THE EFFECT OF HEXAMETHYLENETETRAMINE AND TETRABUTYL AMMONIUM BROMIDE TEMPLATE ON THE LANTHANUM PHOSPHATE SYNTHESIS

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ABSTRACT

LaPO4 synthesis through the sol-gel method and synthesis of LaPO4 with the addition of templates through the hydrothermal method have been successfully carried out. The templates used are hexamethylenetetramine (HMT) and tetrabutylammonium bromide (TBABr). The concentration of precursor, pH, and aging time in the sol-gel method can affect the structure and morphology of LaPO4. In this study, the ratio of La3+: PO43-, pH, and aging were varied to obtain the optimal condition in used sol-gel method. The optimization results show that LaPO4 is formed at pH 9, the ratio of moles La3+: PO43- is 1:1, and the aging time is 72 h. The obtained solids were characterized by X-ray diffraction, FTIR, SEM-EDX, and adsorption-desorption N2. The XRD results showed that LaPO4 without templates (LaP) and LaPO4 with TBABr templates (LaPT) had a hexagonal crystal structure, meanwhile, LaPO4 with HMT templates (LaPH) had a monoclinic crystalline structure. The surface area of LaP, LaPH, and LaPT was 93.28; 69.37; and 107.00 m²/g, respectively, while the pore diameters were 7.04; 16.91; and 8.30 nm, respectively. SEM morphological observations of LaP, LaPH, and LaPT solids are in the form of aggregates that have not been evenly distributed and pore sizes that have not been uniform, and differences are seen between LaP, LaPH, and LaPT.

Keywords: Lanthanum Phosphate, Hexamethylenetetramine, Tetrabutylammonium Bromide

INTRODUCTION

Lanthanum phosphate (LaPO4) has become the center of attention of researchers by exhibiting many potentials, especially for optical applications such as phosphors.1 LaPO4, with excellent physical and chemical properties, was reported to have various applications such as in bio-imaging, bio-labeling,2–5 as catalyst,6 photoluminescence material,7 and hydrophobic nano-coating.8 Many studies have synthesized LaPO4 through hydrothermal,9–11 wet chemistry,12 sonochemistry,13 reverse micelles,14 and sol-gel methods.8,15 Several studies have also produced LaPO4 nanospheres and nanoparticles with irregular shapes, primarily using hydrothermal and precipitation techniques.9,12 The advantages of the hydrothermal technique are easily controlling the size and morphology of the crystals by adjusting the number of precursors, temperature, and reaction time.16 Sol-gel technique also has advantages such as synthesis carried out at room temperature, a more homogeneous final product, and a good technique for doping.15,17,18 Several parameters, such as pH and aging time, affect the synthesis of LaPO4.19 The electrical and optical properties of LaPO4 highly depend on size, shape, structure, and morphology. Many researchers attempted to synthesize LaPO4 with a controllable structure through various approaches. The addition of templates in

http://doi.org/10.31788/RJC.2023.1638472

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the synthesis of LaPO$_4$ could be added as a trapping agent that can control the morphology of the LaPO$_4$.$^{20}$ The addition of HMT is considered to change the morphology and surface area of the obtained powder. HMT is often used as a trapped agent of metal-organic compounds to form various supramolecular structures.$^{21,22}$ The addition of HMT acts as a precipitation agent, nucleation formation control, and regulates reaction pH.$^{23,24}$ Pan et al. reported that the addition of tetrabutylammonium bromide (TBABr) also affects morphology.$^{25}$ HMT and TBABr are known to be good structural and morphological directors.$^{25–27}$ In this study, HMT and TBABr were added to the synthesis of LaPO$_4$ to form a better morphology and structure for the development and increase the application of LaPO$_4$. To study the effect of La: P molar ratio, pH, and aging time on the structure and morphology of LaPO$_4$, the synthesis of LaPO$_4$ was carried out with varying La: P, pH, and aging time. The obtained condition would be used in the synthesis of LaPH and LaPT.

