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Anomaly in structural noncentrosymmetry around T_N in bulk and nanoscale BiFeO$_3$

Sudipta Goswami,[1] Dipten Bhattacharya,[1] Gail N. Iles,[2] Barnali Ghosh,[3] Anastasiia
A. Prytuliak,[4] Benoit Malard,[4] Gopes C. Das,[5] B. Ouladdiaf,[6] and T. Chatterji[6]

[1] *Nanostructured Materials Division, CSIR-Central Glass and Ceramic Research Institute, Kolkata 700032, India*
[2] *Helmholtz-Zentrum Berlin, Berlin, Germany*
[3] *Department of Materials Science, S.N. Bose National Center for Basic Sciences, Kolkata 700098, India*
[4] *European Space Agency, Institut Laue-Langevin, B.P. 156, 38042 Grenoble, France*
[5] *School of Materials Science, Jadavpur University, Kolkata 700032, India*
[6] *Science Division, Institut Laue-Langevin, B.P. 156, Grenoble 38042, France*

Using high resolution powder neutron diffraction data, we show that there is a distinct anomaly in the structural noncentrosymmetry around the magnetic transition point T_N for bulk and nanoscale BiFeO$_3$. It appears that the structural noncentrosymmetry - which gives rise to the ferroelectric polarization - is suppressed by ∼1% in bulk sample and by ∼12% in the nanoscale sample at the onset of magnetic order. This observation shows that the multiferroic coupling improves in nanoscale sample which is expected to brighten the application prospect of nanoscale BiFeO$_3$ in nanospintronics based sensor devices.

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In recent times, clear evidence of strong multiferroic coupling at room temperature has been observed in a single crystal of BiFeO$_3$ in a seminal work.[1] However, whether the ferroelectric order and multiferroic coupling survive in nanoscale system or not has not been clearly determined. The results available in the literature are controversial. While direct determination of ferroelectric domain structure and its switching by piezoforce microscopy (PFM) offers a strong evidence of presence of ferroelectric order in a thin film of just ∼2 nm thickness,[2] results of synchrotron x-ray diffraction, on the other hand, show melting of Bi-sublattice even at a size limit of ∼18 nm.[3] Likewise, while powder neutron diffraction under 5T magnetic field at room temperature yields an evidence of suppression of polarization by ∼7%,[4] x-ray diffraction on a sample of comparable particle size does not show any clear signature of multiferroic coupling.[5] Therefore, a careful experiment appears to be essential in establishing the survival of ferroelectric order and multiferroic coupling in nanoscale BiFeO$_3$. In this paper, we show, with the help of systematic laboratory x-ray, synchrotron x-ray, and powder neutron diffraction data, that indeed multiferroic coupling survives and even improves in the nanoscale BiFeO$_3$. We report our observation of clear anomaly in structural noncentrosymmetry around the magnetic transition point T_N for both bulk and nanoscale BiFeO$_3$. The extent of anomaly increases in the nanoscale.

The precursor powder for bulk and nanoscale BiFeO$_3$ has been synthesized by solution chemistry route.[6] The powder was compacted and sintered at 830°C for 5h for preparing the bulk sample. The nanosized particles were synthesized by heat-treatment at 450°C for 2h. The samples have been characterized by laboratory x-ray diffraction, scanning electron and transmission electron microscopy. The representative SEM image of the bulk sample is shown in Fig.1a while the TEM image for the nano-

sized particles are shown in Fig.1b. The high-resolution TEM image shown in Fig.1c shows the nanosized particles to be single crystalline. The magnetic measurement has been carried out across 300-800 K in order to determine the magnetic transition points T_N of the samples. In Fig. 2, we show the magnetization versus temperature plot. The T_N appears to have dropped down from ∼625 K in bulk to ∼575 K in nanoscale particles. The transition width, of course, has increased from ∼50 K in bulk sample to ∼150 K in nano sample. The broadening of the transition zone results from distribution in the particle size. In order to determine the multiferroic coupling in these samples, laboratory x-ray, synchrotron x-ray, and powder neutron diffraction patterns have been recorded at several temperatures across the respective T_Ns. The synchrotron data have been collected at the ID31 beamline of ESRF, Grenoble while the powder neutron diffraction data were recorded at the E9 diffractometer of HZB, Berlin.

