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Observation of the room temperature magnetoelectric effect in Dy doped BiFeO₃

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Online at stacks.iop.org/JPhysCM/21/012205**Abstract**

Polycrystalline Bi_{1-x}Dy_xFeO₃ ($x = 0.0, 0.03, 0.05, 0.07$ and 0.1) ceramics have been prepared via a mixed oxide route. The effect of Dy substitution on the dielectric, ferroelectric, and magnetic properties of the BiFeO₃ multiferroic perovskite is studied. Experimental results suggest that in the Bi_{1-x}Dy_xFeO₃ system, increase of the Dy concentration leads to effective suppression of the spiral spin structure of BiFeO₃, resulting in the appearance of net magnetization. An anomaly in the dielectric constant (ϵ) was observed in the vicinity of the antiferromagnetic transition temperature. All compositions show saturated polarization–field (P – E) curves. As a result, improved multiferroic properties of Bi_{0.9}Dy_{0.1}FeO₃ ceramics with remnant polarization and magnetization ($2P_r$ and $2M_r$) of $7.98 \mu\text{C cm}^{-2}$ and 0.024 emu g^{-1} , respectively, were established. An enhancement in remnant polarization after poling the samples in the magnetic field was evidence of magnetoelectric coupling at room temperature.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Multiferroic materials exhibit ferroelectric and ferromagnetic/antiferromagnetic properties in the same phase. These materials may also exhibit magnetoelectric effects by virtue of which electric polarization is induced in the material on application of a magnetic field and magnetization is induced on application of an electric effect. This is quite a rare phenomenon since ferroelectricity and ferromagnetism make mutually exclusive groups [1]; still there are a few materials which have attracted a lot of researchers. BiFeO₃ is one such material which shows a lot of potential for research. This material is antiferromagnetic and ferroelectric having an antiferromagnetic Néel temperature (T_N) of 370 °C and a ferroelectric temperature (T_C) of 810 °C. Despite it being a ferroelectric, saturated ferroelectric hysteresis loops have not been obtained for the bulk material due to low resistivity [2]. The resistivity of BiFeO₃ has been increased by rapid liquid phase sintering [3, 4] or by making solid solutions with BaTiO₃ or PbZrTiO₃ [5, 6]. The inhomogeneous spin structure of BiFeO₃ leads to cancellation of the macroscopic magnetization which prohibits the linear magnetoelectric effect from being

observed [7, 8]. This incommensurate spiral spin structure can be suppressed by strain [9], high magnetic field [10] and various dopings [11]. The resistivity and magnetization have to be increased considerably if it is to find applications in technology.

Rare earth dopants have proved successful in improving the magnetization in BiFeO₃. Earlier we have reported the substitution of Gd in place of Bi³⁺ in BiFeO₃ [12]. Samarium doping has also increased the magnetization, as compared to undoped BiFeO₃ [13]. To the best of our knowledge no work has been done on bulk Dy doped BiFeO₃. In this paper we report the synthesis of Dy doped BiFeO₃ samples with composition Bi_{1-x}Dy_xFeO₃, $x = 0.03, 0.05, 0.07, 0.1$ and the effect of Dy substitution on multiferroic properties.

2. Experimental details

Ceramic samples of Bi_{1-x}Dy_xFeO₃, $x = 0.0, 0.03, 0.05, 0.07$ and 0.1 were prepared by a conventional solid state reaction technique. Bi₂O₃, Fe₂O₃ and Dy₂O₃ were used as starting reagents. The ratio of components was taken in accordance with the stoichiometric formula. The calcination of the finely

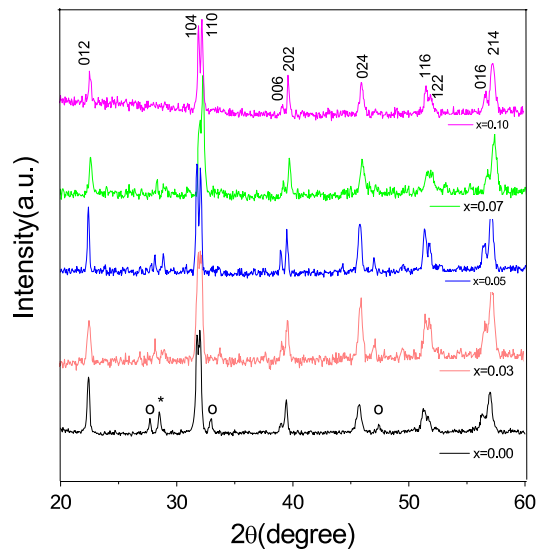


Figure 1. X-ray diffraction pattern for the $\text{Bi}_{1-x}\text{Dy}_x\text{FeO}_3$ system ($x = 0.0, 0.03, 0.05, 0.07, 0.1$); (O) and (*) represent the impurity phases.

