The effect of **high-pressure** on (multi-)ferroics

or

How do distortions behave under pressure? General rules ?

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Outline

A. Introduction & motivation

1. Interest of high-pressure
2. Orders of magnitude

B. Applying High-Pressure

1. Diamond anvil cells
2. Large volume cells
3. Feasable ⇔ unfeasable

C. Illustrations **1** : Ferroic oxides

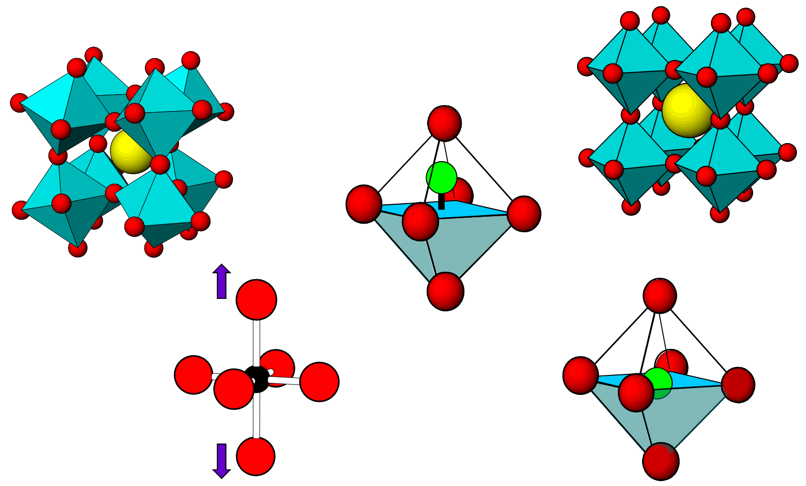
1. Octahedra tilts (ferroelasticity)
2. Cation displacements (ferroelectricity)
3. Disordered materials
4. General rules

D. Illustrations **2** : **Multiferroic oxides**

1. Type 1 MF: $BiFeO_3$
2. Type 2

E. Current trends & conclusions

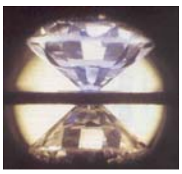
What is the effect of high-pressure ?



High-pressure : Strong modifications of interatomic distances & bond angles

➔ Modificaion / Tuning of coupling and physical properties

Interest of high-pressure studies (p > 1 GPa)



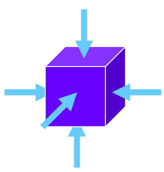
"Clean" parameter (G.A. Samara *et al.*)

- Acts only on interatomic distances
- Important changes in volume (chemical bonding)

  0 to 700 K $\rightarrow \Delta V/V_0 = 1$ % $\leftrightarrow$ 1 bar to 100 GPa $\rightarrow \Delta V/V_0 \approx 25$ %
- Access to new structural & physical phenomena

Estimation and understanding of strain in thin films

- e.g. Estimation of strain via Raman modes in ferroelectrics
- Relation with strain-induced deformations ?



Ab-initio calculations

- Pressure easier simulated than temperature
- Serious test for ab-initio models

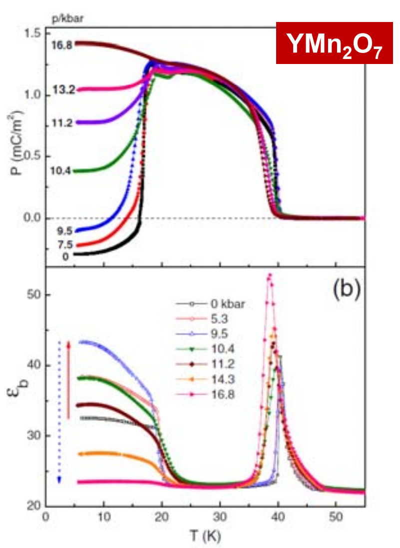
Illustration / Motivation

RAPID COMMUNICATIONS

PHYSICAL REVIEW B 77, 220104(R) (2008)

Pressure-induced polarization reversal in multiferroic YMn_2O_5

Rajit P. Chaudhury,[1] Clarina R. dela Cruz,[2,3] Bernd Lorenz,[1] Yanyi Sun,[1] Ching-Wu Chu,[1,4,5] S. Park,[6] and Sang-W. Cheong[6]



Pressure can

reduce & enhance

ferroelectricity

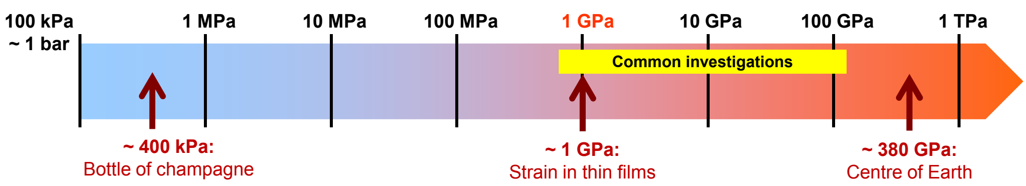
➔ thus acts on m-e coupling

What is high-pressure ?

High-pressure ➔ ΔV / V = 10-25%

1 bar = 1 kg/cm²

50 GPa = 500 kbar = 500 t/cm²



$P = \frac{Force}{Surface}$

Increase F

~ 5 MPa

Reduce S

~ 6 MPa

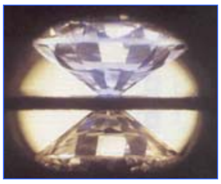
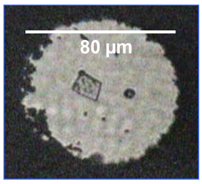
~ 1 GPa

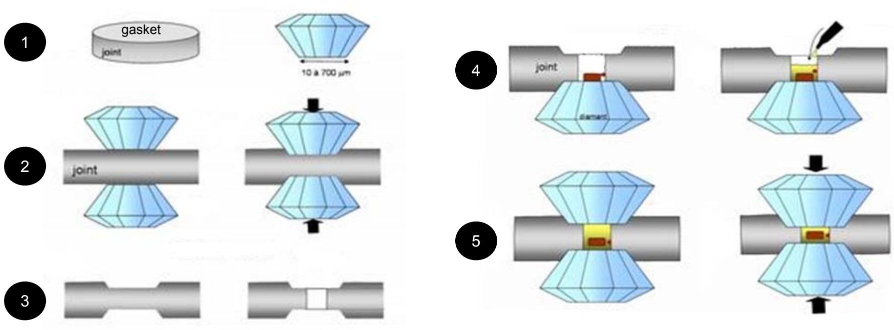
B. Experimental aspects

More elegant ways to apply high-pressure …

1. Diamond anvil cells
2. Large volume cells
3. Feasable ⇔ unfeasable

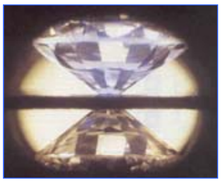
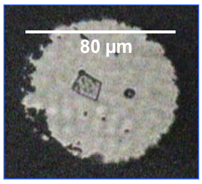
Applying high-pressure in a diamond anvil cell

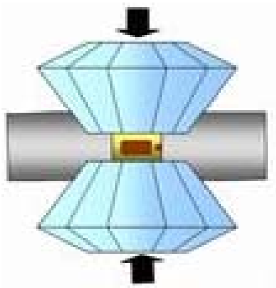






(Pictures: P. Gillet)

Applying high-pressure in a diamond anvil cell



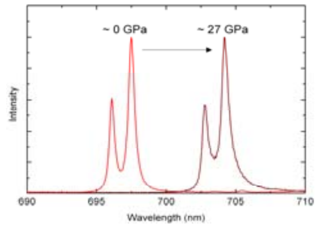
Diamonds
Size, defects…

Gasket
Steel, Rhenium…

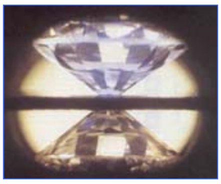
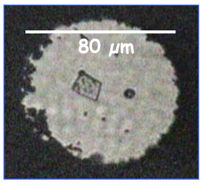
Pression gauge
Ruby, Au…

Transmitting medium
Noble gases (He, Ne)
Alcohol, oil…

Ruby fluorescence line

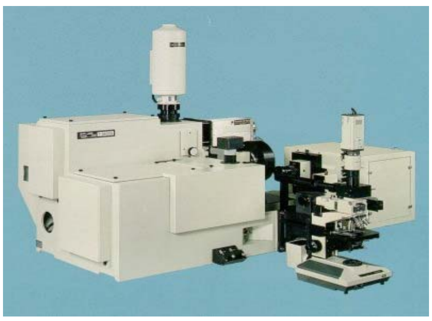


1) Raman spectroscopy and any optical measurement in a DAC

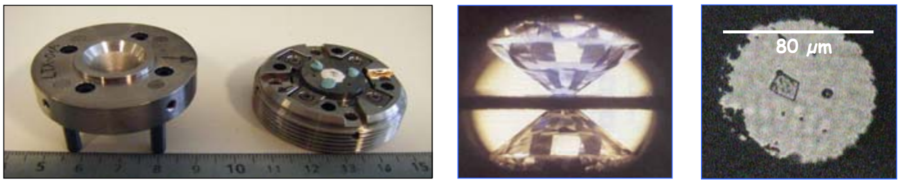
Raman spectroscopy : a probe for
- Phase transitions
- Phonons
- Soft modes

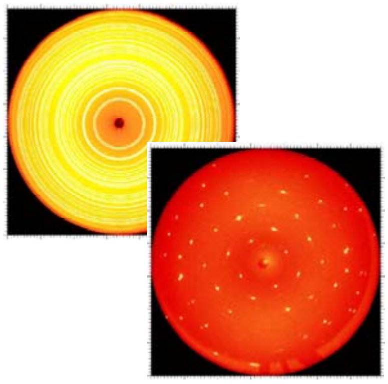
Experimental issues
- Purity of the diamond
- Long focal objective
- Signal of the diamond
- Intensity of the Raman signal



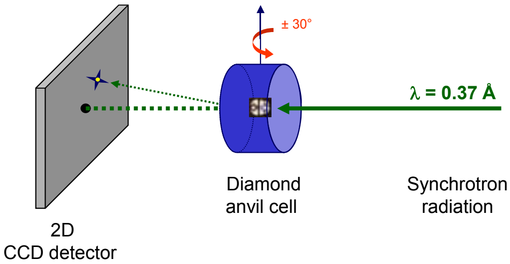
Micro-Raman - T64000 - Jobin-Yvon

2) Synchrotron X-ray diffraction or absorption in a DAC





Synchrotron sources , ex. diffraction



Large Volume cells ex. « Paris-Edinburgh Cell »

