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Reaction study of various mixtures of tetra ethyl ortho silicate and aluminum nitrate

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Abstract Several studies on the formation of amorphous aluminosilicate phase during heating slow hydrolysis (SH) or Type 1 mullite gel prior to formation of 2:1 mullite is briefly reviewed. Tetra ethyl ortho silicate (TEOS) and aluminum nitrate nonahydrate (ANN) are isothermally heated on water bath at 80 °C. It has been shown that these react in an exothermic manner. The resultant isothermally heated gel (ISG) removes organics, moisture on heating and forms alumino silicate (A) precursor phase. Among the various mixtures of the two components, the batch composition corresponds to Al/Si ratio of 3/1 generates highest evolution of heat which suggests that precursor analogous to the composition of 3:2 mullite is most stable. Slow hydrolysis gels of different Al_2O_3:SiO_2 ratios synthesized out of similar sources exhibit 980 °C exotherm on DTA analysis which is a function of Al_2O_3 content. The highest exotherm is observed for the gel/precursor analogous to the same composition of the batch synthesized above by isothermal condition. Corroborating heat evolution behavior of ISG gels with DTA analysis of SH gels, it is suggested that the various compositions of intermediate aluminosilicate (A) phase may form. The composition corresponds to 3:2 mullite may be most stable.

Introduction

In the binary Al_2O_3–SiO_2 phase diagram, mullite of the composition of Al_2O_3:SiO_2 = 3:2 exists as a stable crystalline phase. It has been prepared from different sources of silica and alumina component materials. Roy et al. [1] first used tetra ethyl orthosilicate (TEOS) and aluminum nitrate nonahydrate (ANN) and thereafter these have been widely used till date as an inorganic cum organic source materials for synthesis of mullite precursor via sol–gel route. During the gelation process, TEOS is first hydrolyzed and developed silicic acid gel which physically adsorbed Al^{3+} ions from aluminum nitrate solution in its network. It was presumed that Al^{3+} ions also substituted Si^{4+} ions in the gel structure during both drying and heating process and formed Si–O–Al linkages. The development of such bonds have been investigated and characterized by various instrumental techniques and are briefly described below.

(i) IR studies [2, 3] showed that Si–O stretching vibration for pure silica gel occurred at $\sim 1120\ \text{cm}^{-1}$ and this decreased to $1080\ \text{cm}^{-1}$ in co precipitated gel heated to 900 °C which indicated a considerable effect possibly due to substitution.

(ii) MAS NMR study also showed the formation of aluminosilicate compound during heating mullite. Schneider et al. [4] showed that in the temperature range 600–800 °C, Si NMR of SGM (sol–gel materials) showed symmetrical ^{29}Si resonance at −92 ppm, CM (co-precipitated material) showed an asymmetrical shape of ^{29}Si resonance peak with shoulder towards more negative chemical shift at −95 ppm. Schneider et al. [5] further showed that both NH (no prehydrolysis, Type I) and HB10 (prehydrolysis under basic condition with pH = 13, Type III) samples showed Si resonance at −85 ppm. Both the gels, when heated to 900 °C, showed resonance at −95 ppm. This temperature induced shifting to more negative value was explained by the increase in number of –Si–O–(Si,Al) bridges, corresponding to an increasing degree of

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condensation of the –Si–O–(Si,Al) network. Yoldas [6] in his ^{27}Al MAS NMR spectroscopic studies showed different aluminum environment in polymeric and colloidal gels heated at ~500 °C and suggested two different ultra structures for two gels. Jaymes et al. [7] noted Si peak maxima at ~ -90 ppm for their mullite precursors marked powder A, powder B, powder C and powder E showed the formation of aluminosilicate during heating those gels. Huang et al. [8] also noted two main resonances centered at -81 and -108 ppm with a shoulder at -100 ppm out of two precursors marked M I and M II heated to 450 °C. The resonances were assigned to four aluminum atoms via oxygens Q_o (4Al) sites to Q_4 (0Al) sites. The shoulder at -100 ppm may be due to Q_4 (1Al) environment as discussed earlier by Irwin et al. [9, 10] and Yasumori et al. [11].

