

Nuclear Magnetic Resonance and FTIR Structural Studies on Borosilicate Glasses Containing Iron Oxide

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Abstract

The structure of borosilicate glasses of composition $30\text{Na}_2\text{O}-2\text{Al}_2\text{O}_3-25\text{SiO}_2-x\text{Fe}_2\text{O}_3$ ($43-x$) B_2O_3 has been investigated in the composition range of 0.5 - 20 mol% Fe_2O_3 . ^{27}Al , ^{11}B , ^{29}Si MAS NMR and FTIR spectroscopies have been used to measure the fraction of different structural species in the glasses. It is evidenced from NMR data that both sodium and Fe_2O_3 (in low region up to 7 mol%) are the main glass modifier. Structural determination for borosilicate glasses with a high content of (Fe_2O_3) was carried out by FTIR spectroscopy, where both ^{11}B and ^{29}Si MAS NMR are impossible because of the high quantities of paramagnetic iron (III) species present. NMR analysis was performed on borosilicate glasses containing up to 7 mol% Fe_2O_3 and the N_4 values obtained by FTIR spectroscopy agree within error with the ^{11}B NMR results of the same glass samples. Fe_2O_3 is a main glass modifier in the low- Fe_2O_3 -content region (≤ 6 mol%). On other hand, it plays the role of glass former at higher content of Fe_2O_3 . Increasing both N_4 of boron tetrahedral units and chemical shift of silicon nuclei to reach maxima at 5 mol% Fe_2O_3 confirms the role of Fe_2O_3 as a glass modifier in the low composition region. On the other hand, fast decrease in N_4 with further increasing Fe_2O_3 contents (≥ 6 mol%) is an evidence for iron oxide to inter the glass network as a network former.

Keywords

NMR-FTIR-Spectroscopy-Borosilicate-Glasses

1. Introduction

Ternary and quaternary borosilicate glasses (BSG) have an extended variety of industrial importance due to their different types of applications. They have been used as sealing

components. For example, some of glass compositions have been simply used as sealants in television tubes or bulb lamps. On the other hand, increasing achievements of microelectronics and new demands necessitates new types of glasses. Recent studies have concentrated on borosilicate glasses, which have been developed as sealants, particularly, for molten carbonate fuel cells (MCFC) [1] [2].

Because of the technological advantages, these glasses have long been the subject of structural studies, using different techniques, including ^{29}Si and ^{11}B MAS NMR and FTIR spectroscopy [3]-[7] to offer a quantitative analysis of different structural units forming the glass network. The structure of borosilicate glasses is based on Q^n [SiO_4] units, where n is the number of bridging oxygen atoms per tetrahedron, and [BO_3] and [BO_4] units. The [BO_3] units are triangle boron in both ring and non-ring configuration, while [BO_4] ones are boron atoms in tetrahedral coordination. The oxygen atoms can be bonded to one boron and three silicons (1B, 3Si) or four silicon atoms (0B, 4Si) and have a Na^+ ion as a charge compensator.

The distribution of the borate and silicate structural units depends on two structural factors namely R and K . Generally, R is the ratios of $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ and K is the ratio of $\text{SiO}_2/\text{B}_2\text{O}_3$ [8] [9]. Dell *et al.* [8] proposed a structural model for which the variation of [BO_4] borate units (N_4) is represented as a function of the R parameter. For all K values, N_4 increases up to a maximum in between 0.5 and 0.75 for $R = 1$, and the value of this maximum increases with an increasing K values. Then, the proportion of N_4 slowly decreases for higher R values.

In present study, two individual composition regions of borosilicate glasses were investigated in order to test the possible quantitative use of NMR and FTIR spectroscopy. The first type contains a limited concentration from Fe_2O_3 as a paramagnetic material. In such a case NMR study can easily be applied to obtain values of Q^n and N_4 fraction in the borosilicate glass. On the other hand, the second type of borosilicate glasses contains further high level from Fe_2O_3 (>6 mol%). These concentrations are unsuitable for NMR measurements. This is because the variation in local fields due to the unpaired electron spins produces sufficient broadening of NMR lines [10]. As a result, different contributions cannot be resolved and some may even be unobservable.

FTIR spectroscopy is not affected by the presence of paramagnetic species and therefore it would be a very useful tool for quantitative measurement of structural fractions, such as Q^n in silicate and N_4 in borate networks where NMR is impracticable. In this study, FTIR spectroscopy can be applied for all glass compositions while MAS NMR technique is applied only on glasses of low Fe_2O_3 concentration (≤ 6 mol%).

