Effect of mono-dopants (Mg$^{2+}$) and co-dopants (Mg$^{2+}$, Zr$^{4+}$) on the dielectric, ferroelectric and optical properties of BaTiO$_3$ ceramics

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Abstract

In this work, BaTiO$_3$, Ba(Mg$_{0.01}$Ti$_{0.99}$)O$_3$, Ba(Mg$_{0.015}$Ti$_{0.985}$)O$_3$, Ba(Mg$_{0.02}$Ti$_{0.98}$)O$_3$ and Ba(Mg$_{0.015}$Zr$_{0.15}$Ti$_{0.84}$)O$_3$ ceramics have been prepared through conventional solid-state route to investigate the effects of Mg$^{2+}$ and Zr$^{4+}$ dopants as mono-substitution (only Mg$^{2+}$) and co-substitution (Mg$^{2+}$ and Zr$^{4+}$) of B-site on the structural, electrical and optical properties of BaTiO$_3$ ceramics. Exhibiting perovskite structure, Ba(Mg$_{x}$Ti$_{1-x}$)O$_3$ ceramics revealed a decrement pattern of tetragonality with the increment of the concentration of MgO which was confirmed through Rietveld analysis.

Morphological analysis of the sintered samples by scanning electron microscope showed a grain growth retardation phenomenon with Mg$^{2+}$ addition. Releasing from this retardation process, Ba(Mg$_{0.015}$Zr$_{0.15}$Ti$_{0.84}$)O$_3$ showed a maximum dielectric constant of $\sim$1269.94 due to the enhanced domain wall motion and the confinement within the solubility limit of Mg$^{2+}$. The ferroelectric characteristic of Ba(Mg$_{0.015}$Ti$_{0.985}$)O$_3$ was sluggish due to the effects of grain size and its boundary. The optical band gap for BaTiO$_3$ was found to be decreased from 3.55 eV to 3.06 eV with the addition of Mg$^{2+}$ content but for Ba(Mg$_{0.015}$Zr$_{0.15}$Ti$_{0.84}$)O$_3$, the value increased due to the Burstein-Moss effect. Again the FTIR analysis proved that no impurity phases were formed during the doping phenomenon, but in Ba(Mg$_{0.015}$Zr$_{0.15}$Ti$_{0.84}$)O$_3$ ceramics, a significant reduction of Ti-O bond strength was observed. However, BaTiO$_3$, Ba(Mg$_{0.01}$Ti$_{0.99}$)O$_3$, Ba(Mg$_{0.015}$Ti$_{0.985}$)O$_3$ and Ba(Mg$_{0.02}$Ti$_{0.98}$)O$_3$ ceramics had manifested P-E loop having lower remanent polarization and coercive field compared to Ba(Mg$_{0.015}$Zr$_{0.15}$Ti$_{0.84}$)O$_3$ ceramics with moderate electrical and optical properties. So, co-doping with Mg$^{2+}$ and Zr$^{4+}$ evidenced a favorable accession for the increment of the properties of BaTiO$_3$ ceramics.

1. Introduction

Demonstration of a perovskite structure with relaxor characteristics, Barium Titanate (BaTiO$_3$) (BT) is nominated as a plausible dielectric and ferroelectric material which exhibits environmental friendliness as compared with numerous widely recognized lead (Pb)-based electroceramics, i.e. Pb(Zr,Ti)O$_3$ (PZT), Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$ (PMN), Pb(Zn$_{1/3}$Nb$_{2/3}$)$_3$O$_3$ (PZN), Pb$_2$(Zr$_{1/2}$Ti$_{1/2}$)$_3$O$_7$ (PLZT), etc [1]. As BaTiO$_3$ retains some spanning prominences due to high electrochemical coupling factor, high dielectric constant and low loss factor, it is thoroughly exploited to yield several electronic components such as Multilayer Ceramic Capacitors (MLCCs), Micro-Electro-Mechanical Systems (MEMs), Dynamic Random Access Memories (DRAM), PTC Thermistors, Piezoelectric Transducers, Pyroelectric Sensors, Phase Shifters, Tunable Filters and a variety of electro-optic devices [2].

