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Preparation of lithium aluminosilicate glass–ceramic monolith from metal–alkoxide solution

Part 1 *Preparation and properties of precursor gel monoliths*

JOONG-SIK YANG*, SUMIO SAKKA, TOSHINOBU YOKO, HIROMITSU KOZUKA
Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611, Japan

Crack-free dried gel monoliths of the composition $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ have been prepared as a precursor of lithium aluminosilicate glass–ceramics by the hydrolysis and polycondensation of mixed metal alkoxides in solutions containing $LiOCH_3$, $Al(O\text{-sec}C_4H_9)_3$, $Si(OC_2H_5)_4$, alcohols and water. Higher concentrations of water in the starting solution, close control of reaction conditions and slow drying rates produced crack-free gel monoliths of cylinder shape, 37 mm in diameter and 35 mm in height. Properties of the gel monolith and their change with heating have also been examined.

1. Introduction

The sol–gel process is currently recognized as one of the most attractive methods for preparing glasses, glass–ceramics and ceramics with high homogeneity at lower processing temperatures. In fact, this method has been applied to the synthesis of a variety of bulk glasses, glass–ceramics and ceramics via gel monoliths [1–6]. Glass–ceramics based on the crystalline phases of the composition $Li_2O \cdot Al_2O_3 \cdot nSiO_2$ are famous for ultra-low or even negative thermal expansivity and high thermal stability over an extended temperature range. Recently, the sol–gel technique has been successfully applied to the preparation of lithium aluminosilicate gel monoliths [6–10]. A monolithic gel of the $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ composition, however, has not been synthesized yet.

In this study, gel monoliths of the composition $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ have been prepared by the sol–gel technique. In the preparation of multicomponent monolithic gels, serious problems are often encountered during hydrolysis and polycondensation of metal alkoxides and drying of wet gels. Segregation of specific oxides due to different rates of hydrolysis and crack and bubble formations may occur. To overcome these problems various measures have been taken on hydrolysis of each metal alkoxide, that is, adjusting the water content of the starting solution, close control of the hydrolysis and polycondensation reactions and drying of the wet gel. In the present paper the formation of crack-free monolithic gels and properties of the dried gel are described. The formation of monolithic glass–ceramics from the gel will be reported separately.

2. Experimental procedure

2.1. Preparation of the starting solution and gelation

Gels of the composition corresponding to β-spodumene, $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$, in molar ratio have been prepared by the hydrolysis and polycondensation of metal alkoxides: lithium methoxide, aluminium secondary butoxide (ASB) and silicon tetraethoxide (TEOS). Lithium methoxide was synthesized by reacting lithium metal with excess methanol under refluxing prior to use. ABS and TEOS were supplied by Tokyo Kasei Co. (Tokyo, Japan) and Wako Chemicals Co. (Osaka, Japan), respectively. The compositions of the starting solutions used in the experiment are listed in Table I. Four solutions of different water contents were used.

TABLE I Compositions of starting metal alkoxide solutions

Starting solution	Materials other than water (mol)						H_2O (mol)	$[H_2O]$
	$Si(OC_2H_5)_4$	$Al(OC_4H_9)_3$	Lithium metal	C_2H_5OH	CH_3OH	C_4H_9OH		$[Li_2O \cdot Al_2O_3 \cdot 4SiO_2]$
S1	0.43	0.22	0.22	1.3	1.6	0.4	2.6	24*
S2	0.43	0.22	0.22	1.3	1.6	0.4	5.2	48
S3	0.43	0.22	0.22	1.3	1.6	0.4	7.8	72
S4	0.43	0.22	0.22	1.3	1.6	0.4	10.4	96

*Corresponds to the stoichiometric amount required for hydrolysing alkoxy groups of the metal alkoxides.

