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- REVIEW-—

INTERPRETATION ON THE CHANGES OF CO-ORDINATION
NUMBER OF AL IN THERMAL CHANGES OF KAOLINITE

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ABSTRACT

Analytical results of I.R., XRF and MAS-NMR techniques applied to characterize
the intermediate phases namely metakaolinite and spinel phase have been reviewed

.

The exhaustive analyses showed that no positive evidence has been obtained so as to

conclude that the intermediate 980•Ž spinel is ƒÁ-Al2O3. The major drawback in arriving
to a definite conclusion is probably due to unaccountability of the co-existence of

a substantial amount of amorphous alumino silicate phase at 980•Ž. The measured
AlO4 content of 1000•Ž heated kaolinite by XRF analysis agrees closely with the
theoretically expected global AlO4 value of the 980•Ž reaction where Si-Al spinel and

amorphous alumino silicate phases forms with the liberation of amorphous silica. Lastly
metakaolinite does not have any fixed structure. It transforms to mullite in two parallel
paths as explained from I.R. studies of successive heated kaolinites. First path
corresponds to nucleation of mullite in amorphous alumino-silicate matrix and
subsequent growth thereof which is related to the observation that the ratio of AlO
4 t

o AlO6 does not change too much between the temperature range 1000•‹ to 1400•Ž
in some kaolinite where mullitization predominantly takes place following this path

.

The second path corresponds to the polymorphic transformation of cubic to
orthorhombic form where the global AlO4/AlO6 ratio of 1000•Ž heated kaolinite
changes and subsequently attains to the value close to 3:2 mullite.

INTRODUCTION

The details of earlier work done regarding the intermediate 980•Ž spinel phase in

kaolinite to mullite reaction series have been critically reviewed1) . The old concept was
simple ƒÁ-Al2O3 (Al-spinel) and it developed as per the equation:

Metakaolinite 980•Ž ƒÁ-Al2O3+ 2SiO2(Amorph) 1

The second concept was Si-substituted spinel of the composition of 2Al
2O3 35iO2 (Si
8Al102/3O32) other than the pure Al spinel. With the advent of this concept controversies
brewed up. Researchers belonging to these two groups tried to substantiate their own views
following newer experimental techniques on the one hand and on the other hand

commenting on the views of the other group. During this time, most of researchers in
this field started to believe the old ƒÁ-Al2O3 concept to be true. In the meanwhile, a third

46 A.K. Chakravorty

concept emerged which modified the earlier composition of Si-Al spinel to a composition analogous to that of 3:2 mullite and designated the spinel as cubic mullite which in terms of 32 oxygen is

[Si4.9A13.1] [(Al11.7 4.3) O32]

This concept of mullite like Si-Al spinel shows a partial instead of full substitution of
Al by Si in tetrahedral part of 7-Al2O3 structure. This model has recently been questioned
as to whether it contains 28 wt. per cent SiO2 in reality or it contains about 10 wt. per
cent SiO2. Recently the data of amorphous SiO2 liberated from kaolinite at 980•Ž has
been rechecked and the composition of Si-Al spinel phase has been confirmed as mullite
like and finally the 980•Ž exothermic reaction in case of kaolinite has been established

as follows:

Metakaolinite980•Ž i) 3Al2O3 25iO2 cubic mullite (Si-Al spinel) major phase.
ii) 3Al2O3 2SiO2 orthorhombic mullite weakly
crystalline minor phase.
iii) Alumino silicate (amorphous phase).
iv) SiO2 (Amorphous phase) (2)

During the course of the above 980•Ž transformation the coordination number of Al
in different phases will change. Accordingly, various authors namely Roy et a1.3), Roy
and Stubican4), Dekeyser et al.5), Pampuch66, Freund), Tuszuke8), Percival et a1.9),
Mackenzie10), Okada et al.11) etc. by I.R. Spectroscopic measurements and recently Brown
et al.12) and Sanz et al.13) by MAS-NMR techniques noted relative changes in Al
coordination during each successive stages of decomposition of kaolinite, allophane and
Al2O3-SiO2 gels etc. In this communication the spectroscopic data of the previous authors
have been reviewed first of all and then applied to equations 1 and 2 to show how these
data help in ellucidating the characterization of the spinel phase. Elaborate discussions
to eleminate the ƒÁ-Al2O3 hypothesis which some researchers still believe to be true have

been made.

