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## LETTER TO THE EDITOR

# The effect of Ti substitution on magnetoelectric coupling at room temperature in the $\text{BiFe}_{1-x}\text{Ti}_x\text{O}_3$ system

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## Abstract

Magnetoelectric compounds  $\text{BiFe}_{1-x}\text{Ti}_x\text{O}_3$  ( $x = 0.1, 0.2$  and  $0.3$ ) have been synthesized by the conventional solid state reaction method and the effect of Ti substitution on the ferroelectric and magnetic properties studied. It is seen that Ti substitution does not affect the ferroelectric transition temperature ( $T_c$ ) of the  $\text{BiFe}_{1-x}\text{Ti}_x\text{O}_3$  system. An anomaly in the dielectric constant and dielectric loss in the vicinity of the antiferromagnetic Néel temperature ( $T_N$ ) and a small enhancement in magnetization have been observed. No systematic variation in the antiferromagnetic Néel temperatures has been observed on Ti substitution. Furthermore, it is seen that this system shows coupling between electric and magnetic dipoles exhibiting a magnetoelectric effect at room temperature and possesses a high dielectric constant.

## 1. Introduction

Multiferroics are the class of materials exhibiting coexistence of magnetic and ferroelectric ordering in the same phase [1, 2]. These materials, therefore, have the potential for applications in magnetic as well as ferroelectric devices. The ability to couple to either the electric or the magnetic polarization allows an additional degree of freedom in device design. However, multiferroic materials are rare in nature because the condition for being simultaneously ferroelectric and ferromagnetic is difficult to achieve. In general, the ferroelectric Curie temperature is considerably higher than the magnetic ordering temperature in the most known materials; the latter is below room temperature. Although a material with a large magnetoelectric (ME) coupling at room temperature is desired for practical applications, the ME couplings of most materials are normally small at room temperature and furthermore it is

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rather difficult to find a material with a large ME effect at room temperature. Therefore, the search for single phase compounds exhibiting a magnetoelectric coupling at and above room temperature continues.

As a typical ferroelectric material, BiFeO<sub>3</sub> has been controversial as regards its ferroelectromagnetic property and is reported to exhibit about eight structural transitions [3–5]. It has long been known to be, in its bulk form, an antiferromagnetic ferroelectric multiferroic, with antiferromagnetic Néel temperature  $T_N \sim 370^\circ\text{C}$  with a cycloidal spin arrangement, and ferroelectric Curie temperature  $T_c \sim 830^\circ\text{C}$  [2, 3, 6, 7]. It crystallizes in the rhombohedrally distorted perovskite structure with space group  $R3c$ . The Fe magnetic moments are coupled ferromagnetically within the pseudocubic (111) planes and antiferromagnetically between adjacent planes (so-called G-type antiferromagnetic order). Its low resistivity at room temperature prevents proper electric poling and makes the observation of the ferroelectric hysteresis ( $P-E$ ) loop very difficult [8]. In order to increase the resistivity, Teague *et al* [3] measured the ferroelectric hysteresis loop at liquid nitrogen temperature. They were able to observe a loop on a single crystal at 80 K and obtained a saturation polarization  $P_S$  of  $3.5 \mu\text{C cm}^{-2}$ . Recently, Wang *et al* reported enhanced ferroelectricity in Ti doped BiFeO<sub>3</sub> thin films [9]. In this paper, we report the synthesis, crystal structure and dielectric properties of BiFe<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> compounds along with magnetic properties and magnetoelectric coupling at room temperature of one representative compound, namely, BiFe<sub>0.8</sub>Ti<sub>0.2</sub>O<sub>3</sub>.

