Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of the European Ceramic Society 25 (2005) 1855–1861

www.elsevier.com/locate/jeurceramsoc

FTIR spectroscopy investigation of the crystallisation process in an iron rich glass

Paola Pisciella, Mario Pelino*

Department of Chemical Engineering and Materials, University of L'Aquila, Monteluco di Roio, 67100 L'Aquila, Italy

Received 6 May 2004; received in revised form 15 June 2004; accepted 20 June 2004
Available online 11 November 2004

Abstract

The crystallisation behaviour of an iron rich glass, obtained by recycling zinc hydrometallurgy waste, was investigated by FTIR spectroscopy. The transformations occurring in the glass subjected to different thermal cycles, i.e. liquid–liquid separation and crystallisation, were investigated by FTIR, XRD and TEM. The asymmetric Si–O–Si stretching vibration wave-number, 1016 cm^{-1} in the FTIR spectrum of the glass, increased with the heat treatment temperature and was related to the variation of the coefficient of thermal expansion and density of the glass-ceramic. The magnetite and pyroxene crystalline phase peak, at 638 cm^{-1}, was utilised for determining the degree of crystallisation of the glass-ceramic by measuring the area of the peak as a function of the thermal treatment time; the results were compared with the same evaluation carried out by density measurements.

Keywords: Spectroscopy; Glass ceramics; SiO_2; Crystallisation; Waste materials

1. Introduction

The Fourier Transform Infrared Spectroscopy, FTIR, has been widely applied to the interpretation of the structural modifications occurring in glasses when subjected to a thermal treatment.[1–5] It has been shown[1,2] that the silica glass structure varies with the heat treatment temperature and several properties are affected by this variation. The shifting of the Si–O–Si peak in the FTIR spectra, have been used to evaluate the changes in silica glass properties such as density, reflective index, coefficient of thermal expansion, chemical durability and mechanical properties.[3] Tomozawa and coworkers[4,5] applied the FTIR spectroscopy to aluminium-borosilicate and sodium-silicate glass systems showing that the peak shift appears to be a sensitive tool for detecting the early stage of glass-in-glass phase separation induced by heat treatment. Pernice et al.[6] investigated the crystallisation of the potassium-niobium-silicate glasses by means of FTIR, Differential Thermal Analysis (DTA), X-Ray Diffractometry (XRD), Transmission Electron Microscopy (TEM). In all these studies, shifts in the wave-number of the fundamental vibrational modes in the FTIR spectra of glasses, were observed as a function of the heat treatment.

The FTIR spectrum of silica shows the most intense peak at about 1100 cm^{-1}, assigned to the asymmetric Si–O–Si stretching vibration; a peak at 800 cm^{-1}, assigned to the symmetric stretching vibration, and a peak at 470 cm^{-1} corresponding to the asymmetric bending vibration.[1,7,8]

The band at 1100 cm^{-1}, the most intense in the FTIR spectrum, has been extensively investigated. It has been correlated with glass structure modification and changes in several physical properties of silica glasses. It has been shown that the fundamental band position is correlated to Si–O–Si bond angle[1,2] and that its shifting towards lower wave-number indicates an higher energy level of the bonds.[9,10] Moreover, the deformation of glass network caused by the presence of metallic cations can be highlighted by the shifting of the Si–O–Si peak towards lower wave-number; the amount of the shift depends on the electronegativity of the cations.[9,10]

---

* Corresponding author. Tel.: +39 0862 434224; fax: +39 0862 434233.
E-mail address: pelino@ing.univaq.it (M. Pelino).

0955-2219/$ – see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2004.06.012

In the present study, the FTIR spectroscopy has been applied to investigate the crystallisation process of iron rich glasses obtained by mixing jarosite, a zinc-hydrometallurgy waste, in combination with granite scraps and glass cullet.[11,12] This glass system, when subjected to controlled heat treatment, partially crystallises as pyroxene ($CaO{\cdot}FeO{\cdot}2SiO_2$) and magnetite ($FeO{\cdot}Fe_2O_3$). The modifications of the glass structure have been investigated by recording the changes in wave-number and intensity in the FTIR spectra as a function of heat treatment temperature and time.

