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Phase transitions in lead-free piezoelectric ceramics monitored by the resonance method

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Abstract

Ferroelectrics, like batio$_3$ (bt) or binatio$_3$ (bnt), were studied in the 1950s and are now revisited, due to the need for lead-free piezoceramics, according to worldwide directives for environmental protection. Poling some of these materials has shown a different physical mechanism than ferroelectric domain orientation, involving field-induced structural phase transitions from pseudo-cubic phases to ferro-piezoelectrically active ones. They also depolarize below the curie temperature due to a structural phase transition. Both poling and thermal depoling can be monitored by the measurement of the electromechanical resonances. Depoling of (1-x) bnt-xbt ceramics with x=0.04 (bnbt4) is here considered as a case study.

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1. Introduction

Recent studies revealed the electric field dependent crystal structure of ceramics at the solid-solution system (1-x)($Bi_{0.5}Na_{0.5}$)TiO_3-x$BaTiO_3$ (BNBT100x) near the Morphotropic Phase Boundary (MPB) (Wylie-van Eerd et al., 2010; Fuentes-Cobas et al., 2014), which takes place in the wide composition interval of $0.05< x <0.11$. This is at present focus of interest for many researchers and explains the relatively low ultrasonic transduction of the MPB compositions. Enhanced ultrasonic coupling coefficients were in fact found out of the MPB in this system (Chu et al., 2002; Pardo et al., 2011). Besides, BNBT100x ceramic undergoes a thermal depolarization process (Hiruma et al., 2009) that starts at a temperature, T_d, well below that of the permittivity maximum, $T\varepsilon_{max}$, (T_d=100ºC and $T\varepsilon_{max}$=300ºC for BNBT6) and takes place in a temperature region of existence of a low temperature globally non-polar phase at zero field (LTNPZF) (Pardo et al., 2011). Such a phase shows strong dielectric relaxor behavior and has distinct crystal structure than that of the high temperature non-polar phase that exists above $T\varepsilon_{max}$.

This constitutes a drawback for the practical application of this ceramics. The measurement procedure of T_d and the exact structure of the LTNPZF phase are still a matter of discussion (Montero-Cabrera et al., in press 2014).

Undoped ($Bi_{0.5}Na_{0.5}$)$_{0.96}Ba_{0.04}TiO_3$ (BNBT4) ceramics with expected good performance as ultrasonic transducers (k_p≈20%, k_t≈45% and k_{15}≈40%) were prepared and information on the structural phase transitions underlying the depolarization process was sought in this work. To this aim, in-situ measurements of complex impedance at the planar (or radial) and shear resonances of, respectively, thin disks and shear plates, thickness poled, were performed as the sample temperature was increased.

2. Materials and Measurements Procedures

High density (≈ 96% theor. dens.), submicron structured (<G>≈ 400-450nm) BNBT4 ceramics were prepared from mixed oxides powder by hot-pressing and recrystallization (Pardo et al., 2012). The powder was prepared by mixed oxides method starting from Bi_2O_3 (Aldrich 223891), Na_2CO_3 (Merck 6392), $BaCO_3$(Merck 1714) and TiO_2 (Degussa P25), sieving and milling in ethanol with zirconia milling media for 48h. Calcination was carried out at 800ºC for 1h followed by further milling during 120h. Pellets of the powder of 15 mm diameter and 1 mm thickness were obtained by uniaxial pressure forming followed by cold isostatic pressing at 200 MPa. A combination of hot-pressing at low temperature (700-800ºC for 2h), at 20MPa in air, using heating and cooling rates of 3 ºC.min^{-1} and subsequent recrystallization (Moure et al., 2004) at higher temperature (1100ºC in air) has been applied to sinter the green pellets.

Sintered disks were ground to a thickness (t) to diameter (D) ratio below 1/20 (typically t=0.7 and D=15mm) and Ag paint electrodes were printed on their major faces for the electric poling in thickness and for the impedance measurements at the radial and thickness resonance modes. Rectangular plates of a lateral dimensions (L,w) to thickness (t) aspect ratio below 1/10 (typically t=0.5 and L,w=5mm) were also cut from the sintered ceramic disks, electroded and thickness poled (30-35kV.cm^{-1}, 150ºC in a silicone oil bath). Poling electrodes were mechanically removed and a new pair of electrodes was applied on perpendicular surfaces for the electric measurements.

