IMPACT: International Journal of Research in Applied, Natural and Social Sciences (IMPACT: IJRANSS)
ISSN(E): 2321-8851; ISSN(P): 2347-4580
Vol. 2, Issue 5, May 2014, 37-44

EVOLUTION OF DIELECTRIC CERAMIC $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ (x=0.15) WITH MICROSTRUCTURE AT DIFFERENT SINTERING TEMPERATURES

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ABSTRACT

The doping mechanism of neodymium ion on barium titanate could be promising a new material for applications in miniature microwave technology and mobile communication systems. Microstructural of $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$, with x=0.15 ceramics at different sintering temperatures were investigated. The samples were prepared by the magnetic stirring method and sintered at a temperature range from 600°C to 1300°C. Sintering effects on the crystallite structure and surface morphology were studied and characterized by XRD and FESEM. The transformation of majority of the phase in the system from barium titanate to barium neodymium titanate was confirmed by XRD pattern due to change in sintering temperature. The change in sample densities was determined using Archimede's method. Two activation energies of grain growth were observed by using estimated diffusion process. The activation energies were 0.0698 and 0.3348 eV for low sintering and high sintering temperatures respectively.

KEYWORDS: Evolutions, Microstructure, Surface Morphology, Activation Energy

INTRODUCTION

Miniaturization of electronic components created a new challenge for materials research. To maintain high performance in decreasing the size needs a detailed research on the microstructure and the properties of the materials at nanoscale. The processing of the materials is one of the factors that affect the quality of the materials. There is increased interest to study the materials properties by using magnetic stirring method. Pornprasertsuk et al. [1] reported that magnetic stirring method with a suitable solvent can help to reduce the powder loss during the mixing process compared to solid state reaction method. $BaTiO_3$ is a well known material that has high dielectric constant. However, the properties of doping ion into $BaTiO_3$ are still not clear especially in the sintering process. Kaur et al. [2] found that $BaTiO_3$ ceramic doped with rare-earth element enhanced its dielectric properties.

Snashall [3] reported that nanosize barium neodymium titanate improved processing and sintering time, and provided excellent microwave dielectric properties. Ohsato and Imaeda [4] presented that Sm and Nd doped $BaTiO_3$ ceramics are most suitable for microwave applications such as sensors, memory device, and spintronics [5] due to their good stability and high dielectric constant. The thermal effect does not only influence the microstructure, but also dielectric properties of the materials.

The best sintering temperature for materials is always a question mark for the materials researchers. In the present work, Nd ions was doped on $BaTiO_3$, and the change of microstructure of tungsten bronze type solid solutions $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ by sintering effect was investigated.

In this research, barium and neodymium were selected as electropositive metal, and titanium was chosen as transition metal. As mentioned above, Ba^{2+} and Nd^{3+} are divalent and trivalent cationic form of barium and neodymium respectively. In order to achieve the electrostatic stability, three Ba^{2+} ions can be replaced by two Nd^{3+} ions and a vacancy. The chemical reaction is as follows,

$$3Ba^{2+} \xleftarrow[electrostatic\ stability]{} 2Nd^{3+} + vacancy \quad (1)$$

METHODS

The starting materials used in this research were high purity and nano $BaCO_3$ (99.9%, below 80 nm), Nd_2O_3 (99.9%, 30-45 nm), and TiO_2 (100%, 50 nm) powders. The samples were prepared by magnetic stirring method. The raw materials were weighed by Shimadzu Analytical Balance AY220 according to compositional formula $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ with x=0.15, and mixed together with ethanol using WiseStir MSH-20D Hotplate Magnetic Stirrer. The liquid mixtures were then milled for 24 hours at 30°C with milling speed of 900 rpm in order to get homogenous solutions.

