

PHASE FORMATION AND ELECTRICAL PROPERTIES OF $\text{Ba}_{0.91}\text{Ca}_{0.09}\text{Ti}_{0.916}\text{Sn}_{0.084}\text{O}_3$ -0.1WT%ZnO -0.1WT%MnO₂ LEAD-FREE FERROELECTRIC CERAMICS SYNTHESIZED VIA THE SOLID-STATE COMBUSTION METHOD

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Received: October 25, 2024; Revised: February 08, 2025; Accepted: February 08, 2025

Abstract

This work investigated the effect of firing temperatures on the phase formation, microstructure, and electrical properties of $\text{Ba}_{0.91}\text{Ca}_{0.09}\text{Ti}_{0.916}\text{Sn}_{0.084}\text{O}_3$ -0.1wt%ZnO-0.1wt%MnO₂ (BCTS-ZnMn) lead-free ferroelectric ceramics synthesized via the solid-state combustion method. Glycine was used as fuel to reduce the synthesis temperature. The samples were calcined at temperatures from 1050 to 1250°C (in 50°C increments) for 3 h and sintered from 1250 to 1450°C (in 50°C increments) for 3 h. A pure perovskite phase was found in the powders calcined above 1100°C. The phase structure, microstructure, dielectric and ferroelectric properties of the ceramics were examined. The X-ray diffraction (XRD) analysis for the ceramics revealed the presence of tetragonal (T) and orthorhombic (O) phases in all the ceramics. The average particle size and average grain size increased with increasing firing temperatures. The density, dielectric constant at the Curie temperature (ϵ_c), P_r and P_s tended to increase with increasing sintering temperatures, up to 1400°C, and then decreased at 1450°C. The ceramic sintered at 1400°C exhibited the highest density (5.89 g/cm³), dielectric response ($\epsilon_c = 13324$) and good ferroelectric behavior ($P_r = 8.67 \mu\text{C}/\text{cm}^2$, $P_s = 17.92 \mu\text{C}/\text{cm}^2$ and $E_c = 0.99 \text{ kV}/\text{cm}$).

Keywords: Dielectric; Ferroelectric; Microstructure; Phase formation; Solid-state combustion

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DOI: <https://doi.org/10.55766/sujst11028>

Suranaree J. Sci. Technol. 32(4):030327(1-11)

Introduction

Ferroelectric materials undergo spontaneous polarization without the application of an electric field (Sandi *et al.*, 2016; Mathrmool *et al.*, 2017). In the past century, ferroelectric materials have been discovered and widely applied in various industries. These applications include electronic components such as capacitors, multilayer capacitors (MLCs), sensors, actuators, and energy storage devices (Kongtaweelert *et al.*, 2006). Lead zirconate titanate (PZT) is one of the most popular ferroelectric ceramics because it exhibits an excellent dielectric constant at its Curie temperature ($\epsilon_C \sim 35000$) (Vittayakorn *et al.*, 2007). However, lead-based (Pb-based) ceramics can cause serious harm to humans and also pollute the environment (Sonia *et al.*, 2011; Li *et al.*, 2016; Hu *et al.*, 2017). Recently, lead-free ferroelectric ceramics with a perovskite structure (ABO_3) have been developed to replace lead-based ceramics. Among these potential candidates, BaTiO_3 (BT), $(\text{K},\text{Na})\text{NbO}_3$ (KNN), and $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT) are being researched due to their good electrical properties (Buatip *et al.*, 2020).

Barium titanate (BT) is a ferroelectric ceramic with a good dielectric constant ($\epsilon_C \sim 6800$) around its Curie temperature (T_C) of approximately 120°C , which makes it an attractive candidate (Sonia *et al.*, 2011; Baraskar *et al.*, 2016). To improve the electrical properties of BT ceramics, Li *et al.* synthesized $(\text{Ba}_{0.98}\text{Ca}_{0.02})(\text{Ti}_{0.94}\text{Sn}_{0.06})\text{O}_3$ ceramics via the solid-state reaction method by calcination at 1200°C for 4 h and sintering at 1500°C for 4 h. Ceramics with enhanced dielectric properties ($\epsilon_C \sim 13000$) and a good remanent polarization ($P_r \sim 7 \mu\text{C}/\text{cm}^2$) in a low coercive field ($E_C \sim 2 \text{ kV}/\text{cm}$) were obtained. The increase in the electrical properties of $(\text{Ba}_{0.98}\text{Ca}_{0.02})(\text{Ti}_{0.94}\text{Sn}_{0.06})\text{O}_3$ was due to a polymorphic phase transition (PPT) between the orthorhombic and tetragonal phases, which occurred close to room temperature, was obtained from doping BT based ceramics with Ca and Sn. Ceramics with an optimal composition and good electrical properties for BT based ceramics are typically sintered at temperatures above 1450°C . To reduce the sintering temperature and increase the density, sintering aids such as CuO , MnO_2 , CeO_2 , Pr_2O_3 , and HfO_2 have been added to the ceramics. B. Wu *et al.* synthesized 0.10 wt%ZnO doped $(\text{Ba}_{0.98}\text{Ca}_{0.02})(\text{Ti}_{0.94}\text{Sn}_{0.06})\text{O}_3$ ceramics via the conventional solid-state reaction method by calcining at 1200°C for 2 h and sintering at 1350°C for 3 h. The obtained ceramics showed a tetragonal phase and excellent electrical properties of $d_{33} \sim 428 \text{ pC}/\text{N}$, $P_r \sim 12 \mu\text{C}/\text{cm}^2$ and $E_c \sim 1.5 \text{ kV}/\text{mm}$ (Wu *et al.*, 2015). In addition, Q. Chen *et al.* successfully

