Crystallographic and optical bandgap study of LaFe$_{1-x}$Mg$_x$O$_3$ (x=0.01 and 0.05) nanoparticle

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Abstract In this study, LaFe$_{1-x}$Mg$_x$O$_3$ material with $x = 0.01$ and $x = 0.05$ have been successfully synthesized using the sol-gel method. Characterization of the material was carried out by X-ray Diffraction spectroscopy (XRD), Ultraviolet-Visible Spectrophotometry (UV-VIS), and Fourier Transform Infrared Spectroscopy (FTIR). The XRD data of LaFe$_{1-x}$Mg$_x$O$_3$ was confirmed single-phase with orthorhombic structure and Pbnm space groups for all samples. The lattice parameter value increases with increasing Mg content, which is predicted due to the larger ionic radii Mg$^{2+}$ successfully substituted Fe$^{3+}$. The crystallite size indicated that samples were nano-scale particles. FTIR spectra confirm that the increased Mg substitution increases the distortion of LaFeO$_3$ lattice, which correlates with XRD results. The UV-Vis characterization aimed to measure the optical bandgap energy. The optical bandgap energy value decreases with increasing Mg doping. Lower optical bandgap value makes a positive impact as promising candidates for photocatalytic applications.

1. Introduction

Perovskite has an ABO$_3$ chemical formula in which A-site is filled with rare earth elements, while B-site is filled with elements from transition metals [1]. Perovskite material has been widely studied because of its application in several devices, including electrodes on solid oxide fuel cells, photocatalysts, sensors for detecting gases, and magnetic memory devices. Perovskite type oxide has various types; one of them is LaFeO$_3$, which intensively study until now. LaFeO$_3$ has a bandgap energy of 2.1 eV with a cubic or orthorhombic crystal structure [1]. LaFeO$_3$ is an antiferromagnetic material with the highest Neel TN temperature among the orthoferrite classes, which is 740 K [2]. The substitution of a compound can greatly affect the particle size, surface morphology, and magnetic properties of LaFeO$_3$ [3]. However, the improvement from the original properties of LaFeO$_3$ is the challenge that the researcher intensively studied.

Some review papers related to LaFeO3 have catalytic activity because of its high stability and small bandgap energy [4]. The Mg-substitution with 10% dopant concentration makes positively impacts on the decreasing band gap energy value compared to the LaFeO$_3$-parent compound [5]. The increase in the bond length also confirmed the decrease in bandgap energy. Another previous report also shows that Mg presence improves photocatalytic performance, which correlated with the smaller bandgap energy value obtained [6].
However, to the best of our knowledge, there is still no systematic and comparative study for the effect of Mg substituted Fe-site in the structural and optical properties of LaFeO$_3$. In this work, the crystallography and bandgap properties of Mg-doped LaFeO$_3$ ($\text{LaFe}_{1-x}\text{Mg}_x\text{O}_3$, $x = 0.01$, and 0.05) were investigated.

2. Experimental

LaFe$_{1-x}$Mg$_x$O$_3$ ($x = 0.01$ and 0.05) nanoparticle were prepared using the sol-gel method. In the sol-gel method, the steps taken are mixing and stirring several raw materials such as $\text{La}_2\text{O}_3$, $\text{Fe(NO}_3\text{)}_3$, 9$\text{H}_2\text{O}$, $\text{Mg(NO}_3\text{)}_2$, 6$\text{H}_2\text{O}$, and citric acid monohydrate to obtain the gel phase. The wet gel goes through the "drying" stage at 100°C to remove $\text{H}_2\text{O}$. Then, the next step is the calcination process. The calcination process aims to remove citric acid and other organic compounds that have not been lost in the drying process. At this stage, the dry gel is calcined at 900°C for 6 hours until nanoparticles are formed.

Phase composition and structure were determined using X-ray diffraction (XRD) analysis on a PRO PANalytical X'Pert diffractometer with Cu Kα radiation ($\lambda = 1.5405$ Å), 2θ between 10° and 90°. The refinement of the XRD results was performed using FullProf 2K software. The stretching and bending vibration of the Fe / MgO$_6$ octahedral was analyzed by Fourier transform infrared (FTIR) spectroscopy. The samples' diffused reflectance and absorbance spectra were taken with ultraviolet-visible (UV-Vis) spectroscopy (Agilent Cary 100/300).

