

# Evidence for diffuse ferroelectric phase transition and cooperative tricritical freezing of random-site dipoles due to off-centered $\text{Bi}^{3+}$ ions in the average cubic lattice of $(\text{Ba}_{1-x}\text{Bi}_x)(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_3$

Anar Singh,<sup>1</sup> Chikako Moriyoshi,<sup>2</sup> Yoshihiro Kuroiwa,<sup>2</sup> and Dhananjai Pandey<sup>1,\*</sup>

<sup>1</sup>*School of Materials Science and Technology, Institute of Technology, Banaras Hindu University, Varanasi -221005, India*

<sup>2</sup>*Department of Physical Science, Graduate School of Science, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8526, Japan*

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The mixed solid solution  $(\text{Ba}_{1-x}\text{Bi}_x)(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_3$  (BT- $x$ BF) system exhibits nonrelaxor-type diffuse ferroelectric phase transition whose diffuseness increases with increasing concentration of  $\text{BiFeO}_3$  for  $x \leq 0.40$ . Rietveld analysis of the high-resolution synchrotron x-ray diffraction data reveals that the average cubic symmetry of BT- $x$ BF for  $0.15 \leq x \leq 0.40$  is broken locally by the off-centering of the  $\text{Bi}^{3+}$  ions with respect to the  $\text{Ba}^{2+}$  positions at the perovskite cube corners in the (001) direction. We also show that the random-site dipoles generated by the off-centered Bi ions freeze out cooperatively with a critical exponent of 1/4 characteristic of a tricritical transition. It is argued that the diffuse ferroelectric phase transition in the BT- $x$ BF system is due to the formation of random field domains. The static random fields are generated by the local charge imbalances, strain field, or both caused by the presence of off-valent substituents, even though the overall composition is charge neutral.

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## I. INTRODUCTION

The study of cooperative freezing of random-site electric dipoles in both weakly and highly polarizable crystals has been a time-honored problem in disordered systems<sup>1,2</sup> and continues to attract attention at present.<sup>3-5</sup> The random-site electric dipoles result from off-center impurity ions with respect to the ion of the host lattice for which they substitute because of their much smaller size. The interaction of random-site dipoles depends not only on their position but also their relative orientations. Because of the great spread of local fields experienced by random-site dipoles in weakly polarizable hosts like KCl, these dipoles are known to freeze into a canonical dipole glass state,<sup>1</sup> which has several similarities with canonical spin glass systems like Cu:Mn, although unlike spin glasses, a true equilibrium behavior of dipole glasses has not been confirmed.<sup>6</sup> The random-site dipoles also interact with the host dielectric matrix. This interaction is rather weak in the case of weakly polarizable KCl-like hosts but is quite strong in highly polarizable  $\text{KTaO}_3$ -like hosts because of the presence of a soft-zone center transverse optical phonon mode showing incipient ferroelectric behavior.<sup>1,2</sup> The random-site dipoles in  $\text{KTaO}_3$ -like hosts polarize the surrounding matrix over a length scale,  $r_c$ , which grows with decreasing temperature as the zone center transverse optic mode softens. The polarized region may be regarded as a cluster of dipoles with an effective dipole moment significantly larger than that of the isolated dipole in KCl. At low concentrations of random-site dipoles with  $r_c \ll r$ , where  $r$  is the average separation between the dipoles, the polar regions may freeze into a dipolar glass-like state similar to that in a Li-doped KCl system, except for the larger effective dipole moment associated with the dipoles and the associated longer relaxation times and higher freezing temperatures.<sup>1,2</sup> However, for  $r < r_c$  (i.e., for higher concentrations of the impurity ions), the polar regions can overlap and lead to a long-range ordered ferroelectric state that is probably split into random field (RF) domains under the influence of “static” random fields caused by off-center impurity ions,<sup>1,2</sup> as per the theoretical predictions of Imry and Ma.<sup>7</sup>

While the role of random-site dipoles in weakly polarizable matrices and the highly polarizable incipient ferroelectric matrices has been investigated in great detail, both experimentally and theoretically, the role of random-site dipoles in the highly polarizable regular displacive ferroelectrics like  $\text{BaTiO}_3$  has not been investigated systematically. We present here evidence for  $\text{Bi}^{3+}$  off-centering in the  $\text{BaTiO}_3$  matrix in the mixed solution  $(\text{Ba}_{1-x}\text{Bi}_x)(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_3$  (BT- $x$ BF) system. We also show that the random-site dipoles due to  $\text{Bi}^{3+}$  off-centering in the BT- $x$ BF system lead to a nonrelaxor-type diffuse phase transition (DPT) whose diffuseness increases with the concentration of random-site dipoles. The structure of the mixed BT- $x$ BF system has been reported to be cubic in the composition range  $0.075 \leq x \leq 0.67$ ,<sup>8</sup> which in principle should not exhibit any ferroelectric transition. Rietveld analysis of the high-resolution synchrotron x-ray diffraction (XRD) data, however, reveals that the average cubic symmetry of BT- $x$ BF is broken locally by off-centering of the  $\text{Bi}^{3+}$  ions with respect to the  $\text{Ba}^{2+}$  positions at the perovskite cube corners in six equivalent positions along the (001) direction. More significantly, the off-centered displacement ( $z_{\text{Bi}}$ ) of  $\text{Bi}^{3+}$  is shown to increase with decreasing temperature as  $z_{\text{Bi}} \sim (T_0 - T)^\beta$  in the Curie range with a concomitant change in the average cubic cell parameter on approaching the dielectric peak temperature, suggesting cooperative freezing of  $\text{Bi}^{3+}$  ion-centered dipoles with a mean field exponent of  $\beta = 1/4$ , which is a characteristic of a tricritical transition.<sup>9</sup> We believe that this tricritical transition results from a strong interaction between the  $\text{Bi}^{3+}$ -centered dipoles and the strongly polarizable host matrix. We also propose that the smeared diffuse ferroelectric transition is due to the RF domain formation in the presence of a static random field induced by off-valent substitutions in the  $\text{BaTiO}_3$  matrix as it prepares to undergo ferroelectric phase transition.

