VOL. 11, NO. 2, JANUARY 2016 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences
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EFFECTS OF CITRIC ACID/$BATIO_3$ WEIGHT FRACTIONS AND TIME OF SINTERING IN SOL GEL PROCESS ON ELECTRIC SATURATION POLARIZATION VALUES AND PHASE COMPOSITION

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ABSTRACT

The excellent dielectric and ferroelectric properties of barium titante ($BaTiO_3$/BTO) make it attractive material in the field of electron-ceramic and microelectronics. The aim of this research is to find optimum process condition of sol-gel method for BTO synthesis by varying of citric acid/BTO weight fractions and time of sintering. It is expected to obtain BTO material in nanoparticle, single phase and good electric properties by this method. It was used barium nitrate, titanium oxide, nitrate acid, ammonium nitrate as precursors and citric acid ($C_6H_8O_7$) as a fuel. The parameters which are varied are weight fraction of citric acid/BTO = 1:1, 2:1 and 3:1 and time of sintering 2 and 4 hours at 700 ^oC respectively. To know the temperature of phase transition it was used TGA/DTA (Thermo Gravimetric Analysis/Differential Thermal Analysis) test for BTO gel. Phases formation of material were carried out using X-Ray-Diffraction (XRD) for BTO powder. It was used Particle Size Analyzer (PSA) with Beckman Coulter Delsa^{TM} Nano type to know particle size of BTO powder. "Home made electric instrument by Physics Department of University of Indonesia" was used to know electric properties of BTO powder. XRD results confirm that single phase BTO is obtained on weight fraction of citric acid/BTO =2:1 with time of sintering 2 hours at 700 ^oC. The process condition produces nanoparticle BTO with particle size of 45 nm. Measurement with electric hysteresis loop shows that BTO powder with the process condition has the highest value of electric saturation polarization, 44.84 $\mu C/cm^2$ and good loop of electric hysteresis.

Keywords: sol-gel, nanoparticle, single phase, polarization.

INTRODUCTION

Being a lead free ferroelectric ceramic, barium titanate ($BaTiO_3$/BTO) is an environmentally friendly material, thus making it a good candidate for various applications including capacitors, positive temperature coefficient resistors, high density optical data storage, ultrasonic transducer, piezoelectric devices and semiconductors [1]. The aim of this research is to produce BTO as nanoparticle, single phase dan high value of electric saturation polarization by varying weight fraction of citric acid/BTO and time of sintering in sol-gel method.

Interest in studying the nano-sized particles is influenced by the ability of produce a single phase compounds that could affect the value of crystal parameters and diffraction pattern, which in turn had an effect on his physical properties, especially the electric properties [2].

Synthesis of nanoparticle BTO has already been done by sol-gel process. The advantages of using sol-gel method include : reagents required are simple compound, produces nanoparticles, no special equipment is needed, the elements of dopants could be easily incorporated into the final product, there is little possibility of agglomeration of particles, requires low process temperature and uniform grain shape [3, 4, 5].

LITERATURE REVIEW

Barium titanate ($BaTiO_3$/BTO), which is a typical electronic material, is widely used for multilayer ceramic capacitors because of its high dielectric constant and ferroelectric properties. For the miniaturization and high capacitance of multilayer ceramic capacitors, it is necessary that the particle diameter of BTO powders is less than 100 nm and have a narrow size distribution and high purity.

In the sol-gel synthesis process of fine particles, various researchers have been studied on the control of the powder properties such as a composition , a size of particles and their size distribution, by synthetic conditions; a kind of alcoholic solvent, the solution concentration, a mixed method. Only batch techniques have been utilized in the lab for precipitation of narrow-sized particles, because the uniformity of mixing and the concentrations of reactants can be easily controlled. As an industrial process, sequential batch precipitation is generally undesirable because of high operating costs; low production rates and batch to-batch produce variation.

