Influence of $\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ on the structure, dielectric and ferroelectric properties of $(\text{Ba,Ca})(\text{Zr,Ti})\text{O}_3$ ceramics

DOI:

[10.1016/j.jeurceramsoc.2017.12.063](https://doi.org/10.1016/j.jeurceramsoc.2017.12.063)

Document Version

Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)

Citation for published version (APA):

Al-Aaraji, M., & Hall, D. (2018). Influence of $\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ on the structure, dielectric and ferroelectric properties of $(\text{Ba,Ca})(\text{Zr,Ti})\text{O}_3$ ceramics. *Journal of the European Ceramic Society*.
<https://doi.org/10.1016/j.jeurceramsoc.2017.12.063>

Published in:

Journal of the European Ceramic Society

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Accepted Manuscript

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PII: S0955-2219(17)30872-5
DOI: <https://doi.org/10.1016/j.jeurceramsoc.2017.12.063>
Reference: JECS 11668

To appear in: *Journal of the European Ceramic Society*

Received date: 14-11-2017
Revised date: 27-12-2017
Accepted date: 31-12-2017

Please cite this article as: Al-Aaraji MN, Hall DA, Influence of $K_{0.5}Bi_{0.5}TiO_3$ on the structure, dielectric and ferroelectric properties of $(Ba,Ca)(Zr,Ti)O_3$ ceramics, *Journal of The European Ceramic Society* (2010), <https://doi.org/10.1016/j.jeurceramsoc.2017.12.063>

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Influence of $\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ on the structure, dielectric and ferroelectric properties of $(\text{Ba,Ca})(\text{Zr,Ti})\text{O}_3$ ceramics

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Abstract.

A new lead-free ferroelectric solid solution between $(\text{Ba,Ca})(\text{Zr,Ti})\text{O}_3$ (BCZT) and $\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (KBT) has been systematically investigated in terms of its phase transformations, microstructure, dielectric and ferroelectric properties. The incorporation of KBT into BCZT was found to enhance the sintering behavior, although secondary phases of $\text{K}_4\text{Ti}_3\text{O}_8$ and $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ were detected at high KBT contents. Chemical heterogeneity was also observed in the form of core-shell grain structures comprising tetragonal ferroelectric BCZT-rich cores with pseudo-cubic relaxor ferroelectric KBT-rich shell regions. Temperature-dependent dielectric property measurements revealed that the BCZT-KBT ceramics exhibited both normal and relaxor ferroelectric behaviour simultaneously, associated directly with the core-shell structure. Ferroelectric hysteresis measurements indicated that the remanent polarisation and coercive field were strongly dependent on KBT content. In common with other lead-free relaxor ferroelectrics, increasing temperature led to the formation of constricted polarisation-electric field hysteresis loops, indicating the occurrence of a reversible electric field-induced nanopolar to long-range ordered ferroelectric state.

Keywords: Lead-free ceramics; Ferroelectric; Core-Shell; Relaxor; Dielectric

1. Introduction

Lead zirconate titanate, abbreviated $\text{Pb}(\text{Zr, Ti})\text{O}_3$ or PZT, still represents one of the most important categories of ferroelectrics, despite its long history of use over more than a half century. It is widely used in applications such as electro-mechanical actuators, sensors, ultrasonic transducers and electro-optic devices [1, 2]. PZT ceramics possess outstanding ferroelectric, piezoelectric and pyroelectric properties. However, the high content of lead, which is well-known for its toxicity, has created a strong desire in recent years to remove lead oxide as a component of piezoelectric ceramic products [3-6]. Therefore, it is necessary to develop new lead-free piezoelectric ceramics in order to substitute PZT in certain applications[7, 8]. The

main candidate ceramic materials for this purpose are based on $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (KNN), BaTiO_3 (BT), and $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BNT). Many investigations have been conducted on the synthesis and properties of these materials as pure compounds, modified by minor dopants, or in the form of solid solutions with other ABO_3 perovskites [4, 9].

