Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Published online: 09 Jul 2013.

To cite this article: Amir Abbas Nourbakhsh, Kenneth J. D. Mackenzie & Amin Jamshidi (2013) A Novel Method for the Formation of Lithium Aluminosilicate and Lithium Aluminosilicate-Alumina Matrix Composites by Silicothermal Reaction of Li-Geopolymers, Molecular Crystals and Liquid Crystals, 577:1, 116-126, DOI: 10.1080/15421406.2013.782208

To link to this article: http://dx.doi.org/10.1080/15421406.2013.782208

Mol. Cryst. Liq. Cryst., Vol. 577: pp. 116–126, 2013

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.782208

A Novel Method for the Formation of Lithium Aluminosilicate and Lithium Aluminosilicate-Alumina Matrix Composites by Silicothermal Reaction of Li-Geopolymers

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Li-geopolymer precursors containing silicon were fabricated by a solid-state method and fired in nitrogen at 1100°C–1400°C to produce lithium aluminosilicate (LAS), the amount and crystallinity of which was independent of the silicon used, as shown by X-ray diffraction and solid-state magic angle spinning nuclear magnetic resonance (MAS NMR). LAS/Al_2O_3 composites were formed by adding ρ-Al_2O_3 to the Li-geopolymer precursor and firing under nitrogen at 1400°C. Although no nitride phases were formed under these reaction conditions, scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) showed a small amount of unreacted silicon in the fired samples, suggesting that it may be possible to adapt this procedure to produce LAS-nitride composites.

Keywords LAS-alumina composite; li-inorganic polymer; lithium aluminosilicate; silicothermal reaction

1. Introduction

Materials with very low thermal expansion coefficients have a wide range of engineering applications in fields such as photonics, electronics, and certain structural applications [1]. Compounds in the lithium aluminum silicate (LAS) system show ultralow thermal expansion coefficients, good thermal shock resistance, high thermal stability, and high chemical durability, making them potentially useful materials for further study [2]. There are three important phases in the LAS system, namely, spodumene ($LiAlSi_2O_6$), petalite ($LiAlSi_4O_{10}$), and β-eucryptite ($LiAlSiO_4$) [3]. The first and second phases have close to

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zero thermal expansion coefficients and β-eucryptite has a negative thermal expansion coefficient because of its large negative expansion in the one of its crystallographic directions [1].

Conventionally, LAS phases have been fabricated by glass-processing methods followed by nucleation and crystallization [4,5]. Although crystallizing agents can facilitate nucleation of the ceramic phase, these methods require high temperatures or sintering aids to decrease the firing temperature [3,4]. High-temperature processing is very expensive and the use of additives can increase the thermal expansion [2,6]. This method also requires highly controlled and complicated processing in order to avoid sample heterogeneity. In addition, the high amount of glassy phase can result in relatively poor mechanical properties [1]. Some researchers have tried to improve the mechanical properties, especially at high temperature, by the use of different reinforcing additions. The low thermal expansion coefficients of mullite, alumina, SiC, or Si_3N_4 have led to the use of these ceramics in LAS matrix composites [1,7–14]. Jang et al. reported SiC-whisker reinforced LAS matrix fabrication by a mixed colloidal processing route. The fracture toughness of LAS was thereby increased from 1.3 MPa.m$^{1/2}$ to 5.0 MPa.m$^{1/2}$ for a hot-pressed composite containing 20 wt% SiC whiskers [7].

One possible but relatively unproven method for producing LAS and LAS matrix composites is by silicothermal reaction of an aluminosilicate Li-geopolymer precursor, i.e., the reaction of the geopolymer with elemental silicon under a nitrogen atmosphere. Geopolymers are aluminosilicate materials with ceramic-like properties that are synthesized at room temperature [15] in three steps, identified by Kaps and Buchwald [16] as thermal dehydroxylation of the solid aluminosilicate source (normally kaolinitic clay) to form an X-ray amorphous material. This is then reacted with alkali to form tetrahedral silicate and aluminate monomers which condense to form a polymer network, with or without the addition of an alkali silicate solution. The formation of the three-dimensional geopolymer network causes the material to set and harden to an X-ray amorphous ceramic-like product in which the charge imbalance arising from the presence of the tetrahedral aluminate units is compensated by the presence of the alkali metal ions. The alkali metal hydroxide most commonly used is NaOH [15,17], but KOH is reported to produce a stronger product because of the different silicate speciation it produces [15]. Li-based geopolymers are less accessible by this synthesis route since LiOH is less alkaline, resulting in the much slower dissolution of the solid aluminosilicate than with Na or K [18]. Alternative methods to synthesize a Li-aluminosilicate geopolymer include an ion-exchange method, in which a Na-geopolymer treated with a lithium salt solution results in 81% Li-exchange [19], or a solid-state method [18] in which the clay mineral is reacted with alkali lithium salts, and then hydrated to form the geopolymer. This was the synthesis method of choice here, since the silicothermal reaction involves the addition of elemental silicon which would be destroyed under the highly alkaline conditions of conventional geopolymer synthesis.

