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Edited by
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J. Marty Gregg
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Nanoscale Ferroelectrics and Multiferroics

Key Processing and Characterization Issues, and Nanoscale Effects

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Preface

Multiferroics have been at the cutting edge of research and development in materials for ICTs for over a decade. During this period steady improvements in fundamental knowledge have been made. At the same time, nanoscale phenomena have assumed an increasing importance. Progress has benefited from the strong synergies with activities in nanoscale ferroelectrics, which are at a more mature stage. Multifunctionality and nanoscaling are widely acknowledged at present as the keys to the miniaturization of solid-state electronics, and specifically nanoferronics, which is emerging as a new area with large technological potential. The topic has now reached a maturity level that allows, and actually requires, books that provide a comprehensive revision of the topic, and an in-depth analysis of future trends. These are the objectives of *Nanoscale Ferroelectrics and Multiferroics: Key Processing and Characterization Issues, and Nanoscale Effects.*

It is intended to provide the increasing number of scientists and engineers, who are approaching the topic from a range of backgrounds, with a reference/guide text that should help them to roadmap their R&D activities. The volume reviews the key issues in processing and characterization of nanoscale ferroelectrics and multiferroics, and provides a comprehensive description of their properties. An emphasis is put on differentiating size effects of extrinsic ones like boundary or interface effects. Nanoscale novel, recently described, phenomena that are bound to be behind major advancement in the field during the coming years are also addressed.

The book is devised to stress, and take full advantage of, the synergies between nanoscale ferroelectrics and multiferroics. It covers materials nanostructured at all levels, from ceramic technologies like ferroelectric nanopowders, bulk nanostructured ceramics and thick films, and magnetoelectric nanocomposites, to thin films, either polycrystalline layer heterostructures or epitaxial systems, and to nanoscale free-standing objects with specific geometries, such as nanowires and tubes at different levels of development, but all technologically relevant. Nanostructuring is a requirement of the current tendency to miniaturization of ceramic technologies for microelectronics that imposes stringent conditions on processing, and has a deep impact on functional properties. Also, nanostructuring ultimately results in the ever-decreasing processing temperatures of thin films, a key issue to the integration of these multifunctional oxides with silicon devices and flexoelectronics. Last but not least, a range of novel physical phenomena has been described in nanoscale ferroelectrics and multiferroics that have the potential to enable a range of disruptive technologies, like magnetoelectric memory. Overall, the book reviews the current state of the art of these materials, stressing a range of specific topics at the cutting edge of research.

This project springs from the high-level European scientific knowledge platform built within the COST Action *Single and Multiphase Ferroics and Multiferroics with Restricted*

Geometries (SIMUFER, ref. MP0904), active between March 2010 and May 2014. COST (European Cooperation in Science and Technology) is a pan-European networking instrument that allows researchers from COST member countries and cooperating states to jointly develop their ideas and initiatives in a field or topic of common interest. SIMUFER established a multidisciplinary scientific network of groups from 24 European countries and 7 non-COST countries, experienced in synthesis, advanced characterization, and modeling of all nanoscale ferroics, single-phase multiferroics, and ferroic-based combinations of dissimilar materials. This book project arises primarily from their expertise, though it has been open to world renowned experts when necessary. Chapter contributors have been carefully selected and have all made major contributions to knowledge of the respective topics; overall, they are among the most respected scientists in the field.

Introduction

Why Nanoscale Ferroelectrics and Multiferroics?

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I.1 Ferroics and Multiferroics

Single-phase ferroics are compounds that present one of the three (currently expanded to four) ferroic properties: ferroelectricity, ferromagnetism, or ferroelasticity, to which ferrotoroidicity has recently been added. The common feature of the four types of ferroics is the appearance of the ferroic order; either it is a spontaneous electrical polarization, magnetization, strain, or toroidal moment, in a phase transition from a high-temperature prototype phase to the low-temperature ferroic phase, related by a group/subgroup relationship. This transition is always accompanied by a decrease in symmetry and the splitting of the ferroic phase into domains (regions with a different orientation of the order parameter). A second feature, the direct consequence of the switchable nature of the order parameter and of the domain dynamics, is the characteristic ferroic hysteresis loop; that is, a distinctive hysteretic dependence of the order parameter on its conjugated field (electric or magnetic field, mechanical stress or toroidal source vector, respectively), with two remnant states of opposite sign [1]. The four phenomena are schematically shown in Figure I.1. Ferroics are highly topical, advanced functional materials that have not only enabled a range of mature and ubiquitous related technologies (like magnetic

