

## The Specification of Dielectric Ternary Compound BNT-BKT-BT

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### Abstract

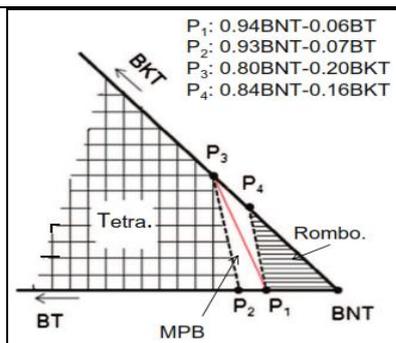
The ternary ceramic compound (BNT-BKT-BT), like 0.855 (Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub>) 0.115 (Bi<sub>0.5</sub>K<sub>0.5</sub>TiO<sub>3</sub>)-0.03 (BaTiO<sub>3</sub>) was prepared by solid-state reaction. Three different calcination processes as a function of temperature and time had been used as the candidate for the structural phase. The crystal structure analysis confirmed a rhombohedral and tetragonal phase regarding diffracted peaks within the morphotropic phase boundary (MPB). The dielectric behavior at different frequencies (1, 10, 100 kHz, and 3 MHz) and temperatures showed a maximum curie temperature at (295 °C) through a frequency (100 kHz). The XRD analyses showed the peak splitting observed around (2θ = 40, and 46) related to the overlapping between many peaks mentioned by different phases. The appearance of the relaxer ferroelectric behavior emphasizes the agreement of the XRD analysis and dielectric measurement.

### 1. Introduction

Piezoelectricity was stated firstly by Curie in 1880 [1]. He stated that there is mechanical stress is applied in such materials as zinc blende, tourmaline, and quartz structures, due to applied force creating electric surface charges and then an electric field created producing electric energy stored [2]. A ferroelectric is appearing an electric polarization in such dielectric material without an electric field applied. The direction of the polarization may be reversed by an electric field [2]. There is a relationship between piezoelectric and ferroelectric, such that the presence of piezoelectric means appearing as ferroelectric [2]. The familiar compound that showed piezo-ferroelectric behavior was Barium Titanite (BaTiO<sub>3</sub>), the structure Perovskite structure which is a special structure of the cubic system. This structure is suitable for producing tetrahedron and octahedron structures within the perovskite structure. The tetrahedron and octahedron are responsible for a piezo-ferroelectric behavior because the net of polarization is coming from the tetrahedron and octahedron structure. The ternary compound BNT-BKT-BT is derivative from the principle compound Barium Titanate (BaTiO<sub>3</sub>) which is one of the most widely used dielectric materials. The reason is related to high dielectric constant, polarization, and piezoelectric constant [3-5].

A morphotropic phase boundary region (MPB) in BNT-BKT-BT system can be determined using the four points in the triple phase diagram [6]. This property is useful in electronic and ultrasonic applications, such as transducers, sensors, actuators, and microelectronic devices [7-9]. The structural nature of that compound is derivative from the

structure of the principle compound BaTiO<sub>3</sub>, which has a perovskite structure in the formula ABO<sub>3</sub>. It is considering the origin of ferroelectrics such as (Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub>) (BNT), KNbO<sub>3</sub>, and NaTaO<sub>3</sub>, they are calling lead free piezoelectric materials [4]. The ferroelectric perovskite crystal structure is a good alternative for lead-free piezoelectric ceramic materials because of anisotropy in the physical properties of piezoelectric, which are predominant in comparison with other ferroelectric [4]. Takenaka and Sasaki et. al.; suggested that the BNT-BKT-BT triple phase system within the MPB region gives superior results compared to those along the MPB line [5]. The MPB region is fixed between two phases represented by tetragonal and rhombohedral within the perovskite structure. There is a tetragonal phase is potassium bismuth titanate Bi<sub>0.5</sub>K<sub>0.5</sub>TiO<sub>3</sub> (BKT) and Barium titanate, BaTiO<sub>3</sub> (BT) [10,11]. The binary system of the piezoelectric ceramic of the compounds BNT-BKT was discussed previously. The MPB region in BNT-BKT-BT system was calculated by the following four points (P<sub>1</sub>-P<sub>4</sub>), as shown in Fig.1. They observed a phase transition from rhombohedral to tetragonal phase with the increasing BKT ratio within the range (12-32% mol). This ratio is a reason to exist an MPB region [12].



