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Enhanced magnetization and suppressed current leakage in BiFeO₃ ceramics prepared by spark plasma sintering of sol–gel derived nanoparticles

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ABSTRACT

BiFeO₃ (BFO) ceramics of different grain size have been synthesized by spark plasma sintering of sol-gel derived nanoparticles. It was found that with decreasing grain size there occurs an enhancement in magnetization and a simultaneous suppression in current leakage. According to systematic materials characterization, the enhanced magnetization is attributed to the enriched grain boundaries where the missing structural order perturbs the spin helix structure of BFO and thus generates uncompensated spins, while the reduced current leakage is ascribed to fewer conduction paths provided by the compacted grain structure.

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1. Introduction

Among the so-called multiferroics [1-3], BiFeO₃ (BFO) has generated increasing interest from the community of science and technology because it possesses spontaneous magnetic and polar orders well above room temperature [4]. In spite of remarkable progress in the development of BFO, some issues relevant to its realistic application demand further investigation. First, the G-type antiferromagnetic (AF) structure of BFO modulated by a spin helix with a period of ~ 62 nm cancels out the total magnetization and disadvantageously disenables the linear magnetoelectric effect [5,6]. Second, it is notorious that BFO bulk ceramics are often not resistive enough to sustain a substantial ferroelectric polarization. From a practical standpoint, it is therefore imperative to acquire macroscopic magnetization while reducing the current leakage.

Recently, enhanced magnetization [7–15] and even strong multiferroic coupling [16] were reported in BFO nanoparticles. Although the nanoscale limits a direct electrical assessment of the polarization [16], the BFO nanoparticle work is inspiring because it would be interesting to fabricate fine-grained ceramics through sintering of BFO nanoparticles. As a newly developed method, the spark plasma sintering (SPS) consolidates powders into bulk material by applying pulsed current and *in situ* pressure. Compared

to the conventional solid state reaction, the SPS process has the salient merits of low sintering temperature and short sintering time. Accordingly, this technique can be exploited to prepare fine-grained samples by avoiding excessive grain growth, and meanwhile the resulting densification should reduce the current leakage [17–19]. In this work, we synthesized BFO bulk ceramics of different grain size through SPS of sol–gel derived nanoparticles. We demonstrate that upon decreasing the grain size there indeed occurs an enhancement in the magnetization and a suppression in the current leakage. Based on systematic sample characterization, we discuss the possible reasons and the perspective of the observed grain-size effect.

2. Experimental

For preparing BFO nanoparticles, analytical grade $Fe(NO_3)_3 \cdot 9H_2O$ and $Bi(NO_3)_3 \cdot 5H_2O$ were first dissolved in deionized water and citric acid ($C_6H_8O_7$), and then mixed with glacial acetic acid (CH_3COOH) as starting materials. Ammonia was successively added to the resulting transparent solution, which was under constant magnetic stirring. The obtained solution was kept at 140 °C for 24 h until a fluffy dried gel was formed. The resultant gel was then transferred to a crucible, and preheated to 300 °C at a heating rate of 5 °C min⁻¹ to remove the organic compounds and NO_3^- . Afterwards, the powders were calcined at 300, 600 and 820 °C, for 10 min before quenching to room temperature. For fabricating BFO ceramics, the sol–gel derived nanoparticles were pressed into



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pellets under 30 MPa in a cylindrical graphite die. The sintering process was performed at 720 °C for 10 min with a heating rate of 100 °C min⁻¹ using an SPS apparatus (SPS-1050). The SPS samples sintered from the fine powders calcined at 300, 600 and 820 °C, are denoted as BFO-300, BFO-600 and BFO-820, respectively.

Phase composition and crystalline structure were investigated by the standard θ – 2θ X-ray diffraction (XRD) using a diffractometer (Rigaku) with Cu K α radiation. The microstructure of the ceramic samples was studied by scanning electron microscopy (SEM) (Hitachi S-4800). The Raman scattering measurements were performed on a high-resolution micro-Raman spectrometer (Jobin Yvon HR800). The magnetization was measured using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design) and a SQUID vibrating sample magnetometer



Fig. 1. X-ray diffraction patterns for the sol-gel derived BiFeO₃ particles calcined at 300, 600 and 820 °C. The asterisks indicate the minor impurity phases of $Bi_2Fe_4O_9$.

