

Status: Preprint has not been submitted for publication

Effect of the synthesis route on the phase formation and dielectric property in Ba,(Zr,Ti)O₃-(Ba,Ca)TiO₃ ceramics

André Bonaventura, Rangel Graudiston Aredes, Renato Boschilia, Eduardo Antonelli

DOI: 10.1590/SciELOPreprints.1232

This preprint was submitted under the following conditions:

- The authors declare that they are aware that they are solely responsible for the content of the preprint and that the deposit in SciELO Preprints does not mean any commitment on the part of SciELO, except its preservation and dissemination.
- The authors declare that the research that originated the manuscript followed good ethical practices and that the necessary approvals from research ethics committees are described in the manuscript, when applicable.
- The authors declare that the necessary Terms of Free and Informed Consent of participants or patients in the research were obtained and are described in the manuscript, when applicable.
- The authors declare that the preparation of the manuscript followed the ethical norms of scientific communication.
- The authors declare that the manuscript was not deposited and/or previously made available on another preprint server.
- The submitting author declares that all authors responsible for preparing the manuscript agree with this deposit.
- The authors declare that in the event that this manuscript has previously been submitted to a journal and being evaluated, they have received the journal's consent to make the deposit on the SciELO Preprints server.
- The submitting author declares that all authors' contributions are included on the manuscript.
- The authors declare that if the manuscript is posted on the SciELO Preprints server, it will be available under a [Creative Commons CC-BY](#) license.
- The deposited manuscript is in PDF format.
- If the manuscript is being reviewed and published by a journal, the authors declare that they have received authorization from the journal to make this deposit.

Submitted on (YYYY-MM-DD): 2020-09-19

Posted on (YYYY-MM-DD): 2020-09-30

Effect of the synthesis route on the phase formation and dielectric property in $\text{Ba}_{1-x}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ -($\text{Ba}_{0.7}\text{Ca}_{0.3}$) TiO_3 ceramics

André L. Bonaventura, Rangel G. Aredes, Renato Boschilia, Eduardo Antonelli

Advanced Ceramic Laboratory, Science and Technology Institute, Universidade Federal de São Paulo, 12231-280, São José dos Campos, SP, Brazil
e-mail: fisico.bonaventura@gmail.com

Keywords: Phase Transition, Ferroelectrics, BCZT, Ceramics.

Abstract

Ceramics of $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ (BZT-BCT) are one of the promising candidates to substitute the lead zirconate titanate (PZT) ceramics. Some authors have named these compositions as $\text{Ba}_{1-x}\text{Ca}_x\text{Ti}_{1-y}\text{Zr}_y\text{O}_3$ (BCZT) while others as BZT-BCT. That way, this terminology can lead the interpretation that ceramics of BCZT were prepared from precursor powders “direct route” (carbonates, oxides, etc), while ceramics of BZT-BCT are synthesized by the mixture of BZT and BCT solid solutions in a “composite route.” Therefore, this paper aims to put light into the influence of the processing route on the properties of these compositions. The method used was the preparation of the ceramics by two routes: BCZT, named as a monophasic system, prepared by the direct route and BZT-BCT, designed polyphasic system, prepared by a composite route. The results show that the processing influences the structure, microstructure, dielectric properties, and phase transitions of the ceramics. These findings are particularly relevant for the discussion of the phase development and compositional complexity of these materials.

1. Introduction

Ceramics with piezoelectric properties are applied as sensors, actuators, and transducers [1]. Traditionally, high piezoelectric coefficients are obtained in Lead zirconate titanate (PZT) based ceramics [2, 3]. However, due to the toxicity of lead, researches have been performed to obtain lead-free ceramics with piezoelectric properties similar to PZT [1, 4].

In 2009 Liu and Ren published a paper about a ceramic system with excellent piezoelectric properties [2]. This paper discusses the case of one composition close to the morphotropic phase boundary, defined as $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$. According to these authors, the material was produced through a pseudo-binary system, called BZT-xBCT, where x is the molar percent of BCT. Since then, many works have been performed to understand the mechanism that explains the high piezoelectric values of these compositions [5, 6, 7]. Nevertheless, the literature has reporting works with the composition $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ using two definitions, BCZT with a direct formulations $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ [8, 9, 10] and BZT-BCT with a composite formulations $(0.5\text{BaTi}_{0.8}\text{Zr}_{0.2}\text{O}_3-0.5\text{Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3)$ [11, 12, 13]. These different definitions referred to the same atomic composition.

