

Study of Density, Molar Volume, X-Ray Diffraction and Infrared Spectra of Phosphate Glasses

Abdulkarim Z. Khalif¹, Ebtihal G. Khadr², Ayoub S. Karim³, Mohammed H. Abbas⁴, Manaf A. Hassan⁵

¹Univesity of Kirkuk, College of Education for Pure Science, Phys.Dept..

²Univesity of Kirkuk, College of Education for Pure Science, Phys.Dept.

³University of Sabah Al-Din , College of Education Phys.Dept.

⁴Univesity of Kirkuk, College of Education for Pure Science, Phys.Dept.,

⁵Univesity of Kirkuk, College of Education for Pure Science, Phys.Dept.,

Abstract

Glasses with compositions

X% V₂O₅ – (50-X)% BaO – (50)% P₂O₅

X% V₂O₅ – (50-X)% CaO – (50)% P₂O₅

X% V₂O₅ – (50-X)% MgO – (50)% P₂O₅

Where $x = 5, 10, 15, \text{ and } 20$ mol%) The result of investigations of density and molar volume ,x-ray diffraction (XRD) and infrared spectra are reported . The density measurements show that the values of the density

increasing with the increasing of V₂O₅ content in the glass systems . From the infrared absorption spectra , it is found that the addition of BaO , CaO and MgO does not introduce any new absorption band in the infrared spectrum of the glass system .

Keyword: Optical properties, Oxide Glasses, Absorption Edge, lead phosphate oxide glasses,

1. Introduction

Now days glasses have a prominent role in the field of the electronics and have wide applications in industry , space research , computer memories etc . Phosphate as glass host possess a lot of advantages such as high thermal expansion coefficient which easily for fiber preparation process [1]. Phosphate glasses have also emerged as a promising group of glasses for optical amplifiers, fibers, laser, etc [2]. Phosphate glasses is an interesting vitreous system that has gained great attention in the past and in recent applications [3].

Phosphate glass types are attractive hosts and also considered to be promising for optical amplifier, fibers, and laser [4]. Many studies on the characterization of phosphate glass types proved that, by adding cation with high value of electrostatic field strength like (Pb²⁺) , the covalence of (P-O-M) bond increases [5,6].

Many transition-metal, alkali-, alkaline- and rare earth oxides form glasses when melted with P₂O₅. Phosphate glasses are technologically important materials because they generally have higher thermal expansion coefficients •, lower transition temperature, and higher electric conductivity than silicate and borate glasses [7]. These glasses have considerable potential for application in optical data transmission, solid state batteries, sensing and laser technologies Van Wazer [8] and Flory [9]. This network is dominated by linkages between PO₄ tetrahedra. In the case of vitreous P₂O₅, these groups are connected to adjacent units by three of their four vertices; one place is occupied by a terminal, double-bonded oxygen atom [10]

Experimental Details

For the present study, glasses with compositions

50-X% BaO – X% V₂O₅– 50)% P₂O₅

50-X% CaO – X% V₂O₅– (50)% P₂O₅

50-X% MgO – X% V₂O₅– (50)% P₂O₅

Where $x=5, 10, 15, \text{ and } 20$ mol% ,were prepared by using a conventional melt quenching method. Chemical powders of reagent grade P₂O₅, V₂O₅, BaO, MgO, and CaO were mixed together for three series of glasses and melted in alumina crucibles placed in an electrically heated muffle furnace at (900_1000)C° for (1h) preheated in an electric furnace for (1h) kepts at 200C° in order to minimize the volatilization. The melts were poured on to stain less plate and pressed to thickness of (3.2)mm at room temperature. The glass powder was mixed with spectroscopically pure KBr. To obtain pellets, the mixed glass samples were pressed in a die and subjected to a pressure of 5tons/cm².

X-ray diffraction (XRD) patterns of the samples were recorded using (X-ray 6000 diffractometer) .

