

# Study of the Structure and Some Physical Properties of Sodium-Boro-Phosphate Glasses Containing Antimony and Iron Oxides

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## Abstract

Boro-phosphate glasses containing transition metal oxides are of special interest. Hence, some sodium-boro-phosphate glasses containing iron and antimony oxides were prepared and investigated.

The structural investigation indicated the presence of different borate groups as well as tetragonal phosphate units. Most of the iron cations were found to occupy the low spin  $Fe^{3+}$  in the tetrahedral coordination state. It was observed that some antimony act as network former cations and some others act as bridges between any two adjacent polyhedra. At high antimony oxide content, the formation of some Sb-Fe bonds was also detected.

The magnetic susceptibility measurements showed a maximum value when antimony oxide reached 15 mol %, but decreased with higher concentration. Between 20 mol % and 30 mol %, the magnetic susceptibility exhibited approximately stable value, indicating that at 15 mol % of antimony oxide content, most iron cations occupy the tetrahedral coordination state. The observed decrease in the magnetic susceptibility at higher concentrations may be due to the formation of some Sb-Fe bonds, which act to pair the iron d-electrons, in addition to the increase of  $Sb_2O_3$  content which has low magnetic properties.

The obtained density and the calculated molar volume values showed approximately linear increase. The increase of the density can be attributed to the differences in the molecular weights of both boron and antimony oxides, while the increase of the molar volume can be ascribed to the radius and the volume effects of the increasing antimony cations.

**Key Words:** Glass structure, Physical properties of glass, Glass containing antimony and iron oxides.

## 1. Introduction

Usually, phosphate glasses are of little interest due to their low chemical durability and high moisture absorbance [1]. But the addition of boron oxide to the phosphorous oxide during melting produces boro-phosphate glass which appears to be of high technological and scientific interest [2]. Moreover, the introduction of selected transition metal ions to the glass network appeared to be very helpful for investigating the glass structure as well as to improve the physical properties of the glass, mainly those properties which are related to electronic movement within amorphous solids.

Iron was classified as the most important transition metal due to its usual presence and wide use [3–6]. On the other hand, antimony oxide was lately classified as a glass former, but only when cooled rapidly [7]; and glasses containing antimony appear now to have much scientific interest [8, 9].

Thus, in this work the structure and some selected physical properties of sodium-boro-phosphate glass system containing antimony and iron oxides were investigated.

## 2. Experimental Work

The composition of the prepared glasses was selected via the criteria that they have the following molecular formula:



where  $x$  takes the values 0, 5, 10, 15, 20, 25 and 30

Chemically pure oxides were used to prepare the glass batches. The obtained batches, after complete mixing, were melted in porcelain crucibles using an electrically heated furnace for 2 h at 1000 °C. The melts were stirred several times to ensure that the obtained glasses are well homogenized. Then the melts were quenched by pouring onto a pre-cooled stainless-steel plate, and after sitting they were directly transferred to the annealing furnace at 300 °C. The glass samples were left for 6 hours in the annealing furnace to obtain strain free samples.

A Fourier transform infrared (FTIR) spectrometer model Bruker-Vector 22 was used to obtain the infrared spectra of these samples using the KBr disc technique [10].

A constant acceleration Mossbauer Effect (ME) spectrometer with a 10 mCi  $^{57}\text{Co}$  radioactive source was used to obtain ME spectra of the investigated samples at room temperature.

The density  $d$  of all samples were measured via Archimedes method, using toluene as an immersing liquid of stable density [0.866 g/cm<sup>3</sup>]. The specific volume  $V_s$  of a sample was then calculated as the inverse of the obtained density value. Multiplying the  $V_s$  of a glass sample by the molecular weight of one mole  $w_m$  of this sample, the molar volume value  $V_m$  was obtained via the formula

$$V_m = w_m \frac{1}{d} \text{ cm}^3/\text{mol}.$$

Gouy method was also applied to obtain the volume magnetic susceptibility  $\Psi_v$  of the glasses under investigation using a one tesla electromagnet supplied by Faraday Instruments Company. The mass magnetic susceptibility  $\Psi_m$  as well as the molar magnetic susceptibility  $\Psi_{mol}$  were then calculated.

## 3. Results and Discussion

The importance of the prepared glasses is due to their valuable uses in the fields of magnetic and semiconducting materials. It is supposed that the presence of iron cations in these glasses acts to increase their magnetic properties while the addition of material such as antimony, with its low magnetic properties, acts to decrease the magnetic properties of the host glasses. Therefore the interaction between the electronic structure of both iron and antimony cations may produce an interesting solid glass having a definite magnetic behavior.

