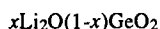


THE NON-ISOTHERMAL DEVITRIFICATION OF LITHIUM GERMANATE GLASSES

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The non-isothermal devitrification of lithium germanate glasses, examined by DTA and XRD, is reported and discussed. The glass compositions are expressed by the general formula:



with $x = 0.050, 0.125, 0.167, 0.200$ and 0.250 . All the glasses studied, unlike GeO_2 glass, exhibit internal crystal nucleation without the addition of any nucleating agent. The devitrification processes occur in one or more steps. Phases which crystallized at each step are identified and crystallization mechanisms proposed. These crystallization mechanisms are related to structures of the crystallizing phases. Activation energy values as well as those for glass transition temperatures, do not vary linearly with increase in Li_2O content but pass through a maximum at $x = 0.200$.

Keyword: crystallization, devitrification process, lithium germanate glasses

Introduction

The ionic size and ionic charge of Ge^{4+} are very similar to that of Si^{4+} and thus the chemical behaviour of silicates and germanates show close resemblance. However, the ionic radius of Ge^{4+} (0.53 \AA) is very close to the limiting cation/anion radius ratio for tetrahedral and octahedral co-ordination and it can therefore assume both fourfold and sixfold co-ordination. Early work on lithium germanate glasses indicated that density and refractive index pass through maxima (about 20 mole%) as the lithium oxide content increases [1, 2]. It was suggested that this behaviour is the result of conversion of the germanium ions from fourfold to sixfold co-ordination with increasing lithium oxide content. The charge of -2 on the GeO_6 octahedron is balanced by the localisation of two lithium ions. No non-bridging oxygens are formed. Eventually, however, the formation of sixfold germanium ions reaches a limiting value and non-bridging

oxygens begin to form in increasing numbers. The competitive effects of formation of sixfold co-ordinated germanium and non-bridging oxygen lead to the observed maxima [3].

In the present study the devitrification behaviour of lithium germanate glasses is investigated with the aid of differential thermal analysis (DTA) and X-ray diffraction (XRD).

Experimental

The glass compositions are expressed by the general formula $x\text{Li}_2\text{O}(1-x)\text{GeO}_2$ with $x = 0.050, 0.125, 0.167, 0.200$ and 0.250 . The glasses were prepared using reagent grade lithium carbonate and germanium oxide in the correct proportions to yield 2 g of glass. The glass was melted in a Pt crucible in an electric oven. The crucible containing the glass was weighed before removing the glass and again

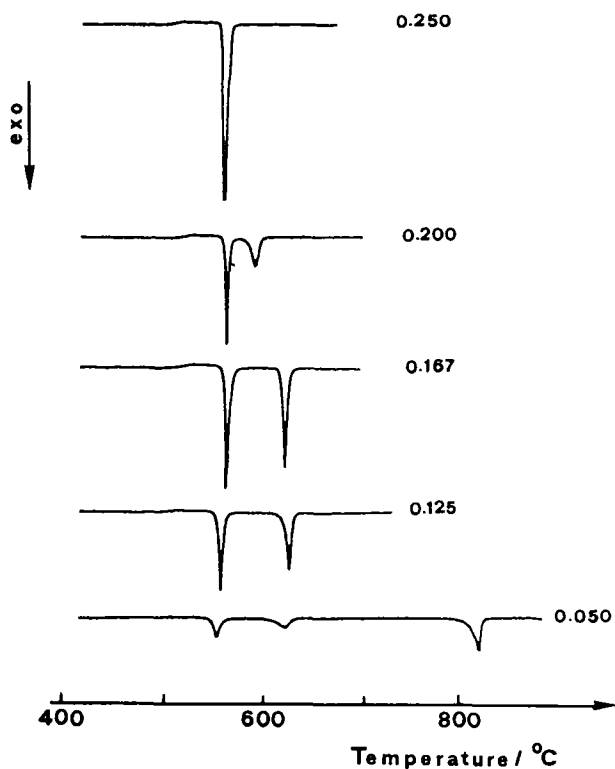


Fig. 1 DTA curves recorded at $10 \text{ deg} \cdot \text{min}^{-1}$

after removing the glass. The weight of glass agreed with that anticipated in the batch calculation. Melts were cast at high cooling rates between two brass plates. Although this resulted in fracture of the glass, pieces of sufficient size for the experimental measurements were obtained by this technique.

DTA curves were recorded in air at different heating rates on bulk specimens of about 60 mg. Powdered Al_2O_3 was added to improve heat transfer between bulk sample and sample holder. A Netzsch High Temperature DSC 404 instrument was used with Al_2O_3 as reference material.

