Raman Studies on Functional Perovskite Oxides

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Aim of the present studies

Structural distortions and their effect on the magnetic properties of rare-earth based oxides

Parameters: Temperature /Pressure

Raman scattering is sensitive to structural distortions and carry information related to the physical properties.

Multifunctional $\textit{R}BO_3$

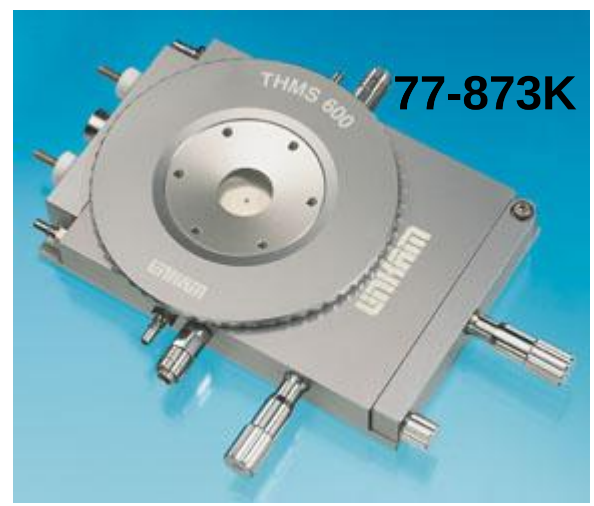
$LaMn_{0.5}Co_{0.5}O_3$	$\textit{R}CrO_3$
Dual magnetic phases	**Multiferroic**
J. Phys. Condens. Matter (2010) J. Appl. Phys. (2014)	Euro. Phys. Lett. (2013) Mater. Res. Exp. (2014)

Experimental facilities

Membrane Diamond Anvil Cell (MDAC)

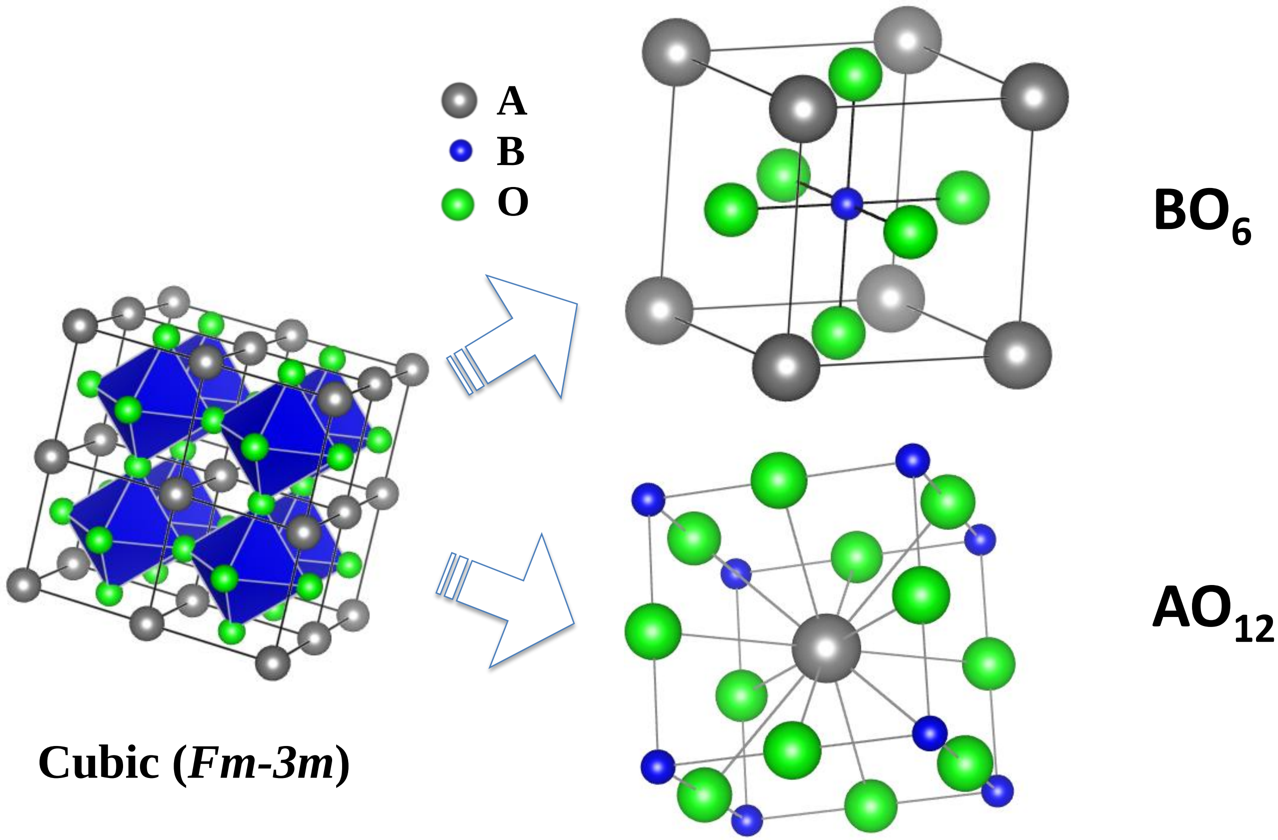
35 GPa

Heating/Cooling stage



Perovskites

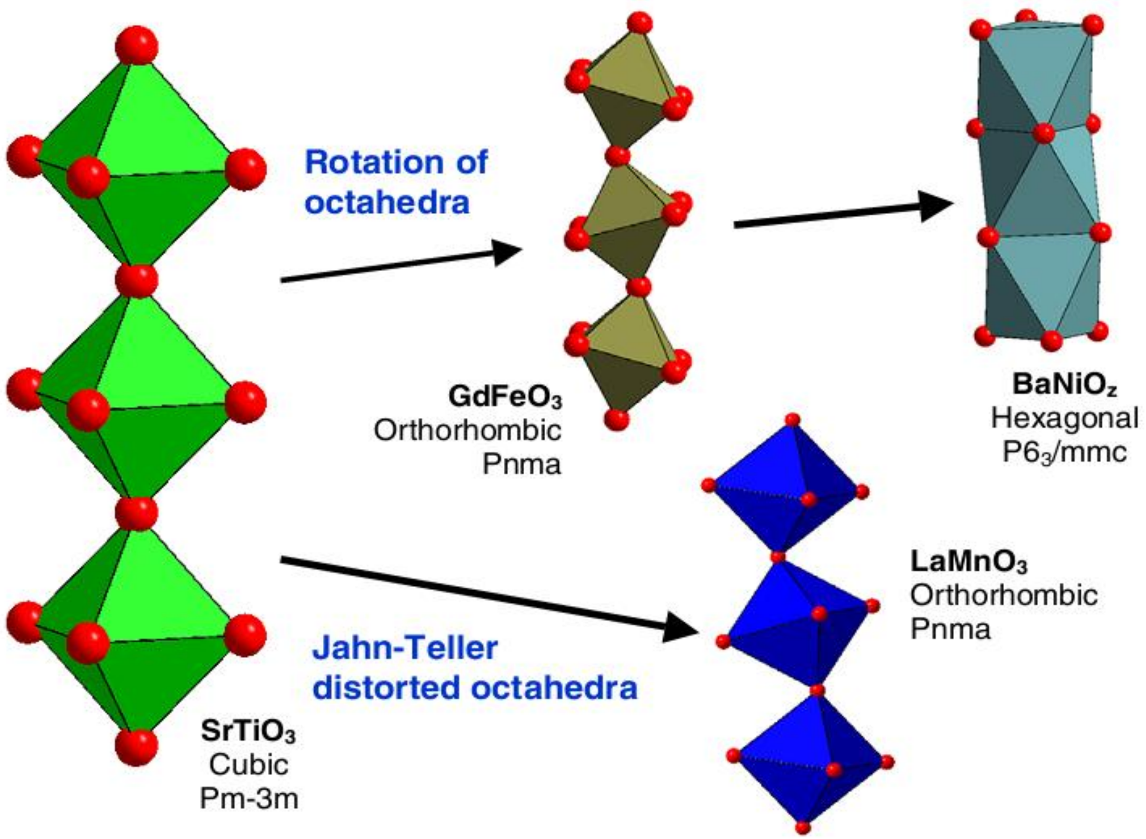
ABO_3 formula



Perovskites

Cationic size mismatch

✓ **Octahedral tilting**
✓ **Cation displacement**



Tolarence factor (t) :

