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Stress-induced phase transition in lead-free relaxor ferroelectric composites



Lukas M. Riemer^a, Lalitha K.V.^a, Xijie Jiang^a, Na Liu^a, Christian Dietz^a, Robert W. Stark^a, Pedro B. Groszewicz^b, Gerd Buntkowsky^b, Jun Chen^c, Shan-Tao Zhang^d, Jürgen Rödel^a, Jurij Koruza^{a,*}

^a Department of Materials and Geoscience, Technische Universität Darmstadt, 64287, Darmstadt, Germany

^b Institute of Physical Chemistry, Technische Universität Darmstadt, 64287, Darmstadt, Germany

^c Department of Physical Chemistry, University of Science and Technology Beijing, Beijing, 100083, China

^d National Laboratory of Solid State Microstructures and Department of Materials Science and Engineering, College of Engineering and Applied Science, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing, 210093, China

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ABSTRACT

Piezoelectric materials are considered an enabling technology generating an annual turnover of about 20 billion \$. At present, lead-based materials dominate the market with the known risk to health and environment. One of the three key competitors for their replacement is the class of sodium bismuth titanate (NBT)-based relaxor ferroelectrics, the use of which is limited by thermal depolarization. An increased thermal stability has recently been experimentally demonstrated for composites of $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ - 6BaTiO_3 with ZnO inclusions (NBT-6BT: $x\text{ZnO}$). However, the exact mechanism for this enhancement still remains to be clarified. In this study, piezoresponse force microscopy and ^{23}Na NMR spectroscopy were used to demonstrate that the incorporation of ZnO leads to a stabilization of the induced ferroelectric state at room temperature. Temperature-dependent measurements of the relative dielectric permittivity $\epsilon'(T)$, the piezoelectric coefficient d_{33} and the strain response revealed an increase of the working temperature by 37 °C. A simple mechanics model suggests that thermal deviatoric stresses stabilize the ferroelectric phase and increase, as well as broaden, the temperature range of depolarization. Our results reveal a generally applicable mechanism of enhancing phase stability in relaxor ferroelectric materials, which is also valid for phase diagrams of other ceramic matrix composites.

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1. Introduction

Ferroelectric materials are essential for piezoelectric applications and modern electronic components. The dominating materials, first and foremost compositions based on $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT), all contain lead [1]. Unfortunately, lead is hazardous and prolonged efforts have been made to advance lead-free alternatives [2]. Among the promising candidates to partially replace PZT are the

$\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ (NBT)-based¹ solid solutions [2], for example with BaTiO_3 (BT) [3]. This system reveals a morphotropic phase boundary (MPB) at a BT content of 6–7 mol.%, wherein the material possesses relaxor ferroelectric properties [4–6].

In the proximity of the MPB, the average structure obtained by X-ray and neutron scattering techniques commonly presents a pseudocubic symmetry [7–9]. However, a phase mixture of rhombohedral and tetragonal symmetry on a local scale was observed by using transmission electron microscopy (TEM) [9,10]. A locally non-cubic structure of NBT- $x\text{BT}$ was further evidenced by recent investigations employing nuclear magnetic resonance

* Corresponding author. Alarich-Weiss-Straße 2, 64287, Darmstadt, Germany.

E-mail addresses: lukas.riemer@gmx.de (L.M. Riemer), venkataraman@ceramics.tu-darmstadt.de (K.V. Lalitha), jiang@pos.tu-darmstadt.de (X. Jiang), liu@pos.tu-darmstadt.de (N. Liu), dietz@pos.tu-darmstadt.de (C. Dietz), stark@pos.tu-darmstadt.de (R.W. Stark), groszewicz@chemie.tu-darmstadt.de (P.B. Groszewicz), gerd.buntkowsky@chemie.tu-darmstadt.de (G. Buntkowsky), junchen@ustb.edu.cn (J. Chen), stzhang@nju.edu.cn (S.-T. Zhang), roedel@ceramics.tu-darmstadt.de (J. Rödel), koruza@ceramics.tu-darmstadt.de (J. Koruza).

