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Crystallization behaviour of β-spodumene in the calcination of Li_2O–Al_2O_3–SiO_2–ZrO_2 gels

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This work was carried out in order to prepare precursor powders with a spodumene composition ($Li_2O \cdot Al_2O_3 \cdot 4SiO_2$, LAS) and to investigate their crystallization behaviours during calcination. A fine β-spodumene type amorphous powder was obtained through sol–gel techniques using $LiOCH_3$, $Al(OC_2H_5)_3$, $Si(OC_2H_5)_4$ and $Zr(OC_2H_5)_4$ as the starting metal alkoxides. The process included well controlled hydrolysis polycondensation of the raw alkoxides. Differential thermal analysis (DTA), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and electron diffraction (ED) analyses were utilized to study the crystallization behaviour of the gels. The activation energy of β-spodumene crystallization was 192 kJ mol^{-1} for LAS gels with 4 wt% ZrO_2, being much smaller than those of LAS gel without ZrO_2, 382 kJ mol^{-1}. For calcination at 800–1200 °C, the crystallized phases comprised a major phase of β-spodumene and a minor phase of zirconia (ZrO_2).

1. Introduction

Over the past several years, much interest has been focused on Li_2O–Al_2O_3–SiO_2 ceramics because they have excellent thermomechanical and electrical properties [1]. They are practically used as industrial furnace material and heat exchangers for gas turbine and packaging [2]. β-spodumene commercially available glass–ceramics are prepared mainly by the recrystallization of solidified glass melt, but it has been impossible to sinter pure β-spodumene powder without proper sintering aid, except for alkoxide-derived precursors [3–5]. The incorporation of a sintering aid resulted in a large thermal expansion. Therefore, the preparation of homogeneous and fine β-spodumene powder has been considered to be indispensable.

The use of metal alkoxide to obtain homogeneous glasses and ceramics via the sol–gel process has been widely explored in recent years [6–9]. The sol–gel method is a chemical technique, which includes the following stages:

1. mixing of metallic alkoxides independently, or in combination with acetates, oxalates and inorganic salts;
2. addition of distilled water, under which hydrolysis and condensation takes place and a sol is formed [9]; and
3. controlled polycondensation into gel by the time of freestanding [9].

Since this technology allows control of manufacturing processes at micro- and macroscopic scales, the sol–gel method of synthesizing glass or ceramics has many advantages over other methods, such as melt processing or solid state reaction sintering. Besides the high purity and lower sintering temperature, a high degree of homogeneity on a molecular scale of the product can be obtained via this method [10, 11].

The chemical composition of Li^+, Al^{3+} and Si^{4+} ions, with a stoichiometric ratio of a bulk β-spodumene phase $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$, LAS), with 4 wt % ZrO_2 was prepared by rapid hydrolysis of an homogeneous alcohol solution of starting materials. In the present paper the crystallization behaviour of β-spodumene in Li_2O–Al_2O_3–Si_2O –ZrO_2 (LASZ) gels was studied, using differential thermal analysis (DTA), X-ray diffraction (XRD). Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and electron diffraction (ED).

To confine the scope of this study, three aspects of the work are presented:

1. production of precursor powders with a spodumene composition in the LASZ system,
2. exploration of crystallization behaviour in the LASZ gels, and
3. structural evolution of the gels with temperature.

2. Experimental procedure

Precursor powders with a spodumene composition were prepared from tetraethylorthosilicate (TEOS), $Al(OC_2H_5)_3$, $LiOCH_3$ and $Zr(OC_2H_5)_4$ as the starting materials. Fig. 1 shows a schematic flowchart of the preparation process [12], using formamide as a drying control chemical additive. TEOS was partially hydrolysed at 60 °C for 60 h. The catalyst used was hydrochloric acid (HCl:TEOS = 0.1). The concentration of the alcoholic solution of metal alkoxides