## II. EXPERIMENT AND ANALYSIS

BT- $x$ BF powders were prepared by solid state reaction route using stoichiometric mixtures of analytical reagent-grade

$\text{Bi}_2\text{O}_3$  (99.5%),  $\text{Fe}_2\text{O}_3$  (99.0%),  $\text{BaCO}_3$  (99.0%) and  $\text{TiO}_2$  (99.0%) powders obtained by ball milling for 6 hours using zirconia zar and balls with acetone as a mixing medium.<sup>10,11</sup> The mixed oxide powders were calcined for 8 hours in open crucibles at different temperatures. The calcination temperature decreased with increasing  $\text{BiFeO}_3$  content in the range 1243 to 1173 K. The calcined powders were confirmed to be monophasic by XRD. The calcined powders were sintered in a closed alumina crucible, using  $\text{MgO}$  powder as a sealant, containing powder of the same composition as spacer powder for preventing the loss of  $\text{Bi}_2\text{O}_3$  during sintering. The weight loss during sintering was found to be less than 0.1%, and the density of the sintered pellets was greater than 96% of the theoretical density. For powder diffraction experiments, the sintered pellets were crushed to fine powder and subsequently annealed at 773 K for 10 hours to remove strains introduced, if any, during crushing.

The temperature-dependent dielectric measurements at various frequencies up to 1 MHz were carried out at a heating rate of 1 K/min using a Nova Control (Alpha-A) high-performance frequency analyzer. High-energy synchrotron x-ray powder diffraction experiments were performed using a large Debye-Scherrer camera equipped with an imaging plate as a two-dimensional detector installed at the BL02B2 beam line in SPring-8<sup>12</sup> at a wavelength of 0.4110 Å for room temperature measurements and 0.3538 Å for high temperatures. These diffraction data are highly sensitive to the small displacement of atoms from the ideal position caused by atomic disorder or thermal vibrations<sup>13</sup> and are therefore ideally suited for the present study. The high-energy synchrotron x-ray powder diffraction data were analyzed with the Rietveld technique using the FULLPROF software package.<sup>14</sup>

### III. RESULTS AND DISCUSSION

#### A. Dielectric studies

##### 1. Evidence for nonrelaxor-type diffuse phase transition in $\text{BT-}x\text{BF}$

Figure 1 depicts the temperature dependence of real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of the dielectric permittivity for several  $\text{BT-}x\text{BF}$  compositions ( $x = 0.0, 0.04, 0.06, 0.10, 0.15, 0.20, 0.30,$  and  $0.40$ ) at 1 MHz. This particular frequency was chosen to get rid of extrinsic contributions to dielectric permittivity due to space charge polarizations at lower relaxation frequencies.<sup>10</sup> Whereas pure  $\text{BaTiO}_3$  shows a sharp phase transition,  $\text{BiFeO}_3$  doped samples exhibit DPT, as is evident from the smeared  $\epsilon'(T)$  response of  $\text{BT-}x\text{BF}$  even for  $x = 0.04$ . The diffuseness of the dielectric [ $\epsilon'(T)$ ] response increases with increasing  $\text{BiFeO}_3$  content ( $x$ ). Furthermore, the peak value of the dielectric permittivity ( $\epsilon'$ ) decreases by an order of magnitude as a result of  $\text{BiFeO}_3$  substitution. On increasing the concentration of  $\text{BiFeO}_3$  to  $0.20 \leq x \leq 0.40$ ,  $\epsilon'(T)$  shows a strong increase at high temperatures due to an increase in conductivity caused by  $\text{BiFeO}_3$  substitution.<sup>15</sup> The contribution of conductivity losses is also revealed by the temperature dependence of  $\epsilon''(T)$ . The  $\epsilon''(T)$  plots show an increasing trend above 475 for  $0.04 \leq x \leq 0.10$ , whereas for  $0.15 \leq x \leq 0.40$ , it starts increasing at  $\sim 400$  K. As a result of the conductivity losses, which obviously increases with

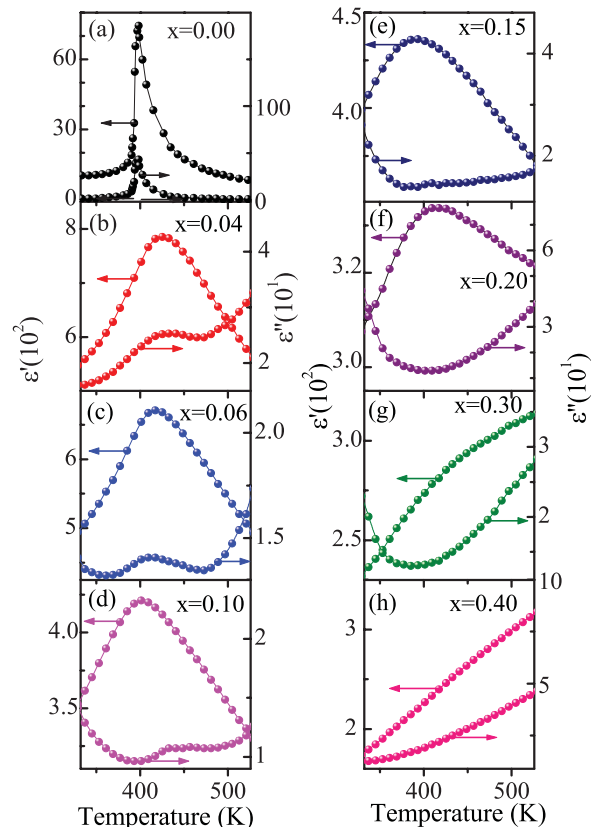


FIG. 1. (Color online) Temperature dependence of real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of the dielectric permittivity of  $\text{BT-}x\text{BF}$  at 1 MHz for  $x =$  (a) 0.00, (b) 0.04, (c) 0.06, (d) 0.10, (e) 0.15, (f) 0.20, (g) 0.30, and (h) 0.40.

increasing  $\text{BiFeO}_3$  content, the diffuse anomaly is partially masked for  $x = 0.30$  and nearly fully masked for  $x = 0.40$ .

