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Moessbauer Effect and Infrared Study of Some Borate Glass Containing Mn and Fe Oxides

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ABSTRACT

Lithium borate glasses containing transition metals appeared now of very high technological and scientific interest. Therefore some lithium borate glasses containing mixed transition metal ions (manganese and iron) were investigated. The glass batches were melted at 1250 ^{o}C for three hours and annealed at 350 ^{o}C -over night- to obtain strain free glasses. Mossbauer Effect spectroscopy and Infrared analysis were employed to investigate the structural changes due to the change of their batches composition. Differential thermal analysis, magnetic susceptibility, density and molar volume measurements were also performed to study the effect of changing both manganese and iron oxides at the expense of boron oxide on these properties. Infrared analysis indicated the presence of different structural groups such as BO_3, BO_4, FeO_4 and MnO_6 as well as different vibrations indicated the presence of various bonds in the glass network. The values of the characteristic temperatures (T_g, T_c and T_m) showed gradual increase except those of the last sample where they showed a decrease. The mid sample showed the lowest stability value. It was found that the molar volume showed its highest value at R=0.33 [where R is the ratio of glass network modifier to the glass network former]. After that it showed gradual linear decrease. The magnetic susceptibility measurements showed approximately stable value between R=0.29 and 0.33, then it increased up to R=0.38, and after that, it decreased up to R= 0.43. The obtained magnetic susceptibility values indicated that all these glasses are paramagnetic. The obtained Mossbauer spectra and the calculated parameters confirmed that iron ions participated in the glass network as network former cations. It confirmed also that all glasses reflect paramagnetic character. The observed structural change were explained and correlated with the change of the measured physical properties.

Key Words: Borate Glasses / Mossbauer Effect / Infrared / Magnetic Susceptibility.

INTRODUCTION

It is established now that Mossbauer Effect (ME) spectroscopy can be successfully used to investigate glass structure [1]. Also infrared (IR) analysis has been extensively employed over the years to study the structure of different glass networks [2].

Due to the wide range of scientific and technological applications of glasses, many valuable studies about their structure together with their physical and chemical properties were done and hence many valuable articles have been published [3-5]. Among these studies those concerning with borate glasses containing transition metal ions appear of special interest due to their uses in many technological uses [6,7].

Inspecting the published papers, there were many articls concerning with the addition of single transition metal ions, while very few concerning with the addition of two different transition

metal ions.

Therefore, in the present study, some lithium borate glasses contaning both manganese and iron oxides were investigated from the structural point of view appling Mossbaur Effect (ME) and infrared (IR) specroscopy. In addition, measurements of some physical properties as density, moler volume (V_m), magnetic susceptibility and the thermal stability were also performed.

EXPERIMENTAL WORK

Chemically pure materials were used to prepare the glass batches. The composition of the batches was selected to give -after melting- solid glasses obying the following molecular formula, [20% Li_2O, (80-2x)% B_2O_3 , x% MnO_2 and x% Fe_2O_3], where x = 0.0, 2.5, 5.0, 7.5 and 10.0. The glass batches, after complete mixing, were then melted in porcelain crucibles in an electrically heated furnace at 1250 ^{o}C for three hours and were then annealed at 350 ^{o}C over night to obtain strain free glasses. The obtained glasses were then powdered and seived to obtain particles less than 200 mech size in order to be sutable for ME, IR, differential thermal analysis (DTA) and magnetic susceptability, while for density measurements, solid glasses were used.

The ME spectra of 50 mg iron/cm^2 absorbers were obtained applying constant acceleration ME spectrometer using 10 mi C ^{57}Co radio active source difused in rhodium matrix. A least square fitting program based on loranzian line shape was used to analyse the obtained ME spectra relative to a metalic iron callibration spectrum.

The infrared spectra have been recorded at room temperature applying KBr disk method using Fourier transform infrared (FTIR) JASCO 5300 spectrometer in the region between 400 and 2000 cm^{-1}.

The DTA thermograms were obtained up to 800°C using a Shimadzu DTA 50 analyser. the glass transition (T_g), crystalization (T_c), and melting (Tm) temperatures were determined from the obtained thermograms and the glass stabilities (T_c-T_g) were then calculated.

Gouy technique was used to obtain the volume magnetic susceptibility (K) values for these glasses using one tesle Faraday electromagnet at room temperature.