3. Result and Discussion

3.1 The XRD Analysis

The XRD spectrum indicated the substitution of Mg in the crystal lattice caused a decrease in the crystal size value. In the Rietveld analysis, structure data parameters were obtained as listed in Table 1. The average crystallite size was calculated using Debye-Scherrer’s method:

$$\langle D \rangle = \frac{0.9\lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

$\langle D \rangle$ is average crystallite size, $\beta$ is the Full Width at Half Maximum (FWHM), $\lambda$ is the wavelength of the X-rays (Cu Kα ($\lambda = 1.5405\text{Å}$)), $\theta$ is the Bragg angle which formed between the detector and the sample.

The results of the geometric sample characterization can show the accuracy of the crystal structure formed by finding the value of the tolerance factor material which has the general formula $\text{AB}_{1-x}\text{B'}_x\text{O}_3$ with the following equation:

$$t = \frac{(r_A+r_X)}{\sqrt{2[(1-x)r_B+xr_{B'}+r_X]}}$$  \hspace{1cm} (2)

where $r_A$, $r_B$ dan $r_X$ are the ionic radius of ions from A-site, B-site, and Oxygen as anion [7]. The value of the tolerance factor for an ideal perovskite is 1.00.

The results of the fitting parameters are shown in Figure 1. Rietveld analysis results confirm that all samples show peaks that correlated with the orthorhombic structure with the $\text{Pbnm}$ space group represented by the peak values (110), (200), (202), (220), (204), (040), and (240). Based on [8], $x=0.0$ with lattice parameters value, crystal structure is consistent with those previously reported for the spectrum of LaFeO$_3$. Based on Figure 1, all of the samples confirmed the single-phase detected from the XRD result.
Figure 1. Le-bail fitting XRD from LaFe$_{1-x}$Mg$_x$O$_3$ ($x = 0.01$ and $0.05$) nanoparticle. The experimental data are indicated by the black dots and the calculated data by the red solid line. The green bottom line shows the difference between experimental and calculated data.

Table 1. Crystallographic parameters of LaFe$_{1-x}$Mg$_x$O$_3$ calcined powder for $x = 0.01$ and $0.05$ as obtained by the Fullprof 2k program.

| Sample | $a$ (Å)       | $b$ (Å)       | $c$ (Å)       | Volume (Å$^3$) | Crystallite size (nm) |
|--------|---------------|---------------|---------------|----------------|------------------------|
| $x = 0.01$ | 5.5516(1)    | 5.5612(1)    | 7.8441(1)    | 242.18(4)     | 78.91(6)               |
| $x = 0.05$ | 5.5512(1)    | 5.5617(1)    | 7.8471(1)    | 242.27(4)     | 69.21(6)               |

The final crystallographic parameters are summarised in Table 1. As the Mg content increased, the lattice parameters changed slightly but with a noticeable overall effect on the cell volume. The lattice parameter increases with increasing Mg content. Because the ionic radius of Mg$^{2+}$ is greater than Fe$^{3+}$. The crystallite size calculated from Debye-Scherrer’s formula based on the (220) highest peak is about 69 - 78 nm. It was indicated that the sample LaFe$_{1-x}$Mg$_x$O$_3$ was nano-scale particle.

The change in bond length and the Fe / Mg - O bond’s angle shows that Mg substitution affects the bonding and dynamic distortion of the FeO$_6$ octahedral. The goodness of fit ($\chi^2$) is the ratio between $R_{wp}$ (weighted profile) and $R_e$ (expected) close to ~ 1.00 (see Table 2) which indicates that the XRD fitting results from the Rietveld refinement are good and usable. $\chi^2$ describes the value of the tolerance factor, $t$ is obtained less than 0.96 [8] confirms the Orthorhombic crystal structure for all samples. The value of $t$ which decreases with doping indicates lattice increasingly distorted in the presence of Mg.
Table 2. Geometrical parameters characterizing the crystal structure of LaFe_{1-x}Mg_xO_3 calcined powder for x = 0.01 and 0.05

