

PHASE FORMATION, MICROSTRUCTURE AND ELECTRIC PROPERTIES OF La^{3+} SUBSTITUTION IN B-SITE OF LEAD-FREE $\text{BaTi}_{0.91}\text{Sn}_{0.09}\text{O}_3$ CERAMICS

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Abstract

The study explored the influence of La^{3+} substitution at the B-site in $\text{BaTi}_{0.91}\text{Sn}_{0.09}\text{O}_3$ (BTS) ceramics on their phase structure, microstructure, and electrical characteristics. La^{3+} -doped BTS ceramics, denoted as $\text{Ba}(\text{Ti}_{0.91}\text{Sn}_{0.09})_{1-x}\text{La}_x\text{O}_3$ (BTSL) with $x = 0, 0.005, 0.010, 0.015$, and 0.020 , were synthesized via the conventional solid-state reaction method. The calcination and sintering processes were carried out at 1200°C for 2 hours and $1400\text{--}1450^\circ\text{C}$ for 4 hours, respectively. Results indicated that the undoped BTSL sample ($x = 0$) exhibited a pure perovskite phase without detectable impurities. However, when x ranged from 0.005 to 0.020 , secondary impurity phases were observed alongside the perovskite structure. Phase analysis revealed that BTSL ceramics consisted of orthorhombic (O) and tetragonal (T) phases for $x = 0\text{--}0.005$, transitioned to a presence of O, T, and cubic (C) phases at $x = 0.010\text{--}0.015$, and exhibited only the C phase at $x = 0.020$. Rietveld refinement confirmed that La^{3+} occupied both A- and B-sites for compositions with $x \geq 0.005$. As La^{3+} concentration increased, the average grain size and remnant polarization initially showed a slight reduction ($x = 0$ to 0.005) before significantly decreasing ($x = 0.010$ to 0.015). The Curie temperature (T_c) was 43°C for $x = 0$, slightly increased to 44°C for $x = 0.005$, and then greatly decreased as x increased to 0.020 .

Keywords: Dielectric; Ferroelectric; Phase Formation; Rietveld Refinement

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Introduction

BaTiO₃ ceramics were the first ferroelectric and piezoelectric ceramics to be developed for commercial applications and are still widely used today. The understanding of ferroelectricity and piezoelectricity in BaTiO₃, as described by Jaffe *et al.* (Jaffe, 1971) and Haertling (Haertling, 1999), led to the development of new ferroelectric materials with the perovskite structure (ABO₃). BaTiO₃ ceramics exhibit excellent piezoelectric coefficient ($d_{33} \sim 200$ pC/N) and high dielectric constant at the Curie temperature ($\epsilon_C \sim 6000$) (Akbarzadeh *et al.*, 2018; Ma *et al.*, 2018; Chen *et al.*, 2020; Jiang *et al.*, 2021). However, they have a low Curie temperature ($T_C \sim 120^\circ\text{C}$) and low dielectric constant at room temperature ($\epsilon_R \sim 2500$) (Sareecha *et al.*, 2017; Lai *et al.*, 2020).

Previous studies have demonstrated that improving the electrical properties of BaTiO₃ ceramics can be achieved through chemical structural modifications, such as substituting ions in the perovskite structure. For example, substitution of ions like Zr⁴⁺, Ho⁴⁺, and Sn⁴⁺ in the B-site of BiTaO₃ have shown significant electrical improvements (Marković *et al.*, 2007; Liu *et al.*, 2017; Khalf and Hall, 2018; Xu and Li, 2020; Zhang *et al.*, 2021). Recently, S. Markovic *et al.* (Marković *et al.*, 2007) reported on the substitution of Sn⁴⁺ ions in the B-site of BaTiO₃ ceramics (BaTi_{1-x}Sn_xO₃; BTS), which resulted in a coexistence of tetragonal and cubic phases and a dielectric constant ranging from 6500 to 7500 as the Sn⁴⁺ concentration increased from 7 to 10 mol%. Additionally, W. Liu *et al.* (Liu *et al.*, 2017) reported on BaTi_{0.91}Sn_{0.09}O₃ (BTS) ceramics, which exhibited a coexisting structure with tetragonal and orthorhombic phases and a high piezoelectric coefficient ($d_{33} \sim 920$ pC/N). However, these BTS ceramics had a low Curie temperature ($T_C \sim 55^\circ\text{C}$) and low density, and other features were also inadequate, indicating a need for further improvement.

