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A STUDY OF OPTICAL PROPERTIES OF PHOSPHATE AND TELLURITE SEMICONDUCTING OXIDE GLASSES

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ABSTRACT

Glass samples in the system 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 where (x = 0, 5, 10, 15,20) were prepared by the melt-quenching technique. Optical absorption spectra of different compositions were recorded in the visible and UV regions and optical parameters such as optical energy gap (E_{opt}) and band tails (E_o) were determined by Urbach formula, the measurements for phosphate glasses of optical energy gap (E_{opt}) $(P_2O_5)_{75}$-$(CuO)_{25-x}$-$(CdO)_x$ have been determined and founded between (3.75-4.185) eV, $(P_2O_5)_{75}$-$(CuO)_{25-x}$-$(ZnO)_x$ the value of optical energy gap is between (3.75-4.25)eV, $(P_2O_5)_{75}$-$(CuO)_{25-x}$-$(V_2O_5)_x$ the (E_{opt}) is between (3.75-4.2)eV. for tellurite glasses the measurements of optical energy gap (E_{opt}) of $(P_2O_5)_{50}$-$(TeO_2)_{50-x}$-$(CdO)_x$ have been determined and founded between (3.825-4.25)eV, $(P_2O_5)_{50}$-$(TeO_2)_{50-x}$-$(ZnO)_x$ the (E_{opt}) is between (4.035-4.2)eV, $(P_2O_5)_{50}$-$(TeO_2)_{50-x}$-$(V_2O_5)_x$ the value of optical energy gap is between (3.875-4.335)eV, It was found that the fundamental absorption of these glasses is dependent upon compositions and arises from forbidden indirect transitions. The most satisfactory results were obtained with the theory Davis and Mott for forbidden indirect transitions.

Keyword: *Optical properties, Oxide Glasses, Absorption Edge.*

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دراسـة الصفات البصرية لزجاجيات اكاسيد الفوسفات والتلريوت الشبه الموصلة

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الملخص

تم تحضير المركبات :

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

البنفسجية وبتراكيز مختلفة X = ٠، ٥، ١٠، ١٥، ٢٠) ، **ثم سجلنا قيم اطياف الامتصاص الضوئي في المناطق المرئية والفوق و قيم لطاقة الفجوة البصرية وطاقة ذيول الحزمة وظهر النتائج لنا بان طاقة الفجوة البصرية تتغير مع تغير تراكيز العناصر ، وقد وجد بان حافة الامتصاص لهذه الزجاجيات يعتمد على المركبات المتغيرة وتنشا من انتقالات غير المباشرة للمناطق المحظورة . ومن الواضح أن النتائج التي تم الحصول عليها من خلال هذه الدراسة تتفق تماما مع نظرية** Davis and Mott

الكلمات الدالة : الصفات البصرية، اكاسيد الزجاجيات، حافة الامتصاص.

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1. INTRODUCTION

Glass can be made with excellent homogeneity in a variety of forms and sizes such as rod tubes, sheets, plates… etc; from small fibers to meter-sized pieces. Furthermore, glass can be doped with rare earth ions and microcrystallines and a wide range of properties can be chosen to meet the needs of various applications. These advantages over crystalline materials are based on the unique structural and thermo dynamical features of glass materials [1]. Glass is in widespread use largely due to the production of glass compositions that are transparent to visible light. In contrast, polycrystalline materials do not generally transmit visible light [2]. The individual crystallites may be transparent, but their facets (grain boundaries) reflect or scatter light resulting in diffuse reflection. In the 21st century, scientists observing the properties of ancient stained glass windows, in which suspended nano particles prevent UV light from causing chemical reactions that change image colors, are developing photographic techniques that use similar stained glass to capture true color images of Mars for the 2019 ESA Mars Rover mission[3].

