

# Switching Dynamics & Mechanisms in Morphotropic $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ from Atomistic Modelling

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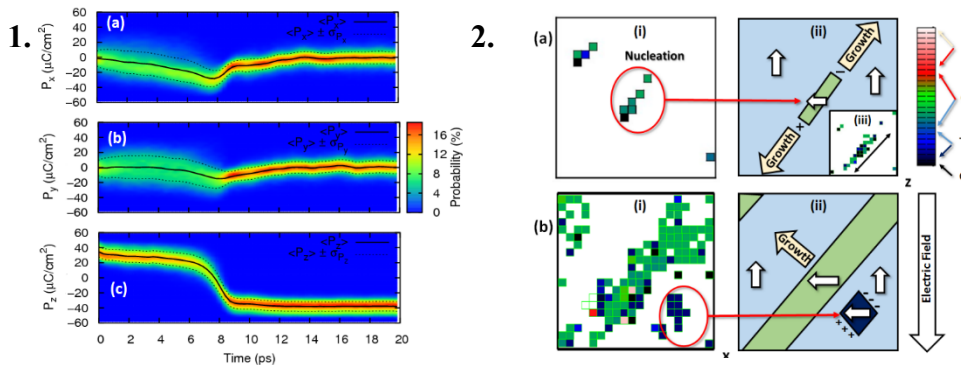
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In this work, we use large scale molecular dynamics using the shell model forcefield of Gindele *et al* [1], to model the dynamic switching behaviour of PZT in the vicinity of the MPB-composition. We show that, in the absence of domain walls, which precludes creep-depinning, the local B-cation disorder is responsible for temperature dependent, competitive switching mechanisms. We model switching of  $x=0.5$  PZT at 100 K and 300 K [2], by pre-poling the simulated sample into a [001] tetragonal phased monodomain and then applying a reverse field to facilitate picosecond switching. At 100 K we show that, in the absence of pre-existing domain walls, diamond-shaped orthorhombic domains, approximately faceted by (101) surfaces, nucleate in the material. These are the 3-dimensional analogues to the beveled nuclei shown as the growth mechanism on 2-dimensional  $180^\circ$  domain walls [3]. For nuclei exceeding a critical radius, fast growth of the facets forming charged domain walls with the [001] bulk occurs to minimize the electrostatic energy cost (Figure 2a). This growth is followed by conventional domain growth via domain wall motion (Figure 2b). Reverse domains then nucleate in the orthorhombic domain which grow until the sample has switched. A switching process via nucleation of orthorhombic domains provides an explanation for experimental studies on  $\text{PbZr}_{0.414}\text{Ti}_{0.585}\text{O}_3$  ceramics, where the double peaks in the switching current were proposed to occur due to non- $180^\circ$  domain switching resulting from the residual stresses developed during forward poling [4].

Further, we identify that the nucleation and switching are facilitated by Zr-site centered unit cells and by extension, Ti within Zr-rich environment. Since  $\text{PbZrO}_3$  has an orthorhombic (AFE) groundstate, these clusters allow for the nucleation of locally orthorhombic domains to facilitate growth via lower energy  $71^\circ$  and  $109^\circ$  domain walls without a large elastic energy penalty [5]. We find Ti in Zr-rich environments have suppressed ferroelectric displacements which may incorrectly be perceived as dead-regions. However, we show these Ti-centred unit cells remain ferroelectrically active due to the oxygen-octahedral displacement in the MPB-composition. At higher temperatures (300 K), the critical nucleus and barriers for reversal become negligible compared to the thermal fluctuation of dipoles enabling the depinning-like process of fast nucleation of switched nanodomains through a paraelectric state (ie tracing the soft  $\Gamma$ -mode as in  $\text{PbTiO}_3$ ).

This work highlights the subtle complex features of the low temperature atomistic switching mechanisms of PZT at the MPB-composition and proves atomistic level insight that is crucial for the development of functional nanoscale control of switching in ferroelectrics.



**Figure 1.** Density of Probability of each component of the order parameter during switching of  $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$  at 100 K. **Figure 2.** (i) Cross-sectional  $xz$  snapshots of the growth and formation of intermittent domains with an orthorhombic local structure to facilitate low temperature switching via low energy domain walls. Each square represents a unit cell with  $P_z < 0$  and a color representing its local structure. (ii) Cartoons of each snapshot.

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[3] Y.H. Shin, I. Grinberg, I.W. Chen & A. M. Rappe, *Nature* **449**, 881 (2007)

[4] T.M.Kamel & G. de With, *J. Appl. Phys.* **102**, 044118 (2007)

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