

Research article

A Simplified Combustion Technique to Synthesize 0.1BLTO-0.9CZFO Nano Powders and Composite Ceramics with a High Magnetoelectric Coefficient

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Abstract

Nano powders and high-performance composite ceramics of 0.1Ba_{0.5}La_{0.5}TiO₃-0.9Co_{0.8}Zn_{0.2}Fe₂O₄ (0.1BLTO-0.9CZFO) were successfully synthesized using a simplified combustion technique, using glycine as the fuel and a short process time with one calcination step. The effect of the firing temperature on the phase formation, microstructure, and density, and the optical, electrical, magnetic, and magnetoelectric properties of the ceramics were investigated. The synthesized powders were calcinated at temperatures between 600 and 1000°C for 2 h and the ceramics were sintered at temperatures in the range of 1200 to 1400°C for 2 h. The 0.1BLTO-0.9CZFO composite powder produced with a calcining temperature of 800°C, for 2 h, had a pure phase and nano sized particles (45 nm) and showed an energy band gap (E_g) of 4.85 eV and excellent magnetic properties ($M_s = 90.54$ emu/g, $M_r = 29.87$ emu/g and $H_c = 310$ Oe). The 0.1BLTO-0.9CZFO composite ceramics showed a pure phase in all samples. The highest %phase of BLTO was 18.54%, and this was obtained with a sintering temperature at 1300°C that formed a well-packed microstructure and also gave the highest density (5.75 g/cm³). Excellent ferroelectric properties ($P_{max} = 1.59$ μ C/cm², $P_{10} = 0.21$ μ C/cm², $E_c = 9.40$ kV/cm), magnetic properties ($M_s = 87.31$ emu/g, $M_r = 20.42$ emu/g, $H_c = 182$ Oe), and magnetoelectric coefficients ($\alpha_{ME} = 6.74$ mV/cm Oe) were also obtained for the sample sintered at 1300°C for 2 h. The 0.1BLTO-0.9CZFO composite ceramics synthesized by the simplified combustion technique showed higher magnetic properties than those synthesized by conventionally sintered ceramics.

Keywords: combustion technique; lead-free multiferroic; magnetoelectric; magnetic; electric

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1. Introduction

Lead-free multiferroic ceramics is a popular research topic in recent years to develop materials to replace Pb-based multiferroic ceramics such as PZT-BF since Pb-based ceramics are extremely toxic to humans and the environment (Rodel et al., 2009; Sadhukhan et al., 2022). Multiferroic materials have at least two coupled ferroic orders, i.e. ferroelectricity, ferromagnetism, or ferroelasticity, which produce the magnetoelectric (ME) effect (Hill, 2000; Rosales-González et al., 2018; Raza et al., 2020). Multiferroic ceramics with high performance and a large ME effect are highly sought for use in a wide range of applications in multifunctional devices such as micro-electromechanical systems (MEMS), magnetic field sensors, current sensors, energy harvesters, transducers, spintronic logics, and microwave interference shielding materials (Esha et al., 2018; Raza et al., 2020.). It is well known that the ME effect can occur either in single phase multiferroic material or composite material, while the ME effect at room temperature in composite materials is larger than in single-phase materials (Pradhan et al., 2005; Esha et al., 2018). To obtain a large ME effect in composite materials, it is imperative to choose strong ferroelectric and ferromagnetic materials with excellent coupling between them. In the past few years, material engineering of lead-free multiferroic ceramics with functional properties has met ever greater requirements for newer applications (Esha et al., 2018; González-Abreu et al., 2023). Thus, development and production are necessary to obtain high-performance lead-free multiferroic ceramics that are reliable and have stable parameters. To satisfy these particular needs, efforts have been made to develop new kinds of lead-free multiferroic composite ceramics and efficient technological processes for producing them. Recently, new composite materials have been designed by mixing lead-free ferroelectric and magnetic phases in multiferroic ceramics, especially using perovskite barium titanate (BaTiO_3) in combination with spinel ferrites-based ceramics to form magnetoelectric composites such as $\text{BaTiO}_3 + \text{CoFe}_2\text{O}_4$ (Shankar et al., 2019), $\text{BaTiO}_3 + \text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ (Lather et al., 2017), and $\text{BaTi}_{0.5}\text{Mn}_{0.5}\text{O}_3 + \text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_{1.85}\text{Sm}_{0.15}\text{O}_4$ (Esha et al., 2020). The highest magnetoelectric coefficient ($\alpha_{\text{ME}} = 4.3 \text{ mV/Oe cm}$) and a high electrical resistivity were obtained with a 20% CoFe_2O_4 /80% BaTiO_3 ceramic composite with a mixture of magnetic and ferroelectric phases using the mechanical ball milling method, as reported by Samghabadi et al. (2021).

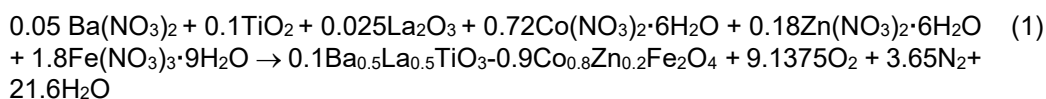
Another important point is the improvement of the magnetic phase and ferroelectric phase for their excellent properties, leading to higher magnetoelectric coefficients in the lead-free multiferroic composite ceramics. The doping of Zn ions into CoFe_2O_4 to form $\text{Co}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ (CZFO) produced a larger magnetic anisotropy and higher magnetostriction coefficients than other undoped ferrites (Kombaiah et al., 2018). Thus, this would be very interesting for the use as a magnetic phase. The doping of La ions at the A-sites in BaTiO_3 was an important development in ferroelectric phase research because the substituted La ions could enhance the dielectric properties and decrease the Curie temperature of BaTiO_3 (Liu et al., 2010; Habiba et al., 2023), which was a key step to solve high electrical conductivity problem for lead-free multiferroic composite ceramics, which have limited application due to their high electrical conductivities. Habiba et al. (2023) investigated $(1-x)\text{Ba}_{0.5}\text{La}_{0.5}\text{TiO}_3$ (BLTO) + $(x)\text{Co}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ (CZFO) composite ceramics with x content of 0.0, 0.1, 0.3, 0.5, 0.7, 0.9, and 1.0, which were synthesized via the solid-state reaction method. They reported that at an x content of 0.90, the composite ceramics showed the highest dielectric constant, the largest saturation magnetization ($M_s = 60 \text{ emu/g}$), and the lowest coercive field ($H_c = 55 \text{ Oe}$), while ferroelectricity was at a satisfactory level. The synthesis process of BLTO+CZFO composite ceramics by the solid-

state reaction method used separate calcination steps for each power. Synthesized BLTO powders were calcined at 850°C for 4 h, and separately the CZFO powders were calcined at 850°C for 4 h. Before the calcination process, the raw materials of each type of powder were hand-milled for 6 h, and then each powder was pressed into disc shapes. When the calcination process was complete, the calcined powder disc shapes were ground for 2.5 h and BLTO ground powders were mixed with the CZFO ground powders at various molar ratios by hand-milling, then pressed into discs and sintered at 1200°C for 4 h. However, this synthesis technique involves multiple steps, a two-step calcination process, and a long manual grinding time, which results in wasted energy and time, and the experimenter may experience fatigue from crushing. Simple and efficient processes for synthesizing ceramic composites to obtain nano powders with high performance are in great demand, especially for preparation processes that use a low preparation temperature, less preparation time, and inexpensive chemicals. The simplified combustion technique can meet these requirements and synthesize high-performance multiferroic composite ceramics and magnetic ceramics. This technique releases energy from the chemical reactions during the calcination process, which promotes the reactions of raw materials and produces calcined powder composed of nanoparticles. Moreover, the technique involved low calcination temperatures and short dwell time, is simple to fabricate, cost effective, and the technique offers improved control over system parameters (Kornphom et al., 2022, 2023a,b; Thongon et al., 2024; Reabreang et al., 2024).

After considering all the literature reviewed above, the preparation of nano powders and high performance lead-free multiferroic composite ceramics with a ferroelectric phase of $\text{Ba}_{0.5}\text{La}_{0.5}\text{TiO}_3$ (BLTO) and a ferromagnetic phase of $\text{Co}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ (CZFO), at a composition of 0.1BLTO-0.9CZFO, were synthesized by the simplified combustion technique, was considered very interesting and has not been reported. Therefore, this research was focused on the study of the effect of firing temperatures and preparation process on the phase formation, microstructure, optical properties, electrical and magnetic properties, and magnetoelectric coefficient synthesized by the simplified combustion technique.

