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The Influence of Thermal Treatment on the Structure and Morphology of Iron Borosilicate Glasses

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تأثير المعالجة الحرارية على بنية وتشكل زجاج البوروسيليكات المحتوي على الحديد

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Abstract:
The effect of heat treatment on the structure and morphology of iron borosilicate glass was analyzed using x-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and high-resolution transmission electron microscopy (TEM) coupled with electron diffraction pattern (EDP) technique. The selected samples were being subjecting to heat treatment at 650^{O}C for 4 hr. FTIR measurements of the heat-treated samples revealed a significant decrease in the peak intensity associated with threefold-coordinated B–O bonds, accompanied by a significant increase in the band intensity corresponding to the tetrahedral units. According to XRD observation, the disappearing of diffraction peaks for the selected samples after heat treatment confirms the vitreous nature of the observed samples. TEM-EDP patterns revealed a reduction in the cluster size with the addition of Fe_2O_3 content, indicating the high ability of iron to withdraw non-bridging oxygens (NBOs) from silicate network and to behave as a glass former. On the other hand, the increasing in the particles number and aggregations that distributed in the internal structure is primarily attributed to the high temperature reached during thermal treatment.

Keywords: Heat treatment, nanoparticles, NBO, iron oxide, glass network

الملخص
اختص هذا البحث بدراسة تأثير المعالجة الحرارية على البنية والتشكل لزجاج البوروسيليكات المحتوي على الحديد باستخدام حيود الأشعة السينية (XRD) وتقنية مطيافية الأشعة تحت الحمراء بتحويل فورييه (FTIR) والمجهر الإلكتروني النافذ عالي الدقة (TEM) والمزود بنماذج حيود الإلكترونات (EDP). خضعت العينات المختارة إلى معالجة حرارية عند درجة حرارة 650° م لمدة 4 ساعات. أظهرت قياسات (FTIR) للعينات المعالجة حرارياً انخفاضاً ملحوظاً في شدة القمم المرتبطة بروابط B–O ثلاثية التناسق مع زيادة واضحة في شدة الحزمة المقابلة للوحدات رباعية السطوح. ايضا، ووفقاً لنتائج (XRD) فإن اختفاء قمم الحيود للعينات المختارة بعد المعالجة الحرارية يؤكد الطبيعة الزجاجية للعيّنات المدروسة. كما كشفت أنماط (TEM-EDP) عن تناقص في حجم تجمعات الجسيمات مع زيادة محتوى أكسيد الحديد في العينات الغير معالجة مما يشير إلى قدرة الحديد العالية على سحب وحدات الأكسجين غير المرتبطة (NBOs) من شبكة السيليكات والعمل كمُحسن لخصائص الزجاج. بالمقابل، فإن هناك زيادة في عدد تجمعات الجسيمات ضمن البنية الداخلية لعينات الزجاج المعالج حراريا كنتيجة لارتفاع درجة الحرارة الناتج عن المعالجات الحرارية.

الكلمات المفتاحية: المعالجة الحرارية، جسيمات النانو، NBO، أكسيد الحديد، الشبكة الزجاجية.

Introduction

Borosilicate glasses are distinguishable materials [1-3] by having their unique properties such as high chemical durability, thermal resistance and low coefficients of thermal expansion. for instance, iron-modified borosilicate glasses can be customized for specific optical, physical and conductivity properties and numerous of technological applications by adjusting their composition concentrations. In iron-borosilicate glasses, the distribution of the modifier cations between the borate and silicate networks is strongly influenced by the ratio of overall glass compositions. The kinetic of this distribution affects the coordination number not only of boron and Q^n in silicon, but also iron coordination links. Iron oxide is a unique component that can be incorporated into the glass structure and modifying both the borate and silicate networks. According to the pieces of literature, Fe_2O_3 can either act as network former and/or modifier inside the glass structure [2,3] based on the components found in the glass network. The addition of low Fe_2O_3 concentration promotes the formation of nonbridging oxygen (NBOs) in silicate and bridging bonds in borate network resulting in changes in the rigidity of the borosilicate network. On the other hand, presence iron with high content causes the formation of its own tetrahedral units connected to the localized network as basic former units which involves a reduction in the fraction of boron tetrahedral units and NBOs in the silicate network.