The density (ρ_G) of glass samples was determined by using Archimede's principal with toulene as an inert buoyant liquid. The glass density (ρ_G) was determined by using the equation.

$$\rho_G = \rho_L \frac{W_{air}}{W_{air} - W_L} \dots \dots \dots (1)$$

where (ρ_L) is the density of immersion liquid which is toluene ($\rho_L=0.86 \text{ g/cm}^3$) , (W_{air}) is the weight sample in air



and (W_L) is the weight sample when immersed in the immersion liquid . The molar volume (V_m) was calculated by using the obtained density (ρ_G) and weight of one mole of the glass sample via the following relation [1]:

$$V_m = \sum_i \frac{X_i M_i}{\rho_G} \dots\dots\dots(2)$$

where (X_i) and (M_i) refers to the molar fraction and molecular weight of the (i^{th}) of the component respectively .

The Infrared (IR) transmission spectra of these glass pellets were measured at room temperature using Perkin_Elmer IR spectrophotometer in the range (400_4000) cm^{-1} .

III. Results and Discussion

A. X-Ray Diffraction (XRD)

X-ray diffraction is a quite useful technique because it is possible to detect it readily crystals in a glassy matrix if the crystals are of dimensions greater than typically 100nm[11]. The X-ray diffraction pattern of an amorphous material is distinctly different from that of crystalline material and consists of a few broad diff use haloes rather than sharp rings . All glass samples were tested and the result showed the absence of crystalline characteristics Fig.4 shows typical XRD patterns of glass simple show a broad halo hump 10° to 40°. Presence of broad halo hum at low angle and absent of existence of crystalline peak indicates that the glass samples are amorphous in nature.

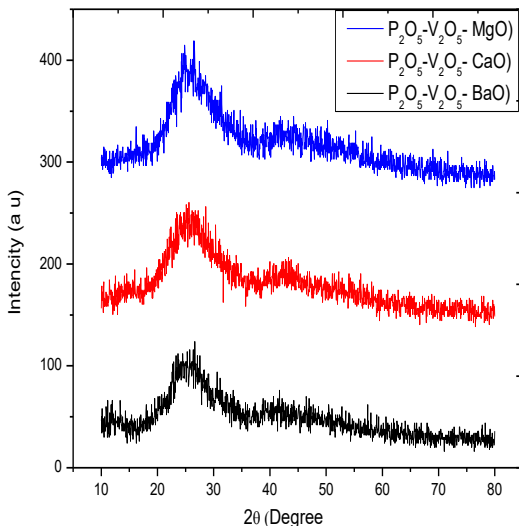


Fig.1: X-Ray Diffraction patterns of three samples of Vanatium phosphate glasses

B. Density Measurements

In the glass systems ($P_2O_5 - V_2O_5 - BaO$), the results showed that the density decreases and the molar volume increases with the increase of V_2O_5 , as shown in

Figure (2). It was noticed that the decrease in the density from 1.205 gm / cm^3 to (1.177 gm / cm^3) And that an increase in the molar volume from 123.4 gm / mol to 130.1 gm / mol with an increase in the ratio of V_2O_5 in the vitreous compound ($P_2O_5 - V_2O_5 - BaO$), the values were listed in Table (1).

Table 1: Composition, density and molar volume for ($P_2O_5 - V_2O_5 - BaO$) glasses.

mol % V_2O_5 content	ρ (gm/ cm^3)	V_m (gm/mol)
5	1.205	123.4
10	1.198	125.4
15	1.188	127.6
20	1.177	130.1

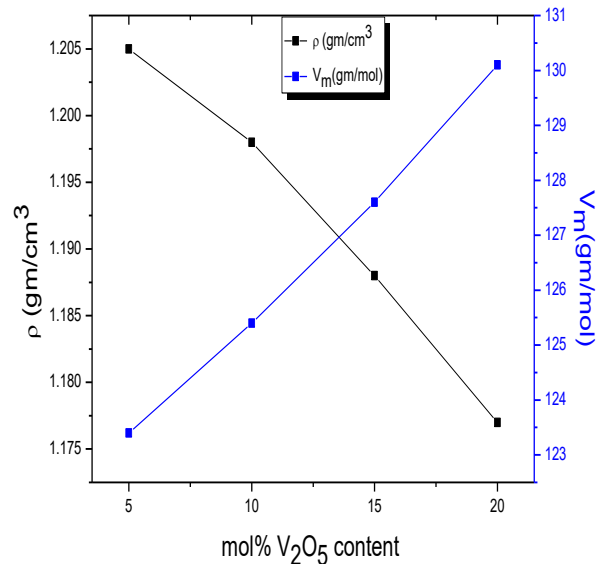


Fig. 2: Relative density and Molar Volume against V_2O_5 content in $P_2O_5 - V_2O_5 - BaO$ glasses

