JOURNAL OF MATERIALS SCIENCE 30 (1995) 4076–4086

Sol–gel processing of lithium disilicate

Part I *Crystalline phase development of gel-derived powders*

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Lithium silicate powders were prepared by several sol–gel routes. Starting solutions contained equimolar amounts of lithium and silicon, but single-phase lithium disilicate ($Li_2Si_2O_5$) formed only when local stoichiometry was maintained through gelation and drying. Gels prepared from solutions containing $LiNO_3$, tetraethylorthosilicate (TEOS), water and ethanol were visibly homogeneous, but on drying the local stoichiometry was upset by the recrystallization of $LiNO_3$. Consequently, a lithium-rich phase (Li_2SiO_3) was the first to crystallize on heating with a lesser amount of $Li_2Si_2O_5$ forming at a higher temperature. Solutions containing TEOS and lithium methoxide formed a precipitate when combined with a water/ethanol hydrolysis solution. The precipitate dissolved before gelation, but the resulting powders crystallized into a mixture of Li_2SiO_3 and $Li_2Si_2O_5$. The relative amount of $Li_2Si_2O_5$ could be increased by adding HNO_3 to the hydrolysis solution and using lower water contents. Precipitation was avoided by partially hydrolysing TEOS before adding the lithium alkoxide; these powders crystallized directly into $Li_2Si_2O_5$ after heating at 550 °C. Gel-derived powders prepared using an Li–Si methoxyethoxide solution also crystallized directly into $Li_2Si_2O_5$.

1. Introduction

The microstructures and crystalline phase contents of glass-ceramics are controlled by manipulating nucleation and growth during heating of a glass [1]. The crystallization of lithium disilicate ($Li_2Si_2O_5$), a prototypical glass-ceramic, from melt-derived glasses, has been studied extensively [1–11]. This literature documents the effects of heating conditions and nucleating agents on nucleation [2–6], crystal growth [7, 8], and crystallization rates [1, 9]. The development of crystalline phases in melt-derived lithium silicate glasses is sensitive to the composition [11–13]. Stoichiometric glasses (i.e. 66.7 mol % SiO_2, 33.3 mol % Li_2O) crystallize directly into lithium disilicate. West and Glasser [13] reported that lithium disilicate has a solid solubility range (62–72 mol % SiO_2); solid solutions are less stable on the Li_2O-rich side. Glass compositions slightly rich in Li_2O crystallize into lithium metasilicate (Li_2SiO_3) in addition to disilicate. Silica-rich compositions undergo amorphous phase separation and crystallize first into lithium disilicate with cristoballite or quartz forming at higher temperatures. The wealth of experimental data and theoretical analyses make lithium disilicate a good model material for crystallization studies [10]. Despite the abundance of studies on melt-derived lithium disilicate, comparatively little work has been done on crystalline phase development of sol–gel derived lithium disilicate prepared from stoichiometric precursors [14–16].

Multicomponent silicate gels, glasses and ceramics are commonly prepared by sol–gel methods [17]. James [18] lists over 40 such binary, ternary, and multicomponent silicate systems. In the sol–gel method, multicomponent solutions are prepared by mixing and reacting alkoxide and salt precursors. The addition of water leads to hydrolysis and condensation, eventually forming a gel network. Examples of hydrolysis (Equation 1) and condensation (Equations 2 and 3) reactions for tetraethylorthosilicate (TEOS) are given by

$$Si(OC_2H_5)_4 + H_2O \rightarrow Si(OH)(OC_2H_5)_3 \quad (1)$$

$$Si(OC_2H_5)_4 + Si(OH)(OC_2H_5)_3 \rightarrow$$
$$(OC_2H_5)_3Si{-}O{-}Si(OC_2H_5)_3 + C_2H_5OH \quad (2)$$

$$Si(OH)(OC_2H_5)_3 + Si(OH)(OC_2H_5)_3 \rightarrow$$
$$(OC_2H_5)_3\,Si{-}O{-}Si(OC_2H_5)_3 + H_2O \quad (3)$$

For multicomponent systems in particular, solution synthesis and gelation conditions influence the distribution of chemical species in the gels and subsequent crystalline phase development during heat treatment (see, for example, [19, 20]). To enhance homogeneity, heterocondensation between silicate and other network forming species (e.g. aluminium and titanium alkoxides) is encouraged by prehydrolysing the less reactive silicon alkoxide (see, for example, [21, 22]). For alkali silicates, achieving chemical homogeneity is

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more challenging because alkali alkoxides are monofunctional and susceptible to hydroxide formation by rapid hydrolysis [23]. Further, Sanchez and McCormick [24] reported that alkali ions become bound by electrostatic forces to the silicate network under base conditions; Si–O^- ··· Li^+ bonds are favoured relative to Si–OH and Si–OEt, but not relative to Si–O–Si. That is, as polymerization continues, lithium cations are more likely to be excluded from the silicate network.

Materials in the Li_2O–SiO_2 and Li_2O–Al_2O_3–SiO_2 systems have been prepared by sol–gel methods using a variety of precursors [14–16, 25–31]. Schwartz *et al.* [25] studied the incorporation of lithium cations into lithium silicate gels (15 mol % Li_2O) prepared by combining a partially hydrolysed TEOS solution with an aqueous $LiNO_3$ solution. Lithium distribution was found to be uniform (without surface segregation), indicating that lithium cations become associated with the silicate network and are not leached out during drying. On heating, lithium nitrate recrystallized and at higher temperatures (600–800 °C) lithium disilicate and quartz formed. In another study [29], the crystallization temperature for lithium silicate gel-derived glasses (15 mol % Li_2O) was found to be lower for gels made using LiOH as compared with those prepared with $LiNO_3$. The high pH of the solution containing LiOH also led to a faster condensation rate for silicate species. Nuclear magnetic resonance (NMR) investigations [29, 30] showed that lithium ions were more strongly attached to the silicate network for the LiOH-prepared materials. Alkoxides have also been used for lithium precursors; for example, Chen and James [31] used a mixture of lithium isopropoxide and partially hydrolysed tetramethylorthosilicate to prepare lithium silicate gels (10 mol % Li_2O).

A few sol–gel studies have included the formation of lithium disilicate from stoichiometric (~33 mol % Li_2O) systems. Smaihi *et al.* [14] prepared lithium silicate gels with a range of lithium contents (0, 33, 66, 80 mol % Li_2O), using solutions of $LiNO_3$ and partially hydrolysed TEOS. For the 33 mol % Li_2O sample, a combination of $Li_2Si_2O_5$ and Li_2SiO_3 formed at 600 °C and by 800 °C, $Li_2Si_2O_5$ was dominant. However, the samples did not convert entirely to lithium disilicate. Beier *et al.* [15] prepared a range of lithium silicate compositions using lithium and silicon alkoxides, and lithium salts and silicon alkoxides. They found that stoichiometric gels formed into a mixture of lithium disilicate and lithium metasilicate. Branda *et al.* [16] formed gels (33 mol % Li_2O) by combining a partially hydrolysed TMOS with a suspension of lithium methoxide in ethanol. Thermal analysis of dried gel-derived powders showed that crystallization occurred at ~550 °C and X-ray diffraction revealed that lithium disilicate formed with a very small amount of lithium metasilicate. A route similar to sol–gel has recently been proposed by Kansal and Laine [32]. In their procedure, a lithium glycolao silicate is prepared, pyrolysed and crystallized into a nearly phase-pure $Li_2Si_2O_5$. Results from previous studies on sol–gel derived lithium silicates show that the crystallization behaviour depends on composition in the Li_2O–SiO_2 system and processing procedures. However, the phase development for stoichiometric sol–gel derived lithium disilicate has not been addressed in detail.