EXPERIMENTAL

Rajmahal kaolinite was heated to successive rise of temperatures, cooled and agated
4 mg of the samples was mixed throughly with 2 g of KBr and ground. 100 mg of this
mixture was charged into vacuum mould to remove free moisture and air and thereafter
it was hydraulically pressed at a pressure of 14,000 lbs per sq. in to form disk. I.R. patterns
were taken in a Pye Unicam spectrophotometer with optimum instrumental setting so
that best possible recordings were obtained. I. R. recordings are shown in Fig. 1. The
patterns are similar to those shown earlier by Freund) in his Fig. 2 and latter by Percival
et a1.8) in their Fig. 4.

DISCUSSION OF EARLIER WORK

Qualitative results of I.R. spectroscopic data of earlier workers have been cited first

Co-ordination Number of Kaolinite 47

FIG. 1. I.R. Studies of
1. Rajmahal Kaolinite
2. -do- heated to 600•Ž
3. Amorphous Silica
4. Rajmahal Kaolinite heated to 1000•Ž
5. ƒÁ-Al2O3
6. Rajmahal Kaolinite heated to 1300•Ž

48 A.K. Chakravorty

of all to show what maximum possible information would be obtained to characterize
the intermediate products and to explain mullitization reactions.

(I) Metakaolinite: During the dehydroxylation of kaolinite, the following band frequency
changes have been noticed. Intensity of different I.R. bands were shown earlier by
Tarte14), Percival et a1.9) and Freund7) etc. (i). Three fold split up bands namely 1108
cm-1, 1035 cm-1, 1012 cm-1 between 1175cm-1 to 950cm-1 due to two dimensional
silica sheet vibration have shifted very little and have merged and formed a broad big
shoulder.

(ii) Three bands namely 540cm-1, 370cm-1 and 345cm-1 due to Si-O vibration
disappeared and the splitting bands at 465cm-1 and 425cm-1 have vanished with the
formation of a broad band at 445cm-1.

(iii) Si-O vibrations in silicon-oxygen layer at 794cm-1, 752cm-1 and 603cm-1 also
disappeared and two new bands appeared at 1150cm-1 and 1080cm-1 which indicated
that the symmetry of Si-O layer has become higher than in kaolinite15).
(iv) Three bands namely 940cm-1, 918cm-1 and 792cm-1 assigned to (A1vi-O)-H
bond have disappeared.
(v) Similarly, 540cm-1 band due to Al(O-(OH)) has disappeared with the appearance
of 810 cm-1 band due to Aliv-O vibration. Change of Aliv co-ordination was shown by
Gastuche et a1.16) to follow a linear relationship with the extent of dehydroxylation.
(vi) Out of four -OH bands, observed in kaolinite three bands namely 3695cm-1,
3670cm-1, 3650cm-1 disappeared on heat treatment. Both 3620cm-1, 3440cm-1 bands
were reduced and became broad. Later, the bands gradually became smaller and finally
disappeared just before 980•Ž exotherm. But the main question regarding Alvi-O-Si bands
connected to (Si2O5)-2 layer and Al(OH)+2 layer cannot be distinguished. According to
Freund), Alvi-O valency vibration from Si-O-Alvi bridge may occur in the range of 900
cm-1 to 700cm-1 and probably at 790cm-1 where other bands due to Si-O and
(Alvi-O)-H also occur. This raises difficulty in the proper identification of Si-O-Alvi band
in kaolinite itself. Therefore, the question whether metakaolinite is a mixture of two oxides
and 980•Ž heated spinel phase is ƒÁ-Al2O3 seems to be unanswerable by I. R. Pumpuch6)
of course, noted that the most characteristic and intense absorption bands for SiO2 at
1190cm-1, 1100cm-1 and 800cm-1 which are absent in metakaolinite but appeared in
subsequent I.R. studies of boiled and HC1 treated metakaolinite. In this way he indirectly
confirmed a connected metakaolinite structure.

