

## A Preliminary Study of BNT-BT Ceramics Prepared by Solid State Reaction

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### ABSTRACT

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In this work, the lead-free ceramics of Bismuth Sodium Titanate-Barium Titanate (BNT-BT) were successfully prepared by solid state reaction. Both compounds were separately milled in a conventional ball milling and subsequently, calcined afterwards. Decomposition temperature was determined by TGA. It was found that the milled powders of BNT and BT were completely stable after 830 and 985oC, respectively. This indicates that the calcination temperature of each powder might be expected to be around at 950oC to form the single-phase formation of BNT and BT with better degree of crystallinity. It was then confirmed by the XRD patterns whereby the diffraction peaks were identified as the formation of single phase BNT and BT, respectively. The SEM images also showed that the calcined powders were formed in hardly agglomeration with micron size scale.

#### Keywords:

BNT-BT, calcination, morphology, solid state reaction

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## 1. Introduction

Lead oxide based materials such as Lead Zirconate Titanate (PZT) is widely used for device application and rapidly gaining interest among researchers [1]. However, the PZT tends to release toxic and high vapour pressure during sintering due to contain of lead up to 60-70% [2-4]. When the textured of potassium sodium niobate (KNN) were developed, the goal were achieved quite readily. It also said that the researchers also achieving into invention of some other lead-free material such as BaTiO<sub>3</sub> and Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> [5,6]. Therefore, the lead free based materials such as Bismuth Sodium Titanate, Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> (BNT), Barium Titanate, BaTiO<sub>3</sub> (BT) Sodium Potassium Niobate (KNN) and others are strongly recommended to be used today. BNT is a ABO<sub>3</sub> type-perovskite material and it has high Curie temperature (320°C), large remnant polarization (38 μC/cm<sup>2</sup>) and high piezoelectric constant (73 pC/N)<sup>6</sup>. However, pure BNT is difficult to pole due to high coercive field (73 kV/cm). In addition, its phase transition (rhombohedral to tetragonal) is lower than the Curie temperature resulting in poor electrical properties [7]. A dense BNT ceramic is difficult to be prepared and need

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to be sintered above 1200°C, resulting in significant loss of bismuth. BNT also exhibits a low depolarization temperature  $\sim 200^\circ\text{C}$ . Therefore, to enhance the properties of BNT ceramics, the incorporation with other  $\text{ABO}_3$  type-perovskite such as BT is possible.

The BNT is usually synthesized via solid state reaction with  $\text{Bi}_2\text{O}_3$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{TiO}_2$  as starting materials that known as easy and non-expensive method. As high temperatures are needed for calcination and sintering, the volatility of  $\text{Bi}_2\text{O}_3$  and  $\text{Na}_2\text{CO}_3$  problems will be occurred. Both materials have low melting points ( $T_m(\text{Bi}_2\text{O}_3) = 826^\circ\text{C}$ ,  $T_m(\text{Na}_2\text{CO}_3) = 851^\circ\text{C}$ ). Therefore, high vapour pressures at processing temperatures resulting loss of A-site cations leads to a non-stoichiometric composition as example a deviation of the A:B ratio from one. This non-stoichiometry causes vacancies; the material can respond with the formation of a secondary phase or volatilization of components to regain stoichiometry [8,9]. To improve the properties of BNT ceramics, it is necessary to reduce the sintering temperature or improve the densification of ceramics. The low sintering temperature is required to maintain the stoichiometry or nominal composition along with the reduction of energy consumption [10]. Thus, to improve electrical properties of BNT either by the doping of some suitable rare earth dopants at A-sites or A and B-sites both by mixing them with other  $\text{ABO}_3$  type compounds, such as  $\text{BaTiO}_3$  [11-16]. Among the BNT-based system,  $(1-x)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-x\text{BaTiO}_3$  possesses a rhombohedral (Fa)-tetragonal (Fb) morphotropic phase boundary (MPB) at  $x = 0.06 - 0.07$ , where the system shows outstanding piezoelectric and dielectric properties [17]. In general, BT has a relatively low Curie temperature ( $120^\circ\text{C}$ ) without the addition of lead. However, BT with lead added could increase the Curie temperature up to  $150^\circ\text{C}$  [18]. As stated earlier, the presence of lead could destabilize the phase transition (orthorhombic to tetragonal) of BT. Therefore; the incorporated of BT into BNT could increase the temperature of phase transition with more variety of applications at a wide range of temperatures [19]. Moreover, BNT-BT ceramics has relatively high piezoelectric properties [20]. In this work, a preliminary study of BNT and BT is necessary to be investigated in terms of decomposition temperature, phase formation and morphology. This study is important prior to start the incorporation of BT into BNT at the next stage of experiment.

