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Multiferroic Properties
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Multiferroic Properties

7.1 Introduction

Multiferroic materials are called magnetoelectrics which have at least two type of ordering: the spontaneous orbital and spin magnetic moments (ferromagnetism) and spontaneous electric dipole moments (ferroelectricity) [23]. In such multiferroic materials, the magnetoelectric (ME) effect arises from the coupling interaction between the ferromagnetic and ferroelectric orderings. Recently these materials have been of particular interest to understand the fundamental links between spin, charge and lattice degrees of freedom. Moreover, magnetoelectrically coupled materials are promising candidates for low energy consumption miniaturized devices wherein polarization/magnetization of the material can be externally controlled by applying a magnetic/electric field. Thus, coupling and controlling the different degrees of freedom in such materials opens unique ways to achieve new functionalities. In this chapter, the multiferroic properties of the compounds at room temperature have been discussed.

7.2 Results and Discussions

7.2.1 Polarization Study

Ferroelectric materials show non-linear relation between polarization (P) and electric field (E) resulting in hysteresis loop. In BFO, the spontaneous polarization occurs because of the hybridization between 6s² lone electron pair of Bi³⁺ ion and the 6p empty orbital of O²⁻ ion. BFO has poor ferroelectric performance due to high leakage current caused by oxygen vacancies and valence fluctuation of Fe ions. Hence measurement of P-E loop has always been difficult. Pure BFO exhibits leaky ferroelectric behavior and so could not withstand applied electric field more than 20 kV/cm due to large leakage current. Poling of pure BFO bulk material is very easy; because large grain size can reduce large stress at grain boundary which originates from polling process. The large grain specimens can easily be poled and have large coupling factors [291]. As the samples under study are of nano-size, the small
grains create the large stress at the grain boundary and polling become difficult. Probably this may be the reason of getting less saturated hysteresis loops.

All the sintered and electroded pellets were poled at room temperature in a silicon oil bath under optimized dc electric field for 6 h using DC poling unit (M/s Marine India, New Delhi) (before taking ferroelectric hysteresis loop measurements). The hysteresis loop of the poled sample was obtained using P–E loop tracer (M/s Marine India Co.).

(i) Ba and Mn co-substituted BFO

![Graphs showing P-E loops for different x values](image)

**Fig. 7.1**: Room temperature P-E loop of (Bi$_{1-x}$Ba$_x$) (Fe$_{1-x}$Mn$_x$)O$_3$ (x = 0.0, 0.05, 0.10, 0.15, 0.20) samples.

The electric field dependence of the electric polarization (ferroelectric hysteresis loops) for (Bi$_{1-x}$Ba$_x$) (Fe$_{1-x}$Mn$_x$)O$_3$ (x = 0.0 - 0.20) is shown in Fig. 7.1. The nature of hysteresis loop behavior indicates ferroelectric character and dynamic polarizability of the samples. The polycrystalline materials are made of a very large number of variously oriented grains; and each grain contains several domains variously oriented among the crystallographically allowable directions of that grain [292]. As the domains in one grain attempt to switch, they are constrained by the differently oriented neighboring grains. So, domain switching in
polycrystalline samples is a highly correlated collective process. When an external electric field is applied, the domains are favorably oriented with respect to the field and the domain wall motion grows at the expense of other less favorably oriented domains [293]. The shape of P–E loops varies greatly with the substitution compositions. It is observed that the value of remnant \( P_r \) and saturation polarization \( P_s \) increases on increasing up to \( x = 0.10 \), but again decreases for \( x = 0.15 \) and 0.20. The increase in \( P_r \) and \( P_s \) value indicates that the domain movement became easier with increase in \( x \) value in the system up to \( x = 0.10 \). This easier orientation of domains is also observed from decrease in \( E_c \) value of the system up to \( x = 0.10 \). This easier orientation of the domain can be understood through the micro structural studies (from chapter 3 Fig. 3.5). The decrease in grain size is observed with increasing value of \( x \); the smaller grains provide the finer domain and higher density in the system. The finer domain can reorient easily with the applied electric field [293]. Again, the value of \( E_c \) increases and \( P_r \) value decrease for the sample \( x = 0.15 \). As observed in micro structural studies, the grain size is very less for samples \( x = 0.15 \) and \( x = 0.20 \), have higher surface strain which makes the harder domain orientation. The observed grain boundary effect may also be the cause of decrease in polarization value and increase in \( E_c \) value [195, 294].

