Transport phenomena and magnetic/crystalline Structure of Manganites

Project Coordinator

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Outline

1 Introducti
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2 Objectiv
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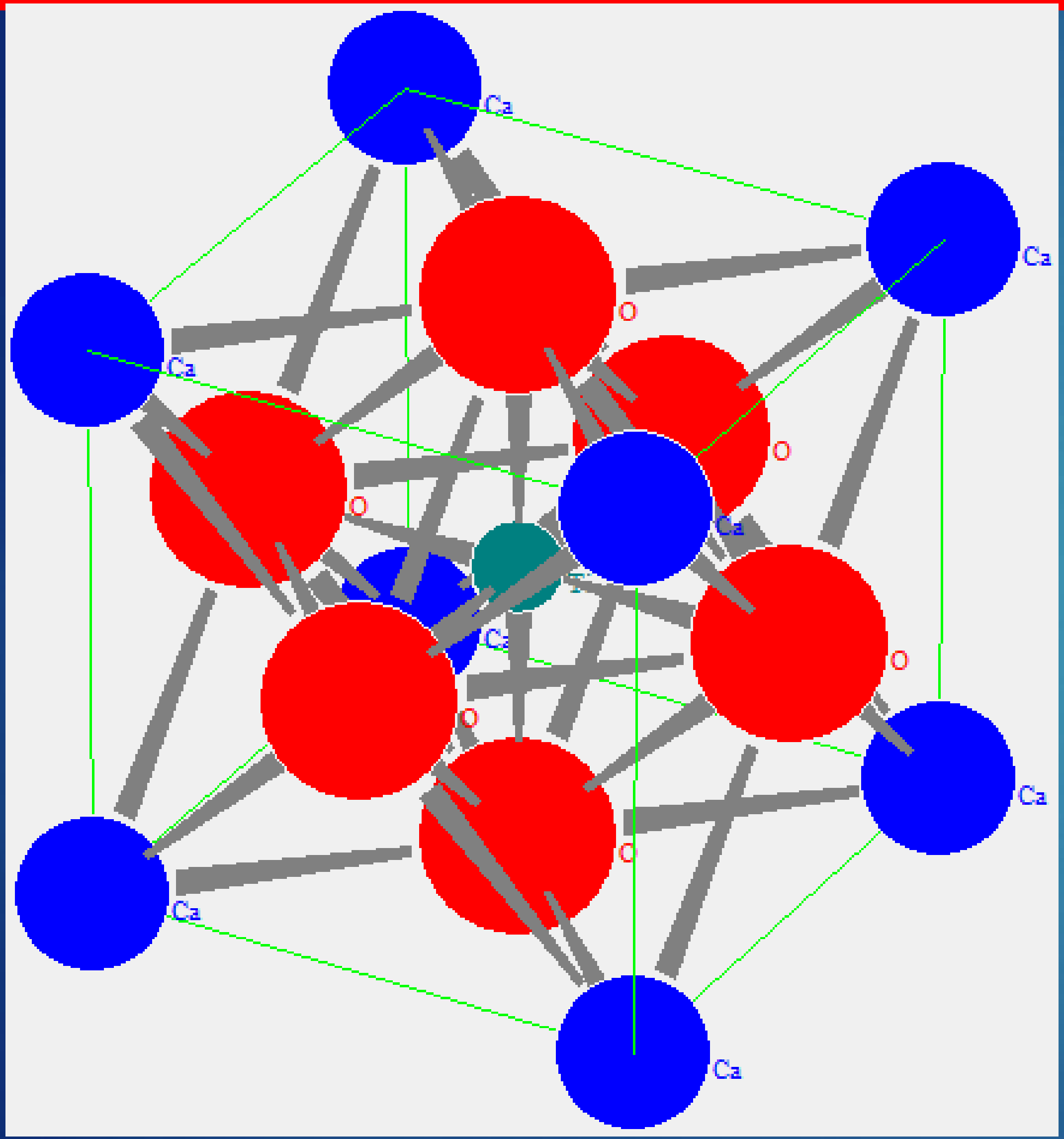
3 Equipment
Description

4 Results

5 Conclusion

Perovskite Parent Structure: $CaTiO_3$



ABO_3

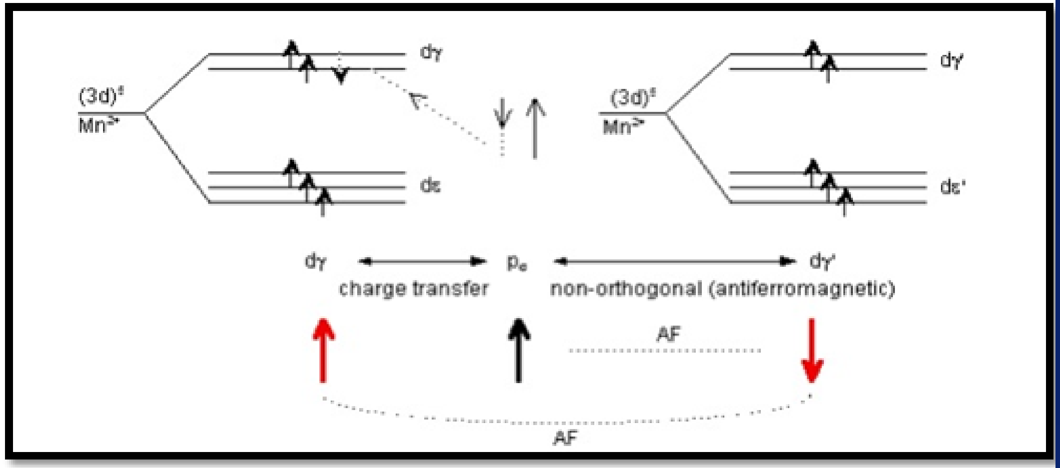
- ✓ (A) cations (such as La, Sr, *Ca*, Pb, etc.) rare earth and alkaline earth.
- ✓ (B) cations (such as *Ti*, Cr, Ni, Fe, Co, Zr, Mn, etc.) transition metals.

Objectives

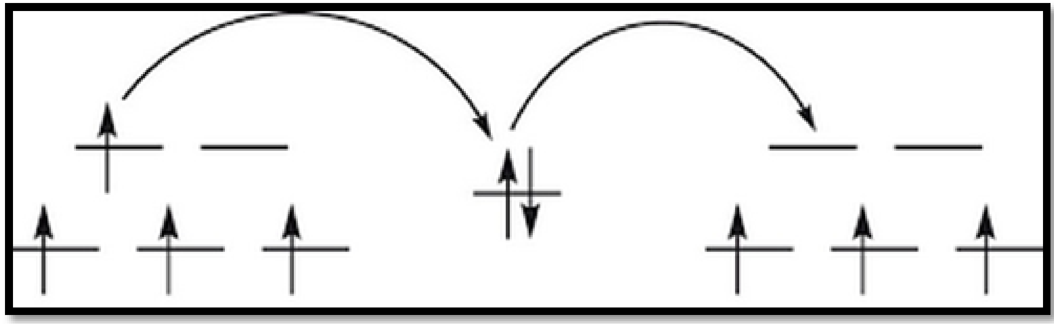
- ✓ Structural analysis of manganites using XRD.
- ✓ Investigate the magnetic and transport phenomena of manganites using VSM and four point probe.

