High stability of properties in morphotropic phase boundary $Bi_{0.5}Na_{0.5}TiO_3$-$BaTiO_3$ piezoceramics

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Abstract

The $(1-x)Bi_{0.5}Na_{0.5}TiO_3$-$xBaTiO_3$ (BNT-xBT) system with composition at its morphotropic phase boundary (MPB) has received significant attention because of their attractive properties as lead-free piezoceramics. Although the basic properties of this system are well-established, reports about the stability of the functional properties of these piezoelectric materials are still lacking. A study on the dielectric and piezoelectric properties of BNT-xBT close to their MPB, with emphasis on material response under high electric field or mechanical stress, is performed in this work. The results indicate that the BNT-BT system exhibits a high stability of dielectric and piezoelectric properties, making it potentially interesting for specific applications. A direct correlation between piezoelectric properties and nonlinear response is evidenced for a wide number of piezoceramics, which is expected due to the extrinsic nature of the piezoelectric response. Finding compositions that show high electromechanical properties and low nonlinear behaviour is a challenge in the search for competitive lead-free piezoceramics.

Keywords: Ferroelectrics; Piezoelectrics materials; Piezoelectric properties; Nonlinear behavior; BNT-BT.

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1. Introduction

Lead-based perovskite-type piezoceramics with compositions close to the morphotropic phase boundary (MPB) have been extensively used as active materials for transducer applications owing to their exceptional functional properties. Despite the excellent properties exhibited by lead-based piezoceramics, and in particular lead zirconate titanate (PZT) based compositions, these materials present some drawbacks that the scientific community has been trying to solve. One critical disadvantage of lead-based piezoceramics is their high lead content, which creates hazards during materials processing and poses a problem of waste disposal. As a consequence, and due to recent regulatory laws about the use of lead, enormous efforts have been made in the last decade in the search for high performance lead-free piezoceramics [1]. A significant number of binary or ternary systems with MPB have been synthesized and characterized, among which high piezoelectric properties and coupling coefficients have been achieved in $(K_{1/2}Na_{1/2})NbO_3$ (KNN) based compositions [2]. However, KNN-based piezoceramics exhibit a markedly nonlinear response, i.e. instability of properties, which limits their applications [3]. Compositional engineering by doping has been the traditional method used to minimize nonlinear effects, but so far only with moderate success in lead-free compositions.

The $(1-x)Bi_{0.5}Na_{0.5}TiO_3$-$xBaTiO_3$ (BNT-xBT) system with composition around MPB ($0.05 \leq x \leq 0.08$) has received significant attention because of its attractive properties ($d_{33} > 150$ pC/N, $k_p > 20\%$, $\tan\delta < 2\%$, $E_c < 30$ kV/mm) [4–6]. Although the basic properties of this system are well-established, and different synthesis routes [6–9] and doping strategies [10–16] have been explored in order to improve the properties, reports about the stability of the functional properties of these piezoelectric materials are still lacking. In this perspective, this work reports the results of a study on dielectric and piezoelectric properties of undoped BNT-*x*BT close to MPB (x = 0.06 and 0.07), with emphasis on material response under high, but sub-switching, electric field or mechanical stress (i.e. nonlinear response), which reflect the real working conditions of these materials in devices. Some aspects related to the piezoelectric response are also discussed in terms of the Rayleigh model.

2. Experimental

$(1-x)Bi_{0.5}Na_{0.5}TiO_3–xBaTiO_3$ (BNT-*x*BT) ceramics with x = 0.06 and 0.07 were prepared by a solid-state reaction route. Details about the materials processing and some basic properties of the synthesized materials can be found in “Supplementary Information”. Nonlinear dielectric response measurements were carried out in a plane capacitor configuration by using a capacitance comparator bridge specially designed for this type of measurement, as described in detail elsewhere [17]. Permittivity was measured by applying a 1 kHz driving ac electric field from 0.06 to 0.6 kV/mm, thereby ensuring a sub-switching range. Nonlinear longitudinal piezoelectric responses (dynamic piezoelectric coefficient) were measured by a Berlincourt-type method, similar to those previously described in the literature [18].