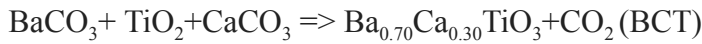
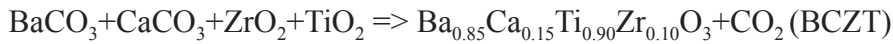
The compositions of BCZT have attracted the attention of researchers due to its high piezoelectric coefficients [9]. However, these coefficients are observed only in a small temperature range due to the phase transitions of the ceramic system. In this context, the excellent properties of these materials are sometimes attributed to phase coexistence [12]. However, the explanation of this phase coexistence is not attributed to a polyphasic material but related to an exotic crystallographic characteristic.

Therefore, this paper aims to put a light in the influence of the route processing on the lead-free ceramics properties, investigating the structures, microstructures, and dielectric

properties of BCZT and BZT-BCT. The method used was the preparation of $0.5\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ceramics by two routes, the direct route (BCZT) defined as a monophasic system, and the composite route (BZT-BCT) defined as a polyphasic system.

2. Experimental Procedure

The ceramics were prepared through the conventional solid-state reaction method, starting from high-purity precursor powders of BaCO_3 (Sigma-Aldrich, 99%), TiO_2 (Sigma-Aldrich, 99%), ZrO_2 (Sigma-Aldrich, 99%) and CaCO_3 (Vetec, 99%). These raw materials were mixed according to the formulations:



The raw materials were ball milled for 24 h and the mixtures were calcined at 1200 °C for 2 h and ball milled again for 24 h into fine powders, compacted into disk-shaped samples, and then sintered at 1380 °C for 3 h. This methodology was named here direct route.

For the composite route, the calcined powders of BZT and BCT were mixed in the proportion of 50% BCT and 50% BZT (BZT-BCT). These powder were ball milled for 24 h and also compacted into disk-shaped samples and then sintered at 1380 °C for 10 min, 3 h, and 24 h. The final density of each sintered specimen was determined by the Archimedes method, showing values of the BaTiO_3 's theoretical density of above 95% in all cases.

The differential scanning calorimetry (DSC) was performed using a NETZSCH STA 449. The experiments were performed in an atmosphere of synthetic air (O_2/N_2 - 1/4), with a heating rate of 10 °C/min using alumina crucible. The crystallographic structure was investigated using a Rigaku Ultima IV diffractometer (with monochromatic $\text{Cu K}\alpha$ radiation,

$\lambda = 1.5406 \text{ \AA}$). The microstructure developments were investigated with a scanning electron microscope (FEI - Inspect S50). The grain size of the ceramics was evaluated by the intercept method directly on the SEM images [14]. Electrical measurements, in terms of impedance ($Z^* = Z' + jZ''$), which was then convertible to complex permittivity as $\varepsilon^* = \varepsilon' + j\varepsilon''$, were carried out from room temperature to about $200 \text{ }^\circ\text{C}$ using a Solartron SI 1260 impedance/gain-phase analyzer in the frequency range of $f = 100 \text{ Hz}$ to 13 MHz . Electric contacts consisted of silver (Ag) paste previously applied on both parallel faces of the pellets and diffused at $550 \text{ }^\circ\text{C}$ for 30 min .

3. Results

Figure 1a and b show the DSC/TG curves obtained from the mixture of the reagents used in the synthesis of BZT and for the combination of the calcinated powders of BCT and BZT, respectively. The curve for the reagents (Figure 1a) exhibits a multi-step process that is completed at about $1300 \text{ }^\circ\text{C}$. Between $1030 \text{ }^\circ\text{C}$ and $1180 \text{ }^\circ\text{C}$ there is a loss of 14% in mass that is attributed to the BaCO_3 decomposition and the CO_2 oxidation. The endothermic peaks observed at $829 \text{ }^\circ\text{C}$ and $986 \text{ }^\circ\text{C}$ are linked with structural phases transitions of the BaCO_3 [15]. The appreciable exothermic reaction at $1200 \text{ }^\circ\text{C}$ was attributed to the BCZT formation. Contrary to the reagents trend, the results obtained from the calcined powders do not show a clear thermodynamic event that can be indicative of reaction between the compositions (Figure 1b). It is essential to point out that, for this experiment, no following thermal treatment was performed after the mixture of BCT and BZT powders. In particular, an endothermic event is observed around $1300 \text{ }^\circ\text{C}$. This event is here attributed to a fusion process and suggests the formation of a Ti^{4+} rich phase during the heating process.

