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THE NON-ISOTHERMAL DEVITRIFICATION OF POTASSIUM GERMANATE GLASSES

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Abstract

The devitrification behaviour of the glasses $K_2O{\cdot}xGeO_2$ with x=4, 7 or 8 was examined by means of differential thermal analysis (DTA), the Fourier transformation infrared (FTIR) transmittance spectra and X-ray diffraction (XRD). The glass transition temperatures were related to the molar ratio GeO_4/GeO_6. For the glass with x=4, metastable $K_4Ge_9O_{20}$ crystals are initially formed and then converted at higher temperatures into stable $K_2Ge_4O_9$ crystals. The glasses with x=7 or 8 both devitrify into $K_2Ge_7O_{15}$ crystals. The effects of the specific surface area of the samples on the devitrification mechanisms were established. Bulk nucleation predominates in the glass with x=4, while the glasses with x=7 or 8 crystallize from the surface. The activation energies for crystal growth were evaluated from the DTA curves.

Keywords: devitrification, glasses, glass transition, potassium germanate

Introduction

Kinetic investigations of the crystallization of glasses are of interest with a view to elucidating the nature of crystal growth and for research into glass-ceramic materials. The present study forms part of a research programme in which the devitrification behaviour of alkali germanate glasses is investigated with the aid of DTA, FTIR spectroscopy and XRD.

Nucleation in glass-forming systems can occur either in the volume or on the surface of the sample. In practice, surface crystal nucleation occurs more easily than internal crystal nucleation and is observed in most compositions. To achieve internal crystal nucleation, it is often necessary to add nucleating agenst. However, certain glass systems nucleate internally without such additions. Surface nucleation is observed to occur without exception on any GeO_2 glass specimen which has been cooled to room temperature for any length of time and then heated to a temperature in the crystallization range [1]. On the other hand, lithium germanate glasses exhibit internal nucleation [2–5]. In the present study, the non-isothermal devitrification of potassium germanate glasses was investigated in order to evaluate the influence of the K_2O content and of the specific surface of the samples on the crystallization mechanism and the activation energy for crystal growth.

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Experimental

The glasses with the compositions $K_2O{\cdot}xGeO_2$ with x=4, 7 or 8 were prepared by mixing appropriate quantities of ultrapure potassium carbonate (Aldrich), and germanium oxide (Heraeus) in batches of size suitable to yield 3 g of glass. In the paper, the glasses are indicated by the corresponding value of x. The glasses were melted in an uncovered Pt crucible in an electric oven. The crucible containing the glass was weighed both before and after the glass was removed. The mass of the glass agreed with that anticipated from the batch calculation. This result indicates that the actual glass composition is close to that based on the glass batch. The melts were quenched by plunging the bottom of the crucible into cold water. Although this resulted in fracture of the glass, for all the compositions pieces of transparent glass of a size sufficient for the experimental measurements were obtained by this technique.

DTA curves were recorded in air at different heating rates (5–20°C min^{-1}) on bulk or finely-powdered (<45 micron) specimens (about 50 mg) form room temperature up to 900°C. Powdered Al_2O_3 was added to improve the heat transfer between the bulk samples and the sample holder. A Netzsch High-Temperature DSC 404 thermoanalyser was used, with Al_2O_3 as reference material. The experimental error in the DTA temperature was ±1°C. The DTA curves were elaborated with Netzsch software.

FTIR absorption spectra were recorded in the range 4000–400 cm^{-1}, using a Mattson 5020 system, equipped with a DTGS KBr (deuterated triglycine sulfate with potassium bromide windows) detector. A spectral resolution of 2 cm^{-1} was chosen. Each test sample was mixed with KBr (1 wt% of glass) in an agate mortar, and then pressed into 200 mg pellets 13 mm in diameter. The spectrum for each sample represents an average of 20 scans, which were normalized to the spectrum of the blank KBr pellet. The FTIR spectra were analysed by Mattson software (FIRST Macros).

The amorphous nature of the as-quenched glass and the nature of the crystallizing phases during the DTA run were ascertained by X-ray diffraction, using a Philips diffractometer. Powders of each sample were scanned in the interval 2Θ=5–60°, using CuK_α radiation. The samples for XRD measurements were heat-treated in a DTA furnace by quenching them directly after a DTA peak had occurred.