In the sol-gel process, BTO gels can be obtained by hydrolyzing the metal alkoxide. The most advantageous characteristics of this method are the high purity and the excellent control of the composition of the resulting powders. To cystallize BTO, the hydrolysis product normally will be calcined at temperatures above

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500 ºC. The advantage of the Pechini process lies in the limitation of segregation of various metal ions, and is achieved by forming stable metal-chelate complexed with a stoichiometric Ba: Ti ratio of 1:1. The pyrolysis of the complexes often occurs at a temperature ranging from 500 to 1000 ºC, which results in aggregated nanosized BTO particles. In hydrothermal synthesis, processing temperature can be much lower, in the range of 100-250 ºC. The prepared BTO with narrow size distributions with the average particle size of larger than 100 nm can be obtained by hydrothermal method. As for the precipitation method, continuous large-scale production of small particle at low temperature can be obtained easily as compared to other synthesis routes.

METHODS

The synthesis of BTO powder uses basic compound pro analysis Merck product with a purity of 99.99%, $Ba(NO_3)_2$, TiO_2, NH_4OH, HNO_3 and citric acid $C_6H_8O_7$ as fuel. The basic compounds dissolved in aquabidestilata which was then heated on a hot plate at 80-90 ºC to form a gel (approximately for 4 to 5 hours). The gel that is formed is then heated in a furnace at a temperature of 150 ºC and 450 ºC respectively for 1 hour and 24 hours. The goal is to evaporate the water and the elements C, N and H. The powder obtained was then carried out by heating the sintering process in the furnace at temperature of 700 ºC respectively for 2 and 4 hours. The flowchart of the synthesis process is shown in Figure-1.

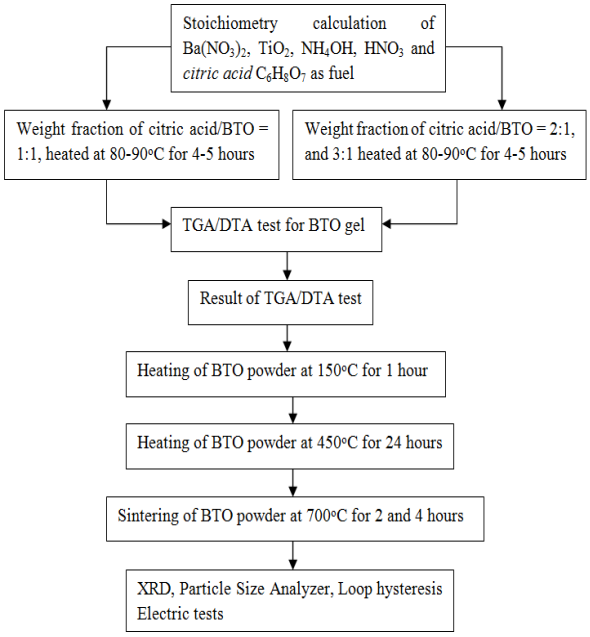

Figure-1. Flowchart of BTO synthesis by Sol-gel method.

Testing by XRD were performed using an XRD PW 1835 Phillips type with diffraction angle of 20º-100º and using CuKα radiation.Characterization of Particle Size Analyzer performed by using a Beckman Coulter instrument DelsaTM Nano by using a solution of Ethyl Alcohol. Characterization using Thermogravimetric Analysis (TGA) / Differential Thermal Analysis (DTA) aimed to observe changes in mass and heat of samples (still in gel form) to the increase in temperature, using a TGA / DTA Thermal Balance Research type LINSEIS L81-Series I / L81- STA (TGA-DTA).

RESULTS AND DISCUSSIONS

To determine the temperatures of calcination and sinter, it has been already done TGA / DTA test as shown in Figure-2.

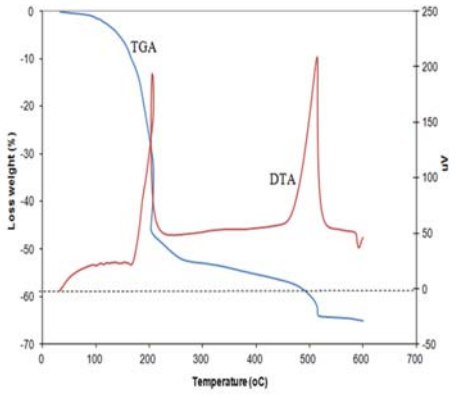

Figure-2. Graph of TGA/DTA test for BTO gel.

