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# Effect of Gamma-Irradiation on Some Boro-Phosphate Glasses Doped with Iron Ions

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**Abstract:** Boro-phosphate oxide glass system doped with iron ions have been prepared by the conventional melting quenching technique, all mixtures are in an agreement with the following chemical formula (25-x) mol% $Na_2O$. x mol% NaCl.15 mol% FeO. 30 mol% $B_2O_3$. 30 mole% $P_2O_5$, where x = 0.0, 05, 10, 15, 20 and 25. Sample of x= 0, only, has been exposed to different doses of gamma rays (0.0, 05, 10 and 20 kGy). Mossbauer Effect ME spectroscopy have been carried out at RT for all irradiated {x =0.0} and for non-irradiated {x> 0.0} samples. ME parameters showed all samples in good glassy state. Also ME parameters showed the iron ions in two different coordination states, where all $Fe^{2+}$ ions and some of $Fe^{3+}$ ions shared the octahedral coordination states, while the tetrahedral coordination states occupied only by $Fe^{3+}$ ions. It was observed that both the gamma irradiation process and the process of replacement $Na_2O$ by NaCl caused the $Fe^{2+}$ ions to oxidize to $Fe^{3+}$ ions.

**Keywords:** Iron Boro-phosphate glasses, Oxides, Glasses, Amorphous Materials, Inorganic Compounds

## 1. Introduction

Borophosphate glasses are highly durable comparing with pure borate or pure phosphate glasses [1, 2]. They have used in many industrial applications as solid electrolytes and glass solders. These glasses offer a possibility to change their structures and properties by changing their composition. Koudelka and Mosner [3, 4] stated that these changes take place in their anionic or/and cationic network elements. In other words, its structures and the properties changed by the changing the concentration of phosphorus and boron cations. The basic building units of these glasses are $BO_4$, $PO_4$ tetrahedral and $BO_3$ triangles, while oxygen anions have six sites, these are B – O – B, P – O – P, B – O – P, (bridging oxygen's), P – $O^-$, B – $O^-$, (non- bridging oxygen's) and P = O (terminal oxygen) [5, 6, 7]. Hadj Youssef [2] showed that in borophosphate glasses of high phosphate and low borate concentrations, the formation of B – O – P bridges causes an increase in the proportion of tetrahedral borate groups. The presence of $BO_4$ tetrahedral groups associated with B – O – P, which induces a random ramification and raises the competence of the borophosphate glass networks [5, 6, and 7]. Also the incorporation of $BO_4$ units into the chain as in phosphate glasses acting to convert the network from one dimensional into three dimensional network, whereas boron ions acting to crosslink the phosphate chains and layers. This cross-linking increases the glass density (ρ) as a result of increasing $B_2O_3$ [7, 8, and 9]. The present work aims to characterize and compare between the effects of both gamma irradiation and chemical structure changes on the Mossbauer atom doped in some sodium boro-phosphate glasses. After this study it hoped to reach a result help in use the structural changes as an indicator to the amount of gamma ray absorbed.

## 2. Experimental

Iron-sodium borophosphate glass samples of the composition of (25-x) mol% $Na_2O$ - x mol% NaCl - 15 mol% FeO - 30 mol% $B_2O_3$. 30 mole% $P_2O_5$ prepared using $FeC_2O_4$, $Na_2CO_3$, $(NH_4)$ $H_2PO_4$ and $H_3BO_3$ as starting materials (with purity not less than 99 %). The raw materials were weighed to the desired compositions and the batches were mixed well and were then melted at 1050°C for 2 h with frequent stirring to ensure complete homogeneity. Melts

were then rapidly quenched onto pre-cooled stainless steel modulus in air. ME spectra were obtained using a constant acceleration Mossbauer Effect ME spectrometer while the ME parameters were calculated relative to metallic iron calibration spectrum. All the free Cl sample exposed to gamma radiation using an Indian $^{60}Co$ gamma ray cell (1000Ci) with a dose rate about 1.2Gy/sec. where the sample was placed in a manner made it subjected to the same irradiation dose. This has been achieved by arranging the sample around a cylinder placed inside the chamber. The required dose achieved by calculating the desired overall dose.

