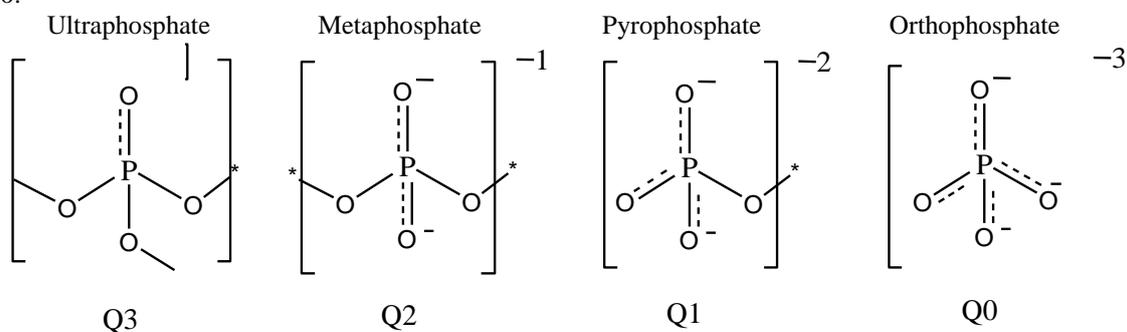


**Effect of MO (CuO, ZnO, and CdO) on the compaction of sodium meta phosphate sealing glass.**<sup>1</sup>A.M . Nassar, <sup>2</sup>M.M. El Oker, <sup>1</sup>Sh. N. Radwan and <sup>1</sup>E. Nabhan<sup>1</sup>Al Azhar University (Girls) Faculty of Science, Cairo, Egypt.<sup>2</sup>Al Azhar University (Boys) Faculty of Science, Cairo, Egypt.**ABSTRACT**

Phosphate glasses are technologically important because they generally have low melting temperature, low glass transition temperature, and high thermal expansion coefficient. Thus, they are of increasing interest for many applications such as sealing glass. However, their relatively poor chemical durability makes them unsuitable for practical applications. The addition of one or more of divalent oxides leads to improvement in the chemical durability, mechanical properties, and thermal expansion by increasing the strength of bonds and the compaction of the phosphate glass system. In the present work the effect of CuO, ZnO, and CdO have been studied in the system of  $(50-x) \text{Na}_2\text{O} - 50 \text{P}_2\text{O}_5 - x \text{MO}$  (CuO, ZnO, and CdO) where  $x=0, 5, 10, 15, 20, 25$  mol % using IR spectroscopy, density, molar volume, and hardness. IR spectra reveals that the formation of P-O-M bonds which replace P...O...Na<sup>+</sup> bonds, while keeping P-O-P fraction as the same, increase the crosslink density. The P-O-P bonds shifts to higher wave number as MO increase reveals that the strength of the matrix increase. This increase is related to the increase of the covalence character of M<sup>2+</sup> ions than Na<sup>+</sup> ion, this increase in the strength will cause shortening of the bonds and so the matrix is compacted as MO increase. The same results have been confirmed by density, molar volume, and hardness measurements.

**Key words:** chemical durability, mechanical properties, phosphate glass, IR spectroscopy**Introduction**

Compared with conventional glasses such as silicate glasses, phosphate glasses based on P<sub>2</sub>O<sub>5</sub> are technologically important materials, primarily due to their superior physical properties such as low glass transition temperatures, low optical dispersion and relatively high thermal expansion coefficients (El-Egili *et al.*, 2003; Xu and Day, 1990; Shin, 2004; Shin *et al.*, 1999). These properties make them useful for many applications, glass to metal seals are one of them (El-Egili *et al.*, 2003; Shin, 2004; Shin *et al.*, 1999). However, their relatively poor chemical durability makes them generally unsuitable for practical applications (Shin *et al.*, 1999; Yung *et al.*, 1997; Reidmeyer *et al.*, 1986). It was suggested Shin *et al.*, (1999) that the addition of one or more modifiers oxides, leads to improve the chemical durability of the modified phosphate glasses. The improved chemical durability is often accompanied by structure changes in the matrix tetrahedral groups as shown in Fig (1). Conversion of P-O-P bridging oxygens to P-O-M<sup>+</sup> non-bridging oxygens takes place, with the formation of Q<sup>2</sup> tetrahedral with two bridging and two non-bridging oxygen atoms Fig. (1). Thus the addition of alkali oxide to vitreous-P<sub>2</sub>O<sub>5</sub> results in the creation of non-bridging oxygens at the expense of bridging oxygens (Wazer, 1958). Recently, (Brow, 2000; Brow *et al.*, 1996; Brow and Tallant, 1997; Brow *et al.*, 1993) gave an excellent review on the structure of simple phosphate glasses by different spectroscopic techniques. They suggested a useful method for comparing the structure of phosphate glasses in terms of their respective O/P ratio.

