Study of LaFe$_{1-x}$Mn$_x$O$_3$ ($x=0.05, 0.1, 0.15, 0.2$) perovskite materials by impedance spectroscopy

A W Anugrah, D Triyono and H Laysandra
Department of Physics, Faculty of Mathematics and Natural Sciences (FMIPA)
Universitas Indonesia, Depok 16424, Indonesia

Corresponding author: djoko.triyono@sci.ui.ac.id

Abstract. We use room-temperature impedance spectroscopy to investigate LaFe$_{1-x}$Mn$_x$O$_3$ ($x=0.05, 0.1, 0.15$ and $0.2$) perovskite-type oxides. The samples were synthesized using the sol-gel method followed by a sintering process to form bulk samples. The microstructural and chemical composition were analyzed using scanning electron microscopy and x-ray fluorescence, with the results indicating a grain size of 373–305 nm and an atomic composition compatible with the chemical formula LaFe$_{1-x}$Mn$_x$O$_3$. Applying impedance spectroscopy to LaFe$_{1-x}$Mn$_x$O$_3$ at room temperature reveals a decreasing impedance and relaxation time with increasing Mn content. The dielectric spectra show an increasing dielectric constant with increasing Mn content.

Keywords: sol-gel method, impedance spectroscopy, LaFe$_{1-x}$Mn$_x$O$_3$

1. Introduction
Perovskites have an ABX$_3$ structure where A and B are cations and X is usually an anion such as LaFeO$_3$, LaMnO$_3$, etc. Lanthanum orthoferrite (LaFeO$_3$), an orthoferrite perovskite compound, is the focus of the present work because of its structural stability and suitability in gas-sensor applications [1]. Previous research has reported substitution into the La and/or Fe sites of LaFeO$_3$, which enhances its electronic properties by producing an increased dielectric constant, decreased dielectric loss, and high thermal stability [2,3]. Cao et al. [2] reported that Na substitution into the La site of La$_{1-x}$Na$_x$FeO$_3$ ($x=0, 0.1, 0.2$) results in a higher dielectric constant, with the maximum being 10 for $x=0.2$. Phokha et al. [3] reported that LaFe$_{1-x}$Ti$_x$O$_3$ ($x=0, 0.1, 0.2$) has a higher dielectric constant, with the maximum at $x=0.2$ being to the order of 10$^4$. In addition, Fe substitution into the Mn site of LaMn$_{1-x}$Fe$_x$O$_3$ ($x=0.15, 0.3, 0.5, 0.7, 1$) was investigated by Karmakar et al. [4], who reported an increasing dielectric constant with increasing Fe content. Zeng et al. [5] reported that LaMn$_{0.5}$Fe$_{0.5}$O$_3$ nanocrystalline materials have crystallite sizes and a dielectric constant of ~25 nm and ~4300 at room temperature, respectively.

Building on previous research, we investigate how Mn doping into the Fe site of LaFe$_{1-x}$Mn$_x$O$_3$ with $x=0.05, 0.1, 0.15, 0.2$ affects the microstructural and dielectric properties at room temperature. The samples were synthesized by using the sol-gel method followed by sintering to form bulk samples. The chemical composition and microstructural properties were examined by using x-ray fluorescence and scanning electron microscopy (SEM), respectively. RLC-Meter FLUKE-PM 6303 with frequency range of 100 Hz to 1 MHz is used to characterize the electrical properties of the samples. The data were analyzed by using impedance spectroscopy and the parallel-plate method.

2. Experimental
By using the sol-gel method, LaFe$_{1-x}$Mn$_x$O$_3$ perovskite compounds were prepared with $x=0.05, 0.10$, 0.15, and 0.20 with lanthanum (III) oxide La$_2$O$_3$, manganese (II) chloride tetrahydrate MnCl$_2$.4H$_2$O, and
Table 1. Results of x-ray fluorescence analysis of LaFe$_{1-x}$Mn$_x$O$_3$ with $x = 0.05, 0.10, 0.15, \text{ and } 0.20$ after calcination at 1173 K.

| LaFe$_{1-x}$Mn$_x$O$_3$ (%) weight | (%) weight experimental | (%) weight calculated |
|----------------------------------|-------------------------|-----------------------|
| $x = 0.05$                       | 65.48                   | 25.50                 |
| $x = 0.10$                       | 61.48                   | 22.70                 |
| $x = 0.15$                       | 63.72                   | 22.16                 |
| $x = 0.20$                       | 65.22                   | 21.25                 |

Figure 1. SEM images of LaFe$_{1-x}$Mn$_x$O$_3$ with $x = (a) 0.05, (b) 0.1, (c) 0.15 \text{ and } (d) 0.2$.

