Microstructure, Morphology, and Dielectric Properties of Ba$_{1-x}$La$_x$TiO$_3$ with Variation Mole Concentration of Lanthanum by Co-Precipitation Method

U Ulfa$^1$, Y Iriani$^{1,2}$, K Kusumandari$^{1,2}$

$^1$Graduate Physics Department, Universitas Sebelas Maret, Jl. Ir. Sutami 36A Kentingan, Surakarta 57126
$^2$Physics Department, Faculty of Mathematics and Natural Sciences, Universitas Sebelas Maret, Jl. Ir. Sutami 36A Kentingan, Surakarta 57126
Email: yofent_iriani@staff.uns.ac.id

Abstract. This study aims to determine the microstructure, morphology, and dielectric properties of Ba$_{1-x}$La$_x$TiO$_3$ modified with variations moles concentration of 10% and 15% Lanthanum at sintering temperatures of 1300$^\circ$C and 1400$^\circ$C for 4 hours. Ba$_{1-x}$La$_x$TiO$_3$ was synthesized using the co-precipitation method. The results of characterization using X-Ray Diffraction (XRD) showed that the greater concentration of La mole caused a diffraction angle shift to the right. The crystallite size decrease as the increasing concentration of La mole and sintering temperature. The smallest crystallite size (36.63 nm) belong to a sample of Ba$_{0.85}$La$_{0.15}$TiO$_3$ sintered at 1400$^\circ$C. The intensity and the crystallinity decreased with increasing concentration of La mole. Scanning Electron Microscopy (SEM) photographs showed that grain size got smaller with increasing La mole concentration. The dielectric constant obtained from the results of characterization using a Resistance Inductance Capacitance meter (RLC meter) showed that the higher the concentration of La mole added, the greater the dielectric constant produced. The highest dielectric constant was 414 belonged to the sample Ba$_{0.85}$La$_{0.15}$TiO$_3$ sintered at 1400$^\circ$C.

1. Introduction

BaTiO$_3$ is a ferroelectric material which has an ABO$_3$ perovskite structure [1]. BaTiO$_3$ is widely applied in the manufacture of electronic devices because it has stable chemical and mechanical properties, eco-friendly [2], and has high dielectric constant ($\geq 1500$ at room temperature) [3]. BaTiO$_3$ material is widely applied as dielectric material on capacitors because it has high dielectric constant [4].

Research regarding BaTiO$_3$ with variations in sintering temperature showed an increase in dielectric constant by increasing the sintering temperature [5]. Besides the sintering temperature, the dielectric constant is influenced by the synthesis method and the other substance substituted in the material [6]. In this research, BaTiO$_3$ was modified using Lanthanum (La). La replaces Ba because it has almost the same radius. It has a radius of 1.15 Å and Ba has a radius of 1.34 Å [7]. Ba$_{1-x}$La$_x$TiO$_3$ was synthesized using the co-precipitation method. This method is combining two or more types of material in the form of solids or liquids [8]. This method has a simple process which means it is easy to control the solubility of the material in solution [8], and able to synthesis material at low temperatures ($<1000^\circ$C) [9].
method has been proven in several studies that can produce homogeneous and high-quality powders [10].

This research was conducted by giving variations of La mol concentration of 10% and 15%. Ba$_{1-x}$La$_x$TiO$_3$ samples were sintered at 1300°C and 1400°C for 4 hours. Samples were characterized using XRD, SEM, RLC meters and the Sawyer-Tower method.

2. Experimental
Ba$_{1-x}$La$_x$TiO$_3$ was synthesized by co-precipitation method. The ingredients used in the synthesis of Ba$_{1-x}$La$_x$TiO$_3$ were Barium Hydroxide [Ba(OH)$_2$] (Sigma Aldrich, 95%), Lanthanum Nitrate [La(NO$_3$)$_3$] (Sigma Aldrich, <99%), Titanium Tetrabutoxide [Ti(C$_4$H$_9$O)$_4$] (Sigma Aldrich, 97%), Oxalic Acid [C$_2$H$_2$O$_4$] (Sigma Aldrich, 99.5%). Preparation of Ba$_{1-x}$La$_x$TiO$_3$ was done by dissolving Titanium tetrabutoxide in IPA, then mixed with Oxalic Acid which has been dissolved in IPA. The solution formed was the solution of Oxalic Titanic Acid (HTO). Barium Hydroxide and Lanthanum Nitrate were put into HTO solution, then stirred continuously using a magnetic stirrer. While stirring, aquades were added by titration and deposited. The sample was hydrolyzed for 5 hours at 100°C using an oven. The sample (powder) was pressed using hydraulic press and sintered at 1300°C and 1400°C for 4 hours.

