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ELECTRICAL PROPERTIES OF $LaYO_3$ CERAMICS: A COMPARATIVE STUDY

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ABSTRACT

Polycrystalline $LaYO_3$ with a monoclinic structure was prepared by conventional solid state synthesis as well as two-step sintering technique. Impedance analysis in the frequency range of 1 Hz – 1 MHz over a wide range of temperature (400 – 700 °C) indicates the electrical properties by bulk contribution. The electrical conductivity measurement of $LaYO_3$ with temperature shows the negative temperature coefficient of resistance (NTCR) behavior. The activation energy (0.48 eV – 0.54 eV) study shows the ionic conduction in all samples. The low activation energies of the samples suggest the presence of oxygen ion vacancies in the conduction process.

Keywords: Polycrystalline, $LaYO_3$; X-ray diffraction (XRD); conductivity; impedance spectroscopy;

INTRODUCTION

Lanthanum-based ceramics such as ($LaYO_3$, $LaGaO_3$, and $LaFeO_3$) have been considered as candidates for solid electrolyte material in solid oxide fuel cell (SOFC) application [1-3]. Lanthanum contained perovskite with general formula ABO_3 is a very interesting material for SOFC since it can be either an electrode or an electrolyte. Extensive researches on perovskite-type oxides structure have received much attention for an electrolyte due to their unique crystal structure. It can tolerate various sizes of cations at both A- and B-cation sublattices and exhibits higher ionic conductivity and better thermal stability. Furthermore, dopant cations can be dissolved in both A- and B-site cation sublattices [1].

$LaGaO_3$ is the most common solid electrolyte material with ABO_3 structure. For example Sr- and Mg-doped $LaGaO_3$ shows relatively higher conductivity of 0.12 S cm^{-1} at 800 ˚C than compared to the commonly used solid electrolytes, Sc-doped ZrO_2 which is exhibits 0.034 S cm^{-1} at 800 ˚C [2, 3]. Thus, many researchers have been focusing on study of $LaGaO_3$. However, due to gallium (Ga) is relatively high cost, there is a need to find and adopt alternative low cost materials to replace Ga in $LaGaO_3$ but offers better properties.

Yttrium (Y) was proposed as a potential candidate to replace Ga as an electrolyte for SOFC. $LaYO_3$ exhibits high ionic conductivity with the oxide ions transport almost unity. Furthermore, Zr-doped $LaYO_3$ exhibited ionic conductivity about 0.012 S cm^{-1} at 1000^{o}C [4].

Different techniques are routinely utilized to synthesis $LaYO_3$ polycrystalline ceramic materials, such as solid state, combustion method and wet chemical methods; sol–gel, co-precipitation, and citrate process [5-8]. In contrast to the above mentioned techniques, solid state method is the most preferred to prepare $LaYO_3$ because of its simplicity, low operation cost and using cheap and easily available oxides as starting materials [9, 10].

However, no further and more detailed experiments have been performed on this $LaYO_3$ material with respected to densification and grain growth for solid electrolyte used in SOFC. Thus, densification and grain growth of this material has yet to be studied because by decreasing the grain size, further improvement in the properties is expected. In order to maintain the grain size it is important to control the growth of the grain. Sintering process is one of the crucial processes that have to give attention. Sintering process is conducted to obtain a material with a high relative density and homogeneous microstructure consisting small grains. The promising approach to obtain fully-dense and fine-grained ceramics has been developed instead of applying conventional single-step sintering (SSS), that grain size can be controlled by applying two-step sintering (TSS) [11-13]. In this regard, we discuss the electrical conductivity and complex modulus spectroscopy of $LaYO_3$ ceramics sintered by TSS.

EXPERIMENTAL

Perovskite $LaYO_3$ was synthesized by solid state synthesis method. La_2O_3 (purity 99.9%) and Y_2O_3 (purity 99.99%) were used to prepare $LaYO_3$. Reagents were dried at the identified drying temperature moisture were weighted in stoichiometric ratio. The reagents were mixed and ground using a pestle and mortar with the addition of acetone. Then, 12 mm diameter pellets were made using uniaxial pressing and fired at 1500 °C in air. After that, the pellets were crushed and ground before analyzed the purity of sample using X-ray Diffraction with Cu Kα radiation (Bruker D2 Phaser equipped with LYNXEYE 1D fast detector).

