

Research Article

Structural and Electrochemical Properties of Lanthanum Silicate Apatites $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ for Solid Oxide Fuel Cells (SOFCs)

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An excellent oxide ion conductivity with high oxygen transportation of lanthanum silicate apatite at the solid oxide fuel cell (SOFC) can be achieved through the solid-state reaction method. The doped $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x = 0.2$ and 0.4) materials sintered at 1600°C accomplished crystallinity and crystal structure of apatite-type. The structural and electrochemical characterizations of $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x = 0.2$ and 0.4) were executed using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and electrochemical impedance spectroscopy (EIS) measurements. The total oxide ion conductivities of $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x = 0.2$ and 0.4) were measured from low to intermediate operating temperature range (450 to 800°C) using electrochemical impedance spectroscopy. Room temperature XRD patterns of $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x = 0.2$ and 0.4) exhibited $\text{La}_{10}\text{Si}_6\text{O}_{27}$ apatite phase with space group $P6_3/m$ as the main phase with the minor appearance of La_2SiO_5 as an impurity phase. The highest total oxide ion conductivity of $3.24 \times 10^{-3} \text{ Scm}^{-1}$ and corresponding activation energy of 0.30 eV at 800°C were obtained for $\text{La}_{10}\text{Si}_{5.6}\text{Al}_{0.2}\text{Zn}_{0.2}\text{O}_{26.7}$ which contains a low concentration of Al^{3+} dopant.

1. Introduction

Solid oxide fuel cells (SOFCs) are now especially popular with everyone for producing renewable or clean energy gadgets for electricity generation [1, 2]. SOFC provides

promising features, such as high performance, environmentally clean power generation, and versatile fuel flexibility (hydrogen, hydrocarbons such as methane, or natural gas [3–8]), as a renewable energy system [9]. One of the most extensively used fuels of SOFC is syngas, produced from the

thermochemical conversion of biomass [10–13]. This electrochemical device is made of dense solid oxide electrolyte located between two perforated electrodes [14–18]. Many researchers have developed new electrolytes that provide stability and high oxide ion or proton conductivity at low to moderate operating temperatures (400 to 700°C) [19–23]. SOFC displays beneficial characteristics at these temperatures, such as a wide variety of materials, longer life and reliability, and low cost. Proton-conducting electrolytes are being tried to substitute yttria-stabilized zirconia (YSZ) [24–27]. One of the recent electrolytes with solid oxide ion conductivity relative to other kinds of materials is lanthanum silicate apatite ($\text{La}_{10}\text{Si}_6\text{O}_{27}$) [27–31]. The conductivity of $\text{La}_{10}\text{Si}_6\text{O}_{27}$ offers oxygen permeability numbers near unity over a wide oxygen partial pressure range and stable electrochemical performance under various gas feedstocks [32–36]. The key challenges affecting the stability and electrochemical efficiency of lanthanum silicate materials have low sinterability and the formation of secondary La_2SiO_5 phase [37–39].

Studies on various dopants that can improve the oxide ion conductivity and the interstitial oxide ion concentrations of $\text{La}_{10}\text{Si}_6\text{O}_{27}$ have been carried out [40–42]. The study shows that doping cations on the Si-site have increased the overall oxide ion conductivity of $\text{La}_{10}\text{Si}_6\text{O}_{27}$ than doping on the La-site [34]. Previous researches have also demonstrated that cation vacancies or excess oxygen have increased the oxide ion conductivity of the lanthanum silicate materials [35, 40, 41, 43–46]. Thus, a wide range of cations doping on both La- and Si-sites can enhance the oxide ion conductivity of $\text{La}_{10}\text{Si}_6\text{O}_{27}$ [47].

Recently, the single-chamber solid oxide fuel cell (SC-SOFC) over the conventional SOFC has attracted researchers due to its numerous advantages. SC-SOFC can be operated using a mixture of fuel (where hydrocarbon fuel can be used directly) without sealing [48]. Electrolyte with a porous microstructure can be used in single-chamber SOFC where the snugness of gas is not essential. In SC-SOFC, the catalytic activity occurs only between the electrodes, the partial oxidation of fuel occurs at the anode, and the oxygen reduction occurs at the cathode. Therefore, due to the uniform gas composition, the electromotive force is generated only between the two electrodes and enhances the cell performance due to the use of a mixture of air and hydrocarbon fuel. In Figure 1, methane and oxygen are separated by a porous membrane. The electrochemical reaction occurs with oxygen ions by producing carbon monoxide (CO) and hydrogen (H_2) due to the partial oxidation [48, 49].

