



A microwave method for the preparation and sintering of β' -SiAlON

M. Panneerselvam, K.J. Rao*

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India

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Abstract

A microwave-assisted carbothermal reduction and nitridation (CTR/N) method has been used for successful preparation of monophasic β' -SiAlON starting from kaolinite and carbon black. Phase pure β' -SiAlON has been obtained in under 60 min in microwave field. The z value of microwave prepared β' -SiAlON is found to be 2.95, which is very close to the expected value from kaolinite composition. Formation of β' -SiAlON has been monitored with XRD and MASNMR of ^{29}Si and ^{27}Al ; the possible reaction mechanism has been discussed. Kaolinite to β' -SiAlON conversion appears to be a very rapid single-step reaction under microwave irradiation. β' -SiAlON powders have been microwave sintered to 98.7% of theoretical density in 30 min.

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1. Introduction

SiAlON is acronym for Silicon Aluminium Oxy-Nitrides. β' -SiAlON has the general formula $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$ and is a structural analogue—or even more appropriately, a derivative—of $\beta\text{-Si}_3\text{N}_4$. $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$ is formed when z silicon atoms in Si_6N_8 ($\equiv 2\text{Si}_3\text{N}_4$) are substituted by aluminium atoms and z nitrogen atoms by oxygen atoms. The charge deficit caused by substituting Al for Si is balanced by the substitution of N by O. The hexagonal structure of $\beta\text{-Si}_3\text{N}_4$ is left unaffected. Therefore, in the structure, the substituted Al atom is 4-coordinated and the O atom is 3-coordinated. β' -SiAlON can be prepared over a wide range of composition with ($0 < z \leq 4.2$). SiAlONs are chemically very stable and enable working temperatures of upto 1600 °C. They possess good mechanical properties such as high strength and high fracture toughness. SiAlONs have, therefore, found wide ranging applications and notably in making cutting tools. Since SiAlON powders are more easily sintered than Si_3N_4 , they hold

* Corresponding author. Tel.: +91-80-360-2897; fax: +91-80-360-1310.

E-mail address: kjr@sscu.iisc.ernet.in (K.J. Rao).

great promise for application in gas turbines and adiabatic engines [1–5]. Therefore, attempts have been made to develop simple and economical procedures to prepare β' -SiAlON [6,7].

Presently synthesis of SiAlON is based on the use mixtures of either Si_3N_4 and Al_2O_3 or SiO_2 and AlN, as starting materials [8–12]. Silica-rich aluminosilicate minerals like kaolinite, halloysite, montmorillonite have also been used as starting materials in combination with Al powder. Carbothermal reduction and nitridation (CTR/N) of these minerals yield SiAlONs [13–22]. The reactions are generally slow and take place at high temperatures of about 1700 °C [19]. Reactions also lead to the formation of mullite, SiC, AlN, and Si_3N_4 as intermediates [13,19,23]. Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) is a layered aluminosilicate containing chemically bound water as OH groups. In terms of component oxides, the formula of kaolinite is $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ and the Al:Si ratio in kaolinite is 1.0. Ideally, the β' -SiAlON obtained from kaolinite corresponds to $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$. In order to prepare β' - $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ from kaolinite, it is required to carry out a clean reaction in which no Si is lost in the form of SiO at the high temperatures of the reaction and no other chemically more stable compound involving Si and Al is allowed to form. Procedures reported in the literature suggest that products other than SiAlON are formed during the reaction [13,19,23] which restrict the use of these approaches particularly when monophasic β' -SiAlON is required. Methods of making Al-rich SiAlONs ($z \geq 3.0$) by introducing additional Al either as Al or Al_2O_3 have also been described in the literature [17].

In recent times, several ceramic materials have been successfully prepared using microwave route [24–26]. Microwaves enable a rapid and fast reaction particularly when a suitable microwave susceptor is present among the reactants. The interaction of microwaves result not only in rapid heating but also in a significant lowering of activation barriers for reactions [27]. Therefore, it is pertinent to explore a microwave route for the synthesis of SiAlON. We expect that microwave irradiation may drastically alter the complex reaction steps involved in the conversion of kaolinite and lead to rapid formation of β' -SiAlON. In this paper, a microwave method for the synthesis of β' -SiAlON is presented in which using microwave-assisted CTR/N reaction kaolinite has been converted to β' -SiAlON in an essentially single-step reaction. We have also presented a microwave method of sintering of β' -SiAlON pellets in extraordinarily short times without the use of any sintering aid or pressure.

