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Iron-induced structural rearrangements and their impact on sulfur solubility in borosilicate-based nuclear waste glasses

Xinyi Xu,¹ Marco Bertani,² Rajan Saini,^{1,3} Saeed Kamali,^{4,5} Daniel R. Neuville,⁶

Randall E. Youngman,⁷ Alfonso Pedone,² Ashutosh Goel^{1,*}

¹ Department of Materials Science and Engineering, Rutgers, The State University of New Jersey, Piscataway, NJ 08854-8065, United States

² Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, via G. Campi 103, 41125, Modena, Italy

³ Department of Physics, Akal University, Talwandi Sabo, Punjab, 151302, India

⁴ Department of Mechanical, Aerospace, and Biomedical Engineering, University of Tennessee Space Institute, Tullahoma, TN 37388, United States

⁵ Department of Physics and Astronomy, Middle Tennessee State University, Murfreesboro, TN 37132, United States

⁶ Institut de Physique du Globe de Paris, CNRS-Géomatériaux, Université Paris Cité, 1 rueJussieu, 75005 Paris, France

⁷ Science and Technology Division, Corning Incorporated, Corning, New York 14831, United States

* Corresponding author

Email: ag1179@soe.rutgers.edu; Ph: +1-848-445-4512

Abstract

The work presented in the article combines the strength of experimental and computational materials science to understand the iron ($\text{Fe}_2\text{O}_3 \leq 3 \text{ mol.}\%$) - induced structural rearrangements in peralkaline aluminoborosilicate glasses and their impact on the solubility of sulfur (as SO_4^{2-}) in the model nuclear waste glasses. The majority (>95%) of iron exists as tetrahedrally coordinated Fe^{3+} (both isolated and clustered) in the investigated glasses, thus acting as a network former being charge compensated by Na^+ , while the remaining exists as tetrahedrally (distorted) coordinated Fe^{2+} . The addition of iron induces re-polymerization in the glass network, thus lowering the sulfur solubility in the glassy matrix. Mössbauer spectroscopy reveals an insignificant impact of sulfur on the redox behavior or environment of iron in the glass structure.

1.0. Introduction

Approximately 56 million gallons of radioactive wastes generated from the production of plutonium in the 1940s-1980s are stored in underground steel tanks at the Hanford site in the State of Washington.¹ In the past, around one-third of these tanks have reported significant leakage incidents, which potentially threaten the nearby ecosystem.¹ For the long-term and safe storage of these radioactive wastes, a Waste Treatment and Immobilization Plant (WTP) is being built at the Hanford site aiming to immobilize the tank waste using the vitrification technology, wherein the waste feed will be mixed with glass-forming precursors followed by melting in the Joule Heated Ceramic Melters (JHCM) at 1150 °C to synthesize durable glasses.² However, during the vitrification process, the waste loading is limited by the accumulation of immiscible salt phases (e.g., alkali- and alkaline-earth-sulfate, -chromates, etc.) on the melt surface (known as "gall" or yellow phase) owing to their low solubility in the vitrified waste form, among which sulfur (as sulfate, SO_4^{2-}) is the dominant participant.^{3,4}

Sulfur was added to the nuclear waste for the complexation of ^{92}U . However, during vitrification, it exhibits poor incorporation (<1 wt.%) in the borosilicate-based waste glasses.³ Upon exceeding its solubility limit, the excess sulfur precipitates as a sulfate-rich salt layer that floats on melt surface, which can disrupt the melters' operation by corroding the sidewalls or short-circuiting the electrodes because of its low-viscosity and high electrically-conductivity.^{3,4} Historically, sulfur was not considered a potential problem in high-level waste (HLW), as it was supposed to be removed from waste feed during the pre-treatment before vitrification. Therefore, most of the effort was directed toward understanding the compositional dependence of sulfur solubility in low-activity waste (LAW) glasses.^{3,5} This effort has resulted in the development of empirical (analytical) models to predict the practical sulfur solubility (as SO_3 or SO_4^{2-}), varying

between 0.15 - 1.83 wt.%, in simulated LAW compositions as a function of feed chemistry.^{3, 6} Nevertheless, with the implementation of the direct feed approach,^{2, 5} the pre-treatment for sulfate removal before vitrification shall be bypassed, due to which not only the sulfate content of the LAW feed will be increased, but a considerable amount of sulfate content will also be accumulated in the HLW waste stream. This is expected to challenge the existing design of glass compositions (LAW and HLW) and the validity of the predictive models owing to their empirical nature and limited compositional diversity, as discussed in our previous article.⁷

The most prudent way to address the abovementioned challenge is to follow a two-pronged approach, where on one hand the focus should be on establishing the composition – structure – sulfur solubility relationships in borosilicate-based glasses over a broad composition space relevant to the LAW and HLW glass chemistries. On the other hand, the knowledge, chemo-structural descriptors and experimental data generated in this process can be used to develop non-empirical models to predict sulfur solubility in both LAW and HLW glasses. While the recent literature on this subject shows some effort in this direction,⁸⁻¹¹ the compositional systems investigated in these studies are significantly less complex than the actual nuclear waste glass composition. Therefore, though these studies lay a solid foundation for our understanding of the structural dependence of sulfur solubility in borosilicate glasses, more work is needed in this direction. Emphasis needs to be laid upon those constituents, which though present in smaller concentrations (0.5 – 5 mol.%), are known to exhibit a significant impact on the sulfur solubility in the nuclear waste glasses, for example, Fe_2O_3 , Cr_2O_3 , V_2O_5 , and Cl^- .^{3, 7, 11-14} In this pursuit, the present study is focused on understanding the iron-induced structural disorder and its impact on sulfur solubility in borosilicate based model nuclear waste glasses.

The literature on the impact of Fe_2O_3 on sulfur solubility in borosilicate glasses is limited and ambiguous. For example, according to Muller et al.⁶ and Xu et al.,⁸ Fe_2O_3 decreases sulfur solubility in borosilicate glasses. However, Vienna et al.³ consider iron's impact on sulfur solubility insignificant. As realized in the previous studies,^{15, 16} the addition of Fe_2O_3 adds a significant degree of compositional and structural complexity to oxide glasses due to its multivalent nature, occurring as both Fe^{3+} and Fe^{2+} , in the glass where its partition in these two valence states is dependent on glass composition, temperature, and oxygen fugacity. The structural environment of Fe in a glass network is complex, as both the cations generally possess a range of coordination states with a high degree of geometric distortion.^{15, 17, 18} For a simplified description, Fe^{2+} tends to act as a network modifier regardless of its coordination state, whereas Fe^{3+} presents itself either as a network former in tetrahedral coordination or as a network modifier in higher coordination.¹⁸⁻²⁰ In particular, when Fe^{3+} participates in the glass structure as a network former cation, it interacts with other framework cations by forming Fe–O–(Si, B) linkages and reorganizing the network structure.²¹ However, the impact of variation in these structural units and linkages induced by Fe addition on the sulfur incorporation in glass is still largely unknown. Further, it has been demonstrated in iron-free sodium borosilicate glasses that sulfur (as SO_4^{2-}) can scavenge Na^+ from the depolymerized regions of borosilicate network, thus inducing re-polymerization in the borosilicate glass network.⁹ In iron-containing glasses, some fraction of Na^+ is also required to charge balance the tetrahedrally coordinated Fe^{3+} ,¹⁸ thus leading to some open questions: Whether there is a preference of Na^+ to charge-compensate FeO_4^- over the SO_4^{2-} group? Is there any preference between Na^+ and Fe^{2+} to charge compensate SO_4^{2-} ? Furthermore, considering that sulfate addition will re-polymerize the glass network by

removing Na^+ from non-bridging oxygen (NBO) sites on both Si and B species for charge compensation,⁹ will the equilibrium of $\text{Fe}^{2+}/\text{Fe}^{3+}$ be altered in this case?

In the present work, we aim to investigate the effect of iron addition on sulfur solubility in alkali aluminoborosilicate glasses. A simplified alkali-rich model nuclear waste glass with a composition of $30\text{Na}_2\text{O}-5\text{Al}_2\text{O}_3-15\text{B}_2\text{O}_3-50\text{SiO}_2$ (mol.%) has been chosen as the baseline for this study.²² Fe_2O_3 has been added to the baseline composition in concentrations varying between 0 – 3 mol.% while maintaining the molar ratios of all the oxides to be constant, i.e., $(100-x)$ $(30\text{Na}_2\text{O}-5\text{Al}_2\text{O}_3-15\text{B}_2\text{O}_3-50\text{SiO}_2)-x\text{Fe}_2\text{O}_3$ ($x = 0, 1, 2, 3$ mol.%). The sulfur solubility in the host glasses was determined by the saturation method (discussed in the next section) and measured by inductively coupled plasma–optical emission spectroscopy (ICP–OES). A suite of state-of-the-art structural characterization techniques (Mössbauer, Raman, and MAS NMR spectroscopies) have been employed in conjunction with molecular dynamic (MD) simulations to elucidate the impact of iron on the short–to–medium–range ordering in the glass structure and sulfur loading in the investigated glass system. The results obtained from this study will not only help to advance our understanding of the composition-structure-property relationships in borosilicate glasses, but they will also contribute to the experimental dataset needed for the design of non-empirical predictive models for the design of advanced nuclear waste glass formulations with enhanced waste loadings.