2. Experimental

A glass with the following wt.% composition: SiO_2 52.9; Al_2O_3 4.1; Fe_2O_3 24.1; CaO 5.2; MgO 1.8; ZnO 2.7; PbO 1.7; Na_2O 6.4; K_2O 1.1 was prepared by mixing jarosite, a hazardous industrial waste arising from the hydrometallurgy of zinc, granite scraps and glass cullet. The melting was carried out in a gas furnace at 1400 °C, utilising mullite crucible. Details pertaining to the characterisation, preliminary treatments of the raw materials and melting were discussed elsewhere.[13] Several 200 mm × 200 mm × 10 mm tiles were obtained and one of them was cut to obtain suitable pieces for the experimental investigations. The thermal behaviour of the initial glass was investigated by Linseis mod L 81 Differential Thermal Analysis (DTA) using a bulk specimens of about 120 mg. The DTA traces were recorded in air at a heating rate of 10°/min. The parent glass was heat treated in isothermal conditions in the range 630–800 °C for 2 h. The amorphous silica, the parent glass and the heat treated samples were investigated by Nicolet Nexus FTIR in transmission mode. The samples were powdered in stainless steel ball mill; the fraction below 45 μm was considered. A 2.5 mg were weighted, mixed in agata mortar with 500 mg KBr, dried at 120 °C for 24 h and then shaped in a 13 mm diameter and 1.3 mm thickness circular tablet. The amorphous silica was dried at 200 °C for 24 h. The spectra were collected in the 400–4000 cm^{-1} wave-number range; data-points were averaged over 64 scans and obtained at an interval of 1.928 cm^{-1}. The kinetic of phase transformation was investigated by isothermal treatments carried out at 660 and 700 °C for different times. The heat treatment temperature range was decided on the basis of DTA investigation, reported in a previous work,[12] in which bulk samples heat treated in air showed the glass transition temperature at about 580 °C and the exothermic peak, corresponding to bulk crystallisation mechanism by evaluation of the Avrami parameter, at temperatures above 700 °C. The degree of crystallisation was evaluated by density measurements by means of AccuPyc 1330 helium pycnometer. The experimental associated error was evaluated as 0.03%. The crystalline phases developed during the thermal treatment were investigated by XRD using a Philips-1830 apparatus and Cu Kα radiation. Transmission Electron Microscopy (a Philips CM 200 operating at 200 keV + EDS) was employed to investigate the crystalline phase formation. The samples used in these studies were thermally treated at different temperatures and then crushed, sieved, suspended in ethylic alcohol and deposited on a copper-carbon grid.

3. Results and discussion

In Fig. 1, the FTIR spectrum of the amorphous silica is reported. It shows the major peak, corresponding to the asymmetric Si–O–Si stretching vibration, at 1108 cm^{-1}. In Fig. 2, the FTIR spectra of the parent glass and the heat-treated sam-

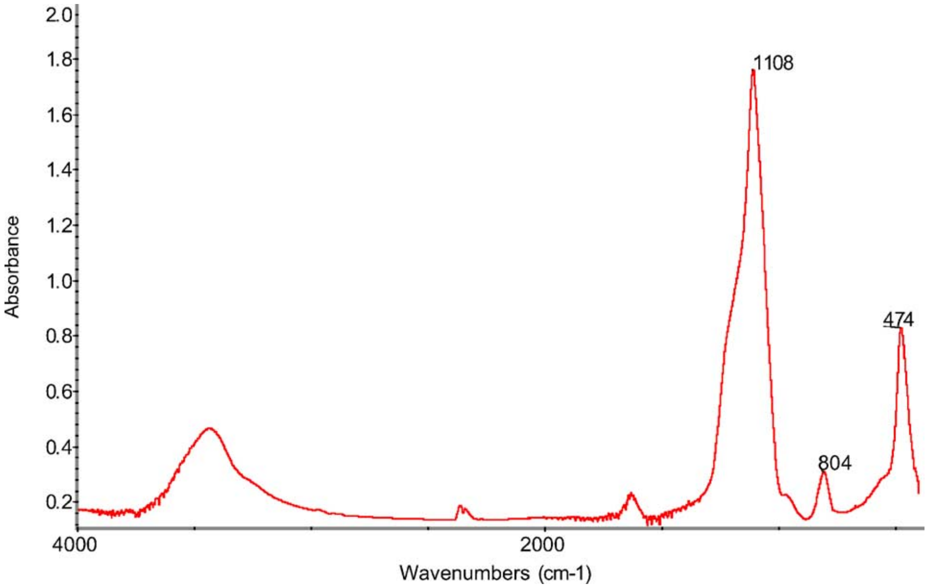

Fig. 1. FTIR spectrum of amorphous silica dried at 200 °C for 24 h.