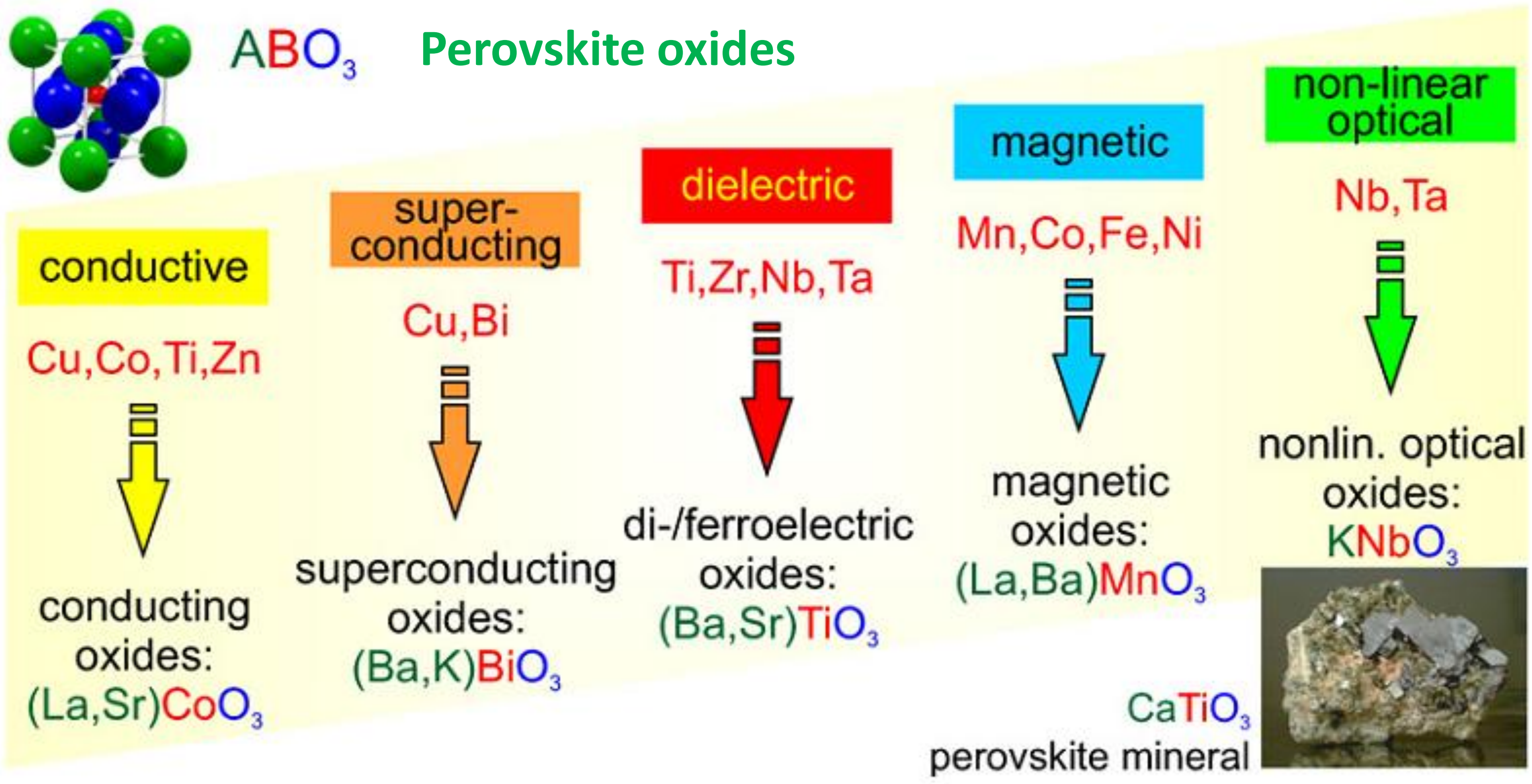
$$\frac{d_{A-O}}{\sqrt{2}d_{B-O}}$$

cubic perovskite: t=1

structural distortion → $t \neq 1$

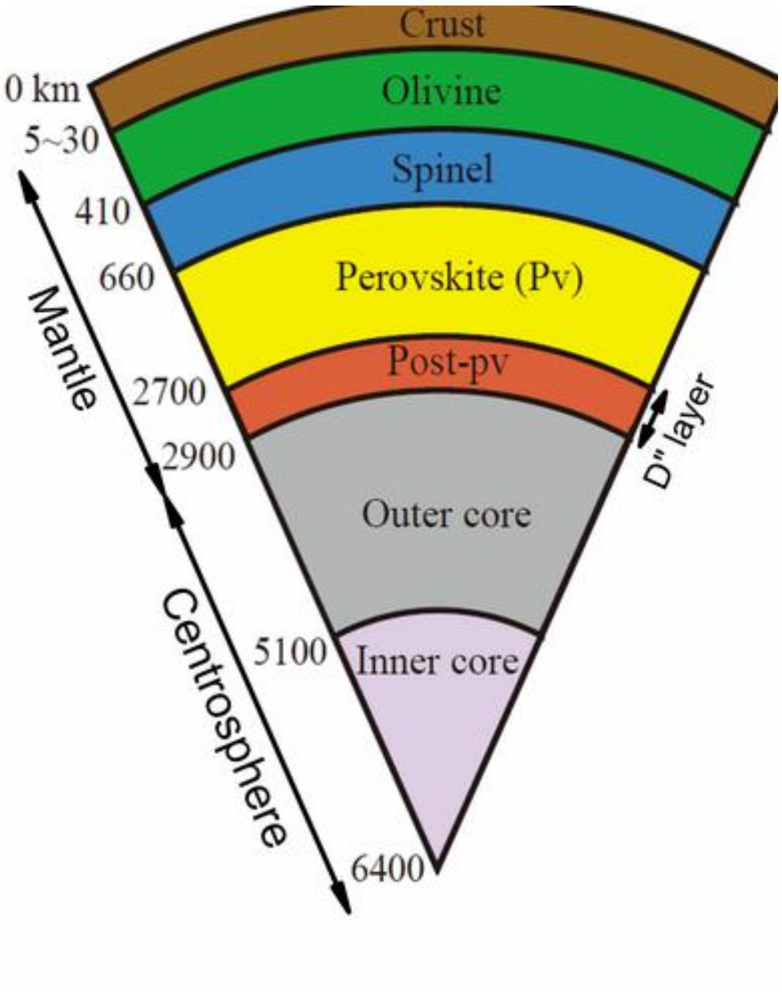
Most common structures are "**Rhombohedral (*R-3c*)**" and "**Orthorhombic (*Pbnm*)**"

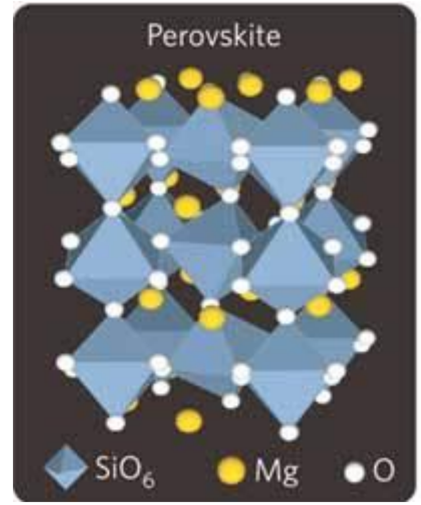
Perovskites



J. Phys. D: Appl. Phys. 45, 033001 (2012)

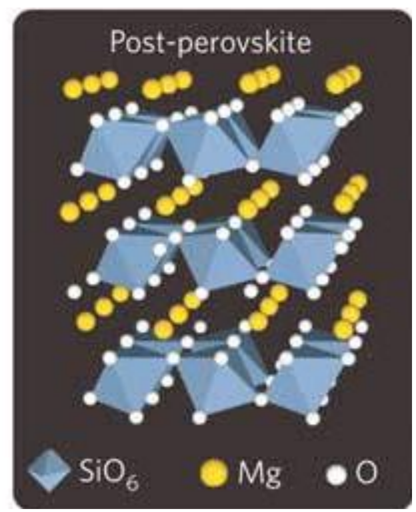
Perovskites





Corundum

R-3c



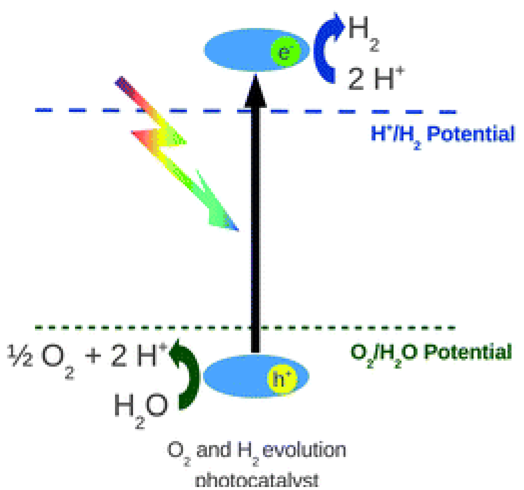
Orthorhombic

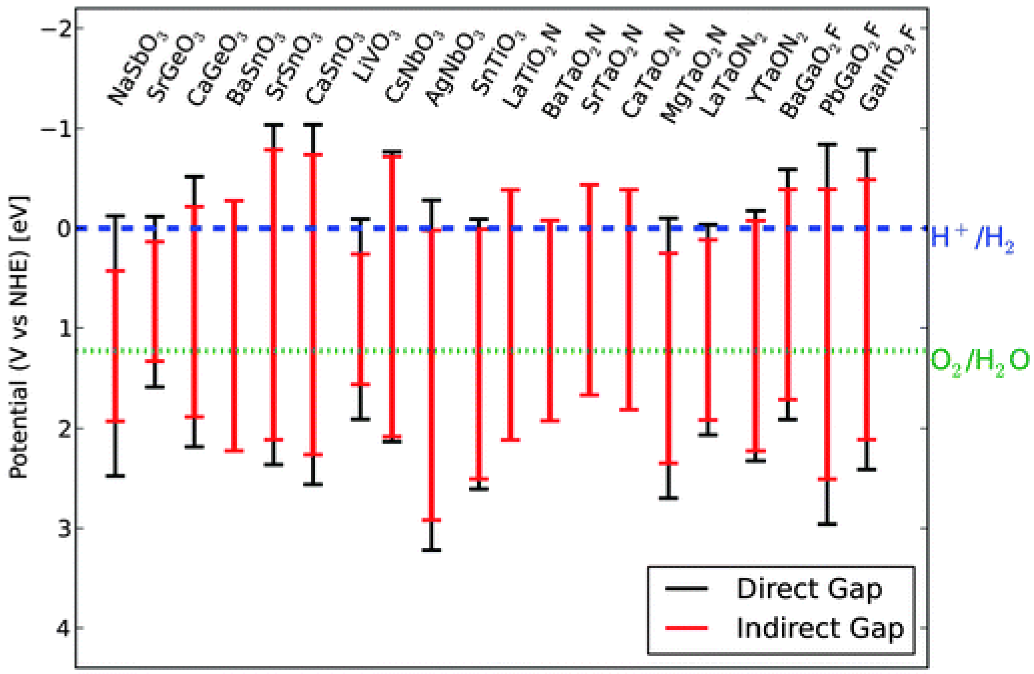
Cmmm

Science, 304, 855 (2004)

Perovskites

Photocatalytic splitting of H_2O for H_2 production

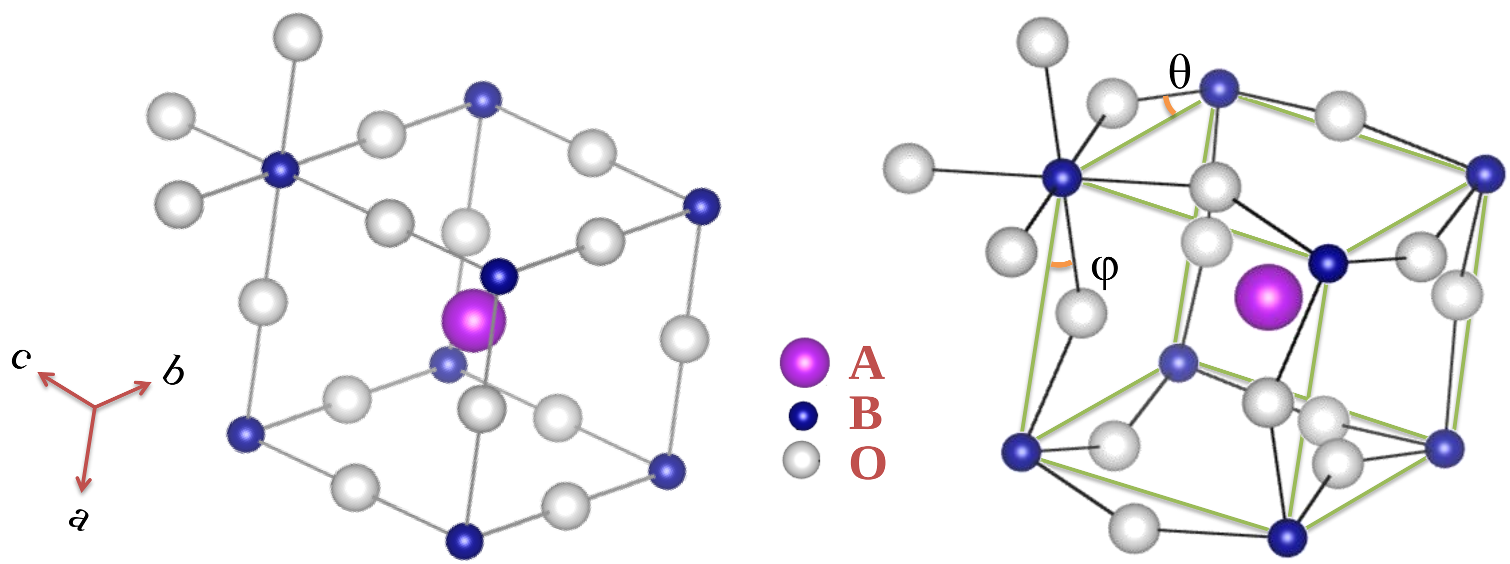




Energy Environ. Sci. 5, 9034 (2012)

Orthorhombic distortion

- ❑ BO_6 tilts around [010] → tilt angle "φ"
  & [101] → tilt angle "θ"
- ❑ A-ion displacement

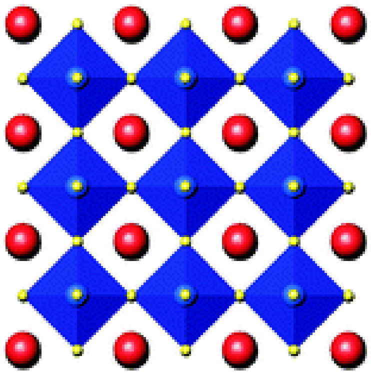


Cubic (*Fm-3m*)

Orthorhombic (*Pnma*)

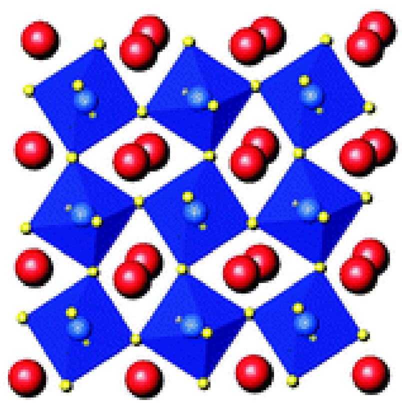
Orthorhombic distortion

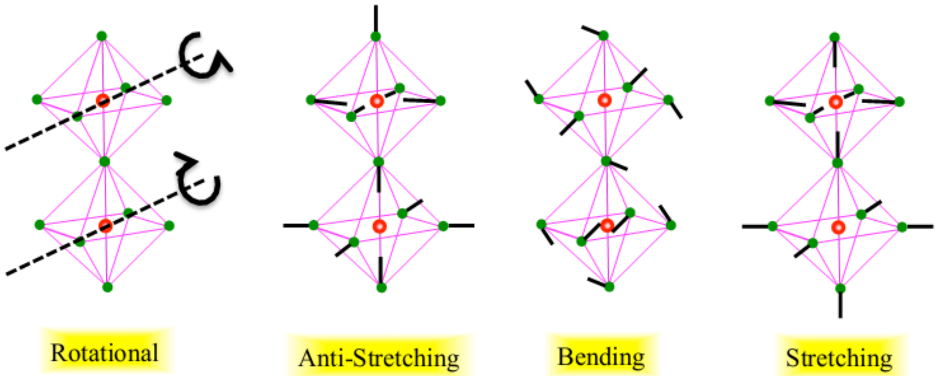
Cubic (*Pm-3m*)



Raman active modes are absent

Orthorhombic (*Pnma*)





24 Raman active modes

Distinct magnetic phases in $LaMn_{0.5}Co_{0.5}O_3$

B-site doped RMO_3 → Spintronic applications

$LaMn_{1-x}Co_xO_3$

$LaMnO_3$
Antiferromagnetic

$LaCoO_3$
Diamagnetic

$LaMn_{0.5}Co_{0.5}O_3$ (LMCO)

Heat above 1300 ^{0}C

Heat upto 800 ^{0}C

LTc
Ferromagnetic
$T_c \sim 142$ K

Ferromagnetic
$T_c \sim 240$ K
HTc

Phys . Rev . B, 67, 014401 (2003)

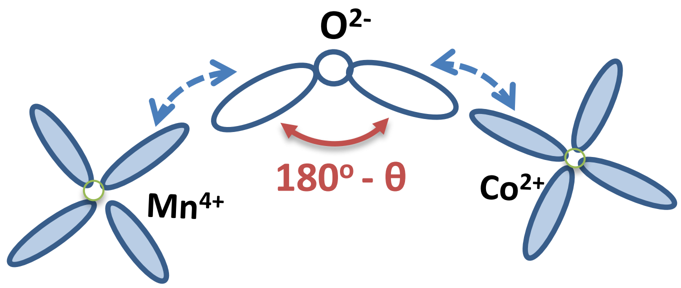
Two different T_C behavior ???

