Piezoelectricity in relaxor-ferroelectrics at cryogenic and elevated temperatures

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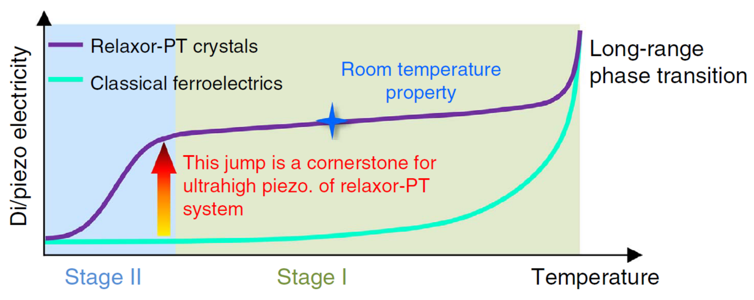
Context

Relaxor-ferroelectric materials are specifically interesting for medical and transducer applications due to their ultrahigh dielectric and piezoelectric properties. In the past two decades however, there has been a growing interest on (1-x)($Bi_{0.5}Na_{0.5}$)TiO_3-x$BaTiO_3$ (BNT-BT) in order to substitute the current lead-based devices due to environmental concerns. Those large properties are thought to be caused by the existence of polar nano-regions (PNRs), arising from inhomogeneous repartition of aliovalent species in the *A*- or *B*-site of the ABO_3 perovskite structure.

A recent cryogenic study[1] on lead-based crystals revealed the role of those regions to the overall structure. Yet, many interrogations still remain on the nature of those PNRs and on the behavior and underlying phenonema of relaxor-ferroelectric materials in general.

