Synthesis and conductivities of the Ti-doped apatite-type phases $\text{La}_{9.33}\text{Si}_{6-x}\text{Ti}_x\text{O}_{26}$

A R Noviyanti$^\text{a}$, D R Eddy$^\text{b}$, F Lastiyanti$^\text{c}$, I Rahayu$^\text{c}$, D G Syarif$^\text{d}$, T Saragi$^\text{d}$ and Risdana$^\text{d}$

$^\text{a}$Department of Chemistry, Faculty of Mathematic and Natural Sciences, Padjadjaran University, Jl. Raya Bandung Sumedang km 21 Jatinangor, West Java, Indonesia 45363
$^\text{b}$PTNBR – BATAN, Jl. Taman Sari 71 Bandung 40132 Indonesia
$^\text{c}$Department of Physics, Faculty of Mathematics and Natural Sciences, Padjadjaran University, Jl. Raya Bandung Sumedang km 21 Jatinangor, West Java, Indonesia 45363

*atiek.noviyanti@unpad.ac.id

Abstract. Solid oxide fuel cell is one of the alternative energy sources with high efficiency and low emissions. Solid oxide electrolyte is an important component of this fuel cell. A new electrolyte that suitable at medium temperature is needed to be developed. Apatite type lanthanum silicate is one of the electrolytes, which can operate at medium temperature. Increasing performance of apatite lanthanum silicate such as ionic conductivity can be achieved by doping. The purpose of the present study was to synthesize the electrolyte of Lanthanum silicates oxide with hydrothermal method and to investigate the effect of Ti$^{4+}$ dopant on apatite electrolyte characteristics such as crystal lattice parameter and conductivity. The results showed that samples of $\text{La}_{9.33}\text{Si}_{6-x}\text{Ti}_x\text{O}_{26}$ with $x = 0.1, 0.2, 0.3$ were successfully synthesized. The value of $c$ on the crystal lattice parameter increases with increasing the doping content of Ti$^{4+}$. Increasing $c$ value on the crystal lattice parameter is directly proportional to the conductivity. Apatite $\text{La}_{9.33}\text{Si}_{5.7}\text{Ti}_{0.3}\text{O}_{26}$ showed the highest conductivity of $2.4 \times 10^{-4}$ S/cm at 700°C.

1. Introduction

Solid oxide fuel cell is one of the alternative energy sources with high efficiency and low emissions. Solid oxide electrolyte is an important component of this fuel cell. Yttria stabilized zirconia is commonly used electrolyte material in solid oxide fuel cells. Unfortunately, operational temperatures of this material were in high temperatures in between 800°C and 1000°C. In order to overcome this problem, new electrolytes that suitable at medium temperature has been developed. Apatite type of lanthanum silicate is one of the electrolytes, which can operate at medium temperature in between 500°C and 700°C.

Lanthanum silicates apatite oxide structure is based on isolated silicate tetrahedral ($\text{SiO}_4$) that share oxygen with La polyhedral to form rigid network. The La cations have two kinds of sites. First site is located at seven-coordinated sites named $6h$ and the second site is located at nine-coordinated sites named $4f$. In these compounds, oxide ions, occupying the centre of one dimensional channels running
along the c-axis, are responsible for ionic conduction [1]. The open structure of oxyapatite suggests that this material should be appropriate for the electrolyte applications for intermediate temperature SOFC (solid oxide fuel cell) [2].

Structure of apatite makes it possible to doped various dopants in both La [3] and Si positions [4]. Structures with stoichiometric compositions for example, La₉Sr₂Si₆O₂₆ have lower conductivity and higher activation energies than cation vacancy structures (La₀.₃₃Si₀.₂₆O₂₆) or excess oxygen (La₀.₃₃₂Si₀.₆₆₋₀.₃O₂₆.₅). The highest conductivity found in excess oxygen-containing samples indicates that the oxygen ions are the result of conduction through an oxygen ion interstitial mechanism [5].

The doping of the lanthanum silicate apatite is well known increasing its conductivity [6-10]. Doping of cations with a relatively low valence for Si site is effective to increase the conductivity of lanthanum silicates apatite when compared to doping for La position [11, 12]. Kendrick et al. [13] reported that a significant number of oxide ions displaced into interstitial positions and significant local structural changes are the reason why the conductivity is increased by doping with Zn²⁺. In addition, doping of trivalent cations such as Al³⁺ and Ga³⁺ for the Si²⁺ site has also a beneficial effect on conductivity [14].