Barium titanate-based solid solutions modified with calcium and zirconium oxides, abbreviated as BCZT have attracted attention in recent years due to their promising piezoelectric properties. Therefore, they represent one of the most promising candidates for lead-free piezoceramic materials [5, 10, 11]. It was reported by Srinivas that the BCZT, $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$, ceramic exhibits a piezoelectric charge coefficient, d_{33} , in the region of 600 pC/N at room temperature, albeit with a low Curie temperature of just 85°C. It was prepared by the conventional solid state reaction method using a sintering temperature of 1500°C [12]. The high piezoelectric coefficient (d_{33}) of this composition is attributed to the coexistence of rhombohedral and tetragonal phases. It is reported that the high piezoelectric activity in such materials is found in the region of the morphotropic phase boundary (MPB) and is associated with enhanced ferroelectric domain wall mobility [13, 14].

The significance of the R-T phase transformation in the MPB region was also recognised by Tian, who investigated the effects of Ca content on the phase transition and electrical properties of the system $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ [15]. Keeble identified an intermediate orthorhombic phase for the same composition, which was found to occur over narrow ranges of composition and temperature [16]. The high piezoelectric response of BCZT ceramics was reported by Sutapun, who investigated the phase boundary between rhombohedral and tetragonal phases for the solid solution $0.87\text{BaTiO}_3-(0.13-x)\text{BaZrO}_3-x\text{CaTiO}_3$ at $x = 0.06$ [14].

On the other hand, it should be recognised that the functional properties of BCZT ceramics are affected significantly by temperature-instability, due to the occurrence of the polymorphic phase transformations, and a relatively low Curie temperature. The need for high sintering temperatures for densification of BCZT is also a serious concern, particularly when considering the compatibility with typical electrode and substrate materials used in thick film fabrication.

It has been proposed that the incorporation of bismuth-based perovskite compounds, such as BiFeO_3 (BF) and $\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (BMT) into BCZT could both reduce the temperature-stability of properties and enhance the densification behavior during sintering. Bai observed that incorporation of BMT into BCZT increases the Curie temperature (T_c) to a maximum value of 218°C for the composition 0.4BCZT-0.6BMT [17]. Similarly, Yi investigated $(1-x)\text{BF}-(x)\text{BCZT}$ solid solutions and reported that the crystal structure transformed from rhombohedral to pseudo-cubic with increasing x . The morphotropic phase boundary was found to be located in the composition range $0.2 \leq x \leq 0.30$. This composition range was also characterized by relatively large grain sizes and Curie temperatures between 380 and 450 °C [18].

Recently, Cai [19] investigated the influence of the tetragonally-distorted perovskite ferroelectric $(\text{K}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ (KBT) on the structural and electrical properties of

$(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Ti}_{0.93}\text{Zr}_{0.07})\text{O}_3$ (BCZT), for KBT contents up to 8 mol%. The ceramics were prepared by conventional solid state reaction method with a sintering temperature of 1280°C. It was reported that the composition 0.96BCZT-0.04KBT exhibits promising ferroelectric and piezoelectric properties, but there was no significant change in the Curie temperature. Yuan also found that KBT was an effective additive to enhance the sintering behaviour of undoped barium titanate ceramics [20].

There are currently no reports on the properties of BCZT-KBT solid solutions for KBT contents greater than 8 mol%, although it is anticipated that useful functional properties could be obtained by tailoring the ratio of these two ferroelectric perovskites. Intermediate compositions in the BCZT-KBT system could potentially combine the high Curie temperature of KBT (~380°C) with the high piezoelectric activity of BCZT, whilst avoiding drawbacks such as problems in the processing of KBT ceramics and the low T_C of BCZT.

The aim of this investigation was to develop new lead-free piezoelectric materials with high performance and high Curie temperature from $(1-y)\text{BCZT}_x-(y)\text{KBT}$ solid solutions. Two BCZT compositions were investigated in the ternary system of $0.87\text{BaTiO}_3-(0.13-x)\text{BaZrO}_3-x\text{CaTiO}_3$ (abbreviated BCZT_x) having two different Ca/Zr contents ($x=0.02, 0.06$), prepared by solid state reaction and conventional sintering. The first composition ($x=0.02, \text{Ca/Zr}=0.18$) was located in the orthorhombic region whereas the second one ($x=0.06, \text{Ca/Zr}=0.86$) was near to the orthorhombic (O)-tetragonal (T) phase boundary. Both of these BCZT ceramics were prepared in the unmodified form and with additions of KBT up to 65 mol%. The evolution from normal ferroelectric to relaxor behaviour with increasing KBT content is discussed in the context of the observed core-shell type microstructures.