Figure 1 (a,b,c and d) exhibits typical IR transmission spectra of some of the obtained spectra for those glasses which contain 0, 10, 20 and 30 mol % of antimony oxide respectively. From this figure, the following bands was observed:

1) A very small shoulder appeared at 413 cm<sup>-1</sup>, but was completely absent in the sample containing 30 mol % Sb<sub>2</sub>O<sub>3</sub>. This shoulder may be due to the presence of little iron cations in the six-fold coordination state [11].

2) A band at about 467cm<sup>-1</sup> appeared in all samples, which may be due to the vibrations of Na cations throughout the glass network [12] as well as the stretching vibrations of the P-O bond [13]. The observed decrease of its intensity on going to higher Sb<sub>2</sub>O<sub>3</sub> content glass may be due to the slower vibrations of the

Na cations, which in turn is due to some rearrangement of the glass network as a result of the decrease of  $B_2O_3$  [12].

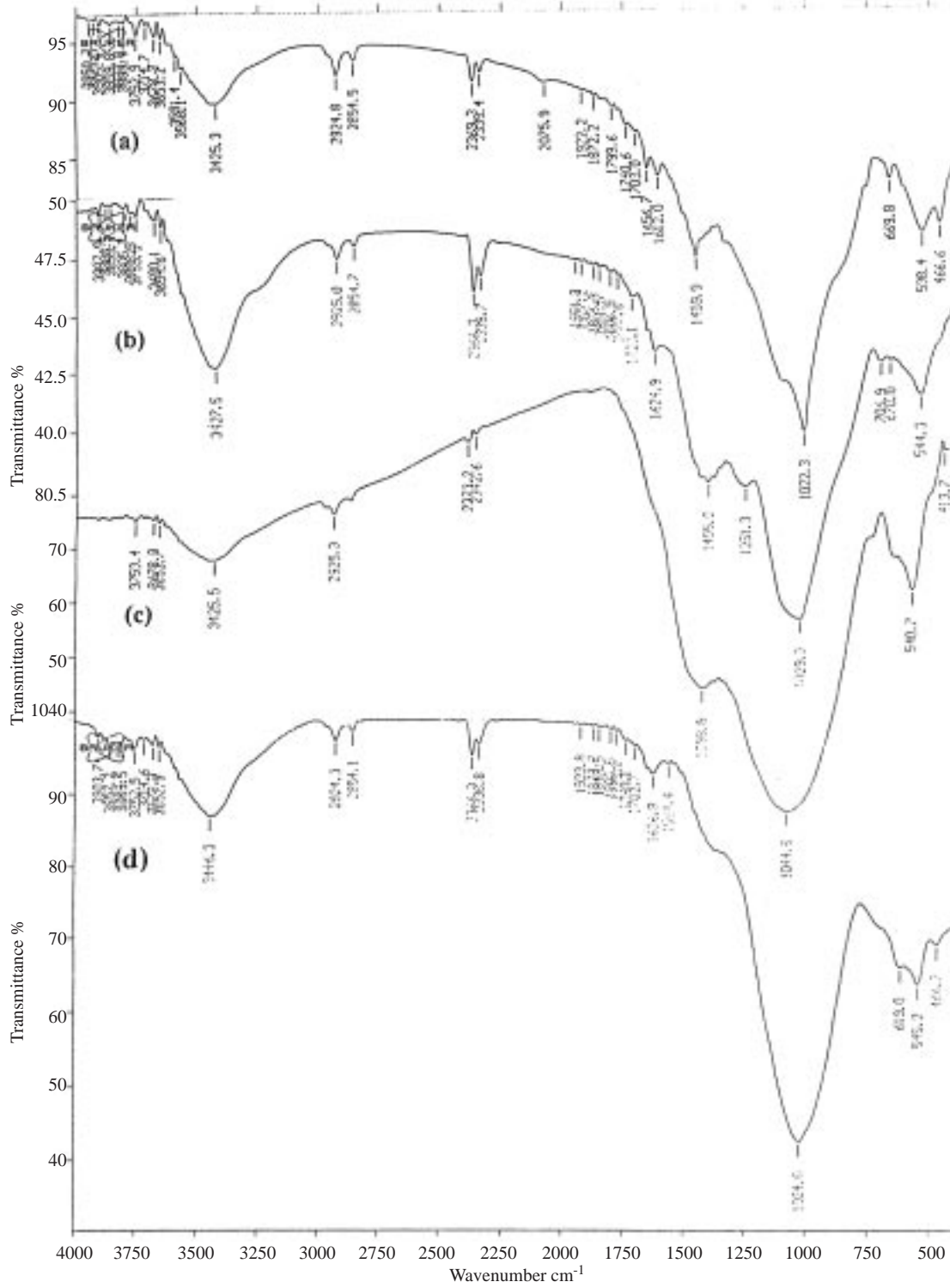


Figure 1. IR Spectral of samples (1), (3), (5) and (7).

3) A band that appeared in the sample free of antimony at about  $538.4\text{ cm}^{-1}$  was found to shift towards higher energy, appearing at  $545.2\text{ cm}^{-1}$ , when  $\text{Sb}_2\text{O}_3$  reached 30 mol %. This band can be attributed to deformation modes of the network structure [14] as well as the vibrations of  $\text{PO}_4$  groups [13, 15].

4) A band at about  $620\text{ cm}^{-1}$  appeared only in the high antimony oxide content (20, 25 and 30 mol %). This may be due to the presence of some iron ions in the four-fold coordination state. That is, the addition of antimony oxide forced the iron cations to transform from  $\text{FeO}_6$  to  $\text{FeO}_4$  positions [11].

5) At low  $\text{Sb}_2\text{O}_3$  content (0 and 10 mol %), a band appeared at  $670\text{ cm}^{-1}$  and at high  $\text{Sb}_2\text{O}_3$  content (20 and 30 mol %) it appeared at  $680\text{ cm}^{-1}$ . This band can be attributed to the vibrations of the present Sb-Fe bonds [6].

