

FT-IR and Thermal Behavior of θ -Type Zirconium- and Hafnium Phosphates and Their Pellicular Membranes

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Summary θ -Type Zirconium Phosphate, $Zr(HPO_4)_2 \cdot 1.88H_2O$ and θ -Type Hafnium Phosphate, $Hf(HPO_4)_2 \cdot 1.61H_2O$, were prepared by direct precipitation method (the HF-method). Their pellicular membranes, $Zr(HPO_4)_2 \cdot 1.35H_2O$ and θ - $Hf(HPO_4)_2 \cdot 1.22H_2O$, were prepared via Intercalation-deintercalation of Arginine into their parent θ -Type materials. All products were characterized by FT-IR, x-ray and thermal analysis. Their exchange capacities were determined by Na^+ ions potentiometric titration. Their FT-IR studies shows the effectiveness of the vibrational spectra in characterizing the resulted products, that supported by TG/DTA and x-ray powder diffraction analysis. From their vibrational spectroscopic investigation it was found the water molecules Characteristic infrared bands that can be assigned to regular hydrogen bonding of each molecule to adjacent OH group(of POH).

Introduction

Inorganic ion exchange materials of M(IV) phosphates have been known as amorphous for some time^(1,2). The discovery of their crystalline layered materials in 1964⁽³⁾ represents a fundamental step in the chemistry of these compounds. The layered materials exist as bi-dimensional (2-D) and three-dimensional (3-D) structures^(4,5). When their chemistry established sufficiently, increase attention has been directed towards their intercalation^(6,7), catalytic properties^(8,9) electrical conductance^(10,11) and as sensors⁽¹²⁾.

Pellicular and fibrous membranes are also known^(13,14). However, the synthesis of Pellicular and fibrous membranes still in its infancy. Layered M(IV) phosphates, exist in α , θ and γ -forms of general formula α -M(IV)(HPO_4)₂.H₂O, θ -M(IV)(HPO_4)₂.I.88-5H₂O

and γ -M(IV).PO₄.H₂PO₄.2H₂O, respectively, (where: M=Ti, Zr, Hf, Sn etc) their protons (the POH groups) have a tendency to be exchanged by other cations^(3,15-17).

Inorganic ion exchange membranes attracted attention, because inorganic materials are usually more stable than those organics toward temperature, oxidizing agents etc⁽²⁾.

Membranes consisting of inorganic polymers are very attractive and could be suitable for use in many of chemical technology.

Metal (IV) phosphates are an interesting materials for the preparation of inorganic ion-exchange membranes, because of their high stability and posses high ion exchange capacities^(13,14).

In our laboratory we are carrying out systematic investigations on new inorganic ion-exchange membranes of metal (IV) phosphates which are prepared by different methods.

This paper presents the studies on FTIR and thermal behavior of pellicular zirconium- and hafnium phosphates membranes, which were prepared by novel method and on their parent θ -type layered materials.

Experimental

Chemicals

ZrOCl₂.8H₂O, H₃PO₄ (85%), Arginine (BDH), HfCl₄ (98%) Aldrich, and HF (40%) of Reidel De-Haen. Other chemicals used were of analytical grade.

Instruments used for characterization

IFS25 FITR Bruker , X-ray diffractometer, D-500 Ni-Filter CuK α -Bruker, Seiko SII instruments Exstra 6000 DTA/TG 6300 thermal analyzer, pH meter CG820.

Preparation of θ -type zirconium -, and hafnium phosphates

50 ml 0.5 M ZrOCl₂.8H₂O (or HfCl₄) in 3M HF were mixed with 200 ml of (4.6 M) H₃PO₄ in Pyrex round bottom flask (prior to mixing the solutions were cooled at ~15°C). The mixture was left at ~15°C for 3days. The resultant precipitate was washed

with distilled water, by addition and decantation of distilled water, up to pH 3, then filtered and dried in air.

Preparation of pellicular zirconium-, and hafnium phosphates membranes via intercalation-deintercalation of arginine

To 0.5 g of θ -type zirconium phosphate(or θ -type hafnium phosphate) 0.05 M arginine aqueous solution was gradually added with stirring at room temperature up to 40% total loading, the stirring was continued for 48 h at room temperature ($\sim 20^{\circ}\text{C}$). The resultant product was protonated by 1 M HCl up to pH \sim 2.2. Then subjected to washing by distilled water, up to pH \sim 3, then filtered on porous plastic filter and dried in air to obtain flexible thin film membrane.