The synthesized sample was then characterized. The sample microstructure was characterized using XRD. The results of XRD characterization are in the form of intensity value data (I) and diffraction angle value (2θ). The data was plotted using Origin software to form a diffraction pattern consisting of diffraction peaks matched with the International Centre for Data Diffraction (ICDD). XRD result data can be used to determine the crystallite size using the Scherrer Equation. In Equation 1,$D$ is the crystallite size (nm), $k$ is Scherrer's constant, wavelength use $\lambda$ (Å), $\beta$ is the Full Maximum Half Width (FWHM) (rad) and $\theta$ is diffraction angle (°) [11].

$$D = \frac{k\lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

The FWHM obtained from the XRD results can be used to determine the value of lattice strain ($\varepsilon$) with equation (2)

$$\varepsilon = \frac{\beta}{4 \tan \theta \tan \theta}$$ \hspace{1cm} (2)

The morphological structure and grain size of the samples were obtained from the results of characterization using Scanning Electron Microscopy (SEM). The dielectric properties of the sample were characterized using RLC meters. The RLC meter characterization results is capacitance data, where the capacitance data are obtained from the dielectric constant from the calculation using Equation 3; where $k$ is the dielectric constant of material, $C$ is the capacitance (F), $d$ is the thickness of the sample (m), $A$ is sample area (m$^2$), and $\varepsilon_0$ is permittivity in vacuum (F.m$^{-1}$) [13].

$$k = \frac{Cd}{A\varepsilon_0}$$ \hspace{1cm} (3)

The ferroelectric properties of the sample were characterized using the Sawyer-Tower method. The Sawyer-Tower characterization results in a hysteresis loop showing the relationship of polarization with the electric field of Ba$_{1-x}$La$_x$TiO$_3$ sample.

3. Results and discussion
Microstructure characterization of Ba$_{1-x}$La$_x$TiO$_3$ was carried out using XRD equipment. The diffraction pattern of the Ba$_{1-x}$La$_x$TiO$_3$ sample is shown in Figures 1 and 2. The formed pattern consists of diffraction peaks. Diffraction peaks show the relationship of intensity (I) and diffraction angle (2θ). Identification of the peak of the characterization results is done by matching the data on ICDD PDF #831880. Figure 1 is a diffraction pattern of Ba$_{1-x}$La$_x$TiO$_3$ synthesized with variations mole concentration of 10% and 15% La at sintering temperature of 1300°C. Figure 2 shows the diffraction pattern.
pattern of $\text{Ba}_{1-x}\text{La}_x\text{TiO}_3$ sample synthesized with variations in the concentration of La mole of 10% and 15% at sintering temperature of 1400°C. Both figure 1 and 2 show that the $\text{Ba}_{1-x}\text{La}_x\text{TiO}_3$ with variations in La mole concentration of 10% and 15% at sintering temperatures of 1300°C and 1400°C has a single phase. This shows that at sintering temperatures of 1300°C and 1400°C the Ba, La, Ti, and O atoms can diffuse completely.

Based on Figure 1, it can be seen that the addition of La mol concentration causes diffraction angle shift ($2\theta$). The angle of the $\text{Ba}_{1-x}\text{La}_x\text{TiO}_3$ diffraction shifts to the right as the mole concentration of La was given. The more concentration of La mol added to $\text{Ba}_{1-x}\text{La}_x\text{TiO}_3$, the diffraction angle will move to the right with greater angle. This angular shift is due to the radius of the La atom being smaller than the radius of the Ba atom. La added to the $\text{Ba}_{1-x}\text{La}_x\text{TiO}_3$ sample replaces Ba atoms in the perovskite structure of $\text{BaTiO}_3$. The addition of $\text{La}^{3+}$ was a donor dopan when occupying the $\text{Ba}^{2+}$ lattice, where $\text{La}^{3+}$ has an ion with more valence than the $\text{Ba}^{2+}$ ion [14].

![Diffraction Pattern](image)

**Figure 1.** $\text{Ba}_{1-x}\text{La}_x\text{TiO}_3$ diffraction pattern with variation mole concentration of La 10% and 15% (a) at sintering temperature of 1300°C and (b) at sintering temperature of 1400°C.

