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The Particle and Crystallite Size Analysis of $BaTiO_3$ Produced by Conventional Solid-state Reaction Process

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Abstract. Synthesis of piezoelectric material $BaTiO_3$ was done by conventional solid-state reaction process, is the process that combine betwen mechanical alloying and sintering process with $BaCO_3$ and TiO_2 precursors. Different samples were prepared by using vibratory ball milling with ball to powder ratio 10:1 and varying the milling time from 1 h to 60 h. The milled powders were investigated with particle size analyzer (PSA). The sintering process was up to 1200^{o}C and the products were examined by X-Ray Diffractometer (XRD) to analyze phase formation and crystallite size. The results showed that the particle size decreases as the function of milling time and reduced to 0,8 µm at 60 h. Single-phase $BaTiO_3$ were succesfully achieved at 1100^{o}C for 10 h holding time of sintering temperature. The crystallite size of $BaTiO_3$ were sintered at 1200^{o}C for 10 h holding time is 106 nm. Crystallite size of $BaTiO_3$ increase as function of temperature and holding time of sintering process.

INTRODUCTION

Barium titanate ($BaTiO_3$) is the first ferroelectric material with an ABO_3 compound structure called perovskite and is a good candidate for a variety of technical applications because it has superior dielectric, ferroelectric and piezoelectric properties [1-4]. According to Stojanovic [5], the *piezoelectric* material can be utilized as *ultrasonic transducers, piezoelectric devices, electrostrictive actuators, relaxors, positive temperature coefficient of resistivity* and other material sensors. $BaTiO_3$ has a cubic structure at above its Curie temperature (120ºC) until 1460ºC [1]. $BaTiO_3$ with perovskite structure is capable of high dielectric constant value[2,6] [2, 6]. This is due to an electric *dipole* caused by the asymmetric location of positive and negative charges when subjected to external force [7-9]. The piezoelectric properties of $BaTiO_3$ can significantly increase if the size of particle and crystallite is made up to the scale of the nanoparticles and nanocrystalline [10].

$BaTiO_3$ can be synthesized from the mixture of $BaCo_3$ and TiO_2 compounds which can be conducted through the mechanical alloying technique [11-13]. This method is commonly used because it has the advantage of cheaper operating costs, more efficient and having the ability to mass produce the material compared with other methods such as *sol-gel* and hydrothermal [14]. The synthesis method of manufacturing BaTiO3 depends on its characteristics and final application, and the method used has a significant influence on the structure and material property of $BaTiO_3$ [1]. The process is then followed by *mechanical alloying* or heating process (sintering) resulting in a *single* phase $BaTiO_3$.

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The synthesis process through the mechanical alloying and *sintering* is expected to result in *piezoelectric* material, $BaTiO_3$, with nanoparticle and nanocrystallite size [15,16]. Varying the *milling* time, temperatures and holding time of *sintering* can produce nanometre - scale particles and crystallites. There were similar researchs, but the difference betwen recent research is on this research the mechanical alloying use the vibratory ball milling for obtain $BaTiO_3$. The objective of this study was to investigate the effect of the length of the mechanical alloying process to the reduction of the size of particle and crystallite, as well as the effect of sintering temperature and holding time on the phase formation and growth of $BaTiO_3$ crystallites.

EXPERIMENTS

The production of $BaTiO_3$ using a mixture of basic compound of $BaCO_3$ and TiO_2 has a purity more than 98%; then it was calculated using stoichiometry to obtain the amount of basic compound in the mixture. The process of mixing both basic compound powder through the mechanical alloying was conducted using type vibratory ball milling for 60 hours with a weight ratio of steel balls to the material that is mixed at 10:1. The weight of particle size after the mechanical alloying process was characterized by using *Particle Size Analyser* (PSA) Coulter LS100. Phase analysis and crystallite size of milled powders were carried out using the Philips X-ray diffractometer equipped. The X-ray diffraction patterns were recorded by "step-scan" method in 2 θ range from 20° to 100°.

After mechanical alloying, sintering process was conducted using Thermolyne furnace 46100 at 1100 ˚C and 1200 ˚C with a holding time of 0, 3, 5 and 10 hours in under atmosphere pressure. Then using the same XRD, to characterize the phase formation and growth of crystallite size of $BaTiO_3$. The Rietveld analysis was performed applying High Score Plus program that is an updated version for Rietveld refinement with PC and mainframe computers. The pseudo-Voigt function was used in the describing of diffraction line profiles at Rietveld refinement. The crystallite size and lattice distortions for $BaCO_3$ and TiO_2 also $BaTiO_3$ phases were estimated using Williamson-Hall method [17]

RESULTS AND DISCUSSION

The results of PSA (Particle Size Analyzer) testing to the particle size of the $BaCO_3$ and TiO_2 powder revealed that the average of the initial size of the $BaCO_3$ particle was 1.979 µm and TiO_2 was 0,795 µm. Figure 1 shows X-ray diffraction pattern for $BaCO_3$ and TiO_2. The diffraction pattern of $BaCO_3$ and TiO_2 on Fig. 1 showed congruity respectively with *Inorganic Crystal Structure Database* (ICSD) number 98-005-6100 and 98-002-4276.

