Feasibility study of ferromagnetic/ferroelectric films for enhanced microwave devices

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Abstract:

This report summarizes exploratory work conducted to assess the feasibility of ferromagnetic/ferroelectric films for next-generation microwave devices. From literature review, it is established that while an increasing number of ferroelectric/ferromagnetic composites are being investigated, a number have transition temperatures that are too low and structures that are not robust enough for low cost, room temperature antenna arrays. On the other hand, several promising systems are identified, including the multiferroic $BiFeO_3$ and a composite system of $Ba/SrTiO_3$ and a related perovskite manganite. It is suggested that when the NASA pulsed laser deposition chamber is fully operational, thin films of these systems be investigated. In preparation for such work, we have reconfirmed several structural features of an existing $Ba/SrTiO_3$ film using the x-ray diffractometer at Oberlin College.

1) Introduction and Outline:

Ferroelectric materials are used in a variety of applications, including nonvolatile memories [1] and microwave frequency devices [2]. In the case of memory devices, the hysteretic character of the polarization with applied electric field is used to store data in the form of two different polarization directions, analogous to the situation for ferromagnetic materials. In the case of microwave-related devices, the ferroelectric material's dielectric constant is tuned by an applied electric field to achieve phase shifting of a microwave signal. Work conducted by Dr. Robert Romanofsky at NASA Glenn has demonstrated that it is feasible to make high quality phased array antennas using the ferroelectric $Ba_xSr_{1-x}TiO_3$ for phase shifters [3]. While these arrays have significant advantages over other technologies in considering power handling and cost issues, there are important limitations based on the particular characteristics (such as the impedance or optimal bias voltage) associated with the chosen ferroelectric material. Thus, it is likely that next generation devices will need to incorporate additional technologies.

Another class of materials already in use for microwave applications is the group of oxides known as ferrites [4]. In this case, the material is controlled through the use of a *magnetic* field as opposed to an *electric* one. Magnetic materials, in general, have become the subject of much attention for storage and data communication devices [5].

In light of this background, we have been interested in exploring the possibility of integrated ferroelectric and ferromagnetic materials for microwave applications. In such composite materials, we could potentially use *both* electric and magnetic fields to tailor the phase shifting in antenna arrays, while minimizing losses. While historically little work has been done on materials that are both ferroelectric and ferromagnetic, there is now a growing interest in such systems which have been termed "multiferroic" [6].

In this study, we review recent results for three classes of multiferroic materials: intrinsically ferromagnetic and ferroelectric ones, described in section 2), extrinsically coupled materials, consisting of separate ferromagnetic and ferroelectric entities, described in section 3), and extrinsically uncoupled materials in which the ferromagnetic and ferroelectric compounds do not interact directly, described in section 4). The most promising materials and systems are identified for future experimental work, in anticipation of a pulsed laser deposition chamber to be upgraded at NASA. In advance of that work, as described in section 5), structural characterization of an existing film of Ba/$SrTiO_3$ has been conducted at Oberlin College to test the suitability of equipment here. Section 6) summarizes the main conclusions of this feasibility study.

2) Intrinsic multiferroic materials:

Intrinsic multiferroic materials are ones in which both ferroelectricity and ferromagnetism (or some type of long range magnetic order) co-exist in the same compound. They are very attractive materials for potential microwave applications, in part due to their simplicity in processing. A single material is responsible for both the electrical and magnetic features, and the coupling between the two is intrinsically controlled by the structure. In comparison to the case of composite systems (described in section 3), there are fewer concerns about controlling the interfaces and minimizing sample inhomogeneities to maintain coupling.

On the other hand, this "all-in one" approach to multiferroism has certain disadvantages. As discussed in a recent review [7], there are relatively few compounds that exhibit both ferroelectricity and ferromagnetism. To support the nonzero polarization, the material must have a noncentrosymmetric crystal structure and must be insulating (at least enough to maintain the polarization). For the magnetic properties, the material must contain either 3d elements such as Fe, Co, Ni, or Mn or rare earth elements such as Ce and the like. This latter constraint is believed to be primarily responsible for the small numbers of multiferroic compounds: while the 3d elements are important from a magnetic standpoint, occupancy of the 3d levels can *destabilize* ferroelectricity as it can make a different type of structural distortion (namely a Jahn-Teller one) more favorable energetically than leaving an off center atom displacement to yield the polarization.

