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Magnetic effects on polarization response in particulate magnetoelectric $Bi_{0.5}Na_{0.5}TiO_3$-$La_{0.67}Sr_{0.33}MnO_3$ composites

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ABSTRACT

Biphase particulate magnetoelectric ceramics (1-x)$Bi_{0.5}Na_{0.5}TiO_3$-$x$$La_{0.67}Sr_{0.33}MnO_3$ (x = 0.05, 0.15, 0.25 and 0.35) were prepared using the powder-in-sol precursor hybrid method. Effect of magnetic field on polarization response in composites was studied, by analyzing the magnetodielectric effect and ferroelectric loops under the applied magnetic field. The switching of magnetodielectric effect and the variation ferroelectric polarization is mainly determined by the competitive mechanisms of magnetoresistance and magnetostriction. Furthermore, the direct magnetoelectric output was carried out and the maximum ME voltage coefficient reached up to 19.1 mV/cm·Oe for the x = 0.15 composite.

1. Introduction

Magnetoelectric (ME) multiferroics, coupling between ferroelectricity and ferromagnetism, have attracted tremendous interest both from the fascinating physics and application-oriented perspective [1–3]. Single-phase multiferroics are restricted to only few systems with weak ME coupling naturally [3,4]. With great design flexibility, the artificially engineered composites combining ferroelectric and ferromagnetic phases yield the strong ME coupling and catch particular attention for the possible practical application [5–7]. Recently, the focus of ongoing research has been on lead-free ME composites [6–8]. As an attractive environmentally-friendly perovskite, $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) exhibits high Curie temperature, large remnant polarization and high piezoelectric response, which is a favorable ferroelectric component for ME composite [8–10]. In parallel, the optimally doped manganite $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) is a typical perovskite-type double exchange system with room-temperature ferromagnetism [11]. It exhibits excellent thermal stability, large anisotropic magnetostriction and unique half-metallic character [12–14]. Due to the perovskite-like structure of the BNT and LSMO, one may expect an enhancement of ME coefficient by combining these two phases.

Manganite LSMO has been demonstrated a large magnetoresistance (MR) material [13,14]. In the particulate BNT-LSMO composites, there exist two major mechanisms acting on the magnetic-field-induced polarization behavior. One is the MR effect [15] and the other is magnetostriction effect [16]. For the MR effect, the varied resistance creates Maxwell-Wagner polarization at the two-phase interface. For the magnetostriction, strain variation of manganite induces a piezoelectric polarization in ferroelectric component. However, it remains unclear how the two mechanisms affect the polarization and ME behavior and which mechanisms deterministically dominate these behaviors as a function of manganite content. Motivated by this, we prepared the particulate (1-x)BNT-xLSMO (x = 0.05, 0.15, 0.25 and 0.35) composites and investigated the magnetic-field-induced polarization response in composites, by measuring the magnetodielectric effect and ferroelectric loops under the applied magnetic field.

2. Experimental details

Ceramic composites of (1-x)BNT-xLSMO (x = 0.05, 0.15, 0.25 and 0.35) were synthesized by a powder-in-sol precursor hybrid method. The LSMO powders were prepared by the sol-gel method using stoichiometric amounts of $La(NO_3)_3{\cdot}6H_2O$, $Sr(NO_3)_2$ and $Mn(NO_3)_2{\cdot}H_2O$ as precursor and acetic/EDTA as complexing agent. The LSMO powder was calcined at 1250 °C for 3 h. BNT precursor was prepared by sol-gel route. $Bi(NO_3)_3{\cdot}5H_2O$, $NaNO_3$ and $Ti(OC_4H_9)_4$ were taken in stoichiometric amounts and dissolved completely in the mixture solution of citric acid and ethylene glycol. The obtained LSMO powder in designed weight ratios was soaked in BNT solution. The resultant precursor solution was subjected to heat and dry. Then the obtained xerogel was pre-sintered and calcined at 950 °C for 2 h. The calcined composite powders were ground, pelleted and finally sintered at 1150 °C for 2 h. The sintered pellets were electrodes using silver paint on the surfaces

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and perpendicularly polarized at an electric field of 2 ~ 5 kV/cm to carry out measurement.

