Magnetoelectric measurements on $Bi_5FeTi_3O_{15}$ and $Bi_6Fe_2Ti_3O_{18}$

1999 J. Phys.: Condens. Matter 11 3335

(http://iopscience.iop.org/0953-8984/11/16/014)

J. Phys.: Condens. Matter **11** (1999) 3335–3340. Printed in the UK PII: S0953-8984(99)00712-2

Magnetoelectric measurements on $Bi_5FeTi_3O_{15}$ and $Bi_6Fe_2Ti_3O_{18}$

A Srinivas, S V Suryanarayana, G S Kumar and M Mahesh Kumar†

Department of Physics, Osmania University, Hyderabad-500 007, India

Received 6 January 1999, in final form 25 February 1999

Abstract. $Bi_5FeTi_3O_{15}$ and $Bi_6Fe_2Ti_3O_{18}$ are members of the Aurivillius family of compounds having simultaneous electrical and magnetic ordering. Magnetoelectric measurements carried out in a linear time-varying magnetic field with an alternating-current field superimposed yielded a non-linear signal. The shift from linearity, which is not usually observed for antiferromagnetic materials, may be due the tilt in the octahedra. The variation of the magnetoelectric output with temperature for $Bi_5FeTi_3O_{15}$ and $Bi_6Fe_2Ti_3O_{18}$ indicated magnetic anomalies with enhanced sensitivity, corresponding to those in magnetization data.

1. Introduction

Bismuth layered-structure ferroelectrics, generally known as the Aurivillius family of compounds, are built from regular intergrowths of $(Bi_2O_2)^{2+}$ and $(A_{n-1}B_nO_{3n+1})^{2-}$ layers, where A $= Bi^{3+}$ and B $= Fe^{3+}$, Ti^{4+} and n refers to the number of perovskite-like packets between Bi_2O_2 layers [1].

$Bi_4Ti_3O_{12}$, a three-layered compound, has a monoclinic symmetry at room temperature with the ferroelectric transition at 675 °C [2]. $BiFeO_3$ also belongs to this class of perovskites, with a rhombohedral symmetry at room temperature. It has a ferroelectric T_C at 850 °C and a simultaneous antiferromagnetic ordering at 370 °C [3]. When one mole of $Bi_4Ti_3O_{12}$ and m moles of $BiFeO_3$, with $m = 1$, 2 and 5, are combined, compounds with four, five and eight layers, $Bi_5FeTi_3O_{15}$, $Bi_6Fe_2Ti_3O_{18}$ and $Bi_9Fe_5Ti_3O_{27}$, are obtained, which are simultaneously ferroelectric and antiferromagnetic [4].

It is reported that in these compounds, with decreasing number of layers, the antiferromagnetic Néel temperature decreases [5]. The Fe–O–Fe-ion superexchange interaction in the perovskites is predominant, when compared to the interaction between the diamagnetic Bi_2O_2 layers and the perovskite. A tilt in the octahedra in the layered structures is reported to give rise to a spontaneous magnetic moment [6]. Apart from this, the random distribution of Fe and Ti ions in the octahedra can be expected to lead to the formation of clusters of Fe ions. These clusters of Fe ions are exchange coupled to the diamagnetic layers, which can be regarded as a thin film. As the temperature is lowered, these clusters have different relaxation times, giving rise to a superparamagnetic behaviour [5].

Of all of the above layered-structure compounds, the most stable are four and five layered. $Bi_5FeTi_3O_{15}$ has a Néel temperature T_N of 80 K, whereas for $Bi_6Fe_2Ti_3O_{18}$ it is 160 K. This

† Now at: Department of Condensed Matter Physics and Materials Science, Tata Institute Fundamental Research, Mumbai-400 005, India.

0953-8984/99/163335+06$19.50

shows an increasing trend in T_N with increasing number of layers, as reported [7]. The value of the magnetic susceptibility measured for $Bi_5FeTi_3O_{15}$ earlier was 1.85×10^{-7} emu mol^{-1}, which is typical for antiferromagnets [8]. Similar five- and six-layered compounds with different dopings at the Ti site are reported to have Néel temperatures of around 110 K and 260 K respectively [5, 9]. Hysteresis loops measured at 60 K showed a non-saturating extremely narrow loop, which may be obtained because of the superparamagnetism reported earlier. The narrow hysteresis loops observed at room temperature are obtained due to a weak ferromagnetic ordering [7].

