

Synthesis of spodumene and spodumene–zirconia composite powders using aqueous sol–gel method

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MS received 5 October 1996; revised 6 January 1997

Abstract. Pure spodumene and spodumene–zirconia (5, 10, 15 mol%) composite powders were prepared using aqueous sol–gel method employing lithium formate, aluminium formate, zirconium formate and tetraethoxy silane (TEOS) as starting materials in aqueous medium. The gels prepared by this method were dried at 100°C for 24h and then calcined for 2h at different temperatures ranging from 500°C to 800°C. X-ray powder diffraction (XRD), differential thermal analysis (DTA), thermogravimetric analysis (TGA) and infra-red spectroscopy analysis (IR) were utilized to characterize the gel powders and calcined powders. Transmission electron microscope (TEM) was used to measure the average particle size of the calcined powders.

Keywords. Sol–gel; spodumene; zirconia; XRD; IR.

1. Introduction

A range of interesting properties makes β -spodumene ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$) useful material for commercial applications. It has been known to exhibit ultra-low thermal expansion, good thermal shock resistance, high-thermal stability and high-chemical durability (Yang *et al* 1991). It is largely used as refractory materials in industrial furnaces and as heat exchangers in gas turbines. Its other applications are found in cook top panels, stove windows, cookware etc (Wang 1994).

β -Spodumene has been commercially prepared by recrystallization of a solidified melt. There have been however, considerable difficulties experienced in sintering β -spodumene, prepared by this melting method, without using any sintering aid. The incorporation of sintering aid results in a large thermal expansion. Therefore, the preparation of homogeneous and fine β -spodumene powder has been considered to be very important (Wang 1994). Recently ZrO_2 particles have been incorporated in the spodumene matrix to prepare ZrO_2 -toughened spodumene (Lathabai *et al* 1996).

Sol–gel method has been widely explored for synthesis of homogeneous multicomponent glass and ceramics (Roy 1987). Extensive studies have been carried out on the synthesis and the processing of spodumene using different precursor compounds. Some of them are (i) partial hydrolysis of tetraethoxy silane (TEOS) coupled with double alkoxide of lithium and aluminium (Suzuki *et al* 1991), (ii) hot pressing of hydrolysed product of TEOS, LiNO_3 and $\text{Al}(\text{OC}_4\text{H}_9)_3$ (Phallipon *et al* 1982; Veltri and Scola 1989), (iii) hydrolysis of alumina sol, silica sol and LiNO_3 (Kobayashi *et al* 1990) and (iv) hydrolysis of TEOS, aluminium-*s*-butoxide and lithium methoxide (Yang *et al* 1991). However, the reactivities of metal alkoxides towards hydrolysis are sometimes very different, and consequently it has been very difficult to build a common molecular network in which various metal ions are included. Different hydrolysis rates of individual alkoxides may result in chemical inhomogeneity in the product leading to higher crystallization temperature or undesired

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crystalline phases (Saha and Pramanik 1995). Tedious laboratory preparation of some metal alkoxides, their high cost and commercial unavailability have led to the use of inorganic salts in sol-gel technique (Oldhman 1968; Levene and Thomas 1972). The most commonly used inorganic precursors are metal nitrates and chlorides. However, when metal halides or nitrates have been used over a certain concentration range (usually about 5 mol%) to prepare silicate gels, the salts separated out during drying, causing chemical inhomogeneity. It has been reported that the use of weak acid salts of metals (e.g. oxalates and formates) caused no such segregation problem when they reacted with TEOS in aqueous medium to form multicomponent silicate gels. This method of preparation of multicomponent silicate gel in aqueous medium was termed as 'aqueous sol-gel method' (Chakraborti and Pramanik 1990; Saha and Pramanik 1993, 1995). In this paper, we report the synthesis of β -spodumene and spodumene-zirconia composite powders using aqueous sol-gel technique. Here lithium formate, aluminium formate, zirconium formate and TEOS were used as starting materials in aqueous medium.