2. Materials and Methods

To synthesize the 0.1 $\text{Ba}_{0.5}\text{La}_{0.5}\text{TiO}_3$ -0.9 $\text{Co}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ (0.1BLTO-0.9CZFO) powders and ceramics by the simplified combustion technique, the raw materials of $\text{Ba}(\text{NO}_3)_2$ (99 %), TiO_2 (99 %), La_2O_3 (99 %), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99 %), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99 %), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99 %) were weighed according to their stoichiometric compositions with following chemical formula;



Then, all stoichiometric powders were mixed with glycine ($\text{C}_2\text{H}_5\text{NO}_2$) in a ratio of 1:1.622 and mixed by hand-stirring with a glass rod for 10 min until a homogeneous solution was obtained. The homogeneous solution was calcined at temperatures between 600 and 1000°C for 2 h in air. After calcination, the powders were sieved through a 400-mesh sieve and then mixed with a polyvinyl butyral (PVB, 2 wt%) binder solution by hand-milled for 10 min. After that, the mixed powders were uniaxially pressed into green bodies (2 mm in thickness and 10 mm in diameter) under 100 MPa. Finally, the green bodies were sintered

in air with temperatures in the range of 1200-1400°C for 2 h. Silver paste was brushed on the two surfaces of the sintered ceramics and heated at 500°C for 20 min to form the electrodes used to investigate the electrical properties. The synthesis procedure of 0.1BLTO-0.9CZFO powders and ceramics is summarized schematically in Figure 1.

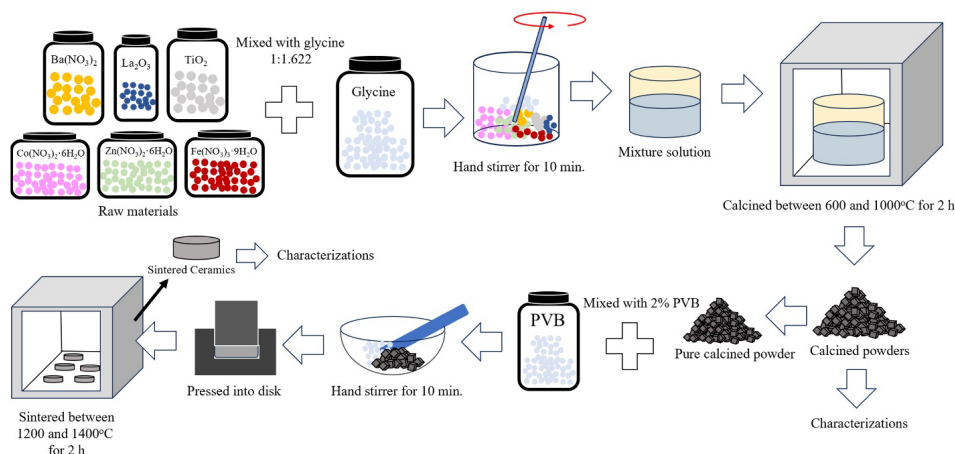


Figure 1. Schematic diagram of the synthesized 0.1Ba_{0.5}La_{0.5}TiO₃-0.9Co_{0.8}Zn_{0.2}Fe₂O₄ powders and ceramics using the simplified combustion technique.

The crystal structure and phase composition at room temperature of the 0.1BLTO-0.9CZFO powders and ceramics, produced with various firing temperatures, were examined by X-ray diffraction (XRD, Rigaku, SmartLab) with Cu-K α radiation ($\lambda = 1.5418$ Å). The microstructure of the powders and the ceramics was observed using scanning electronic microscopy (Thermo Fisher, Apero S). The particle size of the powders was investigated by using transmission electron microscopy (JEM 2100 Plus). The average grain size was counted using Image J software. The optical properties of the powders were investigated by a UV-Visible spectrometer (JASCO V-780). The dielectric behavior at room temperature of the ceramics was measured by an LCR meter (HP, 4284 A). The electric polarization or spontaneous polarization at room temperature was recorded by a computer controlled modified Sawyer-Tower circuit (Radiant, PLC2-1014346). Magnetic field versus magnetization (M–H) loops of the powders and the ceramics were recorded by a vibrating sample magnetometer (EZ9-USA). The magnetoelectric coupling coefficients were determined with a lock-in amplifier (Stanford Research System, model SR830) in which the AC magnetic field was superimposed on the DC biased magnetic field.

3. Results and Discussion

The XRD patterns of the 0.1Ba_{0.5}La_{0.5}TiO₃-0.9Co_{0.8}Zn_{0.2}Fe₂O₄ (0.1BLTO-0.9CZFO) powders calcined at a temperature range of 600-1000°C for 2 h is shown in Figure 2. The XRD patterns of all 0.1BLTO-0.9CZFO powders showed diffraction peaks of two phases, a CZFO spinel and a BLTO perovskite phase, which were matched with JCPDS files no. 221086 (the spinel phase is marked as (•)) and 030725 (the perovskite phase is marked as (♦)) and matched according to the literature (Wang et al., 2012; Goel et al., 2022) confirming the production of a composite powder (Habiba et al., 2023).

An impurity peak of Fe_2O_3 with marking as (♥) was found in the 0.1BLTO-0.9CZFO powders produced with calcination temperatures between 600 and 700°C for 2 h, as seen in Figure 2, indicating that the chemical reaction during calcination was incomplete. The percentage of the purity phase of all 0.1BLTO-0.9CZFO powders can be calculated with equation (2) (Habiba et al., 2023):

$$\% \text{ purity phase} = \frac{I_{\text{perovskite}} + I_{\text{spinel}}}{I_{\text{perovskite}} + I_{\text{spinel}} + I_{\text{impurity}}} \times 100 \quad (2)$$

Where, $I_{\text{perovskite}}$, I_{spinel} and I_{impurity} denote the intensities of the highest perovskite peak of (110), the highest spinel peak of (311), and the highest Fe_2O_3 impurity peak, respectively, which were analyzed from XRD data of all the 0.1BLTO-0.9CZFO powders. It was observed that the percentage of the purity phase increased from 85 to 100% when calcination temperatures was increased from 600 to 800°C as seen in Table 1. A pure phase, with no impurity phase of Fe_2O_3 was obtained for the 0.1BLTO-0.9CZFO powders calcined $\geq 800^\circ\text{C}$ for 2 h (Table 1). The synthesis of 0.1BLTO-0.9CZFO powders by the simplified combustion technique, using one calcination process, decreased hand-mill time by up to 5 h 50 min, decreased the calcination temperature by 50°C, and decreased the dwell time by up to 2 h when compared with the solid-state reaction technique (Habiba et al., 2023). The decrease in hand-milling time occurred because the milling of the raw materials and glycine took only 10 min and formed a single solution that could be further used in the calcination process, removing the need to mill separately calcinated powders together. Moreover, the use of a single solution promoted the chemical reaction of the raw materials during the calcination process, leading to a decrease in the dwell time. The decrease in calcination temperature and dwell time were attributed to the generated combustion energy from an exothermic reaction that occurred in the combustion process, resulting in a reduction in the reaction temperature (Kornphom et al., 2022, 2023a,b; Thongon et al., 2024).