The powder was prepared as pellets and were fired at 1300 °C for 1 minute before quenched into liquid N_2 (denoted as T_1). The quenched pellets were then reheated at 4 different temperatures; 1200 °C, 1150 °C, 1100 °C and 1050 °C (denoted as T_2), for 15 hours. The microstructure of the pellets was analyzed by scanning electron microscope

(SEM, JEOL). For electrical properties using impedance spectroscopy analyzer, surfaces of the pellets were coated with silver paste and been dried for several minutes. The pellets were placed in a ceramic compression jig and placed in tube furnace furnace for measurement of electrical properties at various temperatures. The data were recorded using Solartron 1260 instrument.

RESULTS AND DISCUSSIONS

Figure 1 shows the XRD pattern of $LaYO_3$ that heated at 1500 °C. The result shows that the reflection were matched with ICDD No. 00-053-0649. No impurity was observed in the XRD pattern. The pattern was indexed with monoclinic phase and the obtained lattice parameters are a = 16.925 Å, b = 16.866 Å and c = 16.87 Å. The reflections exhibit the *Pnma* symmetry that indicated the structure comprise of an orthorhombic packed arrangement of the oxide ions and alternating layers of transition metal ions in the monoclinic coordination.

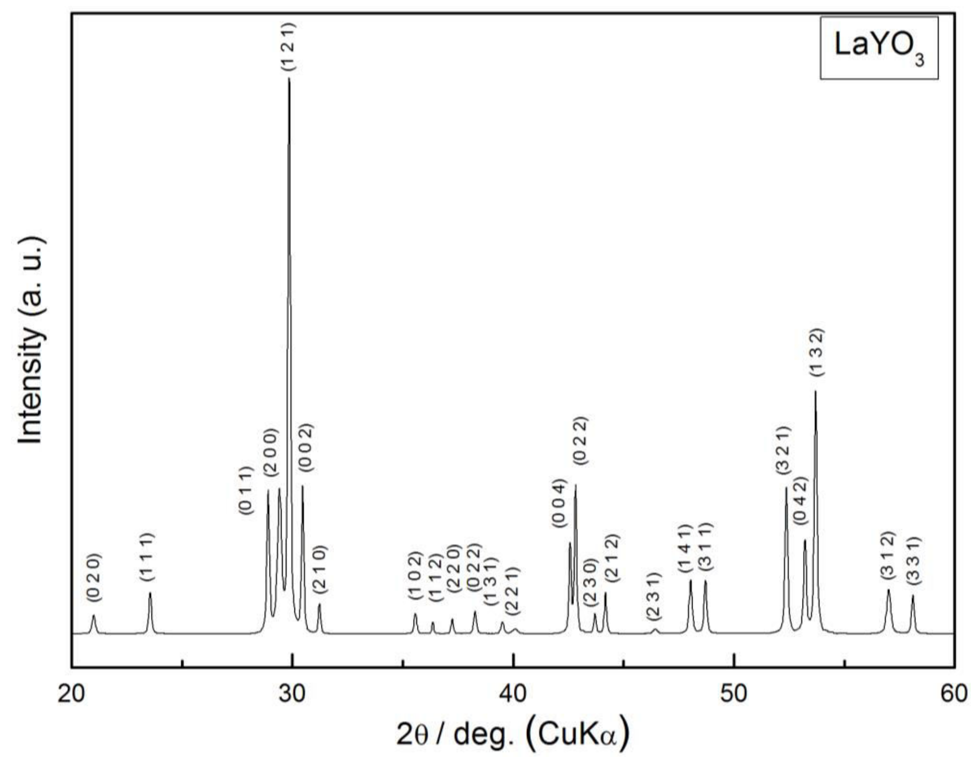

Figure 1: Indexed XRD pattern for $LaYO_3$ powder synthesized at 1500 ºC in air for 10 hours

Figure 2 shows the microstructure of polycrystalline $LaYO_3$ at the different temperature, T_2. The micrographs reveal that well defined grains with variation in grain morphology for all samples. Furthermore, necking formation could be observed and interparticle distance was decreases as the temperature increase. Grain boundary distance decreases as the grain bigger and bulk transport occurs.

