

ELECTRIC AND MAGNETIC PROPERTIES OF $\text{Co}_{0.6}\text{Zn}_{0.4}\text{Fe}_{1.7}\text{Mn}_{0.3}\text{O}_4$ doped $(0.94(\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3)-0.06\text{BaTiO}_3)$ CERAMICS PREPARED BY THE SOLID-STATE COMBUSTION METHOD

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Abstract

In this research paper, we fabricated $(1-x)[0.94(\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3)-0.06\text{BaTiO}_3]-x\text{Co}_{0.6}\text{Zn}_{0.4}\text{Fe}_{1.7}\text{Mn}_{0.3}\text{O}_4$ [(1-x)BNBT-xCZFM] ceramics at $x = 0, 0.05, 0.10, 0.15$, and 0.20 via a method of solid-state combustion. Dielectric, ferroelectric, magnetic, microstructure, and phase formation characteristics were investigated. The BNBT and the CZFM powders were calcined separately at 750°C for 2 h, then their powders were mixed to produce (1-x)BNBT-xCZFM solid solutions with different BNBT and CZFM ratios and sintered at $1,125^\circ\text{C}$ for 2 h. The X-ray diffraction results showed that undoped BNBT ceramics have a typical perovskite structure, with rhombohedral (R) and tetragonal (T) phases coexisting. As the CZFM concentration rose, the ceramics exhibited coexisting rhombohedral (R), tetragonal (T) perovskite, and cubic (C) spinel phases. When x rose from 0 to 0.05, the average grain size of the ceramics greatly increased, while the density and dielectric constant (ϵ) slightly decreased. When x raised from 0.05 to 0.15, average grain size, density and the dielectric constant (ϵ) of the ceramics tended to increase, then they dropped as the CZFM content increased further. CZFM doping into BNBT ceramics reduced the ferroelectric properties by reducing the remnant polarization (P_r) and increasing the E_c values and leakage current. CZFM doping into BNBT ceramics with $x = 0.15$ and 0.20 showed both typical of ferromagnetic and ferroelectric properties.

Keywords: BNBT; CZFM; Combustion method; Ferroelectric; Ferromagnetic

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Introduction

Multiferroic materials are a unique class of materials that simultaneously exhibit two or more ferroic orders, such as ferromagnetism (spontaneous magnetization), ferroelectricity (spontaneous electric polarization), and ferroelasticity (spontaneous strain). These materials have garnered significant scientific and technological interest due to their potential to enable novel functionalities that are unattainable in conventional single-order materials (Spaldin *et al.*, 2010; Matavž *et al.*, 2021). Their potential uses include energy harvesting, low-power memory devices, sensors, spintronics, and transducers (Khomskii, 2006). Multiferroic materials can be classified into single-phase and two-phase composites. Single-phase multiferroic materials consist of single compounds that display both ferroelectric and ferromagnetic properties such as BiFeO₃ ceramics (Jia *et al.*, 2009). On the other hand, two-phase composite multiferroic materials, like BiFeO₃-BaTiO₃ (Futakuchi *et al.*, 2014) derive their characteristics from their compositions of different electromagnetic ceramics. Single-phase multiferroic materials exhibit minimal magnetoelectric response, restricting their use in electronic devices. In contrast, two-phase composite multiferroics demonstrate exceptionally high magnetoelectric properties, making them versatile and well-suited for various applications in the electronics industry (Pradhan *et al.*, 2012; Zhu *et al.*, 2015). Therefore, two-phase composite multiferroic materials are widely studied. The commonly studied multiferroic materials are Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O₃-Ni_{0.8}Zn_{0.2}Fe₂O₄ (BCTZ-NZF), Ba_{0.9}Sr_{0.1}Zr_{0.04}Ti_{0.96}O₃-Ni_{0.8}Zn_{0.2}Fe₂O₄ (BSZT-NZF), Pb(Zr_{0.52}Ti_{0.48})O₃-NiFe₂O₄ (PZT-NF), and Co_{0.8}Cu_{0.2}Fe₂O₄-SrTiO₃ (CCF-ST) (Ryu *et al.*, 2006; Ahmed *et al.*, 2013; Rani *et al.*, 2017; Bansal *et al.*, 2021). In 1970, Van den Boomgaard and Born (1978) were the first to investigate the two-phase composite BaTiO₃-Ni(Co,Mn)Fe₂O₄ which combined an electro ceramic with a perovskite structure (ABO₃) and a magnetic ceramic with a spinel structure (AB₂O₄).

Recently, (Bi_{0.5}Na_{0.5}TiO₃)-BaTiO₃ (BNBT) ceramics have shown great potential as lead-free ferroelectric materials with a perovskite structure (ABO₃) (Swain and Kumar, 2021; Xie *et al.*, 2021; Yang *et al.*, 2022). Their outstanding electrical characteristics, such as the dielectric constant ($\epsilon_r \approx 6000$) and ferroelectric properties ($P_r \approx 38 \mu\text{C}/\text{cm}^2$), make them a promising choice for multiferroic applications. Recently, Thatawong *et al.* (2022) synthesized 0.94(Bi_{0.5}Na_{0.5}TiO₃)-0.06BaTiO₃ ceramics via the solid-state combustion method. It was found that the ceramics had a high

dielectric constant ($\epsilon_m = 5674$), an excellent remnant polarization ($P_r = 38.6 \mu\text{C}/\text{cm}^2$), and a good coercive field ($E_c = 38.9 \text{ kV}/\text{cm}^2$).

