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Deposition barium titanate ($BaTiO_3$) doped lanthanum with chemical solution deposition

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Abstract. Deposition of Barium Titanate ($BaTiO_3$) thin films used Chemical Solution Deposition (CSD) method and prepared with spin coater. $BaTiO_3$ is doped with lanthanum, 1%, 2%, and 3%. The thermal process use annealing temperature 900°C and holding time for 3 hours. The result of characterization with x-ray diffraction (XRD) equipment show that the addition of La^{3+} doped on Barium Titanate caused the change of angle diffraction.The result of refine with GSAS software shows that lanthanum have been included in the structure of $BaTiO_3$. Increasing mol dopant La3+ cause lattice parameter and crystal volume become smaller. Characterization result using Scanning Electron Microscopy (SEM) equipment show that grain size (grain size) become smaller with increasing mole dopant (x) La^{3+}. The result of characterization using Sawyer Tower methods show that all the samples (Barium Titanante and Barium Titanate doped lanthanum) are ferroelectric material. Increasing of mole dopant La^{3+} cause smaller coercive field and remanent polarization increases.

1. Introduction

Perovskite ferroelectric is a large group of ferroelectric material, that has a significance and wide application in electronic industry such as Multi Layer Ceramic Capacitor (MLCC), Ferroelectric Random Access Memory (FRAM), thermistor, optoelectronic devices and actuator [1-9]. Barium Titanate is one kind of ferroelectric material which has a perovskite structure (ABO_3). On the perovskite structure ABO_3, A is a atomic position, that has bigger atomic diameter then atomic diameter on B position. It is similiar with structure of $BaTiO_3$, Ba^{2+} (1.35A) occupied A position and Ti^{4+} (0.68 A) occupied B position. Microstructure, dielectric and ferroelectric properties of perovskite structure could be modificated by modifying of Atomic A or B. Ionic doping for subtituting of A atomic position such is such as ionic La^{3+}, Pb^{2+}, Na^{+}, Ga^{2+}, Nd^{3+}, Th $Cr4^{+}$. B atomic position can be substituted by ionic Zr^{4+}, Fe^{3+}, Al^{3+}, In^{3+}, Cr^{3+}, Nb^{5+}, Ta^{5+}, Sb^{5+}, W^{6+}. This paper presented ionic La^{3+} for subtituting Barium Titanate [10].
A thin film was fabricated by many different method such as Pulsed Laser Deposition (PLD), chemical vapour deposition (CVD), CSD (chemical solution deposition) or Sol-Gel spin coating [11-16]. Every method has advantage and disadvantage. A thin film barium titanate ($\mathrm{BaTiO_3}$) is doped with (La^{3+})

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using metode *Chemical Solution Deposition* (CSD). CSD method is a fabrication method of thin film that combined physic and chemical method. It has step for fabricating thin film : solution development (chemical process), spin coating and annealing process (Physics process). In this research, sol-gel solution material is coated on substrated pt/si using spin coater, then thermal process is done using furnice. Furthermore, the material characterization is done using *X Ray Diffraction* (XRD), *Scanning Electron Microcopy* (SEM-EDX), and electronic characterization is done using Sawyer Tower method for hysteresis properties.

2. Experiment

A Thin film Barium Titanate ($BaTiO_3$) and $BaTiO_3$ with doping lanthanum (BLT) have been fabricated by Chemical Solution Deposition (CSD) method. A thin film Barium Titanate was doped with various molarity of dopant lanthanum (La^{3+}) 1%, 3% and 5%. The precursor material that was used such as Barium acetate ($Ba(CH_3COO)_2$) 99.999%, Strontium acetate ($Sr(CH_3COO)_2$) 99.995%, Titanium (IV) Iso-propoxide ($Ti(C_{12}O_4H_{28})$) 99.000% and Lanthanum acetate ($La(CH_3COOH)_2$). Acetic acid and Methoxy methanol were used as a solvent material. Precursor and solvent material were mixed to be homogeneous solution using magnetic stirrer hotplate. A thin film was deposited $BaTiO_3$ solution (with and without dopant La^{3+}) on Pt/Si Substrate by spin coater instrument with speed 3000 rpm. Furthermore, it was annealed to be crystalline structure using furnace at 900^{o}C with holding time during 3 hours.
Materials properties of sample was investigated by X-Ray Diffraction (XRD) for microstructure and crystallinity analysis. XRD instrument by bruker has a wavelenght λ_{Cu} (1.54056 Å). XRD pattern was analyzed by rietveld method on General Structure Analysis System (GSAS) software that was done for calculation lattice parameter, tetragonality and crystal volume. The morphological investigation included thickness and roughness analysis was done by Scanning Electron Microscopy (SEM). A sawyer tower method was used for investigating of ferroelectric properties.