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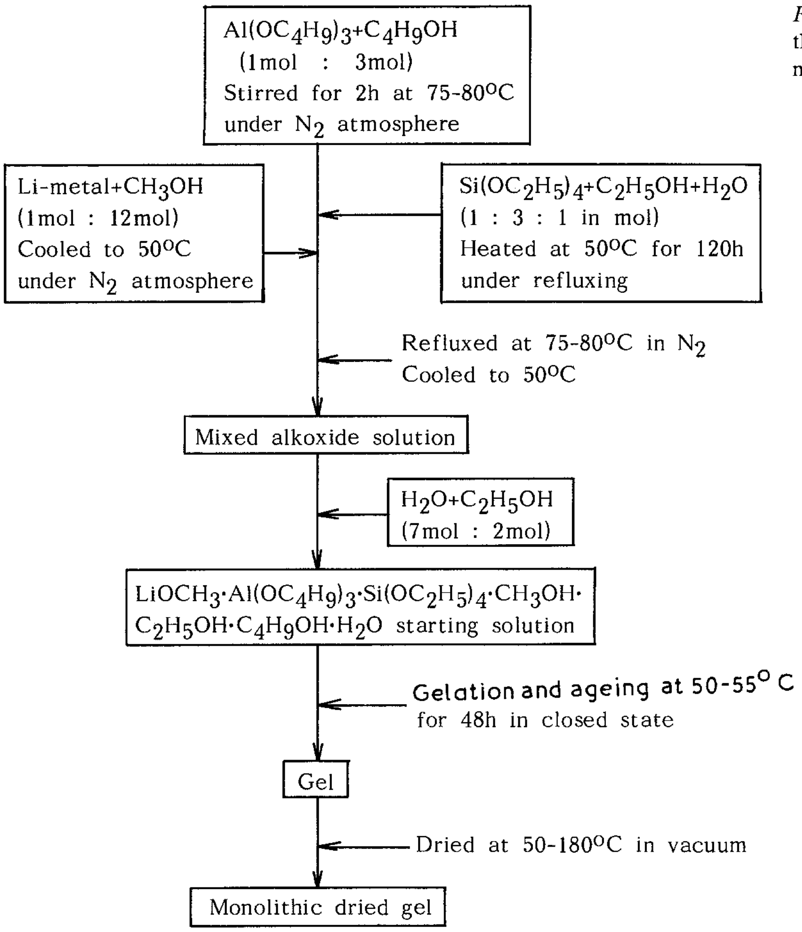

Figure 1 Flow chart for preparing monolithic gel of the oxide composition of $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ from metal alkoxides.

The sol–gel process leading to a gel for dry gel formation is shown in Fig. 1. Because the hydrolysis–polymerization of TEOS is the slowest process among the reactions of the three kinds of metal alkoxide [11], TEOS was partially reacted before the mixing of three different metal alkoxides. For the partial reaction of TEOS a quarter of the water required for full hydrolysis was added to TEOS and the solution was kept at 50° C for 120 h under refluxing.

The lithium methoxide solution was prepared separately by dissolving 1 mol lithium metal in 12 mol methanol. The solution was cooled to 50° C under N_2 atmosphere. A butanol solution of ABS was prepared separately by stirring a butoxide–butanol mixture at 78 to 80° C for 2 h under N_2 atmosphere. The partially hydrolysed TEOS solution was added dropwise to the ASB solution, and then the methanol solution of lithium methoxide was added to this solution

The mixture of the three kinds of metal alkoxide corresponding to the oxide composition of $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ was refluxed at 75 to 80° C for 2 h under N_2 atmosphere for intimate mixing and was cooled down to 50° C. A given amount of water diluted with ethanol was then added to the mixed metal alkoxide solution under vigorous stirring, in order to make a starting solution. The total water content before reaction was changed in the range of 24 to 96 in the molar ratio of water to $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$, as shown in Table I. The ratio 24 corresponds to the stoichiometric amount of water required for hydrolysing alkoxy groups of the metal alkoxides. The pH of the starting solution depended on the water content. The starting solution thus prepared was kept at 50 to 55° C in a closed cylindrical container of glass or polypropylene of 50 to 56 mm inner diameter and 120 to 250 ml volume for the gelling reaction. The gelling point of the solution was determined as the time when no fluidity of the solution was observed on tilting the container.

2.2. Drying of the gel

The wet gel was dried by perforating the sealing cap of the container with a number of small holes of 1 to 2 mm diameter. The drying rate was adjusted with the number of holes. For the first step of drying, the temperature was kept at 50° C in air in an oven.

The evaporation of the solvents took place at a rate of 0 3 to 0.6% h^{-1}. When the total weight loss of the wet gel reached about 80% of the original weight, the cap of the container was removed for the second step of drying. The gel was placed in a vacuum oven, heated up to 180° C at a rate of 0.2° C h^{-1} and kept there for about two weeks. Some of the dried gel monoliths were heated to 400° C at a rate of 0.3° C h^{-1} and kept there for 20 h to remove residual organic matter and water.