synthesized 0.1 wt%Mn doped $\text{Ba}_{0.91}\text{Ca}_{0.09}\text{Ti}_{0.916}\text{Sn}_{0.084}\text{O}_3$ -0.1 wt%Zn (BCTS-ZnMn) ceramics via the solid-state reaction method. The ceramics calcined at 1200°C for 3 h and sintered at 1315°C for 3 h exhibited a tetragonal phase with a high dielectric constant of $\sim 17,000$. Adding a small amount of MnO_2 to the lattice promoted ceramic grain growth in BCTS-0.1wt% ZnO ceramics, resulting in increased polarization (Chen *et al.*, 2014).

A ceramics synthesis method is crucial for creating highly efficient ferroelectric ceramics. The solid-state combustion method is interesting due to its simplicity, energy efficiency, high purity, fine crystalline powder, high density and good electrical properties at a low firing temperature (Julpunthong and Bongkarn, 2011; Feng *et al.*, 2009; George *et al.*, 2009; Phungjitt *et al.*, 2009). The reaction temperature of this technique is lower than the solid-state reaction method because of the released energy from the fuel (such as glycine or urea) accelerates the chemical reaction between the raw materials (Patil *et al.*, 1997; Razak *et al.*, 2011). Moreover, the liquid phase caused from the melting of the fuel creates an easier chemical reaction for the raw materials (Manoharan and Patil, 1992). Therefore, this research focuses on studying the effects of calcination and sintering temperatures on the phase structure, microstructure, and electrical properties of ferroelectric ceramics $\text{Ba}_{0.91}\text{Ca}_{0.09}\text{Ti}_{0.916}\text{Sn}_{0.084}\text{O}_3$ -0.1wt%ZnO-0.1wt%MnO₂ (BCTS-ZnMn) using the solid-state combustion technique.

Materials and Method

$\text{Ba}_{0.91}\text{Ca}_{0.09}\text{Ti}_{0.916}\text{Sn}_{0.084}\text{O}_3$ (BCTS) ceramics were fabricated by the solid-state combustion using glycine as fuel. $\text{Ba}(\text{NO}_3)_2$ (99.00%; Himedia, India), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99.00%; Ajax, Australia), TiO_2 (99.00%; Kemaus, Australia), and SnO_2 (99.90%; Aldrich, UK) were used as the raw materials and weighed to the correct stoichiometry ratio, then mixed in ethanol by ball milling for 24 h. After drying, the powders were mixed with glycine ($\text{C}_2\text{H}_5\text{NO}_2$; Kemaus, Australia) at a ratio of 1:2 in an agate mortar. The mixed powders were calcinated in the temperature range of 1050°C to 1250°C for 3 h in air. The 0.1wt%ZnO (99.00%; Merck, Germany) and 0.1wt%MnO₂ (99.00%; Unilab, Australia) were added to the pure BCTS powders after calcination. The BCTS+0.1wt%ZnMn (BCTS-ZnMn) powders were mixed with an ethanol solution with 3 wt%

polyvinyl butyral (PVB) and crushed in an agate mortar until the ethanol evaporated. The dried mixed powders were pressed into disks 10 mm in diameter and 1 mm in thickness under 80 MPa of pressure. In the end, the disks were sintered in air with temperatures between 1250 and 1450°C for 3 h.

The phase purity and phase formations of the powders and ceramics were examined with an X-ray diffractometer (XRD, Bruker, D2 Phaser) and the Rietveld refinement method. The surface morphology of the sintered samples was investigated using a field emission scanning electron microscope (FESEM, Thermo Scientific Apreo S). The surfaces of the sintered samples were polished with sandpaper and alumina abrasive for the FESEM analysis. Then, the samples were subjected to thermal etching at 100°C below the sintering temperature for 20 min to observe their grain boundaries. The average grain size was determined using the linear interception method. Archimedes method was used to calculate the density using distilled water as the medium. To measure the dielectric properties, silver paste was coated on both sides and fired at 550°C for 30 min to form electrodes. The dielectric properties were determined by an LCR meter (Agilent 4263B) at a frequency of 1, 10 and 100 kHz over a temperature range of 40-140 °C, with a heating rate of 5°C/min and a dwell time of 1 min. The ferroelectric hysteresis (P-E) loops were measured at room temperature using a computer-controlled modified Sawyer-Tower circuit (Radiant, PLC2- 1014346), which measured the ceramics under an electrical field of 12.5 and 50 kV/cm.