In Part I of this report, we investigate the effects of precursor chemistry, gelation conditions and thermal treatment conditions on crystalline phase development of sol–gel derived lithium silicate with a Li : Si molar ratio of 1 : 1. Our main goal was to crystallize lithium disilicate directly from amorphous gel-derived material without second phases. In Part II [33], we investigate crystallization and microstructure control in sol–gel derived lithium disilicate thin films.

2. Experimental procedure

2.1. Solution and gel preparation

All gels prepared in this study contained equimolar amounts of lithium and silicon in order to ideally produce crystalline lithium disilicate ($Li_2Si_2O_5$). Three solution routes were investigated: (i) $LiNO_3$ combined with TEOS, (ii) $LiOCH_3$ combined with TEOS (or partially hydrolysed TEOS) in ethanol, and (iii) $LiOCH_3$ combined with TEOS in 2-methoxyethanol.

For the nitrate route, a stock solution was prepared by combining $LiNO_3$, TEOS, water and ethanol. Lithium nitrate was first dissolved in distilled water and then added to TEOS with dry ethanol added to permit miscibility. The resulting stock solution had a concentration of 1.32 M (in lithium and silicon) and a hydrolysis ratio ($r = [H_2O]/[Si]$) of 5. To produce sols with different hydrolysis ratios and concentrations, hydrolysis solutions containing ethanol and water were mixed with the stock solution. Preliminary experiments were carried out to determine the effect of concentration, r, and temperature on the gelation behaviour. Based on this study, the following procedure was used to prepare samples. Portions of the stock solution were combined with the appropriate hydrolysis solutions to obtain solutions with hydrolysis ratios of 5, 10, 15 and 20 and a constant concentration ($[Li] = [Si] = 1$ M). The combined solutions were immediately sealed and mixed by shaking. Sealed containers were placed in a oven at 65 °C. Gel times (i.e. time at which no flow is observed on tilting the container) were determined. Gels were dried overnight at 65 °C, and then crushed into a powder and stored in sealed containers.

Two methods were used to prepare ethoxide-based solutions. In the first, equimolar amounts on lithium methoxide and TEOS were combined in dry ethanol and refluxed at 70 °C for ~1 h. After refluxing, volatiles (including methanol), were removed by distillation. During the reflux, an alcoholysis reaction occurs according to

$$LiOCH_3 + C_2H_5OH \rightarrow LiOC_2H_5 + CH_3OH \quad (4)$$

The extent of the reaction was not monitored quantitatively. The solution was rediluted with ethanol and the procedure repeated. The final stock solution contained equimolar amounts of lithium and silicon ($[Li] = [Si] = 0.75$ M). In the second method, the

TABLE I Summary of gelation conditions

Route	Concentration[a] (M)	Hydrolysis ratio, r	Additive
Nitrate	1	5, 10, 15, 20	None
Ethoxide	0.05	5	None
	0.1	5	None
	0.25	5	None
	0.30	5	None
	0.375	1, 2, 3, 4, 5	None
	0.375	3	HNO_3 ($a = 0.1, 0.3, 0.5$)
	0.375	3	NH_4OH ($a = 0.1$)
	0.375	3	CH_3COOH ($a = 0.1$)
Ethoxide (partially hydrolysed TEOS)	0.375	3, 5	None
Methoxyethoxide	0.375	3, 5	None

[a] [Li] = [Si].

TEOS was first partially hydrolysed before combination with the lithium alkoxide. The partially hydrolysed solution was prepared by mixing TEOS, ethanol, water and HCl in a molar ratio of 1:3:1:0.0007 at 60 °C for 1.5 h, according a procedure described by Brinker *et al.* [34]. An appropriate amount of lithium methoxide (dissolved in ethanol) was added and the mixture was stirred overnight at room temperature under flowing dry nitrogen. Ethanol was added to give a final concentration of 0.75 M.

Gels were prepared by mixing portions of the ethoxide stock solutions with hydrolysis solutions containing ethanol, water and sometimes an additive (nitric acid, acetic acid, or ammonium hydroxide). The relative amount of additive in the combined solution will be designated by an additive ratio (a = [additive]/[Si]). Several gelation conditions were investigated for the ethoxide system without partial hydrolysis. See Table I for a summary of gelation conditions for all routes. Combinations of stock solution and hydrolysis solution were sealed and held at room temperature. Gelation behaviour was observed and gel times were recorded in most cases. Gels were placed in open containers and dried overnight at 100 °C; dried gels were crushed into powders and stored in sealed containers.

For the methoxyethoxide route, a stock solution was prepared according to a procedure similar to that described above for the first ethoxide route. TEOS and lithium methoxide were combined in 2-methoxyethanol (2-MOE), and refluxed at 125 °C for 1 h. After refluxing, volatiles (including methanol and ethanol) were removed by distillation. Alcoholysis reactions are possible during reflux for both the lithium and silicon alkoxides in 2-MOE. (An NMR investigation of a TEOS solution after reflux with 2-MOE revealed that approximately 80% of ethoxide groups are replaced with methoxyethoxide groups.) The solution was rediluted with 2-MOE and procedure repeated. The final stock solution contained equimolar amounts of lithium and silicon ([Li] = [Si] = 0.75 M). For the methoxyethoxide route, gels were prepared by combining equal volumes of the stock solution with a hydrolysis solution containing 2-MOE and water (see Table I). Gels were dried overnight at 150 °C; dried gels were crushed into powders and stored in sealed containers.

2.2. Heat treatment

Dried gel-derived powders were heat treated in a box furnace. Powders prepared by the nitrate route were heated in air for 60 min at 350–750 °C, using a heating rate of 5 °C min^{-1} to safely decompose nitrates. Specimens were removed from the furnace (air quenched) after the treatment. Gel-derived powders prepared by the ethoxide route were heated for 60 min at 450–650 °C with heating rate of 5 °C min^{-1}. In addition, powders prepared by the ethoxide and methoxyethoxide routes were heated isothermally at 500, 550, and 600 °C for 30 min. In an isothermal treatment, a sample is inserted into a preheated furnace (at the final temperature) and air quenched after 30 min. Some higher temperature and longer term heat treatments were also carried out.

2.3. Characterization

The effects of processing conditions on organic decomposition and crystalline phase development were investigated using differential thermal analysis (DTA) and thermogravimetric analysis (TGA) and X-ray diffraction (XRD). A Perkin–Elmer DTA 1700 system and a Perkin–Elmer 1020 series TGA 7 thermogravimetric system were used. For both thermal analysis techniques, a heating rate of 10 °C min^{-1} was used from 25–800 °C with an air flow rate of 40 cm^3 min^{-1}. The mass of the samples was kept roughly constant. Crystalline phase development of heat-treated powder samples was analysed using a Rigaku D-Max X-ray diffractometer with monochromatic CuK_α radiation. Diffraction patterns were typically recorded from $2\theta = 10°$–$45°$ as this range contained the major peaks from the relevant crystalline phases; data were also taken using wider 2θ ranges.

