A Study of DSC and Raman Spectroscopy of Phosphate- Vanadate Semiconducting Oxide Glasses Containing BaO, MgO and CaO

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Abstract - *Glasses having compositions (50)% P_2O_5–(50-x)%BaO– (x)%V_2O_5, (50)% P_2O_5– (50-X)%CaO–(X)%V_2O_5, (50)% P_2O_5– (50-X)%MgO–(X)%V_2O_5 ,where (x=5,10,15 and 20 mol%) were prepared by the normal melt quenching technique. The thermal parameters, such as the glass transition temperature (Tg), The onset of crystallization temperature (Tc), thermal stability (S) and the thermodynamic fragility (F) we determined. It has been found that the glass transition temperature (Tg) for (P_2O_5-CaO-V_2O_5) and (P_2O_5-MgO-V_2O_5) increase with increasing (V_2O_5) content in the glass matrix but decreases with increasing (V_2O_5) in the glass (P_2O_5-BaO-V_2O_5). The Raman spectroscopy in the range (200-4200)cm^{-1} was used to prove the changes in the structure of the prepared glasses. Strong peak has shown in all glass samples in the range (420-440) cm^{-1} which may be due to symmetrical stretching or bending vibration.*

Keywords, *DSC, Glass transition temperature, Oxide Glasses, Raman spectroscopy, V_2O_5.*

I. INTRODUCTION

Phosphate glasses are both scientifically and technologically important materials because they generally offer unique physical properties which are better than those of other glasses such as high thermal expansion coefficient, low melting and softing temperatures, high electrical conductivity [1,2]. These glasses have a relatively poor chemical durability [3], which often limits their usefulness, but several studies have shown that the chemical durability of phosphate glasses can be improved by the addition of various oxides [4].

Raman spectra of phosphate glasses have been investigated by many researchers [5-8]. They showed that the structure of the phosphate glasses are mainly consisted by (PO_4) tetrahedral. The band at 900 and 525 cm^{-1} are related with asymmetric vibration of P-O-P bridges and bending vibration of P-O bonds, respectively [9].
Differential Scanning Calorimetry (DSC) for bismuth phosphate nanoparticles in glass matrix have been investigated by Eltabey, et al. [10]. They found that the glass transition temperature (Tg) increased with increasing

Bi_2O_3.
The purpose of this paper is to study the important thermal parameters of the prepared glasses as well as to investigate the Raman shifts of such glasses.

II. EXPREMENTAL WORK

The current glass systems had the chemical formula

(50)% P_2O_5– (50-x)%BaO–(x)%V_2O_5

(50)% P_2O_5– (50-x)%CaO–(x)%V_2O_5

(50)% P_2O_5– (50-x)%MgO–(x)%V_2O_5

with (x) equal to 5,10,15 and 20 mol% were prepared via melt quenching method. All the starting chemical constituents were more than 99.5% purity (sigma-Aldrich). The constituents were weighed in alumina crucible and melted at (1050-1100ºC) for 10 minutes then they stirred to obtain a homogeneously mixed melts and returned again to the furnace for 20 minutes. The Raman spectra of prepared samples in the range (200-4200cm^{-1}) using Raman laser (Lab-LS-532nm) with 100mW output power. were reported at the room temperature. The thermal characterization of the prepared glasses was obtained by using DSC (SDT Q600 V20.9 Build 20) to confirm the crystalline phase.

