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

Part II *Conversion of gel to glass-ceramic monoliths and their properties*

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Glass-ceramic monoliths with a composition of $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ have been synthesized by the sol–gel technique using metal alkoxides as starting materials. Heating dried gel monoliths of about 36 mm diameter and height to appropriate temperatures gave glass-ceramic monoliths of about 20 mm diameter and height without the occurrence of cracks, while a melt-derived glass body of the same composition was cracked or softened on heating. The glass-ceramic monoliths obtained by heating gel monoliths at 1000 °C for 40 h were a porous body, whose bulk density and porosity were 1.62 $g\,cm^{-3}$ and 34%, respectively. On heating gel monoliths, β-eucryptite crystals were first precipitated around 750 °C, followed by precipitation of β-spodumene crystals at 830 °C. At higher temperatures the latter grew at the expense of the former phase. The crystallized specimens exhibited very low thermal expansion coefficient ranging from -13–$12 \times 10^{-7}\,°C^{-1}$ at temperatures from room temperature to 700 °C depending on the heat-treatment temperature of gels, indicating that a porous glass-ceramic monolith with ultra-low thermal expansion can be prepared using the present sol–gel method.

1. Introduction

Glass-ceramics consisting of β-spodumene ($Li_2O \cdot Al_2O_3 \cdot 4SiO_2$) and β-eucryptite ($Li_2O \cdot Al_2O_3 \cdot 2SiO_2$) fine crystals are endowed with ultra-low and even negative thermal expansion, high thermal stability and high chemical durability [1]. So far, several attempts have been made to synthesize these glass-ceramics via the sol–gel method [2–6]. However, large glass-ceramic monoliths have not yet been produced, although gel monoliths in the system $Li_2O–Al_2O_3–TiO_2–SiO_2$ were prepared by Orcel and Hench [4] with the help of drying control chemical additives (DCCA).

In the previous work [7], the authors synthesized dried gel monoliths of the composition $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ (LAS) from corresponding sols, not via a powder process. No catalysts such as HCl, HNO_3 and NH_4OH, and DCCA such as *N*,*N*-dimethyl formamide [8] were used. The gel monoliths obtaind by drying the wet ones at 180 °C were 36 mm diameter and 36 mm high.

The purpose of this study was to prepare multicomponent LAS glass-ceramic monoliths without cracks from the corresponding gels. In order to determine the optimum condition, the process of conversion of the gel monoliths into crack-free monolithic glass-ceramics has been investigated using X-ray diffraction (XRD), thermal analysis (DTA) and scanning electron microscopic (SEM) observation.

2. Experimental procedure

2.1. Preparation of gel monolith

The crack-free gel monoliths with an equivalent oxide composition of $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ (mol %) were prepared by the sol–gel process from the starting solution of the composition $2Si(OC_2H_5)_4 \cdot Al(OC_4H_9)_3 \cdot LiOCH_3 \cdot 11CH_3OH \cdot 14C_2H_5OH \cdot 3C_4H_9OH \cdot 36H_2O$ according to the previous study [7].

In order to compare the crystallization behaviour of bulk gels and gel-derived glasses with that of melt-derived glasses of the same composition, glass specimens were also prepared by a conventional melt-quenching technique. A glass batch consisting of SiO_2, $Al(OH)_3$, Li_2CO_3 and TiO_2 powders was melted in a Pt crucible at 1560 °C for 6 h. The melt was cast on an iron plate and annealed at about 600 °C for 1 h. The resultant glass plates were cut to about $0.5 \times 0.5 \times 1.5\ cm^3$ and polished with fused alumina powder.

2.2. Sintering and crystallization

Sintering and crystallization of gels were carried out by heating them at a specified temperature for 5–60 h

