Growth, Electronic Structure, and Electrochemical Properties of Cubic BaTiO3 Synthesized by Low-Pressure Hydrothermal-Assisted Sintering

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Abstract: Cubic BaTiO3 was synthesized through low-pressure hydrothermal-assisted sintering using Ba(OH)2 and TiO2 as precursors with a mol ratio of Ba:Ti = 1.4:1. The single phase of cubic BaTiO3 was produced at a sintering temperature of 800 °C for 2, 4, 8, and 12 h. The absence of diffraction peak splitting at 2θ of 45° was indicated cubic BaTiO3. The crystallite size of BaTiO3 ranged from 80–200 nm, and its size increased with increasing temperatures and sintering times. The micro-strain of the BaTiO3 crystal lattice had a range between 0.27 and 0.68%. The minimum bandgap on the indirect bandgap was about 1.75 eV from point M to Γ, while the direct bandgap was about 1.95 eV from Γ to Γ. Ti–O’s interaction had a covalent character, while that of Ba–O had an ionic character based on the density of state (DOS) calculation. The characteristics of the BaTiO3 voltammogram show an irreversible redox mechanism with a more observable reduction peak in Ti4+/Ti3+. Higher current density at over potential indicated greater BaTiO3 capabilities in Oxygen Evolution Reaction (OER) - Oxygen Reduction Reaction (ORR) electrocatalysis. For that, purified cubic BaTiO3 offers potential application as an electrode for batteries, water splitting systems, and regenerative fuel cells.

Keywords: cubic BaTiO3; bandgap; the density of state; oxygen evolution-reduction; electrocatalyst

INTRODUCTION

Barium titanate (BaTiO3) is widely used as the main material for multilayer capacitors, thermistors, high-density data storage, and electro-optical equipment due to its dielectric and ferroelectric properties as well as environmentally friendly materials. The application of BaTiO3 to electronic materials is closely related to the character of its microstructures. The nano-size of BaTiO3 also exhibits better performance than other sizes. BaTiO3 is also known to have abilities in the electrolysis of oxygen evolution reaction (OER), oxygen reduction reaction (ORR), and hydrogen evolution reaction (HER) [1-2]. Furthermore, it is well-known that a high specific area could increase its catalytic activity by enabling a shorter diffusion distance of its electrons and holes, facilitating the surface redox reaction. Therefore, many studies have been developed to obtain BaTiO3 with microstructure and morphology matching application requirements.

The conventional technique of BaTiO3 synthesis requires high temperatures (~1200 °C) followed by grinding or milling its precursors such as BaO and TiO2 [3]. A disadvantage of this solid technique is the presence of contamination and crystal growth problems during milling and calcination. New techniques are thus being continuously developed, such as sol-gel [4-5], the Pechini process [6], hydrothermal [7], and precipitation [8-9]. These techniques can be categorized as wet techniques that facilitate the crystallization of nano-size...
particles at low temperatures. A synthesis technique for BaTiO$_3$ is required to produce nano-sized particles free of impurities and damage.

The main advantages of low-pressure hydrothermal techniques over solid-phase techniques include lower reaction temperatures and higher product purity. In addition, hydrothermal techniques no longer require thermal treatment for crystallization [10-11], so it is possible to obtain sub-micro or nano-sized materials of BaTiO$_3$. Crystallization via the hydrothermal technique also provides advantages over sol-gel and co-precipitation, such as shorter crystallization times with good control over crystallization, crystallite size, purity, and morphology [12].

Based on the above explanation of the many benefits of BaTiO$_3$ as a ferroelectric material and the advantages of the hydrothermal technique, a study was conducted to obtain cubic BaTiO$_3$ using a low-pressure hydrothermal technique and identify its crystal growth.

■ EXPERIMENTAL SECTION

Materials

All the reagents were obtained from PT Merck Indonesia Tbk, analytical grade, and used without further purification, i.e., Ba(OH)$_2$·8H$_2$O (for analysis-ensure grade, Merck, Germany), TiO$_2$ (for analysis-ensure grade, Merck, Germany), and HNO$_3$ (for analysis-65% purity, Merck, Germany).

Instrumentation

The equipment for synthesis and characterization were oven (Memmert UN55), XRD (Shimadzu XRD-7000), TG/DTA (LINSEISS STA PT 1600), and Potentiostat (Digi-Ivy).

