

Studies on Some Lithium-Borate Glasses Containing Iron and Copper

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Abstract

A lithium-borate-glass system containing iron and copper cations has been thoroughly investigated, in order to obtain information about the structural role of both the iron and copper in such glass hosts.

The amorphous phase of the prepared glass samples was confirmed from their X-ray diffraction. From the infrared spectra it was concluded that the glass networks are highly deformed and boron appeared in both tri- and tetra-hedral coordination states as well as in some ring structure. As copper was introduced, replacing lithium, it acts as a network modifier only while the iron acts as network former (FeO_4).

The molar magnetic susceptibility showed two maxima at 12.5 and 17.5 mol% copper oxide content, and a minimum at 15 mole%. Over the range of $\text{CuO}/\text{Li}_2\text{O}$ mixture fractions investigated, the density and the calculated molar volume values showed a gradual increase. We have attempted to correlate the molar volume values with the molar magnetic susceptibility of these glasses. All the obtained results were discussed on the basis of the glass structure and boron anomaly.

Key Words: Glass structure, Glass containing transition metal ions, Structure and physical properties of glass.

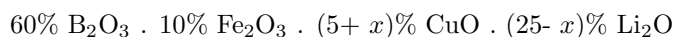
1. Introduction

Nowadays, attention is being drawn to investigate glasses as useful solid materials, especially those containing transition metal cations [1-5]. Early on, boron was identified as an important glass former which can be used in the preparation of glasses for both scientific and technological applications. The addition of alkali oxides may improve the physical properties of these glasses as well as modify— even improve— their preparation conditions. Lithium is an important alkali cation and copper as well as iron are of the most important transition metals. Glasses containing iron and copper oxides are of high interest due to their effects on the physical properties of such glasses, i.e. mainly the electrical and the optical properties [6, 7]. Therefore many studies have been reported in which it was concluded that copper can exist in two different oxidation states (Cu^+ and Cu^{2+}), and that it can also coordinate as CuO_4 or CuO_6 in a glass network [8]. The study of the structural role of iron is also of interest due to the usual presence of iron cations in most industrial glasses.

In this paper, we report on our study of samples of lithium borate glass containing varying concentrations of the two transition metals copper and iron, and characterized via X-ray were prepared and investigated using X-ray diffraction, IR, DTA, magnetic susceptibility, density and molar volume measurements. We have also attempted to correlate the molar susceptibility with the molar volume values of these glasses.

2. Experimental

A lithium-borate glass system with copper and iron oxides was prepared, with component fractions measured according to the following stoichiometric formula:



[where $x = 0, 2.5, 5, \dots, 15$]

The finely mixed batches were melted in porcelain crucibles at 1000 °C for two hours in air. The melts were stirred from time to time to ensure complete homogeneity, and were then poured on a pre-heated stainless steel plate. The glasses were then annealed over night at 350 °C.

The density of the obtained solid glasses was first measured via Archimedes technique. A sample was weighed in air (w_a) and in toluene (w_t) and its density d was then calculated from the equation

$$d = \left(\frac{w_a - w_t}{w_a} \right) d_t, \quad (1)$$

where d_t is the density of toluene.

After obtaining the density of all glasses the specific volume V_s were then calculated using the equation

$$V_s = \frac{1}{d}. \quad (2)$$

Then the molar volume values were calculated using the measured densities and the calculated molecular weight for one mole w_m of glass sample, via the equation

$$V_m = \frac{1}{d} w_m. \quad (3)$$

The solid glasses were then powdered to obtain a glass with particle size less than 160 mesh.

A Bruker Vector-22 Fourier transform infrared (FTIR) spectrometer was used to analyze the present structural units in the glass network

Gouy method was also applied to study the magnetic properties of these glasses using a one Tesla Oxford-electromagnet at RT.

A Shimadzu-50 differential thermal analyzer was used to determine the transition temperatures of these glasses.