2. Experimental procedures

Two BCZT solid solutions, corresponding to the formula $0.87\text{BaTiO}_3-(0.13-x)\text{BaZrO}_3-x\text{CaTiO}_3$ (abbreviated BCZT_x) with $x=0.02$ and 0.06 , were prepared in the form of polycrystalline ceramics using the solid state reaction method. Barium carbonate (BaCO_3), calcium carbonate (CaCO_3), titanium dioxide (TiO_2), and zirconium oxide (ZrO_2) having > 99% purity were used as raw materials. Starting powders were weighed according to the chemical formula of the selected compositions. They were vibro-ball milled with propan-2-ol for 24 h using zirconia balls as milling media. After drying, the mixed powders were calcined at 1300°C for 4 h in a covered alumina crucible.

In parallel, a pure $\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ powder was prepared using potassium carbonate (K_2CO_3), bismuth oxide (Bi_2O_3) and titanium dioxide (TiO_2) having > 99% purity as raw materials. After weighing, ball-milling and drying of powders, the mixture was calcined at 950 °C for 4 h.

Thereafter, the calcined powders of BCZT in both compositions were mixed separately with different contents of KBT according to the formula $(1-y)\text{BCZT}_x-(y)\text{KBT}$, with $y=0, 0.1, 0.35, 0.50, 0.65$ and 1.00 . Then, the mixed powders were ball-milled for 4 h. The powder mixtures were dried and mixed with 2 wt% polyethylene

glycol (PEG) as a lubricant and binder. Afterwards, the mixed calcined powders including binder were uniaxially pressed in a cylindrical steel die into pellets, 10 mm diameter with around 1.5 mm thickness, under a pressure of 35 MPa for 40 s. The pellets were embedded in calcined powders from the same compositions and heat treated at different temperatures in the range between 1125°C and 1500°C for 3 to 4 h, depending on KBT content, to produce the sintered ceramics. This experimental route follows procedures similar to those employed by Yuan [20].

The bulk density of the sintered samples was measured by the Archimedes method using water as the immersion medium. Phase analysis of sintered pellets was achieved by x-ray diffraction (XRD) using a Philips PANalytical X'Pert-Pro with $\text{CuK}\alpha$ radiation having a wavelength of 1.54060 Å. The detection range was 10 to 80 °2 θ with a step size of 0.0167° at room temperature. The surfaces of sintered samples were ground using 1200-grade SiC papers. Then, the samples were annealed at 500 °C for 30 min to eliminate any residual stress that could be induced during preparation. Microstructures of polished and carbon-coated surfaces of sintered samples were characterised by scanning electron microscopy (Philips XL30 FEG-SEM). For electrical measurements, the surfaces of the sintered samples were ground using a similar method to that employed for the XRD samples, to obtain parallel and smooth faces. Then, they were coated with silver paste (C2000107P3, Gwent Electronic Materials) as electrodes. Afterwards, the painted samples were dried in an oven at around 85°C for 20 min for each face and then heat treated at 550°C for 30 min to densify the electrodes and ensure good contact with the ceramic surfaces.

The *low-field* dielectric properties of the sintered samples were studied as functions of both temperature and frequency using an automated dielectric measurement system. The computer-controlled dielectric measurement system consists of an LCR-meter (Hewlett-Packard Precision LCR Meter, HP 4284A) connected to the electroded sample by pure silver probes. Samples were heated in a furnace with a heating rate of 2 °C min⁻¹. The parallel capacitance (C_p) and the dielectric loss tangent ($\tan \delta$) were determined over the temperature range from 25 to 350 °C, using measurement frequencies from 100 Hz to 100 kHz. *High-field* polarization-electric field (P-E) ferroelectric hysteresis measurements were made using a system based on a HP33120A function generator (Hewlett-Packard, Palo Alto, CA) in conjunction with an HVA1B high voltage amplifier (Chevin Research, Otley, UK)[21]. A burst-mode waveform comprising 4 sinusoidal cycles was employed, with a maximum electric field level up to 6 MV m⁻¹. The samples were immersed in silicone oil during these measurements to avoid electrical arcing.

