

γ -Zirconium Titanium-Phosphates – Fibrous Cerium Phosphate / Polyaniline, Polyindole, Polycarbazole and Polyimidazole Nanocomposite Membranes

S. K. Shakshooki (Corresponding Author)

Department of Chemistry, Faculty of Science, University of Tripoli, Tripoli, Libya
Email: shakshooki2002@yahoo.com

F. A. El-Akari

Department of Chemistry, Faculty of Science, University of Tripoli, Tripoli, Libya

Suheila E. Kara

Department of Chemistry, Faculty of Science, University of Tripoli, Tripoli, Libya

M. K. Ellafi

Department of Chemistry, Faculty of Science, University of Tripoli, Tripoli, Libya

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Abstract

Layered nanosized mixed γ -zirconium titanium phosphates and fibrous cerium phosphate, γ -Zr_xTi_(1-x).PO₄.H₂PO₄.2H₂O (γ -ZTP), Ce(HPO₄)₂.2.9H₂O(n CeP_f), respectively, ($x = 0.95, 0.89$), and their $[\gamma$ -Zr_xTi_(1-x).PO₄.H₂PO₄]_{0.3}[Ce(HPO₄)₂]_{0.70}.2H₂O nanocomposite membranes were prepared and characterized by chemical, x-ray diffraction (XRD), thermogravimetric analysis (TGA) and Fourier transform spectroscopy (FT-IR). Novel $[\gamma$ -Zr_xTi_(1-x).PO₄.H₂PO₄]_{0.3}[Ce(HPO₄)₂]_{0.70} / polyaniline, polyindole, polycarbazole, and polyimidazole nanocomposite membranes were prepared via in-situ chemical oxidation of the monomers aniline, indole, carbazole and imidazole, respectively, that was promoted by the reduction of Ce^(IV) ions present on the surface of the inorganic matrix composite. A possible explanation is n CeP_f occurs at the surface of the composite was attacked by the monomers, respectively, converted to cerium (III) orthophosphate (CePO₄). The resultant novel composites were characterized by elemental (C,H,N) analysis and FT-IR. From elemental (C,H,N) analysis the % in weight of the resultant conducting polymers present in $[\gamma$ -Zr_{0.95}Ti_{0.05}.PO₄.H₂PO₄]_{0.3}[Ce(HPO₄)₂]_{0.70} composite were [Pani 19.35, PIn 5.72, PCz 5.8, PIm 23.7]%. The % in weight of the conducting polymers in the composite $[\gamma$ -Zr_{0.9}Ti_{0.11}.PO₄.H₂PO₄]_{0.3}[Ce(HPO₄)₂]_{0.70} were [Pani 8.54, PIn 8.02, PCz 7.72, PIm 22.27]%. The conductivity of the resultant conducting polymers found to be in the range of semiconductors.

Keywords: γ -zirconium titanium phosphates; Fibrous cerium phosphate; Polyaniline; Polyindole; Polycarbazole polyimidazole nanocomposites.

1. Introduction

Zirconium and titanium phosphates in amorphous and crystalline layered α -, γ and θ forms have been known for some time, of general formula M(IV)(HPO₄)₂.3H₂O [1, 2]. And α -M(IV)(HPO₄)₂.H₂O, γ -M(IV). PO₄.H₂PO₄.2H₂O, θ -M(IV) (HPO₄)₂.5H₂O, respectively [3-6] where M = Ti, Zr,. They are very insoluble materials. With good thermal stabilities, and posses high ion exchange capacities. Increase attention direct toward their intercalation [7], catalytic [8], electrical conductance [8], and as sensors [9].

Cerium phosphates have been studied for a long time as ion exchangers, their structures remains unknown until recently [10-12]. The reason is that ,the composition, the structure and the degree of crystallinity of their precipitates results from reaction of solutions containing a Ce(IV) salt is mixed with a solution of phosphoric acid of [(PO₄)/Ce(IV) ratio], strongly dependent on the experimental conditions such as rate and order of mixing of the solutions, stirring, temperature and digestion time, this also implemented on fibrous cerium phosphate [1, 12]. To date most of the work on fibrous cerium phosphate was carried out on its ion exchange [13], intercalation [14] and electrical conductance properties [15].

Conducting polymers (CPs) have become a fascinating area of research due to their very unique characteristic of being organic materials with electrical conductivity. Since their discovery, they have attracted the attention of a large group of researcher [16-18].

The preparation, characterization and application of electrochemically active, electronically conducting polymeric systems are still at the foreground of research CPs have received special attention as promising candidates in many areas of nano science and nanotechnology. They exhibit wide range of electrical conductivity from semiconductors to metallic region by way of doping, show enormous interesting properties like high electrical conductivity, environmental and chemical stability, low cost, easy prepared by chemical oxidative polymerization and electrochemical methods and fast reversible doping and de-doping, accordingly became materials of 21st century [19-24].

However, The preparation, characterization and application of electrochemically active, electronically conducting polymeric systems are still at the foreground of research [16].

Recently we have reported articles on self-support polymerizations of selected organic nitrogen conjugated monomers [25-31].

2. Materials and Methods

2.1. Chemicals

ZrOCl₂.8H₂O, H₃PO₄ (85%), NH₄.H₂PO₄ of (BDH), Ce(SO₄)₂.4H₂O of (Merck), TiCl₄, HF(40%) of (Reidel De-Haen), aniline (99.5%) of (Mindex UK), indole, carbazole and HF(40%) of (Reidel de-Hean), imidazole, Dimethyl sulfoxide (DMSO) of (BDH). Other reagents used were of analytical grade.

2.2. Instruments Used for Analysis

X-ray powder diffractometer. Siemens D-500, using Ni-filtered CuK_α(λ=1.54056Å) XRD with CuK_α radiation at 1.540Å by using PHILIPS PW1710.

TG/DTA SII Extra 6000 Thermogram, TG/DTA Perkin-Elmer.

Scanning electron microscopy (SEM) Jeol SMJ Sm 5610 LV.

Fourier Transform infrared spectrometer FT-IR, FT-IR-6100 and Shimadzu FT-IR Spectrometer in the rang 200-4000cm⁻¹.

Carbon Hydrogen Nitrogen (CHN) automatic analyzer Varian EL III-Elemental, Germany.

pH Meter WGW 521.

The dc conductivity (Scm⁻¹) was measured on compact pellets at (28⁰C) by RC-Circuit., using carbon black electrodes.

2.3. Preparation of γ -Zr_{0.95}Ti_{0.05}PO₄.H₂PO₄.2H₂O (γ -Zr_{0.95}Ti_{0.05} P)

γ -zirconium-titanium phosphate, γ -Zr_{0.95}Ti_{0.05}PO₄.H₂PO₄.2H₂O, was prepared by the reaction of a mixture 35 ml of 1.3M ZrOCl₂.8H₂O in 8M HF and 5ml 1M TiCl₄ in 2.5M HF with 450 ml of 2M NH₄H₂PO₄, in plastic container at room temperature(~20⁰C) for 4 days. The resultant precipitate was filtered on Buchner funnel and subjected to washing with distilled water up to pH4, to obtain the monoammonium form γ -Zr_{0.95}Ti_{0.05}.PO₄.NH₄HPO₄, that was converted to hydrogen form using 1M HCl with vigorous stirring at ~17⁰C for 24 h (for every 3g of γ -Zr_{0.95}Ti_{0.05}.PO₄.NH₄HPO₄, 600 ml 1M HCl were required). The resultant precipitate was washed with distilled water up to pH3, and was dried in air.