Archimedes method was applied to obtain the density (d) values using xylene as an immersing liquid of stable density at room temperature, the molar volume (V_m) were then calculated.

RESULTS AND DISSCUSION

All the obtained experimental results were exhibited as a function of the ratio R, (where R= glass network modifier / glass network former). Fig. (1) show two ME spectra for the samples in which R=0.29 and 0.43.

All the obtained spectra showed only a single paramagnetic doublet, which indicated that iron cations were imbeded in a paramagnetic randomly distrubeted glass host [8]. The computer analysis and fitting indicated that most iron cations occupy mainly high oxydizing state in the tetrahedral coordination. That is to say, most iron cations appeared in the glass network as Fe^{3+} in the former positions [9].

Table (1) represents the obtained ME parameter for iron cations in these glasses as was supplied by computer during analysis. It is appeared from the table that the isomer shift (IS) increased slightly as the ratio R was gradually increased.

This can be attributed to the decrease of the s-electron wave function at the iron nuclei. Such decrease may be due to the decrease in the covalentcy of the glass matrix which may be in turn due to the increase of iron and manganese oxides and the decrease of boron oxide. This act to increase

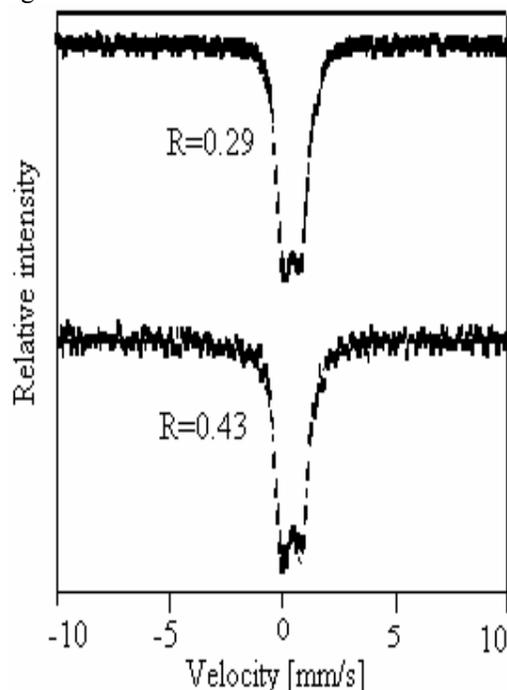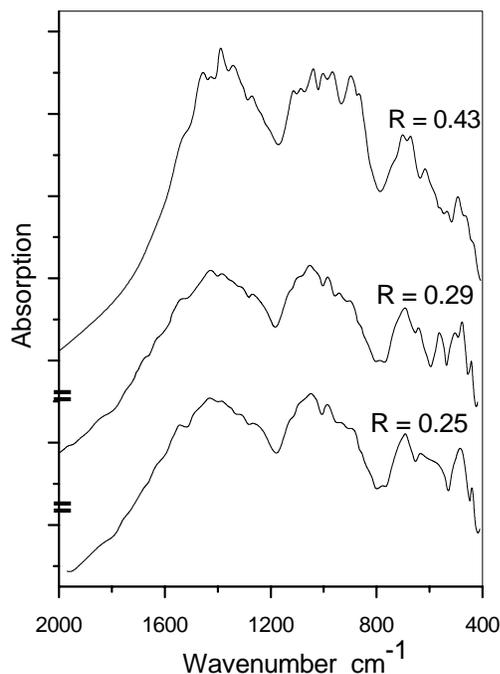the inter atomic distances between iron cations and their surrending oxygon ligands.

Fig. (1)

Fig. (2)

Table (1): ME parameter for iron cations in the glass samples

R	IS	QS	LW
0.29	0.21	0.93	0.57
0.33	0.26	0.91	0.53
0.38	0.29	0.90	0.50
0.43	0.30	0.88	0.49

The quadrapole splitting (QS) values showed a very slight gradual decrease (from 0.93 to 0.88 cm/s). This indicated that there is a little increase in the symetry of the glass matrix arround iron cations, and this in turn act to decrease the electric field gradient due to the network. The calculated line width (LW) values of the obtained ME absorption peaks showed also gradual decrease as R increased. Such decrease confirms the observed slight decrease in the QS values and the slight increase in the symetry arround iron cations. This was supposed to be logic because of the decrease of boron oxide content [which is a glass former covulently bonded to oxygen in the glass network] as well as the increase of both iron and manganese oxides. These oxides act to increase the ionicity in the glass network.