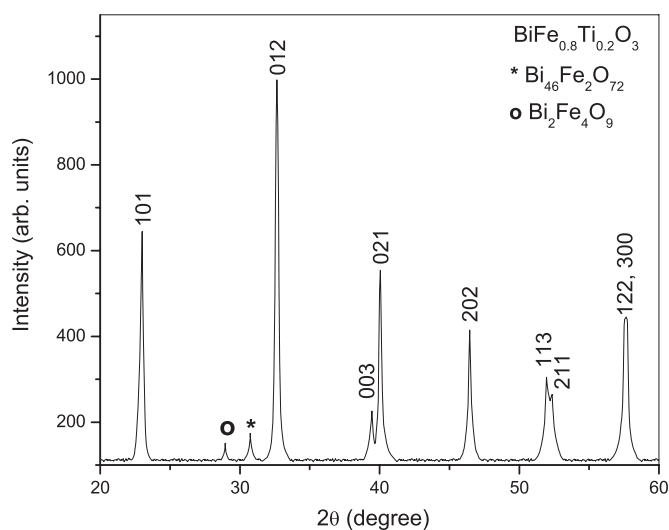
## 2. Experimental details

The BiFe<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> ( $x = 0.1, 0.2$  and  $0.3$ ) samples were synthesized by the conventional solid state reaction method using high purity Bi<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> as starting materials. Both surfaces of the pressed pellets, finally sintered at  $800^\circ\text{C}$ , were coated with silver paste and used as electrodes. X-ray diffraction (XRD) was used for phase identification and differential thermal analysis (DTA) was carried out to determine the ferroelectric transition temperature ( $T_c$ ). Dielectric measurements were carried out using a LCR meter (Model 3532-50, HIKOI) in a temperature range of  $40$ – $550^\circ\text{C}$  at different frequencies. A modified Sawyer–Tower circuit was used to study the ferroelectric hysteresis behaviour. The temperature dependence of the magnetization from room temperature to  $450^\circ\text{C}$  and the magnetic hysteresis ( $B-H$ ) loops were measured using a vibrating sample magnetometer (VSM) supplied by Priston Applied Research.

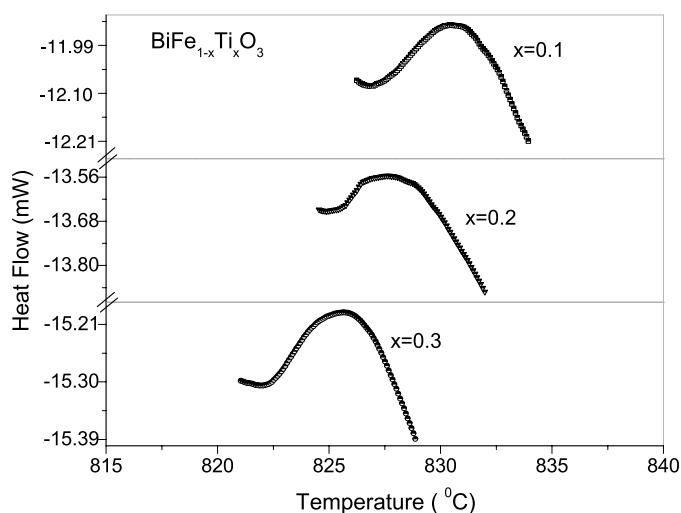
## 3. Results and discussion

From XRD analysis, we observe that the Ti substituted BiFe<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> compounds are single phase materials crystallizing in the same structure as the parent BiFeO<sub>3</sub> compound. Ti substitution for Fe in BiFeO<sub>3</sub> has not affected the structure of the parent compound up to  $x = 0.3$ . A typical XRD pattern of the BiFe<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> sample with  $x = 0.2$  is shown in figure 1. Because of the kinetics of formation, some impurity phases are always obtained along with BiFeO<sub>3</sub> as the major phase during synthesis. The existence of Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> and Bi<sub>46</sub>Fe<sub>2</sub>O<sub>72</sub> as impurity phases was reported by several authors [3, 8]. The resistivity of the BiFe<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> samples was found to be of the order of  $10^{11} \Omega \text{ cm}$  at room temperature.

