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A Topical Review on Magnetoelectric Composite

Rajnish Kumar[1] and ManoranjanKar[1]

[1]Indian Institute of Technology Patna,
Patliputra Colony, Patna
Email: mano@iitp.ac.in

ABSTRACT

Multiferroic materials exhibits at least two properties among ferroic parameters i.e. ferroelectricity, ferromagnetism, and ferroelasticity. Single phase materials which show at least two ferroic properties at a time are very rare. This is because in most ferroelectrics, the mechanism is due to hybridization of empty d-orbital of metal ion and occupied p-orbital of the oxygen ion, causing lack of multiferroic phenomenon. Multiferroics are also magnetoelectric material, in which the phenomenon of coupling between ferroelectric and magnetic order coexist which has a potential application in memory devices, sensors, actuators etc. Recent research activities of manipulating electric field by magnetic field will be discussed. Beginning with the history of Magnetoelectric (ME) effect, limitations of single phase Magnetoelectric compound and need of ME compositesis discussed. Few important works of laminate composite is also discussed. Finally the review ends with proposed applications of ME composites following with some future perspectives.

INTRODUCTION

Multiferroic materials are those materials which simultaneously show at least two properties among ferroic parameters i.e. ferroelectricity, ferromagnetism, and ferroelasticity [1]. Single phase materials which show at least two ferroic properties at a time are very rare. This is because in most ferroelectrics, the mechanism is due to hybridization of empty d-orbital of metal ion and occupied p-orbital of the oxygen ion, causing lack of multiferroic phenomenon. Multiferroic are also known as magnetoelectric material, in which the phenomenon of coupling between ferroelectric and magnetic order coexist which has a potential application in memory devices, sensors, actuators etc. This has encouraged the scientific community to search the subject deeply.

The magnetoelectric effect due to its remarkable ferroelectric and ferromagnetic phenomena has become centre of enthusiasm for research among scientific community. Due to the requirement of large coupling between electrical and magnetic phase in comparison with single phase, laminate composites has attracted great deal of attention recently. Historical perspective, review of the prominent works related with ME effect of last few years observed in materials ranging from bulk composite to thin film laminate composite and proposed applications are discussed in upcoming sections.

Historical Perspective

ME materials are the materials which contain ferroelectric and ferromagnetic orders simultaneously. The credit to observe magnetoelectric effect in 1888 goes to Roentgen [2]. Debye gave the term “Magnetoelectric effect” in 1926 and after sixty years Astrov et al. and V.J. Folen et al. demonstrated experimentally the electric field induced magnetization and vice-versa in Cr_2O_3 (antiferromagnetic material) [3]. After the first observations of ME effect experimentally [3-4], it led to a lot of excitement for research in this area. Few years of the theoretical as well as experimental works in this area was summarized in a book by O’Dell [5] and a conference on "ME interactions and phenomenon in Crystal in 1973 (MEIPIC-1, Seattle, USA, 21-24 may1973)". But, the limited number of compounds showing ME effect, lack of understanding of microscopic origin and difficulty in applications led to fall in the research activity. However the research activity in this field again rising due to increasing understanding of the origin of the phenomenon leading to a conference on ME interactions and phenomenon in Crystal in 1993 (MEIPIC-2, Ascoma, Switzerland, 13-18 September, 1993). The number of publications by year which shows the growing research on Magnetoelectric effect is shown in table 1.

Table 1. Number of Publications by year (Details can be found from www.scopus.com).

