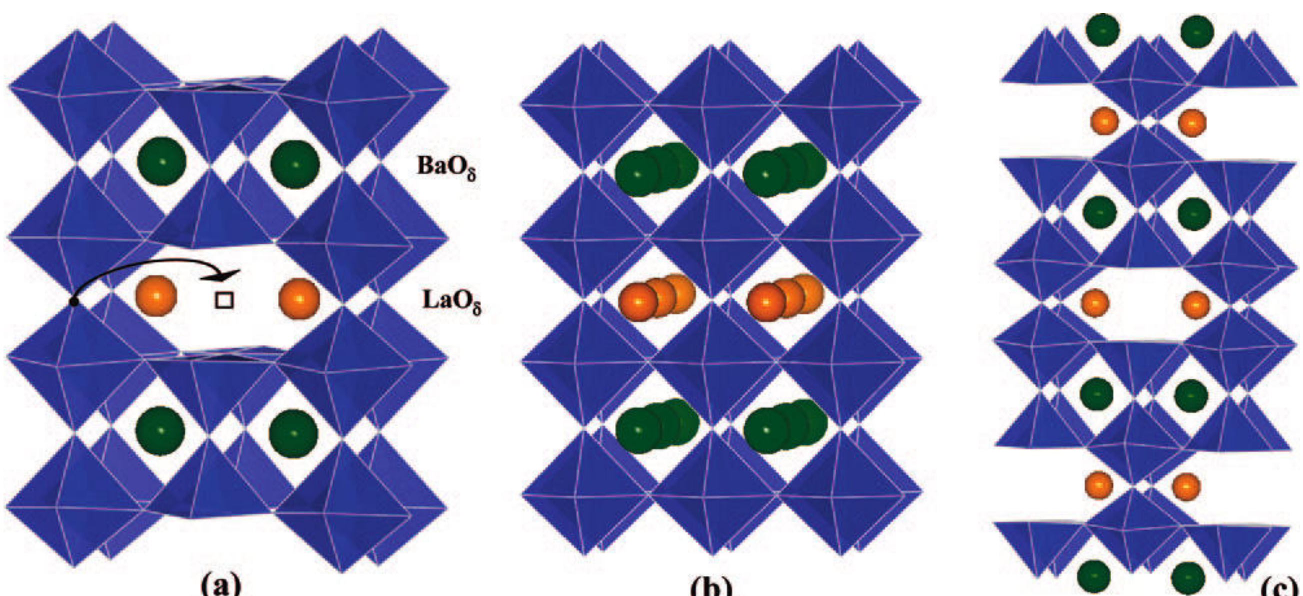
- — **Ba**
- — **Ln**
- — **Co**
- — **O (occupied)**
- — **O (partial occupied)**



$(La, Ba)Co_2O_{5+\delta}$

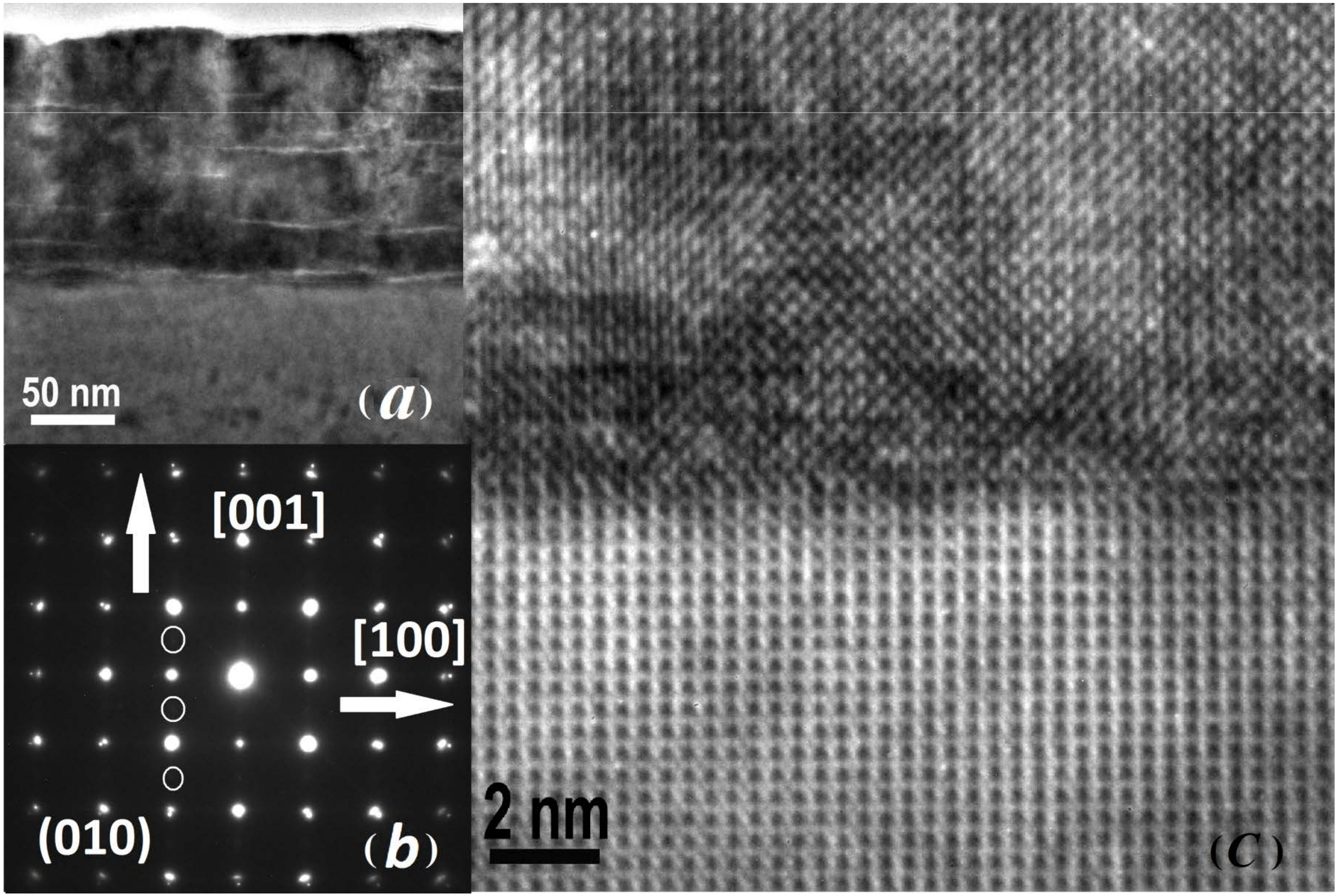
$$Co^{2+} : Co^{3+} = \left(\frac{1}{2} - \delta\right) : \left(\frac{1}{2} + \delta\right) ----- 0 \le \delta \le 0.5$$

$$Co^{4+} : Co^{3+} = \left(\delta - \frac{1}{2}\right) : \left(\frac{3}{2} - \delta\right) ----- 1 \ge \delta \ge 0.5$$



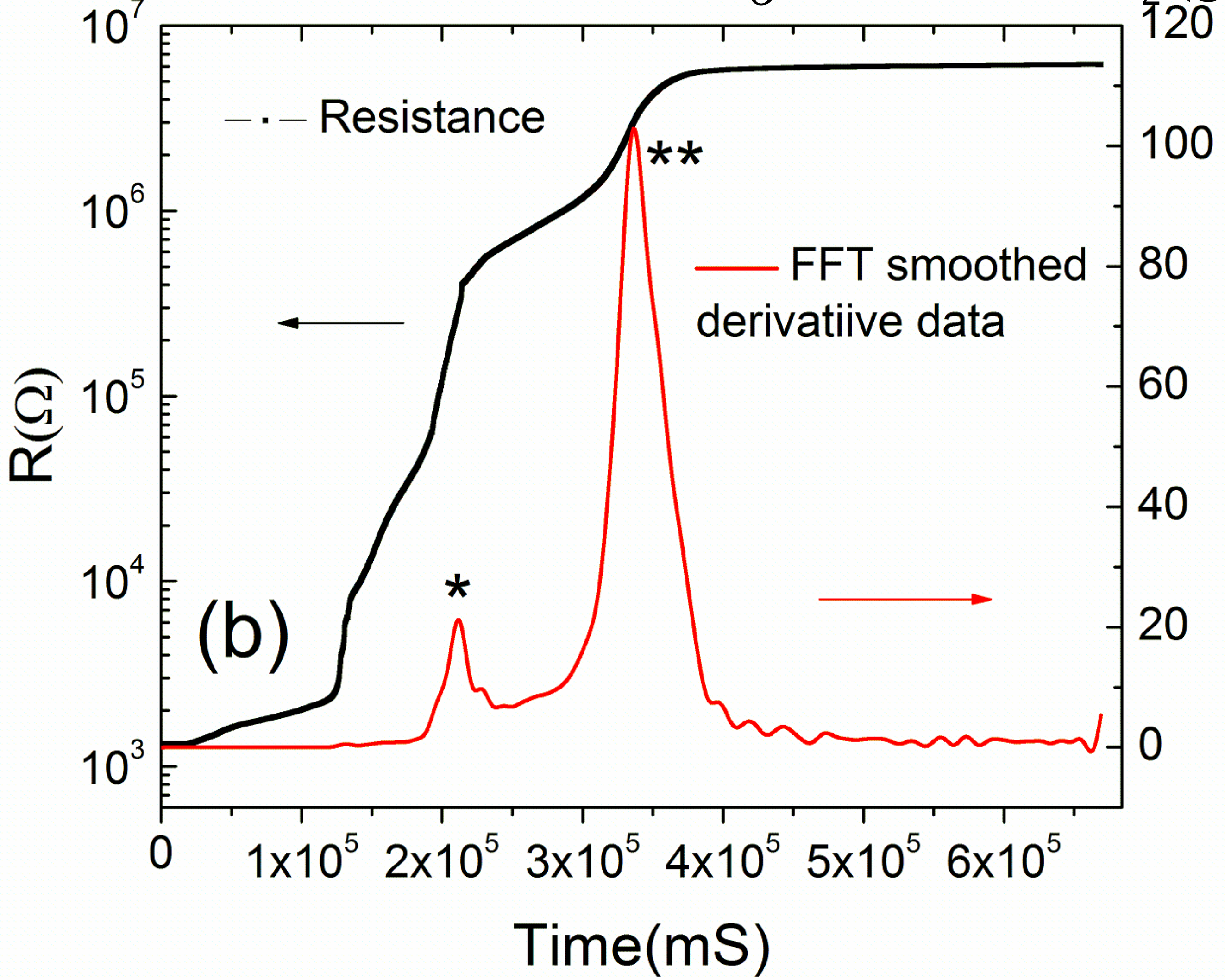
Rautama et , Chem. Mater., Vol. 21, No. 1, 2009.

$LaBaCo_2O_{5+\delta}$ Thin Film on (001)$LaAlO_3$



Transport Properties in 4%H_2 / N_2

$$2O^{2-} + 2Co^{3+} + Co^{4+} \leftrightarrow 2V_O^{\bullet\bullet} + 3Co^{2+} + O_2(g)$$



Transport Properties in O_2

$$LaCoO_3$$

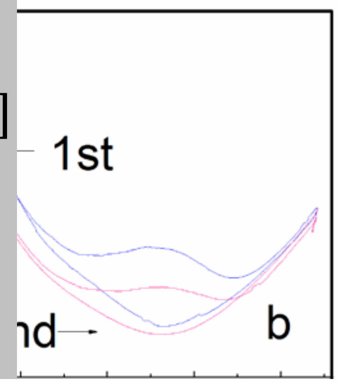
$$2Co^{3+} \leftrightarrow Co^{2+} + Co^{4+}$$