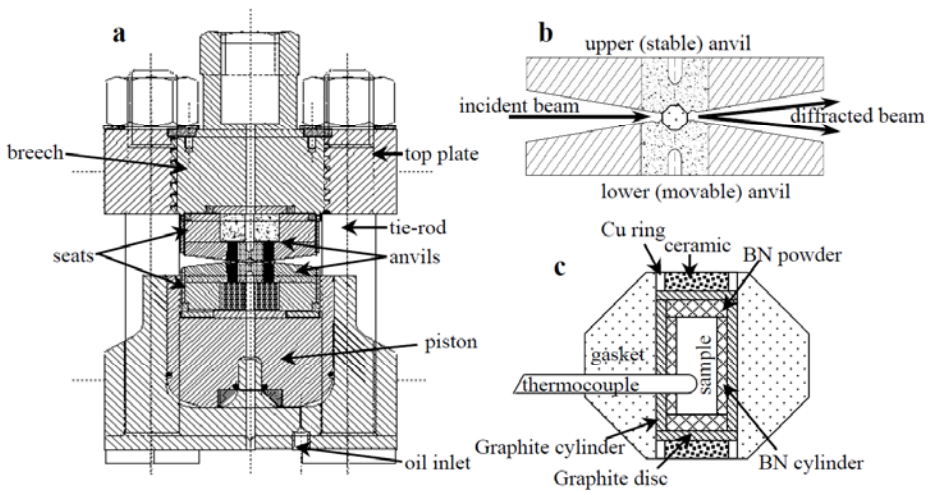


Figure 1: Cross-section of Paris-Edinburgh press (**a**), anvils/sample ensemble (**b**) and sample (**c**).

How does it look like

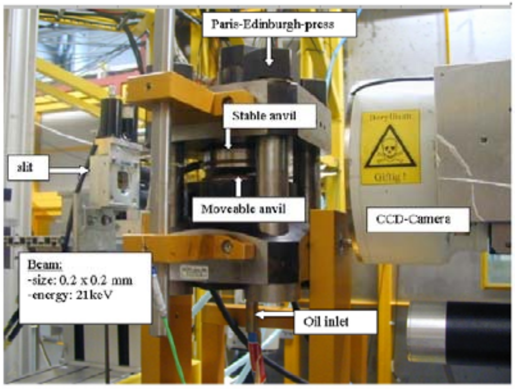


Figure 2: Picture of the set-up at beamline PETRA1.

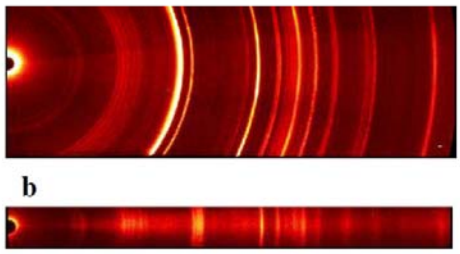


Figure 3: XRD pattern recorded of a $AlSi_{26}Ni_8$ sample at ambient pressure (**a**) and 6.8 GPa (**b**).

Magnetic measurements under pressure

MPMS cell specifications	Hydrostatic		Uniaxial	High pressure		
	MPMS	MPMS	MPMS	PPMS	PPMS	MPMS
Model	LPC-15	MLPC-15	XPC-5	HPC-20	HPC-30	HMD-13
Pressurization system	Hydrostatic		Uniaxial	High pressure		
Maximum applied pressure	1.25 GPa	1.5 GPa	500 MPa	2.0 GPa	3.0 GPa	1.3 GPa
Maximum sample pressure @ 7K	1 GPa	1.2 GPa	400 MPa	1.6 GPa	2.4 GPa	1.0 GPa

Feasible experiments ?

- Type of Measurements ? Optical or not ?
- Wiring needed ?
- Needed size of sample ?
- Pressure range ?

Below 10 GPa
(large volume anvil press', screw press & diamond anvil cells)

➔ Most experiments are feasible 👍
➔ X-ray, neutrons (!), magnetic, electric, optic
➔ Optical experiments either in diamond anvils or by side view

Above 10 GPa
(diamond anvil cells)

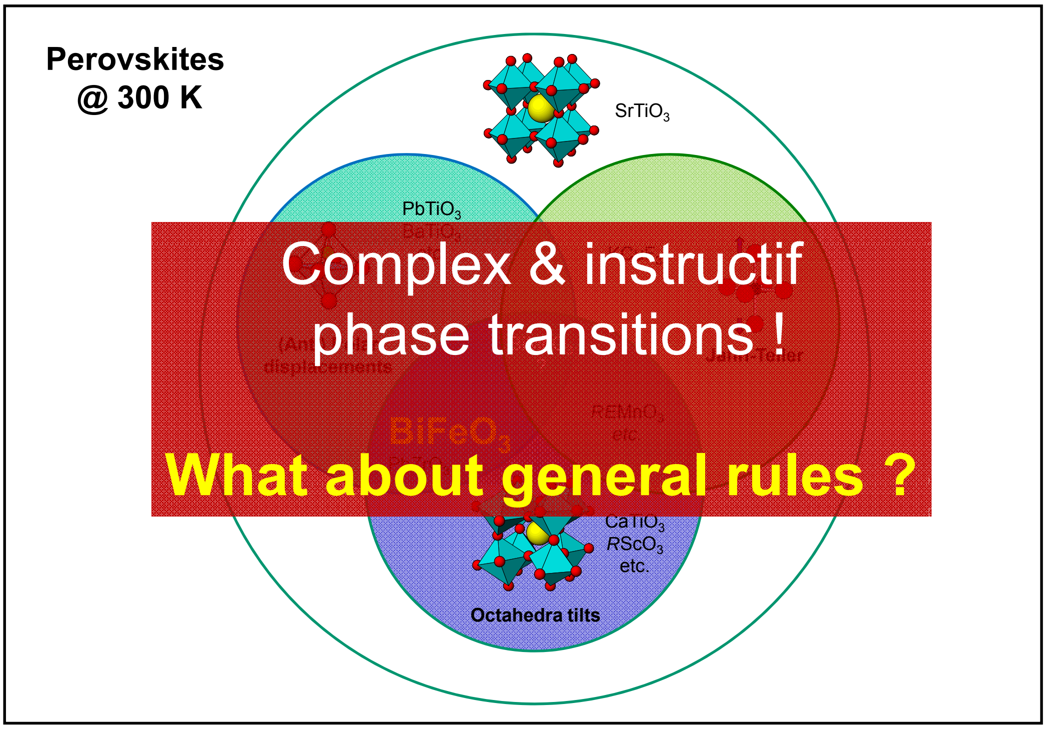
➔ Small samples !
➔ Wiring remains a challenge ! Ferroelectric measurements very difficult 👎
➔ Diffraction, X-ray absorption, Raman, Fluorescence 👍

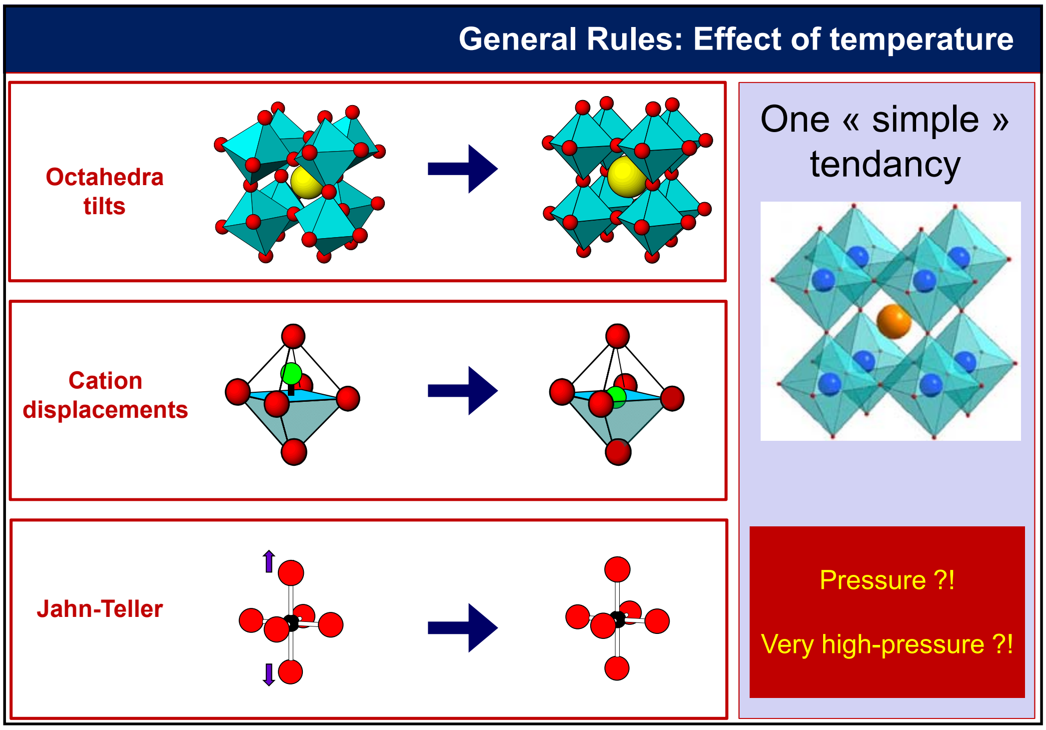
C. Illustrations 1

Effect of high-pressure on ferroic oxides

(or … Understanding individual ferroic orders before looking at multiferroics)

1. Octahedra tilts (ferroelasticity)
2. Cation displacements (ferroelectricity)
3. Jahn-Teller distortion
4. General rules


Perovskites
@ 300 K
$SrTiO_3$
$PbTiO_3$
$BaTiO_3$
Complex & instructif
phase transitions !
displacements
Jahn-Teller
$REMnO_3$
etc
$BiFeO_3$
What about general rules ?
$CaTiO_3$
$RScO_3$
etc.
Octahedra tilts


General Rules: Effect of temperature
Octahedra tilts
Cation displacements
Jahn-Teller
One « simple » tendancy
Pressure ?!
Very high-pressure ?!

