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Influence of barium borosilicate glass on microstructure and dielectric properties of (Ba,Ca)(Zr,Ti)O₃ ceramics

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Abstract

Barium borosilicate (BBS) glass was added as a sintering aid to (Ba_{0.7}Ca_{0.3})TiO₃-Ba(Ti_{0.8}Zr_{0.2})O₃ (BCZT) ceramics at levels from 2 to 15 wt%, yielding enhanced densification. The addition of BBS also induced changes in phase composition, from predominantly tetragonal to orthorhombic at room temperature. It is shown that the changes in phase content are caused by a shift of the orthorhombic to tetragonal phase transformation from below room temperature to ≈ 50 °C. An additional high temperature transition around 120 °C was also identified. These observations are interpreted in terms of the development of chemical heterogeneity associated with the redistribution of dopant elements (particularly Zr and Ca) through the liquid phase during sintering. The relative permittivity and electric field-induced polarisation values were generally degraded by the presence of the glass phase, but a reduction in ferroelectric hysteresis and improved densification behaviour have potential benefits in dielectric energy storage applications.

Keywords: X-ray diffraction, barium titanate, borosilicate, glass, dielectric.

1. Introduction

Ferroelectric ceramic materials are used in a wide range of electrical devices as the basis for electromechanical actuators, sensors, transducers and high energy density capacitors. Ceramic capacitors have traditionally employed BaTiO₃-based ceramics due to their high relative permittivity levels and the ability to tailor the temperature-dependence of dielectric properties to meet various industrial specifications [1, 2]. On the other hand, recent attention has focused on (Ba_{0.7}Ca_{0.3})TiO₃-Ba(Zr_{0.2}Ti_{0.8})O₃ (BCZT) solid solutions as potential lead-free piezoceramic materials due to their promising piezoelectric properties (e.g. $d_{33} > 600$ pC/N), albeit with a low ferroelectric Curie temperature, $T_C \approx 90$ °C [3-7].

Liu and Ren investigated the phase boundaries within the pseudo-binary BCT-BZT solid solution using a combination of temperature-dependent XRD and dielectric measurements; it was reported that the phase diagram is characterised by an MPB between ferroelectric rhombohedral (BZT-rich) and tetragonal (BCT-rich) phases [8]. In addition, a Cubic-Rhombohedral-Tetragonal (C-R-T) triple point was identified for a composition with $x=0.32$ at 57 °C. The phase diagram was subsequently refined by Keeble et al. [9], who identified an intermediate orthorhombic (O) phase for compositions near to $x=0.5$ using high resolution synchrotron x-ray powder diffraction (SXPDP).

The high calcination (≈ 1350 °C) and sintering (≈ 1500 °C) temperatures needed for processing BCZT ceramics can lead to practical difficulties for some applications [4, 10, 11]. Therefore, several approaches have been investigated in order to synthesise such materials at lower sintering temperatures; these have included the addition of sintering aids [12, 13], low melting point oxides [14] and doping of other cations in solid solution [15]. In addition, the use of lower sintering temperatures for BCZT is one of the requirements to make thick films. Bai et al. [16] prepared a fully dense, textured BCZT piezoelectric thick film using a screen printing method, which demonstrated significant improvements in electric field-induced polarisation and strain as a result of preferred grain orientation. However, the films were deposited on platinum substrates and a temperature of 1300 °C was required for sintering.

Glass additives have been identified previously as a potential means to reduce the sintering temperature of BCZT. The fabrication of glass-modified BCZT ceramics was reported by Puli et al. [17], who studied the effect of BaO-B₂O₃-ZnO on the dielectric properties of BCZT with a view to their use as energy storage dielectrics. The resulting samples were composites comprising a mixture of BCZT and glass, yielding dielectric breakdown field strengths of

$\approx 28 \text{ kV mm}^{-1}$ with recoverable energy density values of approximately 0.50 J cm^{-3} . The effect of up to 9 wt% of $\text{CaO-B}_2\text{O}_3\text{-SiO}_2$ (CBS) glass additions on the microstructure and electrical properties of BCZT was also studied by Lai et al [18]. The coexistence of orthorhombic and tetragonal BCZT phases with a small amount of CaTiO_3 secondary phase was observed using XRD. Most of these investigations demonstrate that lower sintering temperatures for BCZT ceramics can be achieved by the use of suitable sintering aids. However, the sintering temperatures employed tend to be in the range higher than 1300°C [12, 15, 19].