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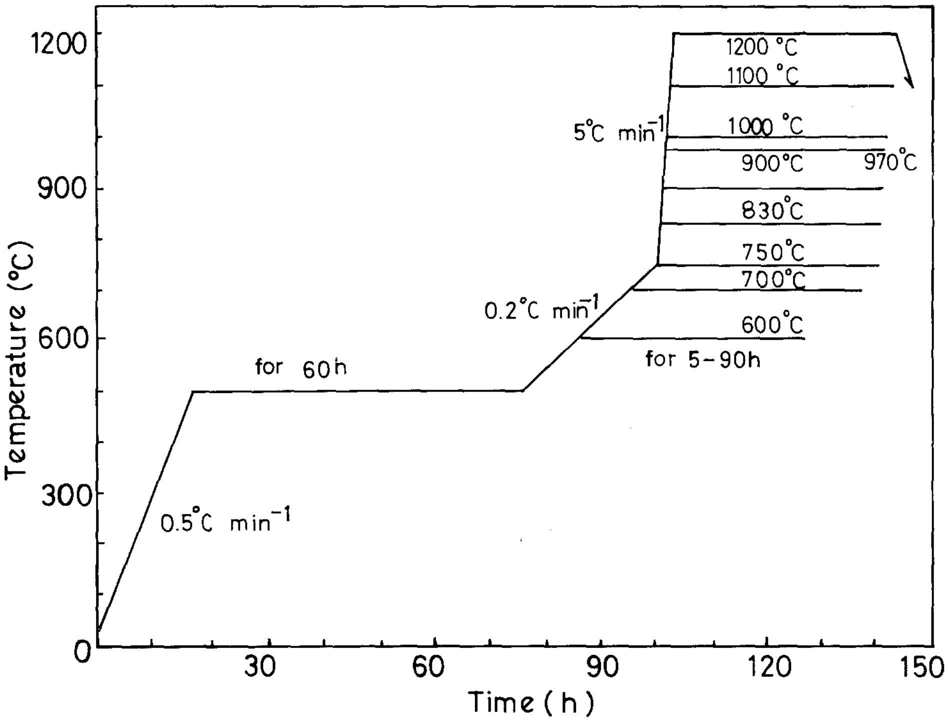

Figure 1 Heating schedule of the sintering process for conversion of gel into glass-ceramics.

in air. The employed heating schedules are schematically illustrated in Fig. 1. The gel dried at 180 °C was first heated at 500 °C for 60 h and then sintered at a given temperature between 600 and 1200 °C for 5–90 h.

2.3. Characterization techniques

Thermal analyses were made using a Rigaku model Thermoflex 100 thermal analyser. Thermogravimetric (TG) and differential thermal analyses (DTA) were performed on the pulverized sample (− 100 + 140 mesh) at a heating rate of 10 °C min^{-1}.

Dilatometric measurements on the heat-treated specimens were conducted using Shimadzu model TMA-30 thermomechanical analyser (quartz glass tube) at a heating rate of 2 °C min^{-1}. The size of the specimen for thermal expansion measurement was about $0.4 \times 0.4 \times 1.5$ cm^3. Small gel pieces 4 mm thick were also used for the measurement for comparison.

Crystalline phases precipitated in the gel specimens which were heated at peak temperatures on the DTA curves were identified using an X-ray diffractometer at room temperature with Ni-filtered Cu$K\alpha$ radiation. Change in the bulk density of gel monoliths with heating was estimated from the weight loss and linear shrinkage. The initial size of the dried gel was about $2.0 \times 1.0 \times 1.0$ cm^3.

The fractured surface of heat-treated specimens was observed by a Hitachi model S-450 scanning electron microscope. The specimens were coated with Pt–Pd prior to observation.

3. Results

3.1. Sintering behaviour

A typical linear contraction for the small gel piece, 4 mm thick, during sintering from room temperature to 1000 °C is given in Fig. 2. The gel was dried at 180 °C beforehand. As seen from Fig. 2, the shrinkage of the gel proceeded very slowly at a rate of 0.026% °C^{-1} in the average linear shrinkage between 150 and 600 °C, and very sharply at a rate of 0.22% °C^{-1} between 600 and 750 °C. No further shrinkage occurred above 750 °C for this gel piece. The total shrinkage amounted to about 44.5%.

Fig. 3 shows changes in linear shrinkage ($\Delta L/L_0$) and density for a larger gel monolith of about 36 mm diameter and height as a function of temperature. The curve indicates that the shrinkage proceeded gradually between 180 and 600 °C and very sharply in the temperature range 600–830 °C. The contraction of the bulk gel appeared to cease at about 900 °C, which is much higher than 750 °C for the small gel piece of 4 mm thickness. The overall linear shrinkage of the gel monoliths during heating to 900–1100 °C was about 51% and the density of the resultant glass-ceramics was about 1.7 g cm^{-3}. It is noticed that this value is

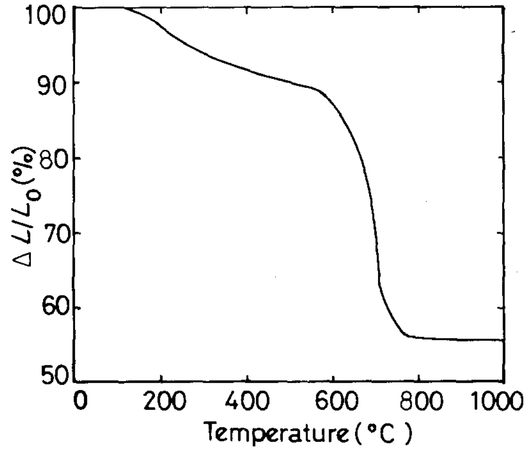

Figure 2 Dilatometric linear shrinkage curve for the gel of 4 mm diameter; heating rate 3 °C min^{-1}.

