Variation of Strontium (Sr) in the Ferroelectric Material Barium Strontium Titanate ($Ba_{1-x}Sr_xTiO_3$) by Co precipitation Method

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Abstract. Barium Strontium Titanate (BST) have been made with variation strontium (Sr) 10%, 30% and 50% by co-precipitation method. This study aims to determine influence addition Sr against the crystal structure, crystallite size, lattice parameter, grain size and dielectric constant. Samples have been made by co-precipitation method and then the samples were sintered by furnace at 1100°C with holding time 4 hours. Characterization of BST use X-Ray Diffraction instrument, Scanning Electron Microscopy and Resistance Capacitance Inductance (RCL meter). Based on result obtained, the larger Sr content cause the diffraction angle shift to the right (the greater) and crystallinity increasing. But, the value of dielectric constant, crystallite size and grain size decreasing with additional Sr content. Measurement of dielectric constant (*K*) performed in the frequency range 1 kHz to 100 kHz and the highest value at Sr content 0.1 i.e. 258.35. The addition of Sr content 30% and 50% change the crystal structure from tetragonal to cubic which has paraelectric phase.

1. Introduction

The development of electric components is one of the factors that support exist as modern technology. One of the material that many applied and continues to be developed is a ferroelectric material. The ferroelectric is a material that can spontaneous polarization if applied external field. Spontaneous polarization is defined as the surface density of the bound charge on the sample surface [1]. The ferroelectric material has a perovskite structure. One of the ferroelectric material often used is Barium Titanate (BT). It has perovskite structure ABO_3.

Barium Titanate has high dielectric constant, there for its often used to electronic component as capacitor [2]. Moreover, BT has a Curie temperature 120°C and environmentally friendly. When the BT is below or above the Curie point, the crystallographic of BT will change [3]. Many research had been done in improving the electric properties as well as the morphology of BT. One of the ways often used i.e give doping. The doping can increase the dielectric constant, decrease the Curie temperature and the ferroelectric properties change. Some dopings are often used for BT i.e Pb, Zr, Ca, Sr, and Sn [4]. The strontium (Sr) is one of the doping that often used because it has an atomic radius similar to the atomic radius of Ba. The Sr caused crystal structure change and increase the dielectric constant of BT. The BT doped with Sr has a chemical formula $Ba_{1-x}Sr_xTiO_3$ (BST). The BST has high dielectric constant, chemical stability and low dielectric losses [5].

The many methods usually used to make BST i.e solid state reaction, sol-gel [4], pulsed laser deposition (PLD), metal organic chemical vapor deposition (MOCVD) [6], chemical solution deposition (CSD) [7], sputtering [8], and co-precipitation [9]. The co-precipitation method is a simple method with low reaction temperature [5]. This paper will discuss on the manufacture of $Ba_{1-x}Sr_xTiO_3$ with variation strontium 10%, 30% and 50% by co-precipitation method. The samples will be sintered by the furnace at 1100 ^oC with holding time 4 hours. The microstructure of the $Ba_{1-x}Sr_xTiO_3$ will be characterized by XRD to obtain lattice parameter and crystallite size. The morphology structure is characterized by SEM, while the dielectric constant is characterized by Resistance Capacitance Inductance (RCL meter).

2. Experimental

The starting materials used for the synthesis of Barium Strontium Titanate ($Ba_{1-x}Sr_xTiO_3$, x = 10%, 30% and 50%) were barium hydroxide (Sigma Aldrich, 95%), strontium nitrate (Sigma Aldrich, ≥ 99%), titanium tetrabutoxide (Sigma Aldrich, 97%), oxalate acid (Sigma Aldrich, ≥ 99%), and isopropanol (IPA). The BST powder was synthesized by the procedure described in the flowchart as given in Fig. 1. Initially, prepared tools and materials. Then the materials were weighed by digital neraca. 0.2 M solution of oxalic acid was dissolved in 35 ml IPA and taken in beaker glass and then stirred continuously. Then the solution of titanium tetrabutoxide (0.1 M) was made by dissolving titanium tetrabutoxide in 18 ml IPA. The solution of titanium tetrabutoxide had been added to a solution of oxalic acid with continuous stirring and then obtained clear solution oxalotitanic acid (HTO). Then barium hydroxide and strontium nitrate were added directly (in solid) to the clear HTO solution. After that, the distilled water was added a dropwise and kept overnight. The precipitate obtained was filtered, washed and dried at 100^oC for 5 hours.

