Study of La(Fe, Zn)O₃ on the structural properties prepared by sol-gel method

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Abstract. Partial substitution of other metallic ions at La and/or Fe sites of LaFeO₃ had been applied to modify the structural properties and for enhancing the properties of its material. In this present work, we prepared LaFeO₃ by replacing a portion of Fe³⁺ with Zn²⁺ with \( x = 0.03; 0.05; \) and 0.07 to study the effect on the structural which prepared by sol-gel method. The samples were identified by X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), Fourier Transform Infrared (FTIR) spectra, Raman spectroscopy, and Ultraviolet-Visible Diffuse Reflectance spectroscopy (UV-Vis DRS). XRD pattern showed all of the samples formed in single crystal and are having an orthorhombic structure with space group Pbnm. The lattice parameters were found to be slightly increased with the increase of Zn concentration. The result of FTIR spectra and Raman spectra also show further information about the formation of LaFeO₃ with the distortion due to the replacement of Zn²⁺ into Fe³⁺. The absorbance and reflectance of samples are measured using UV-Vis DRS and the energy band gap of LaFe₁₋ₓZnₓO₃ (\( x = 0.03; 0.05; \) and 0.07) are determined by Tauc plot using Kubelka-Munk function and was found the energy band gap slightly decreased as the concentration of Zn²⁺ increased.

Keywords: La(Fe,Zn)O₃, perovskite, structural, sol-gel method

1. Introduction

Orthoferrites have attracted a considerable attention due to they can be potentially applied in a wide range applications, namely fuel cells, catalysts, gas sensors, semiconductors, and magnetic materials [1]. The unique distorted perovskite structure, especially in orthoferrites, contributes to the properties that make the high applicability of this material. For enlightenment, perovskite ideal structure B-O-B bond angle is 180°, however, for orthoferrites the angle is deviated from 180° to some lower value because of orthorhombicity in the structure [2]. RFeO₃ orthoferrites, where R belongs to the rare earth elements, with perovskite structure. As LaFeO₃ has an orthorhombic unit cell with the least distortion when compared with other orthoferrites, making this material has the highest Neel temperature \( (T_N = 740 \text{ K}) \). The distortion in this material’s structure is inspected due to the displacement oxygen and rare earth ions from their cubic position, and then the superexchange of Fe³⁺ also contributed to the distortion in the structure [1]. The distorted perovskite LaFeO₃ is a canted antiferromagnetic insulator showing a weak ferromagnetism. Consequently, the structure and physical properties of LaFeO₃ can be modified by the choice of a suitable doping element at La³⁺ or at Fe³⁺ site in LaFeO₃. According to Maria and Gomez [3], doping metals with a 2⁺ oxidation state and radii identical to that of Fe³⁺ (such as Mg²⁺ or Zn²⁺) triggers changes in the structural, electrical and magnetic properties of the pure material and with
using Mg and Zn as dopants in the LaFeO$_3$ perovskite has been proven as an effective strategy for developing application in gas sensors, oxidation catalysts and photocatalysts. In this present work, we prepared LaFe$_{1-x}$Zn$_x$O$_3$ with $x = 0.0; 0.03; 0.05$ and $0.07$ using sol-gel method to analyze the structural of material.

2. Experimental
LaFe$_{1-x}$Zn$_x$O$_3$ ($x = 0.0; 0.03, 0.05$ and $0.07$) materials were prepared by sol-gel method. We used Lanthanum (III) oxide [La$_2$O$_3$], ferric nitrate nonahydrate [Fe(NO$_3$)$_3$·9H$_2$O], and zinc nitrate hexahydrate [Zn(NO$_3$)$_2$. 6H$_2$O] as precursors of material. The required starting materials in stoichiometric amounts were dissolved in aquadest. Citric acid served as a chelating agent was added in the solutions and was maintained with stirring continuously at 120 °C until the gel-phase was obtained. The gel-phase of the material then was dried at 200 °C for 5 h. In the end, the powder was calcined at 900 °C for 3 h.