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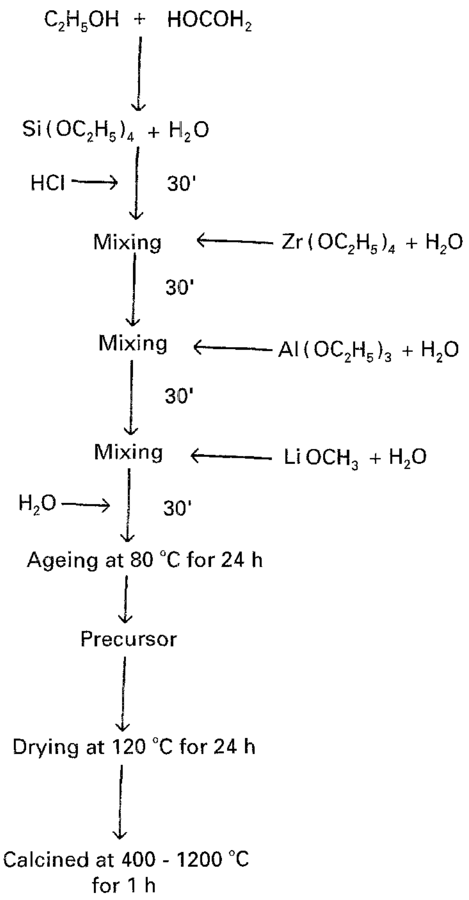

Figure 1 Schematic diagram of the sol–gel process.

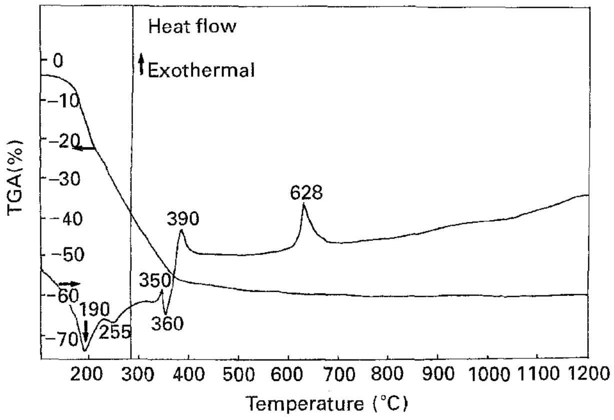

Figure 2 DTA and TGA curves for LASZ gels with 4 wt % ZrO_2 at a heating rate of 10 °C min^{-1}.

was 1 mol l^{-1}. The mole ratios of water to TEOS, $LiOCH_3$, $Al(OC_2H_5)_3$ and $Zr(OC_2H_5)_4$ were 3, 2, 3 and 2, respectively. The TEOS ethanol solution reacted, respectively, with aluminium, lithium and zirconium alkoxides, and resulted in a transparent solution with a cation ratio similar to the composition of spodumene. This solution was completely hydrolysed by adding a large amount of excess water (H_2O:TEOS = 30). The gel was then obtained via the sol. The gel was thoroughly dried at 120 °C for 24 h.

The precursor powders of the LASZ gels, dried at 120 °C for 24 h, and calcined under various conditions, were analysed. Differential thermal and thermogravimetric analyses (DTA–TGA) were carried out in air at various heating rates of 5, 10, 15 and 20 °C min^{-1}, respectively, up to 1000 °C. Crystalline phases were identified by XRD using CuK_α radiation and Ni filter. Lattice constants of β-spodumene were calculated from the angular position of the reflections (2 0 1), (1 1 3), (2 1 3), (3 2 0), (4 0 0) and (4 0 2), using the least-squares method [13]. FTIR analysis was conducted in order to investigate the formation of chemical bonds. FTIR spectra have been recorded in the frequency range 4000–400 cm^{-1} on the precursor powders dispersed in KBr pellets. The fine and homogeneous powders prepared by the sol–gel method were examined by SEM and TEM.

3. Results and discussion

The DTA–TGA curves for LASZ gels at a heating rate of 10 °C min^{-1} are shown in Fig. 2. The exothermic peaks at 350 and 390 °C corresponding to the pyrolysis of the organic ligands, such as CH_3O^- and $C_2H_5O^-$, in the LASZ gel [9]. The endothermic peaks at 190, 255 and 360 °C were due to the release of absorbed water. The amount of weight loss below 360 °C was 60% and levelled off. The exothermic peak at 628 °C is attributed due to the formation of a β-spodumene phase. At this temperature there is no weight loss.