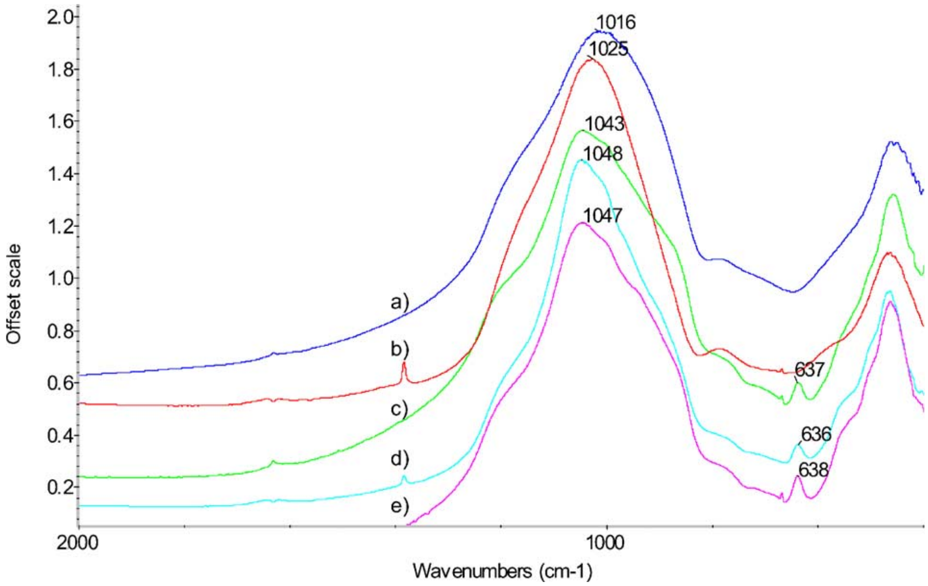

Fig. 2. FTIR spectra of the as quenched glass and 2 h isothermally heat-treated samples: (a) as quenched glass, (b) 630 °C, (c) 660 °C, (d) 700 °C and (e) 800 °C.

ples at different temperature are reported. The as quenched glass shows the Si–O–Si stretching peak at 1016 cm^{-1}, with a shift of 92 cm^{-1} with respect to the amorphous silica, due to the presence of a large amount of metal cations in the glass causing the deformation of the silica network. It can also be noted that all the heat-treated glasses show a peak shift towards higher wave-number with respect to the as quenched one, thus highlighting a lower degree of deformation of the silica network. This behaviour can be attributed to a crystallisation process, i.e. a depleting in metal cations of the residual glass, or a structural rearrangement of the glass network when crystallisation does not occur.[6] Moreover, the spectra reported in Fig. 2 show a peak at 637–638 cm^{-1} in the heat-treated samples which is not evident in the spectra of the as quenched glass and the one heat treated at 630 °C. As reported by Griffths,[14] magnetite and pyroxene show overlapping peaks in this range of wave-number, thus this presence highlights one or both these crystalline phases. In previous investigations, carried out by XRD technique,[11,12] the ratio between pyroxene and magnetite, for bulk samples heath treated at 740 °C for 30 min, resulted to be 3.5.

In order to understand the effect of a thermal treatment on the FTIR spectrum, two glass samples were heat treated at 630 and 700 °C for 2 h, respectively. The 630 FTIR spectrum shows a positive shift of 10 cm^{-1} (towards higher wavenumbers) with respect to the as quenched glass; the peak at 638 cm^{-1} is not evident. The 700 spectrum shows a positive shift of 30 cm^{-1} and the 638 cm^{-1} peak is clearly present.