Relative dielectric permittivity and losses (tanδ) vs. temperature curves in parallel and perpendicular directions to polarization, ε^T_{33} and ε^T_{11}, were carried out at various frequencies from impedance measurements in the range between 1kHz and 1MHz with a HP4194A analyzer. The heating and cooling rates were 2ºC.min^{-1} for disks and 0.5, 1 and 2ºC.min^{-1} for plates, to detect possible artifact in case that heating of these samples were slower, since the metallic electrodes were attached to the minor faces.

Depolarization was monitored by the thermal evolution of the radial and the shear modes of electromechanical resonance in thin disks and plates, both of them thickness poled, measured in-situ as the temperature increases. The evolution of the material coefficients with the temperature was determined by analysis of the impedance curves at resonance using an iterative automatic method (Alemany et al., 1995; Pardo et al., 2011).

3. Results and Discussion

The real part of the complex dielectric permittivity, $\varepsilon^*{}^T_{33}$, and losses (tanδ) vs. temperature curves (Figure 1(a) and (c)) of BNBT4 poled thin disks reveal a peak of the losses and a sharp increase of ε^T_{33} at T≈180ºC. The region

above 180ºC presents a high dispersion and extends to the temperature of the maximum permittivity. Also, the permittivity exhibits a thermal hysteresis with a sharp decrease when measuring on cooling the thermally depoled sample at T≈140ºC. This behaviour is in agreement with that previously found at the rhombohedral side of the MPB of this system (Cracium et al., 2012). The sharp increase of $\varepsilon^{T}{}'_{33}$ in poled samples is ascribed to the transition from the ferro-piezoelectric phase (field-oriented macrodomains with long-range polar order) to a relaxor phase (short-range polar order in nanodomains). In non-poled samples such a jump on heating is also observed for this material (not shown here) and takes place at an intermediate temperature from the jump up on heating of the poled sample and the jump down on cooling of the thermally depoled one. In non-poled samples, this jump is adscribed to the transition from the non-oriented macrodomains of the ferroelectric phase to the nanodomains of the relaxor phase. The sharp decrease of $\varepsilon^{T}{}'_{33}$ on cooling is ascribed to the same nanodomain-macrodomain transition taking place spontaneously, in the absence of electric field, and in a hysteretic way, at a lower temperature.

The complex dielectric permittivity measurements vs. temperature curves (Figure 1(b) and (d)) in the direction perpendicular to the polarization, $\varepsilon^{*T}{}_{11}$, of BNBT4 shear plates reveal a clear displacement towards higher temperatures of all mentioned features in the thermal evolution curves of $\varepsilon^{*T}{}_{33}$. The experiments carried out at different heating rates in poled (not shown here) and depoled samples confirm that this is not an effect of the different sample geometry used in both types of dielectric measurements. Unless other artefacts of the measurement were taking place, there is an anisotropic thermal behavior of the dielectric permittivity. Such thermal anisotropy has been observed also in BNT ceramics (Hiruma et al., 2009).