2. Experimental

We have used lithium carbonate (99 wt%), (BDH Chemicals, India), aluminium nitrate nona hydrate (98.5 wt%), (BDH Chemicals, India), zirconium oxychloride octahydrate (98 wt%) (Aldrich Chemicals), and formic acid (85 wt%), (Qualigen Fine Chemicals, India) for preparation of lithium formate, aluminium formate and zirconium formate. Freshly precipitated aluminium hydroxide, zirconium hydroxide were prepared by adding ammonium hydroxide to the corresponding metal salt solutions. After filtering and washing with distilled water these hydroxides were then reacted with 50% aqueous formic acid solution to give the corresponding metal formate solutions. Lithium formate was prepared by reacting lithium carbonate with aqueous formic acid solution. Metal formate solutions containing the required amount of metal ions were then added to tetraethoxy

Table 1. Experimental details of the preparation of gels of spodumene and spodumene-zirconia systems.

Composition	Sample ^a	Vol ^b (ml)	pH ^c	Temp ^d (°C)	t_{gel}^e (h)
$\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$	SZ0	150	1.3	60	4.5
$\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ with 5 mol% ZrO_2	SZ5	150	1.2	60	5
$\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ with 10 mol% ZrO_2	SZ10	160	1.2	60	5
$\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ with 15 mol% ZrO_2	SZ15	160	1.1	60	5

^aIn all sample solutions, the amount of TEOS used is 10 ml (0.04389 mole) and the amount of constituents are according to their molecular proportions. Aqueous formic acid is used to make the metal formate solutions.

^bInitial volume of the sample solutions including TEOS.

^cInitial pH of the sample solution after adding TEOS to the mixed metal formate solution.

^dTemperature mentioned during the formation of gel.

^e t_{gel} Time required for the formation of gel.

silane (98 wt% of Fluka Chemicals) (TEOS) according to the compositions. The specific conditions and experimental details are listed in table 1. At the beginning of mixing, TEOS and the aqueous solutions of metal formates were immiscible. A homogeneous solution was obtained after about 30 min of hydrolysis of TEOS under rapid stirring using a magnetic stirrer. Slow stirring and heating was continued until the formation of gel.

The gels were dried at 100°C for 24 h on a water bath and then ground to powders. These powders were then gradually heated at 5°C min⁻¹ and calcined in air for 2 h to temperature ranging from 500°C to 800°C.

Infrared spectra of these samples were obtained in KBr medium using Perkin–Elmer 883 IR spectrophotometer. Room temperature X-ray diffraction (XRD) patterns were obtained using a Philips X-ray powder diffractometer PW 11710 and CuK α radiation. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were conducted at a heating rate of 10°C min⁻¹ in air employing Shimadzu DT-40 thermal analyser. The average particle size of the calcined powders were measured using a transmission electron microscope (TEM) of Phillips CM12.

3. Results and discussion

TGA of dried gel powders exhibited three-stage weight loss of the dried gel powders. The total weight loss of the dried gels was about 60 wt%. There was no significant

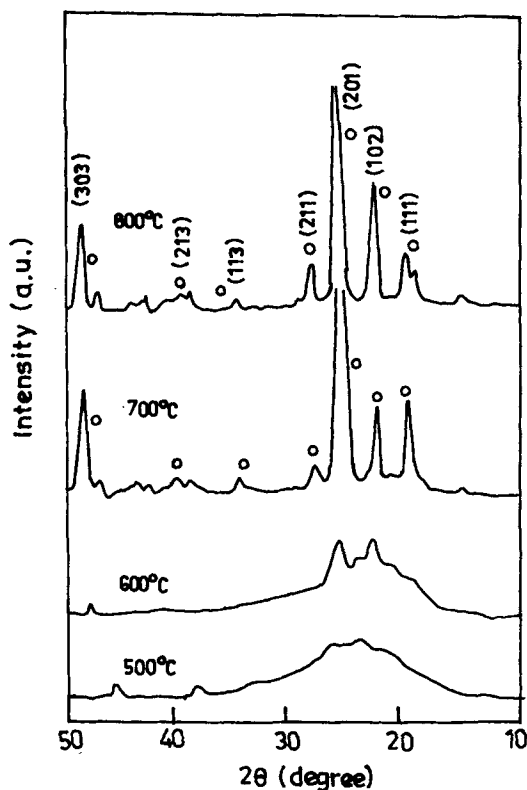


Figure 1. Powder X-ray diffractograms of sample SZ0 after calcination at 500°C, 600°C, 700°C, 800°C, for 2 h. (○): β -spodumene).

