2011

Magnetic and ferroelectric properties of multiferroic Bi2NiMnO6 nanoparticles

Yi Du
University of Wollongong, ydu@uow.edu.au

Zhenxiang Cheng
University of Wollongong, cheng@uow.edu.au

Xiaolin Wang
University of Wollongong, xiaolin@uow.edu.au

Peng Liu
pl990@uowmail.edu.au

S. X. Dou
University of Wollongong, shi@uow.edu.au

Magnetic and ferroelectric properties of multiferroic Bi2NiMnO6 nanoparticles

Y. Du, Z. X. Cheng, X. L. Wang, P. Liu, and S. X. Dou

Citation: J. Appl. Phys. **109**, 07B507 (2011); doi: 10.1063/1.3537943
View online: http://dx.doi.org/10.1063/1.3537943
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v109/i7
Published by the American Institute of Physics.

Magnetic and ferroelectric properties of multiferroic Bi_2NiMnO_6 nanoparticles

Y. Du, Z. X. Cheng, X. L. Wang,[a] P. Liu, and S. X. Dou
Institute for Superconducting and Electronic Materials, University of Wollongong, Wollongong, New South Wales 2522, Australia

(Presented 15 November 2010; received 22 September 2010; accepted 22 October 2010; published online 21 March 2011)

Multiferroic Bi_2NiMnO_6 nanoparticles were synthesized by a simple electrospray method. Bi_2NiMnO_6 nanoparticles crystallize in the monoclinic structure with space group *C121*. The particles show a uniform spherical shape with a diameter of 100 nm to 300 nm. The ferromagnetic transition of Bi_2NiMnO_6 is confirmed at 122 K. The room temperature ferroelectricity of the Bi_2NiMnO_6 nanoparticles is verified by Kelvin probe force microscopy. © *2011 American Institute of Physics*. [doi:10.1063/1.3537943]

I. INTRODUCTION

Multiferroic materials, which show coexistence of ferroelectric and magnetic orderings, have been attracting intense interest due to their interesting fundamental nature and potentially wide applications.[1–3] However, candidate multiferroic materials are very rare because ferromagnetism requires transition metals with unpaired 3*d* electrons and an unfilled 3*d* orbital, while ferroelectricity needs transition metals with filled 3*d* orbitals. Oxide perovskites (ABO_3) have been proposed as potential multiferroic materials with possible A-site ferroelectricity and B-site magnetism. Even though ABO_3 compounds, such as $BiFeO_3$,[4] $BiMnO_3$,[5] and $DyFeO_3$,[6] have demonstrated coupling between the magnetic and ferroelectric orderings, they are characterized by serious current leakage problems or weak magnetoelectric coupling, which makes them very difficult to incorporate into applications. Recently, double-perovskite multiferroic compounds ($A_2BB'O_6$), such as Bi_2FeMnO_6,[7] Bi_2FeCrO_6,[8] and Bi_2NiMnO_6,[9] have been theoretically designed. In these double-perovskite oxides, Bi cations with lone pair s^2 electrons occupy the *A* sites, while two transition metal atoms occupy the *B* and *B'* sites, alternatively. In previous studies, room temperature multiferroic properties were observed in Bi_2FeMnO_6/ Nd:$BiFeO_3$ bilayered films.[10] The strong coupling of magnetism and ferroelectricity was confirmed in a Bi_2NiMnO_6 thin film sample.[11] However, the ferromagnetic transition of the Bi_2NiMnO_6 was not determined due to the large diamagnetic contribution from the $SrTiO_3$ substrate. Moreover, to date, little if any effort has been expended on research associated with the nanostructure of these double-perovskite compounds due to the difficulty in synthesis, which usually needs extremely high pressure and high temperature. The intrinsic magnetic interactions and ferroelectric behaviors of these compounds on the nanoscale are unclear, as yet. Investigations focused on developing advanced structural formulations such as zero-, one-, and two-dimensional (0-D, 1-D, and 2-D) nanostructures of double-perovskite multiferroic materials and studies of their physical properties are still desirable.

