Preparation of Single Phase β -Spodumene Powders by Sol–Gel Processゾル–ゲル プロセス法による β スポジューメン粉体の作製

Shaw-Bing WEN, Sheng YANG, Jen-Min CHEN,* Nang-Chung WU* and Moo-Chin WANG**

Department of Resources Engineering, National Cheng-Kung University, 1, Ta-Hsueh Road, Tainan, 70101 Taiwan, ROC

*Department of Material Science and Engineering, National Cheng-Kung University, 1, Ta-Hsueh Road, Tainan, 70101 Taiwan, ROC

**Department of Mechanical Engineering, National Kaohsiung Institute of Technology, 415, Chien-Kung Road, Kaohsiung, 80782 Taiwan, ROC

The β -spodumene ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$, LAS) powders were prepared by the sol-gel process using a mixture of silica sol, alumina sol and lithium nitrate solution. $\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{Al}(\text{OC}_4\text{H}_9^{\text{sec}})_3$ and LiNO_3 were used as the starting compounds. Thermogravimetric and differential thermal analyses (TG/DTA), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), wavelength-dispersive spectroscopy (WDS), transmission electron microscopy (TEM) and electron diffraction (ED) analysis were utilized to characterize the β -spodumene powders prepared by the sol-gel process. The crystallization temperature of the LAS gel powder estimated by TG/DTA was about 630°C. When the LAS dried gel was heated from 600 to 850°C, the crystallized powders of the single phase β -spodumene were obtained.

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1. Introduction

Over the past several years, much interest has been focused on the $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2$ ceramics with $n=2$ (eucryptite), 4 (spodumene), 6 (lithium orthoclase) and $n=8$ (petalite). With excellent thermomechanical and electrical properties,¹⁾ they have been widely used as thermal shock resistant ceramics in high temperature applications. Conventionally, low thermal expansion coefficient ceramics such as β -spodumene ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$, LAS), are fabricated mainly by the recrystallization of solidified melt, but it is not easy to sinter β -spodumene powders without proper sintering aid except for the alkoxide-derived precursors.^{1)–5)} The incorporation of sintering aid results in a large thermal expansion. Therefore, the preparation of homogeneous fine β -spodumene or eucryptite powders has been considered to be indispensable.

In recent years, sol-gel process has been widely used in the manufacture of ceramics because of its inherent advantages over conventional processes.^{6)–9)} For example, the high surface area of dried gels can result in very high reactivity which permits low process temperatures. By starting with well mixed solutions or sols, chemical homogeneity even on the molecular scale can be obtained.^{10)–13)}

In the present study, oxide gels containing Li^+ , Al^{3+} and Si^{4+} ions in the stoichiometric ratio of β -spodumene phase was prepared by sol-gel process. The scope of the present investigation was to examine the preparation and characterization of the $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2$ gels by thermogravimetric and differential thermal analysis (TG/DTA), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), wavelength-dispersive spectroscopy (WDS), transmission electron microscopy (TEM) and electron diffraction (ED).

The purposes of this investigation are: (1) to examine the effect of water to tetraethylorthosilicate ratio on the gelation time, (2) to study the thermal evolution behavior of the LAS gels, and (3) to evaluate the morphology change during calcination of LAS gels.

2. Experimental procedure

2.1 Gel preparation

The precursor powders for the spodumene phase $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ were prepared from tetraethylorthosilicate (TEOS; $\text{Si}(\text{OC}_2\text{H}_5)_4$), aluminum tri-*sec*-butoxide (ASB,

$\text{Al}(\text{OC}_4\text{H}_9^{\text{sec}})_3$ and lithium nitrate (LiNO_3) as the starting materials, which supplied from Janssen Chemical Co. (Belgium), Aldrich Co. (USA) and Fluka Co. (Switzerland), respectively. A schematic flow chart showing the preparation of LAS ceramic powders through the sol-gel process is illustrated in Fig. 1. The silica sol was prepared by mixing TEOS, ethanol, deionized water and hydrochloric acid in a molar ratio of 1 : 40 : x : 0.3. The alumina sol was prepared by mixing ASB, deionized water and hydrochloric acid in a molar ratio of 1 : 100 : 0.2. The lithium nitrate solution was prepared by dissolving lithium nitrate in deionized water. The LAS precursor powders were prepared firstly by mixing the silica sol and the alumina sol together and then adding the lithium nitrate solution into the mixture. The ratio between the silica sol, alumina sol and lithium nitrate solution was calculated so that the mole ratio of $\text{Li}^+ : \text{Al}^{3+} : \text{Si}^{4+}$ was kept constant at 1 : 1 : 2. Solutions of varied water contents were prepared.