2. Methodology

2.1 Synthesis of baseline glasses and sulfur incorporation

The glasses were synthesized by the melt-quench technique. High-purity powders of Na_2SiO_3 (Alfa Aesar, >99%), Al_2O_3 (Sigma-Aldrich, $\geq 98\%$), H_3BO_3 (Alfa Aesar, $\geq 98\%$), SiO_2 (Alfa

Aesar, $\geq 99.5\%$), Fe_2O_3 (Alfa Aesar, 99%) were used as precursors for glass synthesis. The batches corresponding to 100 g glass were melted in 90%Pt–10%Rh crucibles loosely covered with a Pt lid for 1 h in the air at 1150 °C. The melts were quenched on a copper plate maintained at room temperature. The synthesized sulfur-free glass samples were visibly transparent, and their amorphous nature was confirmed by X-ray diffraction (XRD) (PANalytical-X'Pert Pro; Cu $K\alpha$ radiation; 2θ range 10-90°; step size $0.01313^\circ \text{ s}^{-1}$), as shown in [Figure S1](#).

Na_2SO_4 (Alfa Aesar, 99%) has been used as a precursor for sulfur (SO_3). A multi-step melting process has been followed to ensure the successful incorporation of sulfur in the glasses. Firstly, the batch without sulfate salt (i.e., Na_2SO_4) was melted under conditions similar to those of the sulfur-free baseline glasses (air atmosphere, 1150 °C) for 1 h. Then, Na_2SO_4 was added to the melt, and the mixture was melted for 30 min and quenched on the copper plate. After that, the obtained glass was re-heated for another 30 min before quenching on the copper plate kept at room temperature. As Na_2SO_4 serves as the source for both Na_2O and SO_3 , batch calculations were made to ensure that the total content of Na_2O in the glass remained constant, which was achieved by reducing the corresponding amount of Na_2O added in the first step, as has also been discussed in our previous articles.^{8,9} To saturate the glass with sulfur, the SO_3 concentration has been gradually increased in the increments of 0.25 mol.% until a salt layer floating on the melt is observed. The amorphous nature of the sulfur-loaded glasses and the crystalline phase assemblage of the salt layer were determined using XRD analysis, as shown in [Figure S2](#).

2.2 Compositional analysis of glass samples

The experimental compositions of the as-synthesized glasses were determined using the ICP–OES (PerkinElmer Optima 8300). The sample preparation for the ICP–OES has been discussed in detail in our previous article.⁹ [Table 1](#) compares the batched and experimental

compositions of the glasses, showing a good agreement between them. The sulfur-free glasses are labeled as $x\text{Fe}$, where x represents the molar concentration of Fe_2O_3 (batched) in the glass. Similarly, the sulfur-containing glasses are labeled as $x\text{Fe}-y\text{S}$, where y denotes the amount of SO_3 (in mol.%) added (batched) in the host glass to study the impact of iron on sulfur solubility. Here, it should be noted that the minor discrepancy between the value of y and the reported value of batched SO_3 content in [Table 1](#) is due to the normalization of the glass composition.

2.3 Structural analysis of glasses - Experimental

2.3.1 Density, molar volume, and glass transition (T_g)

The densities of glasses were measured using Archimedes' method, wherein the glass samples were weighed in air and d-limonene (specific gravity at 25 °C = 0.84 g/cc). Each density value reported here averages at least nine measurements (3 samples per composition; each sample was measured thrice). The density values were further used to calculate the molar volume (V_m) of glasses using equation (1):²³

$$V_m = \frac{M_w}{\rho} \quad (1)$$

where M_w and ρ represent the molecular weight and density of the glass, respectively.

The onset of glass-transition temperature (T_g) of the investigated glasses has been determined using differential scanning calorimetry (DSC; STA 449 F5 Jupiter, Netzsch). The glass samples were crushed and sieved to a particle size <45 μm . The DSC scans were obtained in the 60 – 900 °C temperature range at a heating rate of 20 °C min^{-1} under a constant flow of nitrogen gas (20 ml min^{-1}). The reported T_g value for each glass is an average of at least three scans. For sulfur-containing samples with a salt layer formed on the surface, measurements were performed on the glasses after completely removing the salt layer by ultrasonication in acetone.

2.3.2 Mössbauer spectroscopy

The Mössbauer spectra of the as-quenched samples were collected at 298 K and 7 K, respectively, using a constant acceleration spectrometer with a 25 mCi ^{57}Co source in a Rh matrix. Absorbers were prepared from finely ground samples with a particle size $<45\ \mu\text{m}$ to ensure a Mössbauer thickness, $t < 1$. The spectra were measured in the velocity range of $\pm 12\ \text{mm/s}$ relative to $\alpha\text{-Fe}$ and were fitted using the recoil software package to extract the hyperfine parameters.²⁴ Lorentzian doublets were fitted for the superparamagnetic components, and sextets were fitted for the magnetic portion resolved at low temperatures.²⁵ While fitting the spectra, it was assumed that the recoil-free fraction of Fe^{2+} and Fe^{3+} were equal. Therefore, the Fe^{2+} and Fe^{3+} sub-spectra's relative area was proportional to the relative abundance of each redox state in the investigated samples.

2.3.3 Raman Spectroscopy

Unpolarized Raman spectra have been collected using an inVia Renishaw confocal Raman spectrometer equipped with a CCD detector under ambient conditions. The excitation source was the 532 nm line of a green diode laser operating at 500 mW. The laser was directed normal to a smooth sample surface and focused on a spot at a $20\times$ magnification. All spectra have been recorded in the wavenumber range of 300 to $1600\ \text{cm}^{-1}$ with a precision of $\pm 1\ \text{cm}^{-1}$. Each sample is scanned for 10 accumulations with an exposure time of 10 s for each accumulation. The measurements were performed at different positions on the sample surface to ascertain the sample homogeneity. The acquired spectra were subsequently corrected for temperature and frequency-dependent scattering intensity using the correction factor as recommended in the literature,^{26, 27} followed by baseline subtraction and area normalization using OriginPro 2018 software.

2.3.4 MAS NMR Spectroscopy

The ^{27}Al and ^{11}B MAS NMR spectra were acquired on iron-free glasses. The samples were powdered in an agate mortar, packed into 3.2 mm zirconia rotors, and spun at 22 kHz for ^{27}Al and 20 kHz for ^{11}B MAS NMR. ^{27}Al MAS NMR data have been collected at 16.4 T (185.10 MHz resonance frequency) with a 0.6 μs ($\sim\pi/12$ tip angle) pulse width for uniform excitation of the resonances, recycle delay of 2 s and an average of 1000 acquisitions. ^{11}B MAS NMR data has been acquired at 16.4 T (224.52 MHz resonance frequency) using RF pulses of 0.6 μs ($\sim\pi/12$ tip angle). A range of 400-1000 acquisitions are co-added, and the recycle delay is 4 s. The acquired spectra have been processed with minimal apodization and plotted using the normal shielding convention and with shift referencing to aqueous aluminum nitrate (0.0 ppm) and aqueous boric acid (19.6 ppm), respectively. Fitting of the MAS NMR spectra has been performed using DMFit. The CzSimple model, which accounts for distributions in the quadrupolar coupling constant, has been utilized for ^{27}Al MAS NMR spectra.²⁸ For ^{11}B MAS NMR data, "Q MAS $\frac{1}{2}$ " and Gauss/Lorentz functions have been used for fitting the resonances of three- and four-coordinated boron species, respectively. For quantification purposes, N_4 values were calculated from the fractional areas of the peaks attributed to the four-coordinated boron species, while a minor correction due to its overlapping satellite transition was applied.²⁹

2.4 Structural analysis of glasses by molecular dynamics simulations

Classical molecular dynamics (MD) simulations have been employed to investigate the structural features of the studied glasses using the batched compositions reported in [Table 1](#). Three independent replicas of models containing about 3500 atoms have been generated for each composition using the melt-quench approach.³⁰ The exact number of atoms and box dimensions are reported in [Table S1](#).

