

Study of the Effects Due to the Exchange of Na₂O by NaCl on Structure of Some Iron Doped Oxide Glasses

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Abstract

Oxide glasses doped with transition metal ions are of great interest because of their variant applications in both science and technology. Some Borophosphate glasses doped with iron oxide were prepared. Then, a constant acceleration Mossbauer Effect (ME) spectrometer attached with 20 mCi⁵⁷Co radioactive source was used to characterizing the state of iron cations in these glasses. ME parameters had the evidence that the iron occupied two different coordination states. One, of low intensity, characterizing Fe²⁺ in the tetrahedral coordination state, while the other, of high intensity, characterizing Fe³⁺ in the octahedral coordination. In other word, all Fe³⁺ act as a glass network modifiers (GNM), while all Fe²⁺ act as a glass network formers (GNF). Moreover, ME parameters show that the replacement of Na₂O by NaCl causing Fe³⁺ octahedral configuration to transformed to Fe²⁺ tetrahedral configuration.

Key words: Iron Doped oxide glasses, Mossbauer, Na₂O

1. Introduction

Structure, magnetic and electrical properties of glasses doped with transition metal ions have been studied in many previous researches. The interest of the borophosphate glasses coming from the good ability of B₂O₃ and P₂O₅ oxides to form glass when mix with several of many oxides (e.g. alkaline oxides such as Na₂O.....)[1-2]. Borophosphate glasses is one of interesting glassy materials that has many uses, e.g. Zn - Ca borophosphate glasses have been studied as candidates for applications as low-melting glass solders or glass seals [1-3]. These

glasses possess better chemical durability than phosphate glasses due to the cross-linking of phosphate chains by BO_4 groups [2]. Among many previous investigations of borophosphate glasses, it may cite, for instance, studying the effect of replacement of Na_2O on the expense of NaCl on its structural characterization. This done using various techniques (ME Spectra NMR, etc.) [2-3]. Also, Na borophosphate glasses have been investigated but essentially for low sodium concentration [3]. In the present work, Fe borophosphate glass samples of different composition have been prepared to study the effect of replacement of Na_2O by NaCl on its structure characterization.

2. Experimental techniques

The glass samples under investigation were prepared according to the following molecular formula: 30 mole% P_2O_5 - 30 mole% B_2O_3 - 15 mole% Fe_2O_3 - (25 - x) mole% Na_2O - x mole% NaCl , where x= 0, 5, 10, 20, and 25. These samples were investigated from the structural point of view, by applying Mossbauer Effect Spectroscopic Analysis. The glass batches were grounded and mixed well by using agate mortar. Then they were melted in porcelain crucibles using an electric muffle furnace at 1000°C for two hours. Melts were stirred to get a complete mixing and homogeneity. Mossbauer measurements were carried out at room temperature by using 20 mCi ^{57}Co radioactive source in Rh matrix. A constant acceleration transducers is interfaced to a based PC-MCA, metallic iron was used for calibration.

3. Results and discussion

The Mossbauer spectra of the studied glasses plotted as in Fig.(1). The fitting of ME Spectrum of x = 0, as a representative figure is shown in Fig.(2). All samples showed the same behavior with a shift towards the lower velocity as the concentration of x increased. ME analysis indicates that the spectrum, of each sample, can be interpreted as a broad paramagnetic doublet. One, of low intensity, characterized ferrous while the other, of high intensity, characterized ferric. Mossbauer parameters, table (1), reveals that Fe^{3+} Cations occupy, only, the octahedral coordination, while Fe^{2+} Cations occupy, only, the tetrahedral coordination state. In other word, Fe^{3+} Cations act as a glass network modifiers (GNMs), while Fe^{2+} act as a glass network formers (GNFs)[4 -5 -6].