## 3. Results and Discussion

The chemical formula (25-x) mol% $Na_2O$, x mol% NaCl, 15 mol% FeO. 30 mol% $B_2O_3$. 30 mole% $P_2O_5$ have been used to prepared more than glass sample, where x = 0.0, 05, 10, 15, 20 and 25. The first sample {x =0.0} have been divided into four parts. Each part has been irradiated by a single different dose of gamma rays {0, 5, 10 and 20 kGy}, while the other samples with {x > 0.0} have not been irradiated. For each sample, $^{57}Fe$ Mossbauer spectra measurements have been carried out to check the local environment of Fe ions in the structure. Figs. (1, 2) exhibit the ME spectra for both the irradiated {x = 0} and non-irradiated {x > 0.0} samples. Generally, just by looking each spectrum showed two broad peaks each has different intensity, in addition to a small one at the right hand side of the spectrum. The computer program analyzed each spectrum to three paramagnetic doublets, without participation of any magnetic phase. The corresponding Mossbauer parameters, namely, isomer shift (I.S.), quadrupole splitting (Q.S.) and the line width (L.W.), for irradiated {x = 0.0} and non-irradiated {x > 0.0} samples have been recorded in tables 1 and 2, respectively. By studying ME parameters for all samples, It was found that the average L.W. of the paramagnetic doublets is approximately equal to 0.49 mm/s which is twice that of the natural one 0.25 mm/s. this value likely to be associated with the high disorder structure, good glassy state [10, 11]. Many published papers stated the existence of a correlation between I.S. and Fe ions configuration in the glass network [12, 13, and 14]. It is clear from the table (1) that, for irradiated samples {x =0. 0}, the values of I.S. have been found in three separated regions, the first two regions, {1.18-1.27mm/s} and {0.35-0.43mm/s}, refer to ferrous and ferric in octahedral configuration [13, 15], respectively. This mean that, like these ions does not share in the glass network formation but only occupied the interstitial positions [14, 15, and 16]. The third region {0.47-0.50 mm/s} refers to the ferric iron ions in tetrahedral configurations which act as a glass network formers [16, 17]. In similar way, by inspecting table (2) the I.S. values for {x > 0.0} samples have been found in three separated regions. Where the regions {1.06 - 1.12mm/s} and {0.39 - 0.41mm/s} refer to both ferrous and ferric ions in octahedral configurations, respectively [13, 16, 17], While I.S. mean values (0.45 mm/s) refer to ferric ions in tetrahedral configuration [13, 16, and 17].