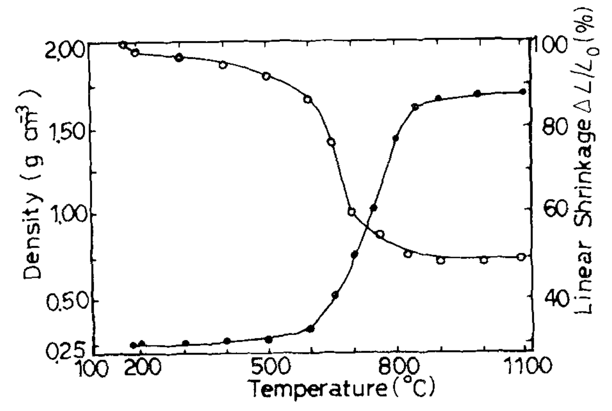

Figure 3 Relationship between (○) linear shrinkage ($\Delta L/L_0$) and (●) density of the large monolithic gel sintered at various temperatures.

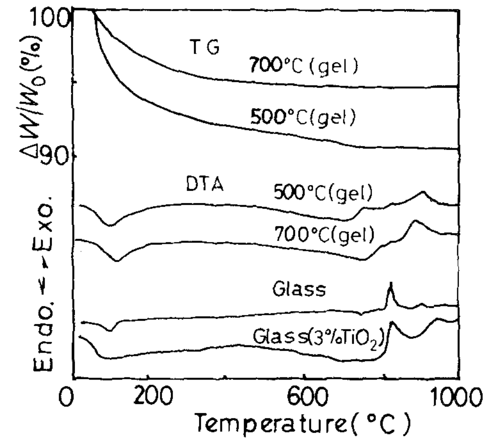

Figure 4 DTA and TG curves for the gel sintered at 500 and 700 °C and DTA curves for the melt-derived glasses.

considerably smaller than that of the dense body (2.5 g cm^{-3}). After being heated up to 1100 °C, the specimens were crack-free and milky white in colour.

3.2. DTA and TG

The DTA and TG curves for the gel-derived glasses obtained by heating at 500 and 700 °C are shown in Fig. 4. The DTA curves for the melt-derived glasses of the same composition $Li_2O{\cdot}Al_2O_3{\cdot}4SiO_2$ with and without 3 wt % TiO_2 are shown for comparison. Three exothermic peaks were observed in a temperature range 750–930 °C for the gel-derived glasses, while two exothermic peaks were seen at 830 and 900–930 °C for the melt-derived glasses.

For the latter glasses the first and second peaks are ascribed to the precipitation of β-eucryptite and β-spodumene, respectively. In the gel-derived glasses, a peak around 750 °C, in addition to two peaks at higher temperatures, suggests the presence of another crystalline phase other than these two crystalline phases. This is not clear at present.

3.3. X-ray diffraction analysis

The XRD patterns of the gel monoliths sintered at various temperatures for 20 h are shown in Fig. 5. Heating at temperatures lower than 700 °C did not cause crystallization of the gels. At 750 °C the peaks due to β-eucryptite were observed. Above 830 °C the peaks due to β-spodumene grew at the expense of those due to β-eucryptite, with increasing heating temperature.

Fig. 6 shows the variation of the XRD patterns of the gel monoliths with heating time at 830 °C. Within 5 h, only the peaks due to β-eucryptite were seen. In addition to these, the peaks due to β-spodumene appeared and grew with increasing heating time.

Fig. 7 shows the XRD patterns for the gel and corresponding glasses heated at 750 °C for 10 h. β-eucryptite was the only crystalline phase precipitated in the gel and glass without TiO_2, while a small amount of β-spodumene crystals was coprecipitated in the glass containing 3 wt % TiO_2 as a nucleating agent.

