

EFFECT OF FIRING TEMPERATURES ON THE PHASE STRUCTURE AND ELECTRICAL PROPERTIES OF BNT-BT-0.1NT CERAMICS SYNTHESIZED VIA THE SOLID-STATE COMBUSTION TECHNIQUE

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Abstract

Lead-free ceramic materials of $0.9(0.92\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-0.08\text{BaTiO}_3)-0.1\text{NaTaO}_3$ or BNT-BT-0.1NT were obtained using glycine as fuel by a solid-state combustion process. The significance of heat treatment conditions, including calcination at 600-800°C for 2 h and sintering at 1075-1175°C for 2 h, on the structure of the phase, microstructure, electrical and energy-storage properties of BNT-BT-0.1NT ceramics were performed. The perovskite phase was presented for all powder samples. BNT-BT-0.1NT powders calcined at the temperature of 750°C for 2 h showed a 100% pure perovskite phase. The particles morphology exhibited spherical shapes with a wide distribution. As the calcination temperature increased, the average particle size grew from 340 nm to 370 nm. Rietveld refinement confirmed that the BNT-BT-0.1NT ceramics possessed a uniform ABO_3 structure with cohabiting of rhombohedral (*R*), tetragonal (*T*), and cubic (*C*) phases. With a rise in sintering temperature, the average grain size expanded from 0.85 μm to 2.66 μm , while the remnant polarization (P_r) and coercive field (E_c) decreased. The samples sintered at 1150°C for 2 h, the ceramic highlighted the highest dielectric constant ($\epsilon_{\text{max}} \sim 1827$), high density of 5.83 g/cm³. Under an applied electric field of 70 kV/cm, the maximum energy storage density reached 0.71 J/cm³.

Keywords: BNT-BT-0.1NT; Energy-Storage; Ferroelectric; Combustion; Dielectric

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Introduction

Energy-storage materials are increasingly being studied because of their promise of application in electronic devices. Especially in dielectric capacitor ceramics, because they charge and discharge rapidly over a large temperature interval (Liu *et al.*, 2010). $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT) ceramics are attractive for use in dielectric capacitors for energy-storage applications, because of their elevated Curie temperature ($T_c \sim 540^\circ\text{C}$) and excellent maximum polarization ($P_{\max} \sim 40 \mu\text{C}/\text{cm}^2$) (Singh *et al.*, 2015), which results in good density of energy-storage in low electric fields. However, BNT ceramics have a significant energy density loss (W_{loss}) due to their high coercive field (E_c) of approximately 73 kV/cm (Takenaka *et al.*, 1991; Herabut and Safari, 1997), which results in a low energy-storage efficiency (η).

Recently, BaTiO_3 (BT) was added to BNT ceramics to produce a unique binary system. Approximately 0.06 and 0.10 mol% BT has been added to the BNT ceramics, which are excellent choices for energy-storage capacitors that operate at high temperatures due to their great electrical properties ($\epsilon_m \sim 7200$, $P_r \sim 35 \mu\text{C}/\text{cm}^2$ and $d_{33} \sim 130 \text{ pC/N}$ (Mahajan *et al.*, 2017)) and reduced coercive field (E_c) of about 22.1 kV/cm (Sung *et al.*, 2010). That lead to a research study on the $0.9(0.92\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3 - 0.08\text{BaTiO}_3) - 0.1\text{NaTaO}_3$ or BNT-BT-0.1NT ceramic prepared by conventional method which was calcined for 2 h at 800°C and a sintered for 2 h at 1150°C . With an electric field of 100 kV/cm applied, an energy storage density of $1.20 \text{ J}/\text{cm}^3$ was attained (Kwon *et al.*, 2011).

According to a review of the literature, many types of ferroelectric ceramics have been used to prepare solid-state reaction techniques (Takenaka *et al.*, 1991; Herabut and Safari, 1997; Kwon *et al.*, 2011; Mahajan *et al.*, 2017). This method makes use of high firing temperatures and an extensive dwell time. It is well known that one of the better processes for synthesizing powders was developed, the solid-state combustion technique (Thongtha *et al.*, 2010; Kwon *et al.*, 2011). It forms powders that are highly fine and have a narrow range of particle sizes that offer outstanding characteristics (high densification $\sim 5.84 \text{ g}/\text{cm}^3$ and good electrical properties; $\epsilon_m \sim 8405$, $d_{33} \sim 161 \text{ pC/N}$, $P_r \sim 28.2 \mu\text{C}/\text{cm}^2$ and $E_c \sim 22.1 \text{ kV}/\text{cm}$ for BNT-0.06BT ceramics (Thatawong *et al.*, 2022). The fuel from the solid-state combustion technique melting to liquid phase, facilitates the basic component having easy diffusion (Bongkarn *et al.*, 2016). It is also an easy technique that uses low-temperature firing with a short dwell time.

Literature review shows that there are no studies on the production of BNT-BT-0.1NT ceramics through the solid-state combustion method. In the context of this study, $0.9(0.92\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3 - 0.08\text{BaTiO}_3) - 0.1\text{NaTaO}_3$ (BNT-BT-0.1NT) ceramics developed using the solid-state combustion technique, with different temperatures for firing and phase content, morphology, and electrical properties of the BNT-BT-0.1NT ceramics were investigated.

Experimental section

The ferroelectric ceramics of $0.9(0.92\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3 - 0.08\text{BaTiO}_3) - 0.1\text{NaTaO}_3$ (BNT-BT-0.1NT) were prepared, which fuels the solid-state combustion process with glycine. The stoichiometric ratios of the raw materials $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (98.5%), NaNO_3 (99.5%), TiO_2 (99.5%), $\text{Ba}(\text{NO}_3)_2$ (99.0%) and Ta_2O_5 (99.9%) were determined by weighing them. The powder mixtures were milled by zirconia grinding balls for 24 h, then dried on a hot plate at 120°C and combined with glycine in an agate mortar at a weight ratio of 1:1.11. The powder mixtures were heated at a rate of 5°C for 2 h in air at temperatures of 600, 650, 700, 750, and 800°C . The pure powders were dried at 120°C after being ball milled for 12 h with polyvinyl alcohol (PVA). The powders were pressed into pellets (15 mm in diameter, 1.2-1.4 mm thick) under 80 MPa. These pellets were then sintered in air for 2 h at $1075\text{--}1175^\circ\text{C}$, with a heating rate of $5^\circ\text{C}/\text{min}$.

