

THE NON-ISOTHERMAL DEVITRIFICATION OF $\text{Na}_2\text{O} \cdot 2 \text{SiO}_2$ GEL-GLASS

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ABSTRACT

The non-isothermal devitrification of $\text{Na}_2\text{O} \cdot 2 \text{SiO}_2$ glass prepared by gel-glass transformation is investigated by differential thermal analysis.

The glass transition temperature, T_g , and the activation energy, E , for the crystal growth are evaluated from DTA and DDTA curves. The results are compared with those obtained for $\text{Na}_2\text{O} \cdot 2 \text{SiO}_2$ prepared by fusion of oxides. The influence of the specific surface area of the samples on devitrification kinetics is also discussed.

INTRODUCTION

The conventional method of making glass is by cooling a melt. A very interesting novel method uses solutions of metal-organic compounds as starting materials. The process involves forming a gel after hydrolysis and polycondensation [1].

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.

The non-isothermal devitrification kinetics of $\text{Na}_2\text{O} \cdot 2 \text{SiO}_2$ glass prepared by gel-glass transformation has been investigated by differential thermal analysis.

Using methods of analysis proposed by the present authors [2–4] the activation energy for the crystal growth has been evaluated from differential thermal analysis (DTA) and derivative differential thermal analysis (DDTA) curves. The results have been compared with those obtained for $\text{Na}_2\text{O} \cdot 2 \text{SiO}_2$ glass prepared using a mixture of oxides as starting materials.

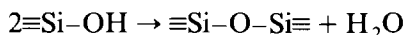
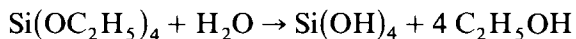
EXPERIMENTAL

$\text{Na}_2\text{O} \cdot 2 \text{SiO}_2$ gel-glass preparation

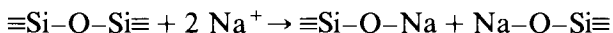
The preparation of the gel is based on the polymerization (i.e., hydrolysis and polycondensation) reaction of tetraethylortosilicate ($\text{Si}(\text{OC}_2\text{H}_5)_4$) con-

taining an alcoholic (C_2H_5OH) solution of sodium methoxide ($NaOCH_3$) in the presence of a controlled amount of water to produce the gel.

Gel formation can be represented, in simplified forms, as follows



The Si-O bonds are partly broken by Na^+ ions



The gel was dehydrated initially at $100^\circ C$ and then dried at $425^\circ C$ for 24 h to remove organic residues. After the thermal treatment the gel is transformed into a porous particulate material suitable for conversion into dense glass by sintering or hot compressing techniques. X-ray powder diffraction analysis showed no crystallinity.

Na₂O · 2 SiO₂ oxide-glass preparation

The glass was prepared by melting pure reagents in a Pt crucible in an electric oven at $1100^\circ C$ for 6 h. The melt was cast with a high cooling rate by plunging the bottom of the crucible in cold water.

The as-quenched glass was well crushed in order to obtain powdered samples with a specific surface area comparable to the gel-glass samples. X-ray powder diffraction analysis showed no crystallinity.

Differential thermal analysis

Differential thermal analysis at different heating rates ($5-20^\circ C \text{ min}^{-1}$) in air of $\sim 100 \text{ mg}$ powdered samples were carried out. Differential thermal analysis (DTA) and derivative differential thermal analysis (DDTA) curves were simultaneously recorded. The reference material was Al_2O_3 . A Netzsch differential thermal analyzer (model 404M) was used.

RESULTS AND DISCUSSION

The DTA and DDTA curves recorded at $20^\circ C \text{ min}^{-1}$ for gel-glass and oxide-glass are reported in the left- and right-hand sides of Fig. 1, respectively. Both glasses exhibit a slope change followed by an exothermic peak.

