

# EXAFS Studies of Fine Particles of Magnetoelectric BiFeO<sub>3</sub>

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## Introduction

Magnetoelectric materials, also called multiferroics, exhibit both ferroelectric and magnetic ordering. Recent interest in these materials is driven by their potential application in sensors and memory devices. BiFeO<sub>3</sub> is one of the few magnetoelectric materials. The ferroelectric properties of BiFeO<sub>3</sub> exist in a wide range of temperatures and vanish at a high Curie temperature (TC) of 820 to 850°C [1, 2]. Size effect studies of the nanoparticulate BiFeO<sub>3</sub> (radius = 23 to 80 nm) indicate that as the particle size decreases, (a) the lattice expands, (b) the Neel temperature (T<sub>N</sub>) decreases from 400 to 339°C, and (c) the antiferromagnetic-to-paramagnetic transition becomes increasingly diffuse [3]. To understand these changes in the physical properties of BiFeO<sub>3</sub> that occur as the particle size decreases, x-ray absorption fine structure (XAFS) measurements have been made at the Fe and Bi edges at several temperatures and on several samples with various particle sizes. This paper reports on the first results from this large collection of data, in which we compare the Fe k-edge data at 20K for the bulk particulate (i.e., BULK, 1400 nm) and nanoparticulate (i.e., NANO, 20 nm) BiFeO<sub>3</sub>. Previous extended x-ray absorption fine structure (EXAFS) studies of a similar material, BaTiO<sub>3</sub>, showed that the magnitude of the Ti atom's off-center displacement does not depend on particle size. We are not aware of any previous EXAFS studies of nanoparticulate BiFeO<sub>3</sub>.

## Methods and Materials

Pure single-phase particles of BiFeO<sub>3</sub> were prepared by using a wet-chemistry coprecipitation technique. The samples were characterized with high-resolution x-ray diffraction (HRXRD) and scanning electron microscopy (SEM) measurements. HRXRD measurements performed at the MR-CAT beamline 10-ID at the APS verified the purity of the sample and accurately determined the lattice parameters and particle sizes of the samples. The samples were packed in capillaries (2 mm in diameter) that were rotated during the measurement in transmission mode. The Fe k-edge EXAFS measurements were also performed at MR-CAT beamline 10-ID [4]. The samples were spread on tape. Several layers were stacked so that the thickness  $x$  of the samples corresponded to  $\Delta\mu x = 0.5$ , where  $\Delta\mu$  is

the jump of the absorption coefficient at the Fe k-edge energy. The samples were then loaded in a dispex and cooled to 20K. The energy of the monochromator was calibrated by simultaneously collecting the XAFS spectra from an iron foil. The undulator parameters (taper and gap) were optimized to obtain a large photon flux with nearly constant intensity within the scanned energy range of 6900 to 8400 eV. The Si(111) double-crystal monochromator was scanned continuously so that the data were collected in quick EXAFS mode. A Rh harmonic rejection mirror was used to eliminate x-rays of higher harmonic energies. The incident and transmission photon intensities were measured by using ion chambers filled with 80:20 He:N<sub>2</sub> and with N<sub>2</sub>. The size of the incident x-ray beam on the sample was 1 mm<sup>2</sup>. The transmission measurements were collected over the scanned energy range of 6900 to 8400 eV with a step size of 0.4 eV and a dwell time of 0.5 second. For each sample, 10 scans were taken and then averaged.

The data was processed by using the FEFFIT package [5]. Background subtraction and data merging was done with Athena [6]. Theoretical models were constructed by using the program FEFF7 [7] and the crystallographic atomic positions of BiFeO<sub>3</sub>.

## Results

HRXRD data showed that the samples are phase pure. The results showed an expansion of the unit cell volume with the decrease in particle size from the BULK to NANO samples. However, this expansion corresponded to changes in distances between the Fe atoms and the neighboring atoms (0.000 to 0.002 Å) that are too small to resolve in an XAFS measurement. This result is confirmed by comparing the average  $\chi(k)\cdot k^2$  data from the NANO and BULK samples. Both data sets show the same phase (as the data sets cross zero at the same points), indicating that although the distances between the Fe atoms and their neighbors are the same for both samples, there is a systematic reduction in the amplitude of the signal from the NANO sample compared with that from the BULK sample, as shown by the arrows in Fig. 1. This reduction in amplitude of the NANO particle signal can be clearly seen in the Fourier transform (FT) of the data shown in Fig. 2 (particularly in the second and third peaks at 3.5 and 5 Å in the FT). Another slight but interesting

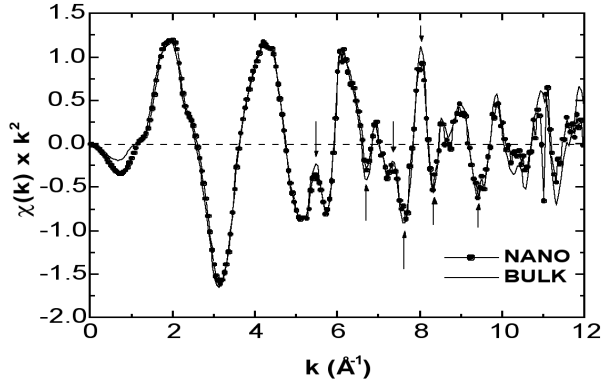


FIG. 1. Comparison of the averaged  $\chi(k) \cdot k^2$  data for the NANO (20 nm) and BULK (1.4  $\mu\text{m}$ ) samples. The arrows mark changes in amplitude.

feature shown in the FT of the first shell is a slight tilting of the signal in a direction consistent with a third cumulant.