3. Results and discussion.

3.1 Density

The temperatures employed for sintering each composition were determined empirically based on the results of bulk density measurements, as shown in Table 1. The theoretical densities were calculated on the basis of the nominal chemical

compositions and the lattice parameters determined from full pattern refinement of the XRD patterns using *Topas* software version 5.0 [22]. Thereafter, the relative densities were calculated, yielding values greater than 92%. It is evident that the required sintering temperatures decreased with increasing KBT content and were greatly reduced (by almost 400 °C), in comparison with pure BCZT ceramics, for the composition with 65% KBT. It has been reported by many researchers that the sinterability of BT-based ceramics at low temperatures can be effectively improved by using single component oxides or other perovskite compounds having low melting points as sintering aids. The enhanced densification behaviour is usually attributed to a liquid phase sintering mechanism.

Hayati [23] investigated the effect of bismuth oxide (melting point ~825°C) on the sintering temperature of $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Zr}_{0.1}\text{Ti}_{0.9}\text{O}_3$ (BCZT) ceramics. The results showed that the presence of 0.1 mol% Bi_2O_3 can allow the sintering temperature to be reduced from 1500°C to 1350°C. Regarding the use of perovskite compounds for this purpose, it was reported that the sintering temperature of BT ceramics modified with KBT can be decreased to 1280°C for 10 mol% KBT [20] and to 1125°C for 65 mol% KBT [24]. In another study, it was found the use of 4 mol% KBT enabled the sintering temperature of $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Ti}_{0.93}\text{Zr}_{0.07})\text{O}_3$ to be reduced from 1500°C to 1280°C [19]. Similarly, several reports have shown that other Bi-based perovskite compounds can effectively enhance the densification of BT-based ceramics. For example, BiAlO_3 [25] and $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ [26] were employed with $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Zr}_{0.1}\text{Ti}_{0.9}\text{O}_3$ (BCZT), while BiScO_3 was used with BT ceramics [27]. Therefore, we suppose that the enhancement of densification behaviour in BCZT-KBT solid solutions can be explained in terms of a liquid phase sintering mechanism due to the presence of the low melting point oxides Bi_2O_3 and K_2O .

Table 1 Densities and sintering temperatures for $(1-y)\text{BCZT}x-(y)\text{KBT}$ ceramics with $x=(0.02, 0.06)$ and $y=(0.00-0.65)$.

Composition (y)	Sintering Temperature °C	x=0.02			x=0.06		
		Absolute density (g/cm ³)	Theoretical density (g/cm ³)	Relative density %	Absolute density (g/cm ³)	Theoretical density (g/cm ³)	Relative density %
0.00	1500	5.83	6.02	97	5.76	5.92	97
0.10	1280	5.71	6.00	95	5.48	5.91	93
0.35	1200	5.69	5.95	96	5.65	5.93	95
0.50	1200	5.5	5.93	93	5.43	5.88	92
0.65	1125	5.52	5.95	93	5.58	6.04	92

3.2 Crystal structure

The XRD patterns of the BCZT-KBT ceramics at room temperature are shown in Figure 1. The results indicate the diffusion of KBT into the lattice of $0.87\text{BaTiO}_3-(0.13-x)\text{BaZrO}_3-x\text{CaTiO}_3$, since the diffraction peaks shifted consistently towards higher angles, indicating a gradual reduction in lattice parameters, with increasing KBT content. A second phase of $\text{K}_4\text{Ti}_3\text{O}_8$ (JCPDS No. 00-041-0167) was identified for compositions with $y \geq 0.35$, while an additional second phase of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$

(JCPDS No. 00-035-0757) became apparent for $y=0.65$. The results of full-pattern refinement for four representative BCZT-KBT compositions are illustrated in the lower part of Figure 1, with emphasis on the pseudo-cubic $\{111\}_p$ and $\{200\}_p$ reflections. A summary of the phase fractions and lattice parameters determined from this analysis is provided in the Tables S1 and S2.

