

EVOLUTION OF PHASE FORMATION, MICROSTRUCTURE, AND ELECTRICAL PROPERTIES OF $\text{BaTi}_{0.91}\text{Sn}_{0.09}\text{O}_3$ LEAD-FREE CERAMICS FOR DIFFERENT CALCINATION AND SINTERING TEMPERATURES

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Abstract

Lead-free $\text{BaTi}_{0.91}\text{Sn}_{0.09}\text{O}_3$ (BTS) ceramics were fabricated by the conventional solid-state reaction method. The evolution of phase, microstructure, dielectric, and ferroelectric properties of BTS powders and ceramics was examined at different calcination (1175°C-1250°C for 4 h.) and sintering (1375°C-1450°C for 2 h.) temperatures. X-ray diffraction (XRD) revealed that the calcined powders had perovskite structures, with a secondary BaSnO_3 impurity phase when calcined below 1200°C. The BTS ceramics displayed a secondary $\text{Ti}_{0.85}\text{Sn}_{0.15}\text{O}_2$ phase at a sintering temperature of 1375°C, while no impurity phases were detected at 1400-1450°C. Rietveld refinement indicated coexisting orthorhombic (O), tetragonal (T), and cubic (C) phases in all samples. The O phase increased with sintering temperatures up to 1425°C before decreasing, while the T and C phases decreased for sintering temperatures up to 1425°C before increasing. When the sintering temperature increased from 1375°C to 1425°C, the density, dielectric constant at the Curie temperature (ϵ_c), and maximum polarization (P_{max}) increased from 5.90 to 5.98 g/cm³, 9,533 to 12,538 and 15.07 to 15.36 $\mu\text{C}/\text{cm}^2$, respectively, before decreasing. In contrast, the dielectric loss ($\tan \delta$), remanent polarization (P_r), and coercive electric field (E_c) decreased from 0.036 to 0.020, 8.42 to 7.48 $\mu\text{C}/\text{cm}^2$, and 3.49 to 1.86 kV/cm, respectively, when the sintering temperature increased from 1375°C to 1425°C, before slightly increasing. The BTS ceramic sintered at 1425°C showed the highest density, a well-packed microstructure, superior dielectric properties, and high P_{max} . The increased orthorhombic phase content reduced P_r and E_c , making this ceramic suitable for dielectric capacitor applications.

Keywords: Phase Evolution; Microstructure; Rietveld Refinement; Ferroelectric Properties

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Introduction

Barium titanate (BaTiO₃-based) were the first ferroelectric and piezoelectric ceramics to be developed. They are widely used in applications such as actuators, sensors, ultrasonic transducers, resonators, filters, and dielectric capacitors, owing to their high piezoelectric properties ($d_{33} \sim 200$ pC/N) and excellent dielectric constant ($\epsilon_C \sim 6000$ at the Curie temperature) (Jaffe, 1958; Haertling, 1999; Ma *et al.*, 2018; Chen *et al.*, 2020; Jiang *et al.*, 2021). However, these ceramics exhibit a relatively low dielectric constant at room temperature ($\epsilon_R \sim 2500$) (Sareecha *et al.*, 2017; Akbarzadeh *et al.*, 2018).

The properties of BaTiO₃ ceramics can be significantly enhanced by tuning the phase ratio and microstructure through ion substitution or adjusting the processing conditions (Kornphom and Bongkarn, 2014; Canu *et al.*, 2018; Hoshina *et al.*, 2018; Sharma *et al.*, 2022). Substituting ions at the B-site of BaTiO₃ ceramics (Xu and Li, 2020; Zhang *et al.*, 2021) has shown significant improvement, as structural changes caused by replacing ions with different radii increases the electrical response. Recently, the substitution of Sn⁴⁺ at the B-site, reported by S. Marković *et al.* (Marković *et al.*, 2007), structure and increased the dielectric constant from 6500 to 7500 when Sn⁴⁺ substitution increased from 7 to 10 mol%. Furthermore, W. Liu *et al.* (Liu *et al.*, 2017) reported that BaTi_{0.91}Sn_{0.09}O₃ (BTS) ceramics synthesized using the conventional solid-state reaction method displayed coexisting tetragonal and orthorhombic phases with a high piezoelectric coefficient ($d_{33} \sim 920$ pC/N). However, BTS ceramics have several drawbacks, including a high dielectric loss and low density. Further development is needed to enhance their electrical properties and expand their potential applications. Furthermore, detailed information on the correlation between the phase ratio, microstructure, and electrical properties of BTS ceramics are currently lacking in the literature.