2.4. Preparation of γ -Zr_{0.9}Ti_{0.11}PO₄.H₂PO₄.2H₂O (γ -Zr_{0.89}Ti_{0.11} P)

γ -zirconium-titanium phosphate, γ -Zr_{0.89}Ti_{0.11}PO₄.H₂PO₄.2H₂O, was prepared by the reaction a mixture of 35 ml of 1.3M ZrOCl₂.8H₂O in 8M HF and 10ml 1M TiCl₄ in 2.5M HF with 450 ml of 2M NH₄H₂PO₄, in Pyrex round bottom flaks at room temperature(~20⁰C) for 4 days. The resultant precipitate was filtered on Buchner funnel and subjected to washing with distilled water up to pH4, to obtain the monoammonium form γ -Zr_{0.89}Ti_{0.11}.PO₄.NH₄HPO₄. It was converted to hydrogen form using 1M HCl with vigorous stirring at ~17⁰C for 24h (for every 3g of (γ -Zr_{0.89}Ti_{0.11}.PO₄.NH₄HPO₄ γ -Zr_{0.89}Ti_{0.11}.PO₄.NH₄HPO₄)600 ml 1M HCl were required). The resultant precipitate was washed with distilled water up to pH3, was dried in air.

2.5. Estimation of Titanium Content

Titanium content was determined spectrophotometrically as described earlier [2, 32].

2.6. Determination of the Exchange Capacities

Exchange capacities of the resultant nanosized γ -Zr_xTi_(1-x)PO₄.H₂PO₄.2H₂O were determined by addition of 25 ml of 0.10 M NaCl solution to 100 mg of the resultant material, with stirring for one h, then titrated with 0.10 M NaOH solution.

2.7. Thermal Analysis

Thermal analysis for the resultant materials were carried out under atmospheric condition, at rate of 10⁰C/min.

2.8. Preparation of Nano Fibrous Cerium Phosphate (nCeP_f)

300ml of 0.05M CeSO₄.4H₂O in 0.5M H₂SO₄ solution were added drop wise to 300ml of 6M H₃PO₄ at 80⁰C with stirring. After complete addition the resultant material left to digest at that temperature for 4h. To that one liter of hot distilled water, (~60⁰C), was added with stirring for 1h. The resultant slurry aqueous solution of nanofibrous cerium phosphate was kept.

2.9. Preparation of [γ -Zr_{0.95}Ti_{0.05} P]_{0.33} [nCeP_f]_{0.67} Nano Composite Membrane

0.6 grams of γ -Zr_{0.95}Ti_{0.05}PO₄.H₂PO₄.2H₂O was dispersed in 150 ml distilled water, with stirring, to that 300 ml of slurry aqueous solution of nanofibrous cerium phosphate (=1.2g nCeP_f) were added at 45⁰C, the stirring was continued for 48h. The resultant product was filtered in Buchner funnel, washed with distilled water and dried

in air. To obtain flexible thin sheet. In similar manner $[\gamma\text{-Zr}_{0.89}\text{Ti}_{0.11}\text{P}]_{0.33}[\text{nCeP}_f]_{0.67}$ nano composite membrane was prepared.

2.10. Preparation of $[\gamma\text{-Zr}_{0.95}\text{Ti}_{0.05}\text{P}]_{0.33}[\text{nCeP}_f]_{0.67}$ / Polyaniline Nano Composite Membrane

0.25g of $[\gamma\text{-Zr}_{0.95}\text{Ti}_{0.05}\text{P}]_{0.33}[\text{nCeP}_f]_{0.67}$ sheet was immersed in 12.5ml 4% aniline in ethanol at room temperature (23°C) for 72h. Then the impregnated sheet was removed, washed with ethanol and left to dry in air. The colour of the resultant product was dark green.

2.11. Preparation of $[\gamma\text{-Zr}_{0.95}\text{Ti}_{0.05}\text{P}]_{0.33}[\text{nCeP}_f]_{0.67}$ / Polyindole Nano Composite Membrane

0.25g of $[\gamma\text{-Zr}_{0.95}\text{Ti}_{0.05}\text{P}]_{0.33}[\text{nCeP}_f]_{0.67}$ sheet was immersed in 15ml 4% indole in ethanol at room temperature (23°C) for 72h. Then the impregnated sheet was removed, washed with ethanol and left to dry in air. The colour of the resultant product was brown.

2.12. Preparation of $[\gamma\text{-Zr}_{0.95}\text{Ti}_{0.05}\text{P}]_{0.33}[\text{nCeP}_f]_{0.67}$ /Polycarbazole Nano Composite Membrane

0.25g of $[\gamma\text{-Zr}_{0.95}\text{Ti}_{0.05}\text{P}]_{0.33}[\text{nCeP}_f]_{0.67}$ sheet was immersed in 21 ml 4% carbazole in tetrahydrofuran (THF) at room temperature (23°C) for 72h. Then the impregnated sheet was removed, washed with THF and left to dry in air. The color of the resultant product was light green.

2.13. Preparation of $[\gamma\text{-Zr}_{0.95}\text{Ti}_{0.05}\text{P}]_{0.33}[\text{nCeP}_f]_{0.67}$ /Polyimidazole Nano Composite Membranes

0.25g of $[\gamma\text{-Zr}_{0.95}\text{Ti}_{0.05}\text{P}]_{0.33}[\text{nCeP}_f]_{0.67}$ sheet was immersed in 6.5 ml 8% imidazole in ethanol at room temperature (23°C) for 72h. Then the impregnated sheet was removed, washed with THF and left to dry in air. The colour of the resultant product was beige.

Following similar experimental parameters shown above, $[\gamma\text{-Zr}_{0.89}\text{Ti}_{0.11}\text{P}]_{0.33}[\text{nCeP}_f]_{0.67}$ / polyaniline-, polyindole-, polycarbazole and polyimidazole nanocomposite membranes were prepared. The colour of the resultant composites were, dark green, dark brown, light green and beige, respectively.

2.13. Measurements of Conducting Polymers

Resultant conducting polymers were subjected for conductivity measurements at room temperature (23°C) using 4510 conductivity meter, JENWAY. Using DMSO solvent.

Typically: 0.1g of the resultant polymers composites were dissolved in 10ml DMSO. After calibration the measurement of samples is carried out by immersing the cell in the samples, allowing the readout to stabilize, and recording the result. The cell were rinsed in deionized water between each sample to avoid contamination, shaken to remove internal droplets, and the outside wiped prior, then by DMSO to immersion in the next sample. On completion of sample measurement the cell were thoroughly rinsed in deionized water. In similar way conductivity measurements were carried out for the rest of samples.

3. Results and Discussion

XRD, SEM, and FT-IR, elemental {CHN} analysis and SEM are well-established techniques for characterization of starting layered materials and conducting polymers composites.