The aim of this research was to investigate the silicothermal reaction of Li-geopolymer as a precursor for LAS and a LAS matrix composite with Al_2O_3. Three different silicon samples were used, which were added after the solid-state generation of the precursor but prior to its hydration and firing. The formation of LAS and other three types of silicon of different particle size and crystallinity were used, shown by X-ray diffraction (XRD) and solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) not to influence the suite of products formed but their amount and crystallinity. The production of an LAS-alumina composite by the addition of ρ-Al_2O_3 was also investigated.

Table 1. Composition of the various samples in this study

Sample	Si type (content/g)	ρ-alumina/g	SiO_2: Al_2O_3	Li_2O: SiO_2	H_2O: Li_2O
1	D (2.71)	...	2.41	0.41	10.1
2	D (5.42)	...	2.41	0.41	10.1
3	Max (2.71)	...	2.41	0.41	10.1
4	Max (5.42)	...	2.41	0.41	10.1
5	Amorphous (2.71)	...	2.41	0.41	10.1
6	Amorphous (5.42)	...	2.41	0.41	10.1
7	Amorphous (2.71)	1.50	1.77	0.41	10.1
8	Amorphous (5.42)	1.50	1.77	0.41	10.1
9	Max (2.71)	5.00	1.09	0.41	10.1

2. Experimental Methods

The solid aluminosilicate source, New Zealand halloysite clay, (Imerys Premium Grade) was mixed with $LiOH.H_2O$ (Pure Science, reagent grade) to give the compositions shown in Table 1. Three types of elemental Si of different particle sizes were used in these experiments, type Max (mean 65 μm), type D (9 μm), and amorphous (mean 7.5 μm) (Sicomil, Kema Nord Engineering Ceramics). The reinforcing agent in the LAS/alumina composites was ρ-alumina (Alphabond, Alcoa). Nine sample compositions were produced (Table 1) as shown in the SiO_2-Al_2O_3-Li_2O ternary phase diagram (Fig. 1).

The Li-geopolymer precursor powder was prepared by dry mixing the halloysite with $LiOH.H_2O$ to give the molar ratio SiO_2: $Al_2O_3 = 2.41$ and Li_2O: $SiO_2 = 0.41$. This mixture was then heated to 570°C–630°C for 24 h in porcelain crucibles before the addition of the Si powder and ρ-Al_2O_3. The mixtures were hardened by the addition of the minimum amount of water, placed in greased moulds, vibrated to remove air bubbles, sealed, and allowed to set at 40°C for typically 2–3 days. The cured samples generally experienced a small degree of shrinkage and were easy to demould. The samples were then fired in a laboratory tube furnace under flowing nitrogen (50 ml.min^{-1}) at a heating rate of l0°C.min^{-1} up to 600°C, held at this temperature for 2 h, then heated at 5°C.min^{-1} to the maximum temperature in the range 1100–1400°C, held for 4 h and finally cooled at the natural furnace rate.

The precursor powder before hydration, the cured samples, and the fired samples were characterized by XRD (Philips PW 1729 computer-controlled goniometer with a graphite monochromator and Co K_α radiation over the 2θ range 10°–80°). The diffraction patterns were identified by comparison with the JCPDS reference data files. The microstructures of the powdered samples were observed by SEM (JEOL JEM6500) at an accelerating voltage of 20 KeV, fitted with an EDS system.

Selected powdered samples were also examined by ^{29}Si and ^{27}Al solid-state MAS NMR at 11.7 T using a Bruker Avance III 500 spectrometer operating at a ^{29}Si frequency of 99.29 MHz with a 5 mm Doty MAS probe and a zirconia rotor spun at ~6 kHz. The excitation pulse for ^{29}Si was 7 μs with a recycle time of 30 s and the spectra referenced with respect to tetramethyl silane. The 11.7 T ^{27}Al solid-state spectra were acquired at an operating frequency of 130.24 MHz using a 4 mm Doty MAS probe with a silicon nitride rotor spun at 10–12 kHz, a 1 μs pulse and a 1 s recycle time. The spectra were referenced with respect to $Al(H_2O)_6^{3+}$.

