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Gel synthesis and crystallization of $Li_2O \cdot 7GeO_2$ glass powders

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Abstract

$Li_2O \cdot 7GeO_2$ gel was synthesized by the hydrolytic polycondensation reactions of germanium ethoxide with lithium methoxide. The crystallization behaviour of the gel, examined by differential thermal analysis and X-ray diffraction, is reported and discussed.

Lithium heptagermanate gel was found to crystallize in two steps. In the primary transformation, microcrystallites of $Li_2Ge_7O_{15}$ are crystallized in an amorphous matrix. In the second transformation, well-shaped $Li_2Ge_7O_{15}$ crystals are formed. The activation energy values for the two stages are found to be 589 and 495 kJ mol^{-1}, respectively. The results are compared with those obtained for conventional lithium heptagermanate glass.

INTRODUCTION

The sol–gel method of making inorganic glasses has been studied intensively in recent years [1]. Interest in this process was partly stimulated by the low preparation temperature involved, compared with the conventional melting method. The preparation involves hydrolysis and polycondensation of organometallic compounds. A gel forms which, on drying, changes into a porous particulate material which differs from the oxide glasses in being highly crosslinked and, perhaps, in containing excess free volume. Therefore, controlled thermal treatments are required to convert the gel into the glass. Binary lithium silicate gel has been prepared in a variety of ways and with a variety of lithium precursors [2]. However binary lithium germanate gels have not been studied.

The ionic size and the ionic change of Ge^{4+} are very similar to those of Si^{4+} and, therefore, the chemistry of the silicates and of the germanates somewhat resemble each other. However, the ionic radius of Ge^{4+} (0.53 Å) is very close to the cation/anion radius ratio limit that separates tetrahedral

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and octahedral co-ordination and, therefore, it can assume both four-fold and six-fold co-ordination. Investigations into the preparation of binary lithium germanate gels and their crystallization behaviour are of interest for elucidating the nature of the crystallizing phases and for research on glass-ceramic materials.

In this study, a lithium heptagermanate gel was prepared and its crystallization behaviour was studied with the aid of X-ray diffraction and differential thermal analysis. This composition was chosen because the crystallization of lithium heptagermanate oxide glass has previously been studied [3]; the results obtained for the gel are compared with those obtained for the conventional glass.

EXPERIMENTAL

The $Li_2O \cdot 7GeO_2$ gel was prepared using $Ge(C_2H_5O)_4$ (TEOG) and $LiOCH_3$ analytical grade reagents as starting materials. Absolute ethanol, obtained by distillation of commercial anhydrous ethanol with metallic sodium, was used because TEOG is a very water-sensitive reagent and in order to control the TEOG/H_2O ratio. Bi-distilled water was used for the hydrolysis reaction. The alcoholic solutions were prepared in a dry-box at room temperature. A flow-chart indicating the preparation procedure and the molar ratios employed is shown in Fig. 1. The alcoholic solution of TEOG was mixed at 0°C with the water–alcohol solution containing lithium methoxide. Under these conditions, complete gelation occurred at room temperature in two days. An opaque homogeneous gel was obtained. The

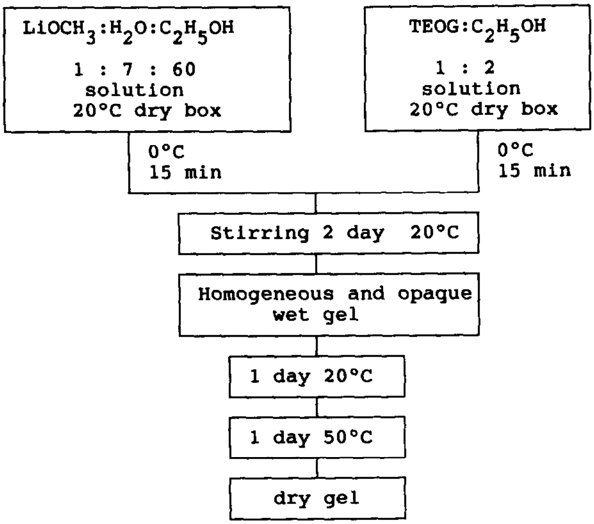

Fig. 1. Flow diagram for the gel preparation procedure.

gelled system was held for one day more at room temperature before drying. After complete drying at 50°C for one day, the gel was an amorphous powder (see trace (a) of Fig. 3, below).

