

## Synthesis and Characterization of Novel Pellicular $\gamma$ -Zirconium Phosphate-Phosphite/Fibrous Cerium Phosphate Nanocomposite Membranes

S. K. Shakshooki<sup>1,\*</sup>, F. A. Elakari<sup>1</sup>, A. M. EL-Hamady<sup>2</sup>, S. M. Elfituri<sup>2</sup> and R. Elghariani<sup>1</sup>.

<sup>1</sup>Department of Chemistry, Faculty of Science, Tripoli University, P.O.Box 13203, Tripoli, Libya.

<sup>2</sup>Advanced laboratory for Chemical Analysis, Tripoli, Libya.

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**Abstract:** Pellicular  $\gamma$ -zirconium phosphate-phosphite and nanofibrous cerium phosphate,  $\gamma$ -Zr.PO<sub>4</sub>.H<sub>2</sub>PO<sub>3</sub>.2H<sub>2</sub>O (p $\gamma$ -ZrPP), Ce(HPO<sub>4</sub>)<sub>2</sub>.2.9H<sub>2</sub>O(nCeP<sub>f</sub>), respectively, were prepared and characterized by chemical, X-ray, thermal analysis and by FT- IR spectra. Composites of pellicular  $\gamma$ -zirconium phosphate-phosphite/nanofibrous cerium phosphate membranes were prepared by mixing slurry aqueous solutions of (p $\gamma$ -ZrPP) and (nCeP<sub>f</sub>) at 45°C for 48h, where the mixing ratios were 33:67 and 25:75 wt/wt%, p $\gamma$ -ZrPP:nCeP<sub>f</sub>, respectively. The resultant composite materials found to be:  $[\gamma\text{-Zr.PO}_4\text{.H}_2\text{PO}_3]_{0.34}[\text{Ce(HPO}_4)_2]_{0.66}\text{.2.86H}_2\text{O}$ , and  $[\gamma\text{-Zr.PO}_4\text{.H}_2\text{PO}_3]_{0.27}[\text{Ce(HPO}_4)_2]_{0.73}\text{.2.17H}_2\text{O}$ , respectively. The composite membranes were homogeneous, flexible thin films with good mechanical texture. The resultant composites were characterized by chemical, x-ray, thermal analysis and by FT- IR spectra. Tailor made of pellicular  $\gamma$ -Zirconium phosphate- phosphite /nanofibrous cerium phosphate composite membranes can be obtained, which mainly depend on wt/wt% mixing ratios of (p $\gamma$ -ZrPP) /(nCeP<sub>f</sub>). These composites can be considered as new ion-exchangers, ionic conductors, and as solid acid catalysts.

**Keywords:** Pellicular  $\gamma$ -Zirconium Phosphate-Phosphite, Fibrous Cerium Phosphate, Nanocomposite Membranes.

### 1 Introduction

Metal phosphates chemistry recently has attracted attention in order to obtain materials with wide range of applications. Among these are tetravalent metal phosphates (TVMP) which are very insoluble compounds. Other than amorphous [1], they exist in two dimensional (2-D) and three dimensional (3-D) structures [2]. Porous layered M<sup>IV</sup> phosphates with  $\alpha$ ,  $\theta$  and  $\gamma$ -structures [3-5],  $\alpha$ -M<sup>IV</sup>(HPO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O,  $\theta$ -M<sup>IV</sup>(HPO<sub>4</sub>)<sub>2</sub>.5H<sub>2</sub>O and  $\gamma$ -M<sup>IV</sup>.PO<sub>4</sub>.H<sub>2</sub>PO<sub>4</sub>.2H<sub>2</sub>O, are well known compounds, (where M = Ti, Zr, Hf, Sn, Ce.....). These materials contain structural POH groups with labile protons and therefore potential conductance [6,7], solid acid catalysts [8] and intercalates [9].

A number of organic membranes are available today. However, very little studies were carried out on inorganic membranes of tetravalent metals. Membranes consists of inorganic polymers such as membrane of M<sup>IV</sup> phosphates are very attractive and could suitable for many processes of chemical technology such as waste disposal of metal ions, intercalates electrical conductance and solid acid catalysts. Fibrous cerium phosphate has been reported [10]. Pellicular

zirconium phosphate, Zr(HPO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O and pellicular hafnium phosphate, Hf(HPO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O were reported [11,12]. The pellicular membranes are two dimensional (2-D) structure membranes.