6) A band at about 707 starts to appear in the sample containing 10 mol % of  $\text{Sb}_2\text{O}_3$  was and found to shift towards higher energy to appear at  $718\text{ cm}^{-1}$  in the sample containing 30 mol % of  $\text{Sb}_2\text{O}_3$ . This band can be attributed to the bending vibrations of the bridging oxygen atoms [16].

7) A band appeared at  $780\text{ cm}^{-1}$  in all glasses, but with the decreasing intensity at higher  $\text{Sb}_2\text{O}_3$  content glass. This band is due to the vibrations of penta- and meta-borate as well as more complex ring structure [2].

8) A band appearing at  $890\text{ cm}^{-1}$  was found to shift towards lower energy on going to high  $\text{Sb}_2\text{O}_3$  content glass, until it disappeared completely from the spectrum of the sample containing 30 mol % of  $\text{Sb}_2\text{O}_3$ . This band can be attributed to the stretching vibrations of tri-, tetra- and penta-borate groups [12] and to modes involving mainly symmetric P-O stretching vibrations in  $\text{PO}_4$  groups [13]. This gradual decrease of the intensity of this band was found to be due to the gradual decrease of  $\text{B}_2\text{O}_3$  down to 10 mol %, that is, in the sample containing 30 mol %  $\text{Sb}_2\text{O}_3$ .

9) A band that appeared at  $1022\text{ cm}^{-1}$  was found to shift towards higher energy on going to high  $\text{Sb}_2\text{O}_3$  content glass. This is due to the asymmetric stretching vibrations of the B-O bond in the tetrahedral borate units [12].

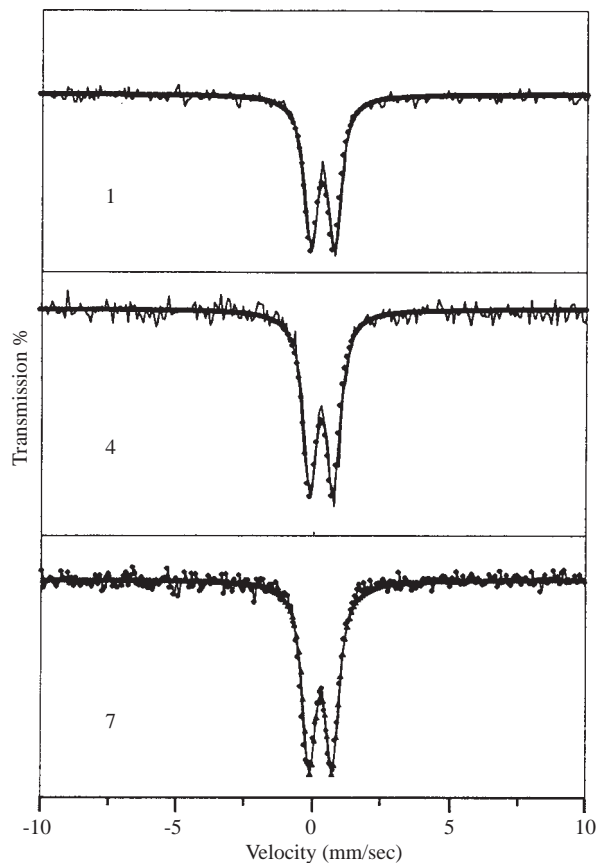
10) In the sample free of antimony, there appeared a band at  $1096\text{ cm}^{-1}$ , which may be due to the stretching vibrations of the B-O bond in the tetrahedral coordination state in the penta-borate groups [12].