2. Experimental

Mixture of kaolinite (BHEL, India) and carbon black in stoichiometric (1:5) proportion was used as the starting material. Two grams of the mixture were ground in acetone media for 30 min and pelletized into a 10 mm diameter and ~3 mm thick pellet. The pellet was embedded in a shallow pit in a SiC block placed inside an insulated quartz set-up (Fig. 1). A gas passing facility was built into quartz set-up. SiC acted as a secondary heater since it is good microwave susceptor. The whole set-up was transferred into a cylindrical cavity of a microwave reactor (MES, France) and exposed to 2.45 GHz microwaves at a power level of 600 W for various reaction times. Reactions were carried out in flowing nitrogen (flow rate of 50 cc/min). Temperature measurement was performed by interrupting the microwave radiation and pushing a Pt–10%Rh thermocouple onto the surface of the pellet. This method of measurement of temperature generally records 20–30 °C lower than the actual value. Use of stoichiometric amount of C, N_2 flow rate of 50 cc/min and microwave power level were found to be the optimum conditions and all these results are presented and discussed. Excess carbon generally remains over and leads sometimes to the formation of excessive SiC.



Fig. 1. A quartz experimental set-up with gas passing facility used for CTR/N.

Reaction products were analyzed using X-ray diffraction (XRD, Jeol-JDX 8P, Japan), infrared spectroscopy (FTIR, Perkin-Elmer, Spectrum1000, UK), Magic Angle Spinning Nuclear Magnetic Resonance Spectroscopy (MASNMR, Bruker-DSX300, Germany), and scanning electron microscopy (SEM, Leica S440I, UK). In order to avoid any reaction of the SiC pit with the pellet material, it was ensured that the pellet did not get stuck to the surface of the pit. For sintering purposes, microwave prepared pellets were pulverized and the powders were pelletized again using 2% polyvinyl alcohol as binder. These pellets were placed in SiC pits and irradiated with microwaves (2.45 GHz) for 35 min. Density of microwave-sintered pellet was determined using Archimedes method. The pellets were polished with 0.25 μm diamond paste and SEM studies were performed to examine the surfaces. Indentation method was used to determine Vickers hardness and fracture toughness (K_{IC}) of the material. Anstis et al.'s [28] formula was used to evaluate the K_{IC} values. Vickers hardness was measured using a load of 100 g for 15 s and K_{IC} was evaluated after initiating cracks using a load of 10 kg for 15 s. Cracks were found to emanate from the corners of the diamond indenter.

3. Results and discussion

The progress of the microwave reaction was followed by arresting the reaction at several intervals and studying their XRD patterns. A typical one is shown in Fig. 2. With just 5 min of microwave

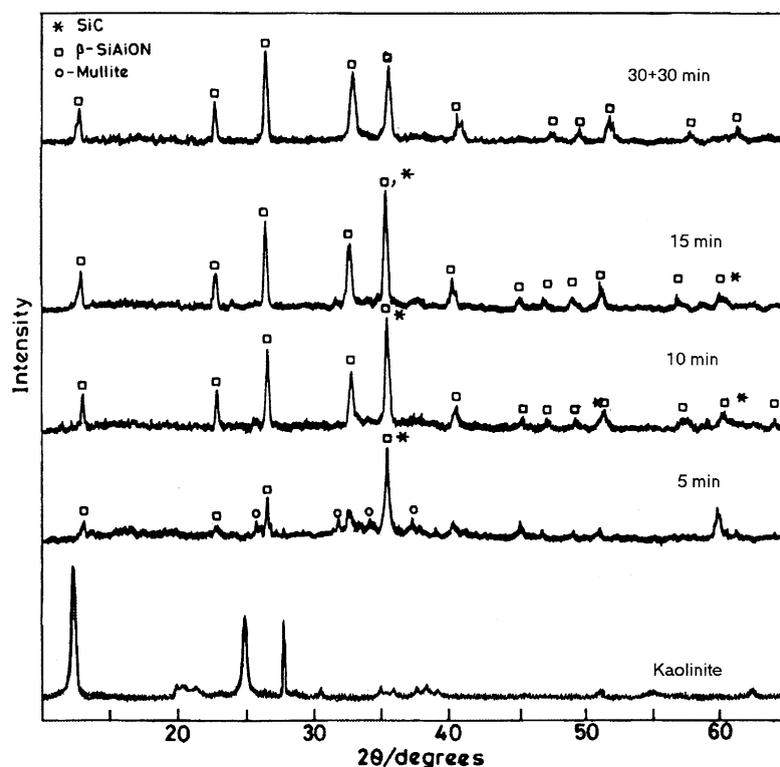


Fig. 2. XRD pattern of microwave irradiated kaolinite–carbon mixture at different intervals of time.

