



Ferroelectric domain evolution in gold nanoparticle-modified perovskite barium titanate ceramics by piezoresponse force microscopy

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ABSTRACT

This work addresses the domain evolution processes in polycrystalline barium titanate (BaTiO₃, BT)-based ceramics containing various amounts of gold nanoparticles (AuNPs) as an additive by using piezoresponse force microscopy (PFM). The obtained PFM images of the AuNPs-modified BT ceramics revealing the change of one spontaneously polarized state to another under various applied direct current (DC) voltage are discussed in terms of their domain topology, PFM phase shift and PFM amplitude. In general, complex microstructures containing almost round-shaped and micron-sized grains, and grain boundary regions are clearly seen in the topographic images of all samples. The obtained results point towards possibility of control the polarization switching of the AuNPs-modified BT ceramics with fined-grains sizes, by a selection of the proper applied DC voltage (V_{DC}). The PFM investigation confirmed good dipole orientation within the AuNPs-modified BT ceramics containing submicron grain size at the elevated external fields and proved the lack of convenient domain switching of the unmodified BT case resulting from their larger grain size.

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1. Introduction

Recently, tremendous utilizations of lead-free ferroelectric ceramics particularly in the development of data storage devices for the next generation of information technology have been realized based on increasing sophisticated ferroelectric domain patterning [1, 2]. Therefore, much attention in the area of domain evolution processes caused by applied electric field and/or mechanical stress has been focused on recording ferroelectric domain patterns and also monitoring domain growth (*i.e.* polarization switching and domain wall motion [2]). In connection with this,

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perovskite BT-based compounds are of particular interest as they are one of the most popular lead-free ferroelectric/piezoelectric materials employed in numerous existing commercial devices [3–5]. For most practical data storage applications, additive modified polycrystalline BT ceramics are more important than single crystal mainly because a good control over grain size and electrical characteristics can be obtained by tailoring the additive type and concentration, which lead to a wide range of applications [6].

In general, each area of the ferroelectric materials in which the spontaneous polarization points in one direction only, so-called “ferroelectric domain”, are separated by a domain wall (*i.e.* domain boundary) [7]. Under static conditions, several techniques may be employed to visualize domain configurations of BT-based ceramics including optical [8] and electron microscopy [3, 9]. One major source of the microscopic behavior of these ferroelectric ceramics for switching processes has been the use of neutron/X-ray/electron backscatter diffractions to indicate reorientation of the crystal lattice [9–11]. However, these techniques do not resolve the individual domains of such materials. Previously, etching in conjunction with a standard optical microscope is a typical approach to obtain an image of the domain structure and can be accomplished in any laboratory without the requirement of any specific facilities. Although, the use of optical microscopy to observe large domains in ferroelectrics is well-known, but this technique is unsuitable for the submicron domains found in fine-grained and opaque BT-based ceramics [12].

As mentioned above, it is fairly difficult to obtain images with ultrafine features of the samples especially in the absence of flat surface. To avoid optical problems such as lens aberration, contrast error and etc., electron microscopy imaging of the etched patterns with significantly higher resolution is appropriate [9]. On the other hand, since the straightforward technique of PFM was introduced by Güthner and Dransfeld in 1992 [13], this technique has become a promising approach for revealing ferroelectric domain patterns with a high lateral resolution of about 10 nm and has also proven to be extremely sensitive as it allows measurement of local surface displacements in the sub-pm regime [14]. Moreover, taking the advantage of the fact that ferroelectricity entails piezoelectricity, the domain pattern can be visualized by its piezomechanical deformation under the application of an electric field. In the case of PFM, the electric field is applied locally to the sample with the help of the tip [2]. Owing to its versatile, easy-to-handle, non-invasive technique for imaging ferroelectric domain patterns on any kind of ferroelectric material without the need of an elaborate sample preparation, PFM technique has been attracting growing attention [2, 12]. To the best of our knowledge, no attempt has been made to use PFM technique to investigate domain patterns and also domain growth of AuNPs-modified BT ceramics which showed significantly almost 3-times-improved dielectric constant maxima and around 2-times-reduced dielectric loss values compared with unmodified BT ceramics, reported in our previous work [15]. Thus, the aim of this work is to explore domain evolution processes in polycrystalline BT-based ceramics containing various amounts of AuNPs. This is of significance because understanding the structure of these polarized BT-based ceramics and

their polarization procedure is a fundamental necessity both for the development of novel materials and to improve their potential device performance [12]. Moreover, to date, no conclusive experimental data of such materials are available.