3. Result and Discussion

The XRD result was shown on figure 1. Based on figure 1, the diffraction pattern was compatible with pattern of Barium Titanate ($BaTiO_3$) on International Center of Diffraction Database (ICDD) with plane orientation (100) and (110). Meanwhile, the other pick diffraction showed plane orientation of Pt/Si substrate.

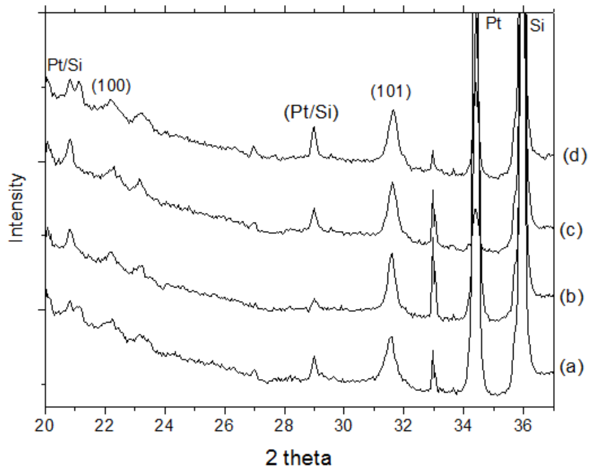


Figure 1. Diffraction pattern of thin film (a) $BaTiO_3$ (b) $Ba_{0,99}La_{0,01}TiO_3$ (c) $Ba_{0,97}La_{0,03}TiO_3$ (d) $Ba_{0,95}La_{0,05}TiO_3$

Based on XRD result, the pick intensity (count) showed crystallinity of thin film Barium Titanate. Table 1 shows pick intensity (count) and shift direction on plane orientation (110). The addition of molarity dopant La^{3+} 1 % will be increase a pick intensity, but the addition molarity dopant La^{3+} (3%, 5%) will be decrease a pick intensity. The dopant La^{3+} was donor dopant with more positive carge (+) than ionic Ba^{2+}. It will substitute ionic Ba^{2+} to be $BaLaTiO_3$. For preserving ionic stability and neutrality, ionic Ti^{4+} released one a positive charge (+), then it effected crystalline deformation especially ionic dislocation of Ti^{4+}. The crystalline deformation changed pattern interference and intensity of XRD.

Tabel 1. Shift direction and Intensity on thin film $BaTiO_3$ and BLT with molarity dopant La^{3+}

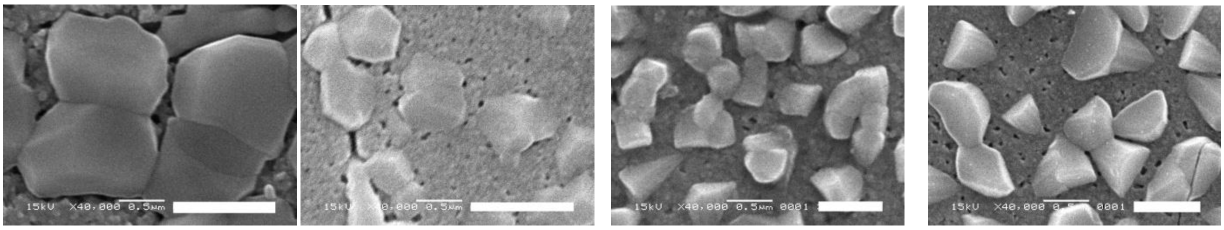
Parameters	Plane Orientation (110)			
	BT	BLT 1%	BLT 3%	BLT 5%
Intensity (count)	8206	8807	8635	8450
Shift direction (^{O})	31.55	31.60	31.60	31.65

Table 1 shows a shift direction on plane orientation of $BaTiO_3$ because of increasing dopant La^{3+}. An ionic La^{3+} has smaller diameter than ionic Ba^{2+}. Furthermore, additional of dopant La^{3+} has decreased crystalline volume and gap between other crystal to more shortly (table 2). Then a lattice parameter of crystalline decreased together additional of dopant La^{3+}. Based on brag law, a decreasing of lattice parameter effected shift angle of diffraction (2θ) into large angle diffraction on plannar orientation (110).