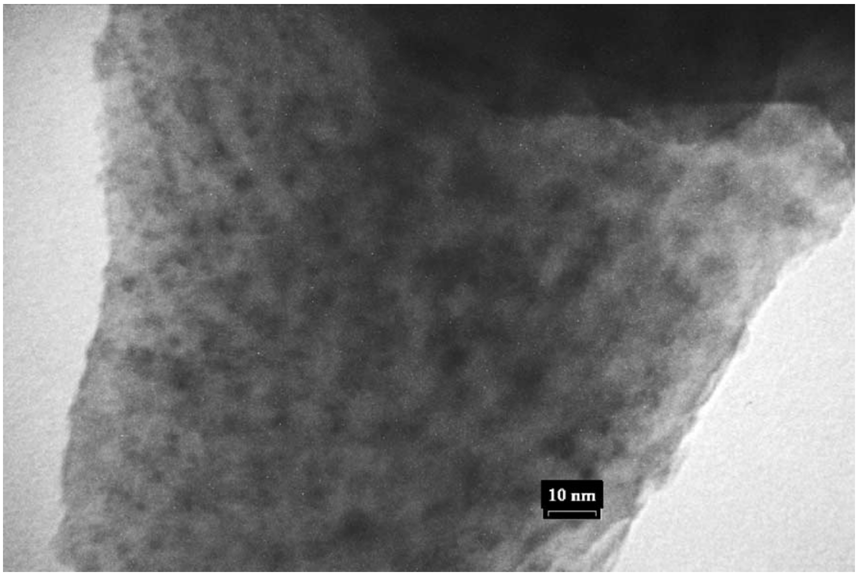

Fig. 3. TEM image of the 630 °C–2 h heat-treated glass (700k× magnification).

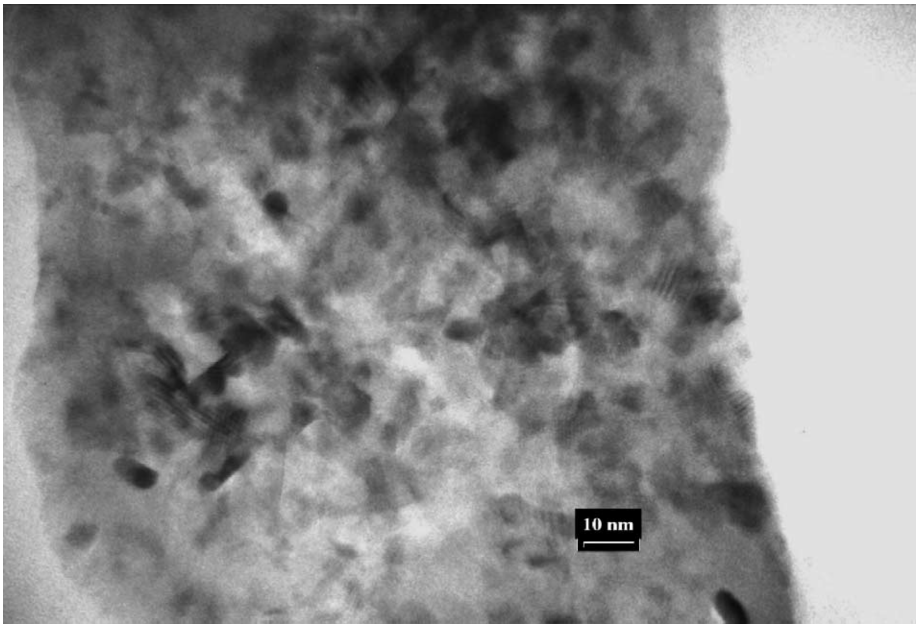

Fig. 4. TEM image of the 700 °C–2 h heat-treated glass (700k× magnification).

TEM, XRD and density measurements were also carried out on both samples. In Figs. 3 and 4 the TEM images of 630 and 700 samples are presented, respectively. The first picture shows two phases with particles uniform in dimensions and distribution, while in the second picture the particles are non-uniform in dimensions and distribution with clear and sharp borders. In Fig. 5, the XRD spectra of the two samples are reported. No relevant crystal phases are noticeable in the 630 sample; the 700 sample shows the peaks relative to magnetite, and pyroxene with a degree of crystallisation of nearly 50%. The density measurements resulted to be 2.872 ± 0.001 g/cm^3 for the 630 sample, i.e. practically identical to the density of the as quenched glass, and 3.233 ± 0.001 g/cm^3 for the 700 sample. These results can be explained by assuming that at 630 °C a liquid–liquid separation takes place in the glassy phase, as highlighted by the TEM observation and by the 10 cm^{-1} shift of the Si–O–Si FTIR peak. At 700 °C, the crystallisation process is evident, as indicated by the presence of the 638 cm^{-1} peak in the FTIR spectrum and is responsible for the 30 cm^{-1} peak shift.

