



Review paper

Development of β -SiAlON based ceramics for radome applications

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Abstract

This paper is a review article covering various methods reported on synthesis of β -SiAlON based ceramic materials and on their net-shape consolidation into radome structures. It also identifies a composition out of a wide-range β -Si_{6-z}Al_zO_zN_{8-z} (where z = 0–4.1) solid solution suitable for radome applications and discusses about various efficient methods reported on fabrication of radome structures out of these compositions. This article also covers the literature pertaining to β -SiAlON-SiO₂ ceramic composites, which are considered to be materials of choice for certain high speed radome applications. Further, successful techniques employed for passivation of AlN powder against hydrolysis are also covered as this powder is one of the starting materials for both β -SiAlON and β -SiAlON-SiO₂ ceramic composites. Surface passivation of AlN is necessary as it decomposes into alumina and ammonia, when it comes into contact with water during aqueous processing of SiAlON based ceramics, thereby not permitting formation of desired SiAlON phase. Finally, the important properties of various commercial radome materials together with those of β -SiAlON and β -SiAlON-SiO₂ ceramic composites are also reviewed and presented in this article.

Keywords: radome material, β -Si₄Al₂O₂N₆, β -SiAlON-SiO₂ composite, near-net shape consolidation

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I. Introduction

1.1 Material selection for radome applications

Development of ceramic materials for radome applications has been the topic of numerous recent investigations and this area of research has received a great deal of attention from materials scientific community [1–21]. Certain missiles that travel at a speeds greater than Mach 5 see a transient temperature of about 1370°C together with high mechanical and aero-thermal loads [1–5]. To withstand these severe environments while transmitting electromagnetic RADAR signals without any disturbance, the materials used for construction of radomes for these high speed missile applications should possess a low dielectric constant, a low loss tangent, a high flexural strength, high thermal shock resistance, high rain erosion and particle impact resistance together with high elastic modulus to keep the thin walls of radomes from buckling [1–13]. A great variety of materials such as, Pyroceram 9606 [2–5], Rayceram 8 [2–5], fused silica [7], barium aluminium silicate (BAS) [8,9], aluminium phosphate (commercially known as Cerablak™ and manufactured by Applied Thin Films, Inc., Evanston, IL, USA) [10,11], SiO₂-AlN ceramics [12], SiO₂-BN ceramics [13], reaction-bonded silicon nitride [14], liquid-phase sintered silicon nitride [15,16], silicon nitride nano-composite (Si₂N₂O, which is also called as SiON) [17], β-Si₄Al₂O₂N₄ [2–5,18–20], β-Si₄Al₂O₂N₄-SiO₂ ceramic composite [1,21], etc., have been investigated so far for these applications. Although all these types of materials have been investigated for these applications only a few materials (as listed in Table 1) have received considerable importance. It can be seen from this table that fused silica possesses excellent dielectric properties (a dielectric constant of 3.9 at 20°C and 4.1 at 1000°C and a loss tangent of 0.0001 at 20°C and <0.01 at 1000°C) making it an ideal material for radome applications [7]. However, its inferior strength (40–50 MPa) and lim-

ited withstanding of high temperatures (<800°C) restrict its use for only certain low speed radome applications. In addition to this, silicon nitride nano-composite (Si₂N₂O or SiON) also possesses good dielectric properties but preparing it with consistent properties repeatedly is not possible as its final chemical composition does not depend on the starting precursor materials composition, but instead depends on the extent of oxidation of α-Si₃N₄ powder that occurs upon calcination in an air atmosphere [6]. The oxidation behaviour of α-Si₃N₄ powder is known to be quite sensitive to several processing parameters such as, atmospheric humidity, the degree of agglomeration of powder particles, temperature fluctuations in furnace, etc. Although, dense sintered silicon nitride possesses exceptionally high flexural strength at room (600–1000 MPa) as well as at high temperatures and withstanding capability together with reasonably acceptable dielectric properties, the major drawback of this material is its poor sintering ability, which requires hot pressing (HP)/hot isostatic pressing (HIP) to achieve desired densification. Nevertheless, the pure Si₃N₄ ceramics cannot be densified under pressureless sintering conditions without using large amount of certain sintering aids. The radome structures consolidated with near-net shape following certain cost-effective techniques like gel-casting cannot be sintered without disturbing the radome structure using HP/HIP techniques. Similarly, silicon nitride-barium aluminium silicate (Si₃N₄/BAS) composite also possesses reasonably high flexural strength (420 MPa) but preparation of radome structures out of this material was found to be quite cumbersome [8]. The only material that can be shaped into radome structures following near-net shape forming techniques like aqueous gelcasting and can also be sintered to full density without disturbing its radome structure is β-SiAlON [2–5]. In the fabrication of β-SiAlON radomes, an aqueous suspension containing required amounts of precursor

Table 1. Commonly employed radome materials and their main characteristics

Material	Fused silica		Silicon nitride based ceramics			
	Phase	SiO ₂ (amorphous)	Si ₃ N ₄	β-SiAlON	Si ₃ N ₄ / BAS [§]	Si ₂ N ₂ O
Temperature withstanding capability [°C]		<800	>1300	>1300	>1300	>1300
Strength [MPa]		40-50	600-1000	266	420	190
Dielectric constant, <i>k</i> (20°C)		3.9	7.96	6.84-7.46	7.50	4.80
Dielectric constant, <i>k</i> (1000°C)		4.01	8.59	7.34	8.16	5.02
Loss tangent, <i>tan δ</i> (20°C)		0.001	0.008	0.0013-0.002	-	0.0014
Loss tangent, <i>tan δ</i> (1000°C)		<0.01	0.013	0.003-0.004	-	0.0025
Processing route		Slip casting + moderate machining	*	‡	†	

* Require hot isostatic pressing (HIP) or hot pressing (HP) followed by extensive diamond grinding

‡ Colloidal processing to near net shape, green machining followed by sintering and final limited diamond grinding / lapping

† Controlling chemical composition is very difficult.

§ Barium aluminium silicate

materials (i.e. α -Si₃N₄, α -Al₂O₃, SiO₂ and AlN together with certain sintering aids such as Y₂O₃) is consolidated in non-porous moulds followed by drying and reaction sintering at elevated temperatures in nitrogen atmosphere [2,22].

Nevertheless, there are two critical issues, which need to be resolved before attempting to fabricate β -SiAlON radomes with near-net shape [18–21]. The first one is fixing of right chemical composition based on the best combination of physical, thermal, dielectric and mechanical properties out of a wide-range of β -Si_{6-z}Al_zO_zN_{8-z} (where $z = 0$ –4.1) solid solution [23]. Furthermore, this composition needs to undergo full densification under pressureless sintering conditions [18–21]. The second one is establishment of suitable net-shape forming technique for making radome structures with desired product yields [19,22]. It is known that processing of β -SiAlON ceramics following aqueous colloidal processing routes is quite difficult as AlN, one of the essential precursor materials of β -SiAlON ($(6-z)$ Si₃N₄ + z Al₂O₃ + z AlN \leftrightarrow 3Si_{6-z}Al_zO_zN_{8-z}, where $0 \leq z \leq 4.1$) decomposes into alumina and ammonia during aqueous processing (AlN + 3H₂O \rightarrow Al(OH)₃ + NH₃) [25]. Despite this problem, Janney *et al.* [2], and Kirby *et al.* [3–5], at Oak Ridge National Laboratory (ORNL), USA, could fabricate β -Si₄Al₂O₂N₆ radomes successfully by utilizing a commercially obtained water processable AlN powder [2]. Furthermore, these radomes were successfully test fired for certain missile applications after sintering [3–5]. Nevertheless, this water processable AlN powder is scarce in the open market. In addition to this, the basis for selecting β -Si₄Al₂O₂N₆ composition by ORNL for these radome applications was not revealed [2]. On the other hand, the dielectric constant (~ 7.3) of β -Si₄Al₂O₂N₆ is also found to be on the higher side for use in radomes for certain high speed vehicles [1–15]. This high dielectric constant value demands the wall thickness of the sintered β -Si₄Al₂O₂N₆ radome to be fixed to ≤ 3.5 mm in order to transmit the electromagnetic waves (i.e., RADAR signals) in the microwave range (~ 17 GHz) without any disturbance [1–15]. However, fabrication of one meter long radomes with about 3.3 mm thickness was found to be a difficult task [2–5]. Most of the commercially available radomes have wall thickness of at least 5 mm. To make 5 mm thick β -Si₄Al₂O₂N₆ radomes, the dielectric constant of β -Si₄Al₂O₂N₆ should be reduced to ≤ 6 while maintaining its flexural strength > 100 MPa [6–17]. In order to confer such properties to this material, many efforts were made to introduce the low dielectric constant SiO₂ into β -SiAlON matrix [1,18–20]. Nevertheless, β -Si₄Al₂O₂N₆-SiO₂ ceramic composites with > 9 wt.% SiO₂ cannot be prepared by following any conventional powder processing route using α -Si₃N₄, α -Al₂O₃ and AlN as precursor materials [18–20]. This is due to the fact that when > 9 wt.%

SiO₂ is to be introduced into SiAlON matrix, in addition to α -Si₃N₄, α -Al₂O₃ and AlN, an additional SiO₂ is required as an additional precursor material. This additional SiO₂ increases the diffusion paths between reactive Si⁴⁺ and Al³⁺ species during sintering that restricts the formation of desired amount of β -SiAlON phase, which is very important to realize high flexural strength for β -Si₄Al₂O₂N₆-SiO₂ ceramic composite [23].

In a study, Gilde *et al.* [6] prepared a silicon oxynitride (Si₂N₂O or SiON) nano-composite by calcining α -Si₃N₄ powder in an open-air atmosphere at 1700°C followed by sintering of this calcined α -Si₃N₄ powder compact in nitrogen atmosphere at $> 1800^\circ\text{C}$. However, in this process the final product could not be prepared repeatedly with consistent properties as mentioned in the first paragraph. In another study, Ganesh *et al.* [18] successfully synthesized β -Si₄Al₂O₂N₆-9.0 wt.% SiO₂ composite by following a reaction sintering process in which a compacted mixture of silicon nitride and alumina was treated at 1750°C for 4 h under ~ 101.63 kPa N₂ atmosphere using 7 wt.% Y₂O₃ as a sintering aid (i.e. 1.5 Si₃N₄ + Al₂O₃ \rightarrow β -Si₄Al₂O₂N₆ + 0.5 SiO₂ (i.e. 9 wt.% SiO₂)). However, none of the compositions of α -Si₃N₄, α -Al₂O₃ and AlN precursors yielded β -Si₄Al₂O₂N₆ with > 9 wt.% SiO₂. Lately, Advanced Materials Organization, Inc., USA, has started producing ceramic composites with a chemical composition of 70 wt.% SiAlON + 30 wt.% fused silica in the form radomes of 25 cm height and 17.8 cm base diameter for certain high speed radome applications [1]. In this process, initially, a green radome was fabricated following a non-aqueous gelcasting of a suspension containing β -SiAlON precursor mixture + 30 wt.% organic fugitive material. After drying, this gelcast green radome was sintered for 2–4 h at $> 1750^\circ\text{C}$ under a N₂ pressure of 50–100 bar to obtain radome with a porosity of about 30% (porosity is formed due to the burning out of the added fugitive material). To fill the generated porosity, fused silica was infiltrated by plasma spraying technique. Fused silica is mainly added to reduce the dielectric constant as well as the density of radome from 3200 kg/m³ to 2200 kg/m³, which is recommended for the above mentioned high speed radome applications [1,6]. Preparation of β -SiAlON radomes with > 30 wt.% fused silica following this route is associated with several practical problems, as it is required to create $> 30\%$ porosity in the sintered radome. Making one-meter long radomes with $> 30\%$ porosity is not an easy step. Additionally, this process has been found to be very laborious and needs highly capital-intensive equipment. Therefore, a simple route for preparing different types of β -SiAlON-SiO₂ ceramic composites with SiO₂ content in the range from 20 to 80 wt.% is highly desired in order to have composites with < 6 dielectric constant and > 100 MPa strength for the intended applications [21,26].

1.2 Surface passivation of AlN powder against hydrolysis

As, AlN is one of the starting materials for β -SiAlON and β -SiAlON-SiO₂ ceramic composites, in order to fabricate radome structures out of these materials with near-net shape following aqueous colloidal processing routes, it is very much necessary to passivate AlN powder against hydrolysis [2–5,18–21]. Otherwise, AlN decomposes during aqueous processing of SiAlONs leading to the coagulation and eventual setting up of the aqueous colloidal slurry in the vessel used for powder de-agglomeration operation thereby not permitting the formation of the targeted final SiAlON composition [2,22]. Owing to the scarcity of water processable AlN powder in the open market, and due to the presence of the hydrophobic substances as coatings on the surfaces of those commercially available water processable AlN powders which hinder achieving high solids loading (>50 vol.%) in particulate (colloidal) suspensions required for net shape consolidation of thin wall radomes, there were several efforts to develop simple and effective techniques to passivate AlN powder against hydrolysis using materials having hydrophilic groups [27–30]. In one study, a di-carboxylic acid (sebacic acid) was utilized to facilitate hydrophilic groups on the surface of treated AlN powder while protecting it against hydrolysis [27]. In another study, aluminium di-hydrogen phosphate, Al(H₂PO₄)₃, was employed to provide a stable phosphate layer on the surface of AlN powder in the aqueous media at pH ~1–3 [28,29]. Yet in another study, a SiO₂ coating was provided on AlN powder in vacuum at 1150–1450°C to protect AlN from hydrolysis [30]. However, all of these processes involve either meticulous control of processing parameters or tedious procedures, thereby making the processes not only complicated but also adversely affecting the environment and the economy of the processes [30–32]. Hence, there is still an open quest to develop ever simpler methods to passivate AlN powder against hydrolysis so that it can be employed in aqueous processing of SiAlON based radome shapes with near-net shape [18–21].