Novel nanosized γ -zirconium-titanium phosphates in homogeneous solid solutions forms., $\gamma\text{-Zr}_{0.95}\text{Ti}_{0.05}\text{PO}_4\cdot\text{H}_2\text{PO}_4\cdot 2\text{H}_2\text{O}$, $\gamma\text{-Zr}_{0.89}\text{Ti}_{0.11}\text{PO}_4\cdot\text{H}_2\text{PO}_4\cdot 2\text{H}_2\text{O}$, were prepared, and characterized by chemical, x-ray diffraction (XRD), thermogravimetric analysis (TGA) and Fourier transform spectroscopy (FT-IR). Their titanium contents were determined spectrophotometrically [28].

3.1. XRD

X-ray diffraction (XRD) is the principle technique used to characterize crystalline materials, and to determine unit cell size of a particular material.

Figures 1, 2 show (XRD) of the resultant nanosized $\gamma\text{-Zr}_x\text{Ti}_{(1-x)}\text{PO}_4\cdot\text{H}_2\text{PO}_4\cdot 2\text{H}_2\text{O}$ ($\gamma\text{-ZTP}$), indicate good degree of crystallinity, where $x = 0.95, 0.89$, respectively. Their interlayer distances (d_{001}) found to be equal to 12.253 Å and 12.238 Å, respectively, The average diameter of $\gamma\text{-Zr}_x\text{Ti}_{(1-x)}\text{PO}_4\cdot\text{H}_2\text{PO}_4\cdot 2\text{H}_2\text{O}$, found to be equal to 33.77, 40.64 nm., respectively, which were calculated from the full width at half maximum of the peak using Scherer's equation; [33]:

$$D = \frac{0.9\lambda}{\beta 2\theta \cos\theta_{\max}}$$

where D is the average crystal size in nm, λ is the characteristic wave length of x-ray used ($\lambda = 1.54056 \text{ \AA}$), θ 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 [33].

Their XRD show the resultant products are in homogeneous solid solution forms [2, 24]. There is no indication of presence of pure α - or γ -titanium phosphates. The (d_{001}) values of α - or γ -TiP in pure forms are 7.56 Å and 11.60 Å, respectively.

Figure-1. XRD of γ -Zr_{0.95}Ti_{0.05}P

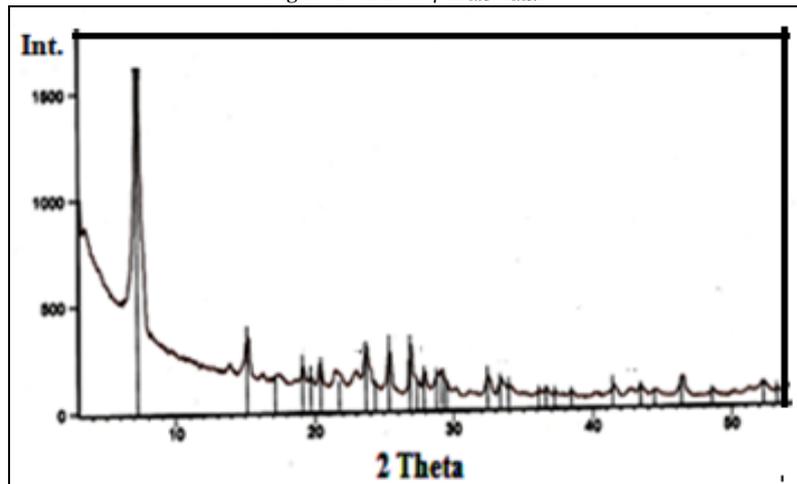
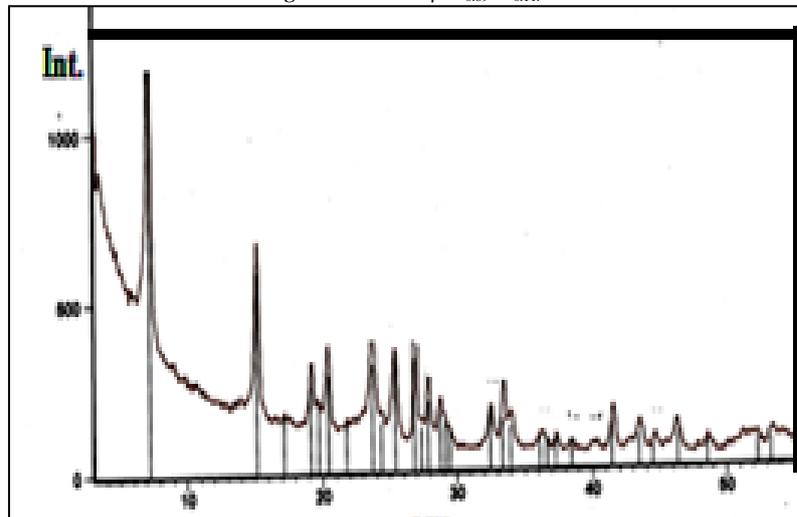


Figure-2. XRD of γ -Zr_{0.89}Ti_{0.11}P



3.2. TGA

Figures 3, 4 show the thermograms of the resultant nanosized γ -Zr_{0.95}Ti_{0.05}. PO₄. H₂PO₄.2H₂O, γ -Zr_{0.9}Ti_{0.1}. PO₄.H₂PO₄.2H₂O, respectively, found to follow almost the same trend. Their total weight losses found to be, 17.02, 17.1, % in wt., respectively. The water of crystallization (two moles) are lost at \sim 100°C. At higher temperature condensation of POH groups occurs resulting in formation of [Zr_xTi_(1-x)]P₂O₇ as final product, the total loss was three molecules of water per unit formula.

Figure-3. TGA of γ -Zr_{0.95}Ti_{0.05}P/

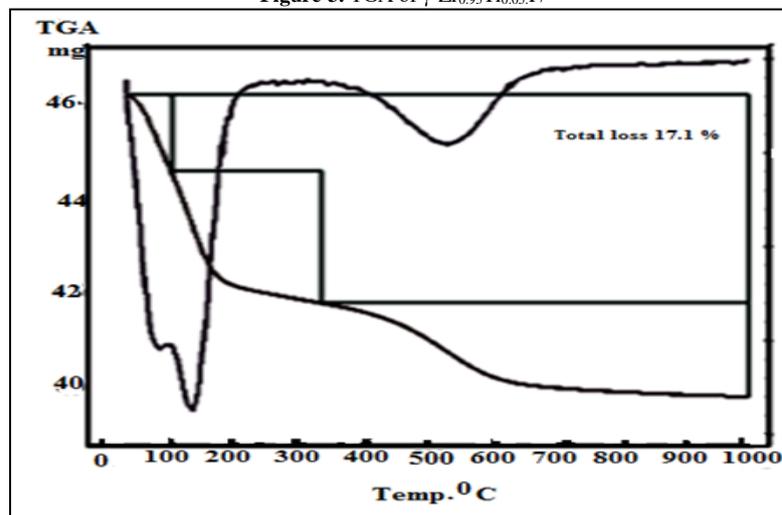
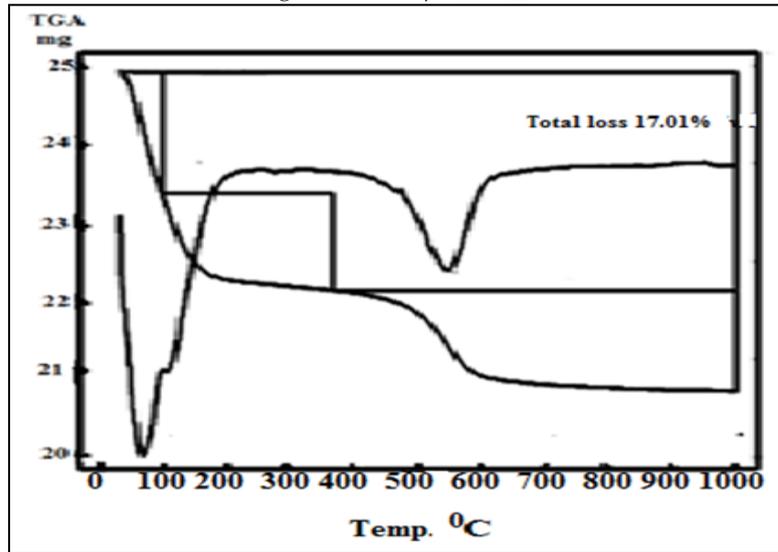


