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Al–Si spinel phase formation in diphasic mullite gels

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Abstract

Diphasic aluminosilicate gels of varying Al_2O_3:SiO_2 ratios were synthesized out of TEOS and ANN in basic condition, heated to different temperatures and finally analyzed for phases. All gels precalcined to ~1000 °C were further calcined after mixing with $CaCO_3$ and analyzed by XRD. XRD intensity of (440) of intermediate spinel phase formed during mullite formation was recorded. It has been shown that the XRD intensity of spinel phase to calcium fluoride is in excess of what is possible if the spinel phase is simply γ-Al_2O_3. This substantiates the view of silicon-incorporation in spinel lattice. This view is verified and extended by the further study of phase development on heating spinel-generated samples with $CaCO_3$. Gehlenite forms in Si-rich gels up to approximately 3:2 mullite composition whereas in more Al-rich gels additional calcium aluminate phases are formed.

Keywords: Al–Si spinel; Phase formation; Mullite gels

1. Introduction

In diphasic gel systems, the nature of the spinel phase prepared under different sets of conditions e.g., pH, water/alcohol mixture using different components of SiO_2 and Al_2O_3 namely boehmite sol, peptized alumina, TEOS, Ludox, fume silica etc. is still a subject of much interest. DTA analysis of diphasic gel exhibits an exothermic peak at ~1300 °C [1,2]. Sequential phase transformation study by XRD technique showed the disappearance of so called γ- or δ-Al_2O_3 peaks with evolution of sharp XRD peaks of mullite at the temperature of exotherm [3–11].

Simply, on the basis of DTA analysis and qualitative identification of spinel phase by X-ray diffractometry, researchers [1–15] believe the solid state reaction between γ- or δ-Al_2O_3 with SiO_2 to be responsible for mullite development in the diphasic gel system. Concerning the mullitization behavior it was noted that growth of mullite in the diphasic gel system was sigmoidal in nature [16]. On the other hand, it was reported to be a parabolic growth curve for oxide mixture [17]. Thus, the course of mullitization in two cases are dissimilar. However, all these mullite formation reactions e.g., from oxide mixture [4], alumina–silica compact [18,19] and diphasic xerogel are diffusion controlled [16].

These results suggest that mullitization in oxide mixtures and in diphasic gels is different. The reason may be either small sizes of the constituent oxide particles are different and lead to different reactivity in solid state diffusion processes or due to incorporation of some silica in γ-Al_2O_3 phase forming Al–Si spinel prior to mullite formation process. Researchers tried to ascertain the content of silicon in γ-Al_2O_3 structure [20,21] by quantitative X-ray diffraction analysis. The following evidence indicates that spinel phase may contain silica: (i) Retardation of the crystallization of alumina polymorphs [16, 22], (ii) inhibition of nucleation and crystallization of θ-, κ-, α-Al_2O_3, (iii) change in crystallization temperature of corundum in some cases. It is well known that X-ray/electron diffraction data are incapable of distinguishing pure γ-Al_2O_3 from Al–Si spinel because of the proximity of their atomic sizes and as a consequence they have nearly identical crystal structure and close lattice parameters.

Experimental evidences in favor of γ- or δ-Al_2O_3 are insignificant. Only with IR study slight differences in absorption peaks are observed. Yamada and Kimura [23] showed by IR technique that the absorption band due to Si–O stretching in the case of pure silica shifts

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from 1120 to 1080 cm^{-1} in heated coprecipitated gel. Substitution of Al^{+3} for Si^{+4} considerably lowers the stretching frequency. This substantiates Al–Si spinel theory. By similar IR spectroscopic study, Okada et al. [24] also conjectured that substitution of SiO_2 by Al_2O_3 in spinel structure is plausible. By IR Study, Hirata et al. [5] and subsequently Sales and Alarcon [25] established a direct confirmatory proof in support of the presence of Si in the spinel lattice. The latter authors showed that IR spectrums of gels heated to 1000 °C are different for three classes of gels synthesized. The IR bend at 1020 cm^{-1} arises by the introduction of Al^{+3} into the silica network. Low and McPherson [26] noted from IR study that spectrum of cubic phases obtained from mullite and alumina gels treated at 1000 and 900 °C show dissimilarity of Al–Si spinel from γ-Al_2O_3 in relation to their bond strength and their composition. Obviously the spectra are not identical. Absorption bands due to AlO_4 tetrahedra are observed to exist in both the cubic phases. By EDS study Schneider et al. [27] tried to analyze this spinel phase and reported that incorporation of Si into γ-Al_2O_3 is feasible and maximum amount of silica introduced would be 18 mol% at 1150 °C and also showed that Si incorporation depended on heat treatment temperature.

