

## Magnetolectricity at room temperature in the $\text{Bi}_{0.9-x}\text{Tb}_x\text{La}_{0.1}\text{FeO}_3$ system

V. R. Palkar,<sup>1,\*</sup> Darshan C. Kundaliya,<sup>1,2</sup> S. K. Malik,<sup>1</sup> and S. Bhattacharya<sup>1</sup>

<sup>1</sup>Department of Condensed Matter Physics & Materials Science, Tata Institute of Fundamental Research, Mumbai 400 005, India

<sup>2</sup>Center for Superconductivity Research, Department of Physics, University of Maryland, College Park, Maryland 20742, USA

(Received 1 December 2003; published 10 June 2004)

Magnetolectric compounds with the general formula,  $\text{Bi}_{0.9-x}\text{R}_x\text{La}_{0.1}\text{FeO}_3$  ( $R = \text{Gd}, \text{Tb}, \text{Dy}, \text{etc.}$ ), have been synthesized. These show the coexistence of ferroelectricity and magnetism, possess high dielectric constant and exhibit magnetolectric coupling at *room temperature*. Such materials may be of great significance in basic as well as applied research.

DOI: 10.1103/PhysRevB.69.212102

PACS number(s): 75.50.-y, 75.80.+q, 77.84.-s

In some insulating materials, an external magnetic field can induce electric polarization and an external electric field can induce changes in magnetization. This phenomenon is known as the magnetolectric (ME) effect and materials exhibiting this effect are called magnetolectrics or Seignette magnets. Thus magnetolectric materials show the coexistence of ferroelectric and magnetic ordering and, therefore, could be used either as ferroelectrics or as magnetic materials in devices since both the properties exist simultaneously. The ability to couple to either the electric or the magnetic polarization allows an additional degree of freedom in device design. However, the ME effect is restricted to insulators and is not so large in magnitude. Further, most of the materials reported so far show the ME effect at temperatures much below room temperature.<sup>1,2</sup> Recently, Wang *et al.*<sup>3</sup> reported an enhancement of polarization and related properties in heteroepitaxially constrained thin films of  $\text{BiFeO}_3$ . However, the observed enhancement in magnetization is thickness dependent (up to 75 nm) and is not a bulk property in the factual sense. Hence, the search for single compounds exhibiting a magnetolectric effect at and above room temperature continues.

During the course of our research on ferroelectric and magnetic materials, we have been successful in synthesizing new compounds showing the ME effect at *room temperature*. The new compounds are based on bismuth ferrite ( $\text{BiFeO}_3$ )—a compound that is known to possess a ferroelectric ordering (transition temperature,  $T_C \sim 840^\circ\text{C}$ ) and an antiferromagnetic ordering (Néel temperature,  $T_N \sim 340^\circ\text{C}$ ) at room temperature. We have synthesized and studied the properties of  $\text{Bi}_{0.9-x}\text{R}_x\text{La}_{0.1}\text{FeO}_3$  compounds, where  $R$  could be Gd, Tb, Dy, etc., and  $x$  varies between 0.05–0.3 (a small amount of La is added to stabilize<sup>4</sup> the perovskite phase of  $\text{BiFeO}_3$ ). In this Brief Report, we report the synthesis and crystal structure of  $\text{Bi}_{0.9-x}\text{Tb}_x\text{La}_{0.1}\text{FeO}_3$  compounds, and ferroelectric and ferromagnetic properties of one representative compound, namely,  $\text{Bi}_{0.825}\text{Tb}_{0.075}\text{La}_{0.1}\text{FeO}_3$ . We also demonstrate the presence of magnetolectric coupling, at room temperature, in this compound.

