Size-dependent infrared phonon modes and ferroelectric phase transition in BiFeO$_3$ nanoparticles

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One emergent property of ferroelectric nanoparticles is the sized-induced structural distortion to a high-symmetry paraelectric phase at small particle sizes. Finite length scale effects can thus be advantageously employed to elucidate ferroelectric transition mechanisms. In this work, we combine infrared spectroscopy with group theory and lattice dynamics calculations to reveal the displacive nature of the ferroelectric transition in BiFeO$_3$, a room temperature multiferroic. Systematic intensity and frequency trends in selected vibrational modes show that the paraelectric phase is $Pm\bar{3}m$ and the lowest frequency $A_1$ feature is the soft mode that drives the first order transition. Finite length scale effects are also evident in the electronic structure with a red shifted band gap in nanoscale BiFeO$_3$ compared with that of the rhombohedral film, a result that can impact the development of ferroelectric photovoltaics and oxide-based electronics. Taken together, these findings demonstrate the foundational importance of size effects for enhancing the rich functionality and broad utility of transition metal oxides.
The interplay between charge, structure, and strain gives rise to interesting cross-coupled properties in polar oxides. Robust ferroelectricity and a large polarization are, in particular, at the heart of many applications. It is well known that the ferroelectric transition is characterized by (i) a soft mode or modes, the frequency of which decreases toward zero on approach to the transition continuously (second order) or discontinuously (first order), and (ii) a displacement eigenvector similar to that in the ferroelectric phase. Direct measurements of phonon mode behavior through the ferroelectric transition thus provide crucial microscopic insight into these processes. One fascinating and potentially useful tendency of nanoscale ferroelectrics is for the size-induced structural distortion to favor the high-symmetry paraelectric phase. In polar oxide nanoparticles, the critical size for the ferroelectric to paraelectric transition varies from, for instance, 7 - 13.8 nm in PbTiO$_3$ and less than 26 - 115 nm in BaTiO$_3$, with even smaller length scales in high quality BaTiO$_3$ wires. In this work, we focus on bismuth ferrite (BiFeO$_3$), a system that has attracted enormous attention as a room temperature multiferroic with many novel properties including magnetoelectric coupling, a large remanent polarization, photovoltaic current, and potential applications in information storage, spintronics, and polar oxide-based solar cells. Despite intense study by traditional methods that employ temperature, pressure, or epitaxial strain to drive the ferroelectric to paraelectric transition in BiFeO$_3$, the mechanism is not yet clearly understood. In this work, we exploit size-dependent trends in the optical properties to reveal the nature of the ferroelectric transition. We also discover band gap tunability that may impact the development of flexible photovoltaics and oxide-based electronics.

Bulk BiFeO$_3$ is ferroelectric ($T_C \sim 1100$ K) and G-type antiferromagnetic ($T_N \sim 640$ K) at room temperature. This polar oxide is a rhombohedrally distorted perovskite with space group $R3c$. The primitive cell contains two formula units that can be described by (i) the displacement of Fe$^{3+}$ and Bi$^{3+}$ cations along the pseudocubic [111] direction, and (ii) an accompanying antiphase rotation of the neighboring FeO$_6$ octahedra. Variable temperature vibrational spectroscopy should, in principle, be ideal for driving into the high temperature paraelectric phase and elucidating the phase transition mechanism. There is, however, no
mechanistic consensus thus far\textsuperscript{20-23}, and a fresh perspective is needed. At the same time, pressure and epitaxial strain are well-known to modify the optical properties of BiFeO\textsubscript{3}\textsuperscript{24,25} and other polar oxides\textsuperscript{26}. Particle size and strain thus provide an opportunity to modulate hybridization and bonding.

