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Redox variations in glass manufacturing: effects of oxygen fugacity and temperature on glass and melt properties

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Abstract:

At the time of the energy transition, it is important to modify the manufacturing conditions of glasses, in particular by reducing the CO₂ footprint. How do changes in the oxygen fugacity of a furnace affect the redox and properties of glass and melts? In this short article, we present redox calculations for some glass compositions and property measurements on a simplified low-iron glass composition. The increase in glass transition temperature by 10°C when the redox ratio $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ changes from 0.4 to 0.73 highlights the role of iron as a network-former in glass.

1. Introduction

Glass is a necessary material for a successful energy transition [1]. However, one of the main challenges we face in the energy transition is reducing the carbon footprint in the manufacturing of tomorrow's materials. To achieve this goal in glass manufacturing practices, there are two well-known levers available:

- the first strategy is to change the sources of raw materials to reduce CO₂ emissions, for example by reducing or eliminating the use of carbonates;
- the second strategy is to modify how furnaces operate. This includes eliminating fuel oil furnaces, reducing the number of gas-fired furnaces, and promoting the use of electric or hybrid furnaces that run partly on hydrogen or biogas [2,3].

However, changing the furnace type can have a major impact on the properties of liquids at high temperature (viscosity, diffusivity), radiation and emissivity within the furnace, and also the properties of finished products (colors, mechanical properties...).

It is therefore important to understand how oxygen fugacity f_{O_2} varies in a furnace, and how this fugacity can influence redox equilibrium. Additionally, it is now recognized that the redox of a glass at room temperature is not necessarily the redox of the parent liquid from which it originated [4-7]. As a reminder, there are many techniques for measuring the redox of a finished product (glass, ceramics) at room temperature. In this short and non-exhaustive paper, we will not present the traditional techniques for measuring the redox ratio of an element, such as wet chemistry analyses, electron microprobe, Mössbauer and optical absorption spectroscopies. A recent

review of redox analyzes is available [8]. Instead, we will mention some results obtained using Raman and X-ray absorption spectroscopies.

In this short article, we will briefly discuss oxygen fugacity measurements at high temperature and how f_{O_2} can affect the redox states of various glass compositions. The aim is to examine how the atmosphere in a furnace can influence redox states and how this, in turn, could affect properties such as viscosity.

2. Samples and experiments

Chemical compositions: Five glass compositions are presented in table 1. The WG composition, close to a window glass composition, is the one that will be studied primarily. For comparison, we report the compositions of commercial E, NC glasses, a commercial green old glass bottle and a Roman glass from the Embiez [9]. WG glass was synthesized and analyzed following previous work [11]. WG was melted at 1400°C in air and nitrogen in large quantities for viscosity measurements, whereas samples melted under oxygen and Ar-2% H_2 were prepared using the microwire technique [12]. E and NC glasses are taken from literature for comparison [10].

Viscosity and Raman are made following the methodology described previously [11,13]. XANES at the Fe K-edge were carried out on FAME Beamline at the ESRF, following the methodology used in previous works [4,5].

3. Results

Using the KC model [14], which has proved its efficiency in calculating redox equilibria on natural and industrial glass compositions [8,4,5], redox evolutions as a function of temperature were calculated for glass compositions and plotted for two different oxygen fugacities (Figure 1).

We can clearly see that, even for industrial glasses with similar composition containing small amount of iron, the redox varies greatly with temperature. This confirms that, during rapid quenching, the redox state of the glass is unlikely to match that of the melts, as shown earlier [4,6,7]. The E-glass shows even greater variations due to its high iron content and its difference in optical basicity.

On the other hand, there is a large difference in oxygen fugacity between a furnace operating in air with oxygen or electric combustion and a furnace operating in reducing conditions. For all compositions, a difference of around 35% is clearly visible in the redox ratio between 1300 and 1600 K for melting in air and with 1 ppm oxygen.