Results and Discussion

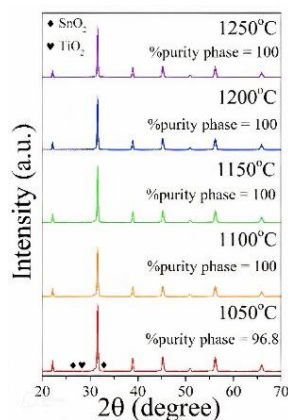


Figure 1. XRD patterns of BCTS-ZnMn powders calcined with temperatures between 1050°C and 1250°C for 3 h with 2θ values of 20° to 70°

Figure 1 shows the X-ray diffraction patterns (XRD) of BCTS-ZnMn powders obtained at various calcination temperatures ranging from 1050°C to 1250°C for 3 h. All samples exhibited a perovskite phase. It was observed that impurity phases, such as SnO₂ and TiO₂, were formed in the XRD patterns of the sample calcined at 1050°C, as seen in Figure 1. The impurity phase was not detected and a pure perovskite structure was obtained by the samples calcined with temperatures ≥1100°C. The purity of the perovskite phase was determined by the relative quantity of perovskite and impurity phases, calculated from the major XRD peak intensities in the perovskite structures using the following equation.

$$\% \text{purity phase} = \frac{I_{\text{max}}}{I_{\text{max}} + I_{\text{SnO}_2} + I_{\text{TiO}_2}} \times 100 \quad (1)$$

The variables, I_{max} , I_{SnO_2} , I_{TiO_2} were defined as the maximum intensity of the highest perovskite peak, and the intensities of the highest SnO₂ and TiO₂ peaks, respectively. It was observed that the %purity phase increased from 96.8 to 100% when the calcination temperature increased from 1050 to 1100°C. The pure samples were achieved at a calcination temperature reduced by approximately 100°C compared to conventional solid-state techniques (Chen *et al.*, 2014). The liquid medium formed when glycine melted, and the energy released from its combustion, reduced the calcination temperature, leading to the disappearance of impurity phases (Kornphom *et al.*, 2018).

Figure 2(a)-(e) presents the FESEM morphology and particle size distributions of BCTS-ZnMn powders calcined between 1050 and 1250°C for 3 h. The particle size distributions were calculated using ImageJ software. It was observed that the powders exhibited small and relatively round particles. All calcined powders showed a wide particle size distribution. The average particle size (d) increased from 0.59 to 0.74 μm as the calcination temperatures increased (Figure 2(a)-(e)). The increase in particle size with increasing calcination temperatures was caused by the following main reasons: (i) As the calcination temperature rises, particles tend to stick together or agglomerate, resulting in larger particle sizes. (ii) The activation energy required for atomic diffusion is easily achieved at high calcination temperatures, which promotes the growth of larger crystals. (iii) Smaller particles have higher surface energy. Increasing calcination temperatures enables these particles to reduce their surface energy by merging into larger particles (Singh *et al.*, 2009; Saikumari *et al.*, 2021).

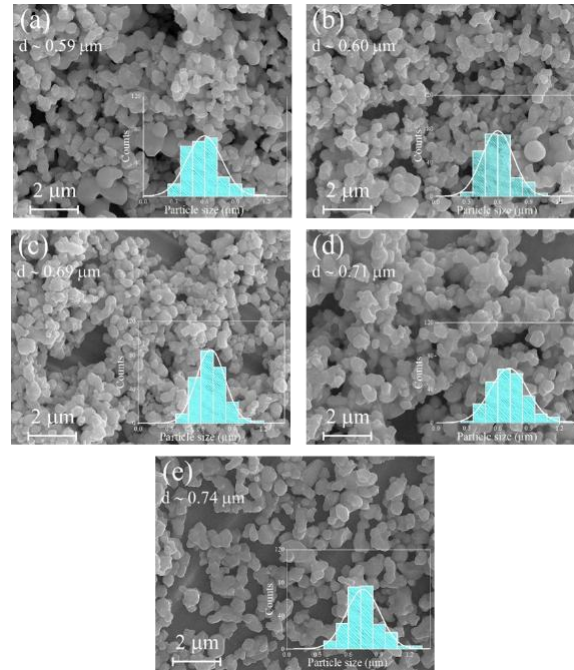


Figure 2. FESEM images and particle size distribution of BCTS-ZnMn powders calcined at (a) 1050, (b) 1100, (c) 1150, (d) 1200 and (e) 1250°C for 3 h

Figure 3 shows the X-ray diffraction (XRD) patterns of BCTS-ZnMn ceramics at room temperature produced with various sintering temperatures, in the 2θ ranges of (a) 20° to 70° and (b) 44° to 47° . The pure BCTS-ZnMn powders calcined at 1100°C for 3 h were pressed into pellets, then sintered between 1250 and 1450°C for 3 h. All ceramics exhibited a pure perovskite structure without any secondary phase, as shown in Figure 3(a). To identify the phase structure of BCTS-ZnMn ceramics, the XRD patterns were expanded in the 2θ range of $\sim 45.5^\circ$, as shown in Figure 3(b). Normally, the orthorhombic (O) phase (JCPDS no. 81-2200) and tetragonal (T) phase (JCPDS no. 74-1956) are characterized by dual peaks of $(022)/(200)_\text{O}$ and $(002)/(200)_\text{T}$ at an angle around 45.5° , respectively. All ceramics exhibited broad dual peaks (Figure 3(b)), which suggested that their phase structure may have contained coexisting O and T phases. The diffraction peaks tended to shift to a higher angle with increased sintering temperatures. This indicated that the unit cell of the ceramics tended to decrease.

