

Studies on the Formation of Mullite from Diphasic Al₂O₃-SiO₂ Gel by Fourier Transform Infrared Spectroscopy

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ABSTRACT: Al₂O₃-SiO₂ diphasic gel was synthesized by sol gel route from aluminium nitrate and silicic acid following aqueous phase colloidal interaction. The precursor gel powder was thoroughly characterized by chemical analysis, measurement of surface area and bulk density measurement. The gel powder was further characterized by thermogravimetry, XRD diffraction study of the heat treated samples and Scanning Electron Microscopic (SEM) study of the fractured surfaces of the heat treated compacts. The gel was observed to be a truly di-phasic in nature and was capable of forming nano-structured well distributed mullite phase in the microstructure of the heat treated sample. The gel powder was heated at different temperatures and the formation of Al-O-Si linkage towards the formation of mullite phase (3Al₂O₃, 2SiO₂) was studied by Fourier Transform Infra Red (FT-IR) spectroscopy. The characteristic Al-O-Si linkage was found to develop after 600°C indicating the formation of mullite gel and at 1600°C the linkage became very strong indicating complete crystallization of mullite.

KEY WORDS: Al₂O₃-SiO₂, Diphasic gel, FTIR, Mullite.

INTRODUCTION

Mullite has achieved outstanding importance as an engineering material for several remarkable physico-chemical properties like, low thermal expansion and thermal conductivity, good thermal and chemical

stability, high melting point, low creep rate, reasonable toughness coupled with strength, thermal shock resistance, infrared transparency etc [1-4]. Owing to these important qualities mullite are widely used in the

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production of heat resistant materials in heat insulation, ceramics, composites, computer chips etc. [5,6] Mullite is basically a non-stoichiometric aluminosilicate compound and its molecular formula can be represented as $Al_2[Al_{2+2x}Si_{2-2x}]O_{10-x}$, where x denotes the number of missing oxygen and atoms per unit cell, varying between 0.17 and 0.59 [7]. Mullite is the only stable crystalline phase formed at atmospheric pressure in the alumina-silica system. The synthesis and characterization of mullite, therefore, have drawn lot of attention from material researchers [8,9]. Among different synthesis methods for advanced materials, the sol-gel process has become one of the most attractive fields of research for material engineers. Employing this process highly pure and homogeneous materials can be produced at relatively lower processing temperature [10,11]. Extensive work has been done in the last two decades related to the processing and characterization of sol-gel derived silica-alumina based materials or mullite [12]. It has been reported that mullite formation depends on the type of precursor gel as well as structural changes occurring during heat treatment [13]. The molecular level mixing during sol-gel processing results in the formation of di-phasic gels whereas the atomic level mixing of the precursors leads to mono-phasic gel formation [14,15]. The temperature of mullite formation was reported to be a function of the size of compositional domains in raw materials [16, 17]. Therefore for micrometric domains of silica and alumina, mullite formation can be observed only in temperature as high as 1500°C, while crystallization of mullite is noted near 1300°C for raw materials having alumina and silica nanometric domains. Otherwise, Al and Si atoms molecularly well-distributed can lead to mullite formation in temperatures near 980°C. The sol-gel method was demonstrated to be capable for production of mullite with nanometric phases [18] and also mullite with a very high degree of homogeneity, where the Al and Si atoms are randomly distributed [19].

Different techniques like XRD, HRTEM, ESR, XANES, Al^{27} and Si^{29} MAS NMR spectroscopy, IR etc have been used for the structural evaluation of mullite [20-25]. Characterization of stoichiometric mullite by FTIR spectroscopy indicates that the variation in intensity of the absorption band in 1100-1200 cm^{-1} region provides useful information regarding the formation of mullite [26, 27].

Table 1: Chemical constituents of the ingredients.

