

Variation in Magnetic Behaviour of Multiferroic Materials for Spintronics

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ABSTRACT

Multiferroic materials show simultaneous ferroelectric and magnetic ordering, exhibit unusual physical properties — and in turn promise new device applications — as a result of the coupling between their dual order parameters. Room-temperature multiferroics are a promising route to design magnetic/electric memories. Over the past decade, there has been a revival of interest in understanding the magnetoelectric coupling due to its possible applications to multifunctional ferroic devices. This is an important step towards controlling magnetization with electric fields, which may enable a new class of electrically controllable spintronic devices and provide a new basis for producing electrically controllable spin-polarized currents. In this paper we review the study of multiferroic materials and focus on the effects of different synthesis methods & doping on their magnetic properties.

Keywords: Multiferroic, magnetoelectric, spintronic and magnetic.

1. INTRODUCTION

Multiferroic materials exhibit simultaneous ferroic properties such as ferroelectricity, ferromagnetism, and ferroelasticity with coupled electric, magnetic, and structural order parameters. Multiferroics materials are of interest because of their potential applications in information storage. The coupling between magnetism and ferroelectricity could be exploited to induce electrical polarization by the application of magnetic fields, and vice versa. BiFeO₃ is a Multiferroic material showing significant promise for future spintronic device applications. The term “spintronics” has come to mean any application of the spin of the electron and is thus dominated by sensor applications for hard-disk read-out. In its original definition, of a development of semiconductor electronics in which the spin could provide additional functionality Multiferroic composite structures in bulk form are explored for high-sensitivity ac magnetic field sensors and electrically tunable microwave devices such as filters, oscillators and phase shifters (in which the ferri-,ferro- or antiferro-magnetic resonance is tuned electrically instead of magnetically). An intense revival and there turn of multiferroicity to the forefront of condensed matter research has been triggered by the invention of a number of frustrated magnets, like manganite rare earths, i.e., RMnO₃, RMn₂O₅ or Ni₃V₂O₈, which are characterized by strong spin frustration due to competing exchange interactions. BiFeO₃ is one of the few materials, along with YMnO₃ and BiMnO₃, that have all the potential applications of both their parent ferroelectric and ferromagnetic materials. Recently, partial substitution of Bi³⁺ ions by lanthanides has been shown to improve ferroelectric properties and magnetization¹, Zhang et al.² and Das et al.³ suggested that La³⁺ substitution for Bi³⁺

eliminates impurity phases and destroys the cycloidal spin structure resulting in uniform canted antiferromagnetic ordering. Zhang et al.² also reported that the structure changes from rhombohedral to orthorhombic at 30 mol% La. In the studies on dopant effects of Sm reported by Nalwa et al.¹ and Yuan⁴ and those of Nd reported by Yuan et al.⁵ in BiFeO₃, changes in the crystal structure of the material were observed, which resulted in improved piezoelectric properties, long-range ferroelectric and canted antiferromagnetic orders. Uniyal and Yadav⁶ claimed on the other hand, that 10 mol% Gd substituted for bismuth in the sample compound did not change the crystal structure but only reduced the volume fraction of impurity phases, while decreasing the Neel temperature T_N to ~150°C from 370°C, and enhancing the magnetization to the extent of allowing the generation of the ferroelectric hysteresis loops⁶. These phenomena also give rise to unusual dynamical effects, which can be observed in optical experiment which offers the means for elucidating of the driving mechanism of the ferroelectric transition and, eventually, its coupling to magnetic ordering⁷.

Several recent discoveries of unusually strong coupling between the ferroelectric (FE) and magnetic order parameters have revived interest in the magnetoelectric effect. Due to the possibility of easily controlling the electric properties using magnetic fields, a class of compounds, in which the magnetic order is incommensurate with the lattice period, is particularly interesting for future applications. Surprisingly, this class of multiferroic materials includes compounds with very diverse crystallographic structures: the perovskite RMnO₃ (R=Gd, Tb, Dy)⁸⁻⁹, orthorhombic RMn₂O₅ (R=Tb, Ho, Dy)¹⁰⁻¹¹, hexagonal Ba_{0.5}Sr_{1.5}Zn₂Fe₁₂O₂₂¹² and kagomé staircase Ni₃V₂O₈¹³. At present, the search for the new multiferroics is being carried out not only among inorganic but also among organic and organometallic compounds.