11) A band at  $1251\text{ cm}^{-1}$  appeared only in the sample containing 10 mol %  $\text{Sb}_2\text{O}_3$ . It is attributed to the B-O stretching vibrations involving mainly the linkage oxygen connecting different groups such as, B-O bridge between  $\text{B}_3\text{O}_6$  rings and  $\text{BO}_3$  triangles [14].

12) In the sample free of  $\text{Sb}_2\text{O}_3$ , a band at  $1349\text{ cm}^{-1}$  was found to shift towards higher energies appearing at 1405, 1398 and  $1373\text{ cm}^{-1}$  in those samples containing 10, 20 and 30 mol %  $\text{Sb}_2\text{O}_3$ , respectively. This band can be attributed to the stretching vibrations of meta-borate groups [17].

13) The higher energy bands may be due to the vibration of  $\text{H}_2\text{O}$  groups or to the stretching vibrations of O-H bonds. The appearance of these bands may be due to the used KBr disk technique and/or due to the present phosphorous in these glasses, since these materials absorb moisture from environmental air [18].

The ME spectroscopy was applied to check the structural role of iron cations and to confirm the obtained results from the infrared analysis. The spectra obtained from samples numbered (1), (4) and (7), containing 0, 15 and 30 mol %  $\text{Sb}_2\text{O}_3$ , respectively are shown in Figure 2. All the obtained spectra showed a symmetrical single doublet, indicating that all these samples exhibited paramagnetic characters. The computer fitting of all the obtained spectra indicated that the iron cations occupy only single phase. The calculated ME parameters for the iron cation in these glasses indicated that most of the iron cations occupy a low spin  $\text{Fe}^{3+}$  in the tetrahedral coordination state imbedded in an amorphous glassy host [6]. This confirms the data obtained from the IR examination, that most of the iron cations occupy the tetrahedral coordination state, and the addition of antimony oxide forced the remain of the iron cations to occupy the tetrahedral coordination state. This means that most of the iron cations occupy the network-former positions.



**Figure 2.** ME spectra of samples (1), (4) and (7).

The obtained ME parameters, Quadrupole splitting (QS), Isomer shift (IS) and line width (LW) are shown graphically in Figure 3 as a function of the gradual increase of antimony Oxide concentration. One can see that the IS increases gradually, indicating that, increasing antimony oxide increases the density of the s-electron wave function on the iron nucleus in these glasses. On the other hand, the gradual decrease of the QS values indicated that the electric field gradient due to the glass network decreased gradually with the gradual decrease of antimony oxide. The line width appeared to be stable at about 0.436 mm/s, indicating that the replacement of boron by antimony does not represent an effective change in the amorphous state of the glass networks [19, 20].

In fact, density was considered early as an important physical property in the field of glass science, especially where glass structure was concerned. It was stated that density measurement is a very sensitive tool that can easily detect any structural changes in a glass.

The obtained density values showed a gradual linear increase as antimony oxide was gradually increased in these glass samples, as shown in Figure 4. It can be supposed that some sort of rearrangement may take place in the network of these glasses. But returning to the ME spectra and the IR results, it is observed that the LW of ME spectra of all glasses appeared highly broadened and approximately stable, while the broadening of the IR bands indicated that there is no detectable change to crystallization. So, the idea of crystallization cannot be confirmed, and hence the increase in density can be attributed only to the differences in the properties of both boron and antimony cations [21].