Just after the first advancement of MLCCs, Ag-Pd was used as an internal electrode [3]. However, a few years later, their usages were minimized due to some costing related issues. Afterward, the Ni electrode was thought to be used as a replacement of the previous electrode [4]. But, during the propagation of Ni electrode into MLCCs through the sintering mode under a partial pressure of oxygen gas ($P_O > 10^{-10}$ MPa), reduction of BaTiO$_3$ and...
evolution of oxygen vacancies with the n-type carries were resulted in accordance with the following reaction [5]:

$$\text{BaTiO}_3 \rightarrow \text{BaTiO}_3 - \delta + \frac{\delta}{2} \text{O}_2 + \delta V_O + 2\delta e'$$

(1)

Where, $V'_o$ prevails an oxygen vacancy into BaTiO$_3$ lattice as derived by Kröger Vink notation [6].

So in order to prevent the afore-mentioned unexpected situation, the structural compositions could be manipulated through the addition of acceptor additives, i.e. Mg$^{2+}$, Al$^{3+}$, Mn$^{3+}$, Fe$^{3+}$ and Co$^{2+}$ in a radical range of 0.54 Å to 0.83 Å [4]. Amongst the acceptor elements, MgO is considered as the most efficient additive for attaining nondeductible compositions in MLCCs with Ni electrodes [3]. Several research works were already performed to dig up the effects of MgO addition on the microstructural and the dielectric properties of BaTiO$_3$ ceramics [7, 8]. Whither, S H Yoon observed a special feature that the accession of Mg$^{2+}$ dominates the rate of grain growth and simultaneously reduces the grain size of BT ceramics [9].

Apart from that, among the doped BaTiO$_3$ systems, Ba(Zr$_{0.01}$Ti$_{0.99}$)O$_3$ ceramics have recently received attention due to their high strain level and piezoelectric effect in both single crystals and polycrystalline ceramics [10]. From the research of Zhi Yu, it is cleared that a distinct phase transition is triggered with Zr enrichment, whereas a merged broad peak corresponds to a three-phase transition [11]. Again, as the replacement of titanium with zirconium takes place, the transition of the polymorphous phase is reconfigured to higher temperatures and also arises the degeneration of the Curie temperature [12]. Besides, regarding higher doping levels (more than 10 mol%), the commencement of the relaxor behavior is obtained which is broadly investigated by C Ciomaga et al [1]. Whereas, Jean Ravez claimed a ferroelectric-relaxor behavior at $x > 0.25$ [13].

However, following the previous researches, we tried to perform further exploration on BT ceramics by adopting variable Mg component (0 mol%, 1 mol%, 1.5 mol%, and 2 mol%) as mono substitution dopants and 15 mol% Zr with 1 mol% Mg as co-dopants, where co-doping (Mg$^{2+}$ + Zr$^{4+}$) supposed to be a new approach which perpetuates the dielectric and ferroelectric behavior of the corresponding ceramics. Moreover, the results were analyzed in terms of crystal anisotropy correlated with the impression of grain size.

2. Methodology

BaTiO$_3$ (BT), BaMg$_{0.01}$Ti$_{0.99}$O$_3$ (BMT1), BaMg$_{0.015}$Ti$_{0.985}$O$_3$ (BMT2), BaMg$_{0.02}$Ti$_{0.98}$O$_3$ (BMT3) and BaMg$_{0.02}$Zr$_{0.025}$O$_{3}$ (BMZT1) solid solutions were prepared via conventional solid-state reaction scheme. Awfully sterling raw materials including BaCO$_3$ (purity > 99%, Merck Specialties, India), MgO (purity > 99%, Merck Specialties, India), ZrO$_2$ (purity > 99%, SRL, India) and TiO$_2$ (purity > 99%, Merck Specialties, India) were used with appropriate stoichiometric ratios. The weighed powders were ball-milled using ethanol (purity > 99%, Merck, Germany) as milling media with yttria-stabilized alumina balls for 20 h. After milling, the slurry was dried in an oven at 100 °C for 2 h. Followed by the incineration at 900 °C for 24 h, the incinerated powder was re-ground, compounded with a binder (2 wt% polyvinyl alcohol) and compacted into disk pellets under an axial pressure of 2.5 tons. The prepared pellets were then sintered at 1250 °C for 4 h. X-ray diffraction (XRD) measurement was carried out at room temperature for phase detection using 40 kV-40 mA (scanning step of 0.01° and counting time of 1 s per step) and Cu-K$_\alpha$ radiation of wavelength $\lambda = 1.54060$ Å and $\theta_{02} = 1.54439$ Å (Panalytical Empyrean, Netherlands) in the range of 10°–80°. Structural refinement was redacted using a standard refinement program ‘Full Prof’. Scanning Electron Microscope (SEM) (JEOL JSM-6510, Netherlands) was devoted to observing the morphologies of the swatches. The average grain size was explored by the linear intercept method and the grain size distribution was attained via Imagej and OriginPro software. Dielectric measurements were effectuated at 500 mV over the frequency range of 100 Hz to 3.17 MHz through Impedance Analyzer (Wayne Kerr 6500B series, UK). Ferroelectric polarization-electric field (P-E) hysteresis loop was obtained using Multifireroic Tester (Radiant Tech., Inc., USA) retaining the reliability on voltage (200 V-1 kV at 1 Hz). The optical band gap energy was assessed using UV–vis spectroscopy (SHIMADZU UV/Vis-1650 PC, Japan) over the range of 200–800 nm. Fourier Transform Infrared spectroscopic measurements were accomplished by using the FTIR spectrometer (JASCO FTIR 6100, Japan) in the wavenumber range of 400–4000 cm$^{-1}$. 

