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Ab-initio calculations of the relaxor ferroelectric $Na_{1/2}Bi_{1/2}TiO_3$ and its solid solutions

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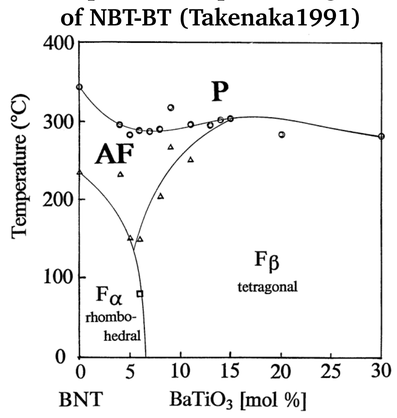
Project C1

Motivation

$Na_{1/2}Bi_{1/2}TiO_3$ (NBT) and its solid solutions with other lead-free perovskite materials have attracted significant interest for applications in actuators, sensors, and transducers due to their excellent piezoelectric properties. Pure $Na_{1/2}Bi_{1/2}TiO_3$ exhibits large remanent polarization of $P_r = 38\ \mu C/cm^2$ (single crystal, Jaffe1971) and a relatively high piezoelectric constant $d_{33} = 72.9$ pC/N (ceramics, Hiruma2009). However, the material is difficult to pole due to the high coercive field of 73 kV/cm (single crystal, Jaffe1971) and electrical conductivity due to the presence of point defects (Hiruma2009, Nagata2008). These shortcomings can be avoided by alloying $Na_{1/2}Bi_{1/2}TiO_3$ with other perovskites. For several of these systems morphotropic phase boundaries (MPBs) similar to the one found in $PbZr_xTi_{(1-x)}O_3$ (PZT) are reported.

There is a long-standing interest in finding design rules for ferroelectric MPB materials. Most of the existing studies focused on lead-based materials; only few attempts were undertaken to predict MPBs in lead-free materials (Lee2009, Miura2010).

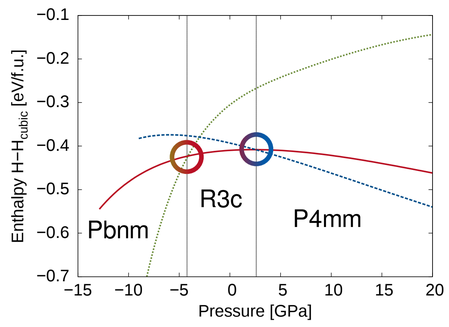
Experimental phase diagram of NBT-BT (Takenaka1991)



To summarize, it is highly desirable to predict promising MPB materials from *ab initio* calculations.

Method

Determination of transition pressures

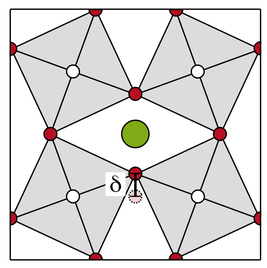


Phase diagram of pure NBT: two phase transitions
Alloying with other lead-free perovskites shifts transition pressures to lower or higher values

Solid solutions investigated

NBT-CT = $Na_{1/2}Bi_{1/2}TiO_3$ - $CaTiO_3$
NBT-BT = $Na_{1/2}Bi_{1/2}TiO_3$ - $BaTiO_3$
NBT-KBT = $Na_{1/2}Bi_{1/2}TiO_3$ - $Li_{1/2}Bi_{1/2}TiO_3$
NBT-LBT = $Na_{1/2}Bi_{1/2}TiO_3$ - $K_{1/2}Bi_{1/2}TiO_3$

Landau analysis of tilt oder parameter



Energy expansion:

