# ME Spectroscopy and Magnetic Susceptibility Studies of Some Sodium-Boro-Phosphate Glasses Doped Two TMIs (Fe and Zn)

## A. M. Abdel_Ghany

*Basic Science Department, Faculty of Engineering Science, Sinai University, El-Arish, Egypt.*

***Abstract:*** *Some sodium-boro-phosphate glasses doped two transition metal cations (Fe, Zn) have been prepared. The effect of replacing $B_2O_3$ by $P_2O_5$ gradually from zero and up to 20 mol % in proportions of 5 mol % has been thoroughly investigated. The obtained ME spectra showed that three different iron states appeared and the obtained ME parameters of this states indicated that all $Fe^{2+}$ occupy the glass network former positions while all $Fe^{3+}$ occupy the glass network modifier positions. It was found that the gradual increase of $P_2O_5$ act to increase both experimental density and molar volume values while the single bond strength was found to decrease. The magnetic susceptibility values were found to increase as $P_2O_5$ was gradually increase also, which may be due to the increase of molar volume and $Fe^{3+}$ cations as well as the decrease of the single bond strength.*
***Keywords:*** *Glass,Magnetic Susceptibility, Mossbauer Spectroscopy, Density and Ion Density.*

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## I. Introduction:

Severalglass families are considered now as interesting solid materials and the attention of most researchers have been then paid to study their structural, physical, mechanical and chemical properties [1- 4]. It is known that, boro-phosphate glass family exhibit useful properties such as large glass-forming region, high thermalexpansion coefficient, low melting temperature and high UVtransparency ….etc. [3-4]. This glass family are also of various interesting uses and important applications, such as infrared transmittance, laser technology and electrolytes in solid stateelectrochemicalcells as well as in biomedical fields and as sealing glass [5-8].It is known also that glasses containing transition metal ions (TMIs) have the major importance in the field of glass science, since these ions affect directly their structure and properties [4, 5]. However, the addition of some TMIs into boro-phosphate glass network makes them also useful in the field of amorphous semiconductor.

On the other hand, glasses doped iron oxides have found important applications as catalysts, gas sensors, and magnetic materials….etc. Therefore the syntheses and characterizations of iron oxide containing glasses have been extensively studied [9].

However, in this article, some sodium-boro-phosphate glasses containing two TMIs (iron and zinc) will be prepared and thoroughly investigated. ME spectroscopy will be used to investigate the hyperfine structure of iron ions in the glass network. The magnetic properties will be also investigated and can be then correlated to the variations observed in the structure of iron cations. The density, molar volume and single bond strength will be also obtained, since they are used for calculating some glass parameters and physical constants as well as they can help to clarify the proposed discussion.

## II. Experimental:

Some boro-phosphate glasses containing constant amounts of sodium, zinc and iron oxides have been prepared. The molecular composition was selected to obey the following formula,

10 mol% FeO - 10 mol% ZnO - 20 mol% $Na_2O$ - (60-x) mol% $B_2O_3$- x mol% $P_2O_5$,

where x = 0, 5, 10, 15 and 20. Boric acid ($H_3BO_3$), ammonium dihydrogen phosphate (($NH_4$)$H_2PO_4$), sodium carbonate ($Na_2CO_3$) and ferrous oxalate ($FeC_2O_4$) were all used as sources for $B_2O_3$, $P_2O_5$, $Na_2O$ and FeO respectively, while zinc oxide was introduced as such.

The liquid displacementmethod was used for density measurements, where each sample was weighted in air ($W_a$) and toluene ($W_t$), and hence the experimental density ($\rho_{exp}$) was then be calculated by applying the following formula:

$$\rho_{\text{exp}} = \rho_t W_a / (W_a - W_t) \,(1)$$

where$\rho_t$is the density of toluene (0.863 g/cm$^3$). Then the empirical density values ($\rho_{emp}$) of the corresponding close packed structural compounds were also calculated applying equation (2),

$$\rho_{emp} = \sum x_i \rho_i \,(2)$$

where $\rho_i$ are the densities of the oxides forming a glass, and $x_i$ is the mole fraction of each oxide.