In this work, we investigate the optical properties of BiFeO\textsubscript{3} as a function of particle size in order to elucidate the nature of the ferroelectric phase transition and the potential for band gap tuning to better match the solar spectrum. Size-dependent trends in the phonon response reveal cubic symmetry in the paraelectric phase and a substantial but incomplete softening of the A\textsubscript{1}(TO1) mode that points to a first order transition and displacive mechanism. Moreover, finite size effects red shift the band gap, a finding that (i) demonstrates the fundamental difference between strain from an uncompensated surface and compressive strain in an epitaxial thin film and (ii) may have important light harvesting and electronic device applications\textsuperscript{15,18,27}. More broadly, we argue that nanoscience provides a fundamentally different approach to these important scientific problems with advantages that both complement traditional physical tuning techniques and extend our understanding of complex materials\textsuperscript{28}.

Group theory predicts that BiFeO\textsubscript{3} in the R\textsubscript{3}c space group should display the following optical phonon modes:

\[ \Gamma(R3c) = 4A\textsubscript{1}^{\text{IR,R}} \oplus 9E^{\text{IR,R}} \oplus 5A\textsubscript{2}. \]

The A\textsubscript{1} and E modes are both infrared (IR) and Raman (R) active, whereas the A\textsubscript{2} modes are silent. Here, the singly-degenerate A\textsubscript{1} modes are z-directed, and the doubly-degenerate E modes are xy-plane polarized\textsuperscript{22,23}. We consider two candidate paraelectric phases\textsuperscript{29}. The first is an ideal perovskite with cubic (Pm\textbar 3m) symmetry. This paraelectric phase presents three triply-degenerate infrared active modes and one triply-degenerate silent mode\textsuperscript{22}:

\[ \Gamma(Pm\textbar 3m) = 3F^{\text{IR}}_{1u} \oplus F_{2u}. \]

The second candidate paraelectric phase has R\bar{3}c symmetry. Group theory predicts infrared-active A\textsubscript{2u} and E\textsubscript{u} features along with additional Raman-active and inactive modes:

\[ \Gamma(R\bar{3}c) = 3A^{\text{IR}}_{2u} \oplus 5E^{\text{IR}}_{u} \oplus A^{\text{R}}_{1g} \oplus 4E^{\text{R}}_{g} \oplus 3A^{2g} \oplus 2A_{1u}. \]
Clearly, the $Pm\bar{3}m$ and $R3c$ structures display very different symmetry characteristics. These differences can be used to identify the most probable paraelectric phase.

Figure 1 displays the 300 K absorption spectrum of bulk and 16 nm BiFeO$_3$. We assign the observed vibrational excitations based on previous first principles calculations and infrared reflectance results$^{21,23}$. The latter$^{21}$ were carried out on a (012)$_h$ plane single crystal in reflectance mode and revealed nine E symmetry vibrational features. As summarized in Table I, we observe eleven transverse optic (TO) vibrational modes in the spectrum of both bulk and nanoparticle BiFeO$_3$. The peaks assigned as E symmetry modes agree very well with those reported by Lobo et al.$^{21}$, and the peaks assigned as $A_1$ symmetry features are in reasonable agreement with calculated results$^{23,30}$. Striking finite length scale effects are evident in the nanoparticle response. Specifically, the $A_1$(TO1) mode red shifts by $\sim$10 cm$^{-1}$, and several E symmetry modes [E(TO1), E(TO3), E(TO7)] are strongly damped in spectrum of the 16 nm particles. With decreasing nanoparticle size, the overall spectral shape also begins to display "three band character", indicative of a size-induced approach to the paraelectric phase in small particles and in line with high temperature infrared reflectance trends$^{22}$. Taken together, these results illustrate the impact of particle size on the vibrational properties of a model polar oxide.

