

ROLE OF $\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ DOPING AND ANNEALING PROCESS ON MECHANICAL, AND ELECTRICAL PERFORMANCES OF $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ LEAD-FREE CERAMICS

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Abstract

Lead-free binary system of $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ - $x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ ceramics referred to $(1-x)\text{BNT}$ - $x\text{BMgT}$ ($x = 0$ - 0.15) have been studied. The optimum sintering temperature was $1,150^\circ\text{C}/4$ h, corresponding to high relative density of 98.46-99.25%. All ceramics had a single perovskite structure. When increasing BMgT, the phase was a change to pseudo-cubic. The relative density and linear shrinkage increased with BMgT, which resulted to an improvement of dielectric and mechanical. The maximum dielectric at RT and mechanical ($HV = 5.56$ GPa, $HK = 5.43$ GPa, $E = 94$ GPa and $K_{IC} = 1.61$ MPa.m^{1/2}) were obtained for the $x = 0.15$. In addition, the $x = 0.05$ had the highest of k_p (0.585) and low-field d_{33} (159 pC/N). Effects of annealing process on densification and dielectric were also studied in this work. After annealed at $1,000^\circ\text{C}$ for 24 h, the $x = 0.05$ had the optimum dielectric improvement ($\epsilon_{\text{max}} = 3,440$), and this value was 45.15% higher than that of the non-annealed sample ($\epsilon_{\text{max}} = 2,370$). The observed results suggested that added-BMgT and annealing process can enhanced mechanical, dielectric, and piezoelectric performances of BNT ceramic.

Keywords: Annealing process; Dielectric; Mechanical; Piezoelectric; Piezoelectric ceramics

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Introduction

Piezoelectric materials have been widely applied in many fields, *i.e.* sensor, brake, and sensitive materials, due to its can conversion between electrical energy and mechanical (Rödel *et al.*, 2015; Chen *et al.*, 2021; Feng *et al.*, 2022). Pb(Zr_{1-x}Ti_x)O₃ (PZT) is one of the most popular piezoelectric material for electronic applications (Jaita and Jarupoom, 2020). However, these materials contain more Pb as a classifiable toxicity (Bell and Deubzer, 2018; Duong *et al.*, 2021; Chen *et al.*, 2022; Feng *et al.*, 2022). Recently, lead-free piezoceramics have studied for new alternatives to lead-based ceramics (Takenaka *et al.*, 1991; Nguyen *et al.*, 2021; Deng and Wu, 2022; Feng *et al.*, 2022; Yang *et al.*, 2022b).

At present, the Ba_{0.5}Na_{0.5}TiO₃ or BNT has been recognized among the most important lead-free materials due to their high Curie temperature ($T_c \sim 320^\circ\text{C}$) (Zhao *et al.*, 2016; Purohit *et al.*, 2018; Hou *et al.*, 2022; Yang *et al.*, 2022a) and large remnant polarization ($P_r \sim 38 \mu\text{C}/\text{cm}^2$) at room temperature (RT) (Purohit *et al.*, 2018; Zhu *et al.*, 2020; Swain *et al.*, 2021; Kuanar *et al.*, 2022). However, it difficult to sintered, poor temperature stability, and high coercive field/electrical conductivity (Bührer, 1962; Wang *et al.*, 2022). Therefore, there are urgent needs for many researchers to improve the properties of BNT ceramic (Liu and Tan, 2016). Bismuth magnesium titanate, Bi(Mg_{0.5}Ti_{0.5})O₃ or BMgT is one of the promising future applications high-temperature antiferroelectric materials due to its octahedral tilting characteristics and its antiferroelectric-like displacement of Bi cations (Schwertfager *et al.*, 2016). It also exhibits good stable ferroelectricity (He *et al.*, 2013). Khalyavin *et al.* prepared BMgT single crystal using 6 GPa high pressure. The crystal structure of this BMgT single crystal was orthorhombic ($Pn\bar{m}$) (Khalyavin *et al.*, 2006). Furthermore, BMgT is used to modify electrical properties of the (K_{0.5}Na_{0.5})NbO₃, BaTiO₃, PbTiO₃ and electrical performances of these materials can be improved (Khalyavin *et al.*, 2006; Rai *et al.*, 2008; Sun *et al.*, 2011; Xiong *et al.*, 2011; Ansell *et al.*, 2012; He *et al.*, 2013). Influence of BMgT on electrical properties of BNT-BT has been studied by Politova *et al.* They reported that small amounts of BMgT-added leads to improvement of dielectric parameters favoring to enhancement of piezoelectric properties (Politova *et al.*, 2017). Wada *et al.* found that the addition of BMgT can improved dielectric and piezoelectric of BT ceramic. The 0.5BT-0.5BMgT ceramic exhibited relaxor-like characteristics with high T_c of 360°C while the 0.4BT-0.6BMgT