3. Results and Discussion

The prepared glass system was firstly examined by X-ray diffraction, from which Figures 1a and 1b show the X-ray patterns for the first and the last samples, respectively. Figure 1a shows two humps at approximately $2\theta = 25^\circ$ and $2\theta = 45^\circ$, while no similar humps are shown in the second figure, and neither figure exhibits any detectable peaks. These two patterns indicated that all the glasses studied are in pure amorphous, non-crystalline phase

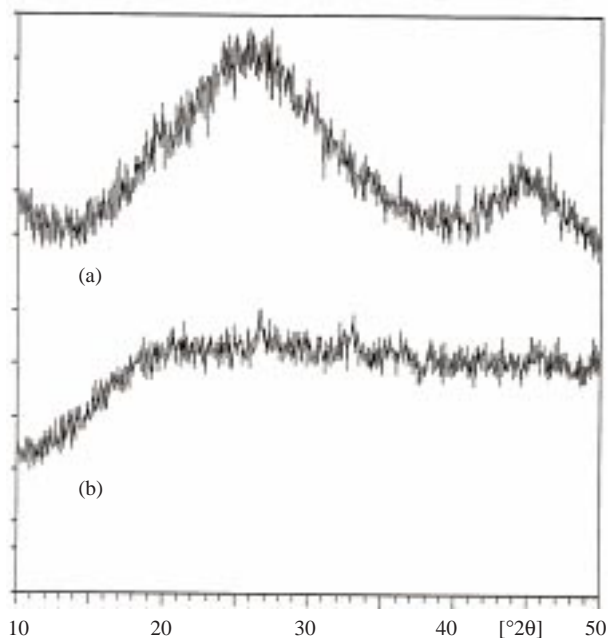


Figure 1. X-ray diffraction patterns.(a) shows the diffraction pattern for sample 1 ($x = 0$) and (b) shows the corresponding pattern for sample 7 ($x = 15\%$).

The density of glasses and amorphous solids are of special importance, especially in the context of the study of their structure. Such importance arises from the ability of the density of a glass to change abruptly when its structure is slightly changed. Hence, the densities of these glasses were measured to show if there is any structural change as the copper oxide was gradually increased at the expense of the lithium oxide. The obtained density values and the calculated specific volume as well as the molar volume values are shown in Table 1.

Table 1. The density, specific volume values versus CuO content.

| Samp. No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|-----------|-------|-------|-------|-------|-------|-------|-------|
| CuO % | 5 | 7.5 | 10 | 12.5 | 15 | 17.5 | 20 |
| Density | 2.61 | 2.62 | 2.64 | 2.65 | 2.65 | 2.67 | 2.71 |
| Sp. vol. | 0.384 | 0.381 | 0.379 | 0.378 | 0.377 | 0.375 | 0.369 |
| Mol. Vol. | 26.6 | 26.8 | 27.1 | 27.5 | 27.9 | 28.2 | 28.3 |

Figure 2 shows the change of the density as a function of copper oxide content. It appears that the density increased gradually from 2.61 to 2.71 gm.cm^{-3} , as copper oxide was gradually increased at the expense of lithium oxide content. The change in the density appeared to be very slight, which can be attributed to the role played by copper oxide that aid the homogeneity of the glasses and in supplying the networks the excess oxygen [9]. The specific volume directly represent the inverse of the density; but the molar volume is of higher interest, since it relates directly to the spatial distribution of the oxygen in the glass network. Figure 3 shows the change in the molar volume values with the increase of copper oxide, exhibiting approximately slight gradual increase. These means that the introduction of copper cations in the glass network act to open the glass structure.

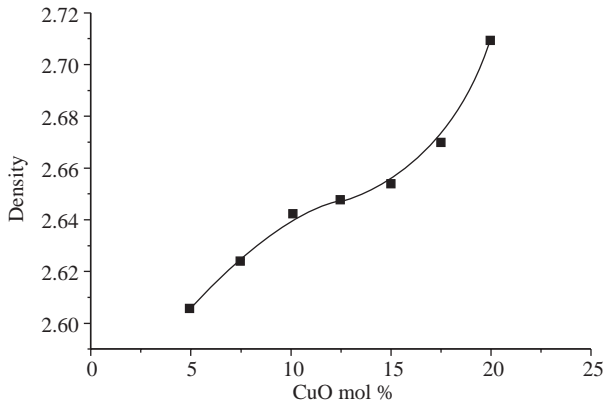


Figure 2. Density versus CuO content.

