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Characterisation and thermal behaviour of a borosilicate glass

M.M. Lima, R. Monteiro*

Department of Materials Science, Centre of Materials Research, Faculty of Sciences and Technology,
New University of Lisbon, 2825-114 Caparica, Portugal

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Abstract

The changes occurring during the heating of a borosilicate glass have been investigated by differential thermal analysis, dilatometric analysis and thermomechanical analysis. The thermal properties of this glass, such as glass transition temperature, dilatometric softening temperature and linear thermal expansion coefficient, have been determined. Viscosity measurements in the temperature range 898–1048 K were performed in a thermomechanical analyser equipped with a penetration attachment for isothermal measurement, and from the temperature dependence of viscosity a value of 290 kJ mol^{-1} was obtained for the activation energy for viscous flow. Devitrification of the glass was observed, specifically in finely powdered glass samples, where the precipitation of cristobalite was identified by X-ray diffraction. Glass powder compacts sintered by viscous flow and cristobalite precipitation reduced strongly the shrinkage rate. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Borosilicate glass; Thermal properties; Cristobalite precipitation; Viscous flow

1. Introduction

Borosilicate glasses, resulting from the addition of small amounts of alkali added to silica and boron oxide, make a family of glasses with a large number of applications particularly due to their low thermal expansion coefficient ($\sim(3-6) \times 10^{-6}\ \text{K}^{-1}$) and to a high resistance to chemical attack [1].

Some borosilicate glasses in the powdered form have aroused considerable interest, either for their use in the production of sintered glass with controlled porosity [2,3], or for their application in the manufacture of composite materials [4–10]. These glasses have a low dielectric constant and a thermal expansion coefficient similar to that of silicon [4,5], and therefore, they are the most commonly used glass materials in glass/ceramic composite substrates for microelectronic packaging [4–6]. Additionally, borosilicate glasses have been used as the matrix component in composites with different types of reinforcement in order to improve their mechanical strength and toughness and to make them suitable for different structural applications [8–10].

This study is part of a more general work about the processing, by powder technology route, of borosilicate glass matrix composites reinforced with ceramic particles. The present study is concerned with the thermal characterisation and behaviour of the borosilicate glass only, which was investigated by various experimental methods such as differential thermal analysis (DTA), X-ray diffraction (XRD), dilatometric analysis and thermomechanical analysis (TMA).

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* Corresponding author. Tel.: +351-21-2948562;
fax: +351-21-2957810.
E-mail address: rcm@mail.fct.unl.pt (R. Monteiro).

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2. Experimental

An amorphous borosilicate glass powder (Corning Glass, France, code 658909) was used in this study. The as-received glass powder had a particle size 80–160 μm, and in order to be used in further work, it was reduced by ball milling, using agate ball media, until a finer powder with a mean particle size ∼10 μm was achieved. The chemical composition, analysed by flame atomic absorption and gravimetric techniques, was as follows: 79.8 wt.% SiO_2, 12.3 wt.% B_2O_3, 2.3 wt.% Al_2O_3, 4.8 wt.% Na_2O and 0.8 wt.% K_2O. The theoretical density of the glass used is 2.23×10^3 kg m^{-3}.

The glass transition temperature (T_g) and the devitrification of the glass were investigated by DTA performed on finely powdered glass samples (∼10 μm) using a Rigaku TAS-100 DTA, model 8121BH. About 40 mg of the sample, contained in the platinum DTA sample holder, was scanned in static air from ambient temperature to 1400 K at a heating rate of 10 K min^{-1}, and powdered calcined alumina was used as the inert reference material.

Bulk glass specimens of suitable size have been prepared to investigate the thermal expansion behaviour and the temperature dependence of viscosity. An amount of about 30 g of the glass powder was put into a platinum crucible and then it was melted in an electric furnace at 1723 K for 1 h. After this time, the melt was removed from the furnace and cooled to room temperature inside the crucible. From the glass lumps withdrawn out of the crucible, which were homogeneous and bubble free, samples with the required dimensions were obtained after cutting and polishing.