X-ray diffraction (XRD) was used to examine the phase structure of the BNT-BT-0.1NT ceramics in the 2θ range = $20\text{--}80^\circ$. To study microstructure, SEM was used after thermally etching the ceramic surfaces at a temperature of 100°C below the sintering temperature for 20 min. The linear intersection approach was applied to determine the average particle and grain sizes. Archimedes' method was used to calculate the density of the sintered ceramics. The ceramics were analyzed using an LCR meter at frequencies of 1 kHz, 10 kHz and 100 kHz over a temperature range of $30\text{--}400^\circ\text{C}$ to investigate dielectric characteristics. At room temperature, all samples exhibited polarization-electric field (P-E) loops at 1 Hz under applied fields of 40 and 70 kV/cm.

Results and Discussion

The XRD patterns of the BNT-BT-0.1NT powders, which were produced at different calcination temperatures that varied from 600 to 800°C for 2 h in the $2\theta = 20^\circ$ - 80° are shown in Figure 1. All the BNT-BT-0.1NT powders showed the perovskite (ABO_3) phase. $\text{Bi}_{1.5}\text{Na}_{0.5}\text{Ti}_7\text{O}_{27}$ (♥), which matched JCPDF file No. 32-1044 and Na_2O (♦) matched JCPDF file No. 02-1285, were identified as impurity peaks in the XRD patterns of the BNT-BT-0.1NT powders at a calcination temperature of 600°C. Due to a lack of energy, the minor phase of Na_2O remained between 650 and 700°C. The BNT-BT-0.1NT powders formed a pure perovskite phase when the calcination temperature rose over 700°C.

According to Figure 1, the percentage that consisted of the proportion of the ABO_3 phase improved from 87% to 100% with a rising firing temperature, which can be calculated with the following equation:

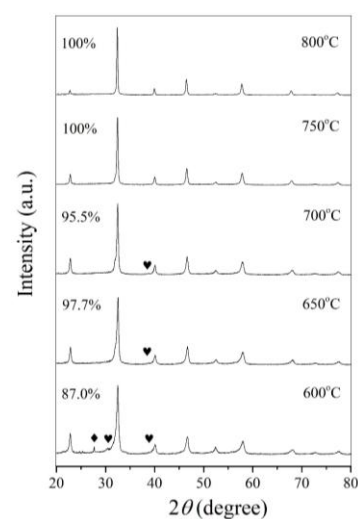


Figure 1. X-ray diffraction patterns of BNT-BT-0.1NT powders with various calcination temperatures, between 600 and 800°C for 2 h in the 2θ range of 20° - 80° .

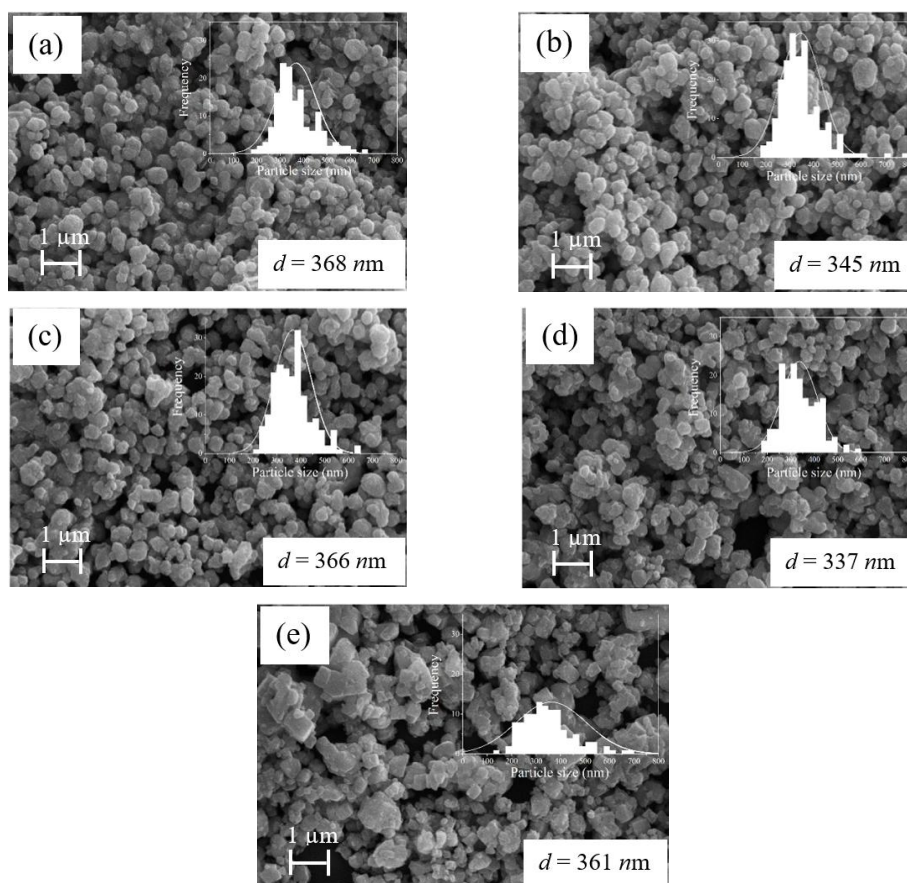


Figure 2. The scanning electron micrographs and particle size distributions of BNT-BT-0.1NT powders with various calcination temperatures of (a) 600°C, (b) 650°C, (c) 700°C, (d) 750°C and (e) 800°C for 2 h.

$$\%perovskitephase = \left(\frac{I_{perovskite}}{I_{perovskite} + I_{impurity}} \right) \times 100 \quad (1)$$

where $I_{perovskite}$ represents the maximum of the perovskite intensity peak and $I_{impurity}$ is the maximum impurity phase peaks of $\text{Bi}_{8.5}\text{Na}_{0.5}\text{Ti}_7\text{O}_{27}$ and Na_2O . The BNT-BT-0.1NT powders were prepared through the solid-state combustion technique, which necessitated a calcination temperature roughly 50°C lower compared to the solid-state reaction method (Kwon *et al.*, 2011). This underscores the solid-state combustion process as an efficient method and well-organized approach for obtaining pure powders at lower firing temperatures.

