

OPTIMUM FIRING TEMPERATURES FOR THE PREPARATION OF $(\text{Ba}_{0.84}\text{Ca}_{0.15}\text{Sr}_{0.01})(\text{Ti}_{0.90}\text{Zr}_{0.09}\text{Sn}_{0.01})\text{O}_3$ CERAMICS BY THE SOLID-STATE COMBUSTION METHOD

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Abstract

The purpose of this research was to investigate the impact of the calcination (1,100°C to 1,300°C for 4 h) and sintering (1,250°C to 1,400°C for 4 h) temperatures on the phase formation, morphology, and electrical behavior of $(\text{Ba}_{0.84}\text{Ca}_{0.15}\text{Sr}_{0.01})(\text{Ti}_{0.90}\text{Zr}_{0.09}\text{Sn}_{0.01})\text{O}_3$ (BCSTZS) lead-free ceramics, synthesized using the solid-state combustion technique with glycine as fuel. The X-ray diffraction (XRD) data of BCSTZS powders exhibited a pure perovskite structure in samples after being calcined at $\geq 1,200^\circ\text{C}$ for 4 h, that was 50°C lower calcination temperature compared to the solid-state reaction technique. The Rietveld refinement analysis of the BCSTZS ceramics confirmed the formation of the orthorhombic phase in all samples. The average grain size expanded from 3.94 to 27.61 μm as the sintering temperature rose. BCSTZS ceramics sintered at 1,300°C exhibited the highest dielectric constant ($\epsilon_r = 2,767$, $\epsilon_c = 8,378$) and decent ferroelectric behavior ($P_r = 10 \mu\text{C}/\text{cm}^2$ and coercive field $E_c = 5.86 \text{ kV}/\text{cm}$).

Keywords: BCSTZS Ceramics; Dielectric; Ferroelectric; Solid-state combustion

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Introduction

Piezoelectric materials can convert mechanical pressure into an electrical current. This conversion occurs when mechanical forces cause stress in the crystal, leading to the alignment of dipole moments in the same direction, a phenomenon known as polarization. Consequently, this alignment results in the generation of an electric current (Thongtha and Bongkarn, 2010). This material is suitable for various applications, such as sensors, actuators and signal converters (transducers) in electronic equipment (Mathrmool *et al.*, 2017). Lead zirconate titanate (PZT) is a widely used piezoelectric ceramic because it exhibits good piezoelectric properties ($d_{33} = 220\text{--}590$ pC/N). Nevertheless, the evaporation of lead oxide during production and disposal is harmful to human health and the environment. To reduce this problem, the European Union (EU) has implemented regulations limiting the amount of lead in electronic equipment to no more than 0.1 wt% (Sonia *et al.*, 2011; Hu *et al.*, 2017; Mathrmool *et al.*, 2017). Consequently, lead-free ceramics, such as BaTiO_3 , KNaNbO_3 , and BiNaTiO_3 , are now used as alternatives to lead-based ceramics (Kumar *et al.*, 2013; ; Shen *et al.*, 2019; Zhao *et al.*, 2021).

Barium titanate (BT) is a lead-free ceramic with a perovskite structure (ABO_3) that has attracted much attention nowadays. This is because BT ceramics exhibit a notable dielectric constant ($\epsilon \sim 6,800$ at the Curie temperature of 130°C) and a high piezoelectric coefficient ($d_{33} \sim 450$ pC/N) (Shen and Li, 2010; Dai *et al.*, 2017). To improve the piezoelectric properties, Sailaja *et al.* synthesized $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Ti}_{0.9}\text{Zr}_{0.1})\text{O}_3$ ceramics and found that at a sintering temperature of $1,450^\circ\text{C}$, the ceramic showed a dielectric constant at the Curie temperature (ϵ_C) of $\sim 7,769$ and a maximum d_{33} of ~ 560 pC/N. The high piezoelectric coefficient was due to an increase in the orthorhombic phase. This could have lowered the energy barrier, making it easier for electric polarization to rotate, leading to a significant amount of strain (Sailaja *et al.* 2019). Afterward, Liu *et al.* reported that the substitution of Sr^{2+} and Sn^{4+} into $(\text{Ba}_{0.84}\text{Ca}_{0.15}\text{Sr}_{0.01})(\text{Ti}_{0.90}\text{Zr}_{0.09}\text{Sn}_{0.01})\text{O}_3$ (BCSTZ) ceramics, when sintered at $1,550^\circ\text{C}$, could enhance the dielectric properties ($\epsilon_C \sim 14,000$) (Liu *et al.* 2015).

