Characterization of Structure-Property-Relationships of electrical Functional Materials with Solid State-NMR

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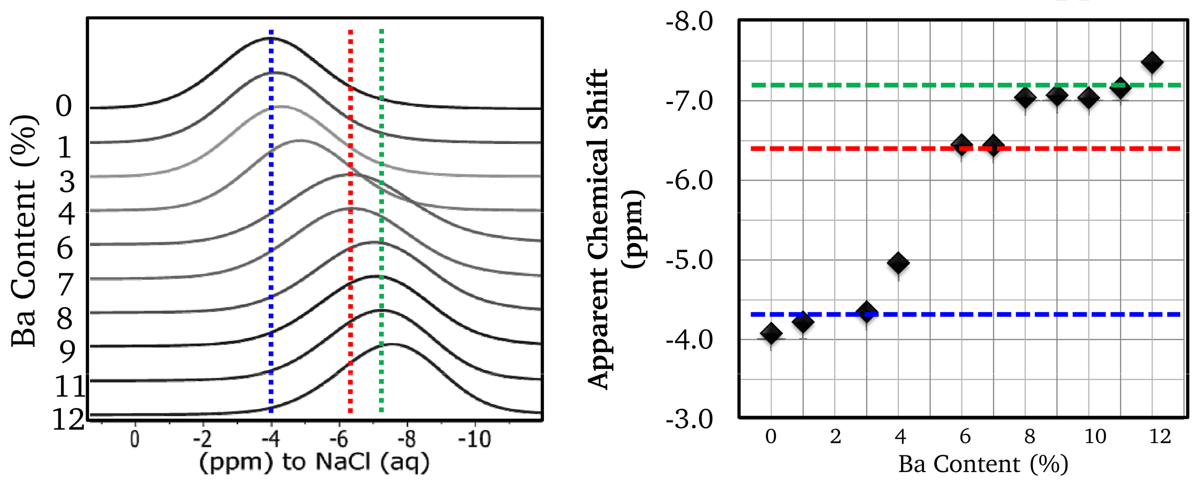
Introduction

The enhanced electric properties of functional electric materials are believed to be direct consequence of their structure. We employed solid-state nuclear magnetic resonance (NMR) in order to better understand these structure-property relationships at a local scale. This technique is a sensitive probe for the local structure because of the very short ranged interactions between nuclei and their close atomic environment.

The chemical shift, one of these interactions, is directly connected to the electronic environment of the nucleus and renders the NMR resonance frequency a fingerprint for the chemical surroundings around the probed nuclei. This feature was employed for lithium speciation in lithium-battery materials. The sensitivity of solid-state NMR to the local structure is further aided by the quadrupolar interaction. It relies on an electrostatic interaction between the nuclear quadrupolar moment and the electric field gradient (EFG) on the nuclear site. Since the EFG is a structural parameter directly connected to the local atomic environment, this technique is capable of detecting minor distortions from the ideal structure, which are responsible for local electric polarization in the investigated perovskite-based functional electric ceramics.

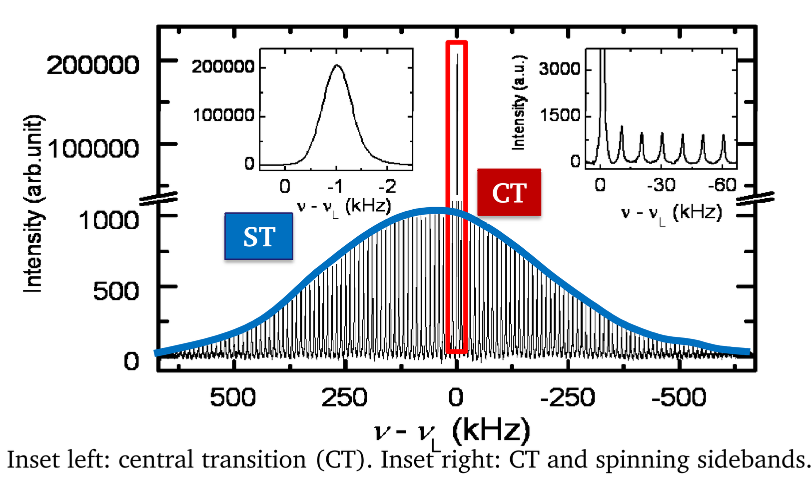
^{23}Na NMR spectra of lead-free piezoelectric ceramics of composition (100-x)$Bi_{1/2}Na_{1/2}TiO_3$-x$BaTiO_3$ with a barium content of $0<x<15$ measured at 14 T under 10 kHz MAS. ^{7}Li and ^{13}C of graphite intercalation compounds and other graphite-based anode materials were measured at 11 T under MAS, in addition do ^{29}Si spectra for ceramic anode materials. Finally, a cathode material, $LiCO_2$, was also investigated by means of ^{7}Li NMR.

