SOLID SOLUBILITY AND IONIC CONDUCTIVITY OF Li_3TaO_4 AND RELATED PHASES

SYAFIQAH BINTI SHARI

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By

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in Fulfilment of the requirement for the degree of Master of Science

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Chair : Tan Kar Ban, PhD
Faculty : Science

Lithium tantalate solid solution, $Li_{3+5x}Ta_{1-x}O_4$ was prepared by conventional solid-state reaction at 925 ^{0}C over 48 h. The x-ray diffraction (XRD) analysis confirmed that these materials crystallised in a monoclinic symmetry, space group of *C2/c* and Z=8, which was similar to the reported International Crystal Diffraction Database (ICDD), 98-006-7675. β-Li_3TaO_4 has a rock-salt structure with a cationic order of $Li^+ : Ta^{5+} = 3 : 1$ over the octahedral sites. The lithium solubility was investigated by varying the lithium content through a proposed formula, $Li_{3+5x}Ta_{1-x}O_4$ ($0 \leq x \leq 0.059$). Ac impedance study releaved that Li_3TaO_4 exhibited the highest conductivity, 3.82 x 10^{-4} S cm^{-1} at 600 ºC. The activation energy in the range 0.63 – 0.68 eV were found in these materials.

In attempt to investigate the correlation between structural and electrical properties of the Li_2O-Ta_2O_5 systems, various chemical doping was performed. Tetravalent dopant, e.g. Ti^{4+} was introduced into the host structure with a proposed formula, $Li_3Ti_xTa_{1-x}O_{4-x}$ ($0.45 \leq x \leq 0.75$) at same synthesis condition. The formation mechanism involved a one-to-one replacement to Ta^{5+} cation by Ti^{4+} cation with the creation of oxygen vacancy for charge compensation. The phase changed from an ordered monoclinic to a disordered cubic phase when x increased from 0 to 0.40. While, a disordered cubic Li_3TaO_4 phase was observed at x = 0.45-0.75. These materials were refined and fully indexed with a space group of Fm-3m, Z=1 with a slightly smaller lattice parameters, a=b=c, in the range 4.1907(2) – 4.1681(2) Å. The unit cell contraction may be attributed to the replacement of larger Ta^{5+} (0.64 Å) by a smaller Ti^{4+} (0.61 Å) at the six-coordination. $Li_3Ta_{0.25}Ti_{0.75}O_{3.625}$ exhibited the highest conductivity among the Ti dopants at all temperatures, i.e. 2.33 x10^{-4} S cm^{-1} at 600 °C. The activation energies of these materials were estimated to be 1.16 - 1.32 eV.

On the other hand, an attempt was made to replace Nb by Ta using a proposed formula of $Li_3Ta_{0.5-x}Nb_xTi_{0.5}O_{3.775}$. A complete substitutional solid solution was formed, which was mainly due to the similar chemical characteristics between these pentavalent cations. The lattice parameters a=b=c were determined to be 4.1866(1) – 4.1849(4) Å.

$Li_3Ta_{0.4}Nb_{0.1}Ti_{0.5}O_{3.75}$ (x = 0.1) was found to exhibited the highest conductivity, i.e. 1.78 x 10^{-3} S cm^{-1} at 600 °C. The activation energies of these materials were estimated to be 1.35 - 1.49 eV.

Selected divalent cation dopants were chemically doped into the β-Li_3TaO_4 monoclinic phase. Both Mg and Zn dopants formed solid solutions with limit up to x = 0.1 only. The chemical formulae of $Li_{3-2x}M_xTaO_4$ (M = Mg or Zn) was proposed wherein two Li^+ ions were substituted by a divalent M^{2+} cation. Both doped samples exhibited relatively higher conductivity than that of parent material, β-Li_3TaO_4. This was probably attributed to the creation of lithium vacancy or well-connected grain. The conductivity values of $Li_{2.8}Mg_{0.1}TaO_4$ and $Li_{2.8}Zn_{0.1}TaO_4$ were determined to be 3.60 x 10^{-4} S cm^{-1} and 5.99 x 10^{-4} S cm^{-1} at 600 °C, respectively. Their resulted activation energies did not change significantly but remained reasonably low, i.e. 0.55 - 0.58 eV.

