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Electric-field-induced polarization and strain in $0.94(Bi_{1/2}Na_{1/2})TiO_3$–$0.06BaTiO_3$ under uniaxial stress

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Abstract

The strain and polarization hystereses of lead-free $0.94Bi_{1/2}Na_{1/2}TiO_3$–$0.06BaTiO_3$ during unipolar electric field loading are obtained from room temperature to 150 °C under uniaxial compressive stress up to 446 MPa. At intermediate temperatures a stress-dependent peak evolves in both the maximum strain and polarization. At 125 °C a large strain with a large-signal piezoelectric coefficient d_{33}^* of 884 pm V^{-1} is observed, which decays upon the application of stress. This behavior is rationalized with a change in the primary strain mechanism from domain switching at low temperatures to a reversible electric field-induced transition from an ergodic relaxor state to a long-range order at high temperatures. Moreover, the energy terms w (the output mechanical work) and e_P (the charged electrical energy density) that are related to the deformation and the polarization, respectively, are analyzed and used to define a large-signal efficiency $\eta^* = w(w + e_P)^{-1}$. It is found that η^* saturates at ~150 MPa but decreases with increasing temperature and electric field. It is furthermore observed that notable strains are achieved at stress levels even far beyond the quasi-statically determined blocking force. Therefore, it is proposed that the presented testing procedure is suited to assess the dynamic actuatoric performance of a piezoceramic.

Keywords: Lead-free piezoceramics; Uniaxial stress; Electromechanical properties; Actuators; Relaxors

1. Introduction

The predominant material of choice for piezoelectric applications is lead zirconate titanate $PbZr_xTi_{1-x}O_3$ (PZT) [1,2] owing to its good electromechanical properties, its adaptability to a wide range of distinct applications, and reliable processing into numerous distinct shapes like bulk, monolithic sheets [3,4], multilayers [5–7], or fibers [8–10]. However, international regulations, such as WEEE [11] and RoHS [12], attempt to reduce the use of hazardous substances like lead for health and environmental reasons. Therefore, a tremendous effort has been invested to find suitable lead-free substitutes for PZT [13–16]. It is likely that a single material will not be able to replace PZT throughout the diverse spectrum of applications; hence, the development of material systems will be highly application-specific.

Lead-free piezoelectrics based on $Bi_{1/2}Na_{1/2}TiO_3$ (BNT) [17,18] appear particularly interesting for actuation applications [19], which require large strokes and forces. Numerous authors have demonstrated that BNT-based solid solutions, such as $Bi_{1/2}Na_{1/2}TiO_3$–$BaTiO_3$ (BNT–BT) [20], $Bi_{1/2}Na_{1/2}TiO_3$–$BaTiO_3$–$K_{0.5}Na_{0.5}NbO_3$ (BNT–BT–KNN) [21], $Bi_{1/2}N_{1/2}TiO_3$–$Bi_{1/2}K_{1/2}TiO_3$–$K_{0.5}Na_{0.5}NbO_3$ (BNT–BKT–KNN) [22], $Bi_{0.5}(Na_{0.78}K_{0.22})_{0.5}(Ti_{1-x}Hf_x)O_3$ [23], $Bi_{1/2}Na_{1/2}TiO_3$–$Bi_{1/2}K_{1/2}TiO_3$–$BiZn_{1/2}Ti_{1/2}O_3$ (BNT–BKT–BZT) [24], etc., are capable of producing large strains that rival PZT at sufficiently high electric fields. In the most well-studied lead-free model material, morphotropic BNT–100xBT with $x = 0.06$, the so-called large-strain behavior emerges at elevated temperatures in

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the vicinity of the depolarization temperature T_d in the range of 100 °C [25,20]. At fields of 6 kV mm^{-1} the ratio (d_{33}^*) of maximum strain S_{max} to maximum applied electric field E_{max} reaches 700 pm V^{-1} [26,27], which is significantly larger than commercially available PIC151 at 500 pm V^{-1}, a highly optimized and co-doped soft PZT [21]. Even though still in discussion, the physical mechanism behind the large strain in BNT–6BT is thought to be the field-induced transition from an ergodic relaxor state [28,29] to a ferroelectric phase, thereby developing macrodomains from polar nano regions [30]. This transition to a long-range order is accompanied by a large increase in strain. With the decrease of the electric field the ferroelectric order collapses, resulting in virtually zero remanent polarization and strain. This lack of remanence gives rise to large unipolar strains that can be harvested during each cycle.