Exchange interaction

- **Superexchange:**
  - Antiferromagnetic interaction
  - Localized non-conducting electrones
  - Change spin orientation due to Hund rules
- **Double Exchange:**
  - Ferromagnetic interaction
  - Delocalization of valence electrons
  - Doped compounds with different number of valence electrons
  - Spin orientation due to polarization
  - Transfer integral



Mn^{2+}- O^{2-} -Mn^{2+}



Mn^{3+} - O^{2-} - Mn^{4+}

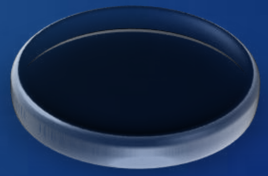
$La_{0.54}Nd_{0.11}Sr_{0.35}Mn_{1-x}Co_xO_3$ Preparation

1. Weighting of the sample

2. Milling and Grinding

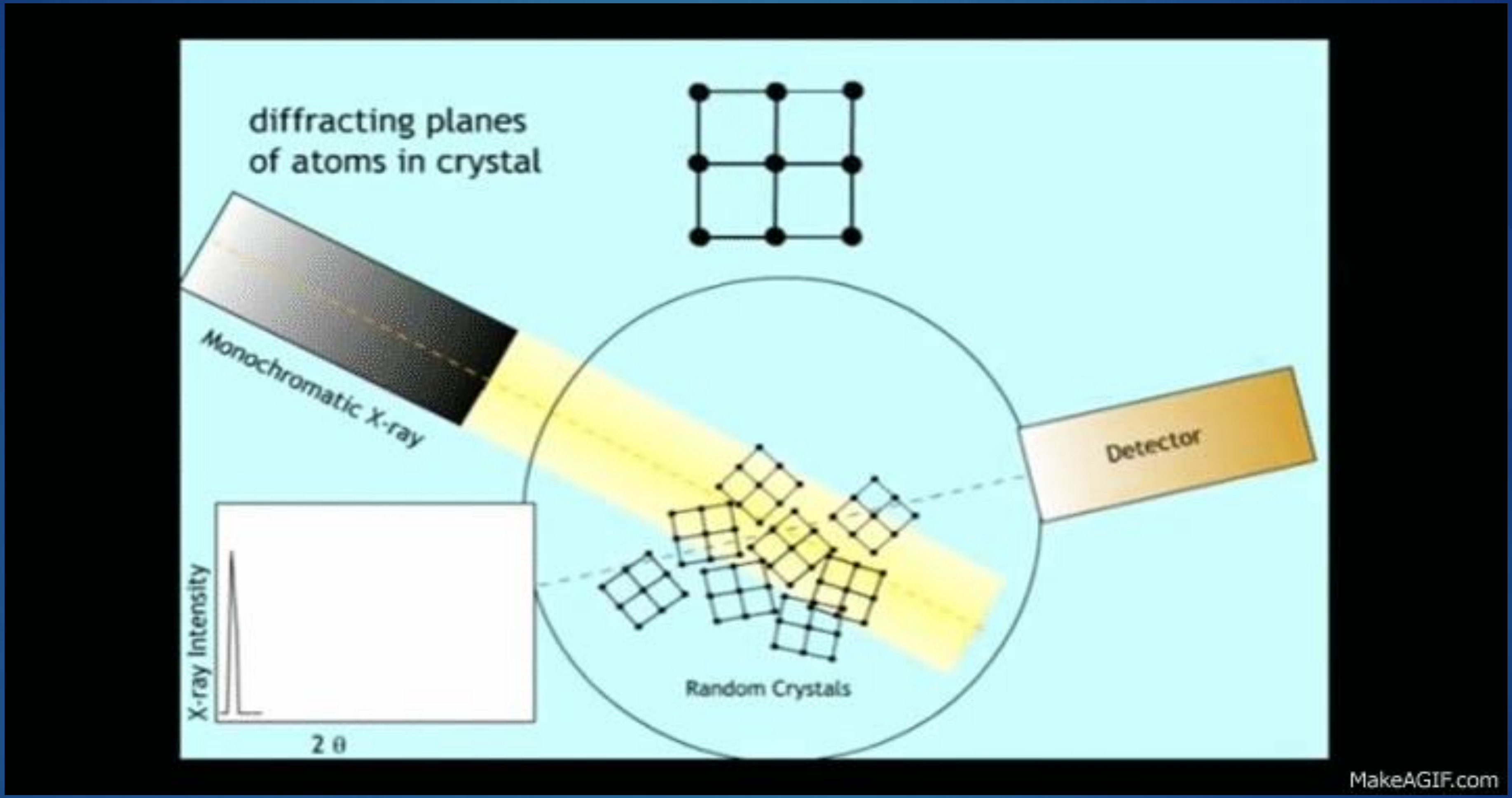
3. Temperature treatment at (800 °C)