## 2. Methodology

The respective amount of  $\text{Na}_2\text{CO}_3$ ,  $\text{BaCO}_3$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{TiO}_2$  (> 99.9 % purity, sigma Aldrich) were weighed according to their stoichiometric. Separately, the first set of powders ( $\text{Na}_2\text{CO}_3$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{TiO}_2$ ) and second set ( $\text{BaCO}_3$  and  $\text{TiO}_2$ ) were milled in the PTFE bottles via conventional ball milling for 3 hours. Each set was then taken out from the PTFE bottles. The milled powders were calcined to form a good degree of crystallinity of BNT and BT, respectively. After calcination, both powders were mixed with ethanol and milled for another 12 hours and then dried in oven at  $100^\circ\text{C}$  for 24 hours. Several characterizations were done. Thermogravimetric analysis (TGA) was performed at a rate of  $5^\circ\text{C}/\text{min}$  to determine the possible calcination temperature to produce a good degree of crystallinity of BNT and BT. This was then confirmed by X-ray diffraction (XRD), whereby the phase formation of BT and BNT was identified. The morphologies of calcined powders were monitored by scanning electron microscopy (SEM).

## 3. Results and Discussions

### 3.1 Thermal Analysis of BNT-BT

Figure 1 and 2 shows the TGA curve of milled BT and BNT powders which was heated up to  $1000^\circ\text{C}$ . As seen in Figure 1, the decomposition temperature of BT was initially detected at  $744^\circ\text{C}$  and the TGA curve was almost stable after  $985^\circ\text{C}$  with total weight loss of about 13%. The DTG peaks

showed a broad endothermic peak from around 744°C to 985°C corresponded to multiple step weight loss in the same temperature range. The decarboxylation of  $\text{BaCO}_3$  was occurred in this stage. Moreover, there is a small endothermic peak around 910°C that contributed to the phase transformation of  $\text{BaTiO}_3$  and the unreacted  $\text{TiO}_2$  to form  $\text{BaTiO}_3$  phase [21]. According to Hsiang, the reaction of  $\text{BaTiO}_3$  in thermogravimetric analysis may be separated into two stages [22]. The first stage occurred an increase in the numbers of reactant contact points of  $\text{BaCO}_3$  and  $\text{TiO}_2$  can enhanced. The second stage is attributed the mainly remaining  $\text{BaCO}_3$  and  $\text{TiO}_2$ . The residual  $\text{TiO}_2$  is completely covered by the product phase and the reaction can only proceed by the slower lattice diffusion. The obvious exothermic peak at 985°C indicated that crystallization of BT.

