

## Multiferroic properties of modified BiFeO<sub>3</sub>-PbTiO<sub>3</sub>-based ceramics: Random-field induced release of latent magnetization and polarization

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It has been found that aliovalent-substituted BiFeO<sub>3</sub>-PbTiO<sub>3</sub>-based polycrystalline materials have significantly enhanced multiferroic properties. Relative to unmodified BiFeO<sub>3</sub>, our results for modified BiFeO<sub>3</sub>-PbTiO<sub>3</sub>-based ceramics reveal: (i) a dramatic increase in the electric-field-induced polarization; and (ii) the establishment of a remanent magnetization. The results evidence the destruction of a space-modulated spin structure in bulk materials, via substituent effects, releasing a latent magnetization locked within the cycloid.

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### I. INTRODUCTION

Multiferroic materials have two or more order parameters.<sup>1,2</sup> Of particular interest is BiFeO<sub>3</sub> (BF), which exhibits the coexistence of ferroelectric and antiferromagnetic (*G*-type) order parameters up to quite high temperatures.<sup>1,3</sup> In bulk single crystals, BiFeO<sub>3</sub> has a ferroelectric Curie temperature of  $T_c=850$  °C,<sup>4-6</sup> and an antiferromagnet Néel temperature of  $T_N=370$  °C.<sup>7,8</sup>

The lattice structure of BiFeO<sub>3</sub> crystals is a rhombohedrally distorted perovskite,<sup>3,6,7,9-12</sup> which belongs to the space group  $R\bar{3}c$  (or  $C_6^{3V}$ ). The rhombohedral unit cell parameters are  $a_r=3.96$  Å and  $\alpha_r=0.6^\circ$ ; and the corresponding hexagonal unit cell parameters are  $a_h=5.58$  Å and  $c_h=13.9$  Å. The hexagonal (001)<sub>h</sub> is equivalent to the pseudocubic (111)<sub>c</sub>, along which there is a three-fold rotation and about which the Bi<sup>3+</sup> and Fe<sup>3+</sup> cations are displaced from their centrosymmetric positions. This distortion is polar and results in a polarization oriented along (111)<sub>c</sub> of  $P_{(111)c}=0.061$  C/m<sup>2</sup>. Along the (001)<sub>h</sub>/(111)<sub>c</sub>, BiFeO<sub>3</sub> has antiferromagnetic order.<sup>8,11</sup>

Microscopically, in BiFeO<sub>3</sub> crystals, the antiferromagnetic spin order is not homogeneous.<sup>12</sup> This is due to a spin rotation plane that is parallel to (110)<sub>h</sub>, which gives rise to an incommensurately modulated spin structure.<sup>12,13</sup> Precise neutron diffraction studies<sup>12,13</sup> have revealed a cycloidal spin structure with a long period wavelength of  $\lambda\sim 600$  Å that is oriented along (110)<sub>h</sub>. Its existence has also been confirmed by line shape analysis of nuclear magnetic resonance (NMR) spectra.<sup>14,15</sup>

As the antiferromagnetic vector is averaged to zero over  $\lambda$ , the remanent magnetization is zero and the induced magnetization is proportional to an applied magnetic field.<sup>16,32</sup> However, application of the high magnetic field ( $H>18$  T) is known to induce a phase transition from the spatially modulated antiferromagnetic spin structure to a homogeneous one.<sup>17-20</sup> This transition results in the establishment of a spontaneous magnetization which is on the order of 0.3 emu/g,<sup>16,32</sup> and the release of the magnetoelectric (ME) interactions locked within the cycloid which was shown to

be on the order of 3.3 V/cm Oe.<sup>20</sup> In addition, an induced phase transition in BiFeO<sub>3</sub> has recently been reported due to epitaxial constraint.<sup>21,22</sup> Dramatic enhancements in the spontaneous magnetization and polarization were found. For example,  $P_{(001)c}$  was increased to 0.6 C/m<sup>2</sup>—which is  $\sim 20\times$  larger than that of a bulk BiFeO<sub>3</sub> crystal projected along the same direction. Clearly, induced phase transitions result in significant property and structural changes.

