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Novel α-Germanium, -α-Vanadyl Phosphates/Polyaniline, Polyindole, Polyimidazole and Polycarbazole Nanocomposites

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Keyword

α-germanium phosphate, α-vanadyl phosphate polyaniline, polyindole, polyimidazole and polycarbazole nanocomposites.

Abstract

Nano sized α-germanium phosphate and α-vanadyl phosphate, α-Ge(HPO4)2.1.84- H2O(GeP), α-VOPO4.2.5H2O(VOP), respectively, were prepared and characterized, composite[α-Ge(HPO4)2.]0.25[α-VOPO4]0.75.2H2O composite was prepared using 25:75 wt/wt% mixing ratios, respectively. Polyaniline(PAni), polyindole(PIn), polyimidazole(PIm) and polycarbazole(PCz)/ [α-Ge (HPO4)2.]0.25[VOPO4]0.75 composites. The polymerization results from part of V+5OP of the inorganic matrix is attacked by the monomers respectively, converted to V+4OP. The resultant materials were characterized and found to be [GePO4)2]0.25[VOPO4]0.75/ PAni 20.71 % in wt, ,PIn 5.99% in wt, PIm 36.0 % in wt, and PCz 10.47% in wt. The color of resultant composites was dark green, greenish-brown, beige and light green, respectively. Color changes support the formation of the resultant nanocomposite. Their conductivity are in range of semiconductors.

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مركبات نانوية جديدة من الجرمانيوم ألفا، وفوسفات ألفا فاناديل/بولي أنيلين، وبولي إندول، وبولي إيميدازول، وبولي كاربازول

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الكلمة المفتاحية: *فوسفات الجرمانيوم ألفا، فوسفات الفاناديل ألفا، بولي أنيلين، بولي إندول، بولي إيميدازول، ومركبات نانوية من بولي كاربازول.*

الملخص

تم تحضير وتوصيف فوسفات الجرمانيوم ألفا وفوسفات الفاناديل ألفا النانوية، α-Ge(HPO4)2.1.84- H2O (GeP) و α-VOPO4.2.5H2O (VOP) على التوالي. تم تحضير المركب [α-Ge(HPO4)2.]0.25[α-VOPO4]0.75.2H2O باستخدام نسب خلط 25:75 وزناً/وزناً. كما تم تحضير مركبات البولي أنيلين (PAni) والبولي إندول (PIn) والبولي إيميدازول (PIm) والبولي كاربازول (PCz)/[α-Ge(HPO4)2.]0.25[VOPO4]0.75. ينتج عن البلمرة تفاعل جزء من V+5OP في المصفوفة غير العضوية مع المونومرات، ليتحول إلى V+4OP. تم توصيف المواد الناتجة، وتبين أنها تتكون من PAni /[GePO4][2]0.25[VOPO4]0.75 بنسبة 20.71% وزناً، وPIn بنسبة 5.99% وزناً، وPIm بنسبة 36.0% وزناً، وPCz بنسبة 10.47% وزناً. وكانت ألوان المركبات الناتجة أخضر داكن، وبني مخضر، وبيج، وأخضر فاتح على التوالي. وتؤكد تغيرات اللون تكوين المركب النانوي الناتج. وتقع موصليتها ضمن نطاق موصلية أشباه الموصلات.

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1.Introduction

Intrinsic conducting, known synthetic metals and materials of 21st century They have high environmental, stability, easy synthesis and low cost of their monomers [1-5]. Proton doping: is one of doping methods in conducting polymers [6,7]. Shows promise applications in various fields [1-5].

Conjugated polymers show both electrical anisotropy with higher charge carrier mobility along the polymer backbone, [6-9].

Conducting polymers can be prepared by: chemical oxidative polymerization, (direct polymerization, or interfacial polymerization) [10], and electrochemical method [11,12].

Metal(iv) phosphates are stable materials good thermal stabilities, good ion exchange properties [12- 16], tendency to intercalate organic polar molecules [17], solid acid catalysts [18] , proton conductance [19] and as sensors[19]. The water molecule of vanadyl phosphate plays an important role in their electrical properties [20-23].. It also shows electrochemical intercalation [24].

2. Materials and Methods

2.1. Chemicals

Vanadium$^{(V)}$oxide (V_2O_5), and HF (40%) of Reidel de-Hean, Germanium tetrachloride ($GeCl_4$) and H_3PO_4(85%) of BDH, Aniline (99.5%) of Mendix, Indole of Park ,Carbazole and Imidazole of Sigma, Dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF) of Park. Others are analytical grade reagents .

2.2. Instrumentals

- XRD.of Siemens D-500 and Philips PW1710.
- (SEM) Jeol SMJ Sm 5610 LV.
- FT-IR, 6100 and Shimadzu
- Elemental analyzer Varian EL III-l, Germany.
- Ultraviolet-Visible (UV-vis) Perkin Elmer Life and Analytical sciences, 710, Bridgeport Shelton, USA.
- pH Meter WGW 521.
- Conductivity meter 4510 from JENWAY.

2.3. Synthesis of α-$VOPO_4.2.5H_2O$

α-$VOPO_4.2.5H_2O$ was prepared by refluxing method as already reported[24].

2.4. Synthesis of α-$Ge(HPO_4)_2.1.18H_2O$

α-$Ge(HPO_4)_2.1.18H_2O$ was reported according to metod reporte earlier[[25].

2.5. Synthesis of $[\alpha\text{-}Ge(HPO_4)_2.]_{0.34}[VOPO_4]_{0.66}.2.16H_2O$ composite

0.15 g of α-$Ge(HPO_4)_2.1.18H_2O$ was mixed with 0.3 g of α-$VOPO_4.2.5H_2O$, in 5ml THF. Ten THF was decanted and left to dry in air.

2.6. $[\alpha\text{-}Ge(HPO_4)_2.]_{0.34}[VOPO_4]_{0.66}$/polyaniline, polyindole, polyimidazole and polycarbazole) composites.

2.6.1. $[\alpha\text{-}Ge(HPO_4)_2.]_{0.34}[VOPO_4]_{0.66}$/polyaniline composite synthesis

To a mixture of 0.15 g α-germanium phosphate and 0.3 g of α-vanadyl phosphate composite 18 ml of 4% aniline in THF were added, with stirring for 48 h. Then filtered, washed twice with THF and dried in air.

