An impedance spectroscopy study of sol-gel prepared La$_{0.9}$Sr$_{0.1}$Fe$_{0.7}$Mo$_{0.3}$O$_3$ perovskite

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Abstract. In this present work, impedance spectroscopy was applied to investigate the electrical properties of La$_{0.9}$Sr$_{0.1}$Fe$_{0.7}$Mo$_{0.3}$O$_3$ (LSFMo) perovskite prepared by sol-gel and sintering methods. SEM analysis reveals the non-uniform grain distributed in samples with average grain size 347 nm. The complex impedance has been examined in the frequency range of 100 Hz–1 MHz and temperature range of 75–250 °C. The Nyquist plots were identified to form single semicircular arc described as grain behavior working in conduction mechanism. The dielectric and complex conductivity is shown depending on the temperature and frequency. The evolution of ln $\sigma_{dc}$ vs 10$^3$/T (K$^{-1}$) satisfies Arrhenius law and the activation energy is found to be 0.45 eV for this conduction mechanism.

Keywords: LSFMo, sol-gel method, dielectric, conductivity, activation energy

1. Introduction

LaFeO$_3$ material and its derivatives become interesting research topics in recent years due to the potential application in many fields such as solid oxide fuel cells, chemical sensors, etc. [1, 2]. Doping on orthorhombic-LaFeO$_3$ has been investigated in many reports resulting in the increase ionic and electronic conductivity, structure and thermal stability as observed in La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_3$ [1], La$_{0.5}$Ca$_{0.5-x}$Pb$_x$FeO$_3$ [2], etc. Doping in La- and Fe-site has been reported increasing the oxygen vacancy concentration related to the oxygen ion conductivity and magnetic-electrical conductivity properties, respectively [1].

This research is focused on the double doping of Sr and Mo on La- and Fe-site of LaFeO$_3$, respectively. Our previous works have investigated its structural, room temperature electrical analysis, and optical properties for La$_{0.9}$Sr$_{0.1}$Fe$_{1-x}$Mo$_x$O$_3$ system [3, 4]. The structural analysis revealed that the orthorhombic system is still preserved under Sr- and Mo-doping variation where the crystallite size and lattice volume increase with addition of Mo-concentration [3]. The room temperature electrical investigation reported the dielectric constant degrades and loss tangent increases with increasing Mo-concentration [3]. Furthermore, the optical analysis revealed the redshift of Fe/MoO$_6$ octahedral bands with increasing Mo-doping confirming the changes in lattice structure in the systems and the increasing the bandgap energy due to Mo content variation [4]. However, there is less or no systematic study of the electrical mechanism on this such system, so that this paper becomes a continuation of previous studies [3, 4] in which will investigate the temperature and frequency effects on electrical
properties of La$_{0.9}$Sr$_{0.1}$Fe$_{0.7}$Mo$_{0.3}$O$_{3}$ sample by applying the alternating current (ac) impedance spectroscopy.

2. Experimental

The La$_{0.9}$Sr$_{0.1}$Fe$_{0.7}$Mo$_{0.3}$O$_{3}$ (LSFMo) sample was prepared by the sol-gel technique using the highly analytical grade of La$_2$O$_3$, Fe(NO$_3$)$_3$.9H$_2$O, Sr(NO$_3$)$_2$, MoO$_3$, and citric acid monohydrate which have stoichiometric amounts ~99.9 % purity. The starting precursor was dissolved into distilled water and then stirred until the dark brown gel was obtained. The obtained gel was heated with the heating rates to obtain the powder form of the sample. Then, the powder was grinded in an agate mortar, pressed using hydraulic pressure into the pellet, and sintered at 1300 °C. The details about the synthesis process have been explained in our previous work [3, 4]. Finally, the sintered pellet was obtained. A silver paste was applied on both sides of the pellet to form the plate capacitor configuration for electrical measurement. By using RLC-Meter Fluke 6306, the electrical and dielectric properties were examined in the temperature of 75–250 °C and frequency range of 102–106 Hz.

3. Results and discussion

3.1. Surface morphology

The scanning electron microscope (SEM) image of LSFMo sample is shown in figure 1a. The image shows that the grain is very small, non-uniform size and shape, and randomly oriented. The average grain size has been calculated by using ImageJ software. The distribution of grain size is shown in figure 1b. The average grain size is found to be 347 nm. Figure 1c shows a typical EDS spectrum of LSFMo sample. It declares that all of elemental compositions (La, Sr, Fe, Mo, and O) in this sample has present. This EDS result also proves that there is no absence of any integrated element during sintering process.

3.2. Electrical properties analysis

The Nyquist plot of LSFMo at different temperatures, we have plotted in figure 2. It is clear that the plots are formed by a single semicircular arc indicating the existence of only grain contribution as the one primary mechanism for the conduction process [5, 6]. The evolution of Nyquist semicircle diameter for variational different temperature indicates the thermal resistance of the sample. Actually, the decrease in diameter of arc with increasing temperature is occurred with an increase in conductivity.