**EXPERIMENTAL**

**Materials**
LaCl$_3$·7H$_2$O (98%, Merck), H$_3$PO$_4$ (99%, Merck), NH$_3$OH (Merck, 25%), HMT (Sigma-Aldrich, 99.5%), TBABr (Sigma-Aldrich, 99%), Ammonium molybdate (Merck, 99%), Hidrazine sulphate (Merck, 99%), and aquabidest (Otsuka) was used without further purification.

**Synthesis of LaPO$_4$**
The LaPO$_4$ was synthesized by the sol-gel method. LaCl$_3$·7H$_2$O was dissolved in aquabidest. Then, KH$_2$PO$_4$ was added dropwise to the LaCl$_3$ solution to get LaPO$_4$ sol with La: P molar ratio = 1:0.5, 1:1, 1:2, 1:3 and 1:4. NH$_3$OH solution was added to adjust the pH levels (6, 7, 8, 9, 10 and 11). The solution was stirred for 3 h to form a gel. The gel was aged for 12, 36, 48, 72, 96, and 120 h until stable gel was obtained. The stable gel was filtered and washed by aquabidest to remove any traces. The washed residue was then dried at 100°C for 18 h. Finally, the dried gel was calcined at 550°C for 4 h. The obtained powder is labeled as LaP. The optimum conditions were based on the LaP formed. The LaP formed was obtained by UV-Vis spectrophotometric method at 715 nm. The optimization results showed that LaPO$_4$ was formed at pH 9, the mole ratio of La$^{3+}$:PO$_4^{3-}$ was 1:1 and the aging time was 72 h. This condition will be used in the synthesis of LaP with templates.

**Synthesis of LaPO$_4$ with Template**
The LaPO$_4$ with templates HMT and TBABr were synthesized by sol-gel and hydrothermal methods. LaCl$_3$·7H$_2$O and template were dissolved in aquabidest. KH$_2$PO$_4$ was added dropwise to the LaCl$_3$ solution to get LaPO$_4$ sol with La: P molar ratio 1:1. NH$_3$OH solution was added to adjust the pH levels 9. The solution was stirred for 3 h to form a gel. The gel was aged for 72 hours until stable gel was obtained. The stable gel was filtered and washed by aquabidest to remove any traces. The washed residue was then dried at 100°C for 18 h. Finally, the dried gel was calcined at 550°C for 4 h. The obtained powder is labeled as LaPT and LaPH.

**Characterization**
The crystal structures of LaP, LaPH, and LaPT were characterized by a Philips X-Pert X-Ray Diffractometer (XRD) equipped with Cu Kα radiation (λ = 1.54178Å). The chemical bonds of the synthesized solids were determined by Fourier Transform Infrared (FTIR) using Shimadzu Instrument Spectrum One 8400s. The nature of acid sites was determined by the Pyridine-FTIR method. Solid morphology was observed by Scanning Electron Microscope–Energy Dispersive X-ray (SEM-EDX) using Hitachi Flexem 100. The Brunauer-Emmet-Teller (BET) surface area and porosity were measured by nitrogen gas adsorption-desorption using Quantachrome Instrument.

**RESULTS AND DISCUSSION**

**Optimization Condition of LaPO$_4$ Synthesis**
Optimization of pH (6, 7, 8, 9, 10 and 11), the mole ratio of La$^{3+}$:PO$_4^{3-}$ (1:0.5, 1:1, 1:2, 1:3 and 1:4), and aging time (12, 36, 48, 72, 96 and 120 h) were investigated to obtain the optimum conditions. The optimum conditions were based on the LaP formed. The LaP formed was obtained by UV-Vis spectrophotometric method at 715 nm. The optimization results showed that LaPO$_4$ was formed at pH 9, the mole ratio of La$^{3+}$:PO$_4^{3-}$ was 1:1 and the aging time was 72 hours (Fig.-1).
SEM-EDX Results

