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Bulk Nucleation and Crystal Growth in Calcium Tetra and Digermanate Glasses

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Abstract

Calcium tetragermanate and calcium digermanate glasses were prepared and studied with the aid of differential thermal analysis, X-ray diffraction and FTIR spectroscopy. The molar ratio of GeO_6/GeO_4 groups increases with the CaO/GeO_2 molar ratio. A two steps crystallisation process was found: initially microcrystals are formed that at higher temperatures are transformed in well shaped crystals. An unidentified phase crystallises in both glasses. $CaGe_2O_5$ crystals also grow in calcium digermanate glass. The influence of the specific surface area of the glass sample and of a heat treatment of nucleation was pointed out. The activation energy for crystal growth in each glass was evaluated by a non isothermal method. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

Although glass formation has been reported in a number of $MO–GeO_2$ systems,[1] very little is known about their devitrification behaviour.

This work is part of a research program in which the devitrification behaviour of $MO–GeO_2$ glasses is investigated with the aid of differential thermal analysis, X-ray diffraction and FTIR spectroscopy.

In previous papers the non isothermal devitrification of barium tetragermanate[2] and lead tetragermanate[3] glasses has been investigated. $BaGe_4O_9$ and $PbGe_4O_9$ crystals have similar structures formed by Ge_3O_9 rings, consisting of three GeO_4 tetrahedra, linked by GeO_6 octahedra giving a three-dimensional network. These structures can be characterised by the formulas $Ba[Ge(GeO_3)_3]$, and $Pb[Ge(GeO_3)_3]$. In spite of these similar struc-

tures two different devitrification mechanisms were found. In barium tetragermanate glass $BaGe_4O_9$ crystals are formed in the bulk without the addition of any nucleating agent.[2] Lead tetragermanate glass devitrifies from the surface forming monoclinic and hexagonal $PbGe_4O_9$ crystals.[3]

In this paper the devitrification behaviour of calcium tetragermanate and calcium digermanate glasses has been investigated.

2 Experimental procedure

Samples of $CaO\cdot2GeO_2$ and $CaO\cdot4GeO_2$ glasses were prepared by mixing appropriate quantities of ultra pure calcium carbonate (Aldrich), and germanium oxide (Heraeus) in batches of a size suitable to yield 2 g of glasses. The glasses were melted in an uncovered Pt crucible in an electric oven at 1450°C. The crucible containing the glasses weighed both before and after the glasses were removed. The weight of the glasses agreed with that anticipated from the batch calculation. This result indicates that the actual glasses composition is close to that based on the glasses batch. The melt were quenched by plunging the bottom of the crucible into cold water. Although this resulted in fracture of the glasses, for both the compositions pieces of transparent glass of size sufficient for the experimental measurements were obtained by this technique.

Differential thermal analysis (DTA) curves were recorded in air at different heating rates (5–20°C min^{-1}) on bulk specimens and powdered ($<45\,\mu$m) of about 60 mg from room temperature to 1200°C. Powdered Al_2O_3 was added to improve heat transfer between bulk sample and sample holder. A Netzsch thermoanalyser high temperature DSC 404 was used with Al_2O_3 as reference material. The experimental error in the DTA temperature is ±1°C. The DTA curves were elaborated by Netzsch software.

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FT-IR transmittance spectra were measured in the 400–1200 cm^{-1} region using a Mattson 5020 system, equipped with a DTGS KBr (deuterated triglycine sulphate with potassium bromide windows) detector, with a resolution of 2 cm^{-1} (20 scans). KBr pelletized disks containing 2·0 mg of the sample and 100 mg KBr were made. The FT-IR spectra were elaborated by Mattson software (FIRST Macros).

To investigate the amorphous nature of the as-quenched glasses and to identify the crystalline phases grown during the DTA runs, the thermally processed sample were finely ground and analysed in a computer-assisted X-ray (Cu K$_\alpha$ powder diffractometer using a Philips model PW 1710 diffractometer, with a scan speed of 1° min^{-1}. To identify the crystallising phases the X-ray diffraction patterns were matched to JCPDS data.