Tolchard et al. [15] reported that calculation of atomic simulations indicates that the doping of M⁴⁺ at the La position is strongly not suitable. That is, Titanium, one of the dopants at the Si position is more suitable because of isovalent M⁴⁺ [16]. In addition, the titanium ionic radius (0.42 Å) is in the range of dopant ionic radii (0.01-0.60 Å) proven for doping the apatite of lanthanum silicate apatite at Si position [17, 18].

Doping of titanium to lanthanum silicate apatites for series of La₀.xSi₀.₆₆Ti₀.₂₆ decrease its conductivity significantly when the dopant content of x > 1 [19, 20]. This is due to the trapped oxygen ions with the higher dopant content. We attempted to prepare Titanium (Ti) doping in lower concentration. Conductivity properties of La₀.₃₃Si₀.₈₆Ti₀.₂₆ with dopant content x = 0.1; 0.2; 0.3 have not been reported in the previous study yet. Here, we reported the effect of Ti⁺⁺ dopant on apatite electrolyte characteristics, namely, crystal structure and conductivity, in lanthanum silicate apatite with dopant content of x = 0.1; 0.2; 0.3.

2. Experiment

High-purity La₂O₃ (Aldrich, 99.999%), Na₂SiO₃ (Sigma, 97%), TiO₂ (Sigma Aldrich 99%) were used to prepare apatite-type phase La₀.xSi₀.xO₂₆ (standard), La₀.₃₃Si₀.₆₆Ti₀.₂₆, La₀.₃₃Si₀.₈₆Ti₀.₂₆ and La₀.₃₃Si₀.₇₆Ti₀.₀₂₆. Sample compositions were chosen to examine the effect of Ti content on the conductivity. A NaOH 3 M solution was used in the preparation of these apatites as mineralizer. The La₂O₃ was pre-calcined at 1100°C for 12 h in order to achieve decarbonation. In a typical experiment for preparing La₀.₃₃Si₀.₂₆, and La₀.₃₃Si₀.₆₆Ti₀.₂₆ (x = 0.1, 0.2, 0.3), The dried starting materials were ground in the appropriate ratios thoroughly mixed and added to the NaOH solution, after which the mixtures were transferred into a stainless-steel autoclave (CIT-HTC230-V100 Co1-Int 125 mL) until 60 % volume of the autoclave was occupied. After heated at 240°C for 3 days, the precipitate was collected by filtration and washed with demineralized water. The resulting powder was dried at 120°C. Phase purity was then examined using powder X-ray diffraction using Cu-Kα radiation. Composition of apatite was measure by using EDAX spectrometer, ionic conductivity was measured using an LCR (GW Instek 61056) at 600°C–700°C and a frequency range of 20 Hz – 5 MHz on the pellet sample that was obtained by applying 6.000 kg cm⁻² pressure, followed by sintering at 1500°C for 3 hours. The value of resistivity (ρ) was calculated by equation (1).

\[ \rho = \frac{R}{A} \]  

where R is the total resistance, A is surface area and l is thickness, respectively. After the value of ρ obtained, the value of conductivity (σ) was calculated by equation (2).

\[ \sigma = \frac{1}{\rho} \]
The activation energy ($E_a$) was calculated by equation (3).

$$k = Ae^{-\frac{E_a}{RT}} \tag{3}$$

where $k$ is the rate constant, $T$ is absolute temperature (in Kelvin), $A$ is the pre-exponential factor, and $R$ is the universal gas constant.

3. Result and Discussion

Figure 1 shows the X-ray diffraction patterns of $La_{9.33}Si_{6-x}Ti_xO_{26}$ with $x = 0.1, 0.2, 0.3$ specimens. All specimens were almost the same as listed in powder diffraction file (JCPDS No. 010760340) reported by Nakayama and Sakamoto [21]. In addition, there are small diffraction peak at $2\theta \sim 15^\circ$ and $44^\circ$ that could be assigned to a secondary phase, these peaks were observed in all the Ti-doped specimens with different intensities.

![Figure 1. X-Ray diffraction patterns of (a) $La_{9.33}Si_6O_{26}$ (JCPDS No 010760340), (b) $La_{9.33}Si_6O_{26}$, (c) $La_{9.33}Si_{5.5}Ti_{0.5}O_{26}$, (d) $La_{9.33}Si_{5.8}Ti_{0.2}O_{26}$ and (e) $La_{9.33}Si_{5.7}Ti_{0.3}O_{26}$.](image)

Table 1 shows lattice parameters for $La_{9.33}Si_{6-x}Ti_xO_{26}$ with $x = 0.1, 0.2, 0.3$. The $c$ parameter increases with increasing Ti content as expected from cation size effects. The largest $c$ parameter was found in the sample of $La_{9.33}Si_{5.7}Ti_{0.3}O_{26}$.