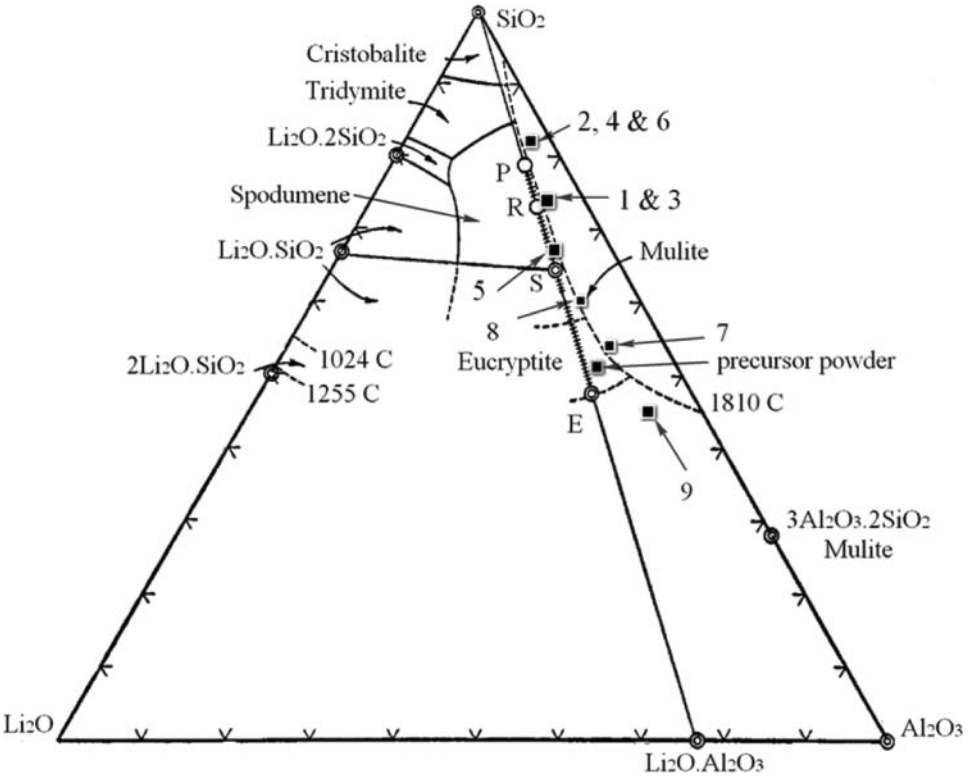

Figure 1. Phase diagram of SiO_2-Al_2O_3-Li_2O system [3] and the position of compounds. P: $Li_2O.Al_2O_3.8SiO_2$ (petalite), R: $Li_2O.Al_2O_3.6SiO_2$ (lithium orthoclase), S: $Li_2O.Al_2O_3.4SiO_2$ (spodumene), E: $Li_2O.Al_2O_3.2SiO_2$ (eucryptite).

3. Results and Discussion

3.1. XRD and MAS-NMR Studies of the Precursor Powders

The XRD patterns of the precursor powders calcined at 570°C and 630°C (Fig. 2) are largely amorphous, especially at the lower temperature, but contain small broad reflections and sharp peaks of crystalline eucryptite and related lithium phases. The ^{29}Si MAS NMR and ^{27}Al MAS NMR spectra of the precursor powders (Figs 3 and 4, respectively) show that the ^{29}Si spectra for both precursor powders are similar, with a single broad peak at about −99 ppm due to dehydroxylated halloysite, together with small peaks at −65, −73, and −76 ppm in the sample calcined at the lower temperature. These peaks correspond to the Q^0, Q^0, and Q^1 sites in lithium silicates [20] (Fig. 3). The precursor calcined at the higher temperature contains small peaks at about −68 and −80 ppm, corresponding to silicon in Q^0 and Q^1 sites respectively in lithium silicates, indicating that increasing the calcining temperature of the precursor powder increases the Q^0 coordination of the Si.

The ^{27}Al MAS NMR spectra (Fig. 4) show both samples contain principal resonances at approximately 80 ppm corresponding to Al in tetrahedral coordination. The lower temperature sample shows additional small peaks at 61 and 40 ppm (CN = 4), 28 ppm (CN = 5), and 3 ppm (CN = 6), whereas the corresponding resonances in the higher temperature sample occur at approximately 66, 56, 28, and 2 ppm (Fig. 4). The relative peak intensities