SEM analyzed the morphology of the obtained powder shown in Fig.-2. The morphology of samples is irregular in shape, with an indefinite particle size. LaP and LaPT have morphology with small particles showing needle-shaped. However, the morphology of LaPH is spherical-shaped. The difference between LaPH and LaPT is related to the particle size of the template used. The presence of four symmetrically placed N atoms and the overall cubic symmetry of the HMT molecule allows the formation of up to four hydrogen bond interactions: N–H··O or O–H···N, O–H···O, C–H···O and N–H···N. This interpretation of the hydrogen bonding pattern creates a three-dimensional supermolecular framework resulting in a slightly larger morphology. In Fig.-2, it can be seen that LaP forms aggregates, whereas LaPH and LaPT have larger and more uniform sizes. It indicates that adding HMT and TBABr produces LaP with a more uniform particle size. EDX observed the composition of elements contained in samples. The EDX spectrum presented in Fig.-3 shows that the obtained powder consists of La, P, and O. It indicates that no other elements were formed during the synthesis process. The composition of elements in LaP, LaPH, and LaPT solids is shown in Table-1. LaPT has the highest La and P content compared to LaP and LaPH.

<table>
<thead>
<tr>
<th>Sample</th>
<th>La (%)</th>
<th>P (%)</th>
<th>O (%)</th>
<th>La (%)</th>
<th>P (%)</th>
<th>O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaP</td>
<td>55.48</td>
<td>12.06</td>
<td>24.67</td>
<td>13.41</td>
<td>13.07</td>
<td>51.76</td>
</tr>
<tr>
<td>LaPH</td>
<td>46.05</td>
<td>10.29</td>
<td>26.07</td>
<td>8.82</td>
<td>8.84</td>
<td>43.36</td>
</tr>
<tr>
<td>LaPT</td>
<td>58.17</td>
<td>13.24</td>
<td>23.96</td>
<td>15.34</td>
<td>15.67</td>
<td>54.93</td>
</tr>
</tbody>
</table>

XRD Results

The XRD patterns of LaP, LaPH, and LaPT are shown in Fig.-4. All the diffraction peaks can be indexed as a hexagonal phase of LaPO₄ (PDF No. 04-0635). A typical peak of hexagonal LaPO₄ is observed at 28.56, 31.36, and 41.58°, which indicate (200), (102), and (211) crystal plane, respectively. The (200) peak is higher than the (102) peak, suggesting a preferential growth direction on the hexagonal c-axis. Compared to other samples, the XRD pattern of LaPH highlights that the (102) peak is more prominent than the (200) peak, indicating no specific direction of growth in LaPH. This case is supported by the difference in powder morphology that shows LaP and LaPT have needle-shaped morphology and LaPH has spherical-shaped morphology. This phenomenon has been reported previously. To ensure the purity of the LaPO₄ powders, we compared their XRD patterns to those of other possible phases like lanthanum chloride, lanthanum hydroxide, and lanthanum oxide from the JCPDS database. We found that the absence of these phases confirms that the LaPO₄ powders are pure. The crystalline size of the obtained powder was determined using the Scherrer equation. Table-2 presents the calculated crystalline size using XRD data. LaP has the largest crystalline size compared to LaPH and
LaPT, indicating that LaP is more crystalline than LaPH and LaPT,\textsuperscript{30} so it was discovered that utilizing a template reduces the crystallite size. In addition, using templates led to solids being more porous and amorphous which is good for catalyst material.

Fig.-2: Scanning Electron Micrograph of (a) LaP (b) LaPH, and (c) LaPT

Fig.-3: EDX Spectrum of (a) LP (b) LPH, and (c) LPT
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Fig.-4: XRD Pattern of LaP, LaPH, and LaPT

Table-2: Particle Size of Obtained Solids

<table>
<thead>
<tr>
<th>Product</th>
<th>Crystalline Sizes (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaP</td>
<td>53.69</td>
</tr>
<tr>
<td>LaPH</td>
<td>19.13</td>
</tr>
<tr>
<td>LaPT</td>
<td>17.86</td>
</tr>
</tbody>
</table>

FTIR Analysis

The FTIR spectra of LaP, LaPH, and LaPT are shown in Fig.-5. The vibration observed at 616–613 cm\(^{-1}\) indicates the O–P–O and O=P–O bending. This result is similar to the research conducted by Wang et al. (2017). The absorption bands at 953–950 and 1047 cm\(^{-1}\) are associated with the P–O symmetric and asymmetric stretching vibration, respectively. The absorption band at 3448–3416 cm\(^{-1}\) is attributed to the O–H stretching vibration supported by the presence of O–H bending vibration at 1637–1629 cm\(^{-1}\). These vibration modes of the hydroxyl group indicated the presence of water vapor physically adsorbed on the solid surface. The absence of HMT and TPABr vibration peaks in LaPH and LaPT indicates that HMT and TPABr decomposed during the calcination process.

