Room temperature electrical impedance analysis of LaFe$_{1-x}$Mg$_x$O$_3$ ($x = 0.01$ and $0.05$) ceramics

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Abstract. The effect of Mg-small doped on the structural and electrical properties of LaFe$_{1-x}$Mg$_x$O$_3$ ceramic materials was studied. A series of LaFe$_{1-x}$Mg$_x$O$_3$ ($x = 0.01$ and $0.05$) perovskite material was synthesized via sol-gel method following by sintering process. Structural properties were investigated by using X-Ray diffraction (XRD). Rietveld refinement analysis have been done using Fullprof software. All of the samples are single-phase with orthorhombic crystal structure and Pnma space group. Lattice parameter slightly increases as the Mg-doping concentration increase. The impedance spectroscopy of the sample was characterized by using the RLC-Meter at a frequency range of 100 Hz - 1 MHz at room temperature. The electrical parameters such as impedance, dielectric constant, tan loss, and conductivity was analyzed using impedance spectroscopy method. The value of the dielectric constant ($\varepsilon'$) decreases with increasing frequency and remains constant at higher frequencies. The dielectric loss shows a decrease in the dielectric constant with increasing Mg doping.

1. Introduction

Perovskite-type oxides have the general formula ABO$_3$ where A = rare earth elements and B = transition metal elements [1]. LaFeO$_3$ (Lanthanum Orthoferrites) from ABO$_3$ type is antiferromagnetic with high Neel Temperatures ($T_N$) around 740 K [2]. LaFeO$_3$ is one of perovskite-type oxide that received great attention nowadays due to the comprehensive physical properties and its various technological applications as functional materials such as gas sensors, fuel cells, solid electrolytes, and superconductors [3].

Properties enhancement of perovskite material can be adjusted by doing partial doping or substitution using new element on the parent-compound (LaFeO$_3$) itself. The previous report describes that metal doping (Zn$^{2+}$ and Bi$^{3+}$) to LaFeO$_3$ causes drastic changes in structural, magnetic, and electrical properties of perovskite material [4, 5]. Another study mentioned that B-site substitution play an important role on electrical properties of perovskite material [6]. It has also been reported that through divalent cation doping, by introducing new element which has $2^+$ oxidation state and a radius similar to Fe$^{3+}$ (such as Mg$^{2+}$ or Zn$^{2+}$), it become a trigger for the change in electrical properties of pure LaFeO$_3$ [7]. Lower band gap value as an improvement in optical properties of LaFeO$_3$ due to the presence of Magnesium also already reported by previous report [8]. Enhancement on the dielectric properties of Mg-doped with average weight concentration ($x = 0.1-0.3$) also has been reported before [9]. However, the effect of Mg-small doped on the electrical properties of LaFe$_{1-x}$Mg$_x$O$_3$ ceramic materials with $x = 0.01$ and $0.05$ at room temperature has not been reported yet.

A series of Lanthanum orthoferrite perovskite (LaFeO$_3$) with Mg substitution on Fe-site with doped variation ($x = 0.01$ and $0.05$) were prepared using a simple sol-gel method and following by pressing
and sintering method to obtain ceramic pellets. This study focused on the electrical properties at room temperature.

2. Method
A series of \( \text{LaFe}_{1-x}\text{Mg}_x\text{O}_3 \) perovskite with \( x = 0.01 \) and 0.05 was synthesized by sol-gel method following sintering process. First, the stoichiometric weight amount of lanthanum oxide, ferrite nitrate nonahydrate, magnesium oxide, and citric acid monohydrate as raw materials were mixed and stirred under certain conditions to form the gel phase was obtained. The gel was dried to remove the remaining elements including water and citric acid to make a sponge. Then the dry-gel was calcined at 1173 K until powder form was achieved. After that, the powder was pressed until bulk form has been reached. Last, the bulk form was heated again at furnace with temperature 1273 K along 6 hours (sintering process) until the \( \text{LaFe}_{1-x}\text{Mg}_x\text{O}_3 \) ceramic materials finally obtained.