The  $\text{Bi}_{0.9-x}\text{Tb}_x\text{La}_{0.1}\text{FeO}_3$  powder samples ( $0 \leq x \leq 0.3$ ) were synthesized by using a novel wet chemical route developed in our laboratory. All the cations were coprecipitated as hydroxides by using NaOH as a precipitating agent. The hydroxy complex thus obtained was calcined at  $550^\circ\text{C}$  to get reacted materials. More preparation details are described

elsewhere.<sup>5</sup> The reacted samples have been characterized by various techniques. X-ray powder diffraction (XRD) was used for phase identification. Differential thermal analysis (DTA) was carried out to determine magnetic and ferroelectric transition temperatures ( $T_M$  and  $T_C$ , respectively). The capacitance of the samples was measured by using an LCZ meter (HP Model 4277A) at a frequency of 10 kHz and field amplitude of 20 mV rms. Ferroelectric hysteresis behavior was studied by using an RT66 Loop Tracer (Radiant Technology) in the Sawyer-Tower mode. The top and bottom surfaces of the sintered pellet were coated with silver and used as electrodes. A SQUID magnetometer (MPMS, Quantum Design) was used for measuring the field dependence of the magnetization of the samples.

The compound  $\text{BiFeO}_3$  crystallizes in the rhombohedrally distorted perovskite structure. From XRD studies, we find that the Tb-substituted  $\text{Bi}_{0.9-x}\text{R}_x\text{La}_{0.1}\text{FeO}_3$  compounds are also single-phase materials crystallizing in the same structure as the parent  $\text{BiFeO}_3$  compound. A typical x-ray pattern for the sample with  $x=0.075$  is shown in Fig. 1. Tb and La substitution has not affected the crystalline structure of the parent compound, and this is important for the ferroelectric properties of the compounds. However, Tb and La substitution leads to a decrease in the unit cell volume from  $186(\text{\AA})^3$  for  $x=0$  to  $183.1(\text{\AA})^3$  for  $x=0.075$ . The decrease in unit cell volume with increasing Tb substitution is expected since the ionic radius of  $\text{Tb}^{+3}$  ( $0.923 \text{\AA}$ ) is smaller than that of  $\text{Bi}^{+3}$

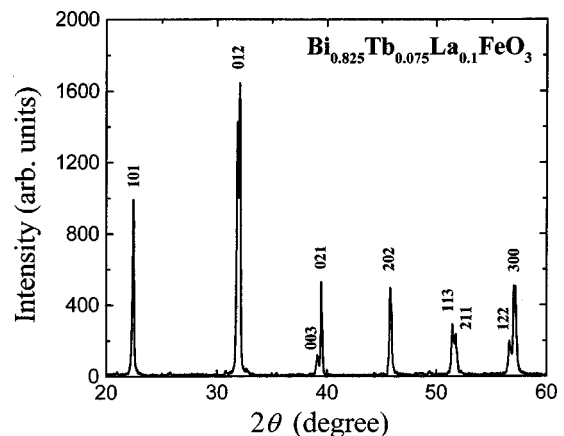


FIG. 1. The XRD pattern of the  $\text{Bi}_{0.825}\text{Tb}_{0.075}\text{La}_{0.1}\text{FeO}_3$  sample indicating the absence of impurity phases.

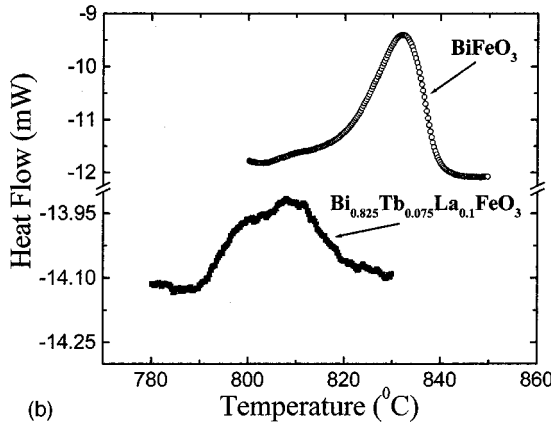
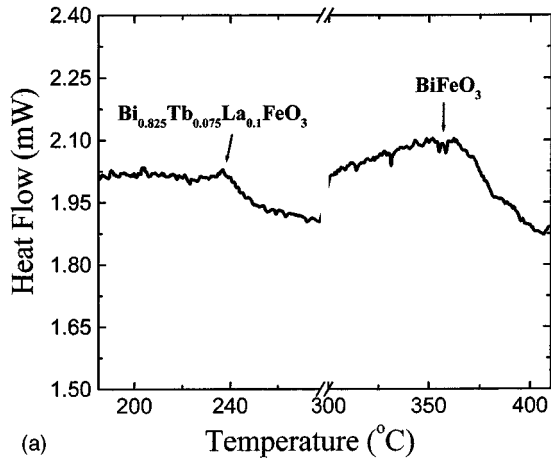