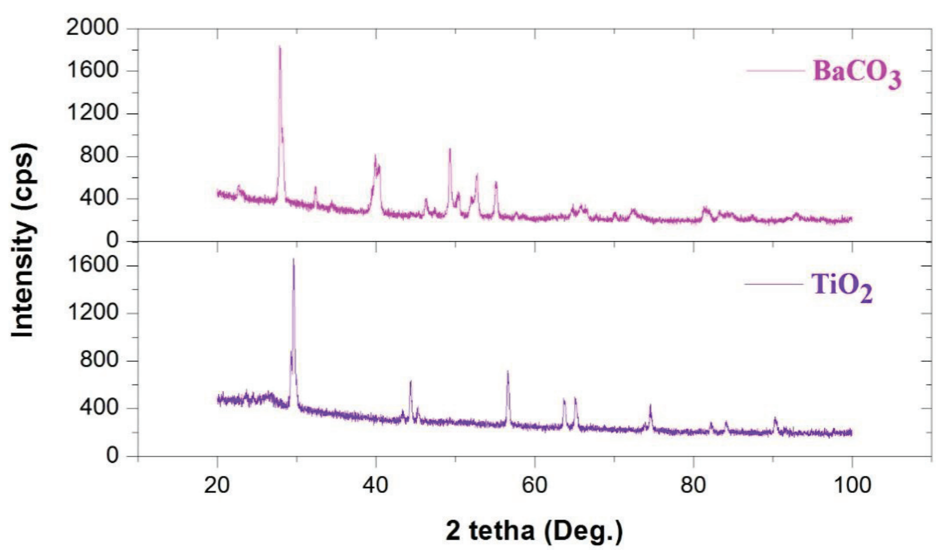

FIGURE 1. X-ray diffraction pattern of $BaCO_3$ and TiO_2.

The results of PSA testing after 60-hour milling is shown in Fig. 2. Figure 2 illustrates that the mixing of the two compounds at an early stage lead to the increase of particle size, during which the size of material increased from 4.7 to 17 µm at the 1-10 hour mixing, the core compounds experienced cold weld, namely the integration of the two particles of the basic compounds to form a close bond between the particles as a consequence of the ball mill impact.

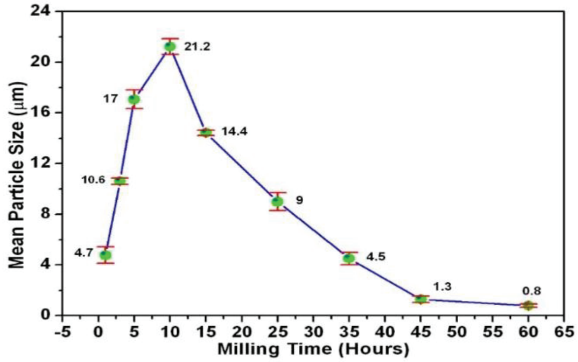

FIGURE 2. The mean particle size of $BaCO_3$ and TiO_2 mixture as a function of milling time.

The impact between ball mills during process continuously occurred. After 1 – 10 hour mixing, both basic compounds formed laminated powder until reaching maximum size 21,2 µm at the milling time of 10 hours [14]. At the 10 hour mixing, the material has reached the homogenization into one alloy, and if the process was continued then mix the two basic compounds, $BaCO_3 + TiO_2$ suffered from embrittlement. Then at the 10 - 45 hour milling time, the mixture entered the third stage which was the stage of continuous *fracture* due to continuous embrittlement of material. It led to significant decrease in size from 21,2 to 1,3 µm. In the third phase, the materials underwent deformation. When the third phase, the continuous impact was given until it reached 60 hours which lead to the final size of the material, 0,8 µm.

Figure 3 shows the X-ray diffraction pattern of a mixture of $BaCO_3$ and TiO_2 which has been milled for 60 hours, where the process of mechanical alloying did not change the diffraction pattern of both compounds. The resulting peak shape can still be identified clearly that the material did not change its phase mixture which is $BaCO_3$ and TiO_2. Based on the form of x-ray diffraction pattern in Fig. 3, the value of the average crystallite size can be seen in Fig. 4.