Results and Discussion

θ -types zirconium phosphate and hafnium phosphate, θ - $\text{Zr}(\text{HPO}_4)_2 \cdot 1.88 \text{H}_2\text{O}$ and θ - $\text{Hf}(\text{HPO}_4)_2 \cdot 1.61 \text{H}_2\text{O}$, respectively, were prepared and characterized by chemical, x-ray and thermal analysis and by FT-IR spectroscopy. Their exchange capacities were determined by Na^+ ions potentiometric titration.

XRD pattern of θ -type materials

X-ray powder diffraction pattern of the θ -types zirconium-, and hafnium phosphates, was found to follow XRD trend of layered bidimensional (2-D) structure of M(IV) phosphates⁽¹⁶⁾, exhibit diffraction maxima with basal spacing equal to 9.85Å and 9.51Å, respectively.

FT-IR Spectra of the θ -type materials

FT-IR become a key tool to investigate structure, specially when x-ray are in applicable like for instance, in those of nanosamples⁽¹⁸⁾. Figures (1,2) Show FT-IR spectra of θ -types zirconium-, and hafnium phosphates, respectively, in the range 4000-400 cm^{-1} .

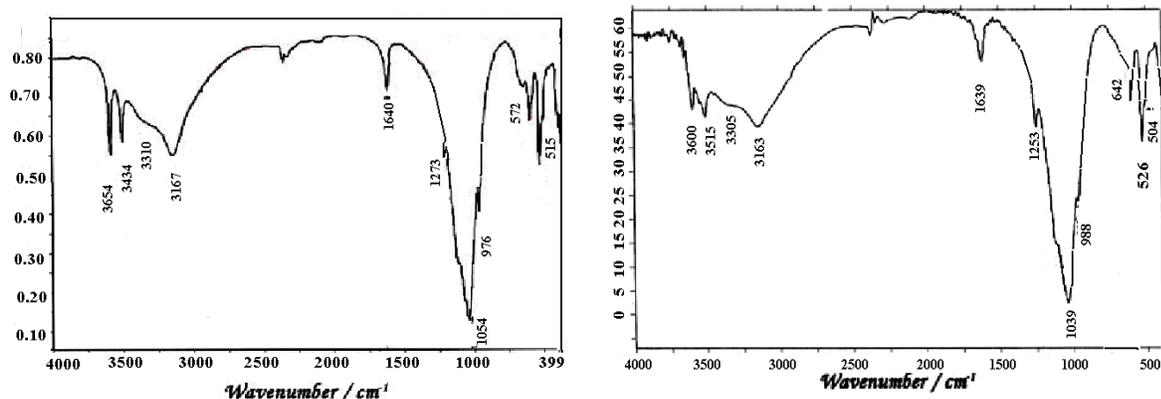


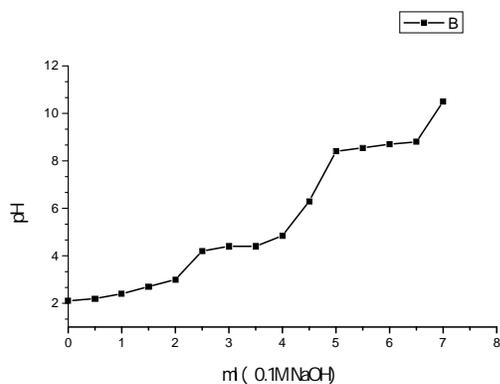
Figure (1) IR-Spectra of θ -type $\text{Zr}(\text{HPO}_4)_2 \cdot 1.88 \text{H}_2\text{O}$ Figure (2) IR-Spectra of $\text{Hf}(\text{HPO}_4)_2 \cdot 1.61 \text{H}_2\text{O}$

A tentative assignment of various vibrational modes is proposed based on previous works performed in other M(IV) phosphate compounds⁽¹⁹⁻²²⁾.