To understand the observed infrared activity and the consequences of that activity for the ferroelectric transition, we performed a series of lattice dynamical calculations$^{31}$. Figure 2c displays the calculated zone-center phonon mode frequencies in the ferroelectric $R3c$ phase of BiFeO$_3$ compared with those of the two candidate paraelectric phases ($Pm\bar{3}m$ and $R\bar{3}c$)$^{29}$. In order to allow structure to change smoothly from the $R3c$ rhombohedral symmetry of bulk BiFeO$_3$ to the $Pm\bar{3}m$ cubic symmetry, we use a single cubic unit cell ($a = 3.87$ Å) and calculated the zone center + zone boundary $k = (111)$ modes.$^{32}$ For the $R3c$ structure, phonon polarization analysis yields four singly-degenerate and nine doubly-degenerate infrared active modes. By comparison, the $Pm\bar{3}m$ structure generates three triply-degenerate infrared active modes, whereas the $R\bar{3}c$ structure yields three singly-degenerate and five doubly-degenerate infrared active modes (Fig. 2c). These results are consistent with the aforementioned group theory predictions, and at the same time, they provide important information on how modes in the $R3c$ phase correlate with those in other symmetry space groups. For instance, through a hypothetical $R3c \rightarrow Pm\bar{3}m$ transition, E(TO2)+$A_1$(TO1), E(TO5)+$A_1$(TO3), and E(TO9)+$A_1$(TO4) combine to form three
triply-degenerate infrared active modes, $E(\text{TO6})$ becomes inactive, and the other features develop into inactive zone boundary modes. In contrast, through a hypothetical $R3c \rightarrow R3c$ transition, four doubly-degenerate infrared active modes [$E(\text{TO3}), E(\text{TO4}), E(\text{TO6}), E(\text{TO8})$] and one singly-degenerate mode [$A_1(\text{TO4})$] become Raman active. Importantly, $E(\text{TO1}), E(\text{TO7})$ and $A_1(\text{TO2})$ modes are predicted to disappear through the ferroelectric $\rightarrow Pm\bar{3}m$ paraelectric transition but remain active through the ferroelectric $\rightarrow R\bar{3}c$ transition. Moreover, $A_1(\text{TO4})$ will remain active in the $Pm\bar{3}m$ phase but disappear in the $R\bar{3}c$ phase. These differences provides a clear test of paraelectric phase symmetry in BiFeO$_3$.

To elucidate the paraelectric phase symmetry, we investigated the intensity of the $E(\text{TO1})$ and $E(\text{TO7})$ modes as a function of particle size [Figs. 3a and c]. We find that mode intensities decrease with decreasing size, disappearing almost completely in the spectrum of the 16 nm nanoparticles. Assuming spherical particles, the size-dependent intensity can be expressed as a function of inverse crystallite diameter as

$$I(d) = A - B/d,$$

where $A$, $B$ are phenomenological constants and $d$ is the particle diameter. To quantify finite size effects on the phonon modes of BiFeO$_3$, we calculated the relative intensities of the $E(\text{TO1})$ and $E(\text{TO7})$ modes and fit the data according to equation (1) [Figs. 3b and d]. Extrapolating the curves to zero intensity, we find critical sizes ($d_c$) of 13.5 and 8.1 nm from our analysis of the $E(\text{TO1})$ and $E(\text{TO7})$ modes, respectively. These results are in good agreement with the 9 nm estimate of $d_c$ from size-dependent $c/a$ crystallographic data by Selbach et al.\textsuperscript{35}. The disappearance of $E(\text{TO1})$ and $E(\text{TO7})$ mode intensity on approach to the critical size regime combined with the presence of $A_1(\text{TO4})$ in the nanoparticle spectrum demonstrates that BiFeO$_3$ displays a rhombohedral $\rightarrow$ cubic distortion with decreasing particle size. Other mode behavior is reasonably consistent with group theory predictions. The paraelectric phase of BiFeO$_3$ could thus, in principle, be stabilized at room temperature with sufficiently small nanoparticles. Importantly, our findings rule out the $R\bar{3}c$ structure for the paraelectric phase.

