Chapter – III
Chemical Synthesis of Doped and Tl(I) Doped Tungsten and Molybdenum Heteropolyoxometalate (HPOM) Thin Films

3.1 Introduction
Several methods are in existence for deposition of the thin films. The choice and selection of a particular deposition technique depends upon several factors such as materials to be deposited, nature of the substrate support required, film thickness, required surface area, structure of the film, application of the film etc. As mentioned earlier, we have used simple chemical growth process for synthesis of the films under study. The process is relatively slow and therefore facilitates better orientation, stoichiometry crystallinity of the thin films. Further it is low temperature process that avoids thermal expansion of the substrate material & intermetallic conversions as well. The well adherent and uniform thin films are obtained by this method.

Among the various methods used for the preparation of transition metal oxide thin films described in chapter I, the most simple and convenient chemical bath deposition technique was employed for the preparation of tungsten and molybdenum HPOM thin films. This chapter is fully devoted to the experimental set up and optimization of experimental conditions for the preparation of tungsten and molybdenum HPOM thin films by the chemical bath deposition technique.

3.2 Theoretical Background and chemistry of transition metal oxide
Before preparation of tungsten and molybdenum HPOM thin films , it is necessary to give detailed theoretical background, chemical and physical properties of phosphotungstic acid (H$_3$PW$_{12}$O$_{40}$), tungsten trioxide (WO$_3$), thallium, phosphomolybdic acid (H$_3$PW$_{12}$O$_{40}$), molybdenum trioxide (MoO$_3$), phosphorus, tungsten, molybdenum.
3.2.1 Phosphotungstic acid

<table>
<thead>
<tr>
<th>Other names</th>
<th>PTA, TPA, tungstophosphoric acid</th>
</tr>
</thead>
</table>

**Properties**

<table>
<thead>
<tr>
<th>Molecular formula</th>
<th>H₃PW₁₂O₄₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass</td>
<td>2880.2 g/mol (anhydrous)</td>
</tr>
<tr>
<td>Melting point</td>
<td>89 °C (hydrate)</td>
</tr>
</tbody>
</table>

A) Nomenclature

Phosphotungstic acid (PTA), tungstophosphoric acid (TPA), is a heteropoly acid with the chemical formula H₃PW₁₂O₄₀. It normally present as a hydrate. It has the appearance of small, colorless-grayish or slightly yellow-green crystals, with melting point 89 °C (24 H₂O hydrate). It is odorless and soluble in water (200 g/100 ml). It is not especially toxic, but is a mild acidic irritant. The compound is known by a variety of different names and acronyms including:-

- Phosphotungstic acid (PTA), (PWA)
- Tungstophosphoric acid (TPA)
- 12-phosphotungstic acid
- 12-tungstophosphoric acid (cited as the IUPAC standard in Cotton and Wilkinson, 2d edition, 1966) [1]
- Dodeca tungstophosphoric acid

In the above the "12" or "dodeca" reflects the fact that the anion contains 12 tungsten atoms. Some early workers who did not know the structure, such as Hsien Wu [2], called it phospho-24-tungstic acid, formulating it as 3H₂O.P₂O₅ 24WO₃.59H₂O, (P₂W₂₅O₈₀H₆).29H₂O, which correctly identifies the atomic
ratios of P, W and O. This formula was still quoted in papers as late as 1970 [3].

B) Structure

Gouzerh summarizes the historical views on the structure of phosphotungstic acid [4] leading up to Keggin’s determination of the structure as:

- $H_7[P(W_2O_7)_6]$ proposed by Miolati and further developed by Rosenheim
- $H_3[PO_4W_{12}O_{40}(OH)_{36}]$ (Pauling)

The structure was determined by J.F Keggin first published in 1933 [5] and then in 1934 [6] and is generally known as the Keggin structure. The anion has full tetrahedral symmetry and comprises a cage of twelve tungsten atoms linked by oxygen atoms with the phosphorus atom at its centre. The following figure shows the octahedral coordination of oxygen atoms around the tungsten atoms, and that the surface of the anion has both bridging and terminal oxygen atoms.

![Fig. 3.4 Keggin structure of $(PW_{12}O_{40})^{3-}$](image)

Further investigation showed that the compound was a hexahydrate not a pentahydrate as Keggin had proposed [7].
C) Preparation and chemical properties

Phosphotungstic acid can be prepared by the reaction of sodium tungstate, \( \text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O} \), with phosphoric acid, \( \text{H}_3\text{PO}_4 \), acidified with hydrochloric acid, \( \text{HCl} \) [2].

