

A Study of Infrared Spectra of Some Semiconducting Oxide Glasses

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ABSTRACT

Glass samples in the systems of $(P_2O_5)_{75}-(CuO)_{25-x}-(CdO)_x$, $(P_2O_5)_{75}-(CuO)_{25-x}-(ZnO)_x$, $(P_2O_5)_{75}-(CuO)_{25-x}-(V_2O_5)_x$, $(P_2O_5)_{50}-(TeO_2)_{50-x}-(ZnO)_x$, $(P_2O_5)_{50}-(TeO_2)_{50-x}-(CdO)_x$ and $(P_2O_5)_{50}-(TeO_2)_{50-x}-(V_2O_5)_x$ of different compositions where $(x=0,5,10,15, 20)$ were prepared by the melt-quenching technique.

Density measurements of $(P_2O_5)_{75}-(CuO)_{25-x}-(CdO)_x$, $(P_2O_5)_{75}-(CuO)_{25-x}-(ZnO)_x$ and $(P_2O_5)_{50}-(TeO_2)_{50-x}-(CdO)_x$ show decreasing in density with the increasing of CdO and ZnO contents. The density of $(P_2O_5)_{75}-(CuO)_{25-x}-(V_2O_5)_x$, $(P_2O_5)_{50}-(TeO_2)_{50-x}-(ZnO)_x$ and $(P_2O_5)_{50}-(TeO_2)_{50-x}-(V_2O_5)_x$ glasses show increasing in density with the increasing of V_2O_5 and ZnO contents in the glass. The infra-red spectra were recorded for $(P_2O_5)_{75}-(CuO)_{25-x}-(CdO)_x$, $(P_2O_5)_{75}-(CuO)_{25-x}-(ZnO)_x$ and $(P_2O_5)_{75}-(CuO)_{25-x}-(V_2O_5)_x$. The band positions of such glasses show that $(475.27-503.15) \text{ cm}^{-1}$ can be attributed to $(PO_4)^{3-}$. The infra-red spectra of $(P_2O_5)_{50}-(TeO_2)_{50-x}-(CdO)_x$, $(P_2O_5)_{50}-(TeO_2)_{50-x}-(ZnO)_x$ and $(P_2O_5)_{50}-(TeO_2)_{50-x}-(V_2O_5)_x$ were recorded in the range $(4000-400) \text{ cm}^{-1}$. The band positions of such glasses shown that $(494.83-498.77) \text{ cm}^{-1}$ can be attributed to Te-O-Te linkages

Keywords: infrared spectra , density, semiconducting oxide glass .

دراسة اطياف اشعة تحت الحمراء لبعض الزجاجيات الشبه الموصلة

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الملخص

حضرت مجموعتين من زجاجيات الاكاسيد وبتراكيز مختلفة للمركبات الاتية :

$(P_2O_5)_{75}-(CuO)_{25-x}-(CdO)_x, (P_2O_5)_{75}-(CuO)_{25-x}-(ZnO)_x, (P_2O_5)_{75}-(CuO)_{25-x}-(V_2O_5)_x,$
 $(P_2O_5)_{50}-(TeO_2)_{50-x}-(ZnO)_x, (P_2O_5)_{50}-(TeO_2)_{50-x}-(CdO)_x$ and $(P_2O_5)_{50}-(TeO_2)_{50-x}-(V_2O_5)_x$

تم قياس كثافة الزجاجيات $(P_2O_5)_{75}-(CuO)_{25-x}-(CdO)_x, (P_2O_5)_{75}-(CuO)_{25-x}-(ZnO)_x, (P_2O_5)_{50}-(TeO_2)_{50-x}-(CdO)_x$ ووجد بان هناك نقصان في الكثافة مع زيادة كمية CdO, ZnO في الزجاجيات. اما بالنسبة للزجاجيات $(P_2O_5)_{75}-(CuO)_{25-x}-(V_2O_5)_x, (P_2O_5)_{50}-(TeO_2)_{50-x}-(ZnO)_x, (P_2O_5)_{50}-(TeO_2)_{50-x}-(V_2O_5)_x$ فقد وجد زيادة في الكثافة مع زيادة كمية V_2O_5, ZnO في الزجاجيات .

كما وتم قياس اطياف الاشعة تحت الحمراء للزجاجيات $(P_2O_5)_{75}-(CuO)_{25-x}-(CdO)_x, (P_2O_5)_{75}-(CuO)_{25-x}-(ZnO)_x, (P_2O_5)_{75}-(CuO)_{25-x}-(V_2O_5)_x$ وقد وجد ان موقع حزمة الامتصاص

عند $cm^{-1} (475.27-503.15)$ تعزى الى $(PO_4)^{3-}$

اما بالنسبة لمجموعة الثانية زجاجيات التيلورايت $(P_2O_5)_{50-x}-(TeO_2)_{50-x}-(ZnO)_x$ ، $(P_2O_5)_{50-x}-(TeO_2)_{50-x}$

$(CdO)_x$ ، $(P_2O_5)_{50-x}-(TeO_2)_{50-x}-(V_2O_5)_x$ قد وجد ان موقع حزمة الامتصاص عند $(494.83-498.77) \text{ cm}^{-1}$

متغير الى $Te-O-Te$

الكلمات الدالة : اطياف الاشعة تحت الحمراء. الكثافة. الشبه الموصلة .

