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Glass Transition Temperature and Crystallisation of Glasses in the $Li_2O{\bullet}4GeO_2$–$K_2O{\bullet}4GeO_2$ Composition Range

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Abstract

The effect of replacing Li_2O by K_2O on the glass transition temperature and on devitrification behaviour in a series of glasses in the lithium tetragermanate–potassium tetragermanate composition range has been studied by differential thermal analysis, X-ray diffraction and Fourier-transform infrared spectra. All glasses studied exhibit internal crystal nucleation. The progressive replacing of Li_2O by K_2O causes the value of the glass transition temperature to go through a minimum at molar ratio $Li_2O/K_2O = 1$. The crystallising phases have been identified and related to the devitrification mechanism. The effect of the specific surface of the glass samples on devitrification processes has also been pointed out. © 1998 Published by Elsevier Science Limited.

1 Introduction

Investigations on glass devitrification are of interest for elucidating the nature of crystallising phases and for research on glass-ceramic materials.

In previous papers[1–3] the non-isothermal devitrification of lithium tetragermanate, sodium tetragermanate and potassium tetragermanate glasses has been investigated. $Li_2Ge_4O_9$, $Na_2Ge_4O_9$, and $K_2Ge_4O_9$ crystals have similar structures[4] 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 formula $M_2[Ge(GeO_3)_3]$. In spite of these similar structures three different devitrification mechanisms were found. All the three glasses devitrify in two steps. In the primary transformation $Li_2Ge_4O_9$ micro crystallites $Na_2Ge_4O_9$ crystals and $K_4Ge_9O_{20}$ crystals are formed and are then converted at higher temperatures into well shaped $Li_2Ge_4O_9$ crystals,[1] $Na_4Ge_9O_{20}$ crystals[2] and $K_2Ge_4O_9$ crystals[3], respectively. It is therefore of interest to study the effect on the glass transition temperature and devitrification behaviour of the progressive substitution of an alkali ion by another one in tetragermanate glasses. The substitution of Na_2O for Li_2O and K_2O for Na_2O causes in both cases the value of the glass transition temperature to go through a minimum at molar ratio $M_2O/M'_2O = 1$ according with the 'mixed alkali effect'.[5,6] In sodium–lithium tetragermanate glasses a ternary compound $LiNaGe_4O_9$ was found among the crystallising phases.[5] In sodium-potassium tetragermanate glasses solid solutions between $Na_4Ge_9O_{20}$ and $K_4Ge_9O_{20}$ crystallise.[6]

In the present work the effect of a progressive replacement of Li_2O by K_2O, on the structure, the glass transition temperature and the devitrification behaviour of tetragermanate glasses have been studied by Fourier-transform infrared spectroscopy (FTIR), Differential Thermal Analysis (DTA) and X-ray diffraction (XRD).

2 Experimental

The glass compositions are expressed by the general formula $(1-x)Li_2O\ xK_2O\ 4GeO_2$ with $x = 0{\cdot}00$; 0·15; 0·25; 0·35; 0·50; 0·65; 0·75; 0·85; 1·00. In the course of the paper each glass is named by the corresponding x value. The glasses were prepared by mixing appropriate quantities of ultra pure lithium carbonate (Aldrich), potassium carbonate (Aldrich) and germanium oxide (Heraeus) in batches of sufficient size to yield 3 g of glass. 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 weight 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 size sufficient for the experimental measurements were obtained by this technique.

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

DTA curves were recorded in air at a heating rate of 10°C min^{-1} on bulk or fine powdered (< 45 micron) specimens (about 50 mg) from room temperature to 800°C. A Netzsch thermoanalyser High Temperature DSC 404 was used with Al_2O_3 as reference material. The experimental error in DTA temperature is ± 1°C.

The DTA curves have been elaborated by a Netzsch software. The amorphous nature of the glasses and the identification of the phases crystallising in the glass during the DTA runs were ascertained by X-ray diffraction (XRD) using a Philips diffractometer. Powders of each glass sample were scanned from $2\Theta = 5$ to 60° using CuK$_\alpha$ radiation. All the samples for XRD measurements were heat treated in DTA furnace by quenching then directly after a DTA peak had occurred.