The Rietveld refinement technique with the Fullprof program was employed to confirm the phase formation using the O (space group $\text{Amm}2$) and T (space group P4mm) phases as initial structural models. Figure 4 shows the XRD patterns of the samples fitted by Rietveld refinement in the 2θ range from 10° to 70° . The scaling factor, background, lattice constants, profile half-width

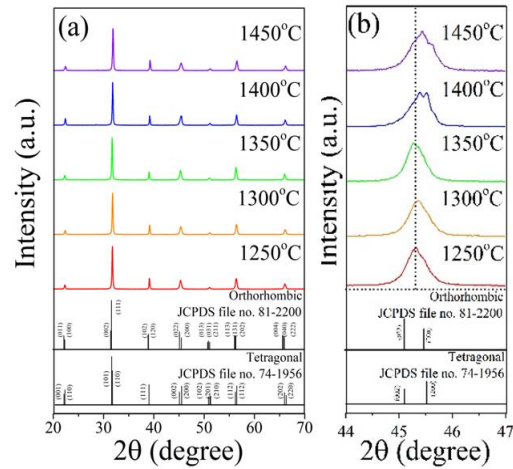


Figure 3. XRD patterns of BCTS-ZnMn ceramics sintered in the range of 1250°C and 1450°C for 3 with 2θ ; (a) 20° to 70° and (b) 44° to 47°

parameters (u , v , and w), atomic functional positions, and occupancy variables of all ceramics were calculated for the XRD fitting process. The Chebyshev polynomial function was used to correct the background and the Pseudo-Voigt function to refine the profile shapes (Marques *et al.*, 2009; Yansen *et al.*, 2015). The following equations were used to calculate the parameters for the weighted-profile R factor (R_{wp}), the pattern reliability factor (R_p), expected R-factor (R_{exp}), and

goodness of fit (χ^2) (Young and Wiles, 1980; Thawong *et al.*, 2019).

$$R_{wp} = \left[\frac{\sum_i w_i |y_{oi} - y_{ci}|}{\sum_i w_i y_{oi}^2} \right]^{1/2} \quad (2)$$

$$R_p = \frac{\sum_i w_i |y_{oi} - y_{ci}|}{\sum_i y_{oi}} \quad (3)$$

$$R_{exp} = \left[\frac{n-p}{\sum_i w_i y_{oi}} \right]^{1/2} \quad (4)$$

$$\chi^2 = \left[\frac{R_{wp}}{R_{exp}} \right]^2 \quad (5)$$

where y_{oi} is the experimental intensities, y_{ci} is the calculated intensities, and $w_i = (1/y_{oi})$ is the weighted experimental observations. Figure 4 also displays the difference between the observed and calculated patterns from the Rietveld refinement process. The value of χ^2 is close to 1, indicating that the fitting procedure fitted the data well (Table 1). The resulting parameter values from the Rietveld refinement are summarized in Table 1. The fitting achieved $R_p \leq 18.6$, $R_{wp} \leq 22.2$, and $\chi^2 \leq 2.92$, indicating a good fit to the experimental data.

The Rietveld refinement results confirm the coexistence of O and T phase structures. The percentage of the T phase increased from 38% to 58% when the sintering temperatures increased from 1250 to 1400°C, then dropped to 45% at 1450°C, as shown in Table 1. The decrease in the percentage of the tetragonal phase with increasing sintering temperatures, reflects the phase's stability. Typically, the orthorhombic phase becomes more stable at higher sintering temperatures, whereas the tetragonal phase remains stable at lower sintering temperatures. The stability of the orthorhombic phase at higher sintering temperatures is due to its lower free energy compared to the tetragonal phase. This stability is improved by reducing lattice strain and increasing atomic displacement (Liu *et al.*, 2022). The average cell volumes of the O and T phases decreased from 131.58 to 128.80 Å³ and from 65.88 to 64.56 Å³, respectively, with increasing sintering temperatures. The lattice parameters of the O and T phases are shown in Table 1. As the sintering temperature increased, the interatomic mobility increased, leading to more rearrangement. This causes the space within the crystal structure to decrease, resulting in a reduction of the unit cell volume (Low *et al.*, 2018). It is noteworthy that the obtained phase structure differs from previous research, which reported that the ceramics exhibited a tetragonal phase when synthesized using the solid-state reaction method (Chen *et al.*, 2014). For example, Ba(Zr_{0.1}Ti_{0.9})O₃