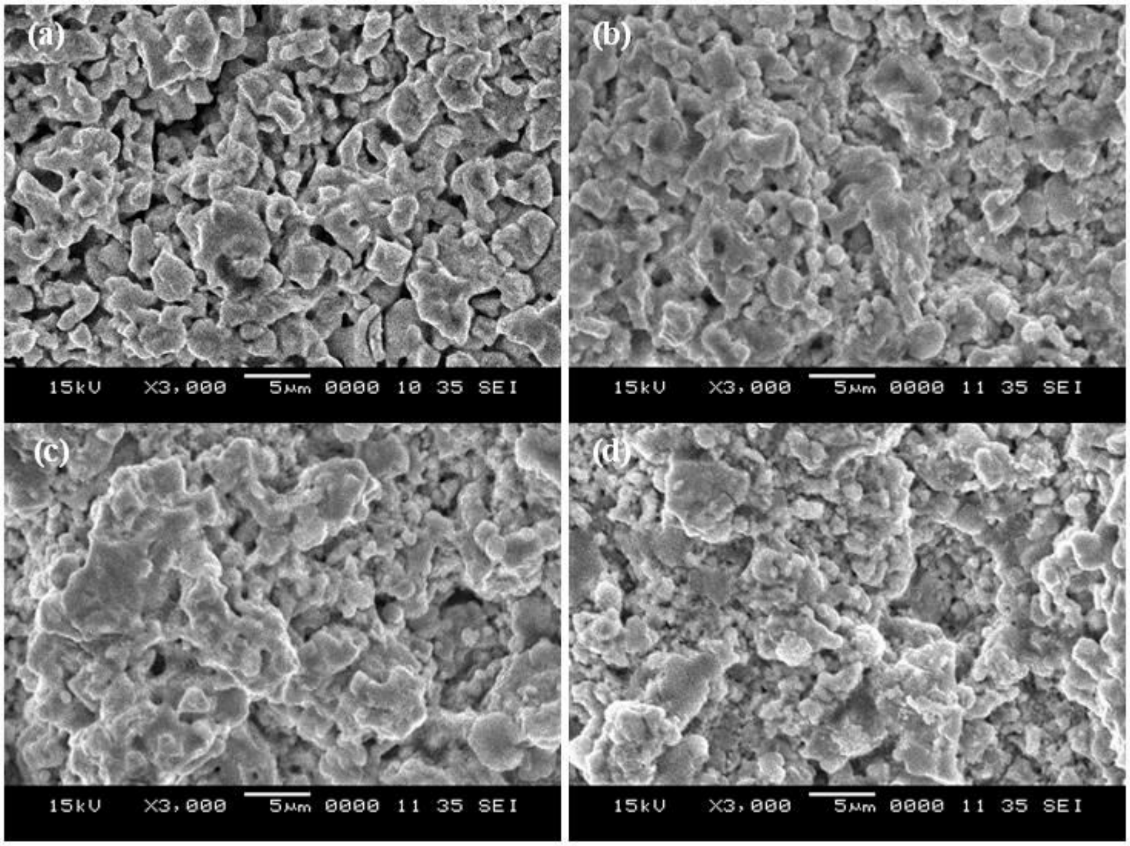

Figure 2: SEM micrographs of $LaYO_3$ by two-step sintering. The samples were sintered at T_2 = (a) 1050 °C (b) 1100 °C (c) 1150 °C (d) 1200 °C for 15 hours, after initial firing at 1300 °C/1 min

Figure 3 shows the complex Cole-Cole plots of the $LaYO_3$ samples at different temperatures. The electrical behavior of the samples were studied over a wide range of temperature between 400 °C and 700 °C with the frequency range from 0.1 Hz to 10 kHz. There is only one semicircle present in the plot which shows only bulk property of the material. The semicircular arc of the complex impedance spectroscopy can be expressed as an equivalent circuit consisting of resistor-capacitor circuits. There is only one semicircle present in the Cole-Cole plot. The presence of one semicircular arc in the impedance spectrum indicates the presence of bulk effects in the material. Therefore, the bulk transport mechanism maybe occurred in the sintered sample. Bulk transport mechanism includes volume diffusion, grain boundary diffusion, plastic flow and viscous flow. Plastic flow, which is the most important, occurs during the heating period where the initial dislocation of density is large. It is usually best verified by compacted powder samples [14]. It has been seen that the sample resistance decreases with increase in measuring temperature which is an effect analogous to the negative temperature coefficient of resistance (NTCR) of the material.