The employed force field is based on the shell model,³¹ where oxygen atoms are split into a massive, positive-charged core and a massless, negative-charged shell linked by a harmonic spring. The sum of the core and shell charges gives the formal charge of the oxygen atoms (-2e). Besides the damped harmonic interaction with the corresponding core, the oxygen shells interact with each other and the other cations through short-range Buckingham terms. In contrast, electrostatic forces act among all species, which bear total formal charges. Three-body screened harmonic potentials control the intra-tetrahedra O–T–O (T = Si, Al, Fe) angles. The full expression of the potential is reported in equation (2):

$$U(r_{ij}, r_{c-s}, \theta_{ijk}) = \frac{z_i z_j e^2}{r_{ij}^2} + A_{ij} e^{-\frac{r_{ij}}{\rho_{ij}}} - \frac{C_{ij}}{r_{ij}^6} + \frac{1}{2} k_s (r_c - S)^2 + \frac{1}{2} k_b (\theta_{ijk} - \theta_{ijk}^0)^2 e^{-\left(\frac{r_{ij}}{\rho} + \frac{r_{jk}}{\rho}\right)} \quad (2)$$

This force field has already been demonstrated to reproduce the medium-range structure of oxide glasses reliably, especially the Si speciation and inter-tetrahedra bond angle distributions.³²⁻³⁶

All the parameters used in this work are reported in [Table S2](#), and have been used in previous investigations except for the Fe³⁺–O parameter set.^{32, 37} The latter has been developed in this work using the relaxed-fitting procedure implemented in GULP³⁸ to fit the experimental crystal structure of Ca₃Fe₂Si₃O₁₂³⁹ and NaFeSi₂O₆.⁴⁰ The new parameters give an error of ±1.7% and ±0.8% on the Fe–O distance and cell parameters, respectively. Since the number of iron atoms in the simulation boxes and the fraction of Fe²⁺ (measured experimentally) is low, all the iron in the simulations has been considered Fe³⁺.

The leapfrog algorithm encoded in the DL_POLY2.14 package⁴¹ has been used to integrate the equation of motion with a timestep of 0.2 fs. The initial configurations have been generated randomly, placing the number of atoms in a cubic box whose dimensions allow the reproduction of the experimental densities. The systems were heated and held at 3200 K for 50 ps in the NVT

ensemble, using the Berendsen thermostat⁴² with a frictional constant of 0.2 ps, to ensure complete melting of the samples. The liquids were then cooled to 300 K with a nominal quench rate of 5 K/ps and equilibrated for 100 ps. Velocity scaling was applied at each step to control the kinetic energy of the shells. The Ewald summation method⁴³ with a cutoff of 8 Å has been applied to calculate the Coulomb interactions, whereas a cutoff of 7.5 Å has been used for the short-range (vdW) interactions.

3. Results

3.1. Structural analysis of sulfur-free glasses - Experimental

3.1.1. Density and molar volume

Figure 1 presents the density and molar volume of the sulfur-free glasses. Upon sequential addition of Fe₂O₃ from 0 to 3 mol.%, the density of glasses increases from 2.49 g/cm³ to 2.55 g/cm³, while the molar volume tends to increase from 25.74 cm³/mol. to 26.32 cm³/mol. These results are consistent with the literature on the variation in density and molar volume with the addition of Fe₂O₃ in silicate⁴⁴ and borosilicate¹⁸ glasses and can be attributed to the following two reasons: (1) the addition of Fe₂O₃ with density (5.24 g/cm³) higher than all the other components in the glass and (2) the structural role of iron in the silicate/borosilicate glass. As discussed earlier, iron manifests itself in silicate glasses as Fe²⁺ and Fe³⁺, where these cations play different roles in the glass structure.^{18, 21} Generally, the four-coordinated Fe³⁺ is incorporated into the glass structure as a network former associated with alkali cations.^{18, 21} As revealed by previous spectroscopic and simulation studies on Fe-containing silicate glasses,^{45, 46} the average length of the Fe–O bond is longer than that of the Si–O bond, together with a wider distribution of bond angles owing to the asymmetric geometry of the Fe species. Therefore,

while the addition of Fe^{3+} tetrahedra in a glass network would lead to a loosening and distortion in the local structure,¹⁹ the Fe^{2+} cations, fitting in the voids as network modifiers, tend to enlarge the voids owing to their large size (0.76 Å).⁴⁷ As a result, the presence of both Fe^{2+} and Fe^{3+} is bound to increase the molar volume of the investigated glasses.

3.1.2. Glass transition temperature

As shown in [Figure 2](#), adding Fe_2O_3 up to 3 mol.% in the glasses results in a slight decrease in their glass transition temperature (T_g) from 484 °C to 478 °C. Given that the T_g is determined by the network connectivity and the corresponding bond strength for viscous flow in the vicinity of liquid-glass transition,²³ the slight change in T_g with increasing Fe_2O_3 content is related to the Fe species and their corresponding role in the glassy structure. As most of the Fe cations in the investigated glasses are present in tetrahedral coordination (discussed in section 3.1.3), thus acting as network formers, adding Fe_2O_3 is expected to reticulate the glass network, thus resulting in a higher T_g . On the contrary, the T_g has been observed to decrease with adding Fe_2O_3 . The observed trend in T_g values can be attributed to the lower bond energy of Fe–O (407 kJ/mol) as compared to that of Al–O (501.9 kJ/mol), Si–O (799.6 kJ/mol) and B–O (536 kJ/mol).⁴⁸ Therefore, the formation of Fe–O–(Si, B)[†] linkages at the expense of (Si, Al, B)–O–(Si, Al, B) bonds would weaken the overall strength of the framework,^{21, 49} thus, decreasing the T_g .

3.1.3 Mössbauer spectroscopy

The iron redox and its local atomic configurations (e.g., coordination number and the distortion of Fe–O polyhedra) in the glasses have been studied by Mössbauer spectroscopy. The Mössbauer spectra of the investigated iron-containing glasses have been acquired at room temperature (RT, 298 K) ([Figure 3](#)) and 7 K ([Figure S3](#)), fitted with 3 and 4 sub-spectra,

[†] We did not mention the possibility of Fe–O–Al linkages in the glass structure as FeO_4^- and AlO_4^- units are known to exhibit a strong tetrahedral avoidance in alkali aluminoborosilicate glasses.²⁰

respectively. The extracted hyperfine parameters, including the centroid shifts (δ , with respect to metallic α -iron at RT), quadrupole splitting (ΔE_Q), Lorentzian linewidth (Γ), intensity (I), and the iron redox in each sample, are summarized in [Tables 2 and S3](#).

The RT spectrum has been fitted with three overlapping doublets, one for Fe^{2+} (S_1) and two (S_2 and S_3) for Fe^{3+} , distinguished by their chemical shifts corresponding to specific environments. The Fe^{2+} doublet (S_1) has a δ value within the 0.93-0.98 mm/s range, and the ΔE_Q values around 2 mm/s, typical for Fe^{2+} in a 4-coordination environment acting as a network modifier, as reported in the previous studies.^{25, 46} Here, it should be noted that the centroid shift δ , screens the average change in the s-electron density, which is related to the coordination environment around Fe nuclei, while the quadrupole splitting describes the degree of asymmetry in the configuration of Fe nuclei.^{25, 50, 51} Therefore, a slight increase in δ from 0.93 mm/s in 1Fe glass to 0.98 mm/s in 3Fe glass along with a large ΔE_Q (as compared to that of Fe^{3+}), suggest the Fe^{2+} cations are predominantly situated in distorted tetrahedral sites acting as network modifier. Similar inferences about the Fe^{2+} environment can also be made from the Mössbauer spectra acquired at 7 K.

Fe^{3+} in the investigated glasses gives rise to both the doublet S_2 and the curved baseline S_3 signals in the Mössbauer spectra ([Figure 3](#)). The paramagnetic Fe^{3+} doublet has δ value of ~ 0.26 mm/s and ΔE_Q value of ~ 0.9 mm/s, indicating the tetrahedral environment with some degree of distortion. According to previous studies,⁵¹⁻⁵³ the Fe^{3+} doublets are produced by the exchange interaction between Fe^{3+} on the adjacent sites, thus referring to the clustered Fe^{3+} involving both $\text{Fe}^{3+}\text{-O-Fe}^{3+}$ and $\text{Fe}^{3+}\text{-O-Fe}^{2+}$ linkages. The curved baseline is from the isolated Fe^{3+} (i.e., when the Fe cations are away from each other), which has been previously reported by Bingham et al.⁵¹ and William et al.⁵⁴ in the silicate glasses. It appears because of the longer relaxation time of

the isolated Fe^{3+} units in comparison to the Mössbauer sensing time due to the lack of spin-spin interaction between Fe^{3+} sites with the dilute iron distribution. According to Williams et al.,⁵⁴ the relaxation arises as a combination of spin-lattice and spin-spin mechanisms. At low iron content, the average distance between Fe^{3+} spins is large, which inhibits the spin exchange interactions, and the spin-lattice mechanism predominates,^{25, 55} giving the paramagnetic hyperfine splitting (p-hfs) signals. The hfs cannot be resolved at ambient temperature as it is smeared out and appears as a broad curve, as shown in Figure 3.⁵⁵ When acquiring the spectra at the temperature of liquid He (~ 4 K), the hfs component can be resolved as the spin-lattice mechanism slows down, thus exhibiting the hyperfine sextet feature in the spectra.⁵⁶ In the present study, the appearance of the sextet peak (S_{L3} in Table S3; Figure S3) and the less significant background (S_{L4} in Table S3 vs. S_3 in Table 2) in the spectra acquired at 7 K suggests that a part of the hfs signal has been magnetically resolved, while the unresolved part is left in the background component. As revealed by the spectral fitting, the δ value of S_3 in RT spectra is 0.26 mm/s (Table 2), which is consistent with that of the sextet peak in 7 K spectra (~ 0.4 mm/s, Table S3) considering the temperature-dependence second-order Doppler (SOD) shift,⁵⁶ thus, implying that the isolated Fe^{3+} cations are in tetrahedral sites. These observations confirm the duality of Fe^{3+} populations (isolated vs clustered) in the investigated glasses that tend to act as network formers (FeO_4^-) being charge compensated by Na^+ .^{18, 53} In addition, the site parameter (Γ) of the isolated Fe^{3+} component is much larger than that of the clustered Fe^{3+} (Table 2) suggesting that the distribution of latter sites is more constrained.^{50, 55}