Phosphotungstic acid solutions decompose as the pH is increased. A step-wise decomposition has been determined and the approximate compositions at various pH values are as follows [8].

<table>
<thead>
<tr>
<th>pH</th>
<th>principal components</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>([\text{PW}<em>{12}\text{O}</em>{40}]^{3-})</td>
</tr>
<tr>
<td>2.2</td>
<td>([\text{PW}<em>{12}\text{O}</em>{40}]^{3-}, [\text{P}<em>2\text{W}</em>{21}\text{O}<em>{71}]^{6-}, [\text{PW}</em>{11}\text{O}_{39}]^{7-})</td>
</tr>
<tr>
<td>3.5</td>
<td>([\text{PW}<em>{12}\text{O}</em>{40}]^{3-}, [\text{P}<em>2\text{W}</em>{21}\text{O}<em>{71}]^{6-}, [\text{PW}</em>{11}\text{O}<em>{39}]^{7-}, [\text{P}<em>2\text{W}</em>{18}\text{O}</em>{62}]^{6-}, [\text{P}<em>2\text{W}</em>{19}\text{O}_{67}]^{10-})</td>
</tr>
<tr>
<td>5.4</td>
<td>([\text{P}<em>2\text{W}</em>{21}\text{O}<em>{71}]^{6-}, [\text{PW}</em>{11}\text{O}<em>{39}]^{7-}, [\text{P}<em>2\text{W}</em>{18}\text{O}</em>{62}]^{6-})</td>
</tr>
<tr>
<td>7.3</td>
<td>([\text{PW}<em>{9}\text{O}</em>{34}]^{9-})</td>
</tr>
<tr>
<td>8.3</td>
<td>(\text{PO}_4^{3-}, \text{WO}_4^{2-})</td>
</tr>
</tbody>
</table>

The species \([\text{PW}_{11}\text{O}_{39}]^{7-}\) is a lacunary, or defective Keggin ion. The \([\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}\) has a Dawson structure. At pH less than 8, the presence of ethanol or acetone stabilizes the anion, \([\text{PW}_{12}\text{O}_{40}]^{3-}\), reducing decomposition [8].

Tungstophosphoric acid is thermally stable up to 400°C, and is more stable than the analogous silicotungstic acid, \(\text{H}_4\text{SiW}_{12}\text{O}_{40}\) [9].
Phosphotungstic acid is less sensitive to reduction than phosphomolybdic acid. Reduction with uric acid or iron (II) sulphate produces a brown coloured compound. The related silicotungstic acid when reduced forms a similar brown compound where one of the four W3 units in the Keggin structure becomes a metal-metal bonded cluster of three edge shared W (IV) octahedra [10].

Phosphotungstic acid is the strongest of heteropolyacids. Its conjugate base is the PW$_{12}$O$_{40}^{3-}$ anion [11]. Its acidity in acetic acid has been investigated and shows that the three protons dissociate independently rather than sequentially and the acid sites are of the same strength [12]. One estimate of the acidity is that the solid has an acidity stronger than $H_0 = -13.16$, [9] which would qualify the compound as a super acid. This acidic strength means that even at low pH the acid is fully dissociated.

**D) Uses**

**i) Catalyst**

In common with the other heteropolyacids, phosphotungstic acid is a catalyst and its high acidity and thermal stability make it a catalyst of choice according to some researchers [13]. It is in solution as a homogeneous catalyst, and as a heterogeneous catalyst “supported” on a substrate e.g. alumina, silica. Some acid catalyzed reactions include:

**ii) Dyeing and pigments**

Phosphotungstic acid has been used to precipitate different types of dyes as "lakes" [14]. Examples are basic dyes and triphenylmethane dyes, e.g. para-rosaaniline derivatives [15].