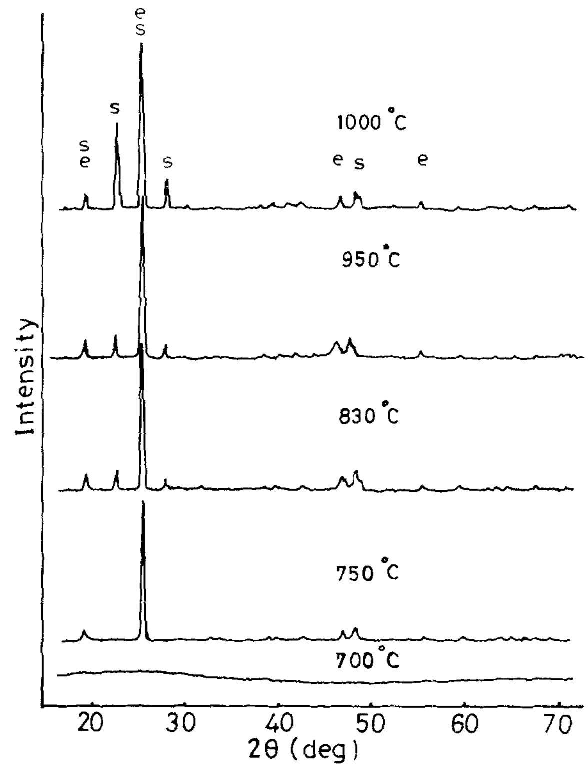

Figure 5 XRD patterns of the monolithic gel heated at various temperatures for 20 h. e, β-eucryptite; s, β-spodumene.

3.4. Thermal expansion

Fig. 8a shows thermal expansion for the specimens sintered below 700 °C for 40–60 h, where they do not crystallize, but remain as a gel or become glassy. The specimens sintered below 600 °C showed complicated shrinkage behaviour. On the other hand, the specimen heated at 700 °C had a relatively large thermal expansion coefficient of $65.7 \times 10^{-7}\,°C^{-1}$, which is almost equal to that of melt-derived glass [9].

The thermal expansion of the specimens crystallized by heating above 830 °C are depicted in Fig. 8b. The specimen heated below 950 °C showed negative thermal expansion over the entire temperature range. The specimen heated at 830 °C showed a sudden shrinkage above 900 °C. As seen from Fig. 8b, the thermal expansion increased with increasing heating temperature and the sign of thermal expansion turned from negative to positive at heating temperatures above 970 °C.

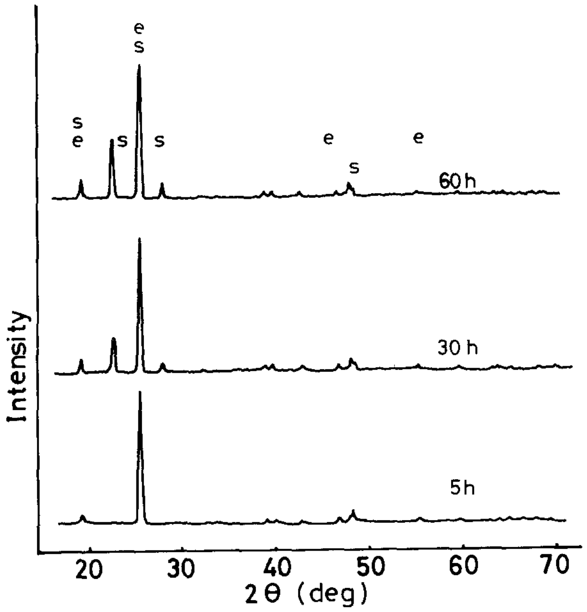

Figure 6 XRD patterns of the monolithic specimen heated at 830 °C for various times. e, β-eucryptite, s, β-spodumene.

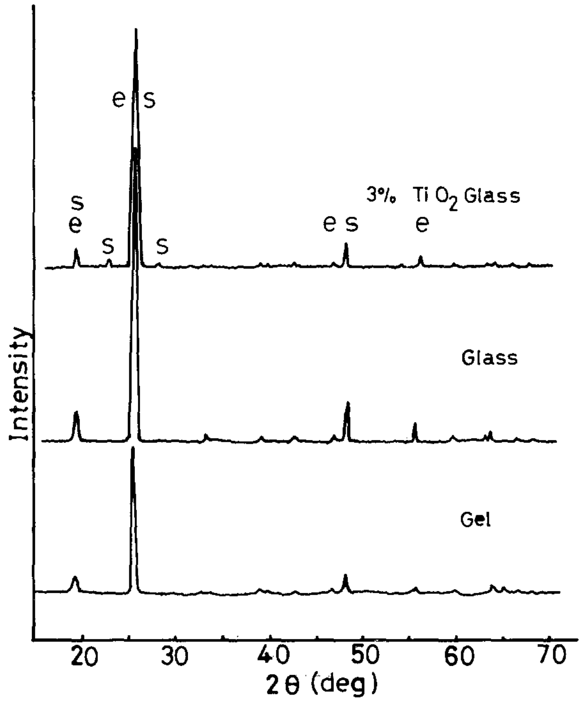

Figure 7 XRD patterns of the gel-derived monolithic specimen and the conventional glasses of the same composition with and without 3 wt % TiO$_2$ heated at 750 °C for 10 h. e, β-eucryptite; s, β-spodumene.