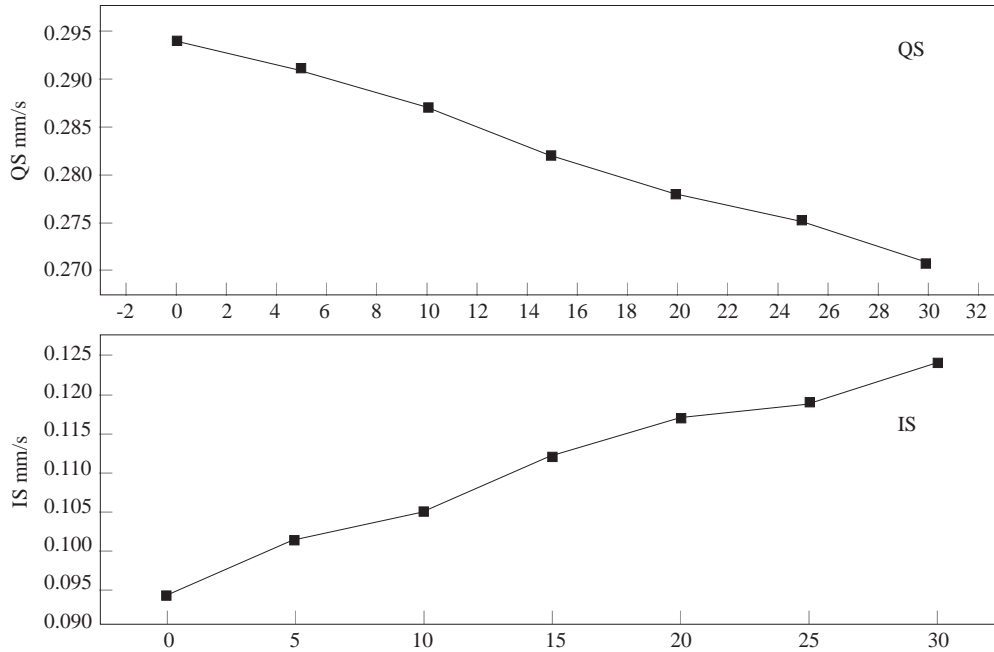


Figure 3. a,b ME parameters versus Sb<sub>2</sub>O<sub>3</sub> content.

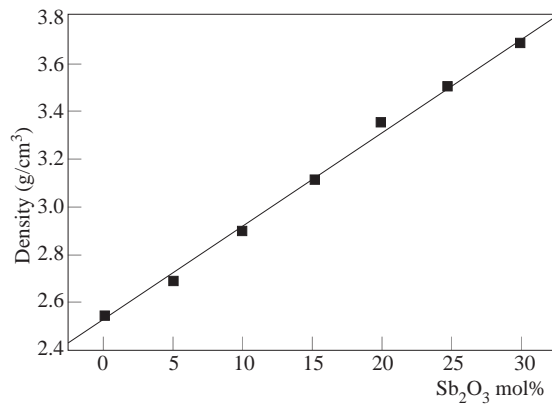


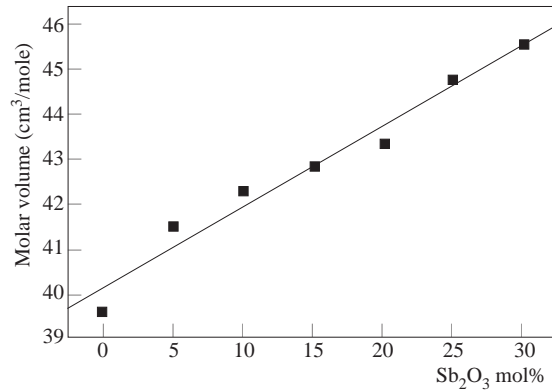
Figure 4. Density versus Sb<sub>2</sub>O<sub>3</sub> content.

Therefore an empirical equation can be applied to the obtained straight line between the density and antimony oxide concentration:

$$d = d_o + mc,$$

where  $d_o$  is the density of the glass sample free of antimony oxide,  $m$  is the slope (the rate of change of density with antimony oxide concentration) and equals  $0.037 \text{ gm cm}^{-3}/\text{mol}$ , and  $c$  is the concentration of antimony oxide.

From Figure 4 one can conclude that the specific volume  $V_s$  represents a gradual linear decrease (the inverse of the density) while the molar volume  $V_m$  showed, as illustrated in Figure 5, a gradual linear increase as B<sub>2</sub>O<sub>3</sub> was gradually replaced by Sb<sub>2</sub>O<sub>3</sub>. This may be also due to the differences between boron and antimony cations in their covalent radii in the glass network [22]. Table (1) summarizes the change in density, specific volume and molar volume of the studied glasses.