3. Results and discussion

3.1. Nitrate route

3.1.1. Gelation behaviour

The effects of concentration and temperature on gel time for sols prepared by the nitrate route are shown in Table II. The gel time decreased as the solution concentration increased (at constant r) and was

TABLE II Gel times for materials prepared by the nitrate route

r	Concentration[a] (M)	Gel time at 25 °C (h)	Gel time at 65 °C (h)
10	0.63	64	6
10	0.70	46	4.5
10	0.80	38	3.7
10	0.94	24	2.2
10	1.13	15	1.5
4.2	0.94		13
7.0	0.94		4.5
10	0.94		2.75
13	0.94		2.0
16	0.94		1.5
19	0.94		1.16

[a] [Li] = [Si].

shorter for 65 °C as compared with 25 °C. The gel time also shortened with increasing hydrolysis ratio (at constant concentration). These trends are expected considering that rates of the hydrolysis and condensation reactions increase with temperature and generally increase with reactant concentration ([Si], [H_2O]). All gels were homogeneous in general appearance and nearly transparent. Interestingly, the gel time for lithium nitrate containing TEOS sols is considerably shorter than TEOS sols alone [17] at the same pH (~3–4). Smaihi *et al.* [14] observed the same effect over a range of $LiNO_3$/TEOS ratios and hypothesized that lithium cations catalyse the condensation of silicate species.

3.1.2. Crystalline phase development

Fig. 1a shows DTA and TGA data for powders prepared by the nitrate route. Powders were dried at 65 °C before analysis. Removal of physically bound water and solvent occurs at 25–120 °C, as evinced by a weight loss in the TGA data and an endotherm in the DTA data. The second endotherm at 255 °C can be assigned to the melting of lithium nitrate. The presence of this endotherm indicates that lithium nitrate recrystallizes, probably around the temperature at which water evaporates. Gels dried at 110 °C contained lithium nitrate (as determined by XRD), while those dried at 65 °C were amorphous. Gradual weight loss from organic decomposition and continued condensation is evident from 120–500 °C. Nitrates decompose in the temperature range 500–650 °C with a corresponding broad endothermic peak in the DTA data at ~550 °C. This endotherm probably masks an exotherm for the crystallization of lithium silicate phases (Li_2SiO_3, $Li_2Si_2O_5$) that are known to form by XRD analysis.

The hydrolysis ratio used for gelation affected the thermal analysis data. The magnitude of the weight loss for water and solvent evaporation (25–120 °C) increased with increasing hydrolysis ratio. Gel-derived powders prepared using higher hydrolysis ratios lost more weight in this first step because greater amounts of water were added initially and more volatiles (i.e. H_2O, C_2H_5OH) were generated by condensation. In the intermediate temperature range (120–500 °C), these powders lost less weight than their lower r counterparts. The endotherm for melting of lithium nitrate decreases in magnitude with increasing hydrolysis ratio, indicating that a lesser amount of nitrate may crystallize in these gels. The nitrate decomposition endotherm at 550 °C and the higher temperature weight loss were not significantly affected by hydrolysis ratio (all samples contain the same amount of nitrate). The weight loss in the final step is slightly less than that predicted based on original sol composition; some nitrates may be removed with the solvent during drying [27].

X-ray diffraction data for powders prepared by the nitrate route are shown in Fig. 1b. As discussed, lithium nitrate recrystallizes at low temperatures and is present in specimens examined after heat treatments up to 400 °C. Lithium metasilicate (Li_2SiO_3) is the first lithium silicate phase to form (~450 °C). Unidentified diffraction peaks near $2\theta = 26°$ and 28° appear in the XRD data for gels prepared with the lower hydrolysis ratio ($r = 5$, 10) and heated to 500 °C. These peaks are not found for powders prepared with higher hydrolysis ratios. Lithium disilicate ($Li_2Si_2O_5$) forms after heat treatments at 550 °C (for $r = 10$, Fig. 1b). The sequence of phase formation is the same for all powders prepared by the nitrate route, but there are some variations with hydrolysis ratio. Gels prepared with lower hydrolysis ratios formed lithium disilicate at lower temperatures (e.g. after the heating at 500 °C for $r = 5$ and 600 °C for $r = 20$). Crystalline SiO_2 (quartz) forms in all at around 750 °C. The relative amount of $Li_2Si_2O_5$ in the mixture was somewhat higher for the specimens prepared with lower hydrolysis ratio.

The recrystallization of lithium nitrate in gel-derived powders results in the formation of local lithium-rich and lithium-poor regions. Therefore, the first lithium silicate phase to form is the lithium-rich lithium metasilicate (Li_2SiO_3) phase. At higher temperatures, lithium disilicate forms either by reaction and diffusion of lithium cations into the silica-rich matrix or by crystallization from regions which have maintained local stoichiometry. The larger scale distribution of lithium is likely to be uniform; Schwartz *et al.* [25] report that the Li^+ distribution remains constant over a bulk gel monolith. The degree of local homogeneity appears to depend on hydrolysis ratio; gels prepared using lower hydrolysis ratios form lithium disilicate at lower temperatures and in slightly greater abundance. Interestingly, DTA appears to show that more nitrate forms in lower hydrolysis ratio gels which seems contrary to the observed lower temperature $Li_2Si_2O_5$ formation. Differences in gel structure and the $LiNO_3$ crystallite size and distribution in the gels with hydrolysis ratio may play a role. Overall, the differences between gels prepared with different hydrolysis ratios are minor in comparison to the gross difference between the expected crystalline phase distribution (100 % $Li_2Si_2O_5$) and the observed mixture of phases.

3.2. Ethoxide routes

3.2.1. Gelation behaviour

The ethoxide-based solution (prepared without partial hydrolysis of the TEOS) underwent a visibly different

