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졸-겔 방법에 의한 Li_2O-Al_2O_3-SiO_2계 저열팽창성 결정화유리의 제조

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Preparation of Ultra-Low Thermal Expansion Li_2O-Al_2O_3-SiO_2 Glass-Ceramics by Sol-gel Technique

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요 약 : Li_2O-Al_2O_3-SiO_2계 결정화유리의 저온합성을 위하여 출발원료로서 각 해당 금속 알콕시드를 사용하였다. 알코올을 용매로 충분히 첨가하고, drying control chemical additive로 dimethyl formamide를 적당량 첨가한 혼합용액을 과잉의 물로 충분히 가수분해시킨 습윤겔을 저온에서 건조하여 균열이 없는 건조된 monolith겔을 합성하였다. 건조겔로부터 750-950℃로 10시간 이상 소결하여 저열팽창성을 나타내는 β-eucrpytite(β-quartz 고용체), $Li_2O \cdot Al_2O_3 \cdot 3SiO_2$ 및 β-spodumene등의 결정상을 석출시켰다.

Abstract : Glass-ceramic monoliths with an ultra-low thermal expansion coefficient have been synthesized by the sol-gel technique using metal alkoxides as starting materials and dimethyl formamide as a drying control chemical additive. The ternary gels: $Li_2O \cdot Al_2O_3 \cdot 2$, 4 or $6SiO_2$ were obtained by hydrolysis and polycondensation reactions of metal alkoxides of silicon, aluminum and lithium. To produce cylindrical crack-free gel monoliths, excess water was used to the starting solutions and drying rates were controlled precisely to prevent cracking. In conversion process β-eucryptite, $Li_2O \cdot Al_2O_3 \cdot 3SiO_2$ and β-spodumene with β-quartz solid solution phase were obtained by heating at the range of 750~1000 ℃. Above 800℃, the β-spodumene phase increased while β-eucryptite phase decreased. The thermal expansion coefficient of the crystallized specimens were $-15 \sim +5 \times 10^{-7}$/℃ over the temperature range from room temperature to 600℃.

1. Introduction

Glass-ceramics based on the crystalline phases of an equivalent oxide composition of β-spodumene($Li_2O \cdot Al_2O_3 \cdot 4SiO_2$) and β-eucryptite($Li_2O \cdot Al_2O_3 \cdot 2SiO_2$) are famous for ultra-low or negative thermal expansion characteristic and high chemical durability.[1] Several attempts have been made to synthesize these glass-ceramics via the sol-gel method.[2~9] In this study, dried gel monoliths which were composed of $Li_2O \cdot Al_2O_3 \cdot 2 \sim 6SiO_2$ have been prepared by the sol-gel technique and converted to glass ceramic monoliths without cracks from the dried gel monoliths. Generally in the preparation of multicomponent monolithic gels, serious problems occur during hydrolysis, polycondensation of metal alkoxides and drying of wet gels. Cracks and bubbles are appeared after segregation of specific oxides due to different rates of hydrolysis. To overcome these problems, this paper suggests the application of N, N-dimethyl formamide(DMP) as drying control chemical additive(DCCA), which had been found effective in producing not only the large gel monoliths but also the glass-ceramic monoliths without the occurrence of crack, fracture and bloating.[10, 11] Ac-

cording to our previous reports of lithium aluminosilicate glass-ceramic prepared by the sol-gel technique, it was found that the optimum quantity of water for the hydrolysis of alkoxides group was three times of the theoretical stoichiometry of water and the conversion temperature of the gel monoliths to glass-ceramic was higher than 800℃.[7-9] We investigated the effect of the composition of gels on crystallization and thermal expansion behavior of the crystallized specimens under the given condition. The solutions were characterized in terms of gelling time. Density and surface area measurements were performed to distinguish the differences in texture of the crystallized monoliths which had the compositions of $Li_2O \cdot Al_2O_3 \cdot 2SiO_2$, $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ and $Li_2O \cdot Al_2O_3 \cdot 6SiO_2$. Thermal characterizations were performed with differential thermal analysis. Finally crystallized monoliths were investigated with X-ray diffractometer, dilatometer and scanning electron micrtoscope.

