

EFFECT OF (AlNb)⁴⁺ B-SITES SUBSTITUTION ON THE PHASE STRUCTURE, MICROSTRUCTURE AND ELECTRICAL PROPERTIES OF Bi_{0.47}Na_{0.47}Ba_{0.06}TiO₃ CERAMICS

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Abstract

Bi_{0.47}Na_{0.47}Ba_{0.06}Ti_{1-x}(Al_{0.5}Nb_{0.5})_xO₃ (abbreviated as BNBT_{1-x}AN_x) lead-free ceramics (x=0-0.05) were synthesized by the solid-state combustion technique. The effect of (AlNb)⁴⁺ content on the phase structure, microstructure and electrical properties was investigated. A pure perovskite structure was obtained from all specimens. Rietveld refinement revealed coexisting rhombohedral and tetragonal phases in all samples and the tetragonal phase increased with increased AlNb content (x). The morphology of the BNBT_{1-x}AN_x ceramics displayed nearly round grains and anisotropic grain growth. Average grain size decreased from 1.8 to 0.7 μm when x increased from 0 to 0.05 and the grain size distribution became narrower. The density, maximum dielectric constant and remnant polarization rapidly decreased with increased x. The deterioration of the electrical properties induced by (AlNb)⁴⁺ substitution was due to shifting away from the morphotropic phase boundary (MPB), poor microstructure and low density.

Keywords: BNBT_{1-x}AN_x; Phase Structure; Dielectric; Ferroelectric

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Introduction

Lead-based ferroelectric ceramics such as Pb(ZrTi)O₃ (PZT) and Pb(MgNb)O₃-PbTiO₃ (PMN-PT), have been widely used in electronic devices, such as sensors, transducers, ultrasound devices and other devices, owing to their superior electrical properties (Park and Shrout, 1997; Barick *et al.*, 2011; Zeng *et al.*, 2017). However, the evaporation of lead oxide at high temperature during the preparation process negatively impacts human health and the environment. Furthermore, the evaporation of lead oxide causes chemical structure instability, resulting in a decrease in the electrical properties. As a result, many researchers have developed lead-free ferroelectric ceramics to replace them.

Bismuth sodium titanate (Bi_{0.5}Na_{0.5}TiO₃; BNT) lead-free ferroelectric ceramics have attracted attention due to their strong ferroelectric behavior and large remnant polarization ($P_r=38 \mu\text{C}/\text{cm}^2$). However, the high coercive field ($E_c=73 \text{ kV}/\text{cm}$) of BNT ceramics causes problems in the poling process, resulting in a low piezoelectric coefficient ($d_{33}=70 \text{ pC}/\text{N}$) (Takenaka *et al.*, 1991). Many researchers have attempted to overcome these disadvantages by adding solid solutions, such as (Ba_{0.7}Sr_{0.3})TiO₃, (Bi_{0.5}K_{0.5})TiO₃, and BaTiO₃ to the BNT ceramics (Takenaka *et al.*, 1991; Sasaki *et al.*, 1999; Lee *et al.*, 2010). B. Thatawong *et al.* (Thatawong *et al.*, 2022) successfully prepared Bi_{0.47}Na_{0.47}Ba_{0.06}TiO₃ ceramics via the solid-state combustion technique with a low firing temperature and short dwell time (calcination temperature of 750°C for 2 h and a sintering temperature of 1150°C for 2 h). The ceramics exhibited a high-density ($\sim 5.84 \text{ g}/\text{cm}^3$) which has good electrical properties with a morphotropic phase boundary (MPB) composition (maximum dielectric constant ($\epsilon_m=8405$), $P_r=28.2 \mu\text{C}/\text{cm}^2$, $E_c=22.1 \text{ kV}/\text{cm}$ and $d_{33}=161 \text{ pC}/\text{N}$).

The substitution of complex ions can change the phase structure, which has a significant impact on the electrical properties of ceramics due to lattice distortions caused by A and B-site ions moving off center and ferroelectric order disruption (Fan *et al.*, 2018; Xie *et al.*, 2018). Moreover, the phase structure can be modified by replacing ions of different radii into B-sites, resulting in a distorted lattice structure (Li *et al.*, 2016a; Shen *et al.*, 2021). L. Li *et al.* (Li *et al.*, 2016b) prepared (Bi_{0.5}Na_{0.5})_{0.935}Ba_{0.065}Ti_{1-x}(Al_{0.5}Sb_{0.5})_xO₃ ceramics with $x=0.005$ -0.020. The ceramic showed good electrical properties ($\epsilon_m\sim 5800$ and $P_r\sim 10 \mu\text{C}/\text{cm}^2$) and excellent strain properties ($S_{\max}=0.46\%$ and $d_{33}^*=573 \text{ pm}/\text{V}$) at $x=0.015$. R. Chen *et al.*

(Cheng *et al.*, 2016) reported that the B-site complex ion (Fe_{0.5}Nb_{0.5})⁴⁺ modified (Bi_{0.5}Na_{0.5})_{0.935}Ba_{0.065}Ti_{1-x}(Fe_{0.5}Nb_{0.5})_xO₃ ceramics with $x=0$ -0.03 and exhibited a high maximum dielectric constant ($\epsilon_m\sim 5500$) and good strain properties ($S_{\max}=0.422\%$ and $d_{33}^*=844 \text{ pm}/\text{V}$) at $x=0.02$. It is reasonable to expect that the B-site complex ion substitution of (A³⁺_{0.5}B⁵⁺_{0.5})⁴⁺ (A=trivalent metal, B=pentavalent metal) for Ti⁴⁺ in BNT-based perovskite ceramics can improve the electrical properties of the resulting ceramics.

In this work, we prepared Bi_{0.47}Na_{0.47}Ba_{0.06}TiO₃ (BNBT) ceramics with (Al_{0.5}Nb_{0.5})⁴⁺ substitution via the solid-state combustion technique and studied the effect of (Al_{0.5}Nb_{0.5})⁴⁺ substituted content on the phase structure, microstructure, and electrical properties of BNBT ceramics.

Experimental

The Bi_{0.47}Na_{0.47}Ba_{0.06}Ti_{1-x}(AlNb)_xO₃ ($x=0, 0.01, 0.02, 0.03, 0.04$ and 0.05 abbreviated as BNBT_{1-x}AN_x) powders were synthesized by the solid-state combustion method. The chemicals, Bi(NO₃)₃·5H₂O (purity~98.5%, Ajax Finechem), NaNO₃ (purity~99%, Ajax Finechem), Ba(NO₃)₂ (purity~99%, Himedia), TiO₂ (purity~99.5%, Kemaus), Al(NO₃)₃·9H₂O (purity~98%, Ajax Finechem) and Nb₂O₅ (purity~99.9%, Eleps) were used as raw materials. The raw materials were mixed and milled for 24 h in alcohol with ZrO₂ balls. The mixed powders of BNBT_{1-x}AN_x were mixed with glycine in a ratio of 1:1.11 (raw materials:fuel) and calcined at 750°C for 2 h. Polyvinyl alcohol (PVA) binder solution (3 wt.%) was added to the calcined powders and compressed into pellets of ~15 mm in diameter and ~1.2 mm in thickness under a pressure of 80 MPa. The green pellets were sintered at 1150°C for 2 h with a heating rate of 5°C/min.

