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Dielectric inspection of $BaZr_{0.2}Ti_{0.8}O_3$ ceramics under bias electric field: A survey of polar nano-regions

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ABSTRACT

The structure and dielectric properties of $BaZr_{0.2}Ti_{0.8}O_3$ ceramics prepared by citrate method were investigated. Structural analysis of the ceramics indicated a cubic perovskite structure and a fine-grained (about 250 nm) microstructure. The ceramics displayed a frequency dispersion of the dielectric loss and a slim polarization versus electric field (*P–E*) hysteresis loop. These results were related to the existence of polar nano-regions (PNRs) embedded in the non-polar matrix of the ceramics. The nonlinear dielectric properties under bias electric field were found to be dependent on holding time of applied bias field. The phenomenon was qualitatively explained with polarization reorientation of PNRs under the bias field. Fitting the dielectric constants under the bias field to a multipolarization mechanism model resolved the contribution of PNRs from the overall dielectric response. From the fitting, the polarization and size of PNRs in the ceramics were determined to be around 0.4 $\mu C/cm^2$ and 9 nm, respectively.

1. Introduction

Lead-free perovskite-type barium zirconate titanate ($BaZr_xTi_{1-x}O_3$, BZT) dielectrics have been the subject of intensive research for their scientific and technological importance. Because of large dielectric constant and high breakdown strength, BZT has found applications in ceramic capacitors [1]. High piezoelectric activity and strain levels of BZT have evoked considerable interest in their utilization in piezoelectric actuators [2–4]. Recently, BZT solid solutions emerged as a promising candidate material for electrically tunable microwave devices due to their strong dielectric nonlinearity under bias electric field and good temperature stability [5,6]. In view of the tunable microwave device applications, the nonlinear dielectric properties of BZT in various forms have been evaluated [7–12].

On the other hand, BZT solid solutions manifest an intriguing evolution in phase transition and dielectric behavior with the change of zirconium content. On increasing temperature, $BaTiO_3$ undergoes three successive phase transitions in the sequence of rhombohedral–orthorhombic (~−90 °C), orthorhombic–tetragonal (~5 °C) and tetragonal–cubic (~120 °C). For BZT solid solutions, the isovalent substitution of Zr^{4+} for Ti^{4+} generates a pinching effect on the temperatures of the phase transitions [3]. The three phase transitions corresponding to pure $BaTiO_3$ are merged into one diffusion phase transition (DPT) at $x = \sim 0.15$ [3]. Further increasing the content of zirconium up to $x = 0.25–0.75$ gives rise to a typical relaxor-like behavior [13,14]. Unlike the classic lead-based perovskite-type ferroelectric relaxors, such as $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) and $PbZn_{1/3}Nb_{2/3}O_3$ (PZN), no cationic ordering is expected for BZT between Zr^{4+} and Ti^{4+} located at the octahedral site of the perovskite structure [14]. Therefore, the origin for the relaxor behavior of the BZT compositions ($x = 0.25–0.75$) has been extensively investigated both experimentally and theoretically [13–19]. It has been recognized that the existence of dynamic polar nano-regions (PNRs) in a non-polar matrix is responsible for the relaxor behavior [13,14,17].

The dielectric properties of BZT are essentially determined by the response of polarization mechanisms of the material with respect to various external physical signals, such as temperature, frequency and electric field [20]. Considering the evolution of the dielectric behavior of BZT family with zirconium content, $BaZr_{0.2}Ti_{0.8}O_3$ ($x = 0.2$) appears as a composition situated at the threshold before the occurrence of a relaxor-like behavior. Up to date, the majority of research on BZT family has been focused on the dielectric properties of the relaxor compositions (e.g. $x = 0.25–0.35$). By contrast, research effort towards the threshold composition remains limited, especially its bias field dependence of dielectric properties [21,22]. A deep insight into such dependence is expected to enhance the understanding on polarization mechanisms and dielectric properties of BZT system.

We prepared $BaZr_{0.2}Ti_{0.8}O_3$ ceramics by a citrate method. In the present work, we study the structure and dielectric properties of the ceramics. The emphasis is placed on the dielectric response of the ceramics under bias electric field.

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2. Experimental

$BaZr_{0.2}Ti_{0.8}O_3$ powder was synthesized by a citrate method. Reagent grade $Ba(NO_3)_2$, $Zr(NO_3)_4{\cdot}5H_2O$, tetrabutyl titanate and citric acid were used as starting materials. Tetrabutyl titanate was first dissolved into a citric acid solution and various nitrates were then added under stirring to yield a transparent aqueous solution. The mole ratio of citric acid to the total metal cation content was 1.5. The precursor solution was heated at 300 °C to form a foam-like solid precursor. The solid precursor was pulverized and calcined at 600 °C for 1 h in air. The synthetic process was basically identical to that previously reported for preparing $Ba_{0.6}Sr_{0.4}TiO_3$ powder [23]. X-ray diffraction (XRD) analysis of the calcined powder certified the formation of a pure perovskite phase (not shown here). The calcined powder was uniaxially pressed under a pressure of 300 MPa into discs of 13 mm in diameter and 1 mm in thickness. The compacted discs were sintered at 1270 °C for 2 h in air. The sintering temperature was determined by a dilatometric analysis of the compacted discs performed at a Netzsch DIL 402C dilatometer.

