# Melting of Bi Sublattice in Nanosized $BiFeO_3$ Perovskite by Resonant X-Ray Diffraction

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Free-standing $BiFeO_3$ perovskite particles with a size ranging from polycrystalline bulk down to 5 nm have been studied by high-energy resonant (Bi $K$ edge) x-ray diffraction coupled to differential atomic pair distribution function analysis. Nanosized $BiFeO_3$ particles are found to exhibit extra, i.e., beyond the usual thermal, structural disorder that increases progressively with diminishing their size. In particles of size smaller than approximately 18 nm the disorder destroys the structural coherence of the Bi sublattice and disturbs that of the Fe-based sublattice in the perovskite structure, substantially affecting the magnetoelectric properties it carries. The new structural information helps better understand the unusual behavior of perovskites structured at the nanoscale.

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Bulk polycrystalline oxides of the perovskite $ABO_3$ family, where $A = K$, Ca, Sr, Ba, Pb, and Bi, and $B =$ Fe, Mn, Ti, Zr, and Nb, exhibit very rich physical properties such as collinear magnetism, high-temperature superconductivity, colossal magnetoresistance, and piezoelectricity, rendering them useful in many important applications. A typical example is bulk $BiFeO_3$, in which electric ($T_c = 1100$ K), and magnetic ($T_N = 643$ K) orders coexist at room temperature allowing for manipulation of magnetism by an applied electric field and vice versa [1]. With new technologies moving quickly toward smaller scales, $ABO_3$ perovskites, including $BiFeO_3$, are increasingly produced in nanosized dimensions. Atoms in nanosized materials, however, often relax to a structure that may be quite different from that exhibited by the respective bulk [2] leading to a modification of the existing [3] or emerging of completely new [4] physical properties. Knowledge of the atomic-scale structure of nanosized $BiFeO_3$ is thus very much needed so that its properties are well understood and fully utilized. Here we report results from a structure study on freestanding $BiFeO_3$ particles with a size ranging from a few $\mu$m down to 5 nm. The study involves resonant high-energy x-ray diffraction (XRD) conducted at the $K$ absorption edge of Bi coupled to differential atomic pair distribution (PDF) function analysis. Atomic PDFs have proven to be very efficient in determining the atomic-scale structure of nanosized materials [5]. High-energy resonant XRD adds chemical specificity [6] which can be invaluable in case of multicomponent materials such as perovskites. We find that nanosized $BiFeO_3$, like other nanosized $ABO_3$ perovskites [7], exhibits extra, i.e., beyond the usual thermal, structural disorder. This extra disorder, however, affects the Bi- and Fe-based sublattices of the underlying perovskite structure and, hence, the electric and magnetic order they carry, respectively, to different extents opening new avenues for nanosized $BiFeO_3$ applications.

Bulk polycrystalline (i.e., $\mu$m-sized particles) $BiFeO_3$ studied here was prepared by a traditional solid-state reaction of $Bi_2O_3$ and $Fe_2O_3$ at 1100 K. Nanosized $BiFeO_3$ particles were prepared by a modified Pechini method using nitrates as metal precursors [8]. Standard XRD, TEM and DSC studies showed that thus obtained very fine powders are phase pure perovskite particles with sizes ranging from 5 to 100 nm, respectively. More details of the sample purity, particle size and average crystal structure determination by in-house XRD can be found in [9].

As prepared polycrystalline and nanosized $BiFeO_3$ particles sandwiched between Kapton foils were subjected to high-energy XRD experiments at the beam line 1-ID at the Advanced Photon Source, Argonne National Laboratory. The experiments were done with x-rays of energy 90.490 keV and 90.190 keV, i.e., 32 eV and 332 eV below the $K$ absorption edge of Bi. By taking the difference of XRD data sets obtained at these two energies the so-called Bi-differential structure functions for each of the samples were obtained. Those are shown in Fig. 1. Their Fourier transforms, the so-called Bi-differential atomic PDFs, are shown in Fig. 2. They reflect only Bi atoms involving correlations, i.e., Bi-Bi, Bi-Fe and Bi-O correlations, in the $BiFeO_3$ samples studied. More details of high-energy resonant XRD experimental procedures and differential atomic PDFs derivation can be found in our recent work [6].