The crystalline structure was identified by X-Ray Diffraction (XRD) type X’Pert PRO PANalytical with source radiation Cu K$_\alpha$ ($\lambda = 1.5405$ Å). Rietveld Refinement was carried out to find the lattice parameters and bond angles by using Fullprof software. The chemical compounds were measured by X-ray fluorescence to determine the ration of each material which form LaFe$_{1-x}$Zn$_x$O$_3$. Raman analysis was performed by Thermo Scientific DXR2 Raman Microscope in the range from 70–800 cm$^{-1}$ with the laser source 532 nm and power 2.0 mW. FTIR spectra were obtained on PerkinElmer type Spectrum Two in the range 250–3500 cm$^{-1}$. The optical band gap energy was determined by UV–Visible diffuse reflectance spectroscopy (Agilent Cary 100/300).

3. Results and discussion
3.1. Structural analysis
The structural properties of the sample have been characterized by X-ray diffraction and were refined by Fullprof software. The XRD pattern of LaFe$_{1-x}$Zn$_x$O$_3$ ($x = 0.0; 0.03; 0.05$ and $0.07$) is shown in figure 1 with a sharp peak in the pattern indicated a well crystallinity of the prepared samples. The XRD pattern was consistent with the pure LaFeO$_3$ (101), (121), (220), (202) and (240) using the standard from No. COD 1526450. There is no additional peaks for impurities which concluded all of the samples were in a single phase with no impurities and have an orthorhombic structure with the Pbnm space group.

The lattice parameter, goodness of fit, tolerance factor and also geometrical parameters were also analyzed using the Fullprof software which is listed in table 1. The lattice parameters of LaFe$_{1-x}$Zn$_x$O$_3$ were observed to be increase with the increase of dopant. This may be caused by the ionic radii of Zn$^{2+}$ ($r_{Zn} = 0.074$ nm) which is larger compared to Fe$^{3+}$ ($r_{Fe} = 0.064$ nm). According to Bhat et al., because Zn$^{2+}$ is a nonmagnetic cation and does not change its valency, hence, when Fe$^{3+}$ was substituted by Zn it may produce an average radius compatible for a perovskite structure, likewise, the ionic radii of Fe$^{3+}$ is 0.064 nm and for Zn$^{2+}$ is 0.074 nm which is clear that unit cell volume would increase as the Zn concentration increases [4]. The effect of doping Zn also changed the geometrical parameters where bond lengths and bond angles of the material were measured. This is because Zn ion exits in the +2 oxidation state, as it replaces part of the Fe which exits in the +3 oxidation state, to maintain the charge balance, Fe$^{3+}$ changes to Fe$^{2+}$ and created the oxygen vacancy in LaFe$_{1-x}$Zn$_x$O$_3$ [2]. As for the oxygen vacancy created, the four octahedra in lanthanum orthoferrite would distort the structure as observed in table 1, where the bond angle and bond length of LaFe$_{1-x}$Zn$_x$O$_3$ increase compared with the pure LaFeO$_3$.

3.2. X-ray fluorescence
XRF elemental analysis was conducted to confirm the stoichiometry of the materials or chemical atoms that were synthesized [5]. Table 2 shows the experimental and calculation of weight percent from the atom which formed LaFe$_{1-x}$Zn$_x$O$_3$. The table clearly shows that the weight percent of Lanthanum (La)
and Iron (Fe) elements were near the calculation result but not for Zinc. The difference result we got from the experiment and calculation could be directed to the characteristic of XRF which generally has modest limits of detection and could be failed from particle size effects and XRF only measured the concentration of the sample in a very superficial region of the sample near the sample surface. As for the big difference of weight percent in Zn it may be due to the weight loss caused by the process of calcination where the samples were heated at 900 °C were higher than the melting point of Zinc ($T_p \approx 419.5 ^\circ C$) for 6 h.

But from the table 2, we could observe the trend of Zn where the weight percentage increases as the value of $x$ increases and no trace amount of any other element was found which confirms the result of XRD which means the purity of LaFe$_{1-x}$Zn$_x$O$_3$ ($x = 0.03; 0.05$ and $0.07$).

### 3.3. Raman spectroscopy

To specify the structure distortion, phase transition, oxygen motion, and the order-disorder effects in the lattice at varied temperatures of perovskite-type materials, the study of the dynamical processes caused by charge carriers, phonons, and spins which affect the properties was conducted [1]. The Raman spectroscopy has been carried out for LaFe$_{1-x}$Zn$_x$O$_3$ ($x = 0.0; 0.03; 0.05$ and $0.07$) at room temperature and are shown in figure 2. From figure 2, where we could compare the Raman plot of pure LaFeO$_3$ and the doped of LaFe$_{1-x}$Zn$_x$O$_3$. There are some peaks which are formed in range ~130 cm$^{-1}$, ~255 cm$^{-1}$, and ~400 cm$^{-1}$. The additional peaks were formed maybe due to the replacement of Zn$^{2+}$ in Fe$^{3+}$ where the dopant distorted the structure and make the effect on the oxygen vacancy formation.