The ternary system $\text{BaO-B}_2\text{O}_3\text{-SiO}_2$ (BBS) exhibits a eutectic reaction at a temperature of 1140°C for the composition 0.55-0.19-0.26; this specific composition was identified by Shukla on the basis of its low ternary eutectic melting point [20]. On cooling such a liquid, crystallisation is generally avoided and an amorphous glassy phase is formed. BBS glasses exhibit high hardness, low thermal expansion coefficient, low dielectric loss and low cost, which means that they are well suited to applications in Low Temperature Co-fired Ceramic (LTCC) technology [21, 22].

The aim of the present work was to evaluate the performance of BBS as a sintering aid in BCZT ceramics. The BBS glass was added to the calcined BCZT powder in varying proportions according to the formula $(1-x)\text{BCZT-xBBS}$, with $x=2, 5, 10$ and $15 \text{ wt\%}$, using sintering temperatures in the range from 1100 to 1300°C . The influence of BBS on densification, phase coexistence, microstructure and dielectric/ferroelectric properties of BCZT were investigated.

2. Experimental procedures

$\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3$ powder, corresponding to the 50-50 BCT-BZT composition, was synthesized by solid state reaction. The precursor materials were BaCO_3 (99 %), CaCO_3 (98 %), ZrO_2 (99 %) and TiO_2 (99 %). These powders were weighed out and mixed by ball milling in propan-2-ol with zirconia milling media for 24 hours. The mixed oxides were dried and then calcined at a temperature of 1000°C for 6 hours.

The BBS glass system was prepared according to the composition $0.546\text{BaO-0.195B}_2\text{O}_3\text{-0.259SiO}_2$ using BaCO_3 (99 %), H_3BO_3 (99.5 %) and SiO_2 (99.5 %) as raw materials. The precursors were mixed and milled using the same procedures employed for the BCZT powder. Then, the mixed oxide powders were dried and melted at a temperature of 1140°C for 60 min in an alumina crucible and quenched in air onto a stainless steel plate having a thickness of 2 mm.

BCZT was mixed with BBS glass as a sintering aid according to the composition $(1-x)\text{BCZT}-x\text{BBS}$, with $x = 2, 5, 10$ and 15 wt%. Here, the BCZT calcined powder and BBS glass powder were mixed and milled for 6 hours in propan-2-ol in a similar way to that described in the preparation of the BCZT powder above. After drying for 24 hours, the mixture was pressed into disks of diameter 10 mm and thickness 2 mm by applying a pressure of 100 MPa in a cylindrical steel die. The green pellets were sintered at temperatures of 1100, 1200 and 1300 °C for 3 hours. In addition, pure BCZT ceramics were prepared by compaction at 100 MPa and subsequent sintering at temperatures up to 1400 °C. The bulk densities for all of the sintered ceramic pellets were determined using the geometric method.

The phase composition of the sintered ceramics was analysed using high resolution SXPD on beamline I11 at the Diamond Light Source, UK, using a wavelength of 0.8259 Å. The crushed ceramic powders were loaded into quartz capillaries of 0.5 mm diameter, and then mounted on the beamline using a spinning brass holder. The Cryostar hot air blower was used to heat the sample from 30 to 150 °C, with a heating rate of 5 °C min⁻¹. Diffraction patterns were recorded using the position sensitive detector (PSD), which was calibrated using a lanthanum hexaboride powder standard. Full-pattern fitting was carried out using Topas v5.0 [23, 24].

Polished sections for microscopic observations were prepared by grinding using 400 to 2400 grade SiC and then polishing using 6, 1, and ¼ micron diamond paste, followed by dilute OPS (Oxide Polishing Suspension) colloidal silica solution for ≈ 90 minutes. Finally, the samples were placed in an ultrasonic bath for cleaning under ethanol for 10 min. A thin conductive carbon coating was applied using a Quorum coater (Q150T). The microstructural examination was carried out using a Quanta FEG 650 SEM, with local chemical information being obtained by EDS analysis. During the experiment, the accelerating voltage was 20 kV and the working distance was approximately 10 mm. For microstructural analysis, the linear intercept method was used in order to determine the grain size of the sintered ceramics [25].

Electrodes were applied to the sintered pellets using a silver paint (C2000107P3, Gwent Electronic Materials, UK), fired-on at a temperature of 550 °C for 30 min. The relative permittivity and loss tangent were measured as a function of temperature at frequencies of 1, 10 and 100 kHz using a Hewlett-Packard HP4284A LCR meter. High field ferroelectric polarisation-electric field (P-E) measurements were conducted at a frequency of 2 Hz under silicone oil over a range of temperatures from 20 to 140 °C using a Hewlett-Packard HP33120A function generator in conjunction with an EHT Amplifier (Chevin Research Ltd,

Otley, UK) and a current amplifier [26]. Simultaneous strain-electric field and polarisation-electric field measurements were also conducted at 20 °C using an AixACCT TF 2000 Ferroelectric Analyzer, with a measurement frequency of 1 Hz.

