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Frequency dependence of polarization and strain in $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$/$Bi_{0.5}(Na_{0.8}K_{0.2})_{0.5}TiO_3$ composites

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ABSTRACT

This study involves the microstructure tailoring of two types of ferroelectric and relaxor composites and their frequency-dependent large-signal properties. The ferroelectric seed of $Bi_{0.5}(NaK)_{0.5}TiO_3$ (BNKT) and a relaxor matrix of 0.74 $Bi_{0.5}Na_{0.5}TiO_3$-0.26$SrTiO_3$ (BNST) with a ratio of 0.1 were synthesized via a solid-state reaction. Two types of BNKT ferroelectric seeds, namely a large-sized template-type (t-BNKT) and small-sized powder-type (c-BNKT), were prepared. Additionally, X-ray diffraction and microstructure analyses revealed that the addition of BNKT to BNST induced the formation of two phases (ferroelectric and relaxor). BNKT/BNST exhibited a combination of relaxor and ferroelectric phases, while the relaxor corresponded to the major phase in pure BNST. The t-BNKT/BNST composite exhibited a large-sized ferroelectric phase in the relaxor matrix with a small population, and the c-BNKT/BNST contained a small-sized ferroelectric phase with a large population of the relaxor matrix in the microstructure. In high-field applications, BNST exhibited pinch-type polarization behavior due to the transition from polar nanocluster to ferroelectric microscale domains in the relaxor matrix. The addition of t-BNKT and c-BNKT accelerated the coexistence of the ferroelectric and relaxor phases, thereby inducing pinch-shaped polarization with high remnant polarization and parabolic strain behavior with high negative strain. The pure BNST and t-BNKT/BNST exhibited a transition from the relaxor to ferroelectric phases at a high-field application over 4 kV/mm. Furthermore, the advent of the ferroelectric phase in c-BNKT/BNST led to a transition from short-range polar ordering to long-range ferroelectric ordering when a lower field (<3 kV/mm) was applied. However, the sample exhibited difficulties in reverse transition upon removal of the applied field. The electromechanical properties of c-BNKT/BNST and t-BNKT/BNST indicated a significant change in the frequency dependence of the polarization and strain, which was related to the presence of the ferroelectric phase. The aforementioned property was evaluated based on the decay in the polarization behavior.

1. Introduction

Piezoelectric/electrostrictive materials and their actuators are widely used in optics, fluid control, and precision machining systems owing to their high generative force, accurate displacement, and fast response to external electric fields [1]. Practical materials with a large piezoelectric/electrostrictive strain mainly correspond to lead-based ferroelectric ceramics such as $Pb(MgNb)O_3$–$PbTiO_3$ and $Pb(ZrNb)O_3$-$PbTiO_3$ [1–3]. In Pb-based antiferroelectric ceramics, such as $(Pb,La,Zr)TiO_3$, high strain is a consequence of a field-induced transition from an antiferroelectric to a ferroelectric phase and/or from a non-polar to polar phase [4,5]. The development of actuators based on ceramic materials that undergo this type of a phase transition under an electric field has attracted significant interest over the past decade.

Given the current requirement of global environmental protection, lead-free materials are an important topic in the study of piezoelectric materials [3,6]. Sodium-potassium-niobate ($KNaNbO_3$) [3,7–10] and bismuth-sodium-titanate ($Bi_{0.5}Na_{0.5}TiO_3$) [11–20] systems are promising ceramic families that can potentially replace lead-based systems. Specifically, $Bi_{0.5}Na_{0.5}TiO_3$-$Bi_{0.5}K_{0.5}TiO_3$-$K_{0.5}Na_{0.5}NbO_3$ (BNT-BKT-KNN) is a bismuth-based

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system that exhibits high strain, which is comparable to that of lead zirconate titanate (PZT). This is attributed to the phase transition from the relaxor phase to the ferroelectric phase. The same strain behaviors are observed in several $Bi_{0.5}Na_{0.5}TiO_3$-based solid solutions. In practical applications, the phase transition materials exhibit the limitation of requiring a high electric field to reach a large strain (0.45% at 80 kV/cm) [11]. Recently, a high strain response under a relatively low field was achieved in lead-free $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) – $SrTiO_3$ (ST) [17]. As indicated by several studies [11–23], the function of ST in the BNT-ST system involves decreasing the phase transition temperature. Thus, a few BNT-ST compositions exhibit a high-temperature relaxor phase at room temperature [14–16]. Specifically, ST is attributed to the distortion in the lattice parameter and disruption of the long-range ferroelectric order due to the existence of nano-polar regions. This change implies the appearance of a ferroelectric order and arrival of a short-range relaxor order [23].

Therefore, BNT-ST exhibits the ferroelectric rhombohedral or rhombohedral + tetragonal phases in a composition range of less than 20% ST. In the range of 20% < ST < 30%, BNT-ST exhibits a combination of ferroelectric (rhombohedral or tetragonal) and relaxor (pseudo-cubic) phases. Furthermore, BNT-ST with ST > 30% mainly exhibits a cubic phase [23–26]. Additionally, with BNT-ST in the range of 20 to 30%, ST exhibits ferroelectric and relaxor phases, which are occasionally formed in core-shell or composite structures [23,25]. The aforementioned structures evoke a large strain on the electric field application and subsequent removal. Thus, BNT-ST can be used as a material for actuator applications since it provides a high strain performance. Hence, the frequency-dependent strain behavior is important to determine the quality of the actuator, because BNT-ST exhibits a relaxor characteristic (time-dependent feature). This is determined by the velocity of the domain wall movement and/or the relaxor-to-ferroelectric phase transition. Furthermore, it is expected that the size and population of the ferroelectric phase can affect the reversion from the nano-polar regions to micro-ferroelectric domains in the relaxor phase (matrix). Therefore, in this study, two shapes of ferroelectric materials (i.e., large-sized $Bi_{0.5}(Na_{0.8}K_{0.2})_{0.5}TiO_3$ (BNKT) template and small-sized BNKT powder) were prepared and added to a $0.74Bi_{0.5}Na_{0.5}TiO_3$–$0.26SrTiO_3$ (BNST) relaxor matrix. Subsequently, BNKT (ferroelectric composition), BNST (relaxor-enriched composition), and combinations of BNKT and BNST were selected, and their high field-induced polarization and strain were investigated as a function of frequency, respectively. The frequency-dependent properties were evaluated by using the kinetics and decay behavior of the polarization.