2.3. Measurements of the gel size during drying

The initial wet gel was approximately 50 to 56 mm in diameter, 45 to 59 mm in height, 110 to 140 ml in volume and 103 to 126 g in weight. The weight and dimensions of the gel were measured at intervals of about 50 to 100 h. The bulk density was estimated from the weight and dimensions. Linear shrinkage in the second step of drying was also measured with callipers.

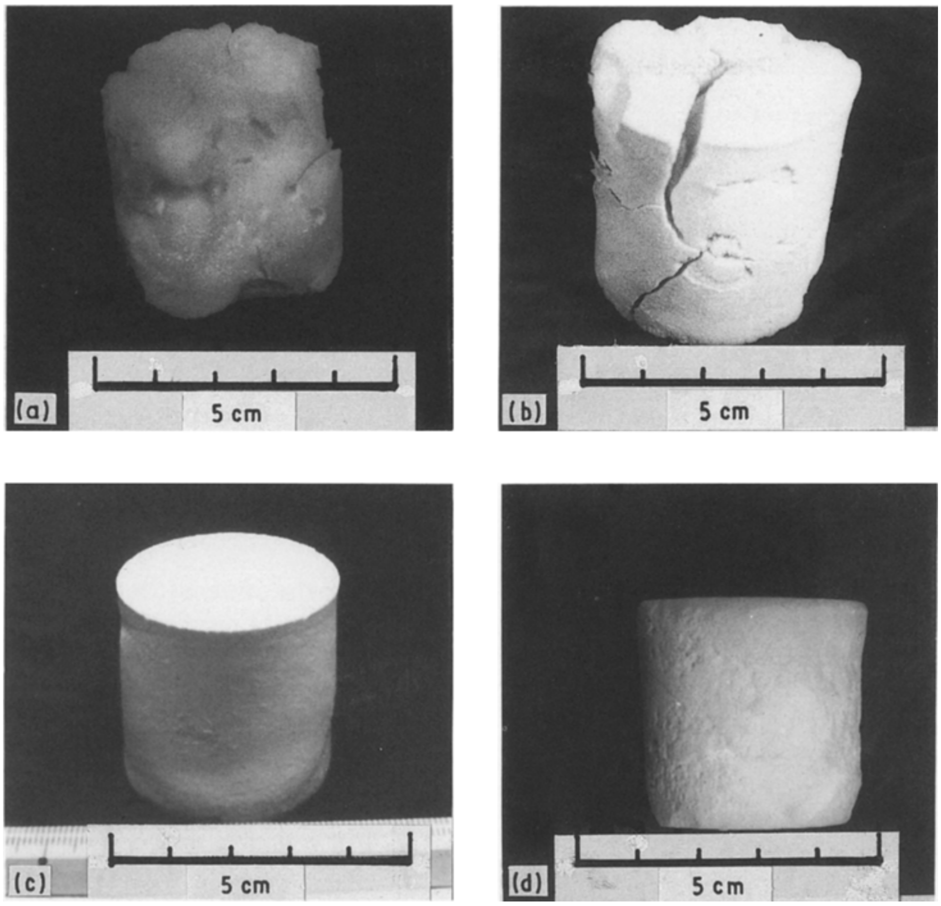

Figure 2 Dried gels prepared by the hydrolysis of alkoxide solutions with various amounts of water: (a) S1 dried at 50° C, (b) S2 dried at 180° C, (c) S3 dried at 180° C, (d) S4 dried at 180° C.

2.4. Characterization of the gel

The microstructure and thermal behaviour of dried gels were characterized. The X-ray diffraction measurements were made at room temperature with nickel-filtered Cu*Kα* radiation. The bulk density of a gel dried at 180° C was estimated from its weight and size. The apparent density was measured by pycnometry with the dry gel after being pulverized and subjected to evacuation to remove the water adsorbed on the surface.

The specific surface area was measured at 77.3 K with a nitrogen adsorption analyser, AccuSorb model 2100E (Micromeritics Co., USA). The gels were pulverized into powders of 75 to 106 mm size and degassed at 150° C for 20 h just before measurement. The specific surface area was calculated from the data of the BET measurements on the basis of the Cranston–Inkley model [12].

Differential thermal analysis (DTA) and thermogravimetric analysis (TG) measurements were performed on gel powders of $-100 + 140$ mesh by a Rigaku Thermoflex model 100 thermal analyser using a heating rate of 10° C min^{-1}. The fractured surface of gels were observed by a Hitachi S-450 scanning electron microscope with the surface coated with Pt–Pd.