The IR spectra in the range from 400 to 2000 cm^{-1} were measured for all samples in order to obtain information about the change in vibration spectra due to the process of coordination variations [10]. Three representative spectra are shown in figure (2), for glasses with R equals 0.25, 0.29 and 0.43. It can be seen from the spectrum of the iron and manganese free glass (R = 0.25), that a band appearead at about 1600 cm^{-1} showed a slight shfit to higher   energy side on going to the spectra of higher R. This band can be attributed to bending vibration   of the present H_2O groups [11]. At about 1504

cm^{-1}, a band appeared in all glasses which can be attributed to the symetric streching

vibration of B-O bond [12]. Other three bands appeared at about 1352, 1400 and 1437 cm^{-1}, and the last one only shifted to higher energy side appeare at 1454 cm^{-1} in the spectrum of the glass in which R = 0.43. This band may be due to the formation of some meta borate groups in the glass network [12, 13]. Another three bands appeared at 1280, 1249 and 1171 cm^{-1} where the first two bands shifted to higher energy side as R was gradually increased while the later band show no shift. These bands can be attributed to B-O streching vibration involved the linkage oxygen with different borate groups as well as the B-O bridge of B_3O_6 ringes . The appeared shift may be due to the gradual change of BO_3 to BO_4 groups [14]. A group of bands appeared between 1100 and 900 cm^{-1} where some shift to the lower energy side can be observed. These bands indicated the presence of B-O asymetric streching vibration of BO_4 in penta-borate groups [15, 16]. A band appeared in these spectra arround 645 cm^{-1} showed a shift to lower energy side as R increased. This band can be attributed to the vibration of some bridging oxygen anaions between a tetrahedron and triangle boron cations in the glass network [12]. A band did not appeared in the spectrum of the sample with R = 0.25, but appeared in all other spectra at 589 cm^{-1}, and it shows a shift to lower energy side as R increased gradually. This band can be attributed to the formation of FeO_4 groups, which indicated that iron cations introduced in these glass as network former [17, 18]. The band appeared arround 450 cm^{-1} in all the obtained spectra can be attributed to lithium vibration in the glass network [16]. There appeared also a band arround 470 cm^{-1} in all spectra except that of R = 0,25. This band can be attributed to the presence of manganese cation as MnO_6 groups, i.e. manganese introduced these glasses as network modifier [19].

The gradual increase of both iron and manganese oxides at the expense of boron oxide showed an increase in the intensity of the bands due to BO_4 groups as well as a decrease of the intensity of the bands due to BO_3 groups, which mean that BO_4 groups increase and BO_3 groups decrease in the glass networks. The intensity of the band due to FeO_4 and MnO_6 showed also gradual increase as R increased gradually, which can be attributed to the gradual increase of both iron and manganese oxides [20].
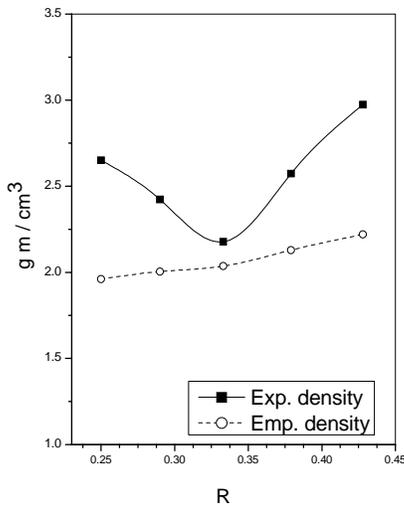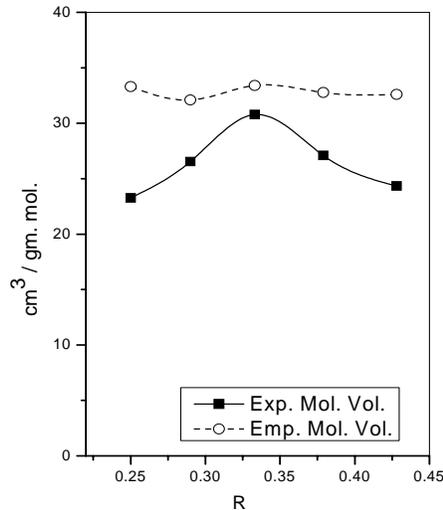

Fig. (3)

Fig. (4)