Atom La can replace the Ba atom because both have atomic radii which are almost the same. Ba has an atomic radius of 1.35 Å and La has atomic radius of 1.15 Å [7]. The more La atoms are added, the
more Ba atoms are replaced. The radius of the smaller substitute atom causes the distance between the atoms to change and the lattice parameter to be smaller. The smaller lattice parameters cause the greater diffraction angle and the more shifts towards right [15]. The reduced lattice parameter cause the distance of the atomic plane in the BaTiO$_3$ structure and will be smaller. The radius of La atom, which is smaller than Ba, can cause the cell unit volume to change[16]. The more La atoms that replace the Ba atoms, the smaller volume of the unit cell is. So that the crystallite size that are formed also shrink. Crystallite size of the Ba$_{1-x}$La$_{x}$TiO$_3$ are shown in Table 1, where the crystallite size decreases as the La mole concentration increase and as the sintering temperature increase. From the SEM results, it shows that the crystallization has decreased, where crystallization shows the level of regularity of the material’s atomic structure [17].

**Table 1. Crystallite size of Ba$_{1-x}$La$_x$TiO$_3$**

| Mole concentration of La | Crystallite size (nm) |
|--------------------------|-----------------------|
|                          | Sintering temperature 1300°C | Sintering temperature 1400°C |
| 10%                      | 40.58                  | 45.80                     |
| 15%                      | 36.63                  | 40.97                     |

**Table 2. Lattice strain of sample Ba$_{1-x}$La$_x$TiO$_3$**

| Mole concentration of La | Lattice strain |
|--------------------------|----------------|
|                          | Sintering temperature 1300°C | Sintering temperature 1400°C |
| 10%                      | 0.00226                  | 0.00403                   |
| 15%                      | 0.00683                  | 0.00495                   |

The effect of variations in the number of moles in La on the crystallite size is about the greater La added cause the crystallite size to be smaller as shown in Table 1. The smaller crystallite size causes the distance of the atoms in the crystal farther away, causing greater lattice strain. It shows the magnitude of the lattice strain in Table 2.
Figure 2 shows SEM photo of Ba$_{1-x}$La$_x$TiO$_3$ sample with magnification of 5000x and 50000x. Based on the SEM photo, it can be seen that the concentration of La mole affects the grain size of the sample. The greater concentration of La mole which is substituted causes the smaller grain size. It because the size of the radius La is smaller than the size of the Ba radius, so the more La atoms that replace Ba atoms, it cause smaller grain size.

Characterization results using RLC meters that show the relationship between frequency and dielectric constant were shown in Figure 3. Based on Figure 3, it shows that the dielectric constant decreases as the frequency increasing. It because when the input frequency is low, the negative charges oscillate with the same frequency as the electric field given. Where the direction of the dipole can adjust to the direction of the electric field, so that the dielectric constant was high. When the frequency given is too high, the dipole can not follow the electric field so that the dielectric constant decreases [17].
Figure 3. Graph of relationship between dielectric constant and frequency at (a) Ba$_{0.90}$La$_{0.10}$TiO$_3$ at sintering temperature of 1300°C, (b) Ba$_{0.90}$La$_{0.10}$TiO$_3$ at sintering temperature of 1400°C, (c) Ba$_{0.85}$La$_{0.15}$TiO$_3$ at sintering temperature 1300°C, (d) Ba$_{0.85}$La$_{0.15}$TiO$_3$ at sintering temperature of 1400°C.

Table 3 shows the dielectric constant of the Ba$_{1-x}$La$_x$TiO$_3$. The dielectric constant is influenced by the concentration of La mol substituted in the Ba$_{1-x}$La$_x$TiO$_3$. The greater concentration of La moles substituted in the Ba$_{1-x}$La$_x$TiO$_3$ sample, the more dielectric constant of the sample increases. The increasing dielectric constant is due to the increasing number of La atoms replacing Ba. Where La has atomic radius that are smaller than Ba, so the volume of cell units formed shrinks and causes the size grains to shrink. The shrinking of volume cell unit causes the increasing of polarization. This is in accordance with the equation of polarization, where the polarization is inversely proportional to the unit cell volume. Increased polarization shows an even greater dipole moment. The more the dipole moment, the more charge is stored.