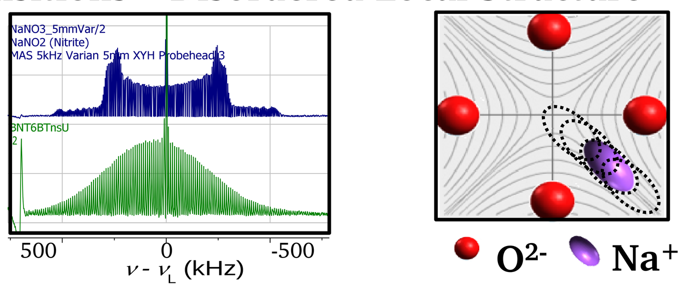
^{23}Na MAS NMR of BNT-xBT – Central Transition – Apparent Chemical Shift



- Three apparent chemical shift ranges identified – dotted lines.
- Correlation with symmetries on BNT-xBT phase diagram.
- P4bm ~ -7 ppm;
- R3c ~ -4 ppm;
- Intermediate range – Morphotropic Phase Boundary (MPB)

^{23}Na MAS NMR of BNT-6BT – Satellite Transitions – Disordered Local Structure



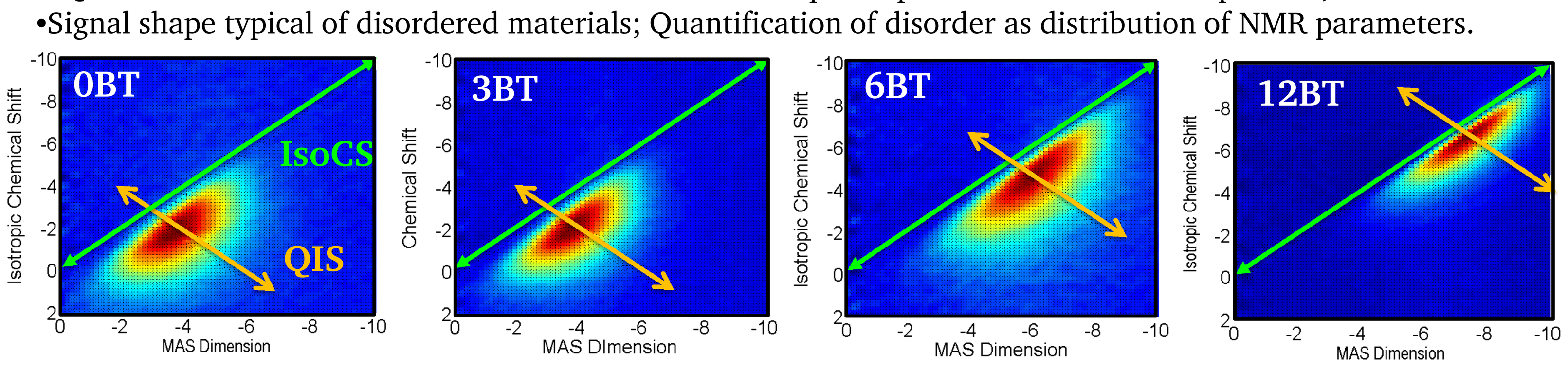


Inset left: central transition (CT). Inset right: CT and spinning sidebands.