3. Results and discussion

Fig. 1 shows the electric field amplitude dependence of the real and imaginary relative dielectric permittivity at 1 kHz and at room temperature for the materials under study. The low-field values of permittivity are reported in “Supplementary Information”. As may be observed, both the real and imaginary parts of the permittivity increase with the increase in the electric field amplitude, and show an expected nonlinear dielectric response [19]. Nevertheless, although a certain instability in the dielectric response is exhibited in BNT-*x*BT, the relative increase in the permittivity of this system is significantly low. Taking as a reference the increase in ε' at E_0 = 0.30 kV/mm, this is lower than 2 % for BNT-*x*BT, while in a well-known lead-free, KNN-based composition it is 35% [3]. In fact, the increment of ε' at E_0 = 0.30 kV/mm is 50 % for a soft commercial PZT (Pz27, from Ferroperm A/S) and 6 % for a hard commercial PZT (PZT4, from Morgan Matroc Ltd.) [17]. It is important to point out that hard PZT are compositional engineered PZT-based materials developed to achieve a high stability of their properties, among other attributes. Thus, the results indicate that the BNT-BT system exhibits a high stability in the dielectric response, which is a not common feature in lead-free piezoceramics.

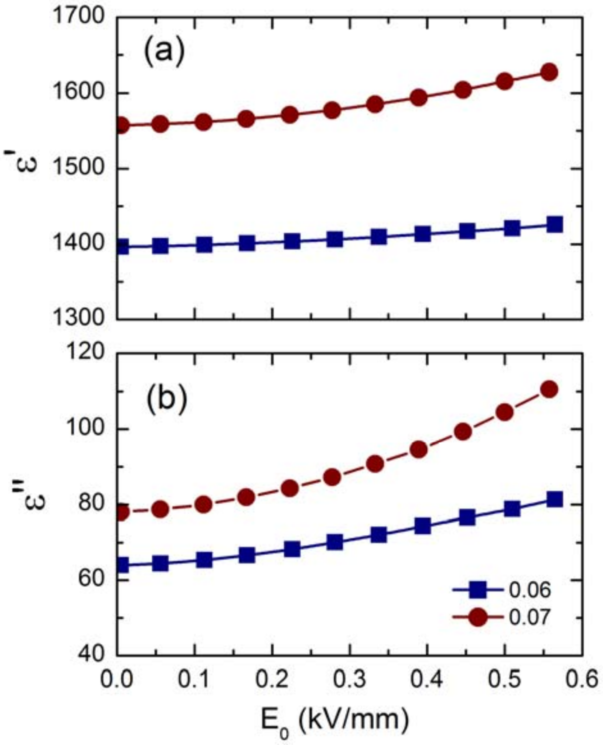

Fig. 1. Nonlinear dielectric response of (1-*x*)$Bi_{0.5}Na_{0.5}TiO_3$–*x*$BaTiO_3$, for *x* = 0.06 and 0.07, at 1 kHz and at room temperature. The real and the imaginary parts of the relative permittivity as a function of the applied ac electric field amplitude are shown in (a) and (b), respectively.

The observed stability of dielectric properties in the BNT-*x*BT system suggests that a high stability of piezoelectric properties may be achieved in these materials, since a common origin of the nonlinear response, either dielectric or piezoelectric, is expected in perovskite piezoceramics [20,21]. From this perspective, Fig. 2a shows the dependence of the longitudinal piezoelectric coefficient d_{33} with the amplitude T_0 of the applied dynamical stress for different 'bias' uniaxial compressive stress T_{DC}. The figure shows this dependence for $x = 0.06$, which is similar to the behaviour for $x = 0.07$. Two main features of piezoelectric response can be highlighted. First, one may observe that when the amplitude T_0 increases d_{33} also increases, thereby displaying a nonlinear behaviour for any T_{DC}. Second, d_{33} decreases for any amplitude T_0 when T_{DC} is increased, which may be explained as a result of the domain wall clamping effect [22]. In particular, the higher the T_{DC}, the lower the d_{33} at zero-stress amplitude (d_{33L}), as shown in Fig. 2b.