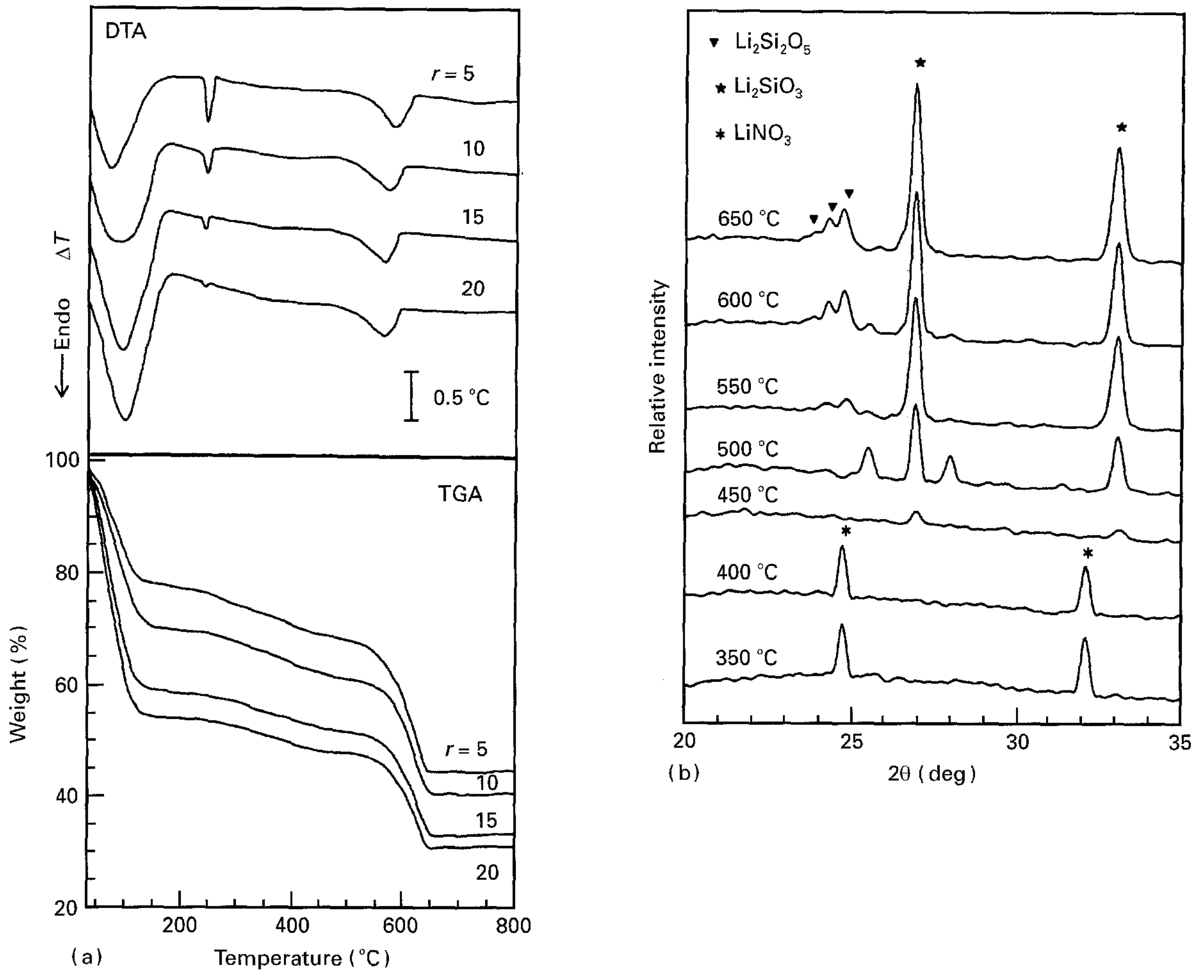


Figure 1 (a) Effect of hydrolysis ratio, (r), on DTA/TGA data for gel-derived powders prepared by the nitrate route. (b) Crystalline phase development for powders prepared by the nitrate route ($r = 10$) and heated (5 °C min^{-1}) to the temperatures given for 1 h.

gelation process than other gels in this study. After combination with the water/ethanol hydrolysis solution, the ethoxide solution changed quickly from clear to cloudy and then, more slowly, back to clear again before gelation. The cloudiness is most likely due to precipitation of lithium hydroxide according to

$$LiOC_2H_5 + H_2O \rightarrow LiOH + C_2H_5OH \qquad (5)$$

This conclusion is supported by the observation that copious amounts of precipitate form when a water/ethanol hydrolysis solution is added to a solution of lithium methoxide in ethanol (without TEOS). The hydroxide precipitate was very fine and did not settle out of suspension. The precipitation time (i.e. the time required for formation of visible precipitate), the dissociation time (i.e. the time required for the solution to clear) and the gel time, are listed in Table III for gels prepared with different hydrolysis ratios. The times for precipitation, dissociation and gelation shortened with increasing hydrolysis ratio. The precipitation reaction was very rapid in all cases except for the lowest hydrolysis ratio ($r = 1$) . Dissociation of the LiOH precipitate ($LiOH \rightarrow Li^+ + OH^-$) was slower. For $r > 1$, only a portion of the water is consumed by the formation of lithium hydroxide; the remainder is available for the hydrolysis and condensation of silicate species. The precipitate dissolution may be linked to the production of water and alcohol by silicate condensation. (LiOH is soluble in water.) Precipitation will lead to local chemical heterogeneity as silicate condensation occurs while lithium is isolated in the precipitate phase. The gelation behaviour of solutions with concentrations ranging from 0.1–0.375 M and a constant hydrolysis ratio of 5 was also studied. These specimens went through the precipitation and dissociation steps before gelation. Gel times decreasing predictably from 35 h to 50 min from least to most concentrated conditions.

TABLE III Gelation behaviour for materials prepared by the ethoxide route[a]

r	Precipitation time	Dissociation time	Gel time (h)
1	168 h	–	–
2	4 min	8 h	–
2.5	2 min	5 h	155
3	1 min	2.5 h	6
4	5 s	50 min	2
5	1 s	15 min	1

[a] Without partial hydrolysis of TEOS, no additives, [Li] = [Si] = 0.375.

Two methods were used to try to eliminate precipitation. In the first, the effect of additives on precipitation, dissolution and gelation phenomena was investigated. Sols were prepared using different additives (HNO_3, CH_3COOH, NH_4OH) with other conditions identical (concentration = 0.375 M, $r = 3$). All of these specimens formed precipitates, but the amount and persistence of the precipitate varied. The addition of NH_4OH increased the apparent amount of precipitate and lengthened the time for dissociation. By contrast, the sol containing HNO_3 had much less precipitate and the slight amount of precipitate dissolved more quickly. The acetic acid additive also decreased the precipitate amount, but to a lesser extent. Thus, acidic conditions were less favourable for the hydroxide formation and aided in precipitation dissolution. Interestingly, the gel time for sols with added NH_4OH, HNO_3 and without additive were nearly the same (~6 h), while the gel time for acetic acid containing sols was longer (~7 h). Chelation with the acetate ligand may lower hydrolysis and condensation rates [35]. The gelation time for the ethoxide sols was much shorter than that for the sols prepared by the nitrate route. For example, at $r = 4$ and [Si] = 0.375 M, the gelation time is 2 h for the ethoxide sols and 13 h for the nitrate sols. A similar contrast was reported for lithium disilicate gels prepared from lithium nitrate and lithium hydroxide precursors, and attributed to the catalytic effect of the OH^- ions on silicate condensation [30].

The effect of nitric acid concentration on gelation behaviour for sols with a hydrolysis ratio of 3 and concentration of 0.375 M was also investigated. With increasing nitric acid concentration, the apparent amount of precipitate decreased and the dissociation occurred more quickly. Nitric acid neutralizes the basic lithium hydroxide. The gel times decreased from 6 h to 1.5 h as the HNO_3 concentration increases from 0.1 M to 0.5 M, presumably due to the enhanced rates of hydrolysis and condensation of silicate species.

The second attempt to enhance homogeneity was partially to hydrolyse TEOS before adding the lithium alkoxide. On addition of the water/ethanol hydrolysis solution to this mixture, uniform gels formed without intermediate precipitate formation. Partially hydrolysed TEOS can react with the added lithium alkoxide according to

$$\begin{aligned} &LiOC_2H_5 + Si(OH)(OC_2H_5)_3 \rightarrow \\ &\quad Li\text{–}O\text{–}Si(OC_2H_5)_3 + C_2H_5OH \qquad (6) \end{aligned}$$

When additional water is added, precipitation does not occur because the lithium alkoxide is no longer free to react. The acidified condition of the partially hydrolysed TEOS may also play a role in preventing precipitation. Gelation occurs more quickly when partially hydrolysed TEOS is used. For example, ethoxide sols with equivalent hydrolysis ratios ($r = 3$) and concentrations (0.375 M) differ by a factor of four in gel time. Consequently, the rate-limiting step in the gelation may be the hydrolysis.