Figure 2 (a)-(e) shows the SEM pictures and particle size distributions of BNT-BT-0.1NT powders with different calcination temperatures. The microstructure of the BNT-BT-0.1NT particles were polyhedron-shaped and agglomerated. Throughout the temperature range of 600°C to 750°C , the powders became more dispersed. Fairly square grains with a broad size dispersion were observed at 800°C . The BNT-BT-0.1NT powders exhibited an average particle size (d) between 337 and 368 nm.

The pure BNT-BT-0.1NT powders, calcined for 2 h at 750°C were pressed in a pellet mold and sintered for 2 h at 1075 to 1175°C . Figure 3(a) displays the XRD patterns of the ceramics sintered at different temperatures, measured within the 2θ range of 20 – 80° . It was none of the compositions that showed any impurity phases. Figure 3(b) presents an enlarged view of the 38 – 48° range from Figure 3(a). The XRD pattern of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$

ceramics with rhombohedral symmetry is typically characterized by a $(202)_R$ single peak at a higher angle of 46.5° and $(003)/(021)_R$ dual peaks at a lower angle of 40° , which corresponds to JCPDS file number 36-0340 (Pookmanee *et al.*, 2004). In contrast, a $(111)_T$ single peak at a lower angle of 40° and the $(002)/(200)_T$ double peaks at a higher angle of 46.5° are distinctive features of tetragonal symmetry, as specified in JCPDS file number 36-0339 (Pookmanee *et al.*, 2004). Moreover, the presence of a cubic phase has been observed in the BT structure (Lu *et al.*, 2000). The characteristic peaks of a normal cubic-phase structure BT include a $(111)_C$ single peak at a lower angle of approximately 38.5° and A prominent $(200)_C$ peak at a higher angle of around 45° , corresponding to JCPDS file number 31-0174 (Lu *et al.*, 2000). In the current investigation, The XRD peaks at roughly 40° and 46.5° for the sample sintered at 1075°C appeared broad without a distinct secondary peak, indicating the dominance of the rhombohedral (R) phase. The diffraction peak at $\sim 40^\circ$ showed broad peaks when the firing temperature was ramped up to 1100°C . However, the peak at $\sim 46.5^\circ$ clearly split into double peaks. This demonstrated that the tetragonal phase (T) was prominent. The dual peaks gradually merged into a single peak upon increasing the sintering temperature from 1125°C to 1175°C . This demonstrated that the predominance of the tetragonal phase (T) was reduced, and it exhibited the cubic (C) phase. Rietveld refinement was employed to further phase-quantify detailed information of the BNT-BT-0.1NT ceramics.

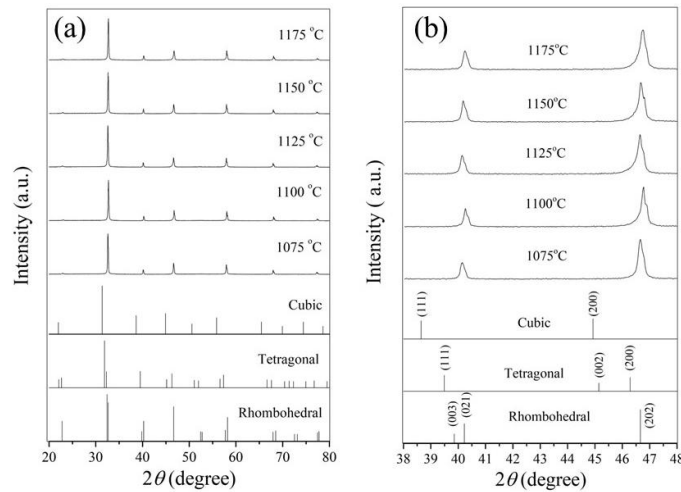


Figure 3. JCPDS file number 36-0340 (Rhombohedral), 36-0339 (Tetragonal), 31-0174 (Cubic) and the X-ray diffraction patterns of BNT-BT-0.1NT ceramics with various sintering temperatures between 1075 – 1175°C for 2 h in the 2θ range of (a) 20 – 80° and (b) 38 – 48° .

All the BNT-BT-0.1NT ceramics performed Rietveld refinement by matching the FullProf program, which was implemented to analyze the XRD data, confirming and validating the XRD analysis. For the starting parameters of the lattice (a , b , c), bond angles (α , β , γ), atomic information and domination were used as reference data. The XRD data of the refinement of BNT-BT-0.1NT ceramics was carried out using a structural model based on $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ characterized by an $R3c$ space group for the rhombohedral phase (R), a $P4bm$ space group for the tetragonal phase (T), and a $Pm3m$ space group for the cubic phase (C). The fitting was performed using a pseudo-Voigt function for the XRD peaks, and a Chebyshev polynomial function was applied to match the background. A variety of parameters were computed to assess the refined fits: R_p is reliability of the profile, R_{wp} is reliability of the weighted pattern, R_{exp} is expected residual and χ^2 is the goodness of fit. Findings of the Rietveld refinement

for different sintering temperatures of BNT-BT-0.1NT ceramics are displayed in Figure 4(a)-(e). In this study, the fitting parameters obtained were $R_p \leq 31.4\%$, $R_{wp} \leq 28.3\%$, $R_{exp} \leq 14.2\%$, and $\chi^2 \leq 3.98$ (Table 1), which indicated that all ceramics had good correspondence with the calculated and observed XRD patterns. The R , T and C phase content, atomic information, lattice parameters, and goodness-of-fit parameters in the BNT-BT-0.1NT ceramics are shown in Table 1. The results obtained from the fitting indicated the presence of R , T and C phases in all samples. At the sintering temperature of 1075°C , the R phase was 80.7% while the T and C phases were observed at 8.0% and 11.3% , respectively. T phase concentration decreased from 71.4% to 34.4% when sintering temperatures increased from 1100°C to 1175°C . The C phase concentration improved from 11.3% to 31.2% when the sintering temperatures changed from 1075°C to 1175°C , according to Table 1.