ceramic has the piezoelectric constant (d_{33}) of 60 pC/N (Wada *et al.*, 2010a; 2010b). Kumar *et al.* have been studied lead-free BMgT-BKT-BNT ceramics. The 5BMgT-40BKT-55BNT composition has large electromechanical strains under high electric fields along with small fatigue under strong electric fields (Kumar *et al.*, 2014).

As above results clearly illustrate, many authors have suggested that BMgT additive can improve electrical properties and electromechanical strains of some lead-free piezoelectric ceramics (Wada *et al.*, 2010a; 2010b; Kumar *et al.*, 2014; Politova *et al.*, 2017). Therefore, the (1-x)(Bi_{0.5}Na_{0.5})TiO₃-xBi(Mg_{0.5}Ti_{0.5})O₃ referred to (1-x)BNT-xBMgT ceramics (0 - 0.15 mol fraction) were synthesized in this research work. The role of BMgT content on physical, phase, mechanical, dielectric, and piezoelectric of BNT ceramic were investigated. Since many researches have focused on annealing process, therefore, effect of aging time and aging rate is also conducted in this research work and discuss in detail.

Experimental Details

The (1-x)(Bi_{0.5}Na_{0.5})TiO₃-xBi(Mg_{0.5}Ti_{0.5})O₃ referred to (1-x)BNT-xBMgT lead-free ceramics ($x = 0, 0.05, 0.10$, and 0.15 mol fraction) was synthesized by a solid-state reaction technique. The reagent-grade powders of Bi₂O₃, MgO, Na₂CO₃, and TiO₂ were starting materials. The mixed powder was calcined for 2 h at 900°C . The green pellets were sintered for 4 h at $1,150^\circ\text{C}$.

The density was determined using Archimedes method. The relative density and linear shrinkage was also determined. Phase evolution was determined by X-ray diffractometer. For mechanical properties, all ceramics were subjected to Vickers (HV) and Knoop (HK) hardness. Young modulus (E) and fracture toughness (K_{IC}) were calculated with method described by Marshall *et al.* (Marshall *et al.*, 1982) and Meredith *et al.* (Meredith *et al.*, 1996). For electrical properties characterization, the planar electromechanical coupling factors (k_p) was measured by impedance analyzer. The piezoelectric coefficient (d_{33}) was recorded using d_{33} -meter after 24-168 h aged ceramic. Dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) were carried out by 4284A LCR-meter. In addition, all ceramics were selected for annealing process at $1,000^\circ\text{C}$ for 24 h. After that, annealed ceramics were re-checked again for densification and dielectric properties.

Results and Discussion

Based on Table 1, the addition of BMgT caused an increase in BNT samples' relative density. High relative density of 98.46-99.25% were obtained for all ceramics after sintering at 1,150°C for 4 h. This result was relate to an increase of linear shrinkage with increasing BMgT.

XRD patterns with different BMgT contents are shown in Figure 1(a). All ceramics had a single perovskite structure with no any secondary/impurity

phases. For detail analyzing, XRD patterns with the narrow angular are presented in Figure 1(b-c). The $x = 0$ ceramic was indexed according to rhombohedral phase, which could be matched with International Centre for Diffraction Data (ICDD) number 00-036-0340 (Kantha and Pisitpipathsin, 2018; Aryal and Choudhary, 2021; Difeo *et al.*, 2021). At higher BMgT content, rhombohedral phase transformed into pseudo-cubic phase. This can be evidenced by the $(003)_R/((021)_R$ rhombohedral peaks at $2\theta = 39\text{-}40.5^\circ$ gradually