For ferromagnetic materials, the spinel ferrites such as MnFe₂O₄-MF (Reddy *et al.*, 2015), ZnFe₂O₄-ZF (Ni *et al.*, 2020), and CoFe₂O₄-CF (Zhou *et al.*, 2008), are magnetic materials having a specific general formula AB₂O₄. CF and ZF are notable for their good magnetic properties and excellent chemical stability. Nevertheless, the ceramics still offer issues due to their high magnetic coercivity (For CF and ZF, $H_c \sim 5,400 \text{ Oe}$ and $\sim 1,200 \text{ Oe}$, respectively). Enhancing the properties of CF and ZF ceramics can be achieved by substituting A-site and B-site ions, in small amounts to effectively improve the magnetic characteristics. Recently, According to Gupta *et al.* (2015), Co_{0.6}Zn_{0.4}Fe_{1.7}Mn_{0.3}O₄ (CZFM) ceramics exhibited low coercivity ($\sim 23.9 \text{ Oe}$) and high saturation magnetization ($\sim 67 \text{ emu/g}$). Furthermore, CZFM ceramics produced using the solid-state combustion process were reported by Thawong *et al.* (2019). It was found that the ceramics exhibited a high saturation magnetization ($M_s = 72.50 \text{ emu/g}$) and low coercive field ($H_c = 4.24 \text{ Oe}$). Therefore, in this work, we used the solid-state combustion technique to fabricate (1-x)[0.94(Bi_{0.5}Na_{0.5}TiO₃)-0.06BaTiO₃]-x Co_{0.6}Zn_{0.4}Fe_{1.7}Mn_{0.3}O₄ [(1-x)BNBT-xCZFM] ceramics at x = 0-0.20 and investigated the influence of CZFM concentration on BNBT ceramics' phase formation, microstructure, electric properties, and magnetic properties.

Experimental

In this study, (1-x)BNBT-xCZFM solid solutions (x = 0, 0.05, 0.10, 0.15, and 0.20 mol%) are produced using the solid-state combustion method with glycine as a fuel. Raw components employed included high purity grade reagents such as Bi(NO₃)₃·5H₂O (>98%, KemAus, AU), NaNO₃ (>99%, Ajax, NZ), Ba(NO₃)₂ (>99%, HiMedia, IN), TiO₂ (>99%, KemAus, AU), Co(NO₃)₂·6H₂O (>99%, Ajax, NZ), ZnO (>99% Merck, DE), Fe(NO₃)₃·9H₂O (>99%, Ajax, NZ) and MnO₂ (>99% Aldrich, MX). The raw materials were weighed to the appropriate stoichiometric ratios for different compositions of 0.94(Bi_{0.5}Na_{0.5}TiO₃)-0.06BaTiO₃ (BNBT) and Co_{0.6}Zn_{0.4}Fe_{1.7}Mn_{0.3}O₄ (CZFM), then ball-milled for 24 h. The suspensions were then dried at 120°C, and the powders were sieved. Glycine and dry BNBT powders were mixed in a 1:1.11 ratio and calcined for 2 h at 750°C

(Thatawong *et al.*, 2022). CZFM powders were mixed with glycine in a 1:0.855 ratio and subsequently calcined for 2 h at 750°C (Thawong *et al.*, 2019). The BNBT calcined powder and the CZFM calcined powder were mixed to produce (1-x)BNBT-xCZFM solid solutions in various compositions. These powders were fully blended with a 3 wt% polyvinyl alcohol (PVA) binder solution after 12 h of ball milling. The slurries were dried, and the calcinated powders were sieved. The powders were pressed into pellets with a diameter of about 15 mm and a thickness of about 1.5 mm using an 80 MPa hydraulic press. After removing the PVA, the pure (1-x)BNBT-xCZFM pellets were sintered at 1,125°C for 2 h, with a heating rate of 5°C per minute and natural cooling.

X-ray diffraction (XRD) using a BRUKER D2 Phaser was conducted to determine the phase composition and crystal structure of (1-x)BNBT-xCZFM ceramics. Scanning electron microscopy (SEM, Leo1455VP) was used to analyze the microstructure. Samples were polished with sandpaper and alumina abrasive, then thermally etched at 100°C below the sintering temperature for 15 min before imaging. Grain size was estimated using the linear interception method. Density was measured using the Archimedes technique with distilled water as the immersion medium. Electrical characterization involved coating both ceramic surfaces with conductive silver paste, firing at 550°C for 15 min, and naturally cooling. Dielectric properties were assessed using an LCR analyzer (HP4284A, Hewlett-Packard) at room temperature over a frequency range of 10 Hz to 1 MHz. Polarization-electric field (P-E) hysteresis loops were recorded at 1 Hz using a modified Sawyer-Tower circuit (Radiant, PLC2-The P-E loop) with computer-controlled data acquisition. The magnetic characteristics of the sample were assessed using a Vibrating Sample Magnetometer (VSM, Versa Lab model, Quantum Design). This instrument evaluates the magnetic response of materials by applying an external magnetic field, which is adjusted to 10,000 Oersted (Oe).

Results and Discussion

Figure 1 displays the patterns of X-ray diffraction (XRD) of the (1-x)[0.94(Bi_{0.5}Na_{0.5}TiO₃)-0.06BaTiO₃]-xCu_{0.6}Zn_{0.4}Fe_{1.7}Mn_{0.3}O₄ [(1-x)BNBT-xCZFM] ceramics with x = 0, 0.05, 0.10, 0.15, and 0.20 at room temperature in the 2θ range between 20-70°. The results showed that the [(1-x)BNBT-xCZFM] ceramic at x = 0 (pure BNBT) exhibited a pure perovskite structure. When CZFM content was added, the ceramics exhibited a perovskite phase,

cubic spinel phase, and secondary phases of Bi₂O₃ and Fe₂O₃ (Figure 1). The XRD measurements agreed with the JCPDS files no. 36-0340, 05-0626, and 01-1121, which correspond to the rhombohedral perovskite, tetragonal perovskite, and cubic spinel phases, respectively.