In this work, nanosized Bi_2NiMnO_6 particles have been successfully fabricated by an electrospray method. The structure, morphology, magnetic properties, and ferroelectric properties have all been investigated. The ferromagnetic transition temperature has been determined as 122 K. Switchable polarizations of the Bi_2NiMnO_6 nanoparticles were also observed.

II. EXPERIMENTAL PROCEDURES

Bi_2NiMnO_6 nanoparticles were synthesized by an electrospray method in a high voltage field (up to 20 kV). Stoichiometric $Bi(NO_3)_3{\cdot}5H_2O$ (99.5%, Sigma-Aldrich), $Mn(CH_3COOH)_2{\cdot}5H_2O$, and $Ni(NO_3)_2{\cdot}3H_2O$ were dissolved in 200 ml 2-methoxyethanol (Sigma-Aldrich) forming a 0.005 *M* clear solution. 0.003 *M* NH_4OH was slowly added to the solution, resulting in a dark brown sol-gel. Then, the precursor was sprayed onto an Si wafer substrate at a temperature of 573 K in an electric field of 16 kV for 2 hours. The as-prepared sample was annealed at 973 K in Ar for 1 hour.

The crystal structure of the samples was examined by X-ray diffraction (XRD; GBC MMA), using Cu-Kα radiation at $\lambda = 1.54056$ Å, operating at 40 kV voltage and 25 mA current. Field-emission scanning electron microscope (SEM) images were obtained, and X-ray energy dispersive spectroscopy (EDS) analysis was conducted using a JEOL-7500 microscope equipped with EDS. Transmission electron microscope (TEM) images were collected on a JEOL-2100 with an acceleration voltage of 200 kV. The magnetic measurements were carried out using a 14 T physical property measurement system (Quantum Design) over a wide temperature range from 5 K to 300 K. The ferroelectricity of the samples was measured by Kelvin probe force microscopy [(KPFM), Asylum Research MFP-3D], using both contact and noncontact modes.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern for the Bi_2NiMnO_6 nanoparticles. It indicates that the Bi_2NiMnO_6 nanoparticles have crystallized in the monoclinic structure with space group *C121*. The lattice parameters are $a = 9.527$ Å,

[a]Author to whom correspondence should be addressed. Electronic mail: xiaolin@uow.edu.au.

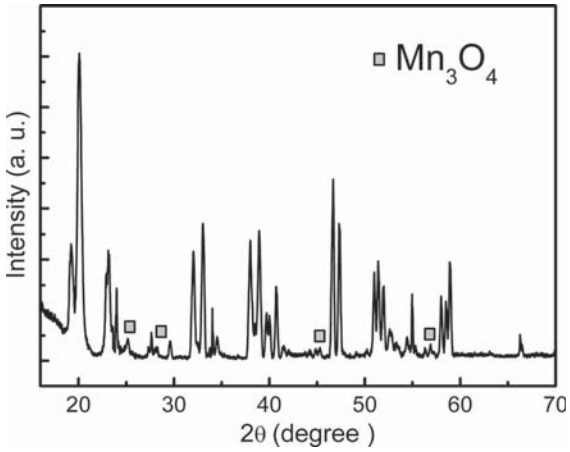

FIG. 1. XRD pattern of Bi_2NiMnO_6 nanoparticles fabricated by the electrospray method.

$b = 5.431$ Å, and $c = 9.552$ Å. The sharp peaks confirm the highly crystalline nature of the as-obtained sample. The impurity peaks are attributed to a small amount of Mn_3O_4.