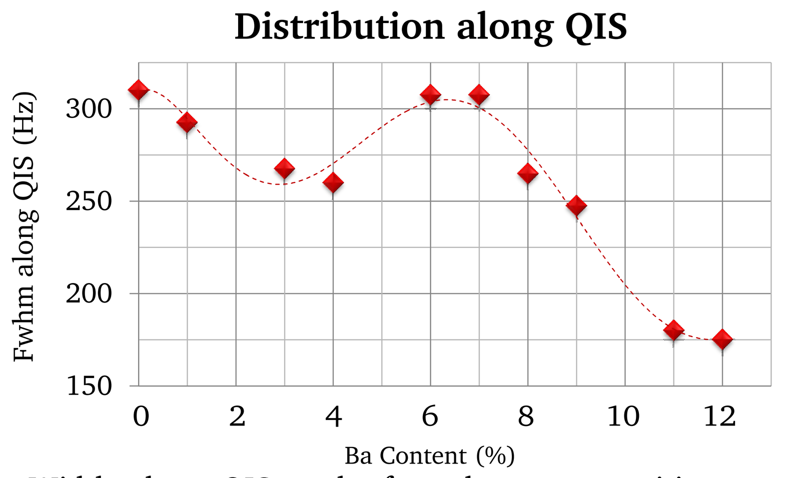
- STs are a fingerprint for non-cubic local symmetry – polar local structure not evidence by diffraction methods.
- Shape of STs indicates partial disorder at the atomic level, as it represents a distribution of Electric Field Gradients (V_{zz}).

^{23}Na 3QMAS NMR of BNT-xBT – Assessment of Local Disorder

- 3QMAS allows the contribution from chemical shift and quadrupole interaction to be separated;
- Signal shape typical of disordered materials; Quantification of disorder as distribution of NMR parameters.

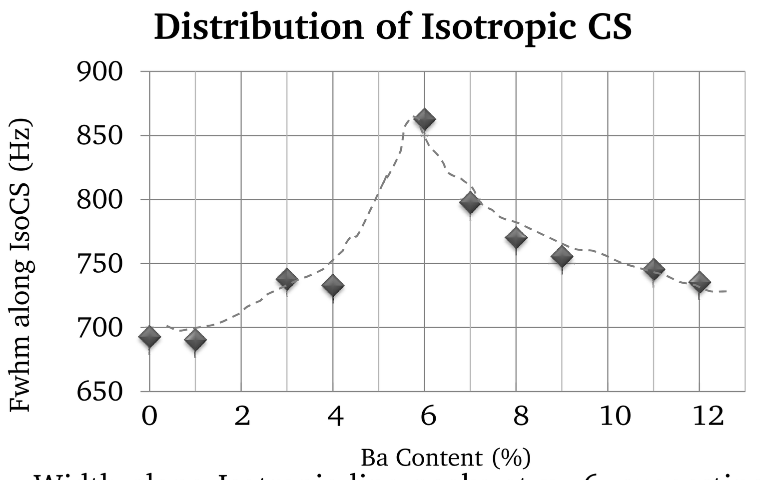


Distribution along QIS



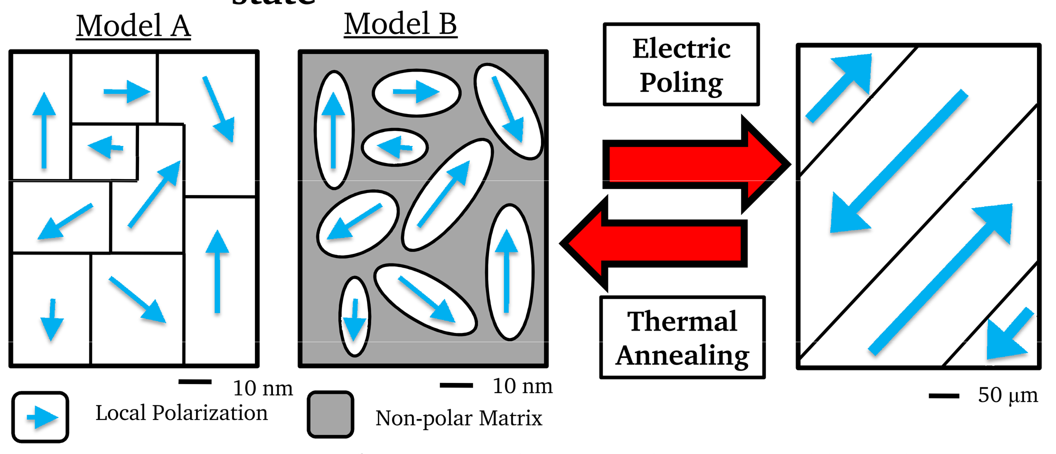
- Width along QIS peaks for relaxor compositions; a lower value is observed for compositions which display a spontaneous ferroelectric state.
- This parameter can be regarded as a measure for the local structure disorder, and correlates to the unusual relaxor-to-ferroelectric crossover observed for this solid solution.