The existence of simultaneous ferroelectricity and magnetic ordering in these materials makes them candidates for exhibiting magnetoelectricity. The magnetoelectric effect (ME) is observed due to the interaction of the magnetic and electric dipoles in a strong magnetic field at a given temperature. The strain-induced magnetic ion in turn applies a stress to the electric dipole, which is realized as an electric field output.

The magnetoelectric effect is rarely reported in the literature on these materials. A quadratic signal was observed for $Bi_5FeTi_3O_{15}$ in strong DC magnetic fields and the value of the maximum output reported is 80 mV cm^{-1} [8], whereas no report is available on $Bi_6Fe_2Ti_3O_{18}$. Furthermore, no data are available on the linear (α) and quadratic (β) coefficients which govern the magnetoelectric interaction [10].

Measurement of the ME by static methods may sometimes lead to incorrect conclusions, as we have shown in an earlier report on $Bi_5FeTi_3O_{15}$, that it is an electret [8]. Instead, a more accurate measurement technique is adopted in the present investigation to calculate the linear and quadratic coefficients for these materials. Also, a temperature scan of the ME output would bring out the magnetic phase transitions occurring in the samples with enhanced sensitivity. The present paper discusses the results obtained on $Bi_5FeTi_3O_{15}$ and $Bi_6Fe_2Ti_3O_{18}$ in a dynamic environment, at room temperature and 77 K. Also, the ME output has been measured as a function of temperature over the range 77–300 K.

2. Experimental procedure

The materials are synthesized by the solid-state sintering route. Phase purity was checked using x-ray diffraction and SEM. The x-ray, electrical, dielectric and static ME properties of $Bi_5FeTi_3O_{15}$ have already been published elsewhere [8, 11].

Magnetoelectric measurements were carried out in a specially fabricated experimental set-up, the details of which are given in reference [12]. The measurements are performed in a DC magnetic field (H) varying linearly with time, with a superimposed AC field (h).

ME measurements were performed at RT and 77 K as functions of DC field (in the range 0–8 kOe) in a superimposed AC field of 18Oe for $Bi_5FeTi_3O_{15}$ and $Bi_6Fe_2Ti_3O_{18}$. Fits to the measurement, to calculate the coefficients α and β, are performed for the data obtained in the increasing magnetic field.

The samples were cooled to liquid nitrogen temperature in a magnetic field of 1.3 kOe and then the ME output was measured as a function of temperature by increasing the temperature at a rate of 3 K min^{-1} over the range 77–300 K. Prior to the measurements, both of the samples were poled electrically at 3 kV cm^{-1} (at 100 °C) and magnetically at room temperature in a DC field of 1.3 kOe. The temperature was measured using a copper–constantan thermocouple and the induced ME output, as a voltage, was measured by a lock-in amplifier (SR530). For the temperature scan of the magnetoelectric output, a fixed AC field of 18 Oe and a DC field of 1.3 kOe were used. The measurements were repeated, to check their reproducibility.

The foremost advantage of the dynamic technique compared to others is the pronounced appearance of the magnetic and dielectric transitions [13]. Magnetic transitions are rarely reported in studies using the magnetoelectric effect in polycrystalline materials [14].

3. Results and discussion

Figure 1 shows the magnetoelectric signal observed for $Bi_5FeTi_3O_{15}$ at room temperature and 77 K. The room temperature signal shows a quadratic output. The value of the ME output decreases with increasing magnetic field and, upon reversal, does not retrace its path, resulting in half of a butterfly loop. The values of the first-order (α) and second-order (β) coefficients calculated are 0.1 mV cm^{-1} Oe^{-1} and 1.37×10^{-5} mV cm^{-1} Oe^{-2} respectively, whereas the value of the maximum $\mathrm{d}E/\mathrm{d}H$ reported by Singh *et al* [8] from static measurements is 17 mV cm^{-1} Oe^{-1} at 8 kOe.

At 77 K, the ME output, with increasing field, gradually increases and, upon decreasing the field, does not retrace its path, and shows a hysteresis. The signal does not show much variation upon reduction of the field. The maximum value of the ME output obtained is 49.8 mV cm^{-1}.