**iii) Histology**

Phosphotungstic acid is used in histology for staining specimens, as a component of phosphotungstic acid haematoxylin, PTAH, and “trichrome”
reagents, and as a negative stain for imaging by a transmission electron microscope.

iv) Phosphotungstic acid haematoxylin
Mallory described the reagent now generally known as PTAH in 1897 [16]. PTAH stains tissues either reddish brown or blue depending on their type. This property of simultaneously staining two different colours is different from other haematoxylin reagents e.g. alum-haematoxylin. The role of phosphotungstic acid and the mechanism of staining is not fully understood. Interestingly the active component of haematoxylin is the oxidized form, haematin, although this rarely acknowledged in the literature which refer to haematoxylin staining. Phosphotungstic acid forms a lake with haematin [17]. The make up of the reagent is uncertain, examination of a year old sample showed there to be three coloured components, blue, red and yellow [18]. These were not identified. Some investigations of “model” systems, reacting various compounds e.g. amino acids, purins, pyrimidines and amines. with PTAH show that they give rise to different colours [19].

v) Trichrome reagents
In these reagents two or three basic dyes are used with phosphotungstic acid, in either a one step or multi-stage procedure. These reagents colour different tissue types different colours. Again the mechanism of staining is not fully understood. Some explanations include the proposal that phosphotungstic acid acts as a mordant to bind the dye to the tissue [20] or that alternatively it binds to tissue blocking it to dye molecules [21].

vi) Negative staining
Adsorption onto tissue or the surface of viruses and its electron density are the bases of phosphotungstic acids action as a negative stain. This electron density arises from the presence of the 12 tungsten atoms which each have an atomic number of 74. The mechanism of the adsorption onto tissue has been proposed as being electrostatic rather than involving hydrogen bonding, as adsorption is not affected by pH [3].
vii) Analysis

The potassium salt is only slightly soluble, unlike most other phosphotungstate salts, and has been proposed as a method for the gravimetric analysis of potassium [22].

viii) Precipitation of proteins

In a number of analytical procedures one of the roles of phosphotungstic acid is to precipitate out proteins. It has been termed a "universal" precipitant for polar proteins [23]. Further studies showed that no precipitation occurred with α-amino groups but did occur with guanidino, ε-amino and imidazole groups [24].

ix) Medicinal

Very little work appears to have been carried out in this area. One example relates to liver necrosis in rats [25].

x) Composite proton exchange membranes

The heteropoly acids, including phosphotungstic acid, are being investigated as materials in composite proton exchange membrane, such as Nafion. The interest lies in the potential of these composite materials in the manufacture of fuel cells as they have improved operating characteristics [26].

3.2.3 Thallium

A) General

Name, Symbol, At. Number
Thallium, Tl, 81

Element category
Poor metal

Group, Period, Block
13,6,P

Standard Atomic Weight
204.3833 g·mol⁻¹
Electron Configuration: [Xe] 4f^{14} 5d^{10} 6s^{2} 6p^{1}

Electrons per Shell: 2, 8, 18, 32, 18, 3

**B) Physical properties**

- Phase: solid
- Density (near r.t.): 11.85 g·cm$^{-3}$
- Melting Point: 577 K (304 °C, 579 °F)

**C) Atomic properties**

- Crystal structure: hexagonal
- Oxidation states: 3, 1 (mildly basic oxide)
- Atomic radius: 190 pm
- Atomic radius (calc.): 156 pm
- Covalent radius: 148 pm

**D) Miscellaneous**

- Magnetic ordering: Diamagnetic
- Electrical resistivity: (20°C) 0.18 µΩ·m
- Thermal conductivity: (300 K) 46.1 W·m$^{-1}$·K$^{-1}$

Thallium is a chemical element with the symbol Tl and atomic number 81. This soft gray malleable poor metal resembles tin but discolors when exposed to air. Approximately 60-70% of thallium production is used in the electronics industry, and the rest is used in the pharmaceutical industry and in glass manufacturing[27,28]. It is also used in infrared detectors. Thallium is highly toxic and is used in rat poisons and insecticides, but its use has been cut back or eliminated in many countries. Because of its use for murder, thallium has gained the nicknames "The Poisoner's Poison" and "Inheritance Powder" (alongside arsenic).
E) Characteristics

Thallium is very soft and malleable and can be cut with a knife at room temperature. It has a metallic luster, but when exposed to air, it quickly tarnishes with a bluish-grey tinge that resembles lead. (It is preserved by keeping it under oil). A heavy layer of oxide builds up on thallium if left in air. In the presence of water, thallium hydroxide is formed.

