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ScienceDirect

Acta Materialia 66 (2014) 340–348

Acta MATERIALIA

www.elsevier.com/locate/actamat

Resolving structural contributions to the electric-field-induced strain in lead-free $(1-x)Ba(Zr_{0.2}Ti_{0.8})O_3 - x(Ba_{0.7}Ca_{0.3})TiO_3$ piezoceramics

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Received 3 September 2013; received in revised form 2 November 2013; accepted 5 November 2013
Available online 3 December 2013

Abstract

The large signal macroscopic strain response during an applied bipolar electric field is calculated from field-dependent in situ XRD data using expressions for, first, a lattice strain contribution and, second, a ferroelastic strain contribution. The lattice strain contribution is estimated using a weighted average of the lattice strains for the observed reflections along the field direction. The ferroelastic strain contribution is calculated by integrating the lattice parameter changes weighted with the ferroelastic domain distribution over all orientations relative to the direction of the applied field. Structural parameters are determined by means of both single peak fitting and Rietveld refinements. A large ferroelastic contribution is found for tetragonal $(1-x)Ba(Zr_{0.2}Ti_{0.8})O_3 - x(Ba_{0.7}Ca_{0.3})TiO_3$ materials that appears to be the dominant origin for the large signal macroscopic strain. The strong changes in lattice parameters and the decrease in tetragonality as a function of orientation and electric field also indicate a large influence of microstructure constraints on the macroscopic strain response. The total strain calculated from X-ray diffraction using both methods is in good agreement with macroscopic strain measurements.

Keywords: Piezoelectricity; Ferroelastic domains; In situ X-ray diffraction

1. Introduction

The development of new lead-free piezoelectric materials for use as actuators, sensors and transducers [1–3] has advanced significantly throughout the past 10 years, driven by the need to replace prominent lead-containing piezoelectric materials such as lead zirconium titanate (PZT) [4–8]. While initial investigations focused mainly on $(K,Na)NbO_3$ (KNN) and $(Bi_{0.5}Na_{0.5})TiO_3$ (BNT) based systems [4], the report in 2009 by Liu and Ren [9] of Ca^{2+}- and Zr^{4+}-substituted $BaTiO_3$ with piezoelectric coefficients larger than 600 pm V^{-1} raised great research interest. In the pseudo-binary phase diagram of $(1-x)Ba(Zr_{0.2}Ti_{0.8})O_3 - x(Ba_{0.7}Ca_{0.3})TiO_3$ (BZT–BCT) there is a strongly temperature-dependent morphotropic phase boundary (MPB) region that separates rhombohedral *R*3*m* from tetragonal *P*4*mm* single phase fields [9] At the MPB the possibility of phase coexistence between those two structures [9–11] or an orthorhombic *Amm*2 structure [12] has been discussed, which apparently enables enhanced piezoelectric performance.

Besides finding a lead-free composition with improved piezoelectric properties, it is important to understand real-world boundary conditions, such as the electric-field-induced response under an applied mechanical load [13], or the effect of electric poling on the properties of the piezoceramics [14–16]. Understanding these properties will require a detailed knowledge about the underlying structural origin of the strain generation. The strain response

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1359-6454/$36.00
http://dx.doi.org/10.1016/j.actamat.2013.11.021

for piezoelectric materials originates from two main contributions: (i) an intrinsic piezoelectric lattice strain; and (ii) an extrinsic ferroelastic strain [17]. Additionally, in PZT- and BNT-based materials an electric-field-induced strain has been reported to originate from field-induced crystallographic phase changes [18–21]. Also, there is always an electrostrictive component that is usually small compared to the piezoelectric response if the material is not used above the Curie temperature [3]. Therefore, the electrostrictive effect is not discussed further. Ideally, the intrinsic piezoelectric effect constitutes the lattice strain, which is in the converse case given by $\varepsilon_{jk} = d_{ijk}E_i$ [22]. Here, ε_{jk} is the strain tensor, d_{ijk} is the piezoelectric tensor and E_i is the applied electric field. However, in a ceramic material, constraints due to the microstructure have to be considered [23]. The extrinsic strain, on the other hand, is caused by the motion of ferroelastic, or non-180°, domain walls that increases the volume fraction of ferroelastic domains aligned in and around the direction of the applied electric field E [17]. This means that in tetragonal materials the domains that have their long unit cell axis c aligned with E will grow at the expense of those domains that have c misaligned with E. As a result, a ferroelastic domain texture is induced, commonly expressed as the multiple of random distribution $f_{00l}(\alpha)$ [24], which is a function of the angle α to E. Having a larger volume fraction of domains with their long c axis being aligned along E leads directly to a strain of the material in the direction of ferroelastic domain alignment.