The gas transportation through the porous electrolyte can be derived mathematically by viscous flow (Π_v) and Knudsen diffusion (Π_k) [50]:

$$\Pi = \Pi_v + \Pi_k = \frac{\varepsilon r^2}{8\eta\tau RTL} Pm + \frac{2\varepsilon\tau}{3\tau\theta_k L} \sqrt{\frac{8}{\pi RMT}}, \quad (1)$$

where ε is the porosity, r is the radius of the pore, η is the gas viscosity, τ is the tortuosity factor, R is the gas constant per mole, T is the temperature, L is the thickness of the porous

medium, Pm is the mean pressure, M is the molar mass of the gas, and θ_k is the parameter coefficient of “hardness” of the walls.

In recent research, transition metal dopant such as Zn^{2+} has been found in $\text{La}_{10}\text{Si}_6\text{O}_{27}$ and improved the oxide ion conductivity of $\text{La}_{10}\text{Si}_6\text{O}_{27}$ as reported by Setsoafia et al. [40]. Other research has found that Al^{3+} dopant can also enhance the oxide ion conductivity of $\text{La}_{10}\text{Si}_6\text{O}_{27}$ as investigated by Yoshioka [41] and even by Cao and Jiang [36]. Hence, in this work, a series of new and novel doped $\text{La}_{10}\text{Si}_6\text{O}_{27}$ materials were prepared by codoping of Al^{3+} and Zn^{2+} on the Si-site through solid-state reaction which observed the correlation between sintering temperature and electrical properties. Prepared lanthanum apatite can be used in single-chamber SOFC effectively as a porous electrolyte. Noteworthy, low-cost and low-temperature cell fabrication is possible with these porous electrolytes. Thus, the lanthanum apatite structures could be a novel approach to use in a porous SC-SOFC system that consisted of a porous electrolyte, anode, and cathode as lanthanum apatite has high oxide ion conduction over a wide range of partial pressure of oxygen from 1 to 10^{-21} atm which may accelerate oxide ion conduction with low activation energy. The purpose of this study is to inspect the effects of codoping, varying concentrations of Al^{3+} with a constant concentration of Zn^{2+} on the structure to reduce the energy consumption and the oxide ion conductivity of the lanthanum silicate materials in SOFC (450 to 800°C).

2. Experimental

2.1. Sample Preparation. Lanthanum silicate of $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x=0.2$ and 0.4) samples were synthesized as apatite structure through the solid-state synthesis method [18, 51–56]. Initially, a total of 10 g of appropriate amount of La_2O_3 , SiO_2 , Al_2O_3 , and ZnO powders were ball milled with 200 g of zirconia balls and 150 ml of ethanol at a rational speed of 250 rpm for 24 hours. After ball milling, the mixtures were then dried completely in an oven at 80°C. The powders were ground and then calcined at 1300°C for 10 hours at 5°C/min heating and cooling rates to get rid of the organics. After calcination, 2.5 g of the powders were pressed uniaxially in a mold at a constant pressure of 50 MPa and a hold-up time of 60 seconds. The produced pellets were sintered at 1600°C for 8 hours at 5°C/min heating and cooling rates.

2.2. Characterization. Structural characterizations of $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x=0.2$ and 0.4) were studied using XRD and SEM, weight %, and atomic % of the elements in the $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x=0.2$ and 0.4) compounds which were measured using EDX. Finally, the electrochemical performances of the electrolytes were investigated using EIS.