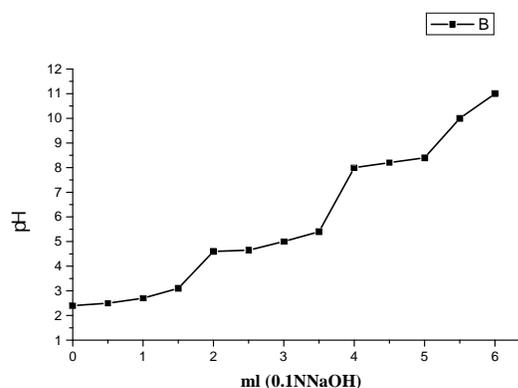
The FT-IR spectra of θ -types materials show the same trend of modes. From figures (1,2), the narrow bands at $\sim(3650)$, 3434 cm^{-1} and $\sim 1640 \text{ cm}^{-1}$ are assigned to vibrational modes of H_2O molecules, suggest that water molecules are located at well defined crystallographic sites. These bands were also attributed to O-H asymmetric modes of interlayer water molecules. The band at $\sim 1640 \text{ cm}^{-1}$ also corresponds to H-O-H bending modes. The broad band at 3147 cm^{-1} assigned to (P)OH stretching mode of the hydrogen bond, it had shoulder at 3310 cm^{-1} attributed to O-H stretching coming from symmetry lowering effect of the H_2O interlayer molecules^(18,19). The bands at the region $1253\text{-}1039 \text{ cm}^{-1}$ are assigned to P-O asymmetry stretching of PO_4 groups, while a band at $\sim 980 \text{ cm}^{-1}$ is characteristic to the bonding in plane of the (P-O). Bands in the region $640\text{-}505 \text{ cm}^{-1}$ ascribed to the presence of $\delta(\text{PO}_4)$. FT-IR modes of the θ -types materials possess same morphological structures.

Exchange capacities of θ -types zirconium-, hafnium phosphates

Na^+ ions potentiometric titration curves of θ -types zirconium-, hafnium phosphates are shown in figures (3,5). The exchange capacities were found to be equal to 6.2 meq/g and 4.95 meq/g, the calculated values are 6.01 meq/g and 4.744 eq/g, respectively. The difference may be due to partial hydrolysis of HPO_4^{2-} groups as a result of pH effect.



Figure(3) Na^+ titration curve of θ -type ZrP



Figure(4) Na^+ titration curve of θ -type HfP

TG/DTA of θ -type materials

Thermal analyses of θ -type materials are shown in figures (5,6) and were carried out at temperature range ~ 25 - 750°C , in air atmosphere, the heating rate was $10^\circ\text{C}/\text{min}$. The thermal decomposition exhibits two weight loss stages, the loss of water of hydration followed by POH groups condensation.

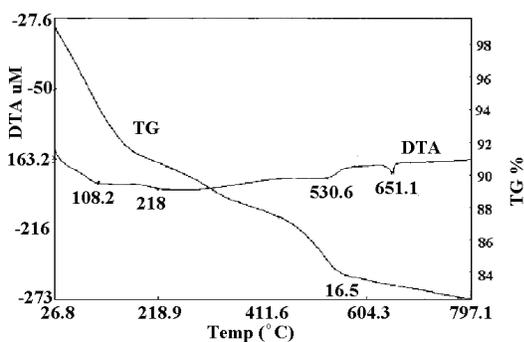


Figure (5) TG/DTA of θ -type $\text{Zr}(\text{HPO}_4)_2 \cdot 1.88 \text{H}_2\text{O}$