Synthesizing ceramics with the solid-state reaction method using high firing temperatures and long soaking times that produce large particles. In contrast, the solid-state combustion method produces high-density ceramics with pure and homogeneous crystalline powders. The small particle sizes are obtained from this method and

the firing temperatures are lower (Manoharan *et al.*, 1992; Kornphom *et al.*, 2016). Atomic diffusion occurs more easily in liquid medium than in a solid one, resulting in faster chemical reaction rates in the liquid phase that is produced in the combustion method by the fuel sources, such as glycine (Lenka *et al.*, 2008; Razak *et al.*, 2011).

This research investigates the influence of firing temperatures on the phase structure, microstructure, and electrical properties of $(\text{Ba}_{0.84}\text{Ca}_{0.15}\text{Sr}_{0.01})(\text{Ti}_{0.90}\text{Zr}_{0.09}\text{Sn}_{0.01})\text{O}_3$ (BCSTZS) ceramics synthesized using the solid-state combustion method.

Experimental

$(\text{Ba}_{0.84}\text{Ca}_{0.15}\text{Sr}_{0.01})(\text{Ti}_{0.90}\text{Zr}_{0.09}\text{Sn}_{0.01})\text{O}_3$ (BCSTZS) ceramics were synthesized via the solid-state combustion method. The raw materials were $\text{Ba}(\text{NO}_3)_2$ (99.00%; Himedia, Ind), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99.00%; Ajax, Aust), SrCO_3 (98.00%; Aldrich, UK), TiO_2 (99.00%; Kemaus, Aust), ZrO_2 (99.00%; Cerac, U.S.A.) and SnO_2 (99.90%; Aldrich, UK). Raw materials were measured and blended by ball milling with zirconia balls using ethanol for a duration of 24 h. Next, the slurry was blended with glycine ($\text{C}_2\text{H}_5\text{NO}_2$; Kemaus, Aust) with a 1:2 ratio using an agate mortar and dried at 120°C , the powders were subsequently calcinated between $1,100^\circ\text{C}$ to $1,300^\circ\text{C}$ for 2 h in atmosphere. Afterward, BCSTZS powders after calcination were blended using polyvinyl butyral (PVB) solution in 3 wt%. The solution mixtures underwent drying and compressed to form pellets (10 mm diameter, 1 mm thickness) at 80 MPa. In the final step, the disks underwent sintering at temperatures between $1,250^\circ\text{C}$ and $1,400^\circ\text{C}$ for 4 h in atmosphere.

The phase evolution and morphology of calcined BCSTZS powders and ceramics were analyzed through an X-ray diffractometer (XRD, Bruker, D2 Phaser) and a Field Emission Scanning Electron Microscope (FESEM), accordingly. The surfaces of sintered samples underwent polishing for the FESEM using sandpaper and alumina. Next, they were thermally imprinted in 100°C temperature below the sintering temperature for 20 min to examine the grain boundaries. The linear interception method was used to measure the grain size and average particle. The density of the ceramics was determined by Archimedes method, using distilled water as the medium. To investigate the electrical properties, silver electrode paste was applied on both sides of

the pellets and was fired at 550°C for 30 min. The dielectric properties were measured using with an LCR meter (Agilent 4263B) at frequencies of 1, 10, and 100 kHz over a temperature between 40°C to 190°C with a heating rate of 5°C/min and a dwell time of 1 min. The ferroelectric hysteresis (P-E) loops underwent examination in ambient temperature with a computer-controlled modified Sawyer-Tower circuit (Radiant, PLC2- 1014346), used to evaluate the ceramics at an electrical field of 40 kV/cm. The piezoelectric properties were measured using a Berlincourt d33 meter (Sinocera, YE2730A).

