Processing and Application of Ceramics 4 [3] (2010) 199–207

Piezoelectric characterization of lead-free ferroelectric ceramics

Lorena Pardo[1,*], Alvaro García[1], Klaus Brebøl[2], Lavinia P. Curecheriu[3], Liliana Mitoseriu[3], Elisa Mercadelli[4], Carmen Galassi[4]

[1]*Instituto de Ciencia de Materiales de Madrid. Consejo Superior de Investigaciones Científicas (ICMM-CSIC). Cantoblanco. 28049- Madrid, Spain*

[2]*Limiel ApS. Langebæk, Denmark*

[3]*Department of Physics, Al. I. Cuza University , 11 Blvd. Carol I, 700506, Iasi, Romania*

[4]*National Research Council Institute of Science and Technology for Ceramics (CNR-ISTEC) via Granarolo 64. I-48018 Faenza, Italy*

Received 15 February 2010; received in revised form 18 May 2010; accepted 22 July 2010

Abstract

The challenge to develop high piezoelectric sensitivity and lead-free composition ferro-piezoelectric ceramics has recently dragged new attention to some classic ferroelectrics. Here, $Ba(Ce_xTi_{1-x})O_3$ (Ce-BT) and $0.94(Bi_{1/2}Na_{1/2})TiO_3$-$0.06BaTiO_3$ (BNBT6) ceramics were piezoelectrically characterized from measurements of complex impedance at electromechanical resonances and their analysis by Alemany et al. software. The reconstruction of the spectra for each resonance is used as an accuracy test of the set of calculated coefficients, quantitatively characterized by the regression factor (R^2) of such reconstruction to the experimental spectrum. Piezoelectric activity at room temperature (RT) was observed for Ce-BT with $x=0.06$ and 0.1, ferroelectrics with $T(\varepsilon'_{max})>RT$, but also for $x=0.2$ with $T(\varepsilon'_{max})<RT$, which confirms its relaxor character ($P_s \neq 0$ for $T \geq T(\varepsilon'_{max})$). BNBT6 fine grained ceramics (~1 μm) were prepared from nanopowder obtained by sol-gel autocombustion. Results obtained for the fine grained ceramic hot-pressed at 800ºC for 2 h and recrystallized at 1050°C for 1 h are $d_{33}=148$ pCN^{-1} and $k_p=26.8\%$. Despite of its lower grain size, the properties of this material are comparable with those reported for coarse grained ceramics obtained by sintering at T>1100°C. Some measurement issues, as the role of the mode coupling on the characterization results, illustrated for the shear mode of a thickness poled plate, are discussed

***Keywords**: piezoelectricity, ferroelectric ceramics, lead-free, $BaTiO_3$, $(Bi_{0.5}Na_{0.5})TiO_3$, impedance, resonance*

I. Introduction

The scientific topics concerning ferro-piezoelectric ceramics are wide, involving from precursor chemistry and processing issues to solid state and applied physics, and they constitute a dynamic area of research, despite of the fact of being a well-established one [1]. Within this area, the development of high piezoelectric sensitivity and lead-free composition materials remains to date as a primary scientific challenge [2,3], driven by the toxicity of lead oxide (PbO) and nowadays directives for environmental protection [4]. Such directives require the elimination of PbO from the composition of ferro-piezoelectric ceramics in devices. This means the substitution of the present commercial ceramics, based in solid solutions containing the ferroelectric $PbTiO_3$ (PT), such as $(Pb,Zr)TiO_3$ (PZT) or $PbMg_{1/3}Nb_{2/3}O_3$-$PbTiO_3$ (PMN-PT). The fact that PT is the ferroelectric material of the highest combination of spontaneous polarization and Curie temperature known to date among mixed oxides with perovskite structure [5] has origin in the specific crystal-chemistry of $PbTiO_3$ [6].

The search for lead-free materials, in addition to the development of new compositions that have reached so far the performances of the so called hard PZT [2] but not those of the highest sensitivity materials based on PT, has driven also to the development of processing routes to increase the ceramic performance. The remanent po-

---

[*] Corresponding author: tel: +34 91 334 90 66
fax: +34 91 372 06 23, e-mail: *lpardo@icmm.csic.es*

larization, P_r, and, consequently the piezoelectric performance in randomly oriented ferroelectric polycrystals, is limited by the symmetry of the crystal structure of the ferroelectric (tetragonal: $P_r^{max} = 0.83 \cdot P_s$, with six <001> equivalent directions of the spontaneous polarization of the crystal, P_s; rhombohedral: $P_r^{max} = 0.87 \cdot P_s$, with eight allowed <111> equivalent directions; orthorhombic: $P_r^{max} = 0.91 \cdot P_s$, with twelve allowed <110> equivalent directions [7,8]). Those solid solution systems with the so called Morphotropic Phase Boundary (MPB), for which composition two symmetries coexist, are desired. This increases the number of equivalent directions of P_s and, consequently, increases the P_r value. It is also possible to increase P_r over the values of the classical randomly oriented ceramics by the processing of textured ceramics or single-crystals. To this end, both the Reactive Templated Grain Growth (RTGG) [2] and the recently developed Solid State Single Crystal Growth (SSSC) [9], a crystal growth technique exploiting the abnormal grain growth in ceramics around a crystal seed, have been applied with success to develop lead-free piezoelectrics based on (K,Na)NbO_3 (KNN), a classical lead-free ferroelectric [10]. Alkaline niobates have high melting point and presence of volatile elements that makes difficult the achievement of single-crystals by the classical, more expensive, methods.

Recently [4], a strong interest has been also focused on two other classical lead-free ferroelectrics (Bi,Na)NbO_3 [11] and $BaTiO_3$ [12] and also on their solid solutions. In particular, ferro-piezoelectric ceramics in the system $(1\text{-}x)(Bi_{0.5}Na_{0.5})TiO_3\text{-}xBaTiO_3$ with $x = 0.06$ (BNBT6), close to the MPB, and prepared from nanopowder obtained by sol-gel autocombustion [13], and $Ba(Ce_xTi_{1-x})O_3$, processed by solid state reaction, will be the subject of this work. Processing from nanopowders allows getting fine grained, submicron structured, ceramics that are of interest both for the basic studies of size-effects in ferro-piezoelectrics and for their use as high frequency ultrasonic transducers.

