

α - Zirconium Titanium Phosphates - Fibrous Cerium Phosphate Composite Membranes and Their 1,10-Phenanthroline Cu(II) Pillared Materials

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Abstract Nanosized fibrous cerium phosphate, $\text{Ce}(\text{HPO}_4)_2 \cdot 2.9\text{H}_2\text{O} (\text{nCeP}_f)$, and α - Zirconium -Titanium Phosphates, $\text{Zr}_x\text{Ti}_{1-x}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O} (\alpha\text{-ZTP})$, where $x = 0.9, 0.8, 0.67, 0.34$, were synthesized. Novel composite membranes $[\text{Zr}_x\text{Ti}_{1-x}(\text{HPO}_4)_2]_{0.25} [\text{Ce}(\text{HPO}_4)_2]_{0.75} \cdot 3.3\text{H}_2\text{O}$ were prepared. Reactions of the resulting composite membranes with 1,10-phenanthroline in ethanol, followed by the addition of 0.1M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, in (1:1) ethanol: aqueous solution, lead to the formation of novel pillared materials: $[(\text{H}_{1.16})\text{Zr}_{0.9}\text{Ti}_{0.1}(\text{PO}_4)_2]_{0.25} [(\text{H}_{1.16})\text{Ce}(\text{PO}_4)_2]_{0.75} (\text{PhenCu})_{0.42} \cdot 2.25\text{H}_2\text{O}$, $[(\text{H}_{1.5})\text{Zr}_{0.8}\text{Ti}_{0.2}(\text{PO}_4)_2]_{0.25} [(\text{H}_{1.5})\text{Ce}(\text{PO}_4)_2]_{0.75} (\text{PhenCu})_{0.25} \cdot 1.77\text{H}_2\text{O}$, $[(\text{H}_{0.3})\text{Zr}_{0.67}\text{Ti}_{0.33}(\text{PO}_4)_2]_{0.25} [(\text{H}_{0.3})\text{Ce}(\text{PO}_4)_2]_{0.75} (\text{PhenCu})_{0.85} \cdot 4\text{H}_2\text{O}$, $[(\text{H}_{1.6})\text{Zr}_{0.34}\text{Ti}_{0.66}(\text{PO}_4)_2]_{0.25} [(\text{H}_{1.6})\text{Ce}(\text{PO}_4)_2]_{0.75} (\text{PhenCu})_{0.2} \cdot 2.22\text{H}_2\text{O}$, respectively. They were characterized by chemical, X-ray diffraction (XRD) and thermal analysis (TGA), accordingly were formulated. XRD patterns of the composite materials retain (d) spacing reflection of α -ZTP and nCeP_f , where $d_{001} = 7.58 \text{ \AA}$ and 11.38 \AA , respectively, The resulting composites are thermally stable and can be considered as novel ecofriendly solid acid catalysts, Ionex changers and ionic conductance materials.

Keywords: pillared, α -zirconium titanium phosphate, fibrous cerium phosphate, composite membranes

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1. Introduction

Layered tetravalent metal phosphates with alpha and gamma structures bear resemblance to clay minerals [1,2,3] Their general formula are $\alpha\text{-M(IV)(HPO}_4)_2 \cdot \text{H}_2\text{O}$, $\theta\text{-M(IV)(HPO}_4)_2 \cdot 5\text{H}_2\text{O}$ and $\gamma\text{-M(IV). PO}_4 \cdot \text{H}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ (where $\text{M} = \text{Ti, Zr, Hf, Sn, Ge, Ce}$). Their structures have been established [4,5,6].

Earlier investigations on intercalating properties of layered α and γ -zirconium phosphates have demonstrated that coordination compounds can be formed between the layers of α -and γ -zirconium phosphates, able to coordinate *in situ* transition metal ions such as Cu(II), Ni(II), Co(II) and Pd(II) [7,8]. These compounds found to behave as catalysts [7,8,9]. Results confirmed the formation of transition metal ions-phenanthroline complex species between the layers [7,8,9].

Synthetic membranes can be fabricated from a large number of different materials. It can be made from organic or inorganic materials including solids such as metal or ceramic, homogeneous films (polymers), heterogeneous

solids (polymeric mixes, mixed glasses), and liquids. Ceramic membranes are produced from inorganic materials such as aluminum oxides, silicon carbide, and zirconium oxide. Their inorganic composite membranes are well known [10,11,12,13].

Inorganic membrane-membrane composites are not a recent invention. Hundreds of scientific papers and few reviews on inorganic membrane composites, examples; $\text{SiO}_2\text{-TiO}_2$, $\text{SiO}_2\text{-ZrO}_2$, $\text{Pd-}\gamma\text{Al}_2\text{O}_3$, Pd thin film deposited on ceramic materials, from metal complexes, from metal alloys, P-type zeolite membrane on porous α -alumina, Pd-Cu membranes supported on ZrO_2 , mesoporous silica membranes containing iron oxide nanocrystallites, $\gamma\text{-Al}_2\text{O}_3\text{-TiO}_2$, and ZrO_2 etc., were published [11,12,13,14]. Most of these type of inorganic membrane composites are prepared by sol-gel method, electrochemical vapour deposition and by chemical vapour deposition metal alloy in gas phase [14,15,16,17].

