Particle size dependence of magnetization and phase transition near $T_N$ in multiferroic BiFeO$_3$

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We report results of a comprehensive study of the phase transition at $T_N$ ($\sim$643 K) as a function of particle size in multiferroic BiFeO$_3$ system. We employed electrical, thermal, and temperature dependent x-ray diffraction studies in order to characterize the transition in a host of samples. We also carried out detailed magnetic measurements over a temperature regime of 2–300 K under a magnetic field of 100–10 000 Oe both on bulk and nanocrystalline systems. While in the bulk system a sharp endothermic peak at $T_N$ together with a broad feature, ranging over nearly $\sim$100 K ($\Delta T$), could be observed in calorimetry, the nanoscale systems exhibit only the broad feature. The characteristic dielectric anomaly, expected at $T_N$, is found to occur both at $T_O$ and $T_N$ across $\Delta T$ in the bulk sample. The Maxwell-Wagner component due to interfaces between heterogenous regions with different conductivities is also present. The magnetic properties, measured at lower temperature, corroborate our observations in calorimetry. The metastability increases in the nanoscale BiFeO$_3$ with divergence between zero-field cooled and field cooled magnetizations below $\sim$100 K and faster magnetic relaxation. Interestingly, in nanoscale BiFeO$_3$ one also observes finite coercivity at lower temperature, which points out that suitable design of particle size and shape may induce ferromagnetism. The inhomogeneous distribution of Bi/Fe ions and/or oxygen nonstoichiometry seems to be giving rise to broad features in thermal, magnetic as well as electrical responses. © 2006 American Institute of Physics. [DOI: 10.1063/1.2229667]

I. INTRODUCTION

The multiferroics, with, at least, two of the three orders or degrees of freedom—(anti)ferromagnetic, (anti)ferroelectric, and ferroelastic—coexisting and often a coupling among them, are rare in nature as transition metal ions with active $d$ electrons often tend to reduce the off-center distortion necessary for ferroelectricity. It has been pointed out by a recent theoretical work that additional electronic mechanism (mainly $s^2$ lone pair at another site) provides the driving force for ferroelectricity. Since the observation by Smolensky et al. in 1958, three different classes of multiferroic systems could be identified—RMnO$_3$ (where $R$ =Dy, Tb, Ho, Y, Lu, etc.), R$_2$Mn$_2$O$_7$ (where $R$ =Nd, Sm, Dy, Tb), and BiBO$_3$-type (where $B$ =Mn, Fe). Such systems depict magnetoelectric coupling and, therefore, magnetic polarization can be achieved by electric field and vice versa. Recently, there has been a renewed interest in multiferroic systems due to the observation of orders of magnitude large magnetoelectric coupling and the application potential of these systems in a range of devices based on “spintronics,” magnetoelectric sensors, electrically driven magnetic data storage and recording devices, magnetocapacitive devices, nonvolatile memories, etc. Direct evidence of linear coupling between electric and magnetic domains could be observed in YMnO$_3$ using nonlinear optics—optical second harmonic generation. However, the temperature range over which the multiferroic behavior is observed varies from system to system. For instance, RMnO$_3$ (space group $P6_3cm$) and R$_2$Mn$_2$O$_7$ (space group $Pbam$) systems depict multiferroic properties at lower temperature (<100 K). In BiMnO$_3$ (space group $C2$) too, ferromagnetic and ferroelectric orders coexist below $\sim$105 K. The BiFeO$_3$ system (space group $R3c$) is interesting, in this respect, as it depicts ferroelectric order below $T_c$ $\sim$1110 K and antiferromagnetic order below $T_N$ $\sim$643 K. Therefore below $T_N$, one expects coupling between electric and magnetic domains.

The multiferroic nature of BiFeO$_3$ is due to stereochemical activity associated with the $6s^2$ lone pair of Bi$^{3+}$. It results in lowering of structural symmetry and hence