3. Results and discussion

3.1 Relative density analysis

The relative densities of the pure BCZT ceramics sintered at 1300, 1350 and 1400 °C were determined as 81, 84 and 91 % respectively, confirming that high sintering temperatures are necessary to achieve significant densification of BCZT in the absence of sintering aids.

Figure 1(a) illustrates the variation in theoretical density of the BCZT-BBS ceramic-glass composite as a function of the BBS content. In order to obtain this figure, the theoretical density of the pure crystalline BCZT phase was calculated first using the nominal composition together with the phase fractions and crystallographic parameters, determined from the full-pattern XRD analysis described in section 3.2 below, while the density of the glass phase was measured by immersion in water using the Archimedes method. Subsequently, the theoretical density of the ceramic-glass composite, ρ_t , was calculated according to the following mixing equation.

$$\frac{1}{\rho_t} = \frac{1-x}{\rho_1} + \frac{x}{\rho_2} \quad (1)$$

where ρ_1 and ρ_2 are the density of the ceramic and glass phases respectively and x is the glass content in wt%.

It was found that the theoretical density of the ceramic-glass composite decreases with glass content, as illustrated in Figure 1(a). This effect can be attributed to the lower density of the glass phase in comparison with BCZT; these were determined as ≈ 4.1 and 5.7 g cm^{-3} respectively.

The relative densities of the BCZT-BBS ceramics sintered at a temperature of 1100 °C, shown in Figure 1(b), were all in the region of 85% or less, indicating poor densification at such low temperatures. Increasing the sintering temperature to 1200 °C resulted in an increase in relative density to values in the range 91 to 94 %, which suggests that the BBS liquid phase can be considered as an effective sintering aid for BCZT. However, reductions in density were observed at the higher sintering temperature of 1300 °C. The latter effect could be due to volatilisation of B_2O_3 at high temperatures, as reported by Lai [18].

For temperatures of 1200 °C and above, the relative density values were moderately independent of BBS content up to approximately 10 wt% BBS. However, significant reductions in density were observed for BBS contents beyond this level. Microstructural observations, described in section 0 below, indicate that the increased porosity in BCZT ceramics prepared with high BBS contents is predominantly in the form of large ($\approx 10 \mu\text{m}$) pores associated with compaction defects. The use of improved processing procedures (e.g. employing lubricants or cold isostatic pressing) could help to prevent the formation of such defects and hence yield further improvements in densification.

Figure 1. Influence of BBS content on (a) theoretical density and (b) relative density of BCZT-BBS ceramics sintered at temperatures ranging from 1100 to 1300 °C.

3.2 Structural studies at room temperature

SXPD patterns of the sintered pure BCZT ceramics are presented in Figure 2 (a). These patterns are consistent with a perovskite phase, with no evidence to indicate the presence of any other crystalline second phases. Asymmetry and/or peak splitting in both of the pseudo-cubic $\{111\}_p$ and $\{200\}_p$ peak profiles suggests the presence of at least 2 different types of structurally-distorted perovskite phases; this observation is consistent with previous reports, which indicate that BCZT ceramics having the present composition are likely to contain coexisting orthorhombic (O) and tetragonal (T) phases at room temperature [9]. The individual peak profiles were generally narrower at the higher sintering temperatures, indicating an improved crystallinity associated with the larger grain sizes.

The incorporation of BBS into BCZT ceramics had relatively little impact on the overall appearance of the SXPD patterns, as shown in Figure 2 (b). The presence of the glass phase did not appear to cause any significant reactions with BCZT or lead to additional crystalline second phases. However, subtle changes in the individual peak profiles are apparent, which could indicate variations in the phase fractions of the coexisting perovskite-type phases. A general narrowing of the peak profiles of the BCZT-BBS ceramics sintered at 1200 °C, in

comparison with those of pure BCZT sintered at 1300 and 1350 °C, was attributed to improved crystallinity; this observation suggests that the presence of the glass phase facilitates grain growth during sintering.

Figure 2. SXPD patterns of (a) pure BCZT ceramics sintered at temperatures from 1300 to 1400 °C (b) BCZT-BBS ceramics with various BBS contents sintered at 1200 °C.

The results of full-pattern fitting, shown in Figure 3 and

Table 1, indicate that the pure BCZT ceramic sintered at 1400 °C comprised coexisting orthorhombic (O) and tetragonal (T) phases with O and T phase fractions of approximately 19 and 81 % respectively. The addition of 5 wt% BBS glass favoured the formation of the orthorhombic (O) and rhombohedral (R) phases, yielding phase fractions of 78 % and 22 % for the coexisting O and R phases respectively. The increase in the proportion of O phase and appearance of the R phase with increasing BBS content is consistent with an increase in the O-T phase transformation temperature, T_{O-T} , as described below in section 3.4, since this acts to stabilise the orthorhombic phase at room temperature. Furthermore, the glass-modified BCZT ceramics prepared with a variety of glass contents yielded similar results for the coexisting O and R phases, albeit with slightly different phase fractions, as shown in

Table 1.