(iii) By radial electron distribution (RED) study of silica–alumina gel heated to 500 °C, Leonard et al. [12] determined the kinds of structure and its defects. They showed that aluminum cations substitute silicon cations in the tetrahedral position. This substantiates the view of aluminosilicate formation. They also showed that some of the aluminum cations were presented in perturbed tetrahedral arrangement. This explained the source of acidity of amorphous silicoaluminous phase. Schneider et al. [13] showed that the peak intensities of short distance RDF pattern of Type I precursor appeared different from the silica glass spectrum. Silica glass displayed four strong peaks assigned to T–O(1), T(1)–T(2), T–O(2) and T(1)–T(3). Mullite precursors exhibited some structural difference from silica glass. They suggested that the increase of T–O (1) and T–O(2) distances in mullite precursors were probably due to isomorphous substitution in tetrahedral position by replacing Si for Al. Far-distance ($R > 6$) RDF pattern provided information on higher coordination spheres corresponding to the structural long-range order of the precursor. Type I precursor exhibited RDF bands at 6.5 and 8.7 Å which indicated –Al–O–Si– matrix networks.

(iv) By X-ray fluorescence spectroscopy (XRF) study Leonard et al. [14] gave a clear picture of changes in coordination number of aluminum in amorphous silicoaluminas. According to Colomban [15], spinel and alumina were poor Raman scatterers to exhibit silica spectra. He opined that there was no segregation during the transformation of the gel to orthorhombic mullite. Instead, a progressive ordering at the local scale might be taking place.

(v) By X-ray absorption fine structure spectroscopy (XAFS) Kamijo et al. [16] found that the coordination environment of oxygen around aluminum in the gel dried at 60 °C was 6 and was reduced to ~4 when gel was further heated in the range of 200–800 °C.

(vi) By large angle X-ray scattering (LAXS) study, Okuno et al. [17] drew radial distribution function $D(r)$ and $G(r)$ curves of heat treated Type I precursor at different temperatures and showed some prominent peaks. At the short-range level, i.e., $R < 0.4$, peaks observed at $r = 0.18$ nm and $= 0.32$ nm of $D(r)$ curves were assigned as T–O and T–T distances, where (T = Al, Si). The amplitudes of both peaks increased and their widths decreased with increasing temperature. The $D(r)$ and $G(r)$ curves of the precursor heated at 800 °C were consistent with the RDF of Type I precursor heated to 900 °C. T–O distance alumina rich glass (Al/Si ratio = 1.78) as found by Morikawa et al. [18] was 0.179 nm. In comparison Type I precursor (Al/Si ratio = 3/1) showed T–O distance = 0.174 nm at 800 °C. For T–T distance (middle range order), i.e., $r = 0.32$ nm, peak intensity increased with temperature. This was attributed to increasing network formation by the condensation of –OH groups. The peak shifts indicated to a successive decrease of bridging angles. For T–O(2), i.e., second neighboring oxygen, i.e., at 0.42 nm, peak intensity increased with increasing temp. This provided evidence for a gradual condensation of precursor network.

The above review displays that during the synthesis of mullite TEOS and ANN have been chosen as source material for more than half a century, but no knowledge regarding the nature of the chemical reaction whether it is endothermic or exothermic occurred when these two are reacting during heating in absence of external uses of hydrolyzing water and acid/base as catalyst is available.

All these techniques, e.g., IR, MAS NMR, RED, XRF, XAFS and LAXS clearly demonstrate that monophasic Al_2O_3–SiO_2 gel at the first stage forms amorphous aluminosilicate phase (marked in the present paper as aluminosilicate (A) phase) during heating in the temperature range at ~400 °C (temperature of first dehydroxylation) to before the commencement of 980 °C (the temperature of first exotherm). However, the composition of it is still unknown and it is not elucidated by previous authors.

In the present study following approaches have been made to explain the above two problems.

(i) To ascertain the nature of the reaction, isothermal heating of a reaction couple consisting of TEOS together with ANN has been carried out and changes in the temperature of the reaction bath have been measured.

(ii) To reveal the composition of aluminosilicate (A) phase, supplementary DTA studies of SH gels of differences in Al_2O_3–SiO_2 compositions synthesized as per Okada and Otsuka [19] have been done and corroborated with the above isothermal study.