Phase formation of the BNBT_{1-x}AN_x ceramics was determined by X-ray diffraction (XRD; Philips PW 3040/60 X'Pert PRO) with CuK α as a radiation source ($\lambda=1.5418 \text{ \AA}$). The microstructure was investigated using a scanning electron microscope (SEM; Leo, 1455VP). The densities of all compositions were determined by Archimedes principle. To make electrical measurements, silver paste was deposited on both sides of the BNBT_{1-x}AN_x ceramics and heated to 500°C for 30 min. The dielectric properties were measured between 30 and 400°C, at the frequencies of 1, 10 and 100 kHz

using a 4263B LCR-meter (HP, 4284 A). The ferroelectric hysteresis (P - E) loops were characterized using a computer controlled modified Sawyer–Tower circuit (Radiant, PLC2-The P - E loop).

Results and Discussion

Figure 1(a) shows the XRD patterns of the $\text{BNBT}_{1-x}\text{AN}_x$ ceramics with x between 0 and 0.05 and a 2θ range of 10 – 70° . All samples exhibited a pure perovskite structure with no secondary phase, indicating that the replaced $(\text{AlNb})^{4+}$ ions diffused completely into the BNBT structure. Generally, the diffraction patterns for a rhombohedral ($R3c$) phase show dual peaks of $(003)_R/(021)_R$ around 40° and a single peak of $(202)_R$ around 46° (JCPDS file No. 36-0340) (Bhupaijit *et al.*, 2019; Bhupaijit *et al.*, 2021), while the diffraction patterns for a tetragonal ($P4bm$) phase show a single peak of $(111)_T$ around 40° and dual peaks of $(002)_T/(200)_T$ around 46° (JCPDS file No. 36-0339) (Bhupaijit *et al.*, 2019; Bhupaijit *et al.*, 2021). The XRD pattern was enlarged to show the phase structure at 2θ around 35 – 50° , as seen in Figure 1(b). For $x=0$, the XRD pattern clearly showed split peaks around 40° and 46° , indicating the coexistence between the rhombohedral and tetragonal phases. Nonetheless, with increasing $(\text{AlNb})^{4+}$ content, it was found that the XRD peak around 40° started to merge, then became a non-symmetric peak, with increased merging occurring as $(\text{AlNb})^{4+}$ increased. The XRD peaks around 46° exhibited two peaks for all samples. These results indicated that increased $(\text{AlNb})^{4+}$ substitution increased the tetragonal phase.

In order to quantify the phase structure, the Rietveld refinement program ‘FullProf’ was used to confirm the phase structure of the $\text{BNBT}_{1-x}\text{AN}_x$ ceramics at $x=0$ – 0.05 as shown in Figure 2. The parameters for the refinement fitting process are the background XRD data, a scale factor, lattice constants, profile half-width parameters (u , v , and w), atomic functional positions, and occupancy. To fit the actual BNT structure, an approximate structural model was required with a tetragonal phase, with $P4bm$ space groups, and a rhombohedral phase, with $R3c$ space groups. The experimental and simulated XRD patterns of all samples from the structural refinement had the fitting parameters $R_p < 31.20\%$, $R_{wp} < 24.40\%$, $R_{exp} < 23.22\%$ and $X^2 < 2.39$, as listed in Table 1. According to the fitting results, the rhombohedral and tetragonal phases coexisted in all samples and the tetragonal phase tended to increase with increased $(\text{AlNb})^{4+}$. The phase ratio of the rhombohedral and tetragonal phases is listed in Table 1.

With increase of x from 0 to 0.05, the unit cell volume (V) demonstrated a relatively small change in the range of 411.4386 – $417.1339 \text{ \AA}^3$ for rhombohedral ($R3c$) phase and slightly increased from 116.3496 to $121.3361 \text{ \AA}^3$ for tetragonal ($P4bm$) phase, as seen in Table 1. In general, when Al^{3+} ($r=0.535 \text{ \AA}$) and Nb^{5+} ($r=0.64 \text{ \AA}$) are substituted into A-sites (Bi^{3+} ; $r=1.03 \text{ \AA}$, Na^+ ; $r=1.39 \text{ \AA}$ and Ba^{2+} ; $r=1.61 \text{ \AA}$), the unit cell volume is dramatically reduced while if the $(\text{AlNb})^{4+}$ is replaced into B site (Ti^{4+} ; $r=0.61 \text{ \AA}$), the unit cell volume is slightly changed. Thus, in our study, the results provide evidence that the $(\text{AlNb})^{4+}$ substitutes into B-site of Ti^{4+} .

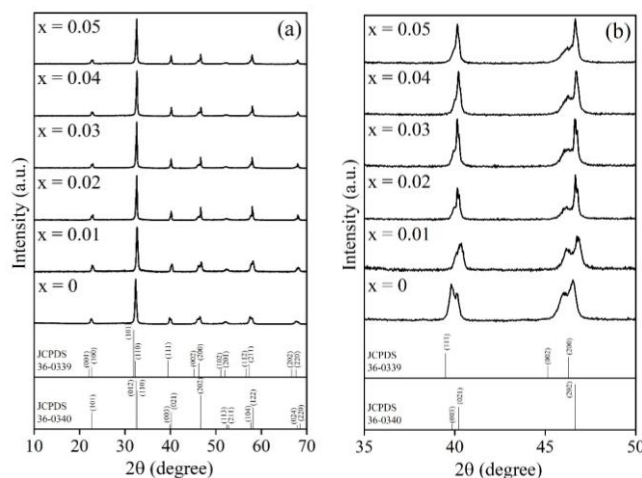


Figure 1. X-ray diffraction (XRD) pattern of $\text{BNBT}_{1-x}\text{AN}_x$ ceramics with $x=0$ – 0.05 within a 2θ range (a) 10 – 70° and (b) 35 – 50°