(Quantum Design). The ferroelectric polarization and the current leakage behavior were measured at room temperature using a Radiant WS-2000 test system. For applying a strong electric field, the ceramic disks were polished into thickness less than 1 mm, and silver (or indium) electrodes with size of approximately 7 mm² were pasted (or pressed) on both surfaces to form metal/oxide/ metal capacitors. Differential thermal analysis (DTA) was performed with a Netzsch STA 449 system in synthetic air with 10 °C min⁻¹ heating and cooling rates.

3. Results and discussion

Fig. 1 shows the XRD patterns of the calcined powders. Besides the peaks associated with the predominant R3c phases for BFO, additional peaks at approximately $2\theta \sim 28^{\circ}$ indicate the presence of minor Bi₂Fe₄O₉ impurities. Nevertheless, by increasing the calcining temperature to 820°, the impurity phase was found to be significantly suppressed (less than 4% estimated from the peak intensity). A higher calcining temperature leads to sharper diffraction peaks and accordingly larger particle size. According to the Scherrer equation, $D_p = 0.94\lambda/(\beta \cos \theta)$, where λ is the X-ray wavelength, and β is the half maximum diffraction peak width, the average particle size D_p can be evaluated using the (024) peak. For the powders calcined at 300, 600 and 820 °C, $D_p \sim 18$, 32, and 46 nm, respectively. In Fig. 2, we show the SEM images of the SPS samples and a referential ceramic sample (BFO-CS) prepared by the conventional solid-phase reaction method. As revealed by the statistical histograms (Fig. 3), the average grain sizes (D_g) for BFO-300, BFO-600, BFO-820 and BFO-CS are approximately 1.2, 2.9, 3.5 and 13 μ m, respectively. Compared to their starting calcined powders, D_gs for all of the SPS samples increase; however, they are still much smaller than that of BFO-CS. Furthermore, with reduction of D_g , more compacted and coherent grain structure is exhibited in BFO-300.

Fig. 4 displays the XRD patterns for the SPS samples. The rhombohedral phase for BFO is well retained. The impurity phase $(Bi_2Fe_4O_9 \text{ and/or } Bi_{25}FeO_{39})$ is present, but still in a minor amount (less than 7 %). The lattice constants for BFO were calculated using



Fig. 2. Scanning electron micrograph of a fresh fractured surface of (a) BFO-300, (b) BFO-600, (c) BFO-820, and (d) BFO-CS which was sintered at 860 °C for 3 h using a conventional solid-state reaction method.

JADE. For BFO-300, *a*=5.5820 Å, *c*=13.8591 Å; for BFO-600, a = 5.5796 Å, c = 13.8666 Å; and for BFO-820, a = 5.5760 Å, c = 13.8781 Å. There is a slight expansion and shrink in a and c axes, respectively, as the grain size is decreased. In Fig. 5, we show the Raman spectra measured at room temperature. According to group theory analysis, the R3c structured BFO permits 13 Raman active phonons that can be summarized by the irreducible representation: $\Gamma = 4A_1 + 9E$ [20–25]. As assigned in the spectrum, three A_1 modes (138, 172.4, 218.7 cm⁻¹) and seven E modes (75.5, 261.1, 277.4, 345.7, 372.4, 476.2, and 523.3 cm⁻¹) can be clearly detected in all of the SPS samples. There is no obvious peak shifting between the spectra. However, the peak intensity for the $A_1 - 2$ mode is relatively decreased in BFO-300. Note that a similar change in peak intensity was observed in $Bi_{1-x}La_xFeO_3$ (x ≤ 0.15) [23] and the A_1 mode has been found to be governed by Bi-O covalent bonds. The observed weakened intensity may reflect some broken Bi-O bonds at the enriched grain boundaries because of the smaller grain size.