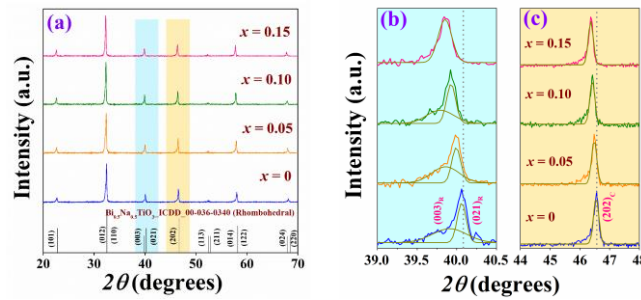


Figure 1. XRD patterns where (a) $2\theta = 20\text{-}70^\circ$ (b) $2\theta = 39.0\text{-}40.5^\circ$, and (c) $2\theta = 44\text{-}48^\circ$

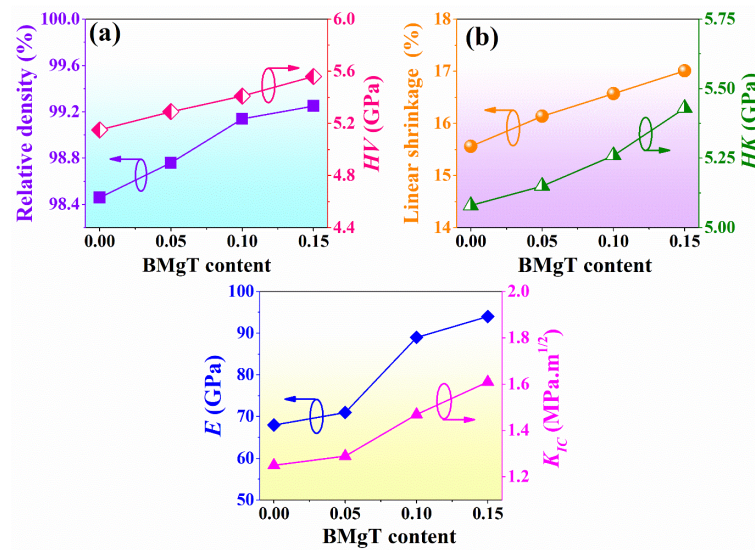


Figure 2 Plots of (a) relative density and HV as a function of BMgT content, (b) linear shrinkage and HK as a function of BMgT content, and (c) E and K_{IC} as a function of BMgT content

Table 1. Physical, phase, and mechanical properties of $(1-x)\text{BNT}-x\text{BMgT}$ ceramics

x	Relative density (%)	Linear Shrinkage (%)	FWHM of (110) (°)	HV (GPa)	HK (GPa)	E (GPa)	K_{IC} (MPa.m ^{1/2})
0	98.46	15.56	0.39	5.15	5.08	68	1.25
0.05	98.76	16.14	0.36	5.29	5.15	71	1.29
0.10	99.14	16.57	0.35	5.41	5.26	89	1.47
0.15	99.25	17.01	0.32	5.56	5.43	94	1.61

merged into a single one and also showed a single one of (202)_c pseudo-cubic peak at $2\theta = 44-48^\circ$ (Kantha and Pisitpipathsin, 2018; Difeo *et al.*, 2021). Due to differences in ionic radius of Na⁺ (1.18 Å), Bi³⁺ (1.17 Å), Ti⁴⁺ (0.605 Å), and Mg²⁺ (0.72 Å) when Mg²⁺ filled Ti⁴⁺ in the B-site position, the lattice distortion was observed. Finally, the diffraction peaks were shifted to lower 2θ angles (Wang *et al.*, 2004). The full width at half maximum (FWHM) was calculated from the (110)-type peak (Cullity, 1978). Based on Table 1, the FWHM of the added-ceramics ($x = 0.05-0.15$) was much smaller than the $x = 0$ ceramic, which suggested that all cations in ceramics were homogeneously distributed (Wada *et al.*, 2010a; 2010b).