The structural properties of \( \text{LaFe}_{1-x}\text{Mg}_x\text{O}_3 \) ceramic materials was performed using X-Ray diffraction spectroscopy type XPert PANalytical diffractometer with a Cu Kα radiation source in the Bragg’s angle range of 10°–90°. Then the experimental pattern was further analyzed using the VESTA software. After that, XRD result was analyzed through Rietveld refinement by using the Fullprof suite 2K software. The chemical composition for each sample was detected by PANalytical XPert PANalytical e, with Ag (source energy 50 kV). The electrical properties of the sample such as impedance, dielectric constant, tan loss, and conductivity were characterized by using the RLC-Meter FLUKE-PM 6306 method at a frequency range of 100 Hz - 1 MHz at room temperature.

3. Results and Discussion

3.1 XRD Analysis

Figure 1 presents the XRD pattern of the \( \text{LaFe}_{1-x}\text{Mg}_x\text{O}_3 \) ceramic materials which sintered at 1273 K for 6 h. Rietveld refinement analysis has been done to obtain the crystal structure, phase, lattice parameters, and crystallite size using Fullprof 2K software. From the figure, it shows that all of \( \text{LaFe}_{1-x}\text{Mg}_x\text{O}_3 \) ceramic materials are single-phase orthorhombic crystal structure with the Pnma space group. Several peaks in figure 1 corresponding to the hkl plane (110), (112), (022), (004), (222), (024), (400), and (116). In figure 2 shows the inset of highest peak (112) hkl at \( 2θ = 31.8° \). From that figure, it can be seen that as long as Mg-dopant increases, the highest peak shift to the lower Bragg angle and also consistent for other peaks. The lower Bragg angle will add the value of lattice parameter. This is evidenced by table 2 which shows the increase in lattice parameter value with peak shift at 2θ smaller. This phenomenon proves that Mg-doping can change in stoichiometric composition and change the structural properties of the \( \text{LaFe}_{1-x}\text{Mg}_x\text{O}_3 \) ceramics compound. Compared to the \( \text{LaFeO}_3 \)-parent compound reported by Triyono et al. [10], this result has a peak shift due to the presence of Mg.

The crystallographic parameters based on the refinement result are summarized in Table 1. The lattice parameter slightly increases as the doping concentration increase. The effect is visible on the cell volume which also increased with increasing Mg concentration. The crystallite size of \( \text{LaFe}_{1-x}\text{Mg}_x\text{O}_3 \) ceramic materials was calculated by using the Scherrer equation [8]:

\[
D_{\text{XRD}} = \frac{0.9λ}{B_{1/2} \cos θ_{hkl}}
\]

Where \( λ \) is the wavelength of Cu-Ka (1.5406 Å), \( B_{1/2} \) is full width at half maximum (FWHM) intensity in degree, and \( θ \) is Bragg angle. Mg-doped increase \( (x = 0.01 \) and 0.05) has caused a decrease in the size of crystallites from 44.79 nm to 44.77 nm.

Table 2 showed the geometrical parameters based on the refinement results. Mg-doped does not make the crystal structure change due in atomic and Wyckoff position does not show any changes. However, the changes in the geometrical parameters (i.e. the Fe–O₂–Fe and Fe–O₁–Fe bond angles increases, the Fe/Mg-O bond length decreases) owing to the Mg substitution indicate that Mg ions are
strongly affected by bonding and dynamics distortion in FeO$_6$ octahedral [9]. $t$ value (tolerance factor) increases as well as the Mg-substitution increases. The tolerance factor is calculated by using relation [8]:

$$t = \frac{A-X}{\sqrt{2(B-X)}}$$ (2)

Where $t$ is the tolerance factor, A - X is the bond distance between A-site cation and X-site anion, and B - X is the bond length between B-site cation and X-site anion. The goodness of fit ($\chi^2$) describes the comparison between Rwp and Re approaching value ~1.00 shows the indication that XRD fitting result from Rietveld refinement was a good result and suitable to be used. But for the concentration of Mg with $x = 0.05$, $\chi^2 = 3.20$ quite far from 1.00.

Figure 1. Rietveld refinement of LaFe$_{1-x}$Mg$_x$O$_3$ ceramic materials, using Fullprof 2K software. The experimental data are indicated by the black dots, the calculated data by the red solid line and the green bottom line shows the difference between experimental and calculated data.