Experimental procedure

Isothermal heating of various mixtures of TEOS–$Al(NO_3)_3 \cdot 9H_2O$

A constant temperature water bath at 80 ± 2 °C was used in this study. Isothermally heated gels (ISGs) of different SiO_2/Al_2O_3 ratios marked as ISG40 (isothermally heated gel containing approx. 40 wt.% alumina), and similarly ISG65, ISG66, ISG72, ISG76 and ISG80 were synthesized in the present study in the following manner. In case of ISG72, 4 mL of TEOS was taken in a round bottomed flask and was placed into the water bath until it attained the temperature of the bath. To this fixed amount of TEOS, different amount of ANN were added to make ISGs of other SiO_2/Al_2O_3 ratios as shown in Table 1. Weighed amount of ANN crystals were taken in a separate beaker and its temperature was raised gradually up to ~80 °C when the solid melted first into a solution and then it concentrated on continued heating. After attainment of constant temperature, the concentrated ANN solution was added into the flask containing TEOS at the same temperature of ~80 °C. The temperature of the mixed solution was found to rise slowly at the beginning and then it rose rapidly just after swirling the flask with simultaneous effervescence of brown fumes of NO_2. During this heat evolution process, the temperature of the solution was noted at regular interval of time using a thermometer from the beginning of the experiment to the end of it. In case of ISG72 gel, the temperature of the reaction mixture was finally reached to a maximum of 89 °C. Thereafter, it decreased slowly with time until the temperature subsided to ~80 °C. Gelation of the reaction mixtures started in this period. On continued heating, the gel gradually dehydrated and decrepitated inside the flask. The product was collected and stored for X-ray analysis. The experiment was repeated for successive batches. The evolved exothermic energy as a measure of rise in the temperature of reaction batches versus time period is plotted. Resultant gels are heated to 500 °C and are analyzed for phases by XRD.

Table 1 Batch composition of ANN/TEOS taken in isothermal heating process

Gel mark	Approx. wt.% Al_2O_3:SiO_2	Amount of TEOS taken (mL)	Amount of ANN taken (g)
ISG40	40/60	4	5
ISG56	56.25/43.75	4	10
ISG66	66.66/33.33	4	15
ISG72	72/28	4	20
ISG76	76.27/23.72	4	25
ISG80	79.41/20.58	4	30

Synthesis of SH gels and DTA studies

(i) DTA study of pure ANN and a mixture of ANN with TEOS as a paste like mass were done at first by using Shimadzu Thermo Mechanical Analyzer System.[1]

(ii) Mullite gels of different Al_2O_3:SiO_2 ratios marked as SH40 (slow hydrolysis gel containing approx. 40 wt.% alumina), and similarly, SH56, SH72 and SH80 were synthesized as carried out by Okada and Otsuka [19]. Weighed amount of two components as shown in Table 1 were dissolved in absolute alcohol for hydrolysis for 3 h and were subsequently gelled slowly by heating in a thermostatically controlled oven at ~60 °C for 2 weeks. Finally, the gels were dried in an air oven for 7 days at ~120 °C. These dried gels were also analyzed in the same Thermo Mechanical Analyzer System. About 40 mg of α-Al_2O_3 was used as reference material. Powder sample was pressed in another platinum cup to the fullest extent by finger tip instead of usual sample preparation method. The relative advantages of this technique of sample preparation was shown earlier by the present author in case of DTA analysis of powdered kaolinite [20]. Rate of heating was 10 °C/min and the analyses were carried out with highest sensitivity at ~(±25 μv). The SH gel after DTA run up to 1000 °C was analyzed for XRD to identify the phase development during the occurrence of 980 °C exotherm.

Results

Isothermal heating study

During heating TEOS and ANN at constant temperature at ~80 °C in water bath, it is observed that the temperature of the reaction medium increases as well as brown fumes of NO_2 emerges out. The two phenomena, e.g., sudden rise of temperature and vigorous evolution of fumes indicate the occurrence of an exothermic reaction during heating of the two reactants. Figure 1 shows that the temperature of the reaction bath increases with the Al_2O_3/SiO_2 ratio of the ISG gels. With increase of wt.% of Al_2O_3 in the ISG gels under study, the apparent area under the

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[1] DTA Schmadzu Thermo Mechanical Analyzer, DA 30 module.