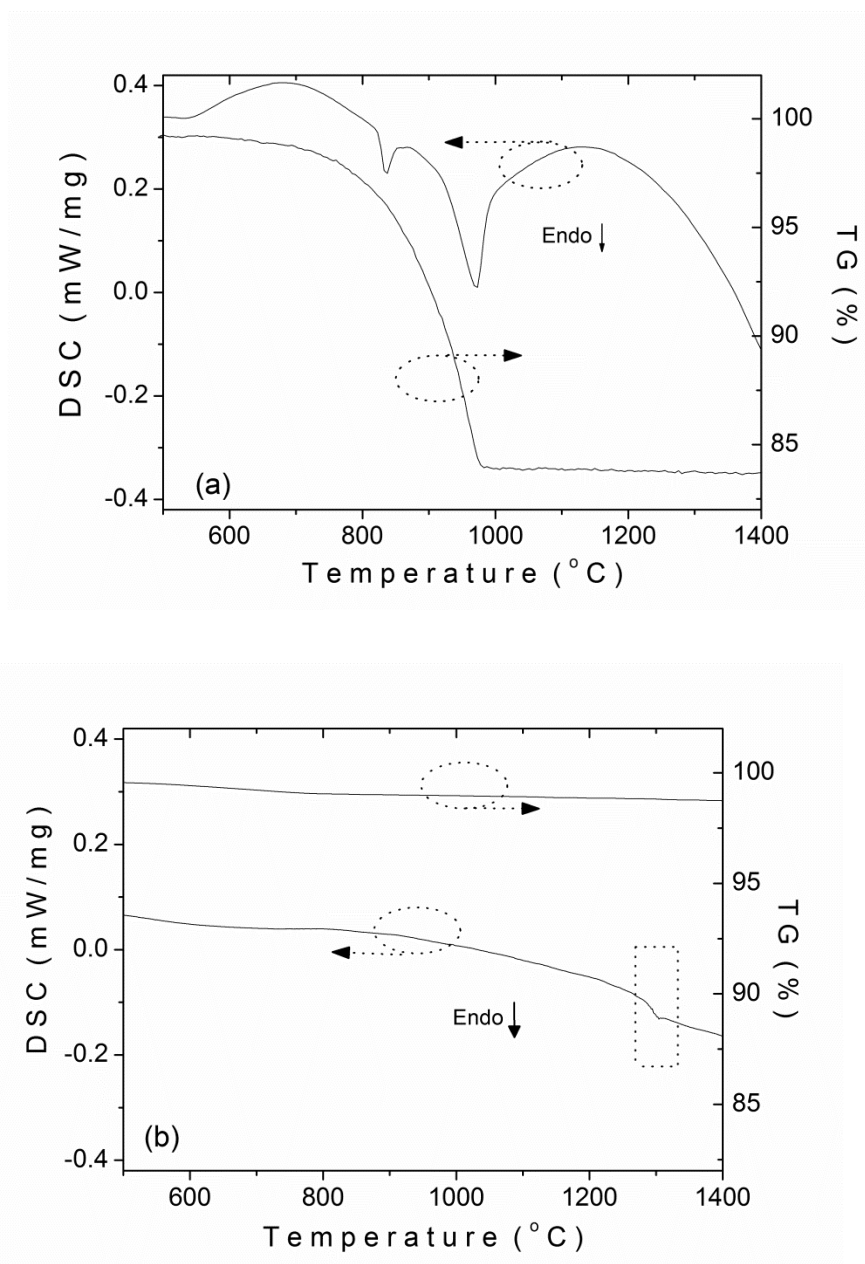


Figure 1 - Simultaneous DSC/TG curves: (a) mixture of the reagents to BZT formation and (b) mixture of the calcinated powders of BZT and BCT (50BCT-50BZT). The experiments were performed in an atmosphere of synthetic air ($O_2/N_2 = 1/4$), with a heating rate of 10 °C/min using alumina crucible.

Figure 2 shows the XRD patterns for BCT, BZT, and BCZT compounds after calcination (at 1200 °C for 2h). The figure also presented the XRD patterns for the BZT-BCT compounds after milling (not performed other calcination). The patterns were compared with files of the Inorganic Crystal Structure Database (ICSD). The patterns for BCT were indexed

with tetragonal symmetry (ICSD-71368) and only one phase was observed. The XRD patterns for BZT reflect the formation of two phases that were identified as majority phase BZT (ICSD-291454) and minority phase BaZrO_3 (BZ) (ICSD-974600). The presence of this phase at the calcined powder is indicative that the temperature should be higher. As expected, the BZT-BCT composition reflects the formation of two distinct phases that were identified to be isostructural with the tetragonal BZT and BCT.