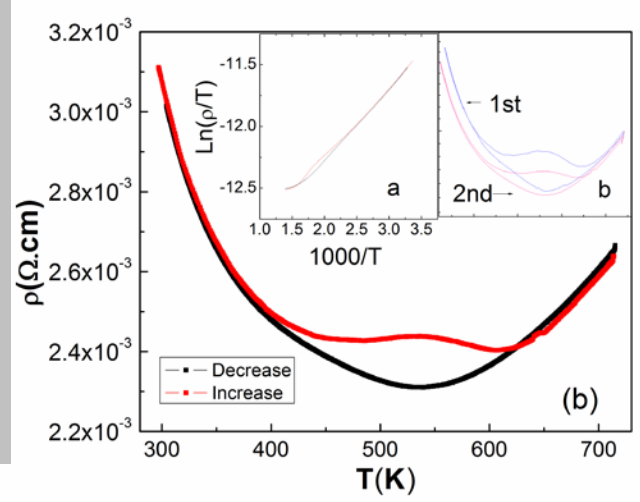
$$Ba^{2+} \Leftrightarrow (La^{3+}Ba^{2+})(Co^{3+}Co^{4+})O_{5+\delta} \mapsto [Co^{4+}] + [V_O]$$

$$O^{2-} + 2Co^{4+} \leftrightarrow V_O + 2Co^{3+} + \frac{1}{2}O_2$$

$$O_{ad}{}^{2-} \leftrightarrow 2e^{-} + \frac{1}{2}O_2$$

$$T\uparrow \Rightarrow [e^{-}]\uparrow \& [h]\downarrow$$





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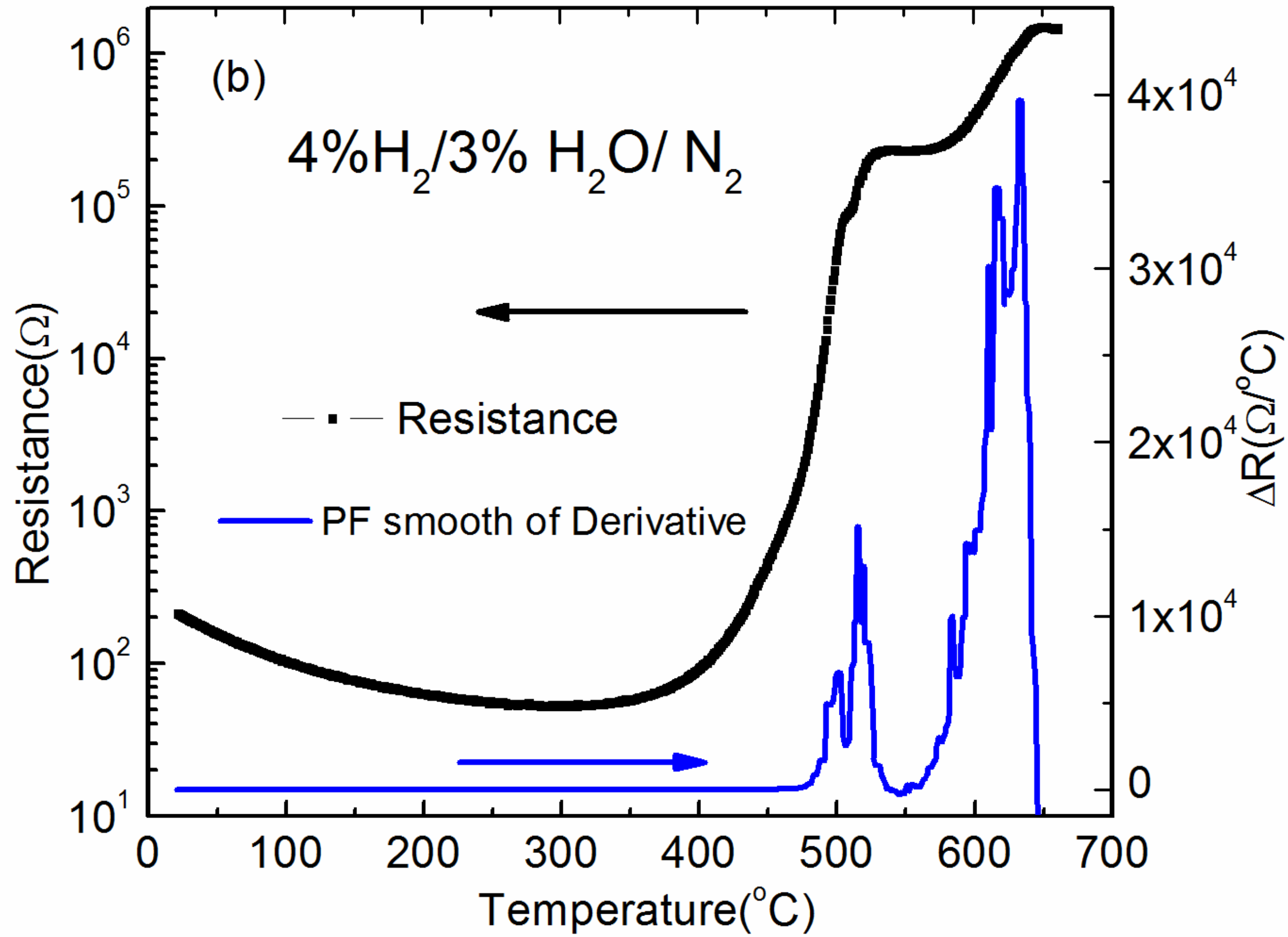
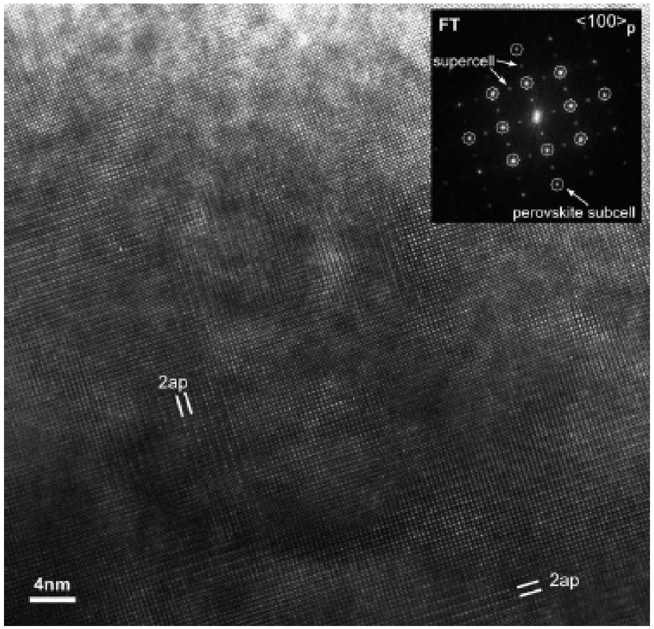
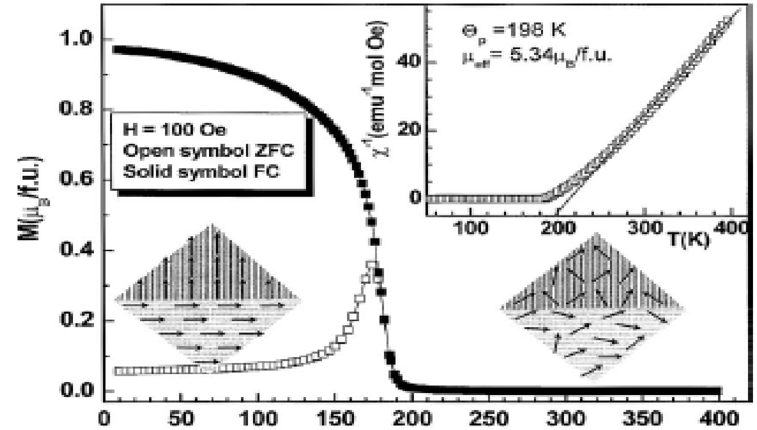
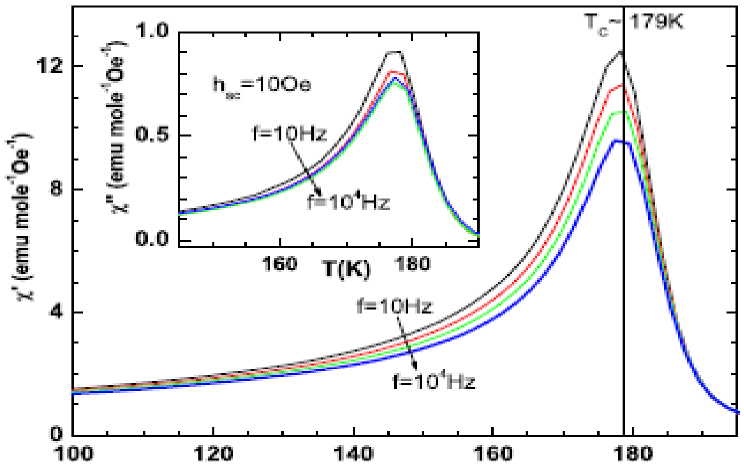
Transport Properties in 4%H_2 / N_2

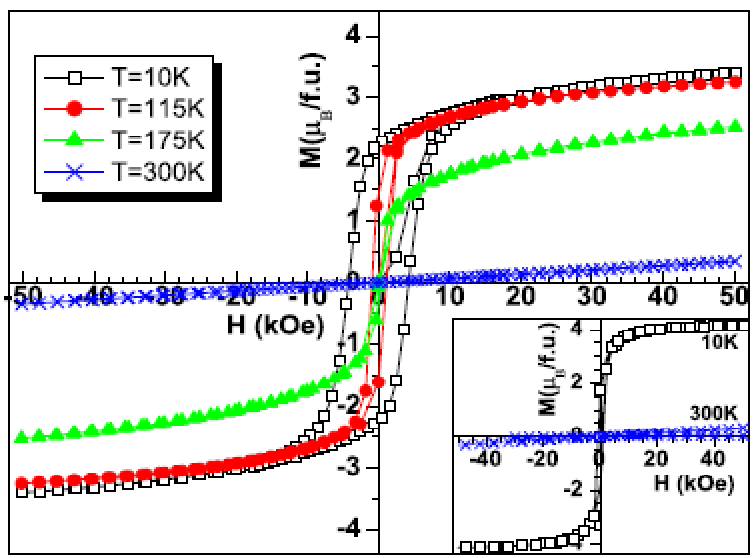


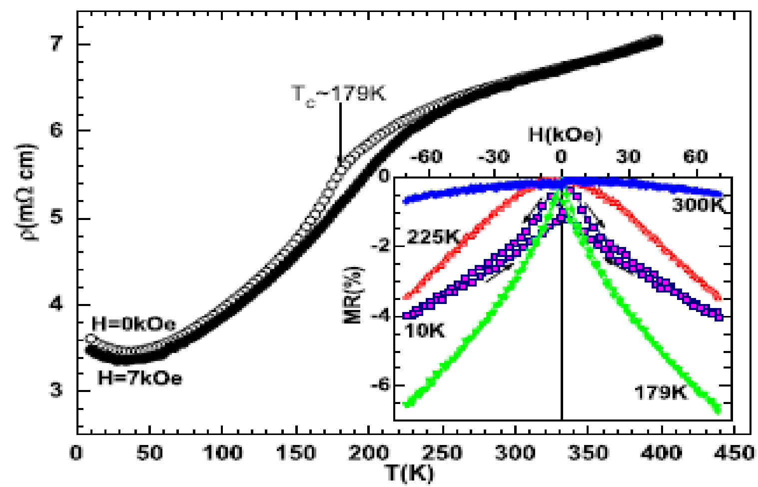
Nanoscale ordered cobaltite $LaBaCo_2O_6$



