

PHASE FORMATION AND ELECTRICAL PROPERTIES OF BCLTS CERAMICS SYNTHESIZED VIA THE SOLID-STATE COMBUSTION TECHNIQUE

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Abstract

Lead-free $\text{Ba}_{0.93}\text{Ca}_{0.04}\text{La}_{0.03}\text{Ti}_{0.90}\text{Sn}_{0.10}\text{O}_3$ (BCLTS) ceramics were fabricated via solid-state combustion technique. The BCLTS powders were calcined in a temperature range of 1075-1175°C for 2 h and sintered in a temperature range of 1350-1450°C for 2 h. The BCLTS powders exhibited a pure perovskite phase when calcined above 1150°C. All BCLTS ceramic samples displayed a perovskite structure with coexisting cubic and tetragonal phases, with a secondary phase observed only at 1450°C. The growth of grain size was increased with increasing sintering temperature (0.42 to 0.65 μm). The highest dielectric and ferroelectric properties ($\epsilon_r=3047$, $\tan \delta_r = 0.029$, $P_{\text{max}} = 9.52 \mu\text{C}/\text{cm}^2$, $P_r = 0.48 \mu\text{C}/\text{cm}^2$, $E_c = 1.04 \text{ kV}/\text{cm}$) were obtained at the sintering temperature of 1400°C. The altered phase structure in this research, compared to earlier studies, results in distinct outcomes for the dielectric and ferroelectric properties.

Keywords: BCLTS; Combustion technique; Ferroelectric; Dielectric

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Introduction

Lead-based perovskite ceramics, such as $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (Lal *et al.*, 1990) and $\text{PbMg}_x\text{Nb}_{1-x}\text{O}_3$ (Bidault *et al.*, 1997), exhibit excellent electrical properties. However, the environmental risks stemming from PbO volatilization during sintering necessitate a focused research effort on the synthesizing and characterization of lead-free ceramic materials as substitutes for their lead-based counterparts. (Haertling, 1999; Xiao *et al.*, 2006; Zeng *et al.*, 2017; Camargo *et al.*, 2018).

BaTiO_3 or BT is recognized as a lead-free ceramic with remarkable piezoelectric and dielectric properties. However, its primary application is as a dielectric material rather than a piezoelectric material, a consequence of the relatively low d_{33} coefficient. (Takahashi *et al.*, 2006; Karaki *et al.*, 2007). BT-based ceramics exhibit high d_{33} , when doped with Zr^{4+} and Ca^{2+} or Sn^{4+} and Ca^{2+} . This characteristic leads to the development of high-performance systems, such as (1-x)BZT-xBCT (Bai *et al.*, 2015) and $(\text{Ba}_{0.9}\text{Ca}_{0.1})(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$ or $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ti}_{0.94}\text{Sn}_{0.06})\text{O}_3$ (Li *et al.*, 2012; Chen *et al.*, 2013). Dopant introduction effectively enhances electrical properties (Wu *et al.*, 2016). La_2O_3 is a well-known dopant that can enhance the piezoelectric properties of $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$, $\text{BaSn}_x\text{Ti}_{1-x}\text{O}_3$ and $(\text{Bi}_{0.5}\text{Na}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ systems (Chou *et al.*, 2008; Kumar *et al.*, 2016; Li *et al.*, 2016). The substitution of A-sites with La^{3+} and Ca^{2+} can be used to tune the piezoelectric and dielectric properties. Chen Zhihui *et al.* (Chen *et al.*, 2017) fabricated $\text{Ba}_{0.97-x}\text{Ca}_x\text{La}_{0.03}\text{Ti}_{0.9}\text{Sn}_{0.1}$ ceramics with $x = 0.02 - 0.10$ via the solid-state reaction technique. The $\text{Ba}_{0.97-x}\text{Ca}_x\text{La}_{0.03}\text{Ti}_{0.9}\text{Sn}_{0.1}$ ceramics were calcined at 1200°C for 4 h and sintered at 1480°C for 2 h, respectively. Coexistence of orthorhombic and tetragonal phases was observed in the ceramics for compositions within the range $x = 0.04 - 0.10$. The maximum d_{33} and dielectric permittivity (ϵ_m) of 541 pC/N and ~ 19000 , respectively, were observed at $x = 0.04$.