irradiation (sample S-5) formation of SiAlON was noticed. Small quantities of mullite and SiC were also found in S-5. SiC gives three peaks at $2\theta = 35.6, 41.4,$ and 60° ; all these three reflections [29] are common with SiAlON peaks and it is, therefore, difficult to ascertain the formation of SiC by XRD alone. Presence of SiC in the product was ascertained using MASNMR. SiC has characteristic ^{29}Si NMR resonance between -16 and -18.5 ppm [13,30]. However, the final product was obtained after microwave irradiation for 30 min followed by a regrinding, repelletizing and re-exposure to microwaves for another 30 min (S-30/30). In the final product, there was no evidence of the presence of SiC (it was made sure that SiC was not the adventitious material from the pit). In samples irradiated for under 30 min (e.g. S-10 and S-15), there was persistence of SiC peak both in XRD and NMR. In the final product (S-30/30), the 100% intensity peak of SiAlON occurs at $2\theta = 26.8^\circ$ and this intensity is lower than that of the 35.6° peak in samples containing SiC. We also wish to point out that kaolinite XRD pattern itself (Fig. 2) was found to vanish completely at the end of 5 min of microwave exposure. Within this time the kaolinite may have amorphized due to escape of water from kaolinite during dehydration (see later). The baseline in XRD of S-5, however, indicates weak humps (see later). The XRD of S-10 reveals the presence of only β' -SiAlON and SiC peaks and XRD features attributable to mullite are totally absent. The $2\theta = 26.8^\circ$ peak and other peaks associated β' -SiAlON exhibit higher intensity in S-15. In the XRD of S-30/30 sample, only β' -SiAlON peaks are observed and the $2\theta = 26.8^\circ$ peak exhibits the highest intensity as expected [31].

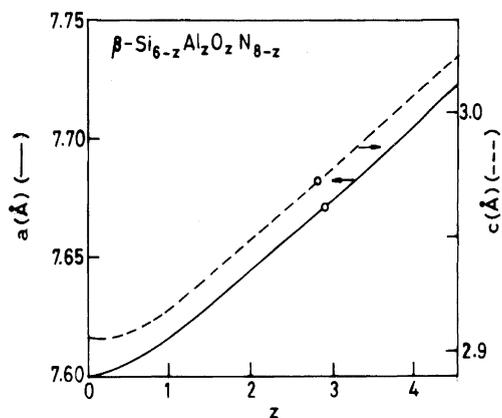


Fig. 3. Plot of lattice parameters (a , c) vs. z for β' -SiAlON (from [1]). Values of a and c of β' -SiAlON from kaolinite (S-30/30) are shown as '○' in the plot.

The crystal parameters of β' -SiAlON were calculated from XRD. The a and c parameters have been interpolated [1] on the known (a , c) versus z (composition) plot in Fig. 3. The observed value of z lies between 2.92 (from a) and 2.87 (from c) as estimated from the corresponding a and c parameters in the figure. This value is very close to the ideal 3.0 which is expected from the composition of kaolinite. The composition of SiAlON was also ascertained from the z -dependent red-shifts of 450 cm^{-1} infrared absorption peak (N–Si–N bending vibrations of $\beta\text{-Si}_3\text{N}_4$) [32]. In the inset in Fig. 4, the observed value of the vibrational frequency has been interpolated on the known frequency versus z plot. z is found to be