3. Results

3.1. Effect of the amount of water

The appearance and crack formation in gels prepared with various amounts of added water are summarized in Table 2. Photographs of dried gels are shown in Fig. 2. Fig. 3 shows the gelling time at 50° C and the pH of the starting solution as a function of water content. Sample S1, to which a stoichiometric amount of water for hydrolysing is added to the solution, gels in 200 to 240 min. The gel cracks during drying at 50° C. Sample S2, to which double the stoichiometric amount of water is added, gels in 2 to 3 min. The gel

TABLE II Appearance and crack formation in gel monoliths prepared with different amounts of water

Starting solution	[H_2O] / [$Li_2O \cdot Al_2O_3 \cdot 4SiO_2$]	Appearance		Crack formation		XRD pattern after heating at 400° C for 20 h
		At gel point	After drying	1st step (drying at 50° C)	2nd step (drying at 50 to 180° C)	
S1	24	Transparent	Opaque	Cracks	–	Amorphous
S2	48	Transparent	Opaque	Crack-free	Cracks	Amorphous
S3	72	Translucent	Very opaque	Crack-free	Crack-free	Amorphous
S4	96	Translucent	Very opaque	Crack-free	Crack-free	Amorphous

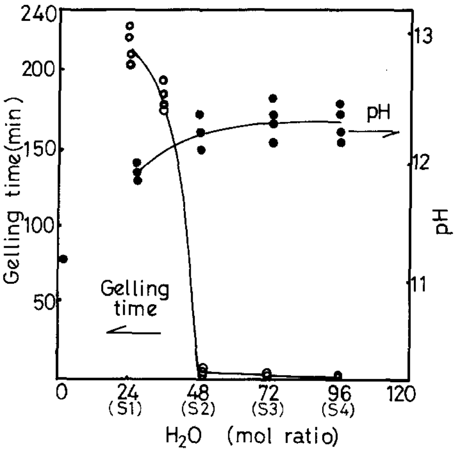

Figure 3 Gelling time at 50° C and pH of the starting solution measured at 24° C against the water content expressed by the $[H_2O]/[Li_2O \cdot Al_2O_3 \cdot 4SiO_2]$ ratio.

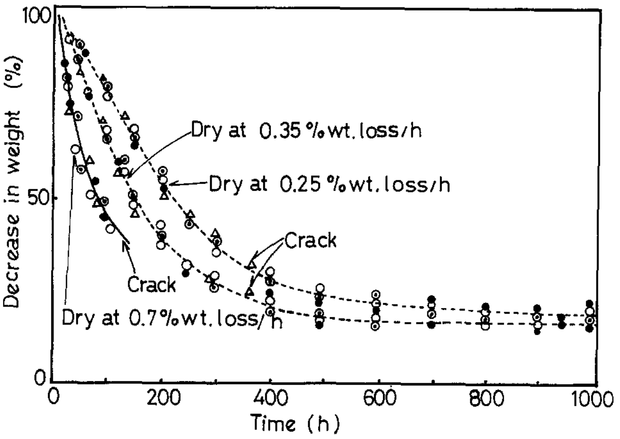

Figure 4 Decrease in weight against time during drying at 50° C for wet gels: (△) S1, (●) S2, (○) S3, (⊙) S4.

obtained is crack-free during drying at 50° C but shows cracks during the subsequent drying at 50 to 180° C. Samples S3 and S4, which contain water at three and four times the stoichiometric amount, respectively, gel in a very short time. The gels are crack-free throughout the drying process. Fig. 3 shows that the gelling time is drastically shortened with increasing water content.

3.2. Drying of gel

The weight losses of wet gels S2, S3 and S4 on drying at 50° C are plotted against time in Fig. 4. At an initial evaporation rate of 0.25 to 0.35% h^{-1}, cracks form in S2 when the weight loss of the gel reaches 70 to 75%, while no cracks are found in samples S3 and S4, leading to the formation of crack-free gel monoliths. On the other hand, when wet gels are dried at an initial evaporation rate of about 0.7% h^{-1}, cracks are formed in all the gels when the weight loss reaches about 60%. Thus crack-free gel monoliths cannot be obtained at such a high initial evaporation rate.

In drying at 0.25 to 0.35% h^{-1}, weight loss of the wet gel continues to occur with decreasing evaporation rate up to about 800 h, reaching a weight loss of about 85 to 90% of the original wet gel. Here gels are in the practically dried state.