The smearing of  $\epsilon'(T)$  of  $\text{BaTiO}_3$  as a result of  $\text{BiFeO}_3$  substitution indicates that the transition from the paraelectric to ferroelectric phase does not occur at a fixed temperature but occurs over a range of temperatures called the Curie range.<sup>16</sup> The systems showing such DPT exhibit significant deviation from the Curie-Weiss law over a wide temperature range above  $T'_{\text{max}}$  at which the real ( $\epsilon'$ ) part of dielectric permittivity peaks.<sup>17,18</sup> Figure 2 shows the temperature dependence of inverse dielectric permittivity for four compositions ( $x = 0, 0.04, 0.10,$  and  $0.15$ ) at 1 MHz. As expected, the Curie-Weiss law is obeyed for temperatures close to  $T'_{\text{max}}$  (see Fig. 2(a)) for pure  $\text{BaTiO}_3$  (i.e.,  $x = 0.0$ ). However, as a result of  $\text{BiFeO}_3$  substitution, significant departure from Curie-Weiss behavior is observed above  $T'_{\text{max}}$  over a temperature range that increases with increasing  $\text{BiFeO}_3$  content. In ferroelectrics with DPT behavior, the following empirical relationship has been suggested to describe the diffuseness of the phase transition,<sup>17-20</sup>

$$1/\epsilon' = 1/\epsilon'_{\text{max}} + [(T - T'_{\text{max}})/C']^\gamma, \quad (1)$$

where  $C'$  and  $\gamma$  are constants. The parameter  $\gamma$  is regarded as a measure of the diffuseness of the phase transition:  $\gamma = 1$  corresponds to normal ferroelectric behavior corresponding to Curie-Weiss law, whereas  $\gamma = 2$  represents complete DPT, as in relaxors.<sup>17-19</sup> In  $\text{BT-}x\text{BF}$ , after fitting Eq. (1) to the inverse

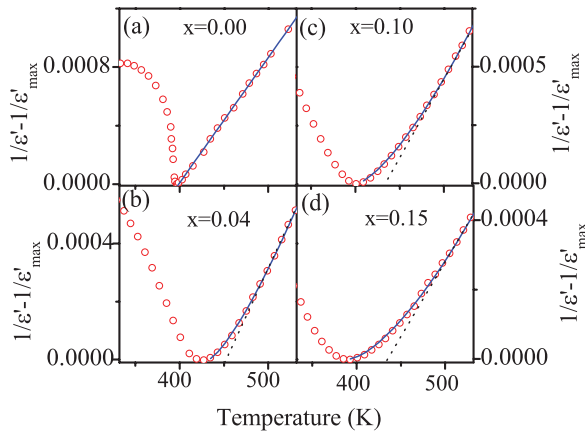


FIG. 2. (Color online) Curie–Weiss plot for BT- $x$ BF for  $x =$  (a) 0.00, (b) 0.04, (c) 0.10, and (d) 0.15 using dielectric data at 1 MHz. The dotted line gives the fit to the Curie–Weiss law, whereas the continuous dark line is the fit to the modified Curie–Weiss law [Eq. (1) in the text] with an exponent  $1 < \gamma < 2$ .

dielectric permittivity, we obtained  $\gamma = 1.31, 1.35, 1.40,$  and  $1.49$  for  $x = 0.04, 0.06, 0.10,$  and  $0.15$ , respectively. The variation of  $\gamma$  with  $x$  is depicted in Fig. 3. The systematic increase in  $\gamma$  with  $x$  is indicative of the increasing DPT behavior with increasing  $x$ . The values of  $\gamma$  for BT- $x$ BF are intermediate to those for regular ferroelectrics and relaxor ferroelectrics.

The DPT in BT- $x$ BF is not due to relaxor ferroelectric freezing. For relaxor ferroelectrics, the temperatures  $T'_{\max}$  and  $T''_{\max}$  corresponding to the peak in  $\epsilon'(T)$  and  $\epsilon''(T)$ , respectively, do not coincide; instead  $T''_{\max} < T'_{\max}$ .<sup>17,18</sup> Additionally, both  $T'_{\max}$  and  $T''_{\max}$  of relaxor ferroelectrics shift to higher temperatures on increasing the measuring frequency. For regular ferroelectric transitions, on the other hand,  $T'_{\max}$  is not only equal to  $T''_{\max}$ , as expected on the basis of the Kramer–Kronig relationship,<sup>21</sup> but is also frequency independent and corresponds to the thermodynamic phase transition temperature ( $T_c$ ). As can be clearly seen from Fig. 1, for the BT- $x$ BF compositions,  $T'_{\max} = T''_{\max}$  for  $x = 0.04$  and  $0.06$ . For higher values of  $x$ , the conductivity losses mask the peak in  $\epsilon''(T)$ . Additionally,  $T'_{\max}$  is independent of frequency, as shown in Fig. 4 for  $x = 0.04$  and  $0.15$ . However, even though  $T'_{\max}$  does not show frequency dependence, one does observe dispersion in the dielectric permittivity. This is due to space

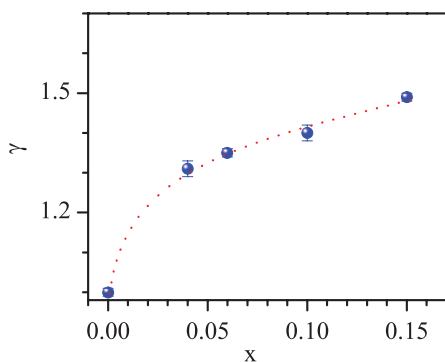


FIG. 3. (Color online) Variation of the diffuseness parameter  $\gamma$  in BT- $x$ BF system as a function of  $x$ .

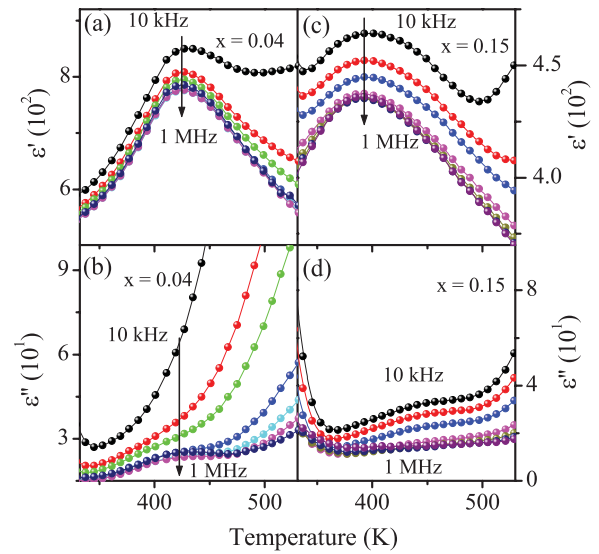


FIG. 4. (Color online) Temperature dependence of real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of dielectric permittivity of BT-0.04BF (a, b) and BT-0.15BF (c, d) at various frequencies (10, 50, 100, 300, 500, 700, and 1000 kHz).

charge relaxation at lower frequencies and conductivity losses, which are significant even at higher frequencies ( $\sim 1$  MHz). The DPT in BT- $x$ BF is thus of nonrelaxor ferroelectric type, similar to that reported in pure  $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  and its solid solutions with  $\text{PbTiO}_3$  (PT).<sup>22</sup>