For determining the accuracy of atom positions, especially of lighter atoms such as oxygen, estimated from the laboratory and synchrotron x-ray data with respect to that determined from the powder neutron diffraction data, we compared the oxygen positions obtained from these experiments for the bulk BiFeO$_3$. In the supplementary document, we provide the patterns and their refinements as well as the atom positions obtained from the refinement.[7] The results of the refinement are given in Table-I of the supplementary document. The comparison of the oxygen position - obtained from three different experiments - shows that while O_x and O_z positions determined from synchrotron x-ray and neutron diffraction data are comparable within ∼0.5%, the laboratory x-ray data yield a result which differs by ∼2-3%. Interestingly, in the case of O_y position, both the laboratory and synchrotron x-ray data yield results comparable within ∼0.5% while result obtained from neutron diffrac-
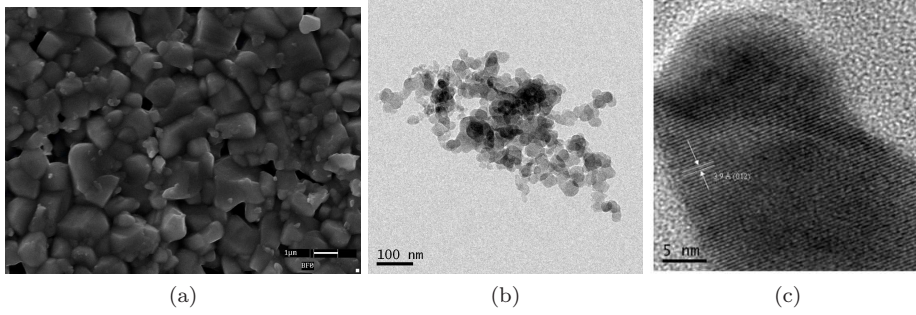
FIG. 1: (color online) (a) The scanning electron microscopic image of the bulk sintered pellet of $BiFeO_3$; the average grain size ~ 0.5 μm; (b) the transmission electron microscopic image of nanoscale particles of BiFeO3; (c) the high resolution transmission electron microscopic image of a nano-sized particle of $BiFeO_3$; the particles are single crystalline with (012) planes perpendicular to beam direction.
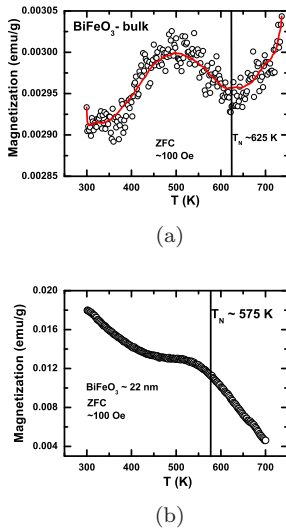

FIG. 2: (color online) (a) The magnetization versus temperature plot for bulk $BiFeO_3$; T_N turns out to be ~ 625 K with transition width ~ 50 K; (b) the magnetization versus temperature plot for nanosized particles (~ 22 nm) of $BiFeO_3$; T_N drops down to ~ 535 K while transition width increases to ~ 150 K.

tion differs by a staggering $\sim 20\%$. This is quite surprising. It appears that the use of laboratory x-ray and even synchrotron x-ray data for determining the position of oxygen atoms cannot lead to a correct result. We have, therefore, restricted ourselves in using powder neutron diffraction data while investigating the structural non-centrosymmetry in bulk and nanoscale $BiFeO_3$. In Fig. 3, we show the representative powder neutron diffraction patterns at several temperatures across the T_Ns and their refinement for both bulk and nanoscale samples. The patterns could be refined by considering the space group R3c with hexagonal unit cell. The space group does not change from bulk to nanoscale. The propagation vec-