Although promising, the multiferroic properties of either BiFeO<sub>3</sub> crystals or ceramics require too high of fields to be considered practical. In particular, it is important that the magnetic field required to induce the transition between modulated and homogeneous spin states be dramatically lowered. Here, we will show that the space modulated spin structure can be destroyed in bulk ceramics by aliovalent substituents, favoring the homogenous spin state.

### II. EXPERIMENTAL PROCEDURE

We have fabricated ceramics of La-modified Bi(Fe,Ga)O<sub>3</sub>- $x\%$ PbTiO<sub>3</sub>, with La concentrations of 10 and 20 at. % and for  $40<x<45$ .<sup>23-26</sup> Starting materials were commercial reagent grades of Bi<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, PbCO<sub>3</sub>, and TiO<sub>2</sub> with 99+ % purity. The oxides were mixed by ball milling for 24 h with stabilized ZrO<sub>2</sub> media, calcined at 750 °C for 4 h, and sintered at 1000–1120 °C for 0.8 h in a sealed crucible. The ceramic specimens used in this study have previously been reported to be single-phase perovskites, have average grain sizes of about 2 μm, and have close to theoretical densities.<sup>25</sup> BiFeO<sub>3</sub>- $x\%$ PbTiO<sub>3</sub> (BF- $x\%$ PT) has been reported to form a continuous solution across its entire range, with a rhombohedral-tetragonal morphotropic phase boundary (MPB) at  $x\sim 30$ .<sup>22-27</sup> The specimen dimensions were 10.4 mm in diameter and 0.5 mm in thickness. Specimens were electroded using a postfired silver paste (Dupont 6160). Some of the disks were poled in a 120 °C oil bath at 40 kV/cm for 10 min.

Dielectric measurements were carried out for  $300<T<600$  °C using a computer controlled HP4284. Ferroelectric hysteresis loops (i.e., *P-E* response) were measured using a

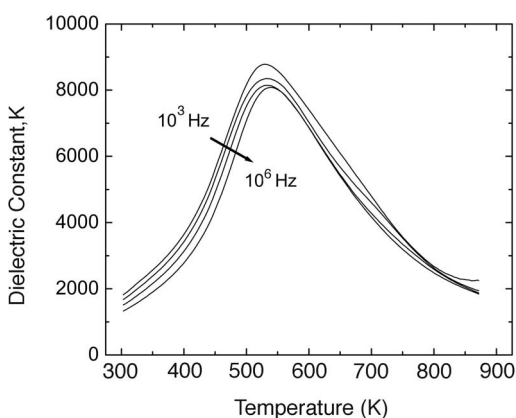


FIG. 1. Dielectric constant of  $(\text{Bi}_{0.8}\text{La}_{0.2})(\text{Fe,Ga})\text{O}_3$ -43% $\text{PbTiO}_3$  as a function of temperature. Data are shown for measurements taken at frequencies of  $10^3$ ,  $10^4$ ,  $10^5$ , and  $10^6$  Hz.

modified Sawyer-Tower circuit. The dc magnetization loops (i.e.,  $B$ - $H$  response) were characterized as a function of  $H$  at various temperatures using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, model XL7). Before magnetization measurements were performed, the electrodes were removed from the specimens.

### III. RESULTS

Two of the main problems of  $\text{BiFeO}_3$ -based materials that have previously limited development are (i) a low resistivity  $\rho$ , which has made it difficult to obtain good dielectric properties; and (ii) a very high coercive field  $E_c$  which makes them difficult to pole. The resistivity of our specimens was on the order of  $10^{12}$   $\Omega$  cm. Consequently, the dielectric properties could be measured. The composition  $(\text{Bi}_{0.8}\text{La}_{0.2})(\text{Fe,Ga})\text{O}_3$ -43% $\text{PbTiO}_3$ , which is close to a morphotropic phase boundary,<sup>23-27</sup> had a room temperature dielectric constant  $K$  and  $\tan \delta(10^3$  Hz) of 1800 and 2.4%, respectively. Figure 1 shows the dependence of  $K$  on temperature ( $T$ ) for this composition. The value of  $T_c$  was  $\sim 500$  K. It is important to note that the temperature dependent response revealed a broad transition region. Also, measurements at various frequencies exhibited low-frequency dielectric-relaxational effects.