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The magnetic order is little complicated with ferromagnetic coupling within a plane and antiferromagnetic coupling between two adjacent planes. Due to antisymmetric Dzyaloshinsky-Moriya (DM) exchange interaction, cant antiferromagnetism may develop. However, a spiral spin structure is superimposed on this antiferromagnetic order in which the antiferromagnetic axis is rotated through the crystal and develops an incommensurate order. The magnetoelectric coefficient \(dE/dH\) is found to vary within 3 V/cm Oe across a temperature range of 77–300 K. The study of crystallographic structure using high temperature x-ray diffraction (XRD) patterns provides the ferroelectric Curie point \(T_C\) to be \(\sim 1110\) K. Direct measurement of polarization \(P\) versus electric field \(E\) loop or dielectric spectroscopy across \(T_C\) is still missing. The magnetic transition temperature \(T_N\) is estimated from magnetic structure study using neutron diffraction patterns and is found to be \(\sim 643\) K. Weak magnetization, however, restricts its large scale use in several devices. One needs to explore whether large magnetization can be induced in these systems by doping and/or structural manipulation. In other words, one needs a thermodynamically stable system with both ferromagnetism and ferroelectricity existing above room temperature. BiFeO\(_3\) could not be exploited for any application for two major problems: (i) weak magnetization as it is essentially an antiferromagnet below \(T_N\) and (ii) large loss factor because of oxygen nonstoichiometry. Therefore, even though magnetoelectric coupling could be observed above room temperature, unlike CdCr\(_2\)S\(_4\) (Ref. 13) complete ferroelectric polarization flop cannot be achieved in BiFeO\(_3\) by magnetic field sweeping. It has recently been observed that in thin film BiFeO\(_3\), finite magnetization of the order of \(\sim 1\) \(\mu_B/Fe\) prevails even above room temperature. The origin of such magnetization is a bit controversial. It has been proposed, however, that such finite magnetization could result from increased canting. A suitable doping at Bi and/or Mn site, on the other hand, helps in minimizing the conductivity and hence the loss factor. It will be interesting to explore whether both the problems can be addressed and tackled in nanoscale BiFeO\(_3\).

In this paper, we report the results of a comprehensive study carried out both on bulk and nanoscale BiFeO\(_3\) for exploring the phase transition features near \(T_N\) as well as the low temperature magnetic properties. We employed dc resistivity, dielectric measurements, differential scanning calorimetry (DSC), differential thermal analyses (DTAs), dilatometry, temperature dependent x-ray diffraction, and detailed magnetic measurements in order to systematically record the behaviors of the bulk and nanosystem below and above the magnetic transition point. It appears that the local inhomogeneity as well as oxygen nonstoichiometry across the sample volume have major roles to play in governing all the properties.

II. EXPERIMENTAL DETAILS

Primarily two types of measurements were carried out on phase pure bulk and nanoparticles of BiFeO\(_3\)—thermal and magnetic. The electrical measurements were carried out only on bulk-sintered samples. All the samples have been prepared by different solution chemistry routes. While bulk \(\sim 1\) \(\mu m\) size particles have been prepared by conventional coprecipitation technique, finer \(4–50\) nm size particles have been prepared by sonochemical and solution evaporation (tartaric acid template or ferrioxalate precursor) techniques. In the sonochemical technique, powders are prepared in solution chemistry route under ultrasonic vibration. A mixed aqueous solution of Bi(NO\(_3\))\(_3\) and Fe(NO\(_3\))\(_2\)—taken in proper stoichiometric ratio—is sonicated by using Ti horn (20 kHz, 1500 W, Vibracell, USA) until the precipitation is complete. A small amount of decalin is used for proper power transfer and sodium dodecyl sulphate (SDS) surfactant is also used for preventing agglomeration. The precipitated powder is collected, washed by alcohol, and dried in a vacuum oven at \(\sim 40^\circ\)C. In the tartaric acid template technique, aqueous solutions of metal nitrates were mixed with tartaric acid. The mixed solution was boiled at 150–160 °C until the liquid evaporated out. The green fluffy powder was heated for 1 h before calcination. The tartaric acid template helps in forming heterometallic polynuclear polymeric arrays where metal ions come in close proximity to yield phase pure BiFeO\(_3\) after \textit{in situ} oxidation. If oxalic acid is used as a template, it forms Bi-ferrioxalate precursor which undergoes decomposition in the presence of oxidizing agent such as HNO\(_3\). In this case too, heteronuclear polymeric array, with metal ions, forms. Other organic acids such as citric acid do not give rise to such phase pure BiFeO\(_3\) as it tends to form dimeric chain instead of polynuclear polymeric chain. It appears, therefore, that the formation of heteronuclear polymeric arrangement prior to oxidation is the key to the formation of phase pure BiFeO\(_3\). The as-prepared powders were calcined at 400–700 °C and the bulk samples were...
sintered at ~820 °C for 10 h. Both the bulk and nanoscale samples were characterized by XRD and scanning electron microscopy (SEM) studies. In addition, the nanoparticles have been studied by transmission electron microscopy (TEM). The specific surface area of the nanoparticles has also been measured. Further details of the sample preparation and the results of the characterization are available elsewhere.\textsuperscript{18,19} The crystallite size of the nanoscale systems could be estimated from x-ray peak broadening by Debye-Scherrer equation using the full width at half maximum (FWHM) data. The particle sizes could be estimated from Brunauer-Emmett-Teller (BET) specific surface area data as well as directly from TEM photographs. A representative TEM photograph for nanoscale BiFeO\textsubscript{3} together with selected area electron diffraction pattern is shown in Fig. 1.