2. Experimental procedure

2.1. Preparation of gel monoliths

Monolithic gels corresponding to $Li_2O \cdot Al_2O_3 \cdot 2SiO_2$(LA2S), $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$(LA4S) and $Li_2O \cdot Al_2O_3 \cdot 6SiO_2$(LA6S) in molar ratio were prepared by the hydrolysis and polycondensation of metal alkoxides: lithium methoxide, aluminum secbutoxide(ASB) and tetraethoxysilane(TEOS). Compositions of the starting solutions used in this experiment are listed in Table 1. Lithium methoxide solution was prepared by dissolving 1 mole of lithium metal in 15 moles of methanol. TEOS was partially reacted before mixing with the three different kinds of metal alkoxies. For the partial reaction of TEOS, a quarter of the water for full hydrolysis was added to alcoholic TEOS solution(TEOS/EtOH=1/5) and kept at 75℃ for 2h. The partially hydrolyzed TEOS soltuion was added drop by drop to the ASB solution, and then the lithium methoxide solution was added to this solution. The mixtures of the three kinds of metal alkoxies corresponding to the oxide compositions of $Li_2O \cdot Al_2O_3 \cdot 2$, 4 or $6SiO_2$ and a desired amount of DMF were refluxed at 80℃ for 1h. And the mixed solutions were cooled to 50℃ under N_2 atmosphere.

For preparing the starting sol, diluted aqueous ethanol(1 : 1) and the metal alkoxides solutions were mixed in a flask with stirring. The total amount of water became 1～5 times of the stoichiometry of water in molar ratio which required for hydrolyzing alkoxy groups of metal alkoxides. The starting sols were kept at 50℃ in a capped cylindrical glass(300ml) for gelling reaction. Gelling point of the sol was determined at the when no fluidity was observed while tilting the container. After sols were gelled, the gels were aged in a drying oven at 50℃ for two days.

2.2. Drying of the gel, sintering and crystallization of the monolithic gel

For the first step of drying, the wet gels were placed in a drying oven and the temperature was raised to 80℃. Drying was started by perforating the sealing cap with a number of small pinholes 1～2mm in diameter. The gels were dried for 340h. The evaporation rate was 4～6%/day. When total weight loss of the wet cap was removed for the second step of dry-

Table 1. Compositions of starting metal alkoxides solutions

Starting solution	Materials of three kinds of metal alkoxides solutions(mole)							
	$Si(OC_2H_5)_4$	C_2H_5OH	H_2O	$Al(OC_4H_9)_3$	C_4H_9OH	Li-metal	CH_3OH	DMF
LA2S	0.1	0.4	0.1	0.1	0.1	0.1	1.5	0.3
LA4S	0.2	0.8	0.2	0.1	0.1	0.1	1.5	0.4
LA6S	0.3	1.2	0.3	0.1	0.1	0.1	1.5	0.5

gel reached at 70% of the original weight, the

ing. The crack-free gel monoliths were heated to 180℃ and rested about two weeks in a vacuum oven. The dried gels were sintered at 550 ℃ for 20h in air. And the sintered gels were crystallized at a given temperature between 750～1000℃ for 20h, respectively. The heating rate was 1℃/h.

2.3. Characterization techniques

DTA and TG were used to characterize micro structure and thermal behavior of gels and crystallized specimens. The dried gels were powdered(-100 mesh) and heated at the rate of 10℃/min. Fractured surface of the dried gels and the crystallized specimens were observed by SEM. Density and surface area were measured by Archimedes and BET methods, respecitively. Thermal expansion coefficients of the crystallized specimens were measured by a thermomechanical analyzer(quartz glass tube) at the heating rate of 2℃/min. Crystallization temperature was determined at the peak temperatures on the DTA curves. X-ray diffractometer with Ni-filtered CuKα radiation was used for qualitative analysis.