Fig. 1. Schematic diagram of the sol-gel process for preparing β -spodumene ceramic powders.

The mixture solution was placed and refluxed in a 70°C water bath to obtain an insoluble gel. The gel was then dried at 50°C for 72–120 h, and then ground to powders. The alumina balls as grinding medium was used as a grinding medium.

2.2 Analysis of the precursor powders

The precursor powders of the LAS gels, dried at 50°C for 72–120 h and calcined under various conditions, were analyzed. Thermogravimetric and differential thermal analysis (TG/DTA) was conducted on a 50 mg powder sample at a heating rate of 3°C/min in air by SETARAM TGA 24 simultaneous symmetrical thermoanalyzer with powder Al_2O_3 as a reference material.

The chemical composition of the calcined LAS gels was identified by wavelength-dispersive spectroscopy (WDS) analysis with $\text{NaAlSi}_3\text{O}_8$ as an internal standard.

FT-IR absorption spectra were obtained by processing on an optical bench of the standard Nicolet's System 800 Fourier transform infrared spectrometer, featured with an SX operation system, on a Model 620 work station and a spectral resolution of 4 cm^{-1} was chosen. Each sample was mixed with KBr (sample : KBr = 1 : 99 in mass ratio), and was pressed into 200 mg pellets of 13 mm in diameter for taking infrared adsorption spectra at a frequency range of $100\text{--}4000\text{ cm}^{-1}$. The composite spectrum for each sample represented an average of 64 scans, normalized to the spectrum of the blank KBr pellets.

The crystalline phase was identified by XRD and ED analyses. The XRD was performed with a Rigaku X-ray diffractometer with $\text{Cu K}\alpha$ radiation and a Ni-filter, at a scanning rate of $2\theta = 0.25^\circ/\text{min}$. The scanning transmission electron microscopy was carried out using a JEM 200 microscope operating at 200 kV. Selected area electron diffraction examinations were made on the calcined samples.

3. Results and discussion

3.1 Effect of the ratio of water to TEOS on gelation time

Hydrochloric acid was used as a catalyst so that the hydrolysis might well be near completion before any significant condensation even at low $\text{H}_2\text{O}/\text{TEOS}$ ratios.¹⁴ The precursor powders with spodumene ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$) composition were prepared by the hydrolysis and polymerization from a LiNO_3 solution and alcoholic solution of ASB and TEOS with different molar ratios of H_2O to TEOS.

The solutions of sol precursors were mixed together as described already in the experimental procedure. The time passed since the beginning of the refluxing until gelation is defined as gelation time. The relationship between the gelation time and the mole ratio of water to TEOS for the LAS solutions is shown in Fig. 2. The gelation time of the LAS solution increases from 40 to 205 min as the $\text{H}_2\text{O}/\text{TEOS}$ mole ratio increases from 10 to 30, whereas the gelation time decreases from 205 to 10 min when $\text{H}_2\text{O}/\text{TEOS}$ ratio increases from 30 to 250.

According to the study of Coltrain et al.,¹⁵ the gelation times of hydrolyzed alkoxysilane solution exhibits a maximum against pH of the reaction solution. Around the isoelectric point of silica with minor dependence on the kind of counter ions. Although the pH values have not been directly measured in this study, the water/catalyst mole ratios employed, from 3 to 7.5, would result in pH values corresponding to above and below the isoelectric point. That is, the drastic change in gelation time with water/catalyst or water/TEOS ratio is mainly due to the pH change in the entire reaction solution.

Fig. 2. Relationship between gelation time and $\text{H}_2\text{O}/\text{TEOS}$ mole ratio in LAS solution.

3.2 Effect of the ratio of water to TEOS on the chemical composition

The analytical contents of Al_2O_3 and SiO_2 in the LAS gels prepared under different hydrolysis conditions are shown in Fig. 3. The Al_2O_3 content is slightly higher and the SiO_2 content is a little less than the expected values from the batch composition. Premature gelation may take place, where ASB is hydrolyzed initially and reacts with slowly hydrolysing TEOS, with the polymerization of the former proceeding.