**Figure 1.** Phase diagram of  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3\text{-BaTiO}_3$  system around the MPB region [12].

The piezoelectric ternary system  $(1-3x)\text{BNT}\text{-}(2x)\text{BKT}\text{-}(x)\text{BT}$  had been studied by using ceramic fabrication processes with different concentrations. They concluded an MPB lies in the range  $(0.025 \leq x \leq 0.035)$  for the system  $(1-3x)\text{NBT}\text{-}2x\text{KBT}\text{-}x\text{BT}$ , which showed a favor piezoelectric constant of about  $(150 \text{ pC/N})$  and the electromechanical coupling factor was  $(0.298)$  at  $(x = 0.035)$  [13,14]. In this work, the ceramic compound  $x\text{BNT}\text{-}y\text{BKT}\text{-}z\text{BT}$  is considering a complement system between three compounds, such that  $(x + y + z = 1)$ , with three perovskite phases was prepared and studied near the MPB region.

#### Experimental procedure

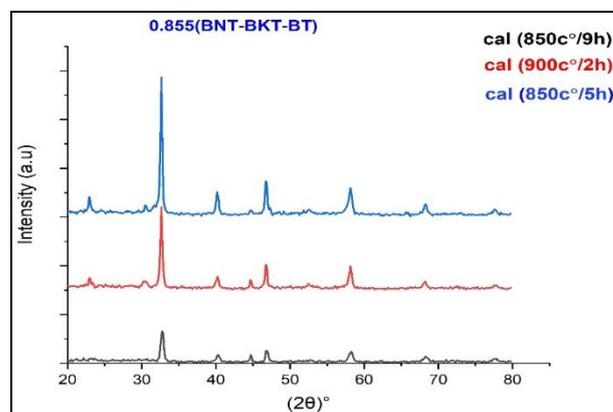
The ternary compound of the system  $(x\text{BNT}\text{-}y\text{BKT}\text{-}z\text{BT})$  was studied through the phase diagram of three compounds such that the summation of the three components represented by  $(x,y,z)$  must be equal to 1. This ternary system was prepared by solid-state reaction. The composition of three compounds was subjected to the formula  $(0.855)\text{BNT}\text{-}(0.115)\text{BKT}\text{-}(0.03)\text{BT}$  at different calcination temperatures and times  $(850 \text{ }^\circ\text{C}/9 \text{ h}, 900 \text{ }^\circ\text{C}/2 \text{ h}, \text{ and } 850 \text{ }^\circ\text{C}/2\text{h})$  to show which one is better during a predominate phase related to perovskite structure. The raw material used Titanium Dioxide  $\text{TiO}_2$ , Bismuth Carbonate  $(\text{BiO})_2\text{CO}_3$ , Barium Carbonate  $(\text{BaCO}_3)$ , Sodium Carbonate  $(\text{Na}_2\text{CO}_3)$ , and Potassium Carbonate  $(\text{K}_2\text{CO}_3)$  as starting materials. Stoichiometry is necessary to investigate the ternary mixture depending on the required weights. The powders were mixed with isopropanol and grinding for  $(5 \text{ hr})$  with a gate mortar. Later, the mixture dried at  $(80 \text{ }^\circ\text{C})$  for  $(1 \text{ hr})$ . The calcination process was applied for the mixture at temperatures  $(850 \text{ }^\circ\text{C}/9\text{h}, 900 \text{ }^\circ\text{C}/2\text{h}, \text{ and } 850 \text{ }^\circ\text{C}/2\text{h})$  by a raising rate equal to  $(60 \text{ }^\circ\text{C}/\text{h})$ . After that, the calcined powder was pressed into a pellet under a pressure  $(200 \text{ MPa})$ . The pellets were sintered at  $950 \text{ }^\circ\text{C}/4 \text{ h}$  with a heating and cooling range of  $(30 \text{ }^\circ\text{C}/\text{h})$  by using a tubular furnace. The three pellets were in a diameter equal to  $1\text{cm}$  and a thickness equal to  $1.6\text{mm}$ . The phase investigation was studied using an X-ray diffractometer XRD, type (PHILIPS), at room temperature with the source  $\text{Cu}_{\text{K}\alpha}$  and wavelength  $(\lambda = 1.5405 \text{ \AA})$ .

