UNIVERSITI PUTRA MALAYSIA

STRUCTURAL, ELECTRICAL, CONDUCTIVITY AND DIELECTRIC RELAXATION BEHAVIOR OF LiMAl(PO4)3 (M = Ti, Hf) NASICON COMPOUND

TASIU ZANGINA

STRUCTURAL, ELECTRICAL, CONDUCTIVITY AND DIELECTRIC RELAXATION BEHAVIOR OF $LiMAl(PO_4)_3$ (M = Ti, Hf) NASICON COMPOUND

By

TASIU ZANGINA

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfillments of the Requirements for the Degree of Doctor of Philosophy

October 2017

DEDICATION

My kind and helpful supervisor and co-supervisors, Associate Professor Dr. Jumiah Hassan, Associate Professor Dr. Khamirul Amin Matori, Dr. Rabaah Syahida Aziz and late Associate Professor Dr. Mansor Hashim

My beloved parent and family for their never-ending support and encouragement.

My seniors, laboratory mate and all my friends for their support, advice and assistance

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the Degree of Doctor of Philosophy

STRUCTURAL, ELECTRICAL, CONDUCTIVITY AND DIELECTRIC RELAXATION BEHAVIOR OF $LiMAl(PO_4)_3$ (M = Ti, Hf) NASICON COMPOUND

By

TASIU ZANGINA

October 2017

Chairman : Associate Professor Jumiah Hassan, PhD
Faculty : Science

Superionic conductors are compounds that exhibit higher values of ionic conductivity within a solid state. The high ionic conductivity of these materials is used in various applications such as rechargeable lithium ion batteries. NASICON is known as sodium super ionic conductor which is a family of NZP (Sodium Zirconium Phosphate). The NASICON-type material has an exceptional property due to its ability to provide accommodation to atoms of various sizes in its lattice sites. However, the conductivity of NZP was found to be low below applicable range. Most studies on NASICONS were conducted on Lithium Titanium system (LTP), but reduction of Ti^{4+} by Li^{+} to Ti^{3+} limits their performance due to the material instability. The Hf^{4+} is more stable and reductive gases toward lithium metal than Ti^{4+}.

In this research work, NASICON-type materials with various composition $Li_{1+x}M_{2-x}Al_x(PO_4)_3$ were prepared via solid-state synthesis technique using raw materials Li_2CO_3, TiO_2, HfO_2, Al_2O_3, $(NH_4)_2HPO_4$ and $NH_4H_2PO_4$. Thermal behavior of the as-prepared Lithium Aluminium Titanium Phosphate (LATP) and Lithium Aluminium Hafnium Phosphate (LAHP) were analysed using TGA technique from room temperature to 1300 ºC. For LTP compound, it was observed that increase in aluminium content lead to sample formation to lower temperature. Unlike, LHP compound where the increase in Al contents or x substitution lead the sample formation toward higher temperature. The finding shows that thermal stability is generally affected by both increase in x-content (Li_2CO_3) and aluminium content.
The XRD Rietvel refinement analysis indicated that increase in Al content in the samples (LTP and LHP) increases the number of secondary phases. It is seen from the analysis that samples with low Al substitution indicated little number of secondary phases.

The FESEM micrographs of un-substituted LTP samples indicated a spherical like morphology with non uniform size and agglomerate as temperature increases. For un-substituted LHP the grains were observed closely attached to one another at all temperatures. Whereas, for the Al subsituted samples, the morphology change from spherical to a glaasy like phase. The technique of elemental analysis (EDX) also confirmed the chemical compositions of all the samples synthesized.

Electrical properties of the optimized compounds sintered at 1100 ^{0}C were examined in the frequency range 40 Hz to 1 MHz at various temperatures from room temperatue to 280 ^{o}C. The findings in the present research indicated that material's dielectric relaxation behavior and variation of ac conductivities with change in frequency is in accordance with the Jonscher's power law. An earlier report showed that, the series $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ with x = 0.3 and 0.45 have the highest conductivity. Whereas, the present research on the $Li_{1+x}Al_xHf_{2-x}(PO_4)_3$ with various compositions showed that sample with x = 0.25 has the highest conductivity $\sigma = 2.5 \times 10^{-3}\ \Omega^{-1}\ m^{-1}$ with low dc activation energy of 0.36 eV. The frequency exponent (n) was found to be within the range $0 \leq n \leq 1$which is in good agreement with the correlated barrier hopping (CBH) model.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

TINGKAH LAKU STRUKTUR, KONDUKTIVITI ELEKTRIKAL DAN PENGENDURAN DIELEKTRIK BAGI SEBATIAN $LiMAl(PO_4)_3$ (M = Ti, Hf) NASICON

Oleh

TASIU ZANGINA

Oktober 2017

Pengerusi : Profesor Madya Jumiah Hassan, PhD
Fakulti : Sains

Konduktor superionik ialah kompaun yang menunjukkan kekonduktivitian ionik yang lebih tinggi dalam keadaan pepejal. Bahan ini mempunyai kekonduktivitian ionik yang tinggi yang digunakan dalam pelbagai aplikasi seperti bateri ion lithium yang boleh dicas semula. NASICON yang dikenali sebagai konduktor superion natrium merupakan kumpulan NZP (Natrium Zirkonium Fosfat. Bahan jenis NASICON memiliki ciri-ciri istimewa disebabkan kemampuannya menampung atom-atom pelbagai saiz dalam kekisinya. Walau bagaimanapun, kekonduktivitian NZP didapati lebih rendah daripada julat yang boleh digunakan dalam aplikasi. Kebanyakan kajian yang dijalankan ke atas NASICON dilakukan ke atas sistem Lithium Titanium (LTP), tetapi penurunan Ti^{4+} kepada Ti^{3+}oleh Li^+ mengehadkan prestasi bahan disebabkan ketidakstabilan bahan itu. Hf^{4+} adalah lebih stabil dan gas-gas penurun terhadap logam lithium berbanding Ti^{4+}.

Dalam kajian ini, bahan jenis NASICON dengan pelbagai komposisi $Li_{1+x}M_{2-x}Al_x(PO_4)_3$ telah disediakan melalui teknik sintesis keadaan pepejal menggunakan Li_2CO_3, TiO_2, HfO_2, Al_2O_3, $(NH_4)_2HPO_4$ and $NH_4H_2PO_4$ sebagai bahan mentah. Sifat termal bahan Lithium Aluminium Titanium Fosfat (LATP) dan Lithium Aluminium Hafnium Fosfat (LAHP) yang disediakan telah dianalisis menggunakan teknik TGA bermula dengan suhu bilik sehingga 1300 ºC. Bagi kompaun LTP, didapati pertambahan kandungan Al atau penggantian x mendorong kepada pembentukan sampel pada suhu lebih rendah. Sebaliknya bagi LHP, pertambahan kandungan aluminium mendorong kepada pembentukan sampel pada suhu lebih tinggi. Dapatan menunjukkan kestabilan terma secara umumnya dipengaruhi oleh pertambahan kandungan kandungan bahan x (Li_2CO_3) dan kandungan aluminium.
Analisis penulenan Reitval menggunakan XRD menunjukkan bahawa pertambahan kandungan Al dalam sampel (LTP dan LHP) meningkatkan bilangan fasa sekunder.