In the glass systems ($P_2O_5 - V_2O_5 - CaO$), the results showed that the density decreases, while the molar volume increases with an increase in the ratio of 5 V_2O_5 , as shown in Figure (3), where Table (4.2.5) shows that the decrease in the density of (1.270 gm / cm^3) to (1.237 gm / cm^3), however, an increase in molar volume was found from 82.93 gm / mol to 100.4 gm / mol with an increase in the ratio of V_2O_5 in the glasses.

Table 2: Composition, density and molar volume for ($P_2O_5 - V_2O_5 - CaO$) glasses.

mol % V_2O_5 content	ρ (gm/ cm^3)	V_m (gm/mol)
------------------------	----------------------	-----------------

5	1.270	82.93
10	1.260	88.55
15	1.249	94.39
20	1.237	100.4

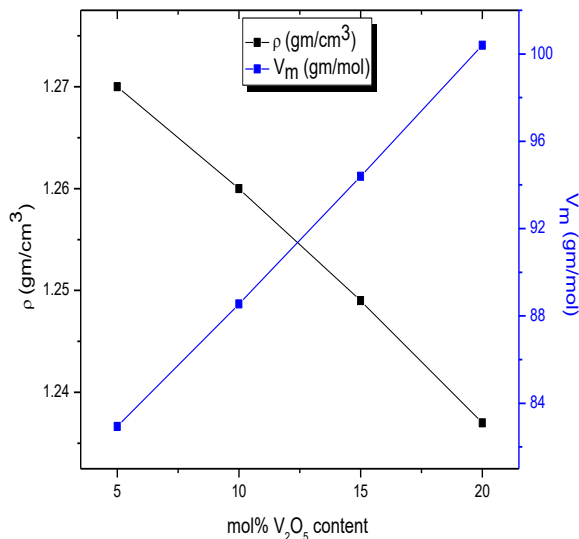


Fig. 3: Relative density and molar volume against V₂O₅ content in P₂O₅ - V₂O₅ - CaO glasses

In the glassy compound (P₂O₅ - V₂O₅ - MgO), the measurement results showed that the density decreases, while the molar volume increases with the increase in the ratio of V₂O₅, as shown in Figure (4.2.6), where it was found that the decrease in the density from 1.270 gm / cm³ to (1.237 gm / cm³) and the increase in the molar volume from gm / mol 82.93 to 100.4 gm / mol with an increase in the percentage of V₂O₅ in the glassy compound, as shown in Table (4.2.6).

Table 3: Composition, density and molar volume for (P₂O₅ - V₂O₅ - MgO) glasses.

mol % V ₂ O ₅ content	ρ (gm/cm ³)	V m (gm/mol)
5	1.318	74.44
10	1.302	80.83
15	1.285	87.37
20	1.271	93.93

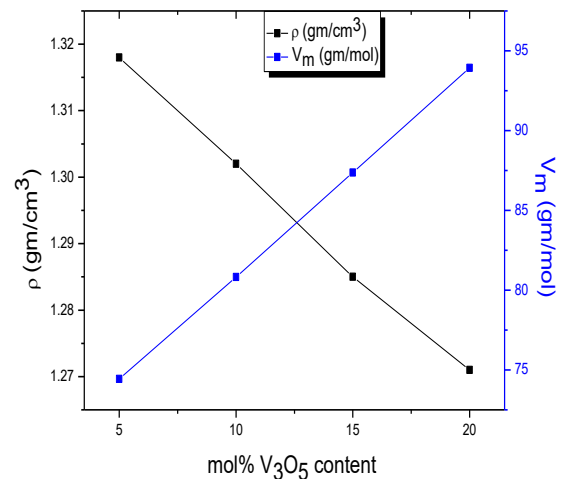


Fig. 4: Relative density and molar volume against V₂O₅ content in (P₂O₅ - V₂O₅ - MgO) glasses