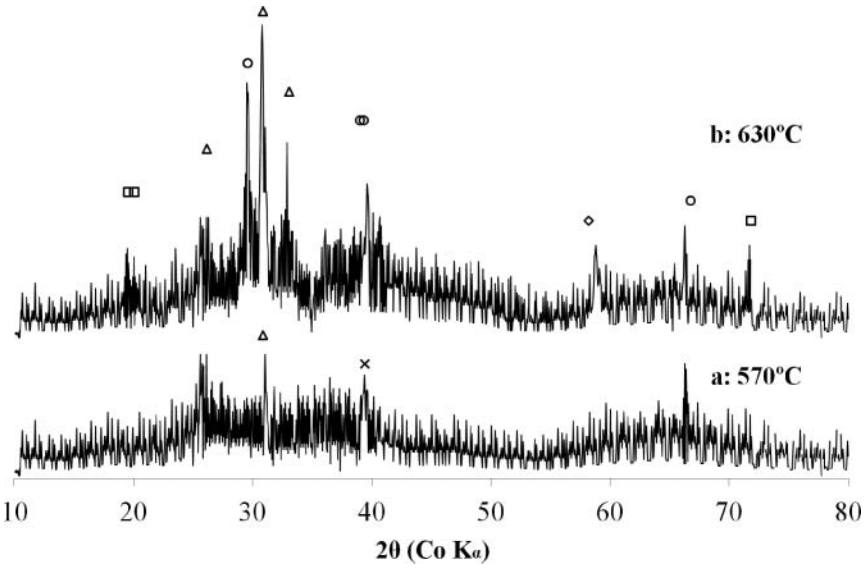

Figure 2. XRD pattern of the precursor powders calcined at 570°C and 630°C. Key: ×: lithium hydroxide hydrate (PDF file No. 25-486), Δ: Eucryptite (PDF file No.14-667), □: lithium silicate (PDF file No. 20-637), ◊: lithium silicate oxide (PDF file No. 17-197), and ○: LAS (PDF file No. 43-230).

indicate significant conversion of octahedral Al to tetrahedral below 570°C, with only a slight increase in the amount of 4 CN Al formed on calcining at 630°C. The lower crystallinity and smaller amount of Si in Q^0 coordination in the precursor calcined at the lower temperature suggests that thermal activation at 570°C is appropriate for the preparation of the precursor powder.

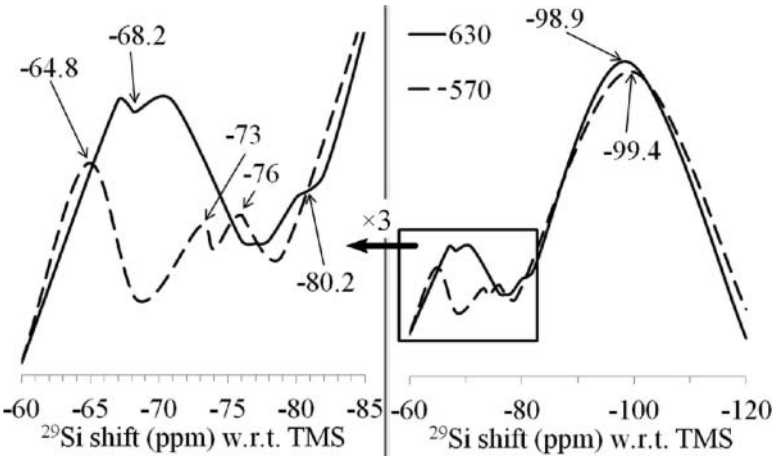

Figure 3. 11.7 T ^{29}Si MAS NMR spectra of precursor powders calcined at 570°C and 630°C.

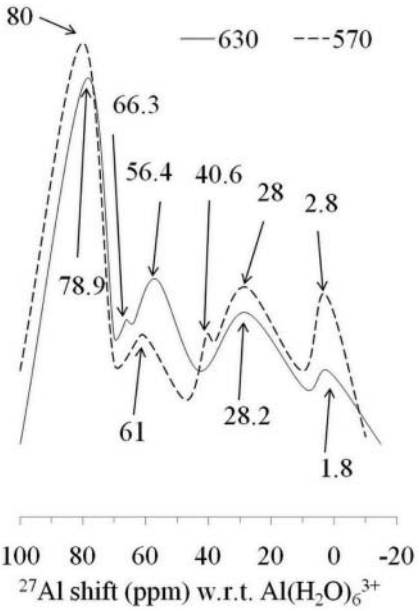

Figure 4. 11.7 T ^{27}Al MAS NMR spectra of precursor powders calcined at 570°C and 630°C.