1. INTRODUCTION

The infrared region of the spectrum extends from the visible unit and overlaps the microwave of short wave radar range. Infrared spectra of zinc doped lead borate glasses have been studied by Motke et al [1] Structural and physical properties of $Fe_2O_3-B_2O_3-V_2O_5$ glasses were studied by Kundu et al [2]. Tellurium oxide (TeO_2) based glasses are of scientific and technological interest on account of their unique properties such as chemical durability, electrical conductivity, transmission capability, high dielectric constant, high refractive indices, good infrared transmission and low melting points [3,4]. Tellurium oxide (TeO_2) is a conditional glass former [4] and forms glass only with a modifier such as alkali, alkaline earth and transitional metal oxides or other glass formers. In binary tellurite glasses, the basic structural unit of TeO_4 is a trigonal bipyramid (tbp) with lone pair of electrons [5]. Nassar and et al [6] studying effect of MO (CuO , ZnO , and CdO) on the compaction of sodium meta phosphate sealing glass. Yajun and et al [7] studying of structures and properties of $ZnO-Sb_2O_3-P_2O_5-Na_2O$ glasses. Khamirul and et al [8] studying the effect of ZnO on physical and elastic properties of $(ZnO)_x(P_2O_5)_{1-x}$ glasses using nondestructive ultrasonic method .

The objective this Research is to studying the infrared (IR) and density of $P_2O_5-CuO-CdO$, $P_2O_5-CuO-ZnO$, $P_2O_5-CuO-V_2O_5$, $P_2O_5-TeO_2-CdO$, $P_2O_5-TeO_2-ZnO$ and $P_2O_5-TeO_2-V_2O_5$

2. Experimental Procedure

For the present study, Six groups of $(P_2O_5)_{75}-(CuO)_{25-x}-(CdO)_x$, $(P_2O_5)_{75}-(CuO)_{25-x}-(ZnO)_x$, $(P_2O_5)_{75}-(CuO)_{25-x}-(V_2O_5)_x$, $(P_2O_5)_{50}-(TeO_2)_{50-x}-(CdO)_x$, $(P_2O_5)_{50}-(TeO_2)_{50-x}-(ZnO)_x$ and $(P_2O_5)_{50}-(TeO_2)_{50-x}-(V_2O_5)_x$ glasses of different compositions ($x=0,5,10,15, 20$) were prepared. The melting temperature used for $(P_2O_5)_{75}-(CuO)_{25-x}-(CdO)_x$ glasses was (950-

1000) °C, (P₂O₅)₇₅-(CuO)_{25-x}-(ZnO) glasses was (1000-1050) °C, (P₂O₅)₇₅-(CuO)_{25-x}-(V₂O₅)_x glasses was (1000-1100) °C, (P₂O₅)₅₀-(TeO₂)_{50-x}-(CdO)_x glasses was (900-950) °C, (P₂O₅)₅₀-(TeO₂)_{50-x}-(ZnO)_x glasses was (850-900) °C, (P₂O₅)₅₀-(TeO₂)_{50-x}-(V₂O₅)_x glasses was (950-1000) °C. All the series of glasses were annealed at 200 °C to relieve mechanical stresses of glasses and minimize cracking. The infra-red spectra were recorded for samples of all series of glasses in the range of 400-4000cm⁻¹ at room temperature in a Perkin–Elmer spectrophotometer. Selected glass samples were ground in a clean mortar into a fine powder and then a few milligrams of glass powder was mixed with a relatively large quantity of KBr. The KBr pellet were made by pressing the mixture at 12 tons for a few minutes under vacuum.

3. Results and discussion

The density can be calculated by using the following formula

$$\rho_G = \rho_L W_a / (W_a - W_L) \quad \dots\dots\dots(1)$$

Where W_a and W_L represent the weight of sample in air and in the liquid respectively. ρ_L is the relative density of the immersion liquid. The density of (P₂O₅)₇₅-(CuO)_{25-x}-(CdO)_x, (P₂O₅)₇₅-(CuO)_{25-x}-(ZnO)_x and (P₂O₅)₅₀-(TeO₂)_{50-x}-(CdO)_x glasses was decreasing with the increasing of TMI contents in the glass as shown in Table (1). Figures (1),(3) shows the decreasing of density with the increasing of CdO and ZnO contents. The decrease in density may be due to a change in the structure caused by the increase of the inter-atomic spacing and hence resulting in a few compact and less dense glasses which means that a structural rearrangement in such glass lattice took place. The density of (P₂O₅)₇₅-(CuO)_{25-x}-(V₂O₅)_x, (P₂O₅)₅₀-(TeO₂)_{50-x}-(ZnO)_x and (P₂O₅)₅₀-(TeO₂)_{50-x}-(V₂O₅)_x glass shown in Table (2). Figures (4),(6) shows that there is a definite increasing in density with the increasing of V₂O₅ and ZnO contents. The increase in density may be due to a change in the structure caused by the decrease of the inter-atomic spacing and hence resulting in a more compact and dense glass which means that a structural rearrangement in such glass lattice took place.