III. RESULTS AND DISCUSSION

A. Deferential Scanning Calorimetry (DSC)
a) Deferential Scanning Calorimetry (DSC) for (P_2O_5–BaO-V_2O_5)

Fig.1 presents DSC profile of the glass samples for the prepared glass series at heating rate 10ºC/min. The transition glass temperature (Tg), the onset crystallization temperature (Tc), the peak crystallization temperature (Tp), the thermal stability (S) and the thermodynamic fragility (F) were calculated and recorded for each glass sample in table (1). The values of (Tg) decreases from 270 to 240ºC as the V_2O_5 content increase from 5 to 20 mol% as shown in Fig.2.This decreasing is referred to the rigidity decreasing in the glass network due to the formation of ionic bonds by replacing the covalent bonds [11,12].The thermal stability (S) for glass samples have been evaluated by using the following equation [13]

$$S = \frac{(Tc-Tg)*(Tp-Tc)}{Tg} \quad \text{-----------(1)}$$

Where (Tg) represents the glass transition temperature, (Tc) crystallization temperature, (Tp) Crystallization peak temperature.

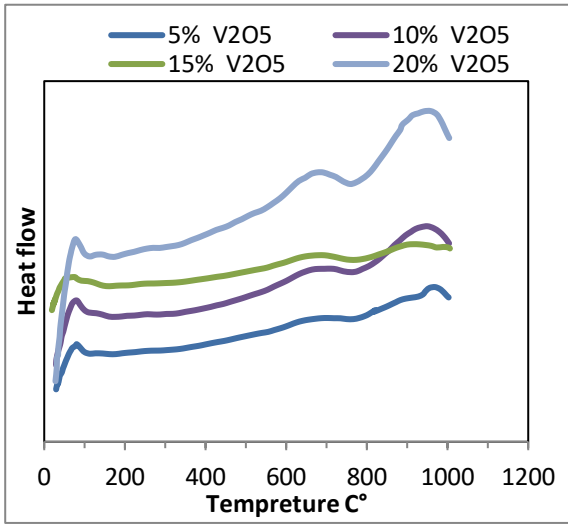**Fig.1: DSC curve of P_2O_5–BaO -V_2O_5 glasses**

Fig.3 shows that the value of (S) increase for 10mol% V_2O_5 and then decreases for 15 and 20 mol% V_2O_5. The thermodynamic fragility (F) can be calculated from relations [14]

$$F = \frac{0.151-X}{0.151+X} \quad \text{--------------(2)}$$

Where

$$X = \frac{\Delta Tg}{Tg} \quad \text{-------------(3)}$$

Fig.4 predicts the variation of fragility with V_2O_5 content in the glass samples as shown from table (1) that the thermodynamic fragility (F) increase with the increasing of V_2O_5 content in the glass samples up to 15 mol% V_2O_5 and then decreases for 20mol % V_2O_5. The difference between crystallization (Tc) and glass transition temperature (Tg) is equal to (ΔT) ($\Delta T=Tc-Tg$) have been calculated and tabulated in Table (1). As show from Fig.5 that the (ΔT) increases with increasing V_2O_5 in glass matrix. This indicates that the addition of V_2O_5 decreases (Tg) values and increases (ΔT) due to the creation of non-bridging oxygen's (NBO) which is a factor that defines the V_2O_5 as a modifier network oxide [15].
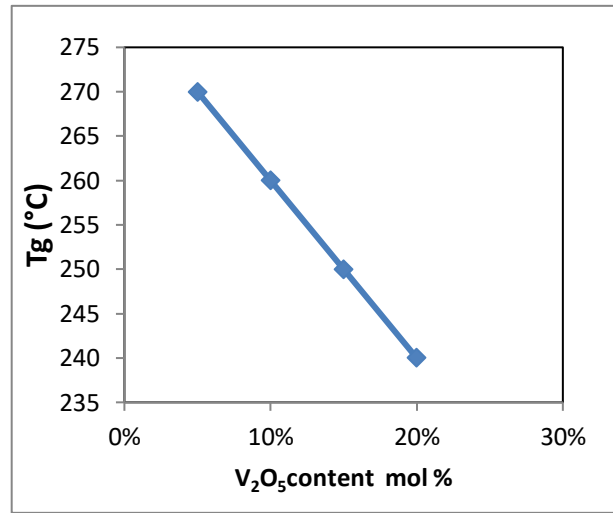

Fig.2: variation of glass transition tempreture (Tg) with V_2O_5 content in (P_2O_5–BaO-V_2O_5) glasses .