The lattice parameters were determined during suitable software used for this analysis. Then, the analysis of XRD-

pattern gives more details about the predicated phase appeared there is much software used for the analysis represented by CrystalDiff.; Originpro 2018, and FullProof Suite toolbar (v.3.00). The database was used for the phase analysis of the sample under study was applied from international center for diffraction Data ICDD [15] with the code (2103295) for  $(\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3)$ , (2102068) for  $(\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3)$ . After the sintering process, the ceramic pellets were polished and then coated with gold on both sides to make a capacitor to get the parameters to function to a dielectric behavior. The dielectric measurement was obtained to enhance the presence of the MPB perovskite structural phase. The dielectric constant  $(\epsilon_r)$  and the loss tangent were measured at different temperatures and frequencies  $(1, 10, 100 \text{ kHz}, \text{ and } 3 \text{ MHz})$ . The measurements were done using (TEGAM-3550 LCR meter at 1 volt).

## 2. Results and Discussion

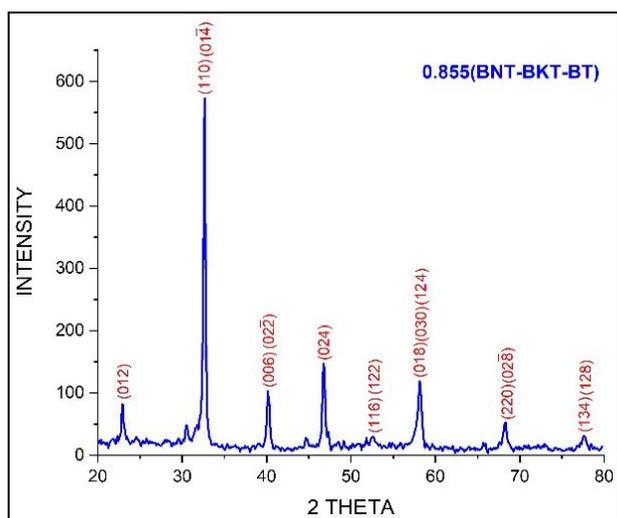
After a successive preparation for all samples under study, the analysis and measurements are necessary to prove the ferroelectric behavior of MPB phases. The first one is XRD analysis during the crystal structure test. The obtainable results showed the formation of the perovskite phase and the coexistence of the rhombohedral and tetragonal phase near the MPB in comparison with a specific database obtained from the crystallography open database. The XRD pattern of  $0.855(\text{BNT}\text{-}\text{BKT}\text{-}\text{BT})$  powder compound prepared at different calcination temperatures  $(850 \text{ }^\circ\text{C}/9 \text{ h}, 900 \text{ }^\circ\text{C}/2 \text{ h}, \text{ and } 850 \text{ }^\circ\text{C}/5 \text{ h})$  is shown in Figure 2.