Table 2. Lattice parameter, tetragonality and crystal volume of thin film $BaTi0_3$ with various mol of dopant La^{3+}

Sampel	Lattice Parameter (Å)		c/a (Tetragonality)	Crystal Volume $(Å)^3$
	a=b	*C*		
$BaTi0_3$	4.008	4.029	1.005	64.722
$Ba_{0,99}La_{0.01}Ti0_3$	4.003	4.015	1.002	64.336
$Ba_{0,97}La_{0.03}Ti0_3$	3.991	4.014	1.005	63.935
$Ba_{0,95}La_{0.05}Ti0_3$	3.996	4.008	1.003	63.999

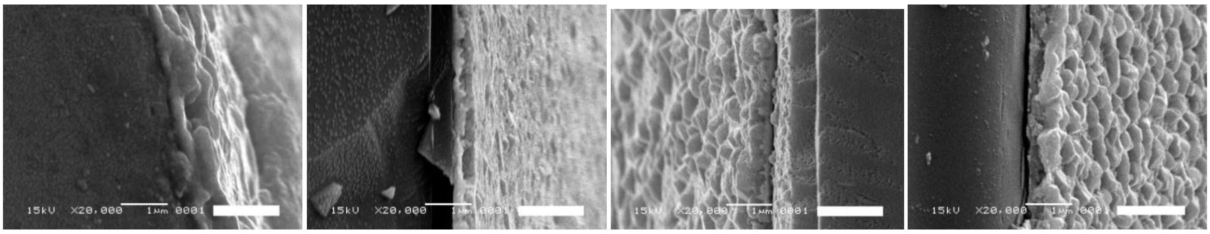
A quantitative analysis was done using GSAS software with refinement tool and rietveld method. The result shows that thin film $BaTiO_3$ was successfully growth on Pt/Si substrate with tetragonal structure of perovskite crystalline. A tetragonal structure has value lattice parameter $a=b \neq c$ and value $c/a \geq 1$. The mean of c/a was tetragonality. Table 2 shows alteration of lattice parameter because of dopant La^{3+} into $BaTiO_3$. The effect of increasing dopant La3+ into BaTiO3 will decrease lattice parameter (a,c). Therefore, the volume of crystal will decrease too.
The SEM with magnitude 40.000x was used for observing thin film $BaTiO_3$ and BLT with various dopant La^{3+} whose annealed at 900°C. Figure 2 and 3 show SEM result. Based on figure 2, the morphological of thin film $BaTiO_3$ shows heterogeneous grain size (1137 nm) and grain distance. The increasing of molarity dopant La^{3+} 1%, 3%, and 5% decreased grain size into 389 nm, 364 nm and 336 nm. It was be parallel with decreasing of crystalline volume (table 2). The result, the additional of dopant morality will be decreased crystalline gap and volume, and grain sice. It occurs because ionic diameter of La^{3+} has a smaller diameter than ionic Ba^{2+} which was substituted it.



(a) (b) (c) (d)

Figure 2. SEM Thin Film $BaTiO_3$ with various mollarity of dopant La^{3+} (a) $BaTiO_3$ (b) $Ba_{0,99}La_{0,01}TiO_3$ (b) $Ba_{0,97}La_{0,03}TiO_3$ (d) $Ba_{0,95}La_{0,05}TiO_3$

