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Fabrication, magnetic, and ferroelectric properties of multiferroic BiFeO₃ hollow nanoparticles

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Abstract

Hollow BiFeO₃ nanoparticles were synthesized by an electrospray route for the first time. The phase purity and structure have been investigated by x-ray diffraction and Raman spectroscopy. Transmission and scanning electron microscope investigations revealed that the as-obtained BiFeO₃ hollow spheres were polycrystalline, with a shell thickness of 35 nm. The formation mechanism can be possibly explained by Ostwald ripening. Raman spectra have verified decreased vibrational frequencies in BiFeO₃ nanoparticles. These hollow and core-shell multiferroic nanoparticles exhibit significantly enhanced ferromagnetism from 5 to 600 K due to a broken spiral spin structure. The ferroelectricity of hollow BiFeO₃ particles exhibits a lower switching electric field, which is confirmed by Kelvin probe force microscopy.

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Du, Y., Cheng, Z. Xiang., Dou, S. Xue., Attard, D. Jon. & Wang, X. (2011). Fabrication, magnetic, and ferroelectric properties of multiferroic BiFeO₃ hollow nanoparticles. *Journal of Applied Physics*, 109 (7), 073903-1-073903-5.

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Citation: *J. Appl. Phys.* **109**, 073903 (2011); doi: 10.1063/1.3561377

View online: <http://dx.doi.org/10.1063/1.3561377>

View Table of Contents: <http://jap.aip.org/resource/1/JAPIAU/v109/i7>

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Fabrication, magnetic, and ferroelectric properties of multiferroic BiFeO₃ hollow nanoparticles

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(Received 16 December 2010; accepted 3 February 2011; published online 1 April 2011)

Hollow BiFeO₃ nanoparticles were synthesized by an electrospray route for the first time. The phase purity and structure have been investigated by x-ray diffraction and Raman spectroscopy. Transmission and scanning electron microscope investigations revealed that the as-obtained BiFeO₃ hollow spheres were polycrystalline, with a shell thickness of 35 nm. The formation mechanism can be possibly explained by Ostwald ripening. Raman spectra have verified decreased vibrational frequencies in BiFeO₃ nanoparticles. These hollow and core-shell multiferroic nanoparticles exhibit significantly enhanced ferromagnetism from 5 to 600 K due to a broken spiral spin structure. The ferroelectricity of hollow BiFeO₃ particles exhibits a lower switching electric field, which is confirmed by Kelvin probe force microscopy. © 2011 American Institute of Physics. [doi:10.1063/1.3561377]

I. INTRODUCTION

Recently, inorganic hollow nanostructures with a thin shell and large interior space have attracted intensive interest due to their high specific surface area, lower density, and excellent permeability, which give them many potential uses in applications involving chemical reactors, sensors, drug delivery, catalysis, and batteries.^{1–4} The conventional approaches to deriving the inorganic hollow nanostructures are the template assisted method and interfacial synthesis.^{5–7} One important process in both approaches is the removal of the template or the core after the shell formation, which results in complication of the preparation and limits their applications. Cracked hollow nanostructures are also unavoidable during the template or core removal process. Several new sonochemical and solvothermal techniques have been reported to simplify the preparation of hollow structures.^{8–10} However, nanosized phase-metastable materials are still difficult to obtain via these techniques. Multiferroic materials are compounds which exhibit (anti-)ferromagnetism (AFM/FM) and ferroelectricity (FE) simultaneously. The mutual control of electrical polarization and magnetic ordering, i.e., magnetoelectric (ME) coupling in these materials, has promise for their application in novel multifunctional devices. It is expected that electric polarization that is controllable by an external magnetic field in multiferroic materials with hollow structures could have benefits for drug delivery and release. The medicine releasing process would be controlled by electric polarization of the material through tuning an external magnetic field. Moreover, the magnetic property of multiferroic compounds would also enhance the contrast in magnetic resonance imaging (MRI).

