Temperature stable electric field-induced strain in Er-doped BNT-BT-BKT ceramics

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Temperature stable electric field-induced strain in Er-doped BNT-BT-BKT ceramics

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Abstract

Dense single-phase Pb-free B-site Erbium doped 80.4BNT-2.6BT-17BKT ceramics were prepared by the conventional solid state route. These ceramics exhibited a stable high unipolar strain of 0.13% under an applied electric field of 60 kV cm^{-1} from room temperature to 175 °C, with a variation no greater than 12%.

KEYWORDS: Pb-free, Piezoelectric, ceramics, strain, Raman, ferroelectric

1. Introduction

Precise controlled mechanical displacements in many devices such as fuel injectors, micro-pumps, ink cartridges and medical instruments is provided by piezoelectric and electrostrictive actuators. Basically, these devices convert directly electrical energy into mechanical displacement. The current market for piezoelectric actuators is in excess of 20 billion dollars.[1] Presently, these actuators are mainly fabricated from ferroelectric $Pb(Zr,Ti)O_3$ (PZT)-based ceramics because they exhibit large field-induced strain combined with large electromechanical coupling coefficients for compositions lying at morphotropic phase boundary between rhombohedral and tetragonal symmetries. Moreover, PZT ceramics also offer a temperature stable electromechanical response, which is a stringent pre-requisite within some technological areas such as aerospace and automotive.

Since the early 2000's there has been a worldwide search for Pb-free piezoceramics, as a response to legislation enacted by the European Union aiming at the elimination of toxic substances from electrical and electronic equipment. Research has been focused in several different approaches, ranging from the search for systems exhibiting morphotropic phase boundaries to materials exhibiting electric field-induced phase transitions, such as incipient piezoelectrics.

In purely ferroelectric ceramics such as PZT, remanent strain due to non-180° domain switching limits the maximum achievable strain under unipolar loading to half of the value measured under bipolar loading. Interestingly, the absence of remanent strain in incipient piezoceramics is accompanied by a so-called "giant" unipolar strain.

Teranishi et al[2] reported a giant strain of ~0.87% under an applied electric field of 40 kV/cm for $Bi_{0.5}Na_{0.5}TiO_3$–$Bi_{0.5}K_{0.5}TiO_3$–$BaTiO_3$ (BNT-BKT-BT) tetragonal single crystals, along [100] direction. A value six times larger than exhibit by PZT. Subsequently, several researchers investigated the

electromechanical response of ceramics in this ternary system. The impact of minor doping has been seldom investigated, but for example, Shieh et al[3] showed Mn additions to sharply decrease induced electrostrain from 0.14% to 0.05% when 2 mol% Mn was added to $Bi_{0.487}Na_{0.427}K_{0.06}Ba_{0.026}TiO_3$ (BNKBT). This detrimental effect of Mn doping contrasts dramatically with the improvement observed by the Obilor et al[4], in $Bi_{0.487}Na_{0.427}K_{0.06}Ba_{0.026}Ti_{0.98}Nb_{0.02}O_3$ (Nb-BKNBT), where substitutional doping of Ti by 2 mol% Nb leads to an increase of the unipolar strain from 0.19% to 0.43% at 75 kV/cm. The temperature dependence of the electric field-induced strain in Nb-BKNBT was found to be field dependent, i.e. the temperature stability of the strain was found to worsen continuously with increasing electrical fields. For example, under an applied field of 40 kV/cm the variation of maximum achievable strain in the 25-170 °C temperature range was no greater than 20%, however under a field of 60 kV/cm and in the same temperature range this variation was greater than 90%. In 2017, Hao et al[5] studied both the electromechanical and up-conversion of $(Bi_{0.5}Na_{0.5})_{0.945}Ba_{0.065}Ti_{1-x}(Er_{0.5}Sb_{0.5})xO_3$ and found a large field-induced strain of 0.40% at 80 kV/cm, but they did not investigate the temperature dependence of this exceptional strain. More recently, Jiang et al[6] investigated the of the up-conversion emission properties of $Na_{0.5}Bi_{0.49}Er_{0.01}TiO_3$ single crystals, but not the electric field induced properties such as polarisation and strain. Here we report the room-temperature structure, vibrational properties and temperature dependence of the electromechanical properties of Er-doped $Bi_{0.487}Na_{0.402}K_{0.085}Ba_{0.026}Ti_{0.98}Er_{0.02}O_3$ ceramics.