2. Experimental

The platelet-shaped samples of AuNPs-modified BT ceramics (AuNPs contents are 0.0, 2.0, 4.0 and 8.0 mol%) were fabricated by employing a simple mixed-oxide method, detailed in [15]. Ferroelectric domain configurations were characterized by commercial PFM model XE-120 (Figure 1). The working principle of PFM is based on the detection of a local piezoelectric vibration signal generated by the converse piezoelectric effect when an external dc voltage is applied between the PFM tip and the sample bottom electrode. The amplitude and phase signal of PFM are directly related to the amplitude of the effective piezoelectric coefficient and the polarization orientation, respectively. A platinum/titanium-coated silicon cantilever with spring constants of 14 N/m and a resonance frequency of 70 kHz was used for domain imaging in PFM on applying a 7.2 kHz, 4.5 V (peak to peak) modulation voltage. All measurements were performed in the ambient environment and room temperature. To characterize the piezoelectric properties, the ceramic specimens were coated with silver paint on the upper and bottom surfaces and fired at 600°C for 20 min.

3. Results and discussion

Representative topographic atomic force microscopy images obtained from BT ceramics containing various amounts of AuNPs additive are given in Figure 2. In general, the bright and dark contrast in these micrographs represent topological variations of the sample's surface, in analogous to the typical scanning electron microscopy (SEM) image where dark areas represent depressions of the surfaces

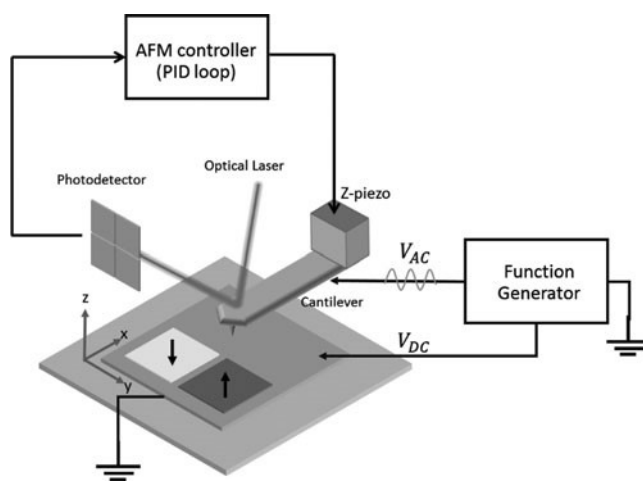


Figure 1. PFM diagram.

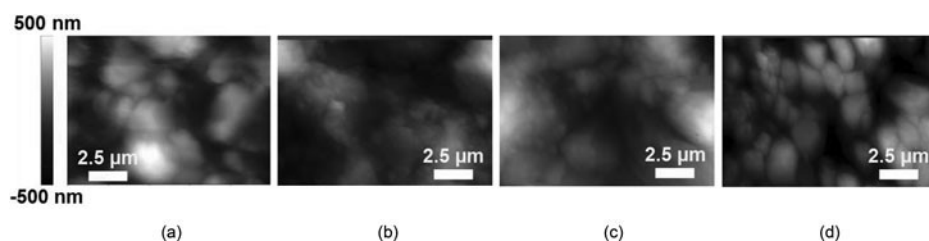


Figure 2. Topographic images of BT ceramics with (a) 0.0 mol%, (b) 2.0 mol%, (c) 4.0 mol% and (d) 8.0 mol% of AuNPs sintered at 1250°C for 2 h.