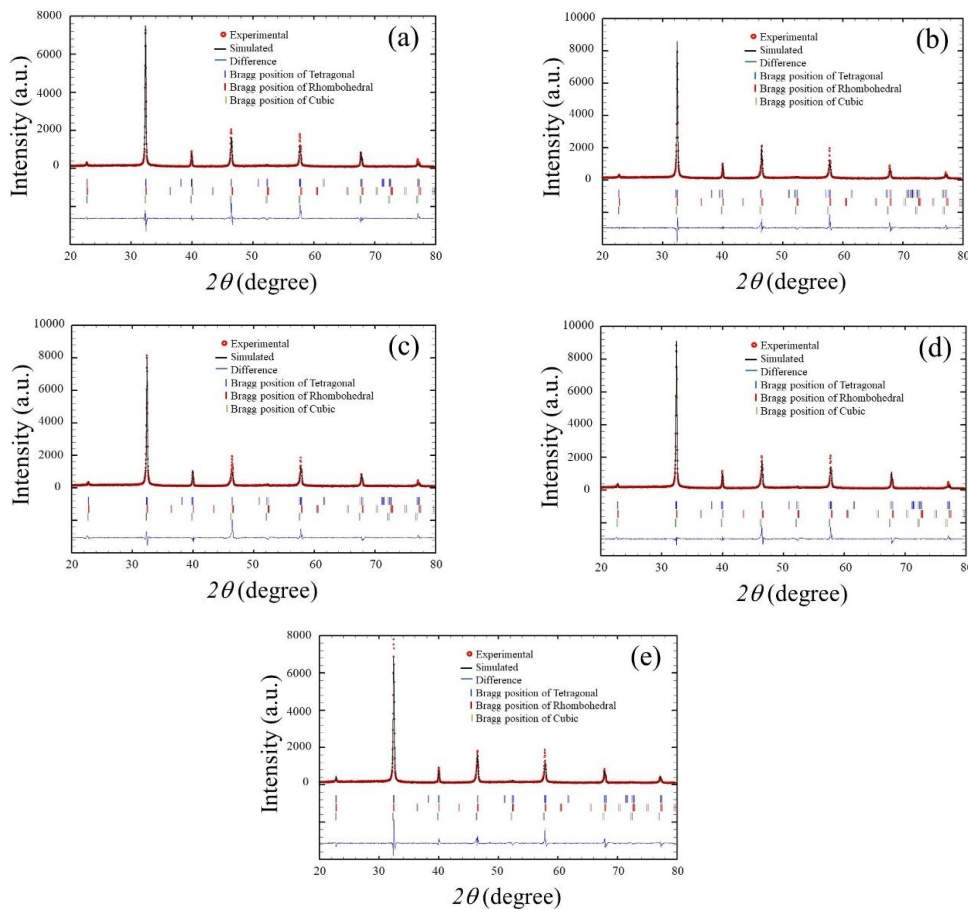


Figure 4. Final plots of the Rietveld refinement, showing the experimental (dots) and calculated (line) intensities of BNT-BT-0.1NT ceramics in the range $20\text{--}80^\circ$ with sintering temperatures of (a) 1075°C , (b) 1100°C , (c) 1125°C , (d) 1150°C , and (e) 1175°C .

Table 1. Goodness-of-fit parameters, lattice parameters, atomic information and the phase content for the BNT-BT-0.1NT ceramics.

