CHAPTER 1- Introduction

In this chapter, an introduction of fast ion conducting materials and NASICON materials is given.

1.1 Introduction – SOLID STATE IONICS

Ions are formed due to dissociation of chemically neutral compounds which generally have ionic bonds or polar molecules. The dissociation results in release of electrochemical energy. The ions thus formed, diffuse and travel across the electrochemical interfaces (and get deposited on the electrodes of opposite polarity – in case of batteries). Solid State Ionics by definition concerns a study of transport properties of charged ions in bulk of a solid material. The field of Solid State Ionics studies the transport of charges across solid interfaces within and across the solid materials. Ionic motion is exhibited in various materials like polymers, glasses, composite materials (a hybrid mix of organic and inorganic materials), ceramics etc.

The transport of positive ions like Ag^+, Na^+, Li^+ and negative ions like F^- and O^{2-} across grains (bulk), grain boundaries are widely studied. The study of transport of charged ions (positive or negative) has wide application value in the fields of electrochemical devices like chemical sensors, batteries, fuel cells and as memory devices in information technology applications (R-RAM), and as electrochromatic displays are well known.

The usage of principles of Solid State Ionics in solid state batteries is well known. The demand of high energy density power sources, which are not only light in weight, chemically stable, leakage proof but also can withstand environmental extremes like very high or low temperatures, pressure (altitude) differences etc., are needed in today's fast paced applications. Today, compact power sources (batteries) are employed in travel, training, medical and industrial applications like laptops, mobile phones, navigation devices like Global Positioning Systems (GPS), palmtops etc. High energy density power sources which are light in weight are desirable in applications like hybrid vehicles, military and communication applications and medical technologies [1-5]. However, the most important short comings of today's power sources remains their short life and their need to be charged frequently. The demand of such ideal power sources is undoubtedly going to soar in years to come.

Although enormous demands have been put on today's battery by ever increasing applications, the basic working principle and construction of a battery remains the same since the time it was first demonstrated by Alessandro Volta (1745-1827) 214 years ago (24th March 1800) at the University of Pavia in Italy [6]

1.1 Working of a battery:

A solid state battery consists of a positive electrode called a cathode, a negative electrode called an anode and a conducting medium called electrolyte. Cathode is located at one end of electrolyte while anode at the other end. These three materials are in good physical contact in their correct sequence. Positive ions released from anode travel via the electrolyte medium to cathode. The cathode due to its special micro structure accommodates positive ions that arrive from anode via electrolyte. Thus there is a ionic charge accumulation within cathode and its overall charge becomes positive.

The half cell reaction at anode during discharging cycle, is as follows:

$$\mathrm{M} \rightarrow M^{n+} + ne^{-} \qquad \text{……..……(1.1)}$$

The electrons are released from anode and travel to cathode. Meanwhile the ions released from anode due to above reaction travel upto cathode and intercalate in its microstructure. The reaction at anode is called oxidation where electrons are released. The electrons are taken in at cathode and this reaction is called reduction. During the discharge mode of the battery, for example, the applications like mobile phone run due to this current in the outer circuit. The current in outer circuit continues until there is ionic charge saturation at the cathode. After charge saturation the cathode can no more accumulate positive charges. Hence the number of electrons reaching cathode in the outer circuit also decreases.

A potential difference from the outer circuit is applied in reverse bias condition to charge the battery again. In this condition, a positive charge at cathode and negative charge at anode is applied so that the ions from cathode migrate back to anode. This restores the battery to its initial state.

The performance of a battery depends, chiefly, on the transport properties of the electrolyte material through which ion migration takes place and the cathode that accepts the ions and releases electrons in the outer/external circuit. It implies that the electrolyte as well as the cathode material both should possess excellent ionic conducting properties and in addition to that the cathode material should also possess good level of electronic conductivity. Hence it is imperative to study the ionic conduction within these solids.