Distribution of Isotropic CS



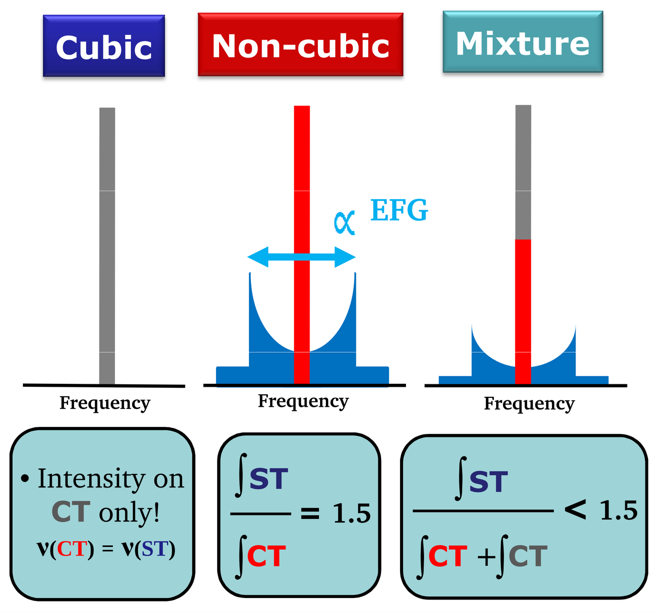
- Width along Isotropic line peaks at x=6, suggesting the overlap of different symmetries.
- Local structure evidence for the MPB concept, which explains enhanced electric properties in this compositional range.
- This composition dependence of this parameter correlates with the piezoelectric coefficient d_{33}.

Models for relaxor ground state / Induced Ferroelectric



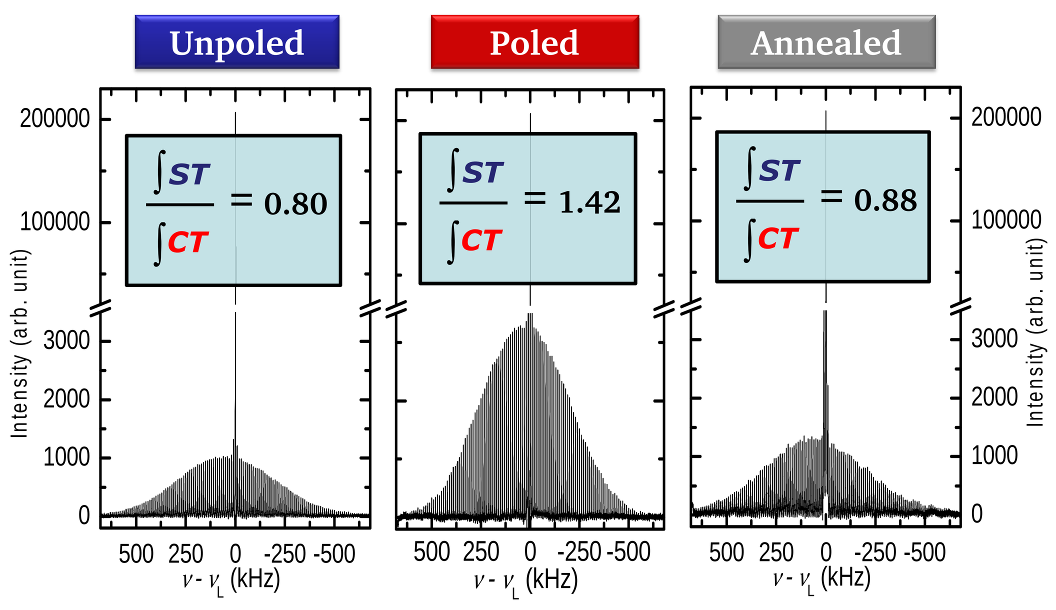
- Whole structure is polar– Ferroelectric nanodomains.
- Polar nanoregions coexist with non-polar matrix.
- Electric Field induces a Relaxor-to-ferroelectric phase transition.

