
STUDY OF THE STRUCTURE AND SOME PHYSICAL PROPERTIES OF IRON MOLYBDENUM PHOSPHATE GLASSES.

W. M. EL-MELIGY, S. M. EL-MOSSALAMY AND H. ELGOHARY*

Physics Dept., Faculty of Science, Al-Azhar University (Girls Branch), Nasr City, Cairo, Egypt.

** Physics Department, Faculty of Science, King Abdul Aziz University, Jeddah, Sudi Arabia.*

Abstract

Structural Studies of iron molybdenum phosphate glasses were carried out using infrared (IR) radiation, density, Vicker hardness measurements and conductivity. Fe_2O_3 concentration ranging from 2.5 to 15 mol% was introduced at the expense of MoO_3 content. The measurements have shown that molybdenum participates predominantly in the six fold coordinated (MoO_6) and four fold coordinated (MoO_4), iron participates also in tetrahedral (FeO_4) and octahedral (FeO_6) concentrations. Small amount of (PO_2) and/or (PO_3), (PO_4) groups are also present in the network former position. The increase in the Fe_2O_3 content lead to the formation of covalent bond between the non bridging oxygen (NBO) ions and iron ions to form (P-O-Fe) units as well as to increase the (MoO_4) groups.

Gradual increase in density, Vicker hardness and number of oxygen ions density are observed with the increase of Fe_2O_3 concentration. There is a proportional relation between the molar volume and electrical conductivity.

Introduction

Molybdenum containing glasses posses a variety of specific features which arouse interest in view of their applications. It is known that MoO_3 adds semiconductor properties with n-type conduction. MoO_3 containing glasses are also used for the development of optical and radiation glasses and crystalline glass materials. There are very reported studies concerning structural details for molybdenum containing iron glasses⁽¹⁻⁴⁾. The density of a material is an important property to understand and make a quality control of commercial glass manufacturing. Density is an intrinsic property, which relates directly to the structure and other properties of the material.

The present paper contains the results of studies of structure and some of physical properties of MoO_3 - P_2O_5 as a function of Fe_2O_3 concentrations by IR techniques, Density, molar volume, hardness measurements and electrical conductivity.

Experimental:

A glass system was prepared according to the formula 20 mol% P_2O_5 , (80-x) mol% MoO_3 and x mol% Fe_2O_3 where x= 2.5, 5.0, 7.5, 10.0, 12.5 and 15. The homogeneous mixture was melted in porcelain crucible at 1000°C for 2 hours and the melt was quenched in air at room temperature (R.T). The (IR) measurements were carried out using Parken Elmer spectrometer, using Fourier transform infrared (FTIR) model RTX with a resolution of 2 cm^{-1} . The IR- absorption spectra were recorded at room temperature applying KBr disk method in the range $400\text{--}4000\text{ cm}^{-1}$

The density of the glass samples was measured at RT using Archimede's technique, which is the most convention used method to accuracy up to $\pm 0.001 \text{ gm/cm}^3$.

Shimadu micro hardness tester type M was used for indentation testing of the glass samples, with parallel and highly polished surfaces. Two samples were examined for each composition. The identification diagonals lengths were measured in micron with estimated accuracy of $\pm 0.5 \mu\text{m}$. At least ten indentations over area of 1 cm^2 were made and measured for each sample. A load of 100 gm was used for indentation keeping the time of indentation of 10 sec in all samples. The micro hardness values (H) was calculated using the formula:

$$H = A(P/d^2) \text{ gm/mm}^2$$

Where A is a constant, that depends on the indenter geometry, equals 1.845 for the used indenter, P is the applied load and d is the average diagonal length.