As a glass is heated its heat capacity, along with other properties, changes abruptly in a narrow temperature range (the glass transition temperature) at which the glass network acquires mobility on changing from a rigid to a plastic structure [5]. When a glass is heated in a DTA furnace and passes through the glass transition temperature range the slope of the DTA curve is

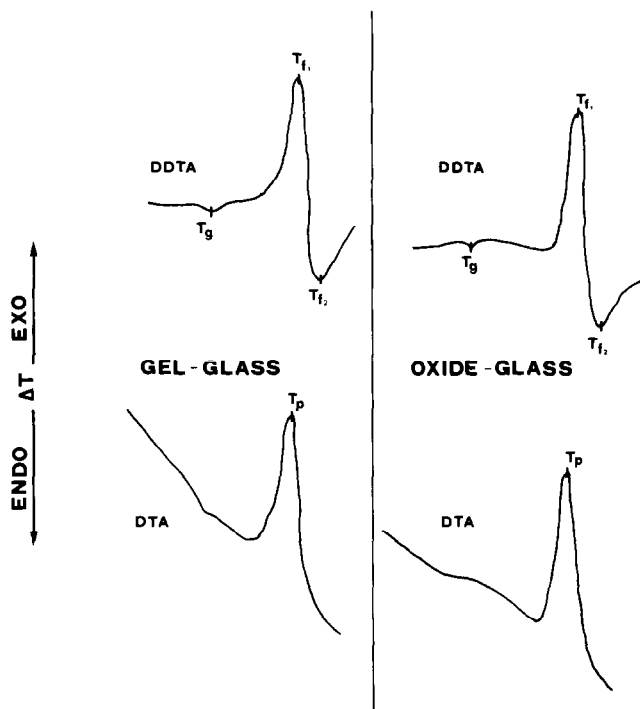


Fig. 1. DTA and DDTA curves of $\text{Na}_2\text{O} \cdot 2 \text{SiO}_2$ gel-glass and oxide-glass.

changed and a peak appears on the DDTA curve, as shown in Fig. 1. In this work the DDTA peak temperature was taken as the glass transition temperature, T_g . The value of $T_g = 472^\circ\text{C}$ for the gel-glass is very close to that for the oxide-glass $T_g = 477^\circ\text{C}$.

At a temperature somewhat higher than the glass transition temperature both glasses devitrify, the heat of crystallization is evolved, and an exothermic peak appears on the DTA curve. The phases crystallized during the DTA runs were identified by X-ray diffraction as $\text{Na}_2\text{O} \cdot 2 \text{SiO}_2$ in both cases.

The difference between the crystallization peak temperature for the oxide-glass is discussed later.

There are two types of crystallization taking place in a glass based on surface and bulk nucleation.

As very fine powders of glass were used in both cases the high specific surface area of the samples makes surface crystallization dominant. The nuclei are formed only on the surface and the crystals grow from the surface to the inside of the glass one-dimensionally.

The crystallization degree α at temperature T in a glass heated at constant heating rate β is well described for surface crystallization by the following

equation [6]

$$1 - (1 - \alpha)^{1/3} = \frac{AN}{\beta} \exp\left(-\frac{E}{RT}\right) \quad (1)$$

where E is the activation energy for crystal growth and A a constant.

The number of nuclei N is proportional to the specific surface area S of the samples

$$N \propto S \quad (2)$$

Assuming that the ΔT deflection from the baseline is proportional at each temperature T to the instantaneous reaction rate [7] the condition exists that at the peak temperature, T_p

$$\frac{d\Delta T}{dT} = 0 \quad (3)$$

and at the inflection points temperature, T_f

$$\frac{d^2\Delta T}{dT^2} = 0 \quad (4)$$

are satisfied, respectively, by

$$x = 1/3 \quad (5)$$

$$9x^2 - 8x + 1 = 0 \quad (6)$$

where

$$x = \frac{AN}{\beta} \exp\left(-\frac{E}{RT}\right) \quad (7)$$

From the two solutions of the quadratic eqn. (6), taking into account eqn. (7), the following relationship between the activation energy E and the two inflection point temperatures T_{f_1} and T_{f_2} can be derived [4]

$$E = \frac{1.59R}{1/T_{f_1} - 1/T_{f_2}} \quad (8)$$

As the two inflection points, i.e., the maximum and minimum slopes of the DTA peak, correspond to the maximum and the minimum of the DDTA double-peak, the temperatures T_{f_1} and T_{f_2} can be easily and precisely detected on the DDTA curves (Fig. 1).

The values of the activation energy E calculated by eqn. (8) for gel-glass and oxide-glass are reported in the first column of Table 1.