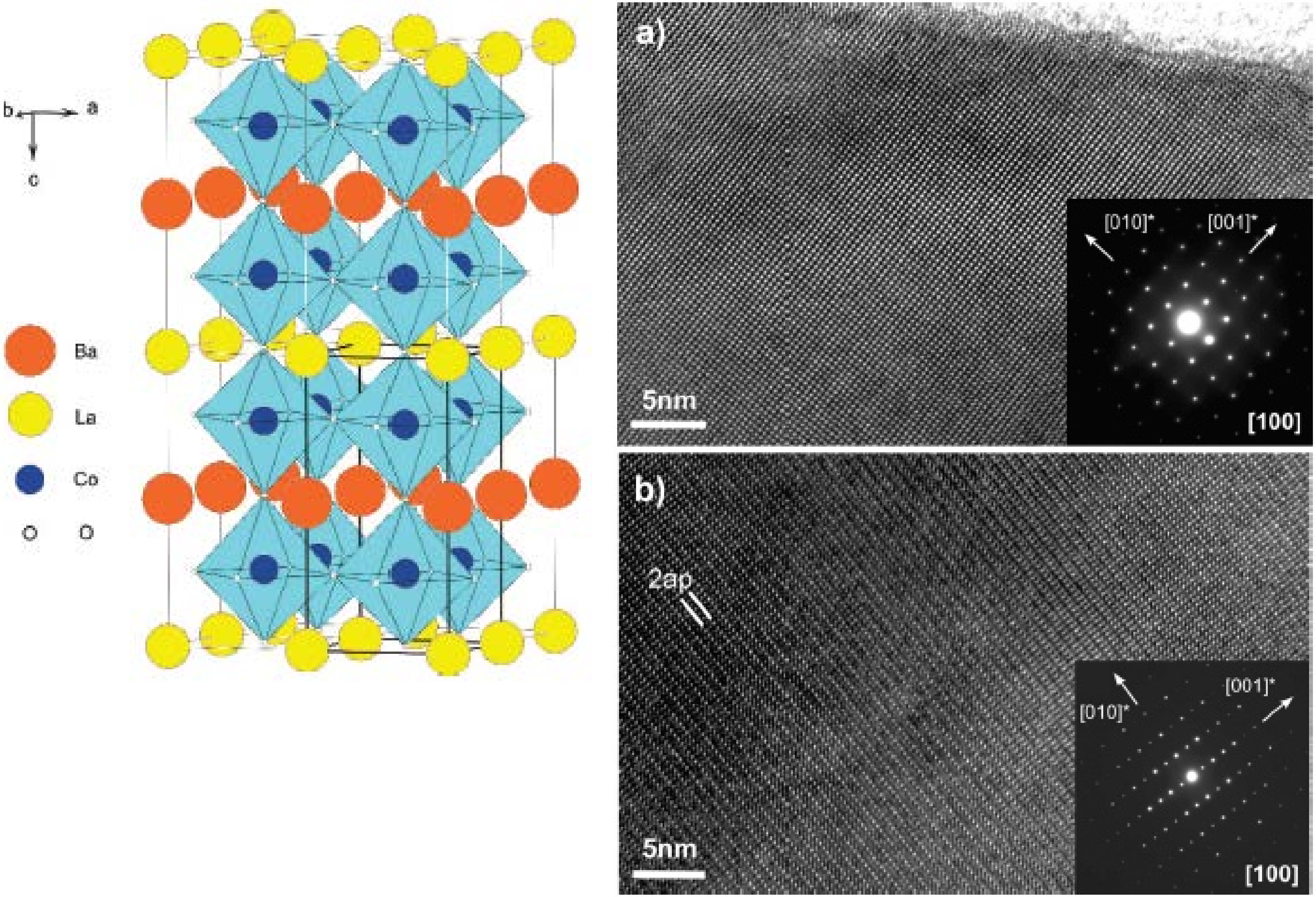




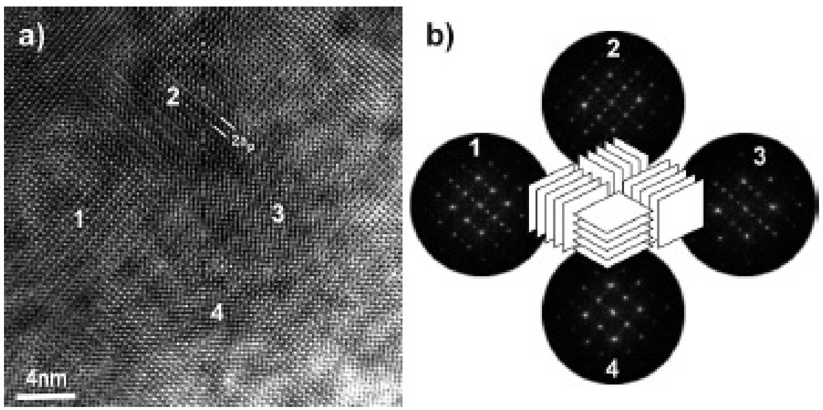


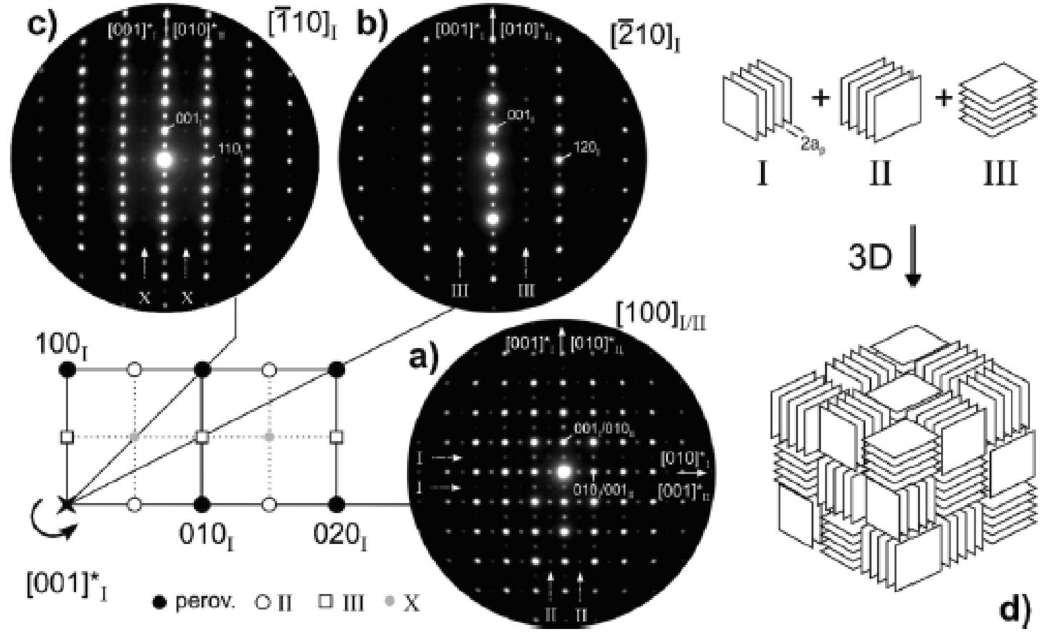


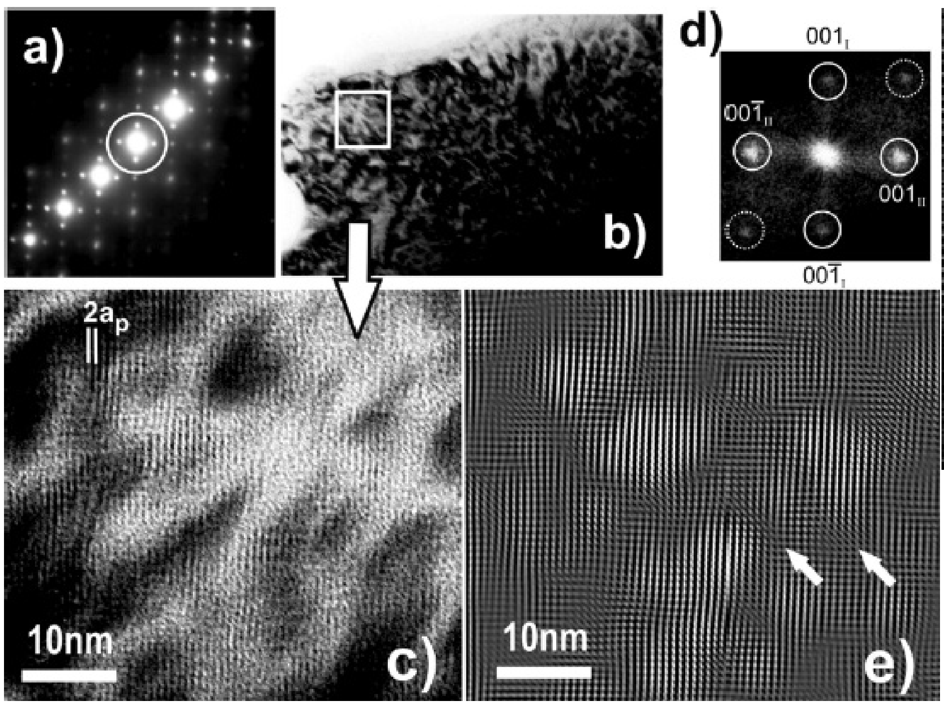
Nanoscale ordered cobaltite $LaBaCo_2O_6$

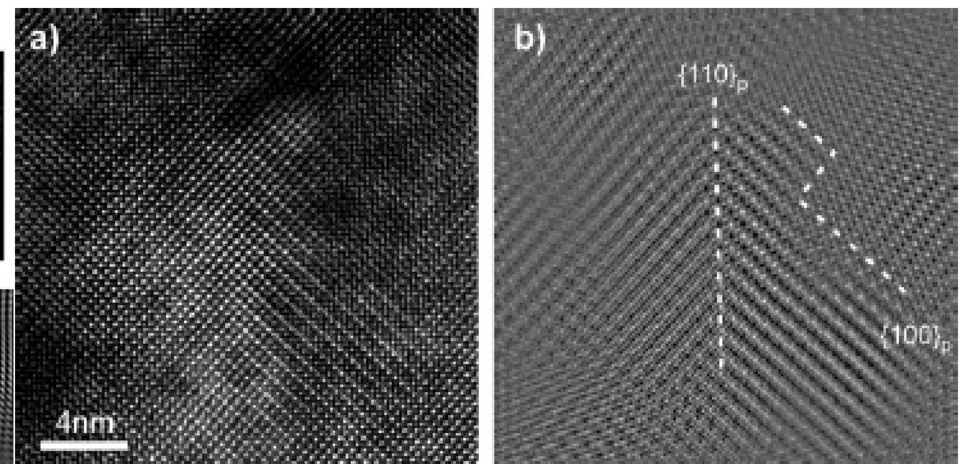


Nanoscale ordered cobaltite $LaBaCo_2O_6$









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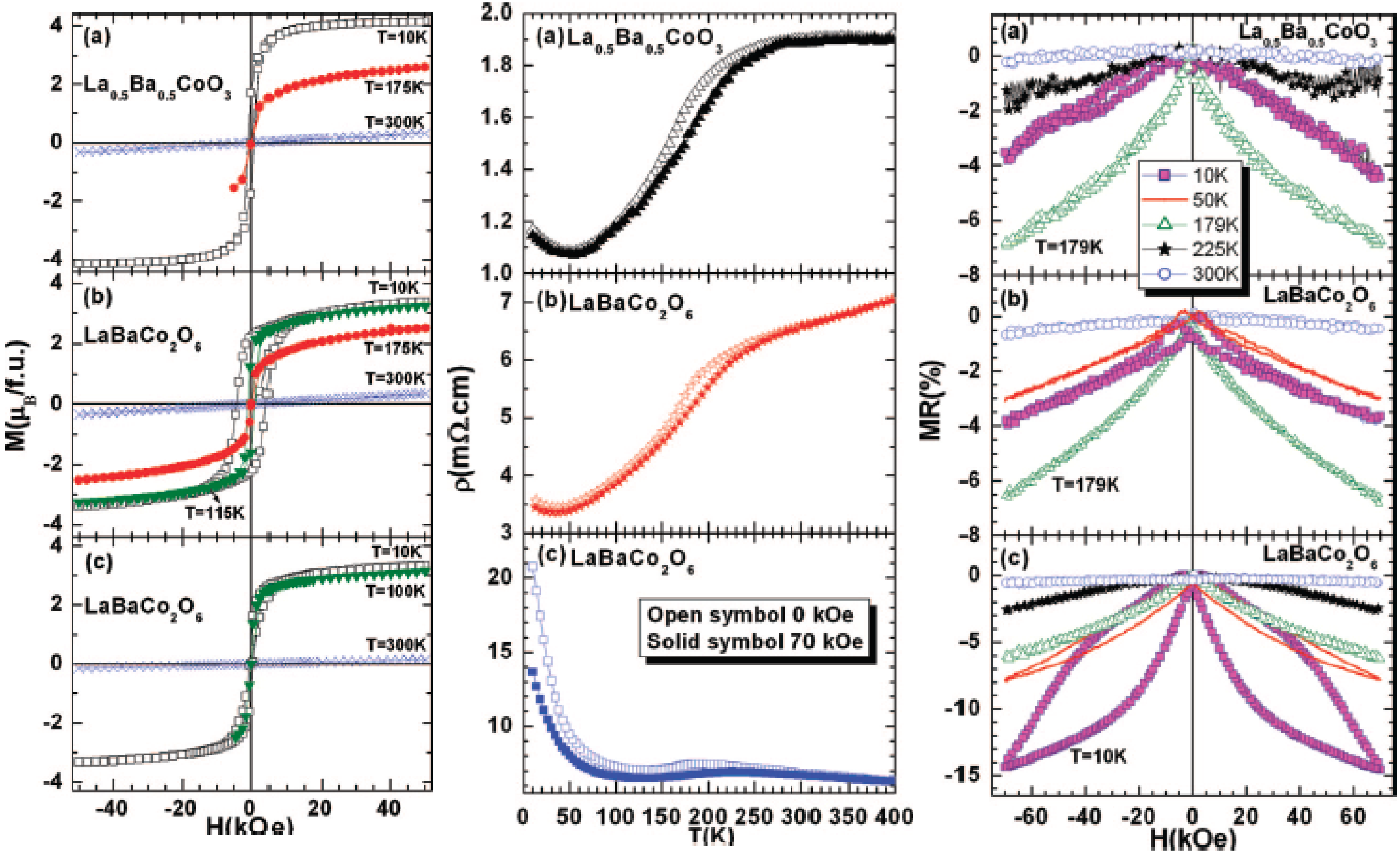
Physical Properties of cobaltite $LaBaCo_2O_6$