From Figure-2 it could be had reference temperatures for heating (150 ºC and 450 ºC) and sintering BTO (700 ºC) due to weight reduction and increasing of energy at those temperatures.

To confirm the formation of BTO phase, it is performed XRD test for all samples and the results are shown in Figure-3.

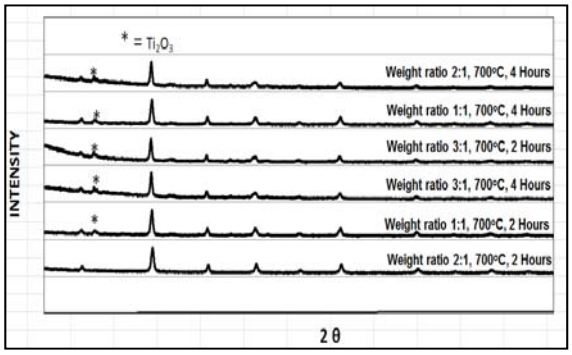

Figure-3. XRD pattern of BTO powder.

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Among all samples in Figure-3, sample with weight fraction of citric acid/BTO = 2:1 with sintering temperatures at 700 ºC for 2 hours has only $BaTiO_3$ phase without Ti_2O_3 phase. Meanwhile another samples has Ti_2O_3 besides $BaTiO_3$ phase. Ti_2O_3 phase is formed because there are a number of Ti^{4+} ions which is not soluble and reoxidized into Ti_2O_3.

Particle size of BTO powder could be known from Particle Size Analyzer (PSA) test which is shown in Figures 4, 5, 6 and 7.

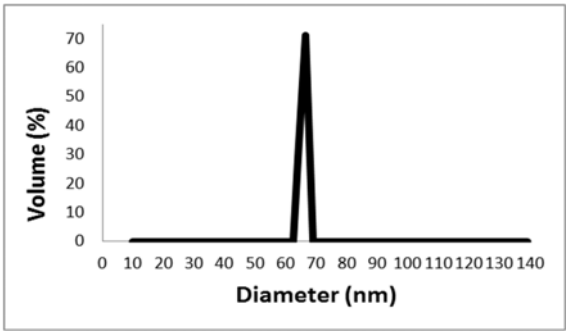

Figure-4. Particle size distribution of ratios 2:1 at 700 ºC for 4 hours.

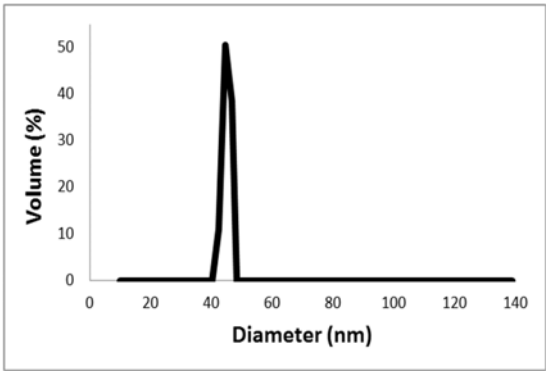

Figure-5. Particle size distribution of ratios 2:1 at 700 ºC 2 hours.

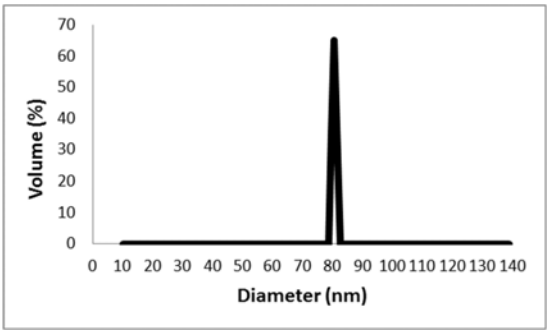

Figure-6. Particle size distribution of ratios 1:1 at 700 ºC for 4 hours.