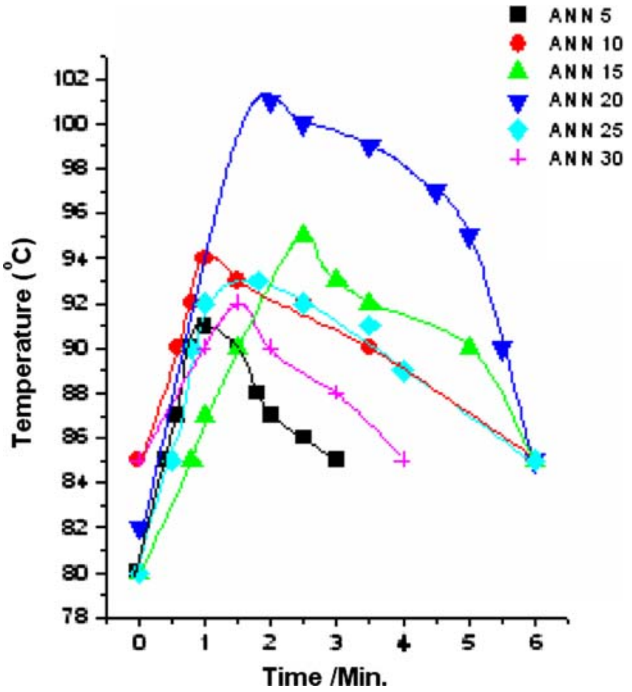


Fig. 1 Time–temperature plot of various mixtures of TEOS-ANN at ~80 °C

time–temperature curve during heat evolution in the temperature range 80–100 °C first increases slowly in ISG40 to ISG56 to ISG66 and then it becomes highest in ISG72. Even with increase of wt.% of Al_2O_3 the said area decreases as noted in the case of ISG76 and it further decreases to ISG80 (Fig. 1).

DTA study

(i) DTA analysis of pure ANN (curve 1) shows a small endotherm at ~95 °C may be due to elimination of free moisture and thereafter a broad endotherm is due to removal of nine molecules of water of crystallization and decomposition of nitrate (Fig. 2).

(ii) DTA run of a mixture of ANN and TEOS in case of ISG72 (curve 2) shows the exhibition of a few exothermic peaks of small in magnitude within the broad endotherm of ANN (Fig. 2). It could also be, and likely to be at least in part, that the released water from ANN is hydrolyzing TEOS to form siloxane.

(iii) Portion of DTA curve for different SH precursors in the vicinity of the first exotherm are shown in Fig. 3. Each of the DTA pattern shows 980 °C exotherm as usual however with different intensity peaks. Significantly, this exotherm begins with an endothermic dip (marked as *D*). This is more marked when DTA analysis was done in high sensitivity scale for SH72 gel as also shown in Fig. 3. Therefore, the nature of the DTA pattern around the exotherm is to be called as endo–exo assembly. Apparently, the present DTA study shows that the geometry of the 980 °C peak

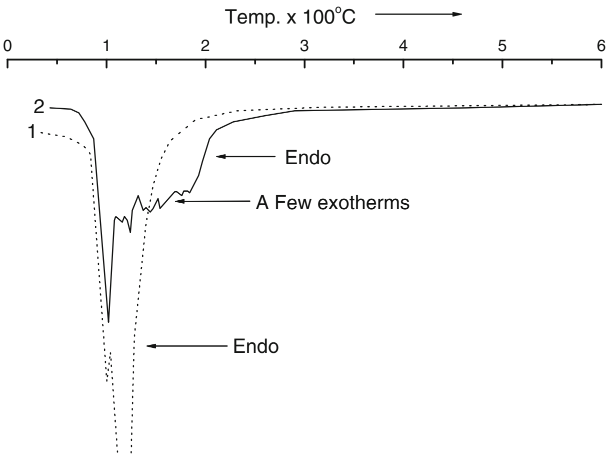


Fig. 2 DTA trace of pure ANN—curve 1, DTA trace of a mixture of ANN and TEOS—curve 2

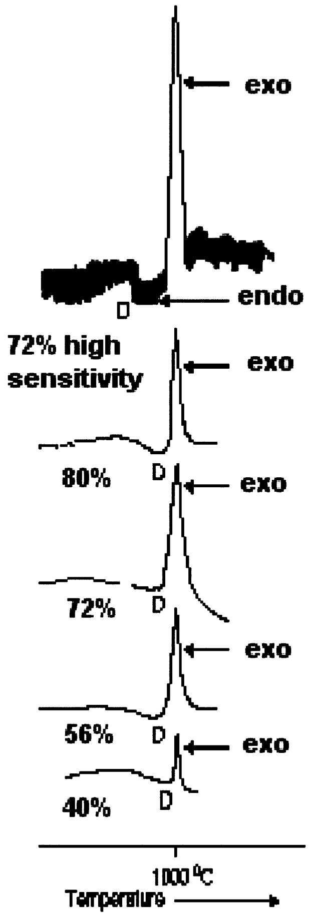


Fig. 3 DTA traces of mullite gels of different alumina content

increases with increase of alumina content from 40 wt.% Al_2O_3 to 56 wt.% Al_2O_3 to 72 wt.% Al_2O_3 of the SH gels and then decreases to SH gel containing 80 wt.% Al_2O_3 gel. Qualitatively, it is found to be maximum for the SH72 gel which corresponds to the composition analogous to the composition of 3:2 mullite.