Raman spectra of glasses made under different oxygen fugacities are shown in figure 2a. Various features are visible and have been described in the literature [15]. The boson peak near 50 cm^{-1} decreases in frequency for the more oxidized glass, indicating an increase in polymerization as already shown [16,11]. The peak near 950 cm^{-1} can be attributed to Q^2 species for the more reduced glass (0, Ar-2% H_2). This peak shifts gradually to higher frequency with increasing oxidation, peaking near 980 cm^{-1} when melted under O_2 . For this latter glass, the band has the highest intensity and is associated with Fe^{3+} in four-fold coordination [17,13,6]. The peak near 1100 cm^{-1} corresponds to Q^3 species and shifts gradually to higher frequency with increasing glass oxidation.

XANES of the two glasses made in air and nitrogen are plotted in the figure 2b. The $Fe^{3+}/(Fe^{2+}+Fe^{3+})$ ratios

were found to be 0.73 and 0.40 for the sample melted in air and nitrogen, respectively. The XANES at the Fe K-edge show consistent results with those observed in the Raman spectra, with an increase of Fe³⁺ in tetrahedral sites when melted in oxidizing conditions.

Raman and XANES spectroscopies are excellent probes for investigating the redox state of glass and melts and their accuracy is within 10%. Additionally, they can be performed in situ at high temperatures [8].

Viscosity measurements for the WG glasses made in air and N₂ are plotted in figure 3. While there is no clear difference at high temperatures, a noticeable difference of 0.4 orders of magnitude is observed at low temperatures, near the glass transition temperature, T_g, determined at 550 °C. The viscosity data are fitted using the Tamann-Vogel-Fulcher (TVF) equation, giving two expressions for the air glass, $\log \eta = -2.6917 + 4025/(T-543.41)$, and the nitrogen glass, $\log \eta = -2.616 + 3938.4/(T-537.34)$. The T_g values are found to be 817.4 K for the air sample and 806.8 K for the nitrogen glass.

4. Discussions

Figure 1 shows that the redox state of glass or melts varies greatly with chemical composition, temperature and oxygen fugacity. This variability is evident even for industrial glasses with similar compositions and for small iron contents, such as around 1 wt%. This similarly applies to other redox couples in dilute conditions, such as cerium [7]. Significant differences in redox ratios were observed between samples prepared in air and under reducing conditions, illustrating the sensitivity of redox equilibria to operational conditions. Raman spectra also reveal that Fe³⁺ is in four-fold coordination, as indicated by the distinct band around 980 cm⁻¹ for soda-lime silicate glasses, corroborating previous findings [17,13].

Viscosity measurements show that oxidized glasses are more viscous than reduced ones, particularly at temperatures near T_g. Although the increase in T_g is only 10°C for a redox change from 0.4 to 0.73 for 1 wt% iron, this observation supports the role of iron as a network-former in the glass structure. This is consistent with the Fe³⁺ tetrahedron vibrational stretching band observed in the ~~silicon~~ vibrational pattern, which contributes to Si-O-Fe³⁺-O-Si stretching vibrations.

5. Conclusion

This study highlights the enormous impact of redox state on the properties of glass and melts, emphasizing the influence of temperature and oxygen fugacity. Our findings demonstrate that the redox state of glass can vary considerably with chemical composition, temperature, and the amount of available oxygen. Even small amounts of iron, around 1 wt%, can cause substantial changes in redox equilibria, which in turn affect the physical properties of the glass. Understanding and controlling redox conditions in glass manufacturing are crucial for optimizing both the process and the final product properties. As the industry moves towards more sustainable practices, such as using electric or hybrid furnaces, monitoring the redox state will be crucial to ensure desired material characteristics and efficient production.

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Table and Figure captions

Table 1: *Chemical composition in wt%. For WG and Bottle, averages over 20 measurement points. The values in brackets correspond to the errors on the last digits. Other values are taken from cited papers.*

Figure 1: Redox variation as a function of temperature for the five glass compositions reported in Table 1.