The crystallite size (D) of the composite powders of BLTO and CZFO produced with various calcination temperatures was investigated using the Debye-Scherrer equation, as seen in equation (3) (Habiba et al., 2023).

$$D = \frac{k \times \lambda}{\beta \times \cos\theta} \quad (3)$$

Where D is the crystallite size, k is Scherer's constant (0.89), λ is the wavelength of the X-rays, β is the full width at half maxima of the (111) peak for BLTO and the (311) peak for CZFO, and θ is the angle in radians. The crystallite size (D) of the composite powders of BLTO and CZFO are shown in Table 1. It was observed that the D values of BLTO and CZFO increased from 34.9 to 87.2 nm and 35.3 to 109.7 nm, respectively, when the calcination temperature increased from 600 to 1000°C for 2 h (Table 1). The larger crystallite size of the composite powders at higher calcination temperatures may be caused by the following main factors: (i) larger crystallites form as smaller ones coalesce and grow at high calcined temperatures, resulting in a larger average crystallite size; (ii) the activation energy required for atomic diffusion is overcome more easily at high calcined temperatures by facilitating the movement of atoms and ions, resulting in an increase in diffusion and

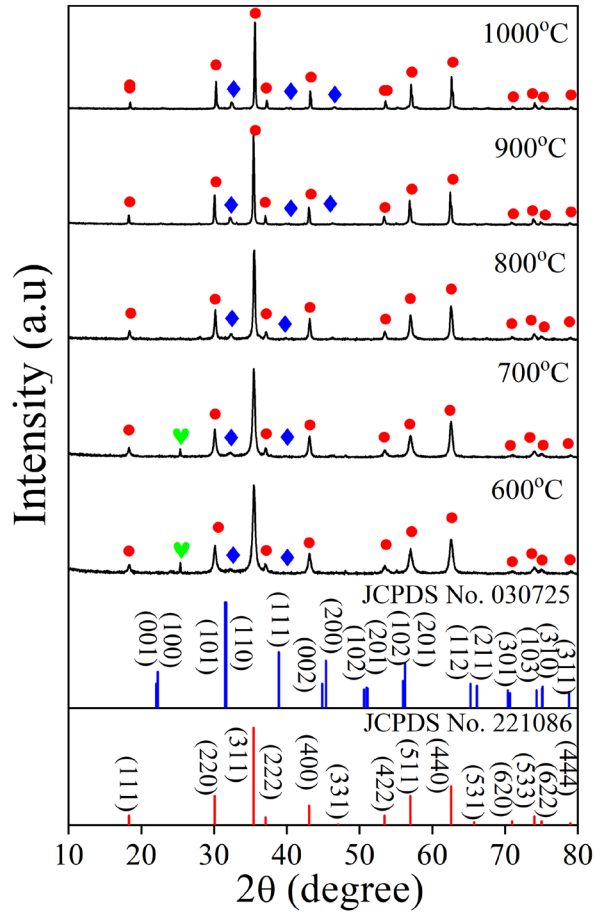


Figure 2. X-ray diffraction pattern of the 0.1BLTO-0.9CZFO powders produced with various calcination temperatures, where the perovskite phase is marked as (♦), spinel phase is marked as (•), and impurity phase of Fe_2O_3 is marked as (♥).

Table 1. % purity phase and D values of the 0.1BLTO-0.9CZFO powders calcined at various temperatures

Calcination Temperature (°C)	% Purity Phase	D (nm)	
		BLTO	CZFO
600	85	34.9	35.3
700	91	42.6	43.6
800	100	53.0	59.7
900	100	70.7	79.8
1000	100	87.2	109.7

contributing to the growth of crystallites; and (iii) the increased kinetic energy at higher calcination temperature excites the nucleation and growth of crystals, which promotes formation of larger crystals during the calcination process (Gaber et al., 2014, Gluchowski et al., 2022).

SEM photographs of the 0.1BLTO-0.9CZFO powders calcined with temperatures between 600 to 1000°C for 2 h are shown in Figures 3(a)-(e). All powders showed densely agglomerated forms, and the particles obviously grew when the calcination temperature was increased from 600 to 1000°C, as can be seen in Figures 3(a)-(e). At low calcination temperatures (600-900°C), the particles of the powders were very small, which made it difficult to observe the particle shape, and the particle size could not be measured from the SEM images (Figures 3(a)-(c)). At a high calcination temperature of 1000°C, the particles of the powder showed a clear spherical shape (Figure 3(e)), and the average particle size measured by SEM image using the Image J program was about 200 nm.

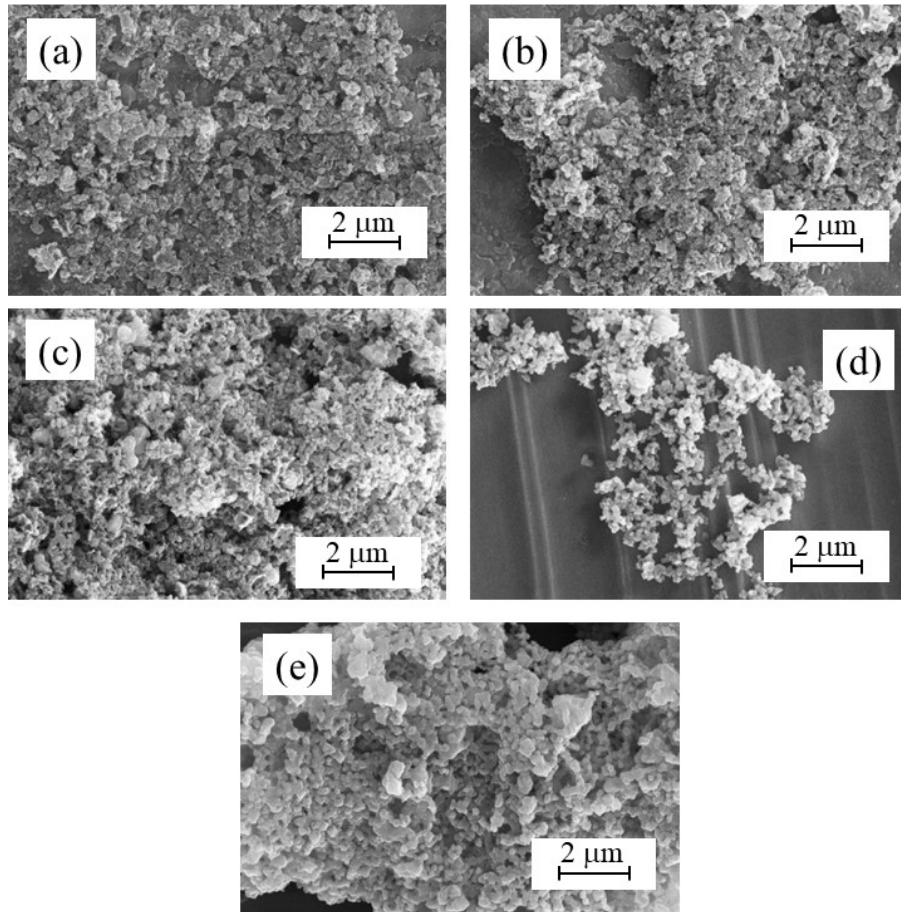


Figure 3. SEM photographs of the 0.1BLTO-0.9CZFO powders calcined with various temperatures: (a) 600°C, (b) 700°C, (c) 800°C, (d) 900°C, and (e) 1000°C for 2 h

TEM photographs of the pure 0.1BLTO-0.9CZFO powders calcined at temperatures between 800 to 900°C are shown in Figures 4(a) and (b). The TEM images confirmed that the powders had an agglomerated form and the particles were of almost spherical shape. The particles of the powder calcined at 800°C exhibited more uniform size than the powder calcined at 900°C, and the average particle size increased from 45 nm to 94 nm when calcination temperatures were increased from 800°C to 900°C. So, the 0.1BLTO-0.9CZFO nanocomposite powder was successfully synthesized by a simplified combustion technique using a calcination temperature of 800°C for 2 h.

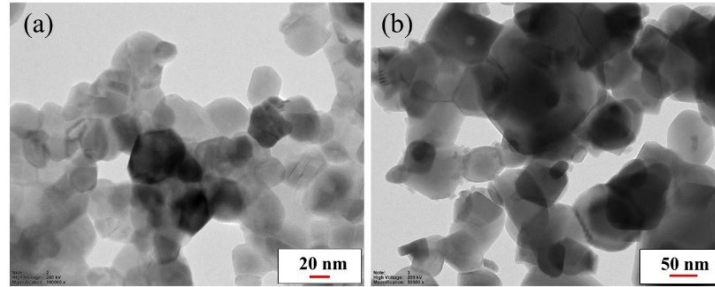


Figure 4. TEM images of the 0.1BLTO-0.9CZFO powders with calcination temperatures of (a) 800°C and (b) 900°C for 2 h

It is well known that BaTiO₃ nanoparticles show good photocatalytic activity with a band gap of 3-4 eV. The dependency of the optical absorption coefficient on the photon energy helps to analyze the band structure and type of electron transitions needed to investigate photocatalytic activity. Thus, investigating the UV-vis absorption is very important to understand the photocatalytic activity of 0.1BLTO-0.9CZFO nanoparticles. UV-vis absorption spectra measured for wavelengths between 300 and 800 nm of the 0.1BLTO-0.9CZFO powders calcined at 800°C and 900°C for 2 h are presented in Figure 5(a). Both powders calcined at 800°C and 900°C exhibited a wide absorption spectral peak around 350 nm (Figure 5(a)), which can be attributed to electron transfer (Kappadan et al., 2016; Madani et al., 2023). UV light is significantly more absorbed by the powder calcined at 800°C than the powder calcined at 900°C, as shown in Figure 5(a). This is because the powder calcined at 800°C had smaller nanoparticles. Generally, variations in particle size can influence quantum confinement effects, thereby impacting the absorption characteristics. Smaller nanoparticles may demonstrate better optical behaviors in contrast to larger ones (Madani et al., 2023).