Perkara tersebut dapat dilihat daripada analisis apabila sampel mempunyai kandungan penggantian Al yang rendah menunjukkan bilangan fasa sekunder yang sedikit.

Mikrograf FESEM bagi LTP tanpa penggantian menunjukkan morfologi berbentuk sfera dengan saiz yang tidak seragam dan mendap apabila suhu bertambah. Bagi LHP tanpa penggantian, dapat diperhatikan bahawa butiran adalah rapat terikat antara satu sama lain pada semua suhu. Manakala untuk sampel dengan penggantian Al, morfologinya bertukar dari sfera kepada seakan-akan fasa kaca. Technique of elemental analysis (EDX) telah digunakan untuk mengesahkan komposisi bagi semua sampel yang disentesis.

Sifat elektrik bagi kompaun yang dioptimum disinter pada suhu 1100 ^{0}C telah diuji pada julat frekuensi antara 40 Hz sehingga 1 MHz pada pelbagai suhu bermula dari suhu bilik sehingga 280 ^{0}C. Dapatan kajian semasa menunjukkan sifat '*dielectric relaxation*' dan variasi kekonduksian ac dengan perubahan frekuensi adalah selaras dengan hukum kuasa Jonscher. Laporan yang lebih awal menunjukkan siri $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ dengan x = 0.3 dan 0.45 mempunyai kekonduktivitian paling tinggi. Sebaliknya, kajian semasa ke atas $Li_{1+x}Al_xHf_{2-x}(PO_4)_3$ pelbagai komposisi menunjukkan sampel dengan x = 0.25 mempunyai kekonduktivitian paling tinggi $\sigma = 2.5 \times 10^{-3}\ \Omega^{-1}\ m^{-1}$ dengan tenaga pengaktifan yang rendah iaitu 0.36 eV. Komponen frekuensi (n) didapati selaras dengan model 'corellated barrier hoping (CBH)' berada dalam julat $0 \leq n \leq 1$.

ACKNOWLEDGEMENTS

Praise be to Allah, the almighty (Subhanahu wataala), the most compassionate, for granting me the opportunity to complete this thesis.

I would like to express my gratitude to those who have immensely contributed in the completion of this research work. It is my pleasure to acknowledge the effort of the chairperson of the supervisory committee, Associate Professor Dr. Jumiah Hassan that provides all the materials needed for the research.

Besides, I would like to extend my sincere appreciation to the supervisory committee members, especially Associate Professor Dr. Khamirul Amin Matori and Dr. Raba'ah Syahidah Azis who are willing to share their knowledge and opinions in promoting the research.

Special thanks also go to my senior colleagues and lab mates who are willing to share their experience and guidance to complete my research, especially Wong Swee Yin, Leow Chun Yan, Tan Foo Khoon, Alex See, Wong Yick Jeng and Dr. Fatin Hana for her contribution in translating the abstract to Malay version. Also, I would like to acknowledge the technical staffs of XRD Unit and Electron Microscopy Unit for their kind assistance.

Finally, I would like to give thanks to Dr. Umaru Ahmadu of Federal University of Technology Minna, Nigeria for his onset guidance and assistance that introduce me to the field of NASICON-type materials. **AlhamduLillah**

This thesis was submitted to the Senate of the Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Jumiah Hassan, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Khamirul Amin Matori, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Raba'ah Syahidah Azis, PhD
Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

ROBIAH BINTI YUNUS, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

TABLE OF CONTENTS

LIST OF TABLES

Table **Page**

LIST OF FIGURES

Figure **Page**

LIST OF SYMBOLS

a, b, c	Lattice parameters or Lattice Constant
hkl	Miller indices
n	Correlation Exponent or Frequency Exponent
σ_{ac}	ac Conductivity
σ_{dc}	dc Conductivity
ΔE	Activation Energy
d	Separation between the plains
T_g	Glass Transition Temperature
T_c	Crystallization Temperature
T_{c2}	Second Crystallization Temperature
T_m	Melting Temperature
f	Frequency
f_{max}	Maximum peak frequency
j	imaginary operator with $(-1)^{1/2}$
t	Thickness
σ	Charge density or conductivity
μ	Dipole moment
δ	Loss angle
τ	Conductivity relaxation time
ε_0	Permittivity of free space
ε	Permittivity of dielectric
ε_r^*	Complex relative permittivity
ε_r'	Real part of relative permittivity
ε_r''	Imaginary part of relative permittivity
ω	Angular frequency

$\tan \delta$	Loss tangent
F	Farad
pF	Picofarad
μF	Microfarad
A	Surface area of the plate
C	Capacitance
C_D	Capacitance of a capacitor filled with dielectric
C_{dl}	Double layer capacitance
C_g	Grain capacitance
C_{gb}	Grain boundary capacitance
C_0	Capacitance of an ideal parallel plate capacitor
D	Flux density with dielectric
E	Electric field
G	Conductance
I_c	Charging current
P	Polarization
Q	Quantity of Charges
R	Resistance
R_g	Grain resistance
R_{gb}	Grain boundary resistance
T	Time or Temperature in Kelvin scale
V	Voltage
V_m	Maximum value of voltage
Y'	Real part of admittance
Y''	Imaginary part of admittance
Z^*	Complex impedance

Z'	Real part of impedance
Z''	Imaginary part of impedance
M^*	Complex dielectric modulus
M'	Real part of dielectric modulus
M''	Imaginary part of dielectric modulus
ρ	Resistivity
Ω	Ohms
χ^2	Chi square
K_B	Boltzman constant
A	pre-exponential factor
Na^+	Sodium ion
P^{3-}	Phosphorus ion
Al^{3+}	Aluminum ion
Ti^{4+}	Titanium ion
Hf^{4+}	Hafnium ion
Zr^{4+}	Zirconia ion
Li^+	Lithium ion