Bi-differential PDFs were obtained and used in the present study for the following reason: bulk $ABO_3$ perovskite may be viewed as a network of corner-sharing B-$O_6$ octahedra with $A$-type atoms occupying the network channels. When the octahedra are perfect and the $A$-type atoms are exactly at the center of the network channels, as shown in Fig. 3 (left), the atomic-scale structure of the bulk perovskite is centrosymmetric. The material then does not show spontaneous polarization. When the B-$O_6$ octahedra are deformed and/or the $A$ atoms displaced from the

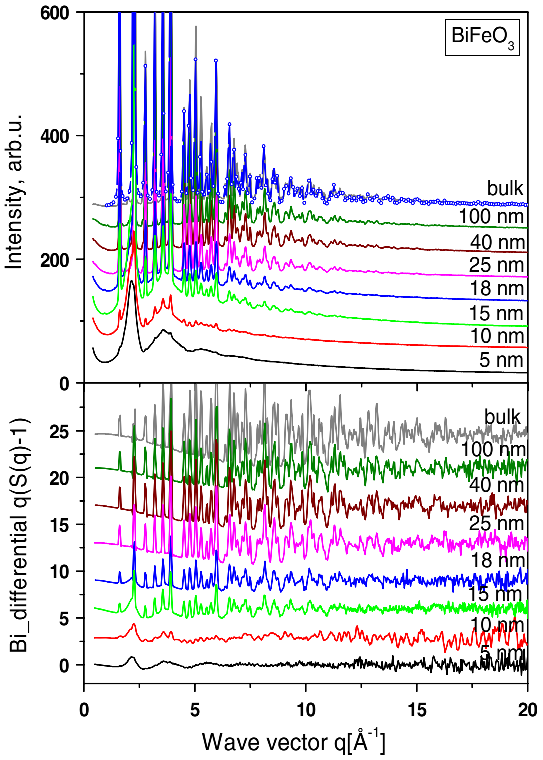

FIG. 1 (color online). Experimental XRD patterns (upper part) and Bi-differential structure functions (lower part) for bulk and nanosized $BiFeO_3$ particles. A model XRD pattern computed from the $R3c$-type structure of $BiFeO_3$ crystal is given as well (symbols in blue, upper part). It fits all peaks in the experimental XRD pattern for bulk $BiFO_3$ confirming that the sample is single phase. The XRD patterns for the nanosized samples are identical to that of bulk $BiFeO_3$ except for the gradual broadening of the respective Bragg peaks confirming that those samples too are single phase perovskites.

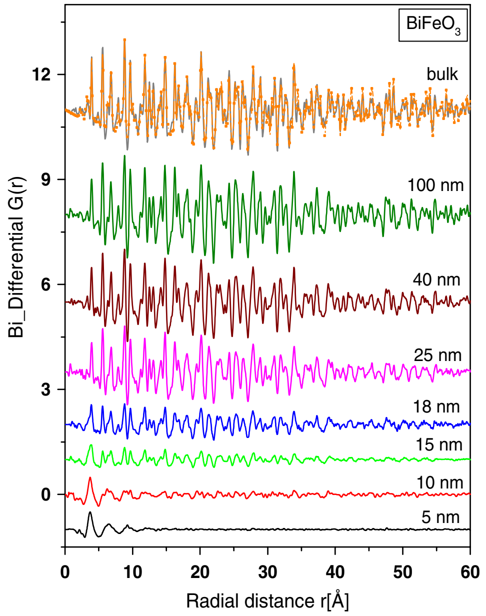

FIG. 2 (color online). Experimental Bi-differential atomic PDFs $G(r)$ for bulk and nanosized $BiFeO_3$ (solid line). A model Bi-differential PDF computed from the $R3c$-type structure of $BiFeO_3$ crystal is given as well (symbols). It reproduces the experimental data for bulk $BiFO_3$ very well. Note even in the smallest size sample the length of structural coherence extends well beyound distances of 1 nm showing the nanocrystalline nature of the material. Only when this length drops below 1 nm a material may be considered to be in an amorphous state.