Nevertheless, the innate attractive feature of a single material with both ferroelectric and magnetic properties has led to a significant amount of research in this area in the past few years. Table 1 (at the end) includes information on a variety of multiferroics, listing in particular transition temperatures and references.

As is evident from the table, the vast majority of multiferroics of current interest are variants of perovskite oxide structures. While some of the materials, like the RMn_2O_5 compounds, have transition temperatures far too low for practical applications [18-19], there are several that show promise for devices. In particular, both $BiMnO_3$ and $BiFeO_3$ have been actively investigated for the magnetoelectric effects that can be quite significant. Specifically for $BiMnO_3$, the ability to write data with different polarization states has been demonstrated recently [14]. $BiFeO_3$ has been shown to have a dE/dH coefficient as high as 3V/cm-Oe [8], although in a quasi-static setup. The iron version is also attractive due to its tunability with doping [10-11]. Furthermore, some of its undoped dielectric properties (including ε of ~ 100, tan δ of ~0.04) are comparable to those of the existing technology based on $Ba/SrTiO_3$ [9].

Recommendation #1: **Given these features and the general difficulty in finding intrinsically multiferroic materials, it is suggested that further work be done to explore the possible use of $BiFeO_3$ thin films as the most promising of existing multiferroic compounds.**

3) Extrinsically coupled multiferroic materials:

As described above, few materials show intrinsically both ferroelectric and magnetic properties. However, it is possible to *extrinsically* couple ferroelectricity and ferromagnetism via structural effects. In particular, one can generate a magnetoelectric effect by combining a magnetostrictive material with a piezoelastic one in the following way. In a magnetostrictive material, an applied magnetic field induces length changes. These changes, if passed on to the piezoelectric material, then result in a change in the (electric) polarization. One can also run the effect the other way: by applying an electric field, one can induce structural changes in the piezoelastic material which are transferred to the magnetostrictive material, resulting in a difference in the magnetization. Note this is a so-called "product property" in that neither constituent is magnetoelectric, but that the two together create via structural effects a new property. To estimate the coupling size, Bichurin et al have made a phenomenological model of the relevant susceptibilities using bulk magnetostrictive and piezoelastic coefficients [21].

In recent years, a significant amount of experimental research has been conducted to investigate and maximize this magnetoelectric coupling in composites of ferromagnetic and ferroelectric materials. In the vast majority of the work, the ferroelectric component has been either $PbZr_xTi_{1-x}O_3$ (PZT) or $Ba_{1-x}Sr_xTiO_3$ (BST), two very well studied ferroelectric compounds. A variety of ferromagnetic materials have been chosen, as listed in Table 2. Note that the rare earth iron alloys have among the highest magnetostrictive coefficients of any material. In principle, they should thus be useful for creating composites with high magnetoelectric coupling. However, in order to do so, there must be a good interfacial match between the magnetostrictive component and the piezoelastic one-else the high magnetostriction does not translate to the ferroelectric material. This has been difficult to achieve due to the very different nature of the metallic alloys vs. the PZT or BST oxides; progress has been made by incorporating a polymer binder as an intermediary [22]. In considering microwave applications, this system now has the added complexity of being three phase, along with the difficulties associated with the metallic character of the ferromagnetic phase.

A more promising approach has been based on either ferrites or manganites [23-32]. While their magnetostrictive coefficients are not nearly as high as those of Terfenol and related materials, they are large with respect to other oxide systems. In the special case of the manganites, the magnetostriction is often closely associated with the unusual structural phase transitions that predominate in the class of colossal magnetoresistive materials. For both sets of magnetic oxides, particularly the manganites, an important feature is the relatively good structural match to PZT and/or BST and better electrical properties in comparison to metallic alloys.

In studies to date, however, it is quite clear that one must have very good control of the FE/FM interface to maximize the magnetoelectric coupling. Even for the ferrites, leakage current and cracking issues have reduced observed coupling values below the predicted ones. For the manganites, issues in interdiffusion in pressed bulk films have been responsible for the coupling reduction [27].

As a result of such concerns, a growing body of work has been conducted on more carefully engineered films [28-31] or nanostructures [26, 32] of ferroelectric and ferromagnetic materials. While the initial emphasis of most of this work has been on the impact of the ferroelectric on the ferromagnetic properties, it should be possible to investigate the reverse, particularly for microwave use.