In our laboratory we under taking systematic studies on different varieties of pellicular membranes with general formulae, M<sup>IV</sup>(HPO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O [11,13], M<sup>IV</sup>.PO<sub>4</sub>.H<sub>2</sub>PO<sub>4</sub>.2H<sub>2</sub>O [14] and Zr<sub>x</sub>Ti<sub>(1-x)</sub>(HPO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O [15] that were prepared by different methods. Recent years have seen upsurge interest in the study of inorganic solid-solid and inorganic solid-organic polymer composite materials. The resultant composite material usually does not have either characteristic of original materials and can be considered as materials with almost new physical and chemical properties [16]. Here we are reporting the synthesis and characterization of novel pellicular  $\gamma$ -zirconium phosphate-phosphite/fibrous cerium phosphate nanocomposite membranes.

### 2 Materials and Methods

#### 2.1 Chemicals

ZrOCl<sub>2</sub>.H<sub>2</sub>O, CeSO<sub>4</sub>.4H<sub>2</sub>O, H<sub>3</sub>PO<sub>4</sub>(85%) of BDH,

\* Corresponding author E-mail: [shakshooki2002@yahoo.com](mailto:shakshooki2002@yahoo.com)

HF (40%) of Reidel De-Haen. Other chemicals used were of analytical grade.

## 2.2 Instruments used for characterization

X-Ray powder diffract meter Siemens D-500, using Ni-filtered  $\text{CuK}\alpha$  ( $\lambda = 1.54056\text{\AA}$ ), TG/DTA SIIExtra6000 TGA Perkin Elmer thermogravimetric analyzer(TGA)US, Fourier Transform IR spectrometer, model IFS 25 FTIR Bruker, Scanning electron microscopy (SEM) Jeol SMJ Sm 5610 LV, Transmission electron microscopy (TEM) Zeiss TEM 10CR, pH Meter WGW 52.

## 2.3 Preparation of nanofibrous cerium phosphate ( $n\text{CeP}_f$ )

200 ml 0.05M  $\text{CeSO}_4 \cdot 4\text{H}_2\text{O}$  in 0.5M  $\text{H}_2\text{SO}_4$  were added drop wise to 200ml 6M  $\text{H}_3\text{PO}_4$  at  $80^\circ\text{C}$  with stirring. The stirring was continued at that temperature for 4h. The resultant product was dispersed in 2 liter distilled water with stirring for 1h. Then subjected to washing by distilled water up to  $\text{pH} \sim 3.5$ . The resultant product kept in 2 liter distilled water to be, as such, in slurry aqueous form.

## 2.4 Preparation of pellicular $\gamma$ -zirconium phosphate ( $p\gamma\text{-ZrP}$ )

$\gamma$ -zirconium phosphate monoammonium form,  $\gamma\text{-Zr.PO}_4 \cdot \text{NH}_4\text{HPO}_4$ , was obtained by reacting 50ml of  $\text{ZrOCl}_2 \cdot 2\text{H}_2\text{O}$  (1.3M in 8M HF) with 450ml of 2M  $\text{NH}_4\text{H}_2\text{PO}_4$  in Pyrex round flask at  $80^\circ\text{C}$  with stirring for 24h. The resulted product was filtered washed with distilled water up to  $\text{pH} \sim 3$ , filtered and air dried. The ammonium form was converted to hydrogen form using 1M HCl with vigorous stirring at  $15^\circ\text{C}$  for 24h (for every 2g of  $\gamma\text{-Zr.PO}_4 \cdot \text{NH}_4\text{HPO}_4$  400ml 1M HCl were required). The major product ( $\sim 90\%$ ) was colloidal like, separated by using large amounts of distilled water for washing up to  $\text{pH} \sim 3$ . Then the suspended colloidal material were filtered through glass sintered funnel and filtered on porous plastic filter ( $1.2\mu$ ) to obtain flexible thin films, the pellicular  $\gamma\text{-Zr.PO}_4 \cdot \text{H}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  ( $p\gamma\text{-ZrP}$ ), and found to be Nanosized. The minor product ( $\sim 10\%$ ) found to be crystalline  $\gamma$ -zirconium phosphate.