FIG. 2. (a) The DTA curve obtained for  $\text{Bi}_{0.825}\text{Tb}_{0.075}\text{La}_{0.1}\text{FeO}_3$  and  $\text{BiFeO}_3$  samples showing the change in the magnetic ordering ( $T_M$ ) temperature. (b) The DTA curve obtained for  $\text{Bi}_{0.825}\text{Tb}_{0.075}\text{La}_{0.1}\text{FeO}_3$  and  $\text{BiFeO}_3$  samples showing the change in the ferroelectric transition ( $T_C$ ) temperature.

(0.96 Å). Figure 2 shows the results of DTA measurements on  $\text{BiFeO}_3$  and  $\text{Bi}_{0.825}\text{Tb}_{0.075}\text{La}_{0.1}\text{FeO}_3$  samples in the (a) 200 °C to 400 °C temperature interval and (b) in the 780 °C to 850 °C temperature interval. For the parent compound, the

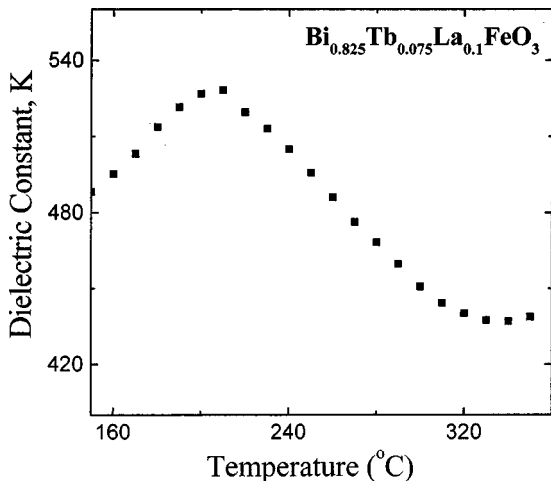


FIG. 3. The dielectric response with temperature measured for the  $\text{Bi}_{0.825}\text{Tb}_{0.075}\text{La}_{0.1}\text{FeO}_3$  sample.

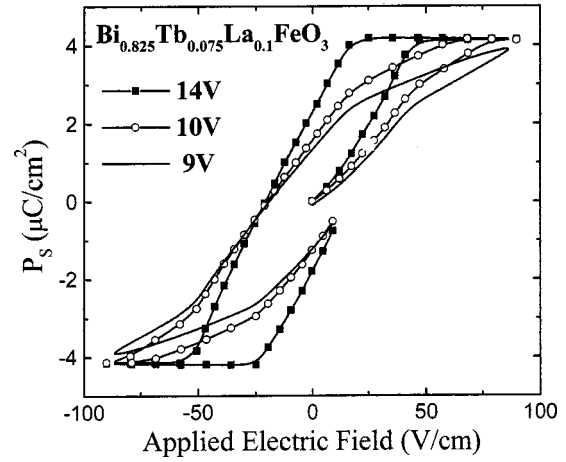


FIG. 4. The saturated ferroelectric hysteresis loop obtained on the  $\text{Bi}_{0.825}\text{Tb}_{0.075}\text{La}_{0.1}\text{FeO}_3$  pellet sample. Resistivity of the sample is  $\sim 10^8 \Omega \text{ cm}$ .

peak obtained in DTA at  $\sim 340 \text{ °C}$  [Fig. 2(a)] is known to be due to magnetic ordering in this compound. The same is shifted down to 245 °C in the Tb-substituted compound. Incidentally, a dielectric anomaly has been also observed near the magnetic transition temperature (Fig. 3). This type of dielectric anomaly in magnetoelectrically ordered systems is predicted by the Landau–Devonshire theory of phase transition as an influence of vanishing magnetic order on the electric order.<sup>6</sup> The peak at  $\sim 806 \text{ °C}$  in DTA [Fig. 2(b)] is attributed to ferroelectric transition and occurs at a slightly lower temperature than that in parent  $\text{BiFeO}_3$ .<sup>7,8</sup> The decrease in ferroelectric transition temperatures ( $T_C$ ) of  $\text{BiFeO}_3$  on Tb substitution may be ascribed to the decrease in unit cell volume caused by Tb.

