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Influence of A-site Mg^{2+} Incorporation on the Structural, Optical, Dielectric, and Ferroelectric Properties of $\text{BaZr}_{0.1}\text{Ti}_{0.9}\text{O}_3$ Perovskite Ceramics

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ABSTRACT

Lead-free ferroelectric ceramics have emerged as critical alternatives to toxic lead-based systems for next-generation dielectric and energy storage applications. In this work, $\text{Ba}_{1-y}\text{Mg}_y\text{Zr}_{0.1}\text{Ti}_{0.9}\text{O}_3$ ($y = 0.00, 0.05, 0.07, 0.10$) ceramics were synthesised via citrate-nitrate auto-combustion and systematically investigated to understand the influence of A-site Mg^{2+} substitution on structural, optical, dielectric, ferroelectric, and energy-storage properties. Rietveld refinement confirmed phase-pure tetragonal symmetry ($P4mm$) across all compositions, with progressive lattice contraction from 4.0266 Å to 3.9909 Å, while average crystallite size decreased from 21.71 nm (BZT) to 17.21 nm (BMZT0.10) as Mg content increased. HR-SEM revealed a monotonically decreasing grain size from 116.87 nm to 112.76 nm, confirming Mg^{2+} as an effective grain growth inhibitor. A tuneable optical bandgap of 3.23-3.31 eV was established from UV-Vis diffuse reflectance spectra. Frequency-dependent dielectric measurements revealed Maxwell-Wagner dominated polarisation behaviour, with BMZT0.05 achieving the highest permittivity (5069.49) and lowest loss factor (0.019). P-E hysteresis analysis confirmed ferroelectric loops across 5-55 kV/cm at 10 and 100 Hz, with BMZT0.05 exhibiting the highest remanent polarisation. Notably, BMZT0.10 achieved an energy-storage efficiency of 85.6% at an ultralow field of 5 kV/cm, attributed to its slim hysteresis loop and enhanced polarisation reversibility. These results establish Mg-engineered BZT ceramics as promising lead-free candidates for low-voltage dielectric capacitors, ferroelectric memory, and microelectronic energy-storage applications.

Keywords: Lead-free ferroelectrics, barium zirconate titanate, A-site substitution, dielectric permittivity, energy storage efficiency

1. INTRODUCTION

The rapid advancement of modern electronic and energy technologies has intensified the demand for high-performance, environmentally sustainable dielectric ceramic materials capable of delivering superior ferroelectric, dielectric, and energy storage characteristics. Lead-based ferroelectrics, particularly lead zirconate titanate (PZT), have long dominated electro-ceramic applications owing to their exceptional piezoelectric and dielectric responses. However, their inherent toxicity and the increasingly stringent environmental regulations governing lead-based compounds have catalysed an urgent worldwide search for viable lead-free alternatives[1].

Among the plethora of lead-free candidates explored to date, Barium Titanate BaTiO_3 (BT) has emerged as one of the most intensively investigated perovskite oxides, distinguished by its simple ABO_3 crystal structure, remarkable dielectric permittivity, well-defined ferroelectric hysteresis, and compatibility with a wide spectrum of ionic dopants at both A (Ba^{2+}) and B (Ti^{4+}) crystallographic sites[2][3]. BaTiO_3 holds many applications, comprising of capacitors, transducers, sensors, actuators, EO modulators, and more. Also, the high dielectric constant of BaTiO_3 enables the fabrication of smaller capacitive elements, which thereby paves the way for more compact electrical devices[4]. Pure BaTiO_3 undergoes a sequence of well-established structural phase transitions as a function of temperature, transforming sequentially from a rhombohedral phase near 88°C , through an orthorhombic phase near 0°C , to a tetragonal ferroelectric phase between approximately 7°C and 130°C , and finally to a cubic paraelectric state above the Curie temperature ($T_C \approx 130^\circ\text{C}$) [3]. The room-temperature tetragonal phase (space group P4mm) is characterised by off-centre displacement of the Ti^{4+} ion within the oxygen octahedra (TiO_6), giving rise to a net spontaneous polarisation that underpins the ferroelectric behaviour of the material. However, despite these promising intrinsic properties, undoped BaTiO_3 suffers from several practical limitations, including a sharp and narrow ferroelectric-to-paraelectric phase transition, relatively modest dielectric permittivity away from T_C , non-negligible dielectric losses at low frequencies, and limited tunability of the Curie temperature for device-relevant operational ranges. These shortcomings have motivated extensive doping and co-substitution strategies aimed at modifying the structural, microstructural, and functional properties of BaTiO_3 in a controlled and systematic fashion. Different dopants like magnesium, zirconium, strontium, gadolinium, neodymium, and manganese have been doped in the A and B sites, as reported by many studies[5][3][6]. A-site substitution of barium titanate has resulted in improved dielectric permittivity. Incorporation

of aliovalent or isovalent ions at the can influence domain dynamics and polarisation reversibility due to the difference in their ionic radii, which are critical factors governing energy storage efficiency[7]. For instance, co-doping aliovalent Gd and Zr in BaTiO₃ (Ba_{1-x}Gd_{2x/3}Zr_{0.05}Ti_{0.95}O₃) with the existence of dual-phase showed an enhanced dielectric behaviour under optimised dopant concentration[8]. Thus, the concentration of the dopants plays a crucial role in determining the functions of the BT-based ceramics. Among B-site dopants, Zr⁴⁺ ions (ionic radius 0.72 Å) are notably larger than Ti⁴⁺ ions (ionic radius 0.605 Å), and their incorporation into the BaTiO₃ lattice to form the barium zirconate titanate (BZT) solid solution produces slight structural distortions that relieve internal strain, enhancing the dielectric constant, stabilising the ferroelectric phase, and minimising electrical losses[9]. In addition to B-site modification, A-site substitution offers an alternative pathway to tune polarisation behaviour, defect chemistry, and microstructural evolution. Furthermore, the addition of acceptor dopants such as Mg²⁺, Co²⁺, Al³⁺ and Mn³⁺ is considered an excellent idea to modify the structure. The substitution of Mg²⁺ at the A-site of Ba(Zr, Ti)O₃, despite being isovalent with Ba²⁺, introduces significant lattice distortion due to the substantial ionic size mismatch. This structural modification alters the tolerance factor and enhances the off-centring of B-site cations, thereby improving the intrinsic polarisation. Consequently, an enhancement in dielectric permittivity and optimised ferroelectric properties are achieved in the studies reported previously [2]. Furthermore, Mg incorporation contributes to controlled grain growth, resulting in a refined microstructure that supports improved dielectric performance and reduced loss. However, systematic studies focusing on the role of A-site Mg²⁺ substitution in BaZr_{0.1}Ti_{0.9}O₃ ceramics to enhance the dielectric and ferroelectric properties and to achieve a good energy storage efficiency, particularly under low electric field conditions, remain limited.

In this context, the present work investigates the effect of Mg²⁺ substitution on the structural, morphological, optical, and electrical properties of BaZr_{0.1}Ti_{0.9}O₃ ceramics synthesised via a citrate-nitrate auto-combustion route. Particular emphasis is placed on understanding the influence of dopant concentration, with Mg content varied in the range of 0.05-0.1 mol%. Furthermore, the dependence of the ferroelectric and dielectric properties on compositional variation is systematically examined to establish the role of Mg incorporation in tuning the functional performance of BaTiO₃-based ceramics.

BaZr_{0.1}Ti_{0.9}O₃, Ba_{0.95}Mg_{0.05}Zr_{0.1}Ti_{0.9}O₃, Ba_{0.93}Mg_{0.07}Zr_{0.1}Ti_{0.9}O₃, Ba_{0.9}Mg_{0.1}Zr_{0.1}Ti_{0.9}O₃ will be named as BZT, BMZT0.05, BMZT0.07, and BMZT0.1 in this work.

2. MATERIALS AND METHODS

2.1. Preparation of Mg-doped BZT

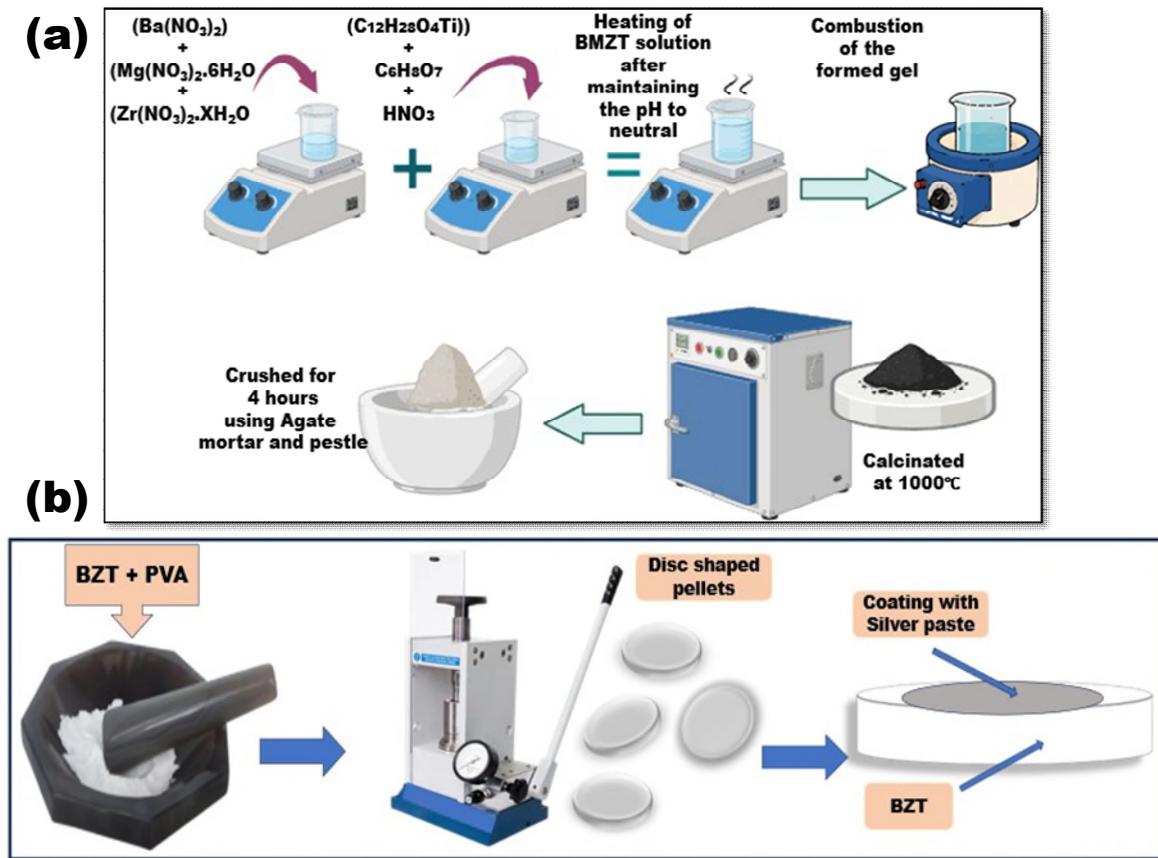


Fig.1.(a) Preparation of BMZT(M=0.05,0.07,0.1) samples via Citrate-nitrate auto-combustion technique and (b) Schematic representation of BZT pellet preparation and Application of Silver Paste Electrodes

The $\text{Ba}_{1-y}\text{Mg}_y\text{Zr}_{0.1}\text{Ti}_{0.9}\text{O}_3$ ($y=0.0, 0.05, 0.07, 0.1$) ceramics were synthesised using a citrate–nitrate auto-combustion route, and the overall preparation scheme is illustrated in Fig.1(a). In the first step, Solution 1 was prepared by dissolving stoichiometric amounts of barium nitrate ($\text{Ba}(\text{NO}_3)_2$, extrapure 98%), zirconyl nitrate hydrate ($\text{Zr}(\text{NO}_3)_2 \cdot \text{XH}_2\text{O}$, and magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, AR, ACS 99%) in distilled water under constant stirring. Separately, solution 2 was formulated by mixing tetra-n-butyl ortho-titanate (TNBT; $\text{C}_{12}\text{H}_{36}\text{O}_4\text{Ti}$) with the required acids to ensure proper hydrolysis and stabilisation. The citric acid to nitric acid ratio is fixed to be 2:2.

Solutions 1 and 2 were then combined and continuously stirred to achieve a uniform sol, and ammonia solution was added dropwise to adjust the pH to 8 and promote controlled gelation. The resulting sol was heat-treated for 2 h to obtain a viscous gel, which subsequently underwent

self-propagating combustion to yield fine precursor powders. The as-combusted powders are calcinated at 1000°C for 5 h to eliminate residual organics, release volatile components, and promote crystallisation. After calcination, the powders were cooled to room temperature and finely ground to reduce particle size and ensure homogeneity. For clarity, $\text{BaZr}_{0.10}\text{Ti}_{0.90}\text{O}_3$ will be denoted as BZT, while $\text{Ba}_{1-y}\text{Mg}_y\text{Zr}_{0.1}\text{Ti}_{0.9}\text{O}_3$ compositions with $y = 0.05, 0.07, \text{ and } 0.10$ are referred to as BMZT0.05, BMZT0.07, and BMZT0.10, respectively, throughout this work.

