**Broadband impedance, dielectric and modulus study of Ti-doped LiSn2(PO4)3**

U. AHMADU**1**, B.A. MAHMOUD**1**, I.K. MOHAMMED**1**, S. IBRAHIM**1**

***1****Department of Physics, Federal University of Technology, P.M.B., 65, Minna, Nigeria*

*mohammedkandiibrahim@gmail.com;sharifat.ibr@futminna.edu.ng;mbamin129@gmail.com*

*Corresponding author: u.ahmadu@yahoo.com*

**Abstract**

LiSn2(PO4)3of composition LiSn1.85Ti0.15(PO4)3 with NASICON structure was prepared by solid-state synthesis. XRD results show the formation of stable phase material of rhombohedral structure with the c space group. Traces of SnO2 unreacted phase and minor impurities of SnP2O7 were detected. Impedance and dielectric study in the microwave range show conductivity enhancement in bulk and grain boundary. The room temperature ionic conductivity is 4.74x10-5 S/cm while the conductivity at 740 K is 2.37x10-3 S/cm. The highest value of dielectric constant obtained is 2000 while the lowest value is 500. Imaginary modulus plot vs temperature indicates the presence of temperature relaxation in the material. The activation energy was calculated from plot of relaxation frequency at different temperatures and found to be 0.23 eV.

***Keywords*: NASICON;Impedance; conductivity; dielectric permittivity; modulus; relaxation**

**1.0 INTRODUCTION**

The discovery of NASICON (Na-Super-Ionic Conductor) by Hong(1976) was a major breakthrough in the tailored making of fast ion conductors (Super-Ionic Conductors) with a covalent framework structure. Apart from their potentials as solid electrolytes they find applications in conversion systems, super capacitors (Sekido and Ninimoya, 1981; Pharm-Thi *et al*,1986) sensors, displays ,nuclear waste disposal, low expansion ceramics, thermal shock resistant materials and have promising catalytic properties (Yamamoto and Abe, 1998; Thangadurai *et al* (2006) studied analogues of NASICON widely used as Li ion conductors for rechargeable Lithium ion batteries for their high ionic conductivity, temperature stability, amongst others. Different systems with general formula LiM2(PO4)3 (M=Ti, Zr, Hf, Ge and Sn) have been reported(Ahmadu, 2014; Ahmadu *et al*, 2011). The Ti-based system is probably the most studied because the smaller tunnels formed with Ti4+ cations are a better fit for the lithium conductors. The Li ion conductivity of Li1+xTi2-x Alx (PO4)3 is up to 10-3 S/cm at room temperature. LiSn2 (PO4)3 was prepared via solid state reaction (Norhaniza *et al*, 2010; Cui *et al*, 2012) and the sintering temperature was reported to be very important. The compound is the least studied amongst members of the NASICON family (Martinez *et al*, 1995, Cui *et al*, 2012) with two crystallographic phases reported so far (Martinez *et al*, 1997). A high temperature rhombohedral symmetry phase with high ionic conductivity and a low temperature phase with triclinic *PI* symmetry or monoclinic *Cc* symmetry with lower conductivity. Stability of the compound has been an issue such that Lazarraga *et al* (2004) used teflon as binder to improve the stability against breakage (due to the structural transition from monoclinic to rhombohedral) in the pellets used for conductivity measurements. However, the value of the conductivity obtained was very low, 10-10 S/m at room temperature. Later, Norhaniza *et al* (2013) succeeded in obtaining stable pellets of LiSn2 (PO4)3 using mechano-chemical ball milling without binder and the ionic conductivity improved to 10-7 S/m at room temperature. Meanwhile, the sol-gel method has been used to overcome some of these problems as it has the advantage of lower sintering temperature, shorter reaction time, good homogeneity and high specific area of material (Adnan *et al*, 2014). Similarly, Norhaniza *et al* (2010) and Mustaffa and Mohammed (2015) synthesized LiSn2 (PO4)3 using low sintering temperature citric acid assisted sol-gel method resulting in minor phase of impurity compared to samples prepared by mechanical ball milling. X-ray diffraction study confirmed the formation of rhombohedral phase LiSn2(PO4)3, after sintering at 873 and 923 K for 48 h while conductivity attained at 873 K was 1.38 x 10-5 S/m at 773 K, which is higher (Mustaffa and Mohammed, 2015).