Piezoelectric characterization of ferroelectric ceramics is commonly achieved by using standard methods [14] from measurements of complex impedance data at electromechanical resonances and their analysis. These have the drawback of not accounting with material losses, reason why alternative methods of analysis of impedance data have been developed. The study of size effects on the piezoelectric activity of submicron- and nanostructured ceramics, or even the evidence of the ferroelectric nature of these, rests on the feasibility of accurate detection of minute changes or minute piezoelectric activity [15], hence the importance of the use of the optimum characterization techniques. To carry out accurate characterization of lossy ferro-piezoceramics at resonance, Alemany *et al.* [16] software has been used in this work for determination of the coefficients associated with thickness and radial resonances of, thickness poled, thin ceramic disks. In this software the material data is determined by solving a set of non-linear equations that results when experimental impedance data at a number of frequencies are introduced into the appropriate analytical solution of the wave equation for a given resonance mode. This set of equations is established for as many frequencies as unknown coefficients. It is worth noting that the proper application of these methods [16] requires strict conditions in terms of the sample geometry and dimensional ratios. These are needed for the applicability of the one-dimensional models from which the analytical expressions of the resonance modes are derived.

II. Piezoelectric characterization of Ce-modified barium titanate ceramics

2.1 Experimental

Four different compositions of $BaCe_xTi_{1-x}O_3$ (Ce-BT) ceramics, with $x = 0.06$, 0.1, 0.2 and 0.3, within the solid solubility range, $x < 0.4$ [17,18], were studied here. The ceramics were prepared by solid state reaction and pressureless sintering at 1500°C for 4 h. All ceramics are single-phase and have tetragonal symmetry crystal structure and bimodal grain size distribution, with increasing mean grain size as the Ce content increases.

In Ce-BT for $x \geq 0.06$, some previous work [19] reports the "pinch off" of the well-known phase transitions of BT from the room temperature tetragonal to the orthorhombic ferroelectric phases and from the orthorhombic (for $T < 0°C$) to the rhombohedral (for $T < -80°C$) ferroelectric phases. The only dielectric anomaly observed for Ce-BT ceramics for $x \geq 0.06$ takes place at a decreasing temperature as the amount of Ce increase ($T(\varepsilon'_{max})$ ~100°C for $x = 0.06$ [19], $T(\varepsilon'_{max})$ ~ 50°C [18,19] for $x = 0.1$, $T(\varepsilon'_{max})$ ~ –30°C [18,19] for $x = 0.2$ and $T(\varepsilon'_{max})$ ~ –100°C for $x = 0.3$ [18,19]). Such dielectric anomaly shows a diffuse character that is common for relaxor ferroelectrics, but also for polycrystals (ceramics) of classical ferroelectrics. This is the case for $(Ba_{1-x}Ce_x)Ti_{1-x/4}(V_{Ti})_{x/4}O_3$ ceramics [20,21] that follow a Curie-Weiss law above $T(\varepsilon'_{max})$, contrarily to relaxors, and do not show the frequency dispersion of the temperature of the maximum, which characterizes the relaxor ferroelectrics. At room temperature samples for $x \geq 0.06$ have pseudo-cubic [19] rather than tetragonal symmetry, but for $0.1 < x < 0.4$ they are better indexed as tetragonal [18].

For Ce-BT with $0.02 \leq x \leq 0.08$, the field-induced strain level is in the range of 0.14–0.19% with a small hysteresis under 60 kV/cm [19], which makes this ceramics a promising lead-free material for the high strain and low hysteresis applications near room temperature or at low temperatures. To date and to the best knowledge of the authors, the performance as ultrasonic transducers of Ce-BT ceramics has not yet been reported, since these are mainly considered for high-K (capacitor) uses due to the proximity to room temperature of the peak of dielectric permittivity.

The piezoelectricity of BT ceramics, isotropic and centrosymmetric, thus, non-piezoelectric, under the action of strong electric fields ("poling") remain unexplained to physicists until 1944. At that time the ferroelectricity of the BT was established and the role of poling, which cause increasing orientation of ferroelectric domains as the poling field and time increases until reach the saturation of P_r, was understood. Poling creates a macroscopic, non-centrosymmetric, 6 mm, ceramic symmetry that leads to piezoelectric activity. Poling remains nowadays as a major issue in the development of high performance lead-free piezoceramics, since for some of these field induced structural transitions to ferro-piezoelectrically active phases have been observed [22,23], which enhances the mere effect of domain orientation during poling and, consequently, the piezoelectric performance. The good piezoelectric behavior found in systems that are in a pseudocubic phase under zero electric field indicates that the search for lead-free alternatives should not exclude such systems.

Ceramics of Ce-BT composition were microstructurally and dielectrically characterized and this study will be reported in detail elsewhere. Here the complex properties at resonance in the ultrasonic range are studied and results discussed in terms of the sample com-