The linear thermal expansion coefficient (α_l), the glass transition temperature (T_g) and the dilatometric softening temperature (T_d) were determined on bulk glass specimens with approximate dimensions 15 mm × 5 mm × 5 mm. These specimens were heated in air from room temperature to 973 K at a heating rate of 10 K min^{-1} in an Adamel Lhomargy dilatometer, model DI24. The viscosity measurements of the glass in the temperature range 898–1048 K were carried out in suitable cylindrical bulk glass samples, with approximately 5 mm diameter and 3 mm height, using a Rigaku TAS-100 TMA, model 8144B, equipped with a penetration attachment for isothermal measurement.

The sinterability of the borosilicate glass powder was also investigated in the dilatometer mentioned above. For this purpose, cylindrical glass powder compacts with 5 mm diameter and approximately 15 mm height were obtained by isostatic pressing of the powders at 200 MPa. These green compacts, which exhibited 55% of the theoretical density of the glass, were then heated in air at 10 K min^{-1} and the curves reporting the linear shrinkage of the glass powder compacts as a function of temperature were obtained. The density of the sintered pellets was measured by the Archimedes' principle, and the relative density was calculated.

Devitrification was investigated using heat-treated samples either in bulk or powdered state, and the choice of the heat treatment schedules has been based on the DTA results. Some glass samples were heated at 10 K min^{-1} from room temperature up to 1003 or 1123 K, while others were submitted to an intermediate heating stage for 3 h at 823 K, for nucleation, and then they were heated at 10 K min^{-1} up to the selected final temperature. In order to allow sufficient crystal growth, some of the samples were hold at the final temperature for 3 h. After the heating stage, the furnace was switched off and the samples were cooled to room temperature inside the furnace.

XRD analyses were performed in heat-treated samples ground at about 10 μm in an agate mortar. The XRD patterns were recorded on a Rigaku Dmax III-C 3 kW diffractometer, using Cu Kα radiation at 40 kV and 20 mA settings in the 2θ range from 20 to 60° at a scanning speed of 2° min^{-1}. The crystalline phases present in heat-treated glass samples were identified by comparing the peak positions and intensities with those listed in the Joint Committee on Powder Diffraction Standards (JCPDS) files.

3. Results and discussion

Fig. 1 shows the DTA curve of a powder sample of the studied glass recorded at 10 K min^{-1}. A slope change is observed at about 800 K at the beginning of the endothermic peak that can be attributed to the glass transformation range. Therefore, from the DTA results it is considered that 800 K is the glass transformation temperature (T_g) of the used borosilicate glass.

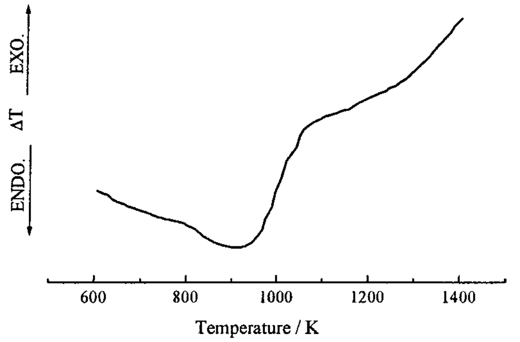

Fig. 1. DTA curve of glass powder recorded at 10 K min^{-1}.

The reported curve does not present a well-defined exothermic peak, but it shows an exothermic bulge centred approximately at 1053 K, which is followed by a successive slope change. This broad exothermic effect is likely associated to the glass crystallisation during the non-isothermal DTA run.

In order to identify clearly the occurrence of glass crystallisation, the DTA results were complemented with XDR analysis performed on various heat-treated samples. The temperatures 1003 and 1123 K, selected for the heat treatment schedules, were, respectively, below and above the peak temperature of the exothermic effect observed in Fig. 1. Some XRD patterns are shown in Fig. 2. Cristobalite [11] was the only crystalline phase identified in the devitrified glass samples. No evidence of cristobalite precipitation was given by the XRD pattern shown in Fig. 2(A), obtained with a powdered glass sample that has been heated at 10 K min^{-1} and stopped just after reaching 1003 K. However, some peaks are already observed in Fig. 2(B), which corresponds to a powdered glass sample that was heated at the same heating rate and hold at 1003 K for 3 h. Comparing the XRD patterns shown in Fig. 2(B) and (C), it is verified that no appreciable change in the cristobalite precipitation occurs when the powdered samples were heated at an intermediate stage for nucleation (at 823 K during 3 h) and then treated under the same final conditions. However, the results revealed a strong effect of the final temperature of heat treatment on the cristobalite precipitation, as observed by comparing the XRD patterns corresponding to glass samples treated at 1003 and 1123 K, Fig. 2(B) and (D), respectively.