(II) Spinel phase - On further heating metakaolinite transforms at and around 980•Ž
to spinel phase. Percival et al.9) noted I.R. bands at 570cm-1, 720cm-1 and 900cm-1
respectively corresponding to the development of phases having AlO6 groups besides the
persistence of AlO4 groups at 810cm-1. They designated the 980•Ž heated spinel phase
as T-Al2O3 which contains both AlO4 and AlO6 groups unlike Si-Al spinel model of
Brindley and Nakahira17) which contains only AlO6 groups vide Table 1. However, it was
pointed out earlier18) that weakly crystalline mullite always formed with spinel phase at
980•Ž and further mullite contains also AlO4 and AlO6 groups. Under this circumstance,
the differentiation of spinel or Si bearing spinel would be inclusive. Similar argument
could be put forward on the NMR work of Brown et al.12). These authors noted from

Co-ordination Number of Kaolinite 49

50 A .K. Chakravorty

their XRD studies the co-existence of spinel phase and mullite at 970•‹ and 1050•Ž
respectively from kaolinite. On comparing the NMR spectra of ƒÁ-Al2O3 with that of
970•Ž heated kaolinite they stated that the two spectra were consistent (Fig. 4, Ref. 12).
Accordingly they proposed that the presence of ƒÁ-Al2O3 in 970•Ž heated kaolinite was
quite feasible. On careful observation one can easily see the following salient features
from those spectra. Positions of tetrahedral and octahedral Al peaks have differed. Nature
of the peaks are obviously dissimilar. They did not explain those in the context of inherent
presence of Si-atom in Si-O-Al network in metakaolinite to that of only A1-O bonding
in pseudo Boehmite during their thermal transformation studies. Lastly A1O4 to A1O6
ratio in the two spectra are definitely different. Similar observation was noted by Sanz
et a1.13). According to them, Al spinel in ƒÁ-Al2O3r phase would contain two peaks centered
at 66 and 6 ppm. However, the position and relative intensity of the component detected
in the 27A1 NMR signal (60, 43 and 1 ppm) vide Fig. 2 ref. 13 were different from the
latter. This ratio is contributed from both spinel and mullite phases. Furthermore it is
also contributed from binary-alumino silicate amorphous phase as detected and semi-
quantitatively estimated by Chakravorty and Ghoshl). Brown et a1.12) were unware of
the development of this phase during 980•Ž reaction. It had been reported earlier199. Now
the question of identification of spinel phase in presence of crystalline and amorphous
alumino-silicate phases becomes more critical. Therefore, their statement "although the
heated kaolinite contains a higher proportions of tetrahedral Al, the presence of -Al2O3r
component is quite feasible" is highly erroneous.

(III) Spinel phase formation from Al2O3-SiO2 gels.
Formation of Si-Al spinel out of kaolinite has been found to be analogous to alumino-
silicate gel during heating20. As such, thermal transformation of Al2O3-SiO2 gels have
been discussed here. Komerneni et al.21,22) tried to characterize the spinel phase produced
during heating the gels by MAS-NMR techniques. Hoffmann et a1.23) and others21,22)
prepared both single phase and diphasic Al2O3-SiO2 gels by using both organic and
inorganic precursors of aluminium and silicon. A part of their results are included in Table
2. It had been shown that 27A1 NMR spectrum of single phase mullite gel heated to
1075•Ž (Fig. 4B), Ref. 21 was virtually indistinguishable from the same in xerogel heated
to 450•Ž (Fig. 2a, Ref. 41) which essentially contained both octahedral and tetrahedral
Al. Moreover, it did not differ from that of ƒÁ-Al2O3 spectra (Fig. 2, Ref. 21). Again 27A1
spectrum of heated diphasic mullite gel at 1010•Ž (Fig. 5, B, Ref. 21) was essentially similar
to ƒÁ-Al2O3. But the most stricking factor is that the phase development in both single
phase and diphasic gels in the vicinity of 980•Ž exotherm were, however, found to be
different (Table 2) e.g. single phase mullite gel showed mullite formation, secondary
deconvoluted NMR data of single phase gel heated to 1025•Ž (tetra/Octa ratio 20.48)
did not predict the formation of 2:1 mullite (tetra/Octa = 1.248) but tallies with
ƒÁ -Al2O3's data. Thus, the results of NMR data do not support x-ray data. Under these
circumstances, the intermediate spinel phase predicted by Komerneni et a1.22) and
Hoffman et al.23) as -Al2O3r is erroneous. Further MAS-NMR data of single phase gel
of high silica content showed both tetrahedral and octahedral Al. These behave as alumino
silicate phase (Si/A1 = 1.26) having Ally-0-Si bonding. On heating these to 1015•Ž the
original Aliv-O bonding persisted and though the NMR pattern was analogous to that