**Fig. 1:** P-tetrahedral sites that can exist in phosphate glasses

In the present study, an effort is made to understand how the structure and strength of metaphosphate glasses are affected by the addition of alkaline earth oxide and CuO. Infrared absorption, density, molar volume, and Vicker's microhardness are the proper direct means of such investigation .

#### *Experimental:*

Analar grade chemicals  $P_2O_5$ ,  $Na_2CO_3$ , CuO, CdO, and ZnO were used to prepare the glass samples, having the composition  $(50 - x) Na_2O - 50 P_2O_5 - x MO$  (CuO, ZnO, and CdO) where  $x=0, 5, 10, 25$  mol %. The traditional melt and quenching method is adopted for samples preparation The melts were casted in an iron mould on an iron plate, and were immediately transferred to the annealing furnace at appropriate temperature depending on the glass composition then gradual self cooling to room temperature. Parts of the prepared samples were grind, the powder were sieved using 200 mesh sieves to be used for different purpose XRD, and IR. The glass samples were kept in a dissector to prevent possible reactions with moisture, and the amorphous state were checked by X-ray diffraction.

#### *2.1) Infrared measurement:*

Infrared measurements were done by using a Beckman 4250 IR spectrometer in the range  $(400-2000) cm^{-1}$ . IR spectra of powdered samples were carried out using potassium bromide (197mg potassium bromide to 3 mg of the sample) pellets for the elimination of errors caused by scattering.

#### *2.2) Density measurements:*

Density of the glass samples was determined by the Archimedes method using toluene as the buoyancy liquid and Sartrous balance measuring up to  $10^{-4}g$ . To avoid the effect of the difference in the atomic masses when replacing the different component among each other. The molar volume  $V_m$  for each glass sample was calculated using the formula:

$$V_m = [\sum M_i x_i] / \rho \quad (1)$$

Where

$V_m$  : is the value of the molar volume.

$M_i$  : is the molecular weight of the constituent oxides

$x_i$  : is the mole percent composition of the different constituent : and

$\rho$  : is the density value for each glass sample.

#### *2.3) Microhardness measurements:*

The microhardness of the glassy samples was determined using a microhardness tester of the type Shimadzu M, (Japan).

High polished flat parallel surfaces was necessary for indentation. Ten indentations were made and measured for each sample. After the first five indentations the sample was repositioned and the remaining five indentations were made for a new area. The measurements were carried out under normal atmospheric conditions at  $\approx 25^\circ C$ . The eye piece on the microscope of the apparatus allowed measurements with estimated accuracy of  $\pm 0.5 \mu m$  for the indenter diagonal . The appropriate loading for the studied groups were found to be 300 gm for duration of 15 sec. the microhardness value was calculated using the formula

$$H_v = A(P/D^2) \text{ kg/mm}^2 \quad (2)$$

where,

A: is a constant takes into account the geometry of the square based diamond indenter.

P : is the load in gm

D : is the average diagonal length in  $\mu m$ .

### *3 Results:*

#### *3.1) IR Results:*

The as measured IR spectra for the different studied glasses are shown in Fig (2). A representative example of a deconvoluted IR spectra is also shown in Fig(5) for samples containing CuO, ZnO or CdO.