For functional characterisation, the powders were pressed into pellets at 3 tonnes using PVA as a temporary binder and sintered at 1100 °C for 5 h. The pellets (~1.5 mm thick) were polished and coated with silver paste electrodes for ferroelectric hysteresis measurements. The pellet preparation procedure for the BZT sample is shown in Fig. 1(b).

2.2. Characterisation Techniques

The information regarding the crystalline structure as well as the phase of the ceramic powders was studied using the X'pert3 powder X-ray Diffractometer, PANalytical. Surface morphology and elemental composition were examined using high-resolution SEM (Thermo Scientific Apreo S) coupled with EDX (Bruker Nano, GmbH, D-12489, Germany). Optical properties, including bandgap estimation, were obtained from UV-Vis diffuse reflectance spectra recorded in the 200-800 nm range (PerkinElmer LAMBDA-35). Functional groups were identified using Fourier Transform Infrared Spectroscopy (FTIR) (FT/IR-4700, Jasco). Room-temperature dielectric studies are measured by utilising an LCR meter, while frequency and electric field-dependent ferroelectric studies were evaluated with a Precision Multiferroic Tester, Radiant Technologies Inc., USA. Energy-storage parameters were calculated by integrating the ferroelectric P-E loops.

3. RESULTS AND DISCUSSION

3.1. Phase Identification and Crystalline Structure Analysis via XRD

Fig. 2 conveys the XRD pattern for the BZT, BMZT0.05, BMZT0.07, and BMZT0.10 samples at room temperature. The directional planes of (100), (110), (111), (200), (210), (211), (220), (300), (310), (113) exhibit the peaks. Also, the perovskite structure of the prepared samples is disclosed, and the identified peaks are found to be in correspondence with the tetragonal phase having the $P4mm$ space group, matching the ICPS card no. 252558. Through this, it is evident that both zirconium and magnesium are well incorporated into the unit cell,

maintaining the perovskite structure of barium titanate, and without any formation of secondary phase.

The average crystallite size (L) was determined by utilising Debye Scherrer's formula, and it is observed that the size decreased with an increase in magnesium content. An inverse correlation between crystallite size and peak intensity has been observed, wherein the most intense diffraction peak corresponds to the smallest crystallite size, and vice versa. A similar decreasing trend was followed for the lattice constant of all the samples, where BZT has the highest value (4.0266), while the Mg-doped samples BMZT0.05, BMZT0.07, and BMZT0.1 have the lowest values (4.0159, 4.0098, 3.9909). This behaviour indicates effective incorporation and uniform diffusion of Mg^{2+} ions within the host lattice, leading to lattice shrinkage. Such contraction arises from the substitution of larger 12-coordinated Ba^{2+} ions (1.61 Å) with comparatively smaller Mg^{2+} ions (1.03 Å). This variation, attributed to peak shifts, is reflected in the XRD patterns, where samples with smaller lattice constants exhibit shifts toward higher 2θ values, [9]. Furthermore, Fig.2b shows the high-resolution scan in the range 31° - 32° , confirming the successful dopant incorporation, resulting in a phase-pure tetragonal structure in the synthesised perovskite. The prepared samples exhibited crystallinity between 63% and 97%, and thus, the magnesium concentration strongly influenced the crystallinity percentage of the sample, where BMZT0.1 attained a crystallinity of 97%. The X-ray density (ρ_x) of the samples increased with Mg substitution, which is likely due to the lesser atomic weight of magnesium than Ba and Zr. The Gold-Schmidt formula was utilised to measure the tolerance factor, and it was found that $0.8 < t < 1.05$ confirms the formation of a stable perovskite structure in the synthesised samples. The measured X-ray densities and tolerance factors are consistent with previously reported values, supporting the structural integrity of the doped perovskite system [10][11].

$$\rho_x = (ZM) / (N_A V) \quad (1)$$

$$t = \frac{r_{A^+} r_O}{\sqrt{2} (r_{B^+} r_O)} \quad (2)$$

Employing size and strain metrics, the microstructural details of Mg-substituted powders were examined by utilising the Williamson-Hall plot. The slope derived from the plot $\sin \theta / \lambda$ and $\beta \cos \theta / \lambda$ gives the lattice strain value is given in the Table 1. Also, in the Fig. 3(a), the positive slope value suggests the existence of tensile strain, which indicates that the lattice elongates and the lattice parameters rise along a specific direction. Furthermore, dislocation density (δ) obtained and the lattice strain (ϵ) are inversely proportional to the average crystalline size.

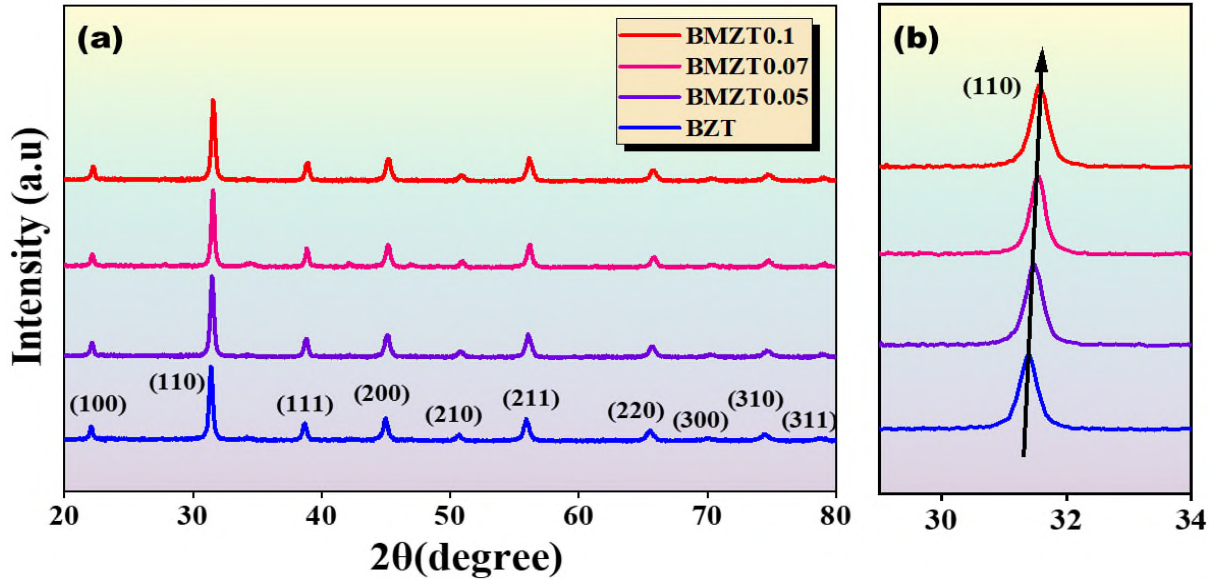


Fig.2. (a) Diffraction patterns of Mg-doped BZT, (b) magnified pattern of the shift in peaks in the θ range 30-32°, 55-57°, and 65-66°

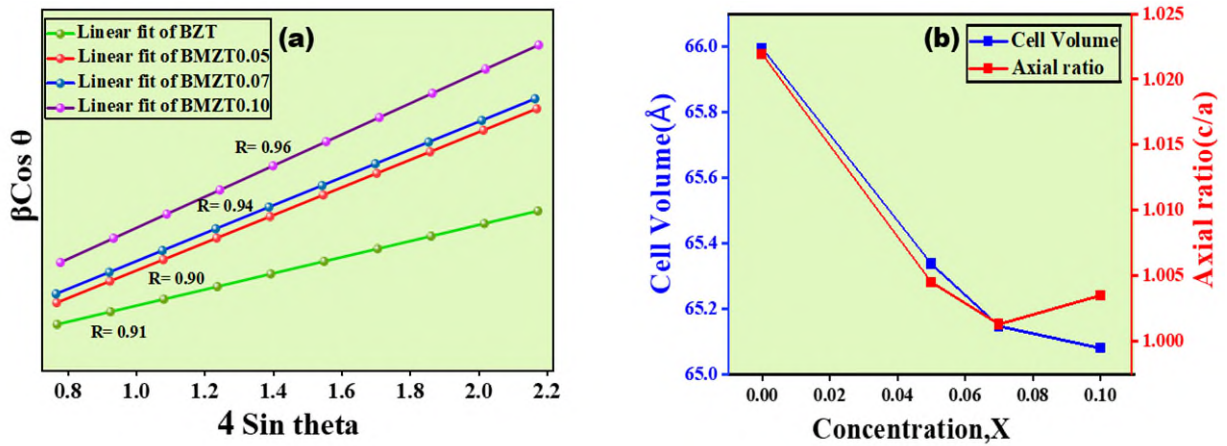


Fig.3. (a) W-H plot and (b) Correlation between cell volume, axial ratio and x

The crystal structure was refined with FullProf Suite using the $P4mm$ space group. Peak fitting with the Pseudo-Voigt function showed close agreement with the experimental data, indicating a tetragonal, single-phase structure. The resulting structural parameters are tabulated in Table 2. Furthermore, by using goodness-of-fit metrics like R_{wp} and χ^2 , the best fit requirement is accomplished. The correlation between axial ratio (c/a) and the volume of the unit cell for the prepared is established in Fig. 3(b). Increasing dopant content reduces the cell volume due to the substitution of smaller Mg^{2+} (1.03 Å) for larger Ba^{2+} (1.61 Å), causing lattice contraction and minor distortion. This trend in lattice constant is consistent with previous reports[12]. The refined patterns are displayed in Fig.4. Furthermore, the diagrammatic representation of the

perovskite structure with the tetragonal phase of the synthesised samples using VESTA software is shown in Fig. 5.

Table 1 Structural parameters of the prepared Pristine BZT and Mg-modified BZT ceramics

Structural parameters	BZT	BMZT0.05	BMZT0.07	BMZT0.1
Crystallite size, L (nm)	21.7119	19.2153	18.8626	17.2093
Lattice constant, a (Å)	4.0266	4.0159	4.0098	3.9909
Volume of the unit cell, V (Å ³)	65.2853	64.7662	64.4715	63.5641
Most intense peak's site	31.3777	31.4660	31.5543	31.7671
X - ray density, ρ_x (gm/cm ³)	6.0854	6.2501	6.3967	6.3211
Lattice strain, ϵ (10 ³)	0.7597	0.8671	0.8770	0.9730
Dislocation density, δ (10 ⁻²)	2.1213	2.7083	2.8105	3.3765
Crystallinity %	63.32	72.35	81.59	97.38
Tolerance factor	1.0550	1.0412	1.0381	1.0304

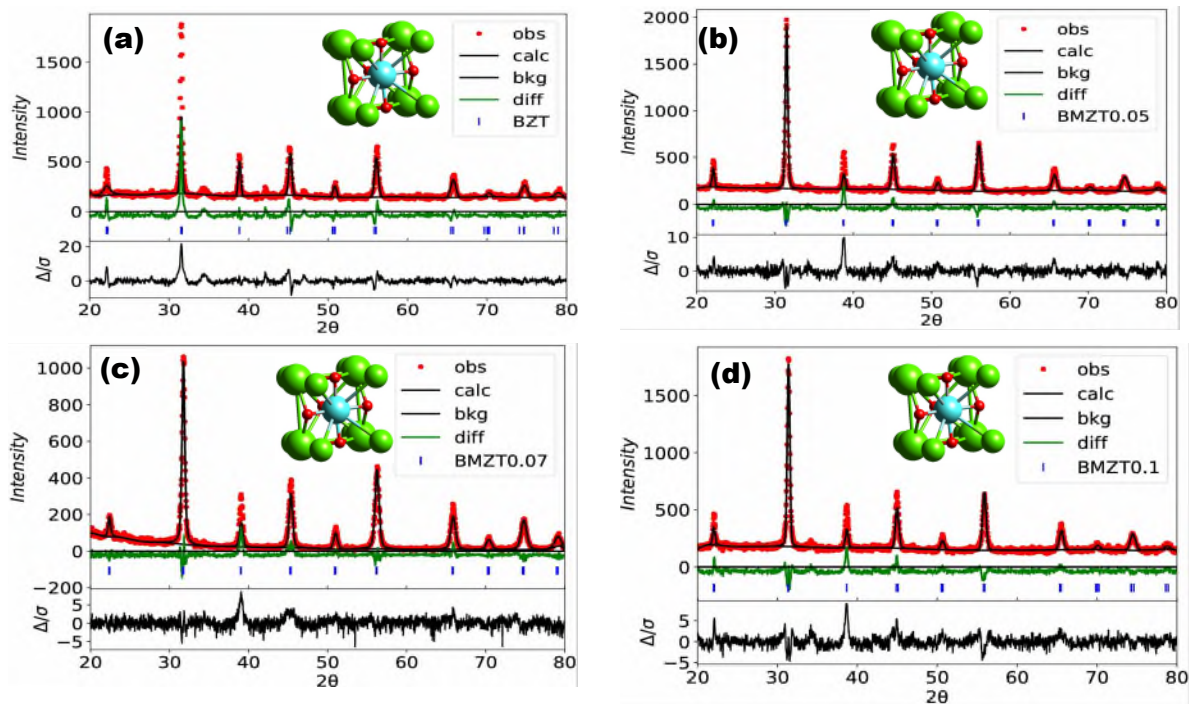


Fig. 4 Rietveld refinement fitting profile of powder XRD patterns

The bond lengths Ba-O increased slightly and dropped significantly in BMZT0.10, which may be reflected due to local distortion or changes in the ionic radius environment due to Mg substitution. The slight reduction in Ti-O bond length observed in Mg-substituted samples

suggests enhanced Ti-O bond strength and modified local lattice strain induced by A-site Mg^{2+} substitution. These local distortions do not alter the global tetragonal symmetry but influence the ferroelectric domain dynamics, contributing to the gradual transition from normal ferroelectric to relaxor-ferroelectric behaviour with increasing Mg concentration. Table 3 shows the bond length of BZT and BMZT samples.