## 2.5 Preparation of pellicular $\gamma$ -zirconium phosphate-phosphite ( $p\gamma\text{-ZrPP}$ )

To 2g of pellicular  $\gamma$ - zirconium phosphate 400ml of 0.1M  $\text{H}_3\text{PO}_4$  were added with stirring at  $80^\circ\text{C}$ . The stirring was continued at that temperature for 20h. The resultant product was washed with distilled water up to  $\text{pH} \sim 3.5$ , then filtered on porous plastic filter ( $1.2\mu$ ) to obtain flexible thin film, the pellicular  $\gamma\text{-Zr.PO}_4 \cdot \text{H}_2\text{PO}_3 \cdot 2\text{H}_2\text{O}$  ( $p\gamma\text{-ZrPP}$ ).

## 2.6 Preparation of pellicular $\gamma$ -zirconium phosphate-phosphite /fibrous cerium phosphate nanocomposite membranes ( $p\gamma\text{-ZrPP}/n\text{CeP}_f$ )

Composites  $[\text{Zr.PO}_4 \cdot \text{H}_2\text{PO}_3]_{0.34}[\text{Ce}(\text{HPO}_4)_2 \cdot 1.6\text{H}_2\text{O}]_{0.66} \cdot 2.86\text{H}_2\text{O}$ ,  $[\gamma\text{-Zr.PO}_4 \cdot \text{H}_2\text{PO}_3]_{0.27}[\text{Ce}(\text{HPO}_4)_2 \cdot 1.6\text{H}_2\text{O}]_{0.73} \cdot 2.17\text{H}_2\text{O}$  membranes were prepared by mixing slurry aqueous solution of  $p\gamma\text{-ZrPP}$  and  $n\text{CeP}_f$  in wt/wt % ratio, 33:67 and 25:75% of  $p\gamma\text{-ZrPP}:n\text{CeP}_f$ , where the mixing weights ratios are 0.15g:0.3g, and 0.1:0.3g, respectively, (in 100ml :300ml distilled water, respectively). The mixing was carried out at  $45^\circ\text{C}$  with stirring for 24h. The resultant products were filtered on filter paper using Buckner funnel, washed with distilled water (50ml) twice and dried in air. The products were homogeneous flexible thin films.

## 2.7 Thermal analysis

Thermal analyses were carried out in atmosphere, the rate was  $10^\circ\text{C}/\text{min}$ .

## 3 Results and Discussion

Nanosized cerium phosphate membrane,  $\text{Ce}(\text{HPO}_4)_2 \cdot 2.9\text{H}_2\text{O}$  ( $n\text{CeP}_f$ ), was prepared and characterized by chemical, XRD, thermal analysis FT-IR, SEM and TEM.

X-ray diffractogram (XRD) pattern of fibrous cerium phosphate membrane is shown in Figure 1 with  $d_{001} = 10.85\text{\AA}$ .

Figure 2 shows its FT-IR spectrum, with a trend similar to the IR spectra of  $\text{M}^{\text{IV}}$  phosphates. Broad band centered at  $3350\text{cm}^{-1}$  is due to OH groups symmetric-asymmetric stretching of  $\text{H}_2\text{O}$ , small sharp band at  $1628\text{cm}^{-1}$  is due to H-O-H bending, sharp broad band centered at  $1045\text{cm}^{-1}$  is related to phosphate groups vibration.

Thermogram of  $\text{Ce}(\text{HPO}_4)_2 \cdot 2.9\text{H}_2\text{O}$  is shown in Figure 3. The thermal decomposition occurs in continuous process almost one step. The thermal analysis was carried out at temperatures between  $10\text{-}750^\circ\text{C}$ , the final product was  $\text{CeP}_2\text{O}_7$ , results from the loss of water of hydration between  $60\text{-}200^\circ\text{C}$ , followed by POH groups condensation. The total weight loss found to be equal to 19.09%.