As the heating rate decreased, the exothermic peak position shifted to a lower temperature. The crystallization kinetics of LASZ gel can be evaluated by the amount of peak shift with different heating rates. Taking into account the maximum exothermic peak temperature, T_c, at a corresponding heating rate, h, as described by the Johnson–Mehl–Avrami equation [14]

$$\ln h = -\frac{Q_c}{RT_c} + \text{constant} \qquad (1)$$

where Q_c is the apparent activation energy for crystallization and R denotes the gas constant.

Plotting the $\ln h$ versus $1/T_c$, a straight line was obtained, as shown in Fig. 3. The apparent activation energy can be calculated from the slope of the straight line as 192 kJ mol^{-1}. This value is much smaller than the activation energy of Li_2O–Al_2O_3–$4SiO_2$ (LAS) gel without ZrO_2, 382 kJ mol^{-1}.

The crystallinity of the β-spodumene phase is improved with increasing temperature. Fig.4 illustrates the X-ray diffraction patterns of the dried LASZ gels at 120 °C for 24 h and those calcined at various temperatures for 1 h. The effect of calcination on the evolution of the major crystalline phase (β-spodumene, $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$) and the minor zirconia phase (ZrO_2) are as follows:

1. the glassy state is maintained in the 120–400 °C runs;
2. at 600 °C, the first appearance of β-spodumene is indicated by the d-spacing of 0.3492 nm ($2\Theta = 25.48°$) which is the most prominent reflection for β-spodumene;

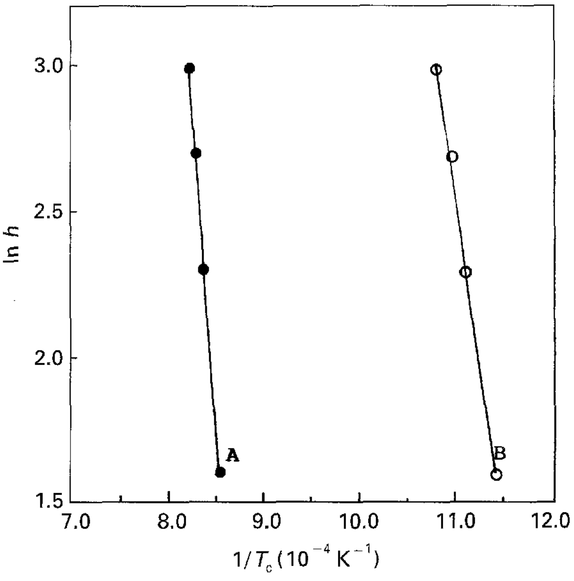

Figure 3 Plot of $\ln h$ versus $1/T_c$: (A) LAS gels, (B) LASZ gels.

3. at 800 °C, the major reflection corresponding to the (1 0 2), (2 0 1), (2 1 1) and (4 0 0) reflections of the β-spodumene type crystal appear [11]; and a minor crystalline phase, zirconia (ZrO_2) also shows up; and
4. for 1000 and 1200 °C runs, X-ray diffraction patterns are representative of the β-spodumene and zirconia, no other phases can be identified.

The phase relationship in the crystallized LAS and LAST (Li_2O–Al_2O_3–SiO_2–TiO_2) gels have been examined earlier using XRD [1, 4, 12, 15–17]. Table I summarizes the phases developed during crystallization of the LAS, LAST and LASZ gel systems.

In practice, β-spodumene is identified in the LASZ gels calcined above 800 °C, resulting in the fluctuation of lattice constant. The values of the lattice parameters for LASZ gels calcined at various temperatures for 1 h are shown in Fig. 5. This confirms the fact that the observed crystalline phase can be isostructural with the β-spodumene phase. Although the values of crystallographic *a* and *c* axes change at different rates in the β-spodumene, the unit cell volume changes only very little through the series. The unit cell is tetragonal geometrically, with a unit cell volume ($V = a^2 \times c$) ranging from 5.184×10^{-1} to 5.232×10^{-1} nm^3.