The study of ionic conduction in solids was for the first time demonstrated through the works of Michael Faraday. He discovered that PbF_2 and Ag_2S were good ionic conductors. Subsequent and systematic research in this field led to the discovery of many other solids which could conduct ions. Based on these studies the ion conducting solids can be classified into three broad categories – the slow ion conducting solids, the normal ion conducting and the fast ion conducting solids. Only the *fast ionic conductors* (FIC) – are used in battery and other applications of electrochemical interest. Following are some of the properties that are needed in a good FIC solid:

1) FICs have ionic conductivities of the order of 10^{-1} to 10^{-6} S/cm.
2) Most of the charge and mass transport within these materials is due to conduction of ions.
3) The FIC contain a large number of conducting ions. Their number increases very less when the temperature is increased (although the ionic conductivity increases rapidly (a few orders of magnitude) with temperature.
4) The activation energy for ionic transport is less compared to other solids.
5) The migration of ions is due to defects within the solid.

The FIC solids can be classified in two broad classes based upon their microstructure. They can either be crystalline with regular and periodic structure or can be amorphous (non crystalline) glassy solids with a short range order (10^{-8} Å). Crystalline materials are generally used in most successful battery applications especially as cathode part.

The conducting ion species used in batteries are Ag^+, Li^+, Na^+, F^- etc. In a typical battery appropriate cathode and anode materials are used to accommodate and help migrate, the ionic charges within the solid materials.

1.2 Devices using FIC materials

FIC materials are used in various applications in today's fast paced domestic and industrial life style. Some appliances of them can be put in broad classes as follows:

1.2.1 Gas sensors

Sensors to detect CO, CO_2, SO_2, NH_3, NO_x and other gases are fabricated using NASICON materials which use oxygen vacancy diffusion. The basic working principle of a sensor is described below:

$$2CO_2 \rightarrow 2CO + O_2 \qquad \text{...........(1.2)}$$

Before the gas reaches the electrode, the dissociation of the gas molecule takes place to liberate oxygen ions. The oxygen ions at the interface of gas and electrode diffuse into the material to occupy oxygen vacancy sites in the electrode while a corresponding positive charge exists at the opposite electrode. Due to the charge accumulation at the two electrodes, a potential is developed in the outer circuit. This potential drop can be measured either in terms of potential difference (for potentiometric sensors) or as current (ampherometric sensors) depending upon the sensitivity of material, the accuracy requirement etc.

1.2.2 Ion Selective Electrode

Ion selective electrodes are employed in bio medical applications to measure the pH or Na^+ ion content in blood to rate kidney function. These electrodes measure the partial pressure due to selected ionic charge on the electrode. The Na^+ forms a space charge layer at the interface of liquid and the electrode and in turn generates a corresponding voltage pulse in the outer circuit which is proportional to the Na^+ content at the interface.

1.2.3 Supercapacitors

Supercapacitors are the devices which are capable of accumulating large number of charges on the plates. They are the materials in which the positive ionic charges are intercalated at one plate of the capacitor with respect to a neutral or negatively charged other plate. The diffusive transport of ions plays an important role in the supercapacitors.

1.2.4 Battery material

The study of transport and electrical properties of ions is also employed for electrolytes and electrodes in a battery. The transport of ion to intercalate and decalate through the cathode material is still a highly persuaded field. Lithium Iron Phosphate ($LiFePO_4$) doped with transition metals like cobalt or nickel have an olivine structure is amongst the most widely studied electrode material while Lithium Titanium Phosphate ($LiTi_2(PO_4)_3$) with a rhombohedral symmetry is a famous example of widely studied electrolyte for lithium ion batteries. Polyethylene oxide (PEO) doped with lithium salts are organic electrolyte materials which are widely studied for lithium ion batteries.