Combined group theory, dynamics, and vibrational property measurements also allow us to analyze the mechanism of the ferroelectric transition. Calculated displacement eigenvectors indicate that Bi centers participate only in the three lowest frequency modes whereas O motion dominates the higher frequency structures\textsuperscript{23}. We focus on the $A_1(\text{TO1})$ vibrational
mode, a feature that is significantly softened in the spectrum of the nanoparticles [Fig. 1, Table I]. As shown in Figs. 2a and b, Bi cations move out-of-phase with respect to the FeO$_6$ octahedra along the polar direction (resulting in ferroelectricity), while the two adjacent FeO$_6$ octahedra counter rotate about the [111] axis (doubling the unit cell). Here, Fe cation displacements are fairly large, so they move off-center in the octahedra. These calculated results point toward a displacive phase transition mechanism$^{23}$ in which atomic displacement changes crystal symmetry$^1$. We can test this prediction by searching for evidence of the displacive phonon. Figure 3e displays the frequency and damping constant of the A$_1$(TO1) mode as a function of particle size. With decreasing crystalline size, this vibrational feature softens by more than 6% and dampens considerably. The systematic red shifting of the A$_1$(TO1) vibrational mode with decreasing size strongly supports its assignment as the soft mode driving the ferroelectric transition. Moreover, this A$_1$ mode is underdamped, even in the 16 nm material, suggesting a first order nature. This result is consistent with the incomplete phonon softening in high temperature infrared$^{22}$ and Raman$^{20}$ measurements.

At a first order phase transition, the soft mode frequency varies with temperature$^{36,37}$ as

$$\omega(d,T) - \omega_0(d,T_C(d)) = A|T_C(d) - T|^{\beta}. \quad (2)$$

Here, $T_C(d)$ is the Curie temperature of the nanoparticles, $\omega_0(d,T_C(d))$ is the soft mode frequency at the ferroelectric to paraelectric transition, $A$ is a constant, and $\beta \simeq \frac{1}{3}$ is the critical exponent$^{36}$. The variation of the transition temperature with particle size$^{4,5,7,10}$ is given by the empirical expression

$$T_C(d) = T_C(\infty) - B/(d - E), \quad (3)$$

where $T_C(\infty)$ is the Curie temperature of the bulk material, $d$ is the particle size, and $B$ and $E$ are constants. Inserting the expression for $T_C(d)$ from equation (3) into equation (2) and incorporating temperature into the constants, we can obtain the soft mode frequency in terms of particle size $d$ at a specific temperature as

$$\omega(d) = \omega_0 + A'|1 - B'/((d - E))|^{\beta}. \quad (4)$$

Here, $A'$ and $B'$ are modified constants, and $\omega_0$ is the soft mode frequency at the critical size. We also assume that $\omega_0[d,T_C(d)]$ in equation 2 is relatively constant across different particle sizes, a reasonable assumption since the structure of the paraelectric phase is expected to be independent of size. With the values of $\beta = 1/3$ and $\omega_0 + A' = 160.23$ cm$^{-1}$.
which is the $A_1$(TO1) mode frequency of the bulk material (when $d = \infty$), we were able to determine constants from equation (4) by a least squares fit of the experimental data yielding the result $\omega(d) = 138.55 + 21.68|1 - 40.08/(d + 32.22)|^{1/3}$. From this expression, we find $\omega_0 = 138.55$ cm$^{-1}$. Notably, this soft mode frequency at the critical size is larger than zero. It is only $\sim 16\%$ lower than that in ferroelectric phase which is a relatively small change compared with traditional ferroelectric perovskites like PbTiO$_3$, BaTiO$_3$, and SrTiO$_3$. The nonzero value of $\omega(d)$ through the transition confirms the first order mechanism, and the modest displacement of the $A_1$(TO1) mode through the size-driven ferroelectric to paraelectric transition explains why phonon softening cannot be observed in high temperature experiments, where thermal expansion and disorder dominate the softening behavior. When $\omega(d) = 138.55$ cm$^{-1}$, we can extract a critical size ($d_c = 7.86$ nm). The latter is in excellent agreement with the values obtained from E(TO1) and E(TO7) mode intensity trends (8.1 and 13.5 nm). As a length scale, the 7.86 nm critical diameter corresponds to about 20 unit cells, which shows that the structure is highly strained. Figure 3g displays the damping coefficient $\gamma$ as a function of particle size. Combining the relationship between $\gamma$ and $T_C$ with equation (3), $\gamma$ can be expressed as

$$\gamma(d) = A'|1 - B'/(d - C)|^{-3/8};$$

where $A', B', C$ are constants. This model fits the experimental data very well, as shown in the curve.

