CHAPTER 1

INTRODUCTION
1.1 INTRODUCTION

Materials are the building blocks for human life. An important goal of materials research, is the ability to synthesize in high yields, new materials whose structure and properties can be predicted, varied and controlled. Materials Science is the science of the relations between processing, structure and properties of materials [1], which affects our life directly in many ways—by lowering the cost and improving the performance of manufactured goods, by leading to development of new structures and devices based on new materials and by providing means for ecological remediation and protection. Materials chemistry is receiving increasing recognition worldwide as a key area of materials research and technology where the emphasis is laid on material synthesis, processing and analysis [2]. It encompasses all the traditional areas of chemistry – Inorganic, Organic, Physical as well as Analytical and Biochemistry. The broad field of materials science, seeks to explain and control one or more of the four basic elements [3]:

i) The structure and composition of a material, including the type of atoms and their arrangement, as viewed over the range of length scales (nano, micro, meso, and macro scale);

ii) The synthesis and processing by which the particular arrangement of atoms is achieved;

iii) The properties of the material, resulting from the atoms and their arrangement that make the material interesting or useful;

iv) The performance of the material, which is the measurement of its usefulness in actual conditions, taking account of economic and social aspects and benefits.

All these factors are interrelated and they can be varied by a better understanding of materials chemistry to develop "Advanced Performance Materials". Advanced performance materials, are materials whose structural and functional properties impart improved performance leading to specific products. These materials are basically divided into ten categories, but they are interrelated in one way or another.
1. Biomaterials
2. Composite materials
3. Superconducting materials
4. Electronic materials
5. Magnetic materials
6. Optical/photonic materials
7. Polymers
8. Catalysts
9. Ceramics
10. Metals

Developing advanced materials, is a science in itself that requires an understanding of the structure/property/processes/function/performance from the viewpoint of the end-user, bearing the cost in mind (figure 1.a).

The ability to design these materials has been built on three pedestals –

i) Development and application of new synthetic techniques including “Soft Chemistry Routes” for cost and pollution minimization.

ii) Better understanding of factors and mechanisms that control molecular architecture and processes.

iii) Improved instrumentation technique to probe the materials at a molecular level.

The recent impacts of chemistry on materials synthesis, include development of synthetic zeolites and their subsequent widespread use as petroleum cracking catalysts, high resolution polymer based lithographic
imaging materials that have lead to amazing reductions in electronic device dimensions, secondary storage devices—batteries which have changed the concept of power storage [2], fuel cells which are zero emission devices and are not limited by the concept of Carnot Efficiency for power generation [4], information exchange devices which have changed the concept of data storage and exchange and development of materials for artificial implantation techniques that has improved the quality of human life [2].

This extraordinary development has been due to an increasing involvement of chemistry in the processing and understanding of materials science through thorough experimentation. The broad applicability of advanced materials, arises from the ability to design and synthesize such materials with the precise functionalities and properties required for a specific application. The design of application specific materials, requires a sound knowledge and understanding of intrinsic and extrinsic properties, property-microstructure relationship which subsequently depends upon the atomic structure and the bonding in the materials. Hence, in the development of an advanced material, a material chemist has to thoroughly understand their compositional, structural and morphological features, based on the knowledge of the principles of chemical bonding and proper characterization of their physical properties [5].

Through a thorough understanding and control of the structure and properties, it is possible to device new materials and technologies or improve the existing ones for applications in the fields such as electronics, optics, automotives and aerospace, building structures and medicine [6] with entirely new levels of performance e.g. by just doping 0.01% of impurity it is possible to change the electrical resistance of a semiconductor 10,000 fold, enabling the development of semiconductor between metallic and insulating behavior [7]. The materials chemist’s understanding of this architecture and control over its structure is of paramount importance in attaining novel materials with improved properties.

