
## Faculty of Manufacturing Engineering

# THE EFFECTS OF PVA BINDER ON THE STRUCTURAL AND DIELECTRIC PROPERTIES OF BNT-BT CERAMICS

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# THE EFFECTS OF PVA BINDER ON THE STRUCTURAL AND DIELECTRIC PROPERTIES OF BNT-BT CERAMICS

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## DECLARATION

I declare that this thesis entitled “The effects of PVA Binder on the Structural and Dielectric Properties of BNT-BT Ceramics” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not currently submitted in candidature of any other degree.

Signature : …….

Name : Nurul Jannah Binti Mohamad

Date : …….

## APPROVAL

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of Master of Science in Manufacturing Engineering.

Signature : …….

Supervisor Name : Associate Professor Ts. Dr. Umar Al-Amani bin Haji Azlan

Date : …….

## DEDICATION

First of all, I express my thanks to my beloved father, the late Mohamad Bin Isnin. I also want to thank my mother, Siti Binti Abdullah that gave me her prayer and blessing and all of her love. Thanks a lot to my lovely siblings Nurul Fatehah Binti Mohamad and Zulkiflee Bin Mohamad that always heard my problem and supported me. I also want to thank my supervisor Associate Professor Ts. Dr. Umar Al-Amani Bin Haji Azlan for endless support and dedication to me to finish this thesis. I want to thanks to Professor Dr. Radzali bin Othman for his advices. This thesis is dedicated for them.

## ABSTRACT

Bismuth Sodium Titanate – Barium Titanate (BNT-BT) is known as a lead-free piezoelectric ceramic with perovskite structure. In this work, the preparation of BNT-BT with different PVA (Poly vinyl alcohol) binder contents using solid state reaction was done. This work is mainly to study the effectiveness of PVA binder on the structural and dielectric properties of BNT-BT ceramics with different sintering temperature. Good sintering temperature can improve the density of material at times. In general, the PVA binder agent is used to form the shape of green body and bind the granules together that can help the materials achieved densification through changes in particle shape with high sintering temperature. The main problem of the BNT-BT ceramic is to have a high density and low porosity, whereby the weight percentage of PVA binder to be added is important. Preparation of BNT-BT with different composition of PVA binder (0.0, 0.1, 0.3, 0.5 and 0.7 wt%) was initially carried out by conventional milling methods; the starting materials of (Barium carbonate- Sodium carbonate- Bismuth oxide- Titanium Oxide) $BaCO_3$-$Na_2CO_3$- $Bi_2O_3$-$TiO_2$ are subsequently milled, calcined and sintered. In this work, X-Ray diffraction (XRD) is used to analysed the phase formation of material. Based on phase analysis using XRD technique, single phase of BNT and BT powder was successfully synthesized at calcination temperature of 950$^oC$ with 4 hours soaking time. After that, single phase of BNT-BT was successfully synthesized for all different compositions with three different sintering temperatures. The peak shifted towards lower angle and get broaden when increasing the composition of PVA content, indicating that the crystallite size is decreasing. Among all of the sample, the BNT-BT with 0.1 wt% composition of BNT-BT has exhibits single phase and has clear distinctive peak of both rhombohedral and tetragonal peak. It also has the highest density when the sintering at 1170$^oC$ which is 96.08%. The sample is also dense and uniform in grain size and turn into spherical in shape indicating a complete BNT-BT perovskite structure. BNT-BT with 0.1 wt% composition of PVA binder also has the highest dielectric constant and lowest dielectric loss at room temperature. Therefore, the lowest PVA amount is simply the good composition in this case. Hence, the dielectric performance of materials can be increased.