3. Experimental Results and Discussion

3.1. Effect of the amount of water

Fig.1 shows the gelling time of three kinds of the starting soultions as function of water content at 50℃. Gelling time of the starting solutions which contained a stoichiometric amount of water shortened with decrease of SiO_2 content. LA2S, LA4S and LA6S gelled in 70-80 min, 310-320 min and 600-620 min respectively. Especially LA2S and LA4S which contained three and four times of the stoichiometric amount of water gelled in very short time. Fig. 1 discloses that the gelling time was drastically shortened with increase of water and TEOS contents. The gelling time of LA6S was much longer, which indicates that the TEOS content was the most important factor for determining the gelling time. Because the hydrolysis-polymerization of TEOS was the slowest process among the reactions of the three kinds of metal alkoxides.[12]

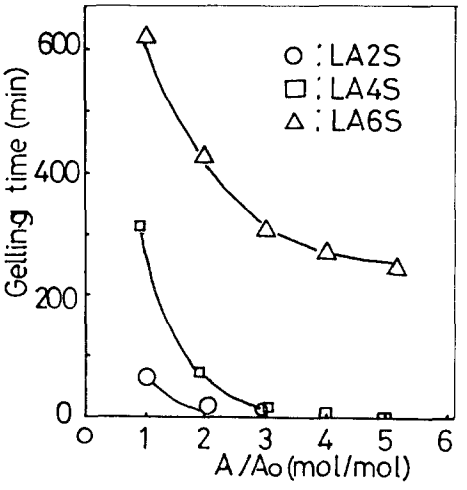

Fig. 1. Gelling time of the sols by hydrolysis.
A_o : Theoretical amount of water for hydrolysis
A : Added water

On the other hand, the increased ASB concentration of the starting solutions was inversely proportional to the gelling time. It was recognized that aluminum alkoxide showed a higher rate of polymerization than silicon alkoxide. Therefore the mixed$(BuO)_2Al$-O-Si$(OTE)_3$ was created during the polycondensation reaction. It should be expected that the increase of Al_2O_3 content affected the increase of the number of Al-O-Al linkage. This tedency was observed in the gels with higher Al_2O_3 content.[12, 13]

3.2. Changes in the volume of the monolithic gels

Fig.2 shows the relationship between volume shrinkage(V/V_o) and weight loss(W/W_o) of the three kinds of gels during the conversion of wet gels to the dried gels at 80℃.

In the region I and Ⅲ the three kinds of gels exhibited similar relationship between(V/V_o) and (W/W_o). And no significant difference was found in the evaporation rate of 4-6%/day at 80℃ throughout the whole drying period. Only in the region Ⅲ the sharp difference in evaporation rate was investigated after re-

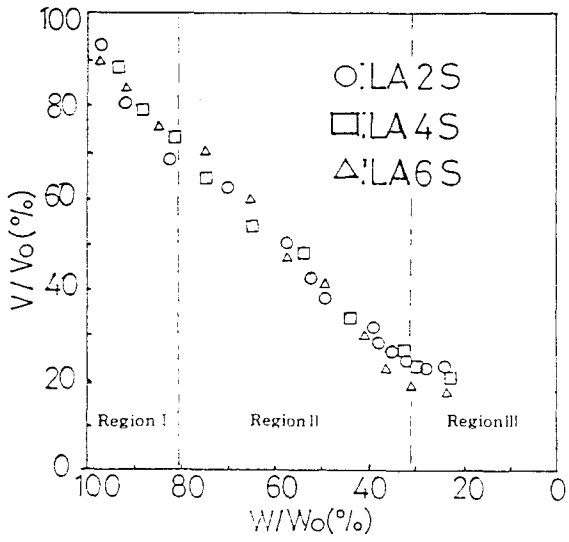

Fig. 2. Volume shrinkage-weight loss curves for gel LA2S, LA4S and LA6S during the drying at 80℃.

moving the cap of gel container. On the other hand, the volume shrinkage of the gels was negligibly small in the region Ⅲ. At the evaporation rate of about 0.25-0.04%, no crack was found in the three kinds of gels which was leading to the formation of crack-free monoliths. According to Scherer,[15] slow rate of drying permitted the relaxation of stress caused by the capillary force and the blurring of interface between the stressed parts due to the effusion of solvents. This phenomenon was confirmed in these experiments, i.e. the three kinds of wet gels could be dried without the formation of cracks when the rate of drying at 80℃ was small as 4-6%/day. On the contrary, it was cracked when the rate of drying was fast as 8%/day in the region.