The purpose of the present investigation is: First, qualitative identification of bonded silica present in diphasic gels heated to ~1000 °C by comparing the intensities of spinel phases formed to the bulk composition of the gels so as to derive the nature of the intermediary spinel phase, Second purpose is to assess the probable composition of spinel phase by performing a solid state reaction study of preheated gels with $CaCO_3$ using X-ray technique.

2. Experimental

2.1. Get preparation

Diphasic gels of different SiO_2/Al_2O_3 ratios marked as DG40 (diphasic gel containing 40% alumina), similarly DG44, DG67, DG72, DG76, DG80 and DG85 were synthesized by using aluminium nitrate nonahydrate (A.R) and tetra ethyl orthosilicate (BDH). Weighed quantities of components of each gel were taken in a Pyrex beaker. To it, 50 ml double distilled water and 10 ml ethyl alcohol were added and warmed to 60 °C with constant swirling till aluminium nitrate went into solution and alcoholic layer disappeared. Ammonium hydroxide (1:10) dilution was added dropwise, stirred vigorously and finally pH was adjusted to 9. The content of the beaker was finally dried at 120 °C.

2.2. Heat treatment

All the samples were heat treated to different temperatures for 2 h soaking in each case, cooled, ground and stored for further experimentation and analysis. Gel samples preheated to 1000 °C/2 h to generate the spinel phase were mixed with calcium carbonate (in the ratio of 1:1 by wt.) and further heated to 1200 °C/h, cooled, ground and stored.

2.3. Qualitative X-ray analysis

All heat-treated diphasic gels and $CaCO_3$ pretreated spinel samples of different compositions heated to 1200 °C were analyzed by XRD to note the phase development.

2.4. QXRD of spinel phase

Semi quantitative estimates of spinel phase were made using the procedure of earlier researchers [16,20]. Spinel samples developed during heating various diphasic gels were mixed with 10 wt.% CaF_2 and ground for 1 h with alcohol and dried. XRD intensities of 0.139 nm peak of Al–Si spinel and 0.164 nm peak of CaF_2 were scanned. Areas under the peaks were measured by planimeter after choosing the background. An average of five such measurements were made for each composition. Ratio of X-ray intensity (peak area) of spinel to CaF_2 was plotted vs. wt.% of Al_2O_3. To compare these data, a pure form of γ-Al_2O_3 was synthesized on heating extra pure ANN at 850 °C/2 h upon a platinum dish followed by X-ray characterization to ensure the maximum formation of γ-Al_2O_3. It was diluted with glass to obtain desired percentages of mixtures. To these mixtures, CaF_2 was added as in the above case and X-ray recordings were made. X-ray intensity of γ-Al_2O_3 to that of CaF_2 vs. % Al_2O_3 was plotted in the same figure and noted as theoretical curve.

3. Results

Phase formation in heated diphasic gels monitored by X-ray are summarized in Table 1. Diphasic gels of different compositions show boehmite as one of the crystalline constituents in association with an amorphous band at ~22° 2θ in X-ray diffractogram indicating the presence of amorphous silica recognizing two phase system. At the first stage of transformation during heating, all these gels form spinel phase/phases. This phase is found up to ~1100 °C. At the second stage, gels starting from DG40 up to DG72 develop mullite only. In addition to mullite, DG76 and DG80 develop some θ- and δ-Al_2O_3 as additional phase/phases. At the third stage, mullite is the predominant phase developed in all gels. Diphasic gel containing silica more than 3:2 composition e.g. DG40 forms cristobalite and the gel containing alumina more than 3:2 composition e.g. DG85 forms corundum as extra phase besides the usual mullite.