2. Experimental

Er-doped $Bi_{0.487}Na_{0.402}K_{0.085}Ba_{0.026}Ti_{0.98}Er_{0.02}O_3$ (Er-BNKBT) ceramics were prepared by the conventional mixed oxide route. The starting materials were high-purity grade Bi_2O_3, Na_2CO_3, K_2CO_3, $BaCO_3$, TiO_2 and Er_2O_3 powders (≥98%, ≥99.9%, 98%, 99.9% and ≥99% purity, respectively, Sigma-Aldrich). The starting chemicals were pre-dried, weighed in the required molar ratio and intimately mixed for 48 h in propanol using a ball mill and zirconia media. Subsequently the dried slurry was calcined in air at 850 °C for 4 h. Purity and crystallinity were determined by x-ray diffraction (XRD) using a high-resolution diffractometer (CuK_α, 1.5418 Å, D8 Empyrean XRD, PANalytical™, Almelo, The Netherlands) operated at 40 kV and 40 mA, in the 2Θ range between 20 and 70, with 2Θ increments of 0.013 and counting time of ~100 s per step.

The calcined powder was finely milled and uniaxially pressed into pellets under an applied pressure of ~150 MPa. The green compacts were fired in air at 1150 °C for 2 hours, using a controlled heating rate of 5 °C /min. Ceramic microstructures were examined using a scanning electron microscope (SEM) (model: Quanta 200, FEI, Brno, Czech Republic) equipped with a W filament. Samples were gold coated before SEM in order to avoid charging.

Depolarized Raman spectra were obtained in back-scattering geometry using a micro-Raman spectrometer (model: DXR™ 2, Thermo Fisher Scientific, Paisley, UK), equipped with a Rayleigh line-rejection edge filter that was set for the 532 nm excitation of an Ar^+ ion laser, which allowed ripple-free measurements down to 50 cm^{-1} from the laser line. Spectra were acquired using a 10× microscope objective and a laser power of 0.1 to 1 mW.

Pt-electrodes were applied to both sides of the fired ceramic disk for subsequent electrical measurements. The polarisation and strain response was recorded by applying a high voltage triangular signal using a ferroelectric tester equipped with a laser interferometer (AixACCT TF 2000). The large signal piezoelectric coefficient was calculated using the maximum achievable strain (S_{max}) normalized by the maximum electric field (S_{max}/E_{max}), where E_{max} is unipolar.

3. Results and Discussion

Room-temperature X-ray diffraction data for Er-BKNBT ceramics fired at 1150°C for 4 h are illustrated in Fig. 1. Ceramics appear to be single-phase within the detection limits of the apparatus, suggesting that Er successfully enters the BKNBT lattice. Their typical microstructure is illustrated in the inset of Fig. 1. Ceramics consist mostly of cube-shaped grains with grain sizes ranging from 0.4 to ~1.5 μm.