F) Applications

The odorless and tasteless thallium sulfate was once widely used as rat poison and ant killer. Since 1975, this use in the United States and many other countries is prohibited due to safety concerns [28]. Other uses:

- Thallium (I) sulfide's electrical conductivity changes with exposure to infrared light therefore making this compound useful in photocells [29].
- Thallium (III) salts, as thallium trinitrate or triacetate, are useful reagents in organic synthesis performing different transformations in aromatics, ketones, olefins, among others.
- Thallium (I) bromide and thallium (I) iodide crystals have been used as infrared optical materials, because they are harder than other common infrared optics, and because they have transmission at significantly longer wavelengths. The trade name KRS-5 refers to this material.[30]
- used in semiconductor materials for selenium rectifiers,[30]
- used as a dopant for sodium iodide crystals in gamma radiation detection equipment, such as scintillation counters,
- high-density liquid used for sink-float separation of minerals,
- used in the treatment of ringworm and other skin infections. However this use has been limited due to the narrow therapeutic index.[30]
- radioactive thallium-201 (half-life of 73 hours) is used for diagnostic purposes in nuclear medicine, particularly in stress tests used for risk stratification in patients with coronary artery disease A(CAD).[30,31] This isotope of thallium can be generated using a transportable generator which is similar to the technetium cow.[32] The generator contains lead-201 (half life 9.33 hours) which decays by electron
capture to the thallium-201. The lead-201 can be produced in a cyclotron by the bombardment of thallium with protons or deuterons by the \((p, 3n)\) and \((d, 4n)\) reactions.[33]

- Thallium oxide has been used to manufacture glasses that have a high index of refraction. Combined with sulfur or selenium and arsenic, thallium has been used in the production of high-density glasses that have low melting points in the range of 125 and 150 °C. These glasses have room temperature properties that are similar to ordinary glasses and are durable, insoluble in water and have unique refractive indices.[34].
- A mercury-thallium alloy, which forms a eutectic at 8.5% thallium, is reported to freeze at \(-60\) °C, some 20 °C below the freezing point of mercury. This allows it used in thermometers and low-temperature switches.[35]
- Thallium is used in the electrodes in dissolved oxygen analyzers.[38]
- Thallium is a constituent of the alloy in the anode plates in magnesium seawater batteries.[34]

In addition, research activity with thallium is ongoing to develop high-temperature superconducting materials for such applications as magnetic resonance imaging, storage of magnetic energy, magnetic propulsion, and electric power generation and transmission. After the discovery of the first thallium barium calcium copper oxide superconductor in 1988 the research in applications started.[35]

**G) Toxicity (Thallium poisoning)**

Thallium and its compounds are extremely toxic, and should be handled with great care. Contact with skin is dangerous, and adequate ventilation should be provided when melting this metal. Thallium (I) compounds have a high aqueous solubility and are readily absorbed through the skin. Exposure to them should not exceed 0.1 mg per m² of skin in an 8-hour time-weighted average (40-hour work week). Thallium is a suspected human carcinogen[36].
H) Treatment and internal decontamination

One of the main methods of removing thallium (both radioactive and normal) from humans is to use Prussian blue, which is a solid ion exchange material which absorbs thallium and releases potassium. Up to 20 g per day of Prussian blue is fed by mouth to the person, and it passes through their digestive system and comes out in the stool. Hemodialysis and hemoperfusion are also used to remove thallium from the blood serum. At later stage of the treatment additional potassium is used to mobilize thallium from the tissue [37-39].

3.3 Experimental

3. 3.1 Thin Film Deposition Chamber used in chemical bath deposition technique:-

This section deals with fabrication of thin film deposition assembly and associated accessories. A thin film deposition chamber was designed and fabricated in our laboratory whose dimensions are 1.8 x 0.8 x 1.0 m. Thin film deposition chamber maintains a clean, ambient atmosphere necessary for the deposition of thin films and protects the deposition system from the physical hazards. Cross-sectional view of deposition bath essentially consist of constant speed AC gear motor, oil bath and constant temperature system with magnetic stirrer, reaction container, substrate holder and temperature controller etc. as shown in Fig.3.1

3.3.2 Constant temperature bath:

The constant temperature bath of the dimension 3½ x 6' having temperature controller attachment was fabricated in our laboratory. In order to obtain uniform deposition temperature, 750 ml paraffin oil was kept in a bath. The constant temperature bath was then agitated using Remi-magnetic stirrer, which was kept on movable stand for adjustment of the height to a required level.
3.3.3 Reaction container:

The reaction container of the dimension 100 mm x 60 mm having 150 ml capacity was fabricated using borosil glass in University Scientific Instrumentation Centre (USIC), Shivaji University, Kolhapur. The reaction mixture was taken into this reaction container provided with magnetic needle at the bottom of the container. The container was kept in constant temperature bath. In order to avoid non-uniform heating of reaction container, glass ring was used to rest the reaction container. Glass ring was used to rest the reaction container in an oil bath.

