Structure-Property Relationships in the Relaxor Ferroelectric $Na_{1/2}Bi_{1/2}TiO_3$

Melanie Gröting, Karsten Albe

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FACHGEBIET MATERIALMODELLIERUNG

International Symposium on Electrical Fatigue in Functional Materials SFB 595
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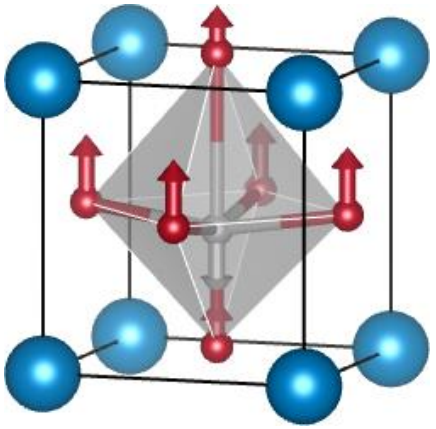

Motivation: Understanding the complexity of $Na_{1/2}Bi_{1/2}TiO_3$ (NBT)

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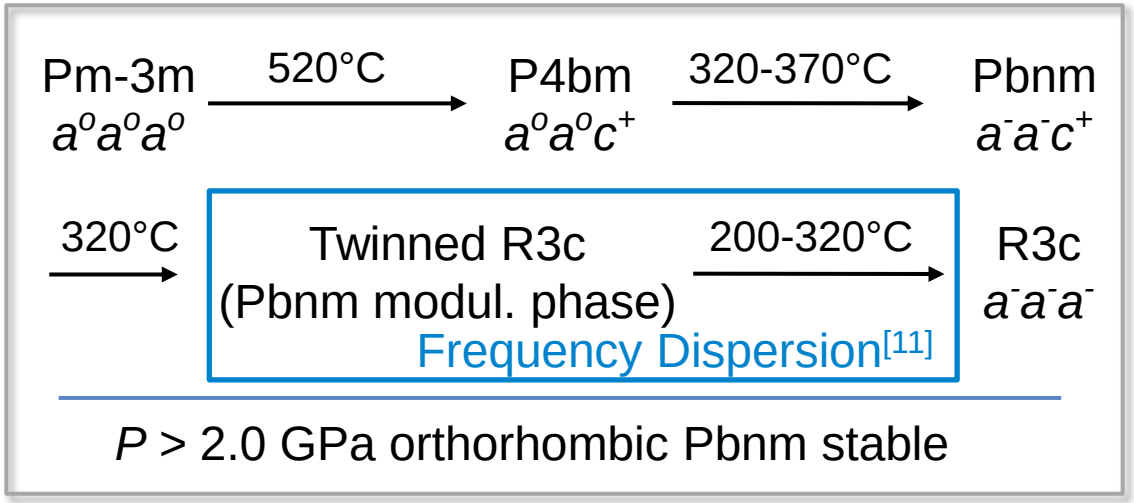
Temperature[1-4]



Deviations from R3c

Strong Diffuse Scattering: ‹100›-like planar defects and modulation (length ~ 40 Å)[5,7,8]

Monoclinic deviation from R3c in single crystals[9] and ceramics[10], *Cc*-phase

[1] G.O. Jones, *Acta. Cryst. B* 58 (2002) 168.
[2] V. Dorcet, Chem. Mater. 20 (2008) 5061.
[3] G. Trolliard, Chem. Mater. 20 (2008) 5074.
[4] V. Dorcet, *J. Magn. Magn. Mat* 321 (2009) 1758.
[5] J. Kreisel, *Phys. Rev. B* 68 (2003) 014113.
[6] P. A. Thomas, *Z. Kristallographie 220* (2005) 545.
[7] P. A. Thomas, *Solid State Sci.* 12 (2010) 311.
[8] J. E. Daniels, Appl. Phys. Lett. 98 (2011) 252904.
[9] S. Gorfman, *J. Appl. Cryst.* 43 (2010) 1409.
[10] E. Aksel, *Appl. Phys. Lett*. 98 (2011) 152901.
[11] Y. Hiruma, *J. Appl. Phys.* 105 (2009) 08411.