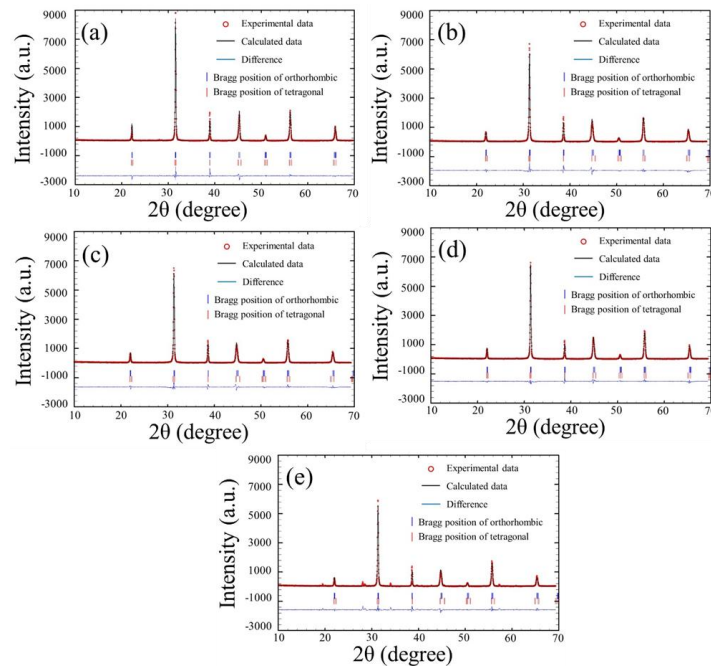


Figure 4. Rietveld refinement of XRD patterns for BCTS-ZnMn ceramics sintered at (a) 1250, (b) 1300, (c) 1350, (d) 1400 and (e) 1450°C for 3 h

Table 1. Refined structural parameters and phase percentages for BCTS-ZnMn ceramics sintered with various temperatures

Sintering temperature (°C)	Goodness of fit	Phase structures	Volume cell (Å ³)		Profile parameters	Atoms information					The percentage of phase
			Amm2	P4mm		La bel	x	y	z	Occ.	
1250	$\chi^2 = 2.30$ $R_p = 16.3\%$ $R_{wp} = 19.3\%$ $R_{exp} = 12.7\%$	Amm2	131.58	65.88	a = 4.050656	Ba	0.0000	0.5000	0.0000	0.7392	62
					b = 5.701902	Ca	0.0000	0.7525	0.0000	0.1289	
					c = 5.696813	Ti	0.5000	0.0000	0.5100	0.9608	
					u = 0.109435	Sn	0.5000	0.0000	0.5100	0.0733	
					v = 0.040225	O1	0.0000	0.4900	0.4900	0.9018	
					w = 0.000355	O2	0.5000	0.7396	0.7396	1.6799	
						Zn	0.5000	0.5100	0.5100	0.0012	
						Mn	0.5000	0.5100	0.5100	0.0028	
		P4mm			a = 4.057979	Ba	0.0000	0.0000	0.0000	0.81809	38
					c = 4.000603	Ca	0.0000	0.0000	0.0000	0.0836	
					c/a = 0.985860	Ti	0.5000	0.5000	0.4820	0.60064	
					u = 1.783562	Sn	0.5000	0.5000	0.4820	0.06566	
					v = -0.328131	O1	0.5000	0.5000	0.0160	1.02237	
					w = 0.065412	O2	0.5000	0.0000	0.5150	1.08337	
						Zn	0.5000	0.5000	0.4820	0.00106	
						Mn	0.5000	0.5000	0.4820	0.00077	
1300	$\chi^2 = 2.14$ $R_p = 15.6\%$ $R_{wp} = 19.0\%$ $R_{exp} = 13.0\%$	Amm2	131.10	65.78	a = 4.043944	Ba	0.0000	0.5000	0.0000	0.7723	54
					b = 5.698087	Ca	0.0000	0.7525	0.0000	0.1084	
					c = 5.689254	Ti	0.5000	0.0000	0.5100	1.0422	
					u = 0.008688	Sn	0.5000	0.0000	0.5100	0.0731	
					v = 0.040307	O1	0.0000	0.4900	0.4900	0.9245	
					w = 0.012162	O2	0.5000	0.7396	0.7396	1.1607	
						Zn	0.5000	0.5100	0.5100	0.0011	
						Mn	0.5000	0.5100	0.5100	0.0031	
		P4mm			a = 4.053685	Ba	0.0000	0.0000	0.0000	0.95437	46
					c = 4.003076	Ca	0.0000	0.0000	0.0000	0.0755	
					c/a = 0.9875153	Ti	0.5000	0.5000	0.4820	0.76945	
					u = 0.391662	Sn	0.5000	0.5000	0.4820	0.06503	
					v = -0.229091	O1	0.5000	0.5000	0.0160	1.08155	
					w = 0.223682	O2	0.5000	0.0000	0.5150	3.35196	
						Zn	0.5000	0.5000	0.4820	0.00148	
						Mn	0.5000	0.5000	0.4820	0.00026	
1400	$\chi^2 = 2.58$ $R_p = 15.3\%$ $R_{wp} = 19.2\%$ $R_{exp} = 11.8\%$	Amm2	129.07	64.65	a = 4.025477	Ba	0.0000	0.5000	0.0000	0.72868	42
					b = 5.665581	Ca	0.0000	0.7525	0.0000	0.09941	
					c = 5.674552	Ti	0.5000	0.0000	0.5100	1.06385	
					u = 0.153693	Sn	0.5000	0.0000	0.5100	0.07405	
					v = 0.003250	O1	0.0000	0.4900	0.4900	1.09635	
					w = 0.007233	O2	0.5000	0.7396	0.7396	3.88518	
						Zn	0.5000	0.5100	0.5100	0.00193	
						Mn	0.5000	0.5100	0.5100	0.00128	
		P4mm			a = 4.02836	Ba	0.0000	0.0000	0.0000	0.90921	58
					c = 3.985989	Ca	0.0000	0.0000	0.0000	0.08777	
					c/a = 0.9894818	Ti	0.5000	0.5000	0.4820	0.62660	
					u = 0.631944	Sn	0.5000	0.5000	0.4820	0.07398	
					v = 0.497348	O1	0.5000	0.5000	0.0160	1.91223	
					w = -0.069465	O2	0.5000	0.0000	0.5150	9.13750	
						Zn	0.5000	0.5000	0.4820	0.00104	
						Mn	0.5000	0.5000	0.4820	0.00220	
1450	$\chi^2 = 2.92$ $R_p = 18.6\%$ $R_{wp} = 22.2\%$ $R_{exp} = 13.4\%$	Amm2	128.80	64.56	a = 4.021176	Ba	0.0000	0.5000	0.0000	0.74967	55
					b = 5.660430	Ca	0.0000	0.7525	0.0000	0.01956	
					c = 5.658789	Ti	0.5000	0.0000	0.5100	0.97082	
					u = 0.141543	Sn	0.5000	0.0000	0.5100	0.08466	
					v = 0.054298	O1	0.0000	0.4900	0.4900	0.84797	
					w = 0.000769	O2	0.5000	0.7396	0.7396	2.39861	
						Zn	0.5000	0.5100	0.5100	0.00230	
						Mn	0.5000	0.5100	0.5100	0.00324	
		P4mm			a = 4.032372	Ba	0.0000	0.0000	0.0000	0.76637	45
					c = 3.970659	Ca	0.0000	0.0000	0.0000	0.01207	
					c/a = 0.9846956	Ti	0.5000	0.5000	0.4820	0.61486	
					u = 1.804668	Sn	0.5000	0.5000	0.4820	0.05628	
					v = -0.289878	O1	0.5000	0.5000	0.0160	2.25284	
					w = 0.053825	O2	0.5000	0.0000	0.5150	3.10355	
						Zn	0.5000	0.5000	0.4820	0.00126	
						Mn	0.5000	0.5000	0.4820	0.00031	