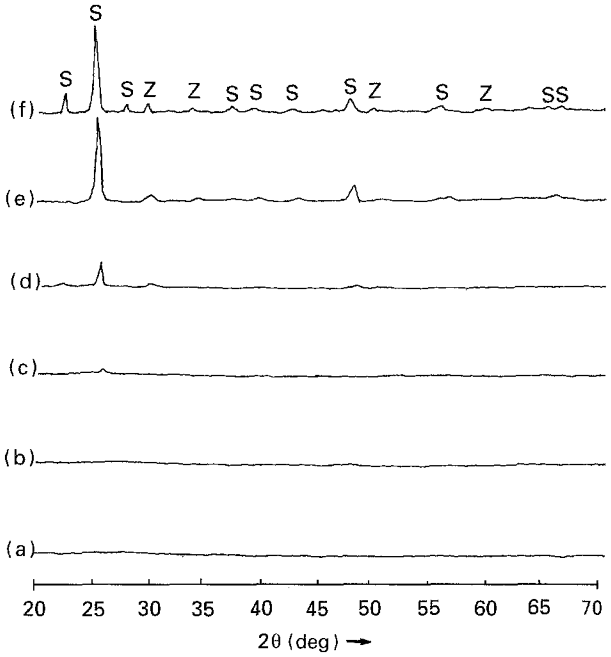

Figure 4 XRD patterns of the LASZ gels dried at 120 °C for 24 h and calcined at various temperatures for 1 h: (a) as-dried at 120 °C, (b) calcined at 400 °C, (c) calcined at 600 °C, (d) calcined at 800 °C, (e) calcined at 1000 °C, (f) calcined at 1200 °C. (s) β-spodumene, (Z) ZrO_2.

In this study, the FTIR spectra for a phase transformation series of the dry gels and the powder calcined at various temperatures for 1 h are shown in Fig. 6. The spectra at around 3650–3200 cm^{-1} in Fig. 6a, b are related to the stretching vibrations of the free hydroxyl group. At 1650 cm^{-1} the OH bend band

TABLE I The crystalline phases in the β-spodumene precursor powder developed during calcination at various temperatures

Starting materials	Temperature (°C)	Index method	Phases	Reference
$Si(OC_2H_5)_4$, $Al(OC_2H_5)_3$ and Li	600	XRD	γ-spodumene (β-eucrytpite/	[1]
	800	TEM	β-quartz solid solution)	
	1200		β-spodumene	
$Si(OCH_3)_4$, $Ti(OCH_3)_4$,	~ 375	XRD	β-spodumene	
$LiOCH_3$ and $Al(OC_3H_7)_3$	400	FTIR		[12]
	1000		β-spodumene	
$Si(OCH_3)_4$, $Al(NO_3)_3$ and $LiNO_3$	460	XRD	Li_2SiO_3, β-spodumene	
	700		β-spodumene, β-quartz	[15]
	800		β-spodumene, $Li_2Si_2O_5$	
$Al(OC_4H_3)_3$, $Si(OC_2H_5)_4$ and $LiNO_3$	1350		β-spodumene	[16]
	(at 6.9 MPa, 15 min)	XRD	Mullite	
Alumina sol, silica sol and	1350	XRD	β-spodumene	[17]
$LiNO_3$		SEM	$LiAlSi_3O_8$	
$Si(OC_2H_5)_4$, $Al(OC_2H_5)_3$,		XRD		This study
$LiOCH_3$ and $Zr(OC_2H_5)_4$	800	TEM	β-spodumene	
		FTIR		
	1000		β-spodumene, ZrO_2	
	1200		β-spodumene, ZrO_2	