Flexibility of the perovskite structure

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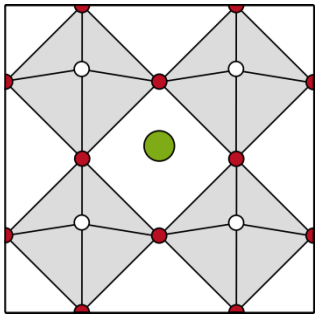
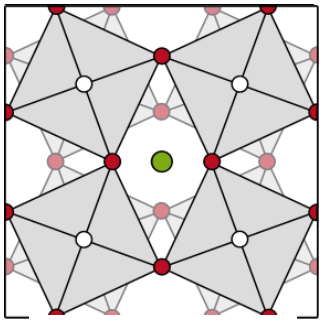
Polarisation

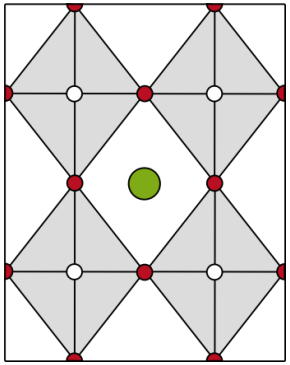


Octahedral Tilt

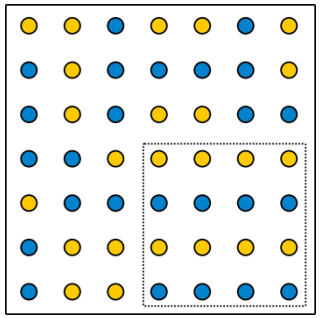


anti-phase

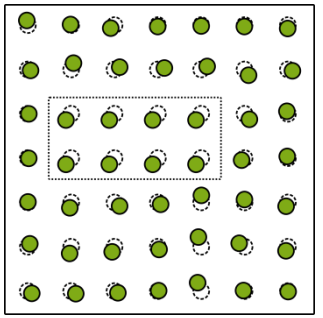
Lattice Strain



Chemical Order



Displacive Order



Cooperation, Competition

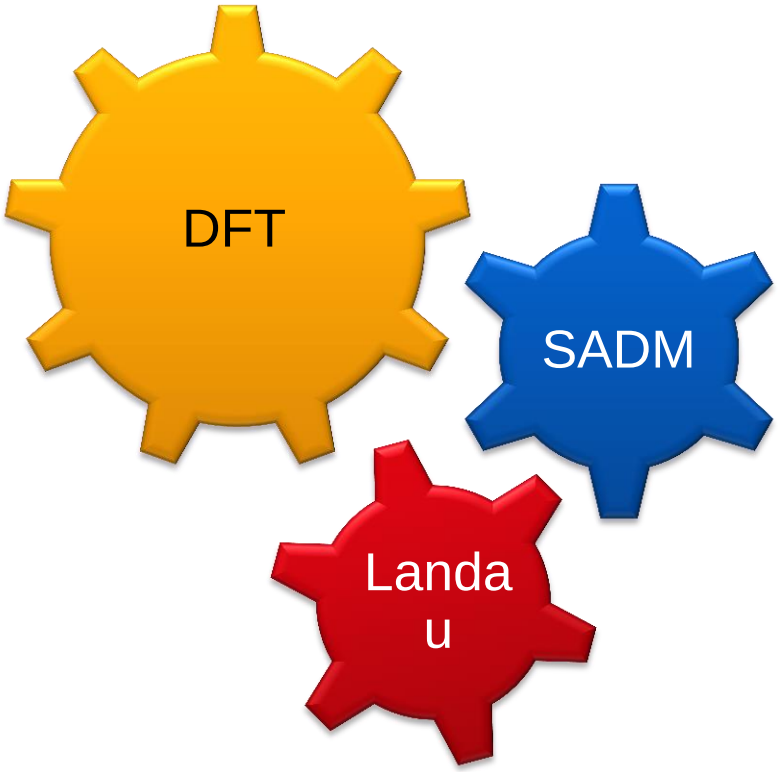
Coupling

Structure-Property-Relationships in $Na_{1/2}Bi_{1/2}TiO_3$

global structure

local structure

Methods



Density functional theory

Quantum mechanics

Optimized crystal structures and relative stabilities

Symmetry-adapted distortion modes

Group theory