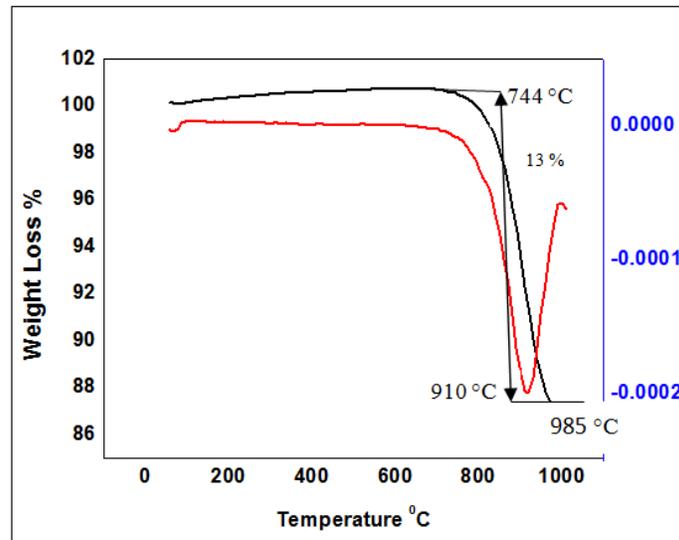


Fig. 1. TG/DTA pattern of BT powder

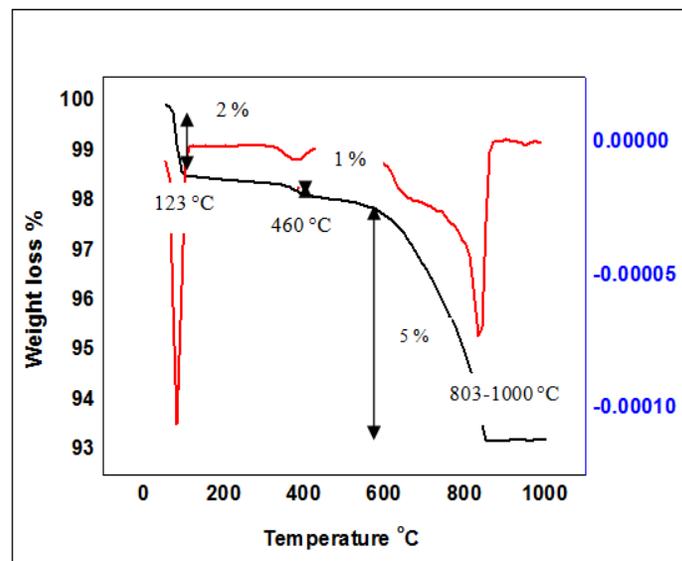


Fig. 2. TG/DTA pattern of BNT powder

Meanwhile, the TGA curve of milled BNT is shown in Figure 2. It was found that the decomposition temperature of BNT was attributed by three different steps. The first step was detected at 123°C, the second step at 460°C and the third step was 830°C. At the first step, a small weight loss occurred about 2% at 123°C is primarily due to vaporization of water. The second and third step at 460°C and 830°C both have major weight loss and attributed to CO<sub>2</sub> loss due to carbonates. The third step at 830°C with an obvious exothermic peak is primarily due to the crystallization of BNT [23]. The curve was then stable after 830°C, indicating that the formation of BNT was completely achieved. In addition, the total weight loss to produce BNT was around 8.0%. Based on DT/TGA results, the calcination temperature of BT and BNT might be possible at around 950°C in order to get single phase formation.

### 3.2 Crystalline Structure of BNT and BT powders

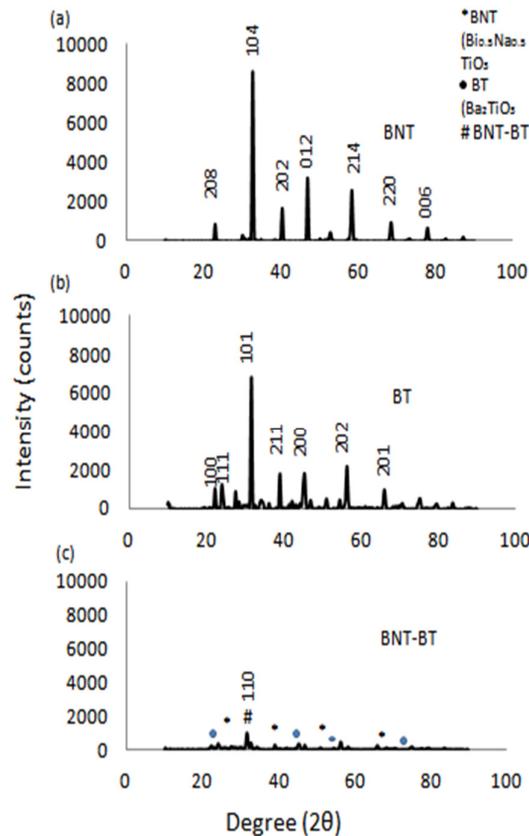
Figure 3(a) shows the XRD pattern of calcined BNT powders at 950°C. The strongest diffraction peak at  $2\theta=32.57^\circ$  which corresponds to a diffraction of  $\langle 104 \rangle$  plane was detected with perovskite structure. As seen, the diffraction peaks of BNT are similar to the master file with rhombohedral structure [24]. In other words, the single phase formation of BNT was achieved with no secondary phase. This is because due to the calcination reaction for stoichiometric BNT. The starting materials were reacted to the perovskite structure and release CO<sub>2</sub>. Thus, with a stoichiometric mixture of starting materials no secondary phase is formed in this reaction step as per XRD results [25]. The reaction that occurred during calcination process is stated by the following equation.



