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Investigation of the magnetoelectric effect in BiFeO₃–BaTiO₃ solid solutions

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Abstract. BiFeO₃ forms solid solutions with BaTiO₃, over the entire compositional range, with different crystal symmetries. Magnetoelectric (ME) measurements carried out with a superimposed alternating-current magnetic field, together with a time-varying direct-current magnetic field in isothermal conditions, indicated non-linearity. The peak observed coincided with a metamagnetic transition in the magnetization data. Rather than the spin flop reported earlier, it is a gradual reorientation of spins towards the field direction that destroys the spiral spin arrangement. With increasing content of BaTiO₃, a quadratic signal was observed, indicating the structural dependence of the magnetoelectric effect. The temperature variation of the ME output in the investigation carried out for $x = 0.75$ indicates magnetic transitions.

1. Introduction

BiFeO₃ belongs to the class of materials which show displacive ferroelectric transitions [1]. In addition, BiFeO₃ is an antiferromagnet with a Néel temperature of 370 °C and shows weak ferromagnetic ordering at room temperature [2, 3]. The existence of both electrical and magnetic ordering makes it a magnetoelectric material.

The magnetoelectric effect (ME) is the observation of an electric field output on the application of a magnetic field, in a material which is ordered electrically and magnetically at a given temperature. Materials showing a ME have technological applications as Hall probes, UHF spin-wave oscillators etc [4].

The ME effect is a secondary ferroic property whose effect can be found in the Gibbs free-energy function

$$dG = -S dT + P_i dE_i + M_i dH_i + \epsilon_{ij} d\sigma_{ij}$$

where S , P , M and ϵ are the entropy, spontaneous polarization, magnetization and elastic strain. E , H and σ are the applied electric field, magnetic field and stress.

In isothermal conditions $S dT$ is zero and when no stress is applied the last term also becomes zero. Expanding the above equation in a Maclaurin two-variable series gives

$$G = P_i E_i + M_i H_i + (1/2)\epsilon_{0ik} E_i E_k + (1/2)\mu_{0ik} H_i H_k + \alpha_{ik} E_i H_k \\ + (1/2)\beta_{ijk} E_i H_j H_k + (1/2)\gamma_{ijk} H_i E_j E_k + \dots$$

where α is the linear magnetoelectric coefficient and β and γ are bilinear coefficients.

Differentiating with respect to E_k , we get the polarization:

$$\partial G / \partial E_k = P_k^s + (1/2)\epsilon_{0ik} E_i + \alpha_{ki} H_i + (1/2)\beta_{kij} H_i H_j + (1/2)\gamma_{ijk} H_i E_j.$$

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When the applied electric field $E = 0$,

$$P_k^s = \alpha_{ki} H_i + (1/2)\beta_{kij} + H_i H_j$$

which is the basic equation for linear and quadratic ME effects.

An ME signal is observed due to the switching of ferroelectric and antiferromagnetic domains. In a magnetic field, the strain-induced magnetic sub-lattice applies a stress on the electrical sub-lattice, which is realized as an ME output. It is measured either as a polarization (charge) or a voltage (P).

A linear ME is observed in usual antiferromagnets. But antiferromagnetic BiFeO₃, because of its spiral spin arrangement, exhibits only a non-linear effect. In the ME measurements on certain BiFeO₃-rich phases of solid solutions, Ismailzade *et al* observed a peak, which they attribute to spin flop. The explanation given is that when a strong magnetic field is applied, the spiral spin arrangement is destroyed; this is observed as a peak. Beyond the peak field, BiFeO₃ behaves as a normal antiferromagnet [5–8]. In contrast to this, Tabares-Munoz *et al* observed, in single-crystal and polycrystalline data, only a quadratic signal and they rule out the possibility of a spin-flop mechanism [9].