BiFeO₃ is an important room temperature multiferroic compound with magnetic transition temperature $T_N \approx 643$ K

and ferroelectric transition temperature $T_C \approx 1093$ K.^{11–16} The hollow BiFeO₃ nanoparticles can be used for multifunctional applications with tunable performance under external magnetic and electric fields at room temperature. However, it is hard to synthesize this multiferroic compound with specific nanostructures due to its metastable phases and complex perovskite structures. In addition, the characterization of intrinsic ferroelectric property of BiFeO₃ nanoparticles is extremely difficult due to their small size. Here, we report a successful fabrication of BiFeO₃ multiferroic hollow nanoparticles using a simple electrospray method.¹⁷ The formation mechanism of BiFeO₃ hollow nanoparticles were revealed by structure and morphologies studies. The ferroelectric polarization of hollow nanoparticles has been observed by a Kelvin probe force microscopy (KPFM) for the first time. The BiFeO₃ hollow nanoparticles exhibit an enhanced magnetic moment at room temperature due to a broken spiral spin structure, which confirmed by the magnetic measurement.

II. EXPERIMENTAL

BiFeO₃ hollow nanoparticles were synthesized by an electrospray method in a high voltage field (20 kV). Stoichiometric Bi(NO₃)₃·5H₂O (99.5%, Sigma-Aldrich) and Fe(NO₃)₃·9H₂O (99.5%, Sigma-Aldrich) were dissolved in 200 ml 2-methoxyethanol (Sigma-Aldrich) forming 0.005 M clear solution; 0.003 M KOH was slowly added to the solution resulting dark brown precursor. The electrospraying system consisted of a substrate holder with a heating element (up to 1073 K), a stainless steel capillary tube with an inner diameter of 160 μm, a solution tank, and a high voltage source (HV, up to 20 kV). The capillary tube was connected to the positive terminal of the HV, while the substrate holder was connected to the negative terminal of the HV. The distance between the substrate and the tip of the capillary tube was 5 cm. The spraying voltage was 16 kV. The temperature of the substrate holder was 873 K.

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FIG. 1. (Color online) Morphology of BiFeO_3 hollow nanoparticles. (a) TEM micrographs of BiFeO_3 hollow nanoparticles synthesized by the electrospray method; the inset 1 is the BiFeO_3 nanoparticles prepared in a spraying duration of 3 min, and the inset 2 is magnified view of a single particle with the fragmentlike dots on the shell, which is formed in a spraying duration of 5 min. The scale bars in both insets represent 100 nm. (b) HRTEM image of a typical portion of a BiFeO_3 hollow nanoparticle; the inset is the corresponding SAED pattern. (c) SEM images of the as-prepared BiFeO_3 nanoparticles with a spraying duration of 5 min; the inset shows a magnified view of a single core-shell particle. (d) Sample prepared with a spraying duration of 10 min; the inset is the EDS result.

The crystal structure of samples was examined by x-ray diffraction (XRD; GBC MMA), using $\text{Cu K}\alpha$ radiation at $\lambda = 1.54056 \text{ \AA}$, operating at 40 kV voltage and 25 mA current. The Raman scattering measurements with shifts ranging from 100 to 2000 cm^{-1} were performed with a laser Raman spectrometer (HR320; HORIBA Jobin Yvon) at room temperature. An Ar^+ laser with wavelength of 632.8 nm was used for excitation of the Raman signals. Field-emission scanning electron microscopy (FE-SEM) images were obtained using a JEOL-7500 microscope operating at 5.0 kV. The x-ray energy dispersive spectroscopy (EDS) analysis was performed using the JEOL-7500. Transmission electron microscopy (TEM) images and the corresponding selected area electron diffraction (SAED) patterns were collected on a JEOL-2100 with an acceleration voltage of 200 kV. The magnetic measurements were carried out using a 5 T magnetic property measurement system (MPMS, Quantum

Design) and a 14 T physical property measurement system (PPMS, Quantum Design) over a wide temperature range from 5 to 700 K. The ferroelectricity of the samples was measured by a Kelvin probe force microscopy (Asylum Research MFP-3D). BiFeO_3 hollow particles were transferred to a silicon (100) wafer before KPFM measurements.

III. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show TEM images for BiFeO_3 hollow spherical nanoparticles synthesized by electrospray method. It reveals that all the particles formed on the substrate with different spraying durations at 600°C show spherical shape. We found that single-phase BiFeO_3 nanoparticles with hollow structures can be formed in spraying duration of more than 10 min. It is believed that there are two steps that convert solid spheres into hollow spheres during the electrospray

FIG. 2. XRD pattern of BiFeO_3 hollow nanoparticles fabricated by the electrospray method. The inset is Raman spectrum for BiFeO_3 nanoparticles.

FIG. 3. (Color online) Magnetization as a function of magnetic field of BiFeO_3 hollow nanoparticles at 5 K. The inset 1 is the M-H loop observed at 300 K. The inset 2 is the temperature dependence of magnetization (field-cooled) measured in a magnetic field of 10 Oe from 325 to 700 K.

FIG. 4. (Color online) KPFM images of BiFeO_3 hollow nanoparticles. (a) The surface potential image of sample after the switching processes with bias voltages of 0.5, 1.0, 3.0, and 5.0 V. (b) The sample surface potential as a function of the bias voltage; the inset is the line potential profiles of the KPFM images of individual BiFeO_3 hollow nanoparticle [corresponding to the blue line in Fig. 4(a)].

process. According to Kirkendall effect and Ostwald ripening mechanism for electrospray method,^{1,18} solid sphere particles consisting of Bi_2O_3 and Fe_2O_3 are formed at the beginning. Then, the reaction between the Bi_2O_3 and Fe_2O_3 takes place at high temperature in situ, forming the BiFeO_3 phase and eventually converting the solid particles into hollow particles completely. Short spraying duration leads to an inadequate diffusion of materials during the formation of the nanoparticles, which results in the coexistence of solid, core-shell, and hollow spheres, as shown in the inset 1 of Fig. 1(a). Large

amounts of BiFeO_3 nanoparticles were formed when the spraying duration was 5 min. However, some remaining fragmentlike dots were found to adhere to the shell of BiFeO_3 hollow nanoparticles, which is indicated in the inset 2 of Fig. 1(a). These dots formed during the shell shrinking process as the precursor droplets became attached to the substrate. When the spraying duration increased to 10 min, nanosized BiFeO_3 with a structure consisting of clear hollow spheres was formed [Fig. 1(a)]. The diameters of the as-obtained nanospheres vary from 50 to 200 nm. The thickness of the

shell is estimated as ~ 20 nm. Furthermore, HRTEM images and SAED patterns confirm that the as-prepared BiFeO₃ particles are polycrystalline. The presence of (101) and (012) plane diffraction fringes in a sample with d -spacings of 3.86 Å and 2.71 Å are shown in Fig. 1(b), which well matches JCPDS Card No. 20-169. The corresponding SAED pattern is shown in the inset. The SEM observations also support the formation process of the BiFeO₃ hollow and core-shell particles, as shown in Figs. 1(c) and 1(d). The EDS result confirmed that the as-obtained nanoparticles contain Bi, Fe, and O with an atomic Bi:Fe:O ratio of $\sim 1:1:3$, which agrees with the expected stoichiometry and XRD results.

Figure 2 shows the XRD pattern for the BiFeO₃ hollow spherical nanoparticles formed on the Al₂O₃ substrate. The diffraction peaks are well indexed by BiFeO₃ phase with a rhombohedral structure and space group $R\bar{3}c$. (The peaks from substrate are also marked.) The XRD peaks indicate the highly crystalline nature of the as-obtained nanoparticles. Raman spectrum of the BiFeO₃ hollow nanoparticles collected at room temperature is shown in the inset of Fig. 2. The irreducible representation for rhombohedral BiFeO₃ with the $R\bar{3}c$ structure at the center of the Brillouin zone is given by $\Gamma_{\text{Raman}, R\bar{3}c} = 4A_1 + 9E$. Eleven unidentified vibration modes, which consist of the four A_1 modes and seven E modes are observed for the hollow nanoparticles, in agreement with what has been reported in BiFeO₃ polycrystalline bulks.¹⁹ However, the Raman peaks of the BiFeO₃ hollow nanoparticles are found to shift to lower wave number, compared to bulk samples. This is because the translational symmetry of crystalline material is broken at grain boundaries, which results in the appearance of specific surface and interface vibrational contributions.²⁰ As the grain size of BiFeO₃ nanoparticles is very tiny, it leads to more surface areas/grain boundaries causing the Raman peaks shifting to low wave numbers.