The ferroelectric polarization behavior was then investigated. It was found that  $E_c$  was pronouncedly decreased to  $< 30$  kV/cm for our modified ceramics, which is much lower than previous reports of  $> 100$  kV/cm. Figure 2(a) shows the  $P$ - $E$  loops. A nonlinear  $P$ - $E$  relationship can be seen for  $E \approx 30$  kV/cm. Saturation of the  $P$ - $E$  loop occurred near  $E \approx 50$  kV/cm, with values of  $P_r$  and  $E_c$  of  $20 \mu\text{C}/\text{cm}^2$  and  $60$  kV/cm, respectively. Conductivity effects were not notable in the  $P$ - $E$  loops. These results clearly demonstrate that our modified  $\text{BiFeO}_3$ - $\text{PbTiO}_3$ -based ceramics can be poled into a ferroelectric state that has remanent and saturation polarizations, which are nearly an order of magnitude higher than that of unmodified  $\text{BiFeO}_3$  crystals.

Next, the magnetization behavior was measured at  $T = 300$  K. Figure 2(b) shows the  $M$ - $H$  response for our modi-

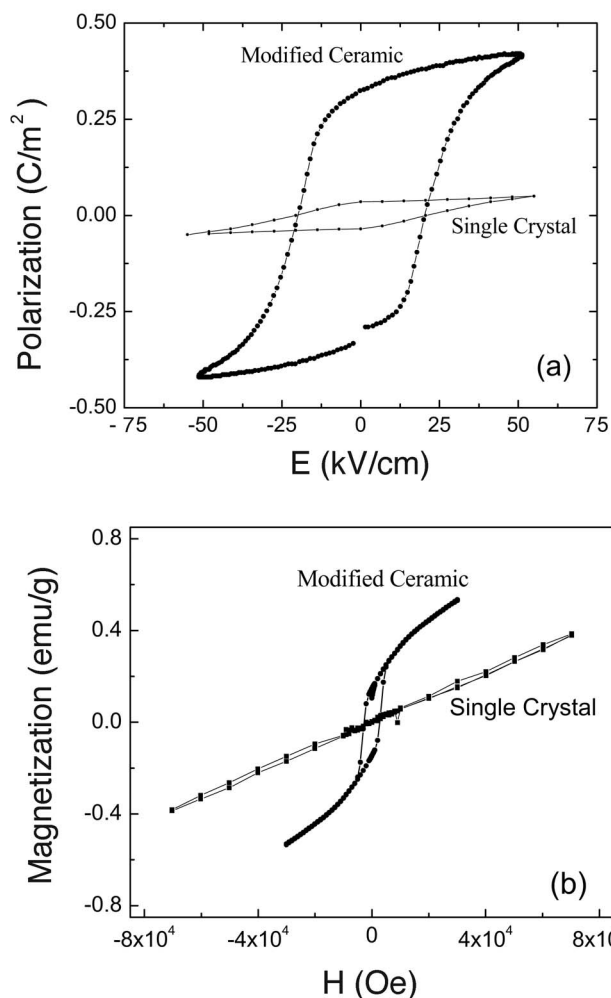


FIG. 2. Induced polarization and magnetization for  $(\text{Bi}_{0.8}\text{La}_{0.2}) \times (\text{Fe,Ga})\text{O}_3$ -43% $\text{PbTiO}_3$  ceramics. (a) Induced polarization as a function of electric field  $E$ ; and (b) induced magnetization as a function of magnetic field  $H$ , corresponding single crystal data is shown for comparisons. These data were all taken at  $T = 300$  K.

modified  $\text{BiFeO}_3$ - $\text{PbTiO}_3$ -based ceramics, along side that of a  $\text{BiFeO}_3$  crystal. The single crystal exhibited a near linear  $M$ - $H$  relationship for  $H < 7 \times 10^4$  Oe, which is what is expected in the presence of cycloidal spin structure in unmodified crystals.<sup>16,32</sup> For our modified  $\text{BiFeO}_3$ - $\text{PbTiO}_3$ -based ceramics, a larger induced (net) magnetization was observed at much lower  $H$ . A ferromagnetic hysteresis loop can be seen in this figure which has a remanent magnetization, saturation magnetization, and coercive field of  $0.25$  emu/g,  $0.3$  emu/g, and  $3 \times 10^3$  Oe, respectively. These results clearly demonstrate that our  $\text{BiFeO}_3$ - $\text{PbTiO}_3$ -based ceramics can be poled into a ferromagnetic state that has remanent and saturation magnetizations, unlike that of unmodified  $\text{BiFeO}_3$  crystals.

