Calcination Effect on Structural Trasformation of Barium Titanite Ferroelectric Ceramic by Sol-Gel Method

A.F. Che Omar, F.F. Hatta, T.I.T. Kudin, M.A. Mohamed, O.H. Hassan

Abstract*: High purity barium titanate BaTiO3 was successfully synthesized by using the sol-gel technique. Barium acetate Ba(CH3COO)2 and tetrabutyl titanate, Ti(C4H9O)4 was dissolved moderately in the solvent of glacial acetic acid and ethanol was added as the chemical modifier. The synthesized BaTiO3 nanoparticle was calcined at the temperature range of 700 ºC to 1100 ºC. The powders were further characterized by X-ray diffraction and scanning electron microscopy (SEM). Fined BaTiO3 powders result indicates the phase of tetragonal structures and high crystallites of BaTiO3. It was observed that the crystallinity and particle size of BaTiO3 is greatly influenced by the calcination temperature.

Keywords*: BaTiO3, sol-gel synthesis, ferroelectric, calcination temperature.

I. INTRODUCTION

Barium titanate (BaTiO3) is widely used in industrial technologies due to its versatility. The BaTiO3 ferroelectric, thermoelectric, and piezoelectric properties when it assumes the tetragonal structure allows it to be widely used in ceramic capacitors, transistor gate dielectrics, waveguide modulators, infrared detectors, electromechanics, and nonlinear optics [1,2]. The ferroelectric property of BaTiO3 is acknowledged to be directly correlated with the size of the materials. Many novel synthesis techniques have been developed to achieve ultrafine BaTiO3 nanoparticles.

Barium titanate ceramics is typically prepared by the solid-state synthesis routes which comprise of the physical mixing of high purity BaCO3 and TiO2 powders at a high sintering temperature followed by grinding and re-sintering again to produce the BaTiO3 [3, 4]. The main disadvantage of solid-state synthesis routes is it requires high energy-consumption, low purity and grain aggregation [5]. Therefore, extensive research efforts have been focused on producing high-quality barium titanate by several methods, including sol-gel, radio frequency sputtering, electrochemical, hydrothermal, and Pulsed Laser Deposition methods [6 – 9]. Amongst all, the sol-gel technique is the most favourable technique due to its low cost, simple chemical composition, low processing temperature and capable of producing highly crystalline BaTiO3 nanoparticles [10, 11].

In the present study, we use a sol-gel based technique for the preparation of tetragonal $BaTiO_3$ nanomaterials by using a combination of acetic acid and ethanol as the solvent and modifying agent, respectively. XRD and SEM were used to investigate the effects on the morphology of the precursor and the effect of the sintering temperature on the nanoparticle crystallinity of the powder.

II. EXPERIMENT

The precursor solution of $BaTiO_3$ sample was prepared by synthesizing it from high purity of barium acetate, $Ba(CH_3COO)_2$ and tetrabutyl titanate, $Ti(C_4H_9O)_4$ with glacial acetic acid and ethanol as the solvent and the chemical modifier, respectively. $Ba(CH_3COO)_2$ was dissolved into the hot heated acetic acid at a temperature of 80°C. Then, $Ti(C_4H_9O)_4$ was added to ethanol and constantly stirred using a magnetic stirrer for 0.5 hour. Complexed barium ion solutions were then dropped into the $Ti(C_4H_9O)_4$ ethanol solution. The $BaTiO_3$ solution was further stirred for another 2 hours at 80°C followed by 24 hours of aging at room temperature. The transparent gel produced was dried at 80°C for another 12 hours to produce the xerogels. Finally, the xerogels were heated at temperatures of 500°C, 700ºC, 900ºC, and 1100°C. Nanopowder was obtained after 2 hours of grinding. Fig. 1 show the sol-gel method of tetragonal $BaTiO_3$. Crystalline structures of the nanocrystals were determined by XRD (BRUKER/D8 ADVANCE). The crystalinity of the nanopodwer was obtained via Brunker X-ray diffraction software (EVA sofware) that evaluated and analyse XRD data. The morphology of the $BaTiO_3$ nanocrystals was obtained by FESEM (ZIESS/SUPRA 55VP).