The optical band gap (E_g) of a system can be estimated by using Tauc's relationship with the following expression (Madani et al., 2023; Chaiworn et al., 2024).

$$(\alpha h\nu)^2 = \beta(h\nu - E_g) \quad (4)$$

Here, $h\nu$ is the incident photon energy, α is the absorption coefficient, β is a constant, and E_g is the optical band gap. The relationship of $(\alpha h\nu)^2$ vs $h\nu$ is plotted in Figures 5(b) and (c). The band gap energy (E_g) can be calculated by extrapolating the straight portion of the curve of $(\alpha h\nu)^2$ vs $h\nu$ at high energies, and the E_g value is indicated on the $h\nu$ axis of the graph as can be seen in Figures 5(b) and (c). It was observed that E_g

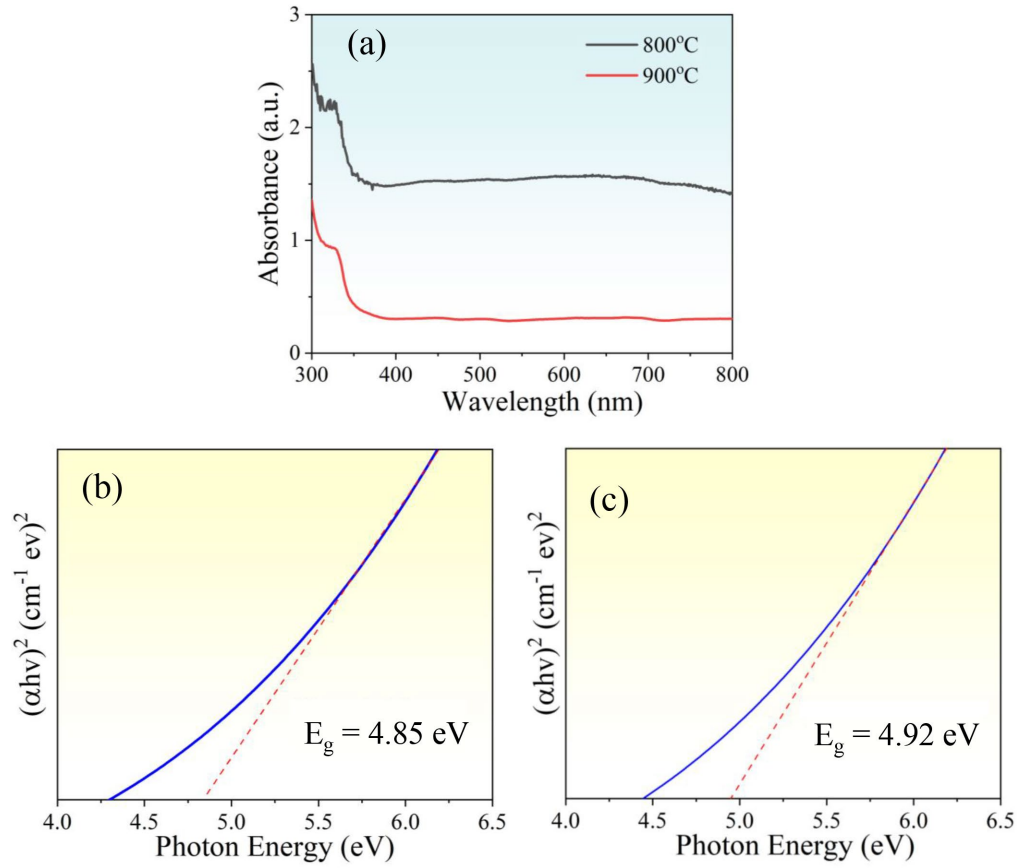


Figure 5. (a) UV–visible absorption spectra of the 0.1BLTO-0.9CZFO powders calcined at 800°C and 900°C for 2 h and the variation of $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) for nano particles of 0.1BLTO-0.9CZFO powders produced at calcination temperatures of (b) 800°C and (c) 900°C

increased from 4.85 to 4.92 eV when the calcination temperature was increased from 800°C to 900°C (Figures 5(b) and (c)). As a result of the increased calcination temperature, the crystallite size of the powders increased, which led to an increase in the band gap due to quantum confinement effects (Madani et al., 2023). Therefore, a lower E_g value was obtained for the 0.1BLTO-0.9CZFO nano powder calcined at 800°C, which was beneficial for the absorption of visible light and produced enhanced photocatalytic activity (Ahamed et al., 2023, Gatasheh et al., 2023).

The magnetic properties with M-H hysteresis loops of the 0.1BLTO-0.9CZFO composite ceramics sintered at various temperatures were analyzed by a vibrating sample magnetometer (VSM), which can be operated by the theoretician magnetic equation (5):

$$\chi_d = \frac{d\vec{M}}{d\vec{H}} \quad (5)$$

Here χ_d is the magnetic susceptibility of materials, M is the ratio of the magnetization of materials, and H is the applied magnetic field strength. The M-H hysteresis loops of the 0.1BLTO-0.9CZFO powders produced with various calcination temperatures, measured at 300 K, under an applied magnetic field (H) of 10 kOe, are displayed in Figure 6(a). It was clearly observed that the M-H loops in Figure 6(a) exhibited typical ferromagnetic curves for all powders. The M-H loops appeared to become narrower (smaller coercivity) when the calcination temperature was increased from 600 to 900°C, indicating these powders had softened ferromagnetism, as seen in insert Figure 6(a). At a calcination temperature of 1000°C, the M-H loop became larger because the coercivity increased, which indicated that the powder had harder ferromagnetism (insert Figure 6(a)). The magnetic parameters, including the saturation magnetization (M_s), remnant magnetization (M_r), and coercivity (H_c), estimated from M-H curves, are shown in Figure 6(b). It was observed that M_s and M_r increased from 54.83 to 90.54 emu/g and 16.37 to 29.87 emu/g, respectively, when the calcination temperature was increased from 600 to 800°C and then dropped in values as seen in Figure 6(b). The H_c values slightly decreased from 393 to 215 Oe when the calcination temperatures were increased from 600 to 900°C and then the values increased (Figure 6(b)). The highest M_s (90.54 emu/g) and M_r (29.87 emu/g) with a low H_c value (310 Oe) were obtained with the powder produced at a calcination temperature of 800°C for 2 h, due to the powders showing a purity phase and the smallest nanoparticle size. Therefore, the 0.1BLTO-0.9CZFO powder with a calcination temperature of 800°C for 2 h was the most suitable synthesizing condition for the simplified combustion technique, and this powder was suitable for further preparation as composite ceramics.

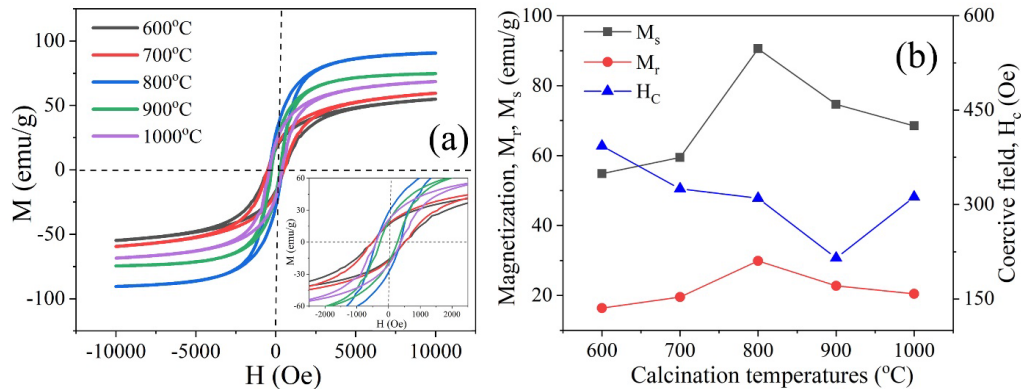


Figure 6. (a) Magnetic hysteresis curves, and (b) magnetization and coercive fields of the 0.1BLTO-0.9CZFO ceramics produced with various calcination temperatures

The XRD patterns of the 0.1BLTO-0.9CZFO ceramics, temperatures between 1200 and 1400°C for 2 h are shown in Figure 7. All XRD patterns showed a pure composite ceramic phase and no traces of an impurity phase were found. The structures matched with JCPDS files no. 221086 (spinel phase is marked as (•)) and 030725 (perovskite phase is marked as (♦)) (Wang et al., 2012; Goel et al., 2022). The XRD results proved that the BLTO and CZFO were successfully formed into composite ceramics.

