



# Structural, dielectric and piezoelectric study of Ca-, Zr-modified BaTiO<sub>3</sub> lead-free ceramics

H MSOUNI<sup>1,3,\*</sup>, A TACHAFINE<sup>2</sup>, M EL AATMANI<sup>1</sup>, D FASQUELLE<sup>2</sup>, J C CARRU<sup>2</sup>,  
M EL HAMMIOU<sup>3</sup>, M RGUITI<sup>4</sup>, A ZEGZOUTI<sup>1</sup>, A OUTZOURHIT<sup>5</sup> and M DAOUD<sup>1</sup>

<sup>1</sup>Equipe Sciences des Matériaux Inorganiques et leurs Applications, Faculté des Sciences Semlalia, Université Cadi Ayyad, BP 2390 Marrakech, Morocco

<sup>2</sup>Unité de Dynamique et de Structure des Matériaux Moléculaires, Université du Littoral Côte d'Opale, BP 717, 62228 Calais, France

<sup>3</sup>Laboratoire Réactivité des Matériaux et Optimisation des Procédés, Faculté des Sciences Semlalia, Université Cadi Ayyad, BP 2390 Marrakech, Morocco

<sup>4</sup>Laboratoire des Matériaux Céramiques et Procédés Associés, Université de Valenciennes et du Hainaut-Cambrésis, 59600 Maubeuge, France

<sup>5</sup>Laboratoire de Physique du Solide et des Couches Minces, Faculté des Sciences Semlalia, Université Cadi Ayyad, BP 2390 Marrakech, Morocco

\*Author for correspondence (houda.msouni@gmail.com)

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**Abstract.** We prepared a lead-free ceramic (Ba<sub>0.85</sub>Ca<sub>0.15</sub>)(Ti<sub>1-x</sub>Zr<sub>x</sub>)O<sub>3</sub> (BCTZ) using the conventional mixed oxide technique. The samples were prepared by an ordinary mixing and sintering technique. In this study we investigated how small amounts of Zr<sup>4+</sup> can affect the crystal structure and microstructure as well as dielectric and piezoelectric properties of BaTiO<sub>3</sub>. X-ray diffraction analysis results indicate that no secondary phase is formed in any of the BCTZ powders for 0 ≤ x ≤ 0.1, suggesting that Zr<sup>4+</sup> diffuses into BaTiO<sub>3</sub> lattices to form a solid solution. Scanning electron microscopy micrographs revealed that the average grain size gradually increased with Zr<sup>4+</sup> content from 9.5 μm for x = 0.02 to 13.5 μm for x = 0.1; Curie temperature decreased due to the small tetragonality caused by Zr<sup>4+</sup> addition. Owing to the polymorphic phase transition from orthorhombic to tetragonal phase around room temperature, it was found that the composition x = 0.09 showed improved electrical properties and reached preferred values of d<sub>33</sub> = 148 pC N<sup>-1</sup> and K<sub>p</sub> = 27%.

**Keywords.** BCTZ; sintering; grain size; dielectric properties; piezoelectric properties.

## 1. Introduction

Ferroelectric materials have attracted the attention of researchers around the world thanks to their high piezoelectric performances. For example, among the ferroelectric compounds, Pb(Zr<sub>1-x</sub>Ti<sub>x</sub>)O<sub>3</sub> (PZT) solid solutions are the best reference materials with respect to their piezoelectric properties [1]. However, the introduction of new standards to eliminate lead-based compound in the implementation of functional materials has opened today an opportunity to develop alternative compounds with equivalent properties. In this regard, BaTiO<sub>3</sub>-based solid solutions are good candidates [2,3]. The most important characteristic of BaTiO<sub>3</sub> is that it can form solid solutions with CaTiO<sub>3</sub> and/or BaZrO<sub>3</sub>, making it possible to tune their properties for various applications.