3.2. XRD, MAS-NMR, and SEM/EDS Studies of the Cured Samples Fired Under Nitrogen

Figure 5 shows the XRD patterns of the samples fired in nitrogen at 1100°C–1400°C. The major crystalline product in all samples is LAS (JCPDS file number 35-797). The similarities between samples 1 and 3 fired at 1100°C and 1200°C suggests that the particle size of the added silicon (type D and Max) does not influence the phases formed during firing, but the samples fired at 1200°C show higher amounts of LAS. Samples 1 and 3 fired at 1100°C and 1200°C contain unreacted silicon and no nitride phases. In order to investigate the effect of the silicon content on the formation of LAS and the possibility of forming nitride phases from these mixtures, samples were prepared containing twice the amount of Si (samples 2 and 4) and fired at 1400°C. The presence of remaining Si and lack of nitride formation in these samples suggests that this high content of Si may dissolve in the amorphous or crystalline phase during firing, thus preventing the nitridation of the Si. The sample containing amorphous Si (sample 5) fired at 1400°C formed a greater amount of LAS, possibly due to an increase in the viscosity of the liquid phase which causes better nucleation of LAS phase by the use of amorphous Si. The XRD peak of elemental Si in the diffractogram of sample 5 (Fig. 5) is attributed to crystallization of the amorphous Si. Sample 6 contained a similar amount of amorphous silicon to samples 2 and 4. Comparison of the XRD patterns of these samples (Fig. 5) shows that increasing the amount of amorphous Si decreases the intensity of the crystalline phases, but in samples fired at 1400°C, the amorphous Si dissolves more readily in the LAS structure than the other types of Si.

Further investigation of the changes occurring in selected samples during setting and firing was carried out by ^{27}Al and ^{29}Si MAS NMR spectroscopy (Figs 6 and 7, respectively). Samples 1 and 3, containing the precursor powder and Si, differ only in the type of silicon used and show identical ^{27}Al NMR spectra (Fig. 6(a)). Comparison of the ^{27}Al MAS NMR

