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## Dielectric relaxation and magneto-dielectric effect in polycrystalline $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_{2.95}$

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We have investigated temperature, frequency, and magnetic field dependent dielectric properties of polycrystalline  $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_{2.95}$ . Two dielectric anomalies, near 65 K and 260 K, were observed with the anomaly near 65 K exhibiting distinct frequency dependence as the peak temperature shifts with increasing frequency. The low-temperature dielectric relaxation data that can be fitted to a Vogel-Fulcher expression yielding a characteristic relaxation time of  $\sim 10^{-8}$  s are four orders larger than that of pure  $\text{BiFeO}_3$  which may be the resultant of the chemical pressure induced by Ca doping. We also observed a switchable magneto-dielectric response in  $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_{2.95}$  at room temperature.

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Multiferroics<sup>1,2</sup> have gained increasing attention due to a wide range of potential applications<sup>3,4</sup> in microelectronic and spintronic devices, and the possibility of controlling magnetic order by electric fields,<sup>5</sup> or electric order by magnetic fields,<sup>6</sup> through magnetoelectric coupling.<sup>7</sup>  $\text{BiFeO}_3$  is termed a multiferroic material due to the coexistence of ferroelasticity, antiferromagnetism, and ferroelectricity.<sup>8-10</sup> A ferroelectric phase transition from the cubic  $Pm\bar{3}m$  to rhombohedral  $R3c$  phase<sup>8</sup> occurs in  $\text{BiFeO}_3$  at  $T_C = 1120$  K, and an antiferromagnetic ordering appears below the Néel temperature,  $T_N = 640$  K.

$\text{BiFeO}_3$  samples typically have a significant residual electrical conductivity, which hampers the study of the intrinsic dielectric properties like polarization and dielectric permittivity at room temperatures and above. Kamba *et al.* have studied the frequency-dependent dielectric properties of  $\text{BiFeO}_3$  ceramics in the temperature range 10-300 K.<sup>11</sup> They observed an anomaly near 250 K in  $\text{BiFeO}_3$  ceramics, which was explained by a Maxwell-Wagner type contribution to the permittivity as a consequence of a relaxation arising at the interfaces between grains and their boundaries.<sup>11,12</sup> At low frequencies or at high temperatures, colossal dielectric constants have also been reported<sup>11,13</sup> with these high values arising due to finite conductivity leading to Maxwell-Wagner (M-W) behavior.<sup>11,13-15</sup> The temperature at which the M-W effect sets in depends on the sample conductivity, and for some samples this effect happens at temperatures as low as 200 K.<sup>11</sup> Recently, Redfern *et al.* conducted low-temperature (below 300 K) dielectric and mechanical measurements of  $\text{BiFeO}_3$  ceramics and single crystals.<sup>16</sup> These studies suggest that the magnetic structure of  $\text{BiFeO}_3$  may shift below room temperature, with evidence for magnetic, magnetoelectric, and magnetoelastic transitions observed at a range of temperatures, including 50 K, 140 K, 210 K, and 230 K.<sup>16</sup> Investigating how these low-temperature transitions evolve with A-site cation substitution may provide additional

insight into distinguishing intrinsic effects from extrinsic mechanisms, such as the M-W effect.<sup>11,12</sup>

We synthesized single-phase polycrystalline  $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_{2.95}$  ceramic sample using a sol-gel approach using a method detailed elsewhere.<sup>17,18</sup> The physical characteristics of the sample, including the structural, magnetic, and ferroelectric properties of sample were also studied.<sup>18</sup> Recently, we investigated the effects of oxygen non-stoichiometry on the low-temperature structural and dielectric properties in the  $\text{BiFeO}_3$  parent compound, as-prepared  $\text{BiFeO}_3$  (BFOAP) and vacuum annealed  $\text{BiFeO}_3$  (BFOVA) ceramics.<sup>19</sup> We found that the coupling among spin, lattice, and dielectric degrees of freedom persists to low temperatures in  $\text{BiFeO}_3$ , and moreover that these properties depend on the degree of oxygen non-stoichiometry.<sup>19</sup> In this letter, we present an investigation of temperature and magnetic field dependent dielectric properties of polycrystalline  $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_{2.95}$  ceramic sample. We measured the temperature and frequency-dependent dielectric constant ( $\epsilon_r$ ) and dielectric loss ( $\tan\delta$ ) of  $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_{2.95}$  sample using an Agilent 4284 A LCR meter attached with physical property measurement system (PPMS, Quantum Design, USA) in a frequency range from 10 kHz to 1 MHz. We also measured room temperature magnetic field dependent dielectric constant of the sample at 30 kHz.

