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THE NON-ISOTHERMAL DEVITRIFICATION OF GEL-DERIVED LITHIUM, SODIUM AND BARIUM DISILICATE GLASSES

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The non-isothermal devitrification kinetics of lithium, sodium and barium disilicate gel-glasses have been investigated by differential thermal analysis. Using methods proposed by the present authors, the kinetic parameters and the mechanism of crystal growth in the studied glasses were evaluated from DTA curves. The results were compared with those obtained for the glasses of the same composition prepared using a mixture of oxides as starting materials and quenching the melts.

Introduction

The sol-gel method of making inorganic glasses was intensively studied in recent years [1]. Interest in this process has been stimulated, in part, by the low preparation temperatures involved compared with the conventional melting method. The preparation involves hydrolysis and polycondensation of organometallic compounds. A gel forms that is changed, by drying, into a porous particulate material. It differs from the oxide glasses by being highly crosslinked and, perhaps, by containing excess free volume. Proper thermal treatments are, therefore, required to convert the gel into the glass. However, it is difficult to obtain glasses containing modifying oxides, because, owing to the high tendency to devitrify, only crystalline materials could be obtained by heating.

The present work is part of a more general study with the ultimate technological objective of determining the suitability and advantages of gels as starting materials for the preparation of glass-ceramics. In the present paper the non-isothermal devitrification kinetics of sodium, lithium, and barium disilicate glasses prepared by gel-glass transformation were investigated by differential thermal analysis.

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Gel synthesis

The preparation of Li$_2$Si$_2$O$_5$, Na$_2$Si$_2$O$_5$ and BaSi$_2$O$_5$ gels involved hydrolysis and polycondensation of organometallic compounds. Tetramethyl orthosilicate (TMOS) or tetraethyl orthosilicate (TEOS), lithium or sodium methylate and barium acetate were used as starting materials.

Gelification is the result of hydrolysis and condensation reactions:

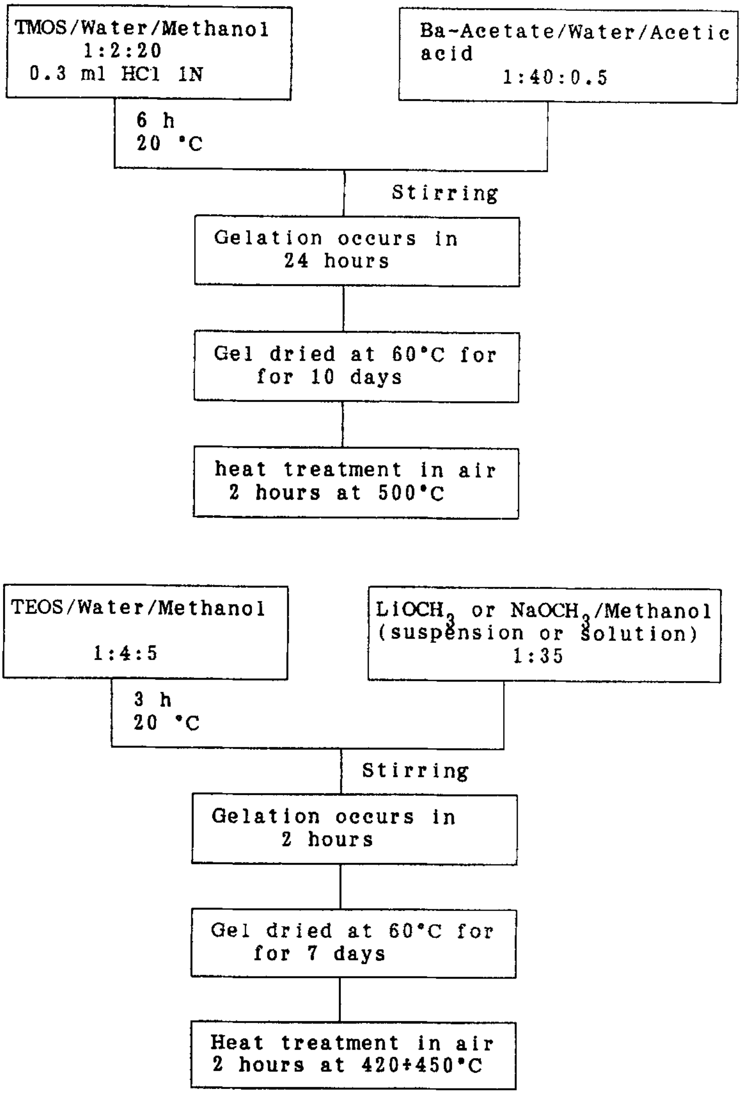

Fig. 1 Flow diagrams of gel-glasses preparation

$$\equiv\mathrm{Si{-}OR} + \mathrm{H_2O} \rightarrow \equiv\mathrm{Si{-}OH} + \mathrm{H{-}OR}$$

$$2\equiv\mathrm{Si{-}OH} \rightarrow \equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{H_2O}$$

the introduction of modifier cations in the gel structure take place according to the following reaction

$$\mathrm{LiOR} + \equiv\mathrm{Si{-}OH} \rightarrow \equiv\mathrm{Si{-}O^-} + \mathrm{Li^+} + \mathrm{ROH}$$

with sodium and barium similar reactions occur. Proper thermal treatments were necessary to convert the gels into the glasses [2–4].