3. Results and discussions

3.1. XRD analysis

Room temperature (RT) XRD patterns of BT, BMT1, BMT2, BMT3 and BMZT1 ceramics sintered at 1250 °C is shown in figure 1 (a). The identified characteristic peaks for BT, BMT1, BMT2, BMT3 and BMZT1 ceramics with high diffraction intensity and sharpness were discovered to be at crystal faces of (100), (110), (111), (002), (200), (210), (211), (220), (221), (301), and (311). All the compositions exhibited a pure perovskite structure without
any trace of impurity phase, indicating that Mg$^{2+}$ and Zr$^{4+}$ have completely incorporated into BT lattices to form complete solid solutions and the reaction for Mg$^{2+}$ as follows [14]:

$$\text{BaO} + \text{MgO} \rightarrow \text{Ba}_{\text{Ba}} + \text{Mg}_{\text{Ti}}'' + 2\text{O}_2 + V''_O$$

(2)

$$\text{Mg}_{\text{Ti}}'' + V''_O \rightarrow (\text{Mg}_{\text{Ti}}'' - \text{O}_2)$$

(3)

Figure 1(b) shows the diffraction spectra attained from the sluggish scanning wreath in the 2$\theta$ range of 44°–46°. The emergence of the splitting of (002) peak of doped BT ceramics confirmed the tetragonal phase. The replacement of Ti$^{4+}$ (0.605 Å, 6 coordinate) with Mg$^{2+}$ (0.720 Å, 6 coordinate) and Zr$^{4+}$ (0.720 Å, 6 coordinate) demonstrated the shifting of (002) peak to lower 2$\theta$ backing the reason of the higher ionic radius of the dopants than that of the replaced ions [15].

Moreover, incorporation of Zr$^{4+}$ into BaTiO$_3$ ceramics usually follows three mechanisms to attain structural stability as revealed through the leading equations [16, 17]:

Consideration for network modifier:

$$[\text{BaO}_{12}']^x + [\text{BaO}_{11} \cdot \text{V}_0^x] \rightarrow [\text{BaO}_{12}']' + [\text{BaO}_{11} \cdot \text{V}_0^x]$$

(4)

$$[\text{BaO}_{12}']^x + [\text{BaO}_{11} \cdot \text{V}_0^x] \rightarrow [\text{BaO}_{12}']' + [\text{BaO}_{11} \cdot \text{V}_0^x]$$

(5)

$$[\text{BaO}_{11} \cdot \text{V}_0^x] + \frac{1}{2}\text{O}_2 \rightarrow [\text{BaO}_{12}]$$

(6)

Consideration for network formers:

$$[\text{TiO}_3]^x + [\text{TiO}_5 \cdot \text{V}_0^x] \rightarrow [\text{TiO}_3]' + [\text{TiO}_5 \cdot \text{V}_0^x]$$

(7)

$$[\text{TiO}_3]^x + [\text{TiO}_5 \cdot \text{V}_0^x] \rightarrow [\text{TiO}_3]' + [\text{TiO}_5 \cdot \text{V}_0^x]$$

(8)

$$[\text{TiO}_3\cdot \text{V}_0^x] + \frac{1}{2}\text{O}_2 \rightarrow [\text{TiO}_4]$$

(9)

$$[\text{ZrO}_2]^x + [\text{ZrO}_3 \cdot \text{V}_0^x] \rightarrow [\text{ZrO}_2]' + [\text{ZrO}_3 \cdot \text{V}_0^x]$$