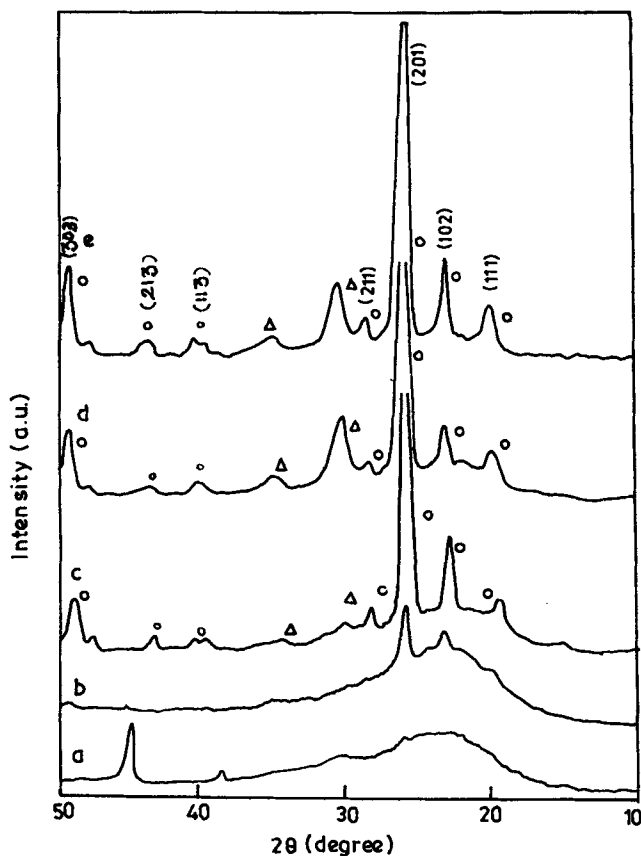


Figure 2. Powder X-ray diffractograms of samples SZ5, SZ10 and SZ15 after calcination at different temperatures for 2h. (a) SZ15 at 700°C, (b) SZ10 at 700°C, (c) SZ5 at 800°C, (d) SZ15 at 800°C, (e) SZ10 at 800°C, (O): β -spodumene, (Δ): tetragonal zirconia.

weight change beyond 550°C. The DTA curves show an endothermic peak at about 90°C corresponding to the release of loosely bound water and an exothermic peak at about 270°C corresponding to the decomposition and oxidation of formate salts.

Room temperature XRD patterns for all the samples calcined at different temperatures were taken and some selected patterns are shown in figures 1 and 2. The effect of calcination on the evolution of β -spodumene phase in sample SZ0 and β -spodumene and zirconia phases in samples SZ5, SZ10 and SZ15 are as follows: (a) all the dried gel powders were amorphous. This amorphous phase was retained when the gel powder of SZ0 was calcined up to 600°C and up to 700°C for the gel powders of SZ5, SZ10 and SZ15, (b) the XRD peaks, corresponding to β -spodumene phase, appeared for sample SZ0 when the calcination temperature was 700°C or above and (c) samples SZ5, SZ10 and SZ15 produced β -spodumene and tetragonal zirconia phases of crystallization when calcined at 800°C for 2h. The crystalline phases of all the samples calcined at different temperatures for 2h are summarized in table 2.

Several structural changes in the gel powders due to calcination at different temperatures were also observed by IR spectroscopic analysis. Figures 3 and 4 show the IR spectra of samples SZ0, SZ5, SZ10 and SZ15 after calcination at different

Table 2. Summary of X-ray powder diffraction studies in the spodumene and spodumene-zirconia composites during heat treatment.

Sample	Temperature of heat treatment (°C) (2h)			
	500	600	700	800
SZ0	A	A	β	β
SZ5	A	A	A	$\beta + t$
SZ10	A	A	A	$\beta + t$
SZ15	A	A	A	$\beta + t$

A: amorphous; β : β -spodumene; t: tetragonal zirconia.