Sample	Goodness of Fit	Phase	Profile parameters	Atomic information					Phase content		
				Lable	x	y	z	Occ.			
1075	c^2	3.752	$R3c$	a	5.531081 Å	Bi	0	0	0.2627	0.35009	80.7%
	R_p	30.2	c	13.561929 Å	Na	0	0	0.2627	0.53889		
	R_{wp}	27.3	c/a	2.451949	Ti	0	0	0.0063	1.05095		
	R_{exp}	14.1	u	0.002774	Ba	0	0	0.2627	0.06291		
			v	0.017504	O	0.126	0.336	0.0833	4.32883		
			w	0.006255	Ta	0	0	0.2627	0.10799		
			a	5.520788 Å	Bi	0	0.5	0.545	0.340561		
			c	3.898160 Å	Na	0	0.5	0.545	0.39585		
			c/a	0.706087	Ti	0	0	0	0.91730		
			u	0.005112	Ba	0	0.5	0.545	0.05883		
			v	0.000405	O1	0	0	0.51	2.28145		
			w	0.000064	O2	0.271	0.229	0.015	4.46622		
					Ta	0	0.5	0.545	0.09960		
			$Pm3m$	a	3.919224 Å	Bi	0	0	0	0.39231	
			c	3.919224 Å	Na	0	0	0	0.51635		
			c/a	1.000000	Ti	0.5	0.5	0.5	0.94886		
			u	0.099400	Ba	0	0	0	0.05226		
			v	0.005840	O1	0.5	0.5	0	3.87611		
			w	0.108660	Ta	0	0	0	0.10000		
	1100	c^2	3.499	$R3c$	a	5.521762 Å	Bi	0	0	0.2627	0.37183
R_p		29.5	c	13.693974 Å	Na	0	0	0.2627	0.50862		
R_{wp}		26.5	c/a	2.480001	Ti	0	0	0.0063	0.93810		
R_{exp}		14.2	u	0.194000	Ba	0	0	0.2627	0.03875		
			v	0.139644	O	0.126	0.336	0.0833	3.15158		
			w	0.006255	Ta	0	0	0.2627	0.12044		
			a	5.521677 Å	Bi	0	0.5	0.545	0.42505		
			c	3.898787 Å	Na	0	0.5	0.545	0.41652		
			c/a	0.7060875	Ti	0	0	0	1.43156		
			u	0.0003220	Ba	0	0.5	0.545	0.06308		
			v	0.0016960	O1	0	0	0.51	1.44656		
			w	0.0000640	O2	0.271	0.229	0.015	3.05769		
					Ta	0	0.5	0.545	0.10042		
			$Pm3m$	a	3.927118 Å	Bi	0	0	0	0.39421	
			c	3.927118 Å	Na	0	0	0	0.56839		
			c/a	1.000000	Ti	0.5	0.5	0.5	0.91051		
			u	0.087700	Ba	0	0	0	0.05198		
			v	1.220934	O1	0.5	0.5	0	1.00910		
			w	0.108660	Ta	0	0	0	0.08149		
1125		c^2	3.98	$R3c$	a	5.525265 Å	Bi	0	0	0.2627	0.30897
	R_p	30.7	c	13.596219 Å	Na	0	0	0.2627	0.53319		
	R_{wp}	28.3	c/a	2.460736	Ti	0	0	0.0063	0.90000		
	R_{exp}	13.8	u	0.063099	Ba	0	0	0.2627	0.05400		
			v	0.003054	O	0.126	0.336	0.0833	3.85766		
			w	0.006255	Ta	0	0	0.2627	0.12044		
			a	5.520745 Å	Bi	0	0.5	0.545	0.41567		
			c	3.898548 Å	Na	0	0.5	0.545	0.47180		
			c/a	0.706163	Ti	0	0	0	1.16541		
			u	0.005226	Ba	0	0.5	0.545	0.06902		
			v	0.003000	O1	0	0	0.51	1.95803		
			w	-0.000666	O2	0.271	0.229	0.015	3.07627		
					Ta	0	0.5	0.545	0.10000		
			$Pm3m$	a	3.927118 Å	Bi	0	0	0	0.42181	
			c	3.927118 Å	Na	0	0	0	0.52300		
			c/a	1.000000	Ti	0.5	0.5	0.5	0.90000		
			u	0.752073	Ba	0	0	0	0.05400		
			v	0.009018	O1	0.5	0.5	0	0.29102		
			w	0.108660	Ta	0	0	0	0.10000		
	1150	c^2	3.58	$R3c$	a	5.525265 Å	Bi	0	0	0.2627	0.30890
R_p		27.1	c	13.596219 Å	Na	0	0	0.2627	0.53319		
R_{wp}		25.2	c/a	2.460736	Ti	0	0	0.0063	0.90000		
R_{exp}		13.3	u	-0.063990	Ba	0	0	0.2627	0.05400		
			v	0.017504	O	0.126	0.336	0.0833	3.85766		
			w	0.006255	Ta	0	0	0.2627	0.12044		
			a	5.520745 Å	Bi	0	0.5	0.545	0.41567		
			c	3.898548 Å	Na	0	0.5	0.545	0.47180		
			c/a	0.706163	Ti	0	0	0	1.16541		
			u	0.003470	Ba	0	0.5	0.545	0.06902		
			v	0.000578	O1	0	0	0.51	1.95803		
			w	0.000064	O2	0.271	0.229	0.015	3.07627		
					Ta	0	0.5	0.545	0.10000		
			$Pm3m$	a	3.927118 Å	Bi	0	0	0	0.42181	
			c	3.927118 Å	Na	0	0	0	0.52300		
			c/a	1.000000	Ti	0.5	0.5	0.5	0.90000		
			u	-0.195108	Ba	0	0	0	0.05400		
			v	0.463717	O1	0.5	0.5	0	0.29102		
			w	0.108660	Ta	0	0	0	0.10000		
1175		c^2	3.813	$R3c$	a	5.515932 Å	Bi	0	0	0.2627	0.29685
	R_p	31.4	c	13.551483 Å	Na	0	0	0.2627	0.49927		
	R_{wp}	27.5	c/a	2.456789	Ti	0	0	0.0063	0.90000		
	R_{exp}	14.1	u	0.312090	Ba	0	0	0.2627	0.05400		
			v	0.000059	O	0.126	0.336	0.0833	1.04196		
			w	0.006255	Ta	0	0	0.2627	0.12044		
			a	5.522316 Å	Bi	0	0.5	0.545	0.41567		
			c	3.899035 Å	Na	0	0.5	0.545	0.38320		
			c/a	0.706051	Ti	0	0	0	1.19889		
			u	0.000000	Ba	0	0.5	0.545	0.05068		
			v	0.005179	O1	0	0	0.51	1.74267		
			w	0.000064	O2	0.271	0.229	0.015	3.18217		
					Ta	0	0.5	0.545	0.10000		
			$Pm3m$	a	3.919473 Å	Bi	0	0	0	0.39060	
			c	3.919473 Å	Na	0	0	0	0.52240		
			c/a	1.000000	Ti	0.5	0.5	0.5	1.44559		
			u	0.000094	Ba	0	0	0	0.05400		
			v	0.971990	O1	0.5	0.5	0	3.12579		
			w	0.108660	Ta	0	0	0	0.10000		

The SEM images of BNT-BT-0.1NT ceramics sintered at different temperatures of 1075°C, 1100°C, 1125°C, 1150°C, and 1175°C for 2 h are shown in Figure 5 (a)-(e). The grains of all ceramics exhibited a polyhedron form. Under lower-temperature sintering conditions of 1075°C, the ceramic contained a large quantity of pores because the particles were not very densely packed (Figure. 5(a)). As the ceramics sintered from 1100°C to 1150°C, the pores decreased. At 1175°C showed

increased grain growth was shown, and grain boundaries were not clearly observed. With increasing sintering temperatures, the average grain size (D) rose from 0.85 to 2.66 μm , as shown in Table 2. The driving force of grain growth is to reduce the total free energy of the grain boundaries, resulting in the movement of the grain boundaries, which causes the grain size to increase during heating (Kovacevic *et al.*, 2020).