Both the experimental molar volume values ($V_{m.exp}$) and the empirical ones ($V_{m.emp}$) were calculated using equation (3 & 4) respectively,

$$V_{m.exp} = M_w / \rho_{exp} \quad (3)$$

$$V_{m.exp} = M_w / \rho_{emp} \quad (4)$$

where $M_w$ is the main molecular weight (g/mol) of a glass sample.

The average single bond strength ($B_{M-O}$) in a glass network was also calculated by applying Dimitrov and Komatsu formula [10-12],

$$B_{M-O} = xB_{A-O} + yB_{B-O} + zB_{C-O} + qB_{D-O} + (1-x-y-z-q)B_{E-O} \quad (5)$$

where x, y, z, q and (1-x-y-z-q) are the molar parts of each oxide in a glass sample.

A conventional constant acceleration Mossbauer spectrometer was used to investigate the role of iron ions in these glasses using 20 m Ci $^{57}$Co radioactive source in Rd matrix. The obtained ME spectra were analyzed using a computer program based on both Lorentzian and Gaussian line shapes. Such program has the facility to calculate the ME parameters like, isomer shift (IS), quadrupole splitting (QS) and line width (LW), for each iron structural state as well as the relative areas under each Mossbauer absorption peeks (A%). The analyses was carried out relative to a standard metallic iron calibration spectrum.

Gouymethod was early established to be a suitable tool for magnetic susceptibility measurements. In such experiment the powder of each sample was inserted in a thin silica tube of fixed length and constant cross sectional area. Such tube was suspended from one arm of an electric balance (with accuracy $10^{-4}$ gm) to be in between the poles of an electro-magnet. The system of measurement was adjusted such that the bottom of the tube must be in between the two poles and on the inter poles axis, where the maximum magnetic field intensity. The tube containing the powder sample was weighed when the magnet is on and when it was turned off, where the difference represents the effect of the magnetic pull.

## III. Results and Discussion:

### 1.1 Density and Molar Volume:

Density of solid materials is a simple property but it is of high interest. It can be used for example, as a factor for quality control during glass manufacturing. Also, density is an effective value that is used to calculate many physical constants and factors of such solid[2]. However, Archimedes technique was used here to measure the density of the studied glasses by applying equation (1),

On the other hand, when the structure of a solid material has been considered, molar volume was directly floated in mind, since it related directly to the internal spatial structure of such solid [2].

The dependence of the density, and molar volume values, on the $P_2O_5$ content of the studied glass system can be shown in Figure (1). From this figure, it appeared that, $\rho_{exp}$ values increased when $P_2O_5$ was gradually increased, which in turn refers that the structure becomes more open when $B_2O_3$ was gradually replaced by $P_2O_5$. On the other hand, $V_m$ increased when $P_2O_5$ was increased, such case may interpret to be due to:

➤ An increase in the average bond length (inter-atomic spacing) between atoms, since the ionic radius of boron ion is much lower than that of phosphorous ion.
➤ The decrease of the average bond energy between ions.
➤ The increase of the number of non-bridging oxygen atoms and hence the increase in the number of terminal oxygen atoms.
➤ The presence of $BO_4$ groups and B-O-P bridges that induce relatively high disordered ratio in the glass network structure.
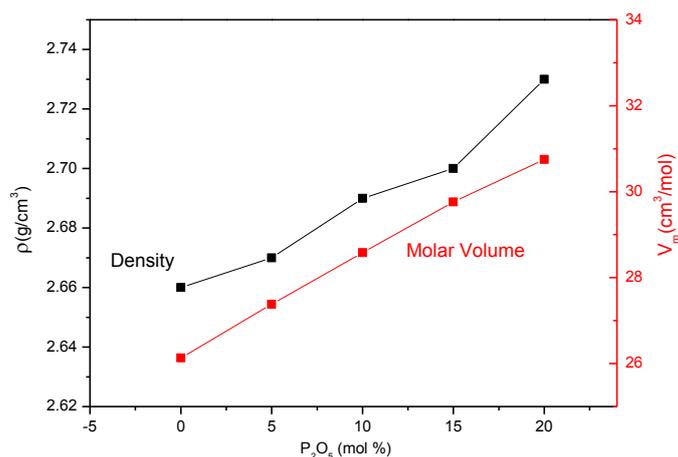
Fig. (1). Density and molar volume as a function of the $P_2O_5$ content.