The liquid mixtures were dried for 24 hours. The mixtures were then compacted into pellets using Carver manual pellet press with pressure of 216 MPa. Each pellet has diameter of 17 mm and thickness of 2.8 mm. The final pellets were sintered for 3 hours in air in a programmable furnace at different sintering temperature in the range from 600°C to 1300°C. The density of the samples was measured by Electronic Densimeter MD-300S which adopted Archimede's principle after each sintering process. The crystalline structure and the formation of the samples were determined by X-ray diffractometer (Phillips Expert Pro PW3040) with CuKα radiation (λ=1.5404Å) in the range of 4 to 90° of Bragg's angles 2θ. The surface morphology of the samples at room temperature was observed by FESEM for every sintering process.

RESULTS AND DISCUSSIONS

Figure 1 showed the XRD pattern of the powders and sintered BNT ceramics with compositional formula $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ with x=0.15 at different sintering temperatures. The results revealed that the powders after milling process presented some individual phases indicating there is low chemical reaction occurring between the components without heating. Small amount of BaO phases were detected in the powders due to the release of CO_2 gaseous from $BaCO_3$ powders. A broad peak was observed from the ceramic sintered at 600°C showing that the ceramic underwent thermal reaction process. The formation of barium titanium oxide at 600°C clearly explained the diminishing of the barium oxide which appeared before the sintering process. $Nd(TiO_3)$ phase was detected at 700 and 800°C sintering temperatures. However, it can be converted to $Nd_2Ti_2O_7$ phase by interaction with BaO from $BaCO_3$ at 900°C.

This is due to the decomposition temperature of $BaCO_3$ at 811°C. The pattern of tungsten bronze structure of BNT can first be observed at 1000°C with some secondary phases. These secondary phases disappeared with increasing sintering temperature. The tungsten bronze type structure of BNT ceramic was fully formed at 1200°C. It clearly shows that the secondary phase of $BaTiO_3$ presented at lower temperature has diminished. The reduction of other phases apparently indicated the increment of the formation of complex tungsten bronze ceramic.

The XRD pattern of the sample was analyzed and showed slightly similar to $BaNd_2Ti_5O_{14}$ phase with orthorhombic crystalline structure. This can be double confirmed by XRD pattern of the ceramic sintered at

1300°C showing similar patterns to the 1200°C, except some of the very small minor peaks have disappeared. It can be concluded that Nd^{3+} ions that filled in A1 site of the tungsten bronze type structure is a thermal driven process due to its high melting and boiling points. This is an interesting finding that the peaks of BNT ceramic shifted to the larger angle from 1000°C to 1100°C, but shifted to lower angle at higher sintering temperatures. This shifting behavior will possibly influence the dielectric properties of BNT ceramic. However, the peaks of the samples became broader and have higher intensity as sintering temperature was increased. This indicated more BNT compounds were formed at higher temperature.

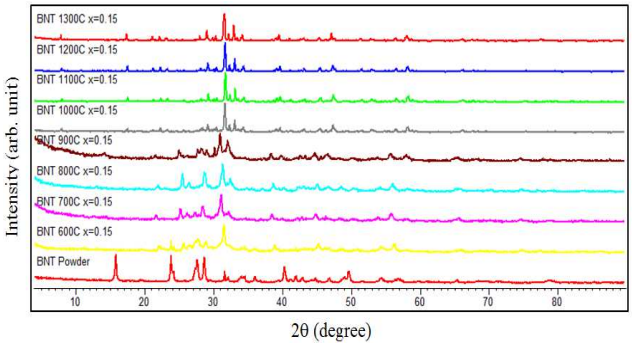


Figure 1: XRD Pattern of BNT Ceramic with x=0.15 for All Sintering Temperatures

The bulk density of barium neodymium titanate with composition x=0.15 as a function of sintering temperature is shown in Figure 2. The results showed that the density of BNT ceramic initially decreases from the starting sintering temperature to 800°C. The decrement of the density at initial stage was due to the mass loss during the sintering process. This was clearly shown in Figure 3 that the mass loss decreases rapidly from 600 to 800°C. Density is proportional to the mass of the object, and inversely proportional to its volume. The reduction in the mass is an important factor that affects the density when there is not much reaction occurring inside the material during the low sintering temperature. The low reaction occurred with less heat treatment of the BNT ceramics was confirmed by XRD results.