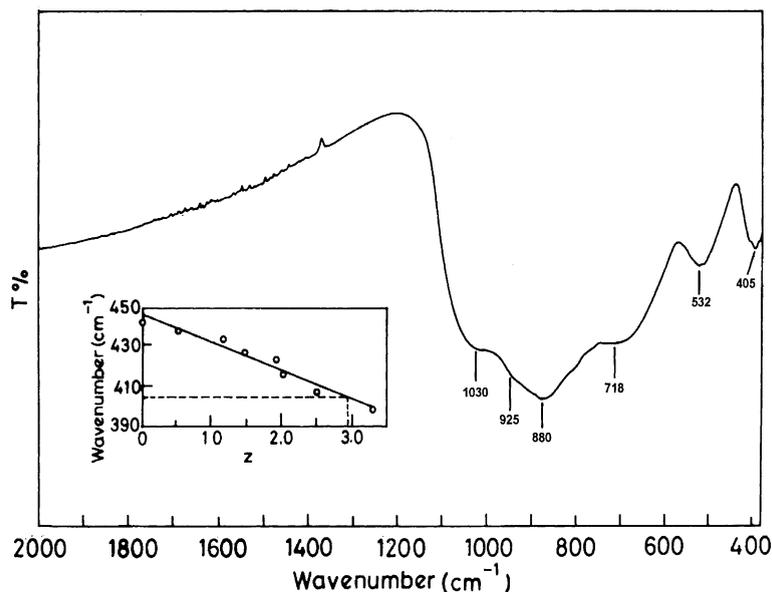


Fig. 4. IR spectrum of S-30/30. Inset shows the variation of wavenumber vs. z (from [35]). Frequency obtained for the β' -SiAlON from kaolinite is indicated by dotted line.

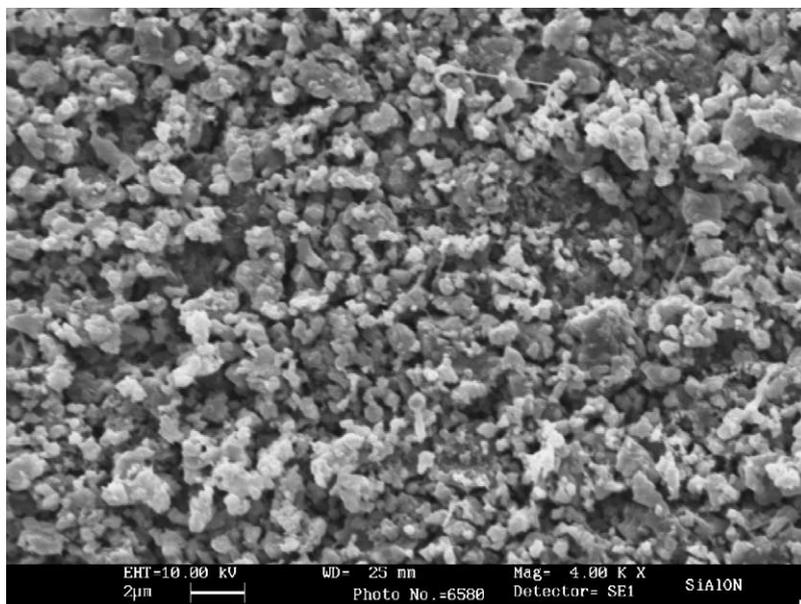


Fig. 5. SEM image of β' -SiAlON powder corresponding to S-30/30.

2.95 which is in good agreement with XRD results [33]. The other peaks observed in IR spectrum (Fig. 4) are those of Si–N stretching ($879, 952, 1030\text{ cm}^{-1}$) Si_3N_4 and Al–O and Al–N stretching (717 cm^{-1}), and the N–Si–N bending (531 cm^{-1}) modes [34,35]. Upon exposure to microwaves, the pellets became almost white-hot and the temperature was found to be around $1400\text{ }^\circ\text{C}$.

The pellet at the end of the reaction was quite friable. The surface was, therefore, mildly abraded and examined under SEM. The micrograph is shown in Fig. 5 and reveals that there has been virtually no sintering and most of the particles themselves are agglomerates of sub-micron size entities.

The reaction leading to the formation of β' -SiAlON was also followed using MASNMR. The MASNMR spectra of ^{29}Si and ^{27}Al are shown in Fig. 6a and b, respectively. The presence of ^{29}Si NMR peak at -18.7 ppm in S-5 is a clear evidence of the presence of SiC. The -109 ppm peak of ^{29}Si is suggestive of the presence of SiO_2 which may be amorphous along with amorphized kaolinite [13,30]. ^{29}Si NMR peak due to SiC in S-5 spectra is very broad. However, ^{29}Si peak expected of SiAlON is not evident in S-5, although it was clearly identified in XRD [13]. The ^{29}Si MASNMR spectra of S-15 reveal the presence of two major peaks, one of SiAlON and the other of SiC. The ^{29}Si peak of SiAlON occurs at a slightly more negative value of -50.5 ppm compared to its value of -48.2 ppm observed in S-30/30. It is suggestive of insufficient substitution of O by N in the β' -SiAlON present in S-15. This is also reflected in the slight shift in the XRD peak at $2\theta = 26.5^\circ$ in S-15 to $2\theta = 26.8^\circ$ in S-30/30. The completion of substitution of O by N and incorporation of Si from SiC in S-30/30 is also indicated by the above observations.