To investigate phase structures, Rietveld refinement was used to estimate the proportions of the R (rhombohedral perovskite), T (tetragonal perovskite), and C (cubic spinel) phases in the [(1-x)BNBT-xCZFM] ceramics by analyzing XRD data with the Fullprof software. The lattice parameters, unit cell diameters, space group, and atomic locations were generated from reference patterns available in the Crystallography Open Database. The first models utilized for the refining of the XRD data of the [(1-x)BNBT-xCZFM] ceramics were based on Bi_{0.5}Na_{0.5}TiO₃ with a rhombohedral perovskite phase (R3c:H space group), BaTiO₃ with a tetragonal perovskite phase (Pm-3m space group), and CoFe₂O₄ with a cubic spinel phase (Fd3m space group). The background signal was fitted using a Chebyshev polynomial function, and the profile shape was represented by a pseudo-Voigt function, which is a hybrid of Lorentzian and Gaussian functions (Sindhu *et al.*, 2012). Several reliability measures were used to assess fit quality, including R_p (profile reliability), R_{wp} (weighted profile reliability), R_{exp} (anticipated

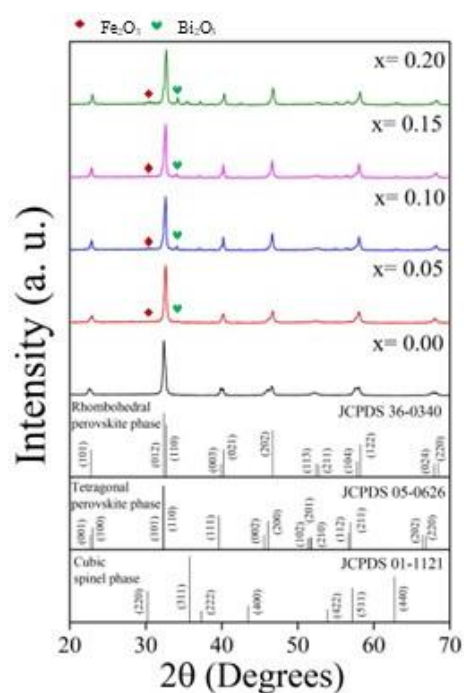


Figure 1. XRD patterns of (1-x)BNBT-xCZFM ceramics with x = 0, 0.05, 0.10, 0.15, and 0.20 in the 2θ range of 20-70°

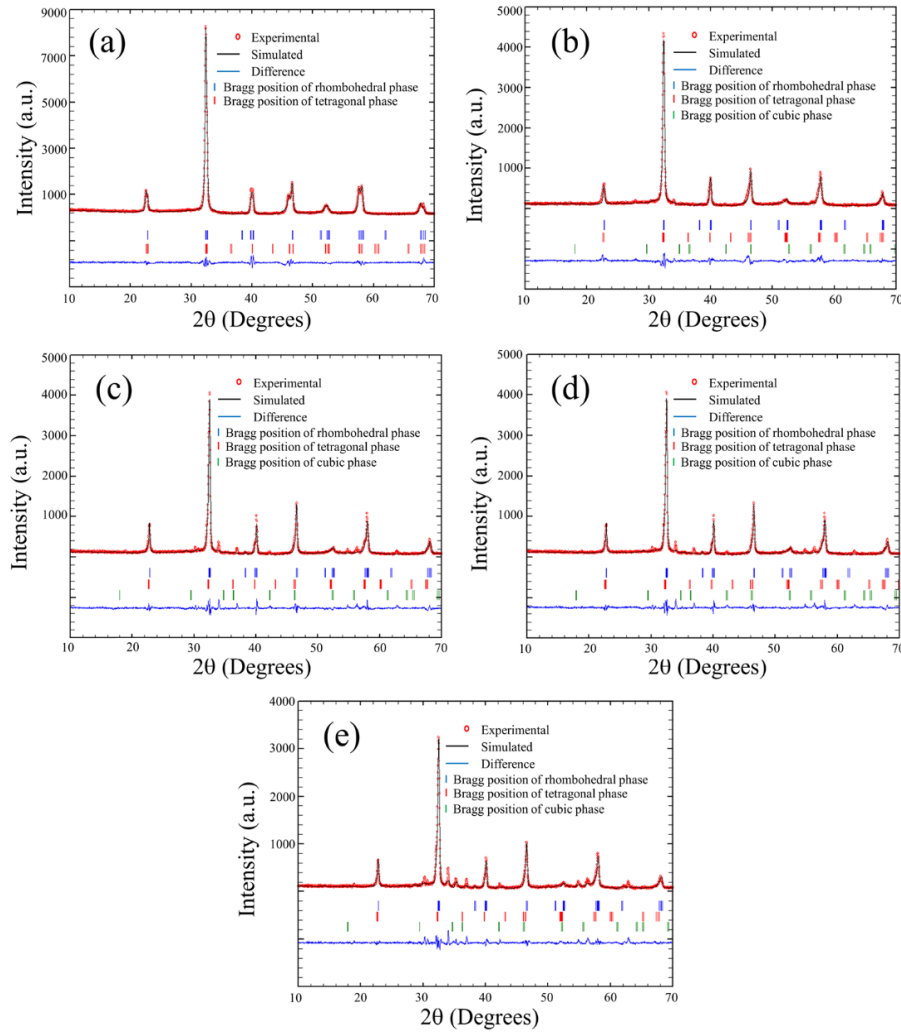


Figure 2. Typical Rietveld refinement analysis for (1-x)BNBT-xCZFM ceramics with different x content; (a) x = 0, (b) x = 0.05, (c) x = 0.10, (d) x = 0.15, and (e) x = 0.20

residual), and χ^2 (goodness of fit). The fit was good, with $R_p \leq 29.40\%$, $R_{wp} \leq 30.10\%$, $R_{exp} \leq 16.98\%$, and $\chi^2 \leq 3.14$ (refer to Table 1). Figure 2 shows the Rietveld refinement of the XRD patterns of the [(1-x)BNBT-xCZFM] ceramics in the range of 2θ from 10 to 70° . The results revealed that undoped ceramic had coexisting R and T perovskite phases. The ceramics with CZFM added exhibited coexisting R, T and C phases. The percentage of the R phase increased from 32 to 84% when x increased from 0 to 0.10, and then dropped as listed in Table 1. When x increased, the percentage of the T phase tended to decrease, while the C phase increased.