centers of the network channels, as shown in Fig. 3 (right), the centers of the positive and negative charge carried by the metal ($A/B$-type atoms) and oxygen atoms, respectively, do not coincide. The material then can show spontaneous polarization, i.e., become ferroelectric. Studies have shown that the net polarization in bulk $BiFeO_3$ and, hence, its ferroelectricity, is predominantly due to the cooperative displacement of $A$ type, i.e., Bi atoms off the center of perovskite network channels [10]. The $B$ type, i.e., Fe atoms have a limited effect on the ferroelecticity [11] but are solely responsible for the magnetic order in $BiFeO_3$ [10]. The relative positioning of Bi- and Fe-based sublattices, i.e., Bi-Fe interatomic distances, in $BiFeO_3$ is thus a very precise indicator of its technologically important ferroelectric behavior. Interatomic distances can be computed from structure models obtained by traditional XRD. The very diffuse nature of the XRD patterns of nanosized $BiFeO_3$ particles (see Fig. 1, upper part), however, renders traditional XRD impossible. On the other hand, structure functions take into account both the Bragg-like and diffuse components of the XRD data to high-wave vectors (see Fig. 1, lower part). Their Fourier transforms, the atomic PDFs (see Fig. 2), show well resolved peaks positioned at actual interatomic distances without any structure modeling at that. Bi-differential PDFs highlight only interatomic distances involving Bi atoms, including Bi-Fe ones, and so are used here as a direct probe of the relative positioning of Bi- and Fe-based sublattices in $BiFeO_3$, from polycrystalline bulk to the nanoscale.

As can be seen in Fig. 2 the experimental Bi-differential PDF for bulk $BiFeO_3$ exhibits a series of well-defined peaks to very high interatomic distances as it should be with a material possessing a perfectly crystalline structure. The experimental data can be reproduced very well with a model featuring the ferroelectric (S.G. $R3c$) phase (see Fig. 3; right) of bulk $BiFeO_3$ [12]. The good agreement between the experimental and model PDF data attests to the very good quality of the present experiments. Note since Bi atoms in bulk ferroelectric $BiFeO_3$ are shifted off the center of the network channels several distinct Bi-Fe first neighbor distances at 3.06, 3.25, 3.56 and 3.90 Å (see Fig. 3; right), exist in this material. They, together with the Bi-Bi first neighbor distances ( $\sim 3.95$ Å) are seen as two distinct peaks in the experimental Bi-differential PDF centered at approximately 3.25 Å and 3.95 Å (see Fig. 4). In an ideal cubic, i.e., not ferroelectric, phase of $BiFeO_3$ perovskite the Bi- and Fe-based sublattices would not be shifted with respect to each other. Accordingly, all Bi-Fe first