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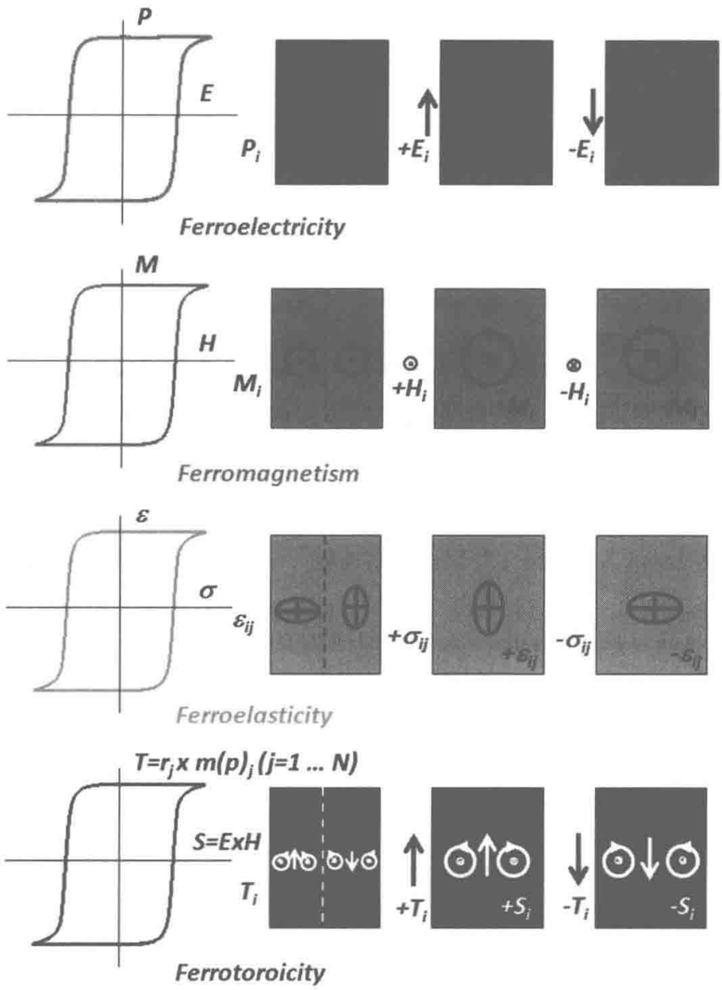

Figure I.1 *Schematics of domains and hysteretic switching for the four ferroic phenomena. Adapted by permission of IOP Publishing from [1].*

or ferroelectric information recording, ceramic ultrasound transducers, or shape memory alloys, to name only a few examples) but are also under extensive research for a number of novel, potentially disruptive, applications [2].

There are also compounds that simultaneously present two (or more) ferroic phenomena, known as multiferroics, among which those showing coexistence of ferroelectricity and ferromagnetism (initially termed ferroelectromagnets) are receiving increasing attention [3,4]. This is not only because of their inherent multifunctionality but also for the fact that they are liable to show magnetoelectric coupling, and have thus the potential to enable the electrical control of magnetism (and the magnetic control of polarization) [5].

This book specifically deals with ferroelectrics and ferroelectromagnets (either robust ferromagnetic materials or canted antiferromagnets showing weak ferromagnetism), though the general term multiferroics will be used following the current tendency to name ferroelectric–ferromagnetic materials, and in general any type of magnetic ordering compounds, in this way.

The choice of addressing them together only acknowledges the deep-rooted relationship between the two sets of materials; multiferroism requires ferroelectricity and thus multiferroics have to be electrically insulating to be functional (an issue not always acknowledged). This feature is not easily found in magnetic materials, most of them being metallic or narrow-band gap semiconductors. Indeed, chemical bonding requirements suggest the two ferroic phenomena to be incompatible [6]; transition metal or rare earth atomic species with partially filled outer *d* or *f* electronic shells (and unpaired electrons) are necessary for magnetism, while model ferroelectric perovskite oxides are characterized by covalently bonded transition metals (to oxygen) with empty *d* orbitals [7]. Nevertheless, an ever-increasing number of multiferroic single-phase materials have been reported over the last decade, exploring alternative mechanisms of ferroelectricity.

I.2 Ferroelectric Materials and Related Technologies

Ferroelectrics are thus materials that present a spontaneous electrical polarization, whose direction can be reversed with an electric field (by nucleation and growth of inversion domains, resulting in the distinctive ferroelectric hysteresis). The ferroic phase appears at a ferroelectric transition, driven by electrical polarization [8], which can be either of a displacive type, the most common one, associated with a crystal structure instability induced by condensation of a transverse optical phonon (the soft mode) [9], or of an order–disorder type. Its macroscopic phenomenological description according to Landau's theory of phase transitions can be found in Chapter 19.