The lithium content in the dried gel was verified using atomic absorption analysis (AAS). A sample of dried gel was placed in a platinum holder which was introduced into an electric oven at 1200°C. After 3 h at this temperature, the molten gel was air-quenched, weighed and dissolved in concentrated HF and diluted in bi-distilled water. A Varian SpectrA-A · 10plus spectrophotometer was used. The analysed Li_2O content (4.14 wt.%) and the theoretical value (3.92 wt.%) are in fairly good agreement.

The nature and the temperatures of the various reactions that occur during the heating of the dried gel were determined using simultaneous thermal analysis (STA). A powder sample, 20 mg of the dried gel, was subjected to a TG/DTA run in N_2, at a heating rate of $10°C\,min^{-1}$ from room temperature to 800 °C. A Stanton-Redcroft STA-780 analyser was used, with powdered Al_2O_3 as the reference material.

The amorphous nature of the dried gel and the identification of the phases crystallizing in the gel-derived glass during the DTA runs, were ascertained by X-ray diffraction (XRD) using a Philips diffractometer. The kinetics of the non-isothermal crystallization of the gel-derived glass were determined by differential thermal analysis (DTA). Powder samples of gel (≈50 mg) were subjected to DTA runs in air at different heating rates (2, 3, 5, 10, $20°C\,min^{-1}$) from room temperature to 800°C. A Netzsch high temperature DSC 404 thermoanalyser was used, with powdered Al_2O_3 was the reference material.

RESULTS AND DISCUSSION

Gelation is the result of hydrolysis and condensation reactions according to the equations

$$\equiv Ge\text{–}OEt + H\text{–}OH = \equiv Ge\text{–}OH + H\text{–}OEt \qquad \text{(hydrolysis)} \qquad (1)$$

$$\equiv Ge\text{–}OEt + HO\text{–}Ge\equiv \; = \; \equiv Ge\text{–}O\text{–}Ge\equiv + H\text{–}OEt \qquad \text{(dealcoholation)} \qquad (2)$$

$$\equiv Ge\text{–}OH + HO\text{–}Ge\equiv \; = \; \equiv Ge\text{–}O\text{–}Ge\equiv + H\text{–}OH \qquad \text{(dehydration)} \qquad (3)$$

$$LiOCH_3 + \equiv Ge\text{–}OH = \equiv Ge\text{–}O^-Li^+ + CH_3\text{–}OH \qquad (4)$$

At room temperature the hydrolysis reaction (eqn. (1)) is much faster than the condensation reactions (eqns. (2) and (3)), so that the number of Ge–O–Ge bridges formed is insufficient for gelation and precipitation of hydrated germanium oxide–alkoxide aggregate occurs. However, mixing at