The iron redox ratio is obtained by the relative areas of the ferrous and ferric absorption peaks recorded at the RT (Table 2). Previous literature suggests that the redox chemistry of iron investigated by Mössbauer spectroscopy to be in good agreement with the wet chemical

analyses,¹⁸ though the presence of hfs could lead to some degree of underestimation of Fe³⁺.⁵⁴ It is worth noting that, though the isolated Fe³⁺ component is better resolved at lower temperatures (7 K), other Fe components (mainly clustered Fe³⁺) could also be magnetically resolved and enter the sextet sub-spectra owing to their saturation magnetization at low temperature,⁵⁷ thus, introducing uncertainty in the quantitative analysis of the 7 K spectra. According to the intensity results (Table 2), the Fe³⁺/∑Fe barely changes with adding Fe₂O₃, and the tetrahedrally coordinated Fe³⁺ remains the predominant species. The highly oxidized condition of Fe species can be correlated to the high theoretical optical basicity of the glass composition brought by the abundance of Na₂O, which favors the higher oxidation state in the Fe²⁺–Fe³⁺ redox couple.⁵⁸ Also, as the Fe₂O₃ content increases, the fraction of clustered Fe³⁺ increases at the expense of the isolated Fe³⁺. This can be explained by the higher probability of Fe in adjacent sites in glassy matrix which allow the spin–spin interaction to take place causing the hfs signal to be transferred to a doublet.^{51, 59}

3.1.4 Raman spectroscopy

Figure 4 depicts the room temperature Raman spectra recorded for sulfur-free glasses with increasing Fe₂O₃ content (up to 3 mol.%). The recorded Raman spectra have been divided into three regions: Region I (low frequency, ~300-820 cm⁻¹), Region II (medium frequency, ~820-1250 cm⁻¹) and Region III (high frequency, ~1250-1600 cm⁻¹).^{9, 60} The Region I (Figure S4a) and Region III (Figure S4b), which are attributed to the mixed stretching and bending modes of T–O–T linkages (T = AlO₄ and SiO₄),⁸ and the stretching vibrations of BO₃ triangles,^{60, 61} respectively, have been deconvoluted following the procedure described by Cochain et al.¹⁸ Region II comprises potentially overlapping contributions from the (1) stretching vibrations of Si–O bonds in the Qⁿ units, where n represents the number of bridging oxygens (BO) in the SiO₄

tetrahedra, (2) $\text{Fe}^{3+}\text{-O}$ stretching vibrations in the FeO_4 groups, and (3) Si-O-(Si, Al, Fe) vibrations in the investigated glasses. Thus, owing to the compositional and structural complexity, it is difficult to differentiate the individual contribution of each vibration mode. Therefore, Region II has not been deconvoluted.

In Region I, a slight increase in the intensity of the shoulder near 400 cm^{-1} is observed with the addition of Fe_2O_3 , indicating the rearrangement of tetrahedral former units.¹⁸ As shown in [Figure S4a](#), the band at $\sim 580\text{ cm}^{-1}$ is characteristic for reedmergnerite units, a four-member ring comprising one BO_4 tetrahedra and three SiO_4 tetrahedra, while the 630 cm^{-1} band is generally assigned to danburite rings where two BO_4 are connected to two SiO_4 .^{60, 62} With an increase in the Fe_2O_3 content from 0 to 3 mol.%, the intensity of the band at 630 cm^{-1} decreases with a simultaneous increase in the intensity of band around the 580 cm^{-1} , thus, suggesting an increasing fraction of reedmergnerite groups at the expense of danburite units in the glass structure. In other words, increased Fe_2O_3 content results in a lower concentration of $\text{Si-O-}^{[4]}\text{B}$ (referred to as BO_4 units) linkages in the glass structure. This structural change can be attributed to the cumulative effect of (1) lowering fraction of BO_4 units, as also corroborated by the MD simulations (discussed in section 3.2.1), and (2) higher affinity of formation of Fe-O-B linkages over Si-O-B linkages, as shown by Zhang et al.²¹ The iron-induced structural changes in the borate network of the glass structure are further corroborated by the decrease in the intensity of Raman bands at 700 and 770 cm^{-1} ([Figure 5a](#)). The intensity of bands at 700 and 770 cm^{-1} is considered to be proportional to the concentration of metaborate rings and pentaborate groups, respectively.^{63, 64} Therefore, a decrease in their intensity with an increase in Fe_2O_3 concentration in glasses suggests breakage of the borate ring structures.

Regarding the evolution of Raman spectra in Region II with increasing Fe_2O_3 concentration in the glasses, the broad band observed in 0Fe glass indicates the co-existence of a variety of Q^n species, where Q^3 is the dominant structural unit with a small fraction of Q^1 , Q^2 and Q^4 species.⁶⁵⁻⁶⁷ An increasing Fe_2O_3 concentration in glasses results in (1) a gradual growth of the band near low-frequency end of this region at around $\sim 950\text{ cm}^{-1}$ (Figure 4), along with some intensity loss of the band at high-frequency side ($\sim 1150\text{ cm}^{-1}$); (2) the appearance of a band at $\sim 980\text{ cm}^{-1}$, most likely originating from the $\text{Fe}^{3+}\text{-O}$ stretching vibrations in the FeO_4 groups,^{18, 68} whose intensity enhances with increasing Fe_2O_3 content suggesting an increasing abundance of FeO_4^- units in glass structure. The Raman spectroscopy results are in good agreement with the Mössbauer spectroscopy results (Table 2), where it has been shown that iron in the investigated glasses predominantly exists as Fe^{3+} and mimics network formers by occurring in tetrahedral coordination. According to the literature,^{18, 69-71} Fe^{3+} tetrahedra (FeO_4) participate in the framework by connecting with SiO_4 , forming $\text{Fe}^{3+}\text{-O-Si}$ linkages. The substitution of Si-O-Si linkages by Fe-O-Si linkages, though it may have minimal impact on the network connectivity in the glass structure, will shift the Raman band to a lower frequency due to a weaker force constant for the transverse motion of the bridging oxygen in the Si-O-Fe bond.⁷² Another explanation for the appearance of lower-frequency band can be the depolymerization (creation of NBOs) in the silicate network. The literature on the structure of iron-containing silicate glasses highlights the network-modifying role of Na^+ and Fe^{2+} (regardless of its coordination state).^{18, 73} Nevertheless, considering the low amount of Fe^{2+} in the investigated glasses (Table 2) and the decreasing availability of Na^+ to associate with NBO pairs due to them being partially consumed to charge-compensate FeO_4^- ,⁷⁴ a lower abundance of Si-O^- bonds, i.e., NBOs, are expected in the iron-rich glasses. These qualitative assertions are supported by the results of the MD simulations

(see Section 3.2.1), where Fe_2O_3 addition to the investigated glass system results in an increased fraction of Q^4 units at the expense of Q^2 and Q^3 units (Table 3). Consequently, the appearance of the lower-frequency bands in Region II (Figure 4) with the addition of Fe_2O_3 has been attributed to the enhanced participation of FeO_4 units in the silicate network.

In Region III, the shoulder band at $\sim 1320\text{ cm}^{-1}$, corresponding to "loose BO_3 ,"^{60,61} grows with an increasing Fe_2O_3 content (Figure S4b). The formation of loose BO_3 groups with increasing Fe_2O_3 is most likely related to the destruction of borate rings,⁶¹ which is consistent with the observed trend of decreasing abundance of pentaborate rings in Region I (Figure 4a). In addition, the broad signals between $1380\text{-}1500\text{ cm}^{-1}$, representing the B-O^- asymmetric vibrations in BO_3 units, shift to lower frequencies with Fe_2O_3 addition (Figure 4). The spectral deconvolution (Figures S4b and 5b) shows that, while the intensity of band near 1380 cm^{-1} — representing $\text{B}_3^2\text{-BO}_4$ linkages, where B_3^n refers to BO_3 units associated with $(3-n)$ NBOs^{18,60} — significantly increases, that of the band near 1460 cm^{-1} , representing $\text{B}_3^2\text{-BO}_3$ linkages, exhibits a moderate decrease in intensity. Considering the simultaneous reduction in the abundance of danburite units (Figure 4a), such a growth of (asymmetric) $\text{B}_3^2\text{-BO}_4$ linkages further implies a rearrangement around BO_4 structural units in the medium-range order. Similar observations have been reported by Cochain et al.¹⁸ in borosilicate glasses and could be attributed to the decreasing concentration of BO_4 units with increasing Fe_2O_3 (discussed further in section 3.1.5). Moreover, the intensity of the 1510 cm^{-1} metaborate band gradually decreases with adding Fe_2O_3 (Figure S3). This shows a lower tendency of the anionic borate formation in the network with the abundance of FeO_4 units, as the Fe tetrahedra require stoichiometrically equivalent amount of Na^+ for charge compensation.⁷⁴