1.3 Near-net shape consolidation of β -SiAlON radome structures

On account of their several useful properties such as, high strength, good oxidation and creep resistance at ambient and elevated temperatures, high elastic modulus, good thermal shock resistance and outstanding rain erosion, particle impact resistance, etc., β -SiAlON ceramics were employed for several applications including radomes for certain high speed missiles [33–40]. β -SiAlON components for these applications are normally fabricated by following a conventional dry-powder pressing (CDPP) of precursor mixtures and then reaction sintering of these compacted precursor mixtures at elevated temperatures in nitrogen atmosphere to achieve the desired density followed by an

extensive and expensive machining to obtain the targeted final shape [33–40]. However, this CDPP technique was found to be quite expensive particularly for making large size and complex-shaped components like turbine rotors and radomes. In order to reduce the processing cost of these components, techniques like slip casting [38], injection moulding [39], temperature induced forming [40], etc., have been tried. However, the productivity and green strength of the parts obtained in these routes have been found to be un-satisfactory. Furthermore, as the forming technique directly impacts the productivity, the ultimate quality and the cost of the manufactured products, particularly in the case of mass production of several advanced ceramics, high productivity with minimum cost must be fulfilled. In view of these reasons, efforts are still needed to be focused on developing simpler and cheaper technologies for processing of β -SiAlON components with near-net shape [19,21,22].

As described by Prof. Evans in a classic review article [41], there are as many as seventy different ways to make ceramic components. Among these numerous ways, only a few methods including powder injection moulding (PIM) [42–47], solid freeform fabrication (SFF) [48–51], and selective laser sintering (SLS) [52–57] have received considerable importance for fabricating certain intricate shaped ceramic products in large quantity on a commercial scale. The efficacy of PIM method was established by German [42–44] as well as by Evans and Edirisinghe [45–49] separately for a great variety of ceramic materials. Although this method has been effectively employed to fabricate certain high end components such as silicon carbide turbochargers and radial rotors for heat engines, alumina thread guides, rare earth magnet pole pieces for hard disk drives, stainless steel gear wheels for electric tooth brushes, etc., it is yet to be tested for manufacturing of large SiAlON radome structures [42–47]. As rightly pointed out by Edirisinghe [49,50] and others [51], the solid freeform fabrication (SFF) is a genus of the manufacturing processes that has been practiced for the fabrication of several three-dimensional ceramic components by assembling their starting materials by point, line or plane. This process has certain advantages over other related processes such as, i) non requirement of any tooling or machining, ii) a dramatic reduction in the time and cost of each design iteration, particularly the first, iii) rapid production of a prototype that could save significant amounts of time and money, iv) dramatic speed up of the entire cycle of designing and bringing a new product to market, v) utilization of a computer aided design (CAD) file to fabricate ceramic components layer by layer, etc.. Nevertheless, this process is yet to be proved for the manufacturing of large SiAlON radome structures [58]. Of late, selective laser sintering (SLS) has also

received a great deal of attention by ceramic community in the manufacturing of near-net shape ceramic components with very high dimensional precision and considerably lower processing times [52–57]. Song *et al.* [52] established a theoretical basis for this process for fabricating three dimensional ceramic components out of several ceramic materials including alumina [55], alumina-zirconia [56], $\text{Al}_2\text{O}_3/\text{SiO}_2$ composite ceramics [57], and yttria-zirconia. However, this process has not been utilized so far in the manufacturing of SiAlON radome structures [58].

It is a well-known fact that aqueous colloidal processing routes offer several environmental and economic benefits apart from the ability to manipulate inter particle forces in aqueous suspensions [2,22,58–67]. On the other hand, as the fracture in the ceramic materials originates from micro-structural imperfections such as pores and inclusions, and leads to poor mechanical reliability, effective de-agglomeration of the powder particles in the slurries is essential. During 1990 period, aqueous gelcasting (GC) has been identified as one of the most efficient near-net-shaping routes, which confers relatively high strength to the green consolidates [2,22]. Furthermore, the green strength of the gelcast part has been found to be three-to-four times higher as compared with that of the compact made by CDPP route [2,22]. However, the drying procedure involved in this process does not allow obtaining crack free green components due to differential shrinkages, particularly when they have different wall thicknesses at different places like in radomes (i.e., nose and wall) [19]. On the other hand, during the same time period, hydrolysis assisted solidification (HAS) has also been identified as a simple and inexpensive net-shaping route that has been employed to consolidate several kinds of ceramics in which alumina is a major or minor constituent [25]. In this process, aluminium hydroxide ($\text{AlN} + 3\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 + \text{NH}_3$) formed by the hydrolysis of AlN which is added to the suspension to promote setting/gelling process acts as cement conferring a relatively high stiffness to the green consolidates. This in turn, keeps the shape of the part intact upon further drying and binder removal operations, thereby minimizing the expensive post-sintering machining operations. Additionally, as this process is not driven by any externally applied pressure or water absorption by an absorptive mould like in the slip casting, it effectively utilizes various thermally activated chemical processes *in situ*. However, the thin wall ceramic components are difficult to fabricate following this process as green parts formed by this method were found to be very brittle [25,59].

In 2009, a new near-net-shaping technique named hydrolysis induced aqueous gelcasting (GCHAS) [19,21,60–63] was successfully developed to address the problems associated with GC and HAS processes.

GCHAS is a combination of aqueous gelcasting (GC) and hydrolysis assisted solidification (HAS) processes. Different kinds of ceramics ($\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ [19], ZTA [60], MgAl_2O_4 [61,62], and Al_2O_3 [63]) consolidated by GCHAS route exhibited significantly higher green strengths in comparison to those consolidated by any other existing technique including original individual techniques GC and HAS. The synergetic effects of these two latter processes are quick setting of the suspension into a stiff gel under ambient conditions with an exceptionally high strength and an absence of differential shrinkage during drying, and thus avoiding cracking of the part. This is a consequence of water being partially consumed by the hydrolysis of AlN ($\text{AlN} + 2\text{H}_2\text{O} \rightarrow \text{AlO}(\text{OH}) + \text{NH}_3$) added to the suspension for room temperature consolidation purpose. The concomitant increase in pH of the system can also favourably change the permeability of the green bodies and minimise the thermal/moisture gradients. These advantages in turn enable fabrication of defect free thick, thin and relatively large components of all ceramics that contain Al_2O_3 as a major or minor component and that utilize and/or tolerate Al_2O_3 as a sintering aid [19,21,60–63].

Considering the importance of net shape consolidation of $\beta\text{-SiAlON}$ and $\beta\text{-SiAlON-SiO}_2$ radomes for certain high-speed missile applications, a systematic study was undertaken recently while keeping the following objectives in mind. i) identification of the best $\beta\text{-SiAlON}$ composition out of a wide-range $\beta\text{-Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$ (where $z = 0 - 4.1$) solid solution based on the physical, dielectric and mechanical properties and the possibility to be sintered to full density under pressureless sintering conditions [42]; ii) development of a simple surface treatment technique for passivating AlN powder against hydrolysis [31,32]; iii) development of a simple powder processing route for preparing dense $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6\text{-SiO}_2$ ceramic composites with SiO_2 in the range of 20–80 wt.% [21,26]; and iv) development of an efficient and simple technique for fabricating $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ and $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6\text{-SiO}_2$ radome structures with near-net shape and with very high product yield [19,21,60–63]. The results published in the literature to address these objectives are reviewed, presented and discussed in this article.

II. Experimental section

The simple and effective experimental procedures reported in the literature on synthesis and net-shape consolidation of $\beta\text{-SiAlON}$ and $\beta\text{-SiAlON-SiO}_2$ ceramic composite radomes, and for surface passivation of AlN powder against hydrolysis are briefly presented in this experimental section.

2.1 Surface passivation of AlN powder

As purchased AlN powder (hereafter termed as A-AlN) could be passivated against hydrolysis following a simple surface treatment method [31,32]. In a

typical experiment, about 175 mL absolute ethanol (99.9%, Les Alcools De Commerce Inc., Ontario) was taken in a 500 mL three-neck round bottom (RB) flask (Duran, India), which was fitted with a condenser, equalization (dropping) funnel and an adapter for passing dry-nitrogen gas from a pressure cylinder. The RB flask was fixed in an oil-bath (the glass dish had 150 mm diameter and 75 mm height, Biotek-Scientific, Hyderabad, containing furnace oil (Thermol-100, -50° to $+250^{\circ}\text{C}$, Biolabs, Hyderabad, India)). The entire set-up was fixed on a magnetic stirrer (5MLH-DX, Remi, India). About 245 g of A-AlN powder was slowly introduced into ethanol present in a RB flask to obtain $\sim 250\text{ cm}^3$ 30 vol.% solids loaded slurry. In a separate experiment, $\sim 2\text{ g}$ $\text{Al}(\text{H}_2\text{PO}_4)_3$ was digested in $\sim 5\text{ mL}$ of hot H_3PO_4 . This solution was then mixed with $\sim 50\text{ mL}$ ethanol and added drop-by-drop to the alcoholic AlN solution (RB flask contents) with the help of an equalization funnel. After completing the addition process, the RB contents were continuously refluxed at 80°C for 24 h while passing nitrogen gas from a pressure cylinder at a rate of $100\text{ cm}^3/\text{min}$. The treated AlN slurry was filtered off and washed with fresh ethanol several times in order to remove any un-reacted/excess H_3PO_4 acid and $\text{Al}(\text{H}_2\text{PO}_4)_3$ from the surface of the treated powder [31,32]. The washing process was continued until the pH of the washed ethanol reached the pH of the fresh ethanol. This powder was then dried at 80°C in an electrically heated oven (Lindberg Blue, USA) over night. The ethanol was repeatedly used several times after subjecting it to the distillation process. Hereafter, the treated powder is termed as T-AlN. The main advantages of this non-aqueous surface passivating process are: i) the formation of a single uni-molecular phosphate monolayer, ii) the excess un-reacted coating agents can be washed away from the powder surface with ethanol, and iii) the ethanol used for washing purpose can be re-used several times after subjecting it to a conventional distillation process. This differs from the existing aqueous acidic solution processing routes that require an excess of H_3PO_4 or $\text{Al}(\text{H}_2\text{PO}_4)_3$ that will remain on the powder surface [31,32].

2.2 Preparation of dense ceramics by conventional dry-powder pressing (CDPP) route

A conventional dry-powder pressing (CDPP) technique was employed to make different types of dense β -SiAlON ceramics and the β -SiAlON-SiO₂ ceramic composites [21,22,24]. The suppliers' details and some of the characteristics of the precursor materials used for the preparation of these β -Si_{6-z}Al_zO_zN_{8-z} ($z = 1, 1.5, 2, 2.5, 3, 3.5$ & 4) ceramics are presented in Table 2. For preparing β -SiAlON-SiO₂ (SiO₂ = 0, 20, 40, 50, 60, 80 & 100 wt.%) ceramic composites, a commercial fused silica powder and a β -Si₄Al₂O₂N₆ powder obtained in a conventional extrusion process followed by reaction sintering were used as the starting raw materials [22]. Prior to pressing into pellets of 30 or 90 mm diameter \times ~ 10 mm height under a pressure of about 200 MPa, $\sim 200\text{ g}$ precursor powders mixtures of both β -SiAlON ceramics and β -SiAlON-SiO₂ ceramic composites (each composition at a time), $\sim 60\text{ g}$ of 5 wt.% aqueous PVA solution and $\sim 200\text{ g}$ of ZrO₂ cylindrical pebbles (10 mm diameter and 12 mm length) were suspended in $\sim 200\text{ mL}$ of toluene in a 500 mL alumina bowl and were ground for 30 min in a planetary ball mill (Retsch, GmbH, Germany) by maintaining 200 rpm. The resultant dough was separated from toluene, dried at $\sim 90^{\circ}\text{C}$ for 12 h in an electrically heated oven and passed through a -30 BSS mesh to obtain granules with less than $595\text{ }\mu\text{m}$ prior to pressing into pellets. Binder burnout was operated at 500°C for 1 h prior to sintering at 1675 – 1700°C for 3–4 h in nitrogen atmosphere (~ 800 – 1100 torr) [19,21,24]. During sintering, these pellets were covered with 50 wt.% Si₃N₄ + 50 wt.% BN to protect them from decomposition and/or deformation.

2.3 Preparation of β -Si₄Al₂O₂N₆ powder by conventional extrusion method

In order to use it as one of the starting materials for preparing β -SiAlON-SiO₂ ceramic composites, the β -Si₄Al₂O₂N₆ powder was synthesized by reaction sintering of extrudates containing a powder mixture of 64.33 wt.% α -Si₃N₄, 23.36 wt.% α -Al₂O₃, 9.37 wt.% AlN (surface passivated against hydrolysis) and 7 wt.% Y₂O₃ (Table 2) at 1675°C for 4 h in N₂ atmos-

Table 2. The details of suppliers and the characteristics (BET surface area and average particle size values and the XRD phases) of various raw materials employed to consolidate β -Si₄Al₂O₂N₆ and β -SiAlON-SiO₂ ceramic composites

Raw material	Supplier and grade of the raw material	BET SA [m ² /g]	Average particle / agglomerate size [μm]	XRD phase
α -Al ₂ O ₃	HP Grade, ACC India Limited, India	1.24	1.39	Corundum
α -Si ₃ N ₄	SicoNide-P95H, VESTA Ceramics AB, Sweden	17.77	6.51	α -Si ₃ N ₄
Y ₂ O ₃	Rhodia Inc., Phoenix, Arizona, USA	3.41	3.23	Y ₂ O ₃
AlN	Grade AT, H.C. Stark, Germany	6.72	7.62	AlN
Fused silica	Chettinad Quartz Products Private Ltd., Chennai, India	-	19.95	Amorphous fused silica

phere [21,22]. In a typical experiment, the required amounts of precursor powders mixture was kneaded in a conventional dough making machine (Sigma Kneader, Prigmayers India Private Limited, India) with 3 wt.% methyl cellulose, 2 wt.% polyethylene glycol (PEG 400) (both are GR grade procured from Loba Chemie, Mumbai, India) and about 30 wt.% double distilled water to obtain an easily extrudable dough [68]. The resultant dough was then extruded through an indigenously designed and fabricated stainless steel die using a ram type extruder at a rate of 50 mm min⁻¹ under a pressure of 10–20 kg/cm² to form extrudates of about 5 mm thickness [68]. These extrudates were allowed to dry in an open-air atmosphere over night under ambient conditions, which were then cut into 5–6 mm length pieces. These cut pieces were then subjected to binder removal for 2 h at 500°C and then sintered for 4 h at 1675°C under a N₂ atmosphere of about 800 torr to form β-Si₄Al₂O₂N₆ extrudates [19]. During sintering, these extrudates were covered with a powder mixture consisting 50 wt.% Si₃N₄ + 50 wt.% BN to protect them against decomposition [18–22]. The sintered extrudates were crushed in a hammer mill followed by wet-grinding in a stainless steel jar (350 mm diameter and 400 mm height) using stainless steel balls with diameters of about 12 mm and 25 mm while maintaining 1:8 weight ratio of charge to balls. This milling operation was continued until the average particle size of β-Si₄Al₂O₂N₆ was around 3 μm [22]. From the resultant ground powder, the iron contamination was removed with the help of several magnets having dimensions of 30 mm diameter and 10 mm height.

