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SYNTHESIS OF BIFEO3 NANOPARTICLE AND SINGLE PHASE BY SOL-GEL PROCESS FOR MULTIFERROIC MATERIAL

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ABSTRACT

The magnetoelectric coupling (ME) in multiferroics i.e. $BiFeO_3$ promises important technological applications in several multifunctional devices like data storage, spinotronics, sensor, actuator devices etc. $BiFeO_3$ was synthesized using a sol - gel process. The aim of this research is to find optimum process condition of sol-gel method for $BiFeO_3$ synthesis by varying of sintering temperature. It is expected to obtain $BiFeO_3$ material in nanoparticle, single phase and shows electric voltage response if given an external magnetic field. It was used $Bi_5O(OH)_9.(NO_3)_4$, $Fe(NO_3)_3.9H_2O$, HNO_3, H_2O as precursor and citric acid ($C_6H_8O_7$) as fuel. It was used 450 ^oC; 500^oC and 550 ^oC as sintering temperature for 10 hours respectively.Phases formation of material were carried out using X-Ray-Diffraction (XRD) for $BiFeO_3$ powder. It was used Particle Size Analyzer (PSA) with Beckman Coulter DelsaTM Nano type to know particle size. "Home made ME instrument by Physics Department of University of Indonesia" was used to know electric voltage response when given an external magnetic field to $BiFeO_3$ powder. XRD results confirm that single phase $BiFeO_3$ is obtained at sintering temperature of 550 ^oC for 10 hours. The smallest particle size was 65 nm. When $BiFeO_3$ powder was given an external magnetic field, it shows electric response. This response shows that the powder has multiferroic characteristic.

Keywords: magnetoelectric, multiferroic, sol-gel, nanoparticle, single phase.

INTRODUCTION

Multiferroics, also called ferroelectromagnets, represent a broad class of materials possessing two or more types of switchable states for memory and transducer applications [1]. In most cases, ferroelectric polarization P, magnetization M and magnetoelectric (ME) coupling between them are the frequently studied topics. It has been expected that fluctuations in P or M can be activated upon applying external magnetic field H or electric field E, respectively. This triggers quite a few proposed novel devices utilizing this additional degree of freedom besides P and M themselves [2, 3]. In one hand, quite a number of single-phase multiferroic compounds have been studied, focusing on the phase transitions associated with ferroelectric ordering and magnetic ordering as well as their coupling, noting that the ME coupling is usually weak [4, 5]. Although the detected polarization change upon a magnetic field H of ~Tesla is only ~nC/cm^2, the well-reproduced polarization reversal induced by the time-varying H is impressive.

$BiFeO_3$ is one of the very few magnetoelectrics with high phase transition temperatures (Curie temperature ~1083 K, and Néel temperature ~657 K). Since its discovery in 1960s, difficult synthesis of $BiFeO_3$ and its current leakage have hampered its practical applications. There is a revival of $BiFeO_3$ because of its possible novel applications [6]. Nowadays, several techniques have been successful in synthesis of pure $BiFeO_3$ ceramics. In the solid state route [7], Bi_2O_3 and Fe_2O_3 are reacted at temperature of 800– 830 °C and impure $Bi_2Fe_4O_9$ phases are removed by washing in HNO_3. The disadvantage of this process lies in the necessary of leaching the unwanted phases using an acid and the impurity appears again in the sintering process. A modified method is rapid liquid phase sintering [8, 9] described by following: Bi_2O_3 and Fe_2O_3 were thoroughly mixed in an agate mortar and the mixture was dried and pressed into the pellets and sintered in air at 860 °C with a high heating rate up to 100 °C/s. This method can result in a high resistivity and polarization value of $BiFeO_3$, but also leads to high dielectric loss and more defects. Another technique for synthesis of $BiFeO_3$ is precipitation/ coprecipitation method [10]. Recently Sushmita [11] successfully synthesized nanosized $BiFeO_3$ via soft chemical route using tartaric acid as a complexing agent. In this work, we report the synthesis of a pure $BiFeO_3$ by sol-gel method. The method is more simple, energy saving, cost effective and requiring lower process temperature than other methods. Another advantage 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, and uniform grain shape [12, 13, 14].