3 Results and discussion

The FT-IR transmittance spectra of vitreous GeO$_2$ and the investigated glasses are shown in Fig. 1. These spectra exhibit broad bands as expected for glassy system.
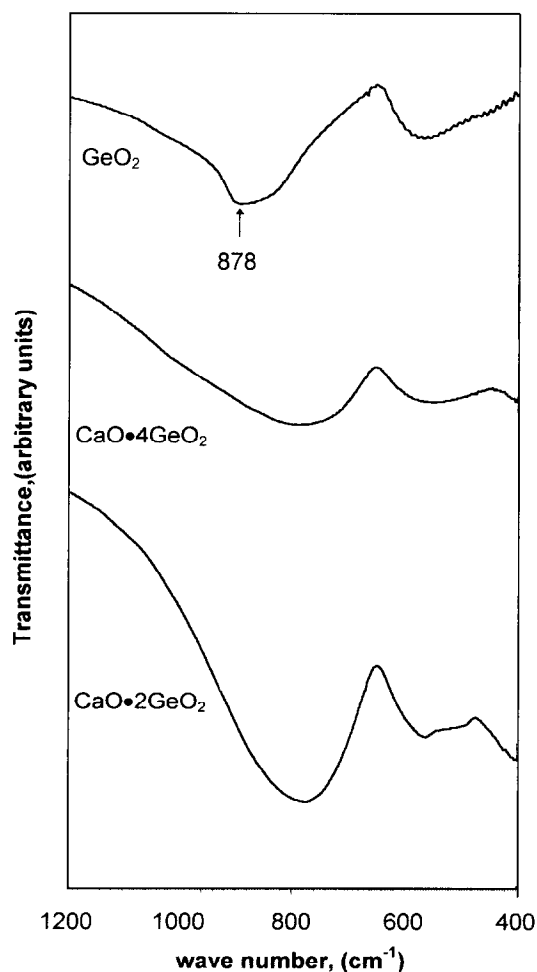
The highest frequency band at 878 cm^{-1} of the GeO$_2$ glass, due to the Ge–O–Ge bond stretching, shows that the co-ordination of Ge in vitreous GeO$_2$ closely resembles that of Ge in hexagonal GeO$_2$, in which Ge is tetrahedrally co-ordinated by oxygen.[4] In the transmittance spectra of the investigated glasses the highest absorption band shifts to a lower frequency. The higher the calcium oxide concentration the greater is the shift.

This shift can be related as in alkali germanate glasses[5] to the change in the co-ordinating number of Ge from 4 to 6. This interpretation is according to the general notion that an increase in the co-ordination number from XO$_4$ to XO$_6$ causes a decrease in X–O–X stretching frequency. It is of interest to remark that in alkali germanate glasses the maximum of the shift was observed at about 20 mol% of M$_2$O[6] whereas the glass containing 33 mol% of CaO exhibit a shift greater then that of the glass containing 20 mol% of CaO. However in CaO·2GeO$_2$ glass the molar ratio of GeO$_6$/GeO$_4$ groups is greater then in CaO·4GeO$_2$ glass.

Figure 2 shows the DTA curves recorded on bulk samples of the as-quenched investigated glasses. Both curves exhibit a slope change followed by two exothermic peaks.
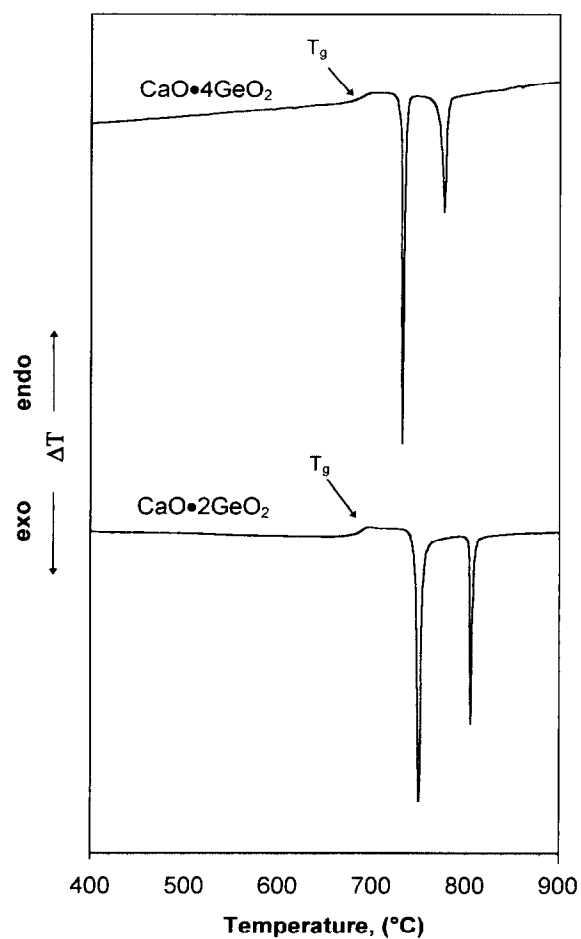