LIST OF ABBREVIATIONS

LTP	Lithium Titanium Phosphate
LHP	Lithium Hafnium Phosphate
LATP	Lithium Aluminum Titanium Phosphate
LAHP	Lithium Aluminum Hafnium Phosphate
TiO_2	Titanium dioxide
AC	Alternating current
CPE	Constant Phase Element
DC	Direct Current
EDX	Energy dispersive x-ray spectroscopy
FESEM	Field emission scanning electron microscopy
ICSD	Inorganic crystal structure database
RF	Radio frequency
SEM	Scanning electron microscopy
XRD	X-ray diffraction
DSC	Differential Scanning Calorimetric
TGA	Thermogravimetric Analysis
DTG	Differential thermogravimetric
HfO_2	Hafnium Oxide
Al_2O_3	Aluminum Oxide
$(NH_4)_2HPO_4$	Diammonium Phosphate
$NH_4H_2PO_4$	Monoammonium Phosphate
TiO_2	Titanium Oxide
Li_2CO_3	Lithium Carbonate
PVA	Polyvinyl Alcohol

CBH	Correlated Barrier Hopping
QMT	Quantum Mechanical Tunneling
OLPT	Overlapping Large Polaron Tunneling
SPT	Small Polaron Tunneling
eV	Electron Volt

CHAPTER 1

INTRODUCTION

1.1 Introduction

The compounds that were developed and used over the course of history serve as an excellent indicator of evolution in technology and civilization as a whole. The earliest materials were those that were readily available in nature, like stone, clay, wood and metals, and the technology involved was to reshaping and restructuring physically these materials to suit specific purposes such as weaponry and utensils and the devices for storing energy. The most complex and difficult process at this stage involved the fabrication of ceramics such as porcelain by baking clays, a process that dates back to the eighteenth century BC. The discovery of procedures for the extraction of metals and fabrication of alloys was a major revolution in the history of materials. It was a situation of complete transformation of physical, chemical and electrical properties of a material. Equally remarkable was the discovery of NASICON-type super ionic conductors; a process in which the conduction properties of the starting substance, normal ionic conductors, was completely modified. Super ionic conductors are part and parcel of our electronic industry, due to the alternative they offer for renewable energy sources and other potential applications.

1.2 Research Background

The key technology in modern society is the battery(Armand and Tarascon, 2008). A device consists of electrochemical cells that transform stored chemical energy into electrical energy. The first battery was invented by Alessando Volta in 1800 and technically improved Daniel cell in 1836 is still a common power source for many household and industrial application according to 2005 estimate (Park *et al.*, 2010) There is a great need for batteries with high power and energy density for advanced researchers to put more effort in this work. At present liquid electrolytes such as $LiClO_4$ dissolved in propylene carbonate are used in lithium batteries. This electrolyte has many disadvantages such as limited temperature range of operation, device failure due to electrode corrosion by electrolyte solution and unsuitable shapes. A suitable solid electrolyte is required to overcome these disadvantages (Thangadurai *et al.*, 1999). Solid electrolytes promise the potential to replace organic electrolytes and thereby improve the safety of next generation high-energy batteries (Kamaya *et al.*, 2011). Two different approaches are pursued for this purpose. In the first, a plasticizer, TiO_2 or Al_2O_3 can be added to make the electrolyte from liquid to solid composite. The second approach is to synthesize solids having desired ionic conductivity and other properties (Anantharamulu *et al.*, 2011). Ionic conducting solids with conductivity of order 10^{-14} to 10^{-6} Scm^{-1} at ambient temperature are known as normal ionic conductors such as KCl and NaCl. The activation process involves energy due to defect formation and energy due to ion migration (Hladik, 1972). Ionic conducting solids with conductivity of order 10^{-6} Scm^{-1}or more with negligible electronic conductivity of order 10^{-12} Scm^{-1} at room temperature as well as high temperature are called super ionic conductors. In this type of conductors, the crystal bonding is ionic (Chandra, 1981), the electrical conductivity is high, the charge carriers are ions, and the electronic conductivity is very low or negligible. The high ionic conductivity of these materials is used in various applications such as rechargeable lithium ion batteries for laptop computers, mobile phones and electrodes and electrolyte materials. It can also be used in making devices such as membranes, fuel cells, and gas sensors. In solid state ionic, ionic conduction occurs due to the imperfections or defects caused by the long- range diffusion of ions in materials. Faraday first observed the effect in 1839 in many materials such as PbF_2 and Ag_2S (Patcheammalle, 2010). The flow of ions through the lattice occurs in two ways i.e. via interstitial sites or hopping through the vacancies at the normal lattice sites (LeClaire and Lidiard, 1956).

1.3 Problem Statement

In NASICON-type material $NaZr_2P_3O_{12}$ (NZP), the conducting mobile ion is Na^+ but there is the problem of stability of sodium ion when in contact with metal electrodes leading to its reduction when in operation in cells. The conductivity of the NZP compound was also reported to be very low, below the applicable range and has poor sinterability. However, the conductivity can be increased by several orders of magnitude if the Na is replaced fully by Lithium (Li) and the Zr and P are replaced by element of different valences and radii (Aono *et al.*, 1991).

Most work were carried out in the titanium system $LiTi_2(PO_4)_3$ (LTP) where the small size of Ti^{4+} cations make the size of the sites in the channels more appropriate for lithium cations (Maldonado-Manso *et al.*, 2005). However, it was observed that, there is also the the problem of poor sinterability and controversial phase transition in the preparation of LTP. It was reported that Hf^{4+} ion is more stable toward a lithium metal and reductive gases than the Ti^{4+} ion, which is an additional advantage for battery applications (Chang *et al.*, 2005).

$LiHf_2(PO_4)_3$ crystallizes in NASICON structure but there is problem for the material to undergo a toptactic and reversible phase transition at low temperature (Losilla *et al.*, 1998). The Li^+ conductivity in $LiHf_2(PO_4)_3$ based solid electrolytes is greatly enhanced by employing spark plasma synthesis (SPS) technique and partial substitution of Hf^{4+} with Al^{3+} resulting in the highest conductivity of $1.1x10^{-4}$ Scm^{-1} by the compound $LiAlHf(PO_4)_3$. The activation energy of the total conductivity (bulk + grain boundary) was reported to reduce from 0.39 to 0.28 eV with Al substitution (Chang *et al.*, 2005). Few works were reported on LHP due to its poor sinterability and controversial phase transition at low temperature during synthesis (Losilla *et al.*, 1997). To overcome such problems, few studies have reported to improve the ionic conductivity of LHP, which includes densification by ionic substitution (Aono *et al.*, 1993; Chang *et al.*, 2005), which involved lithium salt addition (Aono *et al.*, 1993) and Spark Plasma Synthesis technique (Chang *et al.*, 2005).