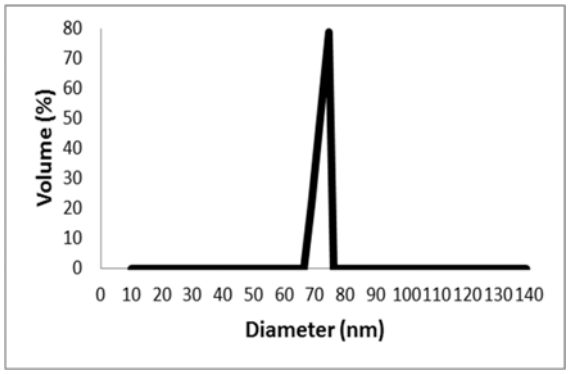

Figure-7. Particle size distribution of ratios 1:1 at 700 ºC for 2 hours.

To know electric characteristic of sample, it is used instrument of electrical hysteresis loop which is shown in Figures 8, 9, 10, 11, 12 and 13.

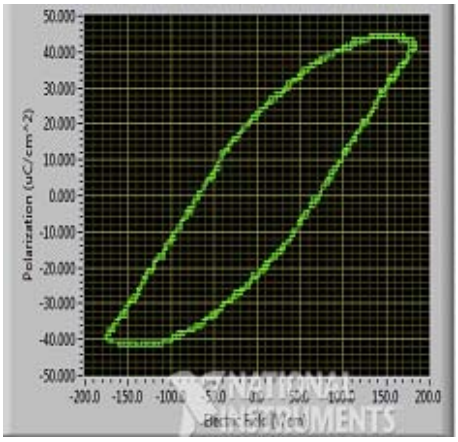

Figure-8. The loop of BTO electric hysteresis ratio 2:1 at 700 ºC for 2 hours.

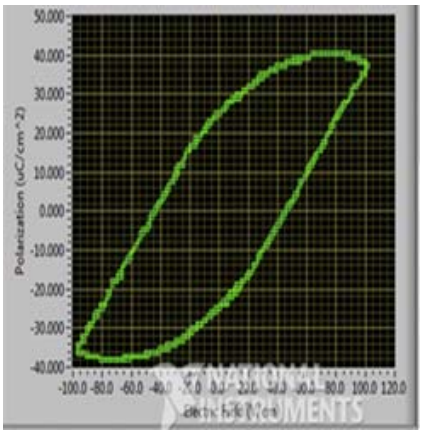

Figure-9. The loop of BTO electric hysteresis ratio 2:1 at 700 ºC for 4 hours.

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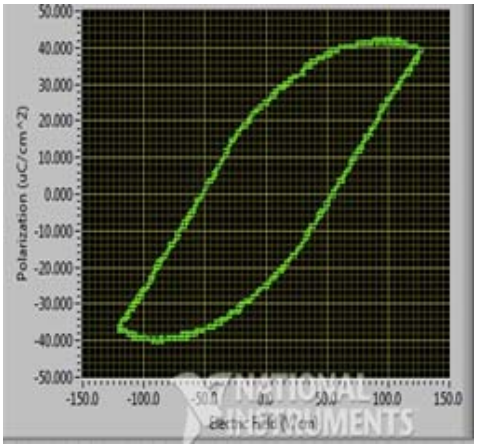

Figure-10. The loop of BTO electric hysteresis ratio 1:1 at 700 ºC for 2 hours.

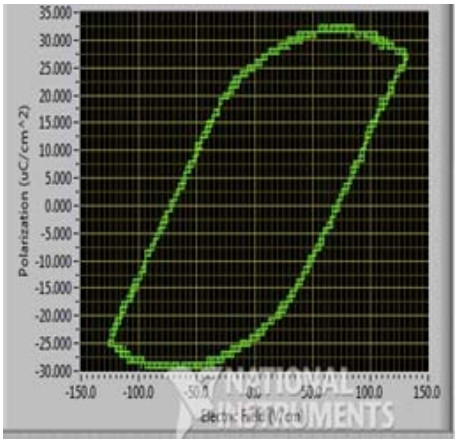

Figure-11. The loop of BTO electric hysteresis ratio 1:1 at 700 ºC for 4 hours.