Results

The X-ray diffraction patterns of the BCSTZS powders calcined between 1,100°C to 1,300°C for 4 h are shown in Figure 1. The phase structure of calcined powders exhibited an orthorhombic (O) perovskite structure in accordance with the Joint Committee on Powder Diffraction Standards

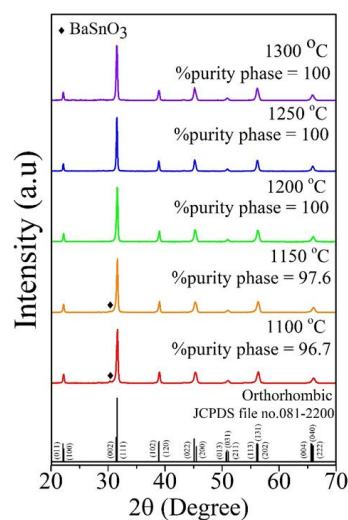


Figure 1. XRD patterns of BCSTZS powders calcined at temperatures between 1,100°C and 1,300°C for 4 h for 2θ values around 20° to 70°

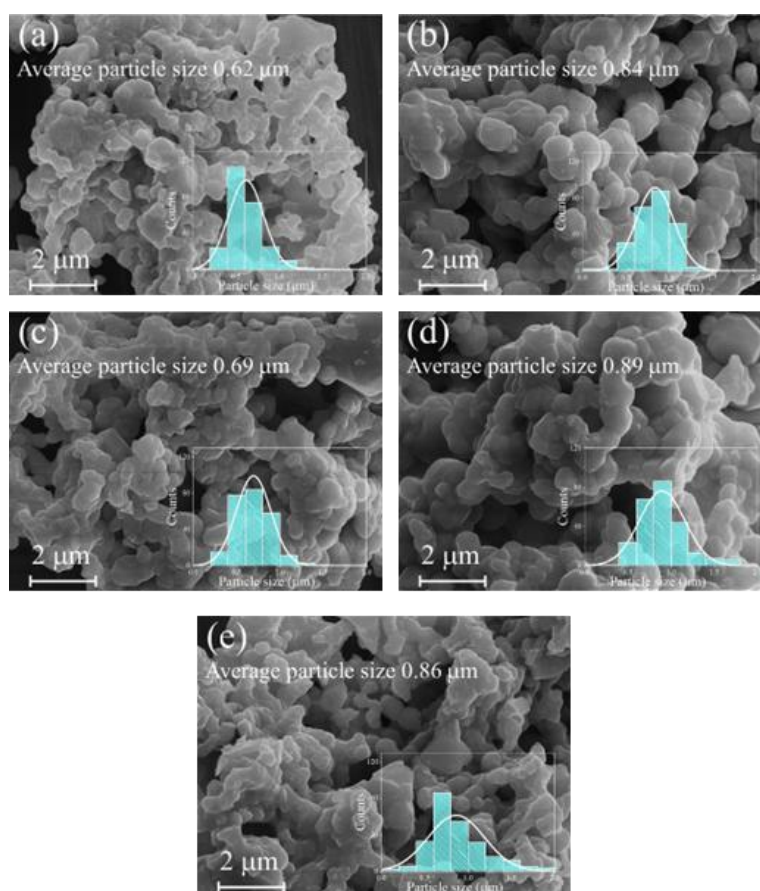


Figure 2. FESEM images of BCSTZS ceramics calcined at (a) 1,100, (b) 1,150, (c) 1,200, (d) 1,250, and (e) 1,300°C for 4 h

(JCPDS) file no. 081-2200 (Figure 1). A trace amount of the BaSnO_3 impurity phase (according to JCPDS file number 074-1300) was detected in the powders calcined at temperatures $\leq 1,150^\circ\text{C}$. A pure perovskite phase was observed when calcined at temperatures $\geq 1,200^\circ\text{C}$. The quality of the perovskite phase structure was characterized through examining the intensity of primary peak of the XRD and the secondary peak. The purity phase percentage of the BCSTZS powders was calculated by the following Equation (1).

$$\% \text{purity phase} = \frac{I_{\max}}{I_{\max} + I_{\text{BaSnO}_3}} \quad (1)$$

Where $I_{\max}$ is the maximum intensity of the primary peak and I_{BaSnO_3} is the highest intensity peak of the secondary phase. The percentage of the perovskite phase increased in the BCSTZS ceramics with higher calcination temperatures as seen in Figure. 1. The powders calcined at $1,200^\circ\text{C}$ for 4 h exhibited a pure perovskite phase, which is below the calcined temperature of the solid-state reaction method by $\sim 50^\circ\text{C}$ (Liu *et al.*, 2015).