Table 2 Structural parameters obtained from the refinement process.

Refinement parameters	BZT	BMZT0.05	BMZT0.07	BMZT0.1
Crystal system	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Space Group	P4mm	P4mm	P4mm	P4mm
Space Group no.	99	99	99	99
$\alpha = \beta = \delta$ (°)	90	90	90	90
a = b (Å)	4.0120	4.0156	4.0219	4.0128
c (Å)	4.1000	4.0337	4.0274	4.0271
Axial ratio (c/a)	1.0219	1.0045	1.0013	1.0035
Cell volume (Å ³)	65.994	65.336	65.146	65.079
Rwp (%)	10.763	9.598	9.392	9.747
χ^2	2.159	1.764	1.591	1.826

Table 3 Bond length between Ba-O and Ti-O of BZT and BMZT samples

Bond length, (Å)	BZT	BMZT0.05	BMZT0.07	BMZT0.10
Ba – O	2.8150	2.8336	2.8191	2.6089
Ti – O	2.049	2.025	2.031	2.032

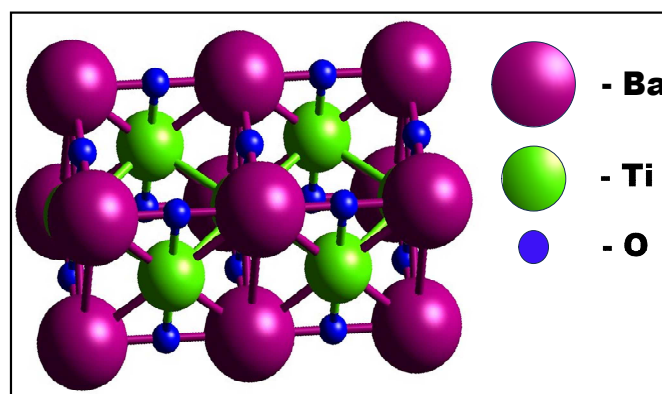


Fig. 5. Crystal structure of Barium Titanate

3.2. Domain structure and Elemental analysis

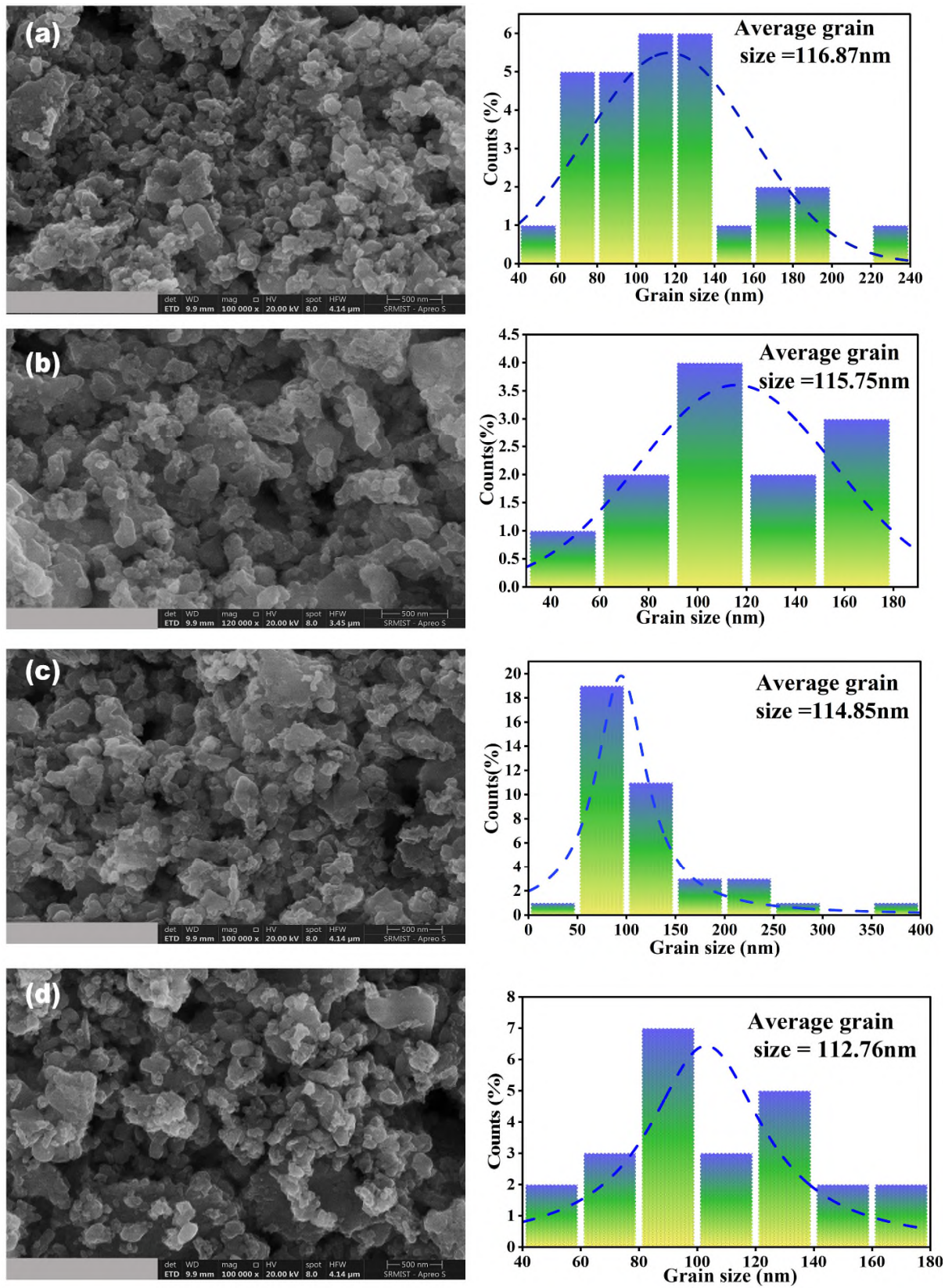


Fig. 6. HRSEM graphs and grain size determination graph of (a) BZT, (b) BMZT0.05, (c) BMZT0.07, (d) BMZT0.1

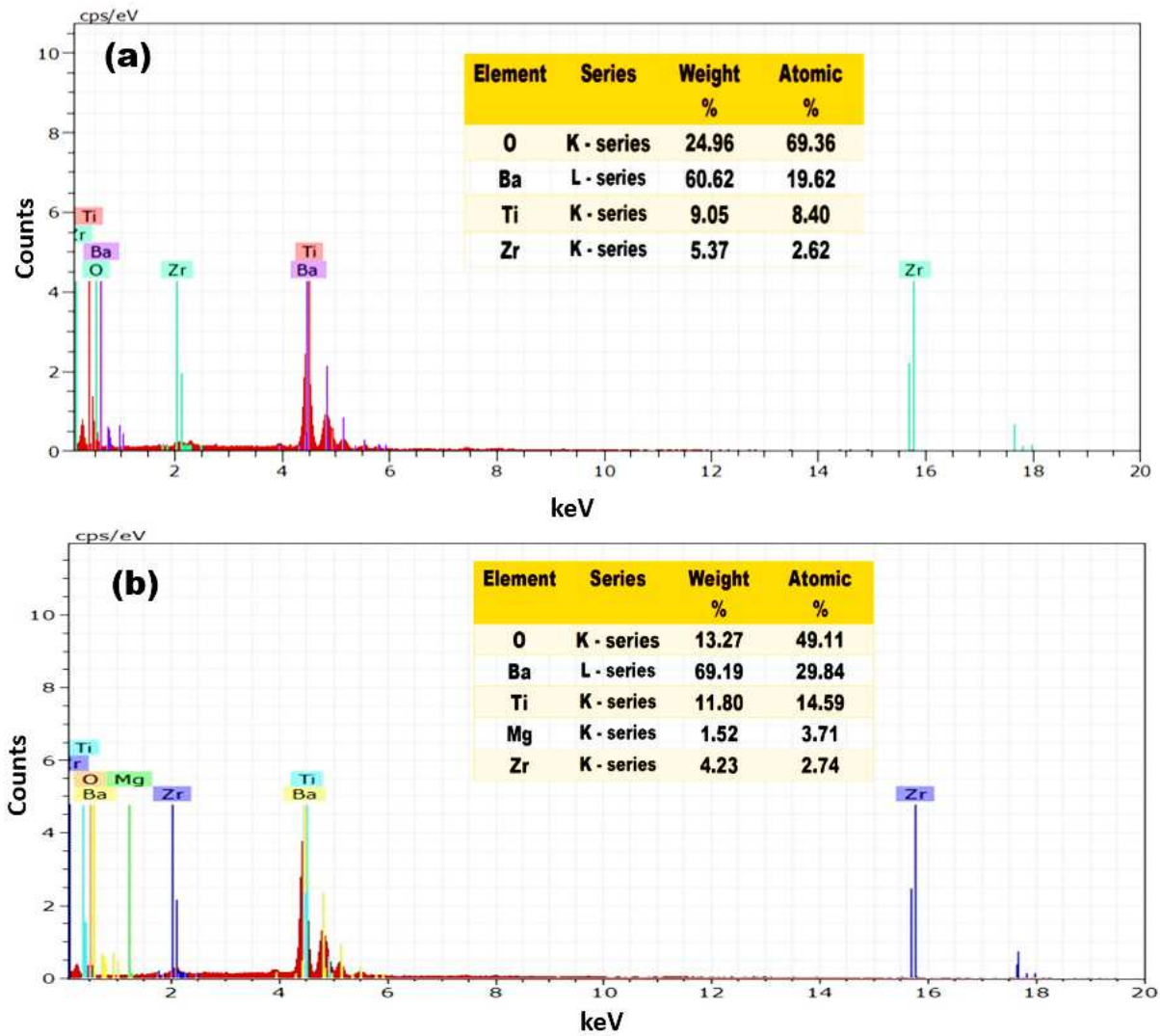


Fig.7. EDX spectrum of (a) BZT and (b)BMZT0.1

Fig. 6(a-d) displays the High-resolution scanning electron microscope (HRSEM) images of pristine BZT and Mg^{2+} doped BZT ceramics. The nanostructure of all the prepared samples is dense and compact. Irregularly shaped particles with minor agglomeration were observed, suggesting that weak Van der Waals interactions may contribute to the formation of these loosely bound aggregates. The percentage of small grains rises as the Mg-doping concentration increases, while the proportion of large grains decreases. This inverse relationship between dopant concentration and grain size is consistent with previous reports [13]. These results indicate that grain growth in BaTiO_3 -based ceramics is effectively suppressed by magnesium incorporation, suggesting its role as a grain growth inhibitor. This behaviour can be attributed to the introduction of Mg^{2+} ions, which promotes the formation of oxygen vacancies, thereby hindering grain boundary mobility and limiting grain growth [6]. The change in grain size was examined by utilising ImageJ software, and the values are found to be 116.87nm, 115.75nm,

114.85nm, and 112.76nm for the pristine BZT, BMZT0.05, BMZT0.07, and BMZT0.1 samples. Also, the reduction can possibly be attributed to the lesser ionic radii of Mg than Ba[14].

