

Li Ion Conduction Studies in Zr Doped Titanate Perovskite Oxides

Saiqua Siddiqui, Priyanka Singh and Brajendra Singh

Materials Chemistry Lab

Centre of Material Sciences, University of Allahabad Prayagraj, India

Email : brajendr@gmail.com, saiqua.siddiqui786@gmail.com, priyankauoa@gmail.com

(Received December 10, 2020)

Abstract: In this study, we report the synthesis and ionic conductivity properties of $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_{3-\delta}$ and $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_{3-\delta}$ Zr doped Lithium Lanthanum Titanates. These samples were made using solid state reaction method. Powder X ray diffraction [$\text{CuK}_{\alpha 1}$ radiation ($\lambda=1.5405\text{\AA}$)] patterns of these materials were recorded to check the phase and inspect the crystal structure of $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_{3-\delta}$ and $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_{3-\delta}$. Conductivity data show the hopping of Li ions at room temperature as well as at higher temperature with higher frequencies. $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_{3-\delta}$ shows 9.72×10^{-4} S/cm conductivity at room temperature (25°C) which increases upto maximum of 1.25×10^{-3} S/cm conductivity at 400°C. $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_{3-\delta}$ shows maximum conductivity 3.71×10^{-4} S/cm at room temperature which further increases to 5.67×10^{-4} S/cm on increasing the temperature upto 400°C. The reported data of Zr doped titanate perovskite oxide shows high ionic conductivity which increases from room temperature to 400°C temperature.

Keywords: Conductivity, High temperature, Impedance, cole cole plot

1. Introduction

Solid state ionic conductors have played an influential aspect in the field of research due to its wide and ongoing developments in rechargeable batteries, solid oxide fuel cells (SOFCs), chemical sensors, photogalvanic solar cells etc¹. Single crystalline, amorphous, composites, polycrystalline and polymers are some of the different kinds of materials that show conduction properties. However, one of the efficient method for attaining suitable conductivity is doping of different elements into the lattice

framework of existent valance ion conductors. Among numerous ions, lithium ions have attracted much attention towards future technologies due to their chemical stability at different temperatures, therefore, solid state lithium ion batteries are of great importance²⁻⁷. However, there are some solid electrolytes that do not have the property of stability due to some reasons. $\text{Li}_{1.3}\text{Al}_{0.3}(\text{PO}_4)_3$ shows high ionic conductivity 3×10^{-4} S/cm, but when it comes in contact with Li metal it becomes unstable due to Ti^{4+} reduction. $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ is unstable in bulk form but shows ionic conductivity of 2.2×10^{-3} S/cm⁸. Different types of Li ion conductors that show different conductivity are NAtrium super ionic conductor (NASICON) $\{10^{-3}\text{S/cm}\}$, garnet type conductor $\{10^{-4}\text{S/cm}\}$, perovskite type conductor $\{10^{-3}\text{S/cm}\}$ and Lithium super ionic conductor (LISICON) $\{10^{-6}\text{S/cm}\}$. Perovskite type structure has gained much advantage due to its vast applications in catalysis, electrochemical sensing etc⁹.

A perovskite is a type of mineral that has same crystal structure as calcium titanium oxide (CaTiO_3). The general formula for perovskite compounds is ABX_3 , where A and B are the cations of different sizes, and X is an anion that binds to both. The idealized form is a cubic structure (Pm3m) which is rarely examined. The orthorhombic (Amm2) and tetragonal (P4mm) phases are the most common non cubic variants¹⁰⁻¹².

Lithium Lanthanum Titanates, $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ are set of those perovskite materials which can be referred as A site deficient perovskites. $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ crystallizes in orthorhombic structure and possess space group Cmmm. Belous et al was the first to report the electrical behaviour and stability of LLTO¹³⁻¹⁶. According to Inaguma et al, LLTO shows a high Li ion conductivity of 10^{-3}S/cm ¹⁷. The high ionic conductivity of LLTO is mainly governed by its bottleneck size and site percolation i.e its high conductivity is due to size of La^+ ion (alkali or alkaline earth), vacancy sites, motion of lithium and behaviour of Ti-O bond. However, the authentic mechanism behind Li ion conductivity is not yet acknowledged¹⁸⁻

²⁰.

