

CHAPTER 1

Introduction

1.1 TETRAVALENT METAL ACID SALTS

“Tetravalent Metal Acid (TMA) Salts” have been researched since the last 50 years, and have emerged as promising advanced materials owing to their good thermal and chemical stability, resistance towards ionizing radiations, and found important applications in the area of ion exchange, catalysis and solid state proton conduction. An extensive literature on TMA salts, exists today, which have been reviewed and detailed in four books.

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- Clearfield A, 1982, *Inorganic Ion Exchange Materials*, CRC Press, Boca Raton, Florida.
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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), Dr. W. H. J. Hogarth (Australia), 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

- TMA salts are cation exchangers, possessing the general formula $M(IV)(HXO_4)_2 \cdot nH_2O$, where $M(IV) = Zr, Ti, Sn, Ce, Th$ etc. and $X = P, Mo, As, Sb, W$ etc.
- The materials possess structural hydroxyl groups, the H^+ of the $-OH$ being the exchangeable sites, due to which the material possesses cation exchange properties.

- TMA salts can be prepared both in amorphous and crystalline forms that exhibit selectivity for certain metal ions.
- The materials possess granular nature and can be obtained in a range of mesh sizes, very suitable for column operations.
- The materials are generally hard and range in physical appearance from totally opaque to transparent.
- TMA salts have shown a great promise in preparative reproducibility and ion exchange behaviour
- TMA salts exhibit both thermal and chemical stability

When a tetravalent metal is treated with phosphoric acid/Na salts of phosphoric acid, M – O – P bonds are formed. In this process, a number of hydroxyl groups do not participate in the condensations which are referred to as pendant hydroxyl groups or defective P – OH, H⁺ of the P – OH contributing to cation exchange [1]. TMA salts are prepared by sol gel routes of different compositions and crystallinities [2-5] varying parameters such as mole ratio of reactants M:X (M = tetravalent metal, X = 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 cation exchange capacity (CEC) thus depends on preparation procedure/parameters varied and hence performance in various applications like ion exchange, catalysis and proton conduction.

From our laboratory, TMA salts have been widely explored as cation exchangers [6-22], as solid acid catalysts [23-36] and solid state proton conductors [37-42]. A literature survey as well as works conducted in our laboratory (outlined above) reveals that phosphates of Zr, Sn and Ti have been widely explored as ion exchangers, solid acid catalysts and solid state proton conductors. However, very few reports are available on synthesis, characterization and application of cerium (IV) phosphate (CP) and thorium (IV) phosphate (TP) as ion exchangers, solid acid catalysts and solid state proton conductors. Much of the works available in literature is related to solving the structures of crystalline CP and TP.

1.3 A LITERATURE SURVEY ON STRUCTURAL ASPECTS OF CERIUM (IV) AND THORIUM (IV) PHOSPHATES

Cerium (IV) Phosphate (CP)

Compared with zirconium, titanium and tin phosphates, which are well-documented materials used in various fields (ion exchange, intercalation, proton conduction, heterogeneous catalysis, molecular sorption) [43-45], CPs appear to be much more complex. Zirconium (IV) phosphate (ZrP) exhibits two well characterized lamellar structures, $Zr(HPO_4)_2 \cdot H_2O$ (α -ZrP)[46] and $Zr(H_2PO_4)(PO_4) \cdot 2H_2O$ (γ -ZrP) [47], based on six-coordinate metal centers. Cerium (IV) phosphates appear to adopt several crystalline structures, with P/Ce ratios ranging from 1.1:1 to 3.0:1. [48-64].