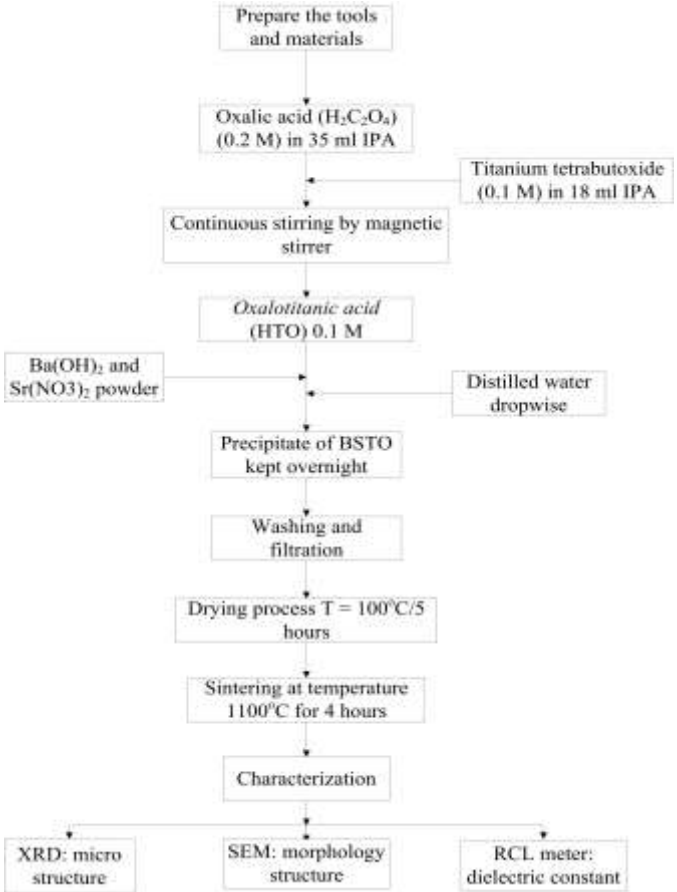

Figure 1. Flowchart procedure of experiment

After the drying process, barium strontium titanate oxalate (BSTO) powder was pressed by the hydraulic pump. The pellets of BSTO were sintered by the furnace at 1100°C with holding time 4 hours. The microstructure will be characterized by XRD with λ Cu = 1.5406Å, the data obtained will be matched with a database ICDD. The morphology structure was characterized by SEM and the dielectric constant was characterized by Resistance Capacitance Inductance (RCL meter).

3. Result and Discussion

The Result obtained from characterization using XRD is diffraction patterns with intensity value and 2θ. They were shown in Fig. 2. The diffraction patterns will be matched with database ICDD number pdf#440093 for $Ba_{0.9}Sr_{0.1}TiO_3$ sample and number pdf#340411 for $Ba_{0.7}Sr_{0.3}TiO_3$, while $Ba_{0.5}Sr_{0.5}TiO_3$ sample will be matched with number pdf#391395. The Fig. 2 shows the peaks formed were only BST peaks and the impurities (BaC_2O_4 and SrC_2O_4) were absent. So, the XRD patterns shown in Fig. 2 were only for single-phase of BST. This shows that the co-precipitation method can produce high purity yield > 99% [9]. It can be seen on the results of high crystallinity. Moreover, the result of GSAS refinement analysis proves that the peaks formed were only BST peaks.

