Effect of zirconium substitution on structural and optical properties of lanthanum orthoferrite

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Abstract. Lanthanum Orthoferrite (LaFeO₃) is one of the perovskite oxide ABO₃ materials. In this study, LaFe₁₋ₓZrₓO₃ (x = 0.01, 0.03 and 0.05) were synthesized by sol-gel method. Synthesized LaFeO₃ with substituted Zr on Fe-site was characterized for crystal structures and optical properties. The X-ray diffraction (XRD) analysis confirms that the LaFe₁₋ₓZrₓO₃ material has an orthorhombic structure with Pnma space group. The local structure of this sample was studied using Raman spectroscopy. Raman analysis shows, there are Zr⁴⁺ substituted effect on the tilt and stretching phonon modes of LaFeO₃. Fourier Transform Infrared (FTIR) characterization test confirmed the effect of substitution on structural properties in terms of the upward shift of tilt, bending, and symmetric stretching of Fe-O-Fe bonds in FeO₆. Optical bandgap has been determined using Kubelka-Munk function with the Tauc connection by the Uv-Vis Spectrophotometer which shows that the energy bands decrease (2.14–2.10 eV) with increased Zr-content.

Keywords: La(Fe,Zr)O₃, sol-gel method, structural properties, optical bandgap.

1. Introduction
Lanthanum orthoferrite (LaFeO₃) is the most common and very known perovskite material that has been investigated for many years [1]. LaFeO₃ has interesting properties because they are the widely used for various applications such as solid oxide fuel cells, sensors, oxygen permeation membranes, environmental catalysts, etc [2]. LaFeO₃ is a G-type antiferromagnetic material possessing high Neel temperature (TN) 480 °C and shows a ferroelectric transition at 200 °C [2]. Perovskite properties are changed into ideal materials to get new materials with desired properties, which can be tuned to reach desired applications through substitution or doping [3]. That can happen because the doping and preparation methods can reduce particle size which causes increased optical properties [5]. Synthesis of LaFeO₃ samples doped with Titanium to determine the structural, optical and magnetic properties was carried out by other researchers [2]. The results show the average crystallite size (Dₓ) between 9 nm and 24.6 nm then, the results of Diffuse Reflectance Spectra (DRS) showed an increase in the bandgap (2.05 and 2.61 eV). Therefore, the Zr⁴⁺ substitution on the Fe-site of LaFeO₃ become an interesting topic to study and explore in this part.
2. Experimental
LaFe$_{1-x}$Zr$_x$O$_3$ ($x = 0.01, 0.03$ and $0.05$) was prepared by sol-gel method. First, the raw materials were calculated stoichiometrically. Here, we used the lanthanum oxide (La$_2$O$_3$) (Merck), Zirconium (IV) chloride octahydrate (Cl$_2$H$_2$O$_9$Zr) (Merck), iron nitrate nonahydrate (Fe(NO$_3$)$_3$.9H$_2$O) (Merck), and citric acid monohydrate as raw materials. Then, the aquadestilation and all of the raw materials were mixed together. Next, using a magnetic stirrer-hotplate, the solvent was stirred until sol-phase changing to gel-phase. After that, the gel was dried using furnace (Vulcan-type 3-1750) at temperature 200 °C for 5 hours, until the sponge-phase was formed. In the next process, the sponge was ground using mortar manually until getting the powder form. Then, the dry-powder calcined at temperature 900 °C along 6 hours till we got the calcined-powder. The calcined-powder then we called as a series of LaFe$_{1-x}$Zr$_x$O$_3$ powder sample. The crystallographic structure was checked by X-ray diffraction using X'Pert PRO PANalytical diffractometer. The X-ray diffraction spectra were analyzed using Highscore plus software at room temperature to obtain parameter structure and crystal phase of the perovskite material. The Raman scattering spectra were recorded using Thermo Scientific DXR2 Raman Microscope in the range from 70–1600 cm$^{-1}$ with a laser source of 532 nm and power 2.0 mW. The molecular and metal-oxide vibration were analyzed using FTIR (PerkinElmer type SpectrumTwo) in the range of 400–4000 cm$^{-1}$. The optical band gap energy was determined by using UV-VIS (Agilent Cary 100/300).

3. Results and discussion

3.1. Structural analysis
Figure 1 shows the XRD pattern of LaFe$_{1-x}$Zr$_x$O$_3$ powder sample ($x = 0.01, 0.03, 0.05$) which calcined at 900 °C. The Rietveld refinement results confirmed that all samples have orthorhombic crystal structure with Pnma space group consistent with structure of LaFeO$_3$ standard from COD (Crystallography Open Database) No. 96-152-6451 and represented by the main peaks in the fields (001), (011), (111), (002), (012), (022) and (013). All samples showed a single phase without additional impurity phase.