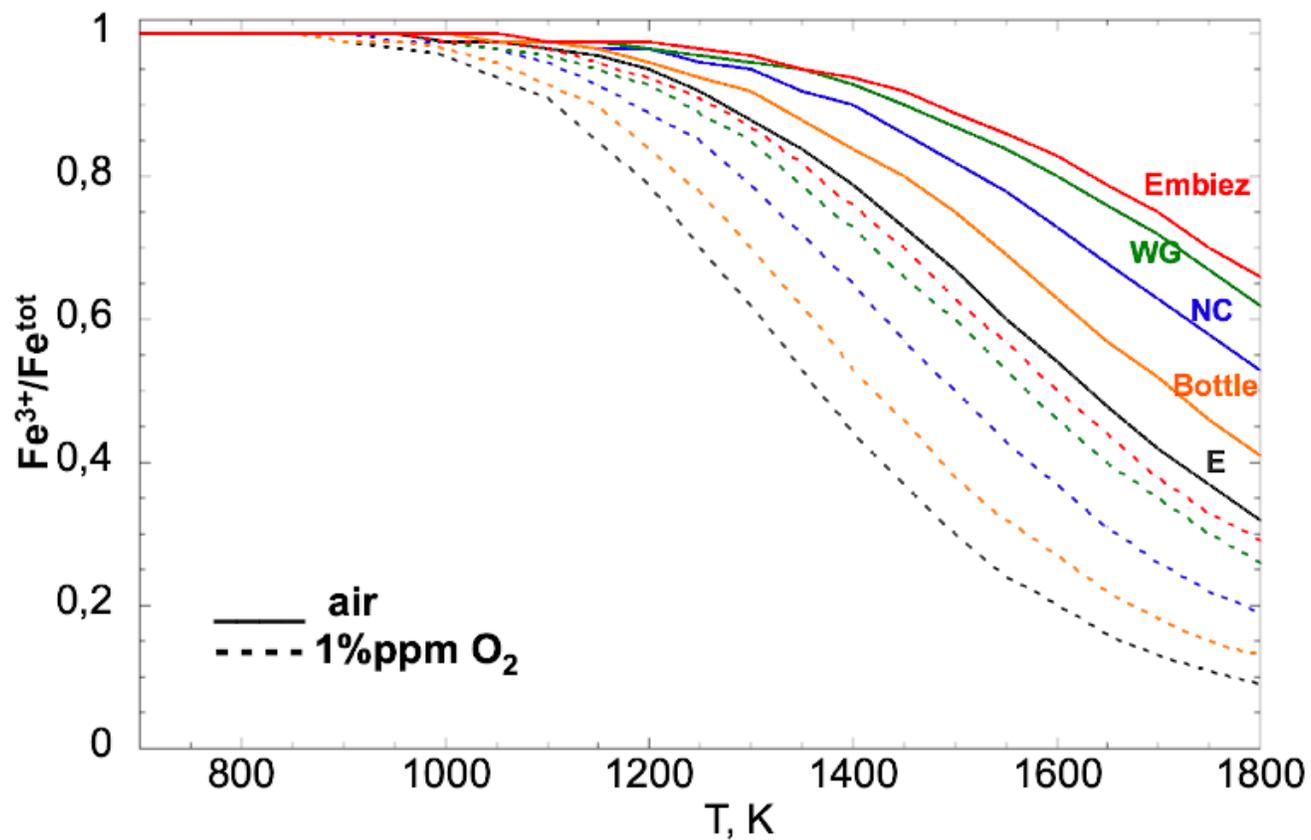