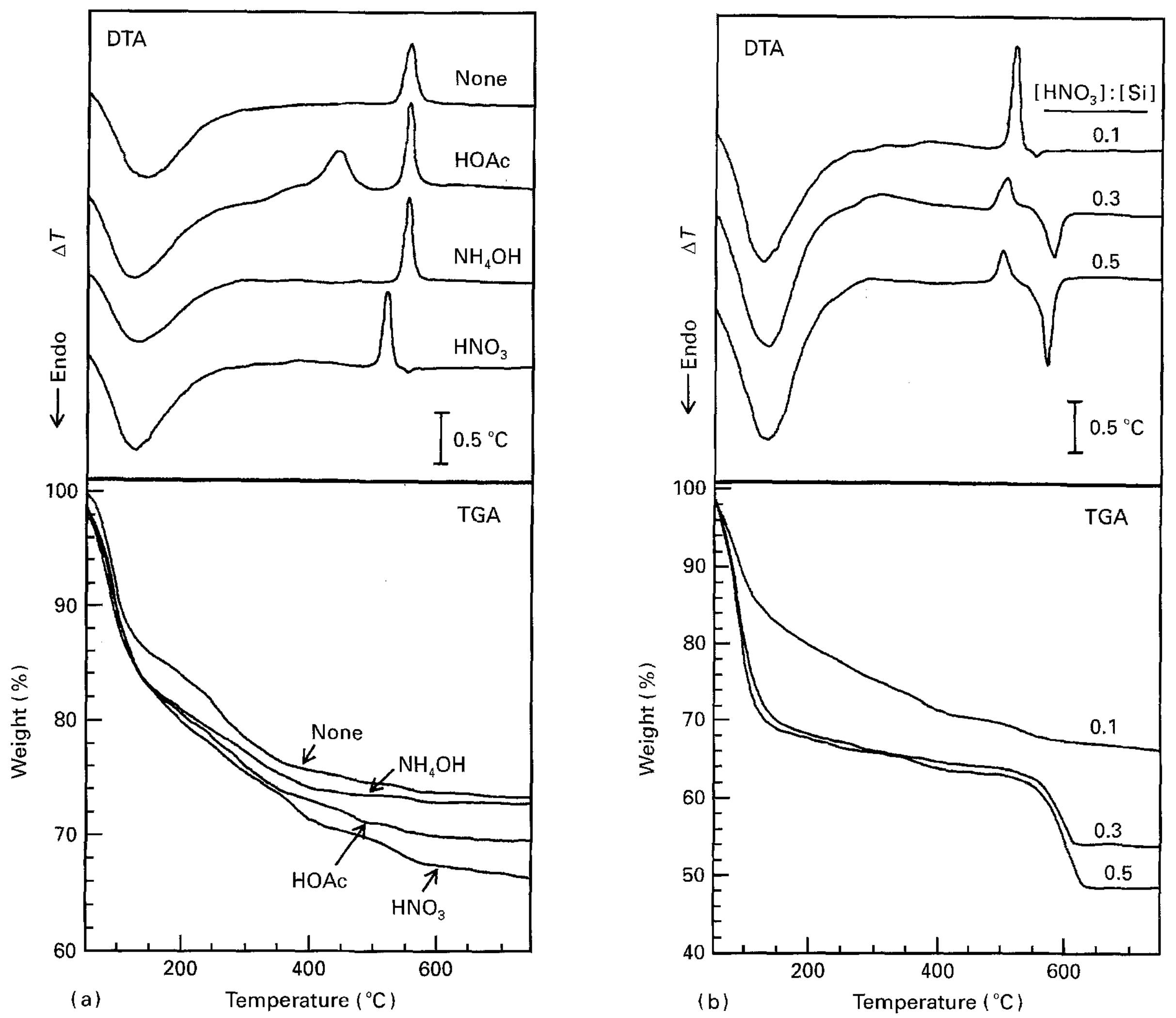
3.2.2. *Crystalline phase development*

Thermal analysis data for gel-derived powders prepared using the ethoxide route without partial hydrolysis are shown in Fig. 2a. First the powder prepared without additive will be considered. Removal of physically bound volatiles occurs at 100 °C with an endotherm in the DTA and weight loss in the TGA data. TGA data shows a more gradual weight loss from 150–550 °C for removal of residual organics. An exothermic peak corresponding to crystallization of lithium silicate phases ($Li_2Si_2O_5$, Li_2SiO_3, see XRD results below) occurs at ~540 °C. Thermal analysis data were also acquired for gel-derived powders prepared without additive and with range of hydrolysis ratios (1–5) and concentrations ([Li] = [Si] = 0.1–0.5 M). Data for these powders have similar features as the data presented in Fig. 2a (curves labelled none); the total weight loss varied only slightly, and the crystallization temperature was not affected significantly. Gel-derived powders prepared with NH_4OH and CH_3COOH additives also had a DTA crystallization temperature of ~540 °C. The additional exotherm (~360 °C) for the gel-derived powders prepared with CH_3COOH is due to acetate decomposition. XRD analysis of the powder after this exotherm showed that the sample was still amorphous.

Gel-derived powders prepared with HNO_3 exhibited distinct decomposition and crystallization behaviour (Fig. 2). The crystallization exotherm occurs at a lower temperature (~500 °C) than other materials in this study. Following this exotherm, an endotherm in the temperature range 550–650 °C appears with a corresponding weight loss in the TGA data. Thus nitrate decomposition occurs after crystallization. Because XRD data indicate that no crystalline nitrate compound formed after the crystallization of lithium disilicate, nitrate species must be trapped in the crystalline structure, pore structure or a residual glassy phase until they are removed. The DTA data show that the crystallization becomes less exothermic, while the decomposition becomes more endothermic with increasing HNO_3 concentration. The lower DTA crystallization temperature relative to other materials in this study and others [16] may reflect a greater chemical homogeneity in the gel. Another possibility is that nitrate anions modify the gel-derived glass structure; Livage *et al.* [36] discuss the potential for network modification by nitrate terminal groups.

Although the TGA data shows that weight loss is complete by ~700 °C, chemical analysis (by inductiively coupled plasma mass spectrometry) of powders heated to 800 °C revealed a small amount of residual carbon. All alkoxide gel-derived powders were brown except the powder prepared with the nitric acid additive which was white. The concentration of carbon is six times higher in samples prepared without additive (0.97 wt %) as compared with samples prepared with HNO_3 (0.17 wt %). The difference may be related to the oxidizing power of HNO_3. All powders became white when heated at 1000 °C in oxygen.

Fig. 3 shows XRD data from powders prepared from the ethoxide route and heat treated at 450–650 °C. The powder is amorphous after the 450 °C treatment; after the 500 °C treatment lithium metasilicate and lithium disilicate crystallize. The presence of both lithium silicate phases indicates that the chemical heterogeneity originating from the lithium hydroxide precipitate persists. With increasing



(a)

(b)

Figure 2 (a) DTA/TGA data for gel-derived powders prepared by the ethoxide route ($r = 3$, [Li] = [Si] = 0.375) without and with additives ($a = 0.10$). (b) Effect of nitric acid additive amount on DTA/TGA data for gel-derived powders prepared by the ethoxide route ($r = 3$, [Li] = [Si] = 0.375).

heat-treatment temperature, the amorphous background diminishes but the relative amount of lithium disilicate does not increase. Because a mixture of Li_2SiO_3 and $Li_2Si_2O_5$ forms, a silica-rich amorphous phase must also be present. The relative amount of the amorphous phase could not be determined exactly due to a small contribution of the glass sample holder to the XRD data. On heating to 800 °C for 1 h, no additional crystalline phases formed. Crystallization was affected by the hydrolysis ratio as shown in Fig. 3b. Gels prepared with lower hydrolysis ratios crystallize into greater amounts of the lithium disilicate. In addition, XRD studies of powders prepared with varying concentration and fixed r show that lithium disilicate formation is favoured for the lower concentration samples. From these data, we infer that the specimens prepared with low hydrolysis ratio and concentration are more chemically homogeneous. These conditions tended to lengthen the gelation process (including the times for precipitate formation, dissociation and gelation) and may have given greater opportunity for the distribution of lithium cations in the silicate network.