Moreover, in order to improve the physical and electrical properties of BaTiO₃ ceramics, acceptor doping or doping of ions with a valence state less than the host ion in the ABO₃ structure has been employed (Bobade *et al.*, 2009; Wang *et al.*, 2016; Buscaglia *et al.*, 2021). Acceptor doping has been found to generate oxygen vacancies and affect features such as grain size, density, Curie temperature (T_C), and electrical properties (Alshoaibi, 2017; Buscaglia *et al.*, 2021). For example, S.M. Bobade *et al.* (Bobade *et al.*, 2009) fabricated Al³⁺ and Ga³⁺ substitution of BaTiO₃ ceramics, showing an increase in T_C and relative density from 130 to 140 °C and 94% to 96%,

respectively, with an increase in Al³⁺ from 0.02 to 0.04 mol%. Meanwhile, the dielectric constant and activation energy decreased with Al³⁺ doping, while they increased with Ga³⁺ doping (6669 to 8566 and 0.25 to 0.43 eV, respectively) as Ga³⁺ increased from 0.02 to 0.04 mol%. Xin Wang *et al.* (Wang *et al.*, 2016) reported the substitution of Y³⁺ in BaTiO₃ (BaTi_{1-x}Y_xO_{3-x/2}; BTY) ceramics, which resulted in an increase in T_C temperature due to the lattice strain caused by a large mismatch of ionic radius between Y³⁺ and Ti⁴⁺. Additionally, Y³⁺ doping was found to restrain oxygen loss. The BTY ceramic exhibited a large electric field-induced strain (0.27%) at an electric field of 65 kV/cm when $x = 0.015$. Furthermore, lanthanum (La³⁺) ion is known to improve the properties of BaTiO₃ ceramics (Morrison *et al.*, 2001; Zechao *et al.*, 2022). Therefore, it is expected that acceptor doping into the B-site of BaTiO₃ ceramics by La³⁺ substitution would enhance its properties. In this study, we fabricated Ba(Ti_{0.91}Sn_{0.09})_{1-x}La_xO₃ (BTSL) ceramics with $x=0, 0.005, 0.010, 0.015$, and 0.020 using the conventional solid-state reaction method. We investigated the effect of B-site lanthanum substitution on the phase formation, microstructure, dielectric, and ferroelectric properties of BTS ceramics.

Experimental

Ba(Ti_{0.91}Sn_{0.09})_{1-x}La_xO₃ (BTSL) ceramics with $x = 0, 0.005, 0.010, 0.015$, and 0.020 were synthesized using the conventional solid-state reaction method. High-purity BaCO₃ (99.0%, HiMedia, IN), TiO₂ (99%, KemAus, AU), SnO₂ (99.9%, Aldrich, MX), and La₂O₃ (99.9%, Aldrich, MX) were used as starting materials. These raw materials were accurately weighed according to the required stoichiometry and mixed by ball milling with zirconia media in ethanol for 24 hours. After milling, the suspensions were dried at 120°C, and the resulting powders were calcined at 1200°C for 2 hours with a heating rate of 5°C/min, followed by natural cooling. The calcined powders were then mixed with 3 wt% polyvinyl alcohol (PVA) as a binder and further milled for 12 hours. The dried powders were sieved and subsequently pressed into pellets with a diameter of 15 mm and a thickness of 1.5 mm under a pressure of approximately 80 MPa using a hydraulic press. The PVA was removed before the pellets were sintered at temperatures ranging from 1400°C to 1450°C for 4 hours, with a heating rate of 5°C/min, followed by natural cooling.

The phase structure of BTSL ceramics was analyzed using X-ray diffraction (XRD, Philips X'Pert Pro) combined with the Rietveld refinement method. The surface morphology was examined using scanning electron microscopy (SEM, Leo1455VP). Prior to SEM observation, the ceramic samples were polished with sandpaper and alumina abrasive. To enhance the visibility of grains and grain boundaries, the polished samples underwent thermal etching at a temperature 100°C lower than the sintering temperature for 15 minutes, with a heating rate of 5°C/min, followed by natural cooling. The average grain size was determined using the linear interception method on SEM images. The bulk density of the ceramics was evaluated using the Archimedes method with distilled water as the immersion medium. For electrical property measurements, both surfaces of the ceramic samples were coated with silver paste and subsequently fired at 550°C for 20 minutes, following a heating rate of 5°C/min and natural cooling. The dielectric properties as a function of temperature were measured using an LCR meter (HP 4284A) at frequencies of 1, 10, and 100 kHz within a temperature range of 35-150°C. Additionally, the polarization-electric field (P-E) hysteresis loops were recorded using a computer-controlled modified Sawyer-Tower circuit at a frequency of 1 Hz (Radiant, PLC2-The P-E loop).