2.6.2. Preparation of $\alpha\text{-}Ge(HPO_4)_2.]_{0.34}[VOPO_4]_{0.66}$/PIn) nanocomposite.

To a mixture of 0.15 g. α-germanium phosphate and 0.3 g of α-vanadyl phosphate composite 22.5 ml of 4% indole in THF were added, with stirring for 48 h. Then filtered, washed twice with THF and dried in air.

2.6.3. Preparation of α-$Ge(HPO_4)_2.]_{0.34}[VOPO_4]_{0.66}$ /PIm) nanocomposite.

To a mixture of 0.15 g α-germanium phosphate and 0.3 g of α-vanadyl phosphate nanocomposite, 13 ml of 4% imidazole in THF were added, with stirring for 48 h. Then filtered, washed twice with THF and dried in air.

2.6.4. Preparation of α-$Ge(HPO_4)_2.]_{0.34}[VOPO_4]_{0.66}$ / polycarbazole (GeP-VOP/PCz) nanocomposite.

32 ml of polycarbazole(4%)in THF were added to a mixture of 0.15 g α-germanium phosphate and 0.3 g of α-vanadyl phosphate nanocomposite, with stirring for 48 h. Then filtered, washed twice with THF and dried in air.

2.7. UV-Vis spectra measurement

DMSO solvent was used for extraction of for UV-vis measurements using 0.02 g of (GeP-VOP)/Conducting polymers composite.

2.8. Electrical conductivity measurements o

Conductivity measurements were carried out at (25°C) using 4510 conductivity meter, JENWAY using0.1 g of each resultant polymers composite dissolved in 10 ml of DMSO solvent..

3. Results and Discussion

3.1. α-Vanadyl phosphate

3.1.1 XRD

XRD of**. α-Vanadyl phosphate is shown in Figure 1.** its d_{001}=6.86 Å.

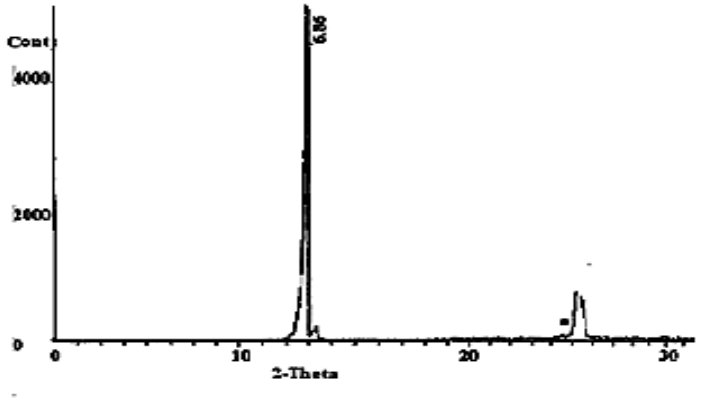


Figure 1: XRD pattern of VOP

3.1.2. VOP FT-IR

FT-IR spectrum of α-$VOPO_4$.2. $5H_2O$, found to follow same trend to that already reported[24].

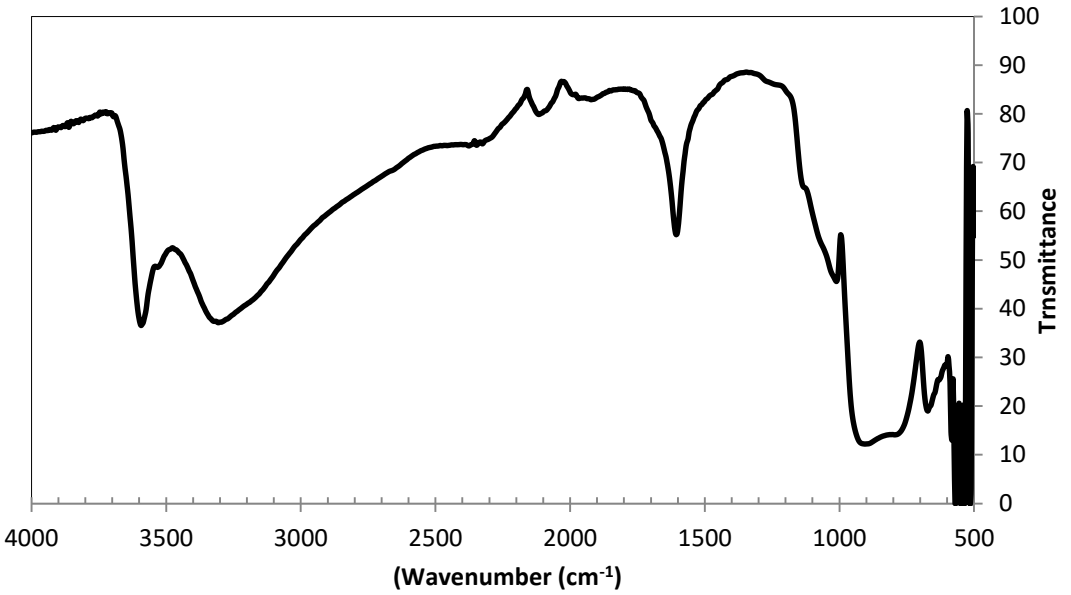


Figure 2: FT-IR spectrum of VOP

Figure 3, Thermal decomposition of α-Vanadyl phosphate is shown in Figure 1. found to follow same trend to that already reported[24].