Both the initial magnetizing curve (M-H) and the hysteresis loop were measured at 5 K. As shown in Fig. 6(a) and its low-field detailed view (Fig. 6(b)), the initial M-H curve of BFO-820 shows a weak level of magnetization with nearly linear behavior at low and high fields, indicating a prevalent AF response. The linear field dependence at low and high fields is still present in BFO-600 and BFO-300. However, with decreasing grain size, a shoulder-like feature appears at approximately 2 kOe in the these two samples, and meanwhile the magnetization was moderately increased in BFO-600 and much enhanced in BFO-300. Fig. 6(c) displays the low-field data of the hysteresis loops, showing that the hysteresis also develops with decreasing grain size. Both the shoulder-like feature and the hysteresis shown in the low-field region clearly indicate an emergent ferromagnetic (FM) component embedded in an AF matrix. Note that a coexistence of FM and AF components would give rise to an exchange bias phenomenon [26]. To check this issue, we compared the hysteresis loops of BFO-300 measured in zero field cooling (ZFC) and field cooling (FC). As illustrated in Fig. 7, the hysteresis loop measured at 5 K under ZFC shows an equivalent left and right coercive fields. In contrast, by FC in 50 kOe which should saturate the FM component and establish a unidirectional exchange anisotropy, an exchange bias behavior manifested by a negative loop shift (\sim 63 Oe) was consistently observed.



Fig. 3. Statistical distribution of the grain size of (a) BFO-300, (b) BFO-600, (c) BFO-820, and (d) BFO-CS, obtained from their SEM images.



Fig. 4. X-ray diffraction patterns for the SPS samples (a) BFO-820, (b) BFO-600, and (c) BFO-300. Note that l/l_{max} is the X-ray intensity normalized by the maximum. The circles and asterisks indicate the minor impurity phases of Bi₂₅FeO₃₉ and Bi₂Fe₄O₉, respectively. The inset shows the XRD profile in the vicinity of the (311) reflection of Fe₃O₄ using a normal scan rate (1 s for 0.02°) and a slow scan rate (10 s for each 0.02°).

It should be mentioned that the FM response previously reported in BFO ceramics and thin films were attributed to impurity phases like Fe₃O₄ [27] and Bi₂₅FeO₃₉ [28]. In our case, no trace for Fe₃O₄ was detected from the XRD patterns (Fig. 4) at a normal scan rate (dwell for 1 s for each 0.02°). To verify whether the sample is truly free from tiny amounts of Fe₃O₄ clusters, we recorded the powder XRD pattern using a very slow scan (dwell for 10 s for each 0.02°) in the vicinity of $2\theta = 36.6^\circ$, at which Fe₃O₄ has the most intense reflection (311). As shown in the inset of Fig. 4, no peak profile was observed in that region. On the other hand, the tiny amounts of Bi₂₅FeO₃₉ as well as Bi₂Fe₄O₉ impurity phases appear at a slightly higher concentration in BFO-820 than in BFO-300, but a linear *M*–*H* behavior is exhibited in the former compound. These facts indicate that the issue of the FM component in BFO-300 is unlikely to involve the impurities.

To shed more light on the enhanced magnetization, we measured the temperature dependence of magnetization (M-T) from 5 to 300 K using an external magnetic field of 1 kOe. As shown in Fig. 8(a), the magnetization of BFO-820 under both ZFC and FC first decreases upon cooling and then increases below



Fig. 5. Raman spectra of the SPS samples measured at room temperature. The vertical lines at the position of the assigned Raman modes are guides for the eyes.

 \sim 120 K, exhibiting only minor thermomagnetic irreversibility. Similar thermomagnetic behavior was also reported in BFO films [29], polycrystalline ceramics [30] and single crystals [31], and the upturn at approximately 120 K was recently attributed to an intrinsic spin-reorientation transition [31]. For BFO-600 and BFO-300 (Fig. 8(b) and (c)), the FC M-T curves are analogous to that of BFO-820, but the ZFC curves deviate remarkably from the FC curves by displaying a drop, which is sharper in BFO-300, at approximately 120 K. Generally, the thermomagnetic irreversibility arises either from nucleation of domains (domain walls) in a FM material [32] or from the freezing of FM and AF clusters in a magnetic glass system [33]. For the present case, the large thermomagnetic irreversibility in BFO-300 agrees well with the existence of FM clusters coupled to an AF matrix. Moreover, the sharper drop of thermomagnetization displayed in BFO-300 (which has a smaller and more coherent grain structure) indicates that the FM clusters are very likely stemming from the grain boundaries, where the missing structural order breaks the spin helix structure of BFO, and accordingly yields uncompensated spins. In BFO and other fine AF particles [34-36], the uncompensated spins would form shell-like FM clusters attached to the AF cores (grains), where the AF-FM interfaces are essential for observation of exchange bias behavior. Because a smaller grain size corresponds to a larger volume of grain boundaries, one naturally observes an obvious FM enhancement in BFO-300.