and brighter areas are relatively higher [16]. Round-shaped and micron-sized grains, and grain boundary regions are clearly seen in the topographic images of all investigated samples [5, 17]. Clearly, the topographic image of unmodified (*i.e.* 0.0 mol% AuNPs) BT ceramics (Figure 2(a)) presents several grains with the grain boundaries distinguished by a sharp change in contrast, in agreement with those observed by Buscaglia et al. [4]. Interestingly, it is likely that individual micron-sized grains of AuNPs-modified samples (Figure 2(b-d)) exhibited the dispersion of nano-sized particles which could be the AuNPs additive. This finding is also similar to those observed by Shen et al. [18]. Moreover, the AuNPs-modified BT samples possessed the uniform microstructure with relatively smaller grain size when compared with the unmodified BT sample, coherent with our previous research regarding their corresponding microstructures obtained by SEM technique [15]. The estimated grain sizes obviously measured from the 8.0 mol% AuNPs-modified BT samples (Fig. 2(d)) are in the range of $\sim 0.6 - 3.1 \mu\text{m}$ while larger grain sizes of unmodified BT ceramics are $\sim 1.0 - 4.0 \mu\text{m}$. This observation strongly supported our previous discussion which was mentioned that tailoring of BT ceramics with AuNPs additive could inhibit the ceramic grain-growth, resulting in an increase of dielectric constant (*i.e.* in this case, the magnitude of the dielectric constant strongly depends on the ease of polarization or the dipole switching [1]) of the ceramics [15]. To further investigate the polarization mechanism related to ferroelectric/piezoelectric properties of the BT ceramics containing various amounts of AuNPs content, PFM technique was conducted for mapping the ferroelectric domains and studying the local polarization switching in which variations in the orientation of the polarization can be distinguished through changes in the phase of the piezoelectric deformation of the sample subjected to the action of an oscillating electric field.

To complete a piezoelectric image, both amplitude and phase parameters have to be carefully monitored as shown in Figure 3. For PFM image recording, the conducting tip is scanned in contact mode with upper surface of samples while different V_{DC} is applied between the tip and Ag electrode at lower surface. As the domains in one grain attempt to switch, they are constrained by the differently oriented neighboring grains. The PFM phase features indicate the changing or inform the information of domain orientation where 0° means in-phase (IP) piezoresponse to the driving voltage, results in an expansion of the domain, while 180° means out-of-phase (OOP) response, results in a contraction of the domain. The PFM phase images for all