In the current work LiSn1.85Ti0.15(PO4)3 has been synthesized using solid state reaction based on a sintering regime that is expected to enhance stability and electrical conductivity in order to resolve some of the above problems. The result of TGA/DTA, X-ray diffraction, impedance spectroscopy, modulus and dielectric studies have been presented.

**2.0 MATERIALS AND METHODS**

LiSn0.85 Ti0.15 was prepared by solid state reaction using agate mortar and pestle using stoichiometric amount of analytical grade Li2CO3 (India > 99%), SnO2 (99.99%), TiO2 (BDH, 99.99%), Methanol CH3OH (BDH, 99.99%), and NH4H2 PO4 (BDH, 99.99%). Appropriate amount of the sample was properly mixed in agate mortar and pestle along with appropriate quantity of methanol to make a homogenous semisolid paste. The homogenous paste was initially calcined at 1173 K for 4 h in order to decompose NH4H2PO4 and initiate its reaction with the carbonate (Lazarraga *et al*, 2004) which results in the emission of carbondioxide, ammonia and water vapour. The mixture was reground to micron size and pressed into a pellet. The dimensions of the pellet was measured and inserted into a steel mould of 16.8 mm diameter by 12 mm thickness in a pelletizing machine. The powder was then pressed in a cold press for 5 min under a hydraulic pressure of 5 N/m2 with the formation of pellets of 16 mm diameter by 1.7 mm thickness. This was sintered at room temperature in alumina crucible at 1173, 1273 and 1373 K for 3 h, successively. 0.5g of sample specimen was used for thermal analysis using DTA/TGA on a TG-DTA machine (Perkin Elmer TGA 400). The data was taken from room temperature to 1113 K. XRD machine (D8 advance, Bruker AXS, 40 kV, 40 mA) with monochromatic Cu-Kα1 (λ = 1.54060Ǻ) was used to characterize the structure and phase composition in the 2Θ range 12 to 40o and step size 0.034o and counts were accumulated for 96 s for each step. Bragg’s law (nλ = 2d sin Θ) was used to calculate the peak positions for diffraction experimentally, where n is an integer, λ is the wavelength of the incident X-rays, d is the inter planer spacing and Θ is the diffraction angle.

Microstructure of surface of sample was determined by SEM (HRSEM, Zeiss) operated at 20 kV and image captured at 5 kV. The ceramic was positioned on an aluminium stage with the aid of carbon adhesive tape and coated with AuPd (Gold-Palladium) using a sputter coater. Impedance measurements were carried out by measurement of complex impedance and complex electric conductivity of the samples using coaxial impedance spectrometer (Kežionis *et al.,* 2011) set-up in the frequency range 300 kHz to 3 GHz. Measurements were taken every 10 K on heating the sample at 1 K per min using a fixed voltage of 200 mV in air atmosphere. The samples were covered with platinum electrode paste and heated to 1073 K. The control and acquisition of data were carried out using Origin graphing software. Temperature range of 300 to 740 K was used for all measurements

**3.0 RESULTS AND DISCUSSION**

Table 1 shows the variation of density with sintering temperature for LiSn1.85Ti0.15(PO4)3 measured using Archimedes’ principle. The unit cell volume of the sample was calculated and the lattice parameters, a *and* *c* were found to be8.6122 and 21.4400, respectively. The density of the sample is 3.5945 g/cm3 (that is more than 70 o/o of its theoretical value). Table 1.Calculated lattice parameters, unit cell volume and densities of LiSn1.85Ti0.15(PO4)3 compared with reference sample.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample | **a(Ao)** | **c(Ao)** | **V(Ao 3)** | **Experimental density(g/cm3)** | **Theoretical density(g/cm3** | **% difference** |
| LiSn1.85Ti0.15(PO4)3 | 8.5281 | 21.6492 | 1363.57 | 2.7568 | 3.5975 | 76.70 |
| LiSn2(PO4)3 | 8.4048 | 21.9621 | 1288.51 | 2.7027 | 3.5788 | 75.52 |

