

# Glass transformation range of iron rich glass and glass ceramics determined by different methods

A. Karamanov,<sup>1</sup> R. Di Gioacchino, P. Piscicella & M. Pelino

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

Manuscript received 3 July 2000

Revision received 29 September 2000

Accepted 6 October 2000

*The glass transformation temperature,  $T_g$ , of an iron rich glass, made up of hazardous industrial wastes, and of the corresponding glass ceramics with different percentages of crystal phase was investigated by differential dilatometry, differential thermal analysis (DTA) and density measurements. The  $T_g$  values, evaluated by different methods, are similar for the parent glass and glass ceramics with a low percent of crystal phase (15, 30 wt%), while for the samples with 50 and 55 wt% of crystal phase the  $T_g$  values obtained by dilatometry are about 100 and 150°C higher than the DTA determined values, respectively. The  $T_g$  values of the parent glass and of the 55 wt% glass ceramic evaluated by density measurements, resulted to be 560 and 600°C, respectively. It was highlighted that the density variation between annealed and nonannealed glass samples was about 0.01 g/cm<sup>3</sup> and that it could be utilised to evaluate the efficiency of the annealing treatment in iron rich black nontransparent glasses. The dilatometric softening point resulted in being dependent on percentage of crystal phase in the glass ceramics.*

The evaluation of the glass transformation interval is of great importance for glass technology and especially for the annealing heat treatment which is carried out in order to remove the internal stresses of glasses. The annealing range is limited by the upper and lower annealing temperatures, corresponding to a viscosity of  $\sim 10^{13}$  and  $\sim 10^{12.5}$  dPa s respectively.<sup>(1-4)</sup> The first temperature is near the glass transformation temperature,  $T_g$ , at which the glass viscosity takes a value of  $\sim 10^{13.3}$  dPa s; the second temperature corresponds to the strain point, i.e. the temperature below which it is assumed that the glass behaves as a solid and elastic material. The efficiency of the annealing heat treatment in removing stresses is usually estimated by observation of the final glass product in polarised light by means of a polariscope.

A further important point is the temperature at which deformation of the glass article may occur under its own weight. This temperature can be evaluated by the dilatometric softening point,  $T_s$ , corresponding to a viscosity of  $\sim 10^{11.3}$  dPa s.

In glass ceramics, due to the presence of crystal phases, the deformation starts at considerably higher temperature than in amorphous glass.<sup>(4-6)</sup> As a result the viscosity might increase by a factor  $\sim 10^3$ – $10^6$  dPa s compared with the expected viscosity of the residual glassy phase.<sup>(7-9)</sup> In this case the viscosity is usually defined as apparent viscosity.<sup>(4,5)</sup> Alternatively, some authors<sup>(10, 11)</sup> use the term effective viscosity which was introduced to define the viscosity of dilute suspensions.

Apparent viscosity acquires a particular importance in the manufacturing process of glass ceramic articles and in the high temperature application of these materials. The heating rate between the nucleation and crystallisation temperatures in the production cycle of glass ceramics depends on the increase of the apparent viscosity as a result of phase transformation; if the heating rate is too high and crystallisation rate slow, the products may deform due to decrease of apparent viscosity.<sup>(4,5)</sup>

In this work the  $T_g$  temperatures of an iron rich glass and of glass ceramics made up of hazardous industrial wastes were measured by a differential dilatometer, differential thermal analysis (DTA) and density measurements. The dilatometric softening point in crystallised glasses was investigated as a function of the percentage of crystal phase formed by different heat treatments.

## Experimental

An iron rich glass having the following composition (wt %): 52.9SiO<sub>2</sub>; 4.1Al<sub>2</sub>O<sub>3</sub>; 24.1(Fe<sub>2</sub>O<sub>3</sub>+FeO); 5.2CaO; 1.8MgO; 2.7ZnO; 1.7PbO; 6.4Na<sub>2</sub>O; 1.1K<sub>2</sub>O was prepared. This glass was obtained by mixing jarosite, a hazardous waste arising from hydrometallurgy of zinc ores, granite scraps and glass cullet. The raw material characterisation and details about the melting condi-

<sup>1</sup> Author to whom correspondence should be addressed. (e-mail: karama@ing.univaq.it)

tions are reported elsewhere.<sup>11,12</sup> The melting was carried out at 1400°C utilising 99.8% corundum crucibles. The melt was poured into a hot stainless steel mould, annealed and then cut in specimens for subsequent thermal treatment.