The density results of the glass compounds (P₂O₅ - V₂O₅ - MgO), (P₂O₅ - V₂O₅ - CaO), (P₂O₅ - V₂O₅ - BaO) showed that the density decreases while the molar volume increases and this indicates that there is an increase in the interstitial distances in the internal composition of the glass compounds. The tripartite number of researchers confirm this finding (Virender). [12] (Kundu) [13] (Tina). [14] They said that the observed changes due to the formation of un-bridged oxygen change the glass structure mainly as increasing the concentration of un-bridged oxygen gives a kind of randomness and disorganization and leads to an increase in the separation between Atoms

C. Infrared spectra

a) Infrared absorption of P₂O₅-V₂O₅-BaO glasses

The infrared absorption spectra of four samples were obtained at room temperature in the wave number range (4000-400)cm⁻¹. The infrared spectra of the glasses are shown in Fig.5. Table (4) shows the positions of the absorption bands obtained in these glasses. The absorption band at (451-495) cm⁻¹ refers to the fundamental frequency (PO₄)⁻³ in the crystalline compound P₂O₅ [15]. The absorption band at (763) cm⁻¹ indicates the extension frequency V-O in the V-O-V ring [19]. The absorption band at (1078-1085) cm⁻¹ refers to the double band frequency V = O [16], or to the extension frequency P-O. The absorption band at the wavelength number (1265-1278) cm⁻¹ indicates the frequency of the double beam extension (P = O). The absorption band position at (900-921) cm⁻¹ also refers to the Ba-O-Ba, P-O-Ba or P-O-P [17] - [19]. An absorption band at (1617-1637) cm⁻¹ yields powder mixing with an amount of KBr [17]. The absorption band at (3454-3664) cm⁻¹ was observed to be due to a small amount of water trapped in the glass [17].

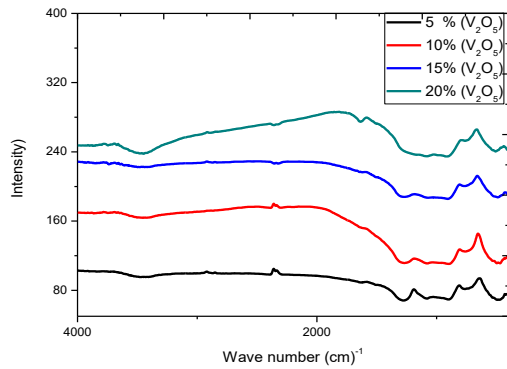


Fig.5: Infrared absorption spectra in (P₂O₅- V₂O₅-BaO) glasses

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

mol% V ₂ O ₅ Content	Band position (cm ⁻¹)						
	400	700	900	1000	1200	1600	3000
5	477	763	903	1085	1274	1631	3455
10	451	763	905	1078	1267	1617	3458
15	491	763	910	1085	1275	1638	3460
20	495	763	917	1080		1637	3664

b) Infrared absorption of P₂O₅-V₂O₅-CaO glasses

The infrared absorption spectra of four samples were obtained at room temperature in the wave number range (4000_400)cm⁻¹. The infrared spectra of the glasses are shown in Fig.(6). Table (5) shows the positions of the absorption bands obtained in these glasses. The absorption band at (458-475) cm⁻¹ refers to the fundamental frequency (PO₄)⁻³ in the crystalline compound P₂O₅ [15]. The absorption band at (640-660) cm⁻¹ refers to the V-O-V ring frequency [18]. The absorption band at (1230-1295) cm⁻¹ indicates the frequency of the double bundle extension (P = O). The absorption band (910-917) cm⁻¹ also indicates the Ca-O-Ca, P-O-Ca or P-O-P [16,18] Tha absorption band at (1784) cm⁻¹ indicates a mixture of a quantity of kBr [17]. Absorption band at (3600-3610) cm⁻¹ was observed due to the presence of an amount Small amounts of water trapped in glass [16].

