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Stress, temperature and electric field effects in the lead-free $(Ba,Ca)(Ti,Zr)O_3$ piezoelectric system

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Abstract

The large signal strain response as a function of uniaxial compressive stress, electric field and temperature is investigated for compositions across the morphotropic phase boundary in the $(Ba,Ca)(Ti,Zr)O_3$ ferroelectric system. The largest piezoelectric coefficient in terms of unipolar strain divided by the maximum applied field, S_u/E_{max}, is 1540 pm V^{-1}, which clearly exceeds the piezoelectric response of most lead zirconate titanate materials. The extraordinarily large piezoelectric properties occur in the vicinity of the morphotropic phase boundary region on the rhombohedral side of the phase diagram. In this material, an electric threshold field is observed that is required to overcome the stress-induced domain clamping and obtain a measurable strain response. Moreover, the study reveals that careful selection of composition, stress and field amplitude allow for large signal piezoelectric coefficients of over 740 pm V^{-1} in the temperature range of 25–75 °C. The extraordinarily large unipolar strain response can be assigned to an electric field-controlled regime, in which the unipolar compressive stress induces non-180° domain switching perpendicular to the applied electric field. During electrical loading, the electric field can realign these domains back into the parallel direction, maximizing non-180° domain switching and enhancing unipolar strain.

Keywords: BZT-BCT; Lead-free; Ferroelectrics; Actuator; Ferroelasticity

1. Introduction

Piezoelectric materials are used in a variety of applications, prominently as actuators, sensors and electromechanical transducers [1–3]. The material of choice for these applications in the past 60 years has been lead zirconate titanate (PZT), because it offers large piezoelectric coefficients, excellent electromechanical performance, a range of properties tunable through doping, and a well-studied and reliable ceramic processing route [1–3]. The global market for piezoelectric actuators alone was reported to be US$6,587 million in 2009, with bulk PZT materials having a market share of over 98% [4]. These numbers are expected to almost double by 2014, when bulk PZT is expected to remain the dominant material with over 95% of the market [4]. This is despite the legislative measures pushed forward by many countries and states, such as the EU [5,6], Japan [7], China [8], Korea [9] and California [10], to minimize and ultimately ban the use of toxic compounds in electronic equipment.

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The search for lead-free alternatives, triggered by the report by Saito et al. in 2004 [11], has led to the development of two major classes of materials that have been heavily investigated and are based on (K,Na)NbO_3 and $(Bi_{0.5}Na_{0.5})$-TiO_3 (BNT) [12–14]. More recently, the report by Liu and Ren [15] on the Ca^{2+}- and Zr^{4+}-substituted barium titanate ((Ba,Ca)(Ti,Zr)O_3; BCTZ) system with piezoelectric coefficients of more than 600 pm V^{-1} has increased research interest. The large signal piezoelectric response, expressed as the unipolar strain divided by the maximum field, S_u/E_{max}, was reported to exceed 1200 pm V^{-1} at 0.5 MV m^{-1} in the stress-free state [16]. This exceptional piezoelectric performance under comparatively small electric fields is ascribed to the presence of the strongly temperature-dependent morphotropic phase boundary (MPB). At the MPB, evidence of the coexistence of rhombohedral $R3m$ and tetragonal $P4mm$ phases [15,17] and an additional intermediate orthorhombic $Amm2$ phase [18,19] has been reported. This can enable a large piezoelectric response through the polarization rotation and extension mechanisms originating from a flattening of the energy landscape [12,15,20]. One major limitation of this system is the comparatively low Curie point, T_c, of approximately 100 °C, at which the ferroelectric to paraelectric phase transition occurs.