This study shows the hopping of ions at room temperature as well as at higher temperature with higher frequencies. Powder X ray diffraction was done to examine the crystal structure with $\text{CuK}\alpha_1$ radiation ($\lambda=1.5405\text{\AA}$) and impedance measurement were recorded using Novacontrol impedance Analyzer (Alpha-A high performance frequency analyzer) in frequency range from 1 Hz to 40 MHz.

2. Methodology

We have prepared Zr doped Titanate perovskite oxide $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_3$ and $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_3$ by solid state method of synthesis. After weighing in stoichiometric amount, precursors were mixed in an agate mortar and grinded for 45 minutes. Grinded powder was again reginded in 25 ml ethanol for 15 minutes for proper mixing. This grinded powder was calcined at 1200°C for 12 hours with heating and cooling rate 5° per minute. After calcination, powder was grounded and pressed to make 10 mm diameter pellet. This pellet was sintered at 1300°C for 12 h with keeping heating and cooling rate of 5° per minute. Powder X-ray diffraction method was used to examine the crystal structure with $\text{CuK}_{\alpha 1}$ radiation ($\lambda = 1.5405 \text{ \AA}$) at 40kV and 30 mA over 10 to 90 degree with data separation 0.02 degree. Conductivity and impedance measurements were recorded using Novacontrol make Impedance analyzer (Alpha-A high performance frequency analyzer) in the frequency range from 1Hz to 40 MHz in ambient atmosphere from room temperature 25°C to 450°C . Silver paste have been applied on both side of the sample to avoid fluctuations in the data.

3. Results and Discussion

In this literature, we have synthesized Zr doped Titanate perovskite $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_{3-\delta}$ and $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_{3-\delta}$ and efforts have been made to enhance the ionic conductivity, structure and composition of the prepared sample by method of doping. On doping Zr, the following changes are recorded .

- (i) Zr being transition metal have a larger ionic radius than La, when doped, escalates the lattice parameter and thus the migration of Li ion is promoted.
- (ii) The concentration of Li ion in $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_{3-\delta}$ and $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_{3-\delta}$ increases.
- (iii) High ionic conductivity is obtained with increasing temperature and conductivity data show hopping of Li ions.

The XRD pattern investigated the orthorhombic crystal structure of the polycrystalline samples $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_{3-\delta}$ and $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_{3-\delta}$.

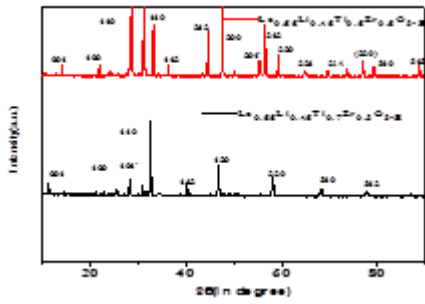


Figure 1. shows the X-ray diffraction pattern of the above reported samples.

XRD pattern of $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_{3-\delta}$ and $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_{3-\delta}$ shows new peak which originates nearly at 30° . The majority of peaks are at higher angles showing doublet. This kind of behaviour has been found in both the compositions. It also indicate the deficiency of oxygen in the lattice.

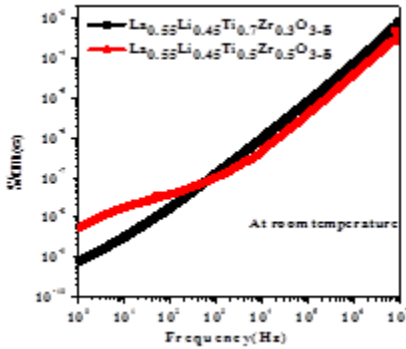


Figure 2. Conductivity plots of sintered pellets of $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_3$ and $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_3$ recorded at room temperature (25°C).

Maximum conductivity of 9.72×10^{-4} S/cm has been found at room temperature for $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_3$ at frequency of 10 MHz. The conductivity value for $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_3$ shows 3.71×10^{-4} S/cm at frequency of 7 MHz. The plotted conductivity represents the sum of the grain boundary and bulk conductivity.