Table.1:values of glass transition temperature(Tg) Crystallization Temperature (Tc) ,and Melting temperature (Tm) and Fragility(F) as a function of V_2O_5 content in P_2O_5–BaO -V_2O_5 S/C glasses

V_2O_5 mol%	Tg (ºC)	Tc (ºC)	Tm (ºC)	Tp (ºC)	$\Delta T=Tc-Tg$ (ºC)	ΔTg (ºC)	S	E
5%	270	550	773	690	280	25	145.18	0.239
10%	260	555	783	795	295	20	158.84	0.325
15%	250	570	785	687	320	15	149.76	0.431
20%	240	585	779	680	345	20	136.56	0.288
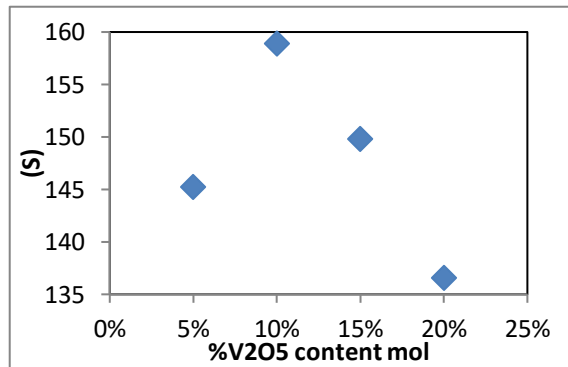
Fig.3:variation of thermal stability(S) with V_2O_5 content in(P_2O_5–BaO-V_2O_5) glasses.
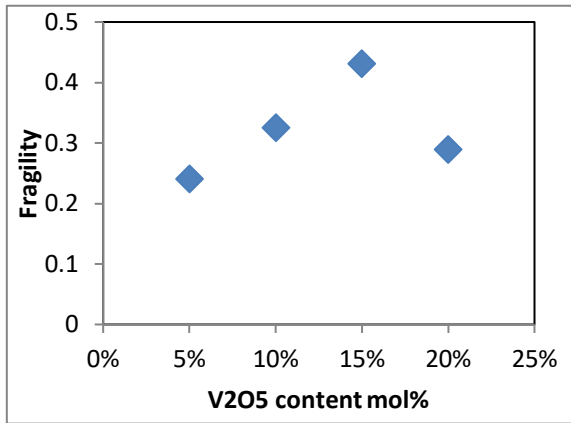
Fig.4:variation of Fragility(F) with V_2O_5 content in (P_2O_5–BaO-V_2O_5) glasses
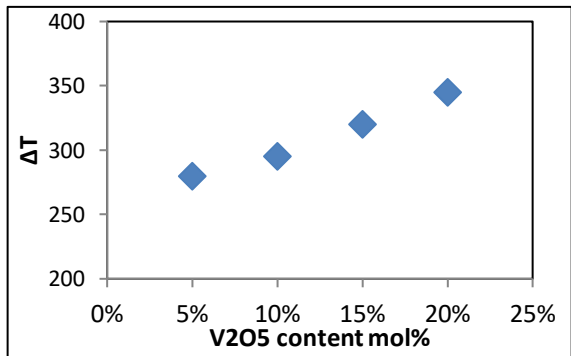
Fig.5:the variation of ΔT with V_2O_5 content in (P_2O_5–BaO-V_2O_5)glasses.