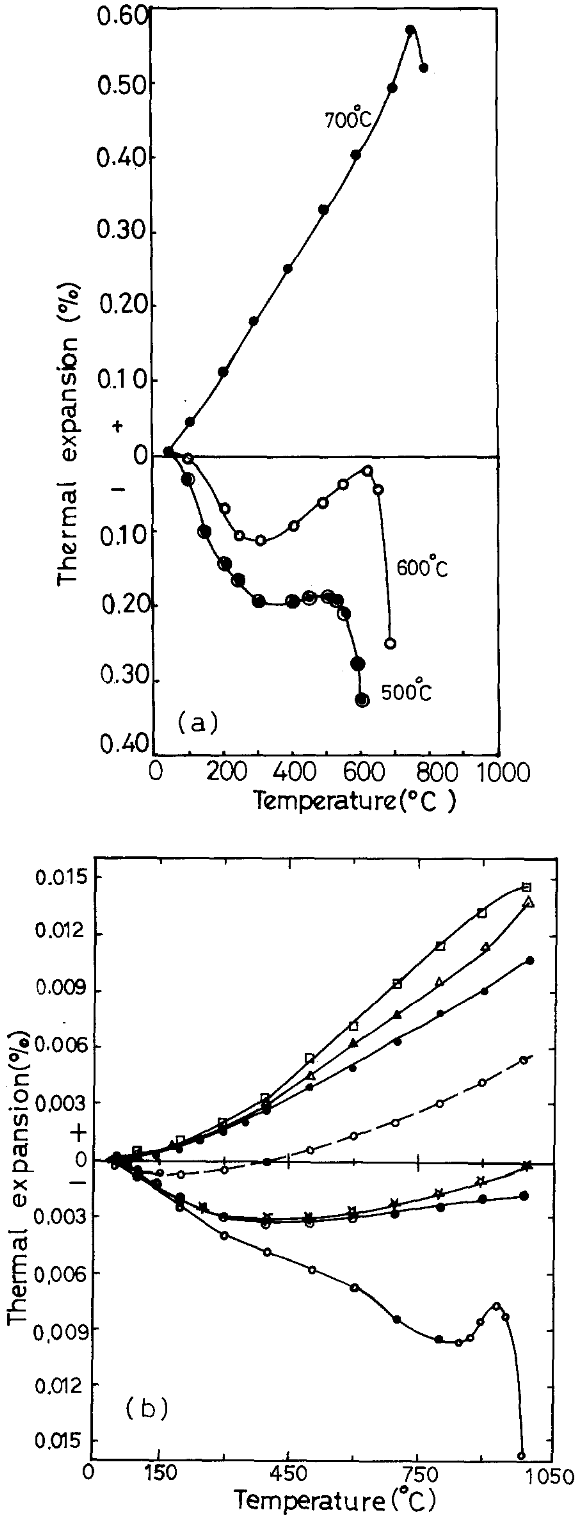

Figure 8 Thermal expansion curves for the specimens sintered (a) below 700 °C and (b) above 830 °C: (○) 830 °C, (⊙) 920 °C, (✡) 950 °C, (– – –○– – –) 970 °C, (●) 1000 °C, (△) 1100 °C, (□) 1200 °C.

3.5. Microstructure of glass-ceramic monoliths

Fig. 9 shows the photographs of the glass-ceramic monoliths prepared by heating gel monoliths at 830 and 1000 °C for 40 h. It is found that the gel monoliths become glass-ceramic monoliths without cracking and deformation, while much cracking and deformation were observed at the surface of melt-derived glass heated at 1000 °C, although the photograph is not shown. Fig. 10 shows scanning electron micrographs of the cross-sections of the gel monolith and melt-derived glass after heating at 750 and 1000 °C, respectively, for crystallization. It is clearly seen that crystallization takes place over the whole of the sample in the gel monolith, while in the melt-derived glasses crystallization occurred only at the surface layers and voids formed between the crystallized surface layer and the uncrystallized bulk. Fig. 11 shows scanning electron micrographs of the fractured surface of glass-ceramics heated at 750, 830, 900 and 1000 °C for 20 h. At 750 °C where β-eucryptite started to precipitate, the sintered body has an open structure consisting of secondary particles of several micrometres in size which are composed of finer primary particles.