Figure 2(a-e) shows the FESEM images and particle size distributions of BCSTZS powders calcined in the temperature between $1,100$ - $1,300^\circ\text{C}$ for 4 h. The software ImageJ was used to determine the particle size distributions. BCSTZS powders consisted of small particles with round shapes and tended to form large agglomerates. The particle size distribution increased as the calcination

temperatures rose. The particle sizes were in the range of 0.62 - $0.89 \mu\text{m}$.

The pure BCSTZS powders calcined at $1,200^\circ\text{C}$ for 4 h were formed into pellets through compaction and underwent sintering in temperatures between $1,250^\circ\text{C}$ to $1,400^\circ\text{C}$ for 4 h, as shown in Figure 3. The BCSTZS ceramics

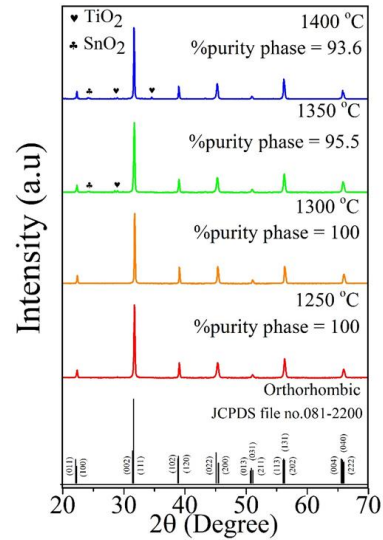


Figure 3. XRD patterns of BCSTZS ceramics sintered in the range of $1,250^\circ\text{C}$ and $1,400^\circ\text{C}$ for 4 h with 2θ between 20° and 70°

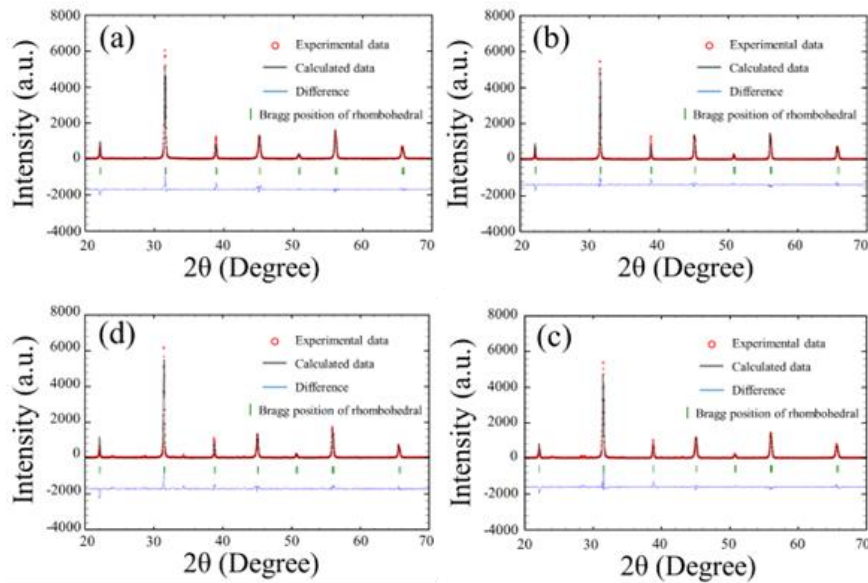


Figure 4. Typical Rietveld refinement analysis for BCSTZS ceramics sintered at (a) $1,250^\circ\text{C}$, (b) $1,300^\circ\text{C}$, (c) $1,350^\circ\text{C}$ and (d) $1,400^\circ\text{C}$ for 4 h

exhibited a typical ABO_3 orthorhombic structure corresponding to JCPDS 081-2200 (Figure 3). The ceramics were sintered at $\leq 1,300^\circ\text{C}$ exhibited a pure perovskite phase. Secondary TiO_2 and SnO_2 phases were detected at sintering temperatures $> 1,300^\circ\text{C}$. The percentage of the BCSTZS perovskite phase is demonstrated in Figure 3.