(BZT) synthesized by the solid-state combustion technique shows cubic and tetragonal phases (Julphunthong and Bongkarn, 2011), while ceramics synthesized the solid-state reaction technique show tetragonal and orthorhombic phases (Kuang *et al.*, 2009). In addition, Na_{0.5}K_{0.5}NbO₃ (KNN) prepared using a partial co-precipitation

synthesis route obtained orthorhombic and monoclinic phases (Kumar and Pattanaik, 2013) while the ceramic produced using the spark plasma sintering technique exhibited the orthorhombic phase (Li *et al.*, 2006).

Figures 5 shows the FESEM images of BCTZ-ZnMn ceramics sintered at various temperatures.

The grain morphology exhibited polygonal grain shapes, with a wide grain size distribution observed in all ceramics (Figures 5(a)-(e)). As the sintering temperatures increased from 1250 to 1400°C, the average grain size (D) increased, the grain boundaries became clearer, and the porosity decreased. However, pores reappeared at a sintering temperature of 1450°C. The average grain size of the ceramics increased from 5.29 to 28.74 μm with increasing sintering temperatures, as shown in Figures 5. The increase in grain size and decrease in porosity with increasing sintering temperatures can be explained by the phenomenological kinetic grain growth equation, expressed as follows (Coble, 1985; Chen *et al.*, 2002).

$$\log G = \frac{1}{n} \log t + \frac{1}{n} \left[\log K_0 - 0.434 \frac{Q}{RT} \right] \quad (6)$$

where G is the average grain size at time t , n is the kinetic grain growth exponent, K_0 is a constant, Q is the apparent activation energy, R is the gas constant, and T is the absolute temperature. The measured

densities of the ceramics sintered at various sintering temperatures are listed in Table 2. The density of the ceramics increased from 5.49 to 5.89 g/cm^3 as the sintering temperature increased from 1250 to 1400°C. Thereafter, the density decreased when the sintering temperature increased to 1450°C. The results of the density measurements corresponded with the results of the morphology seen in the FESEM images. The increase in density with increasing sintering temperatures was due to enhanced atomic diffusion, leading to better particle bonding and reduced porosity (Jana *et al.*, 2018). The reduction in density at the highest sintering temperature (1450°C) was caused by the evaporation of SnO , which has a lower boiling point (1425°C) (Kornphom *et al.*, 2018). This resulted in increased porosity and decreased density. Although SnO evaporated, the X-ray diffraction pattern shows a pure perovskite phase structure because the amount of evaporated SnO was too small to be detected (the detection limits for XRD range from about 0.2 to 0.5 wt%) (Newman *et al.*, 2015).