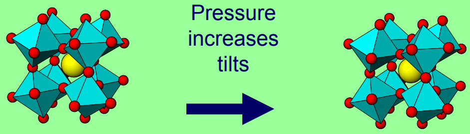
The effect of high pressure on perovskites: ***Samara's rules***

Important Generalization Concerning the Role of Competing Forces in Displacive Phase Transitions

G. A. Samara et al., Phys. Rev. Lett. 35, 1767–1769 (1975)

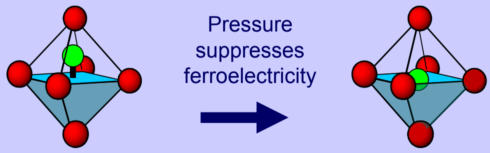
Soft zone **boundary** instabilities

$$\frac{dT_c}{dP} > 0$$

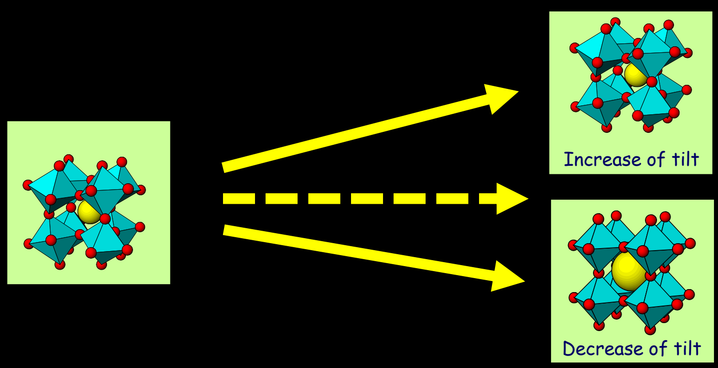


Soft zone **centre** instabilities

$$\frac{dT_c}{dP} < 0$$



Effect of pressure on octahedra tilts ?



Samara rule

G. A. Samara
Phys. Rev. Lett. 35, 1767 (1975)

Compression mechanism ?

Tilts ⇔ Bond compression (A-O, B-O distances ?)

Octahedra rotations (tilts): Important characteristics

R. H. Mitchell, *Perovskites: Modern and ancient ,Almaz Press, Ontario (C), 2002*

Most common type of distortion

Subtle distortion

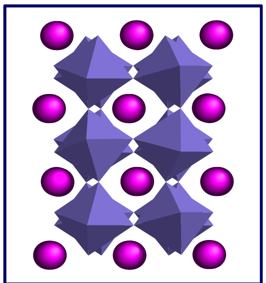
BO_6 close to rigid (⇔ AO_{12})

Tuned by size of *A*-cation

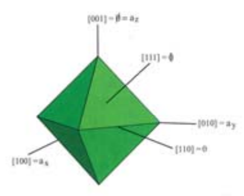
Reduced symmetry

Lattice instability
➔ Tuning by external parameters

Drives physical properties

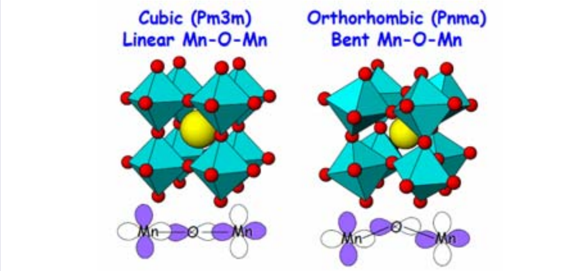


Long-range correlations



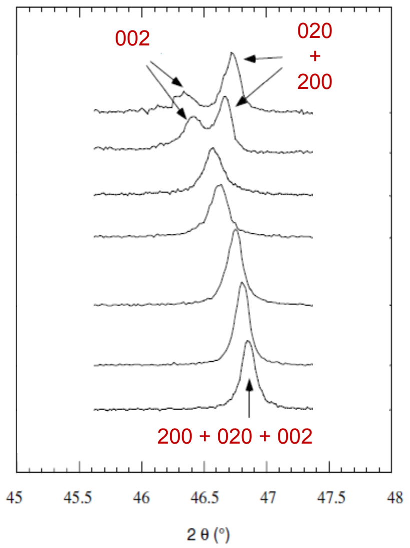
A. M. Glazer
Acta Crystallographica **B 28**, 3384 (1972).

23 different tilt systems !



Detecting tilts with diffraction: 1st step

Peak splitting of Bragg reflections

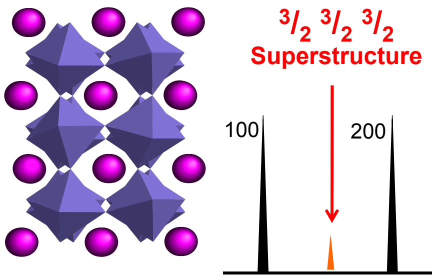


- Crystal system (structure refinement)
- Unit cell strain
- Resolution limited
- Low precision on tilt angles

Tilt	$NaMgF_3$	$GdFeO_3$
From cell dimensions		
ϕ	8.5	9.46
θ	12.3	17.58
Φ	14.9	19.89
From bond angles		
ϕ	10.7	11.32
θ	14.3	16.51
Φ	17.8	19.93
a^{-}_{x}	10.1	11.71
From atomic coordinates		
ϕ	10.4	11.95
θ	14.3	16.51
Φ	17.7	20.28

Investigation of octahedra tilts

Cell doubling ➔ Superstructure « tilt » reflections

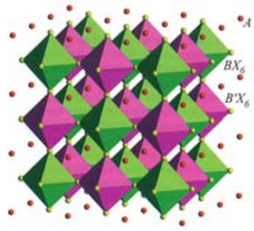


- 👍 Intensity ➔ Tilt angle
- 👍 Selection rules ➔ Type of tilt system
- 👎 Low intensity for X-rays (↔ neutrons)
- 👎 Other cell doubling mechanism

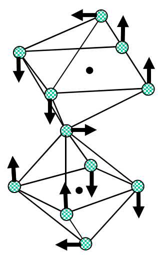
Table 2.6. Reflections Associated With Octahedral Tilts (Glazer 1975)

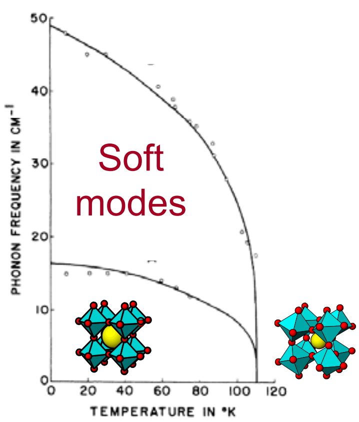
In-phase tilts				Anti-phase tilts			
Tilt	Conditions		Examples*	Tilt	Conditions		Examples*
a^+	eoo	$k \neq l$	013, 031	a^-	ooo	$k \neq l$	131, 113
b^+	oeo	$h \neq l$	103, 301	b^-	ooo	$h \neq l$	113, 311
c^+	ooe	$h \neq k$	130, 310	c^-	ooo	$h \neq k$	131, 311

* All indices given on the basis of a double ($2a_p$) cubic cell.



Raman scattering: Vibrations with rotational pattern



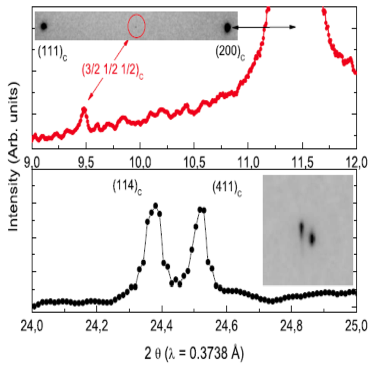


- 👍 Scale to octahedra tilt angle
- 👍 Order parameter, soft mode
- 👎 No structure refinement possible
- 👎 Raman difficult to model

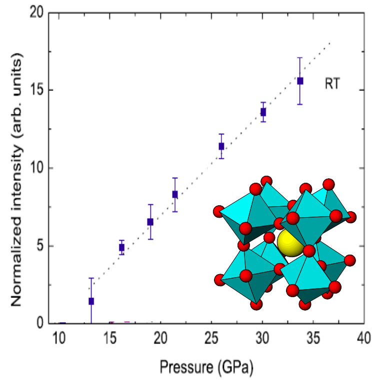
High-pressure X-ray diffraction of $SrTiO_3$

M. Guennou, P. Bouvier, J. Kreisel, and D. Machon, *Phys. Rev. B* **81**, 054115 (2010)

Diffraction at 37 GPa



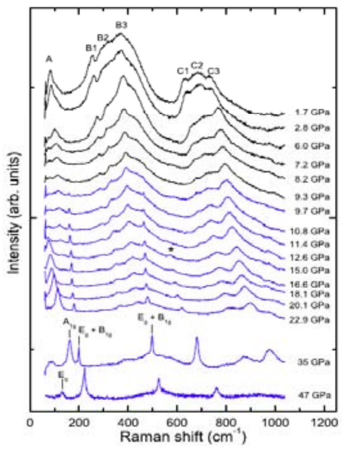
I(P) of superstructure

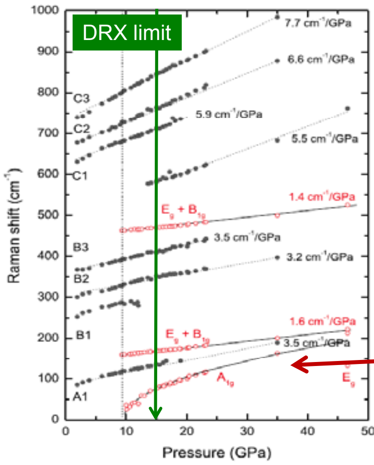


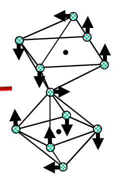
- Clear evidence for distortion
- Identification of symmetry
- Pressure-induced phase transition
- Precision near P_c

High-pressure Raman scattering of $SrTiO_3$

M. Guennou, P. Bouvier, J. Kreisel, and D. Machon, *Phys. Rev. B* **81**, 054115 (2010)



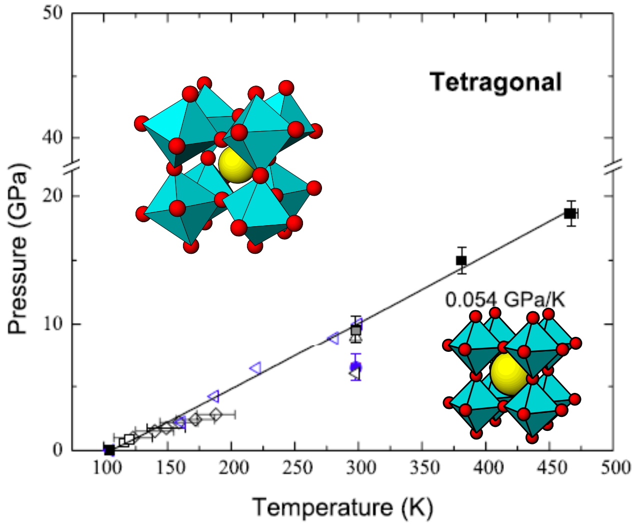




- Identification of P_c
- Soft-mode-driven phase transitions
- Decription with Landau theory

P-T phase diagram

M. Guennou, P. Bouvier, J. Kreisel, *Phys. Rev. B* **81,** 054115 (2010)



Samara model holds

in high-pressure regime

Model system 2: $LaAlO_3$

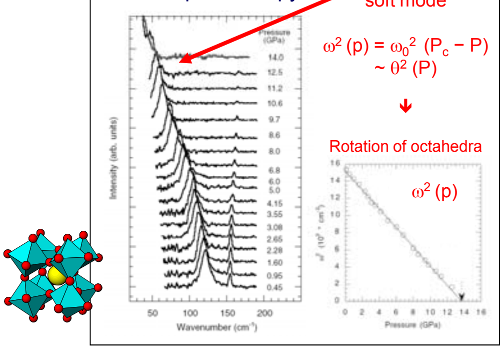
P. Bouvier & J. Kreisel J. Phys.: Condens. Matter **14**, 3981 (2002) & **23**, 395401 (2011).