Additives have a dramatic effect on the crystalline phase development, as shown in Fig. 4. Both lithium silicate phases form in the gel-derived powders prepared using NH_4OH, although the relative amount of disilicate is greater than without additive. This result is curious considering that visibly more precipitate formed when NH_4OH was added. However, the precipitate dissolved before gelation and the distribution of lithium may have been improved by the enhanced tendency for lithium cations to bond to the silicate network in basic conditions [24, 29]. Lithium disilicate is the dominant crystalline phase for powder prepared with the acetic acid additive; this additive decreases the precipitation and may have influenced structure through chelation. The powders prepared using HNO_3 formed lithium disilicate after a 600 °C isothermal heating (see Fig. 4). Powders prepared with a range of nitric acid concentrations (see Table I) showed the same crystalline phase distribution after the 600 °C isothermal heating. The nitric acid additive clearly reduced precipitate formation leading to greater homogeneity. After heating for 4 h at 600 °C, the diffraction peaks sharpened, but no additional crystalline phases appeared. The lithium disilicate (130) diffraction peak ($2\Theta \sim 24°$) was of low intensity for these samples, even after extended heating. West and Glasser [13] found that a similar change in

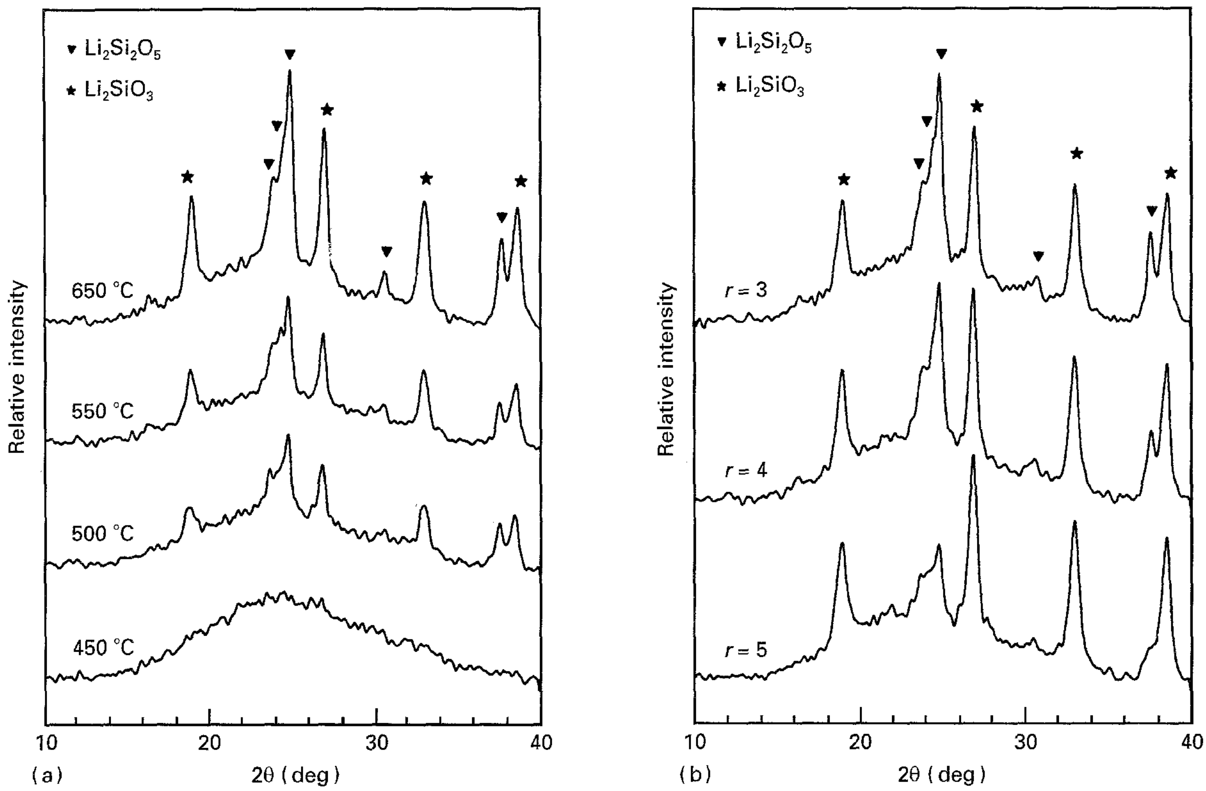


Figure 3 (a) Crystalline phase development for gel-derived powders prepared by the ethoxide route ($r = 3$, [Li] = [Si] = 0.375) and heated (5 °C min^{-1}) to the temperatures given for 1 h. (b) Crystalline phase development of gel-derived powders prepared by the ethoxide route (varying r, [Li] = [Si] = 0.375) and heated isothermally at 600 °C for 30 min. Note that the phase distribution is not sensitive to the heating rate.

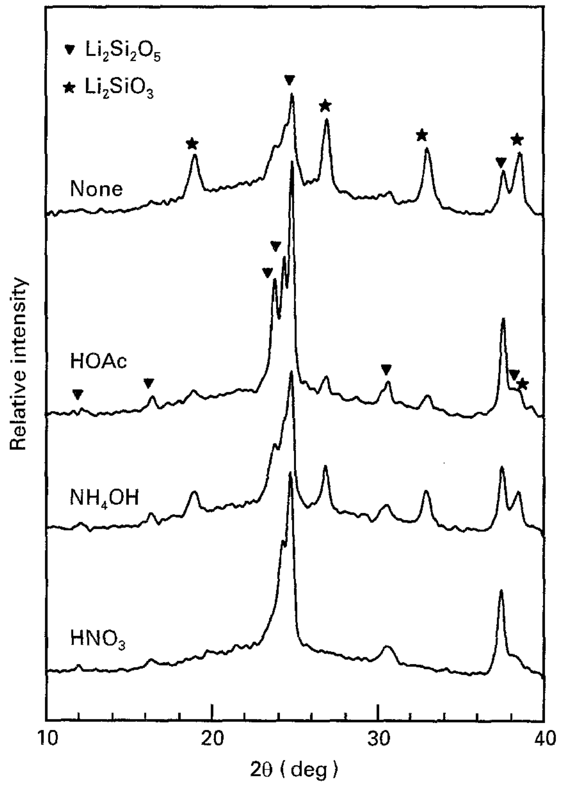


Figure 4 Crystalline phase development for gel-derived powders prepared by the ethoxide route ($r = 3$, [Li] = [Si] = 0.375) with different additives ($a = 0.1$) and heated isothermally at 600 °C for 30 min.

diffraction pattern occurred in slightly silica-rich samples that contain fibular lath-shaped crystals, presumably due to an orientation effect.