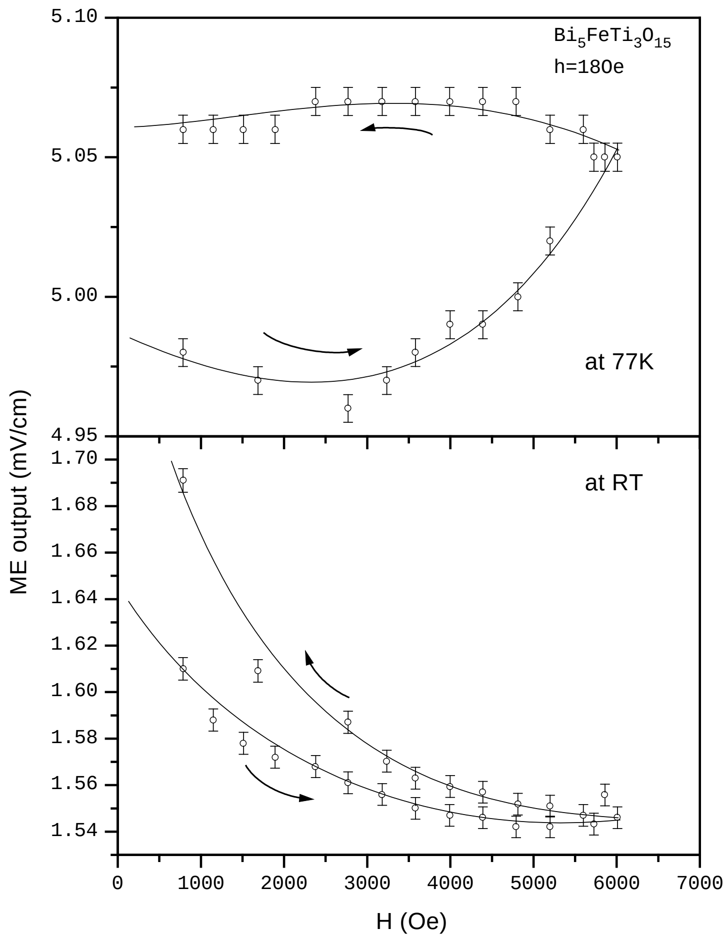

Figure 1. The variation of the magnetoelectric output with field for $Bi_5FeTi_3O_{15}$ at room temperature and 77 K (the curves are fits to the data points).

The values of α and β calculated are 2.8 mV cm^{-1} Oe^{-1} and 5.62×10^{-5} mV cm^{-1} Oe^{-2} respectively.

Figure 2 shows the magnetoelectric output obtained for $Bi_6Fe_2Ti_3O_{18}$, at room temperature and 77 K. The plot indicates the ME output to increase non-linearly. But on reversing the field, this also does not retrace its path, and shows a hysteresis. At 77 K, a quadratic signal was observed. Similarly to the room temperature curve, it too does not retrace its path, and shows a hysteresis. There is a marginal increase in the ME output as compared to the value at room temperature. The values are low compared to that for $Bi_5FeTi_3O_{15}$.