Ingredients	SiO ₂	Al ₂ O ₃	Na ₂ O
Sodium silicate	29.75	-	17.41
Aluminium nitrate	-	12.98	-
Batch composition	27	73	-

Although extensive work has been done on the processing and characterization of sol-gel derived materials having final composition within the alumina-silica system, a complete understanding in terms of the relationship between structures and initial variables of the process has not yet been fully achieved for this system. In the present work alumina-silica di-phasic gel was synthesized by sol gel technique. The gel was characterized by thermogravimetric analyses as well as by XRD and SEM analyses of the heat treated samples. The structural change of alumina-silica di-phasic gel system leading to mullite formation as a function of heat treatment has been thoroughly investigated by FTIR spectroscopy.

EXPERIMENTAL SECTION

The alumina-silica hydrogel was synthesized from the starting materials $Al(NO_3)_3 \cdot 9H_2O$ and liquid sodium silicate (Sp. Gr. 1.6 and molar ratio of $Na_2O: SiO_2 = 1:3$) Both the chemicals used were of analar grade and their chemical compositions are given in Table 1. Silicic acid was prepared by ion exchange process from sodium silicate using Dowex-50 cation exchanging resin in a column exchanger. 7% (w/v) sodium silicate solution was used as the feed with a flow rate of 200 mL/min. Silica sol was prepared by ultrasonic dispersion of the generated silicic acid (5%w/v) in aqueous phase. Silica sol was mixed with 10% (w/v) $Al(NO_3)_3 \cdot 9H_2O$ solution stoichiometrically to attain a molar ratio of 3:2 for Al_2O_3 and SiO_2 in the mixture. The pH of the solution was 2. To the mixed solution 1:1 ammonia solution was added slowly with stirring till a neutral pH was attained. The mixed sol was allowed to age to form the gel. The gel was filtered, washed thoroughly, and dried at 80°C for 24 h. The dried gel was heat treated at different elevated temperatures from 200 to 1600°C with 200°C interval. The gel mass was properly pulverized in a pot mill and was characterized by chemical analysis, measurements of surface area and bulk density and the results are given in Table 2. Thermo Gravimetric Analyses (TGA) of the dried

gel was carried out at four different heating rates (ca, 4, 6, 8 and 10°C/min) from room temperature to 600°C with "METTLER TOLEDO SRAR thermal analysis system (Versions 9.10 and 9.20). X-ray diffraction study of the samples were carried out with Rigaku, desk type powder diffractometer with CuK α target. Scanning electron microscopic analyses of the samples were carried out with FEI Quanta -200 MK2 electron microscope. FTIR spectra of the heat treated gels were taken with a Perkin-Elmer apparatus.

RESULTS AND DISCUSSION

Silica sol is positively charged colloid and after generation by ion exchange process, it did not show any tendency of polymerization. When silica sol was mixed with Al(NO₃)₃ solution, the solution became acidic. With the addition of ammonium hydroxide non-simultaneous formation of the gels aluminum hydroxide and polysilicic acid took place and therefore, the formed aluminosilicate gel was di-phasic in nature. In this system discrete aluminum hydroxide gel particles was likely to be distributed uniformly in the high molecular weight polysilicic acid gel network.

The precursor powder is expected to have considerable surface activity as it had a very low bulk density (0.27g/cm³) and a considerably high surface area (70 m²/g). As the hydro-gel contained significant amount of water (33.91%) it was calcined at 800°C to prevent excessive shrinkage during sintering. The composition of the aluminosilicate was intentionally kept slightly in the alumina rich zone of the mullite to minimize the formation of glassy phase after sintering. After synthesis no deviation was observed from the parent batch composition in the synthesized material.

From the thermogravimetric analyses of the sample it was observed that dehydration loss of the samples at two distinct temperature range (Figs. 1 & 2). Major weight change took place at around 250°C and the minor weight change took place at around 450°C as evident from DTGA diagram. The first peak could be assigned to the dehydration of silicic acid gel whereas the second peak could be assigned to the dehydration of aluminium hydroxide gel. It clearly indicated the true di-phasic nature of the gel.

XRD diagram of the heat treated gel has been presented in Fig. 3. It is evident from the diagram that

Table 2: Physicochemical properties of the hydrogel.