4. Preliminary investigation by XRD

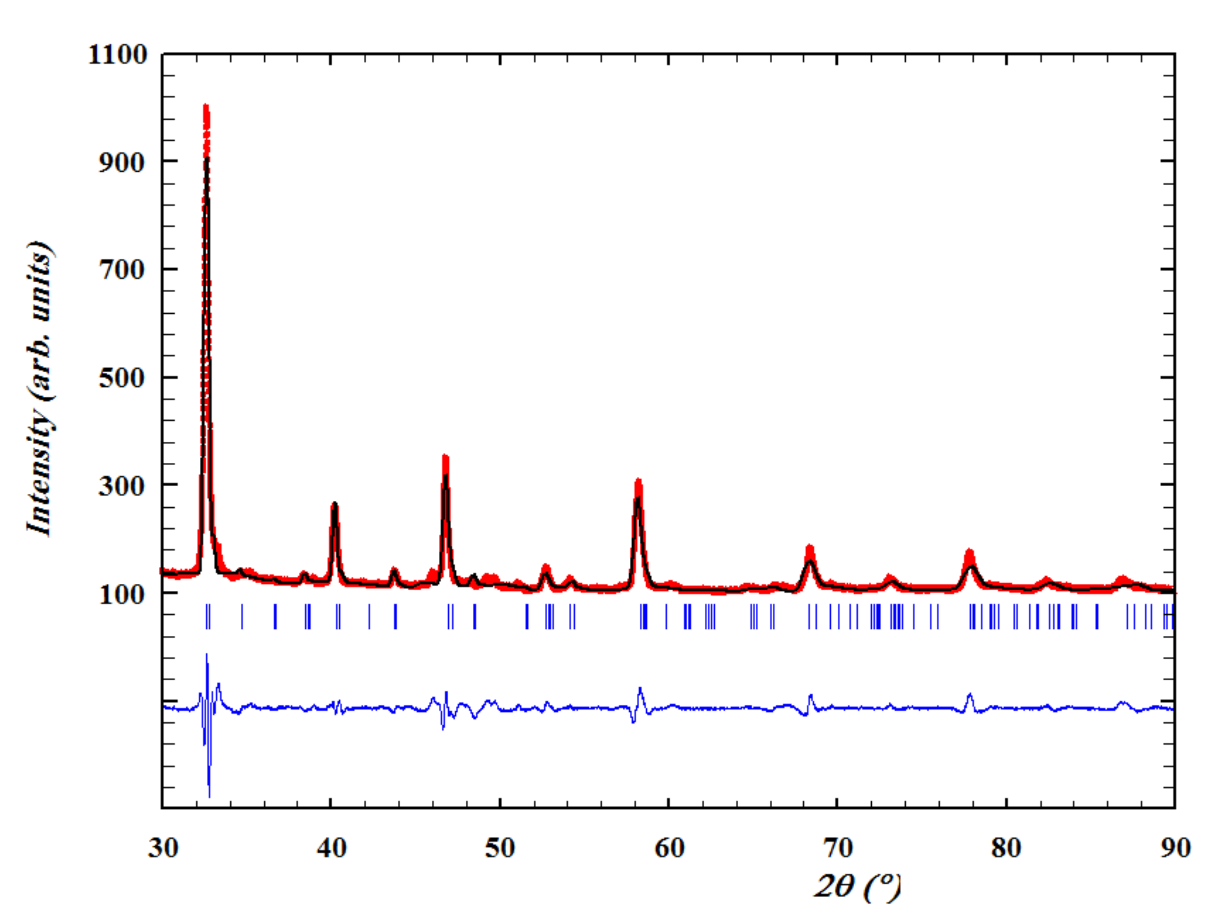


5. Higher temperature sintering (1200 °C)

X-Ray diffraction



XRD of $La_{0.54}Nd_{0.11}Sr_{0.35}Mn_{1-x}Co_xO_3$



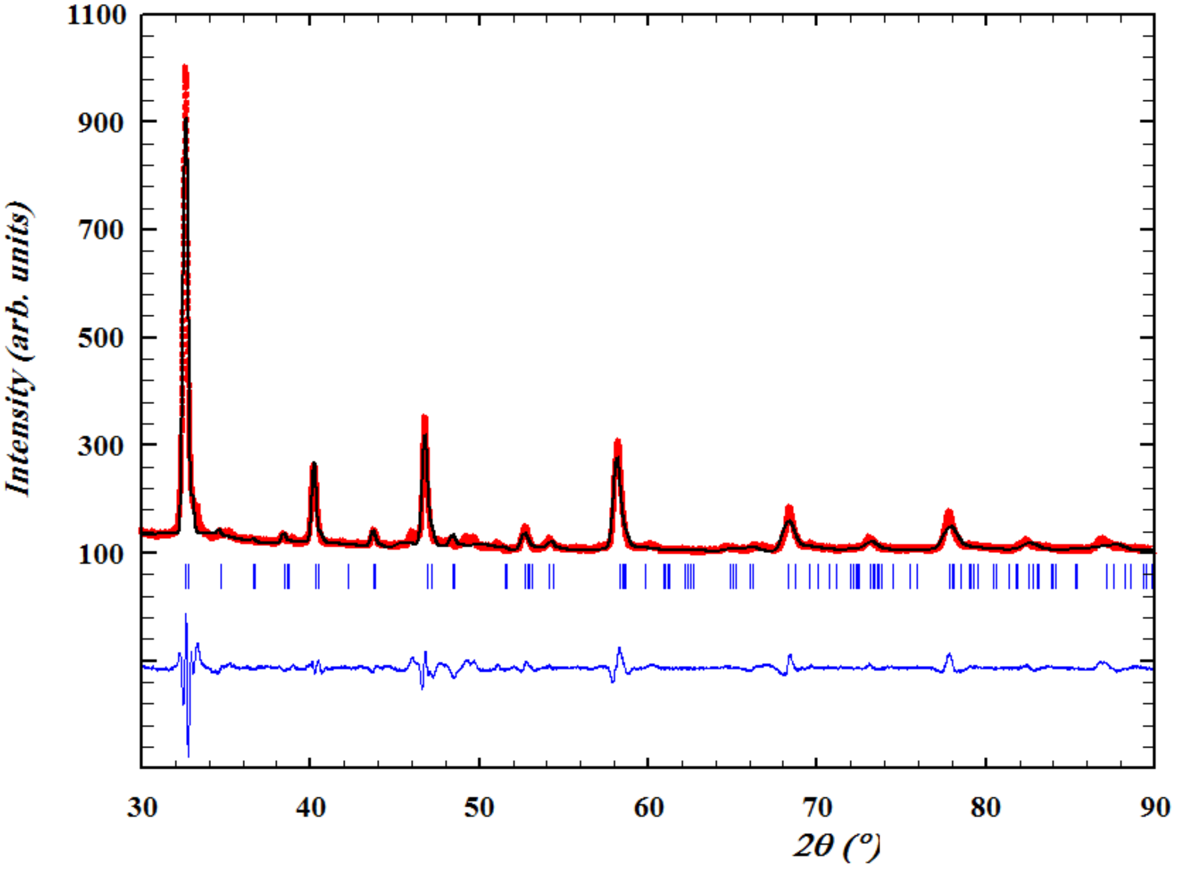
Software Programs

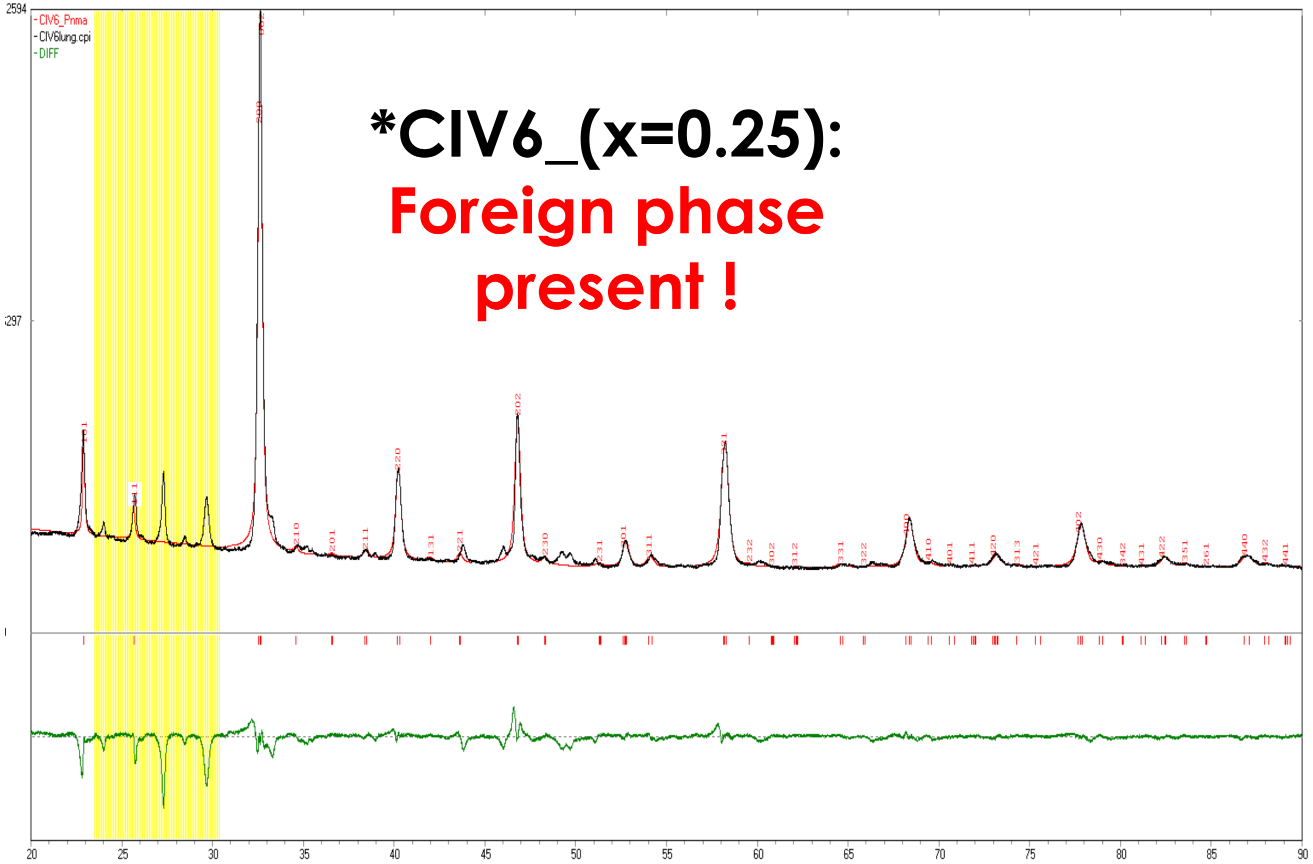
- ✓ Cristalographica
- ✓ Crystallography open database
- ✓ Full Prof suite code
- ✓ Celerf3
- ✓ Powder cell
- ✓ MolCal

Structure Refinement

Molecular Weight Calculation

$La_{0.54}Nd_{0.11}Sr_{0.35}Mn_{0.75}Co_{0.25}O_3$





*CIV6_(x=0.25):

Foreign phase present !

Unit cell for orthorhombic crystal system (Pnma)

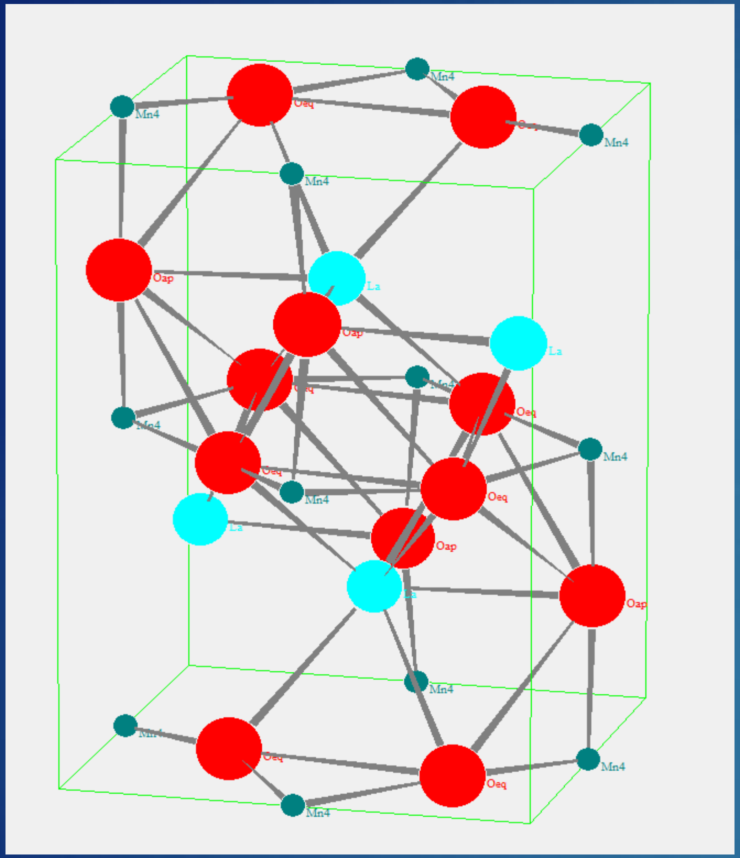


Figure 1 The unit cell of an orthorhombic crystal (system Pn m a)

Manganese

Lanthanum

Oxygen

Cations and anions positions in Pnma unit cell

Name	Cation/ Anion	Wyckoff position	x	y	z	SOF
La	La^{3+}	4c	0.0917	0.2500	0.9950	1
Mn	Mn^{3+}	4b	0	0	0.5000	1
O1	O^{2-}	4c	0.4913	0.2500	0.0838	1
O2	O^{2-}	8d	0.2751	0.0330	0.7245	1

Unit cell parameters for $La_{0.54}Nd_{0.11}Sr_{0.35}Mn_{1-x}Co_xO_3$

x	SG	a (Å)	b(Å)	c (Å)	V (Å^3)
0.00	Pnma	5.4944	7.709	5.4614	231.327
0.05	Pnma	5.4993	7.7099	5.4611	231.546
0.10	Pnma	5.4994	7.7088	5.4649	231.679
0.15	Pnma	5.497	7.7071	5.4624	231.420
0.25	Pnma	5.4907	7.7222	5.4683	231.858