The ^{27}Al MASNMR spectra (Fig. 6b) also support the suggested evolution of β' -SiAlON composition. The ^{27}Al resonance at 1.1 ppm in S-5 indicates the presence of mullite [13]. But this peak is very broad. The resonance at 46.1 ppm originates from oxygen-rich SiAlON. Mullite is absent in S-15. There is concurrent evolution of ^{27}Al resonances due to β' -SiAlON at 10.5 and 60.7 ppm . This evolution appears to become complete in S-30/30. The characteristic ^{27}Al resonance

peaks of β' -SiAlON [13] at 100.5 ppm and -12.4 ppm are also identifiable as shoulders in the spectra. An approximate deconvolution of the spectra is shown in Fig. 6b as an inset.

The microwave preparation of β' -SiAlON from kaolinite indicates that SiC, SiO₂, and mullite are the other products of the reaction. Among them, SiO₂ (amorphous) and mullite are minor products. They both react rapidly and disappear in S-15. Therefore, they are not stable intermediates. The disappearance of SiO₂ is understandable because formation of SiC by carbidation reaction ($\text{SiO}_2 + 3\text{C} \rightarrow \text{SiC} + 2\text{CO}$) is known to be a very fast reaction in microwaves. There is also rapid

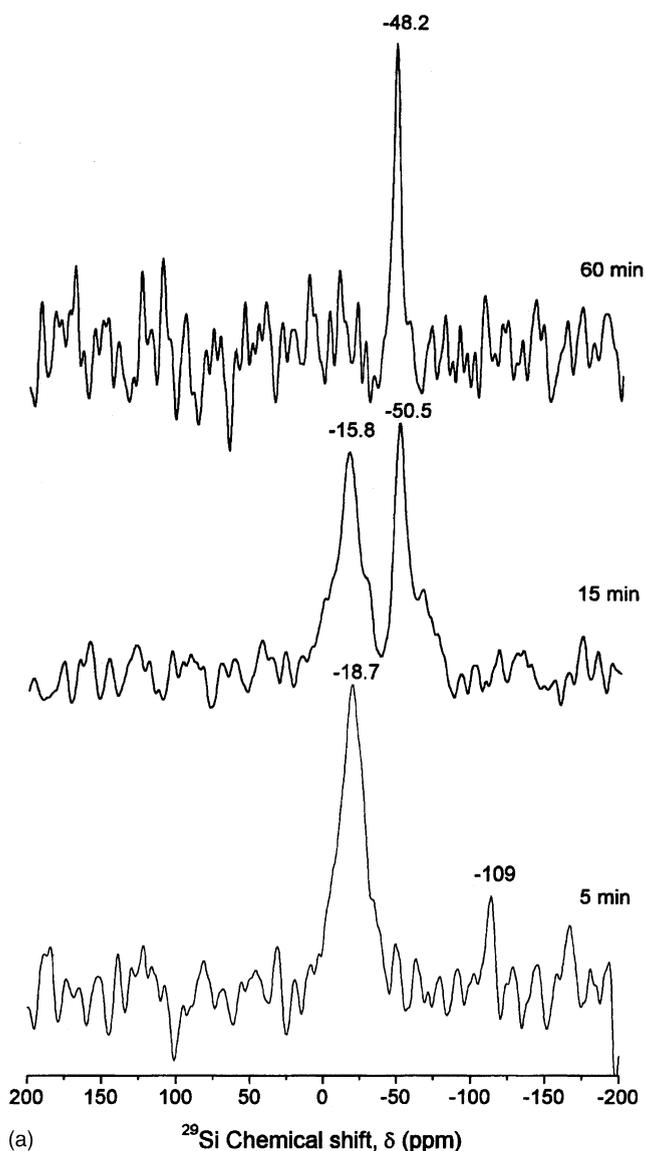


Fig. 6. (a) ^{29}Si MASNMR (b) ^{27}Al MASNMR spectra of microwave irradiated kaolinite-carbon mixture at various intervals of time. Inset is an approximate deconvolution of ^{27}Al MASNMR spectrum corresponding to S-30/30.

