# Infrared and Mössbauer studies of iron in aluminosilicate glasses

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## Abstract

Samples of $10Fe_2O_3 \cdot 10Al_2O_3 \cdot 80SiO_2$ composition were prepared by the sol–gel method and heat-treated between 120 and 1300 °C under oxidising (air) conditions. These samples were studied by Fourier transformer infrared (FTIR) and Mössbauer spectroscopy. The results indicate that $Fe^{3+}$ is in octahedral sites at 250 °C and in tetrahedral sites between 500 and 1300 °C. Goethite and hematite particles are present in the 250 and 500 °C samples and hematite particles in the samples heat-treated between 1000 and 1300 °C. The hematite particles, present in the samples, show a lower hyperfine field ($47.91 \pm 0.08$ T) than that usually seen for hematite (51.5 T). This is due to the fact of $Al^{3+}$ ions take the place of $Fe^{3+}$ ions in hematite particles. © 2001 Elsevier Science B.V. All rights reserved.

## 1. Introduction

In aluminosilicate glasses $Fe^{3+}$ and $Al^{3+}$ can occupy octahedral and/or tetrahedral sites. In silicate glasses $Fe^{3+}$ ions are mainly in tetrahedral sites [1–5]. However, when the iron content is relatively high the iron tends to aggregate forming clusters [3]. Mössbauer and Fourier transformer infrared (FTIR) spectroscopies are good techniques for obtaining information about the structural behaviour of iron in glasses [6]. Mössbauer, data give information about the coordination (isomer shift), symmetry (quadrapole splitting), and content (relative area) of the iron in glasses [7].

Samples of the $10Al_2O_3–10SiO_2–80SiO_2$ composition were already studied by X-ray diffraction (XRD), scanning electron microscopy (SEM),

electron spin resonance (ESR) and ac susceptibility measurements [8,9]. Nevertheless, some aspects of the iron incorporation, in these samples, has remained in doubt. This paper presents results of an investigation using infrared and Mössbauer spectroscopies, in order to detect new aspects of the iron oxide incorporation in gel-derived materials of $10Al_2O_3–10SiO_2–80SiO_2$ composition.

## 2. Experimental procedure

Samples of $10Fe_2O_3 \cdot 10Al_2O_3 \cdot 80SiO_2$ composition (mol%) were prepared from tetraethylorthosilicate (TEOS), $Fe(NO_3)_3 \cdot 9H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$, as sources of silica, iron and aluminium oxide. First, a mixture of TEOS, ethanol and water in a molar ratio 1:3:1 was stirred for one hour at room temperature. After this hydrolysis the two nitrates, which were dissolved in water, were added to give a $H_2O$/TEOS ratio of

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20. This solution was stirred for one hour, poured into Petri dishes and allowed to gel and dried at 60 °C. The gel obtained was heat-treated at 120 °C (48 h), at 250 and 500 °C (4 h) and between 1000 and 1300 °C (2 h) under oxidising (air) conditions.

The structure of the samples was examined using Mössbauer and infrared spectroscopies. Infrared transmission spectra were obtained by KBr method using a FTIR Mattson 7000 spectrometer. The Mössbauer absorbers were prepared by enclosing powdered samples into a plastic holder. $^{57}Fe$ Mössbauer spectra were registered at room temperature in a transmission geometry with a $^{57}Co/Rh$ source of about 30 mCi. The velocity wave had a symmetrical 'sawtooth' shape and the spectrometer was calibrated against $\alpha$-Fe foil absorber. The evaluation of the spectra was done using a least-squares-minimum computer fit to a superposition of Lorentzian line shapes.