Schematic ^{23}Na NMR spectra



- Intensity on CT only! $\nu(CT) = \nu(ST)$
- $\int ST / \int CT = 1.5$
- $\int ST / (\int CT + \int CT) < 1.5$

Effect of Electric Poling & Thermal Annealing BNT-6BT

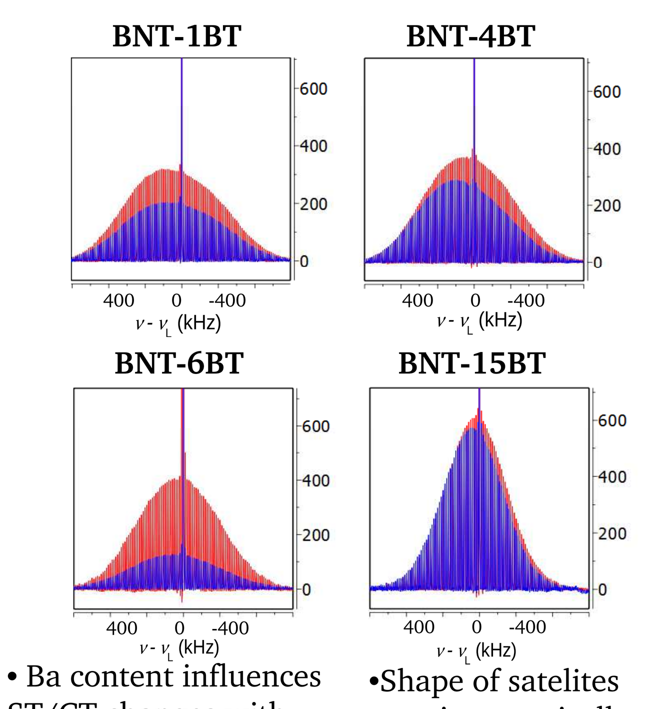


Before Electric Poling:
- Relaxor state;
- ST/CT ratio much lower than theoretical value.

After Electric Poling:
- Ferroelectric state;
- ST/CT ratio pproaches theoretical value of 1.5

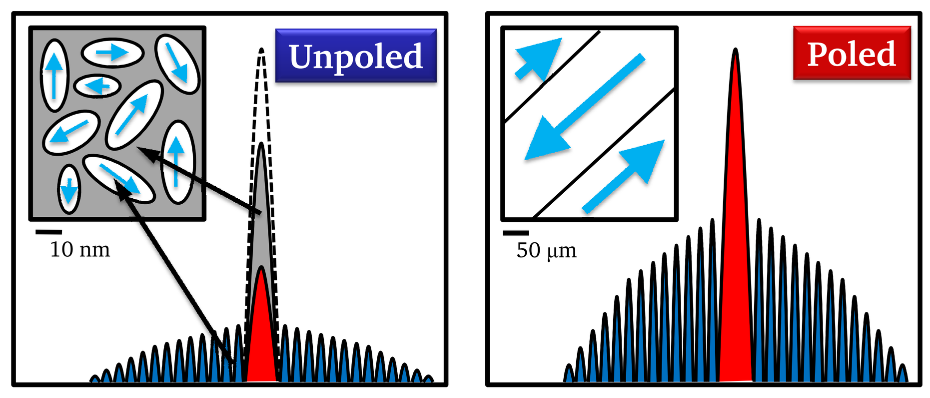
Thermal Annealing:
- Relaxor state re-established;
- ST/CT ratio drops to a value close to the unpoled one.

Effect of Poling on BNT-xBT



- Ba content influences ST/CT changes with poling
- Shape of satelites remains practically unchanged

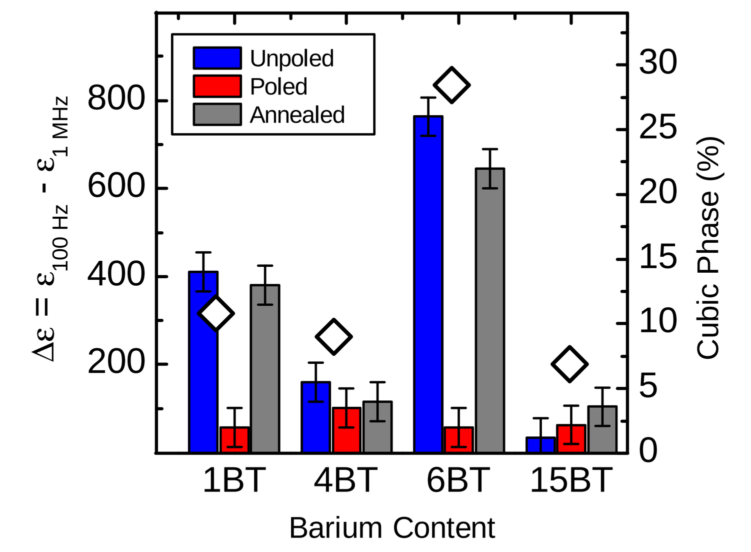
Relaxor state / Ferroelectric state



Relaxor state:
- ST/CT < 1.5
- Coexistence of cubic and non-cubic local symmetries;
- Supports Model B for the ground state of relaxors