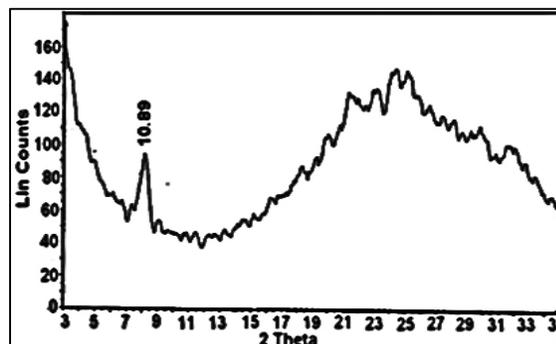


Fig 1: XRD of ( $n\text{CeP}_f$ )

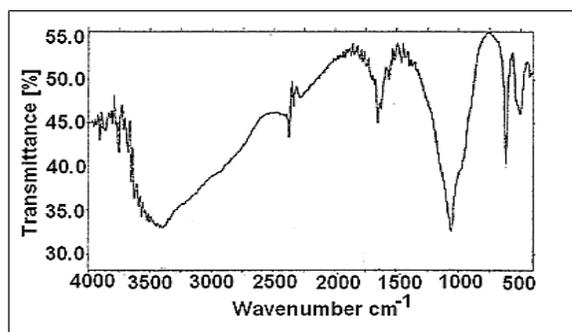


Fig 2: FT-IR spectrum of (nCeP<sub>f</sub>)

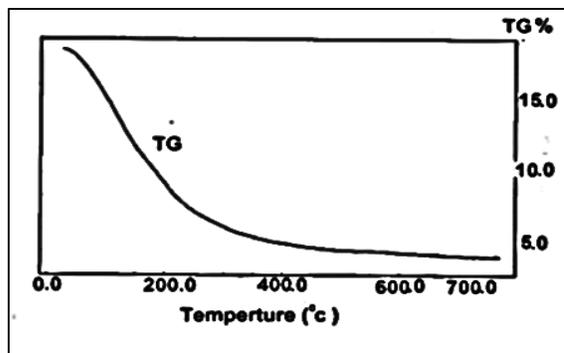


Fig 3: TG of (nCeP<sub>f</sub>).

SEM morphology image of the Nanosized fibrous cerium phosphate (nCeP<sub>f</sub>) is shown in Figure 4. The photograph shows its average size is ~ 20.5 nm. TEM image of the nanosized fibrous cerium phosphate in poly(vinyl alcohol) is shown in Figure 5. The photograph shows its average size is ~ 15 nm. The ion exchange capacity of fibrous cerium phosphate found to be equal to 5.21 meq/g.

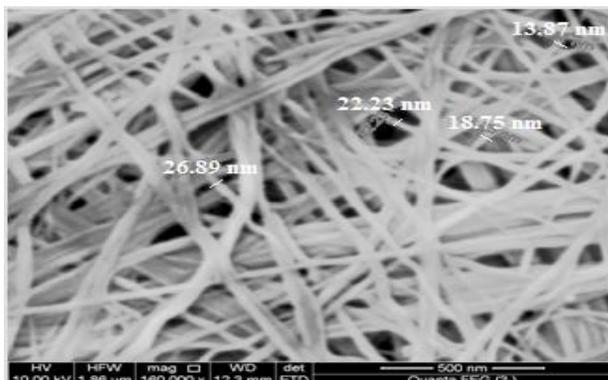


Fig 4: SEM of (nCeP<sub>f</sub>)

Pellicular  $\gamma$ -zirconium phosphate-phosphate membrane,  $\gamma$ -Zr<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (p $\gamma$ -ZrPP), was prepared from the reactions of pellicular  $\gamma$ -zirconium phosphate with 0.1M H<sub>3</sub>PO<sub>3</sub> at 80°C. Its X-ray diffraction pattern (XRD) is shown in Figure 6 with interlayer spacing ( $d_{001}$ ) = 12.2Å. XRD shows the material consists mainly of layers oriented parallel to its surface, so its x-ray diffractogram peaks are similar to that of a highly iso-oriented samples of its parent crystalline layered material.

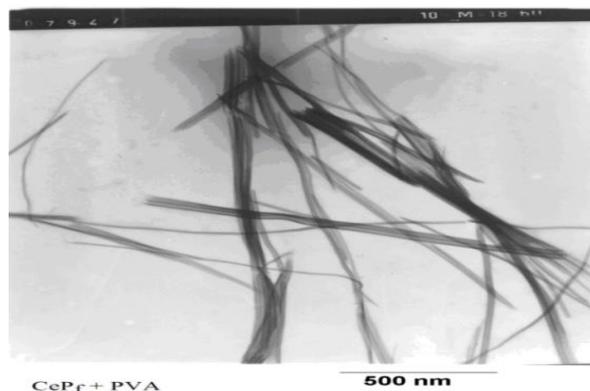


Fig 5: TEM of (nCeP<sub>f</sub>).