Results and Discussion

The X-ray diffraction patterns of $\text{Ba}(\text{Ti}_{0.91}\text{Sn}_{0.09})_{1-x}\text{La}_x\text{O}_3$ (BTSL) ceramics with La^{3+} doping contents ($x = 0, 0.005, 0.010, 0.015$, and 0.020) were obtained at room temperature in the 2θ range of 20-80° and are presented in Figure 1. The diffraction patterns revealed that all the BTSL ceramics exhibited perovskite structures. The BTSL ceramic with $x = 0$ showed a pure perovskite structure without any secondary impurity detected. However, the BTSL ceramics with $x = 0.005-0.015$ showed a secondary phase of La_2O_3 (JCPDS No. 01-083-1349), while the sample with $x = 0.020$ had a secondary phase of $\text{La}_2\text{O}_3 + \text{Ba}_2\text{TiO}_4$ (JCPDS No. 00-038-1481). The percentage of the perovskite phase in the BTSL ceramics was calculated using the equation (1):

$$\% \text{Perovskite} = (I_{\text{perovskite}} \times 100) / (I_{\text{perovskite}} + I_{\text{Bi}_2\text{TiO}_4} + I_{\text{La}_2\text{O}_3}) \quad (1)$$

The parameter $I_{\text{perovskite}}$ is the highest intensity of the BTSL perovskite peak at around 31°, while the parameters $I_{\text{Bi}_2\text{TiO}_4}$ and $I_{\text{La}_2\text{O}_3}$ are the highest intensities of the Bi_2TiO_4 and La_2O_3 impurity phases, respectively, in the XRD result. The results indicated that the percentage of the pure perovskite

structure in the BTSL ceramics increased from 95 to 98% as x increased from 0.005 to 0.015 and then dropped, as shown in Figure 1. These findings suggest that La^{3+} ions can be incorporated into the B-site of the $\text{BaTi}_{0.91}\text{Sn}_{0.09}\text{O}_3$ lattice to form a solid solution with a limit in solubility ($x \geq 0.005$). However, the solubility of La^{3+} ions improved as x increased to 0.010 and 0.015 before dropping. These XRD measurements were consistent with the JCPDS file numbers 01-075-1608, 00-003-0725, and 00-031-0174, which correspond to the orthorhombic, tetragonal, and cubic phases, respectively.

The ratio of the different phases (orthorhombic, tetragonal, and cubic) in BTSL ceramics was analyzed using Rietveld refinement to confirm their formation. This was done by optimizing XRD data with the Fullprof program and reference patterns from the crystallography-open database (COD). Starting models for the refining of BTSL ceramics were BaTiO_3 structures with orthorhombic, tetragonal, and cubic phases and $\text{Amm}2$, $P4mm$, and $Pm3m$ space groups, respectively. The background adjustment was generated using the Chebyshev polynomial function, while the pseudo-voigt function was used to define the profile shape adjustment (Sindhu *et al.*, 2012). The quality values, including R_p , R_{wp} , R_{exp} , and χ^2 , were used as a numerical criterion for refinement. The ceramic structure analysis of BTSL revealed that all ceramics had quality values $R_p \leq 18.30\%$, $R_{wp} \leq 22.60\%$, $R_{exp} \leq 14.31\%$, and $\chi^2 \leq 3.01$ (Table 1), indicating good agreement between the

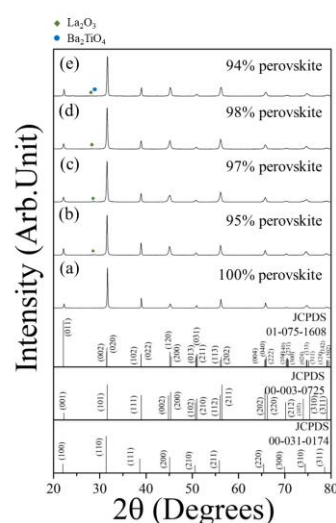


Figure 1. X-ray diffraction patterns of BTSL ceramics in the 2θ range of 20-80°; (a) $x = 0$, (b) $x = 0.005$, (c) $x = 0.010$, (d) $x = 0.015$, and (e) $x = 0.020$