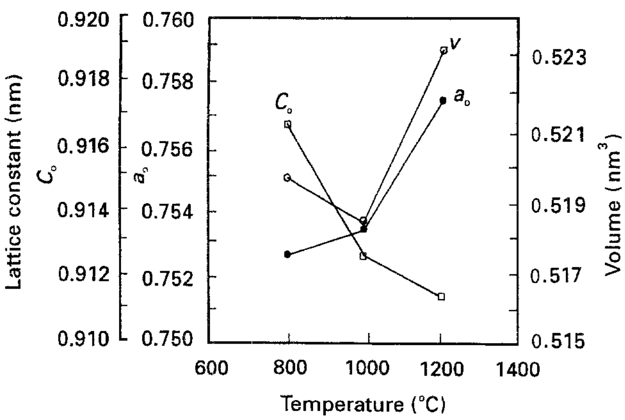

Figure 5 The *a* and *c* lattice parameters for LASZ gels calcined at various temperatures for 1 h: *V*, unit cell volume.

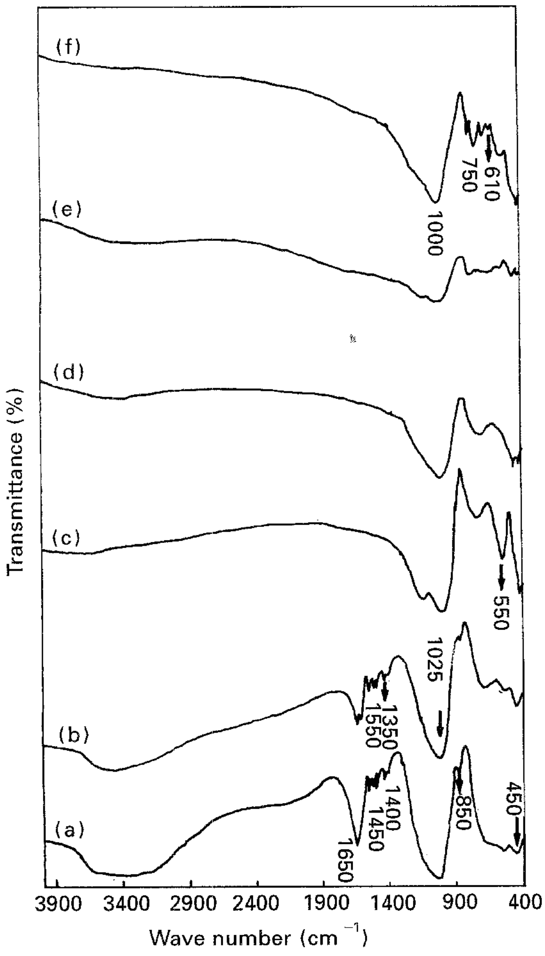

Figure 6 FTIR absorption spectra of the LASZ gels dried at 120 °C for 24 h and calcined at various temperatures for 1 h: (a) as-dried at 120 °C, (b) calcined at 400 °C, (c) calcined at 600 °C, (d) calcined at 800 °C, (e) calcined at 1000 °C, (f) calcined at 1200 °C.

of water in the LASZ gel is observed; in this case the gel was prepared with a higher water concentration and the number of the hydrogen bonds increased. At 1550, 1450, 1400 and 1350 cm^{-1}, the C–H flexion vibration in the C–H band was observed [18]. If the gel was heated to 800 °C and above, the OH stretching band and C–H flexion disappeared.

The low frequency part of the spectrum, under 1200 cm^{-1}, is a complicated combination of bands. The characteristic band corresponding to the Si–O stretching vibration was observed at a lower wave number of about 1025 cm^{-1}, and the absorption peak belonging to the ring structure of SiO_4 tetrahedrons, at about 800 cm^{-1}, cannot be found. These results may suggest that no substantial polymerization of TEOS had occurred [19]. The band at 850 cm^{-1} may be assigned to the stretching of Si–O–Al mode, where Al is in the tetrahedral site. This mode is accompanied by the 550 cm^{-1} band, assigned to AlO_4 tetrahedron vibration, and its appearance characterizes the change of the co-ordination number of Al from six to four [20]. In the FTIR spectra of the LASZ gels, the absorption peak at 464 cm^{-1} is the usual silica rocking vibration [21]. At 450 cm^{-1}, the absorption band is a characteristic caused by stretching of the Si–O–Si bonds [22], and the formation of an ionic bond, which is associated with dehydration polymerization, and ions or ionic substances are fixed in the three-dimensional network of SiO_4 [23].