Procedure

**Synthesis of cubic barium titanate (Cubic BaTiO$_3$)**

Cubic BaTiO$_3$ was synthesized using barium hydroxide (Ba(OH)$_2$·8H$_2$O), titanium oxide (TiO$_2$), and distilled water as precursors. BaTiO$_3$ was synthesized via a low-pressure system hydrothermal method using the mole ratio of Ba:Ti = 1.4:1. The suspension was prepared by mixing 9 g (0.12 mol) of TiO$_2$ and 45 g (0.14 mol) of Ba(OH)$_2$·8H$_2$O in 250 mL of CO$_2$-free-distilled water in a Teflon container. The mixture was stirred evenly and heated in an oven at 150 °C until the water evaporated entirely. Then, the solid was heated at temperatures of 600, 700, and 800 °C for the following durations: (a) for 600 °C = 6, 12, 18, and 24 h, (b) for 700 °C = 4, 8, 12, and 16 h, (c) for 800 °C = 2, 4, 8, 12 h.

The purification of BaTiO$_3$ was conducted by immersing it in 100 mL of 1 N HNO$_3$ solution followed by heating at 60 °C for one hour. Next, the solid was separated, washed with distilled water until being acid-free, and dried at 105 °C for 3 h.

**Phase identification using XRD**

Each product was identified for phase and crystallite size using XRD GBC EMMA software Traces 28 mA, 35 kV with Cu K$_\alpha$ = 1.54056 Å in the 2$\theta$ range of 10 to 90°, step size = 0.02°, and scan rate= 2°/min. An analysis of the XRD data in phase identification and refinement was conducted using HighScore Plus and FullProf software using COD and the ICDD database. The BaTiO$_3$ crystallite size was determined by Scherrer and Williamson-Hall equations using XRD measurement data. The equations are:

Scherrer: $B = \frac{K_\lambda}{D \cos \theta}$

Williamson-Hall: $B = \frac{K_\lambda}{D \cos \theta} + \eta \tan \theta$

then rearranged to $B \cos \theta = \frac{K_\lambda}{D} + \eta \sin \theta$

where $B$ = FWHM peaks after correction by instrumental broadening, $B = \sqrt{B_0^2 - B_s^2}$; $B_0$ = FWHM sample, $B_s$ = FWHM standard (silicon), $D$ = crystallite size, $K$ = constant Scherrer (0.94 for cubic system), and $\eta$=strain. The sizes of the crystallite and strain were determined by making the linear equation between $B\cos \theta$ and $\sin \theta$. The intercept and slope of the linear equations were used to determine the size of the crystal (D) and the strain of a micro-crystal lattice, respectively. The determination of crystal size through the Scherrer equation used FWHM from peaks 111 and 200 because it was close to the standard of the silicon peak [13].

**Study of crystal growth**

The kinetics of BaTiO$_3$ crystal growth was determined using a Burke-Turnbull equation modification based on an isothermal reaction model:

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\[ D_t^b - D_0^b = Ate^{-\frac{E_a}{RT}} \]

this equation was rearranged to:

\[ \ln D_t = -\frac{1}{n} \ln t + \frac{1}{n} (\ln A - \frac{E_a}{RT}) \]

and then rearranged to:

\[ \ln D_t^n = \ln A - \frac{E_a}{R} D_t \]

\( D_t \) and \( D_0 \) are average grain sizes at time \( t \) and original grain size, \( n \) is the grain growth exponent, \( t \) is the sintering time, \( E_a \) is the grain growth activation energy, and \( A \) is the pre-exponential, and \( R \) is the general gas constant.

**Thermal and electrochemical characteristics**

The thermal properties of a low-pressure hydrothermal product prior to sintering were monitored using a TG-DTA pattern in air and oxygen atmospheric with a flow rate of 10 °C/min. In addition, the electrochemical properties of BaTiO\(_3\) were obtained from cyclic voltammetry (CV) and linear sweep voltammetry (LSV). CV was performed using potentiostat DY 2300 digi-ivy, SPCE DS-110 as substrate of BaTiO\(_3\), potential range (-1)–(1) V, scan rate 0.05 V/sec, and sensitivity \(10^{-3}\) A/V in a 1 M NaOH solution.