Multiferroic materials are rare in nature because the physical/structural/chemical conditions for a material to display simultaneously more than one of (anti)ferromagnetism, (anti)-ferroelectricity, and ferroelasticity are generally difficult to be achieved. Especially, ferroelectricity requires that the crystal structure be non-centrosymmetric and the ferroelectric transition is directly related to the structural phase transformation. Therefore, in such intriguing multiferroics, structural characterizations are extremely important. The experimental search for such robust room-temperature multiferroics is proving a major challenge.

2. EFFECT OF METHODS OF SYNTHESIS ON THE PROPERTIES OF MULTIFERROICS

In order to understand the properties of multiferroics like BiFeO_3 and other such samples, it is very important to establish a synthesis procedure in a manner such as to avoid impurity phases. There are several reports on the synthesis of BiFeO_3 . Recently, BiFeO_3 ceramic samples have been synthesized by methods like pulsed laser deposition, sol-gel, solid state reaction simple precipitation rapid liquid phase sintering chemical solution deposition and high-energy ball milling.

The magnetic properties of BiFeO_3 have been improved significantly by chemical manipulations. One of the important goals in multiferroics is to establish a strong coupling of magnetic ordering at room temperature, which can be achieved by chemical substitutions at both the Bi and Fe sites¹⁴. Low-temperature manufacture methods referred to as “soft chemistry”, such as the Pechini method, produce more homogeneous, purer, and more reproducible phases whose microstructure and morphology may be controlled practically at will¹⁵. These aspects play a major role in determining the overall electronic, optical, magnetic and catalytic properties, as well as the applicability of multiple-oxide materials.

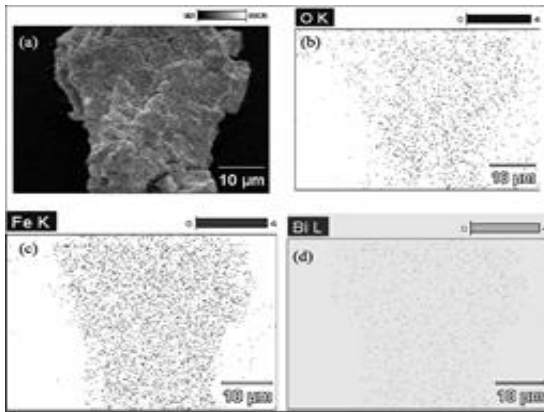


Fig.1(a) Microparticle micrograph. (b), (c), and (d) are O(K), Fe(K), and Bi(L) EDS mappings, respectively. [43]

Most of the investigations on low-dimensional BiFeO_3 focus on thin films, there are some reports on BiFeO_3 nanoparticles produced by hydrothermal synthesis, sol-gel process, or microwave synthesis¹⁶ and BiFeO_3 nanowires synthesized using alumina templates.¹⁷ These studies mainly concern photocatalytic properties of BiFeO_3 because of its small band gap, and the multiferroic properties of nanoparticles and nanowires have not been reported. Sol-gel based electrospinning^{18, 19} offers an attractive alternative to synthesize long BiFeO_3 ultrafine fibers in large quantities that are easier to collect and characterize.

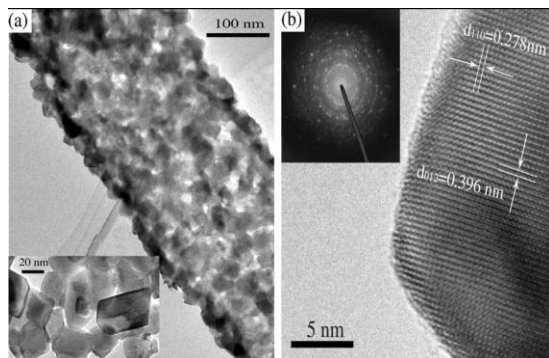


Fig.2(a) TEM image of an ultrafine BiFeO_3 fiber with magnified local image in the inset. (b) HRTEM image of an ultrafine BiFeO_3 fiber with SAED pattern in the inset.