Figure 2 shows SEM and TEM images of the as-prepared Bi_2NiMnO_6 nanoparticles. Clearly, the product consists of a high yield of spherical Bi_2NiMnO_6 nanoparticles. The size of the nanoparticles ranges from 100 nm to 350 nm. Because the charged droplets are self-dispersing in the electric field during the electrospraying process, all of the particles are dispersed without any agglomeration. A magnified SEM image of dispersed Bi_2NiMnO_6 nanoparticles is shown as the inset in Fig. 2(a). The nature of the products was also determined by energy dispersive spectroscopy (EDS) analysis. The EDS results confirmed that the as-obtained products contain Bi, Mn, and Ni with an atomic Bi: Mn: Ni ratio of ~2: 1: 1, which agrees with the expected stoichiometry and XRD results. TEM was used to further confirm the morphology and structure of the Bi_2NiMnO_6 nanoparticles, as shown in Fig. 2(b). A magnified TEM image of an individual Bi_2NiMnO_6 nanoparticle is shown as the inset in Fig. 2(b). The formation mechanism can be explained by the Ostwald ripening model. Initially, the Bi_2NiMnO_6 sol is electrosprayed to form self-dispersing charged droplets in a high-voltage electric field. The solvent will evaporate from the precursor once the droplets become attached to the heated substrate. Then, the nucleation and growth of the Bi_2NiMnO_6 particles take place. Some fragment-like dots

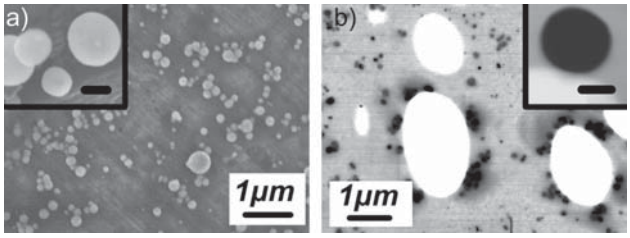

FIG. 2. (a) SEM image of as-prepared Bi_2NiMnO_6 nanoparticles. The inset shows a magnified view of the dispersed particles, on which some fragment-like dots are observed. (b) TEM image of Bi_2NiMnO_6 nanoparticles; the inset is a magnified view of an individual nanoparticle. The scale bars in both insets represent 100 nm.

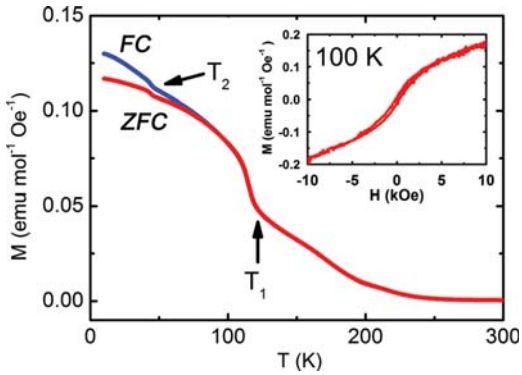

FIG. 3. (Color online) Magnetization as a function of temperature for Bi_2NiMnO_6 nanoparticles measured in the temperature range from 5 K to 300 K in a magnetic field of 100 Oe; the inset is the M-H loop measured at 100 K.

are formed on the nanoparticles [see inset in Fig. 2(a)]. Because the system tries to lower its overall energy, the dots on the surface will diffuse into the particles.

Figure 3 shows the magnetization (M) as a function of temperature (T) for Bi_2NiMnO_6 nanoparticles measured in the temperature range from 5 K to 300 K in a magnetic field of 100 Oe. Both zero-field-cooling and field-cooling measurements were conducted. The magnetic contribution from the substrate has been subtracted from the data. Two magnetic transitions were observed at $T_1 = 122$ K and $T_2 = 44$ K. In a previous study, it was reported that Mn_3O_4 undergoes a ferrimagnetic transition at ~42 K.[12] In our sample, the impurity Mn_3O_4 was detected in the XRD pattern. Therefore, the magnetic transition at T_2 should be attributed to Mn_3O_4 ferrimagnetic ordering. For Bi_2NiMnO_6, it is expected that Ni ions present a valence of +2 with e_g electrons, while Mn ions present a valence of +4 with no e_g electrons. According to the Goodenough-Kanamori rules,[13] the expectation for magnetic interaction between Ni^{2+} and Mn^{4+} should be ferromagnetic ordering with a linear arrangement of Ni-O-Mn. It is believed that T_1 observed in the M-T curve corresponds to the ferromagnetic transition temperature of Bi_2NiMnO_6. To further confirm the aforementioned analysis, the magnetization as a function of magnetic field (H) for Bi_2NiMnO_6 nanoparticles was measured in a magnetic field of 10 kOe at 100 K, as shown in the Fig. 3 inset. The hysteresis in the M-H loop should only be contributed by Bi_2NiMnO_6 at 100 K because it is far higher than the Mn_3O_4 ordering temperature. Clear hysteresis behavior has been observed. The coercive field is found to be 190 Oe.