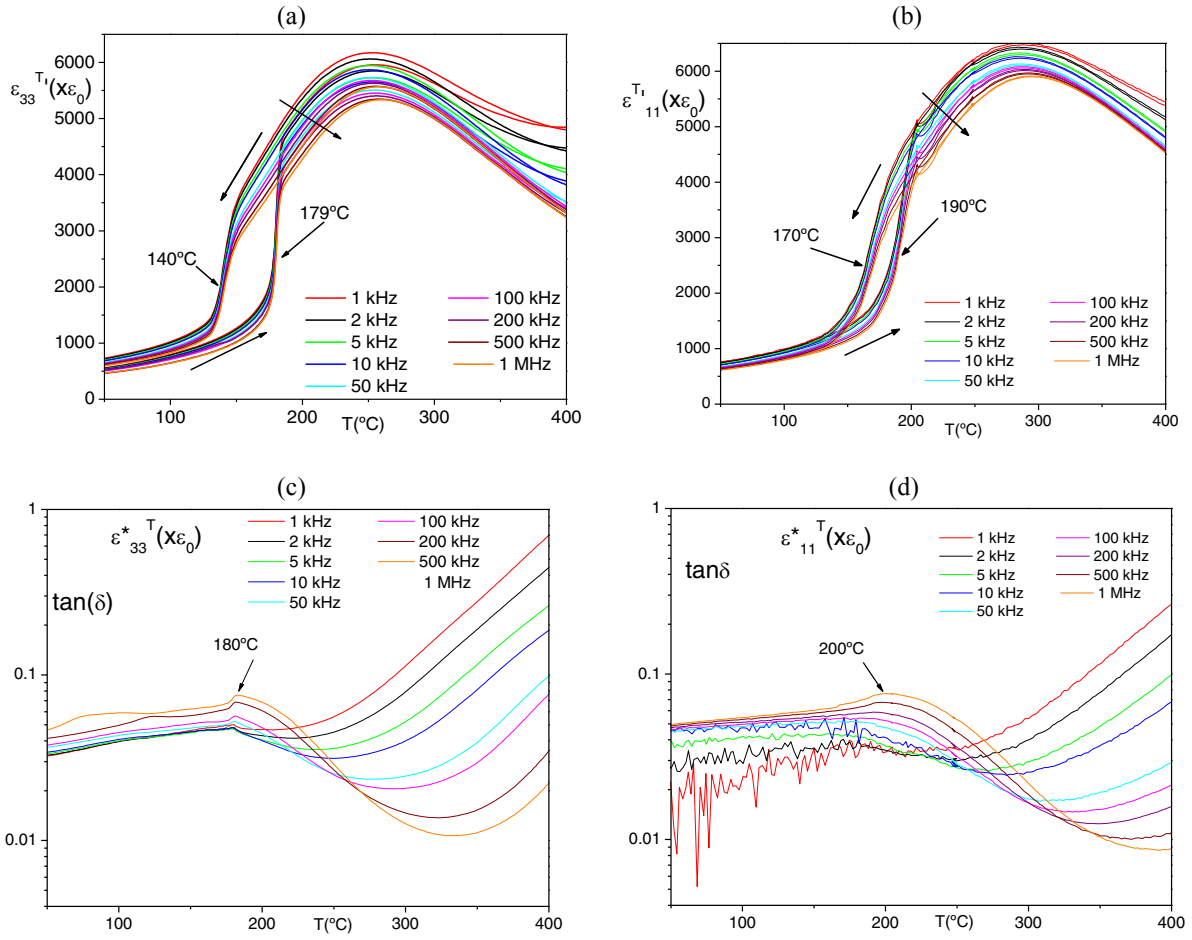

Figure 1. Real part of the dielectric permittivity, ε´, and losses, tan δ (shown only for heating run): (a and c) in parallel direction to polarization ($\varepsilon^{*T}{}_{33}$) for a poled thin disk and (b,d) in perpendicular direction to polarization ($\varepsilon^{*T}{}_{11}$) for a unpoled shear plate (heating rate of 0.5ºC/min.). Arrows indicate heating and cooling runs and the direction of increasing measurement frequency.

Figure 2 shows the thermal evolution of the in–situ measured electric impedance of disks at the radial resonance. Instead of the commonly used modulus (|Z|) and phase (θ) plots for the complex impedance as a function of the frequency, an alternative representation of the resonance spectra was used here. Namely, the resistance (R = $|Z|.\cos\theta$) and conductance ($G=|Z|^{-1}.\cos\theta$) peaks were plot as a function of the temperature. Similarly, Figure 3 shows the plots of the resistance and conductance for the shear resonance as a function of the temperature.

In-situ measurements of the radial resonance during the thermal depolarization process of BNBT4 ceramic disks (Figure 2), and all the coefficients that can be directly calculated from it (Figure 4), shows that for 150ºC the resonance has virtually disappear. It can be seen that the complex impedance signal for the shear resonance of plates and all the coefficients that can be directly obtained from it (Figure 4), decreases at higher temperature than that of the radial resonance of disks. At 150ºC, a shear coupling factor of 80% of the room temperature value (k^{RT}_{15}= 33%) and piezoelectric coefficient of 140% of that value (d^{RT}_{15}=105 pC/N) are obtained, whereas only 58% (of k^{RT}_{p}= 21%) and 110% (of d^{RT}_{31}=- 26 pC/N) remain at such a temperature (Figures 4(a) and (d)). The conductance curve for the shear mode shows also clear signal at 150ºC (Figure 3(b)).