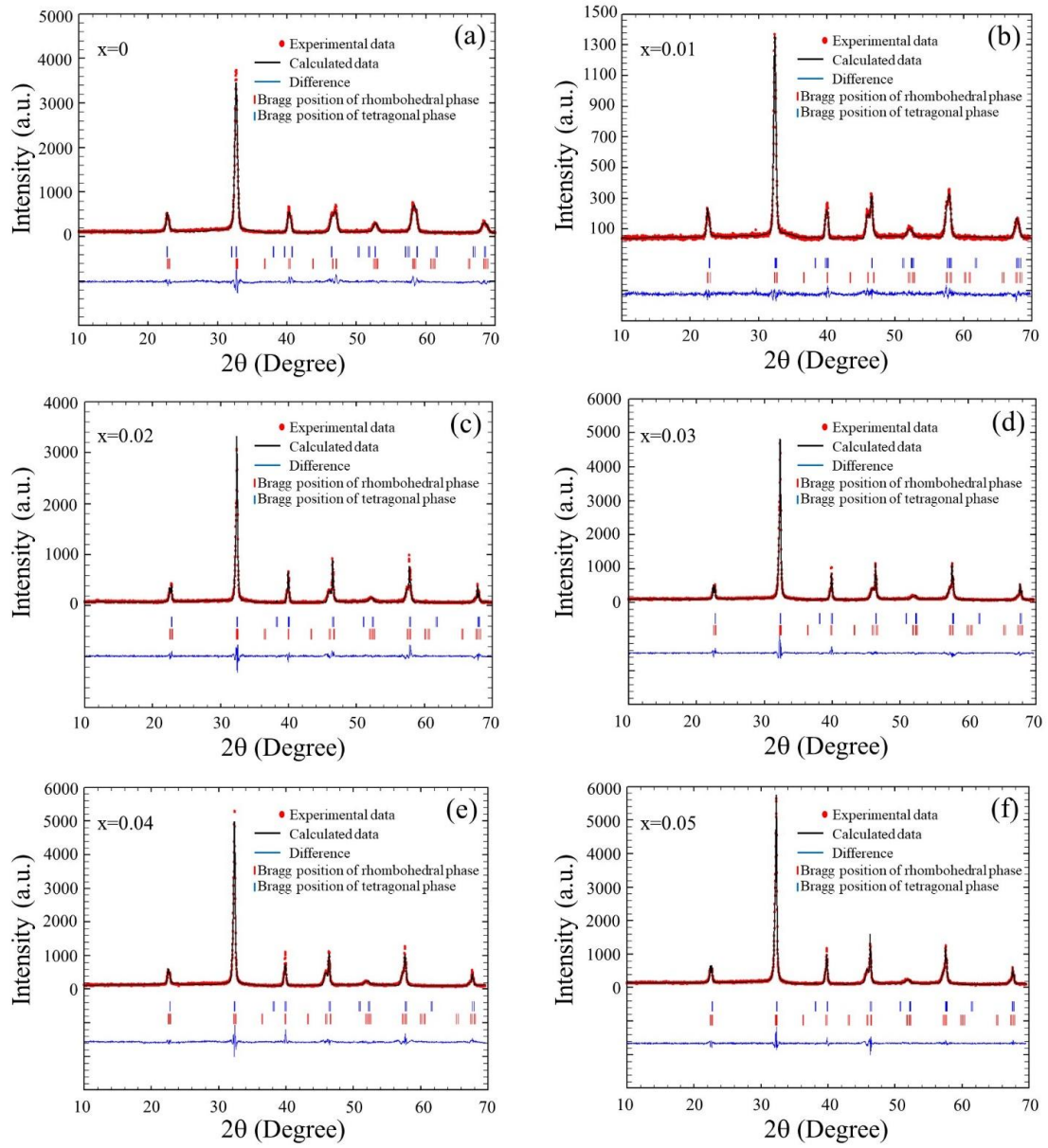


Figure 2. The experimental (dots) and calculated (line) intensities of $\text{BNBT}_{1-x}\text{AN}_x$ in $2\theta=10\text{--}70^\circ$ are seen in the final plots of the Rietveld refinement with (a) $x=0$, (b) $x=0.01$, (c) $x=0.02$, (d) $x=0.03$ (e) $x=0.04$ and (f) $x=0.05$

Table 1. Refined parameters and the percentage of phase for the BNB_T1-xAN_x ceramics with x=0-0.05