The room temperature ferroelectricity of the Bi_2NiMnO_6 nanoparticles was then confirmed by KPFM measurements. To induce the ferroelectric dipoles (poling process), atomic force microscope (AFM) scans were carried out on a sample area of 1.5×1.5 μm^2 (scan speed of 19.6 Hz, 512 lines) in contact mode with the given biases of 0 V, 1 V, 3 V, and 5 V. Then, a second AFM scan of the 1.5×1.5 μm^2 area (scan speed of 19.6 Hz, 512 lines) with a grounded tip was performed on the same area to discharge the screening charge, which had accumulated during the poling process. Due to a reduction of the screening charge by the discharge process, the surface potential directly indicates the ferroelectric

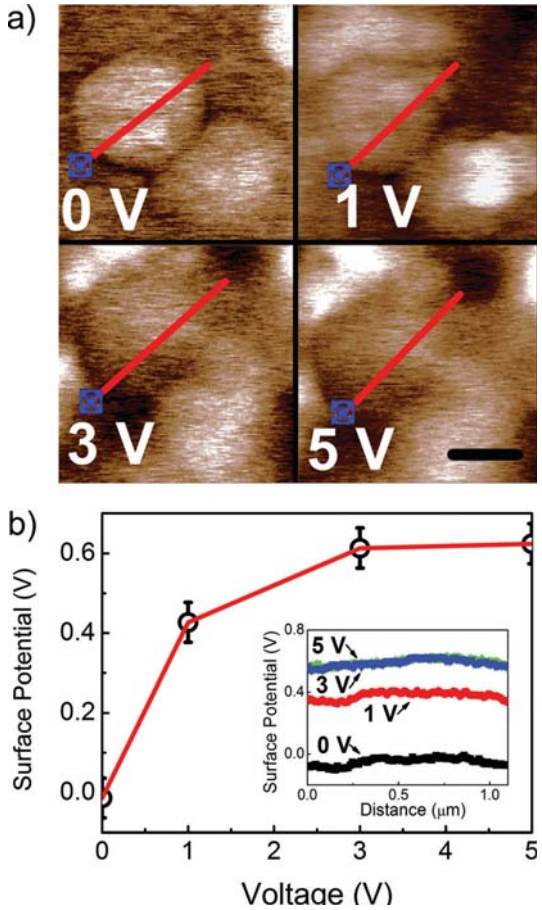

FIG. 4. (Color online) KPFM images of Bi_2NiMnO_6 nanoparticles: (a) Surface potential images of the sample with the given biases of 0 V, 1.0 V, 3.0 V, and 5.0 V. (b) The sample surface potential as a function of the bias voltage; the inset contains the line potential profiles of the KPFM images of an individual nanoparticle [corresponding to the red lines in Fig. 4(a)]. The scale bar represents 0.5 μm.