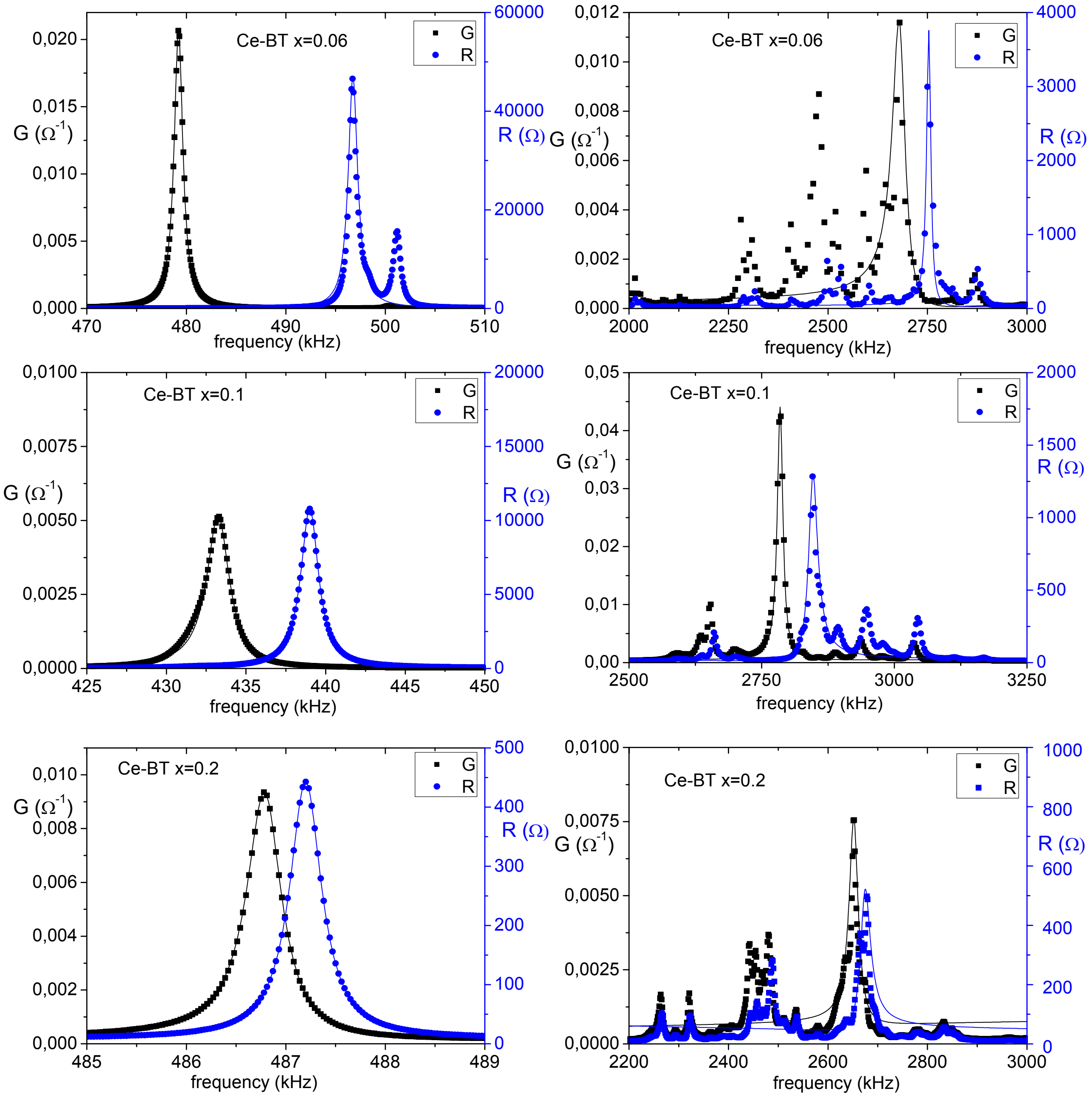


Figure 1. Radial (left column) and thickness (right column) resonance spectra of Ce-BT disks, poled and excited in thickness, showing the experimental data (symbols) and the reconstructed spectra (lines) after calculation of the material parameters

Table 1. Results of the complex characterization at room temperature (*RT*), and regression factors (R^2) of the calculations from the planar (*P*) and thickness (*T*) resonances of ceramic disks, of Ce-BT ceramics under the optimum *RT* poling conditions and comparison with data on $BaTiO_3$ ceramics (For a given complex coefficient $C^* = C' - iC''$, $\tan\delta(C) = C''/C'$; (*) d_{33} values measured in a Berlincourt meter; NA=not applicable).

Processing conditions		$BaCe_xTi_{1-x}O_3$ solid state reaction 1500°C/4h			$BaTiO_3$ [1]
Composition		$x = 0.06$	$x = 0.1$	$x = 0.2$	$x = 0$
Density [g/cm^3]		5.95	5.88	5.97	5.7
Grain size		> 1 µm	> 3 µm	>> 3 µm	coarse
$T(\varepsilon'_{max})$		~ 100°C	~ 50°C	~ –30°C	115°C
d_{33}·[10^{-12}C/N] (*)		150	110	40	190
k_p [%]	P	30.1	18.3	4.6	36
N_p [kHz·mm]	P	2962	3067	3329	---
R^2	P	0.9367	0.9963	0.9997	NA
Poisson ratio	P	0.45	0.38	0.33	---
k_t [%]	T	25.4	22.8	3.6	50
N_t [kHz·mm]	T	2814	2647	2843	---
R^2	T	0.6749	0.8710	0.7057	NA
$\varepsilon^T_{33}/\varepsilon_0$ at ~500 kHz	P	864–13.4i	790–9.3i	5069–205.7i	1700
tan δ (ε^T_{33})	P	0.015	0.012	0.041	0.5
$\varepsilon^S_{33}/\varepsilon_0$ at ~ 2700 kHz	T	706–68.4i	688–67.6i	4677–750.5i	---
tan δ (ε^S_{33})	T	0.097	0.098	0.160	---
h_{33} [10^8 V/m]	T	14.26–0.575i	12.05+1.00i	0.76+0.012i	---
tan δ (h_{33})	T	0.004	0.001	0.016	---
g_{31} [10^{-3} m·V/N]	P	–6.01–0.05i	–3.74+0.05i	–0.34+0.001i	---
tan δ (g_{31})	P	0.008	0.013	0.002	---
d_{31} [10^{-12} C/N]	P	–45.98+0.37i	–26.14+0.65i	–15.31+0.66i	–78
tan δ (d_{31})	P	0.008	0.024	0.04	---
s^E_{11} [10^{-12} m^2/N]	P	11.1–0.025i	9.5–0.038i	7.4–0.007i	9.1
tan δ (s^E_{11})	P	0.002	0.004	0.0009	---
s^E_{12} [10^{-12} m^2/N]	P	–5.0+0.011i	–3.6 + 0.014i	–2.5 + 0.002i	---
tan δ (s^E_{11})	P	0.002	0.004	0.0008	---