The temperature-dependent dielectric constant ( $\epsilon_r$ ) and dielectric loss ( $\tan\delta$ ) were measured in the temperature range of 10–350 K for the  $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_{2.95}$  ceramic sample at 10 kHz (Fig. 1). Two anomalies at 66 K and 260 K can be observed, which are similar to the features seen in pure  $\text{BiFeO}_3$ .<sup>19</sup> The low-temperature dielectric anomaly (inset of Fig. 1), 66 K for the  $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_{2.95}$  sample is shifted to a higher temperature than that of pure  $\text{BiFeO}_3$  ( $\sim 23$  K).<sup>19</sup> The low-temperature dielectric anomaly near 66 K may be due to a short range magnetic ordering with magnetoelectric coupling, which has been observed in  $\text{BiFeO}_3$  ceramics and single crystals.<sup>16,17,19,20</sup> We suggest that this low-temperature feature may result primarily from some structural distortion, leading to a significant dielectric response.<sup>19</sup> The dielectric loss ( $\tan\delta$ ) of the sample was found to be close to that of

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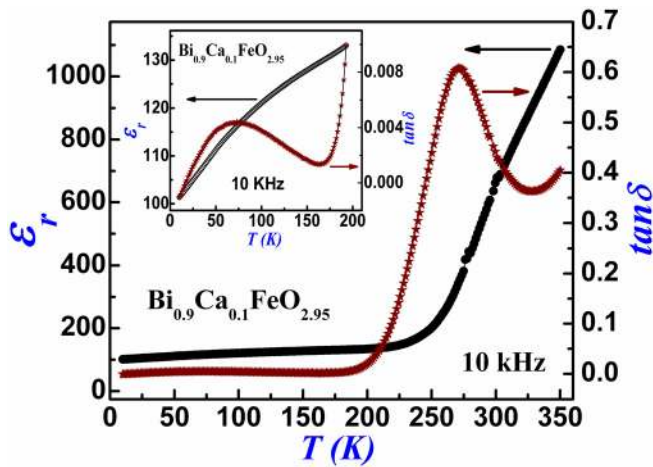


FIG. 1. Temperature-dependent dielectric constant ( $\epsilon_r$ ) and dielectric loss ( $\tan\delta$ ) of polycrystalline  $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_{2.95}$  sample measured at 10 kHz. Inset shows dielectric constant ( $\epsilon_r$ ) and dielectric loss ( $\tan\delta$ ) of the sample below 200 K.

pure  $\text{BiFeO}_3$  below 150 K (Ref. 19) and found to increase abruptly above 200 K in the sample which may be due to Maxwell-Wagner effect.<sup>11,12</sup>

The frequency-dependent dielectric constant ( $\epsilon_r$ ) and dielectric loss ( $\tan\delta$ ) of the polycrystalline  $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_{2.95}$  sample was measured below room temperature in the vicinity of the anomaly near 66 K, as shown in Figs. 2(a) and 2(b). The