### Table 1. Lattice parameters (hexagonal phase) for Ti doped $La_{9.33}Si_{6-x}Ti_xO_{26}$ with $x = 0.1, 0.2, 0.3$.

| Specimens            | $a = b$ / Å | $c$ / Å | Cell volume / Å$^3$ |
|----------------------|-------------|---------|---------------------|
| $La_{9.33}Si_6O_{26}$| 9.7231(1)   | 7.1899(1)| 588.6563(1)        |
| $La_{9.33}Si_{5.9}Ti_{0.1}O_{26}$| 9.6294(1) | 7.1895(1) | 583.8781(1)        |
| $La_{9.33}Si_{5.8}Ti_{0.2}O_{26}$| 9.6928(1) | 7.1920(1) | 585.1637(1)        |
| $La_{9.33}Si_{5.7}Ti_{0.3}O_{26}$| 9.7140(1) | 7.2074(1) | 588.9865(1)        |

Slightly different from the literature [22-25], Ti substitution for Si shows the larger $c$ parameter for larger Ti content samples, but have smaller $a$ and $b$ parameter. This fact proves that the substituted Ti (0.42 Å) occurs at the Si (0.26 Å) position, which confirms that the substitute at Si position is very sensitive to change the $c$ parameter [19].
EDX analysis of composition ratio for $\text{La}_{9.33}\text{Si}_{6-x}\text{Ti}_x\text{O}_{26}$ with $x = 0.1, 0.2, 0.3$ using experimental and theoretical data was shown in table 2.

**Table 2.** EDX analysis for $\text{La}_{9.33}\text{Si}_{6-x}\text{Ti}_x\text{O}_{26}$ with $x = 0.1, 0.2, 0.3$.

| Specimens          | Experimental ratio of La:Si:Ti | Theoretical ratio of La:Si:Ti |
|--------------------|-------------------------------|------------------------------|
| $\text{La}_{9.33}\text{Si}_{5.9}\text{Ti}_{0.1}\text{O}_{26}$ | 9.7231(1)                      | 7.1899(1)                     |
| $\text{La}_{9.33}\text{Si}_{5.8}\text{Ti}_{0.2}\text{O}_{26}$ | 9.6294(1)                      | 7.1895(1)                     |
| $\text{La}_{9.33}\text{Si}_{5.7}\text{Ti}_{0.3}\text{O}_{26}$ | 9.6928(1)                      | 7.1920(1)                     |

Overall, the experimental ratio is lower than the theoretical one, which may result from the small unidentified impurities and homogeneity of specimens. These ratios are reasonable for lanthanide apatites. The presence of impurities is indicated as peak in the XRD pattern at 20 of 15° and 44°.

The Nyquist diagrams at 650°C exhibited single semicircle as shown in Figure 2. As they were difficult to accurately separate grain and grain boundary contributions on the Nyquist diagrams, the reported conductivities were total conductivities. Nyquist diagrams obtained were fitted using the Zview software [26].

**Figure 2.** Nyquist diagram of $\text{La}_{9.33}\text{Si}_{5.9}\text{Ti}_{0.1}\text{O}_{26}$ (red circle) and $\text{La}_{9.33}\text{Si}_{5.8}\text{Ti}_{0.2}\text{O}_{26}$ (black rectangular) specimens sintered at 1500°C.

The conductivity values of $\text{La}_{9.33}\text{Si}_{6-x}\text{Ti}_x\text{O}_{26}$ with $x = 0.1; 0.2; 0.3$ at 600°C, 650°C, and 700°C are presented in table 3. The conductivity increased with increasing of Ti content. Apatite phase of $\text{La}_{9.33}\text{Si}_{5.7}\text{Ti}_{0.3}\text{O}_{26}$ showed the highest conductivity of $2.4 \times 10^{-4}$ S/cm at 700°C.

**Table 3.** Conductivity of $\text{La}_{9.33}\text{Si}_{6-x}\text{Ti}_x\text{O}_{26}$ with $x = 0.1, 0.2, 0.3$ at variation operation temperature.

| Specimens          | Conductivity /(10^5 S/cm) |
|--------------------|--------------------------|
|                    | 600 °C | 650 °C | 700 °C |
| $\text{La}_{9.33}\text{Si}_{5.9}\text{Ti}_{0.1}\text{O}_{26}$ | 0.23     | 0.81   | 0.95   |
| $\text{La}_{9.33}\text{Si}_{5.8}\text{Ti}_{0.2}\text{O}_{26}$ | 0.60     | 1.48   | 2.57   |
| $\text{La}_{9.33}\text{Si}_{5.7}\text{Ti}_{0.3}\text{O}_{26}$ | 9.07     | 17.80  | 24.00  |
Conductivity is still lower than that of standard requirement for solid electrolyte of $10^{-3}$-10 S/cm [27, 28]. It is probably due to low sintering temperature of specimens, resulted lower densification of the oxyapatite [29, 30].