1.2.5 Solid Oxide Fuel Cells (SOFC)

Solid Oxide Fuel Cells are termed as future of domestic, vehicular and industrial power sources. They use hydrogen, oxygen and organic compounds like methane to chemically react and form by-products like water and carbon dioxide. In this process they convert chemical energy into electrical energy. The chemical reactions take place at elevated temperature of 1000 °C or more. Due to such high temperatures the cost of the SOFCs also increases. This is a major bottleneck in the development of the SOFC technology.

1.3 Fast ion conducting materials

Based upon the conducting ionic species, there are following broad classes of inorganic Fast Ion Conducting materials.

1.3.1 Lithium Ion Conductors

Li^+ ion conductors are primarily employed in energy storage applications (mostly batteries) because of the high energy density and high current density the lithium conducting compounds provide. Li^+ is light weight cation and has low activation energy in the compounds in which it is used.

The lithium based crystalline inorganic compounds belong to different categories like like Nasicon, glasses, thin films, polymer compounds etc. A detailed classification and discussion about the different inorganic crystalline Li^+ ion conducting compounds and their applications are presented in section 1.5.

1.3.2 Sodium Ion Conductors

A lot of research is currently going on towards fabricating sodium ion batteries due to its low cost and ease of handling. β-Alumina is perhaps the most well known of the sodium based fast ion conductors which has a room temperature ion conductivity of 10^{-2} S/cm [7,8]. A large number of Na-ion conducting systems like $NaTi_2P_3O_{12}$ and $NaZr_2P_3O_{12}$ have been reported [9, 10, 11]. Thin films formed due to sputtering, glassy amorphous compounds and polymer materials containing Na^+ ions as conducting species are widely studied Fast Ion Conducting conductors.

1.3.3 Silver Ion Conductors

α–AgI is the most well known among the silver ion conducting compounds. Glassy compounds made from modifier and formers like $AgI\text{-}B_2O_3\text{-}V_2O_5$ are ionic in nature. Many workers have used a combination of glass formers like B_2O_3, V_2O_5, P_2O_5, glass modifiers like Ag_2O or Al_2O_3 and dopant salts like AgI, CdI_2 etc. [12, 13, 14] to form silver based fast ion conducting glassy systems. Besides chalcogenide systems like $Ag_2S\text{-}Ag_2Se_3$ have also been found to form amorphous or crystalline FIC solids. Silver based polymer electrolyte systems are also widely studied.

1.3.4 Copper Ion Conductors

Copper ion conducting fast ionic conducting materials are formed by stabilizing highly conducting phase like α–CuI. $CuI\text{-}Cu_2O\text{-}MoO_3$ and $CuI\text{-}Cu_2O\text{-}P_2O_5$ are some of the commonly studied compounds of Cu FICs.

Cu based compounds are also used as mixed ion conducting compounds. Bussereau et al [15] have studied the crystalline structure of compounds like $Cu^{1+}Ti_2(PO_4)_3$ etc.

1.3.5 Fluorine Ion Conductors

PbF_2 was amongst the first ionic compounds to have fast ionic conduction. CaF_2 and SrF_2 have moderate fluoride ion conduction. Owing to its highly electronegative nature and small ionic radii (amongst all halogens), Fluoride ions (F^{-}) are ideal for conduction and used for rechargeable batteries. LaF_3 compounds have exhibited ionic conductivity of up to 10^{-3} S/cm [16].

1.3.6 Proton Conductors

Protons (H^+ ions) are very small in size compared to other ordinary ions. Hence they can pass through passageways and bottlenecks easily. All the same protons cannot move on their own but bind with other molecules to form such units like H_3O^+, NH^{4+} etc which move from one site to the other. Sulfonated fluorocarbons, NAFION, sulfonated polybenzimidazole (SPBI) etc are some well known proton conducting compounds. Proton conducting materials find application in fuel cells, hydrogen and humidity sensors, membranes for water electroanalysers etc.