Figure 3(a-e) shows the SEM images, displaying the microstructure of the polished and thermally etched surfaces of (1-x)[0.94(Bi_{0.5}Na_{0.5}

TiO₃)-0.06BaTiO₃-xCo_{0.6}Zn_{0.4}Fe_{1.7}Mn_{0.3}O₄ [(1-x)BNBT-xCZFM] ceramics (x = 0-0.20). It can be found that the grains of the ceramics exhibited a non-uniform distribution and a polygon shape and no directed grain growth for all samples. The undoped BNBT ceramic had relatively uniform grain sizes (Figure 3(a)). When doped with CZFM, the ceramics displayed a mixture of smaller and larger grain sizes. The smaller grains were found to form between the larger grains' boundaries. When x increased, the number of smaller grains increased, as seen in Figure 3(b-e). As listed in Table 2, the average grain size of the (1-x)BNBT-xCZFM ceramics increased from 1.75 to 5.41 μm when x increased from 0 to 0.15, while the porosity decreased. When x increased to 0.20, the ceramics' average grain size decreased while the porosity increased (Table 2).

Table 1. Goodness of fit, the quality values, lattice parameters and the percentage of phases for (1-x)BNBT-xCZFM ceramics with various x content

Samples	Refine parameters	Phase structures	Profile parameters	Atoms information					The percentage of phase
				Label	x	y	z	Occ.	
x=0	$\chi^2=2.38$ $R_p=17.7\%$ $R_w=16.3\%$ $R_{exp}=10.57\%$	R3c:H	$a=5.49084\text{\AA}$	Bi1	0.00000	0.00000	0.26270	0.32146	32
			$c=13.59055\text{\AA}$	Na1	0.00000	0.00000	0.26270	0.46986	
			$u=0.16382$	Ti1	0.00000	0.00000	0.00630	1.06171	
			$v=0.00107$	Ba1	0.00000	0.00000	0.26270	0.08907	
			$w=0.02098$	O1	0.12600	0.33600	0.08330	0.52045	
		Pm-3m	$a=5.49739\text{\AA}$	Bi1	0.00000	0.50000	0.54500	0.45335	68
			$c=3.93560\text{\AA}$	Na1	0.00000	0.50000	0.54500	0.33061	
			$u=0.17681$	Ti1	0.00000	0.00000	0.00000	0.96727	
			$v=0.53076$	Ba1	0.00000	0.50000	0.54500	0.03756	
			$w=-0.01500$	O1	0.00000	0.00000	0.51000	1.20830	
x=0.05	$\chi^2=2.13$ $R_p=26.6\%$ $R_w=23.5\%$ $R_{exp}=16.09\%$	R3c:H	$a=5.52314\text{\AA}$	Bi1	0.00000	0.00000	0.26270	0.46881	68
			$c=13.54982\text{\AA}$	Na1	0.00000	0.00000	0.26270	0.48471	
			$u=0.09296$	Ti1	0.00000	0.00000	0.00630	0.91367	
			$v=0.04426$	Ba1	0.00000	0.00000	0.26270	0.02534	
			$w=0.10471$	O1	0.12600	0.33600	0.08330	3.44371	
		Pm-3m	$a=5.53031\text{\AA}$	Bi1	0.00000	0.50000	0.54500	0.48327	29
			$c=3.93875\text{\AA}$	Na1	0.00000	0.50000	0.54500	0.34987	
			$u=-0.36838$	Ti1	0.00000	0.00000	0.00000	1.26490	
			$v=0.05578$	Ba1	0.00000	0.50000	0.54500	0.04869	
			$w=0.34012$	O1	0.00000	0.00000	0.51000	1.33227	
		Fd3m	$a=b=c=8.51622\text{\AA}$	O2	0.27100	0.22900	0.01500	0.97406	3
			$u=-0.04715$	O1	0.25000	0.25000	0.25000	0.87087	
			$v=-0.21042$	Fe1	0.12500	0.12500	0.12500	0.74321	
			$w=0.56453$	Fe2	0.50000	0.50000	0.50000	1.05709	
				Mn1	0.12500	0.12500	0.12500	0.17758	
				Mn2	0.50000	0.50000	0.50000	0.13271	
				Zn1	0.12500	0.12500	0.12500	0.18812	
				Zn2	0.50000	0.50000	0.50000	0.19718	
				Co1	0.12500	0.12500	0.12500	0.28115	
				Co2	0.50000	0.50000	0.50000	0.32215	
x=0.10	$\chi^2=2.37$ $R_p=25.1\%$ $R_w=24.6\%$ $R_{exp}=15.94\%$	R3c:H	$a=5.50205\text{\AA}$	Bi1	0.00000	0.00000	0.26270	0.49562	84
			$c=13.57090\text{\AA}$	Na1	0.00000	0.00000	0.26270	0.49664	
			$u=0.15526$	Ti1	0.00000	0.00000	0.00630	0.91636	