In order to confirm the increase in the experimental values of both $\rho$ and $V_m$, the empirical ones were than calculated, and all the obtained values are listed in Table(1) together with these obtained experimentally for composition.

Table (1). Density ($\rho$), molar volume ($V_m$) and average bond length ($R$) for all samples

| $P_2O_5$mol% | 0 | 5 | 10 | 15 | 20 |
|---|---|---|---|---|---|
| $\rho_{exp}$(g/cm$^3$) | 2.66 | 2.67 | 2.69 | 2.7 | 2.73 |
| $\rho_{emp}$(g/cm$^3$) | 3.12 | 3.11 | 3.10 | 3.10 | 3.09 |
| $V_{m.exp}$ (cm$^3$/mol) | 26.13 | 27.38 | 28.58 | 29.76 | 30.75 |
| $V_{m.emp}$ (cm$^3$/mol) | 22.28 | 23.50 | 24.73 | 25.96 | 27.20 |
| $R$ (A) | 2.21 | 2.23 | 2.24 | 2.26 | 2.26 |

It is notice from Table (1) that:
1. The experimental density show gradual increase which may be due to the gradual replacement of $B_2O_3$ by $P_2O_5$ in the glass network, since $P_2O_5$ is of large molecular weight than $B_2O_3$ which increases the mean molecular weight of a glass sample.
2. Also, both experiment and empirical molar volume values show gradual increase.

According to the above mentioned factors, it can be stated that, the increase of both $\rho$ and $V_m$ are logically acceptable.
3. The higher empirical density values in comparison to the experimental ones and the lower empirical molar volume values in comparison to the experimental ones, can be taken as evidences to confirm the amorphous nature and randomness character of the studied glass samples.

**1.2 Single bond strength ($B_{M-O}$):**
The average single bond strength represents the energy of the chemical bonds in glasses. Based on Sun's fundamental condition of glass formation [13], Dimitrov and Komatsu proposed an approach for calculating the average single bond strength ($B_{M-O}$) for oxide glasses [10]. The values of the single bond strength for each simple oxide of the oxides composing a glass under study can be used here [11], taking into consideration the molar part of each oxide in the composition.
However Dimitrov and Komatsu equation [number (5)] will be applied here for calculating the average single bond strength of the studied glasses the following values for the corresponding individual oxides were used 133, 151, 54, 498 and 464 kJ/mol for FeO, ZnO, $Na_2O$, $B_2O_3$ and $P_2O_5$ respectively [11-12].

Figure (2) shows the variation of the single bond strength as a function of $P_2O_5$ where it appeared that, it decreased with increasing $P_2O_5$ content. This may be due to the fact that, the bond strength of $B_2O_3$ is larger than $P_2O_5$.
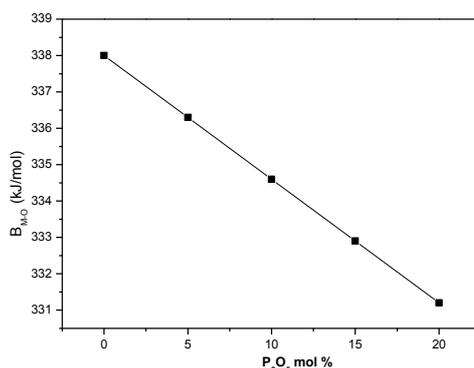


Fig. (2).The variation of single bond strength ($B_{M-O}$) as a function of the $P_2O_5$ content for the studied glasses.