2. Experimental

2.1. Sample Preparation

The modified borosilicate glasses were prepared by melting batches in alumina crucibles at a temperature ranging from 1250°C to 1520°C depending on composition. Then the melt was quenching over a stainless steel plate. The batches were prepared from reagent grade SiO_2 , H_3BO_3 , Na_2CO_3 , Al_2O_3 and Fe_2O_3 .

2.2. Nuclear Magnetic Resonance

All samples were measured with JEOL GSX-500 high-resolution solid-state MAS NMR spectrometer in a magnetic field of 11.4 T. ^{29}Si MAS NMR spectra were recorded at a frequency of 99.3 MHz and a spinning rate of 6 kHz. A cylindrical zirconia sample holder was rotated at a speed depends on the type of the measured nuclei. The applied pulse length was 2.62 μs and a recycle delay of 30 s. typically 1000 - 2000 scans were acquired. ^{11}B MAS NMR spectra were recorded at a frequency of 160.4 MHz and spinning rate of 15 KHz. The glass samples were measured with a single pulse length of 0.5 - 1.0 ms and a pulse delay of 2.5 s, and an accumulation of 100 - 200 scans. ^{27}Al MAS NMR spectra were recorded at a frequency of 130.3 MHz and spinning rate of 6 KHz.

2.3. FTIR Measurements

Fourier transform infrared absorption signals of the studied glasses were measured at room temperature (20°C) in the wavelength range 4000 - 400 cm^{-1} using a computerized recording FTIR spectrometer (Mattson 5000, USA). Fine powdered samples were mixed with KBr in the ratio 1:100 for quantitative analysis and the weighed mixtures were subjected to a load of 5 t/cm^2 in an evocable *i.e.* to produce clear homogenous discs. Then, the IR absorption spectra were immediately measured after preparing the discs to avoid moisture attack.

3. Results and Discussion

There is a wide range of compositions which can form glass in the silicate and borosilicate systems [3] [5] [9] [11]-[14]. The structure of these glasses depends on two factors, namely R and K ($R = \text{modifier}/\text{B}_2\text{O}_3$ and $K = \text{SiO}_2/\text{B}_2\text{O}_3$) [8] [9]. The structural factors of the base glass ($30\text{Na}_2\text{O}-2\text{Al}_2\text{O}_3-25\text{SiO}_2-43\text{B}_2\text{O}_3$) are $R = 0.7$ and $K = 0.58$. The experimental results are mostly obtained on modified borosilicate glasses having $R > K$ in all cases, since R changes between 0.7 and 1 and K changes from 0.58 to 0.67. In this case, the modifier oxide is participated between both the borate and the silicate network.

3.1. Iron Free Borosilicate Glass

It was known that Al_2O_3 plays the role of both glass former and modifier in the network of the glass [15] [16]. This depends upon the type of the glass and the content of Al_2O_3 . In our case, the Al_2O_3 enters the glass as a network former, since the value of chemical shift of the Al spectrum **Figure 1** is 59.6 ppm which assures that the aluminum is found in tetrahedral coordination which means that Al_2O_3 is consumed as a glass former.

Figure 2 presents ^{29}Si NMR spectrum of iron free borosilicate glass. The chemical shift (σ) of base glass is appeared at -88.4 ppm which is related to Q^2 species. This leads that the modifier oxide is consumed to break two bridging bonds as an average per each tetrahedral SiO_4 unit. **Figure 3** shows experimental ^{29}Si MAS NMR for glasses containing different concentrations from Fe_2O_3 (0, 5 mol%). Comparing the two spectra, it can be seen from this figure that there is remarkable shift in the peak position between the spectral lines of ^{29}Si NMR of iron free glass and one contains 5 mol%