Relevant distortion modes and order parameters

Landau theory

Phenomenological theory

Properties depending on order parameters, order parameter coupling

Questions

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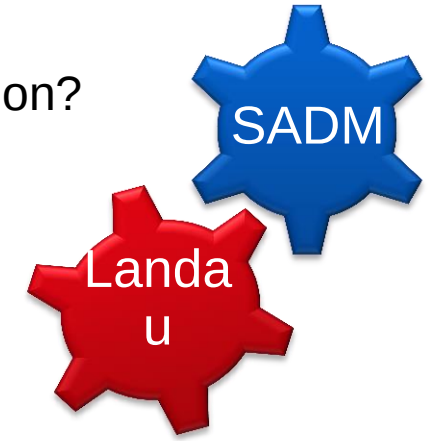
Phase stability and its order/pressure dependence

- Which phases are stable?
- Is phase coexistence possible?
- Consequences?

Structure-property relationships

- Influence of chemical order and octahedral tilts on polarisation?
- Consequences?



Pressure dependence of phase stability

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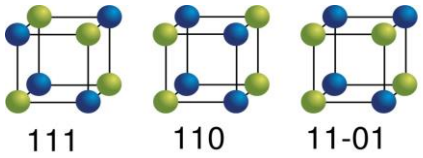
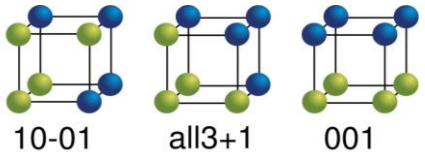
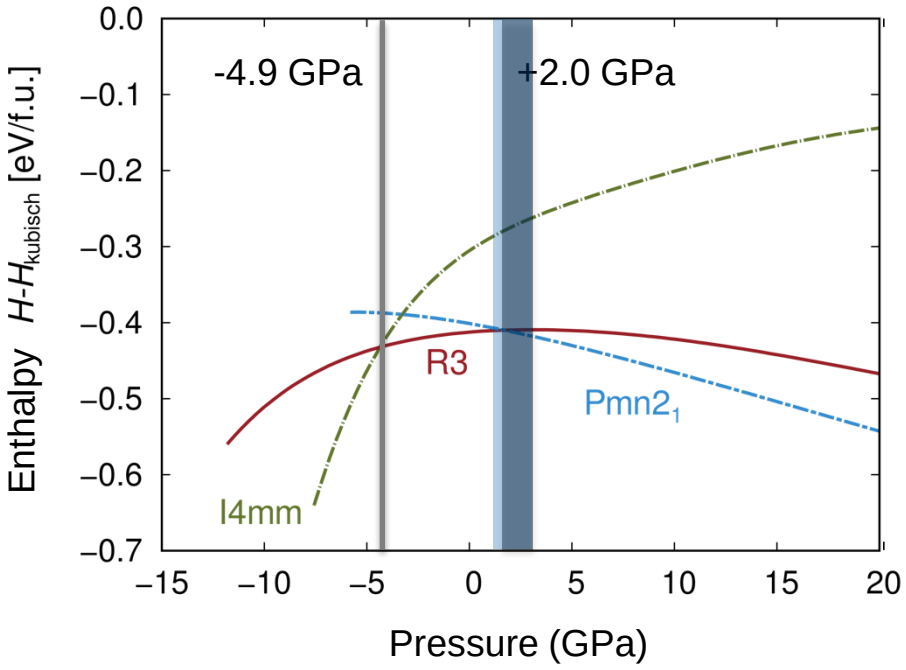
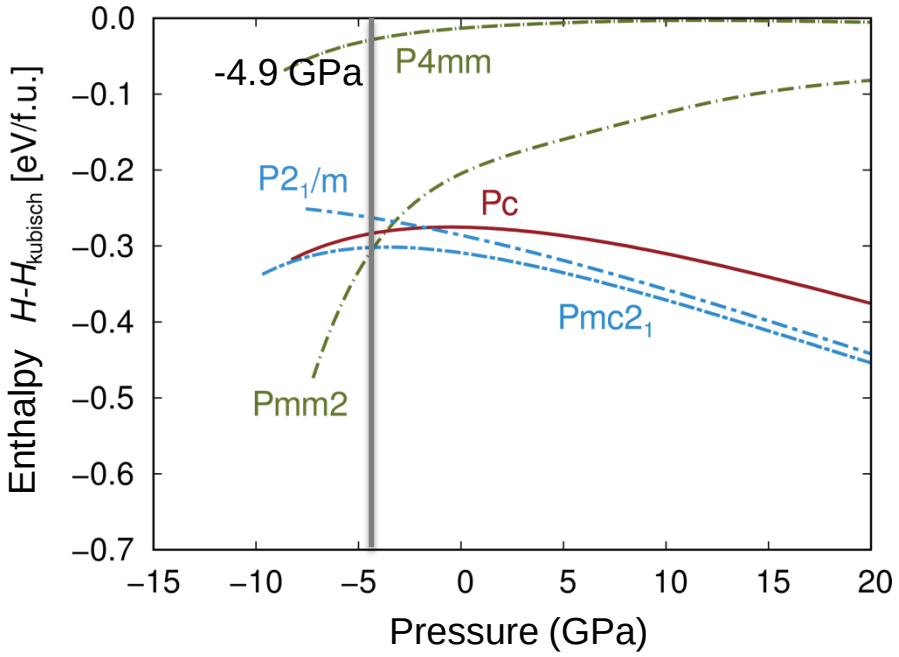
Phase diagrams