ground powder was done at 800°C . The pellet specimens of 1 mm thickness and 7 mm diameter were prepared with an organic binder and sintered at 820°C in air atmosphere. Sintered pellets were polished and flat surfaces were coated with silver paste and then dried at 100°C for 30 min before taking electrical measurements. The phase purity of the materials obtained was examined using the XRD of the sintered pellets. Dielectric characterization was done by using an LCR meter (HIOKI model 3532-50). The room temperature magnetic hysteresis ($M-H$) loops were measured using a superconducting quantum interference device magnetometer (SQUID) with a maximum magnetic field of 70 kOe. The temperature dependence of the magnetization was found using a vibrating sample magnetometer (VSM).

3. Results and discussion

Figure 1 shows the XRD pattern for all the compositions. From the XRD analysis, we observe that $\text{Bi}_{1-x}\text{Dy}_x\text{FeO}_3$ has a majority phase of BiFeO_3 . All the samples show the peaks corresponding to the parent BiFeO_3 . Dy substitution for Bi in BiFeO_3 has not affected the structure of the parent compound up to $x = 0.1$. The lattice parameters (equivalent to hexagonal for $x < 0.10$) of $\text{Bi}_{1-x}\text{Dy}_x\text{FeO}_3$ are: for $x = 0.00$, $a = 5.5736 \text{ \AA}$, $c = 13.921 \text{ \AA}$, for $x = 0.03$, $a = 5.557 \text{ \AA}$, $c = 13.964 \text{ \AA}$, for $x = 0.05$, $a = 5.5416 \text{ \AA}$, $c = 13.747 \text{ \AA}$, for $x = 0.07$, $a = 5.5327 \text{ \AA}$, $c = 13.776 \text{ \AA}$ and for $x = 0.1$, $a = 5.5312 \text{ \AA}$, $c = 13.759 \text{ \AA}$. Because of the kinetics of formation, some impurity phases are always obtained along with BiFeO_3 as the major phase during synthesis. The existence of $\text{Bi}_2\text{Fe}_4\text{O}_9$ and $\text{Bi}_4\text{Fe}_2\text{O}_7$ as impurity phases has been reported by several authors [2, 14]. A small amount of secondary phase was observed in the samples up to $x = 0.05$. The intensity of impurity peaks is reduced with increase in the Dy concentration and we obtained pure phase $\text{Bi}_{0.9}\text{Dy}_{0.1}\text{FeO}_3$.

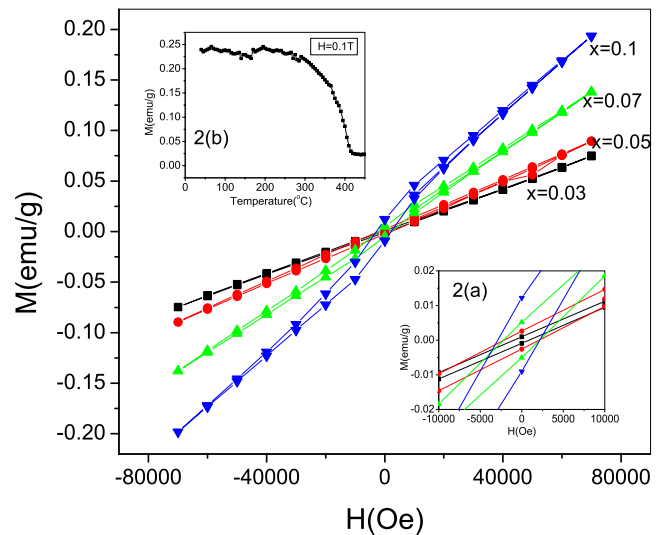


Figure 2. Room temperature magnetic hysteresis plots for all samples. Inset (a) shows an enlarged view of the $M-H$ loops. The $M-T$ curve is shown for $\text{Bi}_{0.9}\text{Dy}_{0.1}\text{FeO}_3$ at 0.1 T in inset (b).

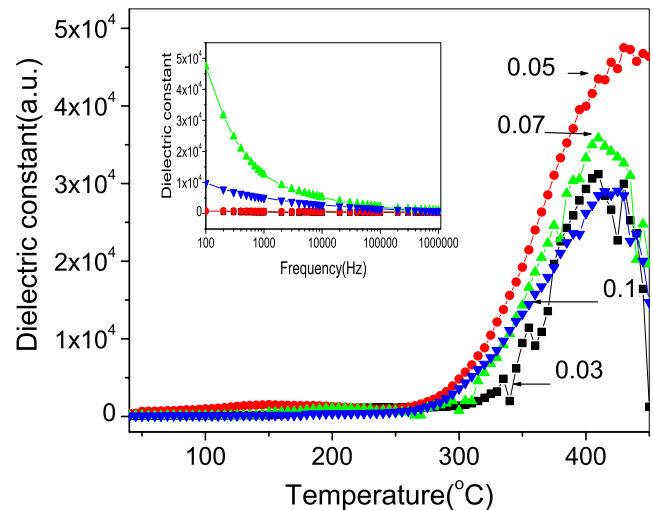


Figure 3. Dielectric constant versus temperature plot for the $\text{Bi}_{1-x}\text{Dy}_x\text{FeO}_3$ system ($x = 0.03, 0.05, 0.07, 0.1$). The inset shows the respective frequency dependences of the dielectric constant.