Crystallisation heat treatments of bulk glass samples were carried out at 650°C for 2, 4, 10 and 20 h. The crystallisation times were selected on the basis of previous investigations, in order to obtain samples with different percentages of crystal phase.<sup>11,12</sup> The crystalline phases were determined by x-ray diffraction (XRD) technique. (Philips PW1830 apparatus and CuK $\alpha$  radiation) and the crystalline fraction was evaluated by measuring the change of the density between the parent glass and the heat treated sample, using a He displacement Pycnometer (Accypyc 1330).<sup>13</sup>

The glass transformation temperature,  $T_g$ , and the dilatometric softening point,  $T_s$ , for the parent glass and crystallised samples were obtained using a Netzsch 402 ED differential dilatometer. In these experiments samples with 3×3×25 (mm<sup>3</sup>) size were treated at 5°C/min and 20°C/min heating rates.

$T_g$  temperatures of the parent glass and crystallised samples were estimated by the DTA technique (Netzsch STA 409 apparatus) using 30–35 mg bulk samples at 20°C/min heating rate.

$T_g$  temperatures of the parent glass and glass ceramics were also evaluated by density measurements. In this series of experiments, 20×20×20 (mm<sup>3</sup>) samples were heat treated for 1 h at different temperatures in the range 450–620°C for the parent glass and 500–680°C for the glass ceramics, respectively, and quenched on cold stainless steel moulds. The density of each sample was measured by He displacement Pycnometer. The experimental error associated to these measurements was evaluated as  $\pm 0.0005$  g/cm<sup>3</sup>.

## Results and discussion

Figure 1 shows the dilatometric traces at 5°C/min heating rate obtained for the parent glass, A, and for the samples crystallised at 650°C for 2, 4, 10 and 20 h and indicated as B, C, D and E, respectively. The crystalline fraction (wt%) evaluated by density measurements<sup>13</sup> resulted to be about 15% for B, 30% for C, 50% for D and 55% for E samples, respectively.

$T_g$  temperatures of the parent glass (A) and crystallised samples B and C are comparable while glass ceramics D and E show a consistently different dilatometric behaviour and much higher  $T_g$  values. With respect to the parent glass, the dilatometric softening point,  $T_s$ , increases about 30 and 50°C for samples B and C and about 150 and 200°C for samples D and E,

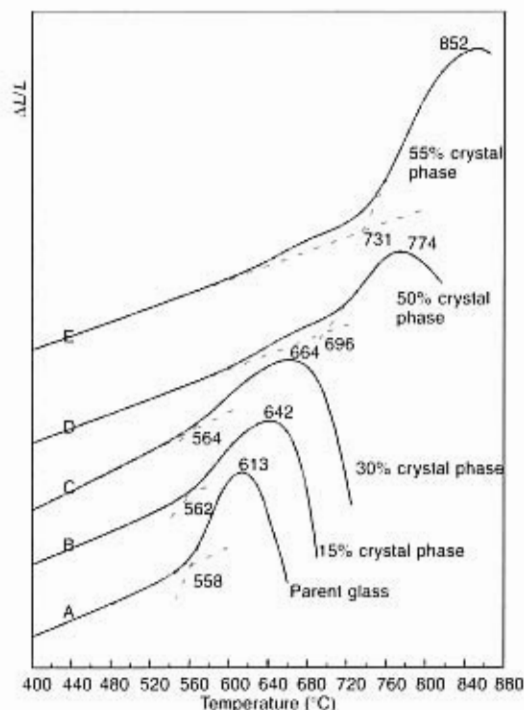


Figure 1. Dilatometric curves of the parent glass (A) and crystallised samples with 15 wt% (B), 30 wt% (C), 50 wt% (D) and 55 wt% (E), respectively

respectively, as also indicated in Figure 1. Dilatometric measurements were also carried out at 20°C/min heating rate. The corresponding  $T_g$  and  $T_s$  occur at about 20–30°C higher than the ones obtained at 5°C/min; the dilatometric traces show a similar behaviour. The results are reported in Table 1.