Figure 3. Comparison of experimental and calculated SXPD peak profiles of (a) pure BCZT ceramic sintered at 1400 °C and (b) BCZT-5 wt% BBS ceramic sintered at 1200 °C.

Table 1. Coexisting phases, phase fractions, lattice parameters, χ^2 and R_{wp} of BCZT ceramics. Numbers in parentheses are statistical standard deviations of the last significant digit.

Composition (sintering T)	Phase fraction / wt%	Lattice parameter				χ^2	R_{wp}
		a / Å	b / Å	c / Å	α / °		
Pure BCZT (1400 °C)	T = 81(2) O = 19(1)	$a_T = 3.9963(3)$ $a_O = 5.6642(2)$	-- $b_O = 3.9972(3)$	$c_T = 4.0139(2)$ $c_O = 5.6673(3)$	-- --	6.1	6.77
BCZT-2BBS (1200 °C)	O = 75(2) R = 25(1)	$a_O = 5.6775(1)$ $a_R = 4.0089(1)$	$b_O = 4.0032(2)$ --	$c_O = 5.6785(3)$ --	-- 89.96(1)	5.19	4.23
BCZT-5BBS (1200 °C)	O = 78(3) R = 22(1)	$a_O = 5.6771(5)$ $a_R = 4.0101(3)$	$b_O = 4.0057(1)$ --	$c_O = 5.6819(4)$ --	89.98(1) --	5.6	4.55
BCZT-10BBS (1200 °C)	O = 82(1) R = 18(2)	$a_O = 5.6789(1)$ $a_R = 4.0103(4)$	$b_O = 4.0052(2)$ --	$c_O = 5.6790(3)$ --	-- 89.97(1)	6.29	4.76

3.3 Microstructure

The SEM micrographs of the pure and BBS-modified BCZT ceramics are shown in Figure 4. Poor densification and a very fine grain size are apparent for the pure BCZT ceramic sintered at 1300 °C, consistent with the low relative density of 81 % reported in section 3.1 above. Increasing the sintering temperature for pure BCZT led to a reduction of porosity and enhanced grain growth, yielding an average grain size of $12.2 \pm 4.1 \mu\text{m}$ for a sintering temperature of 1400 °C. In contrast, significant reductions in porosity and limited grain growth are already apparent at the lower sintering temperature of 1200 °C for the BBS-modified BCZT ceramics.

At a given sintering temperature, the effect of adding BBS was to enhance densification and grain growth. On the other hand, the ultimate grain sizes of the BCZT-BBS ceramics were somewhat lower than those of pure BCZT due to the different ranges of sintering temperatures employed in the present study. For example, the average grain size for the BCZT-10 wt% BBS ceramic, sintered at 1200 °C was $2.9 \pm 0.2 \mu\text{m}$, significantly smaller than that of pure BCZT sintered at 1400 °C. The presence of the glassy phase between the grains became more clearly apparent with increasing BBS content and sintering temperature, as illustrated in Figure 5.

Figure 4. SEM micrographs of BCZT-BBS ceramics with 0, 2 and 10 wt% BBS sintered at temperatures in the range 1100 °C to 1400 °C, imaged using SE mode.

Although densification was much improved in the glass-modified BCZT ceramics, some isolated large pores were present, giving rise to slight reductions in density at high glass contents, as noted in section 3.1 above. The size and morphology of these pores, presented as the insert in Figure 4 (10BBS/1300 °C), suggests that they may originate from the inhomogeneous distribution of the glass phase in the powder and/or compaction defects. EDS mapping was employed to determine the distribution of BCZT and BBS phases in the BCZT-10BBS ceramic, as illustrated by the results shown in Figure 5. It is evident that the heavier metallic elements, represented by Ba and Ti, are distributed uniformly throughout the crystalline BCZT grains while the lighter elements, represented by Si, are concentrated in the glassy BBS phase, which occurs as a continuously connected matrix between the grains.

Figure 5. (a) BSE micrograph of the polished section and (b) to (d) EDS mapping for BCZT-10BBS ceramic sintered at 1300 °C.