## 2. Comparison with other Bi-based systems

It is worth mentioning here that  $\text{Bi}^{3+}$ -induced relaxor ferroelectric behavior has been reported in the past in “A” site-deficient solid solutions  $(\text{Ba}_{1-x}\text{Bi}_{2x/3})/\text{TiO}_3$ .<sup>23–25</sup> The charge neutrality of the overall composition in such solid solutions requires vacancies at the A site.<sup>24–26</sup> Because of the creation of A-site vacancies, the intrinsic ferroelectric behavior of  $\text{BaTiO}_3$  is affected drastically. Our compositions are charge neutral without any vacancies at the A site. Therefore, the DPT behavior in BT- $x$ BF is not linked with A-site vacancies. Recently, smeared  $\epsilon'(T)$  response has been reported in many other Bi-based solid solution systems with a general formula  $(1-x)\text{BaTiO}_3-x\text{BiMO}_3$  (BT- $x$ BM) (where  $M = \text{Sc}^{3+}, \text{Al}^{3+}, (\text{Mg}_{1/2}\text{Ti}_{1/2})^{3+},$  and  $(\text{Zn}_{1/2}\text{Ti}_{1/2})^{3+}$  (Ref. 32)) similar to BT- $x$ BF without A-site vacancies. The  $\epsilon'(T)$  response of all these system is in many ways similar to that for BT- $x$ BF. For example, the  $\text{BiMO}_3$  substitution smears the  $\epsilon'(T)$  plot of pure  $\text{BaTiO}_3$  similar to that for BT- $x$ BF. The  $T'_{\max}$  for all these systems decreases slightly with respect to  $T_c$  of  $\text{BaTiO}_3$  for the tetragonal compositions, similar to that of BT- $x$ BF. Furthermore, with increasing concentration of  $\text{BiMO}_3$ , the room temperature crystal structure changes from tetragonal to pseudocubic.<sup>28,30</sup> Some authors report rhombohedral symmetry for the pseudocubic phase, even though the published XRD data do not reveal clear splitting of hhh-type peaks characteristic of the rhombohedral phase.<sup>29,32</sup> In  $(1-x)\text{BaTiO}_3-x\text{BiScO}_3$  (BT- $x$ BS) system, it has been proposed that the tetragonal and the cubic regions are separated by a two-phase region over which the tetragonal phase coexists with a rhombohedral phase.<sup>27</sup> The BT- $x$ BF

system also reveals a similar change of average symmetry from tetragonal to a pseudocubic phase, as can be seen from Fig. S1 in the supplementary material.<sup>33</sup> The  $T'_{\max}$  for the pseudocubic/rhombohedral compositions increases with increasing BM content, which is also similar to that of BT- $x$ BF.

Notwithstanding the above-mentioned similarities, there are also characteristic differences between BT- $x$ BF and BT- $x$ BM systems. For example, the peak value of dielectric permittivity ( $\epsilon'_{\max}$ ) corresponding to  $T'_{\max}$  in the smeared  $\epsilon'(T)$  response is in general lower for BT- $x$ BF ( $\sim 800$  for  $x = 0.04$ ) compared with other BT- $x$ BM systems ( $\geq 4000$  for  $x = 0.04$  to 0.05<sup>29,30,32</sup>), except for  $(1-x)\text{BaTiO}_3-x\text{BiScO}_3$ , where a  $\epsilon'_{\max}$  value ( $\sim 800$  for  $x = 0.03$ ) comparable to BT- $x$ BF has also been reported.<sup>32</sup> Our measured value of  $\epsilon'_{\max}$  ( $\sim 800$ ) corresponding to  $T'_{\max}$  in BT- $x$ BF for  $x = 0.04$  is in good agreement with the reported value of  $\epsilon'_{\max}$  ( $\sim 800$ ) at  $T'_{\max}$  by Kumar *et al.*<sup>34</sup> for the same composition. It has been argued that the significant difference between the values of  $\epsilon'_{\max}$  of  $(1-x)\text{BaTiO}_3-x\text{BiScO}_3$  and  $(1-x)\text{BaTiO}_3-x\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$  is due to the large ionic radius of  $\text{Sc}^{3+}$  compared with the average radius of  $(\text{Zn}_{1/2}\text{Ti}_{1/2})^{3+}$  at the ‘‘B’’ site.<sup>32</sup> In fact, this idea seems to work for  $(1-x)\text{BaTiO}_3-x\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$  system also, which has  $\epsilon'_{\max}$  values comparable to that of  $(1-x)\text{BaTiO}_3-x\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$  for small values of  $x$  because of comparable average ionic radii of  $(\text{Mg}_{1/2}\text{Ti}_{1/2})^{3+}$  and  $(\text{Zn}_{1/2}\text{Ti}_{1/2})^{3+}$ . In the  $(1-x)\text{BaTiO}_3-x\text{BiAlO}_3$ , although the ionic radius of  $\text{Al}^{3+}$  is much less than those of  $(\text{Mg}_{1/2}\text{Ti}_{1/2})^{3+}$  and  $(\text{Zn}_{1/2}\text{Ti}_{1/2})^{3+}$ , this system does not show higher  $\epsilon'_{\max}$  than those for  $(1-x)\text{BaTiO}_3-x\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$  and  $(1-x)\text{BaTiO}_3-x\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$  systems. Similarly, the ionic radius of  $\text{Fe}^{3+}$  is also less than those of  $(\text{Mg}_{1/2}\text{Ti}_{1/2})^{3+}$  and  $(\text{Zn}_{1/2}\text{Ti}_{1/2})^{3+}$  and comparable to that of  $\text{Al}^{3+}$ , but the BT- $x$ BF system shows a much lower value of  $\epsilon'_{\max}$ . This suggests that the reduction in  $\epsilon'_{\max}$  corresponding to  $T'_{\max}$  may not only depend on the average ionic radius of the B site but also on the chemistry of the B-site cation. We believe that the substantial decrease in  $\epsilon'_{\max}$  value from  $\sim 7500$  in BT- $x$ BF for  $x = 0$  to  $\sim 800$  for  $x = 0.04$  is essentially due to the non- $d^0$ -ness of  $\text{Fe}^{3+}$ , which prevents the hybridization of 3d  $\text{Fe}^{3+}$  with 2p  $\text{O}^{2-}$ ,<sup>35</sup> making  $\text{Fe}^{3+}$  nonferro-active.<sup>36</sup> On the other hand, first principles calculations have revealed hybridization of 4s/4p of  $\text{Zn}^{2+}$ ,<sup>36</sup> 3s/3p of  $\text{Sc}^{3+}$ ,<sup>37</sup> and 2s/2p of  $\text{Al}^{3+}$  (Ref. 37) with 2p orbitals of  $\text{O}^{2-}$  confirming their ferro-active nature. Apart from the difference in  $\epsilon'_{\max}$  values, there is another significant difference between BT- $x$ BF and BT- $x$ BM systems. The DPT in BT- $x$ BF is of nonrelaxor type, whereas it is in general of relaxor<sup>29–32</sup> or reentrant relaxor type<sup>5,38</sup> in other BT- $x$ BM systems.