1.3.7 Oxygen Ion Conductors

The oxide ion conductors like CeO_2, Yttrium Stabilized Zirconia (YSZ), ThO_2, ZrO_2 are commonly known oxide conductors. The conductivity can be enhanced by doping aliovalent oxides like Ca^{2+}, Y^{3+} etc. $La_{1-x}Sr_xGa_{1-y}Mg_y\,O^{3-}_{0.5(x+y)}$ is one of the best oxide conductors. YSZ is extensively studied for its use in fuel cells [17].

1.4 Properties of Cathode Material

The main problem that inhibits growth for lithium ion batteries as a universal technology is the development of proper cathode material. If anode is the source of Lithium ion, the cathode is the sink of Lithium ions. The electrolyte must conduct the lithium ions but must not conduct electrons while keeping anode and cathode separate. Cathode is an important material in case of solid state lithium ion batteries because it must have the following characteristics:

A cathode material must;

a) Contain a readily reducible / oxidizable ion (e.g., transition metal ions)
b) React with Lithium reversibly i.e., structure does not change when Lithium is added or intercalated.
d) React with lithium very rapidly i.e., high power density
e) Has to be a good electronic conductor which means easy addition / removal of electrons.
f) Should be structurally stable during charge-discharge
g) be environmentally safe (‘green’)

Thus the material has to have a closely-packed layered structure where transition metal ions are accessible for redox reaction with Lithium and will result in high energy density cathode materials.

Some of the examples of such materials are the compounds like $LiM(PO_4)_3$ (M = Fe, Mn, Ni) [18, 19, 20], $LiCoO_2$ [21, 22, 23], $LiTi_2(PO_4)_3$ [24] etc.

1.5 Lithium Based Inorganic systems

Below are given some of the classes of inorganic Lithium ion conducting materials with crystalline structure.

1.5.1 Li_4SiO_4 Compounds And Related Phases:

Compounds of the type Li_4SiO_4 have monoclinic structure. When in these solid solutions Si^{4+} is replaced with either by divalent cations like Zn^{2+}, Mg^{2+} etc, the conductivity rises in the order of ~ 10^{-2} S/cm at higher temperatures like 400° [25,26] When Si^{4+} is replaced by trivalent cations like Al^{3+} or Ga^{3+} the ionic conductivity falls as the ionic radius of the replacing ions increases. Compounds like Li_5AlO_4 have applications in high voltage Lithium cells [27].

1.5.2 NASICON Compounds

Ever since the discovery of Na – based Nasicon compounds in 1976 by Hong and Goodenough [28] the Sodium and Lithium based NASICON systems like $Li_{1+x} M_{2-x} M'_x(PO_4)_3$ where M =Ti^{4+}, Ge^{4+} and Hf^{4+} and M' = In^{3+}, Sc^{3+}, Ga^{3+} [29-33]. The NASICON compounds are a widely studied class of materials for their potential uses as sensors, battery electrode etc. Highest conductivity so far for titanium based phosphate NASICON compounds has been ~10^{-3} S/cm when Ti^{4+} is partially replaced by Al^{3+}.

1.5.3 Lithium Rare Earth Titanate Perovskites

Perovskites (general formula ABO_3) and related structures are extremely important solid state materials and have uses in a variety of applications such as high Tc superconductors, cathodes in solid oxide fuel cells, materials with giant magnetoresistors (GMR) and in Ferroelectrics. High lithium-ion conductivity of $1 x 10^{-3}$ S/cm was demonstrated in $Li_{0.5-3x}$ $La_{0.5+x}$

TiO_3 [34–38]. Batteries comprising of $Li_{0.5-3x}$ $La_{0.5+x}$ TiO_3 as electrolyte material have been developed with this kind of structure.