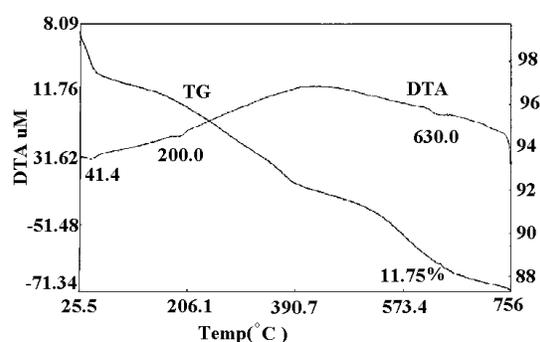


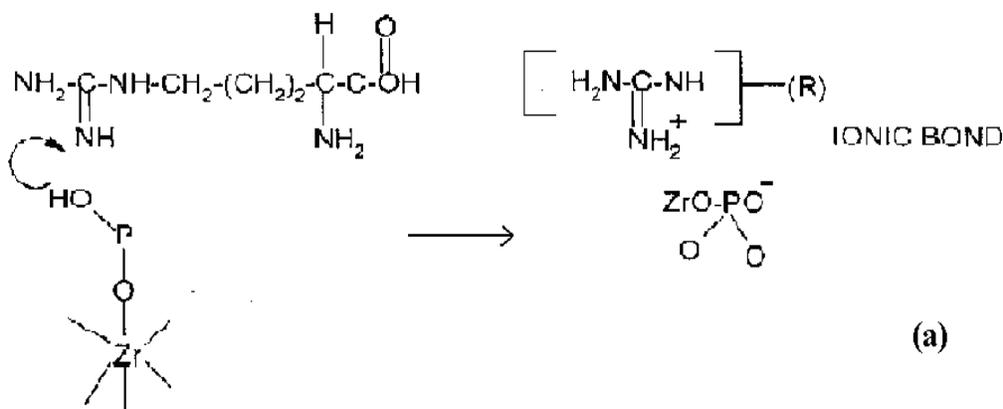
Figure (6) TG/DTA of θ -type $\text{Hf}(\text{HPO}_4)_2 \cdot 1.61 \text{H}_2\text{O}$

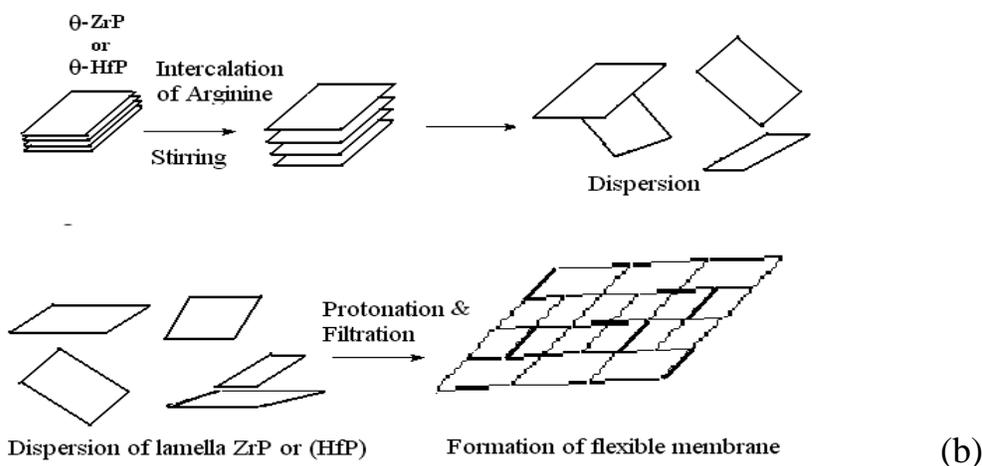
The first stage for θ -type $\text{Zr}(\text{HPO}_4)_2 \cdot 1.88 \text{H}_2\text{O}$ and θ -type $\text{Hf}(\text{HPO}_4)_2 \cdot 1.61 \text{H}_2\text{O}$ compound is accompanied by weight losses equal to 16.52% and 11.78%, respectively, up to 210°C has been attributed to the loss of water of hydration. The second stage in the region 320 - 650°C ascribed to the loss of the structure water due to POH groups condensation. The weight losses were 5.65 and 4.5%, respectively. The final products were the pyrophosphates, ZrP_2O_7 and HfP_2O_7 .

Pellicles zirconium phosphate and hafnium phosphate membranes, $\text{Zr}(\text{HPO}_4)_2 \cdot 1.35 \text{H}_2\text{O}$ and $\text{Hf}(\text{HPO}_4)_2 \cdot 1.22 \text{H}_2\text{O}$, respectively, were prepared via intercalation deintercalation of arginine into their parent crystalline layered θ -type materials.

Previous studies on amino acids intercalation into layered M(IV) phosphates, show that neutral amino acids, existing as Zwitter ions adsorbed on surface, by replacing the surface protons by the terminal NH_3^+ cations. However, basic amino acids bind to the interlayer POH groups of the layered materials are shown in the following sketch. Where arginine likely to anchor through guanidine groups to the POH sites.

Figure (7) shows the intercalation-deintercalation of arginine into θ -type zirconium phosphate (θ -ZrP) and θ -type hafnium phosphate (θ -HfP).