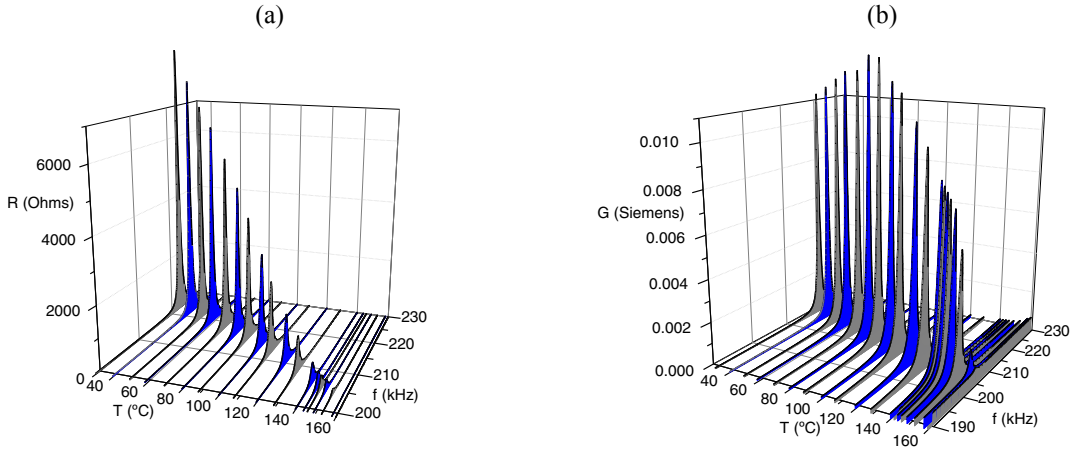

Figure 2. Thermal evolution of the complex impedance at the RADIAL resonance of a BNBT4 thin disk, thickness poled: (a) resistance (R) peak and (b) conductance (G) peak.

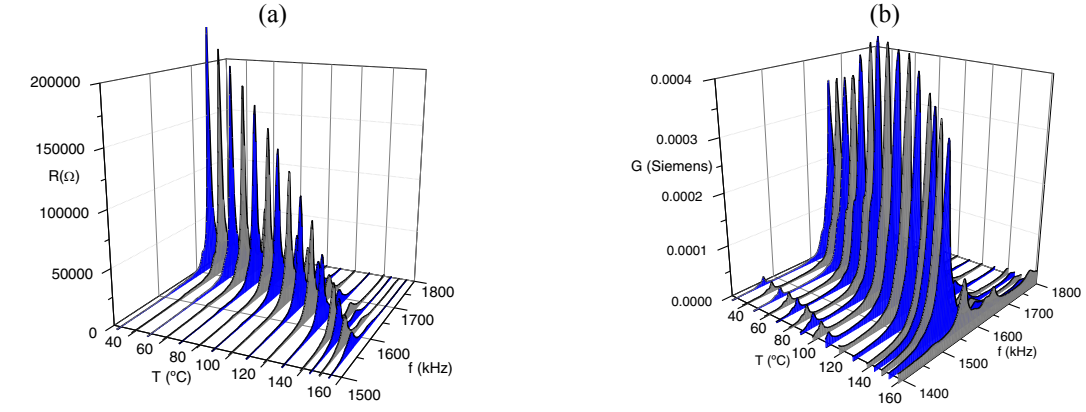

Figure 3. Thermal evolution of the complex impedance at the SHEAR resonance of a BNBT4 shear plate, thickness poled: (a) resistance (R) peak and (b) conductance (G) peak.

We can conclude that the thermal depolarization temperature, T_d, as measured in-situ from shear resonance mode as a function of the temperature is above the one determined from in-situ measurements of the planar resonance mode. This is common for ceramics obtained by hot-pressing and subsequent recrystallization from both sol-gel nanopowders, which showed an enhanced effect (Pardo et al., 2011), and mixed oxides powder here studied. The phase transition underlying the thermal depolarization of BNBT4 (Jo et al., 2013) is a complex process, similar to the one in BNBT6, involving both progressive reduction of the preferential orientation of the ferroelectric phase and a phase transition - which is irreversible, and according to our results anisotropic, to a non-piezoelectric phase, yet locally polar, that takes place below the temperature of the permittivity maximum - above which a LTNPF takes place.