The calculated values of lattice parameters indicate that there is a continual change of lattice constant as a result of replacing the Bi^{3+} ion with the Dy^{3+} ion.

SQUID measurements were performed on the samples in order to study the magnetization hysteresis ($M-H$) loops at room temperature with a maximum applied field of 7 T. The $M-H$ loops are shown in figure 2. Magnetization increases noticeably with increase in the doping content. Inset 2(a) shows that the loop area increases with increase in the Dy concentration. Results show that a sample with $x = 0.03$ shows a narrow magnetic hysteresis loop, a weak ferromagnetic behaviour like that of pure BiFeO_3 , with remnant magnetization (M_r) of $9.5 \times 10^{-4} \text{ emu g}^{-1}$ and a coercive field (H_c) of 693 Oe. Similarly $\text{Bi}_{0.95}\text{Dy}_{0.05}\text{FeO}_3$ also shows a weak ferromagnetic behaviour, with a wider loop. The

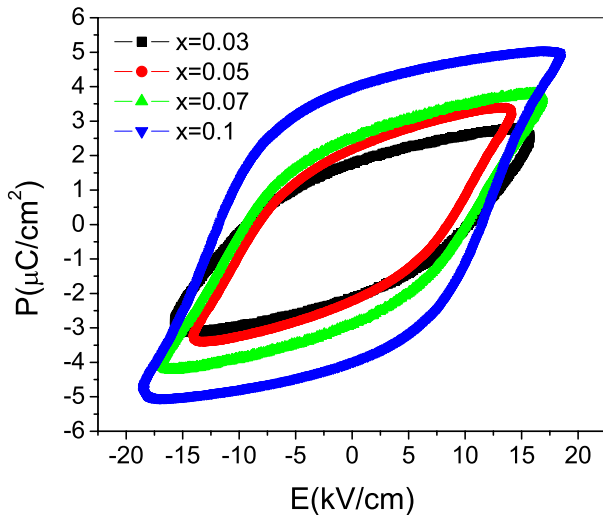


Figure 4. Ferroelectric (P - E) loops for all the samples.

increase in magnetization with dysprosium doping is also in agreement with other experimental reports [8, 12, 13] and has been attributed to suppression in the inhomogeneous magnetic spin structure, and increased canting angle. With further increase in Dy concentration the magnetization is highly enhanced and we obtained $M_r = 0.12 \text{ emu g}^{-1}$ for $x = 0.1$. In inset 2(b), the temperature dependence of the magnetization (M - T) of $\text{Bi}_{0.9}\text{Dy}_{0.1}\text{FeO}_3$ under 1 kOe is presented. From the magnetization variation, the antiferromagnetic transition is observed to take place at 400°C .

Figure 3 shows the temperature dependence of the dielectric constant for all the samples at 10 kHz. Incidentally, a dielectric anomaly in the dielectric constant has also been observed in the vicinity of the Néel temperature for all compositions, indicating magnetoelectric coupling in the $\text{Bi}_{1-x}\text{Dy}_x\text{FeO}_3$ system. Several workers reported a small dielectric anomaly in the vicinity of the Néel temperature for bulk and thin films of BiFeO_3 [15, 16]. 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 electric order [5, 17]. No systematic increase in dielectric constant with increase in the concentration of Dy is observed. The frequency dependence of the dielectric constant (ϵ) is shown in the inset. It is clear that the dielectric constant is strongly frequency dependent. Sigmoidal variation in the low frequency region is observed, followed by a saturation in the high frequency region, for all the temperatures. The high values of the dielectric constant at low frequencies and low values at higher frequencies indicate large dispersion due to a Maxwell-Wagner type of interfacial polarization, in agreement with Koop's phenomenological theory [18, 19]. This is due to the inability of the electric dipoles to be in step with the frequency of the applied electric field. The low frequency dielectric dispersion increases with increase in the Dy concentration and it was maximum for the $x = 0.1$ sample.