Phases which crystallised during the DTA runs were identified by XRD, using a Philips diffractometer, with CuK_α radiation.

Results and discussion

Differential thermal analysis

Figure 1 shows the DTA curves of the five as-quenched glasses. All curves exhibit a slope change that may be attributed to the glass transition.

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

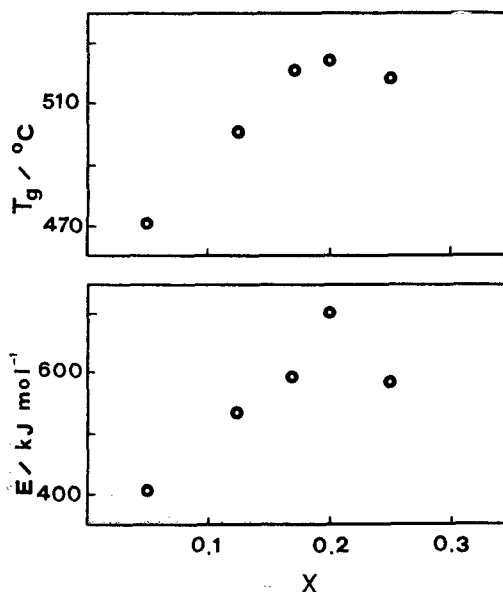


Fig. 2 Glass transition temperature, T_g , and activation energy of crystal growth, E , as function of x

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 was taken as the glass transition temperature, T_g , and values for the five glasses investigated are plotted as function of x in Fig. 2.

When a glass crystallizes during a DTA run, heat is evolved and one or more exothermic peaks appear on the DTA curve. DTA curves of all the compositions showed an exothermic crystallization peak just above the glass transition (at about 560°C). A second exothermic crystallization peak appears, at a higher temperature, on the DTA curves of the first four compositions of the series. A third exothermic crystallization peak appears at an even higher temperature on the DTA curve of the composition $x = 0.050$.

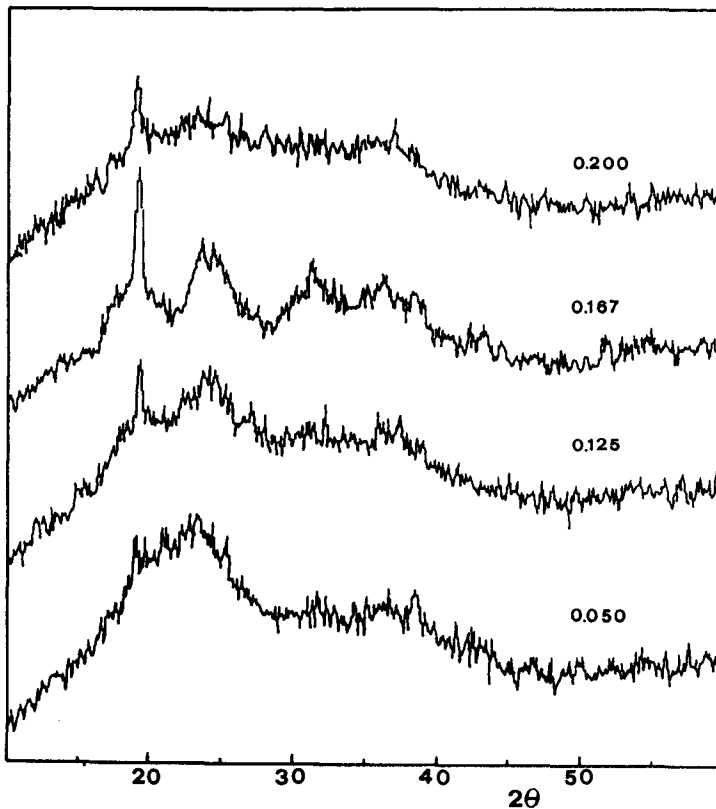


Fig. 3 X-ray diffraction patterns of samples heated up to the temperature of the first DTA peak

X-ray diffraction

To identify the phases crystallizing during the DTA runs, samples of each of the studied glasses were heated in the DTA furnace up to the temperature of each exothermic peak detected on the DTA curves. XRD patterns of all glasses (except $x = 0.250$) heated up to the temperature of the first DTA exothermic peak showed only one sharp reflection in an amorphous background (Fig. 3). These results and the glassy appearance of the samples after heating in spite of the evident thermal effect on DTA curve, suggest precipitation of a large number of microcrystallites dispersed in a non-crystalline matrix. The sharp reflection at $19^\circ 2\theta$ corresponds to one of the stronger reflections ($hkl = 010$) of $\text{Li}_2\text{Ge}_4\text{O}_9$. Sharp lines on all other. XRD patterns could be attributed to other germanium compounds (Table 1).