The pure BaTiO<sub>3</sub> crystal undergoes a series of phase transformations, from cubic to tetragonal at about 120°C, tetragonal to orthorhombic at about 5°C and finally orthorhombic to pseudo-cubic structure at -80°C. It is known that Zr substitution at the Ti-sites in BaTiO<sub>3</sub> shifts the phase transition temperatures of the tetragonal to orthorhombic and

orthorhombic to rhombohedral to high temperatures, while lowering the cubic to tetragonal transition temperature [4]. Yu *et al* [5] have studied the effect of the incorporation of Zr<sup>4+</sup> on the piezoelectric properties of BaTiO<sub>3</sub>. They reported that certain amounts of Zr<sup>4+</sup> in BaTiO<sub>3</sub> may cause the shift of the tetragonal–orthorhombic transition temperature to near room temperature (RT) and thus improve the piezoelectric properties. In fact, they found that the optimum piezoelectric properties are obtained for 5 mol% of Zr<sup>4+</sup>. For this composition, the orthorhombic–tetragonal phase transition temperature reaches 331 K. Li *et al* [6] showed that the piezoelectric properties of Ba(Zr<sub>0.05</sub>Ti<sub>0.95</sub>)O<sub>3</sub> may also be improved by doping with calcium (Ca<sup>2+</sup>). The main advantage of this is that calcium reduces the transition temperature of the tetragonal–orthorhombic and orthorhombic–rhombohedral phase without affecting the cubic–tetragonal transition temperature.

The dielectric and piezoelectric solid solution (Ba<sub>0.85</sub>Ca<sub>0.15</sub>)(Zr<sub>x</sub>Ti<sub>1-x</sub>)O<sub>3</sub> was investigated by some authors [7–9]. However the range of substitution with zirconium was clearly limited around the morphotropic phase boundary (MPB), i.e.,

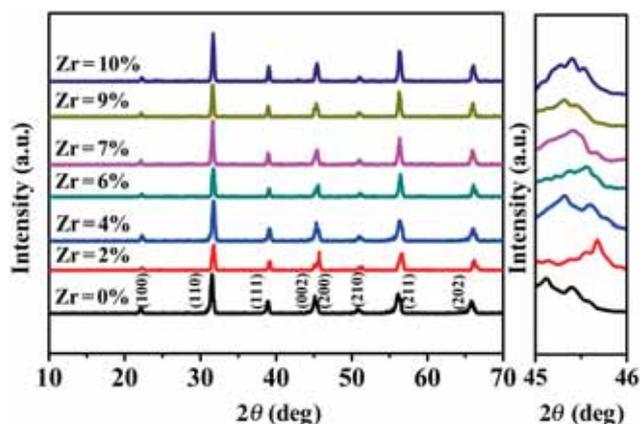


Figure 1. XRD patterns of BCTZ powders.

Zr% = 0, 2.5, 5, 7.5, 10, 12.5, 15, 17.5, 20, 22.5 and 25. In addition, some authors have synthesized those ceramics using an additive for the sintering process [7].

In this work, we carried out a systematic study of  $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  solid solution (BCTZ) by varying  $x$  in small steps in the range of [0–10%] in order to approach the MPB (to approximate and predict) without using any sintering-aid additive. To this end, the evolution of the ferroelectric–paraelectric transition temperature and the structural, dielectric and piezoelectric properties of the solid solution  $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  with  $x$  is studied.

## 2. Experimental

$(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$  (abbreviated as BCTZ) powders were prepared by the solid-state reaction method. Commercial powders of  $\text{BaCO}_3$  (99%, Sinopharm Chemical Reagent),  $\text{CaCO}_3$  (99%, Sigma-Aldrich),  $\text{TiO}_2$  (99.9%, Sigma-Aldrich) and  $\text{ZrO}_2$  (99%, Sigma-Aldrich) were selected as starting materials. These precursors were weighted in stoichiometric proportions, mixed carefully and ground in an agate mortar until an intimate mixture was formed, which was then calcined at  $1350^\circ\text{C}$  for 15 h in air. The resulting calcined powders were ground and then uni-axially compacted at RT to pellets of 6 mm diameter and 1 mm thickness before being sintered at  $1400^\circ\text{C}$  for 10 h in air.

The crystal structure of the samples was studied using an X-ray diffractometer with Cu-K $\alpha$  radiation in the  $2\theta$  range of  $5^\circ$ – $70^\circ$ , with a scan step of  $0.05^\circ$ . The surface morphology of the pellets was observed by scanning electron microscopy (SEM) and also used to estimate the grain size. The ceramics used for the dielectric measurements were made from the same powders used for the X-ray investigation. To perform dielectric measurements, the specimens were polished to obtain parallel surfaces and then coated by silver paste to form the electrodes. The temperature- and frequency-dependent capacitance and conductance were measured using an LCR meter (HP 4284 A) in the frequency range 100 Hz–1 MHz. For measurement of piezoelectric properties, the samples were

Table 1. Dependence of  $c/a$  ratio on zirconium content.