representative for:





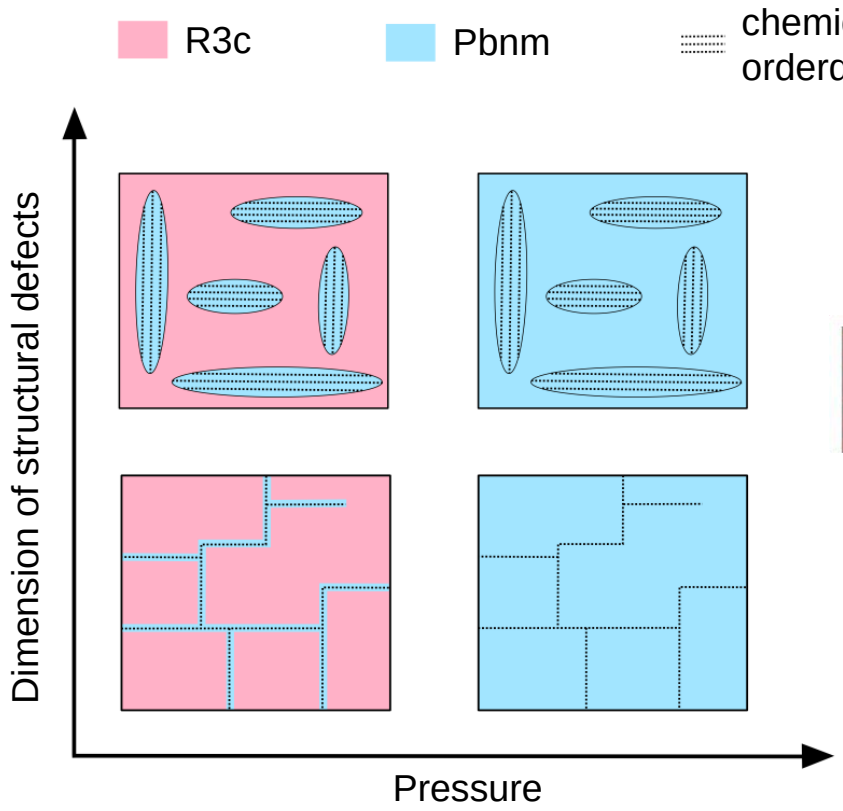


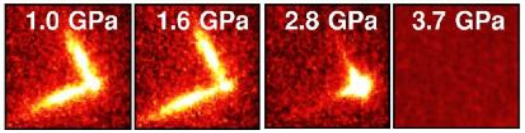


experiment: 1.6-3.3 GPa[1,2]

