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Preparation and characterization of a powder precursor, consisting of oxides of Li–Al–Si in the form of hydroxyhydrogel for synthesis of β-spodumene ceramics☆

S. Mandal, S. Chakrabarti*, S. Ghatak

Central Glass & Ceramic Research Institute, 196, Raja S. C. Mullick Road, PO: Jadavpur University, Kolkata - 700 032, India

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Abstract

Powder precursors of different compositions in the system Li_2O–Al_2O_3–SiO_2 were prepared in the hydroxy-hydrogel form by wet interaction technique in aqueous medium for ultimate synthesis of low expansion ceramics. Properly processed powder precursors were characterized. It was found that the powder precursor produced by this process was in meta-stable state with the aluminium in the tetrahedral as well as in the octahedral co-ordination sites. The confirmation of this finding was made by IR analysis of the prepared powder precursors as well as the heat treated samples. It was further found that the complete dehydroxylation did not occur even after heat treatment at 700 °C. The XRD analysis of the samples, when heat treated at 700 °C confirmed the detection of β-spodumene phase and the formation of this phase was almost complete when the samples were heat treated at 1000 °C.

Keywords: β-Spodumene; Powder precursor; Hydroxy-hydrogel processes

1. Introduction

The “stuffed” β-(high) quartz structure [1] is known to exhibit very interesting physical and technological properties. This name was given to structures in which the mode of linking of the tetrahedral in the quartz structure is retained, but some Si atoms are replaced by Al while cations (Li^+, Mg^{++}) are accommodated in some of the interstices to maintain the charge balance [2]. In the system Li_2O–Al_2O_3–SiO_2, β-quartz solution phases of this type have found tremendous application for low expansion glass ceramics [3]. The high temperature structure of β-eucryptite ($LiAlSiO_4$) can be imagined as a superstructure on β-quartz [4]. For high SiO_2 contents, however, such phases are only metastable precursors of the stable equilibrium phase (β-spodumene solid solution) [5].

This is confirmed by the study on the phase diagram in the system Li_2O–Al_2O_3–SiO_2 reported by Anon [6] in which the stability field of β-eucryptite ($LiAlSiO_4$) solid solution is confined in the range of compositions 1:1:1 to about 1:1:1.60 (Li:Al:Si). D. Mazza et al. [7] reported the high quartz solid solution phases by an unconventional sol-gel technique, by means of the preliminary formation of an amorphous solid (xerogel) with composition $Li_2O.Al_2O_3.nSiO_2$, ($n = 2$–4). Glass-ceramics based on the crystalline phases of the composition $Li_2O.Al_2O_3.nSiO_2$ are famous for ultra-low or even negative thermal expansivity and high thermal stability over an extended temperature range. The sol-gel process is currently recognized as one of the most attractive methods for preparing glass ceramics with high homogeneity at lower processing temperature. But while doing so, serious problems are often encountered during hydrolysis and polycondensation of metal alkoxides and drying of the wet gels. Segregation of specific oxides due to different rates of hydrolysis and crack and bubble formation may occur. However, it is notoriously difficult to prepare the homogeneous precursors of silicates from alkoxides. The different hydrolysis rates of individual alkoxides result in chemical inhomogeneity in the hydrolysis products, leading to higher crystallization

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☆ Patent is pending for the preparation of powder precursor.

* Corresponding author. Fax.: +91-033-2473-0957/2483-8085.
E-mail addresses: chakrabarti_s@cgcri.res.in or chakrabarti_s@hotmail.com(S. Chakrabarti).

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temperature or undesired crystalline phase [8]. Several approaches have been investigated including matching of hydrolysis rates by chemical modification with chelating agents [9]. Attempts have also been made to synthesis β-eucryptite, β-spodumene, Petalite, Virgilite, Lithium Orthoclase, etc. glass ceramics via the sol-gel method. However large glass ceramics monoliths have not yet been produced, although gel monoliths in the system Li_2O–Al_2O_3–SiO_2 were prepared by Orcen and Hench [10] with the help of drying control chemical additives (DCCA). Joong-sil Yang et al. reported [11,12] the synthesis of lithium aluminosilicate glass