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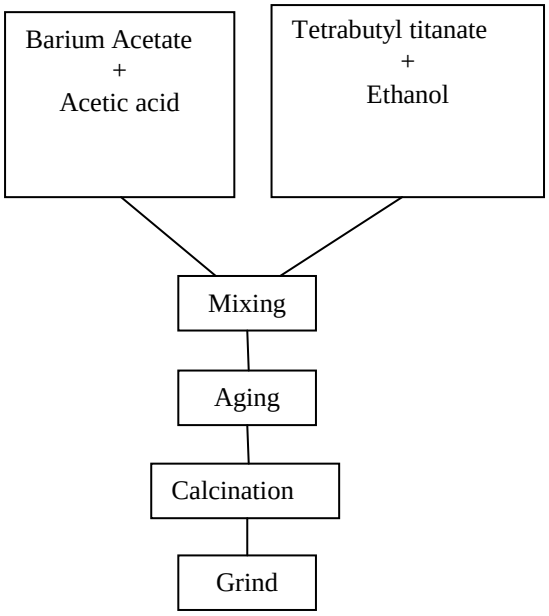

Fig. 1: Flow diagram of the synthesis of $BaTiO_3$ powder by sol-gel technique.

III. RESULT AND DISCUSSION

XRD analysis was carried out for industrial BaTiO3 and synthesized BaTiO3 nanopowder with five different calcination temperature. XRD pattern of industrial BaTiO3 and synthesis BaTiO3 is shown in Fig. 2. The results show a distinctive diffraction peak at 2Θ = 22.2°, 31.4°, 38.8°, 45.4°, 51°, 56.2°, and 65.7°. It directly corresponds to the planes of (100), (110), (111), (200), (210), (211) and (220), respectively. The results indicate that the sol-gel synthesized BaTiO3 powders exhibit a perovskite structure as per literature reports [10, 12]. The XRD pattern shows that the peak of the BaTiO3 narrowed as the calcination temperature increased, in which the BaTiO3 calcined at 1100°C has the highest peak intensity to all planes as compared to other samples.

In Fig. 3, it can be observed that the diffraction peaks (2Θ = 45.4°, 51°, 56.2°, and 65.7°) of BaTiO3 as-calcined at 1100°C broadened and finally split as the calcination temperature increase. This result is consistent with the report by Yu et al. [12], which described that the tetragonal structure of the BaTiO3 phase is formed well at higher calcination temperature. Fig. 4 further shows the diffraction peak in between 2Θ = 44° to 46° for the industrial BaTiO3 and sol-gel synthesized. It can be observed that there is a visible split at peaks of (0 0 2) and (2 0 0) reflection. This reflection implies that the tetragonality class of BaTiO3 parameter occurred at the higher sintering temperature and the nanoparticle ceramic consisted of the tetragonal BaTiO3 phase (JCPDS #No. 5-0626). JCPDS standards indicated the severity of the split peaks where (0 0 2) and (2 0 0) are completely tetragonal [13]. Further analysis of the phases, the crystallinity at each corresponding plane was calculated using the EVA software. By using the software database, synthesized BaTiO3 nanopowder match the database and concluded the identification of BaTiO3 phases. Phases and crystallinity synthesized BaTiO3 nanopowder was tabulated in Table I. The analysis data was tabulated in Table I using the Eva sofware and can be demontrated by using the crystallinity fomula.

The quantitative analysis provided similar data with the XRD software and showed accurate analysis and parameter corresponding to the BaTiO3 phases.

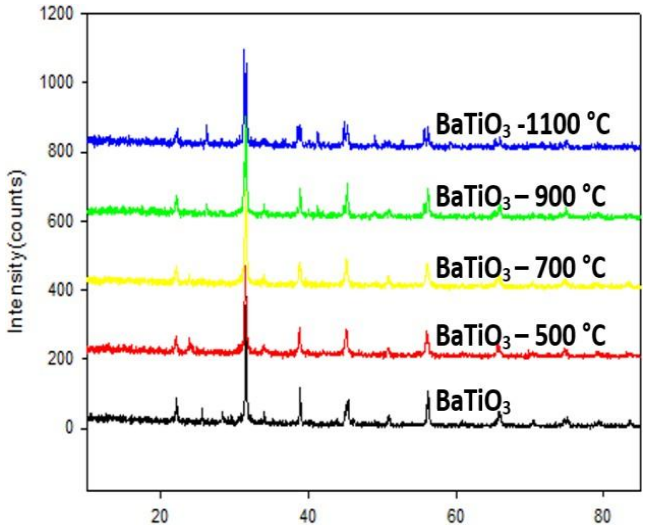

Fig. 2: XRD analysis between Industrial $BaTiO_3$ with synthesis $BaTiO_3$ at different calcination temperatures.