[1] J. Kreisel et al., *Phys. Rev. B* 68 (2003) 014
[2] P. A. Thomas et al., *Z. Kristallographie 220*

Structure models





above 2 GPa pure Pbnm phase
local and global structure become equal

Phase coexistence at atmospheric pressure (R3c+Pbnm)
Chemically ordered Pbnm-regions cause deviations of local structure from global structure

J. Kreisel et al., *Phys. Rev. B* 68 (2003) 014113.

M. Gröting, *Phys. Rev. B.* 86, **2012**, 134118.

Polar displacements influenced by octahedral tilt and chemical order?

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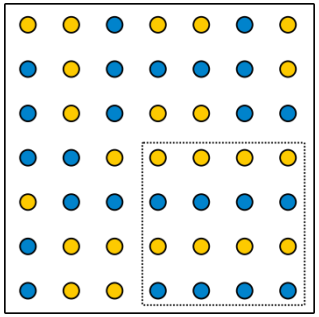
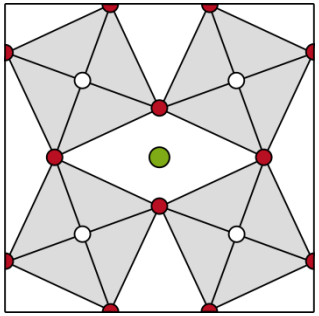
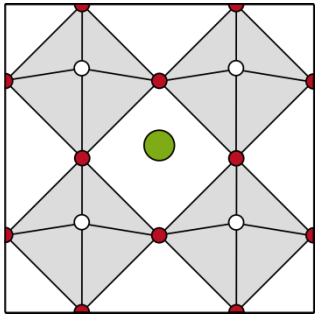
Chemical Order