Figure 3a shows the variation of the real part of impedance for the LSFMo sample as a function of frequency for variational temperatures. The $Z'(f)$ curve reveals that the real impedance value is higher at lower temperature and in the low-frequency range, and then it decreases slowly with increasing frequency. The $Z''$ also become lower with increasing temperature suggesting the increasing in ac conductivity [5]. The merge of the real impedance in the high-frequency range could be caused by space charges release as a consequence of reduction of the barrier properties with increasing temperature [5, 7]. Next, the frequency and temperature dependence on variation of imaginary impedance value is shown in figure 3b. The $Z''$ value reaches one maximum value and that the peaks broaden with increasing temperature indicating the thermal relaxation mechanism. This mechanism is possible due to the release of charge carriers at lower temperature and ionic vacancies formation at higher temperature [8]. Figure 3c shows the Bode plots of the phase as a function of frequency for different temperatures. It reveals the similar curve for all temperature and only has one peak appear in $\theta$ spectrum confirming only one primary contribution to the conduction process [9].

Figure 4 shows the dielectric constant with frequency and temperatures. It reveals the change of dielectric property with frequency and temperature. The dielectric constant value relatively higher in the lower frequency whereas lower and tends to frequency-independent at higher frequency region. This condition might be caused by the influence of higher charge carrier density [5].
Figure 1. (a) SEM image, (b) the distribution of average grain size calculation, and (c) EDS spectrum for LSFMo sample.

Figure 2. Nyquist plot of LSFMo sample at different temperatures.
Figure 3. Bode plots of (a) $Z'(f)$, (b) $Z''(f)$, and $\theta(f)$ of LSFMo sample at different temperatures.

Figure 4. The dielectric constant of LSFMo sample at different temperatures.
Figure 5. Complex conductivity of LSFMo sample at different temperatures.

Figure 6. Temperature dependence of the DC conductivity for LSFMo sample. The inset reveals the evolution of $\ln \sigma_{DC}$ vs $10^3/T$ (K$^{-1}$) to evaluate the activation energy.

Figure 5 shows the frequency-dependence complex conductivity of LSFMo sample. It is noticed that the complex conductivity is consist of two different trends. The first one is that the independent frequency behaviour conductivity value at low-frequency region which is namely dc conductivity whereas the second one is that the frequency-dependence region occurring in the higher frequency region which increases with increasing temperature called ac conductivity.

Now, we turn to evaluate DC conductivity. Figure 6 shows the evolution of DC conductivity as a function of temperature which is resulted from impedance measurement at low frequencies for LSFMo sample. The conductivity increases with increasing temperature. It is obvious that the conductivity is thermally activated which is correspond to the Arrhenius Law [5, 9]. The inset of figure 6 illustrates the evolution of $\ln \sigma_{DC}$ vs $10^3/T$ (K$^{-1}$) and the activation energy is found to be 0.45 eV. As can be seen that only single slope is formed in this temperature range indicating only one mechanism involved in the conduction mechanism which is consistent with the Nyquist plot and bode-phase plot analysis.
4. Conclusion
The La$_{0.9}$Sr$_{0.1}$Fe$_{0.7}$Mo$_{0.3}$O$_3$ (LSFMo) sample was prepared using sol-gel and sintering methods. The SEM image reveals the non-uniform grains with an average grain size of 347 nm. The impedance analysis identifies only one semicircular arc indicating the grain behaviour as single and dominant contribution in electrical mechanism. The elucidation of variational temperature of the imaginary part of impedance peak and DC conductivity has exhibited that the observed electrical mechanism is thermally activated.

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References
[1] Taylor F H, Buckeridge J and Catlow R A 2017 Chem. Mater. 29 8147-57
[2] Benali A, Azizi, S, Bejar M, Dhahri E and Graça M F P 2014 Ceram. Int. 40 14367-73
[3] Rafsanjani R A, Triyono D and Laysandra H 2018 AIP Conf. Proc. 2023 020024
[4] Utami R W, Rafsanjani R A and Triyono D 2019 J. Phys. Conf. Ser. 1153 012072
[5] Omri A, Bejar M, Dhahri E, Es-Souni M, Valente M A, Graça M P F and Costa L C 2012 J. Alloys Compd. 536 173-8
[6] Sen S, Choudhary R N P and Pramanik P 2007 Physica B 387 56-62
[7] Costa M M, Junior G F M P and Sombra A S B 2010 Mater. Chem. Phys. 123 35-9
[8] Lily L, Kumari K, Prasad K and Choudhary R N P 2008 J. Alloys Compd. 453 325-31
[9] Kharrat A B J, Moutia N, Khirouni K and Boujelben W 2018 Mater. Res. Bull. 105 75-83