Amongs the BT- $x$ BM systems, the dielectric response of  $(1-x)\text{BaTiO}_3-x\text{BiScO}_3$  is in some ways similar to that of BT- $x$ BF. For example, as in the case of BT- $x$ BF, the  $\epsilon'_{\max}$  value of BT- $x$ BS reduces drastically as a result of  $\text{BiScO}_3$  substitution compared with other  $\text{BiMO}_3$  substitutions. Furthermore, in both systems, the dependence of  $T'_{\max}$  on  $x$  is slightly nonmonotonic in the sense that  $T'_{\max}$  increases slightly for very small  $x$  values and then decreases. At this point in time, there is no explanation for such nonmonotonic behavior either in BT- $x$ BS or in BT- $x$ BF. The close similarities in the phase transition behavior of BT- $x$ BS and BT- $x$ BF suggest that the smearing of the sharp ferroelectric phase transition of  $\text{BaTiO}_3$

in BT- $x$ BF and BT- $x$ BS is essentially due to Bi substitution at the Ba site, with little role of the substitution at the B site by  $\text{Fe}^{3+}$  or  $\text{Sc}^{3+}$ . It is therefore likely that the DPT in these systems, as well as in other BT- $x$ BM systems, may have a common origin. To investigate further the likely role of Bi substitution on the phase transition behavior of  $\text{BaTiO}_3$ , we carried out detailed structural studies on the BT- $x$ BF system, as discussed in the following section.

## B. Structural studies

### 1. Evidence for off-centered $\text{Bi}^{3+}$ in pseudocubic BT- $x$ BF

Although BT- $x$ BF compositions with  $0.15 \leq x \leq 0.40$  undergo diffuse paraelectric to ferroelectric phase transition, their synchrotron powder diffraction patterns do not show any splitting or asymmetry of the cubic Bragg peaks even for very high order hkl reflections (in the higher  $2\theta$  region), suggesting that the crystal structure is cubic, at least in an average sense. We accordingly carried out Rietveld refinement of the structure of BT-0.15BF using the cubic  $\text{Pm}\bar{3}\text{m}$  space group. Figure 5(a) depicts the fit between observed and calculated profiles of BT-0.15BF obtained after the Rietveld refinement using the  $\text{Pm}\bar{3}\text{m}$  space group. It can be clearly seen from Fig. 5(a) that in the low-angle ( $2\theta$ ) region, the fit between the observed and calculated profiles is good. However, in the higher angle ( $2\theta$ ) region (shown in the inset to Fig. 5(a)), the calculated intensities are lower than the observed intensities, with large discrepancies for most of the reflections. The large discrepancy between the calculated and observed intensities in the higher  $2\theta$  region clearly suggests that the crystal structure

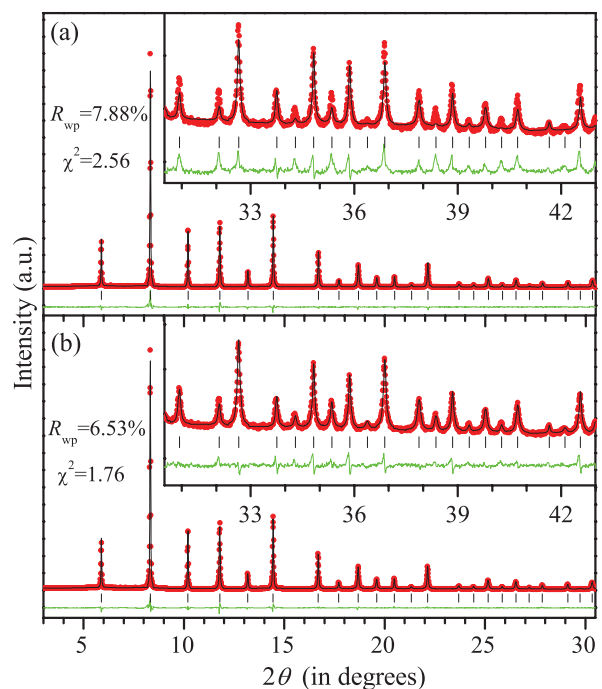


FIG. 5. (Color online) Observed (circles), calculated (line), and difference (bottom line) patterns obtained after Rietveld refinement of BT-0.15BF at room temperature using (a) average cubic structure and (b) disordered  $\text{Bi}^{3+}$  along the  $(001)$  direction in the average cubic structure with the  $\text{Pm}\bar{3}\text{m}$  space group. The vertical tick marks correspond to the positions of Bragg reflections.

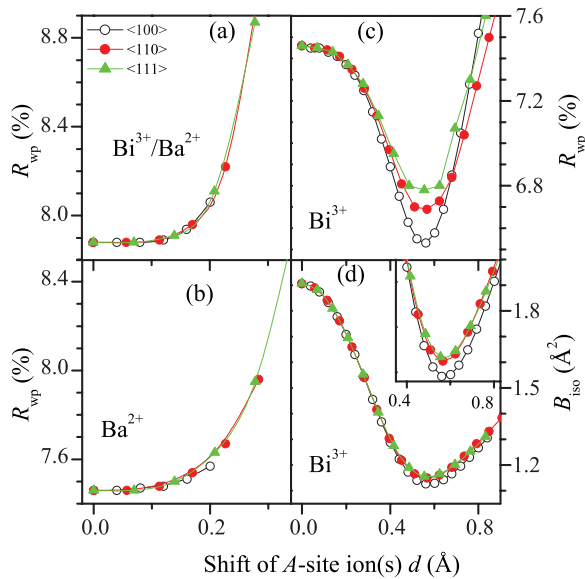


FIG. 6. (Color online) Variation of weighted profile agreement factor  $R_{wp}$  with off-centered displacement of (a) both  $\text{Bi}^{3+}$  and  $\text{Ba}^{2+}$ , (b) only  $\text{Ba}^{2+}$ , and (c) only  $\text{Bi}^{3+}$  along the  $\langle 001 \rangle$ ,  $\langle 110 \rangle$ , and  $\langle 111 \rangle$  directions. (d) Variation of the  $\text{Bi}^{3+}$  thermal parameter with off-center displacement of  $\text{Bi}^{3+}$ . The inset to panel (d) shows the zoomed portion of the minima in  $B_{iso}$ .