A similar kind of decrease in grain size after the inclusion of dopant is reported by [12][15]. Additionally, the elemental composition of the synthesised BZT and BMZT (Z=0.05, 0.07, 0.1) samples is explored using Electron Dispersive X-ray (EDX) spectra. The spectra noticed the presence of Ba, Zr, Ti, O in BZT and Ba, Mg, Zr, Ti, O elements were seen commonly in Mg-doped BZT samples with varying weight percentage. Fig.7(a,b) shows the EDX spectrum of BZT and BMZT0.1, which confirms the above findings.

3.3. Functional Group Mapping Using FT-IR

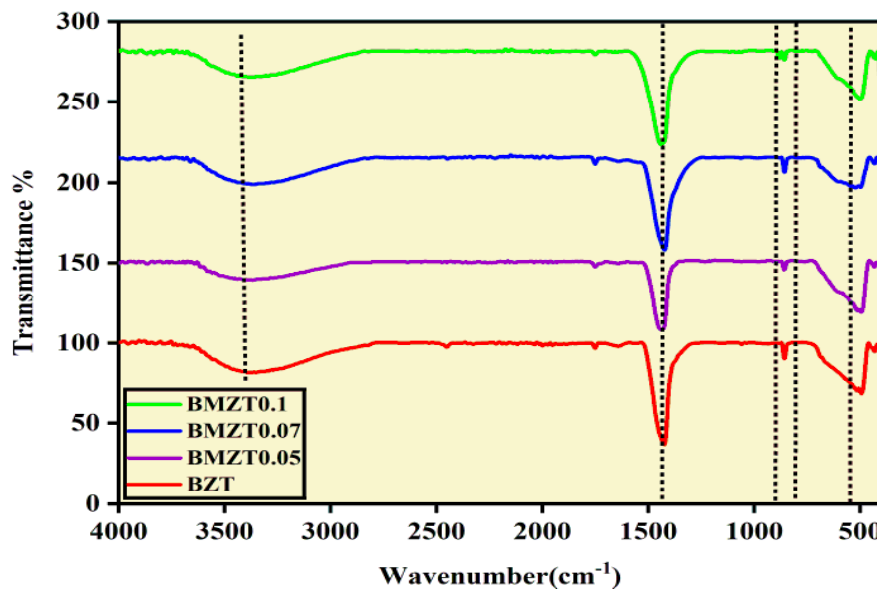


Fig. 8 FTIR spectra of the prepared perovskite ceramics

The structure of the prepared samples is once again confirmed by using Fourier transform infrared spectroscopy (FT-IR). Fig. 8 depicts the graph of FT-IR spectra of the synthesised BZT, BMZT0.05, BMZT0.07 and BMZT0.1 samples in the wavenumber range from 400 cm^{-1} to 4500 cm^{-1} . The presence of absorption bands has been found in four different regions. Initially, the presence of strong peaks at a range of 460-750 cm^{-1} represents the metal-oxygen vibrational stretching of Ti-O-Ti and Zr-O-Zr, M-O, confirming the perovskite structure (ABO_3) of all the prepared samples [4]. The difference in concentration between each sample could be a possible reason for the changing broadness of the bands in this area [11]. Secondly, a small band is measured around 850 cm^{-1} , which is due to the stretching of C-C [16]. Thirdly, a broad medium intensity peak observed in the range of 1300 – 1600 cm^{-1} conveys the

presence of water and carbonate groups. The broadness of the peak shrinks after the addition of Mg in BZT, which can be because of better phase formation and less surface water retention due to increased densification or crystallinity. And finally, a wide absorption band has been detected between the wavenumber 2800-3600 cm^{-1} , indicating the moisture, hydroxyl groups due to the water molecules absorbed in the surface [11].

3.4. Optical Energy bandgap analysis

The UV-Visible absorbance (DRS) spectra of the synthesised Mg-doped BZT samples recorded in the 200nm-800nm range at room temperature are shown in Fig. 9. Maximum light has been absorbed within 200nm to 400nm, gradually decreasing at longer wavelengths. The optical bandgap (E_g) was estimated using the Tauc relation for a direct transition:

$$\alpha h\nu = B (h\nu - E_g)^n \quad (3)$$

where the transition parameter $n = 1/2$ corresponds to direct electronic transitions[2].

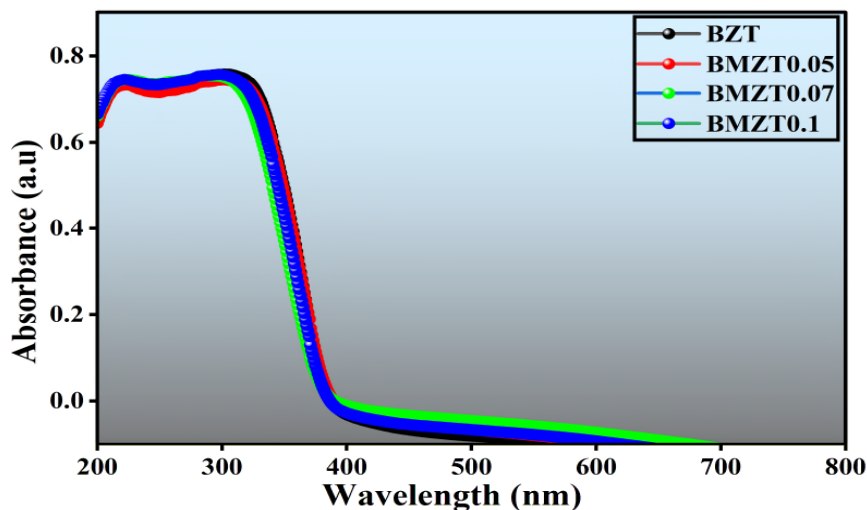


Fig. 9. UV-absorption spectra of pristine BZT and Mg-modified BZT samples

Linear extrapolation of the $(\alpha h\nu)^2$ versus $h\nu$ data indicates a bandgap of 3.24 eV for BZT, while doped samples exhibit E_g values between 3.23 and 3.30 eV. The energy bandgap of the prepared samples obtained in this range matched the trend [6][2]. The incorporation of Mg influenced the bandgap non-monotonically and is shown in Fig.10. Initially, the addition of Mg decreased the bandgap values to 3.23V in BMZT0.05. The main cause for the decrease in energy bandgap can be attributed to the disordered arrangements in BZT, which could have been a result of the rarity of symmetry in O-Ti-O connections and structural distortions [2][5]. Compared to BMZT0.07, the lower band gap of the pristine sample arises from stronger Ti-O hybridisation

and defect states. Mg^{2+} substitution widens the band gap, with BMZT0.07 showing the maximum E_g due to optimal lattice distortion and defect suppression. And finally, for BMZT0.1, the energy bandgap decreased. A similar kind of increase and decrease in bandgap affected by the concentration of the dopant is reported in [5]. The tunable bandgap (3.23-3.31 eV) and ferroelectric behaviour make these ceramics promising for Fe-RAM and opto-ferroelectric applications.

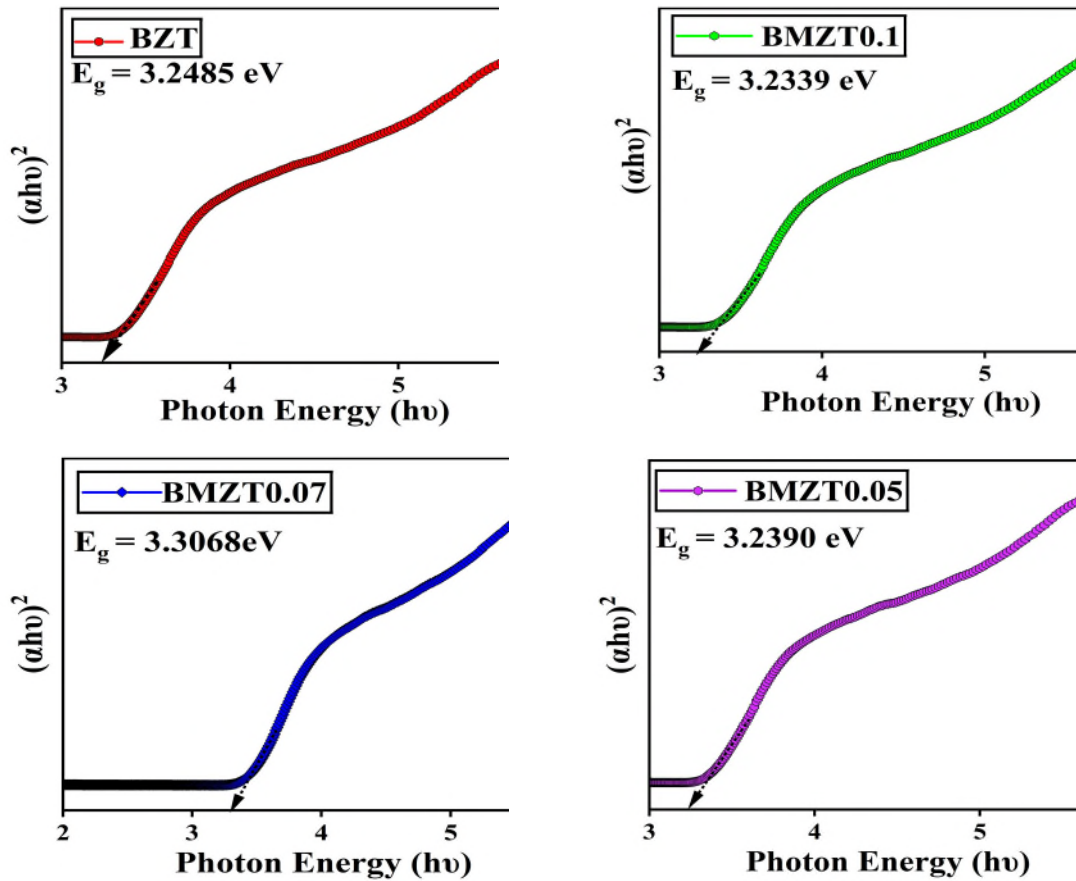


Fig. 10. Determination of energy bandgap of the BZT and BMZT samples

3.5. Dielectric Characterisation

The dielectric stability of materials is crucial for ferroelectric and energy storage applications. Factors such as synthesis route, calcination temperature, structure, and frequency significantly influence the dielectric constant and loss, reflecting various polarisation mechanisms [14]. Barium titanate, with its high permittivity and low energy dissipation, is a promising candidate for high-efficiency capacitors. This work examines the loss factor (δ) and relative dielectric constant (ϵ_r), which indicate a material's ability to store electric energy through polarisation.

3.5.1. Frequency-dependent dielectric study

Fig. 11(a) illustrates the relative dielectric constant (ϵ_r) measurements for both pristine and Mg-doped BZT ceramics as a function of frequency (1Hz - 7MHz) at room temperature. All samples exhibit exceptionally high ϵ_r values at lower frequencies, followed by a rapid decrease with increasing frequency. The enhanced dielectric response at low frequencies originates from space-charge accumulation associated with defects, oxygen vacancies, and dislocations at grain boundaries [2]. The pronounced decline in ϵ_r with increasing frequency indicates relaxation behaviour typical of heterogeneous dielectric systems [3][17]. Maxwell-Wagner interfacial polarisation dominates the dielectric response at low frequencies, while at higher frequencies, the contribution of space-charge polarisation diminishes, and electronic polarisation becomes dominant [3]. At higher frequencies, the dielectric constant approaches a nearly frequency-independent value, often referred to as the static dielectric constant. This behaviour arises from the inability of dipolar entities to respond to the rapidly oscillating electric field, resulting in diminished polarisation contributions due to lagging dipole dynamics and associated damping effects [2].

The obtained results demonstrate a strong correlation between the dielectric constant and the dopant concentration, as shown in Fig. 11(d). Among the compositions, BMZT0.05 exhibited the highest dielectric performance ($\epsilon_r = 5069.49$), surpassing BMZT0.07 ($\epsilon_r = 1649.61$), and BMZT0.1 ($\epsilon_r = 895.09$). Moderate Mg doping enhances ϵ_r by reducing oxygen vacancies and optimising grain size, whereas excessive doping (BMZT0.1) deteriorates dielectric performance. Although the average grain size decreases with increasing Mg concentration, the dielectric constant exhibits a maximum at BMZT0.05. This behaviour can be attributed to an optimal balance between enhanced interfacial (Maxwell-Wagner) polarisation, arising from increased grain boundary density and retention of ferroelectric domain wall mobility at moderate Mg content. At higher Mg concentrations, further grain refinement and increased lattice disorder are likely to restrict the domain wall motion, leading to a reduction in dielectric permittivity. This trend suggests a competing influence of grain interior and grain boundary contributions to the overall polarisation response. Grain boundaries act as space-charge regions, forming depletion layers that enhance interfacial polarisation at low frequencies, while simultaneously generating internal fields that can hinder the effective polarisation response [6]. The dielectric performance of all samples investigated in this work exceeds previously reported values [6][2], which may be attributed to differences in dopant concentration, sintering temperature, crystallite size, defect density, and microstructural

homogeneity [10]. The frequency-dependent dielectric behaviour was further examined using the Universal Dielectric Response (UDR) model. The model indicates that localised charge carriers, moving between spatially inhomogeneous lattice potentials, are responsible for both conductivity and dipole formation [3].

$$F \times \epsilon_r = A(T) \times F^\alpha \quad (4)$$

Here, $A(T)$ represents the temperature constant, and F^α is the frequency exponent. By using this relation, a graph has been plotted for $\ln F$ Vs $\ln (F \epsilon_r)$ and is depicted in Fig. 11(c). A linear trend across the entire frequency range confirms that the UDR model accurately describes the dielectric response of all titanate samples, with excellent fitting ($R^2 \approx 0.99$).