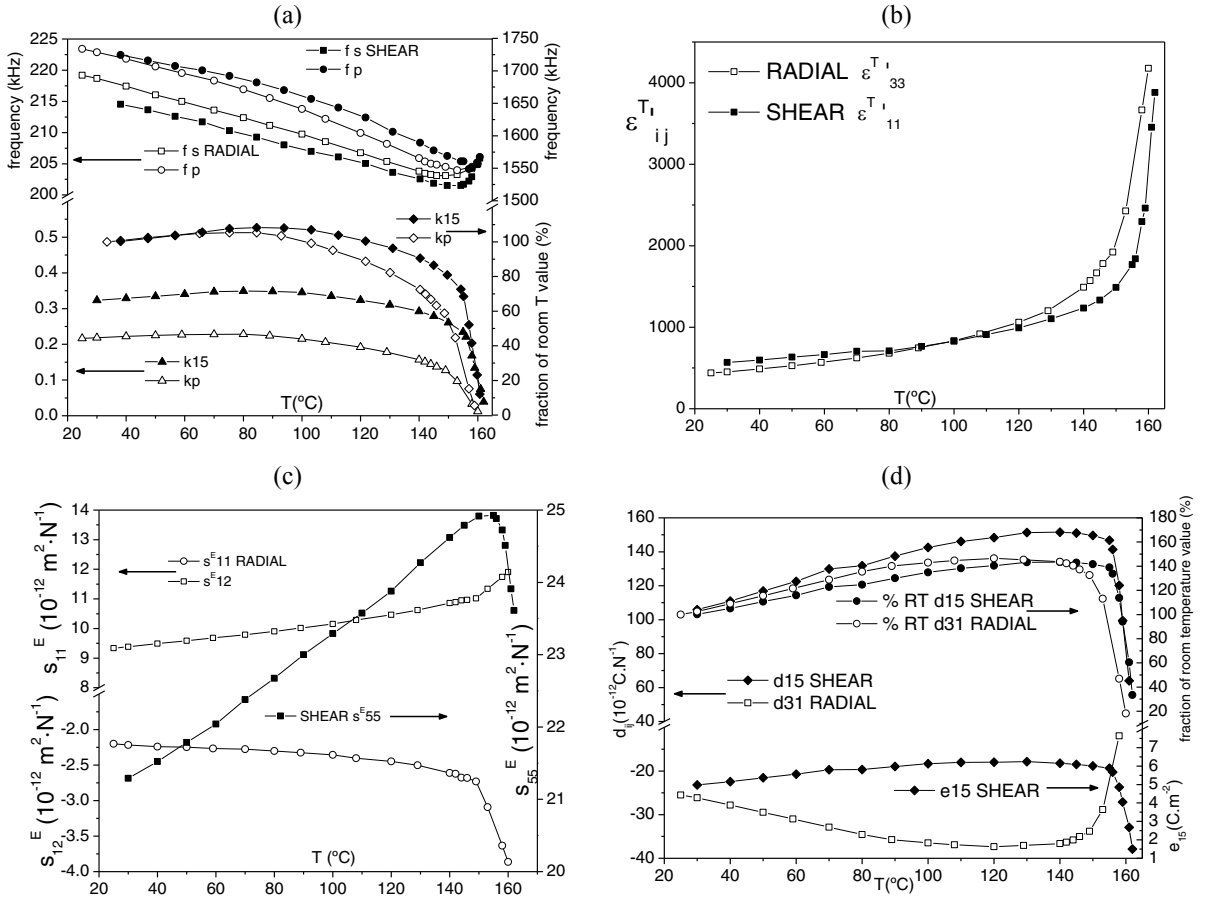

Figure 4. Comparation of the directly calculated coefficients from the RADIAL and SHEAR modes of resonance: (a) series (f_s –from G_{max}) and parallel (f_p-from R_{max}) frequencies and electromechanical coupling coefficients (both in absolute value and as a fraction of the room temperature values); (b) real part of the complex dielectric permittivity at the resonance frequency; (c) real part of the complex elastic compliances; (d) real part of the piezoelectric coefficients.

Finally, the measurement procedure of the depolarization temperature is critical to assess the potential application of a piezoceramics. For applications dealing with the shear resonance of BNBT4, our results allows to conclude that the depolarization temperature in submicron-structured ceramics is higher than the commonly reported, of 150ºC from in-situ measurements on radial modes of resonance of disks.