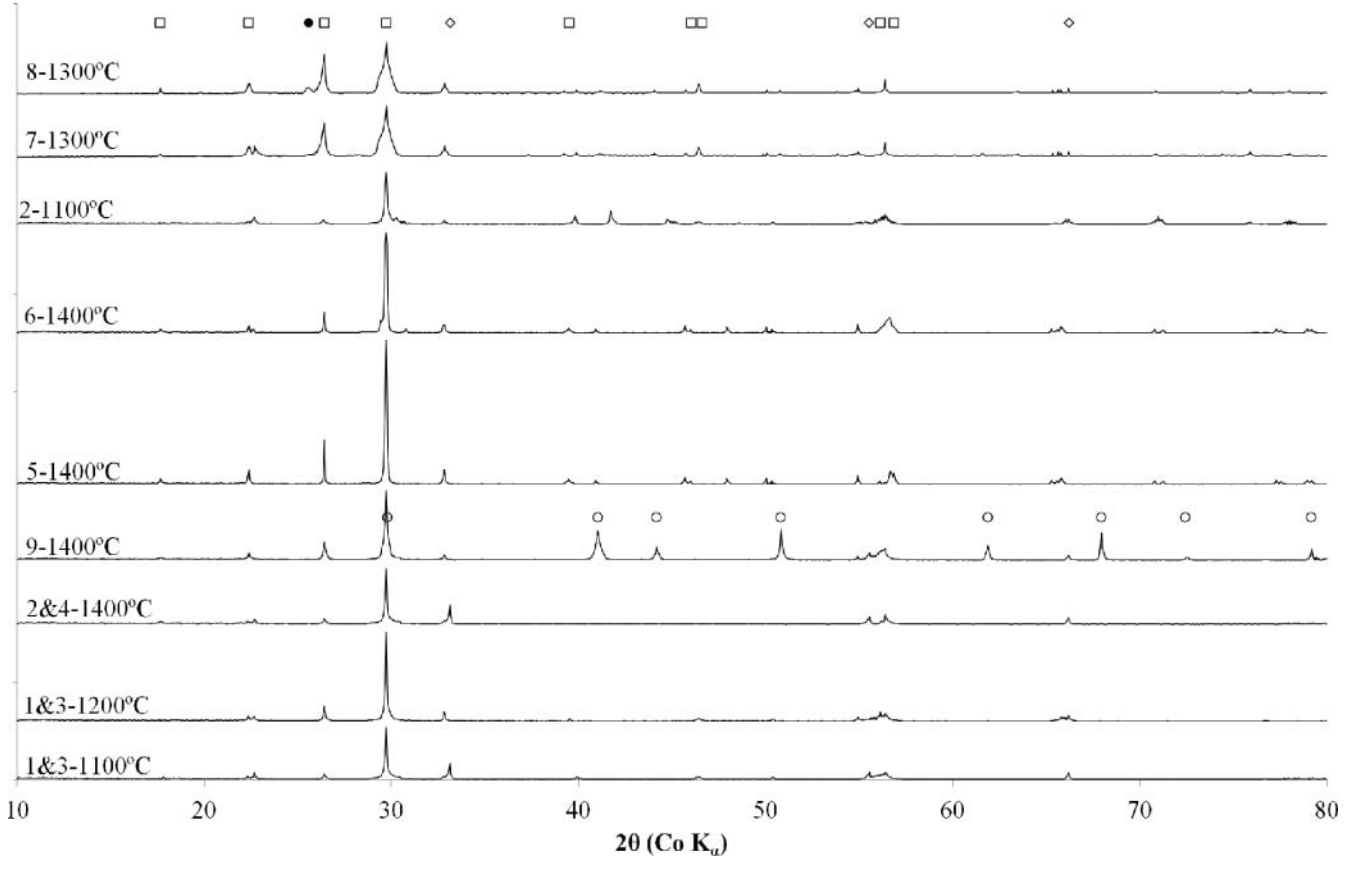

Figure 5. XRD patterns of samples fired under nitrogen at various temperatures. Key: □: LAS (PDF file No. 35-797), ○: corundum (PDF file No. 10-173), ●: cristobalite (PDF file No. 39-1425), and ◇: silicon (PDF file No. 27-1402).

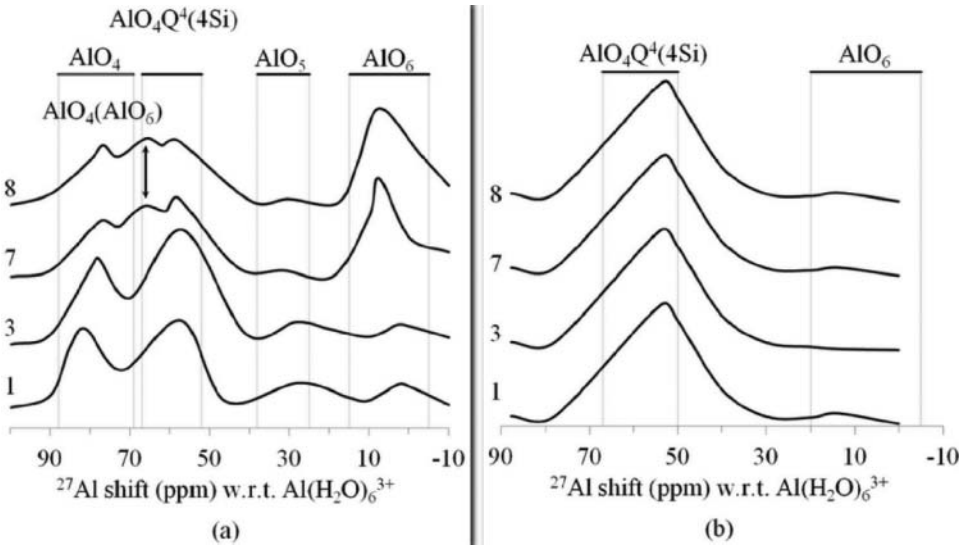

Figure 6. 11.7 T ^{27}Al MAS NMR spectra of the Li geopolymer precursors. (a): before firing and (b): after firing under nitrogen at 1300°C.