All the prepared samples appeared to be thermally stable as there are not thermal event detect in both TGA and DTA thermograms. The chemical stoichiometry of these samples was confirmed by ICP-OES, in which comparable values between theoretical and experimental concentrations were obtained. Structural analysis by FT-IR disclosed that several metal-oxygen bonds were found in the wavenumber range 250 - 1000 cm^{-1}. The irregular shaped grains in the range 0.95 – 10.82 μm were also shown by the SEM micrographs. This was further supported by TEM analysis as the results showed some spherical particles with quadrangle edges were found in the samples.

In attempts to investigate the possibility of new solid solution formation and to determine the electrical performed of the Li_2O-Ta_2O_5 materials, chemical dopants were performed. These materials showed different solid solution limit and moderate lithium ionic conductivity

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KELARUTAN PEPEJAL DAN KEKONDUKSIAN ION BAGI Li_3TaO_4 DAN FASA-FASA BERKAITAN

Oleh

SYAFIQAH BINTI SHARI

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Pengerusi : Tan Kar Ban, PhD
Fakulti : Sains

Larutan pepejal litium tantalat, $Li_{3+5x}Ta_{1-x}O_4$ telah disintesis secara tindak balas keadaan pepejal pada suu 925 ^{0}C dalam 48 jam. Analisis belauan sinar-x (XRD) telah mengesahkan bahan-bahan menghablur dalam simetri monoklinik, kumpulan ruang *C*2/*c* dan Z=8 seperti yang telah dilaporkan di dalam Pangkalan Data Belauan Kristal Antarabangsa (ICDD), 98-006-7675. β-Li_3TaO_4 mempunyai struktur garam batuan dengan tertib kation Li^+ dan Ta^{5+} 3:1 pada tapak oktahedron. Keterlarutan litium telah dikaji dengan pengubahan kandungan litium secara formula, $Li_{3+5x}Ta_{1-x}O_4$ ($0 \leq x \leq 0.059$). Kajian ac impedans Li_3TaO_4 menunjukkan kekonduksian yang paling tinggi, 3.82 x 10^{-4} S cm^{-1} pada 600 ºC. Tenaga pengaktifan dalam julat 0.63 – 0.68 eV ditentukan untuk bahan-bahan ini.

Dalam usaha untuk mengkaji korelasi diantara sifar struktur dan elektrik sistem Li_2O-Ta_2O_5, pelbagai pendopan kimia telah dibuat. Dopan tetravalensi, Ti telah diperkenalkan ke dalam struktur perumah dengan mekanisme, $Li_3Ti_xTa_{1-x}O_{4-x}$ ($0.45 \leq x \leq 0.75$) pada keadaan sintesis yang sama. Mekanisme pembentukan melibatkan penggantian satu kation Ta^{5+} dengan satu kation Ti^{4+} dan juga kekosongan oksigen demi pampasan cas. Peralihan fasa dari monoklinik teratur kepada kubik yang tak teratur berlaku apabila x meningkat dari 0 hingga 0.40. Manakala, fasa kubik Li_3TaO_4 tak teratur ditemui pada x = 0.45-075. Bahan-bahan ini telah diindeks sepenuhnya dengan kumpulan ruang, Fm-3m, Z=1 dan juga pengecilan parameter kekisi, a=b=c, yang berasa dalam julat 4.1907(2) - 4.1681(2) Å. Penyusutan sel unit adalah disebabkan oleh penggantian saiz jejari ion Ta^{5+} (0.64 Å) yang lebih besar jika dibandingkan dengan Ti^{4+} (0.61 Å) pada koordinasi-enam. $Li_3Ta_{0.25}Ti_{0.75}O_{3.625}$ menunjukkan nilai kekonduksian yang paling tinggi di antara dopan Ti pada semua suhu, iaitu 2.33 x10^{-4} S cm^{-1} pada 600 °C. Tenaga pengaktifan untuk bahan-bahan telah dianggarkan dalam julat 1.16 - 1.32 eV.