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References

A. Moure, A. Castro and L. Pardo. "Improvement by Recrystallization of Aurivillius-type Piezoceramics from Mechanochemically Activated Precursors". *Acta Mater*., vol. 52 (2004) 945-957

B. Wylie-van Eerd, D.Damjanovic, N. Klein, N. Setter and J.Trodahl. "Structural complexity of $(Na_{0.5}Bi_{0.5})TiO_3$-$BaTiO_3$ as revealed by Raman spectroscopy". *Physical Review B*, vol. 82 (2010) 104112

B.J. Chu, D.R. Chen, G.R. Li and Q.R. Yin."Electrical properties of $Na_{1/2}Bi_{1/2}TiO_3$–$BaTiO_3$ ceramics". *J. Eur.Ceram. Soc*., vol. 2 (2002) 2115–2121

C. Alemany, A. M. Gónzalez, L. Pardo, B. Jiménez, F. Carmona, J. Mendiola "Automatic determination of complex constants of piezoelectric lossy materials in the radial mode" *J. Phys. D: Appl. Phys*. vol. 28 (1995) 945-956

F. Cracium, C. Galassi and R. Birjega "Electric-field-induced and spontaneous relaxor-ferroelectric phase transitions in $(Na_{1/2}Bi_{1/2})_{1-x}$ Ba_x TiO_3"*J.Appl.Phys.* Vol.112 (2012) 124106

L. E. Fuentes-Cobas, L. Pardo, M. E. Montero-Cabrera, J. R. Plaisier, A. García, K. Brebøl, E. Mercadelli and C. Galassi."The $0.96(Bi_{0.5}Na_{0.5})TiO_3 - 0.04BaTiO_3$ crystal structure: A high-Q, high-counting statistics synchrotron diffraction analysis". *Crystal Research and Technology* 49 (2-3) (2014) 190-194

L. Pardo, A. García, F. Montero de Espinosa and K. Brebøl. "Shear Resonance Mode Decoupling to Determine the Characteristic Matrix of Piezoceramics For 3-D Modelling." *IEEE Trans. Ultrasonics Ferroelectrics and Frequency Control*, vol. 58 (3) (2011) 646-657

L. Pardo, A. García, K. Brebøl, E. Mercadeli and C. Galassi. "Anisotropy and dynamic thermal depolarization of $0.96(Bi_{0.5}Na_{0.5})TiO_3$-$0.04BaTiO_3$ lead-free piezoceramics" *Book Series*: IEEE International Symposium on Applications of Ferroelectrics (2012) DOI: 10.1109/ISAF.2012.6297762.

L. Pardo, A. García, K. Brebøl, E. Mercadelli and C. Galassi. "Enhanced properties for ultrasonic transduction, phase transitions and thermal depoling in $0.96(Bi_{0.5}Na_{0.5})TiO_3$-$0.04BaTiO_3$ submicron structured ceramic". *J. Phys. D: Appl. Phys*., vol. 44 (2011) 335404

L. Pardo, E. Mercadelli, A. García, K. Brebøl and C. Galassi. "Field-Induced Phase Transition and Relaxor Character in Submicron Structured Lead-Free $(Bi_{0.5}Na_{0.5})_{0.94}Ba0.06$ TiO_3 Piezoceramics at the Morphotropic Phase Boundary". *IEEE Trans Ultrasonics Ferroelectrics and Frequency Control*, vol. 58(9) (2011) 1893-1904

M. E. Montero-Cabrera, L. Pardo, A. García, M. E. Fuentes-Montero, M. L. Ballinas-Casarrubias and L.E. Fuentes-Cobas. "The global and local symmetries of nanostructured ferroelectric relaxor $0.94(Bi_{0.5}Na_{0.5})TiO_3$ -$0.06BaTiO_3$" *Ferroelectrics* (in press, 2014).

W. Jo, J. Daniels, D. Damjanovic, W. Kleeman and J. Rödel "Two-stage processes of electrically induced-ferroelectric to relaxor transition in $0.94(Bi_{1/2}Na_{1/2})TiO_3$-$0.06BaTiO_3$"*Appl.Phys.Lett.* vol. 102 (2013) 192903

Y. Hiruma, H. Nagata and T. Takenaka. "Thermal depoling process and piezoelectric properties of bismuth sodium titanate ceramics". J. Appl. Phys, vol. 105 (2009) 084112