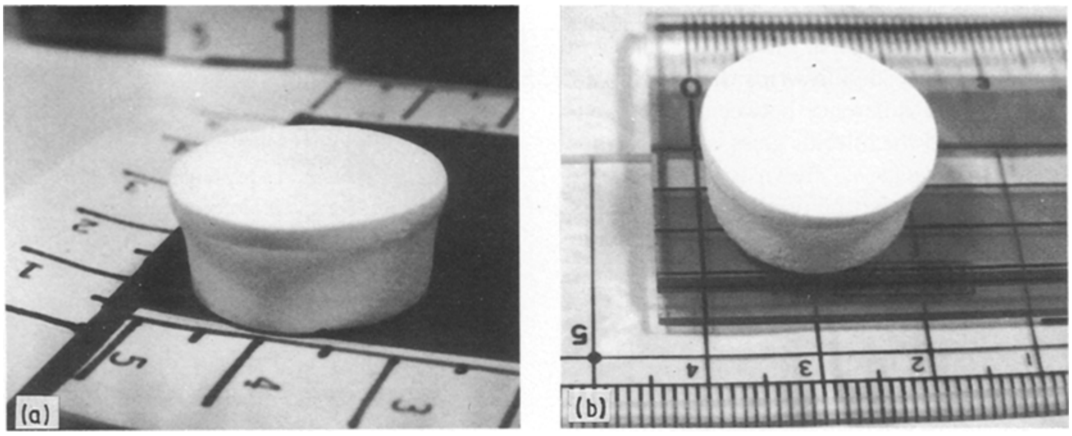

Figure 9 Photographs of the monolithic glass-ceramic obtained by heating the dried gel at (a) 830 °C and (b) 1000 °C.

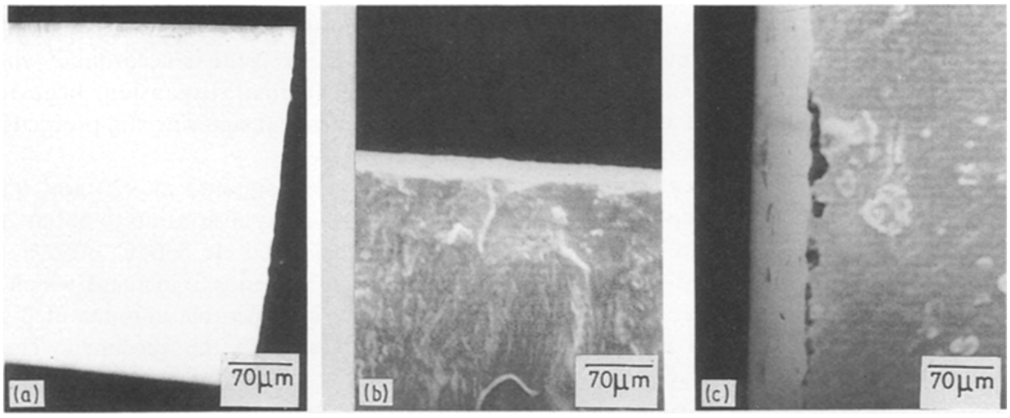

Figure 10 Scanning electron micrographs of the cross-sections of the gel-derived monolithic specimen and the melt-derived glasses heated at 750 °C for 10 h; (a) gel, (b) glass and (c) glass containing 3% TiO_2.

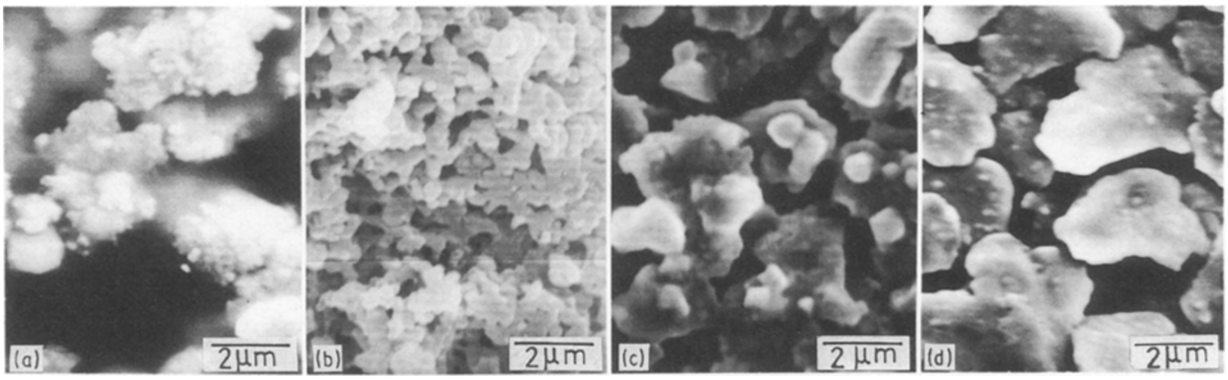

Figure 11 Scanning electron micrograph of the fractured surface of glass-ceramics sintered at (a) 750 °C, (b) 830 °C, (c) 900 °C and (d) 1000 °C for 20 h.