Table 1 X-ray diffraction patterns, observed d spacing (\AA), and their attribution

$x = 0.050$ a)	$x = 0.050$	$x = 0.125$ a)	$x = 0.167$	$x = 0.200$ c)	$x = 0.250$
II exo-peak	III exo-peak	II exo-peak	II exo-peak	II exo-peak	I exo-peak
5.502	5.514 a)	5.519	6.003 c)	7.862	7.880 c)
4.191	4.312 b)	4.188	5.525 a)	6.003	6.007 c)
4.038	4.186 a)	4.034	4.628 c)	4.623	4.824 d)
3.836	4.025 a)	3.836	4.191 a)	3.999	4.628 c)
3.673	3.833 a)	3.678	4.000 c)	3.938	4.003 c)
3.275	3.674 a)	3.275	3.942 c)	3.664	3.940 c)
3.176	3.423 b)	3.182	3.678 a,c)	3.277	3.675 c)
3.013	3.170 a)	3.166	3.279 a,c)	2.855	3.660 c)
2.933	3.010 a)	3.015	3.182 a)	2.521	3.399 d)
2.763	2.929 a)	2.932	3.029 c)	2.447	3.277 c)
2.656	2.763 a)	2.902	3.017 c)	2.440	3.028 c)
2.423	2.654 a)	2.766	2.932 a)	2.325	2.857 c)
2.417	2.489 b)	2.658	2.857 c)	2.315	2.847 c)
2.333	2.418 a)	2.426	2.766 a)	2.286	2.528 c)
2.299	2.359 a)	2.415	2.658 a)	2.271	2.521 c)
2.021	2.331 a)	2.400	2.522 c)	2.006	2.449 c)
1.587	2.280 a,b)	2.334	2.448 c)	1.810	2.439 c,d)
	2.161 b)	2.296	2.419 a)	1.709	2.316 c)
	2.156 b)	2.020	2.334 a)	1.664	2.288 c)
	2.018 a,b)	1.589	2.288 c)		2.006 c)

- a) $\text{Li}_2\text{Ge}_7\text{O}_{15}$ JCPDS card 23-1181, b) GeO_2 JCPDS card 4-0497,
 c) $\text{Li}_2\text{Ge}_4\text{O}_9$ JCPDS card 37-1363, d) Li_2GeO_3 JCPDS card 34-659

These results suggest the following crystallization mechanisms.

All the glasses studied, unlike GeO_2 glass, exhibit internal crystal nucleation without the addition of any nucleating agent.

The glass with $x = 0.050$ devitrifies in three steps. Metastable $\text{Li}_2\text{Ge}_4\text{O}_9$ microcrystallites are formed initially and are then converted at higher temperatures into $\text{Li}_2\text{Ge}_7\text{O}_{15}$ crystals. These latter crystals act as nucleating agents for GeO_2 crystals at an even higher temperature.

The glass with $x = 0.125$ devitrifies in two steps. Metastable $\text{Li}_2\text{Ge}_4\text{O}_9$ microcrystallites are formed initially and are then converted at higher temperature into $\text{Li}_2\text{Ge}_7\text{O}_{15}$ crystals.

The glass with $x = 0.167$ devitrifies in two steps. In the primary transformation, metastable $\text{Li}_2\text{Ge}_4\text{O}_9$ microcrystallites crystallize in an amorphous matrix. In the second transformation a mixture of $\text{Li}_2\text{Ge}_4\text{O}_9$ and well euhedral $\text{Li}_2\text{Ge}_7\text{O}_{15}$ crystals are formed.

The glass with $x = 0.200$ devitrifies in two steps. $\text{Li}_2\text{Ge}_4\text{O}_9$ microcrystallites are formed initially and these are then converted at higher temperature into euhedral $\text{Li}_2\text{Ge}_4\text{O}_9$ crystals.

Finally, the glass with $x = 0.250$ devitrifies in a single stage to form a mixture of $\text{Li}_2\text{Ge}_4\text{O}_9$ and LiGeO_3 crystals.

