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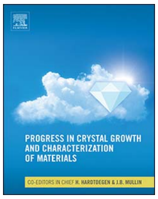

# Synthesis and characterization of electrical features of bismuth manganite and bismuth ferrite: effects of doping in cationic and anionic sublattice: Materials for applications

A. Molak[a,*], D.K. Mahato[b], A.Z. Szeremeta[a]

[a] Institute of Physics, University of Silesia, 75 Pułku Piechoty 1, 41-500 Chorzów, Poland
[b] Department of Physics, National Institute of Technology Patna, Patna, 800 005 Bihar, India

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ABSTRACT

The electrical, magnetic, and structural features of bismuth manganite (BM), e.g., $BiMnO_3$, and bismuth ferrite (BF), e.g., $BiFeO_3$, are reviewed. Induced multiferroicity and enhanced magnetoelectric coupling are required for various modern device applications. BM and BF were synthesized using standard high-temperature sintering and processes such as sol–gel, hydrothermal, or wet chemical methods combined with annealing. The size and morphology of the nanoscale particles were controlled, although they were usually inhomogeneous. BF exhibits structurally stable antiferromagnetic (AFM) and ferroelectric (FE) phases in wide temperature ranges. Ferromagnetic (FM) order was induced in a thick shell around the AFM core of the nanoscale BF particles, which was attributed to a size effect related to surface strains and disorder. BM exhibited both structurally stable and unstable phases. The $BiMnO_3$, $Bi_{12}MnO_{20}$, and $BiMn_2O_5$ structures are nonferroelectric. The perovskite $BiMnO_3$ form was synthesized under high hydrostatic pressure. FM order occurs in BM at low temperatures. $Bi(MnFe)O_3$ solid solution samples exhibited competition between AFM and FM ordering. Doping can decrease the content of unavoidable secondary phases. Doping in the Bi ion sublattice can stabilize the crystal lattice owing to local strains caused by the difference in ionic radius between Bi and the dopant. Doping in the Fe and Mn sublattices affects the electrical features. The main achievement of substitution with tetra- and pentavalent ions is compensation of the oxygen vacancies. In turn, leakage current suppression enables switching of FE domains and polarization of the samples. A significant enhancement of magnetoelectric coupling was observed in composites formed from BF and other FE materials. The leakage currents can be diminished when an insulator polymer matrix blocks percolation. The potential applicability is related to enhanced magnetoelectric coupling. The constructed devices meet the size effect limitations for FE and FM ordering. Resistive switching suggests possible use in nonvolatile memories and gaseous sensors. The sensors can be used for hydrophones and for photovoltaic and photoluminescence applications, and they can be constructed from multiphase materials. Bulk multiferroic solid solutions, composites, and nanoheterostructures have already been tested for use in sensors, transducers, and read/write devices for technical purposes.

## 1. Introduction

### 1.1. Bismuth ferrite and bismuth manganite as potential multiferroics

Bismuth ferrite (BF), e.g., $BiFeO_3$, and bismuth manganite (BM), e.g., $BiMnO_3$, are attracting attention as potential multiferroic (MF) functional materials. The term multiferroics describes materials that exhibit at least two types of order in the same phase. The coexistence of ferroelectric (FE), ferroelastic (FEL), and ferromagnetic (FM) order is of particular interest. Moreover, antiferroelectric (AFE), antiferromagnetic (AFM), spiral ferroic, and ferrotoroidic order are also considered. Coupling between electric and magnetic ordering makes it possible to control the magnetic state with an electric field and the electrical parameters with a magnetic field. Moreover, the electric and magnetic fields can mutually switch the ordered domains and even trigger phase transitions. Use of the electric field for manipulation is easier and more desirable because of the low power consumption, mass, and volume of power supplies. Materials showing sufficient magnetoelectric (ME) coupling are in demand. Significant effects can be expected for interaction between FE and FM subsystems, either direct or at least strain-mediated [1–4].

The perovskite BF, $BiFeO_3$, is a unique single-phase material that

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* Corresponding author.
*E-mail address:* andrzej.molak@us.edu.pl (A. Molak).

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shows AFM, FE, and FEL order over a wide temperature range far above room temperature. It exhibits weak MF coupling because of the AFM ordering. Bulk BM, $BiMnO_3$, is nonpolar, and it shows the required FM order at low temperatures. However, it may still be possible to design functional devices using tuned BF and BM compounds. The occurrence of several stable and metastable phases was reported for various compounds derived from BF and BM. For instance, thin layers of BM showed FE ordering, most likely to be resulting from strains appearing at interfaces. Doping could also affect the crystal lattice structure and ordering of BF and BM samples. For example, ion doping induced a weak FM phase in BF. Therefore, it would be possible to induce the FM and FE states by choosing appropriate synthesis conditions and adequate doping, in combination with the size effect. Consequently, the conditions for sufficiently strong MF coupling should be studied.

### 1.2. Functionality of multiferroics

The coexistence of magnetization and polarization in an MF material allows the material to exhibit bifunctional features. The ME effect is attracting attention because the mutual influence of the magnetic and electric subsystems suggests technological applications. This effect can be observed in single-phase materials, which show coupling between the magnetic and electric order parameters. Moreover, they can be obtained in composite MF materials, in which the ME features correspond to combinations of magnetostrictive, piezomagnetic, electrostrictive, and piezoelectric compounds. MF materials are studied mainly for their applications in spintronic devices and nonvolatile memory elements.

