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 \((\text{Bi}_{x}\text{Na}_{y}\text{TiO}_3)\text{TiO}_2\times\text{B}a\text{TiO}_3\) (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 ialvalent 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 phenomena of relaxor-ferroelectric materials in general.

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 \(a = 3.895 \, \text{Å}\). 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)\(\rightarrow T_c = 100 \, \text{°C}\)
- The transition at \(T_c = 280 \, \text{°C}\) frequency dispersion from PNR dynamics.

Cryogenic Measurements

The dielectric evolution with decreasing, followed by increasing, temperature contains two main 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:
- \(-180° \rightarrow 90°\) 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;
- \(-180° \rightarrow 0°\) 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 be 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