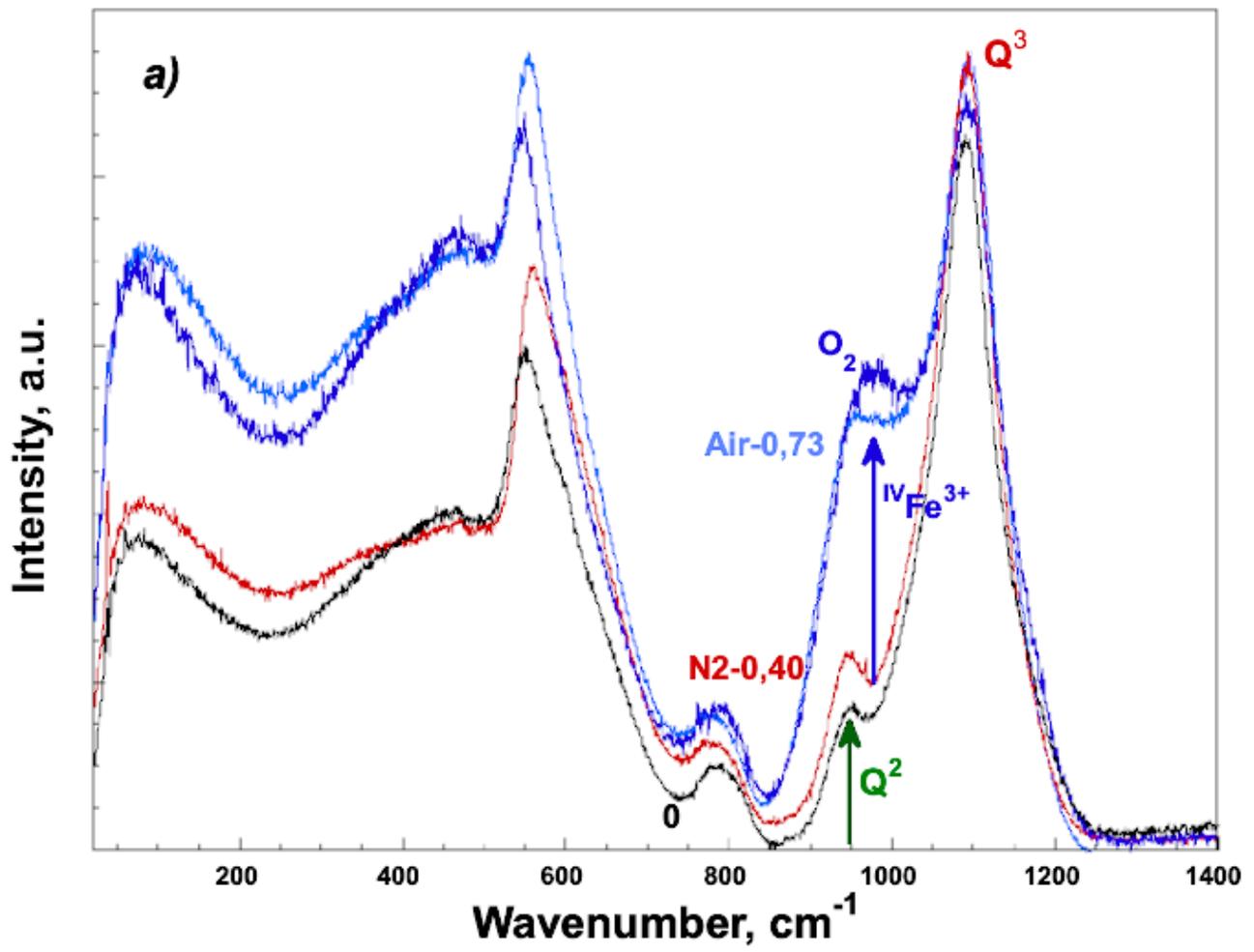