$$E = E_0 + \frac{a}{2}\delta^2 + \frac{b}{4}\delta^4$$

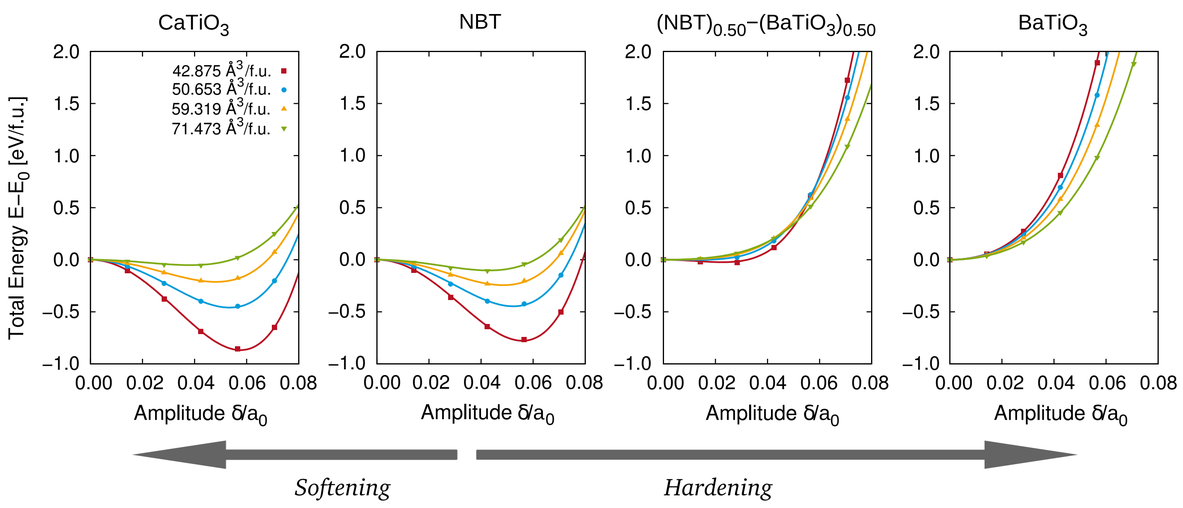
Alloying with cations of different sizes on the A-site (green) influences the tilt soft mode leading to softening or hardening as compared to pure NBT

Ionic radii

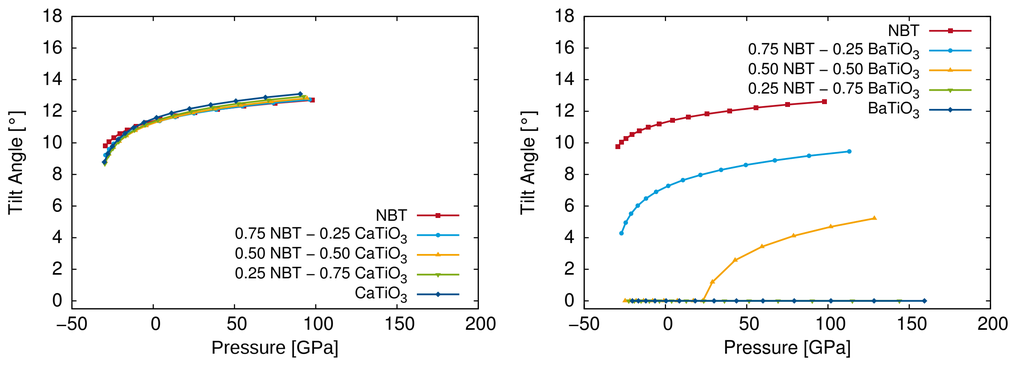
Bi^{3+}	1.45 Å	Ca^{2+}	1.34 Å	Li^+	1.25 Å
Na^+	1.39 Å	Ba^{2+}	1.61 Å	K^+	1.64 Å