**RESULTS AND DISCUSSION**

**Cubic Barium Titanate**

The single-phase was successfully synthesized through low-pressure hydrothermal at 150 °C and sintering at 800 °C for 2, 4, 8, and 12 h based on the XRD measurements (Suppl. 1–3). The BaTiO\(_3\) diffractions show peaks at \( \theta = 45° \) close to BaTiO\(_3\) in the COD database No. 96-210-0863 (Fig. 1). The temperatures of the sintering and distilled water purity could affect the purity of BaTiO\(_3\). The impurities of BaTiO\(_3\) formed at sintering temperatures of between 600 and 700 °C. The impurities were caused by the reaction between Ba(OH)\(_2\) and dissolved CO\(_2\) in distilled water. The use of free-CO\(_2\) distilled water, cleaning with Nitrogen/Argon, or washing with organic acids like formic acid can reduce impurities [7]. In this study, the purification of BaTiO\(_3\) was successfully performed using nitric acid to remove BaCO\(_3\), which was characterized by the absence of BaCO\(_3\) peaks at 23.939, 24.335, 34.143, 42.045, and 43.035° after treatment with nitric acid (Fig. 1). The formation of BaCO\(_3\) impurities indicates the weakness of the synthesis of BaTiO\(_3\) through wet techniques performed at low sintering temperatures [14-15]. Inhibition of BaCO\(_3\) formation is important for obtaining BaTiO\(_3\) with high purity. Small amounts of BaCO\(_3\) impurities were also identified in the hydrothermal synthesis of BaTiO\(_3\) at 200 °C with Ba(OH)\(_2\) and TiO\(_2\)/TiCl\(_4\) as precursors [16].

BaCO\(_3\) was also produced in synthesizing hydrothermal BaTiO\(_3\), with Ba (OH)\(_2\) and TiO\(_2\) as precursors at 220 °C for three days. The impurities of the BaCO\(_3\) phase decreased at the sintering temperature of 800 °C. Based on the Rietveld refinement result, the composition of BaCO\(_3\) was not significantly different at 600 and 700 °C for all durations of sintering (Table 1). Moreover, the sintering temperature of 800 °C caused BaCO\(_3\) to turn into BaO and CO\(_2\).

The synthesized BaTiO\(_3\) had a cubic crystal system based on the XRD diffractogram (Fig. 2), which was indicated by the absence of splitting at the diffraction peak of \( \theta = 45° \), the \{200\} plane into two peaks (i.e., \{200\} and \{002\} planes) (Fig. 1) [17-19]. Sintering at 600, 700, and 800 °C was predicted to be caused by the crystal structure change from tetragonal to cubic. Thermodynamically, BaTiO\(_3\) will form a cubic crystal structure at temperatures above 130 °C.

The reaction equation and mechanism were proposed to explain the formation of BaTiO\(_3\) from Ba(OH)\(_2\) and TiO\(_2\) via the hydrothermal technique.
Table 1. Phase composition in barium titanate synthesis after refinement

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Times (h)</th>
<th>Phase composition (%)</th>
<th>Rietveld refinement (FullProf)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>BaTiO₃</td>
<td>BaCO₃</td>
</tr>
<tr>
<td>600</td>
<td>6</td>
<td>61.4</td>
<td>38.6</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>64.2</td>
<td>35.8</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>61.4</td>
<td>38.6</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>60.1</td>
<td>39.9</td>
</tr>
<tr>
<td>700</td>
<td>4</td>
<td>63.2</td>
<td>36.8</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>65.0</td>
<td>35.0</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>70.5</td>
<td>29.6</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>74.4</td>
<td>25.6</td>
</tr>
<tr>
<td>800</td>
<td>2</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

Fig 2. Crystal structure of purified cubic BaTiO₃

BaTiO₃ formation with Ba(OH)₂ and TiO₂ as precursors could be due to the dissolution-precipitation mechanism. In this mechanism, two-step reactions for BaTiO₃ formation were proposed [18,20]:

Dissolution: TiO₂ + H₂O → [Ti(OH)₄⁻x]x⁺

Precipitation: [Ti(OH)₄⁻x]x⁺ + Ba²⁺ + 2 OH⁻ → BaTiO₃ + 2H₂O

The rate of nucleation and the growth of BaTiO₃ were influenced by the dissolution rate of TiO₂, which is indicated by the surface area dependence of the resulting BaTiO₃ on the size of the TiO₂ precursor [21]. Therefore, the rate of BaTiO₃ formation could be increased by adding KOH or NaOH since the formation of [Ti(OH)₄⁻x]x⁺ ions were accelerated in the alkaline medium. Other explanations for the formation process of BaTiO₃ include the condensation reaction occurring between [Ti(OH)₆]²⁻ and Ba²⁺; the migration of the Ba²⁺ ion into the TiO₂ structure, resulting in the breaking of Ti–O–Ti bonds; and the hydrolysis of Ti–O–Ti in an alkaline medium following the migration of the Ba²⁺ ion [22]. Thermodynamically, hydroxide ions play a role in the nucleation of BaTiO₃ and its function as a catalyst through the transition acceleration of Ba²⁺ ions during the dynamic point of crystallization to form BaTiO₃ crystals. Therefore, increasing the nucleation of BaTiO₃ could increase its growth and cause larger particle size.

