Viewpoint Paper

Prospects for nanostructured multiferroic composite materials

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Abstract—Magnetoelectric multiferroic materials have the potential to transform a range of applications, including tunable microelectronics and multiphase memories. However, the coexistence of ferromagnetism and ferroelectricity in single-phase materials is quite rare, driving the development of composite multiferroic materials. In these composites, the coupling arises from strain transfer across a shared interface between the ferroelectric and ferromagnetic phase. This viewpoint article highlights recent work as well as future challenges in the synthesis and characterization of nanostructured multiferroic materials.
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1. Introduction

Multiferroic materials represent a novel class of material where multiple types of ferroic ordering coexist, and their coupling can lead to additional ordering parameters. These, in turn, can be leveraged to form new multifunctional devices. The ferroic orderings are ferroelectric, ferromagnetic, and ferroelastic and these materials exhibit a spontaneous polarization, magnetization or strain, which can be further controlled by an applied electric, magnetic, or stress field, respectively. In a multiferroic, when multiple types of ferroic ordering are coupled, additional functionalities can arise, including magnetoelectric, piezoelectric and magnetoelastic behaviors. Here, we are interested in magnetoelectric multiferroics that combine ferroelectricity with ferromagnetism. These materials will be the focus of this article, and herein the term multiferroic will refer solely to materials with magnetoeletric behavior.

Single-phase multiferroics, although rare, do exist, but they tend to have both a low permittivity and a low permeability. This rare occurrence of single-phase multiferroics is a result of the often seemingly contradictory material requirements for ferroelectricity and ferromagnetism. Ferroelectric materials must be electrically insulating and require a non-centrosymmetric unit cell, while most ferromagnetic materials tend to be metals. A more complete discussion of these contrasting properties has been reviewed by Hill [1,2]. The single-phase multiferroics that do exist are classified into one of two types, designated as type 1 or type 2, based on the origin of multiferroicity. In type 1

multiferroics the sources for ferroelectricity and ferromagnetism are distinct and independent from one another [3–7]. In type 2 multiferroics the multiferroic behavior arises from magnetic ordering [8]. Although a rich area of research, single-phase multiferroics are plagued by low ordering temperatures, limiting their applications in devices. Single-phase multiferroics have been discussed thoroughly in several outstanding recent review articles and will not be further discussed here [9–13].

To overcome the limitations of these single-phase multiferroics, composite or multi-phase multiferroic materials have been developed. Composite multiferroics are typically heterostructures consisting of a magnetostrictive and a piezoelectric phase. These heterostructures can be readily prepared in a range of composite architectures defined by the connectivity between the two phases by a variety of methods, ranging from thin film to solid-state approaches [14] (Figure 1). For example, a 0-3 composite describes a particulate-based composite where zero-dimensional (0-D) particles are dispersed within a 3-D matrix. Particulate-based composites (0-3) [15], pillars within a 3-D matrix (1-3) [16] and layered heterostructures (2-2) [17–24] represent the most common geometries of magnetoelectric heterostructures (Fig. 1a). In these multiferroic composites the magnetoelectric coupling is mechanical in nature and is based on the fact that piezoelectric and magnetostrictive materials undergo a shape change in an applied electric or magnetic field, respectively. The magnetoelectric effect in these composites can be described by the direct magnetoelectric effect, which is the product of the magnetostrictive effect (magnetic/mechanical) and the piezoelectric effect (mechanical/electrical) [25].

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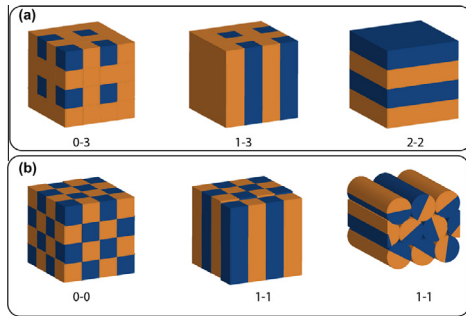
Figure 1. (a) Composite connectivities of composites prepared by traditional routes and (b) connectivities that could be realized with the development of nanostructured building blocks.

$$\text{Direct ME effect} = \frac{\text{magnetic}}{\text{mechanical}} \times \frac{\text{mechanical}}{\text{electric}} \qquad (1)$$

The figure of merit for these materials is the magneto-electric coefficient, α_E, which is determined experimentally by measuring the change in electric field, δE, generated by applying an ac magnetic field, δH, to a biased sample,

$$\alpha_E = \frac{\delta E}{\delta H} \qquad (2)$$

Although these magnetoeletric heterostructures have high theoretically predicted values for α_E, actual experimental values tend to be much lower [20,26–31]. The fact that these experimental coupling values are lower than predicted can be attributed to a variety of factors including the formation of cracks or impurity phases at the interface between the two phases. These heterostructures are also challenged by the low resistivity ferrite phase and substrate effects, which can mechanically clamp the sample [16].