Table 1shows the lattice parameters where it can be easily seen that the cell volume, experimental and theoretical densities of the Ti-doped LiSn2(PO4)3 are in close agreement with those reported by Norhaniza *et al.(*2010) and those calculated from ICSD card no.202157. The average crystallite size of 9.32 is on the high side and is due to the high sintering temperature used.

**3.1 Complex impedance analysis**

 Electrode /ceramic/ electrode can be analysed generally by an equivalent circuit of two parallel resistance-capacitance (RC) element. The Nyquist plot (is a complex impedance plot) for the variation of real and imaginary part of impedance measured at different temperatures and is shown in Figure 1(a-d) for LiSn1.85Ti0.15(PO4)3. Characteristics of impedance spectroscopy, is always displayed by the appearance of the semicircular arcs, whose pattern of evolution changes with rise in temperature. The shape of these plots at 300 K is almost a straight line indicating the insulating behaviour of the sample. These slopes decrease with increasing temperature up to 400 and 600 K in which the curves bend toward the real axis. With further increase in temperature to 740 K the curves become almost semicircular, as shown in figure 4d and are indicative of an increase in the conductivity of the sample. According to Orliukas *et al*.(2006) and Sobiestianskas *et al*.(2000) it is difficult to determine the values of Rg and Rgb from the complex impedance plots due to the overlap semicircles. As an alternative, the value of b was determined by plotting imaginary part of conductivity versus real part of conductivity plots. The intercept of the dispersion curves with the -axis at high and middle frequencies give the values of b(bulk conductivity) and t (total conductivity), respectively. The gb(grain boundary conductivity) is obtained by Subtractingb from t.

Table 2. shows the comparison of conductivity values at different temperatures determined from impedance plots for the sample

|  |
| --- |
| Temp(K) Rb(Ω) Rgb(Ω) b(S/cm)gb(S/cm) t(S/cm) |

300 3.5x103 4.1x104 2.56x10-5 2.18x10-5 4.74x10-5

400 1.50x103 3.75x103 5.98x10-5 2.11x10-5 8.09x10-5

600 1.54x102 3.30x103 2.99x10-4 2.71x10-5 3.26x10-4

740 4.0x101 6.80x102 2.24x10-3 1.32x10-4 2.37x10-3



Figure 1.impedance plots of LiSn1.85Ti0.15(PO4)3 (300 to 740 K), (a) impedance plot of LiSn1.85Ti0.15(PO4)3 at temperatures 300 (b) 400 (c) 600 (d) 740 K, showing the extrapolations for grain and grain boundaries.

**3.2 Plot of real part of impedance vs frequency**

Figure 2 shows the change in real part of impedance () with frequency at different temperatures for Ti-doped LiSn2(PO4)3 compound. On increasing the temperature the value decreased indicating increase ac conductivity as shown in Figure 2. At higher frequencies the value merges for all the temperatures due to the presence of space charge polarization (Suchanicz *et al*., 1998). The higher impedance value at lower frequencies is due to space charge polarization.



Figure 2. variation of real part of impedance with frequency at different temperatures

**3.3 Plot of imaginary part of impedance vs frequency**

Figure 3 shows the loss spectrum at different temperatures. The loss spectrum () decreased with increase in frequency in all the temperature ranges. The peak shifts to higher frequencies with increasing temperature and signifies the presence of temperature dependent electrical relaxation phenomenon in the system. The asymmetric broadening of the peaks may be due to the presence of immobile electron at low temperature and defects/vacancies at higher temperature.