(10)

$$[\text{ZrO}_2]^x + [\text{ZrO}_3 \cdot \text{V}_0^x] \rightarrow [\text{ZrO}_2]' + [\text{ZrO}_3 \cdot \text{V}_0^x]$$

(11)

$$[\text{ZrO}_2\cdot \text{V}_0^x] + \frac{1}{2}\text{O}_2 \rightarrow [\text{ZrO}_3]$$

(12)

The structure reveals that clusters of [BaO$_{12}$, V$_0^x$], [TiO$_3$, V$_0^x$] and [ZrO$_2$, V$_0^x$] belongs to benefactor postulants, whereas [BaO$_{12}$], [ TiO$_3$, V$_0^x$] are acknowledged with promising postulants but [BaO$_{12}$, V$_0^x$], [TiO$_3$, V$_0^x$] and [ZrO$_2$, V$_0^x$] are featuring both characteristics equally. However, the stabilization of defect mechanisms is prompted by the presence of these clusters. Cavalcante and Gurgel believed that the vacancies could be eliminated by the loss of energy of electrons residing into the conduction band and the re-acqurement of the hole in the valence band [16].

Figure 2 shows the final outputs of the Rietveld refinement programs, confirming that the configurations belong to tetragonal symmetry with space group $\text{p4mm}$ which were carried out using ‘FullProf’ and ‘Maud: Materials Analysis Using Diffraction’ software by adopting Wyckoff’s series [18]. The refined lattice parameters and reliability factors (R factors) derived from Rietveld analysis are enlisted in table 1. In consideration of co-doping, an expanded cell volume results in due to the replacement of lower radii Ti$^{4+}$ (0.605 Å) with higher...
radii Zr$^{4+}$ (0.720 Å) and Mg$^{2+}$ (0.605 Å) (table 1) [19]. However, a minor variation in tetragonality takes place as the axial ratio (c/a) alters in the compositional sequence [20].

Debye–Scherrer formula [21] was used to measure the crystallite size (table 2) for the most vivid peak (110). The formula can be expressed as:

$$D = \frac{k\lambda}{\beta \cos \theta}$$

(13)

Hither, $\beta$ is the Full Width at Half Maxima, $k$ being a dimensionless shape factor having a constant value of 0.94 associated with the crystal symmetry, while $\lambda$ and $\theta$ are the wavelengths of Cu K$_\alpha$ radiation (1.54 Å) and Bragg angle respectively.

Through the x-ray diffraction analysis, the degree of crystallinity ($x_c$) can be usually derived by two-phase model according to the following formulae:

$$x_c = \frac{I_{\text{crystalline}}}{I_{\text{crystalline}} + I_{\text{amorphous}}} \times 100$$

(14)
Structural properties of BT, BMT1, BMT2, BMT3, and BMZT1 ceramics.

### Table 1.

| Composition | Space group | Cell parameter | Axial ratio \((c/a)\) | Cell volume \((\text{Å}^3)\) | R factors (%) | GoF | Bragg R factor | RF factors |
|-------------|-------------|----------------|----------------------|-----------------------------|---------------|-----|----------------|------------|
| BT          | P 4 mm     | \(a = 3.997141\) | 1.0037               | 64.328                      | Rp = 6.53     | 1.4 | 2.78           | 1.52       |
|             |             | \(b = 3.997141\) |                      |                             | Rwp = 8.75    |     |                |            |
|             |             | \(c = 4.012226\) |                      |                             | Rexp = 6.33   |     |                |            |
| BMT1        | P 4 mm     | \(a = 4.002433\) | 1.0041               | 64.335                      | Rp = 5.91     | 1.2 | 1.55           | 1.44       |
|             |             | \(b = 4.002433\) |                      |                             | Rwp = 7.84    |     |                |            |
|             |             | \(c = 4.019126\) |                      |                             | Rexp = 6.29   |     |                |            |
| BMT2        | P 4 mm     | \(a = 4.001557\) | 1.0040               | 64.337                      | Rp = 5.92     | 1.2 | 1.56           | 1.58       |
|             |             | \(b = 4.001557\) |                      |                             | Rwp = 7.84    |     |                |            |
|             |             | \(c = 4.017944\) |                      |                             | Rexp = 6.29   |     |                |            |
| BMT3        | P 4 mm     | \(a = 4.001638\) | 1.0039               | 64.368                      | Rp = 5.86     | 1.2 | 2.74           | 2.18       |
|             |             | \(b = 4.001638\) |                      |                             | Rwp = 7.80    |     |                |            |
|             |             | \(c = 4.017632\) |                      |                             | Rexp = 6.45   |     |                |            |
| BMZT1       | P 4 mm     | \(a = 3.997768\) | 1.0043               | 64.935                      | Rp = 6.24     | 1.3 | 1.80           | 1.54       |
|             |             | \(b = 3.997768\) |                      |                             | Rwp = 8.09    |     |                |            |
|             |             | \(c = 4.013503\) |                      |                             | Rexp = 6.03   |     |                |            |