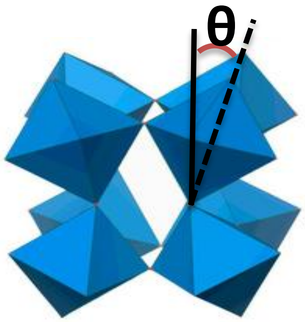
Magnetic ordering temperature

Spin Exchange Interactions

$$T_C = \frac{2nJ_{ex}(J+1)}{3K_B}$$

J_{ex}= exchange energy
J = total angular moment
n = number of nearest neighbors
K_B = Boltzmann constant

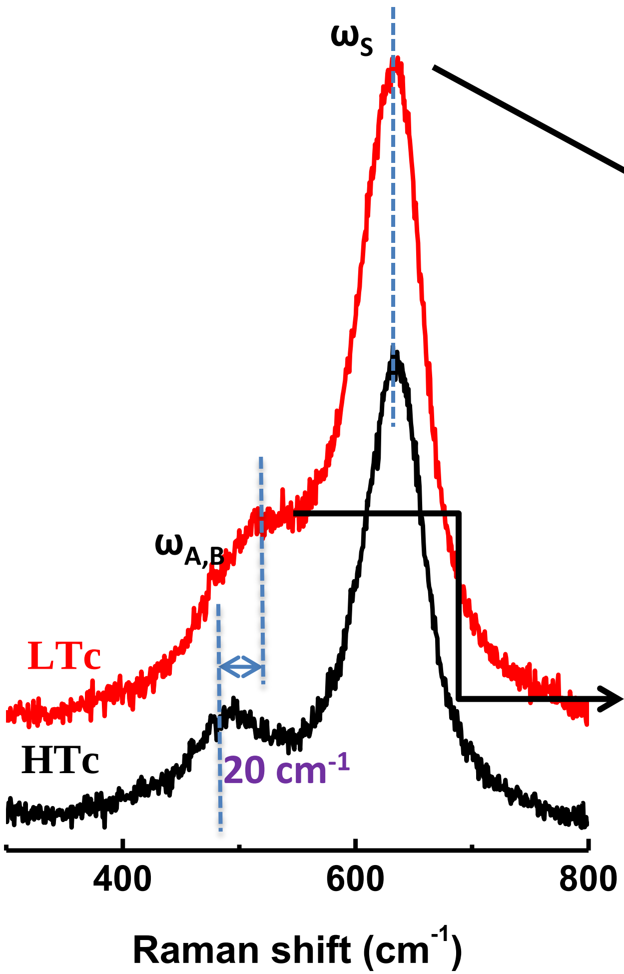




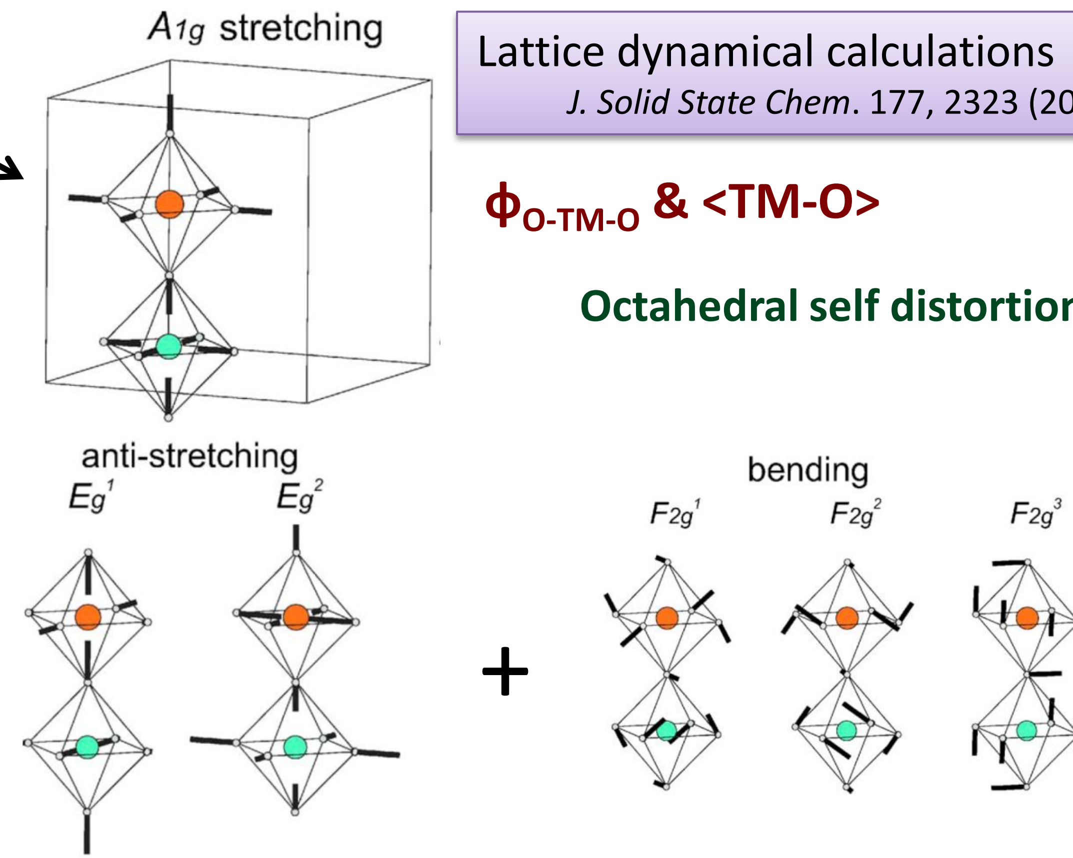
Phys. Rev. Lett. **75, 914 (1995)**

$$J_{ex} \propto \mathrm{Cos}^4(\theta_{avg})$$

Raman studies



Lattice dynamical calculations
J. Solid State Chem. 177, 2323 (2004)



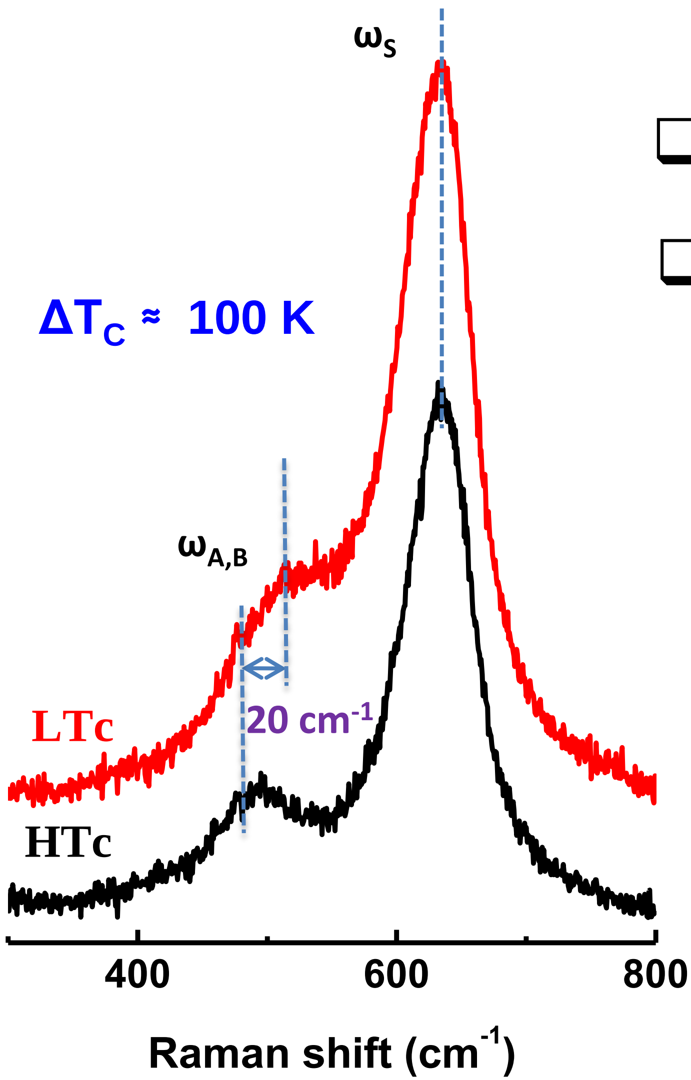
$\phi_{O\text{-}TM\text{-}O}$ & <TM-O>

Octahedral self distortion

θ_{avg} & <La-O>

Octahedral tilting

Difference in T_c values

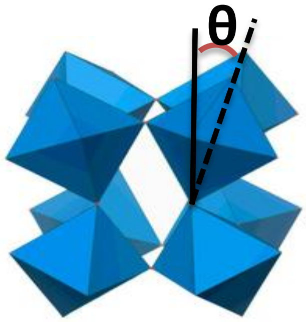


- Octahedral self distortion is same
- Octahedral tilting distortion is different

$\omega_{AB} \propto$ 'θ_{avg}'

$J_{ex} \propto \cos^4(\theta_{avg})$

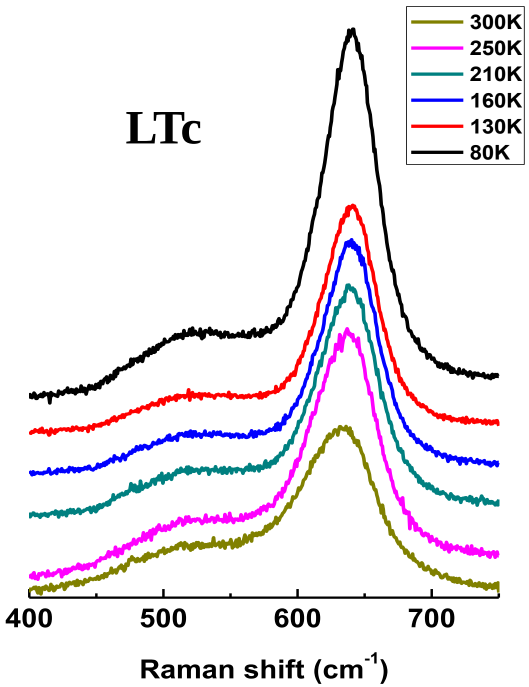
$$T_C = \frac{2nJ_{ex}(J+1)}{3K_B}$$



***Phys. Rev. Lett.* 75, 914 (1995)**

The difference in T_c values can be understood qualitatively using Raman

Temperature dependent Raman scattering



In magnetic materials change in phonon frequency with temperature:

$$\Delta\omega(T) = (\Delta\omega)_{latt} + (\Delta\omega)_{anh} + (\Delta\omega)_{ren} + (\Delta\omega)_{s\text{-}ph}$$

Phys. Rev. B 60, 11879 (1999)