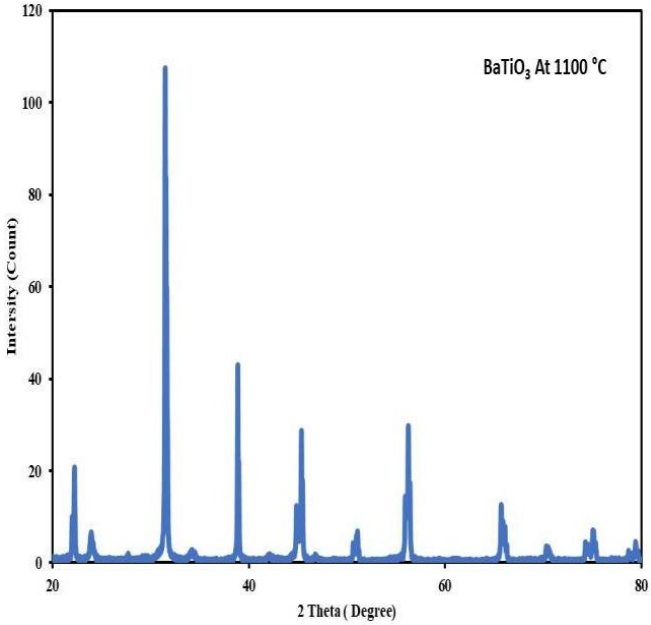

Fig. 3: Narrow and highest peak of $BaTiO_3$ at 1100°C calcination temperature.

Fig. 4 shows the SEM images of $BaTiO_3$ particles sintered at four different temperatures. The micrograph shows the presence of the coarse particles and agglomerations of $BaTiO_3$ at low-temperature sintering of 500°C (Fig. 5). The agglomeration disappeared once the calcination temperature increases to 700°C (Fig. 6) and dense fine particle of $BaTiO_3$ is formed. The amorphous of BaTiO3 was observed to deacrease with increase in heat treatment temperature (Fig. 7 and 8). This was attributed to the finer particle size and physiochemical activation enhancing particle growth during heat treatment [14].

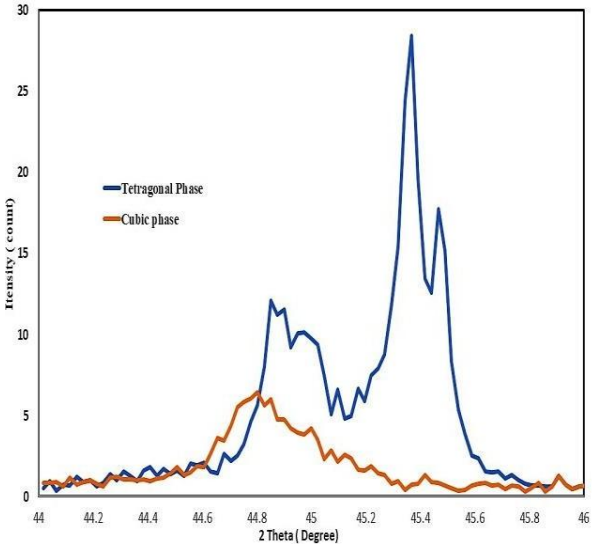

Fig. 4: XRD pattern comparison between cubic and tetragonal at (2 0 0) plane.

Table I: Average crystallinity $BaTiO_3$ sintered at 1100°C

Planes	Crystallinity %	Amorphous %
100	80	20
110	89	11
111	83	17
200	87	13
210	84	16
211	70	30
220	83	17
Average Crystallinity of $BaTiO_3$ = 82%		