It is well-known that the firing process plays a crucial role in ceramic production, significantly affecting the product's strength, durability, density, and shape. When performed optimally, it enhances the desired properties of the ceramics (Panya and Bongkarn, 2009; Wu *et al.*, 2012; Kornphom *et al.*, 2018; Yotthuan *et al.*, 2020). In this work, we fabricated BTS ceramics with different calcination and sintering temperatures by the conventional solid-state reaction method. We then examined the evolution and correlation of the phase formation, microstructure, and dielectric and ferroelectric properties of BaTi_{0.91}Sn_{0.09}O₃ ceramics.

Experimental Procedure

BaTi_{0.91}Sn_{0.09} (BTS) ceramics were synthesized via the solid-state reaction method. High purity oxide and carbonate powders of BaCO₃ (99.0%, HiMedia, IN), TiO₂ (99%, KemAus, AU), and SnO₂ (99.9%, Aldrich, MX) were used as starting materials. The raw components were weighed to the appropriate stoichiometry and mixed in a ball mill using zirconia balls and ethanol for 24 h. The suspensions were dried at 120°C and then calcined at temperatures from 1175 to 1250°C for 4 h. with a heating rate of 5°C/min and allowed to cool down naturally. The calcined BTS powders were mixed with 3 wt% polyvinyl alcohol (PVA) binder solution and re-milled in ethanol for 24 h. The powders were then dried, sieved, and pressed into pellets with a diameter of 15 mm and a thickness of 1.5 mm under 80 MPa pressure. After burning off the PVA, the BTS pellets were sintered at temperatures from 1375°C to 1450°C for 2 h. (with a heating rate of 5°C/min and allowed to cool down naturally).

X-ray diffraction (XRD, BRUKER, D2 Phaser) and the Rietveld refinement method were employed to investigate the phase evolution of the samples. The surface morphologies were examined using a Field Emission Scanning Electron Microscope (FESEM, Thermo Fisher Scientific, Apreo S). The ceramics were polished with sandpaper and an alumina abrasive to prepare the samples for FE-SEM imaging. For the observation of grain boundaries, the ceramics were thermally etched for 20 minutes at 100°C below the sintering temperature, with a heating rate of 5°C/min and a natural cooling rate. The ceramic densities were determined using the Archimedes method with distilled water as the medium. To measure the electrical properties, silver paint was applied to both surfaces of the ceramics, which were then fired at 550°C for 20 minutes (with a heating rate of 5°C/min and allowed to cool naturally). The temperature-dependent dielectric properties were measured using an LCR meter (HP, 4284A) at 1, 10, and 100 kHz over a temperature range of 35°C - 180°C. The polarization-electric field (P-E) hysteresis loops were evaluated using a computer-controlled modified Sawyer-Tower circuit (Radiant, PLC2-The P-E loop).

Results and Discussion

The X-ray diffraction patterns (XRD) of BTS powders, calcined at temperatures between 1175°C and 1250°C for 4 h., are shown in Figure 1. The XRD peaks of all calcined BTS powders showed characteristics of a perovskite structure corresponding to JCPDS files No. 01-075-1608, 00-003-0725, and 00-031-0174. A secondary phase of BaSnO₃ (JCPDS No. 00-015-0780) was detected for calcination temperatures of 1175°C and 1200°C. The ceramics showed a pure perovskite structure when the calcination temperature increased to 1225°C and 1250°C. The percentage of the perovskite phase in the calcined BTS powders can be estimated using the following equation:

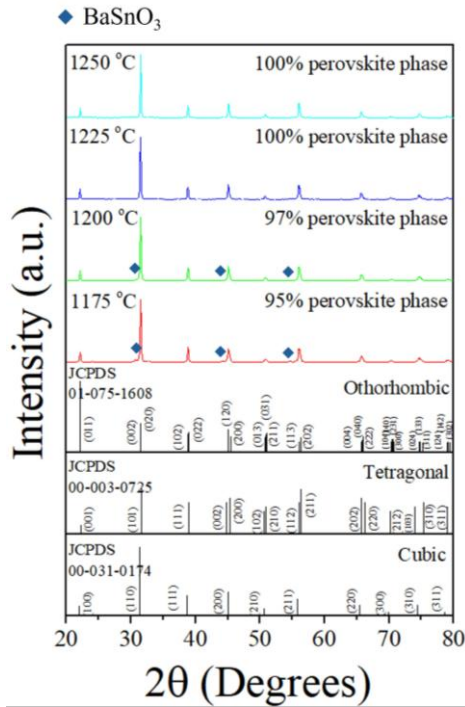


Figure 1. XRD pattern of the BTS powders calcined at temperatures ranging from 1175°C to 1250°C for 4 h.

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

In equation (1), $I_{\text{perovskite}}$ refers to the highest intensity of the BTS perovskite peak, around 32°, while I_{BaSnO_3} represents the highest intensity of the BaSnO₃ impurity phase in the XRD pattern. It was observed that the percentage of the perovskite phase in the BTS powders increased from 95% to 100% when the calcination temperature increased from

1175°C to 1250°C, as shown in Figure 1. Consequently, the optimal BTS powders for synthesizing BTS ceramics were those with the highest perovskite phase content and intensity, obtained by calcining at 1225°C for 4 h.

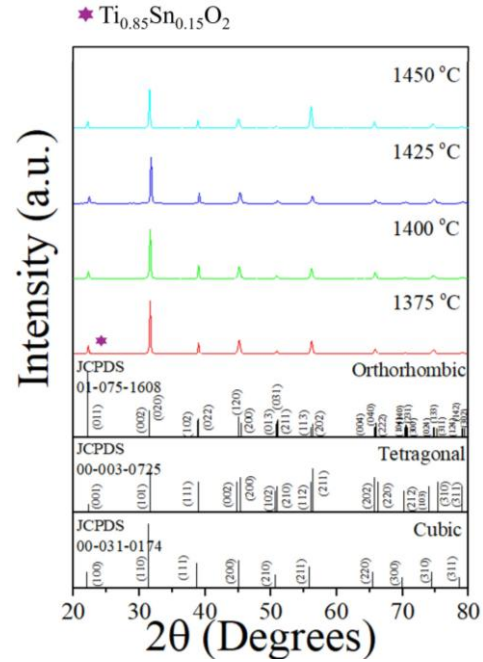


Figure 2. XRD patterns of BTS ceramics sintered at temperatures ranging from 1375°C to 1450°C for 2 h.

Figure 2 presents the XRD patterns of BTS ceramics sintered at temperatures ranging from 1375°C to 1450°C for 2 h. All ceramics exhibited a typical perovskite structure. The secondary phase of $\text{Ti}_{0.85}\text{Sn}_{0.15}\text{O}_2$ was detected in the ceramic sintered at 1375°C, as shown in Figure 2. However, no impurity phases were observed in the BTS ceramics sintered between 1400°C and 1450°C (Figure 2). The phases of all ceramics were consistent with JCPDS files No. 01-075-1608, 00-003-0725, and 00-031-0174, corresponding to the orthorhombic, tetragonal, and cubic phases, respectively.

To investigate the phase formation, the Rietveld refinement technique was applied to all sintered samples using Fullprof software to fit the XRD data. Initial reference values for the cell parameters, lattice constants, space groups, and atomic positions were obtained from the Crystallography Open Database (COD). Structural models based on the BTS composition, including orthorhombic (O), tetragonal (T), and cubic (C) phases with space groups $\text{Amm}2$, P4mm , and