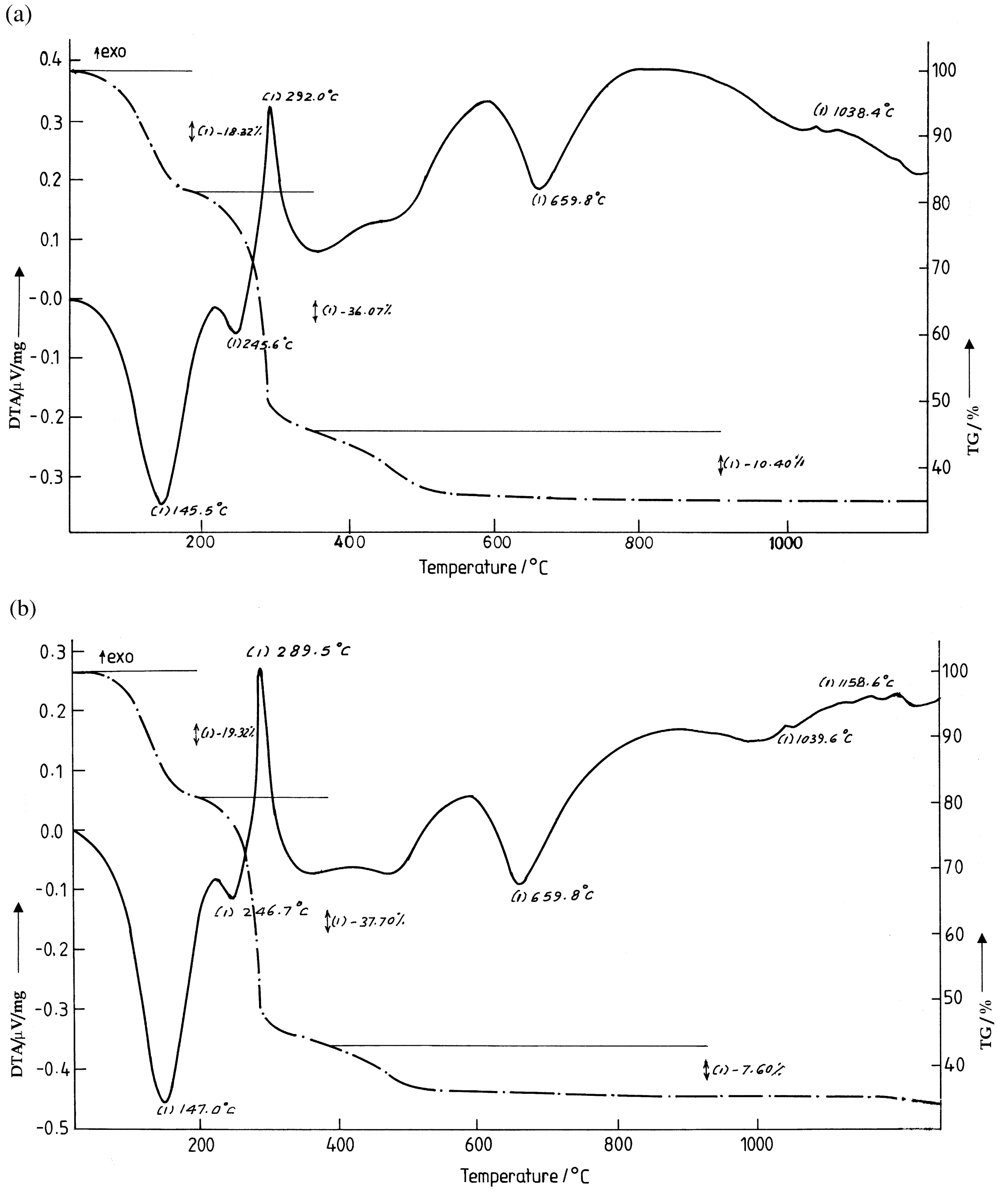

Fig. 1. Differential thermal and thermo-gravimetric analysis of the sample (a) S1, (b) S2, (c) S3 dried at 125±5 °C.

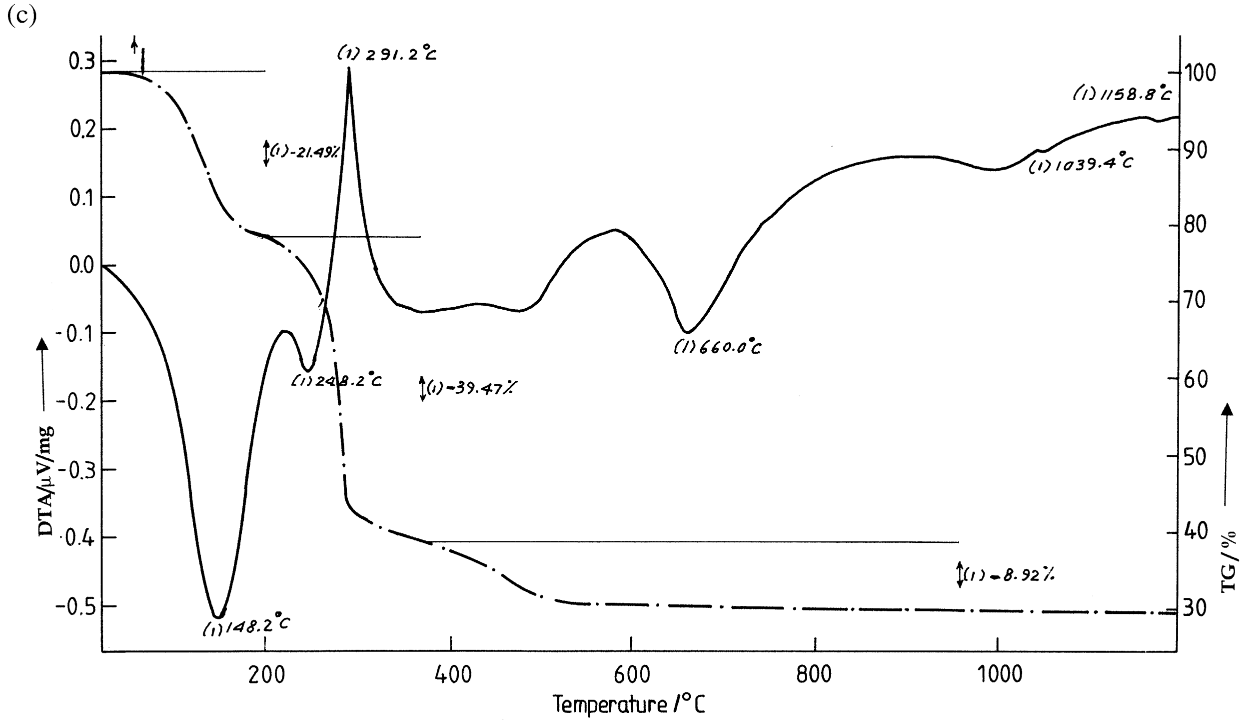

Fig. 1. (*continued*)

ceramics monolith with a composition $Li_2O.Al_2O_3.4SiO_2$ by the sol-gel technique.

The present day method of making the material with low thermal expansion coefficient consists of three main processes i.e. (i) solid–solid interaction (ii) co-precipitation of hydroxides and (iii) sol-gel processing. References for a solid–solid interactive process may be made to Abdel-Fattah et al. [13] wherein lithium carbonate, aluminium oxide and silica or their ores were mixed and sintered to obtain lithium aluminosilicate glass ceramics. References are also made to Ghosh et al. [14] wherein wet interaction techniques were followed by coprecipitating aluminum hydroxide and silicic acid which were mixed with lithium carbonate and sintered at 1300 °C to prepare the same material. The material also could be obtained by sol-gel processing as referred to by Mazza et al. [15] wherein xerogels were prepared as precursor material for the preparation of lithium aluminosilicate materials. This particular technique is implemented by the sol-gel route employing pre-hydrolyzed tetra ethyl orthosilicate and Al, Li nitrate in aqueous solution to obtain amorphous xerogel at 400 °C. From this xerogel, end product is made by calcinations. The drawbacks of the present day methods are namely (i) difficulty in mixing solid materials thus leading to inhomogeneity in the powder precursor (ii) coprecipitation of aluminium hydroxide and silicic acid does not take place at same pH, making the process inaccurate (iii) low reactivity of the powder precursors require higher sintering temperature.

Preparation of lithium aluminosilicate ceramics from reactive precursors prepared in the “Hydroxy Hydrogel” form [16–21] were attempted where desired homogeneity of the reactive precursors were achieved. During sintering two phenomena are likely to be operative, namely (i) formation of solid solution and (ii) densification. Therefore, the entire process may be termed as reaction sintering.