In addition to adjusting the properties of borosilicate glass through controlled content variations, further modification can be effectively achieved by employing heat treatment (HT) process. Heat treatment is one of the key methods for controlling structural and functional properties of glass materials [4-9]. The effectiveness of HT depends on several factors such as glass composition, choice of temperature, heating rate, and cooling rate. It has been shown to be effective in modifying the surface morphology, particle size, shape and distribution, which in turn influences overall material characteristics. In particular, the physical and chemical properties of borosilicate glasses are significantly influenced by the thermal history of the glass samples, particularly heat-induced phase separation.

Heat treatment can modify the glass structure through different mechanisms such as stress relaxation, network reorganization, phase separation [8,9] without necessarily affecting the overall amorphous nature. However, in certain cases, it can also induce a formation of different crystalline phases where crystallization occurs as a result of nucleation and growth.

Several studies based on Nuclear magnetic resonance, neutron diffraction, and Raman spectroscopy [7–10] have proposed that increasing the heating rate in borates, borosilicates, and aluminoborosilicates leads to a noticeable reduction in tetrahedral boron links. The change of coordination environments can induce a substantial contribution to the configurational heat capacity particularly in borate glasses.

Extensive structural data have been obtained for borosilicate glasses revealed that the incorporation of alkali modifiers leads to a thermodynamic competition between the degree of silicate network polymerization and the relative proportion of tri- and tetracoordinate boron. Angeli et al. [8] studied the effect of the heat treatment on the structure of a borosilicate glasses and proposed that, while the temperature has not significant impact on the B-O-B angular distributions of the boroxol rings and the Si-O-Si links, structural disorder becomes evident in the angular distributions of the bonds connecting borate and silicate species. Also, ^{23}Na NMR revealed a reduced homogeneous distribution of sodium atoms when the fictive temperature increases, suggesting that alkali clustering may occur when the glass has insufficient time to be reorganized.

The main objective of this work is to shed more light on the structural changes in $xFe_2O_3.(43-x)B_2O_3.25SiO_2.30Na_2O.2Al_2O_3$ glasses induced by heat treatment. For this purpose, the temperature dependent structural behavior was elucidated using FTIR, XRD, TEM, and EDP techniques. The data analysis and characterization of the as-prepared glass samples have been discussed in detail in a previous work [2,3,11]

Material and methods

Sample preparation

Iron borosilicate glasses of the formula $xFe_2O_3.(43-x)B_2O_3.25SiO_2.30Na_2O.2Al_2O_3$ were prepared using pure chemical reagents of SiO_2, H_3BO_3, Na_2CO_3, Al_2O_3 and Fe_2O_3. The weighted materials were mixed carefully in alumina crucibles and melted using an electric furnace at a temperature ranging from 1250˚C to 1520˚C depending on glass composition. The melt were frequently swirled for several times to produce highly homogeneous glasses.

Heat treatment (HT)

samples containing 0, 3, and 10 mol% Fe_2O_3 were selected for heating procedure. The samples were heated in a muffle furnace (Heraeus KR170) controlled within ± 2 °C at 650 ºC for 4 hours. After heating, the glasses were left in the furnace at the temperature of heat treatment for the desired time followed by normally cooling at room temperature.

X-ray diffraction (XRD)

X-ray diffraction patterns were recorded on a Brucker Axs-D8 diffractometer (λCuK $\alpha = 0.1540600$ nm) at room temperature. Data was collected over a 2θ range of 4˚ - 65˚ with a step size of 0.02° per step and a dwell time of 0.4 seconds. The obtained patterns were matched to standard data compiled by Joint Committee of Powder Diffraction Standards (JCDPS).

Fourier Transform Infrared Spectrophotometer (FTIR)

FTIR signals of the selected samples were recorded at room temperature using Mattson 500 FTIR spectrometer system in the wavelength region 400–2500 cm^{-1} to identify the fundamental functional groups. The specimens were prepared by mixing the powdered samples with KBr (sample to KBr ratio = 1:100). In order to obtain good quality spectra, the weighed mixtures were crushed in an agate mortar and subjected to a load of 5 t/cm^2, then the IR spectra were immediately measured.

Transmission electron microscopy (TEM)

TEM investigations equipped with EDP were performed to determine the size and shape of nanostructured glass under the transmission electron microscope (JEOL-JEM-2100) with an acceleration voltage of 200 kV. In this method, a high energy beam of electrons is passed through a very thin specimen, where the resulting electrons-atoms interactions creating a detailed, high-resolution image of the sample's internal structure.