3.4 Dielectric properties

The temperature-dependence of relative permittivity and loss for pure BCZT ceramics is shown in Figure 6. In the case of the ceramic sintered at 1400 °C, a high relative permittivity in the region of 3800 was obtained at room temperature, consistent with previous reports [27]. Furthermore, a relatively sharp peak was apparent at a temperature of 82 °C. On the basis of previous results, it is assumed that this peak is associated with the ferroelectric Curie point, T_C , and corresponds to the structural transformation from tetragonal (T) to cubic (C). Although the ϵ_r -T curve does not exhibit any obvious anomalies in the region below T_C , small variations in $\tan \delta$ in the temperature range from 30 to 40 °C could be associated with the onset of the lower-temperature O to T transition and therefore may account for the minor orthorhombic phase fraction identified by SXPd, as reported above.

In contrast, the relative permittivity values for the pure BCZT ceramics sintered at 1300 and 1350 °C were significantly lower and did not show such a strong peak at the Curie point. These changes in the ϵ_r -T relationships are attributed to the combination of low density/high porosity and poor crystallinity of these materials.

Figure 6. Influence of sintering temperature on (a) relative permittivity and (b) loss tangent for pure BCZT, measured at a frequency of 100 kHz.

The influence of BBS glass on the dielectric properties of BCZT ceramics is illustrated by the results presented in Figure 7. In common with the case for pure BCZT, the use of higher sintering temperatures yields improved densification and crystallinity, leading to higher relative permittivity values and a more clearly-defined peak at the Curie temperature, as shown in Figure 7 (a) for BCZT-5BBS.

An additional shoulder around 50 °C is clearly apparent on the ϵ_r -T curves for the materials sintered at temperatures above 1200 °C, which is attributed to the thermally-induced O-T transformation. Therefore, it is apparent that the O-T transformation temperature increased from below room temperature to approximately 50 °C as a result of the BBS glass addition. These results are in agreement with the analysis of the SXPD patterns in section 3.2 above, which indicated that the addition of the BBS glass phase led to a change from predominantly tetragonal to orthorhombic phases at room temperature. Furthermore, a similar increase in the R-O transformation temperature could be responsible for the coexisting minor R-phase that was identified by analysis of the SXPD patterns.

For a sintering temperature of 1300 °C, the addition of BBS to BCZT ceramics led to a general reduction in permittivity values as a result of the low permittivity of the BBS glass phase ($\epsilon_r \approx 10.5$), which acts as a screening layer between the higher permittivity BCZT grains. BCZT-BBS ceramics prepared with various BBS contents all exhibited a clear shoulder in their ϵ_r -T curves at temperatures ranging from 40 to 60 °C, as shown in Figure 7 (c).

Furthermore, there was a slight reduction in the position of the main peak at the Curie point and an increase in that of the lower-temperature shoulder with increasing glass content.

The appearance of the O-T transformation in the region above room temperature indicates that the presence of the glass leads to subtle changes in the chemical composition of the crystalline perovskite phase. According to the phase diagram of the BCT-BZT system, even a slight change of the BCT/BZT ratio can lead to significant modification of the phase transformation temperatures [9, 28]. More specifically, reduction of the Ca/Zr ratio in the perovskite phase could be the origin of the observed increase in T_{O-T} , from below room temperature to ≈ 50 °C. One possible mechanism to achieve this could be the selective dissolution of CaTiO_3 into the liquid phase during sintering.

The absence of crystalline second phases in the sintered glass-modified BCZT ceramics suggests that the small amount of additional CaTiO_3 could be incorporated within the glass phase during cooling. This proposal is reasonable given that CaO and TiO_2 are well-known as modifiers for silicate glasses [29, 30]. These observations support the view that the chemical composition of the perovskite phase is significantly affected by the presence of the BBS liquid phase during sintering, resulting in a reduction of the Ca/Zr ratio.

An additional inflection is evident in the ϵ_r -T curves for BCZT-10BBS and BCZT-15BBS at a temperature of approximately 120 °C. Although the origin of this anomaly cannot be decisively identified at present, it could also be caused by chemical heterogeneity. For example, the dissolution of both Ca and Zr from some perovskite BCZT grains could lead to the formation of pure BaTiO_3 grains, which would exhibit a higher Curie temperature, in the range 120 to 130 °C [31]. Therefore, the occurrence of chemical heterogeneity, resulting from the dissolution of dopants into the liquid phase can in principle explain the observed changes in both T_C and T_{O-T} [1, 32]. Further evidence, in the form of more precise micro-chemical analysis, would help to support this argument.

Figure 7. Temperature-dependence of relative permittivity and loss tangent for (a)-(b) BCZT-5BBS sintered at 1100 °C to 1300 °C and (c)-(d) BCZT-BBS sintered at 1300 °C.

3.5 Thermally-induced phase transformations

From the BCT-BZT phase diagram [11], it can be seen that the tilt in the MPB of the BCZT system leads to the possibility to approach the MPB by changing temperature as well as the composition. Therefore, the use of in-situ SXPD during heating provides the means to identify the phase changes that occur on approaching or crossing the MPB.