Raman spectroscopy

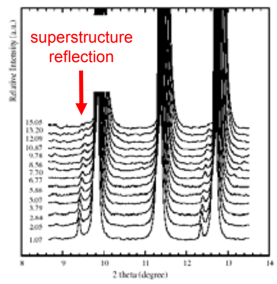
"soft mode"

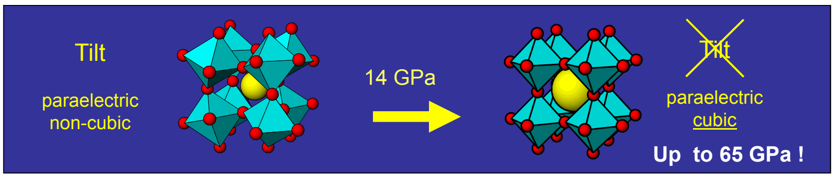
$\omega^2(p) = \omega_0^2 (P_c - P)$
$\sim \theta^2 (P)$

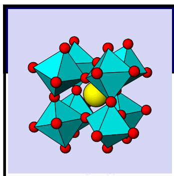
Rotation of octahedra



Powder diffraction
at a synchrotron source

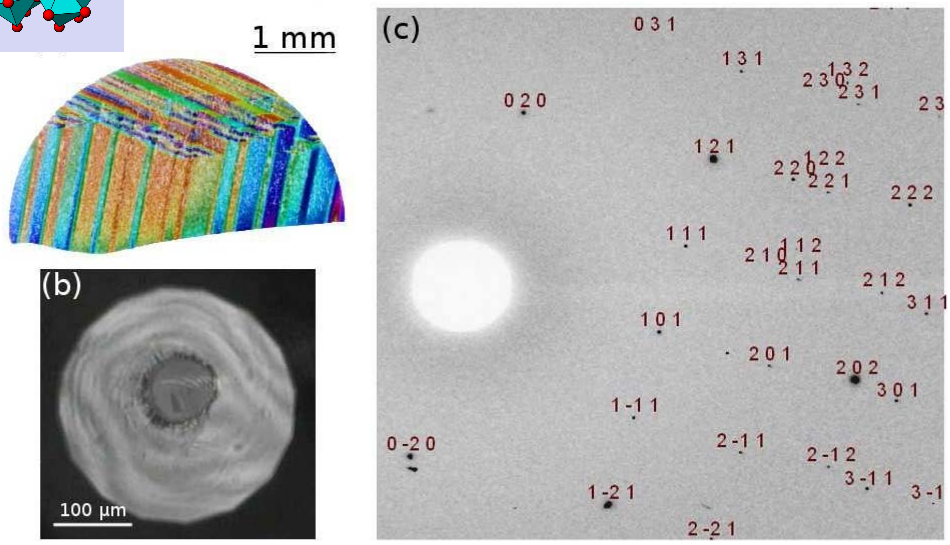






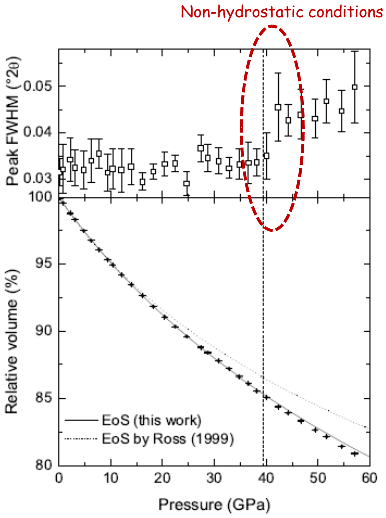
Model system 3 : Orthorhombic *Pnma* $CaTiO_3$

M. Guennou, P. Bouvier, B. Krikler, J. Kreisel, R. Haumont, and G. Garbarino, *Phys. Rev. B* **82**, 134101 (2010).

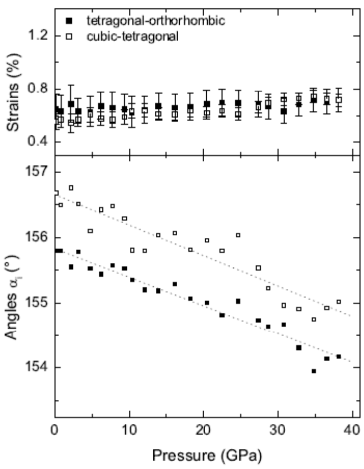


Synchrotron X-ray data analysis

M. Guennou, P. Bouvier, B. Krikler, J. Kreisel, R. Haumont, and G. Garbarino, *Phys. Rev. B* **82**, 134101 (2010).



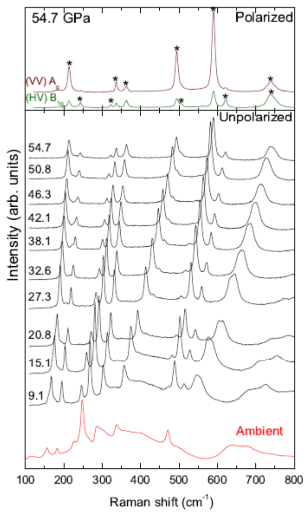
No phase transition !

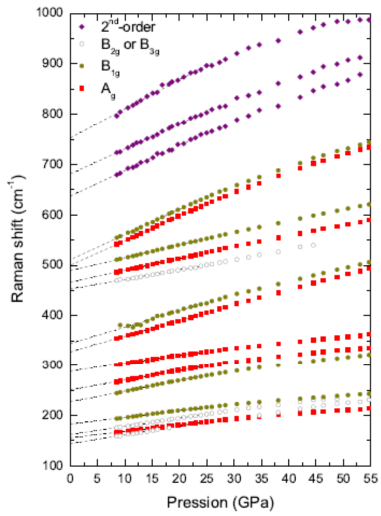


Very little changes in tilt angle

Raman spectroscopy of $CaTiO_3$

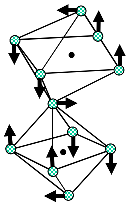
M. Guennou, P. Bouvier, B. Krikler, J. Kreisel, R. Haumont, and G. Garbarino, *Phys. Rev. B* **82**, 134101 (2010).





Ti-O Stretching

Ca-O Stretching



Compression dominated by bond compression not tilts !

Resume: Tilted perovskites under pressure

For perovskites with no distortion but tilts

Rule of thumb

(driven by AO_{12}, BO_6 compressibilities)

The tilt angle under hydrostatic pressure …

… increases for 2+/4+ perovskites,

$SrTiO_3$, $CaTiO_3$

$BaZrO_3$, $SrZrO_3$

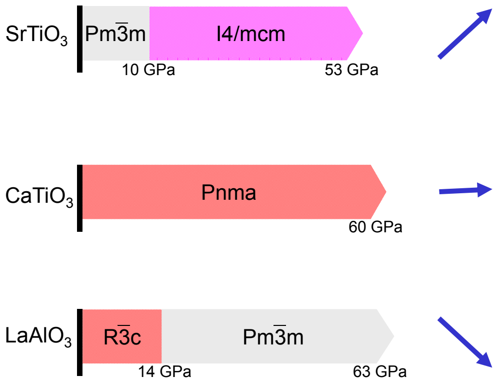
… decreases for 3+/3+ perovskites

REFeO_3

REAlO_3

REGaO_3

R. J. Angel, J. Zhao, N. L. Ross, Phys. Rev. Lett. **95**, 025503 (2005).



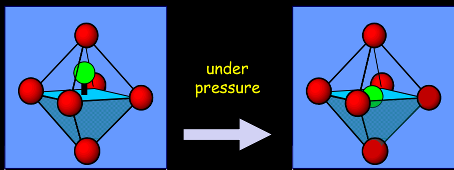
HP-Tilt systems are stable !

Limited number of phase transitions

Effect of pressure on ferroelectrics ?