Figure-4. TGA of $\gamma\text{-Zr}_{0.89}\text{Ti}_{0.11}\text{P}$ 

3.3. FT-IR of $\gamma\text{-Zr}_x\text{Ti}_{(1-x)}\text{PO}_4\cdot\text{H}_2\text{PO}_4\cdot 2\text{H}_2\text{O}$

Fourier transform infrared spectroscopy (FT-IR) is well-established technique to obtain chemical composition by identifying specific bond structure of the studied material's.

Figures 5, 6 show the FT-IR spectra of $\gamma\text{-Zr}_{0.95}\text{Ti}_{0.05}\text{PO}_4\cdot\text{H}_2\text{PO}_4\cdot 2\text{H}_2\text{O}$, and $\gamma\text{-Zr}_{0.89}\text{Ti}_{0.11}\text{PO}_4\cdot\text{H}_2\text{PO}_4\cdot 2\text{H}_2\text{O}$, respectively, with a trend similar to the IR spectra of $\gamma\text{-M}^{\text{IV}}$ phosphates [2, 24, 32]. Shows broad band centered at $\sim 3350\text{ cm}^{-1}$, which is attributed to symmetric and asymmetric -OH stretching while the band at $\sim 1630\text{ cm}^{-1}$ is due to H-O-H bending, Sharp broad band centered at $\sim 1035\text{ cm}^{-1}$ is related to P=O stretching. The bands at the region $630\text{-}515\text{ cm}^{-1}$ are ascribe the presence of $\delta(\text{PO}_4)$ also may be due to Zr-O bond,

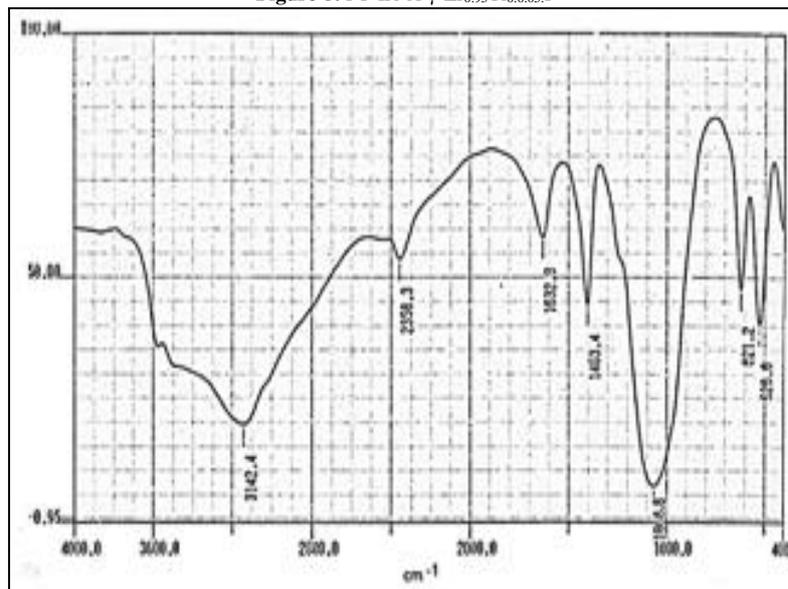
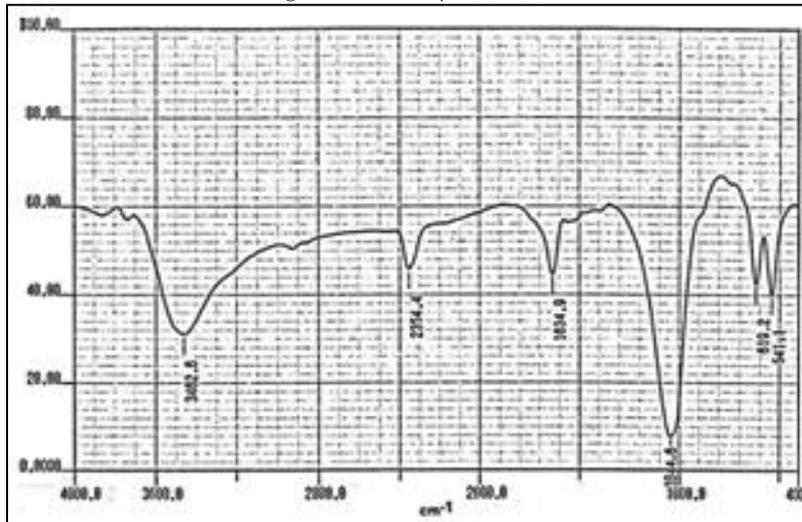
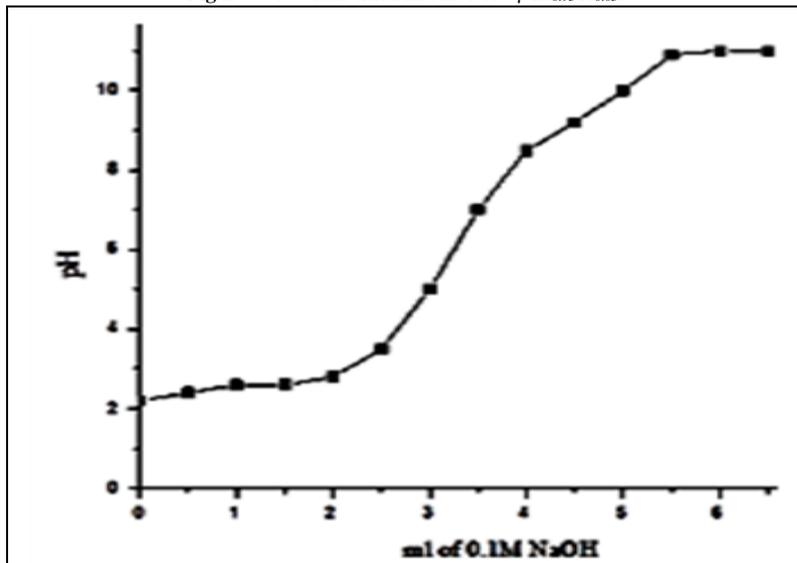
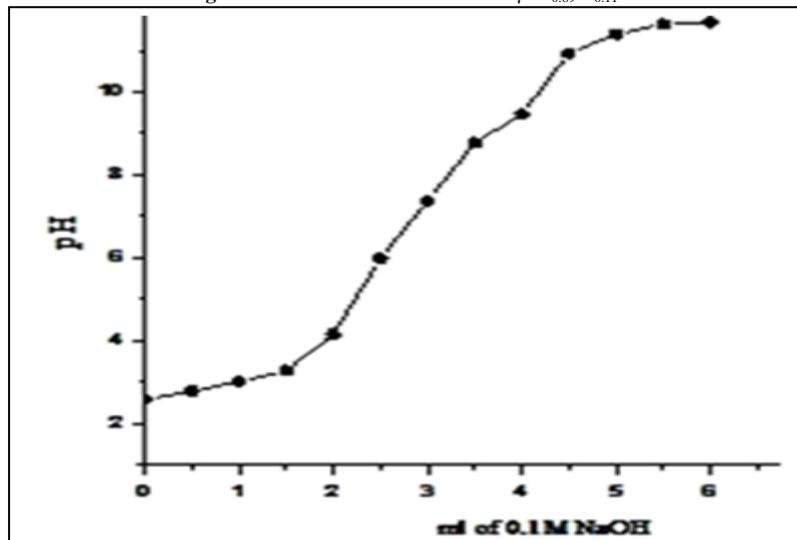
Figure-5. FT-IR of $\gamma\text{-Zr}_{0.95}\text{Ti}_{0.05}\text{P}$ 