Room temperature XRD patterns of the electrolytes were obtained using $\text{Cu-K}\alpha 1$ radiation (wavelength, $\lambda = 1.5406 \text{ \AA}$) with a speed of scan of 2 degrees per minute. Microstructures of the electrolytes were obtained on JEOL

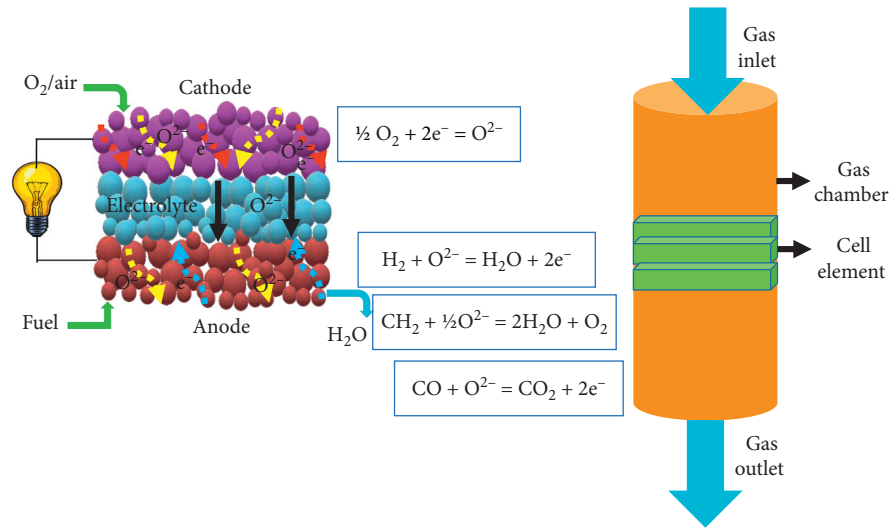


FIGURE 1: Schematic illustration of the all porous single-chamber SOFC. Methane (CH_4) is nourished at the anode side, while air (O_2) is introduced at the cathode and conveyed by the permeable electrolyte to the catalytic anode.

JSM-7610F scanning electron microscopy [57]. EDX is connected to the SEM device to get the weight % and atomic % of the elements in the $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x=0.2$ and 0.4) compounds.

Oxide ion conductivity measurements were performed using a furnace with platinum wires as current collectors. Symmetrical cells with platinum paste coating on the top and bottom surfaces of the pellet were made. A.C. impedance measurements were collected in 50°C steps in the air between 450 and 800°C using a Solartron impedance analyzer system combined with electrochemical interface controlled by Zplot electrochemical impedance software. Total resistance (sum of the bulk and grain boundary resistances) at a certain temperature was obtained from fitting the impedance plot at that temperature. The total oxide ion conductivity σ_{total} was evaluated using the following equation:

$$\sigma_{\text{total}} = \frac{t}{SR}, \quad (2)$$

where t is the thickness of the pellet, S is the surface area of the conducting paste on the pellet, and R is the total resistance. Activation energy was obtained from Arrhenius plot using the following Arrhenius equation:

$$\sigma T = \sigma_o \exp\left(-\frac{E_a}{kT}\right), \quad (3)$$

where σ , σ_o , E_a , k , T are the conductivity (Scm^{-1}), pre-exponential factor, activation energy (eV), Boltzmann constant (8.62×10^{-5} eV/K), and temperature (K), respectively. Equation (3) can be arranged as

$$\log(\sigma T) = -\frac{E_a}{k} \cdot \frac{1}{T} + \log(\sigma_o). \quad (4)$$

3. Results and Discussions

To analyze the apatite structure which was sintered at 1600°C for 8 hours in the air, the X-ray diffraction (XRD) technique

was used and represented in Figure 2. The room temperature XRD patterns of the powder samples confirmed that $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x=0.2$ and 0.4) belongs to an apatite phase of composition $\text{La}_{10}\text{Si}_6\text{O}_{27}$ with space group $P6_3/m$. A small percentage of an impurity phase of La_2SiO_5 was detected from XRD data from the appearance of some additional peaks along with the parent apatite phase. The impurity is difficult to remove once formed even if its appearance in the phase assembly was not thermodynamically favoured [39] and this is the kind of adversity that occurs when a material is made in a solid-state method [58]. The La_2SiO_5 impurity occurred when a secondary phase La_2O_3 formed by decarburization reaction during the calcination reacted with silicate apatite in $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x=0.2$ and 0.4) during the sintering process [29]. La_2SiO_5 crystallizes in the monoclinic symmetry in the $P2_1/c$ space group [59]. The impurity phase is less than 5% which has no significant effect on ionic conduction. The lattice parameters of $\text{La}_{10}\text{Si}_{5.6}\text{Al}_{0.2}\text{Zn}_{0.2}\text{O}_{26.7}$ were found to be $a=b=9.71 \text{ \AA}$ and $c=7.21 \text{ \AA}$ and the lattice parameters of $\text{La}_{10}\text{Si}_{5.4}\text{Al}_{0.4}\text{Zn}_{0.2}\text{O}_{26.6}$ were found to be $a=b=9.73 \text{ \AA}$ and $c=7.21 \text{ \AA}$. The materials have almost similar lattice parameters due to their similar chemical composition and symmetry.