Year	Publications	Year	Publications
1981	9	1999	69
1982	14	2000	146
1983	9	2001	293
1984	8	2002	373
1985	23	2003	405
1986	27	2004	829
1987	38	2005	785
1988	19	2006	632
1989	14	2007	431
1990	31	2008	287
1991	24	2009	234
1992	93	2010	239
1993	54	2011	248
1994	69	2012	188
1995	47	2013	211
1996	57	2014	184
1997	113	2015	4
1998	84		

Magneto Electric Composites

There is intensive research activities have been carried out around 1970's. Efforts were made to design a material with strong magnetoelectric coupling between an electric field and a magnetic field in single-phase compounds [6]. However, it is failed till today. Beside this, in single phase, the magnetic transition temperatures, of both the Curie and Néel temperature are far below the room temperature [7-11]. This was restriction for

Experimentalist to design and fabricate the room temperature single phase magneto-electric materials. This difficulty of observing High ME coupling in a single phase compound is suggested to use two or more single phase compounds in composite structures. The mechanisms of these compounds are a transfer mechanism and indirect coupling through extrinsic mechanical strain.[12]

Depending upon the input and output, magnetoelectric effect in a composite can be broadly classified into two categories. If the input is magnetic field and output is electrical voltage , it is termed as "direct magnetoelectric effect" and it is defined as[12]:

Direct Magnetoelectric Effect=

$$\frac{Electrical}{mechanical} X \frac{Mechanical}{Magnetic} \text{ ……………………..(1)}$$

The above statement simply states that the strain induced by a magnetic field due to magnetostriction of the magnetic phase is passed on to the piezoelectric. This phenomenon results in the induced change of electric polarization.

If the input is Elctric field and output is change in magnetic field , it is termed as "Converse magnetoelectric effect" and it is defined as [12]:

Converse Magnetoelectric Effect=

$$\frac{Magnetic}{mechanical} X \frac{Mechanical}{electrical} \text{ ……………………..(2)}$$

This means that electric field induces mechanical strain in the piezoelectric phase which affects the alignment of magnetization in the piezomagnetic phase.

A systematic study of the ME effect can be studied using the expansion of free energy:

$$F(\vec{E},\vec{H})=F_0-P_i^sE_i-M_i^sH_i-\frac{1}{2}\varepsilon_{ij}\varepsilon_0E_iE_j-\frac{1}{2}\mu_0\mu_{ij}H_iH_j-\alpha_{ij}E_iH_j-\frac{1}{2}\beta_{ijk}E_iH_jH_k-\frac{1}{2}\gamma_{ijk}H_iE_jE_k-\text{....} \text{ …………………(3)}$$

Where E and H as the dielectric and magnetic field respectively. Differentiating Eq. (3), gives polarizations and magnetizations given as [13]:

$$P_i(\vec{E},\vec{H})=P_i^s-\varepsilon_{ij}\varepsilon_0E_j-\alpha_{ij}H_j-\frac{1}{2}\beta_{ijk}H_iH_j-\gamma_{ijk}H_iE_j-\text{....} \text{ ………………….. (4)}$$

$$M_i(\vec{E},\vec{H})=M_i^s-\mu_0\mu_{ij}H_i-\alpha_{ij}E_i-\beta_{ijk}E_iH_j-\frac{1}{2}\gamma_{ijk}E_jE_k-\text{....} \text{ ………………… (5)}$$

Where P^s, M^s, ϵ, μ corresponds to spontaneous polarization, spontaneous magnetization, electric susceptibility, magnetic susceptibility respectively. The tensor α is Linear ME effect.others terminology corresponds to higher order ME effect.

It has been further shown that linear ME effect has been limited by the equation [14]:

$$\alpha_{ij}^2 < \varepsilon_{ij}\mu_{ij} \qquad \text{…………………} (6)$$

Depending on the connectivity schemes, magnetoelectric composites are of the following three types:[12]

(i) 0-3–type particulate composites of piezoelectric and magnetic oxide grains.

(ii) 2-2–type laminate ceramic composites consisting of piezoelectric and magnetic oxide layers.

