



Universität Hamburg, Department of Earth System Sciences / Crystallography

Perovskite-type ferroelectric solid solutions under high pressure: Insights into the nanoscale structure of “green” ferroelectrics

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Online ECA Lunch Seminar, 15.01.2026



Outline

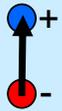
- **Ferroelectrics (FE) and related materials**
 - *basic terms*
 - *perovskite-type (ABO_3) solid solutions with morphotropic phase boundary (MPB)*
 - *seeking for “green” ferroelectrics*

- **What can we learn from high-pressure (HP) studies about FE structure at RT&AP?**
 - *showcase: Pb-based relaxors*
 - *how to do HP experiments*

- **$(1-x)Na_{0.5}Bi_{0.5}TiO_3-xBaTiO_3$ (NBT-xBT) single crystals across **MPB****
 - *structural peculiarities at ambient pressure (AP)*
 - *previous HP XRD studies of pure NBT*
 - *in situ HP Raman spectroscopy for $x = 0, 0.013, 0.048, 0.074$*
 - *in situ HP XRD for $x = 0.013, 0.048, 0.074$*
 - *conclusions*



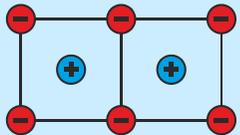
Ferroelectrics : multifunctional materials!



Ferroelectricity: macroscopic polarization \mathbf{P}_S switchable under electric field \mathbf{E}

$$P_i = \epsilon_0 \chi_{ij} E_j + p_i \Delta T + d_{ijk} T_{jk}$$

paraelectric

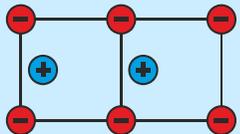


zero-field,
switchable \mathbf{P}

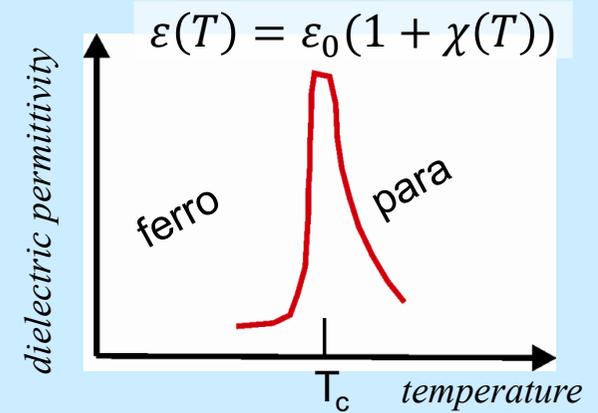
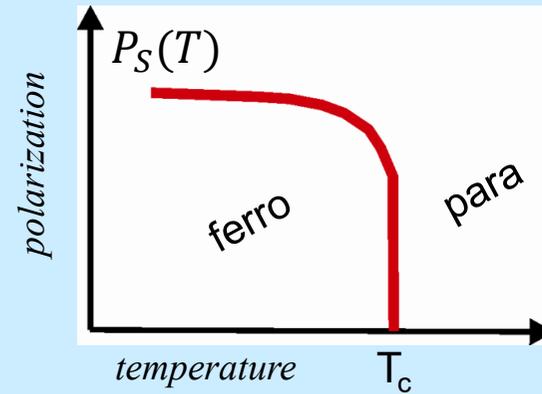
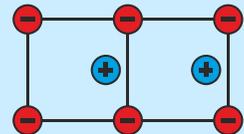
$\downarrow T_c$

$\xrightarrow{\mathbf{E}}$

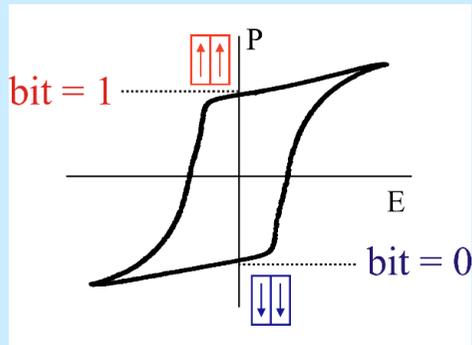
ferroelectric



$\leftarrow a \rightarrow$



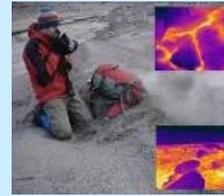
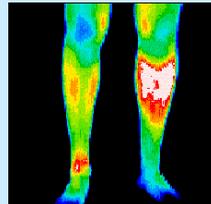
Ferroelectric loop



FE memories



pyroelectricity



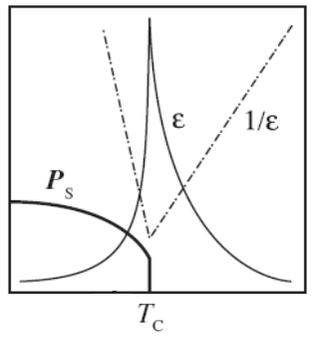
piezoelectricity



Ferroelectricity (switchable P_s) and ergodicity (flipping polar clusters)

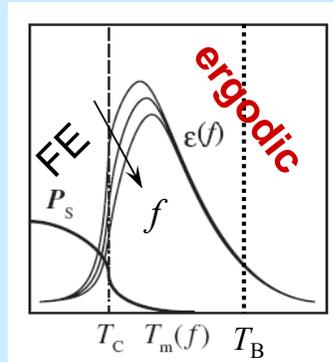
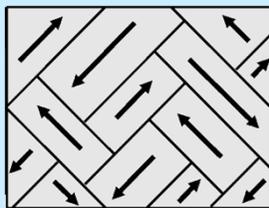
“Normal” ferroelectrics

para-
electric



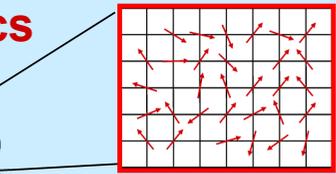
$$T_c \sim T_m$$

ferro-
electric

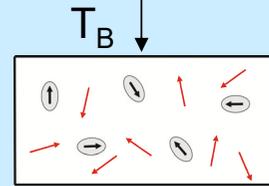


Relaxor ferroelectrics

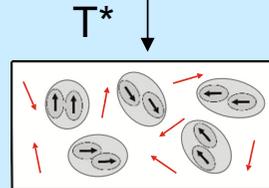
ergodic state: dynamic



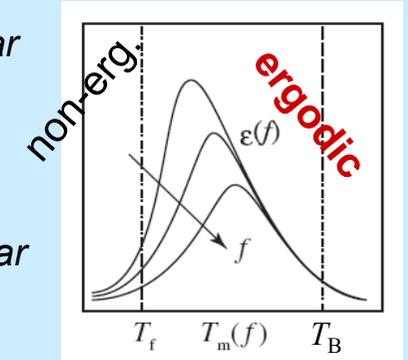
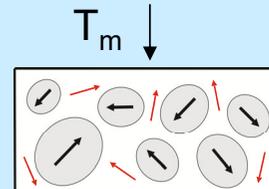
uncoupled atomic polar shifts



small polar clusters



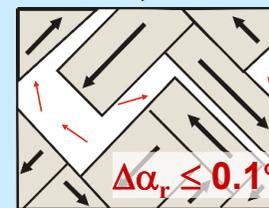
larger polar clusters



$\epsilon(T)$: after Hirota et al, JPSJ, 2006

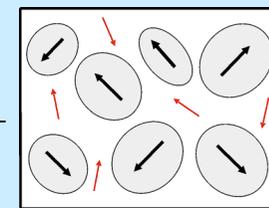
$$T_c \leq T_m$$

T_f (freezing temperature)



FE long-range order

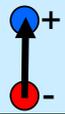
$$\Delta\alpha_r \leq 0.1^\circ$$



static polar nanoregions

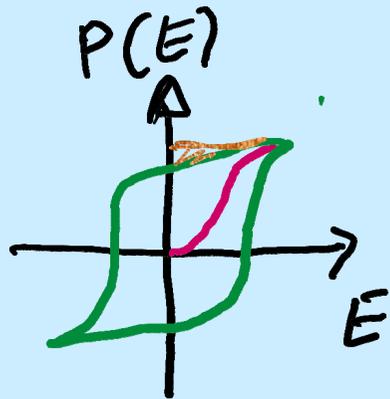
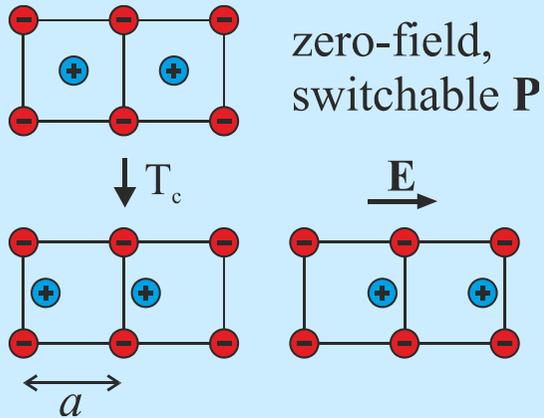
non-ergodic state

E

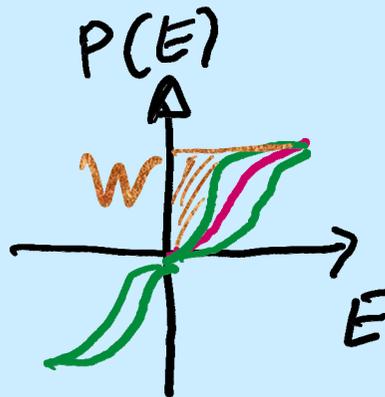
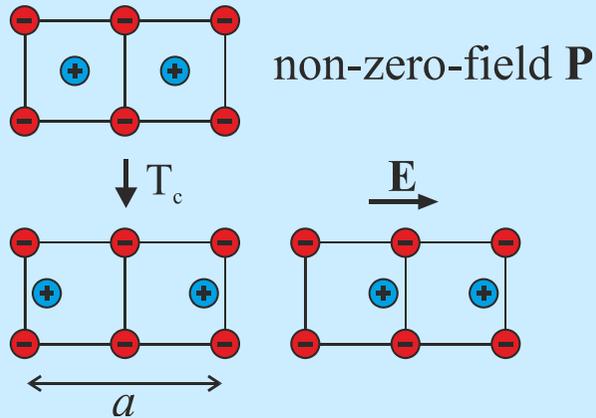


Ferro-, antiferro-, ferri-

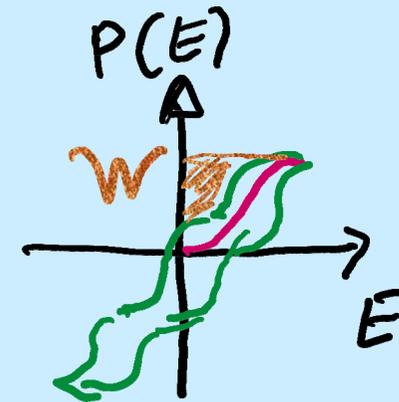
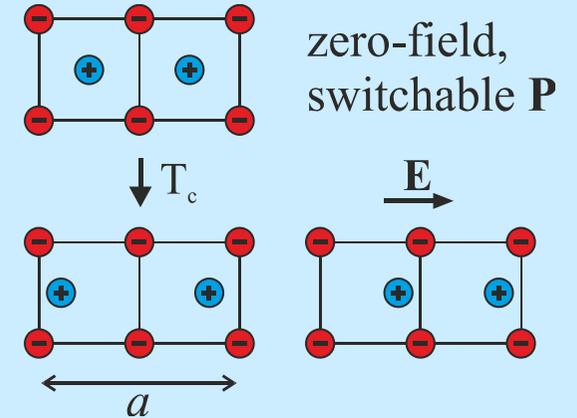
Ferroelectrics (FE)



Anti-ferroelectrics (AFE)

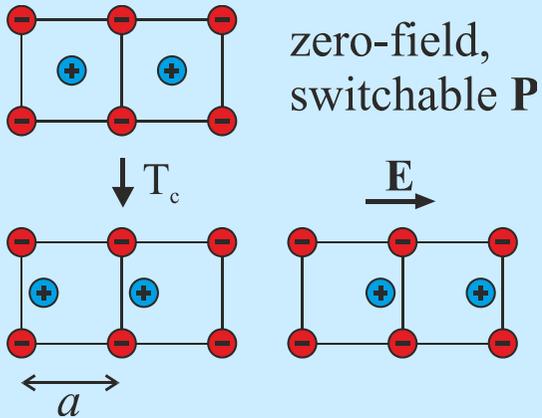


Ferrielectrics

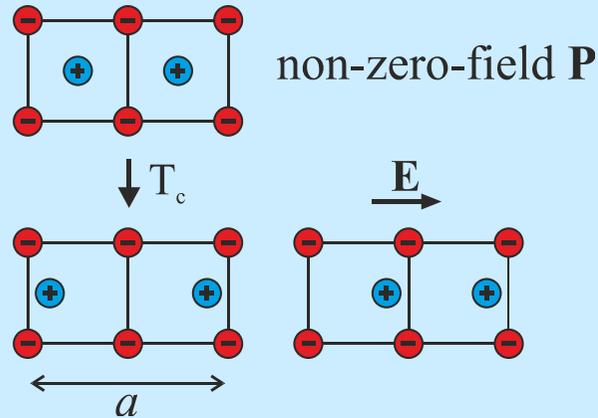


Relaxors: ferro, anti-ferro-, ferri, or?

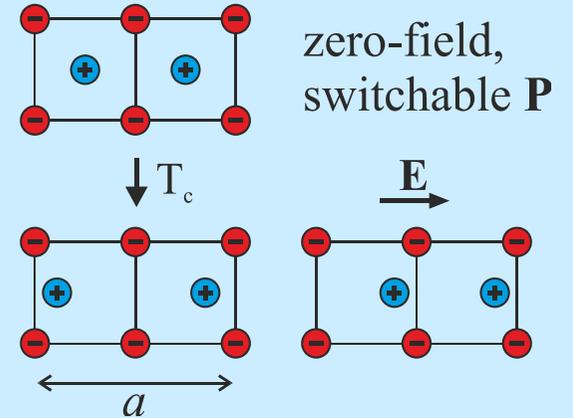
Ferroelectrics (FE)



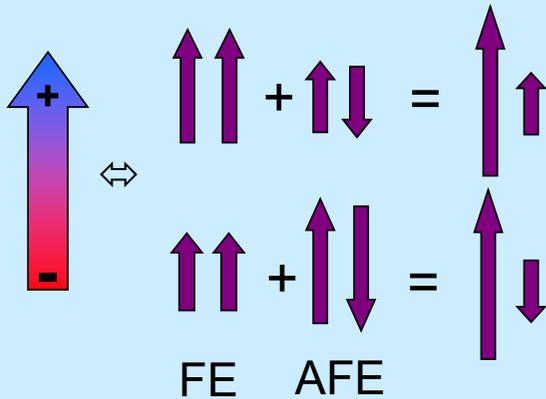
Anti-ferroelectrics (AFE)



Ferrielectrics

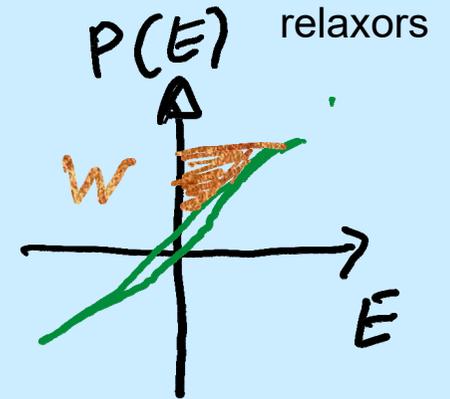


Coexisting orders:
tuning $P(E)$ loop



Doubling of
the unit cell

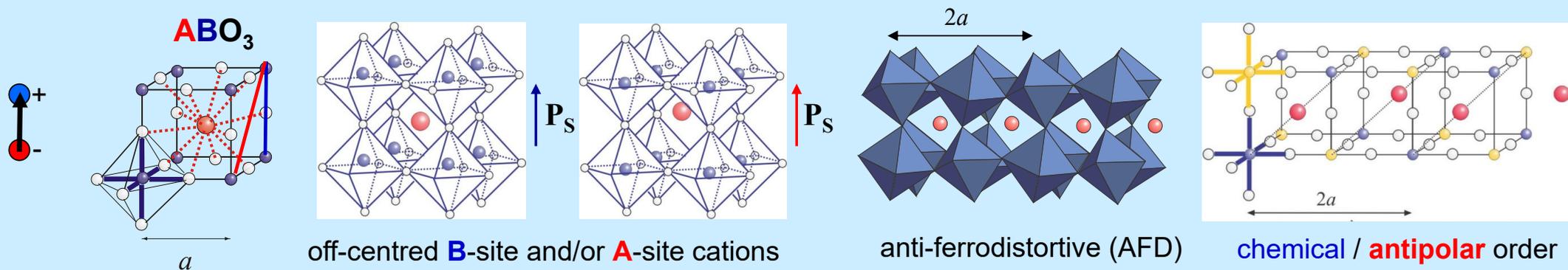
Also if
canted
AFE



➤ How to achieve coexisting orders?