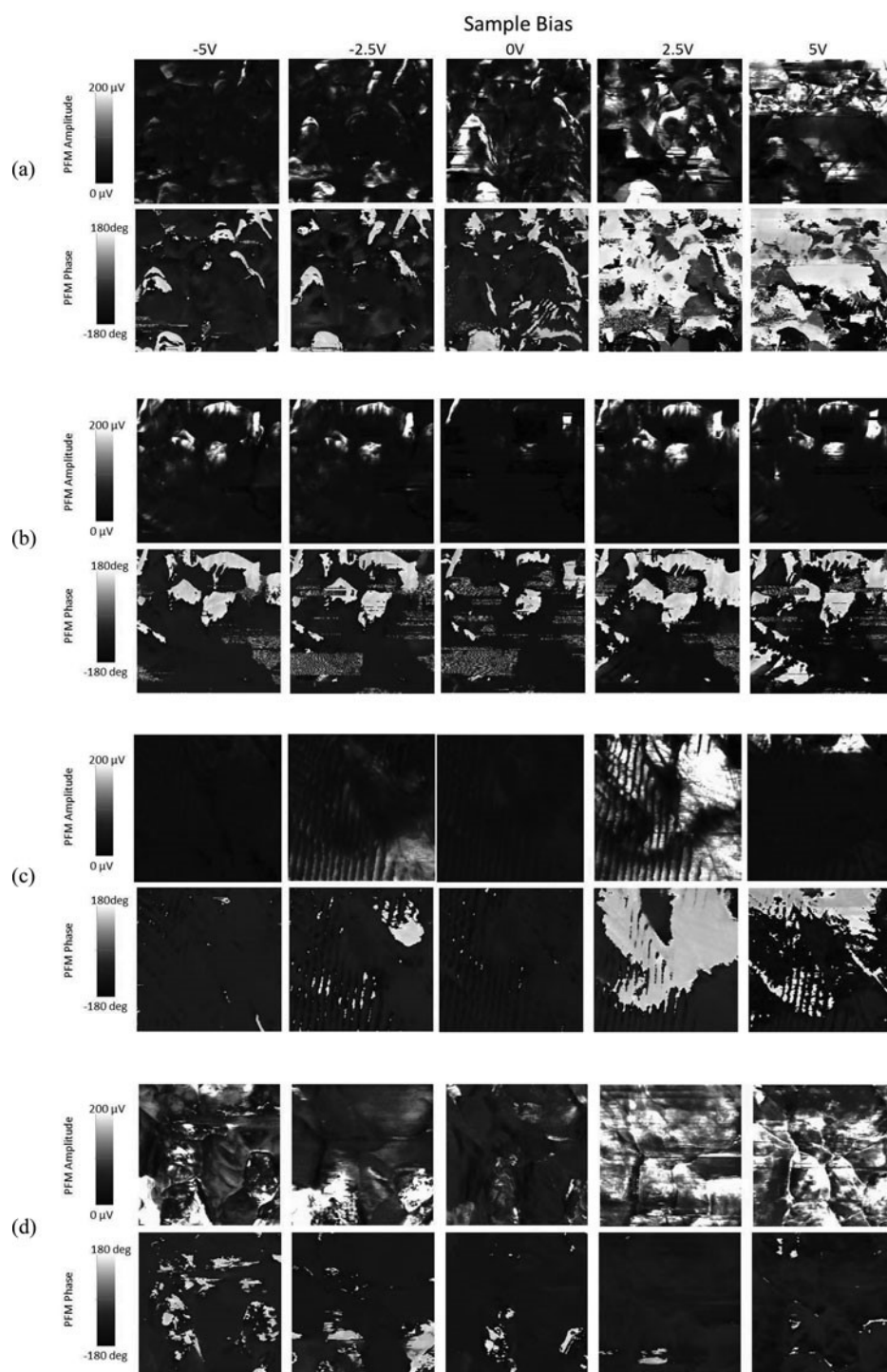


Figure 3. Amplitude (upper panel) and phase contrast (lower panel) PFM images of BT ceramics with (a) 0.0 mol%, (b) 2.0 mol%, (c) 4.0 mol% and (d) 8.0 mol% of AuNPs sintered at 1250°C for 2 h.

samples, except 8 mol% AuNPs-modified BT, indicate that applying positive V_{DC} (up to 5 V) causes significant 180° phase changes, *i.e.* create more OOP domains, more than applying negative V_{DC} (Figure 3, lower panels). It means that before applying voltage, most of domains point upward to the scanned surfaces [19]. Additionally, when the positive V_{DC} was applied to unmodified BT samples, the 90° domains seem to be observed. Both 180° and 90° polarization switching of ferroelectric walls can be ascribed to the minimization of the electrostatic energy and the elastic energy, respectively [20]. However, the most obvious phase shift (180° domains) can be observed from applying positive 2.5 V to 4.0 mol% AuNPs-modified BT ceramics. This information indicates that the amount of AuNPs affected on the orientation polarization, *i.e.* the higher amount of AuNPs additive, the more polarization reversal obviousness when the opposite V_{DC} was applied, revealing superior piezoelectric characteristics. As a consequence, higher dielectric constant values (because of the easier domain switching resulting in higher polarization) could be obtained from the AuNPs-modified BT ceramics than that obtained from unmodified BT sample, as evidence in our earlier work [15]. Nevertheless, applying unsuitable V_{DC} for each condition such as applying positive 5 V to 4.0 mol% AuNPs-modified BT does not provide more phase shift but the opposite result was found. In this case, it might be explained by too much energy from too much applied voltage can cause the creation of newly reverse domains. As a result, their effective piezoelectric coefficients (d_{33}) will cancel each other as the integrated effect of two cylindrical head-to-head (tail-to-tail) domains in agreement with Kholkin et al. [21]. In the same way, the reason for no observed phase change by applying positive V_{DC} only up to 5 V to 8.0 mol% AuNPs-modified BT sample as mentioned above might be due mainly to insufficient energy to create the stable domains of opposite polarity [21]. These observations pointed out that the orientation polarization of the samples might be tailored by applying the negative or positive V_{DC} dependent on their chemical compositions. By the way, since the different shade is referred to the direction of the polarization projection onto the samples, it can be inferred that all investigated samples have average non-zero piezoresponse in this poled state (± 5 V). However, judging from only the phase image cannot provide the exact characteristics such as those found in 8 mol% AuNPs-modified BT case where it looked like that no domains exist in the scanning area. Therefore, it is also important to measure the PFM amplitude.