Samara rule

G. A. Samara Phys. Rev. Lett. 35, 1767 (1975))



ferroelectric
<u>non-cubic</u>

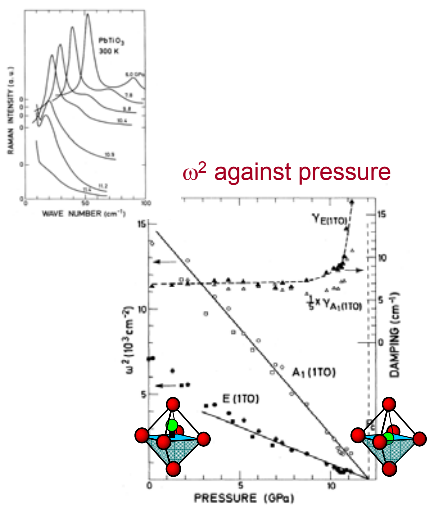
paraelectric
<u>cubic</u>

High-pressure studies of $PbTiO_3$: Literature

High-Pressure Raman data

J.A. Sanjurjo, E. Lopez-Cruz, G. Burns

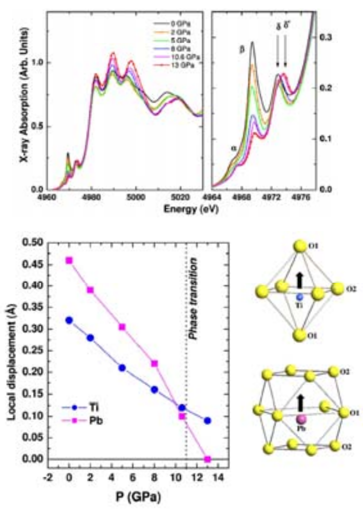
Phys. Rev. B **28**, (1983), p. 7260

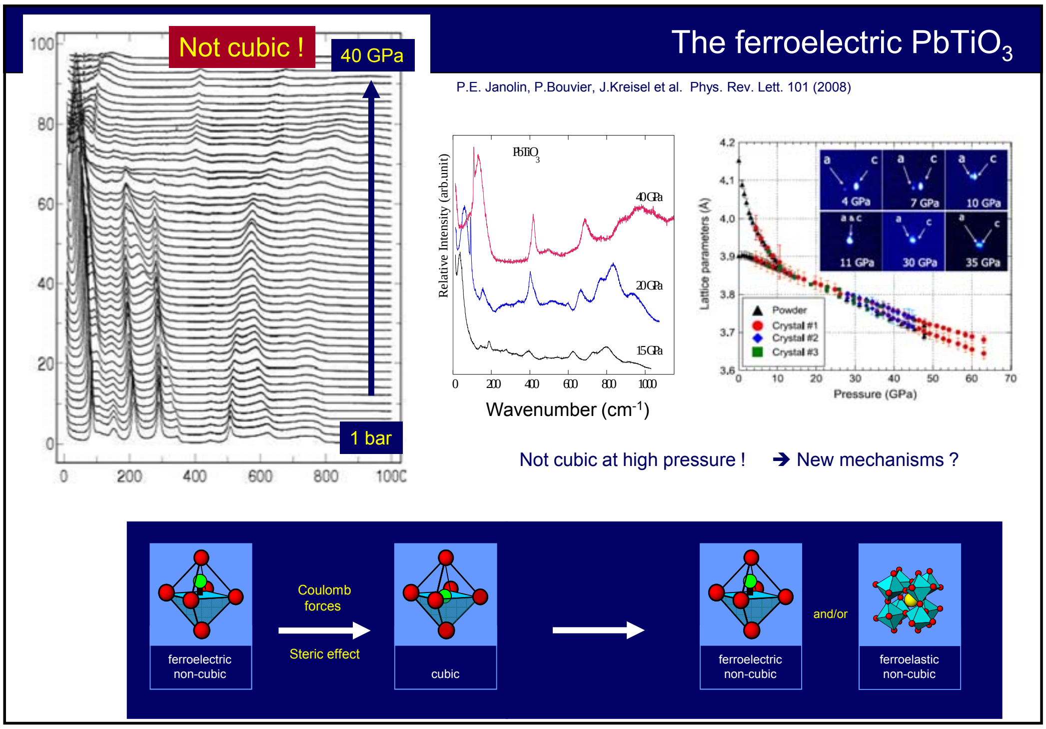


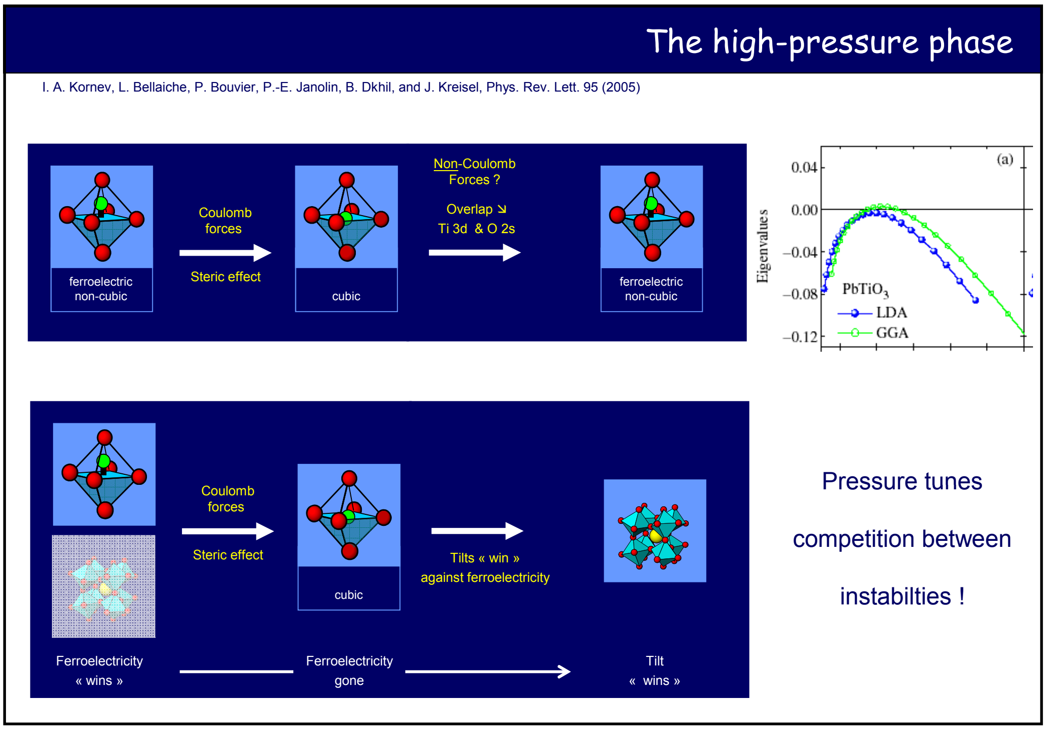
High-pressure X-ray absorption data

N.Jaouen, A.C.Dhaussy, J.P.Itié, A.Rogalev, S.Marinel, Y.Joly

Phys. Rev. B **75** (2007) p. 224115




The ferroelectric PbTiO3
P.E. Janolin, P.Bouvier, J.Kreisel et al. Phys. Rev. Lett. 101 (2008)
Not cubic !
40 GPa
1 bar
Relative Intensity (arb.unit)
PbTiO3
40GPa
20GPa
15GPa
Wavenumber (cm-1)
Lattice parameters (Å)
Pressure (GPa)
Powder
Crystal #1
Crystal #2
Crystal #3
4 GPa
7 GPa
10 GPa
11 GPa
30 GPa
35 GPa
Not cubic at high pressure !
➔ New mechanisms ?
Coulomb forces
Steric effect
ferroelectric non-cubic
cubic
and/or
ferroelectric non-cubic
ferroelastic non-cubic

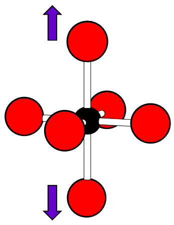

The high-pressure phase
I. A. Kornev, L. Bellaiche, P. Bouvier, P.-E. Janolin, B. Dkhil, and J. Kreisel, Phys. Rev. Lett. 95 (2005)
ferroelectric non-cubic
Coulomb forces
Steric effect
cubic
Non-Coulomb Forces ?
Overlap ↘
Ti 3d & O 2s
ferroelectric non-cubic
Eigenvalues
(a)
PbTiO3
LDA
GGA
Coulomb forces
Steric effect
cubic
Tilts « win » against ferroelectricity
Ferroelectricity « wins »
Ferroelectricity gone
Tilt « wins »
Pressure tunes
competition between
instabilties !

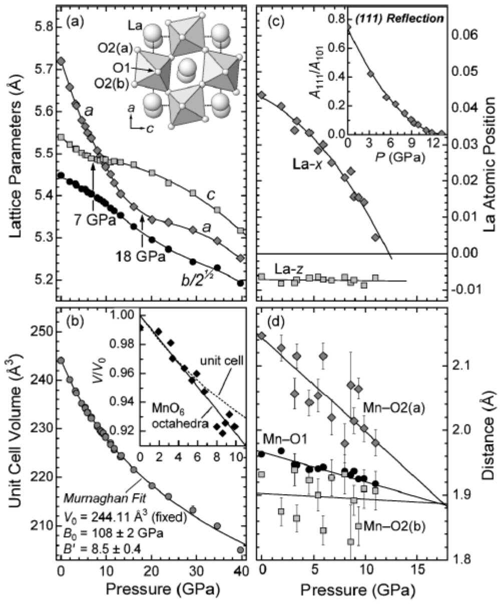
Effect of high-pressure on Jahn-Teller distortion


...e 87, Number 12 PHYSICAL REVIEW LETTERS 17 Septemb...

Pressure-Induced Quenching of the Jahn-Teller Distortion and Insulator-to-Metal Transition in $LaMnO_3$

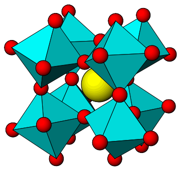
I. Loa,[1] P. Adler,[1] A. Grzechnik,[1] K. Syassen,[1] U. Schwarz,[2] M. Hanfland,[3] G. Kh. Rozenberg,[4] P. Gorodetsky,[4] and M. P. Pasternak[4]





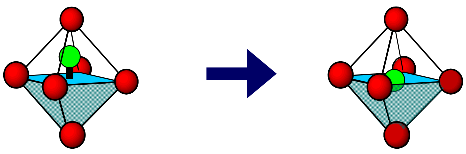
General Rules: Effect of pressure

Octahedra tilts

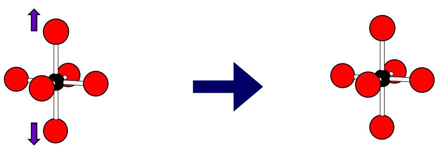


↗ Increase (2+, 4+)
→ Constant
↘ Decrease (3+, 3+)

Cation displacements



Jahn-Teller



More complex than effect of T

Pressure can tune competition tilt ⇔ cation displ.

Watch out for tilts !

Rules in case of co-existence of instabilities ?!

D. Illustrations 2

Effect of high-pressure on multiferroic oxides

1. Primary ferroelectrics (ex. $BiFeO_3$)
2. Secondary ferroelectrics

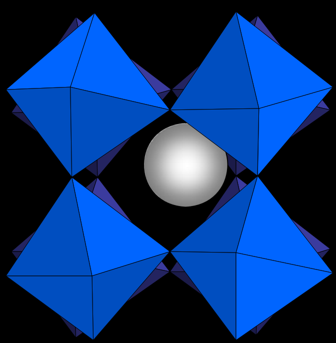
Tilts + Cation displacements + Magnetism

➔ Type I Multiferroics

$BiFeO_3$

(3+, 3+)

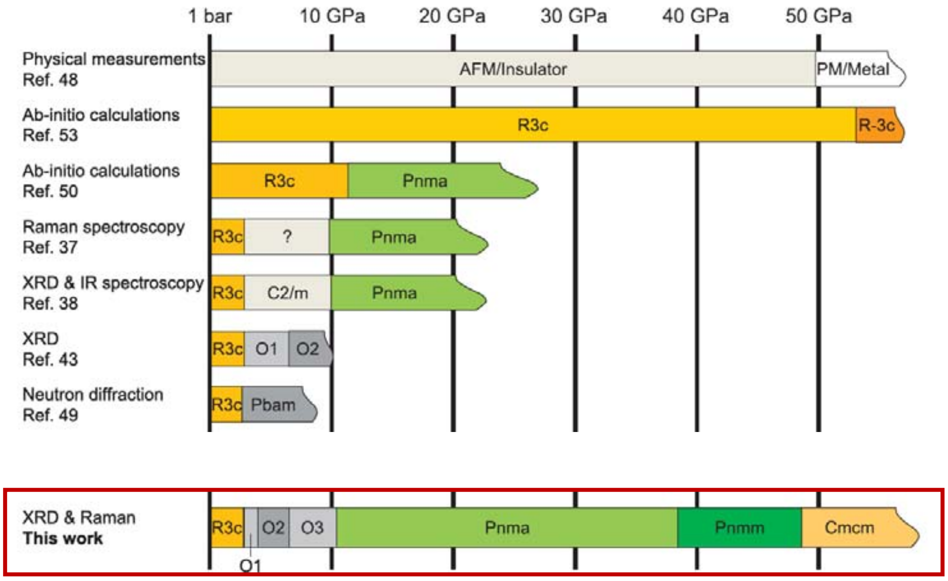
➔ Cubic ?