			$v=-0.03917$	Ba1	0.00000	0.00000	0.26270	0.02379	
			$w=0.02185$	O1	0.12600	0.33600	0.08330	3.46246	
		Pm-3m	$a=5.54533\text{\AA}$	Bi1	0.00000	0.50000	0.54500	0.61309	7
			$c=3.92996\text{\AA}$	Na1	0.00000	0.50000	0.54500	0.35130	
			$u=-0.36838$	Ti1	0.00000	0.00000	0.00000	1.29325	
			$v=-0.10405$	Ba1	0.00000	0.50000	0.54500	0.08227	
			$w=0.34012$	O1	0.00000	0.00000	0.51000	0.87371	
		Fd3m	$a=b=c=8.56169\text{\AA}$	O2	0.27100	0.22900	0.01500	0.97264	9
			$u=0.25604$	O1	0.25000	0.25000	0.25000	0.98635	
			$v=-0.24196$	Fe1	0.12500	0.12500	0.12500	0.74321	
			$w=0.55674$	Fe2	0.50000	0.50000	0.50000	1.09600	
				Mn1	0.12500	0.12500	0.12500	0.14796	
				Mn2	0.50000	0.50000	0.50000	0.09712	
				Zn1	0.12500	0.12500	0.12500	0.17417	
				Zn2	0.50000	0.50000	0.50000	0.17868	
				Co1	0.12500	0.12500	0.12500	0.25836	
				Co2	0.50000	0.50000	0.50000	0.29650	
x=0.15	$\chi^2=2.29$ $R_p=24.6\%$ $R_w=24.1\%$ $R_{exp}=15.94\%$	R3c:H	$a=5.50453\text{\AA}$	Bi1	0.00000	0.00000	0.26270	0.50241	77
			$c=13.57296\text{\AA}$	Na1	0.00000	0.00000	0.26270	0.51321	
			$u=0.15092$	Ti1	0.00000	0.00000	0.00630	0.90891	
			$v=-0.04384$	Ba1	0.00000	0.00000	0.26270	0.01593	
			$w=0.02143$	O1	0.12600	0.33600	0.08330	4.33201	
		Pm-3m	$a=5.54627\text{\AA}$	Bi1	0.00000	0.50000	0.54500	0.66683	7
			$c=3.94702\text{\AA}$	Na1	0.00000	0.50000	0.54500	0.34432	
			$u=-0.05383$	Ti1	0.00000	0.00000	0.00000	1.30936	
			$v=-0.11747$	Ba1	0.00000	0.50000	0.54500	0.09443	
			$w=3.94702$	O1	0.00000	0.00000	0.51000	0.73304	
		Fd3m	$a=b=c=8.57121\text{\AA}$	O2	0.27100	0.22900	0.01500	1.09156	16
			$u=0.21166$	O1	0.25000	0.25000	0.25000	0.91680	
			$v=-0.34907$	Fe1	0.12500	0.12500	0.12500	0.60189	
			$w=0.56641$	Fe2	0.50000	0.50000	0.50000	1.15392	
				Mn1	0.12500	0.12500	0.12500	0.06291	
				Mn2	0.50000	0.50000	0.50000	0.10525	
				Zn1	0.12500	0.12500	0.12500	0.18632	
				Zn2	0.50000	0.50000	0.50000	0.19810	
				Co1	0.12500	0.12500	0.12500	0.25422	
				Co2	0.50000	0.50000	0.50000	0.29454	
x=0.20	$\chi^2=3.14$ $R_p=29.4\%$ $R_w=30.1\%$ $R_{exp}=16.98\%$	R3c:H	$a=5.50183\text{\AA}$	Bi1	0.00000	0.00000	0.26270	0.51488	72
			$c=13.55475\text{\AA}$	Na1	0.00000	0.00000	0.26270	0.52138	
			$u=0.23152$	Ti1	0.00000	0.00000	0.00630	0.89761	
			$v=-0.04362$	Ba1	0.00000	0.00000	0.26270	0.02014	
			$w=13.55475$	O1	0.12600	0.33600	0.08330	3.10736	
		Pm-3m	$a=5.54248\text{\AA}$	Bi1	0.00000	0.50000	0.54500	0.53535	8
			$c=3.94815\text{\AA}$	Na1	0.00000	0.50000	0.54500	0.22416	
			$u=-0.19043$	Ti1	0.00000	0.00000	0.00000	1.38339	
			$v=-0.00184$	Ba1	0.00000	0.50000	0.54500	0.07918	
			$w=0.19235$	O1	0.00000	0.00000	0.51000	0.69441	
		Fd3m	$a=b=c=8.58417\text{\AA}$	O2	0.27100	0.22900	0.01500	1.48365	20
			$u=1.47060$	O1	0.25000	0.25000	0.25000	0.85730	
			$v=-0.43708$	Fe1	0.12500	0.12500	0.12500	0.62229	
			$w=0.30548$	Fe2	0.50000	0.50000	0.50000	1.15443	
				Mn1	0.12500	0.12500	0.12500	0.06394	
				Mn2	0.50000	0.50000	0.50000	0.10581	
				Zn1	0.12500	0.12500	0.12500	0.18621	
				Zn2	0.50000	0.50000	0.50000	0.19848	
				Co1	0.12500	0.12500	0.12500	0.25548	
				Co2	0.50000	0.50000	0.50000	0.29541	

Table 2. Average grain size, density, dielectric, ferroelectric, and magnetic properties of the (1-x)BNBT-xCZFM ceramics various x concentrations

