The effects of sintering temperature on dielectric constant of Barium Titanate (BaTiO$_3$)

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Abstract. Barium Titanate (BT) has been synthesized using solid-state reaction method. Raw materials are Barium Carbonate (BaCO$_3$) and Titanium Dioxide (TiO$_2$). These materials are mixed for 6 h and sintered at a temperature of 1000°C, 1100°C, and 1200°C for 2 h. The sintering temperature was varied to investigate its effects on microstructure and dielectric constant of BT. The XRD patterns showed that BT becomes homogenous, with the large lattice parameter as the increase of sintering temperature. The crystal structure of BT is tetragonal. The crystalline size and crystallinity of BT at a sintering temperature of 1000°C are 37 nm and 97%. Those values for BT at a sintering temperature of 1100°C are 38 nm and 96%. At a sintering temperature of 1200°C, the values are 41 nm and 97%. The dielectric constant of BT at a sintering temperature of 1000°C, 1100°C, and 1200°C are 148, 163, and 185, respectively. It can be concluded that sintering temperature affects microstructure and dielectric constant of BT. High sintering temperature produces a high dielectric constant of BT. It indicates that crystalline size increases.

1. Introduction

The ferroelectric material is a material which undergoes spontaneous polarization without subjected to an electric field [1-2]. In its development, ferroelectric materials become more important as main materials in electronic devices [3]. Barium Titanate (BT) or BT is one of the ferroelectric materials with a high dielectric constant which is most commonly used in the electronic industries. It used to the main materials manufacture of electronic components such as capacitors, multilayer capacitor (MMLc), and energy storage devices [1,4,5].

Curie temperature ($T_C$) of BT is 120°C. When the condition is under $T_C$, BT materials are in ferroelectric phase and dielectric constant increases with increasing temperature, while the condition is above $T_C$, these materials are in paraelectric phase which dielectric constant getting down as temperature increases [1,6]. Ferroelectric phase has a tetragonal crystal, and paraelectric phase has cube crystal [2,7]. The change of BT microstructure affects properties of dielectric while the change of structural of BT is affected by the change of temperature on its fabrication [7].

Several methods which are used to synthesize BT are a sol-gel method, hydrothermal, co-precipitation and solid state reaction method. Compared with other methods, solid state reaction is easy, simple, and low cost. Gomez et al., 2000; Micleaet al., 2007; Pavlovic et al, 2008; Kim et al., 2009;
Othman et al., 2014 using solid state reaction method to fabricate BaTiO3 [8-12]. Their researchers focus on mixing process using ball mill or milling with mixing time variation. The sintering temperature is done under a temperature of 1000°C approximately. XRD patterns of their fabrication showed that there are still peaks of raw materials (BaCO$_3$ and TiO$_2$) with high intensity.

In this paper, BT materials were synthesized using solid-state reaction method. BT was sintered at temperatures of 1000°C, 1100°C, and 1200°C. Its aims are to determine the effects of sintering temperatures on microstructure and dielectric constant of BT.

2. Experiment Method
Barium titanate ceramics has been synthesized using solid-state reaction method. Raw materials of BaCO$_3$ and TiO$_2$ were weighed according to the Equation (1).

$$\text{BaCO}_3 + \text{TiO}_2 \rightarrow \text{BaTiO}_3 + \text{CO}_2$$  \hspace{1cm} (1)

Raw materials were mixed for 6 h in a mortar using the mechanical technique, pressed to form bulk, and sintered for 2 h at a temperature of 1000°C, 1100°C, and 1200°C.

Samples characterization used X-Ray Diffraction (XRD) instrument by Bruker D8 Advance with $\lambda_{\text{Cu}}$ is 1.54056 Å to determine its microstructure. Crystalline size and crystallinity were found using Equation (2) and Equation (3).

$$D = \frac{k\lambda}{B\cos\theta}$$  \hspace{1cm} (2)

$$\text{Crystallinity} = \frac{I_{\text{maxpeak}} - I_{\text{minpeak}}}{I_{\text{maxpeak}}}$$  \hspace{1cm} (3)

$D$ is the crystalline size, $\beta$ is FWHM, $\lambda$ is the wavelength of the X-ray source, $\theta$ is the angle of diffraction peaks, and $k$ is Scherer constant. Scherer constant for cube crystal is 0.94, whereas the other one is 1 [13,14].

Samples also were characterized using LCR-800 Series instrument by Gwinstek. The calculation of dielectric constant is according to Equation (4).

$$\varepsilon = \frac{Cd}{\varepsilon_o A}$$  \hspace{1cm} (4)

$K$ is dielectric constant of BT, $C$ is capacitance, $d$ is thickness of dielectric material (thickness of bulk BT), $A$ is surface area of bulk BT, and $\varepsilon_o$ is permittivity of vacuum (8.85 x 10$^{-12}$ F/m) [15].