New chemical glass compositions or new treatment techniques can be initially investigated in small-scale laboratory experiments. The raw materials for laboratory-scale glass melts are often different from those used in mass production because the cost factor has a low priority. In the laboratory mostly pure chemicals are used. Care must be taken that the raw materials have not reacted with moisture or other chemicals in the environment (such as alkali or alkaline earth metal oxides and hydroxides, or boron oxide), or that the impurities are quantified (loss on ignition) [4]. Evaporation losses during glass melting should be considered during the selection of the raw materials, e.g., sodium selenite may be preferred over easily evaporating SeO_2. Also, more readily reacting raw materials may be preferred over relatively inert ones, such as $Al(OH)_3$ over Al_2O_3. Usually, the melts are carried out in platinum crucibles to reduce contamination from the crucible material. Glass homogeneity is achieved by homogenizing the raw materials mixture (glass batch), by stirring the melt, and by crushing and re-melting the first melt. The obtained glass is usually annealed to prevent breakage during processing [4, 5]

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2. Experimental Work

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 starting materials, namely P_2O_5, CuO, CdO, TeO_2, V_2O_5 and ZnO each of purity 99.99% and in the powder form, were procured from Aldrich Sigma. All the samples were fabricated in air under the same conditions.The appropriate amounts of oxides powder for each glass system were weighed and mixed together in alumina crucibles using an alumina rod and then preheated at about 200 ^oC for one hour in order to minimize material volatilization. The crucible then transferred to a melting furnace for one hour. The melts were stirred from time to time in order to get a homogenous melt. Some of the melt was used to make a thin film by blowing for the optical measurements; the other part of the melt was cast on to a clean stainless steel plate to form a disc 1 cm in diameter. The melting temperature used for $(P_2O_5)_{75}$-$(CuO)_{25-x}$-$(CdO)_x$ glasses was (950-1000) ^oC, $(P_2O_5)_{75}$-$(CuO)_{25-x}$–$(ZnO)_x$ glasses was (1000-1050) ^oC, $(P_2O_5)_{75}$-$(CuO)_{25-x}$-$(V_2O_5)_x$ glasses was (1000-1100) ^oC, $(P_2O_5)_{50}$-$(TeO_2)_{50-x}$-$(CdO)_x$ glasses was (900-950) ^oC, $(P_2O_5)_{50}$-$(TeO_2)_{50-x}$-$(ZnO)_x$ glasses was (850-900) ^oC, $(P_2O_5)_{50}$-$(TeO_2)_{50x}$-$(V_2O_5)_x$ glasses was (950-1000) ^oC. All the series of glasses were annealed at 200 ^oC to relieve mechanical stresses of glasses and minimize cracking. It was believed that the glass preparation history, that is, melting temperature, melting time, annealing temperature, annealing time, rate of cooling and melting atmosphere could affect the properties of glasses and it was decided to keep all these Parameters the same for the samples of the one series. The preparation of the various series of glasses was as stated in the following subsection.

3. RESULTS AND DISCUSSION

The optical absorption coefficient α (ω) near the band edge in many amorphous semiconductors and insulators shows an exponential dependence on photon energy (ħω) and obeys an empirical relation due to Urbach [9]:

$$\alpha(\omega) = \alpha_o \exp(\hbar\omega / E_o) \quad \ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where ω is the angular frequency of the radiation, α_o is a constant and $E_o$is related to the width of the tails of localized states in the band gap. The absorption edge for non-direct

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transitions, having K-constant conservation selection rule in most amorphous and semiconductors [8] can be determined from the relation [10]:

$$\alpha(\omega) = A(\hbar\omega - E_{opt})^n / \hbar\omega \quad \ldots\ldots\ldots\ldots\ldots 2$$

Where A is a constant, n is the power index and E_{opt} is the optical energy gap of the material. Practically the optical absorption coefficient α(ω) can be calculated from the relation:

$$\alpha(\omega) = 1/d \ln(I_t / I_o) \quad \ldots\ldots\ldots\ldots\ldots 3$$

Where I_t and I_o are the intensities of the incident and transmitted beams respectively,corrected for any reflection at the first surface, and d is the thickness of the sample

Optical absorption Edges measurements for 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) made as a function of photon energy at room temperature.