polarization charge distribution. Figure 4(a) shows surface potential images of Bi_2NiMnO_6 nanoparticles with various bias voltages. The polarized particles are brighter than the Si substrate due to their higher potential. The potential line profiles of corresponding individual Bi_2NiMnO_6 particles in Fig. 4(a) are shown in the inset of Fig. 4(b). Results indicate that the surface potential of Bi_2NiMnO_6 particles gradually increases when the applied bias voltage increases from 0.5 V to 5 V. The surface potential as a function of bias voltage for the Bi_2NiMnO_6 nanoparticles is plotted in Fig. 4(b). A nonlinear increase in the surface potential induced by the polarizing voltage is observed, which displays a switchable polarization behavior. The surface potential is saturated when the polarizing voltage is increased up to 3 V. The electric field for the saturation polarization is calculated to be about 600 kV/cm, which is much smaller than that of the Bi_2NiMnO_6 thin film samples,[14] indicating that the electric dipole can be easily switched in the nanoparticles under low electric field.

IV. CONCLUSION

Bi_2NiMnO_6 nanoparticles have been synthesized by a simple electrospray method. It is found that Bi_2NiMnO_6 nanoparticles crystallize in the monoclinic structure with space group *C121*. The self-dispersed nanoparticles show a spherical shape with a diameter of 100 nm to 300 nm. The ferromagnetic transition of Bi_2NiMnO_6 is confirmed at 122 K in the M-T curve. A coercive field of 190 Oe has been observed in the M-H loop. The room temperature ferroelectricity of the Bi_2NiMnO_6 nanoparticles has been investigated using KPFM by applying bias from 0 V to 5 V.

ACKNOWLEDGMENTS

The authors thank the Australian Research Council for providing funding support for this work (DP0987190, DP0558753, and FT 0990287). The authors also thank Dr. Z. P. Guo and Mr. Kouk Hau Seng for their help in sample preparation.

[1]H. Schmid, Ferroelectrics **162**, 317 (1994).
[2]N. Hur, S. Park, P. A. Sharma, J. S. Ahn, S. Guha, and S-W. Cheong, Nature **429**, 392 (2004).
[3]N. Ikeda, H. Ohsumi, K. Ohwada, K. Ishii, T. Inami, K. Kakurai, Y. Murakami, K. Yoshii, S. Mori, Y. Horibe, and H. Kitô, Nature **436**, 1136 (2005).
[4]Z. X. Cheng, X. L. Wang, S. X. Dou, K. Ozawa, and H. Kimura, Phys. Rev. B **77**, 092101 (2008).
[5]T. Kimura, S. Kawamoto, I. Yamada, M. Azuma, M. Takano, and Y. Tokura, Phys. Rev. B **67**, 180401(R) (2003).
[6]Y. Tokunaga, S. Iguchi, T. Arima, and Y. Tokura, Phys. Rev. Lett. **101**, 097205 (2008).
[7]L. Bi, A. R. Taussig, H. Kim, L. Wang, G. F. Dionne, D. Bono, K. Persson, G. D. Ceder, and C. A. Ross, Phys. Rev. B **78**, 104106 (2008).
[8]P. Baettig, C. Ederer, and N. A. Spaldin, Phys. Rev. B **72**, 214105 (2005).
[9]M. Azuma, K. Takata, T. Saito, S. Ishiwata, Y. Shimakawa, and M. Takano, J. Am. Chem. Soc. **127**, 8889 (2005).
[10]H. Zhao, H. Kimura, Z. Cheng, X. Wang, and T. Nishida, Appl. Phys. Lett. **95**, 232904 (2009).
[11]P. Padhan, P. LeClair, A. Gupta, and G. Srinivasan, J. Phys.: Condens. Matter **20**, 355003 (2008).
[12]Y. Q. Chang, X. Y. Xu, X. H. Luo, C. P. Chen, and D. P. Yu, J. Cryst. Growth **264**, 232 (2004).
[13]J. B. Goodenough, *Magnetism and the Chemical Bond* (Wiley, New York, 1963).
[14]M. Sakai, A. Masuno, D. Kan, M. Hashisaka, K. Takata, M. Azuma, M. Takano, and Y. Shimakawa, Appl. Phys. Lett. **90**, 072903 (2007).