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 τ 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_3O_4 powder and grind to form $LaFeO_3.0.1Fe_3O_4$. 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 $LaFeO_3.0.1Fe_3O_4$ 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 (λ =1.54060 Å) radiation source in the 2θ range of 15° to 90°. Electrical properties of $LaFeO_3.0.1Fe_3O_4$ 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 $LaFeO_3.0.1Fe_3O_4$ 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_3O_4 cubic structure as a second phase. The crystallite size of $LaFeO_3.0.1Fe_3O_4$ 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_3O_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.
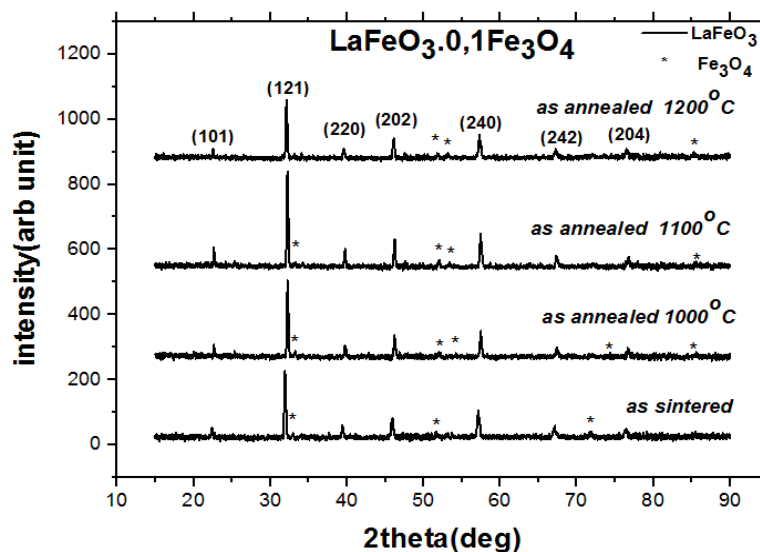

Figure 1. XRD curves of $LaFeO_3.0.1Fe_3O_4$ that sintered and annealed for 12 h.

Table 1. Crystallite size of $LaFeO_3.0.1Fe_3O_4$ 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

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 annealled 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 $LiFeP_2O_7$ 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.
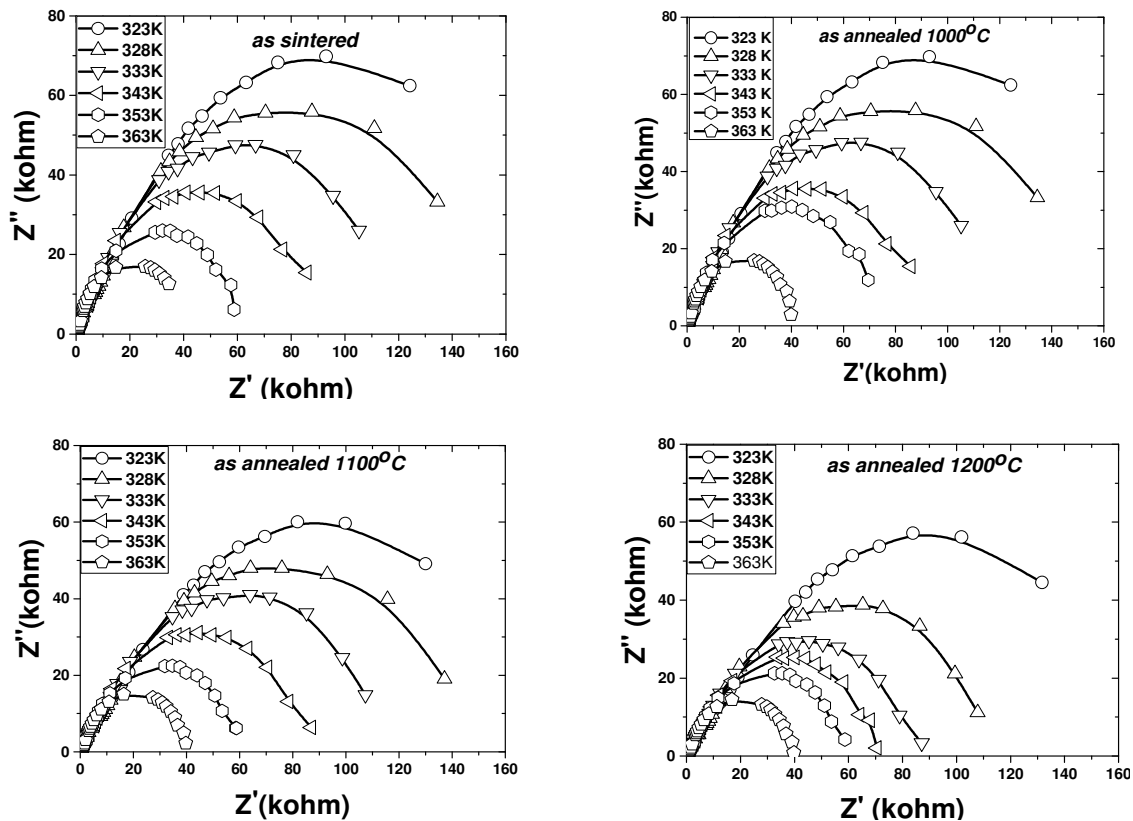