The  $T_g$  temperature was also evaluated by DTA technique by inferring the onset of the endothermic effect in the glass transformation region. The sensitivity of the DTA evaluation depends on the experimental conditions: the higher the heating rate the clearer the endothermic effect. Figure 2 shows the DTA traces, obtained at 20°C/min for the parent glass, A, and for the crystallised samples B and E. In the parent glass,  $T_g$  occurs at about 569°C and the crystallisation exothermic peak at 756°C. In sample B, with 15% crystal phase, the glass transformation temperature of the residual glassy phase can be identified at about 576°C. Due to the preliminary formation of the part of the crystal phase, the crystallisation peak occurs at lower temperature, 728°C, with a reduced thermal effect in comparison to the parent glass. In sample, E, the crystallisation exothermic effect is not evident and the  $T_g$  of the residual glass is not clearly distinguishable. However, the

Table 1.  $T_g$  and  $T_s$  values obtained by dilatometry, differential thermal analysis and estimated by the method of Gehlhoff & Thomas<sup>14</sup>

Sample	$T_g$ (°C)			Gehlhoff & Thomas	$T_s$ (°C)		
	Dilatometry at 5°C/min	Dilatometry at 20°C/min	DTA at 20°C/min		Dilatometry at 5°C/min	Dilatometry at 20°C/min	Gehlhoff & Thomas
A (glass)	558	580	569	558	613	637	613
B (15%)	562	587	580	568	642	670	621
C (30%)	564	601	593	573	664	712	633
D (50%)	696	709	605	574	774	796	635
E (55%)	731	775	607	575	852	868	636

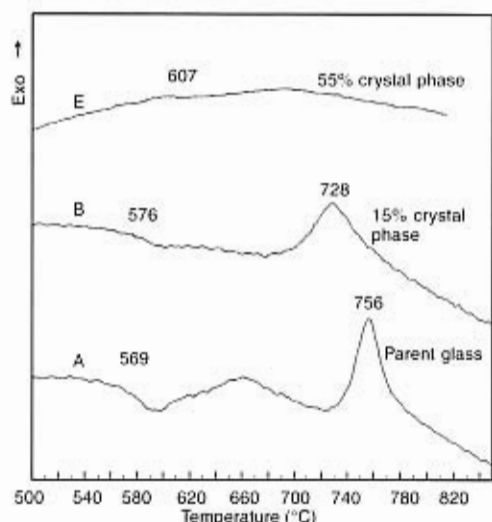


Figure 2. DTA traces of the parent glass (A) and of the crystallised samples B and E

modification of the DTA trace occurring in the temperature range 600–640°C could be considered and  $T_g$  identified at about 607°C.

Results for  $T_g$  and  $T_i$  are plotted as functions of percentage of crystal phase in Figures 3 and 4, respectively. The dashed lines in the figures indicate the values of  $T_g$  and  $T_i$  for the residual glass estimated, for the sake of comparison, by the method of Gehlhoff & Thomas.<sup>(14)</sup> In performing this evaluation the dilatometric values of  $T_g$  and  $T_i$  for the parent glass at 5°C/min, 558 and 613°C, respectively, were used as reference points. It was also assumed that the crystallisation begins with the formation of magnetite followed by growth of pyroxene solid solution.<sup>(12)</sup> The composition of the residual glass was calculated as the difference between the composition of the parent glass and that of the crystal phases formed, 9 wt% of which was taken as magnetite and the remaining as hedenbergite solid solution.

Table 1 summarises the results for  $T_g$  and  $T_i$ , both experimentally obtained and calculated.

$T_g$  values, obtained by dilatometry and DTA are similar for the parent glass and for B and C samples and comparable with the Gehlhoff & Thomas<sup>(14)</sup> esti-

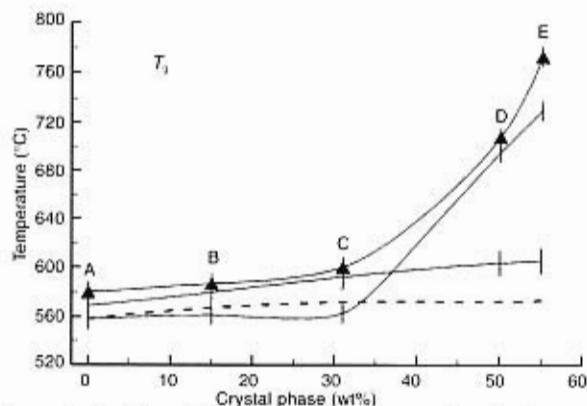


Figure 3. Variation of  $T_g$  as a function of crystalline fraction and comparison with the Gehlhoff & Thomas<sup>(14)</sup> estimated values dashed line – values, calculated by Gehlhoff and Thomas method  $\Delta$  dilatometry at 5°C/min  $\blacktriangle$  dilatometry at 20°C/min  $\diamond$  DTA at 20°C