2.4 Net-shape consolidation of β-Si₄Al₂O₂N₆ and β-SiAlON-SiO₂ ceramics by colloidal processing routes

The precursor mixture compositions employed for consolidating β-Si₄Al₂O₂N₆ and β-Si₄Al₂O₂N₆-9 wt.% SiO₂ composite ceramics by following different routes are summarized in Table 3. For the sake of an easy identification, different codes are given to denote these precursor mixture compositions. CDPP stands for conventional dry-powder pressing; GC stands for aqueous gelcasting; HAS stands for hydrolysis assisted solidification; GCHAS stands for hydrolysis induced aqueous gelcasting; SSC9 stands for β-Si₄Al₂O₂N₆-9 wt.% SiO₂ ceramic composite. Except for SSC9, all other samples' targeted chemical composition was β-Si₄Al₂O₂N₆. In the sample codes numbers (2–10) represent the amount of A-AlN in the precursor mixture, which would hydrolyze (AlN + 3H₂O → Al(OH)₃ + NH₃) in the slurry after casting in the non-porous moulds and the T-AlN stands for AlN powder surface treated against hydrolysis. The experimental procedures involved in consolidation of β-Si₄Al₂O₂N₆, β-Si₄Al₂O₂N₆-9 wt.% SiO₂ and 60 wt.% β-SiAlON + 40 wt.% SiO₂ ceramic composites by GC, HAS and GCHAS are presented briefly in the following sections.

2.4.1 Aqueous gelcasting (GC)

In a typical experiment, a precursor mixture (GC-SSC9 or GC, Table 3) was suspended in a premix solution, which has been prepared by dissolving either 20 wt.% methacrylamide (MAM), methylenebisacrylamide (MBAM) and n-vinylpyrrolidinone (NVP) in 3:1:3 ratio (termed as nonconventional premix solution, NCPM) or 17 wt.%

Table 3. Precursor mixtures used for preparing β-Si₄Al₂O₂N₆ ceramics and β-Si₄Al₂O₂N₆-9 wt.% SiO₂ ceramic composite by following a conventional dry-powder pressing (CDPP), aqueous gelcasting (GC-SSC9 and GC), hydrolysis assisted solidification (HAS-5 to HAS-15) and hydrolysis induced aqueous gelcasting (GCHAS-2 to GCHAS-10) techniques [19]

Sample code [†]	α-Si ₃ N ₄ [wt.%]	A-AlN [wt.%]	α-Al ₂ O ₃ [wt.%]	Y ₂ O ₃ [wt.%]	T-AlN [wt.%]
CDPP	64.33	9.37	23.36	7	-
GC-SSC9	62.77	-	30.22	7	-
HAS-5	64.33	5	18.36	7	9.37
HAS-10	64.33	10	13.36	7	9.37
HAS-15	64.33	15	8.36	7	9.37
GC	64.33	0	23.36	7	9.37
GCHAS-2	64.33	2	21.36	7	9.37
GCHAS-5	64.33	5	18.36	7	9.37
GCHAS-7	64.33	7	13.36	7	9.37
GCHAS-10	64.33	10	8.36	7	9.37

[†] CDPP stands for conventional dry-powder pressing; GC stands for aqueous gelcasting; HAS stands for hydrolysis assisted solidification; GCHAS stands for hydrolysis induced aqueous gelcasting; SSC9 stands for SiAlON-SiO₂ ceramic composite with 9 wt.% SiO₂; Except SSC9 (β-Si₄Al₂O₂N₆-9 wt.% SiO₂), all other samples' targeted chemical composition is β-Si₄Al₂O₂N₆. In the sample codes numbers (2–10) represent the amount of A-AlN in the precursor mixture, which would hydrolyze (AlN + 3H₂O → Al(OH)₃ + NH₃) in the slurry after casting in the non-porous moulds and the T-AlN stands for AlN powder surface treated against hydrolysis.

MAS and MBAM in 6:1 ratio in de-ionized water (termed as conventional premix solution, CPM), to achieve slurries with 45–50 vol.% solids [19,58]. A commercial amino alcohol, a cationic dispersing agent (Dolapix A88, Zschimmer & Schwarz, Berlin, Germany) was employed at the ratio of 25 $\mu\text{L/g}$ of powder mixture to improve the fluidity of the suspension. The resultant suspension was degassed for ~ 2 min after introducing an initiator (10 wt.% aqueous solution of ammonium per-sulphate, APS) and catalyst (tetramethylethylenediamine, TEMED) with the ratio of 4 and 2 μL per gram of slurry, respectively. Afterward, the slurry was cast into non-porous white petroleum jelly coated split-type aluminium moulds (60 mm \times 30 mm \times 30 mm), dried and sintered for 4 h at 1675 $^{\circ}\text{C}$ in N_2 (800 torr) atmosphere. However, by following this (GC) route, the fabrication of the $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ based radomes was found to be very difficult as the formed green radomes always cracked while taking out of the mould due to their very poor strength, hence, the product yield was found to be very low (<5%) [19,58].

The precursor mixture GC-SSC9 (Table 3) leads to the formation of $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6\text{-}0.5\text{SiO}_2$ ceramic composite ($1.5\text{Si}_3\text{N}_4 + \text{Al}_2\text{O}_3 \rightarrow \beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6 + 0.5\text{SiO}_2$) upon reaction sintering at elevated temperatures in N_2 atmosphere [18,19]. The 0.5 mol% silica (which is equivalent to 9.0 wt.%) formed *in situ* during the reaction reduces the dielectric constant and CTE of $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ material considerably because of its relatively low CTE ($<2 \times 10^{-6}/^{\circ}\text{C}$) and dielectric constant (<4) [18]. Since, this composition does not involve AlN as one of the starting raw materials, it is relative-

ly easy to process following aqueous gelcasting (GC) route for making $\beta\text{-SiAlON}$ radomes [18,22].

2.4.2 Hydrolysis assisted solidification (HAS)

In a typical experiment, a precursor mixture of HAS-2 to HAS-15 (Table 3) was initially suspended in doubly distilled water to obtain slurries with 48 to 50 vol.% solids loading [19,58,59]. To improve the dispersion of precursor mixtures and the fluidity of the slurry, Dolapix A88 was added in a ratio of 25 $\mu\text{L/g}$ of powder. All the slurries were degassed for ~ 5 min after milling for 16 h by vacuum pumping. All the above operations were carried out at room temperature. Afterwards, the slurries were cast into non-porous white petroleum jelly coated split-type aluminium moulds ($\sim 100/60$ mm \times 30 mm \times 30 mm), which were then allowed to set under ambient conditions for about 2 h followed by a stage at $\sim 60^{\circ}\text{C}$ till the completion of the setting process. The green bodies thus obtained were de-moulded and dried under controlled humidity (LHL-113; Espec Corporation, Japan) conditions to avoid cracking. These dried consolidates were also sintered along with those samples consolidated by GC route. However, by following this HAS route also the $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ radomes could not be fabricated due to the very brittle nature of the green parts [19,58,59].

2.4.3 Hydrolysis induced aqueous gelcasting (GCHAS)

The hydrolysis induced aqueous gelcasting (GCHAS) process enabled successful fabrication of both $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ as well as $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6\text{-SiO}_2$ ceramic composite radome structures [19,21,58]. In a typical experiment, to obtain $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ or $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6\text{-SiO}_2$ ceramic composite based slurries, respectively, a

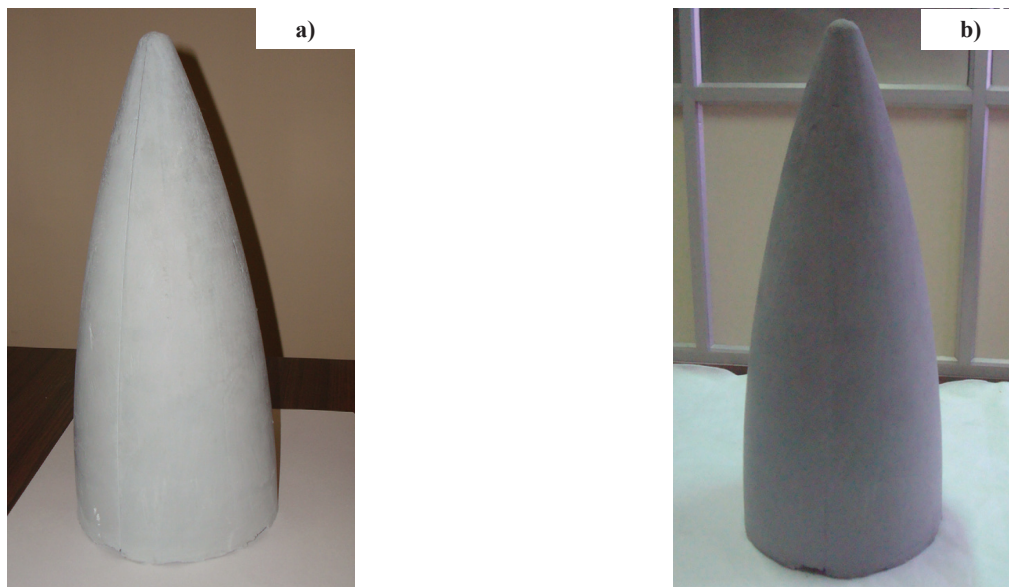


Figure 1. Photographs of green prototype radome shapes (about 290 mm height and 125 mm base diameter) consolidated by GCHAS route using (a) 50 vol.% GCHAS-5 precursor mixture (Table 3) and (b) 50 vol.% precursor mixture consisting 57.56 wt.% $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ + 38.37 wt.% fused silica + 4.06 wt.% as-purchased AlN powders, respectively

precursor mixture of GCHAS-2 to GCHAS-10 (Table 3) or a powders mixture of 60 wt.% β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ and 40 wt.% fused silica was dispersed in NCPM solution with the help of Dolapix A88 added with the ratio of 25 $\mu\text{L/g}$ of powder. After mixing the resultant slurry for ~ 16 h, A-AlN equivalent to 1–5 wt.% of Al_2O_3 was introduced into slurry and the mixing process was continued for further ~ 2 h. The resultant slurry was filtered off and degassed for 5 min by vacuum pumping. The slurry was once again degassed for ~ 2 min after introducing APS and TEMED at the ratio of 4 and 2 μL per gram of slurry, respectively. These degassed slurries were then cast into an indigenously designed and fabricated split type Teflon lined aluminium radome mould, and inserted aluminium solid mandrel into the slurry. After mandrel insertion, the slurry was allowed to gel completely in the mould itself under ambient conditions [19,21,63]. The slurry was constantly poured in excess amounts in the mould so that it overflows from top of the mould in order to remove the formed air/gas bubbles (if any were left after vacuum pumping) while inserting the mandrel into the slurry in the mould. Some rectangular (60 mm \times 30 mm \times 30 mm) pieces were always cast along with radome shape to check the condition of gel before removing the mandrel from the mould [19]. After confirming the gelation of the slurry, the mandrel was removed from the mould and then filled with polyethylene glycol-400 (PEG400) (AR grade, Loba-Chemie, Mumbai, India) [21,63]. Due to high chemical potential difference, the water moves from gel (i.e., from wet radome) into PEG [2]. After about 2 h, the PEG, followed by the wet-green radome was taken out of the mould by simply

tilting the mould up-side down. This wet radome was then placed in an humidity controlled oven (LHL-113; Espec Corporation, Japan), which was pre-set at 40°C and 90% RH [21,63]. Purposefully, the room temperature gelation was performed to avoid the temperature induced reactions between APS and Si_3N_4 raw material, which create a lot of porosity in the cast part, which will manifest even in the sintered parts [19,58]. After drying for 24 h at 40°C, the temperature in the humidity oven was slowly raised to 70°C and then to 90°C. At each of these temperatures the radome was held for ~ 24 h. Two prototype green radome structures formed from precursor mixture of GCHAS-5 (Table 3), and the powder composition of 57.56 wt.% β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ + 38.37 wt.% fused silica + 4.06 wt.% A-AlN, respectively, are shown in Fig. 1. The β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ based samples formed in this (GCHAS) route were sintered along with those formed in CDPP, GC and HAS routes at 1675°C for 4 h [19] and those formed from mixtures of β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ and fused silica were sintered for 3 h at 1750°C in about 900 torr N_2 pressure after subjecting them to binder burnout operation for 2 h at 500°C [21]. The radome structures were subjected to conformal sintering using graphite mandrel (Fig. 2a). A sintered and machined β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ proto-type radome is shown in Fig. 2b. The radome structures product yield in GCHAS process was found to be $>95\%$.

2.5 Characterization

The various techniques employed to characterize the above mentioned powders, suspensions and sintered materials were described in our previously reported papers [18–26,31,59–72].