The crystalline phases were identified by X-ray diffraction (XRD) (Philips X-pert PRO). Micromorphology and composition were studied by scanning electron microscope (SEM) (TESCAN VEGA 3) and energy-dispersive spectroscopy (EDS). Dielectric property was performed by using a HP4284 LCR meter. The magnetostriction coefficients were measured using static strain gauge method. Resistivity was measured using precision LCR meter (TH2829C). The ferroelectric property was evaluated by a ferroelectric tester based on Sawyer Tower circuit. The magnetic field source for resistance, dielectric and ferroelectric properties measurement is used a custom designed magnet and the direction is parallel to the surface of the pellet. The ME measurement were carried out using the lock-in technique [17]. A small alternating magnetic field (f = 1 kHz, H_{ac} = 1.0 Oe) was generated using a solenoid that was superimposed onto a bias magnetic field up to 3.5 kOe.

3. Results and discussion

Fig. 1(a) displays the XRD patterns of the (1-x)BNT-xLSMO (x = 0.05, 0.15, 0.25 and 0.35) composites. XRD patterns of the samples exhibit typical perovskite-based diffraction peak, corresponding to the rhombohedral BNT (JCPDS card No. 36-0340) and LSMO (JCPDS card No. 89-8098) phases. No additional peaks were identified. The micrographs of the composites are presented in Fig. 1(b)–(e). Two distinct and well-crystallized individual light and dark phase are easily observed and they correspond to BNT and LSMO. LSMO grains with average sizes of ~3 μm were well-distributed and segregated over the BNT matrix, confirming a good dispersion. In addition, one can see a very good agreement between the observed and theoretical values of Sr/Ti atomic ratio for all samples, shown in Fig. 1(f).

Since magnetic ordering is coupled to polarization and thus indirectly alters the dielectric constant in multiferroics, magnetodielectric (MD) effect could provide signature of magnetic-dependent polarization. The MD effect is defined as MD = [$\varepsilon'(H) - \varepsilon'(0)] \times 100\%/\varepsilon'(0)$, where $\varepsilon'(H)$ and $\varepsilon'(0)$ are the dielectric constants with and without the applied magnetic field. Fig. 2(a) and (b) plots the frequency dependence of MD at the magnetic field of 0.8T and the magnetic field dependence of MD at the frequency of 1 kHz for composites, respectively. The MD of all composites experiences a continuous decrease with increasing frequency and becomes constant at high frequency. The MD is negative for x = 0.05 and 0.15 samples, while is positive for x = 0.25 and 0.35 samples. Additionally, the magnitude of MD increases with increasing magnetic field at 1 kHz. As mentioned before, the magnetic-dependent dielectric constant relates to the MR and magnetostriction. The decreased resistance (see the inset of Fig. 2(d)) induced by MR effect enhances the interfacial polarization and thus increase ε'. Conversely, tensile stress produced by magnetostriction enhances the polarization of ferroelectric phase and decrease ε'. This reduction of ε' can be explained by the Gridnev model $\varepsilon \propto 1/P^2$ [16], where ε is the dielectric constant and P is the polarization. Considering the result of MD, it is understandable that the negative MD is mainly attributed to the contribution of the magnetostriction effect of LSMO. As increasing x, the negative MD transfers into positive MD. The more MR phases embedding in BNT matrix create abundant interfaces and thereby result in the enhancement of interfacial polarization in the heterogeneity structure [18]. The transformation of MD indicates that the MR induced effect plays a dominant role in the ε' when the x above 0.25.