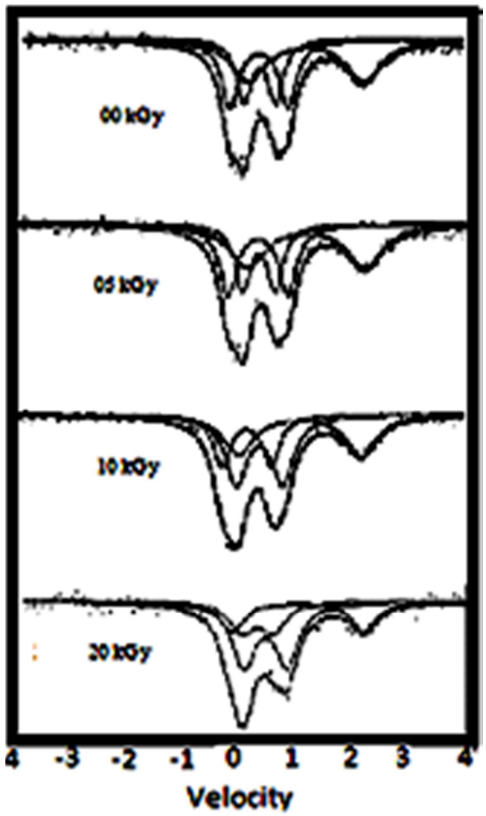


***Fig. 1.*** *ME Spectra of Irradiated samples.*

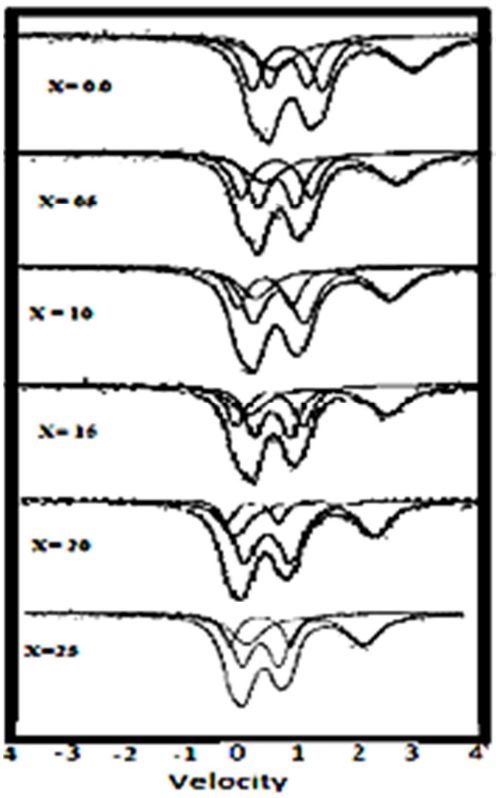


***Fig. 2.*** *ME Spectra of Non-Irradiated samples.*

***Table 1.*** *ME spectra for both the irradiated x = 0 and non-irradiated x > 0.0.*

| Doses kGy | $Fe^{2+}O_6$ | | | | $Fe^{3+}O_6$ | | | | $Fe^{3+}O_4$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | I.S. | Q.S. | L.W. | A% | I.S. | Q.S. | L.W. | A% | I.S. | Q.S. | L.W. | A% |
| 00 | 1.27 | 2.1 | 0.75 | 43 | 0.43 | 0.27 | 0.34 | 29 | 0.50 | 0.68 | 0.37 | 28 |
| 05 | 1.25 | 2.0 | 0.70 | 24 | 0.38 | 0.27 | 0.36 | 38 | 0.48 | 0.58 | 0.42 | 38 |
| 10 | 1.21 | 2.1 | 0.65 | 18 | 0.34 | 0.21 | 0.37 | 42 | 0.50 | 0.71 | 0.46 | 40 |
| 20 | 1.18 | 2.2 | 0.64 | 10 | 0.35 | 0.11 | 0.38 | 50 | 0.47 | 0.58 | 0.48 | 40 |

***Table 2.*** *Effect of $Cl^-$ content on ME Parameters.*

| $Cl^-$ Content | $Fe^{2+}O_6$ | | | | $Fe^{3+}O_6$ | | | | $Fe^{3+}O_4$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | I.S. | Q.S. | L.W. | A% | I.S. | Q.S. | L.W. | A% | I.S. | Q.S. | L.W. | A% |
| 00 | 1.06 | 2.42 | 0.51 | 43 | 0.41 | 0.29 | 0.33 | 32 | 0.45 | 0.70 | 0.39 | 25 |
| 05 | 1.07 | 2.24 | 0.51 | 32 | 0.41 | 0.29 | 0.35 | 40 | 0.45 | 0.70 | 0.38 | 28 |
| 10 | 1.10 | 2.36 | 0.53 | 25 | 0.39 | 0.28 | 0.36 | 45 | 0.45 | 0.75 | 0.38 | 30 |
| 15 | 1.12 | 2.30 | 0.54 | 23 | 0.39 | 0.27 | 0.38 | 46 | 0.45 | 0.71 | 0.35 | 31 |
| 20 | 1.12 | 2.27 | 0.56 | 21 | 0.35 | 0.27 | 0.38 | 48 | 0.44 | 0.78 | 0.35 | 31 |
| 25 | 1.14 | 2.22 | 0.55 | 19 | 0.34 | 0.23 | 0.37 | 50 | 0.44 | 0.75 | 0.34 | 30 |

The non-zero values of Q.S. for both ferrous and ferric ions in octahedral configuration indicate non-spherical electron shell. Therefore, any increase in the deformation of $Fe^{2+}$ sites will be associated with an increase in Q.S. values, and vice versa [14, 16, and 18]. For {x = 0.0} samples, the Q.S. values for the ferrous ions did not change {2.1mm/s} with increasing the irradiation doses, as indicated in table (1).This means that, no distortion change in the ferrous sites had resulted from the increasing of the gamma irradiation doses. In other side with increasing in gamma ray dose the Q.S. values for the octahedral ferric ions have been decreased from 0.27 to 0.11mm/s which caused a decrease in the distortion of their sites. For {x > 0.0} samples, it has been observed that the values of Q.S. for the ferrous ions decreased from 2.4 to 2.2 mm/s, with replacement $Na_2O$ by NaCl. Like this behavior mean a change in the distortion sites of the ferrous ions [18, 19, and 20]. while, the Q.S. values of the octahedral ferric ions showed a decrease from 0.29 to 0.23 mm/s, such behavior indicates a decrease in the distortion sites of the octahedral ferric ions. The relative ratio of both $Fe^{2+}$ and $Fe^{3+}$ with different Gamma irradiation doses and with different Chlorine contents have been calculated and plotted in figs. (3, 4), respectively. In both figures, it is clear that, the $Fe^{2+}$/Fe ratio decreased while $Fe^{3+}$/Fe ratio increased by increasing the irradiation gamma dose or by increasing the chlorine ions content in the glass samples. This similarity in the behavior due to the process of irradiation by different doses or by the process of increasing chlorine ions content in the glass structure may attributed to the oxidation effect of radiation and the oxidation effect of Cl [21, 22, 23 and 24], respectively.