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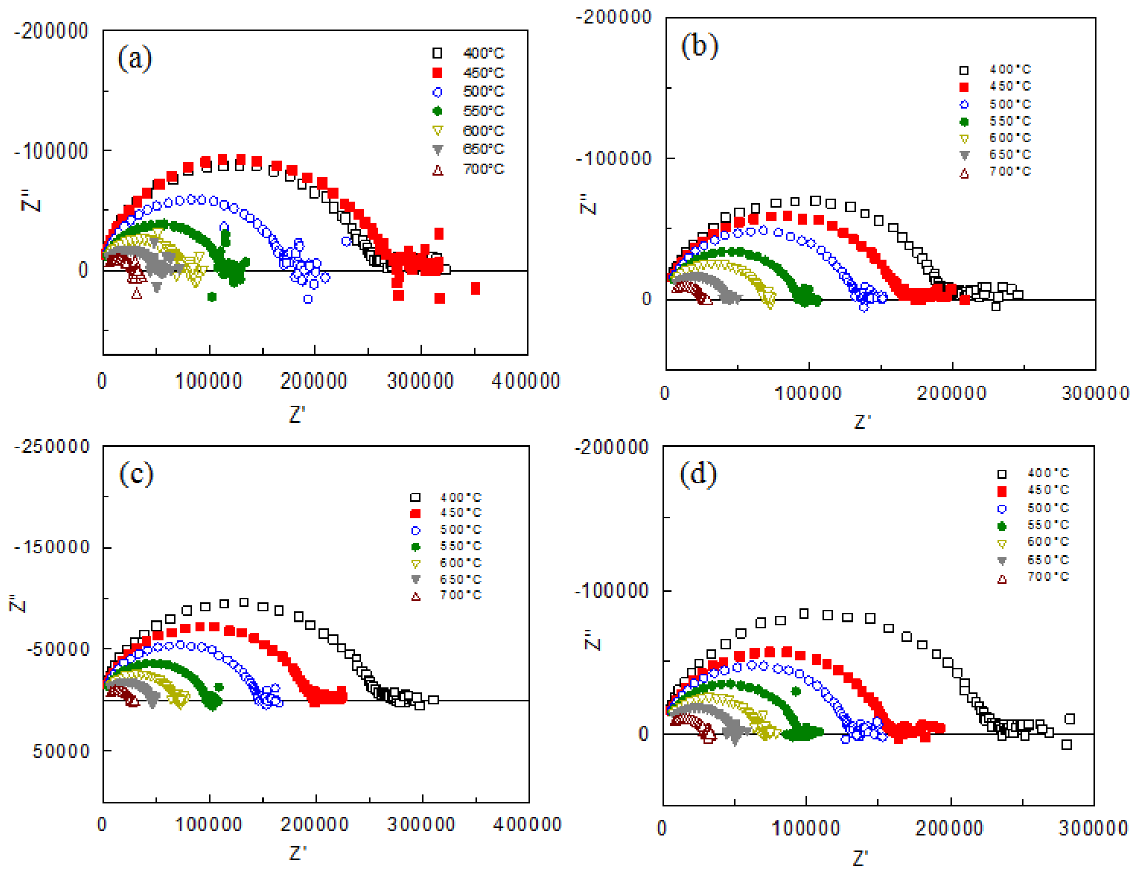

Figure 3: Variations of real (*Z'*) and imaginary (*Z''*) parts of complex impedance of $LaYO_3$ at different T_2 = (a) 1050 °C (b) 1100 °C (c) 1150 °C (d) 1200 °C for 15 hours

Figure 4 shows variations of conductivity with frequency at different temperatures. The conductivity has increased monotonically with frequency from 0.1 Hz to 10 kHz. The slope of the conductivity gives estimation of the amount of charge carries present in the material. It is a function of both temperature and frequency and corresponds to short-range hopping of charge carriers through trap sites separated by energy barriers of different heights.