$Pm3m$, respectively, were used as starting models to fit the XRD patterns of the BTS ceramics. The background was modeled using a Chebyshev polynomial function, and the peak profile was fit by a pseudo-Voigt function, a linear combination of Lorentzian and Gaussian functions (Sindhu *et al.*, 2012). The numerical criteria used to assess the quality of the fits were R_p (profile reliability), R_{wp} (weighed pattern reliability), R_{exp} (anticipated residual), and χ^2 (goodness of fit). Figure 3 (a)-(d) shows examples of the final output from the

Rietveld refinement. The calculated quality values, $R_p \leq 17.8\%$, $R_{wp} \leq 22.10\%$, $R_{exp} \leq 13.47\%$, and $\chi^2 \leq 3.48$ (Table 1), suggest good agreement between the observed and refined intensity profiles for all compositions. The refinement results revealed that all sintered samples exhibited coexisting O, R, and C phases. When the sintering temperature increased from 1375°C to 1425°C, the proportion of the O phase increased and then decreased, while the proportions of the T and C phases decreased and then increased (see Table 1).

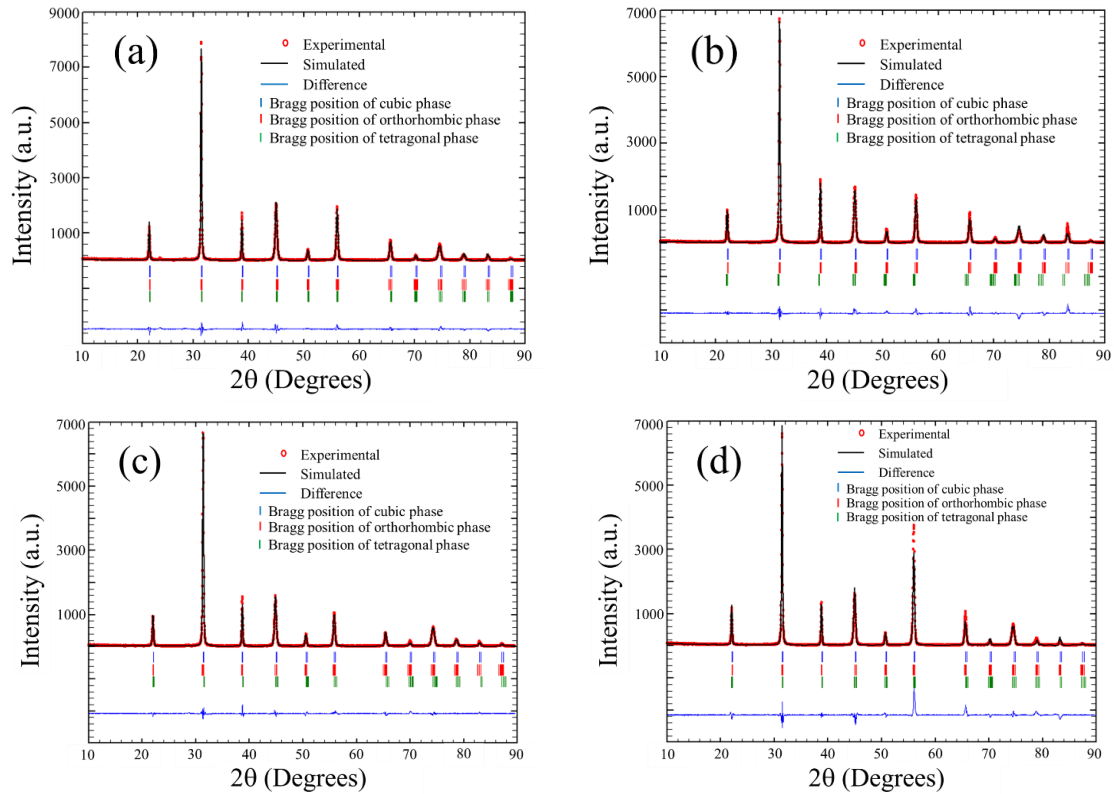


Figure 3. Typical Rietveld refinement analysis for BTS ceramics sintered with different temperatures: (a) 1375°C, (b) 1400°C, (c) 1425°C, and (d) 1450°C

Table 1. Goodness of fit and quality values, lattice parameters, and phase percentages for BTS ceramics as a function of sintering temperature