In our laboratory we are undertaking systematic investigations on new inorganic ion exchange membranes of tetravalent metal phosphates and their transition metal ions-organonitrogen heterocyclic pillared materials, that were prepared by different methods.

Here we are reporting synthesis and characterization of novel α -Mixed zirconium-titanium phosphates-fibrous cerium phosphate composite membranes and their 1,10-phenanthroline Cu(II) pillared products.

2. Materials and Methods

2.1. Chemicals

ZrOCl₂.8H₂O, TiCl₄, CeSO₄.4H₂O, H₃PO₄ (85%), CuCl₂.2H₂O of BDH. Other reagents used were of analytical grade.

2.2. Instruments Used for Characterization

- X-ray powder Diffractometer PW/1710 Philips, using Ni-filtered CuK α ($\lambda = 1.5405\text{\AA}$).
- Scanning electron microscopy (SEM) Jeol SMJ Sm 5610 LV
- Nexus 670 FT-IR Nicolet spectrophotometer
- Derivatograph MOM-C Budapest, Hungary and Shimadzu TGA-60H TG/DTA.
- UV-Visible spectrophotometer, Spectronic
- Atomic Absorption Spectrophotometer Alpha 4 (SPEX)
- pH Meter GWG 521.

2.3. Preparation of Nanofibrous Cerium Phosphate, Ce(HPO₄)₂.2.9H₂O (nCeP_f)

100ml of 0.05M CeSO₄.4H₂O in 0.5M H₂SO₄ solution were added drop wise to 100ml of 6M H₃PO₄ at 80°C with stirring. After complete addition the resultant material left to digest at that temperature for 5h. To that one liter of hot distilled water, (~60°C), was added with stirring for 1h. The resulting fibrous cerium phosphate was subjected to washing by re-slurring several times with distilled water up to pH 3.5, filtered, washed with ethanol and dispersed in distilled water (2 liters), and kept in form of slurry aqueous solution.

2.4. Preparation phosphate α -Zr_xTi_(1-x)(HPO₄)₂.H₂O(α -ZTP)

Crystalline mixed α -zirconium-titanium phosphates, α -Zr_xTi_(1-x)(HPO₄)₂.H₂O (α -ZTP), were prepared, according to method that was reported by shakshooki et al [18], from refluxing Their parent amorphous materials Zr_xTi_(1-x)(HPO₄)₂.3H₂O, in 10 M H₃PO₄ for 100h.

2.5. Preparation of $[\alpha$ -Zr_xTi_(1-x)(HPO₄)₂]_{0.25}[Ce(HPO₄)₂]_{0.75} Composite Membranes

The composite membranes $[\alpha$ -Zr_xTi_(1-x)(HPO₄)₂]_{0.25}[Ce(HPO₄)₂]_{0.75}.3.3H₂O were prepared from reactions of slurry aqueous solution of α -Zr_xTi_(1-x)(HPO₄)₂.H₂O with slurry aqueous solution of fibrous cerium phosphate in wt/wt % mole ratio 1:3, respectively. Typical preparation, 0.25g α -ZTP slurry aqueous solution + 0.75g nCeP_f slurry aqueous solution were used.

2.6. Exchange Capacities Determination of α -ZTP and nCeP_f and Their Composite Materials

To 100 mg of the material 25 ml of 0.1M NaCl solution were added, stirred for 1h, followed by titration with 0.1 M NaOH solution with stirring.

2.7. Estimation of Titanium

Titanium contents in the resulting materials was determined spectrophotometrically as described earlier [18].

2.8. Preparation of Novel $[\alpha$ -Zr_xTi_(1-x)(HPO₄)₂]_{0.25}[Ce(HPO₄)₂]_{0.75}.nH₂O, 1,10-phenanthroline Cu(II) Pillared Materials

The novel pillared materials were prepared from reactions of the composites $[\alpha$ -Zr_xTi_(1-x)(HPO₄)₂]_{0.25}[Ce(HPO₄)₂]_{0.75}.3.3H₂O membranes (0.25g) with (30ml) 0.1M 1,10-phenanthroline in ethanol with stirrings for 24h at room temperature and for 5h at 60°C, followed by the addition of (15ml) 0.05M CuCl₂.2H₂O aqueous solution to the resultant 1,10-Phenanthroline inclusion composite products.

2.9. Estimation the Uptake of Cu²⁺ Metal Ions

The uptake of Cu²⁺ metal ions were determined from the analysis of the original metal ions concentration and on its non equilibrated solution by atomic absorption spectrophotometer.