The first structure of CP, $Ce(PO_4)(HPO_4)$ as crystalline platelets was reported by Nazaraly et al [65, 66]. It can be described as dense $[Ce(PO_4)^+]_n$ slabs, with cerium atoms on both surfaces (**Figures 1.1 to 1.4**), each cerium atom connected to four HPO_4^{2-} tetrahedra belonging to the same side and to one HPO_4^{2-} tetrahedron of the opposite side. These slabs are bridged by HPO_4^{2-} units with water molecules present in the inter slab region, which results in eight-coordinate cerium atoms. This very same compound, according to its X-ray powder diffraction, has been described in previous works as a cerium(IV) hydroxyl (hydrogen)phosphate with the formula $Ce(HPO_4)(PO_4)_{0.5}(OH)_{0.5}$ [54,58,59]. The present structure, and especially the P–O distances, indicate quite clearly that the compound is in fact a cerium(IV)(hydrogen)phosphate hydrate, with the formula $Ce(PO_4)(HPO_4)_{0.5}(H_2O)_{0.5}$.

Nazaraly et al [67] have also reported, $Ce(H_2O)(PO_4)_{1.5}(H_3O)_{0.5}(H_2O)_{0.5}$, the second entry in the structural chemistry of CPs (**Figure 1.5**). The asymmetric unit of this compound contains one cerium atom, two phosphate tetrahedra, one hydronium cation and two water molecules. The cerium atom is eight-coordinate (distorted archimedean antiprism) (**Figure 1.5**) [67]. Its coordination polyhedron is composed of four oxygen atoms of four different phosphate tetrahedra (P1) and three oxygen atoms of two different phosphate tetrahedra (P2) (**Figure 1.5**). The eighth vertex of the cerium coordination polyhedron is occupied by a water molecule (OW1) (**Figure 1.6**).

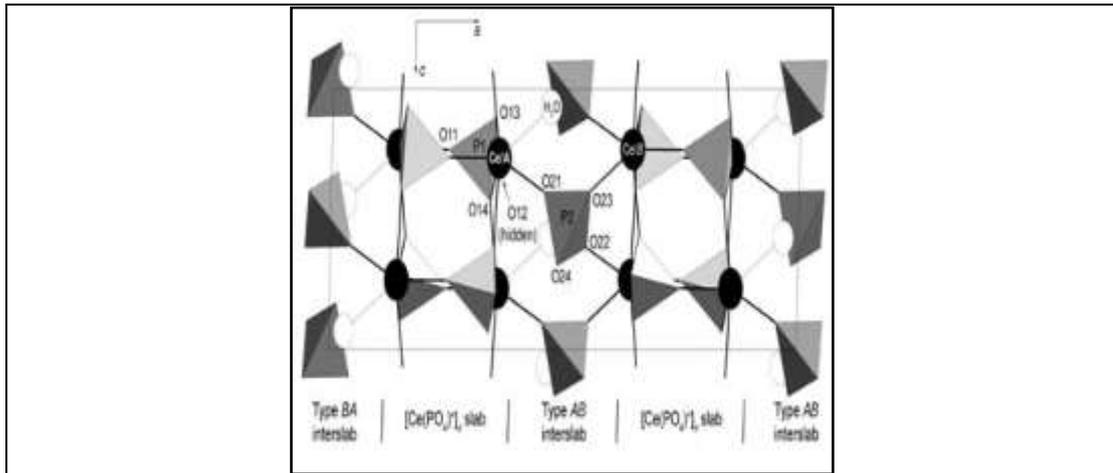


Figure 1.1 $[0\ 1\ 0]$ projection of the $\text{Ce}(\text{PO}_4)(\text{HPO}_4)_{0.5}(\text{H}_2\text{O})_{0.5}$ structure. The random succession of the interslab regions along the stacking a axis illustrates the disorder. [65].