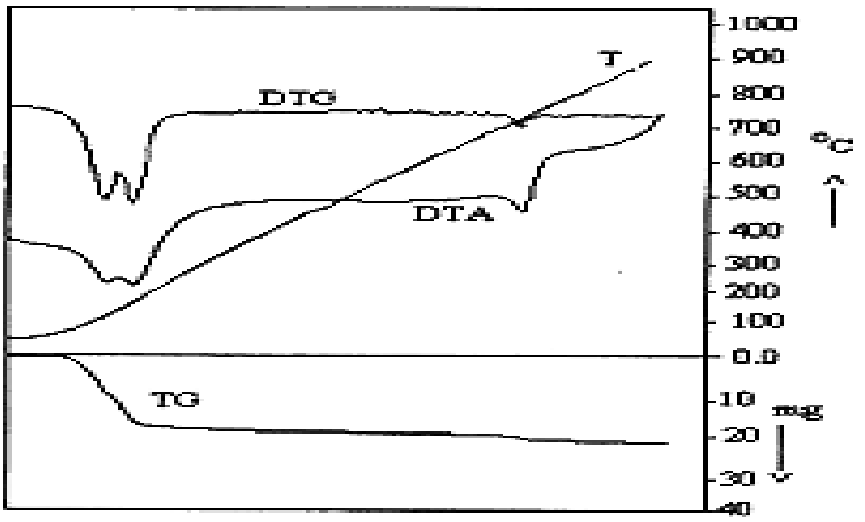


Figure 3: TG/DTA/DTG of VOP

3.1.4 SEM of VOP

SEM of Nano sized α-vanadyl phosphate shown in figure 4. with flake thickness found equal~ 76.2 nm.

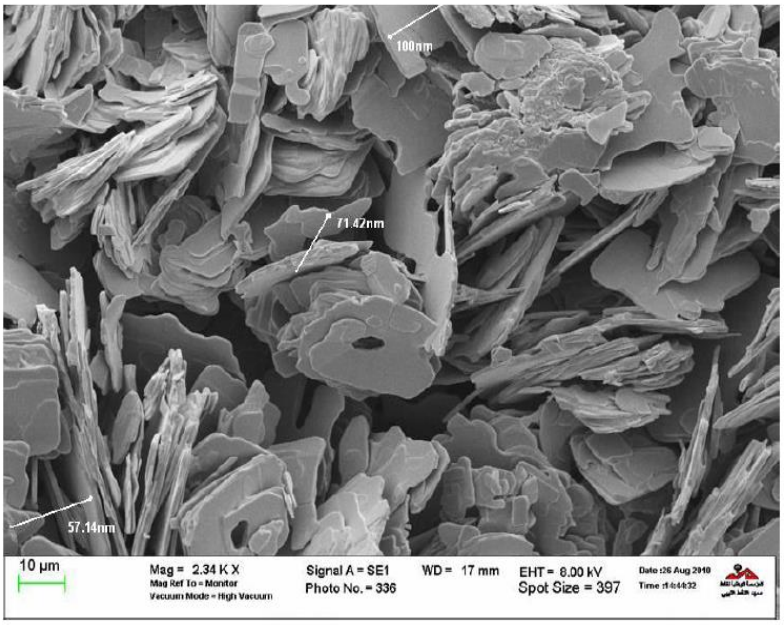


Figure 4: SEM of VOP

3.2. α-$Ge(HPO_4)_2.1.84.H_2O$

3.2.1 XRD of GeP

Figures 5 and 6 are represent XRD of α-$Ge(HPO_4)_2.1.84.H_2O$ its (d_{001}) equal to 7.71 Å , with size of 44.6 nm was calculated using Scherer's equation [25]:

$$D = \frac{0.9\lambda}{B_{2\theta}Cos\theta max}$$

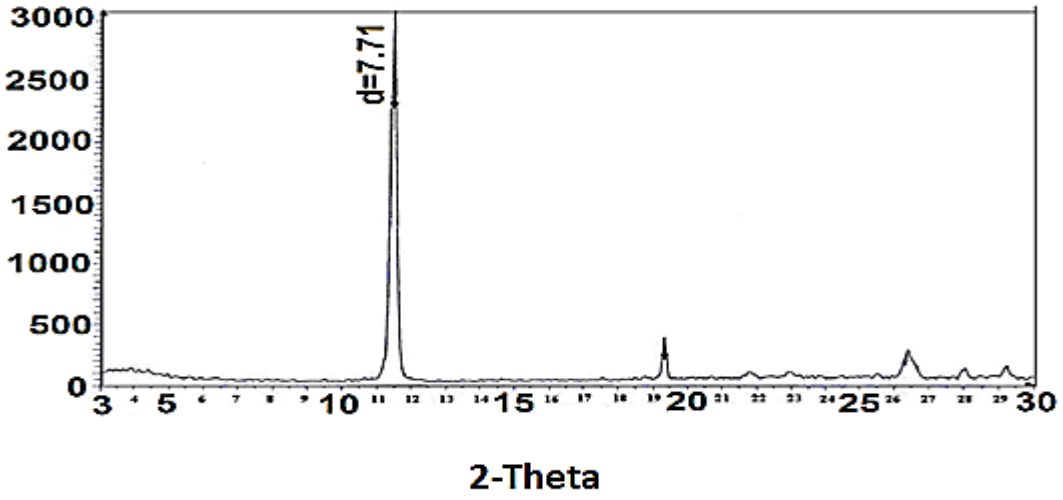


Figure 5: XRD pattern of GeP

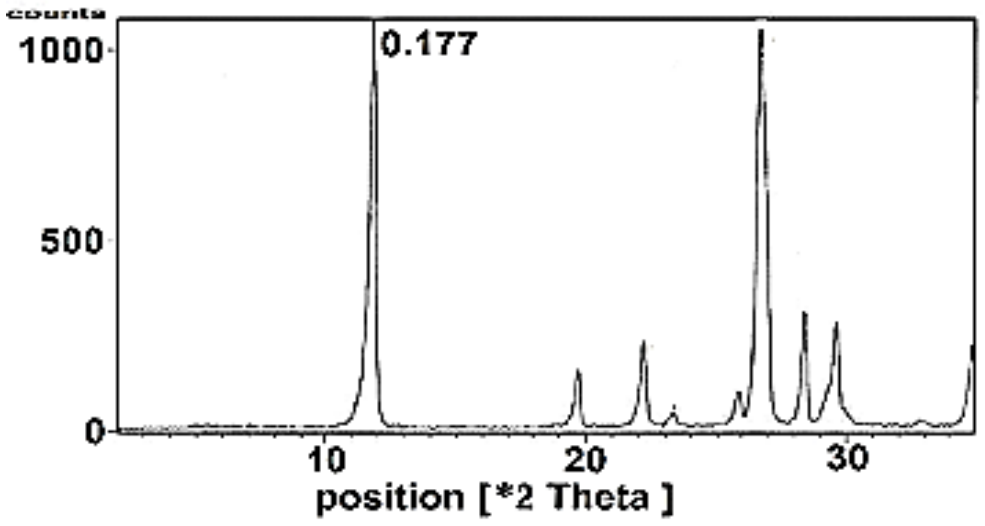


Figure 6: XRD half maximum of the peak

3.2.2. FT-IR of GeP

FT-IR spectra of (GeP),. Is shown in Figure 7 , found to follow same trend to that already reported[26].