## 3. Results

### 3.1. FTIR results

The infrared absorption spectra of the $10Fe_2O_3 \cdot 10Al_2O_3 \cdot 80SiO_2$ sample (Fig. 1) show a band near 1650 $cm^{-1}$ that is due to $H_2O$ presence [10]. This water disappears for heat-treatment temperature higher than 500 °C. The broad absorption band at 3460 $cm^{-1}$ can be assigned to both OH and $H_2O$ vibrations [10]. A peak at 1390 $cm^{-1}$ is assigned to C–H bending vibrations [10,11]. The intensity of this peak is considerably reduced for heat-treatment temperature higher than 120 °C. The band at 1090 $cm^{-1}$ due to the vibration of bridging oxygen present in $SiO_4$ units [12–14] shifts to higher wave numbers with increasing treatment temperature (Fig. 1). A band attributed to the presence of defect bonds in a silicate network [13] is observed at 900 $cm^{-1}$, in the spectra of the 1200 and 1300 °C samples (Fig. 1). The band around 800 $cm^{-1}$ is characteristic of symmetric stretching vibrations of $SiO_4$ units [15]. This band exhibits a shift toward lower wave number at 1200 and 1300 °C. In the spectra of the samples heat-treated at 1000, 1200 and 1300 °C a band near 600 $cm^{-1}$ (Fig. 1) can be attributed to
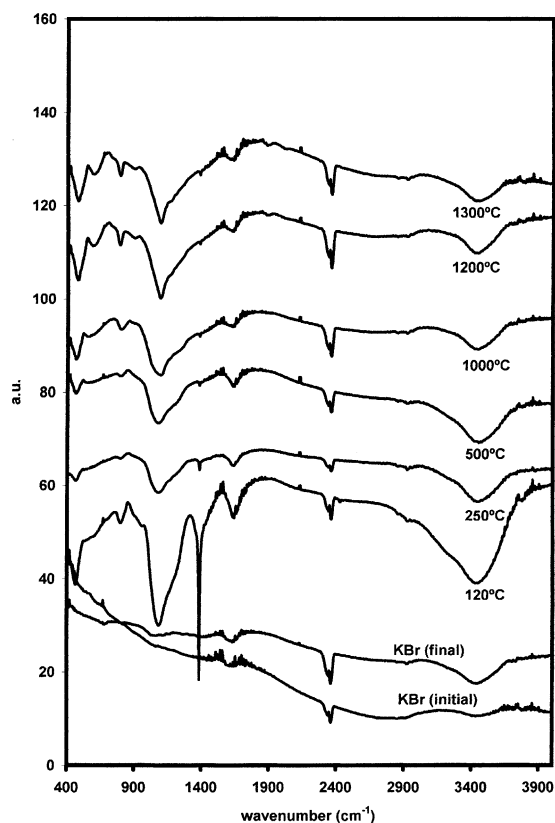


Fig. 1. FTIR spectra of the $10Al_2O_3 \cdot 10Fe_2O_3 \cdot 80SiO_2$ sample heat-treated between 120 and 1300 °C and KBr spectra (before (initial) and after (final) achieving iron spectra).

the vibrations of $FeO_4$ [13], $AlO_4$ or $AlO_6$ [15] units. In all the samples a band near 470 $cm^{-1}$ is present. This band is assigned to the vibration of Si–O–Si bonds [16–18] and $FeO_6$ units [13] and shifts to higher wave number when the temperature increases (Fig. 1). Moreover, EPR results [9] show that $Fe^{3+}$ ions are present in the samples.