(ii) Ca and Mn co-substituted BFO

Usually, the bulk BFO endures a high-leakage current at room temperature. It is due to the involvement of the too high concentrations of oxygen vacancies induced by the loss of bismuth and the mixed valences of Fe (\( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \)) [86, 295]. The oxygen vacancies are one of the major sources of movable charges in BFO, and the mixed valence Fe ions cause increased conductance, possibly through the double exchange mechanism via \( \text{Fe}^{2+}–\text{O}–\text{Fe}^{3+} \) chains [296]. Fig. 7.2 shows room temperature ferroelectric hysteresis loops of the \((\text{Bi}_{1-x}\text{Ca}_x)\) \((\text{Fe}_{1-x}\text{Mn}_x)\)\(_3\) \((x = 0.00 - 0.20)\) samples. It is observed from the loops that the maximum value of polarization as well as the area of the hysteresis loops strongly depends on the value of \( x \) in the modified samples. On the increasing value of \( x \), the behavior of the ferroelectric loops changes noticeably; the value of polarization increases. For the samples with \( x = 0.00, 0.05, 0.10, 0.15 \) and 0.20, remnant polarization \( (2P_r) \) obtained was found to be 0.56, 0.64, 0.77, 0.95 and 0.86 \( \mu \text{C/cm}^2 \) respectively. The contributions to the apparent ferroelectric loop possibly arise from the leakage contributions [196]. For the sample, with \( x = 0.20 \), the value of \( P_r \) decreases which can be understood from the complex impedance analysis discussed in the chapter 5.
Fig. 7.2: Room temperature P-E loop for (Bi$_{1-x}$Ca$_x$)(Fe$_{1-x}$Mn$_x$)O$_3$ (x = 0.0, 0.05, 0.10, 0.15, 0.20) samples.

As observed in complex impedance analysis prominent grain boundary contribution in sample x = 0.20, disrupt the grain to grain correlation and results in less remnant polarization value. The remnant polarization P$_r$ sharply decreases due to increase in grain boundary contribution. It is believed that co-substitution significantly reduces the movable charges and the contribution to leakage current density is also minimized, as a result ferroelectric behaviors of the samples were enhanced.

(iii) Sr and Mn co-substituted BFO

In most of the materials the shape of loop along with the values of coercive field, spontaneous and remnant polarization depends on a number of factors such as mechanical stress, charge defects, preparation conditions, etc. Fig. 7.3 shows room temperature ferroelectric hysteresis loops of the (Bi$_{1-x}$Sr$_x$)(Fe$_{1-x}$Mn$_x$)O$_3$ (x = 0.0 - 0.20) samples. It is observed that the
ferroelectric properties of the modified samples can be enhanced more as compared to that of pure BFO. With the increasing concentration of substituted ions, the value of remnant polarization increases and the remnant polarization and coercive field for the sample (x = 0.20) is $2P_r = 3.08 \mu C/cm^2$ and $2E_c = 3.56 \text{kV/cm}$, respectively. The improved ferroelectric properties are attributed to the lower leakage current density, which is related to oxygen vacancies or valence fluctuation of the transition metal ion [297]. When Bi$^{3+}$ ion is substituted with Ba$^{2+}$ in BFO, oxygen vacancies are created and the system requires charge compensation. Meanwhile Mn$^{4+}$ substitutions at Fe-site suppress oxygen vacancies and thus reduce leakage current. Therefore, co-substitution significantly contributes in the enhancement of ferroelectricity in the modified system [298]. Also, it has been reported in the literature that decrement in grain size increases $E_c$ value [299]. The reason is that each grain is mechanically clamped by its surroundings. This clamping effect in addition to the mechanical
stress accompanying 90° domain rotations, tends to impede the polarization reversal process, and hence, apparently increases $E_c$ [300].