- ✓ Systems with FE-active cations at two different sites
- ✓ Chemically complex systems

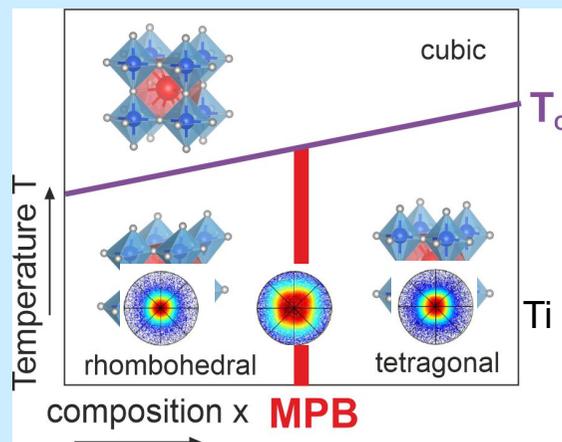
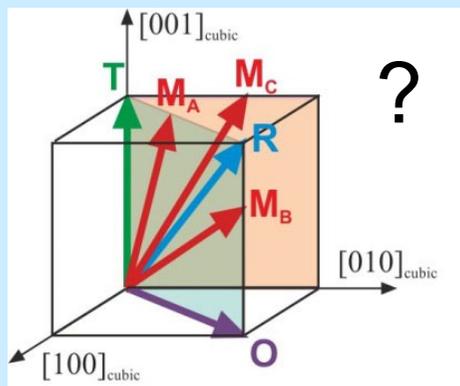
Perovskite-type FEs with morphotropic phase boundary (MPB)



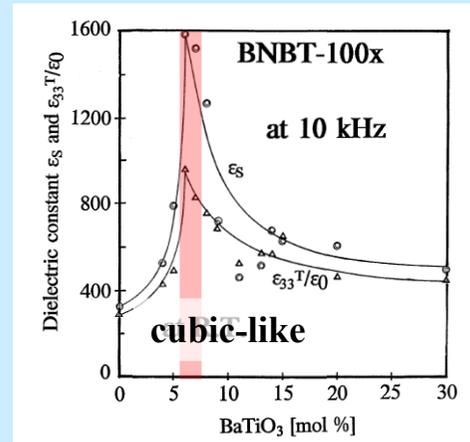
Ferroelectric solid solutions $(1-x)A'B'O_3-xA''B''O_3$, $t = \frac{r_i(A)+r_i(O)}{\sqrt{2}(r_i(B)+r_i(O))} \sim 1$

MPB := **x-driven** FE-FE structural crossover \Leftrightarrow enhanced physical properties

Polarization-rotation model

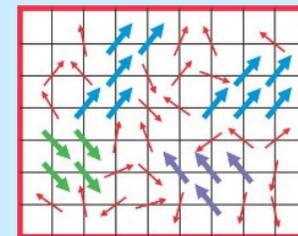


Datta et al, PRL, 119, 207604 (2017)



Takenaka et al, JJAP, 30, 2236 (1991)

multidomain vs mesoscopic-scale structure?



MPB: relaxor-type?

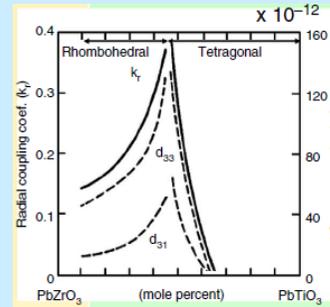


Seeking for “green” FEs as good as the golden $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT)

PZT = $(1-x)\text{PbZrO}_3 - x\text{PbTiO}_3$,
in fact, AFE-FE solid solution

relaxor-based solids solutions with giant d_{ijk} , e.g.

- $(1-x)\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3 - x\text{PbTiO}_3$
- $y\text{PbIn}_{0.5}\text{Nb}_{0.5}\text{O}_3 - (1-x-y)\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3 - x\text{PbTiO}_3$



Jaffe et al. JAP, 25, 809, (1954)



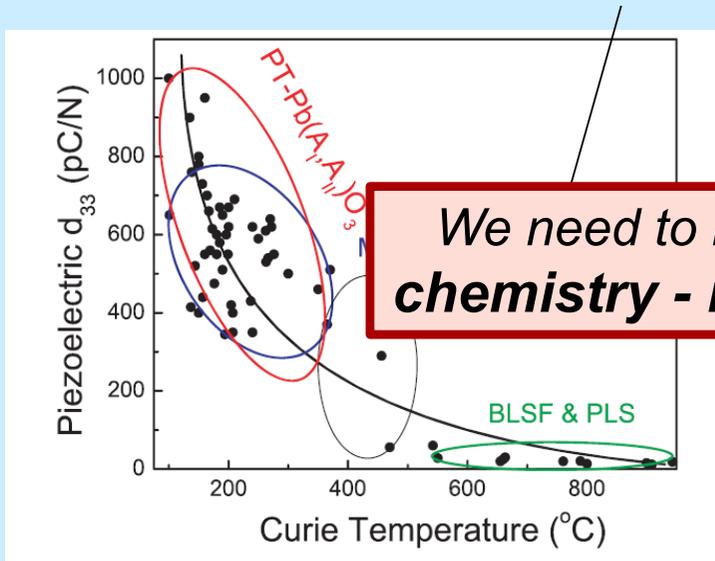
➤ **Pb-reduced:** $(1-x)\text{PbTiO}_3 - x\text{BiMeO}_3$ (PT-BMe)

➤ **Pb-free:** e.g. $(1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3 - x\text{BaTiO}_3$ (NBT-BT)

This is your planet

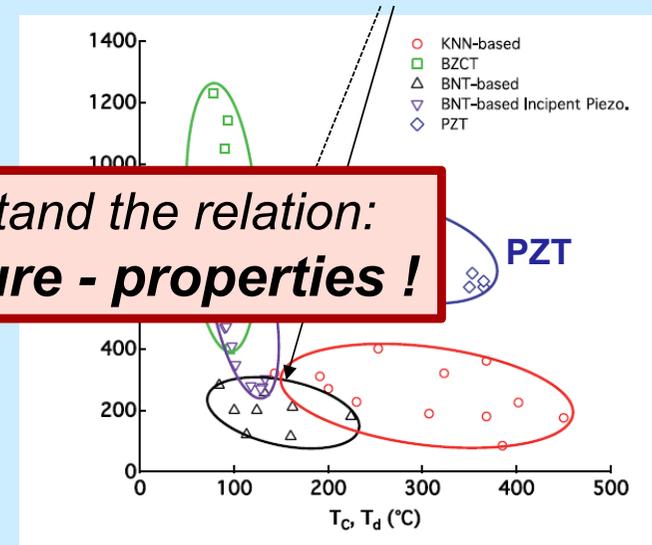


go green!



Shujun Zhang and Fapeng Yu, JACS, 94, 3153, (2011)

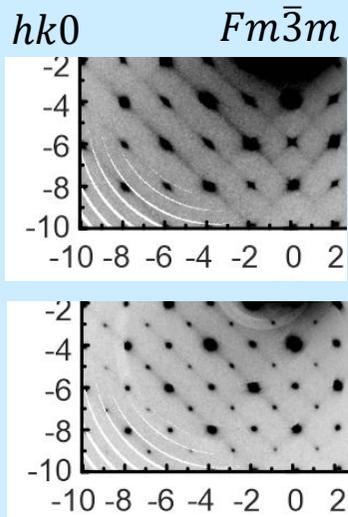
**We need to better understand the relation:
chemistry - nanostructure - properties !**



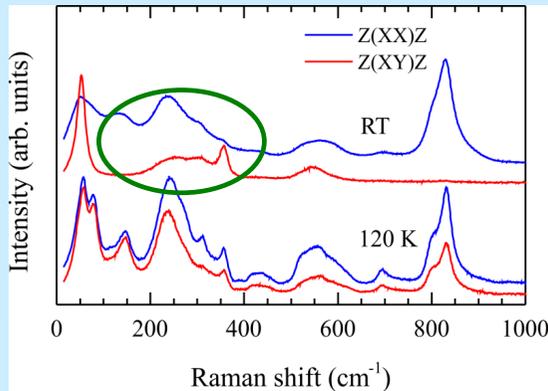
Rödel et al, JECS, 35, 1659, (2015)



Why high pressure?



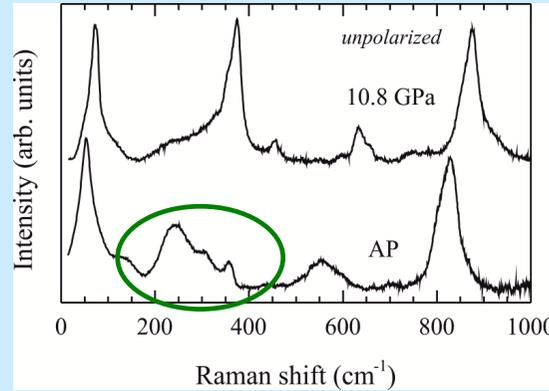
Decreasing temperature



Mihailova et al, PRB 77, 174106 (2008)

(GTA: no Raman peaks in $Pm\bar{3}m$)

Increasing pressure

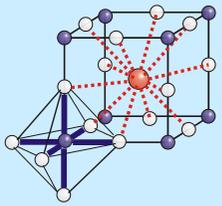
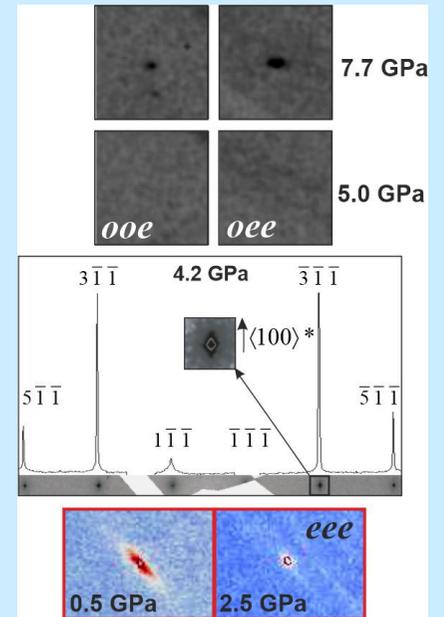


Maier et al, PRB, 84, 174104 (2011)

Maier et al, ACB, 66, 280 (2010),

Mihailova et al, PRL 101, 017602 (2008)

AFD order



Pb-based : ✓ LT: "cubic" → FE LRO

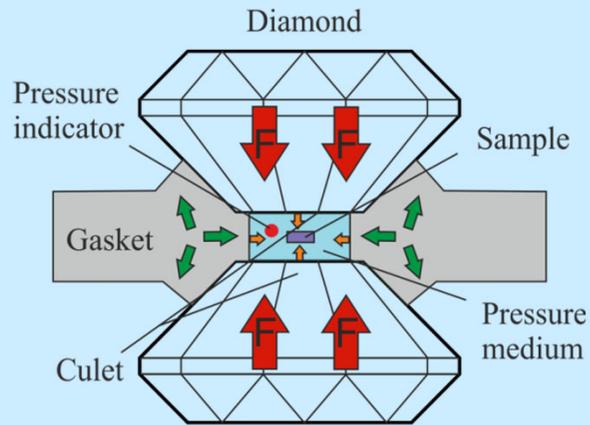
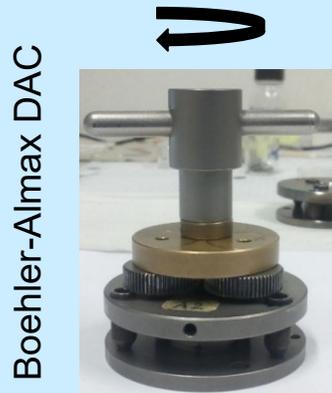
✓ HP: "cubic" → $a^-a^-a^-$ LRO → $a^+b^-b^-$ & $\uparrow\downarrow$ Pb along $[uv0]_{\text{cubic}}$

NBT-xBT single crystals across MPB: complementary HP Raman scattering and XRD

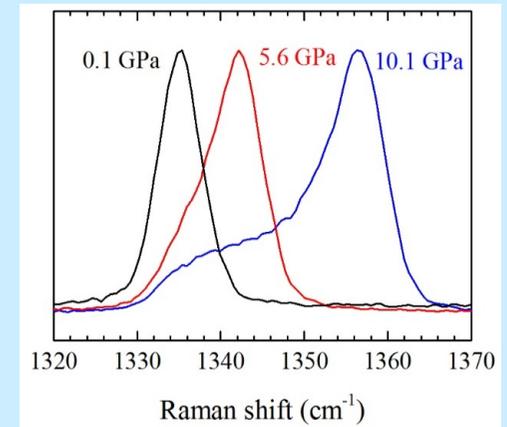
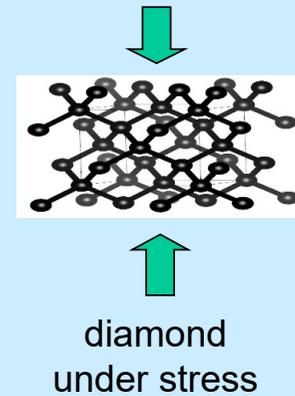
- Mesoscopic-scale structure at RT&AP via revealing the LRO under external HP
- Internal "chemical pressure" (A-site Ba^{2+}) on the NBT matrix, depending on x

Same strategy to "green" FEs

High-pressure experiments: the diamond-anvil-cell (DAC) technique



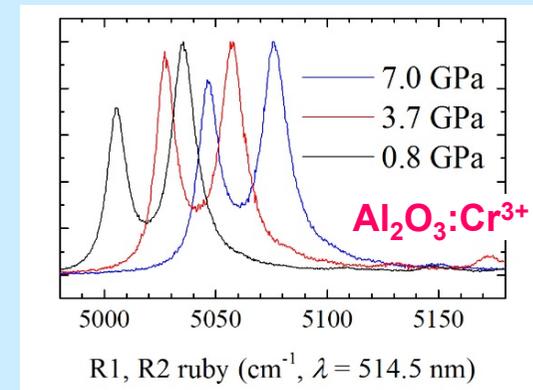
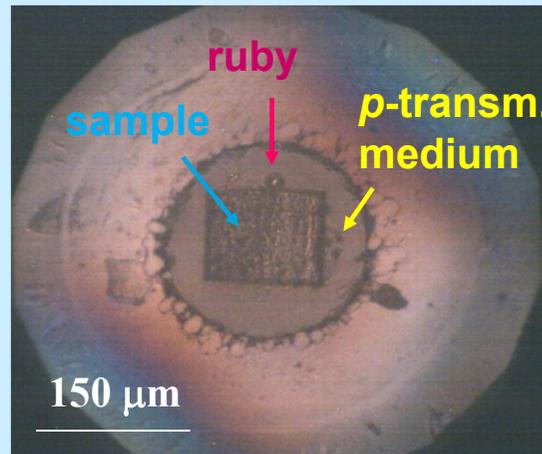
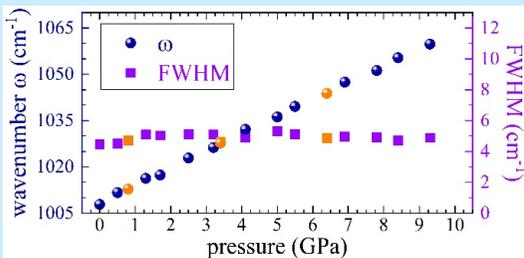
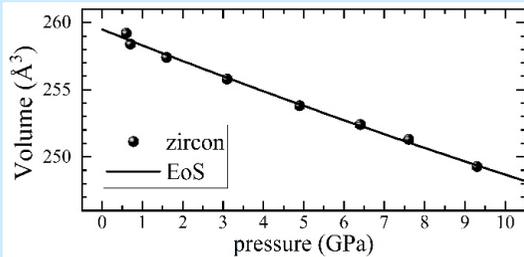
Waeselmann, PhD thesis 2012



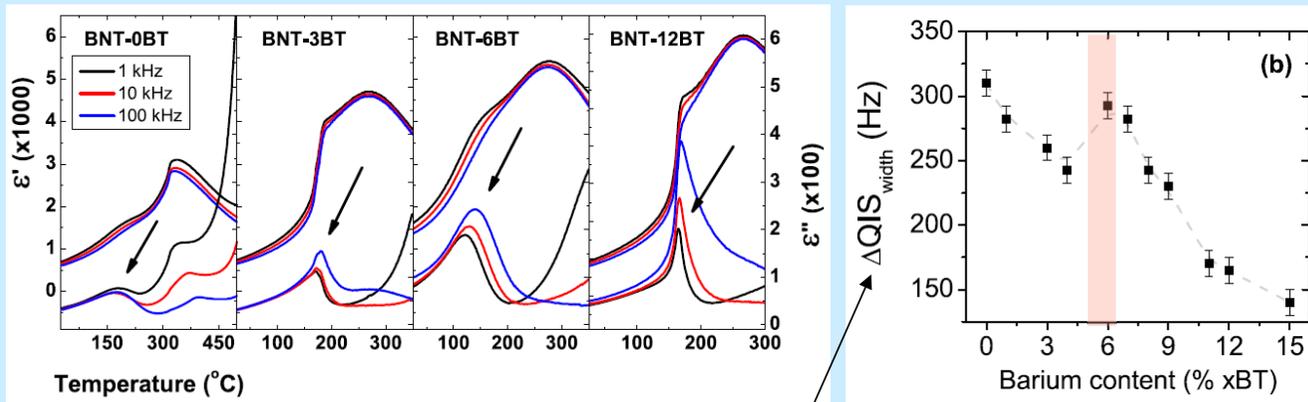
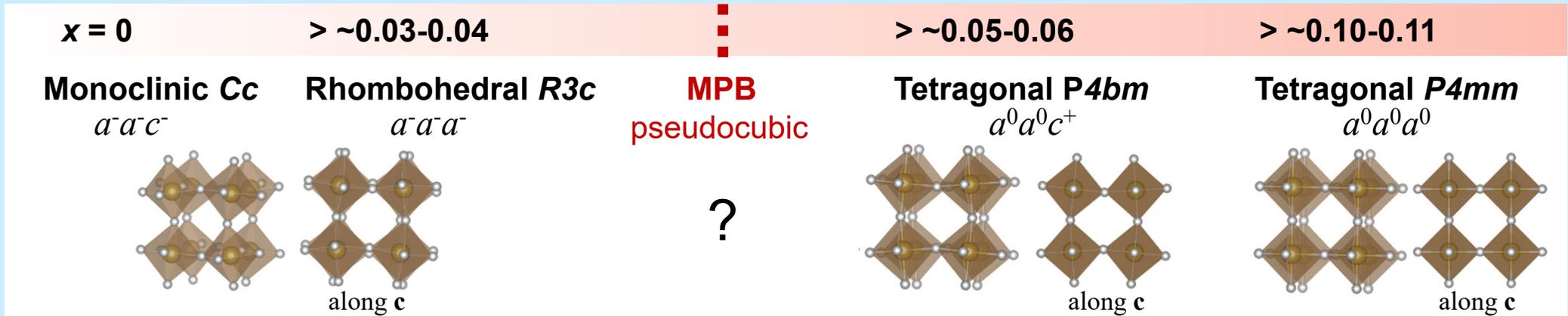
- **p-transmitting media:** He (up to ~ 30 GPa)
Me : Et : H₂O = 16 : 3 : 1 (up to 10.5 GPa)