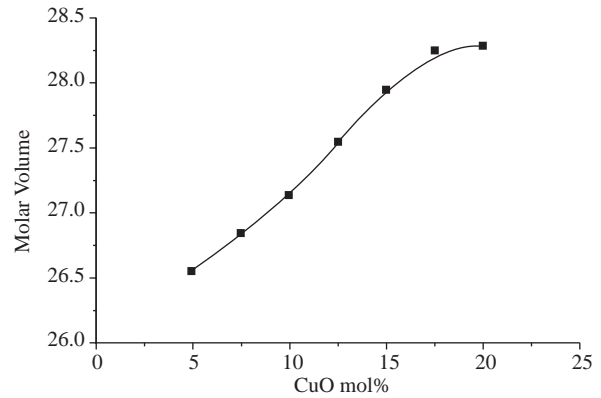


Figure 3. Molar volume against CuO content.

The magnetic properties were also obtained applying the Gouy method, according to which the volume magnetic susceptibility K_v can be given by the equation

$$K_v = K_a + \frac{2\Delta mg}{ah^2}, \quad (4)$$

where

K_a is the volume magnetic susceptibility of air and usually taken to be zero;

Δm is the weight difference due to the magnetic pull of the sample;

g is gravitational acceleration;

a is the cross-section of the tube containing the powdered sample; and

H is the magnetic field intensity

The mass magnetic susceptibility are usually obtained applying the equation

$$K_m = K_v/d, \quad (5)$$

where d is the experimentally obtained density of the sample.

The molar magnetic susceptibility is now calculated by multiplying the mass magnetic susceptibility by the molecular weight of one mole of the glass sample, via

$$K_M = K_m W_t. \quad (6)$$

All the obtained magnetic properties are listed in Table 2.

Table 2. The magnetic properties of the glasses under study.

| Samp. No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|-----------|--------|--------|--------|--------|--------|--------|--------|
| CuO % | 5 | 7.5 | 10 | 12.5 | 15 | 17.5 | 20 |
| Vol. sus. | 3.6E-6 | 3.3E-6 | 3.4E-6 | 3.8E-6 | 2.5E-6 | 3.2E-6 | 2.7E-6 |
| Mas. Sus. | 1.4E-6 | 1.3E-6 | 1.3E-6 | 1.4E-6 | 9.5E-7 | 1.2E-6 | 1.0E-6 |
| Mol. Sus. | 9.4E-5 | 9E-5 | 9.2E-5 | 10E-5 | 7.1E-5 | 9.1E-5 | 7.7E-5 |

Figure 4 shows the change in the molar magnetic susceptibility of these glasses as a function of CuO content. The figure shows two peaks in the magnetic susceptibility at around 12.5 and 17.5 mol% of CuO, while a minimum occurs at 15 mol% CuO. As for the very noticeable decrease at approximately 20 mole% of CuO, this might be an indication that, as the copper oxide replaces lithium cations, more iron come to occupy the network forming positions; that is, the FeO_4 groups increased gradually at the expense of FeO_6 groups.

The gradual increase of the magnetic susceptibility of these glasses can be understood from the fact that the magnetic moment of FeO_4 groups is higher than that of FeO_6 groups. The observed sharp decrease between 12.5 -15 mol% CuO may be due to the gradual increase of the CuO content, since the magnetic moment of Cu^+ cations is less than that of Fe^{3+} cations [10]. The observed maximum magnetic susceptibility at 17.5 mol% CuO content may be due to the appearance of Cu^{2+} cations occupying the interstitial positions. The decrease that follows can be attributed to the participation of some copper cations as network former, since the amount of iron content is limited at 10 mol%.