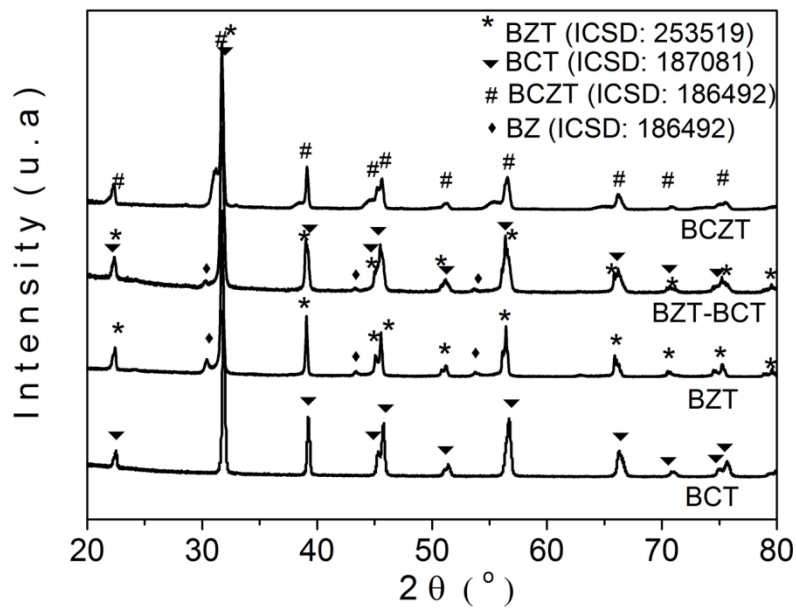


Figure 2 - XRD patterns of BZT, BCT, BCZT calcined at 1200 °C for 2h and the mixture of BZT-BCT

Figure 3 shows the XRD patterns, measured at room temperature, for BCZT and BZT-BCT samples after sintering. The samples were milled to perform the characterizations, and the XRD patterns were compared with the files of ICSD. The XRD result for BCZT indicates that the ceramic is completely crystallized into a single-phase perovskite and isostructural with the ICSD-186490. No traces of the second phase are observed for this composition. However, for BZT-BCT ceramic two phases were identified, being tetragonal (BCT) and orthorhombic (BZT), as shown in figure 3-b.

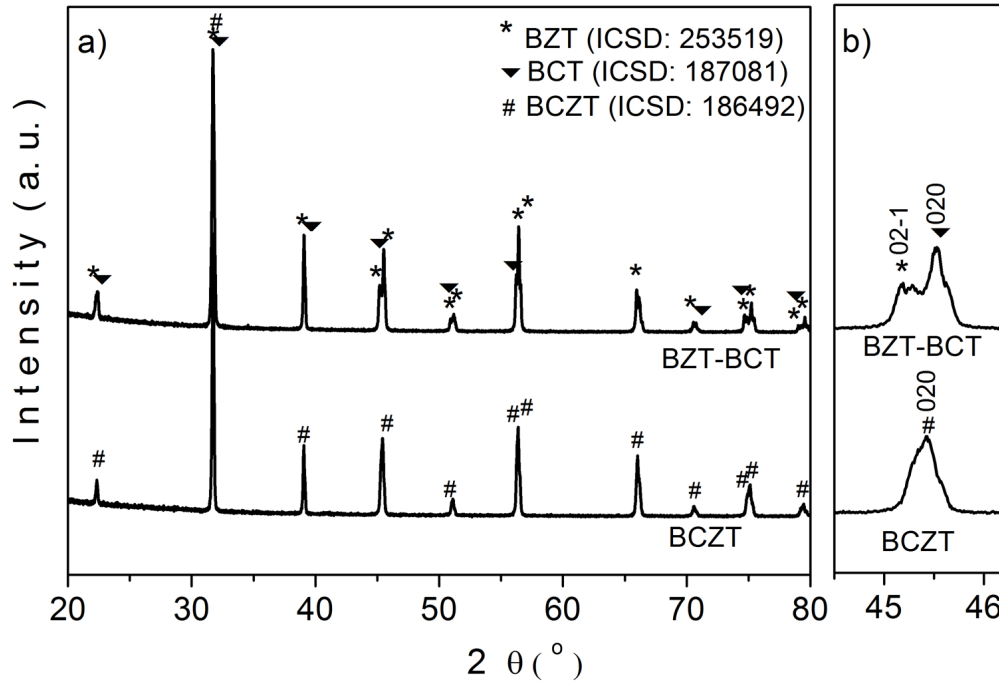


Figure 3 - XRD patterns of BCZT and BZT-BCT ceramics sintered at 1380 °C for 3h a) $2\theta = 20 - 80^\circ$ and b) $2\theta = 44.5 - 46.5^\circ$.