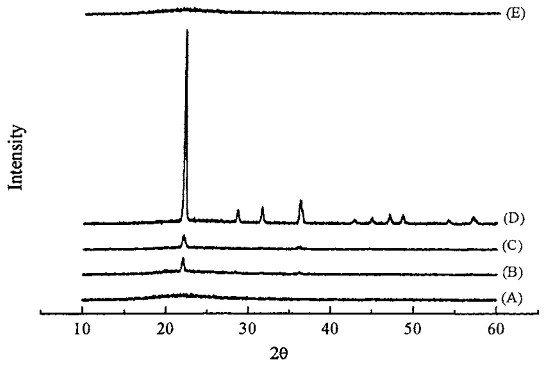

Fig. 2. X-ray diffraction patterns of heat-treated glass: (A) powder sample, 1003 K; (B) powder sample, 1003 K for 3 h; (C) powder sample, 823 K for 3 h and 1003 K for 3 h; (D) powder sample, 1123 K for 3 h; (E) bulk sample, 1123 K for 3 h.

Taking into account the above results, it is considered that the exothermic effect observed in the DTA curve (Fig. 1) is due to crystallisation of the glass, with precipitation of cristobalite during the non-isothermal DTA run. The occurrence of such low and broad DTA exotherm attributable to cristobalite must be due in part to its low enthalpy for crystallisation, quoted in the literature as only -8.2 kJ mol^{-1} [12], and it also implies that cristobalite forms more or less continuously on heating over a very wide temperature range [12].

Glass devitrification is the result of two individual processes: nucleation and crystal growth. Nucleation can occur in the volume or on the surface of the glass sample. The total number of nuclei per unit volume is the sum of surface nuclei, proportional to the specific surface area of the sample, and of the bulk nuclei formed during a heat treatment [13]. The shape of the DTA peak is strongly affected by the crystallisation mechanism. Sharp and broad peaks have been attributed to bulk and surface nucleation, respectively [13], and according to this, the present DTA results suggest that surface crystallisation occurred during the heating of the powdered borosilicate glass.

XRD studies on the devitrification of powdered borosilicate glasses [14,15] have demonstrated that, depending on the duration of the heating stage, cristobalite precipitated at temperatures ranging from 973 to 1273 K [14] and from 1073 to 1373 K [15]. Other studies on the devitrification of an initial amorphous binary glass mixture containing a low-softening borosilicate glass and a high-softening high silica glass indicated that cristobalite precipitated at temperatures ranging from 1073 to 1473 K [16]. In some of those studies it has been found that the precipitation of cristobalite exhibits a characteristic incubation period, which decreases with increasing temperature, from 60–120 min at 973 K to 3–5 min at 1273 K [14]. The XRD results obtained in the present study did not reveal any crystallisation of the glass powders during the non-isothermal treatment up to 1003 K, but they showed the presence of cristobalite after holding this temperature for 3 h.

The devitrification in bulk glass samples was also investigated in the present study. The XRD results demonstrated that the amount of cristobalite formed in the fine glass powder samples was much higher than in bulk glass samples heated under the same experimental conditions. In fact, Fig. 2(E) shows that no cristobalite precipitated on heating a bulk glass sample at 1123 K for 3 h, while the corresponding XRD pattern of a fine powdered sample treated under the same conditions, Fig. 2(D), shows clearly the presence of cristobalite crystals. This indicates that the great increase of specific surface area of a powdered sample allows the surface crystallisation of cristobalite corroborating the suggestion that was given by the appearance of a broad exothermic peak in the DTA curve. In summary, the XRD results obtained in this work show that the devitrification of borosilicate glass can be largely enhanced when powdered glass samples with high surface area are used, where the growth of surface nucleated cristobalite occurs at comparatively lower temperatures than in bulk glass samples.

Fig. 3 shows the linear thermal expansion curve of a bulk glass sample that has been heated at 10 K min^{-1}. The slope changes slightly at 810 K, which corresponds to the glass transformation temperature of the glass (T_g). The difference found between the T_g values determined by the DTA and the dilatometric curves, 800 and 810 K, respectively, both obtained at the same heating rate, may be explained by the fact that this temperature is somewhat dependent upon the property measured and on the sample size used in each measurement method [17].