(more) complex
phase sequence ?

$BiFeO_3$: Impact on the field of multiferroics comparable to that of YBCO on superconductors
Review: G. Catalan & J. F. Scott, Advanced Materials **21**, 1 (2009).

YES !

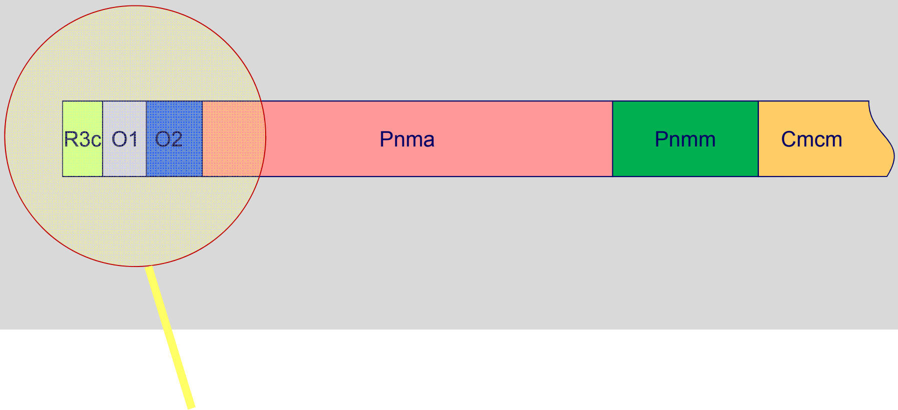


M. Guennou, P. Bouvier, G. S. Chen, R. Haumont, G. Garbarino, and J. Kreisel, *Phys. Rev. B* **84**, 174107 (2011).

M. Guennou, P. Bouvier, G. S. Chen, R. Haumont, G. Garbarino, and J. Kreisel, *Phys. Rev. B* **84**, 174107 (2011).

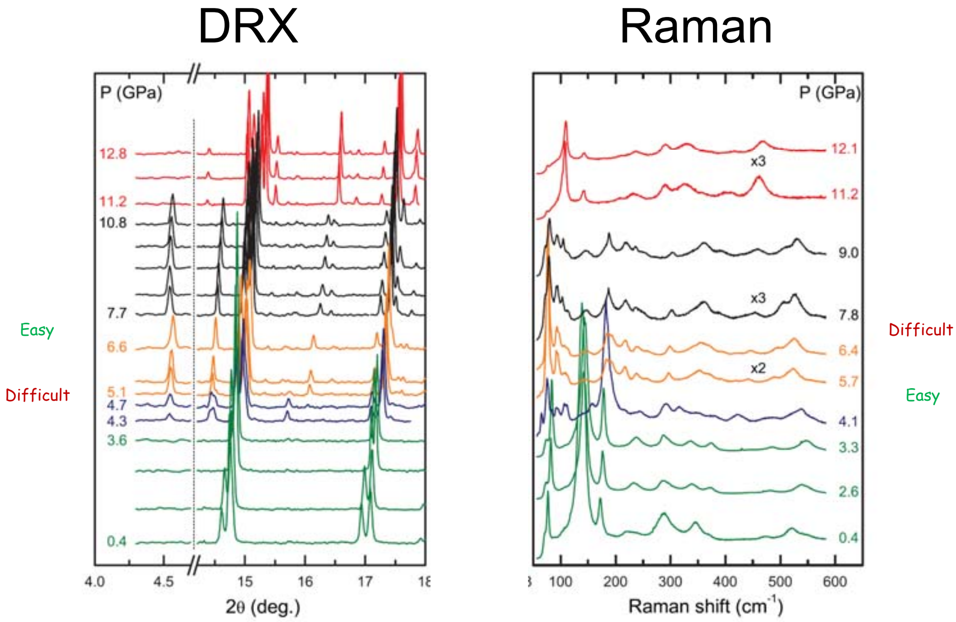
- Low ⇔ High-pressure regime ?
- Polarity of phases ?
- Unusual structures !
- ⇔ other Bi-based perovskites

Expt.	Sample	PTM	Beam line	*P* range (GPa)
XRD 1	Single crystal	Helium	ID09A	0–12
XRD 2	Single crystal	Neon	ID27	12–55
XRD 3	Single crystal	Helium	ID27	30–55
XRD 4	Powder	Helium	ID27	0–52
Raman	Single crystal	Alcohol		0–12

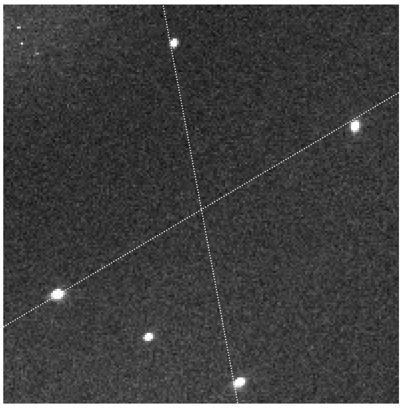


1) Low-pressure regime

An overview



Pressure-dependent single crystal diffraction on $BiFeO_3$



P= 0.4 GPa
Expected R3c, single domain

P= 5 GPa
Orthorhombic, tilts, polar ?

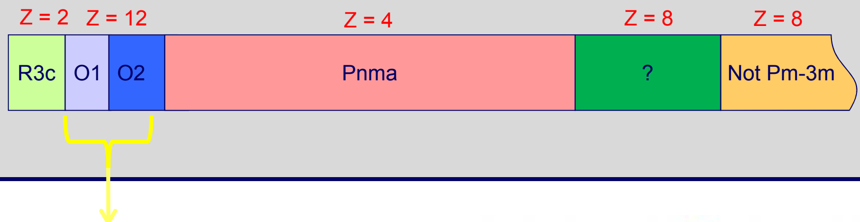
P= 6.7 Gpa
Disappearance of 2 domains
(changes in magnetic structure ?)

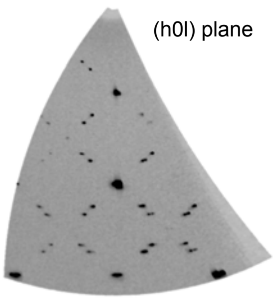
P= 8 GPa
Orthorhombic, tilts, polar ?

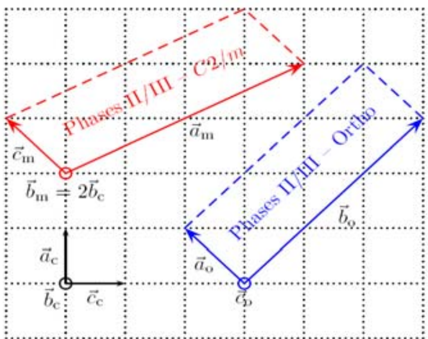
P= 10 GPa
Orthorh. Pnma tilts , non polar

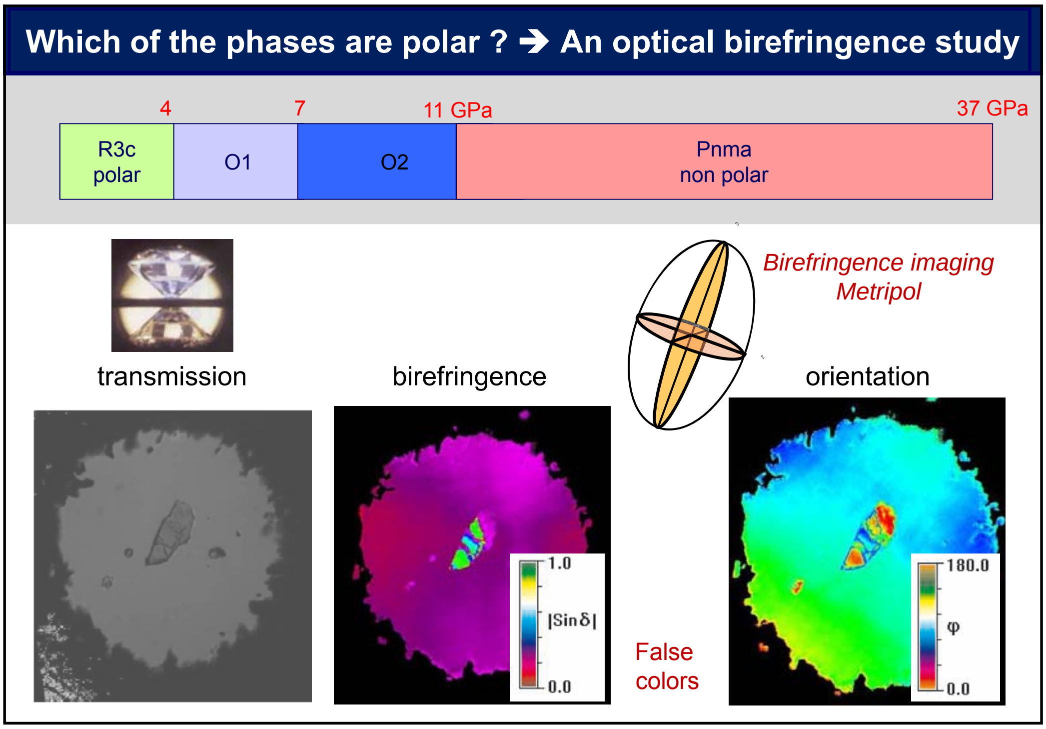
Presence / change of domains are instructive, but complicate the analysis !