Table 3 exhibits the modes of Raman in the range 100–800 cm$^{-1}$ where 9 modes were found around ~130 cm$^{-1}$, ~146 cm$^{-1}$, ~169 cm$^{-1}$, ~255 cm$^{-1}$, ~282 cm$^{-1}$, ~403 cm$^{-1}$, ~421 cm$^{-1}$, ~618 cm$^{-1}$, and ~771 cm$^{-1}$ in LaFe$_{1-x}$Zn$_x$O$_3$ ($x = 0.03; 0.05; 0.07$). These modes are corresponded with pure LaFeO$_3$ where the peak around ~150 cm$^{-1}$ was attributed to the occupying of La in perovskite unit, the Raman shift around ~283 cm$^{-1}$, ~481 cm$^{-1}$ and ~625 cm$^{-1}$ were attributed to the vibration of Fe-O bonds and at ~426 cm$^{-1}$ might be attributed to the existence of the La-O vibration [6]. The modes of Raman for...
LaFe$_{1-x}$Zn$_x$O$_3$ with $x = 0.0; 0.03; 0.05; 0.07$ show a shifting to the higher value due to the increasing of Zn$^{2+}$. Although for some modes in Raman only show a small shifting, in fact there are some modes which have the same result in $x = 0.05$ and $x = 0.07$.

The shifting could be directed to the replacement of Zn$^{2+}$ in Fe$^{3+}$. According to Manzoor and Husain [1], the shift from Raman plot corresponds to the strain in the samples where the shift to the higher value is bound to the compressive stress and tensile stress yields in the shifting to the lower value. The substitution of Zn$^{2+}$ into Fe$^{3+}$ produces a distortion especially in the oxygen bending and stretching vibration. Wanjun et al., also reported the shift in the Raman modes could be due to some factors.

### Table 1. Refinement LaFe$_{1-x}$Zn$_x$O$_3$ with $x = 0.0; 0.03, 0.05$ and $0.07$.

| Parameter | 0.0 | 0.03 | 0.05 | 0.07 |
|-----------|-----|------|------|------|
| Crystallography Parameters |
| Phase (Space group) | Orthorhombic (P b n m) | Orthorhombic (P b n m) | Orthorhombic (P b n m) | Orthorhombic (P b n m) |
| A         | 5.54761 | 5.55319 | 5.55440 | 5.55451 |
| B         | 5.5372 | 5.56228 | 5.56317 | 5.56516 |
| c         | 7.82869 | 7.85461 | 7.85247 | 7.85513 |
| $\chi^2$  | 1.24 | 1.04 | 1.44 | 1.01 |
| t (Tolerance factor) | 0.93 | 0.93 | 0.93 | 0.93 |
| Density (g.cm$^{-3}$) | 6.705 | 6.654 | 6.658 | 6.659 |
| Volume (V/10$^6$ pm$^3$) | 240.485 | 242.616 | 242.642 | 242.816 |
| Geometrical Parameters |
| Bond length(Å) |
| La-O1 | 2.751 | 2.761 | 2.791 | 2.762 |
| La-O2 | 2.565 | 2.578 | 2.593 | 2.579 |
| Fe/Zn-O1 | 1.919 | 1.923 | 1.924 | 1.924 |
| Fe/Zn-O2 | 2.008 | 2.051 | 2.014 | 2.015 |
| Bond Angle(°) |
| La-O1-La | 99.919 | 99.956 | 99.868 | 99.939 |
| La-O2-La | 106.849 | 106.786 | 105.565 | 106.785 |
| Fe/Zn-O1-Fe/Zn | 157.075 | 157.070 | 157.073 | 157.073 |
| Fe/Zn-O2-Fe/Zn | 154.019 | 154.073 | 154.061 | 154.069 |
| R factor (%) |
| Re | 8.48 | 6.15 | 5.84 | 6.17 |
| Rp | 7.34 | 4.89 | 5.37 | 4.88 |
| Rwp | 9.44 | 6.27 | 7.00 | 6.21 |