Results and Discussion:

IR measurements:

Figs. (1a, b) shows the IR spectra of the base glass sample as well as the 20 mol% P_2O_5 , (80-x) mol% MoO_3 and x mol% Fe_2O_3 where x= 2.5, 5.0, 7.5, 10.0, 12.5 and 15 respectively. It can be observed that the intensities of IR band in the region $4000\text{-}1450 \text{ cm}^{-1}$ given evidence that very small contents of water or OH-groups are detected in these samples which have no effect on the structure ⁽⁵⁾. The amount of water present in the samples ia attributed to the intake of water from air moister during preparation of KBr pellets for infrared measurements. Table 1 shows the visual estimation of the band position in the studied glasses.

Table (1): Visual estimation of the band position in the studied glasses.

Iron Content (mol%)	Wave number (cm^{-1})
2.5	508, 650)sm.b, (873,979)v.st.br., (1300)sh, (1457, 1516,1650)m.b(
5.0	(521,625)sm.b, (866,986)v.st.br., (1031,1300)sh, (1457, 1540, 1735)m.b.
7.5	(468)sm.b, (551)sh., (864,972, 1031)v.st, (1300)sh, (1391, 1463, 1540, 1646)m.b
10.0	(488)sm.b., (567)sh, (899.984, 1044)v.st,(1365, 1475, 1600)m.b.
12.5	(488, 567)sm.b., (855. 986, 1041)v.st.b., (1535, 1629)m.b.
15.0	(501)sm.b., (597,694)sh, (815, 959, 1097)v.st.b., (1450, 1627)m.b.

Letters key: m- medium, st- strong, v- very, sh- shoulder, m- medium, sm- small, b-band and br- broad.

From these Fig.1b and table 1, it can be observed the presence of absorption bands which at 508, 650, 873, 979 and 1300 cm^{-1} for the sample with 2.5 mole% Fe_2O_3 , the same bands are observed are present for all samples but with different intensities and small change in band position and appearance a new bands at 1031 cm^{-1} for the samples containing iron oxide $> 2.5 \text{ mol}\%$ and the band at $\sim 486 \text{ cm}^{-1}$ for the glass containing

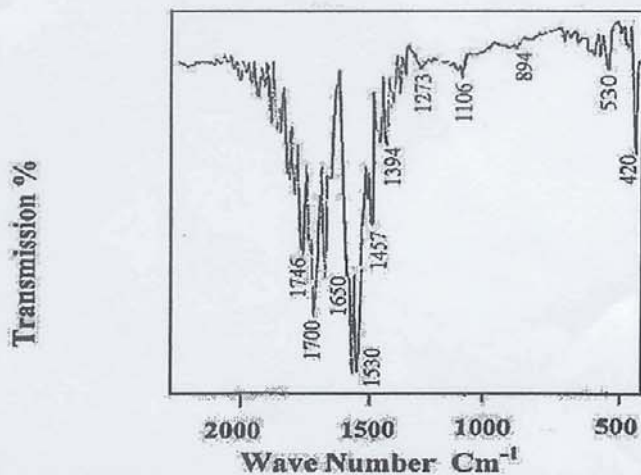


Fig.1a: Infrared spectra of sample glass (80 mol% MoO₃ and 20 mol% P₂O₅).