Disordering

Nano-Ordering

Ordering



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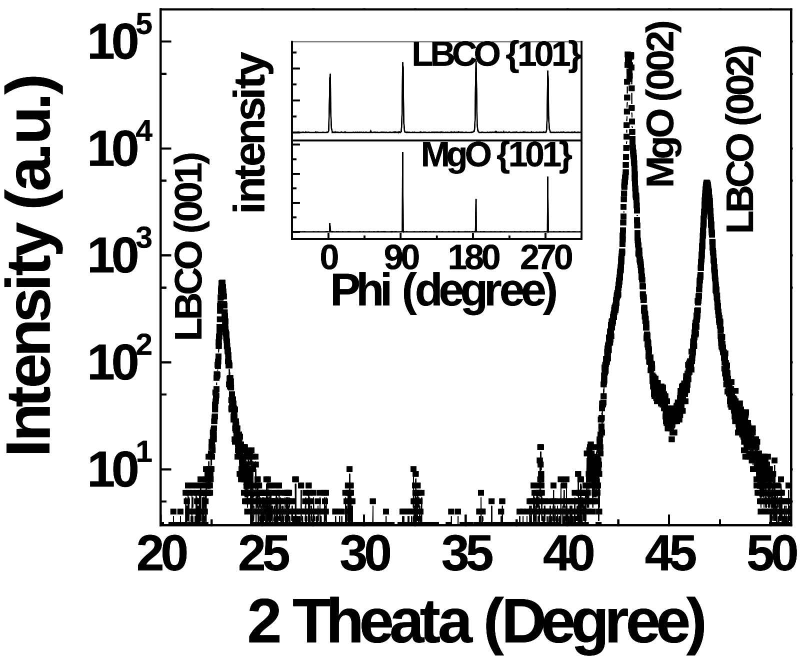
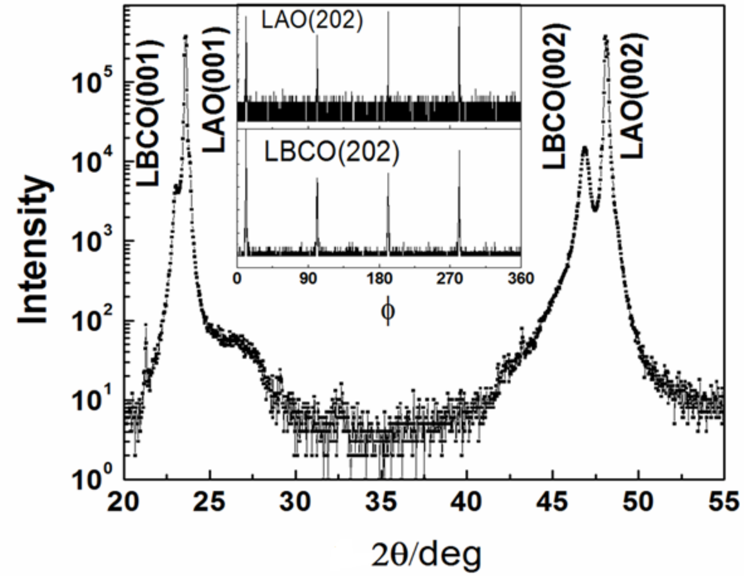
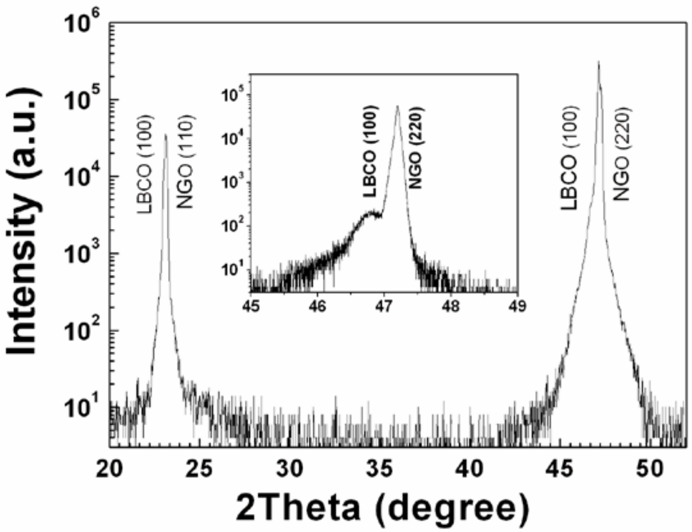
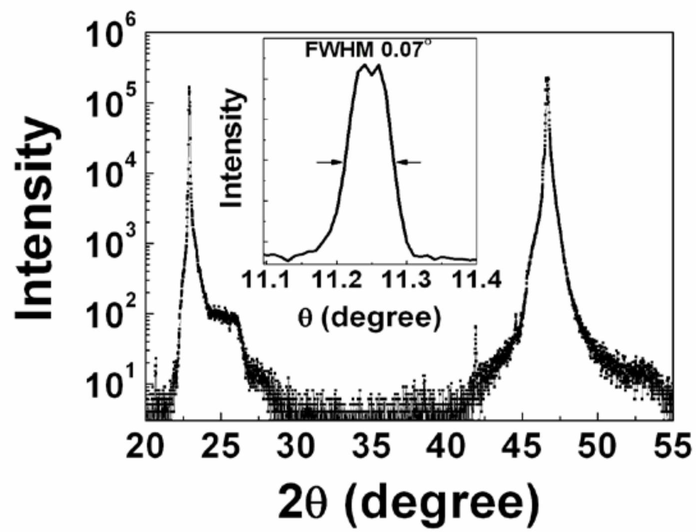
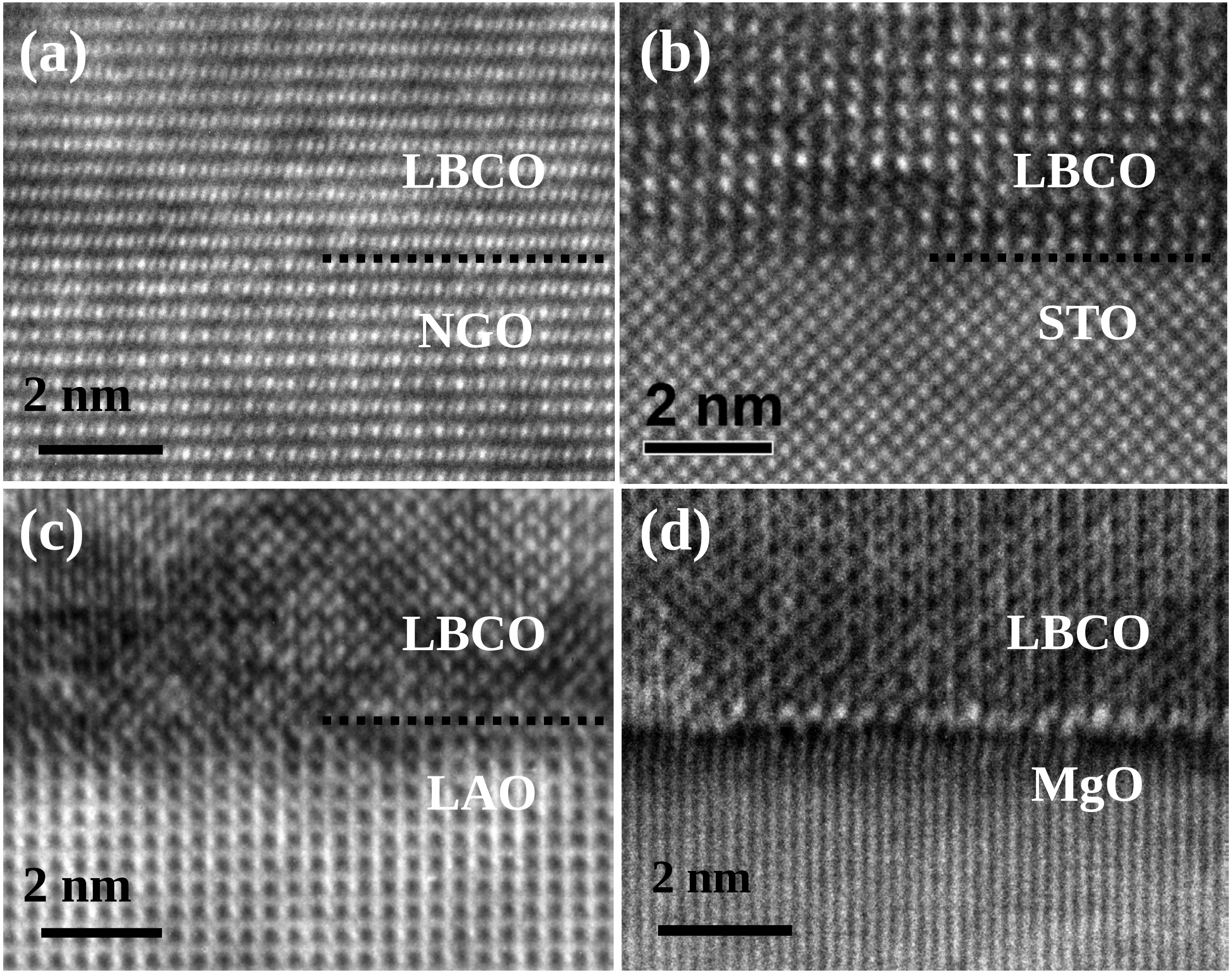

Intensity (a.u.)
2 Theata (Degree)
LBCO (001)
MgO (002)
LBCO (002)
intensity
LBCO {101}
MgO {101}
Phi (degree)


Intensity
2θ/deg
LBCO(001)
LAO(001)
LBCO(002)
LAO(002)
LAO(202)
LBCO(202)
ϕ

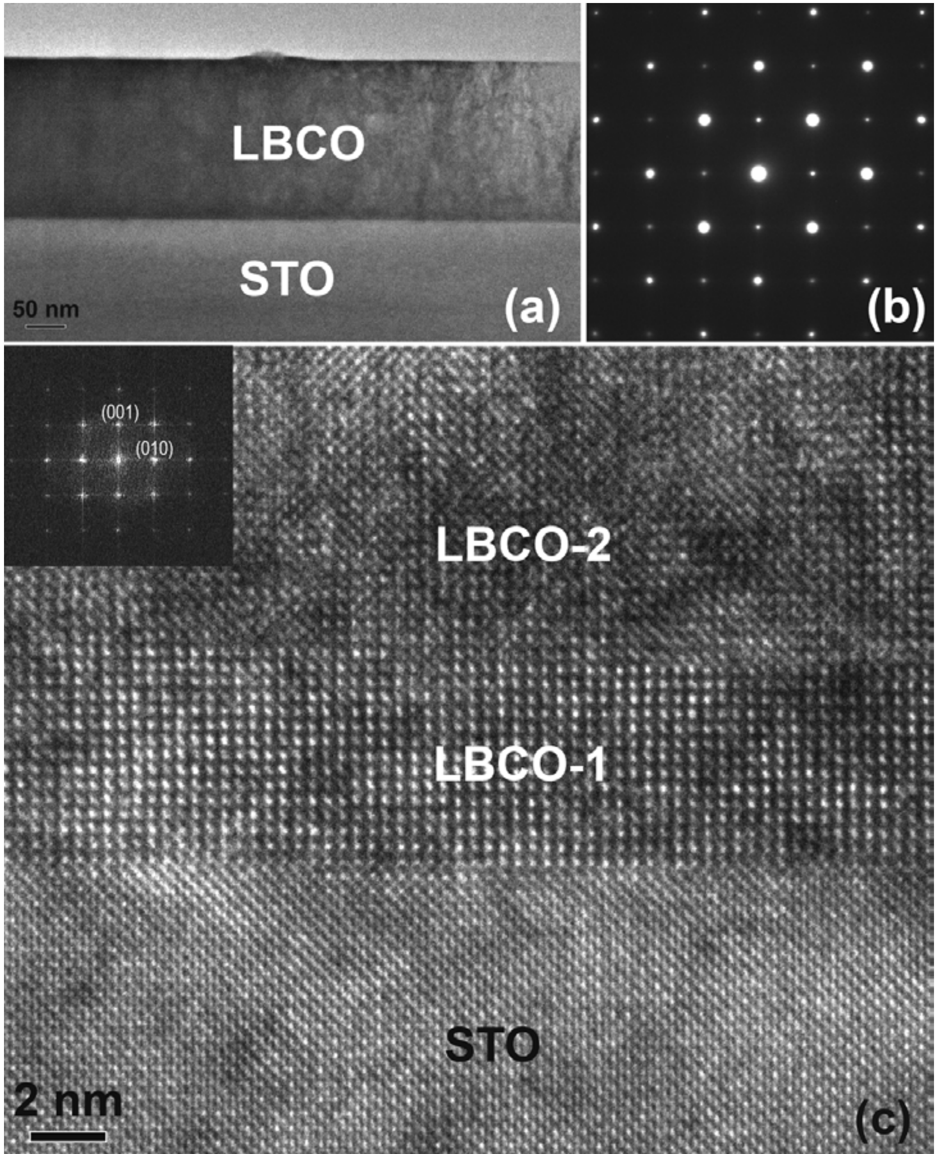

Intensity (a.u.)
2Theta (degree)
LBCO (100)
NGO (110)
LBCO (100)
NGO (220)