Fig.-5: The FTIR spectra of LaP, LaPH, and LaPT

SBET and Porosity Measurement

The surface area and porosity of samples were measured by nitrogen adsorption-desorption technique according to the BET theory and pore size distribution measurements according to the Barret-Joiner-Halenda (BJH) theory. The nitrogen adsorption-desorption is presented in Fig.-6. The results showed that the LaPO\(_4\) solid synthesized with the HMT template (LaPH) and the TBABr template (LaPT) influenced the textural properties. All samples exhibit the type IV isotherm indicating a characteristic of mesoporous materials. The hysteresis loops exhibited by all samples are due to the capillary condensation process on the mesoporous material. LaP and LaPT show a type H3 hysteresis loop at P/P\(_0\) = 0.5–1, which suggests...
that the shape of a pore pinched at both ends or a pore groove formed by flakes-shaped particles. On the contrary, LaPH shows a type H1 hysteresis loop, indicating the presence of large channel-like pores in the narrow range of size or a cylindrical pore shape.  

Table-3: The Measurement Result Using N₂ Adsorption-Desorption Method

<table>
<thead>
<tr>
<th>Powder</th>
<th>S_{BET} (m²/g)</th>
<th>Total Pore Volume (cm³/g)</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaP</td>
<td>93.28</td>
<td>0.16</td>
<td>7.04</td>
</tr>
<tr>
<td>LaPH</td>
<td>69.37</td>
<td>0.29</td>
<td>16.91</td>
</tr>
<tr>
<td>LaPT</td>
<td>107.00</td>
<td>0.22</td>
<td>8.30</td>
</tr>
</tbody>
</table>

Fig.-6: Adsorption isotherm of LaP, LaPH, and LaPT

The surface area of the samples is summarized in Table-3. Comparing LaPH to LaP, the specific surface area of LaPH is smaller, related to its total pore volume. At the constant pore volume, the decrease in pore sizes causes the number of pores to increase, leading to an increase in the specific surface area. Hence, the formation of pores with larger diameters is the reason for the decrease in the surface area of LaPH. In contrast, LaPT showed a slight decrease in the average pore size and a slight increase in specific surface area compared to LaP. It indicates that the LaPT is more porous than others. However, the increase in specific area is not followed by the formation of meso-sized pores, so the overall average pore size will decrease.

Fig.-7: Pore size distribution of LaP, LaPH and LaPT

CONCLUSION

LaP has been successfully synthesized using the sol-gel method, whereas LaPH and LaPT have been synthesized using the hydrothermal method. The optimum conditions for synthesizing LaPO₄ were at pH 9, the mole ratio of La³⁺:PO₄³⁻ was 1:1, and the aging time was 72 hours. XRD characterization results showed that the obtained powders have a monoclinic crystal structure. The solid surface area of LaP, LaPH, and LaPT were 93.28, 69.37, and 107 m²/g, respectively. SEM morphology observations of LaP, LaPH, and LaPT.
and LaPT show that the morphology of all obtained powders is irregular in shape, with an indefinite particle size. In addition, EDX results show that La, P, and O elements are scattered on the solid surface.

ACKNOWLEDGMENTS
This work was supported by the Ministry of Education, Culture, Research, and Technology of the Republic of Indonesia under Penelitian Disertasi Doktor (PDD) research scheme in 2022 with contract number 084/E5/PG.02.00.PT/2022 and 1397/PKS/ITS/2022.

CONFLICT OF INTERESTS
The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS
All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID IDs, given below:

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