Previous studies on NASICON-type such as Lithium Titanium Phosphate (LTP) and Lithium Hafnium Phosphate (LHP) focused on preparation methodologies, structural transformation and dc conductivity of the material. But, other behaviour of the materials such as thermal properties or thermodynamic behaviour, ac conductivity, dielectric and relaxation behaviour of the materials were not fully reported even though they are important to identify proper applicability of the material as an electrolyte. To our knowledge, aluminium substitution in LHP was only reported by Chang *et al.* (2005) using spark plasma sintering technique (SPS). The effect of SPS technique and the ionic substitution with aluminium ion were investigated based on the material densification to enhance the Li^+ ion conductivity, but thermal behaviour of the aluminium substituted composition was not fully discussed by the authors.

1.4 Research Aim and Objectives

In this work, we will study and determine the electrical properties of some NASICON-type materials (LTP and LHP) prepared by conventional solid-state synthesis technique based on the problems stated in Section 1.3. The specific research objectives of the study are as follows;

1. Preparation of the materials (LTP and LHP) using solid state synthesis method and to determine the thermal behaviour from room temperature to 1300 ^{0}C and to examine the phase stability of the materials as Al substitution increases.
2. Evaluation of sintering behaviour, phase composition and structural phase transformation in the temperature range 500 ^{0}C to around the maximum sintering temperature (i.e. 1200 ^{0}C) and to investigate the effect of Al substitution in both LTP and LHP.
3. The sintering characteristics (1000-1200 ^{0}C) for the synthesis of the compounds correlated with microstructure, structural data analysis and to study the effect of Al substitution on the microstructure.
4. The impedance spectroscopy analysis from room temperature to a higher temperature at the frequency range of 40 Hz to 1 MHz. (electrical conductivity and dielectric relaxation behaviour of the materials)

1.5 Scope and Limitations of the Study

This research investigate the effects of aluminium substitution in the $LiTi_2(PO_4)_3$ and $LiHf_2(PO_4)_3$ NASICON-types materials that were prepared out via conventional solid-state synthesis technique. Eight compounds according to the stoichiometric compositions of each $Li_{1+x}Ti_{2-x}Al_x(PO_4)_3$ and $Li_{1+x}Hf_{2-x}Al_x(PO_4)_3$ (x = 0, 0.2, 0.25, 0.3, 0.4, 0.5, 0.75 and 1.0) were prepared. This work is limited to producing a NASICON-type structure with R-3c space group with hexagonal crystal structure. This is because a wide range of stoichiometry of x-value can produce different structure with various electrochemical properties. The sintered materials were characterized by Impedance Spectroscopy, X-Ray Diffraction (XRD), Thermogravimery Analysis TGA, FTIR, and FESEM/EDX. The XRD was used to investigate the crystalline phases, the structural parameters, such as lattice parameters, theoretical and experimental densities. Thermal analysis was carried out on both systems prepared using TGA. Surface morphology and microstructure of the sintered compounds was examined using FESEM/EDX.

1.6 Significance of the Study

At the end of the study, the properties of the synthesized chemical compounds (LATP and LAHP) and the electrical conductivity of the sintered materials will be known. This will provide information for modelling and fabrication of future NASICON materials. The significance of the study is in their application in some areas such as lithium ion rechargeable batteries, electrochemical sensors and fuel cells, among others.

1.7 Outlines of the Chapters

This thesis is designed into six chapters. Chapter 1 gives a general introduction of the research work, comprising of research background, problem statement, aims and objectives, significance of the study and scope and limitation of the work. Chapter 2 presents the previous research and reviews related to superionic conductors such as fast-ionic polymers, fast-ionic composites, amorphous or glassy materials and polycrystalline materials which include Garnet-type, Perovskite-type, LISICON-type and NASICON-type. Properties of NASICON-type materials are also presented which include thermal and thermodynamic properties, structure and physical properties and electrical properties. Chapter 3 covers the fundamentals and theoretical aspects of the subject; structure, phase transformation and electrical properties which include electrical conductivities (ac and dc), complex impedance, complex permittivity formalisms and the complex modulus formalisms. This chapter also explains the theoretical aspect of equivalent circuit modelling and the various types of polarization mechanisms. Chapter 4 deals with materials and sample preparation method and the different characterizations measurements involved in the research are also covered. Chapter 5 presents the results and discussion, whereas Chapter 6 concludes and describes all the major research contributions.

REFERENCES

Adnan, S. and Mohamed, N. (2014). Effects of Sn substitution on the properties of Li 4 SiO 4 ceramic electrolyte. Solid State Ionics, 262, 559-562.

Ahmadu, U. Musa, A. Jonah, S. and Rabiu, N. (2010). Synthesis and thermal characterization of NZP compounds Na1− x Li x Zr2 (PO4) 3 (x= 0.00–0.75). Journal of Thermal analysis and Calorimetry, 101(1), 175-179.

Ahmadu, U. Musa, A. O. Salkus, T. and Isah, K. U. (2011). Electrical and Dielectric Characterization of Na 0.5 Li 0.5 Zr 2 (PO 4) 3. Open Journal of Physical Chemistry, 1(03), 94.

Ahmadu, U. Tomas, Ŝ. Jonah, S. Musa, A. and Rabiu, N. (2012). Equivalent circuit models and analysis of impedance spectra of solid electrolyte. Advance material letters, 4, 185-195

Ahmed, R. Moslehuddin, A. Mahmood, Z. H. and Hossain, A. A. (2015). Weak ferromagnetism and temperature dependent dielectric properties of Zn 0.9 Ni 0.1 O diluted magnetic semiconductor. Materials Research Bulletin, 63, 32-40.

Alamo, J. and Roy, R. (1984). Ultralow-Expansion Ceramics in the System NA2O-ZRO2P2O5-SIO2. Journal of the American Ceramic Society, 67(5).

Almond, D. and West, A. (1983a). Impedance and modulus spectroscopy of “real” dispersive conductors. Solid State Ionics, 11(1), 57-64.

Almond, D. and West, A. (1983b). Mobile ion concentrations in solid electrolytes from an analysis of ac conductivity. Solid State Ionics, 9, 277-282.

Anantha, P. and Hariharan, K. (2005). Ac conductivity analysis and dielectric relaxation behaviour of NaNO 3–Al 2 O 3 composites. Materials Science and Engineering: B, 121(1), 12-19.

Anantharamulu, N. Rao, K. K. Rambabu, G. Kumar, B. V. Radha, V. and Vithal, M. (2011). A wide-ranging review on Nasicon type materials. Journal of materials science, 46(9), 2821-2837.

Aniya, M. (1994). Superionicity as a local fluctuation of the chemical bond. Solid State Ionics, 70, 673-677.

Anuar, N. Adnan, S. and Mohamed, N. (2014). Characterization of Mg 0.5 Zr 2 (PO 4) 3 for potential use as electrolyte in solid state magnesium batteries. Ceramics International, 40(8), 13719-13727.