The polarization ( $P_s$ ) versus applied electric field ( $E$ ) hysteresis loop for the as-sintered  $\text{Bi}_{0.825}\text{Tb}_{0.075}\text{La}_{0.1}\text{FeO}_3$  pellet is shown in Fig. 4. Saturated hysteresis loop seen in this figure reveals the ferroelectric behavior of the as-sintered pellet. Figure 5 shows the variation of magnetization ( $M$ ) with an applied field ( $H$ ) at room temperature for  $\text{BiFeO}_3$  as well as for  $\text{Bi}_{0.825}\text{Tb}_{0.075}\text{La}_{0.1}\text{FeO}_3$  samples. The magnetization for pure  $\text{BiFeO}_3$  is small and varies linearly with the

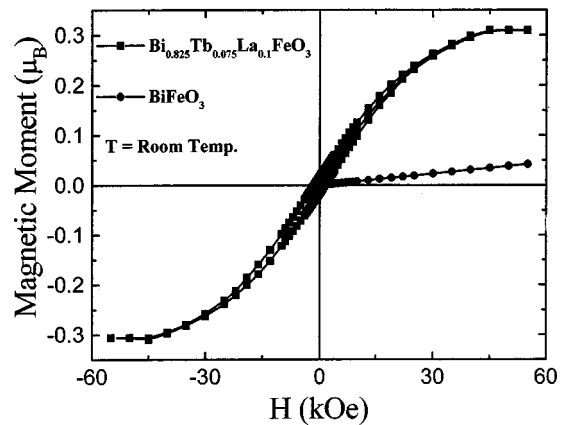


FIG. 5. The  $M (\mu_B/\text{fu})-H$  curve at room temperature for  $\text{Bi}_{0.825}\text{Tb}_{0.075}\text{La}_{0.1}\text{FeO}_3$  and  $\text{BiFeO}_3$  samples.

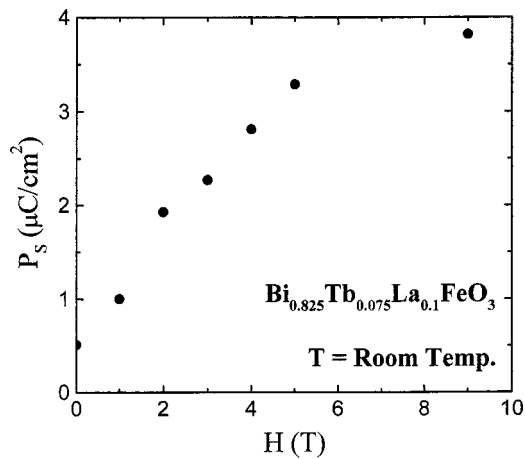


FIG. 6. Saturation polarization ( $P_s$ ) versus the magnetic field used for poling the  $\text{Bi}_{0.825}\text{Tb}_{0.075}\text{La}_{0.1}\text{FeO}_3$  pellet sample.

field as expected for an antiferromagnetic material. In contrast, a saturation in the  $M$ - $H$  curve is obtained at 300 K in  $\text{Bi}_{0.825}\text{Tb}_{0.075}\text{La}_{0.1}\text{FeO}_3$ , which indicates that the sample is ferro- or ferrimagnetically ordered even at room temperature, consistent with the magnetic ordering temperature of 245 °C observed in DTA measurements. Thus ferroelectric and magnetic orders coexist in this compound at room temperature. The ferromagnetic moment at 300 K is estimated to be about  $4\mu_B$  per Tb ion which may increase at lower temperatures and tend toward a  $\text{Tb}^{3+}$ -free ion value.