The thermal and magnetic measurements have been carried out on powder samples while electrical measurements have been carried out on sintered pellets. The DSC study has been carried out in Perkin-Elmer Diamond DSC over a temperature range of 300–800 K while the DTA measurements were carried out in Shimadzu DTA-50. The heating rate was 10 °C/min in all the cases. The thermal expansion has been measured in Orton dilatometer (model 1600). The low-frequency (10 Hz–1 MHz) dielectric measurements have been carried out in an LCR meter (Hioki hi-tester 3652-50). The electrodes have been prepared by silver coating and the coating was cured at ~600 °C in air.

The magnetic measurements have been carried out in a superconducting quantum interference device (SQUID) magnetometer [magnetic property measurement system (MPMS)] of Quantum Design. The zero-field cooled (ZFC) and field cooled (FC) magnetization versus temperature patterns have been studied across a temperature range of 2–300 K while magnetic hysteresis loops over ±10,000 Oe have been recorded at several temperatures. We also carried out magnetic relaxation measurements at ~5 and ~300 K under ~100 and ~10,000 Oe for both bulk and nanoscale samples.

**III. RESULTS AND DISCUSSION**

**A. Thermal studies**

In Fig. 2(a), we show the specific heat \(C_p\) vs temperature patterns—extracted from DSC and DTA data—for both bulk and nanoscale BiFeO\textsubscript{3}. The specific heat is found to be increasing as a function of particle size. This could be because of decrease in surface area to volume ratio and consequent local structural rearrangement with the increase in particle size. A small yet sharp peak—signifying first order transition—could be noticed at ~653 K \((T_N)\) in the case of bulk sample. In the inset of Fig. 2(a), we show the \((C_p/T)\) versus temperature \((T)\) plot of the region around the peak for the bulk sample. The change in entropy \(\Delta S = \int (C_p/T)\,dT\) is estimated to be ~0.0612 J/g K. In Fig. 2(b), we show the thermal expansion data for the bulk sample. The phase transition feature is clearly evident near \(T_N\).

Apart from the rise in specific heat with the increase in particle size, one can also notice a variation in the phase transition feature with the particle size. For finer particles, a very broad feature—spanning nearly 200 K—appears while with the increase in particle size (>50 nm), the broadness reduces a bit, and the feature near \(T_N\) becomes more prominent. The absence of a sharp peak clearly points out local inhomogeneity and broad phase transition across a wide temperature range. Although, such broad feature could be observed in bulk samples as well, simultaneous presence of sharp peak highlights more ordering in bulk sample. It is to be noted in this context that no structural phase transition is noticed across \(T_N\) in BiFeO\textsubscript{3}.\textsuperscript{20} Our high temperature XRD study too does not depict any structural transition at \(T_N\). The magnetic phase transition at \(T_N\), of course, is associated with colossal phonon anomaly as well as anomaly in dielectric

![FIG. 2. (a) The specific heat \((C_p)\) vs temperature \((T)\) plots for the bulk and nanoscale BiFeO\textsubscript{3}; inset: \((C_p/T)\) vs temperature for the bulk sample around \(T_N\); (b) the thermal expansion vs temperature plot for the bulk BiFeO\textsubscript{3} sample. The variation of thermal expansion coefficient \((\alpha)\) with temperature is also shown.](image-url)
response due to magnetoelectric effect. Finite latent heat and change in thermal expansion coefficient as observed in this work could be due to strong spin-phonon coupling.