Sintering temperature (°C)	Refine parameters	Phase structures	Profile parameters	Atoms information					The percentage of phase
				Label	x	y	z	Occ.	
1375	$\chi^2=1.87$ $R_p=12.8\%$ $R_{wp}=16.9\%$ $R_{exp}=12.35\%$	<i>Pm3m</i>	$a=b=c=$ 4.01757Å $u=0.04059$ $v=0.00009$ $w=0.00476$	Ba1	0.00000	0.00000	0.00000	1.08614	30
				Ti1	0.50000	0.50000	0.50000	0.86076	
				Sn1	0.50000	0.50000	0.50000	0.08850	
				O1	0.00000	0.50000	0.50000	1.78039	
		<i>Amm2</i>	$a=4.01101\text{Å}$ $b=5.70982\text{Å}$ $c=5.68482\text{Å}$ $u=0.31447$ $v=-0.08571$ $w=0.02724$	Ba1	0.00000	0.00000	0.00000	1.00536	37
				Ti1	0.50000	0.00000	0.51700	0.91636	
				Sn1	0.50000	0.00000	0.51700	0.08972	
				O1	0.00000	0.00000	0.48900	0.75399	
		<i>P4mm</i>	$a=4.01627\text{Å}$ $c=4.02904\text{Å}$ $u=-0.71856$ $v=1.62097$ $w=-0.13849$	Ba1	0.00000	0.00000	0.00000	0.99547	33
				Ti1	0.50000	0.50000	0.48200	1.45802	
				Sn1	0.50000	0.50000	0.48200	0.09245	
				O1	0.50000	0.50000	0.01600	0.58263	
1400	$\chi^2=2.27$ $R_p=14.9\%$ $R_{wp}=19.2\%$ $R_{exp}=12.71\%$	<i>Pm3m</i>	$a=b=c=4.01576\text{Å}$ $u=0.03653$ $v=-0.00596$ $w=0.01707$	Ba1	0.00000	0.00000	0.00000	0.84906	24
				Ti1	0.50000	0.50000	0.50000	0.71935	
				Sn1	0.50000	0.50000	0.50000	0.08587	
				O1	0.00000	0.50000	0.50000	1.35823	
		<i>Amm2</i>	$a=4.01264\text{Å}$ $b=5.70511\text{Å}$ $c=5.68319\text{Å}$ $u=0.42789$ $v=-0.04462$ $w=0.01759$	Ba1	0.00000	0.00000	0.00000	0.92917	45
				Ti1	0.50000	0.00000	0.51700	0.49670	
				Sn1	0.50000	0.00000	0.51700	0.08889	
				O1	0.00000	0.00000	0.48900	2.87755	
		<i>P4mm</i>	$a=4.061172\text{Å}$ $c=4.02661\text{Å}$ $u=-1.24470$ $v=1.98842$ $w=-0.24820$	Ba1	0.00000	0.00000	0.00000	1.02508	31
				Ti1	0.50000	0.50000	0.48200	1.05520	
				Sn1	0.50000	0.50000	0.48200	0.09185	
				O1	0.50000	0.50000	0.01600	0.65355	
1425	$\chi^2=1.47$ $R_p=11.8\%$ $R_{wp}=16.3\%$ $R_{exp}=13.47\%$	<i>Pm3m</i>	$a=b=c=4.03042\text{Å}$ $u=0.15940$ $v=0.01387$ $w=0.00110$	Ba1	0.00000	0.00000	0.00000	1.06972	20
				Ti1	0.50000	0.50000	0.50000	0.98915	
				Sn1	0.50000	0.50000	0.50000	0.27250	
				O1	0.00000	0.50000	0.50000	1.21607	
		<i>Amm2</i>	$a=4.02995\text{Å}$ $b=5.73446\text{Å}$ $c=5.69920\text{Å}$ $u=0.22065$ $v=-0.00514$ $w=0.02671$	Ba1	0.00000	0.00000	0.00000	0.87710	56
				Ti1	0.50000	0.00000	0.51700	0.37436	
				Sn1	0.50000	0.00000	0.51700	0.11563	
				O1	0.00000	0.00000	0.48900	2.36373	
		<i>P4mm</i>	$a=4.01116\text{Å}$ $c=4.03773\text{Å}$ $u=-1.65725$ $v=1.96058$ $w=-0.17124$	Ba1	0.00000	0.00000	0.00000	1.19212	24
				Ti1	0.50000	0.50000	0.48200	1.05551	
				Sn1	0.50000	0.50000	0.48200	0.09967	
				O1	0.50000	0.50000	0.01600	1.00841	
1450	$\chi^2=3.48$ $R_p=17.8\%$ $R_{wp}=22.1\%$ $R_{exp}=11.86\%$	<i>Pm3m</i>	$a=b=c=4.01745\text{Å}$ $u=0.01061$ $v=0.02625$ $w=0.00865$	Ba1	0.00000	0.00000	0.00000	0.81641	29
				Ti1	0.50000	0.50000	0.50000	0.99069	
				Sn1	0.50000	0.50000	0.50000	0.09367	
				O1	0.00000	0.50000	0.50000	2.00290	
		<i>Amm2</i>	$a=4.01390\text{Å}$ $b=5.69252\text{Å}$ $c=5.70168\text{Å}$ $u=0.12557$ $v=-0.07641$ $w=0.02453$	Ba1	0.00000	0.00000	0.00000	1.17014	27
				Ti1	0.50000	0.00000	0.51700	0.94914	
				Sn1	0.50000	0.00000	0.51700	0.09074	
				O1	0.00000	0.00000	0.48900	6.54707	
		<i>P4mm</i>	$a=4.00827\text{Å}$ $c=4.03516\text{Å}$ $u=-0.50839$ $v=0.82677$ $w=-0.10944$	Ba1	0.00000	0.00000	0.00000	0.65271	44
				Ti1	0.50000	0.50000	0.48200	0.99945	
				Sn1	0.50000	0.50000	0.48200	0.08662	
				O1	0.50000	0.50000	0.01600	4.09989	
				O2	0.50000	0.00000	0.51500	4.17585	