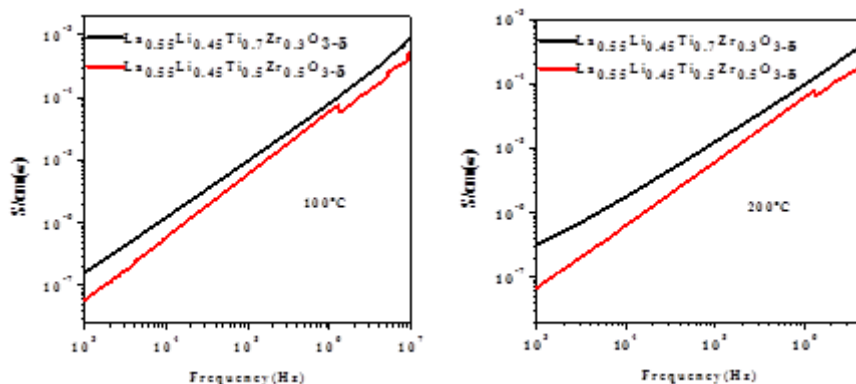


Figure 3. represent the conductivity plots of $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_3$ and $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_3$ at temperature 100°C, 200°C

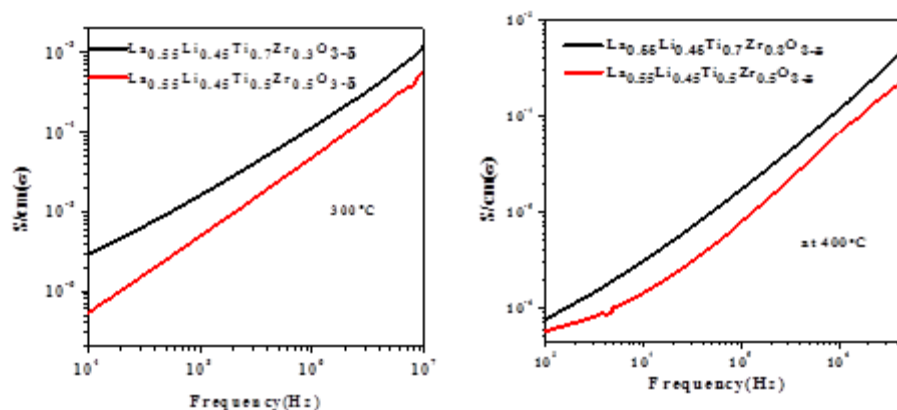


Figure 4. represents 300°C and 400°C in frequency range from 1KHz to 40MHz.

$\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_3$ and $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_3$ sample shows increase in conductivity with increase in temperature from 25 to 400°C. The conductivity recorded at 20MHz and 30MHz shows step increase in comparison to the conductivities recorded at 1MHz. $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_3$ shows increase in conductivity from 25°C to 400°C at frequencies 20MHz and 30MHz.

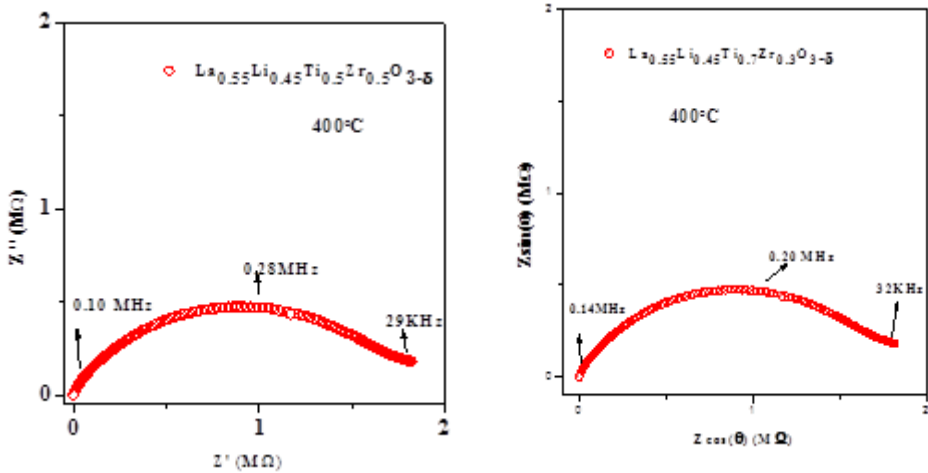


Figure 5. (a) and (b) shows A.c Impedance plots of $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_3$ and $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_3$ recorded at 400°C .