The microstructures from the BCZT and BZT-BCT samples are presented in Figures 4a and b. The grain size determined by the intercept method was $1.5 \pm 0.5 \mu\text{m}$ for BCZT ceramics. Interestingly here, the microstructure of the sintered BZT-BCT presents a homogeneous microstructure with a grain size of $9 \pm 4 \mu\text{m}$. These differences in grain growth suggest the formation of a liquid phase during the BZT-BCT sintering process. The liquid phase normally enhances mass transport between grains, promoting a grain growth process.

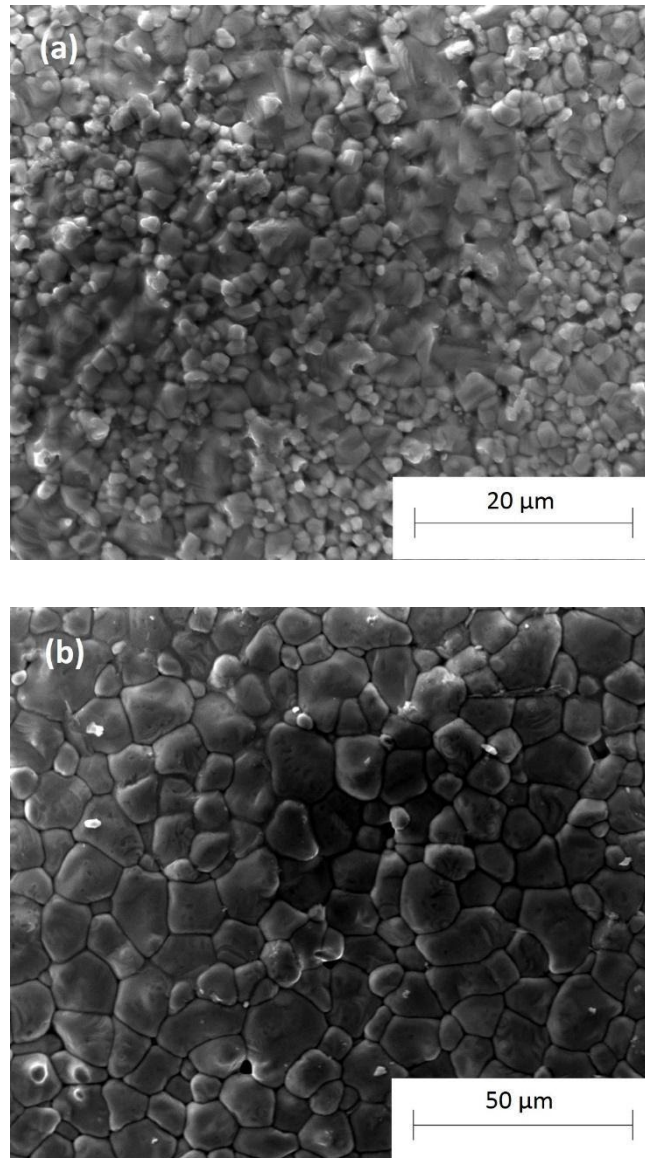


Fig. 4. SEM micrographs of the ceramics sintered at 1380 °C for 3h: a) BCZT and b) BZT-BCT

The temperature dependence of dielectric constants and $\tan(\delta)$ of BCZT and BZT-BCT ceramics, measured at frequencies of 100 Hz, 1 kHz, 10 kHz, and 100 kHz, are presented in Figures 5a and 5b, respectively. The ϵ' curve of BCZT ceramics, at least, exhibit two apparent anomalies that can be related to two phase transitions, the first associated to the Rhombohedral (R) – Tetragonal (T) phase transition, and the second with Tetragonal (T) – Cubic (C) phase transition [1]. This behavior is similar to that observed by Liu et al. [2]. In the figure, it is possible to note that the maximum point in R/T transitions cannot be defined

due to their diffusivity. However, an inflection point at $\sim 50\text{ }^{\circ}\text{C}$ was taken as a reference. The maximum of the anomaly associated with T-C transition was observed at $\sim 83\text{ }^{\circ}\text{C}$. The curve of ϵ'' shows anomalies at $\sim 46\text{ }^{\circ}\text{C}$ and $\sim 77\text{ }^{\circ}\text{C}$. As can be observed in Figure 5b, the composite methodology results in ceramics with different dielectric behavior, once that only one phase transition is observed at $\sim 93\text{ }^{\circ}\text{C}$. This study was conducted on the ceramics of the same composition. Thus it is reasonable to postulate that the observed differences are related to the methodology of synthesis and, therefore, with the trend of phase formation of BZT-BCT.