The temperature-dependent in-situ SXPD patterns for BCZT-5BBS sintered at 1200 °C are shown in Figure 8, which presents the changes in the $\{200\}_p$ peak profile on heating from 30 to 150 °C. It is expected that a chemically-homogeneous BCZT ceramic should transform to a cubic structure at temperatures above the Curie point. In the present case, the transition to the cubic phase occurred above the Curie temperature of ≈ 85 °C. Furthermore, significant changes in the peak profiles are evident in the intermediate temperature range. These results are generally in agreement with the dielectric property measurements, shown in Figure 7 **Error! Reference source not found.** above, where the two transition temperatures, corresponding to the O-T and T-C transformations of BCZT-5BBS, were determined as approximately 50 and 85 °C respectively.

Figure 8. Changes in SXPD peak profile for $\{200\}_p$ reflection of BCZT-5BBS ceramic, sintered at 1200 °C. (a) 3D plot obtained during continuous heating from 30 to 140 °C and (b) 2D plots at selected temperatures. Variations in peak profiles are associated with thermally-induced phase transformations.

Analysis of the temperature-dependent SXPD patterns for the BCZT-5BBS ceramic during heating from 30 to 150 °C, using full-pattern refinement, is illustrated by the $\{111\}_p$ and $\{200\}_p$ peak profiles presented in Figure 9. Increasing temperature caused a gradual transformation from the coexisting O and R phases at 30 °C to a single T phase at 60 °C, as shown by the results presented in Table 2. The presence of the minor rhombohedral phase at 30 °C indicates that the R-O transformation temperature is most likely located slightly below room temperature, in accordance with the results presented by Keeble et al. [9].

It was anticipated that the T to C transformation would occur at the ferroelectric Curie temperature (≈ 85 °C). However, a persistent shoulder was apparent on both the $\{200\}_p$ and $\{111\}_p$ peak profiles at temperatures up to approximately 150 °C. These results are consistent with the presence of chemical heterogeneity in the glass-modified BCZT ceramics, which takes the form of 2 distinct perovskite phases, one being the BCZT solid solution and the other comprising a BT-rich phase, as proposed in section 3.4 above. We suppose that the major BCZT phase transforms to cubic at 85 °C, while the minor BT phase retains the tetragonal structure above 85 °C and transforms to cubic around 120 °C. Above this temperature, the diffraction peak profiles are broadened by the presence of two coexisting cubic phases (BCZT and BT) having slightly different lattice parameters (see Table 2).

Figure 9. Full-pattern refinement of in-situ SXPD peak profiles for BCZT-5BBS during heating from 30 to 150 °C. (a) ϵ_r -T curve and (b)-(f) the measured, calculated and difference data obtained by full-pattern refinement showing $\{111\}_p$ and $\{200\}_p$ reflections. (b) coexisting O-R phases at 30 °C, (c) single T phase at 60 °C, (d)-(e) coexisting C-T phases at 100-120 °C and (f) coexisting C-C phases (BCZT and BT) at 150 °C.

Table 2. Coexisting phases, phase fractions, lattice parameters, χ^2 and R_{wp} obtained by full-pattern refinement for BCZT-5BBS ceramic during heating from 30 to 150 °C. Numbers in parentheses are statistical standard deviations of the last significant digit.

Composition during heating	Phase fraction / wt%	Lattice parameter				χ^2	R_{wp}
		a / Å	b / Å	c / Å	$\alpha / ^\circ$		
30 °C	O = 78(2)	$a_O = 5.6776(2)$	$b_O = 4.0059(3)$	$c_O = 5.6816(3)$	--	5.71	4.53
	R = 22(1)	$a_R = 4.0102(3)$	--	--	89.9		
60 °C	T = 100	$a_T = 4.0128(4)$	--	$c_T = 4.0221(4)$	--	5.98	4.21
100 °C	C = 59(3)	$a_C = 4.0141(3)$	--	--	--	6.71	5.53
	T = 41(2)	$a_T = 4.0131(3)$	--	$c_T = 4.0268(5)$	--		
120 °C	C = 63(2)	$a_C = 4.0150(1)$	--	--	--	7.21	6.57
	T = 37(3)	$a_T = 4.0151(3)$	--	$c_T = 4.0258(4)$	--		
150 °C	C = 73(2)	$a_C = 4.0158(2)$	--	--	--	6.82	6.13
	C = 27(1)	$a_C = 4.0183(3)$	--	--	--		