3. Results and Discussion

Nanofibrous cerium phosphate membrane, Ce(HPO₄)₂.2.9H₂O(nCeP_f), was prepared and characterized by chemical, XRD, TGA, FT-IR and by scanning electron microscopy (SEM).

3.1. XRD

XRD of nanofibrous cerium phosphate membrane is shown in Figure 1, with $d_{001} = 10.89\text{\AA}$.

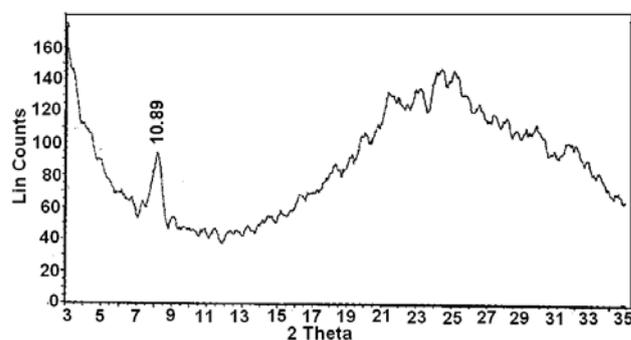


Figure 1. XRD of nanofibrous cerium phosphate

3.2. TGA

The thermal analysis of nanoCe(HPO₄)₂.2.9H₂O was carried out at temperatures between 10-775°C. Its thermogram is shown in Figure 2. The final product was CeP₂O₇, results from the loss of water of hydration between 60-200°C, followed by POH groups condensation. The total weight loss found to be equal to 19.09%.

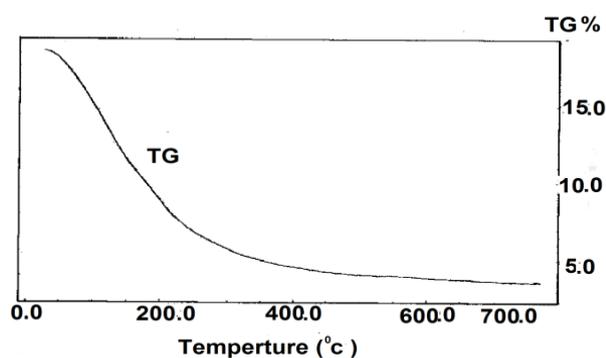


Figure 2. TG A of nanofibrous cerium phosphate

3.3. FT-IR

FT-IR become a key tool to investigate structure of tetravalent metal phosphates. Figure 3, shows FT-IR spectra of fibrous $\text{Ce}(\text{HPO}_4)_2 \cdot 2.9\text{H}_2\text{O}$, with a trend similar to that of $\text{M}(\text{IV})$ phosphates. It consists of broad band centered at 3350cm^{-1} assigned to vibrational modes of H_2O molecules, suggest that water molecules are located at well defined sites, also attributed to an O-H asymmetric

modes of water molecules. Small sharp band at 1628cm^{-1} is related to H-O-H bending, and sharp broad band centered at 1045cm^{-1} is corresponds to phosphate groups vibration. The bands at the region $630\text{--}450\text{cm}^{-1}$ are ascribe the presence of $\delta(\text{PO}_4)$ and to vibrational of water molecules.

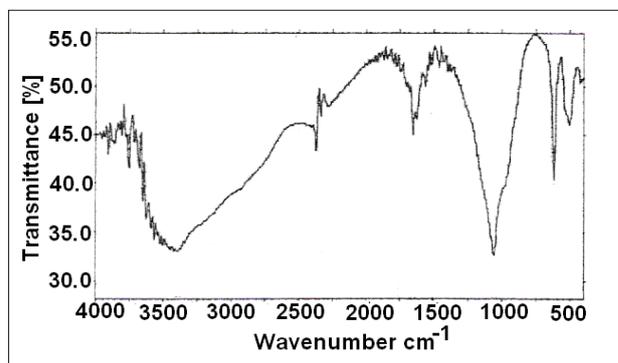


Figure 3. FT-IR spectra of nanofibrous cerium phosphate

3.4. SEM

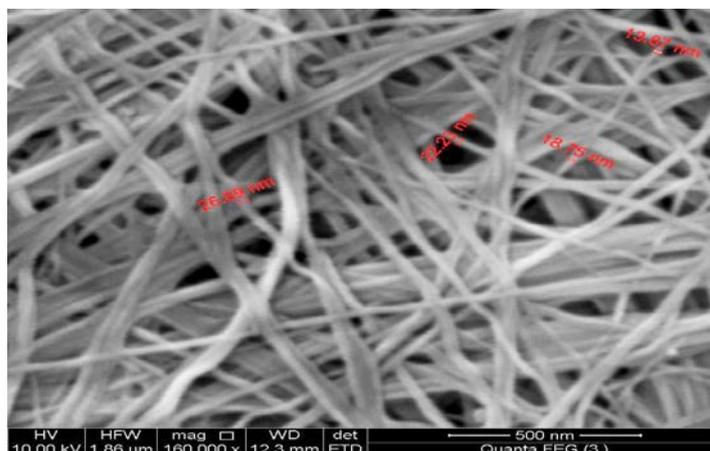


Figure 4. SEM morphology image of (nCeP₇)

SEM morphology image of the nanosized fibrous cerium phosphate (nCeP_7) is shown in Figure 4. The photograph shows its average size is $\sim 20.5\text{ nm}$.