The density values were obtained for these glasses experimentally and imperically. The molar volume values were obtained also experimentally   and imperically. These data were plotted in fig.s (3, 4) for density and molar volume   respectively. The imperical and the

experimental values are presented in the same figuire for comparision.It is shown that as R was gradually increased, the experimental density shows firstly a decrease until R = 0.33, then it show a gradual linear

increase up to R= 0.43. The glass containing higher contents of Fe_2O_3 and MnO_2 showed higher density values rather than those containing smaller contents.
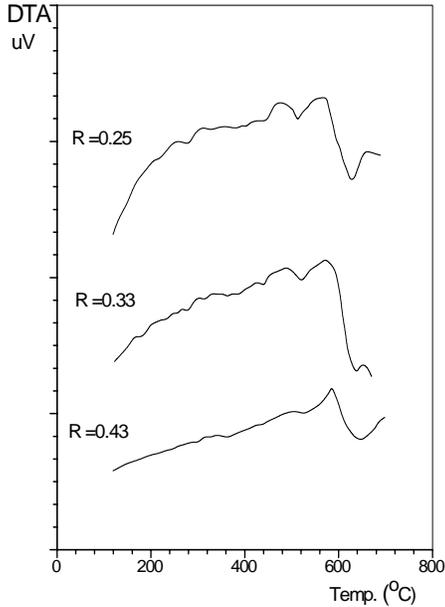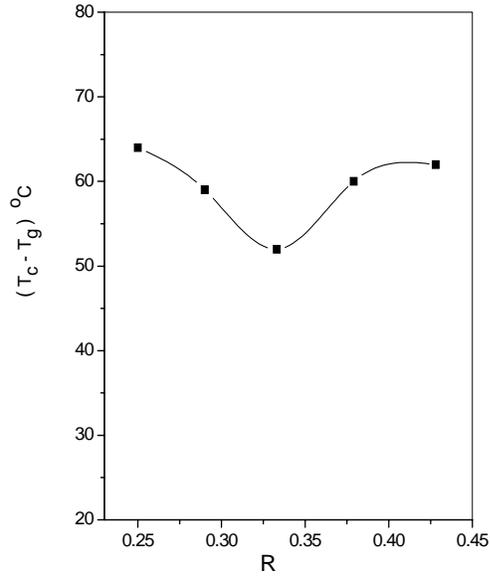

Fig. (5)

Fig. (6)

From the other hand, the emperical density values (close packed density) show gradual linear increase with the gradual increase of R. It can be observed also that the moler volume showed an increase with the gradual increase of R up to 0.33 then it shows a rapid linear decrease up to R=0.43. Accordingly, it is supposed that as R increased between 0.25 and 0.33, the glass network grow up (V_m increased) slightly due to the increase in the oxygen to cation ratio. The observed in the molar volume after that may be due to the formation of somehow compact structure due to the formed non-bridging oxygen and the increase of the ratio R.

Fig. (5) shows three representative DTA thermograms for the samples in which the ratio R = 0.25, 0.33 and 0.43. All the obtained thermograms showed three respective peaks, these are an endothermic peak and exothermic peak followed by a sharp endothermic one. These peaks can be attributed to the glass transition (T_g ^oC), the glass crystallization (T_c ^oC) and the glass melting (T_m ^oC) temperatures respectively. The difference between the crystallization temperature T_c and the glass transition temperatur T_g denote the stability of these glasses [21].

Table (2) represents the variation of the characteristic temperatures T_g, T_c and T_m with the increase of R in the studied samples. It was found that all the values of the characteristic temperatures showed slight gradual increase except the values of the last sample (in which R = 0.43), where a sharp decrease was observed. The stability of these glasses was found also to decrease gradually up to the sample with R = 0.33. Such sample represents the lowest stability value. Increasing R up to 0.43, the stability showed an increase again, as showen in Fig.(6). This change in the stability of these glasses may be due to the increase of the ionic character of the glass network and the decrease of the covalent character. This in turn may be due to the increase in the Fe_2O_3 and MnO_2 and the

decrease in B_2O_3 content. The increase of the stability above R = 0.33 may be due to the participation of most iron cations as glass network formers (covalently bonded to four oxygen iron in the glass matrix) and the gradual transformation to compact structure.

The observed changes in the characteristic temperatures as well as the degree of the glass stability may be due to the increase of Fe_2O_3 and MnO_2. Both manganese and iron oxides represent glass intermediates and from the structural study (ME and IR) it is found that most Fe^{3+} cations introudced in the glass former positions while most of the Mn^{2+} cations participate in the glass modifying positions. Therefore the addition of these transition metal cations increases the ratio of glass modifier to glass former.