The proposed development of ferromagnetic films capabilities at NASA with a pulsed laser deposition system makes this idea especially attractive. Since pulsed laser deposition is a well-established technique to create films of high quality, it should be possible to improve the magnetoelectric coupling over that observed in work with powdered composites or compressed thick films for microwave applications.

***Recommendation #2*:** **In order to maximize the potential gain achieved by better interfacial control, it is suggested that work focus on the manganites in connection with Ba/SrTiO$_3$ since those materials have the most structural similarities. La$_{1-x}$Sr$_x$MnO$_3$ (LSMO) is particularly attractive due to its higher predicted coupling values over other manganites like La$_{1-x}$Ca$_x$MnO$_3$ or Pr$_{1-x}$Ca$_x$MnO$_3$ [27, 31].**

4) Extrinsically uncoupled ferroelectric and ferromagnetic materials:

To this point, this study has focused on materials in which ferroelectric and ferromagnetic properties are either intrinsically or extrinsically coupled, such that we can envision tuning the ferroelectric properties with not only an electric field as is standard but also with a magnetic one.

However, some advantages for microwave applications can also be achieved assuming NO coupling between the two materials and perhaps explicitly separate control might be better. In using a ferroelectric material as a phase shifter, one issue that leads to loss is the change in the associated impedance (Z) as a result of changes in the electric field (to shift the phase). To get around this loss, it has been suggested that if one could at the same time as changing the capacitance (or permittivity) with a ferroelectric material, change the inductance (or permeability) with a ferromagnetic one, one could keep the impedance matched, hence minimizing insertion loss [33-36].

Several experiments have been conducted along these lines to demonstrate aspects of the feasibility of such an approach [33-36]. In the case of [36], which is the furthest along, it has been shown that by combining Ba/SrTiO$_3$ used in the traditional way as a ferroelectric phase shifter and La/SrMnO$_3$ used as ferrite materials typically are, one can increase the tunability and reduce the variation in Z in comparison to just using Ba/SrTiO$_3$. However, there is an important disadvantage to this approach, in that there is a significant amount of patterning that must be done, with regards to the manganite material (as it is used as an inductor). Hence, one of the main advantages of using a ferroelectric material—its simplicity in fabrication—has been removed. In other experiments, the ferromagnetic component has not been patterned [33-35], but it is less clear what the end result is in terms of overall structure performance (effect on Z, etc.)

Recommendation #3: **Given these issues, it would be of significant interest to determine the Z in relatively *unpatterned* structures-with better ease of use. Note that this in some respects can be considered an extension of work on extrinsically coupled ferroelectric/ferromagnetic films as described in section 3) on LSMO/BST films. By varying growth conditions, the interfaces between the two can be modified, resulting in**

differences in coupling. Such experiments would allow us to assess whether high coupling (and a more all-in-one approach to tuning) is more effective than essentially separate components.

5) Assessment of Oberlin College equipment for materials characterization:
Structural characterization:

In preparation for further experimental research regarding ferroelectric/ferromagnetic materials, we have also conducted some structural measurements using a Philips MPD-3040 powder x-ray diffractometer and a Sloan Dektak II profilometer, both at Oberlin College. We have found that the equipment are adequate to provide basic characterization, although currently not capable of further detail.

Specifically, work focused on a portion of a wafer of Ba/$SrTiO_3$, which had already been characterized previously in conjunction with a large study of ferroelectric film quality for microwave applications [3]. In that work, for wafer #3, the lattice constant perpendicular to the film plane was found to be 3.960 Å at the center and 3.965 Å at the film edge, with a full width at half maximum (FWHM) of ~0.1° at the (002) peak. An in-plane lattice constant was also determined by diffraction. Ellipsometry was used to measure a film thickness varying from ~3300 Å (1/4" from the edge) to 3700 Å (at the center).

With the powder diffractometer at Oberlin, eleven different scans were taken at seven different positions on a quarter of wafer #3 (as identified in reference [3]) to measure features perpendicular to the plane of the film, as the in-plane feature can not be scanned with this configuration.

