Atomistic Modelling of Ageing in Ferroelectrics

J.B.J. Chapman[1,2 *], R.E. Cohen[1,3], A.V. Kimmel[1] and D.M. Duffy[1]
[1]Department of Physics, University College London, Gower Street, London, WC1E 6BT, UK
[2]Materials Division, National Physical Laboratory, Hampton Road, Teddington, TW110 LW, UK
[3]Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA
4Ludwig Maximilian University of Munich, 80539 München, Germany
*Jacob Chapman: jacob.chapman.13@ucl.ac.uk

Ferroelectric components are found in many modern technologies, from mobile phones, diesel engine drive injectors and sonar to print heads and non-volatile memory. The change in the material's properties over time, referred to as ageing, can cause severe issues with the operational lifetime of ferroelectric devices.

Acceptor-doped ferroelectrics are known to show novel behaviour when aged including pinched P-E hysteresis, shifts of the hysteresis along the electric field axis and large recoverable non-linear strains [1,2]. Phenomenologically, the large-signal ageing phenomenon is attributed to the stabilization of domain structures from point defects, however, there are still open questions regarding the precise microscopic mechanisms [2]. In particular, it has remained unclear as to whether the microscopic origin is caused by volume effects (the stabilization of the whole domain), domain-wall pinning, boundary effects (defects interacting with interfaces and grain boundaries); or a combination of each. In this work, large scale atomistic molecular dynamics with a core-shell potential [3] is used to perform dynamic simulations of ageing in the prototypical ferroelectic $PbTiO_3$. Introducing different concentrations of dopant-vacancy associates $(B''_{Ti} + V_O^{\bullet\bullet})^X$, we calculate the polarization-field (P-E) and electrostrain (S-E) hysteresis from a poling field under four structural conditions:
(i) defect-free bulk (ii) unaged (iii) aged parallel to the poling field (iv) aged perpendicular to the poling field.

Our results provide fundamental insight into the microscopic mechanism showing all large-signal properties of ageing to be reproduced without any boundary effects. We identify the effect of associates concentration on the hysteresis which may be exploited for novel technological applications. Finally, we show the rich local structure of $PbTiO_3$ above the Curie temperature, similarly noted for $BaTiO_3$ [4], identifying it as a possible mechanism for deviation from the symmetry conforming principle to account for pinched hysteresis of un-poled ferroelectrics.

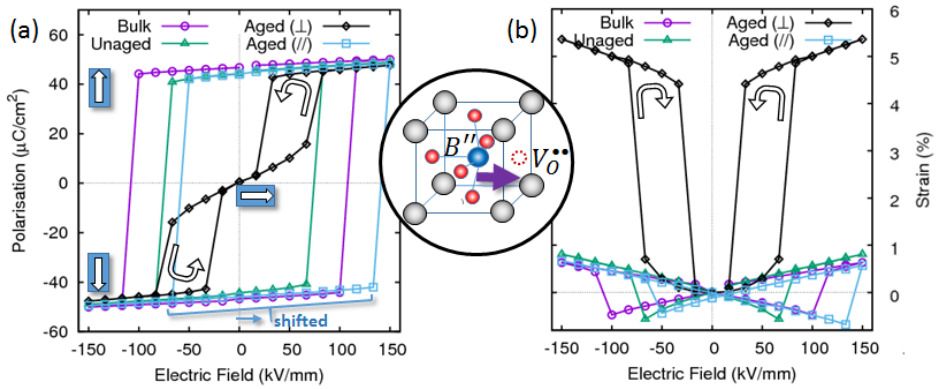

Figure 1. Modelling ageing in Pb-based perovskite ferroelectrics. Hysteresis of (a) polarisation and (b) strain, for defect-free bulk (circle), un-aged (triangle), poling perpendicular to the ageing direction (diamond) and poling parallel to the ageing direction (square). Simulations of samples that have been un-aged recover the square P-E hysteresis of the bulk. Ageing parallel shifts the P-E hysteresis and breaks the symmetry of the S-E loop. Ageing perpendicular pinches the P-E loop, creating a full double hysteresis for large enough defect concentrations, accompanied by a giant recoverable, non-linear strain hysteresis.

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