**7.2.2 Magnetic Study**

The requirement of filled transition metal d state in a compound gives rise to the occurrence of magnetic spin polarization. There exist two sources from which the magnetic moment arises in an electron: one is related to the orbital motion around the nucleus generating a very small magnetic field and having a magnetic moment along its axis of rotation and another magnetic moment arises from the electron spin having a direction along the spin axis. The fundamental carrier of magnetism is electron and possess an intrinsic magnetic moment (i.e. Bohr magnetron $\mu_B = 9.27 \times 10^{-24} \text{ JT}^{-1}$) due to its intrinsic spin angular momentum. If the inner d or f orbital of an atom is incomplete, then the spin and orbital moment of the electrons in the shell do not cancel exactly, hence the atom has a net magnetic moment.

Study of magnetic properties of such type of materials mainly deals with (a) the magnetic moment of the atoms or ions constituting the materials, and (b) the exchange interaction among these magnetic moments. Magnetism in multiferroic materials may arise due to the exchange interactions such as direct, indirect and super exchange interaction. Both the geometrical arrangement and separation of ions are responsible for exchange interaction.

The magnetic measurements of the calcined powders were carried out using PPMS (Physical Property Measurement System)-VSM of Quantum Design model-6000. The main objective of the VSM is to determine magnetic properties according to the applied magnetic field and the temperature. Use of the VSM involves measurement of the harmonic oscillation of the sample in a uniform magnetic field. The magnetization as a function of applied magnetic field was measured at 300 K up to 60 kOe. Magnetization measurements were normalized with respect to sample mass.

(i) **Ba-Mn co-substituted BFO**

The magnetic properties of materials are usually characterized by a hysteresis loop, which determines the behavior of material when excited by an external magnetic field. It is well-known at BFO exhibits antiferromagnetic magnetic ordering, in which the spiral spin structure leads to a cancellation of the macroscopic magnetization. If the spatially modulated spin order is suppressed the latent magnetization will be released, allowing a weak ferromagnetic ordering due to canting of the spins [88].
Fig. 7.4: Room temperature M-H curve of (Bi$_{1-x}$Ba$_x$)(Fe$_{1-x}$Mn$_x$)O$_3$ (x = 0.0, 0.05, 0.10, 0.15, 0.20) samples.

The room-temperature magnetization-field (M~H) curves of (Bi$_{1-x}$Ba$_x$) (Fe$_{1-x}$Mn$_x$)O$_3$ samples with a maximum applied field of 10kOe are shown in Fig. 7.4. It is observed that pure BFO shows very weak FM ordering in room temperature and exhibits enhanced saturation magnetization, $M_s = 0.067$ emu/g. The maximum value of magnetization ($M_s$) are 0.072, 0.085, 0.098 and 0.12 emu/g for x = 0.05, 0.10, 0.15 and 0.20 respectively. There is a small increase in $M_s$ value in the co-substituted samples with the increasing value of x, because the difference in magnetic moment of Mn$^{3+}$ ions interrupts the cycloid spin structure, which results in the enhancement of saturation magnetization of the samples [297, 195]. The hysteresis curves of the samples do not saturate, which suggest their antiferromagnetic nature with weak ferromagnetism [301]. The coercive field ($H_c$) values of the modified samples are reduced as compared to that of pure BFO suggesting the enhancement of soft magnetic property of the prepared system.
(ii) Ca-Mn co-substituted BFO

In BFO the magnetic moments of Fe$^{3+}$ cations are coupled ferromagnetically within the pseudo-cubic plane (111) and antiferromagnetically between adjacent planes, and are surrounded by six O$^{2-}$ ions in the common vertex of two adjacent FeO$_6$ octahedra. Superimposed on anti-ferromagnetic ordering, there is a spiral spin structure due to which the magnetization vanishes [300]. The magnetic field dependence of magnetization loop of the (Bi$_{1-x}$Ca$_x$)(Fe$_{1-x}$Mn$_x$)O$_3$ samples is measured from −10 to 10 kOe at room temperature using vibrating sample magnetometer (VSM) integrated with Quantum designed PPMS and shown in Fig. 7.5.

**Fig. 7.5**: Room temperature M-H curve of (Bi$_{1-x}$Ca$_x$)(Fe$_{1-x}$Mn$_x$)O$_3$ (x = 0.0, 0.05, 0.10, 0.15, 0.20) samples.