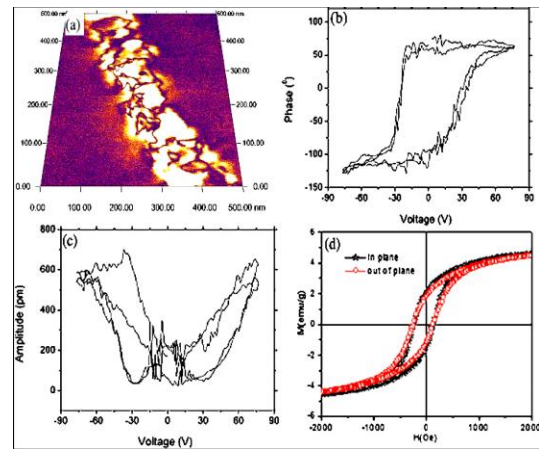


Fig.3 Multiferroic properties of ultrafine BiFeO_3 fiber. (a) PFM amplitude image. (b) PFM phase-voltage hysteresis loop. (c) PFM amplitude-voltage butterfly loop. (d) VSM magnetic hysteresis loop.

Recently, Single phase BiFeO_3 ceramic samples have been synthesized by rapid liquid-phase sintering technique²⁰. These ceramic samples show relatively high resistivity and saturated ferroelectric hysteresis loops at room temperature and could be useful for potential applications. For electronic materials and other applications such as optics, catalysis and thermomechanics, the precise control of the manufacturing process is always crucial, because many physical properties depend on the manufacturing process closely

3. EFFECT OF DOPING ON THE PROPERTIES OF MULTIFERROICS

BiFeO_3 has some inherent problems. In BiFeO_3 , magnetic ordering is of antiferromagnetic type, having a spatially modulated spin structure with an incommensurate long-wavelength period of 62 nm which cancels the macroscopic magnetization and also inhibits the observation of the linear magnetoelectric effect⁴². In addition, the bulk BiFeO_3 is characterized by serious current leakage problems due to the existence of a large number of charge centres caused by oxygen ion vacancies and Bi_2O_3 evaporation during sintering process which makes it difficult to achieve high resistivity. These problems limit the use of BiFeO_3 for fabrication of multifunctional devices. In order to overcome these problems, many attempts have been made recently, which include by minor substitution of Bi^{3+} by ions such as Dy^{3+} [21], Sm^{3+} [22], La^{3+} [23], Nd^{3+} [24], Gd^{3+} [25], Y^{3+} [26], Ca^{2+} , Sr^{2+} , Pb^{2+} , Ba^{2+} [27], by minor substitution of Fe^{3+} by ions such as Cr^{3+} [28], Co^{3+} [29], Mn^{3+} [30-31], Ti^{4+} [32], or by simultaneous minor substitution of Bi^{3+} and Fe^{3+} by ions such as La^{3+} and V^{5+} , respectively [33].

Multiferroic $\text{Bi}_{1-x}\text{Y}_x\text{FeO}_3$ ($x=0.00, 0.05, 0.1, 0.15, 0.2$) ceramics were prepared by conventional solid-state reaction method. The substitution of rare earth Y for Bi was found to decrease the impurity phase in BiFeO_3 ceramics. The effect

of introducing Y^{3+} is shown to increase the optical band gap for doped sample $Bi_{1-x}Y_xFeO_3$. The enhancement of magnetization was observed in Y-doped samples compared to pure $BiFeO_3$.³⁴