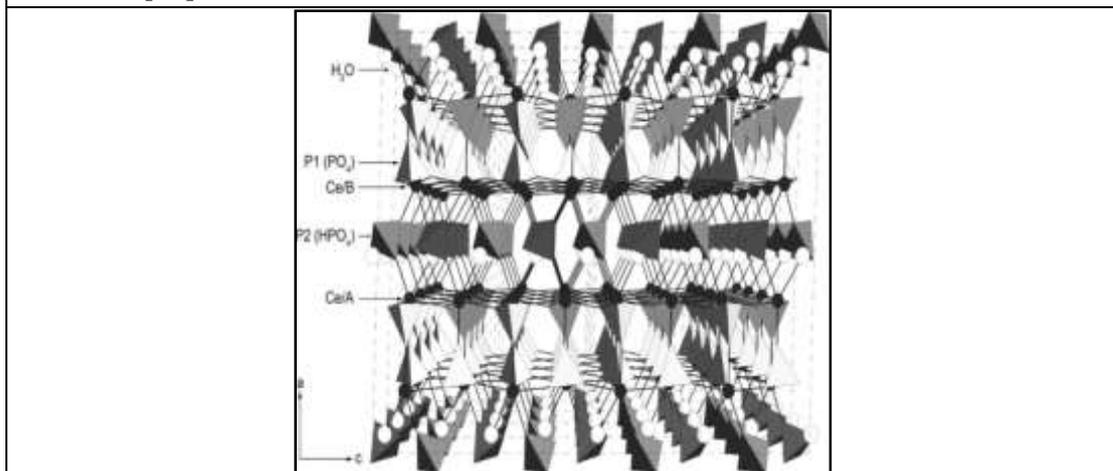


Figure 1.2 View of the structure of $\text{Ce}(\text{PO}_4)(\text{HPO}_4)_{0.5}(\text{H}_2\text{O})$ along $[1\ 0\ 0]$ [66]

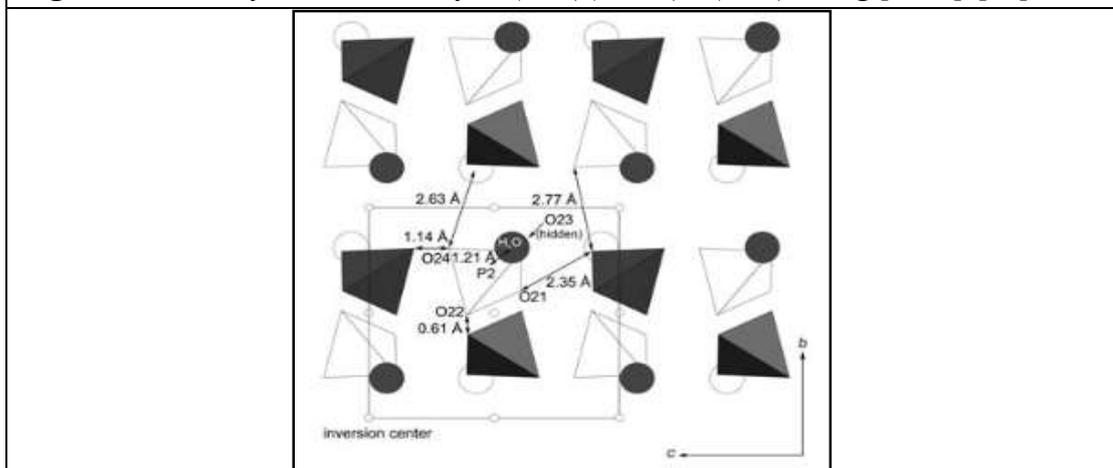


Figure 1.3 $[1\ 0\ 0]$ projection of the interslab regions near $x=0.5$ for the $\text{Ce}(\text{PO}_4)(\text{HPO}_4)_{0.5}(\text{H}_2\text{O})_{0.5}$ structure. White and shaded units $(\text{H}(\text{P}2)\text{O}_4)^{2-}$ tetrahedra and OW (water oxygen atoms) represents the two possible and equiprobable zigzag models [65]