Zr (%)	0	2	4	6	7
$c/a$	1.008	1.008	1.005	1.005	1.005

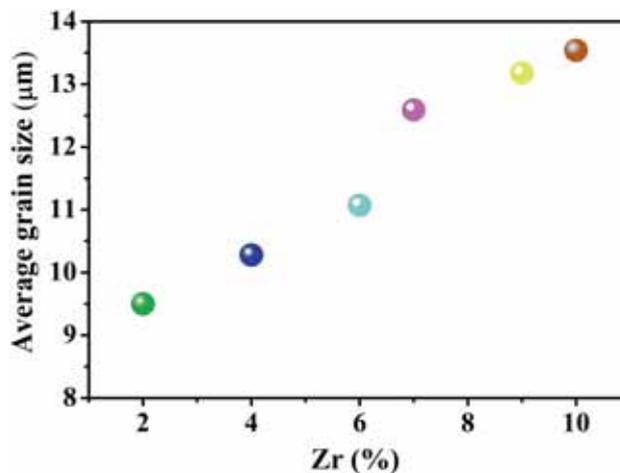


Figure 2. Variation of grain size as a function of zirconium content.

poled at RT ( $20$ – $25^\circ\text{C}$ ) in a silicone oil bath in a DC electric field of  $3\text{ kV mm}^{-1}$ . The piezoelectric coefficient  $d_{33}$  was measured using a piezoelectric  $d_{33}$ -meter (Piezotest PM 200) at a frequency of 100 Hz, 1 day after the polarization. The electromechanical coupling factor  $K_p$  was measured by the resonance and anti-resonance technique using an impedance analyser (HP 4194 A).

## 3. Results and discussion

### 3.1 Phase analysis and microstructure

The X-ray diffraction (XRD) patterns of BCTZ calcined powders recorded at RT are shown in figure 1. As revealed from the recorded patterns, all the samples exhibit pure perovskite structure. The expanded plot in the  $2\theta$  range  $45^\circ$ – $46^\circ$  indicates two overlapping diffraction peaks corresponding to (002) and (200), centred around  $45.5^\circ$ , suggesting the existence of a tetragonal phase at RT for the BCTZ solid solution in the range  $0 \leq x \leq 0.06$ . As the content  $x$  of Zr increases, these two peaks around  $45.5^\circ$  merge to a single peak, suggesting a structural transformation from tetragonal to orthorhombic phase. The variation in the  $c/a$  ratios of the tetragonal phases identified in samples with  $0 \leq x \leq 7\%$  composition is shown in table 1. Samples with  $x = 9$  and  $10\%$  were identified as having an orthorhombic and tetragonal structure, respectively, at around RT, where the MPB of the BCTZ system is located. Thus, it is not easy to determinate the accurate value of the tetragonal distortions. From the table, it can be seen that there is small but distinct linear reduction in  $c/a$  ratio as the Zr content increases. The resulting tetragonal distortion exhibits the

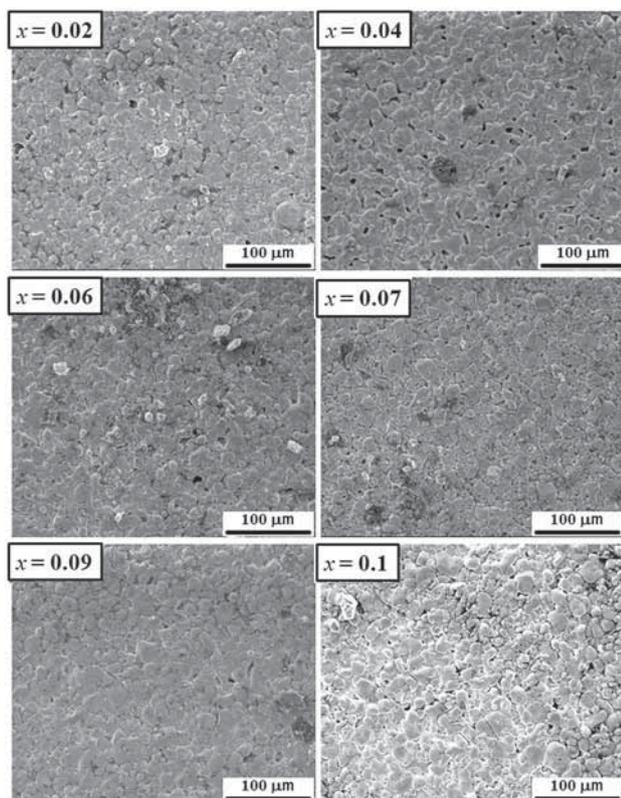


Figure 3. SEM images of  $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$  ceramics.

maximum value of  $\approx 1.008$ . A variation in lattice parameter with composition is to be expected due to the different ion radii of  $\text{Ti}^{2+}$  and  $\text{Zr}^{2+}$ .