For mechanical properties, the H_V , H_K , E , and K_{IC} were calculated with following equations (Marshall *et al.*, 1982; Meredith *et al.*, 1996; Strecker *et al.*, 2005; Domingues *et al.*, 2016; Ghorbal *et al.*, 2017):

$$H_V = \frac{1.854P}{d^2} \quad (1)$$

$$H_K = \frac{14.23P}{d^2} \quad (2)$$

$$E = \frac{\alpha H_K}{[(b/a)-(b'/a')]} \quad (3)$$

$$K_{IC} = 0.016 \left(\frac{E}{H_V} \right)^{1/2} \left(\frac{P}{c^{3/2}} \right) \quad (4)$$

where d is half-length of long diagonal (μm), P is load (N), $\alpha \sim 0.45$ is Marshall Constant, c is crack length (m), b/a is 0.14, and b'/a' is length of H_K indentation with short diagonal/length of H_K indentation with long diagonal. Based on Table 1 and Figure 2(a-b), the H_V and H_K reached the maximum values of 5.56 GPa, and 5.43 GPa, respectively for the $x = 0.15$ ceramic. The E and K_{IC} showed similar trend to that of hardness (Figure 2(c)). The mechanical properties improvement of the ceramics with higher BMgT additive was agree with the densification and linear shrinkage improvement (Jaita *et al.*, 2020). Similar observed by Kruea-In *et al.* for the BNKT/ x NiO system. They also found that the hardness improvement was

partly affected by the density modification (Kruea-In *et al.*, 2017).

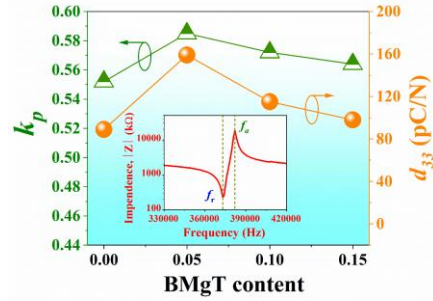


Figure 3 Plots of k_p and low-field d_{33} as a function of BMgT content (inset: Impedance (Z) as a function of frequency)

Plots of k_p and low-field d_{33} as BMgT are shown in Figure 3. Impedance (Z) as frequency (f) is presented in inset of Figure 3. The anti-resonance (f_a) and the resonance (f_r) frequencies, which are the frequencies of the maximum and the minimum impedances, respectively, were used to calculate k_p with following equation (Chen *et al.*, 2004; Zhao *et al.*, 2005; Promsawat *et al.*, 2017):

$$k_p^2 = 2.5 \left[\frac{f_a^2 - f_r^2}{f_r^2} \right] \quad (5)$$

The k_p increased with increasing BMgT and had a maximum value of 0.585 when BMgT was added up to $x = 0.05$. Further increasing BMgT greater than $x = 0.05$, the k_p decreased (see Table 2). Variation of the low-field d_{33} is almost similar to that of k_p , and the optimized BMgT is also about $x = 0.05$, which giving a maximum low-field d_{33} of 159 pC/N (Ullah *et al.*, 2012). The enhancement of piezoelectric properties for the $x = 0.05$ ceramic was possible due to the densification improvement. However, the reduce of the low-field d_{33} and k_p at high BMgT ($x > 0.05$) were observed. This can be ascribed to the induced pseudo-cubic phase, which correlated to the XRD result.

Table 2. Piezoelectric properties of (1- x)BNT- x BMgT ceramics

x	k_p (%)	d_{33}^a (pC/N)	d_{33}^b (pC/N)	Aging rate of d_{33} (%)
0	0.552	89	77	15.96
0.05	0.585	159	154	3.72
0.10	0.571	115	112	3.09
0.15	0.564	98	96	2.42

^a The d_{33} data obtained after aging time 24 h.

^b The d_{33} data obtained after aging time 168 h.

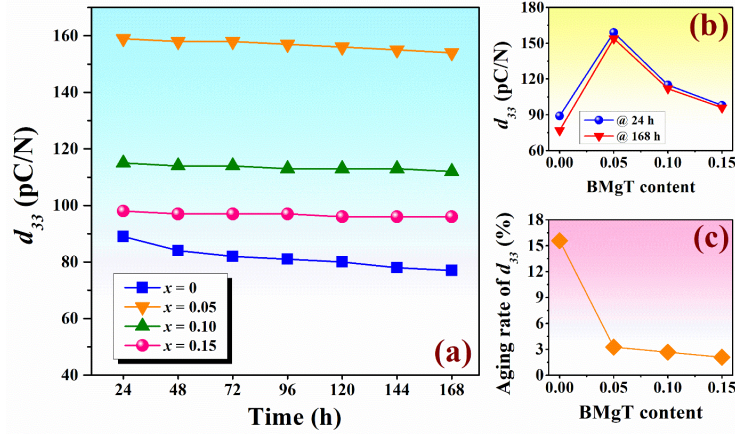


Figure 4 Plots of (a) low-field d_{33} as a function of aging time, (b) low-field d_{33} as a function of BMgT content at difference aging time of 24 h and 168 h, and (c) aging rate as a function of BMgT content