of BT-0.15BF is not an ideal cubic perovskite type, as expected on the basis of the observation of the ferroelectric diffuse phase transition also, which is forbidden for a centrosymmetric space group like  $\text{Pm}\bar{3}\text{m}$ . To capture the departure from the average cubic structure at the local level, we considered displacements of both  $\text{Bi}^{3+}$  and  $\text{Ba}^{2+}$  along the  $\langle 100 \rangle$ ,  $\langle 110 \rangle$ , and  $\langle 111 \rangle$  directions from the perovskite cube corner positions in the refinements using a split site method in the Rietveld refinements.<sup>39</sup> Figure 6(a) shows the weighted profile agreement factor  $R_{wp}$  for various values of off-center displacements of both  $\text{Bi}^{3+}$  and  $\text{Ba}^{2+}$  together. It is evident from this figure that  $R_{wp}$  is nearly unaffected for off-center displacements  $d \leq 0.1 \text{ \AA}$  and increases for  $d \geq 0.1 \text{ \AA}$ . This clearly reveals that an A-site disorder involving off-centering of both  $\text{Bi}^{3+}$  and  $\text{Ba}^{2+}$  is not responsible for the mismatch between the observed and calculated profiles shown in the inset of Fig. 5(a).

As the next step, we considered off-center displacements of  $\text{Ba}^{2+}$  and  $\text{Bi}^{3+}$  separately. For a  $\text{Ba}^{2+}$  off-center displacement, there is no improvement in  $R_{wp}$ , and the nature of  $R_{wp}$  versus the off-center displacement curve is similar to that for an A-site disorder (see Fig. 6(b)). However, when we considered only  $\text{Bi}^{3+}$  off-centering, leaving  $\text{Ba}^{2+}$  at the cube corner site, we observed minima in the  $R_{wp}$  versus off-center displacement plots for displacements along the  $\langle 100 \rangle$ ,  $\langle 110 \rangle$ , and  $\langle 111 \rangle$  directions (Fig. 6(c)). The minimum is deepest for displacements in the  $\langle 100 \rangle$  direction, providing evidence for  $\text{Bi}^{3+}$  off-centering in the  $\langle 100 \rangle$  cubic direction. The variation of the isotropic thermal parameter of  $\text{Bi}^{3+}$  with off-center displacement depicted in Fig. 6(d) also shows a minimum for off-centered displacement along  $\langle 100 \rangle$ , as shown more clearly in the inset. From this analysis, we conclude that only  $\text{Bi}^{3+}$  goes off-center by  $0.56 \text{ \AA}$  from the corner site of the cubic lattice, and the off-centering occurs along

$\langle 100 \rangle$  direction. Using a similar approach, the possibility of B-site cations ( $\text{Fe}^{3+}/\text{Ti}^{4+}$ ) and oxygen disorders from special Wyckoff positions were also considered, but the  $R$  factors and the fitting features did not improve in the Rietveld refinements. Figure 5(b) depicts the profile fit obtained after the Rietveld refinement using the  $\text{Pm}\bar{3}\text{m}$  space group with off-center displacement of the  $\text{Bi}^{3+}$  ion in the  $\langle 100 \rangle$  direction. This model gives a very good fit between the observed and calculated profiles, even at higher  $2\theta$  angles compared with that shown in Fig. 5(a) for an ideal cubic perovskite structure. We believe that the  $\text{Bi}^{3+}$  ion is off-centered in the BT- $x$ BM systems as well, and this off-centering holds the key to the smearing of the  $\varepsilon'(T)$  response in these materials.

The off-centered displacement of  $\text{Bi}^{3+}$  in BT- $x$ BF is indeed expected because of the large difference in the ionic radii of  $\text{Ba}^{2+}$  ( $r_{\text{Ba}^{2+}} = 1.42 \text{ \AA}$ ) and  $\text{Bi}^{3+}$  ( $r_{\text{Bi}^{3+}} \sim 1.11 \text{ \AA}$ ).<sup>40</sup> When  $\text{Bi}^{3+}$  goes off-center, it creates a local dipole, the formation of which will depend on the polarizability of the host matrix. On the other hand, this off-centering enhances the short-range repulsive interaction because of the proximity to the neighboring  $\text{O}^{2-}$  ion. Evidently, the inequality in ionic radius and charge of  $\text{Bi}^{3+}$  and  $\text{Ba}^{2+}$  seems to upset the balance of polarizing and repulsive forces at the centro-symmetric corner point of the unit cell, leading to off-centering of  $\text{Bi}^{3+}$  with respect to the  $\text{Ba}^{2+}$  position.<sup>1</sup> As pointed out earlier,  $\text{Li}^{1+}$  and  $\text{Ca}^{2+}$  in  $\text{KTaO}_3/\text{KCl}$  and  $\text{SrTiO}_3$ , respectively, are also known to be off-centered with respect to the  $\text{K}^{1+}$  and  $\text{Sr}^{2+}$  corner positions in the perovskite unit cell. The off-centering of  $\text{Li}^{1+}$  and  $\text{Ca}^{2+}$  is believed to be induced by a size difference between the substituting ion and the matrix ion. However, in a large class of Pb-based ferroelectric and relaxor ferroelectric perovskites, such as  $\text{PbTiO}_3$ ,<sup>41</sup>  $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ ,<sup>41</sup> and  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ,<sup>42</sup> in which there is only one type of ion ( $\text{Pb}^{2+}$ ) at the unit cell corner position, the  $\text{Pb}^{2+}$  ion is known to occupy the off-centered position in the  $\langle 110 \rangle_{pc}$  direction. It is shifted by  $\sim 0.20$  to  $0.25 \text{ \AA}$  with respect to the special Wyckoff site. This implies that the size difference is not the only factor that can induce off-centering of ions in the pseudocubic perovskites.