3. Results and Discussion
The result of characterization using XRD is shown by Figure 1. XRD patterns were matched with International Commission Data Diffraction (ICDD) database and then How the peaks correspond to the peaks of BT with database number #752116. The peaks with the mark (*) are BaCO$_3$ with database number #5225. They indicate that mixture of BT was still not homogeneous, or raw materials have not reacted perfectly. Increasing temperature does not affect the diffraction angle but affects the peaks of intensity. The peaks of BaCO$_3$ become lower which indicating the higher temperature made BT more homogenous. Due to high sintering temperature provides high energy for raw materials to react (through diffusion), then the mixture becomes more homogenous.

XRD patterns were analyzed using General Structure Analysis System software (GSAS) with Rietveld method to ensure the peaks of XRD pattern is BT. The results of the refinement process using GSAS software shown in Figure 2. The black graph is a graph of data obtained from XRD (observed data) that was incorporated into the GSAS software. The red graph is a graph from ICDD data (data calculation). Blue line is the difference between observed data and calculation data. The green line
is the background. And the orange line is the Chi-square ($\chi^2$). If the data calculation closer to or in agreement with the observed data, Chi-Square line ($\chi^2$) will be straight, and the value will be smaller or close to 1.

The results of refinement process show that the initial allegation is true, that those peaks belong to BT with tetragonal crystal structure which $a=b\neq c$ and $\alpha=\beta=\gamma=90^\circ$. Chi-square ($\chi^2$) of refinement results
of BT samples at sintering temperature of 1000°C, 1100°C, and 1200°C, are 6.065; 5.910; and 12.880, respectively.

**Table 1.** Lattice parameters from the results of refinement process using GSAS software

| Sintering temperature (°C) | Lattice parameter (Å) | \(a=b\) | \(c\) |
|---------------------------|----------------------|-------|------|
| 1000                      | 3.983                | 4.009 |
| 1100                      | 3.987                | 4.015 |
| 1200                      | 3.978                | 4.024 |

**Table 2.** Crystalline size at plane orientation of (1 0 1) and crystallinity of BT with variation of sintering temperature

| Sintering temperature (°C) | Crystalline size (nm) | Crystallinity (%) |
|---------------------------|-----------------------|-------------------|
| 1000                      | 37                    | 97                |
| 1100                      | 38                    | 96                |
| 1200                      | 41                    | 97                |

The results of refinement process confirm lattice parameter of BT. Table 1 shows the lattice parameter of BT, which is influenced by sintering temperature. The lattice parameters of BT tend increasingly longer when the sintering temperature increased.

The peaks of XRD pattern can be used to calculate FWHM values. Then, it used to calculate the crystallite size and crystallinity of BT crystal using Eq. 2 and Eq. 3. Table 2 shows the effect of sintering temperature on the crystalline size and crystallinity. The crystalline size of BT increases as the higher sintering temperature. Sintering temperature gives energy to the atoms diffuse and agglomerates. That energy becomes bigger when the sintering temperature increased, and then more atoms agglomerate, thus, the crystalline size becomes larger [16]. That is why BT’s lattice parameter tends increasingly longer.

The regularity of the atomic arrangement of materials is expressed by crystallinity. Crystallinity is influenced by sintering temperature. The higher sintering temperature causes the energy that is received by atoms to become larger (diffusion rate becomes faster) so that the bond of atoms become strong and regular. The high value of crystallinity shows that atoms bonding are robust and regular. The crystallinity values of BT shown in Table 2.

**Figure 3.** The effect of frequency on dielectric constant of with sintering temperature variation
Capacitance was obtained from characterization using LCR meter instrument. It used to calculate dielectric constant using Eq. 4. Frequency was varied at 0.1 KHz to 50 KHz to find out its effect on dielectric constant. Figure 3 is the graph of the dielectric constant of BT to the change of frequency with variation sintering temperature. The frequency affects capacitance; the higher frequency makes capacitance become lower so that dielectric constant is so. The dielectric constant of ferroelectric materials will be lower as increasing of frequency but tends to be more stable [1].

Increasing of sintering temperature causes the dielectric constant of BT increases. Dielectric constant values of BT, which are measured at a frequency of 1 KHz for samples at a sintering temperature of 1000°C, 1100°C, and 1200°C are 148, 163, and 185, respectively. In ferroelectric materials crystals, there are domains. Domain is the area which has polarization with the same direction. Ferroelectric domains become larger as the larger crystalline size, thus, the polarization becomes stronger. It indicates that dielectric constant of BT increases.

4. Conclusions

BT was synthesized using solid-state reaction method at a sintering temperature of 1000°C, 1100°C, and 1200°C. The sintering temperature affects microstructure and dielectric constant of BT. The higher sintering temperature made a change in lattice parameter. The crystallinity of BT crystals is high for each sintering temperature. The higher sintering temperature made dielectric constant of BT becomes higher because it is considered that the crystalline size becomes larger.

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6. References

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