Figure 2: a) Raman spectra of WG glasses annealed under pure O₂, air, N₂, 0-Ar-2%H₂. b) XANES spectra at the Fe K-edge for WG glasses.



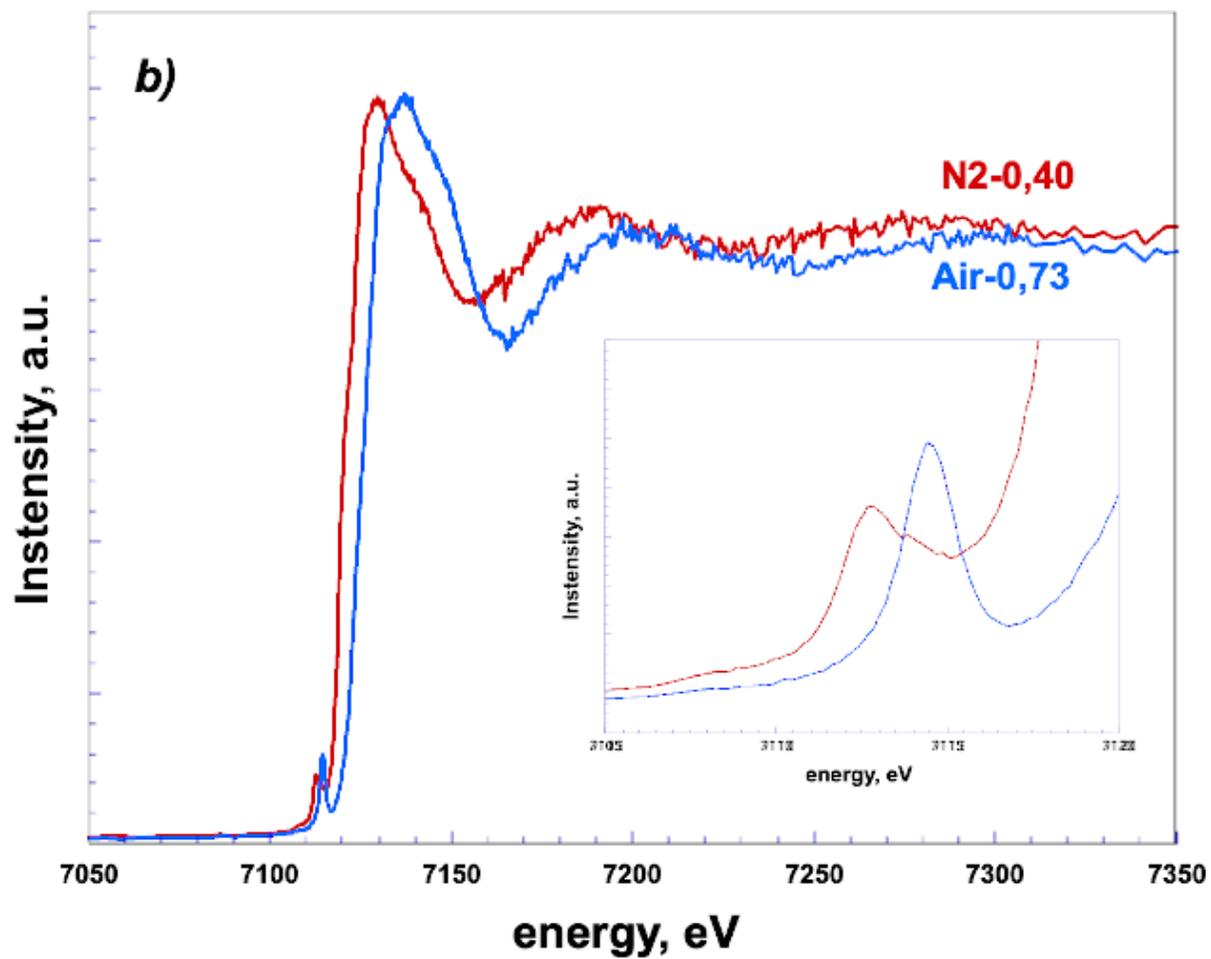


Figure 3: Viscosity measurements for WG composition under different atmospheres.