**Figure 2.** Indicate XRD patterns of the calcined samples  $0.855 (\text{BNT}\text{-}\text{BKT}\text{-}\text{BT})$ .

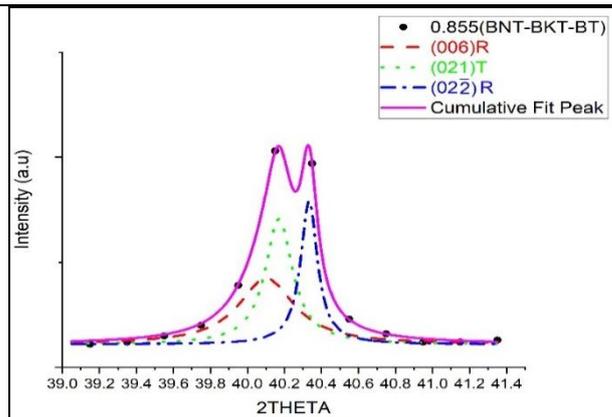
The appropriate phase is predominated at a calcination temperature of  $850 \text{ }^\circ\text{C}/5\text{h}$ . Whereas the calcination temperatures  $(850 \text{ }^\circ\text{C}/9 \text{ h}, 900 \text{ }^\circ\text{C}/2 \text{ h})$  showed a lower density of the phase produced. That was clear from the low intensity of the diffracted peaks. The results showed the appearance of polycrystalline structure with many orientations mentioned by different Miller indices as shown in Figure 3. The XRD analysis aims to examine the existence of rhombohedral and tetragonal both phases are the main reason for creating enhanced ferroelectric properties of the prepared samples. That is mentioned

through the peak's positions and their relative intensities. They have high intensity comparable with the peak intensities mentioned for the calcined powders at (850 °C/9 h and 900 °C/2 h). On the other hand, there is a probability of finding a single perovskite phase for the sample calcined at (850 °C/5 h). That means there is the lowest probability of finding impurities phases. These results are approaches to results obtained previously [3].

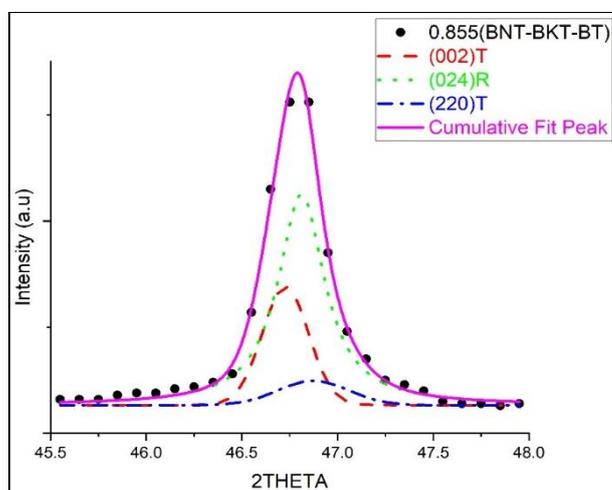


**Figure 3.** Indicate XRD pattern of the calcined 0.855 (BNT-BKT-BT) at 850 °C/5 h.

As mentioned before, Figure 3 showed the MPB behavior during the phase transformation from rhombohedral to tetragonal phase through the splitting around ( $2\theta = 40$ ) which enhances the MPB phases. The Origin PRO-2018 software was used to obtain the peak de-convolution in the overlapping behavior. There is an overlapping between the rhombohedral single peak (022) and tetragonal single peak (021) as appeared in Figure 4. Whereas the peak around ( $2\theta = 46$ ) showed an overlapping between the tetragonal dual peak (220), (002), and rhombohedral single peak (024) as in Fig. 5. The nature of the MPB is responsible for the double structure in a ternary compound (BNT-BKT-BT) [16]. The results exhibited lattice parameters and the volume of a tetragonal and rhombohedral phase was obtained by Rietveld refinement by using Crystal Diffract Software. The concluded lattice parameters for the rhombohedral structure were ( $a = b = c = 5.4679 \text{ \AA}$ ) and unit cell volume ( $V = 349.4 \text{ \AA}^3$ ), whereas the lattice parameters for the tetragonal structure are ( $a = b = 5.4638 \text{ \AA}$ , and  $c = 3.8957 \text{ \AA}$ ) with unit cell volume ( $V = 116.3 \text{ \AA}^3$ ).