Figure(7-a,b) Schematically, intercalation de-intercalation of θ -type (ZrP or HfP)

The intercalated layer thus formed would enlarge the interlayer space of the host crystals. In case of arginine, at certain loading, the interlayer distance increases to $\sim 16\text{\AA}$, that lead to total exfoliation of the original layered material in water giving colloidal dispersion. The layered are stressed and several cracks parallel to the layers occur, i.e delamination occurs. On deintercalation, by portonation, lead to the formation of the pellicular membrane, that what we have found by this novel method, where we obtain flexible thin films, membranes, of the pellicles zirconium- and hafnium phosphates. The resultant pellicles $\text{Zr}(\text{HPO}_4)_2 \cdot 1.35 \text{H}_2\text{O}$ and $\text{Hf}(\text{HPO}_4)_2 \cdot 1.22 \text{H}_2\text{O}$ membranes were characterized by x-ray and thermal analysis and by FT-IR spectroscopy. Their exchange capacities were determined by Na^+ ions potentiometric titration.

The pellicular materials exhibit lamellar structure with morphology similar to their parent θ -type layered materials. The water molecules occupying sites are located almost in the center of interlayer cavities and they are bonded to HPO_4^{2-} groups through hydrogen bonds.

XRD Pattern of pellicles membranes

Figures (8,9) show x-ray diffractograms of pellicles $\text{Zr}(\text{HPO}_4)_2 \cdot 1.35 \text{H}_2\text{O}$ and $\text{Hf}(\text{HPO}_4)_2 \cdot 1.22 \text{H}_2\text{O}$ membranes, having basal spacing equal to 7.65\AA and 7.54\AA , respectively.

The x-ray diffractograms pattern of the pellicles membranes are similar to that of a highly iso-oriented sample of their parent crystalline α -layered materials⁽¹⁸⁾.

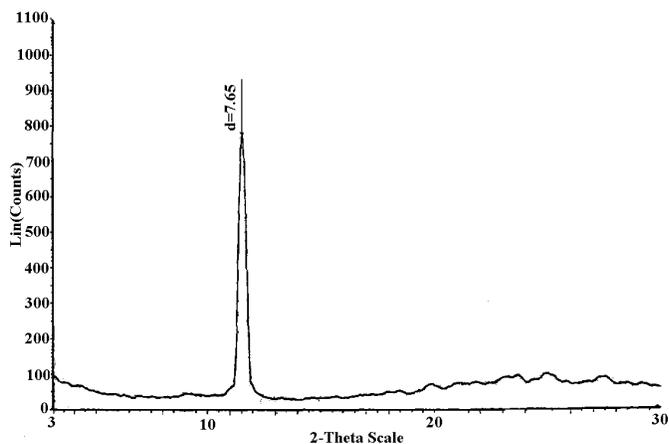


Figure (8) x-ray diffractograms of pellicular $\text{Zr}(\text{HPO}_4)_2 \cdot 1.35 \text{H}_2\text{O}$

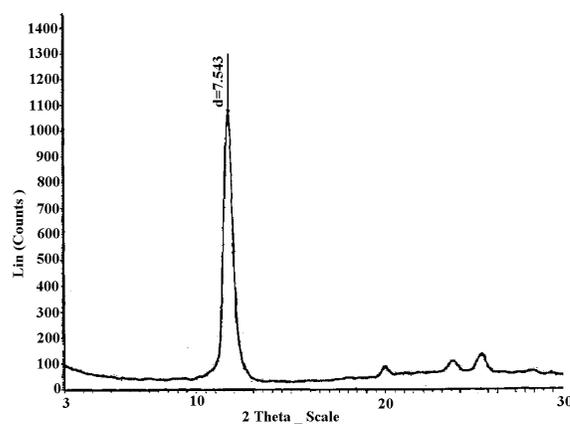
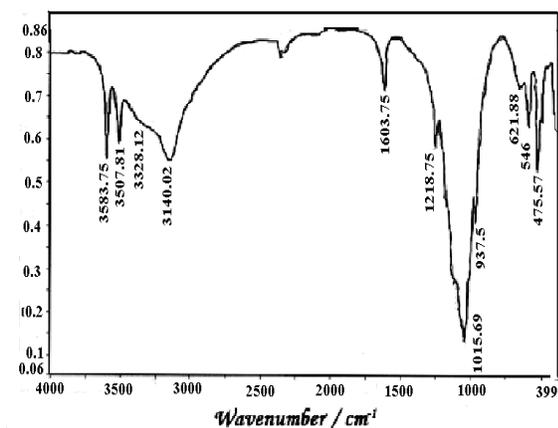