Results and discussion

The FTIR spectra of the three studied glasses and of GeO_2 glass are shown in Fig. 1. The highest-frequency band, at 880 cm^{-1}, due to the Ge–O–Ge bonding in GeO_2 glass is shifted to lower frequency for the investigated glasses. This shift can be related [6] to a change in the coordination number of Ge from 4 to 6. The charge of –2 on the GeO_6 octahedra is balanced by the localization of two K^+

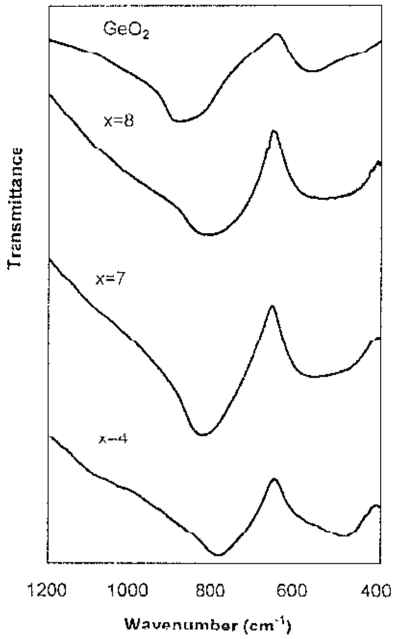

Fig. 1 FTIR transmittance spectra of the studied glasses

ions. The higher the K_2O content, the greater the shift and the molar ratio GeO_6/GeO_4.

Figure 2 shows the DTA curves of the as-quenched bulk glasses. A slope change occurs, followed by one or two exothermic peaks. The slope change may be attributed to the glass transition, while the exothermic effects may be related to the heat evolved during the crystallization processes.

When a 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 in which the glass network acquires mobility, changing from a rigid to a plastic structure. In this work, the temperature of the point of inflection at the change in slope of the DTA curve was taken as the glass transition temperature T_g and is reported in Table 1. In accordance with the increase in the molar ratio GeO_6/GeO_4 indicated by the infrared data, the value of T_g increases with the K_2O content.

The presence of two exothermic peaks during the crystallization of the glass with $x=4$ suggests a two-step crystallization mechanism. Figure 3 shows the XRD patterns of glass with $x=4$ heated in the DTA furnace up to the temperature of the first (trace *a*) or the second (trace *b*) exothermic peak. The diffractogram (*a*) exhibits several sharp lines. The major crystalline phase was found to correspond to $K_4Ge_9O_{20}$. In addition to the peaks due to $K_4Ge_9O_{20}$, three very small

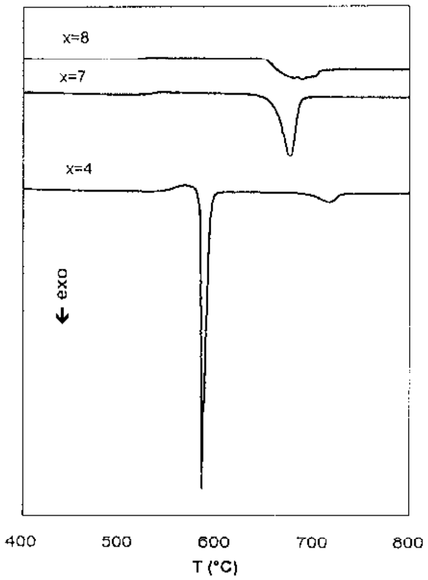

Fig. 2 DTA curves of bulk glasses recorded at a heating rate of 10°C min^{-1}

peaks (indicated in the Figure) corresponding to the strongest reflections of $K_2Ge_4O_9$ were also detected in this pattern. The structure of $K_4Ge_9O_{20}$ contains chains of GeO_4 tetrahedra connected by Ge_4O_{16} groups, which consist of edge-shared GeO_6 octahedra [7]. The structure of $K_2Ge_4O_9$ contains isolated GeO_6 octahedra connected by Ge_3O_9 rings consisting of three GeO_4 tetrahedra to form a three-dimensional network [7]. No reflections of $K_4Ge_9O_{20}$ were found in diffractogram *b*; all peaks were assigned to $K_2Ge_4O_9$. This result indicates a two-step devitrification mechanism. In the primary transformation, metasable $K_4Ge_9O_{20}$ crystals are formed; these are then converted at higher temperatures into thermodynamically stable $K_2Ge_4O_9$ crystals. If more than one crystal is precipitated from a glass, the structure of the metastable phase can be presumed to be more like the mother glass than the stable one. The coalescence of GeO_6 octahedra to Ge_4O_{16} groups by sharing edges has to be already present in the investigated glass.