### 1.3 Mossbauer Effect Spectroscopy:

It is known early that, ME spectroscopy represents an interesting tool for studying the hyperfine structure of iron ions in various solid materials [14]. It can be used to get information in many areas of science such as physics, chemistry, where it can gives very accurate characterization for the chemical, structural and magnetic properties of a material. It reflects also the hyperfine interactions between the iron atom and its environment throughout a solid material. Therefore ME spectroscopy has been employed here, and Figures 3 and 4 show the obtained ME spectra for the samples containing 5 and 15 mol% $P_2O_5$ respectively, as representative figures and all spectra show approximately similar behavior.
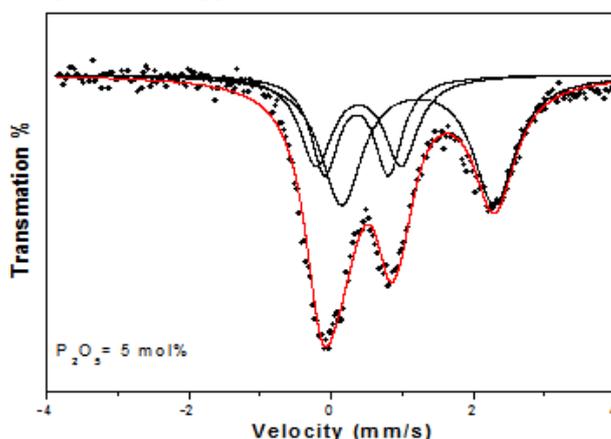


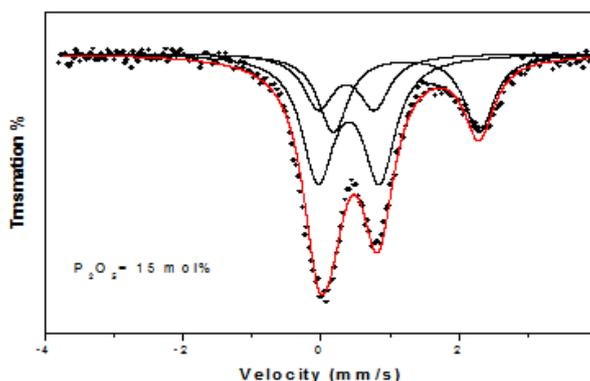**Fig. (3).** ME spectrum of the sample containing 5 mol% $P_2O_5$.



Fig. (4). ME spectrum of the sample containing 15 mol% $P_2O_5$.

All the obtained spectra exhibit three central asymmetric paramagnetic absorption peaks with different intensities, which referred to the absence of any magnetic phases throughout the network of all samples, that is all samples exhibit paramagnetic character.

The computer analysis and fitting of all the obtained ME spectra reviled that:

1. Three different central paramagnetic doublets are present and overlapped with each other in the same spectrum. These three doublets indicated that iron ions occupy three different structural states, and the obtained ME parameters are presented in Table (2).

**Table (2).** ME parameters of the studied glass as a function of $P_2O_5$ content.

| $P_2O_5$ mol% | IS (mm/s) | | | QS (mm/s) | | | LW (mm/s) | | | A% | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $Fe^{2+}O_4$ | $Fe^{3+}O_6$ | | $Fe^{2+}O_4$ | $Fe^{3+}O_6$ | | $Fe^{2+}O_4$ | $Fe^{3+}O_6$ | | $Fe^{2+}O_4$ | $Fe^{3+}O_6$ | |
| 0 | 1.19 | 0.32 | 0.40 | 2.07 | 0.90 | 1.3 | 0.65 | 0.47 | 0.53 | 32.3 | 25.7 | 42.0 |
| 5 | 1.20 | 0.37 | 0.42 | 2.08 | 0.90 | 1.27 | 0.64 | 0.49 | 0.53 | 30.8 | 24 | 45.2 |
| 10 | 1.22 | 0.36 | 0.42 | 2.08 | 0.84 | 1.26 | 0.63 | 0.50 | 0.52 | 29.9 | 20.4 | 49.7 |
| 15 | 1.22 | 0.35 | 0.40 | 2.08 | 0.80 | 1.26 | 0.62 | 0.52 | 0.52 | 29.2 | 20.1 | 50.7 |
| 20 | 1.24 | 0.34 | 0.37 | 2.09 | 0.76 | 1.18 | 0.62 | 0.55 | 0.50 | 28.0 | 20.0 | 52.0 |

2. Inspecting the values in Table (2), it appeared that, the first state of iron occupy a high distorted six coordinated $Fe^{3+}$ state, while the second state of iron occupy a low distorted six coordinated $Fe^{3+}$ state, but the third state of iron appeared in four coordinated $Fe^{2+}$ state.