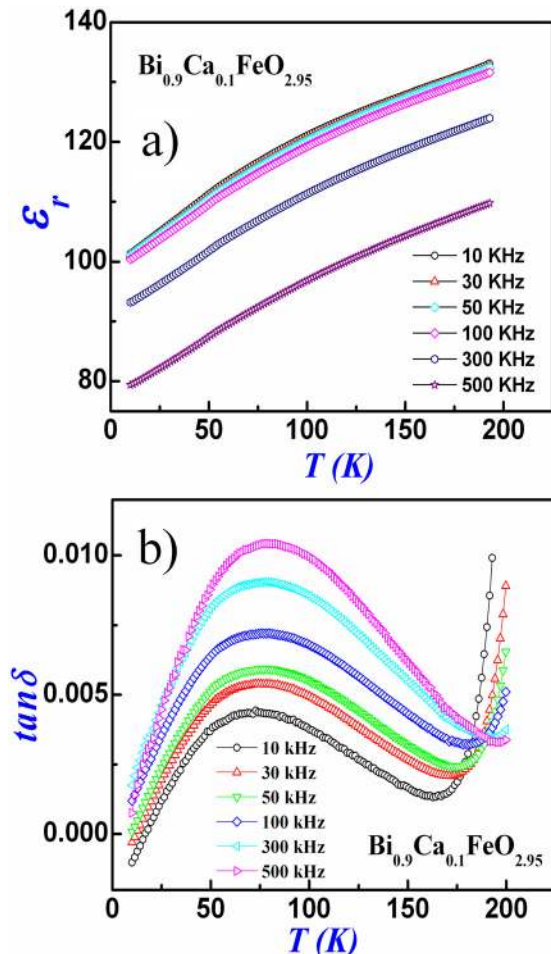


FIG. 2. Temperature and frequency-dependent (a) dielectric constant ( $\epsilon_r$ ) and (b) dielectric loss ( $\tan\delta$ ) of  $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_{2.95}$  sample.

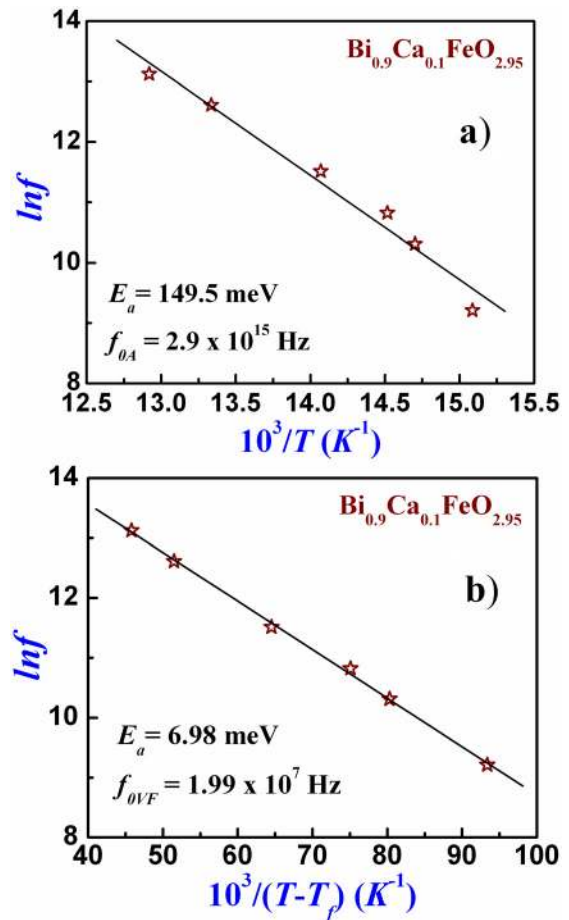


FIG. 3. (a)  $\ln f$  vs  $10^3/T$  and (b)  $\ln f$  vs  $10^3/(T - T_f)$  plots of  $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_{2.95}$  sample in the low-temperature region.