Advanced materials that have revolutionized the materials science scenario are zeolites, clays/pillared clays, fullerenes, optical fibers, high
temperature and high strength fibers and ceramics, electronic polymers, inorganic electronic materials, rapidly solidified metals (metallic glasses) etc.

Though well known and researched since the last 50 years, of late, "Tetravalent Metal Acid (TMA) Salts" have emerged as promising advanced materials as they possess robust properties.

An extensive literature on tma salts, exists today, which have been reviewed and detailed in four books.

4. Amphlett C B 1964 *Inorganic Ion Exchangers* Amsterdam

Systematic studies on their synthesis, structure elucidation and applications in the area of separation science, catalysis and solid electrolytes have been carried out by various groups – Dr. A. Clearfield (USA), Dr. G. Alberti, Dr. U. Costantino (Italy), Dr. D. Whittaker (UK), late Dr. M. Qureshi and Dr. K. G. Varshney (Aligarh Muslim University, India) and Dr. U. V. Chudasama (The M S University of Baroda, India).

1.2 SALIENT FEATURES OF TETRAVALENT METAL ACID (TMA) SALTS

(i) Tma salts are cation exchangers, possessing the general formula M(IV) (H\text{X}O\text{4})_{2}\cdot n\text{H}2\text{O}, where M(IV) = Zr, Ti, Sn, Ce, Th etc. and X = P, Mo, As, Sb, W etc.

(ii) The materials possess structural hydroxyl groups, the H of the –OH being the exchangeable sites, due to which the material possesses cation exchange properties.
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(iii) Tma salts can be prepared both in amorphous and crystalline forms that exhibit selectivity for certain metal ions.

(iv) The materials possess granular nature and can be obtained in a range of mesh sizes, very suitable for column operations.

(v) The materials are generally hard and range in physical appearance from totally opaque to transparent.

(vi) These materials have shown a great promise in preparative reproducibility, ion exchange behavior and stability towards thermal, chemical and ionizing radiations.

1.3 STRUCTURAL ASPECTS OF TMA SALTS

Almost all the possible combinations of tetravalent metals with polybasic acids have been examined and properties of the obtained materials investigated. This has led to an extensive literature on their synthesis, structure and properties. Earlier work was carried out with amorphous materials. The first crystalline α-zirconium phosphate was prepared by Clearfield and Stynes [8,9]. Structure elucidation was first carried out in 1969 [10]. Based on that structure, a large variety of layered compounds has since been developed all over the world [11,12]. Extensive work has been carried out on the structure property relationship and their applications as ion exchangers, catalysts and solid electrolytes, explored.

Much of the earlier work was focused on zirconium phosphate [13]. De Boers [14] reported a gel with P:Zr ratio equal to 2 as zirconium mohydrogen phosphate \( \text{Zr(HPO}_4\text{)}_2 \), but other workers [15,16] argued that under the preparation conditions the formation of a zirconyl salt \( \text{ZrO(H}_2\text{PO}_4\text{)}_2 \) was more likely. Bluementhal [13,16] proposed the following structural formula for the precipitated product (figure 1.b)
Paterson [17] has described the structure of zirconium phosphate as presented in figure 1.c.

According to these structures the H of the -OH groups are the exchangeable protons. Baestle and Pelsemakers [18] suggested the following structure (figure 1.d).

In this case also, the exchange can take place through the hydroxyl groups. Nancollas and Pekarek [19] proposed the following formula for crystalline zirconium phosphate (figure 1.e).
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They represented the semicrystalline zirconium phosphate by the formula shown in figure 1.f

Much of the pioneering work in this area was done by the research group at the Oak Ridge National Laboratory led by K A Kraus [20,21] and in the United Kingdom by C B Amphlett [22,23].