Co-ordination Number of Kaolinite 51

52 A.K. Chakravorty

of ƒÁ-Al2O3 but in practice it actually developed a mixture of poorly crystalline mullite
and spinel phase. From these observations whether an alumino-silicate gel on heating will
decompose into free ƒÁ-Al2O3 and amorphous SiO2 or the A1-O-Si bond which was
previously present in alumino silicate gel itself will persist, is difficult to ascertain by the
mere qualitative detection of A1O6 and A1O4 groups by MAS-NMR studies. Therefore
in spectroscopic studies both A1O6 and A1O4 groups have been detected in 980•Ž heated
alumino silicate gels and kaolinite respectively. These groups account for the formation
of three phases namely mullite, alumino silicate amorphous phase and spinel phase. Now,
one can realize the practical difficulty in interpreting spinel phase as to whether it is
ƒÁ -Al2O3 or Si bearing spinel phase

. The physico-chemical method which helped in
characterizing the spinel phase, developed during 980•Ž heating of kaolinite and
Al2O3-SiO2 gel of the composition of mullite have been reported earlier1). In the present
paper the spectroscopic data have been applied to equation-2 to assess its validity.
Results of quantitative estimations of values of the change of coordination of Al in
the entire reaction series is now being reviewed. The commonly used technique was XRF.
It was based on the findings of White, McKinstry and Bates that K a emission of Al
shifted with its coordination state and secondly from the work of Warlde and Brindley25)
it is indicated that wave length shift was also related to the average A1-O distance. Tentative
values of the change of Al co-ordination based on the works of Brindley and
McKinsky26), Leonard27), Tsuzuke et al.8), Udagawa et a1.28) and Bulens et al.299 on
different heat treated kaolinites have been shown in Table 1.

(a) Metakaolinite. Al in metakaolinite is short of ligands due to elimination of -OH
groups as water molecules during its formation and it automatically acquires four
neighbours. These neighbouring O2 atoms are not expected to be present in a regular
order with respect to Al as per the structures shown either by Tscheischwlli et a1.30) or
Brindley and Nakahira17). During dehydroxylation process one can expect c-axis ordering
but lack of c-axis ordering and continuation of a-b axis is absorbed in single crystal
studies3,17) indicates a hexagonal chain like arrangement which is much more ordered than
in original kaolinite31) with irregular distortions of Aliv-O bond distances as well as bond
angles respectively with the persistance of some localized OH groups as shown by
Pampuch6 and also believed by Freund322. Thus it becomes difficult to estimate the actual
state of metakaolinite. Moreover, it exists between 550•Ž (dehydroxylation peak
temperature) to the last small endothermic dip just before 980•Ž exothermic peak
temperature in DTA. Some well marked I. R. studies (as reviewed earlier 33) indicate
the presence of Aliv-O(OH) bond to the extent of 1.0% as H2O at its formation i.e. the
dehydroxylation completed up to 88% during 550•Ž endothermic peak. Thereafter further
dehydroxylation occurs as a result the concentration of remaining -OH groups also changes
in the abovestability range mentioned earlier. This signifies that as its composition changes
vis-a-vis Aliv-O(OH) varies, the AlO4 to AlO6 ratio also varies. So the measured
co-ordination number of Al in metakaolinite will also vary. The precise measurement in
this range will be most difficult although the calibrant for its measurement were chosen
with utmost care. These suggest one to believe that metakaolinite has no fixed structure
other than suggested by Pampuch6), Iwai et al.34), Mackenzie et al.35) and Sanz et a1.13)
etc. It is worthwhile to mention here the conception of Fripiat36) who thought that