1.5.4 Composite Material

Composite materials comprise an intimate mixture material of lithium-ion conducting solid electrolyte and insulating ceramic powder [39]. First such system to be studied was LiI-AlO for which the conductivity was enhanced significantly with respect to LiI [40]. The enhancement is due to an increase in interfacial transport by one to two orders of magnitude. Other composite systems studied include Li_{16-2x} Zn_x $(GeO_4)_4$ [LISICON]-ZrO_2 [41]; and Li_3PO_4–Al_2O_3 [42]; Li_2SO_4 –Al_2O_3 [43,44]; $LiNO_3$–Al_2O_3 and $LiSO_4$–Al_2O_3 [45]. Relatively less number of conductivity studies have been undertaken for high temperature for this class of materials.

1.5.5 Lithium Metal Halides

The Lithium Metal Halides have a general formula Li_2MCl_4 where M = Mg, Ti, Cd, Cr, Co, Zn and Fe. These compounds have inverse spinel structure in which Li ions occupy tetrahedral and octahedral sites with M^{3+} ions. Almost all the chlorides exhibit phase transitions between 300 - 500°C [46]. Li_2MnCl_4, Li_2MgCl_4 and $LiCdCl_4$ are some of the compounds studied [47-50]

1.5.6 LISICONs

This is an abbreviation for Lithium Super Ionic Conductors. Examples for this class of compounds includes series $Li_{2+2x}Zn_{1-x}(GeO_4)$ has been studied [51,52] of which $Li_{14}Zn(GeO_4)_4$ has the best Li^+ conductivity of 0.125 S/cm. Another group of LISICON compounds is γ-Li_3PO_4. The general formula for another group of LISICON compounds can be written as $Li_{3+x}M_xN_{1-x}O_4$ where M = Si, Ge, Ti and N = P, As, V, Cr [53]. LISICON compounds are chemically stable and have good room temperature conductivities.

1.5.7 Lithium Garnets

The general formula of this class of compounds is $Li_5LaM_2O_{12}$ (where M = Ta, Nb). This class of ionic conductors was discovered by Thangadurai and Weppner [54]. Low valence ions like Ba^{2+}, Sr^{2+} and K^+ can be doped in the above mentioned compound to replace La^{3+} [55, 56]. A maximum conductivity of $4x10^{-5}$ S/cm at room temperature was obtained for $Li_6La_2BaTa_2O_{12}$, $Li_5La_3Ta_2O_{12}$, $Li_5La_3Sb_2O_{12}$ and $Li_6SeLa_2Sb_2O_{12}$ [57] are some other compounds that belong to this category. There is a variation of Li^+ ions occupation at tetrahedral and octahedral sites with temperature within the Li-garnet structure.

Apart from the inorganic solids with crystalline structure, there are amorphous classes of solids which also fall in this category of Lithium based solid fast ionic conductors.

Lithium based glassy electrolytes are generally divided in two types – oxide based glasses and sulphide based glasses. Oxide based glasses are generally prepared by melt quenching technique. Li_2O-Al_2O_3-TiO_2-P_3O_{12} types of Nasicon glassy system are well known from the works of Fu [58] and Mariappan et. al [59-62] are based on the Lithium glassy samples. Lithium aluminosilicate ceramic glass system ($LiAlSi_2O_6$) also falling in this class of compounds, has been well studied [63, 64].

$GeS^{2+}Li_2$ - S^+LiI is a well known Sulphide glass-forming system. Other sulphides like Ga_2S_3 and La_2S_3 are also doped. A maximum Li^+ ionic conductivity of 10^{-3} S/cm at room temperature has been obtained in the sulphide glasses. The sulphide glasses are hygroscopic and hence not very suitable for Lithium batteries. High conductivities were reported for Li_2S–SiS_2 glasses [65, 66] and with P_2S_5 and LiI and especially with Li_4SiO_4 [67]

1.6 LIPON, LISON and LIPOS Glassy Systems

LIPON stands for Lithium Phosphorus Oxinitride (Li_3PO_4) which has a γ phase. This compound was described by Bates et al [68]. Thin films of LIPON can be obtained by RF sputtering by varying nitrogen partial pressure. The principal advantage of LIPON glasses is their recyclability and it is employed in Lithium batteries already [69].