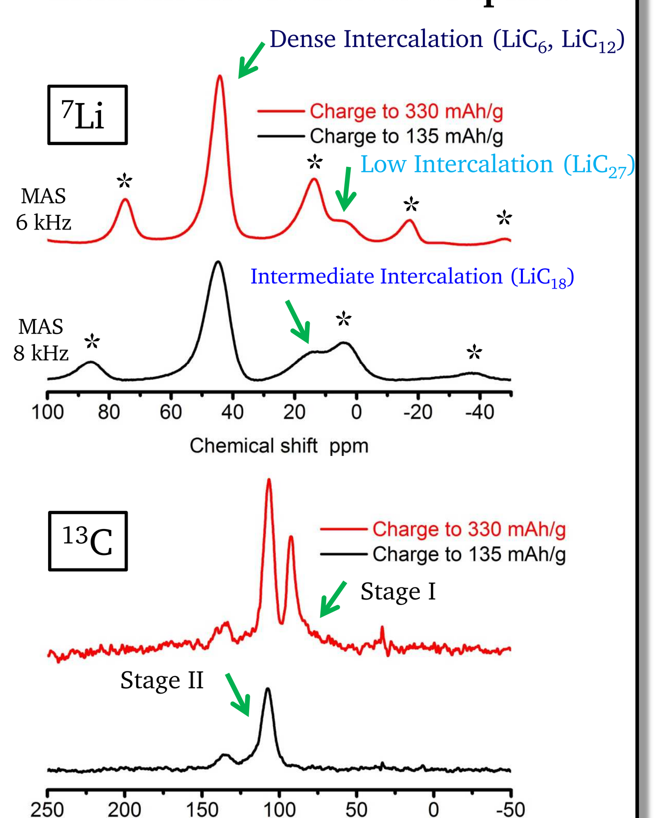
Ferroelectric state:
- ST/CT ≈ 1.5
- Ferroelectric state is completely polarized;
- Structural evidence for Relaxor-to-FE transition

Effect of Barium content



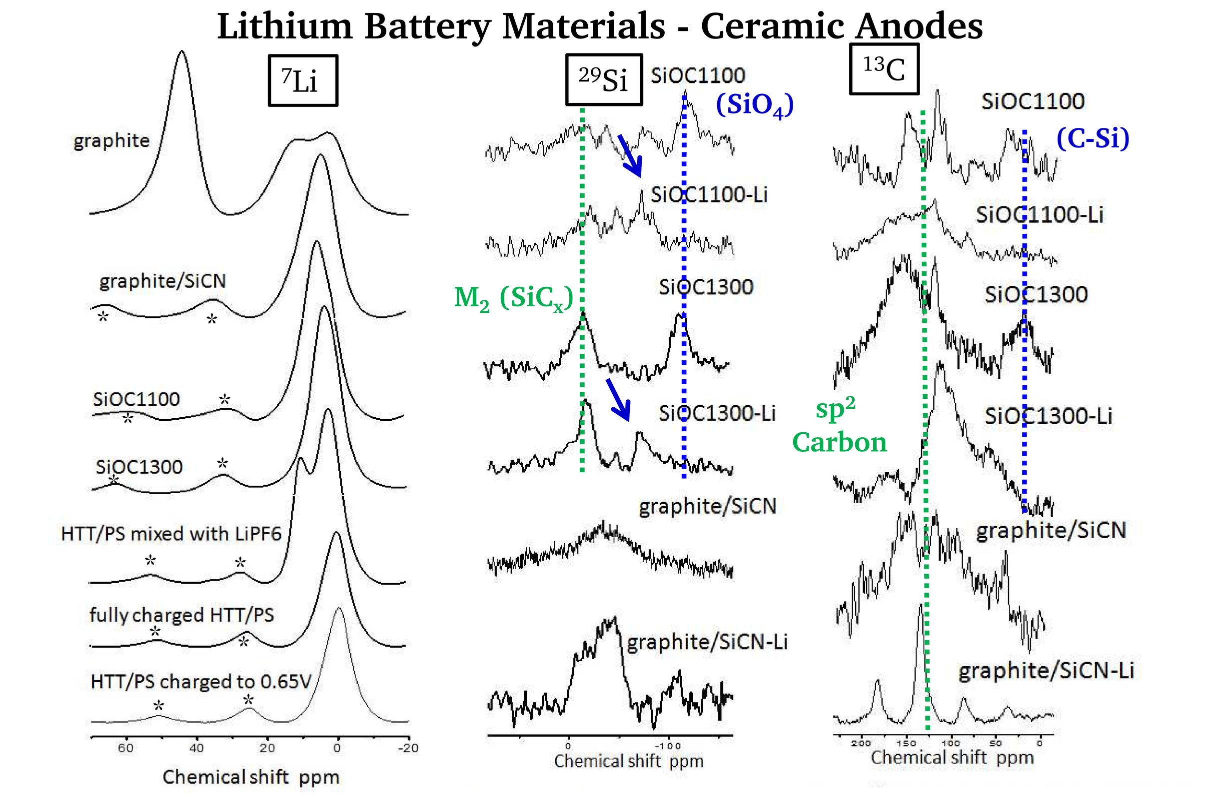
- Compositions with relaxor character (large Δε) exhibit a high relative amount of a cubic phase.