In view of the above arguments, the need to strengthen one of them is apparent. The present investigation of ME properties, along with the necessary magnetization data, will, we believe, provide insight into the non-linearity observed, as ME is a secondary ferroic property involving both spontaneous polarization and magnetization [10].

The problem of the lower value of the resistivity of BiFeO₃ at room temperature has led to the ME output being observed only at low temperatures. But later it was found that when BiFeO₃ forms solid solutions with various other compounds, the resistivity is enhanced. This enabled the observation of the ME output for BiFeO₃-rich phases at room temperature. Extension of the data to pure BiFeO₃ provided the opportunity to arrive at the above conclusions [7, 11, 12].

The BiFeO₃–BaTiO₃ solid-solution system is one such series, where not only is the magnetoelectric property important, but so also are other properties like dielectricity and piezoelectricity. BaTiO₃, which has a high value of the dielectric constant, with a low ferroelectric T_c , was a natural choice as a dopant for BiFeO₃, for studying the variations of dielectric, piezoelectric, magnetic and magnetoelectric properties, which are rarely reported.

Literature available on the solid-solution system reports the existence of three structural phase transitions, with increasing content of BaTiO₃. The structure transforms to cubic at 33 mol% of BaTiO₃ from the rhombohedral symmetry of pure BiFeO₃ and again transforms to tetragonal, as the other end of the system is reached, i.e. BaTiO₃. In addition to the above observations, we have recently reported the existence of field-induced ferromagnetism and ferroelectric properties for this solid-solution system [12–14].

It is interesting to observe that with increasing concentration of BaTiO₃ and with the structure approaching cubic symmetry, the degree of ferromagnetic ordering reduces, and at higher concentrations BaTiO₃ exhibits paramagnetic properties. In addition, our isothermal magnetization measurements at room temperature indicated a metamagnetic state [14] of the BiFeO₃-rich compositions rather than the spin flop reported earlier [15].

Continuing with our investigation on the physical properties of x BiFeO₃–(1 – x)BaTiO₃ solid solutions, magnetoelectric measurements are undertaken on the BiFeO₃-rich phases of the solid-solution system with $x = 0.9, 0.8, 0.75$ and 0.7 , to probe the non-linearity observed with a more accurate technique, where the ME output is measured as a function of the DC magnetic field (which varies linearly with time), in a superimposed AC field. A low-temperature scan of the ME output has been undertaken for $x = 0.75$, to investigate the possible magnetic transitions [16, 17].

2. Experimental procedure

The solid-solution series $x\text{BiFeO}_3-(1-x)\text{BaTiO}_3$ has been prepared by the solid-state reaction method. The samples were found to be phase pure. The series was observed to undergo a structural transition to cubic symmetry after a composition of $x = 0.7$. The synthesis, characterization and dielectric and magnetic properties are reported elsewhere [12, 14].

In the equation for static measurements above, application of an AC field (h_0) together with the DC field (H_0) leads to the total field $H = H_0 + h_0 \sin(\omega t)$, where $\omega = 2\pi f$ (f is the frequency of the input signal). The induced ME signal is measured using a lock-in amplifier (SR530) tuned to the input current phase.

Magnetoelectric measurements have been carried out on an experimental set-up developed in our laboratory, with an AC magnetic field (h_0) superimposed on a time-varying DC magnetic field (H_0) [18]. The AC field employed was 18 Oe, whereas the magnetoelectric measurements were carried out in a DC magnetic field of 0–8 kOe at room temperature and 77 K. The frequency used was 1.001 kHz.

The samples with $x = 0.9, 0.8, 0.75$ and 0.75 were cooled to 77 K in a constant DC magnetic field of 100 Oe and the ME output was measured as a function of temperature in a DC field of 3 kOe with a superimposed AC field of 18 Oe in the range 77–300 K. Though measurements were carried out for all of the samples, only for data $x = 0.75$ are presented, as we obtained similar results for the other samples. The interest in the $x = 0.75$ composition stems from the fact that it is closer to the structural phase boundary.