3.3.4 Constant Speed Motor:

A single phase A.C. gear motor type RU-56-36-HP, 1/8 Amps.1 was used for rotating the substrate at specified speed in a reaction container. A dimerstat-cum-regulator was provided to the motor for better speed control. The speed of the motor can be varied from 40 rpm to 100 rpm. The motor
was fitted to a metallic stand having sufficient height to adjust the position of A.C. gear motor.

Fig.3.2 Cross sectional view of thin film deposition assembly

Fig.3.3.A. Design of the substrate holder

Fig.3.3.B. Cross sectional view of substrate holder.
A rotating shaft-cum-metallic rod of the dimension 20 x 0.5 mm was fitted to the motor and other end of the rod was attached to a substrate holder.

3.3.5 Substrate Holder:

Substrate holder is fabricated by using bakelite material of appropriate thickness in our laboratory and used for holding the substrate in horizontal position as shown in figure. The position of the motor was adjusted to a drilling machine stand in such a way that more than 2/3 portion of the substrates will dip into the solution container and substrates are exactly perpendicular to each other. The substrates were fitted to the bakelite disc of 5.3 cm in diameter and 1 cm thick with 4 slots cut into the disc in such a way that the rotating substrates did not touch the wall of the solution container, which may cause serious damage to the films. Thus continuous and proper bulk churning of the solution in the reaction container was made possible.

3.3.6 Preparation of conducting FTO coatings on glass substrates

The conducting FTO coatings were prepared using pentahydrated stannic chloride (SnCl$_4$·5H$_2$O) (purity 98%) and ammonium fluoride (NH$_4$F) (purity 95%) as precursor salts. The solution was prepared in double distilled water. The FTO coated conducting glass substrates with 90–95% transparency and sheet resistance of 10–15 $\Omega$/cm$^2$ were obtained at 500°C. These FTO-coated glass substrates were further used as conducting substrates for the deposition of electrochromic niobium oxide thin films.

3.3.7 Substrate Cleaning

Cleanliness of the substrates, for thin film deposition is most important factor. It affects the adherence, smoothness and uniformity of the film. The technique to be adopted for cleaning depends on nature of substrates, degree of cleanliness required and nature of contaminants to be removed. The common contaminants are grease, adsorbed water, airborne dust, lint and oil particles. Cleanliness is the process of breaking the bonds between substrates and contaminants without damaging the substrates. There are various methods to supply energy for breaking such bonds, such as heating,
bombarding by ions scrubbing etc. Following cleaning procedure was used for the glass substrates.
1) The substrates were first washed with the neutral detergent solution ‘labolene’ and then with the double distilled water.
2) The substrates were boiled in chromic acid for few minutes.
3) NaOH treatment was given to remove the acidic contaminants.
4) The substrates were again washed with double distilled water.
5) Lastly, the substrates were ultrasonically cleaned.
6) Drying of the substrates were done in the vapors of the alcohol.

this helped in depositing uniform and better orientation of the crystallites.

3.4 Preparation of tungsten heteropolyoxometalate thin films.
3.4.1 Introduction

The heteropolyoxometalate (HPOM) materials of Vanadium, Molybdenum and Tungsten are an exciting class of materials whose properties are intermediate between atoms or molecules and bulk materials. They exhibit size dependent physical and chemical properties largely as a consequence of the confinement of their anionic nature and their unusual molecular structures [40]. Metal ion doped HPOM materials are technologically important due to its high electrical and thermal conductivities [41], redox ion exchange behaviours [42-46]. The applications of HPOM centre depend on there high charge and ionic weights. An enormous patent and journal literature is devoted to the applications of small number of heteropolyanions. The heteropolyanions of V, Mo, and W find applications in biochemical industrial catalysis, proton conductor [47], ion exchange materials, thin layer chromatography, materials for separation of amino acids [48]. Heteropolyoxometalates (HPOM), in addition to their considerable applications in catalysis and medicine, are attracting attention as compounds for advanced materials. The investigation on HPOM complexes with metal ions including Ln (III) ions has important significance due to their antiviral and anti-HIV activity and potential applications in opto-electronic devices [49].
3.4.2 Solutions required for preparing pure and Ti (I) doped tungsten HPOM thin films

Thin films of Ti (I) doped tungsten HPOM were prepared by dissolving following AR grade chemicals in double distilled water.

a) 2% solution of phosphotungstic acid \([H_3 (PW_{12} O_{40})]\) in acetone.

b) 2% aqueous solution of phosphotungstic acid \([H_3 (PW_{12} O_{40})]\).

c) 0.2%, aqueous solution of thallous acetate (CH₃COO- Tl).

d) 0.1% aqueous solution of polyacrylamide (PAM).