Table (1): Decreasing density measurements of (P₂O₅)- TMI glass

(P ₂ O ₅)-(CuO)-(CdO)				(P ₂ O ₅)-(CuO)-(ZnO) (CdO)				(P ₂ O ₅)-(TeO ₂)-			
P ₂ O ₅ %	CuO %	CdO %	ρ _G	P ₂ O ₅ %	CuO %	ZnO %	ρ _G	P ₂ O ₅ %	TeO ₂ %	CdO %	ρ _G
75	25	0	1.317 2	75	25	0	1.3172	50	50	0	1.041 7
75	15	10	1.11	75	20	5	1.26	50	40	10	1.032
75	10	15	1	75	15	10	1.2075	50	35	15	1.027 5
75	5	20	0.88	75	10	15	1.155	50	30	20	1.023
				75	5	20	1.1069				

Table (2): Increasing density measurements of (P₂O₅)-TMI glass

(P ₂ O ₅)-(CuO)-(V ₂ O ₅)				(P ₂ O ₅)-(TeO ₂)-(ZnO)				(P ₂ O ₅)-(TeO ₂)-(V ₂ O ₅)			
P ₂ O ₅ %	CuO %	V ₂ O ₅ %	ρ _G	P ₂ O ₅ %	TeO ₂ %	ZnO %	ρ _G	P ₂ O ₅ %	TeO ₂ %	ZnO %	ρ _G
75	25	0	1.317 2	50	50	0	1.041 7	50	50	0	1.041 7
75	20	5	1.9	50	45	5	1.09	50	45	5	1.05
75	15	10	2.503 5	50	40	10	1.135	50	40	10	1.16
				50	35	15	1.18	50	30	20	1.202
				50	30	20	1.23				

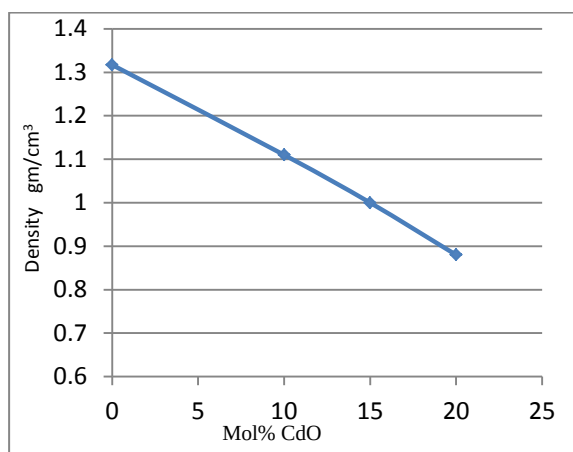


Fig. (1): density variation with the content (CdO) for $(P_2O_5)(CuO)-(CdO)$

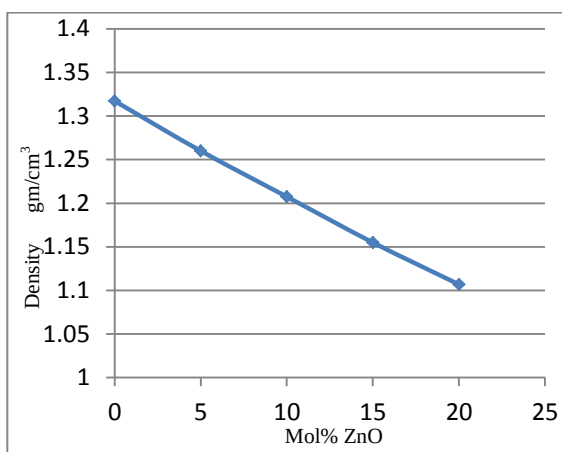


Fig. (2): density variation with the content (ZnO) for $(P_2O_5)-(CuO)-(ZnO)$

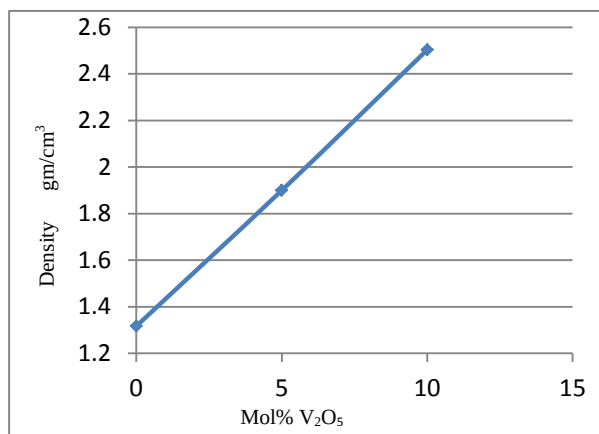


Fig. (4): density variation with the content (V_2O_5) for $(P_2O_5)-(CuO)-(V_2O_5)$

