Project Title : Rediscovering the Fundamental Science of the Archetypal Antiferroelectrics at small scales

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Introduction:

Functional materials form the basis of modern day life and are integral to devices that exploit their unique functionalities. In this context, antiferroelectrics are considered prime candidates for high energy data storage, actuators, transducers and electrocaloric applications. The conventional theory of antiferroelectricity, developed by Kittel in 1950[s], describes antiferroelectric materials through an antiparallel arrangement of dipoles in adjacent unit cells at ground state, which switch to parallel arrangement at high applied electric fields. Such behaviour has been historically associated with the perovskite structure $PbZrO_3$, the archetypal antiferroelectric and has profound implications towards multitude of applications in devices based on them. However, recent work on $PbZrO_3$ suggests a more complex picture, with a range of ferroelectric, ferrielectric and modulated polarization behaviour at the nanoscale and debate about the nature of anti-ferroelectricity in this material has intensified. In this context, our team is uniquely poised to tackle the key challenges of correlated macroscopic and microscopic studies of polar and antipolar states in $PbZrO_3$ thin films, within the range of observational parameters. This work will investigate the existence of a transitional state from classical antiferroelectric states to ferroelectric and paraelectric states in the archetypal antiferroelectric $PbZrO_3$ and $PbHfO_3$. The study will thus for the first time explore the effects of size reduction on such transitional states in dimension-, stress-, and orientation-controlled thin films and nanostructures. The exploration of the limits of the classical Kittel theory of antiferroelectricity will be performed through multipronged theoretical and experimental approaches, pushing the limits of microscopy and will be informed by ab-initio and DFT based atomistic modelling. The insights gained from this project would have direct relevance to broader classes of antiferroelectric materials.

Project description:

The overarching goal of this PhD project is to advance the fundamental understanding of antiferroelectricity in $PbZrO_3$ and $PbHfO_3$ thin films and nanostructures, through multipronged theoretical and experimental studies of nanoscale polarization. Specifically, this work will correlate microscopic structural changes with macroscopic properties in this archetypal antiferroelectric, exploring the stability of classical antiferroelectric (AFE), ferrielectric (FiE), and ferroelectric (FE) behaviour in $PbZrO_3$ thin films and nanostructures as a function of thickness reduction, size confinement in a range of surface-to-volume ratios with reduced lateral constraint, and crystallographic orientation of the films (where a large inherent anisotropy in the material might result in different stabilization criteria for transitions between AFE, FiE and FE behaviours). In parallel, theoretical efforts will evaluate material behaviour at increasing size from the nanoscale, offering insights into transition(s) from the nanoscale-stable ferroelectric phase, to an (intermediate) ferrielectric phase, to the macroscale and bulk-stable and archetypal antiferroelectric one.

The PhD project is relevant to a large collaborative US-Ireland effort between two US-based institutions (Georgia Tech and University of South Florida) and two European counterparts (QUB) in Northern Ireland and TCD in the Republic of Ireland, which attempts to better understand material functionalities across wide (millimeter to nanometer) length scales and will address the nanoscale organization of dielectric dipoles in oxides that can collectively lead to presence or absence of switchable polarization at larger length scales. When successful, this research could enable the next-generation micro- and nano-scale high force and high displacement actuators and transducers, ultra-high energy storage devices, miniaturized voltage regulators, solid-state cooling, electro-optic and electronic devices. The proposed research in this PhD project will be primarily experimental in nature conducted via well-established techniques such as scanning probe microscopy, focused ion-beam milling and high resolution transmission electron microscopy (QUB team has a strong international reputation in the use of such techniques towards novel research in ferroic oxides). The broader ferroelectrics activity at CNM is internationally renowned and the research features in high-impact journals and at international conferences. The student will work with Dr Amit Kumar (as the primary supervisor) and with a vibrant and enthusiastic team of established PhD students and post-doctoral researchers. Dr. Raymond McQuaid (UKRI fellow and co-investigator) will also be part of the supervising team. Applications should be made through the QUB system and informal discussions with Dr Amit Kumar (Email : a.kumar@qub.ac.uk) are encouraged.