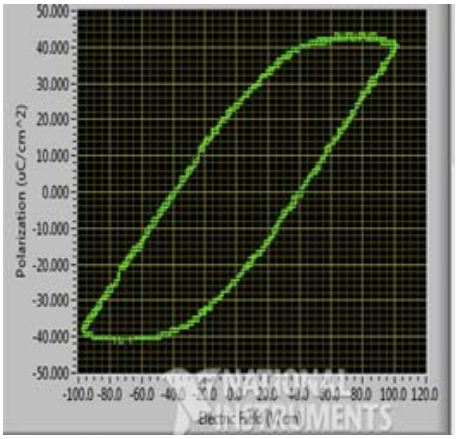

Figure-12. The loop of BTO electric hysteresis ratio 3:1 at 700 ºC for 2 hours.

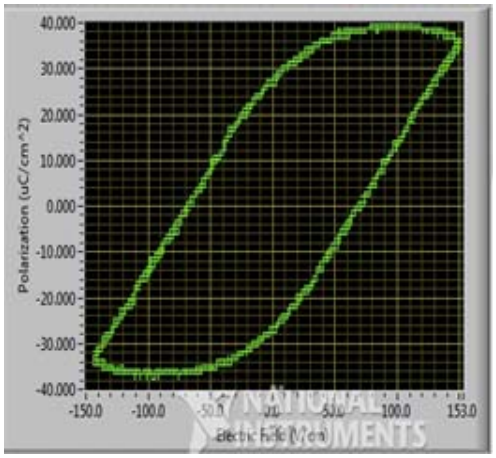

Figure-13. The loop of BTO electric hysteresis ratio 3:1 at 700 ºC for 4 hours.

The value of electric saturation polarization and particle size for all samples could be tabulated in Table-1.

Table-1. Characteristics of BTO powder.

Sinter process	Weight fraction	Polarization ($\mu C/cm^2$)	Phase	Particle size (nm)
700 ºC 2 hours	2:1	44.84	$BaTiO_3$	45
700 ºC 4 hours	2:1	43.82	$BaTiO_3$, Ti_2O_3	65
700 ºC 2 hours	1:1	42.80	$BaTiO_3$, Ti_2O_3	72
700 ºC 4 hours	1:1	40.76	$BaTiO_3$, Ti_2O_3	80
700 ºC 2 hours	3:1	39.75	$BaTiO_3$, Ti_2O_3	82
700 ºC 4 hours	3:1	38.22	$BaTiO_3$, Ti_2O_3	84

Values of electric saturation polarization increase with increasing of weight fraction of citric acid until 2 parts but decrease back when weight fraction of citric acid reaches out 3 parts. BTO with weight fraction of citric acid 2 parts and 2 hours sintering has the highest value of electric saturation polarization, 44.84 $\mu C/cm^2$. Table-1 shows that the highest value of electric saturation polarization is belong to sample in single phase. The presence of other phases besides BTO could decrease value of electric saturation polarization. Single phase BTO with the highest value of electric saturation polarization has the finest particle size. Table-2 confirms that all samples are in nanoparticle (<100 nm).

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CONCLUSIONS

Sol-gel method with weight ratio citric acid/BTO = 2:1 at sinter temperature 700 ^oC for 2 hours could apply for synthesis barium titanate powder in nanosize, single phase, and good electric saturation polarization.The presence of residual phase Ti_2O_3 could decrease value of electric saturation polarization.Weight fraction of citric acid until 3 parts could decreases and increases back value of electric saturation polarization and particle size.

ACKNOWLEDGEMENT

This research is supported financially by Fundamental research grant 2015 through letter of decree No. 0094/E5.1/PE/2015, Ministry for Research and Technology DIKTI, The Republic of Indonesia.

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