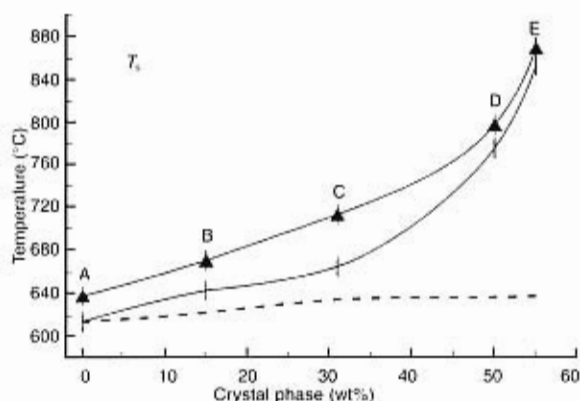


Figure 4. Variation of  $T_i$  as a function of crystalline fraction and comparison with the (dashed line) Gehlhoff & Thomas<sup>(14)</sup> estimated values

$\Delta$  dilatometry at 5°C/min  $\blacktriangle$  dilatometry at 20°C/min

ated values. For D and E samples, however, the dilatometric results are considerably higher than the ones obtained by DTA and the values calculated by the Gehlhoff & Thomas approach.<sup>(14)</sup> It appears that for crystallisation higher than about 30%, the  $T_g$  value obtained by dilatometry is influenced by the crystalline phase so that it can be considered in the sense of ‘apparent viscosity’. Values obtained by this technique and reported in literature<sup>(14–16)</sup> as ‘transformation temperature’ of different glass ceramics should be considered as characteristic of the composite of crystal phase and residual melt;  $T_g$  of the residual glassy phase can be expected at a lower temperature.

Similar consideration also applies for the dilatometric softening point. In this case all values obtained for the glass ceramics (B through E) should be considered as apparent viscosity. In fact, the  $T_i$  of sample B, with only 15% crystal phase, occurs at about 30°C higher than the  $T_i$  of the parent glass. For the sample E, with 55% crystal phase, the variation of  $T_i$  is as much as 250°C corresponding to a viscosity variation of about  $10^4$ – $10^5$  dPas.

The transformation temperature,  $T_g$ , of the parent glass was investigated by density measurements<sup>(15,16)</sup> carried out on glass samples treated for 1 h at different annealing temperatures in the transformation range followed by rapid quenching. The results are depicted in Figure 5 which shows the measured density as a func-

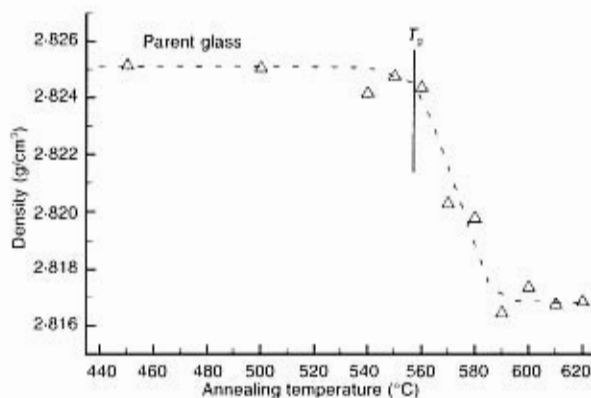


Figure 5. Variation of density as a function of annealing temperature for parent glass (A)

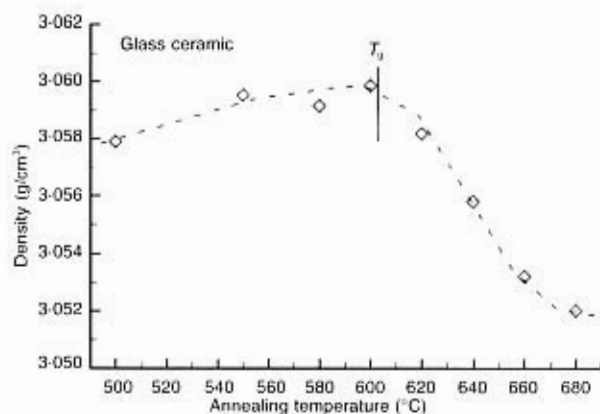


Figure 6. Variation of density as a function of annealing temperature for glass ceramic (E)

tion of annealing temperature. From the figure it appears that a sensible variation of density occurs at about 560°C, a temperature which is coincident with the dilatometric  $T_g$  obtained at 5°/min heating rate. From the figure it appears that 1 h annealing below  $T_g$  does not influence the density of the sample while annealing at a temperature higher than  $T_g$  produces a decrease in the sample density. After annealing at temperatures higher than 590°C the density reaches a constant value because during quenching the relaxation process is fast and follows the temperature variation. For the investigated composition the density variation, as a result of the annealing is about 0.01 g/cm<sup>3</sup> which is about twenty times higher than the sensitivity of the pycnometer.