b) Deferential Scanning Calorimetry (DSC) for (P_2O_5–CaO-V_2O_5) glasses

The thermal behavior of (P_2O_5–BaO-V_2O_5) glass samples is presented by DSC curves and shown in Fig.6. The glass transition temperature (Tg), the crystallization (Tm) have been measured and recorded in Table (2). Generally, (Tg) can be used to indicate the rigidity of prepared glass samples[16]. As shown from Fig.7 that Tg increased from 255 to 268 ºC with addition V2O5 up to 15mol% then decreases to 246 ºC with the further addition of V_2O_5 due to change of coordination number of glass forming atoms[16]. Fig.8 shows that the thermal stability (S) increases from 109.4 to 141.9 with increasing V_2O_5 up to 15mol% and decreases to 122.2 with further increasing of V_2O_5 in the glass matrix. The thermodynamic fragility (F) was calculated according equation (2) and (3) and shown in Fig.9. As shown from table (2) that the thermodynamic fragility (F) is (0.316) for 5mol% V2O5 and decreases to (0.282) for 10mol% V_2O_5 then increases with increasing V2O5 content in the glass matrix up to 15mol%. This variation predicts that a structural changes in glass network took place [17].
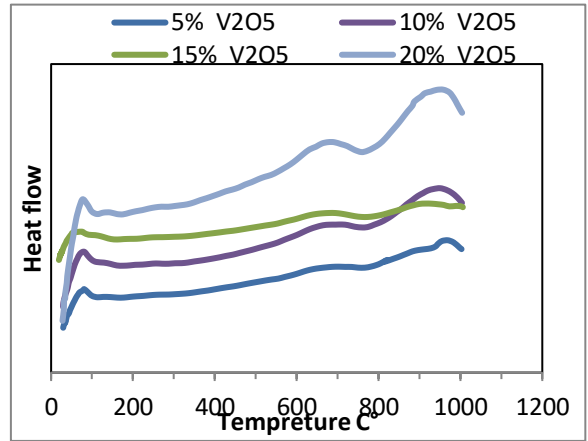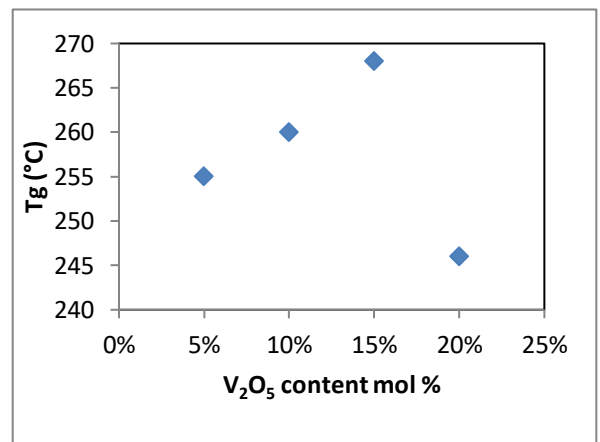

Fig.6: DSC curve of P_2O_5–CaO-V_2O_5 glasses

Fig.7: variation of glass transition tempreture(Tg) with V_2O_5content in (P_2O_5–CaO-V_2O_5)glasses.
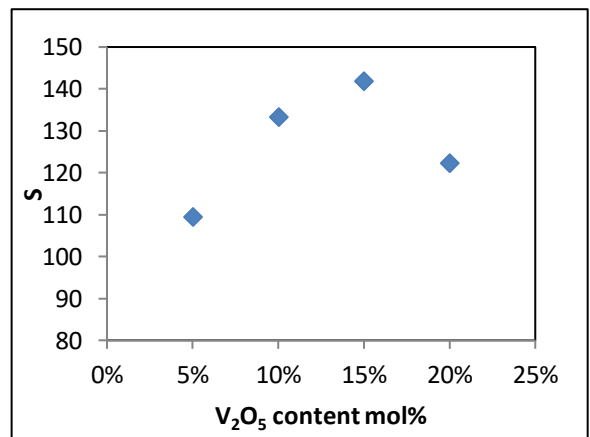
Fig.8:variation of thermal stability (S) with V_2O_5 content in (P_2O_5–CaO-V_2O_5) glasses.

Table.2:values of glass transition temperature(Tg) Crystallization Temperature (Tc) ,and Melting temperature (Tm) and Fragility as a function of V_2O_5 content in P_2O_5-V_2O_5–CaO S/C glasses.