In the present work the powder precursor in the form of hydroxy hydrogel was prepared and was converted to β-spodumene phase and the powder precursor was characterized in relation to the presence of hydro and hydroxy linkages with respect to temperature of heat treatment.

2. Experimental

2.1. *Preparation of β-spodumene powder precursor*

β-Spodumene powder precursor in the form of hydroxy hydrogel of different compositions in the system $Li_2O–Al_2O_3–SiO_2$ was prepared by wet interaction in aqueous medium by flash polycondensation technique [21] using LR grade Li_2CO_3, $Al(NO_3)_3.9H_2O$ and fumed silica as source of Li_2O, Al_2O_3, SiO_2, respectively. A weighed quantity of lithium carbonate was first added to a measured volume of distilled water and then stirred and boiled for sometime. The pH of the aqueous lithium carbonate was adjusted to acidic pH by gradual

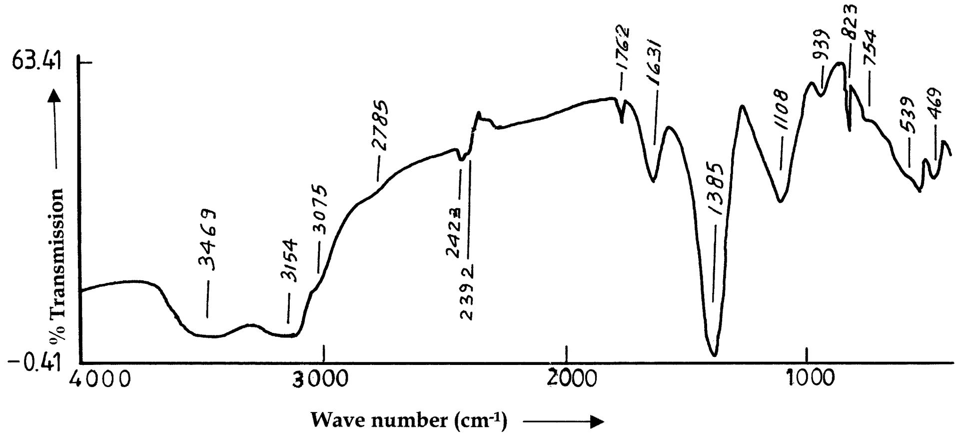

Fig. 2. IR spectra of lithia-alumina-silica powder precursor dried at 125±5 °C.

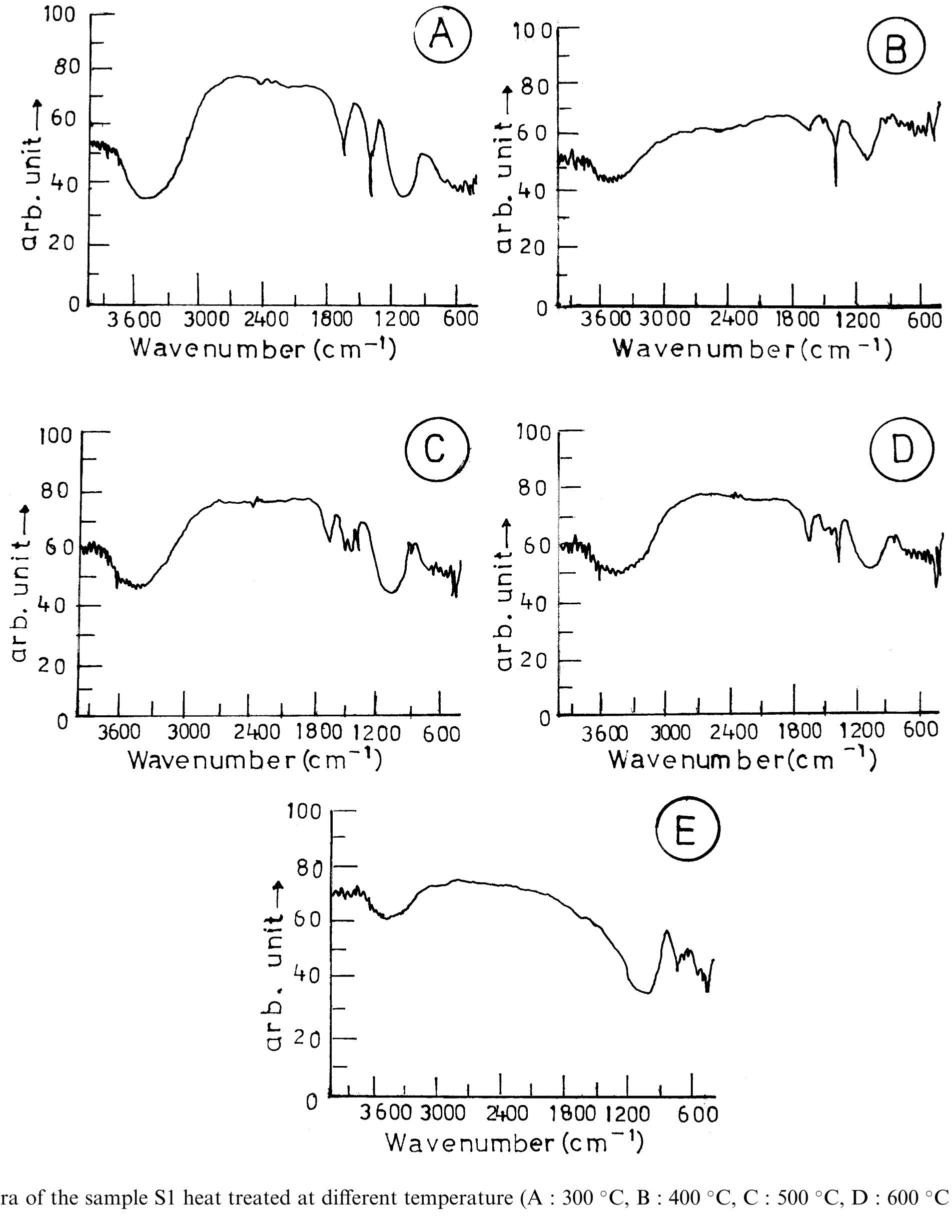

Fig. 3. IR spectra of the sample S1 heat treated at different temperature (A : 300 °C, B : 400 °C, C : 500 °C, D : 600 °C and E : 700 °C).

addition of nitric acid till effervescence ceased. A weighed quantity of LR grade aluminium nitrate was added into this solution with stirring till the complete dissolution of aluminium nitrate into the lithium nitrate solution. A weighed quantity of fumed silica (Cab–O–Sil make, M/s Vaunam Agencies, Kolkata) was added into the mixed solution with continuous stirring to obtain a suspension. The suspension so prepared was poured into a calculated amount of 25% ammonia solution under stirring so that the pH of the mixture after the reaction remains between 4 and 7. The entire mixture took on the consistency of a thick gel like mass. The gel like mass was kept at room temperature for 24 h followed by evaporation to dryness with occasional stirring. The raw materials were taken in such quantities so as to develop LAS (lithium aluminosilicate) in the ratio of (nominal) 1:1:2.5, 1:1:3 and 1:1:3.5 (β-spodumene powder precursor).

