Crystal structure analysis of Lanthanum Orthoferrite doped Zirconium with sol-gel method for solar cell candidate

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Abstract. Lanthanum Orthoferrite (LaFeO$_3$) is one of the perovskite material which has been studied as a candidate for solar cells. Perovskite doped at site-A and site B was expected to increase efficiency in its application as a solar cell. Zirconium as doping at site-B on LaFeO$_3$ used to reduce the size of crystals with nano size. Therefore, this research has synthesized perovskite lanthanum orthoferrite doped zirconium at site-B (LaFe$_{1-x}$Zr$_x$O$_3$ with x=0.075, 0.1 and 0.15) by the sol-gel method and it has not been studied before. The precursors for these materials are lanthanum Oxide (La$_2$O$_3$), Zirconium (IV) chloride octahydrate (Cl$_2$H$_6$O$_9$Zr), iron nitrate nonahydrate (Fe (NO$_3$)$_3$.9H$_2$O). LaFeZrO$_3$ powder was characterized using X-ray diffraction (XRD) to test the crystal structure properties. The results say that the sample has an orthorhombic structure with Pnma space group. The XRD data has been refined and shows that the lattice parameters for 0.075, 0.1 and 0.15 increase with increasing zirconium concentration and crystal size of LaFeZrO$_3$ decreasing and showing nanosize. Nanosize crystals can maximize the absorption of dyes and it can increase the efficiency of solar cells.

1. Introduction

Utilization of solar energy through solar cells that can convert solar energy into electrical energy is one of the alternative energy collisions that currently developing. Various solar cells have been made and commercialized using various materials as active layers such as silicon, gallium arsenide, cadmium telluride, amorphous silicon, solar dye cells, organic-inorganic hybrid, and organic/polymer solar cells [1]. Solar cells with perovskite active material are currently being developed by researchers because they are capable of producing conversion efficiencies above 20%, so they are expected to become solar cells of the future [2]. Morphological control and structure of the perovskite crystals are the main keys to increasing solar cell efficiency and stability to the environment [3].

Perovskite structure is a compound that has a crystal structure associated with the perovskite CaTiO$_3$ mineral. Ideally, perovskite with the chemical formula ABO$_3$ has a cubic crystal structure consisting of [BX$_6$] octahedra with the A cation occupying the 12-fold coordination site formed in the middle of the cube of eight such octahedral [4,5]. Also, perovskite oxides crystals can have broad applications in advanced technologies such as electrode materials, solid oxide fuel cells (SOFC), magnetic materials, catalysts and chemical sensors, etc.

Morphological control and crystal structure are the main keys to increasing the efficiency of solar cells stability to the environment. How to control the morphology and structure of the crystal can be done by supporting the perovskite material. One of the most common perovskite oxides, in over years
LaFeO₃ nanocrystal is a very known material and thus has received intensive investigations. Zr doping using LaFeO₃ perovskite is expected to increase the efficiency of the solar cells. Therefore, this research will be carried out synthesis of LaFeO₃ material doped with Zr at B-site. The Zr concentrations used are 0.075, 0.1 and 0.15 which has never been studied before. Many synthesis methods used to obtain LaFeO₃ perovskite material. In this study LaFe₁₋ₓZrxO₃ (x = 0.075, 0.1, 0.15) was synthesized using the Sol-Gel technique which characterized by X-ray diffraction (XRD) to determine the crystal structure of the material.

2. Methods

First of all, prepare all the precursors for which LaFeZrO₃ material is calculated according to the stoichiometry. These precursors consist of Lanthanum Oxide (La₂O₃), Zirconium (IV) chloride octahydrate (C₂H₁₂O₂Zr), iron nitrate nonahydrate (Fe(NO₃)₃·9H₂O). Next, LaFe₁₋ₓZrxO₃ (x = 0.075, 0.1, 0.15) is made with the Sol-Gel synthesis method which starts by mixing all the material and citric acid monohydrate solution, then the solution is strung using a magnetic stirrer-hotplate with a rotation speed of 700 rpm. wait a few hours for the phase sol to change to phase gel. After the phase gel is formed, the gel phase is dried at 200°C for 5 hours to remove water in the material. LaFeZrO₃ powder form from the dry which has been crushed and then calcined at 900°C for 6 hours. perovskite LaFeZrO₃ powder form has been produced.

Samples that have been formed are then tested for characterization by X-ray diffraction (XRD) using the XPert PRO PANalytical diffractometer. After being tested, the XRD results were analyzed using the highscore PUL software to know the crystal structure and phase parameter data of the material at room temperature. Then, the crystal form is seen using the Vesta application

3. Results and discussion

To know the crystal structure of LaFeZrO₃ we can see in figure 1. Figure 1 shows the X-ray diffraction (XRD) pattern of LaFe₁₋ₓZrxO₃ (x = 0.075, 0.1, 0.15) powder sample which calcined at 900°C. From the analysis results, Rietveld confirmed that all samples showed orthorhombic structure with Pnma symmetry group consistent with the structure of LaFeO₃ in the standard from COD (Crystallography Open Database) No. 96-152-6451 and represented by the main peaks in the fields (101), (200), (220), (202), (321), (400) and (402). All samples showed the La₂O₃ impurity phase, this means that not all La₂O₃ has been converted into perovskite, so it still requires optimization of the manufacture of perovskite that is able to convert the total La₂O₃ into LaFeZrO₃ perovskite. The persistence of La₂O₃ in perovskite can cause obstacles for carrier loads in perovskite to move because La₂O₃ can cause solar cell conversion efficiency to be low.