For $x=0.02$, the pure BCZT was found to possess a predominantly orthorhombic (O) structure, as expected. However, an improved fit could be obtained by introducing a minor rhombohedral (R) phase, with a phase fraction of approximately 12 %, as shown in Figure 1(a). With increasing KBT content, the $\{200\}_p$ peak profile began to show evidence of characteristic splitting, indicating the emergence of the tetragonal (T) phase with a c/a ratio of 1.0146 at $y = 0.65$. In this case, an adequate fit to the overlapping (002) and (200) peaks could be obtained only by the introduction of a minor cubic phase, with a phase fraction of 39 %.

A predominantly orthorhombic structure was also identified for pure BCZT with $x = 0.06$, as shown in Figure 1(b). A minor tetragonal phase, having a phase fraction of approximately 18 %, was also introduced to yield the best fit to the data. Increasing KBT content had a similar effect on the structure for this BCZT composition with a c/a ratio of 1.0164 at $y = 0.65$, although with a lower cubic phase fraction of 30 %.

In view of the microstructural observations and analysis of the ϵ_r - T relationships for the BCZT-KBT ceramics, described below in sections 3.3 and 3.4 respectively, we attribute the centrosymmetric cubic structure to a KBT-rich relaxor ferroelectric (shell) phase and the non-centrosymmetric tetragonal structure to a BCZT-rich normal ferroelectric (core) phase. The emergence of the relaxor ferroelectric pseudo-cubic phase in the KBT-modified BCZT ceramics can be understood in terms of a disruption in ferroelectric ordering due to the presence of aliovalent A-site cations (Bi^{3+} and K^+). Similar effects have been reported previously in many other related solid solutions. For example, it was found that the incorporation of approximately 10 mol% of either $\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ or $\text{Bi}(\text{Zn}_{0.5}\text{Ti}_{0.5})\text{O}_3$ to $(\text{Ba}_{0.8}\text{Ca}_{0.2})\text{TiO}_3$ induced a structural transformation from tetragonal to pseudo-cubic [28, 29]. The relaxor ferroelectric characteristics were reported to become more pronounced with increasing additive levels, similar to the observations made in the present study (section 3.4).

It is evident from the XRD results that increasing KBT content in both BCZT compositions caused a systematic shift of the diffraction peaks to higher 2θ values, indicating a general contraction of the crystal lattice. This trend is also apparent in the results obtained for lattice parameters and unit cell volume, summarized in Table S1. This contraction is consistent with the incorporation of smaller A-site cations, with Ba^{2+} (0.135 nm)/ Ca^{2+} (0.099 nm) being replaced by Bi^{3+} (0.096nm) and K^+ (0.135 nm) [14, 18, 30].

the processing procedures, which involved separate calcination of the BCZT and KBT powders prior to mixing and sintering. The presence of the $K_4Ti_3O_8$ second phase was clearly apparent as darker regions (in BSE imaging mode) and is attributed to the evaporation of bismuth during the sintering process [24, 32, 33].

Further increase of the KBT content to 65% in both BCZT compositions caused the appearance of another second phase, $BaBi_4Ti_4O_{15}$, which was evident as blocky white crystals in the microstructure. It was suggested by Yang that the appearance of this phase could be due to the reaction of residual Bi_2O_3 , TiO_2 , and $BaCO_3$ [24], which might be associated with the use of a relatively short time of mixing the BCZT and KBT powders (4 hours in the present case). The chemical compositions of the BCZT matrix and secondary phases were confirmed by EDX, as shown in Figure S1.

Figure 2 Backscattered electron (BSE) images of polished surface of $(1-y)BCZTx-(y)KBT$ ceramics with $y=0.0, 0.35$ and 0.65 , (a)-(c) for $x=0.02$; (d)-(f) for $x=0.06$. The symbols 'X', 'Y' and 'Z' denote BCZT-KBT, $K_4Ti_3O_8$ and $BaBi_4Ti_4O_{15}$ phases respectively.