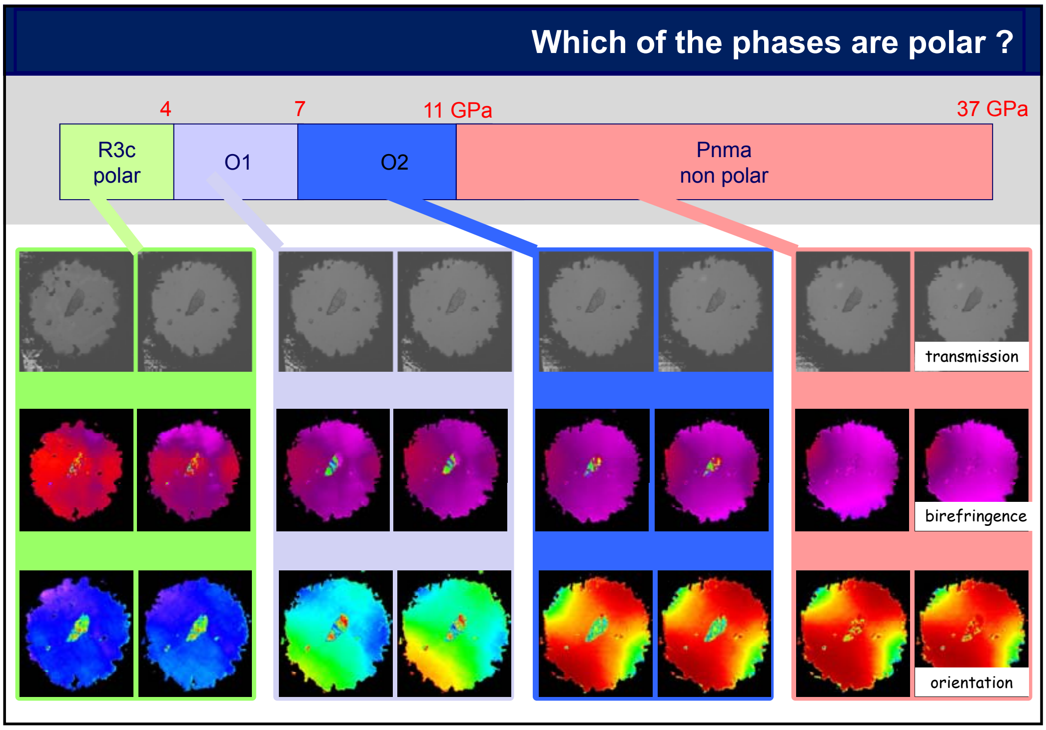
Pressure: Unusual large unit cells ! ≠ PZT-like monoclinic phases

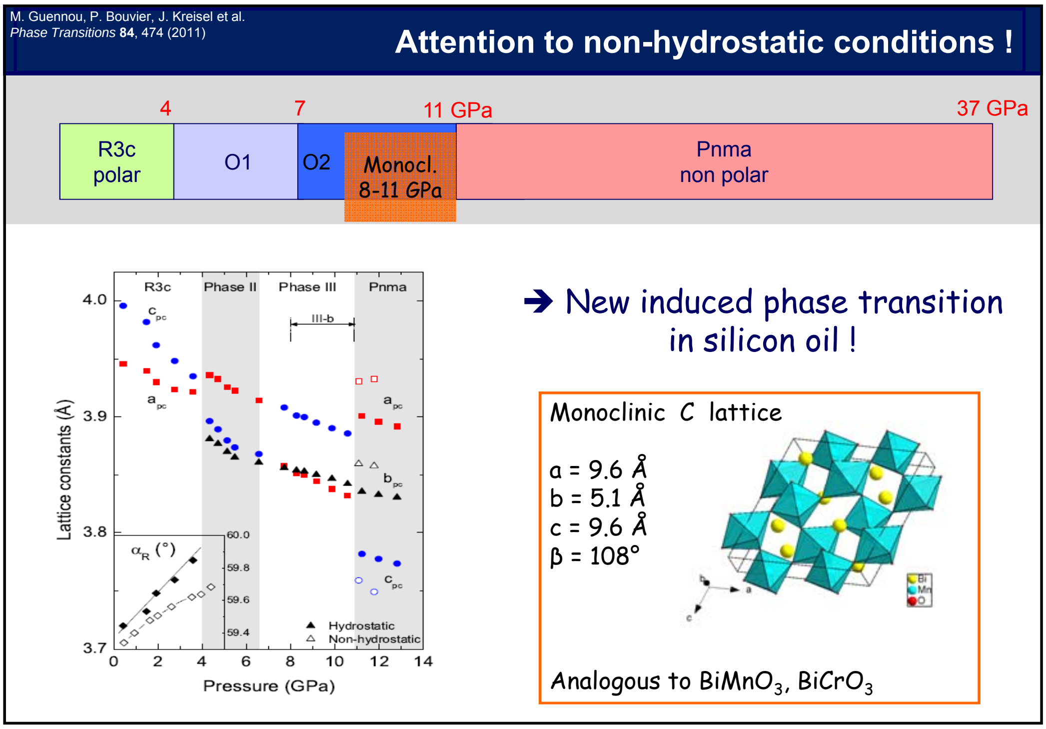


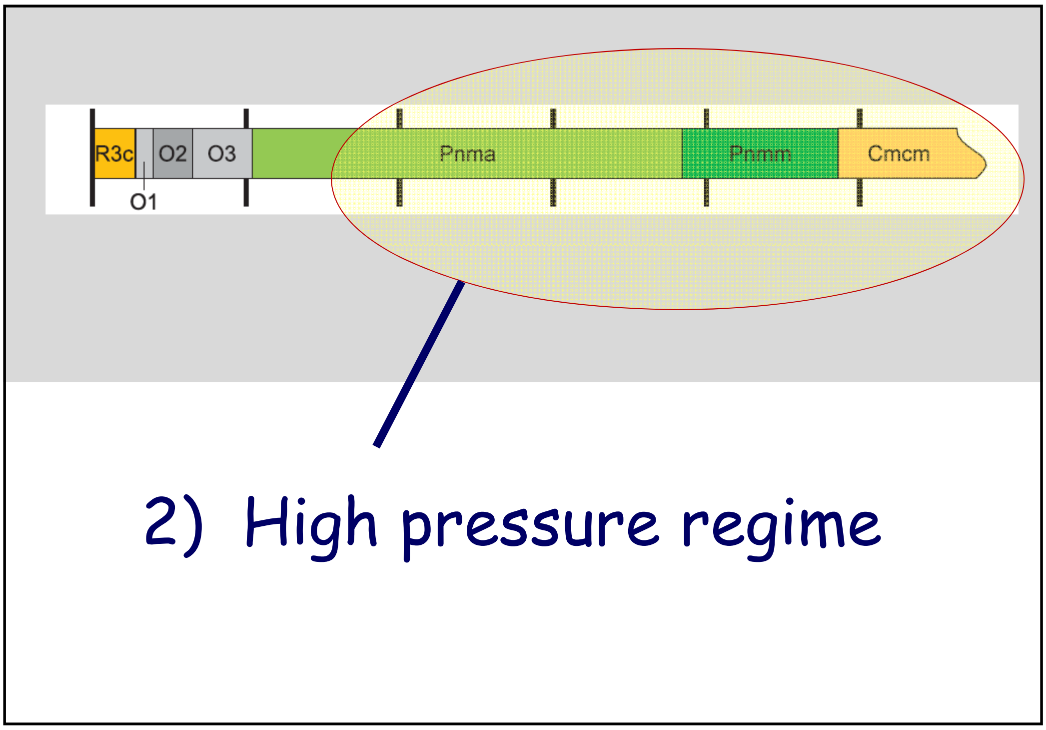




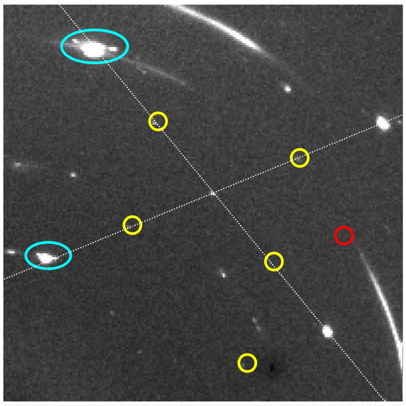

Which of the phases are polar ? ➔ An optical birefringence study
4
7
11 GPa
37 GPa
R3c
polar
O1
O2
Pnma
non polar
Birefringence imaging
Metripol
transmission
birefringence
orientation
1.0
|Sin δ|
0.0
False
colors
180.0
φ
0.0


Which of the phases are polar ?
4
7
11 GPa
37 GPa
R3c
polar
O1
O2
Pnma
non polar
transmission
birefringence
orientation


M. Guennou, P. Bouvier, J. Kreisel et al.
Phase Transitions 84, 474 (2011)
Attention to non-hydrostatic conditions !
4
7
11 GPa
37 GPa
R3c polar
O1
O2
Monocl. 8-11 GPa
Pnma non polar
R3c
Phase II
Phase III
Pnma
III-b
Lattice constants (Å)
Pressure (GPa)
Hydrostatic
Non-hydrostatic
→ New induced phase transition in silicon oil !
Monoclinic C lattice
a = 9.6 Å
b = 5.1 Å
c = 9.6 Å
β = 108°
Analogous to BiMnO3, BiCrO3


R3c
O2
O3
Pnma
Pnmm
Cmcm
O1
2) High pressure regime

High-pressure-regime (P>30 GPa)

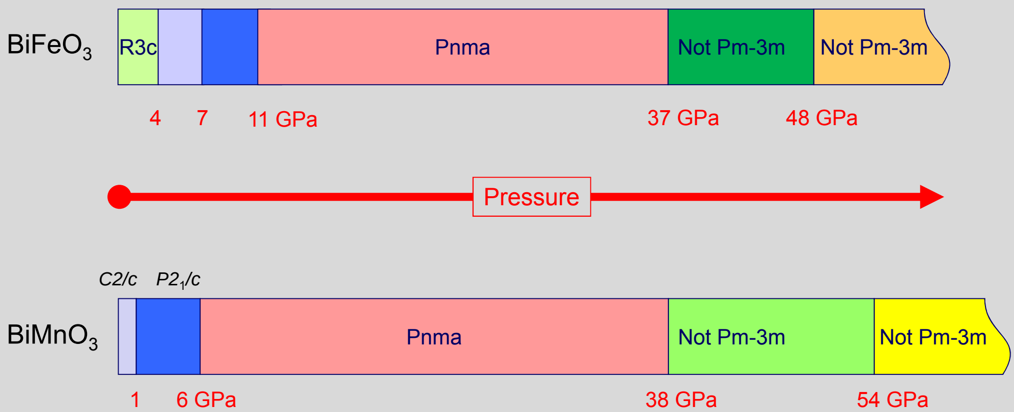


[111] in 2x cubic or
[010] in 2x rhombo

P= 35 GPa
Expected Pnma

P= 37 GPa
Disappearance of super struct.
½ (212) (232) (252)