An important consideration is the magnitude of force that BNT-based materials can produce. A parameter of high interest in actuator design and material selection is the blocking force F_b, which describes the maximum force a device can generate under ideally stiff clamping [31,32]. Recently, we reported on blocking force measurements of BNT–6BT and 0.98(BNT–6BT)–0.02KNN, where it was demonstrated that the observed high strains in this material class are indeed associated with significant blocking forces that can be larger than in PZT [33]. However, a major drawback of blocking force measurements is its quasi-static nature that does not allow for a direct comparison to the actual working environment where the actuator is often operated under dynamic loading conditions, i.e., unipolar or sesquipolar electrical cycling up to the kHz range [34–36]. Moreover, it does not deliver any information on the polarization losses that occur during operation. Knowledge of polarization losses, however, is vital because self-heating is a serious concern at higher frequencies where heat production and temperature increase may cause depoling and even failure of the actuator [35,37]. Therefore, a sound evaluation of a material requires the dynamic measurement of field-induced strain $S(E)$ and polarization $P(E)$ as a function of field amplitude, temperature and uniaxial stress.

Tan et al. [38] reported on the stress dependence of the bipolar polarization $P(E)$ loops for two BNT–BT–KNN compositions and found that stress levels beyond 100 MPa appear to suppress the transition into the long-range ordered state. However, since $S(E)$ was not measured, the stress dependence of actuatoric performance of these materials remains unknown. To the best of our knowledge, a comprehensive, systematic examination of the stress-dependent large-signal properties of a BNT-based piezoceramic is still lacking.

It is known for PZT that moderate compressive stress enhances the usable strain output due to augmented non-180° domain switching [39–41]. This study aims to determine whether the same holds true for BNT–6BT. Due to the temperature dependence, BNT–6BT samples were electrically cycled under a compressive mechanical stress from room temperature up to 150 °C. These results are discussed in terms of domain switching dynamics and the underlying phase transition mechanism.

2. Experimental

The investigated material, $0.94Bi_{1/2}Na_{1/2}TiO_3$–$0.06BaTiO_3$ (BNT–6BT), was produced by the mixed oxide route. Details of the powder processing are given elsewhere [42]. Samples of cylindrical shape were sintered at 1150 °C for 3 h with subsequent round grinding and lapping of the end faces. The final specimens have a diameter of 5.9 mm and a height of 6.0 mm. Thermal annealing was carried out at 450 °C for 30 min in order to minimize residual stress induced during sample preparation. Silver electrodes of ~50 nm thickness were afterwards applied by means of sputtering.

The electromechanical measurements were conducted in a screw-type loading frame equipped with a LVDT-based differential dilatometer and a heating chamber. A detailed description of the measurement technique and the test setup is given by Webber et al. [32,43]. Prior to each measurement, the samples were poled in the same setup with 3 kV mm^{-1} for 3 min under the respective mechanical stress. This was done to account for potential depolarizing effects at elevated temperatures and stress. A high voltage source and a signal generator were used to apply a unipolar cycling at 50 mHz. The input signal contained six subsequent cycles, two cycles each for 3 kV mm^{-1}, 2 kV mm^{-1}, and 1 kV mm^{-1}; the second cycle of each electric field was used for evaluation. Note that the term “field” denotes the electric field throughout this paper.

A total of 20 compressive stress states ranging from the minimum required contact pressure of ~2 MPa up to ~446 MPa were investigated. During unipolar electrical cycling, the stress was kept constant with a force control rate of 100 N s^{-1}. The temperature was increased stepwise from room temperature to 50 °C, 75 °C, 100 °C, 125 °C, and 150 °C. It is known that BNT–6BT displays significant low cycle fatigue under bipolar cycling [44]. For this reason, subsequent to the described testing sequence, the sample was cooled back to room temperature and retested under preload. It was found that the initial (before testing sequence) and the final (following testing sequence) measurements at 2 MPa corresponded well, confirming that the electromechanical properties of the samples had not been altered by the testing procedure, i.e., the sample did not fatigue with unipolar cycling. Moreover, a further sample was used to double-check reproducibility for various selected stress states. For the sake of simplification, measurements that were carried out with minimum contact pressure of 2 MPa are termed “measurements under zero-stress conditions”. Since we are exclusively considering compressive stress, the minus sign is omitted throughout this work.

The controller accuracy of the furnace is ±0.1 °C. Furthermore, the utilized load cell exhibits a calibrated accuracy of less than ±0.5% while the accuracy of the