3598 *Chem. Mater.* **2007,** *19,* 3598−3600

Rapid Synthesis of Multiferroic $BiFeO_3$ Single-Crystalline Nanostructures

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Received March 22, 2007
Revised Manuscript Received June 20, 2007

Multiferroic materials have attracted much attention because of their potential applications for new types of electronic devices, such as multiple-state memories and new data-storage media.[1−3] $BiFeO_3$ is one of the well-known multiferroic compounds having simultaneous ferroelectric ($T_C \approx 830$ °C) and G-type antiferromagnetic ($T_N \approx 370$ °C) properties above room temperature.[3,4] It possesses a rhombohedrally distorted perovskite structure.[4] The spontaneous polarization of $BiFeO_3$ in heteroepitaxially constrained thin films has been enhanced to almost an order of magnitude higher than that of single crystals.[3,5]

Much effort has been made to understand the dependence of physical and chemical properties of the ternary transitional metal oxides, such as $BaTiO_3$, $PbTiO_3$, and $SrTiO_3$, on the size and shape of the crystals in the material.[6,7] The synthesis method used to obtain the desired nanostructures is crucial for exploiting nanoscale electric, magnetic, and thermal properties. For the multiferroic material $BiFeO_3$, however, the limitedly available information relating to the size dependence of the physical properties is mainly due to the difficulty in preparing the pure $BiFeO_3$.[8] During the synthesis of $BiFeO_3$, the kinetics of phase formation in the Bi_2O_3−Fe_2O_3 system can easily lead to the appearance of impurity phases, such as $Bi_{25}FeO_{40}$ and $Bi_2Fe_4O_9$.[9−11] Generally, $BiFeO_3$ can be obtained with the help of leaching out the impurities by the diluted nitric acid.[9,12] Most recently, it was realized in the synthesis of pure $BiFeO_3$ ceramics by a rapid thermal technique.[11] Although previous work mainly involves films[3,13−15] and ceramics,[9,12] it is still a challenge to synthesize pure $BiFeO_3$ nanostructures. Furthermore, the available methods are based on complex solution processes or involve toxic precursors.[8,12,16] Therefore, it is also important to develop an environmentally friendly synthesis method. In the present work, a simple, large-scale synthesis method was performed to prepare $BiFeO_3$ nanostructures in NaCl−Na_2SO_4 salts by rapid sintering and quenching to room temperature in air. The dielectric properties are much enhanced in the $BiFeO_3$ prepared by the present method.

In a typical reaction, Bi_2O_3, Fe_2O_3, NaCl, Na_2SO_4, and NP-9 (nonylphenyl ether) were mixed in a molar ratio of 1:1:5:5:3, ground for 20 min, and then sonicated for 10 min. The mixture was transferred to a crucible, pretreated at 400 °C for 2 h, and then loaded into a furnace, where the temperature was maintained at 800 °C for 20 min before quenching to room temperature in air. Pure $BiFeO_3$ product was obtained after washing the quenched material several times with deionized water to remove the NaCl and Na_2SO_4 salts. The morphology and structure of the material were characterized by scanning electron microscopy (SEM, LEO1530), high-resolution transmission electron microscopy (HRTEM, JEM-2010), and X-ray diffraction (XRD, M21XVHF22). Raman-scattering data were collected using a Raman spectrometer (JY-T64000), and the ion oxidation states were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250). For the measurements of dielectric properties, the $BiFeO_3$ powders were pressed into pellets and then anealed at 760 °C, lower than its decomposition temperature, for 1 h. The dielectric constant and loss were performed on an impedance analyzer (HP-4274A and HP-4275A).

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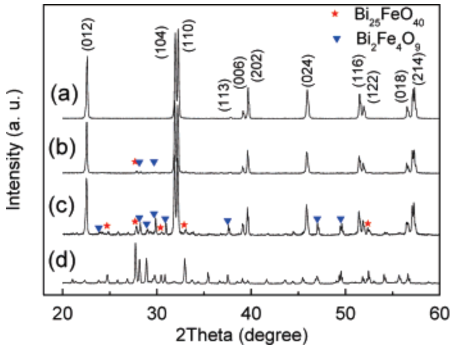

Figure 1. XRD patterns of samples sintered under different conditions: (a) 800 °C, 20 min; (b) 820 °C, 20 min; (c) 840 °C, 20 min; and (d) 800 °C and 20 min with a normal heating rate of 5 °C/min.