Table 1. Goodness of fit, quality values, lattice parameters, atom information and phase percentage for BTSL ceramics with x = 0, 0.005, 0.010, 0.015, and 0.020

Sample	Refine parameters	Phase structures	Profile parameters	Atoms information					The percentage of phase (%)
				Label	x	y	z	Occ.	
x = 0	$\chi^2=2.37$ $R_p=18.30\%$ $R_{wp}=22.00\%$ $R_{exp}=14.31\%$	Amm2	a=4.0149 Å	Ba	0	0	0	0.8783	84
			b=5.6882 Å	Ti	0.5	0	0.5124	0.8501	
			c=5.7019 Å	Sn	0.5	0	0.5124	0.0901	
			V=130.2175 Å ³	O1	0	0	0.4874	1.3744	
			u=-0.0547	O2	0.5	0.2567	0.2485	0.8478	
			v=0.0525						
		w=0.0017							
		P4mm	a=4.3090 Å	Ba	0	0	0	0.9648	16
			c=3.9967 Å	Ti	0.5	0.5	0.482	0.9015	
			c/a=0.9275	Sn	0.5	0.5	0.482	0.0921	
			V= 68.8302 Å ³	O1	0.5	0.5	0.016	1.2877	
			u=0.0823	O2	0.5	0.5	0	0.515	
v=0.0547									
w=0.0198									
x = 0.005	$\chi^2=2.82$ $R_p=17.10\%$ $R_{wp}=21.80\%$ $R_{exp}=12.98\%$	Amm2	a= 4.01093Å,	Ba	0	0	0	1.203	79
			b= 5.71414Å,	La1	0	0	0	0.002	
			c= 5.68724Å	Ti	0.5	0	0.5124	0.795	
			V= 130.346 Å ³	Sn	0.5	0	0.5124	0.092	
			u= 0.11033	La2	0.5	0	0.5124		
			v= 0.08990	O1	0	0	0.4874		
		w= 0.00049	O2	0.5	0.2567	0.2485	2.706		
		P4mm	a= 4.02103Å,	Ba	0	0	0	0.821	21
			c= 4.02964Å,	La1	0	0	0	0.002	
			c/a=1.0021	Ti	0.5	0.5	0.482	1.032	
			V= 65.154 Å ³	Sn	0.5	0.5	0.482	0.088	
			u= -0.10700	La2	0.5	0.5	0.482	0.009	
v= 1.02852	O1		0.5	0.5	0.5	0.016			
w= 0.06345	O2	0.5	0	0.515	0.854				
x = 0.010	$\chi^2=2.53$, $R_p=14.50\%$, $R_{wp}=19.60\%$, $R_{exp}=12.29\%$	Amm2	a=4.0130 Å	Ba	0	0	0	1.025	75
			b= 5.6926 Å	La1	0	0	0	0.013	
			c=5.6730 Å	Ti	0.5	0	0.5124	0.873	
			V= 131.374Å ³	Sn	0.5	0	0.5124	0.09	
			u=0.0048	La2	0.5	0	0.5124	0.01	
			v=0.1863	O1	0	0	0	0.4874	
		w=-.01605	O2	0.5	0.5	0.2567	0.2485		
		P4mm	a= 4.0148 Å,	Ba	0	0	0	0.51	19
			c= 4.0646 Å,	La1	0	0	0	0.014	
			c/a=1.0124	Ti	0.5	0.5	0.482	0.98	
			V= 65.516 Å ³	Sn	0.5	0.5	0.482	0.072	
			u= -0.8959	La2	0.5	0.5	0.482	0.012	
v= 1.1951	O1		0.5	0.5	0.5	0.016			
w= -0.1259	O2	0.5	0	0.515	0.359				
x = 0.015	$\chi^2=2.75$, $R_p=16.00\%$, $R_{wp}=20.50\%$, $R_{exp}=12.33\%$	Amm2	a=4.0343 Å	Ba	0	0	0	0.968	6
			V= 65.660 Å ³	La1	0	0	0	0.01	
			u= -1.8698	Ti	0.5	0.5	0.5	0.829	
			v= 1.5194	Sn	0.5	0.5	0.5	0.5	
			w= 4.0343	La2	0.5	0.5	0.5	0.02	
				O1	0	0	0.5	0.5	
		P4mm	a= 4.0265Å,	Ba	0	0	0	1.025	58
			b= 5.7134Å,	La1	0	0	0	0.013	
			c= 5.7106Å	Ti	0.5	0	0.5124	0.873	
			V= 131.376 Å ³	Sn	0.5	0	0.5124	0.09	
			u= 0.0183	La2	0.5	0.5	0	0.5124	
			v= 0.1039	O1	0	0	0	0.4874	
P4mm	a= 4.0194Å,	Ba	0	0	0	0.676	28		
	c= 4.0558Å,	La1	0	0	0	0.014			
	c/a=1.0090	Ti	0.5	0.5	0.482	0.998			
	V= 65.525 Å ³	Sn	0.5	0.5	0.482	0.072			
	u= -0.7845	La2	0.5	0.5	0.482	0.012			
	v= 1.3334	O1	0.5	0.5	0.5	0.016			
w= -0.2124	O2	0.5	0	0.515	0.303				
x = 0.020	$\chi^2=3.00$, $R_p=14.90\%$, $R_{wp}=20.10\%$, $R_{exp}=11.64\%$	Pm3m	a=4.0112 Å	Ba	0	0	0	0.859	14
			V=65.767 Å ³	La1	0	0	0	0.01	
			u=0.04021	Ti	0.5	0.5	0.5	0.719	
			v=0.0074	Sn	0.5	0.5	0.5	0.5	
			w=0.0221	La2	0.5	0.5	0.5	0.5	
				O1	0	0	0.5	0.5	
		Pm3m	a=4.0177Å	Ba	0	0	0	0.894	100
			V=64.855 Å ³	La1	0	0	0	0.01	
			u= 0.4365	Ti	0.5	0.5	0.5	0.5	
			v= 0.1360	Sn	0.5	0.5	0.5	0.5	
			w= -0.0101	La2	0.5	0.5	0.5	0.02	
				O1	0	0	0.5	0.5	