- Optical pressure marker: **ruby**

Trivial behaviour under HP

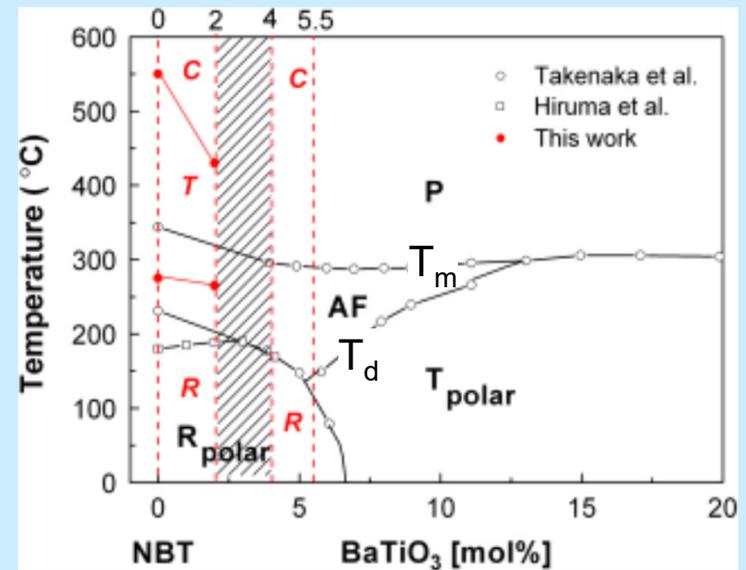


NBT-xBT across the MPB at AP, $x_{MPB} \sim 0.05$: BO_6 tilts



Groszewicz et al, *Sci. Rep.* 6, 31739 (2016)

from ^{23}Na NMR, reflects the local disorder in the BO_6 tilts



Ge et al. *J. Am. Ceram. Soc.* 94, 3084 (2011)

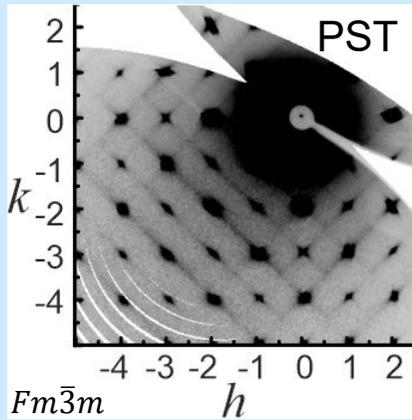
NBT-xBT across the MPB at AP, $x_{MPB} \sim 0.05$: cation off-centring

Pb-based relaxors

versus

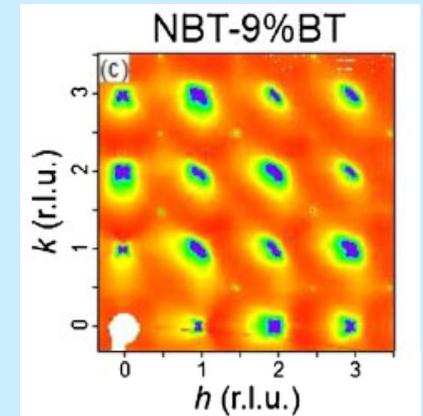
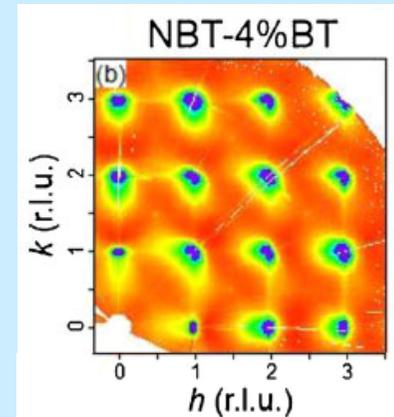
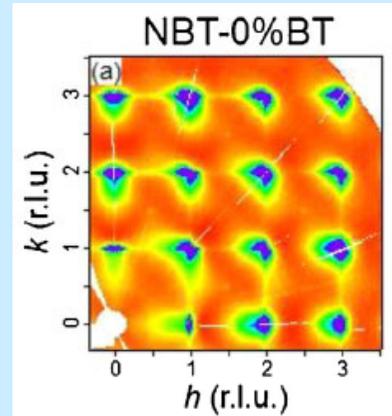
NBT-xBT

$Pm\bar{3}m$



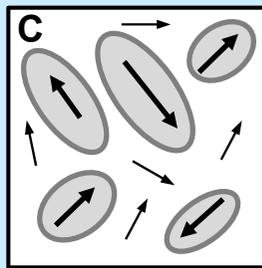
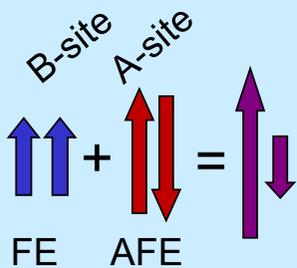
Mihailova et al, PRB 77, 174106 (2008)

$\langle 111 \rangle_c$ cationic shifts correlated within $\{110\}_c$

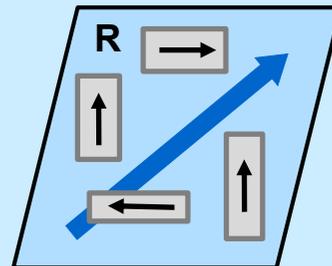


Tung et al, Mat. Res. Bull. 106, 301 (2018)

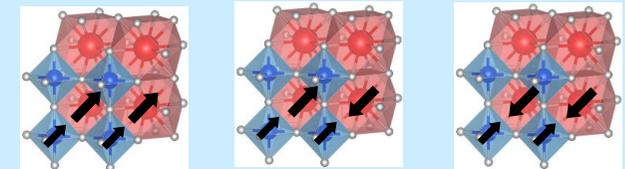
$\langle 001 \rangle_c$ A-site cationic shifts, deviating from the cationic shifts in the matrix



frustrated ferrielectric!



?

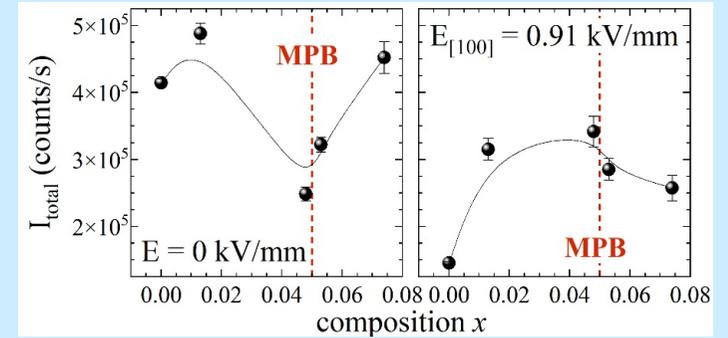
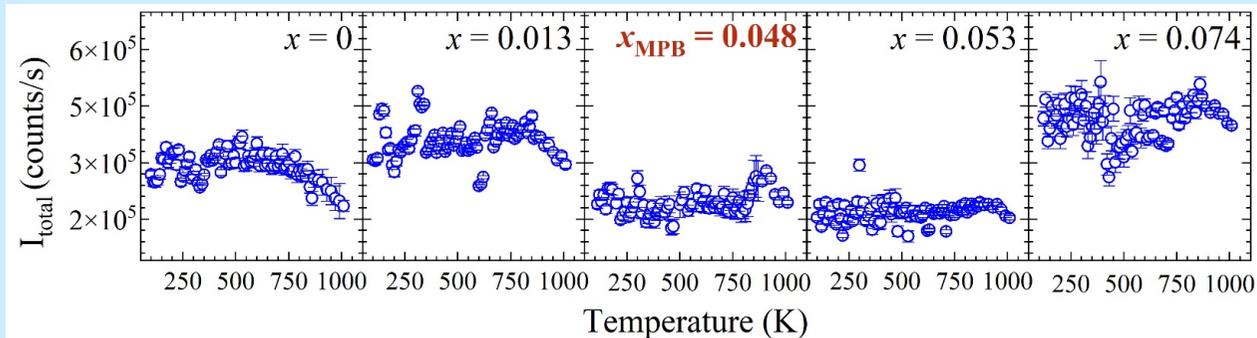


FE or relaxor FE / AFE / ferri or ...?

Review papers: Mihailova et al, HPR 33, 595 (2013),
Mihailova et al., IEEE TUFFC 62, 7 (2015)

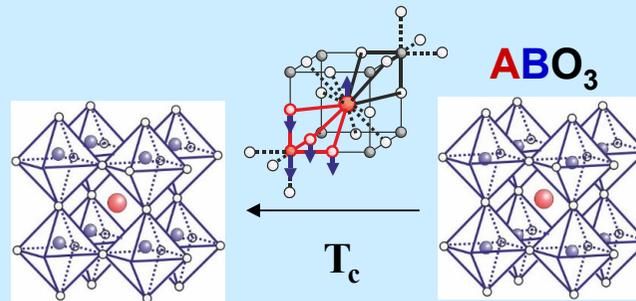
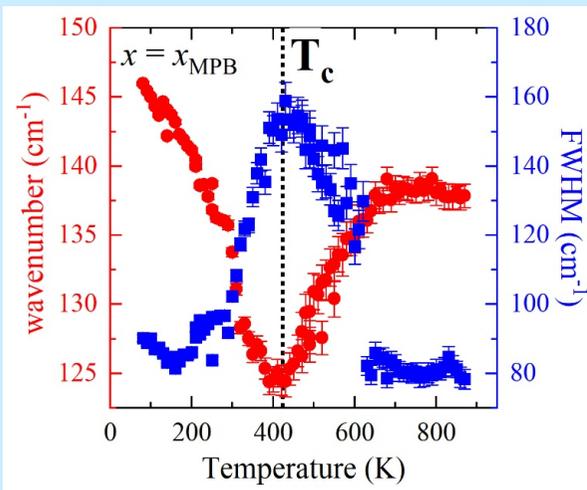
NBT-xBT across the MPB at AP: effect of T or electric field E

no Raman-active modes in $Pm\bar{3}m$! Total Raman intensity \leftrightarrow fraction & magnitude of ferroic distortions

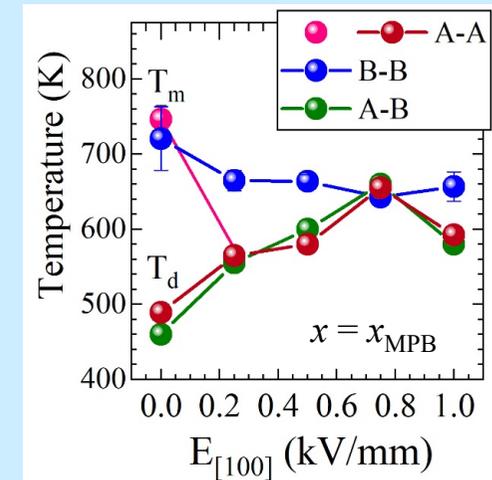


$I_{total}(T) \sim \text{constant} \Rightarrow$ **PE-FE transition: pure order-disorder transition**,
i.e. increasing correlation length of coherent distortions on cooling down

$I_{total}(x=MPB)$: maximum under $E_{[100]}$
 \leftrightarrow **easily realigned polar entities**

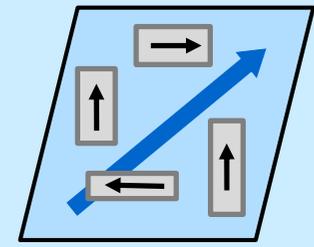
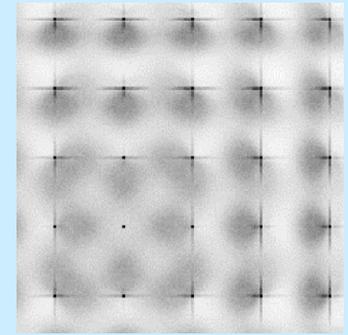
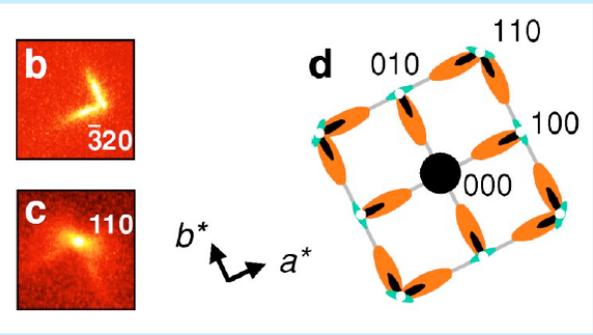
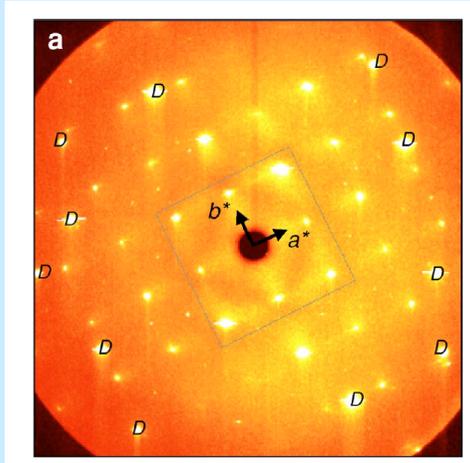


T-induced PE-?-FE, x-induced FE-FE,
E-induced R-T local realignment: *via*
dynamical coupling of A- and B-dipoles!



'hidden' antipolar order?

HP XRD study of pure NBT

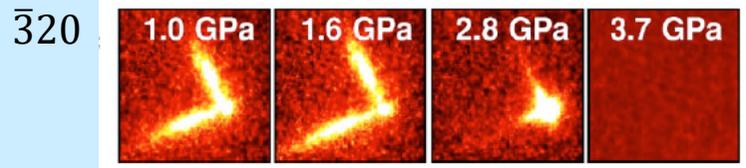


NBT at 0.6 GPa

Monte Carlo modelling of L-shape XDS:

- A-site local dipoles departing from the matrix
- asymmetry due to different charge environment of Bi^{3+} and Na^+ \Leftrightarrow “atomic-size” effect in disordered alloys

$Pm\bar{3}m$



- direction of A-site dipoles in PNRs synchronized with the matrix

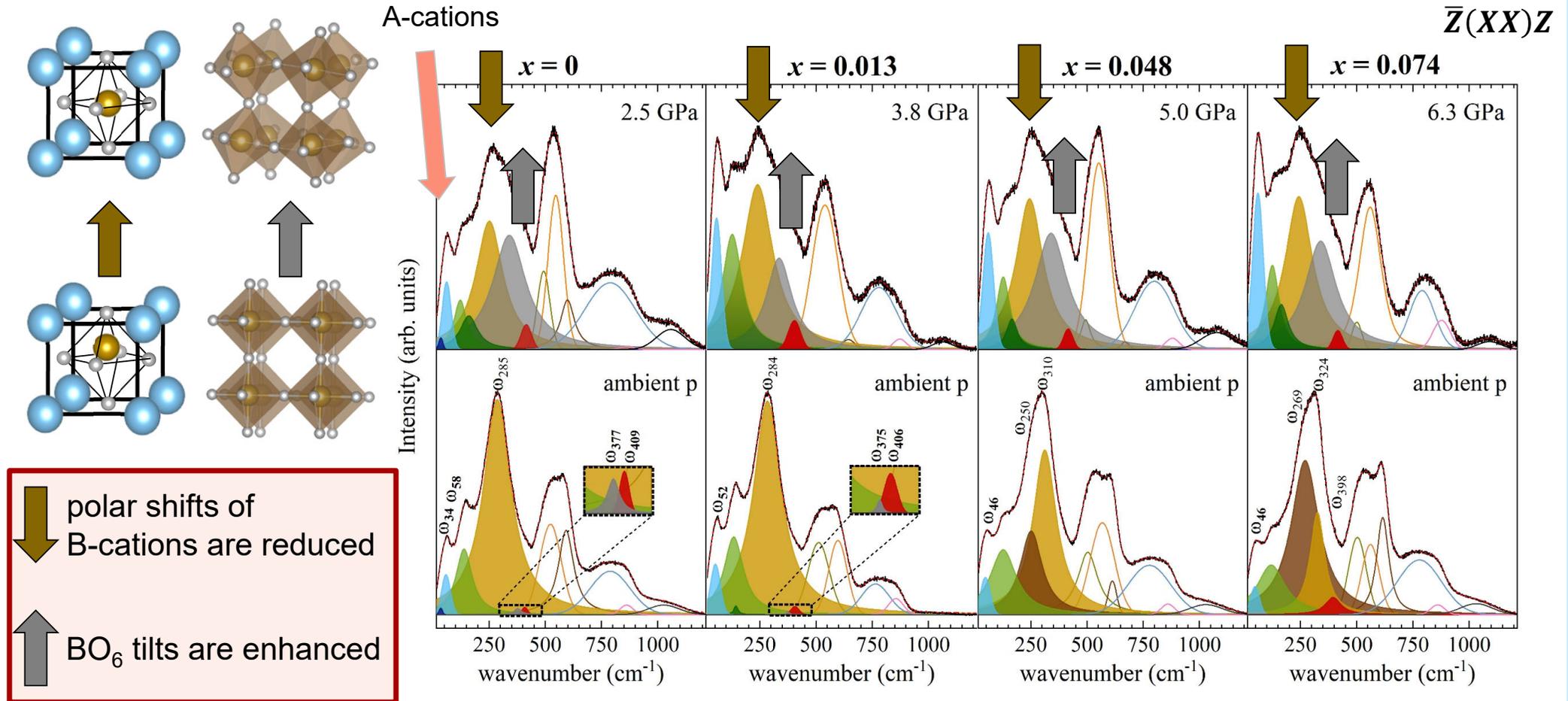


- phase transition to monoclinic or orthorhombic structure

Kreisel et al., PRB 68, 14113 (2003)

Thomas et al., Z. Kristall. 220, 717 (2005): HP phase is $Pnma$

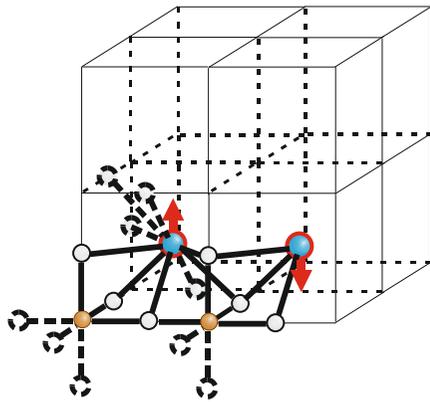
HP Raman spectroscopy of NBT-xBT single crystals