Figure 1 shows flow charts of the chemical preparation procedure and of the heat treatments required for obtaining the gel-glasses. They look as white powder mixed with glassy transparent pieces of few millimeters too, Fig. 2.

Gel-glass devitrification

Kinetic investigations on the crystallization of glass are of interest for elucidating the nature of crystal growth and for research on glass ceramic materials.

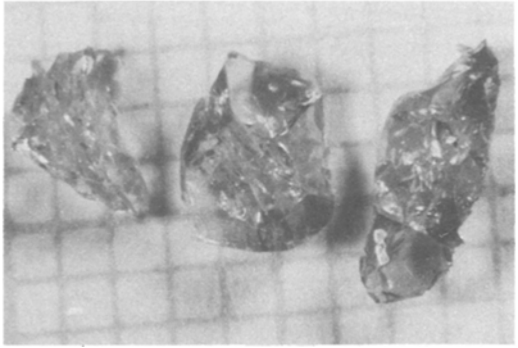

Fig. 2 Barium disilicate gel-glass

Nucleation in glass-forming system 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 agents. However, certain systems nucleate internally without such additions.

The non-isothermal devitrification kinetics of the three desilicate gel-glasses have been investigated by differential thermal analysis. When a glass crystallizes during a DTA run, the heat of crystallization is evolved, and an exothermic peak appears on the DTA curve, see Figs 3, 4.

The process of crystal growth can be described by the following eq. (5):

$$-\ln(1-\alpha) = A(N/\beta^n)\exp(-nE/RT) \qquad (1)$$

where α is the volume fraction crystallized at temperature T, E the activation energy for crystal growth, β the DTA heating rate and A a constant. The n parameter ranges between $n = 1$ for surface crystallization and $n = 3$ for bulk crystallization.

The kinetic parameters E and n can be evaluated from DTA curves by the following Eq. (6)

$$\ln\beta = (E/R)(1/T_p) + \text{const.} \qquad (2)$$

$$\ln\Delta T = -(nE/R)(1/T) + \text{const.} \qquad (3)$$

Equation (2) is based on the assumption [7] that at the peak temperature T_p the degree of crystallization α reaches the same specific value and is not dependent on the heating rate β. Equation (3) is based on the assumption that in the initial part of the DTA crystallization peak the change in temperature T has a much larger effect on the ΔT deflection from the baseline that on the degree of crystallization α [8]. The values of E and n calculated from the slopes of the straight lines obtained by plotting $\ln\beta$ *vs.* $1/T_p$ and $\ln\Delta T$ *vs.* $1/T$ are reported in Table 1.

Table 1 Kinetic parameters E ($kJ \cdot mole^{-1}$) and n for crystal growth

Composition	Gel glasses		Oxide glasses	
	E	n	E	n
$Na_2O \cdot 2SiO_2$	276	1	280	1
$Li_2O \cdot SiO_2$	293	3	272	3
$BaO \cdot SiO_2$	540	3	500	3

These values are very close to those obtained for the glasses of the same composition prepared by the usual method of melting oxides. $Li_2Si_2O_5$ and $BaSi_2O_5$ gel glasses as well the oxides glasses of the same composition exhibit internal bulk crystallization without the addition of any nucleating agent.

The DTA curves In Fig. 3 show that lithium disilicate gel glass (curve *c*) devitrifies at a temperature much lower than that at which does a sample of Li_2SiO_5 oxide glasses, nucleated for 2 h at the temperature of maximum nucleation rate (curve *a*). Moreover the crystallization peak temperature of