3.3. DTA, TG, XRD analysis and thermal expansion

DTA and TG curves for the dried gels obtained by drying at 80℃ are given in Fig. 3. The slow decrease in weight on the TG curves and endothermic peaks on the DTA curves observed below 100℃ could be attributed to the vaporization of water which deposited on the pores surface. The decrease in weight on the TG curves and the endothermic peaks in DTA curves around 200℃, 250℃ and 400℃ might be attributed to the desorption of residual organic materials which were trapped in the micropores, or to the decomposition of unhydrolyzed alkoxy groups. And a few exothermic peaks were observed in the temperature range 750-1000℃ which might be corresponded to crystallization of the gels. The TG curves showed that the gels dried beforehand still lost 20~25% in weight. According to Hummel[16] the first exothermic peak was due to the precipitation of β-eucryptite with β-quartz solid solution and the second exothermic peak was due to the precipitation of β-spodumene phase. As for the gels LA2S, two exothermic peaks appeared at 750℃ and 870 ℃. In the gles LA4S were observed two exothermic peaks at 860℃ and 890℃. And the gels LA6S showed two exothermic peaks at 810℃ and 880℃, respectively.

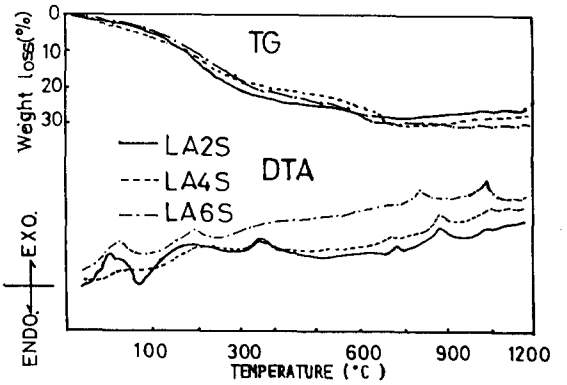

Fig. 3. DTA-TG curves for gel LA2S, LA4S and LA6S dried at 80℃.

XRD patterns of the gel monoliths crystallized at the temperature above 700℃ for 20h are shown in Fig. 4. At the range of 700℃~750℃ the β-eucryptite was predominant in the LA2S monoliths. Above 800℃, small amount of β-spodumene crystals existed. The amorphous material began to crystallize above 700℃,