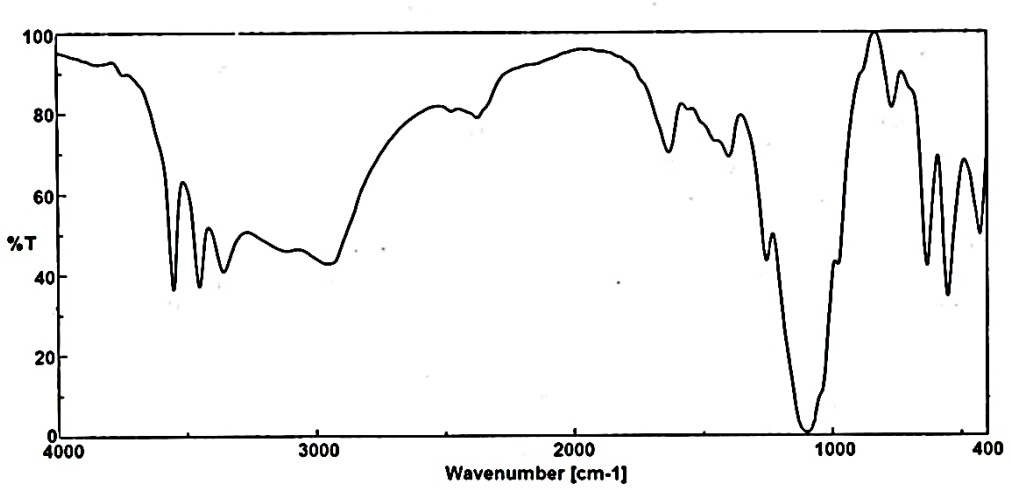


Figure 7: FT-IR of GeP

3.2.3. TGA of GeP

Thermal decomposition of α-Vanadyl phosphate is shown in Figure 8. found to follow same trend to that already reported[26].

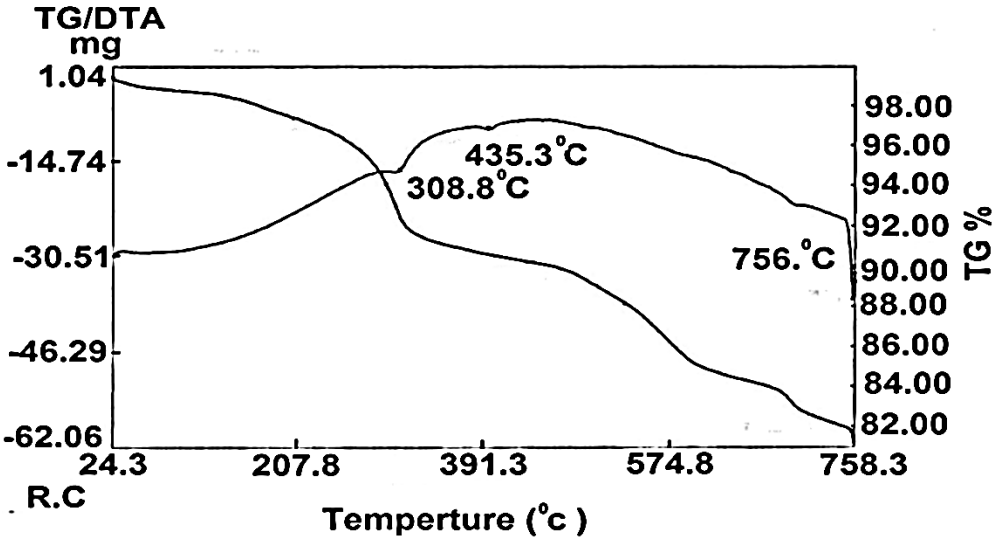


Figure 8: TG/DTA of GeP

3.2.4. SEM image of GeP

Figure 9 shows SEM (GeP/PVA) nanocomposite .Its average size ~ 39.5 nm[26].

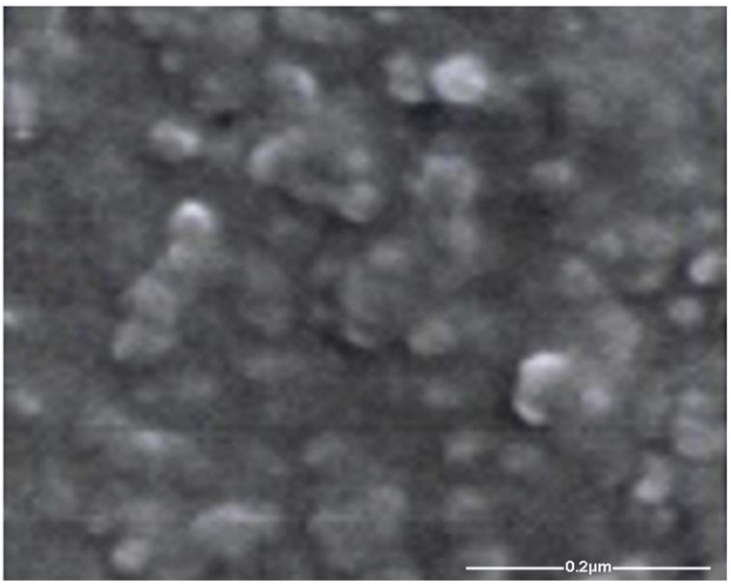


Figure 9: SEM morphology image of GeP

3.3. FT-IR of α-germanium phosphate-α-vanadyl phosphate/ polyaniline, polyindole, polyimidazole and polycarbazole composites

Figures (10-13), show FT-IR spectra of composites(GeP-VOP)/ conducting polymers.

Almost followed same trend .Are all consist of. Broad band in the range 3400 -2700cm^{-1} OH groups symmetric stretching of H_2O super imposed with the N–H stretching of aromatic amines.