In order to investigate the thermal behaviour related to phase changes, DTA results for BiFe<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> samples were obtained and these are presented in figure 2. The peaks obtained around  $830$ ,  $827$  and  $825^\circ\text{C}$  are attributed to the ferroelectric transition temperatures ( $T_c$ ) for BiFe<sub>0.9</sub>Ti<sub>0.1</sub>O<sub>3</sub>, BiFe<sub>0.8</sub>Ti<sub>0.2</sub>O<sub>3</sub> and BiFe<sub>0.7</sub>Ti<sub>0.3</sub>O<sub>3</sub>, respectively. DTA results reveal that the Ti substitution does not affect the ferroelectric transition temperature of BiFe<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> compounds appreciably.

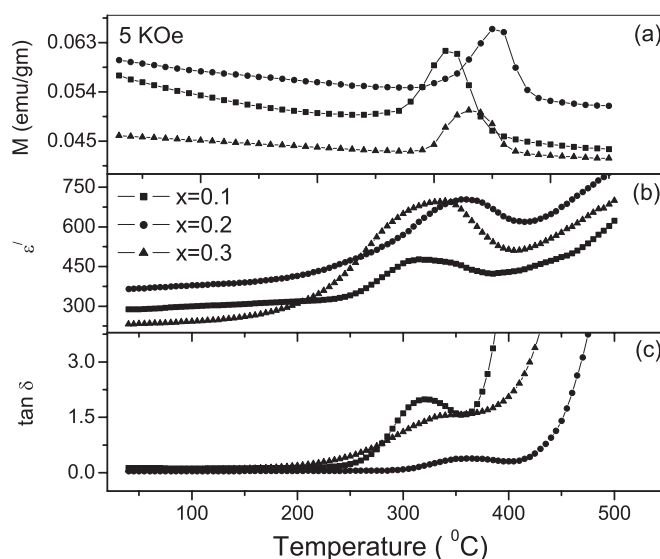


**Figure 1.** X-ray diffraction pattern for  $\text{BiFe}_{0.8}\text{Ti}_{0.2}\text{O}_3$  compound.



**Figure 2.** The DTA curve observed for  $\text{BiFe}_{1-x}\text{Ti}_x\text{O}_3$  compounds showing the ferroelectric transition ( $T_c$ ) temperature.

In figure 3(a), the temperature dependence of the magnetization of  $\text{BiFe}_{1-x}\text{Ti}_x\text{O}_3$  compounds under 5 kOe is presented. From the magnetization variation, the antiferromagnetic transitions are observed to take place at 310, 350 and 330 °C for  $\text{BiFe}_{0.9}\text{Ti}_{0.1}\text{O}_3$ ,  $\text{BiFe}_{0.8}\text{Ti}_{0.2}\text{O}_3$  and  $\text{BiFe}_{0.7}\text{Ti}_{0.3}\text{O}_3$ , respectively. Therefore, no systematic and significant variation in peak position with change in Ti content in  $\text{BiFe}_{1-x}\text{Ti}_x\text{O}_3$  was observed from the magnetization study. Scanning electron microscopy results (not presented here) revealed that Ti substitution in  $\text{BiFeO}_3$  improves the microstructure and reduces the grain size and hence increases the volume fraction of grain boundaries. Therefore, the high value of the dielectric constant ( $\epsilon'$ ) in  $\text{BiFe}_{1-x}\text{Ti}_x\text{O}_3$  samples may be attributed to the interfacial polarization which arises because of the high volume fraction of grain boundaries as observed in SEM. The variation of the