3.6 Ferroelectric properties

The P-E hysteresis loops obtained for pure BCZT and BCZT-BBS ceramics at room temperature are presented in Figure 10. In the case of pure BCZT, Figure 10 (a), a sintering temperature of 1400 °C yielded a well-defined ferroelectric loop having saturation polarisation, P_s , remanent polarisation, P_r , and coercive field, E_c , values of 0.19 C m⁻², 0.09 C m⁻² and 0.30 kV mm⁻¹ respectively. In contrast, the P-E loops of the pure BCZT ceramics sintered at 1300 and 1350 °C were poorly saturated and exhibited a 'rounded' appearance, indicating high losses. Loops of this form are commonly observed in specimens having high porosity and therefore can be attributed to the poor densification achieved in pure BCZT at sintering temperatures lower than 1400 °C. The low polarisation values result from high porosity, poor crystallinity and very fine grain size, while the 'rounding' effect is caused by conduction currents associated with poor insulation resistance.

The influence of sintering temperature on the ferroelectric behaviour of BCZT-5BBS ceramics is illustrated by the results presented in Figure 10 (b). In this case, well-formed P-E loops with relatively high P values were obtained for sintering temperatures of 1200 and 1300 °C, while that of the ceramic sintered at 1100 °C yielded low P values as a result of its lower density. The P values were reduced somewhat relative to the pure BCZT ceramic, due to the presence of the low-permittivity glass phase between the ferroelectric BCZT grains. For example, the BCZT-5BBS ceramic sintered at 1300 °C yielded P_s and P_r values of 0.123 and 0.054 C m⁻² respectively, which were approximately 32 % lower than those of the pure BCZT ceramic sintered at 1400 °C. On the other hand, the BCZT-5BBS ceramic sintered at 1200 °C yielded a slightly higher P_s value of 0.14 C m⁻² but a lower P_r value of 0.040 C m⁻². The observed variations in ferroelectric switching behaviour with sintering temperature can be correlated with the ϵ_r -T relationships shown in Figure 7 (a), where it is apparent that the BCZT-5BBS ceramic sintered at the highest temperature of 1300 °C exhibited a more well-defined Curie point but the relative permittivity at room temperature was slightly higher for the ceramic sintered at 1200 °C.

Figure 10. P-E hysteresis loops obtained for (a) pure BCZT sintered at 1300 °C to 1400 °C, (b) BCZT-5BBS sintered at 1100 °C to 1300 °C and (c) BCZT-BBS sintered at 1300 °C.

For a given sintering temperature of 1200 °C, increasing BBS content had little influence on P_r and E_c , but led to significant reductions in P_s , as shown in Figure 10 (c). The resulting variations in P_s and P_r as a function of BBS content and sintering temperature are illustrated in Figure 11. The highest P_s values were consistently obtained for the BCZT-BBS ceramics sintered at 1200 °C, while the higher sintering temperature of 1300 °C yielded the highest P_r values. Further work is required to optimise the ferroelectric switching behaviour of these materials, and hence to obtain improved remanent polarisation values. This could include investigations into the properties of BCZT-BBS ceramics sintered at intermediate temperatures in the range 1200 to 1300 °C, for example.

Figure 11. Influence of BBS content on (a) P_s and (b) P_r of BCZT-BBS ceramics sintered at temperatures from 1100 to 1300 °C.

The influence of temperature on ferroelectric properties was evaluated by recording the P-E hysteresis loops of pure and glass-modified BCZT ceramics over a range of temperatures from 25 to 140 °C, as illustrated by the results presented in Figure 12. The P-E loops generally decreased in height with increasing temperature but did not collapse fully into linear loss-free behaviour at temperatures up to 140 °C. The P_s values reduced gradually over the full temperature range, while P_r dropped relatively sharply between 80 and 100 °C due to the ferroelectric phase transformation. The coercive field values varied little over this temperature range. Significant nonlinearity and finite P_r values above 100 °C could be caused by electric field-induced paraelectric-ferroelectric phase transformations in the region of T_C .

The temperature-dependent polarisation values obtained for BCZT ceramics with different glass contents are summarised in Figure 12 (c)-(d). The relatively rapid loss of remanent polarisation above 80 °C is clearly apparent in these results. However, it is also clear that significantly nonlinearity and saturation in dielectric properties occurs even above the Curie point. For example, the saturation polarisation, P_s , for BCZT-5BBS at 140 °C was measured as 0.061 C m⁻² at an electric field of 5 kV mm⁻¹. This is somewhat lower than the predicted value of 0.088 C m⁻², calculated by assuming a linear dielectric response with a permittivity of 2000 at an electric field of 5 kV mm⁻¹.

Figure 12. Influence of temperature on P-E hysteresis loops of (a) pure BCZT (1400 °C) and (b) BCZT-5BBS (1300 °C). Variations in (c) P_s and (d) P_r of pure BCZT and BCZT-BBS as a function of temperature. Arrows in (a) and (b) indicate increasing temperature.