Many researchers have found that different methods can produce different structural results in BT ceramics, such as, in $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (BZT) and BCTS ceramics. In the BCT-xBST system, Li-Feng Zhu *et al.* (Zhu *et al.*, 2016) fabricated lead-free BCT-xBST ceramics with various x content ($x = 0.2 - 0.6$) were synthesized via the solid-state reaction technique, with calcination at 1300°C and sintering at 1480°C , both dwell time for 4 h. The BCT-xBST lead-free ceramics had the tricritical point of the orthorhombic, rhombohedral and tetragonal (O-R-T) phase at $x = 0.45$. However, Pavithra *et al.*

(Pavithra *et al.*, 2021) also synthesized BCT-0.45BST ceramics via the solid-state reaction technique, molten-salt methods and sol-gel method. They observed that the BCT-0.45BST ceramics showed a cubic structure phase for all samples. In other research on the BZT system (another BT-based ceramic), certain scholars identified BZT as exhibiting a tetragonal structure (Chen *et al.*, 2008; Huang *et al.*, 2008; Nanakorn *et al.*, 2008). Chen *et al.* fabricated $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ ceramics with various $x = 0.05, 0.10, 0.15$, and 0.20 via the conventional solid-state reaction method. They measured a reduction in tetragonality with higher zirconium content (Huang *et al.*, 2008). Although, multiple other studies have reported an increase in the change from the orthorhombic to the rhombohedral phase with increased zirconium (Nanakorn *et al.*, 2008; Kuang *et al.*, 2009; Binhayeeniyi *et al.*, 2010).

The solid-state combustion method's ability to achieve pure phases with ultrafine, homogeneous particles through low-temperature, short-dwell-time processing has led to its recent rise in popularity for ferroelectric material fabrication. Therefore, ceramics produced through this method exhibit good electrical properties (Mathrmool *et al.*, 2014; Chootin and Bongkarn, 2017; Thawong *et al.*, 2017; Kornphom *et al.*, 2021). This research aims to study the phase formation and electrical properties of $\text{Ba}_{0.93}\text{Ca}_{0.04}\text{La}_{0.03}\text{Ti}_{0.9}\text{Sn}_{0.1}$; BCLTS ceramics fabricated via the solid-state combustion technique.

Experimental

$\text{Ba}_{0.93}\text{Ca}_{0.04}\text{La}_{0.03}\text{Ti}_{0.9}\text{Sn}_{0.1}\text{O}_3$ or BCLTS ceramics were synthesized via the solid-state combustion technique. The raw powders are $\text{Ba}(\text{NO}_3)_2$ (Himedia, 99%), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Ajax Finechem, 99%), La_2O_3 (Aldrich, 99.98%), TiO_2 (Kem Aus, 99%) and SnO_2 (Aldrich, 99.9%). The correct stoichiometric ratio amount of starting compound was ball milled with ZrO_2 balls in ethanol for 24 h. After drying, the mixes were grounded with glycine ($\text{C}_2\text{H}_5\text{NO}_2$) at a ratio of 1:1.1. Then, the mixture was calcined at $1075 - 1175^\circ\text{C}$ for 2 h. After that, the pure calcined powder was mixed with 3% polyvinyl butyrate (PVB) in a ratio of 1:1. These powders were pressed into pellets of ~ 1.3 mm in thickness and 12 mm in diameter using a pressure of 80 MPa. The binder was burned out of the pellets at 400°C for 3 h and then sintered in the range of $1350 - 1450^\circ\text{C}$ for 2 h.

The BCLTS calcined powders and ceramics were characterized for phase structure and microstructure by X-ray diffraction (Bruker D2 Phaser) and field emission scanning electron microscopy (Apreo S), respectively. The linear intercept method was used to calculate the average particle and grain size from the SEM images. The density of the ceramic specimens was determined by Archimedes' method, employing distilled water as the absorption fluid. Before measuring electrical properties, silver plate was coated on both surfaces and fired at 550°C for 30 min. The dielectric properties (dielectric permittivity (ϵ_r) and dielectric loss ($\tan \delta_r$)) were measured using an LCR meter (HP, 4284A) in the temperature range of 35-150°C at frequencies of 1-100 kHz. The ferroelectric hysteresis P-E loops at room temperature were performed at 1 Hz, using ferroelectric tester (Precision Premier II, Radiant USA), under an applied electric field of 50 kV/cm.