Aono, H. Sugimoto, E. Sadaoka, Y. Imanaka, N. and Adachi, G.-y. (1991). Electrical property and sinterability of LiTi2 (PO4) 3 mixed with lithium salt (Li3PO4 or Li3BO3). Solid State Ionics, 47(3-4), 257-264.

Aono, H. Sugimoto, E. Sadaoka, Y. Imanaka, N. and Adachi, G.-y. (1993). Electrical properties and crystal structure of solid electrolyte based on lithium hafnium phosphate LiHf2 (PO4) 3. Solid State Ionics, 62(3-4), 309-316.

Arbi, K. Bucheli, W. Jiménez, R. and Sanz, J. (2015). High lithium ion conducting solid electrolytes based on NASICON Li 1+ x Al x M 2− x (PO 4) 3 materials (M= Ti, Ge and 0≤ x≤ 0.5). Journal of the European Ceramic Society, 35(5), 1477-1484.

Arbi, K. Hoelzel, M. Kuhn, A. García-Alvarado, F. and Sanz, J. (2013). Structural Factors That Enhance Lithium Mobility in Fast-Ion Li1+ x Ti2–x Al x (PO4) 3 (0≤ x≤ 0.4) Conductors Investigated by Neutron Diffraction in the Temperature Range 100–500 K. Inorganic chemistry, 52(16), 9290-9296.

Armand, M. and Tarascon, J. (2008). Building better batteries. Nature, 451(7179), 652-657.

Attia, A. Soliman, H. Saadeldin, M. and Sawaby, K. (2015). AC electrical conductivity and dielectric studies of bulk p-quaterphenyl. Synthetic Metals, 205, 139-144.

Awaka, J. Kijima, N. Hayakawa, H. and Akimoto, J. (2009). Synthesis and structure analysis of tetragonal Li 7 La 3 Zr 2 O 12 with the garnet-related type structure. Journal of solid state chemistry, 182(8), 2046-2052.

Barsoukov, E. and Macdonald, J. R. (2005). *Impedance spectroscopy: theory, experiment, and applications*: John Wiley & Sons.

Begam, K. Michael, M. and Prabaharan, S. (2010). NASICON Open Framework Structured Transition Metal Oxides for Lithium Batteries.

Bisquert, J. Halpern, V. and Henn, F. (2005). Simple model for ac ionic conduction in solids. The Journal of chemical physics, 122(15), 151101.

Bohnke, O. (2008). The fast lithium-ion conducting oxides Li 3x La 2/3− x TiO 3 from fundamentals to application. Solid State Ionics, 179(1), 9-15.

Böttcher, C. J. F. van Belle, O. C. Bordewijk, P. and Rip, A. (1978). *Theory of electric polarization* (Vol. 2): Elsevier Science Ltd.

Brian, S. M. and Mitchell, A. (2004). An introduction to materials engineering and science for chemical and materials engineers. Vol. 1st Edition: Wiley Blackwell.

Bruce, P. and West, A. (1984). Ion trapping and its effect on the conductivity of LISICON and other solid electrolytes. Journal of solid state chemistry, 53(3), 430-434.

Bushiri, M. J. Antony, C. and Aatiq, A. (2008). Raman and FTIR studies of the structural aspects of Nasicon-type crystals; AFeTi (PO 4) 3 [A= Ca, Cd]. Journal of Physics and Chemistry of Solids, 69(8), 1985-1989.

Cao, C. Li, Z.-B. Wang, X.-L. Zhao, X.-B. and Han, W.-Q. (2014). Recent advances in inorganic solid electrolytes for lithium batteries. Frontiers in Energy Research, 2, 25.

Chandra, S. (1981). Superionic solids: principles and applications. North-Holland Publishing Co., xi+ 404, 22 x 15 cm, illustrated.

Chang, C.-M. Hong, S.-H. and Park, H.-M. (2005). Spark plasma sintering of Al substituted LiHf 2 (PO 4) 3 solid electrolytes. Solid State Ionics, 176(35), 2583-2587.

Choudhury, T. R. and Basua, A. (2008). Ac conductivity and dielectric relaxation studies of sandstone-a correlation with its thermoluminescence. Journal of Ovonic Research Vol, 4(2), 35-42.

Corbridge, D. (1956). The crystal structure of magnesium phosphite hexahydrate, MgHPO3. 6H2O. Acta Crystallographica, 9(12), 991-994.

Dieterich, W. (1985). Superionic conductors. Journal of Statistical Physics, 39(5), 583-596.

El-Muraikhi, M. (2009). Complex-impedance response of an Ag/TeO_2–V_2O_5/Ag structure. Materials Chemistry and Physics, 116(1), 52-56.

Elliott, S. (1977). A theory of ac conduction in chalcogenide glasses. Philosophical Magazine, 36(6), 1291-1304.

Fenton, D. E. Parker, J. M. and Wright, P. V. (1973). Complexes of alkali metal ions with poly(ethylene oxide). Polymer, 14(11), 589.

Fluorides, I. S. (1985). Chemistry and Physics: Hagenmuller, P., Ed.

Fröhlich, H. (1958). *Theory of dielectrics: dielectric constant and dielectric loss*: Clarendon Press.

Fuentes, R. Figueiredo, F. Marques, F. and Franco, J. (2001). Processing and electrical properties of NASICON prepared from yttria-doped zirconia precursors. Journal of the European Ceramic Society, 21(6), 737-743.

Fuentes, R. Marques, F. and Franco, J. (1999). Synthesis and properties of NASICON prepared from different zirconia-based precursors. BOLETIN-SOCIEDAD ESPANOLA DE CERAMICA Y VIDRIO, 38(6), 631-634.

Gaber, A. Abdel-Rahim, M. Abdel-Latief, A. and Abdel-Salam, M. N. (2014). Influence of calcination temperature on the structure and porosity of nanocrystalline SnO2 synthesized by a conventional precipitation method. Int J Electrochem Sci, 9(1), 81-95.

Goodenough, J. Hong, H.-P. and Kafalas, J. (1976). Fast Na+-ion transport in skeleton structures. Materials Research Bulletin, 11(2), 203-220.

Govindaraj, G. and Mariappan, C. (2002). Synthesis, characterization and ion dynamic studies of NASICON type glasses. Solid State Ionics, 147(1), 49-59.

Greenwood, N. N. (1968). *Ionic crystals, lattice defects and nonstoichiometry*: Butterworths London.

Griffiths, D. J. and College, R. (1999). *Introduction to electrodynamics* (Vol. 3): prentice Hall Upper Saddle River, NJ.

Hagenmuller, P. (2012). *Preparative methods in solid state chemistry*: Elsevier.