The morphology of the powder was observed at a Hitachi S-4700 filed emission scanning electron microscope (FESEM). The crystal structure of the ceramic specimens was examined by a Philips X'pert PBO X-ray diffractometer using Cu Kα radiation. The microstructure of the ceramic specimens was investigated at a Jeol JSM-5610LV scanning electron microscope (SEM). The grain size of the ceramic specimens was estimated from image analysis using the Image-Pro Plus 6.0 software. The bulk density of the ceramic specimens was measured by the Archimedes method with ethyl alcohol as the medium. The relative density of the ceramic specimens was determined by the measured result and the theoretical density calculated from the XRD data. The temperature dependence of the dielectric constant (ε_r) and the loss ($\tan\delta$) was measured by a TH2828 precision LCR meter (20 Hz-1 MHz) and an SSC-M10 environmental chamber (C4 controller) between −80 and 120 °C. The polarization (P) versus electric field (E) relation was measured at room temperature by a Radiant precision workstation based on the Sawyer-Tower circuit at 50 Hz. The nonlinear dielectric properties were measured at room temperature by a TH2818 automatic component analyzer at 10 kHz under external bias electric field. A blocking circuit was adopted to protect the analyzer from applied bias voltages. The bias electric field was swept from 0 to 20 kV/cm at a step of 1 kV/cm. The measurement was repeated for four times. For each measurement, the dielectric data were recorded after holding at each applied bias field for a constant time. The holding times of the measurements were 10, 60, 300 and 600 s, respectively. Before each measurement, the specimen to be measured was heated at 150 °C for 30 min to ensure an identical initial polarization state.

3. Results and discussion

3.1. Structural analysis

Fig. 1 shows the microstructural images of the synthesized powder and the ceramic specimen. The FESEM image of the powder (Fig. 1a) illustrates a superfine and uniform (50–100 nm) particle morphology. The ceramic specimen displayed a generally dense microstructure with fine and homogeneous grains (Fig. 1b). The Archimedes measurement of the ceramic specimen indicated a relative density of 94.3%. Average grain size of the ceramic specimen was estimated to be about 250 nm. In the case of the conventional solid-state route, BZT ceramics were usually sintered at 1400–1550 °C [5,13,19]. The high sintering temperatures are prone to result in larger grains. The fine-grained microstructure of the ceramic specimen is believed to be due to its superfine starting powder and low sintering temperature (1270 °C).

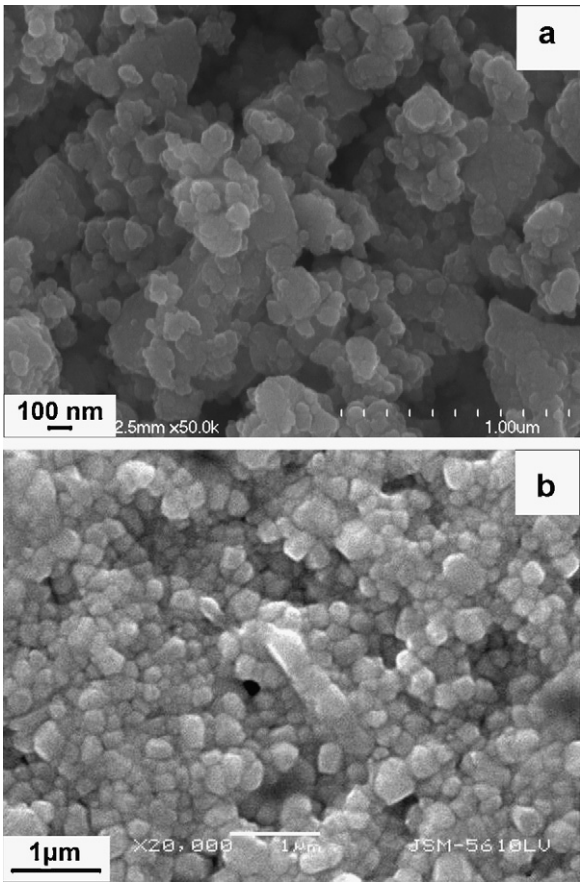

Fig. 1. (a) FESEM image of the synthesized powder and (b) SEM image of the ceramic specimen.

A coexistence of ferroelectric and paraelectric phases has been reported for the structure of BZT compositions adjacent to $x = 0.2$ at room temperature [1,24]. This is due to a small difference in Gibbs free energy between the phases. XRD Reitveld refinement of $BaZr_{0.15}Ti_{0.85}O_3$ ceramics indicated that ~65% cubic phase and ~35% tetragonal phase coexist in the structure [24]. Fig. 2 shows the XRD pattern of the ceramic specimen. The perovskite structure of the ceramic specimen could be indexed with a cubic symmetry. The inset shows the narrow-scanned pattern in the range of 44–46°. Within the resolution of the instrument, no peak splitting

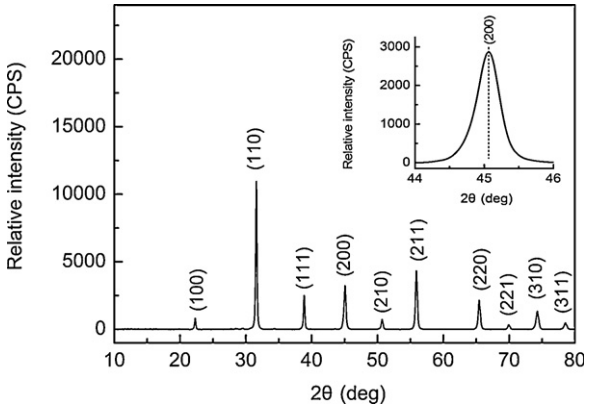

Fig. 2. XRD pattern of the ceramic specimen. The insert shows the narrow-scanned pattern in the range of 44–46°.