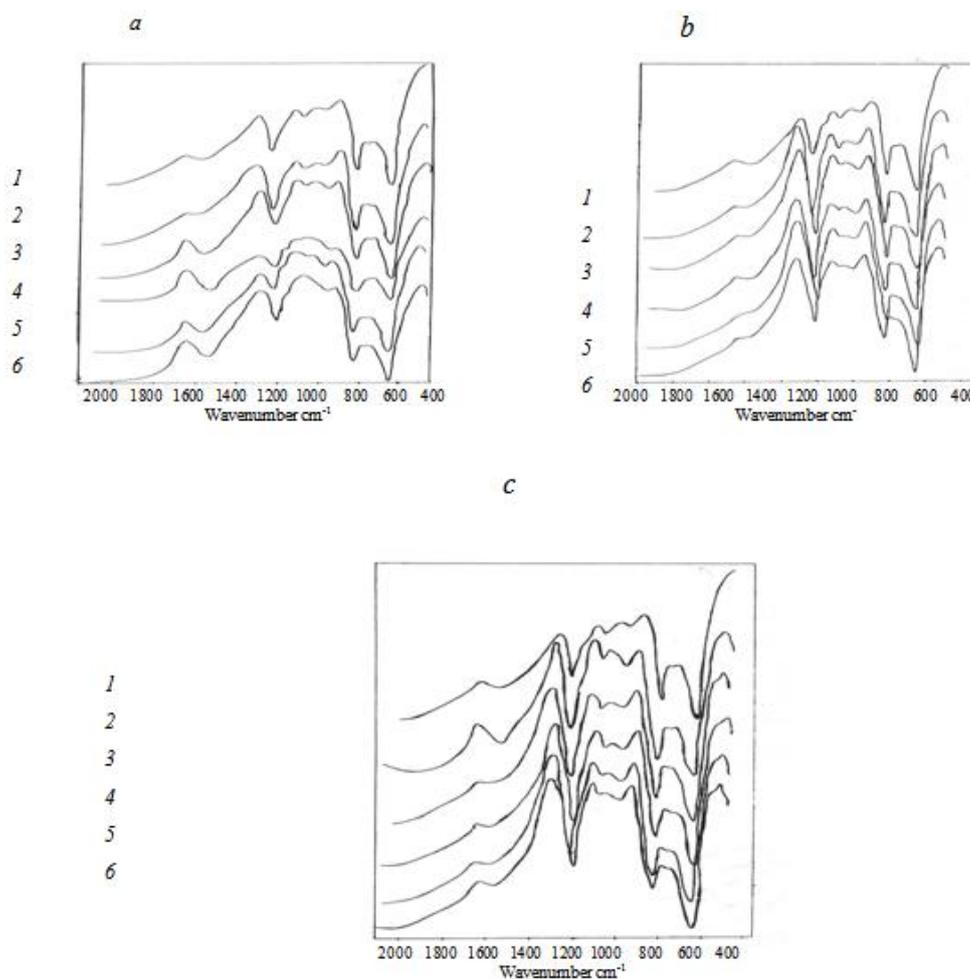
Inspection of the spectra for the three groups in Fig (2) show that these spectra are almost similar without any significant differences except a slight shift of bands position and sometimes changes in the relative intensities of the main bands.

Careful comparison of such spectra and trials following different propositions, based on informations predicted from previous studies (Shin *et al.*, 1998; Shin and Shin 1998; Chahine *et al.*, 2004; Brow *et al.* 1995; Meyer, 1997) leads to the following assignments shown in Table [1]

It is noticed that almost bands around 1000, 900, 750, and 420  $\text{cm}^{-1}$  are slightly shifted to higher wave number as  $\text{Na}_2\text{O}$  is replaced by any one of  $\text{CuO}$ ,  $\text{ZnO}$ , and  $\text{CdO}$ . On the other hand, the bands around 1100, and 1180, 1280  $\text{cm}^{-1}$  are shifted to lower wave number on replacing  $\text{Na}_2\text{O}$  by  $\text{CuO}$ . Also it is clear that the bands at 1000, and 1100  $\text{cm}^{-1}$  tend to overlap as  $\text{Na}_2\text{O}$  is replaced by  $\text{CuO}$  and become one broad band centered at 1050  $\text{cm}^{-1}$  for  $x=25$  mol %, with a noticeable increases in its intensity. Such overlapping changes are not observed on replacing  $\text{Na}_2\text{O}$  by  $\text{ZnO}$  or  $\text{CdO}$ .