The reported thermal expansion curve shows that the dilatometric softening temperature of the glass (T_d) was at 900 K. The linear thermal expansion coefficient of the glass (α_l) was calculated from that curve, and in the temperature range between room temperature and 573 K it measured 3.3×10^{-6} K^{-1}, which is in good agreement with the low thermal expansion coefficient values that have been indicated in the literature for this type of glasses [1,4].

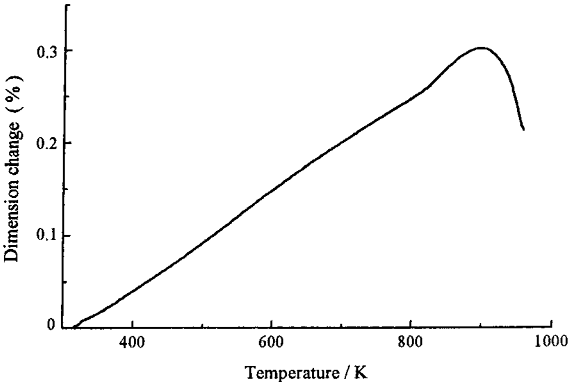

Fig. 3. Linear thermal expansion curve of a bulk glass sample obtained at 10 K min^{-1}.

Knowledge of the viscosity of the glass at the sintering temperature and at the temperature at which the glass crystallises is important for analysis of its behaviour. The viscosity (η) of the borosilicate glass in the temperature region between 898 and 1048 K was measured by TMA equipped with a penetration attachment for isothermal measurement, and it took values that ranged from $10^{9.7}$ to $10^{7.3}$ Pa s. Taking into account the obtained experimental viscosity data, the Arrhenius representation log η versus $1/T$ was made (Fig. 4) and the activation energy for the viscous flow was calculated, giving a value of 290 kJ mol^{-1}.

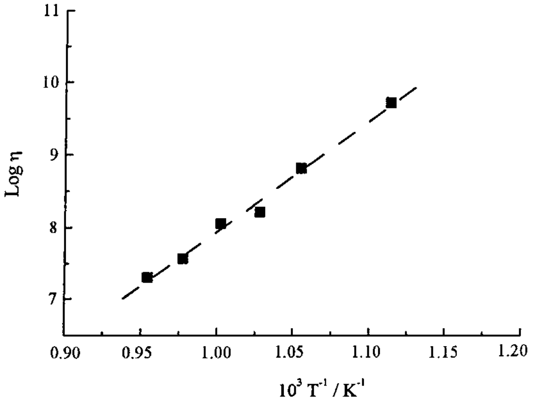

Fig. 4. Viscosity behaviour of the borosilicate glass.

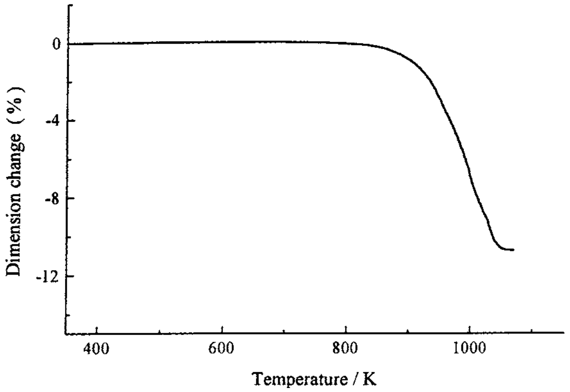

Fig. 5. Linear shrinkage curve of a glass powder compact obtained at 10 K min^{-1}.

This value is within the range between 250 [16] and 303.8 kJ mol^{-1} [8], which were given in the literature as the activation energy for viscous flow of Pyrex glasses that have a similar chemical composition to that of the borosilicate glass investigated in the present study.

The effect of crystallisation on the sintering behaviour of the borosilicate glass powders was investigated by dilatometry. The linear shrinkage curve of a glass powder compact that has been heated at a constant heating rate of 10 K min^{-1} from room temperature up to 1073 K is shown in Fig. 5. A total linear shrinkage of 11% was observed, and the sintered compact achieved 93% of theoretical density. According to the results presented in Fig. 5, the glass powder compact began to shrink at a temperature about 850 K, then the glass powder compact shrank continuously up to about 1050 K, and above this temperature the shrinkage rate was drastically decreased.