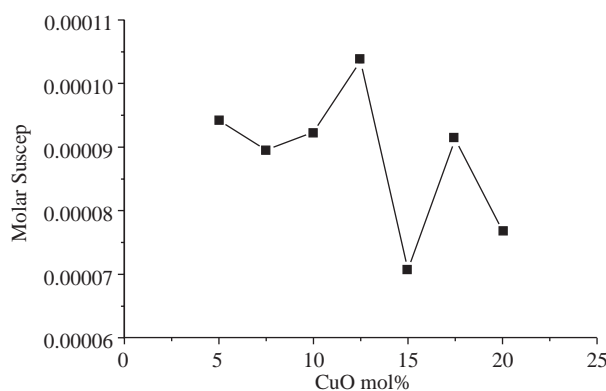


Figure 4. Molar susceptibility against CuO content.

Figure 5 shows the change in molar magnetic susceptibility as a function of the molar volume of these glasses. It shows two maxima for molar volumes of 27.5 and 28.25 cm^3/mole . It can be stated that the gradual increase of molar susceptibility as the molar volume gradually increased may be due to the structural opening, since the ionic volume of the copper cation is as high as that of the lithium cation, until it reach its maxima at 27.5 cm^3/mole . The minimum and the maximum observed at 27.9 and 28.2 cm^3/mole , respectively, may be due to the formation of some non-bridge oxygen which aids to contract slightly the glass structure [11].

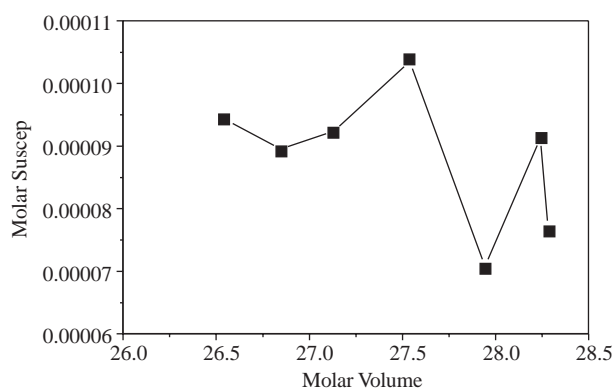


Figure 5. Molar susceptibility against molar volume.

Figure 6 shows some representative infrared absorption spectra of the studied glasses, i.e., for samples 1, 3, 5, and 7. It appeared that a band appeared around 460 cm^{-1} in all sample 5, due to the vibrations of lithium cations through the glass network [12]. Another band appeared around 550 cm^{-1} shifts towards higher energy in sample 3, then shifts towards lower energy sample 5 then disappears completely in sample 7 (i.e. at maximum lithium content). This band can be attributed to some deformation modes of the network structure as well as the vibration of some FeO_4 groups [13,14].