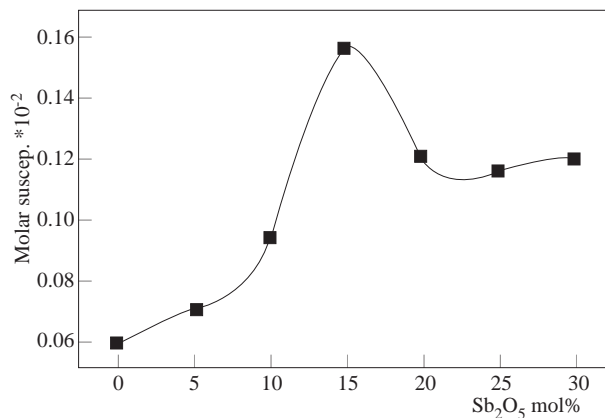


**Figure 5.** Molar volume versus  $\text{Sb}_2\text{O}_3$  content.

**Table 5.** The density, specific volume and molar volume for the different samples.

$\text{Sb}_2\text{O}_3$ content	0	5	10	15	20	25	30
Density	2.54	2.69	2.90	3.12	3.34	3.48	3.66
Specific volume	0.394	0.372	0.345	0.321	0.299	0.287	0.273
Molar volume	39.565	41.483	42.304	42.877	43.375	44.817	45.647

The magnetic susceptibilities of these glasses are presented in Table 2, from which it can be concluded that all glasses are paramagnetic, as confirmed by the ME results. Also from this table, one can see that the molar magnetic susceptibility exhibits a gradual increase which peaks at about 15 mol %  $\text{Sb}_2\text{O}_3$ , then it decreased in the glass sample containing 20 mol %  $\text{Sb}_2\text{O}_3$ . After that it showed approximate stability in the glasses containing antimony oxides between 20 and 30 mol %. This can be attributed to the which antimony acting to change the remainder of the iron ions from  $\text{FeO}_6$  to  $\text{FeO}_4$ , until all iron appears in the four-fold coordination state in the glass, at 15 mol %  $\text{Sb}_2\text{O}_3$ . The observed decrease after that may be due to the formation of some Sb-Fe bonds which may act to pair the d-electrons of the iron cations. The stability of the molar magnetic susceptibilities of the glasses containing high  $\text{Sb}_2\text{O}_3$  content (more than 20 mol %) was supposed to be due to the stabilization of the structural groups constituting the glass networks. [23]. Figure 6 depicts graphically the change in the molar magnetic susceptibility as a function of  $\text{Sb}_2\text{O}_3$  content for all the studied glass samples.



**Figure 6.** Molar suscep. versus  $\text{Sb}_2\text{O}_3$  content.

**Table 2.** The volume, mass and molar magnetic susceptibilities for the different samples.

$\text{Sb}_2\text{O}_3$ mol %	0	5	10	15	20	25	30
Volume suscep. $\times 10^{-7}$	2300	2350	2645	3749	2496	2131	1953
Mass suscep. $\times 10^{-7}$	5842	6322	7671	11697	8337	7416	7148
Molar suscep. $\times 10^{-2}$	5.87	7.05	9.41	15.65	12.08	11.57	11.94

## 4. Conclusion

According to the obtained results and the supposed discussion, it can be concluded that:

- 1) Boron appeared in different borate groups while phosphorous appeared only as PO<sub>4</sub> groups.
- 2) Iron ions appeared mostly as low spin ferric ions in the tetrahedral coordination state.
- 3) Antimony may act as network former and some others may act as bridges between any two adjacent polyhedra.
- 4) It was found also that the gradual replacement of boron by antimony cations increase the effect of the s-electron wave function on the iron nucleus and decrease the electric field gradient due to the networks of these glasses.
- 5) It can be supposed that, at low antimony oxide content glass, the increase in magnetic properties may be due to the change of iron to occupy FeO<sub>4</sub> positions.
- 6) In high antimony oxide glasses, the decrease in magnetic properties may be due to the formation of some Sb-Fe bonds that act to pair the iron d-electrons.
- 7) The gradual linear increase in both the density and the molar volume may be due to differences in the physical constants of both Sb<sub>2</sub>O<sub>3</sub> and B<sub>2</sub>O<sub>3</sub>.

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