The analysis of the main absorption edge of the glasses Series $(P_2O_5)_{75}$-$(CuO)_{25-x}$-$(CdO)_x$ / $(P_2O_5)_{75}$-$(CuO)_{25-x}$ –$(ZnO)_x$ / $(P_2O_5)_{75}$-$(CuO)_{25-x}$-$(V_2O_5)_x$ / $(P_2O_5)_{50}$-$(TeO_2)_{50-x}$ – $(CdO)_x$ / $(P_2O_5)_{50}$-$(TeO_2)_{50-x}$-$(ZnO)_x$ and $(P_2O_5)_{50}$-$(TeO_2)_{50-x}$-$(V_2O_5)_x$ are Based on the theory Davis and Mott [8], As it has been the optical energies gap (E_{opt}) values calculated by this theory, It is clear that the results obtained through this study agree well with the theory Davis and Mott[8], This confirms the occurrence of indirect emission between packages in these glasses. The optical absorption spectra of the phosphate and tellurite glasses as a function of the wavelength for different glass compositions it found firstly there is no sharp absorption edge and secondly the position of the fundamental absorption edge shifts to higher energy (lower wavelength) with increasing CdO, ZnO and V_2O_5 contents, It is likely to be caused by a change in the amount of Oxygen ion (non-bridging Oxygen) is increased with transition metal ions in these glasses. It founded that for the phosphate and tellurite glasses the value of the optical energy gap (E_{opt}) is increasing with increasing CdO, ZnO and V_2O_5 contents, correspond decrease in the band tail (E_o), as shows in Tables (1), (2), (3), (4), (5), (6), This confirms the view of the Hassan [11] Which supports the theory Davis and Mott [8]. The value of the band tails (E_o)of the localized states is found to vary irregularly with increasing CdO, ZnO and V_2O_5 contents where plotted between ln(α) with photon energy (ħω), The values of E_o were determined by using equation (1) and calculated from the slope of the

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straight line of the curve (where E_o= 1/slope). The origin of the exponential dependence of the absorption coefficient on the energy of the photon in the semiconductor crystalline and amorphous Unknown clearly, As Dow and Redfield [12] suggested that the origin of this dependence possibly caused by random fluctuations of the internal field associated with the loss of the structural arrangement in most amorphous solids, While Tauc [13] think that the origin of the exponential dependence of the absorption coefficient on the photon energy caused by electronic transitions between localized states tails of the associated edges of the package, as the density decreases exponentially with energy, Davis and Mott [8] Suppose that the exponential tail are likely to be caused by the effects of the internal electric fields resulting from the charged impurity levels, as well as of the vibrating atoms in the material. The absorption coefficient α (ω) was determined at different photon energies near the optical edge for the whole range of glass compositions and the results may be displayed in a number of ways as a function of photon energy. The most satisfactory results were obtained by plotting the quantity $(\alpha\hbar\omega)^{1/2}$ as a function of photon energy (ħω) for forbidden indirect transitions as suggested by Davis and Mott [8], It observed that all drawings between quantity $(\alpha\hbar\omega)^{1/2}$ and photon energy (ħω) Straight lines appear with some deviations as it consistent explanations Redfield and Afromowitz [14] It is possible to be caused by defects in material, as shows in Figures (1), (2), (3), (4), (5), (6).The absorption specifications in these glasses could be described accepted a general way that the absorption edge is calculated by force oxygen bond in glass composite. The Urbach plots are linear for all the glass samples studied verifying Urbach's law.

Table (1): Optical energy band gap and band tail for (P_2O_5)-(CuO)-(CdO)

Mo1% CdO content	E_{opt} (eV)	E_o (eV)
0	3.75	0.26
5	4.035	0.1375
10	4.1	0.25
15	4.125	0.3
20	4.185	0.38

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Table (2): Optical energy band gap and band tail for (P_2O_5)-(CuO)-(ZnO)

Mo1% ZnO content	E_{opt} (eV)	E_o (eV)
0	3.75	0.26
10	4.05	0.65
15	4.085	0.29
20	4.25	0.25

Table (3): Optical energy band gap and band tail for (P_2O_5)-(CuO)-(V_2O_5)

Mol % V_2O_5 content	E_{opt} (eV)	E_o (eV)
0	3.75	0.26
10	4	0.25
15	4.2	0.593

Table (4): Optical energy band gap and band tail for (P_2O_5)-(TeO_2)-(CdO)

Mo1% CdO content	E_{opt} (eV)	E_o (eV)
10	3.825	0.5
15	3.985	0.308
20	4.25	0.333

Table (5): Optical energy band gap and band tail for (P_2O_5)-(TeO_2)-(ZnO)