Fig. 5 shows thermal analysis and XRD data for gel-derived powders prepared using partially hydrolysed TEOS. TGA data show gradual weight loss up to ~500 °C. The overall weight loss was lower for these gel-derived powders compared to those prepared without partial hydrolysis of TEOS. Partial hydrolysis allowed a greater amount of condensation and thus the elimination of more volatiles during the drying process (100 °C) before TGA analysis. The small difference between the gel-derived powders prepared with different hydrolysis ratios is due to the same effect (i.e. differences in the amount of condensation generated volatiles). The DTA crystallization temperatures were somewhat higher than the other ethoxide-based powders (~562 °C for $r = 3$ and ~575 °C for $r = 5$). XRD data show direct crystallization of the lithium disilicate phase. Lithium disilicate crystallized regardless of the heating rate and the lithium metasilicate phase was not detected by XRD for powders heated up to 600 °C. In this case, reaction between the partially hydrolysed TEOS and lithium alkoxide prevents precipitation and results in bonding of lithium cations to the silicate network. When amorphous gel-derived powder was heated quickly from room temperature to a higher temperature (800 °C) and held for 2 h, a mixture of lithium disilicate and lithium metasilicate formed. However, a sample heated for 4 h at 600 °C and then heated to a higher temperature did not form lithium metasilicate. The rapid heating may not have given adequate time for nucleation and growth of the disilicate; at higher temperatures the greater mobility of Li^+ might allow formation of the simpler lithium metasilicate

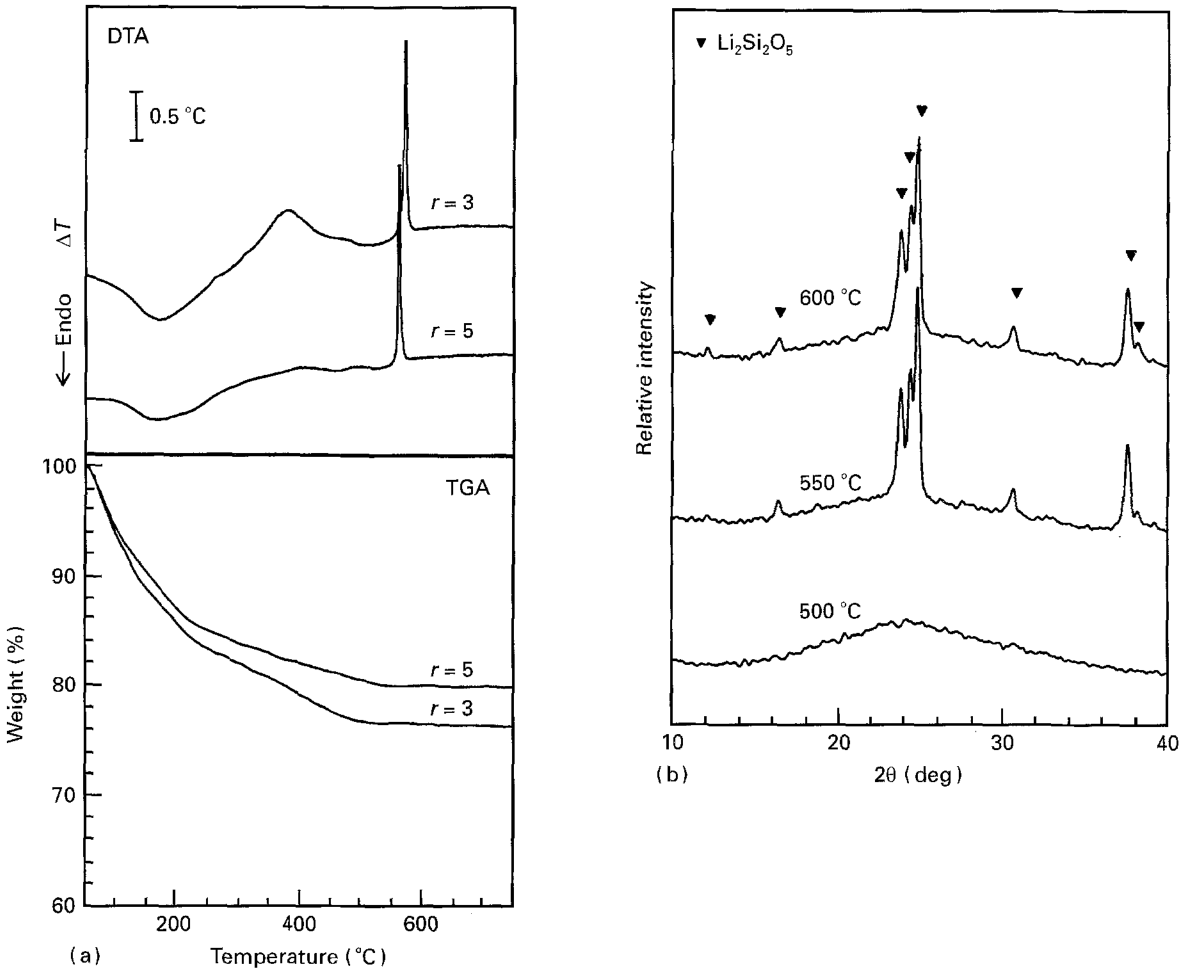


Figure 5 (a) DTA/TGA data for gel-derived powders prepared by the ethoxide route using partially hydrolysed TEOS ($r = 3$ or 5, [Li] = [Si] = 0.375). (b) Crystalline phase development for gel-derived powders prepared by the ethoxide route with partially hydrolysed TEOS ($r = 3$, [Li] = [Si] = 0.375) and heated isothermally at the temperatures given for 30 min.

structure. Similar results were obtained for gel powders prepared with nitric acid addition.

The crystallization of lithium disilicate from gels prepared using stoichiometric Li–Si ethoxide solutions can be interpreted by considering the lithium distribution in the gels. When water is added to the ethoxide solution, immediate hydrolysis of the lithium alkoxide results in precipitation of LiOH. With time this precipitate dissolves, but prior to dissolution, hydrolysis and condensation reactions take place to form silicate oligomers. The degree to which the lithium ions can become associated and distributed in the silicate network is affected by the relative rates of condensation of the silicate species and dissolution of the precipitate. With the higher hydrolysis ratio (and higher concentration), the amount of time between the dissolution and the final gel formation is shortened (for ethoxide route with no additives), increasing the likelihood that the lithium-rich and silicon-rich areas remain in the gel. These conditions result in a less homogeneous gel, as evidenced by lesser amount of disilicate formation. The addition of nitric acid to the hydrolysis solution decreased the amount of precipitate and increased the amount of lithium disilicate. The use of partially hydrolysed TEOS allowed gelation to occur without precipitation-induced heterogeneity. A more uniform distribution of lithium cations in the silicate network was achieved and retained through gelation and drying. As a result, the gel-derived powders crystallize directly into lithium disilicate. NMR investigations of the time evolution of the silicate species before, during and after precipitate dissolution would be helpful to document chemical homogeneity differences further.

3.3. Methoxyethoxide route

3.3.1. Gelation behaviour

Alkoxide solutions based on 2-methoxyethanol formed into uniform gels without the formation of a precipitate. Precipitation was prevented in this case by the lower reactivity of lithium methoxyethoxide as compared with lithium ethoxide. The gel times were generally longer for the methoxyethoxide sols as compared with the ethoxide sols (e.g. for a concentration of 0.25 and $r = 5$, the sol from the methoxyethoxide route had a gel time of 11 h as compared with 8.5 h for the ethoxide route with no additives). The rates of hydrolysis and condensation are likely to be slower for the alkoxides with the more bulky methoxyethoxide ligand. Eichorst [37] found similar comparisons for lithium niobate gels prepared from ethoxide and methoxyethoxide systems.

3.3.2. Crystalline phase development

Fig. 6a shows the thermal analysis and XRD data for dried gels prepared by the methoxyethoxide route.