To verify the phase formation of the BCSTZS ceramics, the XRD of all samples sintered between $1,250^\circ\text{C}$ and $1,400^\circ\text{C}$ were investigated by the Rietveld refinement method and analyzed with the Fullprof software. The Rietveld refinement analysis of the XRD data, is shown in Figure 4. The Rietveld refinement fitting of the XRD data was achieved by varying the scaling factor, lattice constants, background, atomic functional positions (x,y,z), profile half-width parameters (u, v, and w), and occupancy. The initial phase was set to the BaTiO_3 structure with an orthorhombic (space group; Amm2) perovskite structure, referring to JCPDS files no. 081-2200. The background was fitted with a Chebyshev polynomial function. The diffraction peaks were fitted using the pseudo-Voigt function (Chootin and Bongkarn, 2017; Thawong *et al.*, 2019). The profile reliability (R_p),

weight pattern reliability (R_{wp}), expected residual (R_{exp}) and goodness of fit (χ^2) are shown in Table 1. The fitting parameters of, $R_p \leq 32.9\%$, $R_{wp} \leq 34.2\%$, and $\chi^2 \leq 3.83$ demonstrated a good fit between the measured and observed patterns for all samples. The Rietveld refinement results confirmed the formation of an orthorhombic phase, which is consistent with the XRD results. The unit cell volume of the orthogonal phase increased as the sintering temperature increased from $1,250^\circ\text{C}$ to $1,400^\circ\text{C}$, suggesting a gradual expansion of the crystal lattice (Onsri *et al.*, 2022). The lattice parameters of the orthogonal phase are shown in Table 1.

Figure 5 (a-d) shows FESEM images and grain size distributions of BCSTZS ceramics sintered in the temperature between $1,250^\circ\text{C}$ to $1,400^\circ\text{C}$ for 4 h. All the ceramics displayed polygon grain shapes. At a sintering temperature of $1,250^\circ\text{C}$, the sample exhibited small grains and large pores. (Figure 5(a)). An increase in the grain size and a decrease in the porosity was observed at the sintering temperature of $1,300^\circ\text{C}$ (Figure 5(b)). At the sintering temperature of $1,350^\circ\text{C}$, larger grains appeared but pores were once again observed

Table 1. Refined structural parameters and phase percentages for BCSTZS sintered with various temperatures

Sintering temperature ($^\circ\text{C}$)	Refine parameters	Phase structure	Profile parameters	Atoms information				
				Lable	x	y	z	Occ.
1,250	$\chi^2 = 2.95$ $R_p = 19.4\%$ $R_w = 22.7\%$ $R_{exp} = 13.20\%$	R3m	a = 4.023 Å	Ba	0.0000	0.0000	0.0000	0.8400
			b = 5.680 Å	Ca	0.0000	0.0000	0.0000	0.1500
			c = 5.672 Å	Ti	0.5000	0.0000	0.5100	0.9000
			u = 0.301	Sn	0.5000	0.0000	0.5100	0.0100
			v = -0.149	O1	0.0000	0.5000	0.4900	1.0000
			w = 0.043	O2	0.5000	0.7525	0.7396	1.0000
			V = 129.64 Å ³	Sr	0.0000	0.0000	0.0000	0.0100
				Zr	0.5000	0.0000	0.5100	0.0900
1,300	$\chi^2 = 2.24$ $R_p = 20.3\%$ $R_w = 23.0\%$ $R_{exp} = 15.40\%$	R3m	a = 4.020 Å	Ba	0.0000	0.0000	0.0000	0.8400
			b = 5.678 Å	Ca	0.0000	0.0000	0.0000	0.1500
			c = 5.684 Å	Ti	0.5000	0.0000	0.5100	0.9000
			u = 0.021	Sn	0.5000	0.0000	0.5100	0.0100
			v = 0.036	O1	0.0000	0.5000	0.4900	1.0000
			w = 0.006	O2	0.5000	0.7525	0.7396	1.0000
			V = 129.72 Å ³	Sr	0.0000	0.0000	0.0000	0.0100
				Zr	0.5000	0.0000	0.5100	0.0900
1,350	$\chi^2 = 3.83$ $R_p = 24.2\%$ $R_w = 27.7\%$ $R_{exp} = 14.15\%$	R3m	a = 4.027 Å	Ba	0.0000	0.0000	0.0000	0.8400
			b = 5.685 Å	Ca	0.0000	0.0000	0.0000	0.1500
			c = 5.680 Å	Ti	0.5000	0.0000	0.5100	0.9000
			u = 0.207	Sn	0.5000	0.0000	0.5100	0.0100
			v = -0.073	O1	0.0000	0.5000	0.4900	1.0000
			w = 0.035	O2	0.5000	0.7525	0.7396	1.0000
			V = 130.05 Å ³	Sr	0.0000	0.0000	0.0000	0.0100
				Zr	0.5000	0.0000	0.5100	0.0900
1,400	$\chi^2 = 3.53$ $R_p = 24.9\%$ $R_w = 28.0\%$ $R_{exp} = 14.93\%$	R3m	a = 4.026 Å	Ba	0.0000	0.0000	0.0000	0.8400
			b = 5.6882 Å	Ca	0.0000	0.0000	0.0000	0.1500
			c = 5.682 Å	Ti	0.5000	0.0000	0.5100	0.9000
			u = 0.052	Sn	0.5000	0.0000	0.5100	0.0100
			v = 0.006	O1	0.0000	0.5000	0.4900	1.0000
			w = 0.006	O2	0.5000	0.7525	0.7396	1.0000
			V = 130.17 Å ³	Sr	0.0000	0.0000	0.0000	0.0100
				Zr	0.5000	0.0000	0.5100	0.0900