Co-ordination Number of Kaolinite 53

residual protons of the remaining -OH groups in the intermediate metakaolinite stage
were probably able to move from one oxygen to another oxygen in the whole or in part
of the lattice structure, including of course the surface. XRF data of A1O4 content of
metakaolinite (•`59%) shown by Leonardr) seems to be inconsistent. On this issue
Leonard37) stated that the observed value is purely artificial and only characterizes the
unusual situation of Al atoms fully tetrahedrally co-ordinated (2 OH of the gibbsite like
layer are actually and completely removed at least at 800•Ž) in an enlarged oxygen
environment 1.92 A 4..1.77 A (classical Al(iv)-O distance). There is thus no sense in
this particular situation to look after the complementary 40% Alvi content. At least at
800•Ž there are no more Alvi configuration except that the distance A1-O appears to be
octahedral. Similar ambiguity has been observed in NMR study. The 27Al MAS-NMR
spectrum of metakaolinite (Fig. 1 Ref. 12) remains mostly equal even on heating it at
970•Ž. There is only a slight change in relative intensities of tetrahedral to octahedral
resonances of Al. Question is: how does it happen? Theoretical expectation is obviously
different as stated above. In practice Udagawa et ai.28) noted marked difference in the
coordination state of Al in the two stages of the decomposition products of kaolinite

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In this regard Mackenzie et al.35) showed that NMR signal decreased by about 90 per
cent (Fig. 3 Ref. 35) in this stage of transformation. On further heating only slight increase
in the NMR intensity to the extent of 200/o of original value had been observed . This
entails limitation of the use of NMR in detecting the remaining 80% Al occupancies . With
insufficient information, the state of metakaolinite and the characterization of spinel phase
formed thereof are hardly possible. Knowing fully well it is not understood why Mackenzie
et a1.38) claimed when it was seriously opposed by Okada39)

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(b) Cubic Mullite. By using XRF technique Leonardr) showed the quantitative value

of A104 present in 900•Ž/24h heated Zettlitz kaolinite was of the order of 37.9•}10.3%.
This value tallies with the calculated A1O4 content of the 980•Ž decomposition products
of kaolinite comprising of •`25% Si-Al spinel, -40% amorphous alumino silicate
phase and little mullite as per equation 2 and other than equation 1 due to Leonardr)
and others9). This provides an answer to the pertinent question raised regarding the

validity of Chakravorty's mullite like Si-Al spinel (cubic mullite) by Leonard et al.40) and
the expected sharp rise in A1O6 content during metakaolinite to Si-Al spinel
transformation at 980•Ž would not be observed due to the development of the binary
alumino silicate phase.

EXPLANATION OF I.R. RESULTS IN KAOLINITE TRANSFORMATION

To support metakaolinite to Si-Al spinel to mullite reaction mechanism the following
wave number regions of the I. R. spectra of Fig. 1 are discussed below:
(i) Comparatively big and broad absorption band between 1200 to 1000cm-1. In this
region, Si-O-Si vibration and Aliv-O-Alivvibrations superimpose and generally occurs at
1075cm-1 as per Freund). This broad absorption shoulder becomes more and more
sharp from metakaolinite stage to Si-Al spinel stage and thence to mullite stage where
it splits into separate Si-O vibrations at 1160cm-1, 1130cm-1 and Aliv-O vibration at
1075cm-1. So due to mullitization, one can see the decrease in the broad band intensity

54 A.K. Chakravorty

with simultaneous formation of new Alvi-O absorption band.
(ii) Comparatively smaller broad band between 900-700 cm-1. This band due to
corner and edge sharing of A1O4 groups characteristic of metakaolinite decreases in width
during successive heating to higher temperatures. Two new bands appear, one at 725
cm-1 due to the change of Si-O-Aliv to Si-O-Ali during Si-Al spinel formation and
another at 900cm-1 due to Alvi-O vibration in mullite. The remaining portion of A1O4
changes its place and appears at 830cm-1 for isolated A1O4 groups in mullite7,14,41).
(iii) Broad band between 600-400 cm-1. In this range, 445 cm-1 band becomes sharp
and gradually separates into two bands, one at 560 cm-1 due to A1O6 groups because
of formation of mullite and another at 470 cm-1 due to SiO4 groups because of the
exolution of amorphous SiO2 during metakaolin to Si-Al spinel transformation.
It has already been shown that mullitization takes place from Si-Al spinel as well as
from binary alumino silicate phase on further heating. In both the transformations, the
co-ordination number of Al changes. How the question is: whether from the changes of
A1O4 and A1O6 I. R. bands in successive heat treated kaolinite, is it possible to demarcate
from which of the two paths, mullitization is taking place? The basic information which
one gathers from the spectroscopic studies is the disappearance of mostly A1O6 groups
in kaolinite to A1O4 in metakaolinite and then partial development of A1O6 during 980•Ž
reaction and then further decrease of the developed A1O6 with consequent increase of
A1O4 during mullite formation. From this observation, it is difficult to conclude from
which path mullitization occurs. However, major mullite development takes place from
binary alumino silicate phase. Obviously the changes in the contours or shapes of the
three absorption bands e.g. 1200-1000cm-1, 900-700cm-1 and 600 to 400 cm-1 have
been explained to be related to metakaolinite to amorphous alumino-silicate to mullite
reaction which is analogous to the concept of chemical continuity of Si-O-Al bond present
in kaolinite to amorphous alumino silicate phase and lastly to mullite.