(1-x)BNBT-xCZFM	Average grain size (μm)	Density (g/cm^3)	ϵ_r at 10 Hz	$\tan \delta$	P_r (C/cm^2)	E_c (kV/cm)	M_s (emu/g)	H_c (Oe)
x=0	1.75	5.53	824	0.13	35.3	33.0	0.001	-94.15
x=0.05	4.80	5.36	346	0.14	30.5	43.7	0.06	8.07
x=0.10	4.83	5.41	390	0.22	30.9	49.1	0.10	13.45
x=0.15	5.41	5.49	713	0.47	22.4	49.1	0.17	18.82
x=0.20	5.39	5.35	335	0.43	24.0	52.4	1.55	29.59

Table 3. Quantitative results from the energy dispersive X-ray spectrometer (EDS)

(1-x)BNBT-xCZFM	Element	Spot *		Spot *	
		wt%	σ	wt%	σ
x=0	Bi	45.5	0.5	47.1	0.5
	Na	4.8	0.1	5.2	0.2
	Ti	22.9	0.3	23.0	0.3
	Ba	4.0	0.4	4.0	0.4
	O	22.7	0.5	20.8	0.5
x=0.05	Bi	46.7	0.5	2.3	0.2
	Na	5.3	0.2	3.3	0.2
	Ti	21.1	0.3	19.2	0.2
	Ba	1.9	0.4	9.7	0.3
	O	23.4	0.5	38.1	0.4
	Co	0.1	0.1	7.6	0.2
	Zn	0	0.2	6.5	0.2
	Fe	1.2	0.1	10.8	0.2
	Mn	0.1	0.1	2.5	0.1
x=0.10	Bi	47.7	0.5	9.3	0.3
	Na	5.1	0.2	3.1	0.2
	Ti	20.9	0.3	16.3	0.2
	Ba	2.0	0.4	9.3	0.3
	O	22.7	0.6	27.0	0.4
	Co	0	0.1	8.7	0.2
	Zn	0.2	0.2	6.8	0.2
	Fe	1.4	0.1	17.1	0.2
	Mn	0.1	0.1	3.5	0.1
x=0.15	Bi	48.7	0.5	1.1	0.2
	Na	5.0	0.2	2.6	0.2
	Ti	20.2	0.3	15.9	0.2
	Ba	1.7	0.4	10.6	0.3
	O	22.2	0.5	27.9	0.4
	Co	0	0.1	9.7	0.2
	Zn	0.1	0.2	7.0	0.2
	Fe	1.8	0.1	20.8	0.3
	Mn	0.3	0.3	4.2	0.1
x=0.20	Bi	47.9	0.5	6.6	0.3
	Na	5.0	0.2	2.2	0.2
	Ti	20.1	0.3	15.1	0.2
	Ba	1.9	0.4	9.3	0.3
	O	22.3	0.5	25.6	0.4
	Co	0.2	0.1	8.7	0.2
	Zn	0.3	0.2	6.7	0.2
	Fe	2.1	0.1	21.8	0.2
	Mn	0.2	0.1	3.9	0.1

The increase in average grain size may be explained by oxygen vacancies formed by a small amount of Fe^{3+} and Mn^{3+} ions substituting into the B sites of the perovskite structures (acceptor doping), which greatly increased mass transfer and promoted grain growth during the sintering process (Cheng *et al.*, 2015). An energy dispersive X-ray spectrometer (EDS) was used to investigate the microstructural components of the (1-x)BNBT-xCZFM ceramics, as shown in Figure 3. Figure 3 displays the EDS spectrums for the larger grains (Figure 3 (a)*-(e)*, spot *) and the smaller grains (Figure 3 (a)*-(e) *, spot •). It can be observed that the larger grains main components were Bi, Na, Ti, Ba, and O (BNBT), while the smaller grains main components were Co,

Zn, Fe, Mn and O (CZFM), as listed in Table 3. This indicated that high levels of CZFM doping ($x = 0.20$) inhibited grain growth, which led to a reduced average grain size.

The measured density of the (1-x)BNBT-xCZFM ceramics with different CZFM content is listed in Table 2. The measured density increased from 5.36 g/cm^3 to 5.49 g/cm^3 when x increased from 0.05 to 0.015 and then dropped.

Figure 4(a-e) displays the dielectric constant (ϵ) and dielectric loss ($\tan \delta$) of the (1-x)BNBT-xCZFM ceramics at $x = 0-0.20$ as a function of frequency, measured at room temperature in the frequency range of $10-10^6 \text{ Hz}$. It was found that the dielectric constant (ϵ) for each sample decreased