Phase analysis

All these resultant gels obtained by heating TEOS and ANN isothermally are amorphous. XRD pattern of ISG56 shows two broad amorphous bands at ~10° and at 22° 2θ, respectively (Fig. 4a). On heating to 500 °C, it first eliminates a large portion of organics, water and then transforms to aluminosilicate (A) precursor phase. XRD study of ISG56 heated to 500 °C now shows a single broad band at 22° 2θ (Fig. 4b). XRD analysis of a representative DTA run sample, e.g., SH gel (72 wt.% Al_2O_3) shows weakly crystalline mullite as the major phase and Al–Si spinel as the minor phase (Fig. 5).

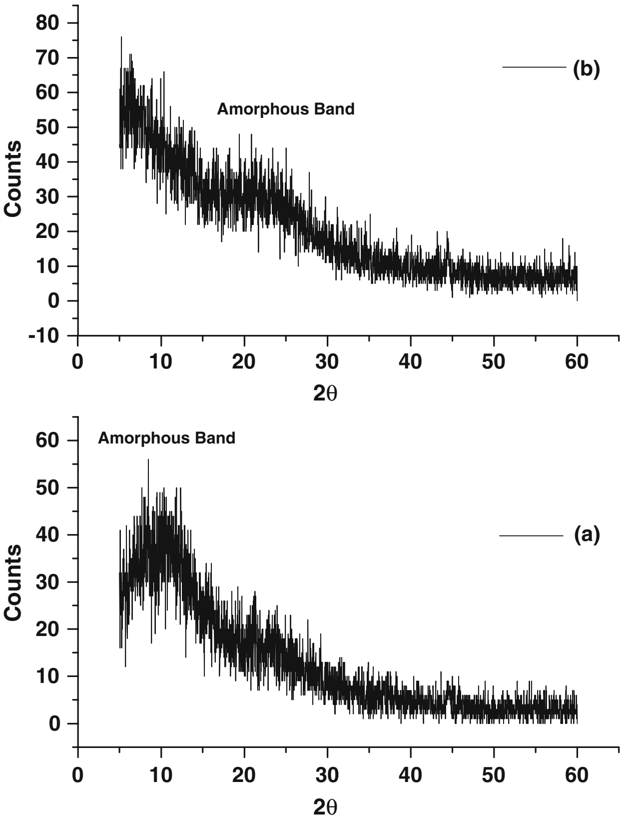


Fig. 4 (**a**) XRD pattern of dried gel obtained after the reaction of gel mark ISG56. (**b**) XRD pattern of precursor obtained after heating ISG56 at 500 °C

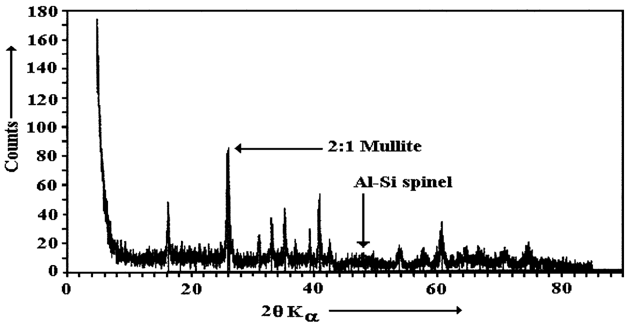


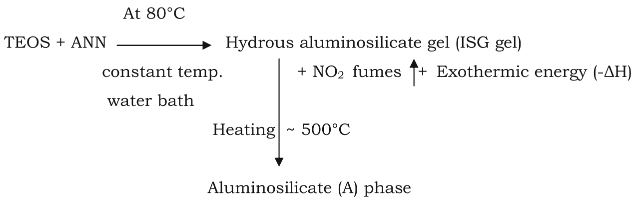
Fig. 5 XRD trace of DTA run sample mark SH gel (~72 wt.% Al_2O_3) up to 1020 °C shows weakly crystalline 2:1 mullite (major) phase and Al–Si spinel as minor phase

Discussion

Nature of the reaction between TEOS and ANN

To understand the course of TEOS and ANN interaction, the mixture of the two components are heat treated at constant temperature water bath at ~80 °C. At the first stage, this reaction couple undergoes heat evolution with the emerge of brown fumes of NO_2 and forms hydrous aluminosilicate gel called as ISG. This physico-chemical behaviors indicate that the components are reacting and the reaction is exothermic in nature. Similar nature of reaction is also ascertained during DTA run of the mixture of two components (curve 2). Exhibition of a few exothermic peaks of small magnitudes when compared with the same for pure ANN (curve 1)indicate the ongoing reaction of the two components with dynamic rise of heating during DTA run.