Density measurements were also carried out on E glass ceramic. Figure 6 shows the density variation as a function of annealing temperature. The obtained plot is similar to that of the parent glass. In this case,  $T_g$  of the residual glassy phase occurs at about 600°C and the density variation is about 0.006 g/cm<sup>3</sup>. Thus in the case of glass ceramics,  $T_g$  obtained by density measurements is in good agreement with the value of about 607°C obtained by DTA and the one evaluated by the Gehlhoff & Thomas<sup>(14)</sup> method (see Table 1).

## Conclusions

The glass transformation temperature of iron rich glass and glass ceramics with different crystalline fractions was investigated by different techniques, i.e. dilatometric curve, DTA trace and density variation. The values obtained for the parent glass and glass ceramics with a

crystal phase lower than 30% are very similar while for the glass ceramics with higher crystallinity the dilatometric  $T_g$  is consistently higher and it should be considered as an apparent viscosity characteristic.

The dilatometric softening point in glass ceramics increases with percentage of crystal phase and also depends on apparent viscosity. For the sample with 15 wt% crystal phase the increase is about 30°C while for the sample with 55 wt% crystal phase is about 250°C.

For nontransparent black iron rich glasses, density measurements could be an efficient tool to evaluate the effect of an annealing heat treatment when polariscopic observation cannot be applied. This is the case in most of the compositions made up of industrial as well as of nuclear wastes where iron content is usually high.

## Acknowledgements

The authors are grateful to the National Council of Research (CNR) for the financial support given to this paper through the project Progetto Finalizzato Materiali Speciali per Tecnologie Avanzate II.

## References

1. Illavae, J. *The technology of glass and ceramics: an introduction*, 1983. Elsevier, Amsterdam.
2. Scholze, H. *Glass nature, structure and properties*, 1990. Springer-Verlag, Berlin.
3. Gutzow, I. & Schmelzer, J. *The vitreous state, thermodynamics, structure, rheology and crystallization*, 1995. Springer-Verlag, Berlin.
4. Pavlushkin, N. M. *The technology of glass and glass-ceramics*, 1983. Strojizdat, Moscow. (In Russian.)
5. Strnad, Z. *Glass-ceramic materials*, 1986. Elsevier, Amsterdam.
6. McMillan, P. W. *Glass-ceramics*, 1979. Academic Press, London.
7. Simons, C. J. & Simons, J. H. High shear rate of single phase and two phase glasses. *Proc. XVII Int. Congr. on Glass*, 1995, Vol. 3, Beijing, China, 413–18.
8. Partridge, G. The use of fibre viscometry to study nucleation and crystallisation phenomena in glass ceramic composition. *Glass Technol.*, 1985, **26** (3), 129–33.
9. Vicente-Mingarro, I., Rincon, J. Ma., Bowles, P., Rawlings R. D. & Rogers, P. S. Viscosity measurements on glass obtained from alkaline volcanic rocks of the Canary Islands. *Glass Technol.*, 1992, **33** (2), 49–52.
10. Fan, Z. & Boccaccini, A. R. A new approach to the effective viscosity of suspension. *J. Mater. Sci.*, 1996, **31**, 2515–21.
11. Kim, K. D. & Lee, S. H. Prediction of viscosity in the two-phase region of a ternary glass-forming system. *J. Mater. Sci.*, 1997, **32**, 6561–5.
12. Karamanov, A., Cantalini, C., Pelino, M. & Hreglich, A. Kinetics of phase formation in Jarosite glass-ceramics. *J. Eur. Ceram. Soc.*, 1999, **19** (4), 527–33.
13. Karamanov, A. & Pelino, M. Evaluation of the degree of crystallisation in glass-ceramics by density measurements. *J. Eur. Ceram. Soc.*, 1999, **19** (5), 649–54.
14. Volf, M. B. *Mathematical approach to glass*, 1988. Elsevier, Amsterdam.
15. Kingery, W. D. *Introduction to ceramics*, 1960. J. Wiley and Sons, New York.
16. Eitel, W. *The physical chemistry of the silicates*, 1954. University of Chicago Press, Chicago.