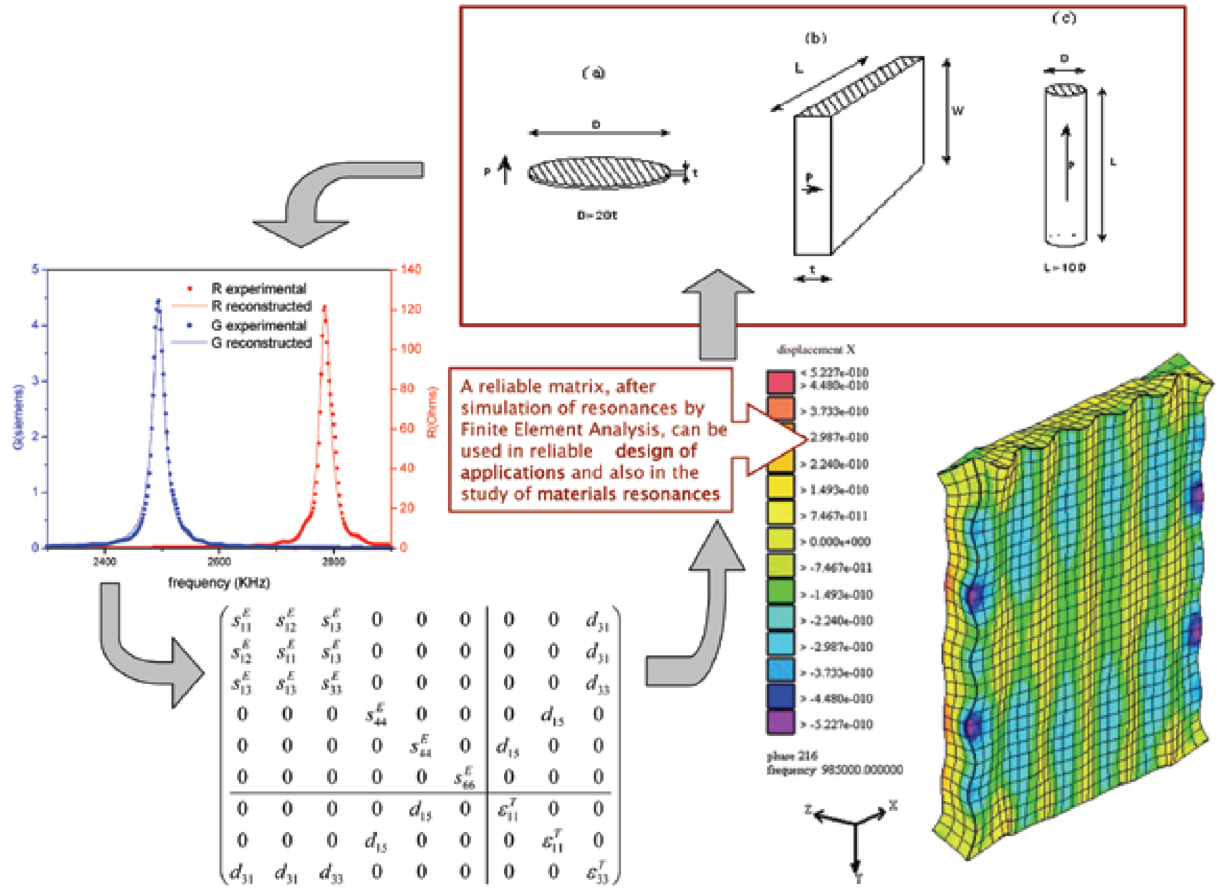
position.

2.2. Results and discussion

Thickness poling of the ceramic thin disks at 160°C did not yield a piezoelectric activity. For all four compositions this is a temperature well above $T(\varepsilon'_{max})$ and this means that the samples are at that temperature in a centrosymmetric, non-piezoelectric, phase. Poling experiments were then carried out at room temperature. Poling field was maintained during 10 minutes. Poling field was increased in steps of 10 kV/cm up to breakdown of the samples. Measurements at the thickness and planar extensional resonances of the disks were carried out at each step. From these, calculation of the dielectric, elastic and piezoelectric complex coefficients, as well as electromechanical coupling factors (k), relevant to each mode were carried out using Alemany *et al.* software. As expected, not even at room temperature the $x = 0.3$ ceramic could be poled ($T(\varepsilon'_{max}) << T_{poling}$).

Fig. 1 shows the measured planar and thickness resonance spectra for the $x = 0.06$, 0.1 and 0.2 samples, of typically 1 mm thickness and 36 mm^2 of electroded area, under the optimum poling conditions. The maxima of the experimental peaks (symbols) of the a.c resistance (R) and conductance (G), the real parts of the impedance ($Z^* = R + iX$) and admittance ($Y^* = G + iB$), respectively, are used to determine two of the frequencies needed for the calculation [16] and the rest of the frequencies are determined automatically by the software. After complex parameters determination, the spectra are reconstructed (lines in Fig. 1) as an accuracy test of the final set of calculated coefficients. This accuracy is also quantitatively characterized by the regression factor (R^2) of such reconstruction to the experimental spectrum. The regression factor is high for the planar mode when a sample is a perfect disk and commonly much lower for the thickness mode. This is mainly due to coupling to overtones of the planar mode, but also to other sort of modes, as edge ones [24]. This coupling, even for a ceramic of optimum microstructure, can only be reduced by using a ratio thickness: diameter >> 1:10 [14]. For this reason, the calculations from spectra in Fig. 1, especially those from the thickness mode, have a restricted validity for characterization purposes. They will be used here, however, to get comparative information from the three compositions studied.

Table 1 shows the results of the complex coefficients obtained for each sample under the optimum poling conditions. The trend of the elastic properties in Table 1, s^E_{11} and s^E_{12} (decrease of the real part of the compliance and the mechanical losses) is related with the trend of the grain size (increase) as the Ce content increases. The trend of the dielectric and piezoelectric properties in Table 1 can be explained in terms of the $T(\varepsilon'_{max})$ for each composition with respect to RT, which is both the poling and the measuring temperature, and in terms of the ferroelectric ($P_s = 0$ for $T > T(\varepsilon'_{max})$) or relaxor ($P_s \neq 0$ for $T \geq T(\varepsilon'_{max})$) character of each composition. The high value, both of the real part and the losses, of the dielectric permittivity ($\varepsilon^{T,S}_{ii}$) for $x = 0.2$ is related to the proximity of $T(\varepsilon'_{max})$ to RT and the high diffusivity of the dielectric anomaly [18,19]. Though often used in the literature to characterize the piezoelectric activity of ceramic compositions, due to the relation between d_{33} and the dielectric permittivity, $d_{ij} = g_{ij}\cdot\varepsilon^T_{jj}$, this is in fact a quite misleading parameter. Since the dielectric permittivity increases from the $x = 0.06$ to $x = 0.2$ compositions the comparison between their d_{33} and d_{31} values indicates