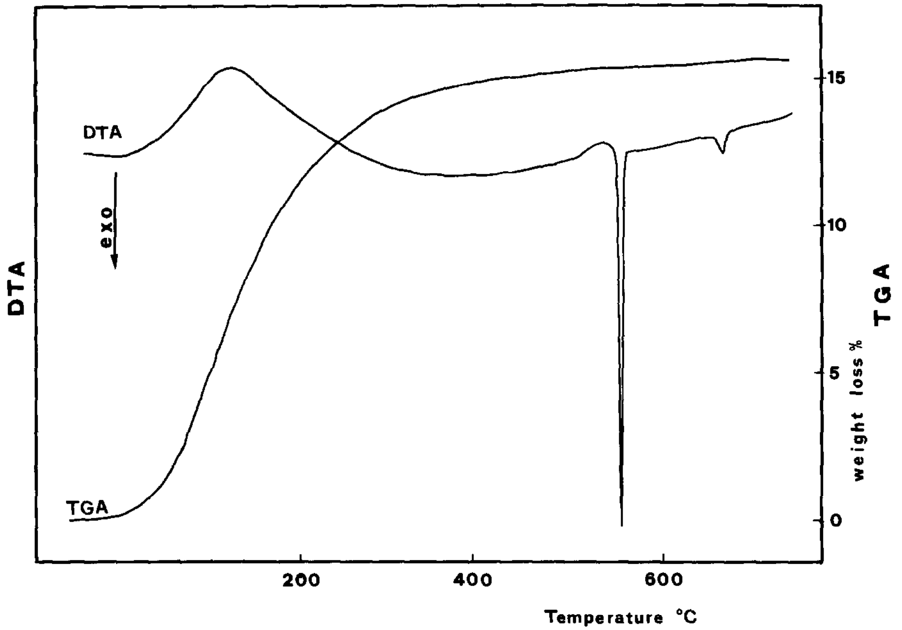

Fig. 2. DTA and TGA curves of the dried gel, recorded in N_2 at 10°C min^{-1}.

a lower temperature (0°C) allows (a) the control of the hydrolytic reactivity of TEOG so that soluble polymeric intermediates are obtained which then undergo further polymerization to form the gel, and (b) the introduction of modifier cation Li^+ into the germanate network according to eqn. (4).

The above reactions can be catalysed by acids or bases. The reaction mechanisms are not clear in every detail; however, it is generally accepted that they proceed through a second-order nucleophilic substitution [4]. The interaction between the electrophilic metal Ge and the nucleofic (H_2O or CH_3O^-) gives rise to addition (eqn. (1)) or substitution (eqn. (4)) reactions, respectively. Lithium methoxide is simultaneously the reagent and catalyst in the substitution reactions.

Figure 2 shows the TG/DTA curve of the dried gel. A large endothermic peak, from room temperature to about 380°C, appears on the DTA curve, with a maximum at about 115°C; a simultaneous weight loss of about 15% occurs in the TG curve. These effects were due to evaporation from open pores of the water and alcohol physically trapped in the gel.

The DTA curve of the gel exhibits a slope change that may be attributed to the glass transition (T_g = 500°C). A high, sharp exothermic peak appears just above the T_g on the DTA curve at 545°C.

At a higher temperature, 673°C, the DTA curve exhibits a second exo peak, smaller and broader than the first. The presence of two exothermic effects on the DTA curve of the studied gel suggests a crystallization process in two steps.