On the other hand, a small density peak was observed at 900°C sintering temperature. The mass loss at 900°C is similar to 800°C indicating the chemical decomposition of $BaCO_3$ and formation of $Nd_2Ti_2O_7$ phases. The former phase that has low density and diminished in the compound is the reason for the increment. The later phase which has high density built up the bulk density of the compound. The density of BNT ceramic sintered at 1000°C showed a decrease again due to the starting of the formation of low density of $BaNd_2Ti_5O_{14}$ phase. Furthermore, the density increase rapidly from 1100°C to 1300°C indicating the ceramic became denser. This behavior was described in the shrinkage of the ceramics due to high sintering temperature and almost constant mass loss.

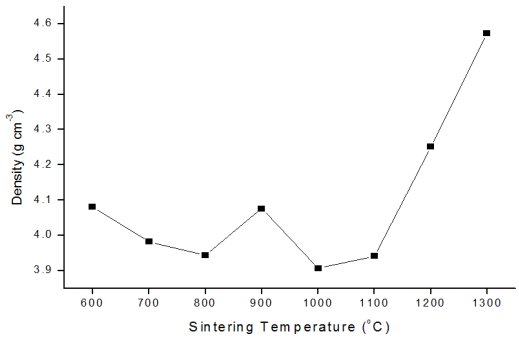


Figure 2: Density of BNT Ceramic with x=0.15 at Different Sintering Temperature

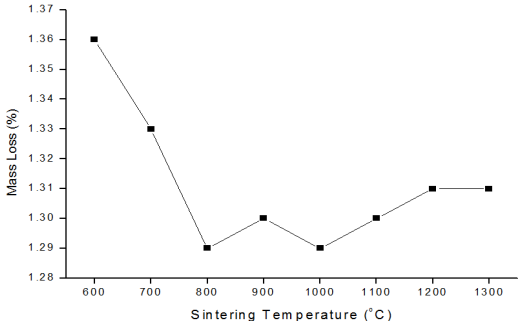


Figure 3: Percentage of Mass Loss of BNT Ceramic with x=0.15 at Different Sintering Temperature