### Table 2. XRF elemental analysis of LaFe$_{1-x}$Zn$_x$O$_3$ ($x = 0.00, 0.03, 0.05$ and $0.07$).

| LaFe$_{1-x}$Zn$_x$O$_3$ (%) experimental weight | (%) weight calculation |
|-----------------------------------------------|------------------------|
| $x = 0.0$ | 63.133 | 26.66 | - | 71.325 | 28.675 | - |
| $x = 0.03$ | 73.61 | 26.30 | 0.09 | 71.220 | 27.774 | 1.005 |
| $x = 0.05$ | 73.66 | 26.24 | 0.10 | 71.151 | 27.175 | 1.674 |
| $x = 0.07$ | 73.43 | 26.46 | 0.11 | 71.081 | 26.577 | 2.342 |
such as the atomic weight, the strength of the corresponding ions and the strength of the chemical bond [6]. The difference of atomic weight between Zn (65.4 g/mol) and Fe (55.845 g/mol) also the difference of ionic radii of Zn (0.074 nm) and Fe (0.064 nm) lead to the strain in the sample which makes the modes shifted to the higher value.

3.4. Fourier transform infrared spectroscopy

FTIR was conducted in all of the samples and are shown in figure 3. Figure 3a shows the result of FTIR in range 250–4000 cm$^{-1}$ where it exhibits peaks around range 490 cm$^{-1}$ and around 540 cm$^{-1}$ then were noted as $\varepsilon_1$ and $\varepsilon_2$. These modes described the establishment of lanthanum orthoferrite where the band around 570 cm$^{-1}$ in the main sample LaFeO$_3$ is attributed to the Fe-O stretching vibration and the band around 410 cm$^{-1}$ corresponds to the O-Fe-O bending vibration [1]. The shifting and the intensity of samples were also observed in the range 450–750 cm$^{-1}$ as shown in figure 3b. The broadening of peaks around 475–525 cm$^{-1}$ become small and sharp as the concentration of Zn$^{2+}$ increase. This is maybe due to the distortion in the structure where the bond angle Fe-O-Fe and bond length change as Zn replaced Fe in LaFeO$_3$. The peaks around 525–550 cm$^{-1}$,
Table 3. Observes and reported raman modes of LaFe$_{1-x}$Zn$_x$O$_3$ in range 100–800 cm$^{-1}$.

| Modes | $x = 0.0$ | Raman shift LaFe$_{1-x}$Zn$_x$O$_3$ (cm$^{-1}$) | $x = 0.03$ | $x = 0.05$ | $x = 0.07$ |
|-------|-----------|-----------------------------------------------|--------|----------|--------|
| $\epsilon_1$ | - | 130.212 | 130.487 | 130.772 |
| $\epsilon_2$ | 146.617 | 146.140 | 146.647 | 147.155 |
| $\epsilon_3$ | 167.669 | 169.026 | 169.614 | 169.473 |
| $\epsilon_4$ | - | 254.864 | 255.739 | 256.456 |
| $\epsilon_5$ | 280.902 | 282.576 | 284.325 | 283.082 |
| $\epsilon_6$ | - | 402.900 | 403.219 | 403.686 |
| $\epsilon_7$ | 427.819 | 421.561 | 422.491 | 422.491 |
| $\epsilon_8$ | 629.323 | 617.722 | 618.783 | 620.027 |
| $\epsilon_9$ | 776.090 | 775.368 | 774.978 | 774.978 |

Figure 3. The FTIR patterns of LaFe$_{1-x}$Zn$_x$O$_3$ ($x = 0.0; 0.03; 0.05; 0.07$), (a) for range 250–3500, and (b) for range 400–1000.

where we could observe the sharp peak with lower intensity. This could be corresponding with the presence of metal-oxygen bond which could be noted as the vibration of Fe-O and O-Fe-O bonding in the octahedral structure of LaFe$_{1-x}$Zn$_x$O$_3$. The samples spectra indicate the two bands shifting toward the lower wavenumber for modes $\epsilon_1$ and $\epsilon_2$ mode shift to the higher wavenumber which could be assigned to the strain of stretching and bending vibration of the metal-oxygen bond. The modes also exhibit the varied of intensity in all of the samples which is shown in figure 3b. The intensity of samples was decrease and the peaks slightly chanted as the concentration of Zn increases. Table 4 shows us the modes of FTIR in range 450–650 cm$^{-1}$ where the vibrations are formed. The modes slightly move to the lower wavelength as the increase of Zn$^{2+}$.