Figure-6. FT-IR of γ -Zr_{0.89}Ti_{0.11}-P

3.4. Exchange Capacities

Exchange capacities of the resultant nanosized γ -Zr_xTi_(1-x).PO₄.H₂PO₄.2H₂O (γ -ZTP), were determined by titration method as described in experimental section, found to be equal to 6.3, 6.33 meq/g, respectively.

Figures 7, 8 show the Na⁺ ions titration curves of nanosized mixed γ -zirconium-titanium phosphates, γ -Zr_{0.95}Ti_{0.05}Zr_{0.95}PO₄.H₂PO₄.2H₂O, γ -Zr_{0.89}Ti_{0.11}.PO₄.H₂PO₄.2H₂O, respectively, found to follow same trend.

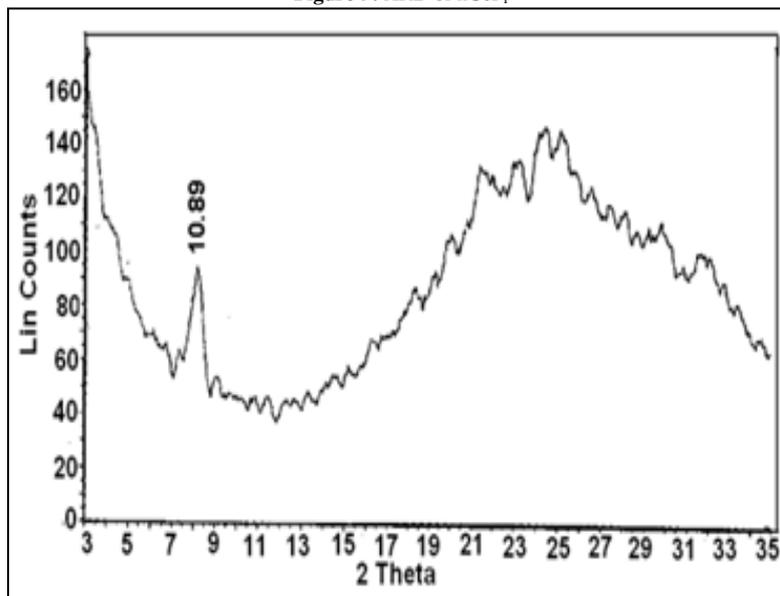
Figure-7. Na⁺ ions titration curve of γ -Zr_{0.95}Ti_{0.05}PFigure-8. Na⁺ ions titration curve of γ -Zr_{0.89}Ti_{0.11}P

Nanofibrous cerium phosphate membrane, $\text{Ce}(\text{HPO}_4)_2 \cdot 2.9\text{H}_2\text{O}$ (nCePf), was prepared, characterized by chemical, XRD, TGA, FT-IR and scanning electron microscopy (SEM).

3.5. XRD of nCePf

XRD of (nCePf) is shown in Figure 9, with $d_{001}=10.89\text{\AA}$.