Selain itu, satu percubaan telah dilakukan untuk menggantikan Nb dengan Ta secara formula, $Li_3Ta_{0.5-x}\ Nb_x\ Ti_{0.5}O_{3.775}$. Larutan pepejal penggantian yang lengkap telah

dihasilkan atas sebab ciri kimia yang sama di antara kation pentavalensi. Parameter kekisi, a=b=c, telah ditentukan dalam julat 4.1866(1) - 4.1849(4) Å. $Li_3Ta_{0.4}Nb_{0.1}Ti_{0.5}O_{3.75}$ (x = 0.1) menunjukkan nilai kekonduksian yang paling tinggi di antara dopan Nb iaitu 1.78 x 10^{-3} S cm^{-1} pada 600 °C. Tenaga pengaktifan untuk bahan-bahan telah dianggarkan dalam julat 1.35 - 1.49 eV.

Dopan kation divalensi yang terpilih telah didopkan secara kaedah kimia ke dalam fasa β-Li_3TaO_4. Kedua-dua Mg dan Zn membentuk larutan pepejal terhad dengan nilai x = 0.1 sahaja. Formula kimia, $Li_{3-2x}M_xTaO_4$ (M = Mg or Zn) telah dicadangkan di mana dua Li^+ telah digantikan dengan M^{2+} kation. Kedua-dua bahan terdop telah menunjukkan kekonduksian yang lebih tinggi dari induk β-Li_3TaO_4. Ini mungkin disebabkan oleh kekosongan litium ataupun butiran yang rapat. Kekonduksian yang diperolehi oleh $Li_{2.8}Mg_{0.1}TaO_4$ dan $Li_{2.8}Zn_{0.1}TaO_4$ ialah 3.60 x 10^{-4} S cm^{-1} dan 5.99 x 10^{-4} S cm^{-1} pada 600 °C. Tenaga pengaktifan yang terhasil tidak menunjukan sebarang perbezaan yang ketara dan kekal rendah iaitu 0.55 -0.58 eV.

Semua sampel yang telah dihasilkan menunjukkan kestabilan terma kerana tiada kejadian terma ditemui di dalam kedua-dua termogram TGA dan DTA. Stoikiometri kimia untuk sampel ini ditentukan oleh ICP-OES, di mana nilai kepekatan diantara diteori dan eksperimen yang diperolehi adalah hampir sama. Analysis struktur oleh FT-IR menemui beberapa ikatan logam-oksigen di dalam julat nombor gelombang 250-1000 cm^{-1}. Bijirin berbentuk tidak teratur ditentukan dalam julat 0.95 -10.82 µm ditentukan dengan menggunakan mikrograp SEM. Ini disokong lagi dengan analisis TEM kerana keputusan menunjukkan zarah sfera bersama segi empat telah ditentukan di dalam sampel.

Dalam usaha untuk menyiasat kemungkinan pembentukan larutan pepejal yang baru dan menentukan prestasi elektrik keatas bahan-bahan Li_2O-Ta_2O_5, pendopan kimia telah dijalankan. Bahan-bahan ini menunjukkan had larutan pepejal yang berbeza dan kekonduksian ionik litium yang sederhana.