The (XRD) of  $\gamma$ -Zr<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O indicate good degree of crystallinity. The average diameter of (p $\gamma$ -ZrPP) was found to be 52 nm, which was calculated from the full width at half maximum of the peak using Scherrer's equation:

$$D = 0.9\lambda / \beta_{2\theta} \cos\theta_{max}$$

Where **D** is the average crystal size in nm,  $\lambda$  is the characteristic wave length of x-ray used ( $\lambda=1.54056 \text{ \AA}$ ),  $\theta$  is the diffraction angle, and the  $\beta_{2\theta}$  is the angular width in the radius at intensity equal to half of the maximum peak intensity [17].

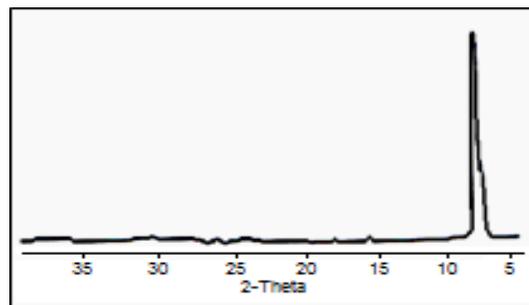
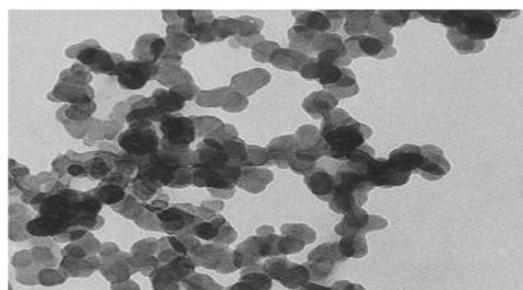


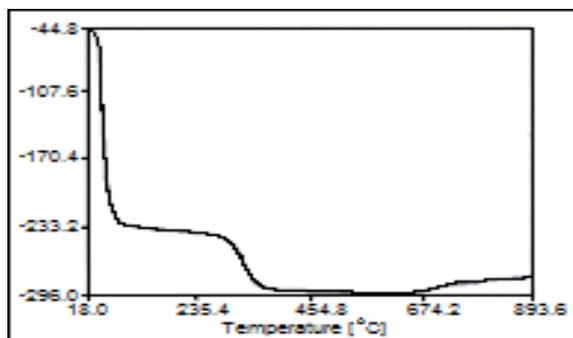
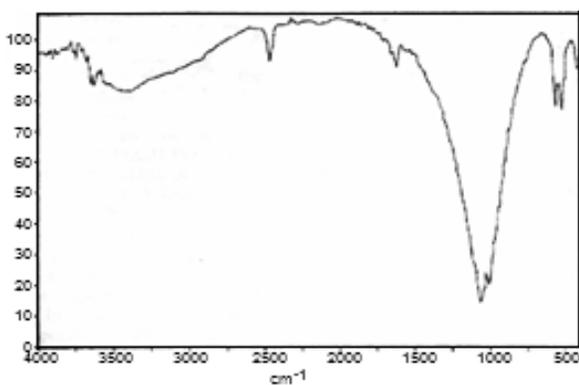
Fig 6: XRD of (p $\gamma$ -ZrPP).

TEM image of Nanosized p $\gamma$ -ZrP precursor of the preparation of pellicular  $\gamma$ -zirconium phosphate-phosphate membrane,  $\gamma$ -Zr<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (p $\gamma$ -ZrPP), is shown in Figure 7. Its average diameter found to be 57.5nm. Figure 8 shows its thermogram, the thermal decomposition occurs mainly in three steps. The weight loss up to 130°C is due to the loss of hydration water. The weight between 300-400°C is related to POH groups condensation while the weight increment above 600°C must be attributed to the calculated value 12.5% oxidation of phosphate groups.

The final product is ZrP<sub>2</sub>O<sub>7</sub>. Its FT-IR spectra is given in Figure 9 with broad band centered at 3370cm<sup>-1</sup> is due to OH groups symmetric-asymmetric stretching of H<sub>2</sub>O. Small sharp bands at 1620, 2335cm<sup>-1</sup> are related to H-O-H bending and phosphite groups, respectively. Sharp broad band centered at 1090cm<sup>-1</sup> is related to phosphate groups vibration.