Fig. 1. FT-IR transmittance spectra.
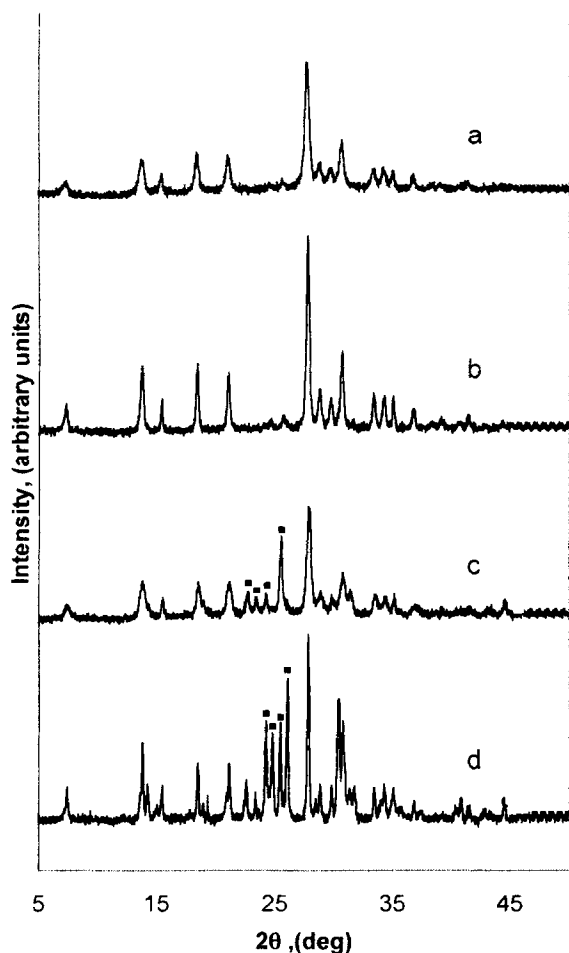

Fig. 2. DTA curves recorded at 10°C min^{-1} on bulk samples.

Fig. 3. XRD patterns of $CaO \cdot 4GeO_2$ glass samples heated up to (a) the first and (b) the second DTA peaks. $CaO \cdot 2GeO_2$ glass samples heated up to (c) the first and (d) the second DTA peaks.

The slope change may be attributed to the glass transition, while the exothermic effects can be related to crystallisation processes. When the glass is heated, its heat capacity, together with other properties, changes abruptly in a narrow temperature range, called the glass transition; this is the transformation temperature range at which the glass network acquires mobility, changing from a rigid to a viscous structure. In this work, the inflection point at the slope-change temperature of the DTA curves were taken as the glass transition temperature, T_g, indicated by an arrow in Fig. 2. The values of $T_g = 688$ and $693°C$ for $CaO \cdot 4GeO_2$ and $CaO \cdot 2GeO_2$ glass, respectively, are very close to those reported by Shelby.[7]

The presence of two exothermic peaks during the crystallisation of these glasses suggests the formation of more than one crystalline phase during the devitrification process or a two steps crystallisation mechanism.

To elucidate this point X-ray diffraction measurements were carried out on samples of both the glasses heated in the DTA furnace up to the temperature of the first and the second DTA exothermic peak.

The XRD pattern of tetragermanate glass heated to the temperature of the first DTA exo-peak shows several reflections (trace a of Fig. 3) that could not be attributed to any known crystalline phase. The XRD pattern of the same glass heated to the temperature of the DTA second exo-peak shows the same reflections (trace b of Fig. 3) but the XRD peaks are higher and sharper. The reflections of the same unknown phase were detected on the XRD pattern of digermanate glass heated to the temperature of the first DTA exo-peak (trace c of Fig. 3). In addition to these reflections the main reflections of $CaGe_2O_5$ crystals were also found. At the temperature of the second DTA exo-peak the XRD peaks become higher and sharper (trace d of Fig. 3). The d-spacing and their relative intensities of the unidentified phase are reported in Table 1.