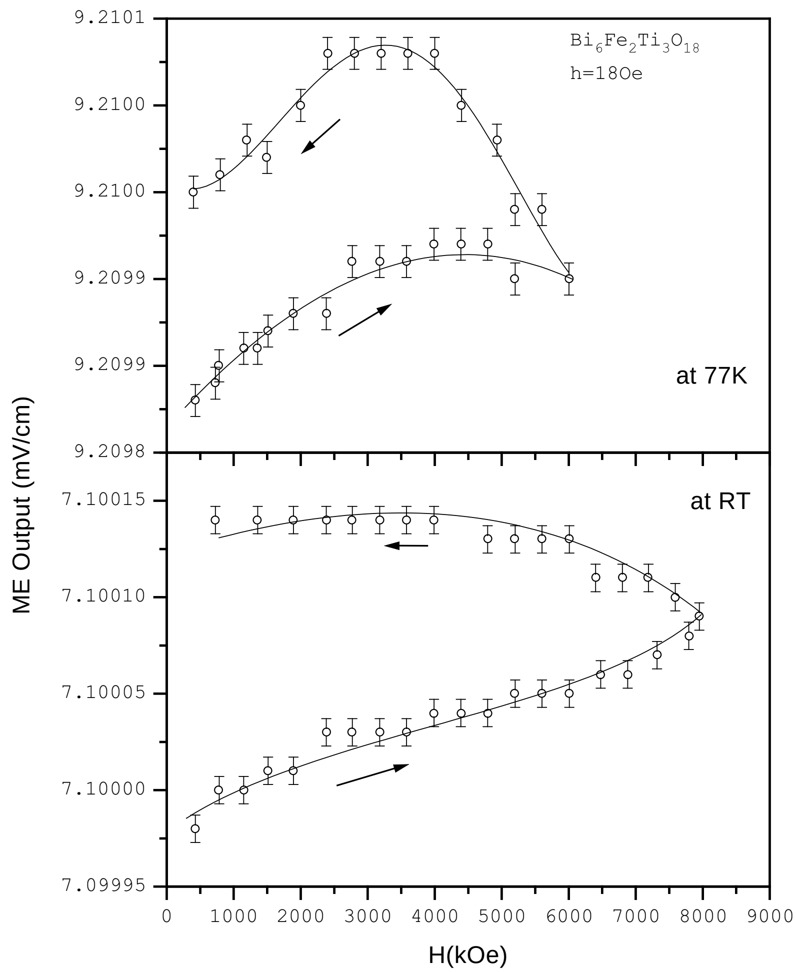

Figure 2. The variation of the magnetoelectric output with field for $Bi_6Fe_2Ti_3O_{18}$ at room temperature and 77 K (the curves are fits to the data points).

The observed irreversibility in the ME output versus *H* looks like the hysteresis loops observed in *B*–*H* measurements in antiferro/ferromagnetic materials. In the light of the hysteresis loops observed at low and high temperatures [7] and also on the basis of reports that Aurivillius phases possess ferro/ferrimagnetic properties [6], it seems possible that a striction-induced polarization is taking place. The presence of Ti^{4+} in the lattice, as reported, can induce bulk magnetization in such perovskites [15].

The antiferromagnetic nature of the above materials should give rise to linear effects, whereas a quadratic signal may be arising due to the slight canting of the Fe–O–Fe chain of spins in the regular octahedra, which is slightly tilted. Apart from this, $BiFeO_3$, which has a cycloidal magnetic spin and incommensurate structure, gives rise only to non-linear effects with a spin flop [16]. Addition of $Bi_4Ti_3O_{12}$ reduces the degree of incommensurate structure, but preserves the non-linearity. The reduced values of the ME outputs for $Bi_6Fe_2Ti_3O_{21}$ may be due to the reduced magnetization, which decreases with increasing number of layers [6].

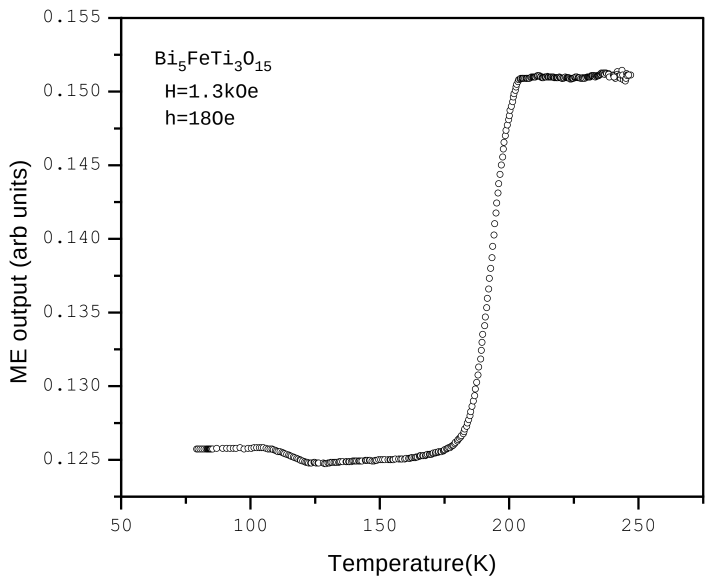

Figure 3. The variation of the magnetoelectric output with temperature for $Bi_5FeTi_3O_{15}$.