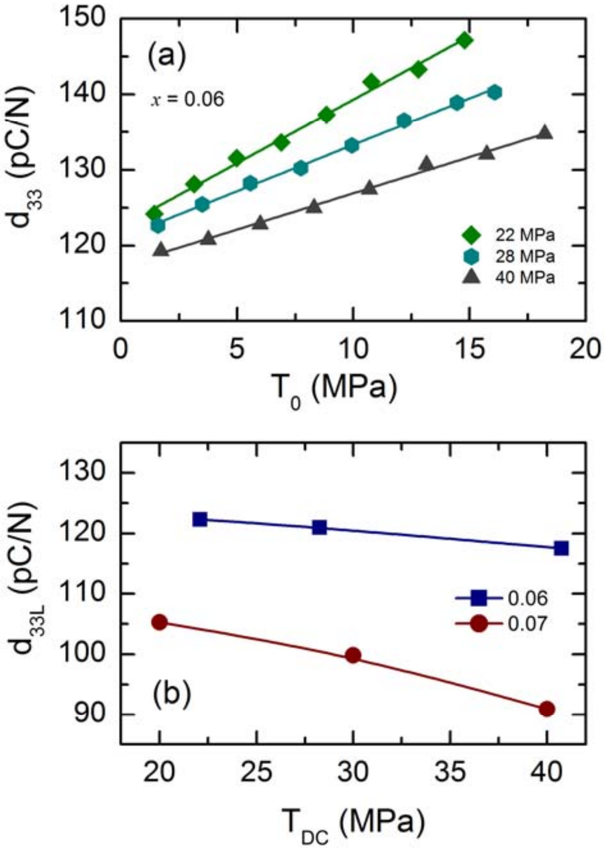

Fig. 2. Direct piezoelectric coefficient of (1-x)$Bi_{0.5}Na_{0.5}TiO_3$–$x$$BaTiO_3$, at 1 Hz and at room temperature, as a function of: (a) the amplitude of the applied dynamical stress for $x = 0.06$; (b) the uniaxial compression pre-stress for $x = 0.06$ and 0.07. In (b) d_{33L} represents the direct piezoelectric coefficient at zero-stress amplitude (T_0=0).

As may be observed in Fig. 2a, the piezoelectric coefficient d_{33} increases linearly as dynamic stress amplitude T_0 increases for all T_{DC}, which is in agreement with the Rayleigh law. This model has been satisfactorily used to describe the nonlinear piezoelectric response in ferroelectric materials [21,23,24]. According to this model, the dynamic stress amplitude dependence of the direct longitudinal piezoelectric coefficient can be expressed as:

$$d_{33} = d_{33L} + \alpha_d T_0 \qquad (1)$$

where α_d is called the Rayleigh coefficient. This is a useful parameter to quantify the instability of the piezoelectric response. The α_d value is easily obtained by a linear fitting of d_{33} versus T_0 curve, for a given T_{DC}.

It is well known that nonlinear response is related to the extrinsic contribution and that this is the main contribution to the material response in perovskite piezoceramics at room temperature [19]. Thus, a correlation between piezoelectric properties and nonlinear response is expected in perovskite polycrystals; e.g., the larger the piezoelectric coefficient the larger the Rayleigh coefficient. Fig. 3 shows the values of the longitudinal piezoelectric coefficient correlated with the Rayleigh coefficient for some piezoceramics. The data are extracted from d_{33} versus T_0 curves measured under a 'bias' uniaxial compressive stress of 20 MPa, at 1 Hz and at room temperature. As may be observed, compositions with a high piezoelectric coefficient exhibit higher values of Rayleigh coefficient, as is the case of the Pz27. A wide number of PZT-based materials are shown in Fig. 3 because the PZT system can be compositionally engineered in order to notably modify its properties. It is therefore possible to achieve such different materials as those denoted by PZT-Fe and PLZT 9/65/35. However, finding a composition whose properties are located in the region indicated as "desired properties" in Fig. 3 poses a challenge, since the nonlinear response is extrinsic in nature in these materials. It appears that lead-free piezoceramics are not unconnected with this issue, which is in line with the trend set by the lead-based compositions.