500 nm

Fig 7: TEM of  $\gamma$ -zirconium phosphateFig 8: TG of ( $\gamma$ -ZrPP)Fig 9: FT-IR of ( $\gamma$ -ZrPP).

### 3.1 Composites of pellicular $\gamma$ -zirconium phosphate-phosphite /nanofibrous cerium phosphate membranes

$[\gamma\text{-Zr.PO}_4\text{.H}_2\text{PO}_3]_{0.34}[\text{Ce}(\text{HPO}_4)_2]_{0.66}\text{.}2.86\text{H}_2\text{O}$  and  $[\gamma\text{-Zr.PO}_4\text{.H}_2\text{PO}_3]_{0.27}[\text{Ce}(\text{HPO}_4)_2]_{0.73}\text{.}2.17\text{H}_2\text{O}$  composite membranes were obtained from mixing slurry aqueous solutions of pellicular  $\gamma$ -zirconium phosphate-phosphite and fibrous cerium phosphate in required wt/wt% mixing ratios. The resultant composite materials were flexible thin films and were designated as compounds (I, II), respectively.

XRD of composite compound (I) is shown in Figure 10 with d spacing reflection at  $12.30\text{\AA}$  and  $10.90\text{\AA}$ , which is a characteristic of XRD pattern of their parent pellicular

$\gamma$ -zirconium phosphate - phosphite and that of fibrous cerium phosphate, respectively. The XRD supports the formulation of the composite membrane.

Its thermogram curve is shown in Figure 11. The thermal decomposition occurs in three steps. First step is relate to the loss of hydration water that occurs between  $65\text{-}240\text{C}$  followed by POH groups condensation and oxidation of hydrogen of H-P (the phosphite groups) to give more  $\text{H}_2\text{O}$  in addition to that due to OH groups condensation this thermal behaviour follow similar TGA trend of M(IV)phosphate-phosphites[12]. The final product was  $[\text{Zr}_{0.34}\text{Ce}_{0.66}]\text{P}_2\text{O}_7$ . The total weight loss found to be equal to 19.2%.

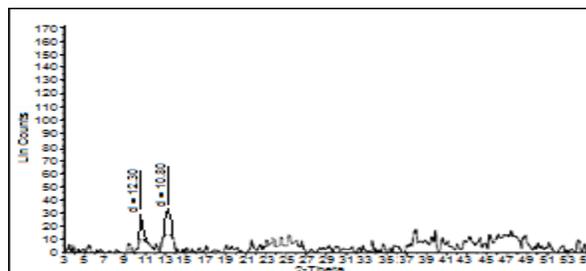
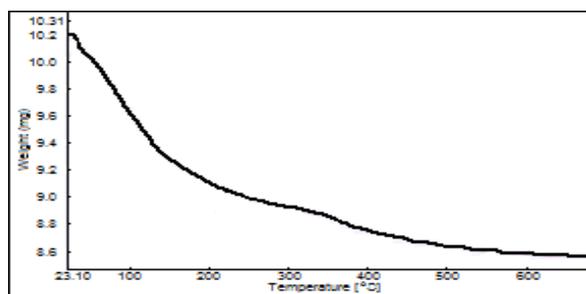
Fig 10: XRD of  $[\gamma\text{-Zr.PO}_4\text{.H}_2\text{PO}_3]_{0.34}[\text{Ce}(\text{HPO}_4)_2]_{0.66}\text{.}2.86\text{H}_2\text{O}$ Fig 11: TG of  $[\gamma\text{-Zr.PO}_4\text{.H}_2\text{PO}_3]_{0.34}[\text{Ce}(\text{HPO}_4)_2]_{0.66}\text{.}2.86\text{H}_2\text{O}$ .

Figure 12 shows the XRD of the composite compound (II) with d spacing reflections at  $12.2\text{\AA}$  and  $11.16\text{\AA}$ , which is a characteristic of XRD pattern of their parent pellicular  $\gamma$ -zirconium phosphate - phosphite and that of fibrous phosphate, respectively.