FE materials show tunable electrical, opto-electrical, and electromechanical features and finite size effects. Their spontaneous polarization, which is switchable in an external applied field, implies numerous applications. For instance, FE polarization is used to encode binary information in ferroelectric random access memories (FeRAMs), which are commercially available.

FM materials exhibit spontaneous magnetization, which finds applications in spintronics and magnetic storage. For example, magnetic random access memories (MRAMs) are proposed for use as nonvolatile memory elements. Although MRAMs show high density, they are still under development to achieve better stability before commercial use. One of the drawbacks of MRAMs is related to the energy-consuming currents needed to switch the spins.

It seems that low power consumption, a crucial characteristic of nanodevices, can be achieved when the write and read procedures are based on application of a voltage and not of a current. Hence, the use of single-phase FE–FM multiferroics provides low energy consumption, as the electric polarization, which is related to the FE component, is switched by an applied voltage, and in turn, ME coupling makes it possible to control the magnetic subsystem by the electric subsystem. A similar effect can also be obtained also in composite materials by effects mediated by the strains emerging at interfaces, i.e., in a combination of electrostrictive (or piezoelectric) and magnetostrictive (or piezomagnetic) materials. Therefore, ME coupling affords possibilities for the design of magnetoelectric random access memories (MERAMs) [5,6].

AFM materials might also be applied in spintronic elements because the AFM ordering exhibits sensitivity to the spin configuration. Moreover, they provide faster spin and magnon responses than FM systems.

FEL materials exhibit a spontaneous strain that is switchable under an applied stress; i.e., either a different orientation phase or a different crystal structure can be induced. The applicability of superelasticity and the shape-memory effect are considered. Moreover, the induced strain can affect the AFM order, magnon dynamics, and magnetoresistance.

Leakage currents and energy dissipation do not originate solely from the low activation energy of charge carriers, which is related to the narrow energy gap in the electronic structure of BF and BM. The currents are enhanced by the charges generated from oxygen vacancies, which are nearly inevitable when standard technology is used. Moreover, the marked leakage current disables spontaneous polarization switching. Therefore, the electrical properties should be tuned by intentional doping, which would provide charge compensation and increased resistivity.

Other characteristics related to FE ordering, namely, the occurrence of FE domains and domain walls, screening, aging and memory effects, and the volume ratio of the FE and other phases, can affect the FE features on the micro- and nanoscale [7,8]. The multiple roles of domain walls and interfaces have been noted, e.g., enhanced electromechanical response due to strains [9]. Moreover, mixed-phase structures resulting from spinodal instabilities can also produce the required piezoelectric strains in heterostructures. The occurrence of charged defect migration toward FE domain walls can lead to electrical conductivity along the formed vortices [10,11]. The elastic interactions depend on residual strains caused by defects, extended defects such as dislocations and glide planes, grain boundaries, and clamping effects. Hence, the effective coupling can be reduced in structurally disordered materials [7,9,12]. The electric ordering is also coupled to the subsystem of defects via nonlinear strain−stress interaction [13]. The strains and elastic fields can change the magnetic order anisotropy via magnetoelastic interaction that affects the magnetic moment. Moreover, magnetic domain walls, residual strains, pinning on defects, and structural disorder may reduce the average magnetization [7,14].

On one hand, it is worth noting that BF and BM are also studied for their applications in gas sensors, resistive switching elements, and photovoltaic devices. On the other hand, these applications are more likely related to spontaneous polarization switching and the resistance response, and not to ME coupling effects.

### 1.3. Methods of synthesis of BF and BM compounds

Several classical methods are used to produce BF and BM samples. Bulky ceramics are obtained from oxides using standard high-temperature sintering. Ceramic pellets are also obtained from nano- and micro-powders obtained by several other methods, e.g., wet chemistry techniques. Hence, the idea of forming multiferroics seems to be straightforward. However, design and production of the desired features are complicated, and achievement of these goals in experiments is difficult. It has been reported that the real microstructure of the samples affects the actual ME coupling.

BF, which shows stable MF features, was obtained using the high-temperature route in air at ambient pressure. This procedure might result in nonstoichiometric products owing to evaporation of the bismuth oxide. Mechano-activation provided much better overall stoichiometry; however, an amorphous phase could appear as a side effect. Wet chemistry methods were more effective. The modified Pechini and hydrothermal syntheses from nitrates, the auto-combustion technique, and the sol–gel technique usually yield the main phase accompanied by impurity phases. Annealing could change their relative content. Note that these impurity phases introduce weak FM ordering, which is required to enhance the ME coupling.

The crystalline perovskite BM form could be effectively sintered under high hydrostatic pressure. However, this perovskite structure of BM is unstable at high temperatures. Two other centrosymmetric phases in equilibrium coexisted when BM was sintered under ambient pressure in air at high temperature. Nano- and micro-sized particles were obtained by low-temperature processing using a hydroxide gel, a hydrothermal procedure, and mechanosynthesis. However, clear FE order was not induced, and disordered or amorphous shells surrounding the particles suppressed the magnetic order.

Ions doped to the Bi sublattice could compensate for oxygen deficiency and suppress transient currents. Such doping enhanced the ME coupling and enabled detection of electric polarization loops in BF. In BM, Bi sublattice doping induced FM clusters that are stable at high temperatures. However, these effects did not always appear.