In  $\text{Pb}^{2+}$ -based perovskites like  $\text{PbTiO}_3$ ,<sup>43</sup> it is now believed that the off-centering of  $\text{Pb}^{2+}$  occurs because of the softening of the short-range repulsive forces by the hybridization of the  $6s^2$  lone pair orbital of  $\text{Pb}^{2+}$  with the  $2p$  orbitals of the oxygen ion. In the case of BT- $x$ BF and other BT- $x$ BM systems,  $\text{Bi}^{3+}$  is not only significantly smaller than  $\text{Ba}^{2+}$  but has  $6s^2$  lone pair orbitals, which also are known to hybridize with the partially filled  $2p$  orbitals of  $\text{O}^{2-}$ , as has been established in pure  $\text{BiFeO}_3$ .<sup>44</sup> Additionally,  $\text{Bi}^{3+}$  is not isovalent with  $\text{Ba}^{2+}$ , unlike  $\text{Li}^{1+}$  or  $\text{Ca}^{2+}$  at  $\text{K}^{1+}$  or  $\text{Sr}^{2+}$  sites. Both the charge difference and the magnitude of the off-center displacement decide the magnitude of the dipole moment. As pointed out earlier, for any off-center displacement to occur, the polarizing forces resulting from the size and charge differences between the impurity and the matrix ion will be opposed by short-range repulsive forces.<sup>1</sup> The magnitude of the off-center displacement will therefore be decided by the balance of these two forces. We believe that the large off-center displacement ( $\sim 0.86 \text{ \AA}$ )<sup>45</sup> of  $\text{Li}^{1+}$  in  $\text{KaTiO}_3$  is essentially a size-induced effect because  $\text{Li}^{1+}$  ( $r_{\text{Li}^{1+}} = 0.92 \text{ \AA}$ ) is very much smaller than  $\text{K}^{1+}$  ( $r_{\text{K}^{1+}} = 1.51 \text{ \AA}$ ), as a result of which, the short-range

repulsive forces are also not so assertive. The size difference between  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$  in the  $(\text{Sr}_{1-x}\text{Ca}_x)\text{TiO}_3$  system is rather small ( $r_{\text{Ca}^{2+}} = 1.12 \text{ \AA}$  and  $r_{\text{Sr}^{2+}} = 1.25 \text{ \AA}$ ), and the off-center displacement of  $\text{Ca}^{2+}$  is also predicted<sup>46</sup> to be much smaller ( $\sim 0.08 \text{ \AA}$ ). In the case of  $\text{Pb}^{2+}$ -based perovskites, the  $\text{Pb}^{2+}$  ions are quite large and have no reason to go off-center in the cubo-octahedral cage of oxygen as a result of a size factor. Here the dominant factor is the tendency of the  $6s^2$  lone pair orbital of  $\text{Pb}^{2+}$  to hybridize with the  $2p$  orbitals<sup>43</sup> of the neighboring  $\text{O}^{2-}$ . In the  $\text{BT-}x\text{BF}$  system, both the size difference, which is somewhat moderate compared with that between  $\text{Li}^{1+}$  and  $\text{K}^{1+}$ , and the lone pair stereochemistry of the  $6s^2$  electrons of  $\text{Bi}^{3+}$ , along with the valence difference between  $\text{Bi}^{3+}$  and  $\text{Ba}^{2+}$ , are responsible for the large off-center displacement of the  $\text{Bi}^{3+}$  ion with respect to the  $\text{Ba}^{2+}$  position compared with that of  $\text{Pb}^{2+}$  in ferroelectric and relaxor ferroelectric perovskites.

The off-center displacement in perovskites may be of dynamic origin too. For example, in  $\text{Pb}^{2+}$ -based ferroelectric and relaxor ferroelectric compounds, it has been argued that the off-centering of  $\text{Pb}^{2+}$  could be due to strong anharmonicity of the on-site potential.<sup>41</sup> A similar study on  $\text{Ba}^{2+}$ -based perovskites has revealed that the absence of off-centering of  $\text{Ba}^{2+}$  ions is essentially due to the quasi-harmonic nature of the on-site potential.<sup>41</sup> The off-center displacement of  $\text{Bi}^{3+}$  in  $\text{BT-}x\text{BF}$  is, however, more than twice that of  $\text{Pb}^{2+}$  in  $\text{Pb}^{2+}$ -based ferroelectric and relaxor ferroelectrics. Such a large displacement is beyond the limit of amplitude of thermal vibrations around a special Wyckoff position, and it should be regarded as static disorder caused by the factors discussed earlier. In case of  $\text{Li}^{1+}$  in  $\text{KTaO}_3$  also, the off-center displacement is very large ( $\sim 0.86 \text{ \AA}$ <sup>45</sup>) and may essentially be due to static disorder.

## 2. Evidence for cooperative tricritical freezing of random-site dipoles in $\text{BT-}x\text{BF}$

To understand the relationship between the diffuse ferroelectric phase transition observed by dielectric measurements and the off-center displacement of  $\text{Bi}^{3+}$  ion in the  $\text{BT-}x\text{BF}$  system, we analyzed the off-center displacement of  $\text{Bi}^{3+}$  in  $\text{BT-}0.15\text{BT}$  as a function of temperature. It is found that although there is no change in the average cubic symmetry on account of the ferroelectric to paraelectric diffuse phase transition, the cubic unit cell parameter and the off-center displacement of  $\text{Bi}^{3+}$  do change as a function of temperature, as can be seen from Fig. 7(a) and 7(b). In particular, the off-center displacement of  $\text{Bi}^{3+}$  shows a monotonic increase on approaching the average Curie temperature (see Fig. 7(b)). The off-center displacement of  $\text{Bi}^{3+}$  would depend on the polarizability of the host matrix, which increases with decreasing temperature on account of the ferroelectric soft mode. Since the ferroelectric soft mode  $\Gamma_4^-$  of  $\text{BaTiO}_3$  also causes displacements of ions in the  $\langle 001 \rangle$  direction during cubic to tetragonal phase transition, the ability of  $\text{Bi}^{3+}$  to go off-center in the  $\langle 001 \rangle$  direction will be further facilitated by the reduction of the force constant in such directions. This will evidently lead to additional off-center displacement, as evident from the monotonic increase in the value of off-center displacement of  $\text{Bi}^{3+}$  on approaching the average Curie temperature in

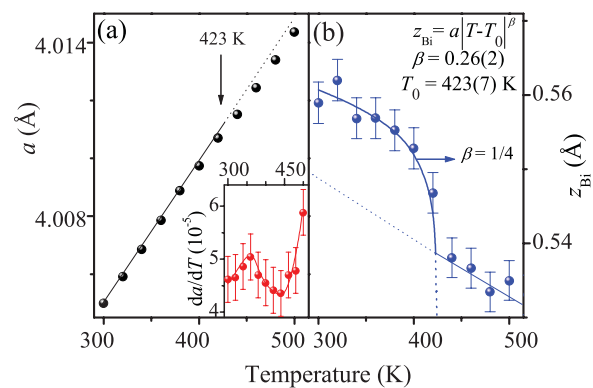


FIG. 7. (Color online) Variation of (a) unit cell parameter and (b) off-center displacement ( $z_{\text{Bi}}$ ) of  $\text{Bi}^{3+}$  along  $\langle 001 \rangle$  with temperature. The continuous line through data points from 300 to 423 K corresponds to the fit for a  $z_{\text{Bi}} = a |T - T_0|^\beta$  type of temperature dependence for the off-center displacements. Inset to panel (a) depicts the first derivative of the variation of the unit cell parameter with temperature.