Figure 3 EDX analyses obtained from different regions of a grain with core-shell structure. Chemical composition is 0.65 BCZTx- 0.35 KBT ceramic, with $x = 0.06$.

3.4 Dielectric properties

The temperature-dependent dielectric properties of the BCZT-KBT ceramics are shown in Figure 4. Two transitions can be observed in the ϵ_r -T results for pure BCZT at $x=0.02$, presented in Figure 4(a). The first of these is associated with the low temperature shoulder on the main peak and corresponds to the phase transformation from orthorhombic to tetragonal (T_{O-T}) at approximately 62 °C while the second is the main tetragonal to cubic transformation at the Curie point (T_C) of approximately 75°C. These transitions are also apparent for pure BCZT with $x=0.06$, as illustrated in Figure 4(e). The phase transition temperatures of T_{O-T} and T_C are approximately 45 °C and 95 °C, respectively. These results are generally in agreement with those of Sutapun, although the interpretation of phase identities differs [14]. Note that the temperatures of the phase transformations for the pure BCZT ceramics are essentially independent of the frequency of measurement, which is a characteristic of conventional long-range ordered ferroelectrics. The shifting of the O-T transformation for pure BCZT with $x=0.02$ to higher temperature, in comparison with the case for $x=0.06$, is related to the higher zirconium content, as explained by Li [30, 34]. The reduction in T_C is also due primarily to the presence of zirconium [34, 35], since it is well-known that calcium substitution does not have a strong effect on the Curie temperature of barium titanate-based dielectrics [36].

The addition of KBT to BCZT led to profound changes in dielectric behaviour, with the ϵ_r -T curves evolving from conventional frequency-independent ferroelectric behaviour for pure BCZT to a classic frequency-dispersive relaxor ferroelectric behaviour for BCZT-KBT with $y=0.65$, as shown in Figure 4(d) and (h). The temperatures associated with the maximum permittivity in the frequency-dependent region, T_m , showed significant positive shifts with increasing KBT content. These effects can be attributed generally to the substitution of divalent Ba^{2+} and Ca^{2+} ions on the A-site of the perovskite lattice by aliovalent but self-compensating Bi^{3+} and K^+ ions. These substitutions disrupt the long-range ferroelectric ordering and lead instead to a disordered nanopolar domain structure [20, 37] .

In the intermediate stage with $y=0.35$ for example, Figure 4(c) and (g), both characteristics were apparent; the frequency-independent Curie point occurred at a

temperature of approximately 110°C, while a frequency-dependent shoulder was also apparent at temperatures around 50°C. Based on the microstructural features described above, specifically the observation of ferroelectric BCZT-rich cores surrounded by featureless KBT-rich shell regions, we attribute the frequency-independent peak and frequency-dependent shoulder in the ϵ_r -T curves to the separate contributions from the normal ferroelectric core and relaxor ferroelectric shell regions respectively. Similar features were discussed previously with respect to BaTiO₃-BiScO₃ [27] and Na_{0.5}K_{0.5}NbO₃-LiTaO₃-BiScO₃ solid solutions [38]. Dielectric characteristics with this form are also well-known in other lead-free ferroelectrics such as Na_{0.5}Bi_{0.5}TiO₃ (NBT) ceramics, which do not necessarily show the tendency for micro-scale chemical heterogeneity reported in the present results[39]. Therefore, the mixed normal and relaxor ferroelectric behaviour, which occurs simultaneously in core-shell structured BCZT-KBT ceramics, could help to elucidate the origin of these dielectric characteristics in NBT and related systems[37].

Figure 4 Temperature dependence of dielectric permittivity and loss for (1-y) BCZTx-(y)KBT ceramics with y=0.0, 0.10, 0.35 and 0.65, for (a)-(d) x=0.02 and (e)-(h) x=0.06.