These results suggest that in both the investigated glasses a devitrification process in two steps, microcrystals are initially formed and are then converted at higher temperatures into well shaped crystals. This hypothesis was confirmed by recording DTA curves at different heating rates. As can be observed in Fig. 4 the higher the heating rate the smaller becomes the second exo-peak. Taking into
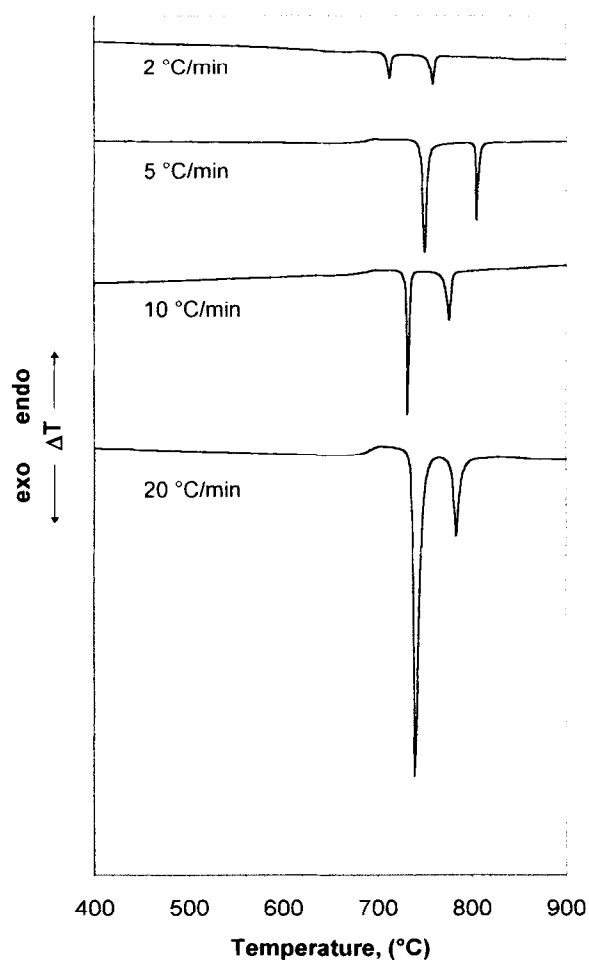

Fig. 4. DTA curves of $CaO \cdot 4GeO_2$ glass samples recorded at difference heating rates.

Table 1. d-spacing of the unknown phase and their relative intensities

5.10_{35}	2.76_{20}	2.32_{15}
4.65_{15}	2.68_{15}	1.77_{15}
4.03_{35}	2.61_{40}	1.75_{25}
3.62_{25}	2.42_{15}	1.68_{15}
2.84_{100}	2.36_{15}	

account that the higher the DTA heating rate the higher is the temperature of the first crystallisation peak the size of the microcrystals formed in this step should be also increase with a consequent decrease of the recrystallisation amount.

The non-isothermal devitrification of glass is the result of two individual processes: nucleation and crystal growth. Nucleation in glass-forming systems can occur either in the volume or on the surface of the sample. In practice, surface nucleation occurs more easily than internal crystal nucleation and it is observed in most compositions. To achieve internal crystal nucleation it is often necessary to add nucleating agents. However, certain systems nucleate internally without such additions. The number of nuclei, N, per unit volume is
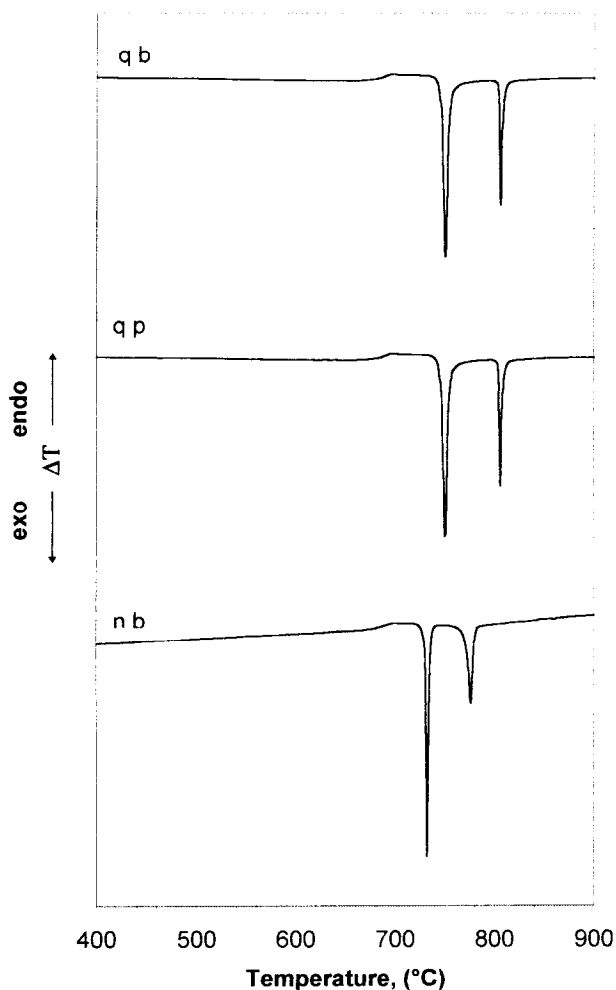
Fig. 6. Ozawa plots of CaO·4GeO2 (◆) and (■) CaO·2GeO₂ glasses.

the sum of surface nuclei proportional to the specific surface area of the sample and bulk nuclei formed during the heat treatments of the samples. The higher the value of N, the lower the temperature, T_p, of the DTA crystallisation peak.[8] The shape of the crystallisation peaks are strongly affected by the crystallisation mechanism[9] to surface and bulk crystallisation correspond broad and sharp peaks, respectively.