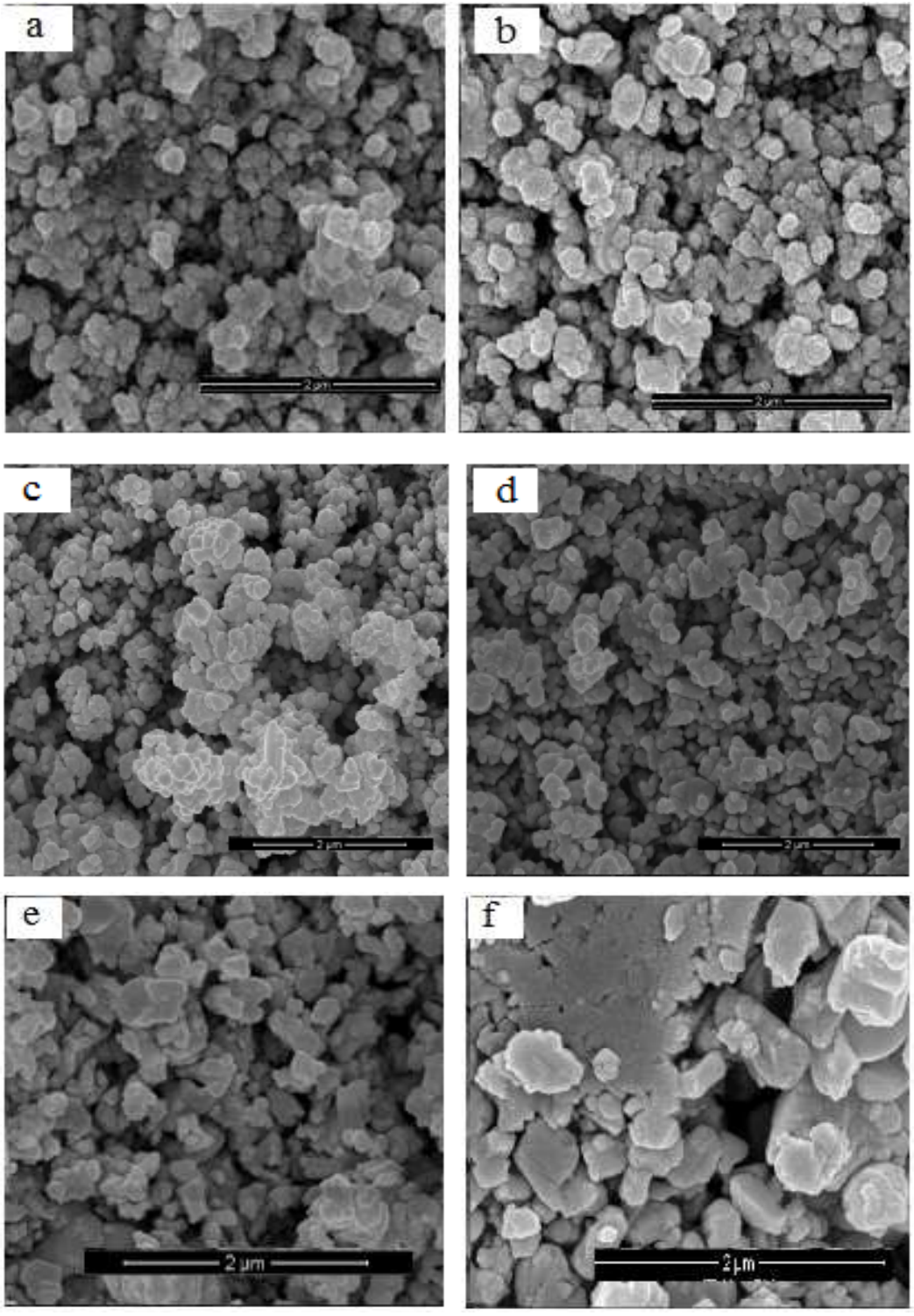
The surface morphology of all sintered ceramics was shown in Figure 4. The estimated grain size was analyzed using linear intercept method by choosing 200 grains inside the sample. The results showed that the grain size increases with increasing sintering temperature. This is very common for ceramic behavior. As shown in Figure 4 (a), the grains inside the ceramic are very small; this is because the particles size of the raw powders used are in the nano range. Normally, a grain is made up by large amount of particles. The combination of particles also will define the shape of the grain. It can be observed that the ceramic sintered at 600°C has the grains almost spherical in shape. Having a lot of small individual grains means that the particles are only connected in a short range. This also indicated that the grains did not interact with the grain surrounding.

This sample showed some pores on the surface. The porous surface of the sample was related to the mass loss during the sintering process. At sintering temperature 700°C, agglomeration occurred due to the combination of the grains, and the grain size became bigger. The particles were initially contacted and some were lost during the process. The necking between the grains also can be seen in Figure 4 (b). The necking behavior can be explained by interaction of two close neighboring grains. Two grains were merged together by diminishing part of the grain boundaries. The ceramic sintered at 800°C showed large agglomerations occurring after the necking process. It can be observed in the agglomerated area that there are many grains combined together. This showed that there is chemical reaction happening inside the compound. The grain diffused to other grains resulting in long range connection.

These three microstructures showed the ceramics only underwent the starting sintering stage which is the adhesion stage. At adhesion stage, the shape of the grain can be deformed. By further increasing the temperature, the agglomeration process was stopped; the shape of the grain can be clearly seen in Figure 4 (d). When the sintering temperature is applied at 1000°C, grain shape of the ceramic is changed to block shape. The transformation of the grain shape can be related to the diffusion of the neodymium ion into the system. This indicated the low formation of the BNT ceramic. The surface characteristic of sample sintered at 1100°C was shown in Figure 4 (f). The grains of the sample have the shape of blocks and large agglomerated grains.