Table 2. Grain size, density, temperature of maximum dielectric, dielectric and ferroelectric properties of BNT-BT-0.1NT ceramics.

Sintering temperatures	Grain size(μm)	Measured density (g/cm^3)	T_{max}	ϵ_{max}	$\tan\delta$ at T_{max}	P_r ($\mu\text{C}/\text{cm}^2$)	P_{max} ($\mu\text{C}/\text{cm}^2$)	E_c (kV/cm)
1075	0.85	4.41	209.0	932	0.017	-	-	-
1100	0.92	4.80	202.4	1137	0.017	-	-	-
1125	0.95	5.34	201.9	1316	0.012	14.52	20.28	16.50
1150	1.50	5.83	185.0	1827	0.011	1.62	11.70	2.64
1175	2.66	5.54	182.9	1815	0.014	1.03	10.23	2.67

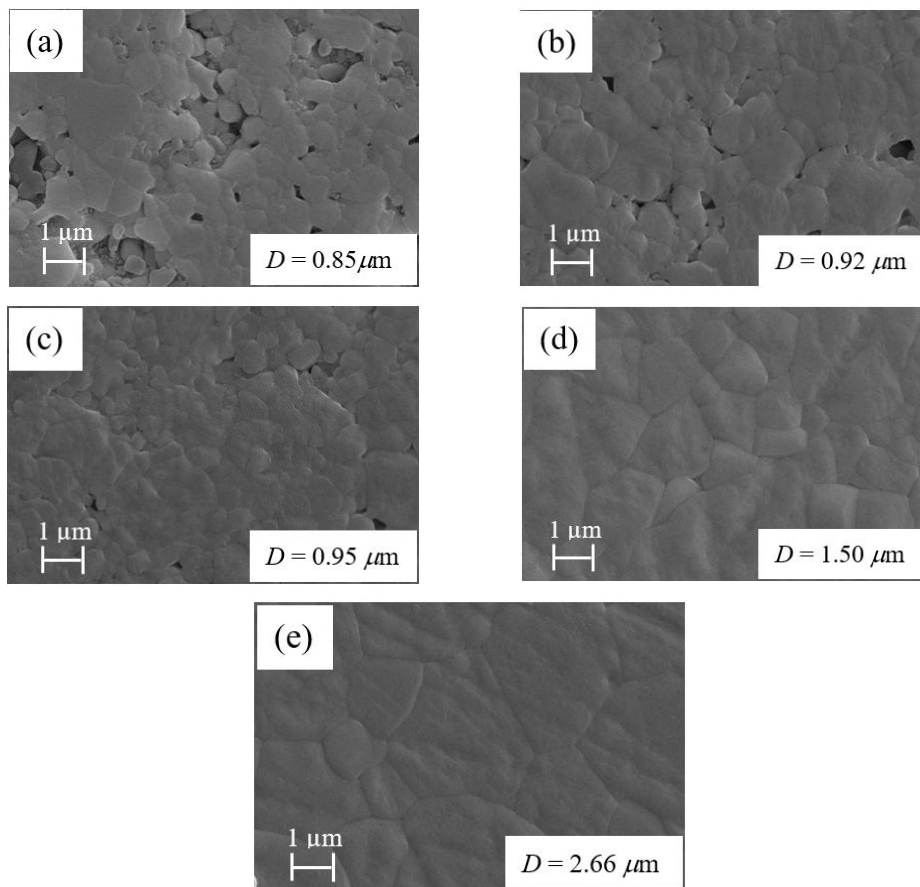


Figure 5. The microstructure of BNT-BT-0.1NT ceramics sintered at (a) 1075°C, (b) 1100°C, (c) 1125°C, (d) 1150°C, and (e) 1175°C for 2 h.

Archimedes' method was used to determine the density of the sintered ceramics, as shown in Table 2. It's determined that the density of ceramics increased as the temperature changed from 1075 to 1150°C. This was due to the reduction of pores in the crystal structure. The particles were rearranged during the sintering process, resulting in more tightly sealed crystal particles. Grain boundaries were displaced, which caused the pores to begin to bond and be eliminated by diffusion from the pores along the grain boundary (Le Claire, 1963). The organic materials' volatilizations and alkali elements contributed to a slight decrease in density when the sintering temperature increased to 1175°C (Fu *et al.*, 2011).

Figure 6 displays the dielectric characteristics of BNT-BT-0.1NT ceramics, which were measured

in frequencies of 1, 10, and 100 kHz as a function of temperature in ranges from 30 to 450°C. A broad dielectric anomaly peak was observed for all samples, which exhibited the depolarization temperature (T_d) and the temperature corresponding to the maximum dielectric constant (T_{max}) merged peaks. As the temperature tended to increase, the T_{max} shifted to lower temperatures. The phase transition has been determined using the modified Curie-Weiss law (Wang *et al.*, 2019) in order to verify the relaxor ferroelectric properties of the BNT-BT-0.1NT ceramics:

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_{max}} = \frac{(T - T_{max})^{\gamma}}{C} \quad (2)$$