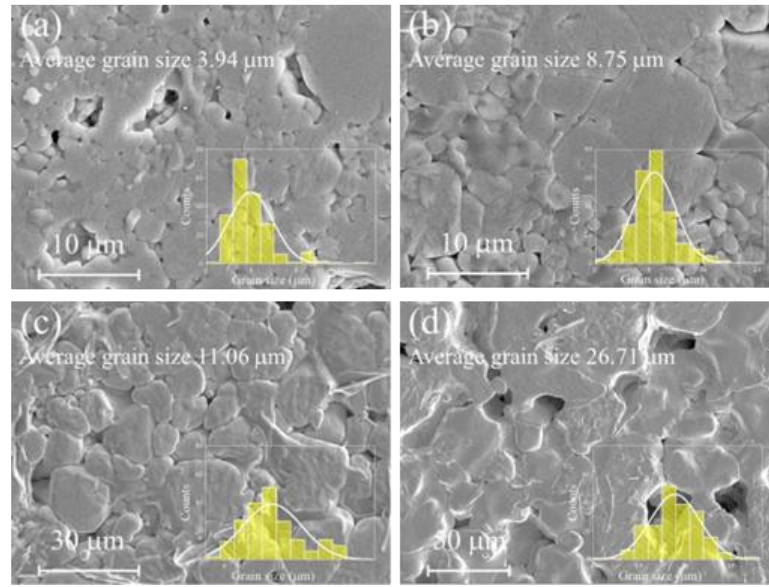


Figure 5. FESEM images of BCSTZS ceramics sintered at (a) 1,250, (b) 1,300, (c) 1,350, and (d) 1,400°C for 4 h

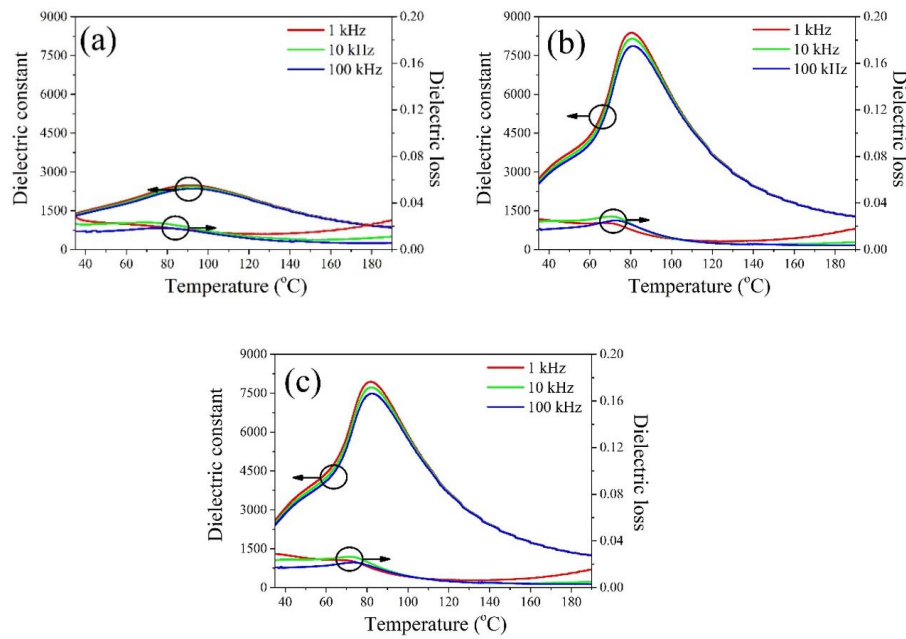


Figure 6. Temperature dependence of the dielectric constant and loss of BCSTZS ceramics sintered at the temperatures of (a) 1,250, (b) 1,300 and (c) 1,350°C for 4 h