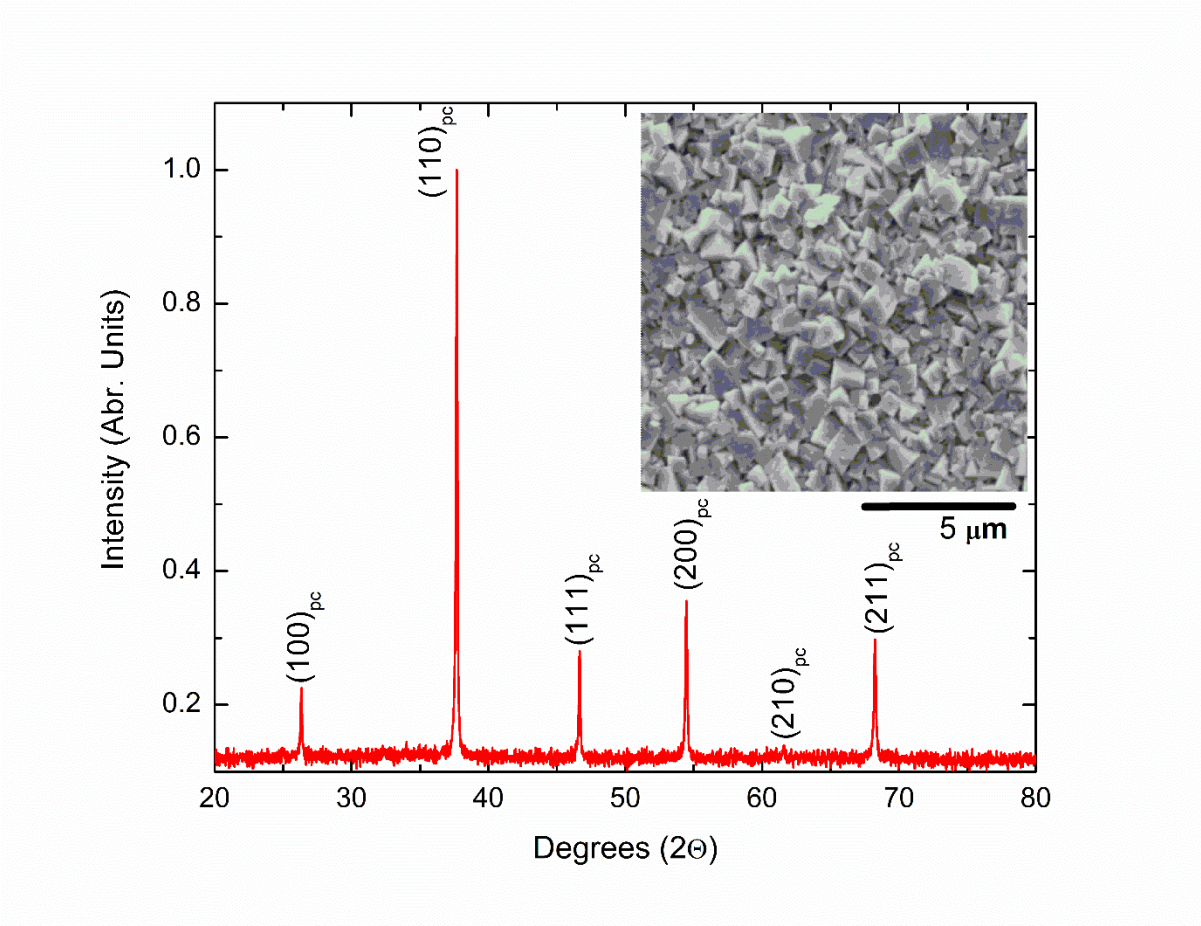

Figure 1 Room-temperature XRD data and microstructure (in the inset) for Er-BKNBT ceramics fired at 1150 ℃ for 4 h.

A pseudocubic crystal structure is corroborated by the appearance of strong Raman modes, as illustrated in Fig. 2, but also by a remarkable electric-field induced strain, as illustrated in Fig. 3. Intense broad modes in the Raman spectra, clearly show that the local crystal symmetry cannot be described by the cubic $Pm\bar{3}m$ space group, as previously discussed by Pascual-Gonzalez et al[7]. The spectrum can be divided into three regions as previously done by Schütz et al[8]. These regions correspond to different types of lattice vibrations described as follows. The < 150 cm^{-1} region can be associated with A-site vibrations, thus involving Bi, Na, K and Ba cations, whereas the 150-450 cm^{-1} region can be associated with Ti–O vibrations, particularly with the bond strength. Finally, high-frequency region above 450 cm^{-1} has been associated with TiO_6 vibrations, namely stretching and breathing of oxygen octahedra. From Fig. 2, in comparison with the work by Obilor et al[4] it becomes apparent that Er doping affects modes associated with Ti–O and TiO_6 vibrations, which corroborates Er incorporation in the B-site.