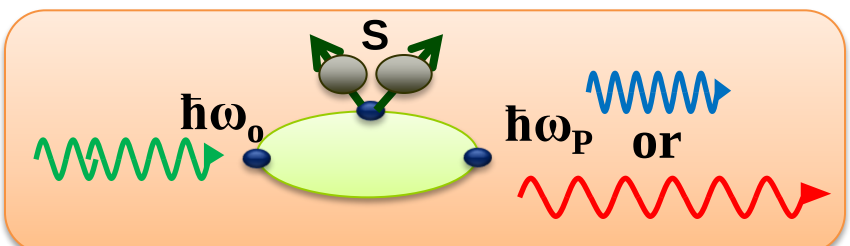
In case of magnetic insulators:

$$\Delta\omega(T) = (\Delta\omega)_{latt} + (\Delta\omega)_{anh} + (\Delta\omega)_{s\text{-}ph}$$

Exchange coupling between magnetic ions contribute as:

$$\Delta\omega_{s\text{-}ph} \approx \pm\lambda \langle S_i.S_j \rangle$$

J. Appl. Phys. 64, 5876 (1988)



In cubic anharmonic process, temperature dependence of phonon frequency:

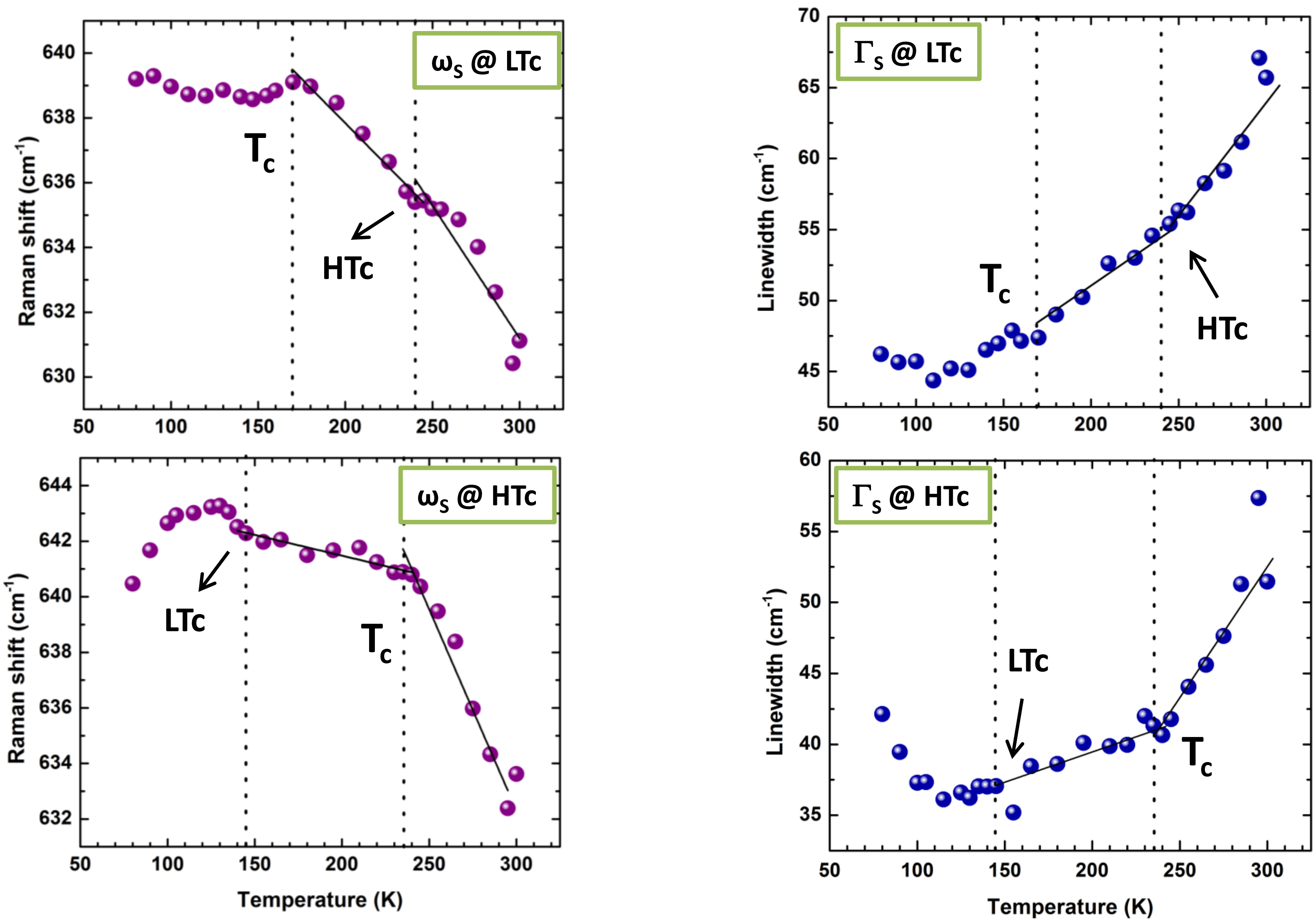
$$\omega_{anh}(T) = \omega_0 - C\left(1 + \left(2/\left(e^{\hbar\omega_0/K_BT} - 1\right)\right)\right)$$

temperature dependence of Raman linewidth:

$$\Gamma_{anh}(T) = \Gamma_0 + C\left(1 + \left(2/\left(e^{\hbar\omega_0/K_BT} - 1\right)\right)\right)$$

Any deviation is considered as due to **spin-phonon coupling.**

Temperature dependent Raman scattering



Co-existance of two magnetic phases is clearly seen from temperature dependent Raman

Conclusions

- ❑ Distortion dependent Raman modes in LMCO could give a qualitative understanding of the two T_C behaviour.

- ❑ Temperature dependence of Raman modes through spin-phonon coupling could show the coexistence of two magnetic phases in LMCO.

Multiferroicity in $RCrO_3$

Transport studies

❑ **Multiferroicity below Néel temperature (T_N) is observed in $RCrO_3$ only in the case of magnetic R^{3+} ion.**

$GdCrO_3$, $SmCrO_3$, $NdCrO_3$ etc. – Multiferroic
$LaCrO_3$, $LuCrO_3$, $TbCrO_3$ etc. – Non-multiferroic

Rajeswaran et.al. Phys. Rev. B (2012)

Applications in spintronics and magnetic memory devices

The mechanism for the occurrence of ferroelectricity in $RCrO_3$

Multiferroicity in *R*CrO_3

Raman studies

A LETTERS JOURNAL EXPLORING THE FRONTIERS OF PHYSICS

January 2013

EPL, **101** (2013) 17008 www.epljournal.org
doi: 10.1209/0295-5075/101/17008

Spin-phonon coupling in multiferroic $RCrO_3$ (R-Y, Lu, Gd, Eu, Sm): A Raman study

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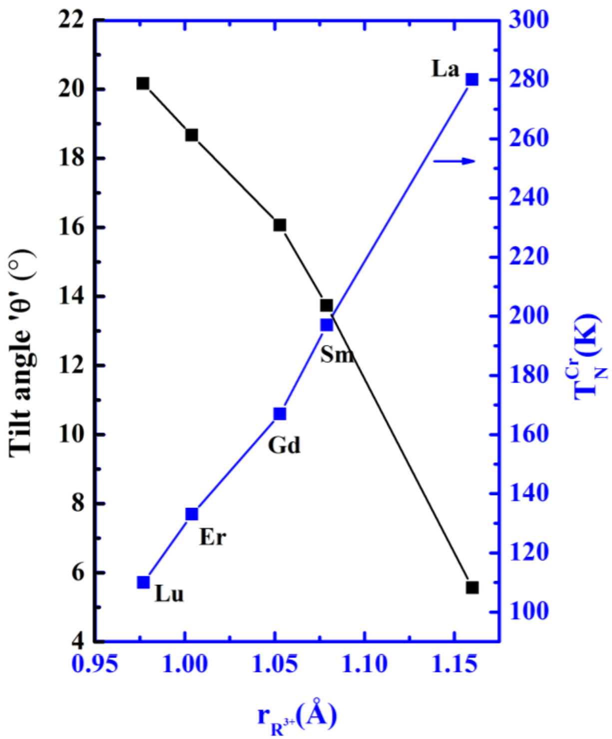
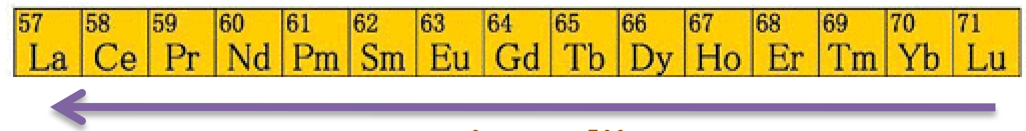
- **Magnetic *R*-Cr interactions mediated spin-phonon coupling could be leading to multiferroicity.**

Motivation for high pressure studies

Orthorhombic $RCrO_3$

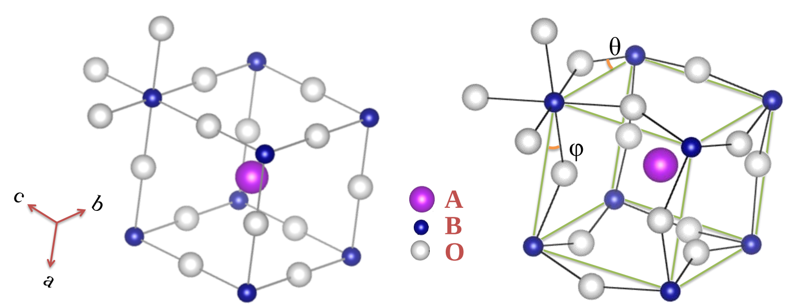




Ionic Radii

$$T_N^{Cr} \propto \cos^4(\theta_{avg})/l^7$$

$\theta_{avg} = (\theta+2\varphi)/2$; $l = \langle Cr - O \rangle$ is constant for all $RCrO_3$



Cubic (*Fm-3m*)

Orthorhombic (*Pnma*)

CrO_6 tilts around
[010] → θ
[101] → φ

Phys. Rev. B 86, 214409 (2012)

Phys. Rev. B, 8, 054303 (2012)

Reduce 'θ_{avg}' & 'l' to increase T_N, but how???

Motivation for high pressure studies

General Rule: with increasing pressure,

$A^{+3} B^{+3} O_3$: distortions increase

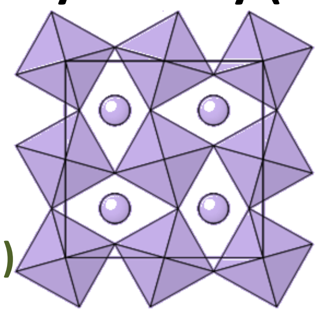
$A^{+2} B^{+4} O_3$: distortions decrease

Phys. Rev. Lett. 95, 025503 (2005)

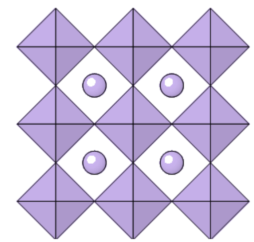
Low symmetry (P*bnm*) **High symmetry (R-*3C*)**

In case of **$LaCrO_3$**

Phys. Rev. Lett. 106, 057201 (2011)



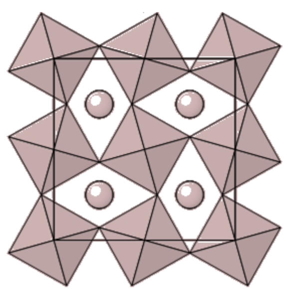
High Pressure



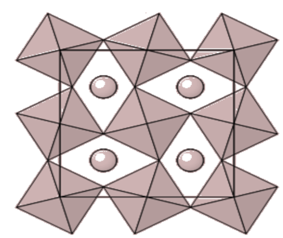
Contrasting Reports! **Role of *R*-ion size!**