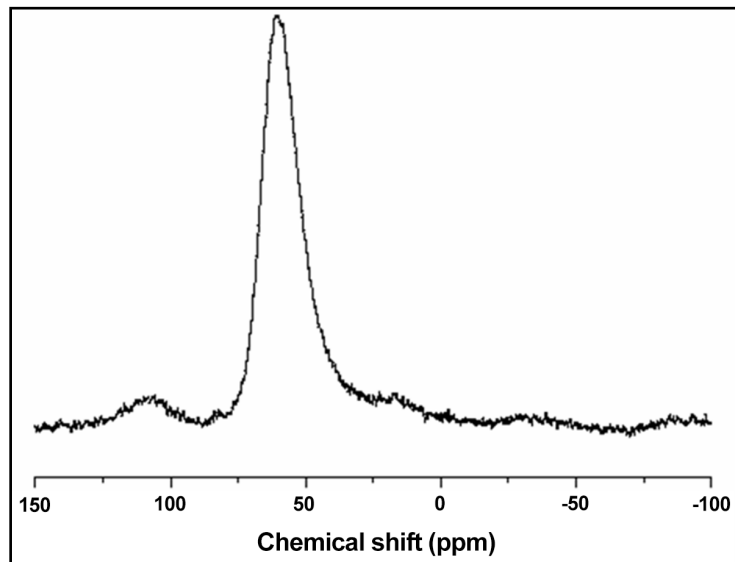


Figure 1. ^{27}Al NMR spectrum of iron free glass.

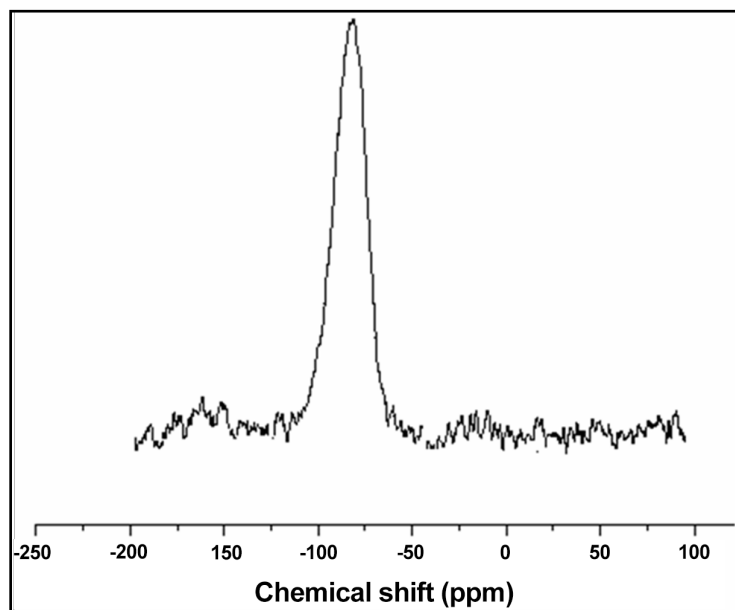


Figure 2. ^{29}Si NMR spectrum of iron free glass.

Fe_2O_3 . The substitution of 5 mol% B_2O_3 by 5 mol% Fe_2O_3 has a clear effect on the chemical shifts (σ) of silicon nuclei. (σ) of base glass is appeared at -88.4 ppm, but the chemical shift value (σ) of glass containing 5 mol% is increased to reach -84.4 ppm upon addition of 5 mol% Fe_2O_3 . This means that most of all of Fe_2O_3 is consumed as suggested above as a modifier, which results in increasing the concentration of NBO in silicate network. Increasing NBO atoms in silicate network is reflected from increasing behavior of chemical shift with increasing Fe_2O_3 content **Figure 4**. This confirms that silicate units are deshielded or depolymerized with increasing iron oxide content in the region up to 6 mol%.

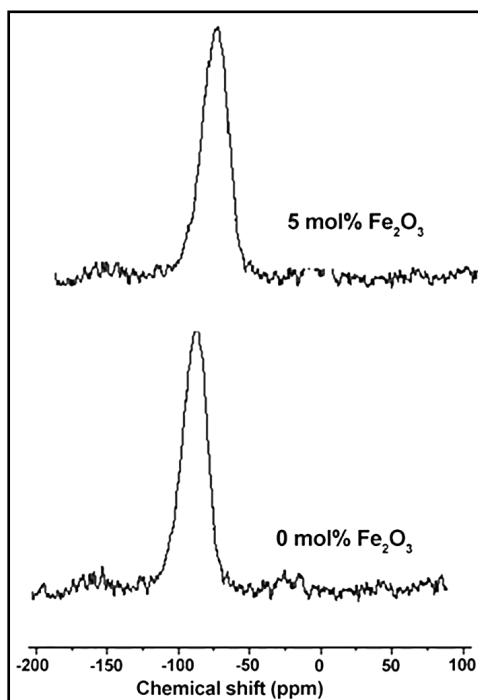


Figure 3. Chemical shift of ^{29}Si NMR spectra of iron free (at bottom) and for glass contains 5 mol% iron oxide.