Halim, Z. Adnan, S. and Mohamed, N. (2016). Effect of sintering temperature on the structural, electrical and electrochemical properties of novel Mg 0.5 Si 2 (PO 4) 3 ceramic electrolytes. Ceramics International, 42(3), 4452-4461.

Hazen, R. Finger, L. Agrawal, D. McKinstry, H. and Perrotta, A. J. (1987). High-temperature crystal chemistry of sodium zirconium phosphate (NZP). Journal of Materials Research, 2(03), 329-337.

Hladik, J. (1972). *Physics of electrolytes*: Acad. Pr.

Hong, H.-P. (1978). Crystal structure and ionic conductivity of Li 14 Zn (GeO 4) 4 and other new Li+ superionic conductors. Materials Research Bulletin, 13(2), 117-124.

Hui, S. R. Roller, J. Yick, S. Zhang, X. Deces-Petit, C. Xie, Y. Maric, R. and Ghosh, D. (2007). A brief review of the ionic conductivity enhancement for selected oxide electrolytes. Journal of Power Sources, 172(2), 493-502.

Hull, S. (2004). Superionics: crystal structures and conduction processes. Reports on Progress in Physics, 67(7), 1233.

Ignaszak, A. Pasierb, P. Gajerski, R. and Komornicki, S. (2005). Synthesis and properties of Nasicon-type materials. Thermochimica acta, 426(1), 7-14.

Jackman, S. D. and Cutler, R. A. (2012). Effect of microcracking on ionic conductivity in LATP. Journal of Power Sources, 218, 65-72.

Jasinski, G. Jasinski, P. Chachulski, B. and Nowakowski, A. (2006). Electrocatalytic gas sensors based on Nasicon and Lisicon. Materials Science-Poland, 24(1).

Jonscher, A. K. (1999). Dielectric relaxation in solids. Journal of Physics D: Applied Physics, 32(14), R57.

Julien, C. Rougier, A. and Nazri, G. (1996). *Synthesis, Structure, Lattice Dynamics and Electrochemistry of Lithiated Manganese Spinel, LiMn 2 O 4.* Paper presented at the MRS Proceedings.

Kamaya, N. Homma, K. Yamakawa, Y. Hirayama, M. Kanno, R. Yonemura, M. Kamiyama, T. Kato, Y. Hama, S. and Kawamoto, K. (2011). A lithium superionic conductor. Nature materials, 10(9), 682-686.

Kang, H.-B. and Cho, N.-H. (1999). Phase formation, sintering behavior, and electrical characteristics of NASICON compounds. Journal of materials science, 34(20), 5005-5013.

Kao, K. C. (2004). *Dielectric phenomena in solids*: Academic press.

Key, B. Schroeder, D. J. Ingram, B. J. and Vaughey, J. T. (2012). Solution-based synthesis and characterization of lithium-ion conducting phosphate ceramics for lithium metal batteries. Chemistry of materials, 24(2), 287-293.

Kim, C. Lee, G. Liou, K. Ryu, K. S. Kang, S.-G. and Chang, S. H. (1999). Polymer electrolytes prepared by polymerizing mixtures of polymerizable PEO-oligomers, copolymer of PVDC and poly (acrylonitrile), and lithium triflate. Solid State Ionics, 123(1), 251-257.

Knauth, P. (2009). Inorganic solid Li ion conductors: An overview. Solid State Ionics, 180(14), 911-916.

Korepina, Y. O. Bigeeva, L. S. Il'in, A. Svitan'ko, A. Novikova, S. and Yaroslavtsev, A. (2013). Cation mobility in Li1+ x Hf2− x Sc x (PO4) 3 NASICON-type phosphates. Inorganic materials, 49(3), 283-287.

Kosova, N. Devyatkina, E. Stepanov, A. and Buzlukov, A. (2008). Lithium conductivity and lithium diffusion in NASICON-type Li1+ xTi2–xAlx (PO4) 3 (x= 0; 0.3) prepared by mechanical activation. Ionics, 14(4), 303-311.

Kothari, D. H. and Kanchan, D. (2015). Study of Study of electrical properties of gallium-doped lithium titanium aluminum phosphate compounds. Ionics, 21(5), 1253-1259.

Kowada, Y. Yamada, Y. Tatsumisago, M. Minami, T. and Adachi, H. (2000). Variation of electronic state of AgI-based superionic conductors with movement of Ag ions. Solid State Ionics, 136, 393-397.

Kumar, A. Dwivedi, R. and Pal, V. (2012). *Dielectric Behavior and Impedance Spectroscopy of Ba1-xBixTi1-xFexO3 System.* Paper presented at the Advanced Materials Research.

Kumar, P. P. and Yashonath, S. (2006). Ionic conduction in the solid state. Journal of Chemical Sciences, 118(1), 135-154.

Kumara, L. Ohara, K. Kawakita, Y. Jóvári, P. Hidaka, M. Sung, N. E. Beuneu, B. and Takeda, S. i. (2011). *Local structure of superionic glass Agx (GeSe3) 1-x, x= 0.565.* Paper presented at the EPJ Web of Conferences.

Kunze, D. and Van Gool, W. (1973). Fast ion transport in solids. North Holland, Amsterdam, 495.

Laskar, A. (2012). *Superionic solids and solid electrolytes recent trends*: Elsevier.

LeClaire, A. and Lidiard, A. (1956). LIII. Correlation effects in diffusion in crystals. Philosophical Magazine, 1(6), 518-527.

Lenain, G. McKinstry, H. Limaye, S. and Woodward, A. (1984). Low thermal expansion of alkali-zirconium phosphates. Materials Research Bulletin, 19(11), 1451-1456.

Liang, C. (1973). Conduction characteristics of the lithium iodide-aluminum oxide solid electrolytes. Journal of the Electrochemical Society, 120(10), 1289-1292.

Limaye, S. Agrawal, D. and McKinstry, H. (1987). Synthesis and thermal expansion of MZr4P6O24 (M= Mg, Ca, Sr, Ba). Journal of the American Ceramic Society, 70(10).

Liu, C. and Angell, C. (1986). Mechanical vs electrical relaxation in Agl-based fast ion conducting glasses. Journal of non-crystalline solids, 83(1), 162-184.

Losilla, E. Bruque, S. Aranda, M. Moreno-Real, L. Morin, E. and Quarton, M. (1998). NASICON to scandium wolframate transition in Li 1+ x M x Hf 2− x (PO 4) 3 (M= Cr, Fe): structure and ionic conductivity. Solid State Ionics, 112(1), 53-62.

Losilla, E. R. Aranda, M. A. Bruque, S. Sanz, J. París, M. A. Campo, J. and West, A. R. (2000). Sodium Mobility in the NASICON Series Na1+ x Zr2-x In x (PO4) 3. Chemistry of materials, 12(8), 2134-2142.