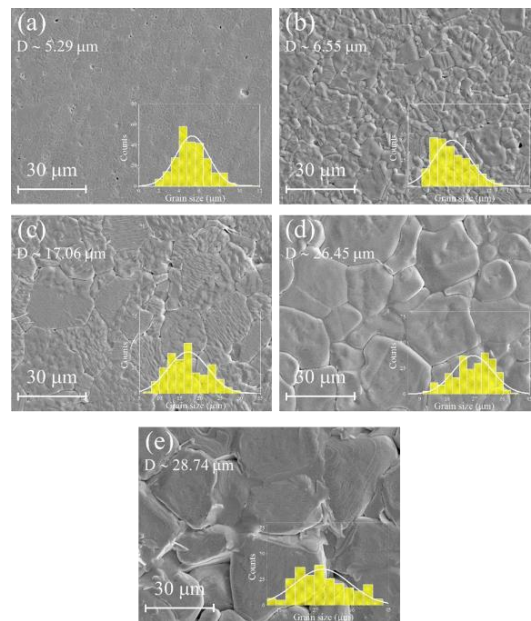


Figure 5. FESEM images and grain size distribution of BCTS-ZnMn ceramics sintered at (a) 1250, (b) 1300, (c) 1350, (d) 1400 and (e) 1450 °C for 3 h

Table 2. Refined structural parameters and phase percentages for BCTS-ZnMn ceramics sintered with various temperatures

Sintering temperatures (°C)	Density (g/cm^3)	Dielectric properties				Ferroelectric properties under an electric field of 50 kV/cm			
		ϵ_r	$\tan \delta$ at T_r	ϵ_c	$\tan \delta$ at T_c	T_c (°C)	P_r ($\mu\text{C}/\text{cm}^2$)	P_s ($\mu\text{C}/\text{cm}^2$)	E_c (kV/cm)
1250	5.49	5153	0.020	10720	0.023	55.94	5.93	17.57	0.76
1300	5.67	5666	0.031	10862	0.045	57.52	6.79	17.88	3.21
1350	5.84	4768	0.024	11804	0.028	58.94	8.14	17.89	0.96
1400	5.89	5325	0.027	13324	0.027	59.30	8.67	17.92	0.99
1450	5.48	4609	0.023	9236	0.021	58.26	8.21	17.72	1.12

Figure 6 shows the temperature dependence of the dielectric constant (ϵ) and dielectric loss ($\tan\delta$) in BCTS-ZnMn ceramics, which were sintered at various temperatures ranging from 1200 to 1450°C and measured at frequencies of 1 kHz, 10 kHz, and 100 kHz. All the ceramics displayed a frequency-independent response, indicating normal ferroelectric behavior (Sonchaopri *et al.*, 2022). Each composition exhibited a single peak corresponding to the phase transition from the tetragonal ferroelectric phase to the cubic paraelectric phase (T_C) (Xue *et al.*, 2011; Yu *et al.*, 2000; Zhi *et al.*, 2002). As the sintering temperature increased from 1250 to 1400°C, the peak shape of the dielectric response changed from broad to sharp. In addition, T_C and the dielectric at T_C (ϵ_C) increased from 55.94 to 59.30°C and 10720 to 13324, respectively. These values decreased when the sintering temperature increased to 1450°C. The dielectric at room temperature (ϵ_r), and $\tan\delta$ at T_r and T_C were in the ranges of 4609-5666, 0.020-0.031 and 0.021-0.045, respectively. As the sintering temperatures increased from 1250 to 1400°C, the dielectric peak became sharper, and the T_C shifted towards a higher temperature, correlating with an increase in the tetragonal phase (Zhang *et al.*, 2013). In contrast, at the sintering temperature of 1450°C, the dielectric peak became broader and the T_C shifted to a lower temperature, corresponding to a decrease in the tetragonal phase as obtained from the Rietveld refinement. The tetragonal phase

features a dominant peak, stability, and an orderly arrangement of dipoles, resulting in an increased dielectric constant (Silveira *et al.*, 2013; Giniyatova *et al.*, 2023; Gouitaa *et al.*, 2023).

Figure 7 shows the ferroelectric (P-E) hysteresis loops for BCTS-ZnMn ceramic samples sintered at different temperatures and measured under electric fields of 12.5 and 50 kV/cm. All ceramics exhibited thin and well-saturated loops, indicating normal ferroelectric behavior consistent with the dielectric results, similar to previous work (Chen *et al.*, 2014). The remnant polarization (P_r), saturation polarization (P_s) and coercive field (E_c) of the ceramics, measured under an electric field of 50 kV/cm, are listed in Table 2. It was found that as the sintering temperature increased from 1250 to 1400°C, P_r and P_s increased from 5.93 to 8.67 $\mu\text{C}/\text{cm}^2$ and from 17.57 to 17.92 $\mu\text{C}/\text{cm}^2$, respectively. However, P_r and P_s decreased when the sintering temperature increased to 1450°C. E_c ranged from 0.76 to 3.21 kV/cm. The rise in sintering temperatures from 1250 to 1400°C led to grain size growth, resulting in increased polarization and improved ferroelectric properties (Cao and Randall, 1996; Smolenskiĭ and Chupis, 1982). At the sintering temperature of 1450°C, although the average grain size increased, large pores formed causing stress in the crystal structure and resulting in a decrease in ferroelectric properties. For a comparative analysis of the ferroelectric and dielectric properties of BCTS-ZnMn synthesized