LISON: $Li_{0.29}S_{0.28}O_{0.35}N_{0.09}$ is another Li^+ ion conducting system with an ionic conductivity $2x10^{-5}$ S/cm [70]. Another glassy system, known as LIPOS ($6LiI$–$4Li_3PO_4$–P_2S_5) also exhibits good Li^+ ion conductivity at room temperature. All of the above systems are unstable in bulk form [71].

Other systems like LiBSO ($0.3LiBO_2$–$0.7Li_2SO_4$) [72] and LiSiPON ($Li_{2.9}Si_{0.45}PO_{1.6}N_{1.3}$) [73] are also well studied for Li^+ ion conductivity; however they have relatively low conductivity and low cyclability.

1.7 A Brief Introduction Of NASICON Materials

NASICONS (Na – Super Ionic Conductors) materials are an important class of crystalline materials which have a structure which is conducive for Lithium or Sodium ion migration. The general, chemical formula of these materials is $ABXO_4$. Hong and Goodenough first predicted the existence of such a class of solid material in 1976 [28]. Since then a substantial body of research has been dedicated into the study of this class of materials as electrolytes for their applications in Lithium ion conducting batteries. Various ionic species like Li^+, Na^+, Ag^+ etc have been investigated for their migration into the NASICON type structure. Lithium Titanium Phosphate with chemical formula $LiTi_2(PO_4)_3$ (LTP) is one of the most extensively studied titanium phosphate NASICON materials. It has a rhombohedral ($R\bar{3}c$) symmetry.

Two cationic vacancy sites M1 and M2 are formed in this phase as a result of sharing of oxygen atoms at the corners from TiO_6 octahedra and PO_4 tetrahedra. M1 vacancy sites are formed between the mutually facing TiO_6 octahedra while M2 sites are formed between the PO_4 tetrahedra joining the parallel chains. M1 sites have more probability of being occupied by Li^+ cation. Li^+ ions diffuse between the M1 and M2 sites within the solid 3D framework of the materials when the Li^+ ions intercalate and decalate during charging and discharging cycles of a battery. In later part of 1980s Aono *et al.* [29] found that doping by trivalent cations like Al^{3+} to replace tetravalent Ti^{4+} cations in the $LiTi_2(PO_4)_3$ (LTP) lattice increases the Li^+ ion conductivity of the system. However this replacement happens only if the tri and tetravalent cationic radii are comparable. Due to the replacement by a cation of different oxidation state, the net charge of the lattice decreases which is compensated by migration of a positive and light weight Li^+. This enhances the Li^+ conductivity in the $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ system. Of all the titanium based systems studied the system with chemical formula $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ has been found to have maximum Li^+ conductivity of 10^{-3} S/cm.