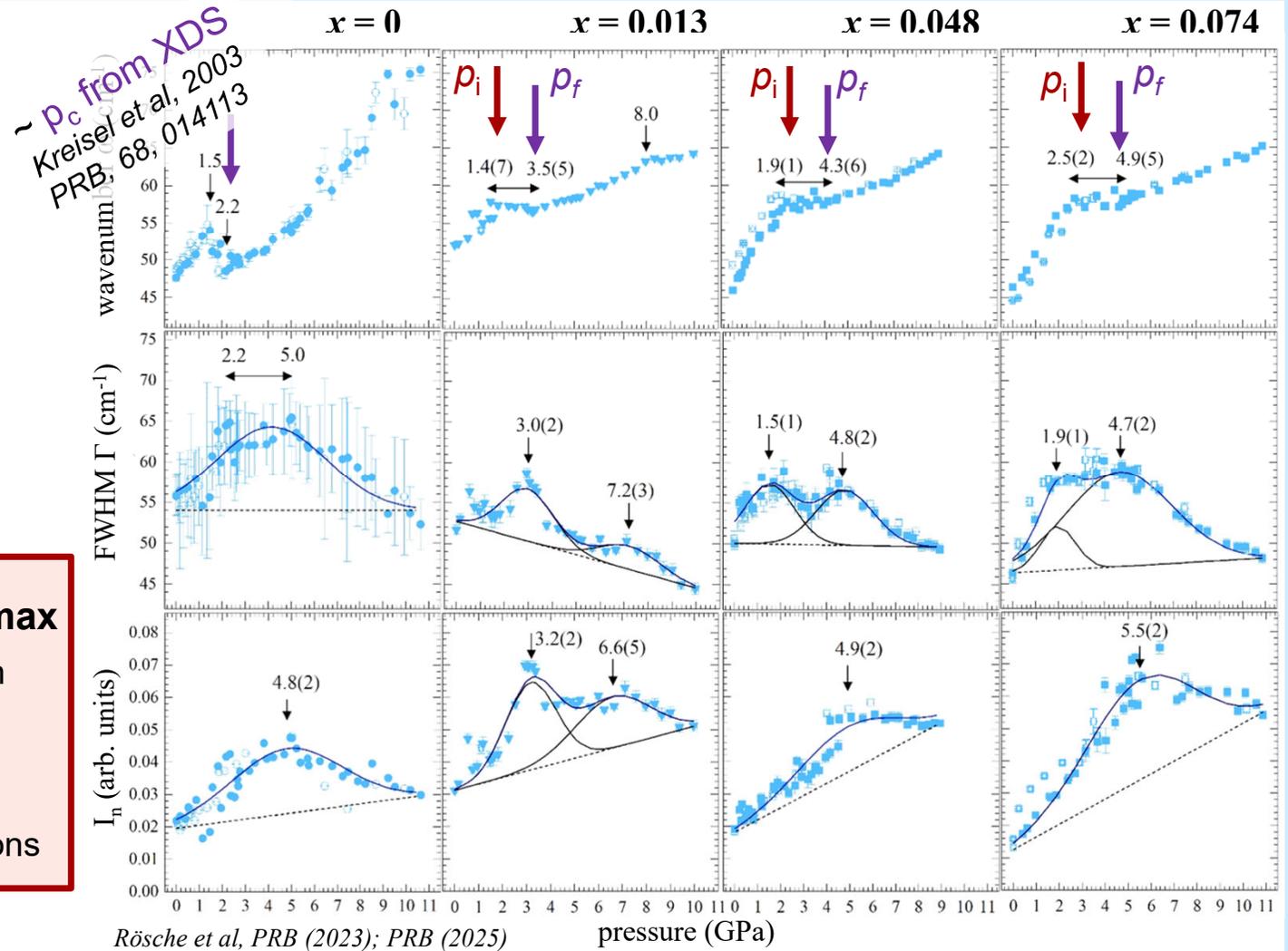
Rösche et al, PRB 108, 094110 (2023), Rösche et al, PRB 112, 184102 (2025)

HP Raman spectroscopy of NBT-xBT single crystals

A-cation off-centering
~30-60 cm⁻¹

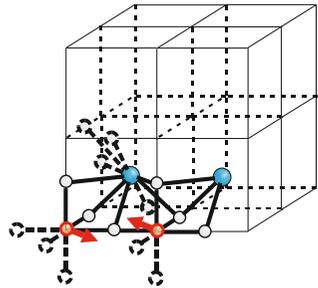


- $\omega(p)$: plateau-like min & $\Gamma(p)$ max
- rearrangements in A-site subsystem
- phase transition as in NBT?
- I_n increase
- increased fraction of off-cent. A-cations

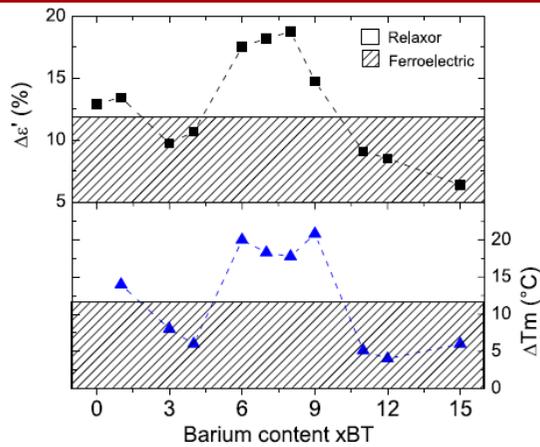


HP Raman spectroscopy of NBT-xBT single crystals

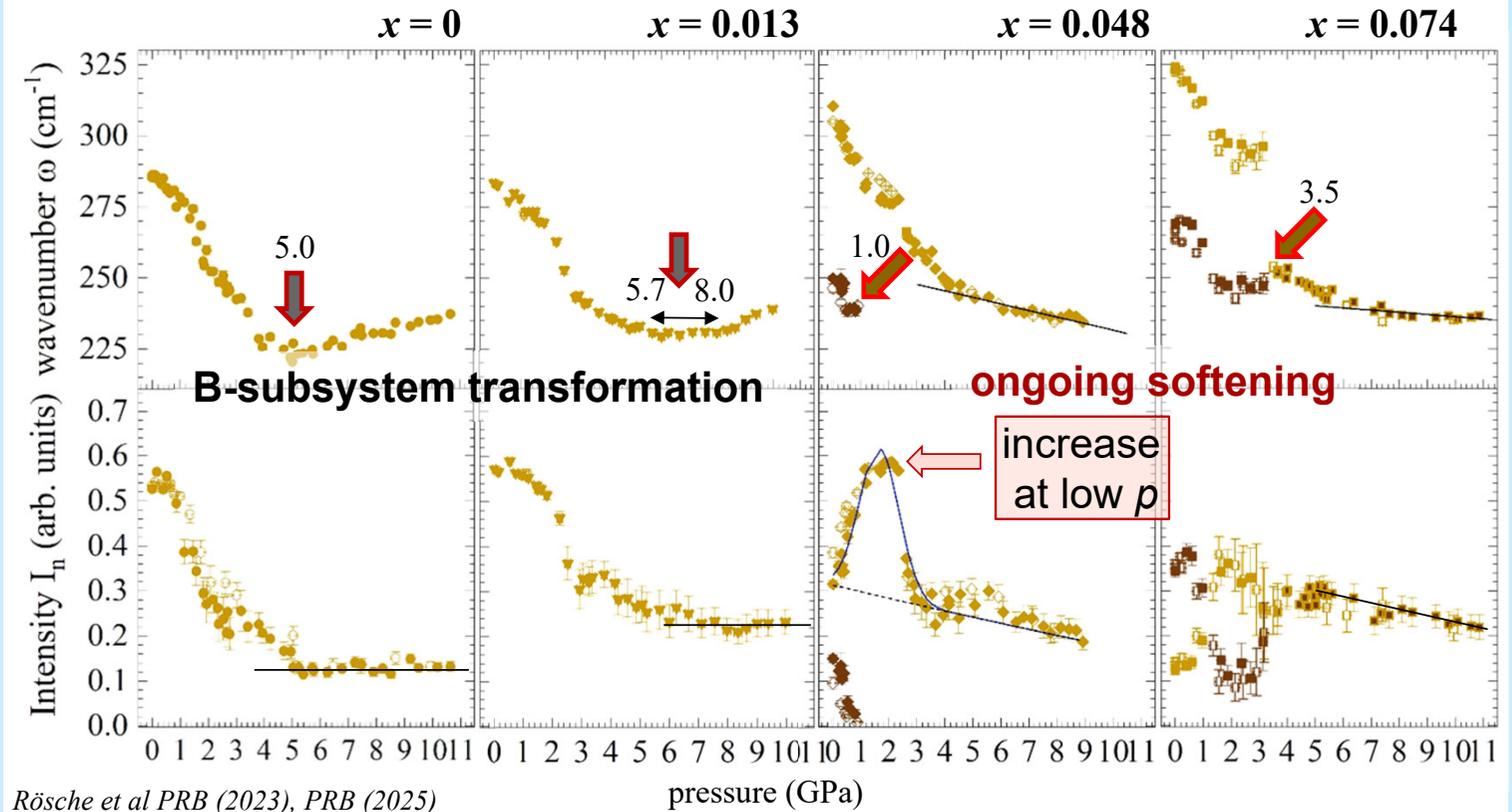
B-cation off-centering
~ 240-325 cm⁻¹



higher B-dipole disorder
corroborates to the Ba²⁺-
enhanced relaxor behaviour



Groszewicz et al, Sci. Rep. 6, 31739 (2016)



Rösche et al PRB (2023), PRB (2025)

- suppression of **B-cation polar shifts**, but they **still exist in the HP phase**
- for $x < \text{MPB}$: rearrangement of the B-site subsystem, no further suppression
- for $x \sim \text{MPB}$: reduced dispersion in local BO₆ anisotropy; same for $x = 0.074$

Synchrotron XRD of NBT-xBT single crystals, DESY/Petra III, P24

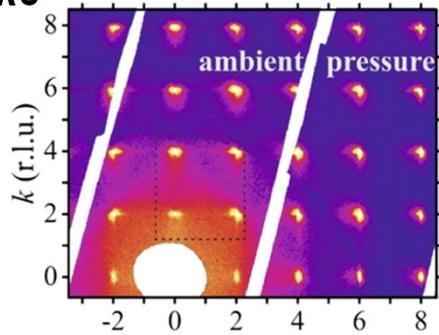
$Fm\bar{3}m$

$x = 0.013$

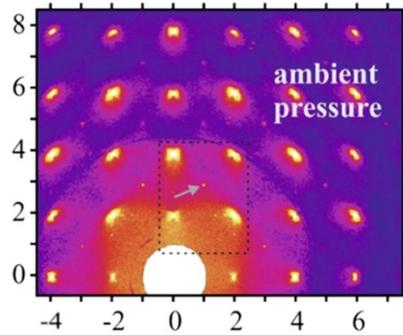
$x_{MPB} = 0.048$

$x = 0.074$

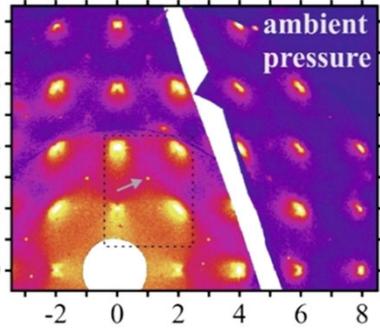
$hk0$



➤ XDS $\parallel \langle 100 \rangle_{pc}$



➤ XDS $\parallel \langle 110 \rangle_{pc}$



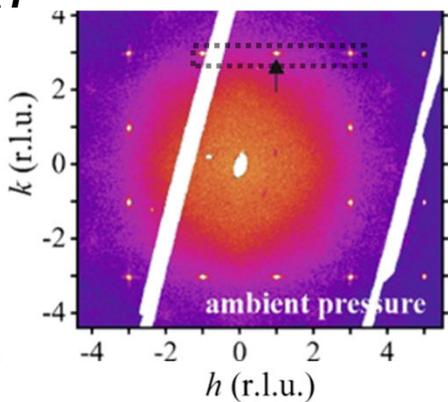
➤ XDS $\parallel \langle 110 \rangle_{pc}$

XRD data ambient pressure,
indices in a doubled cubic perovskite cell

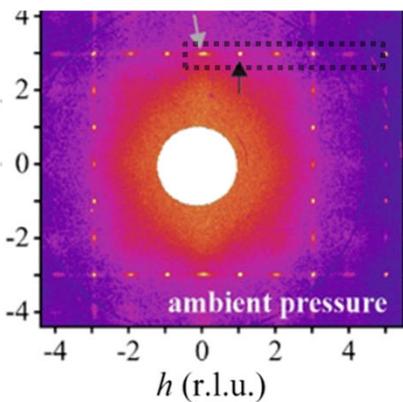
Ba-related internal local stresses:

- ✓ change how the **A-site cationic shifts correlated on nanoscale deviate** from the A-cation shifts of the matrix
- ✓ change the **BO₆ tilt pattern**

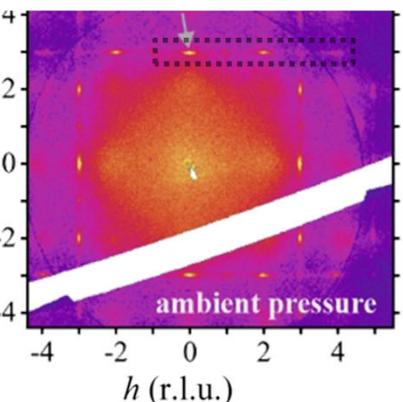
$hk1$



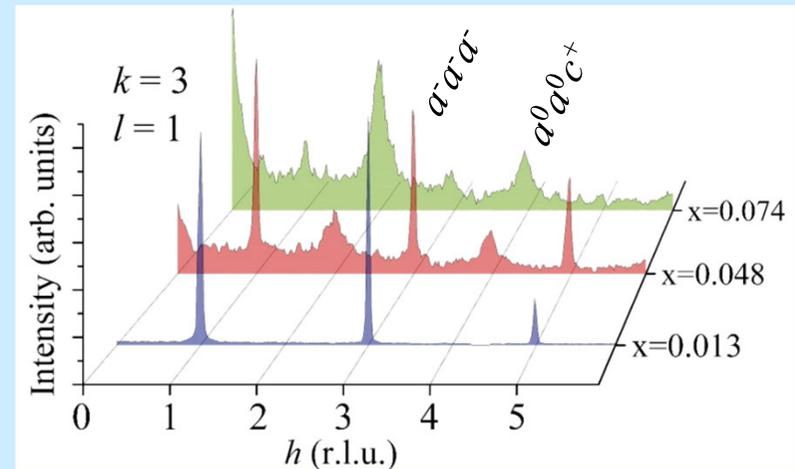
➤ only $a^-a^-a^-$



➤ dominant $a^-a^-a^-$
subordinate $a^0a^0c^+$

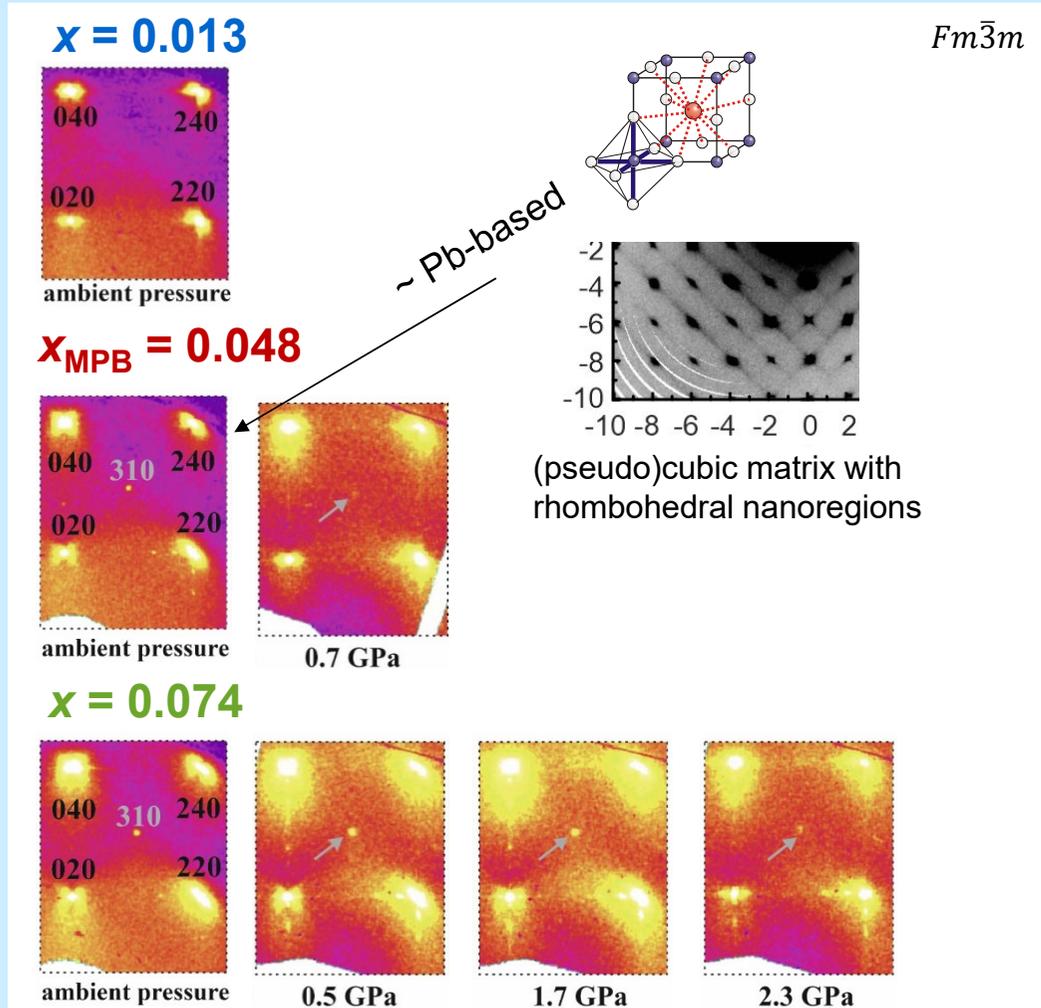


➤ dominant $a^0a^0c^+$
remnant $a^-a^-a^-$



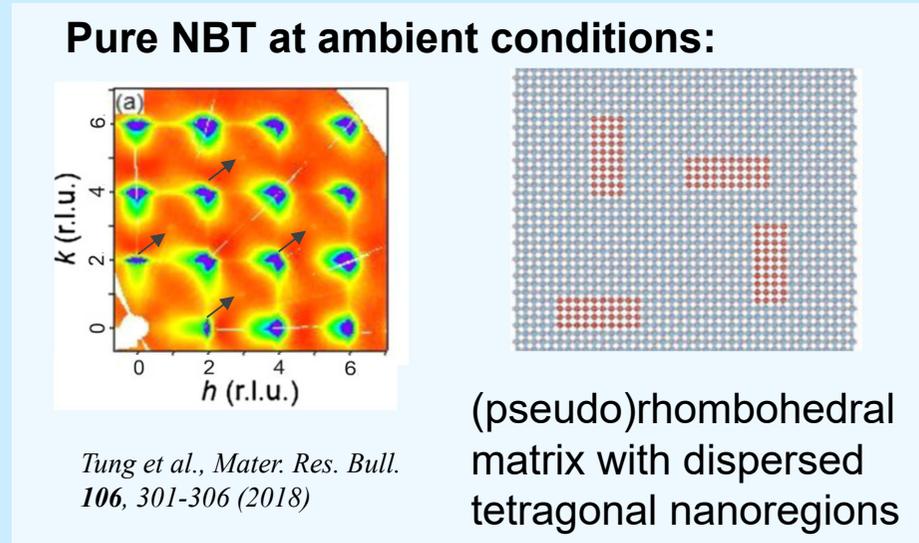
Rösche et al, *Sci. Rep.* 14, 18799 (2024); *PRB*, 112, 184102 (2025)