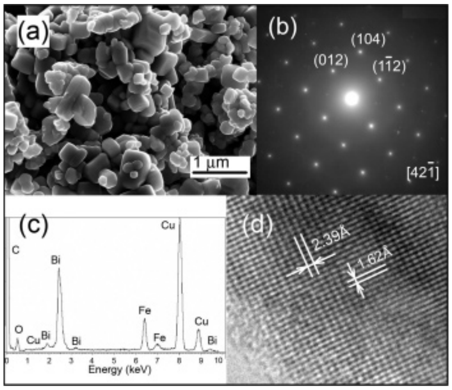

Figure 2. (a) SEM image, (b) selected area electron diffraction (SAED) pattern of a typical individual crystal, (c) EDS, and (d) HRTEM image of a single-crystalline nanocube for $BiFeO_3$.

The synthesis of highly pure $BiFeO_3$ is limited in a very narrow range of sintering conditions in molten $NaCl-Na_2SO_4$ salts. High purity $BiFeO_3$ can be formed only by sintering at a narrow temperature range of 800 ± 10 °C (Figure 1(a)). The XRD pattern of pure-phase $BiFeO_3$ can be indexed in a single phase (space group *R*3*c*, $a = b = 5.578(6)$ Å, $c = 13.866(5)$ Å), in good agreement with the literature data (JCPDS 86-1518). If the sample was sintered at a different temperature, such as 820 or 840 °C, $Bi_{25}FeO_{40}$ and $Bi_2Fe_4O_9$ will exist as impurities (plots b and c in Figure 1). The reaction between Bi_2O_3 and Fe_2O_3 to form $BiFeO_3$ can be completed in a very short time (20 min). Prolonging the sintering time will unexpectedly lead to some of the $BiFeO_3$ decomposing.[10] Another important feature of the present synthesis method is that the sample needs a high heating rate and quenching to room temperature. The high heating rate will avoid the formation of impurities, such as $Bi_{25}FeO_{40}$, during the heating process.[11] Figure 1d shows the XRD data of a sample subjected to a normal heating rate of 5 °C/min. Almost no phase of $BiFeO_3$ could be detected. The impurities formed during the heating process cannot be removed in the following sintering. According to the $Bi_2O_3-Fe_2O_3$ phase diagram, $BiFeO_3$ is an incongruently melting compound.[17] Quenching the sample is helpful in keeping the metastable $BiFeO_3$ single phase to room temperature.

The synthesis of $BiFeO_3$ was also tried in other types of salts, such as LiCl, KCl, NaCl, and their combined salts. However, pure $BiFeO_3$ could not be obtained. The oxygen anions of salts play an important role in the formation of pure $BiFeO_3$. The mechanism of formation needs further investigation. According to the present and previous work on the synthesis of ternary oxides,[6,18,19] it is believed that the type of salt used is an important condition in forming the desirable pure phase. The type of anion in the salt affects not only the crystal shape but also the formation of the products.[20]

Figure 2a presents the SEM image of the as-prepared pure $BiFeO_3$. It can be seen that $BiFeO_3$ mainly consists of cubic structures with an average size of ~300 nm. Some fine particles adhere to the large ones, indicating that the growth of $BiFeO_3$ could be due to the Ostwald ripening mechanism.[21] After the formation of $BiFeO_3$, the fine particles gradually dissolve into the $NaCl/Na_2SO_4$ flux and then redeposit on the larger particles. During the cooling process, the very small amount of dissolved $BiFeO_3$ in the $NaCl/Na_2SO_4$ flux precipitates as the very fine particles. Figure 2b shows a selected-area electron diffraction (SAED) pattern of a typical individual cube of $BiFeO_3$. The sharp diffraction spots indicate that $BiFeO_3$ nanocube is well-developed in the single-crystalline structure. The SAED pattern was indexed with space group *R*3*c* (No. 161) and lattice parameters of $a = b = 5.577$ Å and $c = 13.865$ Å, which are in good agreement with the presently studied XRD result and the literature data (JCPDS 86-1518). The EDS analysis confirms that the chemical composition of as-synthesized $BiFeO_3$ agrees with the nominal one 1:1:3 (Figure 2c). The elements of Cu and C originate from the TEM grid. Further high-resolution TEM (HRTEM) image reveals the nature of single-crystalline $BiFeO_3$ nanocube (Figure 2(d)). The interplanar spacings of about 2.39 and 1.62 Å correspond to (113) and (−330), respectively.