Figure 2. Shift of the diffraction angle of highest peak (112) hkl with respect to intensity of XRD pattern.
Table 1. Crystallographic parameters of the LaFe$_{1-x}$Mg$_x$O$_3$ ceramics ($x = 0.01$ and $0.05$), obtained by the FullProf 2k programme.

| Parameters | $a$ (Å) | $b$ (Å) | $c$ (Å) | Volume (Å$^3$) | Crystallite size (nm) |
|------------|---------|---------|---------|----------------|----------------------|
| $x = 0.01$ | 5.558   | 5.565   | 7.857   | 243.0          | 44.79                |
| $x = 0.05$ | 5.562   | 5.574   | 7.864   | 243.7          | 44.77                |

Table 2. Geometrical parameters characterizing the crystal structure of LaFe$_{1-x}$Mg$_x$O$_3$ ceramics ($x = 0.01$ and $0.05$)

| Parameters | $x = 0.01$ | $x = 0.05$ |
|------------|------------|------------|
| Atomic position | | |
| La (x, y, z) | (0.993, 0.03, 0.25) | (0.993, 0.03, 0.25) |
| Fe/Mg (x, y, z) | (0, 0.5, 0) | (0, 0.5, 0) |
| O1 (x, y, z) | (0.719, 0.302, 0.029) | (0.719, 0.302, 0.029) |
| O2 (x, y, z) | 0.08, 0.485, 0.25 | 0.08, 0.485, 0.25 |
| Wyckoff position | | |
| La | 4c | 4c |
| Fe/Mg | 4b | 4b |
| O1 | 8d | 8d |
| O2 | 4c | 4c |
| Bond angle (°) | | |
| Fe–O2–Fe | 154.0612(6) | 157.8541(0) |
| Fe–O1–Fe | 157.0719(0) | 164.4631(0) |
| Bond length (Å) | | |
| La–O1 (m) | 2.45222(3) | 2.59398(0) |
| La–O1 (l) | 2.76142(3) | 2.64424(0) |
| La–O2 (s) | 2.38642(4) | 2.60908(0) |
| (La – O) | 2.53335(3) | 2.61577(0) |
| Fe/Mg–O1 (l) | 2.08747(3) | 2.00326(0) |
| Fe/Mg–O1 (s) | 1.92484(3) | 1.97054(0) |
| Fe/Mg–O2 (m) | 2.01578(3) | 2.00340(0) |
| (Fe/Mg – O) | 2.00936(3) | 1.99240(0) |
| Tolerance factor | 0.8917 | 0.9285 |
| R-factor’s | | |
| $R_p$ | 4.66 | 5.34 |
| $R_{wp}$ | 6.30 | 7.74 |
| $R_s$ | 4.53 | 4.33 |
| $\chi^2$ | 1.94 | 3.20 |

3.2 XRF Analysis

The composition of the crystal was checked by X-Ray Fluorescence. Table 3 shows the percentage of atomic ratio experimental and atomic ratio calculation for each sample with the chemical formula LaFe$_{1-x}$Mg$_x$O$_3$. Fe atomic ratio tends to decrease in the presence of Mg. Fe atom with Mg-doped $x = 0.05$ it will be smaller than $x = 0.01$ and here it is clear that the Fe atomic ratio percentage for $x = 0.05$ is reduced, this indicates the presence of Magnesium even though the value is not detected due to the calculation of the XRF limit to detect elements with small atomic numbers (light elements) [9]. This result corresponding to the results of XRD analysis that shows a shift 2θ value to the left along with the increase in Mg-doped.
Table 3. Comparison between atomic ratio experimental with atomic ratio calculation for the sample.

| LaFe$_{1-x}$Mg$_x$O$_3$ (%) Atomic ratio experimental | (%) Atomic ratio calculation |
|---|---|
| La | Fe | La | Fe |
| $x = 0.01$ | 1 | 0.88 | 1 | 0.99 |
| $x = 0.05$ | 1 | 0.87 | 1 | 0.95 |

3.3 Impedance Spectroscopy Analysis

Figure 3. Nyquist Plot of LaFe$_{1-x}$Mg$_x$O$_3$ ceramic materials with $x = 0.01$ and 0.05 at room temperature.

Figure 4. Bode plot; (a) absolute, (b) real, and (c) imaginary part of impedance as a function of frequency at room temperature from LaFe$_{1-x}$Mg$_x$O$_3$ ceramic materials with $x = 0.01$ and 0.05.