Results and discussion

XRD patterns of the selected glass samples before and after heat treatment are presented in Figure 1. Consistent with previous reports [11], weak diffraction peaks were observed in the patterns of glasses containing 0 and 3 mol% Fe_2O_3 centered at 2θ = 18.5°, 25.2°, 30°, and 60°, revealing the precipitation of partially ordered Na_2SiO_3 phases within these compositions. According to the previous work [2,3,11], at low iron content, a part of the modifier oxides contributes to increase in the concentration of non-bridging oxygen (NBOs) within the silicate network and promotes the formation of BO4 units in the borate network. The remaining modified ions tend to aggregate as polycrystalline clusters enriched in Na and Fe. Thus, with increasing the content of these modifier oxides the structure becomes less ordered and undergo a transition from amorphous state to one that incorporates sub-crystalline species.

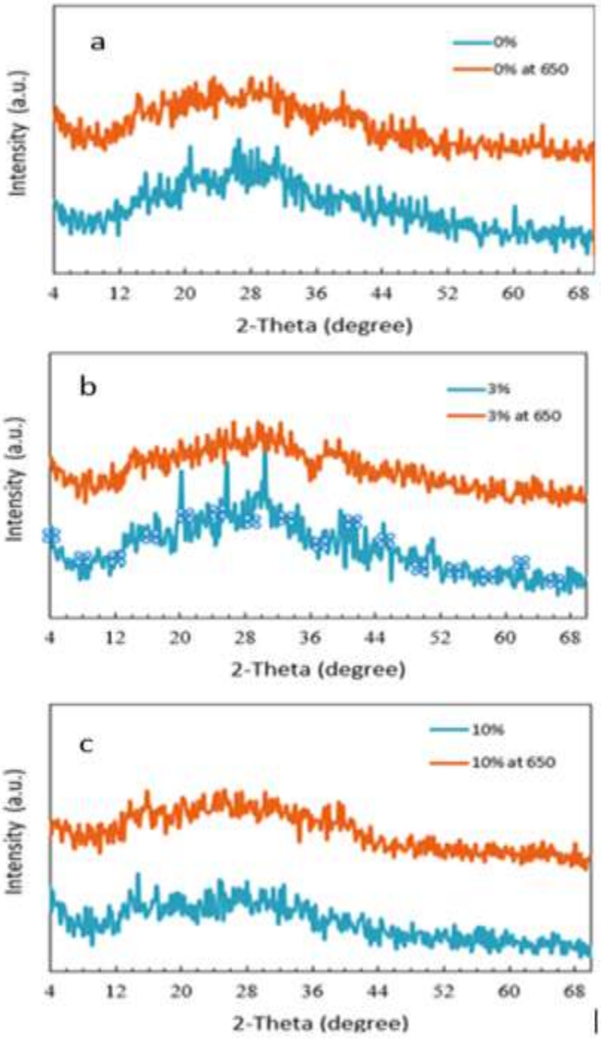

Figure1: X-ray diffraction patterns of the untreated and heat-treated samples at 650°C for 0,3,10 mol% respectively.

On the other hand, the presence of a broad hump free from diffraction peaks in the XRD pattern of 10 mol% sample (Figure1-c). This can be attributed to the reduction of the overall concentration of modifier oxides with increasing Fe_2O_3 content. Consequently, the amount of well-ordered Na_2SiO_3 phases is reduced and a formation of FeO_4 units within borosilicate network increases instead.

Moreover, the X-ray diffraction patterns of the selected samples treated at 650 °C (Figure1) show relatively broad peaks, indicating the absence of crystalline phases of the microcrystalline structure in glass network.

The infrared absorption spectra recorded for the untreated and heat-treated samples containing 0,3,10 mol% Fe_2O_3 are shown in Figure 2 (a, b, and c). The main spectrum of iron borosilicate glass [1-3] displayed three fundamental absorption bands in range of about 600 and 1700 cm^{-1}. The first band located between 600 - 800 cm^{-1} is assigned to symmetric bending vibrations of BO3 bonds. The second band from 800 cm-1 to 1200 cm^{-1} centered around 1000 cm^{-1} is assigned to combined stretching vibration of Si-O-Si and B-O-B tetrahedral structural units formed into silicate and borate network. Meanwhile the third well-defined envelops observed at 1200–1600 cm^{-1} centered at 1350 cm^{-1} is attributed to stretching vibrations of BO3 units with mixed bridging and non-bridging oxygen atoms.