Figure 3 shows the Raman scattering pattern and XPS of Fe2p and O1s for as-prepared $BiFeO_3$. The Raman spectrum of as-synthesized $BiFeO_3$ shows negligible LO-TO splitting of A_1 symmetry in the lower-frequency region, indicating that the short-range interatomic force dominates over the long-range force in the bulk state of $BiFeO_3$ in contrast with epitaxial films.[13] The oxidation state of Fe and O was determined by XPS (Figure 3b). The main peak at 710.9 eV combined with two satellite peaks at 718.9 and 724.4 eV corresponds to Fe^{3+}.[11,22] No peaks of Fe^{2+} can be detected. It can confirm that the oxidation state of Fe ion is Fe^{3+}, but not Fe^{2+}. Furthermore, the symmetrically single XPS peak of O1s (532.2 eV) demonstrates that the $BiFeO_3$ product prepared in this work is a single phase compound, which is in good agreement with the ceramic obtained by the solid-state reaction method (insert of Figure 3b).[11]

Figure 4 shows the dielectric constant and loss of the $BiFeO_3$ ceramic by the present method. The dielectric

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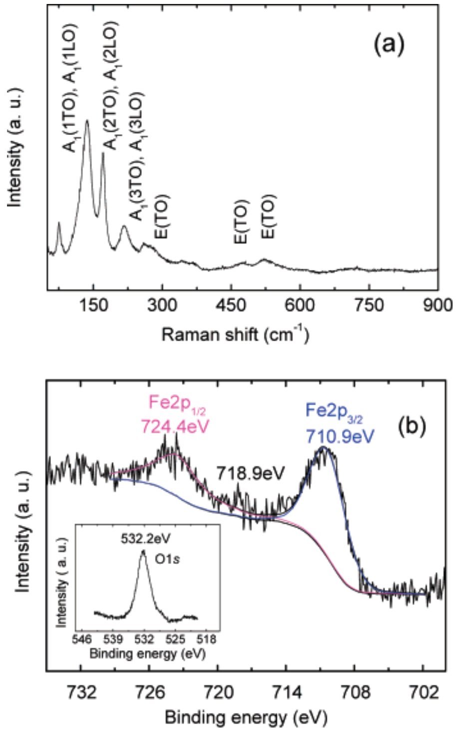

Figure 3. (a) Raman-scattering pattern, and (b) XPS pattern of Fe2*p* and O1*s* for as-prepared $BiFeO_3$.

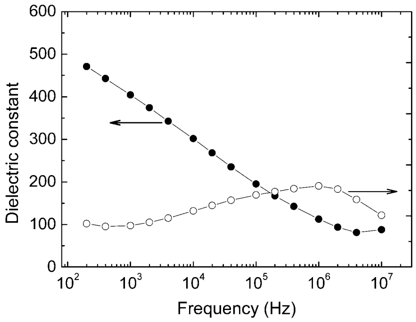

Figure 4. Dielectric constant and loss of $BiFeO_3$ as a function of frequency.

constant decreases almost linearly in the whole frequency range of 200 Hz to 10 MHz. The decrease in the dielectric constant with an increase in frequency reveals the anomalous dispersion of the dielectric constant in low and intermediate frequency range, which can be explained by the phenomenon of dipole relaxation.[23] It needs to be noted that the dielectric constant of $BiFeO_3$ prepared by the present method is much enhanced when compared with those previously reported $BiFeO_3$ in ceramics[9,12,24,25] or films.[14,15] The dielectric constant is in the range of $\epsilon_r < 120$ for the $BiFeO_3$ ceramics prepared by the solid-state reaction and in the range of $\epsilon_r < 300$ for the sol−gel derived thin film[14,15] and the nanotube arrays.[26] For the dielectric loss, a resonance peak is observed at about 1 MHz where the dielectric loss increases with increasing frequency below 1 MHz and then decreases up to 10 MHz. The appearance of such resonance peak can be ascribed to the jumping of ions under external field. A natural frequency exists in the ions jumping between two positions of equal potential energy. As the external alternating electric field equal to this natural frequency, maxium electrical energy is transferred to the oscillation ions and thus dielectric loss increases markedly. It needs to be noted that the dielectric constant for the decomposed $BiFeO_3$ ceramic sintered at a higher temperature, such as 850 °C, decreases dramatically to one tenth that of $BiFeO_3$.

In conclusion, a simple synthesis method has been successfully employed to prepare $BiFeO_3$ nanostructures in a $NaCl-Na_2SO_4$ salt. The pure $BiFeO_3$ forms over a very limited temperature range and a short time. The type of salt anion is an important parameter in pure phase formation. This method could be also exploited to prepare other $BiFeO_3$-based compounds and important multiferroic materials.

Acknowledgment. This work was supported by National Natural Science Foundation of China (20331030, 50374009) and Funds of Ministry of Education of China for PCSIRI.

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