| Parameters               | x = 0.01          | x = 0.05          |
|--------------------------|-------------------|-------------------|
| Atomic position          |                   |                   |
| La                       |                   |                   |
| X                        | 0.993(0)          | 0.993(0)          |
| Y                        | 0.03(0)           | 0.03(0)           |
| Z                        | 0.25(0)           | 0.25(0)           |
| Fe/Mg                    |                   |                   |
| X                        | 0.0(0)            | 0.0(0)            |
| Y                        | 0.5(0)            | 0.5(0)            |
| Z                        | 0.0(0)            | 0.0(0)            |
| O1                       |                   |                   |
| X                        | 0.719(0)          | 0.719(0)          |
| Y                        | 0.302(0)          | 0.302(0)          |
| Z                        | 0.029(0)          | 0.029(0)          |
| O2                       |                   |                   |
| X                        | 0.08(0)           | 0.08(0)           |
| Y                        | 0.485(0)          | 0.485(0)          |
| Z                        | 0.25(0)           | 0.25(0)           |
| Wyckoff position         |                   |                   |
| La                       | 4c                | 4c                |
| Fe/Mg                    | 4b                | 4b                |
| O1                       | 8d                | 8d                |
| O2                       | 4c                | 4c                |
| Bond angle (°)           |                   |                   |
| Fe–O2–Fe                 | 154.05(2)         | 154.06(2)         |
| Fe–O1–Fe                 | 157.08(2)         | 157.08(2)         |
| Bond length (Å)          |                   |                   |
| La–O1 (m)                | 2.4491(1)         | 2.4496(1)         |
| La–O1 (l)                | 2.7581(1)         | 2.6908(1)         |
| La–O2 (s)                | 2.3837(1)         | 2.3835(1)         |
| (La – O)                 | 2.5303(1)         | 2.5080(1)         |
| Fe–O1 (l)                | 2.0858(1)         | 2.0859(1)         |
| Fe–O1 (s)                | 1.9230(1)         | 1.9230(1)         |
| Fe–O2 (m)                | 2.0124(1)         | 2.0131(1)         |
| (Fe – O)                 | 2.0071(1)         | 2.0077(1)         |
| Tolerance factor         | 0.741             | 0.796             |
| R-factors                |                   |                   |
| R_p                      | 4.66              | 4.19              |
| R_wp                     | 6.18              | 5.49              |
| R_e                      | 5.45              | 4.98              |
| χ^2                      | 1.29              | 1.21              |

Based on FullProf 2K software result, it generates data in CIF vesta form. Vesta is useful to help visualize the crystal structure [9]. Figure 2 is a representation of the geometric parameters of the bulk sample crystal structure obtained from the VESTA software using raw data. From the visualization of the image, it is clear that all samples have an orthorhombic distortion structure. The La cation is located at site-A, while Fe / Mg lies at site-B and binds to 6 oxygen anions to form an octahedral.
Figure 2. The crystalline structure of the perovskite orthorhombic material LaFe$_{1-x}$Mg$_x$O$_3$ powder sample (a) $x=0.01$; (b) $x=0.05$

3.1 FTIR Analysis

To order to confirm the structural information obtained by XRD analysis, the FTIR spectra of LaFe$_{1-x}$Mg$_x$O$_3$ ($x=0.01$, and 0.05) nanoparticles were recorded. Several specific FTIR modes are shown in Figure 3 and a list of modes is shown in Table 3. The mode of metal-oxygen (M–O) bond vibration at approximately 400–600 cm$^{-1}$ indicates the formation of a typical perovskite structure (ABO$_3$) [10]. It shows a similar pattern to FTIR spectra in previous studies [11].