Bands ranges about 2246-1948and atrange1800-1200cm^{-1} are related to C-H and C-C , an of C-H (aromatic) , C=C, C-N stretching bonding ,respectively. Band at around 1620 cm^{-1} represent H-O-H bending, and sharp bands at about 1077cm^{-1}, 958cm^{-1} can be related to phosphate groups (PO_4) vibration. of α-germanium and α-vanadyl phosphates,

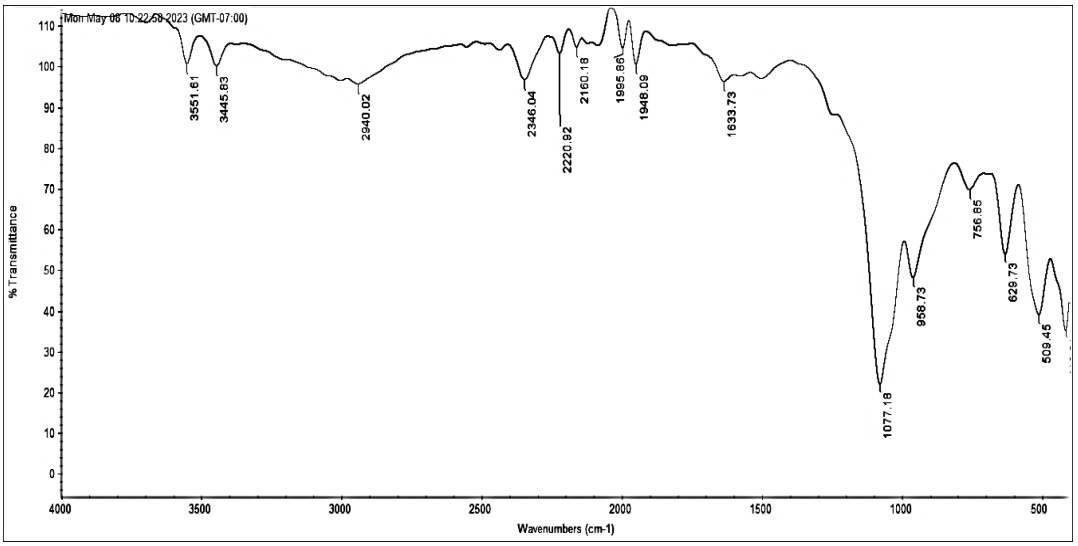


Figure 10: (GeP-VOP) / PAni , FT-IR.

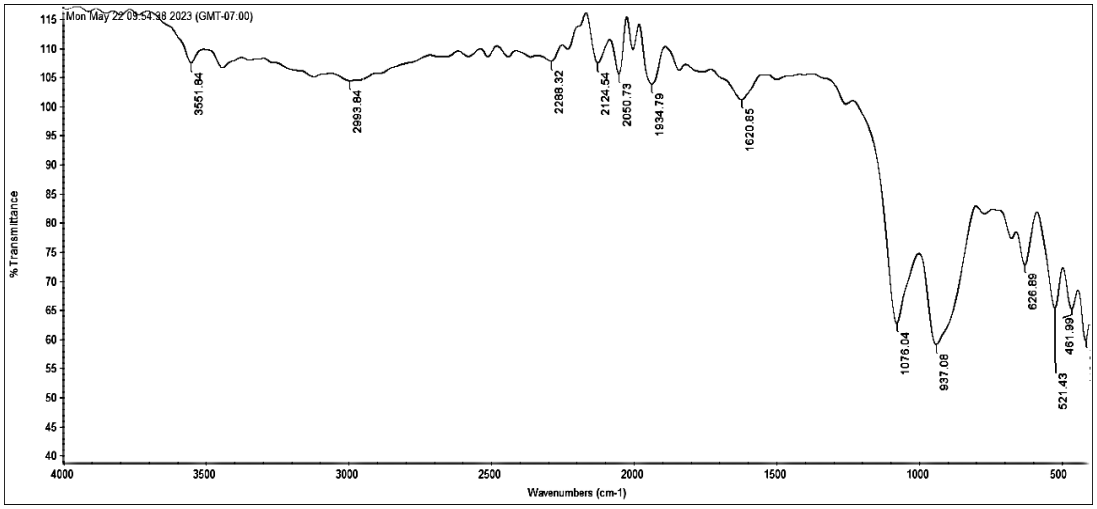
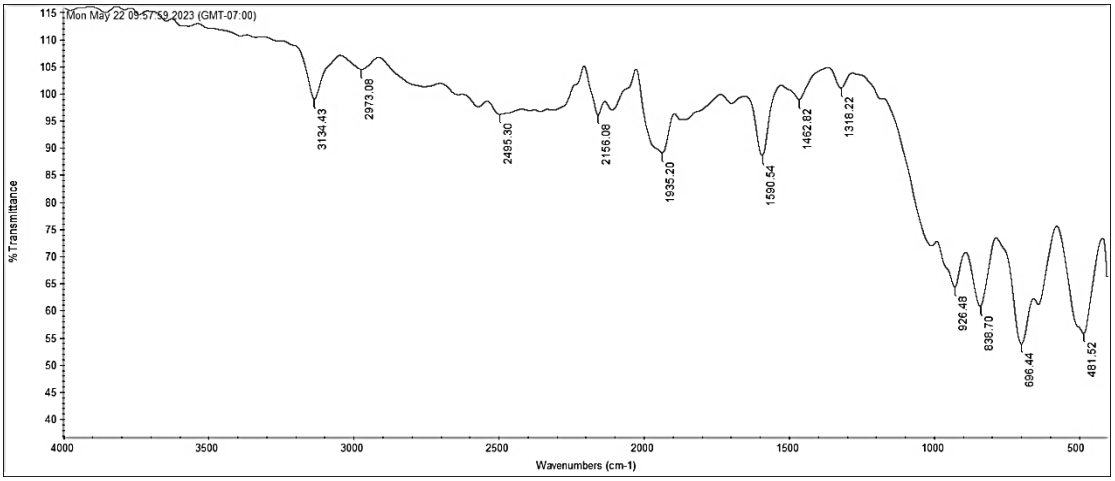
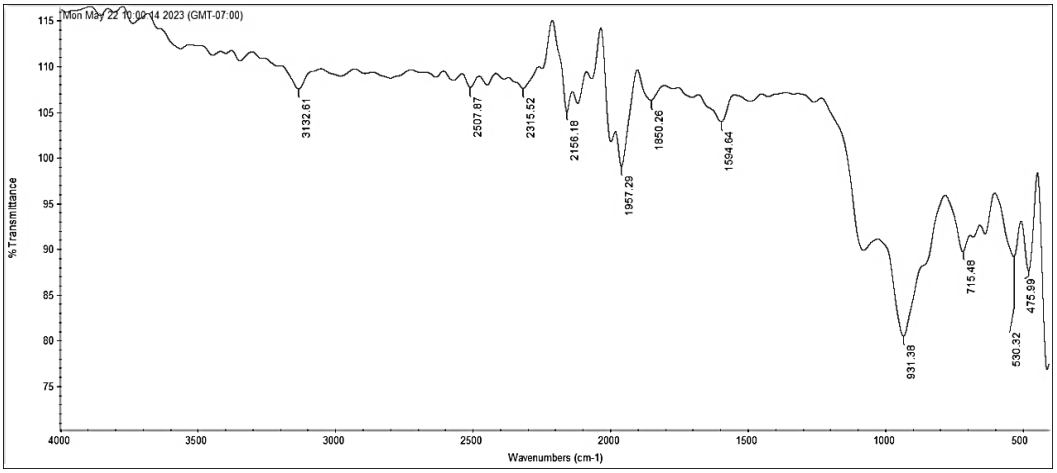