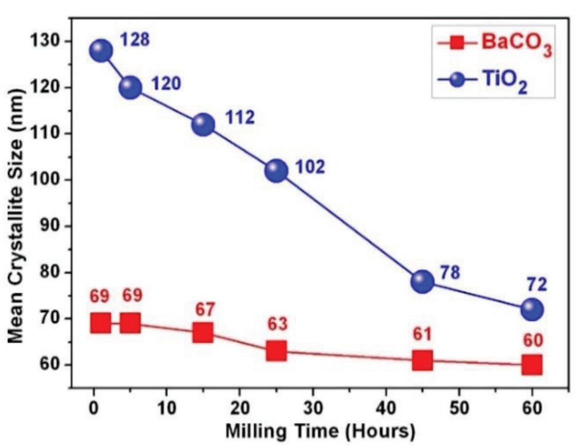

FIGURE 3. *X-Ray* diffraction patterns in the mixture of $BaCO_3 + TiO_2$ on some variation of milling time.

Figure 4 shows that the process of mechanical alloying for 60 hours in a mixture of $BaCO_3$ and TiO_2 lead to a decline in the value of the average crystallite size. The average size of the $BaCO_3$ crystallites decreased not so significantly exponentially with time. In contrast to $BaCO_3$, after mechanical alloying for 60 hours, the crystallite size of TiO_2 decreased significantly, which is about 2 times smaller. It shows that the process of milling up to 60 hours resulted in a more brittle and easily shattered TiO_2 when compared with $BaCO_3$.

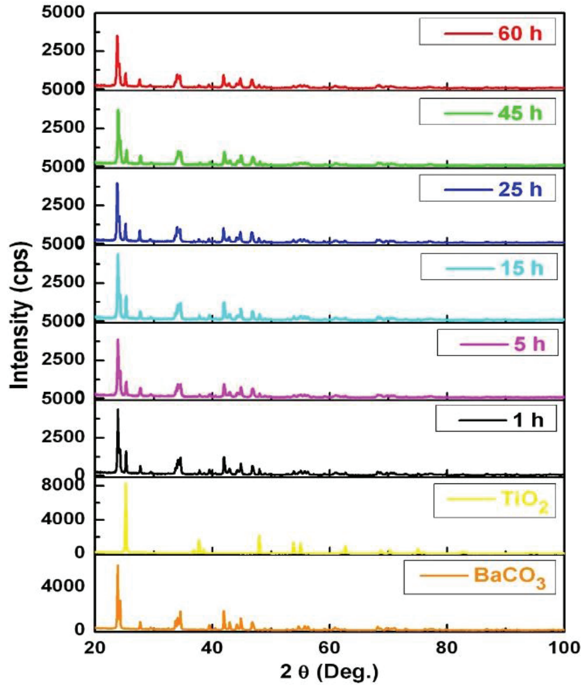

FIGURE 4. The average crystallite size of the mixture $BaCO_3 + TiO_2$.

Figure 5 reveals that diffraction patterns of the mixture of the $BaCO_3 + TiO_2$ samples which has experienced sintering process at 1100 ˚C for 0, 3, 5 and 10 hours. At 1100 ˚C with a holding time 0, 3 and 5 hours, the single phase $BaTiO_3$ has not yet been formed where there is still another phase that is present, $BaCO_3$. Single phase $BaTiO_3$ with tetragonal *perovskite* crystal *structure* was formed after sintering at 1100 °C for 10 hours.

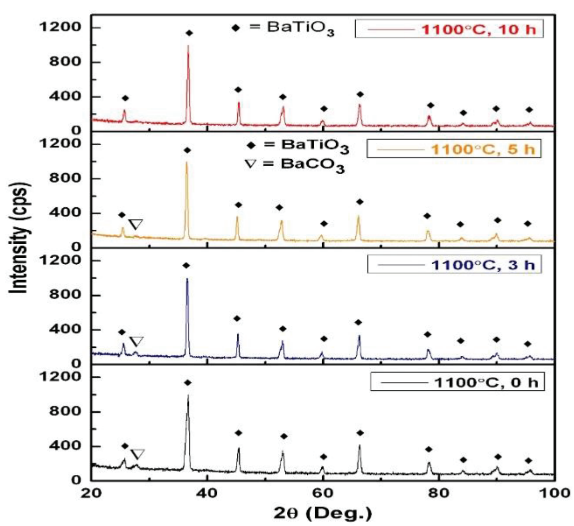

FIGURE 5. *X-ray* diffraction pattern of the powder mixture $BaCO_3 + TiO_2$ that the *sintering* temperature 1100 ˚ C for 0, 3, 5 and 10 hours.

X-ray diffraction pattern of the sample which has undergone Sintering process at 1100^{o}C for 1 hour matched with the data based on the diffraction pattern on Inorganic Crystal Structure Database (ICSD) number 98-007-

3644. Based on Fig. 5, it can be concluded that in addition to temperature High (1100 °C) during the sintering process, it also takes a relatively long holding times (10 hours) to produce a single phase $BaTiO_3$.