To complete data analyses are presented in Figure 5c the results of permittivity as a function of temperature for the sintered BZT-BCT ceramics at the same temperature ($1380\text{ }^{\circ}\text{C}$) and at different times of treatment: 10 min, 3 h, and 24 h. The objective was to check if the BZT-BCT methodology converges to BCZT behavior if the thermodynamic is provided. As can be observed in Figure 5c, when the time of sintering is increased from 10 min to 3 h, one increment on the dielectric values was observed. However, it was not observed significant modifications in the temperature of the phase transition. From 3 h to 24 h, no significant changes are observed, and the conclusion is that the possible phase development is already concluded with 3 h of thermal treatment and the BZT-BCT does not converge to BCZT methodology.

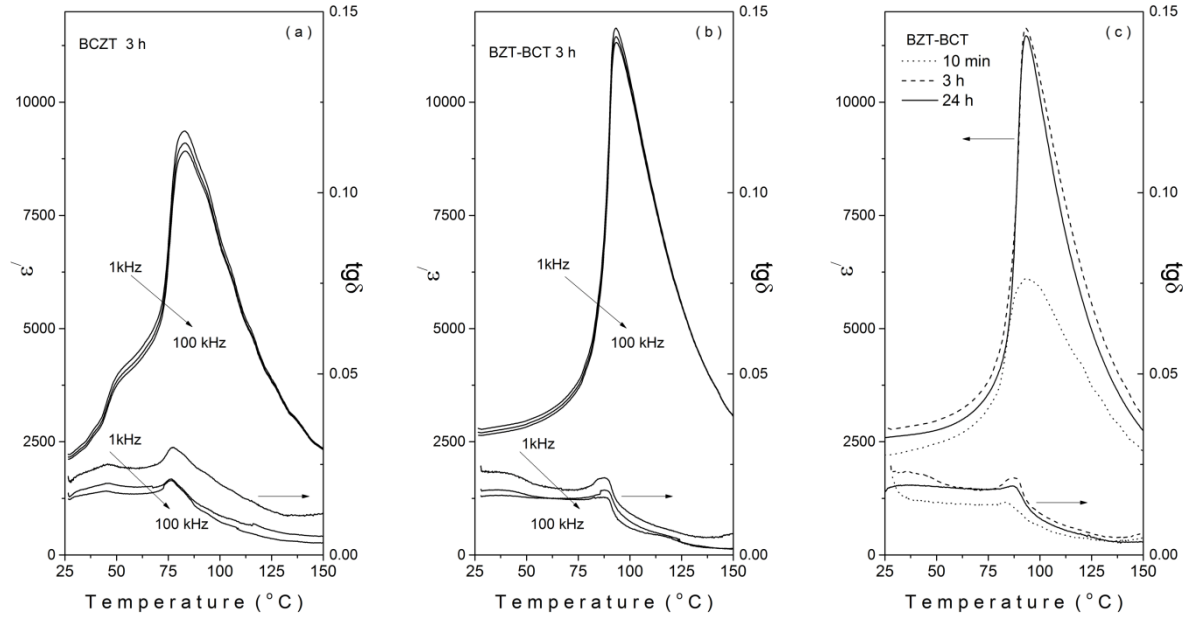


Fig. 5. Temperature dependence of dielectric constant of (a) BCZT and (b) BZT-BCT sintered at 1380 °C for 3 h at 1, 10, 100 kHz. (c) Temperature dependence of the dielectric constant of BZT-BCT sintered at 1380 °C for 10 min, 3 h, and 24 h.