### Table 2.

| Composition | Crystallite size, \(\tau\) (nm) | Tolerance factor, \(t\) | Degree of crystallinity, \(x_c\) (%) | Lattice strain, \(\varepsilon\) (%) | Average grain size (nm) |
|-------------|---------------------------------|--------------------------|--------------------------------------|-------------------------------------|-------------------------|
| BT          | 35.98                           | 1.061542                 | 66.52                                | 0.0016                              | 809.23                  |
| BMT1        | 38.93                           | 1.333495                 | 68.86                                | 0.0019                              | 811.37                  |
| BMT2        | 39.26                           | 1.333015                 | 69.81                                | 0.0020                              | 717.27                  |
| BMT3        | 39.36                           | 1.332535                 | 67.18                                | 0.0022                              | 645.93                  |
| BMZT1       | 24.45                           | 1.319238                 | 63.69                                | 0.0033                              | 873.72                  |

Where, \(I_{\text{crystalline}}\) and \(I_{\text{amorphous}}\) belong to the area of the crystalline and the amorphous peaks respectively. However, BMZT1 exhibits lower \(x_c\) as compared to BT and BMT ceramics which are enlisted into table 2.

The structural transformation could be evaluated by using RD Shannon’s ionic radii table [22] and Goldschmidt’s rule [23]. Following the formula, the tolerance factor \((t)\) could be computed by,

\[
t = \frac{r_A + r_X}{\sqrt{2(r_B + r_X)}}
\]

Where, \(r_A\), \(r_B\), and \(r_X\) are the ionic radii of A-site \([\text{CN} = 12]\), B-site \([\text{CN} = 6]\) and O [\text{CN} = 6] ion correspondingly.

The decrement pattern of \(t\) (table 2) implies that BaTiO\(_3\) doped with MgO and ZrO\(_2\) is attaining structural transformation as well as more stability in the perovskite structure [24]. The value for BMT varies between 1.333495 to 1.332535 inducing the reduction of the tetragonal phase and approaching a cubic phase which will be again evidenced as the discretion of \(c/a\) ratio. Besides, the obtained values of the tolerance factor \((t > 1)\) reflect the presence of the ferroelectric phase at room temperature [25].

The resulted lattice strain arisen in the sample was obtained using Williamson–Hall equation [26],

\[
\frac{\beta \cos \theta}{\lambda} = \frac{1}{D} + \frac{\varepsilon \sin \theta}{\lambda}
\]

Where \(D\) corresponds to crystallite size, \(\lambda\) is the wavelength of Cu-K\(_\alpha\) radiation, \(\beta\) being the Full Width at Half Maximum (FWHM) of diffraction peak, \(\theta\) represents the peak position and \(\varepsilon\) stands for the microstrain present in the sample. The lattice strain values are obtained from the slope of the plot drawn between \(\frac{\beta \cos \theta}{\lambda}\) and \(\frac{\sin \theta}{\lambda}\), which are curtailed in table 2. The presence of tensile strain is indicated by the positive slope value (figure 3) [27]. An enhancement of the tensile strain is emerged with the accession of Mg\(^{2+}\) and Zr\(^{4+}\) due to the lattice alteration sourced from the substitution of Ti\(^{4+}\) ions by larger Mg\(^{2+}\) and Zr\(^{4+}\) ions.