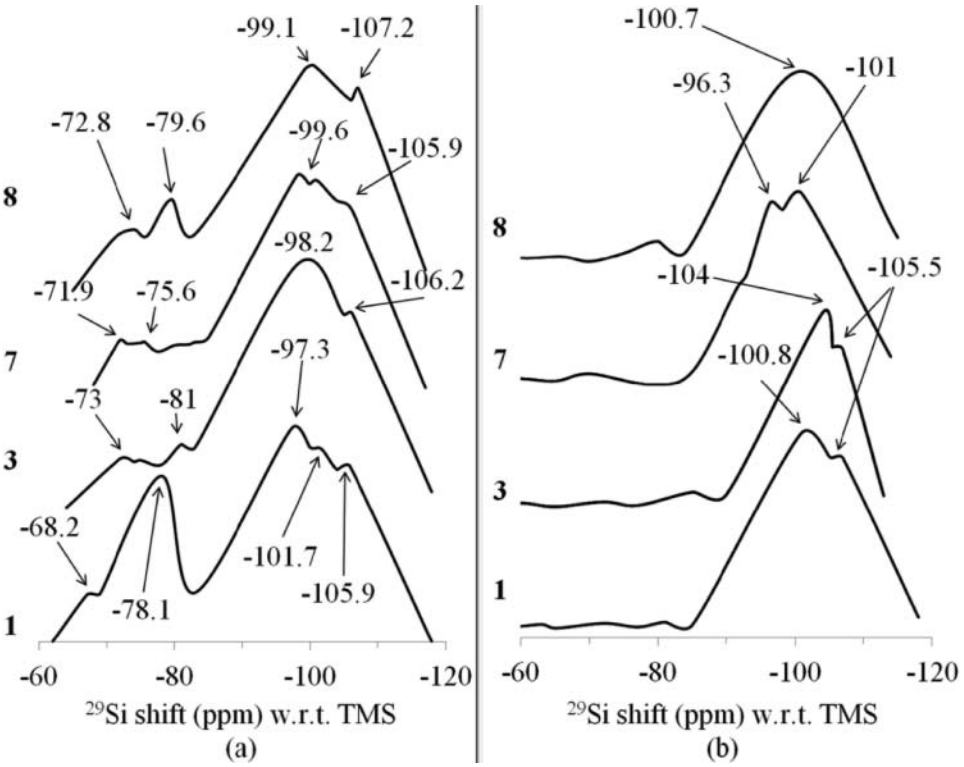

Figure 7. 11.7T ^{29}Si MAS NMR spectra of the Li geopolymer precursors. (a): before firing and (b): after firing under nitrogen at 1300°C.

of the calcined precursor powder (Fig. 4) with Fig. 6(a) shows that that the addition of Si and the curing process produces considerable changes in the ^{27}Al spectrum, indicating that the presence of the silicon significantly alters the geopolymer structure. The principal peak in the precursor at 80 ppm becomes broad and weak in samples 1 and 3. Another change is the emergence of a signal near 60 ppm in samples 1 and 3, attributed to $AlO_4Q^4(4Si)$ and indicating significant conversion of AlO_4 to $AlO_4Q^4(4Si)$ by the addition of Si and the setting reaction.

The spectra of the unreacted precursors 7 and 8 (Fig. 6(a)) contain tetrahedral AlO_4 resonances at approximately 80, 70, and 60 ppm and an octahedral peak at 5 ppm. The peaks at 80 and 60 ppm are similar to those of samples 1 and 3, but the most intense peak in these spectra is the octahedral resonance at 5 ppm. Since the samples 7 and 8 contain added ρ-alumina, the increased intensity of the octahedral peak is probably related to this phase.

Upon firing in nitrogen, the ^{27}Al NMR spectra of all the fired samples contain a broad tetrahedral peak at about 65 ppm Fig. 6(b), suggesting that the silicothermal reaction brings about significant conversion to $AlO_4Q^4(4Si)$.

The ^{29}Si NMR spectra of the unreacted precursors (Fig. 7(a)) contain a broad maximum at about -97 to -99 ppm, suggesting the presence of Si$-$OH groups rather than the expected geopolymer peak at about -92 ppm (although this may be part of the broad envelope). Smaller peaks at about -80 ppm arise from the added silicon; this is the sharpest and most intense in sample 1 (-78 ppm) containing the highest concentration of residual Si of the four, i.e., the greatest stability towards the alkali activation step. Microstructural studies on sample 2 by SEM/EDS (Fig. 8) indicated that the size of the metallic Si relicts