4. Discussion

As can be observed in Figure 2, the milling processing of the mixture of BZT and BCT no offered energy for BCZT phase formation. Thus, the two phases are observed in the XRD of BZT-BCT. These powders, with the two phases, were studied by thermal analyses (Figure 1) and it is possible to conclude that no thermodynamic event can be observed between the BCT and BZT powders during the heating program. Thus, the single phase formation would be expected to occur from a slow diffusion process between the BCT and BZT elements. Besides, a possible fusion is observed in the DTA curves of BZT-BCT at ~1300 °C. This fusion can be related to a possible Ti^{4+} rich phase. A non-homogeneous diffusion of different ions could explain this phase formation during the thermal treatment of the composite. Interestingly here, this Ti^{4+} -rich phase can define the major grain size observed for BZT-BCT

when compared with BCZT ceramics (Figure 3). This increase in grain size in the composite route suggests an intergranular liquid phase that is formed during the materials' sintering process. This effect is often observed in BaTiO_3 -based ceramics treated at temperatures above about 1300 °C [16].

The XRD of the sintered ceramics (1380 °C/3h) reveals that the different routes of processing results in different crystalline structures, and thus, it is reasonable to expect different dielectric behavior. As observed in Figure 5a and b, while the dielectric profile of the BZT-BCT ceramics shows only one anomaly, the BCZT ceramics present two dielectric anomalies. The direct comparison reveals that the BCZT route results in ceramics with structure and behavior similar to that reported by Liu and Ren, 2009 [2]. From this phase diagram would be expected one single phase transition for compositions below the triple point. In other words, the composite route (BZT-BCT) could result in a different composition than that project. As can also be observed in Figure 5a and b, for both the ceramics, only one anomaly associated with the T-C phase transition is determined in temperature spectra. For BCZT the maximum of the curve is observed at ~83 °C while it occurs at ~93 °C for BZT-BCT, thus one shift of ~10 °C. The determination of the temperature of transition by the dielectric curve is largely used as an indicator of the phase and composition of ceramics. This being the case, the shift in the temperature of transition can also be interpreted as differences in compositions.

To advance this discussion, Figure 5c presents the dielectric behavior of the BZT-BCT sintered at different times. The question here is: Could the behavior of BZT-BCT shift to the BCZT if the thermodynamic conditions are provided? Interestingly, even after thermal treatment of 24 h, the samples of BZT-BCT presented the same overall behavior (only one observed phase transition) of the sample sintered for 3 hours. On the other hand, we observed an increase in permittivity values when the time of sintering is increased from 10 min for 3 h.

Consequently, there is some phase development or microstructural changes in this interval of time. However, after 3 h of thermal treatment, no significant alterations were observed. Considering that this study was conducted on ceramics of the same compositions, it is reasonable to postulate that the composite method results in ceramics of different crystalline structures. Thus, the complex crystalline structure of this class of materials is a consequence of intrinsic characteristics. However, it is also dependent on extrinsic characteristics and the methodology of the synthesis.

5. Conclusions

Based on all performed characterizations, we can conclude that the trend of phase development is dependent on the methodology and the composite route (BZT-BCT) does not converge to the direct route (BCZT) being observed by the coexistence of crystalline phases for this methodology. This dynamic results in larger grain size and, principally, in different dielectric behavior.

6. Acknowledgment

This work was supported by CNPq (Grant# 2014/456879-5) and FAPESP (Grant# 2011/08497-6), two Brazilian research- funding agencies.

7. References

- [1] M. Acosta, Strain Mechanisms in Lead-Free Ferroelectrics for Actuators, 2015. doi:10.1007/978-3-319-27756-1.
- [2] W. Liu, X. Ren, Large piezoelectric effect in Pb-free ceramics, Phys. Rev. Lett. 103 (2009) 1–4. doi:10.1103/PhysRevLett.103.257602.
- [3] Y. Zhang, J. Glaum, C. Groh, M.C. Ehmke, J.E. Blendell, K.J. Bowman, M.J. Hoffman, Correlation Between Piezoelectric Properties and Phase Coexistence in (Ba,Ca)(Ti,Zr)O₃ Ceramics, J Am Ceram Soc. 2891 (2014) 2885–2891. doi:10.1111/jace.13047.
- [4] J. Rödel, K.G. Webber, R. Dittmer, W. Jo, M. Kimura, D. Damjanovic, Transferring lead-free piezoelectric ceramics into application, J. Eur. Ceram. Soc. 35 (2015) 1659–1681. doi:10.1016/j.jeurceramsoc.2014.12.013.
- [5] D.S. Keeble, F. Benabdallah, P. a. Thomas, M. Maglione, J. Kreisel, Revised structural phase diagram of (Ba_{0.7}Ca_{0.3}TiO₃)-(BaZr_{0.2}Ti_{0.8}O₃), Appl. Phys. Lett. 102 (2013) 092903. doi:10.1063/1.4793400.
- [6] Y. Tian, L. Wei, X. Chao, Z. Liu, Z. Yang, Phase transition behavior and large piezoelectricity near the morphotropic phase boundary of lead-free (Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O₃ ceramics, J. Am. Ceram. Soc. 96 (2013) 496–502. doi:10.1111/jace.12049.
- [7] D. Damjanovic, A. Biancoli, L. Batooli, A. Vahabzadeh, J. Trodahl, Elastic, dielectric, and piezoelectric anomalies and Raman spectroscopy of 0.5Ba(Ti_{0.8}Zr_{0.2})O₃-0.5(Ba_{0.7}Ca_{0.3})TiO₃, Appl. Phys. Lett. 100 (2012) 7–11. doi:10.1063/1.4714703.
- [8] J. Hao, J. , Bai, W. , Li, W. and Zhai, Correlation Between the Microstructure and Electrical Properties in High-Performance (Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O₃ Lead-Free Piezoelectric Ceramics, J Am Ceram Soc. 95 (2012) 1998–2006. doi:10.1111/j.1551-2916.2012.05146.x.
- [9] Z. Long, P. and Yi, Fabrication and properties of (Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1})O₃ ceramics and their multilayer piezoelectric actuators, Int J Appl Ceram Technol. 14 (2017) 16–21. doi:10.1111/ijac.12611.