### 3.2. Mössbauer spectroscopy

The Mössbauer results for the $10Al_2O_3 \cdot 10Fe_2O_3 \cdot SiO_2$ sample heat-treated between 250 and 1300 °C are shown in Fig. 2 and Table 1. The room temperature Mössbauer spectra of the 250 °C sample show a ferric iron doublet and two sextets (Fig. 2(a)). The isomer shift of the doublet (IS = $0.36 \pm 0.01$, Table 1) is typical of the pres-
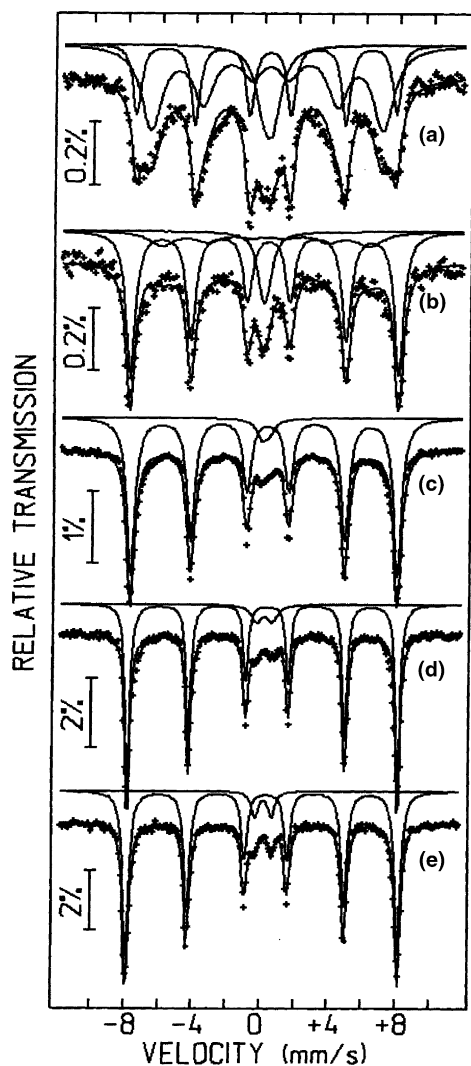
Fig. 2. Mössbauer spectra taken at 300 K of the $10Al_2O_3 \cdot 10Fe_2O_3 \cdot 80SiO_2$ sample heat-treated at: (a) 250 °C; (b) 500 °C; (c) 1000 °C; (d) 1200 °C and (d) 1300 °C.

ence of $Fe^{3+}$ in octahedral sites [19]. The two sextet are related with the presence of goethite and hematite [20]. However, hematite has a low hyperfine field $(47.91 \pm 0.08$ T) than that foreseen for hematite (51.5 T) [20]. The shoulder observed in the 250 °C spectrum cannot be ascribed to a $Fe^{2+}$ site because the introduction of Fe and Al as nitrates produces an efficient oxidation [21,22]. When the heat-treatment temperature increases Mössbauer spectra and parameters (Fig. 2(b)–(e), Table 1)

show a modification in the $Fe^{3+}$ coordination (tetrahedral sites) and the hyperfine field of hematite increases (Fig. 2 and Table 1). In the 500° C sample the isomer shift of $Fe^{3+}$ (IS = $0.22 \pm 0.03$ – Table 1) is lower than the values obtained for the samples heat-treated between 1000 and 1300 °C. The percentage of hematite is higher at 1000 °C than at 1200 or 1300 °C. The central doublet in the Mössbauer spectra is the contribution from $Fe^{3+}$ in the matrix. We have not assigned the central doublet to a supermagnetic behaviour because iron particles, as observed by SEM [8], are too large.

