Crystallite size dependence on electrical properties of LaFeO$_3$.0.1Fe$_3$O$_4$ nanocomposite material

I Rhidwan, D Triyono and H Laysandra

Department of Physics, Faculty of Mathematics and Natural Sciences Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia

Corresponding author's e-mail: djoko.triyono@sci.ui.ac.id.

Abstract. LaFeO$_3$.0.1Fe$_3$O$_4$ nanocomposite was prepared by sintering method. LaFeO$_3$ was synthesized by the sol-gel method and mixed with Fe$_3$O$_4$. The mixture was pressed and then sintered at 1300°C for 1 h resulting nanocomposite. After that, LaFeO$_3$.0.1Fe$_3$O$_4$ nanocomposite was annealed at temperatures of 1000°C, 1100°C, and 1200°C for 12 h. Structural analysis by using X-ray diffraction (XRD) confirm the double phase of LaFeO$_3$ and Fe$_3$O$_4$. The crystallite sizes calculated by using Scherrer’s formula are in the range of 30-60 nm. By using impedance spectroscopy method, the electrical properties were evaluated as functions of frequency (1 kHz-1 MHz) and temperature (RT - 373 K). Electrical properties were represented in Nyquist plot and Bode plot as a function of temperature. Bode plot of $Z''$ vs $f$ shows that relaxation peaks shift to the higher frequency. From the plot of ln $\tau$ vs 1/T, the activation energy was calculated.

1. Introduction
Perovskite oxide materials, especially the orthoferrites, are important class of materials due to the large variety of application in SOFC and chemical sensors [1]. They can be used in various applications because their stable structure, high thermal stability, high dielectric constant, low dielectric loss, and high performances [2]. Among these perovskite oxides, LaFeO$_3$ and doping in La and Fe-site of LaFeO$_3$ have been studied for application in oxide fuel cell cathode, oxygen sensors, etc. [1]. The structural and electrical properties of LaFeO$_3$ is very depend on method of preparation, grainsize, doping and composites, sintering temperature, etc. [3-4]. Study of dielectric properties in this material as a function of frequency and temperature with variation of compositions may provide valuable information to obtain good candidate material for application.

Nanocomposite are drawing attention to investigate the correlation between structural and electrical properties with composition and grain size. In this research, we want to investigate the correlation between crystallite size and electrical properties of LaFeO$_3$.Fe$_3$O$_4$. We have synthesized a homogeneous composites LaFeO$_3$ as a main phase with 0.1 at.% Fe$_3$O$_4$ as a second phase of this composite. We were trying to vary the crystallite size of LaFeO$_3$ phase by annealing treatment. We focused on the effect of annealing treatment on the structural and electrical properties of composites of LaFeO$_3$.0.1Fe$_3$O$_4$ materials.

2. Materials and methods
LaFeO$_3$ was synthesized by the sol-gel method using lanthanum oxide (La$_2$O$_3$), iron (III) nitrate nonahydrate (Fe(NO$_3$)$_3$.9H$_2$O) and citric acid as a precursor. The precursors were mixed into solution. The solution was stirred and heated at 120°C until gel was formed. Then, the gel was calcinated in
900°C for 6 h to form LaFeO$_3$ powder. LaFeO$_3$ powder were mixed with 0.1 at.% of Fe$_3$O$_4$ powder and grind to form LaFeO$_3$.0.1Fe$_3$O$_4$. Finally, the powder was pressed into pellet with diameter of 10 mm at pressure of 5kN and sintered at 1300°C for 1 h. Finally, the LaFeO$_3$.0.1Fe$_3$O$_4$ was annealed at 1000°C, 1100°C, and 1200°C for 12 h. The phase identification was checked by using X-Ray Diffractometer (XRD) with Cu Kα ($\lambda =1.54060$ Å) radiation source in the 2θ range of 15° to 90°. Electrical properties of LaFeO$_3$.0.1Fe$_3$O$_4$ were characterized by RLC-Meter FLUKE-PM6306 at frequency range of 1kHz-1MHz with the temperature range of RT-373K.

3. Results and discussion

3.1. Structure analysis

Figure 1 shows the XRD pattern of LaFeO$_3$.0.1Fe$_3$O$_4$ sintered and annealed at 1000°C, 1100°C, and 1200°C. The XRD analysis data were collected at room temperature, with the 2θ range from 15° to 90° and Cu Kα radiation source. All samples exhibit two phases i.e. LaFeO$_3$ orthorhombic structure as a main phase and Fe$_3$O$_4$ cubic structure as a second phase. The crystallite size of LaFeO$_3$.0.1Fe$_3$O$_4$ is determined by Scherrer method using HighScore plus software as tabulated in Table 1. As shown in Table 1, the crystallite size of LaFeO$_3$ is increasing when annealed at 1000°C, then it starts to decrease when annealing temperature was increased. Decreasing in crystallite size might be due to the phase Fe$_3$O$_4$ that inhibit the grain growth of the main phase of LaFeO$_3$. This is similar to the results of research from Xia et al. [5] that showed the presence of a second phase that is segregated in grain boundary.