The loops obtained for all the modified system shows the presence of an ordered magnetic structure and the spontaneous magnetization originates from unbalanced anti-parallel spins giving rise to small values of coercivity. In the range of weak magnetic fields the above
curves changes its shape and the opening of hysteresis loops in these samples is not prominent due to very low value of coercive field ($H_c$). In all the samples, saturation is achieved at 10 kOe. Thus saturation magnetization ($M_s$) of the above solid solution increases with increase in the value of $x$. The saturation magnetization ($M_s$) are $0.145$, $0.542$, $0.784$ and $0.410$ emu/g for $x = 0.05$, $0.10$, $0.15$ and $0.20$ respectively. The slight enhancement in the value of magnetization is attributed to either the destruction of the spiral spin-modulated incommensurate structure or the increasing of the spin canting angle resulting in the net macroscopic magnetization [66, 302]. There are several other factors responsible for the improvement in the magnetic properties of materials which may be attributed to structural distortion, particle size, the interaction between Fe$^{2+}$ and Fe$^{3+}$, uncompensated anti-parallel lattice magnetization [65, 66]. It is found that at high-temperature calcinations co-existence of Fe$^{2+}$ and Fe$^{3+}$ is unavoidable. So, co-substitution can only suppress but cannot destruct the spin cycloid, which is responsible for the smooth increase of the $M_s$ and $M_r$ values.

(iii) Sr-Mn co-substituted BFO

![Graphs showing M-H curves](image)

Fig. 7.6: Room temperature M-H curve of (Bi$_{1-x}$Sr$_x$)(Fe$_{1-x}$Mn$_x$)O$_3$ ($x = 0.0$, $0.05$, $0.10$, $0.15$, $0.20$) samples.
Fig. 7.6 shows the M-H loops of (Bi$_{1-x}$Sr$_x$(Fe$_{1-x}$Mn$_x$)O$_3$ (x = 0.0 - 0.20) samples recorded at room temperature. All the samples exhibit well saturating loops except x = 0.20. The value of $M_s$ increases steadily with composition (x) variation. However, asymmetry in remnant magnetization ($M_r$) and coercive field ($H_c$) values are observed for almost all materials. This asymmetry indicates magnetic disorder in the surface layer which may contribute to lack of spin alignment even at high field. This magnetic disorder generally introduced into the system by two sources: (i) structural defects in the surface layer, e.g. vacancies in A-sites which causes a local spin canting in B-sites and vice versa [303], (ii) unbalanced distribution in occupation of Fe-ions at A or B-sites which could induce both topological and exchange interaction disorder. The asymmetricity in $H_c$ is maximum for x = 0.15. For material x = 0.20 no asymmetricity is observed which implies that in this sample the magnetic disorder is almost negligible.

The loops of Sr-Mn co-substituted BFO ceramics exhibit the magnetic hysteresis loops with weak ferromagnetic behavior, which means that the antiferromagnetism in BFO is turned into weak ferromagnetism in modified samples with non-zero net magnetization. The tolerance factor (t) in ABO$_3$ type structure is calculated using empirical formula [70], $t = (r_A + r_O)/\sqrt{2}(r_B + r_O)$, where $r_A$ is the average ionic radius of the A-site atoms (Bi$^{+3}$ = 1.03 Å, Sr$^{+2}$ = 1.18 Å), $r_B$ is the average ionic radius of B-site atoms (Fe$^{+3}$ = 0.65 Å, Mn$^{+4}$ = 0.53 Å) and $r_O$ is the ionic radius of O$^{-2}$ = 1.26 Å. For ideal perovskite, the value of t = 1 and for distorted perovskite, this value should be less than or more than 1 [304]. The tolerance factor of the co-substituted samples decreases with the increase in concentration of substituted ions because ionic size of Sr$^{+2}$ is slightly bigger than that of Bi$^{+3}$. This difference in ionic radii results tilting of octahedral unit and the Fe–O–Fe bond angles which, in turn increases the super exchange interaction between the two antiferromagnetically aligned Fe$^{+3}$ with the suppression of cycloid spin structure [305]. The value of $M_s$ and $M_r$ increases on increasing value of x from 0.05 to 0.15, which may be due to the canting of anti-ferromagnetically ordered spins. Due to substitution, the phase evolution gives rise to the continuing collapse of the space-modulated spiral spin structure. As a result, the spiral spin structure is suppressed and the latent magnetization locked within the spiral spin structure is released and accordingly the net magnetization is enhanced [306, 307].
7.2.3 Magnetoelectric effect

