Nanoscale Characterization of Ferroelectric Materials via Piezoresponse Force Microscopy

<u>A. L. Kholkin</u>, I. K. Bdikin, D. K. Kiselev, Jingsong Liu, M. Machado, V. S. Bystrov, I. Delgadillo

Department of Ceramics and Glass Engineering & CICECO, University of Aveiro, 3810-193 Aveiro, Portugal kholkin@ua.pt

Coupling between electrical and mechanical phenomena is very often in nature. Apparently, it underpins the functionality of materials and systems as diversified as ferroelectrics and multiferroics to electroactive molecules to biological materials. In ferroelectrics, electromechanical behavior is directly linked to polarization order parameter and hence can be used to study phenomena ranging from polarization reversal mechanisms, domain wall pinning, cross-coupled phenomena in multiferroics, to direct imaging of electron-lattice coupling. It may be said that electromechanical coupling is also a key component of many electrochemical transformations, in which changes in oxidation state are associated with the variation in molecular shape and bond geometry. Electromechanical energy conversion is an integral part of processes such as triboelectricity, cavitation, and sonoluminescence. It will not be an exaggeration to say that electromechanics, along with mechanics and transport, is one of the fundamental phenomena in nature. Therefore, it forms a basis for numerous device applications, and is thus directly relevant to virtually all existing and emerging aspects of materials and nanoscience.

Recent vears significant growth of interest towards nanoscale showed electromechanical phenomena originating independently in ferroelectric MEMS, biological, nano- and material science, and organic chemistry communities. The interest is stimulated both by development of nanoscience and necessity for efficient electromechanical motion and transformation at the nanoscale, and also recent emergence of scanning probe microscopy techniques capable of addressing electromechanical phenomena at a local level. As a relevant comparison, nanoscale properties are often accessible as a result of evolutionary development from macroscopic probes (e.g. interferometry or Berlincourt meter) to nanoscale, and corresponding macroscopic properties have been studied systematically since the dawn of industrial revolution. Electromechanical properties described by antisymmetric tensors averaged out in macroscopic systems and corresponding coupling coefficients are typically small (~100 pm/V), necessitating precise measurement tools even for macroscopic samples. These two factors resulted in limited quantitative and reproducible macroscopic studies of electromechanics even in single crystals and ceramics, recognized as important for applications (piezotransducers, SAW, sonar, ultrasonic imaging devices). Nanoscale offers a set of novel electromechanical phenomena induced by symmetry breaking at low dimensionality and by unique combination of high electric field and charge in nanovolumes that can lead to anomalous polarization reversal [1].

Ferroelectric materials are being intensively investigated due to their outstanding characteristics useful for various microelectronic devices ranging from nonvolatile ferroelectric random access (FeRAMs) memories to microelectromechanical systems (MEMS). For these applications, the nanoscale properties of ferroelectrics are of crucial importance. Since the feature size of potential devices is currently approaching to the submicron dimensions, local characterization techniques are becoming indispensable to meet the requirements of microelectronic industry. Local properties are expected to deviate from macroscopic ones due to confinement effects, lack of sufficient nucleation, and surface phenomena [2]. Piezoresponse Force Microscopy (PFM) has recently proved its usefulness for high-resolution domain imaging and local electromechanical characterization of ferroelectric materials [3].

In this presentation, the overview of the state-of-art in local ferroelectric characterization via PFM in several piezoelectric important materials (PZT, SBT, PZN-PT) will be given [4]. Local polarization switching and hysteresis [5], cross-sectional domain analysis [6] and polarization patterning [7] will be, in particular, addressed with special emphasis on the effect of PFM instrumentation on the measured properties. Based on these observations, the mechanism of local polarization reversal via PFM tip will be delineated. In the second part of the talk, the nanoscale properties of relaxor ferroelectrics will be shortly addressed. In these materials, the remanent polarization is absent at the macroscopic level due to strong disorder of ferroelectrically active ions. It will be shown that on the nanoscale the properties of relaxors are different due to symmetry breaking [8] and the material typically exhibit a clear piezoelectric contrast with the domain correlation length of the order of tens nm. Long-range order can be induced by applying small dc voltages to the tip [9]. The results confirm great potential of PFM for studying polar structures in ferroelectric and related materials.

References:

[1] A. L. Kholkin, I. K. Bdikin, V. V. Shvartsman, N. A. Pertsev, *Nanotechnology* **18** (2007) p. 095502.

[2] A. Gruverman and A. Kholkin, Rep. Progr. Phys. 69 (2006), pp.1-32.

[3] A. L. Kholkin, S. V. Kalinin, A. Roelofs and A. Gruverman in "Scanning Probe Microscopy: Electrical and Electromechanical Phenomena at the Nanoscale", Eds. S. Kalinin, A. Gruverman, Springer (2007), V. 1, pp. 173-214.

[4] A. L. Kholkin, I. K. Bdikin, D. A. Kiselev, V. V. Shvartsman and S.-H. Kim, J. of *Electroceramics* **19** (2007), pp. 81-94.

[5] I. K. Bdilin, A. L. Kholkin, S. V. Kalinin and A. Morozovska, Appl. Phys. Lett. (submitted).

[6] J. S. Liu, H. Z. Zeng and A. L. Kholkin, J. Phys. D: Appl. Phys. 40 (2007), pp. 7053-7056.
[7] V. S. Bystrov, I. K. Bdikin, D. A. Kiselev, S. Yudin, V. M. Fridkin and A L Kholkin, J. Phys. D. 40 (2007, pp. 4571-4577.

[8] V. V. Shvartsman and A. L. Kholkin, J. Appl. Phys. 101 (2007), p. 064108.

[9] D. A. Kiselev, I. K. Bdikin, E. K. Selezneva, K. Bormanis, A. Sternberg and A. L. Kholkin, J. Phys. D. 40 (2007), pp. 7109-7112.

Figures:





Fig. 1. Local ordering of nanodomains on the surface of disordered PLZT ceramics (a) and corresponding autocorrelation function (b).

Fig. 2. Inverse polarization in PZN-PT [1]

NanoSpain2008

14-18 April, 2008

Braga-Portugal