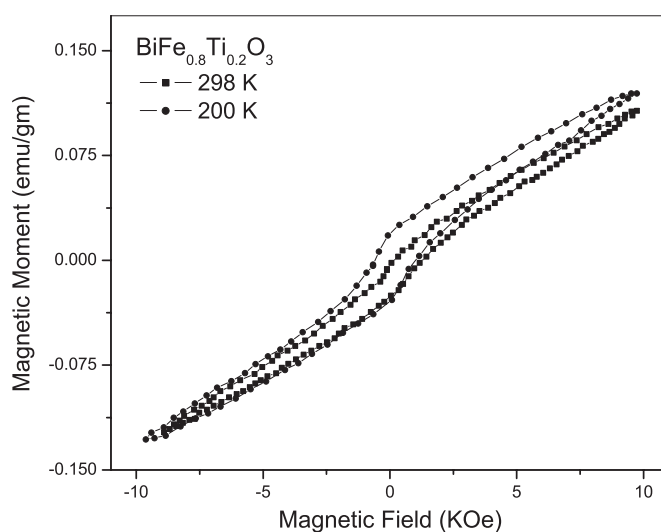


**Figure 3.** Variation of (a) magnetization, (b) dielectric constant and (c) dielectric loss with temperature. The dielectric constant and dielectric loss are measured at 10 kHz frequency.

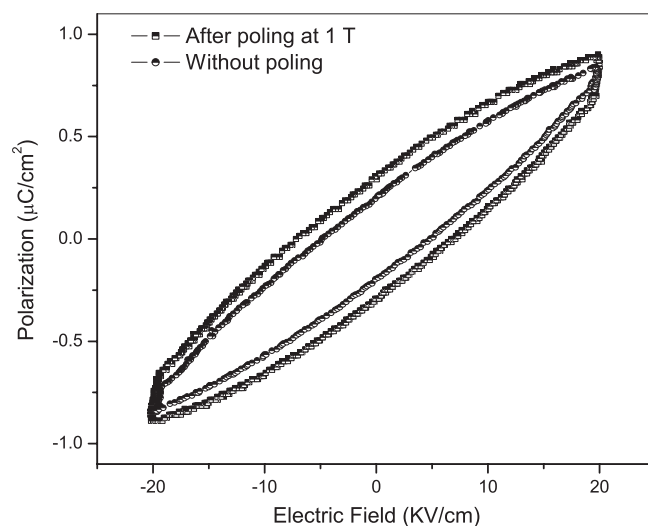
dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\tan \delta$ ) with temperature is shown in figures 3(b) and (c) at 10 kHz. Incidentally, a dielectric anomaly in the dielectric constant and dielectric loss has been also observed in the vicinity of the Néel temperature for all compositions, indicating magnetoelectric coupling in the  $\text{BiFe}_{1-x}\text{Ti}_x\text{O}_3$  system. Several workers reported a small dielectric anomaly in the vicinity of the Néel temperature for bulk and thin films of  $\text{BiFeO}_3$  [7, 10]. The Landau–Devonshire theory of phase transitions predicated this type of dielectric anomaly in magnetoelectrically ordered systems as an effect of vanishing magnetic order on the dielectric order [11].

The magnetization versus applied magnetic field hysteresis ( $B$ – $H$ ) loops for the  $\text{BiFe}_{0.8}\text{Ti}_{0.2}\text{O}_3$  sample at 200 and 298 K are presented in figure 4. However, the loops are not saturated, but the larger loop area at 200 K shows increased magnetization at lower temperature. The magnetization increased with increase in Ti content up to  $x = 0.2$  and thereafter decreased on further increase in Ti content. The maximum magnetization was observed for  $\text{BiFe}_{0.8}\text{Ti}_{0.2}\text{O}_3$  compound and similar results are reported for  $\text{BiFeO}_3$ – $\text{BaTiO}_3$  solid solutions [12]. Remnant magnetizations observed in these compounds are very small compared to those for nominal ferromagnetic compounds. Gehring [13] and Goodenough *et al* [14] suggested that statistical distribution of  $\text{Fe}^{3+}$  and  $\text{Ti}^{4+}$  ions in the octahedra or creation of lattice defects might lead to bulk magnetization and weak ferromagnetism. The charge compensation due to  $\text{Ti}^{4+}$  substitution in  $\text{BiFeO}_3$  can be achieved by filling of oxygen vacancies and/or formation of  $\text{Fe}^{2+}$ . The appearance of weak ferromagnetism in this compound may be attributed to either the canting of the antiferromagnetically ordered spins by a structural distortion [15–17] or the breakdown of the balance between the antiparallel sublattice magnetization of  $\text{Fe}^{3+}$  due to metal ion substitution with a different valence [18, 19]. Further studies are required to understand the magnetic behaviour of this compound.