Density measurement is a sensitive tool to check the fine changes in the batches composition, whereas the molar volume is directly related to the spatial structure of the glass. Table (3) contains the values of both density and molar volume for the studied glass system with different Chlorine content. It is clear from the data that, both of the density and the molar volume have not been changed with the gradually increasing of chlorine content, like behavior may attributed to the small difference between the density of $Na_2O$ (2.27 $gm/cm^3$) and that of NaCl (2.163 $gm/cm^3$) and/or to small difference between the molecular weights of $Na_2O$ (61 amu) and that of NaCl (58 amu). The Constancy in the values of both density and molar volume may be indicated to there is no change in the glass building blocks with replacement $Na_2O$ by NaCl.

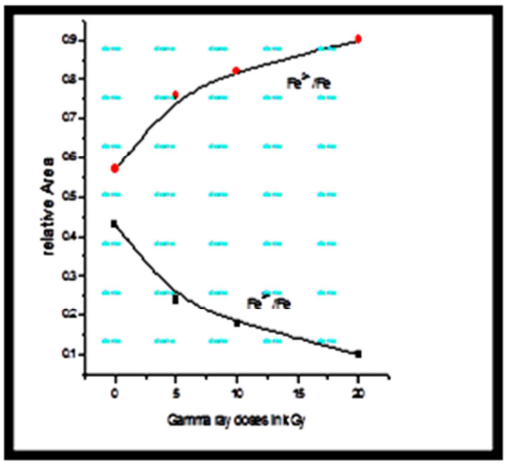


***Fig. 3.*** *Relative area for Irradiated samples.*

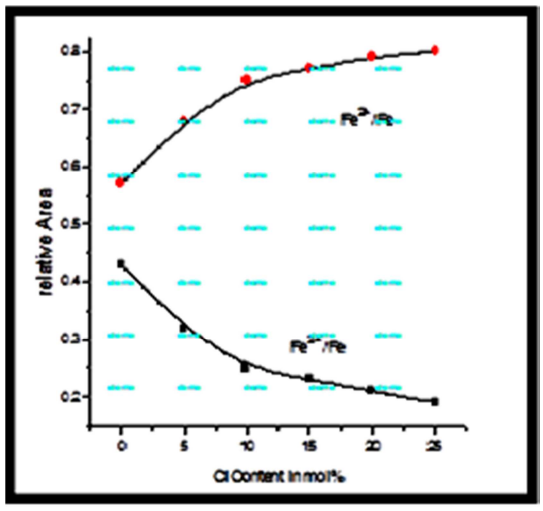


***Fig. 4.*** *Relative area for Non-Irradiated samples.*

***Table 3.*** *Values of the density and molar volume for the studied glasses.*

| Cl content | 0.0 | 05 | 10 | 15 | 20 | 25 |
|---|---|---|---|---|---|---|
| Density (g/cm$^3$) | 2.1 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |
| molar Volume (cm$^3$/mole) | 43.5 | 43.0 | 43.0 | 43.5 | 43.0 | 42.8 |

# 4. Conclusion

The oxide glass system (25-x) mol% $Na_2O$. x mol% NaCl, 15 mol% FeO. 30 mol% $B_2O_3$. 30 mole% $P_2O_5$ has been prepared, where x= 0.0, 05, 10, 15, 20 and 25. Observed effects were as follows

- $^{57}Fe$ Mossbauer spectra and parameters showed all samples in good glassy states
- All $Fe^{2+}$ ions occupied only the octahedral coordination states, some $Fe^{3+}$ ions occupied the octahedral coordination states, while some other occupied tetrahedral coordination states.
- The free Chlorine ions samples (x = 0.0) had subjected to a different doses of gamma radiation 0, 5, 10 and 20 kGy., for the free $Cl^-$ glass, the irradiation causes some of $Fe^{2+}$ ions to oxidize to $Fe^{3+}$ ions.
- For non-irradiated glasses, the increase of $Cl^-$ content causes some of $Fe^{2+}$ ions to oxidize to $Fe^{3+}$ ions. For $Cl^-$ non-irradiated glasses.
- The behavior of both the Density and the molar volume refers to there is no change in the glass building blocks with replacement $Na_2O$ by NaCl.

Finally, it can be concluded that the effect of replacing Na2O with NaCl is the same effect of irradiation. this conclusion has been showed that the irradiation has an oxidation effect.

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