Generally, conductivity values of Ti doped apatite were higher than that of related phases without Ti doping. The order of conductivity value from small to high value is $\text{La}_{9.33}\text{Si}_{6-x}\text{Ti}_x\text{O}_{26}$, $\text{La}_{9.33}\text{Si}_{5.8}\text{Ti}_{0.2}\text{O}_{26}$, and $\text{La}_{9.33}\text{Si}_{5.7}\text{Ti}_{0.3}\text{O}_{26}$, respectively [16]. Effect of Ti content to $c$ parameter and conductivity is displayed in Figure 3.

![Figure 3](image)

**Figure 3.** Effect of Ti content to $c$ parameter and conductivity of $\text{La}_{9.33}\text{Si}_{6-x}\text{Ti}_x\text{O}_{26}$ with x=0.1, 0.2, 0.3.

An interesting feature was the fact that the highest conductivity was observed at higher Ti content and $c$ parameter. In previous studies, generally that the highest conductivities of apatite systems observed at lower Ti [31]. This phenomenon can be probably explained by the fact that the expansion of lattice size is effective increasing the mobility of the oxide ion. The magnitude of the $c$ parameter in the crystal lattice is suspected to extend the oxygen ion channel, and affected the oxygen ion motion that increasing the conductivity.

Figure 4 shows the total conductivity of $\text{La}_{9.33}\text{Si}_{6-x}\text{Ti}_x\text{O}_{26}$ with x = 0.1, 0.2, 0.3 specimen with different Ti contents. Diffusion process of oxide-ions is thermally activated, which is well fitted to the Arrhenius equation.

![Figure 4](image)

**Figure 4.** Arrhenius plot of un-doped (a) $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$, (b) $\text{La}_{9.33}\text{Si}_{5.7}\text{Ti}_{0.3}\text{O}_{26}$, (c) $\text{La}_{9.33}\text{Si}_{5.8}\text{Ti}_{0.2}\text{O}_{26}$ and (d) $\text{La}_{9.33}\text{Si}_{5.7}\text{Ti}_{0.3}\text{O}_{26}$.
The activation energy \((E_a)\) was calculated from the slope and the intercept of the linear fits in the logarithmic form of the Arrhenius equation for all specimens. The value of \(E_a\), for \(\text{La}_{9.33}\text{Si}_{6-x}\text{Ti}_x\text{O}_{26}\) with \(x = 0.1, 0.2, 0.3\) are shown in table 4.

**Table 4.** The activation energy \((E_a)\) of \(\text{La}_{9.33}\text{Si}_{6-x}\text{Ti}_x\text{O}_{26}\) with \(x = 0.1, 0.2, 0.3\).

| Specimens               | Activation Energy /eV |
|-------------------------|-----------------------|
| \(\text{La}_{9.33}\text{Si}_{5.9}\text{Ti}_{0.1}\text{O}_{26}\) | 1.062                 |
| \(\text{La}_{9.33}\text{Si}_{5.8}\text{Ti}_{0.2}\text{O}_{26}\) | 1.061                 |
| \(\text{La}_{9.33}\text{Si}_{5.7}\text{Ti}_{0.3}\text{O}_{26}\) | 0.716                 |
| \(\text{La}_{9.33}\text{Si}_6\text{O}_{26}\)                  | 0.734                 |

Activation energy related to the ion migration mechanism in apatite structure. It was found that the value of activation energy for all specimens was smaller than 1.1 eV indicating the conduction via interstitial mechanism [13, 32].

4. Conclusions

The apatite-type oxide ion conductors of \(\text{La}_{9.33}\text{Si}_{6-x}\text{Ti}_x\text{O}_{26}\) with \(x = 0.1, 0.2, 0.3\) have been successfully synthesized in order to prepared new electrolytes that suitable at medium temperature. It was found that the conductivities of the Ti doped specimens are generally higher than that of undoped samples. From the crystal structure, it was found that the value of \(c\) parameter increased with increasing of Ti content and conductivity. Apatite \(\text{La}_{9.33}\text{Si}_{5.7}\text{Ti}_{0.3}\text{O}_{26}\) showed the highest conductivity of \(2.4 \times 10^{-4}\) S/cm at 700°C. From activation energy, it was found that the value of \(E_a\) was smaller than 1.1 eV indicating the conduction ion via interstitial mechanism.