Meanwhile, Figure 3(b) shows the XRD pattern of calcined BT powders at 950°C. In comparison to master file, the single phase formation of BT was detected in the form of tetragonal structure. As seen, the strongest diffraction peak at  $2\theta=31.59^\circ$  corresponds to  $\langle 101 \rangle$  plane, indicating that the presence of BT phase. In addition, the presence of secondary phase of BT was not detected in this pattern. The small peaks present in this pattern may be formed by orthotitanate phases during the process [26]. This is because a very small amount of intermediate phase was preceded by BaTiO<sub>3</sub> formation appeared in the present results. The temperature at which this trace amount of BaTiO<sub>4</sub> was formed also the same one that this phase retransformed to BaTiO<sub>3</sub>. This behavior mostly depends on the milling time and reactivity of TiO<sub>2</sub> powder [27]. The general reaction of BT can be summarized as the equation below.



For the milled of mixture for both calcined BNT and BT powders (Figure 3(c)), all the peak intensities are relatively low in comparison to the intensities with individual BT and BNT. The high peak indicated the presence of BNT-BT. The powder does not yet achieve in single phase and need to be sintered in high temperature in order the green body more compact and has good electrical properties. It can be concluded that the sintering process has greatly influence on the microstructure of the BNT-BT to real function of piezoelectric material.



**Fig. 3.** XRD patterns of calcined (a) BNT, (b) BT and (c) BNT-BT powders

### 3.3 Morphology of BNT and BT powders

SEM micrograph of individually calcined BNT, BT and calcined BNT-BT powders are shown in Figure 4. In Figure 4(a), the morphology of BNT shows a distribution of nearly cubical or round particles. There is no plate-like particles appeared after calcination that indicating the calcination process is fully transformed all bismuth layered phase into perovskite structure. A similar work was observed by Khairunisak *et al.*, [28] which are during the calcination, there are some unwanted compounds such as water and carbon phases were decomposed. At the same time, diffusion of ions that occur led to the formation of pure compound with stable crystal structure. Thus, all ions in the unstable bismuth-layered phase diffused and formed a more stable cubic or round particle with perovskite structure [28]. The size BNT particles were about 2.04  $\mu\text{m}$  in average. Meanwhile, for BT their size of particles cannot be measured as the powders were too well fine in their size.

The morphology of BT is considered in spherical shape as shown in Figure 4(b). According to Manzoor, the consumption of rod like  $\text{BaCO}_3$  and increase in smaller  $\text{TiO}_2$  particle size is clearly visible. The powder calcined at  $950^\circ\text{C}$  difficult to distinguish between  $\text{BaCO}_3$ ,  $\text{TiO}_2$  and  $\text{BaTiO}_3$  particles [19]. It was also found that the particle size of BT is slightly smaller than the particle size of BNT, probably the size in micron size scale. BNT has the difficulty in maintaining chemical homogeneity. Thus, the particles obtained are poorly uniform with broad size distributions [29]. Interestingly, the morphology of BNT-BT (Figure 4(c)) is almost uniform in shape and size. Ethanol was added as milling media in order to get homogenous powder. This indicates that the mixing and milling of BNT and BT

showed a better result in terms of their morphology. However, the agglomeration of respective powder was obviously observed because of fine in particle size.