Both data sets were simultaneously fit in R-space by using  $k$ -weightings of 1, 2, and 3 in the FT of the data. The path lengths were constrained to the same values for the NANO and BULK data, while the  $\sigma^2$ -values were independently determined. Also, a third cumulant was added to the first shell to account for the tilting of the first shell signal. There were seven common variables and seven independent variables determined in the fit to both data sets, for an average of 10.5

parameters per data set. The additional parameters were an  $S_0^2$  value, a third cumulant for the first and second oxygen shell for both the BULK and NANO data, and an additional energy shift for the NANO data set relative to the BULK data set. With the addition of these two common variables and two independent variables, the final number of parameters per data set was 13.5. This data range results in approximately 18 and 27 independent points for the BULK and NANO data. Figure 2 shows the  $k$ -weighted Fourier transform of the data and best-fit model for the NANO and BULK samples.

The results of the simultaneous fit to the BULK and NANO data sets show a systematic increase in the  $\sigma^2$ -values for the nanoparticulate  $\text{BiFeO}_3$  data relative to the bulk. This is consistent with the change in amplitude of the XAFS spectra observed in the NANO sample with respect to the BULK sample (Fig. 1). We interpret this higher value of  $\sigma^2$  as an increase in static disorder in the NANO sample relative to the BULK sample. It may be interpreted as an indication of a structural phase transition in the NANO sample to a crystal structure with higher symmetry. Another interesting feature is the increase in the values of the third cumulant for the first and second oxygen paths in the nanoparticle sample. In typical transition metal oxides, the magnitude of interaction between the 3d electrons of the metal and the oxygen nucleus is an approximate measure of covalence [8]. The fact that covalence increases with increases in pressure has been confirmed from the measurement of the pressure dependence of the Racah

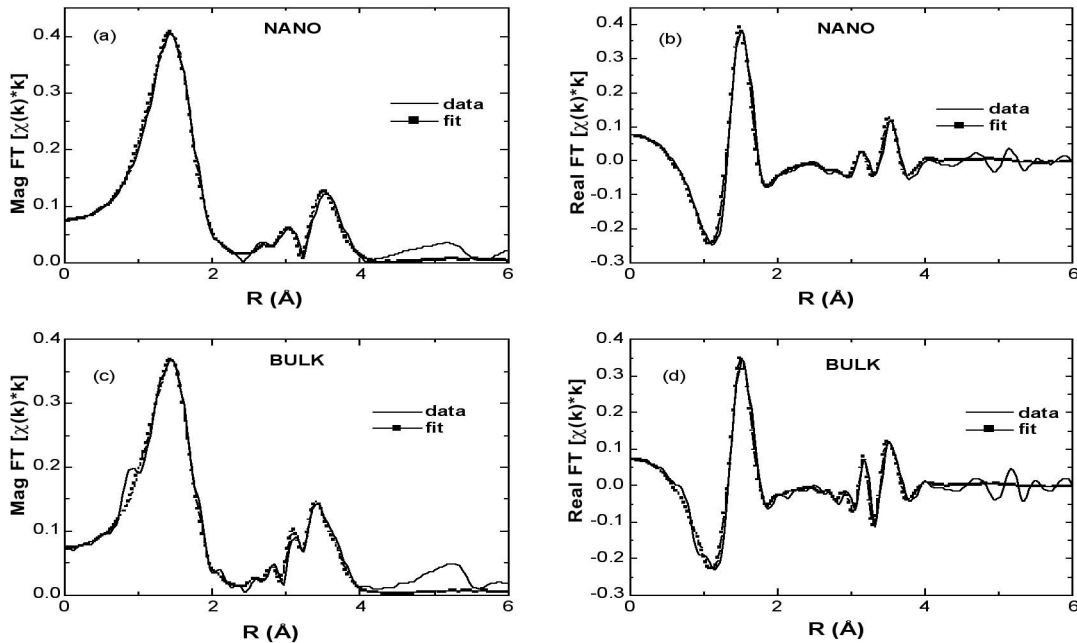


FIG. 2. The magnitude and the real part of the FT of the  $k$ -weighted data and the fit for the NANO and the BULK samples.

parameters (from crystal field theory). An expansion of the unit cell is equivalent to negative pressure. One should therefore expect these systems to become increasingly ionic with decreases in particle size. From our XRD data, we observe an expansion of the unit cell volume with a decrease in size. Hence, we should observe increasing ionicity with a decrease in size. This had been observed before in other partially covalent oxide systems [9]. For our BiFeO<sub>3</sub> nanoparticles, the nonzero third cumulant (third-O2 =  $3.53 \times 10^{-4} \text{ \AA}^3$ ) for the Fe-O2 paths and the increase in the third cumulant value (from 1.32 to  $1.96 \times 10^{-4} \text{ \AA}^3$ ) for the Fe-O1 paths imply an increased ionicity in the NANO as compared to the BULK samples.

### Discussion

In conclusion, our XAFS studies of the magnetoelectric BiFeO<sub>3</sub> system showed that with a decrease in particle size, the disorder in the material increases and the system tends to become increasingly ionic. A more detailed study that is currently in progress, which incorporates XAFS at the Bi L<sub>III</sub> edge and multiple temperature measurements, will enable us to better understand the structural origins of the changes in the physical properties of BiFeO<sub>3</sub> with decreasing particle size.

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