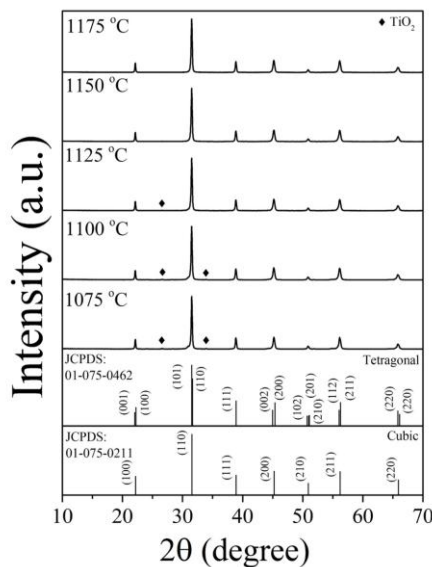


Figure 1. X-ray diffraction patterns of BCLTS powders calcined with various temperatures (1075-1175°C) for 2 h.

Results and discussion

Figure 1 illustrates the XRD patterns of BCLTS powders obtained after calcination for 2 h at varying temperatures from 1075 to 1175°C. The perovskite phase structure observed in all BCLTS powders was

confirmed by JCPDS reference data no. 01-075-0211 and 01-075-0462. At low calcination temperatures (1075-1125°C), an impurity phase of TiO_2 was observed, while at calcination temperatures above 1150°C, a pure perovskite phase was found, which is lower than the solid-state reaction technique (Chen *et al.*, 2017). To quantify the percentage of perovskite phase, the following equation can be used (Kornphom *et al.*, 2021):

$$\% \text{ perovskite} = \left(\frac{I_{\text{perovskite}}}{I_{\text{perovskite}} + I_{\text{TiO}_2}} \right) \times 100$$

Here, $I_{\text{perovskite}}$ represents the highest peak intensity of perovskite structure observed around $2\theta = 32^\circ$ while I_{TiO_2} represents the highest intensities of the TiO_2 peak. The influence of calcination temperature on the perovskite phase percentage was quantified, revealing an increase from 98.6% to 99.17% as the temperature was increased from 1075 to 1125°C. Additionally, a pure perovskite phase was observed at calcination temperatures above 1150°C.

Figure 2 displays the microstructure of the BCLTS powders calcined between 1075-1175°C, analysed at room temperature. The powders exhibited ultrafine particles that were mostly spherical and tended to aggregate. The average particle size of the BCLTS powders was determined to be within the range of 0.27 to 0.39 μm .

Figure 3 illustrates the XRD diffraction patterns of BCLTS ceramics sintered at temperatures ranging from 1350°C to 1450°C for 2 h. The BCLTS ceramics displayed a perovskite phase structure for all of the samples as shown in Figure 3(a). At a sintering temperature of 1450°C, Ba_3SnO was also detected according to JCPDS number 01-083-1868. Key structural phase characteristics are observable in the enlarged 2θ (35–50°) shown in Figure 3(b). The BCLTS ceramics displayed nearly symmetrical single peaks corresponding to the cubic and tetragonal phases at 2θ approximately 39° and 46° , respectively, when sintered at 1350°C. These peaks correspond to JCPDS files no. 01-075-0211 and no. 01-075-0462 which indicated a cubic and tetragonal phase, respectively. From this result, it is suggested that BCLTS ceramics had coexisting cubic and tetragonal phases. As the sintering temperature increased the single peak (200) split into double diffraction peaks. This suggests that the ratio of the tetragonal phase increased with increased sintering temperatures.