SEM is a powerful technique to understand the density, grain boundaries, and phase purity [60]. Figure 3 shows the morphological structure of the lanthanum silicate apatite of $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x=0.2$ and 0.4) porous electrolytes. It shows that the particles of $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ are well connected and form open channels in the electrolyte, which allow gas infiltration through the electrolyte. The cross-section SEM analysis of apatite crystals for the abovementioned compositions showed significant dense solid materials and visible grain size with obvious grain boundaries, which accelerates the exchange of ions indicating electrolytes (Figure 3) [61, 62]. Grain sizes for the samples were approximately $1 \mu\text{m}$. Nonuniform grains of $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x=0.2$ and 0.4) indicated that

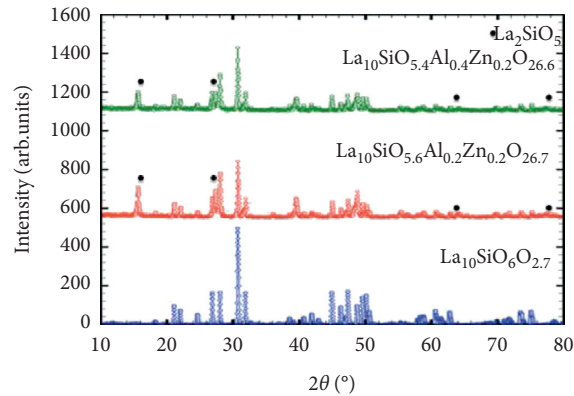


FIGURE 2: Room temperature XRD patterns of $\text{La}_{10}\text{Si}_{5.6}\text{Al}_{0.2}\text{Zn}_{0.2}\text{O}_{26.7}$ and $\text{La}_{10}\text{Si}_{5.4}\text{Al}_{0.4}\text{Zn}_{0.2}\text{O}_{26.6}$ sintered at 1600°C for 8 hours in air compared to room temperature XRD pattern of $\text{La}_{10}\text{Si}_6\text{O}_{27}$ sintered at 1500°C for 10 hours in air obtained.

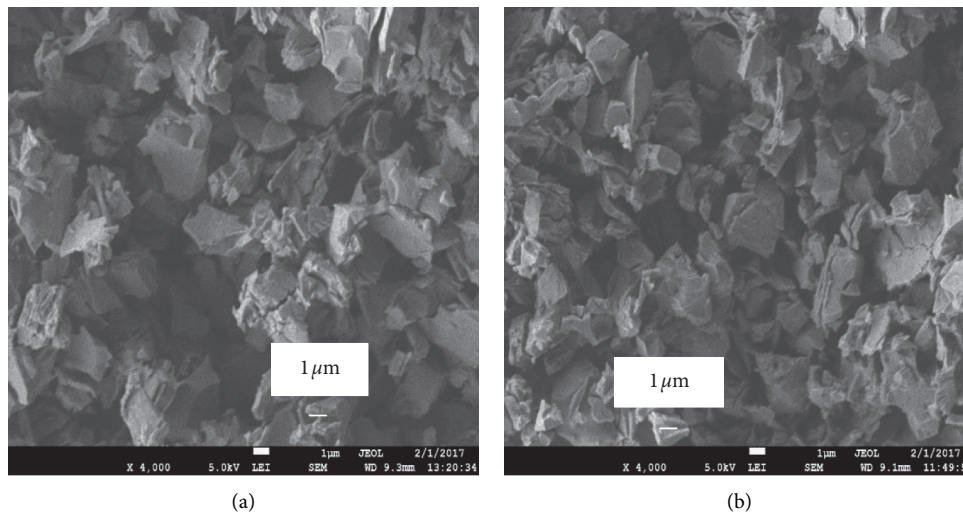


FIGURE 3: SEM images (cross-sectional) of $\text{La}_{10}\text{Si}_{5.6}\text{Al}_{0.2}\text{Zn}_{0.2}\text{O}_{26.7}$ (left) and $\text{La}_{10}\text{Si}_{5.4}\text{Al}_{0.4}\text{Zn}_{0.2}\text{O}_{26.6}$ (right) powders sintered at 1600°C for 8 hours in air.

the milling process had reduced most of the grains into particles of closely related size to each other. This in turn aids in the formation of the apatite structure. Zn and Al codoping at the Si-site increases the density as well as the grain size which increases the ionic conductivity.