3.1.5 MAS NMR spectroscopy

The ^{27}Al and ^{11}B MAS NMR spectroscopy has been performed to better interpret the short-range structural environment in the investigated glasses. However, in preface to the presentation and discussion of the MAS NMR spectroscopy results, it must be highlighted that applying NMR spectroscopy for investigating the structure of glasses containing paramagnetic ions, e.g., Fe^{2+} or Fe^{3+} , is a challenge.²⁸ The unpaired electrons in d-orbitals of iron drastically reduce the spin-lattice relaxation time of its nuclear spins, thus, resulting in an overall loss of NMR signal and significant peak broadening, where the signal loss is dependent on the spatial proximity of the nuclei of interest to Fe.⁷³ For example, in iron-bearing silicate glasses, the nuclear spins within $\sim 3.3 \text{ \AA}$ (cut-off radius) from Fe cannot be observed.⁷³ A recent study focused on investigating the structure of iron-containing alkali aluminoborosilicate glasses using MAS NMR spectroscopy reveals a $\sim 15\%$ and $\sim 80\%$ loss in the observed Al and B signals, respectively, with 5 mol.% addition of Fe_2O_3 .²¹ Further, it is difficult to distinguish the observed broadening induced by real structural changes from that caused by the paramagnetic interaction,⁷⁵ thus forcing a limit over quantitative analysis. Therefore, the MAS NMR spectroscopy results presented in this study should be considered qualitative to understand iron's influence on the structural environment around aluminate and borate sites. The quantitative analysis of aluminum and boron speciation has been performed only on the MAS NMR spectroscopy results of iron-free glass (0Fe) to validate the structural information derived from the MD simulations (see Section 3.2.1). The fitting parameters of the ^{11}B and ^{27}Al MAS NMR spectra of the iron-free glass (0Fe) are summarized in [Table S4](#).

[Figure 6a](#) presents the normalized ^{27}Al MAS NMR spectra of the investigated sulfur-free glasses. A dominant broad peak at ~ 60 ppm is observed in all the spectra and is assigned to tetrahedrally coordinated Al^{3+} ($^{[4]}\text{Al}$).⁷⁶ In the iron-free glass (0Fe), $\sim 96\%$ aluminum is

tetrahedrally coordinated, while the presence of ~4% of five-coordinated aluminum ($^{[5]}\text{Al}$) is confirmed by an additional ^{27}Al MAS NMR signal at ~33 ppm (inset in [Figure 6a](#); [Table 3](#)).⁷⁷ The addition of Fe_2O_3 impacted the ^{27}Al MAS NMR spectra ([Figure 6a](#)) of the glass in the following ways: (1) a significant broadening of $^{[4]}\text{Al}$ peak, making it evolve into a more symmetrical shape, and (2) a subtle shift in the $^{[4]}\text{Al}$ peak towards higher-frequency. The broadening of spectra with the addition of iron in the glass system is in good agreement with the previous literature,^{21, 78} and can be attributed to the paramagnetic effect mainly described by Lorentzian (and thus symmetric) function.^{75, 78} Further, the subtle high-frequency shift in the $^{[4]}\text{Al}$ peak is indicative of the increased chemical shielding of the detected $^{[4]}\text{Al}$, showing a higher number of Al units around the detected $^{[4]}\text{Al}$ centers. Such variation in the Al environment could originate from the rearrangement between tetrahedral structural units and the preferential signal loss of Al–O–Si sites compared to Al–O–Al sites owing to the presence of the paramagnetic Fe nuclei.⁷⁸ According to Zhang et al.²¹, iron has a higher spatial affinity for SiO_4 over AlO_4 units in alkali aluminoborosilicate glasses, which results in a higher signal loss of ^{29}Si nuclei (50%-65%) in comparison to ^{27}Al nuclei (~20%) with 5 mol.% Fe_2O_3 , confirming the significant impact of iron on the silicate environment. The presence/absence of $^{[5]}\text{Al}$ in the iron-containing glasses could not be confirmed due the possible overlap of $^{[5]}\text{Al}$ peak with the spinning sidebands (not shown).

[Figure 6b](#) shows the ^{11}B MAS NMR spectra of the sulfur-free glasses. All the spectra are resolved into two peaks: one is a relatively narrow peak at ~0 ppm, arising from four-coordinated boron ($^{[4]}\text{B}$), and the other one is a broader peak in the region 15-20 ppm, attributed to three-coordinated boron sites ($^{[3]}\text{B}$).⁷⁹ For the iron-free glass (0Fe), the quantitative estimation of $^{[3]}\text{B}$ and $^{[4]}\text{B}$ fractions is achieved by the signal deconvolution, as shown in the inset of [Figure 6b](#).

Two ^{13}B components, labeled as "symmetric" and "asymmetric," identify the threefold boron environment without (i.e., symmetric) and with (i.e., asymmetric) NBOs. To satisfy the area fitting for ^{14}B , three components, referring to those with a different number of Si neighbors (e.g., $^{14}\text{B}_{3\text{B},1\text{Si}}$, $^{14}\text{B}_{2\text{B},2\text{Si}}$, $^{14}\text{B}_{1\text{B},3\text{Si}}$ at 1.1, 0 and -1.7 ppm, respectively) have been fitted.⁸⁰ The fitting parameters are summarized in [Table S4](#). While this deconvolution could be considered artificial, it serves to extract a reliable fraction of 4-fold B units (denoted as N_4) of 60.6% in the 0Fe glass ([Table 3](#)). When Fe_2O_3 is added from 1-3 mol.%, a peak broadening and an increase in the ^{13}B peak intensity are observed ([Figure 6b](#)). Similar to the ^{27}Al MAS NMR spectra, the observed changes in the ^{11}B MAS NMR spectra can be attributed to the structural changes in the glass network and the paramagnetic effect of iron. As mentioned earlier, owing to the paramagnetic interactions with Fe nuclei, some ^{11}B MAS NMR signals from the nuclei located within cut-off distance from Fe nuclei are lost, while the other affected signals are collected but are broadened in line-shape. According to the more pronounced broadening observed for ^{13}B peak, there seems to be a preferential paramagnetic interaction between Fe nuclei and ^{13}B (over ^{14}B), which would induce a larger amount of ^{13}B signal loss. As such, if we assume no variation in B species with Fe_2O_3 addition, the ^{13}B signal intensity should decrease owing to the more enhanced signal loss from the paramagnetic effect of iron. However, the ^{13}B signal intensity shows an apparent increase in the measured spectra, which implies a BO_4 to BO_3 conversion with Fe_2O_3 addition in the framework. Similar results on the variation in borate units as a function of Fe_2O_3 content in borosilicate glasses have also been reported by Cochain et al.,⁷⁴ and may be attributed to any of the following hypotheses: (1) preferential association of Na^+ with FeO_4^- (over BO_4^-) resulting in a higher fraction of BO_3 ; (2) avoidance of $\text{FeO}_4\text{-BO}_4$ linkages (tetrahedral avoidance) resulting in the formation of BO_3 units; (3) structural rearrangement in the borate network, where ring

structures associated with BO_3 units are preferred over BO_4 units. The first hypothesis is not valid in the present study as the investigated glasses are highly peralkaline ($\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 > 1$). Assuming the majority of Al^{3+} in the investigated glasses is in tetrahedral coordination (as shown by ^{27}Al MAS NMR), where FeO_4^- does not effectively compete with AlO_4^- for Na^+ ,²¹ there is enough Na^+ left in the glass composition to charge-compensate both BO_4^- and FeO_4^- . Therefore, there is no need for FeO_4^- to compete with BO_4^- for Na^+ . This assertion is also supported by re-polymerization in the silicate network and the decreasing fraction of asymmetric BO_3 units in the glass structure (as observed by Raman spectroscopy), thus suggesting that FeO_4^- units scavenge Na^+ from the NBO sites. The second and third hypotheses seem more feasible due to the higher affinity of iron to connect with borate units in the glass structure, as has been shown in our previous study.²¹ Considering the linkage between two negatively charged tetrahedral units is energetically unfavorable,⁸¹ it is possible that iron addition to the glass induces some structural rearrangements in the borate/borosilicate network, resulting in an increased fraction of BO_3 units. Further detailed analysis using MD simulations has been presented in section 3.2.2.1.

3.2 Structural analysis of sulfur-free glasses – MD Simulations

Considering the challenges associated with acquiring MAS NMR data on iron-containing glasses, the MD simulations have been performed to compliment the results of Raman and MAS NMR spectroscopy to gain a detailed insight into the impact of iron on the short-to-intermediate range ordering in the structure of glasses. Further, in preface to the presentation/discussion of results obtained from the MD simulations, it needs to be mentioned that due to the low fraction of Fe^{2+} species in the glass structure (as deduced by Mössbauer spectroscopy; [Table 2](#)), the concentration of Fe^{2+} in the simulation box would have been insignificant or statistically

irrelevant. Therefore, the MD simulations have been performed assuming 100% iron in the glasses is in an Fe^{3+} state.