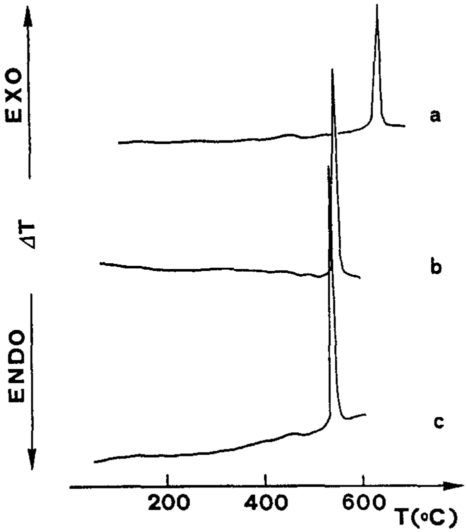

Fig. 3 DTA curves recorded at 10 deg · min^{-1}; (*a*) $Li_2Si_2O_5$ oxide glass after 2 h at 455°C; (*b*) $Li_2Si_2O_5$ oxide glass containing 1% Ag_2O; (*c*) $Li_2Si_2O_5$ gel glass

the gel glass is very close to that of the corresponding oxide glass with the addition of 1% Ag_2O as nucleating agent (curve *b*). The DTA curves in Fig. 4 show that barium disilicate gel glass (curve *c*) devitrifies at the same crystallization peak temperature of the corresponding oxide glass nucleated 2 h at the temperature of maximum nucleation rate (curve *b*). Moreover no shift of the crystallization peak temperature was observed in a gel glass preheated 2 h at this temperature (curve *d*). It was demonstrated in a previous paper [9] that the higher the number of nuclei is, the lower the temperature of the DTA crystallization peak is. Therefore the results reported above suggest that the gel glasses show a nucleation rate higher than that of the gel-glasses and the nature of the phases crystallizing during the DTA runs were acertained by X-ray diffraction. In all cases the crystalline phases have the same composition of the mother glasses.

Conclusions

Lithium, sodium and barium disilicate glasses can be obtained by the sol-gel method. The gels preparation involves hydrolysis and polycondensation of organo-metallic compounds. The gels thus prepared are clear solids containing water and organic residues that are lost on heating. The necessary

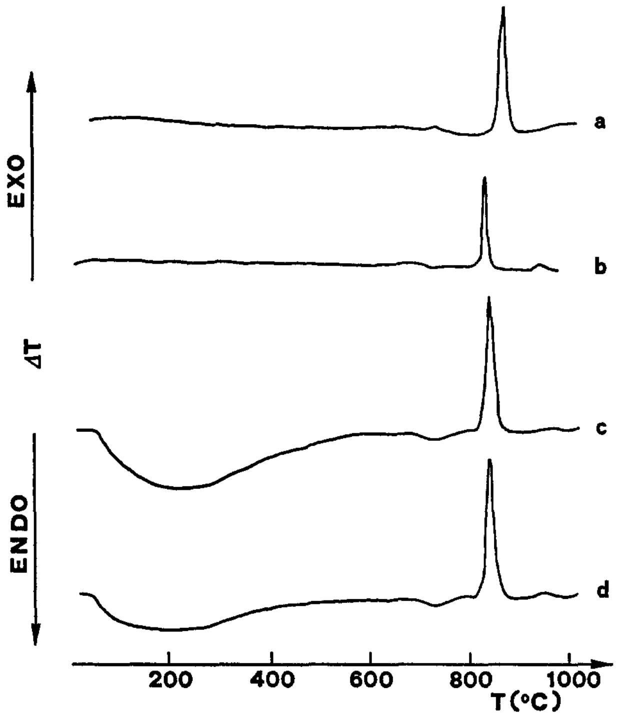

Fig. 4 DTA curves recorded at 20 deg · min^{-1}; (a) as quenched $BaSi_2O_5$ oxide glass; (b) $BaSi_2O_5$ oxide glass after 2 h at 700°C; (c) $BaSi_2O_5$ gel glass; (d) $BaSi_2O_5$ gel glass after 2 h at 700°C

temperatures are well below the glass transition temperature of the glass being formed and therefore, during the heat treatment required for the gel into glass conversion, the gel-glasses are kinetically stable to devitrification. The gel-glass devitrification occurs owing, probably, to the presence of a higher number of nuclei, at temperatures lower than those in the corresponding oxide-glass. These temperatures are in any case well above the glass transition temperature. This suggests the possibility of converting the porous particulate glasses into monolithic dense glasses by sintering or hot-pressing techniques without devitrification phenomena.

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Zusammenfassung — Die nicht-isotherme Entglasungskinetik von Lithium-, Natrium- und Barium Disilicat Gelgläsern wurde mittels Differenzthermoanalyse untersucht. Unter Verwendung der von den Autoren vorgeschlagenen Methoden wurden die kinetischen Parameter und der Mechanismus des Kristallwachstums in den untersuchten Gläsern aus DTA-Kurven bestimmt. Die Resultate wurden mit den an gleich zusammengesetzten, aber ausgehend von Oxidmischungen durch Abschrecken der Schmelze erzeugten Gläsern erhaltenen Ergebnissen verglichen.