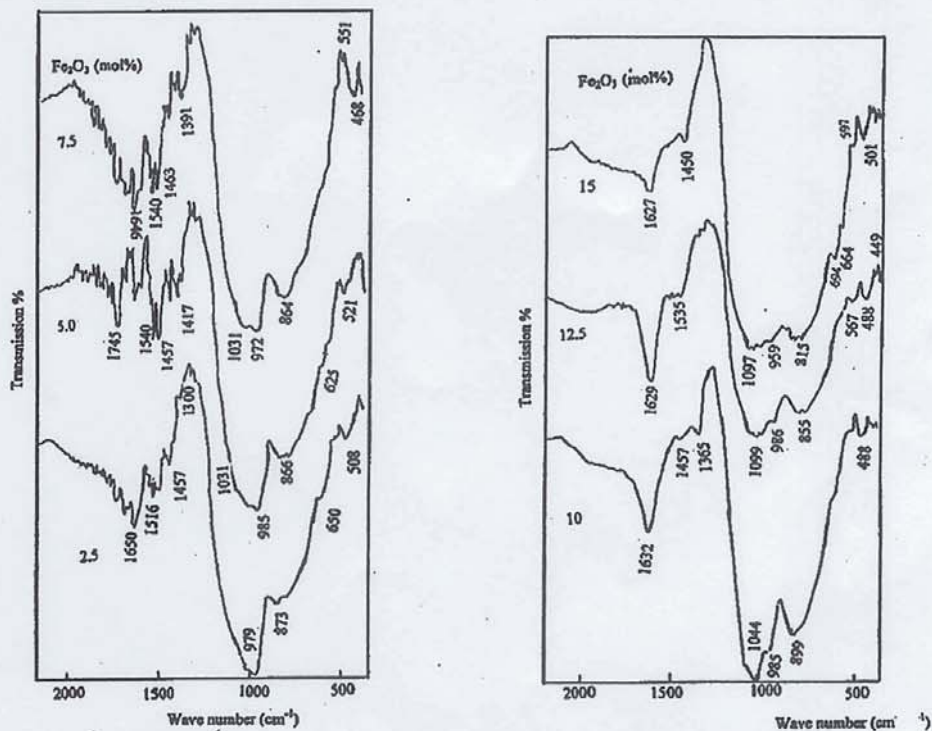


Figure 1b: Infrared spectra of these glasses with different iron contents.

> 5.0 mol%. The fundamental bands of frequencies between 899- 855 cm^{-1} are assumed Iron oxide >5 mol %. The fundamental bands of frequencies between 899 - 855 cm^{-1} are assumed to be the result of activation of vibrations of Mo-O bonds in disordered MoO_4 groups ^(6,4). The strong and broadening in these bands that at 873 and 973 cm^{-1} indicated the formation of a series of complexes with more than one Mo=O bond having vibration frequencies close to each other, so these overlapping bands cannot be resolved. The bands range from 694 to 551 cm^{-1} are characteristic vibrations of FeO_4 groups in these glasses, while the bands that are at 521 to 468 cm^{-1} are due to FeO_6 ⁽⁷⁾. The band at 979 cm^{-1} is shifted to 985 cm^{-1} this band is probably due to the vibration of a short Mo=O bond of deformed MoO_6 groups ⁽³⁾. The band at 815 cm^{-1} is assigned to the anti-symmetric stretching vibration of a Mo-short O long Mo bridge associated with MoO_6 octahedral having Mo=O bond ⁽⁷⁾. The band at 650 cm^{-1} is attributed to bending vibration of FeO_4 ^(8,9) or is assigned to bending modes of the PO_4 groups ⁽¹⁰⁾. The absorption band observed at 508 cm^{-1} is assigned to vibration of FeO_6 ⁽⁴⁾. The band at 1300 cm^{-1} is assigned to asymmetric vibration (ν_{as}) of P-O bonds in O-P-O, i.e., [P=O] in phosphate chains (PO_2), this absorption band is typical of meta phosphate chains ^(11,12). The shoulder band at 1031 cm^{-1} is assigned to P-O⁻ (NBO, non bridging oxygen) stretching vibration of PO_2^- terminal groups (chain terminator) ^(11,13) and /or ν_{as} (PO_3)³⁻ groups (chain end groups). The band at 1031 cm^{-1} is shifted to 1044 cm^{-1} at 10 mol% the iron content . Such shift can be discussed in terms of the formation of covalent bond between the NBO ions and the iron ions to form P-O-Fe units ^(11,14).

Density, Molar Volume, Hardness, and Number of Oxygen ions density Results:

The change in Density (D), Molar Volume (M.V), Hardness and Number of Oxygen ions density Results as a function of iron content in these glasses (table 2) and (figures 2,3&4) are suggested to explain the following structure changes through the formation or the modification process in the glass network.

Table 2: Density, Molar volume, Number of oxygen ions density and hardness of these glasses as a function of iron content.