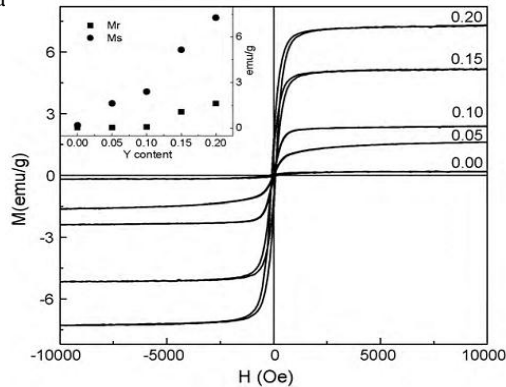
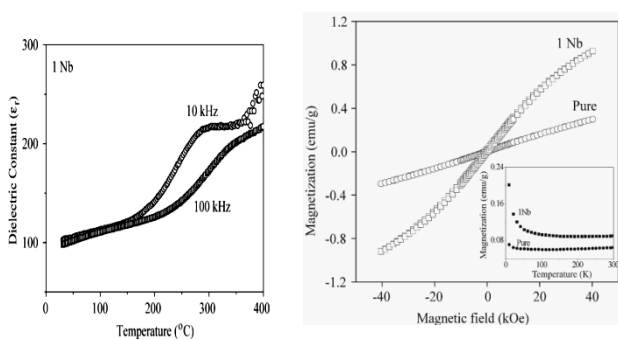


Fig.4 Magnetization vs. magnetic field of $Bi_{1-x}Y_xFeO_3$ samples with $x = 0.00–0.20$. The inset is the saturation magnetization (M_s) and remanent magnetization (M_r) vs. Y content.

Nb-doped $BiFeO_3$ polycrystalline ceramics were synthesized by a solid-state reaction Nb-doping increased the electrical resistivity of $BiFeO_3$ by approximately six orders of magnitude, which allowed the dielectric properties to be determined at room temperature. The room temperature dielectric constant was ~ 100 and the electric hysteresis loops were not really saturated in the Nb-doped $BiFeO_3$ ceramics. Nb-doped $BiFeO_3$ also showed a ferromagnetic-like behavior with $M_r = 0.015 \text{ emu/g}$ and $H_c = 500 \text{ Oe}$, which is similar to the solid solution system of $BiFeO_3$ and $BaTiO_3$.³⁵

Fig.5 Temperature dependence of the dielectric constants for 1 mol% Nb-doped $BiFeO_3$ measured at 10 and 100 kHz and Magnetization versus magnetic field hysteresis loops for Undoped and 1mol% Nb-doped $BiFeO_3$ at 5K



It is shown that Ca^{2+} doping at Bi-site results in the release of weak ferromagnetism in $BiFeO_3$. Structural transformation from rhombohedral to triclinic is observed with 10% Ca doping. The observed weak ferromagnetism and ferroelectric nature at room temperature indicated the multiferroic nature of $Bi_{1-x}Ca_xFeO_3$ ($x=5\%$ and 10%) samples.³⁶

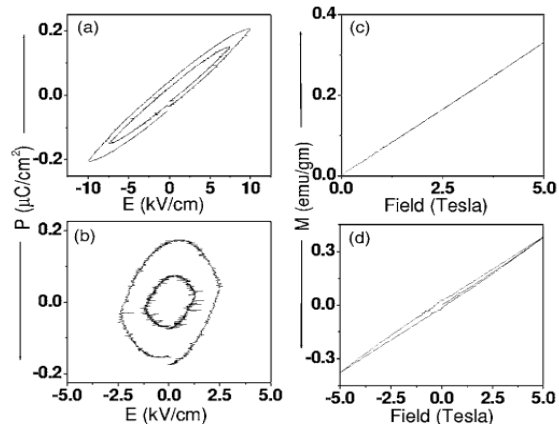


Fig.6 (a) and (b) shows P-E hysteresis loops. (c) and (d) show room temperature M-H curves of Ca0 and Ca10 samples, respectively.

The multiferroic compounds $Bi_{0.9}Sm_{0.1}FeO_3$ (BSFO), $Bi_{0.9}Gd_{0.1}FeO_3$ (BGFO), $Bi_{0.9}Ca_{0.1}FeO_3$ (BCFO), $Bi_{0.9}Sm_{0.05}Ca_{0.05}FeO_3$ (BSCFO), and $Bi_{0.9}Gd_{0.05}Ca_{0.05}FeO_3$ (BGCFO) were prepared by the conventional ceramic method. The improvement of magnetic behavior of the Gd-containing compounds is thought to arise mainly from the partial suppression of the spiral spin structure and the stronger interaction between magnetic ions. The magnetic transition temperatures of the compounds were found to be in the range $300–310^\circ\text{C}$.³⁷

Table1 Some magnetic parameters of the studied compounds.