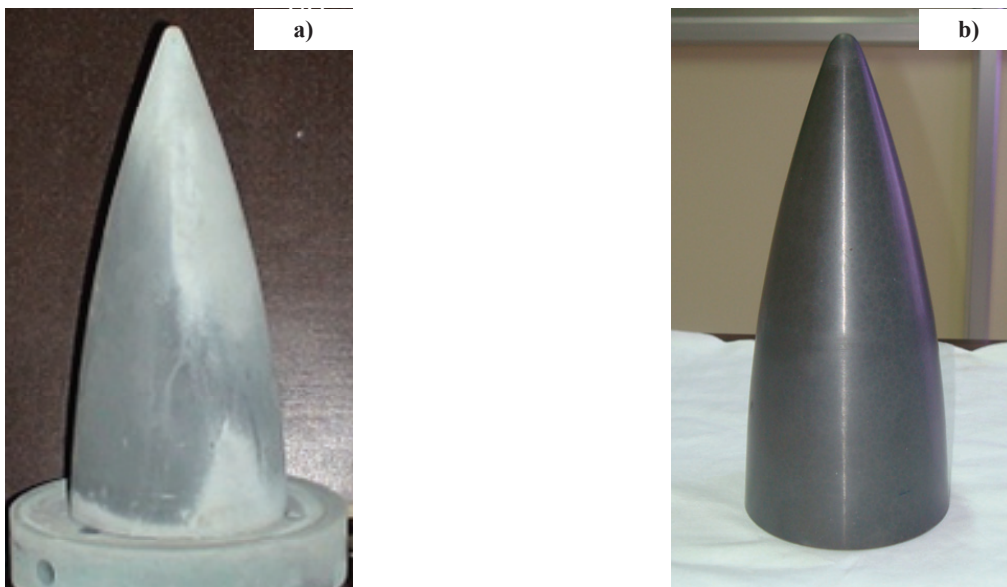


Figure 2. Photographs of (a) graphite mandrel used for conformal sintering of β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ radome structures and (b) conformal sintered (for 4 h at 1675°C in N_2 atmosphere under about 800 torr pressure) and machined β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ radome structure

III. Results and discussion

3.1 Influence of chemical composition on β -SiAlON properties

Figure 3 reveals the XRD patterns of β -SiAlON ceramics formed by reaction sintering of seven different types of precursor mixtures utilizing 7 wt.% Y_2O_3 at 1675°C for 4 h. This figure also lists different codes given to denote the ceramics [24]. In the sample codes, the numbers 1 to 4 represent the z value in the β -Si_{6-z}Al_zO_zN_{8-z} composition and the number 7 represents the concentration of sintering aid on total powder composition basis. It can be seen that all the materials are primarily β -SiAlON ceramics (Si₃Al₃O₃N₅; ICDD File No. 00-036-1333 and Si₄Al₂O₂N₆; ICDD File No. 00-048-1616). They contain some small amounts of impurities such as, Y₂SiAlO₅N [23]. The material, Z1Y7 additionally contain some small amounts of un-reacted alumina as well. With the gradual increase of z value in the composition, the intensity of XRD peaks due to β -SiAlON phase is increased gradually and there is a slight shift in the 2θ values. This small shift could be attributed to the increased contents of aluminium and oxygen ions entered into β -SiAlON unit cell network. Except, Z1Y7 (84.83%) and Z1.5Y7 (88.48%), all other materials exhibited >90% β -SiAlON phase. Interestingly, none of the sintered materials exhibited XRD peaks either due to α - or β -Si₃N₄ material confirming the formation of β -SiAlON phase upon reaction sintering. The increase of β -SiAlON phase with the increase of the z value (i.e. with Al₂O₃ and AlN concentration) could also be attributed to the increased diffusion of ions or to the enhanced reaction of precursor materials in relatively larger amount of tri-oxide eutectic melt (i.e. liquid-phase) formed due to the reactions between Al₂O₃ and Y₂O₃ and/or SiO₂ at <1600°C

[73]. The SiO₂ is a product of the surface oxidation of Si₃N₄, which is difficult to avoid. The amount of Si₃N₄ and Al₂O₃ required for the formation of β -Si₅Al₁O₁N₇ (Z1Y7) are about 80.57% and 11.71%, respective-

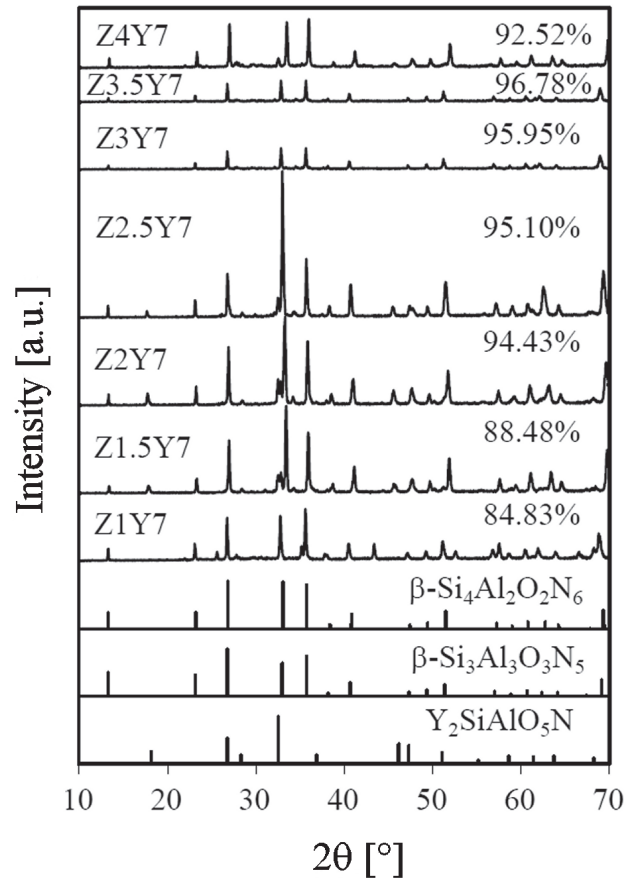


Figure 3. XRD patterns of various β -Si_{6-z}Al_zO_zN_{8-z} ($z = 1-4$) ceramics sintered with 7 wt.% Y_2O_3 at 1675°C for 4 h (Y₂SiAlO₅N - ICDD: 00-048-1627; β -Si₃Al₃O₃N₅ - ICDD: 00-036-1333; β -Si₄Al₂O₂N₆ - ICDD: 00-048-1616)

Table 4. GD of pressed compacts and BD, AP and WA of β -Si_{6-z}Al_zO_zN_{8-z} ($z = 1-4$) ceramics sintered at 1675°C for 4 h with 3 and 5 wt.% Y_2O_3 [24][†]

Composition	Materials sintered with 3 wt.% Y_2O_3					Materials sintered with 5 wt.% Y_2O_3				
	Code [‡]	GD [kg/m ³]	BD [kg/m ³]	AP [%]	WA [%]	Code [‡]	GD [kg/m ³]	BD [kg/m ³]	AP [%]	WA [%]
Si ₅ AlON ₇ (Z1)	Z1Y3	2050	2640	15.31	5.80	Z1Y5	1830	2750	9.34	3.39
Si _{4.5} Al _{1.5} O _{1.5} N _{6.5} (Z1.5)	Z1.5Y3	1850	2780	8.70	3.13	Z1.5Y5	1840	2850	6.33	2.22
Si ₄ Al ₂ O ₂ N ₆ (Z2)	Z2Y3	1880	2800	7.01	0.02	Z2Y5	1860	2930	3.85	1.31
Si _{3.5} Al _{2.5} O _{2.5} N _{5.5} (Z2.5)	Z2.5Y3	2000	2750	5.23	1.37	Z2.5Y5	1920	3010	3.01	1.40
Si ₃ Al ₃ O ₃ N ₅ (Z3)	Z3Y3	2020	2950	4.42	1.50	Z3Y5	1960	3000	3.00	1.55
Si _{2.5} Al _{3.5} O _{3.5} N _{4.5} (Z3.5)	Z3.5Y3	1930	3100	1.86	0.60	Z3.5Y5	1960	2890	2.08	0.71
Si ₂ Al ₄ O ₄ N ₄ (Z4)	Z4Y3	1970	3110	2.48	0.80	Z4Y5	1950	3020	6.15	2.03

[†] Values are derived as mentioned in the experimental section. GD-green density; BD-bulk density; AP-apparent porosity; WA-water absorption capacity.

[‡] In the sample codes, numbers 1, 1.5, 2, 2.5, 3, 3.5 & 4 represent the z value in β -Si_{6-z}Al_zO_zN_{8-z} composition and the numbers 3 and 5 represent the sintering aid (Y_2O_3) concentration in the composites.

ly, whereas, for $\text{Si}_2\text{Al}_4\text{O}_4\text{N}_4$ (Z4Y7), they are only about ~31.92% and 46.4%. Since, the ionic character of Al_2O_3 (63.21%) is higher than that of Si_3N_4 (30.23%), the precursor mixture with higher alumina content is expected to react more readily leading to the improved formation of β -SiAlON phase [73]. Furthermore, as ionic materials possess relatively weaker bonds, they would break up easily during reaction sintering leading to a faster diffusion of ions to form improved β -SiAlON content [73].

Table 4 presents the green density (GD) of consolidates formed in CDP process, and bulk density (BD), apparent porosity (AP) and water absorption (WA) capacity of various β -SiAlON ceramics sintered at 1675°C for 4 h with 3 and 5 wt.% Y_2O_3 . The values of GD, BD, AP, and WA together with the percentage of the ionic character, hardness, fracture toughness, coefficient of thermal expansion (CTE), content of XRD phase and dielectric constant of β -SiAlON ceramics sintered with 7 wt.% Y_2O_3 under identical sintering conditions are presented in Table 5. At the foot notes of these tables, the given sample codes are explained. It can be seen that, in general, the GD and BD values of the consolidates increased with the increase of z value as well as Y_2O_3 in the composition, and as a consequence, their AP and WA capacities values decreased. The increase of GD with the increase of z value could be attributed to the increased content of high density Al_2O_3 (3970 kg/m³) in the compacted consolidate. After sintering for 4 h at 1675°C, only Z3.5Y3, Z4Y3, Z2Y7, Z2.5Y7 and Z3Y7 materials exhibited BD values of >3020 kg/m³ (Tables 4 and 5). Recently, β -SiAlON with a BD of 3020 kg/m³ was found to be suitable for certain radome applications [2–5]. When sintered at 1700°C for 4 h with 7 wt.% Y_2O_3 all compositions except Z1Y7 and Z4Y7, exhibited BD values higher than 3020 kg/m³, and AP and WA capacity values lower than 1 and 0.5%, respectively. The rea-

son for not as good sintering of the extreme compositions of the β -SiAlON (i.e., Z1Y7 and Z4Y7) even with 7 wt.% Y_2O_3 could be mainly attributed to the non-uniform distribution of minor components of precursor mixtures in the pressed compact due to their smaller contents [2–5]. A close look at the data of Tables 4 and 5 reveals two important points. The first - as the z value increases, the sinterability of β -SiAlON ceramics in general increases irrespective of the Y_2O_3 concentration. In the case of materials with $z \geq 3.5$, even 3 wt.% Y_2O_3 is sufficient to densify the material to 3020 kg/m³ (i.e., >98% of theoretical density) at 1675°C for 4 h. The second - all samples, besides the ones with extreme compositions (i.e. β -Si₅AlON₇ and β -Si₂Al₄O₄N₄) in the wide range of β -SiAlON solid solutions [2–5], underwent reasonably acceptable densification upon sintering at 1675°C for 4 h in the presence 7 wt.% Y_2O_3 . The higher densification behaviour of β -SiAlON ceramics with higher alumina content could be explained based by their higher percentage of ionic character. The percentage of ionic character (IC) of Si_3N_4 , Al_2O_3 , AlN and Y_2O_3 were estimated to be 30.23%, 63.21%, 43.02% and 73.33%, respectively, as per the relation: $(\text{IC} = 1 - \exp[-1/4(X_A - X_B)^2])$, where X_A and X_B are the electronegativity of the bonding atoms). The Pauling's electronegativity (EN) data of Si - 1.8; Al - 1.5; Y - 1.2; O - 3.5; N - 3.0 was used in these calculations [74,75]. The percentage of ionic character data of the raw materials was used to calculate the percentage of ionic character of various β -SiAlON ceramics prepared in this study based on the rule of mixture of their values as presented in Table 5. As can be noted from this table, the percentage of ionic character is increased with the increase of alumina concentration. The presence of higher ionic character could be responsible for noted BD values more than 3020 kg/m³ for $\text{Si}_{2.5}\text{Al}_{3.5}\text{O}_{3.5}\text{N}_{4.5}$ (49.981%) and $\text{Si}_2\text{Al}_4\text{O}_4\text{N}_4$ (52.11%) ceramics upon sintering at

Table 5. Physico-mechanical properties of β -SiAlON ceramics sintered at 1675°C for 4 h [24][†]

Sample code [‡]	GD [kg/m ³]	BD [kg/m ³]	AP [%]	WA [%]	Ionic character [%]	CTE ($\times 10^{-6}/^\circ\text{C}$) (30-700°C)	Hardness [kg/mm ²]	Fracture toughness [MPa.m ^{1/2}]	β -SiAlON phase [%]	Dielectric constant at 17 GHz frequency
Z1Y7	1830	2830	7.09	2.50	38.903	-	-	-	84.83	5.67
Z1.5Y7	1880	2960	4.99	1.69	40.973	3.532	-	-	88.48	6.32
Z2Y7	1870	3070	0.01	0.00	43.363	3.628	1317±5	3.30±0.4	94.43	7.206
Z2.5Y7	1960	3050	0.04	0.01	44.958	3.778	1252±4	2.75±0.2	95.10	7.35
Z3Y7	1960	3020	0.01	0.01	47.788	3.827	1276±4	2.64±0.2	94.95	6.82
Z3.5Y7	1980	2990	0.31	0.10	49.981	4.405	1281±5	2.78±0.3	96.78	6.89
Z4Y7	1940	2920	4.72	1.61	52.110	4.657	1278±3	4.34±0.4	92.52	7.67

[†] Values are derived as mentioned in the experimental section; CTE-coefficient of thermal expansion; GD-green density; BD-bulk density; AP-apparent porosity; WA-water absorption capacity

[‡] In the sample codes, numbers 1, 1.5, 2, 2.5, 3, 3.5 & 4 represent the z value in β -Si_{6-z}Al_zO_zN_{8-z} composition and the number 7 represents the sintering aid (Y_2O_3) concentration in the composites.

1675°C for 4 h even with 3 wt.% Y_2O_3 employed. It is also a known fact that materials with higher percentage of ionic character (i.e. $\geq 50\%$) undergo higher densification in comparison to those having lower percentage of ionic character (i.e. $< 50\%$) such as Si_3N_4 , SiC, B_4C , etc. [73–75].

It can also be seen from Table 5 that all the materials exhibited reasonably high hardness (1252 to 1317 kg/mm²) and fracture toughness (2.64 to 4.34 MPa m^{1/2}) values. These fracture toughness values are well comparable with those values reported in the literature for similar ceramics [76]. The hardness of the material decreased and its fracture toughness increased with the increase of z value, i.e. with increase of aluminium and oxygen content in the β -SiAlON network. The three-point bend strength of $Si_4Al_2O_2N_6$ (Z2Y7) was found to be ~ 226 MPa after sintering at 1675°C for 4 h. A value of ~ 260 MPa was reported for the same composition made by an aqueous gelcasting route by ORNL, USA [2–5]. It has also been reported that with the increase of alumina content, the amount of liquid phase to be formed by reactions between Al_2O_3 and SiO_2 at an eutectic temperature of 1587°C is also increased [75]. It is a known fact that the liquid phase favours the formation of elongated grains during sintering operation and that presence in the case of high z materials could be responsible for the observed higher fracture toughness values.