Fe_2O_3 Mol%	D (gm/cm^3)	M.V (cm^3/mol .)	No.of oxygen ion density $\times 10^{21}$	Hardness Kgm/mm^2
2.5	3.14	45.913	44.7535	74.019
5.0	3.15	45.895	44.7989	75.789
7.5	3.61	40.075	51.2320	248.431
10.0	3.68	39.455	52.1120	267.613
12.5	3.79	38.395	53.5528	295.080
15.0	3.74	38.932	49.7452	294.423

From fig.(2,3&4) it is observed that the density of these glasses and the oxygen ions density increases with the increase of iron oxide content from 2.5 to 15 mol% on the expense of molybdenum oxide. This can be attributed to the introduction of

iron cat ions which tend to occupy interstitial sites within the glass network and has greater mass (159.611 a.m.u) than that of molybdenum atom (143.937 a.m.u). So that the increase of the mass of the glass is greater than the increase in its volume. The slight increase of the density for 2.5 and 5 mol% iron oxide can be attributed to slight increase of the degree of bridging corresponding to slight change of the glass network structure. While the large increase in iron oxide content from 5 to 15 mol% can be attributed to an increase of the degree of bridging correlated with a change of the glass matrix (into a three dimensional network structure) which was composed of MoO_6 and MoO_4 tetrahedral instead of MoO_6 only this results consistent with IR result. The large increase in density in this region can be attributed also to the formation of more closed packed structure as a result of the increase of Mo^{4+} ions and also as a result of the interaction of Fe^{3+} with the isolated Mo-O and P-O bonds as can be seen from the change in the intensity and the frequency of the IR stretching band of the Mo-O and P-O.

Fig.4 represents the effect of Fe ion concentration on the O- ion density, where it was found that O- ion density increase with the gradual increase of Fe ions concentration and then decrease again at high iron concentration. This indicated that there is a gradual change in the structure of the glass net work as Fe_2O_3 was gradually increased due to the change in the O-ion density. Thus these results main that polarons become able to hop easily ⁽¹⁶⁾ between Mo and Fe ions at high iron concentration while it become slowly at low iron content. The changes in hardness and density reflect an increase in the structure condensation, increase in bond strength and decrease in flow mobility as will be seen in the electrical conductivity.

Electrical conductivity results

Table 3 and figure 5 showed the electrical conductivity measured at room temperature as function of Fe_2O_3 concentration.

Table 3: Electrical conductivity data of the glasses.

Fe_2O_3 mol%	$\sigma \Omega^{-1} \text{cm}^{-1} \times 10^{-3}$
2.5	7.3800
5.0	8.6731
7.5	4.8661
10.0	4.2589
12.5	5.2457
15.0	6.8863

The decrease in conductivity in the addition of 7.5 and 10 mol% Fe_2O_3 indicates a decrease in the mobility of Mo^{5+} and Fe^{3+} ions which can be attributed to the formation of compact structure and isolated molybdenum ions as can be seen from the IR, density and hardness results. The increase again in the conductivity on the addition of 12.5 and 15 mol% Fe_2O_3 can be attributed to the increase in the number of paramagnetic ions as Effect and ESR measurements ⁽¹⁷⁾ and hence an increase in the hopping mechanism between Fe^{3+} & Fe^{2+} and Mo^{5+} & Mo^{6+} .

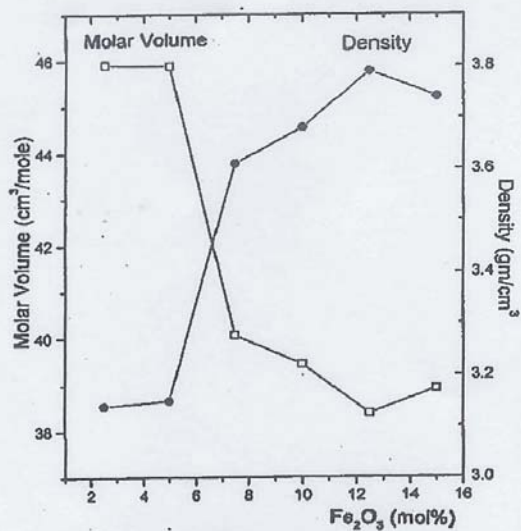


Fig.2. Molar Volume and density versus Fe₂O₃ content.