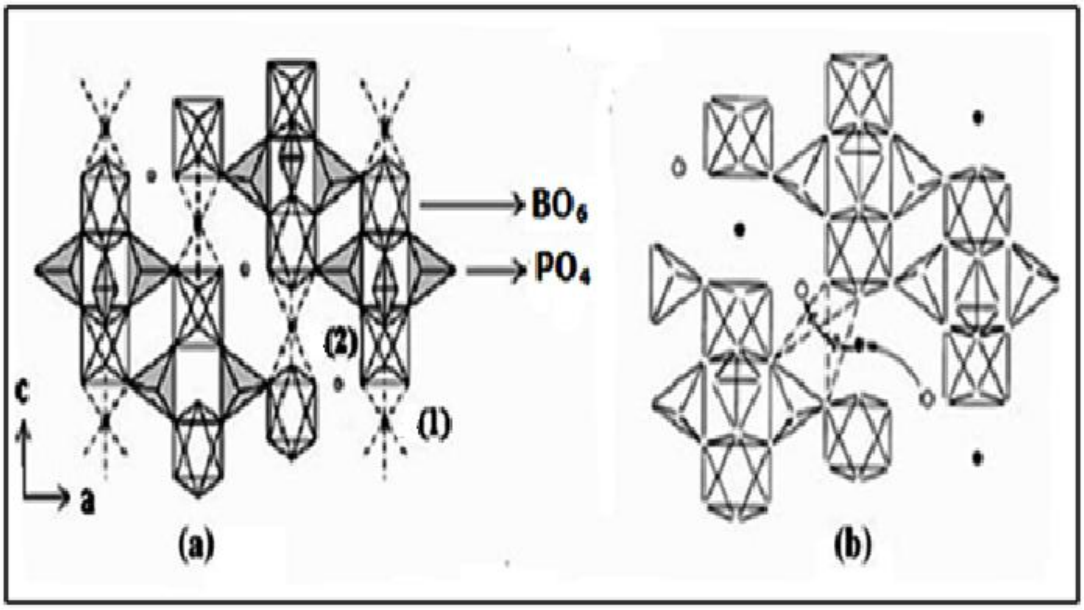

Fig.1.1 A Structure of NASICON which shows (a) (1) as type-1and (2) as type-2 sites in the conduction pathways. (Image from Ref. [74].)

Salkus et al [75] have doped Y^{3+} to replace Al^{3+} in the above mentioned optimized LATP system and found the resultant compound to exhibit NASICON structure.

1.8 Motivation for the Present Work

$LiTi_2(PO_4)_3$ **(**LTP) is a titanium based phosphate NASICON ceramic compound which is widely studied for its Li^+ conducting properties [29-34] for its use in electrode and electrolyte materials in Li batteries. The structure of $LiTi_2(PO_4)_3$ **(**LTP) lattice is a rhombohedral ($R\bar{3}c$) structure [16, 30, 31, 32] in which Li^+ can diffuse and intercalate in the 3D cage structure between cation vacancy sites called M1 and M2 sites. These sites are formed as a result of sharing corner oxygen atoms from two TiO_6 octahedra and six PO_4 tetrahedra. M1 vacancies are formed in the gap between two adjacent octahedral faces. Parallel chains of alternating tetrahedra and octahedra units are formed. The parallel chains are joined to each other due to corner sharing oxygen. The M1 vacancy sites are between the octahedral units. Therefore these vacancies are called inter-chain vacancies whereas M2 sites are vacancies between two tetrahedral units. These units are the ones which join two parallel chains. Hence, they are called intra-chain vacancies. Li^+ intercalates into M1 and M2 sites. LTP retains rhombohedral NASICON structure even after doping of different cations of comparable ionic radii. Hence lithium based NASICON compound $LiTi_2(PO_4)_3$ (LTP) [1-4] had been extensively investigated.

When Al^{3+} is doped in the LTP system, it occupies a position near the PO_4 (the tetrahedral) and TiO_6 (the octahedral sites) which are called Al_T and Al_O respectively [20, 49]. The variation of the concentration in $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP) system has been studied by many workers [10, 16, 33, 49, 76]. It is observed that Li^+ conductivity increases. Various workers have discussed the reasons of enhancement of conductivity due to the changes in the structure of the system. These are enlisted in below:

1) ^{27}Al NMR studies done by [49] in $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$, Al^{3+} replaces the Ti^{4+} cations and occupies the positions at tetrahedral and octahedral sites in the local LTP NASICON structure termed as Al_T and Al_O sites. It was concluded that with increasing amount of doping, the ratio of Al_T / Al_O increases and attains a maximum ratio of 0.3 for $x = 0.7$ of Al concentration and beyond that it starts decreasing. The amorphous phases like $AlPO_4$ are formed and start accumulating at the grain boundary [76]. $AlPO_4$ has different phases also viz. Berlinite, Crystoballite and Tridymite [80] at increasing temperatures. Wong *et al.* [80] observed that the formation of Tridymite phase of $AlPO_4$ due to corner sharing of $[PO_4]^{3-}$ and $[AlO_4]^{5-}$ tetrahedra on basis of ^{27}Al and ^{31}P NMR results above 800° C in a LATP system synthesized by solid state reaction. Peaks corresponding to $AlPO_4$ are visible in the XRD patterns. In general approximately $AlPO_4$ consists of 10% mass in an LATP system [78] synthesized by solid state reaction route. Yan et al [76] have proved that such oxide phases segregate towards grain boundary where they enhance density [29-32]. The phases like AlO_4 and $AlPO_4$ (called Berlinite phases) are irreversible and once formed cannot be disintegrated to be used in the LTP structure.