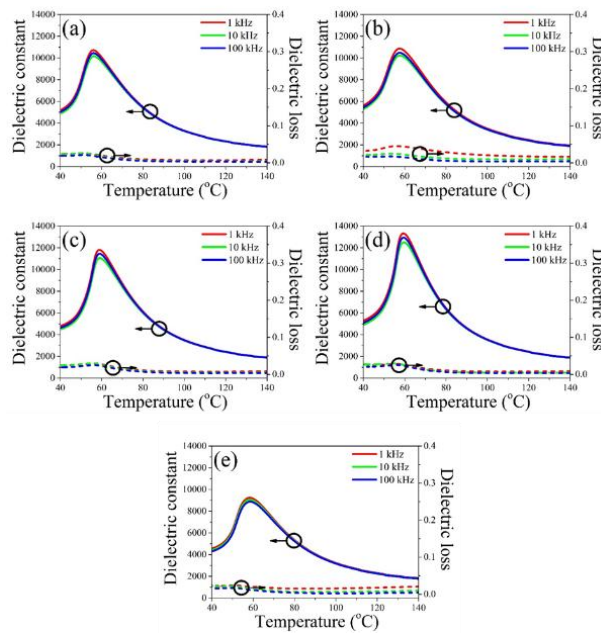


Figure 6. Temperature dependence of the dielectric constant and loss of BCTS-ZnMn ceramics sintered at the temperatures of (a) 1250, (b) 1300, (c) 1350 (d) 1400 and (e) 1450°C for 3 h

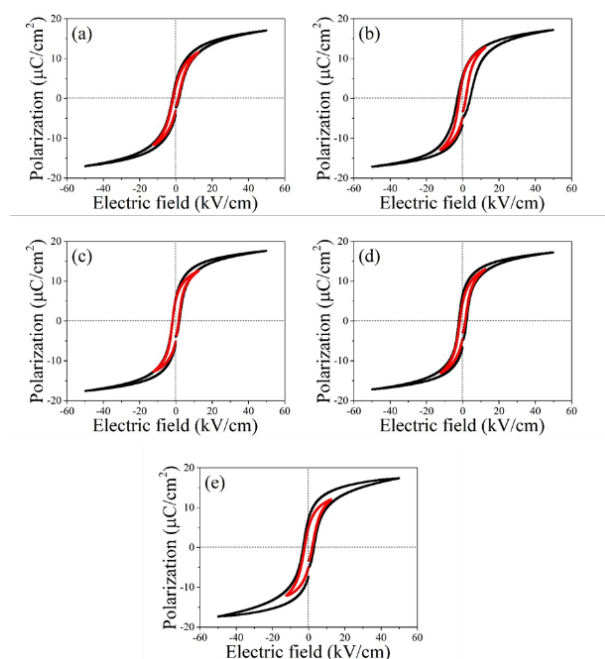


Figure 7. Ferroelectric (P-E) hysteresis loops of BCTS-ZnMn ceramics sintered at temperatures of (a) 1250, (b) 1300, (c) 1350 (d) 1400 and (e) 1450°C for 3 h, measured using electric fields of 12.5 kV/cm (red line) and 50 kV/cm (black line)

using the solid-state combustion technique in this study with those obtained from the solid-state reaction method (Chen *et al.*, 2014), it is found that the ferroelectric properties under an electric field of 12.5 kV/cm for BCTS-ZnMn ceramics from this study ($P_r \sim 5.96 \mu\text{C}/\text{cm}^2$, $P_s \sim 13.20 \mu\text{C}/\text{cm}^2$ and $E_c \sim 1.35 \text{ kV}/\text{cm}$) are similar to previous work (Chen *et al.*, 2014), which reported $P_r \sim 5 \mu\text{C}/\text{cm}^2$, $P_s \sim 13 \mu\text{C}/\text{cm}^2$ and $E_c \sim 1.5 \text{ kV}/\text{cm}$. However, the dielectric constant and T_c obtained from these different preparation methods are quite different due to the distinct phase structures, as similarly reported in previous works (Julpunthong and Bongkarn, 2011; Li *et al.*, 2006; Kuang *et al.*, 2009; Kumar and Pattanaik, 2013).

Conclusions

The BCTS-ZnMn powders and ceramics were synthesized using the solid-state combustion technique with different firing temperatures, with glycine serving as the fuel. A pure perovskite phase of the BCTS-ZnMn powder was achieved at a calcination temperature of 1100°C for 3 h. in air, which represents a reduction of 100°C in calcination temperature compared with the solid-state reaction method. The particles exhibited a round morphology, with an average size ranging from 0.59 to 0.74 μm . All the ceramics showed coexisting

orthorhombic (O) and tetragonal (T) phases, as confirmed by Rietveld refinement. The tetragonality increased from 38% to 58% when the sintering temperature increased from 1250 to 1400°C. The sample sintered at 1400°C exhibited the maximum density (5.89 g/cm³), the highest dielectric constant ($\epsilon_c \sim 13324$ and $\tan\delta \sim 0.027$), and excellent ferroelectric properties ($P_r \sim 8.67 \mu\text{C}/\text{cm}^2$, $P_s \sim 17.92 \mu\text{C}/\text{cm}^2$ and $E_c \sim 0.99 \text{ kV}/\text{cm}$).

Acknowledgements

This project is funded by National Research Council of Thailand (NRCT): (N41A650100), Naresuan University (NU) and National Science, Research and Innovation Fund (NSRF) with Grant No. R2568B022. Appreciations are also given to Asst. Prof. Dr. Kyle V. Lopin for his help in editing the manuscript.

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