Even with an excess amount of water, TEOS does not completely hydrolyse to an "OR" free complex, e.g., $\text{SiO}_{(4-x)/2}(\text{OH})_x$, unlike the aluminium alkoxides, and hence, "OR" and "OH" ligands coexist in the hydrolysed product:¹⁶

Equation (1) is a simplified reaction involving polymerization between "OH" and "OR" ligands and formation of bridging oxygens. For an unhydrolysed TEOS, the stoichiometric SiO_2 content is a $\text{SiO}_2/\text{TEOS} = 28.8\%$ by weight. According to Yoldas's paper,¹⁶ if this material is hydrolyzed without forming any bridging oxygen to form $\text{Si}(\text{OH})_x(\text{OR})_y$ complex the silica content varies from 28.8% for $x=0$ to 62.5% for $y=0$, however, in the presence of bridging oxygen, the polymer contain as much as 85 to 90% of SiO_2 .¹⁶

Fig. 3. Relationship between the analytical Al_2O_3 and SiO_2 content and $\text{H}_2\text{O}/\text{TEOS}$ mole ratio in LAS gels.

3.3 Thermal behavior of the LAS gels

TG/DTA curves of the LAS gels measured at a heating rate of $3^\circ\text{C}/\text{min}$ are shown in Fig. 4. An endothermic peak at 175°C accompanied with a weight loss of 15% is assigned to the vaporization of water and residual organics. An exothermic peak at $250\text{--}270^\circ\text{C}$ is assigned to the combustion of carbonaceous materials.^{17,18} An endothermic reaction peak at $280\text{--}310^\circ\text{C}$ is assigned the evolution of crystalline water. Apparently, the weight loss at $200\text{--}500^\circ\text{C}$ is attributable to the dehydration of the LAS precursor.¹¹ An exothermic reaction peak at around 330°C is attributed to the burning of alkyl group.¹⁸ A sharp exothermic reaction peak at 630°C is due to the formation of β -spodumene crystals.

The FT-IR spectra for the dried gels and the powder calcined at various temperatures for 4 h are shown in Fig. 5. The 3400 cm^{-1} band is attributed to silanol group and adsorbed water.¹⁹ The bands at $2000\text{--}1800\text{ cm}^{-1}$ can not be observed by the KBr method.²⁰ At 2961 , 1384 and 1250 cm^{-1} , the C-H vibration in ethyl and butyl groups is observed.^{17,19,21} These bands indicated that the ethyl and TO groups are retained in the LAS gels because of the incomplete hydrolysis of TEOS.¹⁹ The characteristic band around 1180 and 1050 cm^{-1} corresponds to the LO and TO modes of Si-O-Si asymmetric stretching vibration.¹⁹ The absorption peak belonging to the ring structure of SiO_4 tetrahedra at about 800 cm^{-1} is found.²² These results sug-

Fig. 4. TG/DTA curves for LAS gels ($\text{H}_2\text{O}/\text{TEOS}=40$) measured at a heating rate of $3^\circ\text{C}/\text{min}$.

Fig. 5. FT-IR absorption spectra of LAS gels ($\text{H}_2\text{O}/\text{TEOS}=40$) dried at 50°C for 120 h and calcined at various temperatures for 4 h: (a) as-dried at 50°C , calcined at (b) 550°C , (c) 600°C , (d) 650°C and (e) 750°C .

gest that the polymerization of TEOS has already occurred in gels.¹⁴ The absorption peak at 705 cm^{-1} can be assigned to Al-O stretching vibration.²³ The absorption peak at 475 cm^{-1} seen in the spectra of LAS gels is attributed to the usual silica rocking vibration.²⁴

3.4 Phase evolution of the LAS gels

The phase relationship in the crystallized LAS and LAST ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{TiO}_2$) gels has been examined previously using XRD.^{1,4,25-28} Table 1 summarizes the phases developed during the calcination of the LAS and LAST gel system.

The X-ray diffraction patterns of LAS powders calcined at various temperatures for 4 h are shown in Fig. 6. The effect of calcination temperature on the evolution of the crystalline phases is as follows: (a) at 500°C , the phase is maintained in the amorphous state; (b) at 550°C , the major reflections corresponding to the (201), (100) and (111) of β -spodumene appear; (c) at 600°C , the (211) and (400) reflections of β -spodumene first appear; (d) at $650\text{--}850^\circ\text{C}$, X-ray diffraction patterns are representative of the β -spodumene, where no other phases can be detected. The crystallinity of the β -spodumene phase is improved by increasing temperature.

When LAS gels are calcined at 1350°C for longer than 24 h, the X-ray diffraction peaks of β -spodumene are considerably sharp and no intensity change occurs for the major peak (201). Therefore the intensity of the major peak (2θ from 24.5 to 26.1°) detected in the sample calcined at 1350°C for 24 h can be used as a standard for comparing the crystallinity between different samples. The relative height of (201) peak is shown in Fig. 7 as a function of calcination time at 1350°C . The relative peak height is greater than 90% at 4 h and then reached 100% at 16 h.