Fig. 5 shows the linear shrinkage and bulk density of gel S3 during heating from 50 to 180° C at a rate of 0.2° C h^{-1}. The values for 50° C are those for sample S3 after drying at 50° C for 990 h. The shrinkage and change in density of S2 and S4 are not distinctly different from those of S3.

3.3. Microstructure of dried gel

Fig. 6 shows SEM microphotographs for gel S2 dried at 50° C and S3 dried by heating up to 180° C. Dried gel S3 is found to consist of large particles of about 0.05 to 0.1 μm diameter. Dried gel S2 has a much finer texture and smaller pores than dried gel S3. This comparison is possible because a drastic change in microstructure by heating from 50 to 180° C is not expected. The bulk density, weight loss during drying, specific surface area and porosity of dried gels are summarized in Table III. It is seen that the weight loss reaches about 90% on drying by heating to 180° C. It is also seen that monolithic dried gels S3 and S4, which have no cracks, have a smaller bulk density than S2 which cracks during drying. The specific surface area of S3 is 380 $m^2 g^{-1}$, much larger than that of S2 with 180 $m^2 g^{-1}$.

3.4. Thermal behaviour of dried gel

Fig. 7 shows DTA and TG curves for gels S2, S3 and S4 dried by heating up to 180° C. The rapid decrease in weight on the TG curves and endothermic peaks on the DTA curves observed below 100 to 150° C can be attributed to the vaporization of water adsorbed on the pore surfaces. The decrease in weight in TG and endothermic peaks in DTA at 200 to 250° C and around 400° C may be attributed to the desorption of residual organic materials trapped in the micropores, or to the decomposition of unhydrolysed alkoxy groups. The TG curves show that the gels dried beforehand by heating up to 180° C still show a weight loss of 15 to 19%. The DTA curves have a peak around 800° C, which may correspond to crystallization of the gels.

TABLE III Some properties of typical dried gels

Sample No.	Bulk density (g/cm^{-3})		Weight loss (%)		Surface area after heating to 180° C ($m^2 g^{-1}$)	Porosity after heating to 180° C (%)
	After drying at 50° C	After heating to 180° C	After drying at 50° C	After heating to 180° C		
S2	0.30	0.35	86.75	89.49	180	–
S3*	0.24	0.25	89.46	91.31	380	89.36
S4	0.19	0.20	90.87	92.62	–	–

*Apparent density 2.35 g cm^{-3}.

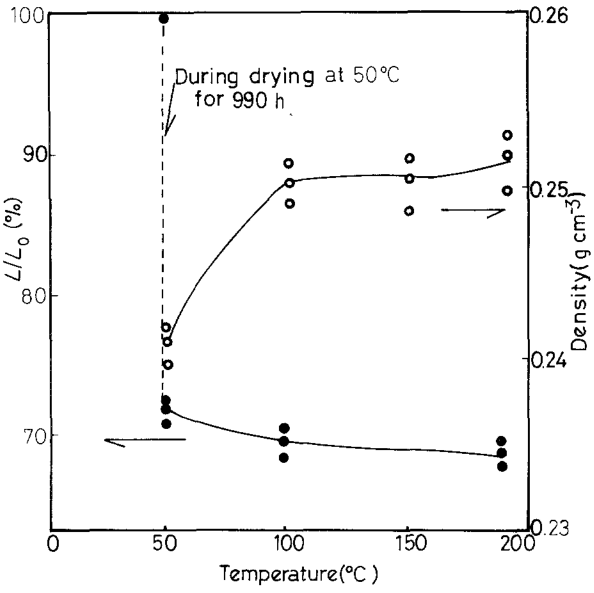

Figure 5 Plot of linear shrinkage and change of density for gel S3 during drying by heating at 50 to 180° C.

4. Discussion

The present experiments have shown that large and crack-free $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ dry gel monoliths can be obtained when the following two conditions are fulfilled:

(i) higher water contents of the starting solution, and

(ii) a slower drying rate in the drying stage at 50° C. Discussion will be centred on these two conditions.

4.1. Effect of water content on gel formation

It is known [1, 9, 13] that a wet gel can be dried without cracks when the particles in the wet gel are large and accordingly pores filled with solvents are large, leading to the stress caused by the capillary force being low. Also, the particles and the skeleton in a wet gel consisting of connected particles should have enough strength to overcome the capillary force.