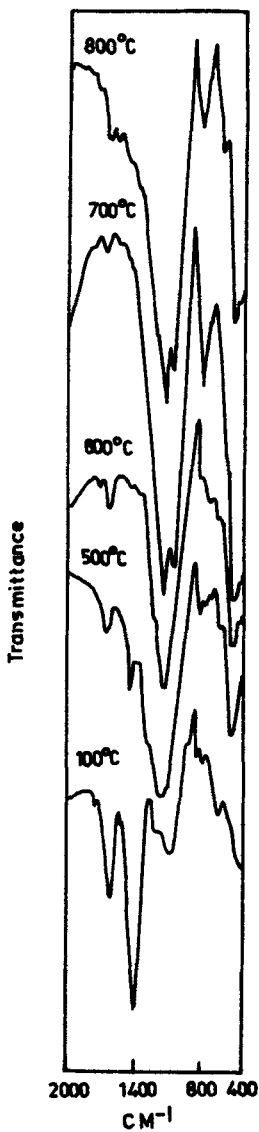


Figure 3. IR spectra of dried gel powder of sample SZ0 at 100°C and after calcination at 500°C, 600°C, 700°C and 800°C for 2h.

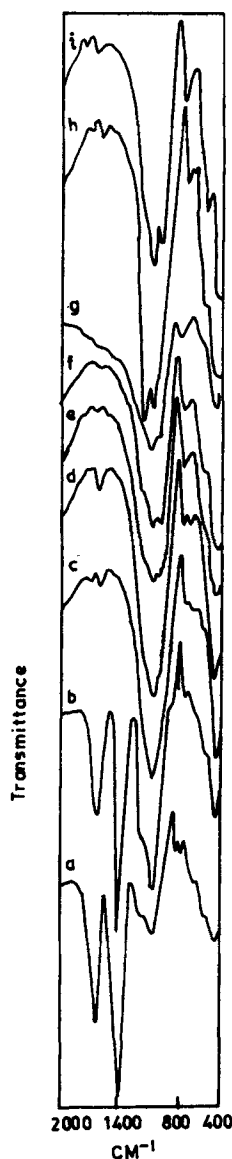


Figure 4. IR spectra of dried gel powders of sample SZ5, SZ10, SZ15 at 100°C and after calcination at different temperatures for 2h. (a) SZ10 at 100°C, (b) SZ5 at 100°C, (c) SZ10 at 600°C, (d) SZ5 at 600°C, (e) SZ5 at 700°C, (f) SZ15 at 700°C, (g) SZ5 at 800°C, (h) SZ10 at 800°C, and (i) SZ15 at 800°C.

temperatures. The vibrational frequencies of the dried gel powders and calcined powders of the samples at different temperatures and their assignments are summarized in table 3. With the increase of calcination temperatures the striking features of IR spectras observed are as follows: (a) in the gel powders dried at 100°C, the characteristic absorption band of the formate group at about 1380 cm^{-1} was observed. The disappearance of this band after calcination at higher temperatures confirmed that

Table 3. IR bands (in cm) of gel powders of SZ0, SZ5, SZ10 and SZ15 after heat treatment.