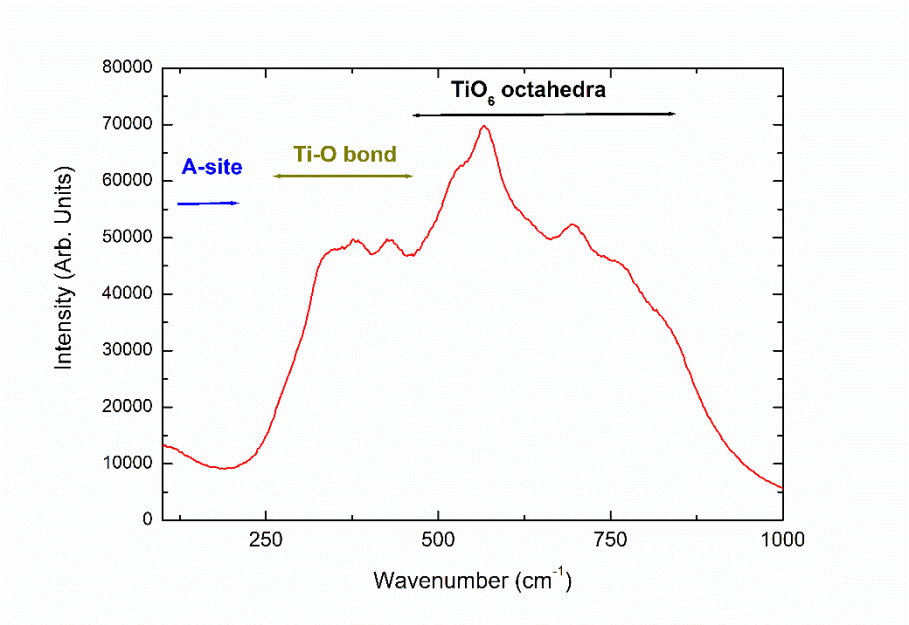

Figure 2 Room-temperature Raman spectroscopy data for Er-BKNBT ceramics fired at 1150 ℃ for 4 h.

The room-temperature field-induced bipolar strain (S-E) and polarisation (P-E) for Er-BKNBT ceramics measured at 1 Hz under an applied electrical field of 60 kV/cm are illustrated in Fig. 3. The S-E curves exhibit reminiscences of a so-called butterfly-shaped strain response, but are closer to a so-called sprout-shaped response. Nevertheless, there are still vestiges of negative strain, which is related to domain back switching, a typical feature in truly ferroelectric materials. The maximum achievable strain is ~0.13%, whereas at zero field the remanent strain is only 0.01%, suggesting destabilisation of ferroelectricity. The P-E loop shows a maximum polarisation of 27.6 μm/cm^2 and a remnant of 10.6 μm/cm^2.

