## **Defects in ferroelectric oxides and at oxide/ferroelectric interfaces** A. V. Kimmel National Physical Laboratory, Teddington, TW11 0LW, U.K.

In ferroic materials, unwanted changes of the ferroelectric, dielectric, and piezoelectric properties, which either occur spontaneously or accumulate in the course of numerous ferroelectric axis switching events, have been attributed to the presence of defects. Understanding the mechanisms of defect-induced atomic scale processes is, therefore, crucial for not only improving the reliability of existing devices but also for utilizing the defect properties and developing new functionalities.

Oxygen vacancies, being the most abundant defects in oxide materials, are known to induce local perturbation of the lattice, affect dielectric properties, conductivity, polarization, and overall lifetime of ferroelectric devices. In this talk I discuss various mechanisms of Oxygen vacancy defects stabilisation in tetragonal ABO<sub>3</sub> ferroelectric compounds.

From symmetry consideration the oxygen axial sites located along the B-O-B chains, oriented along the tetragonal (polar) axis c, and the oxygen equatorial sites located in the BO<sub>2</sub> planes perpendicular to this axis, are not equivalent. Consequently, the oxygen vacancies at these sites, referred to as axial ( $V_{ax}$ ) and equatorial ( $V_{eq}$ ) vacancies, are not iso-energetic and induce strong site-specific lattice relaxation. In particular, the stabilisation may occur via a conventional path of diffusion from metastable to stable configurations. However, an alternative mechanism takes place where the perturbation induced by defect is enough to facilitate the rotation of the polar axis. This mechanism, predicted to dominate in materials with slow oxygen vacancy diffusion and low formation energy of 90° domain walls, can stimulate the formation of domains with their polar axes pinned by the vacancies [1].

We illustrate the material-dependence of these symmetry-conforming properties of defects using a comparative ab initio study of oxygen vacancies in tetragonal phases of BaTiO<sub>3</sub>, KNbO<sub>3</sub> and low energy P4mm phase of solid solution Pb( $Zr_{0.5}Ti_{0.5}$ )O<sub>3</sub> (PZT). We demonstrated that rotation mechanism is efficient in BaTiO<sub>3</sub>, while KNbO<sub>3</sub> exhibits a preference to the diffusion mechanism. The relative stability of oxygen vacancies in PZT strongly depends on the local chemical environment that stabilises a preferential location of defects in material.



Another example of defect-induced properties is related to oxide/ferroelectric interfaces. Oxide interfaces are known to exhibit properties that are not found in the constituent materials when they are considered separately. At the nanoscale, the properties associated with interfaces often define the properties of entire nano-structures. The materials with new properties and functions can be fabricated by assembling complex hetero-structures, such as epitaxial thin films and core-shell (CS) nanoparticles. CS nanoparticles of BaTiO<sub>3</sub> (BTO), in the form of nano-sized (300-500 nm) grains coated with  $\sim$ 5 nm thick silica layer, demonstrated a dielectric constant over  $10^5$  and quite constant in a wide temperature range. These properties make the BTO-SiO<sub>2</sub> nanoparticles promising for the applications that require high dielectric permittivity, such as solid-state energy storage and random access memory devices.

An atomistic model of  $SiO_2/BaTiO_3$  interface was constructed using *ab initio* molecular dynamics. Analysis of its atomistic structure and electronic properties reveals the closure of the band gap at the stoichiometric  $SiO_2/BaTiO_3$  interface that is significantly smaller than that of the bulk BTO and  $SiO_2$ . We showed that the properties of the interfaces significantly depend on perovskite termination. The interfaces with BaO terminated BTO exhibit stable character of interfacial bonds, while that with  $TiO_2$  terminated BTO shows strong covalent bonds. The structure gives rise to the interface polar region with positive and negative charges localized in the BTO and  $SiO_2$  parts of the interface, respectively. In both cases the formation of the interface facilitates the formation of defects. Thus, the interface contains high concentration of oxygen vacancies in the outermost  $TiO_2$  plane of the BaTiO\_3. The high dielectric response, observed experimentally in the SiO\_2-coated nanoparticles of BTO, was proposed to be due to the electron gas formed in oxygen-deficient BTO and localized in the vicinity of the polar interface [2].



1. A.V. Kimmel, P. Weaver, M.G. Cain, P.V. Sushko Phys. Rev. Lett. 117601, 109 (2012).

2. A.V. Kimmel, J. Íñiguez, M.G. Cain, P.V. Sushko J. Phys. Chem. Lett. 4, 333 (2013).