Ratio of X-ray intensity (440) reflection of spinel phase to that of calcium fluoride vs. wt.% of Al_2O_3 is

Table 1
Phase formations in heated diphasic gels

Gel mark	Raw gel	Phases identified on heating to increasing temperatures (°C)						
		900	1000	1100	1200	1300	1400	1600
DG40	B0	Sp	Sp	Sp	Mu	Mu + Cr	Mu + Cr	Mu
DG44	B0	Sp	Sp	Sp	Mu	Mu + Cr	Mu	Mu
DG67	B0	Sp	Sp	Sp	Mu	Mu	Mu	Mu
DG72	B0	Sp	Sp	Sp	Mu	Mu	Mu	Mu
DG76	B0	Sp	Sp	Sp	Mu + θ-Al_2O_3 + δ-Al_2O_3	Mu + θ-Al_2O_3 + α-Al_2O_3	Mu	Mu
DG80	B0	Sp	Sp	Sp	Mu + θ-Al_2O_3	Mu + θ- and α-Al_2O_3	Mu	Mu
DG85	B0	Sp	Sp	Sp + θ-Al_2O_3	Sp + θ-Al_2O_3	Mu + θ-Al_2O_3 + α- Al_2O_3	Mu + α- Al_2O_3	Mu + α- Al_2O_3

Bo—boehmite; Sp—spinel phase; Mu—mullite; Cr—cristobalite.

linear and is shown in Fig. 1. A similar nature of curve is obtained when (400) reflection of spinel is taken for study. If the alumina component of the diphasic gels crystallizes theoretically to γ-Al_2O_3 then two curves should superimpose. On the other hand the calculated curve would lie below the theoretical curve when some quantity of aluminosilicate glassy phase is generated. These two observations are not noted, on the contrary is observed. XRD patterns of heated $CaCO_3$ pretreated samples are shown in Fig. 2a–d. Results of X-ray analysis of reheating $CaCO_3$ treated products of different diphasic gels are summarized in Table 2. XRD shows the usual formation of spinel phase during heating DG72 at 1000 °C. On further heating of this spinel-derived sample to 1200 °C by admixing with $CaCO_3$ develops gehlenite and anorthite (Fig. 2a). On the contrary, an artificial amorphous mixture of silica, alumina (in the ratio of 3:2 mullite) and calcium carbonate as above on heating to 1200 °C develops calcium silicate, calcium aluminate and free corundum and no compounds bearing calcium oxide–aluminium oxide–silicon oxide (Fig. 2b). When raw diphasic gel DG72 was heated to the same temperature and treated similarly with $CaCO_3$ it did not develop any calcium aluminosilicate compound and formed only calcium aluminates (Fig. 2c). Formation of calcium aluminosilicate phase or phases like gehlenite or anorthite indicates that heated DG72 sample which contains only spinel as a single constituent is an aluminosilicate other than pure γ-Al_2O_3. In the case of DG85 a fraction of γ-Al_2O_3 forms in addition to the usual spinel phase since it develops corundum at a latter stage of heating.

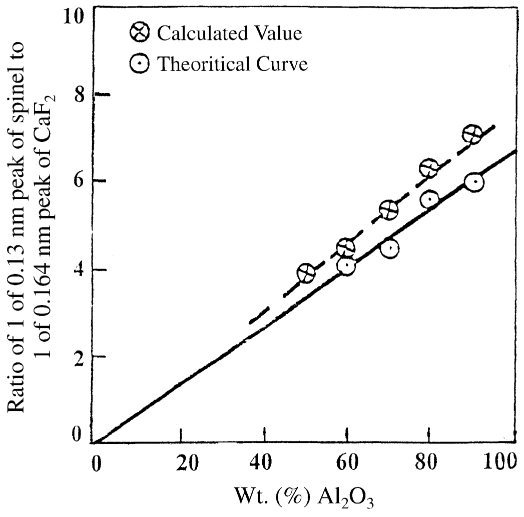

Fig. 1. Relation between the intensity ratio of 0.139 nm peak of spinel phase to 0.164 nm peak of CaF_2 to bulk composition of starting material.