## 4. Discussion

The FTIR 1390 $cm^{-1}$ peak (Fig. 1) has a low intensity at temperature higher than 120 °C because the residual alkoxy groups present in the sample are removed by oxidation [10,11]. The 1090 and 470 $cm^{-1}$ bands shifts to larger wave numbers at higher temperature due to an increasing of the strength of Si–O bonds with the progressive polycondensation of the gel-sample. The glass network formed by the sol–gel method is initially porous [23]. At 250 and 500 °C the samples are porous but, around 800 °C, the porous network densifies and the pores, water and OH groups are eliminated (Fig. 1). Isomer shift data (Table 1) show that at 250 °C iron ions are in octahedral sites (IS = $0.36 \pm 0.01$ mm/s; $I(\%) = 15.01$). The octahedral symmetry of $Fe^{3+}$ ions can be understood considering that, at 250 °C, the network is porous and $Fe^{3+}$ ions are in the pores as $[Fe(H_2O)_x(OH)_{6-x}]^{3+}$ or/and $[Fe(H_2O)_6]^{3+}$ complexes. At 500 °C iron ions are in the pores in tetrahedral sites as $[Fe(OH)_4]^{3+}$ (IS = $0.22 \pm 0.03$; $I(\%) = 15.51$). Most of water has gone out between 120 and 500 °C (Fig. 1). The isomer shift, quadrupole splitting and the relative area values, for $Fe^{3+}$, at 500 and 1000 °C (Table 1) suggest that iron ions are not in a similar place. From 1000 °C the glass structure is densified, as observed by SEM [8], and $Fe^{3+}$ ions are incorporated in the silicate structure as a network former. The quadrapole splitting has a value higher at 1000 °C than at 500 °C because the tetrahedral site is less

Table 1

Mössbauer parameters fitted to the spectra taken at 300 K of the $10Fe_2O_3 \cdot 10Al_2O_3 \cdot 80SiO_2$ sample

| | IS (mm/s) | QS (mm/s) | $\Gamma$ (mm/s) | $H$ (T) | $I$ (%) |
|---|---|---|---|---|---|
| **250 °C** | | | | | |
| $Fe^{3+}$ | $0.36 \pm 0.01$ | $0.56 \pm 0.05$ | $1.01 \pm 0.05$ | – | 15.01 |
| Goethite ($\alpha$-FeOOH) | $0.38 \pm 0.02$ | $-0.17 \pm 0.03$ | $1.49 \pm 0.06$ | $42.73 \pm 0.19$ | 55.24 |
| Hematite ($\alpha$-Fe$_2$O$_3$) | $0.37 \pm 0.01$ | $-0.22 \pm 0.02$ | $0.60 \pm 0.04$ | $47.91 \pm 0.08$ | 29.75 |
| **500 °C** | | | | | |
| $Fe^{3+}$ | $0.23 \pm 0.01$ | $0.28 \pm 0.08$ | $0.80 \pm 0.01$ | – | 12.86 |
| Goethite ($\alpha$-FeOOH) | $0.35 \pm 0.01$ | $-0.15 \pm 0.01$ | $1.65 \pm 0.15$ | $38.42 \pm 0.06$ | 15.06 |
| Hematite ($\alpha$-Fe$_2$O$_3$) | $0.35 \pm 0.01$ | $-0.23 \pm 0.01$ | $0.67 \pm 0.02$ | $49.55 \pm 0.04$ | 72.08 |
| **1000 °C** | | | | | |
| $Fe^{3+}$ | $0.31 \pm 0.02$ | $0.45 \pm 0.05$ | $0.80 \pm 0.01$ | – | 5.50 |
| Hematite ($\alpha$-Fe$_2$O$_3$) | $0.36 \pm 0.01$ | $-0.21 \pm 0.01$ | $0.57 \pm 0.01$ | $49.36 \pm 0.01$ | 94.50 |
| **200 °C** | | | | | |
| $Fe^{3+}$ | $0.30 \pm 0.02$ | $0.95 \pm 0.04$ | $0.60 \pm 0.01$ | – | 8.72 |
| Hematite ($\alpha$-Fe$_2$O$_3$) | $0.36 \pm 0.01$ | $-0.22 \pm 0.01$ | $0.38 \pm 0.01$ | $50.01 \pm 0.07$ | 91.28 |
| **1300 °C** | | | | | |
| $Fe^{3+}$ | $0.29 \pm 0.01$ | $0.99 \pm 0.02$ | $0.49 \pm 0.03$ | – | 7.84 |
| Hematite ($\alpha$-Fe$_2$O$_3$) | $0.36 \pm 0.01$ | $-0.21 \pm 0.01$ | $0.40 \pm 0.03$ | $50.25 \pm 0.01$ | 92.16 |