LITERATURE REVIEW

Multiferroics have been known as materials exhibiting ferromagnetic and ferroelectric properties at the same time, which have exhibited interesting physical properties as well as possibility of practical applications

for new memory devices. The rhombohedrally distorted simple perovskite structure of $BiFeO_3$ is one of the representative multiferroic materials and has been much interested due to the antiferromagnetic behavior with a relatively high Neel temperature and the ferroelectric behavior with a high curie temperature.

Multiferroic materials, owing to the coexistence of ferroelectricity, ferromagnetism and even ferroelasticity in the same phase, have shown promising applications in nonvolatile information storages, spintronic devices and magnetoelectric sensors. Among the multiferroic materials studied so far, $BiFeO_3$ (BFO) is known to have a rhombohedrally distorted perovskite structure with a R3c symmetry. It has two order parameters at room temperature: (i) a ferroelectric ordering with a high Curie temperature T_C of 1103K, (ii) a antiferromagnetic ordering of the G-type with a magnetic transition temperature T_N of 643K. As the only one single phase multiferroic material which simultaneously possesses the ferroelectric and ferromagnetic properties at room temperature, BFO has been one of the most interesting materials studied. At present, the ceramics and thin films of BFO have been extensively investigated.

Although rhombohedral $BiFeO_3$ (BFO R-phase) has been studied extensively since first discovery in 1960s, electrical properties of the pure BFO R-phase have been rarely reported due to its high conductivity, which may originated from uncertain oxygen stoichiometry, high defect density and poor sample quality. In order to understand the properties of multiferroic BFO, it is very important that the fabrication of pure BFO R-phase should be established. If temperature and oxygen parsial pressure were not controlled accurately during crystallization of the BFO R-phases, the kinetics of phase formation always lead to other impurity phases in Bi-Fe-O system such as $Bi_2Fe_4O_9$, $Bi_2O_{2.75}$ and $Bi_{46}Fe_2O_{72}$.

Wet chemical methods are a promising route to prepare fine and homogeneous powder. Various wet chemical methods such as hydrothermal, co-precipitation, combustion synthesis, molten-salt method, thermal decomposition, and sol–gel process have been developed and designed to prepare pure $BiFeO_3$ nanopowder.

Recently, acid-assisted gel strategy has been proved to be an effective way to synthesize metastable $BiFeO_3$ nanopowder. Pure $BiFeO_3$ phase could be obtained by leaching out the minor Bi_2O_3 phase using diluted nitric acid. Pure $BiFeO_3$ powder can be directly synthesized through the acetic acid-assisted or the tartaric acid-assisted sol-gel method. However, $BiFeO_3$ powder synthesized by the organic acid-assisted sol-gel method maybe have relatively low purity resulting from the easy formation of bismutite phase during calcining. Therefore, mineral acid should be considered as an adjuvant to prepare $BiFeO_3$ nanopowder. In the present paper, a nitric acid-assisted gel route has been introduced in the synthesis of $BiFeO_3$ nanopowder.

METHODS

The synthesis of $BiFeO_3$ powder uses basic compound pro analysis Merck product with a purity of 99.99% $Bi_5O(OH)_9.(NO_3)_4$, $Fe(NO_3)_3.9H_2O$, HNO_3, H_2O 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 180 ^oC for 2 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 450,500 and 550^o C for 10 hours respectively. The flowchart of the synthesis process is shown in Figure-1.

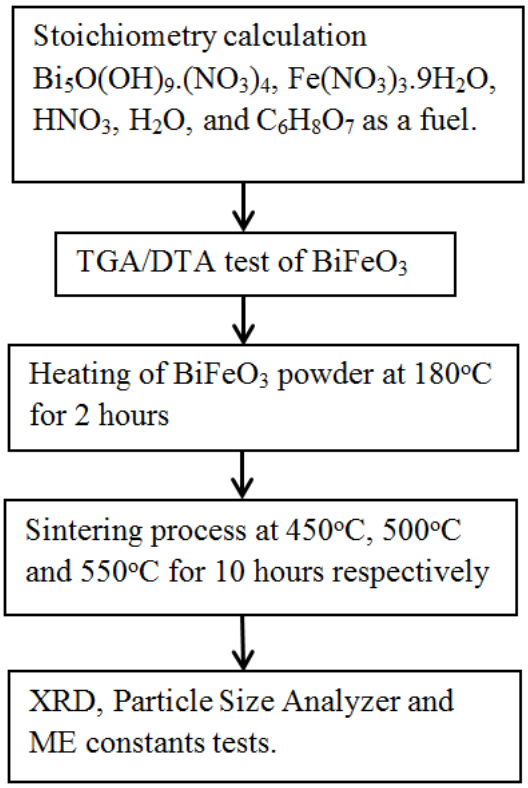

Figure-1. Flowchart of $BiFeO_3$ synthesis by Sol-gel method.