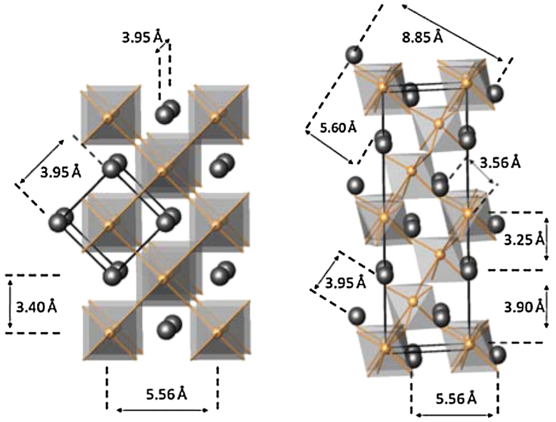

FIG. 3 (color online). Fragments from an ideal $Pm$-$3m$/cubic (left) and $R3c$/trigonal (right) type structures of bulk $BiFeO_3$. The structures feature corner shared $Fe$-$O_6$ units with Bi (black circles) atoms between them. Also shown are several Bi-involving interatomic distances occurring in the structures. Note the vertical direction of the structure fragment on the left is along $[001]_{cub}$ of the cubic lattice while that of the fragment on the right—along the $[001]_{hex}$ of the hexagonal unit cell of $R3c$. $[001]_{hex}$ is parallel to $[111]_{cub}$ of an ideal perovskite.

neighbor distances would be the same and occurring at about 3.4 Å (see Fig. 3; left).

The experimental Bi-differential PDFs for nanosized $BiFeO_3$ also show a series of well-defined peaks but those peaks become increasingly broader with the decrease in particles size, signaling an increasing local structural disorder. The disorder is strong, reducing the length of structural coherence in the nanosized $BiFeO_3$ studied, which is measured by the real-space distance at which the experimental PDFs decay to zero, to distances substantially shorter than the average nanoparticles size (see Fig. 2). A very similar effect has been observed in other nanosized perovskites such as $BaTiO_3$ [7], semiconductor quantum dots [13] and metallic nanoparticles [2]. The effects is universal and often stronger than the usual thermal disorder [7]. It is seen as an extra increase in the root-mean-square (rms) fluctuations of atomic positions when the physical size of a system is gradually reduced to the nanoscale.

A careful analysis of the experimental Bi-differential PDFs, however, shows that though universal the loss of structural coherence in nanosized $BiFeO_3$ is not quite uniform. In particular, with the decrease in particles size the PDF peaks at 3.95, 5.56, 8.85, and 14.8 Å smear out at a much faster rate than those at 6.3 and 10.5 Å. The former PDF peaks presumably reflect Bi-Bi and the latter—Bi-Fe interatomic correlations. As can be seen in Fig. 3 (right) those correlations are between first and more distant Bi-(Bi/Fe) neighbors across a range of directions in the perovskite structure. Obviously the extra rms fluctuations of Bi atoms are larger than those of Fe atoms and so Bi-Bi correlations weakened faster than Bi-Fe ones. Also, the weakening does not occur along a particular direction but, like a melting process, spreads over all sites and directions of the Bi-sublattice in nanosized $BiFeO_3$.

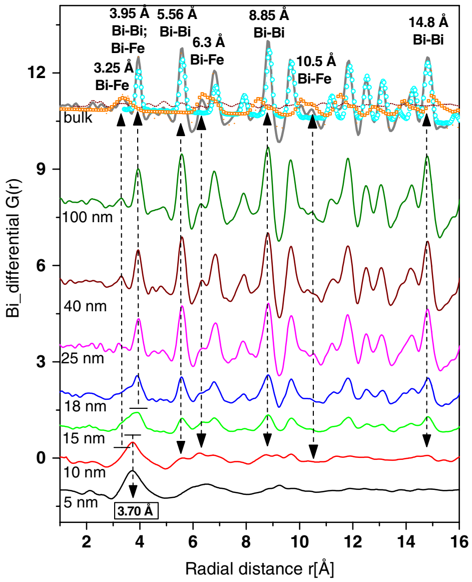

FIG. 4 (color online). Low-$r$ part of the experimental Bi differential $G(r)s$ (full line) for bulk and nanosized $BiFeO_3$. Bi-O (broken line), Bi-Fe (full symbols/brown) and Bi-Bi (open symbols/cyan) partial $G(r)s$ computed from the $R3c$-type structure of $BiFeO_3$ crystal are given as well. Several PDFs peaks (marked with arrows) are labeled with the respective atomic pair distances.