IS – isomer shift; QS – quadrupole splitting; $\Gamma$ – line width; $H$ – average magnetic hyperfine field; $I$ – relative area.

symmetric when $Fe^{3+}$ ions are incorporated in the silicate structure. The amount of $Fe^{3+}$, incorporated as a former, is higher at 1200 and 1300 °C than at 1000 °C (see Section 3.2). This indicates the dissolution of hematite particles present in all the samples [8,9]. The shift of the FTIR band at 800 cm$^{-1}$, to lower wave numbers, at 1200 and 1300 °C (Fig. 1), confirms the increasing in the incorporation of iron as a network former. The shift is due to the fact that Fe–O bonds are more ionic than Si–O bond, which gives rise to a reducing in the tensile of the Si–O–Si bonds at the expense of the distortion of FeO$_4$ units [13]. Only a little part of the iron oxide is incorporated in the silicate network the rest is dispersed as hematite (in all the samples) and goethite (250 and 500 °C) particles. The sextet present in all the Mössbauer spectra (Fig. 2) are characteristic of the goethite and hematite presence. The average magnetic hyperfine data (Table 1), for hematite, indicates that a small amount of iron was replaced by aluminium in these particles [20,24]. As shown by Janot [24] in the $(Fe_{1-x}, Al_x)_2O_3$ (hematite) particles, the hyperfine field decreases linearly with $x$. For the samples in study the H and $x$ values are registered in Table 2. The $x$

Table 2

Average hyperfine field and $x$ values for the $(Fe_{1-x}, Al_x)_2O_3$ (hematite) particles

| $T$ (°C) | $H$ (T) | $x^{a}$ |
|---|---|---|
| 250 | $47.91 \pm 0.08$ | 0.42 |
| 500 | $49.55 \pm 0.04$ | 0.21 |
| 1000 | $49.36 \pm 0.01$ | 0.24 |
| 1200 | $50.01 \pm 0.01$ | 0.15 |
| 1300 | $50.25 \pm 0.01$ | 0.12 |

[a] $x$ is obtained using the equation $H = -7.69x + 51.17$ [20].

value is higher at 250 °C. This result can be understood by considering that, as confirmed by SEM and EPR [8,9], between 250 and 1000 °C, iron particles suffer a decrease in dimensions. This indicates dissolution of hematite particles with increasing heat treatment. Nevertheless, there is a corresponding network closing with segregation of iron oxide particles. At 1000 °C the network closing seems to reach a maximum. For this reason, at 1000 °C, the amount of iron incorporated as tetrahedral $Fe^{3+}$ is minimum ($I(\%) = 5.50$ – Table 1) and that of hematite maximum ($I (\%) = 94.50$ – Table 1). The tetrahedral $Fe^{3+}$ inserted in the glass matrix increases at 1200 and 1300 °C, due to the dissolution of hematite particles (Table 1).

In all the samples, iron is incorporated as $Fe^{3+}$ because the introduction of Fe and Al as nitrates seems to prevent Fe3+ to $Fe^{2+}$ reduction between 120 and 1300 °C.

## 5. Conclusions

This study shows that:

(a) The glass network formed by the sol–gel method is porous between 120 and 500 °C. At 800 °C the presence of pores was not detected.

(b) At 250 °C, $Fe^{3+}$ ions are in the pores as octahedral $[Fe(H_2O)_x(OH)_{6-x}]^{3+}$ and/or $[Fe(H_2O)_6]^{3+}$ complexes.

(c) At 500 °C, $Fe^{3+}$ ions are in the pores as tetrahedral $[Fe(OH)_4]^{3+}$ complexes.

(d) From 1000 °C, $Fe^{3+}$ ions are incorporated in the silicate network as press formers.

(e) In the 250 and 500 °C samples, goethite particles are detected.

(f) In all the samples, hematite particles are present. However, a small amount of iron is replaced by aluminium in these particles.

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