In Fig. 6 the asymmetric stretching Si–O–Si wavenumber, the density and the coefficient of thermal expansion of the samples, are reported together. The three curves show a similar trend highlighting that a good correlation is obtainable between the modifications in the FTIR spectrum and the properties of high iron content glasses. In order to

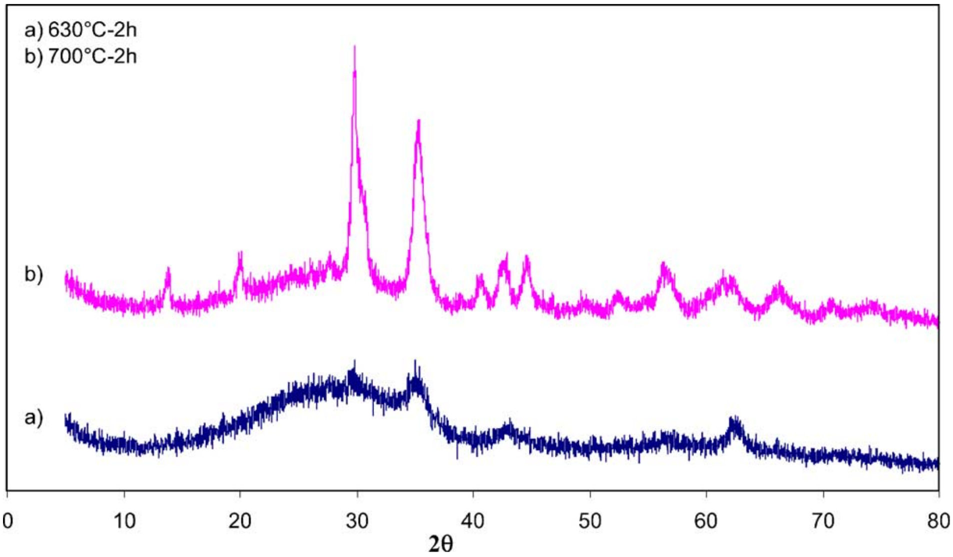

Fig. 5. XRD spectra of: (a) 630 °C and (b) 700 °C–2 h heat-treated samples.

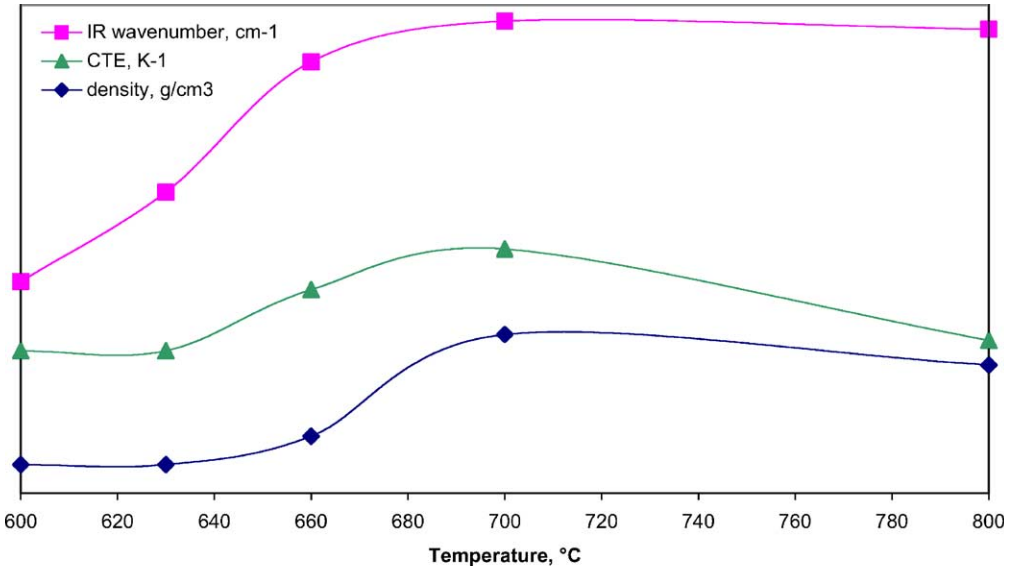

Fig. 6. FTIR Si—O—Si major peak wave-number, coefficient of thermal expansion and density vs. heat treatment temperature of the glass.