Zirconium is known to have an effect on the grain size of the ceramic. In fact the ceramics that are rich in zirconium have larger grains size, in contrast with ceramics that are poor in zirconium. The literature reports that the average grain size gradually increases with a rate of  $1 \mu\text{m}$  per 1% of zirconium [8]. Figure 2 depicts the evolution of the average grain size, which was estimated by calculating the average of 20 grains selected from the SEM micrographs, as a function of zirconium content. The average grain size of the BCTZ ceramics increased with the doping level in the range of  $9.5\text{--}13.5 \mu\text{m}$ . This small size can be explained by the fact that the sintering temperature required for a material containing zirconium, known to be refractory, must be very high, in contrast with materials free of this component.

Figure 3 depicts the SEM images of the samples. The grains have an irregular shape with small grains size in the range of  $9.5\text{--}13.5 \mu\text{m}$ . This confirms that it is difficult to get dense BCTZ ceramics below  $1500^\circ\text{C}$  since zirconium is refractory. Wang *et al* [10] have shown that by optimizing the sintering temperature, one can obtain the required microstructure necessary for high-performance piezoelectric ceramics. Yang *et al* [11] showed that the density has a far less effect on the piezoelectric properties of PZT ceramics than the grain size.

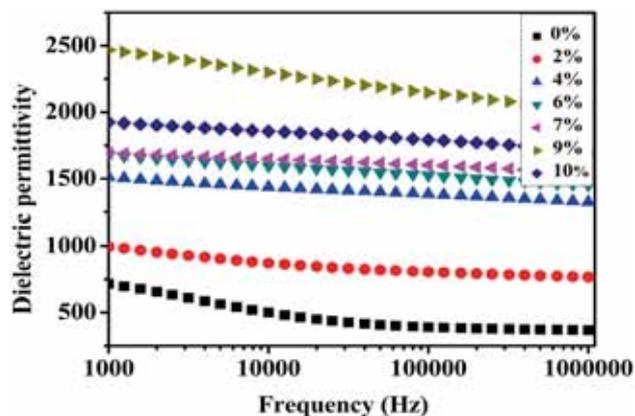


Figure 4. Dielectric constant as a function of frequency for the BCTZ solid solution.

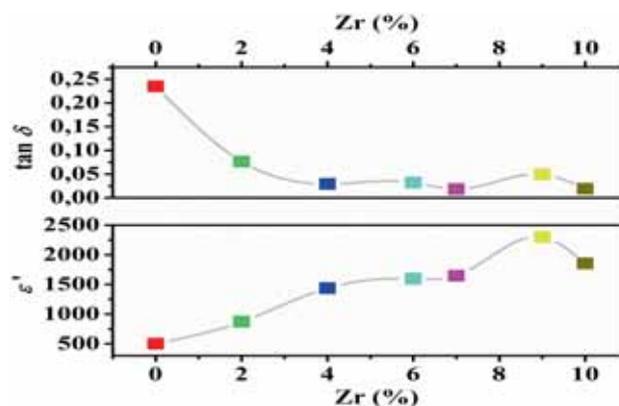


Figure 5. Variation of dielectric properties with zirconium content.

Benabdallah *et al* [12] recently found that BCTZ ceramics with large grain size and low density have better dielectric and piezoelectric properties than the BCTZ ceramics with finer grains but high density.

### 3.2 Dielectric study

Variation of the dielectric constant of the BCTZ ceramics as a function of frequency is shown in figure 4. All the ceramics show a dispersion of permittivity up to 10 kHz. One can see that the maximum permittivity value of 2467 is observed for the composition with 9% of zirconium at 1 kHz. The low-frequency behaviour of permittivity can be attributed to the ionic conduction, which contributes to the polarization process. In fact, at low frequencies the charge carriers, usually impurity ions, diffuse up to the interface and build up the surface charge. In contrast, at low frequencies the mobile charges are more sensitive to the frequency of the applied field and can no longer follow the field at high frequencies, resulting in a decrease of polarization.