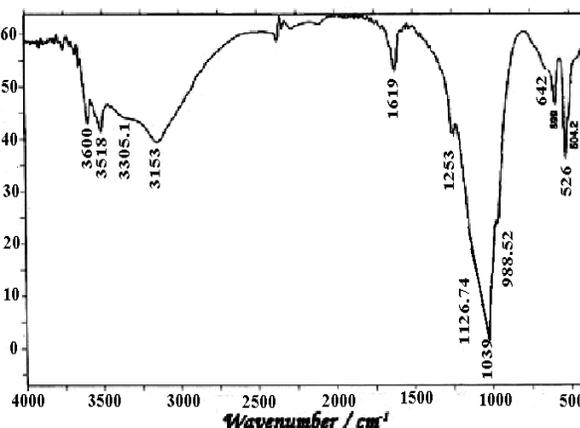
Figure (9) x-ray diffractograms of pellicular $\text{Hf}(\text{HPO}_4)_2 \cdot 1.22 \text{H}_2\text{O}$

FT-IR spectra of pellicles materials

Figures (10,11) Show FT-IR spectra of pellicles zirconium-,hafnium phosphates, in the range $4000\text{-}400 \text{ cm}^{-1}$ membranes. Their FT-IR spectra exhibit the same trend of mode.



Figure(10) FT-IR. Spectra of pellicular $\text{Zr}(\text{HPO}_4)_2 \cdot 1.35\text{H}_2\text{O}$



Figure(11) FT-IR. Spectra of pellicular $\text{Hf}(\text{HPO}_4)_2 \cdot 1.22\text{H}_2\text{O}$

The narrow bands at $\sim(3600) 3520 \text{ cm}^{-1}$ and $\sim 1600 \text{ cm}^{-1}$ assigned to vibrational modes of H_2O molecules. These bands were also attributed to an O-H asymmetric modes of interlayer water molecules and the band at $\sim 1600 \text{ cm}^{-1}$ corresponds also to H-O-H

bending modes The water molecules present in the pellicular materials show very characteristic infrared bands in both the OH stretching and bending region, as that observed in case of their θ -type parent materials, and can be assigned to regular hydrogen bonding of each molecule to OH adjacent group.

The broad band at $\sim 3140\text{cm}^{-1}$, assigned to (P)OH stretching mode of the hydrogen bond, had a shoulder at, $\sim 3320\text{cm}^{-1}$ attributed to an O-H stretching coming from symmetry lowering effect of the interlayer water molecules.

The bands in the region $1250\text{-}1015\text{cm}^{-1}$ are assigned to P-O asymmetric stretching of PO_4 groups, while a band at 937cm^{-1} (or 956cm^{-1}) is characteristic of the (P-O) bond. The bands at the region $620\text{-}438\text{cm}^{-1}$ ascribed to the presence of $\delta(\text{PO}_4)$ and to vibrational of water molecules.

These results are in good correlation both with structural composition of θ -type and pellicular materials, and also with literature data concerning different M(IV) phosphate materials(¹⁹⁻²²).

Na^+ ions potentiometric titration curves of pellicles zirconium-, hafnium phosphates are shown in figures (12,13). Their exchange capacities were found to be equal to 6.2 meq/g and 4.95 meq/g.

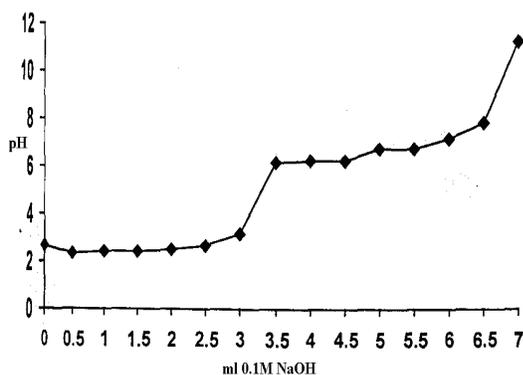


Figure (12) Na^+ titration curve of pellicular $\text{Zr}(\text{HPO}_4)_2 \cdot 1.35\text{H}_2\text{O}$