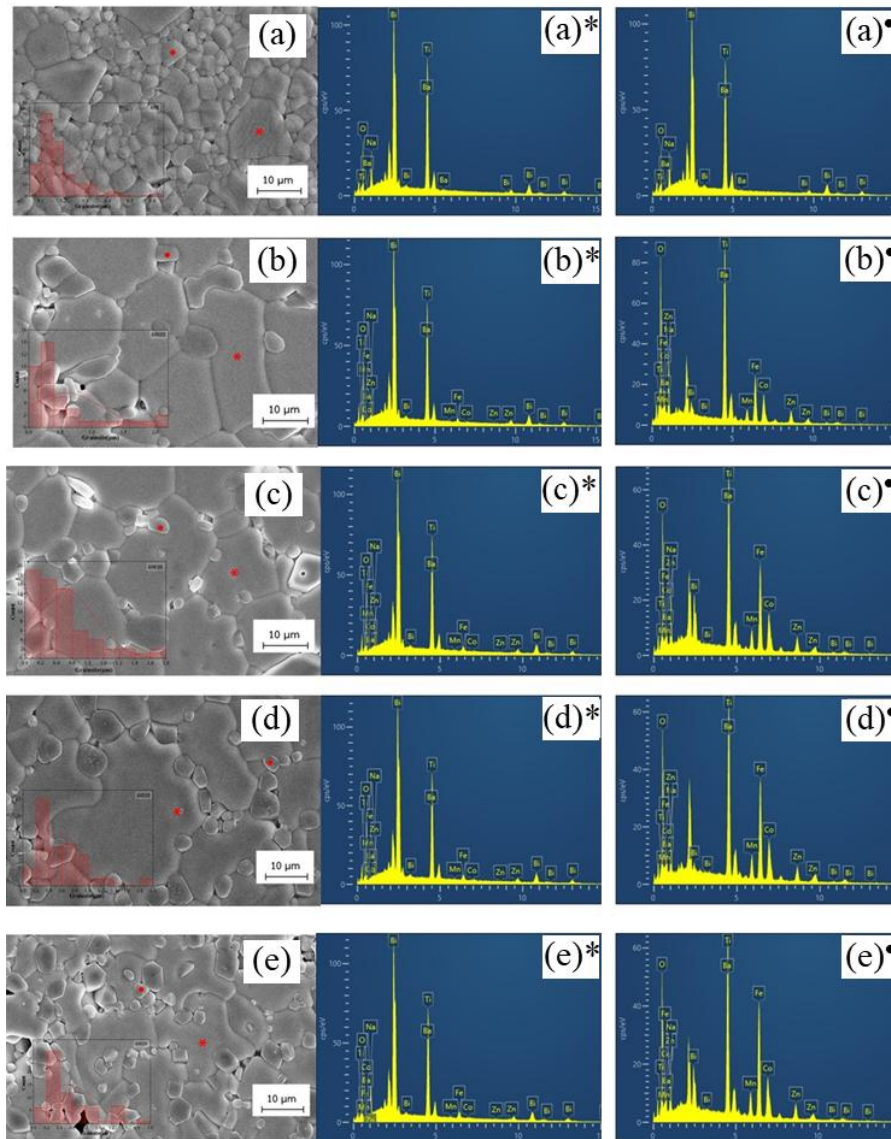


Figure 3. SEM images for (1-x)BNBT-xCZFM ceramics with different x content; (a) $x = 0$, (b) $x = 0.05$, (c) $x = 0.10$, (d) $x = 0.15$ and (e) $x = 0.20$. (a)*-(e)* EDS spectra of the larger grain at $x = 0-0.20$. (a)•-(e)• EDS spectra of the smaller grain at $x = 0-0.20$

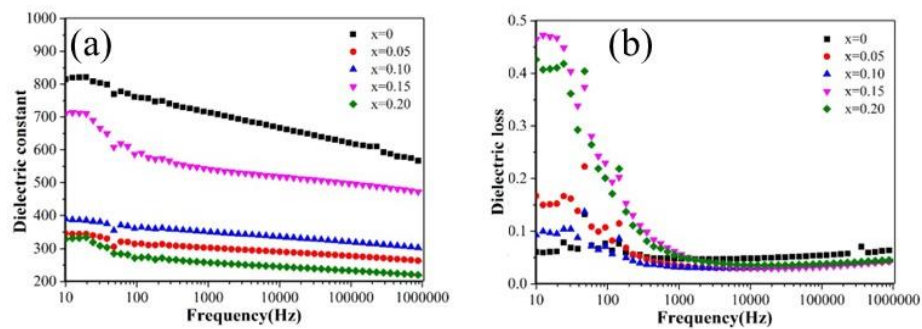


Figure 4. Frequency dependence of the dielectric constant and dielectric loss of the (1-x)BNBT-xCZFM ceramics measured at room temperature; (a) $x = 0$, (b) $x = 0.05$, (c) $x = 0.10$, (d) $x = 0.015$, and (e) $x = 0.20$

with increased frequency (Figure 4(a-e)). This decline resulted from the space charge polarization effect being lessened (Rayssi *et al.*, 2018). When x increased from 0 to 0.05, the dielectric constant (ϵ) of the ceramics, at 10 Hz, decreased from 824 to 346 (Table 2). The dielectric constant (ϵ) of the ceramics at 10 Hz increased when x increased from 0.10 to

0.15 and then dropped (Table 2). The results can be explained by the low dielectric of CZFM, which caused the dielectric to decrease significantly when the ceramics CZFM content increased. However, higher doping produced the $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ ion transition during the sintering process, causing an increase in Fe^{2+} ions at the grain boundaries. This caused

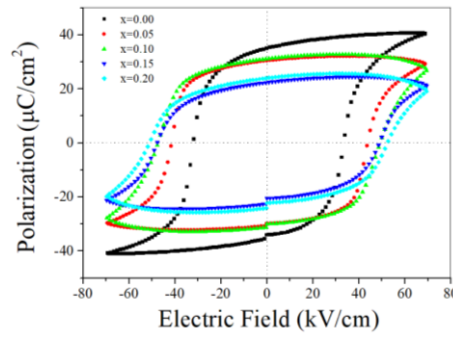


Figure 5. Plot of electric polarization against electric field of (1-x)BNBT-xCZFM ceramics with different x content