Table 3. Dielectric properties of (1-x)BNT-xBMgT ceramics

x	ϵ_r^a	$\tan \delta^a$	$\epsilon_{\max}^b$	$\tan \delta^b$	$\epsilon_{\max}^c$	$\tan \delta^c$	$\Delta \epsilon_{\max}$ (%)
0	741	0.0426	3150	0.0318	3650	0.0422	15.87
0.05	788	0.0322	2370	0.0206	3440	0.0266	45.15
0.10	794	0.0294	2330	0.0233	2880	0.0262	23.61
0.15	818	0.0233	1880	0.0142	2320	0.0218	23.40

^a Dielectric data at RT (25°C) @ 1 kHz.

^b Dielectric data at HT (25-500°C) @ 100 Hz.

^c Dielectric data at HT (25-500°C) @ 100 Hz (after annealing 1,000°C for 24 h).

Plots of low-field d_{33} as time (t) are shown in Figure 4(a). The low-field d_{33} slightly decreased for all ceramics with increasing time, especially for 168 h (Figure 4(b)). The percentage of aging rate was calculated as a logarithmic function (Jones *et al.*, 1996; Promsawat *et al.*, 2017):

$$\text{Aging rate} = \frac{1}{\log(t_2) - \log(t_1)} \left(\frac{P_2 - P_1}{P_1} \right) \quad (6)$$

where t_1 and t_2 are numbers of hours just after poling 24 h and 168 h. The P_1 and P_2 are piezoelectric performances measured at t_1 and t_2 . Plot of aging rate as a function of BMgT are shown in Figure 4(c). The percentage of aging rate decreased with increasing BMgT. The aging rate of the $x = 0$ ceramic is faster than that of the modified-ceramics ($x = 0.05-0.15$). For this system, the different of oxygen vacancy (O_2 vacancy) concentration is believed to be the important cause for the different aging behaviors. When addition of BMgT into BNT, Mg^{2+} filled Ti^{4+} at B-site position, thus created more O_2 vacancies, and resulted to small aging rate for added-samples (Carl and Härdtl, 1978; Jones *et al.*, 1996). Promsawat *et al.* also found that hard PZT (which has a higher interaction between defects and

domains due to its large number of O_2 vacancies) also had small aging rate when compare to that of soft PZT ceramic (lower number of O_2 vacancies) (Promsawat *et al.*, 2017).

Plots of ϵ_r and $\tan \delta$ at RT at various frequencies are shown in Figure 5(a-b). The ϵ_r decreased whereas $\tan \delta$ increased with increasing frequency for all ceramics. This behavior is normally followed by almost all dielectric materials (Moulson and Herbert, 2003; Kumari *et al.*, 2016). The ϵ_r of all ceramic exhibited decreasing with measuring higher frequencies may be cause by the active presence of all types of polarization in dielectric materials as mention in (Moulson and Herbert, 2003). At low frequencies, all four types' mechanism of polarization contributes to the total polarization of material, therefore higher ϵ_r occurs. At high frequencies, the dipoles with large relaxation times break to respond with the applied frequency, thus decrease in ϵ_r is observed (Kumari *et al.*, 2016). Plot of the ϵ_r and $\tan \delta$ @ 1 kHz are also shown in Figure 5(c). The ϵ_r showed a maximum value of 818 for the $x = 0.15$ ceramic (Table 3). The densification was an important factor for dielectric improvement, *i.e.* higher relative