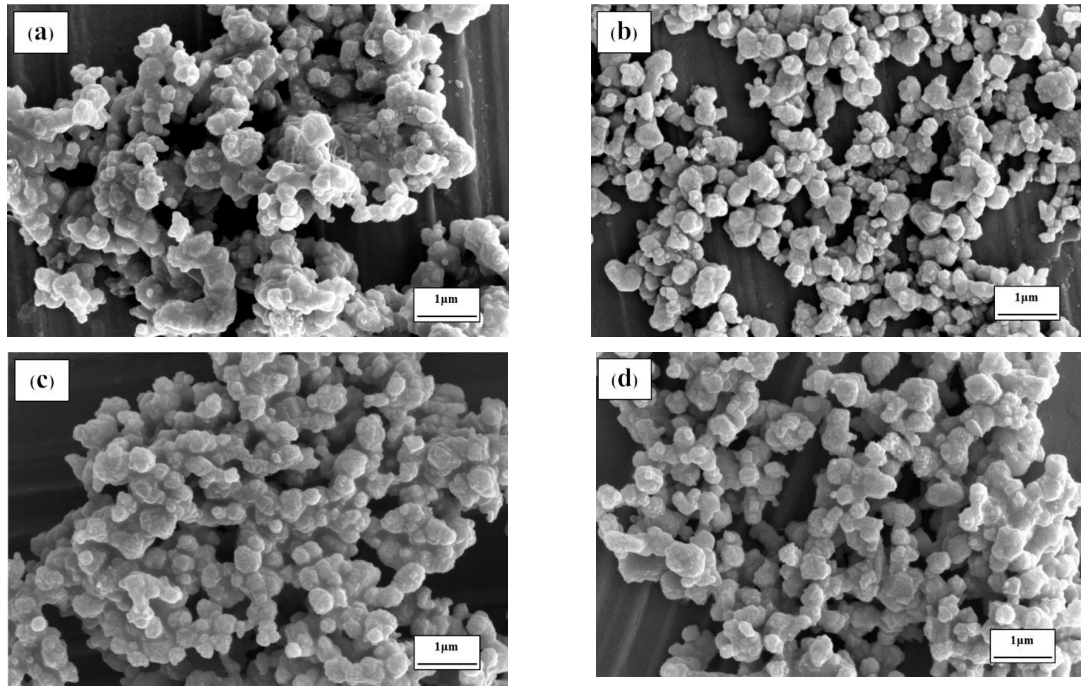


Figure 2. The SEM micrographs of BCLTS powders calcined at (a) 1075°C, (b) 1100°C, (c) 1125°C and (d) 1175°C.

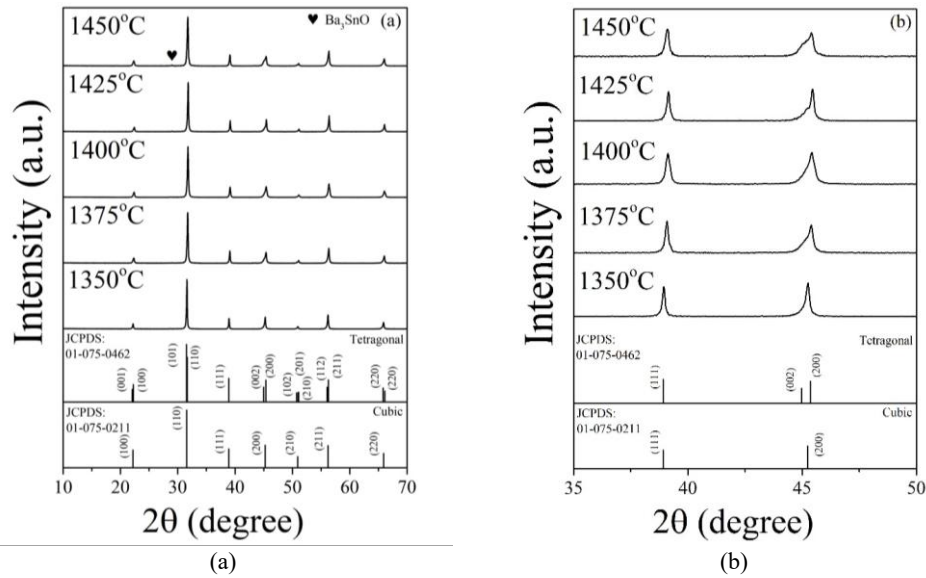


Figure 3. X-ray diffraction patterns of BCLTS ceramics produced with different sintering temperatures within a 2θ range of (a) 10–70° and (b) 35–50°.