Spontaneous magnetoelectric (ME) effect in rhombohedrally distorted perovskites can be described according to Landau’s theory, which are invariable with respect to the elements of a parent centrosymmetrical group R3c (for BFO). This symmetry allows the following lowest order ME invariants linear on electric polarization [308].

\[
F_{1\text{ME}}^1 = \gamma_1 P [L(\nabla L) + L \times (\nabla \times L)] \\
F_{1\text{ME}}^2 = \gamma_2 P [L \times M]
\]  

(7.1)  
(7.2)

where \(L\) is antiferromagnetic vector, \(M\) is magnetic moment, \(P\) is polarization and \(\gamma_1\) and \(\gamma_2\) are constants related to magnetoelectric effect. The first relation is responsible for the spin cycloid structure with a period of 62 nm in BFO, and \(F_{1\text{ME}}^1\) is a relativistic Lifshitz like invariant [309]. The inhomogeneous magnetic structure in BFO appears due to magnetoelectric interactions and its appearance is possible only when the spontaneous polarization takes place. The spin cycloid structure can be observed in the ferroelectric state below \(T_N < T_C\), whereas the second relation shows the possibility of a weak ferromagnetism (WFM) and linear magnetoelectric effect (LMEE) in the antiferromagnetic–ferroelectric state below \(T_N\). However neither weak ferromagnetism nor linear magnetoelectric effect is observed in a bulk BFO due to its inhomogeneous magnetic structure leading to zero value of the net \(M_s\) and \(\alpha_{ik}\) (linear magnetoelectric coefficient). The essential condition for the manifestation of higher magnetoelectric effect in BFO is the suppression of the spin cycloid, which can be achieved by the ionic substitution [310].

In order to estimate the magnitude of the coupling coefficients \(\alpha_{ik}\), it is necessary to understand the microscopic mechanism driving ME behavior. The generalization of this approach with a compilation of magnetic interaction mechanisms, their modification by an electric field and the consequences for different types of magnetic ordering are proposed by Gehring [311]. The rarest co-existence of ferromagnetic and ferroelectric order in a material is multiferroicity and will allow coupling between two orders through mechanical forces. A magnetic field applied to the material will produce a deformation due to magnetostriiction, which will be coupled to the piezoelectric phase and result in an induced polarization [312].

In the present study for ME coefficient analysis, the dynamic lock-in technique was adopted as discussed in chapter 2. The measurement was performed on a sintered pellet at a constant frequency of 1 kHz and a constant bias ac magnetic field (15 Oe). The ME coefficient of the samples was carried out with a time varying dc magnetic field in the presence of an ac field; and was obtained by dividing the measured output voltage by the magnitude of applied ac field and the thickness of the pellet sample.
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The linear coefficient ‘α’ is determined at fixed dc magnetic field along with simultaneous sweeping of the ac magnetic field. A quadratic coefficient ‘β’ has been measured by fixing the ac magnetic field while sweeping the dc magnetic field [313, 314]. When a dc magnetic field is applied, ME output voltage (V) in the material, showing second order effect can be given by following relation:

\[ V \propto \alpha H + \beta H^2 \]  \hspace{1cm} (7.3)

The ME voltage coefficient in terms of voltage equation was given by Rivera [175]. Using this equation α and β can be calculated as follows:

\[ \alpha_{ME} = \frac{V_{out}}{h_0 t} \quad \text{and} \quad \beta = \frac{V_{out}}{h_0^2 t^2} \]  \hspace{1cm} (7.4)

where \( t \) is the sample thickness, \( V_{out} \) is the induced ME voltage and \( h_0 \) is ac magnetic field magnitude.

(i) Ba-Mn co-substituted BFO

Magnetoelectric coupling in antiferromagnetic compounds having complex spin arrangements have been explained based on the exchange interactions in canted spins [315-317]. Sakhnenko et al have proposed a microscopic model to explain ME coupling in some magnetoelectrics and showed that the spin–orbit coupling leads to spin-dependent electric dipole moments of the electron orbitals of those ions located in noncentrosymmetric surroundings, which results in non-vanishing polarization for certain spin configurations [318]. We have not proposed any model for explaining ME effect in BFO; based on the existing ME theory it is expected that the local interactions between local spin moments with disordered electric dipole moments interaction results ME coupling in BFO.