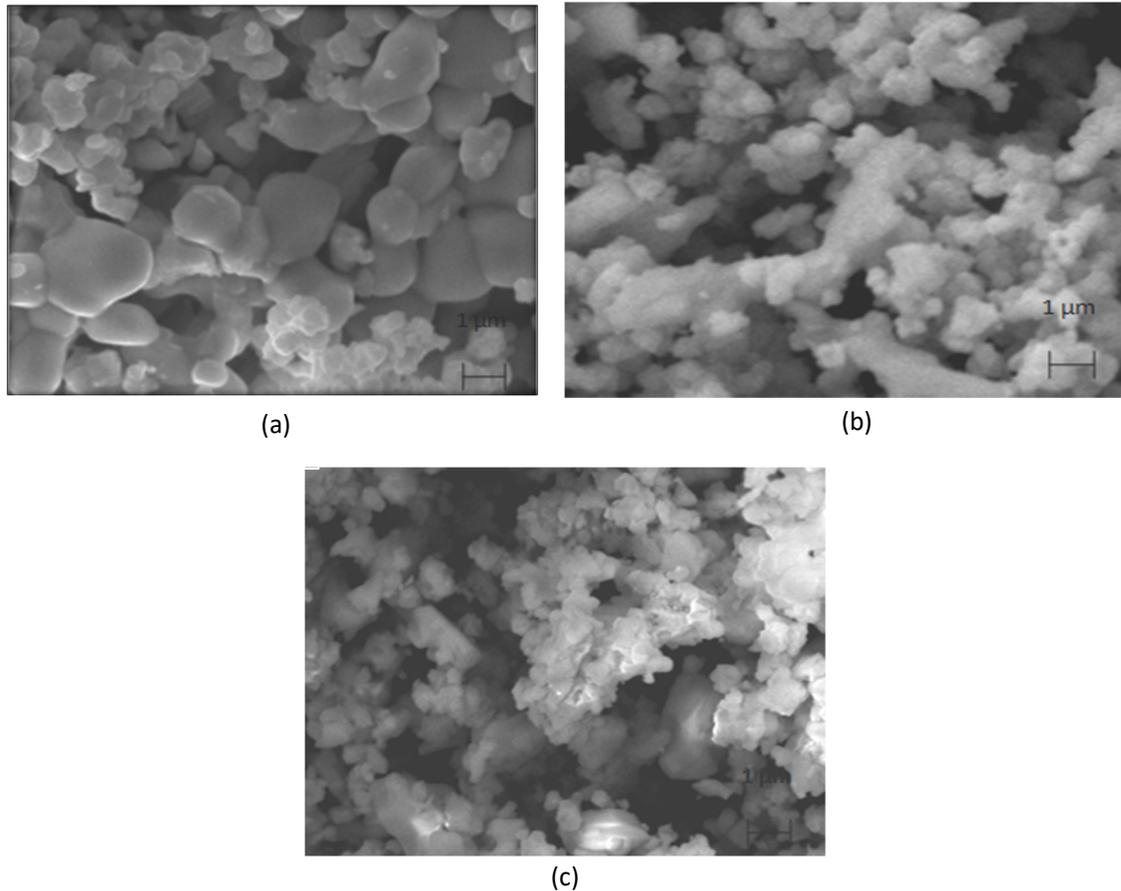


Fig. 4. Morphology of calcined (a) BNT, (b) BT and (c) BNT-BT powders

#### 4. Conclusion

Based on TGA analysis, the calcination temperature of both samples could be determined. Both samples of BNT and BT were calcined at 950°C. The single phase of BNT and BT were successfully formed without secondary phase. The morphology of each powder was found to be formed in different size and shape.

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