Losilla, E. R. Aranda, M. A. Martínez-Lara, M. and Bruque, S. (1997). Reversible triclinic-rhombohedral phase transition in LiHf2 (PO4) 3: Crystal structures from neutron powder diffraction. Chemistry of materials, 9(7), 1678-1685.

Lu, T. and Fleck, N. (1998). The thermal shock resistance of solids. Acta materialia, 46(13), 4755-4768.

Lvovich, V. F. (2012). *Impedance spectroscopy: applications to electrochemical and dielectric phenomena*: John Wiley & Sons.

Macdonald, J. R. and Johnson, W. B. (2005). Fundamentals of impedance spectroscopy. Impedance Spectroscopy: Theory, Experiment, and Applications, Second Edition, 1-26.

Maier, J. (1995). Ionic conduction in space charge regions. Progress in solid state chemistry, 23(3), 171-263.

Maldonado-Manso, P. Aranda, M. A. Bruque, S. Sanz, J. and Losilla, E. R. (2005). Nominal vs. actual stoichiometries in AL-doped NASICONs: a study of the Na 1.4 Al 0.4 M 1.6 (PO 4) 3 (M= Ge, Sn, Ti, Hf, Zr) family. Solid State Ionics, 176(17), 1613-1625.

Mariappan, C. Govindaraj, G. Rathan, S. V. and Prakash, G. V. (2005). Preparation, characterization, ac conductivity and permittivity studies on vitreous M 4 AlCdP 3 O 12 (M= Li, Na, K) system. Materials Science and Engineering: B, 121(1), 2-8.

Martínez-Juárez, A. Amarilla, J. Iglesias, J. and Rojo, J. (1997). Ionic conductivity of LiHf2 (PO4) 3 with NASICON-type structure and its possible application as electrolyte in lithium batteries. Journal of the Brazilian Chemical Society, 8(3), 261-264.

Martinsen, O. G. Grimnes, S. and Schwan, H. P. (2002). Interface phenomena and dielectric properties of biological tissue. Encyclopedia of surface and colloid science, 20, 2643-2653.

Matula, R. A. (1979). Electrical resistivity of copper, gold, palladium, and silver. Journal of Physical and Chemical Reference Data, 8(4), 1147-1298.

McCrum, N. G. Read, B. E. and Williams, G. (1967). Anelastic and dielectric effects in polymeric solids.

Morimoto, H. Hirukawa, M. Matsumoto, A. Kurahayashi, T. Nobukiyo, I. and Tobishima, S.-i. (2014). Lithium ion conductivities of NASICON-type Li1+ xAlxTi2− x (PO4) 3 solid electrolytes prepared from amorphous powder using a mechanochemical method. Electrochemistry, 82(10), 870-874.

Mouahid, F. Zahir, M. Maldonado-Manso, P. Bruque, S. Losilla, E. Aranda, M. Rivera, A. Leon, C. and Santamaria, J. (2001). Na–Li exchange of Na1+ xTi2− xAlx (PO4) 3 (0.6≤ x≤ 0.9) NASICON series: a Rietveld and impedance studyElectronic supplementary information (ESI) available: Selected bond angles for the (Li, Na) 1+ xTi2− xAlx (PO4) 3 series. See http://www. rsc. org/suppdata/jm/b1/b102918p. Journal of Materials Chemistry, 11(12), 3258-3263.

Mustaffa, N. Adnan, S. Sulaiman, M. and Mohamed, N. (2015). Low-temperature sintering effects on NASICON-structured LiSn2P3O12 solid electrolytes prepared via citric acid-assisted sol-gel method. Ionics, 21(4), 955-965.

Naik, A. Thakkar, N. Dharwadkar, S. Mudher, K. S. and Venugopal, V. (2004). Microwave assisted low temperature synthesis of sodium zirconium phosphate (NaZr2P3O12). Journal of Thermal analysis and Calorimetry, 78(3), 707-713.

Note, A. A. (2006). Agilent Basics of Measuring the Dielectric Properties of Materials. Agilent Literature Number.

PANalytical, B. (2012). 'Pert HighScore Plus software, version 3.0 e. Almelo: Netherlands.

Papaioannou, G. (2010). The impact of dielectric material and temperature on dielectric charging in RF MEMS capacitive switches *Advanced Materials and Technologies for Micro/Nano-Devices, Sensors and Actuators* (pp. 141-153): Springer.

Paris, M. Martínez-Juárez, A. Iglesias, J. Rojo, J. and Sanz, J. (1997). Phase Transition and Ionic Mobility in LiHf2 (PO4) 3 with NASICON Structure. Chemistry of materials, 9(6), 1430-1436.

Park, M. Zhang, X. Chung, M. Less, G. B. and Sastry, A. M. (2010). A review of conduction phenomena in Li-ion batteries. Journal of Power Sources, 195(24), 7904-7929.

Paściak, G. Chmielowiec, J. and Bujło, P. (2005). New ceramic superionic materials for IT-SOFC applications. Materials Science-Poland, 23(1), 209-219.

Patcheammalle, R. (2010). Impedance, electric modulus and solid state battery studies of silver based fast ionic conductors.

Patil, V. Patil, A. Yoon, S.-J. and Choi, J.-W. (2013). Structural and electrical properties of NASICON type solid electrolyte nanoscaled glass-ceramic powder by mechanical milling for thin film batteries. Journal of nanoscience and nanotechnology, 13(5), 3665-3668.

Pereira, N. Klein, L. and Amatucci, G. (2002). The Electrochemistry of Zn3 N 2 and LiZnN A Lithium Reaction Mechanism for Metal Nitride Electrodes. Journal of the Electrochemical Society, 149(3), A262-A271.

Pet'kov, V. and Orlova, A. (2003). Crystal-chemical approach to predicting the thermal expansion of compounds in the NZP family. Inorganic materials, 39(10), 1013-1023.

Pet'kov, V. Orlova, A. Trubach, I. Asabina, Y. Demarin, V. and Kurazhkovskaya, V. (2003). Immobilisation of nuclear waste materials containing different alkali elements into single-phase NZP-based ceramics. Czechoslovak Journal of Physics, 53(1), A639-A648.

Pet’kov, V. Asabina, E. Markin, A. and Smirnova, N. (2008). Synthesis, characterization and thermodynamic data of compounds with NZP structure. Journal of Thermal analysis and Calorimetry, 91(1), 155-161.

Ramaraghavulu, R. and Buddhudu, S. (2011). Analysis of structural, thermal and dielectric properties of LiTi 2 (PO 4) 3 ceramic powders. Ceramics International, 37(8), 3651-3656.