3.4.3 Deposition of Phosphotungstic acid \([H_3 (PW_{12} O_{40})]\) thin films

For the deposition of thin films of phosphotungstic acid \([H_3 (PW_{12} O_{40})]\), 2% solution of phosphotungstic acid in acetone was taken in 150 cm³ glass beaker. The cleaned and dried glass as well as FTO substrates were fitted to bakelite substrate holder and dipped in this solution. The speed of substrate rotation was kept 50-60 rpm. After half hour, there was white colored and uniform deposition of \([H_3 (PW_{12} O_{40})]\) on glass and FTO substrates. As deposited thin films were dried in constant temperature oven at 80 °C. After cooling at room temperature, these films were dipped in 0.1% aqueous solution of polyacrylamide (PAM) in order to get the adhesive thin films. Thickness of the as deposited films was measured by surface profilometer and it was 508.2 nm.

3.4.4 Deposition of Ti (I) doped phosphotungstic acid \([Ti_3 (PMo_{12} O_{40})]\) thin films.

90 cm³ 2 % aqueous solution of phosphotungstic acid was taken in 150 cm³ capacity beaker having side arm and temperature of this solution was kept at 55 °C. The clean & dry glass as well as FTO substrates were fitted to bakelite substrate holder and dipped in the phosphotungstic acid solution. After five minutes 0.2% aqueous solution of thallous acetate was added drop wise through side arm in phosphotungstic acid solution. The speed of substrate rotation was kept 50-60 rpm. After 1½ hour, there was white colored and uniform deposition of \([Ti_3 (PW_{12} O_{40})]\) HPOM on glass and FTO substrates. As deposited thin films were dried in constant temperature oven at
80 °C. After cooling at room temperature, these films were dipped in 0.1% aqueous solution of polyacrylamide (PAM) in order to get the adhesive thin films. Thickness of the as deposited films was measured by surface profiler and it was 371.8 nm.

Fig. 3.5 Photograph of as deposited Tungsten HPOM Thin film

The reactions involved during the growth of tungsten HPOM thin films are---

(i) \[ H_3(PW_{12}O_{40}) \rightarrow (PW_{12}O_{40})^{3-} + 3H^+ \]
phosphotungastic acid \hspace{1cm} phosphotungstate anion

(ii) \[ 3\text{CH}_3\text{–COO–Tl} \rightarrow 3\text{CH}_3\text{–COO}^- + 3\text{Tl}^+ \]
Thallous Acetate \hspace{1cm} Acetate ion

(iii) \[ 3\text{CH}_3\text{–COO}^- + 3H^+ \rightarrow 3\text{CH}_3\text{–COOH} \]
Acetate ion \hspace{1cm} Acetic acid

(iv) \[ H_3(PW_{12}O_{40})^{3-} + 3\text{Tl}^+ \]
phosphotungstate anion \hspace{1cm} Thallous ion
Ion by ion condensation

\[ \text{Tl}_3(PW_{12}O_{40}) \]
Thallium (I) doped Tungsten HPOM.
The overall reaction is,

\[ \text{H}_3(\text{PW}_{12}\text{O}_{40}) + 3 \text{CH}_3-\text{COO} - \text{Tl} \xrightarrow{(v)} \text{Tl}_3(\text{PW}_{12}\text{O}_{40}) + 3\text{CH}_3^-\text{COOH} \]

Temp. = 55°C

3.5 Preparation of molybdenum heteropolyoxometalate thin films.

3.5.1 Introduction

The heteropolyoxometalate (HPOM) materials of vanadium, molybdenum and tungsten are an exciting class of materials whose properties are intermediate between atoms or molecules and bulk materials. They exhibit size dependent physical and chemical properties largely as a consequence of the confinement of their anionic nature and their unusual molecular structures [48]. Due to high electrical conductivity, thermal conductivity and redox ion exchange behaviors, metal ion doped heteropolyoxometalates are found to be technologically important. The applications of HPOM centre depend on their high charge and ionic weights. An enormous patent and journal literature is devoted to the applications of small number of heteropolyanions. The heteropolyanions of V, Mo, and W find applications in biochemical industrial catalysis, proton conductor, ion exchange materials, thin layer chromatography, materials for separation of amino acids [58].