Figure 4 shows the electric hysteresis loops of $\text{Bi}_{1-x}\text{Dy}_x\text{FeO}_3$. As indicated in the figure, all samples show distinct hysteresis characteristics. Because of the different breakdown fields for different samples, varied drive fields were applied to the samples. For the samples with $x = 0.03, 0.05, 0.07$ and 0.1 , the remnant polarization (P_r) obtained was $1.75 \mu\text{C cm}^{-2}$, $2.25 \mu\text{C cm}^{-2}$ and $2.5 \mu\text{C cm}^{-2}$ and $4 \mu\text{C cm}^{-2}$ respectively. The above results indicate that the substitution of Dy in place of Bi in BiFeO_3 results in enhanced ferroelectricity and increased breakdown field. The P_r value for the sample is much more than that of the $x\text{BiFeO}_3-(1-x)\text{BaTiO}_3$ thin film with $x = 0.03$ obtained by the pulsed laser deposition method [20]; Liu *et al* reported a P_r of $2.05 \mu\text{C cm}^{-2}$ for BFPT films prepared by the sol-gel method [21].

The coupling between electric and magnetic dipoles at room temperature is demonstrated in figure 5, obtained by measuring the effect of magnetic poling on the ferroelectric hysteresis loop. Not much significant change has been observed in the P - E loops of samples with smaller concentration of Dy. After poling the sample at 1 T DC magnetic field, the samples with $x = 0.07$ and 0.1 showed an increase in loop area, as shown in figure 5.

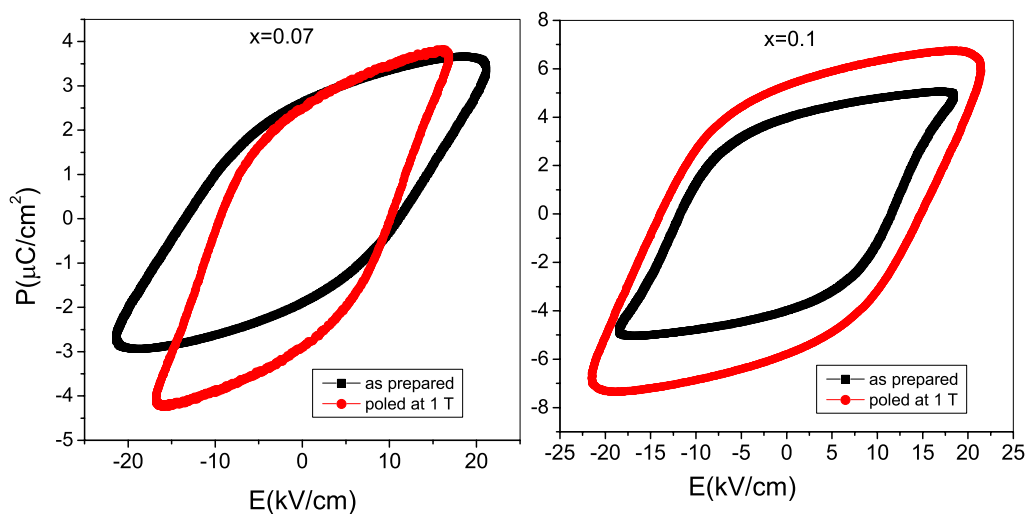


Figure 5. Magnetic field dependence of P - E loops for $\text{Bi}_{1-x}\text{Dy}_x\text{FeO}_3$ ($x = 0.07$ and 0.1) at room temperature.

The ferroelectric hysteresis loop showed an enhancement in the $2P_r$ from 4.5 to 5.3 $\mu\text{C cm}^{-2}$ for $x = 0.07$ and 7.98 to 11.2 $\mu\text{C cm}^{-2}$ for $x = 0.1$ sample. According to Wang *et al*, apart from inducing magnetization that is approximately proportional to a magnetic field H , an applied magnetic field results in a polarization change in the BiFeO_3 particles due to the ME effect and that the destruction of a cycloid results in a significant enhancement in the spontaneous polarization [22]. From the magnetization hysteresis loops, it is clear that the magnetization is increased with increase in the Dy concentration in the BiFeO_3 system, suggesting gradual increase in suppression of the spin spiral. So we can say that $\text{Bi}_{0.9}\text{Dy}_{0.1}\text{FeO}_3$ shows maximum magnetization, i.e. maximum suppression of the spin spiral, and hence shows maximum ferroelectricity and also maximum magnetoelectric coupling.

4. Conclusion

In summary, we have been successful in synthesizing a new system exhibiting enhanced multiferroic properties. An anomaly was observed in the dielectric constant near the antiferromagnetic Néel temperature (T_N). T_N was further confirmed by a sharp decrease in the $M-T$ curve. Saturated $P-E$ loops with high P_r values have been reported for the bulk BiFeO_3 system for the first time. The results of magnetic and ferroelectric measurements point to coupling between magnetic dipoles and electric dipoles at room temperature. The material characteristic (magnetoelectric coupling at room temperature) may be highly useful in numerous devices.

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