All ferroelectrics are also pyroelectric and piezoelectric, as well as electrooptic, which turns them into a prototype of multifunctionality (even before magnetic order is added). Moreover, they are the only materials that can present these properties, intrinsically linked to the crystal structure, in polycrystalline form (thanks to the ability to reorient the polarization under an electric field).

Though ferroelectricity was first described for hydrogen-bonded compounds (Rochelle salt being the first one in 1921), and there are also examples among tellurides, fluorides, and iodides [10], a number of electroactive polymers like poly(vinylidene fluoride) [11], and recent reports of ferroelectric metal organic frameworks [12], clearly oxides stand out as the ones that have enabled a range of successful ferroelectric technologies.

I.2.1 Ferroelectric Bulk Technologies

Perhaps the best-known ferroelectric, and also the first oxide shown to be so in 1944, is $BaTiO_3$ with a perovskite structure. This model compound presents the ferroelectric transition at ~393 K and a succession of low-temperature polymorphic phase transitions between ferroelectric phases with decreasing symmetry, from tetragonal to orthorhombic and to rhombohedral, for which the polar axis (and thus the direction of the spontaneous polarization defined by the displacement of the Ti^{4+} cation from the centre of the oxygen octahedra) changes. Polymorphism is a quite common phenomenon in ferroelectric perovskite oxides and plays a very important role in their functionality. $BaTiO_3$ is also the base composition of multilayer ceramic capacitors (after the chemical tailoring of the ferroelectric transition down to room temperature), one of the two large-scale, mature bulk ceramic ferroelectric technologies. This material and its modifications are extensively addressed in this book (see Chapters 1, 11, 12, 15, and 18), for the miniaturization of these capacitors is a case study of the current trends in microelectronics that require the nanostructuring of the ceramic layers. In the last few years, nanostructured $BaTiO_3$ and its solid solutions have become the main candidates for active materials used in capacitive building blocks for energy storage applications.

The second successful technology is piezoelectric ceramics for electromechanical transduction. The state of the art material for these applications, which range from sensors and actuators (like accelerometers or positioning systems for scanning probe microscopy, respectively) and their combination in smart systems (to implement active vibration damping), to ultrasound generation and sensing (for medical imaging or non-destructive testing), and to submarine acoustics, is $Pb(Zr,Ti)O_3$, which also has a perovskite structure. This is an oxide solid solution, for which the best properties are found at a morphotropic phase boundary (MPB) between rhombohedral and tetragonal ferroelectric polymorphs, for which a monoclinic phase has been recently described [13]. This material can be regarded as a modification of $PbTiO_3$, a second model ferroelectric oxide that also shows a succession of polymorphic phase transitions, yet induced by hydrostatic pressure instead of temperature [14], which has been placed at one of these ferroelectric instabilities (the MPB) by building up chemical pressure (achieved by substitution of Zr^{4+} for Ti^{4+}). As a matter of fact, the very good electromechanical response of this material is a combination of two effects, a crystal contribution, associated with the existence of a transverse lattice instability at the monoclinic tetragonal boundary [15], and an extrinsic contribution, associated with the fact that ferroelectric perovskite oxides are also ferroelastic (and therefore multiferroic, but not ferroelectromagnets). The spontaneous strain develops at the ferroelectric transition along with the polarization (the two parameters are intrinsically coupled), and as a consequence ferrroelectric–ferroelastic domains appear (in addition to polarization inversion domains).The non-180° (90° in the tetragonal case) domain walls are mobile under stress and electric field (unlike 180° walls that only move under an electric field), giving way to a wall contribution to the piezoelectric effect [16]. Moreover, the domain dynamics is enhanced at the morphotropic phase boundary. In addition, chemical (or doping) engineering of $Pb(Zr,Ti)O_3$ has been developed that enables a range of soft and hard piezoelectric ceramics with tailored properties for specific applications. Piezoelectric ceramics are also being considered for novel applications, such as energy harvesting [17] and magnetoelectric composites (see later). Further explanations of the mechanisms, along with a review of alternative materials, can be found in Chapter 16. This technology is not oblivious to the general miniaturization trend and nanostructuring can also be anticipated.

Other examples of ferroelectric ceramic bulk technologies are infrared (IR) cameras for night vision (and, in general, IR detectors for a range of applications exploiting the pyroelectric effect) and electrooptic devices. Modifications of $PbTiO_3$ like $(Pb,La)TiO_3$ and transparent $(Pb,La)(Zr,Ti)O_3$ are usually the material choices, respectively. An excellent review of ferroelectric ceramics and related technologies can be found in [18].

Also successful ferroelectric single-crystal technologies are presently available. The best examples are surface acoustic wave (SAW) devices for radio frequency and microwave signal conditioning, based on ferroelectric $LiNbO_3$ substrates. At the very end of the