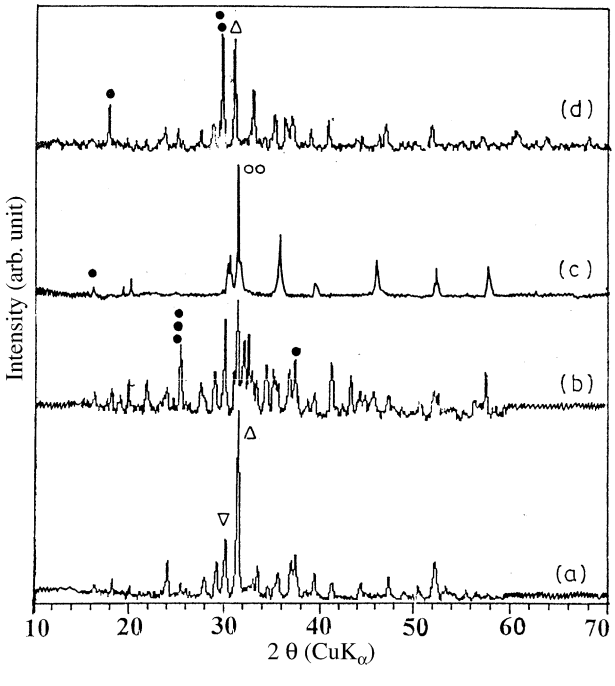

Fig. 2. (a) XRD pattern of diphasic get DG72 to 1000 °C, then treated with CaO and reheated to 1200 °C showing C_2AS (gehlenite, △) and CAS (anorthite); (b) XRD pattern of mechanical mixture of amorphous silica, alumina and CaO heated to 1200 °C showing β-C_2S (dicalcium silicate) + C_3A (tricalcium aluminate, ○○) + Al_2O_3 (corundum, ●●●); (c) XRD pattern of raw diphasic gel DG72 treated with CaO and heated to 1200 °C showing $C_3A + C_{12}A_7$ (12-calcium–7-aluminate, ●); (d) XRD pattern of diphasic gel DG85 to 1000 °C, then treated with CaO and reheated to 1200 °C showing gehlenite, anorthite, calcium aluminate (CA, ●●) and $C_{12}A_7$.

Furthermore it shows development of some calcium aluminate phases in addition to gehlenite (Fig. 2d).

4. Discussion

4.1. Phase transformation sequences

XRD results (Table 1) clearly show three distinct cases of phase transformations behavior of diphasic gels of varying compositions. First one is 3:2 composition of mullite, where mullite is the only crystalline phase to occur in this case >1200 °C. Diphasic gels below this composition i.e. richer in silica show cristobalite in addition to usual mullite on heating at a temperature >1200 °C. Finally, gel above the composition of mullite, richer in alumina, show corundum in addition to mullite. These results are in accordance with the predicted phase formation for compositions in Al_2O_3–SiO_2 phase diagram.

4.1.1. Characterization of spinel phase

In the formation process of mullite out of diphasic "in situ" gel system, spinel forms as an intermediary phase. XRD intensity ratio of (440) reflection of spinel to (311) reflection of CaF_2 shows a linear relationship with the composition of the gel. This curve lies above the theoretically expected curve for γ-Al_2O_3 formation (Fig. 1). This observation definitely indicates that Si has entered into the γ-Al_2O_3 spinel lattice. Higher XRD intensities are observed for each case of diphasic gels in comparison to the amount of alumina taken during getation processes or theoretically expected intensities for γ-Al_2O_3 crystallization.

This figure is compared with that of Fig. 3 of Okada et al. [20] and Fig. 7 of Wei and Halloran [16]. Okada et al. [20] noted similar straight line relationship with the bulk composition of different Al_2O_3–SiO_2 gels. But they did not compare it with theoretical values for γ-Al_2O_3 formation out of those gels. According to them, the amount of spinel phase would be maximum where the composition of the spinel phase coincided with that of starting material. With this concept, they noted maximum X-ray intensity for the composition $SiO_2 \cdot 6\ Al_2O_3$ which corresponded to ~ 8 wt.% SiO_2 for monophasic gel marked SH and for RH gel too. From the present study, it is not likely to conclude that composition of spinel phase coincides with the bulk composition. Exhibition of higher X-ray intensity value for each composition indicates that there is a good possibility of substitution of Al by Si in the spinel structure. Secondly gels of high alumina composition show θ- and κ-polymorphs of Al_2O_3 besides some γ- or δ-Al_2O_3 phases and Si-bearing spinel. As a consequence, there is every possibility of showing reduced X-ray intensity of 0.139 nm peak.

The observed high intensity values of the 0.139 nm peak of spinel phase for each type of diphasic gel indicate that amorphous alumina formed just after the

Table 2
Summary of phases developed on heating diphasic gels first heated to 1000 °C and then treated with CaO and finally reheated to 1200 °C