Figure 3. Imaginary part of impedance with frequency

**3.4 Complex electrical conductivity vs temperature**

Electrical conduction in dielectric material is a thermally activated process and is due to the ordered motion of weakly bound charged particles under the influence of an electric field. It depends on the nature of the charge carriers that dominate the conduction process such as electrons/holes or cations/anions and follow the Arrhenius law. The bulk conductivity (b) and grain boundary conductivity (gb) of the compound can be evaluated from the impedance data using the relation, σb = , where Rb is the bulk resistance, d the thickness and A the area of the electrode deposited on the sample. Rb is obtained from the value of the low frequency intercept of the semicircle on the real axis () on the complex impedance plot. The conductivity plots shown in figure 3 consist of a semicircle and two dispersion curves at low and high regions at the same time. The point of intersection of the dispersion curves with axis at high frequency gives the bulk conductivity value, b.



Figure 4. Complex conductivity plots of LiSn1.85Ti0.15(PO4)3 at different temperatures: (a) 300 (b) 400 (c) 600 and (d) 740 K showing extrapolations for real part of conductivity. The real part of conductivity increases with temperature.

**3.5 Ac conductivity vs temperature**

Frequency dependent conductivity is due to the relaxation of ionic atmosphere after the movement of the particle (Jonscher, 1977). The variation of ac conductivity as function of log of frequency at different temperatures is shown in figure 5. Jonscher explained ac conductivity using the following universal power law (Vijayakumar *et al.*, 2003):

 (ω)= (0) +Aωn. (1)

where (0) is the “dc” or frequency independent part related to dc conductivity and the second term is of constant phase element (CPE) type; n is a frequency exponent in the range of 0≤n≤1. the correlation exponent n can be determined from the slop of lnac versus ln f(Ahmadu *et al*., 2013, ).

The plot of σac vs log ω for Ti-doped LiSn2(PO4)3 is shown in figure 5. The plot consists of a spike in low-frequency region due to the electrode polarization effects which are related to blocking of ions between the electrodes and sample. An intermediate plateau frequency region is due to frequency independent conductivity corresponding to dc conductivity and dispersion in high frequency region (Mariappan and Govindara, 2005). The transition from the dc plateau to ac conductivity dispersion region shifts towards higher frequencies when temperature increases. At high frequencies the power law feature is observed (Adnan and Mohamed, 2012). According to Almond and *et al.* (1983), the ac conductivity data can also be used to estimate the ionic hopping rate, in a material to clarify the ionic conduction of the samples. Figure 5 shows the frequency dependent of ac conductivity from 300 to 740 K.

****

Figure 5. Variation of ac conductivity with frequency of LiSn1.85Ti0.15(PO4)3 at different temperatures.

**3.6 Dielectric vs temperature and frequency**

Figure 6a shows the plot of imaginary part of dielectric permittivity,versus real part of dielectric permittivity which increase with temperature. The value of the imaginary part of dielectric permittivity is very high (2000) while that of real part of dielectric constant is very low (340) due to the effect of space charge polarization and/or conducting ionic motion (Suchanicz *et al*., 1998).The asymmetric broadening of the peaks may be due to the presence of immobile electron at low temperature and defects/vacancies at high temperature (Schanicz *et* *al.,* 1998).

  

1. (b) (c)

Figure 6. (a) plot of dielectric constant () versus dielectric loss () of Ti-doped LiSn2(PO4) at different temperature (300 to 740 K) (b) plot of relative dielectric constant () of Ti-doped LiSn2(PO4)3 as a function of log f at different temperatures and (c) plot of dielectric constant () of Ti-doped LiSn2(PO4)3 as a function of log f at different temperatures