3.5 TEM of the LAS gels

TEM picture of the as-dried samples ($\text{H}_2\text{O}/\text{TEOS}=40$) is shown in Fig. 8(a). The aggregation of the small particles probably occurs as they are concentrated on the grid by drying. TEM pictures of the LAS powders ($\text{H}_2\text{O}/\text{TEOS}=40$) calcined at 550°C and 850°C for 4 h are shown in Fig. 8(b) and Fig. 8(c), respectively. A lot of grains have been crystallized and grown. Fine grains are gradually grown into large grains with increasing calcination temperatures. Figures 8(d) and 8(e) show the bright and

Table 1. Crystalline Phases in the β -Spodumene Precursor Powder Developed during Calcination at Various Temperature

Starting materials	Temp. ($^\circ\text{C}$)	Index method	Phases	Ref.
$\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{Al}(\text{OC}_2\text{H}_5)_3$, and Li	600	XRD	γ -spodumene(β -	1
	800	TEM	eucryptite/ β -Quartz solid solution)	
	1200		β -spodumene	
$\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{Al}(\text{OC}_4\text{H}_9^{\text{sec}})_3$, and Li	750	XRD	β -spodumene, β -eucryptite	4
	880		β -spodumene, β -eucryptite	
	1000		β -spodumene, β -eucryptite	
$\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{Al}(\text{OC}_2\text{H}_5)_3$, and LiOCH_3	800	XRD	β -spodumene, β -eucryptite	25
	1200		β -spodumene	
			β -spodumene	
$\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{Al}(\text{OC}_2\text{H}_5)_3$, LiOCH_3 and $\text{Ti}(\text{OC}_2\text{H}_5)_4$	800	XRD	β -spodumene	26
	1000	TEM	β -spodumene, TiO_2	
	1200		β -spodumene, TiO_2	
$\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{Al}(\text{OC}_4\text{H}_9^{\text{sec}})_3$, and LiOCH_3	1350, at 6.9Mpa HP	XRD	β -spodumene, mullite	27
	15 min.			
Alumina sol, silica sol and LiNO_3	1350	XRD	β -spodumene, $\text{LiAlSi}_3\text{O}_8$	28
		SEM		
$\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{Al}(\text{OC}_4\text{H}_9^{\text{sec}})_3$, and LiNO_3	800	XRD	β -spodumene	This study
		TEM

Fig. 6. XRD patterns of the LAS gels ($H_2O/TEOS=40$) calcined at various temperatures for 4 h: calcined at (a) 500°C, (b) 550°C, (c) 600°C, (d) 650°C, (e) 750°C and (f) 850°C.

Fig. 7. Relative height of β -spodumene (201) peak as a function of calcination time at 1350°C.

dark fields of LAS powders calcined at 850°C for 4 h, respectively, and Fig. 8(f) shows the corresponding ED pattern. The ED pattern also reveals the presence of β -spodumene in this system.

4. Conclusions

Fine and homogeneous β -spodumene ceramic powders were prepared by the hydrolysis of $Si(OC_2H_5)_4$, $Al(OC_2H_5)_3$, and $LiNO_3$ in solution in the presence of hydrochloric acid as a catalyst and with different $H_2O/TEOS$ mole ratios. The results in the present study are summarized as follows:

(1) β -spodumene ceramic powders were formed through calcination from a solution of alumina sol, silica sol and lithium nitrate solution in the mole ratio of $Li^+ : Al^{3+} : Si^{4+}$ is 1 : 1 : 2.

Fig. 8. TEM images and ED pattern of LAS powders heat-treated at various temperatures: (a) the aggregation of the small particles on the grid by drying; (b) calcined at 550°C for 4 h; (c) calcined at 850°C for 4 h; (d) calcined at 850°C for 4 h showing the BF image; (e) DF image by using circular spot of (f); (f) ED pattern indexing corresponding β -spodumene.

(2) The gelation time of the LAS solution increases from 40 to 205 min as the mole ratio $H_2O/TEOS$ increases from 10 to 30, whereas if the ratio of $H_2O/TEOS$ increases from 30 to 250 mol/mol, the gelation time decreases from 205 to 10 min.

(3) By heating the dried gels from 600 to 850°C, crystallization of β -spodumene gradually occurs, excluding the formation of eucryptite, γ -spodumene and β -quartz.

(4) When LAS gels were heated at 1350°C for 16 h, XRD peak intensity become saturated, while the peak intensity has already reached 90% of the saturated value on 4 h heating.

(5) The initial primary LAS particles is observed less than 10 nm and gradually grown into large crystalline grains with increasing calcination temperature. The electron diffraction pattern shows the presence of the β -spodumene phase in the sample calcined at 850°C for 4 h.

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