![Figure 1. Rietveld refinement of XRD patterns of LaFe₁₋ₓZrxO₃ (x = 0.075, 0.1 and 0.15) using HighscorePlus software.](image-url)
Table 1. LaFe$_{1-x}$Zr$_x$O$_3$ ($x = 0.075, 0.1$ and $0.15$) structural parameters.

| Parameter                        | LaFe$_{1-x}$Zr$_x$O$_3$ | $x = 0.075$ | $x = 0.1$ | $x = 0.15$ |
|----------------------------------|--------------------------|-------------|-----------|------------|
| **Crystallography parameters**   |                          |             |           |            |
| a (Å)                            | 5.578                    | 5.567       | 5.570     |            |
| b (Å)                            | 7.867                    | 7.861       | 7.860     |            |
| c (Å)                            | 5.567                    | 5.563       | 5.5623    |            |
| Volume (Å$^3$)                   | 244.308                  | 243.424     | 243.553   |            |
| Crystallite size (nm)            | 51.22                    | 66.38       | 47.5      |            |
| **Geometrical parameters**       |                          |             |           |            |
| Fe/Zr–O1 (Å)                     | 1.929                    | 1.926       | 1.90      |            |
| Fe/Zr–O1 (Å)                     | 2.092                    | 2.089       | 2.11      |            |
| Fe/Zr–O2 (Å)                     | 2.018                    | 2.017       | 2.016     |            |
| Bond angle (°)                   |                          |             |           |            |
| Fe/Zr–O1 – Fe/Zr                 | 157.078                  | 157.074     | 158       |            |
| Fe/Zr–O2 – Fe/Zr                 | 154.049                  | 154.050     | 154.050   |            |
| Factor of Tolerance <$t$>        | 0.846705                 | 0.845984    | 0.844547  |            |

Table 1 shows the structural parameter data obtained from XRD that have been analyzed using the Rietveld refinement method to treat entire slices of the tomograph as single refined datasets, allowing extraction of real structural parameters from all voxels of the reconstruction [6,7]. We can see that the lattice parameters slightly decrease 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 [8]. Decreasing the value of the lattice parameter causes an increased value of the bond distance. Zr which has +4 oxidation number will replace Fe which has +3 oxidation state, so to maintain charge neutrality, Fe$^{3+}$ changes to Fe$^{4+}$. This will cause vacancy of oxygen [9]. The creation of an oxygen vacancy causes changes in the length of the Fe - O bonds that have been observed in Table 1. The tolerance factor value also decreases with increasing Zr, this indicates that the crystal is increasingly distorted to achieve stability and proves that Zr has entered the Fe-site, Then, Zr will remove Fe ions which have a lot of oxygen [10]. The same thing was report by C. Sasikala et al, Patricia et al and S. Pokha et al, when Ti doping on LaFeO$_3$ material, then Ti will replace Fe in the material [10-14].
Figure 2. XRD sample LaFe$_{1-x}$Zr$_x$O$_3$ ($x = 0.075$, $0.1$ and $0.15$) at peak (200).

Figure 2. shows An increase in Zr concentration causes pressure on the internal crystal structure of the LaFeO$_3$ and observed as a shift to a higher 2θ value in the XRD pattern. As mentioned, theoretical studies on the optical properties of perovskite NaOsO$_3$ were reported to have a strong relationship with strains [15]. Therefore, the observed shift in peak position and widening was investigated due to changes in size and strain effect [16].

Figure 3 is a representation of the geometric parameters of the crystal structure obtained from the VESTA software. The data used is raw data from Rietveld highscore plus which is converted into a .cif (Crystal Information File) extension. From the visualization of the image, it appears that all samples have a distorted orthorhombic structure. Cation La is located at site-A, while Fe / Zr is located at site-B and binds with 6 oxygen anions to form octahedral (shown using the polyhedral model).

When the value of $t$ is smaller than the ideal value and is smaller than 1, [BO$_3$] octahedra will be tilted to fill the space [17]. When the cubic structure has a value of 0.89 <t <1 but it turns out that in this sample it has a lower t then it will decrease the symmetry of the Crystal structure. As in the LaFeZrO$_3$ sample which has a tolerance value of less than 1 so the crystal structure is orthorhombic seen in Figure 3. As in GdFeO$_3$ with t = 0.81 is an orthorhombic structure [18].

4. Conclusion
The LaFeZrO$_3$ material has been synthesized by the sol-gel method. The sample shows the crystal structure is Orthorhombic with $Pnma$ symmetry group. The XRD results is decrease in lattice parameters, bond length and bond angle because of changes in Zr concentration as doping in Fe-size. All samples also showed the impurity of La$_2$O$_3$ which caused efficiency as a candidate for solar cell applications to decrease. Thus, it is recommended to do temperature changes during synthesis at the calcination stage which aims to eliminate the impurity of La$_2$O$_3$. Then, as a candidate for solar cell applications, it is expected that the sample in the form of powder is transformed into a form of thin-film and needs to be characterized for optical and dielectric properties.

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