Heteropolyoxometalates (HPOM), in addition to their considerable applications in catalysis and medicine, are attracting attention as compounds for advanced materials. The investigation of HPOM complexes with metal ions including Ln (III) ions has important significance due to their antiviral, anti-HIV activity and potential applications in opto-electronic devices [57]. The literature survey and internet search of heteropolyoxometalates of molybdenum and tungsten have shown that there is no report available on thin films prepared by chemical growth process. In the present investigation, we report preparation and characterization of chemically deposited thallium (I) doped molybdenum \([\text{Tl}_3(\text{PMo}_{12}\text{O}_{40})]\) and tungsten \([\text{Tl}_3(\text{PW}_{12}\text{O}_{40})]\)
heteropolyoxometalate thin films. The experimental procedure used for the preparation of these thin films is given as bellow.

3.5.2 Preparation of Solutions

Thin films of Ti (I) doped molybdenum HPOM were prepared by dissolving following AR grade chemicals in double distilled water.

a) 2% solution of phosphomolybdic acid. [H₃(PMo₁₂O₄₀)] in acetone.
b) 2% aqueous solution of phosphomolybdic acid. [H₃(PMo₁₂O₄₀)]
c) 0.2%, aqueous solution of thallous acetate (CH₃COO· Ti)
d) 0.1 % aqueous solution of polyacrylamide (PAM)

3.5.3 Deposition of pure Phosphomolybdic acid thin films [H₃(PMo₁₂O₄₀)].

For the deposition of thin films of pure phosphomolybdic acid [H₃(PMo₁₂O₄₀)], 2% solution of phosphomolybdic acid in acetone was taken in 50 cm³ glass beaker. The cleaned and dried glass as well as FTO substrates were fitted to bakelite substrate holder and dipped in the in this solution. The speed of substrate rotation was kept 50-60 rpm. After half hour, there was yellow colored and uniform deposition of [ H₃ (PMo₁₂ O₄₀) ] on glass and FTO substrates. As deposited thin films were dried in constant temperature oven at 110 °C. After cooling at room temperature, these films were dipped in 0.1% aqueous solution of polyacrylamide (PAM) in order to get the adhesive thin films. Thickness of the as deposited films was measured by surface profilometer and it was 517.3 nm.

3.5.4 Deposition of Ti (I) doped Phosphomolybdic acid [Ti₃(PMo₁₂O₄₀)] thin films.

90 cm³ 2 % aqueous solution of phosphomolybdic acid was taken in 150 cm³ capacity beaker having side arm and temperature of this solution was kept at 60 °C. The clean & dry glass as well as FTO substrates were fitted to bakelite substrate holder and dipped in the phosphomolybdic acid solution. After five minutes 0.2% aqueous solution of thallous acetate was added drop wise through side arm in phosphomolybdic acid solution. The speed of substrate rotation was kept 50-60 rpm. After 1½ hour, there was yellow
colored and uniform deposition of \[ \text{[Tl}_3 (\text{PMo}_{12} \text{O}_{40}) \] } \text{HPOM on glass substrates. As deposited thin films were dried in constant temperature oven at 110 } ^\circ \text{C. After cooling at room temperature, these films were dipped in 0.1% aqueous solution of polyacrylamide (PAM) in order to get the adhesive thin films. Thickness of the as deposited films was measured by surface profiler and it was 408.3 nm.}

![Fig.3.6 Photograph of as deposited molybdenum HPOM Thin film](image_url)

The reactions involved during the growth of molybdenum HPOM thin films are

\[ \text{H}_3 (\text{PMo}_{12} \text{O}_{40}) \rightarrow (\text{PMo}_{12} \text{O}_{40})^{3-} + 3\text{H}^+ \quad (i) \]

Phosphomolybdic acid \hspace{1cm} Phosphomolybdate anion

\[ 3\text{CH}_3\text{–COO–Tl} \rightarrow 3\text{CH}_3\text{–COO}^- + 3\text{Ti}^+ \quad (ii) \]

Thallous Acetate \hspace{1cm} Acetate ion

\[ 3\text{CH}_3\text{–COO}^- + 3\text{H}^+ \rightarrow 3\text{CH}_3\text{–COOH} \quad (iii) \]

Acetate ion \hspace{1cm} Acetic acid

\[ \text{H}_3(\text{PMo}_{12}\text{O}_{40})^{3-} + 3\text{Ti}^+ \]