Testing by XRD were performed using an XRD PW 1835 Phillips type with diffraction angle of 20^o-100^o 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). To know the

multiferroic properties, it is used "Home made instrument" of Magnetoelectric constant.

RESULTS AND DISCUSSIONS

The synthesis stages of $BiFeO_3$ powder is described by Figure-2.

Figure-2. Sol-gel process to synthesize $BiFeO_3$.

Figure-2 shows that process starts with heating the solution of $Bi_5O(OH)_9.(NO_3)_4$, $Fe(NO_3)_3.9H_2O$, HNO_3, H_2O, and $C_6H_8O_7$ as a fuel until gel formed. After sintering it is produced nanoparticle $BiFeO_3$ powder.To determine the temperatures of sintering, it has been already done TGA / DTA test and the result shows that phase transition occurs at 400 ^oC – 600 ^oC due to weight reduction and increasing of energy at those temperatures.

To confirm the formation of $BiFeO_3$ phase, it is performed XRD test for all samples and the results are shown in Figures 3, 4 and 5

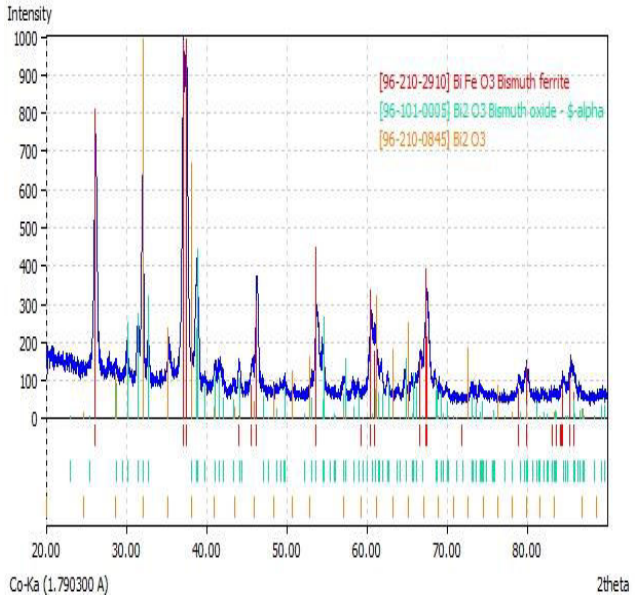

Figure-3. XRD pattern of $BiFeO_3$ powder at sintering of 450 ^oC for 10 hours.

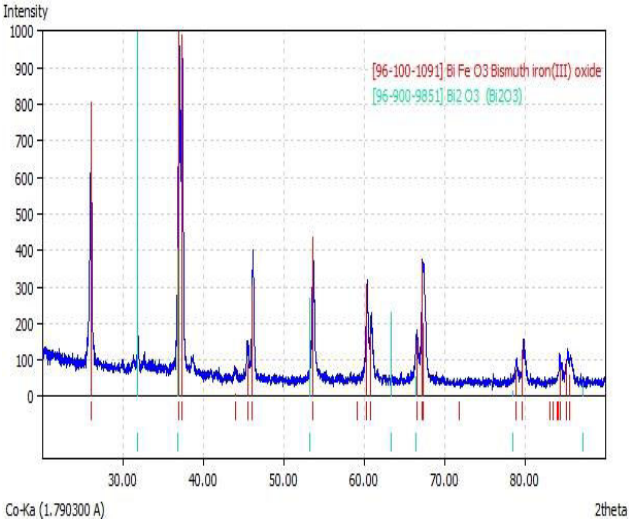

Figure-4. XRD pattern of $BiFeO_3$ powder at sintering of 500 ^oC for 10 hours.