In case of **$YCrO_3$**

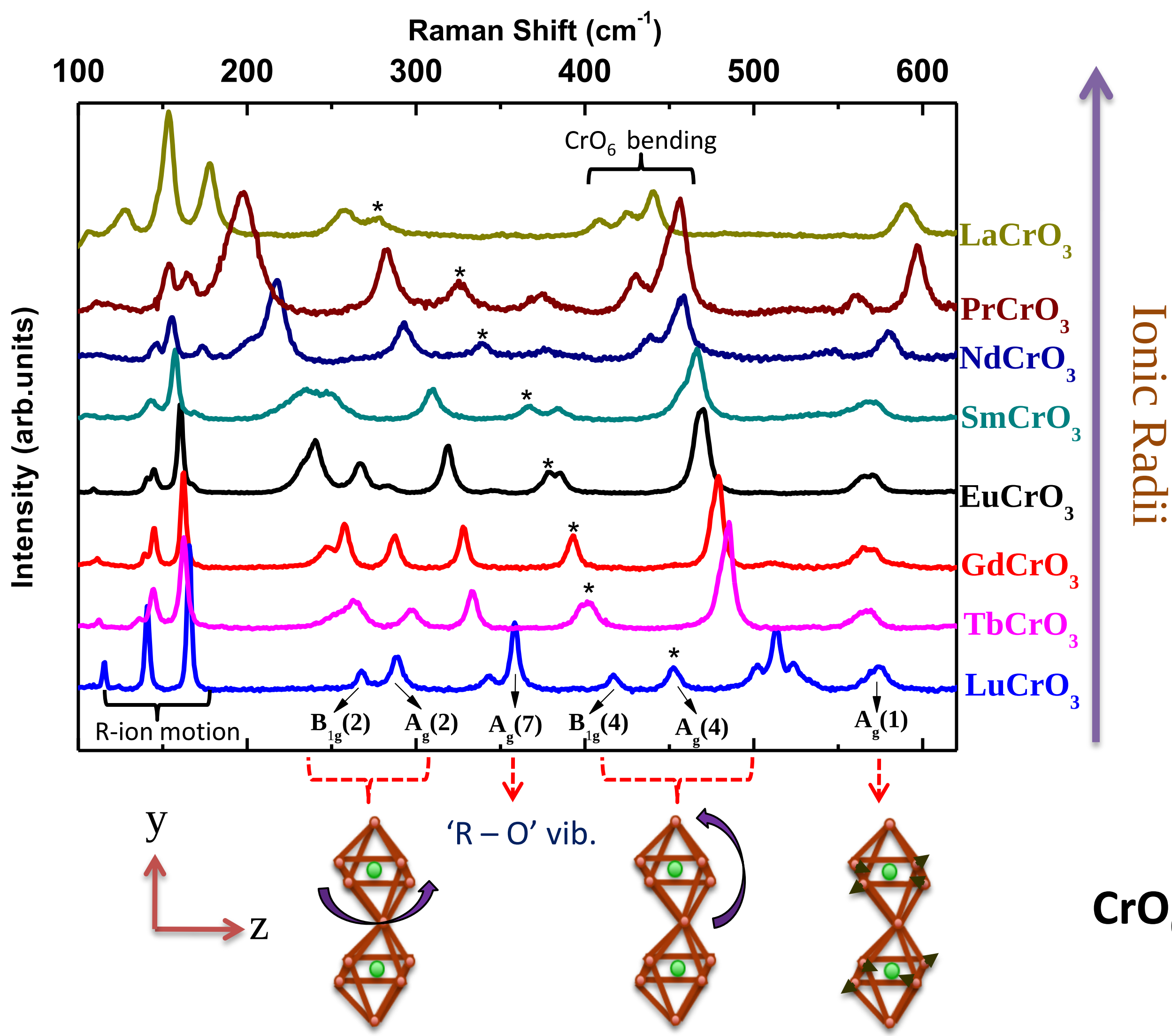
Phys. Rev. B 82, 064109 (2010)



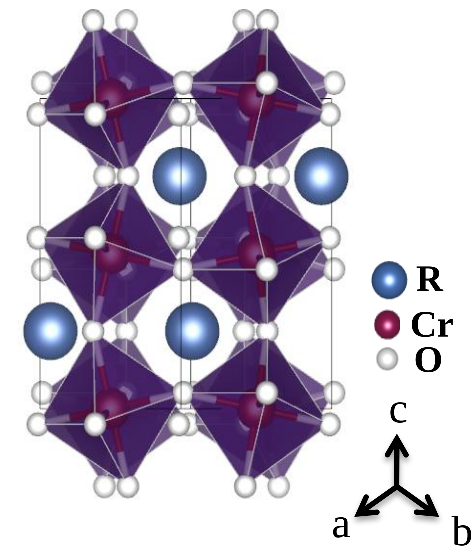
High Pressure



Raman spectra of $RCrO_3$



Orthorhombic *Pnma*

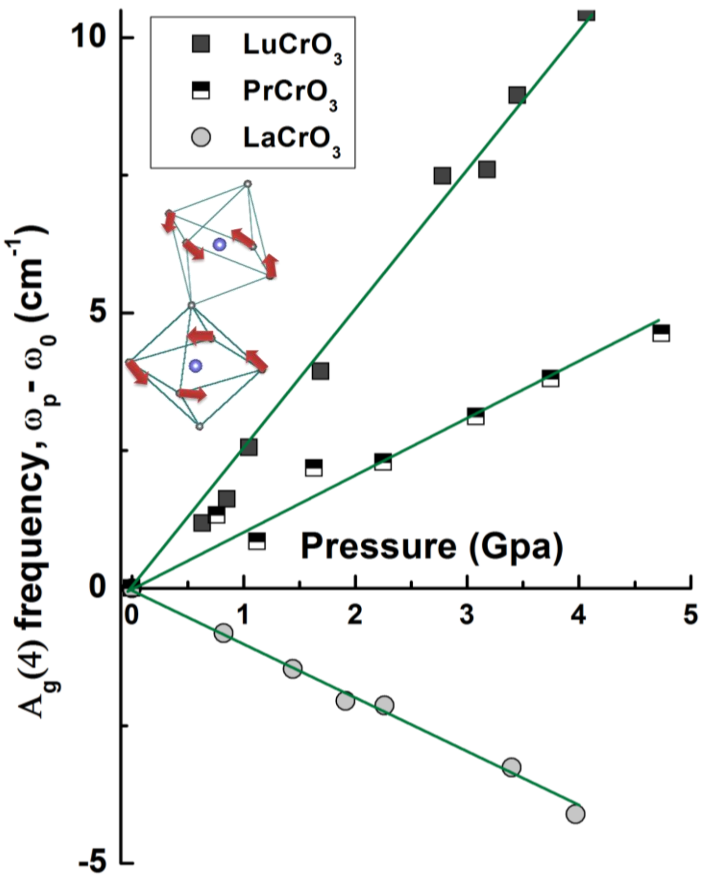


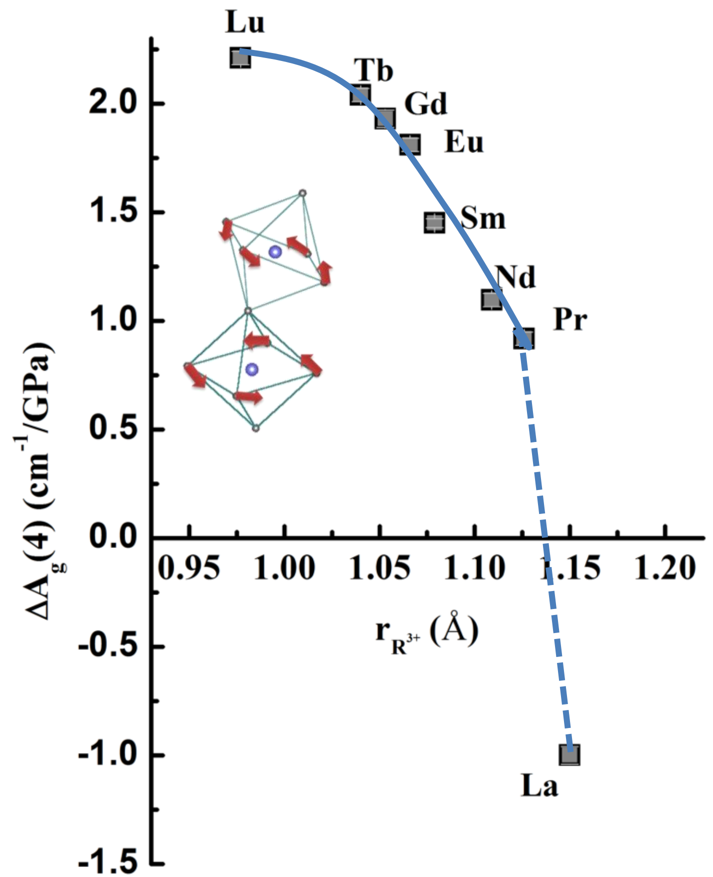
"θ" "ϕ"

CrO_6 tilts around [010] & [101]

- $A_g(2)$ and $A_g(4)$ are soft modes whose frequency vary linearly with "φ" and "θ" respectively.