For particles of size smaller than 18 nm the "melting" of Bi-sublattice seems to be complete as manifested by the disappearance of the respective peaks in the experimental Bi-differential PDF (see Fig. 4). Especially notable is the disappearance of the distinct Bi-Fe and Bi-Bi first neighbor coordination spheres occurring at 3.25 Å and 3.95 Å in bulk $BiFeO_3$. All Bi-Bi/Fe first neighbor distances are seen to merge into a single and very broad coordination sphere centered at about 3.7 Å. Since Bi- and Fe-based sublattices are not anymore displaced in a distinctive way cooperative phenomena involving both sublattices, such as ferroelectric order, could hardly exist in $BiFeO_3$ nanoparticles of size smaller than approximately 18 nm.

Independent Raman studies have also indicated that cooperative lattice vibrations involving Bi atoms that control the ferrolectric behavior of $BiFeO_3$ are strongly quenched when the material is nanosized [14]. On the other hand, since the Fe-based sublattice, although also subject to increased disorder, survives in nanosized $BiFeO_3$ [15] it still can host cooperative phenomena, which is indeed the case. Studies [9,15] have shown that the magnetic order is weakened (e.g., compare $T_N = 620$ K in 10 nm particles with $T_N = 640$ K in bulk $BiFeO_3$) and highly frustrated [14] but survives in nanosized $BiFeO_3$. Note, amorphous $BiFeO_3$, where the Fe-based sublattice may be considered to be as highly disorganized as the Bi-based one, exhibits magnetic behavior [16] substantially different from that seen in nanosized $BeFeO_3$ [14].

What emerges from this and previous studies [7,9,17] on nanosized $ABO_3$ perovskites ($A =$ Bi, Ba; $B =$ Fe, Ti) is that finite nanosize effects gradually weaken their ferroelectricity to a point where it disappears as a measurable cooperative property. There are, however, notable differences in the way this happens in different $ABO_3$ perovskites. Ferroelectricity in $BaTiO_3$ is due to a tetragonal distortion of Ti-$O_6$ octahedra and those distortions are found to increase [7,17] with diminishing particles size. However, instead of being enhanced, ferroelecticity virtually disappears since the extra rms atomic fluctuations in the nanosized particles frustrate the long-range ordering between the (Ti-$O_6$)-based electric dipoles. Ferroelectricity in $BiFeO_3$ is mainly due to a cooperative displacement of Bi sublattice with respect to the Fe-based oxygen octahedra. The extra rms atomic fluctuations in the nanoparticles virtually melt the Bi-sublattice and, hence, the ferroelectric order of which it is a vital part disappears. That different $ABO_3$ perovskites react differently to the extra structural disorder emerging at the nanoscale has very much to do with their different structural stability. It is measured by the so-called tolerance factor, $t$, where $t = (r_A + r_O)/\sqrt{2}(r_B + r_O)$ and $r_{A,B}$ and $r_O$ are the ionic radii of metal ($A/B$) and oxygen atoms, respectively. The tolerance factor for the ideal cubic perovskite shown in Fig. 3 (left) is one; it is 0.96 for $BiFeO_3$ and 1.06 for $BaTiO_3$. The relatively lower structural stability of $BiFeO_3$ is due to the fact that Bi ions are somewhat small ($r_{\mathrm{Bi}} = 1.17$ Å) to fit tightly inside the perovskite network channels and, hence, are quite susceptible to structural disorder [18]. This is not the case with the larger Ba ions ($r_{\mathrm{Ba}} = 1.34$ Å) and so they remain coupled in a structurally coherent sublattice even when subjected to increased rms fluctuations.