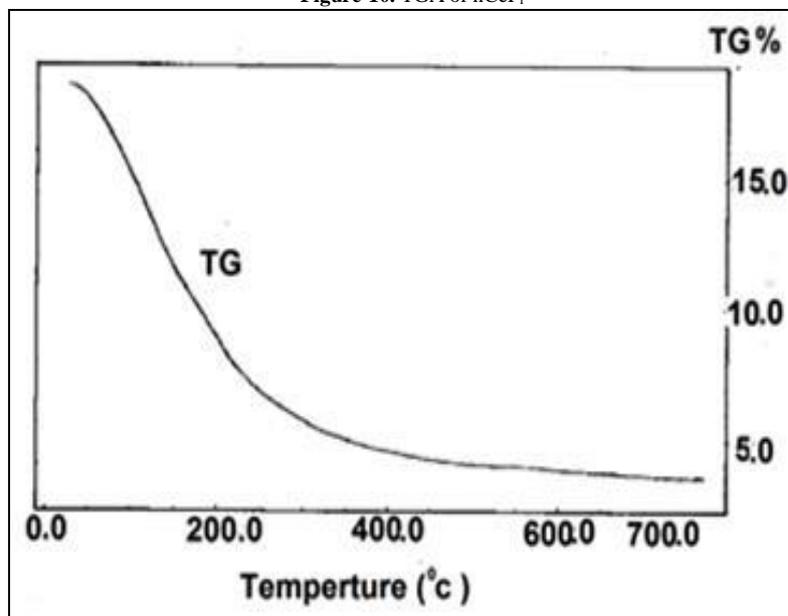
Figure-9. XRD of nCePf



3.6 TGA of nCePf

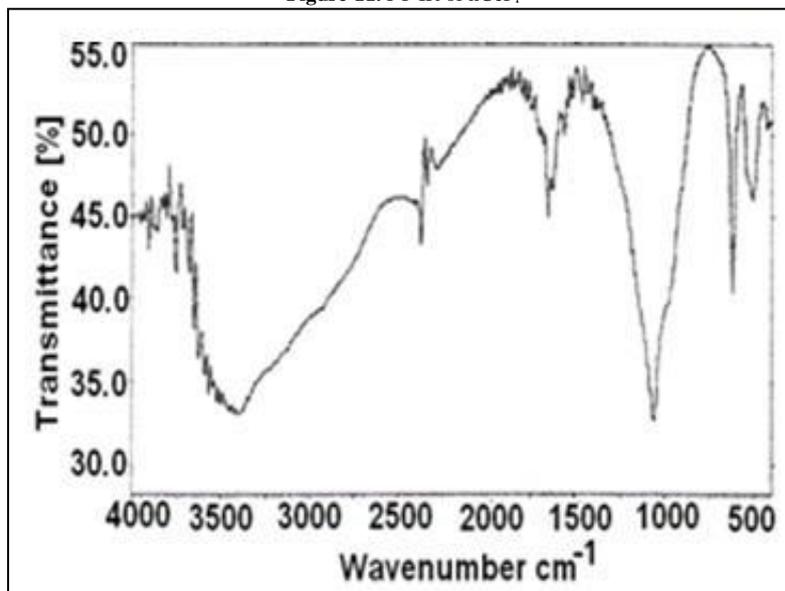
Thermogram of (nCePf) is shown in Figure 10. The thermal decomposition occurs in continuous process, The thermal analysis was carried out at temperatures between 10-775°C, the final product was $\text{Ce}_2\text{P}_2\text{O}_7$. Loss of water of hydration occurs between 60-200°C, followed by POH groups condensation. The total weight loss found to be equal to 19.09%.

Figure-10. TGA of nCePf



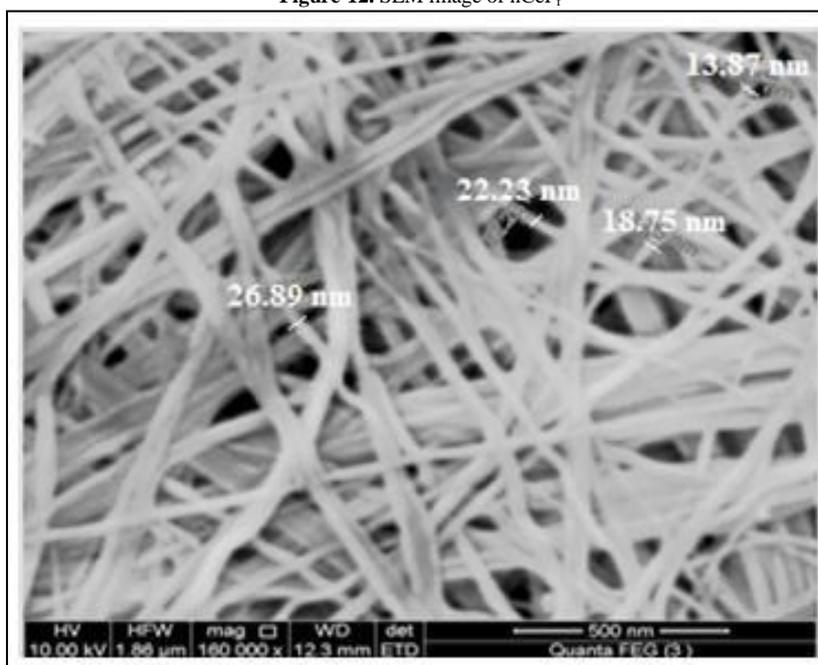
3.7. FT-IR of nCePf

Figure 11 shows FT-IR spectrum of fibrous $\text{Ce}(\text{HPO}_4)_2 \cdot 2.9\text{H}_2\text{O}$, with a trend similar to that of M(IV) phosphates. It consists of broad band centered at 3350cm^{-1} is due to symmetric and asymmetric -OH stretching while the band at $\sim 1628\text{cm}^{-1}$ is due to H-O-H bending, Sharp broad band centered at $\sim 1045\text{cm}^{-1}$ is related to P=O stretching. The bands at the region $630\text{-}515\text{cm}^{-1}$ are ascribe the presence of $\delta(\text{PO}_4)$ also may be due to Ce-O bond.

Figure-11. FT-IR of nCeP_f

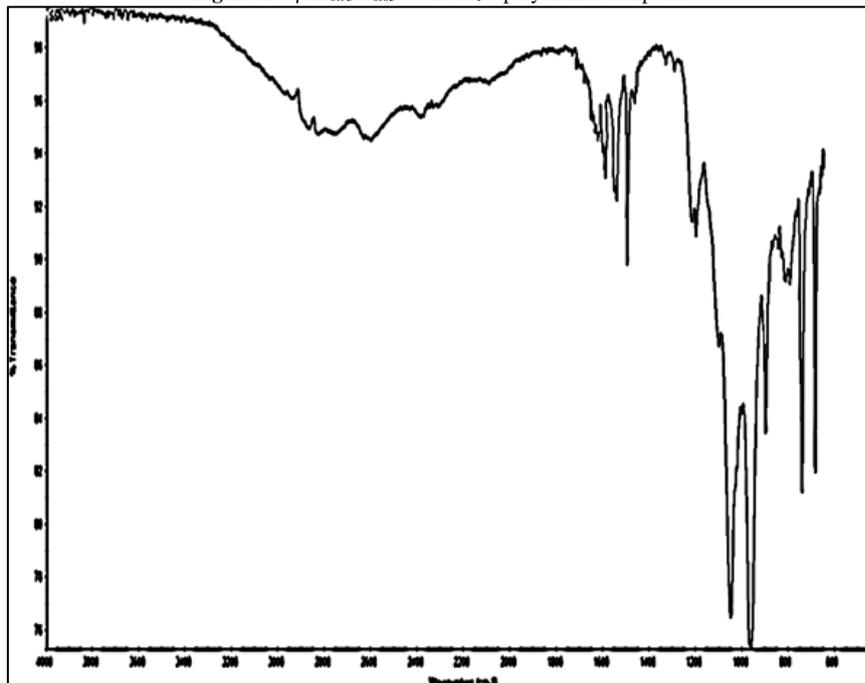
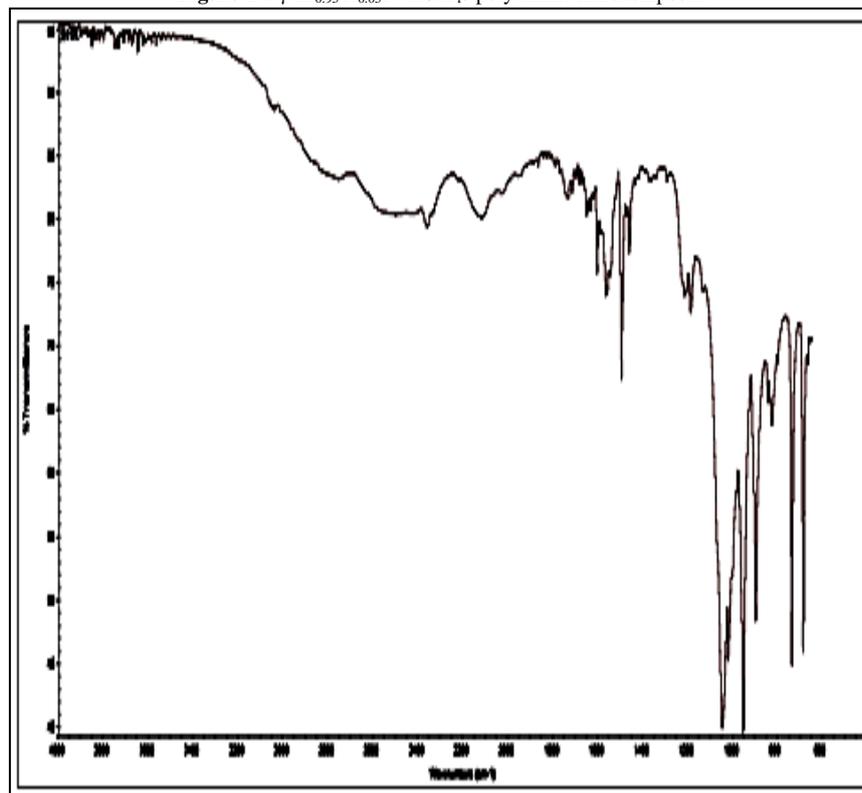
3.8. SEM of nCeP_f

SEM morphology image of the nanosized fibrous cerium phosphate (nCeP_f) is shown in Figure 12. The photograph shows its average size is ~20.5 nm.