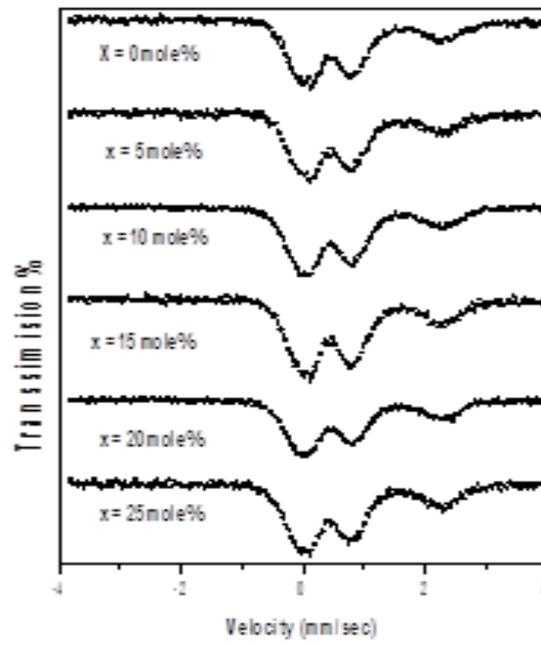


Figure 1. Mossbauer carts for all samples

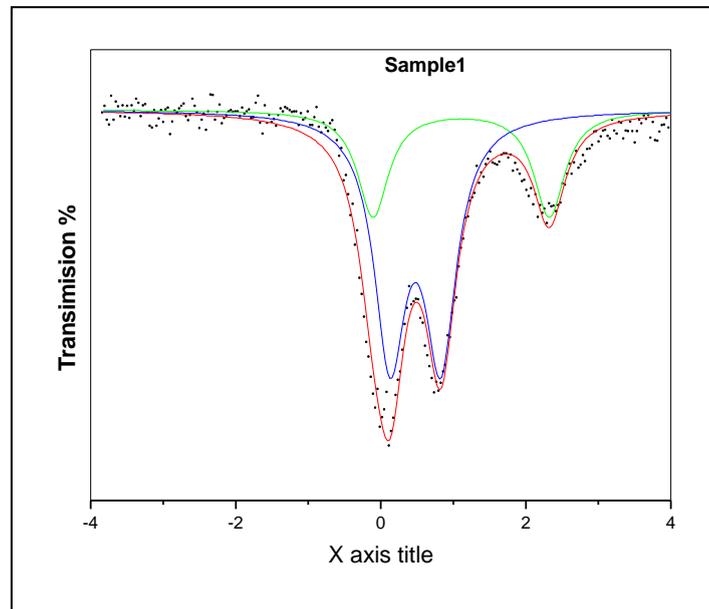


Figure 2 Mossbauer spectra in addition to its analysis for sample (1)

Table 1. ME Parameters

x mole %	Phase I (Fe^{2+})				Phase II (Fe^{3+})			
	QS1 mm/sec	IS1 mm/sec	LW1 mm/sec	A1 %	QS2 mm/sec	IS2 mm/sec	LW2 mm/sec	A2 %
0	2.42	1.06	0.51	29	0.71	0.47	0.53	71
5	2.42	1.07	0.51	30	0.71	0.47	0.52	70
10	2.36	1.10	0.53	31	0.75	0.45	0.52	69
15	2.30	1.12	0.54	32	0.75	0.45	0.53	68
20	2.27	1.12	0.55	33	0.77	0.44	0.53	67
25	2.22	1.14	0.56	34	0.78	0.43	0.53	66

By inspecting table (1) it is noticeable, for all studied samples, that the line width LW values appeared to be highly broadened in comparison with the natural line width of iron [0.25 mm/s], indicating a good homogenous glasses [7]. By inspect ME Parameters that summarized in table (1), as x increased the value of Fe^{2+} isomer shift (IS_1) was observed to be approximately unchanged, while the value of Fe^{3+} isomer shift (IS_2) was observed to decrease. Generally, it was established that the change of the iron from 6-fold to 4-fold coordination states for either Fe^{2+} and Fe^{3+} would result in a decrease of IS values [8-9]. Therefore, for the present study it can be stated that, the decrease of IS values indicates that Fe^{3+} (6-fold), GNM, has been transformed to Fe^{2+} (4-fold), GNF. In other word, the replacement of Na_2O by NaCl cause the iron to change both its oxidation and coordination states, where Fe^{3+} octahedral change to Fe^{2+} tetrahedral. This may due to the formation of more of $\text{Fe}^{2+}\text{-Cl}$ and $\text{Fe}^{3+}\text{-Cl}$ dangling bounds and/or the decrease of Na^+ ions as a result of replacing Na_2O by NaCl . Quadrupole Splitting (QS) is defined as the interaction between the nuclear quadrupole moment, of the Moessbauer atoms (irons), and the gradient of the electric field due to other charges in the structure matrix. This means that, the Quadrupole Splitting expressing the charges distribution around the Mossbauer atoms, where the symmetric distribution has zero Quadrupole Splitting. Q.S Values of both Fe^{2+} (QS_1) and Fe^{3+} (QS_2) are summarized also in table (1). The changes of QS_1 and QS_2 can be attributed to the variations in the symmetry and asymmetry, respectively, around each iron in the different sites [10-11] as a result of a variations in the electric field gradient of the lattice, which affected by replace a divalent ion O^{2-} of high electro-negativity by mono-valence of low one. Also, it is clear from

table (1) that, the relative area, A%, of ME phases exhibits a change in its value, by increasing the x value, where a noticeable gradual increasing in Fe^{2+} content and a gradual decreasing in Fe^{3+} content occurred by the replacement of Na_2O by NaCl . This behavior is in agreement with that predicts by the IS.

4. Conclusion

In oxide glasses of composition 30 mole% P_2O_5 - 30 mole% B_2O_3 - 15 mole% Fe_2O_3 - (25 - x) mole% Na_2O - x mole% NaCl , where x= 0, 5,10, 20, 25. The replacement of Na_2O by NaCl affect the Mossbauer atoms (iron) causing them to change its oxidation and its coordination states, in other words, Fe^{3+} octahedral configuration have been changed to Fe^{2+} tetrahedral configuration.

5. References

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