Composition	Properties
SiO ₂	17.86
Al ₂ O ₃	48.23
Ignition Loss	33.91
Bulk density (g/cm ³)	0.27
Specific surface area (m ² /g)	70

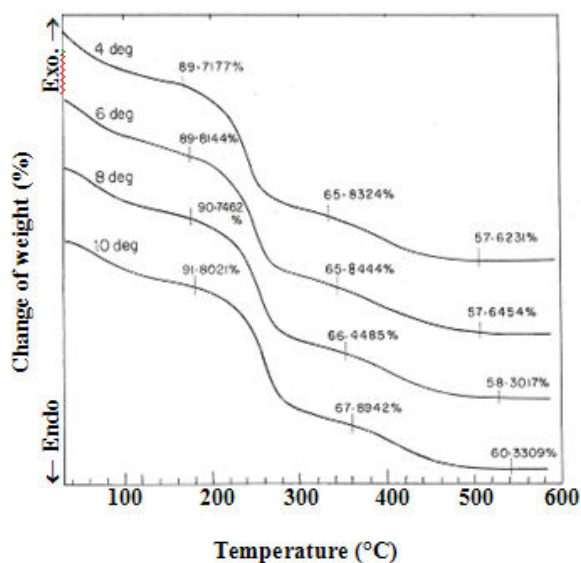


Fig. 1: TGA scan of dried gel at different heating rate from room temperature to 600°C.

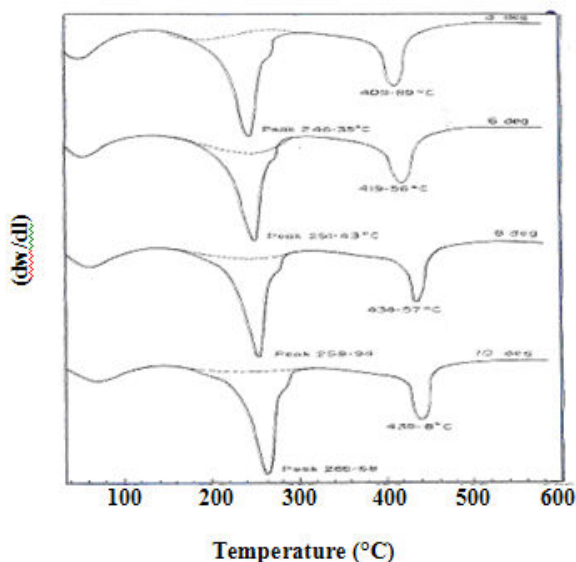


Fig. 2: DTGA scan of dried gel at different heating rate from room temperature to 600°C.

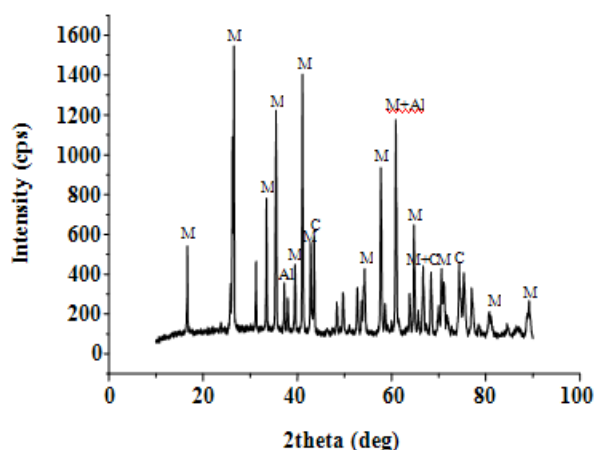


Fig. 3: XRD diagram of heat treated gel at 1600 °C.