Sample characteristic	Phases formed
DG40 heated to 1000 °C/2 h, mixed with CaO in the wt. ratio of 1:1 and reheated to 1200 °C/2 h	Gehlenite (C_2AS)
DG44 heated to 1000 °C/2 h, mixed with CaO in the wt. ratio of 1:1 and reheated to 1200 °C/2 h	Gehlenite (C_2AS)
DG67 heated to 1000 °C/2 h, mixed with CaO in the wt. ratio of 1:1 and reheated to 1200 °C/2 h	Gehlenite (C_2AS)
DG72 heated to 1000 °C/2 h, mixed with CaO in the wt. ratio of 1:1 and reheated to 1200 °C/2 h	Gehlenite (C_2AS)
DG76 heated to 1000 °C/2 h, mixed with CaO in the wt. ratio of 1:1 and reheated to 1200 °C/2 h	Gehlenite (C_2AS) + anorthite (CAS_2) + calcium aluminate (CA) + 12-calcium–7-aluminate ($C_{12}A_7$)
DG80 heated to 1000 °C/2 h, mixed with CaO in the wt. ratio of 1:1 and reheated to 1200 °C/2 h	Gehlenite (C_2AS) + anorthite (CAS_2) + calcium aluminate (CA) + 12-calcium–7-aluminate ($C_{12}A_7$)
DG85 heated to 1000 °C/2 h, mixed with CaO in the wt. ratio of 1:1 and reheated to 1200 °C/2 h	Gehlenite (C_2AS) + anorthite (CAS_2) + calcium aluminate (CA) + 12-calcium–7-aluminate ($C_{12}A_7$)
Mechanical mixture of [silica gel, Al_2O_3 (amorph) in the wt. ratio of 2:3] and CaO further heated to 1200 °C/2 h	Dicalcium silicate (β-C_2S) + α-Al_2O_3 + tricalcium aluminate (C_3A)
Raw DG72 mixed with CaO in the wt. ratio of 1:1 and heated to 1200°/2 h	Tricalcium aluminate (C_3A) + 12-calcium–7-aluminate ($C_{12}A_7$)

dehydration of boehmite in the temperature of 400–500 °C reacted with amorphous silica formed out of dehydroxylation of silica gel. This solid state reaction continues with increase of temperature and crystallizes as spinel phase. XRD intensities of it increase with rise of temperature from 900 to 1100 °C and on continued heating to 1200 °C the spinel phase starts transforming to mullite. Observed high X-ray intensity value of spinel phase noted for each composition of gel in the present study is unlike the estimated data of spinel derived out of heating diphasic get as shown by Wel and Halloran [16] in their Fig. 7. They said that diphasic gel ($Si/Al=1/3$) formed γ-Al_2O_3 in the intermediate stage and it did not change and remained constant value ~72 wt.% prior to mullitization. However, on careful scrutiny of their spinel formation curve, a higher quantity of so called γ-Al_2O_3 would actually be shown if their Fig. 7 is carefully redrawn by joining the mid points of the estimated quantity of spinel formed out of diphasic gel heated to different time/temperature schedule. On the contrary, they simply drew a dotted straight line through 72 wt.% Al_2O_3 only and concluded that the amount of spinel did not change on heat treatment of diphasic gel. Therefore, spinel phase which is formed as an intermediary in the present study is more likely Al–Si spinel.

4.1.2. *Composition of spinel phase*

Regarding the composition of spinel phase, the program of reheating diphasic gels of varying compositions heated to 1000 °C with calcium carbonate has led to a definite indication and is given below.

Nature of spinel phase whether it is simple γ-Al_2O_3 or Al–Si spinel and its composition are one of the well-debated subjects in mullite literature. The present study shows that solid state reactions take place when spinel phase is heated with $CaCO_3$. When the product is a calcium aluminosilicate (gehlenite) then the mother reactant (spinel in this case) must be aluminosilicate. Therefore, spinel is not simple γ- Al_2O_3 but it is an aluminosilicate phase. Now, it is to be seen to what extent of the Al_2O_3/SiO_2 ratio of the preheated diphasic gel reacted with $CaCO_3$ and produced calcium alumino silicate alone?

Table 2 shows that all the heated diphasic gel samples form gehlenite when treated with $CaCO_3$. But there is a characteristic difference in forming phase out of gels of alumina compositions up to 3:2 mullite composition and again the phases developing from gels of alumina compositions beyond 3:2 mullite composition.

In the first case, gehlenite is the only phase whereas in the other cases in addition to gehlenite, calcium aluminates are gradually developing.