3.5. UV-Vis spectroscopy

UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS) was done to determine the band gap of material LaFe$_{1-x}$Zn$_x$O$_3$ ($x = 0.03; 0.05$ and $0.07$). The radiation which is impinged on material would penetrate the sample and some portion will be reflected. The part which penetrates through the sample is scattered and transmitted, and the portion of this radiation which is reflected on the surface of the sample is regarded as the diffuse reflectance. Figure 4 shows the absorbance of material LaFe$_{1-x}$Zn$_x$O$_3$ ($x = 0.0$;
0.03; 0.05 and 0.07) in range 350–800 nm. The absorbance for all of samples increases as the concentration of \( \text{Zn}^{2+} \) increases, may be due to the color of samples which is the darkest by the addition of Zn. The increase of absorbance indicated that all of doped samples could be performed in visible light compared with the pure LaFeO_3.

The bandgap energy (\( E_g \)) can be determined from the absorbance data using the Tauc relation as:

\[
ahv = A (h\nu - E_g)^{1/n}
\]

| Modes | 0.0 | 0.03 | 0.05 | 0.07 |
|-------|-----|------|------|------|
| \( \varepsilon_1 \) | 500.115 | 498.299 | 497.627 | 497.030 |
| \( \varepsilon_2 \) | 535.143 | 536.143 | 537.337 | 534.874 |

**Table 4.** The observes of FTIR spectra modes of LaFe\(_{1-x}\)Zn\(_x\)O\(_3\) in range 450–650 cm\(^{-1}\).

**Figure 4.** UV-vis (a) absorbance and (b) reflectance spectra of LaFe\(_{1-x}\)Zn\(_x\)O\(_3\)  
\( (x = 0.0, 0.03, 0.05 \text{ and } 0.07) \).

**Figure 5.** The energy band gap of material LaFe\(_{1-x}\)Zn\(_x\)O\(_3\) \( (x = 0.0, 0.03, 0.05, 0.07) \).
Where $A$ could be noted as a constant called the band tailing parameter, $E_g$ symbolizes the optical energy gap, and $n$ refers to the interband transition which are depended upon the materials nature, in case the material is amorphous or crystalline and the photon transition [7]. By using the absorbance data of all the samples to determine the energy gap and were plotted between $(\alpha h\nu)^n$ and $(h\nu)$ for $n = 2$ as the best denounced in the literature which LaFeO$_3$ has a direct allowed bandgap [2]. The example of plotted as shown in figure 5a for $x = 0.03$ (LaFeO$_3$ with smallest doped) and figure 5b corresponds to the energy gap for all samples ($x = 0.0; 0.03; 0.05; 0.07$).

Figure 5b shows the bandgap energy of material LaFe$_{1-x}$Zn$_x$O$_3$ ($x = 0.0, 0.03, 0.05, 0.07$) decreases as the concentration of Zn$^{2+}$ increases, it may be due to the creation of oxygen vacancy which formed because of the replacement of Zn in Fe. A possibility of the oxygen vacancy formation could be the additional energy levels near the conducting band [2]. Further enhancement of the hopping of electron and could be applied as photocatalyst or photocathode.

4. Conclusion

Lanthanum orthoferrites doped by Zinc have been successfully prepared by the sol-gel method. XRD result shows that all of the materials are single phase with an orthorhombic structure and $Pbnm$ space group. The lattice parameter, density and also the volume of samples slightly increase due to the concentration of dopant. It might be caused by the ionic radii dopant (Zn$^{2+} = 0.074$ nm) which is larger than (Fe$^{3+} = 0.064$ nm). The vibration of the particle in the material is also observed by FTIR and Raman spectroscopy which give further information about the formation of LaFe$_{1-x}$Zn$_x$O$_3$ ($x = 0.03; 0.05; 0.07$). In FTIR results, the vibration modes shift to a lower intensity and slightly chanted as the concentration of Zn increases, corresponds to the presence of metal-oxygen bond which could be noted as the vibration of Fe-O and O-Fe-O bonding in the octahedral structure of LaFe$_{1-x}$Zn$_x$O$_3$. Raman spectra detect the Zn$^{2+}$ dopant in Fe$^{3+}$ produces a distortion mainly in the oxygen bending and stretching vibration. The energy band gap of samples is observed to decrease as the concentration of Zn$^{2+}$ increases. It is related to the changing in structural properties, such as lattice parameter increment and shift of vibration modes caused by Zinc dopant.

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