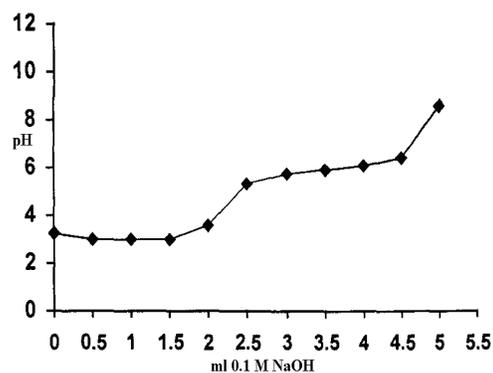


Figure (13) Na^+ titration curve of pellicular $\text{Hf}(\text{HPO}_4)_2 \cdot 1.22\text{H}_2\text{O}$

TG/DTA of pellicular materials

The thermograms presented in figures (14,15) are concern to the thermal decomposition behavior of pellicles zirconium-, hafnium phosphate, $\text{Zr}(\text{HPO}_4)_2 \cdot 1.35 \text{H}_2\text{O}$ and $\text{Hf}(\text{HPO}_4)_2 \cdot 1.22 \text{H}_2\text{O}$, respectively, show the same feature as obtained for crystalline α -layered M(IV) phosphate materials⁽⁴⁾

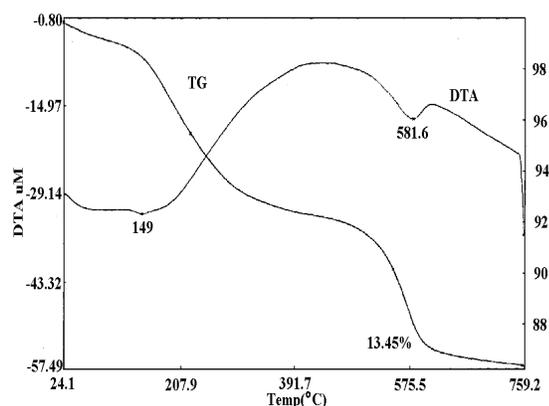


Figure (14) TG/DTA of pellicular $\text{Zr}(\text{HPO}_4)_2 \cdot 1.35 \text{H}_2\text{O}$

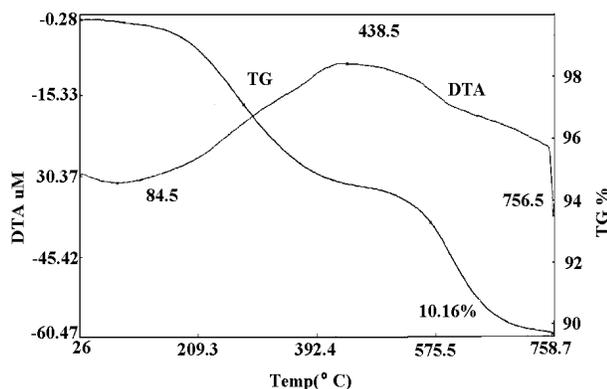


Figure (15) TG/DTA of pellicular $\text{Hf}(\text{HPO}_4)_2 \cdot 1.22 \text{H}_2\text{O}$

Thermal decomposition occurs in two stages, the first stage concerns with the loss of water of hydration up to 210 °C, followed by POH groups condensation (300-750 °C). The final products were ZrP_2O_7 and HfP_2O_7 , with total percent weight losses equal to 13.45 and 10.16%, respectively, found to be in agreement with the calculated values.

Conclusion

The FT-IR spectra is a key tool to detect the presence of water molecules as well as to investigate the H-bonds in layered M (IV) phosphate and membrane forms.

No vibrational spectroscopic investigation have been made in order to understand the H-bonding structure in α -layered M(IV) phosphates only that reported by Casciola et al.⁽¹⁹⁾

However, from this study we show the effectiveness of the vibrational spectra in characterizing the θ -type and the pellicular membranes, giving also the indicator about their morphology.

We have found that the water molecules in the studied materials present very characteristic infrared bands in both the OH stretching and bending region, and can be assigned to regular hydrogen bonding of each molecule to adjacent OH group. The TGA and x-ray results supports the formulation of θ -type and the pellicular membranes.

This study shows the possibility to obtain inorganic ion exchange membranes of pellicular zirconium phosphate and hafnium phosphate, by intercalation-deintercalation of arginine into their parent θ -type materials. This novel method can be explored further with other layered metal (IV) phosphates.

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