Figure 11: (GeP-VOP)/PIn , FT-IR.



ᵻFigure 12: (GeP-VOP)/ PIm , FT-IR.



{ᵻFigure 13: FT-IR Spectrum of (GeP-VOP)/PCz , FT-IR.

3.4. SEM of (GeP-VOP)/polyaniline, polyindole, polyimidazole and polycarbazole composites

Figures (14-17), represent SEM morphology images of (GeP-VOP)/polyaniline, polyindole, polyimidazole and polycarbazole composites, respectively. The polymers is disperse in the inorganic matrix

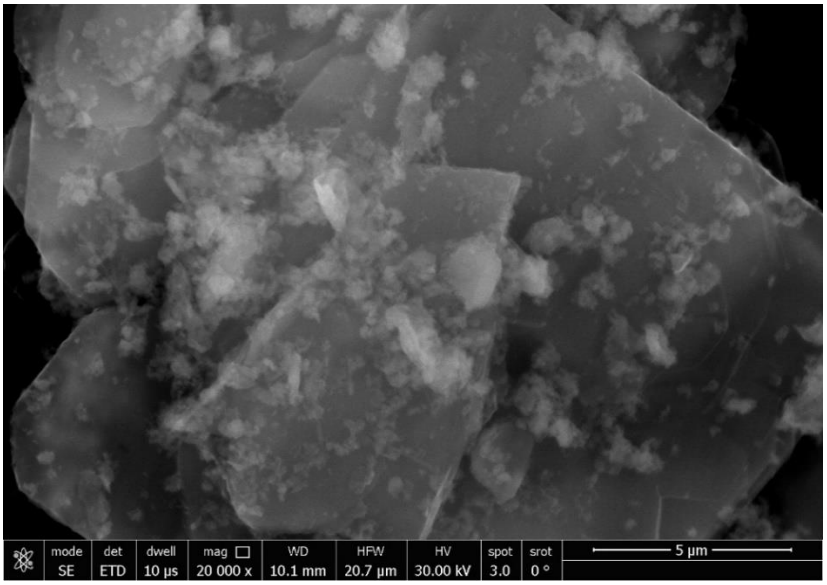


Figure 14: (GeP-VOP)/PAni composite, SEM.