Octahedral Tilt



Polarisation



Polar mode in R3c structure

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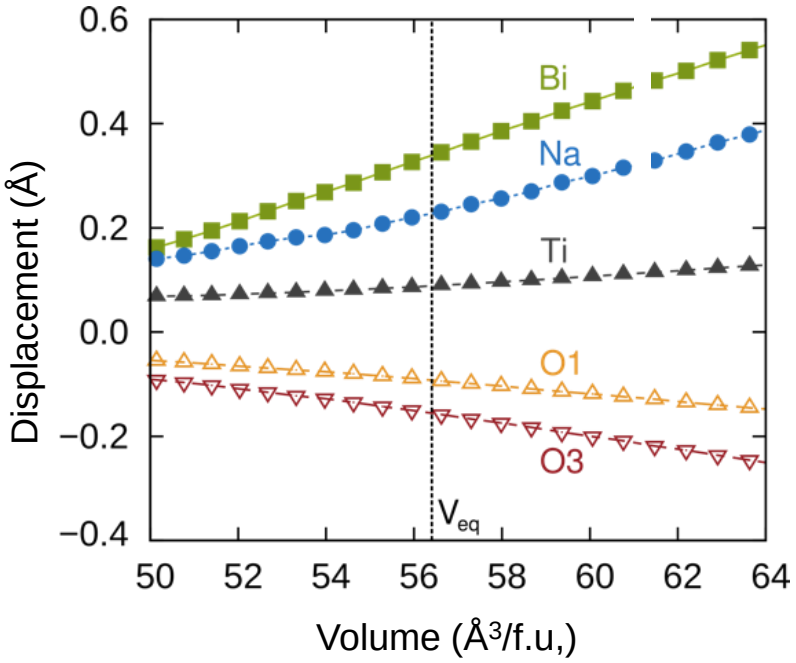
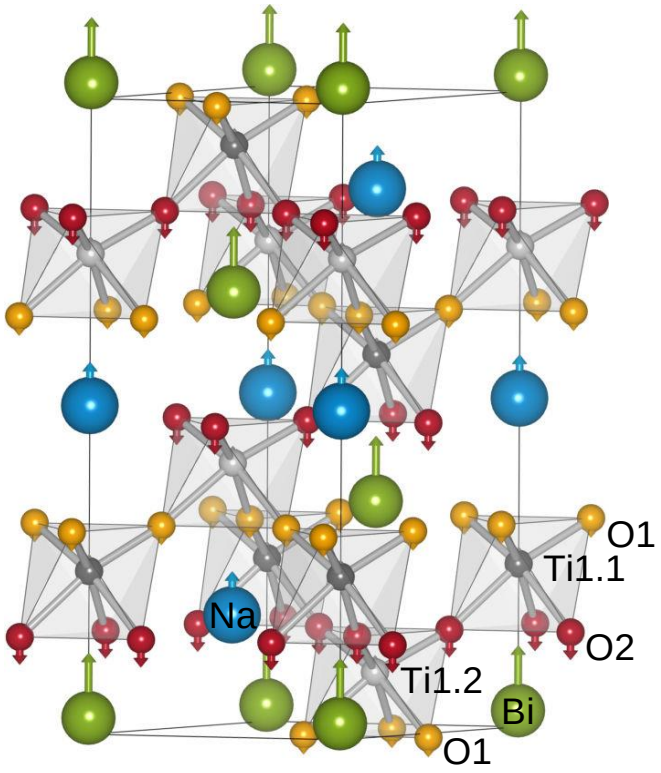
Atomic displacements





polarisation in rhombohedral direction $[111]_{pc}$

Polar mode in Pbnm structure

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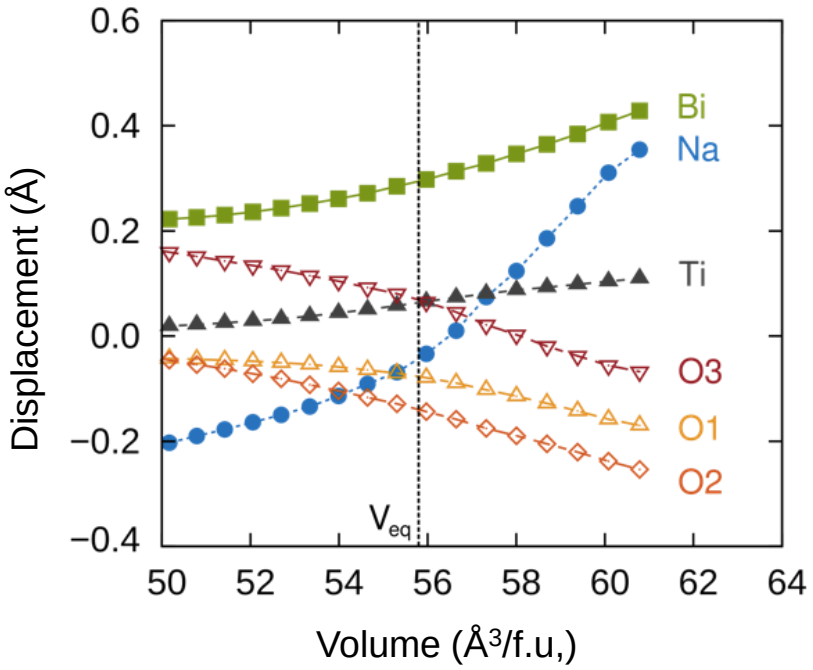
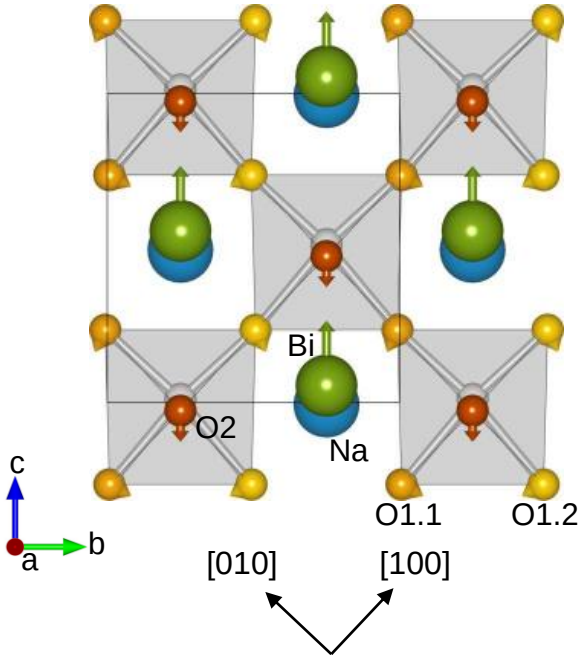
Atomic displacements