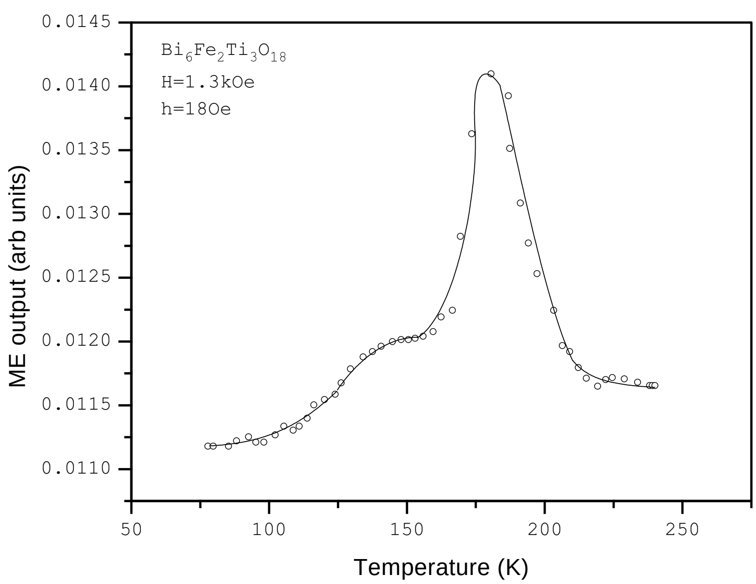

Figure 4. The variation of the magnetoelectric output with temperature for $Bi_6Fe_2Ti_3O_{18}$.

Figure 3 shows the variation of the ME output with temperature for $Bi_5FeTi_3O_{15}$. It shows an anomaly at around 85 K. Later, the output increases and gets saturated at around a temperature of 175 K. Similarly, for $Bi_6Fe_2Ti_3O_{18}$, the ME output increases non-linearly, shows a hump at around 140 K, then rises and shows an anomaly at 180 K (figure 4). The origin of the saturation in the case of $Bi_5FeTi_3O_{15}$ is not known. The anomalies observed correspond to antiferromagnetic and ferromagnetic transitions, such as have been observed in the magnetization data [7]. The magnetoelectric effect is a 'recomforting' property of electrical and magnetic phase transitions.

In conclusion, $Bi_5FeTi_3O_{15}$ and $Bi_6Fe_2Ti_3O_{18}$ show non-linear ME effects. They show hysteretic effects on the reversal of the field. Measurements of the ME output versus temperature for $Bi_5FeTi_3O_{15}$ and $Bi_6Fe_2Ti_3O_{18}$ show anomalies at around the temperatures of the magnetic phase transitions.

Acknowledgments

The authors thank DRDO, UGC, for financial assistance. AS and MMK thank CSIR, Government of India, for fellowships. They also thank Dr R S Singh, now at JNCASR, Bangalore, for providing the samples.

References

[1] Aurivillius B 1949 *Ark. Kemi* **1** 463
[2] Subba Rao E C 1961 *Phys. Rev.* **122** 804
[3] Sosnowska I, Peterlin-Neumaier T and Steichele E 1982 *J. Phys. C: Solid State Phys.* **15** 4835
[4] Ismailzade I G, Nesterenko V I, Mirshili F A and Rustamov P A 1967 *Sov. Phys.–Crystallogr.* **12** 400
[5] Sultanov G D, Guseinov N G, Ismailzade I, Mirzababaev R M and Aliev L A 1975 *Sov. Phys.–Solid State* **17** 1271
[6] Kizaev S A, Sultanov G D and Mirshili F A 1973 *Sov. Phys.–Solid State* **15** 214
[7] Singh R S 1996 Structure property correlations in some magnetically ordered Aurivillius phases *PhD Thesis* Osmania University, Hyderabad
[8] Singh R S, Bhimasankaram T, Kumar G S and Suryanarayana S V 1994 *Solid State Commun.* **91** 567
[9] Mahesh Kumar M, Srinivas A, Kumar G S and Suryanarayana S V 1997 *Solid State Commun.* **104** 741
[10] Rivera J P 1994 *Ferroelectrics* **161** 165
[11] Singh R S, Bhimasankaram T, Kumar G S and Suryanarayana S V 1998 *Ferroelectrics* at press
[12] Mahesh Kumar M, Srinivas A, Suryanarayana S V, Kumar G S and Bhimasankaram T 1998 *Bull. Mater. Sci.* **21** 251
[13] Ikeda N, Kazuhiro S, Kohn K, Kito H, Akimitsu J and Siratori K 1994 *Ferroelectrics* **161** 111
[14] Saito K and Kohn K 1995 *J. Phys.: Condens. Matter* **7** 2855
[15] Gehring G A 1994 *Ferroelectrics* **161** 275
[16] Popov Yu F, Kadomtseva A M, Vorob'ev G P and Zvezdin A K 1994 *Ferroelectrics* **162** 483