As observed in Figure 2, heat treatment induced structural changes, manifested by a broad and asymmetric widening of the band in the 800–1200 cm^{-1} region. This behavior indicates an enhanced conversion of BO_3 to BO_4 units and the formation of (non-bridging bonds) in different silicate networks. This tendency is likely attributed to the structural modifications in the material, which are often induced by heat treatment.

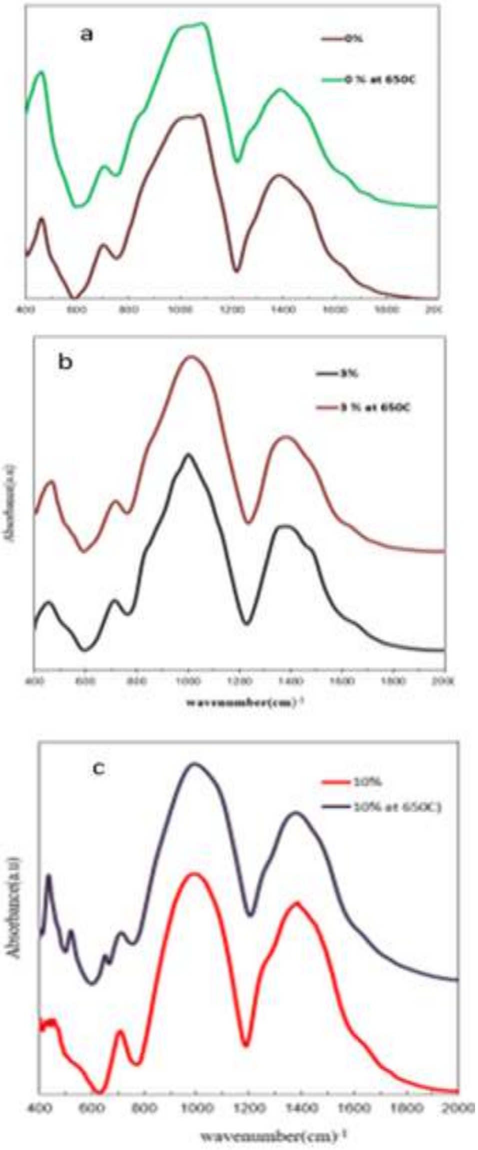

Figure 2: Infrared absorption spectra of the untreated and heat-treated samples at 650ºC for 0,3,10 mol% respectively.

It can also be noticed that with the increase of the iron content (10mol%), the envelope observed at around 800 cm⁻¹ which attributed to the vibrations of NBO bonds in the silicate network has completely disappeared. Meanwhile, a new IR peak emerges at approximately 1285 cm⁻¹ assigned to stretching vibration of Fe-O, as glass forming groups in the spectrum for both before and after heat treatment cases. This observation confirms the formation of Fe–O bonds in iron–silicate and borate species, at the expense of NBO formation in the glass network. This may lead to conclude that, heat treatment, together with the increased Fe_2O_3 content, promotes the development of more shielded units containing mixed three- and four- (BO_4 and FeO_4) coordinated bonds.