It is assumed that these can be achieved in the present case when the water content of the starting solution is high. As seen in Fig. 3, the pH of the solution is increased when the amount of water is increased and reaches a constant value of about 12 for solutions S2, S3 and S4. This can be attributed to a shift of the equilibrium of the following hydrolysis reaction toward the right-hand side:

$$LiOCH_3 + H_2O \;=\; Li^+ + OH^- + CH_3OH \qquad (1)$$

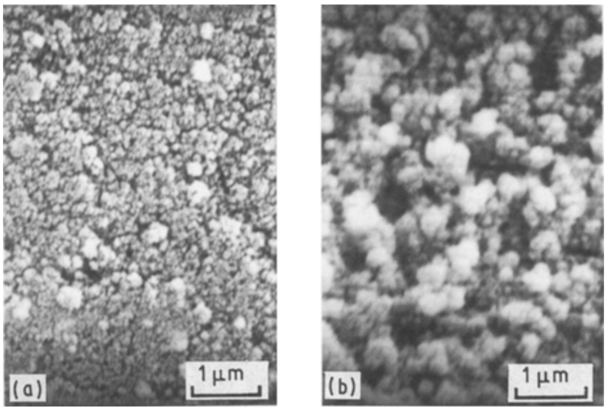

Figure 6 Scanning electron microphotographs of the dried gels: (a) S2 dried at 50° C, (b) S3 heated up to 180° C.

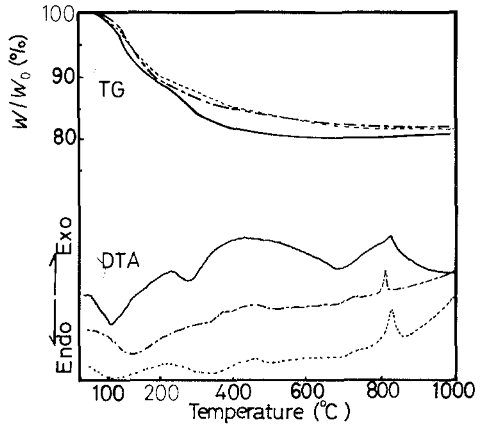

Figure 7 DTA and TG curves of gels dried by heating up to 180° C. Thermal analyses have been made by heating samples at a rate of 10° C min^{-1}. (——) S2, (–·–·–·–) S3, (– – –) S4.

It is known that $LiOCH_3$ and $Al(OC_4H_9)_3$ undergo hydrolysis more rapidly than TEOS. In the solutions of higher water contents, a considerable amount of water remains after their hydrolysis and this makes it possible for TEOS to be hydrolysed and polycondensed. Since the solution is highly alkaline, one can expect to obtain larger particles. This is actually seen in Fig. 2. Larger particles make the pore size larger, which reduces the capillary force due to surface tension of the liquid filling the pores during drying, thus preventing crack formation. The higher pH would also be useful for making silica skeletons stronger by promoting the connection of silica particles [14].

On the other hand, when the water content of the starting solution is low, for example at a quantity which is just enough for the hydrolysis of the metal alkoxides, the amount of water left for the hydrolysis of TEOS is very limited. This will cause a delay in the growth of silica particles, leading to smaller particles and a larger capillary force. A crack-free gel monolith cannot be obtained when the amount of water added to the metal alkoxide mixture is small.

4.2. Effect of drying rate

It has been shown by Scherer [15] that the rate of drying of the wet gel should be small in order to avoid crack formation during drying. According to Scherer, slower rates of drying permit the relaxation of dangerous stress caused by the capillary force and the blurring of the interface between stressed and non-stressed parts as a result of the diffusion of solvents. In the present experiments this was confirmed, that is, wet gels S3 and S4 could be dried without the formation of cracks when the rate of drying at 50° C was small at 0.25 to 0.35 wt % h^{-1}. Contrary to this, they were cracked when the rate of drying was fast at 0.7 wt % h^{-1}.

5. Conclusions

Lithium aluminosilicate gels of the composition $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ can be prepared successfully in a monolithic form without cracking by subjecting a starting solution of the composition $LiOCH_3 \cdot Al(OC_4H_9)_3 \cdot 2Si(OC_2H_5)_4 \cdot 11CH_3OH \cdot 14C_2H_5OH \cdot C_3H_9OH \cdot xH_2O$ ($x = 30$ to 48), to hydrolysis and polymerization reactions and drying the resultant wet gel. The most important conditions for the formation of dry gel monoliths were higher water contents of the starting solution and slower drying rates.

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