**Figure 4.** Indicate the peak de-convolution around  $2\theta = 40$  for 0.855(BNT-BKT-BT) compound.



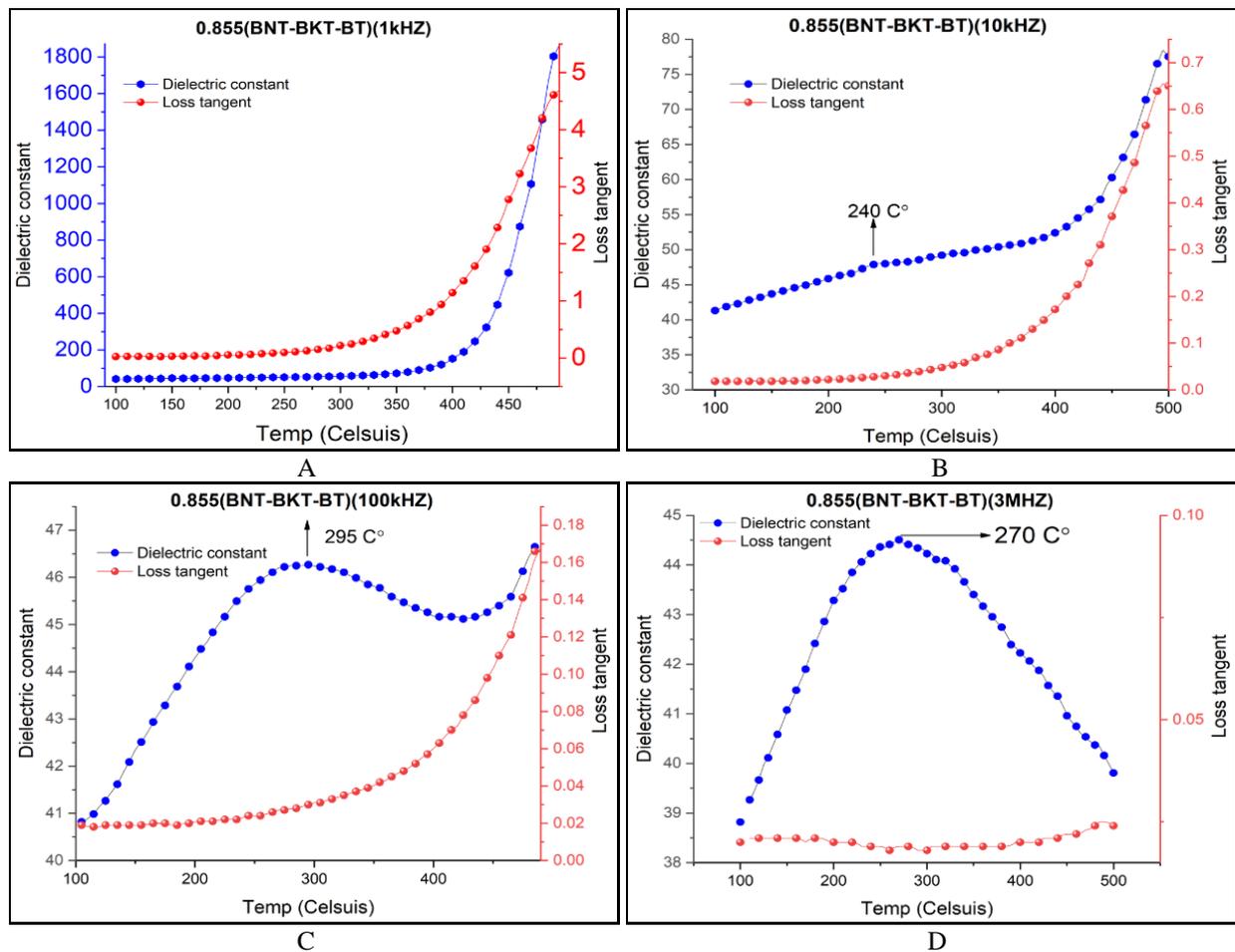
**Figure 5.** Indicates a peak de-convolution around  $2\theta = 46$  for 0.855(BNT-BKT-BT) compound.