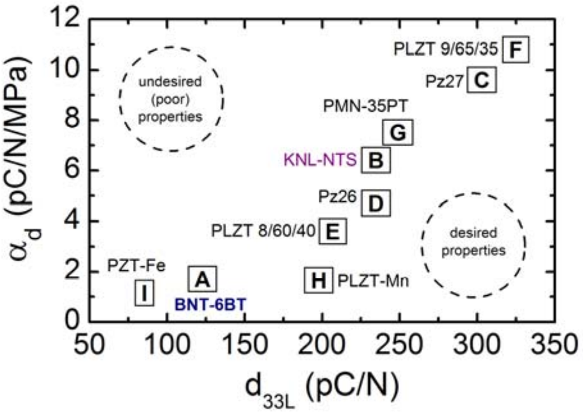

Fig. 3. Correlation between the Rayleigh coefficient and the zero-stress amplitude piezoelectric coefficient for some piezoelectric materials, measured at 1 Hz and under a uniaxial mechanical stress of 20 MPa. Data for A are extracted from Fig. 2(a); data for B, C and D are extracted from Fig. 1S (Supplementary Information); data for E, F, G, H and I are extracted from Refs. [25–28].

4. Conclusion

Not only are high values of electromechanical coefficients desirable in the race to obtain competitive lead-free piezoelectric ceramics, but also a high stability of these properties is needed to effectively replace lead-based compositions in high power applications. In this context, BNT-*x*BT ceramics with a composition around the morphotropic phase boundary are studied in order to evaluate the performance of these materials when they work under a high electric field or mechanical stress. Results indicate that BNT-*x*BT exhibits a high stability of dielectric and piezoelectric responses, which may make this system suitable for specific applications. Since the origin of the piezoelectric response is extrinsic in nature, a direct correlation between the longitudinal piezoelectric coefficient and the Rayleigh coefficient is evidenced for a wide number of piezoceramics. Desirable properties of piezoceramics include a high and stable piezoelectric response together with low losses, which constitutes an ongoing challenge in material science.

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High stability of properties in morphotropic phase boundary $Bi_{0.5}Na_{0.5}TiO_3$-$BaTiO_3$ piezoceramics

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Supplementary information

Details of the synthesis and basic properties of the materials

(1-*x*)$Bi_{0.5}Na_{0.5}TiO_3$–*x*$BaTiO_3$ (BNT-*x*BT) ceramics with x = 0.06 and 0.07 were prepared by a solid-state reaction route. Bi_2O_3 (99.9%), Na_2CO_3 (99.5%), $BaCO_3$ (99%), and TiO_2 (99.9%) were used as the starting raw materials. The raw reagents were weighed according to the desired composition and ball-milled with yttria-stabilized zirconia balls in absolute ethanol medium at 300 rpm for 8h. The solution was dispersed and then dried. The obtained powders were calcined at 700ºC for 2h and then milled again for 8h. The final powders were mixed with a binder solution, dried and then pressed at 700 MPa to produce disc-shaped (13 mm diameter and 0.5 mm thick) and bar-shaped (16 mm long, 4 mm wide and 0.8 mm thick) samples. The pellets were sintered in air at 1200ºC for 2h in covered platinum crucibles. As-sintered samples showed relative densities over 95% measured by Archimedes' method.

Room temperature X-ray diffraction measurement of powder of sintered samples were carried out to verify the structure of the studied compositions. The results show a pure perovskite structure with a mixture of rhombohedral and tetragonal crystal structures for both composition, as may be expected for BNT-BT system around their morphotropic phase boundary. Microstructural analysis by field-emission scanning electron microscopy revealed the polycrystalline nature of the samples with grains that are rounded, irregular shaped and inhomogeneous in size.