investigate the kinetic of crystallisation of the glass, samples were heat treated at 660 and 700 °C constant temperature for times ranging between 30 and 600 min; the FTIR spectra were then recorded. The kinetic of phase transformation was investigated by evaluating the shift of the Si–O–Si peak as a function of thermal treatment time at 660 and 700 °C, respectively. The results are depicted in Fig. 7and do not present a coherent relationship between the shift of the Si–O–Si peak and the duration of the thermal treatment. A similar results were obtained by other authors for different glass systems.[4] On the other hand it was observed that the intensity and the area of the magnetite/pyroxene peaks at 638 cm^{-1} changes as a function of the heat treatment time. This behaviour is evident in Fig. 8 where the FTIR spectra of the samples heat treated at 660 °C constant temperature for different times are reported in the wave-number range of pyroxene/magnetite. The kinetic of crystallisation was, therefore, investigated by measuring the magnetite/pyroxene peak area in the FTIR spectra. The degree of crystallisation was evaluated by the following equation:

$$X = \frac{A_t}{A_{\max}} \tag{1}$$

where A_t is the peak area at heat treatment time t and $A_{\max}$ is the maximum peak area. It was demonstrated in previous studies[13] that, for high iron content glasses, the density variation can be employed to evaluate the degree of crystallisation; the following equation was used:

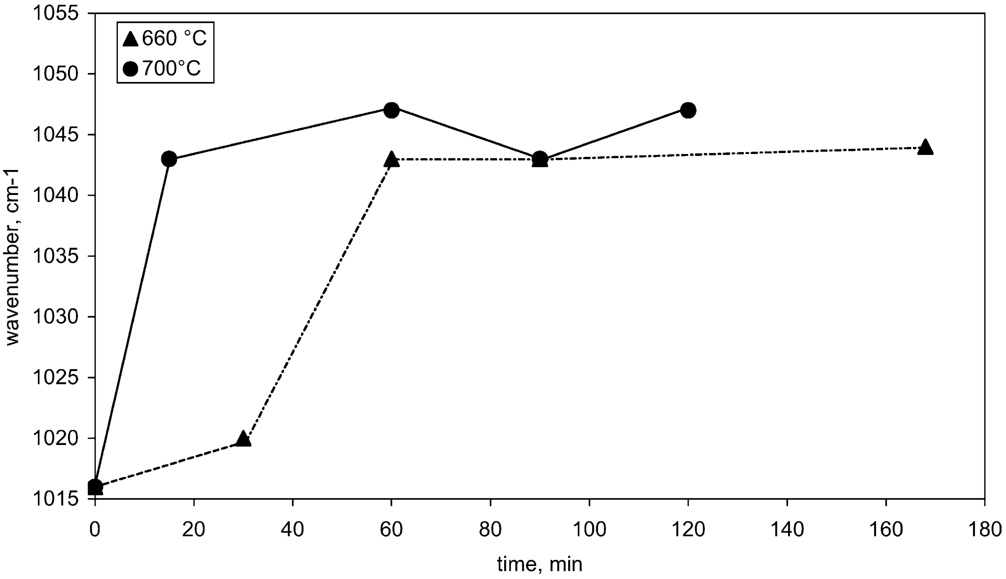

Fig. 7. FTIR Si—O—Si major peak wave-number of the glass samples heat treated at 660 °C (dashed line) and 700 °C (solid line) as a function of time.