The dielectric measurements are another tool to emphasize the presence of the ferroelectric behavior in the ternary system 0.855(BKT, BNT, BT) as shown in Figure 6 A-D. It explains the dependence of the dielectric constant ( $\epsilon_r$ ) and loss tangent as a function of temperature at different frequencies (1, 10, 100 kHz, and 3 MHz). There is a peak that appeared in the behavior related to phase transition from ferroelectric to paraelectric mentioned by Curie temperature recorded in the range (240-295 °C). Normally, the value of the dielectric constant is a function of the concentration of electric dipoles created and the number of octahedrons or tetrahedrons produce per unit cell, and both are a function of the strength of ferroelectric behavior in the MPB phases. From Figure 6, there is a low value of dielectric constants at Curie temperature in comparison with the previous studies [9-13], this is a sign of low density of ferroelectric behavior appeared. The sequences curves in Figure 6 A-D are showing the reduction of the dielectric constant as a function of frequency such that the high frequency recorded a low dielectric constant and low polarization density in MPB phases [17]. That is attributed to the probability of reducing the polarization in the MPB

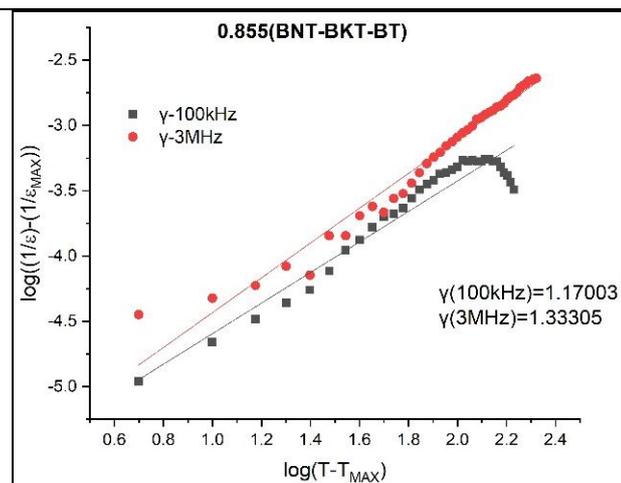
phase and the last return to reducing the built-in potential produced. Whereas, at the Curie temperature the dielectric constant takes the maximum value compared with the literature review [18]. On the other hand, as the frequency increased the peak is sharper. That emphasized the story of reducing the polarization and the possibility to transfer from ferroelectric to paraelectric is more satisfying. When the frequency increases the relaxation process in dielectric material occurred with increasing the dielectric loss [19].

The composition 0.855(BNT-BKT-BT) is acting as a relaxer because it exhibited a relaxer diffusion coefficient in the range of (1.1-1.3) at frequencies (100 kHz, and 3 MHz) as shown in Fig. 7. Normally, the relaxer diffusion

coefficient takes a theoretical value between (1-2), such that  $\gamma = 1$  it means a normal ferroelectric and  $\gamma = 2$  indicates to the relaxer ferroelectric [20,21]. Given what was mentioned above, there was a coincidence in the relaxer diffusion coefficient for the ceramic compound 0.855 (BKT-BNT-BT). Where  $\gamma$  increases from 1.17 at 100 kHz to 1.33 at 3 MHz, going toward the ideal relaxer ferroelectric. That means the presence of the relaxer behavior of ferroelectricity is a sign of the MPB region. The last enhanced the story of the presence of a piezoelectric-ferroelectric behavior in a ternary compound 0.855 (BKT-BNT-BT).



**Figure 6.** Indicates a dielectric constant and loss factor vs. temperature for 0.855 (BKT, BNT, BT) at different frequencies, A-1 kHz, B-10 kHz, C-100 kHz, and D-3 MHz.



**Figure 7.** The relaxer diffusion coefficient of 0.855 (BKT, BNT, BT) ceramic.

### 3. Conclusions

The composition of (0.855) BNT-(0.115) BKT-(0.03) BT lead-free piezoelectric ceramics were synthesized at different calcination temperatures by a conventional solid-state reaction method. The best value of calcination temperature was about (850 °C/5 h). The resultant powder was crystallized and belongs to the perovskite phase with the MPB ferroelectricity behavior phase. The XRD analysis emphasized the presence of the MPB behavior where the (rhombohedral-tetragonal) in the perovskite crystal structure. The observation of the peaks splitting around ( $2\theta = 40$ , and  $46$ ) is related to the double electric structure in the MPB region. The maximum Curie temperature was about (295 °C) at a frequency of (100 kHz). The analysis from the XRD reinforced the results of the dielectric measurements, where the appearance of the relaxer ferroelectric behavior enhances the MPB Nature.

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