Figure 4 (a)-(d) presents the FE-SEM images of the microstructure of BTS ceramics sintered with different temperatures. The ceramic grains had a non-uniform distribution and irregular shapes. At a sintering temperature of 1375°C, the ceramics exhibited unclear grain boundaries, small grain sizes, and numerous pores (Figure 4(a)). When the sintering temperature increased to 1400°C, the grain boundaries remained unclear, but the grain size increased significantly, and the porosity decreased (Figure 4(b)). At 1425°C, the sample showed clear grain boundaries, large grain sizes, and minimal porosity (Figure 4(c)). However, at 1450°C, the grain boundaries began to melt, causing a decrease in grain size and an increase in porosity (Figure 4(d)). The increase in grain size with higher temperatures can be attributed to the enhanced driving force at the grain boundaries during heating, promoting continuous grain growth (Kang, 2004). However, at higher sintering temperatures ($\geq 1450^\circ\text{C}$), excessive heat damaged the grain boundaries, leading to a reduction in grain size and increased porosity. The density of BTS ceramics increased from 5.90 g/cm³ to 5.98 g/cm³ as the sintering temperature rose from 1375°C to 1425°C and then dropped, as shown in Table 2.

The temperature dependence of the permittivity (ϵ) and dielectric loss ($\tan \delta$) of the BTS ceramics, measured at frequencies of 1, 10, and 100 kHz over the temperature range of 35°C-180°C, are shown in Figure 5 (a)-(d). It was observed that the dielectric constant of all BTS samples decreased as the frequency increased from 1 kHz to 100 kHz. This decrease is attributed to reduced space charge polarization effects (Rayssi *et al.*, 2018). The BTS ceramics exhibited a dielectric anomaly corresponding to the ferroelectric to the cubic paraelectric phase transition (T_C) (Liu *et al.*, 2017). As the sintering temperature increased from 1375°C to 1450°C, T_C ranged from 44.5°C to 47.2°C, as shown in Table 2. When the sintering temperature increased from 1375°C to 1425°C, the dielectric constant at T_C (ϵ_C) increased from 9533 to 12538, while the dielectric loss at T_C ($\tan \delta$) decreased from 0.036 to 0.020. This result may be due to a well-developed microstructure and the highest density sample (Bongkarn *et al.*, 2009). However, the dielectric properties degraded when the sintering temperature increased to 1450°C