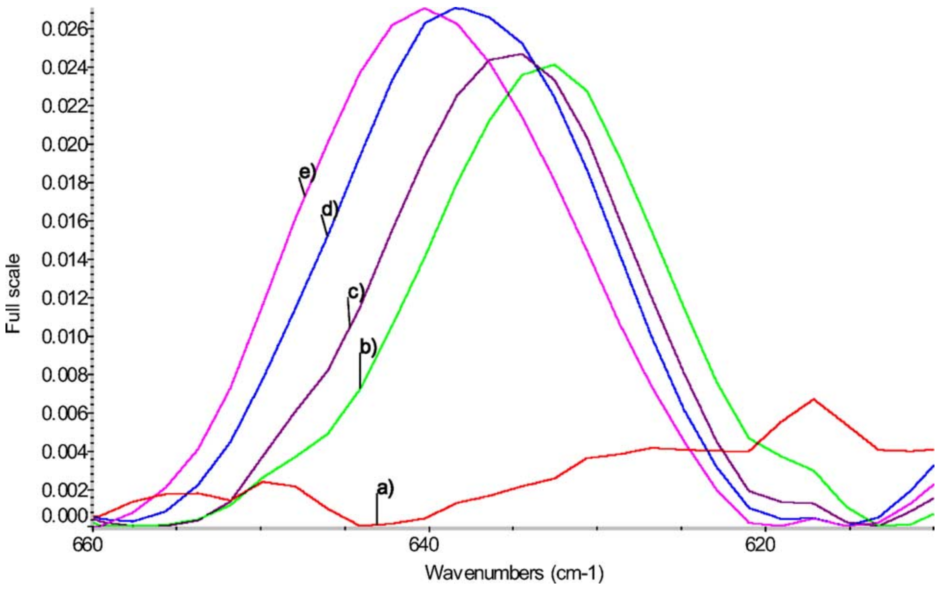

Fig. 8. Peaks at wave-number 638 cm^{-1} (pyroxene and magnetite range) of glass samples heat treated at 660 °C for a time of: (a) 30 min, (b) 60 min, (c) 90 min, (d) 120 min and (e) 600 min.

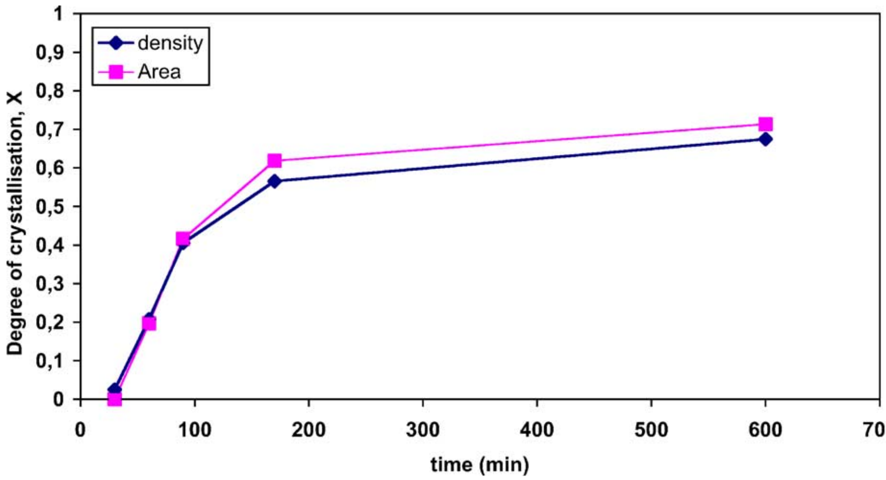

Fig. 9. Degree of crystallisation calculated by peak area at 638 cm^{-1} and density measurements.

$$X = \frac{\rho_t - \rho_0}{\rho_t}\frac{\rho_{\max}}{\rho_{\max} - \rho_0} \qquad (2)$$

where ρ_t is the density after treatment at a specific temperature for a time t, ρ_0 is the density of parent glass and $\rho_{\max}$ the maximum density. In Table 1 , the area of the 638 cm^{-1} peak, the density of the samples and the degree of crystallisation calculated by the two methods are reported as a function of the thermal treatment time. The experimental error associated to the peak measurement was evaluated as ±0.05. The maximum area, $A_{\max}$, resulted to be 1.73 ± 0.05 and the maximum density, $\rho_{\max}$, 3.233 ± 0.001. The degree of crystallisation data, calculated by Eqs. (1) and (2), are depicted in Fig. 9, showing a very good agreement between the two methods.