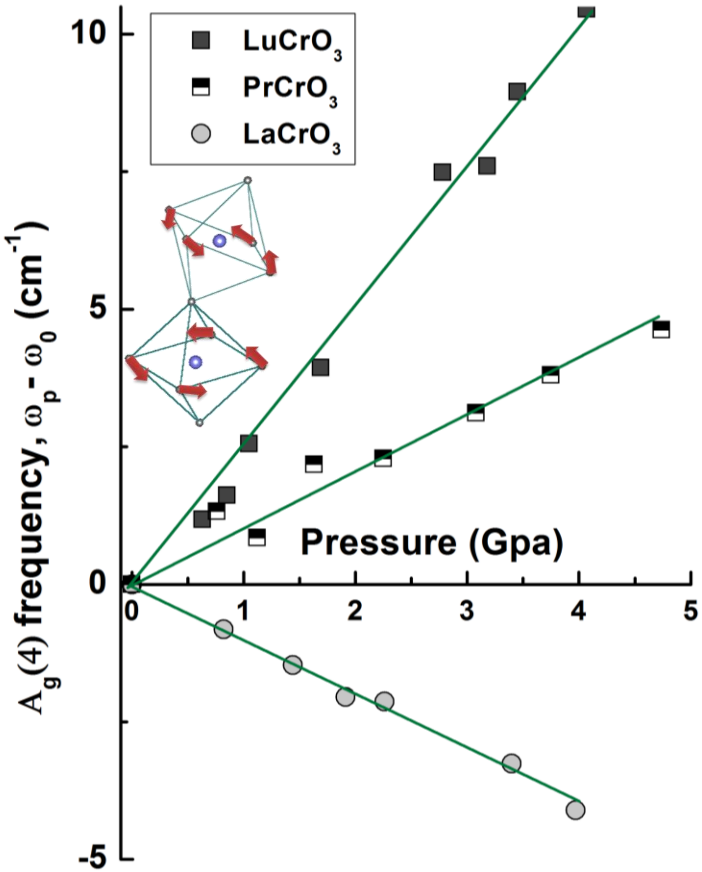
Pressure dependent Raman studies

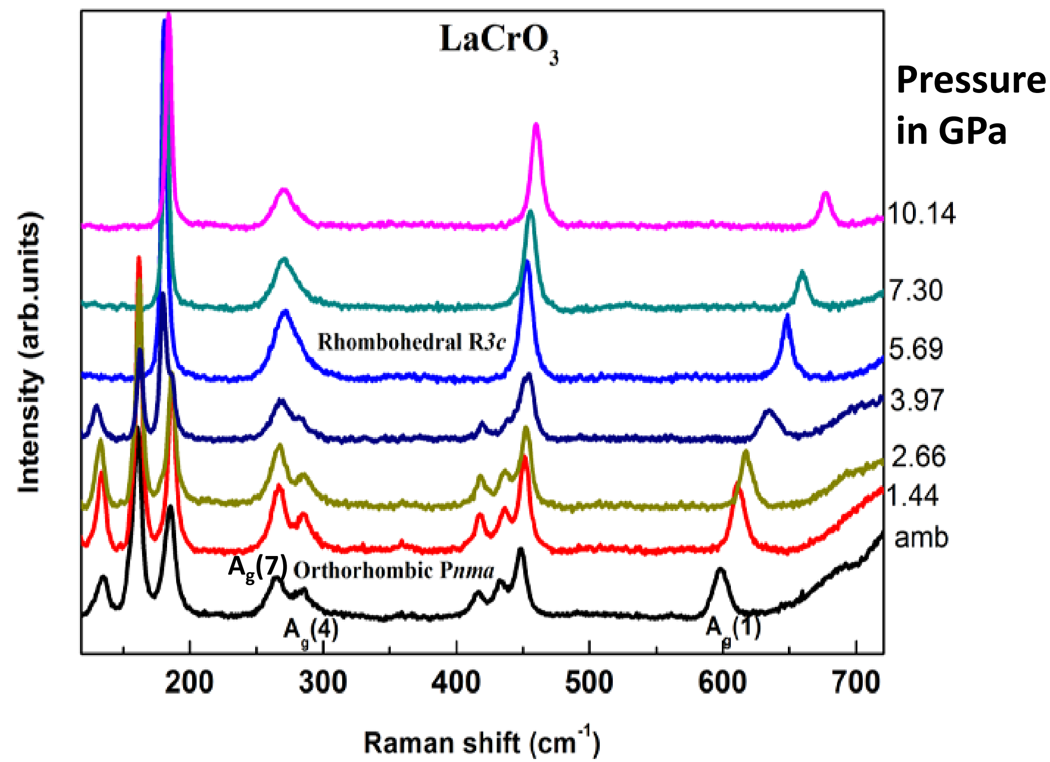




Only in $LaCrO_3$, distortions reduce with increase in pressure

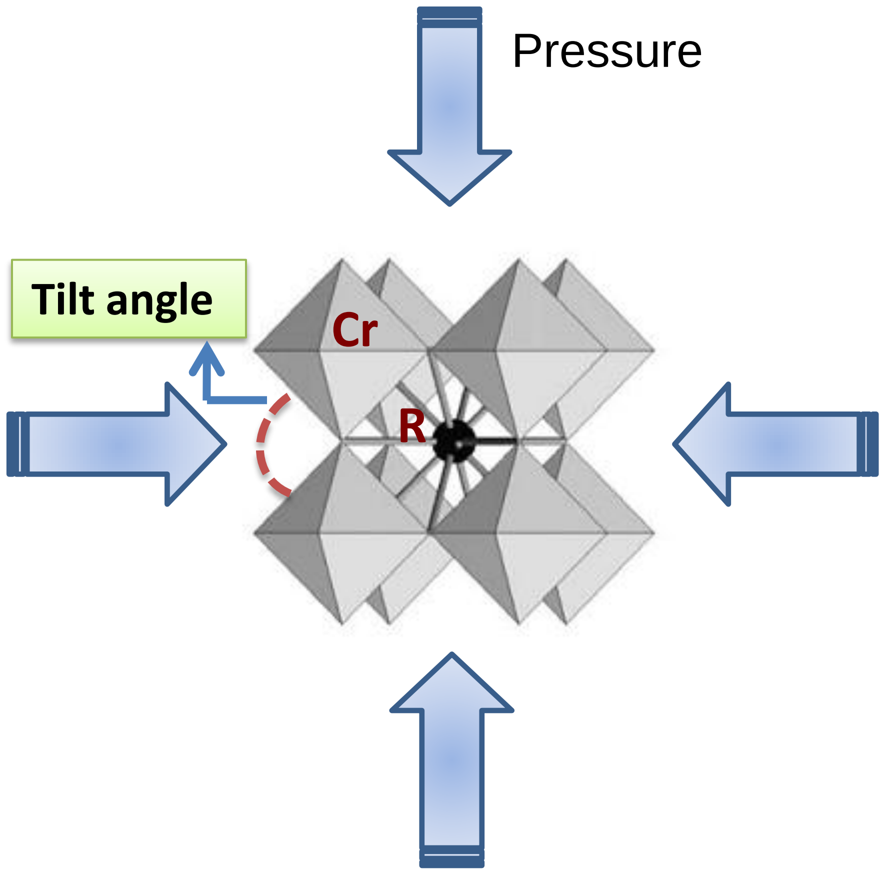
Pressure dependent Raman studies





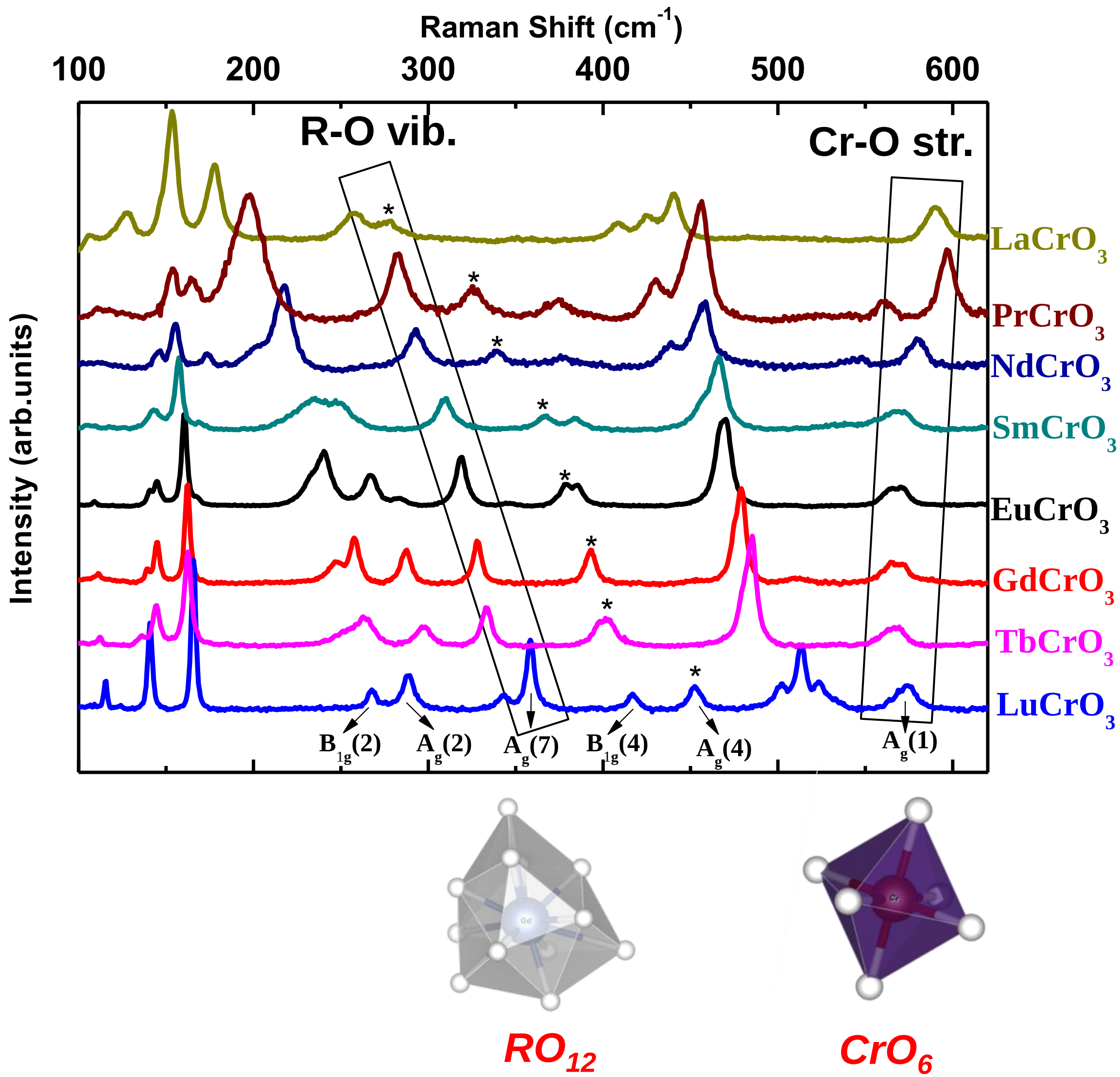
Only in $LaCrO_3$, distortions reduce with increase in pressure

Compressibility : CrO_6 vs RO_{12}

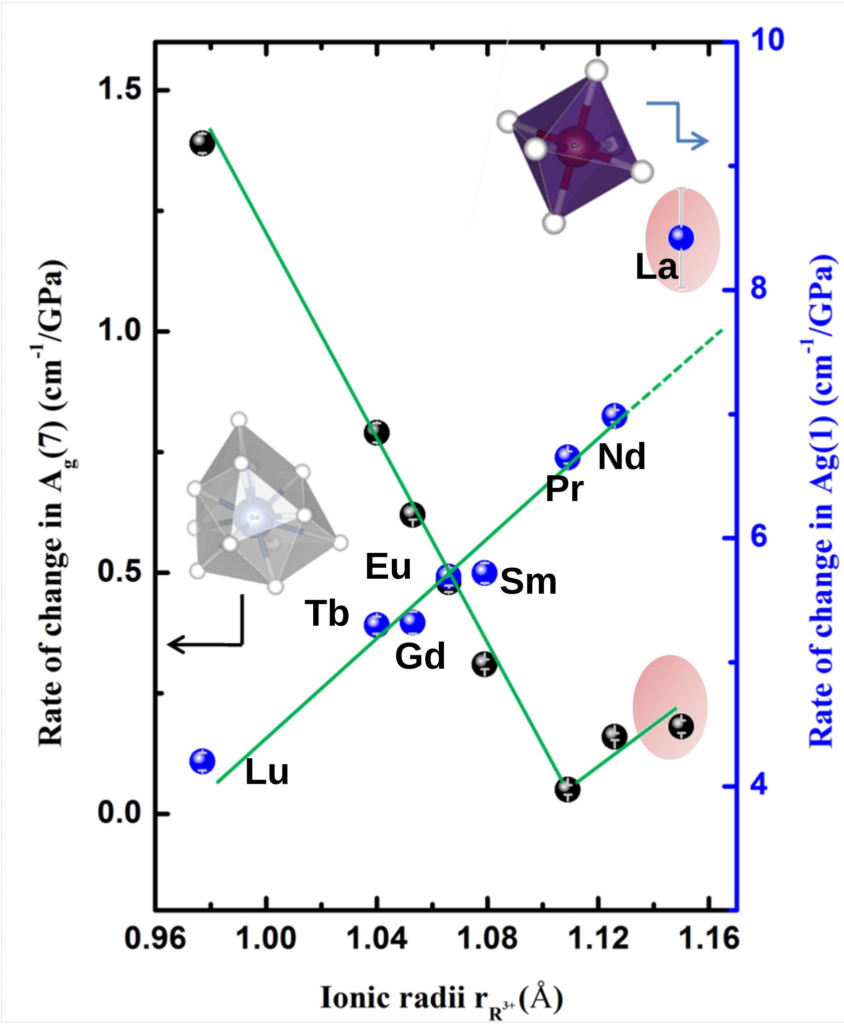


Difference in compressions at Cr and R sites alters the octahedral tilting

Compressibility : CrO_6 vs RO_{12}



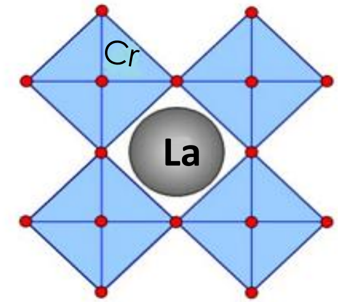
Compressibility : CrO_6 vs RO_{12}



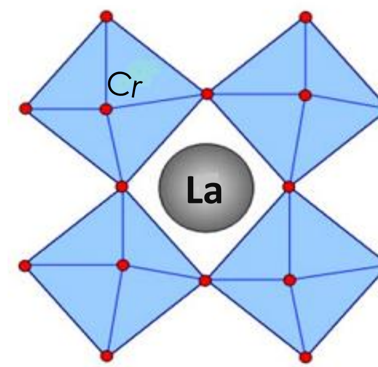
$LaCrO_3$

Less compressible at ‘La’

More compressible at ‘Cr’