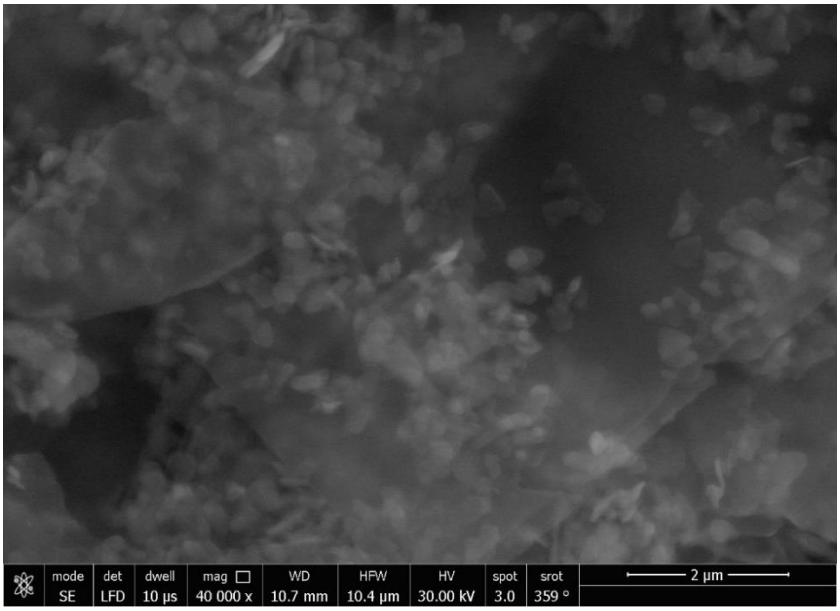
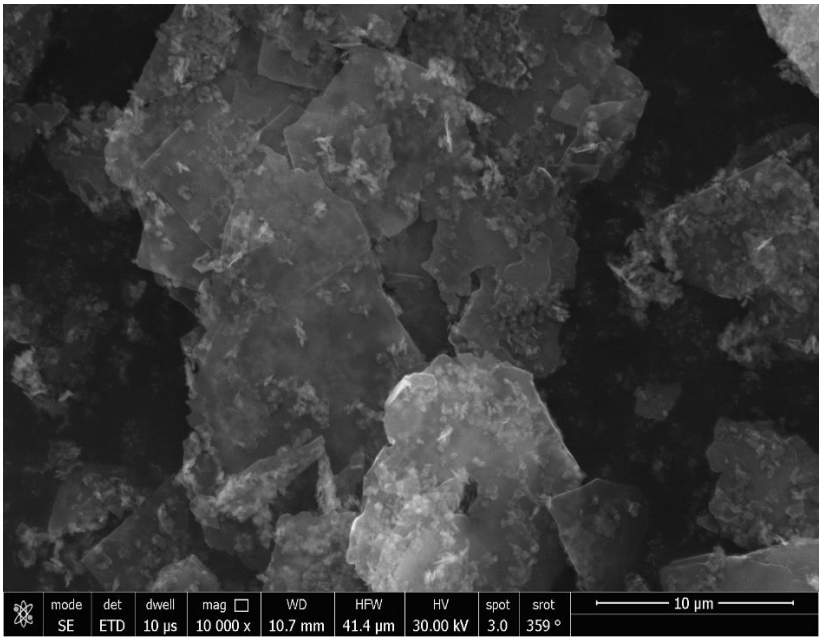
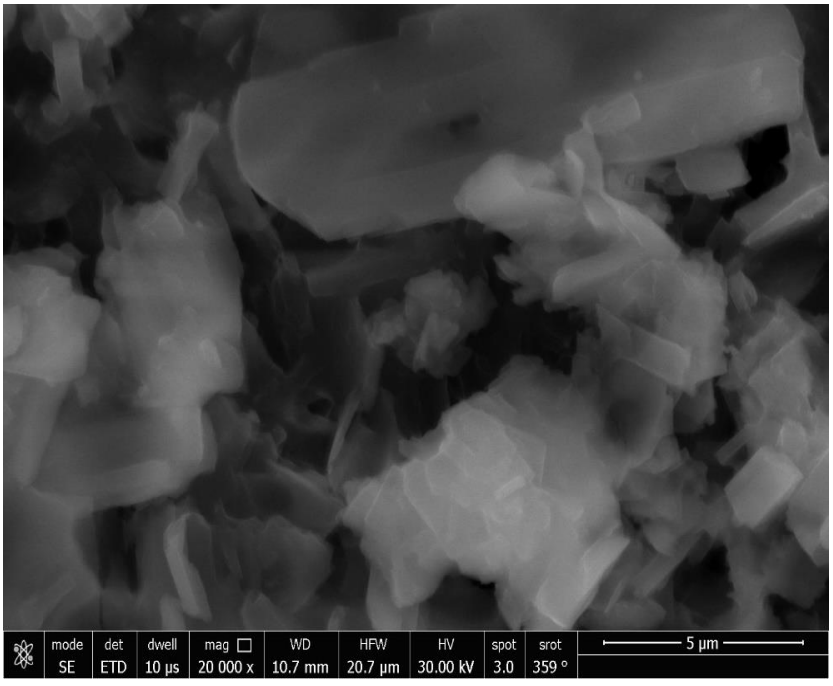


Figure 14: (GeP-VOP)/PIne composite .SEM.



Figures 16: of (GeP-VOP/PCz composite, SEM



Figures 17: (GeP-VOP)/ PCz compositel SEM.

3.8. UV-Vis Spectra o of (GeP-VOP)/polyaniline, polyindole, polyimidazole and polycarbazole composites[27].

3.8.1 UV-Vis Spectra of polyaniline

Figure 18, shows UV-Vis of extracted polyaniline by DMSO from polyaniline composite, shows absorption peaks at 234, 300 nm and broad peak at range 400 – 475 nm and broad peak at range 525 -575 nm are related to PAni , which indicate PAni was in the emeraldine salt form , corresponded to a π–π* transition in the benzenoid and it is also described to exciton formation in the quinoid rings [28]. That prove aniline has already been polymerized.

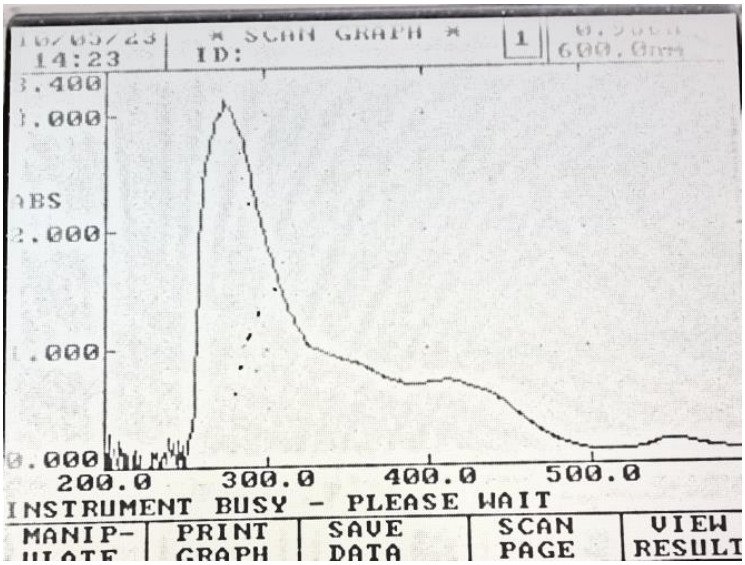


Figure 18: UV-Vis spectra of polyaniline

3.8.21 UV-Vis Spectra of polyindole

Figure 19, shows UV–vis spectra of extracted poly indole by DMSO of polyindole. from polyindole composite, UV-Vis spectra shows absorption peaks at 245, 300 nm, and broad peak commenced at 305 nm, to 350nm and small broad peak at 550 nm found to follow same trend of that reported in literature [29], that prove indole has already been polymerized.