In situ X-ray diffraction (XRD) has been demonstrated to be an exceptionally powerful method for quantifying these individual processes, and has thereby advanced the understanding of piezoelectric materials under an applied electric field [20,21,23–28]. Here we show that electric-field-dependent in situ XRD can be successfully used to not only characterize individual structural processes, but also successfully resolve the macroscopic large signal strain response. For new lead-free BZT–BCT materials, a large extrinsic contribution is identified as the dominant macroscopic strain origin that impacts the stress states for grains with different orientations to E individually and, as a result, also impacts the orientation-dependent lattice responses. The work can significantly advance the understanding of lattice and domain processes present in piezoelectric materials, which could help to advance the development of materials that constitute a feasible alternative to lead-containing piezoelectrics such as PZT.

2. Experimental

Tetragonal BZT–BCT piezoelectric ceramics with the chemical formula $(1-x)Ba(Zr_{0.2}Ti_{0.8})O_3 - x(Ba_{0.7}Ca_{0.3})TiO_3$, where $x = 0.6$, were produced using a conventional solid oxide route, described in detail elsewhere [10]. The samples were fired for 3 h in air at 1450 °C. Sample surfaces were ground with 1200 grit SiC paper and then annealed at 600 °C to release residual stresses. Samples used for strain experiments were disk-shaped, with a diameter of ca. 10 mm and a thickness of 1 mm. The density of the samples is 5.4 ± 0.1 g cm^{-3} and was determined using Archimedes' principle [29]. The average grain size is 19 ± 4 μm and was estimated from a scanning electron microscope image using the mean lineal intercept method. Silver electrodes were applied by means of sputtering. For the in situ XRD, bar-shaped samples with dimensions of approximately 0.8 mm × 1 mm × 7 mm were cut from the ceramic disks. Silver paint electrodes were applied to the 1 mm × 7 mm faces.

The in situ XRD experiments were carried out at beamline 5-BM-D at the Advanced Photon Source of Argonne National Lab. A transmission geometry with a spot size on the sample of 0.5 mm × 0.5 mm and a photon energy of 65 keV (0.19074 Å) was used. The sample was mounted in a custom-made sample holder, in which silicon oil protects it from arcing during field application. The electric field was applied at discrete steps in the direction perpendicular to the beam using a Matsusada (Kusatsu-City, Japan) AMS-10B2 high-voltage amplifier connected to an Agilent (Santa Clara, CA) 33220A arbitrary waveform generator. The peak fields were $E_{max} = |1.84$ MV/m|, which corresponds to approximately four times the coercive field, $4 \times E_c$ [15]. Angular diffraction data for a complete bipolar cycle was collected using a flat-panel MAR345 detector (Marresearch GmbH, Norderstedt, Germany). The intensity is integrated over 10° azimuthal sectors. In this geometry, each azimuth represents scattering from lattice planes at an angle $\alpha \pm 5°$ away from the field direction, with $\alpha = 0°$ being parallel and $\alpha = 90°$ being perpendicular to E. Data collection at each electric field step took 3 min. During collection, the sample was translated perpendicular to both the beam and the electric field to increase the grain sampling statistics. The diffraction peaks were fitted using Gaussian peak profile functions. Errors of quantities calculated from the XRD data are all calculated from the errors of the peak fitting parameters according to error propagation. The results from the peak fitting are denoted with the superscript F from here on. In addition, the Rietveld software "Materials Analysis Using Diffraction" (MAUD) [30] is used to determine the structural parameters and compare them to the results from the single peak fitting. For MAUD, all 36 sectors are used to first determine the ferroelastic domain textures $f_{hkl}(\alpha)$ using a fourth-order harmonic texture model, assuming fiber texture and a *P*4*mm* structure model [11,12]. After refining $f_{hkl}(\alpha)$ at all E, the texture parameters were fixed and only the lattice parameters a and c were refined at all E. For this, all sectors with different orientations to E were refined individually to account correctly for anisotropic structural changes, but equivalent directions were refined simultaneously to increase the signal to noise ratio. Equivalent sectors are those that are oriented at equivalent angles to E, e.g. (0°/180°), (90°/270°), (10°/350°/170°/190°), (20°/340°/160°/200°), and ideally give the same results due to their symmetrical relationship. Since the reflections at a given angle