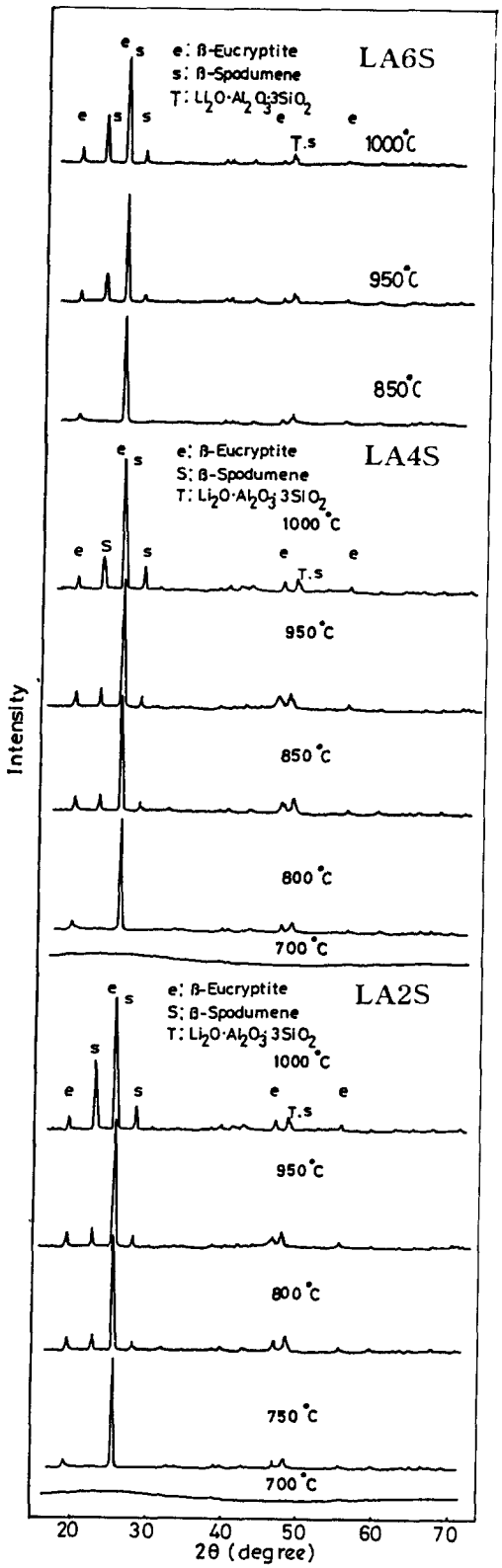

Fig. 4. XRD patterns of the monolithic gels heated at various temperatures for 20h.

but it was not crystallized completely below 850℃. At the range of 800～820℃, LA4S and LA6S monoliths contained β-eucryptite crystals. At the range of 880～900℃ the peaks for β-eucryptite and β-spodumene existed. Above 900℃ β-spodumene increased while β-eucryptite decreased in both monoliths with increase of temperature. Both the XRD analysis and DTA data revealed the same sequence of events.

The composition of the gels used in this study corresponded to that of so-called $Li_2O \cdot Al_2O_3 \cdot SiO_2$ glass system. It is well know 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.[17, 18] This phenomenon is explained by the metastable phase separation of the glass into phases rich and poor in SiO_2, on heating.[18] That is, out of the latter phase with lower SiO_2 coontent β-eucryptite crysatals are precipitated, which then transform into β-spodumene by taking up the SiO_2 from the SiO_2-rich phase at higher temperatures.

In this sense, it can be said that the crystallization behavior of the gel with a composition $Li_2O \cdot Al_2O_3 \cdot 2\text{-}6SiO_2$ prepared in this study is almost the same as that of a melt-derived glass,[16] although the crystallization temperature of gels is slightly lower than that of a melt-derived glass.[8] This means that although

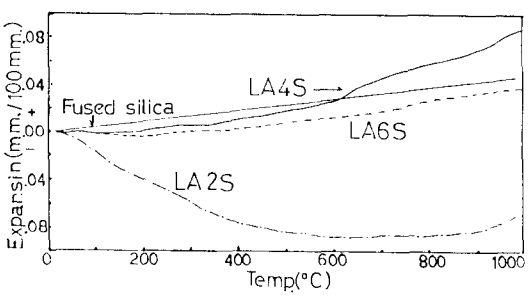

Fig. 5. Thermal expansion curves for the specimens crystallized at 950℃ for 20h.

the hydrolysis rates of three kinds of metal alkoxides are very different, an intimate mixing of the respective elements can be attained 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,[19] where precipitation of Li_2SiO_3, $Li_2Si_2O_5$ and β-quartz were observed at lower temperatures.

Orcel and Hench[4] ovserved the precipitation of β-eucryptite phase(not β-spodumene) as low as 375-400℃, which is by about 350℃ lower than this case. This is possibly ascribed to the addition of 6% TiO_2 as a nucleating agent and not that of DCCA.[20, 21]