The nanocrystalline samples contain primarily inhomogeneous phases where lattice defects, oxygen nonstoichiometry, etc., appear to be sizable. In addition, lattice strain is also high in nanocrystalline system. The combined effect has given rise to even smaller scale of homogeneity in nanosystem. Such inhomogeneity together with increased surface to volume ratio in nanosized particles could give rise to suppression of antiferromagnetic order especially for 11 nm particles. As a result, at least in global calorimetry, no clear endothermic peak could be observed. In the absence of a sharp peak in nanocrystalline samples, it is difficult to identify the phase transition temperature and its shift as a function of particle size. Of course, for a particle size range of 20–50 nm, Chattopadhyay et al. have observed decrease in $T_N$ down to $\sim 603$ K.

B. Electrical studies

In Fig. 3, we show the real part of the dielectric permittivity versus temperature for the bulk BiFeO$_3$ sample. It appears that there are two dielectric anomalies across a temperature range $\Delta T \sim 100$ K.

FIG. 3. The real part of the dielectric permittivity vs temperature for the bulk BiFeO$_3$ sample. It appears that there are two dielectric anomalies across a temperature range $\Delta T \sim 100$ K.

FIG. 4. The real and imaginary impedances vs frequency plot at several temperatures for the bulk BiFeO$_3$.

FIG. 5. (Color online) The dielectric loss spectra at different temperatures for the bulk BiFeO$_3$.
these data and analyses, it can be established that inhomogeneity, even in the bulk BiFeO₃ sample, leads to broadening of the transition at $T_N$.

We now turn to the dielectric relaxation process and estimation of relaxation time in bulk BiFeO₃. It has been observed in the impedance or dielectric loss spectra that the relaxation process here is essentially non-Debye; the full width at half maximum for the relaxation peaks is always higher than 1.144 decade, which is expected in Debye relaxation model. In such a relaxation process, one expects a spectrum of relaxation times with three prominent modes $\tau_{Z}$, $\tau_{e}$, and $\tau_{M}$, where $\tau_{Z}$, $\tau_{e}$, and $\tau_{M}$ are the average relaxation times estimated from impedance, dielectric, and modulus spectra, respectively. It is generally observed that $\tau_{Z} \approx \tau_{e} \approx \tau_{M}$. The elements such as resistance ($R$) and capacitance ($C$) become inherently frequency dependent. The exponent of the frequency dependence of these parameters can be extracted from the analysis of depression of the center of semicircle below the abscissa in complex-plane impedance spectra plot (Fig. 6). The estimated frequency dependence of $R$ and $C$ helps in collapsing the relaxation peaks in impedance, dielectric, and modulus spectra onto a single peak frequency. Of course, in the case of Debye relaxation with dielectric relaxation strength $\Delta \varepsilon = 0$, one observes convergence of these three relaxation time scales. Rigorous derivation of $\tau_{Z}$, $\tau_{e}$, and $\tau_{M}$ and their correlation under different conditions—Debye and non-Debye—are available in Ref. 24. Detailed study on correlation among inhomogeneity, wider transition range ($\Delta T$), and dielectric relaxation process for a series of bulk BiFeO₃ will be reported elsewhere. For the present case, we have analyzed the impedance as well as dielectric loss spectra in order to figure out the relaxation time scales. The intrinsic relaxation time scales $\tau_{Z}$ and $\tau_{e}$ are plotted as a function of temperature ($T$) in Fig. 8. Since $\tau_{e}$ becomes smaller than the frequency window used in this work beyond $\approx 473$ K, we could not estimate $\tau_{e}$ across $T_{N}$. A broad anomaly quite akin to that observed in the case of $\varepsilon'(\omega, T)$ vs $T$ (Fig. 3), however, is observed in the case of $\tau_{Z}$ vs $T$ pattern. Below the anomaly at $T_{O}$, the $\tau_{Z}$ vs $T$ pattern turns out to be nearly Arrhenius while above the anomaly too, the pattern appears to be Arrhenius. In the inset of Fig. 8 we show the natural log of four-probe dc resistivity vs $1/T$ pattern. The activation energies from both $\tau_{Z}$, $1/T$ and resistivity vs $1/T$ patterns have been calculated. While the activation energies, calculated from resistivity data, turn out to be $\approx 0.88$ and 0.19 eV at below $T_{O}$ and above, they are 0.46 and 0.9 eV over the same temperature ranges when estimated from relaxation time scale vs temperature data. The difference in the values of the activation energies, calculated from resistivity and relaxation time data, signifies that the mechanism of relaxation of the electric polarization is different from simple polaron hopping. Dielectric relaxation is taking place through a complicated and correlated process of local structural rearrangement along with hopping of charge carriers.