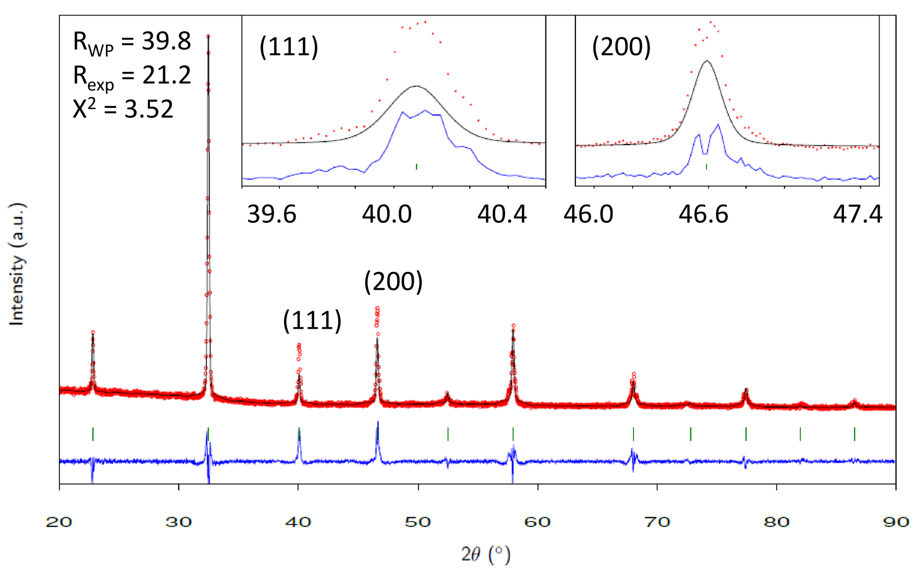


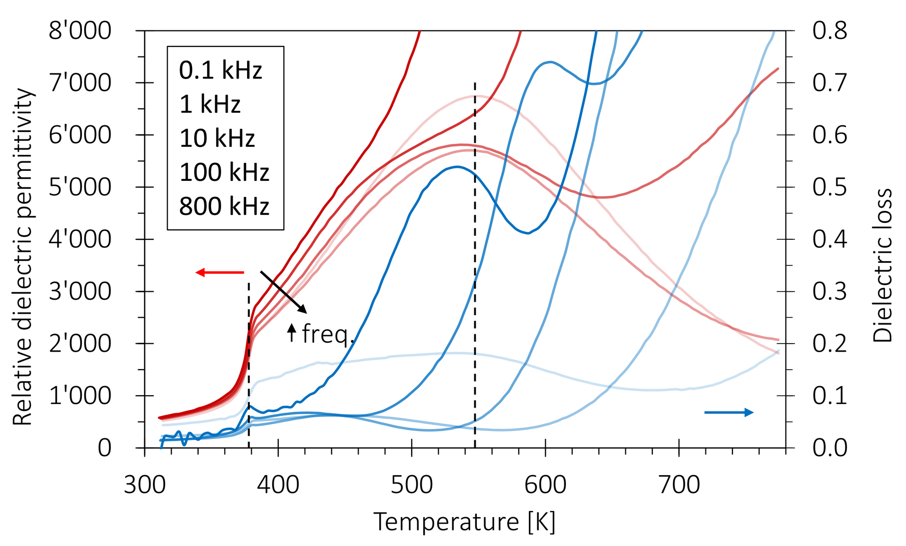
Objectives

This project aims to investigate the contribution of PNRs to the ultrahigh properties of relaxor-ferroelectric materials. To this end, ceramics of 0.94($Bi_{0.5}Na_{0.5}$)TiO_3-0.06$BaTiO_3$ are first fabricated via a standard mixed oxide route and characterized with XRD and dielectric measurements. Then, their dielectric properties are measured at cryogenic temperatures and compared with the behavior of lead-based relaxor-ferroelectrics. Finally, its macroscopic nonlinear dynamics are measured in order to better understand relaxor-ferroelectric materials and the impact from PNRs to the surrounding matrix. The evolution of the third harmonic phase angle with electric field specifically is of great interest to understand its behavior.

Sample Characterization

Rietveld refinement of the XRD pattern using a cubic symmetry reveals the single phase perovskite and pseudocubic structure of the BNT-6BT ceramics, with lattice parameter a_{pc}=3.895 Å. However, it is evident that lower symmetry phases are present, as shown by the peak distortions of the (111) and (200) reflections, characteristic of rhombohedral and tetragonal symmetries. It is likely that the structure consists of ferroelectric domains with embedded PNRs.





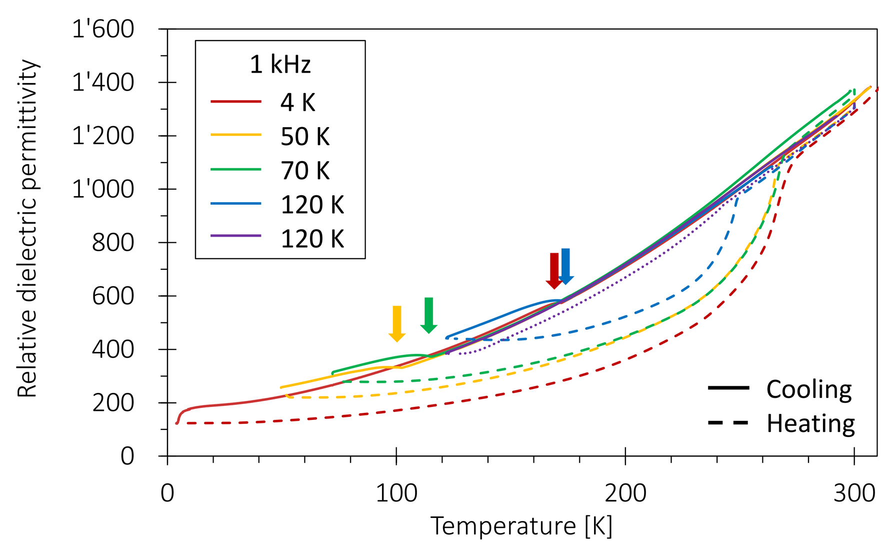
The dielectric properties of the poled ceramics reveal two main features:

- The relaxor-ferroelectric behavior of BNT-BT (in contrast to ferroelectrics)
  - → T_d ≈ 100 °C
  - → T_m ≈ 280 °C
  - → frequency dispersion from PNR dynamics
- Conductive behavior at elevated temperatures characteristic of non-stoichiometric composition. Most likely due to losses of volatile *Bi* or *Na* during sintering.

Cryogenic Measurements

The dielectric evolution with decreasing, followed by increasing, temperature contains two mains features: the appearance of a shoulder upon cooling followed by a step-like transition upon heating reminding the reported jump for lead-based relaxor-ferroelectrics. Several points can be made:

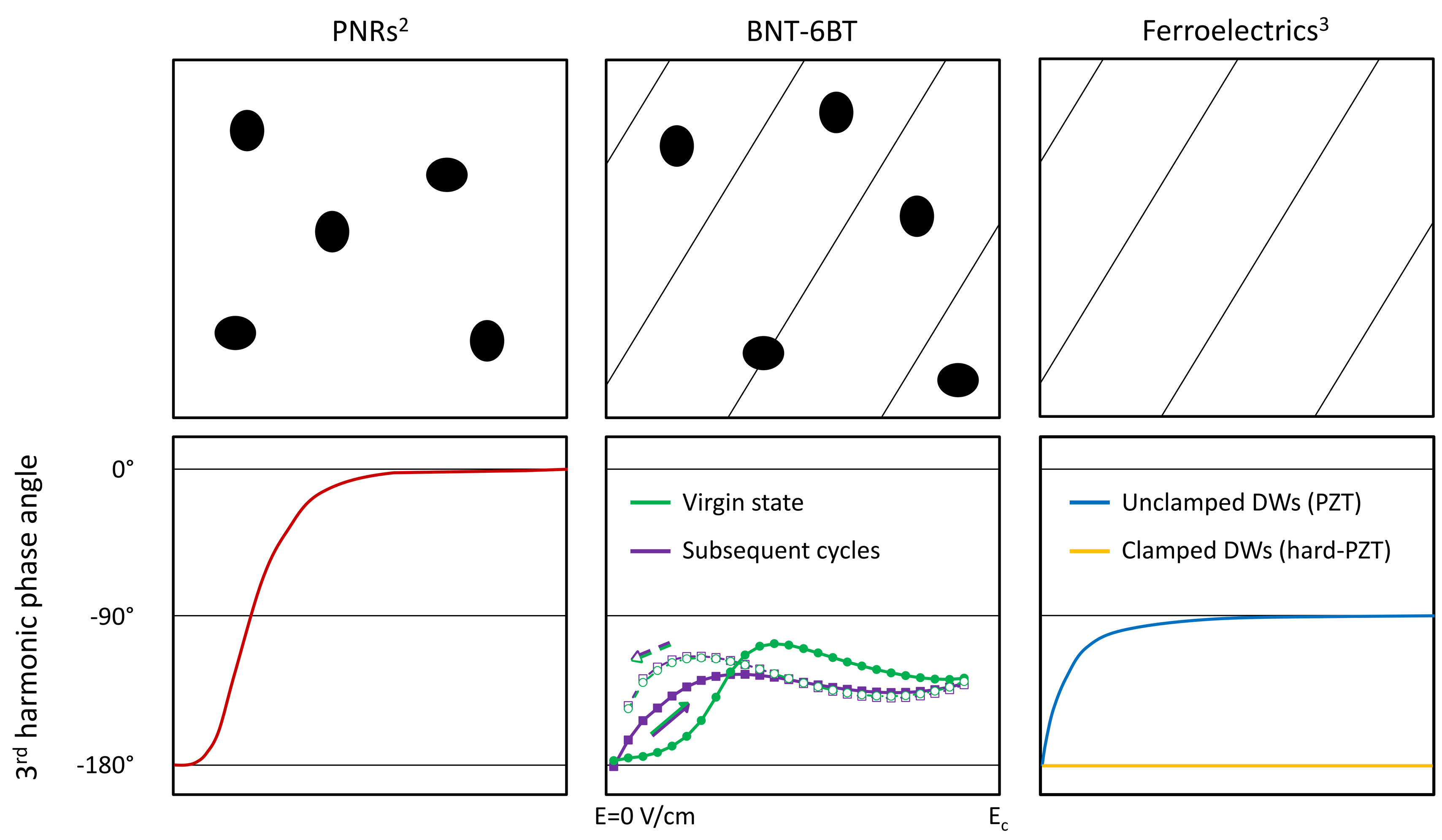
- The shoulder and step transition are linked, with the later only observed if the former occurs. Their absence or presence could be related to the history of the sample;
- Similarly to lead-based materials, the step behavior could be explained by the dynamics of PNRs transitioning from a metastable frozen state into a more stable state. The shoulder on cooling could thus represent, or be related to, the freezing of these PNRs;
- These two features could still however be artifacts and not directly caused by the intrinsic behavior of BNT-6BT or relaxor-ferroelectrics in general. They could be due to the setup configuration and sample connection to the circuit (silver paint) for example.



Nonlinear Dynamics

The dynamics of polar materials can be described using the third harmonic phase angle of the polarization response of a sample subjected to an alternating electric field. Several case scenarios can be determined:

- **-180° → -90° transition**: describes a Rayleigh-type mechanism, which occurs for initially clamped interfaces moving through a random energy landscape, such as domain walls (DWs) pinned by charge defects;
- **-180° → 0° transition**: describes the dynamics of PNRs for example, which do not follow Rayleigh behavior;
- **Transition between -180° and -90°**: the obtained results for BNT-6BT suggest a predominantly non-Rayleigh behavior of relaxor-ferroelectric materials. It is possible that an intermediate behavior between unclamped and clamped ferroelectrics mechanisms takes place due to the pinning of DWs by PNRs.



Conclusions

The low temperature dielectric properties suggest two possibilities:

- Similarly to relaxor-PT materials, the properties of BNT-6BT at room temperature are largely due to PNRs activity and interaction with the surrounding matrix;
- The measured step-like behavior of the BNT-6BT ceramics is an artifact. The measured jump in relaxor-PT crystals reported in the literature would thus not by specific to relaxor-ferroelectrics in general, but rather could be linked to lead and/or *B*-site atomic doping.

The nonlinear dynamics of BNT-6BT suggest however that PNRs might still have an influence on the overall behavior of relaxor-ferroelectric, as shown by the non-Rayleigh-like evolution of the third harmonic phase angle.

Further Work

Further investigations are needed to clearly understand the behavior of BNT-6BT at cryogenic temperatures. More, measuring its nonlinear dynamics at cryogenic and elevated temperatures could help understand the dynamics of PNRs specifically.

References

1. Li *et al.*, *Nature Communications*, 2016
2. Hashemizadeh *et al.*, *Applied Physics* Letter, 2016
3. Morozov, PhD thesis, *Ecole Polytechnique Fédérale de Lausanne*, 2005