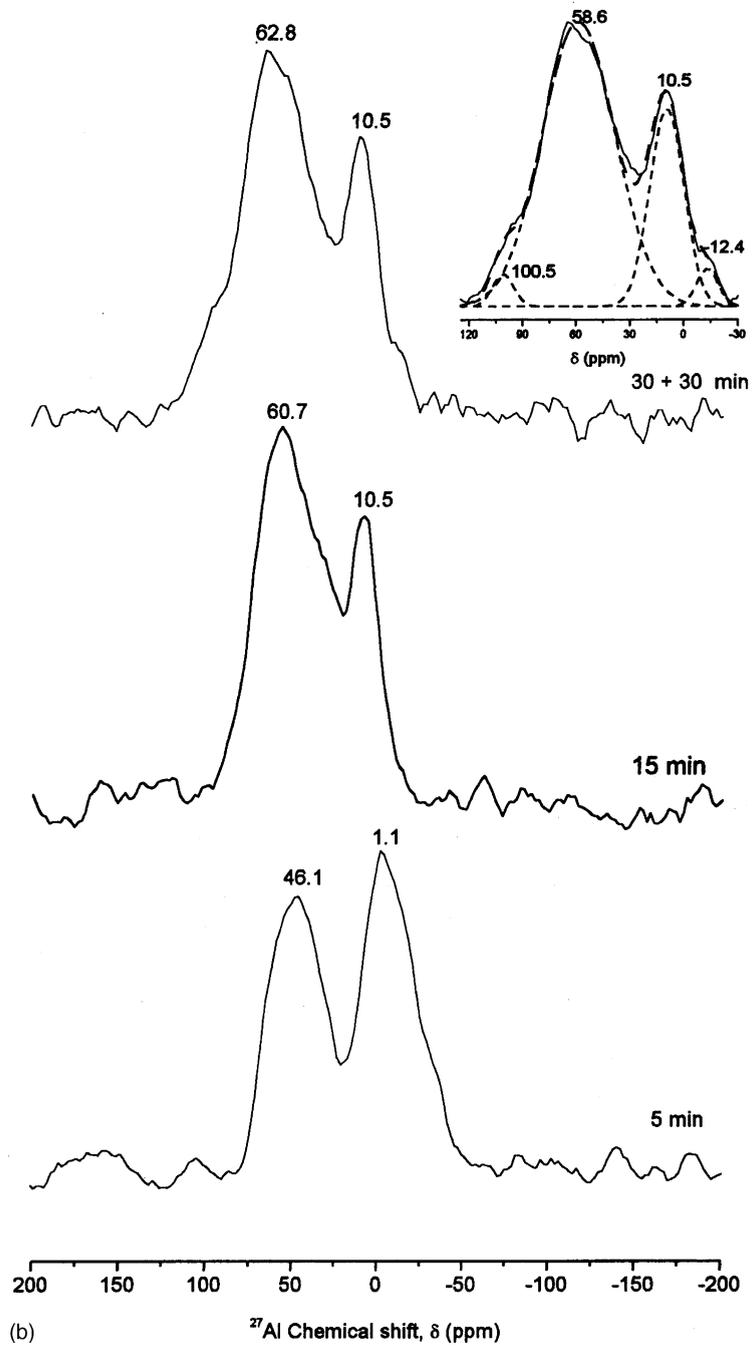


Fig. 6. (Continued).

conversion of mullite into SiAlON which requires re-incorporation of Si from both SiO₂ and SiC and substitution of O by N. Absence of NMR resonances of ²⁹Si and ²⁷Al expected from SiO₂ and mullite in S-15 is an indication that the corresponding reactions are extremely fast. However, SiC appears to persist even in S-15. SiC may be converted into Si₃N₄ or an oxynitride intermediate by its reaction with N₂. The oxygen required for the elimination of C as CO is provided in a concerted reaction by the oxygen-rich SiAlON which has already formed. Incorporation of such nitrated silicon into SiAlON structure may also occur simultaneously. These [SiN_{(4-n)/3}O_{n/2}] units are perhaps not in sufficient concentration at any time in the structure and, therefore, are not observed either in NMR or XRD. Therefore, XRD and NMR observations together suggest that the final stage of the reaction involves a slow step in which SiC, N₂, and oxygen-rich SiAlON react together. The slow kinetics may be a consequence of the difficulty of randomizing the positions of N atoms from the incorporated [SiN_{(4-n)/3}O_{n/2}] units into the structure by exchange with oxygen in the structure and of inducing the bridging and non-bridging oxygens into 3-coordinated nitrogen like positions.