HP synchrotron XRD of NBT-xBT single crystals, DESY/Petra III, P24



external hydrostatic pressure:

- suppresses Ba-induced XDS $\parallel \langle 110 \rangle_{pc}$ and enhances XDS $\parallel \langle 100 \rangle_{pc} \Rightarrow$
- ✓ **pressure reverses the structural state to that of pure NBT at AP**

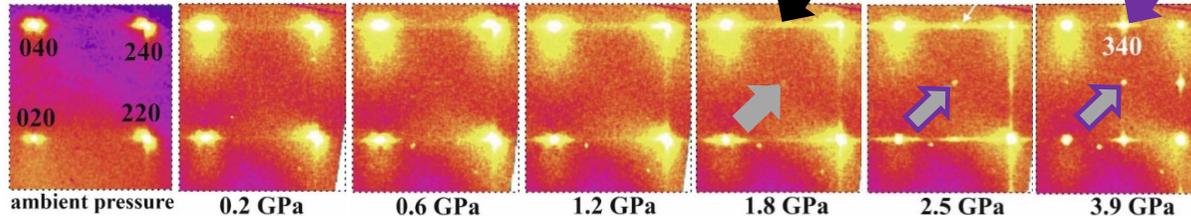


Rösche et al, *Sci. Rep.* 14, 18799 (2024), Rösche et al, *PRB* 112, 184102 (2025)

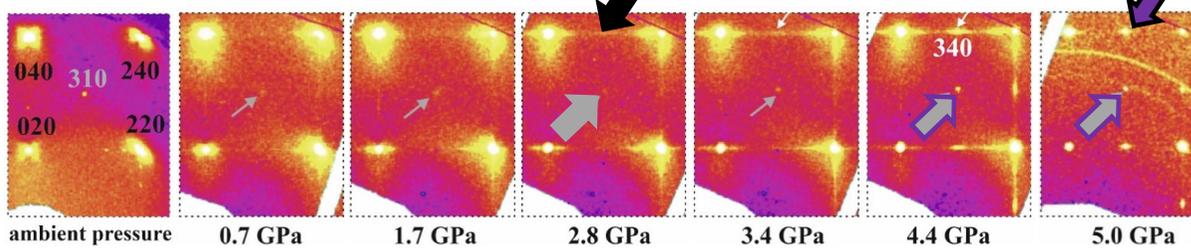
HP synchrotron XRD of NBT-xBT single crystals, DESY/Petra III, P24

Fm3m

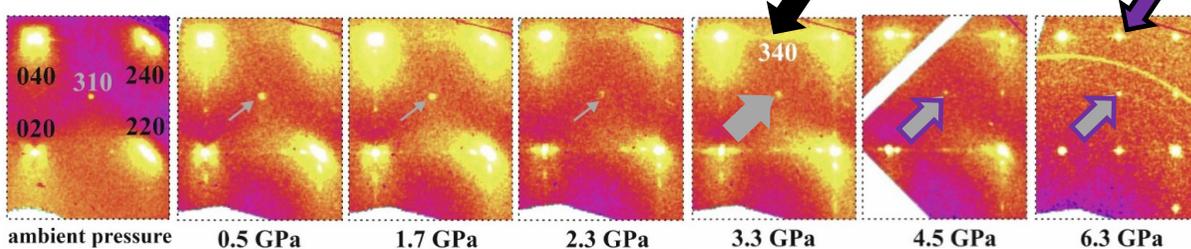
x = 0.013



x_{MPB} = 0.048



x = 0.074



External hydrostatic pressure:

- alters XDS from $\parallel \langle 110 \rangle_{pc}$ to $\parallel \langle 100 \rangle_{pc}$
- alters the tilt correlation lengths
- induces ooe + oee precursors at $p^* \sim 1.8 / 2.8 / 3.3$ GPa
(p^* correlates with $p_{initial}$ derived from $\omega(p)$ of the A-cation phonon mode)
- **Phase Transition**
(structure refinements: **Pnma** for all x)
 $p_c \in (2.5, 3.9) / (4.4, 5.0) / (4.5, 6.3)$ GPa
(p_c correlates with p_{final} derived from $\omega(p)$ of the A-cation phonon mode)
⇒ **A-cation driven phase transition**

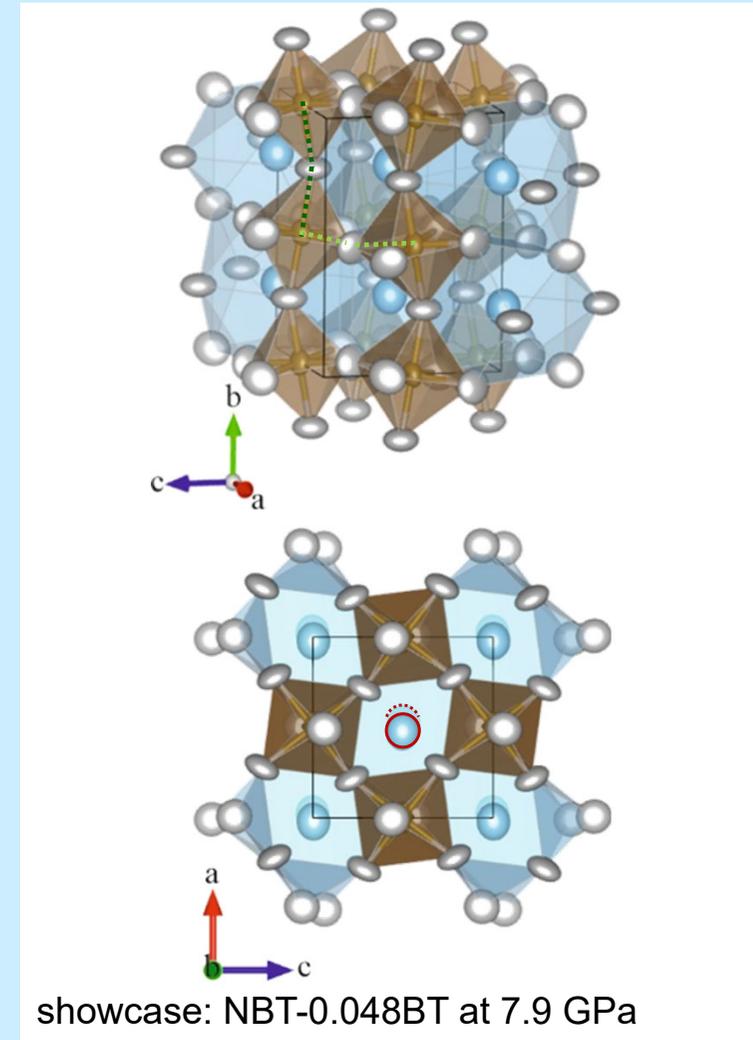
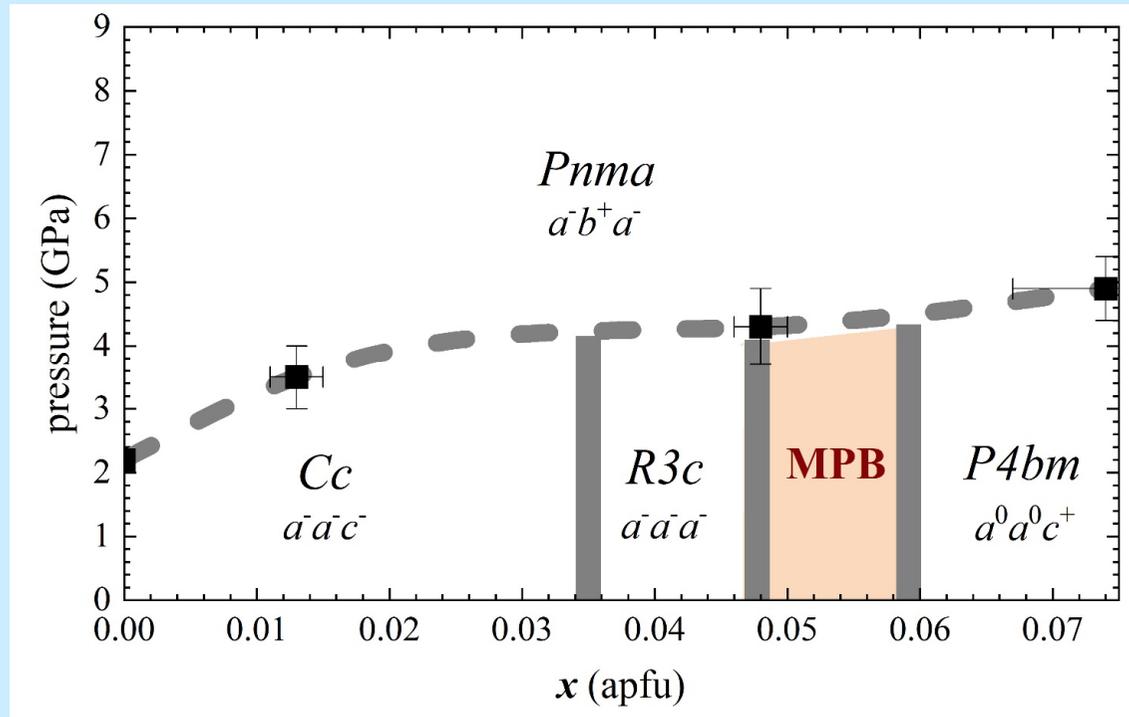
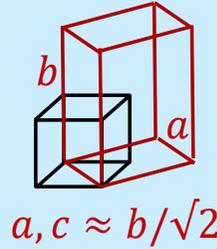
Rösche et al, *Sci. Rep.* 14, 18799 (2024), Rösche et al, *PRB* 112, 184102 (2025)

Phase Transition : reversible, but with a **time hysteresis** on the length-scale sensitivity of **XRD and XDS**, **immediately**, on the length-scale sensitivity of **Raman scattering** ⇒ **of order-disorder type**

Take home message 1: Pressure-induced phase transition

HP structure: orthorhombic *Pnma*

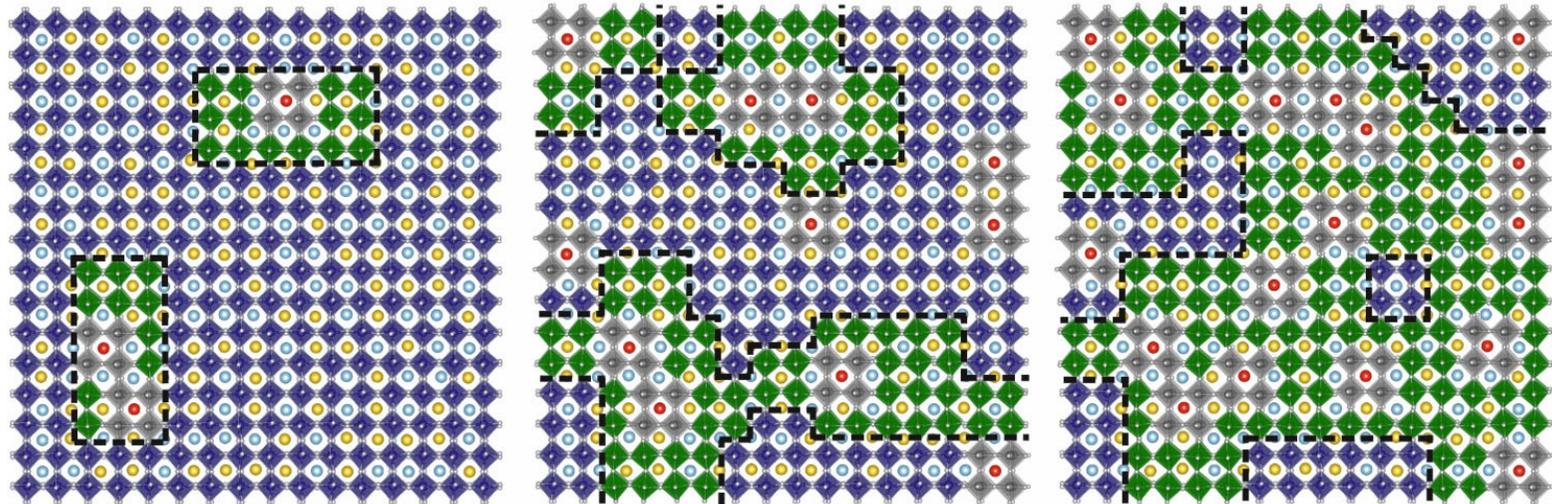
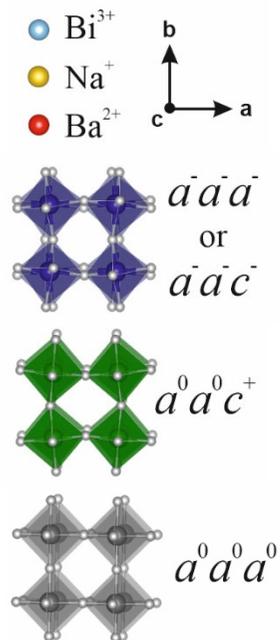
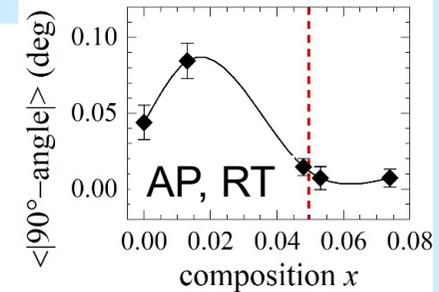
- mixed octahedral tilt pattern: $a^-b^+a^-$
- antipolar A-cation shifts mainly along $[110]_{\text{cubic}}$
- uncorrelated B-cation shifts of reduced magnitude



Take home message 2.1: NBT-xBT at ambient pressure and RT

Ba²⁺ is incorporated in the NBT matrix in a different way:

- **x = 0.013** : only the tetragonal regions, causing stress on the rhombohedral matrix
- **x_{MPB} = 0.048** : in both the rhombohedral (*a*-*a*-*a*⁻) and tetragonal (*a*⁰*a*⁰*c*⁺) fraction
- **x = 0.074**: same as for x_{MPB}, but the tetragonal fraction dominates



Ba²⁺ incorporation near **MPB** at AP and RT:

- ✓ the (pseudo)rhombohedral matrix is fractioned to rhombohedral PNR and tetragonal nanoregions are altered to polarizable (pseudo)cubic areas
- ✓ B-site local dipoles: easily switchable upon low mechanical compressions

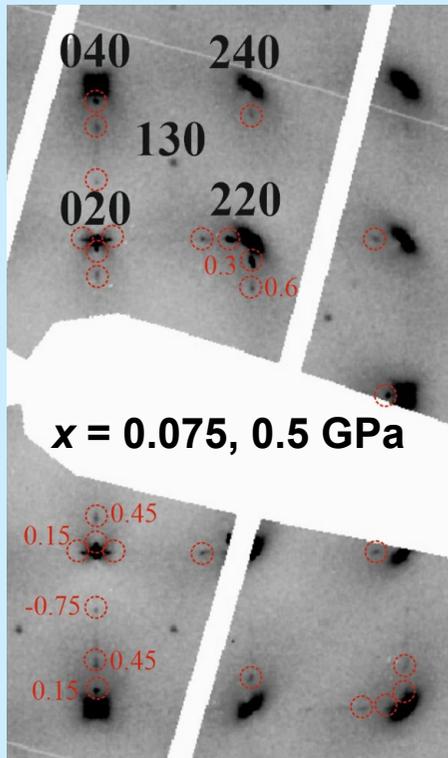
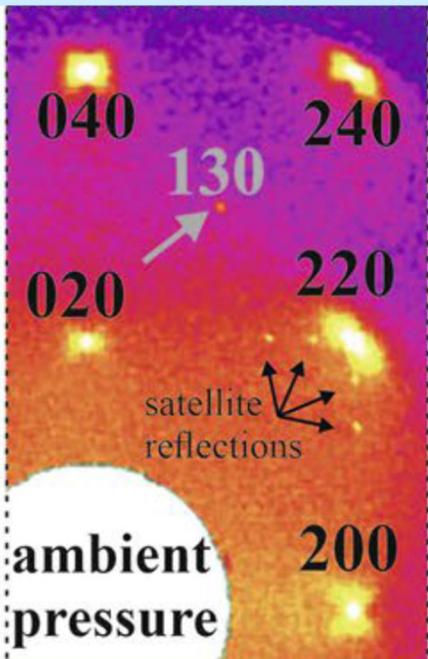
Take home message 2.2: NBT-xBT at ambient pressure and RT

Incommensurate modulated structures

lattice period and modulation period are incompatible

Bragg peak: $H = ha^* + kb^* + lc^* + m_1q_1 + m_2q_2 + \dots$

$x = 0.048$



Satellite Bragg peaks for $x_{MPB} = 0.048$ and 0.074

➤ $p < p_c$: no change with p

➤ $p > p_c$: no such in the $Pnma$ phase

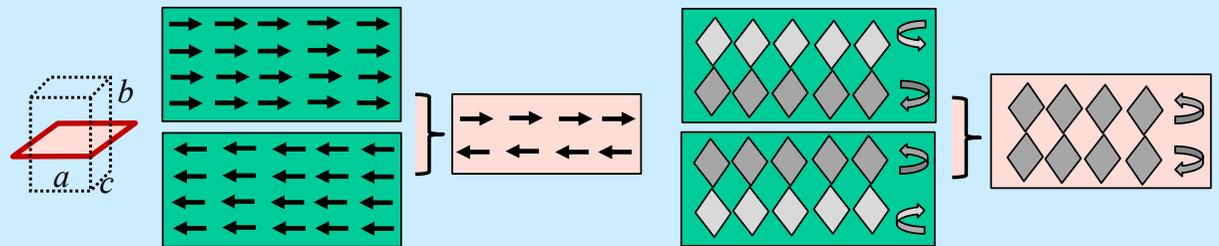
($Pnma$: mixed $a^-b^+a^-$ tilts + $\uparrow\downarrow$ order of A-cation shifts || a_{ortho})

Pure NBT at HT (near T_c of $Cc \leftrightarrow P4bm$ phase transition):

➤ 1D modulation due to $Pnma$ -like layers to relax the strain between adjacent domains with opposite $a^-a^-a^-$ BO_6 tilts.