During calcination, the residual hydroxide ions, or residual organic radicals, disappear and chemical bonds among the elements increase their regularity [23]. After crystallization of the amorphous product, two bands are found at 1000 and 750 cm^{-1} characteristic of the β-spodumene lattice. This change in the spectrum could be taken as indirect proof for building up the crystalline network of the LASZ gel. It is concluded by Girin [20] that the spectral indications of LASZ gel crystallization and separation of β-spodumene in the powder are the appearance of sharp peaks at 750 and 1000 cm^{-1}. The 610 cm^{-1} band is suitable for spectroscopic determination of the presence of ZrO_2 in the LASZ gels after calcining at 1000 and 1200 °C for 1 h, respectively.

Fig. 7 shows bright and dark field TEM micrographs and the corresponding ED pattern of the LASZ gel calcined at 400 and 1000 °C for 1 h, respectively. For the gel calcined at 400 °C for 1 h, very fine powder, with a primary particle size of about 30 nm, and a glassy state were noticed in Fig. 7a, b. The ED patterns of β-spodumene calcined at 1000 °C are superimposed, indicating that a lot of particles have been incorporated and crystallized. Fine particles were gradually incorporated into large particles with increasing calcination temperatures. The ED pattern also provides evidence for the presence of β-spodumene and ZrO_2 in this system. Synthesis was completed in the temperature from 1000 to 1200 °C; no other crystalline phases can be detected except β-spodumene, with a particle size up to 50 nm, and zirconia, with a particle size of 20 nm.

Since the LASZ gel powders were prepared through wet chemical routes, during processing, i.e. drying and/or subsequent steps, agglomeration can take place. Fig. 8 shows typical scanning electron micrographs of LASZ gels dried at 120 °C for 24 h and calcined at 400 and 1200 °C for 1 h, respectively. In these cases, extensive large aggregates are observed, and become more substantial after calcination. During calcination, the most common types of agglomerates in conventional powders are due to solid bonds formed between particles.