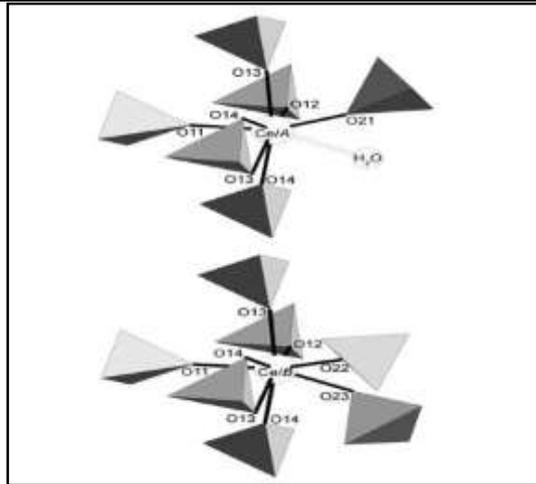


Figure 1.4. The two possible and equiprobable environments of the cerium atom in the $\text{Ce}(\text{PO}_4)(\text{HPO}_4)_{0.5}(\text{H}_2\text{O})_{0.5}$ structure [65].

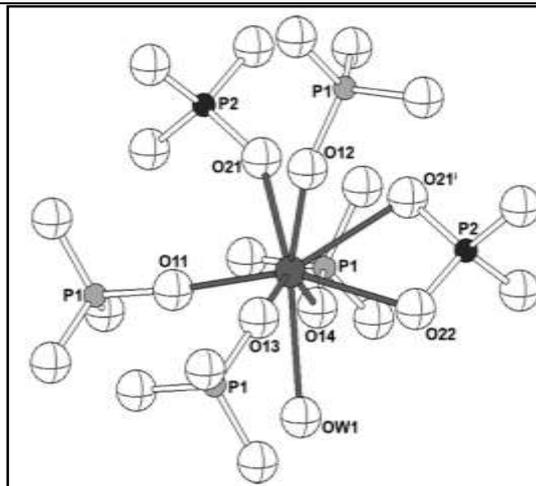


Figure 1.5. Environment of the cerium atom in $\text{Ce}(\text{H}_2\text{O})(\text{PO}_4)_{1.5}(\text{H}_3\text{O})_{0.5}(\text{H}_2\text{O})_{0.5}$ [67].

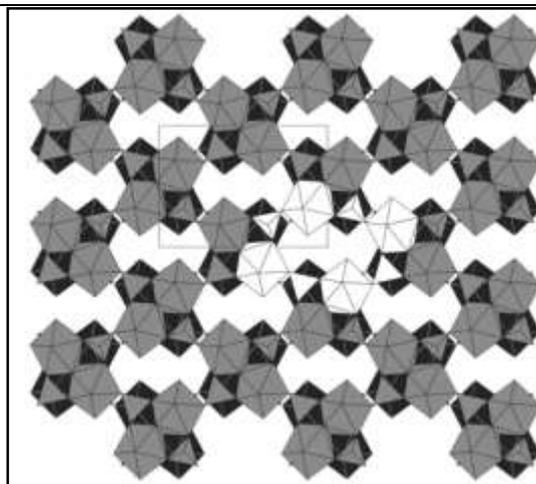


Figure 1.6. View along c of the structure of $\text{Ce}(\text{H}_2\text{O})(\text{PO}_4)_{1.5}(\text{H}_3\text{O})_{0.5}(\text{H}_2\text{O})_{0.5}$ showing two planes of rings ($a+c$ and b). The front and back planes are in light grey and dark grey, respectively. The rings are composed of four Ce atoms and four PO_4 tetrahedra (P1), one ring is highlighted in the front plane (white). [67].

Miguel et al [68] have resolved the structure of $(\text{NH}_4)_2\text{Ce}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ by XRD. The structure was solved by X-ray powder diffraction. The compound was found initially to be tetragonal with a strong cell elongation along the c -axis, consistent with the elongated octahedral habit of crystallites. This structure bears absolutely no resemblance with the α - or γ -ZrP structures [46,47].