Table 1 shows the structural parameter data obtained from the Rietveld analysis. We can see that the lattice parameters slightly increase with increasing Zr content, this is caused by the ionic radii of Zr$^{4+}$ (0.74 Å) ions occupying in Fe-site are larger than Fe$^{3+}$ (0.65 Å) ions [3]. Increasing the value of the lattice parameter causes an increased value of the bond distance. Iron possible vacancies are Fe$^{4+}$, Fe$^{3+}$ and Fe$^{2+}$. To ensure the charge neutrality and stable orthorhombic structure, Fe$^{4+}$ ions should necessarily be formed in the lattice structure because of the 4+ valence of zirconium. So, it will remove Fe ions which have a lot of oxygen [4]. When doping with Zr, Fe will be replaced with Zr. The same phenomenon has reported by C. Sasikala et al, when Ti doping on LaFeO$_3$ material, then Ti will replace Fe in the material [5]. The tolerance factor decreases with increasing Zr content indicating Zr-ions occupying in Fe-site causes the crystal becomes more distorted to achieve stability.

3.2. Raman scattering analysis
Figure 2 shows the Raman spectrum for LaFe$_{1-x}$Zr$_x$O$_3$ ($x = 0.01, 0.03$ and $0.05$) and some specific modes for Raman phonon modes are tabulated in table 2. Modes $A_g$, $B_{1g}$, $B_{2g}$ and $B_{3g}$ are Raman active and modes $A_u$, $B_{1u}$, $B_{2u}$, $B_{3u}$ and $B_{4u}$ are infrared active [6]. Modes are indicated by the La vibrations which are shown by modes below 200, namely $\omega_1$ and $\omega_2$. Modes between 200 and 400 cm$^{-1}$ are oxygen octahedral tilt modes at La which are $\omega_3$, $\omega_4$ and $\omega_5$. Modes between 400 and 450 are oxygen octahedral bending vibrations which are marked with modes $\omega_6$. Modes above 500 cm$^{-1}$ are oxygen stretching vibrations which are marked with modes $\omega_7$, $\omega_8$, $\omega_9$ and $\omega_{10}$.

It can be seen from the spectra that the Zr doping effects of the oxygen tilt, stretching and bending modes of vibration. Then, table 2 shows the changes in the stretching and bending modes of vibration due to the Zirconium doping effect. It appears that the higher the Zirconium doping appears and the
higher the intensity of the shutter for modes $\omega_9$ and $\omega_{10}$. This shift in wavenumber and the variation in their intensities may be influenced by lattice strain, defects and crystallite size [7].

![Figure 1](image.png)

**Figure 1.** Rietveld refinement of XRD patterns of LaFe$_{1-x}$Zr$_x$O$_3$ using HighscorePlus software.

**Table 1.** The structural parameters of LaFe$_{1-x}$Zr$_x$O$_3$ ($x = 0.01, 0.03$ and $0.05$) nanoparticle.

| Parameter | $x = 0.01$ | $x = 0.03$ | $x = 0.05$ |
|-----------|------------|------------|------------|
| Crystallography parameters | LaFe$_{1-x}$Zr$_x$O$_3$ | LaFe$_{1-x}$Zr$_x$O$_3$ | LaFe$_{1-x}$Zr$_x$O$_3$ |
| Lattice parameters | | | |
| $a$ (Å) | 5.569 | 5.586 | 5.588 |
| $b$ (Å) | 7.856 | 7.859 | 7.863 |
| $c$ (Å) | 5.561 | 5.562 | 5.566 |
| Volume (Å$^3$) | 243.345 | 244.138 | 244.559 |
| Crystallite size (nm) | 453.2 | 429.1 | 394.4 |
| Density g/cm$^3$ | 6.635 | 6.632 | 6.640 |
| Geometrical parameters | | | |
| Bond length (Å) | | | |
| Fe/Zr–O1 (s) | 1.92616 | 1.92812 | 1.92927 |
| Fe/Zr–O1 (l) | 2.08910 | 2.09311 | 2.09417 |
| Fe/Zr–O2 (m) | 2.01562 | 2.01612 | 2.01738 |
| $<$Fe/Zr–O$>$ | | | |
| Bond angle ($^\circ$) | | | |
| Fe/Zr–O1 – Fe/Zr | 157.0782 | 157.0865 | 157.0860 |
| Fe/Zr–O2 – Fe/Zr | 154.043 | 154.045 | 154.043 |
| Tolerance factor $<t>$ | 0.848583 | 0.848004 | 0.847426 |
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Figure 2. The Raman Spectra of LaFe$_{1-x}$Zr$_x$O$_3$ for (a) $x = 0.01$; (b) $x = 0.03$ and (c) $x = 0.05$; calcined at 900 °C for 6 h.