Crystalline α -mixed zirconium-titanium phosphates $\alpha\text{-Zr}_x\text{Ti}_{(1-x)}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ (where $x = 0.9, 0.8, 0.67, \text{ and } 0.34$) were prepared and characterized by XRD, TGA, and by FTIR Spectroscopy. The materials found to be α -layered type materials.

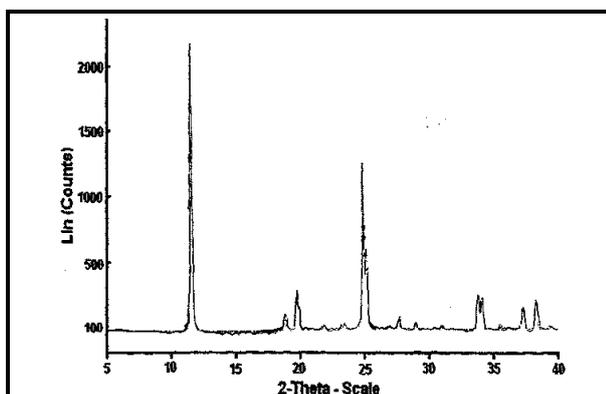


Figure 5. XRD of $\text{Zr}_{0.8}\text{Ti}_{0.2}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$

3.5. XRD

Figure 5 shows typical X-ray diffractogram of mixed zirconium titanium phosphates, $\text{Zr}_{0.8}\text{Ti}_{0.2}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, with basal spacing (d_{001}) = 7.56 \AA .

3.6. TGA

The investigated samples found to have similar thermal decomposition mechanism, consisting of the following stages:

- Loss of crystalline water (water of hydration) up to 200°C .
- Loss of the structural water due to POH groups condensation, start to occur $>300^\circ\text{C}$.
- Finally formation of pyrophosphates of general formula $[\text{Zr}_x\text{Ti}_{(1-x)}]\text{P}_2\text{O}_7$ at $\sim 650\text{--}700^\circ\text{C}$.

Typical thermogram of zirconium titanium phosphates, $\alpha\text{-Zr}_{0.8}\text{Ti}_{0.2}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, is shown in Figure 6. The thermal decomposition found to occur in two stages, which concern with the loss of water of hydration between $70\text{--}200^\circ\text{C}$, followed by POH groups condensation. The total weight loss found to be equal to 12.32% , the final product was $(\text{Zr}_{0.8}\text{Ti}_{0.2})\text{P}_2\text{O}_7$.

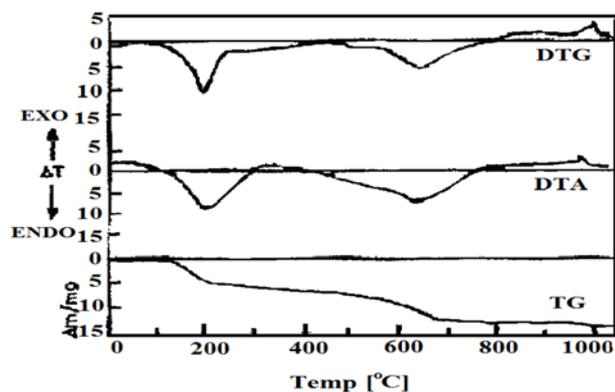


Figure 6. TGA of $\alpha\text{-Zr}_{0.8}\text{Ti}_{0.2}(\text{HPO}_4)_2\cdot\text{H}_2\text{O}$

3.7. FT-IR

Figure 7 shows typical FT-IR spectrum of mixed zirconium titanium phosphates, $\alpha\text{-Zr}_{0.8}\text{Ti}_{0.2}(\text{HPO}_4)_2\cdot\text{H}_2\text{O}$, with a trend similar to the FT-IR spectra of tetravalent metal phosphates. Two sharp bands at ~ 3600 , 3500 cm^{-1} and band at 1638 cm^{-1} are assigned to vibrational modes of H_2O molecules, suggest that water molecules are located at well defined crystallographic sites. The bands at ~ 3600 , 3500 cm^{-1} were also attributed to an O-H asymmetric modes of interlayer water molecules. The band at 1638 cm^{-1} also corresponds to H-O-H bending modes. The bands in the region $608\text{-}510\text{ cm}^{-1}$ ascribed to the presence of $\delta(\text{PO}_4)$ and to vibrational of water molecules, follow trend similar to the FT-IR spectra of tetravalent metal phosphates [18,19].