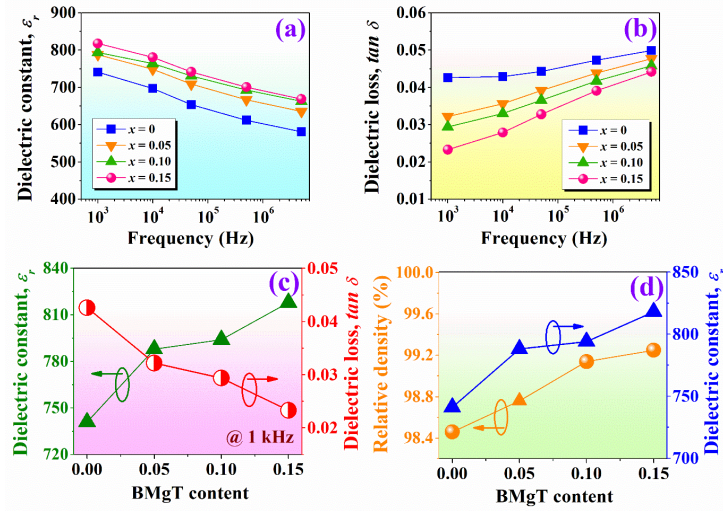


Figure 5 Plots of (a) ϵ_r as a function of frequency, (b) $\tan \delta$ as a function of frequency, (c) ϵ_r and $\tan \delta$ @ 1 kHz as a function of BMgT content, and (d) relative density and ϵ_r as a function of BMgT content

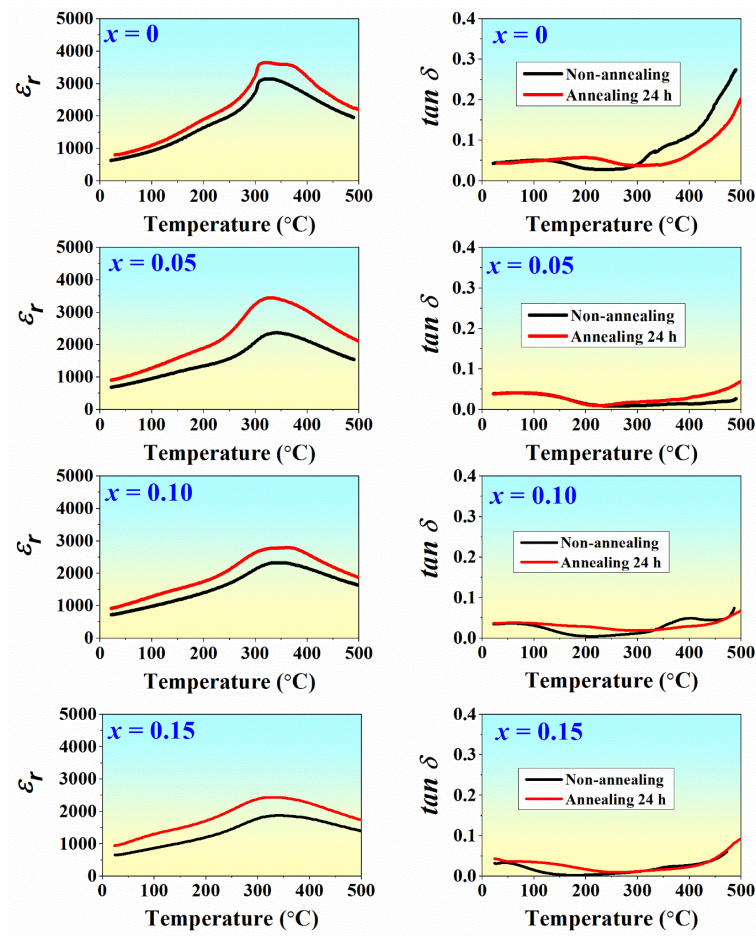


Figure 6 Temperature dependence on ϵ_r and $\tan \delta$ at 100 Hz, measurement before and after annealing process at 1,000 °C for 24 h

density resulted in higher dielectric (Figure 5(d)) (Xia *et al.*, 2002; Mudinepalli *et al.*, 2015). Similar behavior observed in recent investigation of BNKT-SFT and $(\text{Bi}_{0.4871}\text{Na}_{0.4871}\text{La}_{0.0172})\text{TiO}_3-(\text{Ba}_{0.7}\text{Sr}_{0.3})\text{TiO}_3$ ceramics (Jaita *et al.*, 2021; Inthong and Kruea-In, 2022). Hajra *et al.* also mentioned that densification enhancement was an important factor in higher dielectric (Hajra *et al.*, 2019).