The crystallinity seems very poor. At 830 °C, fine crystalline particles are seen. As the sintering temperature is raised to 900 and 1000 °C, they grow in size. However, it is noticed that large pores still remain, indicating that the glass-ceramic monoliths obtained in the present work are porous.

4. Discussion

4.1. Crack-free crystallization of the gel monolith

It has been shown in Fig. 9 that the gel monolith of the $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ can be converted by heating to the glass-ceramic monolith without cracks and deformation of the shape, whereas glasses of the same composition with and without 3 wt % TiO_2 show cracks and deformation during crystallization on heating. The crack-free crystallization of the gel monolith is attributed to the fact that crystallization takes place at the same time throughout the gel monolith, as shown in Fig. 10. This means that nucleation occurs in the bulk because the gel monolith has many pores whose surfaces provide nucleation sites. It is well known [10] that crystallization of a glass often takes place at the surface.

In the present work, crystallization of bulk glasses has taken place at the surface of the glass article, and crystal growth has proceeded towards the inside. This gives rise to a volume difference between the crystallized surface layer and the interior glass, causing voids between them and cracks as shown in Fig. 9. If the temperature becomes higher before the completion of crystallization, the non-crystallized region softens and the whole article may be deformed.

4.2. Sintering process

The dried gel monoliths used for making glass-ceramics were quite porous, the surface area being about 380 $m^2 g^{-1}$. The noticeable densification was found to start at 600 °C and end at 830 °C as seen from Fig. 8a. It is assumed that the sharp shrinkage found in the temperature range 600–830 °C is probably caused by viscous flow. In this temperature range glasses are being studied because the gel-to-glass conversion occurs around 600 °C. The shrinkage, however, ceases at 830 °C because of the precipitation of crystalline phases. After being sintered at 1100 °C, densification is not completed. In order to obtain well-sintered glass-ceramics without porosity, heat treatment at temperatures much higher than 1100 °C may be required.

The composition of the gels used in the present study corresponds to that of so-called β-spodumene, $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$. It is well known that the primary crystalline phase precipitated out of a melt-derived glass with a composition of $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ is β-eucryptite phase, followed by the precipitation of the thermodynamically stable β-spodumene phase at higher temperatures [11, 12]. This phenomenon is explained by the metastable phase separation of the glass into phases rich and poor in SiO_2, on heating [12]. That is, out of the latter phase with lower SiO_2 content β-eucryptite crystals are precipitated, which then transform into β-spodumene by taking up SiO_2 from the SiO_2-rich phase at higher temperatures.

In this sense, it can be said that the crystallization behaviour of the gel with a composition $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ prepared in the present study is almost the same as that of a melt-derived glass, although the crystallization temperatures of gels is slightly lower than that of a melt-derived glass. This means that although the hydrolysis rates of three kinds of metal alkoxide are very different, an intimate mixing of the respective elements can be attained very well in a liquid state and even in a gel state, in contrast to the works of Phalippou *et al.* [2] and De Lambilly and Klein [6], where precipitation of Li_2SiO_3, $Li_2Si_2O_5$ and β-quartz are observed at lower temperatures.

Orcel and Hench [4] observed the precipitation of β-eucryptite phase (not β-spodumene as stated in their paper) from the gels at temperatures as low as 375–400 °C, which is by about 350 °C lower than the present case. This is possibly ascribed to the addition of 6 wt % TiO_2 as a nucleating agent and not to that of DCCA.

4.3. Thermal expansion

The glass-ceramics of lithium aluminosilicate are widely known for ultra-low or negative thermal expansion [13–15]. Therefore, the thermal expansion behaviour of lithium aluminosilicate gels sintered at various temperatures is of great interest.

As can be clearly seen from Fig. 8a, gel to glass conversion is not completed by sintering below 600 °C, because a drastic contraction can be observed at about 500–600 °C during heating. On the other hand, the gel sintered at 700 °C becomes completely glassy because the thermal expansion coefficient is exactly the same as that of a melt-derived glass as stated above [9]. Hanging in the curve is not due to softening but due to crystallization as deduced from the XRD (Fig. 5) and DTA (Fig. 4) results.