Lithium Intercalated Graphite



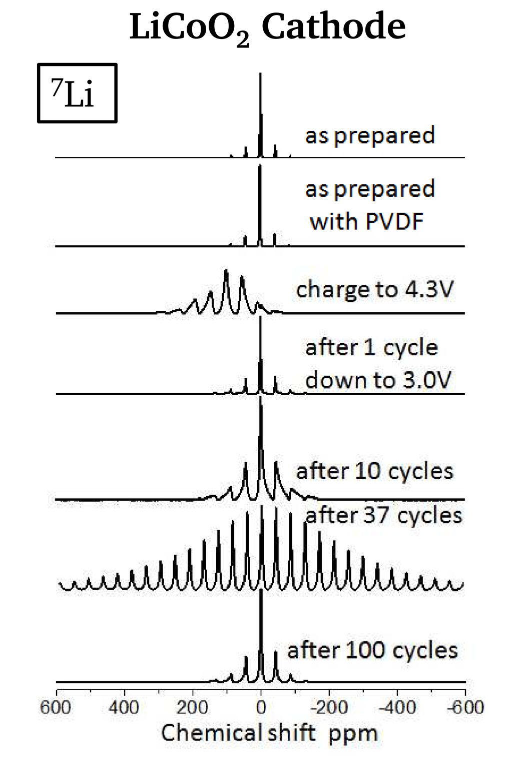
- Different stages of lithium intercalation in graphite

Lithium Battery Materials - Ceramic Anodes



- Graphene based: Intercalation verified.
- Ceramics: too narrow chemical shift range for ^{7}Li.
- SiOC based: Indication of prefered interaction between lithium and Q_4 groups.
- Graphite based: T1 effect on signal
- SiOC based: lithium interacts with ceramic part.

$LiCoO_2$ Cathode



- Charging influenced the quadrupolar coupling.
- Cycling might have colapsed the structure, however, not irreversilbily

Conclusion

For BNT-xBT ceramics, a correlation was found between the ^{23}Na apparent chemical shift and the symmetries observed for different regions of its phase diagram. Additionally, evidence of local disorder was found for these materials, which was asserted by means of 3QMAS NMR spectra. While the distribution of the chemical shift supported the concept of an MPB, the distribution of quadrupolar constants, a parameter that might be related to local electric polarizations, correlated to the unusual relaxor-to-ferroelectric cross-over observed for these compositions.

The quadrupolar interaction also provided insight into the local symmetry around ^{23}Na nuclei. It revealed the coexistence of cubic and non-cubic phases in relaxor compositions of BNT-xBT and afforded the first direct evidence of a non-polar matrix in relaxor ferroelectrics.

Solid state NMR also revealed microscopic details of lithium storage in the electrode materials. ^{7}Li and ^{13}C results of charged graphite showed the various stages of lithium intercalation, while ^{29}Si results of anode ceramic materials indicated lithium is possibly located near Q_4 silicon. ^{7}Li spectra also suggested a reversible collapse of the structure of $LiCO_2$ cathode materials during the charge-discharge process.

Acknowledgement

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