These crystallization mechanisms are related to the structures of the crystallizing phases. In the first four glass compositions of the series the primary phase consists of $\text{Li}_2\text{Ge}_4\text{O}_9$ microcrystallites. This phase does not appear in the $\text{Li}_2\text{O}-\text{GeO}_2$ phase diagram [1]. This compound contains chains of GeO_4 tetrahedra linked by GeO_6 octahedra forming a three-dimensional network [4]. This structure is quite similar to that of $\text{Li}_2\text{Ge}_7\text{O}_{15}$ which contains layers of GeO_4 tetrahedra linked by GeO_6 octahedra forming a three-dimensional network [5]. The $\text{Li}_2\text{Ge}_4\text{O}_9$ crystals have a simpler structure and are therefore kinetically favoured with respect to the $\text{Li}_2\text{Ge}_7\text{O}_{15}$ crystals but they are similar enough to allow, in the compositions $x = 0.050$, 0.125 and 0.167 , rapid conversion.

The crystallization mechanism of the composition $x = 0.250$ is remarkably different from that of the other compositions of the series. The glass $x = 0.250$ fully devitrifies in a single stage close to the temperature at which in the other compositions only precipitation of microcrystallites occurs. This behaviour can be attributed to the presence of non-bridging oxygens in the structure of this glass that leads to a more fragmented network. This allows easier formation of chains of GeO_4 tetrahedra that give rise to Li_2GeO_3 crystals (infinite chains of GeO_4 tetrahedra [3]) and $\text{Li}_2\text{Ge}_4\text{O}_9$ crystals (chains of GeO_4 tetrahedra linked by GeO_6 octahedra).

Activation energy of crystal growth

The activation energy E for crystal growth of the first crystallization step of all the studied glasses has been evaluated from a set of DTA curves recorded at different heating rates β by the following equation [6]:

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

This equation is based on the assumption that, at the temperature T_p of the DTA crystallization peak, the degree of crystallization attains the same specific value independent of heating rate. The values of E were calculated from the slopes of the straight lines obtained by plotting $\ln(\beta)$ against $1/T_p$.

Activation energy values, as well as glass transition temperature values, do not change linearly with increase in Li_2O content but pass through a maximum at $x = 0.200$ (Fig. 2). This behaviour is the result of the conversion of the germanium ions from fourfold to sixfold co-ordination with increasing lithium oxide content in the first four compositions of the series, where no non-bridging oxygens are formed. At the composition $x = 0.200$, formation of sixfold germanium ions reaches a limiting value and in the next composition $x = 250$ non-bridging oxygens are formed. The competitive effects of formation of sixfold co-ordinated germanium and non-bridging oxygens lead to the maxima observed.

Conclusions

The following conclusions can be drawn:

- a) All glasses studied exhibit internal crystal nucleation without the addition of nucleating agent.
- b) The first four compositions of the series crystallize in many steps.
- c) Progressive increase of lithium oxide content causes the value of the glass transition temperature and the value of activation energy for crystal growth to pass through a maximum at $x = 0.200$.

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References

- 1 M. K. Murthy and J. Ip, *J. Am. Ceram. Soc.*, 47 (1964) 328.
- 2 J. E. Shelby and J. Ruller, *Physics Chem. Glasses*, 28 (1987) 262.
- 3 H. Verweij and J. H. J. M. Buster, *J. Non-crystalline Solids*, 34 (1979) 81.
- 4 A. Wittmann and E. Modern, *Mh. Chem.*, 96 (1965) 581.
- 5 H. Vollehnle, A. Wittmann and H. Nowotny, *Mh. Chem.*, 101 (1970) 46.
- 6 T. Ozawa, *Polymer*, 12 (1971) 150.

Zusammenfassung — Es wird die nichtisotherme Entglasung von Lithiumgermanat-Gläsern, untersucht mittels DTA und Röntgendiffraktion, beschrieben und diskutiert. Die Glaszusammensetzungen entsprechen der allgemeinen Formel $x\text{Li}_2\text{O}(1-x)\text{GeO}_2$ mit $x=0.050, 0.125, 0.167, 0.200$ und 0.250 . Anders als GeO_2 zeigen alle untersuchten Gläser eine interne Kristallkeimbildung ohne den Einsatz von Keimbildungsmitteln. Der Entglasungsprozeß verläuft in einem oder mehreren Schritten. Die in den einzelnen Schritten kristallisierten Phasen wurden identifiziert und ein Kristallisationsmechanismus vorgeschlagen. Diese Kristallisationsmechanismen werden mit den Strukturen der kristallisierenden Phasen in Verbindung gebracht. Weder die Werte für die Aktivierungsenergie noch für die Glasumwandlungstemperaturen ändern sich linear mit dem Ansteigen des Li_2O -Gehaltes, durchlaufen aber ein Maximum bei $x=0.200$.