At the second stage, the ISGs remove volatile combustibles during further heating to 500 °C and forms X-ray amorphous aluminosilicate phase (Fig. 4a,b). A schematic reaction process is given below.



Therefore, evolution of heat as noted during isothermal heating experiment agrees with the exhibition of a few exothermic peaks during DTA study of the mixture of two components. This reaction process definitely suggest formation of binary aluminosilicate (A) phase. As the batch composition of the two components changes (Table 1), it is expected that varying composition of aluminosilicate (A) phase likely develop.

Formation of aluminosilicate (A) phase in SH gels

During synthesis of SH gel, present study shows that at the first step an immiscible solution was noted by adding TEOS in alcoholic mixture of ANN. At the second step, hydrolysis of TEOS occurs over a course of time during warming condition at water bath at ~60 °C. As a result immiscibility disappears, a clear sol is obtained which indicates the ongoing process of hydrolysis. Besides the presence of Al^{3+}, NO_3^-, hydrolysis products of TEOS such as silicon hydroxide monomers, dimmers and other bigger molecules etc. are also evident [21]. The state of solution consists of different polymeric molecules of silicon hydroxides as colloidal silica sols, Al^{3+}, NO_3^- in aqueous state. At the third step, this silica sols set to a transparent glassy like gel at ~60 °C at the water bath condition and is called as SH gel. Therefore, the SH gel behaves as silicon hydroxide network in which both Al^{3+} and NO_3^- radicals, a large amount of water and alcohol are trapped homogeneously in the wet stage. After drying and dehydroxylation of silica gel network during heating, bond generation takes place and leads to develop aluminosilicate (A) phase as per the experimental evidence shown by the present author earlier [22]. It is not probable that SH precursor contains two oxide components mixed in atomic scale as conceived by previous authors. In case of diphasic gel, aluminum component is rapidly precipitated by NH_4OH solution as aluminum hydroxide may be of varying colloidal sizes in which TEOS molecules are trapped. Hydrolysis of TEOS and poly condensation thereafter occur during continued drying at air oven. Dried diphasic gel is a homogeneous mixture of silicon hydroxides and aluminum hydroxides (present as pseudo boehmite) likely in nano scale which on subsequent dehydroxylation during heating beyond 400 °C develops Si–O–Al linkages and also forms aluminosilicate (A) phase [22]. Sacks et al. [23] in their review showed that scale of mixing of the two components in aqueous or alcoholic medium largely influence the phase formation behavior during 980 °C exotherm of two type of mullite precursors. They believed that SH gel and Type 1 mullite precursor are possessing atomic scale mixing, i.e., these precursors have atomic level of homogeneity and as a result it transforms to t-mullite at 980 °C exotherm. Contrary, diphasic gel and RH gel possess nanometer scale (1–100 nm) of homogeneity and as a consequence, these do not exhibit 980 °C exotherm but form transient spinel phase. The later phase transforms to mullite at 1250 °C. Atomic scale mixing of two oxide components may not be the valid concept as discussed above, the reason for the variations in phase evolution behavior and exhibition of 980 °C peak in both cases of SH gel and diphasic gel may be due to some other causes. Yoldas [6] conceived that sol–gel methods likely produce different levels of homogeneity and different type of ultra structure in their pre-ceramic gels. However, he is of the opinion that when soluble salt such ANN was used, a high degree of homogeneity may be obtained but without any network connectivity. Jaymes et al. [24] filtered and subsequently washed the weak gel obtained after hydrolysis of TEOS in presence of ANN. Energy dispersive X-ray spectroscopy (EDS) study showed the presence of silicon in dried gel and presence of aluminum in the dried filtrate. They concluded that no reaction was occurred between silicic gel and aluminum nitrate solution. According to latest literature by Schmuecker and Schneider [25], information on the gelation process of Al_2O_3–SiO_2 are very little. However, both present study and earlier studies [2–18] showed that this SH gel forms aluminosilicate (A) phase on heating. As like as in SH gel, even in the case of diphasic gel, the intermediate amorphous phase formed during heating above 400 °C and it was concluded by the present author that it is a compound instead of free mixture of two oxides [22, 26]. It was shown that gehlenite was formed when dried SH gels were heat treated with $CaCO_3$. If intimate mixture concept is valid, it would crystallize to calcium aluminate (CA) rather than gehlenite. The experimental evidence on the phase transformation studies of dried and heat treated both SH and diphasic gels during heating with $CaCO_3$ at ~1000 °C absolutely confirm the presence of connectivity between two component oxides whether it is an aluminosilicate gel as occur in case of drying SH gel or a homogeneous mixture of oxides in nanometer scale formed during heating diphasic gel heated >400 °C. It was demonstrated further that differences in phase evolution behavior and exhibition of 980 °C exotherm between two types of mullite gels suggest us to believe that internal structure of intermediate aluminosilicate (A) phase formed in two cases may be different. Question is: when linkage between Si and Al actually starts during heating precursors? Fukuoka et al. [27] indicated a relationship between removal of NO_3 groups with formation of Si–O–Al bonds. They showed that the above bond is not formed in the sol or in wet gel state. It is formed during drying of the wet gel. It was shown by IR spectra that intensity of NO_3 group occurs at ~1380 cm^{-1} decreases slowly during heating from 200 to 300 °C and is completed eliminated at 400 °C. More extensive observation is noted by Li and Thomson [28]. They showed that bands due to NO_3 group situated at 1650 cm^{-1}, 1380 cm^{-1} in IR spectra of single phase gel are removed gradually during heating it from 25 to 300° and at 500 °C. This result indicates that Si–O–Al bond formation increases with increase of heating temperature of single phase gel followed by the removal of NO_3 groups. Therefore, NO_3 groups are not present in SH gel network in free state. Aluminum nitrate does not crystallize even when gel is dried. Retention of NO_3 groups to a temperature as high as 500 °C indicates that a weak bond likely develops during gelation process of hydrolysed silicon hydroxide sol containing both Al^{3+} and NO_3^-. To generate some kinds of weak bonding between silicon hydroxide with Al^{3+} a long heating as long as 2 weeks is required at ~60 °C during the synthesis of single phase gel. During the course of heating SH gel between 400 and ~900 °C, dehydration, subsequent condensation of gel network and finally interaction leads to the Si–O–Al bonds formation with elimination of nitrous gases. However, Li and Thomson (28) showed that the single phase gel appeared amorphous until mullite formation begins. In a sharp contrast to our finding of bond development between two constituents, they conjectured that amorphous phase consists of mixtures amorphous Al_2O_3 and amorphous SiO_2 and believed in the hypothesis of intimate mixture. Accordingly, they further expressed the mullite formation reaction as the recombination of those two phases at >940 °C. However, they did not explain why these two reactants reacted sharply and completed at the said temperature of exotherm itself.