(Cc : antiphase BO_6 tilts, $P4bm$: $\uparrow\uparrow$ A-site polar shifts)

- ✓ **$Pnma$ -like layers** relax intrinsic strains between adjacent domains with
 - **opposite antiphase BO_6 tilts** as well as with
 - **opposite polar shifts of A-site cations**
- ✓ **Ba content** varies the **temperature range of stability** of the 1D incommensurate modulated structure



*Acknowledgements: all co-authors!
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Carsten Paulmann, Gemma de la Flor, Kaustuv Datta,
Naemi Waesermann, Bernd Maier, Anna-Maria Welsch etc.*

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The two (former) PhD students who worked on FE solid solutions over the last 5 years:

Dr. Constanze Rösche

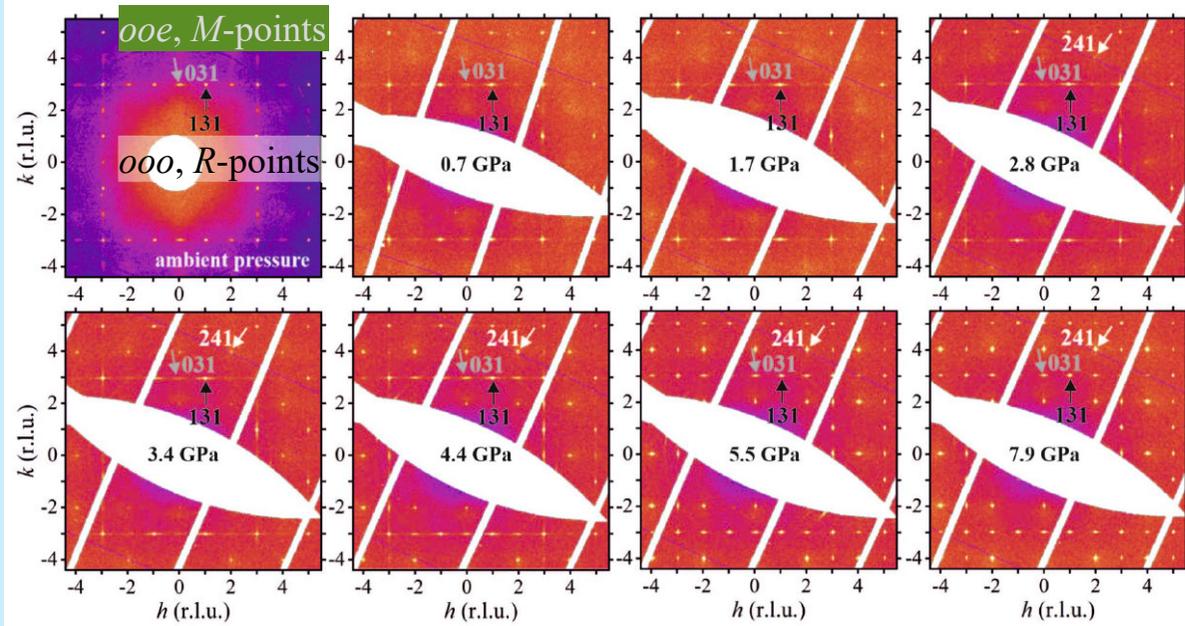
Dr. Irina Margaritescu (now Schablack)

Thank you for your attention!



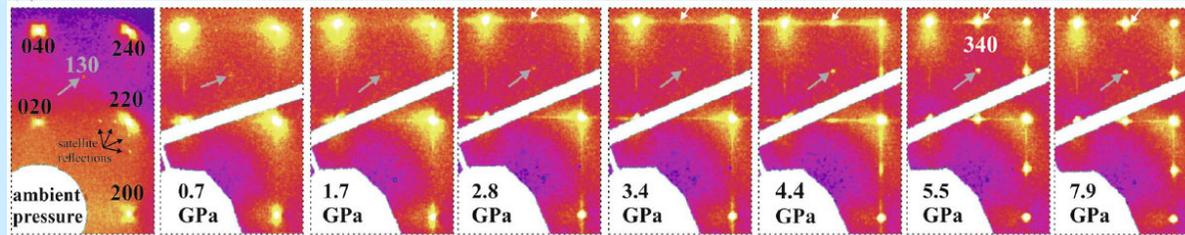
HP synchrotron XRD of NBT-xBT single crystals, DESY/Petra III, P24

$hk1$ in $Fm\bar{3}m$

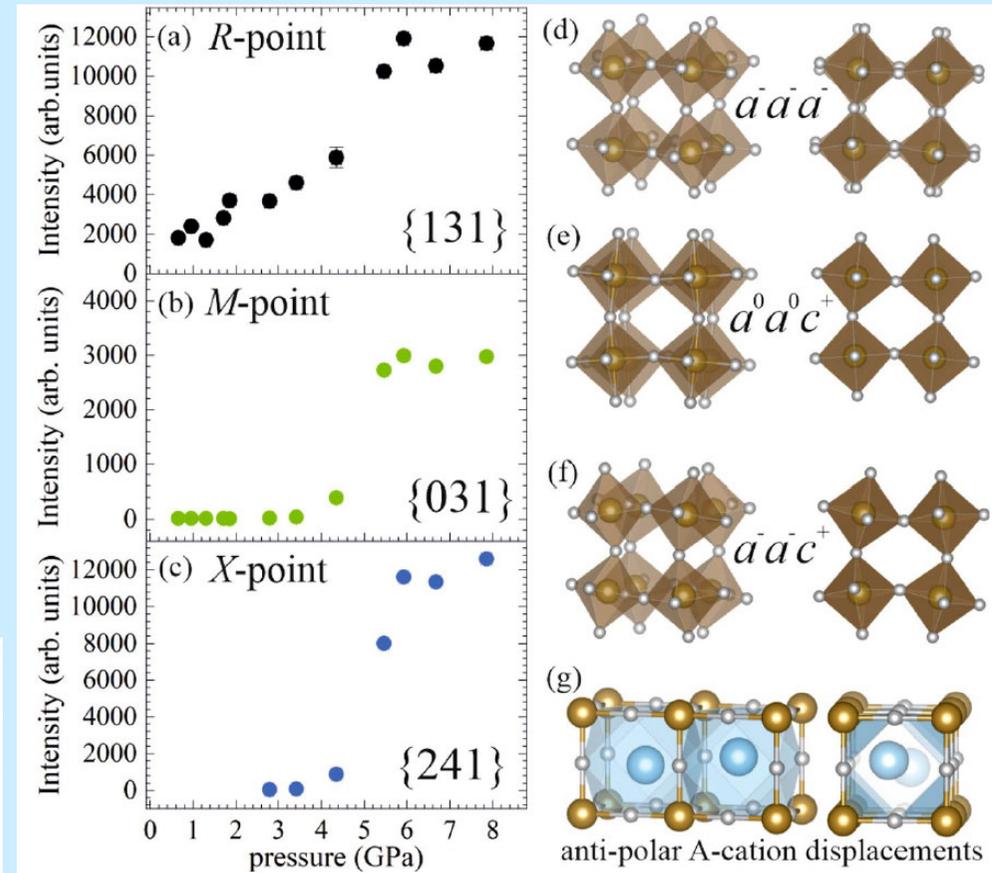


$hk0$ in $Fm\bar{3}m$

ooe, X-points

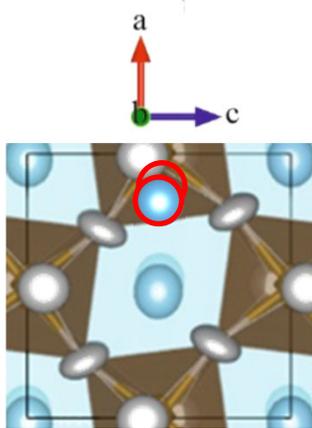
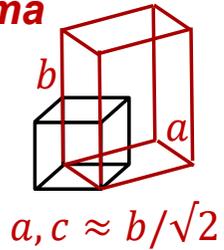


$NBT-xBT$, $x = x_{MPB}$



HP synchrotron XRD of NBT-xBT single crystals, DESY/Petra III, P24

Pnma

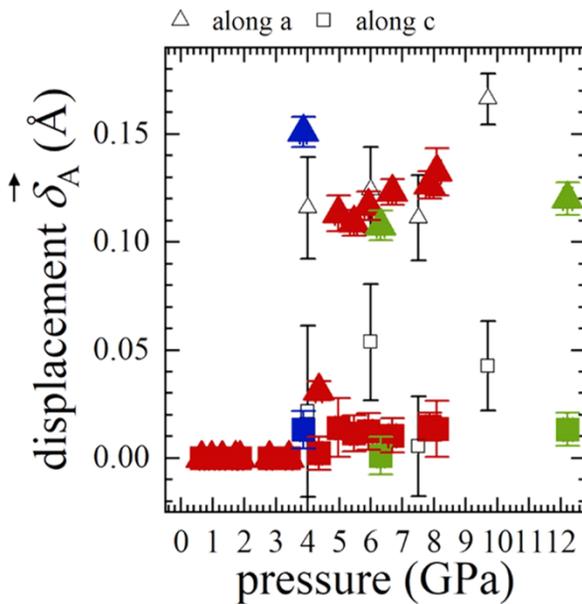


$x = 0.048$
at 7.9 GPa

A-cation off-centre displacements

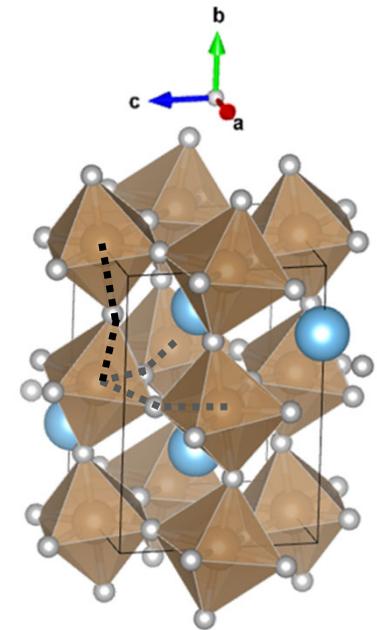
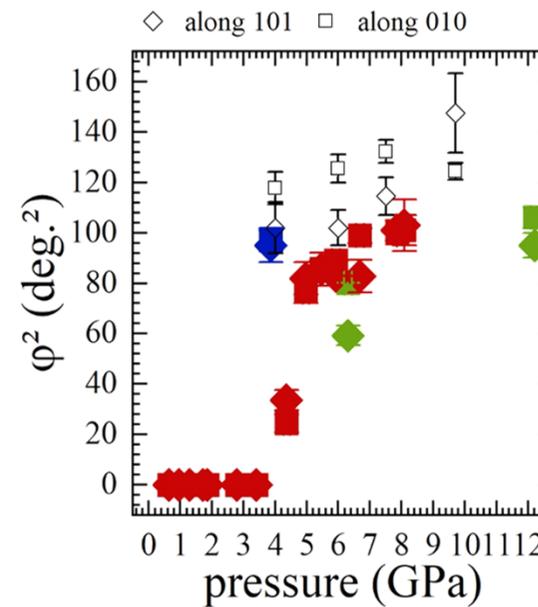
$$\vec{\delta}_A = \vec{r}_A - \frac{1}{12} \sum_{i=1}^{12} \vec{r}_{iO}$$

$x = \square 0 \quad \blacksquare 0.013 \quad \blacksquare 0.048 \quad \blacksquare 0.074$



squared octahedral tilt angle

$$\varphi^2 = \left(\frac{180 - \angle(B' - O - B'')}{2} \right)^2$$



$x = 0.048$
at 7.9 GPa

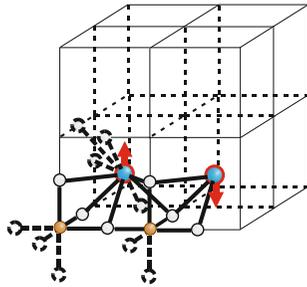
Rösche et al, *Sci. Rep.* 14, 18799 (2024), Rösche et al, *PRB* 112, 184102 (2025)

data on pure NBT: after Thomas et al., *Z. Kristall.* 220, 717 (2005)

HP Raman spectroscopy of NBT-xBT single crystals

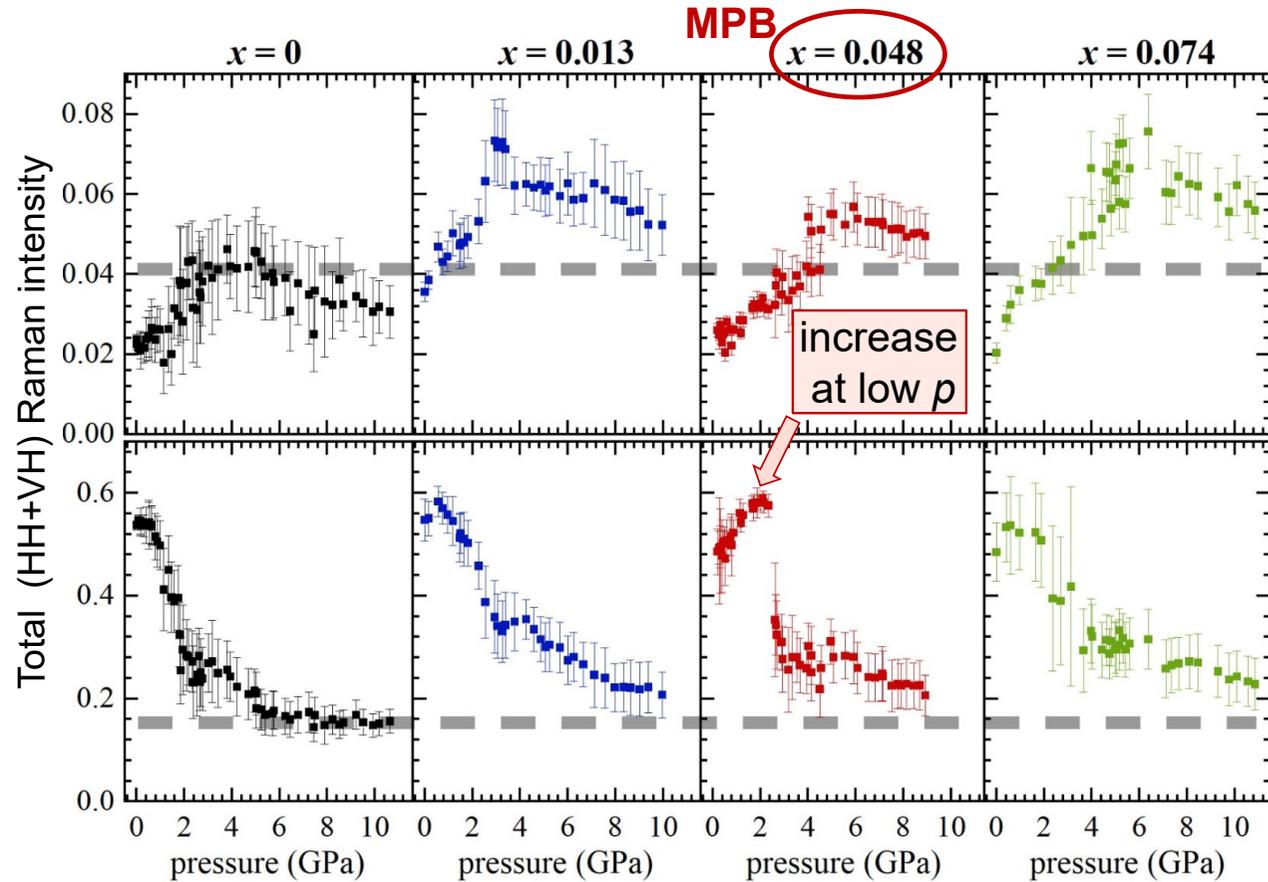
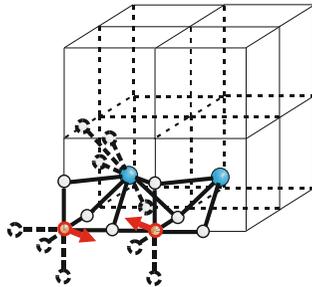
A-cation off-centering

~30-60 cm⁻¹



B-cation off-centering

~ 240-325 cm⁻¹



Ba²⁺: favours A-cation off-centering & hinders *p*-ind. reduction of B-cation off-centering

NBT-BT: atomic dynamics vs atomic statics

Grüneisen parameter:

$$\gamma_V = \frac{\beta_\omega}{\beta_V}$$

Phonon compressibility:

$$\beta_\omega = \frac{1}{\omega_0} \frac{d\omega}{dp}$$

Volume compressibility:

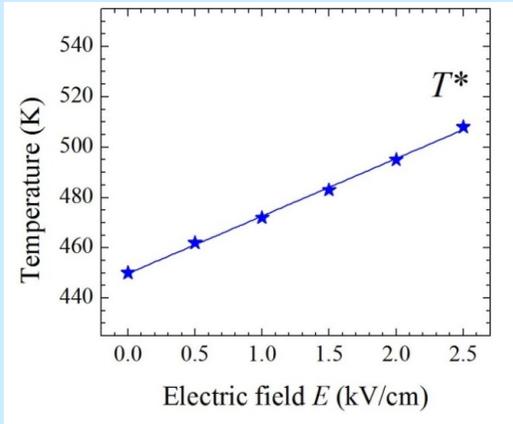
$$\beta_V = -\frac{1}{V_0} \frac{dV}{dp}$$

$x = 0$		$x = 0.013$		$x = 0.048$		$x = 0.074$		mode assignment
ω_0	γ_T	ω_0	γ_T	ω_0	γ_T	ω_0	γ_T	
47.6(4)	8.1(8)	52.1(1)	6.0(1.0)	46.0(1)	10.9(7)	46.4(2)	8.2(5)	A-cation localized mode
286.1(1)	-2.5(5)	283.5(1)	-2.4(3)	310.5(5)	-6.1(2)	324.3(3)	-3.2(1)	B-cation localized mode
788.1(1.3)	0.2(1)	763.9(2.2)	0.3(1)	777.3(1.3)	0.5(1)	781.7(2.2)	0.4(1)	internal BO ₆ stretching mode
861.7(7)	0.2(1)	855.1(1.0)	0.4(1)	859.9(7)	0.2(1)	861.7(1.0)	0.3(1)	internal BO ₆ stretching mode