This type of microstructure can be considered as the intermediate sintering stage. The coarsening behavior of the sample is more dominant than the densification due to the pore being larger and rounded the grains. In addition, the measured density of this sintered sample is quite low that also supported the coarsening effect. In view of higher sintering temperature, BNT ceramic sintered at 1200°C showed the grains have rectangular shape. The block shape of the ceramic was elongated by increasing sintering temperature. The behavior can be considered as the thermal expansion and the combination of the grains. Figure 4 (g) showed that the densification is more in favor than coarsening.

This is because the pore size was minimized and the grain size increased. This also indicated that the sample approached full densification. However, some of agglomerated grains were also observed from the results. Figure 4 (h) revealed the ceramic sintered at 1300°C are rectangular shapes. As can be seen from the result, the pore shrunk with increasing grain size showing that this ceramic reached the final sintering stage. The grain boundaries of this ceramic also can be seen very clearly. The full densification of BNT ceramic was demonstrated in this sample. According to the measured density results, this sintered ceramic obtained the highest density among the samples.



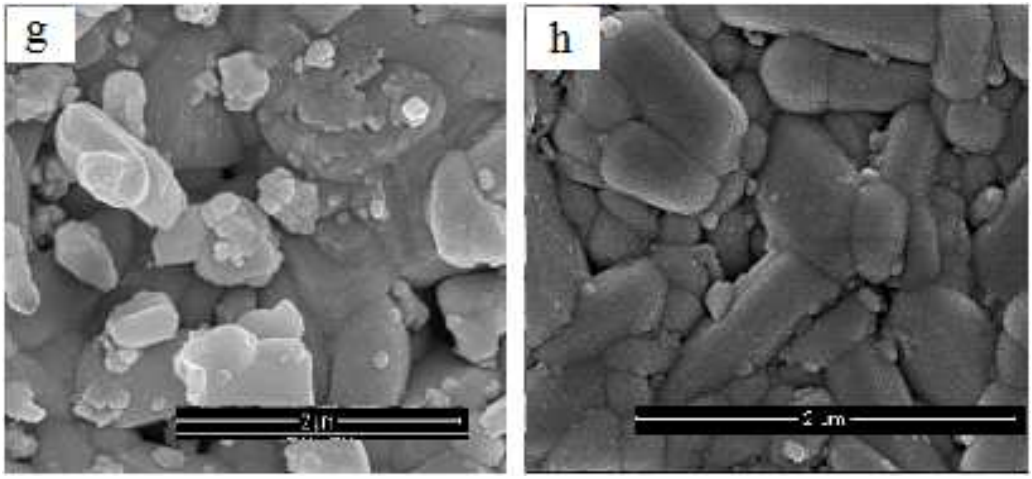


Figure 4: Microstructure of BNT Ceramic for All Sintering Temperatures; (a) 600°C, (b) 700°C, (c) 800°C, (d) 900°C, (e) 1000°C, (f) 1100°C, (g) 1200°C, and (h) 1300°C

Table 1: Microstructure and Dielectric Properties of BNT Ceramic at All Sintering Temperatures

Sintering Temperature (°C)	Average Grain Size (um)	Density (g cm^{-3})
600	0.131	4.08
700	0.185	3.982
800	0.197	3.944
900	0.207	4.076
1000	0.322	3.907
1100	0.456	3.941
1200	0.687	4.251
1300	0.754	4.572

The average grain size as a function of sintering temperature can be used to predict the activation energy of grain growth of the materials [6]. It could be calculated by using equation (2).

$$\log D = \log D_o + \frac{Q_a}{2.3R}\left(\frac{1}{T}\right) \quad (2)$$

Where D is the average grain size of ceramic, Q_a is activation energy of grain growth, D_o is temperature independent grain size, R is gas constant, and T is sintering temperature. As can be seen from Figure 5, two activation energies can be found from 600 to 1300°C. This is because there are two different slopes in the range of the sintering temperature.