At the same time, while running SEM, the energy dispersive X-ray (EDX) analysis was performed with an utterly vacuum atmosphere. The EDX spectra (Figure 4) clearly describes that in addition to a small amount of Al and Zn components, the material contains La, Si, Al, Zn, and O. The particle sizes of $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x = 0.2$ and 0.4) were about $1\mu\text{m}$. Weight % and atomic % of the sintered powders obtained from EDX spectroscopy are listed in Table 1. Greater weight % of aluminium in $\text{La}_{10}\text{Si}_{5.4}\text{Al}_{0.4}\text{Zn}_{0.2}\text{O}_{26.6}$ is when the theoretical aluminium content of the $\text{La}_{10}\text{Si}_{5.4}\text{Al}_{0.4}\text{Zn}_{0.2}\text{O}_{26.6}$ compound is greater than $\text{La}_{10}\text{Si}_{5.6}\text{Al}_{0.2}\text{Zn}_{0.2}\text{O}_{26.7}$, whereas the weight % of silicon and oxygen are greater in $\text{La}_{10}\text{Si}_{5.6}\text{Al}_{0.2}\text{Zn}_{0.2}\text{O}_{26.7}$ when the theoretical silicon and oxygen contents of the $\text{La}_{10}\text{Si}_{5.6}\text{Al}_{0.2}\text{Zn}_{0.2}\text{O}_{26.7}$ compound are greater than the

$\text{La}_{10}\text{Si}_{5.4}\text{Al}_{0.4}\text{Zn}_{0.2}\text{O}_{26.6}$ compound. The weight % of lanthanum and zinc in $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x = 0.2$ and 0.4) are closely related values to each other as the theoretical compositions of lanthanum and zinc in $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x = 0.2$ and 0.4) compounds are the same. The results show an approximate match between the weight % of elements in a compound and the theoretical composition of the elements in the compound [63].

Figure 5 compares the EIS plots of $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x = 0.2$ and 0.4) pellets at 800°C with corresponding equivalent circuit used for fitting the Nyquist plots. The two semicircles of the Nyquist plots represent the grain conductivity and the grain boundary conductivity. The high frequency regime belongs to the grain contribution to the conductivity and the medium range frequency belongs to the grain boundary contribution to the conductivity of $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x = 0.2$ and 0.4) [38,64]. The total oxide ion conductivity of $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x = 0.2$ and 0.4) at a certain operating temperature was calculated using equation (2) where the total resistance was obtained by fitting