Bringing these results together, we propose that size effects in ultrafine BiFeO$_3$ particles can be understood within the soft mode picture in which cubic structure dominates below $d_c$. To obtain the distorted ferroelectric phase, one of the TO modes with $F_{1u}$ symmetry becomes soft and unstable. The important distortions consist of opposite polar displacements of Bi cations and FeO$_6$ octahedra combined with counter-rotation of adjacent FeO$_6$ octahedra around the [111] axis. As a consequence, the cubic symmetry transforms into rhombohedral. This transition is driven by the competition between short-range overlap and long-range Coulomb forces. Surface tension $\delta$ impacts the latter. It can be expressed in terms of particle diameter as

$$\delta = Pd/4,$$

where $P$ is the internal pressure. We can estimate $P$ from previous high pressure studies that show BiFeO$_3$ becomes metallic above 47 GPa. Employing a critical size
of 7.86 nm (obtained from our frequency shift analysis of the A₁(TO1) mode which is more reliable than values determined from intensity trends), we extract δ = 92 N/m. Similar results are obtained in other polar oxides such as PbTiO₃ and BaTiO₃.

The electronic properties of complex oxides provide fundamental information on chemical bonding, hybridization, and the interplay between charge, structure, and strain. Certainly, applied pressure induces electronic structure changes in BiFeO₃ through the phase transition. The consequences of surface strain induced by finite size effects are of complementary importance. Figure 4 displays the optical absorption spectrum of the 16 nm BiFeO₃ nanoparticles. Compared to the response of an epitaxially grown rhombohedral thin film, the familiar 3.2 and 4.5 eV electronic bands, assigned as minority channel dipole-allowed charge transfer excitations split into multiplets. For instance, the 3.2 eV band splits to reveal features centered at 2.9 and 3.4 eV. The splitting of these strongly hybridized O 2p to Fe 3d excitations is due to distortions of the FeO₆ octahedra that, from a local perspective, reflects the strained nature of small sized particles and reveals the diminished structural coherence at small particle sizes in conjunction with this tendency toward average cubic structure. We extract the direct band gap via a linear extrapolation of (αE)² vs. E plots to zero (inset, Fig. 4). The gap in the nanoparticles (2.43 eV) is significantly reduced compared with that in the film (2.67 eV). This is a consequence of the aforementioned splitting of the 3.2 eV charge transfer excitation due to symmetry breaking. A red shifted gap (2.5 eV) is also observed in BiFeO₃ nanowires, although tetragonal BiFeO₃ (stabilized by compressive strain) displays a larger 3.1 eV gap that is again determined by the location of the lowest energy charge transfer edge. That these are structural rather than chemical disorder-induced effects is supported by direct crystallographic studies as well as our vibrational properties work that demonstrates small BiFeO₃ particles tend toward the cubic structure. In principle, the gap of the nanomaterial can also be affected by quantum confinement (which scales as d⁻²). We do not, however, expect to observe this effect here because even the smallest particle size in this experiment (16 nm) is still too large to display quantum confinement. The long near infrared tail below 2.3 eV in optical absorption spectrum of the nanoparticles is due to scattering and reflectance contributions, artifacts that can be corrected in certain cases (epitaxial thin films, single crystals), but are difficult to quantify for a sample in powder form. Moreover, our experiments show no explicit size-dependent band gap for particles between 16 and 61 nm, indicating that the
FeO₆ local structure distortion is of similar magnitude in this size range. Recent reports of photoconductivity, a photovoltaic effect, and a 0.8-0.9 V open circuit voltage combined with 10% external quantum efficiency above the band gap in a working ferroelectric solar device illustrate the potential of polar oxides like BiFeO₃ as active photovoltaic materials¹⁵,¹⁸,²⁷. The optical response of the BiFeO₃ nanoparticles (Fig. 4) shows a smaller band gap and an improved match to the solar spectrum which translates into a broader active wavelength range in a photovoltaic device. It also illustrates the far-reaching potential of finite size effects for band gap modification of functional oxides.