Table 2. The mode assignment of some specific Raman phonon modes for LaFe$_{1-x}$Zr$_x$O$_3$ ($x = 0.01, 0.03$ and $0.05$) Raman shift in cm$^{-1}$.

|        | $x = 0.01$     | $x = 0.03$     | $x = 0.05$     | Mode       |
|--------|----------------|----------------|----------------|------------|
| $\omega_1$ | 156.188        | 158.387        | 156.188        | B$_{1g}$   |
| $\omega_2$ | 177.983        | 177.983        | 177.983        | B$_{1g}$   |
| $\omega_3$ | 262.964        | 258.765        | 267.363        | A$_g$      |
| $\omega_4$ | 295.756        | 297.956        | 293.557        | A$_g$      |
| $\omega_5$ | 382.937        | 382.937        | 385.137        | A$_g$      |
| $\omega_6$ | 433.126        | 433.124        | 435.325        | B$_{3g}$   |
| $\omega_7$ | 603.288        | 596.689        | 577.094        | B$_{1g}$   |
| $\omega_8$ | 646.878        | 649.078        | 646.878        | B$_{1g}$   |
| $\omega_9$ | 675.272        | 686.269        |                | B$_{1g}$   |
| $\omega_{10}$ | 762.653        | 762.653        |                |            |

3.3. UV-Vis spectroscopy analysis

The UV-Visible reflectivity spectrum of LaFe$_{1-x}$Zr$_x$O$_3$ ($x = 0.01, 0.03$ and $0.05$) is shown in figure 3. The UV-Vis spectrum can be used to find bandgaps from the material using the functions of Kubelka-Munk. Bandgap can be described by Tauc plots or extrapolating slop plots ($F^2$ vs. $h\nu$) shown in
The bandgap value decreases with increasing doping constants, the value is from the range 2.14–2.10 eV. This might be caused by doping Zr$^{4+}$ to Fe$^{3+}$ which has smaller ion radii, bond length increases so that the atomic bond gets weaker so that the energy needed by the electron to detach from the bond, facilitates movement of excited and exciting carriers from the valence band to the conduction band easy so that it will reduce the bandgap energy. The small bandgap of LaFeO$_3$ is interesting for application in photocatalytic [4]. Figure 3a shows the calculation of the bandgap value of LaFe$_{1-x}$Zr$_x$O$_3$ ($x = 0.01, 0.03$ and $0.05$) material and summarized in figure 3b.

3.4. Fourier Transform Infrared Spectroscopy (FTIR) analysis

The FTIR transmittance of LaFe$_{1-x}$Zr$_x$O$_3$ ($x = 0.01, 0.03$ and $0.05$) is shown in figure 4. Several types of modes observed are presented in table 3. Changes in metal-oxide stretching and bending vibrations may be related to changes in chemical mass in the material due to Zr substitution [8]. Fe/Zr–O stretching vibration and Fe/Zr–O–Fe/Zr bending showed that Zr was substituted on the Fe site. Also, the change in mode position shows a change in the Fe/Zr–O distance bond and Fe/Zr–O–Fe/Zr bond angle confirmed by XRD data in table 1.

![Figure 3](image1.png)

**Figure 3.** (a) The plot of $(F)^2$ vs. $h\nu$ from a series of LaFe$_{1-x}$Zr$_x$O$_3$ ($x = 0.01, 0.03$ and $0.05$), (b) Value of bandgap.

![Figure 4](image2.png)

**Figure 4.** The FTIR patterns of LaFe$_{1-x}$Zr$_x$O$_3$ ($x = 0.01, 0.03$ and $0.05$) nanoparticles.
Table 3. FTIR band assignment of some specific absorption modes for LaFe$_{1-x}$Zr$_x$O$_3$

(\(x = 0.01, 0.03\) and 0.5).

| LaFe$_{1-x}$Zr$_x$O$_3$ | FT-IR band positions |
|------------------------|---------------------|
|                        | O–Fe/Zr–O           | Fe/Zr–O–Fe/Zr | Fe/Zr–O                 |
|                        | Bending             | Bending       | Stretching              |
| \(x = 0.01\)          | 466                 | 508           | 539                     |
| \(x = 0.03\)          | 463                 | 506           | 540                     |
| \(x = 0.05\)          | 460                 | 505           | 542                     |

4. Conclusion
The series of LaFe$_{1-x}$Zr$_x$O$_3$ with \((x = 0.01, 0.03\) and 0.05) had been successfully synthesized using sol-gel method. The XRD analysis reveals the single phase of the orthorhombic crystal structure with \(Pnma\) space group. The addition of Zr content leads to the increasing of lattice constant and volume, distortion, and decreasing of crystallite size with increasing Zr content. The Local structure of this sample was studied using Raman spectroscopy. Raman analysis shows, there are Zr$^{4+}$ substituted effect on the tilt and stretching phonon modes of LaFeO$_3$. Fourier Transform Infrared (FTIR) confirmed the effect of substitution on structural properties in terms of the upward shift of tilt, bending, and symmetric stretching of Fe–O–Fe bonds in FeO$_6$. Optical bandgap has been determined by the UV-Vis Spectrophotometer which shows that the energy bands decrease (2.14–2.10 eV) with increased Zr-content.

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