3.5 Ferroelectric properties

The influence of KBT on the ferroelectric behaviour of BCZT ceramics is illustrated by the P-E hysteresis loops presented in Figure 5 and the derived parameters

(remanent and saturation polarisation, P_r and P_s , and coercive field, E_c) shown in

Figure 6. The unmodified BCZT ceramics exhibited saturated P-E loops having well-defined switching points and low coercive fields in the region of 0.3 to 0.4 MV m⁻¹. The addition of KBT led to the formation of slim and inclined P-E loops, typical of those reported in relaxor ferroelectrics. However, much wider loops with high remanent polarisation and coercive field were evident for the highest KBT content at $y = 0.65$.

Figure 5. P-E hysteresis loops for $(1-y)\text{BCZT}_x\text{-(}y\text{)KBT}$ ceramics at room temperature, for (a) $x=0.02$, (b) $x=0.06$.

For both BCZT compositions, P_s reduced by approximately 50% with increasing KBT content, yielding a value around $10 \mu\text{C.m}^{-2}$ for $y = 0.5$, followed by a recovery to the initial level around $20 \mu\text{C.m}^{-2}$ for $y = 0.65$, as shown in Figure 6. The P_r values followed a similar trend, but with enhanced variations. On the other hand, the coercive field remained relatively low (below 0.5 MV m^{-1}) for low KBT contents, but increased dramatically to values in the range 2 to 3 MV m^{-1} as y increased from 0.50 to 0.65. The P_s and P_r values exhibited similar step changes over the same compositional range, indicating improvements in the stability of the ferroelectric ordering.

These results are consistent with previous reports for the end members of the solid solution, BCZT and KBT, both of which exhibit a well-saturated ferroelectric loop at room temperature [40-42]. However, the intermediate compositions yielded slim P-E loops that are tilted strongly with respect to the polarisation axis, giving rise to greatly

reduced P_r and P_s values. This behaviour is typical of relaxor ferroelectrics, which are characterised by polar nano-regions (PNRs) rather than long-range ordered ferroelectric domains. On the other hand, the recovery of P_r and P_s (at room temperature) for higher KBT contents could be related to the substantial increase in T_m reported in section 3.4 above, since relaxor ferroelectrics tend to show a transition towards normal ferroelectric behaviour at temperatures well below T_m .

Generally higher polarisation and coercive field values were obtained for the BCZT composition with $x = 0.06$ (in comparison with $x = 0.02$), which suggests that the higher Ca/Zr ratio helps to stabilise the ferroelectric tetragonal phase in the BCZT-KBT solid solution. These effects can be correlated with the peak in dielectric permittivity at the Curie point, which was more prominent in the BCZT-KBT ceramics with $x = 0.06$, for the compositional range $0.10 < y < 0.50$. This observation is also consistent with the XRD results reported in section 3.2 above, which indicate a slightly higher c/a ratio for $x = 0.06$.

Based on the microstructural observations described in section 3.3 above, the observed changes in ferroelectric switching behaviour must be due to a combination of effects involving both the core and shell regions. Further investigations, involving the use of in-situ XRD and PFM methods for example, are required in order to identify the relative importance of the underlying polarisation mechanisms.

Figure 6 Influence of KBT content on saturation and remanent polarisation (P_s , P_r) and coercive field (E_c) of $(1-y)\text{BCZT}_x\text{-(}y\text{)KBT}$ ceramics at room temperature, (a) $x=0.02$, (b) $x=0.06$.

Ferroelectric domain switching in the $\text{BCZT}_x\text{-KBT}$ ceramics with $y = 0.65$ was also investigated by comparing the XRD patterns obtained from the surfaces of the pellets before and after application of a high electric field, as shown in Figure S2. These results show a qualitative increase in the proportion of c -axis oriented domains after poling at 6 MV m^{-1} , indicated by the changes in the relative intensities of the $(002)_p$ and $(200)_p$ diffraction peaks, for the composition with $x = 0.06$. In contrast, there were no significant changes for $x=0.02$, suggesting that the non-zero remanent polarisation for this composition, shown in Figure 6(a), might be unstable. Further studies of the

thermal depolarisation characteristics, including its dependence on composition and poling procedures, would help to clarify this point.