To summarize, we investigated the optical properties of a model polar oxide, BiFeO₃, as a function of particle size in order to elucidate the nature of the ferroelectric phase transition and the potential for band gap tuning to better match the solar spectrum. Intensity trends in selected phonon modes reveal that the paraelectric phase is cubic, and A₁(TO1) mode softening with decreasing size points to a displacive mechanism. Moreover, finite size effects red shift the band gap, a finding that may have applications in flexible ferroelectric photovoltaic devices and oxide-based electronics. Taken together, this work reveals the importance of size effects as a complement to more traditional physical tuning via temperature, pressure, and magnetic field for understanding ferroelectricity and for exploring both existing and emergent properties of correlated oxides.

**Methods**

Single-crystalline BiFeO₃ nanoparticles were prepared by sol-gel techniques as described previously⁵⁰ and detailed in the Supplementary Information section. Particle sizes are 16 ± 4, 31 ± 15, 47 ± 10, 85 ± 21, and 215 ± 60 nm, respectively, determined from transmission electron microscopy (TEM), scanning electron microscopy, and x-ray diffraction. A typical TEM image of an individual 16 nm BiFeO₃ is shown in the inset of Fig. 1. Additional representative TEM and SEM data confirming the nanoparticulate nature of our samples are shown in Fig. S1(a) and (b) of the Supplementary Information section and in Ref. 50. The minimum size of 16 nm arises from the need to anneal to a temperature of 400°C in order to achieve sufficient crystallinity and satisfactorily remove any organic material remaining. The distribution of sizes is intrinsic to the thermal anneal process, causing a thermodynamic distribution of sizes. This effect has been previously reported in other bismuth ferrite
systems\textsuperscript{51}. The single crystalline nature of particles prepared by these methods was previously established by selected area diffraction and high resolution TEM,\textsuperscript{50} and a detailed chemical analysis points to the appropriate Bi/Fe ratio and few oxygen vacancies. Characterization details are available in Ref. 50 and the attached Supplementary Information. The nanoparticles were mixed with paraffin or KBr to form isotropic composites appropriate for transmittance experiments at 300 K. We measured the optical properties of these samples using a series of spectrometers including Bruker IFS 113v Fourier transform infrared spectrometer (20 - 5000 cm\textsuperscript{-1}) and a Perkin-Elmer Lambda-900 spectrometer (4000 - 52,670 cm\textsuperscript{-1}). Spectral resolution was 1 cm\textsuperscript{-1} in the far-infrared and 2 nm in the visible and near-ultraviolet. The absorption coefficient was obtained as $\alpha(\omega) = -\frac{1}{hd} \ln T(\omega)$, where $h$ is the loading, $d$ is the thickness, and $T(\omega)$ is the measured transmittance. While the comprehensive analysis of powdered samples in the ultraviolet-visible range presents certain inherent challenges (such as scattering, light leakage, reflectance corrections, penetration depth issues, and optical density effects that derive from large error bars on loading and effective thickness), there are many intrinsic aspects of the optical response such as peak position and band gap that can be readily and reliably extracted, even if the aforementioned effects impact the absolute value of $\alpha(E)$ or the spectral shape. Traditional peak fitting methods were employed as appropriate. Lattice dynamical calculations were performed based on a real-space summation involving a spherical cut-off boundary\textsuperscript{31} and Coulomb potential between Fe and O ions with nominal valencies.

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30 The observed $E$(TO1) and $E$(TO2) mode frequencies are $\sim25\%$ lower than the calculated values whereas $A_1$(TO4) mode frequency is $\sim12\%$ higher which may due to the anharmonicity effects$^{23}$. $E$(TO4) and $A_1$(TO2) are not identified in our experiment result which is the consequence of their strong overlap with $E$(TO3) and $E$(TO5) modes.


32 Zone center and zone boundary $k = (111)$ modes in the single cubic unit cell are equivalent to zone center modes in the 10-atom unit cell which is doubled along the [111] direction.


34 Relative intensity is defined as the fractional area of the whole spectrum needed to minimize the error bar associated with the nanoparticle size distribution and the experimental method.