Table 1
Area of the 638 cm^{-1} peak, A_t, density, ρ_t, and degree of crystallisation, $X(A)$ and $X(\rho)$ calculated by the two methods

Time (min)	A_t	ρ_t (g/cm^3)	$X(A)$	$X(\rho)$
0	0.00	2.872 ± 0.001	0.00	0.00
30	0.00	2.885 ± 0.001	0.00	0.04
60	0.34 ± 0.05	2.940 ± 0.001	0.20	0.21
90	0.72 ± 0.05	3.008 ± 0.001	0.42	0.40
170	1.07 ± 0.05	3.065 ± 0.001	0.62	0.56
600	1.23 ± 0.05	3.106 ± 0.001	0.71	0.67

4. Conclusions

The FTIR spectroscopy was successfully applied to investigate the crystallisation process in iron rich glasses. Compared to the as quenched glass, the Si–O–Si asymmetric stretching vibration was shifted towards higher wavenumbers as a function of the heat treatment temperature.

This behaviour was attributed to liquid–liquid separation and metal cations depleting in the residual glassy phase due to the precipitation of magnetite and pyroxene. Moreover, the shifting of the peak was related to the variation of the coefficient of thermal expansion and density of the glass-ceramic.

The magnetite and pyroxene crystalline phase peak, at $638\,\mathrm{cm}^{-1}$, was utilised for determining the degree of crystallisation of the glass-ceramic by measuring the area of the peak as a function of the thermal treatment time. The results were comparable with the same evaluation carried out by density measurements.

References

1. Devine, R. A. B., Ion implantation and radiation induced structural modifications in amorphous SiO_2. *J. Non-Cryst. Solids*, 1993, **152**, 50.
2. Agarwal, A., Davis, K. M. and Tomozawa, M., A simple IR spectroscopic method for determining fictive temperature of silica glasses. *J. Non-Cryst. Solids*, 1995, **185**, 191–198.
3. Agarwal, A. and Tomozawa, M., Correlation of silica glass properties with the infrared spectra. *J. Non-Cryst. Solids*, 1997, **209**, 166–174.
4. Kato, Y., Yamazaky, H. and Tomozawa, M., Detection of phase separation by FTIR in a liquid-crystal-display substrate aluminoborosilicate glass. *J. Am. Ceram. Soc.*, 2001, **84**(9), 2111–2116.
5. Fujita, S., Kato, Y. and Tomozawa, M., IR peak shift due to phase separation of Na_2O-SiO_2 system glasses. *J. Non-Cryst. Solids*, 2003, **328**, 64–70.
6. Pernice, P., Aronne, A., Sigaev, V. and Kupriyanova, M., Crystallization of the $K_2O{\cdot}Nb_2O_5{\cdot}2SiO_2$. *J. Non-Cryst. Solids*, 2000, **275**, 216–224.
7. Handke, M. and Mozgawa, W., Model quasi-molecule Si_2O as an approach in the IR spectra description glassy and crystalline framework silicate. *J. Mol. Struct.*, 1995, **348**, 341–344.
8. Rokita, M., Handke, M. and Mozgawa, Spectroscopic studies of the amorphous SiO_2-$AlPO_4$ materials. *J. Mol. Struct.*, 1999, **511/512**, 277–280.
9. Strens, R. G. J., IR study of cation ordering and clustering in some (Fe,Mg) amphibole solid solutions. *Chem. Com.*, 1966, **15**, 519–520.
10. Osswald, J. and Snethlage, R., The hardening process in silicate paints. In *Proceedings of 8th International Congress on Deterioration and Conservation of Stones, Berlin*, ed. Joseph Riederer, 1996, pp. 1265–1275.
11. Karamanov, A. and Pelino, M., Evaluation of the degree of crystallization in glass-ceramics by density measurements. *J. Eur. Ceram. Soc.*, 1999, **19**, 649–654.
12. Karamanov, A., Pisciella, P. and Pelino, M., The crystallization kinetics of iron rich glass in different atmosphere. *J. Eur. Ceram. Soc.*, 2000, **20**, 2233–2237.
13. Karamanov, A., Canalini, C., Pelino, M. and Hreglich, A., Kinetics of phase formation in jarosite glass-ceramics. *J. Eur. Ceram. Soc.*, 1999, **19**(4), 527–533.
14. Griffths, P. R., Recent commercial instrumental developments in Fourier transform infrared spectrometry. In *Advances in Infrared and Raman Spectroscopy*, ed. R. J. H. Clark and R. E. Hester. Heyden Ltd., London, 1987, pp. 277–306.