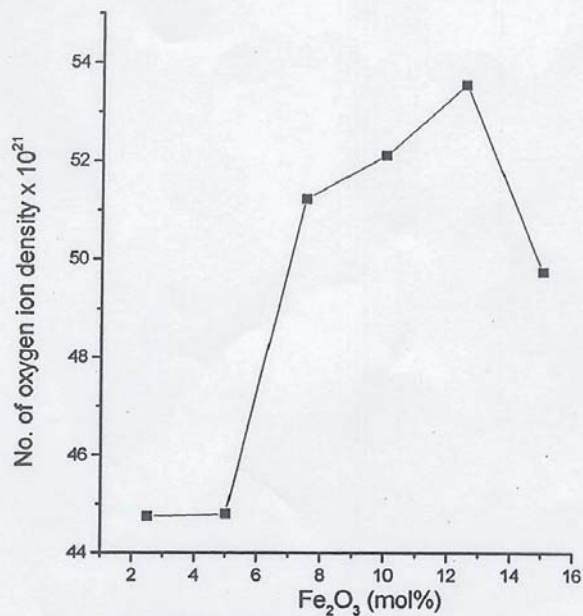


Fig.3: Relation between No. of oxygen ion density and Fe₂O₃ contents.

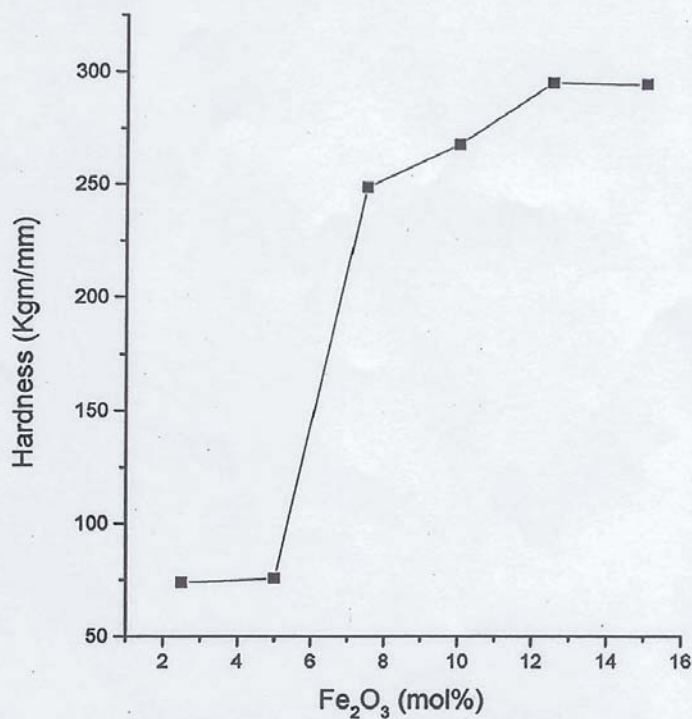


Fig.4: Relation between Hardness and iron contents in these glasses.