Table (2):The change in the characteristic temperatures (T_g, T_c and T_m)
with the increase of R

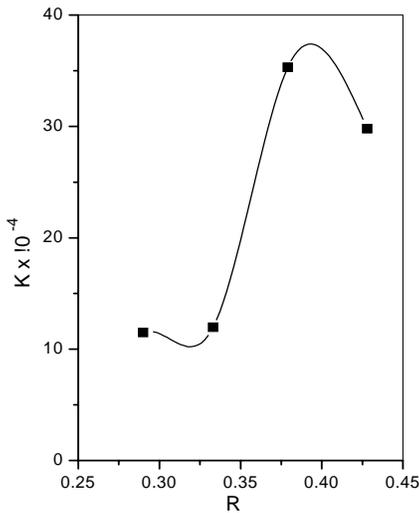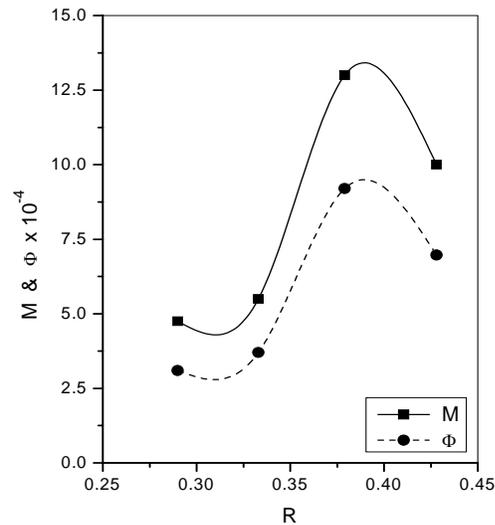| R	T_g ^oC	T_c ^oC	T_m ^oC
0.25	506	570	612
0.29	515	574	625
0.33	527	579	646
0.38	528	588	658
0.43	509	571	637

Fig. (7)

Fig. (8)

The change in the volume magnetic susceptibility is presented in fig. (7) as a function of R. It was appeared that the sample with R = 0.25 (free of iron and manganese) show a very low volume susceptibility (out of scale). In between R = 0.29 and R = 0.335, a stable value is observed. Then it elevated sharply up to R = 0.38 while after that it show a slight decrease. Both the mass magnetic susceptability and the molar magnetic susceptibility exhabit the same trend, and they are presented in fig.(8).Inspecting these figures, it can be concluded that the iron and manganese free sample is not displayed on the graph since it showed very lower value in comparison with other samples (K= $3x10^{-9}$). The observed stability 0.29 and 0.33 can be attributed to the low iron and manganese content, then the sharp increase of the susceptability up to 0.38 may be reasonably due to the formation of FeO_4 groups, since it is a group of higher magnetic moment.

The observed decrease after that may be due the dispersion of iron and manganese cations throw the slightly compact glass network and the formation of MnO_6 in this range of composition, since it is a group of low magnetic moment than MnO_4 group[22].

CONCLUSION

From this study it can be concluded that:

1] From the stractural point of view it was found that most iron cations occupy the network forming positions while most manganese cations occupy the network modifying positions.

2] It was found also that BO_4 units increases and BO_3 units decreases as a result to the gradual replacement of boron oxide by iron and manganese oxide. This may be due to the increase of the ratio R [glass modifier / glass former].

3] The decrease in the experimental density (d) and the increase in the experimental molar volume (Vm) up to R = 0.33, may be due to the decrease in the covalency and the increase in the ionicity of the glass networks as was concluded from ME parameters. After this ratio the increase of density and the decrease of molar volume may be due to the formation of somewhere compact structure.

4] The lowest stability value of the sample in which R = 0.33 relative to the stability of other samples can be attributed to increase of the bond length which in turn decrease the bond energy. This was confirmed by the high molar volume value of this sample.

5] The gradual increase of the susceptability values between R=0.33 and R= 0.38 may be due to the gradual formation of FeO_4 groups while the observed decreased between R=0.38 and 0.43 may be due to the formation of MnO_6 group which is of low magnetic properties and the change of the structure to become slightly compact.

The ME and DTA measurements were carried in Al-Azhar university center for material science research and glass,Al-Azhar university, Cairo, Egypt.

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