peak temperature ( $T_p$ ) of the anomaly below 150 K shifts to higher temperature systematically from 66 K to 77 K, as the frequency increases from 10 kHz to 500 kHz. In order to determine the activation energy ( $E_a$ ) and characteristic relaxation frequency ( $f_0$ ) for relaxation behavior of  $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_{2.95}$  sample, we fitted the frequency dependence of the peak temperature to an Arrhenius expression,  $f = f_0 \exp(-E_a/k_B T)$ , where  $f_0$  is the relaxation frequency,  $E_a$  is the activation energy, and  $k_B$  is the Boltzmann constant. We plot  $\ln f$  as a function of  $10^3/T$  in Fig. 3(a). The estimated activation energy ( $E_a$ ) and relaxation frequency ( $f_0$ ) for the anomaly near 66 K are found to be about  $\sim 150$  meV and  $1.5 \times 10^{15}$  Hz, respectively. The activation energy barrier of the Ca doped  $\text{BiFeO}_3$  was estimated to be approximately 1740 K, which is five times larger than that of pure  $\text{BiFeO}_3$  ( $\sim 340$  K).<sup>19</sup> However, a better curve-fit was obtained using Vogel-Fulcher relaxation equation,  $f = f_0 \exp(-E_a/k_B(T - T_f))$ , where  $T_f$  is freezing temperature (55.6 K), as shown in Fig. 3(b). The estimated activation energy ( $E_a$ ) and relaxation frequency ( $f_0$ ) are found to be about  $\sim 7$  meV and  $\sim 2 \times 10^7$  Hz, respectively. This dramatic change in the activation energy and relaxation frequency is consistent with the higher relaxation temperature and its broader characteristics in Ca doped  $\text{BiFeO}_3$  as compared to pure  $\text{BiFeO}_3$ , and may be the resultant of the chemical pressure induced by Ca substitution, which can serve to brace the lattice.<sup>19,21</sup> This dielectric relaxation can potentially be related to relaxor ferroelectric properties involving strongly interacting relaxing clusters.<sup>22</sup> These strong

interactions produce Vogel-Fulcher relaxation rather than Arrhenius, implying glassy behavior rather than superparaelectric, albeit with a slightly enhanced relaxation time, which we find to be  $\sim 10^{-8}$  s.

These relaxation features developing at low temperature near 66 K in Ca doped  $\text{BiFeO}_3$  are related to those observed in pure  $\text{BiFeO}_3$  (23 K)<sup>19</sup> and may be related to the magnetic glassy behavior near 30 K in  $\text{BiFeO}_3$  single crystals.<sup>21</sup> In this context, the microscopic origins of the relaxation features in  $\text{BiFeO}_3$  and  $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_{2.95}$  may differ from those in relaxor ferroelectrics<sup>22</sup> (which would not have a magnetic contribution), but still exhibit qualitatively similar behavior. These features could also be related to the 38 K anomaly seen in previous magneto-caloric measurements in  $\text{BiFeO}_3$ .<sup>17</sup> This dielectric anomaly is found to be very sensitive to disorder/doping, as indicated by the shift from 23 K ( $\text{BiFeO}_3$ ) to 66 K ( $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_{2.95}$ ) on doping, illustrating the strong coupling between charge, spin, and lattice degrees of freedom in  $\text{BiFeO}_3$ .

We also probed possible spin-charge coupling at room temperature using magneto-dielectric measurements. We plot the magnetic field dependence of the change in dielectric constant of  $\text{BiFeO}_3$  and  $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_{2.95}$  samples at 300 K in Figs. 4(a) and 4(b), using a measuring frequency of 30 kHz. Magneto-dielectric effect in pure  $\text{BiFeO}_3$  corresponds to linear increase of magnetization with increasing magnetic field and this behavior changes upon substitution of Ca. For higher magnetic fields ( $>44$  kOe), the magneto-dielectric effect begins to saturate in the  $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_{2.95}$ , which can be attributed to the saturation of the magnetization at higher magnetic fields.<sup>18</sup>  $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_{2.95}$  exhibits a dis-

torted butterfly loop whereas pure sample shows no signature of butterfly-like behavior (Fig. 4). These measurements confirm that the magneto-dielectric effect in Ca doped  $\text{BiFeO}_3$  is improved compared to parent undoped  $\text{BiFeO}_3$ . Figure 4(b) shows a quadratic magneto-dielectric coupling in the  $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_{2.95}$  sample which exhibits shifts in the dielectric constant proportional to the magnetic field ( $H$ ) in the magnetically ordered phase.