To acquired more information on the dynamic properties of the ion in the material, the frequency dependence of the dielectric constant and for the LiSn1.85Ti0.15(PO4)3 NASICON at different temperatures are depicted in figure 6(b, c). At low frequencies the high value of dielectric (the highest value of at 500) is due to the contribution of charge carrier accumulation at the interface of electrode and LiSn2(PO4)3 material. Also at high frequencies the dielectric constant and decrease to a constant value. Meanwhile, the values of dielectric loss is very high (the highest value of being 2000) at these frequencies because the electrical energy loss is high (some of their energy is lost to the lattice as heat) due to the ions motion (Mahato *et al*., 2011). At high frequencies the value of dielectric constant and dielectric loss is low and decreases to a constant value due to high periodic reversal of the field and to limitations of dielectric loss sources (ion vibration only), respectively (Hegab *et al*., 2007).The and increase with temperature indicating the bound charge carriers get sufficient excitation energy to be able to follow the charge in external field more easily. This in turn increases their contribution to polarization resulting in increase in and (El-Metwally *et al*., 2008; Mahato *et al*., 2011).

**3.7 Tan vs frequency plot at various temperatures.**

Figure 9 is the plot of frequency dependence of tan at different temperatures and indicates a peaking behaviour for some temperatures. As the temperature increases, the tan peaks are shifted towards higher frequencies. The peaks are expected when the hopping frequency of ions is approximately equal to the external applied electric field. In this, case=1, where is the relaxation time of the hopping process and is the angular frequency of the external field (=2).



Figure 9. The plot of frequency dependence of tan vs log w at different temperatures

The frequency dependence of at different temperature has been plotted (figure 10a) in other to determine the relaxation frequencies. The imaginary part of electric modulus is indicative of energy loss under electric field. As rises smoothly to a peak value, two of the peaks decrease at high frequency. The low frequency side of the peaks is an indication of long range motion in which the ions drift to a long distance and the position of the peaks may be attributed to transition from short range to long range mobility with decreasing frequency (that is hopping from one site to another neighbouring site).The shift in maxima indicates the presence of temperature relaxation process in the material. When the conductivity plots frequency are analysed, the shifts in frequency of the peaks correspond to conductivity relaxation phenomenon (Venkateswara *et al*., 2014). The real part of electric modulus () represent the ability of a material to store energy and increase with increase in temperature at low frequencies (figure 10b). The maxima of falls with increase in temperature in all the plots and tends to lower values, confirming that electrode effects make negligible contribution and may be ignored in the modulus at low frequencies and temperatures (Ahmadu *et al*., 2011). The frequency independent variation of at high frequencies may be attributed to absence of charge effects due to inhomogeneities in composition.



1. (b) (c)

Figure 10.(a) plot of frequency dependence on at different temperatures indicating the relaxation process(b) plot of real part of electric modulus () versus frequency at different temperatures (c) plot of the peaks of ln (fmax) vs 1000/T

The obtained values of peaks of (i.e., fmax) are plotted in figure 10c against 1000/T. Peaks are expected when the hopping frequency of the ions is approximately equal to the external applied electric field. In the case ωτ =1, where τ is the relaxation time of hopping process, ω the angular frequency of the external field (ω = 2ᴨfmax), τ = . The natural logarithm of the relaxation frequencies at different temperatures have been plotted against reciprocal temperature. It was fitted to the Arrhenius equation of the form 2ᴨfmax = foexp ( ), where fo is the pre-exponential factor, the activation energy for relaxation, k the Boltzmann constant and T is the absolute temperature. From slope the value of ~ 0.23eV.

**3.8 CONCLUSION**

Powdered LiSn1.85Ti0.15(PO4)3 has been prepared by conventional solid-state reaction. XRD patterns of calcined at 1173 K for 4 h and sintered at 1373 K for 3 h showed the formation of rhombohedral symmetry with space group *Rc* and SnO2 unreacted phase coexisting with triclinic SnP2O7. XRD analysis shows decrease in lattice parameter *c*, while *a*, the unit cell volume (V) and the densities for both experimental and theoretical, increased compared with reference (pristine). The experimental density is ~3.6 g/cm3, amounting to ~77o/o of theoretical density. The crystallite size and the particle size of the sample decreased comparatively. Electrical conductivity studies show conductivity of order of 4.74x10-5 S/cm at room temperature, which is two orders of magnitude higher than that reported by other workers. The highest conductivity achieved was 2.37x10-3 S/cm at 740 K and is two orders of magnitude higher than that reported by other workers. These results are an indication that the sintering temperature was instrumental in the structural stability of the pellets and enhancement in electrical conductivity. This shows that the sample may be applied as solid electrolyte at high temperatures.