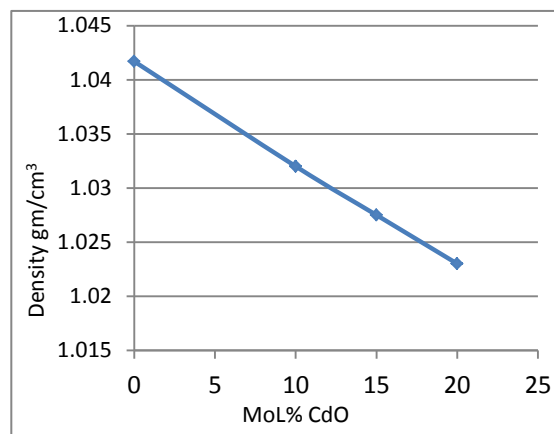


Fig. (3): density variation with the content (CdO) for $(P_2O_5)-(TeO_2)-(CdO)$

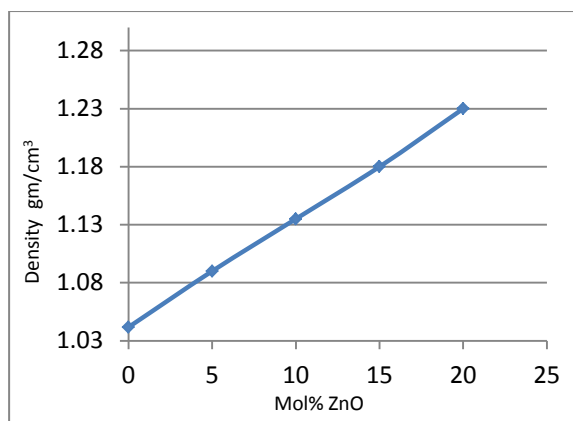


Fig. (5): density variation with the content (ZnO) for $(P_2O_5)-(TeO_2)-(ZnO)$

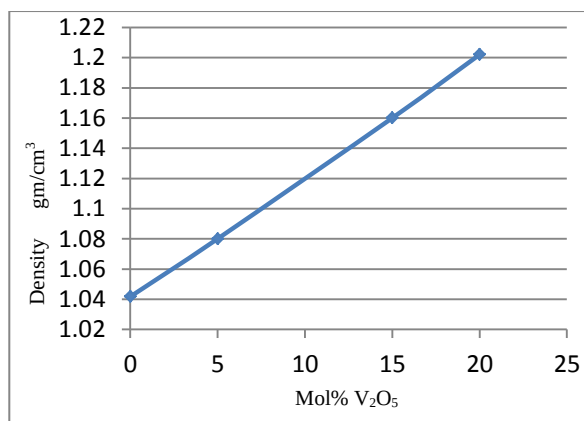


Fig. (6): density variation with the content (V_2O_5) for $(P_2O_5)-(V_2O_5)$

Infra-red spectra for $(P_2O_5)_{75}-(CuO)_{25-x}-(CdO)_x$ glasses of different compositions ($x=0, 5, 10, 15, 20$) are shown in Fig.(7) and the band positions of P_2O_5 -CuO-CdO have been tabulated in Table (3). The absorption band at $(475.27-503.15) \text{ cm}^{-1}$, which appear in this compound corresponds to the glass absorption band at 500 cm^{-1} of the (P_2O_5) and knowledge at the main frequency group $(PO_4)^{-3}$ [9] . The absorption band observed at $(748.89 - 751.93) \text{ cm}^{-1}$ would seem to be attribute to the P-O-P ring frequency, which is in close agreement with other results [10] and the strong broad band at $(905-955.5) \text{ cm}^{-1}$ are assigned to P-O stretching in phosphate[11] . Infra-red spectra for $(P_2O_5)_{75}-(CuO)_{25-x}-(ZnO)_x$ glasses of different compositions ($x= 5, 10, 15, 20$) are shown in Fig.(8) and the band positions of P_2O_5 -CuO-ZnO have been tabulated in Table (4) .The absorption band position in $(739.65-780) \text{ cm}^{-1}$ a symmetric vibration due the P-O-P chains [12] . The absorption band at $(494.96-502.57) \text{ cm}^{-1}$, is due to the $(PO_4)^{-3}$, ν^3 -normal tetrahedral ion also, IR investigations showed that the phosphate tetrahedral unit, PO_4 ,dominate the structure of the glasses which contain metal oxide[13]. The band position at $(1150-1170) \text{ cm}^{-1}$ is associated with the formation of covalent P–O–Zn linkages, which give rise to an increase of connectivity and the cross-linking of the network linkages [14,15]. The absorption band position at $(993.39-999.40) \text{ cm}^{-1}$ could be due to the P-O stretching frequency [16].Infra-red spectra for $(P_2O_5)_{75}-(CuO)_{25-x}-(V_2O_5)_x$ glasses of different compositions ($x=5,10, 15$) are shown in Fig.(9). and the band positions of P_2O_5 -CuO- V_2O_5 have been tabulated in Table (5). The absorption band positions at 475.07 cm^{-1} to 499.16 cm^{-1} is due to the $(PO_4)^{-3}$ which observed in the high frequency region and shifts to lower wave number with the increase of V_2O_5 [17]. The presence of P-O band at $(914.93-918.77) \text{ cm}^{-1}$ may be identified as the characteristic of vanadium pyrophosphate[17] . Infra-red spectra for $(P_2O_5)_{50}-(TeO_2)_{50-x}-(CdO)_x$ glasses of different compositions ($x=10, 15, 20$) are shown in Fig.