3 Results and Discussion

The FTIR transmittance spectra of glasses with $x = 0{\cdot}00$; 0·25; 0·50; 0·75 and 1·00 and vitreous GeO_2 are shown in Fig. 1. These spectra exhibit broad bands as expected for glassy systems. The infrared spectra of a number of compositions in alkali germanate systems show that in each system the highest frequency band at 878 cm^{-1}, due to Ge–O–Ge bond stretching is shifted to lower frequencies. This shift is related to the change in the co-ordination number of Ge from 4 to 6. The higher the alkali concentration the greater is the shift.[7] The infrared spectra of the studied glasses, shown in Fig. 1, exhibit the same shift. This result suggests a similar GeO_4/GeO_6 molar ratio in all the glasses of the series.

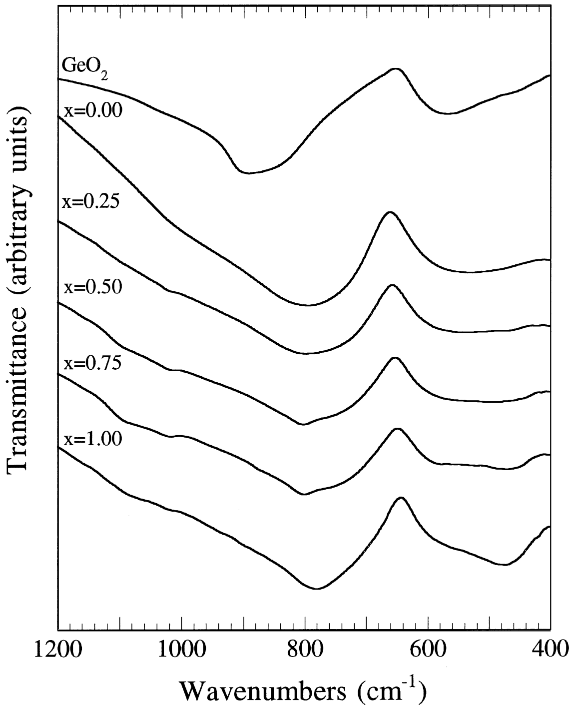

Fig. 1. FT-IR transmittance spectra of the studied glasses.

Figure 2 shows the DTA curves of the as-quenched glasses with $x = 0{\cdot}00$; 0·25; 0·50; 0·75; 1·00 recorded on bulk samples. A slope change followed by an exothermic peak occurs on all curves. The slope change may be attributed to the glass transition. When a glass is heated, its heat capacity,

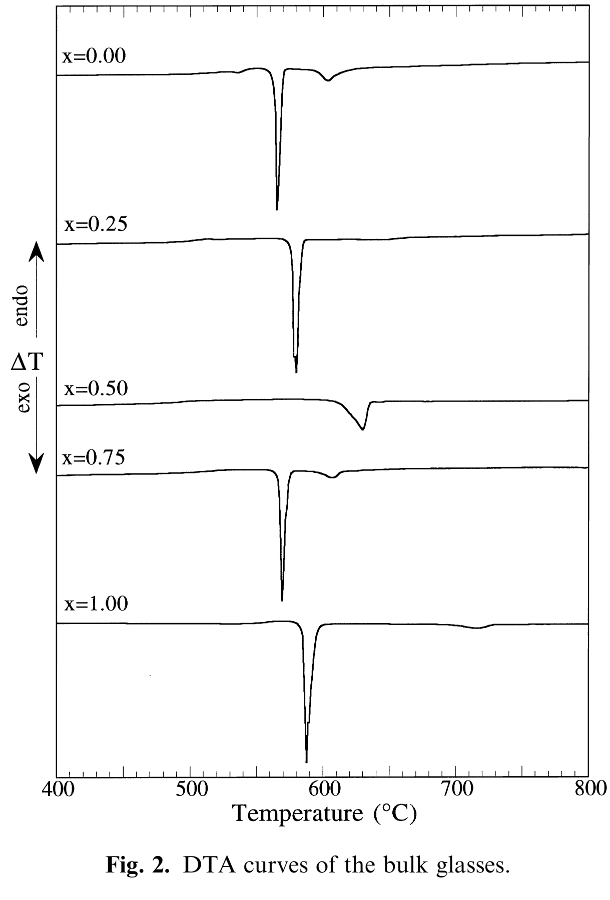

Fig. 2. DTA curves of the bulk glasses.

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 plastic structure. In this work, the inflection point at the slope change temperature of the DTA curve, Fig. 3 was taken as the glass transition temperature, T_g. The values of T_g of the nine investigated glasses are plotted as a function of x in Fig. 4.