Phosphomolybdate anion \hspace{1cm} Thallous ion

\[ \text{ion by ion condensation} \]

\[ \text{Tl}_3 (\text{PMo}_{12} \text{O}_{40}) \]

Thallium (I) doped Molybdenum HPOM.
The overall reaction is,

\[ \text{P}^H = 1.0 \]
\[ \text{H}_3 (\text{PMo}_{12} \text{O}_{40}) + 3 \text{CH}_3 - \text{COO-Tl} \rightarrow \text{Tl}_3 (\text{PMo}_{12} \text{O}_{40}) + 3 \text{CH}_3 - \text{COOH} \]

\[ \text{Temp.} = 60^\circ \text{C} \]

3.6 Effect of preparative parameters:

The chemical bath deposition technique i.e. solution growth process is now proved to be most suited method for deposition of metal oxide thin films. However growth of the metal oxide film is found to be influenced by the various preparative parameters such as geometry of the substrate holder, speed of substrate rotation, bath composition, the \( \text{P}^H \), deposition time and deposition temperature.

3.6.1 Geometry of the substrate holder:

A specially designed substrate holder as shown in figure 3.3 was used for holding the substrate in vertical position. The holder was fabricated by using bakelite material of appropriate thickness. It is a circular disc slotted to fix the substrate in such a fashion that each of the substrate was exactly perpendicular to each other. The continuous proper bulk churning of the solution in the reaction container was made possible which help in depositing uniform and better orientation of the crystallites. In order to rotate the substrate in a reaction container the substrate holder is attached to rotating shaft of constant speed, A. C. gear Remi make electric motor.

3.6.2 Speed of Substrate Rotation:

The deposition of the metal oxide thin film on the substrate material is greatly influenced by the speed of substrate rotation, at lower speed (say below 40 rpm) thick, porous and non adherent films were obtained at higher speeds (say above 70rpm) very thin adherent and reflecting film deposition was obtained. Hence in the present investigation the speed of the substrate rotation was kept at optimum value of 50-60 rpm so as to obtain uniform and adherent metal oxide films on the substrate surface.
3.6.3 Bath Composition:-

The growth rate and quality of the deposited films was greatly influenced by the concentration of the reacting species. Therefore we have studied the effect of concentration of reacting species for various concentrations. The film deposited by using low concentration was thin and non-uniform. This shows that the insufficient supply of ionic species at such concentration level. On the other hand when concentration of species was increased, the quality and uniformity of the films goes on increasing and films were thick. This is true up to a certain level of concentration and then saturation in the growth process was observed.

3.6.4 pH:-

The simple chemical bath deposition process used for growth of oxide thin films largely depends on pH value of reacting solution. The oxides are well known to be pH sensitive. Increase in the pH value causes increase in the relative molecular surface area and solubility. At acidic pH uniform crystallite size and uniform thin films were observed.

3.6.5 Deposition Time: -

The growth rate was also studied for various deposition durations. Growth of the thin film is time dependent; hence the deposition of the film was varied from half hour to one and half hour depending upon the thickness of film. The deposition time of half hour for pure and one and half hour for Tl (I) doped HPOM was therefore kept constant throughout the experiment.

3.6.6 Deposition Temperature:

The temperature dependence of growth rate shown by literature survey that the rate of deposition increases with bath temperature resulting in formation of fine grained structure. Hence optimum temperature selected for the deposition is 50-60 °C.

3.7 Conclusions-

The chemical bath deposition technique is found to be most convenient and simple method for the preparation of tungsten and molybdenum heteropolyoxometalate thin films. The deposited films are compact, homogeneous and adherent.
References

[24]. M. Z. Sternberg, Biotech. and Bioengineering 12, 1, (1970), 1 - 17
[31]. Thallium Test from Walter Reed Army Medical Center Oxford University Press. (2004) 326.
[32]. Thallium Stress Test from the American Heart Association
[34]. Thallium-201 production from Harvard Medical School's Joint Program in Nuclear Medicine
[36]. "Biology of Thallium". Web elements.
[37]. Prussian blue fact sheet from the Centers for Disease Control and Prevention

[40]. Ying-Hua Sun, Ji-Qing Xu, Ling Ye, Xiao-Bing Cui, Yong Li, Hai-Hui Yu, Guang-Hua Li, Guang-Di Yang and Yan Chen J. Mol. Str. 740 (2005) 193.