Mo1% ZnO content	E_{opt} (eV)	E_o (eV)
5	4.035	0.15
10	4.015	0.13
15	4.175	0.18
20	4.2	0.98

Table (6): Optical energy band gap and band tail for (P_2O_5)-(TeO_2) (V_2O_5)

Mo1% TeO_2 content	E_{opt} (eV)	E_o (eV)
5	3.875	0.49
10	4	0.48
15	4.285	0.37
20	4.335	0.41

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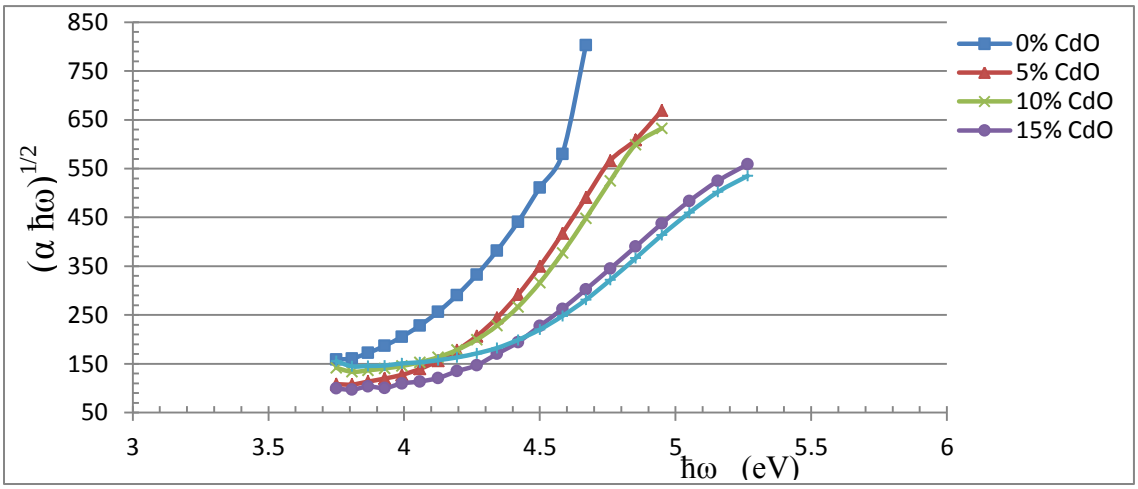

Fig. (1): $(\alpha\ \hbar\omega)^{1/2}$ against $(\hbar\omega)$ for (P_2O_5) - (CuO) - (CdO) glasses.

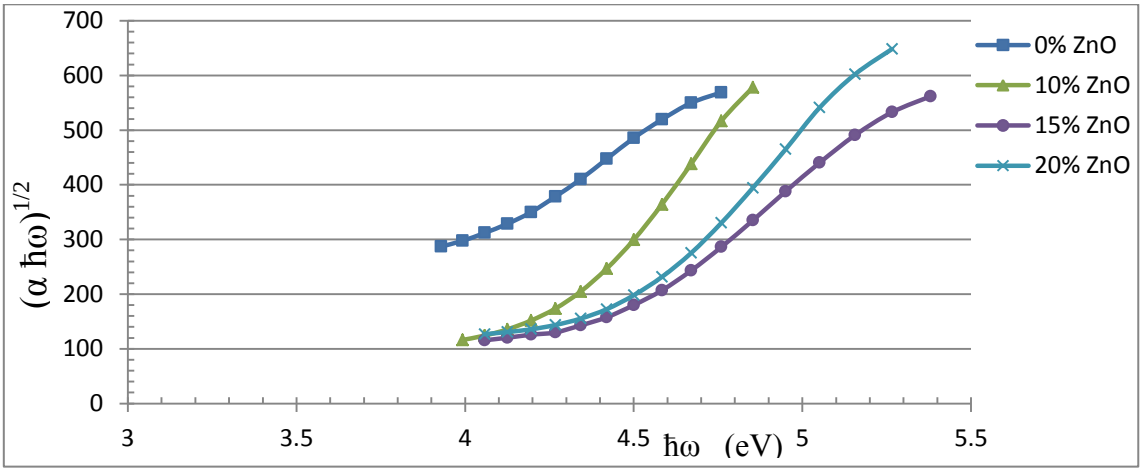

Fig. (2): $(\alpha\ \hbar\omega)^{1/2}$ against $(\hbar\omega)$ for (P_2O_5)-(CuO)-(ZnO) glasses.