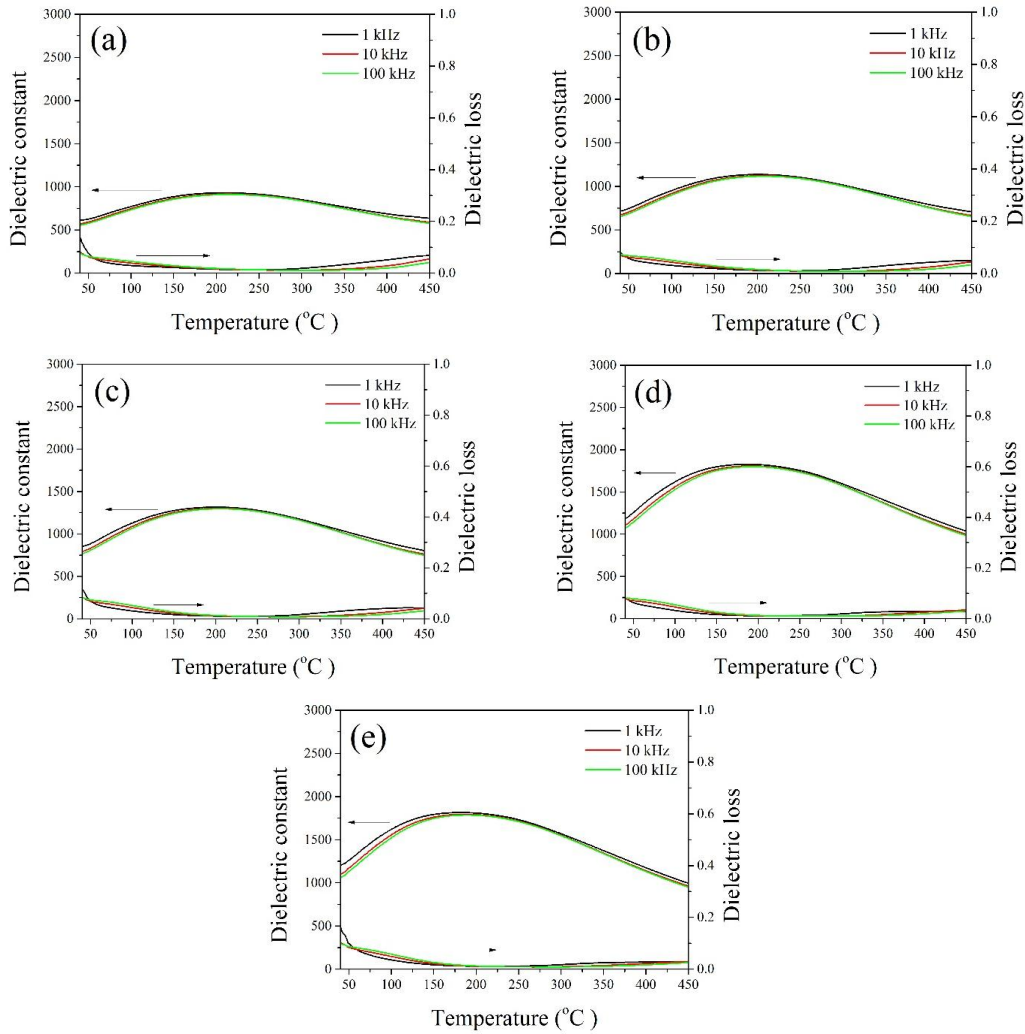


Figure 6. Dielectric constant (ε) and dielectric loss ($\tan\delta$) of BNT-BT-0.1NT ceramics measured at different frequencies between 1 kHz, 10 kHz and 100 kHz with sintering temperatures of (a) 1075°C, (b) 1100°C, (c) 1125°C, (d) 1150°C, and (e) 1175°C.

In this context, ε denotes the dielectric constant, $\varepsilon_{\max}$ represents the maximum dielectric constant, C refers to the modified Curie-Weiss constant and γ is the exponent. The properties of relaxor ferroelectrics and normal ferroelectrics are typically described by the γ value in this equation, which is typically close to 1 and 2, respectively. The γ -values of the BNT-BT-0.1NT ceramics sintered between 1075°C and 1175°C are shown in Figure 7, in which the fluctuation of $\log(1/\varepsilon - 1/\varepsilon_{\max})$ with $\log(T - T_{\max})$ is shown. It was evident from the γ -values, which ranged between 1.80 and 1.98, that the BNT-BT-0.1NT ceramics exhibited relaxor ferroelectric behavior. When the ceramics sintered, the temperature increased from 1075°C to 1150°C, the $\varepsilon_{\max}$ increased from 932 to 1827. However, at the sintering temperature of 1175°C, it reduced to 1815. The increasing temperature to 1150°C resulted in an increase of density and a decrease of the porosity, which made it obtain a significantly high dielectric constant (Zeng *et al.*, 2006). BNT-0.06BT ceramics fabricated by the solid-state combustion method showed a similar pattern (Thatawong *et al.*, 2022). According to Table 2, the dielectric loss ranged between 0.011 and 0.017.

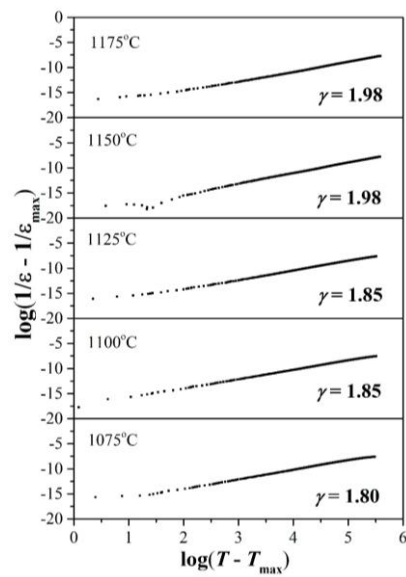


Figure 7. Variation of $\log(1/\varepsilon - 1/\varepsilon_{\max})$ versus $\log(T - T_{\max})$ and γ -values of the BNT-BT-0.1NT ceramics sintered between 1075°C and 1175°C.