α=β=
γ =90°

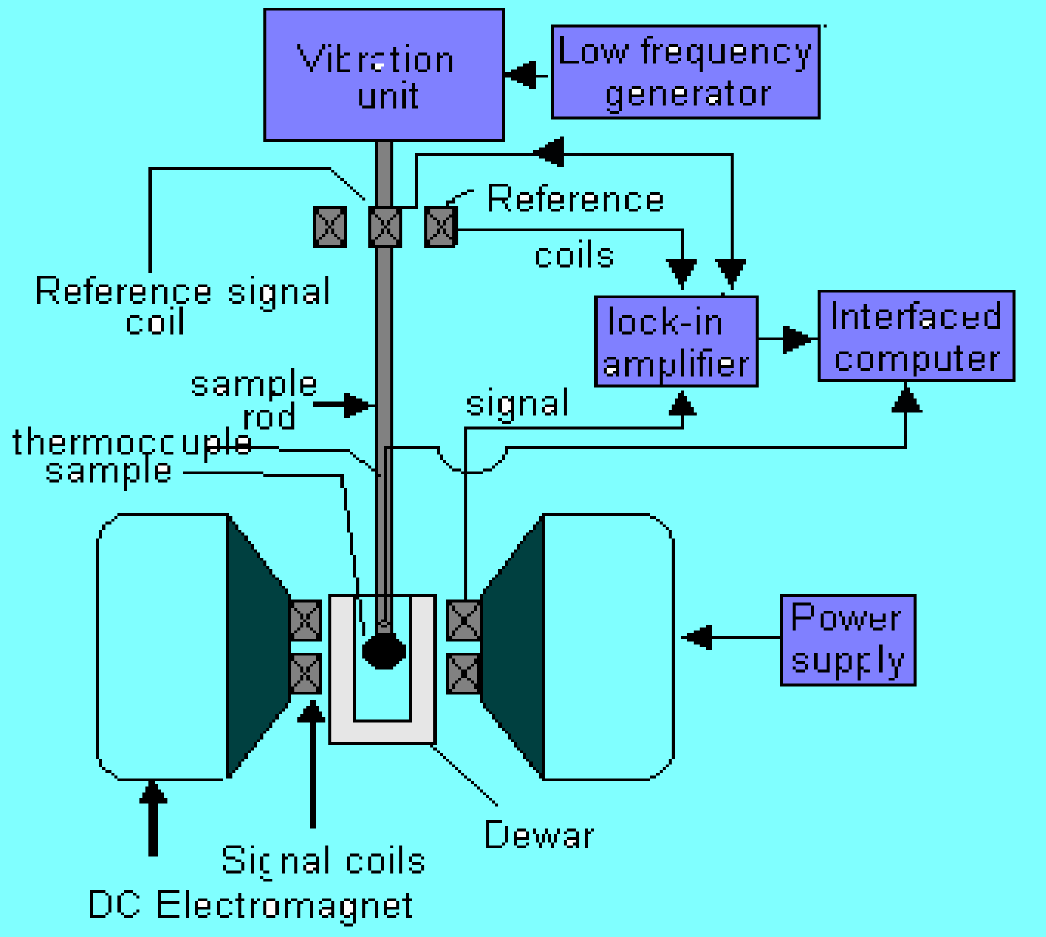
Microstructural parameters for $La_{0.54}Nd_{0.11}Sr_{0.35}Mn_{1-x}Co_xO_3$

x	SG	ε	D(nm)
0.00	Pnma	0.000240	68.81
0.05	Pnma	0.000883	84.28
0.10	Pnma	0.000639	104.75
0.15	Pnma	0.000617	106.24
0.25	Pnma	0.002214	65.15

*CIV6_(x=0.25):
Foreign phase present !