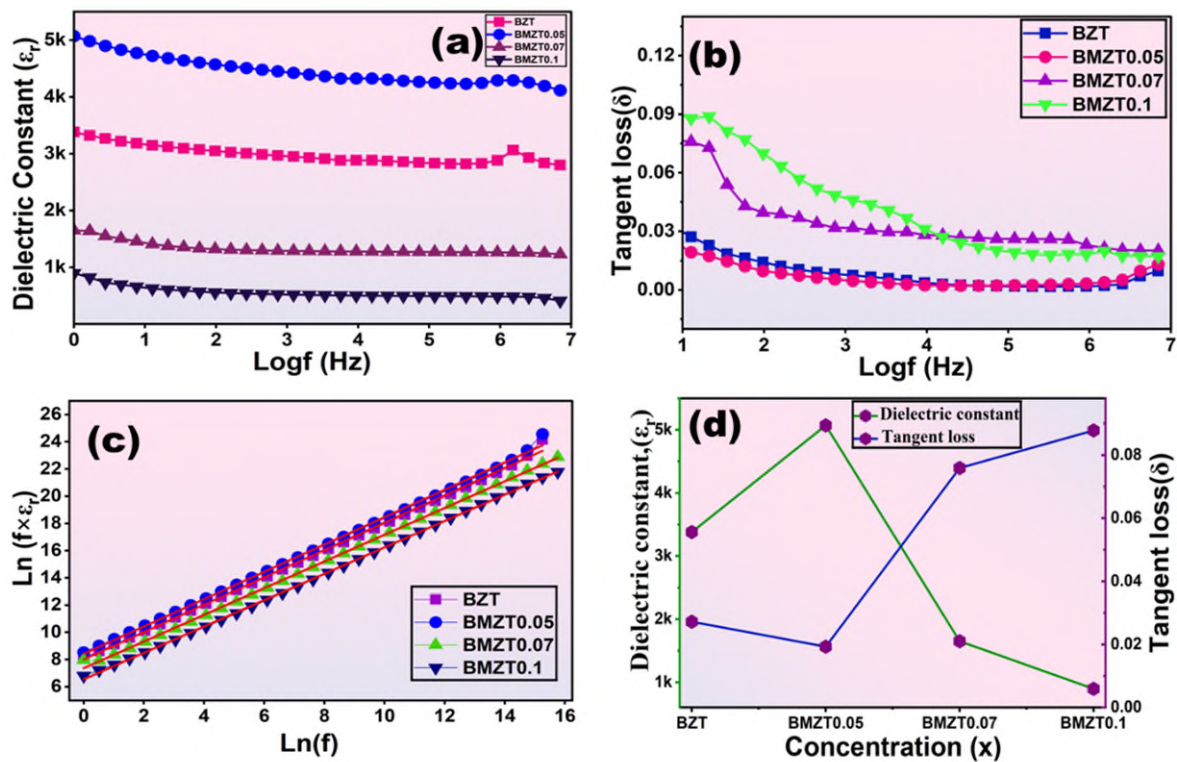


Fig. 11 (a) - Representing the Dielectric constant, (b) - tangent loss, (c) Dielectric response versus frequency fitted with the UDR model and (d) Variation of ϵ_r and δ Vs Concentration (X)

Fig. 11(b) shows the tangent loss ($\tan \delta$) for the titanate samples. All samples exhibit a high loss factor at low frequencies, which decreases with increasing frequency and becomes constant at higher frequencies, likely due to conductivity effects. As shown in Fig. 11(d) ϵ_r and $\tan \delta$ display an inverse relationship with varying dopant concentrations. The higher $\tan \delta$ values at low frequencies may result from imperfections and impurities generating absorption

currents, which diminish as frequency increases, leading to lower $\tan \delta$. Among all samples, BMZT0.05 shows the lowest dissipation energy of $\delta=0.019$ and exhibits a superior ferroelectric loop.

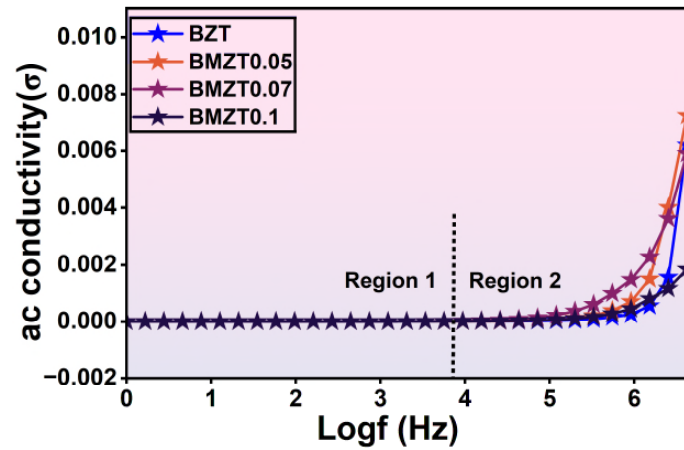


Fig. 12. (a) Frequency-dependent ac conductivity of BZT and Mg-doped samples

3.6. Electrical behaviour

The movement of free charge carriers in response to the applied electric field causes the polarising action or distortion factor in the nearby lattice, which influences the ac conductivity. AC conductivity (σ_{ac}) as a function of frequency at room temperature is tested, and the results are depicted in Fig. 12. The decrease in ac conductivity is due to the large polaron hopping, whereas the increased value is attributed to the smaller polaron hopping [10]. The σ_{ac} -frequency plot (1Hz-7MHz) can be divided into two distinct regions: at low frequencies, σ_{ac} remains nearly constant, indicating frequency-independent behaviour corresponding to DC conductivity (σ_{dc}) and long-range charge movement; at high frequencies, σ_{ac} increases with frequency due to short-range hopping of localised charges. All samples display a linear rise in σ_{ac} at higher frequencies, confirming that the conduction mechanism is governed by small polaron hopping, consistent with earlier reports [18]. The results confirm that a small amount of magnesium incorporation significantly enhances the conductivity of the BZT sample. The frequency dependence of AC conductivity can be described using the AC power-law expression:

$$\sigma_{ac} = A\omega^s \quad (5)$$

A is dimensionless, whereas s denotes a constant. In Fig. 13, a graph has been plotted for $\text{Log } \omega$ against $\text{Log } \sigma$, and the slope of the resulting linear fit provides the value of s. For all the

prepared samples, $s > 0$, indicating a strong frequency dependence of the conductivity consistent with hopping conduction of localised charge carriers.

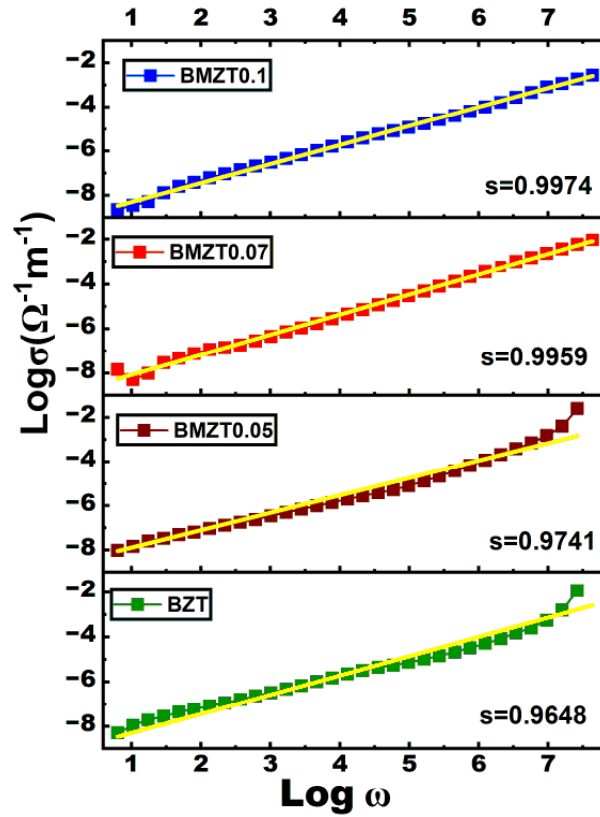


Fig. 13. Linear Fitting of $\text{Log } \sigma$ against $\text{Log } \omega$.

3.7. Ferroelectric Characterisation

Due to the ion off-centring in its tetragonal ($P4mm$) structure, barium titanate ceramics exhibit noteworthy ferroelectric properties at ambient temperature. Fig. 13 and Fig. 14 present the P-E hysteresis loops of BZT titanate samples measured at 10 Hz and 100 Hz. Ferroelectric behaviour is influenced by several factors, including grain size, porosity, defects, imperfections, applied electric field, and microstructural uniformity [14].

3.7.1. Electric field dependent P-E hysteresis loop

The observed P-E loops display both remanent and non-remnant characteristics, the former indicating the material's ability to retain polarisation after field removal. As shown in the figures, the hysteresis loops become more developed with increasing electric field. All samples exhibit saturated loops when subjected to fields ranging from 5-55 kV/cm at both frequencies. Under an applied field, cationic and anionic sites shift toward opposite electrodes, forming dipoles. Increasing the field enhances the separation between charge sites, thereby increasing

the dipole moment and promoting dipole alignment, which raises both maximum polarisation ($P_{\max}$) and remanent polarisation (P_r). These observations confirm that the polarisation behaviour of all samples strongly depends on the applied electric field.

Table 4 shows the values of $P_{\max}$, P_r , and E_c for the BZT, BMZT0.05, BMZT0.07 and BMZT0.1 samples. A P_r of $0.249 \mu\text{C}/\text{cm}^2$ is observed at $5\text{kV}/\text{cm}$, increasing to $3.14 \mu\text{C}/\text{cm}^2$ at $55\text{kV}/\text{cm}$ for the BZT sample. The hysteresis loop drift, indicating leakage, increased with higher Mg content. Among the samples, BMZT0.05 showed the highest P_r and E_c values under all applied fields. Fig. 15 presents the variation of E_c , $P_{\max}$, and P_r with the electric field for BMZT0.05 at 10 Hz and 100 Hz.