Orlova et al [69] have reported structure of cadmium-CP as $\text{Cd}_{0.5}\text{Ce}_2(\text{PO}_4)_3$. The phosphate $\text{Cd}_{0.5}\text{Ce}_2(\text{PO}_4)_3$, like its analog CePO_4 , has a framework structure. $\text{Na}_{10}\text{Ce}_2\text{P}_6\text{O}_{24}$ is the first structurally characterized CP with a P/Ce ratio of 3 [70]. Ru Yang et al [71] have reported the phase composition and crystal structure of $\text{Ce}(\text{H}_2\text{O})(\text{PO}_4)_{1.5}(\text{H}_2\text{O})_{0.5}(\text{H}_2\text{O})_{0.5}$ by XRD. Two CPs with a P/Ce ratio of 3 have been reported by Xu et al [72], namely, $\text{Ce}(\text{HPO}_4)(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_5\text{Ce}(\text{PO}_4)_3$.

Thorium (IV) Phosphate (TP)

Miguel et al [73] have reported first structurally characterized thorium hydrogenphosphate. The structure of $\text{Th}_2(\text{PO}_4)_2(\text{HPO}_4)_4 \cdot \text{H}_2\text{O}$ (**Figure 1.7**) can be described as layers including both thorium atoms and two (PO_4) groups, alternating with a layer formed by a third set of PO_4 groups with the water molecules filling the spaces left in the layer (**Figure 1.8**).

This phosphate group could be identified to the hydrogenphosphate one (HPO_4), and then this layer would be held by a strong hydrogen bond network between HPO_4 entities and water molecules. The Th1 atom is surrounded by seven oxygen atoms in a distance range 2.268(24)-2.695(24) Å, involving five monodentate and one bidentate phosphate groups. This environment could be described as a highly distorted pentagonal bipyramid (**Figure 1.9**). The Th2 atom is also surrounded by seven oxygen atoms in a distance range 2.21(4)-2.676(28) Å involving seven monodentate phosphate groups. This environment could be described as a monocapped trigonal prism (**Figure 1.10**). The next closest atom is an oxygen belonging to a water molecule at 2.813(25) Å. Therefore, the coordination of both thorium atoms in this compound is seven as opposed to the more usual eight coordination in $\text{Th}_4(\text{PO}_4)_4\text{P}_2\text{O}_7$ or the rare octahedral coordination in cubic ThP_2O_7 [74]. Th1 and Th2 polyhedra, through sharing one edge (O12 and O34) and one vertex (O32), form chains running along the direction $[0\ 1\ 0]$.

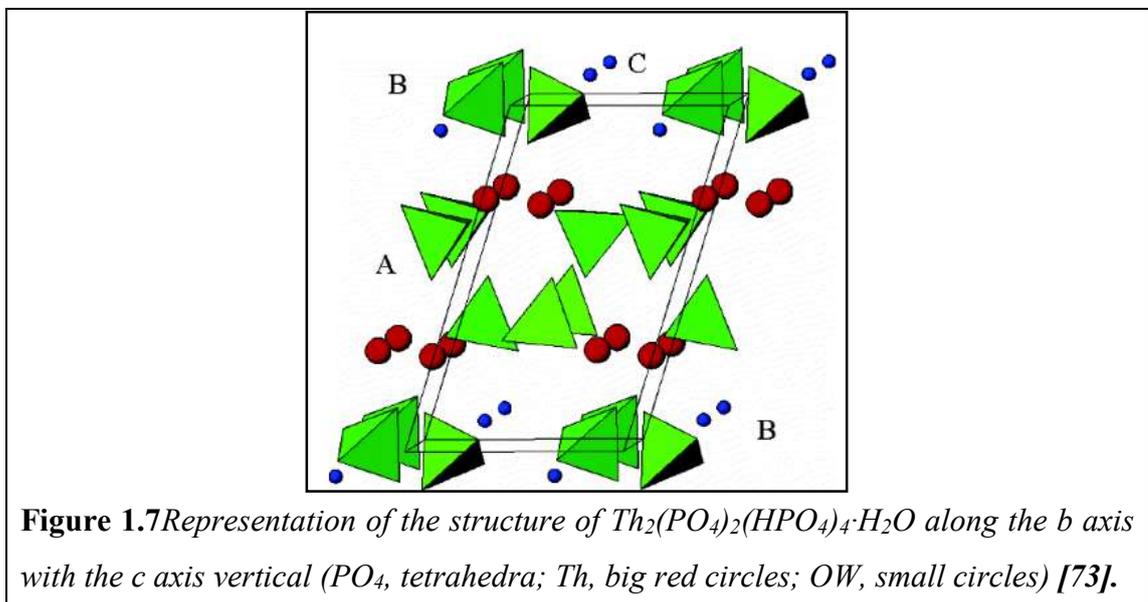
The phosphate $(\text{PO}_4)_1$ is surrounded by five thorium atoms, three Th1 and two Th2, acting always as a monodentate group. The O12 atom acts as a bridge between

