Supplementary Material (ESI) for Chemical Communications

Supplementary Information

"Synthesis and Characterization of Multiferroic $BiFeO_3$ nanotubes"

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Figure S1. (A) Powder X-ray diffraction (XRD) of the bulk $BiFeO_3$ (a), $BiFeO_3$ NTs (b), and comparison with literature results (JCPDS#20-0169) (c). (B) $BiFeO_3$ NTs' X-ray diffraction patterns (c) were deduced by subtracting the diffraction signal of the alumina template/$BiFeO_3$ (a) from that of the alumina template itself (b).

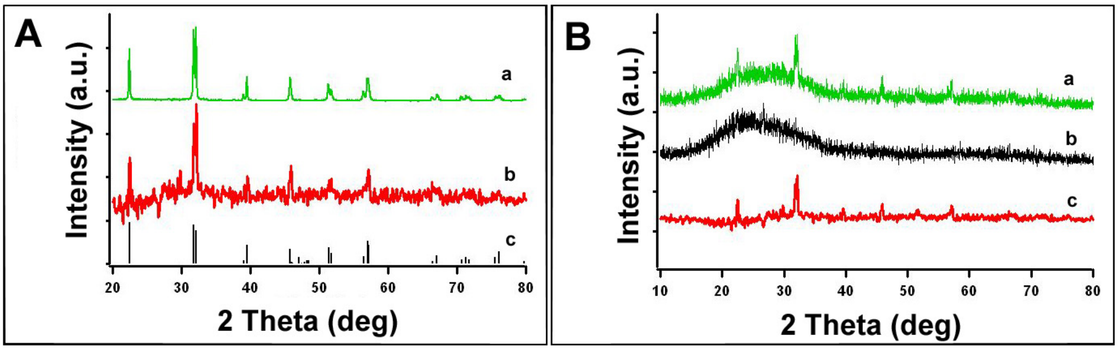


Figure S2. Scanning electron microscopy (SEM) images of the bulk $BiFeO_3$ prepared using identical experimental procedures.

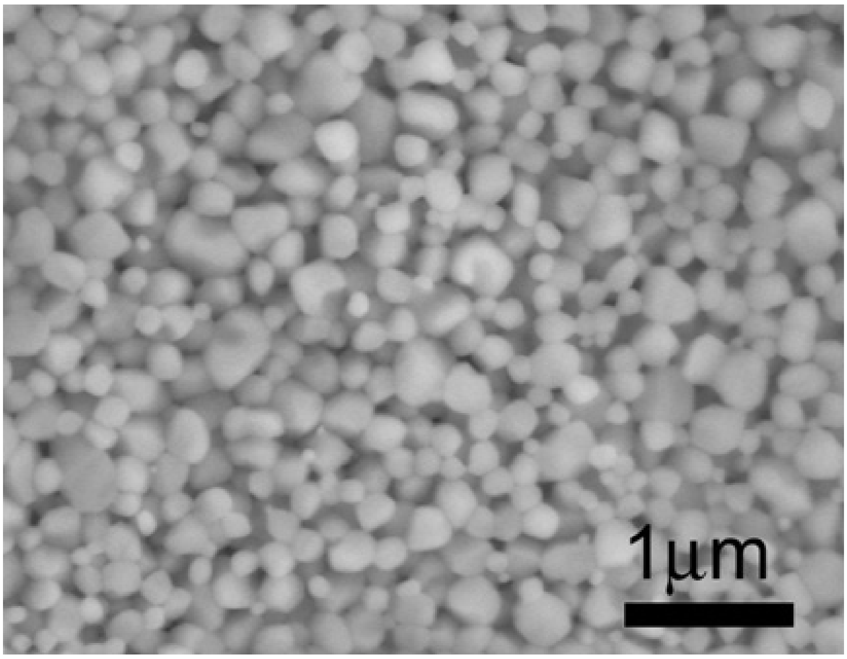
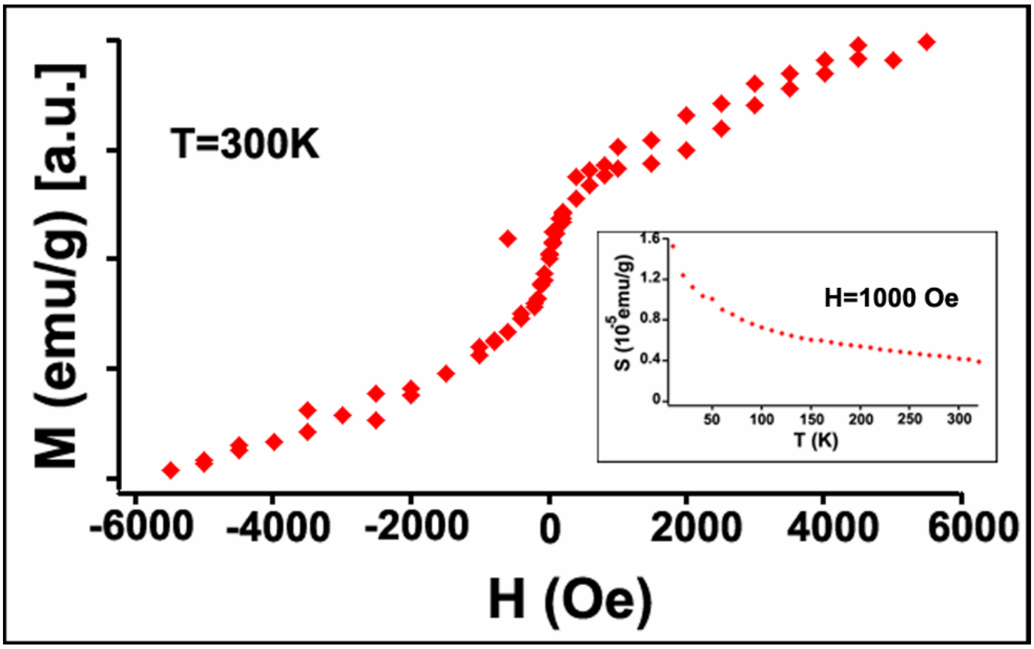


