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Non-180° domain contributions in $Bi_{0.5}(Na_{0.82}K_{0.18})_{0.5}TiO_3$ lead-free piezoelectric thick films

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Abstract

Piezoelectric responses of $Bi_{0.5}(Na_{0.82}K_{0.18})_{0.5}TiO_3$ (NKBT) ceramic films with thickness of 10–100 μm have been studied in a wide range of ac electric field and frequency. By the Rayleigh law fit, the typical irreversible Rayleigh coefficient, α, for piezoelectric response is $39.69 \pm 0.41 \times 10^{-18}$ m^2 V^{-2}, which is much larger than that of the piezoelectric thin films, indicating significantly enhanced non-180° domain wall motions in NKBT thick films. The logarithmic frequency dependence of the piezoelectric response is associated with domain wall pinning in NKBT thick films, and the frequency dispersion increases with increasing ac field amplitude, which is attributed to the relaxation of non-180° domains.

Keywords: Lead-free piezoelectrics; Thick films; Domain wall motions; Bismuth sodium titanate; Piezoelectric response

1. Introduction

In the past two decades, there have been tremendous efforts in developing lead-free piezoelectric materials due to increasing environmental concerns [1,2]. Various perovskite lead-free piezoelectrics such as $BaTiO_3$-, $(Bi_{0.5}Na_{0.5})TiO_3$-, KNO_3-, and $BiFeO_3$-based systems as well as bismuth layer-structured ferroelectrics, $Bi_4Ti_3O_{12}$- and Bi_3TiTaO_9-based systems have been extensively studied [3–10]. The $Bi_{0.5}(Na_{1-x}K_x)_{0.5}TiO_3$ (NKBT) lead-free system which was firstly reported by Sasaki et al. [11] demonstrates a high piezoelectric response due to the morphotropic phase boundary (MPB) structure between rhombohedral $Bi_{0.5}Na_{0.5}TiO_3$(NBT) and tetragonal $Bi_{0.5}K_{0.5}TiO_3$(KBT). However, the studies on NBT-based lead-free materials are almost limited in bulk ceramics, only a few attempts at the fabrication of lead-free piezoelectric thin film have been made [12–14]. Recently the researches on large-strain or temperature-insensitive lead-free piezoceramics and applications in multilayer actuators attract great attentions [15–18]. For multilayer actuator applications, the microstructures and piezoelectric responses of the thick-film piezoelectric layers (with thickness of 40–100 μm) are extremely important. There is a lack of reports on the study of the lead-free piezoelectric thick films. Piezoelectric thick films with thickness in the range of 10–100 μm have been the subject of ongoing experimental and theoretical investigations due to their fundamental scientific interest and their importance in technological applications [19–22]. Our previous studies [23,24] reported that the screen-printed NBT-based lead-free piezoelectric thick films exhibit high remanent polarization and effective longitudinal piezoelectric coefficient.

Most recently, we found pronounced nonlinear behaviors of the piezoelectric responses for NKBT thick films measured under ac electric field. Because 180° domain wall motions do not cause any change in strain, and it contribute only to the dielectric responses. The non-180° domain wall motion is a major source

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of piezoelectric nonlinearity and strain hysteresis in piezoelectric bulk ceramics [25–27]. However, for ferroelectric thin films (< 1 μm), the non-180° domain wall motion is very heavily clamped and cannot contribute to the nonlinear piezoelectric response [28–31]. Even though several studies suggest that 180° domain wall motion can also contribute to nonlinear piezoelectric response in ferroelectric thin films due to a dynamic poling mechanism [32,33]. It is widely believed that the non-180° domain wall motions and its contribution to nonlinear piezoelectric response are enhanced with increasing film thickness [34–37]. Xu et al. [36] found that the extrinsic contributions to the piezoelectric response were small in fine grain lead zirconate titanate (PZT) thin films with thickness smaller than 1.5 μm, whereas the nonlinear behavior between the converse piezoelectric coefficient and the electric driving field amplitude was observed in PZT films with thickness larger than 5 μm. Their results imply that the pinning of non-180° domain walls is very strong in films with thicknesses less than 2 μm, and the non-180° domain switching are evidenced when the poling field exceeded a threshold field for thicker films. Kholkin et al. [34] demonstrated that 7–8 μm thick PZT films exhibited relatively stronger nonlinearity comparable to that of hard PZT ceramics.