Fig. 7(b). On entering the Curie range, the polarizability of the matrix increases suddenly because of the  $\Gamma_4^-$  mode freezing at the transition temperature. Since the off-center displacement of the  $\text{Bi}^{3+}$  ion is dependent on the polarizability of the host matrix, it also shows a sudden increase on entering the Curie range. We tried to fit the following function, which is known to describe the temperature dependence of spontaneous polarization in ferroelectrics,

$$z_{\text{Bi}} = a |T - T_0|^\beta, \quad (2)$$

where  $\beta$  is 0.5 for a second-order phase transition.<sup>21</sup> Interestingly, least squares fit to the experimentally observed  $z_{\text{Bi}}$  versus  $T$  plot gives a value of  $\beta = 0.26(2)$  and  $T_0 = 423(7)$  K. The fitted curve with of  $\beta = 0.26(2)$  and  $T_0 = 423(7)$  K is shown in Fig. 7(a). The case in which  $\beta = 0.25$  is characteristic of a tricritical phase transition.<sup>9</sup> Our results thus suggest that the temperature dependence of the off-center displacement of  $\text{Bi}^{3+}$  ions exhibits a tricritical behavior. With the increase in off-center displacement of  $\text{Bi}^{3+}$  in the Curie range, the cubic cell parameter also shows a diffuse anomaly that is more clearly seen in the  $da/dT$  plot shown in the inset of Fig. 7(a). All these observations clearly point towards the occurrence of a diffuse cooperative phenomenon associated with the freezing of  $\text{Bi}^{3+}$ -centered dipoles.

## 3. Possible role of random fields in the diffuse phase transition behavior of $\text{BT-}x\text{BF}$

In pure  $\text{BaTiO}_3$ , freezing of the  $\Gamma_4^-$  mode leads to tetragonal distortion of the cubic paraelectric phase. This distortion, however, is not revealed in  $\text{BT-}x\text{BF}$  for  $0.15 \leq x \leq 0.40$  at the macroscopic level. We believe that this is because of the formation of RF-induced small domains that not only mask the tetragonal distortion but also make the phase transition diffuse because of the size effect. It was shown by Imry and Ma<sup>7</sup> in a pioneering paper that in the presence of small quenched-in random field, long-range order breaks into small RF domains to minimize the overall energy. This concept has been used for smeared transition in dipolar glasses<sup>1,2</sup> and

relaxor ferroelectrics,<sup>19</sup> besides the magnetic system for which it was originally proposed.<sup>7</sup> What are the possible sources of random field in BT- $x$ BF system? Random field can originate from the random strain ( $e_{ij}$ ) coupling to local  $\text{Bi}^{3+}$  polarization with terms like  $e_{ij}P_mP_n$ , as has been proposed in the context of the  $(\text{Sr}_{1-x}\text{Ca}_x)\text{TiO}_3$  system.<sup>47</sup> Additionally, random field can also arise due to “local” charge imbalance if, in some of the unit cells, the oxygen octahedral cage center is occupied by  $\text{Fe}^{3+}$  while the oxygen cubo-octahedral cage center is occupied by  $\text{Ba}^{2+}$ . Alternatively, oxygen octahedral cage center occupied by  $\text{Ti}^{4+}$  and the oxygen cubo-octahedral cage occupied by  $\text{Bi}^{3+}$  may also give rise to a local charge imbalance. Such situations cannot be ruled out for random solid solutions. Since such excess or deficient –ve local charges occur randomly, the overall charge neutrality of the samples is not affected but can lead to random fields.

The model proposed here is similar to what has been observed in the canonical relaxor ferroelectric compound  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PMN), which also exhibits smeared  $\epsilon'(T)$  response. In PMN, a ferroelectric soft mode has been reported below Burn’s temperature  $T_B$ , which is well above the Curie range.<sup>48,49</sup> This soft mode, however, gets overdamped in the Curie range and reappears as a hard mode outside the Curie range.<sup>48</sup> There is no signature of macroscopic symmetry breaking in the diffraction data of PMN despite the freezing of the ferroelectric  $\Gamma_4^-$  mode. One of the models of relaxor ferroelectrics attributes the smeared  $\epsilon'(T)$  response to the formation of RF domains in the Curie range, induced by the random field generated by local charge imbalance at the B site of the  $\text{ABO}_3$  perovskite structure.<sup>19</sup> Such RF domains have been observed in PMN.<sup>50</sup> The conversion of such RF domains into regular ferroelectric domains, bearing a definite crystallographic orientation relationship, with  $\text{PbTiO}_3$  substitution causes gradual crossover from diffuse to sharp ferroelectric transition.<sup>50,51</sup> Although the DPT in BT- $x$ BF and the smeared  $\epsilon'(T)$  response in relaxor ferroelectrics like PMN with no signature of symmetry breaking at the macroscopic level may both be due to the formation of RF domains, there is a significant difference in terms of the dynamics of the RF

domains. In PMN-like relaxor ferroelectrics, the RF domains are small enough to show relaxational freezing in the Curie range, leading to frequency-dependent  $T'_{\text{max}}$  and  $T''_{\text{max}}$ , but there is no evidence for such relaxational dynamics of the RF domains in BT- $x$ BF. This may be because of the larger size of RF domains in BT- $x$ BF compared with that in PMN, which are big enough not to undergo thermal fluctuations because of insufficient thermal energy ( $k_B T$ ) in the Curie range but small enough so as not to reveal symmetry breaking in a diffraction profile.

#### IV. CONCLUSIONS

To summarize, we have presented evidence for a nonrelaxor-type diffuse ferroelectric to paraelectric phase transition as a result of  $\text{BiFeO}_3$  substitution in  $\text{BaTiO}_3$  [i.e., the  $(\text{Ba}_{1-x}\text{Bi}_x)(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_3$  system] and off-center displacement of  $\text{Bi}^{3+}$  ions in the  $\langle 001 \rangle_{\text{pc}}$  direction of the average cubic lattice for  $0.15 \leq x \leq 0.40$ . We have also shown that random-site dipoles associated with the off-centered Bi ions freeze cooperatively with a critical exponent of 1/4 which is the characteristic of a tricritical transition. It is proposed that the presence of static random fields generated by the local charge imbalances, strain fields, or both lead to the diffuse  $\epsilon'(T)$  response.

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\*dp.mst1979@gmail.com

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