## *ABSTRAK*

*Bismut Natrium Titanat- Barium Titanat (BNT-BT) lebih dikenali sebagai bahan piezoelektrik seramik yang bebas daripada plumbum dengan struktur perovskit. Dalam kajian ini penyediaan BNT-BT dengan pelbagai komposisi pengikat PVA (Polivinil Alkohol ) dilakukan melalui proses reaksi keadaan pepejal. Fokus kajian ini adalah untuk mengkaji keberkesanan pengikat PVA terhadap struktur dan ciri dielektrik seramik BNT-BT dengan suhu sinter yang berlainan. Suhu sinter yang sesuai boleh menambah baik ketumpatan bahan. Secara umumnya, ejen pengikat PVA digunakan untuk membentuk dan mencantum partikel kecil untuk membantu mencapai densifikasi melalui perubahan bentuk zarah pada suhu yang tinggi. Masalah utama BNT-BT seramik adalah mempunyai nilai ketumpatan yang tinggi dan jisim berongga yang rendah, di mana peratusan berat pengikat PVA yang di tambah adalah penting. Penyediaan BNT-BT dan pelbagai komposisi pengikat PVA iaitu 0.0, 0.1, 0.3, 0.3, 0.5 and 0.7 wt% telah dijalankan dengan kaedah pengisaran bebola secara konvensional; bahan mentah seperti (Barium karbonat- Natrium karbonat- Bismut oksida- Titanium Oksida)* $BaCO_3$-$Na_2CO_3$- $Bi_2O_3$-$TiO_2$ *telah dicampur, dikalsin, dibentuk serta disinter. Dalam kajian ini, difraksi sinar-x (XRD) telah digunakan untuk menganalisa fasa bahan. Berdasarkan analisis fasa menggunakan XRD teknik, fasa tunggal BNT dan BT telah berjaya dihasilkan pada suhu pengkalsinan selama 4 jam. Fasa tunggal BNT-BT juga telah berjaya dihasilkan dengan pelbagai komposisi PVA melalui tiga suhu sinter berlainan. Graf XRD menunjukkan posisi telah beralih kepada sudut yang rendah dan pola graf semakin membesar. Sampel BNT-BT dengan komposisi 0.1 wt% telah menunjukkan fasa tunggal rombohedral dan tetragonal dengan jelas. Sampel juga menunjukkan nilai ketumpatan yang tinggi apabila disinter pada suhu* $1170^oC$ *dengan nilai 96.08%. BNT-BT sampel juga menunjukkan saiz partikel yang tersusun dan bertukar menjadi bentuk sfera yang menunjukkan ia telah sepenuhnya bertukar menjadi BNT-BT struktur perovskit. Sampel itu juga mempunyai nilai pemalar dielektrik yang tinggi dan kehilangan dielektrik yang sedikit pada suhu bilik. Kepentingan pengikat adalah untuk menambah baik produk yang ingin dibentuk sebelum bahan itu didensifikasikan melalui sinter. Oleh itu, jumlah pengikat yang sedikit adalah komposisi yang sesuai digunakan dalam kajian ini. Dengan itu, prestasi dielektrik sesuatu bahan akan meningkat.*

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## LIST OF ABBREVIATIONS

| | | |
|---|---|---|
| BNT | - | Bismuth sodium titanate |
| BNT-BT | - | Sodium bismuth-barium titanate |
| BT | - | Barium titanate |
| PVA | - | Polyvinyl alcohol |
| PZT | - | Lead zirconate titanate |
| SEM | - | Scanning electron microscopy |
| SPS | - | Spark plasma sintering |
| SSR | - | Solid state reaction |
| TGA | - | Thermal gravimetric analysis |
| XRD | - | X-ray diffraction |

## LIST OF PUBLICATIONS

1. Mohamad N.J., Azlan U.A.A. and. Harun M.H., 2018. Preliminary Study of BNT-BT Ceramics Prepared by Solid State Reaction, *Journal of Advanced Research in Fluid Mechanics and Thermal Science,* 48 (2), pp. 133-140.
2. Mohamad N.J., Azlan U.A.A. and M.R. Othman., 2017. Review of BNT-BT Ceramics for Piezoelectric Applications, *Proceedings of Innovative Research and Industrial Dialogue'16*, pp 159-160.

# CHAPTER 1

# INTRODUCTION

## 1.1 Research background

Ceramics in general were often used for piezoelectric applications. The so-called *piezoceramics* are known to have unique characteristics in which the polarization was contributed from mechanical stress instead of electrical field. Since lead base piezoelectric materials released toxic and high vapor pressure during sintering, it is inevitable to change them with lead-free materials (Parija et al., 2013). Bismuth Sodium Titanate, ($(Bi_{0.5}\ Na_{0.5})\ TiO_3$ or BNT), Barium Titanate ($BaTiO_3$ or BT) and Potassium Sodium Niobate ($(K_{0.5}Na_{0.5})\ NbO_3$ or KNN) is an example of perovskite material and lead-free piezoelectric ceramics that had been thoroughly studied based on good piezoelectric properties (Yantao et al., 2015).