Taking into account this shrinkage behaviour, it is considered that the softening of the glass chiefly influences the sinterability of the glass powder. Indeed, the glass has a finite viscosity above the glass transition temperature and is then capable of viscous flow. The results obtained in studies on the sintering of different type of glasses, performed through dilatometric measurements and by the application of low uniaxial stresses [18,19], demonstrated the occurrence of viscous sintering, and densification was attributed to viscous flow during the sintering of the glass. Under the non-isothermal heating conditions used in the present study, the shrinkage of the glass powder compact occurs mainly up to about 1050 K, before the crystallisation of the glass, and pore removal with consequent densification of the compact is by viscous flow. When the glass powder is heated above 1050 K, the single-phase glass is no longer stable, and two competitive processes will occur simultaneously, namely viscous flow and growth of surface nucleated cristobalite. Therefore, at high temperature, cristobalite precipitation makes the compact more difficult to densify, and the shrinkage rate is largely reduced.

4. Conclusions

Basic thermal properties such as the glass transition temperature, the dilatometric softening temperature and the linear thermal expansion coefficient of a borosilicate glass have been determined by DTA or dilatometric analysis. The temperature–viscosity dependence was studied by TMA with a penetration attachment for isothermal measurement, and the activation energy for viscous flow in the glass transformation range was evaluated.

Cristobalite precipitation occurred when the glass was heated over a wide temperature range, particularly if fine powdered samples were used. The sintering behaviour of the glass powder, investigated by dilatometry, indicated that densification of powder compacts was by viscous flow and that the shrinkage rate is strongly reduced after cristobalite precipitation.

Acknowledgements

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References

[1] A.K. Varshneya, Fundamentals of Inorganic Glasses, Academic Press, New York, 1994, p. 4.

[2] J.C. Knight, T.F. Page, Br. Ceram. Trans. J. 86 (1987) 154.

[3] K. Nakashima, K. Noda, K. Mori, J. Am. Ceram. Soc. 80 (1997) 1101.

[4] J.-H. Park, S.-J. Lee, J. Am. Ceram. Soc. 78 (1995) 1128.

[5] R.R. Tummala, J. Am. Ceram. Soc. 74 (1991) 895.

[6] K. Kata, Y. Shimada, H. Takamizawa, IEEE Trans. Comp. Hybrids Manufac. Tech. 13 (1990) 448.

[7] M.M. Lima, R. Monteiro, Ceramics-processing: reliability, tribology and wear, in: G. Muller (Ed.), Euromat, Vol. 12, Wiley/VCH, Weinheim, 2000, p. 178.

[8] M.J. Pascual, L. Pascual, A. Durán, in: A. Helebrant, M. Maryska, S. Kasa (Eds.), Proceedings of the 5th European Society of Glass Science and Technology Conference, Prague, Czech Republic, 1999, p. C2-63 (CD-ROM).

[9] A.R. Boccacini, P.A. Trusty, J. Mater. Sci. Lett. 15 (1996) 60.

[10] I. Dlouhy, A.R. Boccacini, Composites Sci. Technol. 56 (1996) 1415.

[11] Powder Diffraction File, card no. 39-1425, 1996 Joint Committee on Powder Diffraction Standards, International Centre for Diffraction Data, Swarthmore, PA, USA.

[12] W.F. Hammetter, R.E. Loehman, J. Am. Ceram. Soc. 70 (1987) 577.

[13] A. Marotta, A. Buri, Thermochim. Acta 40 (1980) 397.

[14] J.-H. Jean, T.K. Gupta, J. Am. Ceram. Soc. 76 (1993) 2010.

[15] Y. Imanaka, S. Aoki, N. Kamehara, K. Niwa, J. Am. Ceram. Soc. 78 (1995) 1265.

[16] J.-H. Jean, T.K. Gupta, J. Mater. Res. 7 (1992) 3103.

[17] J.E. Shelby, Introduction to Glass Science and Technology, The Royal Society of Chemistry, 1997, p. 110.

[18] M.N. Rahaman, L.C. De Jonghe, J. Am. Ceram. Soc. 73 (1990) 707.

[19] M.N. Rahaman, L.C. De Jonghe, G.W. Scherer, R.J. Brook, J. Am. Ceram. Soc. 70 (1987) 766.