tor for the magnetic structure is (0, 0, 0) both for bulk and nanoscale samples. The refinement of the diffraction patterns yields the structural details as well as magnetic moment per Fe ion in Bohr magneton (μ_B). For the bulk sample, the magnetic moment increases from ~ 3.239 μ_B/Fe at room temperature to ~ 3.979 μ_B/Fe at T_N whereas for the nanoscale sample it is ~ 3.979 μ_B/Fe at room temperature and reaches ~ 4.143 μ_B/Fe around T_N and then drops sharply. In Fig. 4, we show the variation of the structural parameters such as lattice volume, bond length, and angle across T_Ns for both the samples. Evidently, in both the cases clear anomaly could be seen around respective T_Ns. Therefore, onset of magnetic order appears to have influenced the structural parameters significantly. This could result from magnetostrictive effect. The lattice volume depicts a mere change in slope in variation with temperature across T_N for bulk sample while a clear volume contraction could be noticed around T_N in nanoscale sample signifying first order nature of the transition in nanoscale. It is also possible to note that at any given temperature the lattice volume increases from bulk to nanoscale. And while there are two types of (Bi-O) bonds - long and short - within a unit cell for bulk sample, in nanoscale sample, one observes long and short (Fe-O) bonds. The long (Bi-O) bond shortens with the decrease in temperature below T_N and the length of the short one increases in bulk sample. Likewise, in nanoscale sample, the long (Fe-O) bond shortens while the short bond stretches with the drop in temperature below T_N. Therefore, there is an anisotropy in the striction effect both in between two types of bond as well as in between Bi-O and Fe-O bonds. When two types of bond merge into one, it depicts a drop in length both in bulk and nanoscale sample.

The off-center displacement has also been calculated by noting the center of positive and negative charges in a unit cell.[5] The plot of net off-center displacement as a function of temperature is shown in Fig. 5. *This is the central result of this paper.* For both the bulk and nanoscale samples, clear anomaly could be seen
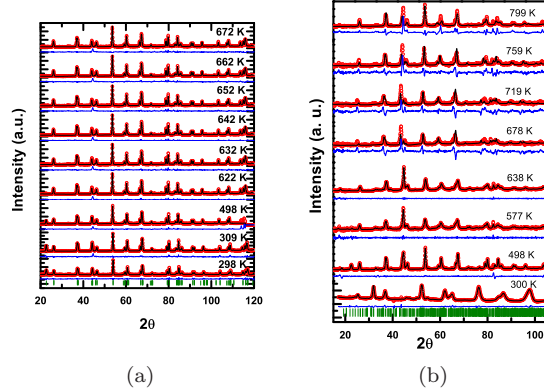
FIG. 3: (color online) The powder neutron diffraction data and their refinement at several temperatures across T_N for (a) bulk and (b) nanoscale $BiFeO_3$.
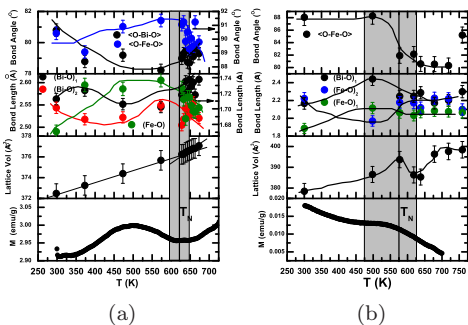

FIG. 4: (color online) The structural parameters such as lattice volume, bond lengths, and angles determined from the Rietveld refinement of the powder neutron diffraction data for (a) bulk and (b) nanoscale ($\sim$22 nm) $BiFeO_3$.

around the magnetic transition points. The off-center displacement appears to have been suppressed at the onset of magnetic order around T_N. While the extent of suppression for the bulk sample is $\sim$1%, in nanoscale sample it shoots up to $\sim$12%. Earlier x-ray diffraction data by others did not show any clear anomaly in off-center displacement around T_N even for a bulk sample.[5] Therefore, it appears that the high resolution powder neutron diffraction data are more useful in determining the position of the oxygen ions and hence the off-center displacement in a cell accurately.