Sample	Refine parameters	Phase structures	Profile parameters	Atoms information					The percentage of phase
				Label	x	y	z	Occ.	
x=0	$\chi^2=1.73$ $R_p=19.9\%$ $R_{wp}=17.7\%$ $R_{exp}=12.8\%$	<i>R3c:H</i>	$a=5.5938\text{\AA}$	Bi	0	0	0.2627	0.42310	53
			$c=13.3016\text{\AA}$	Na	0	0	0.2627	0.36575	
			$c/a=2.3778$	Ti	0	0	0.0063	1.05992	
			$V=416.2150\text{ \AA}^3$	O	0.1260	0.3360	0.0833	0.90314	
			$u=0.0821$	Ba	0	0	0.2627	0.06105	
			$v=0.1357$	Al	0	0	0.0063	0	
			$w=0.1285$	Nb	0	0	0.0063	0	
		<i>P4bm</i>	$a=5.4617\text{\AA}$	Bi	0	0.5	0.5450	0.44565	47
			$c=3.9004\text{\AA}$	Na	0	0.5	0.5450	0.47245	
			$c/a=0.7141$	Ti	0	0	0	0.095867	
			$V=116.3496\text{ \AA}^3$	O1	0	0	0.5100	1.37665	
			$u=1.2668$	O2	0.2710	0.2290	0.0150	1.22850	
			$v=0.1364$	Ba	0	0.5	0.5450	0.04292	
			$w=0.009$	Al	0	0	0	0	
x=0.01	$\chi^2=1.11$ $R_p=31.20\%$ $R_{wp}=24.40\%$ $R_{exp}=23.22\%$	<i>R3c:H</i>	$a=5.5038\text{\AA}$	Bi	0	0	0.2627	0.3873	45
			$c=13.5825\text{\AA}$	Na	0	0	0.2627	0.4633	
			$c/a=2.4678$	Ti	0	0	0.0063	1.0324	
			$V=411.4386\text{ \AA}^3$	O	0.1260	0.3360	0.0833	1.1022	
			$u=-0.0990$	Ba	0	0	0.2627	0.0807	
			$v=0.2173$	Al	0	0	0.0063	0.0018	
			$w=0.0119$	Nb	0	0	0.0063	0.0029	
		<i>P4bm</i>	$a=5.4902\text{\AA}$	Bi	0	0.5	0.5450	0.5241	55
			$c=3.9476\text{\AA}$	Na	0	0.5	0.5450	0.4391	
			$c/a=0.7190$	Ti	0	0	0	0.7817	
			$V=118.9898\text{ \AA}^3$	O1	0	0	0.5100	1.0351	
			$u=1.0248$	O2	0.2710	0.2290	0.0150	1.8985	
			$v=0.6169$	Ba	0	0.5	0.5450	0.0672	
			$w=-0.0932$	Al	0	0	0	0.0013	
x=0.02	$\chi^2=1.38$ $R_p=30.10\%$ $R_{wp}=22.20\%$ $R_{exp}=18.88\%$	<i>R3c:H</i>	$a=5.5208\text{\AA}$	Bi	0	0	0.2627	0.4171	44
			$c=13.5292\text{\AA}$	Na	0	0	0.2627	0.5460	
			$c/a=2.4505$	Ti	0	0	0.0063	0.9806	
			$V=412.3596\text{ \AA}^3$	O	0.1260	0.3360	0.0833	3.0386	
			$u=-0.0705$	Ba	0	0	0.2627	0.0632	
			$v=0.0859$	Al	0	0	0.0063	0.0062	
			$w=-0.0130$	Nb	0	0	0.0063	0.0066	
		<i>P4bm</i>	$a=5.5089\text{\AA}$	Bi	0	0.5	0.5450	0.4091	56
			$c=3.9449\text{\AA}$	Na	0	0.5	0.5450	0.6361	
			$c/a=0.7161$	Ti	0	0	0	0.9735	
			$V=119.7197\text{ \AA}^3$	O1	0	0	0.5100	1.0095	
			$u=0.4515$	O2	0.2710	0.2290	0.1500	1.1989	
			$v=0.9238$	Ba	0	0.5	0.5450	0.0450	
			$w=-0.1884$	Al	0	0	0	0.0051	
x=0.03	$\chi^2=1.53$ $R_p=25.30\%$ $R_{wp}=19.60\%$ $R_{exp}=15.84\%$	<i>R3c:H</i>	$a=5.5352\text{\AA}$	Bi	0	0	0.2627	0.4026	38
			$c=13.5551\text{\AA}$	Na	0	0	0.2627	0.4968	
			$c/a=2.4489$	Ti	0	0	0.0063	0.9954	
			$V=415.3071\text{ \AA}^3$	O	0.1260	0.3360	0.0833	2.9814	
			$u=-0.0239$	Ba	0	0	0.2627	0.0752	
			$v=0.0499$	Al	0	0	0.0063	0.0068	
			$w=-0.0068$	Nb	0	0	0.0063	0.0072	
		<i>P4bm</i>	$a=5.5239\text{\AA}$	Bi	0	0.5	0.5450	0.3752	62
			$c=3.9531\text{\AA}$	Na	0	0.5	0.5450	0.5475	
			$c/a=0.7156$	Ti	0	0	0	0.9773	
			$V=120.6228\text{ \AA}^3$	O1	0	0	0.5100	0.9162	
			$u=0.9266$	O2	0.2710	0.2290	0.0150	1.3150	
			$v=0.9758$	Ba	0	0.5	0.5450	0.0671	
			$w=-0.2134$	Al	0	0	0	0.0072	
x=0.04	$\chi^2=2.39$ $R_p=31.00\%$ $R_{wp}=22.20\%$ $R_{exp}=14.39\%$	<i>R3c:H</i>	$a=5.5373\text{\AA}$	Bi	0	0	0.2627	0.4141	34
			$c=13.5361\text{\AA}$	Na	0	0	0.2627	0.5127	
			$c/a=2.4445$	Ti	0	0	0.0063	1.0049	
			$V=415.0397\text{ \AA}^3$	O	0.1260	0.3360	0.0833	1.7041	
			$u=-0.0345$	Ba	0	0	0.2627	0.0690	
			$v=-0.0044$	Al	0	0	0.0063	0.0129	
			$w=0.0398$	Nb	0	0	0.0063	0.0125	
		<i>P4bm</i>	$a=5.5176\text{\AA}$	Bi	0	0.5	0.5450	0.4261	66
			$c=3.9525\text{\AA}$	Na	0	0.5	0.5450	0.5118	
			$c/a=0.7163$	Ti	0	0	0	1.1333	
			$V=120.3296\text{ \AA}^3$	O1	0	0	0.5100	2.7219	
			$u=0.6764$	O2	0.2710	0.2290	0.0150	3.3672	
			$v=0.9177$	Ba	0	0.5	0.5450	0.0882	
			$w=-0.1776$	Al	0	0	0	0.0143	
x=0.05	$\chi^2=1.25$ $R_p=18.80\%$ $R_{wp}=15.30\%$ $R_{exp}=13.74\%$	<i>R3c:H</i>	$a=5.5446\text{\AA}$	Bi	0	0	0.2627	0.4191	32
			$c=13.5686\text{\AA}$	Na	0	0	0.2627	0.4406	
			$c/a=2.4471$	Ti	0	0	0.0063	0.9865	
			$V=417.1339\text{ \AA}^3$	O	0.1260	0.3360	0.0833	3.2729	
			$u=0.0260$	Ba	0	0	0.2627	0.0807	
			$v=-0.0031$	Al	0	0	0.0063	0.0195	
			$w=0.0005$	Nb	0	0	0.0063	0.0734	
		<i>P4bm</i>	$a=5.5358\text{\AA}$	Bi	0	0.5	0.5450	0.4257	68
			$c=3.9594\text{\AA}$	Na	0	0.5	0.5450	0.4553	
			$c/a=0.7152$	Ti	0	0	0	0.9397	
			$V=121.3361\text{ \AA}^3$	O1	0	0	0.5100	0.9871	
			$u=0.2895$	O2	0.2710	0.2290	0.0150	2.1075	
			$v=0.8392$	Ba	0	0.5	0.5450	0.0715	
			$w=-0.1418$	Al	0	0	0	0.0123	
				Nb	0	0	0	0.0134	