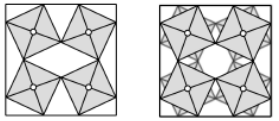




polarisation in orthorhombic direction $[110]_{pc}$

Induced polarisation in 001-ordered Pbnm-structure

$$E = E(P) + E(\phi) + E(\theta) + E(P,\phi) + E(P,\theta) + E(\phi,\theta) + E(P,\phi,\theta)$$

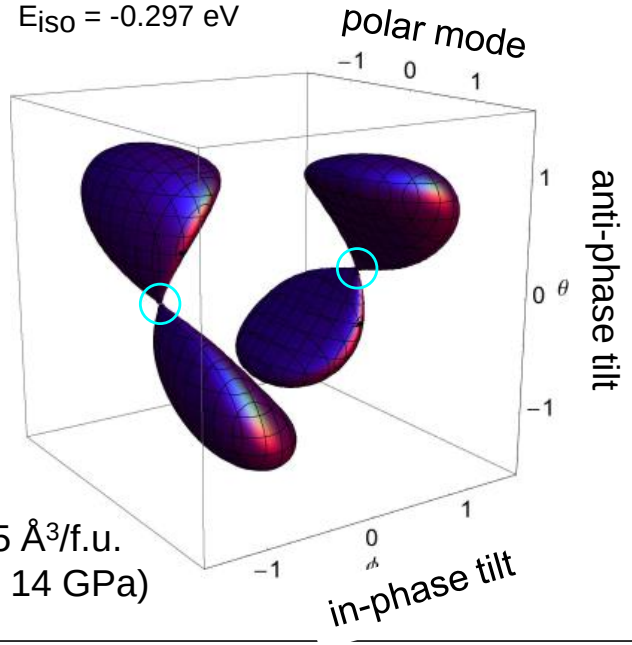


common even terms

$$E(P,f,q) = d_{111}Pf\,q + e_{311}P^3f\,q + e_{131}Pf^3q + e_{113}Pf\,q^3 + c_{222}P^2f^2q^2$$

odd terms can soften otherwise hard modes

E_{iso} = -0.297 eV



52.5 Å^3/f.u.
(ca. 14 GPa)

At small volumes polarisation is induced

High-pressure phase might be improper ferroelectric instead of antiferroelectric

Answers

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Phase stability and its pressure dependence

- Which phases are stable? **P4mm, R3c/Pbnm, Pbnm**
- Is phase coexistence possible? **R3c/Pbnm coexistence**
- Consequences? **tilt and displacive order/disorder**

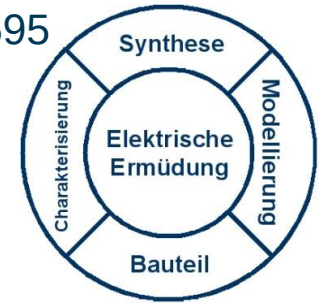
Structure-property relationships

- Influence of chemical order and octahedral tilts on polarisation? **strong**
- Consequences? **polar disorder**
  improper FE in ordered regions

Acknowledgment

Financial support from

SFB 595



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