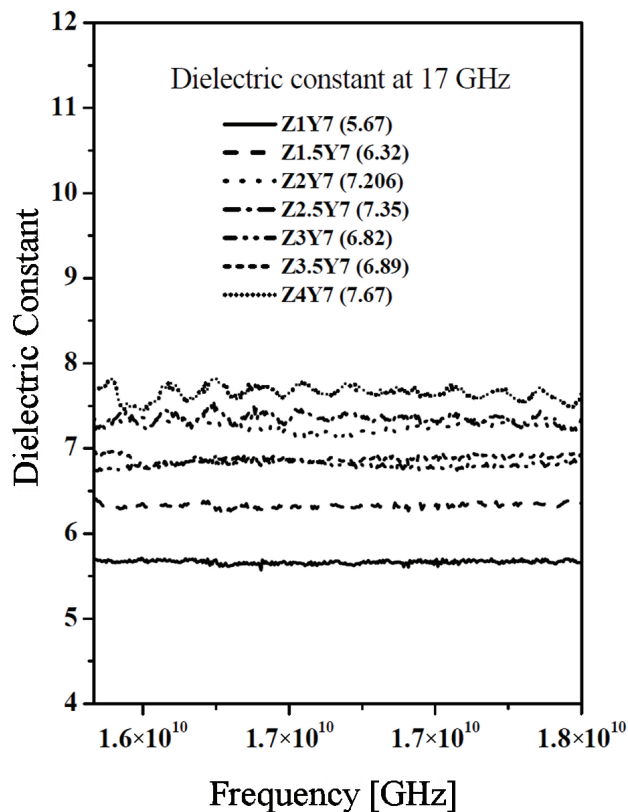


Figure 4. Influence of chemical composition on dielectric constant of β - $Si_{6-z}Al_zO_zN_{8-z}$ ($z = 1-4$) ceramics sintered with 7 wt.% Y_2O_3 at 1675°C for 4 h [24]

The SEM study of β - $Si_{6-z}Al_zO_zN_{8-z}$ ($z = 1, 1.5, 2, 2.5, 3, 3.5$ and 4) ceramics sintered with 7 wt.% Y_2O_3 at 1675°C for 4 h revealed the presence of only elongated (2 to 10 μm in length and 2 to 3 μm in diameter) grains in ceramics with $z = 2.5, 3, 3.5$ and 4, whereas, the combination of elongated and equi-axed grains (about $< 5 \mu m$ in diameter) in those with $z = 1, 1.5$ and 2 [24]. This study further revealed that there is a gradual decrease of porosity percentage in the micrographs with the increase of z value in β - $Si_{6-z}Al_zO_zN_{8-z}$. The ceramics with $z \leq 2.5$ had considerable amount of glassy phase. These results are also inline to the information reported in the literature [2–5].

Dielectric constants of β -SiAlON ceramics (Z1Y7-Z4Y7, Table 5) sintered at 1675°C for 4 h are recorded in the frequency range of 16 to 18 GHz and the corresponding profiles are presented in Fig. 4. It can be seen that all the materials exhibited reasonably stable and low dielectric constant values. At 17 GHz, the dielectric constant of these materials varied between 5.67 and 7.67. It is known that the overall dielectric constant of a material originates from different polarisation mechanisms such as electronic (P_e), ionic (P_i), orientation (P_o), space charge (P_{sc}), etc., and it is also highly influenced by the material composition, frequency of applied field, temperature of the dielectric, humidity, crystal structure, etc., and by other external factors including porosity [77,78]. Further, the polarisations from P_e and P_i are mostly composition dependent, instantaneous, or nearly frequency independent for most dielectrics and only marginally affected by temperature, and on the hand the P_o is both frequency (time) and temperature dependent. This polarisation is slower than the ionic polarisation. The P_{sc} is associated with ion migration, presence of grain boundary or inhomogeneous phases in the dielectric and is the slowest process [77]. Since, in the present case, the applied frequency is varied through 16 to 18 GHz at ambient conditions, the operative polarisations are mainly electronic, and ionic [77,78]. As there is no apparent correlation between the porosity and dielectric constant data of the β -SiAlON ceramics (Table 5), the observed differences in the dielectric constant values could be related to the differences mainly in the chemical compositions. For example, materials with $z = 3, 3.5$ and 4 have apparent porosity (AP) values of 0.01, 0.31 and 4.72%, respectively, whereas, their corresponding dielectric constant values are 6.82, 6.89 and 7.67, respectively. If the porosity had a strong influence on the measured dielectric constant of these materials, there should have been a decreasing trend in the dielectric constant values with the increase of porosity. However, such trend is absent in the present case (Table 5). Thus, it can be inferred from these results that the presence of negligible amount of porosity could be responsible for not finding any correlation between AP and dielectric constant values of these materials. The die-

1133) indicating that the surface treated AlN powder is quite stable in water. SEM micrograph and EDAX spectra of T-AlN-72h are presented in Fig. 8a,c and of A-AlN-72h in Fig. 8b,d, respectively. The A-AlN powder (having average particle size of $\sim 7.62 \mu\text{m}$) converted into relatively large sized agglomerates ($>50 \mu\text{m}$) after suspending in water for 72 h. A close look at its micrograph (Fig. 8b) gives an impression that the fine A-AlN-72h particles are fused together to form continuous cement like network after suspending in water for 72 h. EDAX results reveal that T-AlN-72h (Fig. 8c) consists nitrogen as a major element, whereas, A-AlN-72 h (Fig. 8d) consists Al and O as major constituents. The XRD, SEM and EDAX study confirmed that a major part of the as-purchased AlN (A-AlN) was converted into $\text{Al}(\text{OH})_3$ upon suspending in water for 72 h, whereas the T-AlN is quite stable after being suspended in water for 3 days [31,32].

3.3 Properties of aqueous processed $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ ceramics

The component making capability of GC, HAS and GCHAS processes from aqueous $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ precursor mixtures' slurries could be seen from Table 6 [19,58]. This table also shows the medium employed for each slurry preparation, the conditions of green radomes/crucibles/tubes and rectangular bars formed in each process, the amount of time taken for each process and the solids loading and absolute viscosity of the slurry. Many details pertaining to these slurries' preparations are given at the footnotes of this table. The precursor mixtures compositions employed for preparing each of suspensions are presented in Table 3 [19]. Nor-

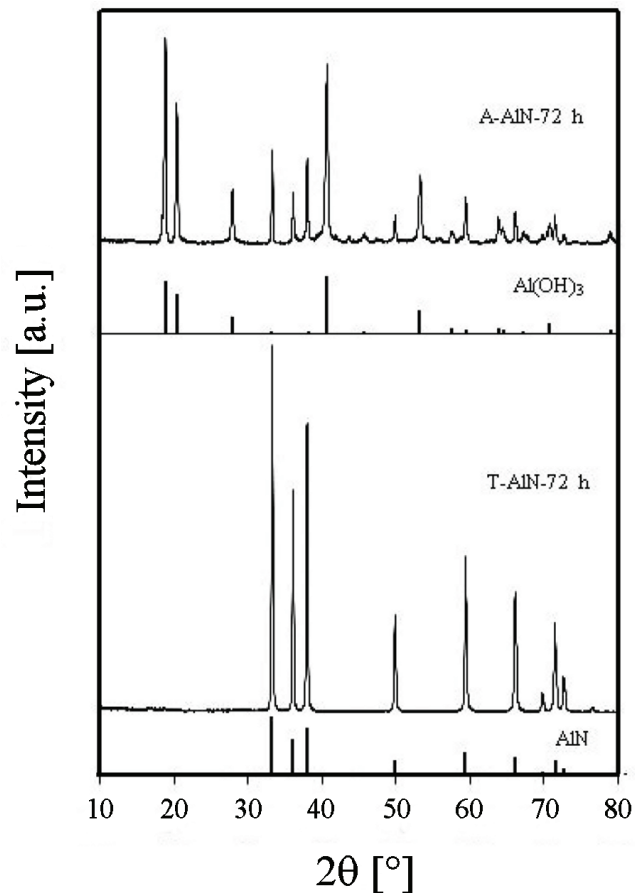


Figure 7. XRD patterns of different AlN powders (AlN - ICDD: 00-025-1133; and $\text{Al}(\text{OH})_3$ - ICDD: 00-020-0011) [19]

Table 6. Slurry characteristics and condition of green radomes, crucibles, tubes and rectangular bars consolidated from aqueous particulate slurries containing 48-50 vol.% $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ precursors mixtures by following HAS (HAS-5 to HAS-15), GC (GC-SSC9 and GC) and GCHAS (GCHAS-2 to GCHAS-10) routes [19]

Sample code	Solids loading [vol.%]	Viscosity [mPa·s]	Slurry medium [†]	Gelation conditions	Condition of the green rectangular bar	Condition of green crucible/tube/radome
GC-SSC9	48	288.5	CPM / NCPM	3 h at 30°C	Acceptable	Acceptable
HAS-5	50	299.6	Water	3 h at 30°C followed by 6 h at 60°C	Acceptable	Not acceptable
HAS-10	50	514.5	Water	3 h at 30°C followed by 6 h at 60°C	Not acceptable	Not acceptable
HAS-15	50	823.0	Water	3 h at 30°C followed by 6 h at 60°C	Not acceptable	Not acceptable
GC [‡]	48	678.0	NCPM	3 h at 30°C followed by 2 h at 60°C	Acceptable	Acceptable
GC [§]	50	246.0	NCPM	3 h at 30°C followed by 6 h at 60°C	Acceptable	Not acceptable
GCHAS-2	50	248.4	CPM / NCPM	3 h at 30°C followed by 2 h at 60°C	Acceptable	Acceptable
GCHAS-5	50	276.8	CPM / NCPM	20 min at 30°C	Acceptable	Acceptable
GCHAS-7	50	512.7	CPM / NCPM	15 min at 30°C	Acceptable	Acceptable
GCHAS-10	50	717.8	CPM / NCPM	15 min at 30°C	Not acceptable	Not acceptable

[‡]Details are given in the experimental section; [§]Involves treated AlN powder without washing.

[†]Involves treated AlN (T-AlN) powder after washing with absolute ethanol for 48 h.

[‡]NCPM stands for non-conventional premix solution formed by the dissolution of 20 wt.% MAM, MBAM, and NVP in 3:1:3 ratio in distilled water, CPM stands for conventional premix solution formed by the dissolution of 17 wt.% MAM and MBAM in 3:1 ratio in distilled water.

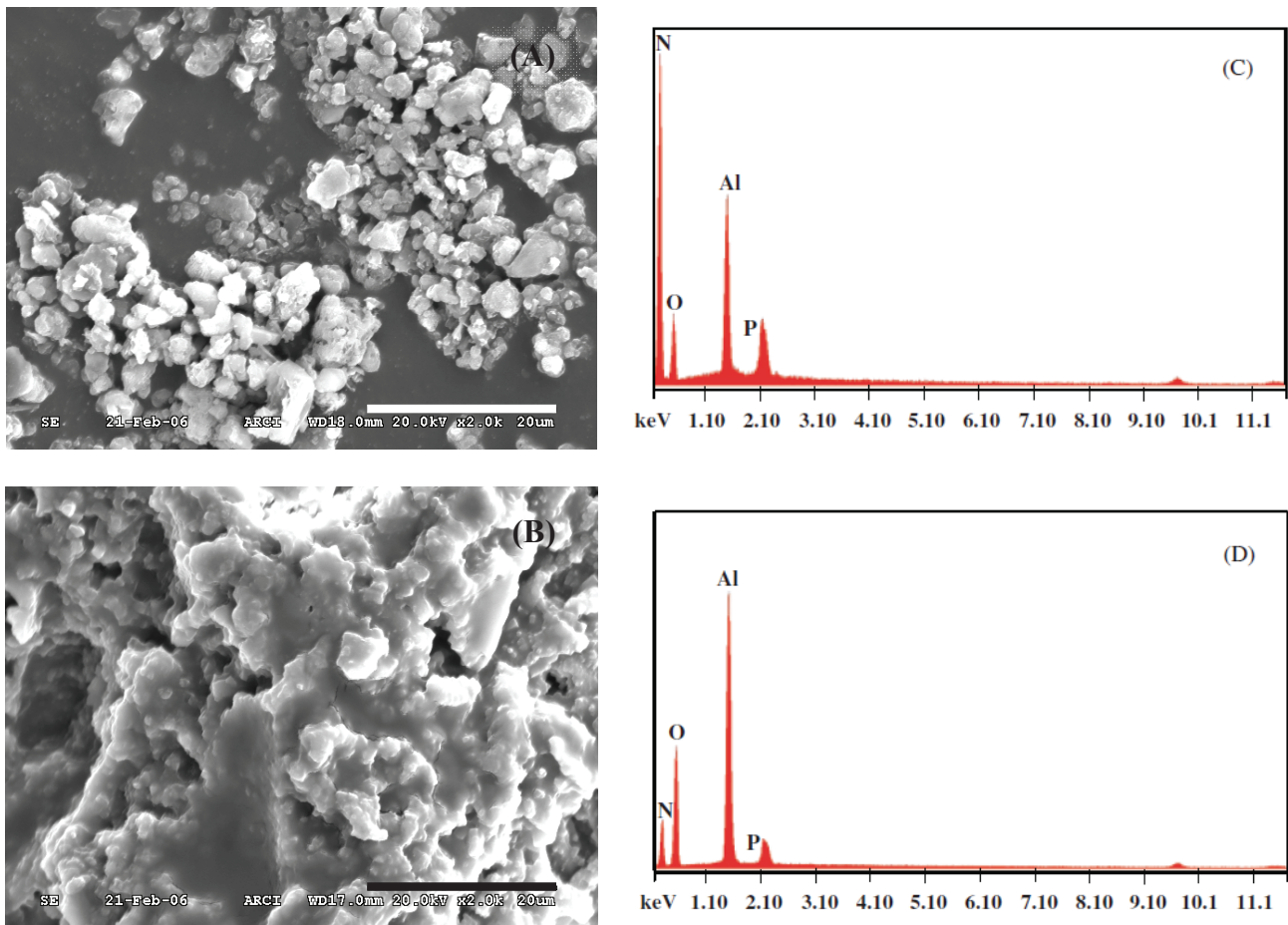


Figure 8. SEM micrograph and EDAX spectra of T-AlN-72h (a & b), and A-AlN-72h (c & d), respectively [19]

mally, to obtain a defect free consolidate by any colloidal processing route, the viscosity of the slurry should be kept ≤ 300 mPa·s [22]. Although aqueous gelcasting (GC) is known for providing exceptionally high flexural strength to the green bodies, fabrication of certain structures such as radomes, crucibles, tubes, etc., following this route is relatively difficult. This is due to the fact that the mandrel needs to be removed from the mould prior to the cast part gets completely gelled/dried, which causes breaking of the part within the mould due to excess shrinkage of the part when the solids loading in the slurry is not optimum. The minimum solids loading required for making defect free radomes, crucibles and tubes out of β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ precursor mixtures' slurries was found to be 48 vol.% [19,58]. When the solids loading was less than this ratio, the slurry took more time to get gelled to the required extent. Furthermore, in this case, the gelled parts were always found to be cracked as the mandrel could not allow the part to shrink to get the enough strength.