To better characterize the ceramics, the lattice parameters and phase ratios of the BCLTS ceramics were determined through Rietveld refinement, a quantitative analytical methodology implemented via the Fullprof software. Structural parameters,

including lattice constants, profile half-width parameters, scaling factors, site occupancies, and atomic positions, were obtained from the Crystallography Open Database (COD). Initial models for the refinement were based on the P4mm

(Tetragonal phase) and Pm-3m (Cubic phase) space groups. Figure 4 displays the refined XRD patterns, while Table 1 presents the parameters for the pattern R_p , expected R-factor (R_{exp}), the weighted-profile R factor (R_{wp}), and goodness of fit (χ^2) for the BCLTS ceramics. It can be seen that the fitting parameters of $R_p \leq 17.7\%$, $R_{wp} \leq 22.0\%$, $R_{exp} \leq 12.95\%$ and $\chi^2 \leq 2.96$ showed good agreement between the observed and calculated patterns for all samples. As a result, it is shown that all BCLTS ceramics

exhibited coexisting cubic and tetragonal phases. The phase ratio between the cubic (C) and tetragonal (T) phases was found to be 79:21, 73:27, 56:44, 39:61 and 24:76 for sintering temperatures of 1350, 1375, 1400, 1425 and 1450°C, respectively. However, it differs from previous work [16] where Zhi-hui Chen *et al.* reported that BCLTS has coexisting orthorhombic and tetragonal phases, when synthesized via the conventional solid-state sintering process.

Table 1 Fitted parameters, phase ratio and lattice parameters of the BCLTS ceramics.

Samples	χ^2	R_p	R_{wp}	R_{exp}	The percentage of phase		Structure	
					Cubic	Tetragonal	Cubic (Pm-3m)	Tetragonal (P4mm)
1350	1.57	13.1	16.1	12.85	79	21	$a=b=c=4.014 \text{ \AA}$,	$a=4.027 \text{ \AA}$, $c=3.996 \text{ \AA}$, $c/a=0.992$
1375	2.11	16.1	18.5	12.74	73	27	$a=b=c=4.014 \text{ \AA}$,	$a=4.032 \text{ \AA}$, $c=3.989 \text{ \AA}$, $c/a=0.989$
1400	2.44	15.7	19.6	12.53	56	44	$a=b=c=4.015 \text{ \AA}$,	$a=4.032 \text{ \AA}$, $c=3.996 \text{ \AA}$, $c/a=0.991$
1425	2.57	17.0	20.8	12.95	39	61	$a=b=c=4.017 \text{ \AA}$,	$a=4.032 \text{ \AA}$, $c=4.003 \text{ \AA}$, $c/a=0.993$
1450	2.96	17.7	22.0	12.79	24	76	$a=b=c=4.005 \text{ \AA}$,	$a=4.023 \text{ \AA}$, $c=3.985 \text{ \AA}$, $c/a=0.990$