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Tan Kar Ban, PhD
Associate Professor
Faculty of science
Universiti Putra Malaysia
(Chairperson)

Zulkarnain Zainal, PhD
Professor
Faculty of science
Universiti Putra Malaysia
(Member)

Khaw Chwin Chieh, PhD
Lecturer
Lee Kong Chian Faculty of Engineering and Science
Universiti Tunku Abdul Rahman
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School of Graduate Studies
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Name of Member of Supervisory Committee : Prof. Dr. Zulkarnain Zainal

Signature : _____
Name of Member of Supervisory Committee : Dr. Khaw Chwin Chieh

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3D	Three dimensions
ac	Alternating current
DTA	differential thermal analysis
FT-IR	Fourier-transform infrared
ICDD	international centre for diffraction data
ICP-AES	inductively-coupled plasma-atomic emission spectrometry
JCPDS	Joint Committee on Powder Diffraction standards
SEM	scanning electron microscopy
TEM	transmition electron microscopy
TGA	thermogravimetry analysis
XRD	X-ray diffraction
A, b, c, α, β, γ	lattice constant
A	area
A_w	Warburg coefficient
C	Capacitance
C_b	Bulk capacitance
C_{dl}	Double-layer capacitance
C_{gb}	Grain boundary capacitance
C_o	Vacuum capacitance
d	d-spacing
D	Density
e	Charge of the conducting species
e_o	Permittivity of free space
E	Electric field
E_o	Activation energy
ε'	Relative permittivity
ε^*	Complex permittivity
f	Frequency
F	Faraday constant
h, k, l	Miller indice
I	Current
j	Flux of charge
J	Density of the current
τ	Thickness
λ	Wavelength
M	Dopant introduced
M'	Real part of modulus
M"	Imaginary part of modulus
M*	Complex modulus
μ	Mobility of the species
R	Resistance
R_b	Bulk resistance
R_{gb}	Grain boundary resistance
σ	Bragg angle

ι	Electrical relaxation times
T	temperature
ω	Angular frequency
Z	Formula unit
Z	Impedance
Z′	Real part of impedance
Z′′	Imaginary part of impedance
Z*	Complex impedance

CHAPTER 1

INTRODUCTION

1.1 Electroceramics

Electroceramics are advanced materials which are used in electrical, optical and magnetic applications (Bharadwaj *et al.*, 2012). This includes several groups of dielectric and conductive ceramics. In general, dielectric ceramics counting a large number of materials which can be divided either linear or non-linear dielectric. On the contrary, conductive ceramics are more numerous, including superconductors, semiconductors and conductors of which the charge carrier could be either ions or electrons (Setter, 2001).

There are two categories of conductive ceramics which are either electrically homogeneous or heterogeneous (Table 1.1). The electrically homogeneous materials, e.g. ionically conducting ceramics or microwave dielectrics, usually have high dense microstructure of which the grain boundaries have less influence on their electrical properties. On the contrary, electrically heterogeneous materials, e.g. varistors and barrier capacitors, have properties which are controlled by the structure of interfacial region at grain boundaries and grain surface. In additional, these materials rely strongly on the control processing control by a series of post-sintering heat treatments, so that the correct defect segregation, degree oxidation or reduction at the grain boundaries and surfaces could be achieved (West *et al.*, 2004).

Ceramic materials have been used in a wide range of industrial applications, e.g. electrical and electronic components, superconductors, catalysts, and automobile components. These materials are generally polycrystalline, which are comprised of inorganic, non-metallic, non-water soluble compounds that show ionic contribution in their chemical bond. Other examples of applications including transportation, industrial production, power engineering, medicine and health care, consumer electronic and communication (Setter and Waser, 2000).

Table 1.1: Electrical microstructure of electroceramics (West *et al.*, 2004)

Electrically homogeneous	**Electrically heterogeneous (grain boundary controlled)**
Ionic conductors	Varistors
Mixed conductors	Barrier layer capacitors
High T_c superconductors	PTC thermistors
Microwave dielectric	Gas sensors

1.2 Solid Solution

A solid solution is mostly a crystalline material that has variable composition and its properties usually vary with composition. Generally, a simple solid solution could divide into two types either substitutional solid solution or interstitial solid solution. For substitutional solid solution, atoms or ions that replace each other must have the same charge in the parent structure. On the other hand, interstitial solid solution has introduced species that to occupy a site that is normally empty and no ions or atoms are left out in the crystal structure.