3.2.1 *Reproducing the short-range glass structure by MD simulations*

According to the MD simulations, the majority (97%-98%) of iron in the investigated glasses is present as FeO_4 units, while the remaining is present in five-coordination (FeO_5) (Table 3). These results are in good agreement with the Mössbauer spectroscopy results, given the Mössbauer spectroscopy probes the average structural features of a variety of possible iron sites. The MD simulations also reveal the average Fe–O bond length to be ~ 1.83 Å, consistent with the tetrahedral Fe^{3+} –O length of 1.85-1.86 Å, reported by Henderson et al.⁸² in alkali silicate glasses. This further supports the 4-fold coordination environment of Fe^{3+} as a network former, charge-balanced by Na^+ .

For the 0Fe glass, the simulated Al and B speciation data closely matches the experimental (MAS NMR) results, with a $\sim 4\%$ and 5% difference for AlO_4 and N_4 fractions, respectively (Table 3). Adding Fe_2O_3 to the investigated glasses does not impact the aluminum coordination, as 100% Al is tetrahedrally coordinated in the glass structure. This agrees with the results of ^{27}Al MAS NMR spectroscopy, where only a subtle shift in the NMR peak has been observed with increased Fe_2O_3 concentration in glasses (Figure 6a). The major change in the glass structure due to Fe_2O_3 addition can be observed in borate and silicate speciation (Table 3), where the N_3 fraction increases from $\sim 44\%$ to $\sim 49\%$ (with the fraction of B_3^3 increasing with increasing Fe_2O_3 content, while B_3^2 and B_3^1 staying almost constant), and the fraction of Q^4 silicate units increase at the expense of Q^3 and Q^2 units, thus resulting in a polymerized glass structure. These results are supported by the qualitative trends observed via Raman spectroscopy, as discussed in Section 3.1.4.

In addition, the MD simulation results suggest the existence of NBOs in the borate and silicate network, where, in agreement with our previous study on borosilicate glasses,⁸³ the highest fraction of NBOs are associated with trigonal borate units followed by silicate units, and a few NBOs associated with BO_4 units, as shown in [Figure S5](#). Here, it needs to be mentioned that though the formation of NBOs on BO_4 units is counterintuitive to our conventional understanding of the structure of borate and borosilicate glasses, their existence has been experimentally demonstrated in borate glasses, for example, by Winterstein-Beckmann et al.⁸⁴

3.2.2 Predicting the intermediate – to – medium-range structure by MD simulations

3.2.2.1 Connectivity between network-forming moieties

The connectivity among network-forming species, as extracted from the MD simulations, in terms of the fractional populations of the corresponding linkages, has been summarized in [Figure 7](#). As evident from [Figure 7a](#), Fe^{3+} (as FeO_4^-) preferentially connects with SiO_4 units followed by borate species, particularly BO_3 units, while the fraction of Fe–O–Al remains small (if not insignificant). Similar trends (at the qualitative level) for the preferential interaction between FeO_4 units with other network-forming moieties have been experimentally demonstrated, using MAS NMR spectroscopy, by Zhang et al.²¹ in sodium aluminoborosilicate glasses. In the present study, the fraction of these linkages gradually increases with an increased (absolute) abundance of Fe^{3+} in the glass structure, which agrees with the spectral broadening observed in in ^{11}B and ^{27}Al MAS NMR spectra (see Section 3.1.5), thus suggesting the spatial proximity of network forming species to Fe. It is worth noting that though the amount of Fe–O–Fe linkage remains low in the investigated glasses, the average Fe–Fe distance decreases as a function of Fe_2O_3 addition from 4.59 Å in 1Fe glass to 4.25 Å in 3Fe glass. This suggests a stronger exchange interaction

between adjacent Fe cations and, consequently, a higher possibility of forming Fe clusters, thus supporting the more intense doublet signals in Mössbauer spectra.

Further, adding iron influences the overall mixing among the framework cations. As evident from [Figure 7b](#), in iron-free glass (0Fe), AlO_4 units prefer to associate with SiO_4 units, leading to the formation of Al–O–Si linkages followed by the formation of Al–O–B linkages, where nearly equal fraction of BO_3 and BO_4 units tend to associate with AlO_4 units despite the potential tetrahedral avoidance rule ([Figure 7b inset](#)). Due to its highly peralkaline nature, the fraction of Al–O–Al linkages in 0Fe glass is small (if not insignificant). The addition of Fe_2O_3 to the glass induces the following structural changes: (1) a decrease in the fraction of Si–O–Al ([Figure 7b](#)) and Si–O–Si linkages ([Figure 7c](#)) is compensated by a corresponding steep increase in Si–O–Fe ([Figure 7a](#)) and a slight increase in Al–O–Fe linkages in the glass structure ([Figure 7b](#)); (2) a concomitant decrease in B–O–B and Si–O–B linkages (primarily Si–O– BO_4 ; [Figure 7c inset](#)) in the glass structure is compensated by an increase in the Fe–O–B linkages ([Figures 7a and 7d](#)), while the fraction of Al–O–B linkages remains almost constant irrespective of Fe_2O_3 content ([Figure 7b](#)).

Besides impacting the mixing between different network-forming moieties, adding Fe_2O_3 also promotes the restructuring of the borate network, as hypothesized in section 3.1.5 and described below.

(1) As shown in [Figure 7d \(inset\)](#), Fe_2O_3 addition has a minimal impact on the fraction of BO_3 – BO_3 linkages (corresponding to boroxol rings) in the structure of investigated glasses. The concentration of these linkages (as calculated by the MD simulations) is low or negligible in all the investigated glasses, thus suggesting the low-fraction (or absence) of

boroxol rings in the modifier-rich borosilicate-based glasses – in agreement with our previous study.⁹

- (2) Although energetically unfavorable, the $\text{BO}_4\text{--BO}_4$ linkages are present in the investigated glasses, and their concentration decreases with increasing Fe_2O_3 content. Meanwhile, the fraction of $\text{BO}_3\text{--BO}_4$ linkages, signifying the super-borate units,^{80, 85} decreases with the addition of Fe_2O_3 , indicating a destruction of big borate rings. This is in agreement with the destruction of pentaborate groups and the growth of loose BO_3 units, as observed in Raman spectroscopy (Figure 5).
- (3) According to the MD simulations, boron participates predominantly in 4-6 membered rings, as shown in Figure S6. When Fe_2O_3 concentration increases from 0 to 3 mol.%, the fraction of boron in the 4-6 membered rings decreases from ~18% to ~15% (Table S5), suggesting a general decrease in the abundance of boron present in the ring structure. This agrees with the qualitative results from Raman spectroscopy, where a reduction in metaborate and pentaborate ring structures has been observed with increasing Fe_2O_3 concentration (Figure S4). Accordingly, an increase in the average ring size from 6.23 (members) in 0Fe glass to 7.84 membered rings in 3Fe glass (Table S5) suggests the formation of larger borate rings with the participation of loose BO_3 units.⁸⁶

The structural trends observed in the MD simulations are in good agreement with the literature, where it has been shown that the addition of Fe^{3+} can alter the $\text{SiO}_4\text{--AlO}_4$ and $\text{SiO}_4\text{--BO}_3/\text{BO}_4$ intermixing in the glass network by the formation of Fe--O--(Si, B) bonds, thus, introducing a higher degree of structural disorder.^{21, 78} It must be emphasized that unlike the fraction of $\text{SiO}_4\text{--BO}_3$ linkages, which seems to remain almost unchanged with an increase in Fe_2O_3 concentration, the fraction of $\text{SiO}_4\text{--BO}_4$ linkages decreases significantly (Figure 7c inset).

The observed trend is in good agreement with the results of Raman spectroscopy, where a decreasing fraction of danburite units, four-membered ring structures comprising interlinked BO_4 and SiO_4 tetrahedra, in the investigated glasses with increasing Fe_2O_3 concentration has been reported (Figure 5).