Nyquist plot of LaFe$_{1-x}$Mg$_x$O$_3$ ceramic materials with $x = 0.01$ and 0.05 at room temperature were shown in figure 3 above. As can be seen, the diameter of the semicircle becomes larger when the Mg-doped increases. And can be indicated that resistance is increases by increasing Mg-doping. Figure 4 shows the Bode plot of LaFe$_{1-x}$Mg$_x$O$_3$ ceramic materials with $x = 0.01$ and 0.05 at room temperature. Figure 4a shows the absolute part of the impedance ($Z(f)$) as a function of frequency at room temperature. For sample $x = 0.01$ indicates that the constant value of $Z'$ then decreases with increasing frequency and $x = 0.05$ indicates that the value of $Z'$ decreases drastically with increasing frequency. Figure 4b shows the real part of the impedance ($Z'(f)$) as a function of frequency at room temperature. ($Z'(f)$) indicates a value equal to ($Z(f)$) however at high frequencies the value of real impedance merges and becomes independent toward frequency indicating the possibility of charge polarization [11]. Figure 4c shows the imaginary part of the impedance ($Z''(f)$) as a function of frequency at room temperature. $Z''$ increases with increasing frequency then decreases for both samples ($x = 0.01$ and 0.05). The presence of the peak indicates the existence of electrical properties in terms of the relaxation process in this material [11].
Figure 5 shows the dielectric constant (ε’) of LaFe\textsubscript{1-x}Mg\textsubscript{x}O\textsubscript{3} ceramics as a function of frequency in the frequency range from 100 Hz-1 MHz at room temperature. The trend of dielectric material displays from the value of dielectric constant (ε’) decreases rapidly at the frequency region between 100 Hz and 100 kHz and then become constants at high-frequency region is a normal trend of dielectric material [9]. Figure 5b shows the dielectric loss of LaFe\textsubscript{1-x}Mg\textsubscript{x}O\textsubscript{3} perovskite material with x = 0.01 and 0.05. Sample with doping Mg x = 0.01 are higher but overlap at 50 Hz frequency and become lower. The higher doping, the less energy is absorbed. The dielectric loss shows a increase with increasing Mg doping. Figure 5c displays the total conductivity σ at different frequencies (100 Hz-1 MHz). The conductivity of the sample is relatively constant in low frequency areas and increases linearly in high frequency areas. Increased conductivity in these samples indicates a better response as Mg doping increases. Conductivity in high and low frequency areas is associated with hopping charge carriers and successive jumping from mobile ions from one site to another in lattice sequentially [12].

4. Conclusion
The LaFe\textsubscript{1-x}Mg\textsubscript{x}O\textsubscript{3} ceramic materials with x = 0.01 and 0.05 was successfully prepared by sol-gel method. The XRD characterization showing the single-phase orthorhombic crystal structure with the Pnma space group. The chemical composition was confirmed by X-ray Fluorescence resulting in the incompatibility of atomic composition with the chemical formula of LaFe\textsubscript{1-x}Mg\textsubscript{x}O\textsubscript{3}. As doping concentration increases, the resistance increases so that the energy absorbed is less and it can be indicated that Mg-doping with x = 0.01 higher conductivity.

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References
[1] Kanta and Kumar D 2014 Int. J. Innov. Sci. Res. Technol. 3 1
[2] Falcon H, Goeta A E, Punte G and Carbonio R E 1997 J. Solid. State. Chem. 133 379
[3] Tang P, Tong Y, Chen H, Cao F and Pan G 2012 Curr. Appl. Phys. 13 340
[4] Bhat I, Husain S, Khan W and Patil S I 2013 Mater. Res. Bull. 48 4506
[5] Ahmed M A, Azab A A and El-Khawas E H 2015 J. Mater. Sci. 26 1
[6] Nath V O, Jha P K and Singh P 2017 J. Appl. Phys. 122 225106-1
[7] Isabel D-G M and Roberto G Dr 2017 Chem. Sus. Chem. 10 2457
[8] Triyono D, Hanifah U and Laysandra H. 2020 Results in Physics. 16 102995
[9] Hanifah U and Triyono D 2020 AIP. Conf. Proc. 2242 020004-2
[10] Triyono D, Laysandra H, Liu H L and Anugrah A W 2019 J. Mater. Sci. 30 18587
[11] Ray A, Basu T, Behera B, Kumar M, Thapa R and Nayak P 2018 J. Alloys. Compd. 768 198-213
[12] Dubey S and Kuchania R 2015 Bull. Mater. Sci. 38 1887