In this connection, the amplitude piezoresponse images of these samples are also given in Figure 3 (upper panels). The different shade in images exhibited different piezoresponses (weak; the darker area and strong; the brighter area) or degree of effective d_{33} coefficient. By applying positive, all samples exhibit apparently strong piezoresponse more than applying negative V_{DC} . The strong piezoresponse areas (*i.e.* the brighter area) in 4.0 mol% and 8.0 mol% AuNPs-modified BT ceramics are much larger than that of unmodified and 2.0 mol% AuNPs-modified BT cases. These variations could certainly support the differences in their dielectric properties, as mentioned earlier. This finding especially for 4.0 mol% AuNPs-modified BT sample which show the most obvious phase change as described above could be

comparable to Zhao et al. research [22]. In this case, they applied a negative bias to Pb-based perovskite ferroelectric system of lead magnesium niobate-lead titanate (PMN-PT) ceramics, with various ratios of PMN/PT, from -10 to -70 V to create a reversed polarity domain and found that the fluctuation of PT content affected on the domain configurations and domain dynamic response. They reported that the reversed polarization of macrodomain area in PMN-35%PT and PMN-25%PT exhibited a relatively higher response behavior and better polarization retention performance than that of microdomain in PMN-10%PT and PMN-20%PT. Again, it was noticeable that applying positive 5 V to 4 mol% AuNPs-modified BT ceramics causes the decreasing of effective d_{33} coefficient compared with applying only $+2.5$ V. This finding supports the previous explanation related to the cancellation of the oppositely poled grains exist after applying more than $+2.5$ V. In contrary to 8 mol% AuNPs-modified BT case, although there were not phase changes found in the previous discussion, this sample showed the highest amplitude among others. These results emphasize that it is possible to control the piezoresponse of the AuNPs-modified BT ceramics by selection the proper applied V_{DC} for each AuNPs content. Moreover, it is likely that homogeneous polarization state of the ceramics could be induced by applying high bias and/or increasing AuNPs content. However, to obtain a better understanding on ferroelectric domain evolutions and local polarization switchings, further research on applying higher voltage as found in Zhao et al. [22] is therefore attractive. Additionally, Kim et al. [12] work which study the ferroelastic domain evolution under compressive loading in polycrystalline lead zirconate titanate (PZT) ceramics by using PFM also provided the interesting point to apply this method for our AuNPs-modified BT samples because their results confirmed that applying different compressive loading revealed the involved multiple domain switching processes. With these understandings, the fundamental necessity both for the development of novel materials and an improvement of their potential device performances as aimed could be surely achieved.

4. Conclusion

Piezoresponse force microscopy was adopted to study the complex domain evolution in polycrystalline BT-based ceramics containing various amounts of AuNPs additives. Complex microstructures that are agglomerations of a very large number of variously oriented grains were evidenced. Additive content dependence was noticable in AuNPs-modified BT ceramics where higher amplitude can be observed from applying positive V_{DC} to 4.0 mol% AuNPs-modified BT ceramics, compared to other samples, revealing more polarization reversal obviousness, *i.e.* superior piezoelectric characteristics. The amplitude piezoresponse images indicate that most samples exhibit stronger piezoresponse by applying positive V_{DC} than that by negative V_{DC} . Interestingly, the strong piezoresponse areas of AuNPs-modified BT ceramics are larger than that of unmodified BT case indicating the possibility of control the polarization switching of the AuNPs-modified BT ceramics by a selection of the proper applied V_{DC} .

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