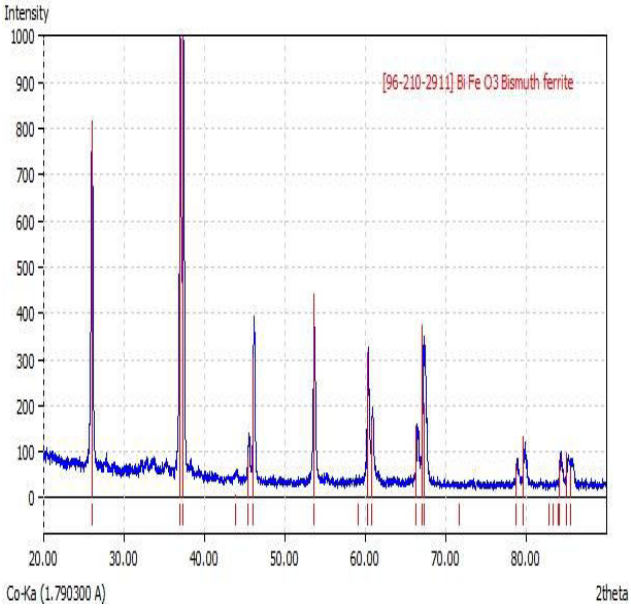

Figure-5. XRD pattern of $BiFeO_3$ powder at sintering of 550 ^oC for 10 hours.

Figure 3, 4 and 5 shows that there is an impurity phase Bi_2O_3 for powder at sintering temperature of 450 ^oC and 500 ^oC for 10 hours. There is no impurity phase at sintering temperature of 550 ^oC for 10 hours. It has 100% $BiFeO_3$ phase. Bi_2O_3 phase is formed because there are a number of Bi^{3+} ions which is not soluble and reoxidized into Bi_2O_3 during temperature of 450 ^oC – 500 ^oC.

Particle size of $BiFeO_3$ powder could be known from Particle Size Analyzer (PSA) test which is shown in Figures 6, 7 and 8.

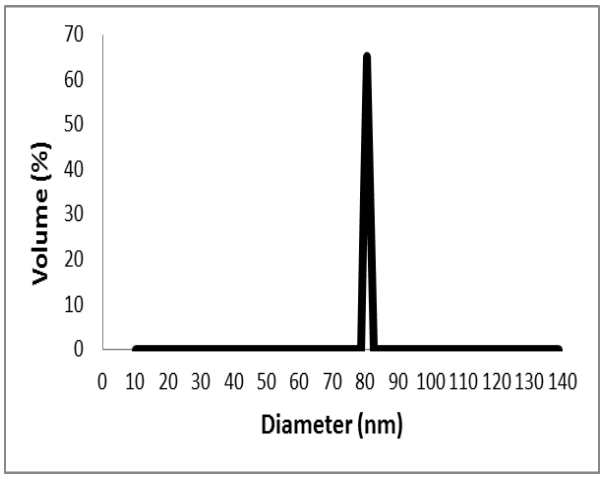

Figure-6. Particle size distribution of sintering at 450 °C for 10 hours.

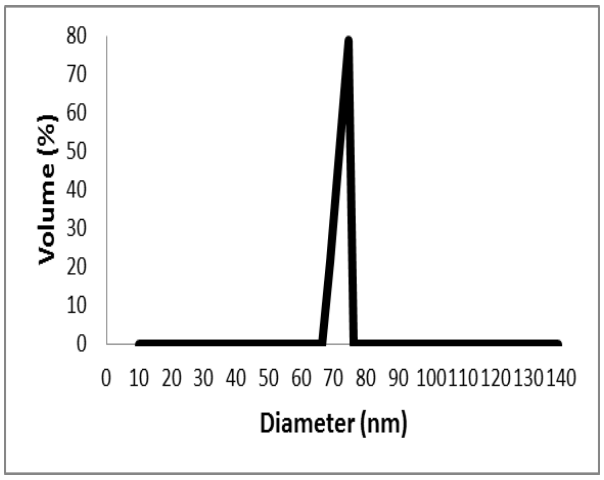

Figure-7. Particle size distribution of sintering at 500 °C for 10 hours.