V_2O_5 mol%	Tg (ºC)	Tc (ºC)	Tm (ºC)	Tp (ºC)	ΔT=Tc-Tg (ºC)	ΔTg (ºC)	Thermal stability(S)	Fragility (F)
5%	255	565	773	655	310	20	109.4	0.316
10%	260	575	783	685	315	22	133.3	0.282
15%	268	565	785	693	297	20	141.9	0.338
20%	246	580	779	670	334	20	122.2	0.3
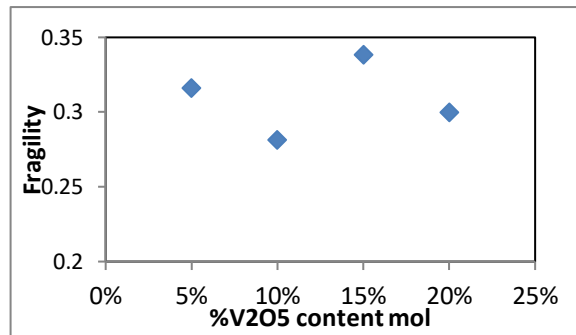
Fig.9:variation of Fragility(F) with V_2O_5 content in (P_2O_5–BaO-V_2O_5)glasses.

c) Deferential Scanning Calorimetry (DSC) for (P_2O_5– MgO-V_2O_5) glasses

Fig.10 shows the respective DSC curves within 20-1200 ºC temperature range for all fabricated samples. From these DSC patterns, the carefully identified Tg, Tc, Tm, and Tp values are listed in table (3). In general, the curves show abroad endothermic peak between 249 and 270 ºC which represents the glass transition temperature (Tg). The thermal parameters estimated from these curves are collected in table (3). Generally, Tg is very sensitive to variation in network forming atoms, in this case , P and Mg coordination number and non-bridging oxygen's bond strength [18].
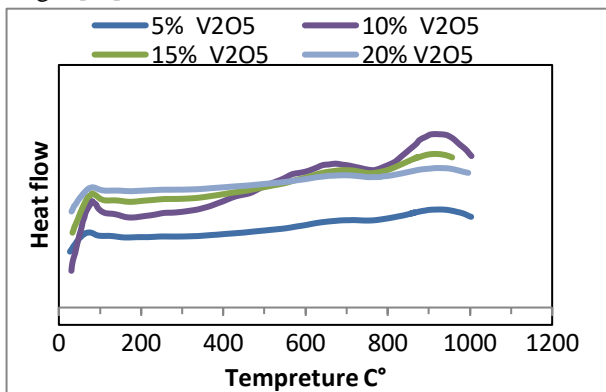
From Fig.11 and Table 3, can notice that the addition of V2O5 into the glass structure cause an increase of the Tg, indicating the glass network close-packed structure and rigidity increment, which is in an agreement with the glassy density data for (TeO2-Ag2O-WO3) glass system [17]. The variation of thermal stability (S) with V2O5 content in the glass network is shown in Fig.12.
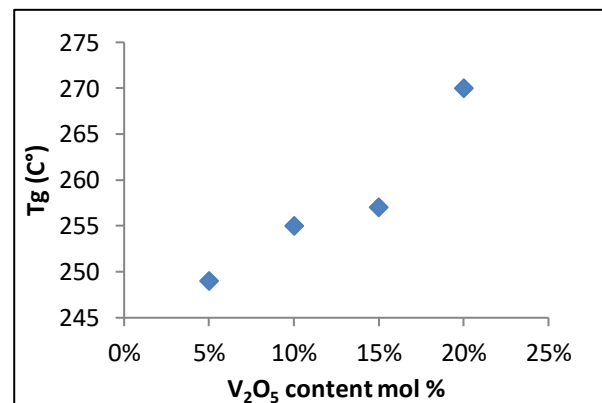

Fig.10: DSC curve of P_2O_5-V_2O_5–MgO glasses

Fig.11: variation of glass transition temperature Tg with increase V_2O_5 content