Because of antiferromagnetic spin cycloid in bulk $BiFeO_3$, it was predicted that the linear multiferroic coupling could be nearly zero.[8] Indeed, the polycrystalline samples investigated in the past did not depict a strong coupling.[9] However, in a single crystal of $BiFeO_3$ one observes a very strong coupling.[1] The origin of this strong multiferroic coupling in bulk $BiFeO_3$ appears to lie in the coupling between polarization resulting from

the spin cycloid[10] and that from the polar domains. In the nanoscale sample of size smaller than 62 nm, the spin cycloid becomes incomplete and hence one should observe a weak coupling. However, it has been observed that incomplete spin spiral gives rise to a ferromagnetic component and hence larger magnetization. Large magnetization is associated with the rotation of nonferroelectric oxygen octahedra around the [111] axis via Dzyaloshinskii-Moriya exchange interaction.[11] This rotation, in turn, is coupled with the rotation of the polar domains. Therefore, enhanced magnetization could give rise to an enhanced multiferroic coupling.

Improved multiferroic coupling in nanoscale ($\sim$22 nm) $BiFeO_3$ brightens the prospect of using this system in nanospintronics-based devices. It remains to be seen, however, whether the multiferroic coupling improves further as the size is reduced or does it decrease because of fluctuations in the magnetic and ferroelectric domain structures. The optimum size limit at which one observes strong multiferroic coupling needs to be determined and is a future challenge.
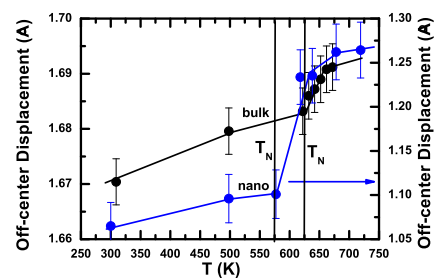

FIG. 5: The anomaly in noncentrosymmetry around T_N both for bulk and nanoscale $BiFeO_3$.

In summary, we report here that from high resolu-

tion powder neutron diffraction data, we could see clear anomaly in off-center displacement around the magnetic transition point T_N for both bulk and nanoscale ($\sim$22 nm) $BiFeO_3$. This was not observed earlier from the x-ray diffraction data. The extent of anomaly, i.e., suppression of polarization at the onset of magnetic order increases from $\sim$1% in bulk to $\sim$12% in nanoscale. The coupling between the spin cycloid driven polarization and polarization from polar domains gives rise to the multiferroicity in bulk system. In nanoscale system, on the other hand, enhanced magnetization due to suppression of spin spiral leads to an enhanced rotation of nonferroelectric oxygen octahedra around the [111] axis. This rotation, in turn, gives rise to the multiferroic coupling observed via interactions between nonferroelectric and ferroelectric domains. It remains to be seen whether the coupling improves further or not if the particle size is reduced further.

[1] D. Lebeugle, D. Colson, A. Forget, M. Viret, A.M. Bataille, and A. Gukasov, Phys. Rev. Lett. **100**, 227602 (2008).
[2] Y.-H. Chu *et al.*, Appl. Phys. Lett. **90**, 252906 (2007).
[3] V. Petkov *et al.*, Phys. Rev. Lett. **105**, 185501 (2010).
[4] S. Goswami *et al.*, Appl. Phys. Lett. **91**, 073106 (2011).
[5] S.-M. Selbach, T. Tybell, M-A. Einarsrud, and T. Grande, Adv. Mater. **20**, 3692 (2008).
[6] S. Goswami, D. Bhattacharya, and P. Choudhury, J. Appl. Phys. **109**, 07D737 (2011).
[7] Supplementary data are available at this url.
[8] C. Tabarez-Munoz, Jpn. J. Appl. Phys. **24**, 1051 (1985).
[9] Y.F. Popov *et al.*, JETP Lett. **57**, 69 (1993).
[10] M. Mostovoy, Phys. Rev. Lett. **96**, 067601 (2006).
[11] C. Ederer and N.A. Spaldin, Phys. Rev. B **71**, 060401(R) (2005).