A reliable matrix, after simulation of resonances by Finite Element Analysis, can be used in reliable design of applications and also in the study of materials resonances

$$\left(\begin{array}{cccccc|ccc}
s^E_{11} & s^E_{12} & s^E_{13} & 0 & 0 & 0 & 0 & 0 & d_{31} \\
s^E_{12} & s^E_{11} & s^E_{13} & 0 & 0 & 0 & 0 & 0 & d_{31} \\
s^E_{13} & s^E_{13} & s^E_{33} & 0 & 0 & 0 & 0 & 0 & d_{33} \\
0 & 0 & 0 & s^E_{44} & 0 & 0 & 0 & d_{15} & 0 \\
0 & 0 & 0 & 0 & s^E_{44} & 0 & d_{15} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & s^E_{66} & 0 & 0 & 0 \\
\hline
0 & 0 & 0 & 0 & d_{15} & 0 & \varepsilon^T_{11} & 0 & 0 \\
0 & 0 & 0 & d_{15} & 0 & 0 & 0 & \varepsilon^T_{11} & 0 \\
d_{31} & d_{31} & d_{33} & 0 & 0 & 0 & 0 & 0 & \varepsilon^T_{33}
\end{array}\right)$$

Figure 2. Diagram explaining the process for the full matrix characterization of poled ferro-piezoelectric ceramics (6 mm symmetry) for 3-D modelling. Three samples and measurements of complex impedance on four resonance modes (*R* and *G* curves vs. frequency) of these are required. Alemany *et al.* software [16,32] provides for each mode a discrete number of material coefficients, including all losses, namely: thickness (h_{33}, ε^S_{33}, c^D_{33}) and planar (d_{31}, ε^T_{33}, s^E_{11}, s^E_{12}) extensional modes of thin disks (a); shear mode (e_{15}, ε^S_{11}, s^E_{55}) of thickness poled plate(b); length extensional mode (g_{33}, ε^T_{33}, s^D_{33}) of length poled bars (c). A Finite Element Analysis (FEA) tool can be used to reproduce the previously studied spectra, using as input data the whole matrix, as validity test of this. The FEA generated pattern of the shear strain at resonance (highly exaggerated) of a thickness poled plate is shown here [32].

Table 2. Results of the characterization of BNBT6 hot-pressed and recrystallised ceramics from sol-gel autocombustion nanopowder, showing: the thickness dependence of the properties obtained from the shear resonance of thickness poled plates (*SH*) (in bold the most reliable results), the properties from planar (*P*) and thickness (*T*) resonances of thin disks and the comparison with data in the literature on similar ceramics. ((*) d_{33} values measured in a Berlincourt meter; (**) dielectric permitivity value for unpoled sample; NA=not applicable).

Composition and synthesis route		BNBT6 sol-gel autocombustion				BNBT6 [33] mixed oxides	BNT [34] mixed oxides
Processing conditions		Hot pressed at 800°C/2h + recryst. 1050°C/1h				sintered 1200°C/2h	sintered 1100°C/2h
Hot pressed density [g/cm^3]		5.37				---	---
Final density [g/cm^3]		5.49 - 5.65				5.82	---
Grain size		~1 µm				> 1 µm	> 1 µm
Poling conditions		40 - 60 kV/cm, 180°C				30 kV/cm, 60°C	55 kV/cm, 60°C
d_{33} [10^{-12}C/N] (*)		148				125	72.9
k_p [%]	P	26.8				20	16.8
N_p [kHz·mm]	P	2933				2975	3260
R^2	P	0.9999				NA	NA
k_t [%]	T	40.4				52	45.5
N_t [kHz·mm]	T	2281				2600	2780
R^2	T	0.9548				NA	NA
Thickness [mm]	SH	0.89	0.87	0.85	**0.83**	---	---
R^2	SH	0.6003	0.8580	0.9670	**0.9847**	NA	NA
k_{15} [%]	SH	49.60	39.65	39.71	**40.2**	49.8	36.2
N_{15} [kHz·mm]	SH	1340	1395	1384	**1373**	1586	1650
$\varepsilon^T_{33}/\varepsilon_0$	P	641–31i				580** (1kHz)	343 (1MHz)
$\tan\delta$	P	0.048				0.013 (1kHz)	0.028 (1MHz)
$\varepsilon^T_{11}/\varepsilon_0$	SH	775–69i	718–59i	712–41i	**726 - 40i**	373	367 (1MHz)
d_{31} [10^{-12} C/N]	P	–37.0+1.33i				–40	–15
d_{15} [10^{-12}C/N]	SH	203.25–24.8i	151.84–19.2i	153.6–9.82i	**158.3– 8.31i**	194	87.3
s^E_{11} [10^{-12} m^2/N]	P	9.73–0.07i				8.59	7.07
s^E_{12} [10^{-12} m^2/N]	P	–3.02+0.02i				---	–1.88
s^E_{55} [10^{-12} m^2/N]	SH	24.73–1.22i	23.35–0.80i	23.79–0.42i	**24.17–0.42i**	23.3	17.9

a much higher relative piezoelectric activity of the latter than the actual one. This can be better determined by comparing all other piezoelectric parameters (k, h_{ij}, e_{ij}) in Table 1.

The overall properties at room temperature of the ferroelectric $x = 0.06$ composition from the planar mode compare well with those for classical BT ceramics [1]. Recently, however, these values have been enhanced by processing of fine grained [25], domain engineered [26] or textured [27] ceramics, which, via grain size effect or increase of $P_r^{\text{máx}}$ over the one for a random distribution of domains, increase the piezoelectric performance. For the relaxor composition $x = 0.2$ the fact that a small piezoelectric activity is measurable provides the basic information that, even above $T(\varepsilon'_{max})$, a stable ferroelectric long-range order can be induced by poling.