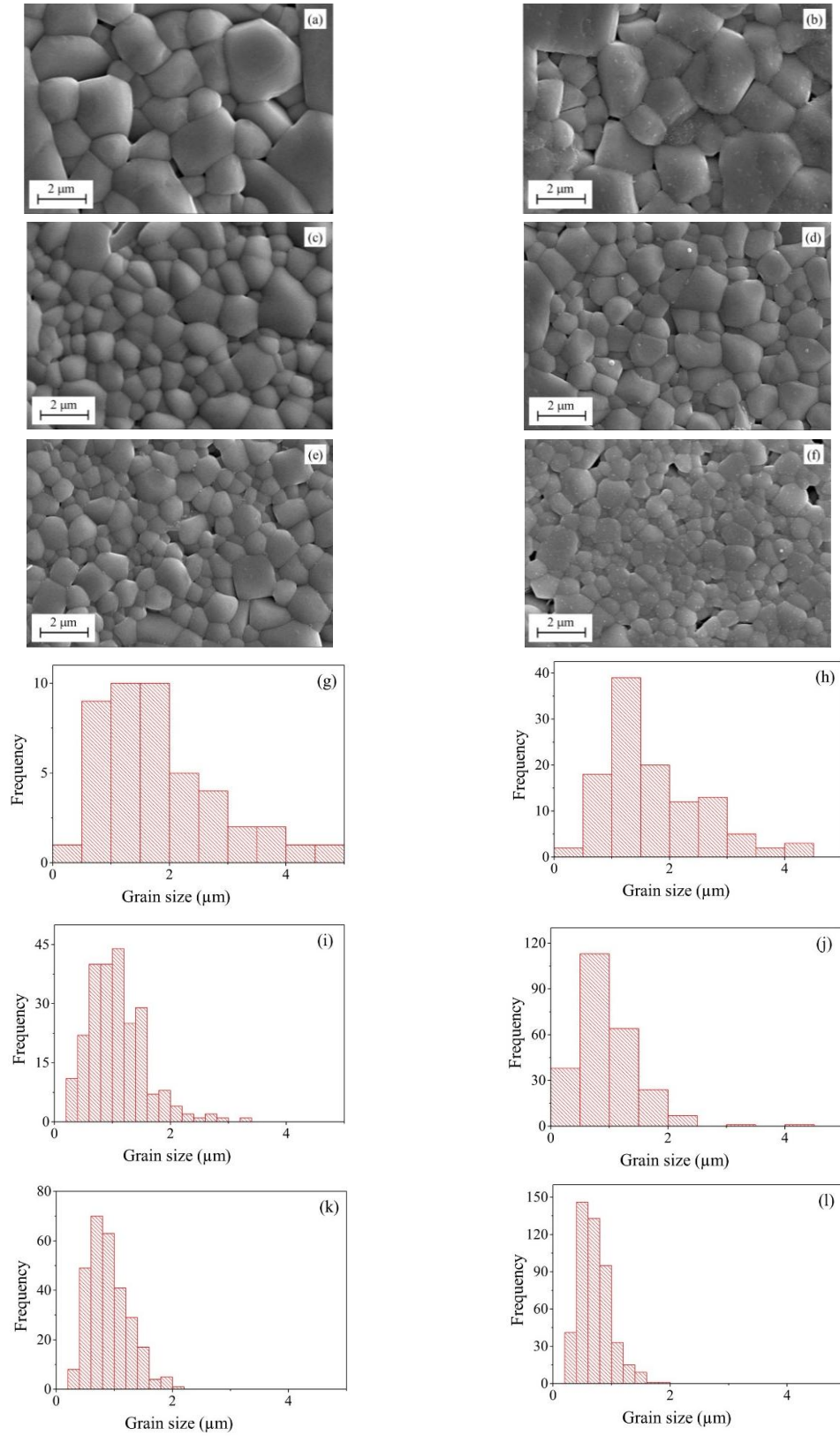


Figure 3. The morphology of surfaces and grain size distributions of $\text{BNBT}_{1-x}\text{AN}_x$ ceramics with (a), (g) $x=0$, (b), (h) $x=0.01$, (c), (i) $x=0.02$, (d), (j) $x=0.03$, (e), (k) $x=0.04$ and (f), (l) $x=0.05$

The SEM micrographs and the grain size distributions of the $\text{BNBT}_{1-x}\text{AN}_x$ ceramics with $x=0-0.05$ are displayed in Figure 3(a)-(f) and 3(g)-(1), respectively. The surface morphology exhibited nearly-spherical shaped grains with anisotropic grain growth in all samples. As listed in Table 2, the average grain size decreased from 1.8 to 0.7 μm when $(\text{AlNb})^{4+}$ content increased from 0 to 0.05, which is probably due to inhibition of grain growth

by $(\text{AlNb})^{4+}$ at the grain boundaries. With increased $(\text{AlNb})^{4+}$, the pores tended to increase and were clearly enhanced at $x=0.05$, as seen in Figure 3(a)-(f). The grain size distribution became narrower as $(\text{AlNb})^{4+}$ increased, as shown in Figure 3(g)-(1). It was found that the measured density of $\text{BNBT}_{1-x}(\text{AN})_x$ ceramics significantly decreased from 5.84 to 5.54 g/cm^3 when x increased from 0 to 0.05, as listed in Table 2.

Table 2. The average grain size, measured density, dielectric and ferroelectric properties of $\text{BNBT}_{1-x}\text{AN}_x$ ceramics with $x=0-0.05$

samples	Average grain size (μm)	Measured density (g/cm^3)	T_d ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	ϵ_m	$\tan\delta$ at T_m	P_r ($\mu\text{C/cm}^2$)	E_c (kV/cm)
$x=0$	1.8	5.84	165	272	5745	0.02	21.2	23.0
$x=0.01$	1.7	5.71	153	270	5390	0.01	17.4	15.8
$x=0.02$	1.2	5.70	151	264	5124	0.01	10.7	22.6
$x=0.03$	1.0	5.67	138	268	4627	0.02	10.6	23.4
$x=0.04$	0.8	5.59	129	264	4619	0.01	10.0	13.8
$x=0.05$	0.7	5.54	120	264	4484	0.01	7.7	10.6