The slurries consisting of precursor mixtures of GC-SSC9, HAS-5, GCHAS-2, GCHAS-5, and GC with partially washed T-AlN (Table 6) exhibited absolute viscosity values < 300 mPa·s. The green parts cast out of all of these slurries had shape integrity upon drying, and they exhibited green densities $> 50\%$ of the theoret-

ical density (TD) upon drying. The HAS-5 slurry exhibited a viscosity < 300 mPa·s, which was responsible for forming acceptable quality rectangular bars (Table 6). Although the rectangular bars formed out of HAS-10 and HAS-15 were found to be very strong, they had considerable amount of porosity in them. Further, none of the HAS suspensions led to the formation of defect free radome/crucible/tube structures.

In the case of GC slurries (Table 6), they needed ~ 10 μL of APS (initiator) and ~ 10 μL of TEMED (catalyst) per gram of slurry to convert into gel. Furthermore, this slurry could not be converted into gel under ambient conditions but converted at ~ 55 – 60°C in an electrically heated oven. Furthermore, in this case, the surface passivated AlN powder against hydrolysis (T-AlN) had a strong influence on the slurry viscosity and on its gelation behaviour. When T-AlN was not washed thoroughly with absolute ethanol in order to remove the un-reacted excess phosphate ions from its surface completely, an improved gelation of slurry was noted in comparison to the one involved the fully washed T-AlN powder [19]. These results suggest that prolonged washing of T-AlN with absolute ethanol creates certain specific sites, which preferentially interact with APS free radicals during polymerisation of organic gelcast monomers, i.e. MAM, MBAM and NVP. In this case, the number of

APS free radicals available for initiating the polymerization reaction of organic monomers would be lowered, hence a delayed or weak gelation. However, when the as treated T-AlN was employed without much washing, the slurry underwent relatively faster gelation though it has restricted the maximum achievable solids loading in the slurry to only 48 vol.% only. In addition to this, this slurry (GC) also consumed about 2 to 6 h time at 55–60°C to undergo complete gelation. The temperature induced gelation is not recommended for SiAlON ceramics as there will be considerable number of gas releasing reactions between Si_3N_4 and APS/TEMED that creates a lot of porosity in the green body. Nevertheless, GC could not lead to any radome or crucible shape even upon temperature induced gelation (Table 6) [19].

On the other hand, the slurries, GCHAS-2 to GCHAS-7 exhibited faster gelling behaviour upon introducing APS and TEMED even at the ratio of 2 and 4 μL per gram of slurry, respectively, under simple ambient conditions (Table 6). The time consumed in setting of GCHAS-5 at ambient conditions was found to be <20 min. Nevertheless, this time could always be delayed by adding relatively smaller amounts of APS and TEMED or by cooling the slurry close to $\sim 5^\circ\text{C}$ in a refrigerator prior to introducing APS and TEMED [22]. The improved gelation in the case of GCHAS process could be ascribed to the synergy of HAS and GC processes. The gelled parts of GCHAS-5 and GCHAS-7 slurries were found to be like a strong rubber until they were completely dried. These parts were also found to be relatively stronger than those formed out of GC and HAS slurries. Thus, these results clearly reveal that the GCHAS is a more promising technique for making thin wall $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ radomes, crucibles, tubes, etc., with near-net shape in comparison to HAS and GC processes.

Table 7 reveals the values of bulk density (BD), apparent porosity (AP), water absorption capacity (WA), total linear shrinkage (LS), hardness, fracture toughness and $\beta\text{-SiAlON}$ phase contents of $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ ceramics consolidated from slurries containing HAS-5, GC and

GCHAS-5 precursor mixtures (Table 3) and sintered for 4 h at 1675°C , and of $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ -9 wt.% SiO_2 ceramic composite consolidated from a slurry having GC-SSC9 precursor mixture and sintered for 4 h at 1750°C along with the green density (GD) values of these consolidates [19]. It can be seen that both $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_4$ and

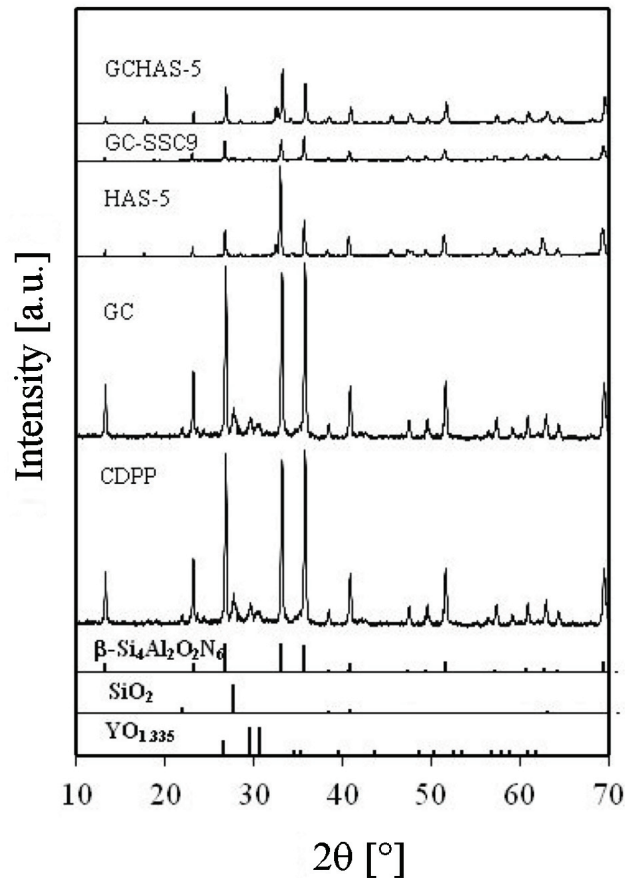


Figure 9. XRD patterns of $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ ceramics formed from (a) HAS-5, (b) GC and (c) GCHAS-5 precursor mixtures and of $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ -9 wt.% SiO_2 ceramic composite formed from (d) GC-SSC9 precursor mixture, sintered at 1675°C and 1750°C , respectively (YO_{1.335} - ICDD: 00-039-1065; SiO₂ - ICDD: 01-085-0462; $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ - ICDD: 00-48-1616)

Table 7. Properties of $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ (HAS-5, GC and GCHAS-5) ceramics and $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ -9 wt.% SiO_2 ceramic composites (GC-SSC9) sintered at 1675°C and 1750°C for 4 h, respectively [19]

Sample codes [§]	GD [kg/m ³]	BD [kg/m ³]	AP [%]	WA [%]	Total linear shrinkage [%]	$\beta\text{-SiAlON}$ phase [%]	Hardness [kg/mm ²]	Fracture toughness [MPa·m ^{1/2}]
GC-SSC9 [‡]	1750	3130	1.0	1.0	~17	~90	1356±8	3.42±0.3
HAS-5	1730	3120	0.47	0.16	~14	~94	1571±11	3.42±0.2
GC	1860	3070	0.13	0.04	<16	~93	1423±4	3.95±0.3
GCHAS-5	1960	3150	0.01	0.01	<16	~94	1495±7	3.56±0.2

[§] SSC9 stands for SiAlON-SiO₂ ceramic composite having 9 wt.% SiO₂; GC stands for aqueous gelcasting; HAS stands for hydrolysis assisted solidification; GCHAS stands for hydrolysis induced aqueous gelcasting; 0 and 5 indicates AlN content in the precursor mixtures; GD-green density; BD-bulk density; AP-apparent porosity; WA-water absorption capacity

[‡] Made using slurry containing 48 vol.% precursor solids, and the rest are made used slurries containing 50 vol.% precursor solids loading.

β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ -9 wt.% SiO_2 ceramics exhibited BD values $>3020 \text{ kg/m}^3$. The small difference seen in the GD values seems to have little effect on their densification behaviour upon sintering as all these sintered ceramics exhibited almost similar BD values (i.e., 3070 to 3150 kg/m^3). The total LS associated with ceramics made from slurries containing HAS-5, GC and GCHAS-5 precursor mixtures were found to be less than 17%, which is well within the acceptable range for making complex-shaped parts [2,22]. The higher sintering behaviour of β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ precursor mixtures used in this study could be attributed not only to the use of higher sintering temperature (1675°C for 4 h) and the Y_2O_3 content (7 wt.%), but also to the involvement of high purity powders having small average particle sizes. The reason for requiring higher sintering temperature (i.e. at 1750°C for 4 h) for β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ -9 wt.% SiO_2 ceramic composite in comparison to β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ ceramics could be attributed to the excess 9.0 wt.% SiO_2 present in the former material. The SiO_2 is known for restricting grain diffusion to some extent by forming a high viscous liquid during sintering thereby demanding the higher sintering temperatures [18,23,34–37,73].

XRD patterns of various β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ ceramics sintered for 4 h at 1675°C, and of β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ -9 wt.% SiO_2 ceramic composite sintered for 4 h at 1750°C are presented in Fig. 9 [19]. It can be seen that all the materials are fully crystalline and are mainly ($>90\%$) β - SiAlON ceramics (ICDD File No.: 00-48-1616) phase. The formation of $\text{Y}_2\text{SiAlO}_5\text{N}$ (ICDD File No.: 00-048-1627) is expected in these materials due to the reactions between SiO_2 , Al_2O_3 and Y_2O_3 at sintering temperature; however, no characteristic peaks belonging to this phase are noticed. The probable reason for not detecting any characteristic peaks of this phase is the crystallite size of this material could be below the detection limit of XRD technique. However, some minor peaks belonging to SiO_2 (ICDD File No.: 00-085-0462) and $\text{YO}_{1.335}$ (ICDD File No.: 00-039-1065) are revealed by ceramics consolidated from CDPP and GC precursor mixtures, both of which are the starting materials for $\text{Y}_2\text{SiAlO}_5\text{N}$ formation. These XRD results are well-comparable with those reported by Janney and others [3–5]. Although β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ -9 wt.% SiO_2 ceramic composite contains $\sim 9 \text{ wt.}\%$ free SiO_2 , no characteristics XRD peaks due to this silica phase are seen [18]. It has been reported that

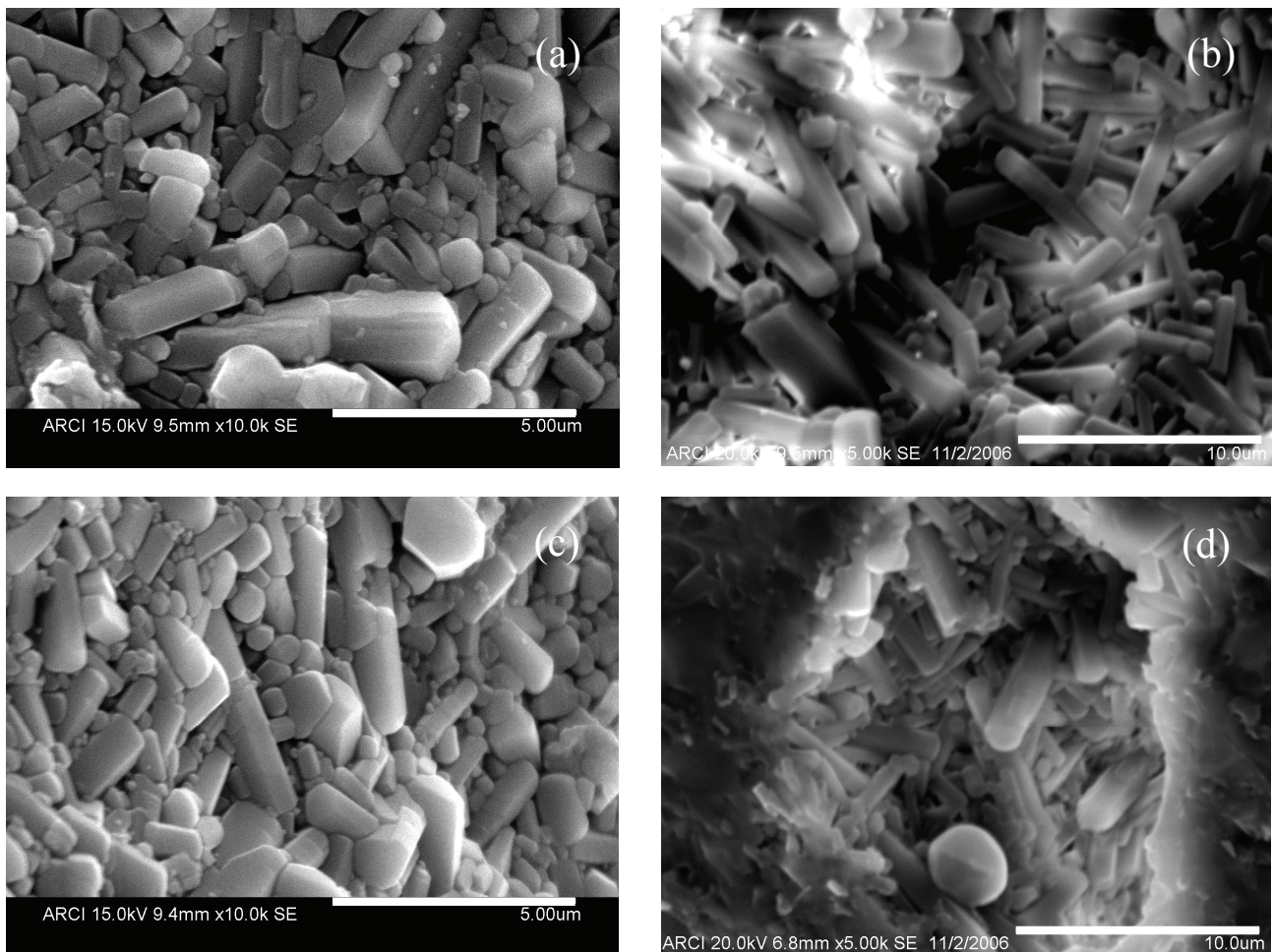


Figure 10. SEM micrographs of different types of β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ ceramics formed from (a) HAS-5, (b) GC and (c) GCHAS-5 precursor mixtures and of β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ -9 wt.% SiO_2 ceramic composite formed from (d) GC-SSC9 precursor mixture, sintered at 1675°C and 1750°C, respectively [19]