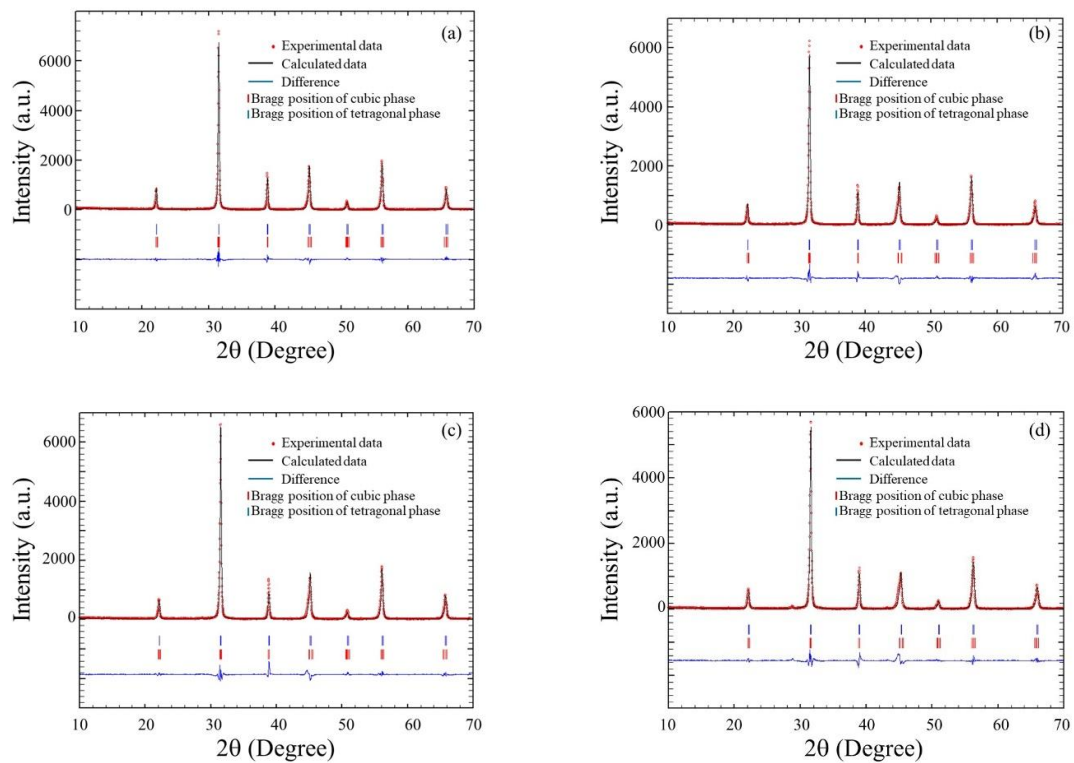


Figure 4. Rietveld refinement analysis for BCLTS ceramics sintered at (a) 1350°C, (b) 1375°C, (c) 1400°C and (d) 1450°C for 2 h.

Table 2 The average grain size, density, relative dielectric measured at a frequency of 1 kHz and ferroelectric properties of BCLTS ceramics produced with different sintering temperatures measured under an electric field of 50 kV/cm.

Temperature	Grain size (μm)	ρ (g/cm^3)	ϵ_r	$\tan \delta_r$	P_{max} ($\mu\text{C/cm}^2$)	P_r ($\mu\text{C/cm}^2$)	E_c (kV/cm)
1350	0.42	3.77	2320	0.006	8.28	0.82	2.34
1375	0.47	3.80	2743	0.009	8.89	0.46	1.18
1400	0.50	4.06	3047	0.029	9.52	0.48	1.04
1425	0.60	3.98	2472	0.008	8.71	0.47	1.29
1450	0.65	3.92	2392	0.009	8.54	0.68	1.59