Size and Kinetics of Crystal Growth

The crystallite size of the synthesized BaTiO₃ was measured using the Scherrer equation. The size of the obtained crystals ranged from 82 to 169 nm, 100 to 198 nm, and 82 to 149 nm for sintering temperatures of 600, 700, and 800 °C (Table 2). The crystallite size increased in line with the duration of sintering time. The crystallite size and structure of the crystal were also influenced by the particle size and TiO₂ precursor type, with a smaller particle size of the TiO₂ precursor resulting in smaller-sized BaTiO₃ as well. Other studies were conducted for BaTiO₃ hydrothermal synthesis at 96 °C with Ba(OH)₂ and TiO₂ precursors obtaining a crystallite size of 70 nm [23]. Additives, such as Polyacrylate, PVA, and fructose...
Table 2. Crystallite size, rate parameter, and $E_a$, crystal growth of cubic BaTiO₃

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Crystallite size (nm)</th>
<th>Micro-strain ($\eta$, %)</th>
<th>Crystal growth exponent (n)</th>
<th>$E_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>Time (h)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>6</td>
<td>82</td>
<td>0.27</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>118</td>
<td>0.64</td>
<td></td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>131</td>
<td>0.58</td>
<td></td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>169</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>4</td>
<td>100</td>
<td>0.51</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>134</td>
<td>0.59</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>148</td>
<td>0.63</td>
<td></td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>198</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>2</td>
<td>82</td>
<td>0.31</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>110</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>126</td>
<td>0.68</td>
<td></td>
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<tr>
<td></td>
<td>8</td>
<td>149</td>
<td>0.65</td>
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</tr>
</tbody>
</table>

to the hydrothermal process, could reduce particle size [23]. BaTiO$_3$ with a crystallite size of 75 nm (48 h of treatment) and 130 nm (72 h of treatment) were obtained using hydrothermal techniques followed by plasma spark sintering [24].

The XRD pattern could be used to calculate microstrains from the crystal lattice. One of the top causes of expansion at peak X-ray diffraction is the microstrain. BaTiO$_3$, obtained with low hydrothermal pressure at 150 °C, a sintering temperature between 600 to 800 °C, and a sintering time of 2 to 24 h has a microstrain of 0.27 to 0.68% (Table 2). Microstrains can occur due to the uniform distortion of the crystal lattice, dislocation, anti-phase domain boundaries, or deformation faulting.

The size of the crystallite material is closely related to its chemical and physical properties, so it needs to be studied to identify its crystal growth. Information on crystal growth kinetics can be used to control the desired crystal size of the material. The crystals/grains from BaTiO$_3$ growth via low-pressure hydrothermal methods were studied at sintering temperatures of 600, 700, 800 °C for different time durations. Based on the linear plot between $\ln(D)$ and $\ln(t)$ of the Burke-Turnbull equation changes, $n$ values were 2.0, 2.2, and 2.5, respectively, for sintering temperatures 600, 700, and 800 °C. In general, the value of $n$ ranged from 2 to 6, but there were up to 10 [24]. The exponent of crystallite growth was obtained at $n = 3.4$ (matrix) and $n = 9.7$ (template) for the growth kinetics of the ceramic-textured BaTiO$_3$ through template techniques [25]. The greater value of $n$ indicates the crystal growth is constrained, resulting in the slower growth of the crystal.

A correlation between the crystal growth exponent and the grain mechanism was proposed (i.e., $n \leq 3$ due to pore controlled lattice diffusion, pore controlled vapor transport with constant vapor pressure, boundary controlled coalescence of the second phase particles for a system containing second phase particles, and boundary controlled solute drag for the doped system. Based on the value of the grain growth exponent, the growth mechanism of BaTiO$_3$ synthesized with low-pressure hydrothermal-assisted sintering was due to poorly controlled lattice diffusion. On the other hand, the sintering temperature change did not affect the grain growth exponent, which means that temperature changes do not affect the diffusion mechanism [26].