The thermal expansion curves for the specimens sintered above 830 °C in which β-eucryptite and β-spodumene are coprecipitated are shown in Fig. 8b. The specimen sintered at 830 °C shows a negative thermal expansion, indicating that the major crystalline phase is β-eucryptite in accordance with the XRD results. The thermal expansion behaviour above 900 °C indicates that sintering still proceeds above this temperature.

The specimens sintered at 920 and 950 °C show negative thermal expansions up to about 200 °C, similar to that sintered at 830 °C. Above 200 °C the thermal expansion tends to increase, which reflects the presence of a considerable amount of β-spodumene phase precipitated in the specimen. The specimen sintered at 970 °C has almost zero (i.e. zero to slightly negative) thermal expansion between room temperature and 400 °C. By heating above 1000 °C the specimens have positive thermal expansion coefficients over a wide temperature range from room temperature to 1000 °C just like β-spodumene crystal.

These results obviously indicate that the lithium aluminosilicate glass-ceramic monoliths with a desired thermal expansion coefficient of negative ($-13 \times 10^{-7}\,°C^{-1}$) to zero to positive ($12 \times 10^{-7}\,°C^{-1}$) values can be easily prepared by controlling the fraction of β-eucryptite and β-spodumene phases.

5. Conclusions

Lithium aluminosilicate glass-ceramic monoliths with a composition of $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ have been prepared from the corresponding monolithic gels dried at 180 °C. The gel monoliths were converted to glass-ceramic monoliths without the occurrence of cracks and softening, in contrast with melt-derived glass bodies which cracked and were deformed due to softening. The glass-ceramic monolith obtained by heating at 1000 °C for 40 h was a porous body, whose bulk density and porosity were 1.62 $g\,cm^{-3}$ and 34%, respectively. β-eucryptite crystals were first precipitated around 750 °C and then β-spodumene precipitated at 830 °C and higher temperatures. The crystallized specimens exhibited very low thermal expansion coefficient ranging from -13–$12 \times 10^{-7}\,°C^{-1}$ at temperatures from room temperature to 700 °C, depending on the heat-treatment temperature of gels. Non-occurrence of cracks in gel monoliths during heating for crystallization can be attributed to the bulk crystallization which may take place as a result of crystal nucleation at the internal surfaces of fine pores. Thus, it was found that crack-free porous glass-ceramics with ultra-low thermal expansion coefficient can be prepared using the present sol–gel method.

References

1. P. W. McMILLAN, Glass Ceramics (Academic Press, New York, 1979).
2. J. PHALIPPOU, M. PRASSAS and J. ZARZYCKI, *J. Non-Cryst. Solids* **48** (1982) 17.
3. G. ORCEL, J. PHALIPPOU and L. L. HENCH, *ibid.* **82** (1986) 301.
4. G. ORCEL and L. L. HENCH, in "Science of Ceramic Chemical Processing", edited by L. L. Hench and D. R. Ulrich (Wiley, New York, 1986) p. 224.
5. J. COVINO, F. G. A. DE LAAT and R. A. WELSBIE, *J. Non-Cryst. Solids* **82** (1986) 329.
6. H. DE LAMBILLY and L. C. KLEIN, *ibid.* **102** (1988) 269.
7. J. S. YANG, S. SAKKA, T. YOKO and H. KOZUKA, *J. Mater. Sci.* **25** (1990) 1773.
8. T. ADACHI and S. SAKKA, *ibid.* **99** (1988) 118.
9. C. E. BRACKBILL, H. A. McKINSTRY and F. A. HUMMEL, *J. Amer. Ceram. Soc.* **34** (1951) 107.
10. P. F. JAMES, "Nucleation and Crystallization in Glasses", "Advances in Ceramics", Vol. 4, edited by J. H. Simmons, D. R. Uhlmann and G. H. Beall (American Ceramic Society, Columbus, Ohio, 1982) p. 1.
11. P. E. DOHERTY, D. W. LEE and R. S. DAVIS, *J. Amer. Ceram. Soc.* **50** (1967) 77.
12. N. NAKAGAWA and T. IZUMITANI, *J. Non-Cryst. Solids* **7** (1972) 168.
13. F. A. HUMMEL, *J. Am. Ceram. Soc.* **34** (1951) 236.
14. W. OSTERTAG, G. R. FISHER and J. P. WILLIAMS, *ibid.* **51** (1968) 651.
15. H. SCHULZ, *ibid.* **57** (1972) 313.

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