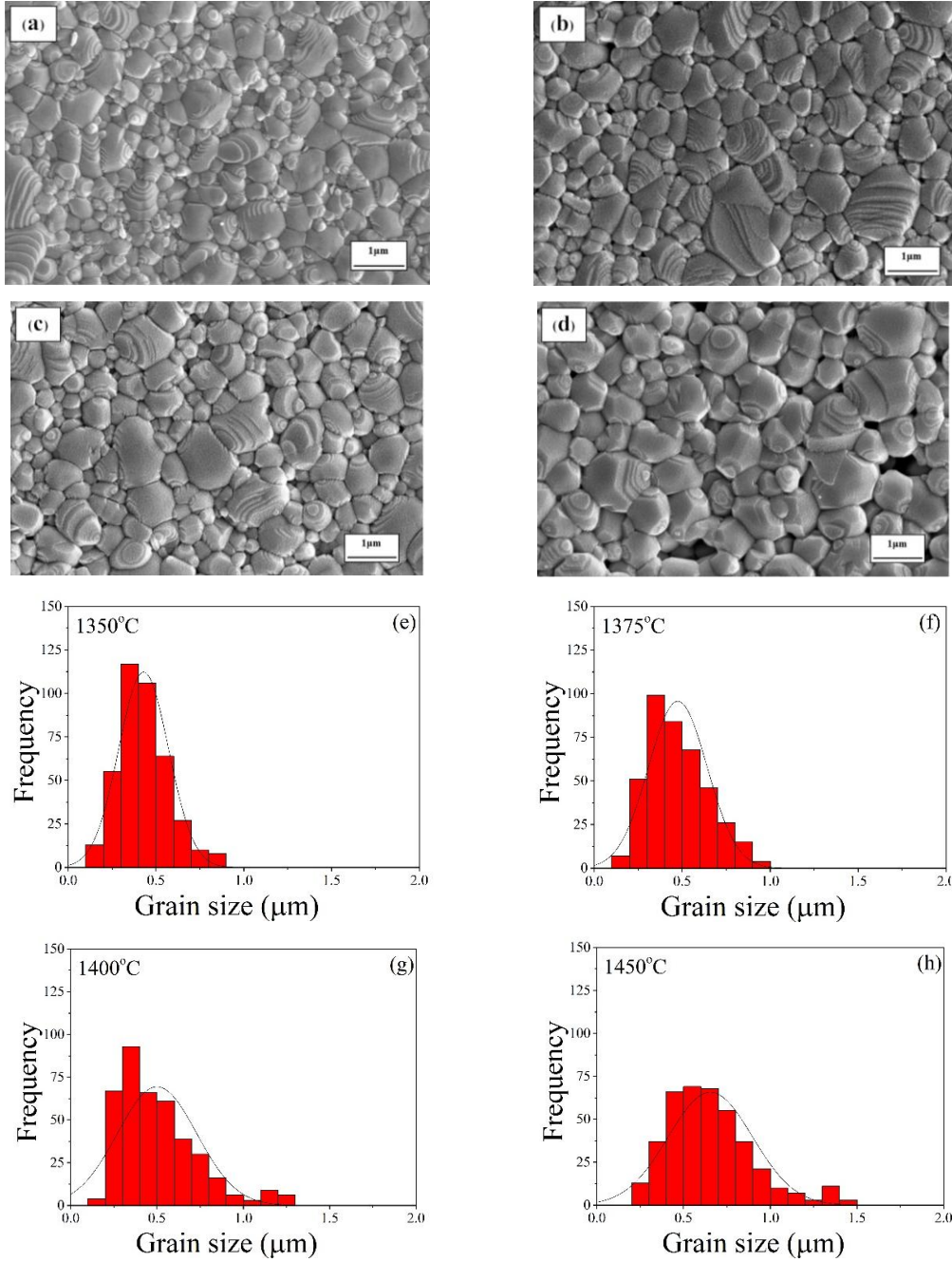


Figure 5. The morphology of BCLTS ceramic surfaces and grain size distributions sintered at: (a, e) 1350°C, (b, f) 1375°C, (c, g) 1400°C and (d, h) 1450°C.

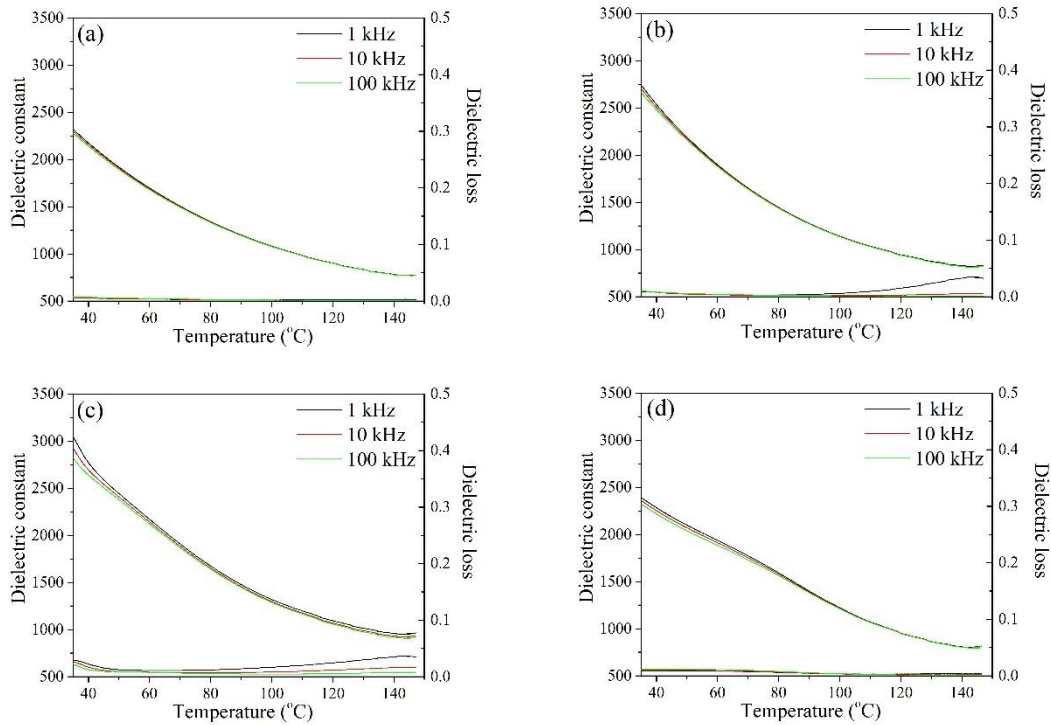


Figure 6. Temperature dependences of dielectric constant of BCLTS ceramics sintered at: (a) 1350°C, (b) 1375°C, (c) 1400°C and (d) 1450°C.