FLNP

Magnetic measurements using VSM



$$\sigma = k\frac{U}{m}$$

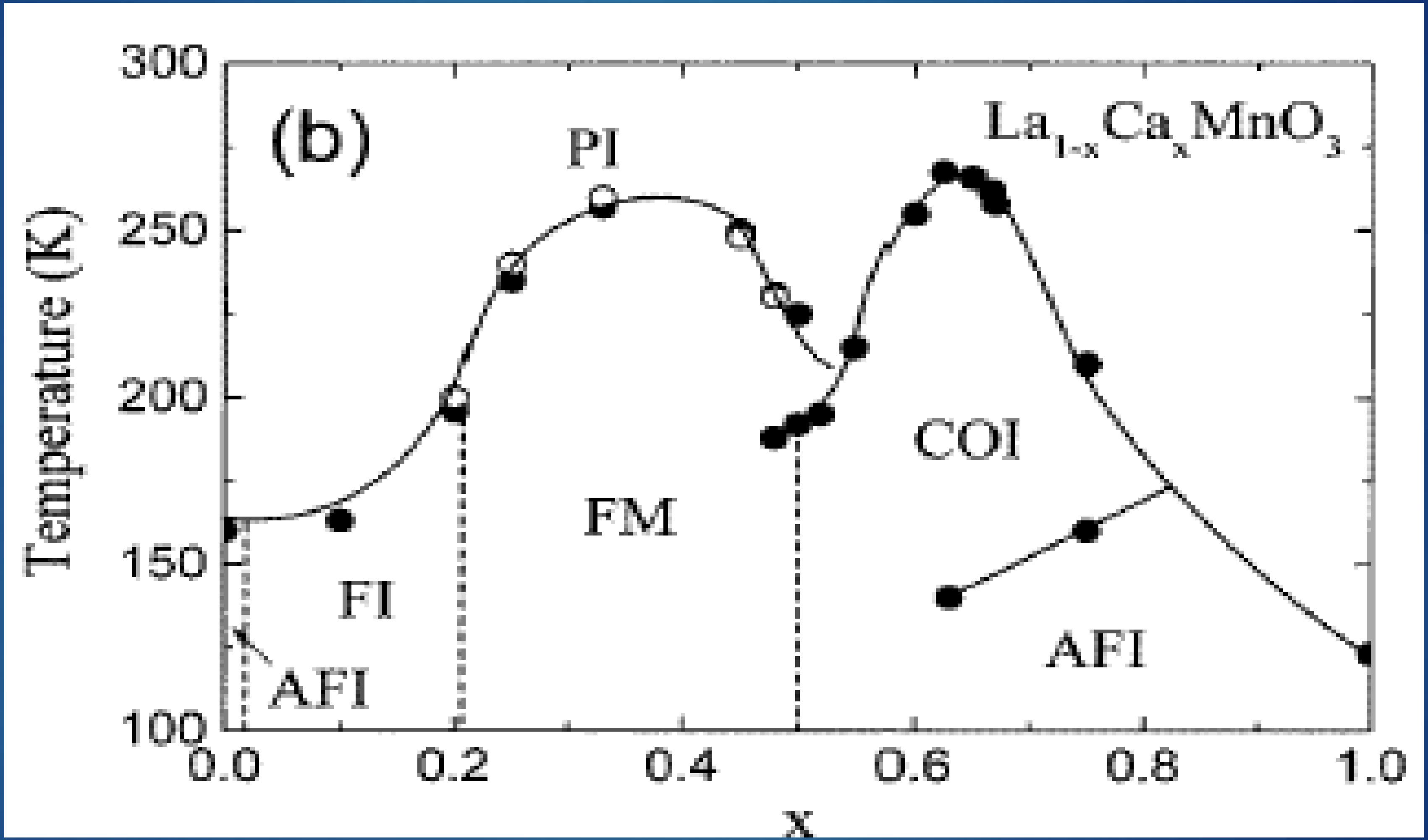
(σ) specific magnetization

(U) voltage drop across the coils

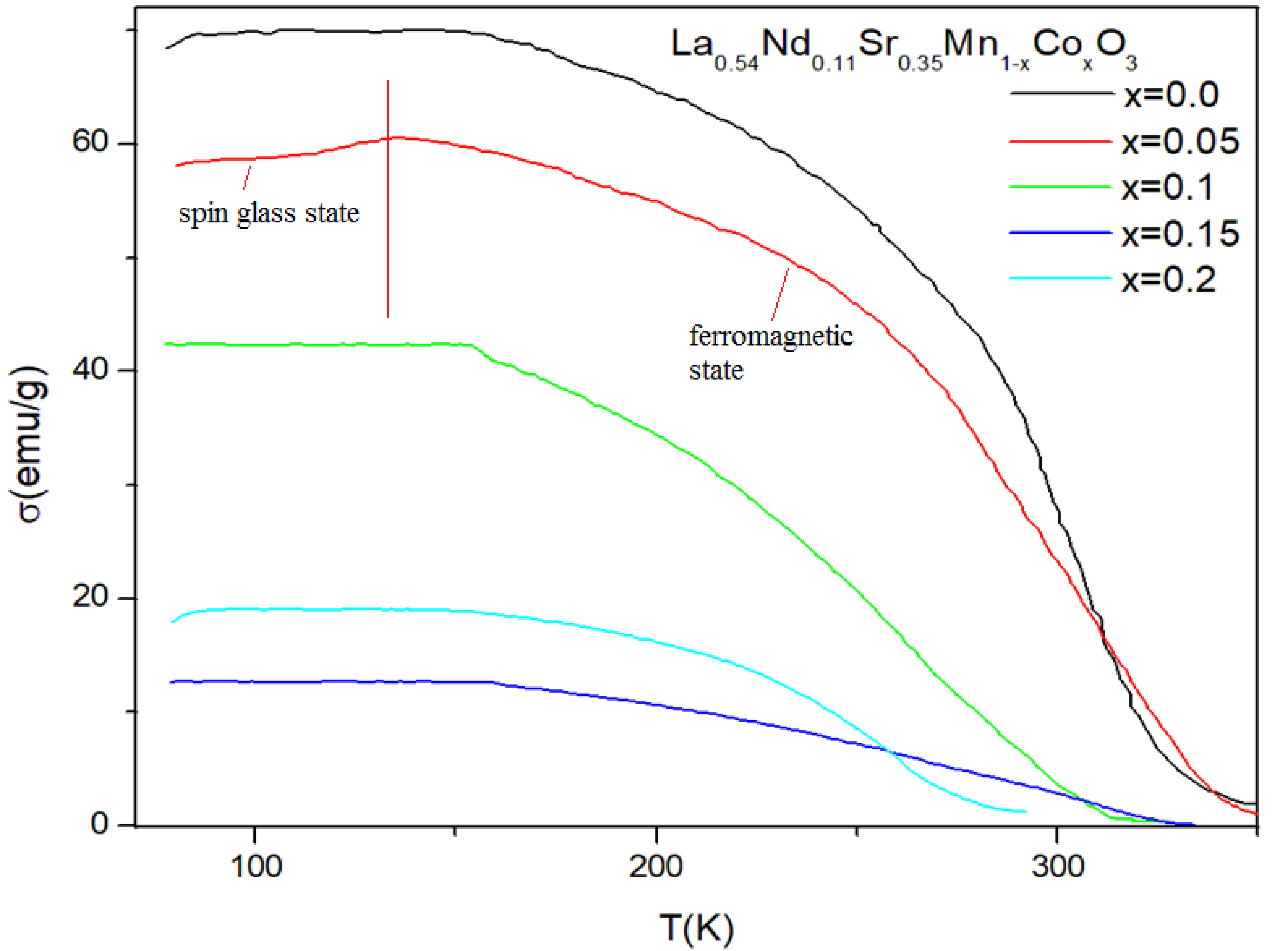
(m) sample weight

(k) constant of the instrument

Phase diagram of Manganites



Uehara, Mori, Chen and Cheong, Nature399, 560 (1999).



Specific magnetization (σ) vs temperature (T) for the sam-ples of the system **$La_{0.54}Nd_{0.11}Sr_{0.35}Mn_{1-x}Co_xO_3$**

The variation of σ vs T presents two regions: for high temperature (T>200 K) we have ferromagnetic behavior, while for low temperature can be observed a transition from the ferromagnetic to the spin glass state.

Magnetic parameters for $La_{0.54}Nd_{0.11}Sr_{0.35}Mn_{1-x}Co_xO_3$

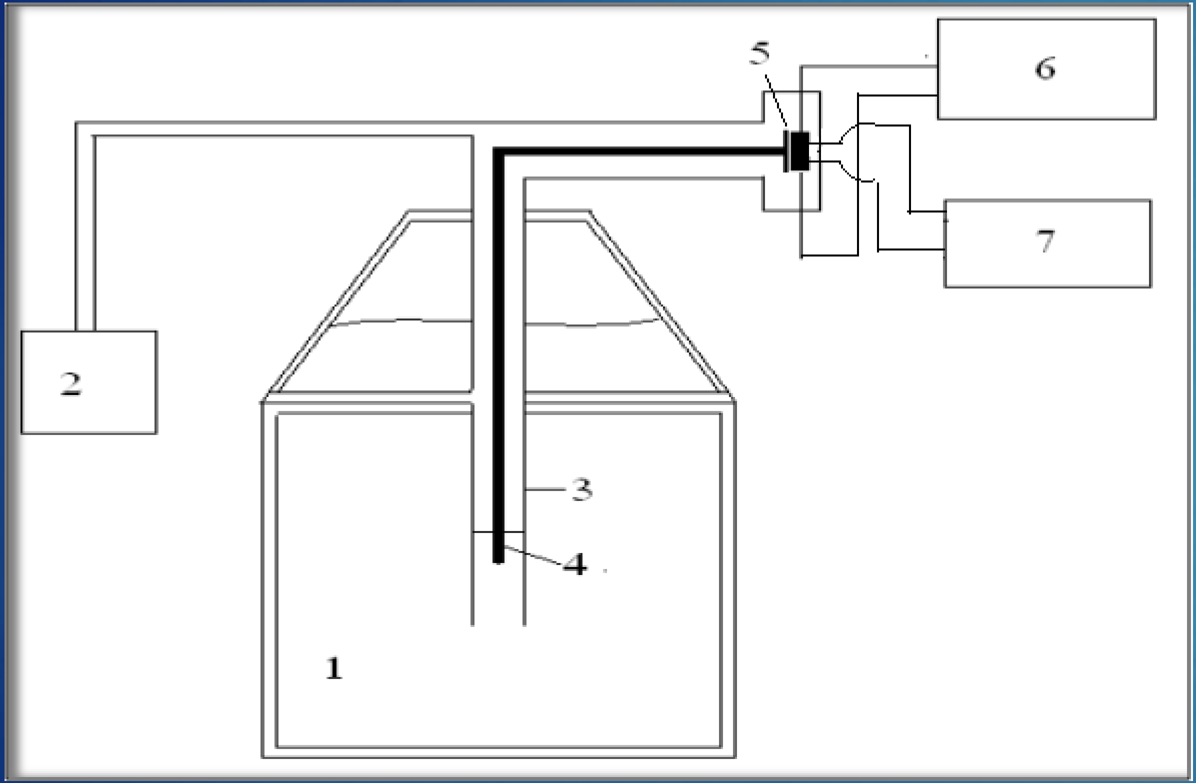
(Curie temperature – T_C; specific magnetization - σ)

Co concentration	T_c (K)	σ (emu/g)
x=0.00	304.5	70.5
x=0.05	310.0	60.6
x=0.10	266.5	42.4
x=0.15	264.0	12.7
x=0.20	255.0	19.1

We observed that the Curie temperature have a small decrease with the Co concentration: the distances between the magnetic moments remain practically unchanged. In the same time , a very quick change appears in the specific magnetization, that means a decrease of the magnetic phase concentration , implicitly of the metallic phase concentration.