The structure of crystalline $\alpha$-ZrP [10] was solved by Clearfield and Smith in 1969. Zirconium phosphate has a layered structure. The structure of $\alpha$-ZrP is monoclinic: $a = 9.06 \AA$, $b = 5.30 \AA$, $c = 16.19 \AA$, $\beta = 111.42^\circ$ and space group $P2_1/c$ [10,24]. Zirconium atoms lie slightly above and below the $ab$ plane as shown in figure 1.g and are bridged by the phosphate groups. These are situated alternatively above and below the metal atom plane. Three oxygen atoms of each phosphate, are bonded to three adjacent metal atoms, forming a distorted equilateral triangle [25]. Each zirconium atom is thus octahedrally coordinated by oxygens. Lamellar macroanions $[\text{Zr}_6(\text{PO}_4)_{22}]^{2n-}$ (figure 1.h) have charge balancing protons ($\text{H}^+$) bonded to oxygens adjacent to the interlayer region. These protons are responsible for the ion exchange, surface acidity and
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proton conductivity of $\alpha$-ZrP [75]. Crystal water molecules are located close to the centre of the interlayer cavities, held by hydrogen bonds with phosphates of both adjacent layers [26]. An idealized picture of a portion of the layer is given in figure 1.h

![Figure 1.h Idealized diagram showing arrangement of Zr and P](image)

Figure 1.g $ab$ layer of $\alpha$-ZrP structure, showing the approximate position of the monoclinic cell [27].
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Zirconium phosphate, the most extensively studied tma salt of the crystalline type can be prepared as fibrous, layered or as three-dimensional structures [9]. The layered acid salts, in turn, may be obtained in at least two different modifications, usually known as α-ZrP and γ-ZrP having the formula Zr(HPO$_4$)$_2$. H$_2$O and Zr(PO$_4$)(H$_2$PO$_4$).2H$_2$O respectively [28]. The structure of the α-ZrP (figure 1.i) arises from the ABAB stacking of layers, each of which is formed by zirconium atoms lying in a nearly ideal plane and sandwiched between O$_3$POH groups, with the exchangeable proton pointing into the interlayer region as P–OH [25]. The interlayer distance is 0.76 nm, the free area surrounding each POH group is ~0.24 nm$^2$ and there are 6.64 mmol of exchangeable proton per gram. The layers of the γ-ZrP are made up of zirconium atoms laying in two parallel ideal planes and bridged by PO$_4$ groups, while O$_2$P(OH)$_2$ groups are directed towards the interlayer region [29,30]. The layers in the γ-ZrP are thus thicker (0.92 nm) than those in α-ZrP (0.64 nm), and the OH groups bound to the same phosphorous atoms have different acidities. The interlayer distance is 1.22 nm and the free area surrounding each P(OH)$_2$ group is ~0.33 nm$^2$, with an ion exchange capacity of 6.27 mmol/g. A new phase of zirconium phosphate known as τ-ZrP has been reported, having composition identical to α-ZrP [31]. Extensive information on the chemistry of

Figure 1.i Schematic diagram of the arrangement of two adjacent macroanions in α-ZrP. Protons & water molecules are not shown [27].
group IV metal phosphates with $\alpha$ and $\gamma$ type structures has been compiled in reviews and books [32,33].

1.4 HYBRID MATERIALS

There is currently high interest in engineering mixed materials (organic/inorganic) where features of the organic and inorganic components complement each other, leading to the formation of new solid-state structures and materials with new composite properties [34]. Organic-inorganic hybrids have been attracting significant attention as a new class of materials, since the combination of an inorganic component and an organic component has the potential to provide improved and tunable properties [35-39].

The synthesis of novel organic–inorganic hybrid materials, has received extensive attention in recent years [40-43]. Hybrid materials in general can be obtained through intercalation/anchoring/ pillaring/encapsulation or sol-gel method.