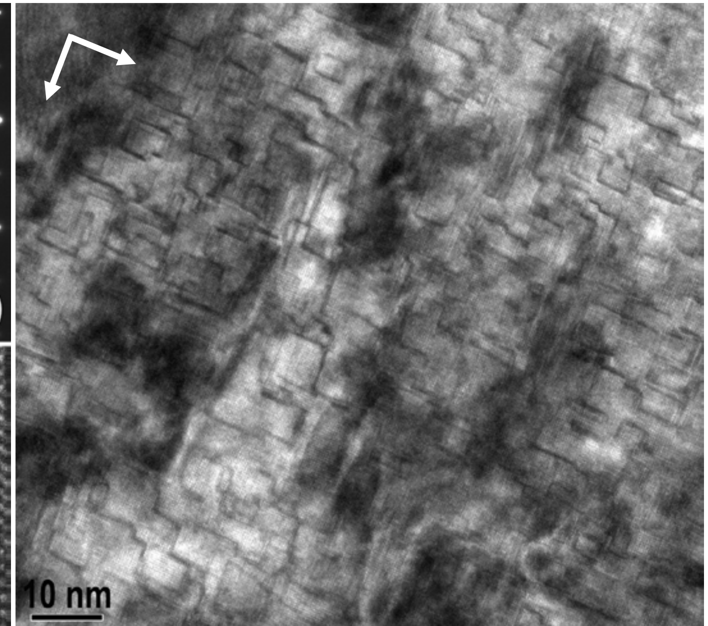

Intensity
2θ (degree)
FWHM 0.07°
θ (degree)

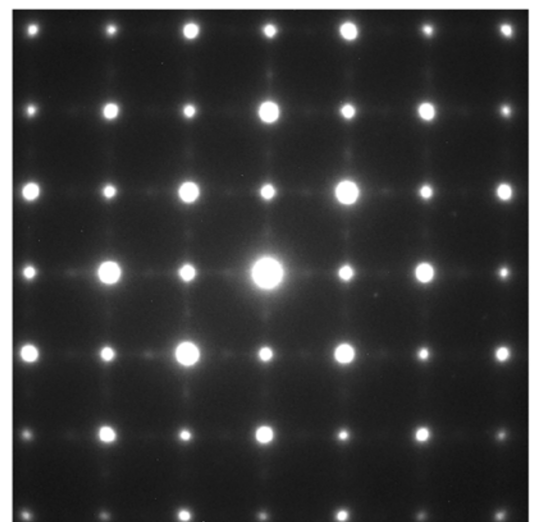
Nanoscale ordered cobaltite LaBaCo2O6



Highly epitaxial nanoscale ordered cobaltite $LaBaCo_2O_6$ thin films







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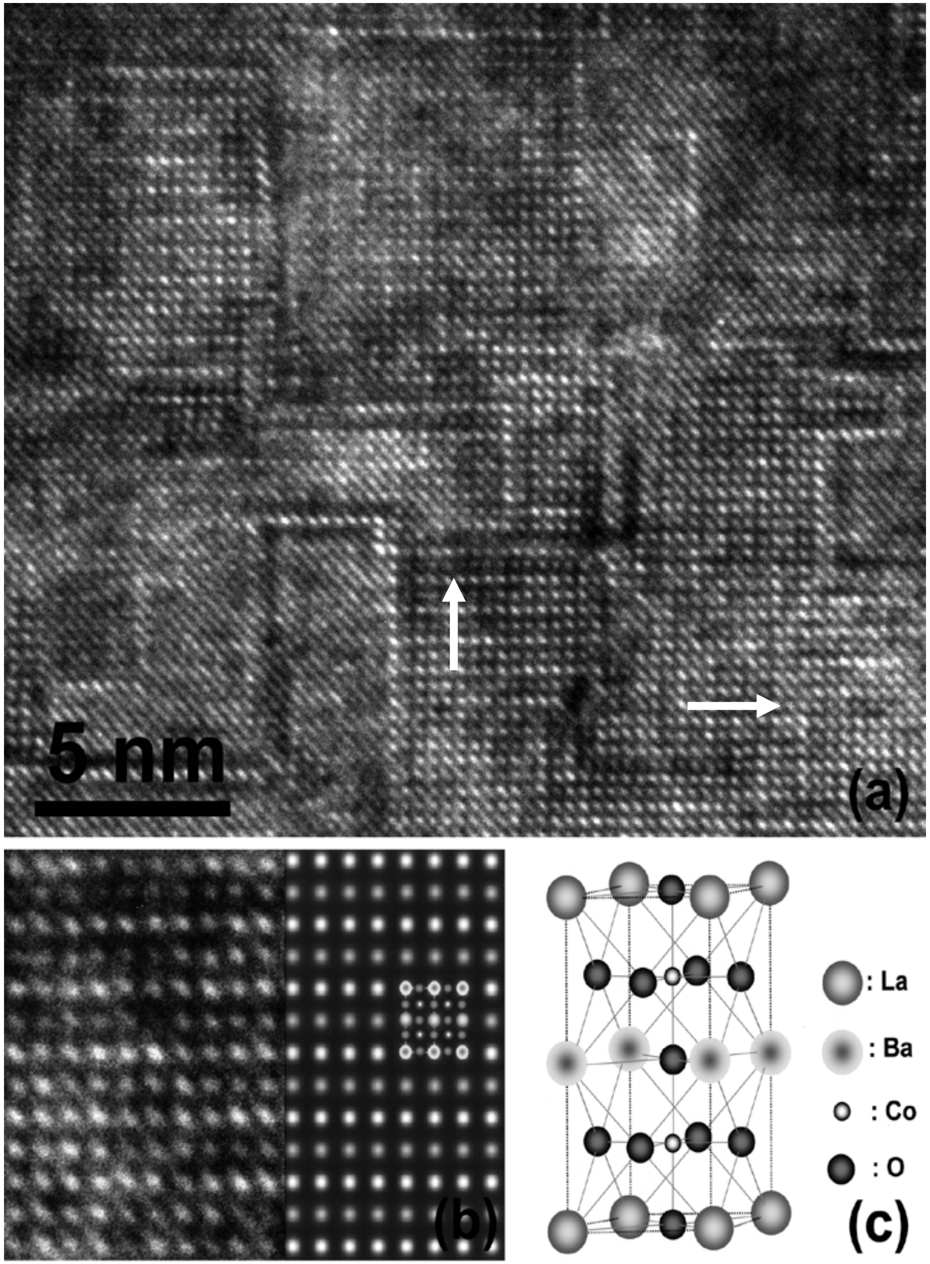
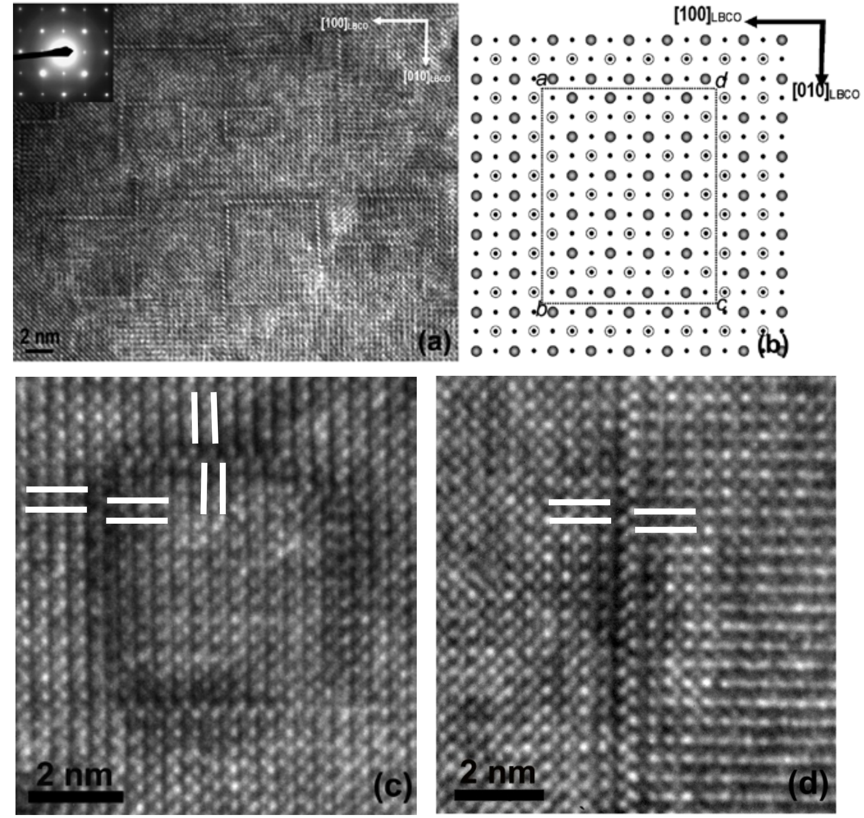
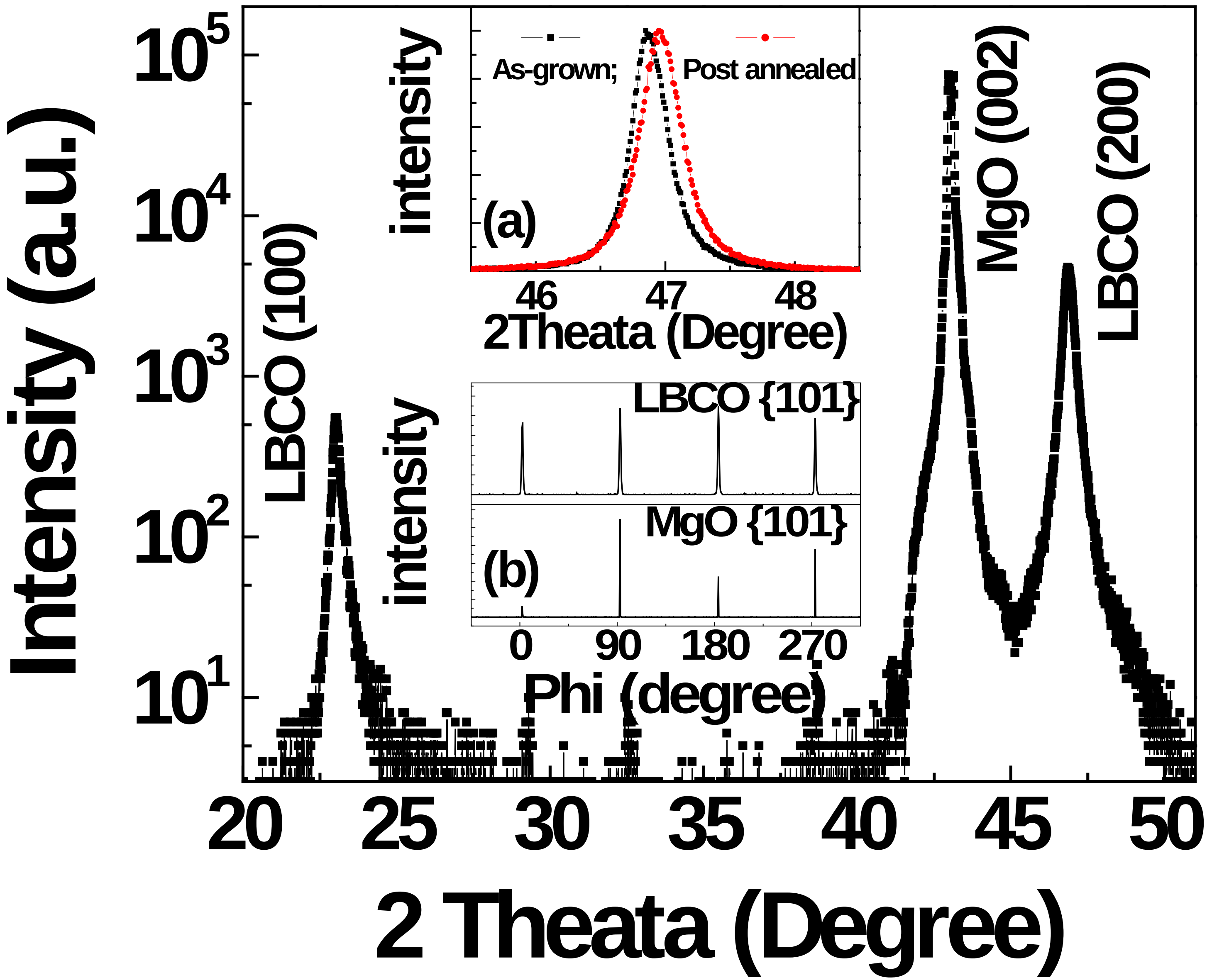
Nanoscale ordered $LaBaCo_2O_6$ thin films