FLNP

Transport measurements by four probe method



(1)Cryostat

(2)Vacuum pump

(3)Evacuated tube

(4)Copper rod

(5)Sample

(6)Current source

(7)Voltmeter

Conductivity models

Depends on density of localized states near E_F.

$T>T_C$

Activated behaviour

$$\rho(T)\alpha\exp(\frac{E_0}{kT})$$

where E_0 – activation energy and k – Boltzmann constant

Polaronic hopping

$$\rho(T)\alpha T\exp(\frac{E_0}{kT})$$

VRH- variable range hoping

Coulomb energy between charge carriers excess Jahn- Teller energy gap .

Localized states with sufficient energy.

Hops beyond nearest neighbor are energetically favourable.

$$\rho(T)=\rho_0\exp\left\{\left[\frac{T_0}{T}\right]^{1/4}\right\}$$

There is no agreement concerning the conductivity models at high temperature

$T<T_C$

Ferromagnetic region

$$\rho(T)=\rho_0+AT^2+BT^{4.5}$$

Dominant lowering of density of localized states

The AT^2 term represents the electron-electron scattering processes, while the third is due to the two magnon (collective excitation spin structure) processes.

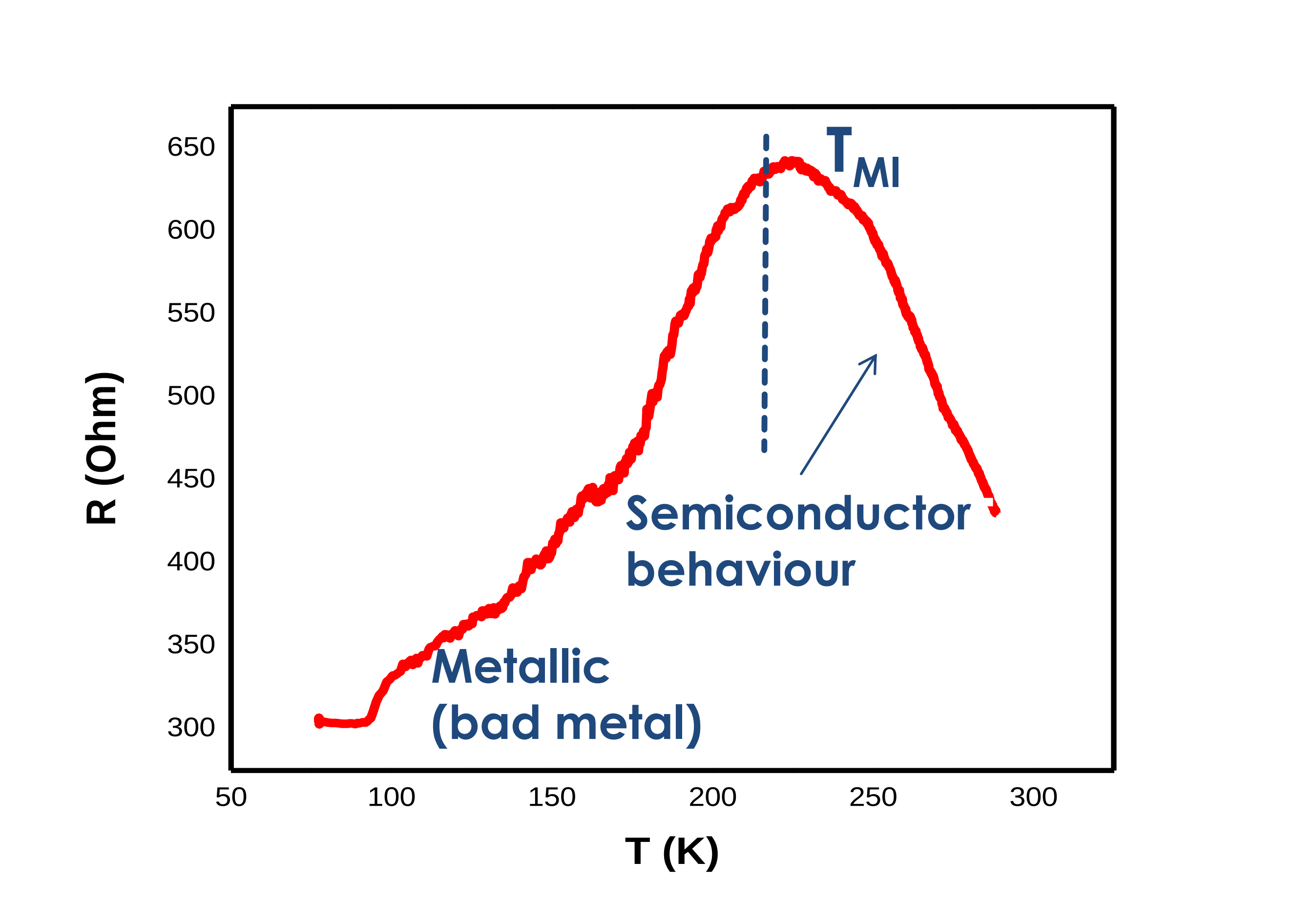
Conductivity models

- ✓ Thermal Activation model (T_A)