Table 2. Density, dielectric, and ferroelectric properties of BTS ceramics sintered at different temperatures

Sintering Temperature (°C)	Density (g/cm ³)	T_C (°C)	ϵ_C	$\tan \delta$ at T_C	P_r ($\mu\text{C}/\text{cm}^2$)	$P_{\max}$ ($\mu\text{C}/\text{cm}^2$)	E_c (kV/cm)
1375	5.90	46.3	9533	0.036	8.42	15.07	3.49
1400	5.95	44.5	10919	0.027	8.14	15.20	2.12
1425	5.98	46.7	12538	0.020	7.48	15.36	1.86
1450	5.86	47.2	10375	0.022	7.96	15.31	2.15

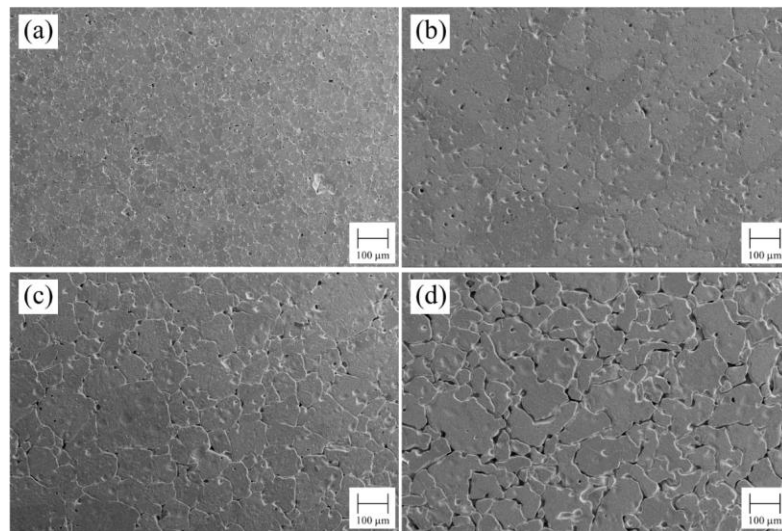


Figure 4. SEM images of BTS ceramics sintered with different temperatures: (a) 1375°C, (b) 1400°C, (c) 1425°C, and (d) 1450°C

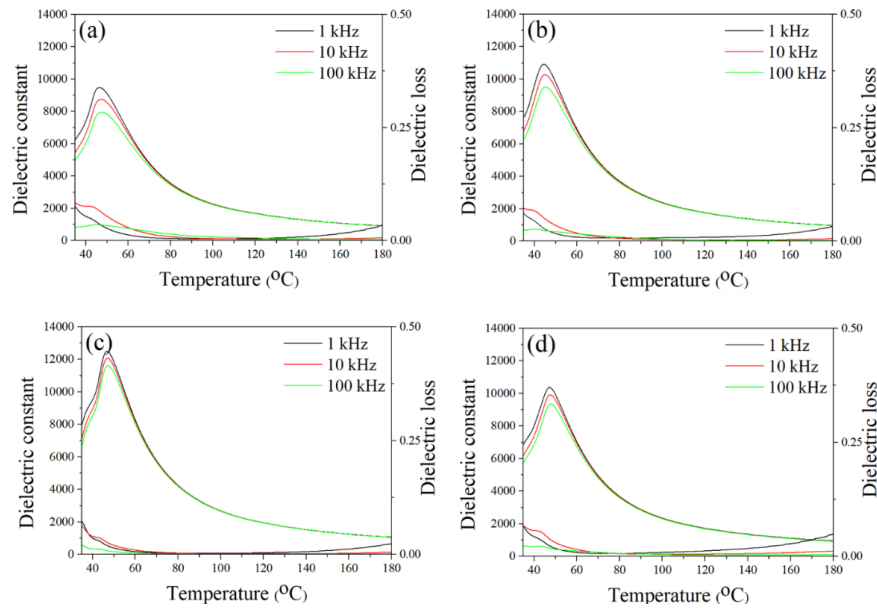


Figure 5. Temperature dependence of the dielectric constant (ϵ) and dielectric loss ($\tan\delta$) of the BTS ceramics, measured at the frequencies of 1, 10, and 100 kHz, fabricated with sintering temperatures of (a) 1375°C, (b) 1400°C, (c) 1425°C, and (d) 1450°C