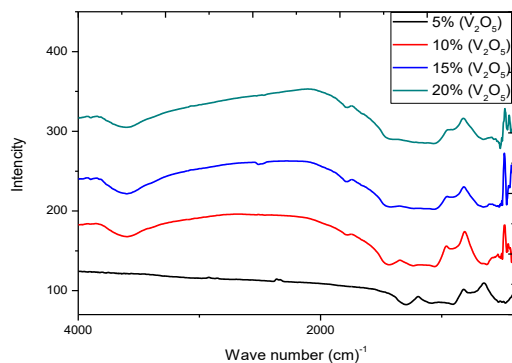


Fig.6: Infrared absorption spectra in (P₂O₅-V₂O₅-CaO) glasses

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

mol% V ₂ O ₅ Content	Band position (cm ⁻¹)						
	400	600	900	1000	1200	1400	3000
5	475		910	1078	1295	1483	
10	458	640	917	1064	1240	1434	3600
15	466	655	915	1065	1230	1420	3610
20	460	660	910	1060		1434	3600

c) Infrared absorption of P₂O₅-V₂O₅-MgO glasses

The infrared absorption spectra of four samples were obtained at room temperature in the wave number range (4000_400)cm⁻¹. The infrared spectra of the glasses are shown in Fig.(6). Table (5) shows the positions of the absorption bands obtained in these glasses. The absorption beam at (485-495) cm⁻¹ refers to the fundamental frequency (PO₄)⁻³ in the crystalline compound P₂O₅ [15]. The absorption band at (770-780) cm⁻¹ indicates the extension frequency V-O in the V-O-V ring [18]. The absorption band at (1260-1295) cm⁻¹ indicates the frequency of the double beam extension (P = O). Also, the absorption band at (917-924) cm⁻¹ indicates an Mg-O-Mg, P-O-Mg or P-O-P band [16,18,19]. absorption band at (1635-1639) cm⁻¹ produces powder mixing with an amount of kBr [17]. An absorption band at (3448-3462) cm⁻¹ indicates the presence of a small amount of water trapped in the glass [16,20].

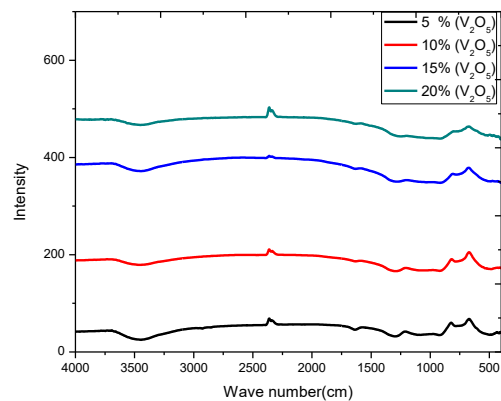


Fig.7: Infrared absorption spectra in (P₂O₅-V₂O₅-MgO) glasses

Table. 6: Band positions in (P₂O₅- V₂O₅-MgO) glasses

mol% V ₂ O ₅ Content	Band position (cm ⁻¹)					
	400	700	900	1200	1600	3000
5	485	777	924	1295	1638	3448
10	490	780	917	1288	1638	3450
15	490	777	924	1285	1639	3455
20	495	770	917	1260	1635	3462

IR spectra of all the samples showed large water peaks. This moisture effect could disrupt the whole spectrum and add general noise. It would be useful to remove these peaks to improve the results obtained from IR spectra. One way of removing the water is by heating the sample for about 2 hours prior to the IR measurements[21].