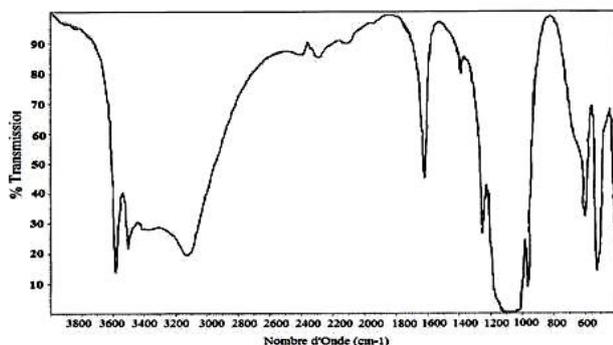


Figure 7. FT-IR spectra of $\alpha\text{-Zr}_{0.8}\text{Ti}_{0.2}(\text{HPO}_4)_2\cdot\text{H}_2\text{O}$

3.8. Ion Exchange Capacity

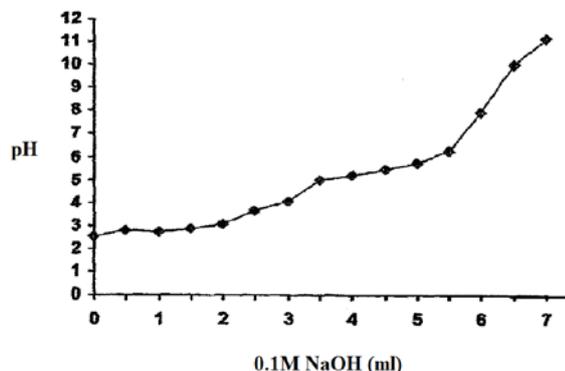


Figure 8. Na^+ ions titration curve of $\alpha\text{-Zr}_{0.8}\text{Ti}_{0.2}(\text{HPO}_4)_2\cdot\text{H}_2\text{O}$

Figure 8 shows typical Na^+ ions titration curve of $\alpha\text{-Zr}_x\text{Ti}_{1-x}(\text{HPO}_4)_2\cdot\text{H}_2\text{O}$, and found to follow similar trend

to that of crystalline layered mixed zirconium-titanium phosphates [18].

3.9. $[\alpha\text{-Zr}_x\text{Ti}_{1-x}(\text{HPO}_4)_2]_{0.25} [\text{Ce}(\text{HPO}_4)_2]_{0.75}$ Composite Membranes

The composite membranes $[\alpha\text{-Zr}_x\text{Ti}_{1-x}(\text{HPO}_4)_2]_{0.25} [\text{Ce}(\text{HPO}_4)_2]_{0.75}\cdot 3.3\text{H}_2\text{O}$ were prepared and characterized. The resultant composites were flexible homogeneous thin films with good mechanical properties. Its XRD, FT-IR and TGA are shown in Figure 9, Figure 10, Figure 11, respectively.

3.10. XRD

Figure 9 shows typical X-ray diffraction pattern of composite $[\alpha\text{-Zr}_{0.8}\text{Ti}_{0.2}(\text{HPO}_4)_2]_{0.25} [\text{Ce}(\text{HPO}_4)_2]_{0.75}\cdot 3.3\text{H}_2\text{O}$ with d spacing reflections at 11.38\AA , 7.58\AA , which are related to $\alpha\text{-Zr}_{0.8}\text{Ti}_{0.2}(\text{HPO}_4)_2\cdot\text{H}_2\text{O}$ and fibrous cerium phosphate, respectively, found to be typical for the X-ray patterns expected for such type of composite materials, where the composite materials retain their XRD patterns of their parent materials.

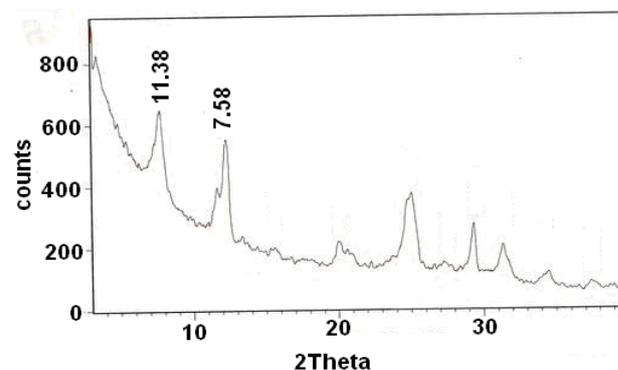


Figure 9. FT-IR spectra of $[\alpha\text{-Zr}_{0.8}\text{Ti}_{0.2}(\text{HPO}_4)_2]_{0.25} [\text{Ce}(\text{HPO}_4)_2]_{0.75}\cdot 3.3\text{H}_2\text{O}$