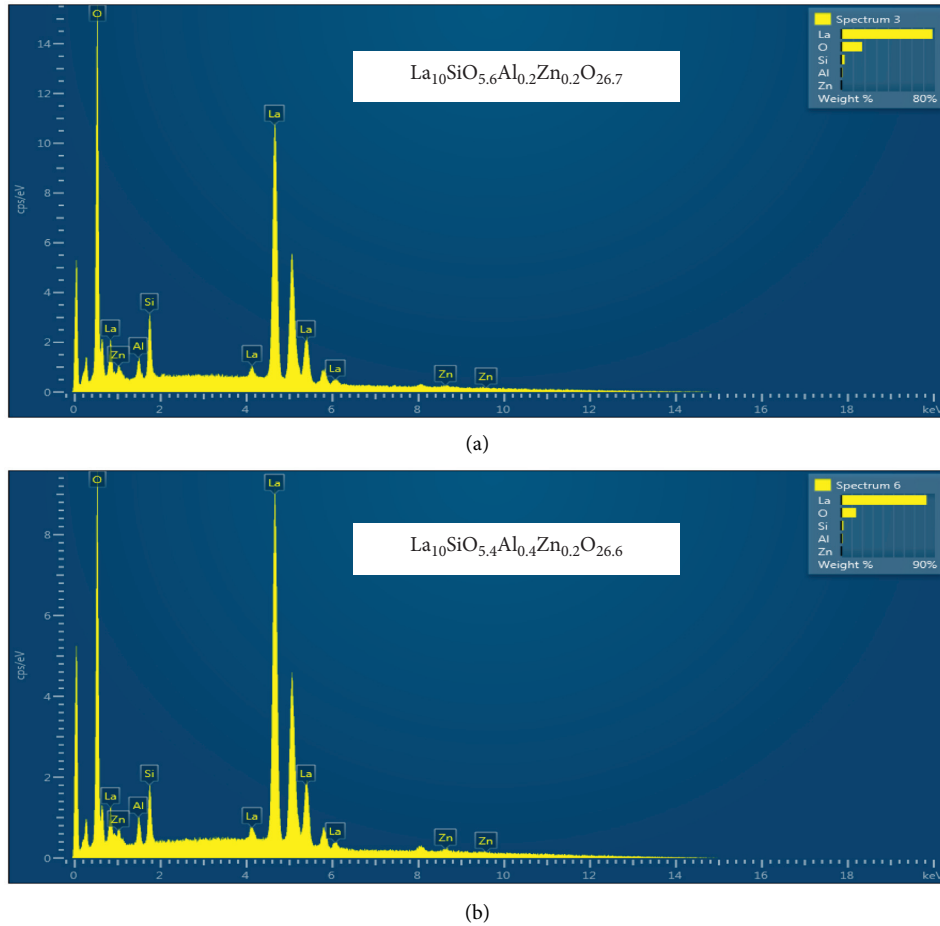


FIGURE 4: EDX spectra of $\text{La}_{10}\text{Si}_{5.6}\text{Al}_{0.2}\text{Zn}_{0.2}\text{O}_{26.7}$ (top) and $\text{La}_{10}\text{Si}_{5.4}\text{Al}_{0.4}\text{Zn}_{0.2}\text{O}_{26.6}$ (bottom) powders sintered at 1600°C for 8 hours in air.

TABLE 1: Elemental distribution of $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x = 0.2$ and 0.4) through EDX.

Element symbol	Composition	$x = 0.2$		$x = 0.4$	
		F %	EDX %	F %	EDX %
La	10	77.88	30.73	81.99	36.62
Si	5.6	2.96	5.78	2.16	4.77
Al	0.2	0.98	2	1.17	2.7
Zn	0.2	0.31	0.26	0.35	0.33
O	26.7	17.87	61.24	14.33	55.58

the impedance plot with equivalent circuit model shown as an inset in Figure 5. Total conductivity of different compositions reported in this work and in the literature from 500 to 800°C are listed in Table 2. Overall, it can be stated that the total oxide ion conductivity of $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x = 0.2$ and 0.4) pellets gradually increases with increasing temperature as shown in Table 2, which demonstrates that the ionic diffusion process is thermally activated [41]. $\text{La}_{10}\text{Si}_{5.6}\text{Al}_{0.2}\text{Zn}_{0.2}\text{O}_{26.7}$ obtains the highest total oxide ion conductivity of $3.24 \times 10^{-3} \text{ Scm}^{-1}$ at 800°C than $\text{La}_{10}\text{Si}_{5.4}\text{Al}_{0.4}\text{Zn}_{0.2}\text{O}_{26.6}$ of $2.08 \times 10^{-3} \text{ Scm}^{-1}$. The addition of small weight % of aluminium and sintering temperature of 1600°C for 8 hours in air resulted in a good conductivity achieved at the intermediate operating temperature of 800°C . Unfortunately, total oxide ion

conductivity measurements of fully sintered $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x = 0.2$ and 0.4) pellets could not be obtained because the pellets are not fully sintered even after heating at the maximum temperature (1600°C) of the furnace, whilst the samples have porous electrolyte nature, but the grain growth is obviously aging at elevated temperature which can be correlated with the conductivity results [66]. Normally, Zn doping in oxides increases the sintering behavior and density of the materials [67]. A wet chemical method using azeotropic distillation was used to densify lanthanum silicate. The particle size was about 10 nm which helps to densify the material [68]. Figure 6 presents the Arrhenius plots of $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x = 0.2$ and 0.4) pellets. Straight lines can be drawn from the Arrhenius plots that are well fitted to the