observed and calculated intensity profiles. The XRD pattern of the BTSL ceramics in the range of 2θ from 20 to 90° is shown in Figure 2. The analysis revealed that ceramics with $x = 0$ and 0.005 had coexisting O and T phases, while ceramics with $x = 0.010$ -0.015 had coexisting O, T, and C phases. Ceramics with $x = 0.020$ had only C phase. The percentage of O phase decreased with increasing x , while the T phase increased from 16 to 21% with increasing x from 0 to 0.005, and then significantly decreased as listed in Table 1. B-site substitution is difficult due to the huge difference in ion radii between La^{3+} and $\text{Ti}^{4+}/\text{Sn}^{4+}$ (ion radii of La^{3+} , Ti^{4+} , and Sn^{4+} are 1.36, 0.605, and 0.69 Å, respectively), whereas A-site substitution is possible due to the

similarity in ion radii between La^{3+} and Ba^{2+} (ion radii of Ba^{2+} =1.61 Å). Therefore, the refinements needed to consider the presence of La in the A-site. The refinement results revealed the cation occupancy of La^{3+} both in the A-site and B-site with La^{3+} doping, with greater A-site occupancy when $x \geq 0.010$. In addition, F. Han *et al.* (Han *et al.*, 2016) reported that La^{3+} had strong stability in the A-site of rare earth doped BaTiO_3 ceramics due to the similarity in ion radii size.

The SEM microstructure of the polished and thermal-etched surfaces of the BTSL ceramics is shown in Figure 3. The figure shows that all the samples had ceramics with grains that were irregular in shape, non-uniformly distributed, and unequal in