3.11. FT-IR

Figure 10 shows FT-IR spectrum of the typical composite $[\alpha\text{-Zr}_{0.8}\text{Ti}_{0.2}(\text{HPO}_4)_2]_{0.25} [\text{Ce}(\text{HPO}_4)_2]_{0.75}\cdot 3.3\text{H}_2\text{O}$, with a trend similar to that of M(IV) phosphates [18]. It consists of broad band centered at 3400 cm^{-1} which is due to OH groups symmetric stretching of H_2O , small sharp band at 1630 cm^{-1} is related to H-O-H bending, and sharp broad band centered at 1030 cm^{-1} is corresponds to phosphate groups vibration. The bands at the region $600\text{-}450\text{ cm}^{-1}$ are ascribe the presence of $\delta(\text{PO}_4)$.

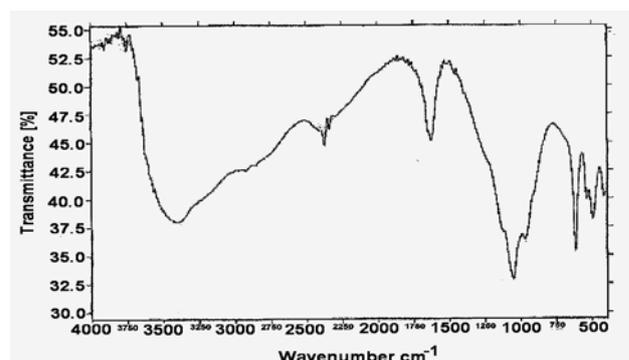


Figure 10. FT-IR spectra of $[\alpha\text{-Zr}_{0.8}\text{Ti}_{0.2}(\text{HPO}_4)_2]_{0.25} [\text{Ce}(\text{HPO}_4)_2]_{0.75}\cdot 3.3\text{H}_2\text{O}$

3.12. TGA

Thermogram of typical composite membrane [α -Zr_{0.8}Ti_{0.2}(HPO₄)₂]_{0.25} [Ce(HPO₄)₂]_{0.75}·3.3H₂O is shown in Figure 11. The thermal decomposition occurs in three stages. First two stages concern the loss of hydrated water of hydration between 65-300 °C, followed by POH groups condensation up to 750 °C. Total weight loss was 20.42 %. Found to be in agreement with formulation of the composite material. The final products were (α -Zr_{0.8}Ti_{0.20})_{0.25} P₂O₇ and [(Ce)_{0.75}]P₂O₇.

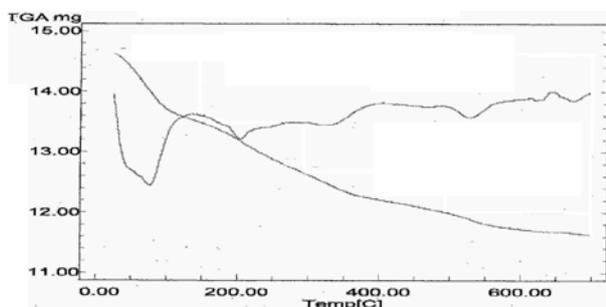


Figure 11. TGA of [α -Zr_{0.8}Ti_{0.2}(H)_{1.5}(PO₄)₂]_{0.25}[Ce(H)_{1.5}(PO₄)₂]_{0.75}·3.3H₂O

3.13. Novel Pillared Materials

[(H_{1.16}) Zr_{0.9}Ti_{0.1} (PO₄)₂]_{0.25}[(H_{1.16}) Ce (PO₄)₂]_{0.75}(PhenCu)_{0.42}·2.25H₂O, [(H_{1.5})Zr_{0.8}Ti_{0.2} (PO₄)₂]_{0.25} [(H_{1.5})Ce (PO₄)₂]_{0.75} (Phen Cu)_{0.25}·1.77H₂O

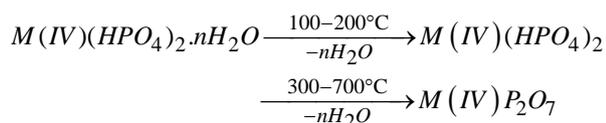
[(H_{0.3}) Zr_{0.67}Ti (PO₄)₂]_{0.25} [(H_{0.3}) Ce (PO₄)₂]_{0.75}·(Phen Cu)_{0.85}·4 H₂O, [(H_{1.6})Zr_{0.34}Ti_{0.66} (PO₄)₂]_{0.25} [(H_{1.6}) Ce(PO₄)₂]_{0.75}·(PhenCu)_{0.2}·2.22 H₂O

were prepared and characterized by chemical, TGA analysis and FT-IR spectra. Their Cu²⁺ ions content were determined by atomic absorption spectroscopy.