### 3.2. Structural analysis

Figures 4(a)–(e) displays the SEM micrographs of the empirical formulas of BaTiO\(_3\) ceramics doped with Mg and Zr. The average grain size was enumerated by using the linear intersection method [28]. At a lower proportion of MgO (1.0 mol%), inhabiting in the solubility range of MgO in BT, the microstructure shows aesthetic conformation, with an average grain size of 811.37 nm [4]. But a significant reduction in grain size is observed when the MgO content is above 1.0 mol% (table 2) [14]. This result reveals that the grain growth of BT
ceramics is suppressed by Mg which designates it as the grain growth inhibitor \[29\]. It is due to the fact that the incorporation of Mg\(^{2+}\) ions persuades the formation of oxygen vacancy \((V_\text{O})\). Simultaneously, the generated \(V_\text{O}\) introduces a motion into the crystal lattices which attempts to consume some energy. However, the consumption of the energy is benefited as the segregation of the solutes \((\text{Mg}^{2+})\) is manifested in the grain boundary. Positioning themselves into the grain boundary, Mg\(^{2+}\) ions counteract the motion of the boundary resulting the suppression of the grain growth. Besides, in consideration of Zr embodiment, a symbolical enhancement in the grain size is observed accompanied by more effectiveness in the densification mechanisms as shown in figure 4(d) \[30\]. This can be caused by the accelerated matter transport mechanism which is generally materialized at the interim locus of the grains during the densification course \[17\]. A narrative scatter diagram associated with the distribution contour of the grain size distribution (appraised by exploiting ImageJ software and OriginPro 2018 software) are stereotyped in figures 4(a)–(d) \[31\].

Furthermore, from the quantitative Energy-dispersive x-ray spectroscopy (EDS), the weight percentage of the elements in the samples were computed (table 3). The curves as stereotyped in the inset of figure 5 reveal the elemental provinces of the perovskite phases of un-doped and doped BT ceramics. However, the tabulated values ensure the absence of impure phases in the experimental specimens and also dispel the burden of losing any ingredients during its formulation \[32, 33\].

3.3. Dielectric properties

Figure 6(a) shows the frequency dependence of dielectric constant \((\kappa)\) of the experimental ceramics in the frequency range of 100 Hz to 3.17 MHz at room temperature. All the samples exhibited a high dielectric constant at the starting frequency which is abstracted into table 4. This phenomenon results from the ability of readjustment of the dipolar complex \((\text{Mg}^{2+} - V_\text{O})\) and the dynamism of the oxygen vacancies \((V_\text{O})\) allowing rotation around the centrum of impurity \((\text{Mg}^{2+})\) for retaining the drift of poling actions \[34\]. But proceeding at high frequencies, the dipoles show incapability to provide sufficient response to the imposed field resulting in degradable dielectric constant. The observed dielectric behavior at the low frequencies due to the oxygen vacancies can be coordinated with the Maxwell-Wagner interfacial polarization model with Koop’s phenomenological theory. According to the hypothesis, the dielectric structure comprises two layers, i.e. layers of immensely conducting grains and layers of flimsy conducting grain boundaries, where the grain boundaries become more enterprise than the grains at a lower frequency and only the grains withhold their distinctiveness at the higher frequencies \[35\].

Besides, the acquired data confirms a strong relationship between \(\kappa\) and dopant \%. Enhanced dielectricity is observed at 1 mol\% MgO, while further increment of MgO demonstrates a declined \(\kappa\) value \[14\]. It is backed by the dominance of grain size and grain boundary permittivity. Generally, Grain boundary comprises space charges which exclude polarization charges from the grain surface and creates a depletion layer on it. However, the layer introduces a depolarization field which lowers the polarization value simultaneously. Whereas, in consideration of the ZrO\(_2\) accession into BT, a maximal value of the relative permittivity is demonstrated by the emergence of the largest grain size as well as the dominance of maximum tetragonality \[36\].
Figure 6(b) interprets the dielectric loss factor ($\tan\delta$) as a function of frequency and the $\tan\delta$ values for BMT and BMZT ceramics at 100 Hz are tabulated into Table 4. Actually, there involves two mechanisms contributing to the loss factor, i.e. resistive loss and relaxation loss. For the consideration of resistive loss, a certain quantity of energy is devoured by the whirling charge bearers, while for later one, the contribution results from the relaxation of electric doublets. However, the dependence of the dielectric loss on frequency turns into nonpartisan at the higher frequency range [37].
3.4. Ferroelectric property

