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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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 ferroelectricity [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. $R_3c$) 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. 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 $R_3c$-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 BiFeO$_3$ 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 $R_3c$-type structure of BiFeO$_3$ crystal is given as well (symbols). It reproduces the experimental data for bulk BiFeO$_3$ 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.]
The right—along the $\frac{1}{2}$—structural coherence in the nanosized order. The disorder is strong, reducing the length of structural PDFs decay to zero, to distances substantially measured by the real-space distance at which 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 ferroelectric 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 ($A = \text{Bi, Ba}; B = \text{Fe, Ti}$) 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, ferroelectricity 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 $t = (r_A + r_O)/\sqrt{2(r_F + r_O)}$ 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 ($r_{\text{Bi}} = 1.17$ 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 ($r_{\text{Ba}} = 1.34$ 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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