Figure 3. FTIR spectra pattern of LaFe$_{1-x}$Mg$_x$O$_3$ $x=0.01$, 0.05 perovskite powder material perovskite. The dashed lines show vibrations of symmetry bonds on the lattice. $\gamma_1$, $\gamma_2$, $\gamma_3$ symbolized the Fe/Mg cation in the lattice.
Table 3. FTIR band assignment of some specific absorption modes for $LaFe_{1-x}Mg_xO_3$

| FT-IR band positions | $\gamma^3$ | $\gamma^2$ | $\gamma^1$ |
|----------------------|-----------|-----------|-----------|
|                      | O-Fe/Mg-O | Fe/Mg-O-Fe/Mg | Fe/Mg-O |
| LaFe$_{1-x}$Mg$_x$O$_3$ ($x = 0.01$) | 445 | 497 | 535 |
| LaFe$_{1-x}$Mg$_x$O$_3$ ($x = 0.05$) | 445 | 498 | 544 |

Based on Table 3, the absorption band is in the range 400-500 cm$^{-1}$ shows the stretching and bending vibration of the tape Fe/Mg−O−Fe/Mg which corresponds to the deformation of the Fe/MgO$_6$ octahedral and changes in the Fe/Mg−O−Fe/Mg bond angle. The bands are in the range of about 500–600 cm$^{-1}$ identified as Fe/Mg−O stretching vibration covering the internal motion of change in Fe/Mg−O bond length. A slight shift in the vibratory band on wavenumber is greater along with the increase in the number of Mg substitutes. Because Mg substitution reduces symmetry and increases distortion in the grid as confirmed by XRD analysis. A little change in the tape position confirms the change in bond angle and bond length the results of previous XRD data analysis.

3.2 UV-VIS Analysis

The results of characterization using UV-vis spectroscopy produced raw data in the form of absorbance, reflectance. The LaFe$_{1-x}$Mg$_x$O$_3$ sample's absorbance patterns with x = 0.01 and 0.05 are shown in Figure 4. The absorbance pattern in the visible light region range above 500 nm indicates that as Mg doping increases, the absorbance pattern tends to increase.

From the absorbance data, the calculation of the direct bandgap energy ($E_g$) can be obtained using the equation $\alpha h\nu = A (h\nu - E_g)^{1/2}$, where $\alpha$ is the optical absorption coefficient, $h\nu$ is the photon energy, $A$ is a constant, and $E_g$ is the direct bandgap. By extrapolating the curve towards zero ($ah\nu$)$^{1/2}$ from the plot of $(ah\nu)^2$ vs. $h\nu$ as shown in Figure 5. It shows the optical bandgap ($E_g$) of LaFe$_{1-x}$Mg$_x$O$_3$ with $x = 0.01$ and 0.05. In previous research, it has been mentioned that bandgap LaFeO$_3$ with $x = 0.0$ is 2.13, $x = 0.1$ is 1.51, $x = 0.2$ is 1.39, and $x = 0.3$ is 1.29[10]. The optical bandgap energy value decreases
with increasing Mg doping probably because the increased conduction response is associated with absorption from the charge carrier space to balance the Coulomb interactions at the substitution site.

![Graph](image)

**Figure 5.** The plot of \((\alpha h \nu)^2\) vs. \(h \nu\) of LaFe\(_{1-x}\)Mg\(_x\)O\(_3\) \((x = 0.01\) and \(0.05)\)

**Table 4.** The results of optical bandgap energy \((E_{gap})\) value from LaFe\(_{1-x}\)Mg\(_x\)O\(_3\)

| Sample \(x\)  | \(E_{gap}\) value |
|--------------|-----------------|
| \(x = 0.01\) | 2.06            |
| \(x = 0.05\) | 1.73            |

Table 4 is a summary of the optical bandgap energy materials LaFe\(_{1-x}\)Mg\(_x\)O\(_3\) with \(x = 0.01,\) and \(0.05\). \(E_{gap}\) was found in the range of 2.06-1.73 eV. The substitution of Mg causes a decrease in the value of the bandgap energy.

**4. Conclusion**
The LaFe\(_{1-x}\)Mg\(_x\)O\(_3\) material \((x = 0.01\) and \(0.05)\) had been successfully synthesized using the sol-gel method. XRD characterization showed the single-phase orthorhombic crystal structure with the \(Pbnm\) space group. The FTIR results also confirmed the increase in bond value and bond angle as Mg substitution at the Fe site. The bandgap value decreases with increasing doping constant. The optical bandgap energy value decreases with increasing Mg doping correlated to the increased conduction response associated with absorption from the charge carrier space to balance the Coulomb interactions at the substitution site. This lower optical band gap value makes a positive impact as promising candidates for photocatalytic applications.

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