Figure 5 shows experimental ^{11}B MAS NMR for glasses containing different concentrations from Fe_2O_3 . The spectrum at the bottom was obtained from sodium borosilicate glass (free from Fe_2O_3) with $R = 0.7$ and $K = 0.58$. The second two spectra were obtained from a glass containing 3 and 5 mol% Fe_2O_3 with R around 0.9. It can be seen from this figure that there is no remarkable shift in the peak position of the spectral lines of ^{11}B NMR. Substitution of 5 mol% B_2O_3 by 5 mol% Fe_2O_3 has no effect on the chemical shifts (σ) of boron nuclei. Chemical shift of BO_4 is appeared at 0 ppm for all investigated samples. But the fraction of boron tetrahedral units (N_4) is only affected, since it changed from 0.52 to 0.65 upon addition of 5 mol% Fe_2O_3 , see **Figure 6**. This means that substitution of B_2O_3 by Fe_2O_3 results in increasing the concentration of bridging bonds in the borate network through transformation of BO_3 triangle units to BO_4 groups.

Fe_2O_3 is therefore played the role of glass modifier in the region between 0 and 5 mol%. This based on the difference between the values of N_4 for sample free from Fe_2O_3 and the other containing 5 mol%, since glasses containing Fe_2O_3 showed higher values of N_4 compared with that of iron free glass, see **Figure 6**.

Higher concentrations of Fe_2O_3 (8 - 20 mol%) are unsuitable for both ^{11}B and ^{29}Si NMR measurements [10]. This is because the high level of paramagnetic oxides which can induce local fields due to the unpaired electron spins which in turns produces sufficient broadening of NMR lines. Therefore, structure of glasses in the higher composition region has to be investigated by FTIR absorbance spectroscopy.

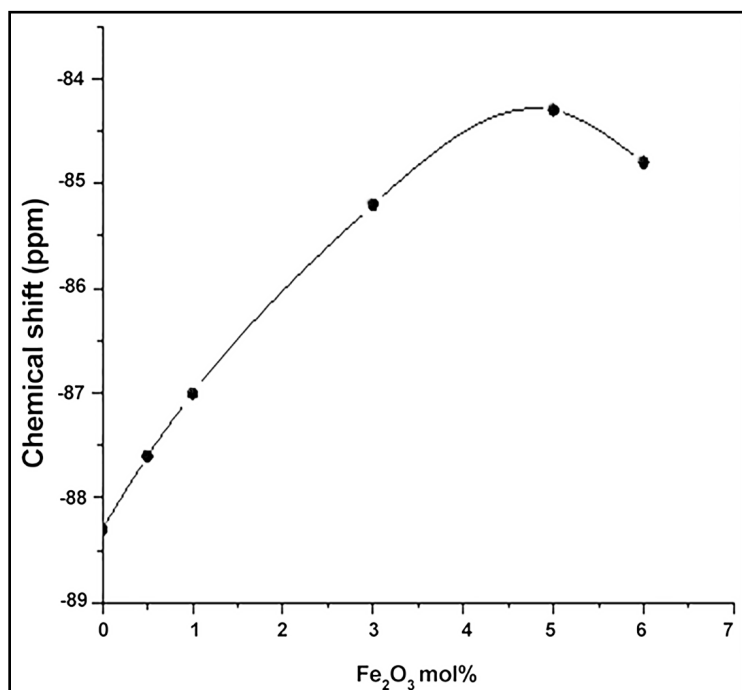


Figure 4. Chemical shift of ^{29}Si NMR spectra as a function of Fe_2O_3 contents.