Table 3. Dielectric constant of Ba$_{1-x}$La$_x$TiO$_3$

| Mole concentration of La (x) | Dielectric constant |
|-----------------------------|---------------------|
|                             | Sintering temperature 1300°C | Sintering temperature 1400°C |
| 10 %                        | 272                  | 412                  |
| 15%                         | 301                  | 414                  |

Based on Equation 3 states that the higher the capacitance, the greater the dielectric constant. This is shown in Table 6 where the dielectric constant increases as the concentration of La mol added to Ba$_{1-x}$La$_x$TiO$_3$ increase. The increasing dielectric constant occurs because the radius of La atom (1.15 Å) is smaller than the Ba atom (1.35 Å) which causes the grain size to be smaller [18].
Figure 4. Hysteresis loop of (a) $\text{Ba}_{0.90}\text{La}_{0.10}\text{TiO}_3$ at sintering temperature 1300°C, (b) $\text{Ba}_{0.90}\text{La}_{0.10}\text{TiO}_3$ at sintering temperature 1400°C, (c) $\text{Ba}_{0.85}\text{La}_{0.15}\text{TiO}_3$ at sintering temperature 1300°C, (d) $\text{Ba}_{0.85}\text{La}_{0.15}\text{TiO}_3$ at sintering temperature 1400°C.

Figure 4 is hysteresis loop from the characterization of $\text{Ba}_{1-x}\text{La}_x\text{TiO}_3$ using the Sawyer-Tower method. Remanent polarization increase with increasing mol concentration of La. The coercive field does not appear to change with the increase in the number of moles of La. Remanent polarization increase with increasing number of moles of La. $\text{Ba}_{0.85}\text{La}_{0.15}\text{TiO}_3$ shown in Figure 4 (d) has the highest polarization value, it shows that the dipole moment is formed more and more. A side from the hysteresis loop, the more formation of dipole moments can also be seen from the value of the dielectric constant. The increasing remanent polarization because of dopant $\text{La}^{3+}$ (1.15 Å) has smaller radius $\text{Ba}^{2+}$ (1.35 Å).

In the perovskite structure $\text{Ba}_{1-x}\text{La}_x\text{TiO}_3$, $\text{La}^{3+}$ ion replaces $\text{Ba}^{2+}$, because it is replaced by ions which have smaller radii, causing the crystallite size and volume of cell units to shrink [18].

4. Conclusion
The greater concentration of La mole added causes the diffraction angle shift to the right. The crystallite sizes gets smaller as the concentration of La mol is added and the sintering temperature increases. The smallest crystallite size (36.63 nm) is owned by a sample of $\text{Ba}_{0.85}\text{La}_{0.15}\text{TiO}_3$ which is sintered at 1300°C. Intensity and crystallinity decrease with increasing La mol concentration. SEM photo results show that grain size gets smaller with increasing La mol concentration. The dielectric constant obtained from the characterization results using the RLC meter shows that the greater concentration of La mol added, the greater the dielectric constant produced. $\text{Ba}_{0.85}\text{La}_{0.15}\text{TiO}_3$ owned the highest dielectric constant (414) which was sintered at 1400°C.

References
[1] Prado, L.R., Resende, N.S., Silva, R.S., Egues, S.M.S., Salazar G.R., 2015. Influence of the synthesis method on the preparation of barium titanate nanoparticle. *Chemical Engineering and Processing*. Vol 30, 490-970.

[2] Vijatovic, M.M., Stojanovic, B.D., Bobic, J.D., Ramoska, T., Bowen, P. 2010. Properties Lanthanum Doped BaTiO3 Produced from nanopowder. *Ceramic International*. Vol 36, 1817-1824.

[3] Vijatovic, M.M., Bobic, J.D., & Stojanovic, B.D. 2008. History and Challenges of Barium Titanate: Part II. *Science of Sintering*, 40, 235-244.
[4] Sun, Z., Zhang, L., Dang, F., Liu, Y., Fei, Z., Shao, Q., Lin, H., Guo, J., Xiang, L., Yerra, N., Guo, Z. 2017. Experimental and Simulation-based understanding of morphology controlled barium titanate nanoparticles under co-adsorption of surfactants. *Royal Society of Chemistry.* Vol 19, 3288-3298.

[5] Ulfa, U., Kusumandari, K., Iriani Y. 2019. The Effect of Temperature and Holding Time Sintering Process on Microstructure and Dielectric Properties of Barium Titanate by Co-precipitation Method. *AIP Conf. Proceedings.* Vol 2202, 020036.