Gold electrodes were sputtered on parallel polished faces of the samples. A precision LCR meter (Agilent E4980A) was used to obtain the real and imaginary parts of the permittivity of unpoled samples at selected frequencies from 100 Hz to 1 MHz. Samples were then poled in a silicone bath at 25 ºC under a dc electric field of 4 kV/mm for 30 minutes. Before measurements, samples were aged for a week in order to prevent the influence of aging processes. The static longitudinal piezoelectric coefficient was measured with a d_{33} meter (KCF Technologies PM3500). A precision impedance analyzer (Agilent 4294A) was employed to measure resonance and anti-resonance frequencies of the main vibration extensional mode of bar-shape samples as well as their capacitance value at the frequency where the motional admittance is null. The elastic compliance s^E_{11}, the piezoelectric coefficient d_{31}, and the electromechanical coupling factor k_{31} were determined on the basis of IEEE standards. **Table S1** summarizes some basic room temperature functional properties of the synthesized materials.

Table S1. Room temperature values of the dielectric constant, ε', dielectric losses, $\tan\delta$, elastic compliance, s^E_{11}, piezoelectric coefficients, d_{33} and d_{31}, and electromechanical coupling factor k_{31} of (1-x)$Bi_{0.5}Na_{0.5}TiO_3$–$x$$BaTiO_3$, for x = 0.06 and 0.07.

x	ε'	$\tan\delta$ (%)	d_{33} (pC/N)	d_{31} (pC/N)	s^E_{11} (10^{-12}/Pa)	k_{31}
0.06	1397	4.6	147	34	8.5	0.17
0.07	1557	5.0	180	37	8.0	0.17

Nonlinear piezoelectric response of some piezoelectric ceramics

Figure S1 shows the dependence of the longitudinal piezoelectric coefficient d_{33} with the amplitude T_0 of the applied dynamical stress, measured under a ‘bias’ uniaxial compressive stress of 20 MPa, at 1 Hz and at room temperature. The piezoelectric coefficient d_{33} increases linearly as dynamic stress amplitude T_0 increases; thus, $d_{33} = d_{33L} + \alpha_d T_0$. The values of α_d are obtained by a linear fitting of d_{33} versus T_0 curve for each material. In the figure, Pz26 and Pz27 are commercial hard and soft $Pb(Zr,Ti)O_3$-based materials (Ferroperm Piezoceramics S/A) and KNL-NTS is the well-known KNN-based composition $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.10}Sb_{0.06})O_3$.

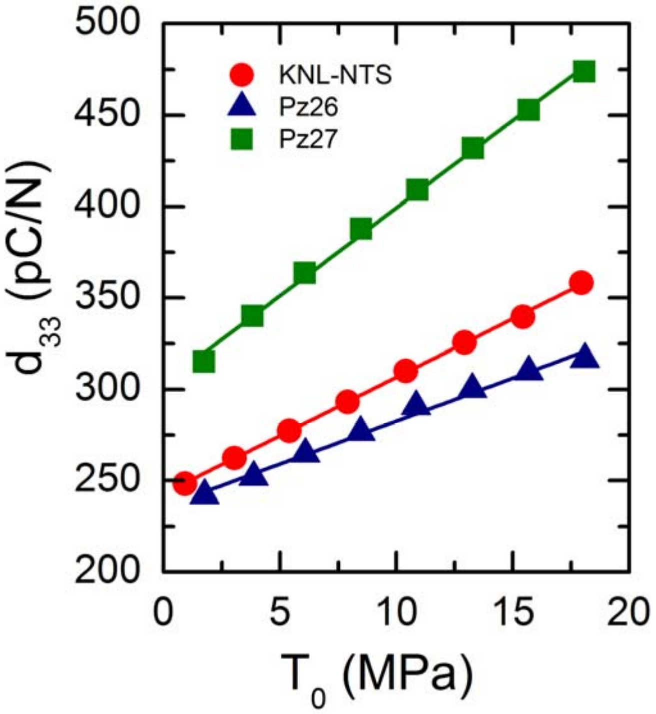

Fig. 2. Direct piezoelectric coefficient of some representative piezoceramics as a function of the amplitude of the applied dynamical stress, at 1 Hz and at room temperature. All measurement were performed under a uniaxial pre-stress of 20 Ma.