42 Gavriliuk, A. G.; Struzhkin, V. V.; Lyubutin, I. S.; Ovchinnikov, S. G.; Hu, M. Y.; P. Chow,
In a traditional oscillator fit, the center frequency and trends in the center frequency are always more reliable than the line width or intensity (and trends in these quantities). Partial superposition of features impacts the latter as well.

Penetration depth is \(2/\alpha\), where \(\alpha\) is absorption coefficient. Since \(\alpha \approx 3 \cdot 10^5 \text{ cm}^{-1}\) for BiFeO\(_3\), the maximum penetration depth is \(\sim 67 \text{ nm}\).

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A PDF file describing synthesis and characterization of BiFeO\(_3\) nanoparticles is available free of charge via the Internet at http://pubs.acs.org.
Tables

TABLE I: Frequencies (cm$^{-1}$) and assignments of transverse optic (TO) phonon modes in BiFeO$_3$ using the notation of Hermet et. al. (Ref. 23). We quantify mode softening in the nanoparticles compared to the bulk material as $\Delta \omega/\omega = (\omega_{\text{bulk}} - \omega_{\text{nano}})/\omega_{\text{bulk}}$. Calculated$^{23}$ and single crystal reflectance$^{21}$ results are shown for comparison as well.

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<th>Mode</th>
<th>Calc.$^{23}$</th>
<th>Crystal$^{21}$</th>
<th>Bulk</th>
<th>16 nm</th>
<th>$\Delta \omega/\omega$(%)</th>
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<tr>
<td>E(TO1)</td>
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<td>66</td>
<td>76.4</td>
<td>77.3</td>
<td>-1.18</td>
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<td>126</td>
<td>114.7</td>
<td>113.9</td>
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<td>160.2</td>
<td>150.5</td>
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<tr>
<td>E(TO3)</td>
<td>237</td>
<td>240</td>
<td>227.6</td>
<td>226.2</td>
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<td>E(TO4)</td>
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<td>580.3</td>
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**Figure Legends**

**Fig. 1.** (Color online) 300 K absorption coefficient $\alpha(\omega)$ of bulk (thin solid line) and 16 nm (solid line) BiFeO$_3$. The spectrum of the bulk materials is offset by $6 \times 10^2$ cm$^{-1}$ along the y-axis for clarity. Peak positions in the bulk are identical to those of 7500 nm particles. Three modes of particular interest [E(TO1), A$_1$(TO1), E(TO7)] are labeled. Inset: TEM image of an individual, isolated 16 nm nanoparticle annealed at 400°C. Additional information on the particulate nature of these samples, their crystallinity, and their chemical composition is available in the Methods section, the Supplementary Information section, and in Ref. 50.

**Fig. 2.** (Color online) Schematic representation of the calculated A$_1$(TO1) displacement vectors in rhombohedral BiFeO$_3$: a, Bi, Fe vectors along [111] direction and b, O vectors projected in (111) plane. c, Calculated phonon mode frequencies for cubic ($Pm\bar{3}m$) and rhombohedral ($R\bar{3}c$) structures$^{29}$ (paraelectric phases) compared with those of the rhombohedral ($R\bar{3}c$) (ferroelectric phase) system$^{52}$. Blue circles represent acoustic and silent modes (here, we use the phrase “silent modes” for simplicity to represent all infrared inactive modes, whether they be formally silent or Raman active), green squares represent infrared active modes, and red diamonds mark the silent $\rightarrow$ active modes at the $Pm\bar{3}m \rightarrow R\bar{3}c$ phase transition. Several modes of interest are labeled. Degenerate modes are connected by a bold line.

**Fig. 3.** (Color online) Close-up view of selected phonon modes of BiFeO$_3$ as a function of size (diameter) at 300 K. These modes include features of (a) E(TO1), (c) E(TO7), and (e) A$_1$(TO1) symmetries. Important trends quantified include (b) the relative intensity of the E(TO1) mode vs. size, (d) the relative intensity of the E(TO7) mode vs. size, (f) the frequency of the A$_1$(TO1) mode vs. size, and (g) the damping of the A$_1$(TO1) mode vs. size. The green solid lines are the calculated curves fit to the data, described in the text. Red triangles mark the critical sizes (13.5 nm and 8.1 nm) for the E(TO1) and E(TO7) modes, respectively.