one Th1 and one Th2 atoms. The phosphate (PO_4)₃ is surrounded by five thorium atoms, two Th1 and three Th2, and acts as bidentate ligand for one Th1 atom with the two oxygen atoms involved (O32 and O34) acting also as bridges between the Th1 and two Th2 atoms (**Figure 1.9**). The hydrogenphosphate (PO_4)₂ is surrounded by three thorium atoms, one Th1 and two Th2, acting always as a monodentate group. The oxygen atom O22 does not belong to the coordination environment of thorium atoms and it is close to the oxygen of water molecule. Then, it is plausible that this atom holds the hydrogen atom of the HPO_4 group.

Wallez et al [75] have reported structure evolution of crystallized precursor thorium phosphate hydrogenphosphate hydrate $\{\text{Th}(\text{PO}_4)_4(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}\}$ (TPHPH) and intermediate α -thorium phosphate diphosphate (α -TPD) and its hydrate (α -TPDH) have been resolved ab initio by Rietveld analysis of their synchrotron diffraction patterns.

As could be inferred from their powder patterns, the three compounds show a remarkable similarity in the structure of their $[\text{Th}_4(\text{PO}_4)_4]^{4+}$ slabs. The thorium atom is bonded to six oxygen atoms of the $\text{P}(1)\text{O}_4$ groups, forming hemispheric polyhedron. The close packing of Th and $\text{P}(1)\text{O}_4$ in the slabs differs from the monazite type by the orientation of the tetrahedra, which share two edges with the other anionic polyhedra in the latter and only one in the title compounds.

Clevier and Walleze [76] have reported synthesis, Raman and Rietveld analysis of thorium diphosphate. The obtained structure is analogous to those of the other $\text{M}^{\text{IV}}\text{P}_2\text{O}_7$ compounds.



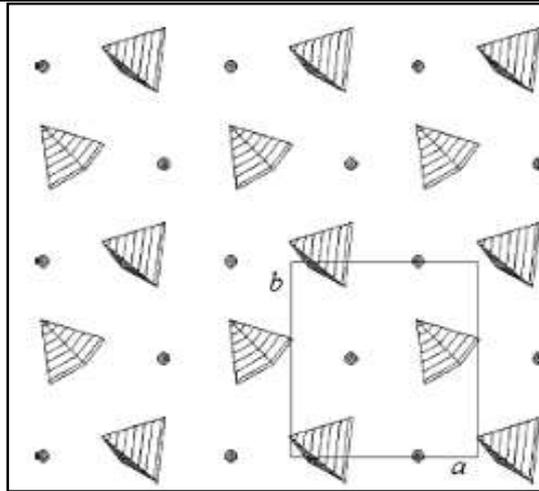


Figure 1.8 Perpendicular view of one hydrogenphosphate water layer of $Th_2(PO_4)_2(HPO_4)_4 \cdot H_2O$ [73].