**Table 1:** Assignments of the observed bands of the studied glasses

Band positions $\text{cm}^{-1}$	Suggested assignment	References
1640	Deformation vibration of free water	14
1280-1260	Asymmetric stretching vibration of P-O bonds in O-P-O groups ( $\text{PO}_2$ ) asymmetric in the $\text{Q}^2$ tetrahedra	12,13,14,15,16
1180	The symmetric stretching vibration. of P-O in ( $\text{PO}_2$ ) symmetric of $\text{Q}^2$ tetrahedra	12,13,14,15,16
1100	Assigned to P-O groups, the phosphate- non- bridging oxygen portion of $\text{PO}_4$ tetrahedra structure P-O asymmetric	13,14
1000	Symmetric stretching vibration. of P-O in $\text{PO}_4$ tetrahedra	13,14
880-900	Asymmetric stretching mode of P-O-P linkage	13,14
~ 750	Symmetric stretching mode of P-O-P linkage	13,14
400-500	Deformation mode of $\text{PO}_4$	13,14



**Fig. 2:** IR spectra of  $50\text{P}_2\text{O}_5-(50-x)\text{Na}_2\text{O}-x\text{MO}$  glass system where (MO a-  $\text{CuO}$ , B-  $\text{ZnO}$ , C -  $\text{CdO}$ )

$x = 0, 5, 10, 15, 20, 25$  mol% for samples (1-6) respectively.

• Finally it is clear that the IR spectra of the three groups are free from any of the characteristic absorption bands for CuO, ZnO, or CdO as network former (N.W.F) groups.

• The IR spectra of the three groups are free from any characterization band for P=O, the band which was always observed in many of the previous studies on phosphate systems (Hudgens *et al.*, 1998 ; Metwalli *et al.*, 2004) and is expected to appear at  $1380\text{ cm}^{-1}$

### 3.2) Density and Molar volume Results:

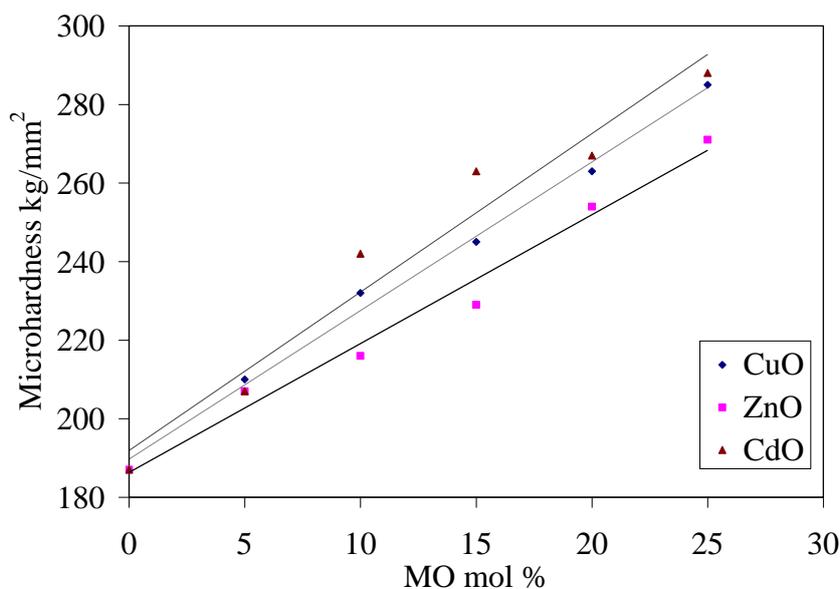
The experimentally determined density and the corresponding theoretically calculated values are given in Table [2]. It is clear that generally, The replacement of Na<sub>2</sub>O by any of the three studied oxides causes an increase in the density with the consequent decrease in molar volume.