References

- [1] Yaacob, S. N. S., Sahar, M. R., Sazali, E. S., & Sulhadi, S. (2019). The Polarizability and Optical Characteristics of Zinc Phosphate Glasses Doped Terbium Embedded with Copper Oxide Nanoparticles. In *Solid State Phenomena* (Vol. 290, pp. 35-40). Trans Tech Publications Ltd.
- [2] Ravikumar, R. V. S. S. N., Komatsu, R., Ikeda, K., Chandrasekhar, A. V., Reddy, B. J., Reddy, Y. P., & Rao, P. S. (2003). EPR and optical studies on transition metal doped LiRbB4O7 glasses. *Journal of Physics and Chemistry of Solids*, 64(2) 261-264.
- [3] Ibrahim, S., & Marzouk, M. A. (2017). Structural characteristics and electrical conductivity of vanadium-doped lithium ultraphosphate glasses. *Silicon*, 9(3) 403-410.
- [4] Ravikumar, R. V. S. S. N., Chandrasekhar, A. V., Ramamoorthy, L., Reddy, B. J., Reddy, Y. P., Yamauchi, J., & Rao, P. S. (2004). Spectroscopic studies of transition metal doped sodium phosphate glasses. *Journal of alloys and compounds*, 364(1-2) 176-179.
- [5] Brow, R. K., & Tallant, D. R. (1997). Structural design of sealing glasses. *Journal of Non-Crystalline Solids*, 222, 396-406.
- [6] Ray, N. H., NH, R., & CJ, L. (1973). Oxide glasses of very low softening point. I. Preparation and properties of some lead phosphate glasses.
- [7] Sidek, H. A. A., Collier, I. T., Hampton, R. N., Saunders, G. A., & Bridge, B. (1989). Electrical conductivity and dielectric constant of samarium phosphate glasses. *Philosophical Magazine B*, 59(2) 221-232.
- [8] Wazer, J. R. V. (1950). Structure and properties of the condensed phosphates. II. A theory of the molecular structure of sodium phosphate glasses. *Journal of the American Chemical Society*, 72(2) 644-647.
- [9] Flory, P. J. (1953). *Principles of polymer chemistry*. Cornell University Press.
- [10] Prasad, P. S., Rao, V. H., Babu, M. M., Rao, P. V., Raju, G. N., & Laxmikanth, C. (2015). Spectroscopic investigations of the PbO–MoO3–P2O5: V2O5 glass system. *Physics and Chemistry of Glasses-European Journal of Glass Science and Technology Part B*, 56(4) 169-174.
- [11] Anderson, G. W., & Luehrs Jr, F. U. (1968). Structural Characterization of and Phase Separation in Vanadate Glasses. *Journal of Applied Physics*, 39(3) 1634-1638.
- [12] Kundu, V., Dhiman, R. L., Maan, A. S., & Goyal, D. R. (2008). Structural and Physical Properties of Fe2 O3-B2 O3-V2 O5 Glasses. *Advances in Condensed Matter Physics*, 2008.
- [13] Kundu, R. S., Dhankhar, S., Punia, R., Sharma, S., & Kishore, N. (2013). ZnCl2 modified physical and optical properties of barium tellurite glasses. *Transactions of the Indian Ceramic Society*, 72(3) 206-210.
- [14] Tasheva, T., & Dimitrov, V. (2017). Synthesis, Optical properties and structure of NiO-BaO-V 2 O 5 glasses. *Journal of Chemical Technology & Metallurgy*, 52(2).
- [15] Richard, A. (1971). *Nyquist and Ronald O Kagel. IR Spectra of Inorganic Compounds* (New York and London: Academic Press. Aynur, B.k., & Hassan, M.A., J .Education science to be published
- [16] Dogra, M., Singh, K. J., Kaur, K., & Anand, V. (2018). Gamma ray shielding properties at 129.5 MBq and structural investigations of the Bi2O3–B2O3–K2O–Li2O–V2O5 glass system. *Physics and Chemistry of Glasses-European Journal of Glass Science and Technology Part B*, 59(6) 293-300.
- [17] Prasad, P. S., Rao, V. H., Babu, M. M., Rao, P. V., Raju, G. N., & Laxmikanth, C. (2015). Spectroscopic investigations of the PbO–MoO3–P2O5: V2O5 glass system. *Physics and Chemistry of Glasses-European Journal of Glass Science and Technology Part B*, 56(4) 169-174.
- [18] Obed, S. A., & Hassan, M. A. (2016). A Study of Infrared Spectra of Some Semiconducting Oxide Glasses. *kirkuk university journal for scientific studies*, 11(3).
- [19] Lakshmikantha, R., Rajaramakrishna, R., Anavekar, R. V., & Ayachit, N. H. (2012). Characterization and structural studies of vanadium doped lithium–barium–phosphate glasses. *Canadian journal of physics*, 90(3) 235-239.
- [20] Dhyghm A. Ibrahim Najat A. Dahham, Manaf A. Hassan (2020) Optical Properties of Lead-Phosphate Glasses *International Journal of Applied Physics (SSRG-IJAP)* V7I3P103
- [21] Mohammed H . Abbas Manaf A . Hassan Optical Properties of Phosphate Glasses *International Journal of Applied Physics (SSRG-IJAP)* V7I3P105