Figure 2. Nyquist plots of $LaFeO_3.0.1Fe_3O_4$ that sintered and annealed for 12 h.

Table 2. R_g of $LaFeO_3.0.1Fe_3O_4$ that sintered and annealed for 12 h at 323 K.

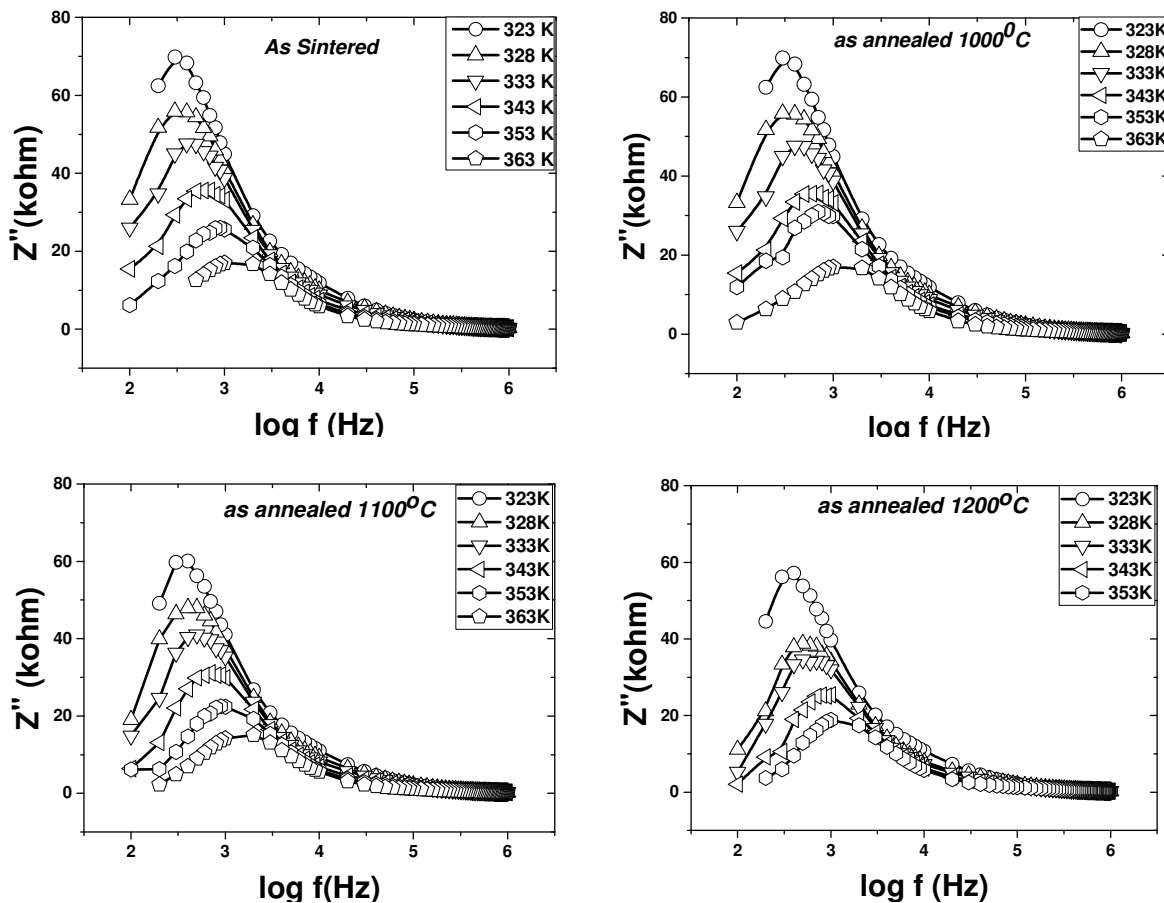| R_g (kOhm)	323 K
As Sintered	108.7
As Annealed 1000°C	129.9
As Annealed 1100°C	113.0
As Annealed 1200°C	112.9