Point contacts were made on both sides of the samples with silver paint using epoxy resin. Prior to the measurement, all of the samples were poled electrically to align the dipoles in the direction of the field, in a field of 35 kV cm^{-1} at 90°C for 1/2 h, and magnetically at 8 kOe at room temperature for 1 h. The temperature was measured using a Lakeshore DT470 diode sensor.

3. Results and discussion

Figure 1 shows the variation of the magnetoelectric output with field for $x = 0.9$. At room temperature, the ME output rises up to a field of 5.2 kOe and then shows a decreasing trend. The value of the ME output is 0.55 mV cm^{-1} at the peak. At 77 K, the curve shows a non-linear increase up to 4 kOe beyond which an anomaly appears. The anomaly is not as pronounced as at room temperature and the value of the ME output has more than doubled around the anomaly. This may be due to the increased magnetic ordering at 77 K.

The anomaly in the room temperature data is similar in shape to that observed by Ismailzade *et al* [7, 15], which they report as due to spin flop for $x = 0.95$. In order to check this claim, we have carried out isothermal magnetization measurements at room temperature for $x = 0.9$. The inset of figure 1 shows the M - H isotherm, which is close to $x = 0.95$. The figure shows a gradual increase in the magnetization at low fields, before it appears to saturate at high fields. The curve corresponds to metamagnetism, contrary to the earlier claim of a spin flop, where the magnetization should show a sudden increase at a certain field.

Figure 2 shows the magnetoelectric output observed for $x = 0.8$ at room temperature and 77 K. At room temperature, the curve increases non-linearly up to a field of 5.5 kOe and then starts rising linearly, whereas at 77 K an anomaly is observed at 7 kOe. The values of the ME output do not vary much at the fields given above for both of the temperatures (1.7 mV cm^{-1}).

In figure 3 we show the ME output for $x = 0.75$ obtained at room temperature with increasing magnetic field. The value of the ME output shows a small variation up to a field of 4.3 kOe. At still higher fields, the output increases sharply. The initial decrease in the