![XRD curves of LaFeO$_3$.0.1Fe$_3$O$_4$ that sintered and annealed for 12 h.](image)

**Figure 1.** XRD curves of LaFeO$_3$.0.1Fe$_3$O$_4$ that sintered and annealed for 12 h.

| Sample               | Crystallite size (nm) |
|----------------------|------------------------|
| As Sintered          | 38.1                   |
| As Annealed 1000°C   | 60.1                   |
| As Annealed 1100°C   | 58.2                   |
| As Annealed 1200°C   | 40.6                   |

**Table 1.** Crystallite size of LaFeO$_3$.0.1Fe$_3$O$_4$ that sintered and annealed for 12 h.
3.2. Electrical properties

Impedance spectroscopy method is commonly used to characterize electrical properties of ceramic material. The impedance data is represented by Nyquist plot and Bode plot [6, 7]. The variation of imaginary part and real part of impedance (Nyquist plot) for both sintered and annealed samples (1000°C, 1100°C, 1200°C) is given in figure 2. Nyquist plot show that the diameter of semicircle decreases with increasing temperature. The similar phenomenon was reported by Nasri et al. [8] on LiFeP$_2$O$_7$ ceramic. The high-frequency semicircle is caused by the grain contribution and at low frequencies is caused by grain boundary contribution that arising due to equivalent circuits of two parallel resistance-capacitance (RC) elements similar as reported by Triyono et al. [9] for Sr$_2$(Fe,Ti)O$_6$ compounds. From the figure 2, it can be seen that the radius of the semicircle at low frequencies is greater than the semicircle at high frequencies. This means the effect of grain boundaries to resistance is more effective than grains at temperature range for all samples.

Using Zsimpwin 7.0 software, the grain resistance ($R_g$) for all samples can be calculated. Table 2 shows the value of $R_g$ at 323 K. It can be shown that the $R_g$ is decreasing when the annealing temperature increases indicating that grain resistance in the system is affected by crystallite size.

![Nyquist plots](image_url)

**Figure 2.** Nyquist plots of LaFeO$_3$.0.1Fe$_3$O$_4$ that sintered and annealed for 12 h.

**Table 2.** $R_g$ of LaFeO$_3$.0.1Fe$_3$O$_4$ that sintered and annealed for 12 h at 323 K.

| $R_g$ (kOhm) | 323 K |
|--------------|-------|
| As Sintered  | 108.7 |
| As Annealed 1000°C | 129.9 |
| As Annealed 1100°C | 113.0 |
| As Annealed 1200°C | 112.9 |
Figure 3 shows that imaginary part of impedance, $Z''(f)$ at different temperatures for LaFeO$_3$.0.1Fe$_3$O$_4$ for both sintered and annealed samples (1000°C, 1100°C, 1200°C). $Z''$ values increase with increasing of frequency in all temperature range, and exhibited a maximum value before starts decreasing rapidly. From figure 3, it can also be noted that the maximum value show relaxation peak. The $Z''$ peak shifts towards higher frequency with the increase of temperature which indicate the relaxation phenomenon [8]. The activation energy for relaxation process was calculated from plot of $\ln \tau$ vs $1/T$ following Arrhenius law. The observed relaxation times and activation energies [9] are shown in figure 4. It is observed that the value of $\tau$ decreases with rise of temperature. Activation energy indicates the type of charge carrier related to the relaxation process which is accepted that for n-type polaron $E_a < 0.2$ eV, whereas for p-type polaron $E_a > 0.2$ eV [10]. The activation energies for all samples have been calculated. They show that the relaxation process is accepted for n-type polaron. Activation energies for all samples are similar indicates that the crystallite size has no effect for type of charge carrier.

4. Conclusions
Nanocomposite LaFeO$_3$.0.1Fe$_3$O$_4$ has been successfully synthesized. All samples exhibit two phases i.e. LaFeO$_3$ orthorhombic structure as a main phase and Fe$_3$O$_4$ cubic structure as a second phase. The grain resistance is affected by crystallite size. The relaxation peak as shown in bode plot $Z''$ vs $f$ shifts...
Figure 4. Plot between In $\tau$ vs 1/T for LaFeO$_{3.0,1}$Fe$_3$O$_4$ that sintered and annealed for 12 h.

to the higher frequency indicates relaxation phenomenon. From $\tau$ as a function of a temperature, the activation energy for all samples was calculated and its values indicate as n-type polaron.

Acknowledgements
The authors would like thanks to HIBAH PITTA (2007/UN2.R12/HKP.05.00/2016) from Universitas Indonesia for financial support.

References
[1] Benali A, Bejar M, Dhahri, Graça M F P and Costa L C 2015 J. Alloys and Compounds 653 506-12
[2] Cui X, Li S and Zhu X 2014 Mater. Lett. 130 267-70
[3] Shen M, Ge S and Cao W 2001 Appl. Phys. 34 2935-8
[4] Waernhus I, Grande T and Wiik K 2005 Solid State Ionic 176 2609-16
[5] Xia Z C, Yuan S L, Feng W, Zhang L J and Zhang G H 2003 Solid State Comm. 126 567-71
[6] MacDonald J R 1987 Impedance Spectroscopy Emphasising Solid Materials and Systems (New York: Wiley)
[7] Sutar B C, Choudhary R N P, Das P R 2013 J. Ceram. Int. 40 7791-8
[8] Nasri S, Megdiche M and Gargouri M 2016 Ceram. Int. 42 943-51
[9] Triyono D and Laysandra H 2016 AIP Conference Proceedings 1729 20-2
[10] Devi Chandrasekhar K, Mallesh S, Krishna Murthy J, Das A K and Venimadhav A 2014 Physica B 448 304-11