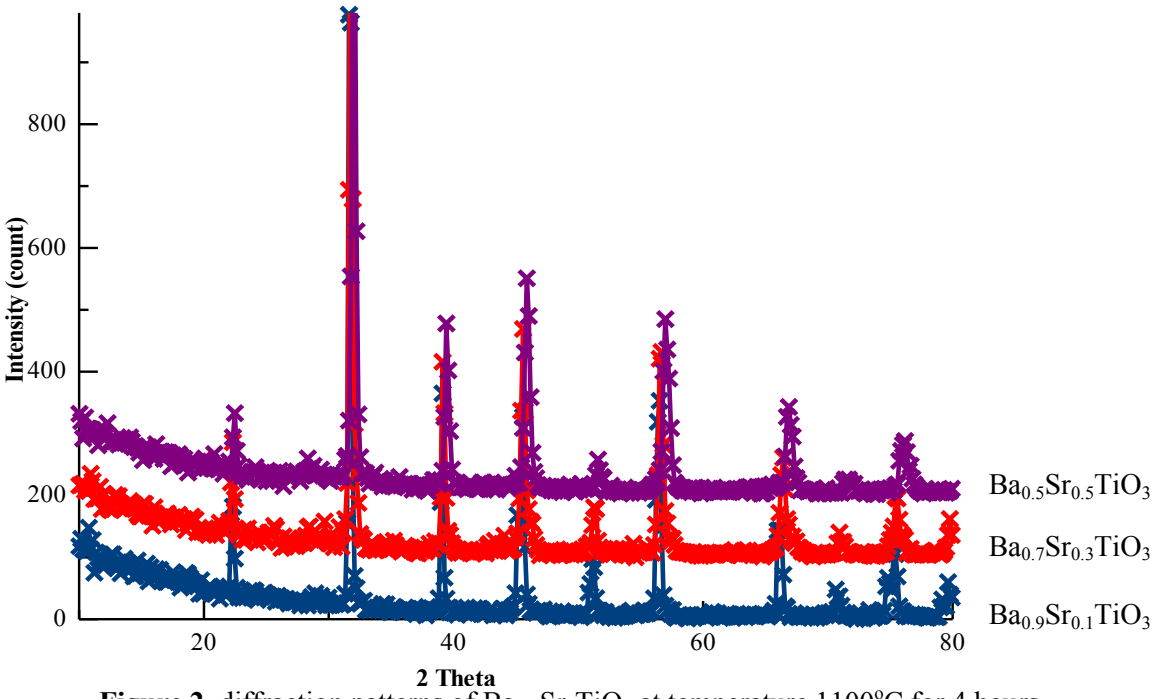

Figure 2. diffraction patterns of $Ba_{1-x}Sr_xTiO_3$ at temperature 1100°C for 4 hours

Fig. 2 shows that the addition mole percent Sr shift the diffraction angle to the right or increase. This is due to the smaller atomic radius of Sr compared to atomic radius of Ba. The Sr will replace Ba atom position in the structure of $Ba_{1-x}Sr_xTiO_3$. The effect of Sr was shown in the lattice parameter change. The lattice parameter of BST was calculated by GSAS refinement analysis (in Table 1).

Table 1. Lattice parameter of refinement obtained by GSAS software

$Ba_{0.9}Sr_{0.1}TiO_3$		$Ba_{0.7}Sr_{0.3}TiO_3$		$Ba_{0.5}Sr_{0.5}TiO_3$	
2θ	Lattice Parameter (Å)	2θ	Lattice Parameter (Å)	2θ	Lattice Parameter (Å)
31.625 45.575 56.525	a = b = 3.9762 c = 4.0026	31.775 45.575 56.675	a = b = c = 3.9693	31.925 45.875 56.975	a = b = c = 3.9510

Based on Table 1 shows that the addition mole percent of Sr affected on the crystal structure. The increase of Sr will decrease the lattice parameter. This is caused crystal structure change from tetragonal to the cubic structure. At additional mole percent of Sr 10% has tetragonal structure, space group p 4 m m and ferroelectric phase. But, when the addition mole percent of Sr 30% and 50%, the crystal structure is transformed into cubic, space group p m 3 m and paraelectric phase. The BST has a tetragonal structure and ferroelectric phase if mole percent of Ba $\geq$ 0.75. Mean while, the BST has a cubic structure and paraelectric phase if the mole percent of Ba < 0.75 [10].

We can obtain the crystallite size of BST through the result of XRD peaks. Table 2 shows crystallite size and crystallinity were influenced by composition mole of Sr. The increasing mole of Sr will decrease the crystallite size. The decreasing crystallite size is caused the atomic radius of Sr which smaller than Ba. Therefor the substitution of Sr in the unit cell Ba causes the volume of the unit cell and the crystallite size become smaller.

Table 2. Crystallite size and crystallinity of $Ba_{1-x}Sr_xTiO_3$

Sample	Crystallite size (nm)	Crystallinity (%)
$Ba_{0.9}Sr_{0.1}TiO_3$	36.99	95.09
$Ba_{0.7}Sr_{0.3}TiO_3$	33.95	96.96
$Ba_{0.5}Sr_{0.5}TiO_3$	21.49	97.32

Table 2 also shows the crystallinity of BST. The highest crystallinity was obtained at the sample with the composition of Sr 50%, while in the composition of Sr 10% obtained the lowest value of crystallinity. It also can be seen in the SEM photos. The value of crystallinity shows the level of regularity atomic structure on a material.

The dielectric constant value was obtained from measurement Resistance Capacitance Inductance (RCL meter) by giving input frequency 1 kHz to 100 kHz. Based on the Fig. 3, increasing frequency will decrease the dielectric constant. While the increasing the composition of Sr will decrease the dielectric constant. This is caused the greater composition of Sr will change crystal structure into cubic and become paraelectric phase. The paraelectric material has the dielectric constant which smaller than the ferroelectric material.