**Acknowledgements**

This work was supported by the Tertiary Education Trustfund (Tetfund) under project no: TETFUND/ FUTMINNA/2014/04. One of the authors, U. Ahmadu is grateful to Professor Tomas alkus, Vilnius University, Lithuania for help with Broadband impedance and dielectric spectroscopy characterisation.

**References**

Ahmadu, U.(2014). NASICON: Synthesis, Structure and Electrical Characterisation, in *Advanced*

 *Sensor and Detection Materials.* eds., A. Tiwari and Mustafa M. Demir, WILEY-Scrivener

 publishing, U.S.A.pp.265-300.

Ahmadu, U., Tomas, S., Jonah, S. A., Musa, A. O., & Rabiu, N. (2013). Equivalent circuit models and analysis of impedance spectra of solid electrolyte Na0.25Li0.75Zr2(PO4)3, *Advanced Materials Letters,* 4(3), 185-195. doi:10.5185/amlett.2012.7396.

Ahmadu, U., Salkus, T., Abubakar, O. M. and Kasim, U.I.(2011). Electrical and dielectric characterization of Na0.5Li0.5Zr2(PO4)3. *Open journal of physical chemistry*, 1, 94-103.

Adnan, S.B.R, & Mohamed, N.S., (2012) Conductivity and dielectric studies of Li2ZnSiO4 ceramic electrolyte synthesized via citrate sol-gel method. *International Journal of Electrochemical Science* 7, 9844

 Adnan, S. B. R., & Mohamed, N. S. (2014). Properties of novel Li4−3xCrxSiO4 ceramic electrolyte. *Ceramic International,* 40, 5033.

Almond, D. P,, Duncan, G. K., & West, A. R,(1983). Anomalous prefators in fast ion conductors – Nature. *Solid State Ionics,* 8, 159-164.

Catti, M., Stramare, S., Ibberson, R. (1999). [Lithium location in NASICON-type Li+conductors by neutron diffraction. Triclinic alpha LiZr2(PO4)3,](http://serials.unibo.it/cgi-ser/start/en/spogli/df-s.tcl?prog_art=6384617&language=ENGLISH&view=articoli) *Solid State Ionics,* 123, 173–180.

Cui, W. J., Yi, J., Chen, L, Wang, C. X., & Xia,Y. Y. (2012). Synthesis and electrochemical characteristics of NASICON structured LiSn2(PO4)3 anode material for lithium-ion batteries. *Journal of Power Sources* 217,77. doi:10.1016/j.jpowsour.2012.05.117

El-Metwally, E. G., Fadel, M., Shakra, A.M. &.Afifi, J. (2008) Optoelectronics and Advanced Materials, 10, 1320.

Hegab, N. A., Bekheet, A. E, Afifi, M. A., Wahaba L. A., & Shehata, .H. A.(2007). Effect of Cd addition on the AC conductivity and dielectric properties of Ge 70 Te films *Journal of electronic Resources*, 30, 3- 71.

Hong, H. Y. P. (1976). Crystal structures and crystal chemical in the system Na1+xZr2SixP3-xO12. *Material Research Bulletin,* 11, 173–182. doi:10.1016/0025-5408 (76) 90073-8.