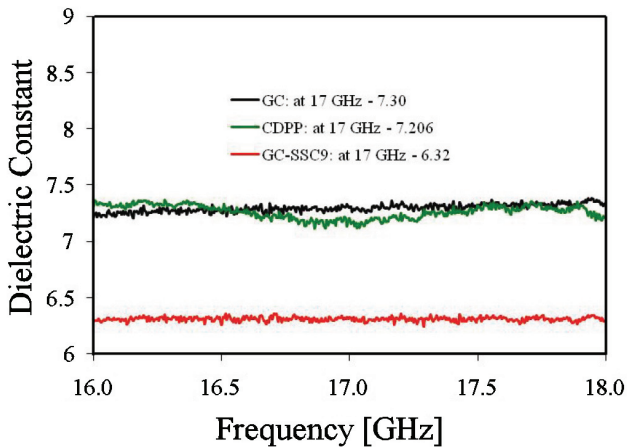


Figure 11. Dielectric constant profiles of different types of $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ ceramics formed from GC and CDPP precursor mixtures and of $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ -9 wt.% SiO_2 ceramic composite formed from GC-SSC9 precursor mixture, sintered at 1675°C and 1750°C, respectively [19]

SiO_2 formed by the surface oxidation of Si_3N_4 is always in the form of amorphous phase and it reveals no characteristic XRD lines. Furthermore all these sintered materials exhibited reasonably high hardness (1317–1571 kg/mm^2) and fracture toughness (3.30–3.95 $\text{MPa}\cdot\text{m}^{1/2}$) values (Table 7) [2].

The SEM micrographs of the colloidal processed $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ ceramics formed from HAS-5, GC and GCHAS-5 precursor mixtures at 1675°C for 4 h, and the $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ -9 wt.% SiO_2 ceramic composite formed from GC-SSC9 precursor mixture at 1750°C for 4h are presented in Fig. 10. It can be seen that ceramics formed from HAS-5 (Fig. 10a) and GCHAS-5 (Fig. 10c) precursor mixtures consist of similar microstructures having a bimodal grains (one type being in the size range of 1–2 μm and others being $\sim 5 \mu\text{m}$). Interestingly, the ceramic formed from GC precursor mixture (Fig. 10b) con-

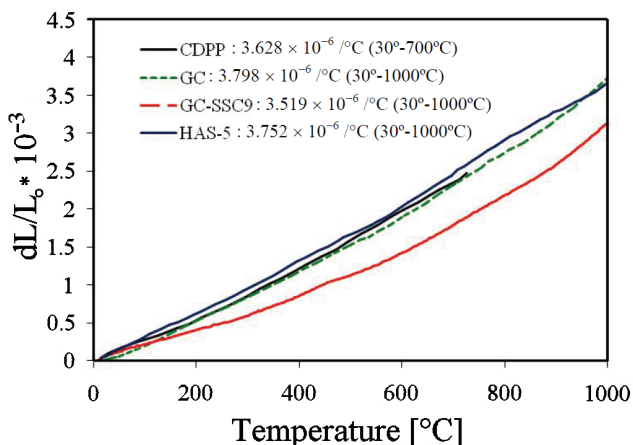


Figure 12. CTE profiles of different types of $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ ceramics formed from CDPP, GC and HAS-5 precursor mixtures and of $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ -9 wt.% SiO_2 ceramic composite formed from GC-SSC9 precursor mixture, sintered at 1675°C and 1750°C, respectively [19]

sist of almost mono-modal hexagonal grains with 1–2 μm in diameter and 5–10 μm in length. Although, the $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ -9 wt.% SiO_2 ceramic composite (Fig. 10d) also consist of similar type of grains, it has some additional grains with equi-axed shape. Further, this latter material contains some pores with $\sim 10 \mu\text{m}$ diameter in size. These SEM findings are inline to those reported for $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ ceramics formed in CDPP technique [24].

Dielectric constant profiles recorded for $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ ceramics formed from GC and CDPP precursor mixtures at 1675°C for 4 h and for $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ -9 wt.% SiO_2 ceramic composite formed from GC-SSC9 at 1750°C for 4 h are presented in Fig. 11 in the frequency range of 16 to 18 GHz. It can be seen that these three materials exhibited reasonably stable and low dielectric constant values. At 17 GHz, the ceramics formed from CDPP and GC precursor mixtures exhibited 7.206 and 7.30 dielectric constant values, respectively, whereas, the one formed from GC-SSC9 exhibited a value of 6.32. Since, in the present case, the applied frequency is varied from 16 to 18 GHz at ambient temperature, the operative polarisation mechanisms are mainly electronic, and ionic [75,76]. Furthermore, as these three materials exhibited very similar apparent porosity values (Table 7), the differences observed in their dielectric values do not seem to be influenced by the porosity alone but also by the chemical composition and other factors. The difference between the AP values of GC-SSC9 and others is only about 0.65% (Table 7), whereas the difference in their dielectric constant values at 17 GHz is $\sim 13\%$. This data clearly indicates that the reason for difference in dielectric constant values measured for these ceramics is mainly the chemical composition as GC-SSC9 has ~ 9 wt.% excess SiO_2 in it when compared with $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ ceramics. The dielectric constant reported for a gelcast $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ varied from 6.84 to 7.46 [6–8]. Thus, the observed dielectric constant values for these synthesized materials are comparable with the reported results in the literature [6–8].

CTE profiles recorded in the range of 30–1000°C for aqueous colloidal processed $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ ceramics formed from CDPP, GC and HAS-5 precursor mixtures at 1675°C for 4 h and for $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ -9 wt.% SiO_2 ceramic composite formed from GC-SSC9 precursor mixture at 1750°C for 4 h are presented in Fig. 12. The CTE values recorded for these ceramics are $3.628 \times 10^{-6}/^\circ\text{C}$ (30–700°C), $3.798 \times 10^{-6}/^\circ\text{C}$, $3.752 \times 10^{-6}/^\circ\text{C}$, and $3.519 \times 10^{-6}/^\circ\text{C}$, respectively. The GC-SSC9 exhibited a relatively low CTE value ($3.519 \times 10^{-6}/^\circ\text{C}$) due to the presence of excess 9.0 wt.% SiO_2 in it, while the other materials exhibited CTE values comparable to those reported in the literature for $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ [2–5]. A gelcast $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ exhibited a value of $4.1 \times 10^{-6}/^\circ\text{C}$ between 25 and 1000°C [2]. Thus, this CTE study also reveals that $\beta\text{-Si}_4\text{Al}_2\text{O}_2\text{N}_6$ ceramics consolidated by CDPP, HAS, and GC routes are well comparable.

Table 8. The raw materials composition, the values of green density of pressed pellets and of various properties of reaction sintered β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ (SS), β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ densified from its powder (SSC0), ceramic composites (SSC20 to SSC80) prepared from β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ and fused silica powder mixtures, and of pure fused silica (SSC100) sintered for 3–4 h at 1500 to 1750°C under ~ 101.63 kPa N_2 pressure [21]

Ceramic composite (code) †	SSC0	SSC20	SSC40	SSC50	SSC60	SSC80	SSC100	SS
* β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ [wt.%]	100	80	60	50	40	20	0	α - Si_3N_4 , α - Al_2O_3 ,
*Fused silica [wt.%]	0	20	40	50	60	80	100	AlN & Y_2O_3
Green density of pressed compact [kg/m^3]	1720	1890	1830	1660	1520	1630	1140	1770
Sintering condition employed [$^\circ\text{C}/\text{h}$]	1750/3	1750/3	1750/3	1500/4	1500/4	1500/4	1675/4	1675/4
BD [kg/m^3]	3210	2840	2510	2450	2480	2260	1970	3080
AP [%]	0.01	2.47	5.44	2.15	3.29	4.72	10.72	0.19
WA [%]	0.01	0.87	2.16	0.87	1.32	2.08	5.44	0.12
LS [%]	10.15	10.29	10.68	8.77	9.99	10.69	12.41	14.0
Hardness [kg/mm^2]	1407	1347	1319	957	931	766	407	1317
Mass loss upon sintering [%]	4.86	8.03	16.69	5.57	3.35	5.03	3.90	4.46

† Values were obtained as mentioned in the experimental section.

* Starting raw materials utilized

‡ In the sample codes, SS stands for reaction sintered stoichiometric β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ prepared from the precursor mixture of α - Si_3N_4 , α - Al_2O_3 , AlN and Y_2O_3 , and the SSC stands for ceramic composites prepared from a powder mixture of β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ and fused silica, and the numbers 0–100 represent the fused silica content in the β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ and fused silica mixtures employed to prepare these ceramic composites; BD-bulk density; AP-apparent porosity; WA-water absorption capacity

3.4 Properties of dense β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ - SiO_2 ceramic composites (SSC0 to SSC100)

Table 8 lists the raw materials compositions and the values of green density (GD) of consolidates made by CDPP route, and of bulk density (BD), apparent porosity (AP), water absorption (WA) capacity, linear shrinkage (LS), hardness and percentage of mass loss (ML) occurred upon sintering of β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ - SiO_2 ceramic composites at 1500–1750°C for 3–4 h. For the sake of an easy identification, different codes are also given to denote these ceramic composites. In the sample codes SS stands for the reaction sintered stoichiometric β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ ceramic, and the SSC stands for ceramic composite formed from the powder mixture of β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ and fused silica, and the numbers 0–100 represent the fused silica (SiO_2) content in the starting raw materials compositions. Prior to measuring the properties presented in Table 8, and in order to find the optimum sintering condition needed to densify each composition, all samples consolidated by CDPP route were sintered at temperatures in the range of 1500°C to 1750°C for 3–4 h, and then characterised to evaluate their shape integrity (i.e. whether the material got melted/deformed or not) and the sintered density. The characterization results of these sintered ceramic composites revealed the following observations. (i) There is a gradual increase in the value of green density of the pressed consolidate with the increase of β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ content in it (Table 8). This is due to the fact that the fused silica possesses a lower bulk density ($2200 \text{ kg}/\text{m}^3$) than that of β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ ($3100 \text{ kg}/\text{m}^3$). (ii) In general, the compositions having ≥ 50 wt.% fused silica (i.e. SSC50, SSC60

and SSC80) underwent early densification at relatively lower temperatures (at about 1500°C) in comparison to β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ rich compositions (i.e., SSC20 and SSC40), and to the pure fused silica (SSC100). The latter compositions exhibited best-sintered properties only upon sintering at 1750°C and 1675°C, respectively. The reason for early densification of fused silica rich compositions in comparison to the pure fused silica could be the formation of eutectic melts out of Y_2O_3 , Al_2O_3 and SiO_2 at 1350°C during sintering. (iii) The green density values estimated based on dimensions of these pressed pellets varied in the range of $1140 \text{ kg}/\text{m}^3$ (for pure fused silica consolidated by CDPP route, SSC100) to $1890 \text{ kg}/\text{m}^3$ (for SSC20). These green density values are comparable with those reported for similar kinds of ceramics consolidated by CDPP route [2–5,21,22] (iv) The β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ densified from its same powder (i.e. SSC0) exhibited a very low apparent porosity value of $<0.5\%$ after sintering at 1750°C, whereas, all the remaining ceramic composites exhibited significantly higher apparent porosity values (up to 10.72% for SSC100) even after sintering at such high temperatures. (v) Among all the sintered samples, the reaction sintered β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ (SS) exhibited the highest degree of linear shrinkage (about 14%) followed by the pure sintered fused silica (SSC100), i.e. 12.41% [2–7,21,30]. The remaining sintered composites exhibited linear shrinkage values which are comparable to those reported for similar materials consolidated by CDPP followed by sintering [21,22]. It can also be seen from Table 8 that SSC0 to SSC40 exhibited relatively higher hardness ($>1310 \text{ kg}/\text{mm}^2$) values in comparison to others,

which showed values in the range of 407 to 957 kg/mm². The presence of relatively densely packed elongated grains (discussed in the following paragraphs) in the case of β -Si₄Al₂O₂N₆ rich composites (i.e. SSC0 to SSC40) could be responsible for the such higher measured hardness values. Furthermore, all the SiAlON-SiO₂ ceramic composites exhibited considerable amounts of mass losses upon sintering which was to be expected for Si₃N₄ based ceramics [21,22]. Among the various sintered composites, the SSC40 exhibited the highest mass loss (16.69±0.32%) followed by SSC20 (8.03±0.21%), incidentally these two ceramic composites were sintered at highest sintering temperature employed in this study (i.e. at 1750°C for 3 h) together with SSC0 (exhibited a mass loss of 4.86±0.16%). Not only the higher sintering temperature employed could be responsible for these higher mass losses, but also the presence of certain low melting phases including Y₂SiAlO₅N and the iron based silicates formed due to iron impurities that entered during the milling of the sintered β -Si₄Al₂O₂N₆ extrudates. Some melted spherical grains of SSC40 had small amounts of iron (found by EDAX study, not presented here). However, on the whole the percentage of this iron based impurity grains was found to be < 1 wt.%. Furthermore, this iron impurity contamination was found to be drastically reduced when the relatively harder grinding media such as Al₂O₃ and ZTA (zirconia toughened alumina) was used in place of steel balls.