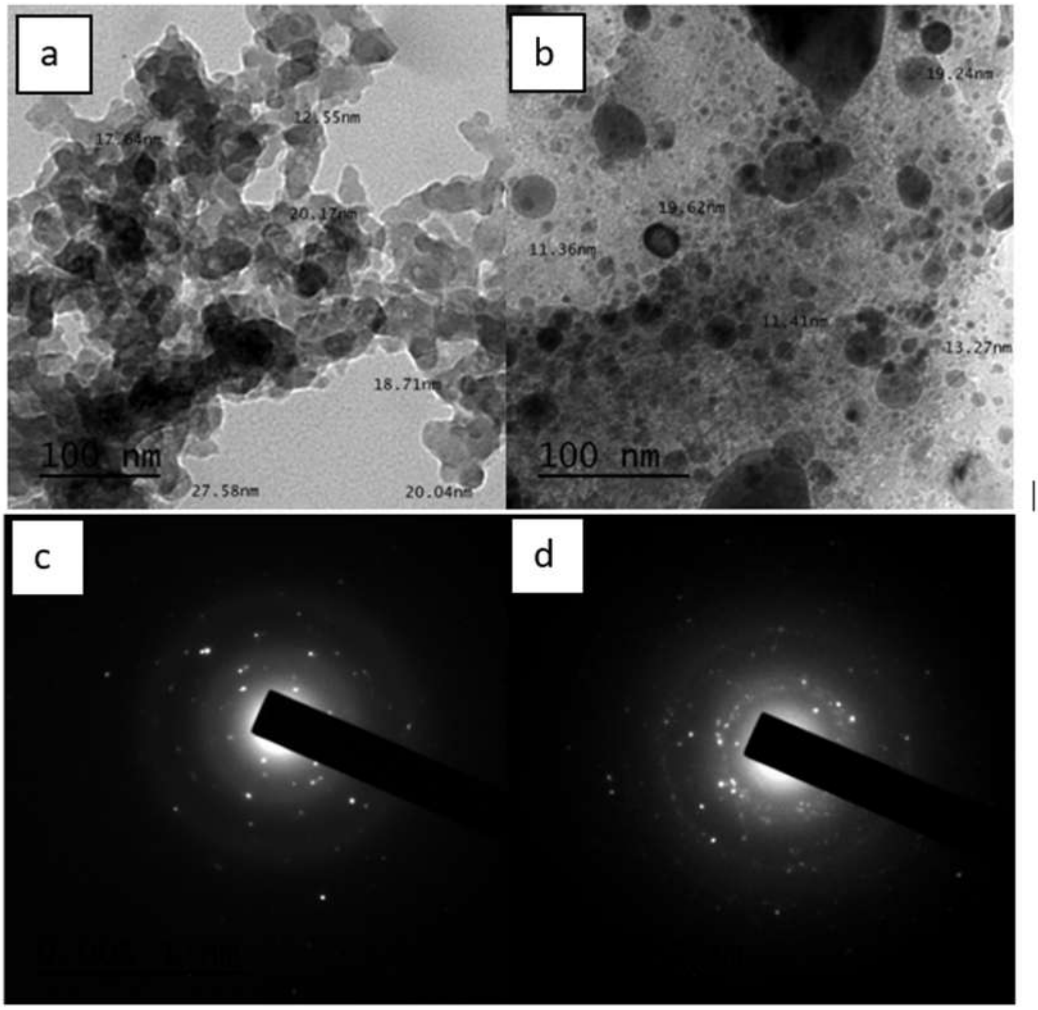

Figure 3: TEM (a,b) and EDP (c,d) images of glass containing 3 mol % Fe_2O_3 of the untreated (a,c) and heat-treated (b,d) samples at 650°C .

Figure 3 and Figure 4 show TEM and EDP analysis for two different compassions (3 and 10 mol% Fe_2O_3) before and after heat treatment at 650 °C for 4hours . The image of the as-prepared samples reveals the presence of sub-crystallized species distributed within the glassy matrix. The size of the crystalline nanoparticles decreases with increasing Fe_2O_3 content, from 21–37 nm at 3 mol% Fe_2O_3 to 5–11 nm at 10 mol%. The reduction in cluster size with higher Fe_2O_3 concentration confirms the strong ability of iron to acts as a network former by taking up NBOs from the silicate network and build its own units [11]. The incorporation of FeO4 groups [2,3,11] into the sodium silicate phase induces mismatching among the structural units within the glass network. As a result, glasses with higher Fe_2O_3 concentrations are characterized by increased disorder and reduced crystallinity. This interpretation is agreed with the XRD and FTIR findings presented above.