In multiferroics, when a magnetic field is applied, the materials are strained. Due to the coupling between the magnetic and ferroelectric domain, the strain does induce stress that in turn generates additional charges on the ferroelectric domain. The measurement of ME output at low temperatures might be beneficial due to the fact the magnetic ordering will increase resulting in the strengthening of the sub-lattice interaction. A small ac magnetic field \( H_{ac} \) (15 Oe) was generated by a solenoid and was superimposed onto a magnetic bias \( H_{bias} \) up to 5 kOe. The variations of \( \alpha_{ME} \) with \( H_{bias} \) for \((\text{Bi}_{1-x}\text{Ba}_x)(\text{Fe}_{1-x}\text{Mn}_x)\text{O}_3 \) (\( x = 0.0 - 0.20 \)) samples are shown in Fig. 7.7. For pure BFO, an initial ME coefficient value of 1.926 mV/cm.Oe is obtained near zero magnetic bias. As the magnetic field is increased, the ME coefficient of BFO sample shows a linear increase with magnetic field and attains a maximum value of 1.929 mV/cm.Oe at dc magnetic field of ~ 1296 Oe. The ME coefficient value saturates and
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then decreases with further incremental field after 1500 Oe. The optimum dc bias field at which the maximum ME coupling occurs is the critical parameter for the operation of multiferroic sensors and devices to maximize the energy conversion between the fields.

![Graph showing ME coefficient vs. DC bias magnetic field for samples](image)

**Fig. 7.7:** Room temperature dc bias magnetic field dependence of magnetoelectric coefficients ($\alpha_{ME}$) for $(\text{Bi}_{1-x}\text{Ba}_x)(\text{Fe}_{1-x}\text{Mn}_x)\text{O}_3$ ($x = 0.0, 0.05, 0.10, 0.15, 0.20$) samples.

As it can be seen in Fig. 7.7, for all the samples the $\alpha_{ME}$ value strongly depends on the magnetic bias field: at first increases, attains a maxima ($\alpha_{ME_{\text{max}}}$) and after that decreases. This trend of $\alpha_{ME}$ is attributed to the piezomagnetic phase, since its magnetostriction increases with the field until saturation. The saturated magnetostrictive strain is transferred to the piezoelectric phase and a constant electrical signal is generated in spite of the increasing magnetic field [315]. It is also evident that co-substitution of Ba-Mn results in higher ME coefficient [184]. The higher value of ME in the modified systems is attributed to the increase in magnetic ordering with co-substitution. The maximum value of $\alpha_{ME}$ for samples with $x = 0.05, 0.10, 0.15, 0.20$ are 2.491, 2.974, 3.193 and 2.254 mV/cm.Oe respectively. At this stage ME coupling magnitude significantly depends on the intrinsic magnetization of the material. More is magnetization more is the ME coupling due to presence of more magnetic dipoles. It
is also well known that large interfacial area and good phase connectivity play a role in contributing to the strong ME effect. From the SEM analysis it can be understood that smaller sizes of grains can induce large interfacial area, which favours elastic interactions between the ferroelectric and ferromagnetic phases. Hence, the smaller grain sized systems contribute enhance ME effect than pure BFO.

(ii) Ca-Mn co-substituted BFO

![Graphs showing ME coefficient vs. DC Bias Magnetic Field for different x values](image)

**Fig. 7.8:** Room temperature dc bias magnetic field dependence of magnetoelectric coefficients ($\alpha_{\text{ME}}$) for $(\text{Bi}_{1-x}\text{Ca}_x)(\text{Fe}_{1-x}\text{Mn}_x)\text{O}_3$ ($x = 0.0, 0.05, 0.10, 0.15, 0.20$) samples.