The magnetic property measurements were performed on bismuth ferrite hollow nanoparticles on a Quantum Design superconducting quantum interference device (SQUID), and the results are shown in Fig. 3. The magnetic contribution from the substrate has been subtracted from all the data. The magnetic hysteresis loops for BiFeO₃ hollow nanoparticles measured at both 5 and 300 K are shown in Fig. 3. It reveals that the BiFeO₃ hollow particles exhibit weak ferromagnetic behavior with magnetic moment of ~ 0.07 emu/g at 5 K and 0.045 emu/g at 300 K in magnetic field of 0.1 T. The coercive field of sample is found to be 200 Oe at 5 K. These values are much larger than what has been observed in undoped bulk BiFeO₃ samples.²¹ Since the grain size of BiFeO₃ forming the hollow particles is ~ 40 nm, which is smaller than the period of the spin spiral structure (64 nm), enhanced magnetization is expected for the BiFeO₃ hollow particles due to uncompensated spins as a results of the broken period of the spiral spin structure.¹³ Moreover, the defects, such as oxygen vacancies, can induce the formation of dangling bonds on the BiFeO₃ particle surface, which enhance the magnetic moments of these hollow particles. The temperature dependence of the field cooled (FC) magnetization for the BiFeO₃ nanoparticles from 325 to 700 K is shown in the inset 2 of Fig. 3. It shows

a transition around 600 K, which corresponds to the bulk antiferromagnetic transition temperature of BiFeO₃.

The room temperature ferroelectricity of the BiFeO₃ hollow nanoparticles is confirmed by the KPFM measurement^{22–24} on a sample area of $1.98 \mu\text{m} \times 1.98 \mu\text{m}$ with scan speed of 1 Hz. Figure 4(a) is surface potential images of BiFeO₃ hollow nanoparticles under different bias voltages.²⁵ The polarized particles are brighter in the potential images than the Si substrate area due to their higher potential. The potential line profile of corresponding individual BiFeO₃ particles in Fig. 4(a) is shown in the inset of Fig. 4(b). Results show that the surface potential of BiFeO₃ hollow particles increases gradually when applied bias voltage increases from 0.5 to 5 V. The surface potential as a function of bias voltage for the BiFeO₃ hollow nanoparticles is plotted in Fig. 4(b). A nonlinear increase of surface potential induced by the bias was observed, which indicates a switchable polarization behavior. The surface potential is saturated at 800 mV when the bias voltage is increased up to 1 V. The electric field for the saturation polarization is calculated to be about 70 kV/cm, which is much smaller than that of BiFeO₃ bulk samples,¹³ indicating that the electric dipole can be easily switched in the hollow nanoparticles under low electric field.

IV. CONCLUSION

In summary, multiferroic BiFeO₃ hollow spherical nanoparticles were successfully synthesized by the electro-spray method. The diameter of BiFeO₃ hollow nanoparticles was found to be approximately 100 nm with a shell thickness of ~ 35 nm. The Raman peaks of the as-prepared nanoparticles shift to lower frequency due to increased surface areas and grain boundaries. The hollow BiFeO₃ particles exhibit ferroelectricity with lower switching electric field and enhanced magnetic moment at room temperature compared to BiFeO₃ bulks and thin films.

ACKNOWLEDGMENTS

This work is supported by the Australian Research Council through projects DP0987190, FT0990287, and DP0770205. The authors acknowledge Dr. Z. P. Guo and Mr. P. Zhang for assistance in using the electrospray system.

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