3.2.2.2 Distribution of non-framework moieties in the glass structure

Table 4 presents the average coordination number (CN) of Na^+ in the investigated glasses and the average number of NBOs (N_{NBO}) and BOs (N_{BO}) coordinated by Na^+ in the glass structure, as derived from MD simulations. A slight increase in the CN from 5.82 (0Fe) to 5.86 (3Fe) can be observed with increasing Fe_2O_3 content in glasses. In parallel, N_{BO} increases from 3.72 to 4.03, while N_{NBO} decreases from 1.84 to 1.58 with increasing iron content in glasses. As per our conventional understanding of the structure of alkali aluminoborosilicate glasses,^{9, 83} Na^+ can play a dual role in the glass structure, i.e., it can either act as a charge compensator interacting with BO within anionic former units (e.g., BO_4^- , AlO_4^- , FeO_4^-) or as a network modifier interacting with NBOs in the borate and silicate network. Accordingly, the observed variation in Na^+ coordination number suggests a gradual shift in its structural role from a network modifier to a charge compensator with the incorporation of FeO_4^- units.⁸⁷

The distribution of Na^+ in the local environment of each network former cation has been calculated with Na-(Al/B/Si/Fe) cut-off radius taken from the end of the first peak in the corresponding partial radial distribution function and is plotted as a function of Fe_2O_3 concentration in Figure 8. It is observed that with the Fe_2O_3 addition, Na^+ are increasingly brought in the surroundings of Fe^{3+} , leaving less amount of Na^+ in the second coordination environment of Si and B. At the same time, the amount of Na^+ around AlO_4 stays relatively constant. The noticeable changes in Na^+ distribution are attributed to its relative affinity to

different former units, as presented in [Table S6](#). As shown, the values of Al/B, Al/Si, and Al/Fe are >1 , thus indicating a higher (preferential) tendency of Na^+ to stay closer to AlO_4^- units over other network former groups. Therefore, the distribution of Na^+ around Al^{3+} remains almost unaffected by the Fe_2O_3 addition. Meanwhile, Fe^{3+} shows a stronger affinity towards Na^+ in comparison to Si^{4+} and B^{3+} (for both BO_3 and BO_4) (see [Table S6](#)). These results suggest that the reduction in the average number of Na^+ around B^{3+} and Si^{4+} could stem from (1) Na^+ preferentially charge compensating FeO_4^- instead of BO_4 and/or (2) a fraction of Na^+ participating in the creation of NBOs in the silicate and borate network are removed to charge-compensate FeO_4^- units. In the present study, we observe both the abovementioned trends by MD simulations (corroborated by experimental studies). Nevertheless, more detailed experimental and computational studies investigating the structure of iron-containing borosilicate glasses over a broader compositional domain are needed to confirm the occurrence of either or both of the abovementioned structural changes about the redistribution of Na^+ in the glass structure.

It should be noted here, Fe^{2+} , which is not involved in the present MD simulations, is commonly considered as non-framework cation in the glass structure, exhibiting proximity with NBOs.⁷⁸ However, the distribution of Fe^{2+} in the glass network is still ambiguous and needs further investigation.

3.3 Sulfur in iron-containing borosilicate glasses

3.3.1. Impact of iron on the solubility of sulfur in borosilicate glasses

The sulfur solubility is defined as the concentration of sulfur at an established equilibrium between dissolved and atmospheric sulfur in the form of SO_3 and/or SO_4^{2-} , which is dynamic and difficult to reach and record in the actual glass melting process. Therefore, in the present study, sulfur (as SO_3) has been added to the $x\text{Fe}-y\text{S}$ glasses (starting from 0.25 mol.% SO_3) until it supersaturates in the melt and appears as a salt layer on the glass surface. The highest

concentration of SO_3 , which dissolves in a glass without altering its amorphous nature (as analyzed by XRD analysis), has been defined as its solubility limit. Once the SO_3 solubility limit has been reached, the excess sulfate partitions out of the melt in the form of salt and floats on the melt surface. Upon quenching the melt, the salt layer tends to stick to the surface of the transparent and XRD amorphous glass. All the sulfur-containing glasses (within the solubility limit) are XRD amorphous, as shown in [Figure S2a](#). The XRD analysis of the white salt layer reveals the formation of Na_2SO_4 [PDF# 97-006-3077] as the only phase ([Figure S2b](#)).

[Table 1](#) presents the compositions of the sulfur-free ($x\text{Fe}$) and sulfur-containing ($x\text{Fe}-y\text{S}$) glasses analyzed by ICP-OES. The solubility limit of SO_3 in glasses has been determined by the compositional analysis of the sulfur-containing glasses supersaturated with SO_3 . Therefore, the SO_3 concentrations for glasses 0Fe-1.25S, 1Fe-1S, 2Fe-1S, and 3Fe-0.75S, as reported in [Table 1](#), should be considered as the solubility limit of sulfate ions in the respective glasses under the given experimental conditions. Here, it needs to be emphasized that we did consider the possibility of sulfur volatilization from the glass melts as a probable cause for the difference between the batched and measured SO_3 concentrations in glasses supersaturated with sulfur. Based on the literature,^{9, 88} there should be minimal volatilization of sulfur from the glass melts in the present study due to the lower batch melting temperature, i.e., 1150 °C. Nonetheless, to confirm/negate any possibility of sulfur volatilization from the glass melts, the glass samples unsaturated with SO_3 , i.e., 0Fe-1S, 1Fe-0.75S, 2Fe-0.75S, and 3Fe-0.5S, were analyzed for their sulfur content using the ICP-OES. As evident from [Table 1 \(and Figure 9\)](#), the batched and experimental SO_3 concentrations in these glasses are in good agreement. These results help negate the effect of volatilization from the SO_3 solubility values reported in [Table 1](#). Thus, the lower SO_3 values (compared to batched SO_3) in the supersaturated glasses have been attributed

to sulfur solubility in the glass structure, while the insoluble SO_3 results in the formation of Na_2SO_4 -based salt phase on the melt surface. Since the formation of Na_2SO_4 requires the removal of Na^+ from the melt (to charge-compensate SO_4^{2-}), the experimental composition of supersaturated glasses exhibits a slight decrease in their Na_2O content.

3.3.2. *Impact of sulfur on the structure of iron-containing borosilicate glasses*

Table 5 presents the variation in density (ρ) and molar volume (V_m) of $1\text{Fe}-y\text{S}$ glasses, where y varies between 0 mol.% and 0.75 mol.%. An increase in the SO_3 content has an insignificant effect on the density of glasses, most likely due to its low content. Similarly, though the molar volume of glasses shows a slight increase with increasing SO_3 content, the values overlap each other in the range of experimental uncertainty, thus making the observed changes insignificant at a quantitative level. In general, the addition of SO_3 to alkali borosilicate and aluminoborosilicate glasses has been shown to increase their density and molar volume^{8,9} – a qualitative trend also observed in the present study and has been attributed to the presence of Na^+ neutralized sulfate (SO_4^{2-}) units in the interstitial space, which enhances the network connectivity due to structural re-polymerization (since SO_4^{2-} scavenges Na^+ from the NBO sites in the borosilicate network⁹) resulting in higher T_g , as shown in **Table 5**. Similar structural changes can also be expected in other Fe-containing glasses.

Figures 3b and S3b present the room temperature (RT) and low-temperature (LT) Mössbauer spectra of $1\text{Fe}-y\text{S}$ glasses, respectively. The fittings for these spectra have been performed following the methodology used for the sulfur-free glasses, and the extracted parameters are listed in **Tables 2 and S3**. A comparison between the results of Mössbauer spectroscopy on sulfur-containing and sulfur-containing glasses reveals insignificant changes in the redox behavior of iron as a function of SO_3 content in glasses, thus suggesting a minimal interaction

between iron and sulfur in the investigated glass system under the given experimental conditions. It is noteworthy that sulfur addition to the glasses has been shown to impact the redox behavior of iron, for example, as reported by El-Desoky et al.,⁸⁹ where sulfur addition (from 0 to 8 mol.%) to 40 Fe₂O₃ – 60 P₂O₅ glass increased the Fe²⁺/∑Fe. The observed disagreement between our results and those reported by El-Desoky et al.⁸⁹ can be attributed to the different sources of sulfur used, i.e., crystalline elemental sulfur (S) in Ref.⁸⁹ vs. SO₃ (as Na₂SO₄ → Na₂O + SO₃) in the present study. Therefore, while the melting conditions in the study performed by El-Desoky et al.⁸⁹ were reducing, the melt conditions in the present study were relatively oxidizing. However, it must be emphasized here that the glasses investigated in the present study are peralkaline, i.e., an excess of Na⁺ is available to charge-compensate AlO₄⁻, BO₄⁻, FeO₄⁻ and SO₄⁻, respectively. The observed trend of minimal impact of sulfur addition on iron redox may not be valid for metaluminous or peraluminous glasses, where BO₄⁻, FeO₄⁻ and SO₄⁻ will be competing for charge compensation by Na⁺ – this warrants further investigation.

The Raman spectra of 1Fe-yS glasses are shown in [Figure 10](#). In comparison to the sulfur-free glass (1Fe), the sulfur addition gives rise to the appearance of a relatively narrow band near 990 cm⁻¹ corresponding to symmetric S–O stretching vibration of SO₄²⁻ tetrahedra, whose intensity increases with an increase in the SO₃ content in the glass.^{13, 90-93} In agreement with our previous studies,^{8, 9} no band corresponding to any other sulfur species was observed with increasing sulfur content in the investigated glasses.