The influence of BBS glass on the longitudinal strain-electric field response at room temperature is illustrated by the results presented in Figure 13 (a). The dramatic reductions in strain with increasing glass content are consistent with the P-E measurements reported above and are attributed to the electric field screening effect caused by the low-permittivity BBS glass phase between the BCZT grains. By utilising the simultaneous measurements of the strain and polarisation components, x_{33} and P_3 respectively, it is also possible to evaluate the influence of glass content on electrostrictive behaviour. The method used here follows a similar approach to that described by Weaver et al., who examined the electrostrictive responses of a soft PZT ceramic as a function of temperature [33].

In the present case, the strain and polarisation data obtained on decreasing the electric field in the partly-saturated region, between 4 and 1 kV mm⁻¹, were re-plotted to illustrate the linear electrostrictive x_{33} - P_3^2 relationships, as shown in Figure 13 (b). These results were then employed to calculate the longitudinal electrostrictive coefficient, Q_{3333} , by a linear least-squares fitting procedure, according to the definition given in equation 2.

$$x_{33} = Q_{3333} P_3^2 \quad (2)$$

Somewhat surprisingly, it was found that the values of the electrostrictive coefficient were affected strongly by the BBS glass content. For example, the pure BCZT and BCZT-2BBS ceramics yielded Q_{3333} values of approximately 0.025 and 0.054 $\text{C}^{-2} \text{m}^4$ respectively. The value of Q_{3333} continued to increase systematically with further increases in glass content, reaching a value of 0.084 $\text{C}^{-2} \text{m}^4$ for the BCZT-15BBS ceramic. The origin of these variations in Q_{3333} with glass content is not immediately obvious, but it could be associated with changes in phase composition (as listed in

Table 1) or alternatively with changes in the polarisation mechanisms associated with particle crystallinity and grain size variations. Irrespective of its origin, this could be an important factor to consider for the applications of such materials in dielectric energy storage devices, where a high electrostrictive coefficient could potentially create undesirable mechanical stresses at high electric field/polarisation levels.

Figure 13. Influence of BBS on (a) strain-electric field loops and (b) strain- P^2 relationships. The latter are plotted to enable determination of the longitudinal electrostrictive coefficient; results for pure BCZT are omitted for clarity.

The P-E loops and recoverable (stored) energy density, U_{rec} , values, calculated from the area between the P-E curve and the polarisation axis for the pure and glass-modified BCZT ceramics, are shown in Figure 14. It is evident that the addition of the BBS glass led to a significant reduction in P_s (from 0.187 to 0.102 C m^{-2}), but the U_{rec} values for pure BCZT and the BCZT-2BBS ceramics are similar. This effect is attributed to the concomitant reduction in P_r (from 0.096 to 0.035 C m^{-2}). Both the pure and glass-modified BCZT ceramics showed a tendency for saturation in the P-E loops, giving rise to sub-linear $U_{\text{rec}}-E_{\text{max}}$ relationships, but the incorporation of BBS glass could potentially yield a higher breakdown field strength and hence enable the use of higher E_{max} values in order to enhance U_{rec} .

Figure 14 (a) P-E hysteresis loops obtained for pure BCZT and BCZT-2BBS and (b) the recoverable (stored) energy density of pure BCZT and BCZT-2BBS, sintered at temperatures of 1400 and 1200 °C respectively, as a function of the maximum electric field.

4. Conclusions

BBS glass was shown to be an effective sintering aid for BCZT ceramics, enhancing densification at relatively low processing temperatures (≈ 1200 °C). The presence of the low permittivity glass phase between the ferroelectric BCZT grains led to significant reductions in relative permittivity and electric field-induced polarisation, these effects becoming more pronounced with increasing glass content. Additional inflections were observed in the dielectric permittivity-temperature curves of the glass-modified BCZT ceramics, indicating the occurrence of further phase transformations that were not apparent in the unmodified material.

Structural studies using SXPD suggested that the unmodified and glass-modified BCZT ceramics were predominantly tetragonal with minor orthorhombic phase and orthorhombic with minor rhombohedral phase respectively. These changes in phase composition are explained on the basis that the incorporation of the BBS glass caused an increase in $T_{\text{O-T}}$, from below room temperature to ≈ 50 °C. Furthermore, the diffraction peaks retained a pronounced asymmetry at high temperatures extending into the paraelectric cubic region, indicating the presence of chemical heterogeneity within the crystalline perovskite phases. It is proposed that the heterogeneity is a result of redistribution of the dopants by dissolution and reprecipitation mechanisms through the liquid phase during sintering.

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6. References

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