Presence of mullite in only S-5 and its total absence in other samples admits of a possibility that the main reaction leading to conversion of (dehydrated) kaolinite to β'-SiAlON may not involve any intermediates at all. The layered kaolinite structure [36] is represented in Fig. 7. Fragments of graphitic carbon in the reactant (carbon black) can indeed enter into the interlayer regions of layered oxides and selectively remove oxygens under microwave irradiation. We visualize such a reduction and simultaneous nitridation in the interlayer regions of kaolinite also as shown schematically in Fig. 7. The bridging oxygen atoms in the inter-layer region present in either as Si–O–Al or Si–O–Si linkages are readily removed as CO during the reaction and are replaced by equivalent number of nitrogens. The oxygen atoms present in hydroxyl groups first undergo a condensation which results in the removal of water and are, therefore, unreactive towards carbon. These oxygen atoms are likely to be retained in the structure. The condensation step which involves loss of oxygen atoms may also induce the remaining oxygens to re-organize such that Al acquires tetrahedral coordination. The change of coordination

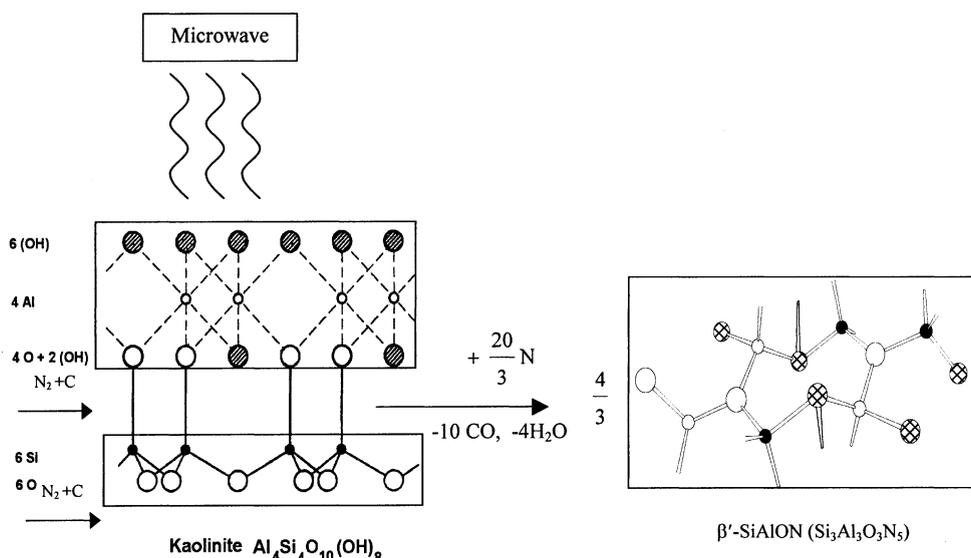


Fig. 7. Schematic representation of a possible single-step conversion of kaolinite to β'-SiAlON under microwave irradiation.

geometry from octahedron containing only four oxygen atoms to a tetrahedron does not require any relaxation of volume around Al and should be, therefore, spontaneous. The net consequence of the reactions is that in each block in the layered structure of kaolinite the 10 bridging oxygens are removed by reaction with carbon and are replaced by equivalent 20/3 nitrogens and the 8 hydroxyls and condense so as to lose four water molecules leaving behind four oxygens in the structure. The reaction may be written as:



The reason why only the bridging oxygens, and not the hydroxyls, are involved in the reaction with carbon is that bridging oxygens carry less charge (the partial charge on oxygen, $\Delta_{\text{O}} = -0.2141$ and -0.266 for the oxygen atoms in Si–O–Si and Al–O–Si links, respectively) in comparison to the oxygen in hydroxyl which is bound to Al and H (in Al–O–H) ($\Delta_{\text{O}} = -0.308$). These partial charges on oxygen are calculated using Sanderson procedure [37]. Therefore, the approach of carbon to within reactive distances is more likely to happen with the bridging oxygens. Further, water elimination reaction (condensation) may also occur simultaneously and the oxygen left behind in its nascent state may be a non-bridging oxygen ($-\text{O}^-$) which is far less reactive towards carbon.