The ferroelectric hysteresis loops (P - E loops) of BNT-BT-0.1NT ceramics, produced at various sintering temperatures, with an applied electric field of 40 kV/cm are displayed in Figure 8 (a)-(c). At sintering temperatures of 1075°C and 1100°C, the

ceramics were highly porous, resulting in a breakdown of the electric field and unobservable hysteresis loop. At a sintering temperature of 1125°C, the hysteresis loop was quite square-shaped and had an unsaturated leakage current, resulting in a high remanent polarization (P_r) and high coercive electric field (E_c), indicating a typical ferroelectric character, as shown in Figure 8(a). At a sintering temperature of 1150°C, the P - E loop of the sample becomes slanted and slim with the lowest E_c and a low P_r . For 1175°C, E_c slightly increased from 2.64 to 2.67 kV/cm as shown in Table 2. This was due to the formation of pores.

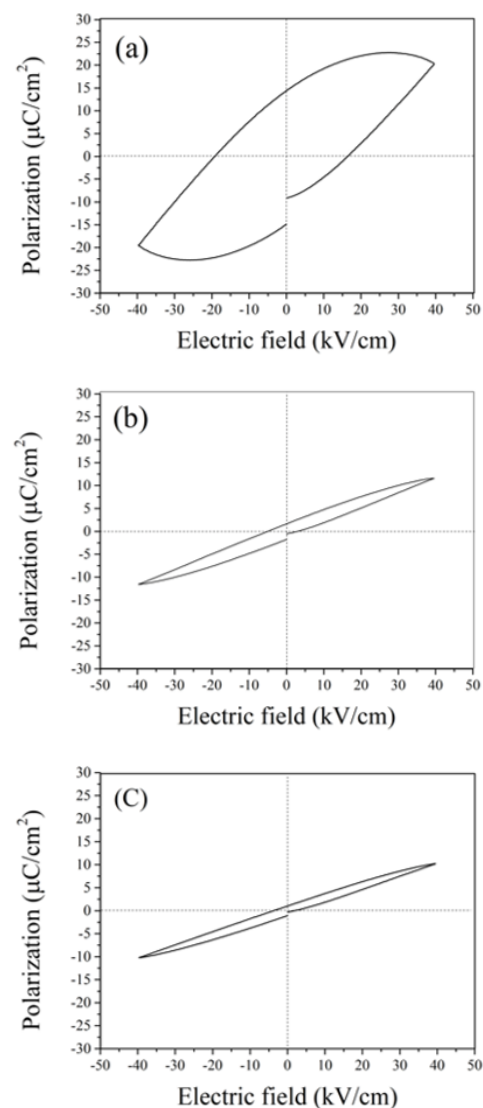


Figure 8. The polarization-electric field (P - E) hysteresis loops of the BNT-BT-0.1NT ceramics with sintering temperature of (a) 1125°C, (b) 1150°C and (c) 1175°C under an electric field of 40 kV/cm.

The P - E loop of the BNT-BT-0.1NT ceramics sintered at 1150°C, under an electric field of 70 kV/cm was measured and is shown in Figure 9. With the same electric field, the ceramics with sintering temperatures at 1125°C and 1175°C were broken. Energy storage parameters of the ceramic sintered at 1150°C were obtained using the P - E hysteresis loop. The energy storage density (W) was determined by calculating the operational area enclosed between the polarization axis and the charging curve. Similarly, the recoverable energy storage density (W_{rec}) was obtained from the operational area between the polarization axis and the discharging curve (Palneedi *et al.*, 2018). The energy loss density (W_{loss}) corresponds to the area of the P - E loop. The energy storage efficiency (η), an essential parameter for energy storage capacitor dielectrics, is defined by the following equations:

$$W = \int_0^{P_{max}} E dP \quad (3)$$

$$W_{rec} = \int_{P_r}^{P_{max}} E dP \quad (4)$$

$$\eta = \frac{W_{rec}}{W} \times 100\% \quad (5)$$

In equations (3), (4) and (5), E represents the electric field, and P denotes the polarization. After calculation, the energy storage density was found to be 0.71 J/cm³ with an energy storage efficiency of 64.5% under a measured electric field of 70 kV/cm. These values are similar to BNT-BT-0.1NT ceramics produced by solid-state reaction method (Kwon *et al.*, 2011).

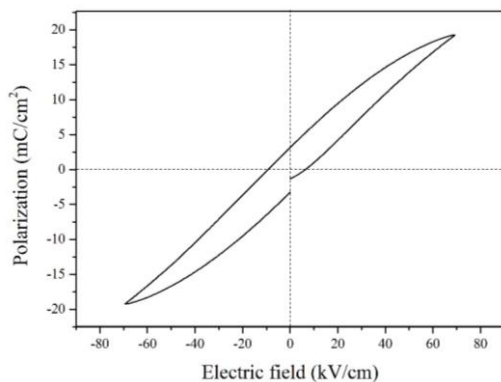


Figure 9. P - E loop of the BNT-BT-0.1NT ceramic, sintered at 1150°C, measured under an electric field of 70 kV/cm.

Conclusions

Throughout this study, BNT-BT-0.1NT ceramics were developed with success by the solid-state combustion process. A well-defined perovskite phase was obtained after calcination at 750°C for 2 h, which was reduced compared to the temperature required for powders synthesized by the solid-state reaction method. The crystallographic structure, microstructure, bulk density, electrical properties and energy storage characteristics were strongly affected by the firing temperatures. The rhombohedral, tetragonal and cubic phases were observed in all ceramics and verified by Rietveld refinement. When sintering temperatures increased, the average grain size increased from 0.85 to 2.66 μ m. The density of the BNT-BT-0.1NT ceramics increased with rising sintering temperatures. The ceramic was sintered at 1150°C, the highest value of dielectric constant (1827) and favorable ferroelectric properties were observed, leading to a high energy storage efficiency ($\eta \sim 64.5\%$) and substantial usable energy storage density ($W \sim 0.71$ J/cm³) with 70 kV/cm for an applied electric field.

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