(10) and the band positions of P_2O_5 - TeO_2 -CdO have been tabulated the Table (6).The bands located in the range of the $(494.83-498.77) \text{ cm}^{-1}$, and are assigned to the bending mode of Te-O-Te linkages, and to stretching mode $[TeO_4]$ trigonal pyramidal with bridging oxygen the last band may be overlapped with a band attributed to the stretching mode of $[TeO_3]$ trigonal pyramidal with non-bridging oxygen as a result, some of the TeO_4 groups are transformed into TeO_3 [18]. The absorption band position at $(982.16-994.42) \text{ cm}^{-1}$ have been assigned to P-O groups (chain terminator)[19] . Infra-red spectra for $(P_2O_5)_{50}-(TeO_2)_{50-x}-(ZnO)_x$ glasses of different compositions ($x=0, 5, 10, 15, 20$) are shown in Fig.(11) and the band positions of P_2O_5 - TeO_2 -ZnO have been tabulated

in Table (7). The vibration absorption bands observed for P_2O_5 - TeO_2 - ZnO glasses are listed in Table (7). The absorption band at $(602.77-660) \text{ cm}^{-1}$ which appears in all the compositions studied could possibly be assigned to stretching vibrations of the Te-O bonds[20]. The bands of $(495.60-496.32) \text{ cm}^{-1}$ of such glass are assigned to the stretching mode of the TeO_3 trigonal pyramid (tp) with non-bridging oxygen (NBOS) atoms, TeO_4 tbp with ZnO and bending mode of Te-O-Te or O-Te-O linkages [21]. The absorption band position at $(979.39-987.19) \text{ cm}^{-1}$ group is nearly unaffected with the increase of ZnO the slight increase in band position can be attributed to shortening of P-O bond due to the increase in the network packing[17]. Infra-red spectra for $(P_2O_5)_{50}-(TeO_2)_{50-x}-(V_2O_5)_x$ glasses of different compositions ($x = 0, 5, 10, 15, 20$) are shown in Fig.(12) and the band positions of P_2O_5 - TeO_2 - V_2O_5 have been tabulated in Table (8). The weak band centered at 495.31 cm^{-1} disappears proving that the Te-O-Te bridging are broken leading to an increase of the amount of the nonbridging oxygen atoms (NBO) introducing a network modifier into the glass matrix changes the Te coordination polyhedron from TeO_4 to TeO_3 by breaking Te-O-Te bonds, along with the formation of non-bridging oxygen (NBOs) atoms[22]. The absorption band in $(727.49-751.82) \text{ cm}^{-1}$ are assigned to the symmetric stretching modes of P-O-P linkages,[23]. The absorption band position at $(910-967.26) \text{ cm}^{-1}$ the ionic character of phosphate group can be explained by formation of the P-O groups[17].