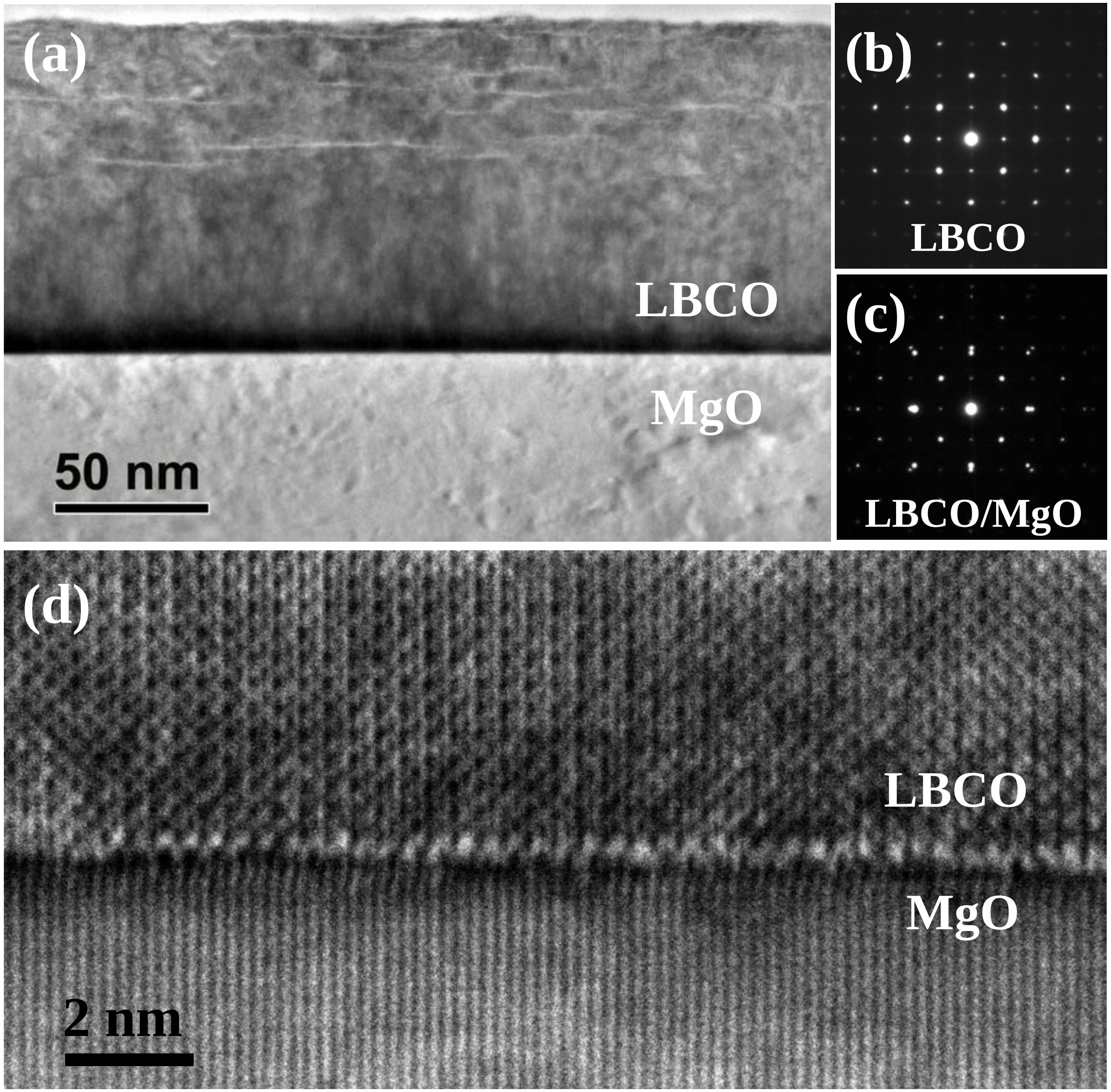


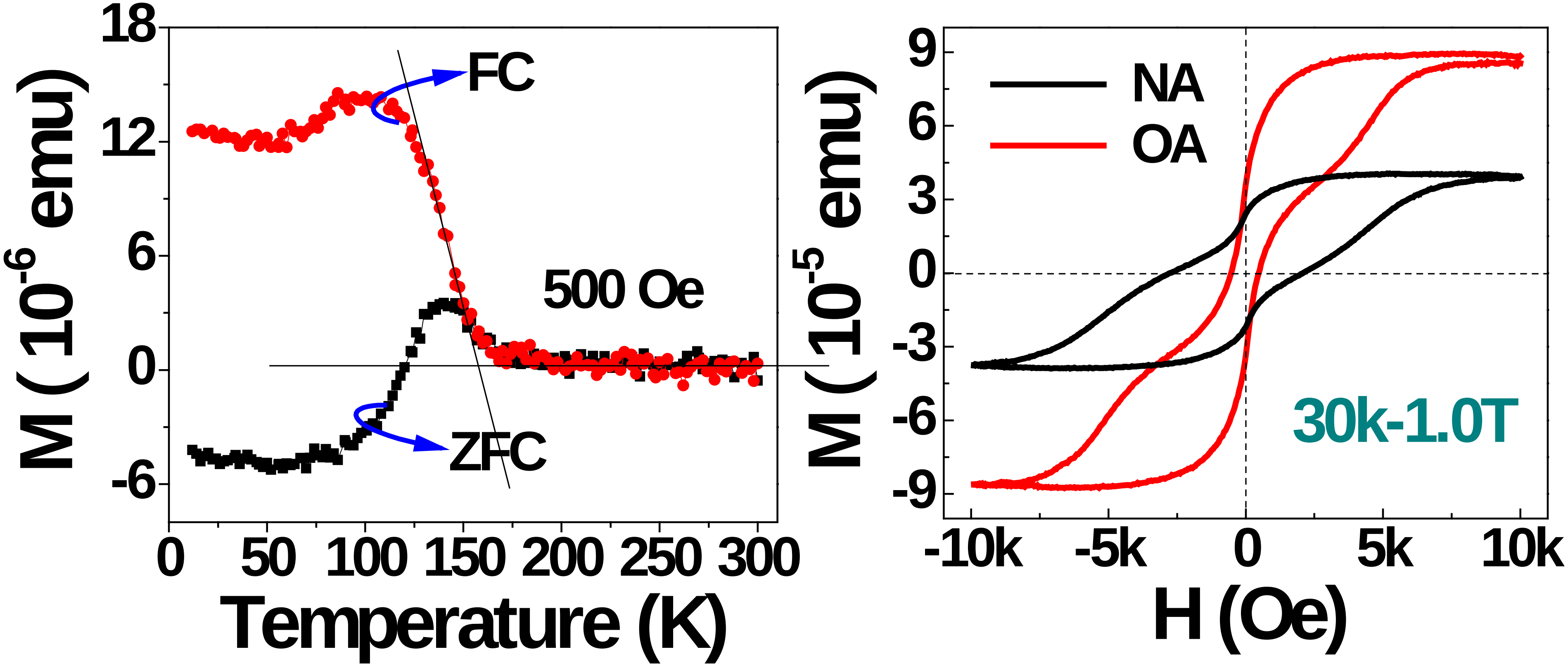


Appl. Phys. Let., 96 (2010) 132106

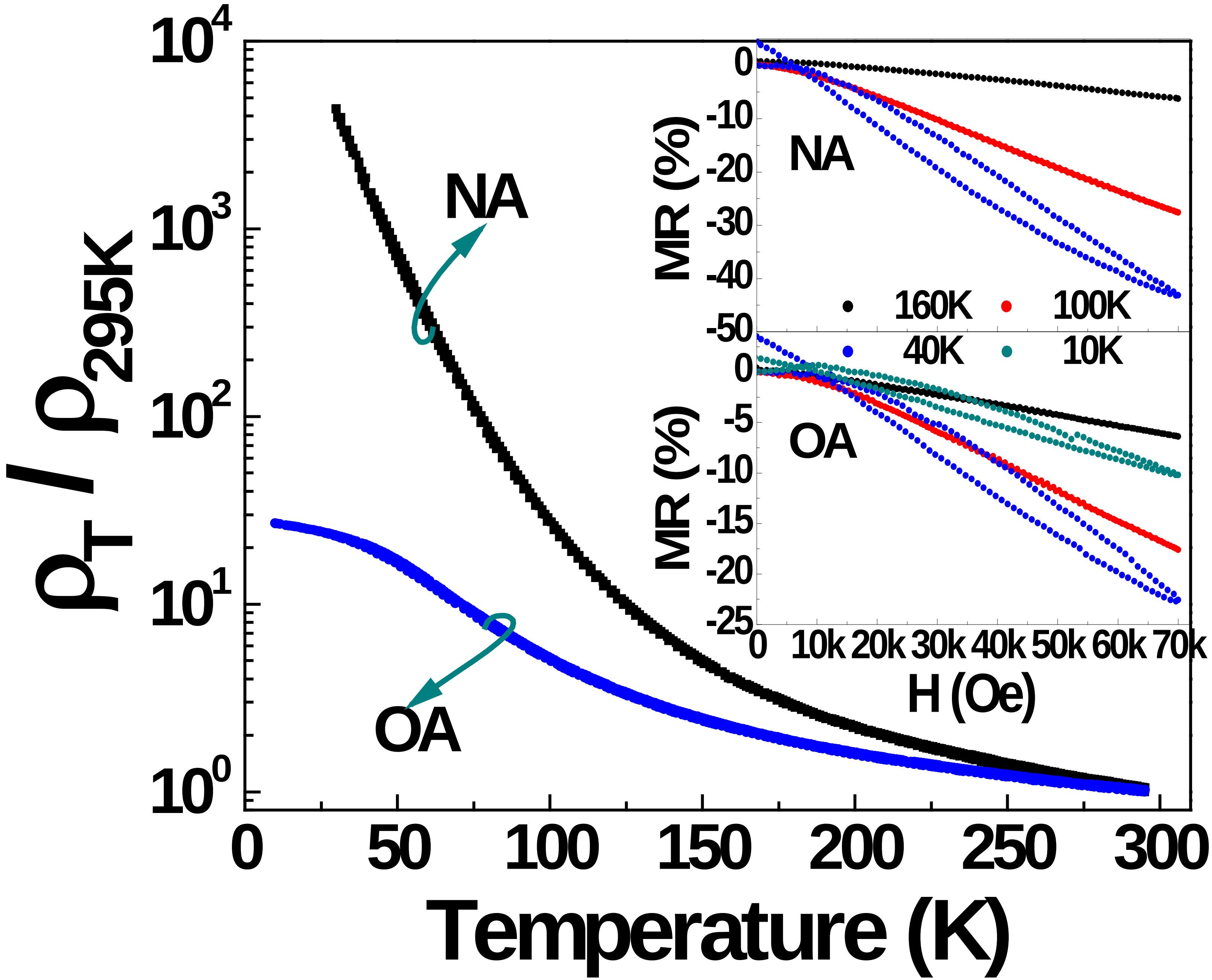


Intensity (a.u.)
10^5
10^4
10^3
10^2
10^1
20
25
30
35
40
45
50
2 Theata (Degree)
LBCO (100)
MgO (002)
LBCO (200)
intensity
As-grown;
Post annealed
(a)
46
47
48
2Theata (Degree)
LBCO {101}
MgO {101}
intensity
(b)
0
90
180
270
Phi (degree)

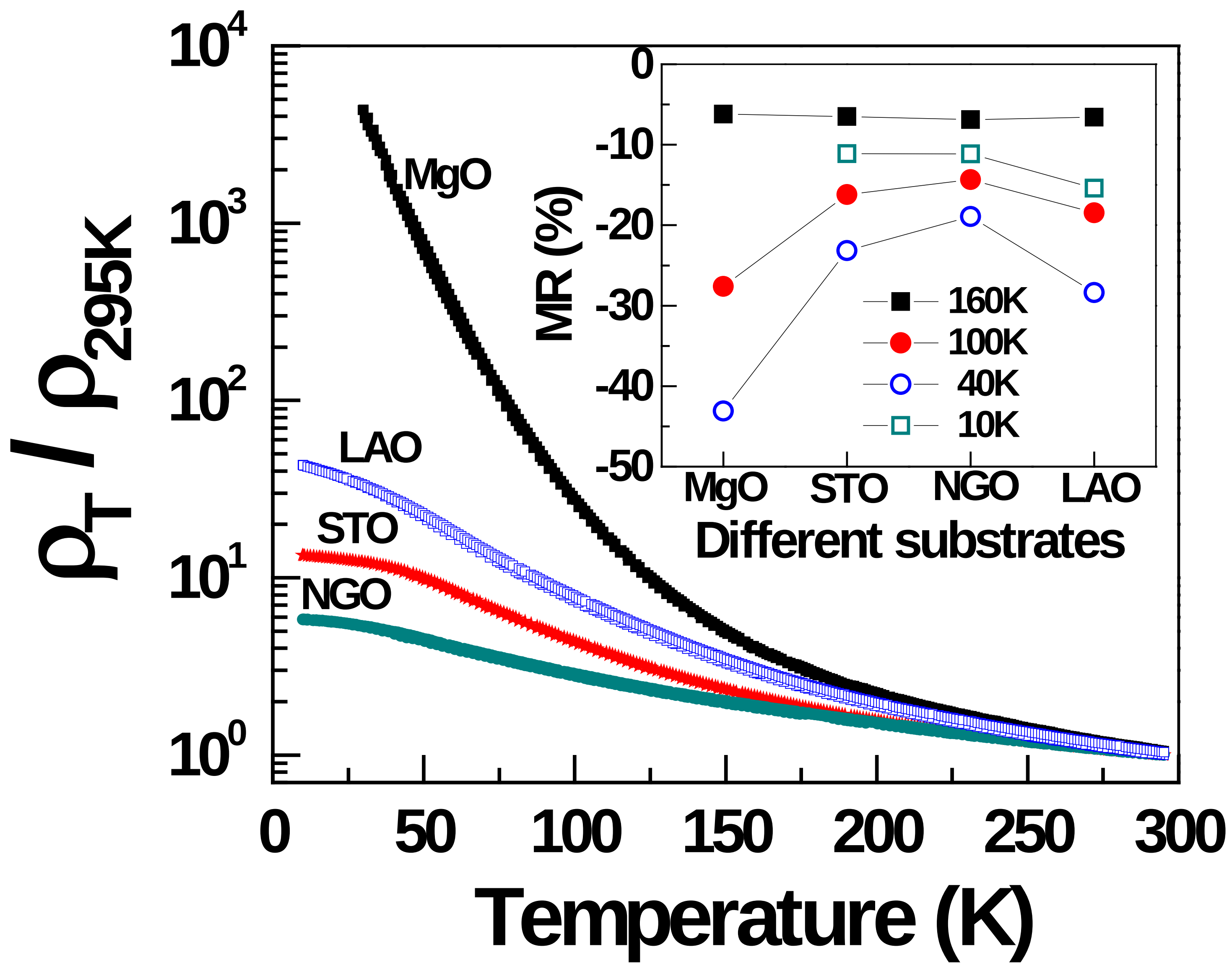

(a)
LBCO
MgO
50 nm
(b)
LBCO
(c)
LBCO/MgO
(d)
LBCO
MgO
2 nm



FC
ZFC
500 Oe
M (10-6 emu)
Temperature (K)
NA
OA
30k-1.0T
M (10-5 emu)
H (Oe)