3. However, it can be stated that, all the studied samples exhibits pure amorphous state (glassy solid phase) [18-19].

4. The analyses of all spectra and regarding the obtained ME parameters of all the analyzed sub-spectra, it can be stated that all ferric ions occupy the glass network modifier positions, while all ferrous ions occupy the glass network former positions.

The variation of IS and QS parameters as well as the relative area as a function of $P_2O_5$ content are exhibited graphically in Figures 5, 6 and 7 respectively.
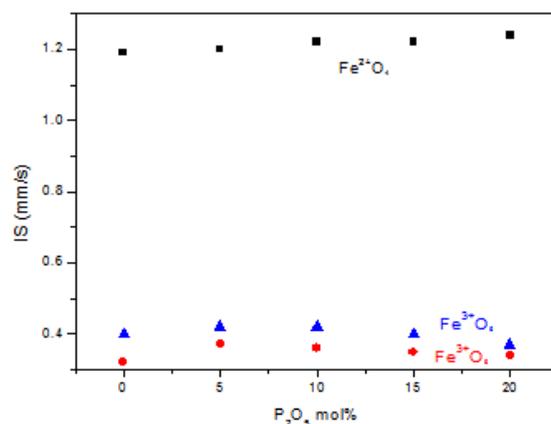


Fig. (5). The variation of the IS values as a function of $P_2O_5$ content, for the three iron states.
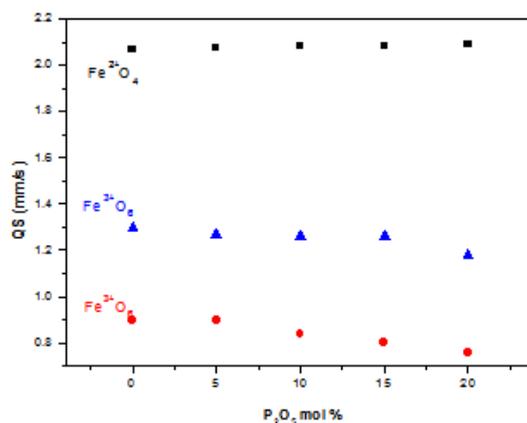


Fig. (6). The variation of the QS values as a function of $P_2O_5$ content, for the three iron state.

It can be seen that, both the values of the IS and QS of the ferrous states exhibit approximate stability. On the other hand the IS values of both ferric states fluctuated around 0.35 and 0.40 (mm/s) for the low- and high- distorted states, respectively, while the QS values show very slight decrease.
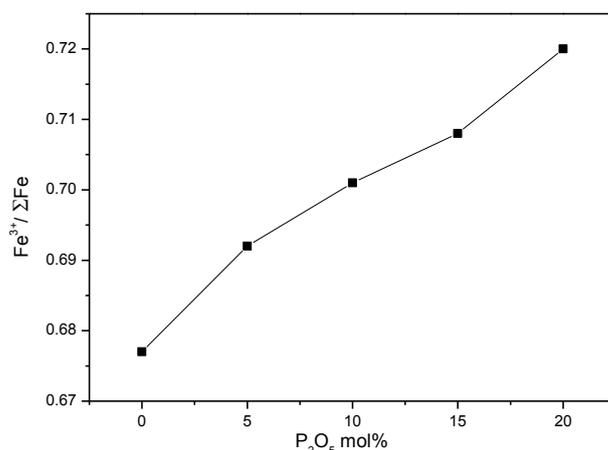


Fig. (7). The variation of the relative area of $[Fe^{3+}/\sum Fe]$ as a function of the $P_2O_5$ content.

Also, it was observed for all spectra of all samples that the value of the line width is much higher than the value of the natural line width (0.25 mm/s), which reflects the high level of randomness character and amorphous nature of the studied glasses [20-22].

From Figure (7), it is seen that, the relative area of $Fe^{3+}$ increased gradually as $P_2O_5$ was gradually increased, while that of $Fe^{2+}$ decreased. It is supposed that such behavior may be due to the variation of the number of oxygen and iron ion densities. However both the number of oxygen ion density as well as the number of iron ion density will be then calculated by applying equation (6) [23],

$$N = a\left[\left(\frac{\rho_{exp} X_i}{M_w}\right) N_A\right] \qquad (6)$$

where $a$ is the number of formula units, $\rho_{exp}$ is the experimental density of a glass sample, $X_i$ is the weight fraction of an elements in each sample, $M_w$ is the molecular weight of such glass sample and $N_A$ is Avogadro number.