The observed magneto-dielectric effects in the  $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_{2.95}$  sample can be explained by considering the enhancement of weak ferromagnetic moments<sup>18</sup> to the energy gain of the Dzyaloshinskii-Moriya (DM) interaction under an external magnetic field ( $H$ ).<sup>23,24</sup> Since weak ferromagnetism in this system is associated with the rotation of the oxygen octahedral, the enhanced weak ferromagnetism in Ca substituted  $\text{BiFeO}_3$  implies an increase of the relative rotation of the oxygen octahedral. Ederer and Spaldin suggested that the weak DM magnetic moment  $M$  was directly related to the relative rotation of the two oxygen octahedral in the  $R3c$  unit cell around the polarization [111] axis.<sup>23</sup> Therefore, it is plausible that the external magnetic field does increase the polarization in Ca doped  $\text{BiFeO}_3$  sample through the DM interaction. Whereas, the observed magneto-dielectric effect in pure  $\text{BiFeO}_3$  shows that the change in dielectric constant with magnetic field (Fig. 4(a)) is not due to coupling of spontaneous polarization and magnetization, as expected in magnetoelectrics, but may be due to a combination of the magneto-resistance and Maxwell-Wagner effect,<sup>11</sup> and the linear shift in dielectric constant at certain applied magnetic field reflects some background effect and not the intrinsic properties of pure  $\text{BiFeO}_3$ . Whereas in the case of Ca doped  $\text{BiFeO}_3$ , the switchable magneto-dielectric behavior may arise from the terms  $P^2M^2$  in Ginzburg-Landau free energy which are always allowed by symmetry.

In conclusion, we investigated the temperature, frequency, and magnetic field dependent dielectric responses of the polycrystalline  $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_{2.95}$  ceramic sample. The dielectric anomaly near 66 K was shifted to higher temperature than that of pure  $\text{BiFeO}_3$ . This anomaly shifts to higher temperatures monotonically with an increase in measurement frequency, consistent with ferroelectric relaxor-like behavior mediated by strong interacting ferroelectric domains. The estimated relaxation time for  $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_{2.95}$ ,  $\sim 10^{-8}$  s, is four orders larger than that of pure  $\text{BiFeO}_3$  which may be the resultant of the chemical pressure induced by Ca doping. We also observed a switchable magneto-dielectric effect in  $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_{2.95}$  at room temperature which makes this compound interesting material for magnetoelectric multiferroic applications.

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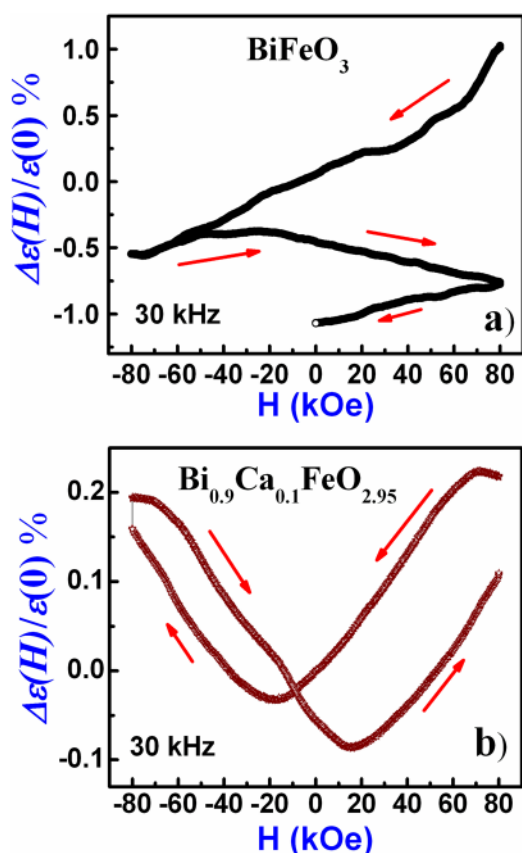


FIG. 4. Room temperature magnetic field dependent the change in dielectric constant of  $\text{BiFeO}_3$  and  $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_{2.95}$  samples measured at 30 kHz.

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