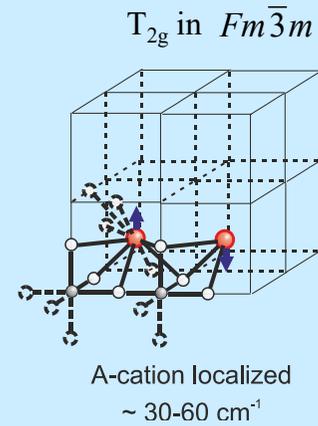
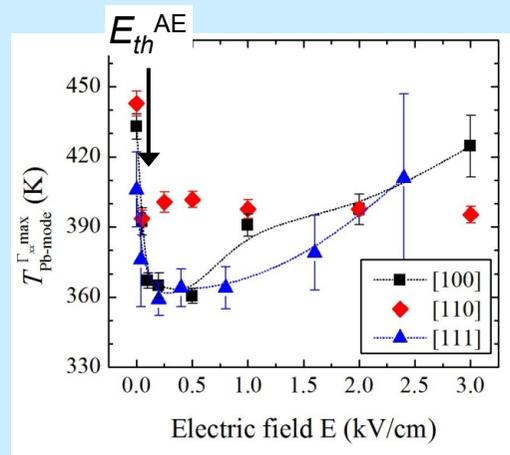
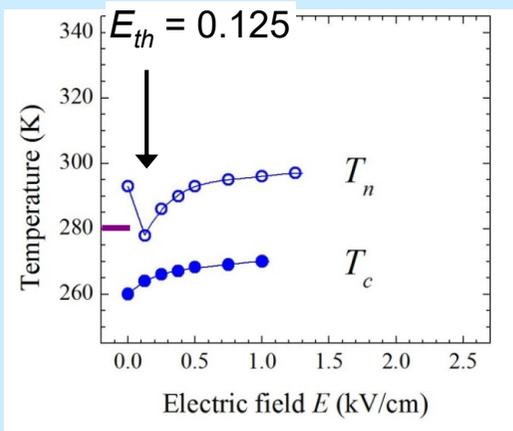
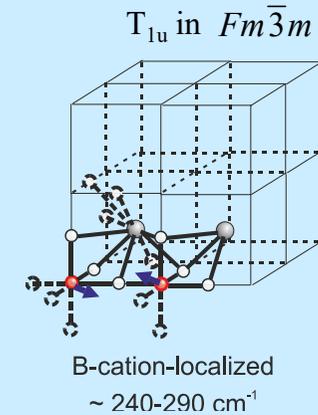
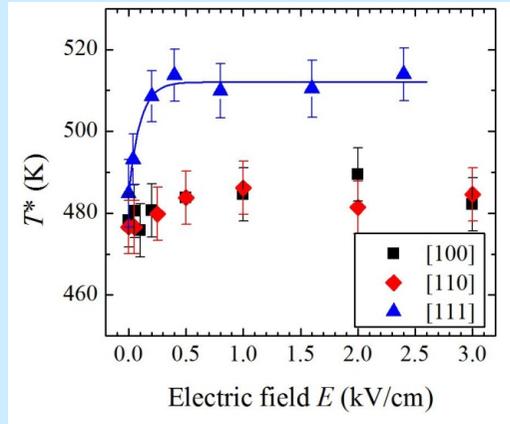
- atomic dynamics of off-centred A-cations are atomistic driving force for the phase transition
- **elastic response (particularly for B-cations) is highest at MPB**

Raman and AE under electric field (locally, coexisting FE & AFE)

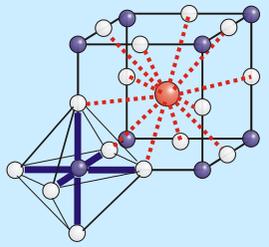
Acoustic emission



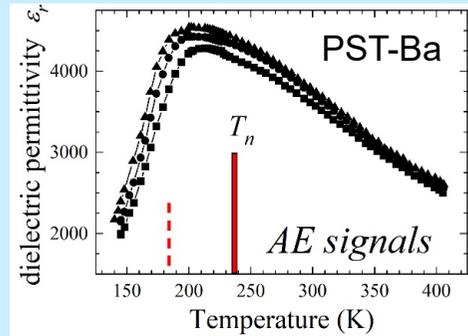
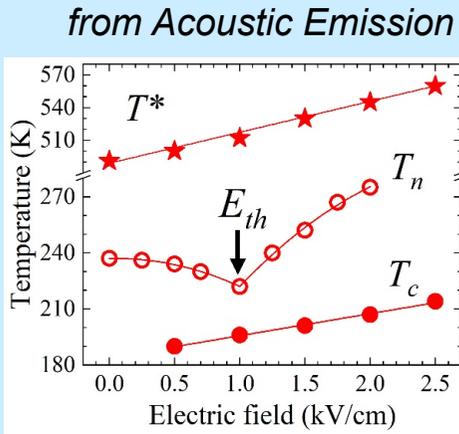
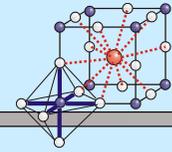
Raman spectroscopy (via $\Gamma_{\max}(T)$)



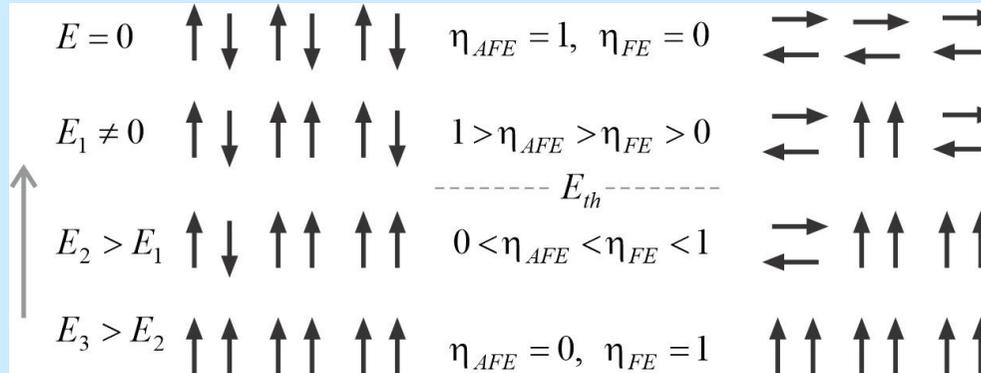
Coexistence of FE (B-site) and AFE(A-site) order on the mesoscopic scale



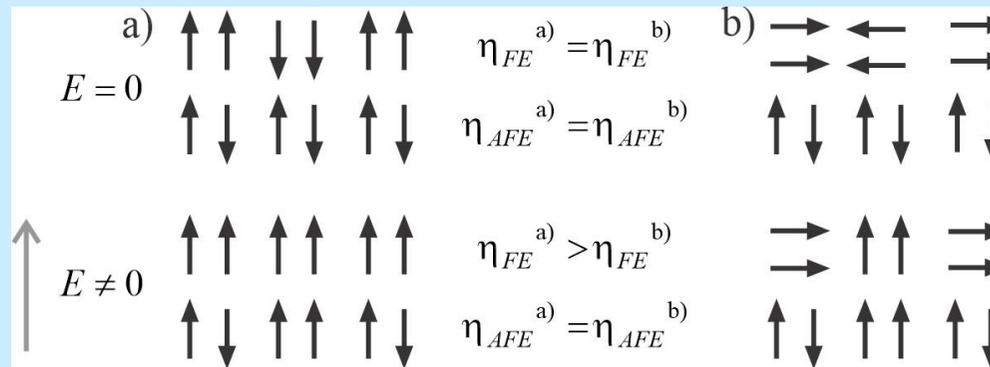
Coexisting competing order parameters



AFE system under E



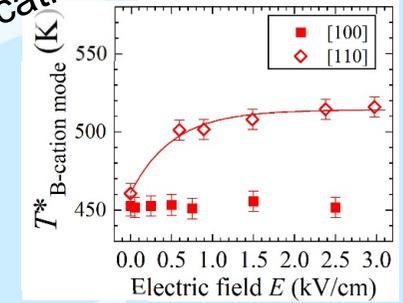
FE & AFE subsystems under E



(anisotropy in E_{th})

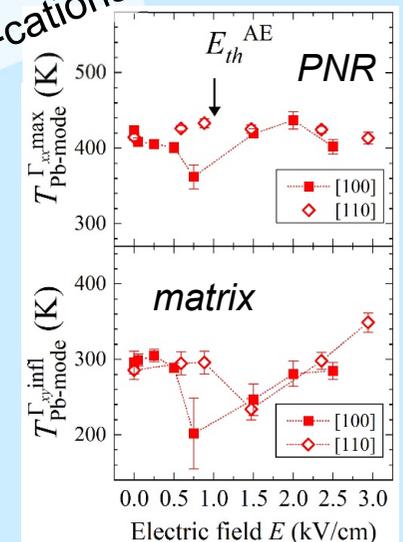
B-cations

from Raman



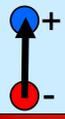
ferro

A-cations



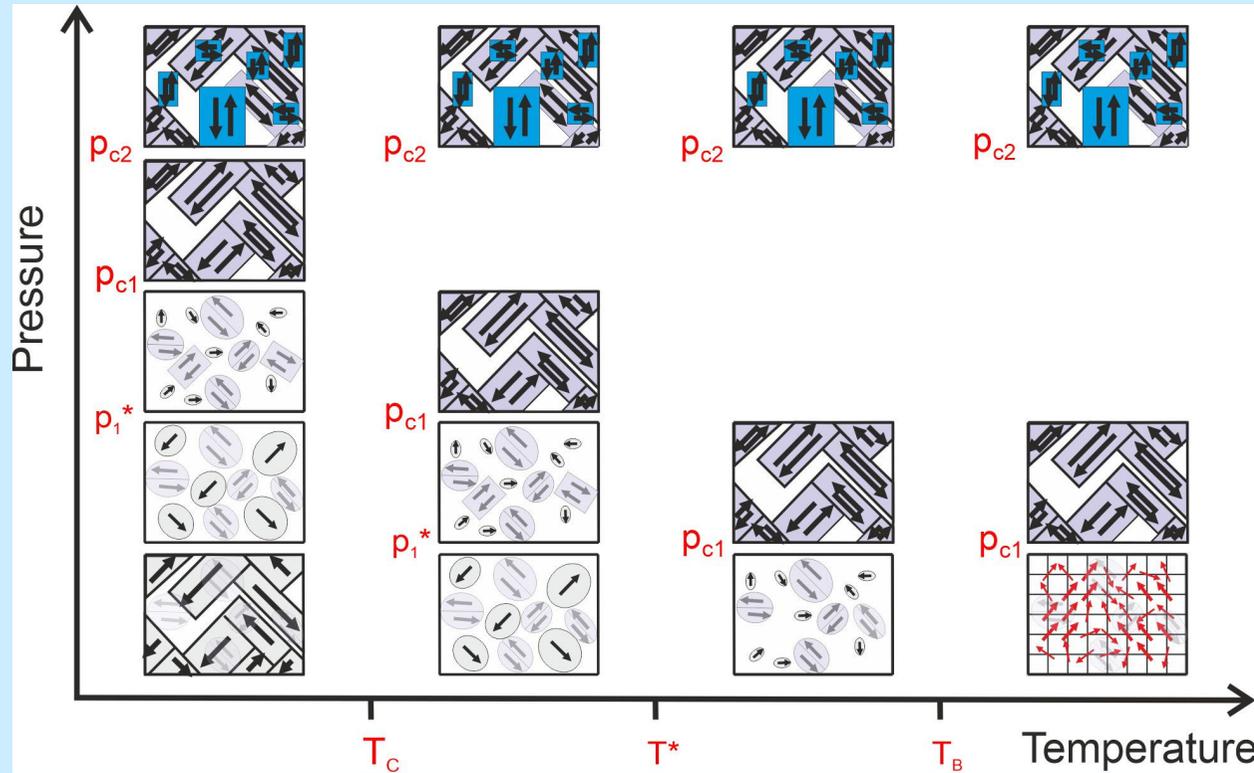
anti-ferro

local dipoles couple in different directions



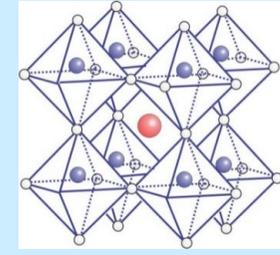
p-T diagram of Pb-based relaxors with ABO_3 structure

Based on complementary single-crystal XRD and Raman scattering:

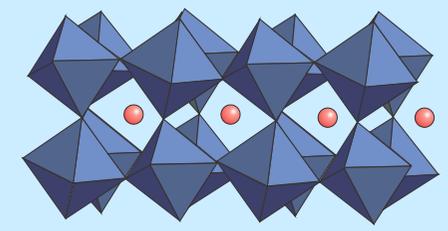


Relaxors: frustrated ferrielectrics!

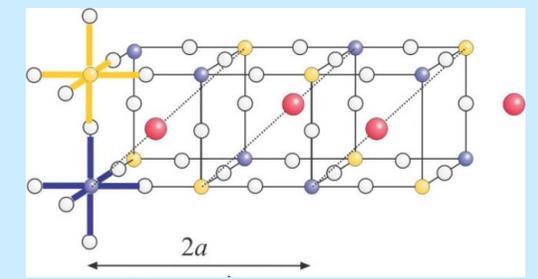
Prevailing FE or AFE/AFD
→ depending on p, T, x



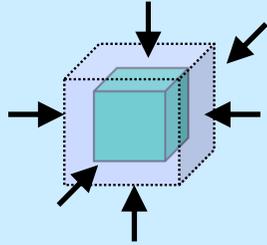
B-site dipoles: **FE** order



BO_6 tilts: anti-ferrodistortive (**AFD**)



A-site dipoles: **AFE** order



compressibility: $\beta_{ij} = -\frac{S_{ij}}{dp}$ (2nd order *matter tensor*)

$$\begin{pmatrix} \beta_{11} & \beta_{12} & \beta_{13} \\ \beta_{12} & \beta_{22} & \beta_{23} \\ \beta_{13} & \beta_{23} & \beta_{33} \end{pmatrix}$$

(elastic compliances under hydrostatic pressure: $S_{ij} = -s_{ijkl}\delta_{kl}dp$)

volume compressibility: $\beta = -\frac{1}{V} \frac{dV}{dp}$

Bulk modulus: $K = -V \frac{dp}{dV}$

Equation of state (EoS): $V = f(p, T)$

e.g. ideal gas: $pV = nRT$

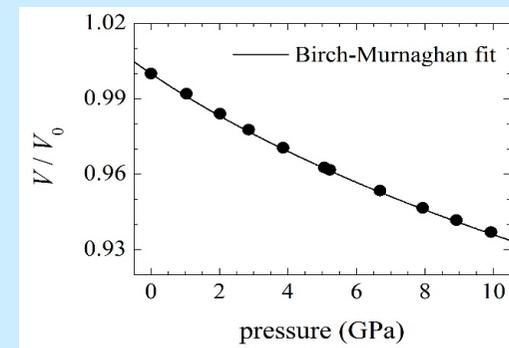
Isothermal EoS: $V = f(p)$

solids: many approximations

Birch-Murnaghan, via the **Eulerian strain** $f = [(V_0/V)^{2/3} - 1]/2$
 3rd-order: (with respect to the strained state)

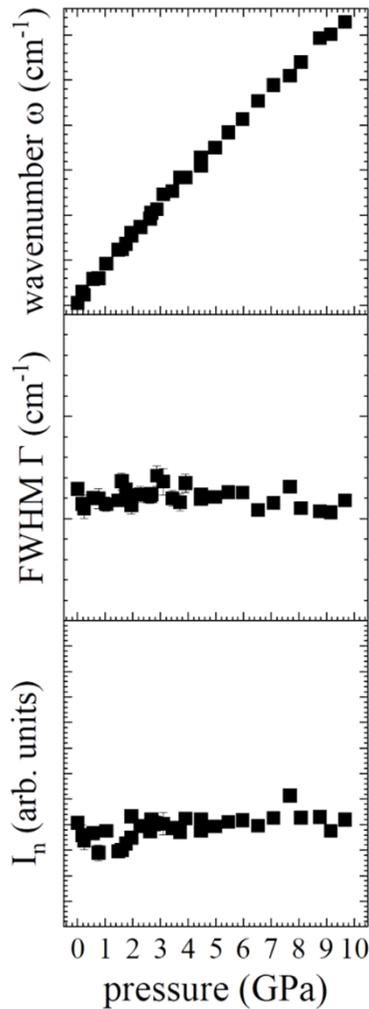
$$p(V) = \frac{3K_0}{2} \left[\left(\frac{V_0}{V} \right)^{7/3} - \left(\frac{V_0}{V} \right)^{5/3} \right] \left\{ 1 + \frac{3}{4} (K'_0 - 4) \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right] \right\}$$

$$K_0 = -V \left(\frac{\partial p}{\partial V} \right)_{p=0} \quad K'_0 = \left(\frac{\partial K}{\partial V} \right)_{p=0}$$



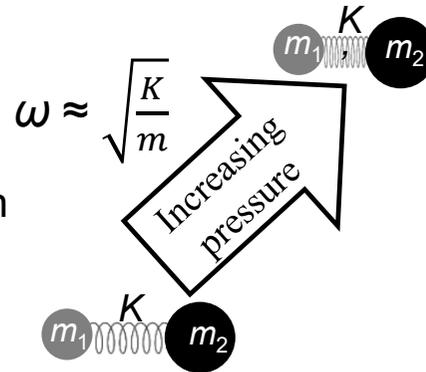
Welsh et al, PRB **80**, 104118 (2009)

What can we learn from high-pressure Raman spectroscopy?