The powder precursors, dried at 125 °C±5 °C were calcined at 750 °C for 2 h. Content of Li_2O, Al_2O_3 and SiO_2 after calcinations were analyzed chemically. From the analyzed composition, molar ratio of Li_2O:Al_2O_3:SiO_2 was calculated and shown in Table 1.

2.2. Thermal analysis

DT and TG analysis of the powder precursor dried at 125±5 °C in an air oven at ambient atmospheric

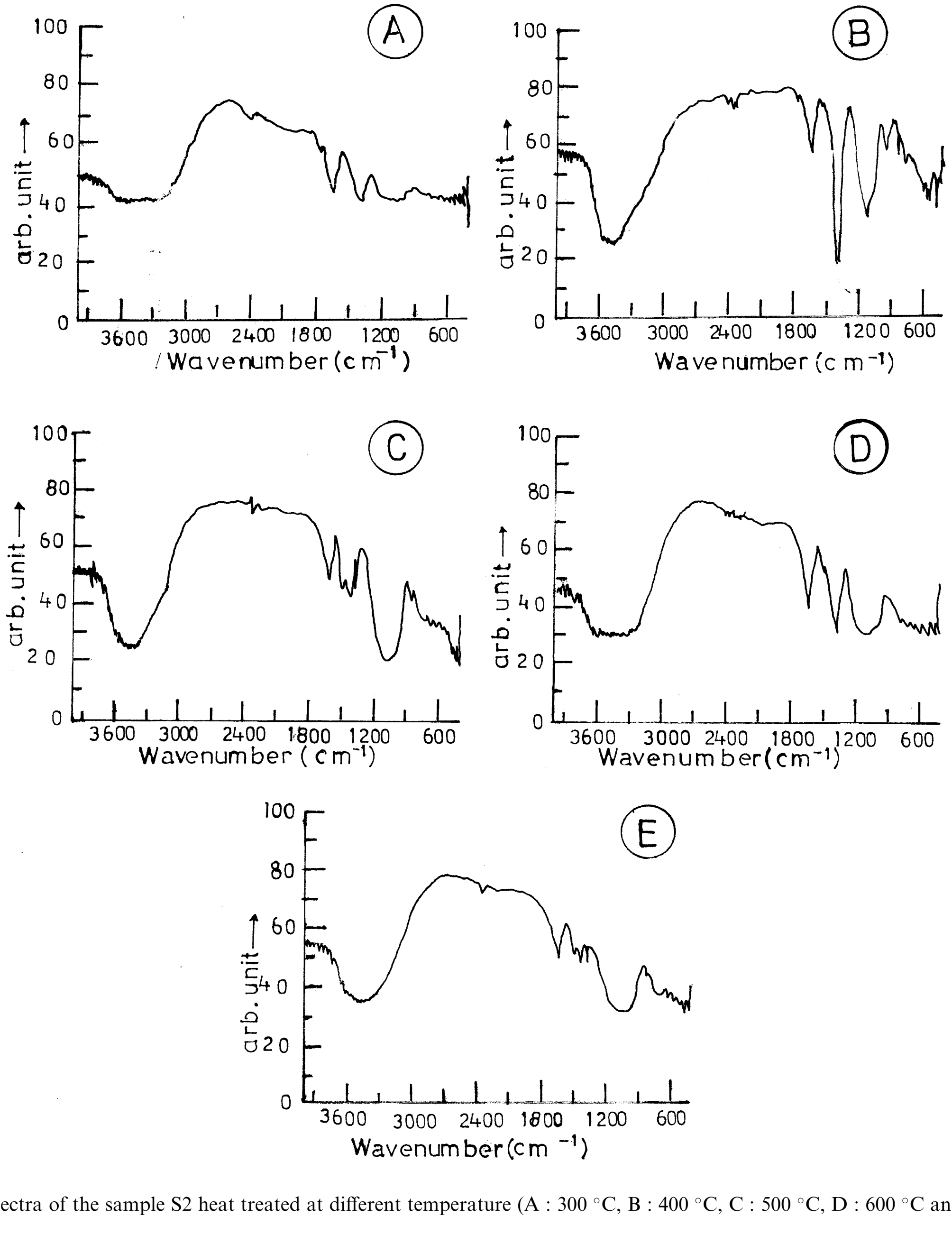

Fig. 4. IR spectra of the sample S2 heat treated at different temperature (A : 300 °C, B : 400 °C, C : 500 °C, D : 600 °C and E : 700 °C).

conditions was carried out by NETSCH Thermal Analyzer, Model 4045 upto 1200 °C at a heating rate of 10 °C/min. The results obtained are shown in Fig. 1A–C.

Table 1
Compositional analysis after ignition at 750 °C

Constituents	Composition (wt.%) of the samples			Molar ratio
	S1	S2	S3	
Li_2O	10.54	9.17	8.71	S1 = LAS 1:1.01:2.52
Al_2O_3	36.21	34.37	30.18	S2 = LAS 1:1.10:3.04
SiO_2	53.25	56.46	61.11	S3 = LAS 1:1.02:3.51

LAS = lithia aluminosilicate.

2.3. *IR analysis*

IR study of the powder precursor and of the heat treated samples was done in the range 4000–400 cm^{-1} by means of the Perkin-Elmer model No. 1615 FTIR spectometer using KBr and the results are shown in Figs. 2 and 3–5 respectively.

2.4. *XRD analysis of the powder precursor*

The dried powder precursors, fired at 300, 500, 700 and 1000 °C for 2 h were taken for XRD analysis. The XRD analysis for all the samples were carried out using a Philips PW-1730 with Cu K_α radiation and Ni filter and the patterns are shown in Figs. 7–9 and 10 respectively.