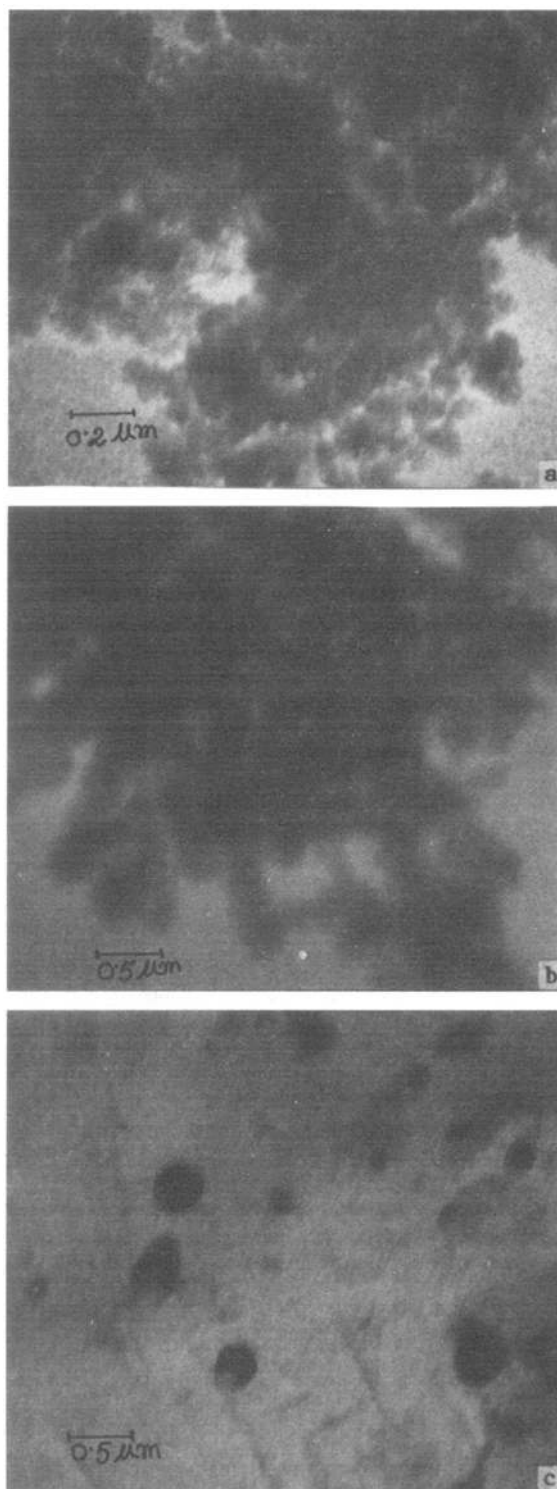
Relevant assignment lit data	Temp. (°C)	Samples			
		SZ0	SZ5	SZ10	SZ15
1380 Carb	100	1392s	1387s	1397s	1390s
	500	1385vw	—	—	—
1200 SiOSiLO	100	1200sh	1180sh	1200sh	1190sh
	500	1206sh	1189sh	1200sh	1189sh
	600	1206sh	1200sh	1199sh	1198sh
	700	1206sh	1200sh	1200sh	1200sh
	800	1210sh	1186sh	1190sh	1190sh
1080 SiOSiTO	100	1072b	1070s	1053m	1070s
	500	1079b	1075s	1060m	1075s
	600	1070s	1075s	1070m	1075s
	700	1080vs	1074vs	1084vs	1079vs
	800	1079vs	1083vs	1079vs	1081vs
1070 Sp	700	1009s	—	—	—
	800	1015s	1009s	1008s	1007s
800 SiOSism	100	826w	790w	809w	800w
	500	790w	785w	805w	800w
	600	762w	789w	785w	790w
	700	771s	789w	784sh	791sh
	800	773s	780m	761m	764m
655 form	100	—	660s	652sh	655d
600 tetra	800	—	600	599wsh	599wsh
560 Sp	800	554	560sh	555sh	—
460 SiOSibm	100	451m	451m	456m	450m
	500	467mb	450m	456m	445m
	600	466s	455m	450m	455m
	700	432s	465s	460s	465s
	800	439s	447s	445s	446s

a) Carb: Carboxylate group; SiOSiLO: Asymmetric stretching vibration-longitudinal optics; SiOSism: Network Si–O–Si symmetric stretching vibration; SiOSiTO: asymmetric stretching vibration–transverse optics; SiOSibm: Network Si–O–Si bending vibration; form: zirconium-formate; tetra: tetragonal zirconia; Sp: spodumene.

b) v: very; w: weak; m: medium; s: strong; sh: shoulder.

the decomposition of metal formates occurs due to calcination, (b) the characteristic bands of β -spodumene at about 1017, 765, 560 cm^{-1} (Gadsden 1975) were observed in the calcined powders of sample SZ0 when calcined at 600°C and in the calcined powders of sample SZ5, SZ10 and SZ15 when calcined at 700°C and higher temperatures. The characteristic peak of tetragonal zirconia (Saha and Pramanik 1993) at about 600 cm^{-1} was observed in the sample SZ5, SZ10 and SZ15 when calcination temperature was 800°C.

The average particle size of the calcined powders were measured using TEM. The particle sizes of spodumene and spodumene–zirconia composite are listed in table 4. The average size of the particles were in nanometre scale and were observed to increase with increase in calcination temperature (figure 5). The crystallite sizes of β -spodumene and tetragonal zirconia phases were also calculated by X-ray peak broadening method and the crystallite sizes are listed in table 5.