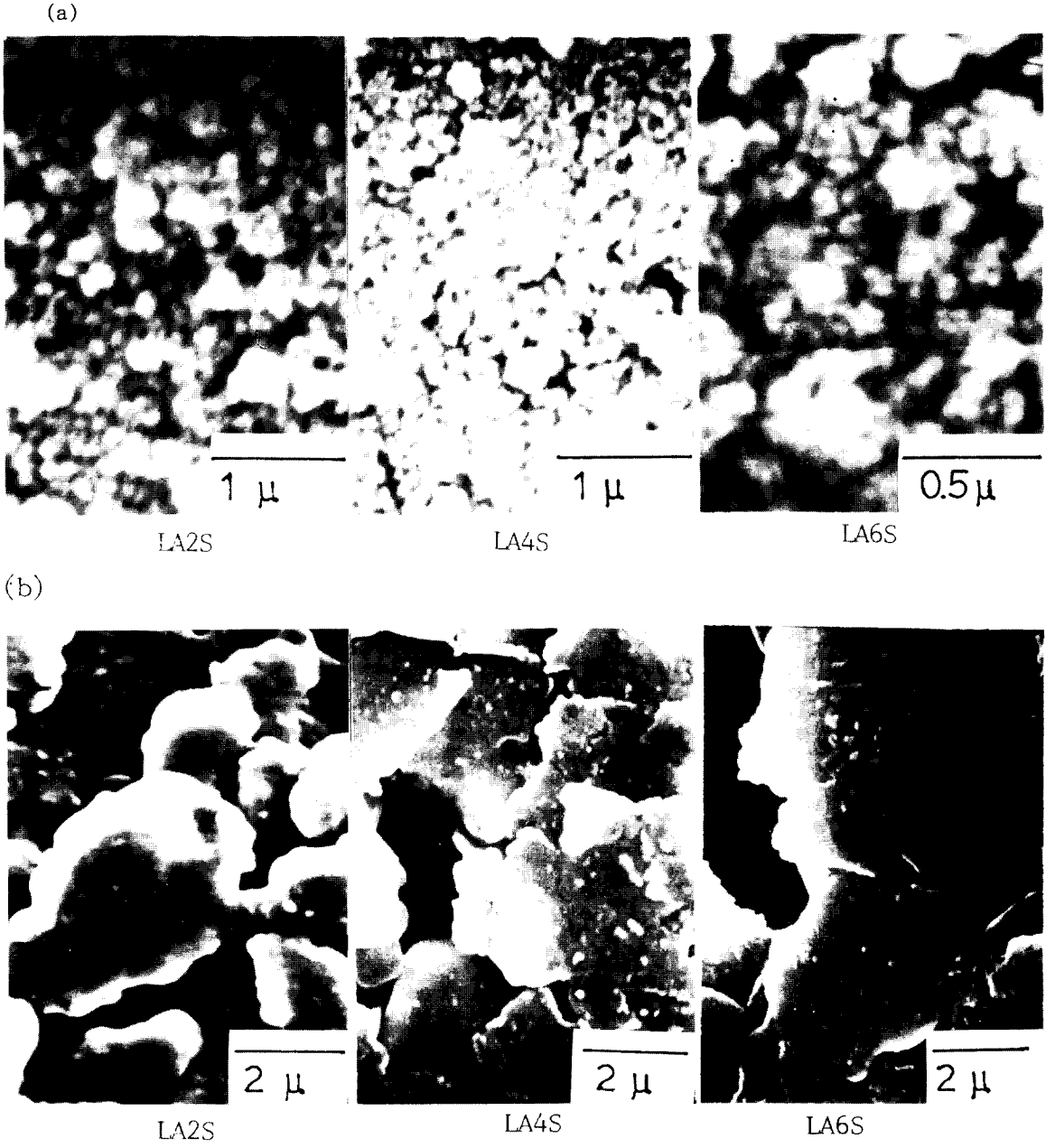

Fig. 6. SEM of the fractured surface of dried gels(a) at 80℃ and glass-ceramics(b) sintered at 950℃ for 20h.

Fig. 5 discloses thermal expansion characteristics of the specimens crystallized at 950℃ for 10h. The specimens LA2S showed negative thermal expansion coefficients to 1000℃. The β-eucryptite and β-spodumene phases around 950℃ which were the equilibrium phases in the range of these gel compositions were very desirable since they had a negative thermal expansion coefficients. The glass-ceramics of lithium aluminosilicate are widely known for ultra-low or negative thermal expansion.[16-18] By heating the gels above 850℃, three kinds of gels yielded a glass-ceramics with very low or even negative thermal expansion coefficients. These results obviously indicate that the lithium aluminosilicate glass-ceramic monoliths with a desired thermal expansion coefficient of negative(-15×10^{-7}/℃) to positive (5×10^{-7}/℃) values can be easily prepared by controlling the fraction of β-eucryptite and β-spodumene phases.