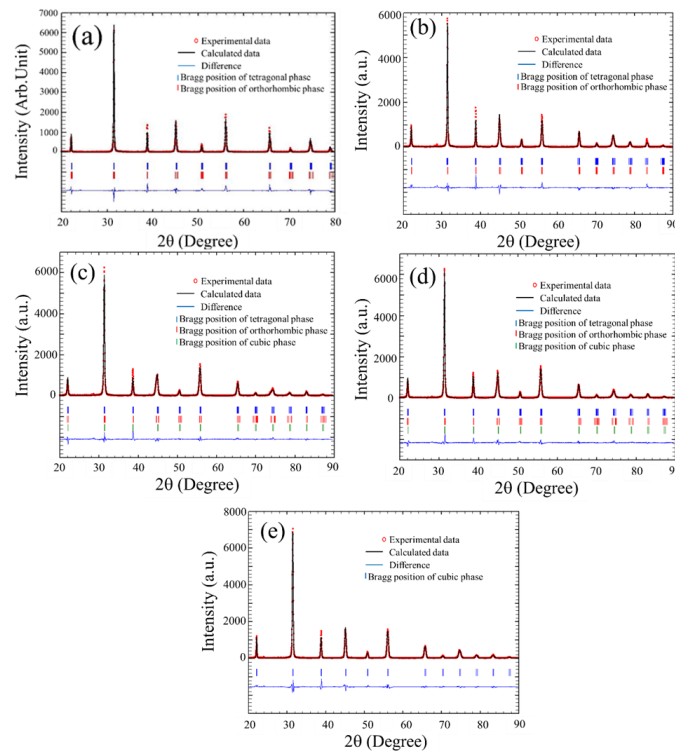


Figure 2. Typical Rietveld refinement analysis for BTSL ceramics: (a) $x = 0$, (b) $x = 0.005$, (c) $x = 0.010$, (d) $x = 0.015$ and (e) $x = 0.020$

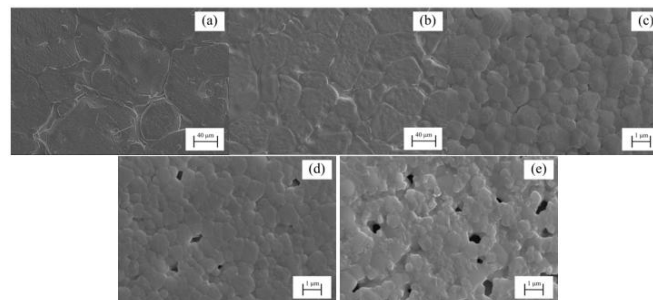


Figure 3. (a)-(e) SEM images of BTSL ceramic surfaces; (a) $x = 0$, (b) $x = 0.005$, (c) $x = 0.010$, (d) $x = 0.015$ and (e) $x = 0.020$

size. The BTSL ceramic with $x = 0$ (Figure 3(a)) had large grain size with unclear grain boundaries. However, the grain size decreased, and the grain boundaries became clearer as x increased to 0.005 (Table 2). The grain size significantly decreased (from 29.0 μm to 0.8 μm) when $x = 0.010$, but the grain boundaries remained clear. On the other hand, the BTSL ceramics with $x = 0.015$ and 0.020 had very fine grain, unclear grain boundary, and numerous pores. These observations suggest that the addition of La³⁺ inhibited grain growth. Nevertheless, the small amount of La³⁺ substituted in the B-site ($x = 0.005$) had little effect on grain size due to the oxygen vacancy existing caused by acceptor doping, which is beneficial to grain

growth. Conversely, $x \geq 0.01$ of La³⁺ doping had a major effect on grain size due to reduced oxygen vacancy, which might be due to diffusion of La³⁺ in the A-site (Buscaglia *et al.*, 2021). Furthermore, the density of the BTSL ceramics decreased with increasing x as listed in Table 2. Porosity increased with the increase of x due to grain growth inhibition, resulting in decreased density (Kang, 2004).

The temperature dependence of the dielectric constant (ϵ) and dielectric loss ($\tan \delta$) of the BTSL ceramics at 1, 10, and 100 kHz within the temperature range of 35–150 °C is presented in Figure 4. It was observed that the dielectric constant decreased with an increase in frequency. The BTSL ceramics containing $x = 0$ and 0.005 displayed