The ratio of the number of oxygen ion density to the number of iron ion density was also obtained and all the obtained values are listed in Table (3).

Table (3). The number of oxygen and iron ion densities ($N$) for all samples.

| $P_2O_5$ mol% | 0 | 5 | 10 | 15 | 20 |
|---|---|---|---|---|---|
| N(O) $10^{21}$ (cm$^{-3}$) | 50.71 | 50.58 | 50.58 | 50.6 | 50.91 |
| N(Fe) $10^{21}$ (cm$^{-3}$) | 2.31 | 2.2 | 2.11 | 2.02 | 1.96 |
| N(O)/N(Fe) | 22.0 | 23.0 | 24.0 | 25.0 | 26.0 |

**1.4 Magnetic Susceptibility:**

The magnetic susceptibility measurements of the studied glasses were carried out using one tesla electromagnet at room temperature. Figure (8) shows the change in the mass ($\Delta m$) as a function of the square value of the applied magnetic field intensity ($H^2$), where $\Delta m$ was found to increase gradually and linearly as $H^2$ was increased. The slopes were then calculated and equation (7) was also applied to compute the volume magnetic susceptibility of all glasses. The mass- and molar- magnetic susceptibilities were also calculated using equations (8, 9) respectively [24].

$$k = (2g/A)slope \qquad (7)$$
$$M = k/\rho_{exp.} \qquad (8)$$

$$\phi = k \ / V_{m \ exp} \qquad (9)$$

where $g$ and $A$ are the acceleration gravity and the cross sectional area of the used tubes.

All the obtained values for all the studied glass samples are presented in Table (4).

Table (4). The obtained magnetic susceptibility parameters for all the studied glasses.

| $P_2O_5$mol% | $k10^{-5}$ | $M10^{-5}(cm^3/g)$ | $\phi10^{-5}(cm^3/mol)$ |
|---|---|---|---|
| 0 | 0.104 | 0.039 | 2.722 |
| 5 | 0.117 | 0.044 | 3.215 |
| 10 | 0.130 | 0.048 | 3.707 |
| 15 | 0.139 | 0.051 | 4.124 |
| 20 | 0.154 | 0.056 | 4.731 |

It appeared that the oxygen molar volume increased with respect to iron and such increase act to oxygen iron from $Fe^{2+}$ to $Fe^{3+}$.

Figure (9) indicate that, the molar magnetic susceptibility increased as $B_2O_3$ was gradually replaced by $P_2O_5$ which may be due to the transformation of $Fe^{2+}$ to $Fe^{3+}$ as drown from ME analyses. Also, the introduced phosphorus act to form some layer and chain phosphate structure.
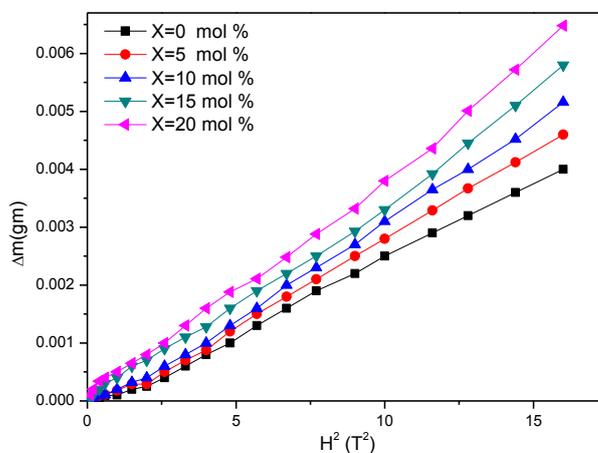