Figure 3. Variation of imaginary part of impedance with frequencies at different temperatures for LaFeO$_3$.0.1Fe$_3$O$_4$ that sintered and annealed for 12 h.

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 annealled 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 τ 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 τ 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 Ea < 0.2 eV, whereas for p-type polaron Ea > 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
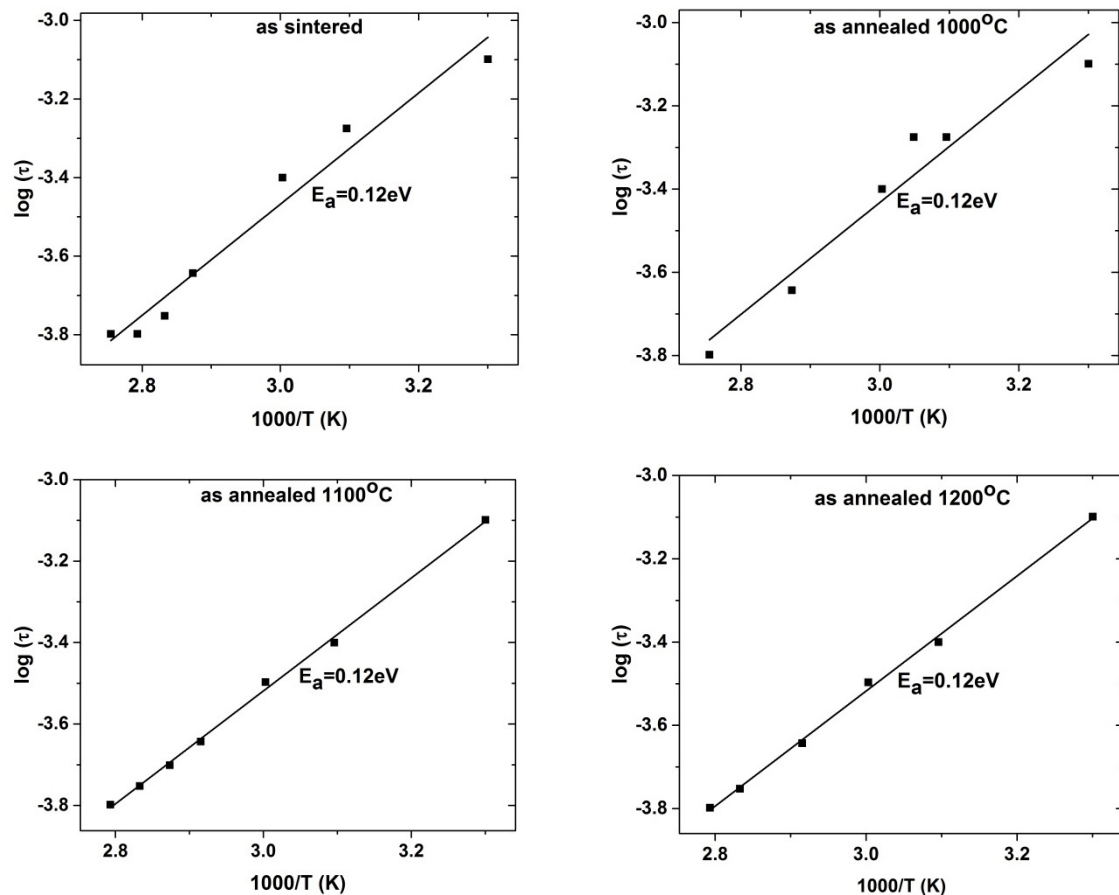
Figure 4. Plot between $\ln \tau$ vs $1/T$ for $LaFeO_3.0,1Fe_3O_4$ that sintered and annealed for 12 h.

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

Acknowledgements

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