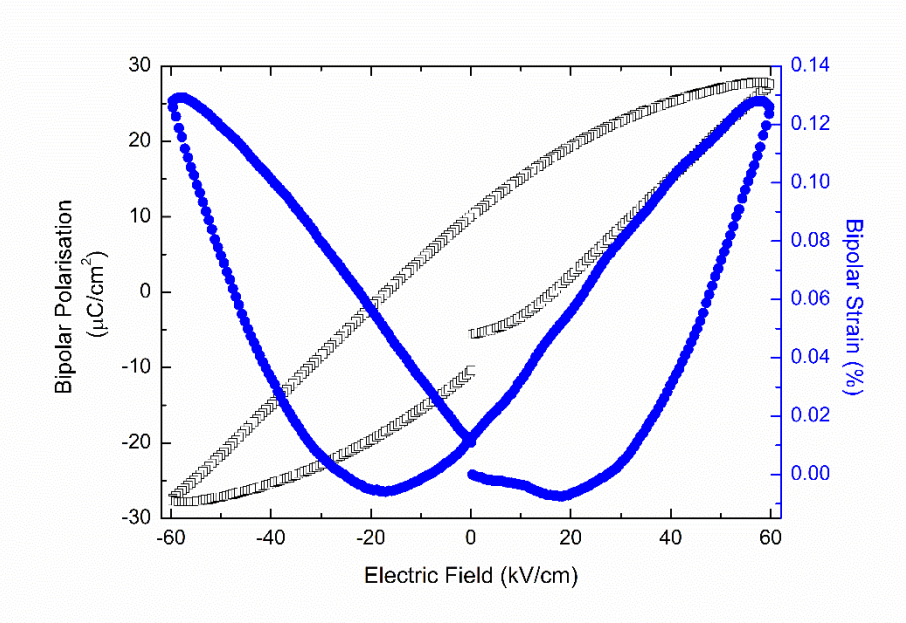

Figure 3 Bipolar field-induced polarisation and strain for Er-BKNBT ceramics fired at 1150 ℃ for 4 h.

Only positive strains are usable in actuator devices and many large-volume applications require stable unipolar electrostrain over extended temperature ranges. Hence, temperature dependent measurements of the unipolar strain for Er-BKNBT ceramics were carried out to evaluate and compare the potential of those ceramics as an actuator material. Measurements carried out under an applied field of 60 kV/cm up to 175°C are illustrated in Fig. 4. The polarisation values vary from 19.9 to 28.4 μC/cm^2, whereas the electrostrain exhibits a higher degree of stability over the temperature range.

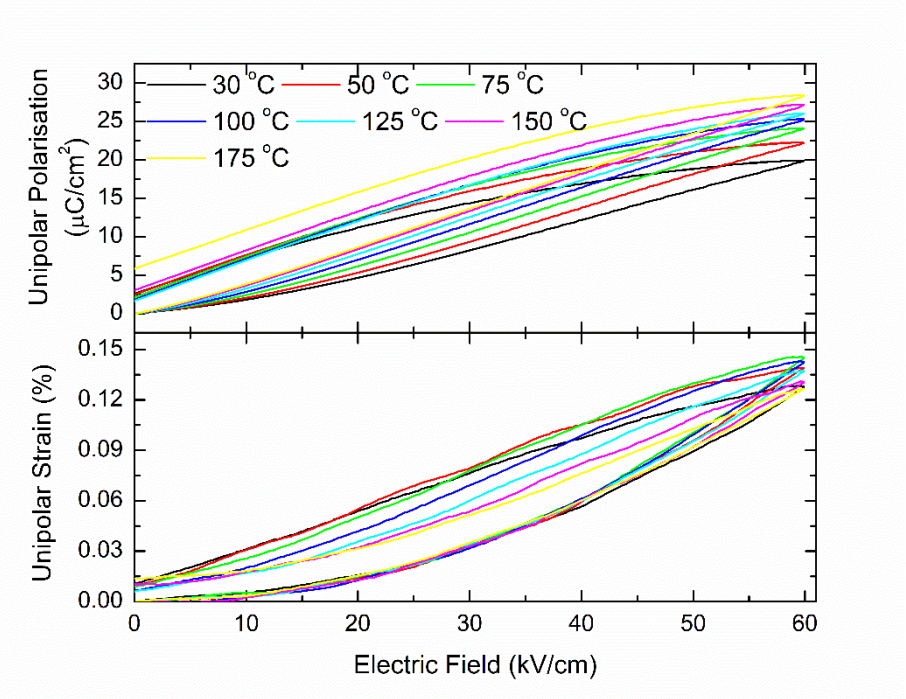

Figure 4 Temperature dependence of the unipolar field-induced strain for Er-BKNBT ceramics fired at 1150 ℃ for 4 h.

Finally, Fig. 5 summarises the temperature dependence of both the unipolar strain and the S_{max}/E_{max} for Er-BKNBT ceramics obtained from the unipolar measurements. At room temperature, ceramics exhibit a field-induced strain of 0.13% and a S_{max}/E_{max} of ~ 213 pm/V. In the entire temperature range those parameters do vary less than 15%. The maximum field-induced strain is lower compared with $(Bi_{0.5}Na_{0.5})_{0.945}Ba_{0.065}Ti_{1-x}(Er_{0.5}Sb_{0.5})xO_3$[5] but it shows a good temperature stability. A comprehensive study of Er-BKNBT of different Bi/K/Na/Ba ratios will be presented elsewhere, showing how stability and the maximum achievable strains are correlated.