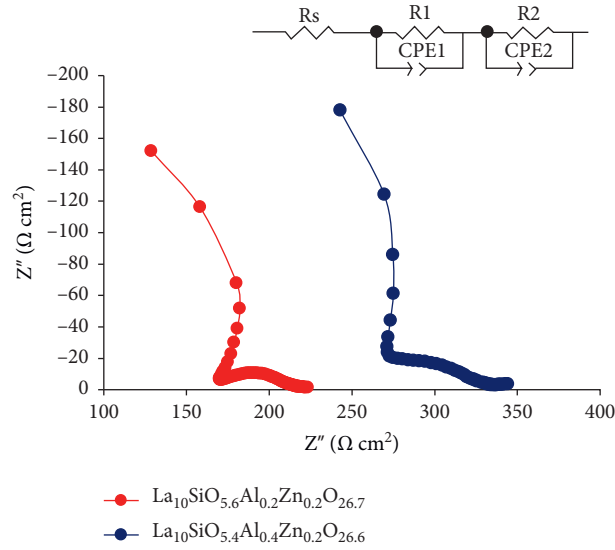


FIGURE 5: A.C. impedance plots of $\text{La}_{10}\text{Si}_{5.6}\text{Al}_{0.2}\text{Zn}_{0.2}\text{O}_{26.7}$ (left) and $\text{La}_{10}\text{Si}_{5.4}\text{Al}_{0.4}\text{Zn}_{0.2}\text{O}_{26.6}$ (right) at intermediate operating temperature of 800°C and the equivalent circuit.

TABLE 2: Total conductivity of different compositions reported in this work and in the literature.

Sample compositions	500°C (Scm^{-1})	600°C (Scm^{-1})	700°C (Scm^{-1})	800°C (Scm^{-1})	Ref.
$\text{La}_{10}\text{Si}_{5.4}\text{Al}_{0.4}\text{Zn}_{0.2}\text{O}_{26.6}$	1.35×10^{-4}	5.67×10^{-4}	1.38×10^{-3}	2.08×10^{-3}	This work
$\text{La}_{10}\text{Si}_{5.6}\text{Al}_{0.2}\text{Zn}_{0.2}\text{O}_{26.7}$	1.61×10^{-4}	7.23×10^{-4}	1.76×10^{-3}	3.24×10^{-3}	This work
$\text{La}_{9.67}\text{Si}_6\text{O}_{26.5}$	0.40×10^{-3}	—	—	7.10×10^{-3}	[41]
$\text{La}_{9.533}(\text{Si}_{5.4}\text{Al}_{0.6})\text{O}_{26}$	0.60×10^{-3}	—	—	7.80×10^{-3}	[41]
$\text{La}_{9.8}\text{Si}_{5.7}\text{Mg}_{0.3}\text{O}_{26.4}$	—	—	—	7.40×10^{-2}	[45]
$\text{La}_{10}\text{Si}_{5.8}\text{Mg}_{0.2}\text{O}_{26.8}$	—	—	—	8.8×10^{-2}	[45]
$\text{La}_9\text{BaSi}_6\text{O}_{26.5}$	—	—	—	11.4×10^{-3}	[43]
$\text{La}_9\text{SrSi}_6\text{O}_{26.5}$	—	—	—	8.7×10^{-3}	[43]
$\text{La}_{9.67}\text{Si}_5\text{AlO}_{26}$	—	—	—	7.9×10^{-3}	[65]

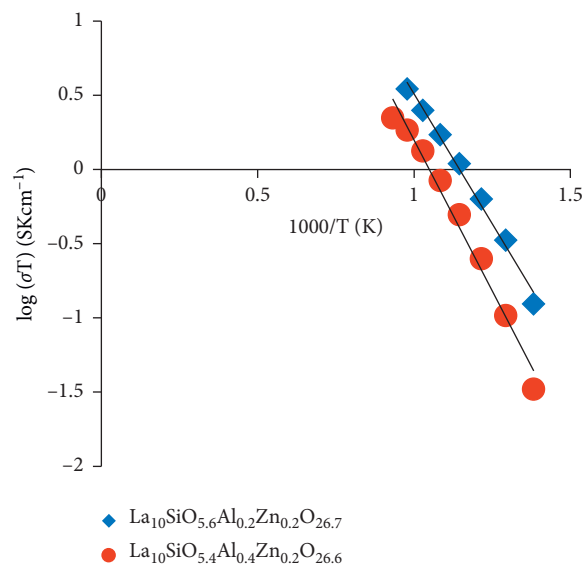


FIGURE 6: Arrhenius plots of total oxide ion conductivity of $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x=0.2$ and 0.4).