**Fig. 4.** (Color online) 300 K absorption coefficient $\alpha(E)$ of 16 nm BiFeO$_3$ nanoparticles as compared with that of an epitaxially grown rhombohedral thin film$^{27}$. Blue dashed arrows denote the charge transfer excitation split by 0.5 eV. Inset: Direct band gap analysis of the thin film and the nanoparticles. The triangle marks the 2.67 eV charge gap of the
rhombohedral film whereas the square marks the 2.43 eV gap of 16 nm BiFeO$_3$.  

FIG. 1:
FIG. 2:

(a) 160 cm$^{-1}$ $A_1$(TO1)

(b) $E$(TO1)

(c) $T = 300$ K

Frequency (Arb. Units)

Mode index
FIG. 4:

Absorption ($10^5$ cm$^{-1}$)

Energy (eV)

$T = 300$ K

16 nm BiFeO$_3$

rhombohedral film
Supplementary information: Size-dependent infrared phonon modes and ferroelectric phase transition in BiFeO₃ nanoparticles

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Synthesis and characterization of BiFeO₃ nanoparticles:
Single-crystalline BiFeO₃ nanoparticles were prepared by sol-gel techniques as described by Park et al.¹ In a typical synthesis of BiFeO₃ nanoparticles, 5 mmol of Bi(NO₃)₃·5H₂O and Fe(NO₃)₃·9H₂O was added successively to 12 ml of ethylene glycol. The mixture was stirred at 80°C, after which a yellow-brown sol was recovered upon evaporation of the excess ethylene glycol. Thereafter, the resultant gel samples were preheated to 400°C in three separate runs at a ramp-rate of 5°C/min in order to remove excess hydrocarbons and NOₓ impurities. To obtain reasonable size variation, samples were further annealed at 400, 425, 460, 595, 635, and 800°C for 30 minutes, respectively. The purity and crystallinity of as-prepared BiFeO₃ nanoparticles were examined by X-ray powder diffraction (XRD) measurements, as shown in Fig. S1(c). The XRD results are in excellent agreement with those of the original report¹ for the new sizes that were not previously reported, and it is evident that the observed patterns of the 16 nm displayed all of the expected peaks emanating from the BiFeO₃ structure, with no impurity peaks. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images reveal the morphologies of as-prepared BiFeO₃ products (Fig. S1(a) and (b)). Additional supporting data are shown in Fig. S2 of Ref. 1. The single crystalline nature of these nanoparticles was previously established with selective area diffraction and high resolution TEM.¹ The Bi/Fe ratio and oxygen stoichiometry was also assessed.¹ Briefly, energy dispersive X-ray spectroscopy (EDS), taken at a number of se-
lected positions on the sample, indicated the expected presence of Bi, Fe, and O. Mössbauer spectroscopy detected no significant amount of Fe$^{2+}$, a result that points to few oxygen vacancies. The sizes of our as-prepared BiFeO$_3$ nanostructures annealed at 400, 425, 460, 595, 635, and 800$^\circ$C, were measured to be 16 ± 4, 31 ± 15, 47 ± 10, 85 ± 21, 215 ± 60 nm and bulk, respectively. These values are in reasonable agreement with those obtained by the Debye-Scherrer analysis of the XRD data. Our middle infrared spectroscopy indicates no significant –OH absorption, although small molecule absorption to nanostructured surfaces$^1$ is anticipated to increase over time, particularly under atmospheric conditions.

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FIG. S1: (Color online) Representative TEM (A) and SEM (B) images of the as-prepared 16 nm nanoparticles after sonication. A representative XRD pattern (red) of 16 nm nanoparticles with the corresponding JCPDS standard (black) for bismuth ferrite (JCPDS #20-0169) shown immediately below.