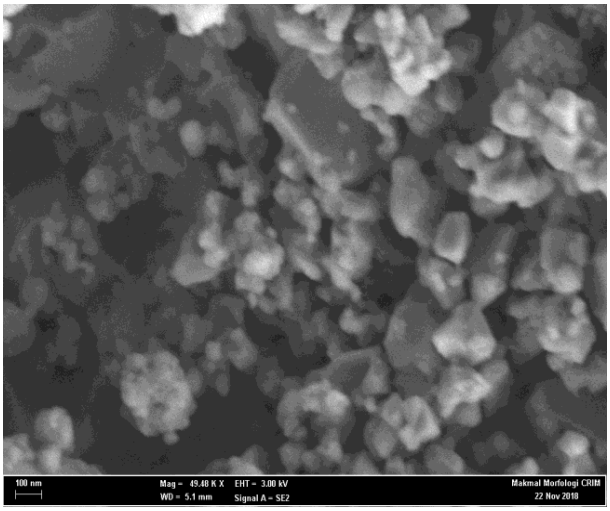

Fig. 5: Microstructure development of the $BaTiO_3$ sintered at the 500°C

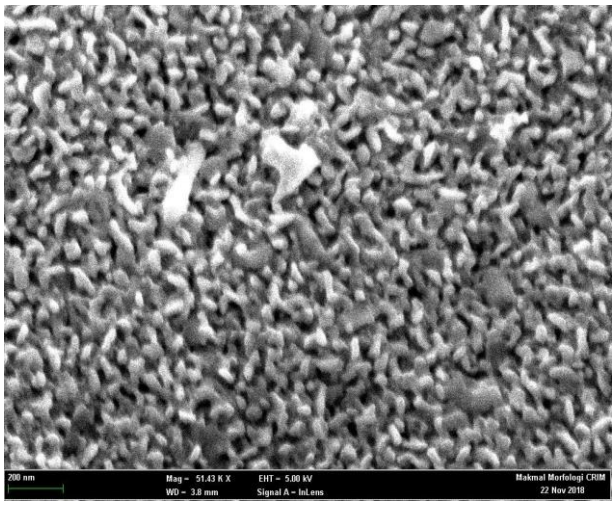

Fig. 6: Microstructure development of the $BaTiO_3$ sintered at the 700°C

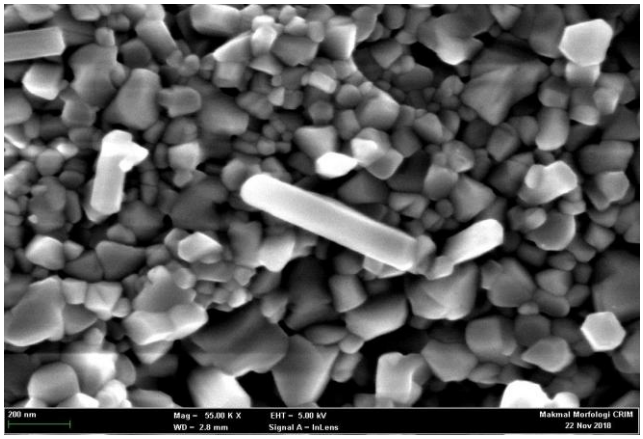

Fig. 7: Microstructure development of the $BaTiO_3$ sintered at the 900°C

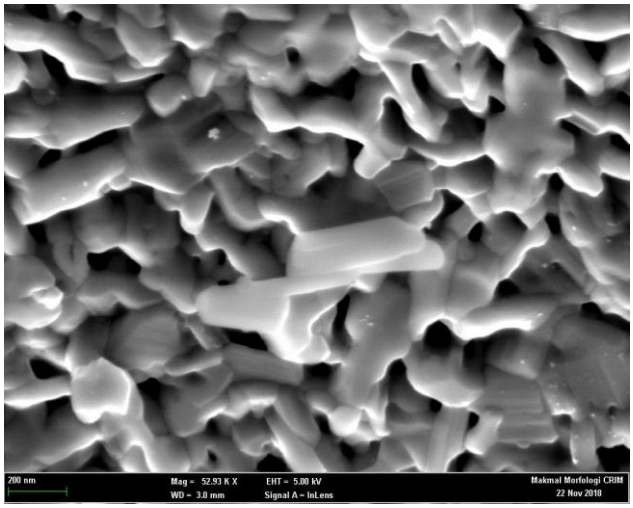

Fig. 8: Microstructure development of the $BaTiO_3$ sintered at the 1100°C

IV. CONCLUSION

A simple aqueous sol-gel technique was investigated for synthesizing BaTiO3 ceramics. Homogeneous monolithic gels were achieved by complexing barium ions with acetic acid and ethanol as a modifying agent. X-ray diffraction and SEM analysis of the BaTiO3 ceramics revealed that a tetragonal phase and finer particles of BaTiO3 were formed at higher temperatures of calcination.

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