$$R = R_o \exp(-E_a/kT)$$

- ✓ Single magnon process

$$R=R_0+AT^2$$



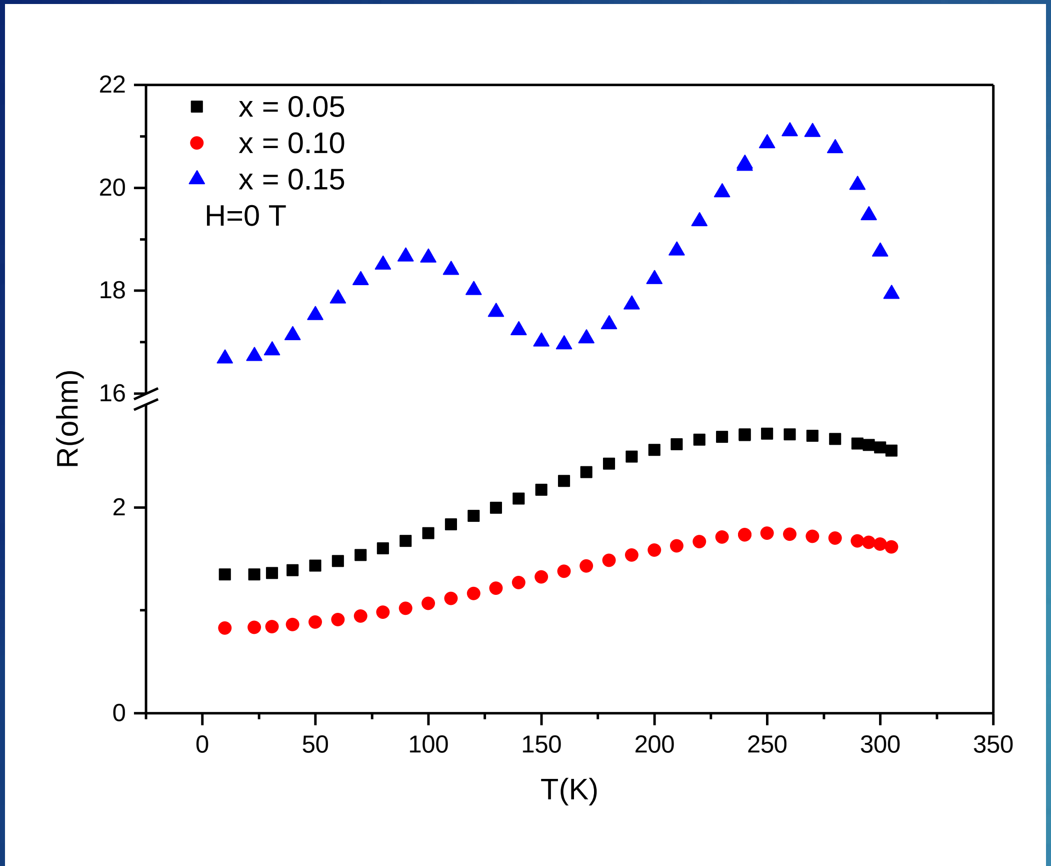


Figure 4. Variation of resistance vs temperature for $La_{0.54}Nd_{0.11}Sr_{0.35}Mn_{1-x}Co_xO_3$ manganites

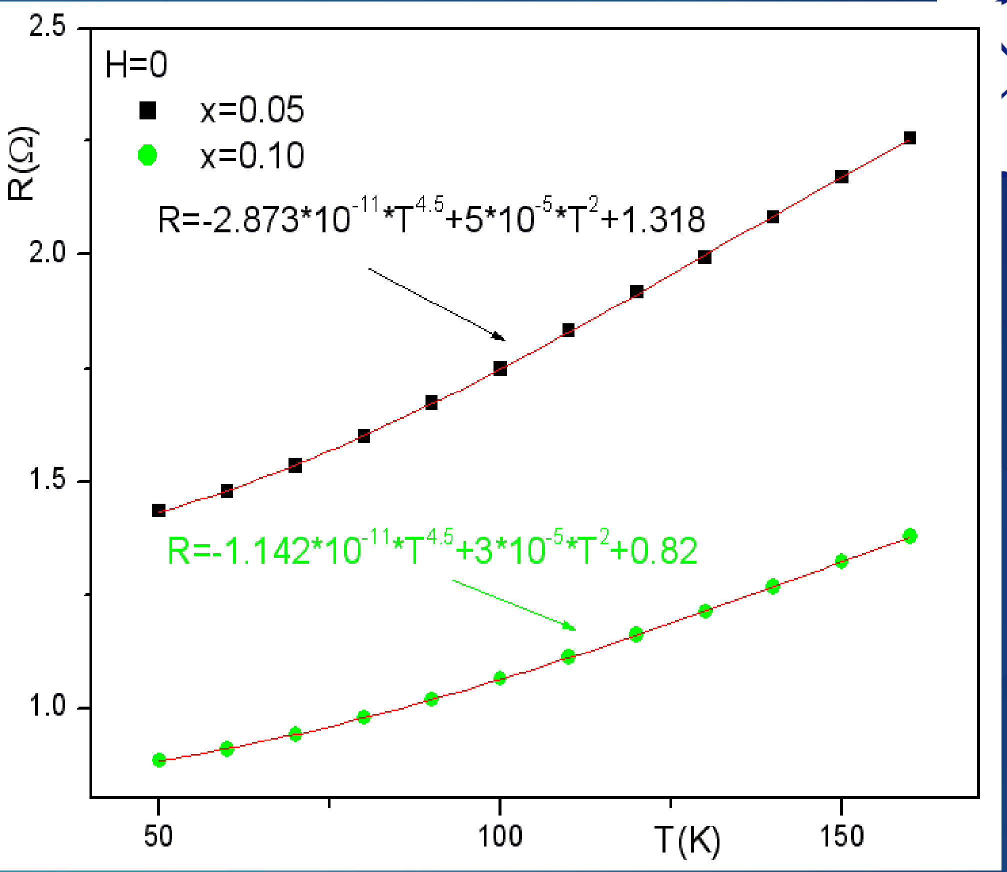


Figure 5. Variation of resistance vs temperature and Co concentration for $La_{0.54}Nd_{0.11}Sr_{0.35}Mn_{1-x}Co_xO_3$ manganites at low temperatures (***two magnon processes***)

Magnetic and transport parameters of some $La_{0.54}Nd_{0.11}Sr_{0.35}Mn_{1-x}Co_xO_3$ manganites

x	T_c [K]	$T_{IM,extrinsic}$(K)	$T_{MI, intrinsic}$[K]	E_o[eV]
0.00	304.5	216	-	0.051
0.05	310.0	239	293	0.026
0.10	266.5	-	-	-
0.15	264.0	210	303	0.029
0.20	255.0	241	-	0.033

Conclusion

- ✓ *$La_{0.54}Nd_{0.11}Sr_{0.35}Mn_{1-x}Co_xO_3$ manganites have been synthesized by ceramic method and the Pnma structure was confirmed by XRD for all x values, except of the one corresponding to x=0.25*

- ✓ *Orthorhombic structure with space group (Pnma) was observed for all investigated samples*

- ✓ *The variation of the unit cell volume is due to the: 1)the increase of the Mn^{3+} concentration with the increase of oxygen concentration and 2)the increase of the Co concentration, which have a smaller radii as the manganse*

- ✓ *Manganite samples behave as metals for temperature lower than T_{MI} and semiconductor for temperature higher than T_{MI}*
- ✓ *At low temperature all the samples support a transition from the ferromagnetic to spin-glass state*

- ✓ *For the studied manganites was observed a large difference between the Curie and transition temperature, attributed to the presence of an important amount of defaults, present in the boundaries layers.*

- ✓ *The present of a boundary layer with a large amount of defaults and characterized by a lower Curie temperature and a high resistivity as the "crystalline core" avoids the observation of the transition temperature of the "crystalline core". The observed behavior of resistance with temperature at very low temperatures can be attributed to the intergranular spin polarized tunneling mechanism.*

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Thank you for your attention !!