Figure-12. SEM image of nCeP_f

3.9. FT-IR of γ -Zr_{0.95}Ti_{0.05}P = nCeP_f / Polyaniline, Polyindole Polycarbazole and Polyimidazole Nanocomposites

Figures 13, 14 show FT-IR spectra, of γ -Zr_{0.95}Ti_{0.05}P = nCeP_f / polyaniline and γ -Zr_{0.95}Ti_{0.05}P = nCeP_f / polyaniline nanocomposites. found to be almost identical. Consists of bands in the range 2900-2250cm⁻¹ corresponds to C-H stretching bonds. Other bands in the range 1600-1250cm⁻¹ correspond to the non-symmetric C₆ ring stretching modes and bands related to C-C bonds C-H stretching, C=C stretching, C-N stretching of the resultant polyaniline nanocomposites. Strong sharp doublet bands at 980-1050m cm⁻¹ assigned to P=O stretching. The bands at the region 850-500 cm⁻¹ are ascribe the presence of $\delta(\text{PO}_4)$, metal oxide and the polyaniline. Thus FT-IR spectra confirms the formation of polymerization.

Figure-13. γ -Zr_{0.95}Ti_{0.05}P = nCeP_f / polyaniline compositeFigure-14. γ -Zr_{0.95}Ti_{0.05}P = nCeP_f / polyaniline nanocomposite

Figures 15, 17 show typical FT-IR spectra of the resultant γ -Zr_xTi_(1-x)P-nCeP_f / polyindole, polycarbazole and polyimidazole nanocomposites, consists of small bands in the range 1700-1250 cm⁻¹, represent Fingerprint of FT-IR spectra of conducting conjugated polymers, which are correspond to C-C bonds C-H stretching, C=C stretching, C-N stretching of the resultant polymers. Strong sharp doublet band centered at about 1000 cm⁻¹ assigned to P=O stretching. The bands at the region 850-500 cm⁻¹ are ascribe the presence of $\delta(\text{PO}_4)$, metal oxide and the conducting polymer. Thus FT-IR spectra confirms the formation of polymerization

Figure-15. γ -Zr_{0.95}Ti_{0.05}P= nCeP_r/ polyindole nanocomposite

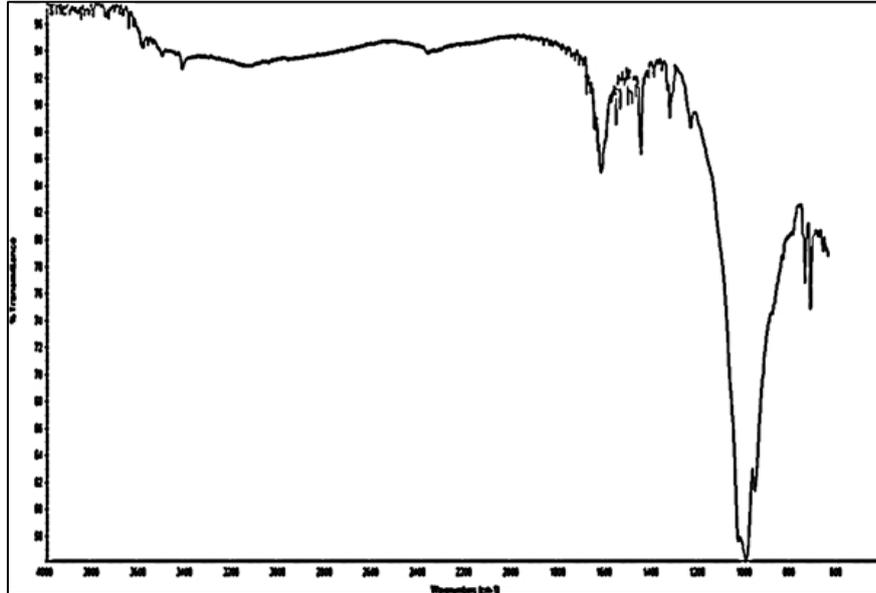


Figure-16. γ -Zr_{0.95}Ti_{0.05}P= nCeP_r/ polycarbazole nanocomposite

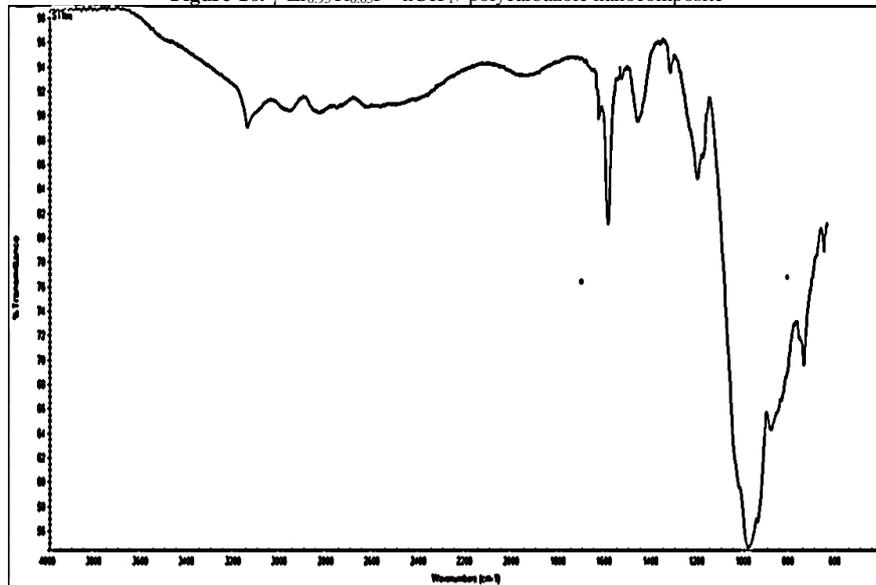
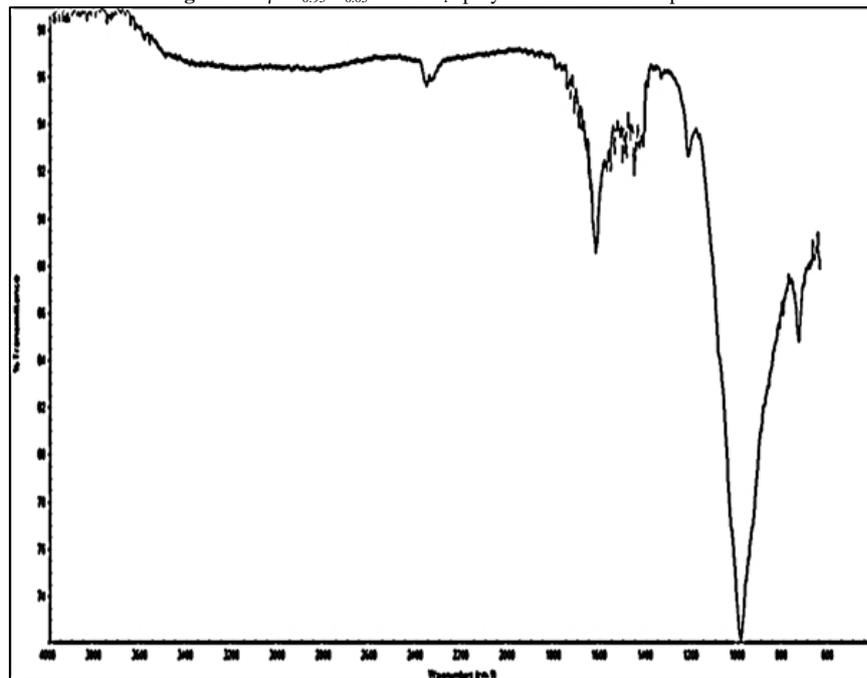