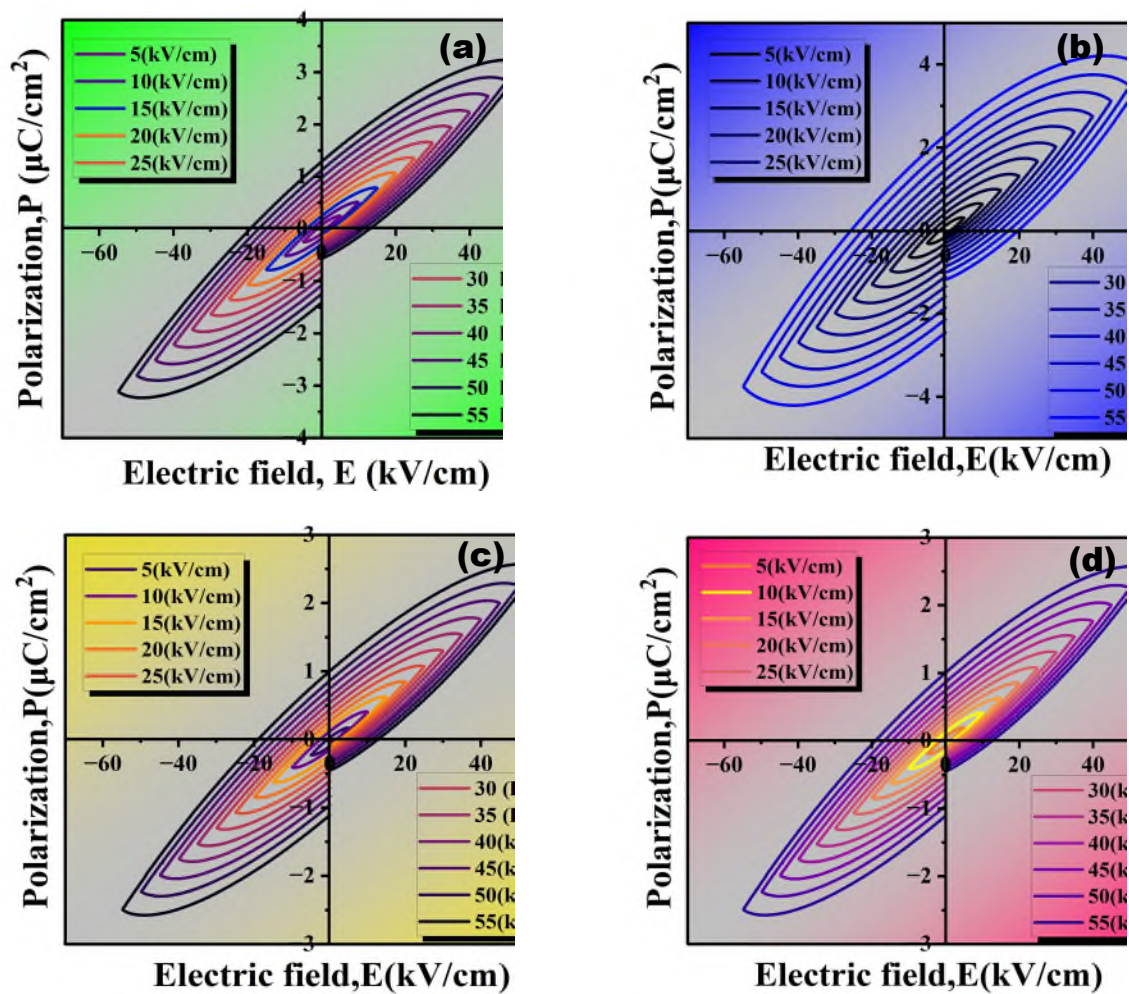


Fig. 13. PE loop recorded at 10Hz under applied electric fields ranging from of 5-55kV/cm

When 0.1% of Mg^{2+} ions replaced the Ba^{2+} site, a clear decrease in $P_{\max}$ ($2.52 \mu\text{C}/\text{cm}^2$), P_r ($1.00 \mu\text{C}/\text{cm}^2$) and E_c (12.6) was observed at 10Hz under $55\text{kV}/\text{cm}$. The reduced loop size at higher Mg levels is attributed to lattice disruption and increased defect density, which degrade

ferroelectric performance. Acceptor ion doping generates localised dipoles that align with the applied field, and higher Mg^{2+} content (BMZT0.1) further raises defect density, restricting spontaneous polarisation switching. Additionally, the smaller grain size of BMZT0.1, which was confirmed from HRSEM, limits domain growth and domain wall motion, resulting in lower polarisation and coercive field [12]. Similar reductions in polarisation with higher dopant levels have been reported [19][20].

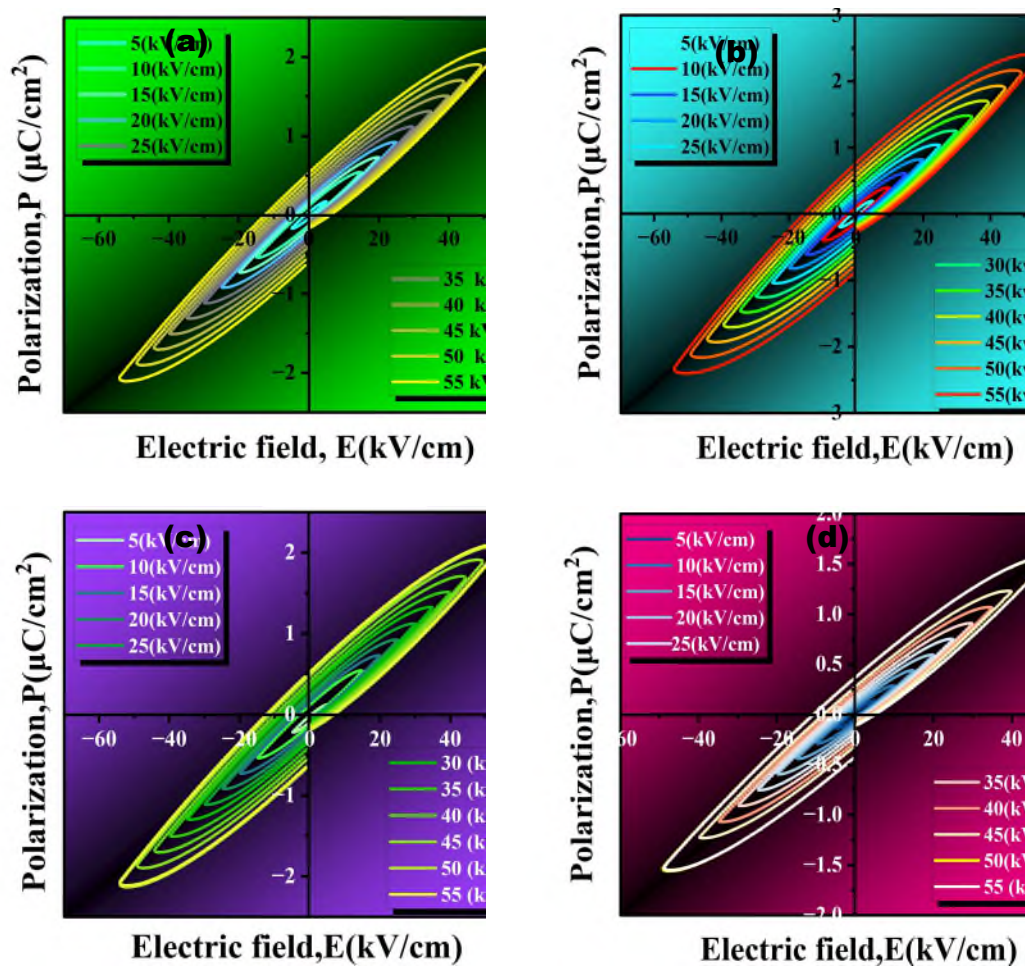


Fig. 14. PE loop obtained at 100Hz under applied electric fields ranging from of 5-55kV/cm-(a)BZT, (b)BMZT0.05, (c)BMZT0.07, and (d)BMZT0.1

Fig. 16 shows the instantaneous I-E characteristics at 10 Hz under an applied field of 5 kV/cm of the ceramics. The presence of current peaks near E_c indicates gradual polarisation switching. The BZT and BMZT0.05 samples exhibit broader loops with higher current response, indicating stronger domain wall activity and higher conduction. With increasing Mg content (BMZT0.07 and BMZT0.1), the loops become slimmer, and the current magnitude decreases, suggesting suppressed domain switching and reduced leakage. This reduction in current

contributes to lower energy loss and improved electrical stability in the higher Mg-containing compositions [21].

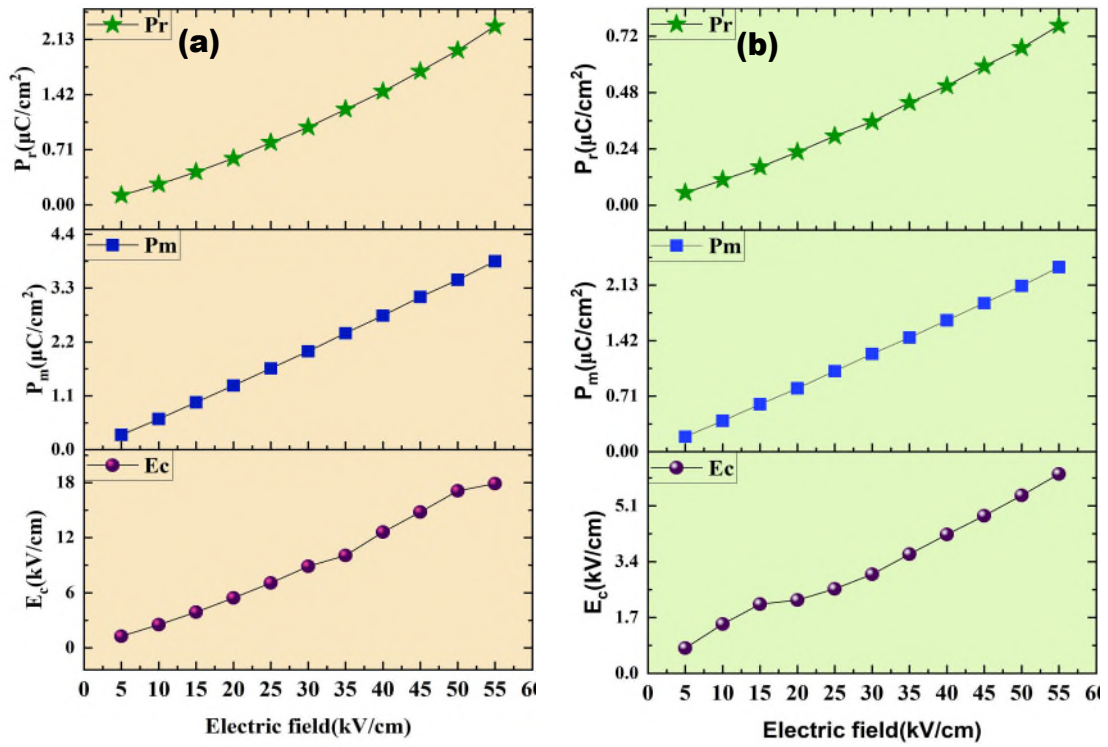


Fig. 15. Emergence of E_c , P_m and P_r with increasing applied electric field for BMZT0.05 at (a) 10Hz and (b) 100Hz

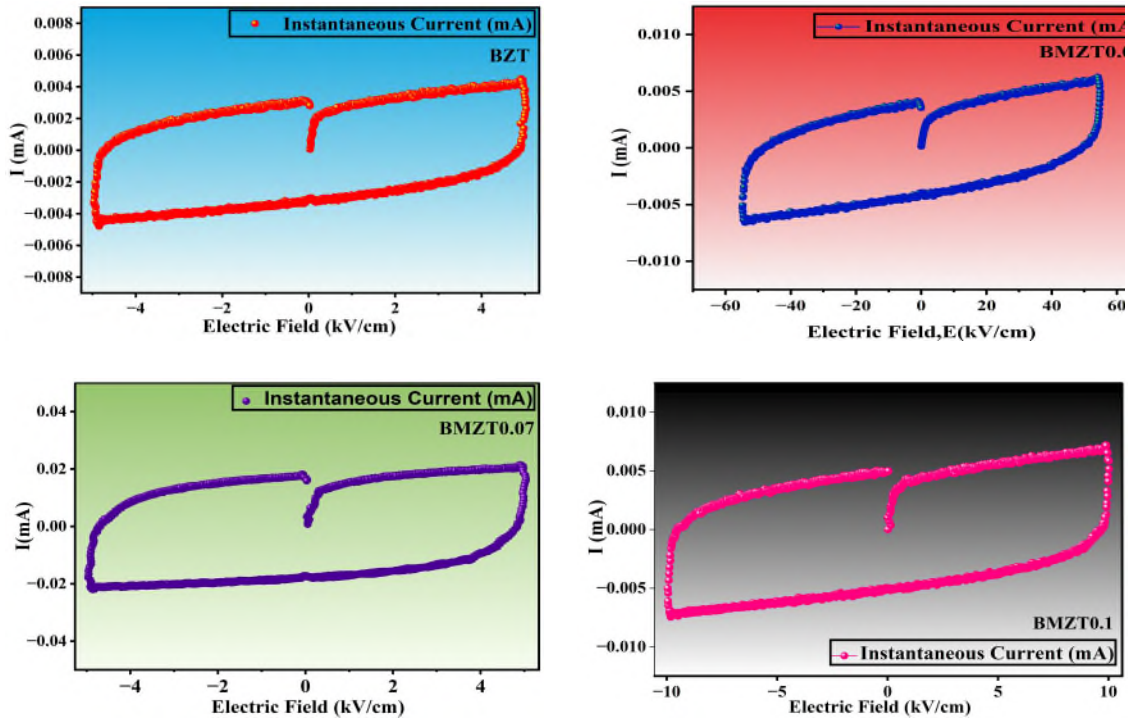


Fig. 16. I-E response of samples at 10 Hz with 5 kV/cm applied field

3.7.2. Frequency-dependent P-E hysteresis loop

The P-E hysteresis loops measured at 10 Hz and 100 Hz at room temperature shows that, frequency strongly affects the loop area, shape, and polarisation parameters. At 10 Hz, the loops are wider and higher polarisation, while at 100 Hz, they are narrower and slimmer, resulting in lower $P_{\max}$ and P_r and higher E_c . This indicates that the ferroelectric domains in BZT ceramics switch more easily under low-frequency fields [22]. As frequency increases, domains cannot reorient quickly, reducing macroscopic polarisation and energy per switching cycle [23]. Furthermore, the leakage decreases, and the loop becomes more linear at 100 Hz, highlighting the dominant capacitive behaviour. A visible change in $P_{\max}$ and P_r is seen in Fig.15. For BZT, the value of $P_{\max}$ dropped from 3.04×10^{-1} to $1.93 \times 10^{-1} \mu\text{C}/\text{cm}^2$ and the value of P_r reduced from 5.33×10^{-2} to $1.23 \times 10^{-1} \mu\text{C}/\text{cm}^2$ at $5 \text{ kV}/\text{cm}$ for an increase in frequency. Also, they represented a decline even when a higher electric field was applied at 100 Hz. This reduction in P_r and P_m with an increase in E_c at higher frequency is also reported in [22][23]. However, the prepared BMZT ceramics are promising candidates for ferroelectric random access memory applications [24].