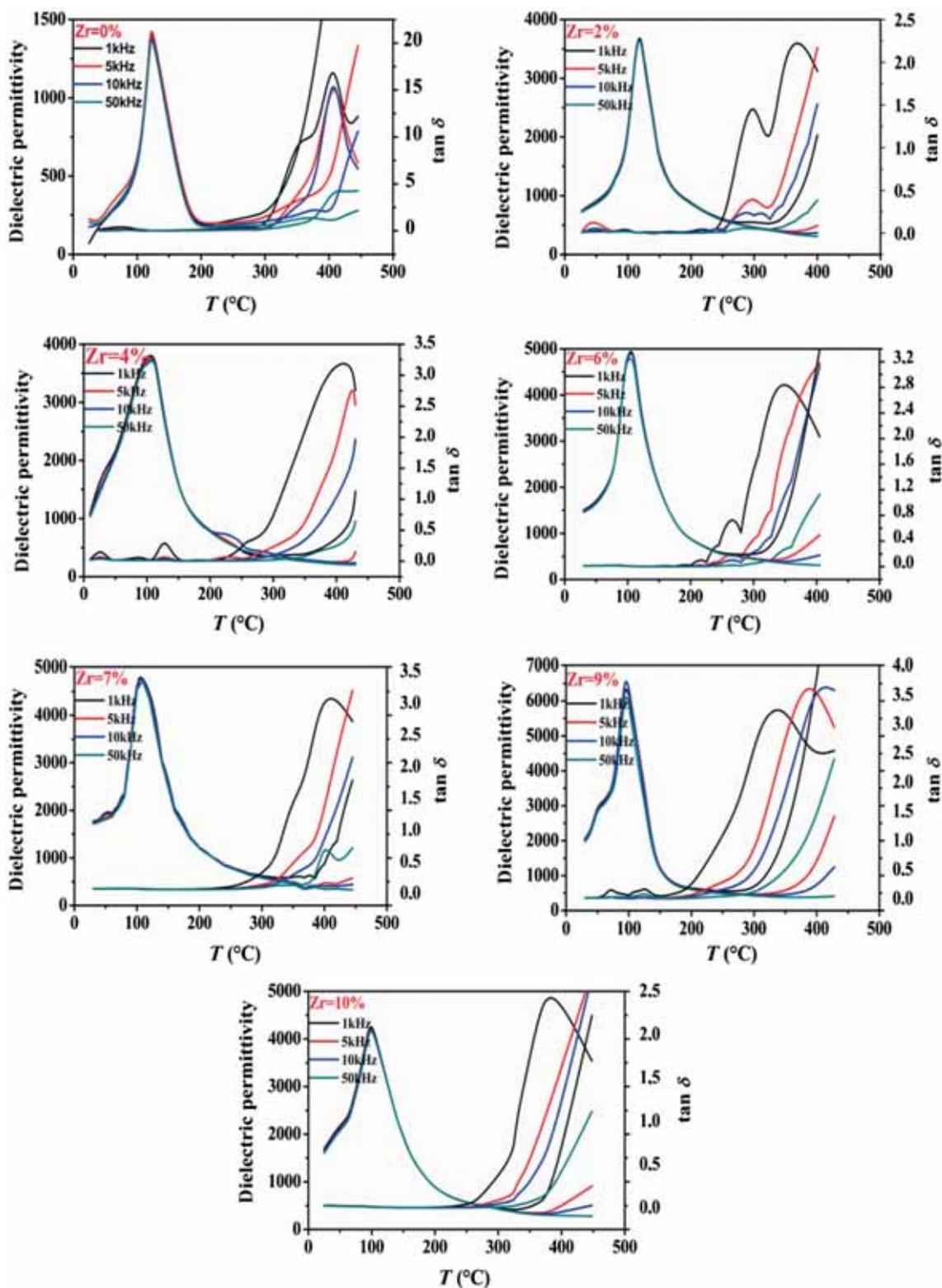


Figure 6. Dielectric properties vs. temperature at different frequencies for the BCTZ solid solution.