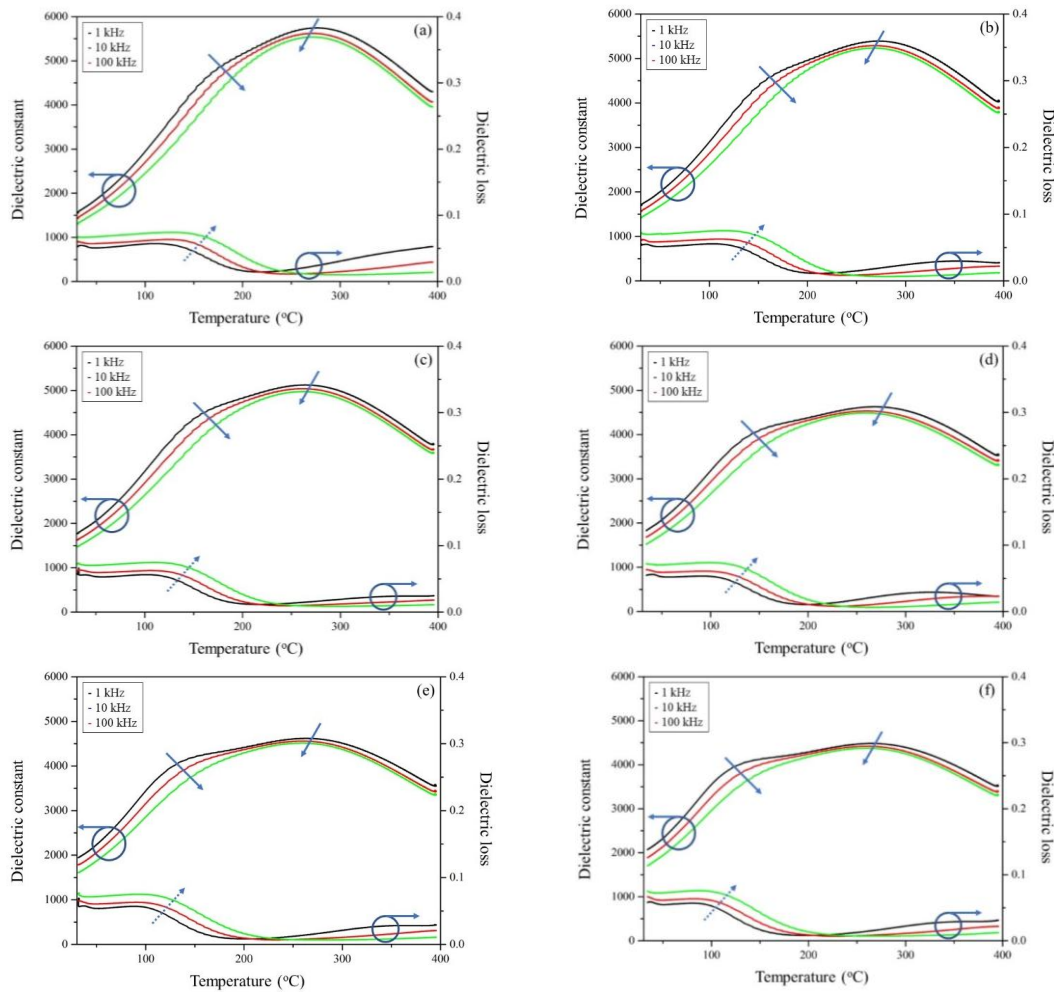


Figure 4. Temperature dependence of the dielectric constant (ϵ_r) and dielectric loss ($\tan\delta$) of $\text{BNBT}_{1-x}\text{AN}_x$ ceramics with (a) $x=0$, (b) $x=0.01$, (c) $x=0.02$, (d) $x=0.03$, (e) $x=0.04$ and (f) $x=0.05$ at various frequencies

Figure 4(a)-(f) show the temperature dependence of the dielectric constant (ϵ_r) and dielectric loss ($\tan\delta$) of BNBT_{1-x}AN_x ceramics with $x=0-0.05$, measured at various frequencies (1, 10, and 100 kHz). BNT-based ceramics, in general, present two dielectric anomalies, one at the depolarization temperature (T_d) corresponding to the thermal evolution of the polar nano-regions (PNRs) from a rhombohedral structure with $R3c$ symmetry to a tetragonal structure with $P4bm$ symmetry at that occurs at low temperatures (Pan *et al.*, 2011; Badapanda *et al.*, 2017) and the second an anomaly at the temperature of the maximum dielectric constant (T_m), at higher temperatures (Pan *et al.*, 2011; Badapanda *et al.*, 2017). The dielectric curve showed broad transition peaks and strong frequency dispersion around T_d and T_m for all samples. T_d shifted to a higher temperature as the frequency increased from 1 to 100 kHz whereas T_m shifted to a lower temperature, according to the arrow in Figure 4(a-e). Moreover, as shown by the dashed arrow in Figure 4(a-e), the $\tan\delta$ at T_d increased as the frequency increased from 1 to 100 kHz. According to these results, all samples can be classified as relaxor ferroelectrics. At 1 kHz, T_d decreased significantly to a lower temperature, from 165°C to 120°C, as listed in Table 2. The downward shift of T_d may be due to the distortion of the structure caused by (AlNb)⁴⁺ substitution into B-sites, indicating a phase transition from the ferroelectric to relaxor ferroelectric, which is similar to the results of (MgNb)⁴⁺ substituted into B-sites on BNKT ceramics by H. Xie *et al.* (Xie *et al.*, 2018). The T_m was in the range of 264-272°C at 1 kHz, as listed in Table 2.

According to Table 2, the maximum dielectric constant at T_m (ϵ_m) of BNBT_{1-x}AN_x ceramics gradually decreased from 5745 to 4484 as (AlNb)⁴⁺ increased from 0 to 0.05, owing to a deviation in the phase ratio from an MPB (nearly equal R:T), a poorer microstructure, and lower density. The dielectric loss ($\tan\delta$) did not significantly change with (AlNb)⁴⁺ content, and the $\tan\delta$ was around 0.01 in all ceramics, as listed in Table 2.

Figure 5(a)-(f) displays the hysteresis loops (P-E) of BNBT_{1-x}AN_x ceramics with $x=0-0.05$, measured under an electrical field of 40 kV/cm⁻¹. All ceramics showed saturated loops, implying a ferroelectric characteristic. In general, BNT-based ceramics exhibit ergodic relaxor behavior, which is a type of relaxor behavior in which the field-induced ferroelectric order turns back to normal ferroelectric behavior when the electric field is removed, as opposed to non-ergodic relaxor behavior, which exhibits ferroelectric-like behavior and turns irreversibly into normal ferroelectric behavior (Bhupaijit *et al.*, 2021). A nearly-rectangular shape was observed in the pure BNBT ceramic ($x=0$), with a large maximum polarization (P_{max}) and remnant polarization (P_r), suggesting non-ergodic relaxor behavior, which is consistent with the studies of B. Thatawong *et al.* (Thatawong *et al.*, 2022). It was seen that the loops gradually became slimmer while P_{max} and P_r tended to decrease with increased (AlNb)⁴⁺, implying that domain switching was easier, which also confirms the appearance of the ergodic relaxor behavior. The substitution with (AlNb)⁴⁺ distorted the long-range ferroelectric order, resulting in a shift from non-ergodic to ergodic relaxor behavior and domain structure transformation from macrodomain to microdomain (Qi and Zuo, 2019; Li *et al.*, 2020). The P_r and E_c of the BNBT_{1-x}AN_x ceramics are listed in Table 2. Both of them tended to decrease with increased (AlNb)⁴⁺ content. This can be explained by (AlNb)⁴⁺ substitution significantly disrupted the ferroelectric order of BNBT ceramics, leading to a decrease in the stability of the electric dipole, resulting in ferroelectric property degradation (Jin *et al.*, 2014).

The degenerate electrical properties with (AlNb)⁴⁺ substitution is due to the smaller grains, which provide a lot of insulating grain boundaries and more grain-grain interface contact area (Bongkarn *et al.*, 2016; Yotthuan *et al.*, 2019). Inclusive, the shift in the phase ratio and poor microstructure consequently contributed to the inferior electrical properties.