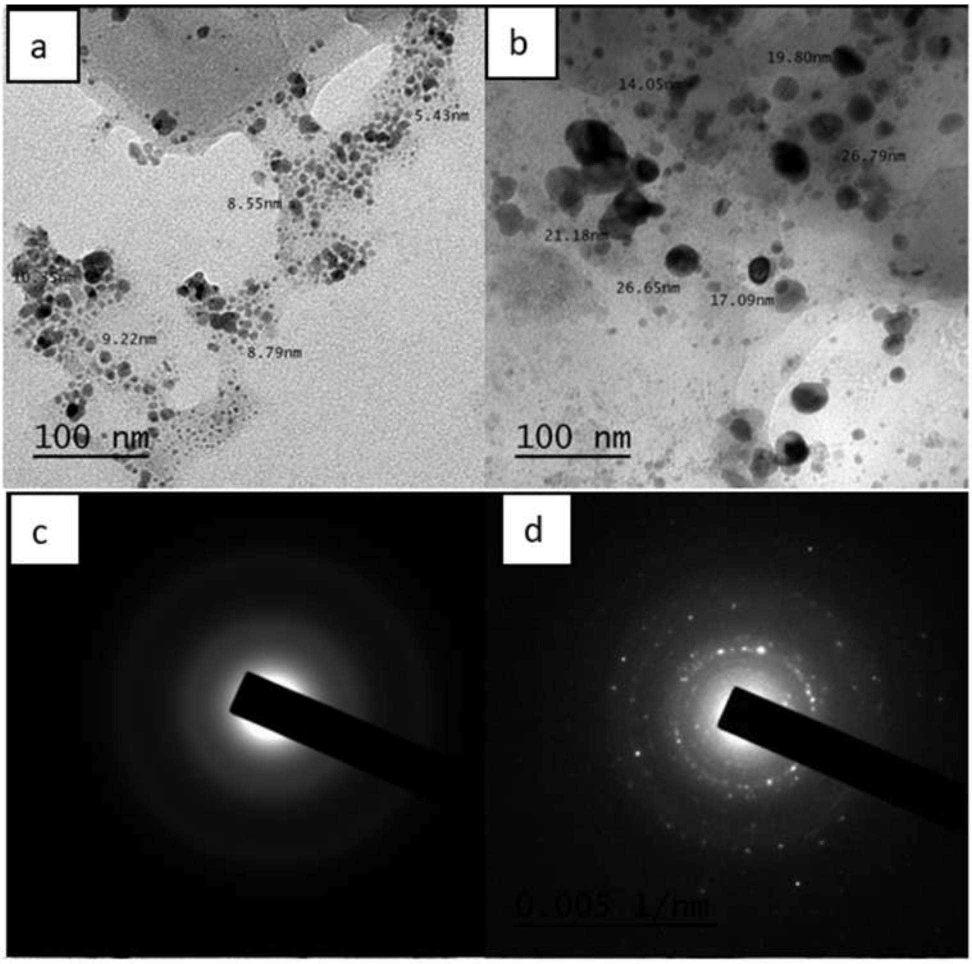

Figure 4 : TEM (a,b) and EDP (c,d) images of glass containing 10 mol % Fe_2O_3 of the untreated (a,c) and heat-treated (b,d) samples at 650° C.

In contrast, a relatively weak increment in the number of nanoparticles that are part of internal borosilicate network was observed after the heat treatment. As it can be detectable from Figures 3 and 4, both heat-treated samples show a grown in of the aggregated species with increasing amount of iron oxide.

To give an illustration to this, heat treatment process can either increase or decrease the number of nanoparticles [8-10,13]. Heat treatment can affect the crystal growth, potentially decreasing the total number of individual nanoparticles. Besides, it can also lead to nucleation and the formation of new nanoparticles, particularly at higher temperatures.

The EDP obtained results (Figure 3 and Figure 4) are in agreement with those from TEM micrographs showing a greater number of aggregated species in the heat-treated samples than in the as-prepared samples.

Conclusion

Based on the obtained experimental results, the following conclusions can be summarized:

•The absence of distinct diffraction peaks in the XRD spectrum demonstrates that the heat-treated samples are fully amorphous with no detectable crystallization phases.

•According to FTIR results, heat treatment process had a notable effect on structural bonds of the selected samples and confirmed that the basic network structure consists of BO3/trigonal and SiO4/BO4 tetrahedral units. The sharp increasing in intensity band composed of both iron and silicon and boron tetrahedral units accompanied by a noticeable decrease in the peak intensity assigned to threefold-coordinated B–O bonds after being subjecting to a heat treatment. This behavior is interpreted in terms of the role of heat treatment in enhancing the structural function of iron oxide within the local network. Heat treatment may either promote or suppress the conversion between trigonal and tetrahedral units depending mainly on iron oxide content as well heating temperature and time.

•XRD and FTIR analysis revealed that, the modified structure of iron oxide consists of BO3, BO4 and NBOs species meanwhile Fe-rich borosilicate glasses exhibit reduced concentrations of both NBOs and modification within the borosilicate network. These findings indicate that the structural role of iron within the glass network contributes to strengthening the glass and regulating the precipitation of the main forming species in the borosilicate network.

- TEM-EDP micrographs indicated the presence of nanoparticles species within the sample. The number of dispersed particles within the glassy matrix increased with rising Fe_2O_3 concentration after thermal treatment. With iron oxide increment, iron enhances the disorder of the aggregated species, while heat treatment promotes crystallization of the glass through nucleation and subsequent crystal growth.

Compliance with ethical standards

Disclosure of conflict of interest

The authors declare that they have no conflict of interest.

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