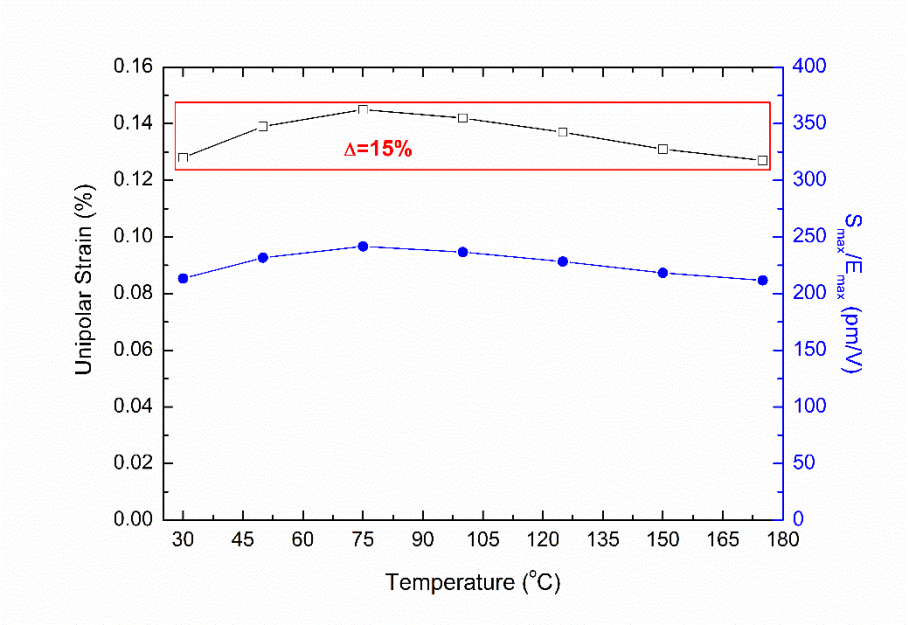

Figure 5 Temperature dependence of the field induced strain and S_{max}/E_{max} for Er-BKNBT ceramics fired at 1150 ℃ for 4 h.

4. Conclusions

In summary, a Pb-free ceramic exhibiting a unipolar strain of 0.13% (S_{max}/E_{max} =213 pm/V) at room-temperature under applied electric field of 60 kV/cm was obtained by chemical substitution of Ti by 2 mol % Er in the parent $Bi_{0.487}Na_{0.402}K_{0.085}Ba_{0.026}TiO_3$ composition. The material shows a variation of the electrical field-induced strain no greater than 12% in the 25-175 °C temperature range.

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References

[1] A. Khesro, D. W. Wang, F. Hussain, D. C. Sinclair, A. Feteira, and I. M. Reaney, Applied Physics Letters **109** (14), 142907 (2016).

[2] S. Teranishi, M. Suzuki, Y. Noguchi, M. Miyayama, C. Moriyoshi, Y. Kuroiwa, K. Tawa, and S. Mori, Applied Physics Letters **92** (18) (2008).
[3] J Shieh, YC Lin, and CS Chen, Journal of Physics D-Applied Physics **43** (2) (2010).
[4] U. Obilor, C. Pascual-Gonzalez, S. Murakami, I. M. Reaney, and A. Feteira, Materials Research Bulletin **97**, 385 (2018).
[5] J. G. Hao, Z. J. Xu, R. Q. Chu, S. Chu, W. Li, P. Fu, J. Du, and C. C. Hu, Materials Letters **193**, 138 (2017).
[6] L. W. Jiang, Z. H. Wang, Y. P. Chen, P. Chen, L. H. Luo, and H. B. Chen, Materials Letters **210**, 158 (2018).
[7] Cristina Pascual-Gonzalez, Giorgio Schileo, Amir Khesro, Iasmi Sterianou, Dawei Wang, Ian. M. Reaney, and Antonio Feteira, Journal of Materials Chemistry C, 1990 (2017).
[8] D Schuetz, M Deluca, W Krauss, A Feteira, T Jackson, and K Reichmann, Advanced Functional Materials **22** (11), 2285 (2012).