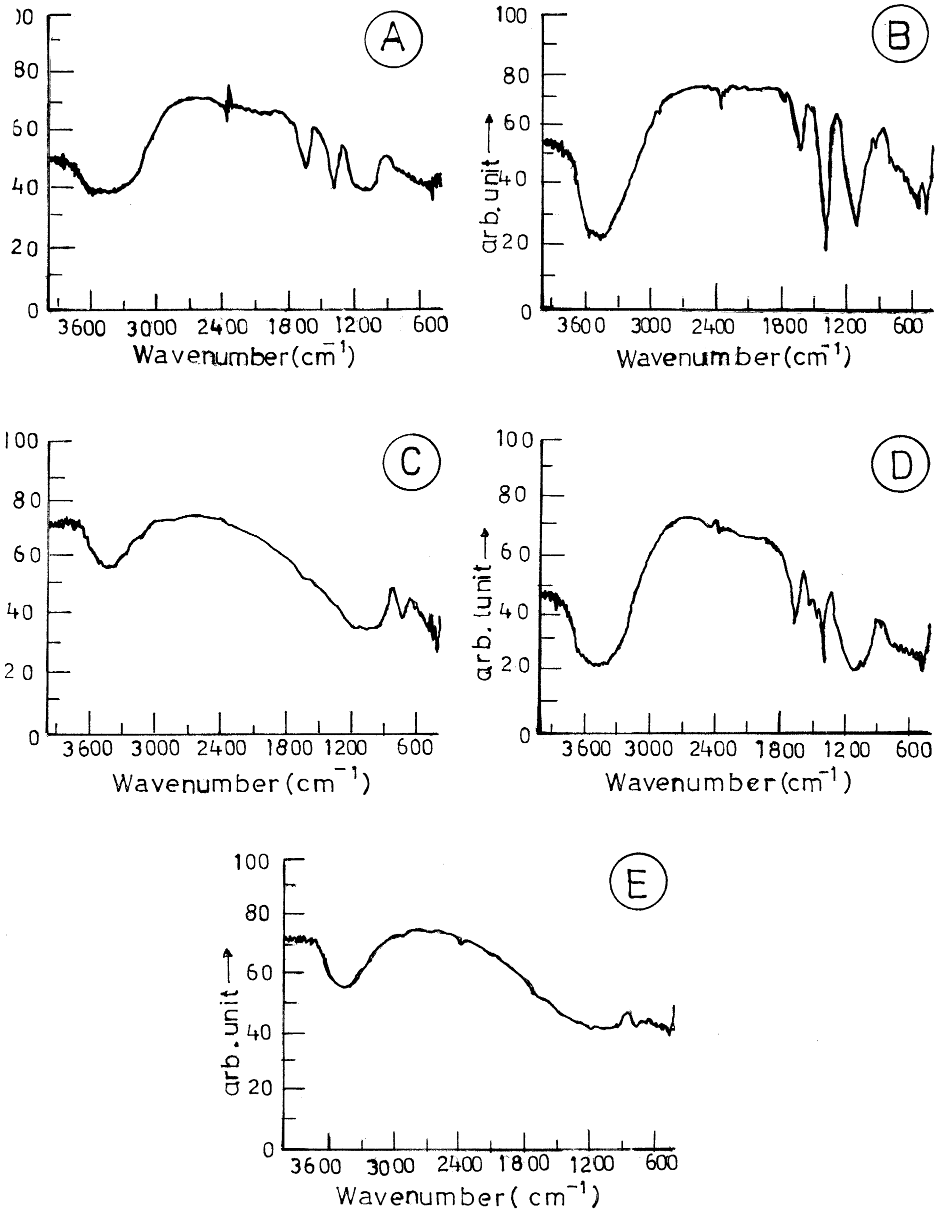

Fig. 5. IR spectra of the sample S3 heat treated at different temperature (A : 300 °C, B : 400 °C, C : 500 °C, D : 600 °C and E : 700 °C).

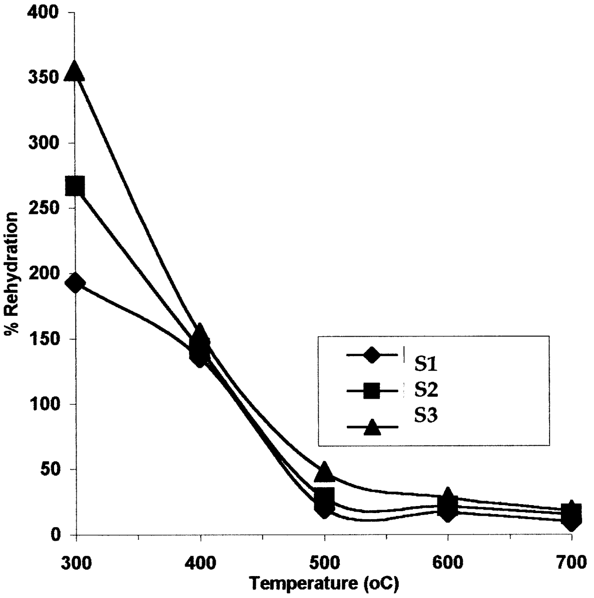

Fig. 6. Rehydration characteristics of samples heat treated at different temperature and equilibrated at 100% RH.

3. Results and discussion

3.1. DTA/TGA

From the DTA/TGA curves (Fig. 1A–C) it was found that loosely bound physically absorbed water escaped at around 150 °C. The amount of loosely bound water was around 20%. Nearly 40% of the hydroxylated water escaped the system at around 300 °C. It appeared from Table 2 that the loosely bound water present in different samples escaped in varying amounts (18.32–21.49%) up to a temperature of 150 °C. Maximum loss of water (21.49%) occurred in the case of the sample S3 at 150 °C. Loss of water at 150 °C for the other two samples was more or less same. In the intermediate temperature range i.e. 150–300 °C a similar trend was noticed. It also appeared from Table 2 that although the sample S3, containing a larger amount of silica, contains more water molecules in its network but the sample S1 containing a lesser amount of silica retained water molecules more firmly up to 1000 °C.Thus, it may be said that silica in the network structure has a considerable role in the bonding of water to the network structure. However, more specific and detailed investigations are needed for exact evaluation of this phenomenon.