Acknowledgement

Authors are grateful to Directorate General for Higher Education, Ministry of Ristek Dikti through PUPT no 718/UN6.3.1/PL/2017, Universitas Padjadjaran for research Grant of Academic Leader Grant No.872/UN6.3.1/PL/2017 as a financial support. A part of this research also supported by PKM No. 547/UN6.1.1/KM/2017.

References

[1] Gasparyan H, Neophytides S, Niakolas D and Stathopoulos. V 2011 *Solid State Ionics* **192** 158
[2] Cao X G and Jiang S P 2014 *J Materi Chem A* **2** 20739
[3] Ma Y, Fenineche N, Elkedim O, Moliere M, Liao H, and Briois P 2016 *Int J Hydrogen Energy* **41** 9993
[4] Ding X, Hua G, Ding D, Zhu W and Wang H 2016 *J Power Sources* **306** 630
[5] Kioupis D and Kakali G 2015 *J Ceram Int.* **42** 9333
[6] Najib A and Sansom J E H 2004 *Dalton T* **3106** 3106
[7] Vincent A, Savignat S B and Gervais F 2007 *J Eur Ceram Soc* **27** 1187
[8] Kharlamova T, Pavlova S, Sadykov a V, Lapina O and Khabibulin D 2008 *Solid State Ionics* **179** 1018
[9] Xiang J, Jia-Hu O, and Zhan-Guo G 2015 *J Power Sources* **284** 49
[10] Noviyanti A R, Ismunandar, Prijamboedi B and Marsih I N 2012 *ITB J Sci* **44** 193
[11] Qingle S and Hua Z 2012 J Rare Earths **30**
[12] Marrero-López D, Martín-Sedeno M C, Pena-Martínez J, Ruiz-Morales J C and Núñez P 2010 *J Power Sources* **195**
[13] Kendrick E, Islam M S and Slater P R 2007 *J Mater Chem* **17** 3104
[14] Kendrick E, Islam M S and Slater P R 2007 *Solid State Ionics* **177** 3411
[15] Tolchard J R 2007 *Adv FuncMater* **17** 2564
[16] Sansom J E H, Sermon P A and Slater P R 2005 *Solid State Ionics* **176** 1765
[17] Kendrick E, Sansom J E H, Tolchard J R, Islam M S and Slater P R 2007 Faraday Discuss 134 181
[18] Shannon R D 1976 Acta Cryst A 32
[19] Al-Yasari A, Jones A, Orera A, Apperley D C and Driscoll D 2009 J Mater Chem. 19 5003
[20] Sansom J E H, Sermon P A and Slater P R 2005 Solid State Ionics 176 1765
[21] Nakayama S, Aono H and Sadaoka Y 1995 Chem. Lett. 24 431
[22] Tolchard J, Sansom J, Islam M and Slater P 2004 Ionics 10 353
[23] Sansom J E H, Rudge-Pickard H A, Smith G, Slater P R and Islam M S 2004 Solid State Ionics 175 99
[24] Sansom J E H, Najib A and Slater P R 2004 Solid State Ionics 175 353
[25] Noviyanti A R, Ismunandar, Prijamboedi B, Marsih I N and Mukti R R 2011 (ICICI-BME Bandung Indonesia)
[26] Bonhomme C, Beaudet-Savignat S, Chartier T, Maître A, Sauvet A L and Soulestin B 2009 Solid State Ionics 180 1593
[27] Goodenough J B 2003 Annl Rev Mater 33 91
[28] Noviyanti A R, Hastiawan I, Irwansyah F S, Hidayat S, Hardian A, Syarif D G and Yuliyati Y B 2016 AIP Conf Proceedings Bandung Indonesia, 050002-1--6.
[29] Xiang J, Liu Z G, Ouyang J H and Yan F Y 2014 Jornal of Power Sources 251 305-10
[30] Rahayu I, Hidayat S, Noviyanti A R, Rakhmawaty D and Ernawati E 2017 IOP Conf Series: J Phys: Conf. Series 812 1
[31] León-Reina L, Porras-Vázquez J M, Losilla E R and Aranda M A G 2006 Solid State Ionics 177 1307
[32] Noviyanti A R, Hastiawan I, Yuliyati Y B, Rahayu I, Rosyani D and Gustaman S D 2017 AIP Conf. Proceedings 0400011