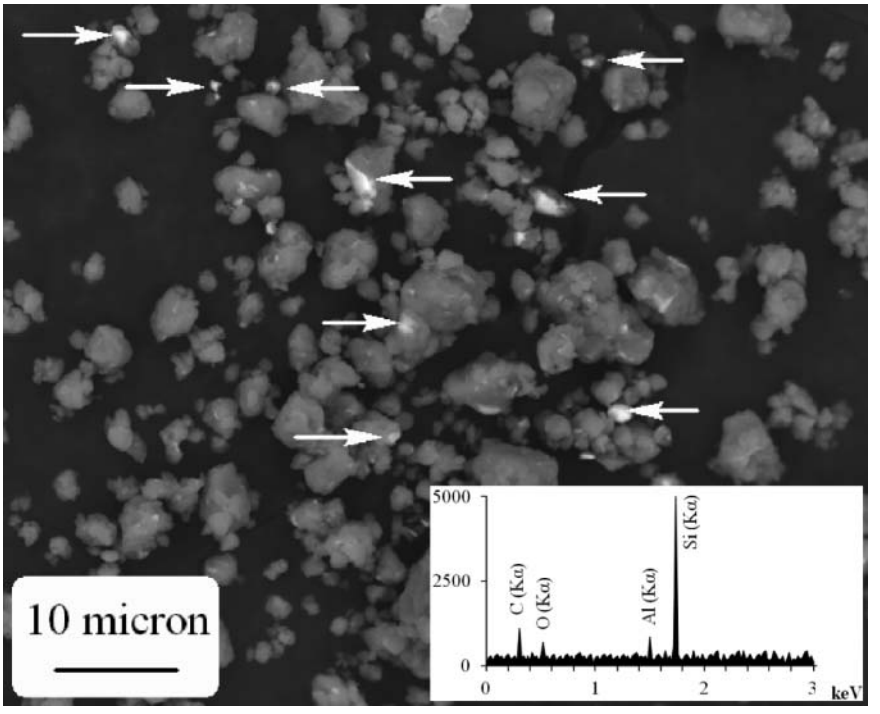

Figure 8. Backscattered SEM image of sample 2 fired at 1400°C under N_2 atmosphere.

is about 3 μm. These results suggest that to extend this method to the production of nitride phases, a procedure is needed to maintain the residual silicon in a reactive form in the presence of the lithium. This has not been possible to accomplish under the present reaction conditions.

Although the larger particle size of the type Max silicon used in sample 3 might have been expected to provide more protection from alkali attack than the type D silicon used in sample 1, the greater chemical purity of the latter may explain its greater inertness. Both samples 7 and 8 contain the same amorphous silicon of small particle size, but the persistence of a small amount of residual silicon in the unfired precursor sample 8 reflects the fact that this sample contains double the amount of silicon than in sample 7. The small sharp shoulders at about -106 ppm in the unfired precursors arise from the quartz and cristobalite impurities present in the original clay. After firing, the spectra of all the samples (Fig. 7(b)) remain broad, with centre-of-gravity positions at about -100 ppm. The broad envelopes of these spectra may mask the presence of LAS, whose ^{29}Si resonance occurs at about -91 ppm in both spodumene and eucryptite [20], but the fired spectra indicate the substantial disappearance of the elemental silicon upon firing, notwithstanding the XRD and SEM/EDS evidences of unreacted silicon. No evidence is present in these spectra of the formation of nitride phases whose resonances would appear at about -48 ppm [20].

The inset shows a typical EDS analysis of the white grains indicated by the arrows indicating these to be unreacted silicon.

3.3. Formation of LAS-alumina Matrix Composites

The absence of evidence of nitridation of any of the above mixtures suggests the possible viability of this method for producing alumina-containing LAS composites from samples in the mullite region of the phase diagram (Fig. 1). This was attempted by the addition of Si and ρ-Al_2O_3 to the precursor powder (samples 7, 8, and 9, Table 1). The XRD patterns of samples 7 and 8 after firing (Fig. 5) show broad LAS peaks arising from a large amount of glassy phase. Sample 7 contains LAS and Si whereas sample 8 contains LAS, Si and a trace of SiO_2. The formation of SiO_2 suggests the Si is being oxidized rather than being retained in either the crystalline form or dissolved in the liquid phase as in the previous samples.

Sample 9 contains crystalline Si of larger particle size (type Max) rather than amorphous Si as in samples 7 and 8, and a higher content of ρ-Al_2O_3 than in samples 7 and 8. This combination was hoped to produce a compound with a high Al content in the ternary phase diagram with high melting temperature. The XRD pattern of the product fired at 1400°C (Fig. 5) shows the formation of LAS, corundum and a small amount of residual Si, but no trace of SiO_2 or Si_3N_4. Thus, the silicothermal reaction of a Li-geopolymer with the addition of an appropriate alumina source such as ρ-Al_2O_3 is suitable for producing composites of LAS and alumina, provided a crystalline form of silicon is used, and the sample composition is maintained within the mullite region of the ternary phase diagram.

4. Conclusions

A novel method has been demonstrated for the production of LAS and LAS-alumina matrix composites by silicothermal reaction of Li-geopolymer precursors fabricated by a solid-state method to avoid destroying the elemental silicon. LAS formation occurs at relatively low temperatures (between 1100°C and 1400°C, with an optimum reaction temperature of

1200°C). The type and amount of Si used in the silicothermal reaction does not affect the phases formed in the fired samples, but the crystallinity of the products is influenced by the silicon used. Below 1100°C, the Si particles are surrounded by a liquid phase, hindering further reaction with nitrogen, but ^{29}Si NMR shows that crystalline Si of 9-μm particle size was the most alkali-stable.

LAS/Al_2O_3 composites can be formed by adding ρ-Al_2O_3 to Li-geopolymer precursors and firing the mixture under a nitrogen atmosphere at 1400°C.

Since a small amount of silicon is retained in all the fired samples, it may be possible to adapt this procedure to produce nitride phases or LAS-nitride composites if the residual Si could be maintained in a reactive form in the alkaline environment of the geopolymer precursors.

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