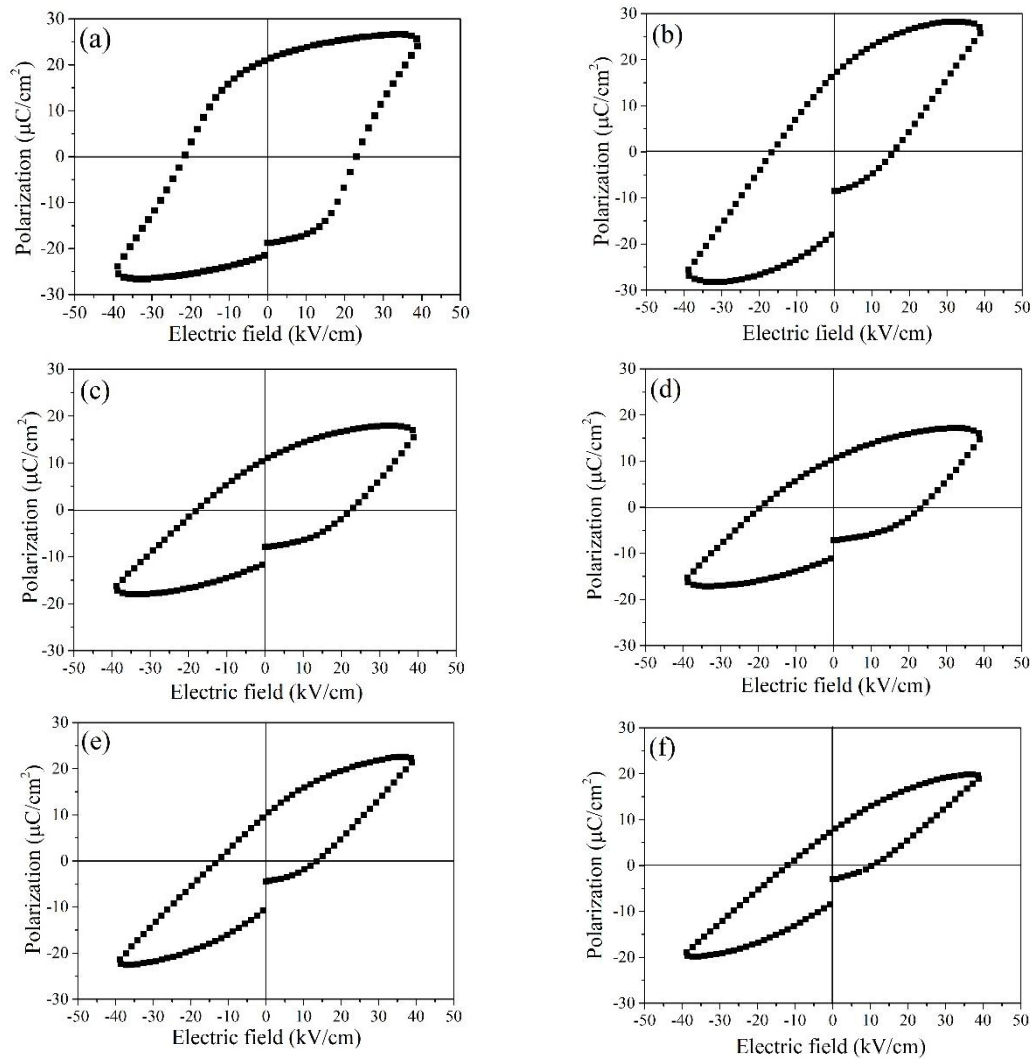


Figure 5. The hysteresis (P-E) loops for BNBT_{1-x}AN_x ceramics with (a) $x=0$, (b) $x=0.01$, (c) $x=0.02$, (d) $x=0.03$, (e) $x=0.04$ and (f) $x=0.05$

Conclusions

In summary, lead-free BNBT_{1-x}AN_x ceramics with $x=0-0.05$ were fabricated using the solid-state combustion technique. The effects of (AlNb)⁴⁺ substitution into B-sites on the phase formation, microstructure, and electrical properties was systematically investigated. The coexistence of the rhombohedral and tetragonal phases was observed in all BNBT_{1-x}AN_x ceramics, and the tetragonal phase increased as (AlNb)⁴⁺ increased, as seen in the Rietveld refinement. The surface morphology displayed nearly spherical shaped grains for all samples. When (AlNb)⁴⁺ content increased from 0 to 0.05, the average grain size and measured density

decreased rapidly from 1.8 to 0.7 μm and 5.84 to 5.54 g/cm^3 , respectively. All of the ceramics displayed a strong frequency dispersion, implying that these ceramics are relaxor ferroelectrics. The deviation of the phase ratio from MPB, poor microstructure and a decrease in the density with (AlNb)⁴⁺ substitution resulted in weakened dielectric properties. The transition from a non-ergodic to an ergodic relaxor ferroelectric state was obtained with (AlNb)⁴⁺ substitution. The decreases in density and electrical properties make BNBT ceramics with (AlNb)⁴⁺ substitution into B-sites are unsuitable for further application.

