Fabrication of barium titanate doped strontium using co-precipitation method

Y Iriani, M A Yasin and R Suryana*

Department of Physics, Faculty of Mathematics and Natural Sciences, Sebelas Maret University, Jl. Ir. Sutami 36A Kentingan Surakarta 57126 Indonesia

*E-mail: rsuryana@staff.uns.ac.id

Abstract. Fabrication of barium titanate (BaTiO3/BT) doped strontium (Sr) using co-precipitation method has been successfully conducted. The research aim is to get the best mole variation of Sr doping to ferroelectric material properties. Doping Sr was varied at 1%, 2%, 3%, 4%, and 5% in BaTiO3. Each sample was sintered at temperature of 1100°C with holding time for 6 h and temperature rate at 10°C/min. They were then characterized by XRD instrument to investigate the crystal structure, LCR meter to measure the dielectric constant, and Sawyer Tower circuit to reveal the hysteresis curve. The peaks of XRD shift towards larger angle when mole doping Sr increase. The crystallinity of all samples is above 90% and the crystallite size is in the range of 27 nm to 34 nm. Hysteresis curve from Sawyer Tower testing confirms that all samples are ferroelectric material. The RLC measurement results reveal that the less frequency leads to the higher dielectric constant while the highest dielectric constant belongs to the BT doped 3% of Sr. Therefore, it is the best variation obtained in this research.

1. Introduction

Ferroelectric materials can be used as a dielectric material. It is able to change the electric polarization spontaneously when an external electric field is applied [1-2]. That condition is marked by the formation of a hysteresis curve which is the curve between the electric polarization and the electric field. Ferroelectric material has perovskite structure with ABO3 formula where A is cation with valence of 1 and 2, B is cation with valence of 4 and 5, and O is oxygen [3].

Ferroelectric material has three types of property those are pyroelectric, dielectric and piezoelectric properties. Pyroelectric property is able to be used as a sensor that will produce voltage when it is applied in certain temperature. The dielectric property, by utilizing the ferroelectric properties, is widely used as a memory storage application that is Ferroelectric Random Access Memories (FRAM) [4].

One of ferroelectric materials is barium strontium titanate (Ba1-xSr3TiO3/ BST) obtained from BT doped by strontium (Sr) atoms. The dielectric constant of BST has been attained between the range of 578 to 2854, and the highest dielectric constant is produced by Ba0.71Sr0.29TiO3 [5]. One of methods to fabricate BST is co-precipitation method [6-9]. The advantage of this method is simply and only required the room temperature in the reaction experiments. In this research, BT doped by Sr with mole variation of Sr concentration has been synthesized by co-precipitation method. This research aims to find the best result of Sr mole variation in BT to ferroelectric properties.
2. Experimental Method

BT doped Sr was fabricated by co-precipitation method. The mole composition of Sr in BT was varied i.e. 1%, 2%, 3%, 4% and 5%. The raw material involved barium hydroxide (Sigma Aldrich, 95%), strontium nitrate (Sigma Aldrich, ≥ 99%), titanium tetrabutoxide (Sigma Aldrich, 97%), oxalic acid (Sigma Aldrich, ≥ 99%), and isopropanol (IPA). 0.2 M solution of oxalic acid was dissolved into 35 ml of IPA in beaker glass then stirred continuously (named solution 1). The solution of titanium tetrabutoxide (0.1 M) was dissolved in 18 ml IPA (named solution 2). The solution 2 then was poured into the solution 1 then obtained clear solution of oxalotitanic acid (HTO) (named solution 3). Finally, barium hydroxide was added into the solution 3 then dried to get powder sample.