The conjunction of layered material and intercalation technique has the possibility of providing new organic–inorganic hybrid materials. The chemistry of intercalation is a research area that has been widely investigated and plays a very important part in applications in many academic and technological fields, such as those related to catalysis, ion-exchange processes, magnetic determinations and supports for catalytic methods [44-49]. A wide variety of natural and synthetic inorganic compounds are susceptible to intercalation processes, whose final properties are connected to their respective structures, specially the distribution of the inorganic backbone in a lamellar arrangement. One of the most important inherent properties of these types of layered materials, is the fact that they can expand the interlamellar space, when exposed to guest species [44,50,51]. The crystalline layered compounds, exhibit some attractive properties such as, high thermal stability, resistance to oxidation, high selectivity to a series of ions and molecules and convenience for chemical modifications [50]. In this class of materials, natural clays [52], phyllosilicates [53], double hydroxides [50], silicic crystalline acids [51],
polymeric silicates [54], transition metals oxides [55] metallic phosphates and phosphonates [44-46] are included, all of which can accommodate various molecules in free interlamellar space. The hybridization of layered metal (IV) phosphates has been extensively studied because of their applications in the field of photochemistry, electrochemistry, molecular recognition, ion exchange and catalysis [56-63].

In addition to selection of an appropriate combination of inorganic and organic components, achieving desirable properties, requires that their interfaces and nanostructures are carefully designed. The reactivity of both the organic and inorganic precursors are usually quite different and phase separation tends to occur. The general tendency is therefore to create intimate mixing, thereby increasing the interfacial interactions or interpenetration between organic and inorganic networks. Organic-inorganic hybrids can be classified into two groups, based on their interfaces:[35,36,38]

Class I hybrids with weak interactions such as van der Waals forces or hydrogen bonds or electrostatic interactions created between organic and inorganic phases. This class involves mainly small organic species embedded with an oxide matrix.

Class II hybrids where in the inorganic and organic components are bonded through strong bonds, such as covalent bonds. For the production of class II hybrids [35] selection of the preparation process and starting compounds is extremely important.

1.5 HYBRID MATERIALS INVOLVING TMA SALTS AS BACKBONE

A major development in the class of tma salts occurred in 1978 when Alberti [64] prepared the first hybrid material based on zirconium phosphate backbone. The discovery of zirconium phenyl phosphonate, opened up the possibilities of further modification and control of the structure and properties of such materials [65]. Several compounds have been subsequently prepared [66-68]. Layered phosphonates are inorgano-organic materials in which the
organic moieties are bridged through the phosphorous atoms to an inorganic
two dimensional matrix. They are represented by the general formula
M(03PR)_2.S where R can be alkyl or aryl group, bearing ionogenic functional
groups such as − COOH, −OH, −SO_3H, −PO_3H etc. Interest in such materials
stem from the fact that the inorganic backbone, provides a stable and relatively
inert support for the organic moiety. In fact, these materials can be regarded as
inorganic sheets with functional organic groups (R) on the surface. Depending
on the nature of the R group, these compounds could lead to different
applications [69] in the field of chromatography, catalysis, photochemistry,
tailor made molecular sieves and proton conduction.

Hybrid materials with tma salts as the backbone is of particular interest,
since the resulting material has the added advantage of both its counterparts in
terms of thermal and chemical stability and ion exchange capacity. Moreover,
it is also stable towards acidic and oxidizing media. The loading potential of
the inorganic backbone is as high as two alkyl groups per zirconium atom.

Zr(IV) phosphate has shown a number of advantages as an ideal host
lattice. In the tetrahedral moiety of phosphoric acid, PO(OH)_3, if H or OH is
replaced by R ( where R = alkyl, aryl containing functional groups such as
amino, alcoholic, carboxylic, sulphonic etc.), phosphonic acids are obtained,
which when treated with tetravalent metals such as Zr, Ti, Sn, Th, Ce, etc. give
rise to metal phosphonates. In these compounds, the organic moieties are
bridged through phosphorous atoms to an inorganic two dimensional matrix,
leaving the structure of the parent phosphate unchanged. Amongst various
metal phosphonates, the zirconium derivatives are of special interest, as they
are very insoluble compounds and their structure and reactivity, can be
modified and tailored for specific purposes [38]. Depending on the complexity
of the phosphonate used, the material gives rise to two or three dimensional
hybrid polymeric structures.