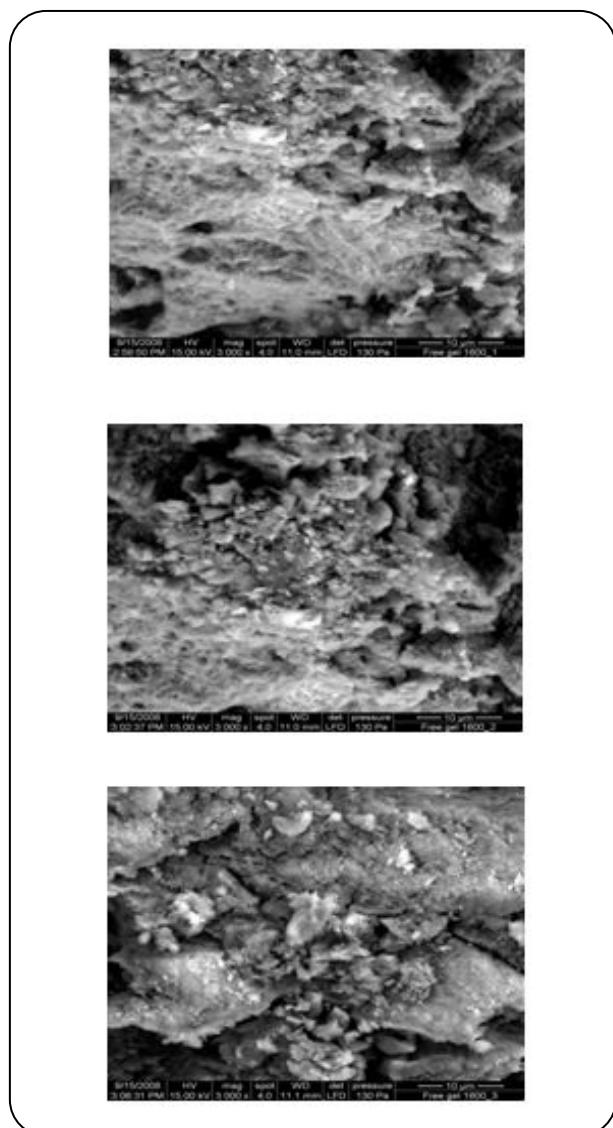


Fig. 4: SEM photomicrographs of heat treated gel at 1600 °C.

the heat treated mass contained mullite as the major crystalline phase. It indicated the activity of the synthesized gel towards stoichiometric solid state reaction as major part of the gel has been converted to the desired solid phase mullite. The minor amount of unreacted silica and alumina were converted to cristobalite and corundum phases after heat treatment. The grain size of the heat treated sample was calculated by using Scherrer's equation, $d = 0.9\lambda/B\cos\theta$, where d is the grain size, λ is the wavelength of the XRD radiation, B is the full width at half maxima (FWHM) of the XRD peak and θ is the diffraction angle of the corresponding peak. The grain size of mullite was observed to be 20 nm in the heat treated sample. It indicated that the synthesized di-phasic gel is capable of developing nano-structured materials.

From the SEM micrographs of the un-etched fractured surfaces of the heat treated compacts at 1600°C (Fig. 4), the needlelike mullite crystals were observed to be well distributed in the microstructure. A minor amount of vitreous phases generated from silica was also observed in the microstructure.

In the FTIR spectra of the gel sample (Fig. 5) the broad hump at 3464cm^{-1} was assigned to the stretching mode of adsorbed water. The corresponding bending mode was observed at 1640cm^{-1} . The precursor gel was prepared under basic conditions where the gelation occurred rapidly. In this system the $\text{Al}(\text{OH})_3$ was precipitated out in colloidal form along with the precipitates of $\text{Si}(\text{OH})_4$ and they grow rapidly side by side without forming aluminosilicate compound. The irregularity in the shape of the band may be related to the randomness in the vibration of different energy bearing -OH groups. The band at 3151cm^{-1} was assigned to the OH^- stretching mode of these hydroxides, particularly Al-OH. Corresponding OH^- bending vibration was observed at 1104cm^{-1} . The presence of the shoulder at 1104cm^{-1} indicated the overlapping of the stretching vibration of Si-O-Si of SiO_4 tetrahedra in the gel structure with the OH^- bending vibration [28]. The corresponding bending mode of Si-O-Si vibration was observed at 477cm^{-1} . As the starting material was $\text{Al}(\text{NO}_3)_3$, the gel contained some traces of NO_3^- ions and the peak at 1388cm^{-1} was assigned to the stretching of the entrapped nitrate ions in the gel structure. The peak at 747cm^{-1} indicates the stretching mode of Al-O-Al linkage [29].