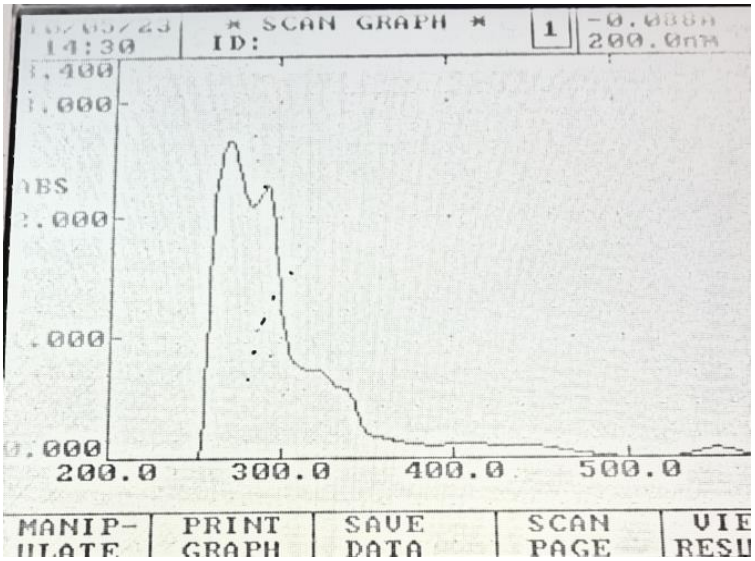


Figure 19: UV-Vis spectra of polyindole

3.8.3 UV-Vis Spectra of polyimidazole

Figure 20, shows UV–Vis spectra of extracted polyimidazole by DMSO, from polyimidazole composite. UV-Vis spectra shows absorption peak at 300 nm and small broad peak at about 400 nm also shows broad peak commenced at 525 nm to 570 nm, that prove imidazole has already been polymerized. Found to follow same trend of that reported in literature [30].

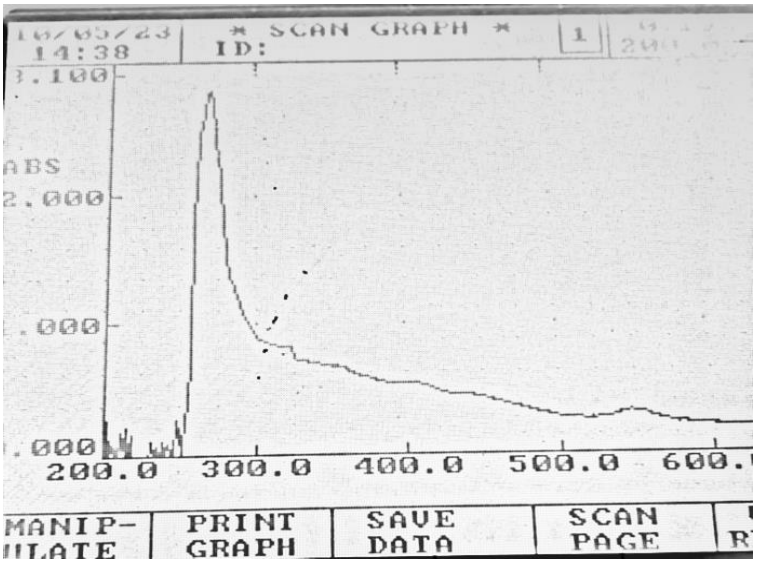


Figure20: UV-Vis spectra of polyimidazole

3.8.4. UV-Vis Spectra of polycarbazole]

Figure 21, shows UV–vis spectra of extracted polycarbazole by DMSO from polycarbazole composite. UV-Vis shows absorption peaks at 235, 300, 330 nm and broad

band commenced 425 nm. That prove carbazole has already been polymerized. Found to follow same trend of that reported in literature [31].

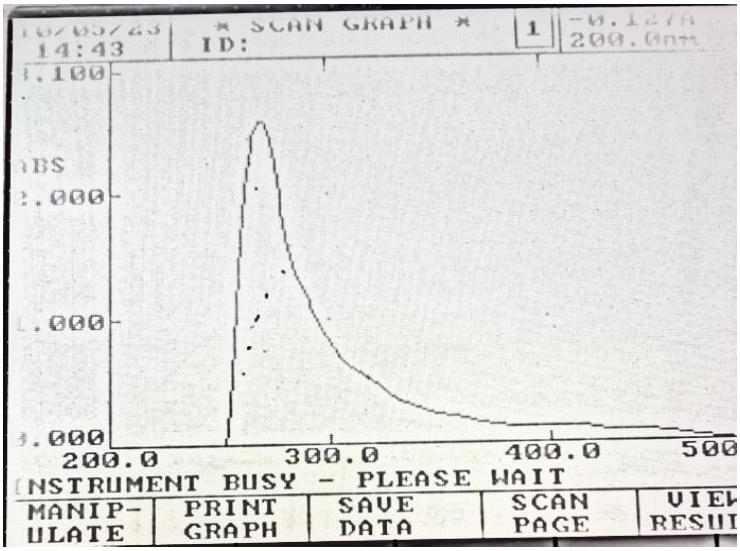


Figure 21: UV-Vis spectra of polycarbazole

3.9. Electrical conductivity of (GeP-VOP)/polyaniline, polyindole, polyim-idazole and polycarbazole composites

In this work the resultant DMSO extracted polyaniline, polyindole polyimidazole and poly carbazole from (GeP-VOP) composites were investigated for their electrical conductivity, shows the resultant composite in range of semi conductance.

Table 1, shows electrical conductivity of polyaniline, polyindole, polyimidazole and polycarbazole extracted by DMSO from their composites.

Table 1: Electrical conductivity of the polyaniline, polyindole, polyimidazole and polycarbazole

Extracted CPs	Conductivity (Scm^{-1})
Pani	~ 1.0×10^{-6}
PIn	~ 1.0×10^{-5}
PIm	6.9×10^{-6}
PCz	1.21×10^{-5}

Conclusion

α-$VOPO_4.2.5H_2O$(VOP), and α-germanium phosphate, α-$Ge(PO_4)_2 1.84H_2O$(GeP), were prepared and characterized. Composite$[GeP]_{0.25}[VOP]_{0.75}$ e was prepared and characterized. Novel $[GeP]]_{0.25}[VOP]_{0.75}$/PAni, PIn. , PIM and PCz, composites were

prepared and characterized.α-$V^{(v)}OPO_4.2.5H_2O$ act as self-support polymerization of the monomers($V^{(v)}$converted to $V^{(IV)}$). The protons (H^+) of (O_3POH) groups were act as self-doping

Color changes support the formation of the resultant novel conducting composites,. The electrical conductivity found to be in range of semiconductor.

Beneficial of these novel composites, are as novel ion exchangers and as sensors.

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