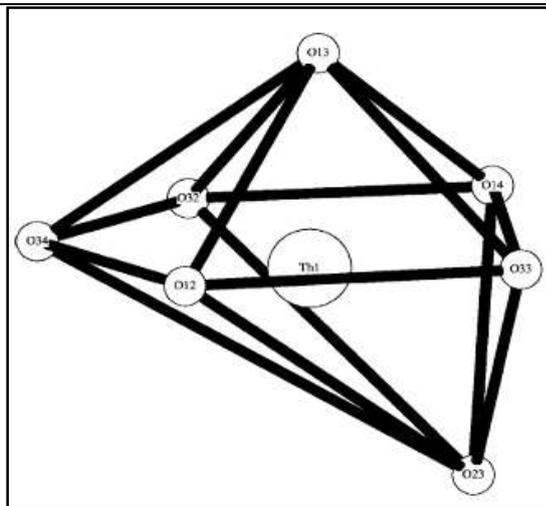


Figure 1.9 Representation of the Th1 polyhedra [73].

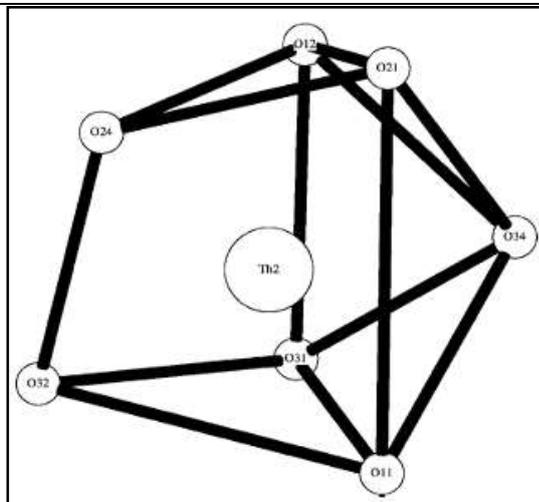


Figure 1.10 Representation of the Th2 polyhedra [73].

1.4 AIM AND SCOPE OF THE PRESENT WORK

The present work is focused towards synthesis, characterization and applications of amorphous CP and TP as cation exchangers, solid acid catalysts and solid state proton conductors.

Ion exchange is an excellent technique for removal of toxic metals from effluents. Ion exchange materials have played a vital role in waste water treatment and found extensive application in analytical/industrial chemistry. Various ion exchange materials are being studied, to improve efficiency and economy in its application to metal separations and removal/recovery. TMA salts possess structural hydroxyl groups (the H^+ of the $-OH$ being the exchangeable sites), due to which they behave as cation exchangers. The potential applications of TMA salts CP and TP can be explored as **cation exchangers** in separation science.

Catalysts and catalyst based technologies have undergone tremendous changes and the present trends in catalysis research and industrial catalysis is the materials approach and catalysts that are environment friendly. In the ongoing search for catalysts that are environment friendly, solid acid catalysts are making a huge impact. Due to presence of structural hydroxyl protons in TMA salts, surface acidity is expected, giving rise to solid acid characteristics. TMA salts CP and TP can therefore be explored as **environment friendly solid acid catalysts**.

Discovering new proton conductors and studying the mechanism of their conduction is an area of current interest, the potential use of such compounds being in fuel cells. The protons present in the structural hydroxyl groups indicates good potential for TMA salts CP and TP to be explored as **solid state proton conductors**.

Chapter II of the thesis is entitled is “*Synthesis and Characterization of Cerium (IV) and Thorium (IV) Phosphates*”. Amorphous CP and TP have been synthesized by sol-gel route. Further, the gels were subjected to microwave (MW) irradiation for optimum time and temperature to yield CP_M and TP_M . These materials have been characterized for **physical characteristics** {appearance, percentage moisture content, particle size, apparent density, true density, nature of exchanger and chemical stability}, **ion exchange characteristics** {CEC, effect of calcination on CEC, void volume fraction, concentration of fixed ionogenic groups and volume capacity of the resin}, **instrumental methods of characterization** {elemental analysis (ICP-AES), thermal analysis (TGA and DSC), spectral analysis (FTIR), X-ray

diffraction studies, SEM and EDX}, and **Catalyst characterization** {surface area measurements (BET method) and surface acidity (NH₃-TPD method)}.