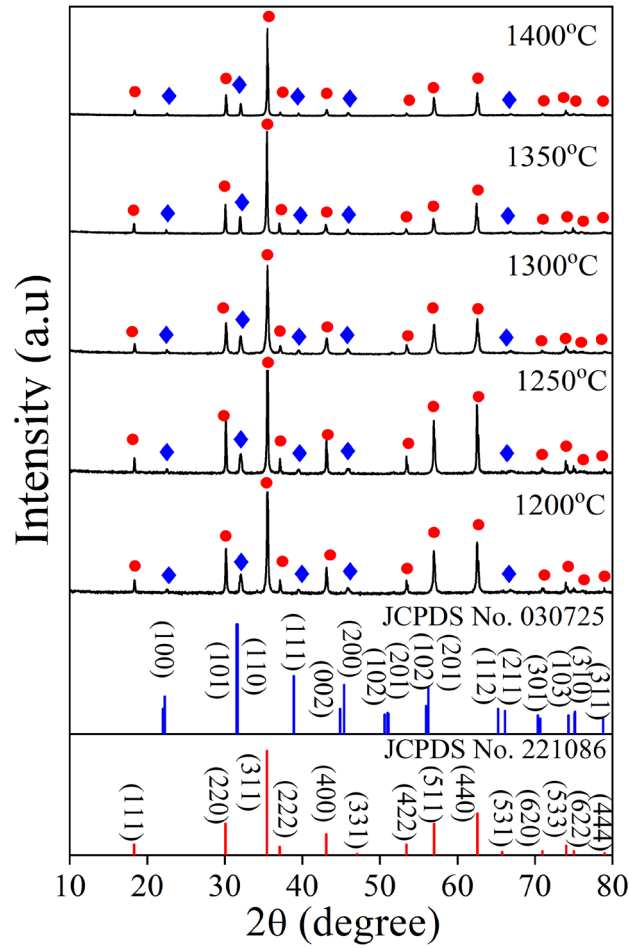


Figure 7. X-ray diffraction pattern of the 0.1BLTO-0.9CZFO ceramics at various sintering temperatures, where the perovskite phase is marked as (♦) and spinel phase is marked as (●)

The XRD spectrum of all ceramics was used to calculate the fraction of BLTO and CZFO phases within the composite ceramics produced with various sintering temperatures using the intensity of the sharpest (110) BLTO and (311) CZFO peaks following equations (6) and (7) (Habiba et al., 2023).

$$\% \text{Phase fraction of BLTO} = \frac{I_{\text{BLTO (110)}}}{I_{\text{BLTO (110)}} + I_{\text{CZFO (311)}}} \times 100 \quad (6)$$

$$\% \text{Phase fraction of CZFO} = \frac{I_{\text{CZFO (311)}}}{I_{\text{CZFO (311)}} + I_{\text{BLTO (110)}}} \times 100 \quad (7)$$

The %phase fraction of BLTO increased from 11.76 to 18.54% when the sintering temperature was increased from 1200 to 1300°C and then decreased. The phase fraction of CZFO showed the opposite trend, as seen in Table 2. The variation of the %phase fractions of BLTO and CZFO with sintering temperatures may be caused by three factors; (i) the diffusion of atoms within the material becomes more pronounced at higher temperatures, which leads to the rearrangement of atoms at the grain boundaries, affecting the phase distribution, (ii) grain growth during sintering at high temperatures can cause changes in the microstructure, influencing the distribution of different phases within the ceramics, and (iii) the degree of porosity can impact the phase distribution of the ceramics, as the presence of pores can influence local chemical and physical conditions (Kornphom et al., 2023a,b).

Table 2. %phase fractions, average grain size and density of the 0.1BLTO-0.9CZFO ceramics produced with various sintering temperatures

Sintering Temperature (°C)	%Phase Fractions		Average Grain Size (μm)		Density (g/cm ³)	ϵ_r at 1 kHz	tan δ_r at 1 kHz
	BLTO	CZFO	Small Grain	Large Grain			
1200	11.76	88.24	0.51±0.08	1.60±0.28	5.12	16.21	3.55
1250	14.67	85.33	0.59±0.12	1.71±0.24	5.44	44.92	1.51
1300	18.54	81.46	0.69±0.13	2.16±0.32	5.75	52.19	1.30
1350	15.27	84.73	3.41±0.78	11.20±3.07	5.61	-	-
1400	12.84	87.16	4.17±1.10	14.42±3.41	5.50	-	-

The SEM images of the surface morphologies of the polished and thermally etched 0.1BLTO-0.9CZFO ceramics, for all sintering temperatures, are displayed in Figures 8(a)-(e). The SEM images showed an inhomogeneous grain morphology, in which large grains were mixed with polygon-shapes and small grains with almost spherical shapes, in all ceramics (Figures 8(a)-(e)). From previous work, the large grains were identified as the spinel structure of CZFO and small grains identified the perovskite structure of BLTO (Lather et al., 2017). It was observed that the small grains were interspersed at the grain boundaries of the large grains, which is clearly seen in the marking of Figures 8(c) and (d). At a low sintering temperature of 1200°C, both grain shapes were small, and many porous structures were formed, as seen in Figure 8(a). When the sintering temperature was increased from 1250°C to 1300°C, these ceramics had denser morphology and the grains sizes increased while the porous structures decreased, as seen in Figures 8(b) and (c). Porous structure, abnormal grains, and rapid grain growth were observed in the ceramics sintered at the higher temperatures of 1350°C and 1400°C (Figures 8(d) and (e)), probably due to the excessive sintering temperatures causing some grains to grow faster than others, leading to porosity and inhibiting other grain growth.

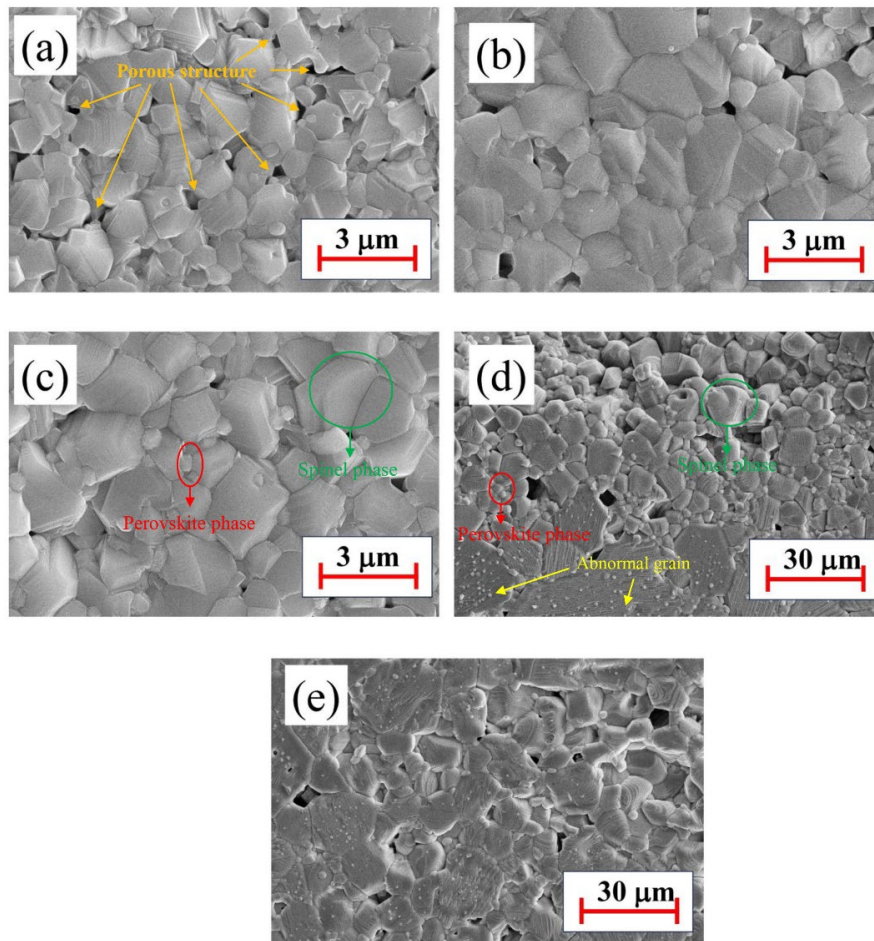


Figure 8. SEM micrograph of the 0.1BLTO-0.9CZFO ceramics produced with various sintering temperatures; (a) 1200°C, (b) 1250°C, (c) 1300°C, (d) 1300°C and (e) 1400°C for 2 h