3.4. Micro structure of sintered gels and crystallized monoliths

Fig. 6 shows SEM microphotographs of the three kinds of dried gel monoliths by heated up to 80℃ and those of the crystallized monoliths prepared by heating gel monoliths at 950℃ for 20h. The dried gel LA2S consisted of large particles whose diameter was less than 0.01㎛. And dried gels LA4S and LA6S had a much fine texture and small pores. It was found that the gel-glass monoliths became glass-ceramic monoliths without cracking and deformation. The crystallized specimens at 950℃ had an open structure consisted of secondary particles of several micrometers in size, which were composed of finer primary particles. At 950℃, fine crystalline particles were appeared.

The crystallinity seemed very poor. The bulk density, specific surface area and porosity of three kinds of the sintered gels and the glass-ceramic monoliths are summarized in Table 2.

Table 2. Some properties of typical crystallized specimens

sample No.	Bulk density (gcm^{-3})	Surface area (m^2g^{-1})	Porosity (%)	Appearance
LA2S	2.00	354	31.4	opaque
LA4S	2.10	312	28.0	opaque
LA5S	2.14	288	27.0	opaque

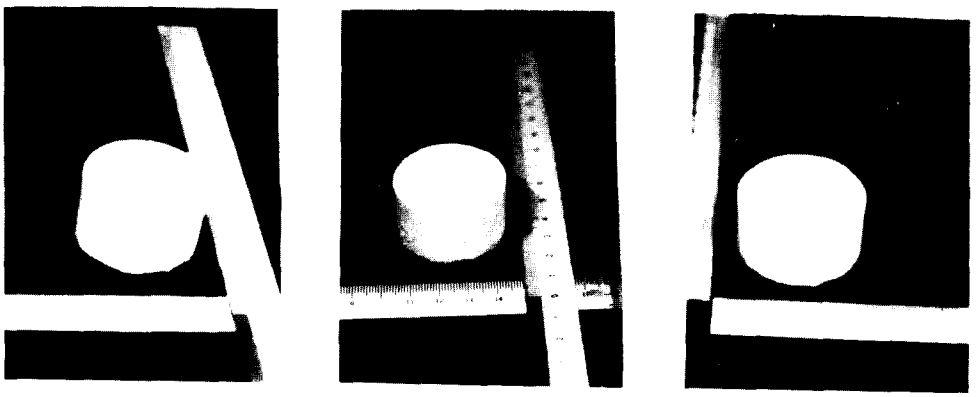

Fig. 7. Photographs of the monolith glass-ceramics obtained by heated gels at 1000℃ for 10h.

After being sintered at 950℃, densification was not completed. Many pores remianed, indicating that the monolithic glass-ceramics obtained in the processing work were porous.[7, 8] Fig. 7 shows the photographs of the glass-ceramic monoliths prepared by heating gel monoliths at 950℃ for 20h. It was found that the corresponding gel monoliths became glass-ceramic monoliths without cracking and deformation. It was clearly seen that crystallization took place homogeneously over the whole sample in the gel monolith. The samples were visibly opaque by heated up to 850℃.

4. Conclusion

Lithium aluminosilicate glass-ceramics with the composition Li_2O $Al_2O_3$2, 4 or 6SiO_2 were prepared in monolithic form. The three kinds of gels which contained water three times of the stoichiometric amount were crack-free througout drying process at the evaporation rate of 4～6%/day. It was found that the use of DMF was necessary to produce crack-free gel monoliths. The glass-ceramic monoliths obtained by heating at the range of 750～850℃ for 10h were porous whose bulk density and porosity were 1.8～2.0g/cm^3 and 34～36%, respectively. β-Eucryptite crystals were precitated first at the range of 750～850℃. And then β-spodumene precipitated at the temperature above 850℃. The crystallized specimens at 950℃ for 10h exhibited very low thermal expansion coefficient ranging -15～+5×10^{-7}/℃ from 10h exhibited very low thermal expansion coefficient ranging -15～+5×10^{-7}/℃ from room temperature to 600℃. It was found that crack-free porous glass-ceramics with ultra-low thermal expansion coefficient could be prepared by using the sol-gel method.

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