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Lead-free $Bi_{1/2}(Na_{0.82}K_{0.18})_{1/2}TiO_3$ relaxor ferroelectrics with temperature insensitive electrostrictive coefficient

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Abstract

The electric field-induced strain of $Bi_{1/2}(Na_{0.82}K_{0.18})_{1/2}TiO_3$ (BNKT) ceramics modified with $BaZrO_3$ (BZ) was investigated as a function of composition and temperature. Unmodified BNKT ceramics revealed a typical ferroelectric butterfly-shaped bipolar *S–E* loop at room temperature, whose normalized strain (S_{max}/E_{max}) showed a significant temperature coefficient of 0.38 pm/V/K. As the BZ content increased in the solid solution up to 5 mol%, the ferroelectric BNKT gradually transformed to a relaxor. Finally, 5 mol% BZ-modified BNKT ceramics showed a typical electrostrictive behavior with a thermally stable electrostrictive coefficient (Q_{33}) of 0.025 m^4/C^2, which is comparable to that of $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) ceramics that have been primarily used as Pb-based electrostrictive materials.

Keywords: C. Dielectric properties; C. Piezoelectric properties; D. Perovskites; E. Actuators

1. Introduction

Relaxor ferroelectrics (RFEs) are a special class of ferroelectrics (FE) that have peculiar properties: frequency-dependent dielectric permittivity maxima; Curie-Weiss dependence of the permittivity versus temperature at temperature fairly higher than the maximum dielectric constant temperature (T_m) [1–4]. Relaxors have been widely studied not only due to their behaviors and properties but also due to various applications such as electromechanical sensors and actuators [5]. RFE behaviors were found in many Pb-based materials: $Pb(Mg_{1/3}Ta_{2/3})O_3$ [1], $Pb_3Fe_2WO_3-PbTiO_3$ [3], $Pb(Fe_{2/3}W_{1/3})O_3-Pb(Mg_{1/3}Ta_{2/3})O_3$ [6], $Pb(MgW)_{1/2}O_3-Pb(FeTa)_{1/2}O_3$ [6], $Pb_3MgNb_2O_9-PbTiO_3$ [7], $Pb_{1-x}La_x(Zr_{1-y}Ti_y)_{1-x/4}O_3$ [8], $Pb(Fe_{2/3}W_{1/3})O_3-PbTiO_3$ [9], $Pb(Zn_{1/3}Nb_{2/3})O_3-Pb(Zr_{0.55}Ti_{0.45})O_3$ [10], and $Pb_3MgNb_2O_9-PbZr_{0.47}Ti_{0.53}O_3$ [11]. Recently, RFE phenomena were reported on lead-free materials including $(Bi_{1/2}Na_{1/2})_{1-x}Ba_xZr_yTi_{1-y}O_3$ [12], $Ba(Ti_{1-x}Zr_x)O_3$ [13], (K,Na)(Nb,Sb)$O_3-LiTaO_3-BaZrO_3$ [14], and $Bi_{1/2}Na_{1/2}TiO_3-Bi_{1/2}K_{1/2}TiO_3-Bi(Zn_{1/2}Ti_{1/2})O_3$ [15].

Increasing demand for environmentally friendly materials in electronic industry leads researchers to exploit new lead-free materials which can replace Pb-based ceramics. Among various lead-free systems, solid solutions between $Bi_{1/2}Na_{1/2}TiO_3$ (BNT) and $Bi_{1/2}K_{1/2}TiO_3$ (BKT), hereafter abbreviated as BNKT, are considered as potential candidates due to their excellent electromechanical properties near the rhombohedral-tetragonal phase boundary [16,17]. In particular, recent studies on BNKT ceramics have reported large electric field-induced strains over 500 pm/V when modified with Sn [18,19], Nb [20], Ta [21], or co-doping with both Li and Ta [22].

On the other hand, the thermal stability of electric field-induced strain in a wide temperature range is important in highly reliable precision mechatronic systems. Seifert et al. [23] reported temperature-insensitive strains in BNKT–(K,Na)NbO_3 (KNN) ceramics by suppressing their converse piezoelectric effect via substitution of KNN for BNT. This work investigated temperature dependent electric field-induced strain properties of BNKT ceramics modified with $BaZrO_3$ (BZ) that is known to induce relaxor behaviors in BNT [12] as well as in $BaTiO_3$ [13]. Here we report a new lead-free RFE showing a temperature stable electrostrictive coefficient in the BZ-modified BNKT system.

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2. Experiments

Ceramic powders with compositions of $(1-x)Bi_{1/2}(Na_{0.82}K_{0.18})_{1/2}TiO_3$–$xBaZrO_3$ (BZ100x: x=0, 0.01, 0.02, 0.03, 0.04, and 0.05) were synthesized using a conventional solid state reaction route. Reagent grade Bi_2O_3, Na_2CO_3, K_2CO_3, TiO_2 (99.9%, High Purity Chemicals, Japan), $BaCO_3$, and ZrO_2 (99.9%, Cerac Specialty Inorganics, WI) powders were used as raw materials. The reagents were put in the oven at 100 °C for 24 h to remove moisture and then weighed according to the formula. The powders were mixed in ethanol with zirconia balls by ball milling for 24 h, dried at 80 °C for 24 h, and calcined at 850 °C for 2 h in an alumina crucible. After calcination, the powder was mixed with polyvinyl alcohol as a binder and then pressed into green discs with a diameter of 12 mm under a uniaxial pressure of 98 MPa. The green pellets were sintered at 1200 °C in covered alumina crucibles for 2 h in air.