iron (III) nitrate nanohydrate Fe(NO$_3$)$_3$·9H$_2$O (analytical grade) as raw materials. The materials were mixed stoichiometrically with aquades and citric acid monohydrate as a solvent and stirred at 393 K until a gel formed. The gel was dried at 473 K for 5 h then calcined at 1173 K to obtain the nanoparticle form. To obtain nanocrystalline form, the material was pressed into bulk samples by applying 3 kN/m$^2$ and sintered at 1273 K for 12 h. The chemical composition was checked by x-ray fluorescence. The morphology was analyzed by using SEM (FEI QUANTA 650). To apply the parallel-plate capacitor model, the materials were coated with carbon by using a Quorum K975x Turbo Evaporator. RLC-Meter FLUKE-PM 6303 with frequency of 100 Hz to 1 MHz is used to measured the electrical properties of the samples at room temperature.

3. Results and discussion

X-ray fluorescence analysis confirms an atomic composition consistent with the chemical formula LaFe$_{1-x}$Mn$_x$O$_3$. Table 1 shows the composition of LaFe$_{1-x}$Mn$_x$O$_3$ with $x = 0.05, 0.10, 0.15, 0.20$ after calcination at 1173 K. The results of these measurements differ slightly from the calculation, which may be attributed to preparation conditions and insufficient measurement accuracy.

Figure 1 shows typical SEM images of Mn-doped LaFeO$_3$ sintered at 1273 K for 12 h. The average grain sizes are in the range of 373–305 nm. The SEM images show a homogenous surface morphology with spherical grains [6]. Zeng et al. [5] reported a similar morphology for LaFe$_{1-x}$Mn$_x$O$_3$. 
The grain size and dielectric constant of LaFe$_{1-x}$Mn$_x$O$_3$ increases with increasing Mn content. The dielectric constant also increases with increasing Mn content. Figure 4a shows the dielectric constant $\varepsilon'(f)$ for all materials, which increases with increasing frequency and Mn content. This phenomenon is similar to that in BaTi$_{1-x}$Mn$_x$O$_3$ (with $x = 0.00, 0.01, 0.02, 0.03, 0.04$) [7], where the dielectric constant also increases with increasing Mn content. Figure 4b shows the dielectric loss tan $\delta(f)$ of LaFe$_{1-x}$Mn$_x$O$_3$ at room temperature, which shows that the dielectric loss depends on Mn content. In addition, all materials exhibit the dielectric-relaxation phenomenon. The varying dielectric constant and dielectric loss may be due to the number of grain boundaries and to the Mn doping. LaFe$_{1-x}$Mn$_x$O$_3$ has a higher dielectric constant than the others, which indicates that it has a smaller grain size and fewer grain boundaries. Riaz et al. [8] reported variations in dielectric constant and dielectric loss due to several factors, including grain size and grain boundaries. The decrease in grain size reportedly changes the dielectric constant in BiFe$_{1-x}$Mn$_x$O$_3$. In addition, Islam et al. [7] reported a decrease in the dielectric constant of BaMnTi$_{1-x}$O$_4$ with increasing Mn content and increasing grain size, and Verma et al. [9] reported a small dielectric constant resulting from a large number of grain boundaries. Riaz et al. [8] also reported increased dielectric parameter values due to a large number of grain boundaries and Mn doping.

Figure 2. (a) Nyquist plot and (b) impedance $Z$ as a function of frequency for LaFe$_{1-x}$Mn$_x$O$_3$ with $x = 0.05, 0.1, 0.15$, and $0.2$ at room temperature.

Figure 3. (a) Real and (b) imaginary part of impedance as a function of frequency (Bode plot) for LaFe$_{1-x}$Mn$_x$O$_3$ with $x = 0.05, 0.1, 0.15$, and $0.2$ at room temperature.
Figure 4. Frequency dependence of the (a) real part of dielectric constant and (b) dielectric loss of LaFe$_{1-x}$Mn$_x$O$_3$ with $x = 0.05$, 0.1, 0.15, and 0.2 at room temperature.

4. Conclusions
Perovskites LaFe$_{1-x}$Mn$_x$O$_3$ with four variations of Mn ($x = 0.05$, 0.1, 0.15, and 0.2) were successfully synthesized by using the sol-gel technique followed by sintering. The results of x-ray fluorescence spectroscopy indicate an atomic composition consistent with the chemical formula LaFe$_{1-x}$Mn$_x$O$_3$. SEM images show a morphology consisting of homogeneously distributed spherical grains. The average grain size decreases with increasing Mn content, and Mn doping decreases the impedance and increases the dielectric constant.

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