Because this coupling involves mechanical coupling across the interface between the magnetostrictive and piezoelectric phase, it follows that one route to enhance the magnetoelectric coupling is by maximizing the interfacial area between the two phases [32]. One way to accomplish this is to use nanoscale materials due to their large surface to volume ratio. The first example of coupling in multiferroic nanostructures was demonstrated by Zheng et al. [16], who embedded $CoFe_2O_4$ nanopillars epitaxially in a $BaTiO_3$ thin film matrix. However, it is worth noting that here the $CoFe_2O_4$ rods are nanoscale in diameter only. Since this seminal work, much effort has been done to develop new nanostructured building blocks for the formation of the next generation of multiferroic materials. The focus of this viewpoint article will be to describe and review the development of nanostructured multiferroic building blocks that can be assembled into higher order multiferroic structures and devices, while also addressing the needs to develop and utilize novel characterization methods to fully study these systems.

2. Synthesis and characterization of nanostructured multiferroic materials

2.1. Zero-dimensional (nanoparticles)

One of the challenges in fabricating multiferroic composites with magnetoelectric coupling values approaching the theoretically predicted values is the low resistivity of the ferrite phase. In many of the theoretical models the optimum volume fraction of ferrite is at high volume fractions ($\sim$0.5–0.9) [26]. However, at such high loadings the leaky ferrite phase makes it challenging to pole the material. Therefore, much effort has been made to isolate the leaky ferrite phase within a ferroelectric matrix (0-3 connectivity). This can be accomplished via a multitude of routes with a range of synthetic complexities. The simplest methods involve mechanically mixing particles followed by densification via solid-state methods [33–37], or mixing solutions of ferroelectric and piezoelectric particles followed by spin-coating and calcination [38], and molten-salt based synthetic routes [39,40]. Thin film approaches such as pulsed laser deposition have also been used to fabricate particulate composites [41]. Novel one-pot synthesis strategies have also been developed to more fully control the synthesis and microstructure of composite multiferroics [33,42–46]. However, using many of these routes, it remains a challenge to isolate the ferrite phase at the high volume fractions required to obtain high performance magnetoelectric composites. In many of these routes the device performance drops off at volume fractions of ferrite between 0.2 and 0.5, corresponding with percolation of the ferrite phase [47–49]. Core–shell magnetoelectric particles have been synthesized to address this challenge of isolating the ferrite phase while maintaining a high overall volume fraction of ferrite. These novel particles consist of a ferrite core ($CoFe_2O_4$, Fe_3O_4, $Ni_{0.5}Zn_{0.5}Fe_2O_4$) surrounded by (i.e. electrically isolated by) a ferroelectric shell [51–53,55–59]. The ferrite core is typically synthesized via either a hydrothermal or co-precipitation method, and is subsequently coated using sol–gel methods with a $BaTiO_3$ shell. These particles are then calcined and/or sintered at elevated temperatures (650–1300 °C). Duong et al. have reported the longitudinal and transverse maximum magnetoelectric (ME) coupling coefficients as 3.4 mV cm^{-1} Oe^{-1} and 2 mV cm^{-1} Oe^{-1} respectively for sintered pellets of these core-shell nanoparticles [52,56,57]. However, they found that by varying pressure, sintering temperature and sintering duration, these values were further increased to 3.53 mV cm^{-1} Oe^{-1} and 2.23 mV cm^{-1} Oe^{-1}.

Duong et al. [57] also synthesized a structure using barium titanate as the core and cobalt ferrite as the shell. The barium titanate was synthesized using sol–gel methods, then suspended in a solution containing a chelating agent and the elements to form cobalt ferrite. As expected, in these materials where the $CoFe_2O_4$ was not isolated in the core, the ME coefficient was found to be 4.2 times lower than a comparable sample with cobalt ferrite as the core [57].

All the synthesis examples outlined above require calcining steps to produce crystalline tetragonal perovskite barium titanate from the amorphous barium titanium sol, which is needed for piezoelectric behavior. The exact temperatures varied from 650 to 1000 °C. All of the reported ME measurements were made on samples that underwent additional sintering for further densification [53,52,56–59]. Though some groups use transmission electron microscopy (TEM) and SEM to confirm the core–shell particles, the particles are agglomerated because of the high temperature processing [51,55]. One of