Fig. (8). Thevariation of the mass difference ($\Delta$m) versus the magnetic field intensity ($H^2$) for all glasses.
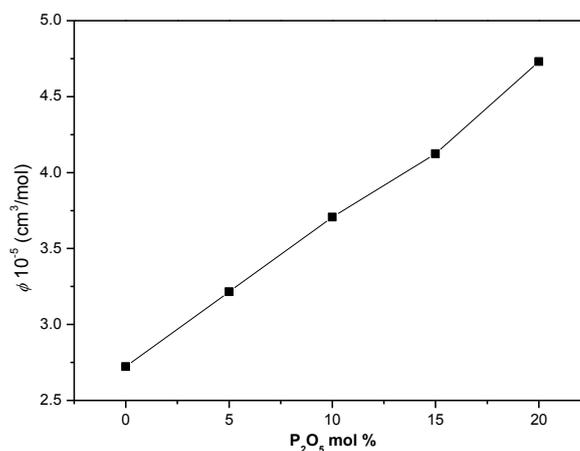


Fig. (9). The variation of the molar magnetic susceptibility ($\phi$) as a function of the $P_2O_5$ content.

Inspecting the values in Table (4) and the variation of the molar magnetic susceptibility with $P_2O_5$ content (as exhibited in Figure (9)), it is notice that, all the magnetic susceptibility values increased gradually with the gradual replacement of $B_2O_3$ by $P_2O_5$. But since this is not the effective reason for such increase, therefore the following effects can be proposed:

i. The gradual increase of the molar volume values which means that the network structure becomes open which in turn act to permit the orientation of the present iron cations, which was found in agreement with the data presented in ref. [24].

ii. The gradual decrease of the single bond strength of the studied glasses, that act also to open the glass structure and act to permit the orientation of iron in the glass network.

iii. The gradual increase of the relative ratio of ferric to total iron ($Fe^{3+}/\sum Fe$) since $Fe^{3+}$ is of higher magnetic moment.

It can be stated that all the above mention effects act to increase the magnetic susceptibility values, and all these effects are presented graphically in Figure (10).
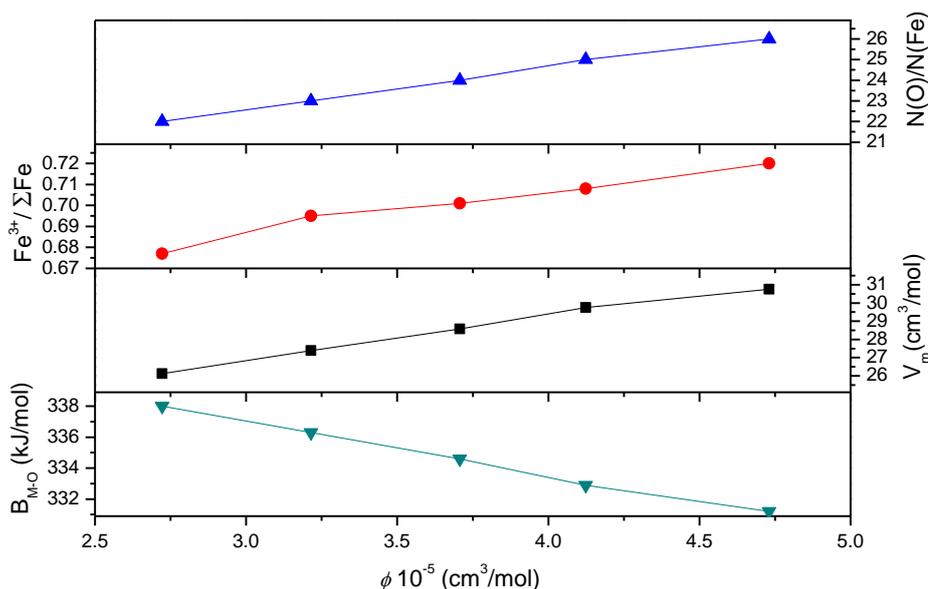


Fig. (10). N(O)/N(Fe), relative area of [$Fe^{3+}/\sum Fe$ ], molar volume ($V_m$) and single bond strength ($B_{M-O}$) as a function of molar magnetic susceptibility ($\phi$) for the studied glasses.

## IV. Conclusion

Some sodium-boro-phosphate glass containing two TMIs (Fe and Zn) have been prepared and investigated by measuring density, ME spectra and magnetic susceptibility as well as by calculating the empirical density, molar volume and the average bond strength of all glasses. According to the obtained results and the proposal discussion, it can be concluded that:

1. The broadening of the LW values of all ME spectra indicated the amorphous nature and the randomness character of the studied glasses.