Kaolinite crystals
(having Si-O-Al bonds)

Alumino silicate phase (amorphous) into which nuclei
of alumino-silicate originates

Mullite crystals (persistence of Si-O-Al bonds)

The results of Udagawa et al.28) supports the above view. They showed that the ratios

of A1O4/A1O6 of 970•Ž and 1250•Ž heated kaolinite were found to be nearly close. This
leads us to believe that the coordination state of Al analogous to that of mullite has already
been attained in the matrix of 1000•Ž heated kaolinite and wherein nucleation has started
,

only slight heating or soaking is necessary for the mobility of atoms to have sufficient
growth of the size of crystals to be revealed by XRD analysis.
In some kaolinites eg. Zettlitz kaolinite referred by Leonard27), Rajmahal kaolinite
referred by Chakravorty and Ghoshl) and Mgo mineralized kaolinite29) the relative ratio
of A1O4/A1O6 changes gradually and approaches towards the AlO4/AlO6 ratio of mullite
with the development of more and more mullite as well as increase in its crystallinity .
This indicates that Al sites in 1000•Ž heated kaolinites are reorganized on further heat
treatment to develop more AlO4 groups connected with remaining AlO6 chains which is
necessary for building up of mullite structure. This type of transformation is related to

Co-ordination Number of Kaolinite 55

the polymorphic change of Si-Al spinel ((cubic) to mullite (orthorhombic) as shown earlier)
by Chakravorty and Ghoshl). The predominance of either of the two paths of
metakaolinite's transformation may be dependent upon various factors as revealed from
the analysis of different kaolinites studied by various workers all over the world e.g.
crystallinity of kaolinite, size of the particles of inherent oxides present in the clay mineral.
As such these are indirectly related to the origin/source of clay mineral.

CONCLUSION

The change of coordination number of Al in successive heat treated kaolinites by
different spectroscopic studies have been reviewed. Literature study indicates that kaolinite
transforms first into metakaolinite followed by change of co-ordination of Al from
octahedral to mostly tetrahedral at•`600•Ž with very little amount of Al in Alvi-O (OH)
stage. At 980•Ž metakaolinite decomposes into spinel phase with release of SiO2 by
elimination of last traces of OH. This intermediate spinel phase was disputed in earlier
days. On accounting of the binary alumino silicate phase to the extent of•`40% as one
of products of the 980•Ž phases developed, spectroscopic studies do not conclusively
characterize the spinel phase as ƒÁ-Al2O3. Similar conclusion has been drawn in case of
Al2O3-SiO2 gel's transformation. On the other hand the measured co-ordination number
data of Al by XRF technique of 980•Ž heated kaolinite is found to be consistent with
the concept of Si-Al spinel model. From I.R. studies, the decomposition of metakaolinite
to mullite by two parallel paths have been explained. The first path constitutes the
decomposition of metakaolinite to an amorphous alumino silicate phase, nucleation of
mullite into that amorphous matrix and subsequently the growth of these nuclei into larger
detectable mullite crystals. In this process of mullitization sharp spectral bands disappeared
and are converted into broad bands. These gradually became sharp as heating progresses
followed by the rise in crystallinity of mullite.
In the second path, metakaolinite decomposes into Si-Al spinel. This on subsequent
heating to•`1250•Ž transforms topotactically into mullite phase. In this process, the ratio
of tetrahedral to octahedral Al co-ordination changes sharply from 21 per cent AlO4 to
55 per cent approximately.
In general both the two processes of mullitization take place on gradual heat treatment.
It is not taking place in a way that one started and then completed after reaching a specific
temperature thereafter another process commences.
The predominance of either of the two paths depends on the origin of the kaolinite.

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56 A. K. Chakravorty

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