(iii) 1-3–type fiber composites with fibers of one phase embedded in the matrix of another phase

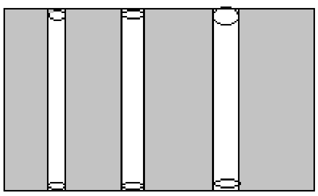
Magnetoelectric voltage coefficient in a composite is larger than the single phase multiferroics which has drawn the research interest on multiferroic composites. The simplest ME composite is 0-3 type particulate composite. However there are certain issues which has limited the ME voltage coefficients of particulate composite below the theoretically expected value. These issues are:

1. Chemical reaction between the piezoelectric and magnetostrictive materials during sintering processes.

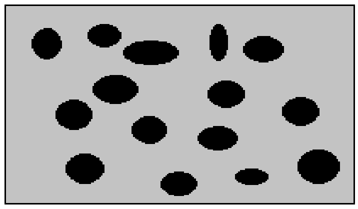
2. Potential developed due to mechanical defects caused by lattice mismatch

Figure 2. Schematic illustration of three bulk composites with the three common connectivity schemes

(a) 0-3 particulate composite



(b) 2-2 laminate composite



(c) 1-3 fibre/rod composite

<u>Review on ME laminate composites</u>

The issues related with particulate composites have been avoided to a greater extent by using laminate composites consisting of ferroelectric and ferromagnetic plates. Ryu et al. [15] have reported the magnetoelectric effect in a laminate composite consisting of Terfenol-D (magnetostrictive material) and a ferroelectric PZT (lead zirconatetitanate, $Pb[Zr_xTi_{1-x}]O_3$ $0\leq x\leq 1$) with magnetoelectric voltage coefficient α = 4680mVcm^{-1}Oe^{-1}. Plate laminate composites were made by combining a Terfenol-D plate and a ferroelectric PZT plate with silver epoxy. N. Cai et al. [16] in 2004 reported multiferroic three phases laminate composite with a Terfenol-D/PVDF composite sandwiched between two layers of PZT/PVDF composite prepared by simple hot molding technique with $\alpha \sim$ 3000mVcm^{-1}Oe^{-1}. S. G. Lu et al [17] observed α=12Vcm^{-1}Oe^{-1} in laminate composite of PVDF-hexafluropropylene-metglass.

While the above discussed reports deals with bulk property measurements, the last few years have seen a giant march towards the research on laminate composite by making thin film (multilayer or bilayer) for enhancing ME coefficient by controlling the nanoscale domain.

Thin film deposition of $BiFeO_3$ (BFO) for ME study has remain centre of attraction due to the required properties at room temperature compared with other counterparts. Wang et .[18] deposited BFO on (100) using ulse laser deposition. enhanced ferroelectric and ferromagnetic property compared with bulk properties. However the enhancement is not smart enough to be employed for technological exploration. So researchers' move was towards laminated thin films composite. Zheng et al.[19] deposited 2-2 laminate composite and 1-3 nanopillar structure of $CoFe_2O_4$ (CFO) and $BaTiO_3$ (BTO) on single crystal $SrTiO_3$ (100). ME coupling was more in the 1-3 nanopillar structure due to reduced clamping effect from the substrate. Liu et al.[20,21] deposited Fe_3O_4 and $Zn_{0.1}Fe_{2.9}O_4$ film on piezoelectric substrate lead magnesium niobate and lead titanate (PMN-PT) demonstrating strong ME coupling. A large ME coefficient of 100 Oe cm/ kV in plane and 68 Oe cm / kV out of plane for the first case and large electric-field induced field shift of up to 140 Oe was observed, corresponding to an ME coefficient of 23 Oe cm/ kV for the second case. Similarly Li et al.[22] have studied thick film of $NiFe_2O_4$ (NFO) on PMN-PT substrate and, observed ferromagnetic resonance field shifts of 125–130 Oe and, ME coefficient of 16 Oe cm/KV which was in the well agreement with calculated theoretical value. Zheng et al.[23] deposited bilayer of Ni and PZT on single crystal Si substrate. They demonstrated using AC-mode magneto optical Kerr effect that magnetization induced from electric voltage is dependent on the thickness of Ni layer. Nickel layer of 40nm presented a dominative strain mediated ME coupling. Chin Jui Hsu et al.[24] made thin film of $Ni/(PMN)_{0.68}$-$(PT)_{0.32}$ (100) (heterostructure) and reported partial and reversible out of plane magnetization change. This phenomenon is depending on the thickness of the Ni layer showing no out of plane magnetization for thickness of 100nm. Yu et al.[25] have fabricated BFO/CoFe bilayer with different BFO structure by chemical solution deposition and sputtering method. They studied temperature dependence of exchange bias as well as coercivity. It has been found that temperature dependence of the exchange bias is dominated by the direct interface coupling while crystallinity of BFO has no remarkable effect. Sreenivasulu et al.[26] have fabricated bilayer and trilayer of piezoelectric quartz and magnetostrictive alloy of Fe-Co-V and showed that ME voltage co-efficient is higher in quartz based composite than traditional ferroelectric based ME composite. Venkataiah et al.[27] have demonstrated magnetization switching in Fe/BTO heterostructure due to the interface lattice distortion caused by the structural phase transition of BTO. The switching process is more succeptible in small negative applied field than zero.