Table.3:values of glass transition temperature(Tg) Crystallization Temperature (Tc) ,and Melting temperature (Tm) and Fragility as afunction of V_2O_5 content in P_2O_5-V_2O_5–MgO S/C glasses

V_2O_5 mol%	Tg (C°)	Tc (C°)	Tm (C°)	Tp (C°)	ΔT=Tc-Tg (C°)	ΔTg (C°)	S	Fragility
5%	249	595	773	655	346	35	83.37	0.036
10%	255	600	783	647	345	25	63.59	0.213
15%	257	580	785	590	323	15	12.57	0.442
20%	270	575	779	651	305	20	85.85	0.342

As shown from Table (3) that the values of (S) decreases from 83.37 to 12.57 for 5mol% V_2O_5 and 15mol% V2O5 then with the addition of further V_2O_5 content in the glass matrix the value of (S) increasing abruptly to 85.85, which indicates a changes in structural of glass network.
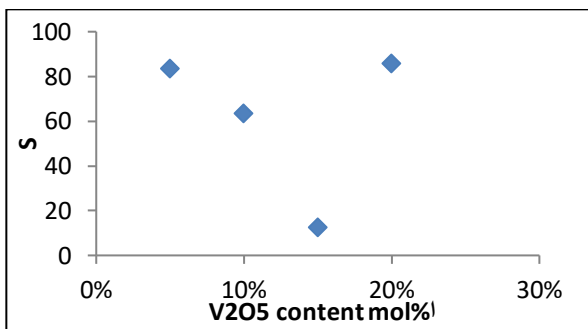

Fig.12:variation of thermal stability (S) with V_2O_5 content in (P_2O_5–MgO-V_2O_5) glasses.

The thermodynamic fragility (F) have been estimated and reported in Table 3 and drawn in Fig.13. The same variation between (F) and V_2O_5 content in the glass network was predict as a variation of (S) with the addition of V_2O_5 in the glass matrix.Thermodynamic fragility is found to increase with increasing V2O5 content for 5≤x≤15; this can be attributed to the glass network getting lossely packed with increasing of V2O5 content in this range. Such conclusion has been drawn in the case of (CaO-V2O5-TeO2) [19].
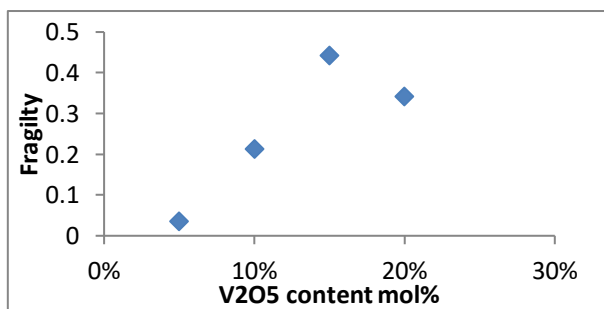

Fig.13:variation of Fragility (F) with V_2O_5 content in (P_2O_5–MgO-V_2O_5)glasses.

B. Raman Spectroscopy

Raman spectroscopy is used for determination of the structure, environment and dynamics of glassy materials. Raman bands arise from a change in the polarizability [20].

Phosphate network is formed by various structural units of phosphate . The phosphate glasses are formed at low temperature in comparison to silicate glasses are formed at low temperature in comparison to silicate glasses. The vibrational units of phosphate networks are Q_p^n groups of PO_4 tetrahedra (n= number of bridging oxygen per PO_4 tetrahedron), symmetric stretching of P-O, asymmetric stretching vibration of P-O, P-O-P symmetric vibrations, bending vibrations of phosphate polyhedral and O-P-O bending modes [21].The phosphate glasses are much sensitive in ionizing particles. This property of phosphate glasses enables the use for identification of heavy ions [22].The phosphate networks are shown in Fg.14 [23]