Table 1 Glass transition temperatures T_g (°C) and activation energies for crystal growth E (kJ mol^{-1})

Glasses	T_g	E 1st exo	E 2nd exo
x=4	556	558	207
x=7	520	268	
x=8	518	258	

In the glass with x=7, the major crystalline phase was found to correspond to $K_2Ge_7O_{15}$. In addition to the peaks due to $K_2Ge_7O_{15}$, the three strongest reflections of $K_2Ge_4O_9$ were also found in this pattern (trace *c* in Fig. 3). The growth of a small amount of $K_2Ge_4O_9$ crystals is due to their simpler (and therefore kinetically favoured) structure than that of $K_2Ge_7O_{15}$ crystals [7]. In the glass with x=8, all the reflections were assigned to $K_2Ge_7O_{15}$ crystals (trace *d* in Fig. 3). The lower K_2O content makes the growth of $K_2Ge_4O_9$ crystals in this glass more difficult.

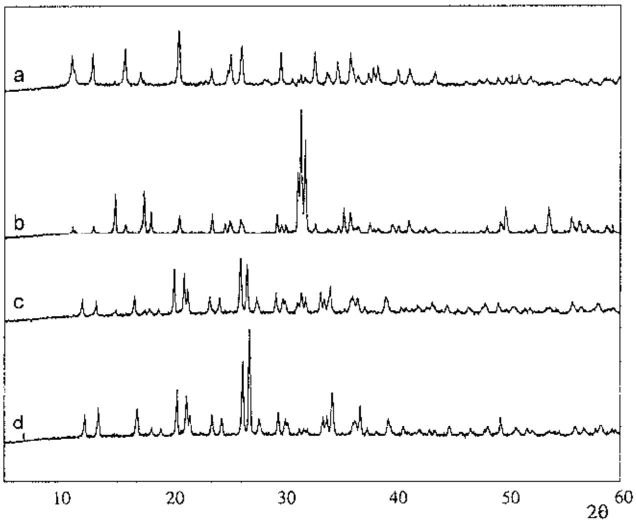

Fig. 3 XRD patterns of bulk glasses with x=4 (a), x=7 (c) and x=8 (d) heated up to the temperature of the first exothermic DTA peak, and the bulk glass with x=4 (b) heated up to the temperature of the second exothermic DTA peak

There are two types of crystallization which take place in a glass, based on surface and bulk nucleation. The number of nuclei, N, is the sum of the surface nuclei (proportional to the specific surface area of the sample) and the bulk nuclei formed during heat treatment of the sample. The higher the value of N, the lower the temperature, T_p, of the DTA crystallization peak [8].

To evaluate the influence of the specific surface area of a sample on the devitrification mechanism, DTA curves of very finely-powdered samples were recorded. In the glass with x=4, no appreciable difference in the temperature or in the shape of the peak was found. This result suggests a predominant bulk nucleation in this glass. In the glass with x=7, the DTA curve of the powdered sample (Fig. 4) shows two partially overlapping exothermic peaks at 602 and 632°C. This result suggests different crystallization mechanisms in bulk and powdered samples. To clarify this point, XRD measurements were carried out on powdered samples heated in the DTA furnace to 600 and 700°C and then quenched at room