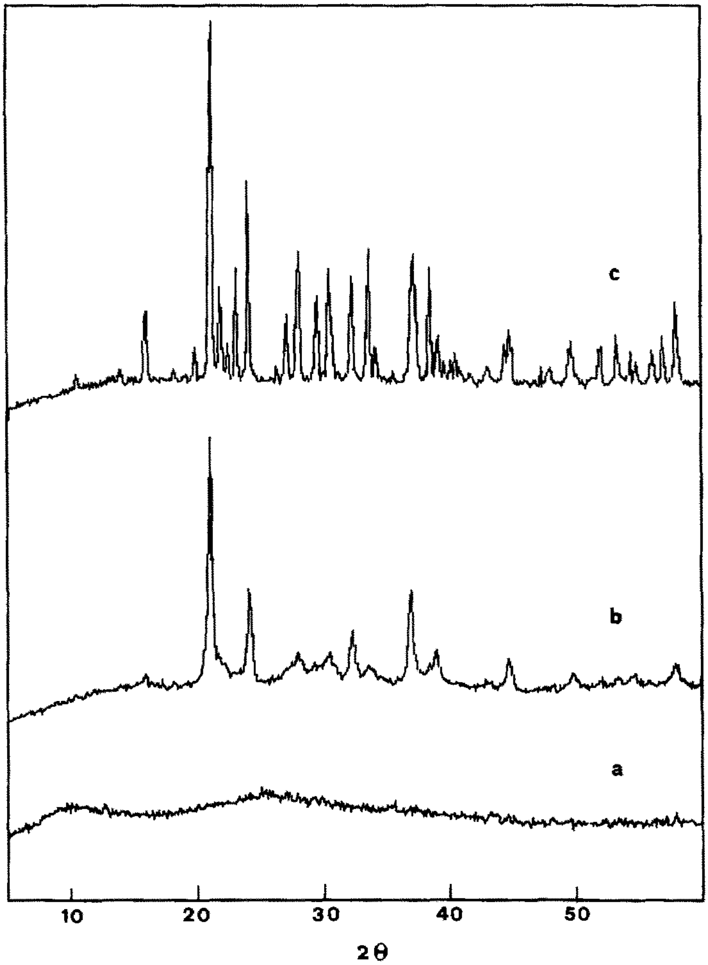

Fig. 3. Powder X-ray diffraction pattern for (curve a) dried gel; (curve b) sample of dried gel heated in DTA furnace up to the temperature of the first exo-peak; (curve c) sample of the dried gel after a DTA run from room temperature to 700°C.

X-ray diffraction analysis was used to identify the crystallizing phases. Only a few broad reflections of $Li_2Ge_7O_{15}$ can be detected on the XRD pattern of a gel sample heated in the DTA furnace up to the temperature (545°C) of the first exothermic peak (see trace (b) of Fig. 3). This result, in spite of the strong thermal effect on the DTA curve, suggests the precipitation of a high number of very small crystals. The XRD pattern (trace (c) of Fig. 3) of a gel sample heated in the DTA furnace up to the temperature (673°C) of the second exothermic peak exhibits a high number of sharp reflections that can all be assigned to $Li_2Ge_7O_{15}$ crystals (ASTM card 23-1180). This result indicates that the small second exothermic peak is due to a recrystallization process.

The DTA curves of $Li_2O \cdot 7GeO_2$ gel and oxide glass are compared in

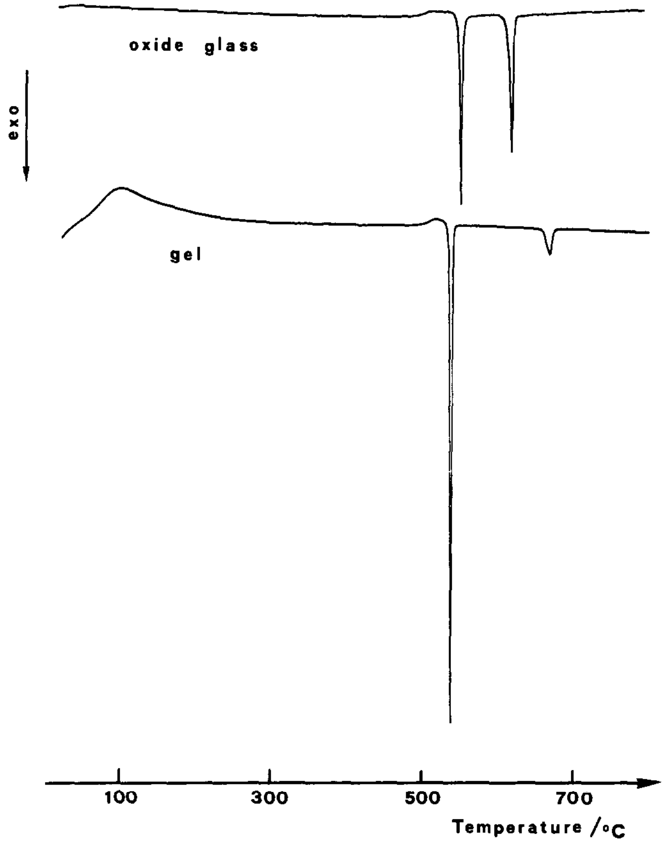

Fig. 4. DTA curves recorded in air at 5°C $\min^{-1}$.