### d) Hardness Results:

• Fig(3) represents the hardness of the three studied groups as a function of MO content. The values of the two hardness increase as MO content increase

**Table 2:** The experimental density , calculated molar volume, of the studied glasses and Vicker's microhardness value

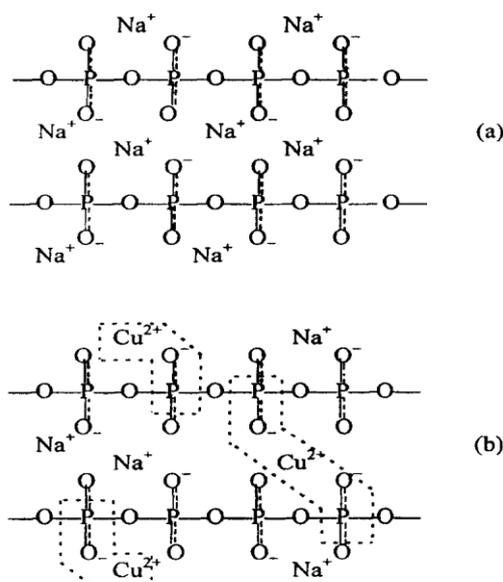
Composition % P <sub>2</sub> O <sub>5</sub> -Na <sub>2</sub> O-MO	.Density gm/cm <sup>3</sup>		Molar volume cm <sup>3</sup> /mol		Vicker's micro hardness kg/mm <sup>2</sup>
	Exp.	Theo.	Exp.	Theo.	
50- 50 - 0	2.304	2.447	41.67	44.25	187
50 - 45-5CuO	2.368	2.538	40.52	43.43	210
50 - 40 - 10	2.436	2.619	39.60	42.58	232
50 - 35 - 15	2.505	2.689	38.90	41.76	245
50 - 30 - 20	2.578	2.761	38.20	40.91	263
50 - 25 - 25	2.654	2.811	37.83	40.15	285
50 - 45- 5ZnO	2.366	2.528	40.72	43.50	207
50 - 40 - 10	2.428	2.587	40.16	42.79	216
50 - 35 - 15	2.493	2.655	39.40	42.07	229
50 - 30 - 20	2.561	2.704	39.14	41.33	254
50 - 25 - 25	2.631	2.758	38.73	40.60	271
50 - 45 - 5CdO	2.417	2.547	41.42	43.55	207
50 - 40 - 10	2.534	2.641	41.12	42.85	237
50 - 35 - 15	2.649	2.743	40.81	42.23	255
50 - 30 - 20	2.772	2.846	40.50	41.55	267
50 - 25 - 25	2.899	2.976	39.84	40.88	288



**Fig. 3:** The relation between MO mol % and microhardness of the three studied groups

## Discussion:

It is worthy remembering that, many previous studies using different techniques such as FTIR, Raman (Onyiriuk, 1993 and Gresch *et al.*, 1979) and neutron diffraction, Suzuki and Ueno, (1985) and Hoppe *et al.* (1996), suggested the absence of the P=O bond in these glasses. Neutron diffraction analysis also suggested the presence of two spectroscopically indistinguishable non-bridging oxygen on each phosphate tetrahedral instead of the P=O bond. As all of the present glasses studied are of meta-phosphate chemical composition as given in Table [2], it is thus normally observing the absence of the P=O characteristic bond of their IR spectra. Further the consequent suggested presence of the n.b.o can be considered to be realized by the bands observed at 1000, 1100  $\text{cm}^{-1}$  which are attributed to symmetric and asymmetric stretching vibration of P-O-. Again this is also suggested by Gresch *et al.* (1979) Fig (4) which indicate that on addition of the modifier oxides to  $\text{P}_2\text{O}_5$  the  $\pi$  bond the P=O group becomes distributed across the new non-bridging oxygen. Such delocalization of the  $\pi$  bonding on the  $\text{Q}^3$  tetrahedra as it interact with the modifier oxide is expected to result in strengthening of the other P-O bonds in the resulting tetrahedral as shown in Fig(4). The strengthening of the P-O bonds in the resulting tetrahedral is supported by the observed slight shift of their characteristic bands towards higher wavenumbers. Similar IR bands shift was also observed by Shin and Shin *et al.* (1998) and confirmed by Raman spectroscopic studied of some alkali phosphate glasses (Hudgens *et al.*, 1998). The shift towards lower wavenumber of both the asymmetric and symmetric vibration bands of  $\text{PO}_2$  at 1280, 1180  $\text{cm}^{-1}$  respectively, as  $\text{Na}_2\text{O}$  is replaced by  $\text{CuO}$  may be attributed to the role played by  $\text{Cu}^{2+}$  cations in crosslinking phosphate chains across  $\text{Q}^2$  tetrahedra. Chahin *et al.* (2004) expected that since phosphate chains interact more strongly with  $\text{Cu}^{2+}$  than  $\text{Na}^+$  due to the higher electronegativity of  $\text{Cu}^{2+}$  than that of  $\text{Na}^+$ , i.e, higher degree of covalency as shown in Table [3]. Thus the phosphate – oxygen bond linked to  $\text{M}^{2+}$  ions in P---O- $\text{M}^{2+}$  would be longer than the bonds in P-O---(Na) and causing the observed band shift to lower wavenumber.