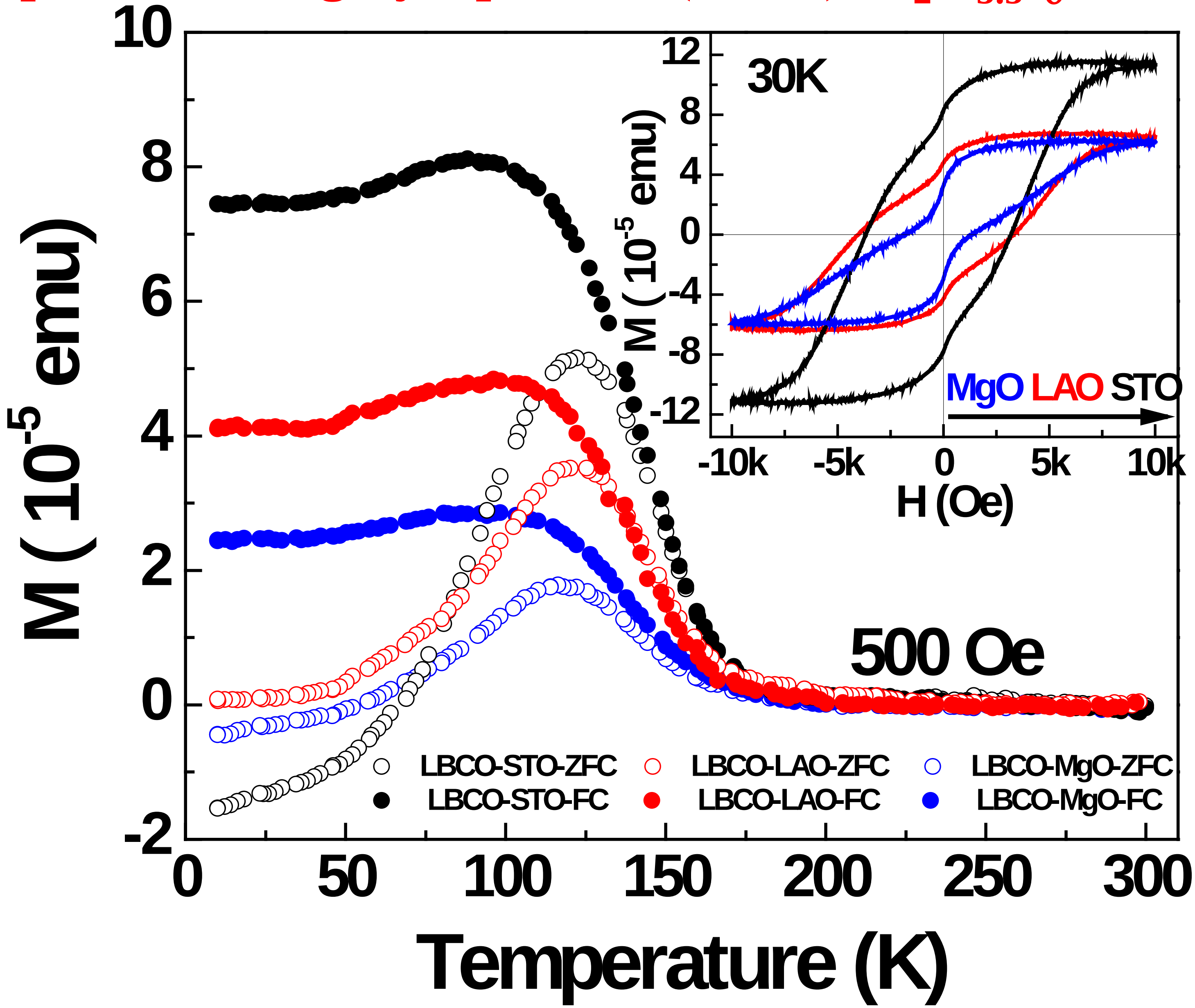


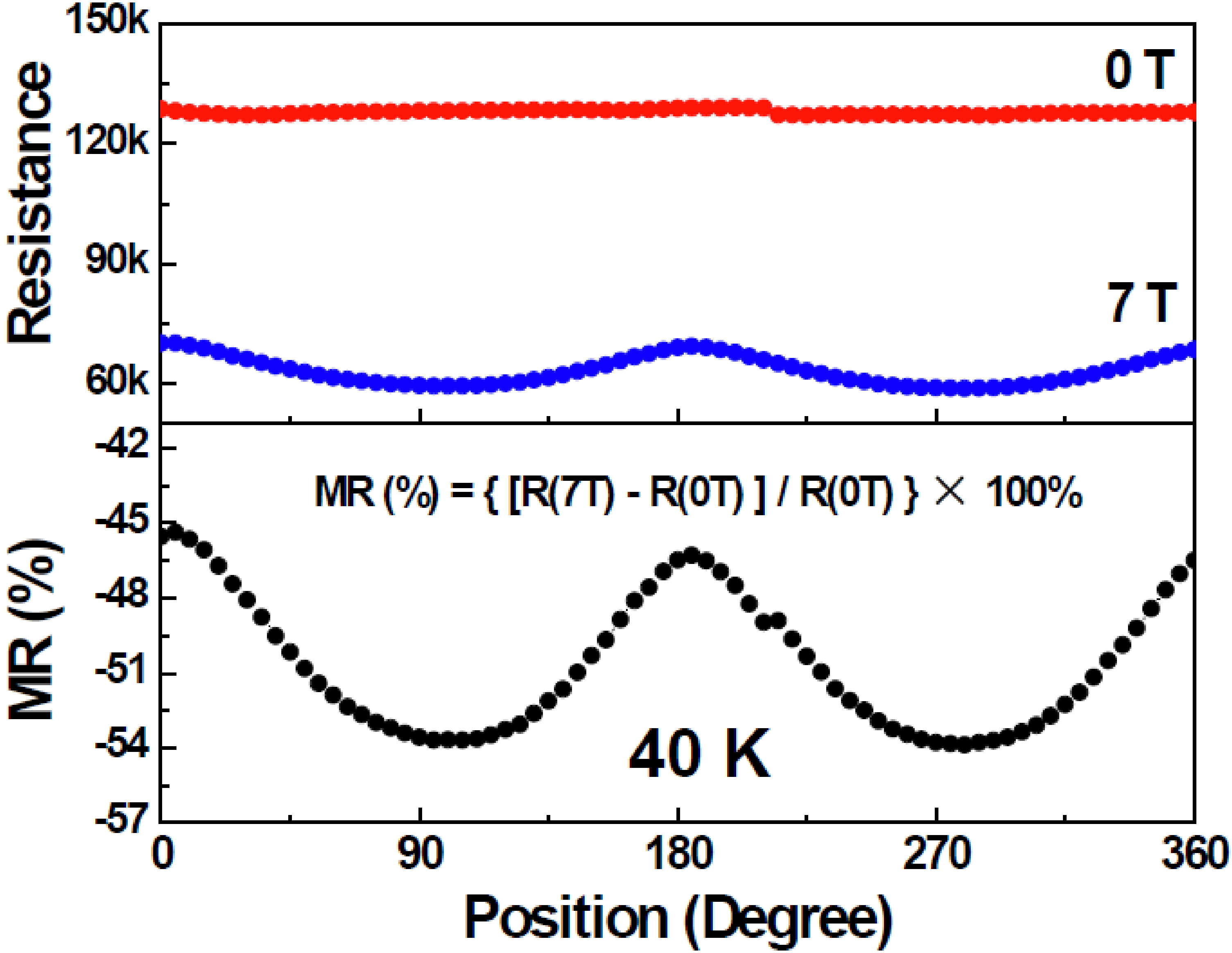
ρ_T / ρ_{295K}
Temperature (K)
NA
OA
MR (%)
H (Oe)
160K
100K
40K
10K



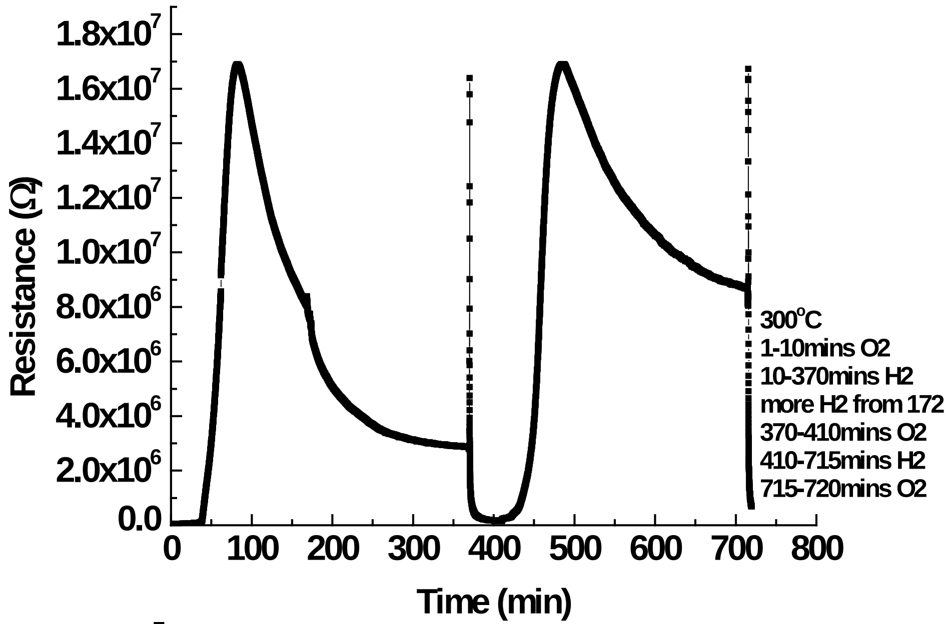
ρ_T / ρ_{295K}
Temperature (K)
0
50
100
150
200
250
300
10^0
10^1
10^2
10^3
10^4
MgO
LAO
STO
NGO
MR (%)
0
-10
-20
-30
-40
-50
160K
100K
40K
10K
MgO
STO
NGO
LAO
Different substrates

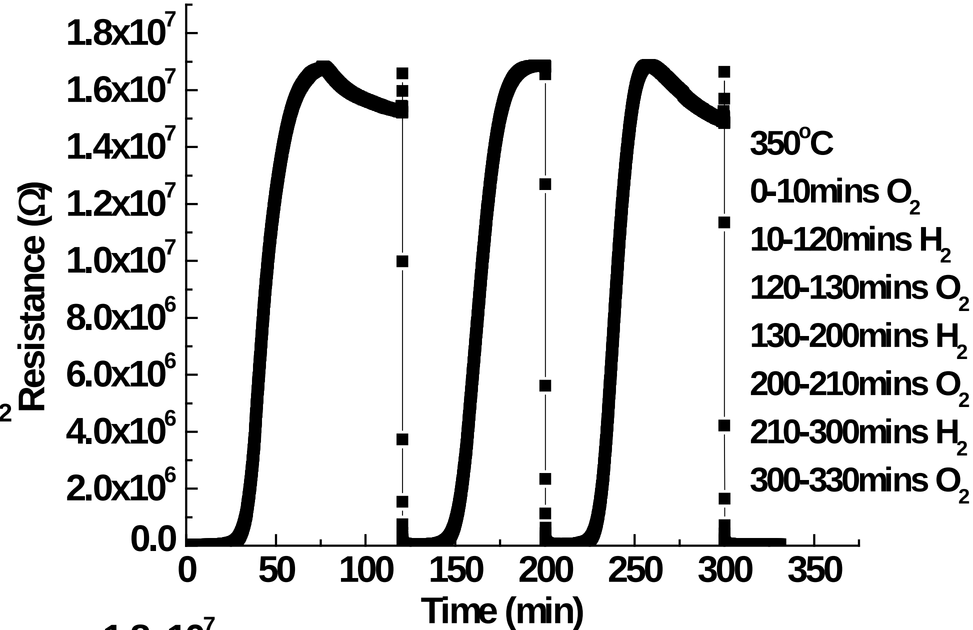
Substrate-induced Strain on Transport Behavior and Magnetic Properties of Highly Epitaxial (LaBa)$Co_2O_{5.5+\delta}$ Thin Films