III. Piezoelectric characterization of BNBT6 ceramics from sol-gel combustion

3.1 Experimental

The composition near the MPB of the system (1-x)(Bi$_{0.5}$Na$_{0.5}$)TiO$_3$-xBaTiO$_3$ with $x = 0.06$ (BNBT6) was found to have interesting properties as lead-free piezoelectric ceramic [28]. Nanometric (15–30 nm) powder of BNBT6 was synthesized by a citrate nitrate sol gel auto-combustion method, details of which are explained elsewhere [13]. In this process, the pure perovskite phase is directly obtained by combusting the gel at 500°C. It is a well-known fact that the properties of ceramics are strongly dependent on the starting powders used, as well as on the final microstructures. Highly dense ceramics with controlled grain size, be-low 1μm, also preventing off-stoichiometry, have been obtained by a combination of hot-pressing at reduced temperature (700–950°C) and subsequent recrystallization [29] at moderately higher temperature (1000–1050°C for 1 h in air). Results obtained for the fine grained ceramic hot-pressed at 800°C for 2 h and recrystallized at 1050°C for 1 h are d_{33} = 148 pCN^{-1} and k_p = 26.8%. Despite of its lower grain size, the properties of this material are comparable with those reported for coarse grained ceramics obtained by sintering at temperatures higher than 1100°C. The full report of the study of these materials will be published elsewhere, while some characterization issues, scarcely considered in the literature but of primary importance, will be stressed in this work.

The accurate modeling of ferro-piezoelectric ceramics rests on the accuracy of the material coefficients used (Fig. 2). The knowledge of shear coefficients is needed for the full matrix characterization of piezoceramics [30], which allows simulation by numerical methods (like Finite Element Analysis) of devices in the design of new applications and in the study of material resonances. However, the shear coefficients have been scarcely reported in the literature for BNBT compositions. This is due to the complexity of the achievement of the in-plane poled geometry required for the standard methods of measurement and to the problem of dynamic clamping and underestimation of the ceramic coefficients associated to it [30,31]. To accurately determine shear coefficients at resonance, including losses, an alternative shear characterization method, which uses thickness-poled samples (Fig. 2b) and Alemany *et al.* software [32], has been developed and has been used in this work.

3.2. Results and discussion

Table 2 shows measured data for BNBT ceramic hot-pressed at 800°C for 2 h and recrystallized at 1050°C for 1 h. The disks used have 0.99 mm thickness and 143 mm^2. To the best knowledge of the authors, shear resonance related complex material coefficients have not yet been reported for BNBT ceramics. In the study of complex coefficients, one must keep in mind that their determination requires the knowledge of accurate values of impedance around the characteristic frequencies [16,32], thus mode coupling is always undesired. However, regardeless of the sample aspect ratio, the electrically driven thickness-shear mode excites, mechanically, the different overtones of plate waves (*n*, *n*+1, *n*+2, etc.) when corresponding frequencies get close giving place to more or less severe mode coupling. For shear plates, instead of a universal threshold value of the sample dimensional ratio

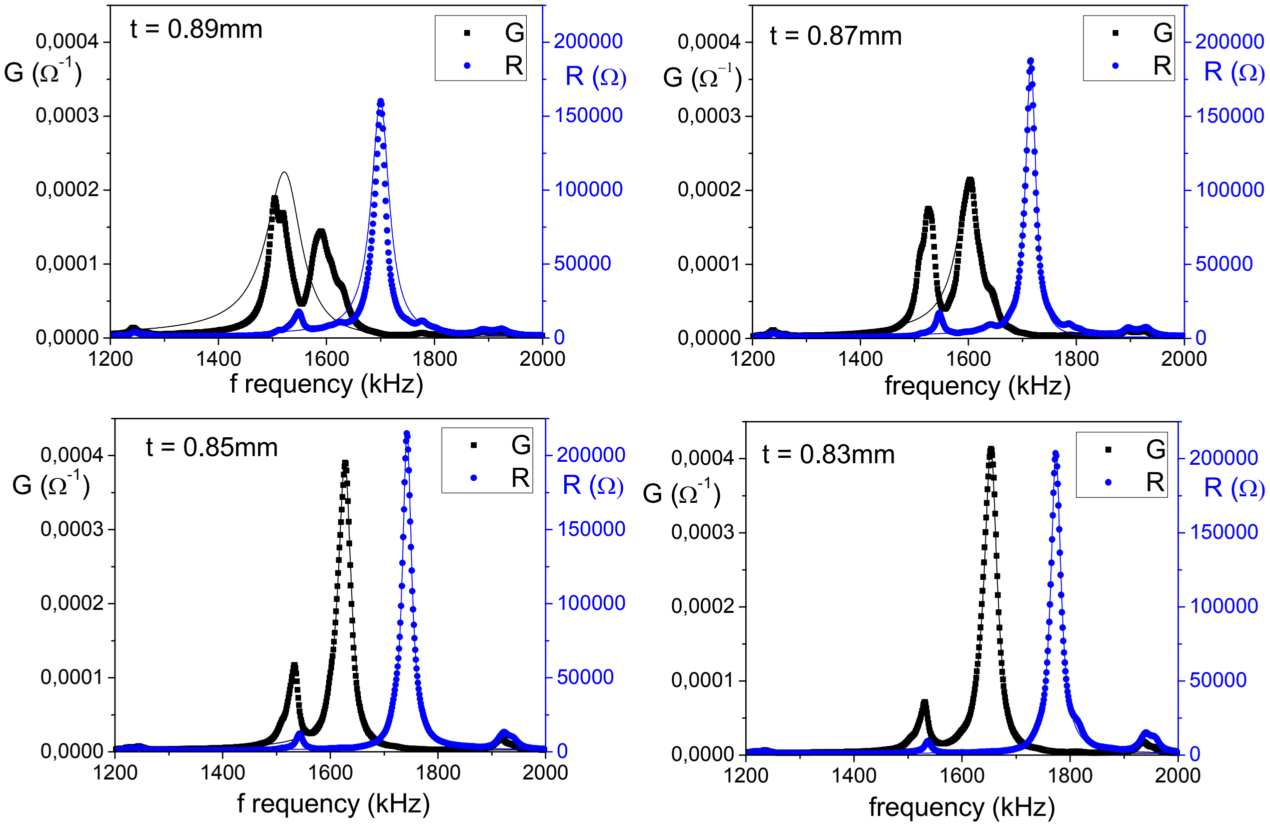


Figure 3. Illustration of the process to get the best aspect ratio for the calculation of the parameters related to the thickness shear resonace for a BNBT6 ceramic. The resonance spectra correspond to a 9.43 mm × 9.53 mm plate, thickness poled, with initial thickness of 0.89 mm. Optimum ratio for minimum mode coupling and higher regression factor (R^2) of the reconstructed spectra by Alemany software to the experimental one is found for 0.83 mm.