The magnetoelectric coefficient ($\alpha_{\text{ME}}$) of $(\text{Bi}_{1-x}\text{Ca}_x)(\text{Fe}_{1-x}\text{Mn}_x)\text{O}_3$ ($x = 0.0 \text{ to } 0.20$) samples as a function of bias dc magnetic field at room temperature are shown in Fig.7.8. The nature of all plots reveals hysteretic behavior, as observed in case of magnetic field cycles. As observed from the plots, the ME coefficient value initially increases with increase in the magnetic field, attains a maximum and then decreases with further increase in the magnetic field. All the samples exhibit peak at magnetic field nearly 2 kOe and height of the peak is related to the strength of the ME coupling. The ME coefficient of the samples in the series is dependent on the value of $x$. The value of $\alpha_{\text{ME}}$ increases significantly with increase in the value of $x$ up to $x = 0.15$ and then drops. This enhancement in the ME coefficient might be ascribed to the
increase of the mechanical deformation in the magnetostrictive phase \[319\]. The maximum value of \(\alpha_{\text{ME}}\) is 2.187 mV/cm.Oe at 1.5 kOe obtained for the sample with \(x = 0.15\), may result from the uniform distribution and better mechanical coupling of the constituent phases. The above results are in good agreement with the M-H study where maximum value of saturation is obtained for the same sample \((x=0.15)\). The comparatively lower value of ME coefficient for \(x = 0.20\) is due to the reduction of the ME response of the sample which may be ascribed to lower value of saturation magnetization \((M_s)\) compared to the sample with \(x = 0.15\).

(iii) **Sr-Mn co-substituted BFO**

Magnetoelectric coupling coefficient determination is carried out to reveal extent of intimate interaction between electric and magnetic dipoles interaction in a material. The best results are obtained by electrically poling the sample initially to orient electric dipoles and subsequently sample is put in dc and ac magnetic field simultaneously.

![Graph showing ME coefficients](image)

**Fig. 7.9:** Room temperature dc bias magnetic field dependence of magnetoelectric coefficients \((\alpha_{\text{ME}})\) for \((\text{Bi}_{1-x}\text{Sr}_x)(\text{Fe}_{1-x}\text{Mn}_x)\text{O}_3\) \((x = 0.0, 0.05, 0.10, 0.15, 0.20)\) samples.
Fig. 7.9 shows the magnetic field ($H_{dc}$) dependence of ME voltage coefficient ($\alpha_{ME}$) measured by superimposing an ac magnetic field for all the compositions of the series ($\text{Bi}_{1-x}\text{Sr}_x(\text{Fe}_{1-x}\text{Mn}_x)\text{O}_3$). The ME coefficient increases initially with the bias magnetic field, reaches a maximum around 1.5 kOe and after that a decreasing trend is observed. On reversing the direction of the field through zero, ME coefficient exhibits a hysteretic behavior. It can also be observed that increasing content of x to BFO resulted in an improved ME coefficient. The maximum value of $\alpha_{ME}$ for samples with $x = 0.05, 0.10, 0.15, 0.20$ are $2.076, 2.344, 2.983$ and $2.285$ mV/cm.Oe respectively. The enhancement in $\alpha_{ME}$ may be attributed to the substitution of divalent (Sr) A-site and tetravalent (Mn) B-site in BFO; which allows an increased canting angle on the account of crystallochemical strain resulting in the enhanced magnetization. These results can well be correlated with the magnetic study as well as the ferroelectric study discussed on the same series of samples. Thus enhanced ME coupling is obtained under the magnetic field by means of spin exchange magnetostriction [320].

### 7.3 Conclusion

On the basis of above results the following conclusions have been drawn:

- Appearance of ferroelectric hysteresis loop in all the samples at room temperature confirms the presence of ferroelectricity in the compounds.
- The Ba-Mn co-substituted BFO samples showed anti-ferromagnetic nature with weak ferromagnetism at room temperature.
- The Ca-Mn modified BFO showed unsaturated hysteresis loops with enhanced ferromagnetism observed for $x = 0.15$ which may be due to the destruction of cycloid spin structure.
- The appearance of hysteresis loops in Sr-Mn co-substituted samples (up to $x = 0.15$) may be attributed to the canting canting of anti-ferromagnetically ordered spins.
- Room temperature occurrence of ferromagnetism and ferroelectricity further supports the observation of multiferrosim and magnetoelectric coupling in the BiFeO$_3$.
- The nature plot for ME voltage co-efficient of pure and modified BFO showed hysteretic behavior.
- The highest value of ME co-efficient is obtained for Sr-Mn co-substituted BFO with $x = 0.15$ which is correlated to its enhanced magnetic properties.

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