Finally, the magnetization behavior was measured at  $T = 5$  K for both a modified  $\text{BiFeO}_3$ - $\text{PbTiO}_3$ -based ceramic and a  $\text{BiFeO}_3$  crystal. Figure 3(a) shows the  $M$ - $H$  response for the  $\text{BiFeO}_3$  single crystal (data for  $T = 300$  K is shown for comparisons). The  $M$ - $H$  behavior can be seen to be temperature independent between  $5 < T < 300$  K, over the field range

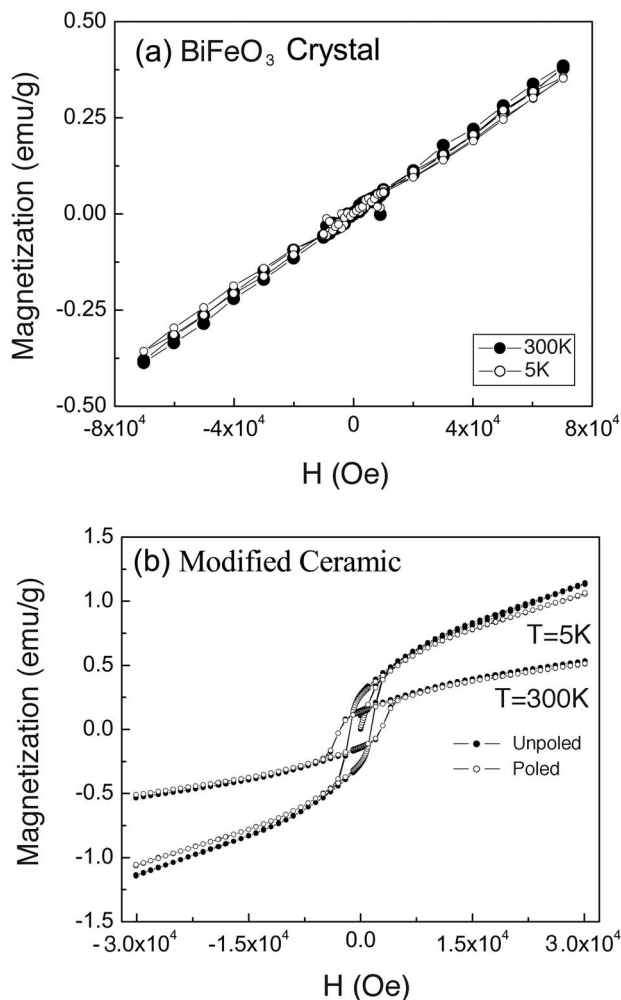


FIG. 3. Effect of temperature and electrical poling on the induced magnetization as a function of magnetic field  $H$ . (a) BiFeO<sub>3</sub> single crystal in the electrically unpoled condition. Data are shown in both figures for  $T=5$  and 300 K; and (b) (Bi<sub>0.8</sub>La<sub>0.2</sub>)(Fe, Ga)O<sub>3</sub>-45% PbTiO<sub>3</sub> ceramic, in both the electrically poled and unpoled conditions.

investigated. However, the magnetization behavior of our modified BiFeO<sub>3</sub>-PbTiO<sub>3</sub>-based ceramic was found to be notably temperature dependent. Figure 3(b) shows the  $M$ - $H$  response for the ceramic taken at both  $T=5$  and 300 K. The saturation and remanent magnetization were both increased on cooling to  $T=5$  K; however, interestingly, the coercive field was decreased with decreasing temperature. It is also important to note in Fig. 3(b) that both electrically unpoled and poled specimens yielded similar  $M$ - $H$  responses. The results in Fig. 3 clearly demonstrate an important difference in the temperature-dependent magnetization between BiFeO<sub>3</sub> crystals and modified ceramics.