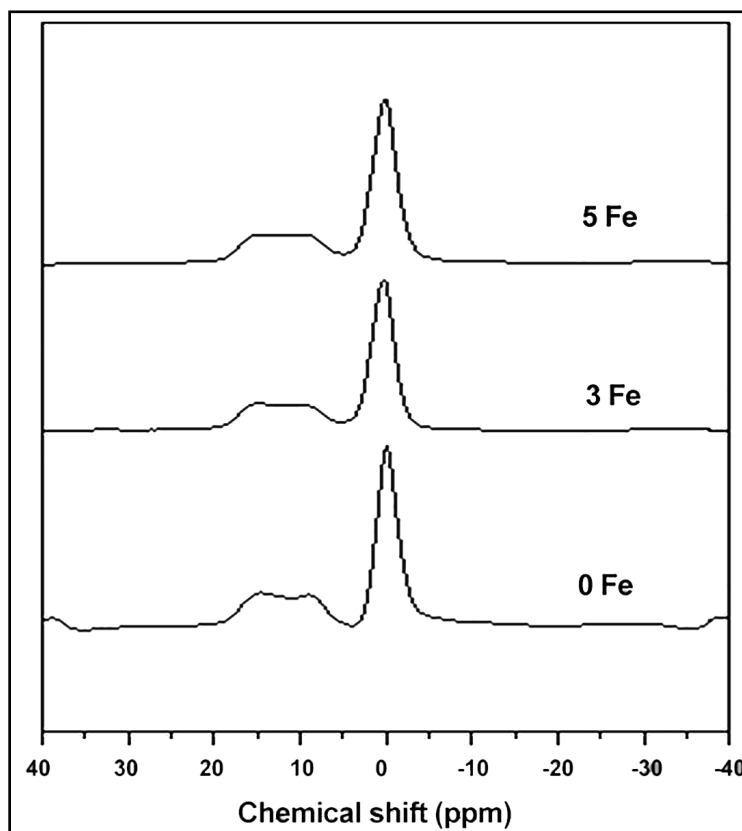


Figure 5. ^{11}B NMR spectra of selected composition of modified borosilicate glasses containing Fe_2O_3 .

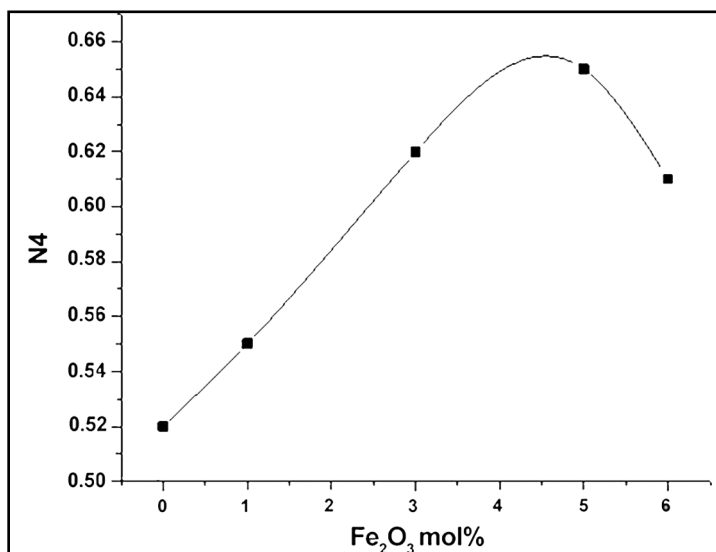


Figure 6. Fraction of boron tetrahedral as a function of Fe₂O₃ concentration.

3.2. FTIR Spectroscopic Analysis

Figure 7 shows FTIR spectra obtained for the studied sodium borosilicate glasses containing different concentrations from Fe₂O₃. It can be realized from this figure that there are well defined FTIR envelopes appeared at about 800 and 1580 cm⁻¹ in glasses containing up to 6 mol% Fe₂O₃ concentrations. The FTIR envelop cited at about 800 cm⁻¹ is assigned to NBO atoms in Q² and Q¹ species. This envelop is totally disappeared and the new IR peak at about 1285 cm⁻¹ is clearly seen at higher Fe₂O₃ concentrations. The well-defined envelopes at 800 cm⁻¹ and 1580 cm⁻¹ are assigned to vibration of Si-O (non-bridging bonds) in different silicate networks [11] [13] [17] as a result of addition of Fe₂O₃ (up to 6 mol%). Disappearing of these envelopes and appearance of new one at 1285 cm⁻¹ leads that concentration of NBO in the silicate network is reduced upon more addition of Fe₂O₃ (≥6 mol%). The appearance of the envelop at about 1285 cm⁻¹ is assigned to stretching vibration of Fe-O in iron silicate and borate species, as a glass forming groups [18]-[21]. On other wards, Fe₂O₃ in such situation plays, as suggested above, the role of glass former. It can remove NBO from the silicate network and as a result it consumes part of the modifier to form FeO₄ groups. In such situation, Si-O-Fe bonds are constructed and it played the role of shielding silicate units.