Electromechanical applications, such as stack actuators, require large field-induced displacements as well as the development of a large force during actuation that can act against external elements [1,21,22]. In order to evaluate how the material performs against external mechanical constraints, the blocking force can be determined. By definition, it is the maximum force at a given electric field acting against an infinitely stiff external clamping and is used by actuator manufactureres as a figure of merit [23–27]. Experiments conducted on soft PZT- and BNT-based materials demonstrate the corresponding blocking forces [24,25]. It must be noted, however, that these experiments represent quasi-static behavior. A real-world scenario constitutes the dynamic interplay between mechanical stress and electric field application acting on the obtainable strain response. Here, unipolar electric field measurements under constant stress for compositions across the MPB in the BCTZ system are reported. The stress- and electric-field-dependent properties at different temperatures are analyzed and contrasted to previous experiments on soft PZT- and BNT-based materials to give insight into the viability of this material system for actuator applications [26,27].

2. Experimental

BCTZ materials with the chemical formula $(1-x)Ba(Zr_{0.2}Ti_{0.8})O_3 - x(Ba_{0.7}Ca_{0.3})TiO_3$ were produced using a solid oxide and carbonate processing route. The compositions are $x = 0.4$ (40BCT), $x = 0.5$ (50BCT) and $x = 0.6$ (60BCT) [15–19,28]. The starting materials were high-purity $BaZrO_3$ (99.5%, Sigma Aldrich), $CaCO_3$ (99.0%, Sigma–Aldrich), $BaCO_3$ (99.8%, Alfa Aesar) and TiO_2 (99.8%, Sigma–Aldrich). The starting powders were ball-milled for 24 h in ethanol, dried, calcined for 2 h at 1350 °C, ball-milled for another 24 h in ethanol, dried and the resulting agglomerates broken up with a ceramic mortar and pestle. The ceramic powders were passed through a 70-mesh (0.212 mm) sieve, before they were compacted using a double-acting uniaxial pressing die. Sintering was carried out for 5 h in air at 1450 °C. The phases present were confirmed by X-ray diffraction (XRD) using a Bruker D8 Focus diffractometer with Cu K_α radiation. The compositions at room temperature span from single-phase rhombohedral (40BCT) through one variant of phase mixtures of rhombohedral, tetragonal and orthorhombic (50BCT) to single-phase tetragonal (60BCT). The sintered ceramics were machined to cylinders with a height of 6 ± 0.02 mm and a diameter of 5.8 ± 0.02 mm. Prior to testing, the samples were annealed at 400 °C to depolarize the materials. Silver electrodes were applied using sputter coating.

The electromechanical experiments were carried out using a screw-type load frame (Zwick Roell Z010) with a customized sample environment that allows the simultaneous application of compressive mechanical stresses and electric fields at elevated temperature up to 800 °C. A thermocouple is positioned in the base of the sample holder approximately 6 mm from the sample that was used to regulate the temperature. The experimental setup and the reproducibility of the measurements are presented in detail elsewhere [25,29]. Electric fields were applied using an arbitrary waveform generator (Agilent 33220) connected to a high-voltage power supply (TREK 20/20C). The strain was measured using a linear variable differential transformer located outside of the heating chamber. Various other experimental arrangements have previously been used to investigate the electric-field-dependent ferroelasticity of PZT [30–34], although these setups have typically relied on the use of strain gages, which has limited the application of temperature [35].

A virgin sample was used for measurements at 25 °C. The contact stress, i.e. the smallest stress applied without losing contact to the sample, was $\sigma_0 = 3$ MPa using a force control mode. Note that the minus sign is omitted as only compressive stresses are considered during the following discussion. Nine consecutive triangular unipolar electric field cycles were applied at a frequency of 50 mHz, where the first three cycles had a field amplitude of 2 MV m^{-1}, the next three cycles had a field amplitude of 1 MV m^{-1} and the last three cycles had a field amplitude of 0.5 MV m^{-1}. In that way, the cycling at 2 MV m^{-1} determines the amount of poling and the consecutive cycles at lower fields probe the response under the same poling conditions at smaller electric fields. For each field amplitude, the third cycle was used for data analysis. The mechanical load was subsequently increased stepwise to 250 MPa. At each stress level the same nine consecutive electric field cycles were applied and the strain was measured. The displacement sensor zero point was referenced to the