Recent investigations of the magnetization of BiFeO<sub>3</sub> crystals under high pulsed magnetic fields of  $H \leq 20$  T,<sup>16,32</sup> for  $T=5$  K, have demonstrated an induced transition in the  $M$ - $H$  response, as shown in Fig. 4. The saturation magnetization was  $\sim 0.3$  emu/g, as shown by the dashed line in the figure. This is the cycloidal-to-homogeneous-spin transition.<sup>17-20</sup> Comparisons of the results in Fig. 4<sup>16,32</sup> to

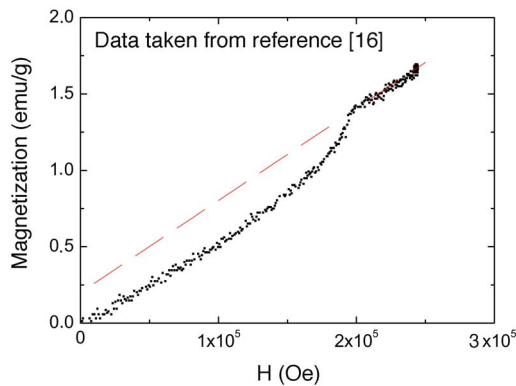


FIG. 4. (Color online) High-field magnetization as a function of the amplitude of a pulsed magnetic field for  $H \leq 25$  T for a BiFeO<sub>3</sub> crystal. These data were taken at  $T=10$  K (Refs. 16 and 32).

that in Fig. 3 provide evidence that in the modified ceramics, the cycloidal-spin structure is suppressed, and that the homogeneous-spin state is favored.

## IV. DISCUSSION AND SUMMARY

### A. Enhancement of polarization

The significant enhancement in the polarization cannot be understood by a simple dipolar defect model, but rather must reflect important changes in the spontaneous polarization and, consequently, the ferroelectric stability. An important consideration emerges upon examination of  $P_s$  of BiFeO<sub>3</sub> crystals, as previously noted:<sup>9</sup> the parent compound of our crystalline solution has a  $P_s$  that is significantly smaller than what might normally be expected for a ferroelectric with such a high  $T_c$  (for example, PbTiO<sub>3</sub>, with  $T_c=763$  K and a  $P_s=80-100 \mu\text{C}/\text{cm}^2$ ). Rather, we conjecture that ferroelectric order may prevent the manifestation of a full spontaneous polarization, resulting in significant cancellation of the polar vector moments. Introduction of substituents into a ferroelectric could then result in dramatic changes in  $P_s$ , by favoring ferroelectric order.

### B. Onset of spontaneous magnetization, due to destruction of spin cycloid

Microscopically, the antiferromagnetic spin order of BiFeO<sub>3</sub> single crystals is not homogeneous. Rather, an incommensurately modulated spin structure is present,<sup>12</sup> which manifests itself as an incommensurate cycloid with a long wavelength  $\lambda$  of  $\sim 600 \text{ \AA}$ .<sup>12,13</sup> The spin spiral is directed along the  $[110]_h$  and is dependent on the applied magnetic field and temperature.<sup>14</sup> Breaking of the translational symmetry of the spiral spin modulation might be achieved by the substituent effect in perovskites.<sup>28-30</sup> We attempt to understand these changes by the Landau-Ginzburg (LG) formalism for the free energy,<sup>20</sup> given as

$$F = F_{exch} + F_L + F_{an} + F_m, \quad (1)$$

where  $F_{exch}$  is the inhomogeneous exchange energy,  $F_L$  is the magnetoelectric coupling that is linear in gradient (i.e., Lif-

shitz invariant),  $F_{an}$  is the magnetic anisotropy energy, and  $F_m$  is the magnetic energy. The individual terms in the sum of (1) have previously been given in Refs. 17 and 20.