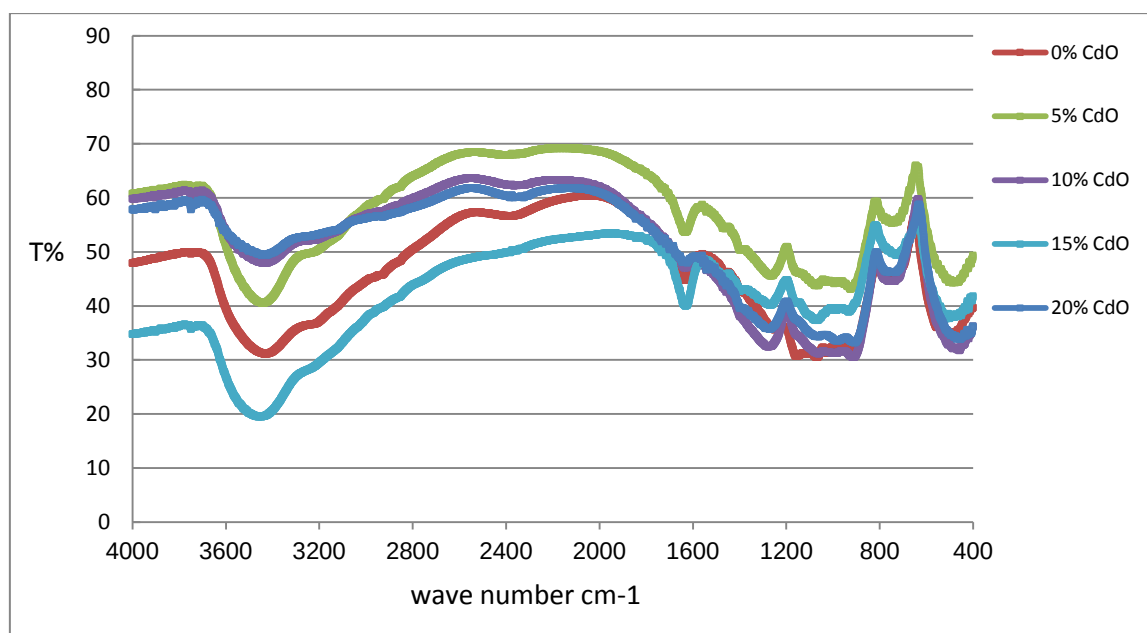


Fig.(7) : infrared transmission spectra of (P_2O_5) -(CuO)-(CdO) glass.

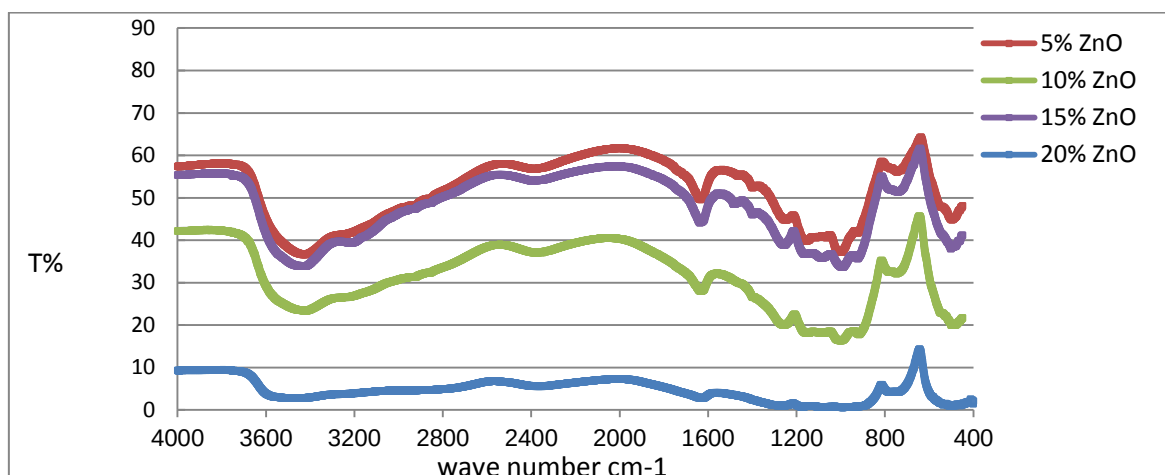


Fig. (8): infrared transmission spectra of $(P_2O_5)-(CuO)-(ZnO)$ glass.