Quantitatively, **Figure 8** presents change of the fitted areas representing NBO and concentration of FeO₄ as a glass former against Fe₂O₃ content. The relative area of the peak centered at about 800 cm⁻¹ is clearly seen to increase with increasing Fe₂O₃ content, see **Figure 8** (between 0 and 5 mol%). On the other hand, at higher Fe₂O₃ content the envelope at 800 cm⁻¹ is decreased and vanished and other envelop at 1280 cm⁻¹ is rather appeared. The increasing behavior of relative area (at 800 cm⁻¹) may indicate an increase of the number of non-bridging oxygen atoms upon addition of Fe₂O₃ in silicate network. Higher area means higher concentration of modifier in the silicate network upon addition of 6 mol% Fe₂O₃. In this case we suggest that most of Fe₂O₃ enter the

borosilicate network as an effective modifier. The relative area of the envelope at 1280 cm^{-1} (see **Figure 8**) is remarked to increase upon addition of more Fe_2O_3 ($>5\text{ mol}\%$). These features are suggested to be due to reducing the content of modifier and NBO in the network of the glasses due to changing the structure role of iron from modifier to former. Presence of the well resolved envelope at about 1280 cm^{-1} confirms the presence of iron as a former units connected to BO_3 groups as basic former units. Presence of Fe_2O_3 as a glass former should in turns reduce the fraction of boron tetrahedral units and NBO in the silicate network.

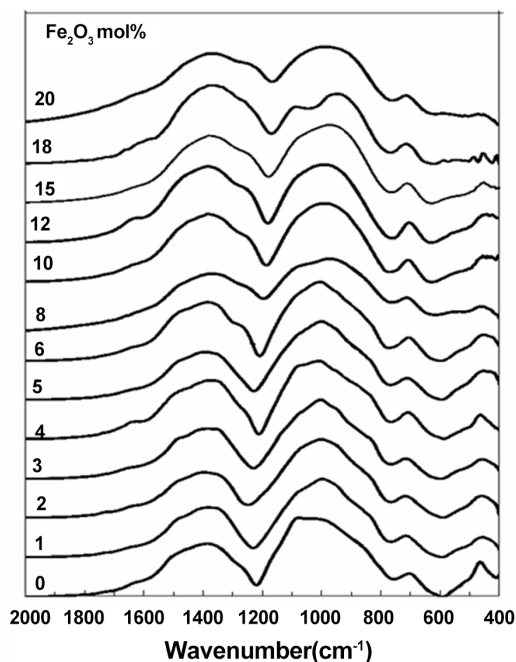


Figure 7. FTIR absorbance spectra of borosilicate glasses containing different Fe_2O_3 concentrations.

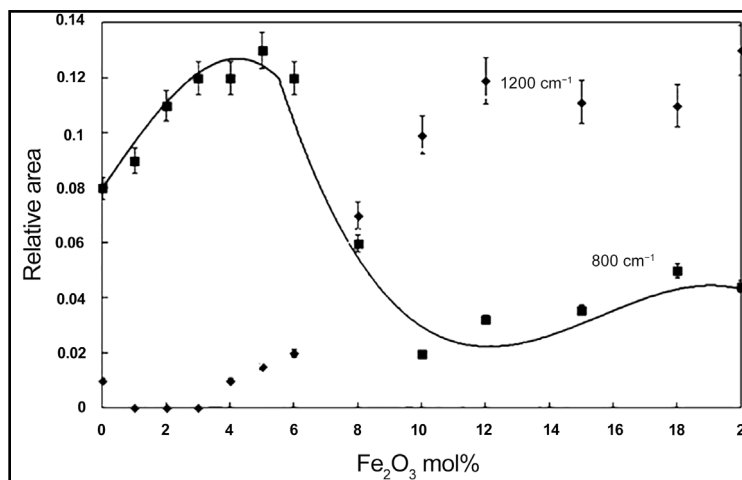


Figure 8. Changes of relative area of both IR peaks centered at 800 cm^{-1} and 1280 cm^{-1} .

4. Conclusion

Borosilicate glasses containing different concentrations from Fe_2O_3 have been prepared and investigated with FTIR and NMR spectroscopy. At low concentration from Fe_2O_3 (≤ 6 mol%), iron oxide enters the glass network as a modifier. On the other hand, Fe_2O_3 is consumed as a glass former at higher concentration. The modifier part of iron oxide is consumed to form NBO in silicate and bridging bond in borate network. As a result Q^2 was found as the main units in silicate network. The fraction of boron tetrahedral N_4 was found to increase in glasses of up to 6 mol% iron oxide. At higher concentration N_4 decreases due to the action of Fe_2O_3 as a glass former.

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