Table 4 $P_{\max}$, P_r , E_c for the BZT, BMZT0.05, BMZT0.07 and BMZT0.1 samples

Samples	Electric field applied (kV/cm)	Maximum polarisation, $P_{\max}$ ($\mu\text{C}/\text{cm}^2$)		Remanent Polarisation, P_r ($\mu\text{C}/\text{cm}^2$)		Coercive field, E_c (kV/cm)	
		At 10Hz	At 100Hz	At 10Hz	At 100Hz	At 10 Hz	At 100Hz
BZT	5	0.249	0.169	0.073	0.034	0.916	0.513
	10	0.510	0.349	0.156	0.072	1.79	1.040
	15	0.780	0.539	0.248	0.114	2.75	1.520
	20	1.06	0.725	0.347	0.154	3.72	2.00
	25	1.35	0.917	0.457	0.202	4.76	2.57
	30	1.64	1.11	0.571	0.247	5.89	3.02
	35	1.94	1.31	0.697	0.298	7.14	3.63
	40	2.22	1.50	0.832	0.352	8.42	4.28
	45	2.53	1.68	0.976	0.409	9.85	4.80
	50	2.82	1.88	1.12	0.470	11.3	5.42
	55	3.14	2.07	1.29	0.533	13.0	6.07

BMZT0.05	5	0.304	0.193	0.123	0.053	1.25	0.773
	10	0.629	0.395	0.266	0.108	2.52	1.50
	15	0.968	0.606	0.424	0.163	3.88	2.11
	20	1.31	0.817	0.599	0.227	5.44	2.83
	25	1.61	1.03	0.802	0.295	7.06	3.59
	30	2.01	1.25	1.00	0.356	8.88	4.54
	35	2.38	1.46	1.23	0.437	11.07	5.02
	40	2.74	1.68	1.46	0.509	12.6	5.94
	45	3.12	1.90	1.72	0.593	14.8	6.72
	50	3.47	2.12	1.99	0.671	17.1	7.61
	55	3.85	2.36	2.30	0.766	17.9	8.55
BMZT0.07	5	0.168	0.119	0.036	0.024	1.776	1.68
	10	0.404	0.542	0.120	0.115	1.905	1.89
	15	0.619	0.729	0.186	0.158	2.751	1.95
	20	0.844	0.917	0.274	0.209	3.479	2.09
	25	1.067	1.110	0.364	0.255	4.706	2.37
	30	1.296	1.319	0.449	0.313	5.92	3.89
	35	1.538	1.504	0.549	0.351	7.14	3.95
	40	1.752	1.687	0.660	0.404	8.56	4.47
	45	1.999	1.894	0.758	0.466	9.74	5.70
	50	2.250	2.055	0.868	0.508	11.12	6.07
	55	2.522	2.075	1.006	0.541	13.53	6.21
BMZT0.1	5	0.199	0.138	0.056	0.028	0.089	0.557
	10	0.407	0.287	0.122	0.058	1.81	1.02
	15	0.621	0.438	0.191	0.080	2.73	1.52
	20	0.844	0.592	0.261	0.121	3.70	1.93
	25	1.07	0.750	0.351	0.157	4.85	2.42
	30	1.30	0.904	0.439	0.194	5.92	2.99
	35	1.53	1.06	0.539	0.237	7.14	3.50
	40	1.76	1.23	0.634	0.277	8.56	4.03
	45	2.00	1.39	0.748	0.320	9.74	4.59
	50	2.25	1.54	0.862	0.370	11.12	5.04
	55	2.52	1.55	1.00	0.376	12.6	5.07

3.8. Energy storage density and Efficiency

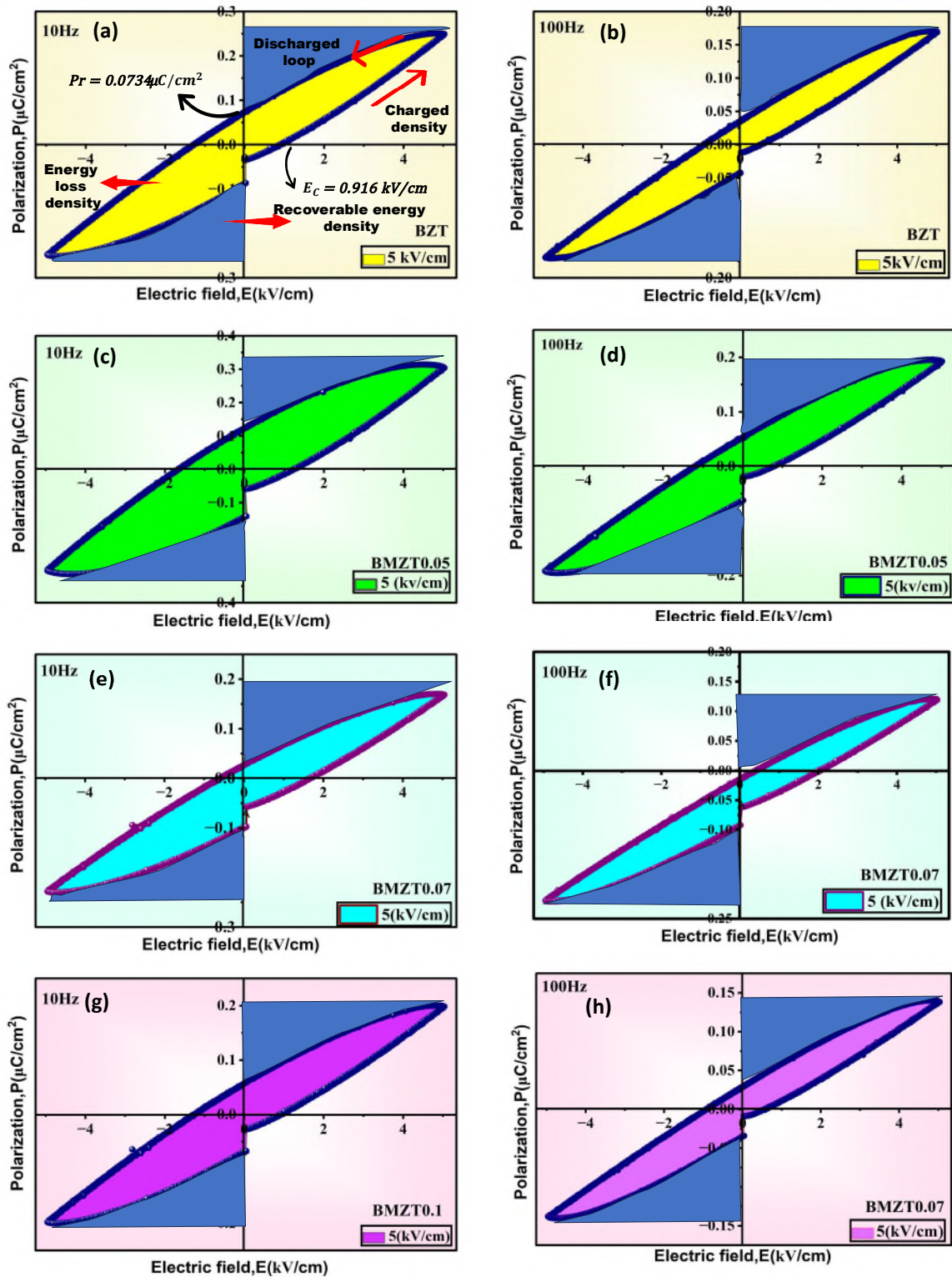


Fig. 17. Evaluation of energy storage density from room-temperature PE hysteresis,

In general, ferroelectric ceramics are widely used as energy storage materials in electric power systems and other electronic devices due to their excellent properties such as fast charging and

discharging speeds, higher energy storage density, lower tangent loss and better breakdown behaviour. The energy storage capacity and the efficiency (η) of the samples are determined from the ferroelectric hysteresis loop by integrating the applied electric field with the measured polarisation values [25].

$$W_{total} = \int_0^{P_{max}} E dp \quad (6)$$

$$W_r = \int_{P_r}^{P_{max}} E dp \quad (7)$$

$$\eta \% = \frac{W_r}{W_{total}} \quad (8)$$

W_{total} denotes the total energy density, and W_r represents the recoverable energy density. Fig. 17 presents the magnified hysteresis loops of pristine and Mg-doped BZT samples, measured at 5 kV/cm under frequencies of 10 Hz and 100 Hz, illustrating the polarisation behaviour. Here, the area shaded in vibrant colours inside the loop represents the total energy loss that occurs during the charging and discharging process, while the blue shaded part indicates the energy density (recoverable).

Using the obtained P_r (0.0734 $\mu\text{C}/\text{cm}^2$) and P_{max} (0.249 $\mu\text{C}/\text{cm}^2$), W_r is found to be 0.88 (mJ/cm^3) with $\eta = 70.7\%$ for the pristine BZT at 10Hz for an applied electric field of 5kV/cm. In the same way, W_{total} , W_r , and η values are calculated for all the samples for both the frequencies (10 and 100Hz) and for the varying electric field (5kV/cm-55kV/cm). Fig. 18 shows the progressive increase in W_{total} and W_r with increasing applied electric field, which is accompanied by modest variation in efficiency.

Enhanced energy storage efficiency is associated with a higher P_{max} and lower P_r . Specifically, BMZT0.1 exhibits the highest energy storage efficiency of 85.7% at 5 kV/cm, corresponding to the maximum ΔP ($P_{max}-P_r$). This calculated efficiency is greater than the efficiency (56%) obtained for $\text{SrTiO}_3\text{-BaZr}_{0.15}\text{Ti}_{0.85}\text{O}_3$ composite at 20kV/cm BZT-STO. In contrast, BMZT0.05, with a significantly low ΔP , shows the lowest efficiency of 40.3%. The P_{max} and the ΔP ($P_{max}-P_r$) increase with increasing applied electric field. Thus, to increase the storage of BZT and Mg^{2+} doped BZT, it is important to have a notable difference between the remanent polarisation and maximum polarisation [20]. Even though the BMZT composition exhibits a higher dielectric constant and P_{max} , its relatively large P_r and broader hysteresis loop result in significant energy loss, thereby limiting its efficiency. In contrast, BMZT0.1, despite showing a comparatively lower P_{max} , possesses a much smaller P_r and a slim hysteresis loop. This leads

to a larger difference between $P_{\max}$ and P_r , enhancing the recoverable energy density and significantly reducing hysteresis loss.