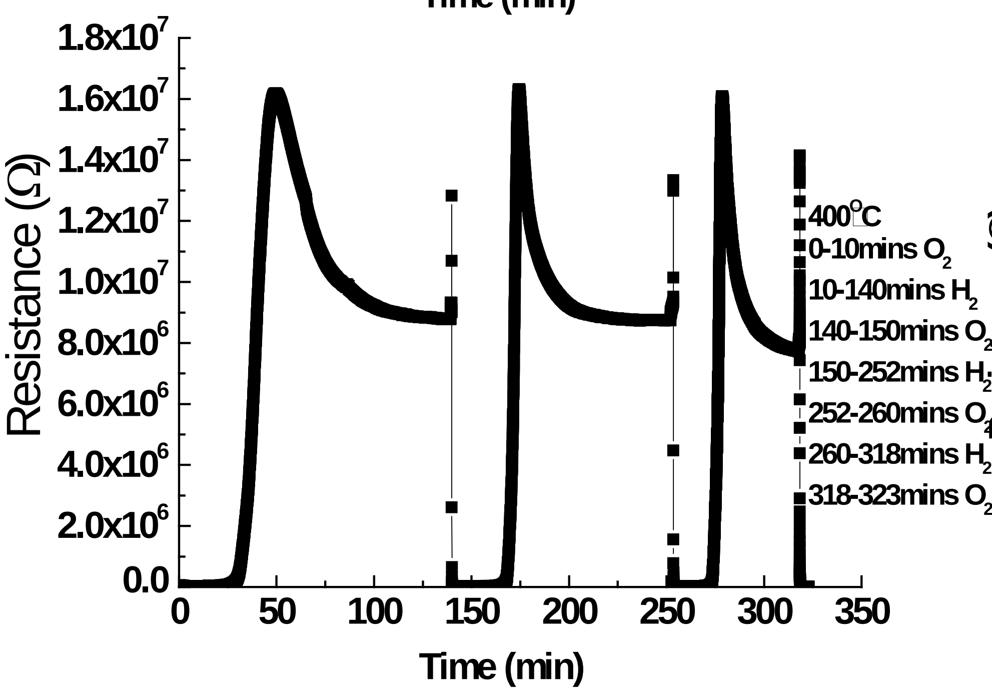


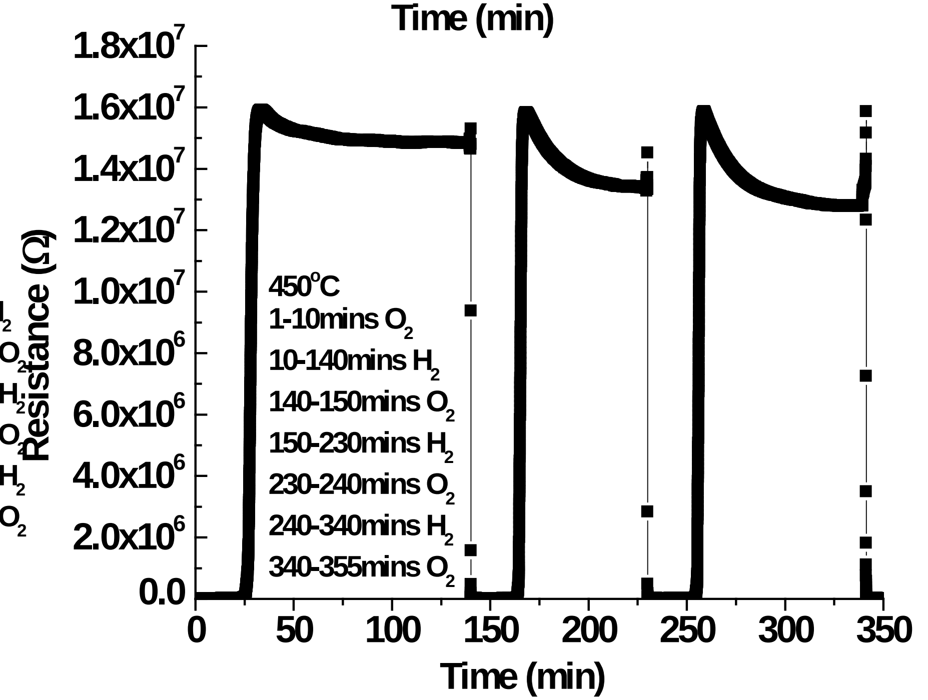

150k
120k
90k
60k
Resistance
0 T
7 T
-42
-45
-48
-51
-54
-57
MR (%)
MR (%) = { [R(7T) - R(0T)] / R(0T) } × 100%
40 K
0
90
180
270
360
Position (Degree)

Characterization of LBCO Films in O_2/4%H_2+N_2

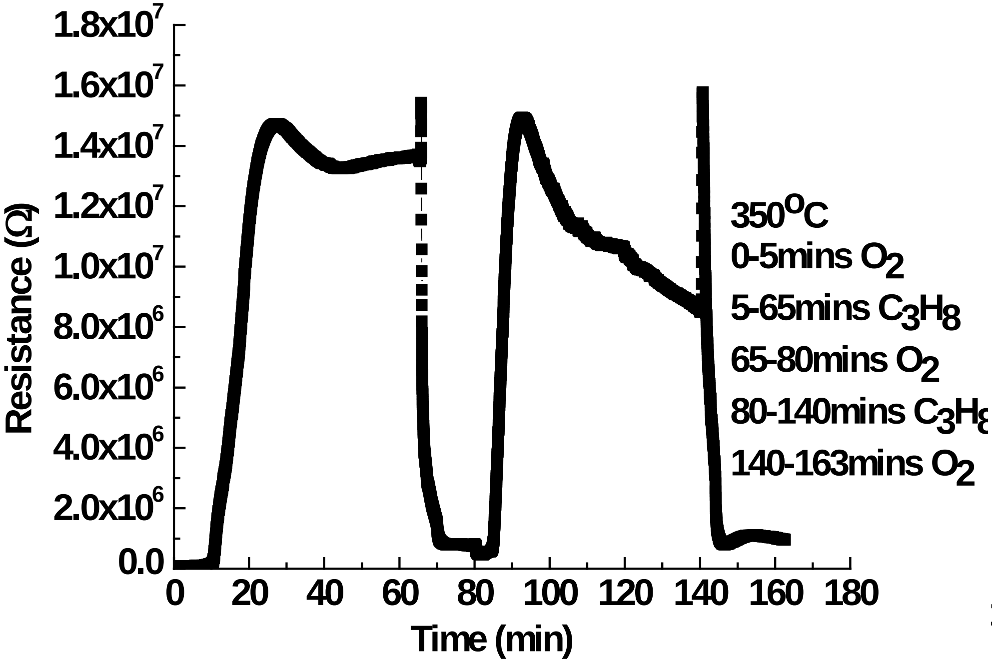


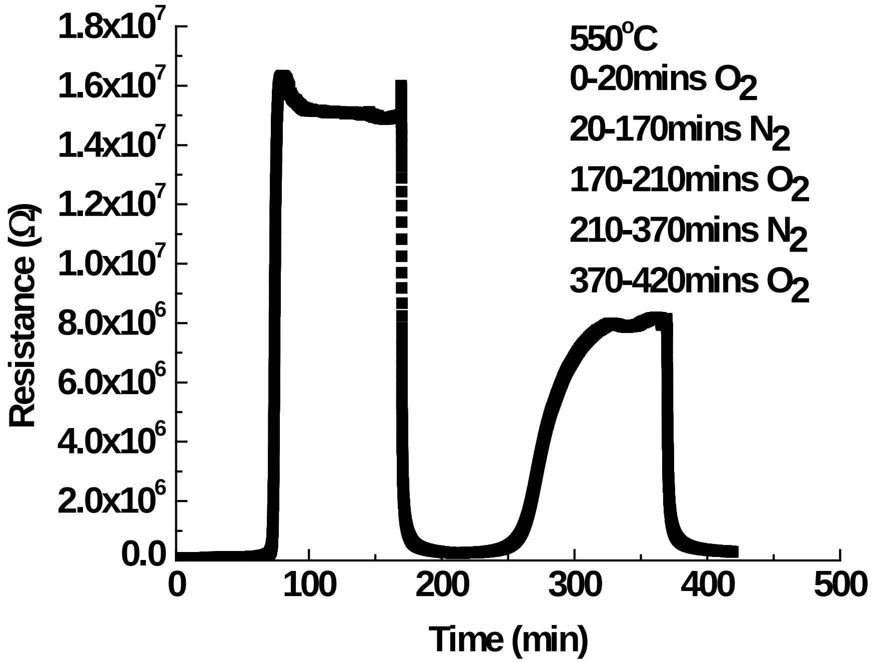






LBCO Films in Other O_2/Fuel Systems





Future Research

- Continually study physical properties of LBCO thin films at various chemical environments (gases, pressures,
- Design and characterize the full scale (low & high temperature) chemical sensors
- Explore novel materials for the development of new sensors and transducers
- Fundamentally understand the sensing mechanisms

Publications – published/revised

- C. L. Chen and J. Liu, "**US61/351,576** (06/04/2010): Highly Epitaxail Thin Films for High Temperature/Highly Sensitive Chemical Sensors for Critical and Reducing Environment".
- Jian Liu, Gregory Collins, Ming Liu, Chonglin Chen,* Jie He, Jiechao Jiang, and Efstathios I. Meletis, **"**Ultrafast Oxygen Exchange Kinetics on Highly Epitaxial $PrBaCo_2O_{5+d}$ Thin Films", ***Appl. Phys. Lett***., **100** (2012) 193903.
- Chunrui Ma, Ming Liu, Gregory Collins, Jian Liu, Chonglin Chen,* Jie He, Jiechao Jiang, E. I. Meletis : "Thickness Effects on Magnetic and Electrical Transport Properties of Highly Epitaxial $LaBaCo_2O_{5.5+\delta}$ Thin Films on MgO Substrates", ***Appl. Phys. Lett***. (Suggested Minor Revision)
- M. Liu, C. R. Ma, J. Liu, G. Collins, Y. M. Zhang, C. L. Chen,* J. He, J. C. Jiang, E.I. Meletis, Y. Lin, Li Sun, A. J. Jacobson, and Q. Y. Zhang, "Magnetic properties and anomalous transport phenomena in highly epitaxial double perovskite nano-ordering $(LaBa)Co_2O_{5.5+d}$ thin films on (001) MgO", ***Phys. Rev. Lett***., (Under revision)

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- C. R. Ma, M. Liu, J. Liu, G. Collins, Y. M. Zhang, H. B. Wang, C. L. Chen, Y. Lin, J. He, J. C. Jiang, E. I. Meletis, "Interface Strain Induced Anomalous Electronic Transport Behavior in Highly Epitaxial $LaBaCo_2O_{5.5+d}$ Films", ***Appl. Phys. Lett***. (submitted)
- M. Liu, C. R. Ma, E. Enriquez, H. B. Wang, C. L. Chen, Y. Lin, "Physical Properties of Highly Mixed Conductive $LaBaCo_2O_{5.5+d}$ Thin Films directly Integrated on Si (100)", ***Appl. Mat & Interfaces*** (submitted)
- Chunrui Ma, Ming Liu, Gregory Collins, Jian Liu, Y. M. Zhang, Chonglin Chen, Jie He, Jiechao Jiang, E. I. Meletis, "Magnetic and Electrical Transport Properties of Highly Epitaxial $LaBaCo_2O_{5.5+\delta}$ Thin Films on Vicinal (001) $SrTiO_3$ Surfaces", ***Appl. Phys. Lett***., (to be submitted)
- Several other manuscripts are preparing for publication

Summary

- Mixed ionic/electronic conductive double perovskite $LaBaCo_2O_{5.5}$ thin films have been successfully grown on various substrates for full scale chemical sensors.
- Transport property studies indicate that the physical properties of the highly epitaxial LBCO are highly dependent upon the interface strain
- New/interesting physical phenomena have been found and achieved in the LBCO materials.
- More experimental and theoretical works are needed to understand the superfast chemical oxidation/redox dynamics and to explore the interface physics.

Thank you very much for your attention!