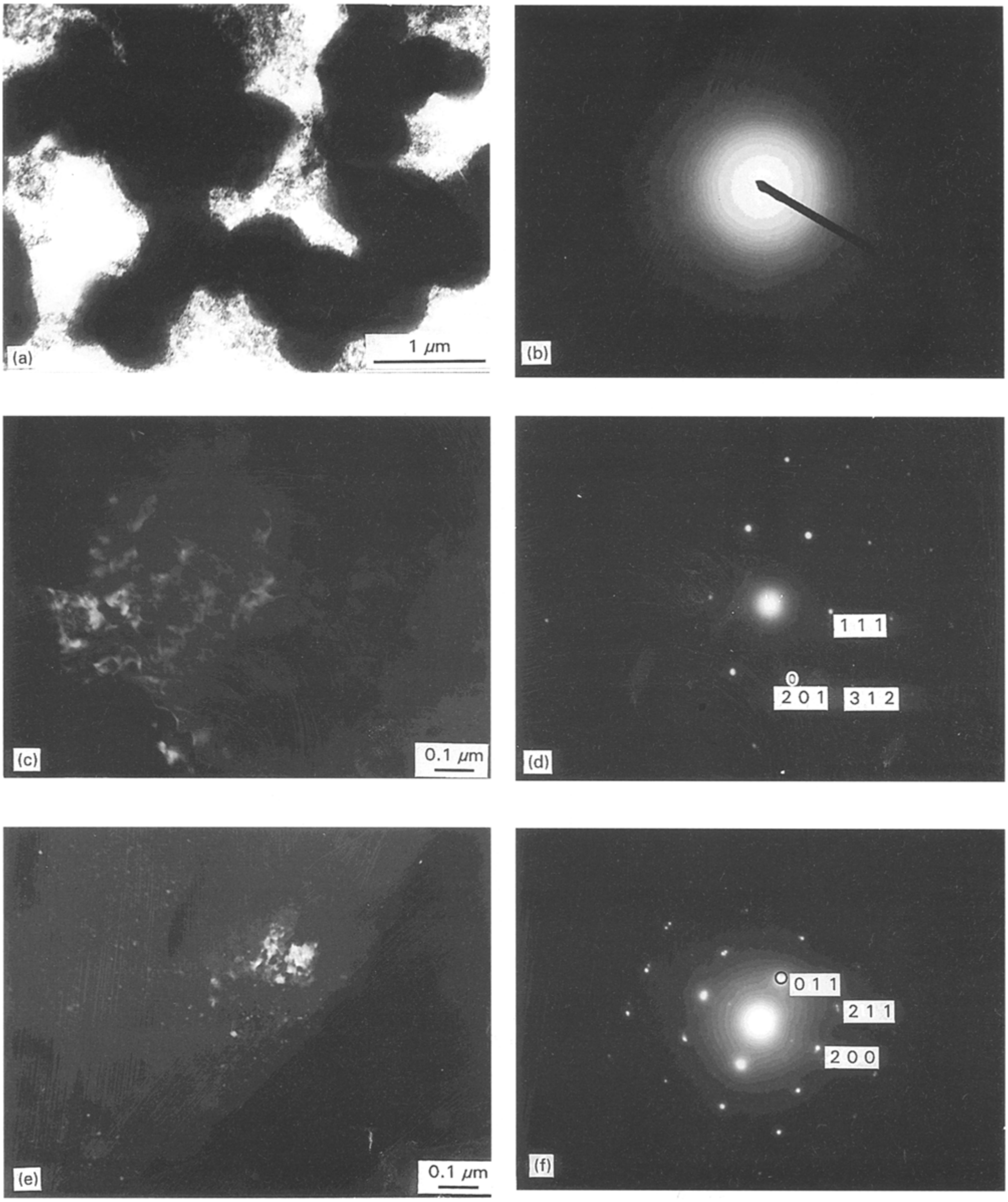

Figure 7 TEM micrographs and ED patterns of the dried LASZ gels calcined at various temperatures: (a) calcined at 400 °C for 1 h; (b) corresponding ED pattern showing the glassy state; (c) calcined at 1000 °C for 1 h, dark field image using circled spot of (d); (d) corresponding ED pattern showing the β-spodumene phase; (e) calcined at 1000 °C for 1 h, dark field image using circled spot of (d); and (f) ED pattern corresponding to ZrO_2 phase.

4. Conclusions

Fine and homogeneous β-spodumene ceramic powders were prepared by hydrolysis of a solution containing a mixture of $LiOCH_3$, $Al(OC_2H_5)_3$, $Si(OC_2H_5)_4$ and $Zr(OC_2H_5)_4$ in the presence of hydrochloric acid as a catalyst and with a large excess of water, leading to a gel powder which was properly controlled. Differential thermal analyses, X-ray diffraction, Fourier transform infrared spectroscopy, transmission electron microscopy and electron diffraction analyses were utilized to characterize and identify the crystallization behaviour and crystalline phases in calcining precursor powders of the Li_2O–Al_2O_3–SiO_2–ZrO_2 system. The activation energy of