(Figure 5(c)). In Figure 5(d), the grain boundaries of the ceramics started to melt and large pores at the grain boundaries were detected in the sample sintered at 1,400°C. The average grain size of the ceramics rapidly increased from 3.94 to 26.71 μm when the sintering temperature increased from 1,250°C to 1,400°C, as shown in Figure 5(a-d). The density of the sample increased from 5.67 g/cm^3

to 5.89 g/cm^3 when the sintering temperature increased from 1,250°C to 1,300°C. The density of ceramics decreased as sintering temperatures increased above 1,300°C. The reduction in density at the higher sintering temperatures could be attributed to the evaporation of certain elements (Kornphom *et al.*, 2018; Onsri *et al.*, 2022), in accordance with the FESEM results.

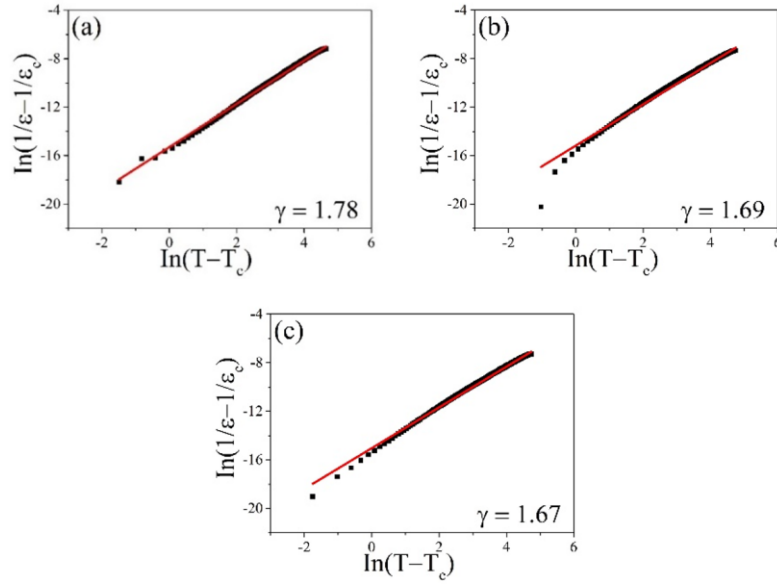


Figure 7. Plot of $\ln(1/\varepsilon - 1/\varepsilon_c)$ as a function of $\ln(T - T_c)$ for BCSTZS ceramics sintered at (a) 1,250, (b) 1,300 and (c) 1,350°C for 4 h

Figure 6(a-c) plots the temperature dependence of the dielectric constant (ε) and dielectric loss ($\tan\delta$) in BCSTZS ceramics sintered at temperatures between 1,250°C and 1,350°C for 4 h and measured at the frequencies of 1, 10, and 100 kHz. For samples sintered at 1,400°C, the electrical properties could not be measured due to high porosity and low density. The dielectric curve exhibited two peaks across all samples, that corresponded to the temperatures of the phase transition of the rhombohedral ferroelectric phase to the tetragonal ferroelectric phase (T_p) at the lower temperature and the tetragonal ferroelectric phase to the cubic paraelectric phase (T_c) at the higher temperature (Kornphom *et al.*, 2016). All sintering temperatures produced ceramics that had a frequency-dependent response with T_c shifting to higher temperatures with increased frequency, indicating relaxor ferroelectric behavior (Bokov and Ye, 2006; Buatip *et al.*, 2018). The values of T_p and T_c tended to decrease as the sintering temperatures rose, as shown in Table 2. The sample sintered at 1,300°C achieved the highest ε_r of 2,767 and ε_c of 8,378, respectively, which can be explained by this sample also having the highest density. The $\tan\delta$ at room temperature (T_r) and T_c were in the range of 0.026-0.033 and 0.017-0.025, respectively.