Fig.14: Network units of phosphate glasses [23].
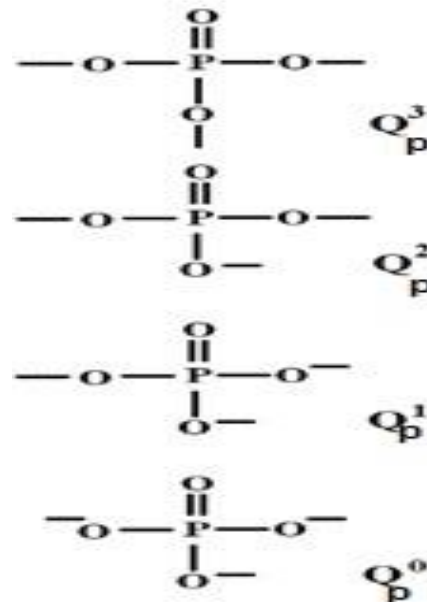
a) Raman Spectroscopy for (P_2O_5-BaO-V_2O_5) glasses

The typical Raman Spectra of (P_2O_5-BaO-V_2O_5) glasses are shown in Fig.15. The glass system have bands near 250-265, 415-425, 675-690, 1105-1120 and 1700-1740

cm^{-1}. The band in range 1105-1120 cm^{-1} is assigned due to symmetric stretching vibrations of PO$_3$ groups [24]. The band at 415-425 cm^{-1} is related to bending vibrations of P-O bonds [9]. The vibration due to PO$_2$ bending and in chains of O-P-O bending motions is assigned at 250-265 cm^{-1} respectively [25]. The presence of band at 675-690 cm^{-1} is attributed to V-O-V vibration [26]. Finally the band at 1700-1740cm^{-1} is due to stretching vibration of P=O bond [26].All bands are listed in Table (4).
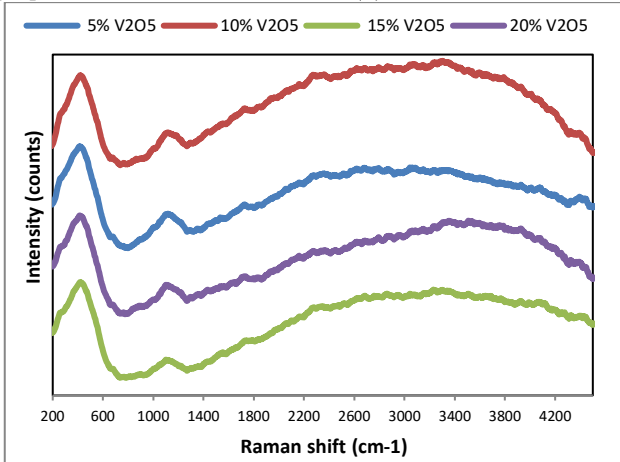

Fig.15: Raman spectra of (P₂O₅-V₂O₅–BaO) glasses.

Table.4: Band positions in P₂O₅-V₂O₅–BaO glasses

V$_2$O$_5$ mol % content	Band position (cm-1)				
5%	265	420	690	1120	1725
10%	255	425	675	1105	1700
15%	250	415	685	1100	1730
20%	260	420	680	1110	1740

b) Raman Spectroscopy for (P₂O₅-CaO-V₂O₅) glasses

Raman spectra for all studied glasses are shown in Fig.16 and were employed for more investigation of the glass structural units. Table (5) predicts all the bands of such glasses. The analysis of these bands leads to following points:

1. The peak identified at 250-260 cm^{-1} are attributed to heavy metal oxygen (P-O, V-O) vibrational modes, stretching vibrational of P-O-V linkage [18]. The peaks at 410-425 cm^{-1} could be assigned to symmetric bending vibration of P-O-P and O-P-O linkages in PO4 and vibration of V-O bonds of VO4 groups [27].
2. Bands identified at 680- 690 cm^{-1} could be belong to bending vibration of P-O and P-O-P linkages [28].
3. The spectral peaks at 1100-1130 cm^{-1} are due to P-O stretching vibration bonds of PO$_3$ [28].
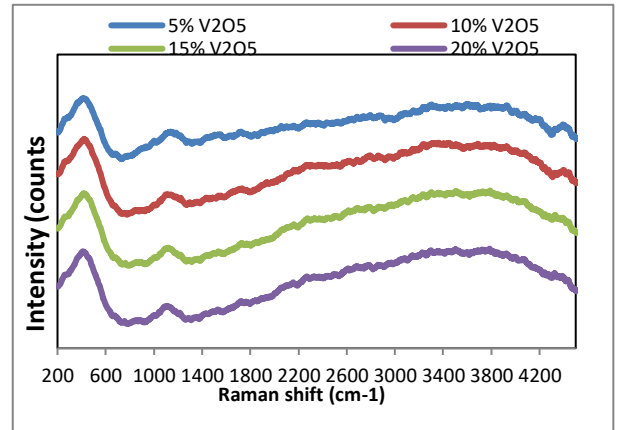4. The bands identified at 1710-1735 cm^{-1}could be assigned to P=O stretching of terminal oxygen [9].

Fig.16: Raman spectra of (P₂O₅-V₂O₅–CaO) glasses.

Table. 5: Band positions in P₂O₅-V₂O₅–CaO glasses

V$_2$O$_5$ mol % content	Band position (cm-1)				
5%	250	415	690	1130	1720
10%	255	425	680	1100	1735
15%	260	420	690	1125	1720
20%	255	410	680	1120	1710

c) Raman Spectroscopy for (P₂O₅_MgO_V₂O₅) glasses

Raman spectra for (P₂O₅_MgO_V₂O₅) glasses of different compositions are shown in Fig.17. Raman spectra of such glass samples have bands near 230_240 cm^{-1}, 415-440 cm^{-1}, 675-690 cm^{-1}, 1090-1100 cm^{-1}, and 1715-1740 cm^{-1} as shown in Table (6). The band at 230_240 cm^{-1} is due to the bending vibration of V-O-V in the VO$_4$ units [29]. The presence of Raman band in the rang at 675-690 cm^{-1} has been attributed to pentophosphate groups in the phosphate glasses. The Raman bands in the high frequency range 1715_1740 cm^{-1} has been assigned to stretching of P-O bonds attached to large number of phosphate groups [30]. The Raman band in the range 415-440 cm^{-1} is assigned to in plane-bending mode of PO$_3^{3-}$ units [31]. The Raman band in the range 1090-1100 cm^{-1} is assigned to V-O single bond stretching vibrations within V-O-V bonded units [32].
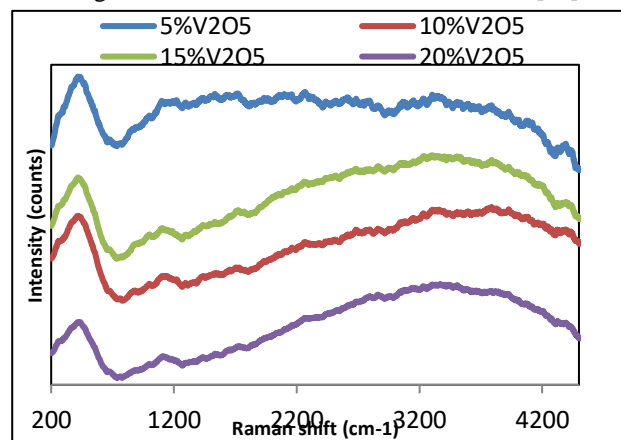

Fig.17: Raman spectra of (P₂O₅-V₂O₅–MgO) glasses.

Table.6: Band positions in P_2O_5-V_2O_5–BaO glasses

V_2O_5 mol %	Band position (cm-1)				
5%	240	420	675	1090	1730
10%	230	420	690	1100	1740
15%	235	415	685	1100	1715
20%	230	440	680	1100	1720

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