Figure 7 represents the characteristic polarization versus electric field (P-E) loops of BT, BMT1, BMT2, BMT3, and BMZT1 ceramics. The arisen of interruption at 0 V coupling with the generation of an unsaturated hysteresis loop express the appearance of leakage current into the samples. Actually, P-E loops describe a total polarization value comprising of remanent and non-remanent polarization. The remanent polarization is concerned with switchable dipoles which retain their polarization in the removal of the applied field. While for the non-remanent polarization, it is mainly influenced by the dielectric linear capacitance and its loss factor accompanied by the non-retainable polarized dipoles. The obtained remanent polarization ($P_r$) and the coercive field ($E_c$) are enlisted in table 4. However, the maximal value of remanent polarization ($P_r$) of 0.21 μC/cm² with a field of maximum coercive value ($E_c$) of 2.10 kV/cm were found for BMZT solid solution. It is caused by the presence of Zr⁴⁺ which influences to generate the space charges and in the meantime preserve the domain configuration resulting in the higher poling efficiency as well as enhanced remanent polarization value. Moreover, the graphs (figures 7(a)–(c)) for BMT exhibit a decreased pattern of $P_r$ with the increment of the mol% of Mg. Actually, reduction of poling proficiency can be usually caused by the effects of grain size, grain boundary, internal stress, depolarizing field and also the mutual interaction between the domain walls and their clamping characteristics. Again, the larger area of the grain boundaries results in enhanced electrical insulation associated with a haphazard arrangement of space charges that interrupts and lowers the polarizability.
3.5. Optical property

The UV-Visible spectra of BT, BMT1, BMT2, BMT3, and BMZT1 ceramics are interpreted in figure 8(a). The optical band gap energy was computed via allowed direct inter-band transition between valence and conduction bands by adopting Tauc’s Law [38]:

\[(\alpha h\nu)^2 = A(\nu^2 - E_g)\]

Where, \(A\) is a constant, \(\alpha\) being the absorption coefficient, \(h\nu\) stands for the photon energy and \(E_g\) represents the optical band gap energy. \(E_g\) can be attained from the \((\alpha h\nu)^2\) versus \(h\nu\) plot and the extrapolation of the graphical segment of the trajectory to \((\alpha h\nu)^2 = 0\) as shown in the inset of figure 8(b). With proceeding from BMT1 to BMT3, the band gap significantly reduces from 3.18 to 3.06 eV while for BT, the value is 3.55 eV (table 4).

Generally, the obtained \(E_g\) values are strongly dominated by the appearance of ordered or disordered patterns into the lattice structure. The disordered arrangement is mainly caused due to the presence of asymmetry into the O-Ti-O bond or due to the misrepresentation of the TiO\(_6\) clusters. Again, another contributing factor is the

![Figure 6](image)

(a) Dielectric constant (inset of (a) shows dielectric constant versus log frequency curves between 100 Hz to 1 MHz) and (b) Dielectric loss (loss tangent) as a function of log frequency of BT, BMT1, BMT2, BMT3, and BMZT1 ceramics.

| Composition | Dielectric constant (\(\kappa\)) at 200 kHz | Dielectric loss \((\tan\delta)\) | Remanent polarization \(P_r\) \((\mu C/cm^2)\) | Coercive field \(E_c\) \((kV/cm)\) | Optical band gap energy, \(E_g\) \((eV)\) |
|-------------|-------------------------------------------|-------------------------------|----------------------------------|---------------------|-------------------------------|
| BT          | 438.48                                    | 0.06                          | 0.09                             | 1.48                | 3.55                          |
| BMT1        | 907.32                                    | 0.17                          | 0.10                             | 1.25                | 3.18                          |
| BMT2        | 858.31                                    | 0.15                          | 0.09                             | 1.45                | 3.14                          |
| BMT3        | 817.84                                    | 0.14                          | 0.07                             | 1.43                | 3.06                          |
| BMZT1       | 1269.94                                   | 0.26                          | 0.21                             | 2.10                | 3.71                          |

3.5. Optical property

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\[(\alpha h\nu)^2 = A(\nu^2 - E_g)\]  

Where, \(A\) is a constant, \(\alpha\) being the absorption coefficient, \(h\nu\) stands for the photon energy and \(E_g\) represents the optical band gap energy. \(E_g\) can be attained from the \((\alpha h\nu)^2\) versus \(h\nu\) plot and the extrapolation of the graphical segment of the trajectory to \((\alpha h\nu)^2 = 0\) as shown in the inset of figure 8(b). With proceeding from BMT1 to BMT3, the band gap significantly reduces from 3.18 to 3.06 eV while for BT, the value is 3.55 eV (table 4).