**Fig. 4:** Schematic structures of sodium –copper –meta phosphate glasses (a) Binary sodium-metaphosphate (50- $\text{Na}_2\text{O}$ -50 $\text{P}_2\text{O}_5$ ) linear resonance chain structure and P-non-bridging oxygen bonds are marked by P---O, (b) Sodium ions are replaced in part by copper ions After Gresch *et al.*<sup>(21)</sup>

The decrease in the intensities of the two bands at 1100 and 1000  $\text{cm}^{-1}$  assigned as, asymmetric and symmetric P-O<sup>-</sup> in  $\text{Q}^1$  tetrahedra, as MO content increase may reveal increase in crosslink density as MO increase. This suggestion is supported by the analysis of the deconvoluted IR spectra of the different samples Fig.(5). As the area corresponding to P-O<sup>-</sup> in  $\text{Q}^1$  decreased with the increase of MO content as shown in Fig(4) indicates decrease in  $\text{Q}^1$  concentration. This is in agreement with the structural model suggested by Gresch *et al.* (1979) Fig(4b) which reveals that  $\text{M}^{2+}$  cations decrease the (n.b.o) and increase the crosslink density without breaking P-O-P chain.

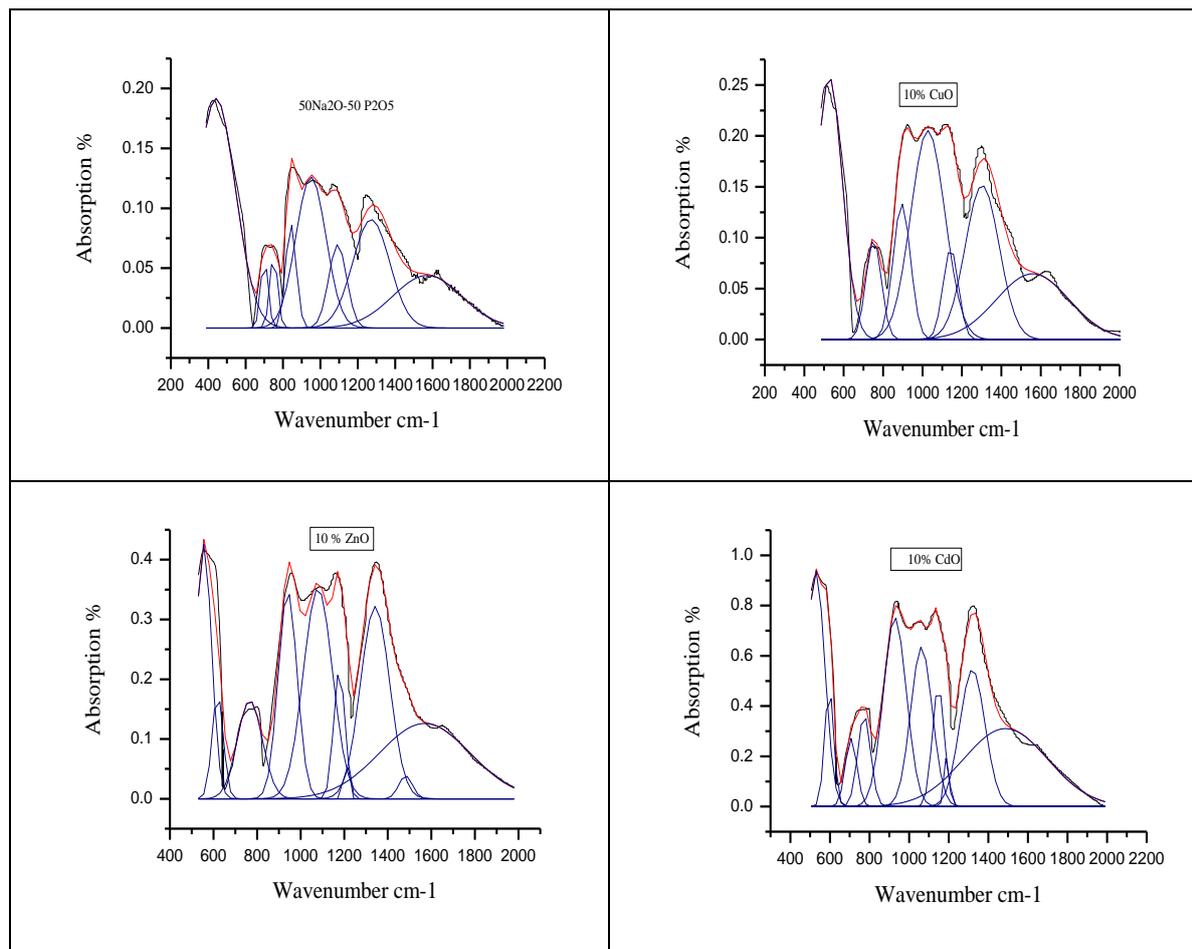
The above suggested increase in crosslinking as  $\text{Na}_2\text{O}$  is replaced by MO, is in agreement with the resulting compaction revealed from results of densities and molar volume given in Table [2]. Such compaction can be realized through one or more of the following factors:-