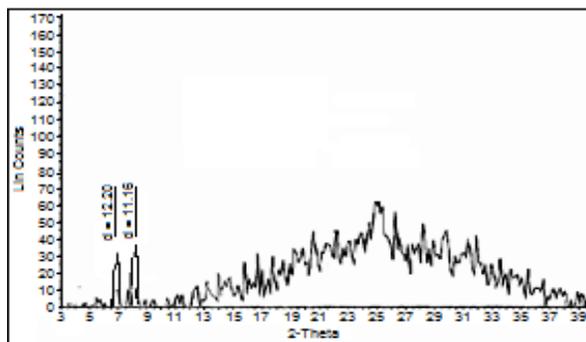
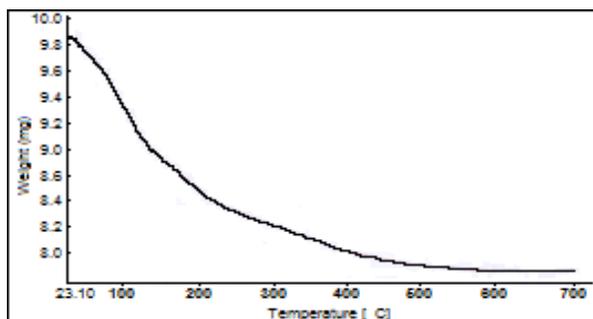
Figure 12. TG of  $[\gamma\text{-Zr.PO}_4\text{.H}_2\text{PO}_3]_{0.27}[\text{Ce}(\text{HPO}_4)_2]_{0.73}\text{.}2.17\text{H}_2\text{O}$ .

Figure 13 shows the thermogram curve of compound (II). The thermal decomposition occurs in three steps. First step is relate to the loss of hydration water that occurs between 70-240°C followed by POH groups condensation and oxidation of hydrogen of H-P (the phosphite groups) to give more H<sub>2</sub>O in addition to that due to be OH group condensation this thermal behavior follow similar TGA trend of M(IV)phosphate-phosphites. The final product was [Zr<sub>0.27</sub>Ce<sub>0.73</sub>]P<sub>2</sub>O<sub>7</sub>. The total weight loss found to be equal to 15.49%.



**Fig 13:** XRD of  $[\gamma\text{-Zr.PO}_4\text{.H}_2\text{PO}_3\text{.}]_{0.27}[\text{Ce}(\text{HPO}_4)_2]_{0.73}\text{.2.17H}_2\text{O}$ .

## 4 Conclusion

Novel Nanosized cerium phosphate membrane,  $\text{Ce}(\text{HPO}_4)_2\text{.2.9H}_2\text{O}(\text{nCeP}_f)$ , and pellicular  $\gamma$ -zirconium phosphate-phosphite,  $\gamma\text{-Zr.PO}_4\text{.H}_2\text{PO}_3\text{.2H}_2\text{O}$ , Nanosized, were prepared and characterized. The study shows pellicular  $\gamma$ -zirconium phosphate-phosphite/nanofibrous cerium phosphate composite membranes,  $[\gamma\text{-Zr.PO}_4\text{.H}_2\text{PO}_3]_{0.34}[\text{Ce}(\text{HPO}_4)_2]_{0.66}\text{.2.86H}_2\text{O}$  and  $[\gamma\text{-Zr.PO}_4\text{.H}_2\text{PO}_3]_{0.27}[\text{Ce}(\text{HPO}_4)_2]_{0.73}\text{.2.17H}_2\text{O}$  were obtained by mixing slurry aqueous solution of their membranes in required wt/wt% mixing ratios. The resultant compounds were flexible homogeneous thin films. The resultant composite material usually does not have either characteristic of original materials and can be considered as materials with almost new physical and chemical properties [18]. XRD of the resultant composites show it is possible to obtain tailor made inorganic membrane-membrane composites, where their XRD patterns shows two d spacing reflections which are related to the d spacing reflection of their parent compounds. The XRD retain the d spacing of their parent materials. FT-IR spectrum of composite materials are similar to the FT-IR spectra of their original materials. These novel composite membranes can be considered for potential applications as solid acid catalysts, inorganic ion exchangers and as proton conductance materials. Cerium phosphate [19,20] and its /exfoliated zirconium phosphate nanocomposite membranes were utilized as self-support polymerization aniline, indole and its aniline and pyrrole copolymers[21]. So the possibility of application of the resultant cerium phosphate/ pellicular  $\gamma$ -zirconium phosphate - phosphite can be considered for

self-support polymerization of the monomers such as aniline, indole and pyrrole.

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