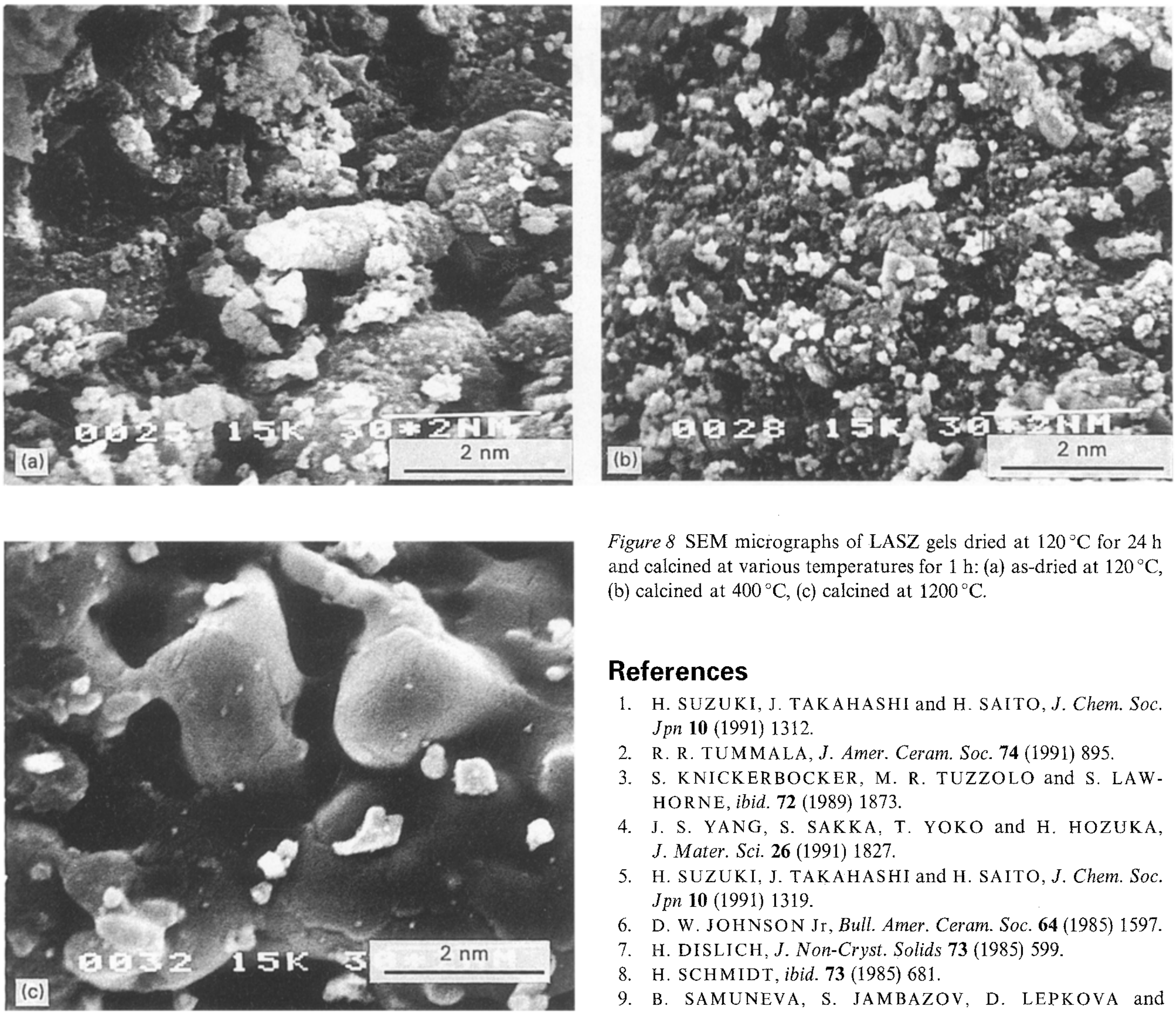

Figure 8 SEM micrographs of LASZ gels dried at 120 °C for 24 h and calcined at various temperatures for 1 h: (a) as-dried at 120 °C, (b) calcined at 400 °C, (c) calcined at 1200 °C.

β-spodumene crystallization was 192 kJ mol^{-1} for LASZ gels with 4 wt % ZrO_2. For calcinations at 800–1200 °C, the crystallized phases were comprised of a major phase of β-spodumene and a minor phase of zirconia oxide (ZrO_2). In the FTIR spectra, evidence of crystallization and separation of β-spodumene in the powder is provided by the appearance of a sharp band at 750 cm^{-1} and of a structure in the band at 1000 cm^{-1}. The synthesis was completed in the temperature range 1000–1200 °C, no other crystalline phases were detected, except β-spodumene, with a particle size up to 50 nm, and zirconia, with a particle size of 20 nm.

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