There are many studies focused on BNT as a ceramic as replacement for PZT (Lead, Zirconium and Titanium) in industrial applications especially in energy harvesting (Shrout and Zhang, 2007; Panda, 2009). The Bismuth Sodium Titanate, ($(Bi\ Na)\ TiO_3$) or known as BNT is perovskite structure. Perovskite is a family name of a group of materials of Calcium Titanate ($CaTiO_3$), having the general formula, $ABO_3$. BNT is the most studied in the past because it had high temperature of dielectric constant and it is able to work well without the addition of lead or known as lead-free material. Besides, Bismuth, Bi is known as non-toxic in its oxide forms (Vijayeta et al., 2013).

Besides that, BNT is favorable in the field of lead-free piezo-ceramics due to the high Curie temperature in about $T_c$ ~ 320°C among various lead-free piezoelectric ceramics

materials (Parija et al., 2013b). After that, BNT most literally can be synthesized under ordinary processing conditions. Thus, in order to enhance electrical properties of BNT is either by doping with some suitable rare earth dopants at A- sites or A and B- sites both by mixing them with other $ABO_3$ type compounds, such as $BaTiO_3$ (Vijayeta et al., 2012).

Curie temperature is a temperature at which certain magnetic materials undergo a sharp change in their magnetic properties (Yang et al., 2015). The room temperature is taken to be about 20ºC. BT materials has relatively low Curie temperature ($T_C \sim 120$ºC). The BT material possessed orthorhombic–tetragonal (O-T) phase transition at about 5º and caused a poor stability of temperature in electrical properties (Meera and Yadav, 2013). Thus, it is needed to shift the O-T phase transition away and increase the Curie temperature from application of temperature range. Lead additions can increase the Curie temperature up to about 150°C (Ciceron et al., 2011). However, present of lead can destabilize the low temperature phase transitions. Thus, by adding some of BNT, the Curie temperature can be increased.

Solid state reaction is normally used high sintering temperature whereas the densification process is attained through particle shape that changes without presence of liquid or the particle rearrangement. The grain growth in particles can affect the density of materials because microstructures or polycrystalline ceramics that have been heated at sufficiently high temperatures often shows abnormal grain growth (Veronika, 2013). Thus, binder is believed to be used for shape forming of green body and binds the granules together. In the process of compacting oxide materials, Polyvinyl Alcohol (PVA) binder is the most commonly used among researchers because it has strong affinity of adsorption on oxide particles dispersed in water (Yuan and Li, 2011; Holloway et al., 2013). In this project, a study on difference in concentration of polyvinyl alcohol (PVA) will be used to investigated the effect of binder on structural and dielectric properties of BNT-BT ceramics

and sintering temperature was used to enhance the density and dielectric properties of ceramic. As a result, the improved ceramics is believed to have a good result in microstructure and dielectric properties of BNT-BT. Various composition of samples with different PVA contents will be prepared in this work.

## 1.2 Problem statement

BNT (bismuth sodium titanate) has several poor properties that need to be enhanced by doping the substances with other materials such as rare earth or other perovskite material itself. BNT has high Curie temperature at about $T_c \sim 320°C$ and need to be fabricated at high sintering temperature (Jiang et al., 2013). Dense BNT is difficult to be prepared due to high sintering temperature above 1200$^oC$ that resulted in significant loss of Bismuth, Bi. Thus, at sintering temperature >1000$^oC$, $Bi_2O_3$ (bismuth oxide) and $Na_2O$ (sodium oxide) become volatiles which can caused changes in the stoichiometry. Hence, the volatility issue for BNT process was approached using shorter heating times and lower temperatures for synthesis and sintering (Rodrigo et al., 2017). BT (barium titanate) has a relatively low Curie temperature ($T_c \sim 120^oC$). Hence, it is necessary to be doped with BNT to increase the Curie temperature for further used of BT (Liu et al., 2010). Due to these poor properties of both BNT and BT, the doping of material need to be improved by using PVA binder to make the compaction of BNT-BT more effective. However, excessive used of PVA binder can lead to porosity.

PVA (polyvinyl alcohol) binder is the most commonly used for compaction of oxide materials. PVA possessed a strong affinity of adsorption on oxide particles that dispersed in water. The main used of binders is to bind the granules together and help to improve the green strength and handling of ceramics before sintering. PVA binder has melting point at