An exothermic peak around 290 °C indicated structural rearrangement with the exclusion of energy towards more stability (Fig. 1A–C). Though it was found that almost all the water molecules were expelled from the structure below 600 °C, strong endothermic peak at around 650 °C indicated rupture of hydroxyl bond and forming a metastable structure. Therefore the powder precursor, heat treated at 600–650 °C resulted in a material which is thermodynamically metastable with a lesser amount of hydroxyl bonding which may ultimately produce low pore or pore free micro-structure in the sintered compacts. A representative IR result of the processed powder precursor, shown in Fig. 2A, indicated the presence of hydroxylated water (3469 cm^{-1}) [22]. Aluminium present in the structure is tetrahedral as well as in octahedral form which was indicated by the presence of peaks at frequencies 469, 539 and 754 cm^{-1} (Fig. 2) [23]. Therefore, at this stage it may be concluded that the powder precursor produced by this process was in thermodynamically meta-stable state with the aluminium in the tetrahedral as well as in the octahedral co-ordination sites.

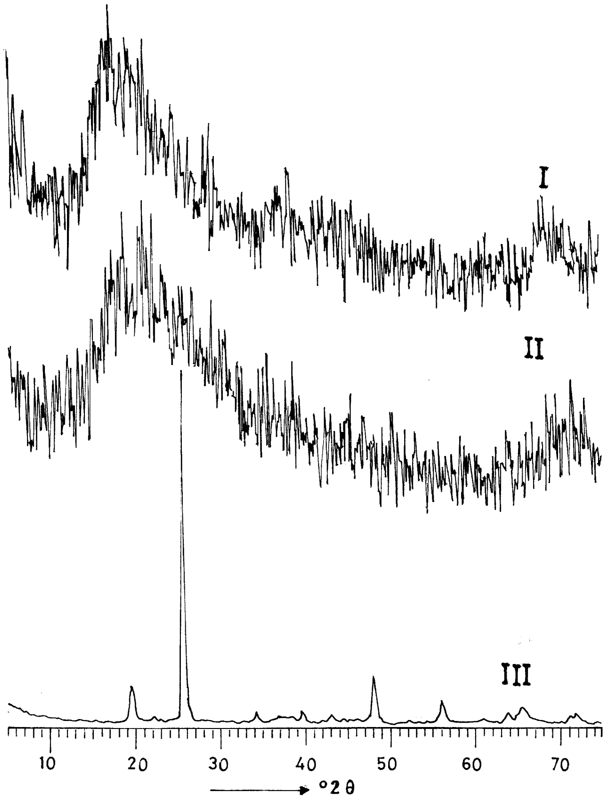

Fig. 7. XRD pattern of the sample S1 heat treated at different temperature (I : 300 °C, II : 500 °C, and III : 700 °C).

3.2. IR characterization and analysis

The IR spectra of the processed powder precursor, dried at 125±5 °C and of the heat treated samples (300–700 °C with an interval of 100 °C) were shown in Figs. 2 and 3–5 respectively. Fig. 2 is the representative IR curve of the samples S1, S2 and S3 in the hydroxy hydrogel form when dried at 125±5 °C. The observed spectra were shown in Table 2. From Table 2 it was evident that the strong band at 469 cm^{-1} is assigned to the deformation mode of the β-quartz type frame work and gives an indication of SiO_4 tetrahedral bending vibration [24]. The shifting of the band at 754 cm^{-1} to

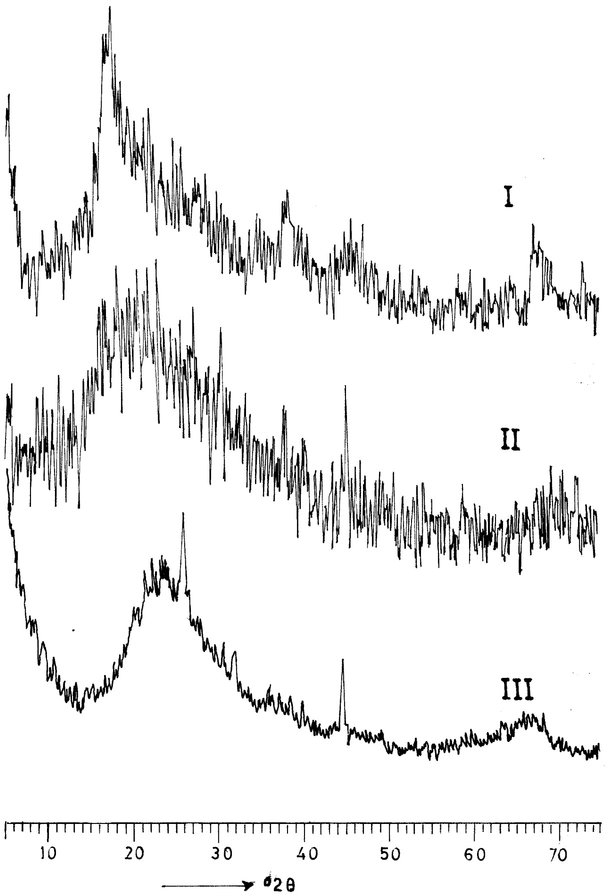

Fig. 8. XRD pattern of the sample S2 heat treated at different temperature (I : 300 °C, II : 500 °C, and III : 700 °C).