The electric hysteresis (*P*–*E*) loops for the BFO ceramics were measured at different applied electric fields. For BFO-CS, its low resistivity ($\sim 10^6 \Omega$ cm) makes the ferroelectric measurements difficult. In contrast, the ferroelectric *P*–*E* loops with an unsaturated polarization can be obtained for all of the SPS specimens. As shown in Fig. 9(a), application of higher electric fields (>4.8 kV/cm) was restricted in BFO-820. However, the breakdown fields in BFO-600 and BFO-300 were markedly increased (Fig. 9(b) and (c)), indicating that the current leakage should be efficiently suppressed in these compounds. To further confirm this explanation, the leakage behavior was directly measured, and Fig. 10 plots the leakage current density versus the electric field (*J*–*E*) curves. It can be seen that the current leakage was indeed



Fig. 6. (a) Initial magnetization vs. magnetic field (M-H) curves of BFO-300, BFO-600 and BFO-820 measured at 5 K. (b) A detailed view of the low-field behavior of the initial M-H curves shown in (a). The straight lines shown in (a) and (b) are linear fits of M-H at low- and high-fields, respectively. (c) Magnetization hysteresis loops measured at 5 K, where only low-field regions are shown for viewing the developing hysteresis.



Fig. 7. Magnetization hysteresis loop of BFO-300 measured at 5 K after FC in 50 kOe and ZFC from 300 K. The insets magnify the low-field region of the ZFC and FC loops. Note that a remnant magnetic field of \sim 7 Oe for the superconductor magnet has been taken into account in the calculation of the exchange bias field.

greatly decreased with decreasing grain size. Fig. 11 shows the DTA curves measured for the SPS ceramics. In all specimens the first-order ferroelectric transition occurs at nearly the same Curie temperatures (T_c) assigned by the endothermic peaks at T_{endo} in cooling and by the exothermic peaks at T_{exo} in heating. For BFO-300, T_{endo} =824.4 °C, T_{exo} =808.3 °C; for BFO-600, T_{endo} =825.8 °C, T_{exo} =809.3 °C; and for BFO-820, T_{endo} =823.3 °C, T_{exo} =810.5 °C. They are close to those reported in BFO single crystals [37]. This fact indicates that the suppressed current leakage should not be linked with an effect of a phase transition [38]. As supported by the SEM observations, we argue that the experimental results can be explained by the fact that the more compacted grain structure provides fewer conduction avenues in fine-grained samples.



Fig. 8. Temperature dependence of magnetization measured in 1 kOe under ZFC and FC for (a) BFO-820, (b) BFO-600, and (c) BFO-300.



Fig. 9. Room temperature P-E loops of (a) BFO-820, (b) BFO-600, and (c) BFO-300 measured at 1 kHz up to different electric fields.



Fig. 10. Current leakage density vs. electric field (J-E) curves measured for In/BFO/ In capacitors at room temperature.



Fig. 11. Differential thermal analysis of (a) BFO-820, (b) BFO-600, and (c) BFO-300.

4. Summary

To summarize, BFO ceramics of different grain size have been successfully prepared by the SPS technique using sol-gel derived nanoparticles. With decreasing grain size, the magnetization is enhanced, while the current leakage is suppressed. Note that the present magnetization and polarization values are still far from ideal for BFO. However, by optimizing the SPS parameters, e.g., exploiting higher heating rate, larger *in situ* pressure, and even lower sintering temperature, one may fabricate *nanograined* BFO bulk ceramics with further improved magnetization and polarization.

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