There have been several tricks adopted by researchers to increase ME coefficients. In an attempt to demonstrate the transfer of strain mediated effect from one phase to other phase via some other material, Rahul C kambale et al.[28] fabricated trilayer ME composite of $Pb(ZrTi)O_3/LaNiO_3/Ni$ (PZT/LNO/Ni). Here LNO transfer the stress generated in magnetostrictive part Ni to piezostrictive part PZT. ME coefficients of $1Vcm^{-1}Oe^{-1}$ at biasing field of 30 Oe and $8.5Vcm^{-1}Oe^{-1}$ at a magnetomechanical resonance frequency of 204 KHz corresponding to Ni substrate have been observed. Continuing this idea for mediator material, Matthias C Krantz and his co-researchers[29] gave a theory for ME coefficient at resonance for magnetostrictive and piezostrictive layer on opposite of a substrate. They fabricated Metglas-Si-AlN system and found unexpected additional enhancement of the ME coefficient.Research went on further for fabrication of laminated composite with different geometries. Pan et al.[30] have fabricated laminate composite with cylindrical geometry by electro deposition. Material was Ni-P/Ni/PZT with lower optimal magnetic field and higher ME coefficient due to compressive stress in the Ni layers induced by the high permeability Ni-P layers. There has been also an attempt to increase ME coefficient by substituting or doping the elements of the compound in participating phase of the composite. One such step has been adopted by Li et al.[30] by varying concentration of Mg in $Co_{1-x}Mg_xFe_2O_4/0.68Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.32PbTiO_3$ (CMFO-PMN-PT) laminate composite fabricated on $Pt/Ti/Si/SiO_2$ by sol-gel technique. They showed that increasing Mg concentration can improve the ME coefficient of the bilayer composite. There are several reports available on ME phenomenon dealing with basic origin of ME effect as well as proposed applications. However it is not possible to discuss all of them in a single paper.

Application Of ME Composite

Several technological applications have been proposed to use ME composites [12,31,32]. Due to the hysteretic nature of the ME effect, the composites may find applications in memory devices. The linear ME effect has a positive or a negative sign, depending on the annealing conditions (parallel or anti-parallel magnetic and electric fields). Thus the coupling could lead to design a read and write memory technology. It can also be used as transformer and gyrator. ME transformers or gyrators have important applications as voltage gain devices, current sensors, and other power conversion devices. Several other technological applications includes: Magnetic Sensors, Microwave device, Energy harvesting etc.

Future Directions

There are many future challenges, but two most important challenges which needed to be solved first are as follows:

1.To obtain particulate composite with good dispersion of piezoelectric phase in piezomagnetic phase (and vice-versa) by avoiding the above mentioned limitations is still a challenge.

2.To obtain laminate composite with good interfacial contact without diffusion is still a challenge.

Summary

Various aspects of ME effect have been reviewed. Although this phenomenon has been predicted almost a century ago and detected experimentally in 1960, but the research in this area goes on peak after 1993 when researchers start understanding the microscopic origin of ME effect. But due to various limitations and lack of proper materials, ME composite still needs more research to make it suitable for technological exploration.

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