- Shortening of bond length as indicated by the observed shift in P-O-P asymmetric and symmetric vibrations at 880 and 750  $\text{cm}^{-1}$  respectively towards higher wavenumber.

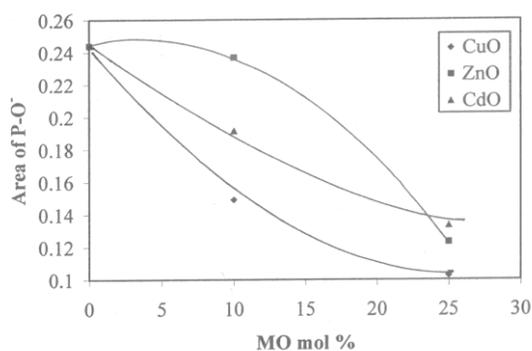
- The role of  $M^{2+}$  cations in crosslinking the phosphate chains, with the corresponding decrease in the concentration of n.b.o as illustrated in Fig(4b)

**Table 3:** The fractional bond character of the studied oxides according to either Pauling, (1960), and/or Hannay and Smyth depending on the electronegativity of the constituting ions.

Oxide	Pauling	Hannay and Smyth	Bond character
Na-O	0.82	0.65	Covalency ↓ ↑ Ionicity
Cd-O	0.69	0.49	
Zn-O	0.57	0.42	
Cu-O	0.53	0.39	



**Fig. 5:** Deconvoluted IR spectra for some studied samples containing (CuO, ZnO, or CdO)



**Fig. 6:** the relation between MO mol% and the area of P-O- in  $Q^1$  tetrahedra for the three studied groups

Further support for the suggested compaction factors is realized by the observed progressive increase in hardness shown in Table[2], for the hardness is a measure for the immobility of matrix elements suggested by Fen and Linzhang, (1980) from Viscosity measurements

#### Concolusion:

From the above the following can be concluded:-

- \* Absence of the P=O bond in these studied glass samples.
- \*\* The three divalent oxides (CuO, ZnO, or CdO) play the role of network modifier.
- \*\*\* Replacement of Na<sub>2</sub>O by MO increase the covalency of the P-O-P bonds and so enhance the strength of the studied glasses.
- \*\*\*\* As MO content increase n.b.o decrease.
- \*\*\*\*\* The suggested increase in the covalency of P-O-P bonds and the decrease in the n.b.o as MO increase enhance the density and hardness to increase and the molar volume to decrease.

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