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References

- Badapanda, T., Sahoo, S., and Nayak, P. (2017). Dielectric, ferroelectric, and piezoelectric study of BNT-BT solid solutions around the MPB region. *Materials Science and Engineering*, 178:012032. <https://doi.org/10.1088/1757-899X/178/1/012032>
- Barick, B.K., Mishra, K.K., Arora, A.K., Choudhary, R.N.P., and Pradhan, D.K. (2011). Impedance and Raman spectroscopic studies of (Na_{0.5}Bi_{0.5})TiO₃. *Journal of Physics D: Applied Physics*, 44(35):355402. <https://doi.org/10.1088/0022-3727/44/35/355402>
- Bhupaijit, P., Kornphom, C., Kidkhunthod, P., Nuntawong, N., and Bongkarn, T. (2019). Structural study of (1-x)BNKLT-xBZT ceramics using XRD, Raman spectroscopy, and XAS. *Integrated Ferroelectrics*, 195:144-153. <https://doi.org/10.1080/10584587.2019.1570028>
- Bhupaijit, P., Nuntawong, N., Kidkhunthod, P., Pinitsoontorn, S., and Bongkarn, T. (2021). Enhanced electrical properties near the morphotropic phase boundary in lead-free Bi_{0.5}Na_{0.34}K_{0.11}Li_{0.05}Ti_{1-x}Ni_xO_{3-δ} ceramics. *Radiation Physics and Chemistry*, 189:109716. <https://doi.org/10.1016/j.radphyschem.2021.109716>
- Bongkarn, T., Chootin, S., Pinitsoontorn, S., and Maensiri, S. (2016). Excellent piezoelectric and ferroelectric properties of KNLNTS ceramics with Fe₂O₃ doping synthesized by the solid state combustion technique. *Journal of Alloys and Compounds*, 682:14-18. <https://doi.org/10.1016/j.jallcom.2016.04.285>
- Cheng, R., Xu, Z., Chu, R., Hao, J., Du, J., and Li, G. (2016). Electric field-induced ultrahigh strain and large piezoelectric effect in Bi_{1/2}Na_{1/2}TiO₃-based lead-free piezoceramics. *Journal of the European Ceramic Society*, 36(3):489-496. <https://doi.org/10.1016/j.jeurceramsoc.2015.09.043>
- Fan, P., Zhang, Y., Xie, B., Zhu, Y., Ma, W., Wang, C., Yang, B., Xu, J., Xiao, J., and Zhang, H. (2018). Large electric-field-induced strain in B-site complex-ion (Fe_{0.5}Nb_{0.5})⁴⁺-doped Bi_{1/2}(Na_{0.82}K_{0.12})_{1/2}TiO₃ lead-free piezoceramics. *Ceramics International*, 44(3):3,211-3,217. <https://doi.org/10.1016/j.ceramint.2017.11.092>
- Jin, C.C., Wang, F.F., Wei, L.L., Tang, J., Li, Y., Yao, Q.R., Tian, C.Y., and Shi, W.Z. (2014). Influence of B-site complex-ion substitution on the structure and electrical properties in Bi_{0.5}Na_{0.5}TiO₃-based lead-free solid solutions. *Journal of Alloys and Compounds*, 585:185-191. <https://doi.org/10.1016/j.jallcom.2013.09.152>
- Lee, W.C., Huang, C.Y., Tsao, L.K., and Wu, Y.C. (2010). Crystal Structure, dielectric and ferroelectric properties of (Bi_{0.5}Na_{0.5})TiO₃-(Ba,Sr)TiO₃ lead-free piezoelectric ceramics. *Journal of Alloys and Compounds*, 492(1-2):307-312. <https://doi.org/10.1016/j.jallcom.2009.11.083>
- Li, D., Shen, Z.Y., Li, Z., Luo, W., Wang, X., Wang, Z., Song, F., and Li, Y. (2020). *P-E* hysteresis loop going slim in Ba_{0.5}Sr_{0.7}TiO₃-modified Bi_{0.5}Na_{0.5}TiO₃ ceramics for energy storage applications. *Journal of Advanced Ceramics*, 9(2):183-192. <https://doi.org/10.1007/s40145-020-0358-9>
- Li, L., Hao, J., Chu, R., Xu, Z., Li, W., Du, J., and Fu, P. (2016a). Dielectric, ferroelectric and field-induced strain response of lead-free (Fe, Sb)-modified (Bi_{0.5}Na_{0.5})_{0.935}Ba_{0.065}TiO₃ ceramics. *Ceramics International*, 42:9419-9425. <https://doi.org/10.1016/j.ceramint.2016.02.168>
- Li, L., Hao, J., Xu, Z., Li, W., and Chu, R. (2016b). 0.46% unipolar strain in lead-free BNT-BT system modified with Al and Sb. *Materials Letters*, 184:152-156. <https://doi.org/10.1016/j.matlet.2016.07.150>
- Pan, H., Hou, Y., Chao, X., Wei, L., and Yang, Z. (2011). Microstructure and electrical properties of La₂O₃-doped Bi_{0.5}(Na_{0.68}K_{0.22}Li_{0.1})_{0.5}TiO₃ lead-free piezoelectric ceramics. *Current Applied Physics*, 11(3):888-892. <https://doi.org/10.1016/j.cap.2010.12.013>
- Park, S.E. and Shrout, T.R. (1997). Ultrahigh strain and piezoelectric behavior in relaxor based ferroelectric single crystals. *Journal of Applied Physics*, 82:1,804-1,811. <https://doi.org/10.1063/1.365983>
- Qi, H. and Zuo, R. (2019). Linear-like lead-free relaxor antiferroelectric (Bi_{0.5}Na_{0.5})TiO₃-NaNbO₃ with giant energy storage density/efficiency and super stability against temperature and frequency. *Journal of Materials Chemistry A*, 7(8):3,971-3,978. <https://doi.org/10.1039/C8TA12232F>
- Sasaki, A., Chiba, T., Mamiya, Y., and Otsuki, E. (1999). Dielectric and Piezoelectric Properties of (Bi_{0.5}Na_{0.5})TiO₃-(Bi_{0.5}K_{0.5})TiO₃ Systems. *Japanese Journal of Applied Physics*, 38:5,564-5,567. <https://doi.org/10.1143/JJAP.38.5564>
- Shen, Y., Xie, H., Sun, Y., Xu, J., Yang, L., Pan, X., Zhou, C., and Wang, H. (2021). High piezoelectric properties of 0.82(Bi_{0.5}Na_{0.5})TiO₃-0.18(Bi_{0.5}K_{0.5})TiO₃ lead-free ceramics modified by (Mn_{1/3}Nb_{2/3})⁴⁺ complex ions. *Bulletin of Materials Science*, 44:1-8. <https://doi.org/10.1007/s12034-021-02389-3>
- Takenaka, T., Maruyama, K., and Sakata, K. (1991). (Bi_{1/2}Na_{1/2})TiO₃-BaTiO₃ System for Lead-Free Piezoelectric Ceramics. *Japanese Journal of Applied Physics*, 30(9B):2,236-2,239. <https://doi.org/10.1143/JJAP.30.2236>
- Thatawong, B., Bhupaijit, P., Lamyai, Y., Vittayakorn, N., and Bongkarn, T. (2022). Dielectric and piezoelectric properties near the morphotropic phase boundary for 0.94BNT-0.06BT ceramics synthesized by the solid-state combustion technique. *Ferroelectrics*, 586(1):199-212. <https://doi.org/10.1080/00150193.2021.2014271>
- Xie, H., Zhao, Y., Xu, J., Yang, L., Zhou, C., Zhang, H., Zhang, X., Qiu, W., and Wang, H. (2018). Photoluminescence efficiency significantly enhanced by surface modification of SiO₂ coating on β-sialon:Eu²⁺ phosphor particle. *Journal of Alloys and Compounds*, 741:454-458. <https://doi.org/10.1016/j.jallcom.2018.01.153>
- Yothuan, S., Kornphom, C., Prasertpalichat, S., Suriwong, T., Pinitsoontorn, S., and Bongkarn, T. (2019). Phase ratio, dielectric, ferroelectric, and magnetic properties of BCTZ ceramics with CuO doping synthesized by the solid-state combustion technique. *Physica Status Solidi A*, 216(11). <https://doi.org/10.1002/pssa.201800803>
- Zeng, W., Li, Q., Zhou, C., Xu, J., Yuan, C., and Chen, G. (2017). A new insight onto structure complexity in ferroelectric ceramics. *Journal of Advanced Ceramics*, 6:262-268. <https://doi.org/10.1007/s40145-017-0237-1>