SEM images and grain size distributions of BCLTS ceramics produced with various sintering temperature (1350-1450°C) are presented in Figure 5. Unclear grain boundaries were observed in the ceramic sintered at 1350°C, as illustrated in Figure 5(a). However, upon increasing the sintering temperature above 1375°C, the ceramics displayed clear grain boundaries, with no observed porosity, except at the sintering temperature of 1450°C, as exhibited in Figure 5(b-d). Furthermore, the average grain size increased from 0.42 to 0.65 μm , as listed in Table 2, with increased sintering temperatures. An increase in sintering temperature markedly augmented grain growth and contributed to the densification of the microstructure. (Sumang *et al.*, 2016). It was observed that grain size distribution broadened with increasing sintering temperature, as depicted in Figure 5(e-h). The density of the BCLTS ceramics exhibited an increase from 3.77 to 4.06 g/cm^3 as the sintering temperature up to 1400°C, subsequently decreasing thereafter, as detailed in Table 2, attributed to pore formation observed in the SEM results. The temperature dependence of the dielectric permittivity (ϵ_r) and dielectric loss ($\tan \delta_r$) of BCLTS ceramics, measured in the temperature range of 35-150°C with frequencies of 1 - 100 kHz, are shown in Figure 6. At sintering temperatures

above 1400°C, BCLTS ceramics exhibited an anomalies peak at a temperature around 60°C as seen in Figure 6 (c, d). However, the specific phase transition remains undetermined, necessitating further investigation. When the sintering temperature was increased from 1350°C to 1400°C, the dielectric constant (ϵ_r) and dielectric loss ($\tan \delta_r$) at room temperature increased from 2320 to 3047 and from 0.006 to 0.029, respectively, measured under a frequency of 1 kHz. After that, both values decreased as listed in Table 2. The degradation of the dielectric properties of the BCLTS ceramics, sintered at raised temperatures, was attributed to enhanced electrical conductivity resulting from porosity, as supported by SEM results (Kornphom *et al.*, 2016).

The room temperature P-E hysteresis loops of BCLTS ceramics fabricated with different sintering temperatures (1350-1450°C) under the applied electric field of 50 kV/cm and 1 Hz are shown in Figure 7. All the P-E hysteresis curves exhibited well-formed loops and showed typical ferroelectric properties. The coercive field (E_c) decreased from 2.47 to 1.04 kV/cm when the sintering temperature was increased to 1400°C and then increased again to 1.29 and 1.59 kV/cm at the sintering temperatures of 1425, 1450°C, respectively. The maximum polarization (P_{max}) tended to increase from 8.28 to

9.52 $\mu\text{C}/\text{cm}^2$ as the sintering temperature increased from 1350 to 1400°C, and then dropped as listed in Table 2. Due to the differing phase structure of this research from previous studies, the dielectric and ferroelectric properties yield distinct results.

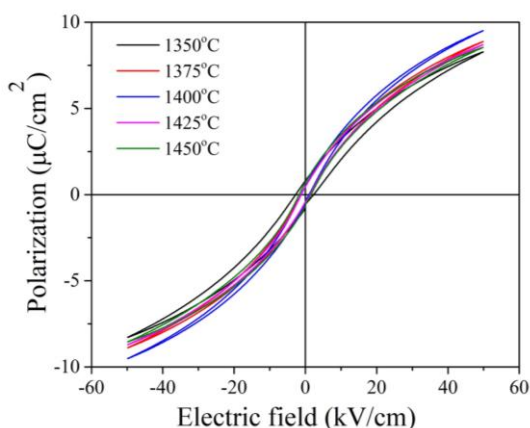


Figure 7. The polarization-electric field (P-E) hysteresis loops of the BCLTS ceramics produced with difference sintering temperatures under an electric field of 50 kV/cm.

Conclusions

The BCLTS lead-free ceramics have been prepared via the solid state combustion method. XRD analysis showed all BCLTS powders to exhibit a perovskite structure, with a pure perovskite phase obtained at calcination temperatures above 1150°C. All BCLTS ceramic samples exhibited a pure perovskite phase structure, with the remarkable exception of those sintered at 1450°C. Coexisting cubic and tetragonal phases were observed in all BCLTS ceramics. With an increase in sintering temperature, the tetragonal phase increased. The maximum values for the density, dielectric constant and P_{max} were observed at the sintering temperature of 1400°C, with values of 4.06 g/cm³, 3047, and 9.52 $\mu\text{C}/\text{cm}^2$, respectively.

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