The substitution of one alkali for the other causes the value of T_g to go through a minimum. This behaviour is known in alkali silicate glasses as the 'mixed alkali effect'.[8,9] According to Ray,[10] the effect of any cation on T_g is related to the following factors: (i) reduction in density of covalent cross-linking; (ii) change in oxygen density of the network; (iii) number and strength of the cross-links between oxygen and the cation. In the glasses studied the O/Ge ratio is constant (i.e. O/Ge = 2·25) and the GeO_4/GeO_6 molar ratio is near the same, therefore the cross-link density does not change. The strength and the number of the cross-links between oxygen and the cations are related to the radius and to the co-ordination number of the cations. The radii of Li^+ and K^+ ions are 0·60 Å and 1·33 Å, respectively. The co-ordination numbers are 4 and 9 for Li^+ and K^+.[10] Therefore, the non-linear trend with a minimum of the T_g versus x curve observed in Fig. 3 may be explained assuming that at low substitutions K^+ is forced into 4-co-ordination, with M–O strength reduced consequent on the larger radius of K^+ compared with Li^+, while at large substitution it goes into 9-co-ordination giving a large number of bonds which more than compensate for their reduced strength.

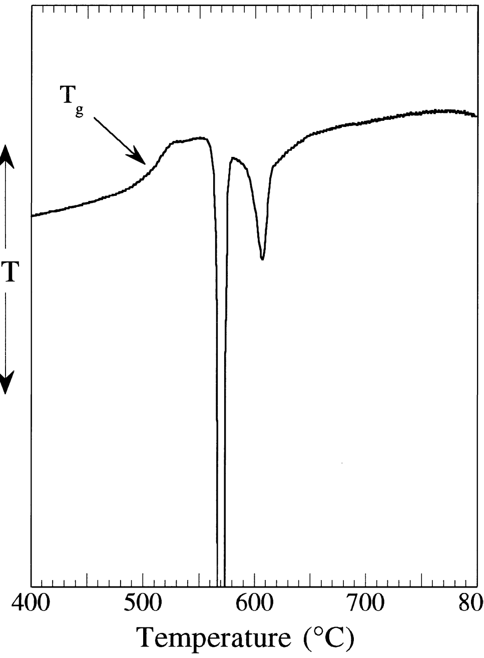

Fig. 3. DTA curve of the glass $x = 0{\cdot}75$ with an expanded ordinate scale to display the slope change attributed to the glass transition.

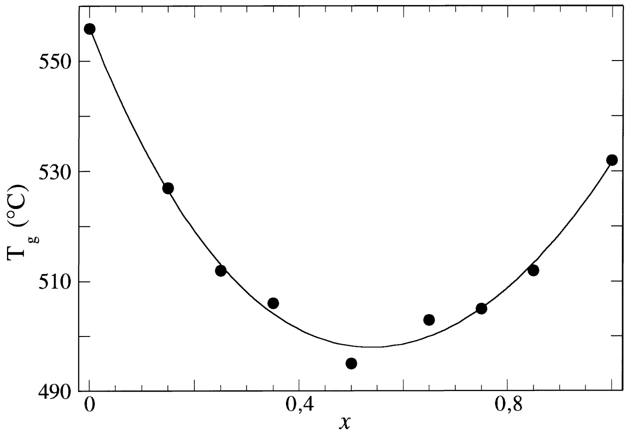

Fig. 4. Glass transition temperature, T_g, as function of glass composition.

When a glass crystallises during a DTA run, the heat of crystallisation is evolved and an exothermic peak appear on the DTA curve. The DTA curves of all glasses studied exhibit an exothermic crystallisation peak at temperatures ranging between 560 and 630°C. Nucleation in glass-forming systems can occur either in the volume or on the surface of the sample. In practice, surface crystal nucleation occur more easily and is observed in most compositions. To achieve internal crystal nucleation it is often necessary to add nucleating agents. However certain glass systems nucleate internally without such additions. The number of nuclei, N, is the sum of the number N_s of surface nuclei proportional to the specific surface area of the samples, and of the number N_b bulk nuclei formed during the heat treatments of the samples.[11] The higher the number of N, the lower is the temperature of the DTA crystallisation peak.[12] Moreover the shape of the DTA crystallisation peak is strongly affected by the crystallisation mechanism to surface and bulk crystallisation, corresponding to broad and sharp peaks, respectively.[11]

The shape of the crystallisation peaks on the DTA curves, carried out on bulk samples (low specific surface area), Fig. 2, indicates that in glasses with $x = 0{\cdot}00$, 0·25, 0·75 and 1·00 internal crystal nucleation occurs without the addition of any nucleating agent. The small and broad crystallisation peak of the glass with $x = 0{\cdot}50$ indicates a dominant surface crystallisation. To investigate the influence on the devitrification process of the specific surface area of the samples, DTA curves were also recorded on very fine powdered samples. In glasses with $x = 0{\cdot}00$, 0·25, 0·75 and 1·00 no appreciable differences of the temperature, T_p, and the shape of the crystallisation peak were found.