The shape of the first exothermic peak shown in Fig. 2 suggests a dominant bulk crystallisation in both the investigated glasses. To confirm this conclusion DTA curves on very fine powdered samples and on previously nucleated bulk samples of tetragermanateglass were recorded Fig. 5 No appreciable difference in the temperature or in the shape of the peaks were found. On the other hand a DTA curve carried out on a bulk glass sample previously held 4 h at T_g, a temperature where the bulk nucleation rates are usually high, shows a shift toward a lower temperature of the first crystallisation peak. These results confirm an internal bulk nucleation in this glass. A similar behaviour were also observed for the digermanate glass.

Fig. 5. DTA curves recorded on as-quenched bulk (qb) and powdered (qp) samples and on nucleated bulk (nb) sample of CaO·4GeO₂ glass.

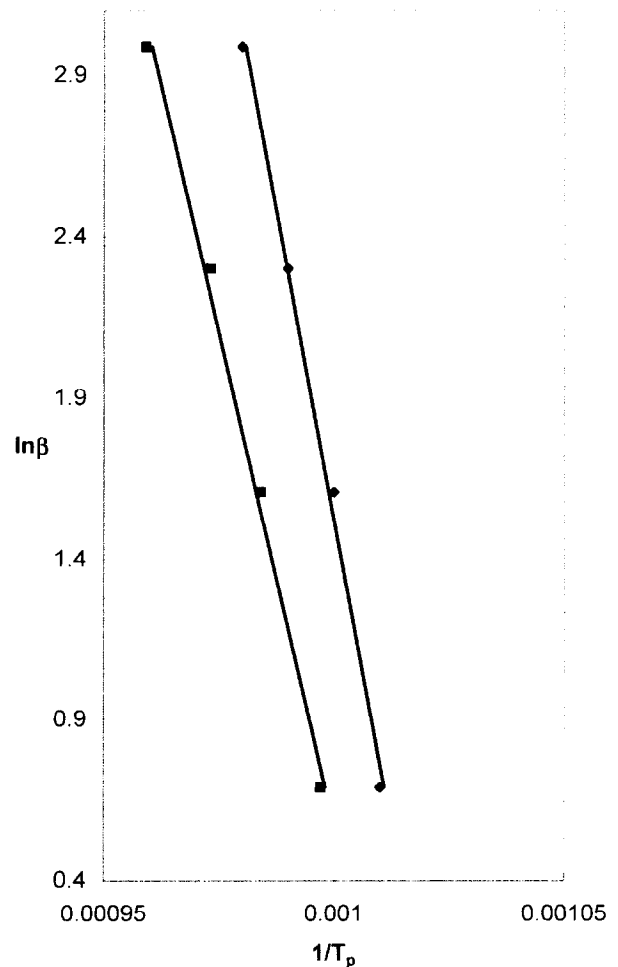The activation energy E for crystal growth was evaluated from the DTA curves using the equation:[10]

$$\ln \beta = -(E/R)(1/T_p) + \text{const}$$

This equation is based on the temperature shift of the DTA peak T_p as the DTA heating rate β is changed. Multiple DTA runs were recorded in air at different heating rates on bulk samples of the two studied glasses. Plots of $\ln \beta$ against $1/T_p$ (Fig. 6) give straight lines in both cases. From their slopes values of $E = 686$ and $673\,\text{kJ mol}^{-1}$ were calculated for $CaO \cdot 4GeO_2$ and $CaO \cdot 2GeO_2$ glass, respectively. As the difference between the two values is less than the experimental error the crystals of the unidentified phase grow in both the studied glasses with the same activation energy.

4 Conclusions

From the experimental results the following conclusions can be drawn. The structure of digermanate glass contains a GeO_6/GeO_4 molar ratio greater than that of tetragermanate glass. Both the studied glasses exhibit: (a) near the same glass transition temperature (b) internal crystal nucleation without the addition of any nucleating agent, and (c) a crystallisation process in two steps. Microcrystals are initially formed in the glassy matrix that are then converted at higher temperatures into well shaped crystals.

The main crystallising phase was found to be the same in the two glasses. This phase was not identified among those reported in the literature therefore further investigations are required to its composition and structure. In digermanate glass $CaGe_2O_5$ crystals are also formed.

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