Fabrication and Magnetic Properties of Multiferroic $BiFeO_3$ Nanotube Arrays

Xueqin Xu, Tian Qian, Genqiang Zhang, Tao Zhang, Guang Li, Wei Wang, and Xiaoguang Li*
Hefei National Laboratory for Physical Sciences at Microscale, Department of Physics, University of Science and Technology of China, Hefei 230026, P. R. China

(Received September 19, 2006; CL-061084; E-mail: lixg@ustc.edu.cn)

Multiferroic $BiFeO_3$ nanotube arrays have been successfully prepared by means of a sol–gel method utilizing porous anodic alumina templates. The magnetic field and temperature dependencies of magnetizations demonstrate the superparamagnetism behavior with the most sound evidence, which can be attributed to the uncompensated surface spins induced by the size effect.

Multiferroics are materials possessing a spontaneous polarization, magnetization, and piezoelectricity that can be switched on by an applied electric field and magnetic field, respectively. Recently, increasing efforts have been made to fabricate and understand multiferroics nanostructures because of their promising application in nanoscale devices, such as high-density magnetically recorded ferroelectric memory.[1–6]

Of particular interest is $BiFeO_3$ (BFO), which exhibits the coexistence of ferroelectric and antiferromagnetic orders up to quite high temperature.[7] For example, thin films of pure BFO shows good multiferroics properties that both ferroelectricity and magnetism are significantly enhanced with respect to that of bulk materials.[2] Nanoparticles have been prepared by a sol–gel method and show enhanced magnetic properties due to reduction of size.[1] The fabrication of one-dimensional nanostructures of BFO and investigating size correlation of the basic physical properties of these materials are of fundamental importance. Recently, the BFO nanotubes and nanowires were fabricated using a sol–gel template method and show significant ferroelectric and piezoelectric characteristics.[5,8,9] However, the magnetic property of the BFO nanotubes has not been reported. In present work, we report the fabrication of BFO nanotube arrays using a modulated sol–gel template method. The presence of superparamagnetism in the BFO nanotubes has been revealed.

The homemade porous anodic alumina membrane (PAAM) templates were prepared using a two-step anodization process,[10,11] and the BFO nanotubes were prepared by sol–gel method utilizing PAAM templates. In a typical experiment, $Bi(NO_3)_3 \cdot 5H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ were initially dissolved in 2-methoxyethanol ($C_3H_8O_2$),[12] and the solution was stirred for 1 h at room temperature. PAAM templates were put into a jar containing a lot of sol. Then, the jar was vacuumized for vacuum perfusion. The resultant samples, i.e., PAAM templates containing the precursor, were subsequently oven-dried at 140 °C for 1 h and then preheated to 600 °C for 10 h in order to get rid of excess hydrocarbons and NO_x impurities. A higher nanopore filling efficiency of BFO nanotubes was achieved by repeating the perfusion and heating treatment cycles. After deposition (3–4 times), the samples were annealed at 700 °C for 1 h.

The crystal structure of the BFO nanotubes was characterized using a MXP18AHF powder X-ray diffractometer (MAC Science Co., Ltd., Japan) with Cu Kα ($\lambda = 1.54056$ Å) radiation and a transmission electron microscope (TEM, Hitachi-800). The morphology of the samples was obtained by field-emission scanning electron microscopy (FE-SEM, JEOL, JSM-6700F). The magnetic measurements were performed using a superconducting quantum-interference device (SQUID) magnetometer (MPMS 5, Quantum Design).

X-ray diffraction pattern obtained from the as-prepared sample is shown in Figure 1. All the peaks can be indexed to a rhombohedrally distorted perovskite structure with space group $R3c$. It should be noted that in the pattern of as-prepared sample, the abnormally strong intensity of (024) and (220) is the contribution of the superposition of the intrinsic diffraction peak of the BFO nanotubes and partly crystallized Al_2O_3 after annealing at 700 °C for 1 h, and the broad peaks in the range from 20 to 40° is the only contribution of Al_2O_3.

Figures 2a and 2b are a top view and a cross-sectional FE-SEM images of the nanotube arrays after the PAAM template has been etched in 2 M NaOH for 10 min, respectively. They clearly display the nanotube structure of the BFO samples. Figure 2c is a typical FE-SEM cross-sectional image of the samples with an eroding time of 20 min, which reveals that the BFO products consist of nanotubes with lengths up to 50 μm. An important feature of the present system is that the BFO nanotubes are continuous and uniform in diameter and length.