2. The comparison between the experimental and empirical values of both density and molar volume values confirm also the homogenies glassy state of the studied samples.

3. It was confirmed by ME parameters that all $Fe^{2+}$ act as glass network former while all $Fe^{3+}$ act as glass network modifier.

4. As $P_2O_5$ increased gradually replacing $B_2O_3$, $Fe^{2+}$ change gradually to $Fe^{3+}$.

5. Both the experimental density and molar volume values increased with the gradual increase of $P_2O_5$.

6. The calculated average single bond strength decreased gradually with the increase of $P_2O_5$.

**7.** It is concluded also that some parameters act to increase the magnetic susceptibility values such as the increase of the molar volume, the gradual increase of $Fe^{3+}$ cations, the gradual increase of the number of oxygen to the number of iron ratio and the decrease of the average single bond strength of these glasses.

## References:

[1]. T. Nishida, J. Non-Cryst. Solids, 108 (1989) 87.
[2]. S. A. El-badry, Al-Azhar bull.Sci., 16(2) (2005) 1.
[3]. Praveen Jha, Satwinder Singh Danewalia, Gaurav Sharma and K. Singh, J. Mater. Sci.& Engineering, 86(C)(2018) 9.
[4]. Young_Seok Kim, Won_Gyu Choi, and Bong_KiRyu, Glass Phys. Chem., 40(4) (2014) 408.
[5]. G. I. Patronov, I. P. Kostova, D. T. andTonchev, Bulgarian Che. Comm., 49(A) (2017) 40.
[6]. P. Pascuta, G. Borodi, N. Jumate, I. Vida-Simiti, D. Viorel and E. Culea, J. Alloys Compounds, 479(14) (2010) 504.
[7]. U. Hoppe, J. Non_Cryst. Solids, 195 (1996) 138.
[8]. J. M. Clinton and W. W. Coffeen, Am. Ceram. Soc. Bull., 63(11) (1984) 1401.
[9]. MarijanGotic and Svetozar Music, J. Molecular Structure, (834–836) (2007) 445.
[10]. V. Dimitrov, T. Komatsu, Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B, 46 (2005) 521.
[11]. V. Dimitrov, T. Komatsu, J. Uni. Chem. Tech. &Meta., 45 (2010) 3.
[12]. T. R. Tasheva and V. V. Dimitrov, Bulgarian Chemical Communications, 49(G)(2017) 43.
[13]. K. H. Sun, J. Am. Ceram. Soc., 30 (1947) 277.
[14]. M. Villa, M. Scogliolti and G. Childeli, J. Non-Cryst. Solids, 94 (1987) 101.
[15]. A. G. Mostafa, M. A. Salem and Z. A. El-Hadi, J. Mater. Sci. Tech., 18(5) (2002) 391.
[16]. F. Abdel-Wahab, A. G. Mostafa, A. E. Belal and E. M. El-Agwany, Mater. Chem. Phys., 93 (2005) 243.
[17]. A. M. Abdel-Ghany, T. Z. Amer, A. A. Bendary, A. G. Mostafa, J.Nuclear& Particle Phys., 5(6) (2015) 101.
[18]. Hossam M. Gomaa, J. Non-Cryst. Solids, 481(2018) 51.
[19]. S. Sindhu, S. Sanghi, A. Agarwal, V.P. Seth, N. Kishore, J. Spectrochim. Acta A, 64 (2006) 196.
[20]. M.Y. Hassaan, M.M. EL-Desoky, S.M. Salem, S.H. Salah, J. Radoanal. Nucl. Chem. 290(3) (2001) 595.
[21]. T. Nishida, J. Non-Cryst. Solids 177 (1994) 257.
[22]. N. Hadj Youssef, M. S. Belkhiria, J. J. Videau and M. Ben Amara, J. Mater.Lett., 44(5)(2000) 269.
[23]. A. M. Abdel-Ghany, IOSR J, Applied Phys., 10(3)(2018)66.
[24]. A. M. Abdel-Ghany, Al-Azhar bull. Sci., 29(1) (2018) 1.