Dopants are generally introduced into a host structure in order to enhance the electrical properties (Moulson and Herbert, 2003). Several requirements must be met: first, the ions that replace each other must have the same charge to maintain elecroneutrality, else a structural change involving either vacancies or interstitial is required. Second, the replacing ion must be fairly similar in size. For example, the formation of metal alloy would allow 15 % difference in the ionic radii. In the case of extensive solid solution, ions of similar size may substitute each other easily and the resulted solid solution is stable at all temperatures.

On the other hand, doping with aliovalent cations (the replacing and replaceable ion have difference oxidation states) would require creation of vacancies or interstitials (ionic compensation) or electron or holes (electronic compensation). Therefore, substitution of a cation with lower valence may result in either anion (oxide ion) vacancies or interstitial cations. Meanwhile, for substitution by higher valence cations would give interstitial anions and cation vacancies (West, 1999).

In this study, few dopants with different charges have been introduced into host structure in order to investigate the influence of these on doping mechanism and electrical properties. The dopants are chosen, e.g. Mg^{2+}, Zn^{2+}, Ti^{4+}, and Nb^{5+}. The selection of these dopants is mainly based on their chemical and physical properties. These are the determining factors that influence the formation of new solid solution. Divalent cations, Mg^{2+} and Zn^{2+} are expected to form an extensive solid solution due to the factor of charge as the introduction of these dopants may create lithium vacancies for charge compensation, where two Li^{+} ions are substituted by one divalent ion. Meanwhile, a tetravalent cation, (e.g. Ti^{4+}) is selected due to the size of ionic radii between the guest and host is less than 15%, therefore the formation of an extensive solid solution may be possible. This Ti^{4+} is used as a dopant for substitution at the Ta-site of β-Li_3TaO_4. The formation will create more oxygen vacancies for the charge compensation in order to preserve the overall electroneutrality of the system. Lastly, pentavalent cations are chosen due to the replacing ion Nb^{5+} directly replaces the same charge Ta^{5+} ion in the parent structure, thus neither vacancies nor intersitialcies are required to maintain the overall electroneutrality of the system. Furthermore, both $Nb^{5+}$and Ta^{5+} have an identical ionic radii (r= 0.64 Å) at the six coordination, thus the extensive solid solution are expected to form. In this study, the effects of all dopant are determined in term of solid solubility, structural and electrical properties.

1.3 Ionic Conductivity and Solid Electrolytes

The first observation of conductivity in solid electrolytes was more than 150 years ago. Ionic conductivity occurs in materials known as solid electrolytes, superionic conductors or fast ion conductors with ions acting as charge carriers. While, for mixed conduction usually refers to the materials with good electronic conduction. Superionic conductor or fast ion conductor is good for ionic conduction with negligible electronic conductivity (Kumar and Yashonath, 2006).

In solid electrolytes, either cations or anions are free to move throughout the structure, i.e. they are not confined to specific lattice sites. Therefore, solid electrolytes are well known as intermediate between typical ionic solids, all ions are fixed on their lattice sites in a regular 3 dimensional structures. On the contrary, all ions are mobile in liquid electrolyte which does not have a regular structure. Usually solid electrolytes are stable at high temperature, while on cooling may they transform to a polymorph with a low ionic conductivity at low temperatures. The types of crystal structure shown are Figure 1.1.