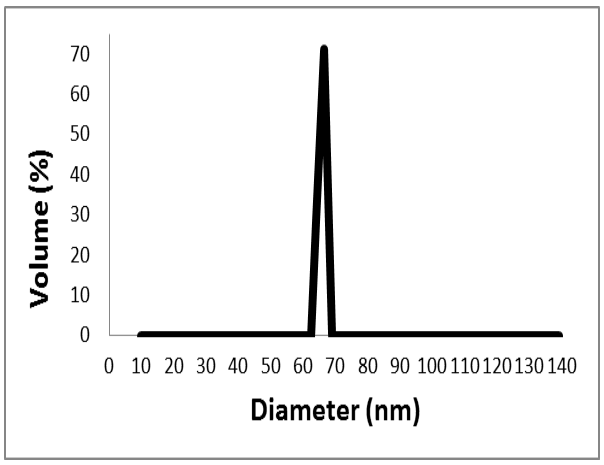

Figure-8. Particle size distribution of sintering at 550 °C for 10 hours.

Figure 6, 7 and 8 show that $BiFeO_3$ powder at sintering temperature of 550 °C has the smallest particle of 65 nm. The lower sintering temperature, the greater particle size. It could be seen that there is a relation between particle size and phase composition as shown in Table-1.

Table-1. Particle size and phase composition of $BiFeO_3$ powder.

Sinter Process	$BiFeO_3$ Phase (%)	Bi_2O_3 Phase (%)	Particle Size (nm)
450 °C 10 hours	56	44	82
500 °C 10 hours	92	8	72
550 °C 10 hours	100	0	65

Table-1 shows that $BiFeO_3$ powder with the smallest particle has no impurity phase. However all samples with sintering temperature 450 °C, 500 °C and 550 °C are nanoparticle powder due to particle size < 100 nm.

Magneto Electric (ME) coupling is one of the characteristics of multiferroic material. To know whether there is ME coupling, it will shows electric voltage response when the powder is given an external magnetic field. The response is shown in Figure-9.

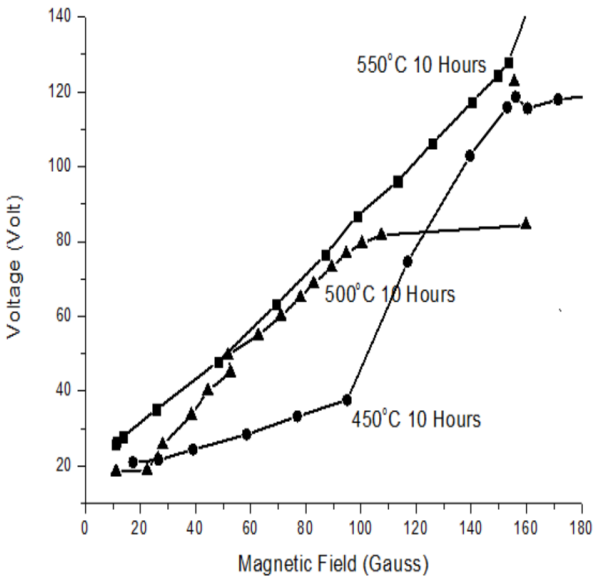

Figure-9. The electric voltage response of $BiFeO_3$ at 450 °C, 500 °C and 550 °C.

Figure-9 shows that $BiFeO_3$ powder with sintering temperature of 550 °C for 10 hours has the most

powerful multiferroic properties when given external magnetic field. The weakest multiferroic properties owned by powder sintering temperature of 450 ^{o}C and 500 ^{o}C. Strong inter-phase contact in powder material certainly cause interactions around the surface of the crystal. The average size in the nanometer material causes the interact surface fraction will increase as well as with the decrease size of the grain size.

CONCLUSIONS

Sol-gel method at sintering temperature of 45^{o}C - 550^{o}C could produce nanoparticle and single phase $BiFeO_3$, with the smallest particle owned by powder at sintering temperature of 550 ^{o}C for 10 hours. The powder has also single phase without impurity. The presence of residual phase Bi_2O_3 could decrease electric voltage response and increase particle size. All samples could apply as a multiferroic material due to given an external magnetic field around the sample provide a response in the form of electrical voltage effects.

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