The structure of the BFO nanotubes is further examined by TEM after dissolving away the template by NaOH solution, as shown in Figures 2d–2f. A large amount of straight and long nanotubes are observed with uniform outside and inside diameters of about 100 and 80 nm, respectively. Figure 2e shows the selected area electron diffraction pattern taken from a single nanotube, which reveals the polycrystalline nature of the BFO nanotubes. Similar result has been reported in ref 8 and has been attributed to the sol–gel method. It is also seen that the polycrystalline nanotubes are composed of very fine particles.

Small particles of antiferromagnetic materials are expected to be superparamagnetic just as fine particles of ferromagnetic or ferrimagnetic materials.[13,14] The temperature dependence of

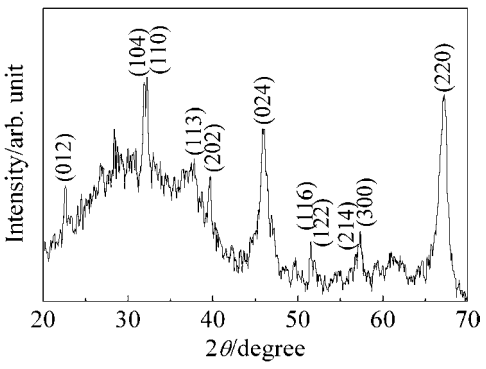

Figure 1. X-ray diffraction pattern of the BFO nanotubes.

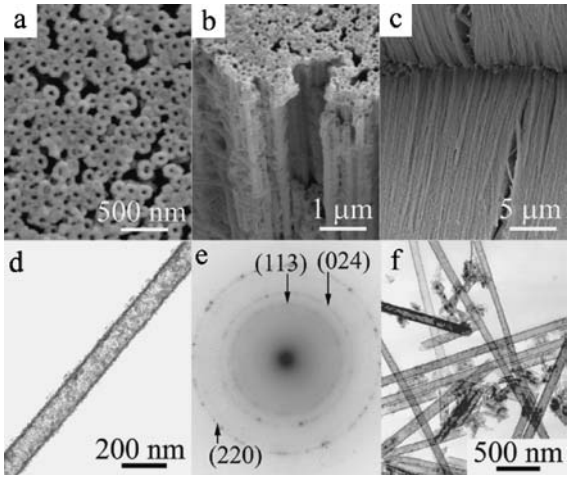

Figure 2. SEM images of (a) top view of the BFO nanotubes, (b) and (c) the cross section of BFO nanotube arrays, (d) and (f) TEM images of the BFO nanotubes after removing the alumina template, (e) the corresponding SAED pattern of a single nanotube.

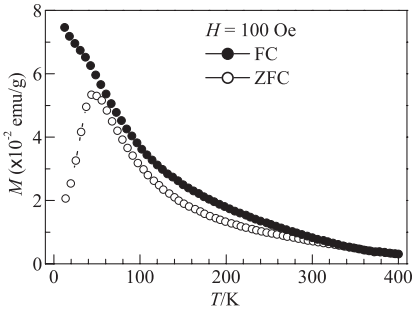

Figure 3. Temperature dependence of ZFC (open symbol) and FC (solid symbol) magnetization measured under magnetic field of 100 Oe for the BFO nanotubes.

field-cooled (FC) and zero-field-cooled (ZFC) magnetization (M–T) curves for the BFO nanotubes measured under a magnetic field of 100 Oe are shown in Figure 3. The ZFC curve exhibits a maximum at 46.5 K while the FC one increases gradually with decreasing temperature. Similar results were also reported for the antiferromagnetic NiO and MnO nanoparticles which are superparamagnets.[15,16] These indicate that the current nanotubes can be also viewed as superparamagnets. In addition, there is a distinct irreversibility below $T_{irr} = 340$ K, i.e., splitting between the FC and ZFC M–T curves. At high temperature (above T_{irr}), the thermal fluctuations are very strong leading to the reversibility of M–T curves. With decreasing temperature (below T_{irr}) the thermal fluctuations slow down and the magnetic moments block progressively because of a distribution of the particle size, giving rise to the irreversibility in the M–T curves.[15]

The superparamagnetic behavior of the BFO nanotubes was further confirmed by magnetic hysteresis loops (M–H) measured at 10 and 300 K, as shown in Figure 4a. A hysteresis loop is clearly observed in the inset of Figure 4a at 10 K, whereas the curve at 300 K is nonlinear with no coercive field and no hysteresis although there is a manifest irreversibility between the ZFC and FC M–T curves.