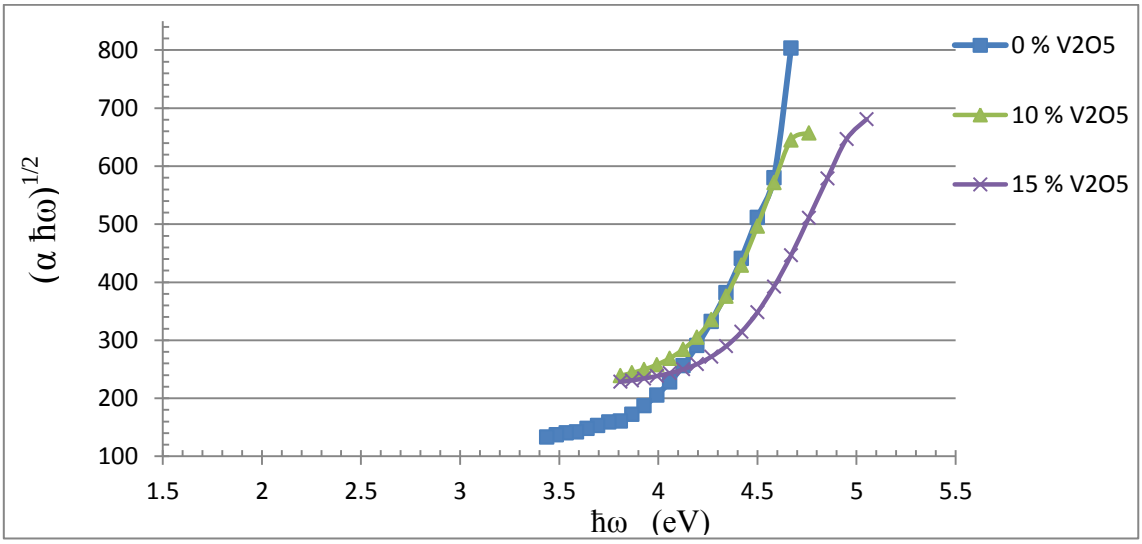

Fig. (3): $(\alpha\ \hbar\omega)^{1/2}$ against $(\hbar\omega)$ for (P_2O_5)-(CuO)-(V_2O_5) glasses.

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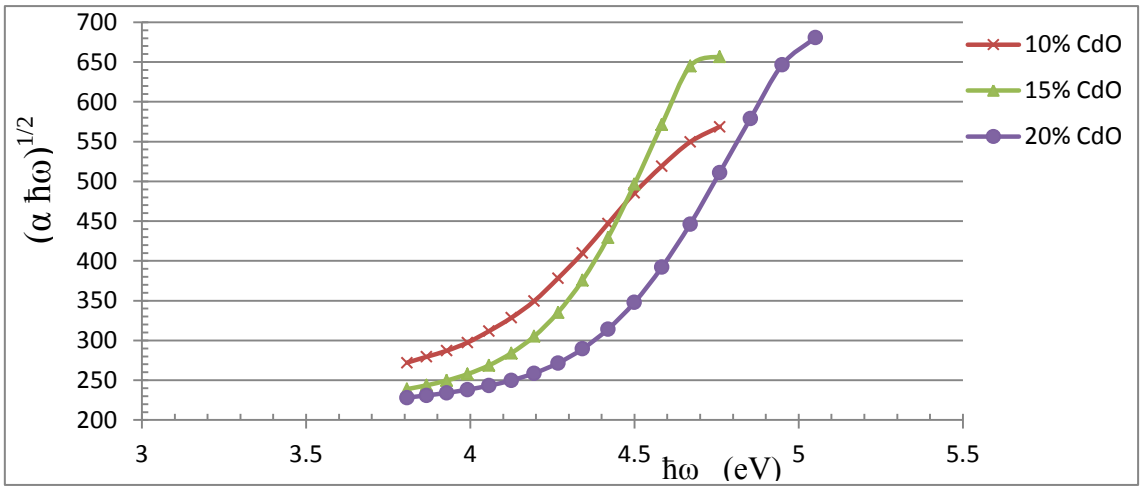

Fig. (4): $(\alpha\ \hbar\omega)^{1/2}$ against $(\hbar\omega)$ for (P_2O_5)-(TeO_2)-(CdO) glasses.