Crystal growth is influenced by the crystal-boundary curvature mechanism, lattice diffusion, crystal-bound diffusion, interfacial diffusion, evaporative agglomeration, the dissolving-settling mechanism, and super-saturation (concentrations of reactant, temperature, and mixing conditions) [25]. The size of the initial crystal affects the crystal formation process and its growth rate. In this research, BaTiO$_3$ had
an initial crystallite size that did not differ significantly among the materials (82 and 100 nm) and grew to 198 nm during sintering, with an activation energy of 119.8 kJ/mol (Table 2). This activation energy was in line with the growth rate. Based on our references, activation energies of 190, 202, and 196 kJ/mol for BaTiO₃ were produced using the milling technique for BaCO₃ and TiO₂ [27]. Activation energies of 364 kJ/mol (matrix) and 918 kJ/mol (template) for BaTiO₃ produced by the template method [25].

**Electronic Structure of BaTiO₃**

The bandgap and density of state (DOS) of the cubic BaTiO₃, calculated using quantum espresso with Burai as the graphical user interface (GUI), are shown in Fig. 3 and 4. For band structure, the maximum of the valence band and the minimum of the conduction band are located at the M and Γ band, respectively, with the smallest value of the direct bandgap about 1.9 eV at the Γ to Γ band and the indirect bandgap from M to Γ band being about 1.75 eV. This result was in line with Rohj et al. [28], who used DFT+U approximations for BaTiO₃ with values of 1.67 eV at the Γ band, and Taib et al. [29], who used the using LDA+U method for BaTiO₃ with a value of about 1.778 eV for the indirect bandgap. Orbital O 2p dominated the highest valence band (VB), while orbital Ti 3d dominated the lowest conduction band. Details on the electron density of cubic BaTiO₃ were explained using the DOS data.

The DOS of cubic BaTiO₃ exhibited a symmetric type (Fig. 4). The valence band (VB) from -6 to 0 eV consisted of an O 2p state with a small contribution from the Ti 3d and Ba 5p states. The conduction band minimum from 0 to 5 eV was dominated by the Ti 3d state, with a small contribution from the O 2p state, which

![Fig 3. Band structure of cubic BaTiO₃](image)

![Fig 4. The total density of state (DOS) for cubic BaTiO₃](image)
indicates that some electrons moved from the valence band of the O 2p orbital to the conduction band of Ti 3d and hybridized to form a covalent bond. The Ba state was not influenced by the valence band even when separated from the other bands. The Ba and O states were much larger than the O and Ti states in DOS, which indicates that the Ba–O interaction takes on an ionic character, while the Ti–O interaction takes on a covalent character.

**Thermal Characteristics and Electrochemical Properties**

Thermal analysis can be used to explain the process of forming barium titanate from its precursors. Theoretically, the formation of BaTiO₃ from Ba(OH)₂ and TiO₂ precursors will release 7.17% w/w H₂O molecules so that the BaTiO₃ material quantity after a water loss is 92.83% w/w. The study of thermal analysis using TG/DTA showed that the percentage loss of weight at 1000 °C by 8% (airflow) and 6.7% (oxygen flow) were in line with theoretical calculations (Fig. 5(a) and 5(b)). The weight loss occurred slowly until reaching a temperature of 650 °C and then increased sharply until reaching the temperature of 950 °C.

The temperature achieved for weight loss acceleration in the airflow was lower than that of the oxygen flow, indicating that airflow can accelerate BaTiO₃ formation. This phenomenon followed the TG-DTA pattern of BTO from BaCO₃ and TiO₂ and exhibited that the phase transition temperature during BaTiO₃ formation will be from 650 °C to 950 °C [30].

Endothermic peaks appeared in a TG-DTA pattern, which indicates a phase change during the formation of BaTiO₃. In the airflow, phase transition more frequently occurs, which is possible due to the effects of the chemical components contained in the air, such as N₂, O₂, CO₂, and CO. Ba₂TiO₄ is a possible phase, which occurs due to the reaction between BaTiO₃ and BaCO₃. This phase will react again with TiO₂ to form BaTiO₃ [30]. Endothermic peaks in oxygen flow occur at 750 °C and 900 °C, with sharper characters than airflow. An endothermic DTA peak above 800 °C was associated with CO₂ release due to a reaction between BaCO₃ and Ba₂TiO₄ to form Ba₂TiO₆. On the other hand, water released in the formation of BaTiO₃ from the Ba(OH)₂ and TiO₂ precursors requires high temperatures, indicating a strong OH chemisorption in the lattice perovskite [31].