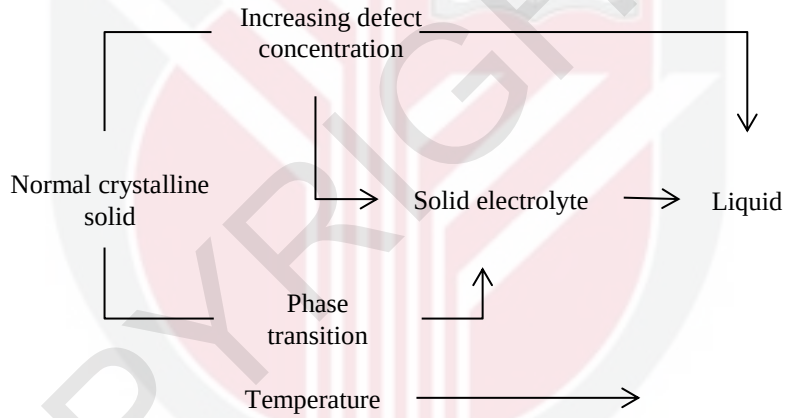

Figure 1.1: Solid electrolytes as intermediate between normal crystalline solids and liquids (West, 1999)

In addition, ionic conductivity is related to the presence of defects or disordered structure that may have a variation of positions by replacement of certain ion in the crystal structure. These materials have a high ionic conductivity can be classified into four groups with thermally induced defects, impurity-induced defects, crystal structure disorder and amorphous character (Koller, 1994).

1.3.1 Ionic Conductors

Solid ionic conductors are generally polycrystalline compounds in which electric current is carried by charged atoms, i.e. by ions. The passage of current is associated with mass transfer and such ionic conductors are called solid electrolytes. Examples of

solid ionic conductor including doped ZrO_2, AgI, β-Al_2O_3 and CaF_2. Ionic conduction in ceramic materials is associated with the movement of ionic point defect, the creation or movement requires energy. The conductivity increases with increasing temperature for all materials except metal and superconductors. Therefore, ceramic solid electrolytes are suitable for high temperature application. (Rickert, 1978; Moulson and Herbert, 2003). The examples of ionic and electronic materials are tabulated in Table 1.2.

Table 1.2: Typical values of electrical conductivity of ionic and electronic materials (West, 1999)

Conduction mechanism	**Materials**	**Conductivity, σ (ohm^{-1} cm^{-1})**
Ionic conduction	Ionic crystals	$< 10^{-18} – 10^{-4}$
	Solid electrolytes	$10^{-3} – 10^{4}$
	Strong (liquid) electrolyte	$10^{-3} – 10^{4}$
Electronic conduction	Metals	$10^{-1} – 10^{5}$
	Semiconductors	$10^{-5} – 10^{2}$
	Insulators	$< 10^{-12}$

In ionic solids, ions are trapped on their lattice sites and they rarely have enough thermal energy to escape from their lattice site but to vibrate continuously. In The process of migration, hopping or diffusion is required, therefore ions must be able to escape and move into adjacent lattice sites. If some sites are vacant, the adjacent ions can hop into these vacancies, thus leaving their own sites vacant or some ions in interstitial sites which can hop into adjacent interstitial sites. Thus, ionic conduction is easier at high temperatures especially ions could vibrate more vigorously and the defect concentrations are higher (West, 1999).

For any material and charge carrier, the specific conductivity, σ proportionality constant between the current density, j and the electric field, E is given by

$$j/E = \sigma = \sum_i n_i e_i \mu_i \tag{1.1}$$

While, for ionic conductivity, σ

$$\sigma = N_{ion} e\ \mu_{ion} \tag{1.2}$$

Where N_{ion} is the number of ion which can change their position under the influence of electric field, μ_{ion} is the mobility of these ions and *e* is the elementary charge.

Factors that influence the conductivity are the concentration of charge carrier, temperature, the availability of vacant-accessible sites (which is controlled by the

density of defects in the crystal) and ease of jumping of ions to another site. The numbers of jumping or hopping ions to a neighboring site is controlled by activation energy. The activation energy is a phenomenological quantity as it indicates the free energy barrier an ion has to overcome for a successful jump between the sites. Among the various factors that influence the ionic conductivity of a materials the activation energy is the utmost important factor since its dependence is exponential from Arrhenius expression (Kumar and Yashonath, 2006). The temperature dependence ionic conductivity is usually deduced by using Arrhenius equation, where the graph of $\log_e \sigma$ against 1/T should give a straight line with the slope $-E_a/R$.

$$\sigma = A \exp(-E_a/RT) \tag{1.3}$$

Where σ is the conductivity at temperature T in Kelvin, K, R is the Boltzman's constant, E_a is the activation energy and A is called the pre-exponential factor, which depends on the vibration frequency of the potential mobile ions and same structural parameter (West,1999).