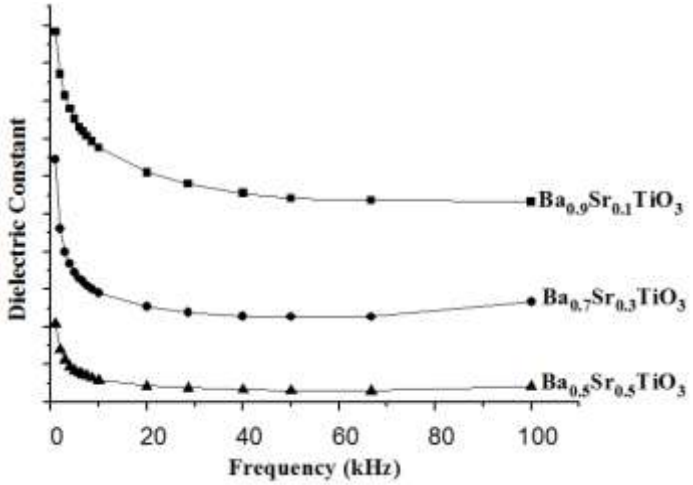

Figure 3. Graphic the dielectric constant of $Ba_{1-x}Sr_xTiO_3$

The morphology characterization results of BST is shown in Fig. 4. The addition of Sr to the BST decrease the grain size and increase homogeneous. It is also can be seen from the XRD characterization results. The grain size of $Ba_{0.9}Sr_{0.1}TiO_3$ with 80.000x magnitude, $Ba_{0.7}Sr_{0.3}TiO_3$ with 80.000x magnitude and $Ba_{0.5}Sr_{0.5}TiO_3$ with 40.000x magnitude are about 230 nm, 166 nm, and 113 nm, respectively.

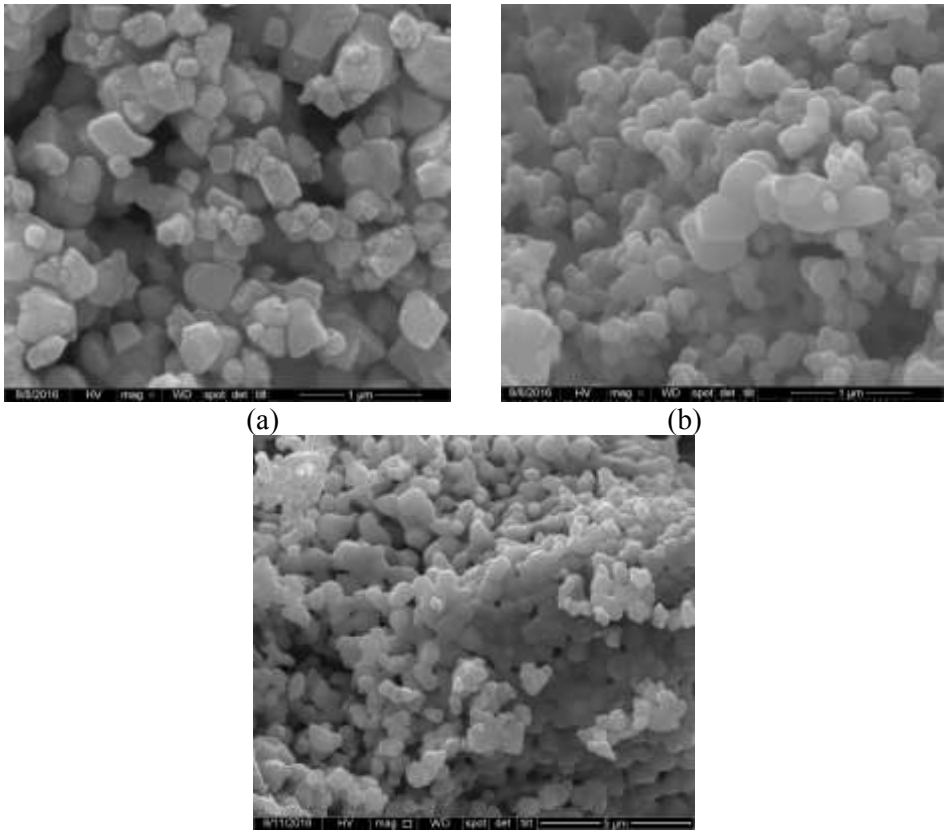

Figure 4. SEM photos of $Ba_{1-x}Sr_xTiO_3$ at temperature 1100 ^oC (a) $Ba_{0.9}Sr_{0.1}TiO_3$, (b) $Ba_{0.7}Sr_{0.3}TiO_3$ and (c) $Ba_{0.5}Sr_{0.5}TiO_3$

All samples show uniformity and homogeneous morphologies. Moreover, the sintering at high temperature has two effects, grain growth and slight reduction of lattice parameter [11]. This one like Fig. 4 the $Ba_{1-x}Sr_xTiO_3$ samples at temperature 1100 ^oC shows less porosity. It shows growth the grain. The decreasing grain size was caused the addition mole percent of Sr. It also can be seen in the crystallite size decrease. Because the grain size, crystallite size and lattice parameter were comparable.

4. Conclusion

Ferroelectric BST material (x = 10%, 30% and 50%) has been made by co-precipitation method. It can be concluded that the increasing mol of Sr shift diffraction angle to the right (the greater) and the crystallinity also gets bigger. But, the dielectric constant value, the crystallite size and grain size decrease along with the addition of Sr. The addition of Sr 30% and 50% change the crystal structure become cubic which has paraelectric phase.

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