Figure S2 shows an image of the surface of $BiFeO_3$ bulk samples prepared by identical experimental protocols (but without a template) to that of $BiFeO_3$ NTs to demonstrate the efficacy of our procedure. In comparison with previous SEM images of bulk samples, the surface morphologies of our bulk $BiFeO_3$ are similar to those of thin films grown on $Pt/TiO_2/SiO_2/Si$ substrate using a pulsed-laser deposition (PLD) technique.[1] However, the grain sizes of particles in our samples are much smaller (range of 100-500 nm), as compared with samples (range of 1-3 μm) prepared by a typical solid state reaction method.[2]

Figure S3. Hysteresis loop at 300 K of as-prepared $BiFeO_3$ NTs, grown in AAO membranes having 100 nm sized pores. Inset shows the magnetic susceptibility of $BiFeO_3$ nanotubes as a function of temperature with the magnetic field set at 1000 Oe.



These preliminary data were taken using the superconducting quantum interference device (SQUID). As further experimental details, we note that the alumina template was not removed in these experiments. Hence, since the sample (the template/$BiFeO_3$) contains small quantities of nanotubes, sample data shown are presented after an appropriate, mass-corrected background subtraction of the signal due to the alumina template itself and hence, reflect genuine magnetic behavior of the nanotubes themselves.

The net result is that there does indeed appear to be a small though appreciable level of magnetization, unlike bulk pure $BiFeO_3$ which does not show any spontaneous moment even up to very high fields and low temperatures.[3] The precise nature of this nanoscale effect, however, has not as yet been fully discerned as more comprehensive data on our nanotubes are still being taken. Moreover, a detailed comparative evaluation with the bulk is limited because of the lack of any published data on single crystals.[4]

References

(1) Palkar, V. R.; John, J.; Pinto, R., *Appl. Phys. Lett.,* 2002, **80**, 1628.

(2) Kumar, M. M.; Palkar, V. R.; Srinivas, K.; Suryanarayana, S. V., *Appl. Phys. Lett.,* 2000, **76**, 2764.

(3) Kumar, M. M.; Srinath, S.; Kumar, G. S.; Suryanarayana, S. V., *J. Magn. Magn. Mater.,* 1998, **188**, 203.

(4) Wang, J.; Neaton, J. B.; Zheng, H.; Nagarajan, V.; Ogale, S. B.; Liu, B.; Viehland, D.; Vaithyanathan, V.; Schlom, D. G.; Waghmare, U. V.; Spaldin, N. A.; Rabe, K. M.; Wuttig, M.; Ramesh, R., *Science,* 2003, **299**, 1719.

Materials Characterization. The products were characterized by a number of different methodologies, including X-ray diffraction, transmission electron microscopy (TEM), scanning electron microscopy (SEM), as well as by selected area electron diffraction (SAED) and energy dispersive X-ray spectroscopy (EDS).

X-ray diffraction. Crystallographic information on $BiFeO_3$ and AAO template samples were obtained on a Scintag diffractometer, operating in the Bragg configuration using Cu Kα radiation ($\lambda = 1.54$ Å). The samples were obtained by grinding thoroughly in ethanol using a mortar and pestle, followed by loading onto glass slides and subsequent drying in air. The diffraction patterns were collected from 20 to 80^o at a scanning rate of 2^o per minute with a step size of 0.02^o. Parameters used for slit widths and accelerating voltage were identical for all samples.

Electron Microscopy. The particle size and morphology of the resulting $BiFeO_3$ products were initially characterized using a field emission SEM (Leo 1550) at accelerating voltages of 15 kV, which was equipped with the energy dispersion X-ray spectroscopy (EDX) capabilities. Specifically, $BiFeO_3$ samples were deposited onto copper tapes, which were attached to the surface of SEM brass stubs. These samples were then conductively coated with gold by sputtering them for 20 seconds to minimize charging effects under SEM imaging.

Specimens for transmission electron microscopy (TEM) and high resolution TEM (HRTEM) were obtained by drying $BiFeO_3$ NTs sample droplets from an ethanolic dispersion onto a 300 mesh Cu grid coated with a lacey carbon film. Transmission electron microscope (TEM) images were taken at an accelerating voltage of 120 kV on a Philip CM12 instrument. High-resolution images were obtained on a JEOL 2010F

HRTEM at an accelerating voltage of 200 kV. This instrument was equipped with an Oxford INCA EDS system with the potential of performing selected area electron diffraction (SAED) to further characterize individual $BiFeO_3$ nanostructures.