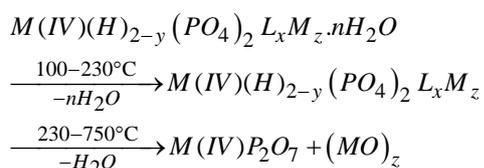
The resulting pillared products are porous materials where the divalent transition metal ions exchanged with the H⁺ of the POH groups and the organic ligand inserted in the interlayer region, where the presence of metal ion and the ligand act as pillars, that facilitate the access to the interlayer region of different reactants.

This pillaring process gives rise to porous solids can be tailor made by suitable choosing of the layered inorganic material [17]. Thermal analysis, TGA, is a good tool for characterization of M(IV) phosphates and their intercalated materials [6,18,19,20], where at high temperature combustion of the complexes occurs to give the M(IV) pyrophosphate (in case of M(IV) phosphates) and M(IV) pyrophosphate + M oxide, in case of intercalated complex materials. So it is easy to formulate the product according to equations shown below:

a



b



(Where y= exchanged proton, L_x= ligand loading, n= water of hydration and z= metal ion mole content).

From the (a, b) the weight losses can be calculated. The content of metal ions was determined by atomic absorption spectroscopy analysis [20].

3.14. TGA of Pillared Materials

Figure 12 shows the thermogram of pillared compound [α -Zr_{0.9}Ti_{0.1} (HPO₄)₂]_{0.25} [Ce(HPO₄)₂]_{0.75} (Phen Cu)_{0.42}·2.25H₂O. The thermal decomposition found to occur in 3 stages. First stage concern with the loss of water of hydration up to ~180°C, followed by organic ligand decomposition and POH groups condensation as well as the formation of CuO, up to ~760°C.

The thermal decomposition of the organic ligand and oxidation of Cu ions found to superimpose to that of the POH groups condensation. The final products were [(Zr_{0.9}Ti_{0.1})_{0.25}(Ce)_{0.75}]P₂O₇ + (CuO)_{0.42}. The total weight loss found to be equal to (28.98 %), the calculated value was (28.766%).

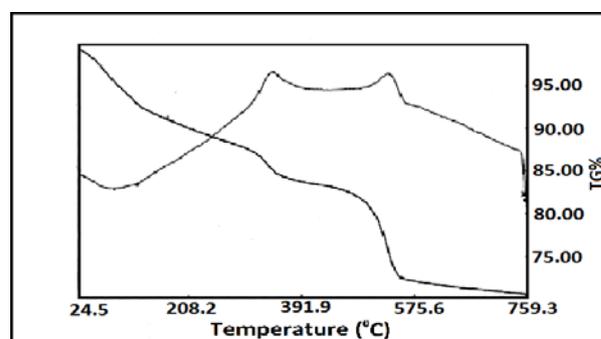


Figure 12. TG/DTA of [(H_{1.16}) Zr_{0.9}Ti_{0.1} (PO₄)₂]_{0.25} [(H_{1.16}) Ce (PO₄)₂]_{0.75} (PhenCu)_{0.42}·2.25H₂O

Figure 13 shows the thermogram of pillared compound [α -Zr_{0.8}Ti_{0.2}(H)_{1.5}(PO₄)₂]_{0.25} [(H_{1.5})Ce (PO₄)₂]_{0.75} (PhenCu)_{0.25}·1.77 H₂O. The thermal decomposition found to occur in 3 stages. first stage is relating to the loss of water of hydration up to ~180°C, followed by organic ligand decomposition and POH groups condensation, as well as the formation of CuO, up to ~760°C. The final products were [(Zr_{0.8}Ti_{0.2})_{0.25}(Ce)_{0.75}]P₂O₇ + (CuO)_{0.25}. The total weight loss found to be equal to (23.01 %), the calculated value was (23.03%).

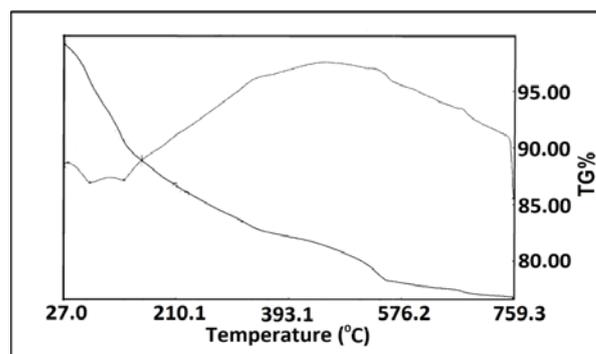


Figure 13. TG/DTA of [(H_{1.5})Zr_{0.8}Ti_{0.2} (PO₄)₂]_{0.25} [(H_{1.5})Ce (PO₄)₂]_{0.75} (Phen Cu)_{0.25}·1.77H₂O

Thermogram of [α -Zr_{0.67}Ti_{0.33}(H)_{0.3}(PO₄)₂]_{0.25} [Ce(H)_{1.5}(PO₄)₂]_{0.75} (Phen Cu)_{0.85}·4H₂O, is shown in Figure 14. The thermal decomposition found to occur in three stages. The first stage concerns the loss of water of hydration up to ~180°C, followed by organic ligand

decomposition and POH groups condensation, and the formation of CuO, up to $\sim 760^\circ\text{C}$. The final products were $[(\text{Zr}_{0.67}\text{Ti}_{0.33})_{0.25}(\text{Ce})_{0.75}]\text{P}_2\text{O}_7 + (\text{CuO})_{0.85}$. The total weight loss found to be equal to (41.13 %), the calculated value was (40.78 %).