The free energy density of the cycloid structure ( $f_{cycloid}$ ) that takes into account all terms in (1) can be derived following Ref. 20, as:

$$f_{cycloid} = Aq^2 - \gamma P_z q + K'_u \sin^2 \theta, \quad (2)$$

where the first term  $Aq^2$  corresponds to the exchange energy,  $q$  is the wave vector of the modulation,  $A$  is the stiffness constant of the cycloid, the second term  $\gamma P_z q$  originates from the Lifshitz invariant,  $\gamma$  is the inhomogeneous magnetoelectric constant,  $z$  is directed along the trigonal axis (which is the spontaneous polarization  $P_s$  direction), and  $K'_u$  is the effective uniaxial anisotropy constant. This effective uniaxial anisotropy constant takes into account the true anisotropy  $K_u$  and a contribution due to a linear homogeneous magnetoelectric effect, given as

$$K'_u = K_u - \chi_{\perp} \frac{(\beta P_z)^2}{2}, \quad (3)$$

where  $\beta$  is the homogenous magnetoelectric coefficient that relates the Dzyaloshinsky-Moria magnetic field and the spontaneous polarization, i.e.,  $H_{DM} = \beta P_z$ ; and  $\chi_{\perp}$  is the magnetic susceptibility in the direction perpendicular to the antiferromagnetic vector.

In the presence of an external magnetic field  $H$  applied along the  $c$  axis, Eq. (3) for the effective anisotropy takes the form of

$$K'_u = K_u - \chi_{\perp} \frac{(\beta P_z)^2}{2} - \chi_{\perp} \frac{H_z^2}{2}. \quad (4)$$

The volume averaged energy of the cycloid is then

$$\langle f_{cycloid} \rangle = Aq^2 - \gamma P_z q + \frac{K'_u}{2}. \quad (5)$$

In Eq. (5), it has been taken into account that averaging must be done over the entire length of the cycloid, i.e.,  $\langle \sin^2 \theta \rangle = \frac{1}{2}$ . The phase transition to the homogenous state takes place when the modulated structure becomes energetically unfavorable, relative to the homogenous state, which occurs at

$$f_{hom} = K'_u. \quad (6)$$

In single crystals, the phase transition to the homogeneous spin state can be induced by application of a large magnetic field in excess of  $H_c = 180$  kOe = 18 T.<sup>16,17,19,20,32</sup>

As can be seen in Eq. (3), destruction of the spin cycloid results in a significant enhancement in the spontaneous polarization. We estimate the minimum spontaneous polarization change ( $P_z^{mod}$ ) resulting from the destruction of the cycloid, using the following condition:

$$\chi_{\perp} \frac{(\beta P_z^{mod})^2}{2} \geq \chi_{\perp} \frac{(\beta P_z^0)^2}{2} + \chi_{\perp} \frac{H_c^2}{2}, \quad (7)$$

where  $P_z^{mod}$  is the polarization of the modified ceramic, and  $P_z^0$  is the polarization of the unmodified BiFeO<sub>3</sub> crystal. Using the reported values of  $H_{DM} = \beta P_z^0 = 12$  T,  $H_c = 18$  T, and

$\beta = H_{DM}/P_z^0 \approx 197$  (T m<sup>2</sup>)/C,<sup>20</sup> the minimum polarization condition for the ceramic is obeyed if  $P_z^{mod} > 0.1$  C/m<sup>2</sup>.

Clearly, substituents perturbate the spiral spin structure, via magnetoelectric interactions that couple to the change in  $P_s$ . The cycloid destruction induced by the high magnetic field results in the release of the latent magnetization  $M_{spont} \sim 0.3$  emu/g (see Fig. 4) that is trapped within the cycloid. In the modified ceramic, this latent magnetization is expressed as a remanent magnetization of  $M_{rem} \sim 0.3$  emu/g (see Fig. 3).

### C. Enhanced magnetic susceptibility

The susceptibility can be determined from the slope of the  $M$ - $H$  curve at  $H=0$ . Inspection of Fig. 2(b) will reveal that the slope is about  $3\times$  higher for the modified ceramic, relative to the unmodified crystal. This requires a simple explanation: the high dielectric constant subsystem enhances the magnetic one, via magnetoelectric interactions. Now let us consider this in more detail.