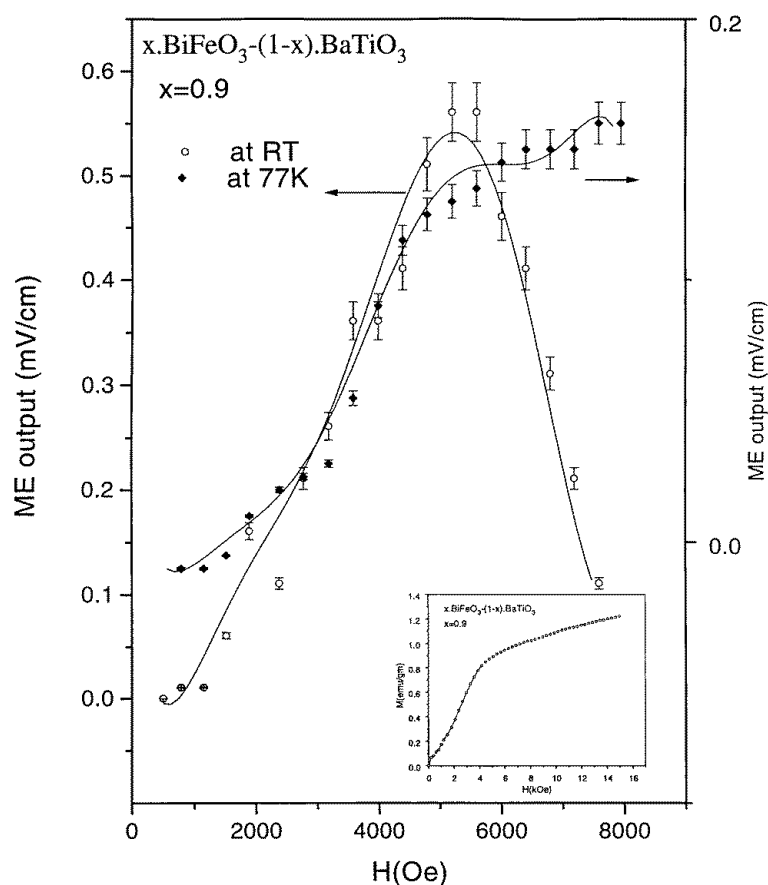


Figure 1. The variation of the magnetoelectric output with field for $x = 0.9$ at room temperature and 77 K (inset: the isothermal magnetization measured at room temperature).

ME output may be due to a polarization reversal, which is usually observed in ferroelectric materials.

Figure 4 shows the variation of the ME output with magnetic field for $x = 0.7$ at room temperature and 77 K. The ME signal saturates at a certain field at 77 K. Unlike the case for other samples, the curve does not show an anomaly, but indicates a quadratic nature. The value of the ME output decreases with this composition.

As discussed in the introduction, samples with compositions below $x = 0.7$ are in the cubic phase and are non-ferroelectric. Consequently, the ME effect is absent for these compositions.

The variation of the ME output with temperature for $x = 0.75$ is shown in figure 5. The plot indicates an ME output independent of temperature up to 145 K which sharply rises thereafter, giving rise to an anomaly at 183 K. The ME output shows another anomaly at a temperature of 273 K.

Figure 6 shows the dependence of the inverse susceptibility on temperature for $x = 0.75$, measured at a field of 1.6 kOe in a PAR VSM, in the temperature range 14–300 K. The figure shows ferromagnetic ordering at low temperatures. As the temperature is increased, the susceptibility does not approach zero. The extrapolation of the high-temperature data

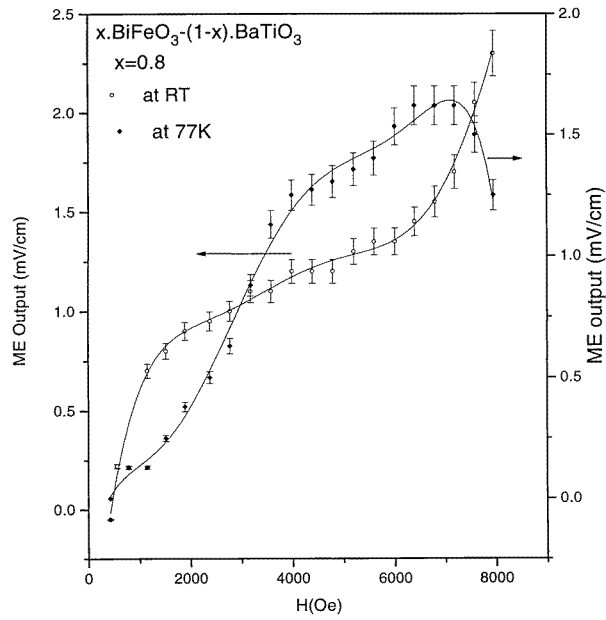


Figure 2. The variation of the magnetoelectric output with field for $x = 0.8$ at room temperature and 77 K.

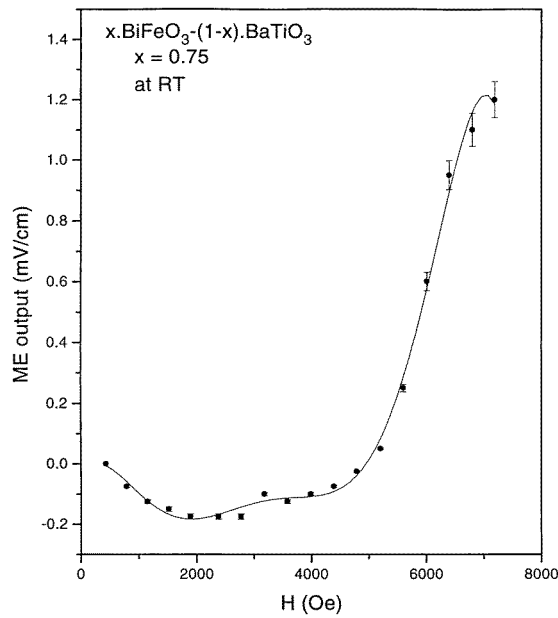


Figure 3. The variation of the magnetoelectric output with field for $x = 0.75$ at room temperature.