**Figure 5. a-c.**

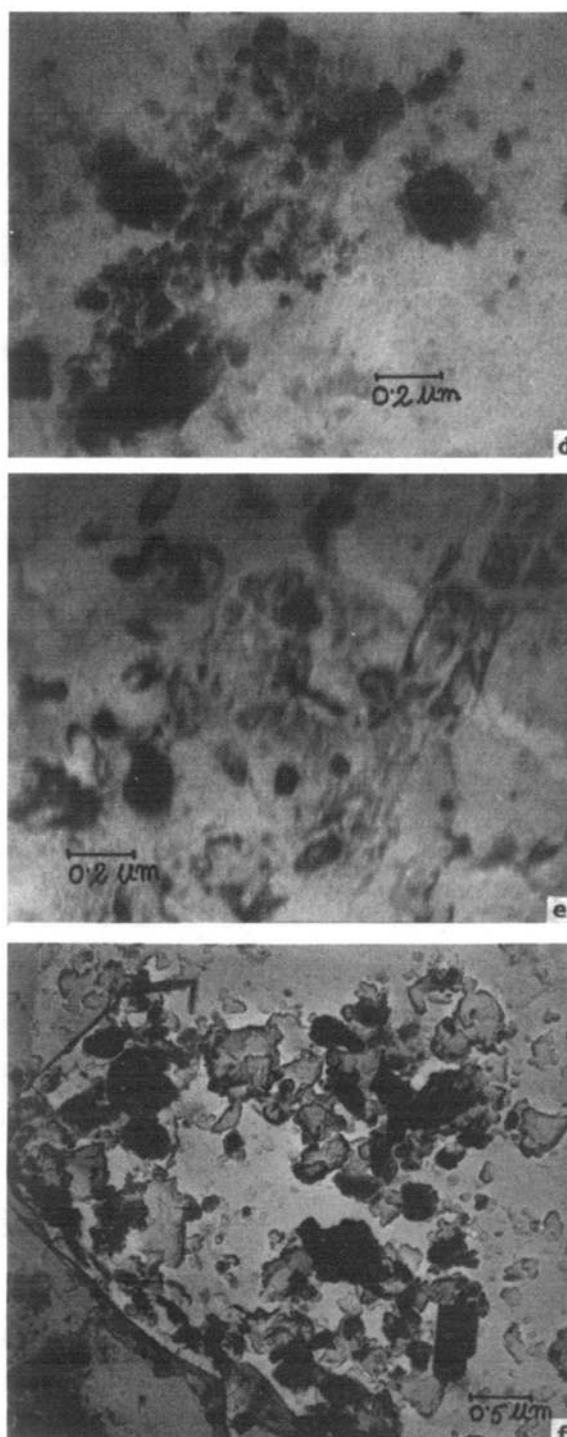


Figure 5. TEM micrographs of spodumene and spodumene–zirconia composite powders after calcination at different temperatures: (a) SZ0 at 600°C, (b) SZ0 at 700°C, (c) SZ0 at 800°C, (d) SZ5 at 800°C, (e) SZ10 at 800°C and (f) SZ15 at 800°C.

Table 4. Average particle size (± 10 nm) of the samples after calcination at different temperatures obtained from TEM.

Samples	Temperature of heat treatment ($^{\circ}\text{C}$) (2h)		
	600	700	800
SZ0	150 nm	170 nm	200 nm
SZ5	160 nm	200 nm	310 nm
SZ10	175 nm	190 nm	330 nm
SZ15	190 nm	230 nm	275 nm

Table 5. Average particle size of the powders calcined at 800°C for 2h measured by X-ray peak broadening.

Sample	Particle size
SZ0	β (180 nm)
SZ5	β (250 nm) + t(25 nm)
SZ10	β (280 nm) + t(40 nm)
SZ15	β (285 nm) + t(45 nm)

β : β -spodumene; t: tetragonal zirconia.

4. Conclusion

Ultrafine β -spodumene and spodumene–zirconia composite powders were easily synthesized by using aqueous sol–gel method. X-ray diffraction patterns and IR spectras confirm the formation of β -spodumene phase and tetragonal zirconia phase occurring due to calcination of dried gel powders. The formation of β -spodumene and tetragonal zirconia phase occurs at comparatively low temperature due to the atomic scale mixing of the constituent elements in gels.

In conclusion, it can be stated that, this method of using aqueous solutions of metal formate salts for preparation of multicomponent gel offers a cost-effective and technically simpler alternative to the rather expensive all alkoxide route.

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