higher wave number at 1108 cm^{-1} (Fig. 2) is indicative for the symmetric stretching mode of SiO_4 tetrahedral coordination [25]. The presence of IR absorption bands at 3154 and at 1385 cm^{-1} (Fig. 2) was ascribed to NH_4^+ ion (ammonium nitrate) [26] for which a DTA exothermic peak is observed at around 290 °C (Fig. 1A–C). The retention of these two particular peaks indicates that the representative powder precursor contains ammonium nitrate significantly. The difference in the band intensities between the stretching modes of OH groups and H_2O molecules centered at 3469 cm^{-1} (presence of hydroxylated water) and the bending mode of H_2O molecules centered at 1631 cm^{-1} (Fig. 2) is in agreement with the presence of both, H_2O and OH groups [27]. The peak at 3469 cm^{-1} is contributed mainly by aluminium hydroxide gel [28]. Therefore, the physical identity of both the $Al(OH)_3$ and the ammonium nitrate was retained in the powder precursor. The presence of peaks at frequencies 539, 823 and 939 cm^{-1} (Fig. 2) of the hydroxy hydrogel powder precursor indicated the presence of aluminium in both octahedral and tetrahedral form [29], which was not destroyed during the subsequent stages of heat treatment of the powder precursor (Figs. 3–5). From Figs. 3–5 it is evident that on heat treatment of the powder precursors in the temperature range between 300 and 700 °C, the absorption band at 3154 cm^{-1} [26], responsible for NH^{4+} ion is eliminated for the samples (S1, S2 and S3) and the peak intensity for other type of IR band (1385 cm^{-1}, responsible for IR absorption band for NH^{4+} ion) is found to be substantially reduced in the case of sample S2, but in the case of the other two samples (S1 and S3) the peak at 1385 cm^{-1} is finally disappeared on heat treatment at 700 °C (Figs. 3–5). The peak at 3469 cm^{-1} was assigned mainly to stretching mode of the OH group (Al-hydroxide gel) and water molecules [30]. The presence of this peak after heat treatment at 700 °C indicated that OH groups are still present in association with the structural network for all the samples. Thus it may be said that the metal hydroxyl bond did not rupture completely. The 1645 cm^{-1} peak (assigned to bending mode of water molecules), [30] is noticed for all the samples when heat treated in the temperature range of 300–700 °C. The intensity of this peak indicates that with the increase of heat treatment temperature water molecule is gradually eliminated and the total elimination took place at the maximum temperature of heat treatment i.e. at 700 °C. So from the IR study of the heat treated powder precursor (Figs. 3–5), it may be concluded that (i) in general the complete dehydroxylation

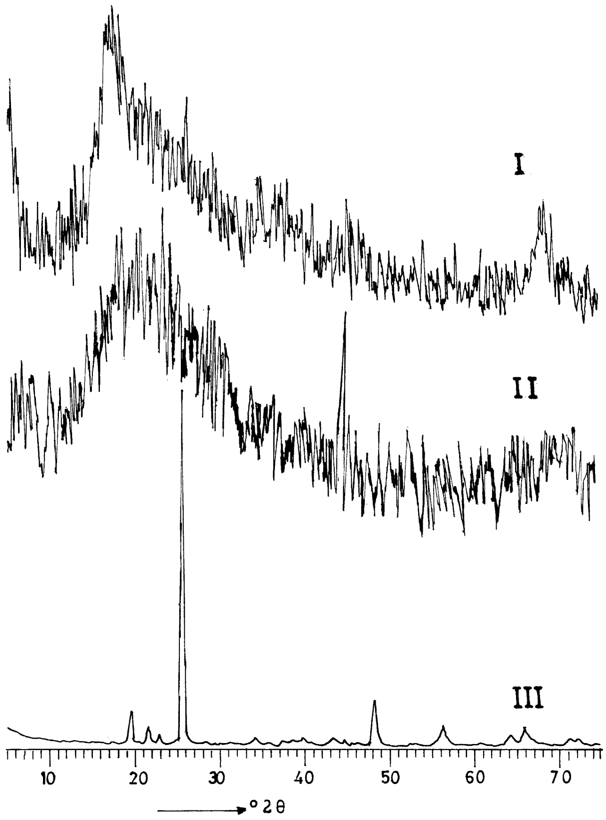

Fig. 9. XRD pattern of the sample S3 heat treated at different temperature (I : 300 °C, II : 500 °C, and III : 700 °C).

did not occur even after heat treatment at 700 °C, (ii) presence of SiO_4 tetrahedral are indicated for the samples S1 and S2 at 300–700 °C temperature of heat treatment and for S3 up to 600 °C.

3.3. XRD analysis

The X-ray diffraction of the samples heat treated at different temperature (300, 500, 700 °C) were shown in Figs. 7–9. It was indicated that crystallization of β-spodumene ($Li_2O.Al_2O_3.\ 4SiO_2$) though initiated at 300 °C but well defined formation could be noted for samples heat treated at 700 °C. Formation of this phase was found to be more or less complete when the samples were heat treated at 1000 °C (Fig. 10).

4. General discussion

In the present system, fumed silica polymerizes on addition of water in which both aluminium nitrate and lithium nitrate remain in solution producing Al^{3+}, Li^{+} and NO^{3-} ions in solution. This system during ageing adjust itself so that cations and anions assume favourable equilibrium position. Since Al^{3+} remains in octahedral coordination in aqueous solution, it is likely that in the present system, under the above-mentioned condition, octahedral coordination will be retained. During flash polycondensation, the entire system polymerizes almost instantaneously where most of the aluminium cation is expected to maintain its octahedral coordination. However, some conversions of octahedral aluminium into