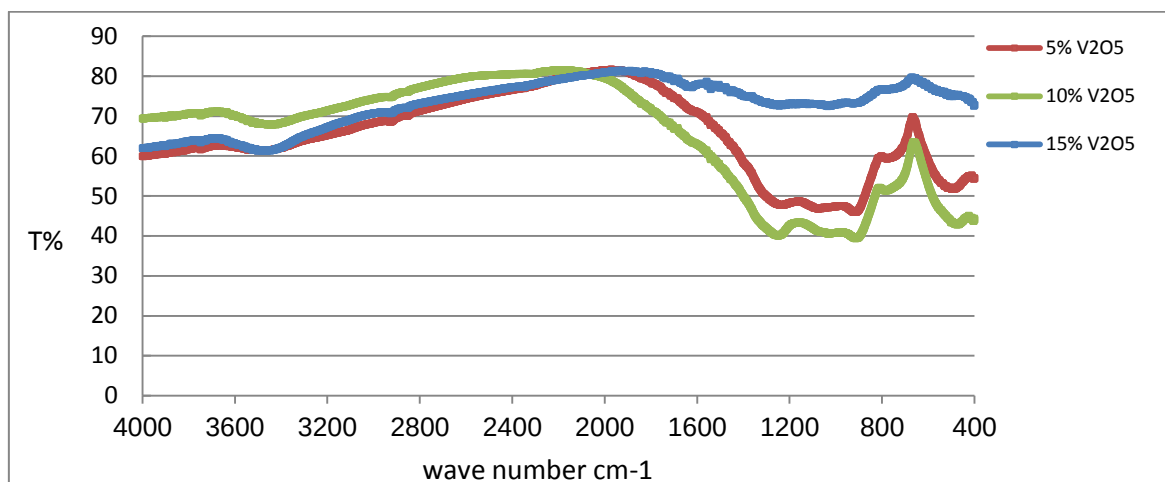


Fig. (9): infrared transmission spectra of $(P_2O_5)-(CuO)-(V_2O_5)$ glass.

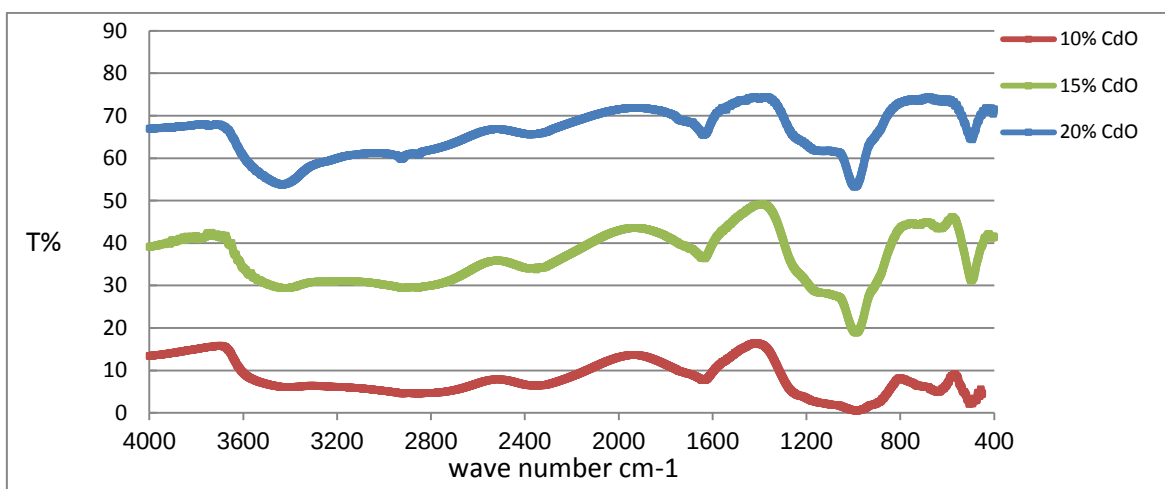


Fig. (10): infrared transmission spectra of $(P_2O_5)-(TeO_2)-(CdO)$ glass.

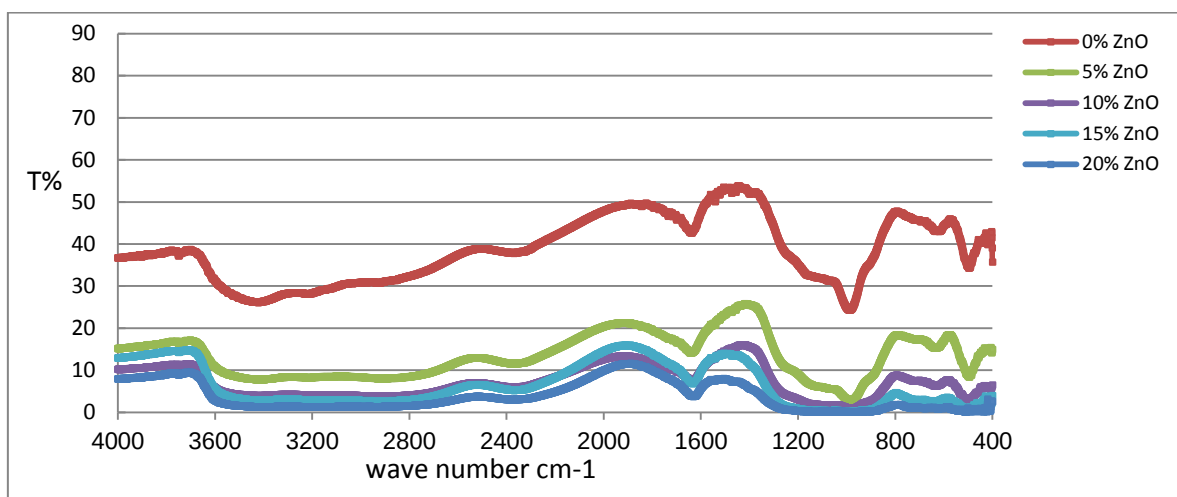


Fig. (11): infrared transmission spectra of $(P_2O_5)-(TeO_2)-(ZnO)$ glass.