Three oxygens of each phosphate group are bound to three different
zirconium atoms while the fourth oxygen bears the proton that can be easily
replaced by other cations. Compounds in which the tetrahedral P − OH groups
are replaced by $P - R$ or $P - OR$ groups ($R = \text{alkyl/aryl radical}$) are reported [70]. Derivatization of tma salts, depends on the nature of the inorganic matrix. If the material is crystalline and hence layered, then the organic molecules are incorporated into the layers, whereas in amorphous or non-layered materials, the organic moieties are anchored or sorbed on the surface [71]. The advantage in these materials, is that they have the rigidity of the inorganic backbone and flexibility of the organic moiety.

Though several metal phosphonates have been synthesized and characterized, the focus has been on structure elucidation [64,72,73]. These materials are interesting because of their potential utility as sorbents and supports [74], in the area of catalysis [75], as ion exchangers [76], proton conduction [77], intercalation chemistry [78], photochemistry [79] and materials chemistry [80].

TMA salts with varying water content, composition and crystallinity [81-85] can be obtained depending on various factors viz. mole ratio of reactants $M:X$ ($M = \text{tetravalent metal, } X = \text{polyvalent anion}$), temperature of mixing, mode of mixing (metal salt solution to anion salt solution or vice versa), pH and rate of mixing. Variation in any of these parameters yields materials with different characteristics. The preparation procedure affects the structural hydroxyl groups, which is reflected in their performance in various applications like ion exchange, catalysis and proton conduction. Thus, the area of study of tma salts is evergreen and much remains to be investigated.

The present thesis deals with synthesis and characterization of advanced materials of the class of “tma salts” and exploring their possible use in the area of catalysis and solid state proton conduction.

1.6 LITERATURE SURVEY ON THE CURRENT AREA OF STUDY

Tma salts have been known for a long time, but of late, there has been increased interest in these compounds. This revived interest is chiefly due to their good ion exchange properties and their high chemical and thermal
stability as well as resistance towards ionizing radiations. Due to these properties they find use in varied fields like nuclear technology, ion exchangers, catalysis and solid electrolytes.

Tma salts in both amorphous and crystalline forms have been extensively explored since early days as ion exchangers and in separation science, due to the high selectivity for certain metal ions [22,86-92]. As mentioned earlier in the text, various groups all over the world have been working on these materials. The work carried out in the area of ion exchange and sorption has been on alkali metal ions and other cations [86,87,90], in nuclear technology [86], development of quantitative separation procedures [93,94], detection and estimation of metal ions in ayurvedic and antacid drugs, multivitamin formulations [95-97] and sorption and recovery of metal ions [98-100].

Of late, besides their applications as ion exchangers, tma salts are extensively being explored in the area of catalysis. They are either used as solid acids, solid bases (alkali metal exchange) or as supports in heterogenised homogeneous catalysis, mainly because they possess surface protonic sites which are labile and hence exchangeable. Various applications of tma salts as catalysts and as supports have been summarized by Clearfield in his review [101]. The alkali metal exchanged phases have been explored in solid base reaction like Knoevenagel condensation reactions, hydrolysis of sterically hindered phenolic silyl ether, cyanosilylation of carbonyl compounds and synthesis of nitro alkanols [102-105]. As solid acids they have been explored in numerous reactions viz. dehydration, conversion of ethylbenzene to styrene, hydration, amination, esterification and isomerization [106-114]. Tma salts have also been explored as supports in heterogenised homogeneous catalysis [115-122].

Tma salts also find application as solid electrolytes in proton conduction. They behave as proton conductors due to the exchangeable and diffusible H⁺ sites present on the surface. Extensive literature is available, wherein both phosphates and phosphonates exhibit promising results [123-
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Some of them are found to have favourable value of proton conductance to be used as solid electrolytes in fuel cells, sensors, electrochromic displays, solid state batteries etc. Several reviews have been published pertaining to the possible use of tma salts in the area of proton conduction and solid electrolytes [130-133].