Both E values are very close to the value $E_\eta = 60 \text{ kcal mol}^{-1}$ of the activation energy for the viscous flow of $\text{Na}_2\text{O} \cdot 2 \text{ SiO}_2$ glass [8].

Taking into account eqn. (7) the logarithms of eqn. (5) lead to

$$\ln N - \ln \beta = \frac{E}{R} \frac{1}{T_p} + \text{const.} \quad (9)$$

TABLE 1

Activation energy E (kcal mol⁻¹) for crystal growth

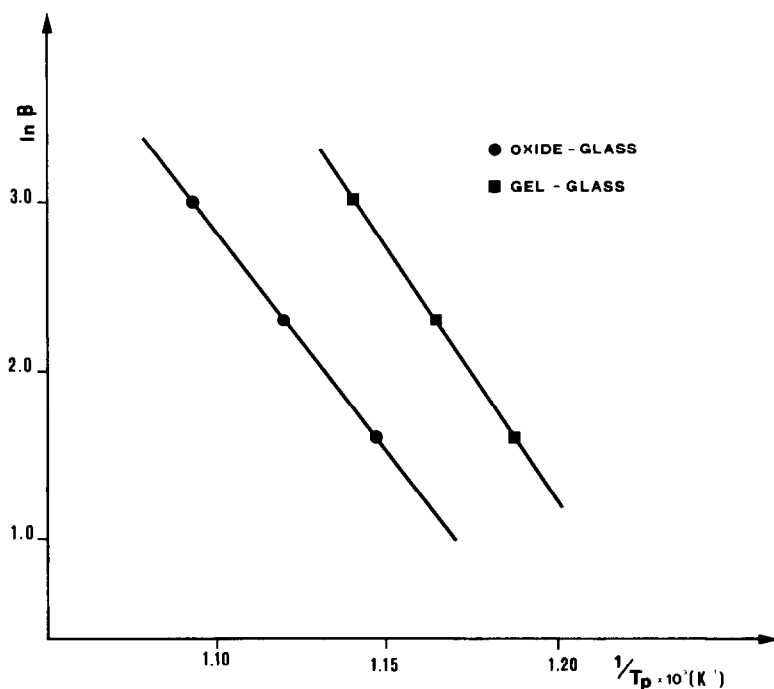
Samples	Eqn. (8)	Ozawa plot
Gel-glass	66	58
Oxide-glass	67	51

Taking into account eqn. (2), as the activation energy, E , is nearly the same for gel-glass and oxide-glass, the peak temperatures T_{p_1} and T_{p_2} detected on DTA curves recorded at the same heating rate β for the gel-glass and for the oxide-glass, respectively, can be related to the specific surface areas S_1 and S_2 of the two types of glass

$$\ln \frac{S_1}{S_2} = \frac{E}{R} \left(\frac{1}{T_{p_1}} - \frac{1}{T_{p_2}} \right) \quad (10)$$

The above mentioned difference between the peak temperatures T_{p_1} and T_{p_2} of the two types of glass can, therefore, be attributed to a difference between the specific surface areas of the two glasses.

By plotting $\ln \beta$ against $1/T_p$ (Ozawa plot) straight lines were obtained for both glasses (Fig. 2). The values of the activation energy E calculated from their slopes are reported in the second column of Table 1.

Fig. 2. Plot of $\ln \beta$ vs. $1/T_p$.

These values are lower than those calculated by eqn. (8). This discrepancy can be attributed (eqn. (9)) to a linear decrease of the number of nuclei N with the increase of the DTA heating rate, i.e., with the decrease of the time of heating in the nucleating temperature range.

CONCLUSIONS

From the DTA study described the following conclusions can be drawn. $\text{Na}_2\text{O} \cdot 2 \text{SiO}_2$ gel-glass and $\text{Na}_2\text{O} \cdot 2 \text{SiO}_2$ oxide-glass show:

- (a) the same value of glass transition temperature;
- (b) the same value of activation energy for the crystal growth very close to that for the viscous flow;
- (c) the same crystallized phase after the DTA run.

Owing to their higher specific surface area gel-glass samples devitrify at temperatures lower than those of the oxide-glass samples.

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