This phenomenon can be explained using the Maxwell–Wagner mechanism [13] and Koops theory [14]. According to the Koops theory, all ceramics have a heterogeneous

microstructure consisting of semiconductor grains and insulator grain boundaries. The semiconducting nature of grain was explained as the result of low oxygen level during the

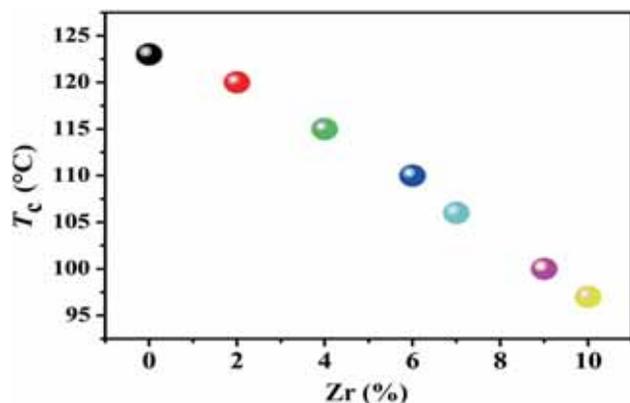


Figure 7. Variation of  $T_c$  as a function of zirconium content.

ceramics sintering process. According to this model, at low frequencies the main contribution to the permittivity is due to the grains, which have a high dielectric constant, and to grains at high frequencies, which have a small dielectric constant.

Figure 5 describes the variation of permittivity and dielectric loss as a function of Zr doping level at 10 kHz. The dielectric constant value increases significantly from 500 at  $x = 0$  to 1437 at  $x = 0.04$  and changes slightly with raising doping level, before reaching a maximum of 2300 at  $x = 0.09$  and finally decreases at  $x = 0.1$ .

The observed value for BCTZ-7% and BCTZ-10% ceramics at 100 kHz is greater than the value found by Sindhu *et al* [15]. The dielectric loss tangent of all the samples is below the value of 0.24 with a maximum at  $x = 0$  and a slight variation in the range of 2–10% of zirconium. The high values of loss tangent may be due to the small grains size, resulting in large number of grains boundaries and consequently high dielectric loss.

Figure 6 shows the effect of temperature on the dielectric behaviour of the BCTZ solid solution at different frequencies: 1, 5, 10 and 50 kHz. All the ceramics show weak frequency dispersion. The maximum value of the dielectric constant at the medium frequency (10 kHz) was found to be around 1408 at  $x = 0$ , 3753 at  $x = 0.02$ , 3813 at  $x = 0.04$ , 5043 at  $x = 0.06$ , 5301 at  $x = 0.07$ , 5964 at  $x = 0.09$  and 4241 at  $x = 0.1$ .

The dielectric losses significantly increased at high temperature due to the increasing conduction, which occurs because of the substitution of  $Ti^{4+}$  cations on B-sites. The transition from the tetragonal structure to the cubic structure ( $T_c$ ) was observed in all ceramics, while the orthorhombic to tetragonal transition could be clearly observed around RT for  $x = 0.09$  and slightly observed for  $x = 0.1$ . This can be explained by the pinched nature of the phase transition, which is similar to that observed for the  $Ba(Ti_{1-x}Zr_x)O_3$  ceramics [16]. Huang *et al* [17] also reported that a zirconium content greater than or equal to 10% leads to the appearance of the cubic phase with a gradual disappearance of the orthorhombic–tetragonal phase transition.

Figure 7 illustrates the variation of the Curie temperature *vs.* doping level in zirconium. The transition temperature varies

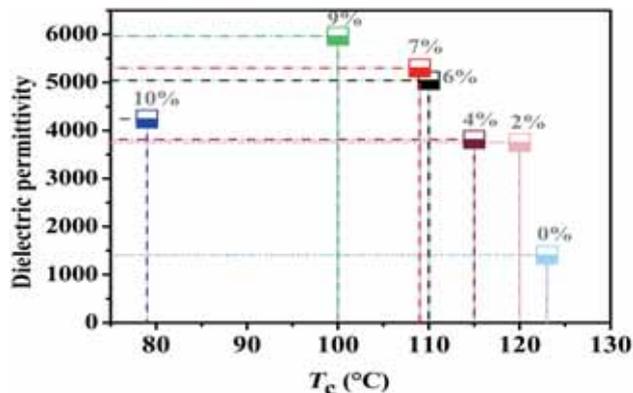


Figure 8. Variation of the dielectric permittivity at 10 kHz as a function of  $T_c$  for the BCTZ solid solution.