1.7 AIM AND SCOPE OF THE PRESENT WORK

In the present endeavor M(IV) phosphates and phosphonates have been prepared using soft chemistry routes – sol-gel method of synthesis. Further, metal exchanged phases of zirconium phosphate have been prepared by ion exchange method. The utility of these materials have been explored in catalysis and as solid electrolytes.

Chapter II of the thesis deals with the synthesis of amorphous tma salts ZrPA, SnPA and TiPA as well as crystalline phase of zirconium phosphate – ZrPC. Further, metal exchanged phases have been obtained by exchanging Cu$^{2+}$, Li$^+$, Ru$^{3+}$ and Pd$^{2+}$ onto ZrPA. Ru$^{3+}$ and Pd$^{2+}$ have also been exchanged onto ZrPC. The metal exchanged phases have been abbreviated as CuZrPA, LiZrPA, RuZrPA and PdZrPA for exchange with amorphous zirconium phosphate and as RuZrPC and PdZrPC for exchange with crystalline zirconium phosphate. Phosphonates of zirconium have been synthesized by treating zirconium oxychloride with phosphonic acids namely HEDP (Hydroxyethylidenediphosphonic acid), ATMP [Aminotris (methylenephosphonic acid)] and DETPMP [Diethylenetriamine pentakis(methylene phosphonic acid)] to yield ZrHEDP, ZrATMP and ZrDETPMP respectively. These materials have been characterized for elemental analysis, thermal analysis (TGA/DSC), spectral analysis (FTIR), X-ray analysis, BET surface area measurement, acidity measurement (NH$_3$TPD) and SEM analysis. Chemical resistivity of the synthesized materials has been accessed in various acids, bases and organic solvent media. Ion exchange capacity of the materials has been determined and the effect of heating on ion exchange capacity studied.
Chapter III of the thesis, deals with the utility of ZrPA and ZrPC in the area of catalysis. This chapter is divided into two sections.

Section I deals with the utility of ZrPA and ZrPC as solid acid catalysts by selecting esterification as a model reaction wherein monoesters and diesters have been prepared. The monoesters prepared are ethyl acetate (EA), propyl acetate (PA), butyl acetate (BA) and benzyl acetate (BzA). The diesters prepared are dioctyl phthalate (DOP) and dibutyl phthalate (DBP). The reaction conditions have been optimized and the yields compared.

Section II deals with the utility of ZrPA and ZrPC as supports in heterogenised homogeneous catalysis. RuZrPA and RuZrPC have been accessed as oxidation catalysts for oxidation of benzyl alcohol and styrene. The reaction parameters have been optimized and the yields compared. RuZrPA, RuZrPC, PdZrPA and PdZrPC have been explored as hydrogenation catalysts for hydrogenation of 1-octene and cyclohexanone. The reaction parameters have been optimized and results compared.

In Chapter IV, the performance of tma salts as solid state protonic conductors has been investigated under the following categories:
1) A comparative study of the proton transport properties of Metal (IV) Phosphates – ZrPA, SnPA and TiPA.
2) A comparative study of the proton transport properties of Metal exchanged phases of ZrPA – CuZrPA and LiZrPA.
3) A comparative study of the proton transport properties of Zr(IV) Phosphonates – ZrHEDP, ZrATMP and ZrDETPMP.

Proton conductivity of these materials, have been measured in the temperature range 30–120 °C, at 10 °C intervals, using SOLARTRON DATASET impedance analyzer (SI 1260) over a frequency range 1 Hz–10 MHz at a signal level below 1 V, interfaced to a minicomputer for data collection. Based on the specific conductance data obtained, a suitable mechanism has been proposed and the values compared.
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