to avoid mode coupling, we must consider the optimum length and thickness of the plate for a given material to obtain uncoupled modes. The minimum length should be the one where the distance between two plate resonances is the same as the distance between the maximum of the conductance and the maximum of the resistance for the thickness-shear resonance. Such distance is determined by the shear electromechanical coupling factor of the material. Optimum thicknesses are the ones that place both maxima halfway between given overtones of the plate resonances, minimizing the coupling between the plate and shear waves.

Fig. 3 shows an example of the measurement of the complex impedance (*R* and *G* curves) vs. frequency at the shear resonance. The process to get the most accurate shear coefficients is illustrated. A rectangular, thickness poled, plate that has, initially, 0.89×9.43 mm^2 area of electroded surface and 9.53 mm of distance between measuring electrodes, is reduced in thickness in steps of 0.02 mm, measuring the resonance spectrum at each step. Practically, as the thickness of the sample is reduced by grinding, a spectrum that fulfils the above mentioned condition is found for the ceramic under study (Fig. 2d) at a sample thickness of 0.83. The shear mode related complex coefficients and the regression factors of the experimental curves to the reconstructed ones in Table 2 are calculated from these measurements and compared with values in the literature [33,34]. It must be noticed the wide range of values of the shear properties, both the piezoelectric coefficient (d_{15}) and the electromechanical coupling factor (k_{15}), obtained for BNBT6 sample by changing the dimensional ratio and, thus, changing the mode coupling. The most reliable coefficients for material characterization, the ones with higher R^2 value corresponding to the measurement for uncoupled modes (Fig. 3d), however, are not the highest ones. The comparison with the reported values in the literature is not straightforward, both because of literature values come from in-plane poled samples and standard calculation methods and because of measurement artifacts, as the mode coupling just shown, can overestimate actual material parameters. However, the overall performance of the obtained ceramics from sol-gel combustion nanopowders, by hot-pressing and recrystallization, can be considered similar to the one reported for coarser grained ceramics [33] and competitive with those of BNT with controlled stoichiometry [34]. This fine grained ceramic has suitable properties in the range needed to consider it as promising lead-free piezoelectric material for industrial applications.

Acknowledgements: ELENA COST539 Action (ESF), in particular, for the funding Short Term Scientific Missions to ICMM-CSIC of E. Mercadelli (COST-STSM-539-02122) and L.P. Curecheriu (COST-STSM-539-04682). L. Pardo and K. Brebøl express they gratitude to late Dr. Carlos Alemany (1940-2008) for thoughtful discussions regarding the software. Authors also acknowledge the funding of CNCSIS grant PN II_RU_TE_187/2010 for young researchers and NoE-MIND CE FP6 515757-2 that promotes the European Piezoinstitute.

References

1. G.H. Haertling "Ferroelectric ceramics: History and technology", *J. Am. Ceram. Soc.*, **82** [4] (1999) 797–818.
2. Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, M. Nakamura. "Lead-free piezoceramics", *Nature*, **432** (2004) 84–87.
3. J. Rödel, A.B.N. Kounga, M.Weissenberger-Eibl, D. Koch, A. Bierwisch, W. Rossner, M.J. Hoffmann, R. Danzer, G. Schneider, "Development of a roadmap for advanced ceramics: 2010–2025", *J. Eur. Ceram. Soc.*, **29** [9] (2009) 1549–1560.
4. J. Rödel, W. Jo, K.T.P. Seifert, E.M. Anton, T. Granzow, D. Damjanovic, "Perspective on the development of lead-free piezoceramics", *J. Am. Ceram. Soc.*, **92** [6] (2009) 1153–1177.
5. B.A. Tuttle, D.A. Payne, J.L. Mukherjee, "Spontaneous Polarization for ferroelectric materials", *MRS Bull.*, **19** [7] (1994) 20.
6. R.E. Cohen, "Origin of ferroelectricity in perovskite oxides", *Nature*, **358** (1992) 136–138.
7. E.C. Subbarao, M.C. McQuarrie, W.R. Buessem, "Domain effects in polycrystalline barium titanate", *J. Appl. Phys.*, **28** [10] (1957) 1194–1200.
8. H.G. Baerwald, "Thermodynamic theory of ferroelectric ceramics", *Phys. Rev.*, **105** [2] (1957) 480–486.
9. J.G. Fisher, A. Benčan, M. Kosec, S. Vernay, D. Rytz, "Growth of dense single crystals of potassium sodium niobate by a combination of solid-state crystal growth and hot pressing", *J. Am. Ceram. Soc.*, **91** [5] (2008) 1503–1507.
10. G. Shirane, R.E. Newnham, R. Pepinsky, "Dielectric properties and phase transitions of $NaNbO_3$ and (Na, K)NbO_3", *Phys. Rev.*, **96** [1] (1954) 581–588.
11. G.A. Smolenskii, V.A. Isupov, A.I. Agranovskaya, N.N. Krainik, "New ferroelectrics of complex composition IV", *Soviet Phys. Solid State*, **2** [11] (1961) 2651–2654.
12. A. von Hippel, "Ferroelectricity, domain structure, and phase transitions of barium titanate". *Rev. Mod. Phys.*, **22** [3] (1950) 221–237.
13. E. Mercadelli, C. Galassi, A.L. Costa, S. Albonetti, A. Sanson, "Sol-gel combustion synthesis of BNBT powders", *J. Sol-Gel Sci. Technol.*, **46** [1] (2008) 39–45.
14. "IEEE Standard on piezoelectricity". *ANSI/IEEE Std.* 176-1987. "Piezoelectric properties of ceramic materials and components. Part 2: methods of measurement - Low power", *European Standard CENELEC*, EN 50324-2 (2002).