	M_r (emu/g)	H_c (Oe)	T_N ($^\circ\text{C}$)
BSFO	7.8×10^{-3}	257	310
BGFO	1.3×10^{-2}	351	305
BCFO	5.6×10^{-3}	173	310
BSCFO	3.6×10^{-3}	131	305
BGCFO	2.9×10^{-2}	207	300

Multiferroic $Bi_{1-x}Ca_xFeO_3$ was prepared by sol-gel method with the rapid thermal process. The remanent polarization and magnetization of $Bi_{0.7}Ca_{0.3}FeO_3$ ceramics are $4 \mu\text{C}/\text{cm}^2$ and 0.153 emu/g , respectively.³⁸ Li et al.³⁹ have shown that Sr doping (at the Bi site) resulted in samples being oxygen sub-stoichiometric, and with increasing Sr concentration, transition to a $SrFeO_3$ phase accompanied by a decrease in magnetization. Khomchenko et al.⁴⁰ have observed similar behaviour in Ca and Ba-doped $BiFeO_3$ samples without any enhancement in magnetization. On the other hand, Pb^{2+} doping in $BiFeO_3$ showed weak ferromagnetism with an increase in magnetization.⁴⁰

Bucci had earlier prepared $BiCo_{1-x}Fe_xO_3$ and indicated a limiting value of 0.64 for x to obtain single phase material. Vasudevan had also synthesized $BiCo_{1-x}Fe_xO_3$. Band confirmed that sample of $BiCo_{1-x}Fe_xO_3$ ($x \leq 0.7$) show complex magnetic behavior.⁴¹ The magnetic behavior of sample with $x < 0.1$ is similar to that of $BiCoO_3$. When $0.1 \leq x \leq 0.2$, the sample show a slight field dependence of susceptibility. The samples with $0.5 \leq x \leq 0.7$ are ferromagnetic at room temperature. Magnetic hysteresis measurements behaved a value of 79.6 Oe for saturation magnetization in the $x = 0.7$ sample. When $x > 0.7$ were found to be biphasic. Therefore, it is worth while to experimentally investigate the effect of the substitution of Co

for Fe on the physical properties of BiFeO₃. Doping with transition metals has been proved to be very effective in improving the ferroelectric property of samples through improving their insulating property. However, information on how the magnetic properties are modified by the transition metal doping is very inadequate. Further investigation of the magnetic enhancement in these doped BiFeO₃ systems is warranted.

4. CONCLUSION

This review is an attempt to cover as fully as possible the existing variety of multiferroics and briefly describe those that are of most interest as regards the mechanism of origination of the coupling between the electric and magnetic types of ordering. The crystal chemical features of these materials and the methods for their synthesis are considered. The multiferroic subject is tightly connected with complex, often poorly studied, physical processes in crystals; therefore, it was necessary to consider the characteristic physical properties of these compounds. It is reasonable to expect that new multiferroics and new physical mechanisms of interaction of magnetic and ferroelectric orderings will be discovered in the future. As far as applications are concerned, multiferroics have a great potential in spintronics using the magnetoelectric effect to control a magnetization with an electric field. In the field of spintronics the spin of an electron, rather than (or in addition to) its charge is used to carry information. Spintronic devices, therefore, can retain information without an applied electric current (i.e. are non-volatile) and so have a much lower power consumption than typical charge-based devices. Spintronics could theoretically be used for magnetic random access memory (MRAM). The ability to change the magnetisation state of a sample with an applied electric field would mean that less power is used, and so multiferroic materials could prove to be very important to this field. Despite lots of new ideas and achievements that appeared in recent years in the field of design of composite multiferroics, many challenges are still waiting to be solved, in particular some fundamental problems.

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