cuts the negative axis, indicating the antiferromagnetic nature. To confirm this, we have measured the magnetization as a function of applied field for $x = 0.75$ at room temperature

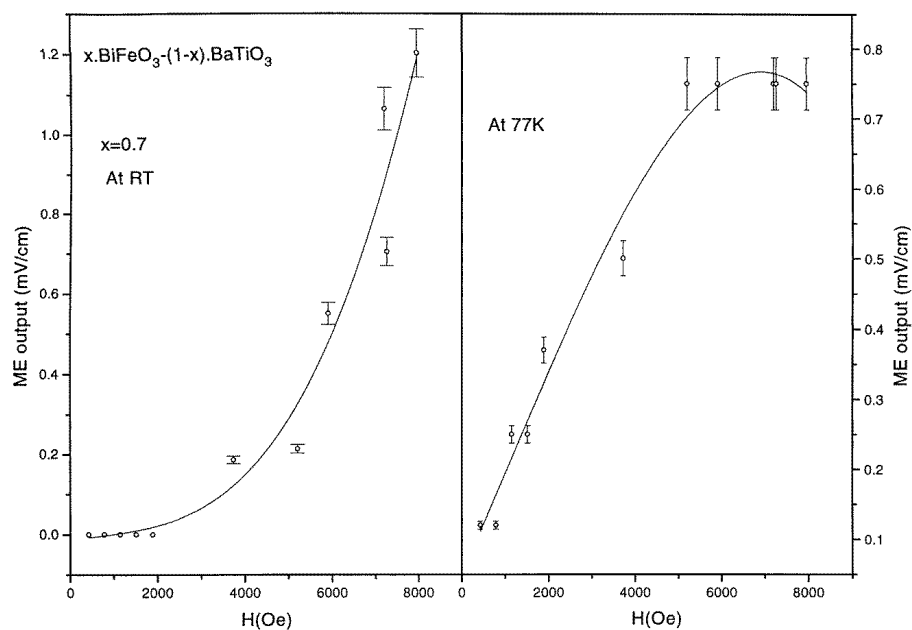


Figure 4. The variation of the magnetoelectric output with field for $x = 0.7$ at room temperature and 77 K.

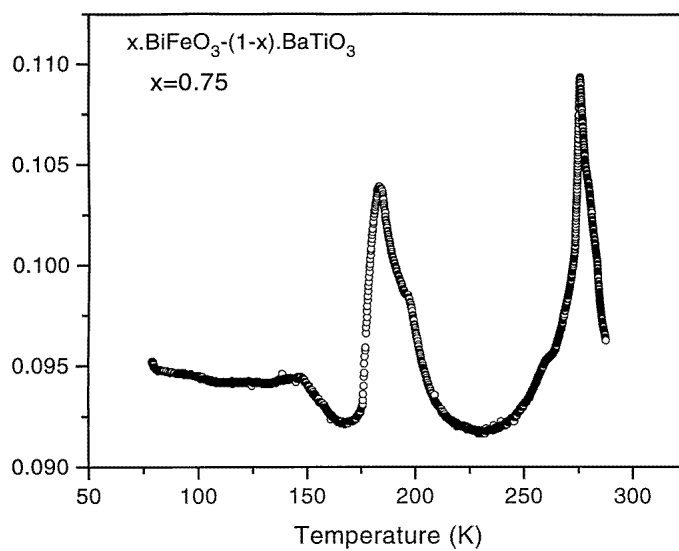


Figure 5. The variation of the magnetoelectric output with temperature for $x = 0.75$.