TABLE 3: Comparison of activation energy E_a and preexponential factor k of $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x=0.2$ and 0.4) with literatures.

	$\text{La}_{10}\text{Si}_{5.4}\text{Al}_{0.4}\text{Zn}_{0.2}\text{O}_{26.6}$ (this work)	$\text{La}_{10}\text{Si}_{5.6}\text{Al}_{0.2}\text{Zn}_{0.2}\text{O}_{26.7}$ (this work)	$\text{La}_{9.6}\text{Si}_{5.7}\text{Mg}_{0.3}\text{O}_{26.1}$ [44]	$\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ [39]	$\text{La}_{10}\text{Si}_6\text{O}_{27}$ [70]	$\text{La}_{9.50}\text{Si}_6\text{O}_{26.25}$ [70]
Activation energy, E_a (eV)	0.35	0.30	0.43	0.65 ± 0.1	0.67	0.35
Preexponential factor, k (Skcm^{-1})	18281	10216	—	—	—	—

Arrhenius equation. The fitted lines indicate that the diffusion process of oxide ions is thermally activated [45].

The activation energy described by Arrhenius in 1889 is the minimum amount of energy required to conduct a chemical reaction [69], i.e., as less energy is used, the lower the cost. According to the Meyer–Neldel rule, activation energy is related to the preexponential factor, i.e., with the decrease in activation energy, the preexponential factor will increase and the ionic conductivity is affected by temperature significantly compared to the activation energy. From the slope and the intercept of the linear fit in the Arrhenius plots, the activation energy E_a and preexponential factor k of the materials can be obtained using equation (3). The values of activation energy E_a and preexponential factor k of $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x=0.2$ and 0.4) pellets are compared with another apatite structure in Table 3. $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x=0.2$ and 0.4) apatite materials resulted in a significant improvement on the total oxide ion conductivity at the operating temperature of 800°C . It is noteworthy in this work that we got a large value of preexponential factor which may be explicated a higher coordination number between lanthanum (La) and oxygen (O) [71]. Hence, $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x=0.2$ and 0.4) apatite materials maybe useful as electrolyte materials of SOFCs [65]. Recently, lanthanum silicate-based materials were used to measure power density at intermediate temperature [72, 73].

4. Conclusion

In summary, the apatite-type hexagonal $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x=0.2$ and 0.4) crystals were examined as promising electrolytes for SOFCs. Nonetheless, the operational challenges associated with its high sintering temperature. XRD patterns of the sintered $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ ($x=0.2$ and 0.4) materials revealed the apatite phase with $P6_3/m$ space group with a small amount of impurity. The milling process has reduced most of the large grains into microsize grains closely related to each other, which aids in the formation of the hexagonal apatite structure. $\text{La}_{10}\text{Si}_{5.6}\text{Al}_{0.2}\text{Zn}_{0.2}\text{O}_{26.7}$ gives the highest total oxide ion conductivity of $3.24 \times 10^{-3} \text{Scm}^{-1}$ at the intermediate operating temperature of 800°C . The activation energy was decreasing with increasing the preexponential factor and the lowest activation energy was 0.30eV for $\text{La}_{10}\text{Si}_{5.6}\text{Al}_{0.2}\text{Zn}_{0.2}\text{O}_{26.7}$ which was one of the lowest activation energies among the lanthanum silicate-ion conductors. Thus, the apatite-type $\text{La}_{10}\text{Si}_{6-x-0.2}\text{Al}_x\text{Zn}_{0.2}\text{O}_{27-\delta}$ can be used in SC-SOFCs due to its porous microstructure.

Data Availability

The data used in this study are available on request.

Conflicts of Interest

The authors declare that there are no financial or personal conflicts of interest for this publication.

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