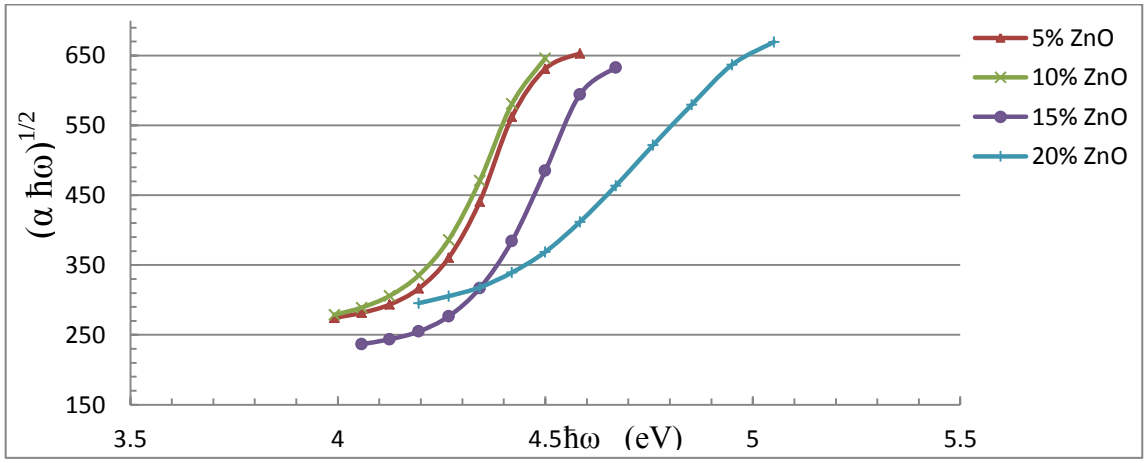

Fig. (5): $(\alpha\ \hbar\omega)^{1/2}$ against $(\hbar\omega)$ for (P_2O_5)-(TeO_2)-(ZnO) glasses.

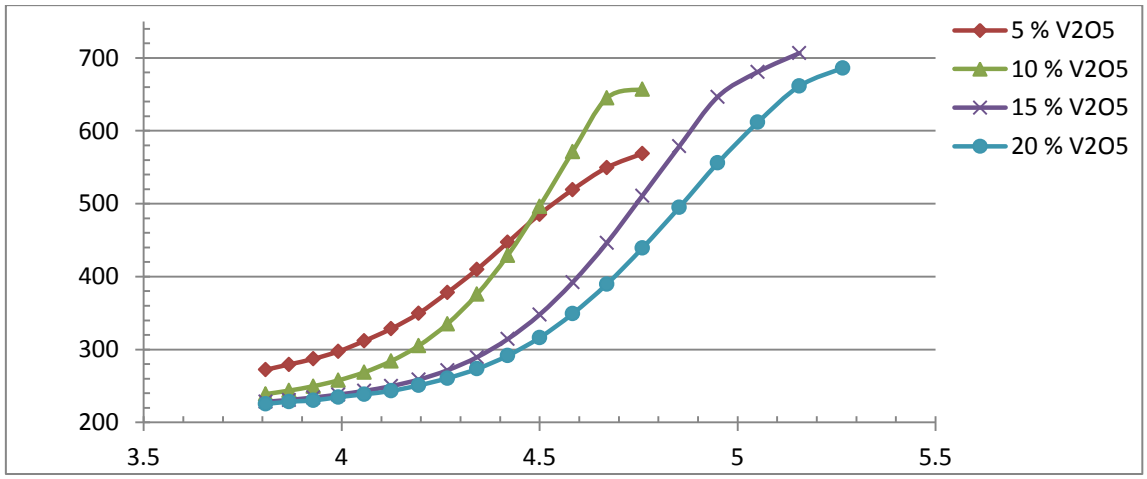

Fig. (6): $(\alpha\ \hbar\omega)^{1/2}$ against $(\hbar\omega)$ for (P_2O_5)-(TeO_2)-(V_2O_5) glasses.

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