Therefore, the overall dielectric response appears to be consisting of both interface and intrinsic polarization components. Clear dielectric anomaly could be observed near $T_{N}$ due to magnetoelectric effect in BiFeO₃. However, the transition region becomes broad, spanning over a temperature range $\Delta T$, due to inhomogeneity and/or oxygen nonstoichi-
mometry. Because of such inhomogeneity, a spectrum of relaxation times with $\tau_2 < \tau_c$ could be noticed in the present case. The inhomogeneity results from volatility of Bi near the processing temperature of 820–850 °C and/or oxygen nonstoichiometry inherent in the complicated crystal chemistry of BiFeO$_3$. In fact, the polarization ($P$) vs field ($E$) loop in the case of pure BiFeO$_3$ appears to reflect the lossy nature. The inhomogeneity results in smaller ferroelectric domains with faster relaxation dynamics. It would have been interesting to study the relaxation dynamics and transition point in nanoscale system where the scale of inhomogeneity is higher and the homogeneous cluster size is small. Since sintering leads to growth of nanograins into micron size, no electrical measurement could be done on nanocrystalline samples.

C. Magnetic studies

We have measured ZFC and FC magnetizations versus temperature patterns under different fields as well as hysteresis loops at several temperatures across a range of 2–300 K. The magnetic relaxation pattern has also been observed at different temperatures and under different fields. In Fig. 9, we show the ZFC and FC magnetizations versus temperature patterns for both the bulk and nanocrystalline BiFeO$_3$. The bulk system exhibits antiferromagnetic order below $T_N \sim 643$ K. Therefore, we could not study the magnetization across the transition point. The magnetization at $\sim 2$ K is found to be $\sim 0.016 \mu_B$/Fe atom under $\sim 100$ Oe and $\sim 1.5 \mu_B$/Fe atom under $\sim 10,000$ Oe for the bulk sample. It drops down to $\sim 0.008 \mu_B$/Fe atom and $0.7 \mu_B$/Fe atom, respectively at $\sim 300$ K. On the other hand, for nanoscale sample, the low temperature magnetization (at $\sim 2$ K) is found to be nearly equal to what has been observed in the case of bulk sample. But, at $\sim 300$ K, the magnetization is higher by a factor of 2. For high spin ($S = 5/2$) Fe$^{3+}$ ions, the effective magnetization should be $\sim 5.92 \mu_B$. Therefore, it appears that the spin configuration per Fe ion is far from parallel. There are several other important points worthy of noting in the magnetization versus temperature data: (i) no divergence between ZFC and FC data in the case of the bulk sample; (ii) the magnetization changes with magnetic field; (iii) in the case of nanoscale sample, the ZFC and FC magnetization data diverge below $\sim 100$ K; (iv) in all the cases—bulk and nano—the magnetization rises with decrease in temperature; (v) the temperature below which the magnetization starts rising is $\sim 50$ K for the bulk sample and $\sim 10$ K for the nanoscale sample. The sharp rise in magnetization below $\sim 50$ K, in bulk sample, could result from free Fe ions. In the absence of high temperature magnetization data above $T_N$, this Curie-Weiss paramagnetism due to free Fe ions could not be quantitatively estimated. Interestingly, in the case of bulk sample an anomaly near $65$ K could be observed in the low-field ZFC data. The FC as well as high-field data, of course, do not depict any such anomaly. This seems to be because of an impurity phase Bi$_2$Fe$_3$O$_9$. Of course, such a phase could not be detected in x-ray diffraction pattern. The absence of the peak in FC data signifies metastability of that phase under field. The nanoparticles of the BiFeO$_3$ do not depict any anomaly around $\sim 65$ K.

Because of stable antiferromagnetic order within the temperature range of 2–300 K, no divergence between ZFC and FC magnetization versus temperature plots could be noticed in the case of bulk sample. The nanoscale sample, on the other hand, exhibits divergence between ZFC and FC magnetization data below $\sim 100$ K, which could be due to the onset of spin glass state. The magnetization at any temperature, within this regime, depends on history effect—the path followed for reaching the point. The ZFC data exhibit a broad cusplike feature below $\sim 100$ K which is typical of nanoscale antiferromagnetic system. 26