In summary, high-energy resonant XRD and differential atomic PDFs allow us to reveal the presence of notable differences between the atomic ordering of bulk and nanosized $BiFeO_3$. The differences are based on pure experimental observations and so are unbiased toward any model considerations which is impossible to achieve with traditional XRD. In particular, results from the present study show that, at the atomic scale, freestanding nanosized $BiFeO_3$ particles may be viewed as an assembly of highly and not so disordered Bi and Fe-O sublattices of a perovskite-type structure, respectively. The Bi sublattice loses structural coherence and so becomes uncorrelated with the Fe-O one in particles of size smaller than approximately 18 nm. The picture is somewhat different from that in nanosized $BaTiO_3$ [7] where the Ba- and Ti-O sublattices of the underlying perovskite structure also suffer extra structural disorder but retain their structural integrity. Once the ground-state structure of freestanding nanoparticles is known in good detail the technologically important ferroelectric properties of $ABO_3$ perovskites are easier to understand and, hence, take control of. It is plausible to assume that by applying of external unidirectional strain, e.g., by using appropriate substrates, the frustrated but existing (Ti-$O_6$) electric dipoles in nanostructured $BaTiO_3$ can be forced to line up and exhibit cooperative ferroelectricity. Studies have shown that this exactly what happens [19]. The origin of ferroelectricity in $BiFeO_3$ does not survive in very small size particles so it is unlikely to be restored by simply applying an unidirectional strain. Such strain though, depending of its magnitude and direction (i.e., compressive or tensile), may be able to drive the "molten" Bi sublattice into other structural states, more ordered at the nanoscale, and, hence, drive the whole $BiFeO_3$ system into novel phases, existing at the nanoscale only, opening opportunities for new applications. Research to explore this scenario has begun and results achieved are very promising [20]. Another possibility to stabilize the Bi sublattice in nanosized $BiFeO_3$ is to dope it with other metal atom species [21]. The success of all these efforts depends critically on the availability of precise knowledge about the atomic-scale structure of nanosized $ABO_3$ perovskites. The present study shows that high-energy resonant XRD and differential atomic PDFs can deliver it with success.

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[1] T. Zhao *et al.*, Nature Mater. **5**, 823 (2006); D. Lebeugle *et al.*, Phys. Rev. Lett. **103**, 257601 (2009).
[2] V. Petkov *et al.*, J. Phys. Chem. C **112**, 8907 (2008).
[3] I. Naumov *et al.*, Nature (London) **432**, 737 (2004).
[4] M. D. Hudges *et al.*, Nature (London) **437**, 1132 (2005).
[5] T. Egami and S. J. L. Billinge, *Underneath the Bragg peaks* (Pergamon Press, Amsterdam, 2003).
[6] V. Petkov and S. D. Shastri, Phys. Rev. B **81**, 165428 (2010).
[7] V. Petkov *et al.*, Phys. Rev. B **78**, 054107 (2008).
[8] S. M. Selbach *et al.*, J. Am. Ceram. Soc. **90**, 2649 (2007).
[9] S. M. Selbach *et al.*, Chem. Mater. **19**, 6478 (2007).
[10] P. Ravindran *et al.*, Phys. Rev. B **74**, 224412 (2006).
[11] R. Saeterli *et al.*, Phys. Rev. B **82**, 064102 (2010).
[12] F. Kubel and H. Schmid, Acta Crystallogr. Sect. B **46**, 698 (1990).
[13] B. Gilbert *et al.*, Science **305**, 651 (2004); V. Petkov *et al.*, Phys. Rev. B **81**, 241304 (2010).
[14] T.-J. Park *et al.*, Nano Lett. **7**, 766 (2007).
[15] Note the EXAFS studies of S. Chattopadhyay *et al.*, Phys. Scr. **T115**, 709 (2005) also show that Fe-sublattice in $BiFeO_3$ disorders but does not change drastically with nanoparticle's size.
[16] S. Nakamura *et al.*, J. Appl. Phys. **74**, 5652 (1993).
[17] K. Page *et al.*, Chem. Mater. **22**, 4386 (2010).
[18] A. Palewicz *et al.*, Acta Crystallogr. Sect. B **63**, 537 (2007).
[19] K. J. Choi *et al.*, Science **306**, 1005 (2004).
[20] R. J. Zeches *et al.*, Science **326**, 977 (2009).
[21] S. M. Selbach, M.-A. Einarsrud, and T. Grande, Chem. Mater. **21**, 169 (2009).