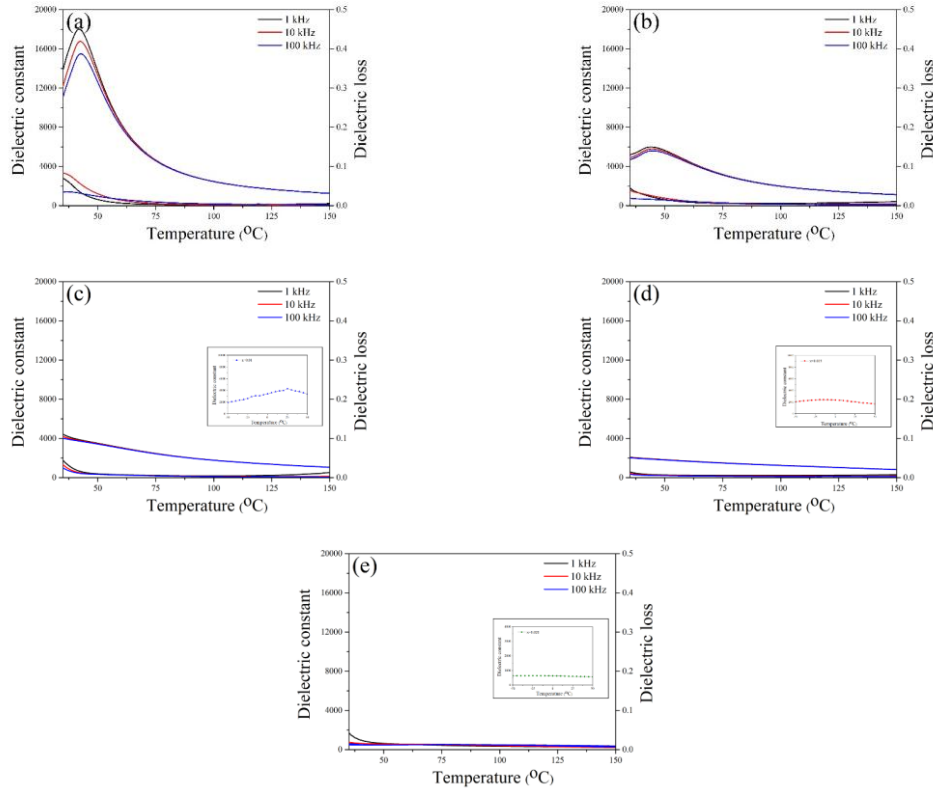


Figure 4. Temperature dependence of the dielectric constant (ϵ) and dielectric loss ($\tan \delta$) of the BTSL ceramics measured at the frequencies of 1, 10 and 100 kHz: (a) $x = 0$, (b) $x = 0.005$, (c) $x = 0.010$, (d) $x = 0.015$ and (e) $x = 0.020$. The figure inside Figure 4 (c-e) shows the dielectric constant in the -50 to 50 °C temperature range

Table 2. The average grain size, density, Curie temperature, dielectric, and ferroelectric properties of BTSL ceramics as a function of x concentration

Ba(Ti _{0.91} Sn _{0.09}) 1- x La _{x} O ₃	Average grain size (μm)	Density (g/cm ³)	T_c (°C)	ϵ_c	$\tan \delta$ at T_c	P_s ($\mu\text{C}/\text{cm}^2$)	P_r ($\mu\text{C}/\text{cm}^2$)	E_c (kV/cm)
$x = 0$	47	5.98	43	18023	0.034	14.56	7.42	1.79
$x = 0.005$	29	5.95	44	5990	0.022	12.41	5.65	3.22
$x = 0.010$	0.8	5.80	25	4293	-	10.21	1.26	1.34
$x = 0.015$	0.7	5.72	-15	2420	-	7.89	0.61	1.02
$x = 0.020$	0.6	5.66	-	-	-	2.82	1.29	7.88

a dielectric anomaly that corresponded to the cubic paraelectric phase transition (T_C) (Liu *et al.*, 2017), as listed in Table 2. The T_C values were 43°C and 44°C for the samples with $x = 0$ and 0.005, respectively. However, as the concentration of La^{3+} increased to 0.020, there was a significant decrease in the T_C values due to structural distortion (Han *et al.*, 2016). At low concentrations, the substitution of La^{3+} had a minor effect on the structural distortion, but at higher concentrations, the distortion became more pronounced, leading to a significant decrease in the T_C values. Table 2 shows the dielectric constant and dielectric loss at the T_C of the BTSL ceramics. The decrease in dielectric constant can be attributed to the decrease in density and tetragonality (Zechao *et al.*, 2022).

Furthermore, it was revealed that when x increased, the dielectric peak at T_C of the BTSL

ceramics became broader (Figure 4 (a) - (d)). This result suggested the formation of a diffuse phase transition. The diffuse phase transition can be described by the modified Curie-Weiss law following the equation (2)

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_C} = \frac{(T-T_C)^\gamma}{C} \quad (2)$$

Where ε is the temperature-dependent dielectric constant, C is the Curie-like coefficient, and γ is the degree of diffuseness. The ideal γ number is approximately one for a normal Curie-Weiss law and approximately two for a complete diffuse phase transition (Palei and Kumar, 2012). The plot of $\ln(1/\varepsilon - 1/\varepsilon_C)$ as a function of $\ln(T-T_C)$ for these ceramics at 1 kHz are shown in Figure 5 ((a)-(d)). The γ values of the BTSL ceramics with $x = 0$ -0.015 were found to increased significantly. This indicated that when x increased, the ceramics showed an increasing diffuse phase transition. This phenomenon can explain by the compositional fluctuations and cationic disorder (Zhu *et al.*, 2018).