For electrical measurements, a silver paste was screen-printed on both sides of a specimen and subsequently fired at 700 °C for 30 min. Temperature dependent dielectric properties were characterized using an impedance analyzer (HP4192A, Agilent, CA) attached with a computer programmable electric furnace at different frequencies (0.1–10 MHz) in a temperature range of 30–550 °C at heating and cooling rate of 2 °C/min. Their electrical polarization (P) and electromechanical strain (S) as a function of external electric field (E) were measured at 0.1 Hz with a 15 μF measurement capacitance using a Sawyer-Tower circuit equipped with an optical sensor (Philtec, MD). Temperature dependent $P(E)$ and $S(E)$ were measured by using a commercial aixPES setup (aixACCT Systems GmbH, Germany).

3. Results and discussion

Fig. 1 shows the temperature dependent dielectric constant of BNKT modified with BZ measured at different frequencies. The dielectric maxima (ε_m) and peak temperature (T_m) decreased with increasing frequency for all samples, indicating that they are typical RFEs. The degree of frequency dispersion is more clearly explained by introducing a parameter ΔT_{relax} that has been applied to investigate the relaxation degree of ferroelectric ceramics [24,25].

$$\Delta T_{relax} = T_m(1\text{ kHz}) - T_m(100\text{ kHz}) \quad (1)$$

Based on the experimental data, the value of ΔT_{relax} was calculated to be about 2 K for BZ0, 4 K for BZ3 and 5 K for BZ5, respectively. This result indicates that the frequency dispersion increases with BZ-modification.

The inverse dielectric constant at 100 kHz as a function of temperature was plotted in Fig. 2. From the curves, it is seen that the dielectric permittivity deviates from the Curie-Weiss law which can be represented by ΔT_m that is given by the following equation [3].

$$\Delta T_m = T_{cw} - T_m \quad (2)$$

where T_{cw} is defined as the temperature at which the dielectric permittivity starts to deviate from the Curie-Weiss law. When $T < T_{cw}$, the paraelectric phase transforms into an ergodic relaxor state and thus starts to form polar nanoregions [3,4,24]. The ΔT_m was found to be 201 K for BZ0, 144 K for BZ3, and about 166 K for BZ5, respectively.

For a ferroelectric with broad dielectric maxima, it is known that the diffuseness can be described by a modified Curie-Weiss law [3] as follows.

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T-T_m)^\gamma}{C}, \quad 1 \le \gamma \le 2 \quad (3)$$

where C is the Curie constant and γ the indicator of diffuseness: if γ is near 1, the material is a normal ferroelectric; if γ is 2, the material can be considered as a perfect relaxor [3,14,24]. From the slope in the logarithmic plot of $(1/\varepsilon - 1/\varepsilon_m)$ vs. $(T-T_m)$, as shown in insets of Fig. 2, γ can be determined. The γ was estimated to be 1.77 for BZ0, 1.87 for BZ3 and 2.00 for BZ5, suggesting that there happened a FE–RFE transition with increasing BZ content. Such a composition-induced FE–RFE crossover was also reported in other lead-free piezoelectric ceramics [13–15].

Fig. 3 presents the P–E hysteresis loops of BNKT–BZ ceramics as a function of BZ concentration and temperature. At room temperature (RT), both undoped and 1 mol% BZ-doped BNKT specimens revealed saturated P–E hysteresis loops with significant P_r and E_c values that were distinctive in normal ferroelectrics. On the other hand, specimens with higher BZ content (BZ4 and BZ5)

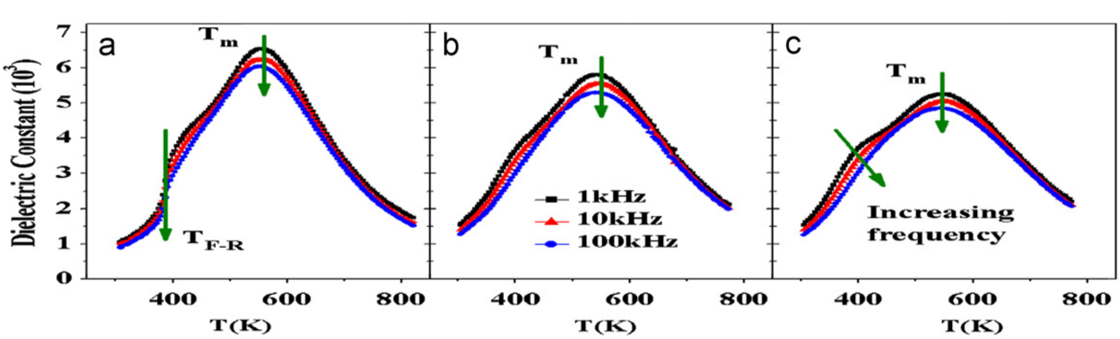

Fig. 1. Dielectric constant of BZ-modified BNKT ceramics as a function of temperature and frequency for: (a) BZ0, (b) BZ3, and (c) BZ5.