¹ The authors would like to point out that according to IUPAC recommendations, with electronegativity taken as the ordering principle, the preferable nomenclature is $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ - 6BaTiO_3 (NBT) and not $\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ - 6BaTiO_3 (BNT) as is often used in literature for historical reasons.

spectroscopy of sodium (^{23}Na NMR) [5,11]. For the MPB composition $0.94\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3\text{-}0.06\text{BaTiO}_3$ (NBT-6BT), an irreversible electric-field-induced transition from a non-polar (non-ergodic relaxor) to a long-range ordered ferroelectric state with macroscopic remanent polarization was observed [12,13] and an electric field-temperature phase diagram was reported [14]. Analogous to the electric-field-induced phase transitions, stress-induced transitions were also detected and a corresponding stress-temperature phase diagram was constructed [15].

A major challenge for the technological use of NBT-based systems is a pronounced reduction of macroscopic piezoelectric properties at the depolarization temperature, which for the NBT-6BT composition occurs at about $100\text{ }^\circ\text{C}$ [2,16]. Various techniques have been discussed to assess the depolarization temperature [17]. The depolarization is initiated through a randomization of domain structure as evidenced by piezoelectric and ferroelectric measurements at the depolarization temperature T_d and is finalized by a ferroelectric to relaxor transition at T_{F-R} [18].

T_d can be increased by applying an external electric field during heating [19]. An increase in T_d of NBT-BT by chemical modifications is not expected without considerably decreasing the piezoelectric properties. Moreover, a natural mutual interdependence between good piezoelectric properties and enhanced thermal stability was established for a variety of ferroelectric solid solutions and doped systems [2,20,21]. At the same time, anisotropic flattening of the Gibbs free energy near a phase transition promotes a high piezoelectric response, but reduces the stability of domain orientation causing premature depolarization [21,22]. A solution for this quandary was recently demonstrated by the development of (3–0)-type composites without thermal depolarization up to $130\text{ }^\circ\text{C}$ [23]. These composites consisted of the relaxor ferroelectric NBT-6BT and the semiconductor ZnO. Isothermal bipolar hysteresis loops, temperature-dependent measurements of the relative dielectric permittivity $\epsilon'(T)$, and retained d_{33} measurements were used to quantify the depolarization behavior. A charge order model was proposed that explains the enhanced thermal stability with a partial compensation of the depolarization fields at pores and interfaces by the free electrons of ZnO.

In this study, unpoled NBT-6BT: x ZnO composites were investigated by means of polarization and strain analysis, piezoresponse force microscopy (PFM), Kelvin probe force microscopy (KPFM) and ^{23}Na NMR at room temperature. A single particle model is used to estimate the thermal stresses in the composites in order to assess its influence on the relaxor to ferroelectric transformation. Furthermore, temperature-dependent in situ d_{33} , dielectric permittivity, and large-signal strain measurements were used to gain further insight into the thermal depolarization behavior.

2. Experimental section

2.1. Sample preparation

$0.94\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3\text{-}0.06\text{BaTiO}_3$ powder was prepared by means of the conventional solid-state synthesis method. Stoichiometric amounts of powders of Bi_2O_3 (99.975%), BaCO_3 (99.8%), Na_2CO_3 (99.5%), and TiO_2 (99.6%) (all Alfa Aesar), were weighed and milled for 24 h in ethanol at 250 rpm in a planetary ball mill (Fritsch Pulverisette 5). The dried powders were calcined in closed alumina crucibles at $900\text{ }^\circ\text{C}$ for 3 h with a heating rate of 5 K min^{-1} . The obtained NBT-6BT powder was ground by mortar and pestle, milled for 24 h in ethanol at 250 rpm, and subsequently dried. The powder was sieved with a $160\text{ }\mu\text{m}$ nylon sieve and annealed in closed alumina crucibles at $1100\text{ }^\circ\text{C}$ for 3 h in order to coarsen the particles.