Wavenumber ω

- energy level of phonon mode

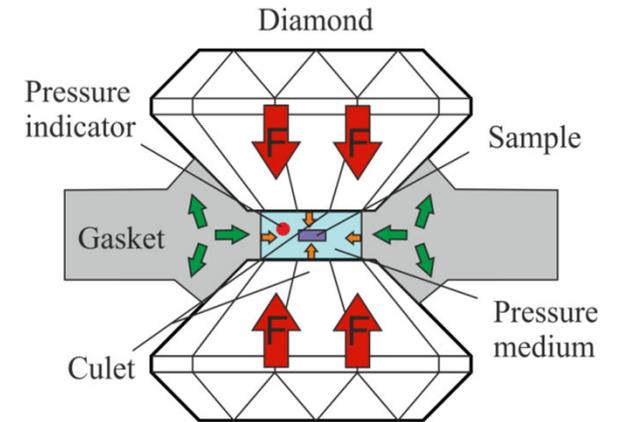


Full width at half maximum Γ

- lifetime of harmonic oscillation
- local structural disorder

Fractional intensity I_n

- $I_n(i) = \frac{I(i)}{\sum_i I(i)}$
- number of structural species
- probability of the event

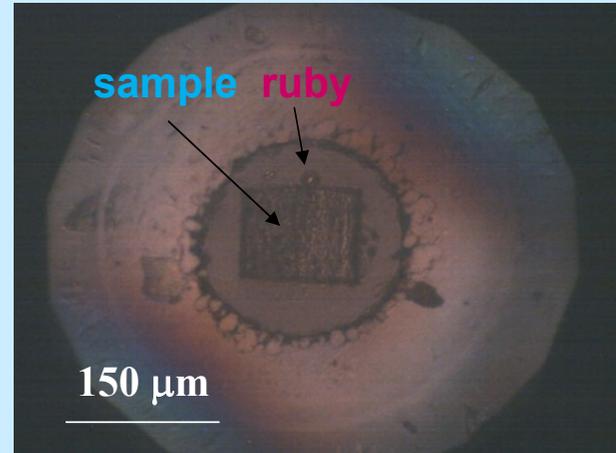
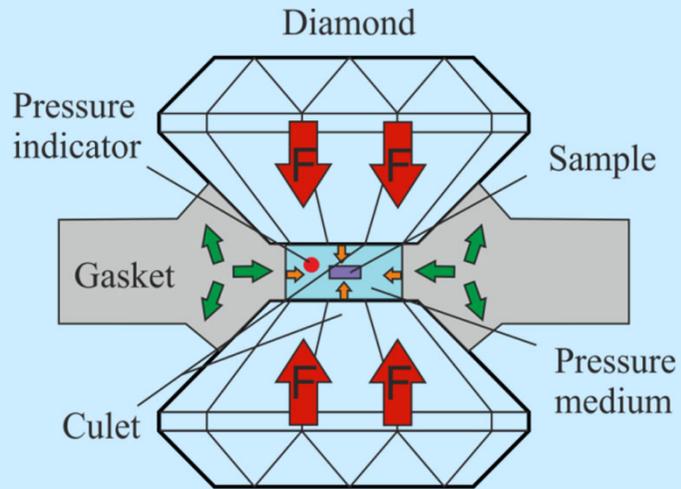


Deviation from trivial $\omega(p)/\Gamma(p)/I_n(p)$ trends

↔

Structural transformation

HP experiments with a Diamond Anvil Cell (DAC)

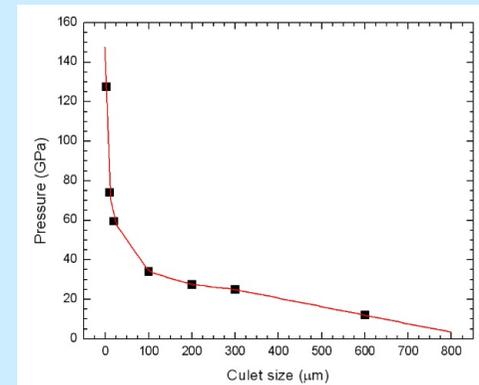


Waesermann, PhD thesis 2012

$$\begin{pmatrix} T & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \xrightarrow[\text{fluid, no shear strain}]{p\text{-transmitting medium}} \begin{pmatrix} -T & 0 & 0 \\ 0 & -T & 0 \\ 0 & 0 & -T \end{pmatrix}$$

- small culet size ($\sim 500 \mu\text{m}$) ensures pressures $\sim 50 \text{ GPa}$;
the exact correlation depends also on the DAC design

$$p_{\text{max}} (\text{GPa}) \approx 12.5/d_{\text{culet}}^2 (\text{mm}^2)$$

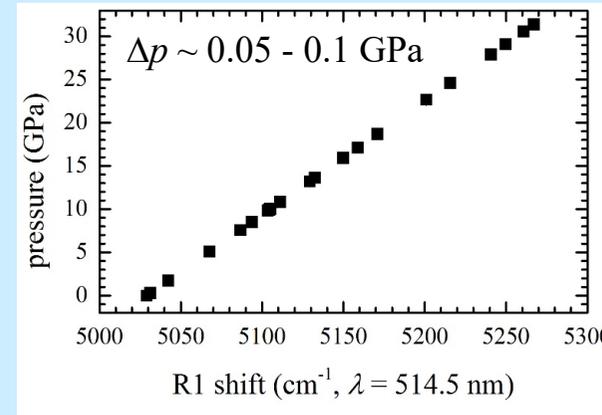


Weslich, PhD thesis 2009

DAC: “pressure-meters”

- Optical markers:
ruby ($\text{Al}_2\text{O}_3:\text{Cr}^{3+}$) calibration

e.g.
$$p = A\left(\frac{\Delta\lambda}{\lambda}\right) + B\left(\frac{\Delta\lambda}{\lambda}\right)^2$$



Calibration methods:

- absolute p measurement via the free-piston gauge
 (also against critical pressures determined like that) $p = \frac{F}{A}$ ($< \sim 3$ GPa)

- thermodynamic relations between physical properties

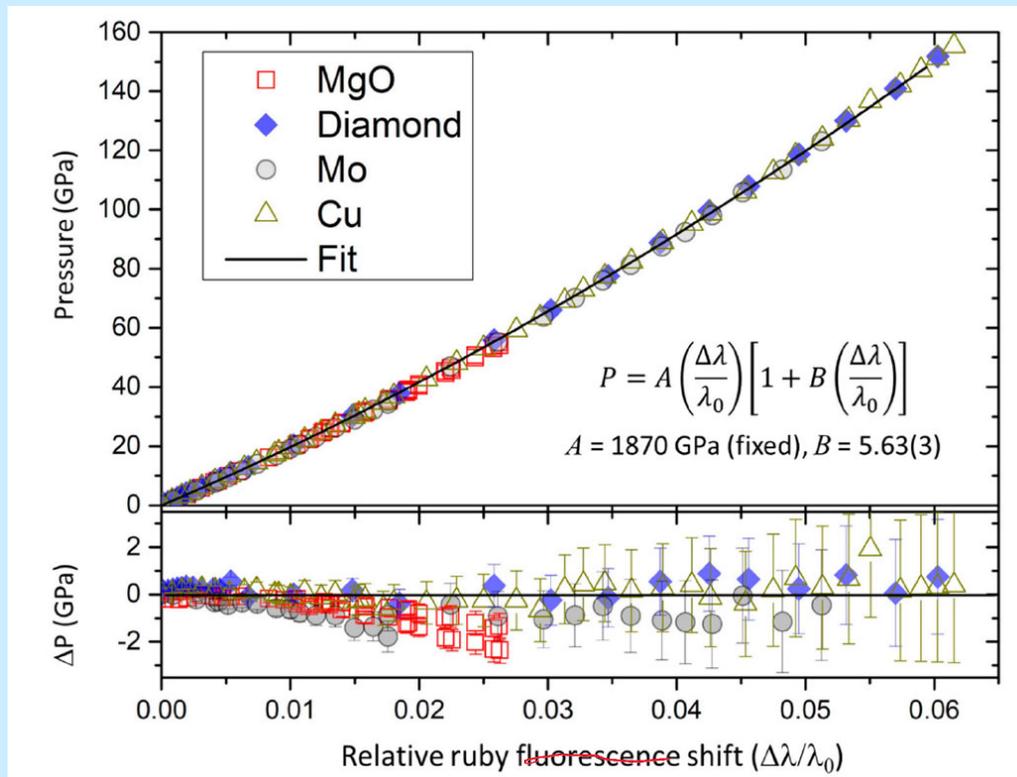
$$K_T = -V\left(\frac{\partial p}{\partial V}\right)_T = K_S / (1 + \alpha^2 V K_S T / C_p)$$

Zha et al., PNAS, 97, 13494 (2000):
 XRD and Brill. Sp. of MgO: **R1(p) up to 55 GPa**

- EoSs from shock-wave-reduced isotherms (conditions close to those in DAC)
- extrapolation of EoSs

DAC: “pressure-meters”

The currently recommended $p(R1)$ calibration: by Shen et al, High pressure Research, 2020, 40, 299-314 up to 150 GPa at RT, using representative EoS data for ionic, covalent, and metallic materials, (EoS: V/V_0 is measured, then theoretical model for p vs V/V_0 is applied)



luminescence

The error in pressure depends on:

- Errors in the coefficients of the $p(R1)$ relations
- Experimental accuracy in $R1$ position
- Quality of the ruby crystals used

Recommended:

- a level of 0.3%-Cr doping;
- annealed spheres to release internal strain

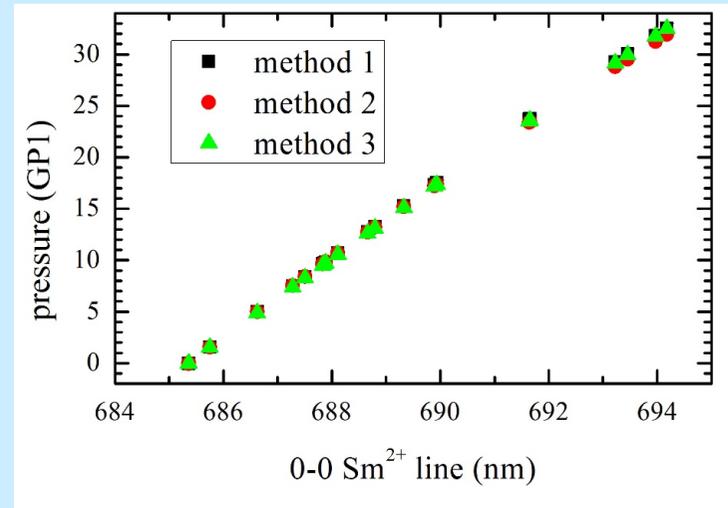
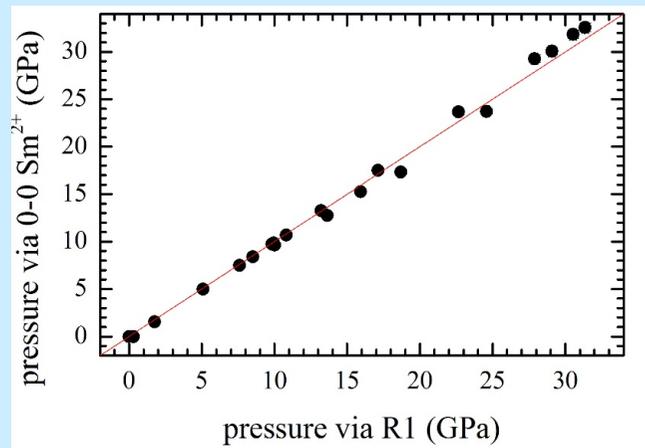
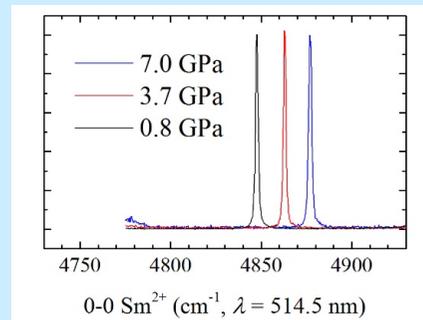
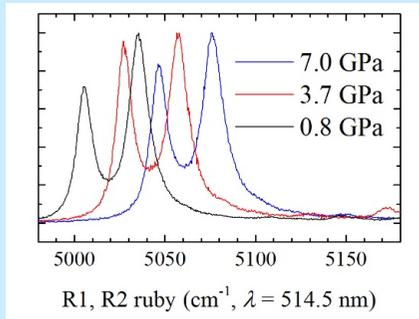
DAC: “pressure-meters”

- Optical markers at HT and HP:

ruby calibration, disadvantages: strong T dependence

SrB₄O₇:Sm²⁺ calibration, advantage: negligible T dependence

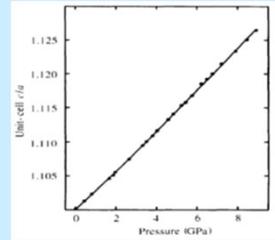
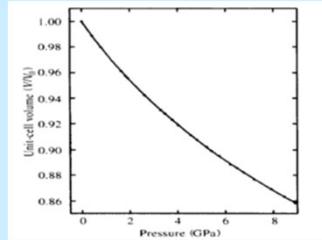
Datchi et al. *J. Appl. Phys.* **81**, 333 (1997)



DAC: “pressure-meters”

- EoS via XRD of quartz (slow but more precise $\Delta p \sim 0.01$ GPa)

calibration via $V(p)$ of CaF_2

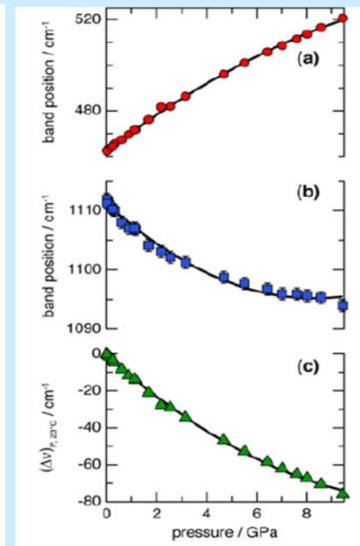
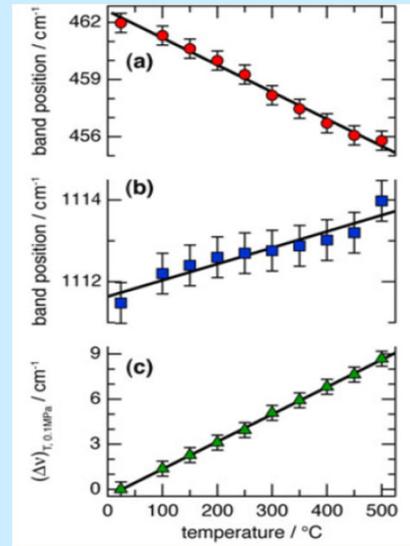
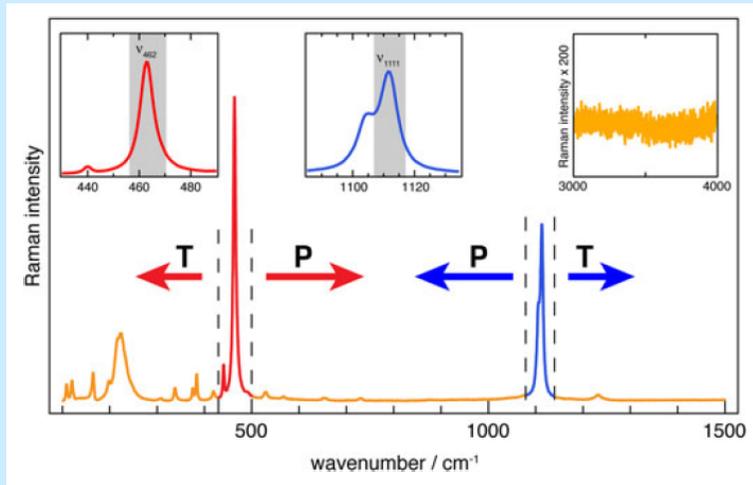


Angel et al,
J. Appl. Cryst. **30**, 461 (1997)

- Raman pressure sensor: quartz (SiO_2), berlinite (AlPO_4), zircon (ZrSiO_4)

Alignment of the spectrometer is not so critical if $\omega_1 - \omega_2$ is considered

berlinite

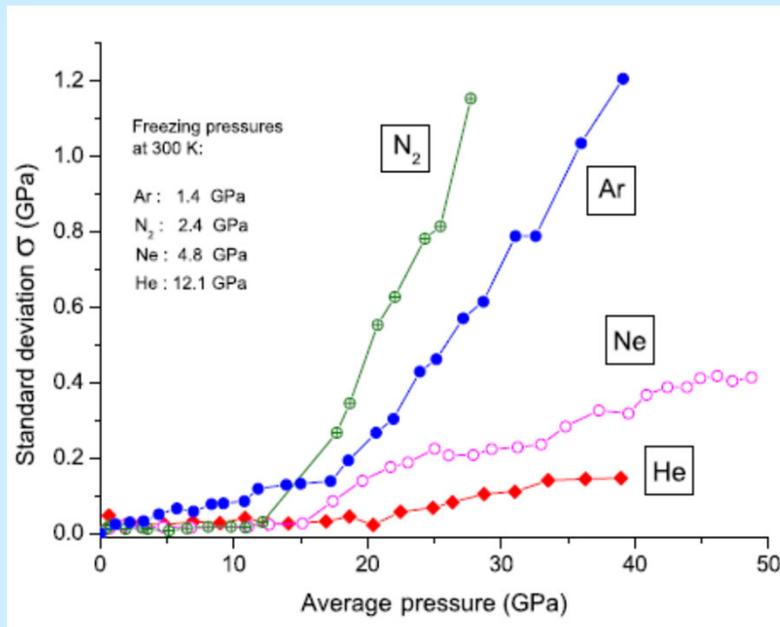


Watenphul & Schmidt, *J. Raman Spectr.* **43**, 564 (2012)



DAC: pressure-transmitting medium

- **alcohol mixtures:** Methanol : Ethanol = 4 : 1 ($p_{\max} = 9.8$ GPa)
Me : Et : H₂O = 16 : 3 : 1 ($p_{\max} = 10.5$ GPa)
- **gases:** Ar, N₂, Ne, He, H₂ (best for VHP but can damage the anvils)



Klotz et al., *J. Phys. D: Appl. Phys.* **42**, 075413 (2009)

Medium	Hydrostatic limit (GPa)
4:1 Methanol-ethanol	9.8
Anhydrous 2-propanol	4.2
Argon	1.9
Nitrogen	3.0
Glycerol	1.4
Silicone oil, viscosity 0.65 cSt	0.9
Silicone oil, viscosity 37 cSt	0.9

Angel et al., *J. Appl. Cryst.* **40**, 26 (2007)

- **alkali halides** (pseudo-hydrostatic): NaCl, KCl, KBr, CsI (appropriate for HT-HP experiments with external heater)