Fig. 3(a) presents the ferroelectric hysteresis loops of the composites. The maximum saturation polarization P_s and remnant polarization P_r was obtained in x = 0.05 sample. Further increasing x leads to a decrease in polarization, which is caused by the dilution of the non-ferroelectric phase of LSMO. The sample with high LSMO content exhibited some curvature near saturation, mainly arising from the leakage current developed in ferroelectric regions through low-resistance manganite grains. Fig. 3(b) shows the variation of the P_s and P_r with x in absence and presence of an external magnetic field of 0.8T, respectively. One may clearly notice that a slight increase in P_s and P_r with low LSMO content ($x \leq 0.15$) and an obvious decrease in P_s and P_r with high LSMO percent ($x \geq$

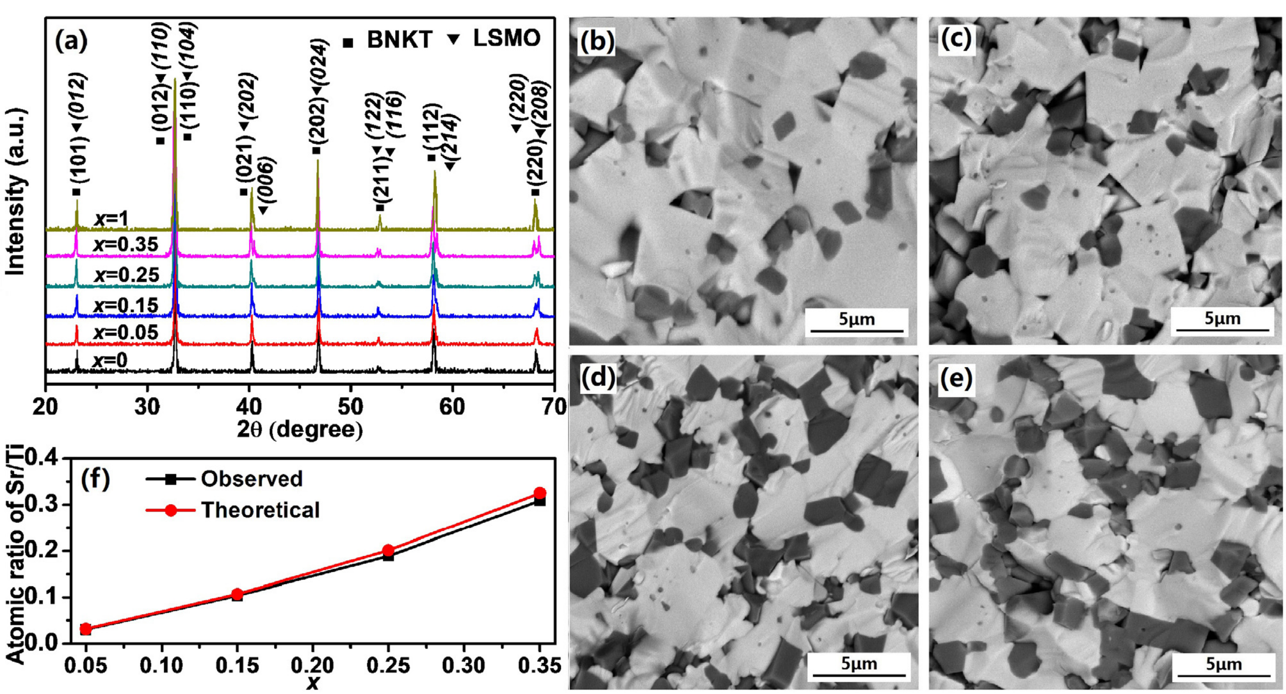

Fig. 1. (a) XRD patterns of the (1-x)BNT-xLSMO composites. Micrographs of the composite: (b) x = 0.05, (c) x = 0.15, (d) x = 0.25 and (e) x = 0.35. (f) Atomic ratio of Sr/Ti as a function of x.