1.4 Application of Ionic Conductivity

There are numerous examples of materials with high ionic conductivity in the solid state, e.g. Ag^+ ions in $RbAg_4I_5$, Li^+ ions in α-Li_2SO_4 (> 570 ºC) and Na^+ ions in β,β''-alumina. The high ionic conductivity value are found in the range 10^{-3}- 10^1 Ω^{-1} cm^{-1} with activation energies in the range 0.1-0.3 eV (Lee and West, 1991). The applications of solid electrolytes in electrochemical devices have several advantages and this includes a long life, high energy density etc. Therefore, there are suitable for compact power batteries used in pace-maker, mobile telephones, laptops etc. Besides, they are can used to study thermodynamics and kinetics problems, and to build fuel cell, batteries, sensors and chemotronic components (Rickert, 1978).

In addition, ionic conduction material is also found in sodium-sulfur cell. The cell systems have been developed with other solid electrolytes, some of these being characterised by very long lifetime. The storage time is more than ten years, whose lifetime cannot be even approached with conversional batteries. Rickert (1978) found that the energy density of the sodium-sulfur cell is much greater than the customary lead accumulators. Moreover, the cell can be recharged by reversing the direction of the current. These reasons present the great interest in this sodium-sulfur cell for large-scale energy storage and for electric motor vehicles well known as electrotraction.

Ionic conducting ceramic such as cubic ZrO_2 which has heavily doped acceptor, are used for electrochemical oxygen sensors in car and for high-temperature solid oxide fuel cells (SOFCs). In addition, SOFC could produce electricity directly from oxidising a fuel. It is about 2-3 times more efficient if compared to a thermal engine as SOFC converts chemical potential to the electrical energy. By, reversing the current flow this can induce the full cell to be an electrolyser and energy storage (Setter and Waser, 2000).

In 1972, a cardiac pacemaker was first implanted into a human, which was powered by Li/I_2. Lithium/iodine pacemaker battery worked even though the electrolytes have a low conductivity 10^{-7} S/cm at room temperature. The battery was suitable as the application required an isothermal operation at 37 ºC, at a very low rate (10-year rate). The cell was a Wilson Greatbatch Model 702/C. To date, there are several million persons have benefited from these implantable devices (Ginnings *et al.*, 1930; Owens *et al.*, 1986).

1.5 Problem Statement

Intensive research has been focused on the materials of $LiTaO_3$ and $LiNbO_3$ systems due to their interesting optical properties. However, a structurally related β-Li_3TaO_4 has received less attention and limited information is available in literature review specifically about the structural and electrical properties. Few reported compositions may have been a mixture that contain trace amount of other secondary phases. Besides that, the study concerning chemical doping of the β-Li_3TaO_4 is rarely reported. Therefore, this research is undertaken to study the formation mechanism and to determine the optimised synthesis condition for the sample preparation. The effect of chemical doping on the electrical properties is also part of the investigation. Hence, the correlation between composition and the electrical properties of various phases and other related solid solution in the Li_2O – Ta_2O_5 systems has been discussed systematically.

1.6 Objectives

The objectives of this research are:

1. To synthesise β-Li_3TaO_4 phase and other new related phases in the Li_2O-Ta_2O_5 system.
2. To study the thermal stability, structure and subsolidus solution of the prepared samples.
3. To investigate the effect of chemical dopants, e.g. TiO_2, Nb_2O_5, MgO and ZnO in the Li_2O-Ta_2O_5 system as to explore the possibility of new solid solution formation and determine their electrical performance by using ac impedance spectroscopy.

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