To analyze the difference between large grains with polygon-shapes and small grains with almost spherical shapes, the electron scanning technique of energy dispersive spectrometry (EDS) was used to examine the different grains on the surface of the ceramics, sintered at 1300°C for 2 h, as displayed in Figure 9(a) and (b). The EDS results of the large grains (Spot I) and small grains (Spot II) showed the characteristic peaks of Fe, O, Co, Zn, Ti, La, and Ba, for 0.1BLTO-0.9CZFO ceramics as seen in Figures 9(a) and (b). The small grains showed a higher wt% of Ba, La, and Ti elements than the large grains (Figure 9(b)), which confirmed that the small grains were composed of BLTO perovskite ceramics. The large grains exhibited a low wt% of Ba, La, and Ti elements, confirming they were composed of CZFO spinel ceramics (Figure 9(b)). The EDS results indicated that both grains were mostly composed of the different compounds that had been used to produce the composite ceramic.

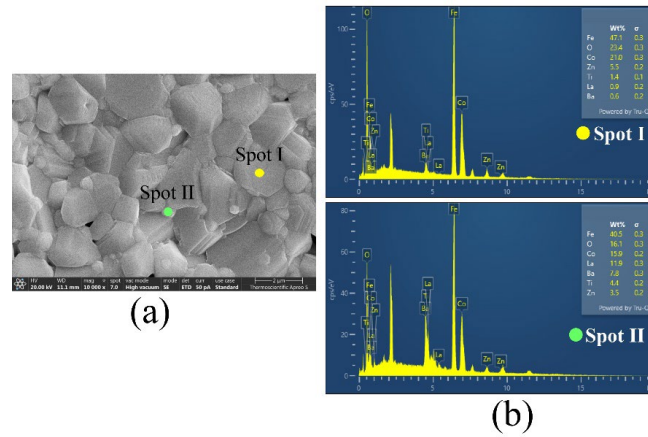


Figure 9. (a) SEM image (b) EDS spectra of spot I and spot II of the 0.1BLTO-0.9CZFO ceramics sintered at 1300°C for 2 h

The average size of the 0.1BLTO-0.9CZFO ceramics, produced with various sintering temperatures, was measured using the ImageJ program after dividing the grains into two groups, the small spherical grains, and the large polygon grains. The average size of the small spherical and large polygon grains increased from 0.51 to 4.17 μm and 1.60 to 14.42 μm , respectively, when the sintering temperatures increased from 1200 to 1400°C, as listed in Table 2. The SEM results revealed the results of pore formation and grain growth at each sintering temperature, which supported the phase fraction variations seen in the XRD results of the ceramics. The measured density of all ceramics was analyzed by the Archimedes technique. The measured density of the sintered ceramics increased from 5.12 to 5.75 g/cm^3 when the sintering temperatures increased from 1200 to 1300°C, and then the density decreased, as seen in Table 2. The decrease in density was likely caused by an increase in the amount of porous structure present, corresponding with the SEM images.

The temperature dependency of the dielectric permittivity of the 0.1BLTO-0.9CZFO ceramics, sintered at temperatures between 1200 and 1300°C for 2 h, as a function of temperature (30-350°C) and frequency (1-100 kHz), is presented in Figures 10(a)-(c). The dielectric constant (ϵ) and dielectric loss ($\tan\delta$) curves of the sintered ceramics showed higher values and higher dispersion with different frequencies when the temperature was increased, as seen in Figures 10(a)-(c), which was similar to previous work (Habiba et al., 2023). This behavior was indicative of cobalt ferrite-based ceramics which exhibited low ϵ values and high $\tan\delta$ values at room temperature, and the ϵ and $\tan\delta$ values rose rapidly upon heating (Rather et al., 2019; Habiba et al., 2023). The dielectric constant and dielectric loss at room temperature (ϵ_r and $\tan\delta_r$) of the ceramics measuring at 1 kHz are listed in Table 2. It was observed that ϵ_r values increased from 16.21 to 52.19, while $\tan\delta_r$ values decreased from 3.55 to 1.30 (Table 2). The highest ϵ_r and $\tan\delta_r$ values were obtained from the ceramics sintered at 1300°C for 2 h because the ceramics had the best microstructure and the highest density. Moreover, the ceramics sintered between 1350 and 1400°C could not have their dielectric properties measured because the ceramics exhibited large conductivity, inferior microstructure, and low density. The dielectric properties of the 0.1BLTO-0.9CZFO ceramics, produced with various sintering temperatures, corresponded to the microstructure and density results.

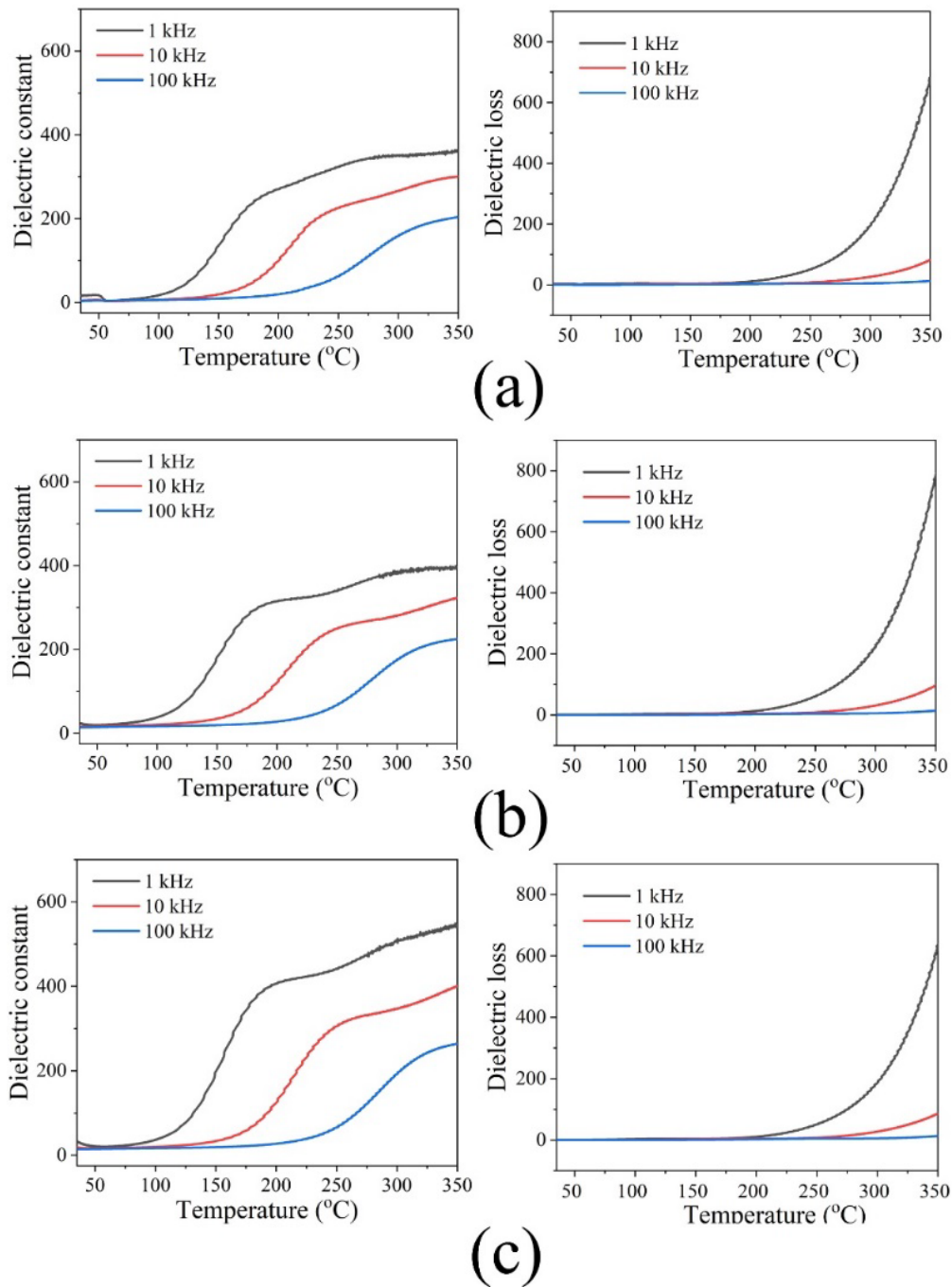


Figure 10. Temperature dependence of the dielectric properties measured between 1 and 100 kHz of the 0.1BLTO-0.9CZFO ceramics sintered at (a) 1200°C, (b) 1250°C, and (c) 1300°C