(see the inset of figure 6). There is a clear hysteresis at low fields and we have observed that the magnetization does not saturate even at high fields. This indicates the antiferromagnetic nature of the material at room temperature. Similar results were obtained for other samples of the solid-solution system. The above observation makes it clear that the samples exhibit ferromagnetism

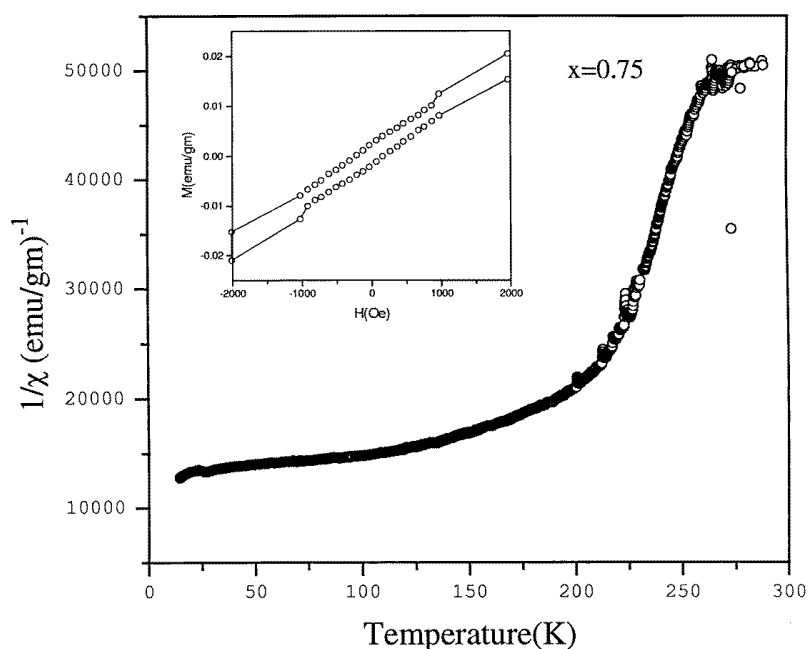


Figure 6. The temperature dependence of the inverse magnetic susceptibility for $x\text{BiFeO}_3\text{-(1-x)BaTiO}_3$ (inset: the low-field hysteresis loop at room temperature).

at low temperatures and antiferromagnetism at high temperatures, corroborating our earlier published data [14].

In BiFeO_3 , the d shell of Fe^{3+} is half-filled and each orbital contains an integral number of spins. This lifts the degeneracy and results in the interaction between the electrons in the overlap of like atomic orbitals between two Fe^{3+} ions. In such a situation, electron transfer takes place only if the spins in the neighbouring atoms are antiparallel due to Pauli's exclusion principle. This leads to an Fe–O–Fe antiparallel arrangement in BiFeO_3 leading to a G-type antiferromagnetic ordering. Each Fe^{3+} is surrounded by six antiparallel nearest neighbours. The spiral rotation plane is (110) [19, 20].

The space group $R3c$ of BiFeO_3 with the rhombohedral distorted perovskite structure allows both ferroelectric atomic displacements and a weak ferromagnetic ordering, due to the spin arrangement. In this kind of arrangement the Fe–O–Fe bond angle is much less than 180° and this results in canting of the spins and a weak ferromagnetic ordering [1].

The core electron polarization of Bi^{3+} in BiFeO_3 , which causes ferroelectricity, also leads to the distortion in the ideal perovskite structure. The Bi^{3+} ion moves in the (111) direction to stabilize strongly the p_π orbital of the oxygen, thus making the symmetry rhombohedral. Progressive addition of Ba^{2+} at the A site reduces this polarization and, at a particular composition ($x = 0.67$), the movement of Bi^{3+} completely ceases, giving rise to an ideal cubic perovskite. At this point, the octahedral distortion reduces and, as a consequence, the Fe–O–Fe bond angle reaches 180° and the ferromagnetism disappears [19].