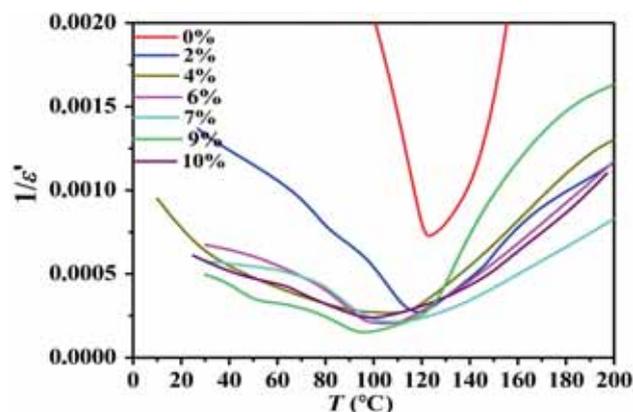


Figure 9. Inverse of dielectric constant  $1/\epsilon'$  as a function of temperature at 10 kHz.

from 123 to 97°C, suggesting a strong dependence of the Curie temperature on zirconium content. The BCT ceramic exhibits a dielectric constant maximum at 123°C. With increasing content of Zr, the  $T_m$  decreased gradually from 120°C at 2% to 97°C at 10%. This decrease was attributed to the low value of the jump force between B-sites and oxygen ions and to the distortion of the octahedron in the perovskite  $ABO_3$  due to the substitution of  $Ti^{4+}$  by  $Zr^{4+}$  [16].

Figure 8 shows the temperature dependence of the dielectric constant of BCTZ ceramics at 10 kHz. The  $(Ba_{0.85}Ca_{0.15})(Ti_{0.91}Zr_{0.09})O_3$  ceramic with orthorhombic–tetragonal phase transition around RT has the highest dielectric constant value of 5964, which tends to decrease with increasing Zr content. It is known that the maximum dielectric constant is often obtained around the MPB in both lead-based and lead-free materials, and this was attributed to the movement of domains and walls in particular [18,19]. Similar observations were reported by Wu *et al* [8] for the  $(Ba_{0.85}Ca_{0.15})(Ti_{0.90}Zr_{0.10})O_3$  ceramic.

In figure 9 we plot the inverse of permittivity *vs.* temperature at 10 kHz fitted to the Curie–Weiss law described by the

**Table 2.** Curie–Weiss temperature ( $T_{cw}$ ), the temperature where the dielectric constant starts to follow the Curie–Weiss law ( $T_0$ ), the temperature at the dielectric constant maximum ( $T_m$ ) and the deviation from the Curie–Weiss law ( $\Delta T_m$ ) at 10 kHz.

Zr (%)	$T_{cw}$ (°C)	$T_0$ (°C)	$T_m$ (°C)	$\Delta T_m$ (°C)
0	153	146	123	30
2	132	104	119	13
4	129	56	113	16
6	138	111	110	28
7	137	118	108	29
9	130	119	100	30
10	146	115	97	49

relation

$$1/\varepsilon' = (T - T_0)/C, \quad (1)$$

where  $T_0$  is the Curie–Weiss temperature and  $C$  is the Curie–Weiss constant. The parameter  $\Delta T_m$  describes the degree of deviation from the Curie–Weiss law and is defined as

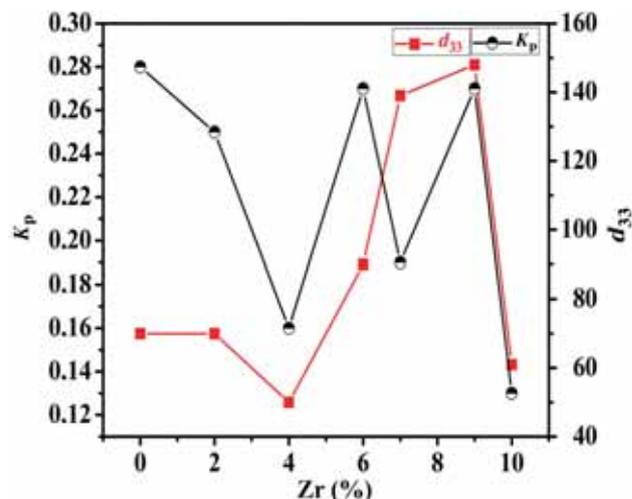
$$\Delta T_m = T_{cw} - T_m, \quad (2)$$

where  $T_{cw}$  illustrates the temperature from which the permittivity starts deviating from the Curie–Weiss law and  $T_m$  represents the temperature of the maximum value of permittivity.