The influence of temperature on the ferroelectric properties of 0.35BCZTx- 0.65KBT ceramics, represented in terms of the polarisation (P-E) and current density (J-E) loops, is shown in

Figure 7. At room temperature, two sharp peaks in the J-E curves obtained for $x=0.06$ are a clear indication of polarisation reversal due to ferroelectric domain switching around the coercive field, E_c . On the other hand and in view of the ϵ_r -T relationships shown in Figure 4(h), it should be recognised that this behaviour is consistent that of a relaxor ferroelectric in a *non-ergodic* state i.e. the application of the high electric field induces an irreversible transformation from polar nanoregions (PNRs) to ordered ferroelectric domains[37]. In contrast, broadening and splitting of the J-E curves, as observed for $x=0.02$, is a typical characteristic of relaxor ferroelectrics in the *ergodic* state and is associated with a more reversible transformation between PNRs and ordered ferroelectric domains. This behaviour is also consistent with the XRD patterns obtained for this composition, which showed no significant changes after poling, as shown in Figure S2.

Progressive constriction in the P-E loops, accompanied by the presence of multiple peaks in the J-E loops, during heating for the 0.35 BCZTx- 0.65 KBT ceramic for $x=0.06$, as shown in

Figure 7b, indicates disruption of the long-range ordered ferroelectric state to form polar nano-regions (PNR). In other words, application of the high electric field at room temperature induces irreversible switching from short-range ordered PNRs to long-range ordered ferroelectric domains; this process becomes reversible at higher temperatures, indicating the transformation from the non-ergodic to ergodic relaxor ferroelectric behaviour.

Figure 7 P-E and J-E loops of 0.35BCZTx-0.65KBT ceramics (a) $x=0.02$, (b) $x=0.06$ at different temperatures under an electric field of 6 MV m^{-1} and frequency of 2 Hz. Blue arrows indicate the development of constricted P-E loops, which are accompanied by the appearance of split switching peaks in the J-E curves.

The changes in remanent polarization (P_r) with temperature for all of the BCZT-KBT ceramics are illustrated in Figure 8. The P_r values are generally less than $10 \mu\text{C.m}^{-2}$ and decay gradually to levels below $3 \mu\text{C.m}^{-2}$ above 100°C , indicating relatively low depolarization temperatures. On the other hand, higher P_r , P_s and E_c values and substantially improved temperature stability were obtained for the 0.35BCZTx-0.65KBT ceramic with $x=0.06$, in comparison with $x = 0.02$, due to the higher Ca/Zr ratio. In the former case, P_r retained approximately 80% of its initial value up to 100°C , decreasing gradually at higher temperatures. This behaviour is attributed to the improved long-range ordering of ferroelectric domains, which is associated with the *non-ergodic* relaxor ferroelectric state of this composition at room temperature and the transition to an *ergodic* state at elevated temperatures.

Figure 8 Temperature dependence of P_r for $(1-y)\text{BCZTx}-(y)\text{KBT}$ ceramics with $y=0.10, 0.35, 0.50$ and 0.65 ; (a) $x=0.02$, (b) $x=0.06$.

4. Conclusions

The structural and electrical properties of BCZT-KBT ceramics were studied. XRD results indicate that the addition of KBT to BCZT stabilises the tetragonal phase, although a coexisting pseudo-cubic phase is also present. Density measurements and microstructure observations demonstrated that the sinterability was enhanced significantly by the addition of KBT, albeit with the occurrence of some secondary phases. Further refinement of processing procedures is necessary to eliminate such second phases. The addition of KBT also led to the formation of core-shell type microstructures comprising a KBT-rich relaxor ferroelectric shell and a BCZT-rich normal ferroelectric core. Dielectric measurements demonstrated the evolution from normal to relaxor ferroelectric behaviour with increasing KBT content, with intermediate compositions exhibiting both types of characteristic simultaneously. Both constricted and well-saturated P-E hysteresis loops were obtained for the BCZT-KBT ceramics, depending on the BCZT composition and KBT content, indicating either ergodic or non-ergodic relaxor ferroelectric behaviour respectively.

Acknowledgements:

The authors would like to thank the Iraqi Ministry of Higher Education and Scientific Research (MOHESR), University of Babylon for sponsoring this work.

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