For the first activation energy of grain growth, the slope obtained is the low sintering region which is from 600 to 900°C with the value of 0.0698 eV. It can be seen from Figures 4(a) to (d) that the rate of grain growth is smaller. The small value of activation energy showed the diffusive motion of atoms in the ceramic is high. In view of the electrical properties, the potential barrier of an electron to jump to other state is low in these ceramics.

Therefore, the diffusive motions provided the conducting behavior which can be seen in the dielectric loss factor. On the other hand, the high temperature sintered ceramics obtained higher activation energy of 0.3348 eV where the grain growth is faster. Contrast to low sintered ceramics, the diffusive motion is low, and the potential barrier is high. In order to

excite the electron to cross over the barrier, a large amount of energy should be applied. The rapid increase in the grain size for high temperature sintered ceramics leads it to insulating properties.

The different activation energies can also be used to distinguish the formation of the tungsten bronze type structure of BNT ceramic. As indicated from the results, large value of activation for high sintered ceramics showed the material is no more conducting and have insulating properties.

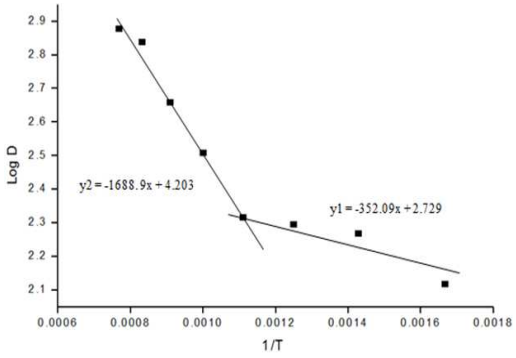


Figure 5: Activation Energies of Grain Growth

CONCLUSIONS

In conclusion, BNT with x=0.15 ceramics were successfully fabricated using wet solid state reaction method. The formation of BNT ceramic started at 1000°C, and the densification could be achieved at 1300°C. The increment of grain size can be controlled by thermal energy such as sintering process. BNT ceramic sintered at 1300°C obtained the grain in rectangular shape. The activation energy was found to be increased from low to high sintering temperature. This also indicated that the diffusive motion of the atoms showed smaller in tungsten bronze structure.

ACKNOWLEDGEMENTS

This research was financially supported from the Research University Grant Scheme (RUGS) Project No.: 05-02-12-2180RU, Universiti Putra Malaysia (UPM). The authors also acknowledged the Department of Physics, Faculty of Science, UPM and Institute of Advanced Technology (ITMA), UPM.

REFERENCES

1. Pornprasertsuk, R., et al. (2012). Preparation of doped $BaZrO_3$ and $BaCeO_3$ from nanopowders. *International Journal of Precision Engineering and Manufacturing, 13(10)*, 1813-1819.
2. Kaur, D., et al. (2006). Processing, dielectric behavior and conductivity of some complex tungsten-bronze dielectric ceramics. *Journal of Ceramic Processing & Research, 7(1)*, 31-36.
3. Snashall, et al. (2012). Phase analysis and microwave dielectric properties of $BaO–Nd_2O_3–5TiO_2$ composite ceramics using variable size TiO_2 reagents. *Ceramics International, 38, Supplement 1(0)*, S153-S157.
4. Ohsato, H., & Imaeda, M. (2003). The quality factor of the microwave dielectric materials based on the crystal structure—as an example: The $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = rare earth) solid solutions. *Materials Chemistry and Physics, 79(2–3)*, 208-212.

5. Ohsato, H. (2001). Science of tungstenbronze-type like $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R=rare earth) microwave dielectric solid solutions. *Journal of the European Ceramic Society, 21(15)*, 2703-2711.

6. Callister, W.D., & Rethwisch, D.G. (2010) *Materials science and engineering: an introduction 8th edition*. John Wiley & Sons, Inc: United States, America, pp. 133.