Table 1. Crystallising phases during a DTA run from room temperature to 800°C. (mc) Microcrystal, (tc) traces

Glasses	*First DTA peak*	*After DTA run*
$x = 0{\cdot}00$	$Li_2Ge_4O_{9(mc)}$	$Li_2Ge_4O_9$
$x = 0{\cdot}25$	$Li_4Ge_9O_{20}$	$Li_2Ge_4O_9$
$x = 0{\cdot}50$	$K_2Ge_7O_{15} + K_2Ge_4O_{9(tc)}$	$K_2Ge_4O_9 + K_2Ge_7O_{15(tc)}$
$x = 0{\cdot}75$	$K_2Ge_7O_{15} + K_2Ge_4O_{9(tc)}$	$K_2Ge_4O_9 + K_2Ge_7O_{15(tc)}$
$x = 1{\cdot}00$	$K_4Ge_9O_{20}$	$K_2Ge_4O_9$

Taking into account the great increase of the number of surface nuclei due to the high specific surface area of the samples this result confirms that in these glasses bulk nucleation is dominant. On the other hand in the powdered glass with $x = 0{\cdot}50$ the crystallisation peak is shifted towards a lower temperature (597°C) than that (630°C) of the correspondent bulk sample.

The XRD patterns of the as-quenched glasses show broad humps characteristic of their amorphous state. To identify the phases crystallising during the DTA runs, XRD measurements were carried out on glasses with $x = 0{\cdot}00$; $0{\cdot}25$; $0{\cdot}50$; $0{\cdot}75$ and $1{\cdot}00$. Samples quenched after heating in the DTA furnace up to the temperature of the DTA exothermic peak and samples quenched after a DTA run to 800°C were studied. The XRD patterns exhibit several sharp reflections that were assigned to the crystalline phases reported in Table 1. Owing to the great difference of L^+ and K^+ radii no intermediate compound or solid solutions between lithium and potassium germanate phases were found.

As observed in Fig. 5 the more the composition of the crystallising phases differs from that of the mother glass the greater the difference between T_p and T_g temperatures. The simultaneous presence of the large K^+ cation and the small Li^+ one in the glass network makes it hard to achieve nucleation and crystallisation without a decrease of the viscosity that allows the required rearrangement of network.

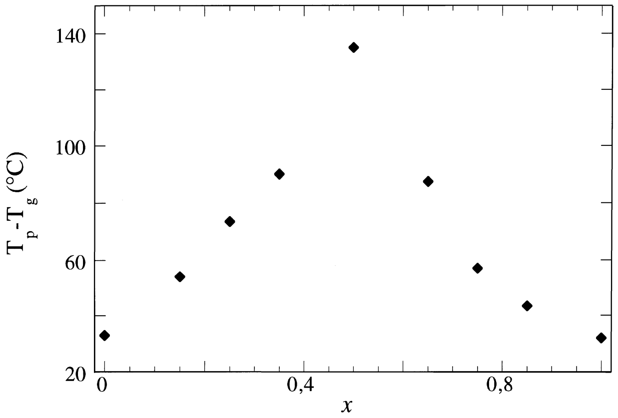

Fig. 5. T_p–T_g versus glass composition.

4 Conclusions

From the experimental results the following conclusions can be drawn:

1. The structures of the glasses contain GeO_4 and GeO_6 groups in near the same molar ratio.
2. The progressive replacing of Li_2O by K_2O causes the value of the glass transition temperature to go through a minimum at molar ratio $Li_2O/K_2O = 1$ according with the 'mixed alkali effect'.
3. All glasses exhibit internal crystal nucleation except in the glass with $x = 0{\cdot}50$ where surface crystallisation is dominant.
4. The glass stability increases with the increase of the difference between crystallising phases and mother glass compositions.

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