In Figure 6, the P-E hysteresis loop of the BTSL ceramics was measured at a frequency of 1 Hz under an electric field of 30 kV/cm. The ceramics with $x = 0$ -0.015 showed saturated P-E hysteresis loops, while the ceramic with $x = 0.020$ exhibited an unsaturated loop. As x increased from 0 to 0.005, both the saturated polarization (P_s) and the remnant polarization (P_r) decreased from 14.56 to 12.41 $\mu\text{C}/\text{cm}^2$ and 7.42 to 5.65 $\mu\text{C}/\text{cm}^2$, respectively, while the coercive field (E_c) increased from 1.79 to 3.22 kV/cm (Table 2). This observation may be due to acceptor doping on the B-site, which produces oxygen vacancies, immobilizing domain motion, and making switching polarity difficult, resulting in a high coercive electric field (Jin *et al.*, 2014). As x increased from 0.010 to 0.015, P_s , P_r , and E_c decreased (Table 2). This result may be related to different ions occupying the A-site (Ba^{2+} and La^{3+}), breaking the long-range ferroelectric order and generating different domain structures (Li *et al.*, 2020). The unsaturated loop in the BTSL ceramic with $x = 0.020$ may be due to poor density and dielectric properties, resulting in the energy stored in the material being lost due to current leakage (Maraj *et al.*, 2019).

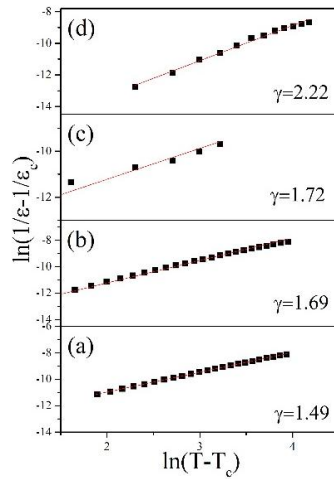


Figure 5. Plots of $\ln(1/\varepsilon - 1/\varepsilon_C)$ as a function of $\ln(T-T_C)$ at 1 kHz for the BTSL ceramics; (a) $x = 0$ (b) $x = 0.005$ (c) $x = 0.010$ and (d) $x = 0.015$

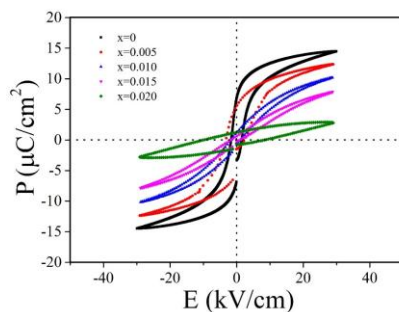


Figure 6. Plot of electric polarization against electric field of BTSL ceramics measured under an electric field of 30 kV/cm

Conclusions

The $\text{Ba}(\text{Ti}_{0.91}\text{Sn}_{0.09})_{1-x}\text{La}_x\text{O}_3$ (BTSL) ceramics with La^{3+} substitutions were synthesized using the conventional solid-state reaction method. The samples with $x = 0$ exhibited pure perovskite structures and O+T phases, whereas the ceramics

with $x \geq 0.005$ showed impurity phases. The ceramics with $x = 0-0.005$, $x = 0.010-0.015$, and $x = 0.020$ had O+T, O+T+C, and only C phases, respectively. La³⁺ was found to occupy both A- and B-sites, with greater occupancy at the A-site for $x \geq 0.010$. The substitution of La³⁺ significantly inhibited grain growth. For samples with low La³⁺ content ($x = 0.005$), La³⁺ was predominantly located at the B-site, which resulted in a slight decrease in grain size, density, and remnant polarization (P_r), as well as an increase in coercive field (E_c). Conversely, for samples with high La³⁺ content ($x \geq 0.010$), La³⁺ was mainly located at the A-site, leading to a significant decrease in grain size, density, Curie temperature (T_c), remnant polarization (P_r), and coercive field (E_c). These changes were likely caused by the reduction of oxygen vacancies and structural distortion.

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