2) The presence of aluminum in the tetrahedral (PO_4) and octahedral (TiO_6) positions to replace phosphorus (P) and titanium respectively [26, 49] results in broadening of the bottlenecks [16, 77, 78, 79] and expands the lattice along ***a*** and ***c*** axis to accommodate the aluminum in the LATP system. Due to this the mobility of Li^+ near the M1 and M2 vacancy sites increases.

3) The bond angle between Ti-P-O(1) and Ti-P-O(2) becomes more tilted due to electropositive repulsive influence of Al^{3+} [78] at octahedral sites (Al_O). Due to this, the electropositive repulsive influence at M1 sites increases. This causes an increase in the mobility of Li^+ at M1 sites resulting in higher conductivity. Some workers [16] have proposed that for a concentration (x = 0.3), optimum number of Al atoms at octahedral sites (Al_O) are accumulated. Due to their electropositive repulsion, bottlenecks (the pathways or channels joining the M1–M1 or M1–M2 vacancy sites, in which Li^+ ions migrate) open up for the Li^+ to pass easily.

4) The overall Li^+ conductivity of LATP samples at all temperatures is higher than parent system LTP. Besides, according to Arbi et al [77], the Li^+ ions trapped in amorphous phases like $LiTiPO_5$ release Li^+ when the samples are subjected to increasing temperatures because Li^+ ions can overcome the activation barrier and diffuse over some distances. This enhances the overall conductivity with temperature.

Due to the above reasons, the optimized system $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) has been chosen as reference system. When Al^{3+} in this optimized system is replaced at tetrahedral and octahedral sites, by trivalent cations with increasing ionic radii – like Y^{3+}(0.93 Å), Ga^{3+} (0.64 Å) and Sc^{3+} (0.74 Å) in the LATP system can result in changes of microstructure with grain and at grain boundaries. These are described and discussed in the following sections.

The substitution is possible when the ionic radii of the dopant and host cations are comparable. In our case, Ga^{3+} and Sc^{3+} have a comparable ionic radius to Al^{3+} compared to Y^{3+} and are likely to replace Al. Y^{3+} due to its large size is likely to block the conducting pathways. Keeping in view these facts, the series of compounds with the following configurations have been synthesized:

a) $\mathbf{Li_{1.3}Al_xY_{0.3-x}Ti_{1.7}(PO_4)_3}$ (x = 0.01, 0.03, 0.05, 0.07, 0.1, 0.15)

b) $\mathbf{Li_{1.3}Al_xGa_{0.3-x}Ti_{1.7}(PO_4)_3}$ (x = 0.01, 0.03, 0.05, 0.07)

c) $\mathbf{Li_{1.3}Al_xSc_{0.3-x}Ti_{1.7}(PO_4)_3}$ (x = 0.01, 0.03, 0.05, 0.07)

Besides, investigations have been carried out to study the properties of yttrium as a sintering material. Samples for two concentrations (*x* = 0.01 and 0.15) of series-**a**, were subjected to heat treatment at a temperature of 1273 K for 2 and 3 hrs and their Li^+ ion conducting properties were investigated.

The x-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy were performed to understand the microstructure and chemical composition of the material. Density measurements using Archimedes principle was also performed. Impedance spectroscopy and transport number measurement techniques were used to find the ion transport properties of the material.

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