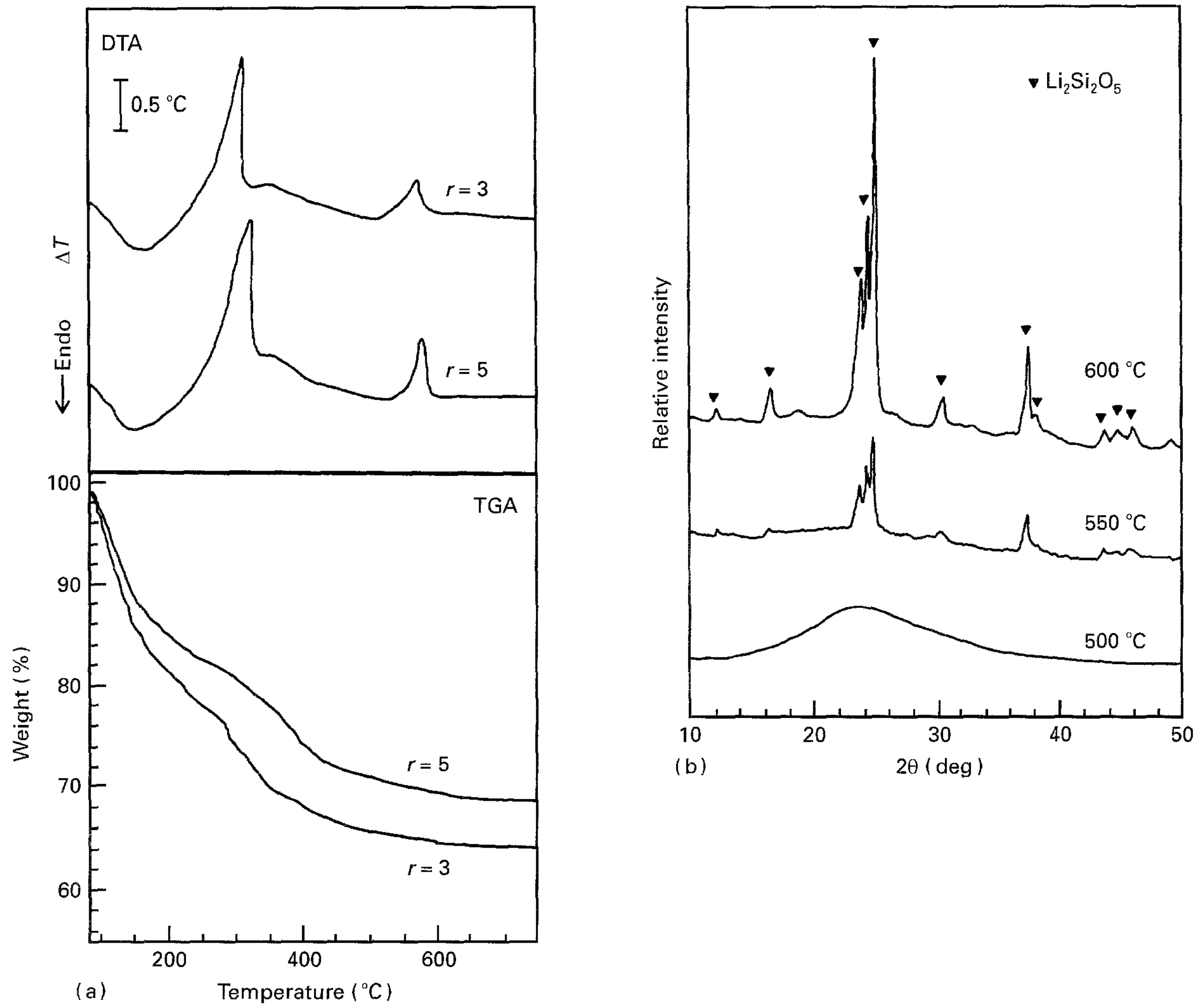


Figure 6 (a) DTA/TGA data for gel-derived powders prepared by the methoxyethoxide route ($r = 3$ or 5, [Li] = [Si] = 0.375). (b) Crystalline phase development for gel-derived powders prepared by the methoxyethoxide route ($r = 3$, [Li] = [Si] = 0.375) and heated isothermally at the temperatures given for 30 min.

The decomposition of residual organics is accompanied by an exothermic peak at approximately 250 °C in the DTA data and a weight loss in the TGA data (in addition to a weight loss associated with the removal of solvent and water at ~110 °C). Greater amounts of weight loss were observed for lower r values for the same reasons mentioned previously for ethoxide gels. DTA crystallization temperatures are slightly higher compared with the ethoxide route. Direct crystallization into the lithium disilicate phase is confirmed by XRD data (Fig. 6b); a trace of metasilicate can also be found in the sample heated to 600 °C. Similar to above, heating the amorphous powder quickly to 800 °C resulted in a mixture of metasilicate and disilicate. The methoxyethoxide route also gives homogeneous gelation and crystallization into the lithium disilicate phase. The uniform chemical distribution necessary for lithium disilicate formation may be inferred from the lack of precipitate. In addition, the ether oxygen on the methoxyethoxide ligand ($-OCH_2CH_2OCH_3$) may play a role in achieving a uniform distribution of lithium in the silicate network. In other methoxyethoxides, the ether oxygens bond to metals and influence structure, as observed in single-crystal structures [38, 39].

4. Conclusion

Several sol–gel routes were investigated with the goal of crystallizing lithium disilicate ($Li_2Si_2O_5$) from a gel-derived amorphous material. The route using lithium nitrate and TEOS did not fulfil this goal; recrystallization of the lithium nitrate early in the heating process resulted in local chemical heterogeneity. With heating to higher temperatures, the lithium-rich Li_2SiO_3 phase formed followed by lithium disilicate and quartz. A route based on ethoxides was successful in preparing lithium disilicate if measures were taken to avoid precipitation of lithium hydroxide. The precipitation occurred when a water/ethanol hydrolysis solution was added to a solution of TEOS and lithium ethoxide. Although the precipitate disappeared before gelation, the heterogeneity remained, as evidenced by the initial crystallization of a mixture of Li_2SiO_3 and $Li_2Si_2O_5$. When nitric acid was added to the hydrolysis solution, the amount of precipitate decreased and lithium disilicate increased dramatically. Precipitation was eliminated entirely by using partially hydrolysed TEOS before adding the lithium alkoxide; this route appeared to encourage the lithium cations to become associated with the partially hydrolysed TEOS monomers. Lithium disilicate crystallized directly from the amorphous powder (at ~550 °C, by XRD). Although these powders crystallized fully into lithium disilicate when heated at 550–600 °C, quick heating of the amorphous powder to a higher temperature (800 °C) resulted in the formation of Li_2SiO_3 in addition to $Li_2Si_2O_5$. A route based on 2-methoxyethoxides also resulted in powders that crystallized into lithium disilicate; a trace of metasilicate formed at higher temperatures. In this system, the more bulky alkoxy ligand decreased hydrolysis rates and allowed homogenous gel formation.

The results of this study of the gelation behaviour and crystalline phase development of gel-derived powders indicate that the ethoxide route (with nitric acid additive or partially hydrolysed TEOS) and the methoxyethoxide route are ideal for the study of crystallization and microstructure of thin-film lithium disilicate [33].

Acknowledgements

We gratefully acknowledge support from the Shell Oil Company Foundation, 3M Company and NSF Center for Interfacial Engineering.

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Received 13 July 1994
and accepted 21 February 1995