It has been found that conductivity is increasing with frequency upto 30MHz at 400°C . These conductivity properties shows that the samples are activated by thermal movements of molecules and ions bounce into unoccupied neighbouring sites. The cole-cole plot (a.c impedance plot) represents the presence of bulk resistances and absence of grain boundary resistances for the reported samples. These cole cole plots represent the ionic conduction mechanism properties in $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_3$ and $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_3$.

4. Conclusion

We have successfully reported the synthesis of Zr doped titanate perovskite $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_3$ and $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_3$ by method of solid state synthesis. XRD pattern indicate that the samples crystallizes into orthorhombic system. Conductivity value has been found to increase with increase in temperature for $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_3$ and $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_3$. sintered pellets of $\text{La}_{0.55}\text{Li}_{0.45}\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_3$ shows the conductivity value 9.72×10^{-4} S/cm conductivity at room temperature (25°C) which increases upto maximum of 1.25×10^{-3} S/cm as the temperature is increased to 400°C .

References

1. O. Bohnke, *Solid State Ion.*, **179** (2008), 9–15.
2. P. Knauth and H. L. Tuller, Solid-State Ionics: Roots, Status, and Future Prospects, *J. Am. Ceram. Soc.*, **85** (2002), 1654–1680.
3. Y. Inaguma and M. Nakashima, *J. Power Sources*, **228** (2013), 250–255.
4. A. Belous, E. Pashkova, O. Gavrilenko, O. V'yunov and L. Kovalenko, *J. Eur. Ceram. Soc.*, **24** (2004), 1301–1304.
5. K. Takada, *Acta Mater.*, **61** (2013), 759–770.
6. V. Thangadurai and W. Weppner, *J. Am. Ceram. Soc.*, **88** (2005), 411–418.
7. R. Murugan, V. Thangadurai and W. Weppner, *Angew. Chem. Int. Ed.*, **46** (2007), 7778–7781.
8. P. Knauth, *Solid State Ionics.*, **180** (2009), 911–916.
9. J. Fergus, *Solid State Ionics.*, **227** (2012), 102–112.
10. M. Yedukondalu, J. Anirudha, H. Chang and Ru-Shi Liu, *ACS Energy Lett.*, **2** (2017), 2734–2751.
11. J. Wolfenstine, H. Jo, Y. H. Cho, I. N. David, P. Askeland, E. D. Case, H. Kim, H. Choe and J. Sakamoto, *Mater. Lett.*, **96** (2013), 117–120.
12. B. Singh, S. Nishad and S. Siddiqui, *Orissa Journal of Physics*, **27** (2020), 15–26.
13. M. Itoh, Y. Inaguma, W. H. Jung, L. Chen and T. Nakamura, *Solid State Ion.*, **70–71** (1994), 203–207.
14. X. Gao, C. A. J. Fisher, T. Kimura, Y. H. Ikuhara, H. Moriwake, A. Kuwabara, H. Oki, T. Tojigamori, R. Huang and Y. Ikuhara, *Chem. Mater.*, **25** (2013), 1607–1614.
15. E. R. Losilla, M. A. Aranda, S. Bruque, J. Sanz, M. A. París, J. Campo and A. R. West, *Chem. Mater.*, **12** (2000), 2134–2142.
16. C. H. Chen and K. Amine, *Solid State Ion.*, **144** (2001), 51–57.
17. X. Gao, C. A. J. Fisher, T. Kimura, Y. H. Ikuhara, A. Kuwabara, H. Moriwake, H. Oki, T. Tojigamori, K. Kohama and Y. Ikuhara, *J. Mater. Chem.*, **A 2** (2014), 843–852.
18. H. Zhang, X. Liu, Y. Qi, V. Liu, *J. Alloy. Compd.*, **577** (2013), 57–63.
19. V. Thangadurai and W. Weppner, *Solid state Ionics.*, **12** (2006), 81–92.
20. A. Nadiri, G. Le Flem and C. Delmas, *J. Solid State Chem.*, **73** (1988), 338–347.