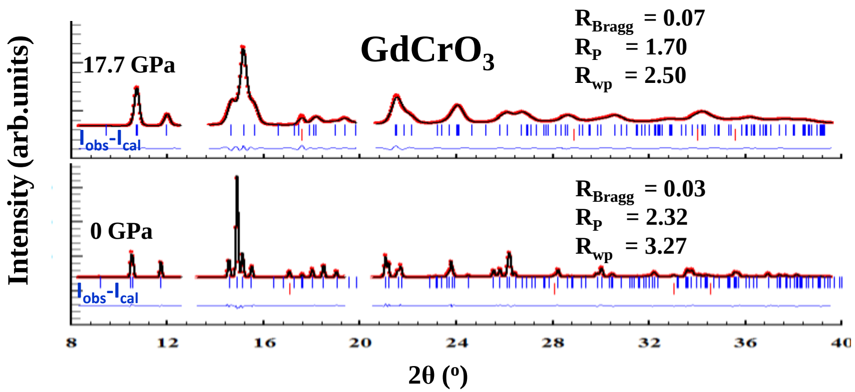


P



‘Unique’ analysis of Raman modes ➡ Role of *R*-ion size

XRD pattern



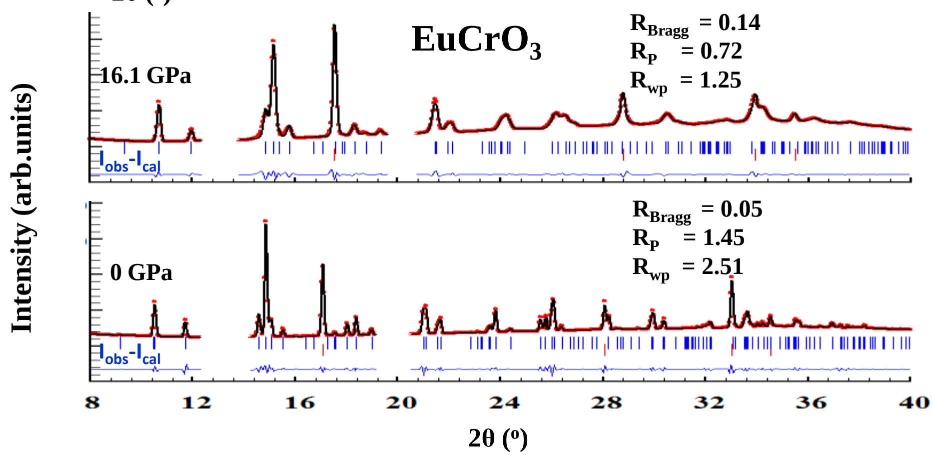
Profile matching with Le Bail fit

FullProf Suite

Crystallographic tools for Rietveld, profile matching & integrated intensity refinements of X-Ray and/or neutron data

a= 5.3238(1)Å
b=5.5279(1) Å
C=7.6184(1)Å

a= 5.3714(2) Å
b=5.5255(2)Å
C=7.6372(3)Å



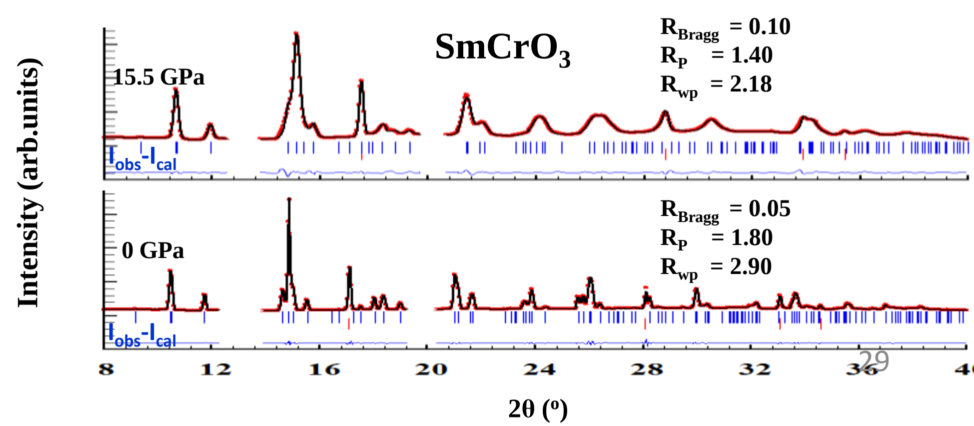
Orthorhombic (*Pbnm*)

Elettra Sincrotrone Trieste

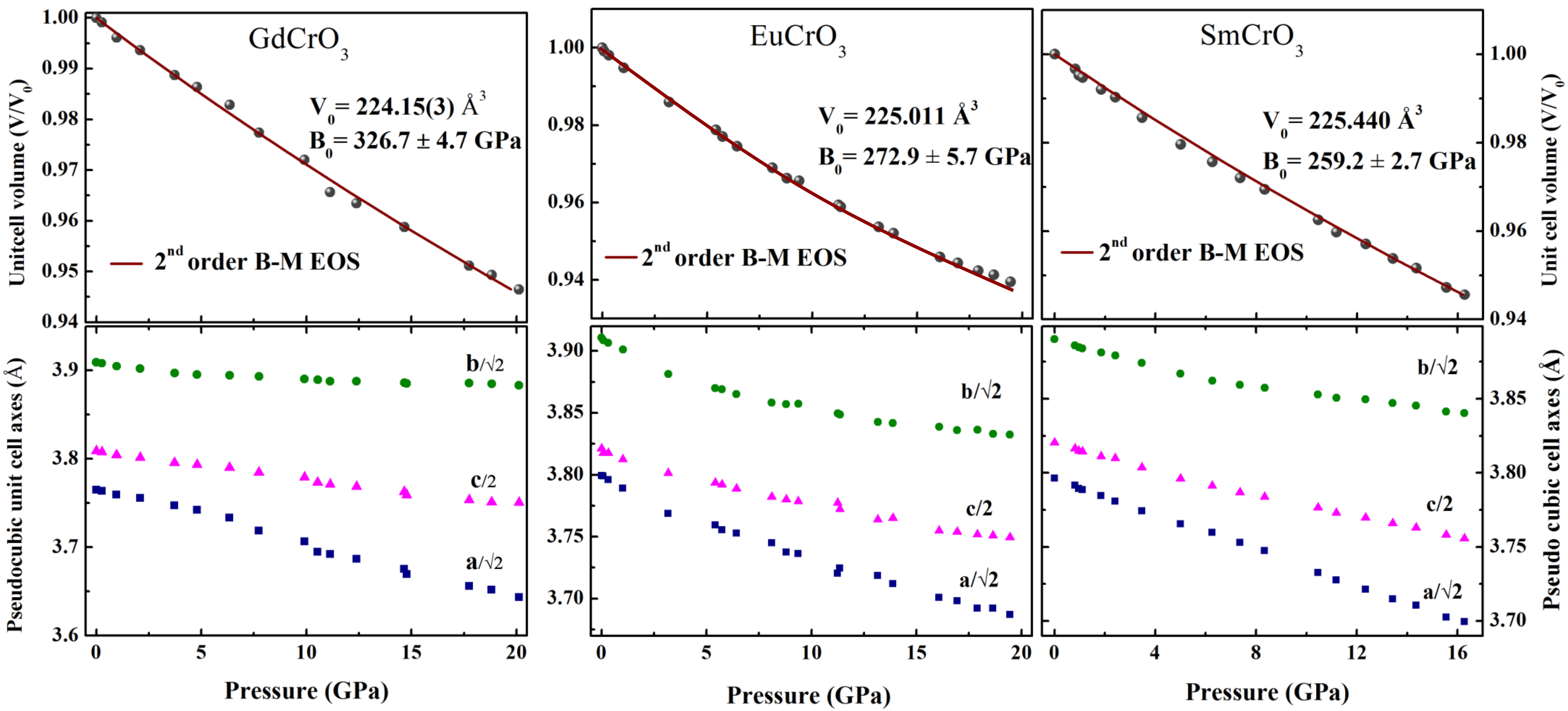
Monochromatic

λ = 0.7 Å

a= 5.3698(3) Å
b=5.5143(1)Å
C=7.6512(1)Å



Lattice parameters

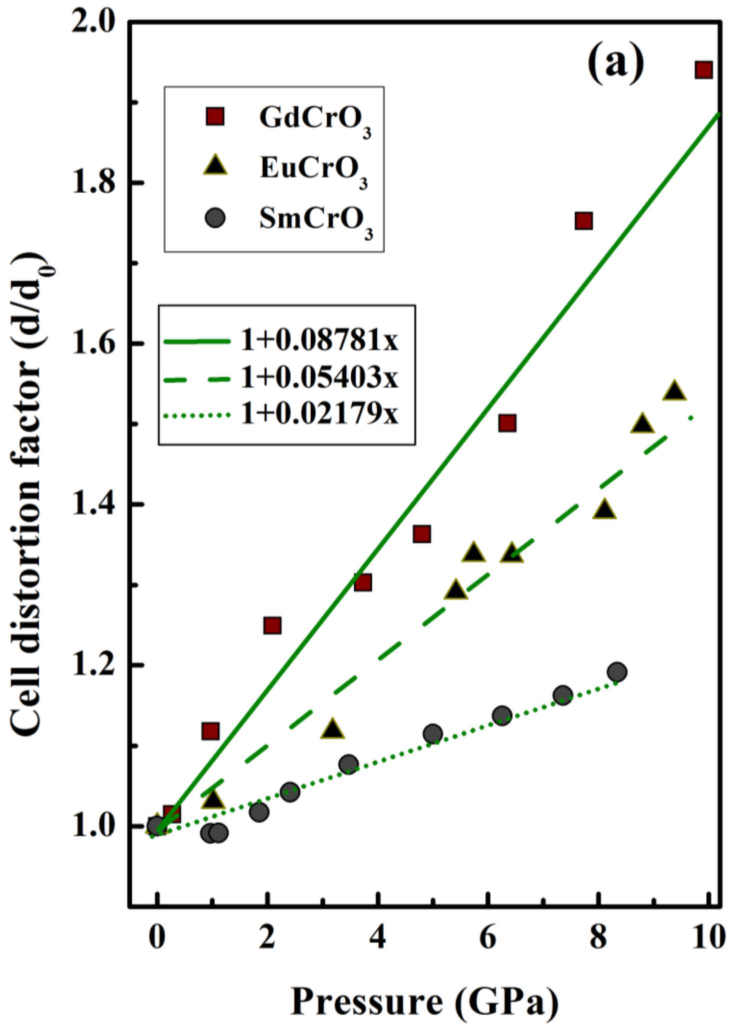


No structural transition is observed

2nd order Birch-Murnagham EOS $P = \frac{3B_0}{2}\left[\left(\frac{V_0}{V}\right)^{\frac{7}{2}} - \left(\frac{V_0}{V}\right)^{\frac{5}{2}}\right]$

B_0= bulk modulus

Cell distortion factor

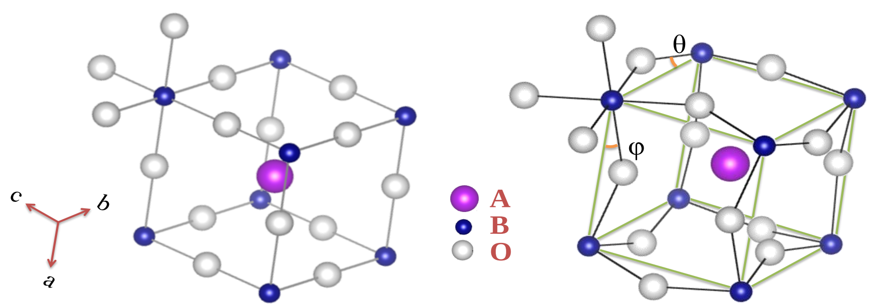


$$d = \frac{\left[\left(\frac{a}{\sqrt{2}} - a_p\right)^2 + \left(\frac{b}{\sqrt{2}} - a_p\right)^2 + \left(\frac{c}{2} - a_p\right)^2\right]}{3a_p^2 \times 10^4}$$

Where

$$a_p = \frac{\left(\frac{a}{\sqrt{2}} + \frac{b}{\sqrt{2}} + \frac{c}{2}\right)}{3}$$

Am. Mineral., 68, 1189 (1983)



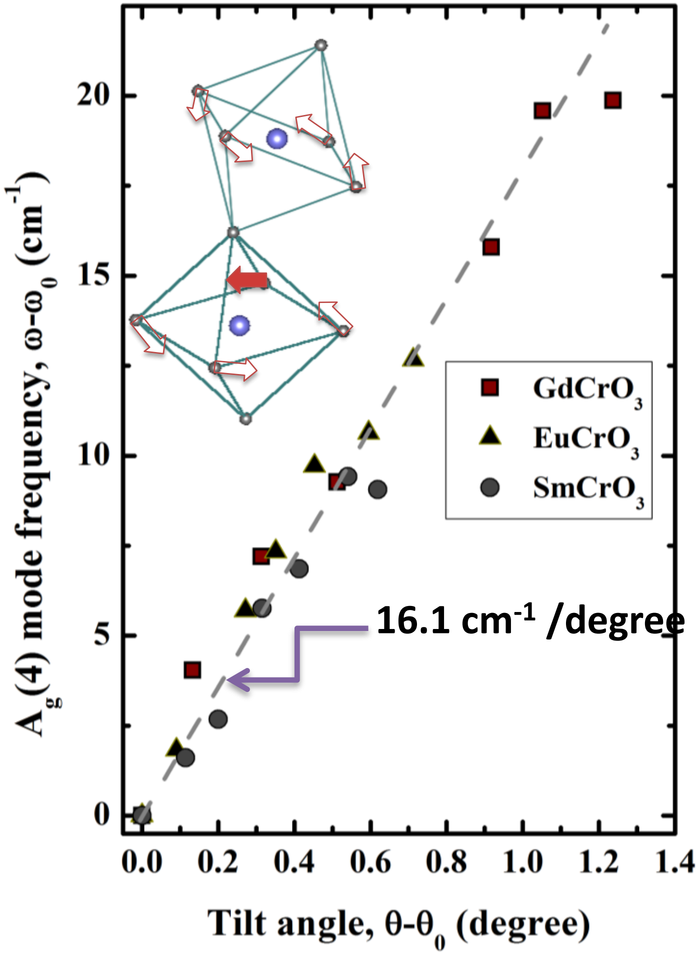
Cubic (*Fm-3m*)