The ferroelectric properties of the P-E hysteresis loops, at room temperature, of the 0.1BLTO-0.9CZFO composite ceramics, produced with sintering temperatures between 1200 and 1300°C for 2 h, were investigated under an applied electric field of 10 kV and are shown in Figure 11. The P-E loops showed unsaturated and bloated hysteresis loops, which can be attributed to a large leakage of current in this composite ceramic, as can be seen in Figure 11, the P-E loops are similar to previous work (Habiba et al., 2023). The maximum polarization values ($P_{\max}$) of the ceramics were observed at the applied electric field at 0 kV, and the polarization values increased from 0.90 to 1.59 $\mu\text{C}/\text{cm}^2$, while polarization values at the highest applied electric field of 10 kV (P_{10}) were in the range of 0.18-0.22 $\mu\text{C}/\text{cm}^2$, as seen in Table 3. The highest polarizations were obtained for the ceramics sintered at 1300°C.

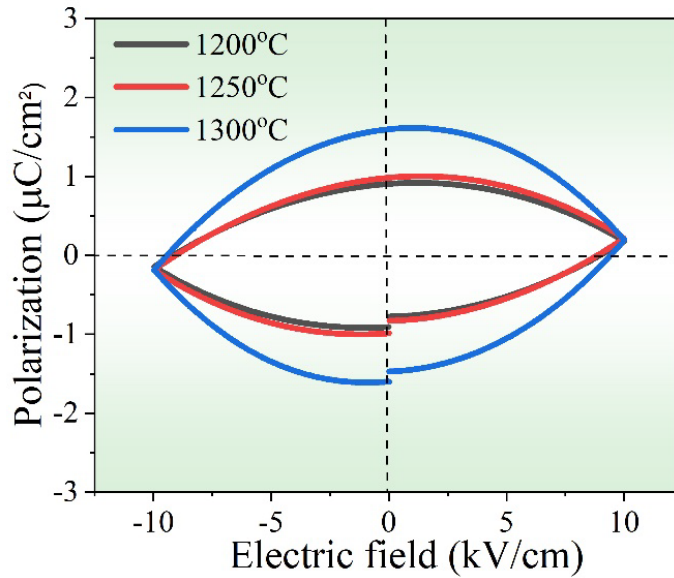


Figure 11. P-E loops at room temperature of the 0.1BLTO-0.9CZFO composite ceramics produced with sintering temperatures of 1200-1300°C for 2 h

Table 3. Ferroelectric and magnetic properties, and magnetoelectric coefficients of the 0.1BLTO-0.9CZFO composite ceramics produced with various sintering temperatures

Sintering Temperature (°C)	Maximum Polarization ($P_{\max}$) ($\mu\text{C}/\text{cm}^2$)	Polarization at Applied Electric Field of 10 kV (P_{10}) ($\mu\text{C}/\text{cm}^2$)	Coercive Field (E_c) (kV/cm)	Saturated Magnetization (M_s) (emu/g)	Remnant Magnetization (M_r) (emu/g)	Coercivity (H_c) (Oe)	Magnetoelectric Voltage Coefficient (α_{ME}) (mV/cm Oe)
1200	0.90	0.18	8.86	82.03	13.12	195	6.30
1250	0.98	0.20	8.99	83.56	15.50	200	6.55
1300	1.59	0.22	9.40	87.31	20.42	182	6.74
1350	-	-	-	79.14	16.73	142	1.76
1400	-	-	-	74.63	12.34	121	0.49

The shape of the P-E hysteresis loops and polarization values of these ceramics under an applied electric field were caused by two main factors: (i) the bloated hysteresis loops and high $P_{\max}$ values resulted from the lattice mismatch between ferroelectric and ferromagnetic phases (Rather et al., 2019; Habiba et al., 2023); and (ii) the increased polarization with sintering temperatures increasing from 1200 to 1300°C resulted from the enhancement of magnetostriction and strain, which influenced the formation of space charges and promoted strong ferromagnetic interactions, leading to enhanced polarization (Wang et al., 2012; Rather et al., 2019). The coercive field (E_c) of the 0.1BLTO-0.9CZFO composite ceramics increased from 8.86 to 9.40 kV/cm when the sintering temperature was increased from 1200 to 1300°C, and E_c values were larger than the polarization values. This result may be linked to the existence of the ferromagnetic phase, the formation of porous structures, and the growth of grains, which prevented and stopped the motion of the domain wall of the ferroelectric phase (Wang et al., 2012; Rather et al., 2019).

The M-H hysteresis loops, measured at room temperature, of the 0.1BLTO-0.9CZFO composite ceramics produced with various sintering temperatures are displayed in Figure 12. From the M-H hysteresis loops, it was found that the ceramics exhibited saturated M-H loops and soft ferromagnetic behavior with high saturated magnetization (M_s), small remnant magnetization (M_r), and small coercivity (H_c). The values of M_s , M_r , and H_c were examined using the M-H hysteresis loops and are listed in Table 3. It is observed that the M_s and M_r values increased from 82.03 to 87.31 emu/g and 13.12 to 20.42 emu/g, respectively, when the sintering temperatures were increased from 1200 to 1300°C and then dropped in value, as seen in Table 3. The H_c values tended to decrease with increased sintering temperature, as observed in Table 3. The increase in magnetization and decrease in coercivity may be caused by an increase in sintering temperature, which results in more grain growth with larger grains, leading to improved alignment of the magnetic domains and a more ordered arrangement of magnetic moments, enhancing the overall magnetic properties, and increasing magnetization (Wang et al., 2012; Sharma et al., 2021; Goel et al., 2022; Kornphom et al., 2023a,b). Moreover, extremely high sintering temperatures can induce porous structures and excessive grain growth, which increases the non-magnetic regions and disrupts magnetic coupling between neighboring magnetic domains, reducing the overall magnetic response and magnetization in the ceramics (Li et al., 2019; Sharma et al., 2021; Goel et al., 2022; Kornphom et al., 2023a,b). The magnetic properties correspond to the microstructure and density of the ceramics at various sintering temperatures. The best magnetic properties, such as the highest M_s (87.31 emu/g), M_r (20.42 emu/g), and low H_c (182 Oe), were obtained for the 0.1BLTO-0.9CZFO composite ceramics sintered at a temperature of 1300°C for 2 h, which had the best microstructure and the highest density. The M_s value (87.31 emu/g) of the ceramics prepared by a simplified combustion technique, with one-step calcination, was higher than the ceramic prepared by the solid-state reaction method (M_s = 60 emu/g) (Habiba et al., 2023).