Chapter III of the thesis is entitled as “*Applicability of Cerium (IV) and Thorium (IV) Phosphates as Cation Exchangers*”. The equilibrium exchange of transition metal ions (Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺) and heavy metal ions (Cd²⁺, Hg²⁺, Pb²⁺) ions with H⁺ ions contained in CP and TP have been studied varying temperature (303 K, 313 K, 323 K and 333 K), at constant ionic strength. Thermodynamic parameters equilibrium constant (K), standard Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) have been evaluated and correlated.

Adsorption isotherms (Langmuir and Freundlich) have been studied by varying metal ion concentration, pH, contact time and temperature. Langmuir constants (b and V_m) and Freundlich constants (K and $1/n$) have been evaluated using Langmuir and Freundlich isotherms respectively. R² value (goodness of fit criterion) has been computed by linear regression for both types of isotherms.

Distribution coefficient (K_d) has been determined at optimized conditions (optimum pH, optimum metal ion concentration and optimum equilibrium time) in aqueous as well as various electrolytes media/concentration (HNO₃, NH₄NO₃, HClO₄ and CH₃COOH of 0.2 M and 0.02 M).

Breakthrough curves have been plotted, breakthrough capacity (BTC) determined and compared with K_d values to confirm the selectivity order of metal ions.

Elution behaviour of metal ions has been studied using acids and electrolytes (HNO₃, NH₄NO₃, HClO₄ and CH₃COOH of 0.2 M and 0.02 M). Based on the separation factor α a few binary and ternary metal ion separations have been performed.

To explore the performance ability, CP and TP have been regenerated and reused.

Chapter IV of the thesis is entitled as “*Applicability of Cerium (IV) and Thorium (IV) Phosphates as Solid Acid Catalysts*”. The potential use of CP, TP, CP_M and TP_M as solid acid catalysts has been explored by studying esterification and acetal formation as model reactions.

Monoesters ethyl acetate (EA), propyl acetate (PA), butyl acetate (BA), benzyl acetate (BzAc) and diesters diethyl malonate (DEM), diethyl succinate (DES), dibutyl phthalate (DBP), dioctyl phthalate (DOP) have been synthesized.

A simple, efficient and highly eco-friendly protocol is described for the acetalization of benzaldehyde, cyclohexanone, acetophenone and benzophenone with pentaerythritol(PET) {2,2-bis(hydroxymethyl)propane-1,3-diol}.

In both cases (esterification and acetal formation), reaction conditions were optimized by varying parameters such as reaction time, catalyst amount and mole ratio of reactants. A study on regeneration and reuse of catalyst has been performed. The catalytic activity of CP, TP, CP_M and TP_M has been compared and correlated with surface properties of the materials. A reaction mechanism has been proposed and discussed for solid acid catalyzed esterification and acetalization reactions.

Chapter V of the thesis is entitled as “*Applicability of Cerium (IV) and Thorium (IV) Phosphates as Solid State Proton Conductors*”. Proton transport properties of CP, TP, CP_M and TP_M have been investigated by measuring specific conductance at different temperatures in the range of 30 - 120 °C at 10 °C intervals using an impedance analyzer {Solartron Impedance Analyzer (SI 1260) over a frequency range 1 Hz - 32 MHz at a signal level below 1 V}.

Trends in specific conductance of CP, TP, CP_M and TP_M has been compared and correlated based on CEC values and surface acidity. Mechanism of conductance in these materials has been discussed based on conductivity (σ) data and activation energy (E_a).

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