- [10] D.A. Ochoa, A. Reyes-montero, F. Su, L. Pardo, J.E. García, M.E. Villafuerte-castrej, Assessment of the functional properties stability in $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ piezoceramics: Huge dielectric and piezoelectric nonlinearity, *J. Alloys Compd.* 774 (2019) 410–417. doi:10.1016/j.jallcom.2018.10.060.
- [11] L. Zhang, M. Zhang, L. Wang, C. Zhou, Z. Zhang, Y. Yao, L. Zhang, D. Xue, X. Lou, X. Ren, Phase transitions and the piezoelectricity around morphotropic phase boundary in $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3\text{-x}(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ lead-free solid solution, *Appl. Phys. Lett.* 105 (2014) 162908. doi:10.1063/1.4899125.
- [12] M. Acosta, N. Novak, W. Jo, J. Rödel, Relationship between electromechanical properties and phase diagram in the $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3\text{-x}(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ lead-free piezoceramic, *Acta Mater.* 80 (2014) 48–55. doi:10.1016/j.actamat.2014.07.058.
- [13] X. Liu, M. Zhu, Z. Chen, B. Fang, J. Ding, X. Zhao, H. Xu, Structure and electrical properties of Li-doped $\text{BaTiO}_3\text{-CaTiO}_3\text{-BaZrO}_3$ lead-free ceramics prepared by citrate method, *J. Alloys Compd.* 613 (2014) 219–225. doi:10.1016/j.jallcom.2014.06.046.
- [14] American Society for Testing and Materials – ASTM.E1382. Standard test methods for determining average grain size using semiautomatic and automatic image analysis. v. 03.01. Annual Book of ASTM Standards, ASTM; 1991., n.d.
- [15] E. Antonelli, M.I.B. Bernardi, A.C. Hernandez, Pós nanométricos de BaZrO_3 (BaZrO_3 nanometric powders): preparação e caracterização de cerâmicas, *Cerâmica.* 51 (2005) 430–435. doi:10.1590/S0366-69132005000400019.
- [16] E. Antonelli, M. Letonturier, J.C. M'Peko, a. C. Hernandez, Microstructural, structural and dielectric properties of Er^{3+} -modified $\text{BaTi}_{0.85}\text{Zr}_{0.15}\text{O}_3$ ceramics, *J. Eur. Ceram. Soc.* 29 (2009) 1449–1455. doi:10.1016/j.jeurceramsoc.2008.09.009.

Informações para SciELO Preprints:

Contribuições dos autores no manuscrito:

Todos os autores contribuíram igualmente para o manuscrito apresentado.

Declaração de conflito de interesses no manuscrito

Todos os autores declaram que não há conflito de interesses.

ORCID de todos os autores:

André L. Bonaventura (ORCID: 0000-0001-9255-4737)

<https://orcid.org/0000-0001-9255-4737>

Rangel G. Aredes (ORCID: 0000-0003-0459-1023)

<https://orcid.org/0000-0003-0459-1023>

Renato Boschilia (ORCID: 0000-0002-2737-9511)

<https://orcid.org/0000-0002-2737-9511>

Eduardo Antonelli (ORCID: 0000-0001-5029-1115)

<https://orcid.org/0000-0001-5029-1115>