In order to demonstrate the coupling between electric and magnetic polarizations in  $\text{Bi}_{0.825}\text{Tb}_{0.075}\text{La}_{0.1}\text{FeO}_3$ , we have carried out two experiments, namely, (a) the measurement of electric polarization after poling the sample in a magnetic field, and (b) *in situ* changes in capacitance with the application of a magnetic field. Figure 6 shows the change in saturation polarization ( $P_s$ ) values for the sample after poling at different magnetic fields. A continuous increase in  $P_s$  is seen with an increase in the poling field before  $P_s$  eventually saturates. This is indicative of the coupling between the two polarizations. An increase in the dielectric constant with an increase in the magnetic field is observed (Fig. 7), and this is also a signature of the ME conversion occurring in the sample. The magnetoelectric coupling observed at room

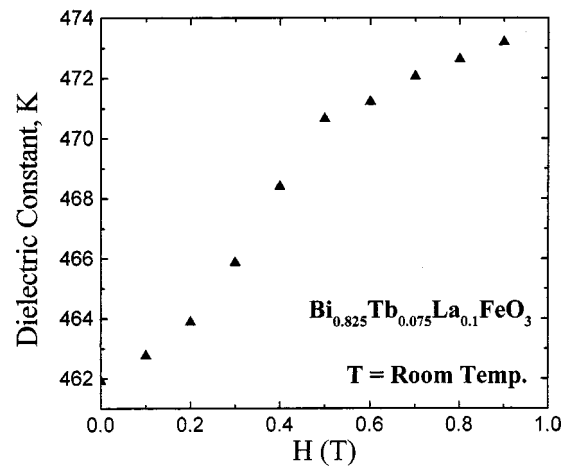


FIG. 7. Dielectric constant  $K$  versus the magnetic field ( $H$ ) curve for the  $\text{Bi}_{0.825}\text{Tb}_{0.075}\text{La}_{0.1}\text{FeO}_3$  pellet sample.

temperature and the observed reduction in lattice parameters indirectly confirm that Tb is not remaining isolated in the matrix of the compound but enters the lattice. Although the theory of magnetoelectric media<sup>9</sup> is based on symmetry arguments, which are not yet available for our novel ferromagnetic-ferroelectric compound, the essence of magnetoelectric coupling may be envisaged as follows. When a magnetic field is applied to a magnetoelectric material, the material is strained. This strain induces a stress on the piezoelectric (all ferroelectrics are piezoelectrics), which generates the electric field. This field could orient the ferroelectric domains, leading to an increase in polarization value. Such magnetoelectric coupling and the large dielectric constant observed in the present system could be useful in device applications.

In summary, we have been successful in synthesizing a new system exhibiting magnetoelectric coupling and large dielectric constant at room temperature. The material characteristics may be highly useful in numerous devices. We have also been able to grow thin films of the same material with similar properties and the result will be published elsewhere.

The authors wish to thank A. V. Gurjar, J. John, B. A. Chalke, and D. Buddhikot for experimental help.

\*Corresponding author. Electronic mail: palkar@tifr.res.in

<sup>1</sup>N. A. Hill, *J. Phys. Chem. B* **104**, 6694 (2000).

<sup>2</sup>K. Uchino, *Comprehensive Composite Materials* (Elsevier, Amsterdam, 2000), Vol. 5, Chap. 5.24, p. 523.

<sup>3</sup>J. Wang, B. J. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wutting, and R. Ramesh, *Science* **299**, 1719 (2003).

<sup>4</sup>I. Sosnowska, T. Peterlin-Neumaier, and E. Steichele, *J. Phys. C* **15**, 4835 (1982).

<sup>5</sup>V. R. Palkar, Darshan C. Kundaliya, and S. K. Malik, Indian Patent Application No. 409/MUM/2003, dated 24 April 2003.

<sup>6</sup>L. Benguigui, *Solid State Commun.* **11**, 825 (1972).

<sup>7</sup>M. Polomska, W. Kaczmarek, and Z. Pajak, *Phys. Status Solidi A* **28**, 567 (1974).

<sup>8</sup>W. Kaczmarek, Z. Pajak, and M. Polomska, *Solid State Commun.* **17**, 807 (1975).

<sup>9</sup>T. H. O'Dell, *The Electrodynamics of Magneto-Electric Media* (North-Holland, Amsterdam, 1970).