Orthorhombic (*Pnma*)

Support for Raman results

Softmode vs Tilt angle

External pressure



By neglecting the self distortion of the CrO_6

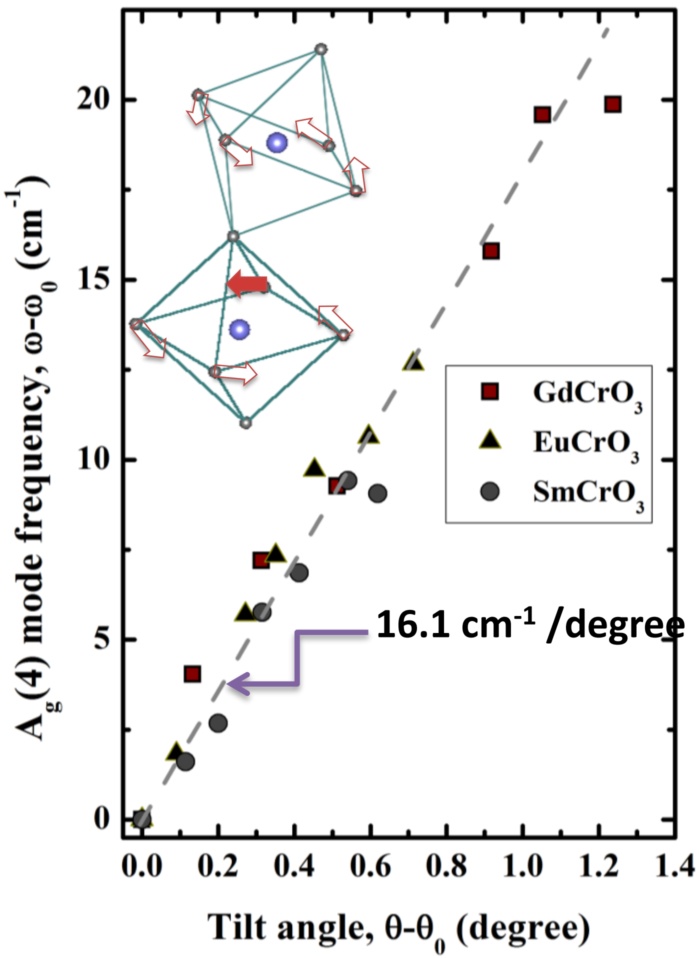
$$\varphi = \cos^{-1}\left(\frac{a}{\sqrt{2}c}\right)$$

$$\theta = \cos^{-1}\left(\frac{a}{b}\right)$$

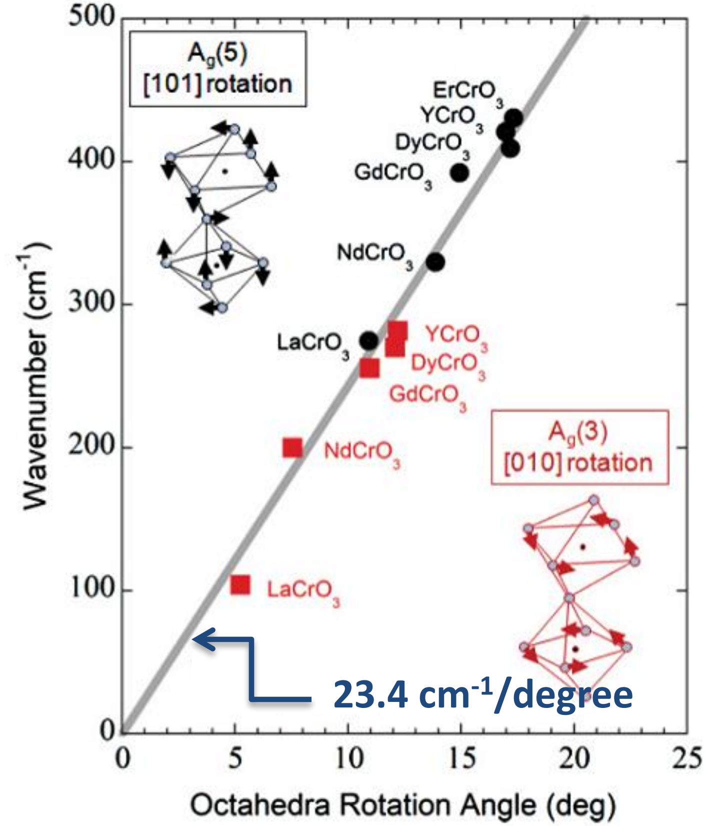
Phys. Earth. Planet. Inter. 76, 1 (1993)

Softmode vs Tilt angle

External pressure



Chemical pressure



Phys. Rev. B 85, 054303 (2012)

Behavior of octahedral distortions w.r.t. chemical pressure (*R*-ion size) and external pressure is different.

Pressure effects on the Néel temperature

Bloch's rule: Based on the change in lattice volume with pressure,

$$\frac{dT_N}{dP} = 3.3T_N\kappa$$ 'κ' is the compressibility

J. Phys. Chem. Solids, 27, 881 (1965)

$$\frac{dT_N}{dP} = (1.561)_{Gd} < (2.543)_{Eu} < (2.691)_{Sm} \text{ degree/GPa}$$

$$T_N^{Cr} \propto cos^4(\alpha)/l^7$$

Phys. Rev. B 81, 214115 (2010)

where $\alpha = \frac{\theta+2\varphi}{2}$ and $l = \langle Cr - O\rangle$

Explicit relation

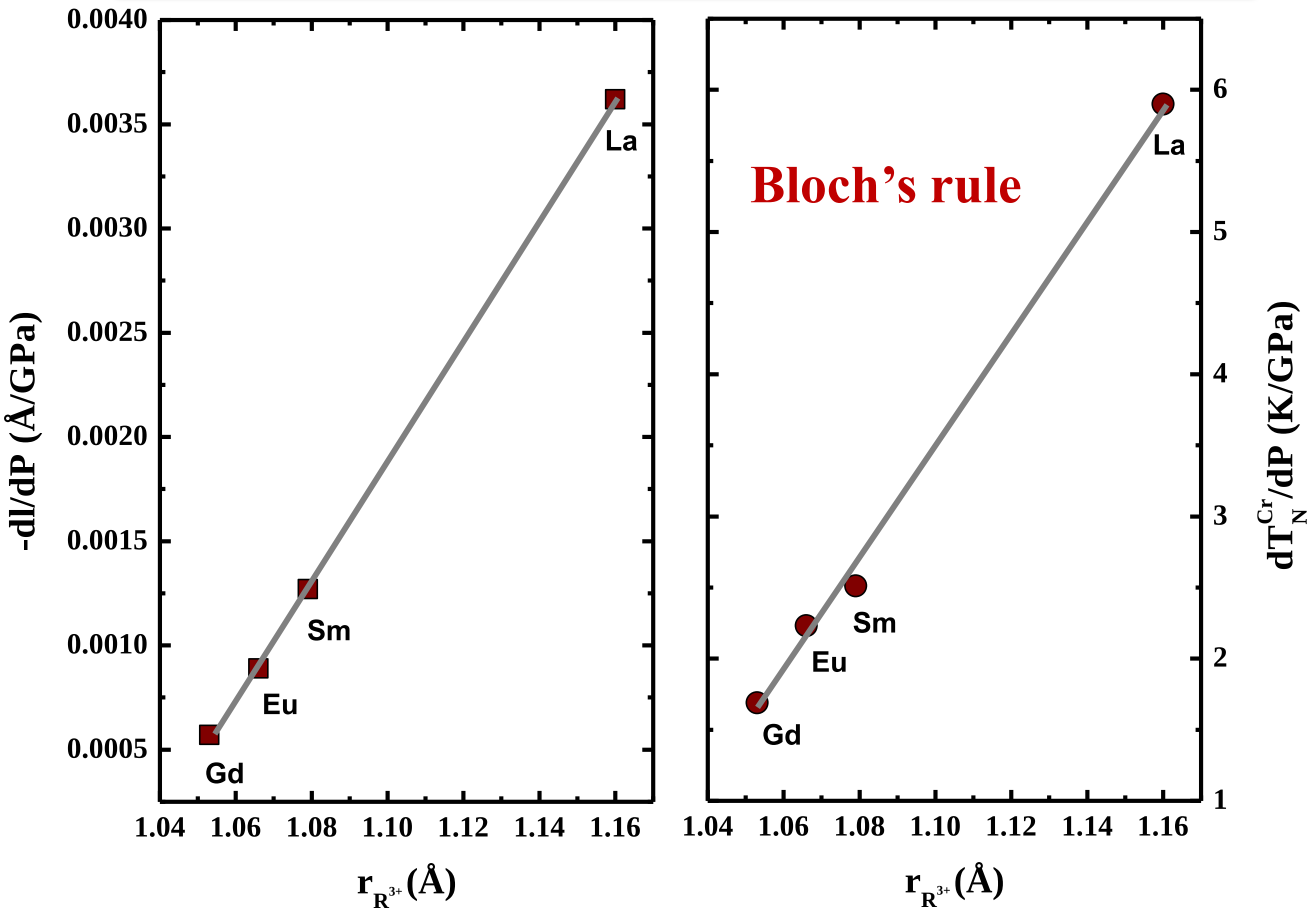
$$\frac{dT_N^{Cr}}{dP} = -T_N\left[\frac{7}{l}\frac{dl}{dP} + \left(2\tan\left(\frac{\theta+2\varphi}{2}\right)\left(\frac{d\theta}{dP} + 2\frac{d\varphi}{dP}\right)\right)\right]$$

Negative quantity

Positive/negative quantity (Raman data)

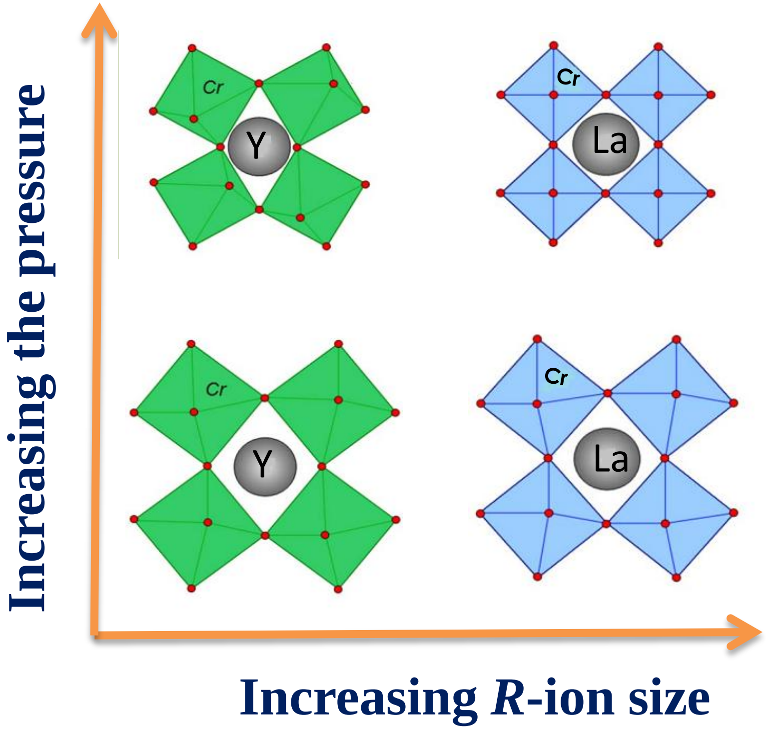
Pressure effects on the Néel temperature

$$\frac{dT_N^{Cr}}{dP} = -T_N\left[\frac{7}{l}\frac{dl}{dP} + \left(2\tan\left(\frac{\theta+2\varphi}{2}\right)\left(\frac{d\theta}{dP} + 2\frac{d\varphi}{dP}\right)\right)\right]$$



$\frac{dT_N}{dP}$ is more sensitive to compression of Cr-O under external pressure

Conclusions



Pressure effects on perovskite distortions

- ✓Role of *R*-ion size
- ✓Effect on the magnetic properties
- ✓Chemical pressure vs external pressure

V. S. Bhadram et al, *Mater. Res. Express* 1, 026111 (2014)
V. S. Bhadram et al (unpublished results)

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Thank you