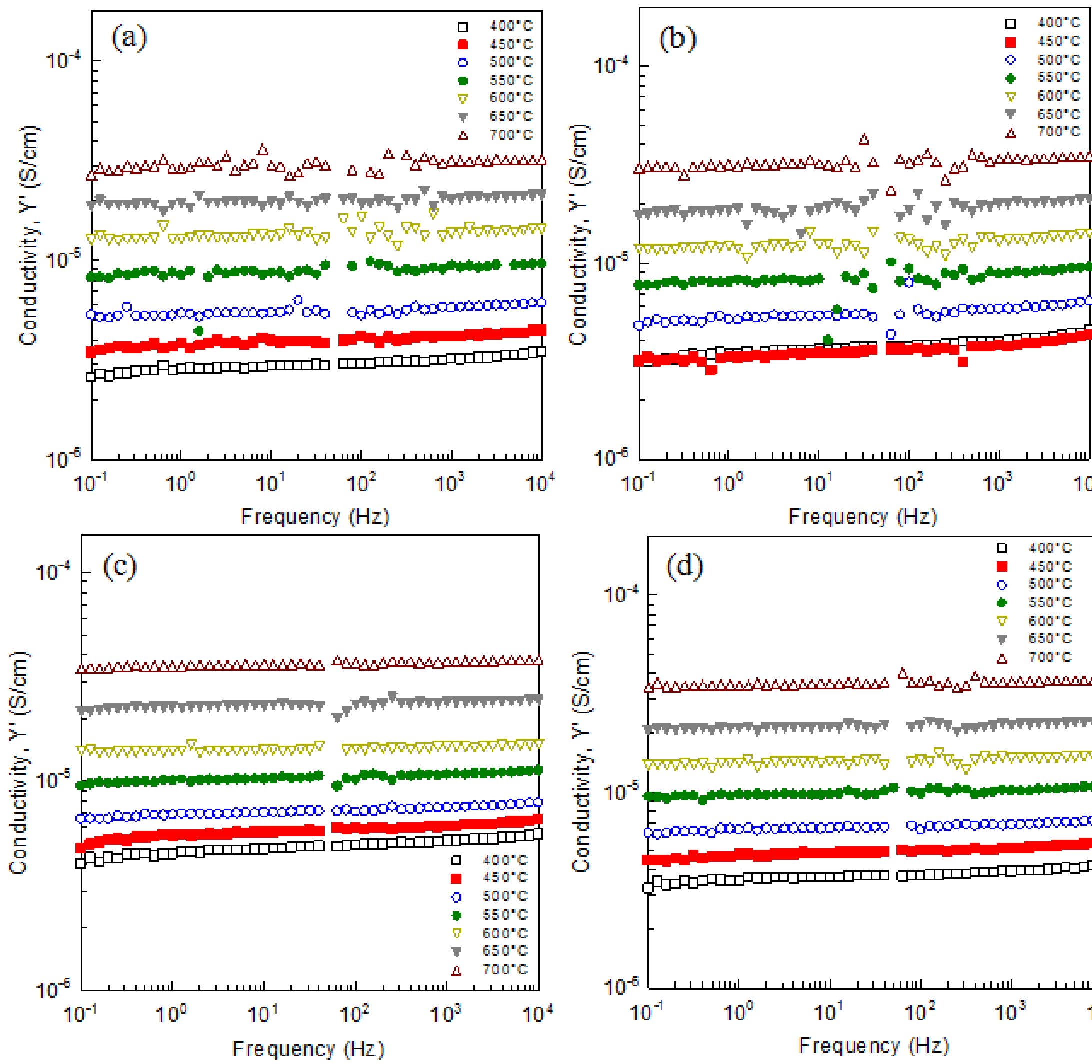

Figure 4: Variations of conductivity of of $LaYO_3$ with frequency at different T_2 = (a) 1050 °C (b) 1100 °C (c) 1150 °C (d) 1200 °C for 15 hours

Figure 5 shows variations of DC conductivity with temperature at different frequencies. The bulk electrical conductivity can be written as

$$\sigma_b = \frac{1}{R_b} \times \frac{l}{A} \qquad (1)$$

where *l* is the thickness; *A* is the area of the electode deposited in the sample. The values of bulk resistance R_b are obtained from the high-frequency and low-frequency intercepts of the semicircle on the real axis in the complex impedance plot.