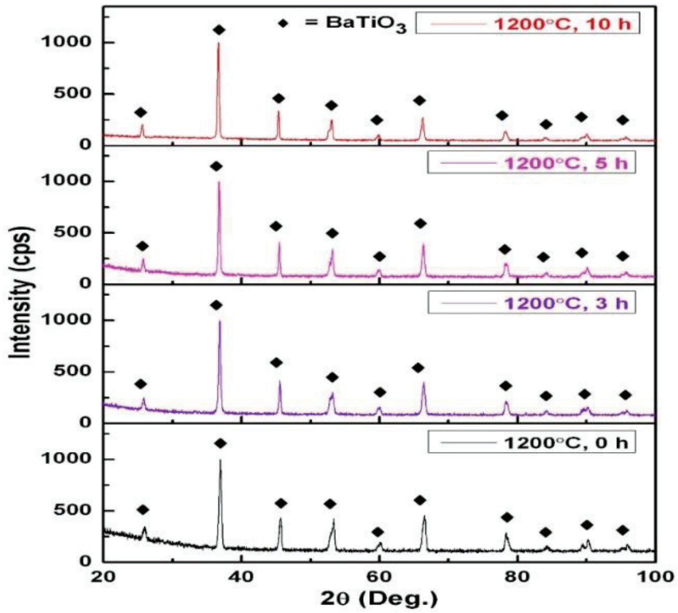

FIGURE 6. *X-ray* diffraction pattern of the powder mixture of $BaCO_3 + TiO_2$ at the *sintering* temperature 1200° C for 0, 3, 5 and 10 hours.

Figure 6 shows the X-ray diffraction pattern of the sample mixture of $BaCO_3 + TiO_2$ which underwent *sintering* process at temperature 1200°C for 0, 3, 5 and 10 hours, where a single phase $BaTiO_3$ was fully formed. The crystal structure of single phase $BaTiO_3$ is *tetragonal perovskite*, which is similar to the result at 1100°C with a 10-hour holding time. The structure matches with the $BaTiO_3$ that can be used in various applications. Based on the x-ray diffraction patterns in Figure 5 and 6, the average size of crystallites of each phase can be found, where the result is shown in Fig. 7. In the same holding time which is 0 hours, the average size of $BaTiO_3$ crystallites was 24 nm and 33 nm after the sintering process. At 1000°C sintering temperature with the holding time of 10 hours, the average size of $BaTiO_3$ crystallites grew significantly into 46 nm and 106 nm at 1200°C

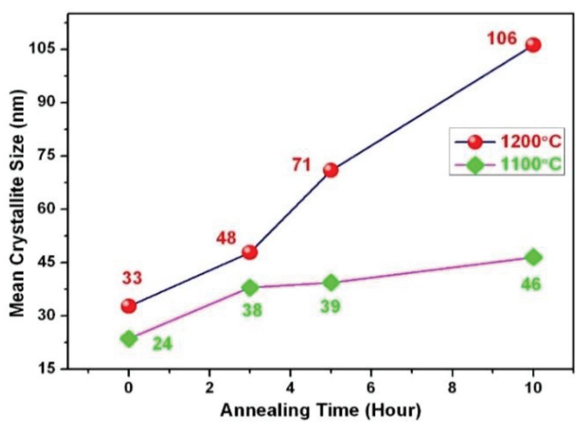

FIGURE 7. The size of crystallites $BaTiO_3$ phase which underwent sintering process at a temperature of 1100°C and 1200°C respectively for 0, 3, 5, and 10 hours.

Based on Fig. 7, it can be concluded that the average size of crystallites $BaTiO_3$ increased exponentially as the rising of sintering temperature and holding times. The growth of $BaTiO_3$ crystallite size is a function of the temperature and time of sintering [10].

CONCLUSION

Tests on a mixture of $BaCO_3$ and TiO_2 as a piezoelectric material, $BaTiO_3$, after undergoing a process of milling and sintering resulted in several conclusions, which are:

1. Mechanical alloying process for 60 hours in a mixture of $BaCO_3 + TiO_2$ caused the mixture of the two compounds decreased their average particle size to 0.8 μm and a crystallite size of 60 nm and 72 nm, respectively. The reduction of the size of particle and crystallite was the result of the continuous collision between sample powder and ball mill. As a consequence, the samples underwent embrittlement and deformation.
2. The sintering process at a temperature of 1100°C for 10 hours or 1200°C produced a single phase $BaTiO_3$ with nanometer sized crystallites. The growth of $BaTiO_3$ crystallite size is a function of the temperature and time of sintering.

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