The annealed NBT-6BT powder was ground by mortar and pestle, sieved ($160\text{ }\mu\text{m}$ sieve) and weighed together with ZnO nano-

sized powder (25 nm, 99.5%, PlasmaChem GmbH, Berlin) to form mixtures with ZnO/NBT-6BT mole ratios of $x = 0.1, 0.2, 0.3,$ and 0.4 . A final milling step of 24 h in ethanol at 250 rpm was used to obtain the final powder mixture.

For analytical purposes, disks with a diameter of 10 mm were manually cold-pressed, cold isostatically compacted at 40 MPa and sintered in closed alumina crucibles at $1012\text{ }^\circ\text{C}$ for 1 h with a heating rate of 9 K min^{-1} . As a reference, 10 mm NBT-6BT disks from non-coarsened powder were sintered in closed alumina crucibles at $1150\text{ }^\circ\text{C}$ for 3 h with a heating rate of 5 K min^{-1} . To avoid volatilization of bismuth and sodium during sintering, all the samples were embedded in atmospheric powders with the same composition.

2.2. Methods

The microstructure was characterized by scanning electron microscopy (SEM) (Philips XL30 FEG) and density measurements (Archimedes method). XRD measurements were performed on ground and annealed samples with a Bruker D8 diffractometer in Bragg-Brentano geometry and locked couple mode using Cu-K α radiation. For electrical measurements, the samples were ground to a thickness of 0.6 mm and coated with a layer of silver paste. The burn-in of the electrodes and the annealing of the samples were performed simultaneously at $550\text{ }^\circ\text{C}$ for 30 min with a heating rate of 5 K min^{-1} and slow cooling. Samples were poled at room temperature for 20 min at 6 kV min^{-1} , 24 h before measurement.

Polarization and strain as a function of electric field were measured with a triangular field up to 6 kV mm^{-1} at 1 Hz using a Sawyer-Tower circuit equipped with an optical sensor. The same electric field was also used to investigate the temperature-range between 25 and $140\text{ }^\circ\text{C}$ with a TF Analyzer 2000 (AixACCT systems).

PFM and KPFM measurements for the characterization of the local domain morphology and surface potential, respectively, were performed using a MFP-3D atomic force microscope (Asylum Research). The measurements were acquired using electrically conductive cantilevers of the type ASYELEC-01 and AC240TM, (Asylum Research) with nominal free resonance frequencies of 70 kHz and 60 kHz, respectively, and nominal force constants of 2 N m^{-1} . Images were taken at a scan rate of 0.5 Hz with a resolution of 256×256 pixels. For the overview PFM measurements, an *ac* driving voltage of 3 V (peak amplitude), and a drive frequency close to the tip-sample contact resonance frequency which was approximately 300 kHz in the single frequency PFM mode were used. For the high-resolution PFM images, we used the dual *ac* resonance tracking mode [24] applying two drive frequencies f_1 and f_2 close to the contact resonance frequency (frequency difference $\Delta f = f_1 - f_2 = 8\text{ kHz}$, drive voltages for both signals 5 V). KPFM [25] was performed in standard lift mode using a lift height of 50 nm. The sample was polished as described in Ref. [26].

Temperature and frequency-dependent permittivity measurements were performed with a Hewlett Packard 4192 LF Impedance Analyzer from room temperature to $450\text{ }^\circ\text{C}$ and a heating rate of 2 K min^{-1} . In situ d_{33} values as a function of temperature were measured by the converse method with a Polytec VDD-E-600 Vibrometer Front-End and a Polytec OFV-505 Sensor Head using an amplitude of 20 V_{pp} , a frequency of 1 kHz, and a heating rate of 2 K min^{-1} .

^{23}Na magic angle spinning (MAS) NMR spectra were recorded with a Bruker AVANCE III 600 MHz spectrometer operated at a frequency of 158.745787 MHz. A 4 mm MAS probe was employed for spinning prism-shaped (1 mm thick) ceramic samples at 10 kHz. A single-pulse experiment with a pulse length of 0.75 μs , a recycle delay of 1.0 s and a dwell time of 0.2 μs ensured appropriate excitation and recording of the spectra. The spectrum of NBT-15BT was

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