The obtained results are given in table 2, which shows that the dielectric constant of all samples deviates from the Curie–Weiss law above the Curie temperature. Furthermore,  $\Delta T_m$  increases with increasing Zr content, suggesting that the diffuse nature of the transition is related to Zr cations. This kind of phase transition may be related to the occupancy of  $Zr^{4+}$  ions at B-site of  $Ba_{0.85}Ca_{0.15}TiO_3$  cell, which can induce a disorder in the crystal structure. This can be explained by the larger ionic radius and lower polarization of  $Zr^{4+}$  than that of  $Ti^{4+}$  ions [20,21]. The local distortion of the lattice leads to increase of polar nanoregions (PNRs), which can hardly be detected by the X-ray diffractometer due to their small size. However, one can suppose that those PNRs may show a large size since the relaxor behaviour of our samples is very weak [22].

### 3.3 Piezoelectric study

Figure 10 shows the evolution of piezoelectric properties as a function of zirconium content. The maximum  $d_{33}$  and  $K_p$  are observed for the composition  $x = 0.09$ . This ceramic has the greatest value of dielectric constant and a ferroelectric phase transition at  $T_{O-T}$  (orthorhombic–tetragonal) close to ambient temperature. Besides, the lattice constants  $a$  and  $b$  for samples with Zr content in the range  $0.09 \leq x \leq 0.1$ , where the orthorhombic structure is located, were estimated from XRD



**Figure 10.** Variations of  $d_{33}$  and  $K_p$  with  $x$  for the BCTZ ceramics.

**Table 3.** Correlation between zirconium content and structural distortion.

Zirconium content (%)	Orthorhombicity factor
9	0.3485
10	0.3455

patterns and are presented in table 3. The orthorhombic factor  $2 \frac{|a-b|}{a+b}$  reflects the degree of lattice distortion. As one can see, the decrease in orthorhombicity implies that the coexistence of the tetragonal and orthorhombic phases starts to disappear for the sample with 10% of zirconium, confirming the results discussed earlier.

It has been explained by several authors that compositions inducing a phase transition near RT are very promising for high piezoelectric properties [23–25]. This is due to the instability of the polarization direction at the transition temperature, which is easily influenced by the application of an electric field [26–29]. Moreover, it is believed that relaxor behaviour tends to decrease the energy and external stress required for the ferroelectric polarization [30–32], resulting in high piezoelectricity. These combined effects together affect the piezoelectric properties positively and lead to a relatively high  $d_{33}$  value in the BCTZ-0.09 ceramic.

The decrease of piezoelectric response with higher Zr content may be due to many factors: the diffuse nature of the transition, which tends to be stronger for the ceramic with 10% of Zr than for the ceramic with 9%, the decrease of permittivity value and finally, the coexistence of orthorhombic and tetragonal phases, which tends to decrease with further increase in Zr content ( $x \geq 0.10$ ).

However, the piezoelectric response is lower than the predicted value for BCTZ single crystal due to the polycrystallinity and the porosity of the textured BCTZ ceramics. These parameters are known to influence the electrical and

electromechanical properties of the material, which are highly dependent on the microstructure. Process optimization should be studied further to improve the density, texture and piezoelectric properties of this system. In addition, it was found that the sintered grain size, which can be altered by the initial powder particle size, contributes also to the enhanced  $d_{33}$  value because the domain rotation becomes easier for the specimens with large sintered grains [33]. In fact, Bai *et al* [34] found that particle size of calcined powder is an important factor and should be chosen with care in order to maximize the  $c/a$  ratios in the sintered ceramics.

#### 4. Conclusion

In this study, BCTZ solid solution was synthesized using the conventional solid-state method, leading to a single perovskite structure. All the ceramics have a porous microstructure with grain size in the range of 9.5–13.5  $\mu\text{m}$ . The dielectric measurements exhibit paraelectric–ferroelectric phase transition with a slight dependence on frequency. The deviation from Curie–Weiss law increases with increasing zirconium content. The evolution of piezoelectric properties with zirconium content was discussed and correlated with XRD, SEM and dielectric results. Because of the phase transition near RT and the MPB, the ceramic with  $x = 0.09$  exhibits optimum piezoelectric properties: a piezoelectric constant  $d_{33} = 148 \text{ pC N}^{-1}$  and an electromechanical coupling factor  $K_p = 27\%$ .

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