[6] Wang, Y., Pu, Y., Li, X., Zheng, H., & Ga, Z. (2016). Evolution from Ferroelectric to Diffused Ferroelectric and Relaxor Ferroelectric in BaTiO₃ – BiFeO₃ solid solution. *School of Materials Science & Engineering.* Shaanxi University of Science and Technology, China.

[7] Wang, Y., Cui, B. Liu, Y. Zhao, X.T. Hu, Z.Y. Yan, Q.Q. Wu, T. Zhao, L.L. Wang, Y.Y. 2014. Fabrication of submicron La₂O₃-coated BaTiO₃ particles and fine-grained ceramics with temperature-stable dielectric properties. *Scripta Materialia.* Vol 90-91, 49-52.

[8] Shamsipur, M., Roushani, M., & Pourmortazavi, S. M. 2013. Electrochemical Synthesis and Characterization of Zinc Oxalate Nanoparticles. *Materials Research Bulletin,* 48, 1275-1280.

[9] You, Z., Yue, K., Zhang, J., Pan, K., Danyu, G., Guo, Q., & Luo, W. (2018). Effects of Atmosphere and Temperature on Luminescence Property of YAG:Ce synthesized by Co-precipitation Method. *School of Environmental and Chemical Engineering,* Shanghai University, Shanghai 200444, China.

[10] Pookmanee P. & Phanichphant S. 2010. Characterization of Ba₀.₇₇Sr₀.₂₃TiO₃ Powder Prepared from an Oxalate Co-precipitation and an Impregnation Method. *Ceramic Processing Research,* vol. 11, no. 3, hlm. 384-387.

[11] Callister, W.D.Jr., dan Rethwisch, DG. 2010. *Materials Science and Engineering An Introduction, Eighth Edition.* United States of America: John Wiley & Sons, Inc.

[12] Bindu, P., & Thomas, S. (2009). Estimation of lattice strain in ZnO nanoparticles: X-ray peak profile analysis. *Journal of the Chilean Chemical Society,* 54, 2.

[13] Uchino, K. 2000. *Ferroelektrik Devices.* USA: Marcel Dekker, Inc

[14] Iriani, Y., Jamaludin, A., Nurhadi, N. 2016. Deposition Barium Titanat (BaTiO₃) dped Lanthanum with chemical solution deposition. *Journal of Physics : Conference Series.* Vol. 776, 012064.

[15] Alkathy, M.S and Raju, K.C. 2018. Structural, Dielectric, Electromechanical, Piezoelectric, Elastic and Ferroelectric Properties of Lanthanum and Sodium Co-substituted Barium Titanate Ceramics. *Journal of Alloys and Compounds.* Vol 17, 6.

[16] Wang, Y., Miao, K, Wang, W., Qin, Y. 2017. Fabrication of Lanthanum Doped BaTiO₃ Fine-Grained Ceramics with a high Dielectric Constant and Temperature-Stable Dielectric properties Using Hydro-phase Method at Atmospheric Pressure. *Journal of The European Ceramic Society.* Vol 37, 2385-2390.

[17] Subarwanti, Y., Safitri R.D., Supriyanto, A., Iriani, Y., Jamaludin A. 2016. Variation of Strontium (Sr) in the Ferroelectric Material Barium Strontium Titanat (Ba₁₋ₓSrₓTiO₃) by Co-precipitation Method. *IOP Conf. Ser. : Material Science and Engineering.*

[18] Sonia, Chandrasekhar, M. Kumar, P. 2016. Microwave sintered sol-gel derived BaTiO₃ and Ba₀.₉₅La₀.₅TiO₃ ceramic samples for capacitor applications. *Ceram.Int.* Vol 42, 10587-10592.

[19] Noviastuti, M.D., Iriani Y., Kusumandari K. 2018. Electrical Properties of Barium Titanate Doped Lanthanum (Ba₁₋ₓLaₓTiO₃) Fabricated Using Co-precipitation Method. *Material Science and Engineering.* Vol 578, 012033.

[20] Vijatovic, M.M., Stojanovic, B.D., Bobic, J.D., Ramoska, T., Bowen, P. 2010. Properties Lanthanum Doped BaTiO₃ Produced from nanopowder. *Ceramic International.* Vol 36,1817-1824.