Our magnetic susceptibility measurements, which have already been published [14], indicate a reduction in ferromagnetic ordering with increasing content of BaTiO_3 . The isothermal magnetization for $x = 0.9$ at room temperature indicates a gradual reorientation of the antiparallel-aligned spins towards the field direction. Hence, the spiral magnetic arrangement

gradually makes way for a normal antiferromagnetic nature. This differs from a spin flop, where a sudden flipping of the spins take place.

It was pointed out by Gehring [21] that in magnetoelectric materials, a bulk magnetization may result due to the presence of an electrically polarizable ion. The increase in the ME values at low temperatures may be attributed to this increased magnetization, which results in an increased interaction between the two sub-lattices. As the content of BaTiO₃ increases, the role of the Ti⁴⁺ ion, which is non-magnetic, dominates, resulting in the reduction in the bulk magnetization.

In view of the above arguments, it is clear that the anomaly in the ME data is not due to spin flop. This finding corroborates the observation of Tabares-Munoz *et al* [9] that BiFeO₃ exhibits non-linear ME properties, which are essentially not due to spin flop.

The increase in the ME values at low temperatures is due to the increased magnetic ordering, which makes the sub-lattice interaction strong, giving rise to a larger value of the ME output.

Furthermore, the dependence of the ME on the structure is obvious from the results. As the BaTiO₃ content increases, the structural distortion reduces, making the unit cell simpler. A cubic unit cell cannot possess spontaneous polarization; the sub-lattice interaction ceases, thereby reducing the chances of observing ME at higher concentrations of BaTiO₃.

From the above observations, it is evident that, at room temperature with increasing content of BaTiO₃, the field at which the anomaly is observed in the ME decreases, confirming earlier reports [15]. With increasing concentration of BaTiO₃, the solid-solution system shows a quadratic behaviour. This indicates not only strong magnetic fields, but also that excess addition of BaTiO₃ destroys the spiral magnetic ordering, making BiFeO₃ a normal homogeneous antiferromagnet. Due to the decrease in magnetization with increasing content of BaTiO₃, the anomaly in the ME output at room temperature disappears.

From the Gibbs free-energy function it is clear that, on the varying temperature scale, due to the change in entropy, the spontaneous polarization and spontaneous magnetization are interdependent. Hence the pronounced indications of ferroelectric and magnetic transitions in the ME data [17].

The anomalies observed for $x = 0.75$ in the temperature dependence of the ME output indicate magnetic anomalies. The anomalies in the ME output at particular temperatures may be due to the minute magnetic phase transitions occurring in the sample. The first (at 183 K) can be attributed to a weakly ordered ferromagnetic state, whereas the second may have its origin in the antiferromagnetism. The temperature variation of the magnetic susceptibility confirms this. Similar observations were made by Ikeda *et al* [16] for polycrystalline Eu₂FeO₄ and Rivera for single-crystal boracite [17], indicating the usefulness of ME as regards obtaining information on minute magnetic phase transitions. The anomalies may be due to the fluctuating valence states of the Fe ion, which is also the cause of the ferromagnetism [16].

4. Conclusions

The present study of the magnetoelectric effect in the BiFeO₃-rich phases of the BiFeO₃-BaTiO₃ solid-solution system indicates that BiFeO₃ does not exhibit spin flop. It can be concluded that the spiral spin arrangements are destroyed in strong magnetic fields and with the addition of BaTiO₃. As the structure becomes simpler the spontaneous polarization reduces and, hence, so does the ME. The magnetoelectric output depends on the structure. As the structure becomes simpler, only a quadratic output results, indicating the onset of a normal antiferromagnetic nature. Magnetoelectric data are useful in finding the magnetic anomalies.

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