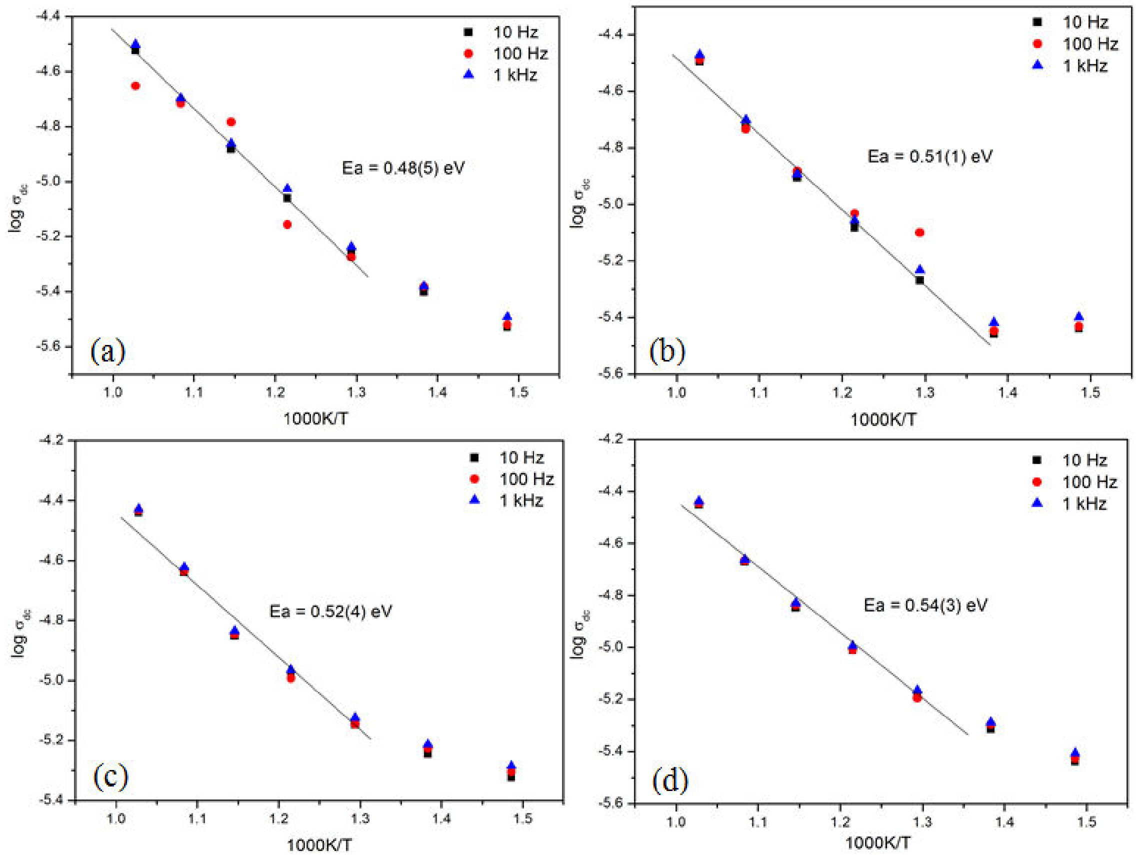

Figure 5: Arrhenius plots of DC conductivity of $LaYO_3$ at different T_2 = (a) 1050 °C (b) 1100 °C (c) 1150 °C (d) 1200 °C for 15 hours

In ceramic samples, oxygen vacancies are usually considered as one of the mobile charge carriers. The ionization of oxygen vacancies creates conducting electrons, which are easily thermally activated. From the results of conduction and the value of activation energy for conduction, it clearly suggests a possibility that the conduction of charge carriers in the high-temperature range maybe oxygen vacancies. The conductivity variation indicates an increase of conductivity with rise in temperature with a typical Arrhenius-type behavior having linear dependence on logarithm of frequency. The type of temperature dependence of DC conductivity indicates that the electrical conduction in the material is a thermally activated process [14].

CONCLUSION

Perovskite $LaYO_3$ can be synthesis using solid state reaction method. Preparation of $LaYO_3$ with monoclinic phase require high temperature which is about 1500 °C and long time (10 h), which may be impossible to be used as low temperature co-fired ceramic (LTCC) application. A comparative investigation of $LaYO_3$ sintered by TSS method has been performed and found that the lowest T_2 are more prominent as charge carriers which it gives more conduction. Activation energy is greatly improved from

0.48 eV to 0.54 eV when T_2 temperature increased which in turn improves the conductivity. One semicircle reflects bulk conduction in the material due to bulk effects by the bulk transport mechanism. In summary, we have performed a comparative investigation of $LaYO_3$ ceramics from the point of view on its electrical conductivity and complex modulus spectroscopy.

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