P= 48 GPa
New super struct. + splitting
➔ not cubic Pm-3m



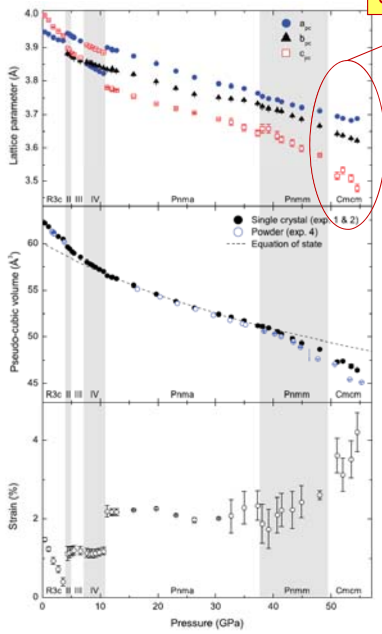
- Low-pressure ⇔ high-pressure regime

- Intermediate *Pnma* structure (stable but not that stable …)

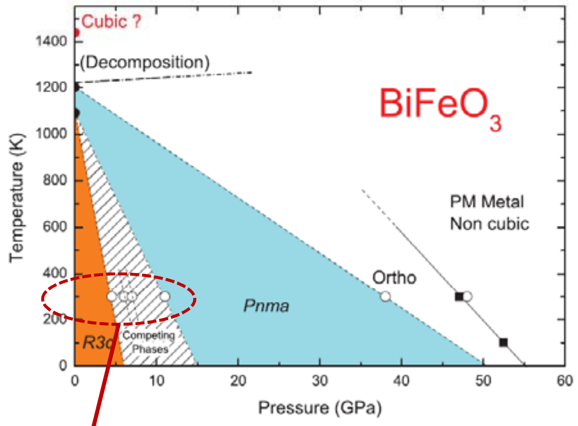
- Common transition at high-pressure - a coincidence !?

Resume for $BiFeO_3$

Not towards cubic structure



Schematic P-T phase diagram

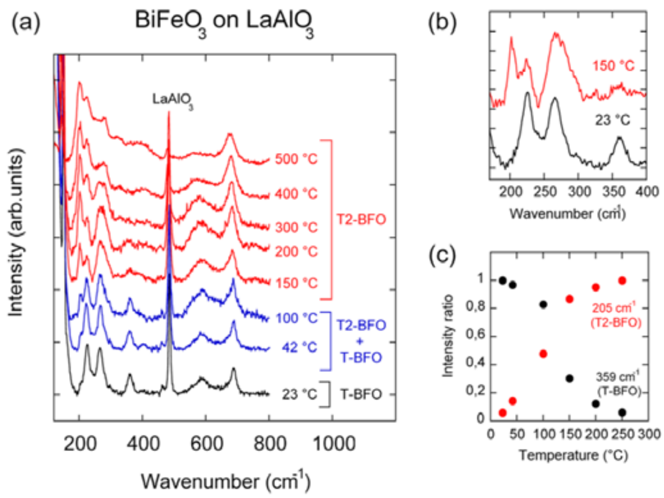


R3c structure ➔ stable under T
… but not under strong deformations !

Highly-strained tetragonal-like BFO thin films on $LaAlO_3$

J. Kreisel, P. Jadhav, O. Chaix-Pluchery, M. Varela, N. Dix, F. Sánchez, and J. Fontcuberta, Journal of Physics: Condensed Matter 23, 342202 (2011).

A phase transition close to room temperature in $BiFeO_3$ thin films



Strong strain tunes phase transitions to room temperature

Tilts + Ferroelectricity + Magnetism

➔ Type II Multiferroics

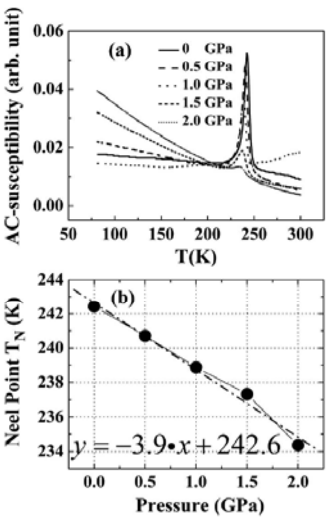
➔ Ferroelectricity driven by Magnetism / CO

Same rules ?

APPLIED PHYSICS LETTERS 96, 102909 (2010)

Pressure effects on multiferroic $LuFe_2O_4$

X. Shen, C. H. Xu,[a] C. H. Li, Y. Zhang, Q. Zhao,[a] H. X. Yang, Y. Sun, J. Q. Li, C. Q. Jin, and R. C. Yu[b]

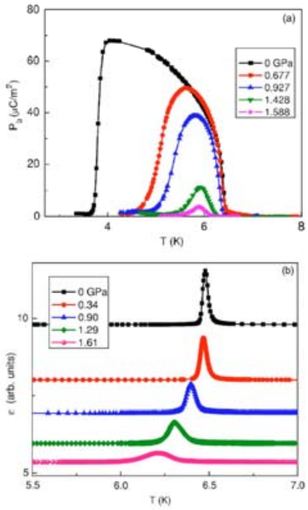


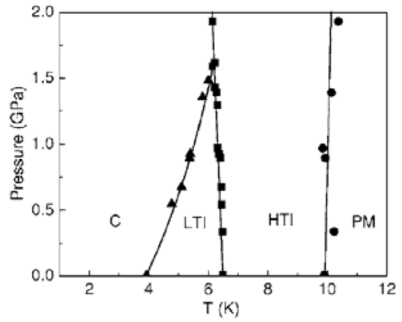
Little changes

PHYSICAL REVIEW B **75**, 012407 (2007)

Pressure-temperature phase diagram of multiferroic $Ni_3V_2O_8$

R. P. Chaudhury,[1] F. Yen,[1] C. R. dela Cruz,[1] B. Lorenz,[1] Y. Q. Wang,[1] Y. Y. Sun,[1] and C. W. Chu[1,2,3]





Ferroelectricity reduced by pressure !

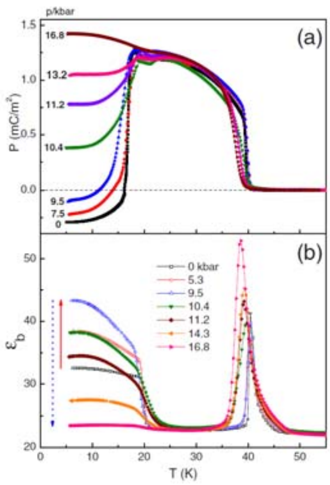
Same as previous rule ??

RAPID COMMUNICATIONS

PHYSICAL REVIEW B **77**, 220104(R) (2008)

Pressure-induced polarization reversal in multiferroic YMn_2O_5

Rajit P. Chaudhury,[1] Clarina R. dela Cruz,[2,3] Bernd Lorenz,[1] Yanyi Sun,[1] Ching-Wu Chu,[1,4,5] S. Park,[6] and Sang-W. Cheong[6]



Pressure can
reduce & enhance
ferroelectricity

⇔ Multiferroics type 1 !

Bond angle changes
➔ Changes in Magnetism
➔ Changes in Ferroelectricity

➔ What's about strain in films ?!

Some interesting directions …

Uniaxial pressure

PRL **107**, 067203 (2011) PHYSICAL REVIEW LETTERS week ending 5 AUGUST 2011

Giant Effect of Uniaxial Pressure on Magnetic Domain Populations in Multiferroic Bismuth Ferrite

M. Ramazanoglu,[1] W. Ratcliff II,[2] H. T. Yi,[1] A. A. Sirenko,[3] S.-W. Cheong,[1] and V. Kiryukhin[1]

High-pressure synthesis

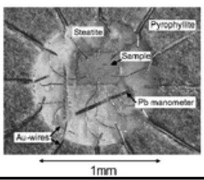
APPLIED PHYSICS LETTERS **90**, 112909 (2007)

High pressure bulk synthesis and characterization of the predicted multiferroic $Bi(Fe_{1/2}Cr_{1/2})O_3$

Matthew R. Suchomel, Chris I. Thomas, Mathieu Allix, Matthew J. Rosseinsky,[a] and Andrew M. Fogg
Department of Chemistry, The University of Liverpool, Liverpool L69 7ZD, United Kingdom

Michael F. Thomas
Department of Physics, The University of Liverpool, Liverpool L69 7ZE, United Kingdom

Pressure on films



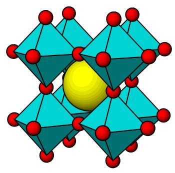
APPLIED PHYSICS LETTERS VOLUME 80, NUMBER 13 1 APRIL 2002

Magnetic behavior of epitaxial $SrRuO_3$ thin films under pressure up to 23 GPa

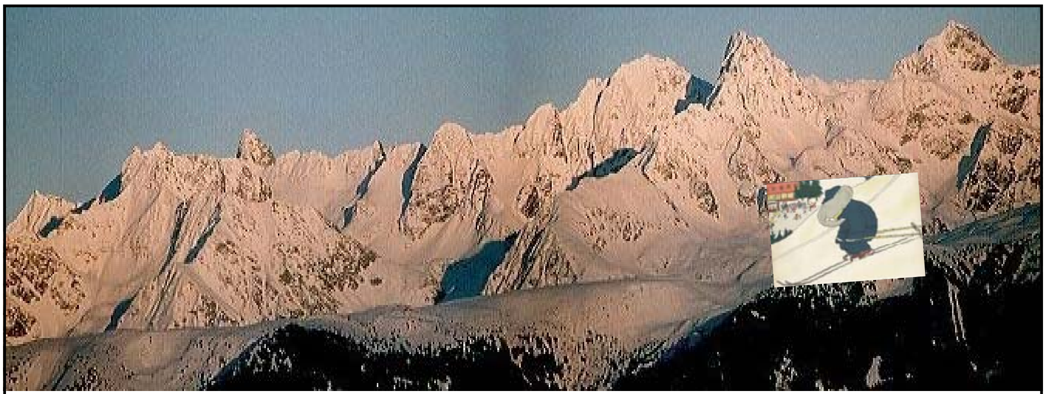
F. Le Marrec,[a] A. Demuer,[b] D. Jaccard, and J.-M. Triscone
DPMC, University of Geneva, 24 quai Ernest Ansermet, 1211 Geneva 4, Switzerland

M. K. Lee and C. B. Eom
Department of Materials Science and Engineering, University of Wisconsin–Madison, 1500 Engineering Drive, Madison, Wisconsin 53706

Concluding remarks



- Pressure is a useful parameter for tuning and understanding instabilities
- Guiding rules are more complex for pressure than for T (tilts not so simple)
- Competing instabilities remain to be understood (➔ multiferroics)
- Very-high pressure regime should receive more attention



“Decompressing” in Grenoble ...

(thank you for your attention !)