Jimenez, R.., Martin, P. D., Ibanez, J., & Rojo, J. M. (1997). Spectrochim Acta Part A. *Journal of Physical Condense Matter*, 54, 1869–1878

Jonscher, A. K. (1977). The Universal dielectric response. *Nature,* 276, 673–679

[Kezionis A](https://www.cheric.org/research/tech/periodicals/searchresult.php?articlesearch=Kezionis%20A&searchtype=author), [Kazakevicius E](https://www.cheric.org/research/tech/periodicals/searchresult.php?articlesearch=Kazakevicius%20E&searchtype=author" \o "저자 Kazakevicius E 검색), [Salkus T](https://www.cheric.org/research/tech/periodicals/searchresult.php?articlesearch=Salkus%20T&searchtype=author" \o "저자 Salkus T 검색), [Orliukas A](https://www.cheric.org/research/tech/periodicals/searchresult.php?articlesearch=Orliukas%20A&searchtype=author" \o "저자 Orliukas A 검색).(2011). Broadband high frequency impedance

 spectrometer with working temperatures up to 1200 K. Solid State Ionics, 188, 10-113

Lazarraga, M.G., Iban˜ez, J., Tabellout, M., & Rojo, J. M. (2004). On the aggregation process of ceramic LiSn2P3O12 particles embedded in Teflon matrix . *Compose Science Technology,* 64 (5), 759.

MahatoDev, K., Dutta ,A. l., Sinha T. P. (2011). Physics B, 406- 2703

Martinez-juarez, A., Rojo, J. M, Iglesias, J. E., & Sanz, J. (1995). Reversible monoclinic-rhombohedral transformation in LiSn2(PO4)3 with NASICON-type structure. *Chemical Matter,* 7, 1857.

Martinez, J. A., Amarilla, J. M., Iglesias, J. E., & Rojo, J. M. (1997). Ionic conductivity

of LiHf 2(PO4)3 NASICON type structure and its Possible Application as Electrolyte in Lithium Batteries. *Journal of Chemical Society*, 8(3), 261-264.

Mariappan, C., & Govindaraj, G. (2005). Conductivity and ion dynamic studies in the

 Na4+7xTi1-3x(PO4)3.3-x (0≤≤0.6) NASICON material. *Solid State Ionics,* 176, 1311

Mustaffa, N. A., & Mohamed, N. S. (2015). Properties of Stannum-Based Li NASICON-Structured Solid Electrolytes for Potential Application in Electrochemical Devices. *International Journal of. Electrochemical Science,.*10, 5382 – 5394

Norhaniza, R.,Subban, R.H.Y., & Mohamed, N. S. (2010) Advanced Material Resourses129–131:338 and icdc.

Norhaniza, R., Subban, R. H. Y., & Mohamed, N. S. (2013). Cr and V substituted

 LiSn2P3O12. *Journal of power sources,* 244, 300-305.

Orliukas, A. F,,Dindune, A, Kanepe,. Z, Ronis, J., Bagdonas., B., & Kezionis, A. (2006).*Electrochemical Acta*, 51, 6194.

Pham-Thi, M., Velasco, G. & Colomban, P. H.,(1986). *Journal of Material Science.* *Letter,* 5,415

Sekido, S. & Ninimoya, Y.(1981). Fast Ionic Conductors and Their Theoretical

models. *Solid State Ionics*, 34, 15315

Sobiestianskas, R., Dindune, A., Kanepe, Z., Ronis, J., Kezionis, A.,Kazakev, E., & Orliukas, A. (2000). *Material Science Engineering B*, 76, 184-533

Suchanicz, J. (1998). Material Science Engineering B, 55, 114.

Thangadurai, V., & Weppner, W. **(**2002) Solid state lithium ion conductors, Design considerations by thermodynamic approach. *Solid State Ionics*, 8, 281–292.

Venkateswara Rao, A., Veeraiah, A., Prasada Rao, V., Kishore Babu, B., &

 Brahmayya, M. (2014). Spectroscopic characterization and conductivity of Sn-substituted LiTi2(PO4)3. *Resources on Chemical Intermediate*, 40, 2

Vijayakumar, M., Hirankumar, G., Bhuvaneswari, M. S, Selvasekarapandian, S. (2003).

 Influence of B2O3 doping on conductivity of LiTiO2 electrode material. *Journal*

 *of Power Sources*, 117, 43

Yamamoto, K. & Abe, Y. (1998).*Journal of American Ceramic. Society*.81-2201