Intralayer reaction products being H_2O and CO , they open up the kaolinite layers rapidly creating more surfaces in the process. The formation of SiC and mullite may, therefore, occur primarily from surface reactions of clay particles and not as bulk reactions. The increased surface area not only enhances reaction rates but also the formation of SiC which is why the persistence of SiC in S-15. Formation of SiC makes the β' -SiAlON oxygen rich. Therefore, it requires grinding and re-reaction which is carried out during the 30 min of the second-stage microwave operation. Thus we visualize kaolinite \rightarrow β' -SiAlON conversion process as an essentially one-step reaction in microwaves and this is schematically shown in Fig. 7. This is in contrast to conventional reactions which occur in stages and often leads to the formation of different types of SiAlON.

The as-prepared β' -SiAlON is powdery. It is, however, easily sintered in microwaves. β' -SiAlON is not a good susceptor of microwaves at the laboratory temperature. As described in the experimental section β' -SiAlON powder was pelletized and heated in a SiC pit to about 500°C . Above this temperature, β' -SiAlON becomes quite susceptible to microwaves. Sintering of pellets required less than 30 min. In Fig. 8, the SEM of sintered pellet is presented. The surface of the sintered pellet was etched with HF and coated with gold before obtaining the SEM micrograph. It is seen that the degree of sintering is remarkable and there is no indication of any connected porosity. The monolith-like blocks, A and B, are marked on the micrograph. Pits like C and D are primarily a consequence of etching rather than of retained porosity. Density was found to be 3.02 g/cc which corresponds to 98.7% of theoretical density. The Vickers hardness and fracture toughness (K_{IC}) values were found to be 15.03 GPa and $4.41 \text{ MPa m}^{1/2}$, respectively which is in very good agreement with literature reports [23].

The sintering feature of β' -SiAlON is truly extraordinary. Microwave sintering is known to involve field-assisted mass transport on the grain surfaces into surrounding cavities [27,38–41]. Formation of monolith-like blocks is, therefore, a truly microwave effect. Presence of tetrahedral Al ($[\text{AlO}_4]^{1-}$) and 3-coordinated oxygen ($[\text{OM}_{3/2}]^{1+}$) units where M can be Al or Si creates dipoles in β' -SiAlON structure which at high temperature may become responsible for escalated microwave absorption.

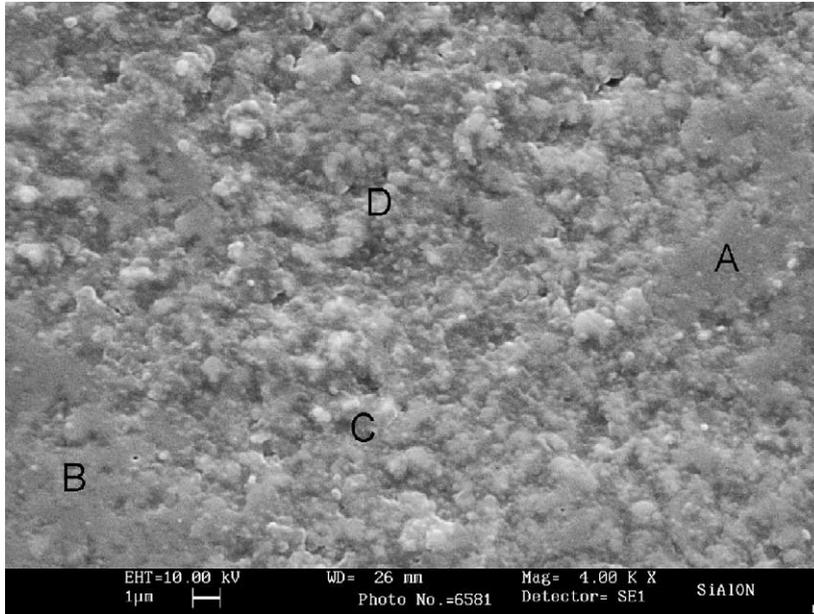


Fig. 8. SEM image of microwave-sintered β' -SiAlON. Regions marked A and B are monolith-like blocks, C and D are pits formed by deep etching.

4. Conclusions

Kaolinite to β' -SiAlON reaction occurs very rapidly under microwave irradiation. XRD and ^{29}Si MASNMR reveals the formation of SiC, mullite, and glassy SiO_2 in small amounts during the initial stages of CTR/N reaction. CTR/N leading to β' -SiAlON involves removal of bridging oxygens and replacement by nitrogens. The retained oxygens in the β' -SiAlON structure appear to be those left behind after water removal by condensation. β' -SiAlON undergoes a rapid microwave sintering and attains 98.7% of theoretical density in under 30 min. Vickers hardness and fracture toughness of microwave-sintered β' -SiAlON are comparable with conventionally sintered products.

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