The powder sample was then pressed by a hydraulic pump with the pressure of 5 Pa. The pellets of sample were sintered using furnace at temperature of 1100°C with holding time for 6 h and the temperature rate at 10°C/min. The microstructure of sample then was characterized via XRD with λ Cu of 1.5406Å. The XRD data were then matched with ICDD database to investigate the crystal structure. The crystallinity was calculated by Eq. 1. $I_{peak\ max}$ is the maximum intensity and $I_{peak\ min}$ is the minimum intensity.

$$ \text{Crystallinity} = \frac{I_{peak\ max} - I_{peak\ min}}{I_{peak\ max}} \quad (1) $$

The crystallite size of BaTiO$_3$ doped Sr was obtained by using Scherrer equation in Eq. 2 [10]. In which, β is FWHM value, θ is the diffraction angle, k is Scherrer constant that is 0.9; and λ is the wavelength of X-ray.

$$ D = \frac{k \lambda}{\beta \cos \theta} \quad (2) $$

LCR meter was then performed in the samples to measure the dielectric constant. In addition, to reveal the hysteresis curve, the samples were then test by Sawyer Tower circuit.

3. Results and discussion

Fig. 1 is the diffractogram of BT doped Sr. ICDD database confirms that the peaks belong to BT (#831880) with tetragonal structure. It indicates that the Sr doping process in BT has been successfully conducted. The peaks are dominated by crystal orientation of (101), (111), (002) and (211). An undesirable BaCO$_3$ (*) at diffraction angle about 24° appears in all samples. BaCO$_3$ was usually present at lower temperature of synthesis [11]. The more Sr mole causes the peaks shift the right side, in other word leading to the larger angle diffraction, but it does not change the crystal structure (tetragonal).

Table 1 is the crystallinity and the crystallite size of BT doped Sr with mole variation. All samples have a high crystallinity confirmed by the value that is above 90%. The highest crystallinity is showed by BT doped 2% and 5% of Sr mole. All samples show the similar crystallite size except BT doped 3% of Sr mole and BT doped 4% and 5% of Sr mole show the largest crystallite size.

Fig. 2 is the hysteresis curve of BT doped Sr. This hysteresis curve was applied using Sawyer Tower method. The hysteresis curve formed indicates that all samples of BT doped Sr are ferroelectric material.
Figure 1. Diffrac
togram of BT doped Sr at variation of Sr mole

Table 1. Crystallinity and crystallite size of BT doped Sr

| Percentage of Sr mole in BT | Crystallinity (%) | Crystallite size (nm) |
|-----------------------------|-------------------|----------------------|
| 1%                          | 94                | 30                   |
| 2%                          | 96                | 32                   |
| 3%                          | 91                | 27                   |
| 4%                          | 95                | 34                   |
| 5%                          | 96                | 34                   |

Fig. 3 is the graph of dielectric constant in various frequencies. The greater the frequency decreases the dielectric constant. Each sample has the high value of dielectric constant at the frequency of 0.1 kHz. Fig. 4 is the graph of the dielectric constant of BT doped Sr at frequency of 0.1 kHz. Variations of mole doping Sr will tend to increase the dielectric constant. The highest dielectric constant was obtained in 3% mole doping Sr. This is caused by the radius Sr smaller than Ba, so that will reduce the volume of atoms that affect dielectric constant. However, in the number of moles of doping Sr 4% the dielectric constant decreases. This is possible because Sr doping results in crystal defects.
Figure 2. Hysteresis curve of BT doped Sr, a. 1% b. 2% c. 3% d. 4% e. 5%

Figure 3. The dielectric constant for each frequency at percent doping variation Sr
Figure 4. Dielectric constant of BT doped Sr at frequency of 0.1 kHz

4. Conclusion

BT doped Sr ferroelectric material has been successfully fabricated. The more of Sr mole resulted in the larger diffraction angle. The crystallinity of the sample is above 90% and the crystallite size is in the range of 27 nm-34 nm. The hysteresis curve confirms that all samples are ferroelectric material. The greater frequency tends to decrease the dielectric constant. The highest dielectric constant at frequency of 0.1 kHz occurs at doping 3% Sr. Therefore, the best variation obtained in this research is BT with doping of 3% Sr

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