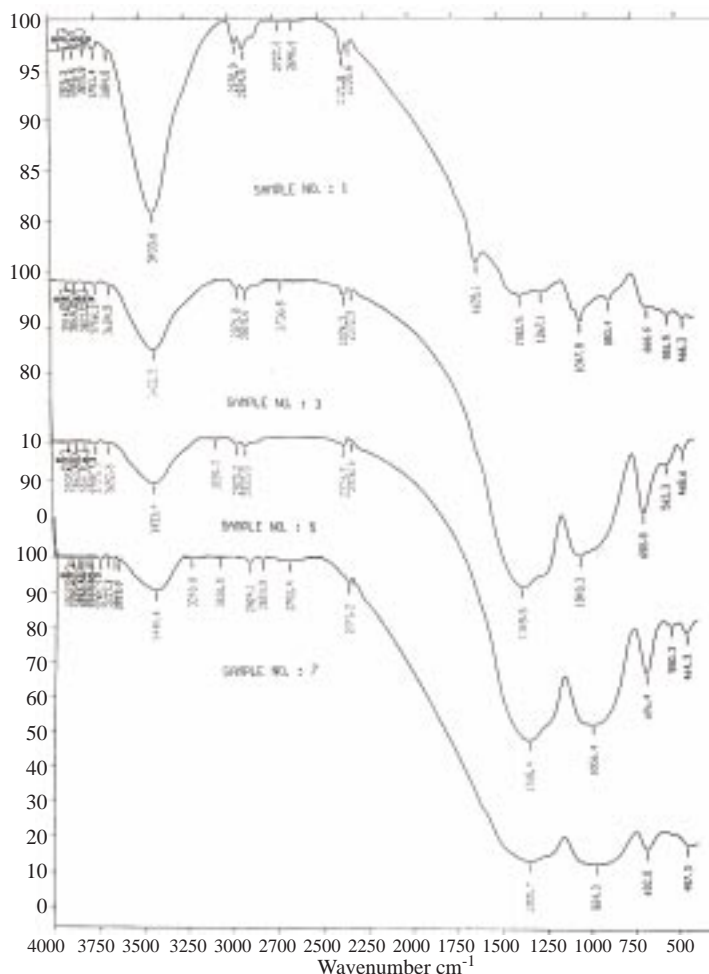


Figure 6. IR Spectra of samples (1, 3, 5 and 7).

A band that appeared at 666 cm^{-1} in sample 1 was found to shift towards higher energy, to appear at 692 cm^{-1} in sample 7. This band can be attributed to the bond bending vibrations of the bridging oxygen anions [15]. There is also a band that appeared only in sample 1 at 883.4 cm^{-1} and may due to the vibrations of different borate groups [12].

A band appeared at 1047 cm^{-1} in samples 1 and 2, and appeared to shift towards lower energy on going to sample number 7. This band can be attributed to vibrations of diborate bridging to penta borate groups, and to the asymmetric and stretching vibrations of BO_4 groups [12].

The band that appeared at 1267 cm^{-1} in sample 1 was found to shift to lower energy, to appear at 1250 cm^{-1} in sample number 7. This can be attributed to B-O bond stretching vibrations involving mainly the linkages between oxygen and different groups as well as the B-O bridging between B_3O_6 rings and BO_3 triangles [13,16,17].

A band that appeared at 1382 cm^{-1} in sample 1 was found to shift toward higher energy and appear at 1355 cm^{-1} . This band can be attributed to the B-O symmetric stretching vibrations of various borate groups [16].

The bands appeared after that are attributed to the presence of water groups and O-H bond vibrations [18, 19].

The observed shift toward lower energy as Li^+ cations increase may be due to the high polarizing power of lithium cations.

Table 3. The glass transition temperature obtained from DTA.

| | | | | | | | |
|----------------|-----|-----|-----|------|-----|------|-----|
| Samp. No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| CuO % | 5 | 7.5 | 10 | 12.5 | 15 | 17.5 | 20 |
| T _g | 594 | 601 | 608 | 617 | 624 | 633 | 642 |

The glass transition temperatures are given in Table 3, and shows a gradual increase from 594 °C to 642 °C as copper oxide content was gradually increased. The observed increase may be due to the increase in copper cations content which act to stabilize the glass network ,since it possess lower electronegative values and higher ionic volumes in the comparison to lithium cations [20].

4. Conclusion

The glass samples were checked by X-ray diffraction, where the obtained patterns indicated that all the studies glasses are in pure non-crystalline phase. From the above results it can be concluded that:

1. The magnetic susceptibility showed a minimum for the sample containing 15 mol% CuO, and showed two maxima at 12.5, 17.5 mol% CuO.
2. On relating the molar susceptibility and the molar volume it appeared that two maxima were obtained at 27.5 and 28.25 cm³/ mole.
3. It was concluded that groups like BO₃, BO₄ and FeO₄ acted as network structural groups while copper and lithium appeared in the interstitial positions.
4. The DTA analysis indicated that the glass transition temperature increase from 594 °C to 642 °C as copper oxide was gradually increased from 5 to 20 mol%.

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