As like as in ISG gels, present study suggests that formation of the aluminosilicate (A) phase also occurs during heating Type 1 or SH mullite gel in the temperature range 150° to ~900 °C as shown earlier by IR, MAS NMR, RED, XRF, XAFS and LAXS studies [3–16]. Present study suggests that Si–O–Al bond formation influences crystallization of aluminosilicate (A) phase to 2:1 mullite of large XRD intensity (Fig. 5).

Composition of aluminosilicate (A) phases

Apparent increment in temperature (area under the time–temperature curve) is noted during isothermal heating of all cases of TEOS/ANN mixture (Fig. 1). It increases from batch composition marked ISG40 to ISG56 to ISG66 to ISG72 and thereafter it decreases to ISG76 and lastly to ISG79. The rise in temperature in isothermal reaction condition of TEOS and ANN mixture is found to be related to alumina content of the batch. The maximum or highest rise in temperature is found for the synthesis of gel of composition corresponding to Al/Si ratio = 3/1, i.e., for the case of ISG72. The maximum heat evolution data draw two findings. (i) Interaction between TEOS with melted aluminum nitrate crystals occurs for the batch composition marked ISG72 having Al_2O_3/SiO_2 ratio around 3:2 mullite approximately is most intense. (ii) The resultant product of interaction will be most stable. Thus, it is conjectured that several compositions of aluminosilicate phase (A) may form during heating ISG gels of varying compositions at ~500 °C (Table 1). Among these, the aluminosilicate (A) precursor of the composition analogous to 3:2 mullite is probably most stable.

In case of DTA study of various compositions of SH gels, the present study also shows that geometry of the 980 °C exothem increases with increase of wt. (%) alumina content (Fig. 3). It is found to be maximum for the gel containing 72 wt.% alumina. Therefore, it is interpreted that SH gel of 3:2 mullite composition forms aluminosilicate (A) phase of similar composition and which crystallizes to t-mullite on heating at 980 °C exotherm.

Thus, highest heat evolution data in case of isothermally heated batch composition (ISG72) concur with DTA studies of SH72 gel. As both of them are 3:2 mullite like composition, aluminosilicate (A) phase would also be similar in composition.