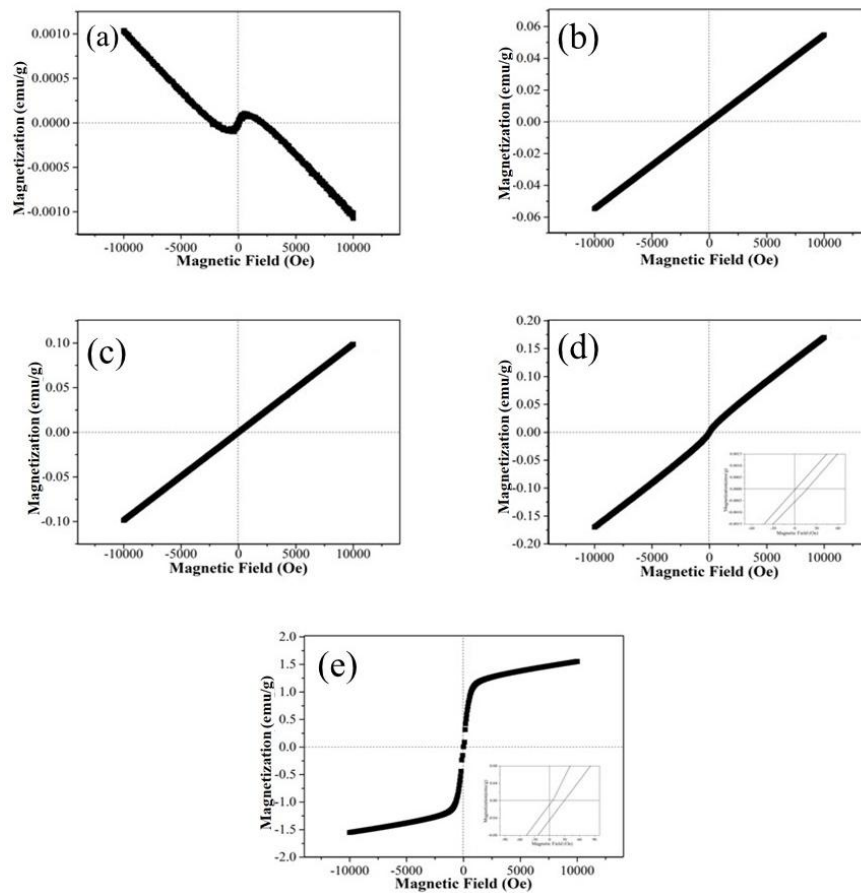


Figure 6. The M-H loops of the (1-x)BNBT-xCZFM ceramics at (a) $x = 0$, (b) $x = 0.05$, (c) $x = 0.10$, (d) $x = 0.015$, and (e) $x = 0.20$

an increase in polarization which enhanced the dielectric constant (Su *et al.*, 2012). Furthermore, the dielectric constant is significantly related to the microstructure and density of the ceramics (Thawong *et al.*, 2021). The dielectric loss ($\tan \delta$) tended to increase when x increased (Table 2). This is due to an increase in the defect concentration or oxygen vacancies in the samples, which resulted in increased mobility of space charges (Peláiz-Barranco *et al.*, 2008; Pichitra *et al.*, 2020).

Figure 5 illustrates the polarization as a function of electric field (P-E hysteresis loops) for (1-x)BNBT-xCZFM ceramics, measured at a frequency of 1 Hz and under an electric field of 70 kV/cm. All ceramics displayed saturated P-E loops. When $x = 0.05$ -0.20, the ceramics exhibited leakage current. The values of the remnant polarization (P_r) tended to decrease, from 35.3 to 22.4 $\mu\text{C}/\text{cm}^2$ when x increased from 0-0.15, and then slightly increased, as seen in Table 2. The coercive field (E_c) of the ceramics increased from 33.0 to 52.4 kV/cm when the CZFM doping increased (Table 2). This result suggested that the BNBT ceramics with CZFM doping causes a deterioration of the ferroelectric properties. This is probably due to the domain pinning by the ferromagnetic phase of CZFM, which limited the domain walls motion of the ferroelectric phase (Jin *et al.*, 2014).

The room-temperature magnetization as a function of the magnetic field (M-H loops) for (1-x)BNBT-xCZFM ceramics at various CZFM concentrations was shown in Figure 6(a-e), measured with a maximum applied field of 10 kOe. The M-H loop in the undoped ceramic (Figure 6(a)) showed a linear trend with a negative slope, indicating diamagnetic behavior. As the CZFM concentration increased from $x = 0.05$ to $x = 0.10$, the M-H loops changed to a linear relationship with a positive slope, indicating that the ceramics were paramagnetic. When x increased from 0.15 to 0.20, the ceramics showed ferromagnetic properties where the saturation magnetization (M_s) and coercive field (H_c) values increased from 0.17 to 1.55 emu/g and 18.82 to 29.59 Oe, respectively as listed in Table 2. The results suggested that CZFM doping into BNBT ceramics with $x = 0.15$ and 0.20 was the optimal composition to produce magnetoelectric materials that simultaneously exhibit ferromagnetic and ferroelectric properties.

Conclusions

The phase structure, microstructure, dielectric properties, ferroelectric properties, and magnetic properties of (1-x)[0.94(Bi_{0.5}Na_{0.5}TiO₃)-0.06BaTiO₃]

-xCu_{0.6}Zn_{0.4}Fe_{1.7}Mn_{0.3}O₄] [(1-x)BNBT-xCZFM] ceramics, fabricated by the solid-state combustion method were investigated. At $x = 0$, the (1-x)BNBT-xCZFM ceramic showed a typical perovskite structure, with rhombohedral and tetragonal phases coexisting. When x increased, the ceramics showed coexisting rhombohedral-tetragonal perovskite and cubic spinel phases, as revealed by XRD patterns. The (1-x)BNBT-xCZFM ceramics' average grain size rose from 1.75 to 5.41 μm as the x content increased from 0 to 0.15 due to oxygen vacancies. At $x = 0.05$, the dielectric constant (ϵ) of the ceramics greatly decreased from 824 to 346, while x increased from 0.10 to 0.15, the ceramics' dielectric constant (ϵ) slight increased and then dropped. The CZFM doped into BNBT ceramics increased the coercive electric field and leakage current, probably due to domain pinning by the ferromagnetic phase. Ferromagnetic characteristics were found in the ceramics with $x = 0.15$ and 0.20, where they also exhibited ferroelectric properties.

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