XRD patterns of $CaCO_3$ treated spinel samples show that the intensities of $C_{12}A_7$ and CA decrease with the decrease of wt.% of Al_2O_3 content. The X-ray intensities of those phases e.g. 0.490 nm peak of $C_{12}A_7$ is noted to be of the following order as DG85≫DG80 > DG76. And formation of those two phases are found to be absent in the case of diphasic gel of composition approx. to 3:2 mullite. With this observation, the composition of spinel could be predicted as nearly analogous to 3:2 composition of mullite. Formation of calcium aluminate out of gel marked DG85 indicates that in addition to formation of some usual Al–Si spinel phase some portion of aluminium oxide remains as excess as γ-Al_2O_3 and θ-Al_2O_3 during heating DG85 to 1000 °C. This alumina which had remained as free reacted with calcium carbonate. So formation of calcium aluminate in this case is responsible for solid state reaction between the portion of alumina left out after reaction of Al–Si spinel with calcium carbonate. On the contrary, bonded alumina forms calcium aluminosilicate. So these results indicate that alumina was bonded previously with silica in heat treated diphasic gels. Therefore, Al–Si spinel containing ~28 wt.% silica is a more feasible proposition. However, the data of some earlier studies are varying. By TEM study. Okada et al. [28] analyzed the chemical composition of the phase obtained by using specimen fired at 1000 °C and leached with 7 wt.% NaOH solution by boiling for 40 min in analytical TEM with EDX-type analyzer and obtained a value of ~8 wt.% SiO_2. By similar TEM study, Schneider et al. [27] showed that during heating diphasic gel, Si is gradually introduced into the γ-Al_2O_3 lattice. They estimated the silica content of the nano crystalline spinel phase at different temperature on heating precursor by EDX analysis. The silica content of the spinel phase at 500 °C is ~12 mol%. It increases to 18 mol% at 1150 °C (their Fig. 7). With this result they suggested that the maximum silica incorporation into γ-Al_2O_3 is 18 mol% (11.5 wt.%) at 1150 °C. On the contrary Suzuki et al. [29] presented the electron diffraction pattern of Al–Si spinel phase. The composition of the spinel was analyzed by EDS in TEM and was similar to stoichiometric mullite composition. This spinel phase converted to yield ultrafine mullite during heating at 1200 °C with the same stoichiometric composition.

According to Okada et al. [20] the decomposition reaction of gel into spinel phase and amorphous compound is as follows.

$$x\mathrm{SiO_2}.(1-x)\mathrm{Al_2O_3} \rightarrow \mathrm{m(SiO_2.6Al_2O_3)} + n\mathrm{(6SiO_2.Al_2O_3)}$$

Had the composition of the spinel phase been nearly $SiO_2{\cdot}6Al_2O_3$ (8–10 wt.% SiO_2) then the diphasic gels beyond 3:2 composition e.g. gels like DG76, DG80, and DG85 of the present study would not show any free crystallization of θ-Al_2O_3/α-Al_2O_3 during heating as shown in Table 1. Since sufficient alumina is present in those gels to form spinel phase of the composition ($SiO_2 \cdot 6Al_2O_3$). With the similar reason these preheated gels would not show any formation of calcium aluminates during solid state reaction with $CaCO_3$ (Table 2). Qualitative identification of formation of free corundum out of gel just beyond 3:2 composition and likely the formation of calcium aluminates during spinel–calcium carbonate reaction predict that the limiting stage of Al_2O_3/SiO_2 ratio for Al–Si spinel composition would be 3:2. Thus, the composition of Al–Si spinel would be analogous to the composition of 3:2 mullite suggested by other authors.

5. Conclusion

In situ diphasic gels of varying Al_2O_3:SiO_2 ratios have been synthesized out of TEOS arid ANN at ammoniacal condition. On heating two discrete phases first dehydrate. Solid state reaction among them starts and leads to crystallization to spinel phase . XRD intensities of spinel phase increase with continued heating up to ~1200 °C and rapidly decomposes to weakly crystalline mullite phase which grows at high temperature heat treatment.

Results show that measured X-ray intensities of spinel phase formed out of diphasic gels are much greater than that of the theoretical intensity expected for γ-Al_2O_3 formation. This indicates that increase in intensity of spinel phase on heat treatment is probably due to incorporation of Si in the γ-Al_2O_3 phase.

In addition results also show that spinel phase formed from all diphasic gels up the composition of 3:2 mullite form calcium aluminosilicate rather than calcium aluminate. This observation more definitely indicate that spinel phase is Al–Si spinel other than simple γ-Al_2O_3. Calcium aluminate starts forming from spinel derived diphasic gels of composition beyond 3:2 composition of mullite. This further indicate that probable composition of Al–Si spinel is analogous to the composition of 3:2 mulilte.

Finally, it is predicted that if boehmite is precipitated during gelification process by using ammonia in a solution mixture of TEOS and ANN, the resultant gel would be diphasic in character and it would transform to Al–Si spinel as an intermediary phase as noted occasionally in transformation of some monophasic gels.

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