An applied magnetic field will have two effects on BiFeO<sub>3</sub> subsystem. The first is that it will induce a magnetization that is approximately proportional to a magnetic field  $H$ , given as

$$M^H = f\chi H, \quad (8)$$

where  $f$  is BiFeO<sub>3</sub> filling factor, and  $\chi$  is magnetic susceptibility. The second is that this will result in a polarization change in the BiFeO<sub>3</sub> particles due to the ME effect, approximately given as

$$P^H = \frac{\alpha}{4\pi} fH, \quad (9)$$

where  $\alpha$  is magnetoelectric coefficient.

This polarization gives rise to the effective electric field that induces polarization of the medium

$$P^{Total} = (\epsilon_{eff} - 1)P^H, \quad (10)$$

where  $\epsilon_{eff}$  is the effective dielectric constant of the solution, which we approximate simply by use of the dielectric mixing rules given as

$$\epsilon_{eff} = (1 - f)\epsilon_1 + f\epsilon_2, \quad (11)$$

where  $\epsilon_1$  is dielectric constant of PbTiO<sub>3</sub> and  $\epsilon_2$  is dielectric constant of BiFeO<sub>3</sub>. Using experimental values for PbTiO<sub>3</sub> of  $\epsilon_1 = 10^3$ , for BiFeO<sub>3</sub> of  $\epsilon_2 = 0.5 \times 10^2$ ,<sup>6</sup> and the fact that  $f = 0.6$  in our BF-40%PT ceramic, we have the effective dielectric constant for the solid solution of  $\epsilon_{eff} \approx 430$ . From Eq. (10) it follows that polarization is enhanced by the PbTiO<sub>3</sub> constituent of solid solution by factor of 30.

The ME-induced polarization change  $P^{PT}$  will further induce an additional magnetization contribution in the BiFeO<sub>3</sub> subsystem due to ME effect, approximately given as

$$M^{ME} = \frac{\langle \alpha \rangle}{4\pi} P^{Total} = \left( \frac{\langle \alpha \rangle}{4\pi} \right)^2 (\epsilon_{eff} - 1) fH. \quad (12)$$

Thus, an approximation of the total magnetization of the crystalline solution is

$$\delta M = \chi H f + f M^{ME}, \quad (13)$$

and the approximate effective magnetic susceptibility of the composite media is

$$\chi_{eff} \sim f\chi + \left(\frac{\langle\alpha\rangle}{4\pi}\right)^2 (\epsilon_{eff} - 1)f^2. \quad (14)$$

Using values for  $f=0.6$ ,  $\chi=4.7\times 10^{-5}$ ,<sup>31</sup> and  $\langle\alpha\rangle\approx 10^{-2}$  (calculated from magnetization induced by the electric field of the spontaneous polarization in bulk BiFeO<sub>3</sub> crystals,<sup>32</sup> and independently by high magnetic field studies of bulk BiFeO<sub>3</sub> single crystals<sup>20</sup>), the effective magnetic susceptibility can be estimated as  $\chi_{eff}\approx 1.2\times 10^{-4}$  (or  $1.5\times 10^{-5}$  emu/g Oe). This is  $3\times$  larger than the value of the magnetic susceptibility of BiFeO<sub>3</sub> single crystals, which is  $0.6\times 10^{-5}$  emu/g Oe. Thus, we can attribute the enhanced magnetic susceptibility in modified ceramics to the release of the latent ME interactions, due to random fields associated with aliovalent substituents.

#### D. Summary

In summary, aliovalent modified BiFeO<sub>3</sub>-based ceramics have been found to have significantly enhanced multiferroic

properties, relative to nonsubstituted BiFeO<sub>3</sub> single crystals. Dramatic enhancements in the electric-field-induced polarization and magnetic susceptibility at the onset of spontaneous magnetization have both been found. The observed enhancements are shown to be equal to the predicted ones, using a thermodynamic model that includes a magnetoelectric coupling. The onset of spontaneous magnetization is caused by the destruction of a cycloidal spin structure by the random fields associated with substituents, which couples to the polarization of the ferroelectric phase, via ME exchange.

Recently, a related paper was published.<sup>33</sup>

#### ACKNOWLEDGMENTS

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