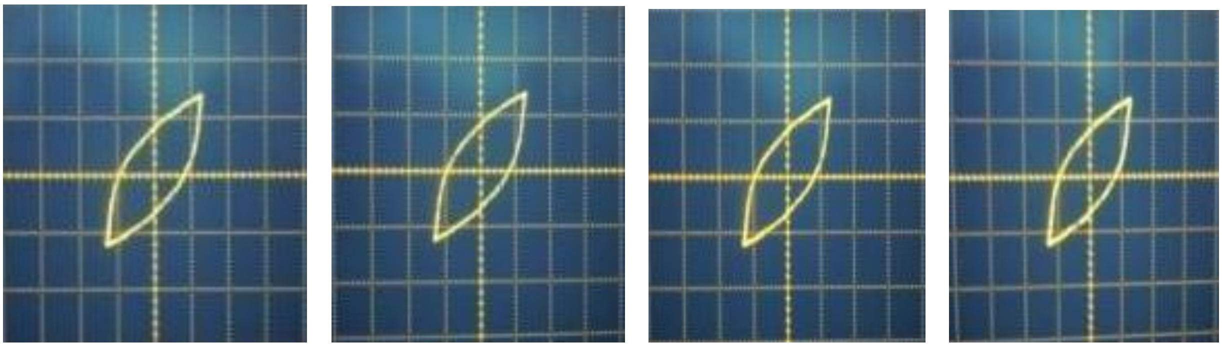
The cross section of thin film was investigated by SEM with 20.000X magnitude. It was done for knowing a thickness of thin film $BaTiO_3$. Figure 3 shows a cross section of thin film $BaTiO_3$ and $BaTiO_3$ with dopant La^{3+} on substrate Pt/Si. Figure 3 (a) shows thin film $BaTiO_3$ without dopant that was deposited on Pt/Si substrate. Thin film $BaTiO_3$ appeared visible roughness film and non-homogeneous thickness. The thickness calculation of $BaTiO_3$ was average of 705 nm. Figure 3 (b), (c) and (d) show cross section of thin film $BaTiO_3$ with various dopant La^{3+} 1%, 2%, 3%. The thickness calculation of it was average 409 nm for dopant La^{3+} 1%, 484 nm for dopant La^{3+} 3% and 646 nm for dopant La^{3+} 5%.



(a) (b) (c) (d)

Figure 3. Cross section of thin film $BaTiO_3$ with various dopant La^{3+} (a) $BaTiO_3$ (b) $Ba_{0,99}La_{0,01}TiO_3$ (b) $Ba_{0,97}La_{0,03}TiO_3$ (d) $Ba_{0,95}La_{0,05}TiO_3$

The Sawyer Tower method was done for investigation of ferroelectric material properties. A ferroelectric properties of material was shown by hysteresis curve while it was given external electric field. Figure 4 shows hysteresis curve of thin film $BaTiO_3$ and with dopant La^{3+} 1%, 3% dan 5%. The increasing doping La^{3+} into $BaTiO_3$ when annealed at temperature 900°C was not significantly influence of hysteresis curve. The coercive field was not change while add molarity of dopant La^{3+}. Furthermore, additional molarity of dopant La^{3+} changed value of remanent polarity. The alteration of remanen polarity was effected by non-uniform grain size. While external electric field offered on sample, domain orientation of sample was not same direction because of non-uniform grain size. When grain size was under critical grain size, domain structure transition happened from multi-domain into mono-domain. A mono-domain structure was a stable domain, so domain orientation transition will be difficulty offered external electric filed.



(a) (b) (c) (d)

Figure 4. Hysteresis Curve of Thin film $BaTiO_3$ with various dopant La^{3+} (a) $BaTiO_3$ (b) $Ba_{0,99}La_{0,01}TiO_3$ (c) $Ba_{0,97}La_{0,03}TiO_3$ (d) $Ba_{0,95}La_{0,05}TiO_3$

4. Summary

The addition of La^{3+} doped on Barium Titanate caused the change of angle diffraction.The result of refine with GSAS software shows that lanthanum have been included in the structure of $BaTiO_3$. The addition of molarity dopant La^{3+} 1 % will be increase a pick intensity, but the addition molarity dopant La^{3+} (3%, 5%) will be decrease a pick intensity. Increasing mol dopant La3+ cause lattice parameter and crystal volume become smaller. Grain size become smaller with increasing mole dopant (x) La^{3+}. The result of characterization using Sawyer Tower methods show that all the samples (Barium Titanante and Barium Titanate doped lanthanum) are ferroelectric material. Increasing of mole dopant La^{3+} cause smaller coercive field and remanent polarization increases.

5. Acknowledgments

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