The coupling between electric and magnetic dipoles at room temperature is demonstrated in figures 5 and 6, obtained by measuring the effect of magnetic poling on the ferroelectric hysteresis loop and the variation of the dielectric constant as a function of the magnetic field. After poling the sample at 1 T DC magnetic field, the ferroelectric hysteresis loop showed

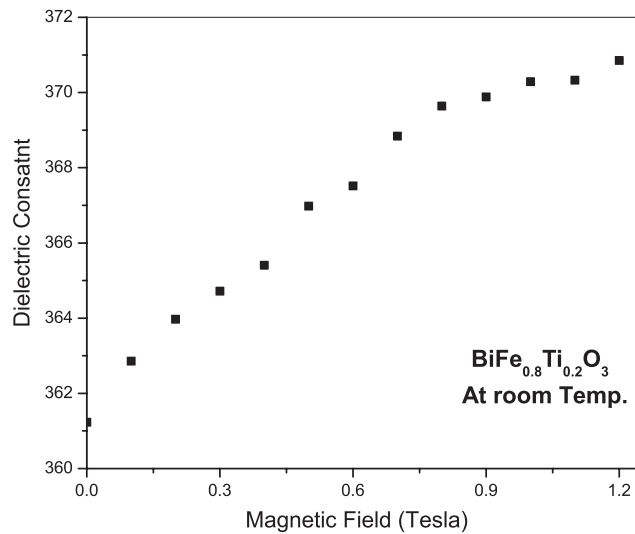


**Figure 4.** Magnetic hysteresis loops of  $\text{BiFe}_{0.8}\text{Ti}_{0.2}\text{O}_3$  samples at 298 and 200 K.



**Figure 5.** Ferroelectric hysteresis loops of  $\text{BiFe}_{0.8}\text{Ti}_{0.2}\text{O}_3$  sample without poling and after poling at 1 T DC magnetic field.

an enhancement in the remnant polarization from  $0.202$  to  $0.296 \mu\text{C cm}^{-2}$  and the coercivity increased from  $4.87$  to  $7.21 \text{ kV cm}^{-1}$ . In addition, the measurements of the dielectric constant as a function of magnetic field showed an enhancement in dielectric constant with increase in the applied magnetic field, which clearly indicates coupling between electric and magnetic dipoles at room temperature. Catalan *et al* [20] discussed the influence of magnetoresistance on magnetocapacitance. To see the influence of magnetoresistance on the magnetodielectric effect observed in figure 6, we studied the variation in magnetoresistance with magnetic field up to 1.2 T. We did not observe any change in the magnetoresistance with the increase in magnetic field up to 1.2 T. Therefore, the magnetodielectric effect shown in figure 6 is solely because of magnetoelectric coupling and not due to the influence of magnetoresistance.



**Figure 6.** Dielectric constant versus the magnetic field curve for  $\text{BiFe}_{0.8}\text{Ti}_{0.2}\text{O}_3$  sample.

#### 4. Conclusion

In summary, we have studied the effect of Ti substitution on ferroelectric and magnetic properties of the  $\text{BiFe}_{1-x}\text{Ti}_x\text{O}_3$  system. We have been successful in synthesizing a new  $\text{BiFe}_{1-x}\text{Ti}_x\text{O}_3$  system that possesses a large dielectric constant and exhibits ME coupling at room temperature. It would, therefore, be interesting to realize thin films of the same system and study their properties with a view to device applications.

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