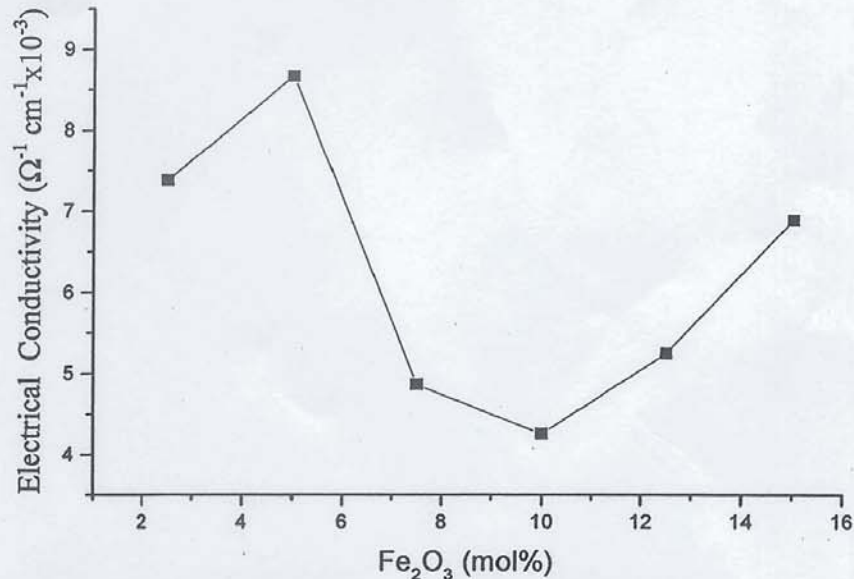


Fig.5: relation between Electrical conductivity and iron contents in these glasses.

Conclusion

The measurements have shown that the structural net of these glasses consist mainly of MoO₆, MoO₄, PO₂, PO₃, FeO₄ and FeO₆. The increase of Fe₂O₃ concentration in the composition led to the formation of covalent bond between the NBO ions and iron ions to form P-O-Fe units, as well as an increase in MoO₄ groups.

This increase up to 10 mole% led to a decrease in the conductivity due to the formation of compact structure. More increase than 10 mol% led to an increase again in the conductivity due to an increase in the hopping processes between Fe²⁺ & Fe³⁺ and Mo³⁺ & Mo⁶⁺.

References

1. N.M.Bobkova, I.L.Rakov and N.P.Solovie, J.Non Cryst.Solids, 111,98(1989).
2. R.Iordanova, Y.Dimitriev, V.Dimitrov, S.Kassabov and D.Klissurski, J.Non. Cryst. Solids, 231, 227(1998).
3. R.Iordanova, V.Dimitrov, Y.Dimitriev and D.Klissurski, J.Non Cryst. Solids, 180, 58(1994).
4. R.Iordanova, Y.Dimitriev, V.Dimitrov and D.Klissurski, J. Non Cryst. Solids,

- 167,74(1994).
5. K. Marinaga, Y.Suginohara, Y.Yanagase, J. Jpn.Inst. Met., 40, 775 (1976).
 6. W.Jeitschko, W.Sleight, W.Mc.clellan, J.Weither, Acta crystallogr. B.32, 1163(1976).
 7. I.Beattie, T.Gilson, J.Chem.Soc.A, 2322(1969).
 8. A.A.Sattar, A.H.Wafik and E.M.El-Sayed, Phys.State Sol. (a) 186, No.3, 415(2001).
 9. T.Nishida, M.Suzuki, S.Kubuki and M.Katata, J.Non Cryst.Solids, 194,23(1996).
 10. B.Bridge and N.D.Patel, J.Non Cryst.Solids,91,27 (1987).
 11. M.Abid, M.Et.tabirou and M.Taibi, J.Materials Science and Engineering B97, 20(2003).
 12. A.Shaim, M.Et-Tabirou, L.Montagne and G.Palavit, J.materials Research Bulletin, 37, 2459 (2002).
 13. T.Jermoumi, M.Hafid, N.Niegish, M.Mennig, A.Sabir and N.Toreis, J.Materials Research Bulletin,37, 49(2002).
 14. R.F.Bartholomey, J.Non Cryst. Solids, 7,221(1972).
 15. H. Mori, H. matsuno, H. Sakata, J. Non Cryst. Solids, 276, 78 (2000)
 16. F. Abdel- wahab, M. S.Aziz,A.G.Mostafa and D.M.Ahmed, J. Materials Science and Engineering B, 134, 1 (2006).
 17. N.A.Eissa, S.M.ELMossalamy, W.M.El-Meligy and H.A.Sallam, J. physics and chemistry of Glasses, Vol. 47,No.6,665 (2006).