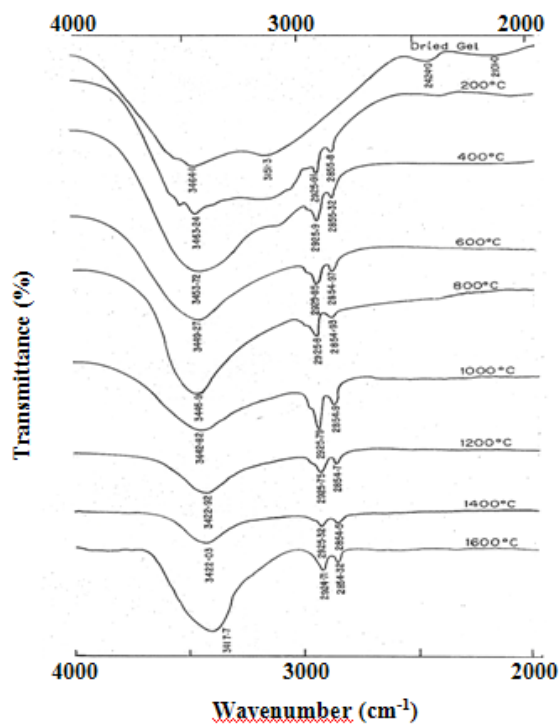


Fig. 5: FTIR spectra of the $\text{Al}_2\text{O}_3\text{-SiO}_2$ gel after heat treating at different temperatures within $2000\text{-}4000\text{cm}^{-1}$.

After heating at 200°C (Fig.6), the peaks at 3151cm^{-1} was shifted to 2926cm^{-1} and a new peak appeared at 2855cm^{-1} . It indicates removal of some water from the gel structure as a result of which the charge density on Al^{3+} increased and the vibration frequency of Al-OH bonds are shifted to the lower wave number. The new peak at 2855cm^{-1} was assigned to Si-OH stretching vibration. The intensity of the stretching vibration of Si-O-Si increased at 1105cm^{-1} as observed from the increase in the peak height. It can be related to the combination of the stretching vibrations of Si-O-Si and Si-O-Al linkages. The corresponding bending vibration intensity was also found to increase. The intensity of Al-O-Al linkage was also found to increase due to the combination of both octahedrally coordinated Al-O and tetrahedrally coordinated Al-O stretching modes. The sharpness of the peak at 1384cm^{-1} was reduced indicating the weakening of the NO_3^- bonds in the gel structure.

After heating at 400°C , the hump at 3453cm^{-1} assumed a more regular shape, indicating a more regularity in the vibration of the -OH groups. It suggested that the energy of the -OH groups assumed some similarity.

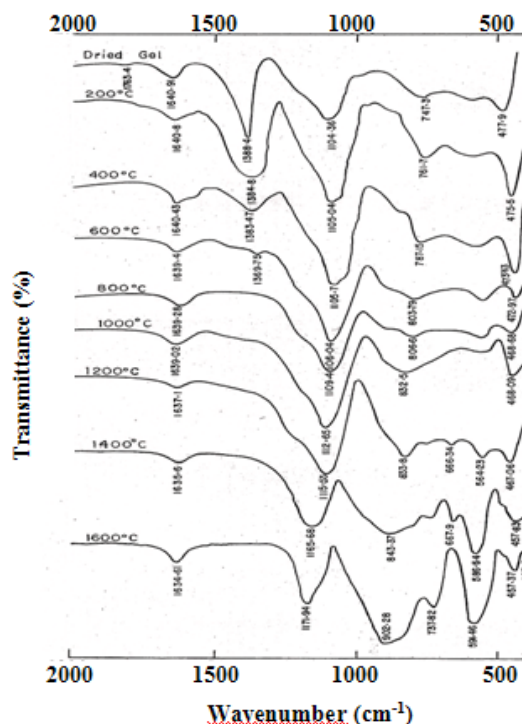


Fig. 6: FTIR spectra of the $\text{Al}_2\text{O}_3\text{-SiO}_2$ gel after heat treating at different temperatures within $400\text{-}2000\text{cm}^{-1}$.