The magnetoelectric effect (ME) of the 0.1BLTO-0.9CZFO composite ceramics produced with various sintering temperatures can be explained by the magnetoelectric voltage coefficient (α_{ME}), which is calculated by the following equation, equation (8):

$$\alpha_{ME} = \left(\frac{\partial E}{\partial H} \right) = \frac{V_0}{t_p \times H_{ac}} \quad (8)$$

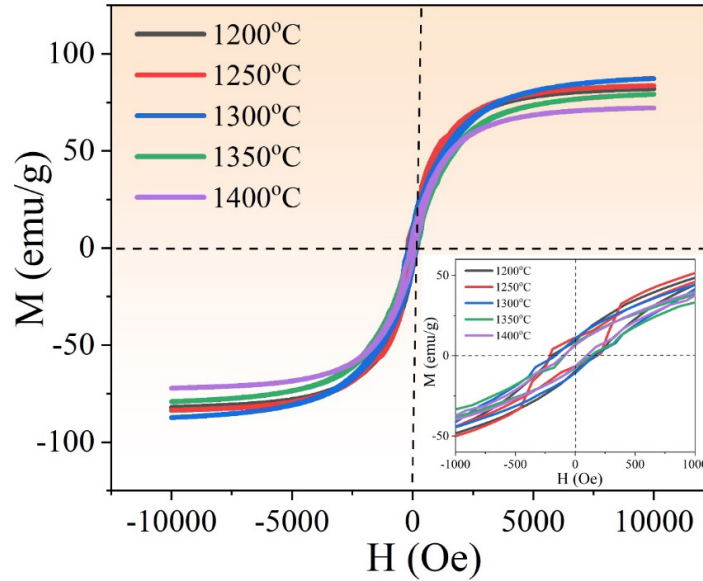


Figure 12. M-H hysteresis of the 0.1BLTO-0.9CZFO ceramics for the various sintering temperatures

Here V_o is the induced output voltage, t_p is the thickness of the ceramics, and H_{ac} is the applied ac magnetic field (Kornphom et al., 2023a,b). Figure 13 demonstrates the performance of the magnetoelectric coefficient (α_{ME}) of the 0.1BLTO-0.9CZFO composite ceramics, for various sintering temperatures, which were determined under a H_{ac} field of ~ 10 Oe, a frequency of ~ 1 kHz, and a varying H_{dc} field in the range of 0-4500 Oe (Kornphom et al., 2023a,b). The α_{ME} values of each sintered sample showed almost unchanged values when H_{dc} increased from 0 to 2500 Oe, as observed in Figure 13. When sintering temperatures increased from 1200 to 1300°C, the α_{ME} values slightly increased from 6.30 to 6.74 mV/cm Oe, as seen in Table 3. Then, the α_{ME} values rapidly decreased to 1.76 and 0.49 mV/cm Oe with increased sintering temperatures of 1350 and 1400°C, respectively (Table 3). The variation in the α_{ME} values of the 0.1BLTO-0.9CZFO composite ceramics produced with various temperatures could be due to three main possible factors: the phase fractions, porous structure, and grain growth. These factors affected the electrical and magnetic properties, as described in the above sections, leading to a change in the magnetoelectric coefficient. The 0.1BLTO-0.9CZFO composite ceramics with a sintering temperature of 1300°C showed the highest α_{ME} value of 6.74 mV/cm Oe and this ceramic showed the best microstructure, the highest density, and excellent electrical and magnetic properties. Thus, nano powders and high performance multiferroic 0.1BLTO-0.9CZFO composite ceramics were successfully synthesized by a simplified combustion technique with only one calcination step.

A comparison of the α_{ME} value of the 0.1BLTO-0.9CZFO composite ceramics in this work with lead free multiferroic ceramic composites from previous research are summarized in Table 4. It was observed that the 0.1BLTO-0.9CZFO composite ceramic exhibited a higher α_E value than the composite ceramics of previous work. It is confirmed that the 0.1BLTO-0.9CZFO composite is a potential lead-free multiferroic with possible future applications in multifunctional electronic devices.

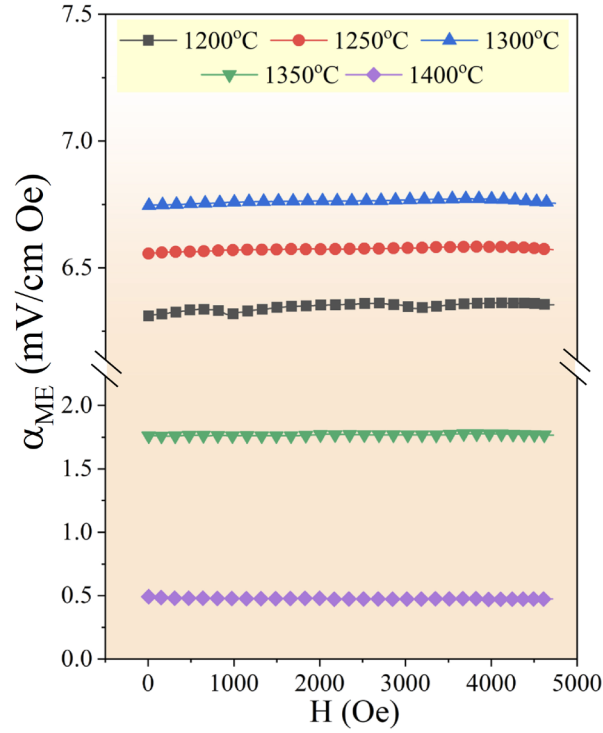


Figure 13. Variation of α_{ME} with H_{dc} of the 0.1BLTO-0.9CZFO composite ceramics for various sintering temperatures

Table 4. Comparison of the α_{ME} value of the 0.1BLTO-0.9CZFO composite ceramics in this work and related composite ceramics reported in previous work.

Optimized Composition	α_{ME} (mV/cm Oe)	Ref.
0.1BLTO-0.9CZFO	6.74	-
$\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-CoCr}_{0.4}\text{Fe}_{1.6}\text{O}_4$	4.87	Goel et al., 2022
$\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Ti}_{0.90}\text{Zr}_{0.10}\text{O}_3\text{-CoFe}_2\text{O}_4$	1.99	Sharma et al., 2021
BCZT/LCMO/BCZT	1.07	Li et al., 2019
$0.8 \text{ Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}0.2 \text{ Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$,	3.16	Reddy et al., 2024
$0.3 \text{ NiFe}_2\text{O}_4\text{-}0.7\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$	3.82	Chavan et al., 2021
$(\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4)_{0.3}\text{-(Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6)_{0.7}$	0.18	Köferstein et al., 2024
$(\text{Na}_{0.41}\text{K}_{0.09}\text{Bi}_{0.5}\text{TiO}_3\text{-Ba}_{0.85}\text{Ca}_{0.15}\text{Zr}_{0.1}\text{Ti}_{0.9}\text{O}_3)\text{-}(\text{CoFe}_2\text{O}_4)$	4.09	Pal et al., 2024
$0.6\text{Pb}_{0.4}\text{La}_{0.6}\text{Zr}_{0.6}\text{Ti}_{0.4}\text{O}_3\text{-}0.4\text{CoFe}_2\text{O}_4$	0.45	Vandana et al., 2023
$(\text{NiFe}_2\text{O}_4)_{0.3}\text{-(Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6\text{-LiNbO}_3)_{0.7}$	0.803	Köferstein et al., 2023

4. Conclusions

In summary, the effect of firing temperatures on the phase formation, microstructure, density, optical, electrical, magnetic, and magnetoelectric properties of 0.1Ba_{0.5}La_{0.5}TiO₃-0.9Co_{0.8}Zn_{0.2}Fe₂O₄ (0.1BLTO-0.9CZFO) ceramics, synthesized by a simplified combustion technique, with glycine as the fuel, using a one-step calcination process with short processing times, was studied. A 0.1BLTO-0.9CZFO nano powder, with a pure phase, an average particle size of 45 nm and a band gap energy (E_g) of 4.85 eV that produced enhanced photocatalytic activity, was successfully synthesized using a calcination temperature of 800°C for 2 h. The 0.1BLTO-0.9CZFO ceramics sintered at temperatures of 1200-1400°C for 2 h showed a pure phase with a mixture of perovskite and spinel phases, forming the composite ceramics. At a sintering temperature of 1300°C for 2 h, the 0.1BLTO-0.9CZFO ceramic demonstrated a well-packed microstructure, the highest density (5.75 g/cm³), excellent electric properties ($\epsilon_r = 52.19$, $\tan\delta_r = 1.30$, $P_{\max} = 1.59$ $\mu\text{C}/\text{cm}^2$, $P_{10} = 0.21$ $\mu\text{C}/\text{cm}^2$ and $E_c = 9.40$ kV/cm), excellent magnetic properties ($M_s = 90.54$ emu/g, $M_r = 29.87$ emu/g and $H_c = 310$ Oe) and the highest magnetoelectric coupling coefficient ($\alpha_E = 6.74$ mV/cm Oe). This work successfully synthesized nano powders and high-performance composite ceramics of 0.1BLTO-0.9CZFO by a simplified combustion technique with one calcination step, low temperatures and short dwell times which might be helpful for further preparation and application of magnetoelectric materials.

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6. Conflicts of Interest

The authors and the institutes where the work has been carried out declare that there are no conflicts of interest regarding the publication of this article.

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