Rao, K. Sobha, K. and Kumar, S. (2001). Infrared and Raman spectroscopic studies of glasses with NASICON-type chemistry. Journal of Chemical Sciences, 113(5-6), 497-514.

Razeghi, M. (2009). *Fundamentals of solid state engineering*: Springer Science & Business Media.

Rodrigo, J. Carrasco, P. and Alamo, J. (1989). Thermal expansion of NaTi2 (PO4) 3 studied by rietveld method from X-ray diffraction data. Materials Research Bulletin, 24(5), 611-618.

Rulmont, A. Cahay, R. Liegeoisduyckaerts, M. and Tarte, P. (1991). Vibrational spectroscopy of phosphates-some general correlations between structure and spectra. European Journal of Solid State and Inorganic Chemistry, 28(1), 207-219.

Rusdi, H. Azilah, A. R. Subban, R. H. Y. and Mohamed, N. (2012). *Characterisation of Lithium Aluminium Titanium Phosphate as Solid Electrolytes Synthesized by Mechanical Milling Method.* Paper presented at the Advanced Materials Research.

Sayer, M. and Mansingh, A. (1972). Transport properties of semiconducting phosphate glasses. Physical Review B, 6(12), 4629.

Shannon, R. t. (1976). Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography, 32(5), 751-767.

Shukla, N. Thakur, A. K. Shukla, A. and Marx, D. T. (2014). Ion conduction mechanism in solid polymer electrolyte: an applicability of Almond–West formalism. Int J Electrochem Sci, 9, 7644-7659.

Skaudzius, R. Pinkas, J. Raudonis, R. Selskis, A. Juskenas, R. and Kareiva, A. (2012). On the limitary radius of garnet structure compounds Y 3 Al 5− x M x O 12 (M= Cr, Co, Mn, Ni, Cu) and Y 3 Fe 5− x Co x O 12 (0≤ x≤ 2.75) synthesized by sol–gel method. Materials Chemistry and Physics, 135(2), 479-485.

Solymar, L. and Walsh, D. (1993). Lectures on the electrical properties of materials.

Subramanian, M. Subramanian, R. and Clearfield, A. (1986). Lithium ion conductors in the system AB (IV) 2 (PO 4) 3 (B= Ti, Zr and Hf). Solid State Ionics, 18, 562-569.

Sun, F. Wang, R. Jiang, H. and Zhou, W. (2013). Synthesis of sodium titanium phosphate at ultra-low temperature. Research on Chemical Intermediates, 39(4), 1857-1864.

Tan, F. K. Hassan, J. and Wahab, Z. A. (2016). Electrical conductivity and dielectric behaviour of manganese and vanadium mixed oxide prepared by conventional solid state method. Engineering Science and Technology, an International Journal, 19(4), 2081-2087.

Taylor, B. English, A. and Berzins, T. (1977). New solid ionic conductors. Materials Research Bulletin, 12(2), 171-181.

Thangadurai, V. Shukla, A. K. and Gopalakrishnan, J. (1999). New lithium-ion conductors based on the NASICON structure. Journal of Materials Chemistry, 9(3), 739-741.

Tsagarakis, E. D. (2004). *Investigation of kinetic processes of gas-solid-ionic-conductor-interfaces with respect to potential application in chemical sensors*. Christian-Albrechts Universität Kiel.

Tsangaris, G. M. Psarras, G. C. and Kouloumbi, N. (1998). Electric modulus and interfacial polarization in composite polymeric systems. Journal of materials science, 33(8), 2027-2037.

Vijayan, L. and Govindaraj, G. (2009). Impedance spectroscopic studies of planetary ball-milled lithium titanium phosphate material. Physica B: Condensed Matter, 404(20), 3539-3543.

Vijayan, L. and Govindaraj, G. (2011). Structural and electrical properties of high-energy ball-milled NASICON type Li 1.3 Ti 1.7 Al 0.3 (PO 4) 2.9 (VO 4) 0.1 ceramics. Journal of Physics and Chemistry of Solids, 72(6), 613-619.

Wang, G. Bradhurst, D. Dou, S. and Liu, H. (2003). LiTi 2 (PO 4) 3 with NASICON-type structure as lithium-storage materials. Journal of Power Sources, 124(1), 231-236.

Wang, Y. Pu, Y. and Zhang, P. (2015). Investigation of dielectric relaxation in BaTiO 3 ceramics modified with BiYO 3 by impedance spectroscopy. Journal of Alloys and Compounds, 653, 596-603.

Will, G. (2006). *Powder diffraction: The Rietveld method and the two stage method to determine and refine crystal structures from powder diffraction data*: Springer Science & Business Media.

Winie, T. and Arof, A. (2004). Dielectric behaviour and AC conductivity of LiCF3SO3 doped H-chitosan polymer films. Ionics, 10(3-4), 193-199.

Wright, P. V. (1975). Electrical conductivity in ionic complexes of poly (ethylene oxide). British Polymer Journal, 7(5), 319-327.

Wu, F. Liu, Y. Chen, R. Chen, S. and Wang, G. (2009). Preparation and performance of novel Li–Ti–Si–P–O–N thin-film electrolyte for thin-film lithium batteries. Journal of Power Sources, 189(1), 467-470.

Wu, X. Lai, F. Lin, L. Li, Y. Lin, L. Qu, Y. and Huang, Z. (2008). Influence of thermal cycling on structural, optical and electrical properties of vanadium oxide thin films. Applied Surface Science, 255(5), 2840-2844.

Xu, X. Wen, Z. Yang, X. and Chen, L. (2008). Dense nanostructured solid electrolyte with high Li-ion conductivity by spark plasma sintering technique. Materials Research Bulletin, 43(8), 2334-2341.

Yu, S. Mertens, A. Gao, X. Gunduz, D. C. Schierholz, R. Benning, S. Hausen, F. Mertens, J. Kungl, H. and Tempel, H. (2016). Influence of microstructure and AlPO4 secondary-phase on the ionic conductivity of Li 1. 3 Al 0. 3 Ti 1. 7 (PO 4) 3 solid-state electrolyte. Functional Materials Letters, 9(05), 1650066.

Zangina, T. Hassan, J. Matori, K. A. Ahmadu, U. and See, A. (2016). Sintering behavior, ac conductivity and dielectric relaxation of Li 1.3 Ti 1.7 Al 0.3 (PO 4) 3 NASICON compound. Results in Physics, 6, 719-725.

许晓雄 温兆银 and 杨学林. (2007). Preparation and electrical properties of NASICON-type structured Li1. 4Al0. 4Ti1. 6 (PO4) 3 glass-ceramics by the citric acid-assisted sol–gel method.