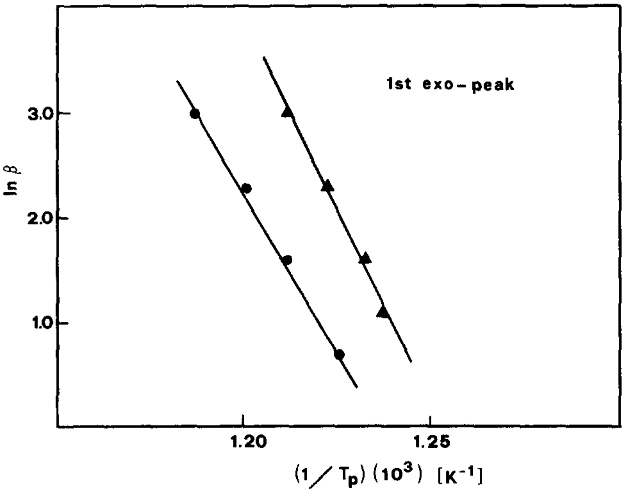

Fig. 5. Plot of ln β against $1/T_p$; (▲) gel; (●) oxide glass.

Fig. 4. The curves exhibit a slope change due to the glass transition at almost the same temperature, 500 and 491°C respectively, followed by two exothermic effects. In the gel glass, the second exothermic peak is much smaller than the first, while in the oxide glass the two exothermic peaks are the same size. This result is consistent with the crystallization mechanism.

In the gel glass a high number of microcrystallites of $Li_2Ge_7O_{15}$ are first formed that are then converted, at higher temperature, into well-shaped $Li_2Ge_7O_{15}$ crystals. The second crystallization step involves only the growth of the microcrystallites formed during the first step.

This crystallization behaviour is rather different from that of the corresponding oxide glass. Metastable microcrystallites of $Li_2Ge_4O_9$ in an amorphous matrix are first formed which are then converted at higher temperature into $Li_2Ge_7O_{15}$ crystals [3]. The second crystallization step involves a solid-state reaction in the oxide glass that is more complicated than that taking place in the gel glass.

The activation energy E for crystallization was evaluated from the DTA curves using the equation [5]

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

This equation is based on the temperature shift of the DTA crystallization peak T_p as the DTA heating rate β is changed. Multiple DTA runs were recorded in air at different heating rates on samples of powdered gel and bulk oxide glass. Plots of $\ln \beta$ against $1/T_p$ (Figs 5 and 6) give straight lines in all cases. The values of the activation energy calculated from their slopes are reported in Table 1. It can be observed that the values of E for the two crystallization steps of the gel are close to those of the oxide glass. Moreover, the value of E for the second crystallization step of the gel glass

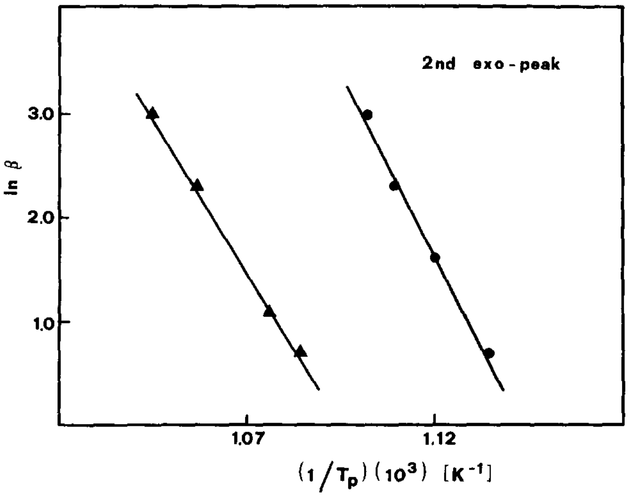

Fig. 6. Plot of $\ln \beta$ against $1/T_p$: (▲) gel; (●) oxide glass.

TABLE 1

Activation energy E (kJ mol^{-1}) for crystallization

Composition	First step	Second step
Gel	589	495
Oxide glass	531	523

is lower than that for the first crystallization step. This result is consistent with the XRD analysis and with the crystallization mechanism discussed above.

CONCLUSIONS

The gel preparation involves hydrolysis and polycondensation of germanium ethoxide with lithium methoxide. The gel thus prepared is an amorphous solid containing water and organic residues that are lost on heating. The temperatures required are well below the glass transition temperature of the glass being formed and, therefore, the gel is kinetically stable to crystallization during the heat treatment necessary for the conversion of the gel into glass. In the $Li_2O \cdot 7GeO_2$ gel heated at constant heating rate during a DTA run, the crystallization occurs in two steps, as in the corresponding oxide glass.

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