Based on only the (002) peak, lattice parameters for the film were calculated at different locations, with values of 3.960 Å at the center and 3.965 Å at the edge, in excellent agreement with previous results. However, this agreement is also somewhat fortuitous; repeated measurements of the same position revealed an associated uncertainty on the order of that difference. Overall, considering all three (00l) reflections for the film (in the range of 10-70° in 2θ) and the different positions on the wafer, an average value of 3.958 Å was obtained with an uncertainty of ~ 0.002 Å. It is most likely not possible to distinguish amongst different values throughout wafer, either because the spot size of the x-ray beam might not have been sufficient to constrain it-or the differences might have been simply too small.

The FWHM for the (002) peak was found to be ~0.15°, slightly above the reported value of ~0.1°. The discrepancy might stem from some issues associated with the cleavages. It was found that scans at the cut edges were sometimes distorted, partly due to a geometry issue in the measurement of the wafer.

To determine the thickness of the film, we used a Sloan Dektak II profilometer to measure the step at the edge of the film as opposed to doing an ellipsometry experiment. We obtained a value of ~7500 Å, which is significantly larger than the 3500 Å from ellipsometry. Note that any overlayers and any shimming on the edges of the substrate would have increased our thickness values from the ellipsometry value. Hence, it is difficult to assess how useful the profilometry method might be. Nevertheless, as it is very quick, it might be of import in gross characterization of film quality.

To obtain further information about the film such as its interfacial roughness, we have begun to look into x-ray diffraction measurements at low angle. X-ray reflectivity is now a well-established method to get information about film thickness, surface roughness, and compositional differences [37]. In order to obtain high quality reflectivity data, however, it is necessary to pay close attention to alignment issues as well as geometrical factors [38]. Additional stages have been purchased to facilitate a better sample positioning. A test multilayer sample from Philips has been used to investigate reflectivity on the powder diffractometer. A new upgrade to the software has been installed to augment the analysis capabilities. In principle, it will allow for a better characterization of interfacial quality—a particularly important feature, given the previous discussions on the impact on magnetoelectric coupling.

Magnetic characterization:

In examining the existing literature for multiferroics, we can see a range in the magnetic properties associated with the materials. We note that while some clearly require very low temperature and high sensitivity such as in the case of investigating RMn_2O_5 materials [15], a significant number can be studied with less precision [cf. for instance, ref. 8, 22, 35]. At Oberlin, we have a Lakeshore VSM with a sensitivity of ~ 10^{-5} emu and a temperature range from 4-1273 K. This should be adequate to investigate the proposed materials.

6) Summary:

In summary, materials with both ferroelectric and ferromagnetic properties do appear to be promising for enhanced microwave devices. It is suggested that further work be conducted with the multiferroic $BiFeO_3$ as well as with thin films of the ferroelectric $BaSr/TiO_3$ combined with the ferromagnetic $La/SrMnO_3$ manganite perovskite.

Existing equipment at Oberlin College should be sufficient to provide some good insight into basic structural and magnetic properties. In addition, the improved sample stage and software tested in the last months of this grant should enhance the structural characterization of interfacial quality-a feature that may be critical for this work, due to its effect on magnetoelectric coupling.

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Table 1: Multiferroics of current interest

Compound	**Ferroelectric T_c in K**	**Magnetic T_c or T_n**	**Reference #**
$BiFeO_3$	1103	643 (canted AFM)	8-11
$BiMnO_3$	450, 750 (true transition)	100 (FM)	12-14
$HoMnO_3$	875	75 (AFM), 4 (FM)	15
$Pb(Ta_{0.5}Fe_{0.5})O_3$	220-270	133-180 (AFM)	16
$Pb(Nb_{0.5}Fe_{0.5})O_3$	380	150, 9 (AFM)	17
(Tb, Gd, Eu) Mn_2O_5	30's	20-40 (AFM)	18-19
$YMnO_3$	570-990	70-130 (AFM)	20

Table 2: Ferromagnetic materials of current interest in extrinsically coupled systems.

Class	**Examples**	**Magnetostriction, ppm***	**References**
Terbium alloys	Terfenol, $TbFe_2$ Terfenol-D, $Tb_{1-x}Dy_xFe_2$	~ 1000-2000	22
Ferrites	MFe_2O_4, M=Ni, Co, Li, Cu $Y_3Fe_5O_{12}$	~20-40	23-26
Manganites	$La_{1-x}Sr_xMnO_3$ $La_{1-x}Ca_xMnO_3$ $Pr_{1-x}Ca_xMnO_3$	<20-30	27-32

* Actual value depends on orientation, temperature, etc…