Results

Stability of tilts in different perovskites



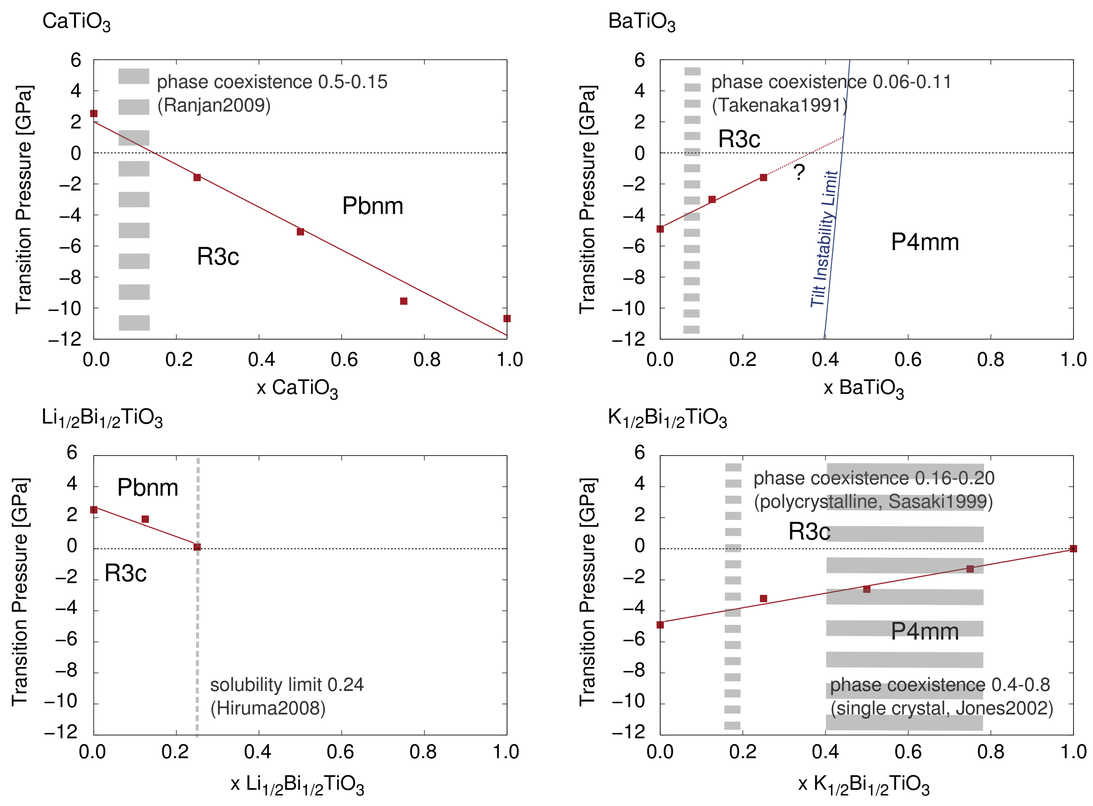
Tilt angles in NBT-CT and NBT-BT



NBT-CT
Tilts are not influenced by $CaTiO_3$ substitution

NBT-BT
Barium cations block tilts for $BaTiO_3$ contents higher than about 50%

Phase diagrams of solid solutions (comparison with experiment)



Smaller cations (Li^+, Ca^{2+}) shift phase transition Pbnm - R3c to ambient pressure.
Larger cations (K^+, Ba^{2+}) shift phase transition R3c - P4mm to ambient pressure.

Predicted data correspond to 0 Kelvin conditions, experimental data to room temperature.
The agreement with experimental data is better for the smaller cations. This is probably due to the neglect of phonon contributions, which are expected to have higher impact on the phase transition R3c - P4mm.

We developed a method based on *ab initio* calculations to predict compositions at morphotropic phase boundaries in lead-free perovskite solid solutions. This method utilizes the concept of flat free energy surfaces and involves the monitoring of pressure-induced phase transitions as a function of composition.

Publications last funding period

- M. Gröting, S. Hayn, K. Albe, "Comparative study of A-site order in the lead-free bismuth titanates $M_{1/2}Bi_{1/2}TiO_3$ (M=Li,Na,K,Rb,Cs,Ag,Tl) from first-principles", *J. Solid State Chem.* 184 (2011) 2041.
- M. Gröting, I. Kornev, B. Dkhil, K. Albe, "Theoretical prediction of morphotropic compositions in $Na_{1/2}Bi_{1/2}TiO_3$-based solid solutions from transition pressures", *Phys. Rev. B* 86 (2012) 134118.
- P. M. Diehm, P. Ágoston, K. Albe, "Size-Dependent Lattice Expansion in Nanoparticles: Reality or Anomaly?", *ChemPhysChem* 13 (2012) 2443-2454.
- S. Li, J. Morasch, A. Klein *et al.*,"Influence of orbital contributions to the valence band alignment of Bi_2O_3, Fe_2O_3, $BiFeO_3$, and $Bi_{0.5}Na_{0.5}TiO_3$", *Phys. Rev. B* 88 (2013) 045428.
- P. Erhart, P. Träskelin, K. Albe, "Formation and switching of defect-dipoles in acceptor-doped lead titanate: A kinetic model based on first-principles calculations", *Phys. Rev. B* 88 (2013) 024107.
- M. Gröting, K. Albe, "Pressure-induced phase transitions and structure of chemically ordered nano-regions in the lead-free relaxor ferroelectric $Na_{1/2}Bi_{1/2}TiO_3$", *Phys. Rev. B* 89 (2014) 054105.
- M. Gröting, K. Albe,"Chemical order and local structure of the lead-free relaxor ferroelectric $Na_{1/2}Bi_{1/2}TiO_3$", *J. Solid State Chem.* 213 (2014) 138-144.

5 key publications (2003-2014)

- H. Mestric, R. A. Eichel, T. Kloss *et al.*, "Iron-oxygen vacancy defect centers in $PbTiO_3$: Newman superposition model analysis and density functional calculations", *Phys. Rev. B* 71 (2005) 134109.
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- P. Erhart, K. Albe, "Modeling the electrical conductivity in $BaTiO_3$ on the basis of first-principles calculations", *J. Appl. Phys.* 104 (2008) 044315.
- So. Laubach, St. Laubach, P. C. Schmidt *et al.*, "Changes in the crystal and electronic structure of $LiCoO_2$ and $LiNiO_2$ upon Li intercalcation and de-intercalation", *Phys. Chem. Chem. Phys.* 11 (2009) 3278-3289.