2. Experimental section

The ceramics were fabricated via a conventional solid reaction. Bi_2O_3 (99.975%, Sigma Aldrich Co.), Na_2CO_3 (99.9%, Sigma Aldrich Co.), TiO_2 (99.9%, Sigma Aldrich Co.), and $SrCO_3$ (99%, Sigma Aldrich Co.) were mixed to fabricate stoichiometric $0.74Bi_{0.5}Na_{0.5}TiO_3$–$0.26SrTiO_3$ (BNST) and $Bi_{0.5}(Na_{0.8}K_{0.2})_{0.5}TiO_3$ (BNKT) [17,20].

Two types of ferroelectric particles were prepared – BNKT template and normal powders. The BNKT templates with grain sizes exceeding 5 μm were fabricated by a molten salt method [27,28]. In the first reaction, Bi_2O_3 (99.9%, Sigma Aldrich Co.) and TiO_2 (99.9%, Sigma Aldrich Co.) powders were reacted in a NaCl and KCl (99.9%, Sigma Aldrich Co.) flux at 1100 °C for 30 min to obtain plate-like $Bi_4Ti_3O_{12}$ precursor particles. In the second reaction, BNKT single particles were formed by reacting plate-like $Bi_4Ti_3O_{12}$, Bi_2O_3, K_2CO_3, Na_2CO_3, and TiO_2 powders in a KCl and NaCl flux at 1100 °C for 30 min. Normal BNKT powders were fabricated by a conventional solid-state reaction. The resulting solution was dried at 90 °C for 12 h. The resulting powders were calcined at 850 °C for 2 h.

In order to fabricate the composites, the selected powders including BNST and BNKT template (t-BNKT), and the conventional BNKT powder (c-BNKT) were mixed and ball-milled again with ethanol and a zirconia ball (diameter of 3 mm). Following the drying process, the powders were compacted via pressing. The compacts were sintered at 1150 °C for 4 h. The BNST and t-BNKT composite (t-BNKT/BNST), and the BNST and c-BNKT composite (c-BNKT/BNST) were polished, electroded with silver paste, and heated at 700 °C for 30 min.

X-ray diffraction (XRD) patterns were measured from 20° to 80° (2θ) (step interval of 0.01°) with the Panalytical X'pert PRO MPD system equipped with an X'celerator detector using graphite monochromatic (Cu Kα1) radiation (λ = 1.54056 Å). Rietveld refinement of the XRD patterns was performed using the HighScore Plus software. The fitting was conducted by comparing the experimental data with the reserved data (stored in the ICSD structure database). The space group of each phase was selected with a minimal value of goodness of fit (χ^2) from the reserved data of the space group. Field-emission scanning electron microscopy (Hitachi FE-SEM S4800, Japan) was performed for microstructural inspection. With respect to transmission electron microscopy (TEM), the specimen was prepared by the conventional method. TEM (JEM–3000 F, JEOL, Tokyo, Japan) was performed using a transmission electron microscope equipped with a field-emission gun. The TEM sample was prepared via the conventional method that included polishing, dimpling, and argon ion-milling. The sample was annealed at 250 °C to reduce the residual stress accumulated during polishing.

A precision LCR Meter 4192 A (Hewlett Packard Corporation, Palo Alto, CA) was used to measure the dielectric constant with respect to temperature. The electromechanical coupling factor was measured as per the IEEE standard. The polarization-electric field (P—E) hysteresis loops were measured via a modified Sawyer-Tower circuit at 0.1–100 Hz. The field-induced strains were measured using a laser interferometer-type displacement sensor (SIOS GmbH, SP-120).

3. Results and discussion

3.1. SEM and XRD

Fig. 1 shows the secondary electron images of scanning micrographs for the BNKT/BNST samples sintered at 1150 °C for 4 h. In the secondary electron images, a combination of enlarged and small grains is observed in t-BNKT/BNST. The large grains are ferroelectric BNKT and are identified by energy dispersive X-ray spectroscopy, as shown in Fig. 1(c) (Sr deficiency and K enrich mapping), and the relaxor BNST is in the small grains. In the backscattered electron images, a large ferroelectric BNKT phase is observed for t-BNKT/BNST (BNKT does not exhibit Sr content, which led to a different contrast in the BSE mode). Furthermore, a small and different contrast as identified with ferroelectric BNKT was detected in c-BNKT/BNST. The relaxor BNST and ferroelectric BNKT are also observed in the TEM image of Fig. 1(d). The enlarged image on the right shows the ferroelectric domains, indicating that a large-sized ferroelectric phase with a small population is formed in t-BNKT/BNST, whereas a small-sized ferroelectric phase with a large population is formed in c-BNKT/BNST.

As indicated in previous studies [23,25], the phase exhibits a rhombohedral structure in BNT-ST with ST < 20%, a mixed state of rhombohedral and cubic structures exists in the range corresponding to 20% < ST < 30%, and a cubic structure exists for ST > 30%. The addition of ST to BNT weakens the long-range ferroelectric ordering. Based on the Rietveld refinement of the XRD pattern shown