In Figs. 10 and 11 we show the hysteresis loops for bulk and nanoparticle systems. For the bulk BiFeO$_3$ sample, the hysteresis loops at several temperatures exhibit patterns typical of an antiferromagnetic system with no hysteresis and nearly zero coercivity. Small diamagnetic component ob-
served in the hysteresis data at very low field is due to the contribution from the sample holder. It becomes prominent in the case of antiferromagnetic sample with very small magnetic moment. The nanoparticle system, on the other hand, exhibits sizable hysteresis and finite coercivity below ~100 K. In fact, one can easily notice a deviation from linearity and formation of a ferromagnetic loop at a lower field. The coercivity at ~5 K is found to be ~450 Oe. An observation of such high coercivity in nanoscale BiFeO$_3$ is quite significant. This could be because of lattice strain-induced spin canting or ferromagnetism in nanoscale. It has been reported earlier that lattice strain in thin film gives rise to higher magnetism ($\sim 1\mu_B/\text{Fe}$). The observation of higher coercivity in nanoscale may help in finding a way for improving magnetization in BiFeO$_3$, which, in turn, will lead to many applications.

In order to find out the stability of the magnetic phases—both at low temperature (~5 K) and room temperature (~300 K)—in the nanoparticle vis-à-vis bulk system, we measured the magnetic relaxation pattern over a time scale of ~36,000 s. The relaxation patterns are shown in Fig. 12. In all the cases of the relaxation measurements, the zero-field cooling protocol has been used. The temperature of the sample is set at the desired point under zero magnetic field. Once the temperature is reached, the field is applied and the relaxation of the magnetic moment is measured over a time scale of ~36,000 s without switching off the applied field. The amount of variation in initial magnetization ($M_0$) with time ($t$) varies with temperature, applied field, and sample type—bulk or nanoparticle systems. The initial magnetization decreases with time in the case of low field (~100 Oe) while it increases with time in the case of higher field (~10,000 Oe). In all the cases, however, the pattern of variation is logarithmic in nature where the magnetization at any time $t$ follows $M(t,T) = M_0(T) ± S(T)\ln(t/\tau_m)$ equation; $S$ is magnetic viscosity and is related to the activation energy, and $\tau_m$ is a characteristic time scale. This is a typical flux-creep pattern. The extent of relaxation in the bulk system is negligible at low temperature and is very small (~0.53%) at

![Graphs of magnetic hysteresis loops at different temperatures](image)
high temperature highlighting the stability of the phase. The nanoparticle system, of course, exhibits large relaxation ($\sim 0.61\%$) at low temperature and nearly an order of magnitude higher relaxation ($\sim 3.7\%$) than that of the bulk system at high temperature. The high-field relaxation patterns depict a rise in magnetization. This could be due to metastability in the system. The activation energies are found to be varying over $\sim 0.08–0.25$ eV with field ($100–10,000$ Oe) at $\sim 5$ K and over $1.4–10.0$ eV at $\sim 300$ K. In bulk sample, of course, the variation in the magnetization is very small both at $\sim 5$ and $\sim 300$ K. The activation energies for the bulk systems are found to be enormous—of the order of $\sim 10^4$ eV—reflecting the stability of the magnetic phases.

These results point out that a magnetic state with a higher magnetization and a finite coercivity develop in the case of nanoscale samples. Of course, the magnetic state is metastable with lower activation energy and higher relaxation rate. The metastability is possibly due to spin frustration in nanoscale.

IV. SUMMARY

In summary, we have studied the phase transition near $T_N$ as a function of particle size in multiferroic BiFeO$_3$ system by employing calorimetry, dielectric, and temperature dependent x-ray diffraction studies. Because of inhomogeneity, the phase transition at $T_N$ is found to become broader—both in bulk and in nanoscale samples. The inhomogeneity possibly arises from volatility of Bi near the processing temperature as well as susceptibility of the lattice structure for developing oxygen nonstoichiometry. Such broader transition gives rise to two anomalies in dielectric permittivity across a range $\Delta T$ in the case of bulk sample. The magnetization versus temperature data depict a rise in magnetization at lower temperature for both the cases while an onset of spin glass state in the case of nanoscale sample below $\sim 100$ K. The magnetization in the latter case relaxes at a faster rate and yields lower activation energy. One interesting observation is the ferromagnetism and finite coercivity at lower temperature ($<100$ K) in nanoscale, which possibly results from
enhanced lattice strain. This result points out that suitable design of BiFeO$_3$ particles—size and shape—can improve the magnetization of the system.

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