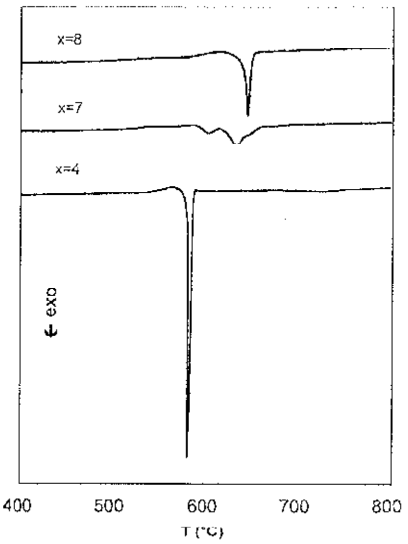

Fig. 4 DTA curves of powdered glasses recorded at a heating rate of 10°C min^{-1}

temperature. The XRD pattern of the powdered sample heated up to 600°C (trace *a* in Fig. 5) exhibits a few sharp peaks that cannot be attributed to any known crystalline phase. The interplanar spacing and the relative intensities corresponding to the three strongest lines of this pattern are d=5.522$_{(100)}$; 3.376$_{(100)}$; 2.897$_{(90)}$. The XRD pattern of the powdered sample heated up to 700°C shows the same peaks as those in the XRD pattern of the bulk sample reported in Fig. 3. All attempts to apply different heat treatment to achieve the growth of the unknown crystalline phase in bulk samples with low specific surface failed. As the number of surface nuclei is proportional to the specific surface area of a sample, the growth of the unknown crystalline phase is probably catalysed by the great increases in the number of surface nuclei in very finely-powdered samples owing to their high specific surface. These results indicate that in bulk and powdered samples two different crystallization mechanisms occur. Bulk samples devitrify directly into $K_2Ge_7O_{15}$ crystals. In very finely-powdered samples, crystals of an unknown metastable phase are initially formed on the surface and are then converted at higher temperatures into the thermodynamically stable $K_2Ge_7O_{15}$ crystals. The crystallization peak in the DTA curve of a powdered sample of glass with x=8 is shifted to a lower temperature than that in the DTA curve of the bulk sample. This shift can be related (as in the glass with x=7) to the increase in the number of surface nuclei due to the increase in specific surface area of the sample, and indicates that in these two glasses surface nucleation predominates. The crystallizing phase (trace *b* in Fig. 5) is as in the bulk sample $K_2Ge_7O_{15}$.

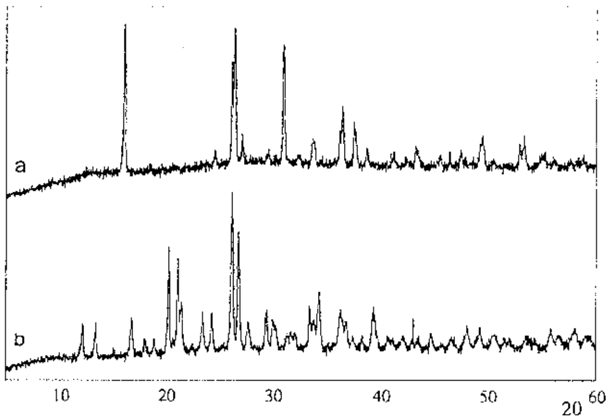

Fig. 5 XRD patterns of the bulk glasses with $x=7$ (a) and $x=8$ (b) heated up to the temperature of the first exothermic DTA peak

The activation energies, E, of crystal growth in bulk samples of the investigated glasses were evaluated from a set of DTA curves recorded at different heating rates, β, via the equation [9]

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

This equation is based on the assumption that the degree of crystallization at the temperature T_p of the DTA crystallization peak has the same specific value, independently of the DTA heating rate [9]. The values of E calculated from the slopes of the straight lines obtained by plotting $\ln\beta$ *vs.* $1/T_p$ are reported in Table 1. In the glass with $x=4$, the activation energy for the second step is much lower than that for the first step. This result and the small size of the second exothermic peak are consistent with the proposed crystallization mechanism. The second step actually involves only a recrystallization process. $K_2Ge_7O_{15}$ crystals grow in the glasses with $x=7$ and 8 with the same value of activation energy.

Conclusions

The experimental results permit the following conclusions:

a) The glass $K_2O\cdot 4GeO_2$ exhibits internal crystal nucleation and devitrifies in two steps. Metastable $K_4Ge_9O_{20}$ crystals are initially formed and then converted at higher temperatures into stable $K_2Ge_4O_9$ crystals.

b) The glasses $K_2O\cdot 7GeO_2$ and $K_2O\cdot 8GeO_2$ devitrify from the surface into $K_2Ge_7O_{15}$ crystals. In finely-powdered samples of the glass $K_2O\cdot 7GeO_2$, a metastable unidentified crystalline phase is initially formed.

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