15. A. Moure, T. Hungría, A. Castro, L. Pardo, "Microstructural effects on the phase transitions and the thermal evolution of elastic and piezoelectric properties in highly dense, submicron structured $NaNbO_3$ ceramics", *J. Mater. Sci.*, **45** (2010) 1211–1219.
16. C. Alemany, L. Pardo, B. Jiménez, F. Carmona, J. Mendiola, A.M. González, "Automatic iterative evaluation of complex material constants in piezoelectric ceramics", *J. Phys. D: Appl. Phys.,* **27** (1994) 148–155; C. Alemany, A.M. Gónzalez, L. Pardo, B. Jiménez, F. Carmona, J. Mendiola, *J. Phys. D: Appl. Phys.*, **28** (1995) 945–956; software avaliable at http://www.icmm.csic.es/gf2/medidas.htm
17. D. Makovec, Z. Samardzija, D. Kolar, "Solid solubility of cerium in $BaTiO_3$", *J. Solid State Chem.*, **123** (1996) 30–38.
18. A. Chen, Y. Zhi, J. Zhi, P.M. Vilarinho, J.L. Baptista, "Synthesis and characterization of $Ba(Ti_{1-x}Ce_x)O_3$ ceramics", *J. Eur. Ceram. Soc.*, **17** [10] (1997) 1217–1221.
19. C. Ang, Z. Yu, Z. Jing, R. Guo, A. S. Bhalla, L.E. Cross, "Piezoelectric and electrostrictive strain behavior of Ce-doped $BaTiO_3$ ceramics", *J. Appl. Phys.*, **80** (2002) 3424–3426.
20. Z. Jing, Z. Yu, C. Ang, "Crystalline structure and dielectric behaviour of $(Ce,Ba)TiO_3$ ceramics". *J. Mater. Res.*, **17** [11] (2002) 2787–2793.
21. M. Cernea, O. Monnereau, P. Llewellyn, L. Tortet, C. Galassi, "Sol-gel synthesis and characterization of Ce doped-$BaTiO_3$", *J. Eur. Ceram. Soc.*, **26** [15] (2006) 3241–3246.
22. W. Jo, T. Granzow, E. Aulbach, J. Rödel, D. Damjanovic, "Origin of the large strain response in $K_{0.5}Na_{0.5}NbO_3$ modified $Bi_{0.5}Na_{0.5}TiO_3$-$BaTiO_3$ lead-free piezoceramics", *J. Appl. Phys*., **105** (2009) 094102.
23. F. Rubio-Marcos, J.J. Romero, D.A. Ochoa, J.E. García, R. Perez, J.F. Fernandez, "Effects of poling process on KNN-modified piezoceramic properties", *J. Am. Ceram. Soc.*, **93** [2] (2010) 318–321.
24. S. Ueha, S. Sakuma, E. Mori, "Measurements of vibration velocity distributions and mode analysis of thick disks of $Pb(Zr,Ti)O_3$", *J. Acoustic Soc. Am*., **73** [5] (1983) 1842–1847.
25. H. Maiwa, "Electromechanical properties of $BaTiO_3$ ceramics prepared by spark plasma sintering and other methods", *Jap. J. Appl. Phys*., **48** [9K] (2009) 09KD04-1–4; H. Takahashi, Y. Numamoto, J. Tani, S. Tsurekawa, "Considerations for $BaTiO_3$ ceramics with high piezoelectric properties fabricated by microwave sintering method", *Jap. J. Appl. Phys.*, **45** [9B] (2006) 7405–7408.
26. T. Karaki, K. Yan, M. Adachi, "Subgrain Microstructure in high-performance $BaTiO_3$ piezoelectric ceramics". *Appl. Phys. Express*, **1** [11] (2008) 111402; S. Shao, J. Zhang, Z. Zhang, P. Zheng, M. Zhao, J. Li, C. Wang, "High piezoelectric properties and domain configuration in $BaTiO_3$ ceramics obtained through the solid-state reaction route". *J. Phys. D: Appl. Phys.*, **41** [12] (2008) 125408.
27. S. Wada, K. Takeda, T. Muraishi, H. Kakemoto, T. Tsurumi, T. Kimura, "Preparation of [110] grain oriented barium titanate ceramics by templated grain growth method and their piezoelectric properties", *Jap. J. Appl. Phys.*, **46** [10B] (2007) 7039–7043.
28. T. Takenaka, K. Maruyama, K. Sakata. "$(Bi_{1/2}Na_{1/2})TiO_3$-$BaTiO_3$ system for lead-free piezoelectric ceramics", *Jap. J. Appl. Phys.*, **30** [9B] (1991) 2236–2239.
29. A. Moure, A. Castro, L. Pardo, "Improvement by recrystallization of Aurivillius-type piezoceramics from mechanochemically activated precursors", *Acta Mater.*, **52** (2004) 945–957.
30. L. Pardo, A. García, K. Brebøl, D. Piazza, C. Galassi, "Key issues in the matrix characterization of porous PZT based ceramics with morphotropic phase boundary composition", *J. Electroceram.*, **19** [4] (2007) 413–418.
31. L. Pardo, F. Montero de Espinosa, K. Brebøl, "Study by laser interferometry of the resonance modes of the shear plate used in the Standards characterization of piezoceramics", *J. Electroceram.*, **19** [4] (2007) 437–442.
32. L. Pardo, A. García, F. Montero de Espinosa, K. Brebøl, "Choosing the best geometries for the linear characterization of lossy piezoceramics: Study of the thickness poled shear plate", *Appl. Phys. Lett.* **92** (2008) 172907; software avaliable at http://www.icmm.csic.es/gf2/medidas.htm
33. T. Takenaka, A. Huzumi, T. Hata, K. Sakata, "Mechanical properties of $(Bi_{1/2}Na_{1/2})TiO_3$-based piezoelectric ceramics", *Silicates Ind.*, **7** [8] (1993) 136–142.
34. Y. Hiruma, H. Nagata, T. Takenaka, "Thermal depoling process and piezoelectric properties of bismuth sodium titanate ceramics", *J. Appl. Phys*., **105** (2009) 084112.