It should be mentioned that the nanotubes for these magnetization measurements in Figures 3 and 4a are randomly orientated. Since large length-to-diameter ratio in the nanotubes might lead to large shape anisotropy, we measured the magnetic hysteresis loops under fields parallel and perpendicular to the nanotubes for the as-prepared samples at 10 K, as shown in Figure 4b. It is clear that the coercivity value for the field parallel to the nanotubes is greater than that for the perpendicular case, which confirms the large shape anisotropy.

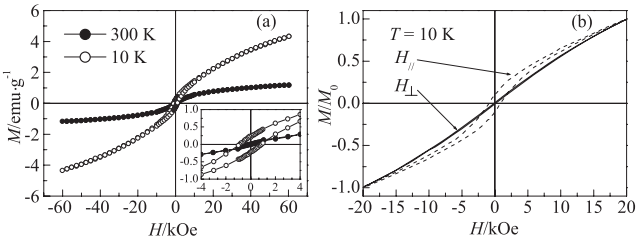

Figure 4. (a) M–H loops at 10 and 300 K for BFO nanotubes. The inset shows the enlargement of the low-field data. (b) M/M_0–H loops of the as-prepared sampes at 10 K under fields parallel ($H_{//}$) and perpendicular ($H_{\perp}$) to the nanotubes. M_0 is the magnetization at 20 kOe in each loop.

This work was supported by the National Natural Science Foundation of China and the National Basic Research Program of China.

References

1 J. Li, H. He, F. Lü, Y. Duan, D. Song, *Mater. Res. Soc. Symp. Proc.* **2002**, *676*, Y7.7.1.
2 J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, R. Ramesh, *Science* **2003**, *299*, 1719.
3 H. Zheng, J. Wang, S. E. Lofland, Z. Ma, L. Mohaddes-Ardabili, T. Zhao, L. Salamanca-Riba, S. R. Shinde, S. B. Ogale, F. Bai, D. Viehland, Y. Jia, D. G. Schlom, M. Wuttig, A. Roytburd, R. Ramesh, *Science* **2004**, *303*, 661.
4 F. Zavaliche, H. Zheng, L. Mohaddes-Ardabili, S. Y. Yang, Q. Zhan, P. Shafer, E. Reilly, R. Chopdekar, Y. Jia, P. Wright, D. G. Schlom, Y. Suzuki, R. Ramesh, *Nano Lett.* **2005**, *5*, 1793.
5 X. Y. Zhang, C. W. Lai, X. Zhao, D. Y. Wang, J. Y. Dai, *Appl. Phys. Lett.* **2005**, *87*, 143102.
6 H. Béa, S. Fusil, K. Bouzehouane, M. Bibes, M. Sirena, G. Herranz, E. Jacquet, J.-P. Contour, A. Barthélémy, *Jpn. J. Appl. Phys., Part 2* **2006**, *45*, L187.
7 I. Sosnowska, T. Peterlin-Neumaier, E. Streichele, *J. Phys. C* **1982**, *15*, 4835.
8 T. J. Park, Y. Mao, S. S. Wong, *Chem. Commun.* **2004**, 2708.
9 F. Gao, Y. Yuan, K. F. Wang, X. Y. Chen, F. Chen, J.-M. Liu, Z. F. Ren, *Appl. Phys. Lett.* **2006**, *89*, 102506.
10 H. Masuda, K. Fukuda, *Science* **1995**, *268*, 1466.
11 X. P. Hoyer, H. Masuda, *J. Mater. Sci. Lett.* **1996**, *15*, 1228.
12 T. Kanai, S. Ohkoshi, K. Hashimoto, *J. Phys. Chem. Solids* **2003**, *64*, 391.
13 L. Neel, in *Low Temperature Physics*, ed. by C. Dewitt, B. Dreyfus, P. D. de Gennes, New York Gordon and Beach, **1962**, p. 413.
14 S. D. Tiwari, K. P. Rajeev, *Phys. Rev. B* **2005**, *72*, 104433.
15 E. Winkler, R. D. Zysler, M. Vasquez Mansilla, D. Fiorani, *Phys. Rev. B* **2005**, *72*, 132409.
16 S. Sako, Y. Umemura, K. Ohshima, M. Sakai, S. Bandow, *J. Phys. Soc. Jpn.* **1996**, *65*, 280.

Published on the web (Advance View) December 2, 2006; doi:10.1246/cl.2007.112