The voltammogram of BaTiO₃ indicated an irreversible redox system in the alkaline medium (Fig. 6(a)). A reduction peak appeared at -0.4 V vs. Ag/AgCl, and an oxidation peak appeared at 0.6 V vs. Ag/AgCl, indicating the behavior of Ti³⁺/Ti⁴⁺ redox on an electrode surface. On the other hand, the redox system of the BaTiO₃ electrode surface caused an oxygen evolution/reduction reaction (OER/ORR) and a hydrogen evolution reaction (HER). Positive potential is the OER/ORR region, while the negative potential is the HER region. The current at a positive potential is higher than negative potential indicating that BaTiO₃ is more active as an OER/ORR electrocatalyst. The OER/ORR
bifunctional electrocatalyst of BaTiO$_3$ has been studied previously [32] due to the oxygen vacancy of BaTiO$_3$ that changes its crystal structure from cubic to hexagonal. Mechanistic of OER, ORR, and HER are initiated via OH adsorption on the Ti atom, the formation of the O–O bond, and O$_2^{2-}$/OH exchange. The OER/ORR mechanism of the perovskite has also been previously studied, and a proposed mechanism of OER in an alkaline medium is as follows:

\[
\begin{align*}
M + \cdot \text{OH} & \rightarrow \text{MOH} \\
\text{MOH} + \cdot \text{OH} & \rightarrow \text{MO} + \text{H}_2\text{O} \\
2\text{MO} & \rightarrow 2\text{M} + \text{O}_2(g) \\
\text{MO} + \cdot \text{OH} & \rightarrow \text{MOOH} + \cdot \text{e}^- \\
\text{MOOH} + \cdot \text{OH} & \rightarrow \text{M} + \text{O}_2(g) + \text{H}_2\text{O}
\end{align*}
\]

Good electrocatalyst was indicated by Tafel slope value and also may provide insightful information about the OER mechanism. Suen et al. [33] was reviewed various OER mechanisms that correlated with Tafel slope value. Tafel slope value can be linked to the rate-determining step and implicates to some pattern may exist. The same rate-determining steps could have several values of Tafel slope, dependent on different coverage degree of intermediate. OER mechanism included intermediate such o xo, peroxide and superoxide group on surface electrocatalyst.

The OER ability of BaTiO$_3$ can be attributed to the electron configuration system of the Ti atom, in which the d orbitals of Ti are not filled (d$^0$), so it is possible to interact with more reactive ligands, such as –OH at the initial stage. Based on Hard-Soft Acid Base (HSAB) theory, The Ti ion is categorized as a hard acid, while O$_2^-$ and –OH are categorized as hard bases. –OH ions are preferred for interacting with Ti compared to O$_2^-$ ions due to their having a larger degree of basicity. To study the OER mechanism of BaTiO$_3$, the calculation of reaction Gibbs free energy using MMFF-based molecular mechanics was calculated (Fig. 7). The energy profile showed that the OOH stage is the rate
Fig 7. Profile of Gibbs Free Energy in oxygen evolution reaction
determining step, allowing for oxygen evolution in the base medium. The calculation of Gibbs free energy in Fig. 7 was used a mechanism of OER proposed by Hong et al. [34] for perovskite surface.

■ CONCLUSION

The hydrothermal technique of low-pressure systems followed by sintering at 600, 700, and 800 °C can be used to synthesize BaTiO3 with Ba(OH)2 and TiO2 precursors. Sintering temperatures of 600 and 700 °C still contain BaCO3 impurities sourced from distilled water and air. The crystal size of BaTiO3 ranged from 82 to 198 nm based on the Williamson-Hall equation with strains from 0.27 to 0.68%. BaTiO3 crystal growth following lattice diffusion is controlled by pore size based on the exponent value of 2-2.5. The band structure of cubic BaTiO3 exhibited an indirect band from the M to Γ band of about 1.75 eV and a direct bandgap of about 1.9 eV at Γ to Γ. The density of state (DOS) indicated the covalent character on the Ti–O interaction and the ionic character on the Ba–O interaction. Electrochemical measurements indicated that BaTiO3 has OER electrocatalytic capabilities in an alkaline medium. The purified cubic BaTiO3 offers potential application in electrocatalyst for energy storage and conversion as an electrode for batteries, water splitting systems, and regenerative fuel cells.

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■ REFERENCES