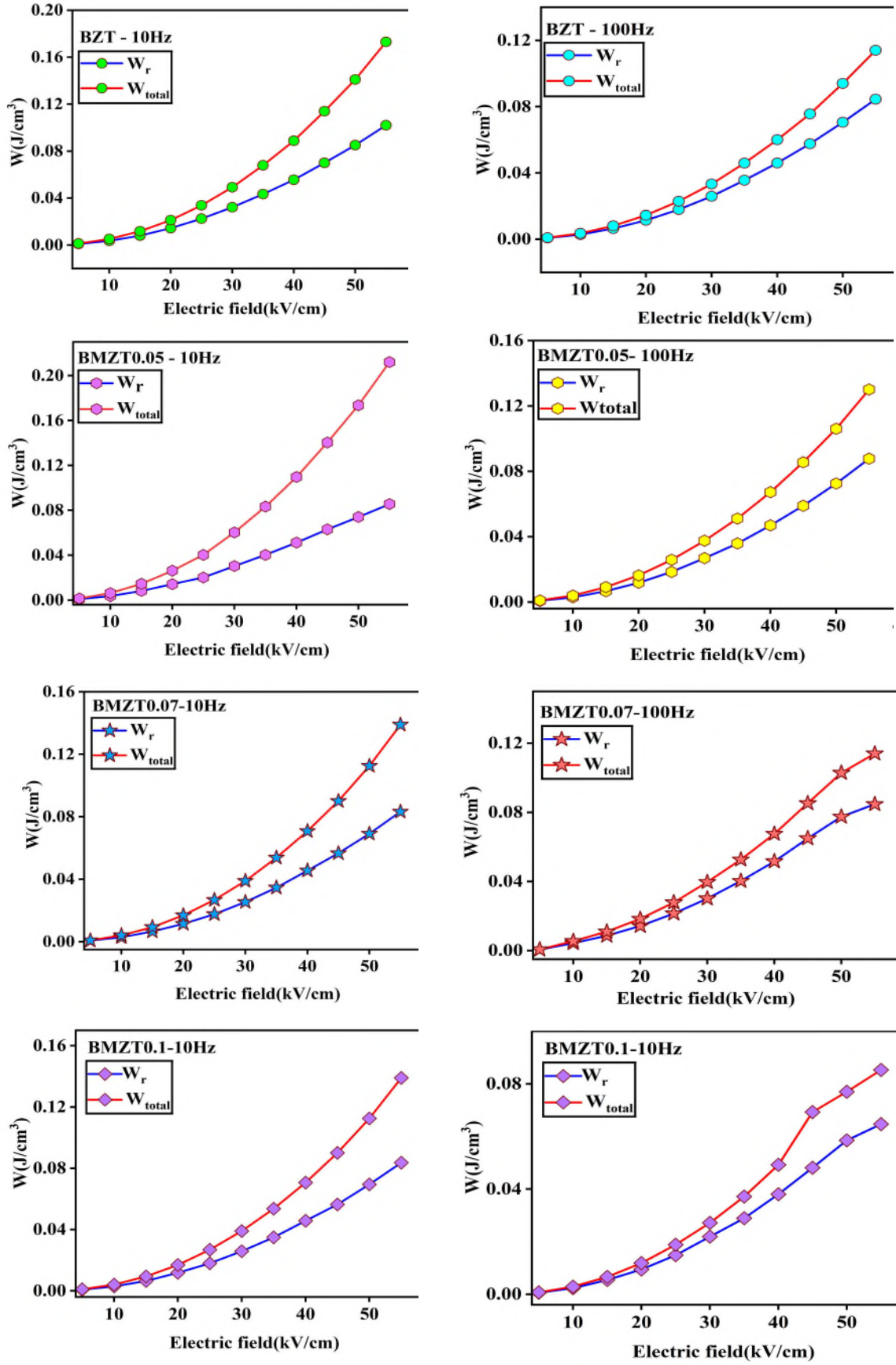


Fig. 18. Variation of W_{total} & W_r of BZT samples with electric field (5–55 kV/cm)

As a result, BMZT0.1 exhibits superior energy storage efficiency, demonstrating that minimised remanent polarisation and improved polarisation reversibility are more critical than high polarisation magnitude for achieving efficient energy storage performance. Thus, optimising the balance between polarisation magnitude and hysteresis loss is essential for high-performance dielectric energy storage materials.

Moreover, all samples exhibited higher energy storage efficiency at lower applied electric fields compared to higher fields, as the polarisation response is nearly linear with minimal hysteresis. At higher fields, increased domain switching and remanent polarisation widen the P-E loops, causing greater energy loss and reduced efficiency. Increasing Mg content further enhanced the storage efficiency, reflecting the electric field and frequency-dependent behaviour of the BZT ceramics. This makes them promising candidates for low-field energy storage applications. The energy storage efficiency ($\eta\%$) is compared with the energy storage density (W_r , J/cm^3) of the samples measured at an applied electric field of 5 and 55 kV/cm, showing its field dependency. From the Fig. 19, it is very clear that at different frequencies and lower values of energy storage density have yielded maximum storage capacity. This increasing behaviour could be related to the breakdown of long-range ferroelectric ordering [26].

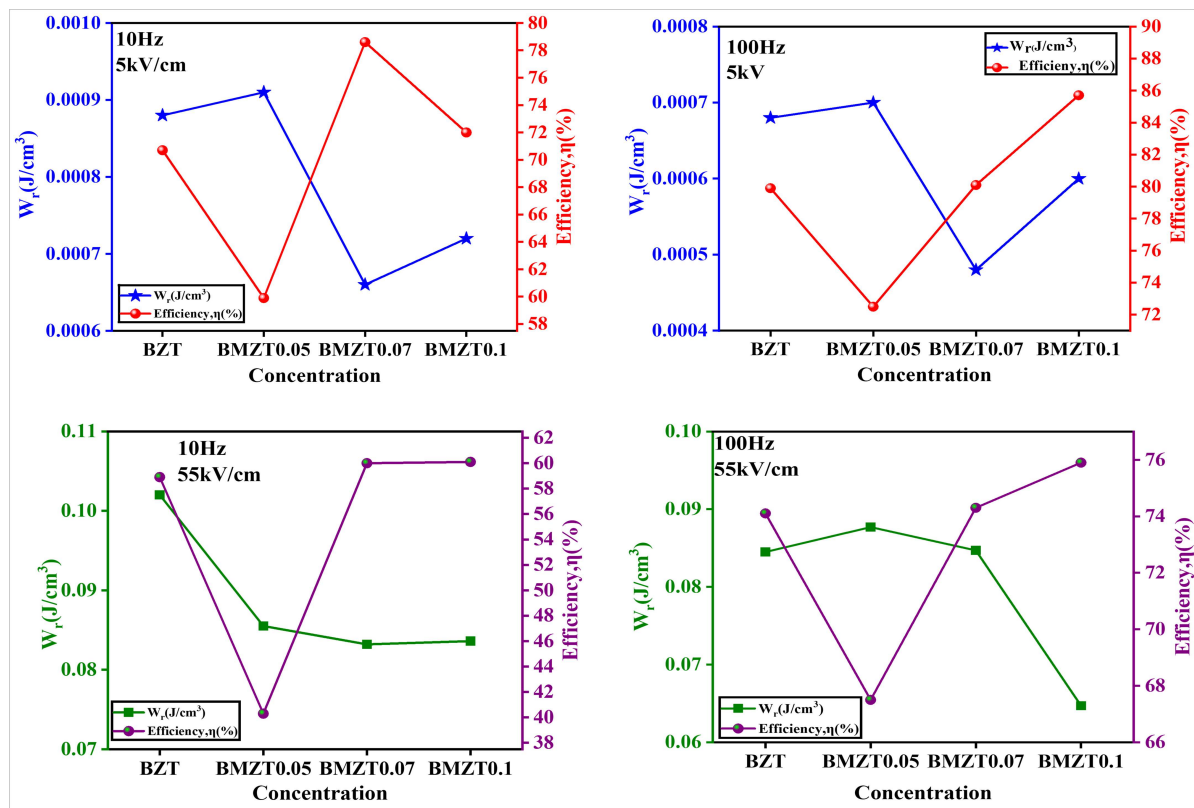


Fig. 19. Variation of W_r and η (%) with Concentration (X) at 5kV/cm and 55kV/cm

These findings demonstrate that BMZT0.1 can deliver an efficiency of 85.1% at a very low applied electric field of only 5kV/cm, underscoring its potential for low voltage applications. Further research will be conducted on this material to enhance its storage efficiency.

Hence, for real-life uses, Mg-doped BZT stands as an excellent lead-free ferroelectric ceramic for energy storage applications. The calculated efficiency (%) of the samples at 10Hz and 100Hz under an applied electric field ranging from 5kV/cm to 55kV/cm in this work is shown in Fig. 20. Such efficient energy storage behaviour at comparatively low operating fields suggests that Mg substitution effectively enhances polarisation reversibility in BZT ceramics, making them attractive for practical low-voltage energy-storage devices.

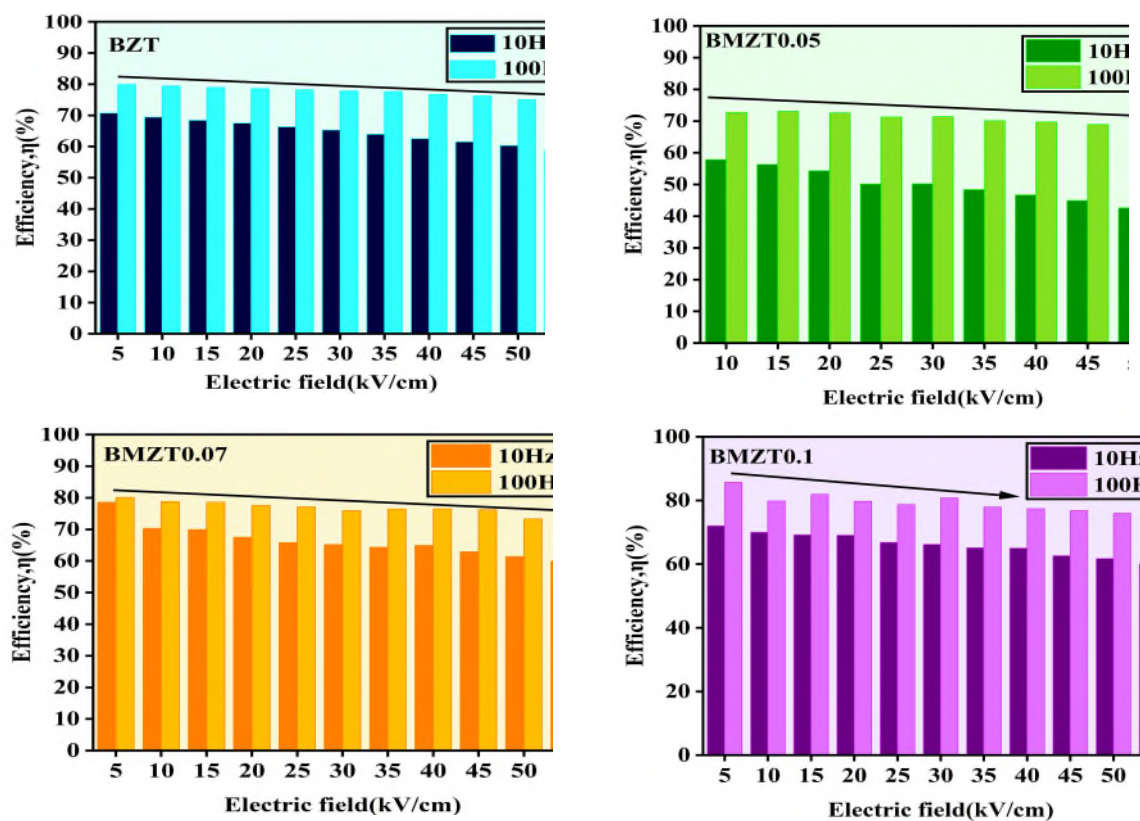


Fig. 20. Calculated $\eta\%$ of the samples at 10Hz and 100Hz for varying applied fields

4. CONCLUSION

A-site Mg^{2+} substitution in $\text{BaZr}_{0.1}\text{Ti}_{0.9}\text{O}_3$ ceramics, synthesised via a citrate–nitrate auto-combustion route, is demonstrated as an effective strategy to tailor structural, dielectric, ferroelectric, and energy-storage properties. Rietveld refinement confirms phase-pure tetragonal symmetry ($P4mm$) across all compositions, with systematic lattice contraction and enhanced crystallinity indicating successful Mg^{2+} incorporation at Ba^{2+} sites. Williamson-Hall

analysis reveals increasing tensile lattice strain with dopant concentration, while tolerance factor values (1.03-1.06) confirm the stability of the perovskite framework. HR-SEM shows a gradual reduction in grain size with increasing Mg content, attributed to inhibited grain boundary mobility associated with defect formation. Dielectric measurements identify BMZT0.05 as the optimal composition, exhibiting the highest permittivity ($\epsilon_r = 5069.49$) and lowest loss ($\delta = 0.019$) due to a favourable balance between interfacial polarisation and domain wall mobility. At higher Mg concentrations, suppressed domain dynamics and increased lattice disorder reduce dielectric response. Ferroelectric analysis reveals a transition from well-saturated to slimmer P-E loops with increasing Mg content, reflecting reduced remanent polarisation and enhanced reversibility. Consequently, BMZT0.10 delivers the highest energy-storage efficiency ($\approx 85.6\%$ at 5 kV/cm), driven by a large ΔP and minimal hysteresis loss, despite its comparatively lower polarisation magnitude. These results establish that energy-storage performance is governed primarily by polarisation reversibility and reduced hysteresis loss rather than high polarisation alone. The present study highlights Mg-modified BZT ceramics as promising lead-free candidates for low-field dielectric energy storage applications, offering a viable pathway for the design of high-efficiency capacitive materials.

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Data availability

On request, data would be made available.

Competing Interests

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Author Contributions

Anitha G: Writing - original draft, Writing - review & editing, Software, Methodology, Investigation, Formal analysis. Pavithra G: Writing - review & editing, Methodology, Formal analysis. Geetha D: Writing – review & editing, Validation, Supervision, Investigation, Formal analysis, Conceptualisation. Giridharan N V: Software, Resources, Formal analysis.