Figure-17. γ -Zr_{0.95}Ti_{0.05}P= nCeP_r/ polyimidazole nanocomposite



Electrical conductivity from resultant polymer composites were investigated using DMSO solvent. The resultant organic polymers have conjugated structure which are necessary to become intrinsically conducting. The polymer to be electronically conductive they possess not only charge carriers to move. However, their conjugated structure can meet the second requirement through a continuous overlapping of orbitals along the polymer backbone [25, 34].

The dc conductivity are measure for all samples at room temperature (RT) about 23°C using the following relation:

$\sigma = (1/R \text{ for sample} - 1/R \text{ for solvent}) \times L/A$, where $1/R$ is electrical conductance, L/A is cell constant ($= 1.036 \text{ cm}^{-1}$) and electrical conductance for DMSO as solvent $= 3.75 \mu\text{S}$. The conductivity (σ) of the selected samples are listed in the Table 1.

Table-1. Conductivity

Compounds	Conductivity (Scm^{-1})
$[\gamma\text{-Zr}_{0.95}\text{Ti}_{0.05}\text{PO}_4\cdot\text{H}_2\text{PO}_4]_{0.3} [\text{Ce}(\text{HPO}_4)_2]_{0.70}/\text{Pani}$ (19.35%)	7.12×10^{-6}
$[\gamma\text{-Zr}_{0.95}\text{Ti}_{0.05}\text{PO}_4\cdot\text{H}_2\text{PO}_4]_{0.3} [\text{Ce}(\text{HPO}_4)_2]_{0.70}/\text{PIn}$ (5.72%)	2.6×10^{-6}
$[\gamma\text{-Zr}_{0.95}\text{Ti}_{0.05}\text{PO}_4\cdot\text{H}_2\text{PO}_4]_{0.3} [\text{Ce}(\text{HPO}_4)_2]_{0.70}/\text{PCz}$ (5.80%)	1.4×10^{-6}
$[\gamma\text{-Zr}_{0.95}\text{Ti}_{0.05}\text{PO}_4\cdot\text{H}_2\text{PO}_4]_{0.3} [\text{Ce}(\text{HPO}_4)_2]_{0.70}/\text{PIIm}$ (23.70%)	1.1×10^{-5}
$[\gamma\text{-Zr}_{0.89}\text{Ti}_{0.11}\text{PO}_4\cdot\text{H}_2\text{PO}_4]_{0.3} [\text{Ce}(\text{HPO}_4)_2]_{0.70}/\text{Pani}$ (8.54%)	8.04×10^{-6}
$[\gamma\text{-Zr}_{0.89}\text{Ti}_{0.11}\text{PO}_4\cdot\text{H}_2\text{PO}_4]_{0.3} [\text{Ce}(\text{HPO}_4)_2]_{0.70}/\text{PIn}$ (8.02%)	4.8×10^{-6}
$[\gamma\text{-Zr}_{0.89}\text{Ti}_{0.11}\text{PO}_4\cdot\text{H}_2\text{PO}_4]_{0.3} [\text{Ce}(\text{HPO}_4)_2]_{0.70}/\text{PCz}$ (7.72%)	2.8×10^{-7}
$[\gamma\text{-Zr}_{0.89}\text{Ti}_{0.11}\text{PO}_4\cdot\text{H}_2\text{PO}_4]_{0.3} [\text{Ce}(\text{HPO}_4)_2]_{0.70}/\text{PIIm}$ (22.27%)	1.584×10^{-5}

From the above dc conductance (Table 1) the conductivity of resultant conducting polymers composites indicate their semi conductance properties.

4. Conclusions

Novel nanosized mixed γ -zirconium– titanium phosphates, $\gamma\text{-Zr}_{0.95}\text{Ti}_{0.05}\text{PO}_4\cdot\text{H}_2\text{PO}_4\cdot 2\text{H}_2\text{O}$ $\gamma\text{-Zr}_{0.89}\text{Ti}_{0.11}\text{PO}_4\cdot\text{H}_2\text{PO}_4\cdot 2\text{H}_2\text{O}$, were prepared and characterized. Their XRD show the resultant products are in homogeneous solid solution forms. There is no indication of presence of α - or γ -titanium phosphates in pure forms. Their nanosized found to be equal to 33.77, 40.64 nm, respectively. The nanosized (γ -ZTP) were formulated according to their chemical, XRD, TGA analysis and the estimation of their titanium contents.

Their novel $\gamma\text{-Zr}_x\text{Ti}_{(1-x)}\text{P-nCeP}_f$ / polyaniline, polyindole polycarbazole and polyimidazole nanocomposite membranes were prepared by in-situ chemical oxidation, promoted by self support polymerization which involve reduction of Ce(IV) ions present in the inorganic matrix of ($\gamma\text{-Zr}_x\text{Ti}_{(1-x)}\text{P-nCeP}_f$) nanocomposite membrane. The presence of Ce(IV) ions allows redox reactions necessary to oxidative polymerization to occur. A possible explanation is that polymerization of monomers is a result the attacking of the monomers on nCeP_f on the surface of inorganic matrix composite membranes, respectively, converted to cerium(III) orthophosphate (CePO_4).

The formulation of the resultant conducting polymers nanocomposites was supported by elemental(C,H,N) analysis, FT-IR spectra, and colour changes, We suggest self doping occurred on polymerization, which is due to labile proton (H^+) present in (POH) groups. Their electrical conductivity measurements shows the resultant conducting polymers are in range of semiconductors.

Beneficial properties of the resultant nanocomposites can be considered these composites as novel conducting inorganic-organic composites, and as ion exchangers.

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