The corresponding bending vibration at 1640cm^{-1} was also more prominent. The band at 1106cm^{-1} became sharper indicating the loss of -OH groups from the gel structure. The Al-O-Al stretching vibration in tetrahedral and octahedral co-ordination at 787cm^{-1} also increased.

After heating at $600\text{-}800^\circ\text{C}$, the major change in the spectra was observed in the shifting of peak at $803\text{-}806\text{cm}^{-1}$ from 787cm^{-1} . It was related to the symmetric stretching vibration of Si-O-Al linkages. It indicated the onset of Al-Si spinel formation in the gel structure.

After heating at 1000°C the peak was shifted to 832cm^{-1} and was converted to a broad shoulder indicating an extensive formation of Al-Si spinel. The vibration at 1112cm^{-1} became sharper due to the anti-symmetric stretching vibrations of Si-O-Si in amorphous silica and Si-O-Al networks. The peaks at 2925cm^{-1} and 2554cm^{-1} progressively became sharper and uniform due to symmetric stretching vibration of Si-O and Al-O in the structure.

After heating at 1200°C the major change in spectral was observed in the appearance of peaks at 564cm^{-1} and

666 cm^{-1} due to the development of stretching mode of Al-O vibration in octahedral coordination. The appearance of multiple peaks in low wave numbers indicated the formation of highly disordered octahedron. The peak at 833 cm^{-1} also became wider indicating formation of more Si-O-Al linkages resulting in the crystallization of more mullite phases.

On further heating to 1400 $^{\circ}\text{C}$ the peak at 843 cm^{-1} became wider indicating an increase in the tetrahedrally coordinated aluminum atom. It suggests the more crystallization of mullite with the formation of more Si-O-Al linkages in the mullite structure [30]. The peak due to stretching vibration of octahedrally coordinated Al at 586 cm^{-1} became sharper indicating the development of Al_2O_3 in the structure.

After heating at 1600 $^{\circ}\text{C}$ the peak due to the vibration of Si-O-Al became wider compared to the peak at 1171 cm^{-1} . It indicates complete crystallization of mullite with less amount of SiO_2 . The peak at 591 cm^{-1} became more prominent indicating the existence of Al_2O_3 and $\text{Al}_2\text{O}_3\text{SiO}_2$ agglomeration in the structure. Crystallization of silica was noticed from the appearance of the peak at 423 cm^{-1} corresponding to Si-O-Si stretching frequency. Crystallization of alumina was also noticed from the peak at 737 cm^{-1} corresponding to Al-O-Al stretching frequency for octahedrally coordinated aluminum.

CONCLUSIONS

Diphasic $\text{Al}_2\text{O}_3\text{-SiO}_2$ gel was generated by sol-gel technique. Thermogravimetric analyses of the gel samples confirmed the formation of two co-existing phases of aluminium hydroxide and silicic acid in the synthesized gel samples. XRD analysis of the gel samples heat treated at elevated temperature indicated the formation of nano-mullite as the major crystalline phase. The mullite phase was also observed to be well distributed in the microstructure from the SEM diagram of the heat treated sample. The gel was further heat treated at different temperatures to study the formation of mullite phase by Fourier transformed infrared spectroscopy. After 600 $^{\circ}\text{C}$ of heating the Si-O-Al bonds started to develop in the structure from the linkage of Al-O tetrahedron with Si-O tetrahedron. The mullite phase started to crystallize after heating at 1200 $^{\circ}\text{C}$ and after heating at 1600 $^{\circ}\text{C}$ complete crystallization of the mullite

phase was noticed with the formation of Al_2O_3 and SiO_2 crystals also separately in the structure.

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