However, all of these researches are focused on Pb-based ferroelectric materials, and almost all are limited to bulk ceramics or thin film (< 1 μm). There is a dearth of investigations on domain wall motions and its contribution to piezoelectric nonlinearity for the lead-free piezoelectric materials or piezoelectric thick films (> 10 μm). Moreover, compared with piezoelectric bulk ceramics, the nonlinearity of piezoelectric properties for thick films is more significant because piezoelectric thick films normally operate at high electric fields even for small driving voltages due to their small thickness [38]. The understanding of the mechanism of non-180° domain wall motion and nonlinear piezoelectric properties is important in order to predict the behaviors of film-based devices especially of the lead-free piezoelectric devices. Thus the non-180° domain wall motions and their contributions to the nonlinear piezoelectric properties of NKBT thick films with various thickness and different dopants were systematically studied in the present work. The investigations on microstructures, dielectric, ferroelectric and piezoelectric properties could be found in our previous work [23,39–42].

2. Experimental procedure

A conventional solid-state reaction method was used to prepare the NKBT ceramic powders. Commercially available reagent grade powders TiO_2, Bi_2O_3, Na_2CO_3, and K_2CO_3 were used as starting materials and mixed according to chemical formula $Bi_{0.5}(Na_{0.82}K_{0.18})_{0.5}TiO_3$. These oxide and carbonate powders were mixed in ethanol and ball milled for 24 h. After calcining at 850 °C for 4 h, the powder mix was again ball-milled for 48 h with the addition of ethanol. After the second ball milling, the ground ceramic powders were dried at 60 °C for 24 h. The resulting NKBT powder was ball milled for 4 h with the addition of 20–40 wt% of organic vehicle. The organic vehicle usually consists of a binder (ethyl cellulose), a solvent (α-terpineol), a plasticizer (polyethylene glycol) and a dispersing agent (butoxyethoxyethyl acetate). After the third ball-milling, the viscosity of the prepared screen-printable pastes was adjusted in the range 20–80 Pa s for shear rate 18 s^{-1}. NKBT layers were screen-printed with a 320 mesh screen mask on 96% alumina substrates ($20 \times 15 \times 0.5$ mm^3), which were firstly electroded with an Pt paste. In order to fire the organic vehicle the layers precalcined at 550 °C for 5 min with a heating rate of 180 °C/min in rapid thermal processor (RTP). After sintering, the single printed layer is around 4 μm. These processes from printing to firing were repeated seven times to obtain various thicknesses. At last the thick films were sintered at 1000–1100 °C for 30 min in atmosphere.

The microstructures of the thick films were examined by field-emission scanning electron microscopy (FESEM, Sirion 200, FEI Ltd., Eindhoven, the Netherlands). For dielectric, ferroelectric, and piezoelectric measurements, platinum top electrodes with diameters of 0.8 mm and thickness of 0.3 μm were sputtered onto the sintered NKBT thick films. Ferroelectric properties were measured by a modified Sawyer–Tower circuit, and a dual-beam laser interferometer for the longitudinal piezoelectric charge coefficient measurements. The thick films were driven with ac field, $E=E_{ac}$ sin (ωt), and the electrically induced charges were converted into voltage via a charge amplifier. The input and output signals were analyzed with an oscilloscope. The maximum amplitude of applied ac field was 30 kV/cm which is about half of the coercive field for NKBT thick films.

3. Results and discussion

As shown in Fig. 1, from the curves of longitudinal piezoelectric coefficient, d_{33}, measured as a function of the amplitude of ac driving electric field, a threshold field, E_{th}, is apparent because there are no mobile domain walls contributing irreversibly to the extrinsic piezoelectric responses. It has been reported that the piezoelectric coefficient increased with increasing amplitude of ac applied field when the field beyond a certain threshold field, E_{th} [43]. The longitudinal piezoelectric coefficient becomes a function of the applied-field

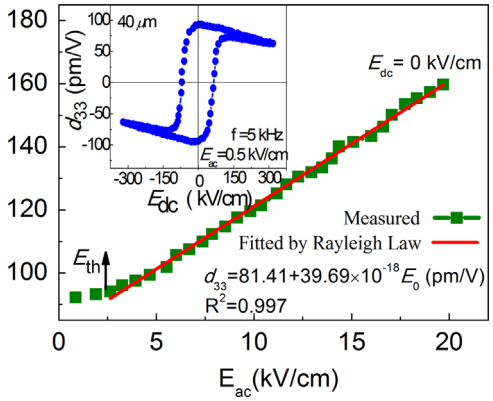

Fig. 1. Longitudinal piezoelectric coefficient d_{33} measured as a function of ac driving electric field amplitude at 5 kHz. The inset figure shows longitudinal piezoelectric coefficient d_{33} measured as a function of dc electric field.