Generally, the obtained \(E_g\) values are strongly dominated by the appearance of ordered or disordered patterns into the lattice structure. The disordered arrangement is mainly caused due to the presence of asymmetry into the O-Ti-O bond or due to the misrepresentation of the TiO\(_6\) clusters. Again, another contributing factor is the
defect mechanisms into the structure [39, 40]. However, the inauguration of lattice defects into the crystal structure allows for the establishment of certain intermediate energy levels (comprising of oxygen 2p, titanium 3d, and magnesium 3p orbitals) between the valence band and the conduction band (as shown in figure 9) which reduce the band gap energy significantly. Moreover, as the amount of Mg increases, the corresponding defect mechanism enhances which triggers the shifting of $E_g$ to a lower extent for BMT ceramics.

On the other hand, in consideration of Zr$^{4+}$ addition, the $E_g$ shifts to a higher extent value (3.71 eV) as compared to BMT. Whenever these materials are heavily doped, the electrons seize themselves into the lowest

![Figure 7. Polarization versus electric field curves (P-E loop) of (a) BT, (b) BMT1, (c) BMT2, (d) BMT3 and (e) BMZT1 ceramics at RT.](image-url)
Figure 8. (a) UV-Visible spectra of BT, BMT1, BMT2, BMT3, and BMZT1 ceramics and (b) $(\alpha \ h \ \nu)^2$ versus photon energy plot for determining the corresponding band gap energy of the samples ((inset shows the extrapolation of the trajectory to $(\alpha \ h \ \nu)^2 = 0$).  

Figure 9. Band model having deep and shallow holes within the band gap.
potency level adjacent to the conduction band which is ordinarily commenced from the defect mechanisms i.e. oxygen vacancy and this phenomenon is considered as Burstein-Moss effect \[41\]. Another contributing factor known as crystallite size also affects the optical band gap energy significantly. Whereas, reduced band gap results from the cause of increment in the crystallite size of BT ceramics doped with Mg\(^{2+}\) and Zr\(^{4+}\) as derived from the XRD analysis \[42\].

Figure 10 illustrates the room temperature transmittance spectra of BT, BMT1, BMT2, BMT3, and BMZT1 ceramics. All of the samples (except BMT1) exhibit a broad absorption band at 3250 cm\(^{-1}\) due to the stretching vibration of water molecules \[43\]. However, the characteristic band at 2452 cm\(^{-1}\) is employed for the asymmetric stretching of CO\(_2\) \[44\]. Moreover, the absorption band at 1630 cm\(^{-1}\) appears due to the bending vibration of H\(_2\)O molecules \[45\]. The band at 585 cm\(^{-1}\) is caused due to the stretching vibration of TiO\(_6\) with barium, while for the bending vibration of Ti-O bond in [TiO\(_6\)]\(^{2-}\) octahedron, the band at 475 cm\(^{-1}\) has appeared. In addition, for BMT1, BMT2, BMT3 and BMZT1 ceramics, the maximum absorption occurs at the band of 578 cm\(^{-1}\), 576 cm\(^{-1}\), 571 cm\(^{-1}\), and 583 cm\(^{-1}\) respectively. It is observed that as the incorporation rate of MgO increases, the absorption band of BMT ceramics shifts to a lower extent. It is mainly caused due to the weakening of the Ti-O bond \[46\] and this weakening behavior is mainly caused by two reasons. The first one involves the replacement of Ti\(^{4+}\) ions with Mg\(^{2+}\) and Zr\(^{4+}\) ions having higher ionic radius than that of the replaced ions and the second one involves the formation of oxygen vacancies (V\(_{O}\)) for retaining the electric charge balance into the crystal lattice \[47\]. Whereas, for BMZT1, the absorption band increased due to the higher stabilization mechanism of Zr\(^{4+}\) as well as having a lower concentration of Mg\(^{2+}\).

### 4. Conclusion

In summary, BT doped with 0, 1, 1.5, 2 mol\% Mg and co-doped with 1 mol\% Mg and 15 mol\% Zr ceramics were successfully fabricated by conventional solid-state reaction method. A single perovskite tetragonal phase was found in all the ceramic specimens without the evidence of any additional phase which was simultaneously proved by XRD and FTIR analysis. An occurrence of retardation in grain growth of BMT ceramics was exhibited whenever the MgO content is >1 mol\%. The dielectric behaviors were predominantly attributed to the existence of oxygen vacancies, experiencing the extensive motion of V\(_{O}\) accompanied by the pinning phenomena derived by Mg\(_{6Ti}^{6+}\). However, due to the effect of larger grain size, BMZT1 exhibits enhanced relative permittivity value along with the appearance of higher remanent polarization as compared with other synthesized samples. However, the obtained optical band gap energy of the samples increases its probability to use in optoelectronic purposes.
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