Figure 6 presents the polarization-electric field (P - E) hysteresis loop of the BTS ceramics measured under a 40 kV/cm electric field at a frequency of 1 Hz. All ceramics exhibited saturated P - E hysteresis loops. As the sintering temperature increased from 1375°C to 1425°C, the maximum polarization (P_{max}) of BTS ceramics increased from 15.07 to 15.36 $\mu\text{C}/\text{cm}^2$, then dropped, while the remanent polarization (P_r) and coercive electric field (E_c) decreased from 8.42 to 7.48 $\mu\text{C}/\text{cm}^2$ and from 3.49 to 1.86 kV/cm, respectively, before increasing again, as shown in Table 2. The P_{max} value is strongly related to the dielectric constant, so increasing the dielectric constant increases the P_{max} value (Li *et al.*, 2020). Meanwhile, the decrease in P_r and E_c is linked to the phase structure. In the orthorhombic phase, the lower symmetry makes it harder to align the polarization, reducing P_r as the orthorhombic content increases. This also lowers E_c , as a lower electric field is needed to switch the polarization direction, as shown in Table 1 (Weng, 2009).

The results indicated that the optimal sintering temperature for BTS ceramics is 1425°C. At this temperature, the ceramics exhibited the highest density, well-packed microstructure, superior dielectric properties, and high P_{max} . The results from this study were better than those reported by Marković *et al.* (Marković *et al.*, 2007) for $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ ceramics. This could be due to the presence of three phases (orthorhombic, tetragonal,

and cubic), while $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ only exhibited two phases (tetragonal and cubic). Additionally, the increased orthorhombic phase content reduced the P_r and E_c of the ceramic, making them suitable for dielectric capacitor applications.

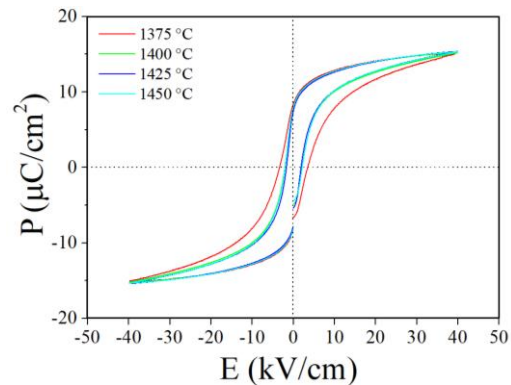


Figure 6. Plot of electric polarization versus electric field for BTS ceramics measured under an electrical field of 40 kV/cm

Conclusions

In this study, BTS ceramics with good dielectric characteristics were produced with the solid-state reaction method. A calcination temperature of 1225°C for 4 h. produced pure perovskite phase

BTS powders. The phase evolution, morphology, density, and electrical properties were examined. Rietveld refinement confirmed that the BTS ceramics had coexisting orthorhombic (O), tetragonal (T), and cubic (C) phases. The percentage of the O phase increased as sintering temperatures increased from 1375°C to 1425°C, then decreased. Meanwhile, the percentage of T and C phases decreased as the sintering temperature increased from 1375°C to 1425°C and then increased. The dielectric constant at T_C (ϵ_C) and maximum polarization (P_{max}) increased from 9533 to 12538 and from 15.07 to 15.36 $\mu\text{C}/\text{cm}^2$, respectively, as sintering temperatures increased from 1375°C to 1425°C and then dropped. The dielectric loss ($\tan \delta$), remnant polarization (P_r), and coercive field (E_c) of the BTS ceramics decreased as the sintering temperature increased from 1375 to 1425°C, and then increased. The results indicate that firing condition affects the phase evolution, microstructure and density, which in turn play an important role in the dielectric and ferroelectric properties of BTS ceramics.

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