Effect of thermal annealing process on dielectric performance was also investigated in this work. Temperature dependence on ϵ_r and $\tan \delta$ at 100 Hz, measurement before (non-annealing) and after annealing process at 1,000°C for 24 h are shown in Figure 6. The annealed ceramic showed better both ϵ_r and $\tan \delta$ when compared to that of the non-annealed ceramics (Figure 7(a-b)). After annealed at 1,000°C for 24 h, the $x = 0.05$ ceramic had the maximum dielectric improvement ($\epsilon_{\max} = 3,440$), and this value was 45.15% ($\Delta\epsilon_{\max}$) higher than that of the unannealed sample ($\epsilon_{\max} = 2,370$). The observed dielectric enhancement after annealing process can be attributed to an extrinsic contribution which induced by domain wall motion. The pinning effects caused by internal stress on domain wall motion and O_2 vacancies were largely eliminated after annealing process. Therefore, a greatly increased dielectric performances and a significantly increased polarization level were observed (Wang *et al.*, 2008). Xia *et al.* also reported that after annealing, the pinning effects caused by oxygen vacancies and internal stress on domain wall motion were largely eliminated (Xia *et al.*, 2002). Therefore, a greatly increased dielectric constant were observed (Xia

et al., 2002). After the annealing process, the relative density was determined again (Figure 7(c)). The data clearly showed that the relative density enhanced after annealing process which high relative density sample is responsible for enhanced dielectric properties as expected (Ghasemifard *et al.*, 2013; Hajra *et al.*, 2018).

Conclusions

In this work, the $(1-x)\text{BNT}-x\text{BMgT}$ ceramics were successfully synthesized using a solid-state reaction technique. This study has been conducted to investigate the influence of BMgT adding on physical, mechanical, and electrical responses of BNT ceramic. High relative density of 98.46-99.25% was achieved for all samples. All ceramics exhibited a single perovskite structure. Rhombohedral phase transformed into pseudo-cubic phase with increasing BMgT. The $x = 0.15$ ceramic showed the maximum dielectric ($\epsilon_r = 818$, $\tan \delta = 0.0233$) and mechanical ($HV = 5.56$ GPa, $HK = 5.43$ GPa, $E = 94$ GPa and $K_{IC} = 1.61$ $\text{MPa}\cdot\text{m}^{1/2}$). The $x = 0.05$ had the maximum of k_p (0.585) and low-field d_{33} (159 pC/N). Moreover, the $x = 0.05$ ceramic had the maximum dielectric improvement after annealed at 1,000°C for 24 h ($\epsilon_{\max} = 3,440$), and this value was $\sim 45.15\%$ higher than that of the unannealed ceramic ($\epsilon_{\max} = 2,370$). This results suggested that BMgT-added and annealing process can enhanced the mechanical and electrical properties of BNT ceramic.

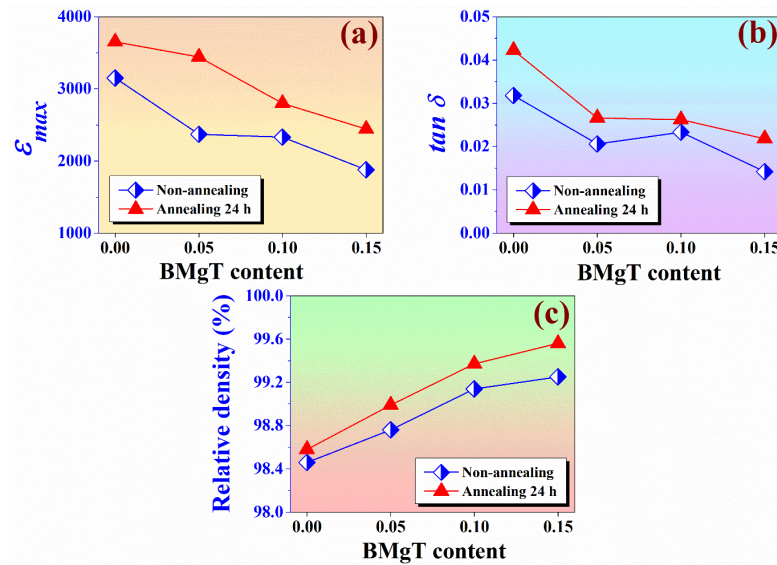


Figure 7. Plots of (a) $\epsilon_{\max}$ as a function of BMgT content, (b) $\tan \delta$ as a function of BMgT content, and (c) relative density before and after annealing process as a function of BMgT content

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