In mullite literature, a varying inter-relationship between height of 980 °C peak of Al_2O_3–SiO_2 gel with its alumina content is found to exist. It requires discussion in context of present conclusion. On careful observation it is revealed that such deviations are related to various causes as outlined below

(i) Gealtion time

Using the same source of starting materials, e.g., TEOS and ANN, variation of height of 980 °C exothermic peak was due to the weight ratio of aluminum nitrate to ethanol (N/E ratio) used during synthesis process [29, 30]. According to Li and Thomson [28], the sharpness and intensity of a DTA peak only measures how fast a reaction rate rises and falls, and gives no indication of the extent of conversion. These authors and Hoffman et al. [29] pointed out the dependence of the 980 °C exothermic peak intensities on gelation time, i.e., indirectly on the gel volume. Intensity of this exothermic peak decreases with increase of amount of ethanol used during gelation process. Enthalpy of crystallization of 3:1 mullite gel was calculated from DTA peak area and it was found to be 85 J/g.

(ii) Choice of components

Horte and Wiegmann [31] showed the occurrence of highest exotherm noted in gel corresponded to sillimanite composition. On the other hand, first exotherm of highest magnitude was shown by Demediuk and Cole [32] for the composition corresponding to 3:2 mullite.

Taylor and Holland [33] used TEOS and aluminum isopropoxide in presence of butan-1-ol and isopropyl alcohol, i.e., in water free approach. They showed the change in the shape of the exothermic peak observed at 980 °C is related to the homogeneity coefficient, i.e., intensity of reflection from (331) plane of mullite (P_m) to (440) plane of spinel (P_s) of the gel.

Sales and Alarcon [34] synthesized three mullite gels with Al/Si atomic ratios of 2:3, 3:1 and 9:1 out of same source of starting chemicals, e.g., TEOS and aluminum ethoxide. Unlike to the present study, DTA study showed that the intensity of exothermic peak increased only slightly from gel of composition containing 36 wt.%

alumina to gel of 72 wt.% alumina and again it decreased abruptly to gel containing 82% alumina. XRD analysis of former two gels after the exothermic peak indicated the formation of mullite only whereas in later case it forms both mullite and γ-alumina.

(iii) Hydrolysis conditions

Jaymes et al. [7] synthesized five mullite precursors by changing both use of source of component and with variation of hydrolysis conditions. They measured the enthalpy of crystallization by DSC experiments. They showed a large variation in enthalpy 169 to 310 J/g and this is related to character of the basic gel whether it is monophasic or diphasic and method of preparation conditions.

However, using the same source of component, the result of present study agrees with earlier study by Okada and Otsuka [19]. They used TEOS and ANN and showed that exothermic peak was sharpest and highest at the composition $2SiO_2 \cdot 3Al_2O_3$. It was diffused and weakened as the composition deviated from it. XRD showed formation of only mullite when fired just above the temperature of exothermic peak. SH gels richer in alumina than $3Al_2O_32SiO_2$ showed reflections of both mullite and spinel phase.

(iv) Method of synthesis

Douy [35] synthesized spray dried precursors in the entire range of composition of Al_2O_3–SiO_2 system out of TEOS and ANN by usual procedure. During DSC experimentations, he observed that quantitative enthalpy value for crystallization is maximum for a narrow range of composition from 60 to 80 mole% (72–85 wt.%) Al_2O_3. In the present qualitative study, highest exothermic enthalpy value is shown for 60 mole% (72 wt.%) alumina of SH gel during DTA study and also for similar composition obtained out of TEOS–ANN mixture in isothermal heating study. This value lies in the above range and confirms the quantitative enthalpy value shown earlier by Douy [35]. Therefore, the conclusion that the composition of intermediate aluminosilicate (A) phase analogous to that of 3:2 mullite may hold true.

Conclusions

The following conclusions have been drawn in the present study.

1. Various mixtures of TEOS and ANN react vigorously at ~80 °C at water bath in isothermal condition with evolution of exothermic energy as heat and subsequently form aluminosilicate (A) phase on further heating. Maximum heat evolution occurs in mixture marked ISG72 which corresponds to the composition of 3:2 mullite.
2. Slow hydrolysis gels also form intermediate aluminosilicate (A) phases during heating in the temperature range 400 to ~900 °C other than present as an intimate mixture of amorphous silicon and aluminum oxides. These phases exhibit 980 °C exotherm during DTA study. The peak height is a function of the alumina content of the respective gels and it is maximum for the gel of composition of Al/Si = 3/1.

Thus, the maximum heat evolution data of isothermally heated mixture is analogous to DTA observation of SH gel of 3:2 mullite like composition. The corroborative studies postulate that the composition of aluminosilicate (A) phase analogous the composition of mullite is most stable.

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