Besides the appearance of the band corresponding to SO₄²⁻ species, the sulfur addition also induces some additional structural changes, especially in the mid-frequency region (Region II), where the intensity of low-frequency bands at 950 cm⁻¹ and 1050 cm⁻¹ decreases, along with the growth of a tail near 1150 cm⁻¹. As discussed in Section 3.1.4, the low-frequency bands in

Region II could arise from (1) Si–BO (bridging oxygen) modified by weak network former cations, e.g., Fe–O–Si linkages, and/or (2) Si–NBO vibrations involved in depolymerized silicate tetrahedra. Based on Mössbauer spectroscopy results (Table 2), sulfur addition has a minimal impact on iron's redox behavior and structural role in the investigated glasses. Meanwhile, the unchanged peak width in ^{27}Al MAS NMR and ^{11}B MAS NMR spectra of the 1Fe-yS glasses (Figure S7), contributing to the uniform degree of paramagnetic interaction, also implies a similar spatial proximity between Fe, Al, and B in these glasses.⁷³ Therefore, Mössbauer and MAS NMR spectroscopy results collectively suggest a relatively constant environment of iron around other framework cations in the glass network as a function of sulfur content. Thus, the variation in the intensity of the abovementioned Raman bands in Region II most likely reflects a more polymerized silicate network formed upon sulfur incorporation. As discussed in our earlier study on iron-free sulfur-containing aluminoborosilicate glasses,⁸ such a change is associated with Na^+ at NBO sites being preferentially taken by SO_4^{2-} for charge compensation

4. Discussion

4.1 Impact of iron on the structure of alkali aluminoborosilicate glasses

In the investigated glass system and under the given melting conditions, $\geq 96\%$ iron tends to exist as Fe^{3+} in the glass structure irrespective of the total Fe_2O_3 concentration (Table 2). Similar redox behavior of iron has been reported in our previous studies and is widely discussed in the literature.^{21, 53, 94} Further, as revealed by the results of Mössbauer spectroscopy and MD simulations, both the cations, i.e., Fe^{2+} and Fe^{3+} , exist in tetrahedral coordination in the glass structure, where Fe^{2+} plays the role of a network modifying cation while Fe^{3+} acts as a network

former (FeO_4^-). Here, it needs to be emphasized that though Fe^{2+} is primarily known to exist in 5-6 coordination in silicate/borosilicate glasses, its existence in four-coordination (and still acting as a network modifier) has been reported in glasses with low-iron content.¹⁶ Mössbauer spectroscopy also suggests the possible existence of Fe^{3+} in two forms, i.e., isolated units and clustered ($\text{Fe}^{2+}\text{-O-Fe}^{3+}$ and/or $\text{Fe}^{3+}\text{-O-Fe}^{3+}$), where the fraction of the latter increases with increasing Fe_2O_3 concentration in the glass structure — a result that the MD simulations could not corroborate due to the low concentration of Fe_2O_3 in glasses and accordingly, lower number of iron atoms (and that too only Fe^{3+}) in the simulation boxes.

Concerning the impact of iron on the structure of alkali aluminoborosilicate glasses, the framework of an iron-free peralkaline sodium aluminoborosilicate glass is a cross-linked network for several network-forming moieties, namely SiO_4 , AlO_4^- , BO_4^- and BO_3 (symmetric and asymmetric), where Na^+ plays a dual role of charge compensator (preferentially for AlO_4^- followed by BO_4^-) and network modifier (creating NBOs in silicate and borate network). The addition of Fe_2O_3 brings in Fe^{2+} as another non-framework cation in the glass network. Therefore, a pool of Na^+ and Fe^{2+} exists in the glass network, where according to the random network hypothesis, both the cations should be randomly distributed and should not exhibit a preference for the role of charge compensator vs. network modifier. However, as has been reported in the literature,^{53, 95-97} this is not the case as the cation with lower ionic field strength will preferentially act as a charge compensator, while the one with higher ionic field strength will act as a network modifier and associate itself with NBOs. Considering the higher ionic field strength of Fe^{2+} (0.36 \AA^{-2}) compared to Na^+ (0.18 \AA^{-2}), the anionic groups, e.g., AlO_4^- , BO_4^- and FeO_4^- , are expected to charge-balanced by Na^+ , while Fe^{2+} and the leftover Na^+ would act as network-modifiers. Meanwhile, Fe^{3+} , as FeO_4^- , associates itself with the borosilicate network, as evident

from Table 7a and experimentally demonstrated in our previous study.²¹ Therefore, the formation of FeO_4^- - Na^+ association not only reduces the amount of Na^+ spent on creating the NBO attached to either silicate or borate units (as evident from the decreasing NBO/T from MD simulations) but also results in (1) the substitution of Si-O-(Al, B) linkages with Si-O-Fe and B-O-Fe linkages; (2) a decrease in the N_4 fraction (Table 3); and (3) destruction of metaborate and pentaborate rings resulting in the formation of “loose BO_3 ” units. This results in an increase in the directional bonding and molar volume with increasing Fe_2O_3 content in glasses. Here, it should be highlighted that Al speciation is insensitive to Fe_2O_3 addition due to the high stabilization of AlO_4^- - Na^+ association caused by its high electrostatic force, which allows AlO_4^- to be preferentially satisfied by Na^+ .⁹⁸

4.2 Impact of iron on the sulfur solubility in alkali aluminoborosilicate glasses

When discussing the impact of the iron-induced structural rearrangements on the solubility of sulfur, it is well known that SO_4^{2-} does not reticulate with the borosilicate or aluminoborosilicate network. Instead, it scavenges alkali/alkaline-earth cations from the depolymerized regions in the glassy network to charge-compensate its negative charge. Therefore, an increased degree of polymerization (decreasing NBO/T and increasing molar volume) with increasing Fe_2O_3 content helps explain the decreasing solubility of SO_4^{2-} in the glass structure. Nonetheless, two questions that still need to be answered are: (1) From our previous studies, it is known that SO_4^{2-} cannot effectively compete with AlO_4^- and BO_4^- for charge compensation by Na^+ . Can it compete with FeO_4^- for charge compensation by Na^+ ? (2) Despite the presence of Na^+ and Fe^{2+} as possible charge compensators, why does SO_4^{2-} preferentially associate with Na^+ , as evident from the formation of Na_2SO_4 salt (instead of FeSO_4) in the melts oversaturated with SO_3 ?

If SO_4^{2-} is preferentially charge compensated by Na^+ over FeO_4^- , either the $\text{Fe}^{3+}/\sum\text{Fe}$ in sulfur-containing glasses will be lower compared to sulfur-free glasses, or there will be a shift in the coordination of Fe^{3+} from four to six. As evident from the Mössbauer spectroscopy, the addition of SO_3 to the glasses has a minimal – to – no impact on the redox behavior of iron, thus negating the possibility of SO_4^{2-} being preferentially charge compensated over FeO_4^- .

The preference of SO_4^{2-} to be charge compensated by Na^+ over Fe^{2+} in the investigated glasses can be attributed to the following reasons: (1) Na^+ has lower ionic field strength than Fe^{2+} . Therefore, it is preferred by SO_4^{2-} for charge compensation; (2) The inventory of Fe^{2+} in the glass network is significantly lower than Na^+ . Consequently, it is easier for SO_4^{2-} to find Na^+ for charge compensation; (3) It is energetically favorable for SO_4^{2-} to associate with Na^+ (over Fe^{2+}), resulting in the formation of Na_2SO_4 as salt phase over FeSO_4 , as evident from the enthalpy of formation (ΔH_f) of the two salts: $\Delta H_f(\text{Na}_2\text{SO}_4) = -1387.56 \text{ kJ mol}^{-1}$; $\Delta H_f(\text{FeSO}_4) = -928.85 \text{ kJ mol}^{-1}$ [NIST Chemistry WebBook, SRD 69].

5. Conclusion

A suite of state-of-the-art spectroscopic characterization techniques, including Mössbauer, Raman, and ^{11}B , ^{27}Al MAS NMR, have been employed in conjunction with MD simulations to understand the impact of iron on the structure of peralkaline glasses designed in $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ based glass system, and unearth the structural descriptors controlling the sulfur (as SO_4^{2-}) solubility in these glasses. The majority ($\geq 96\%$) of iron exists as tetrahedrally coordinated Fe^{3+} (both isolated and clustered) in the investigated glasses, thus acting as a network former being charge compensated by Na^+ , while the remaining exists as tetrahedrally (distorted) coordinated Fe^{2+} . An increasing concentration of Fe_2O_3 (from 0 to 3

mol.%) results in the re-polymerization of the glass network by (1) scavenging of Na^+ by FeO_4^- units for charge compensation (most likely from the NBO sites), as evidenced by the decreasing NBO/T, and (2) formation of Fe–O–(Si, B) linkages larger-sized borate ring structures at the expense of metaborate and pentaborate rings. Since SO_4^{2-} is unable to effectively compete with AlO_4^- , BO_4^- and FeO_4^- for preferential charge compensation by Na^+ , the decreasing availability of NBO-associated Na^+ (with increasing Fe_2O_3) in the glassy matrix results in lower sulfur solubility. Finally, the presence of sulfur exhibited a minimal impact on the redox behavior and environment of iron in the glass structure owing to the oxidizing nature of the glass melt, and SO_4^{2-} prefers to be charge-compensated by Na^+ over Fe^{2+} .

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