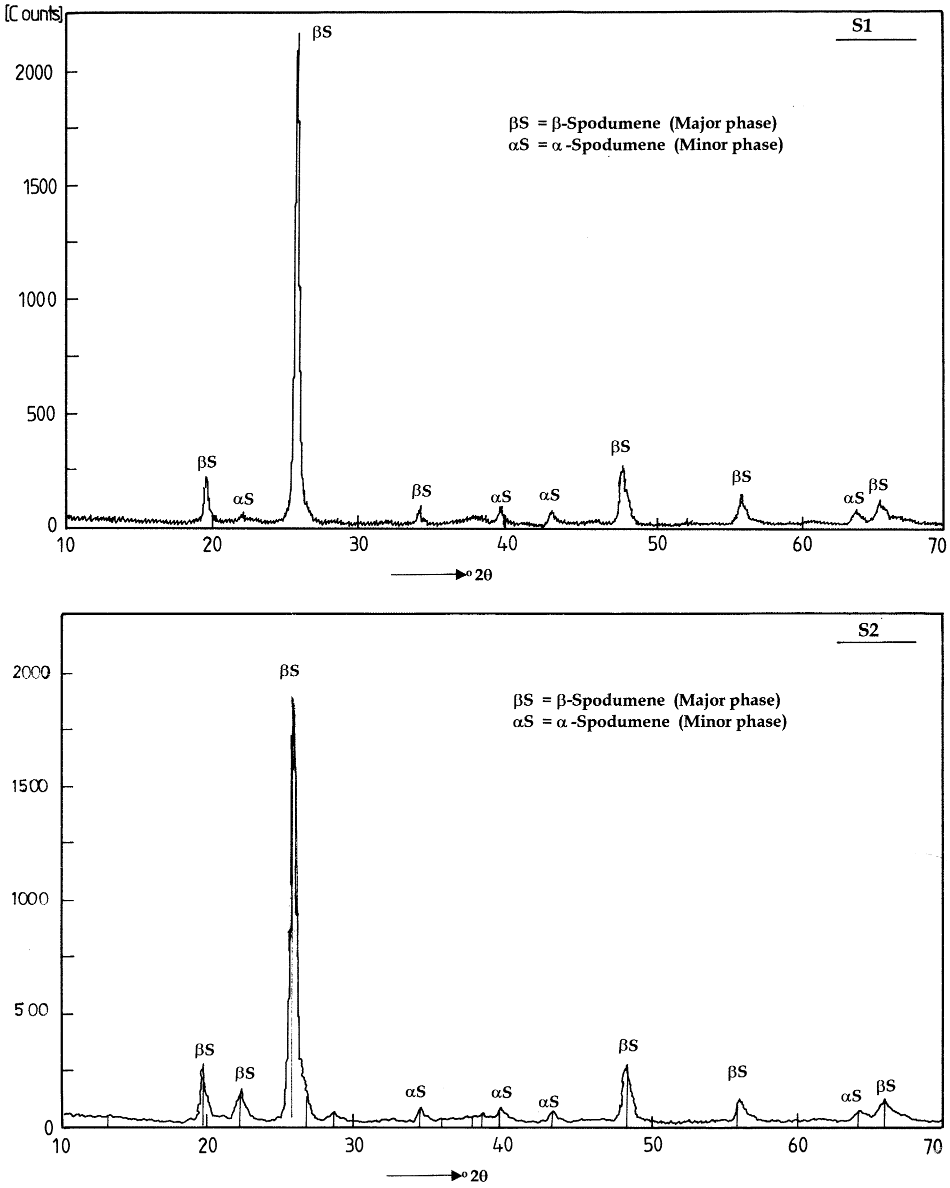

Fig. 10. XRD patterns of the samples (S1, S2 and S3) fired at 1000 °C.

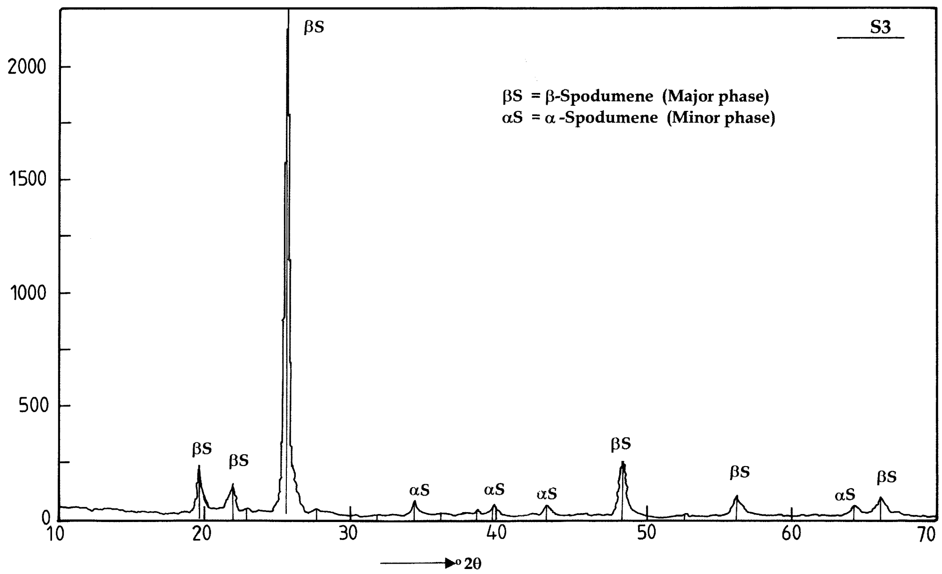

Fig. 10. (*continued*)

Table 2
Loss of water (wt.%) of the samples at different temperature as reflected in the TG curve

Sample No.	Up to 150 °C	150–300 °C	300–1000 °C	Total (%)
S1	18.32	36.07	10.40	64.79
S2	19.32	37.70	7.60	64.62
S3	21.49	39.47	8.92	69.88

Table 3
Band position (cm^{-1}) obtained from the IR curve (Fig. 2) (stretch: stretching vibration), bend:bending vibration)

Band position (cm−1)	Band assignment Refs. [23–30]
469	O–Si–O stretch (SiO_4 tetrahedra)
539	Al–O stretch (AlO_6 Octahedra)
754	Si–O stretch (SiO_4 tetrahedra)
823	Al–O stretch (AlO_4 tetrahedra)
939	Al–O stretch (AlO_4 tetrahedra)
1108	Si–O stretch (SiO_4 tetrahedra)
1385	NH_4^+ ion (absorption band for ammonium nitrate)
1631	H_2O bending mode
1762	H–O–H vibration band
3154	NH_4^+ ion (absorption band for ammonium nitrate)
3469	Stretching mode of OH groups and H_2O molecules

tetrahedral aluminium can not be ruled out and was observed in reality. The confirmation of the above suggestion is found by IR analysis of the prepared materials as well as the heat treated samples where the existence of both octahedral and tetrahedral aluminum was noted.

During dehydration and dehydroxylation, the water molecules were first eliminated from the system leaving behind cavities, putting the structure in non-equilibrium state. This was confirmed by rehydration experiments where heat treated samples were progressively kept in different humidity chambers and were found to reabsorb the lost water to the extent which was related to the humidity level maintained. A representative curve showing the rehydration characteristics of the samples heat treated at different temperature and equilibrated at 100% RH was shown in Fig. 6. This rehydration behavior depends primarily on the structure of the material. The extent of rehydration decreases with increasing extent of structural collapse i.e. break down of the cavities and pore channels during heat treatment [31].

Even after total collapses of the structure, the hydroxy linkages were found to be present as is evident from IR analysis (Figs. 3–5) of the samples heat treated at different temperature up to 700 °C. The entire phenomenon leads to a material which was found to be highly reactive and produced β-spodumene phase at a temperature as low as 700 °C, detected by XRD analysis (Figs. 7–9).

5. Conclusions

1. Lithium aluminosilicate powder precursor in the hydroxy hydrogel form was found to be suitable for making material where the dominant phase may be β-spodumene.
2. Destabilization of hydroxy hydrogel network structure was initiated at 400 °C and almost complete rupture occurred at a temperature between 400 and 500 °C.
3. Dehydration and dehydroxylation resulted in a

metastable and reactive structure that favoured β-spodumene formation on heat treatment at 700 °C.

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