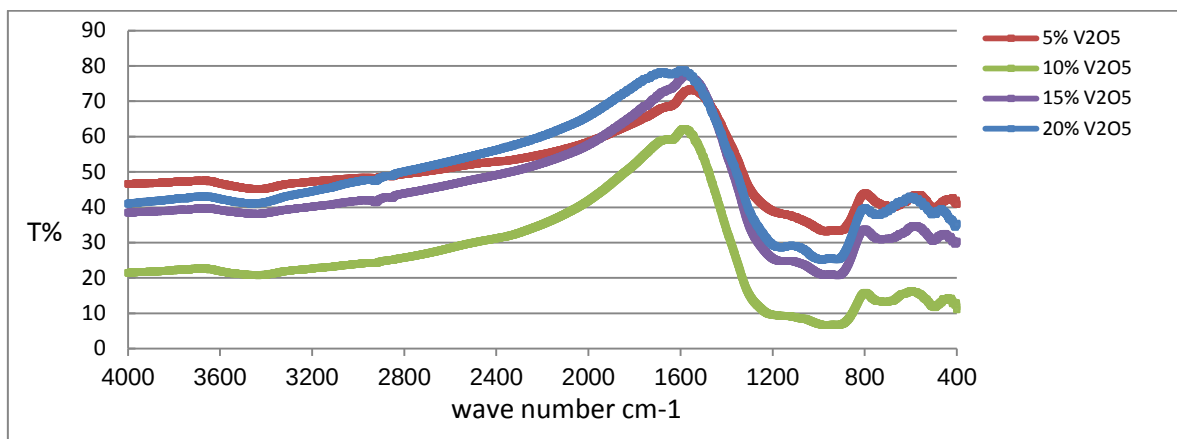


Fig. (12): infrared transmission spectra of $(P_2O_5)-(TeO_2)-(V_2O_5)$ glass.

Table (3): Band positions of (P₂O₅)-(CuO)-(CdO) glasses.

Mol% CdO	Band position cm ⁻¹						
0	503.15	751.93	905	1067.51	1240	1636.21	3430.38
5	475.27	748.89	924.92	1095	1259.82	1630.69	
10	458.61	738.53	911.19	1070	1279.22	1660	3444.34
15	514.32	730.09	955.5	1067.23	1270.96	1630.58	3459.79
20	455.34	732.32	908.20	1070	1270.75	1650	3445.01

Table (4): Band positions of (P₂O₅)-(CuO)-(ZnO) glasses

Mol% ZnO	Band position cm ⁻¹						
5	494.96	745.72	999.22	1150	1230	1635.66	3430.03
10		747.92	999.40	1150	1258.97	1632.34	3421.46
15	502.57	739.65	993.77		1255.91	1636.61	3422.59
20		780	993.39	1170	1270	1620	3483.05

Table (5): Band positions of (P₂O₅)-(CuO)-(V₂O₅) glasses

Mol % V ₂ O ₅	Band position (cm ⁻¹)				
5	499.16	918.77	1070	1240	3480
10	475.07	914.93		1250.91	3446.09
15			1035.38		3466.97

Table (6): Band positions of (P₂O₅)-(TeO₂)-(CdO) glasses

Mol% CdO	Band position cm ⁻¹			
10	505.15	982.16	1638.24	3380
15	498.77	987.60	1634.95	3400
20	494.83	994.42	1640.92	3436.18

Table (7): Band positions of (P₂O₅)-(TeO₂)-(ZnO) glasses

Mol% V ₂ O ₅	Band position cm ⁻¹				
5	495.31	675.08	967.08	1650	3434.03
10	495.38	707.02	967.26	1630	
15	503.80	727.49	919.05		
20		751.82	910	1630	3467.19

Table (8): Band positions of (P₂O₅)-(TeO₂)-(V₂O₅) glasses

Mol% ZnO	Band position cm ⁻¹				
0	496.32	602.77	987.19	1637.12	3421.16
5	495.60	635.47	981.07	1641.07	3421.63
10	502.61	660	979.39	1640.59	3440
15	516.31		980.02	1635.45	3420
20	512.65	630		1630.46	3193.87

4. Conclusions

- 1- Density measurements of (P₂O₅)-(CuO)-(CdO) , (P₂O₅)-(CuO)-(ZnO) and (P₂O₅)-(TeO₂)-(CdO) decreasing whether (P₂O₅)-(CuO)-(V₂O₅), (P₂O₅)-(TeO₂)-(ZnO) and (P₂O₅)-(TeO₂)-(V₂O₅) increasing
- 2- IR the absorption band at (475.27-503.15) cm⁻¹ , at 500 cm⁻¹ can be attributed to (PO₄)⁻³, whether the bands at (494.83-498.77) cm⁻¹ , can be attributed to Te-O-Te

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