The diffuseness of the ferroelectric phase transition can be calculated using the modified Curie Weiss law (Yotthuan *et al.*, 2020) according to Equation (2):

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_c} = (T - T_c)^\gamma / C \quad (2)$$

where ε represents the dielectric constant depends on temperature and C is a constant and γ refers to the degree of diffuseness, which ranges from 1 to 2. $\gamma = 1$ describes a regular ferroelectric, while $\gamma = 2$ indicates a completely diffuse phase transition (Yotthuan *et al.*, 2020). The slope of the fitted curves of $\ln(1/\varepsilon - 1/\varepsilon_c)$ versus $\ln(T - T_c)$ at 1 kHz of the ceramics were employed to determine the γ values, as seen in Figure 7(a-c). The γ values decreased from 1.78 to 1.67 with increased sintering temperatures (Figure 7), which confirms a relaxor ferroelectric behavior in the ceramics. The decrease in γ indicated a transition from a relaxor ferroelectric to a normal ferroelectric phase as the sintering temperature increased. The decrease in the relaxor behaviour with increased grain size is attributed to the weakening of long-range ferroelectric interactions (Sailaja *et al.*, 2019).

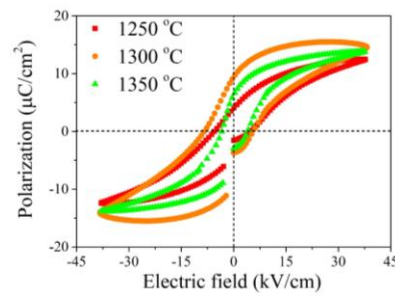


Figure 8. Ferroelectric hysteresis (P-E) loops of BCSTZ ceramics sintered between 1,250-1,350°C for 4 h

Table 2. The density, dielectric, ferroelectric and piezoelectric properties of BCSTZS ceramics

Sintering temperatures (°C)	Density (g/cm ³)	Dielectric at the frequency 1 kHz						Ferroelectric properties		d_{33} (pC/N)
		ϵ_r	$\tan\delta$ at T_r	ϵ_c	$\tan\delta$ at T_c	T_p (°C)	T_c (°C)	P_r ($\mu\text{C}/\text{cm}^2$)	E_c (kV/cm)	
1,250	5.67	1,426	0.031	2483	0.017	53.12	91.38	3.66	5.89	108
1,300	5.89	2,767	0.026	8378	0.025	43.35	80.35	10.00	5.86	156
1,350	5.84	2,606	0.029	7936	0.017	44.75	81.81	6.67	4.71	124
1,400	5.49	-	-	-	-	-	-	-	-	-

Figure 8 shows the ferroelectric hysteresis loops of polarization versus electric field (P-E) of the BCSTZS ceramics sintered in the range of 1,250–1,350°C for 4 h, measured at room temperature using a maximum electric field of 40 kV/cm. All samples exhibited a relaxor ferroelectric behavior with saturated and slim loops. The remnant polarization (P_r), saturation polarization (P_s) and coercive fields (E_c) values of ceramics are tabulated in Table 2. The BCSTZS ceramics underwent sintering at 1,300°C exhibited the optimal ferroelectric properties, with $P_r = 10.00 \mu\text{C}/\text{cm}^2$ and $E_c = 5.9 \text{ kV}/\text{cm}$.

The piezoelectric properties (d_{33}) values of the BCSTZS ceramics obtained at various sintering temperatures are presented in Table 2. A maximum value of $d_{33} = 156 \text{ pC}/\text{N}$ was achieved at the sintering temperature of 1,300°C. The synthesis of BCSTZS ceramics by the solid-state combustion method led to a phase structure different from that of ceramics made by the solid-state reaction technique, resulting in reduced electrical properties.

Conclusions

This study produced BCSTZS ceramics synthesized via the solid-state combustion technique and investigated the impact of firing temperatures between 1,100°C to 1,300°C for calcination and 1,250°C to 1,400°C for sintering with a duration of 4 h, respectively. Pure BCSTZS powder was obtained at a calcination temperature of 1,200°C, for 4 h, which is 50°C lower than the solid-state reaction method. The BCSTZS ceramics exhibited an orthorhombic perovskite phase, which was confirmed by the Rietveld refinement technique. All calcined powders exhibited a rounded grain shape. The average grain size expanded as sintering temperatures were raised. The maximum density (5.89 g/cm³), highest dielectric constant ($\epsilon_r \sim 2,767$ and $\epsilon_c \sim 8,378$), decent ferroelectric properties ($P_r = 10 \mu\text{C}/\text{cm}^2$ and $E_c = 5.86 \text{ kV}/\text{cm}$) and highest piezoelectric ($d_{33} \sim 156 \text{ pC}/\text{N}$) were found in the sample sintered at 1,300°C.

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