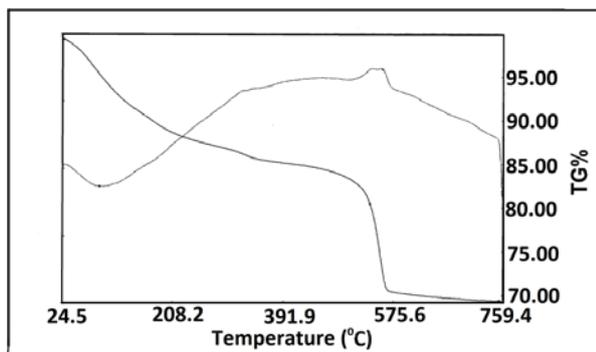


Figure 14. TGA/DTA $[(\text{H}_{0.3}) \text{Zr}_{0.67}\text{Ti} (\text{PO}_4)_2]_{0.25}[(\text{H}_{0.3})\text{Ce} (\text{PO}_4)_2]_{0.7} (\text{Phen Cu})_{0.85} \cdot 4 \text{H}_2\text{O}$

Figure 15 shows the thermogram of the pillared $[\alpha\text{-Zr}_{0.34}\text{Ti}_{0.66}(\text{H})_{1.6}(\text{PO}_4)_2]_{0.25}[\text{Ce}(\text{H})_{1.6}(\text{PO}_4)_2]_{0.75}(\text{PhenCu})_{0.2} \cdot 2.2\text{H}_2\text{O}$. The thermal decomposition found to occur in 3 stages. first stage concerns the loss of water of hydration up to $\sim 180^\circ\text{C}$, followed by organic ligand decomposition and POH groups condensation, as well as the formation of CuO, up to $\sim 760^\circ\text{C}$. The final products were $[(\text{Zr}_{0.34}\text{Ti}_{0.66})_{0.25}(\text{Ce})_{0.75}]\text{P}_2\text{O}_7 + (\text{CuO})_{0.2}$. The total weight loss found to be equal to (22.56 %), the calculated value was (23.16 %).

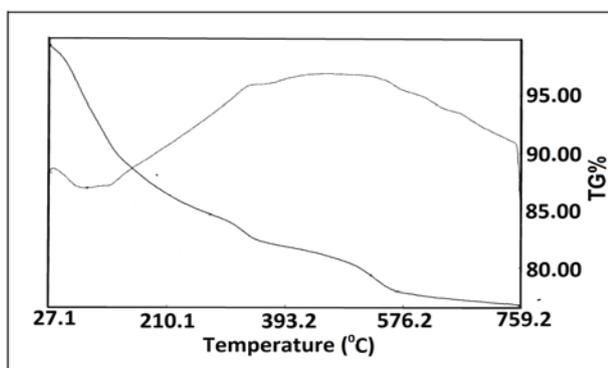


Figure 15. TG/DTA of $[(\text{H}_{1.6})\text{Zr}_{0.34}\text{Ti}_{0.66} (\text{PO}_4)_2]_{0.25}[(\text{H}_{1.6}) \text{Ce}(\text{PO}_4)_2]_{0.75} (\text{PhenCu})_{0.2} \cdot 2.22 \text{H}_2\text{O}$

4. Conclusion

This study shows that α -zirconium titanium phosphates-nanofibrous cerium phosphate composite membranes can be obtained by mixing slurry aqueous solution of their parent materials in required wt / wt % mixing ratios. The resultant composites were flexible homogeneous thin films with good mechanical properties. XRD of the composites show that it is possible to obtain tailor made inorganic membrane-membrane composites, where their XRD patterns show two d spacing reflections which are related to the d spacing reflection of their parent compounds. i.e. their XRD retain the d spacing of their parent materials. The formulation of the investigated pillared materials is based on a fact that M(IV) phosphates are stable materials and extremely insoluble. The final

products from thermal treatment are the pyrophosphates. The titanium % contents found to retain its molar ratio in hydrogen form, in pillars forms or when the materials used as ion exchangers, i.e. in its counter ions adsorbed forms. The pillared materials shows the increase of their thermal stability which can be related to metal ions effect. These materials can be considered as new solid acid catalysts, inorganic ion exchangers and as ionic conductance materials.

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