XRD patterns of sintered SSC_x ($x = 0, 20, 40, 60, 80$ and 100) samples are presented in Fig. 13. It can be seen that SSC0 is a fully crystalline material and that the major portion of it is β -SiAlON (ICDD File No.: 00-048-1616) together with some impurities like Y₂SiAlO₅N (ICDD File No: 00-048-1627) and certain other un-known phases [2,23]. The SSC20 is a mixture of β -SiAlON and Si₂N₂O (ICDD File No: 00-047-1627), whereas, the SSC40 is fully Si₂N₂O. Upon sintering, the fused silica (SSC100) was completely converted into cristobalite form. Although SSC50 was prepared from a powder mixture of 50 wt.% β -Si₄Al₂O₂N₆ + 50 wt.% fused silica, upon sintered it was converted into a mixture of cristobalite, β -Si₄Al₂O₂N₆ and Si₂N₂O. On the other hand, both SSC60 and SSC80 consists of cristobalite, β -Si₄Al₂O₂N₆ and Si₂N₂O with cristobalite being the major content. Interestingly, in these latter composites the starting material β -Si₄Al₂O₂N₆ is higher than that of Si₂N₂O. The considerable amount of viscous liquid melt formed in these two composites during sintering could not have allowed moving of the relatively isolated β -Si₄Al₂O₂N₆ particles with enough speed to react with and form Si₂N₂O phase [73].

As mentioned in the introduction section, certain high speed (> Mach 5) radomes see a transient temperature of about 1300°C in service. Therefore, the construction materials of these radomes should be able to withstand a temperature of at least 1300°C and also

should have dielectric constants preferably less than 6 [1–15]. Among the various SiAlON-SiO₂ ceramic composites prepared in this study (as listed in Table 8), only SSC40 is expected to meet both of these requirements, i.e., the high temperature withstanding capability and the dielectric constant as it was sintered at highest sintering temperature employed in this study (1750°C) for achieving the maximum density. Furthermore, among those sintered at 1750°C, only this SSC40 contains the maximum amount of fused silica, i.e. a low dielectric constant material. Considering these facts, SSC40 was selected to consolidate into near-net shape components by following the GCHAS route, as this technique allows the fabrication of thin wall radomes with near-net shape and very high green strength (i.e. >20 MPa) [19,21,58,59–63].

The compositions of precursor mixtures utilized in the consolidation of SSC40 ceramic composites by following GCHAS route, the values of viscosity of the prepared slurries at a shear rate ($\dot{\gamma}$) of 141 s⁻¹, the setting time of slurries, as well as the values of green density, percentage linear shrinkage occurred upon casting followed by drying, and the green flexural (4-point bend) strength of consolidates are presented in Table 9. In sample codes given to denote these composites, SSC40 indicates the ceramic composite formed from a

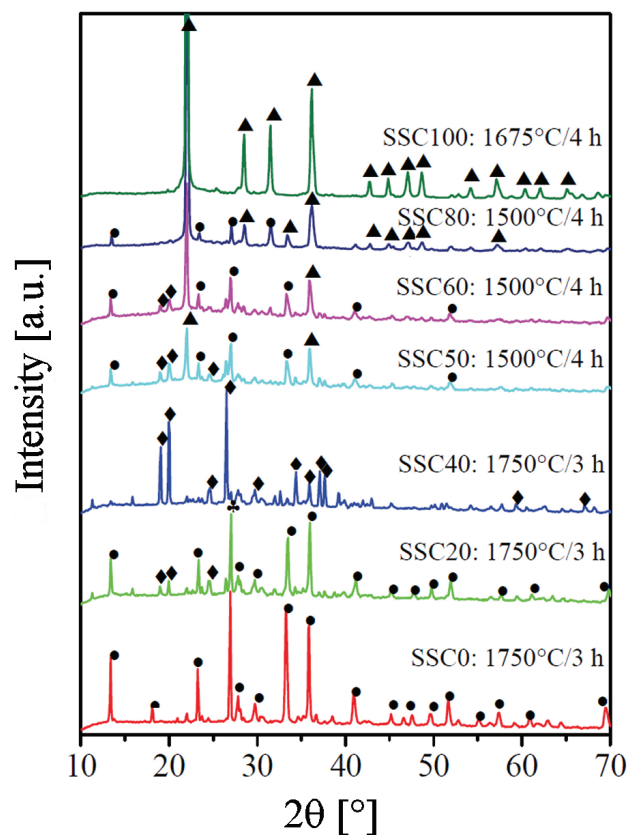


Figure 13. XRD patterns of SSC_x ($x = 0, 20, 40, 60, 80$ and 100) ceramic composites sintered at different temperatures under N₂ atmosphere of >900 torr. (● - β -Si₄Al₂O₂N₆; ◆ - Si₂N₂O; ▲ - Cristobalite) [21]

Table 9. Properties of suspensions and of green bodies of 60 wt.% β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ + 40 wt.% fused silica consolidated by following GCHAS route using AlN equivalent to 1–5 wt.% Al_2O_3 [21]

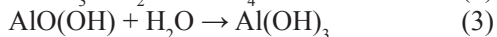
Ceramic composite [‡]	Precursor mixture				Suspension viscosity at $\gamma = 141 \text{ s}^{-1}$ [mPa s]	Suspension setting time [min]	Green strength [MPa]	Green density [kg/m ³]	Linear shrinkage from casting to drying [%]
	β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ [%]	Fused silica [%]	A-AlN [%]	α - Al_2O_3 [wt%] [†]					
SSC40-1	59.51	39.67	0.80	1	503	~11	14.13±1.87	1830±0.06	2.32±0.23
SSC40-2	59.03	39.35	1.61	2	467	~10	15.32±2.17	1820±0.04	2.33±0.11
SSC40-3	58.52	39.01	2.47	3	433	~8	16.72±2.32	1820±0.05	2.33±0.32
SSC40-4	58.06	38.70	3.24	4	416	~6	18.42±2.48	1810±0.03	2.34±0.27
SSC40-5	57.56	38.37	4.06	5	409	~5	20.25±2.66	1800±0.05	2.34±0.21

[†] Values were obtained as explained in the experimental section. Suspensions were prepared by dispersing powder mixtures of 60 wt.% β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ + 40 wt.% fused silica in NCPM (non-convectonal premix) solution using 10 μL Dolapix CE 64 dispersing agent per gram of powder mixture.

^{*} Formed upon hydrolysis and firing of added A-AlN

[‡] In sample codes, SSC40 indicates the ceramic composite formed from a powder mixture of 60 wt.% β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ + 40 wt.% fused silica; the numbers 1–5 represent the AlN content equivalent to 1–5 wt.% Al_2O_3 on total powder basis added to the suspensions; A-AlN stands for as purchased AlN powder, which was not passivated against hydrolysis

powder mixture of 60 wt.% β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ and 40 wt.% fused silica; the numbers 1–5 represent the content of AlN added (equivalent to 1–5 wt.% Al_2O_3) into the slurry on total powder weight percent basis; A-AlN stands for as purchased AlN powder that was not passivated against hydrolysis. The viscosity of the slurries considerably decreased with the increasing concentrations of AlN in the slurry reaching the lowest value of 406 mPa s for SSC40-5. Usually, when AlN is introduced into aqueous slurry the following three reactions (equations (1-3)) take place.



It consumes water, releases ammonia, and forms aluminium hydroxides. This released ammonia changes the pH and rheological characteristics of aqueous slurries [29,59]. In the present case, the generated ammonia gas increases the pH of the slurry away from the iso-electric-point of the dispersed powders thereby increases the stability and fluidity of slurry by decreasing their viscosities [29,59]. The slurry, SSC40-1, took about 11 minutes for completely converting into a gel after introducing APS, TEMED and AlN equivalent to 1 wt.% of Al_2O_3 . On the other hand, the slurry, SSC40-5, took only about 5 min after introducing APS, TEMED and AlN equivalent to 5 wt.% of Al_2O_3 . These results indicate that AlN concentration in the slurry drastically reduces the setting time of slurries under ambient conditions [29]. In all three events (equations 1-3), water is consumed and solids content is increased. These events support the early setting of slurries when higher amounts of AlN are introduced into them [19,59]. The flexural strength of green bodies also increased

with the AlN content. In GCHAS process, strength not only comes from polymerization of organic monomers present in the slurry but also by the cementing action of boehmite formed by the hydrolysis of AlN added to the slurry [19,21,29,59]. The generated boehmite connects the ceramic particles into a stiff body and the content of this boehmite increases with the concentration of AlN in the slurry [29]. Due to the involvement of both strengthening mechanisms, the green SSC40-5 consolidates exhibited the highest green strength value of 20.25±2.66 MPa.

A gradual decrease in the values of green density (from 2830 to 2800 kg/m³) and a gradual increase in the values of percentage linear shrinkage (from 2.32 to 2.34%) with the increasing AlN concentration in slurry can be seen from the data of Table 9. The decrease of green density with the increase of AlN concentration in the slurry could be attributed to the amount of NH_3 gas released in the slurry due to AlN hydrolysis (equation 1). Normally, some of the ammonia gas remains entrapped in the slurry having a viscosity of >400 mPa s, even after vacuum pumping. This entrapped gas leads to the formation of fine pores in the green bodies, which in turn are responsible for lower densities of consolidates. Nevertheless, these green density values are well-comparable with the one (2820 kg/m³) measured for consolidate formed by CDPP route having the same composition of β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ and fused silica (SSC40).

The SSC40 consolidated by CDPP route followed by sintering for 3 h at 1750°C exhibited a bulk density of 2510 kg/m³, apparent porosity of 5.445%, water absorption capacity of 2.168%, linear shrinkage of 10.68%, hardness of 1319 kg/mm², fracture toughness of 3.22 MPa·m^{1/2}, and flexural strength of 113 MPa. On the other hand, the pure stoichiometric β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ formed

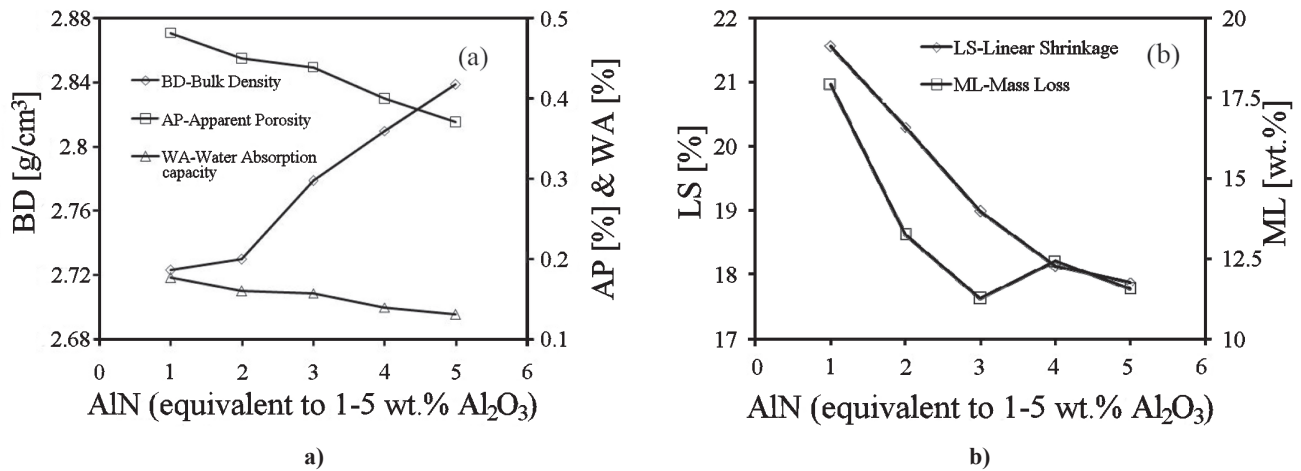


Figure 14. (a) Bulk density (BD), apparent porosity (AP) and water absorption capacity (WA), and (b) linear shrinkage (LS) and mass loss (ML) of SSC40-1 to SSC40-5 sintered for 3 h at 1750°C (Table 9) [21]

by the reaction sintering (at 1675°C for 4 h) of extrudates consisting α - Si_3N_4 , α - Al_2O_3 , surface passivated AlN against hydrolysis and Y_2O_3 (7 wt.%) exhibited a bulk density of 3080 kg/m³, apparent porosity of 0.19%, water absorption capacity of 0.12%, linear shrinkage of 14%, hardness of 1317 kg/mm², fracture toughness of 3.30 MPa·m^{1/2}, and flexural strength of 216 MPa. Although the hardness and fracture toughness values of these two differently sintered materials are comparable, there is a large gap between their flexural (4-point bend) strength values (β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ had a strength 226 MPa, whereas, the SSC40, $\text{Si}_2\text{N}_2\text{O}$, had only about 113 MPa).

The kinds of bonds and the amounts of porosity present in them could be responsible for the measured different flexural strength values [23].

The values of bulk density, apparent porosity and water absorption capacity, and the values of linear shrinkage and mass loss of SSC40-1 to SSC40-5 sintered for 3 h at 1750°C are plotted in Fig. 14a,b, respectively. Their corresponding hardness and fracture toughness values, and the flexural strength and Young's modulus values are plotted in Fig. 15a,b, respectively, as a function of the amount of AlN added to their corresponding slurries. In general, all these properties ap-

Table 10. Sintered properties of SSC40-5 and of various commercial radome materials [21]

Materials trade ad manufacturers [†]	Basic chemical composition	BD [kg/m ³]	Elastic modulus [GPa]	Flexural strength [MPa]	CTE [10 ⁻⁶ /°C]	Dielectric permittivity [ϵ']	tan δ	Ref.
Pyoceram 9606 (Corning Inc., USA)	Cordierite	2600	121	240	4.7	5.5	0.0005	[3]
Fused silica (Ceradyne, Inc., USA)	SiO_2	2000	37	43	0.7	3.3	0.003	[2]
IRBAS (Lockheed Martin Inc., USA)	Si_3N_4	3180	280	550	3.2	7.6	0.002	[78]
Ceralloy 147-31N (Ceradyne, Inc., USA)	Si_3N_4	3210	310	800	-	8	0.002	[78]
Ceralloy 147-01EXP (Ceradyne, Inc., USA)	Reaction bonded Si_3N_4	1800-2500	50-200	180	3.1	4-6	0.002-0.005	[78]
β -SiAlON (ORNL, USA)	β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$	3020	230	260	4.1	7.4	0.003	[3,6]
Cerablak™, (Applied Thin Films, Inc., USA)	Al_2O_3 - P_2O_5 composite	2000-2500	-	-	5.0	3.3-5	-	[10]
Invisicone (AMO, USA)	β -SiAlON- SiO_2	2200	-	532	2.0	4.9	0.002	[4]
SSC40-5 (material of this study, Table 8)	$\text{Si}_2\text{N}_2\text{O}$	2810	214	140	3.50	5.896	0.002-0.003	-

[†] ORNL stands for Oak Ridge National Laboratory and AMO stands for Advanced Materials Organization; CTE-coefficient of thermal expansion; BD-bulk density.

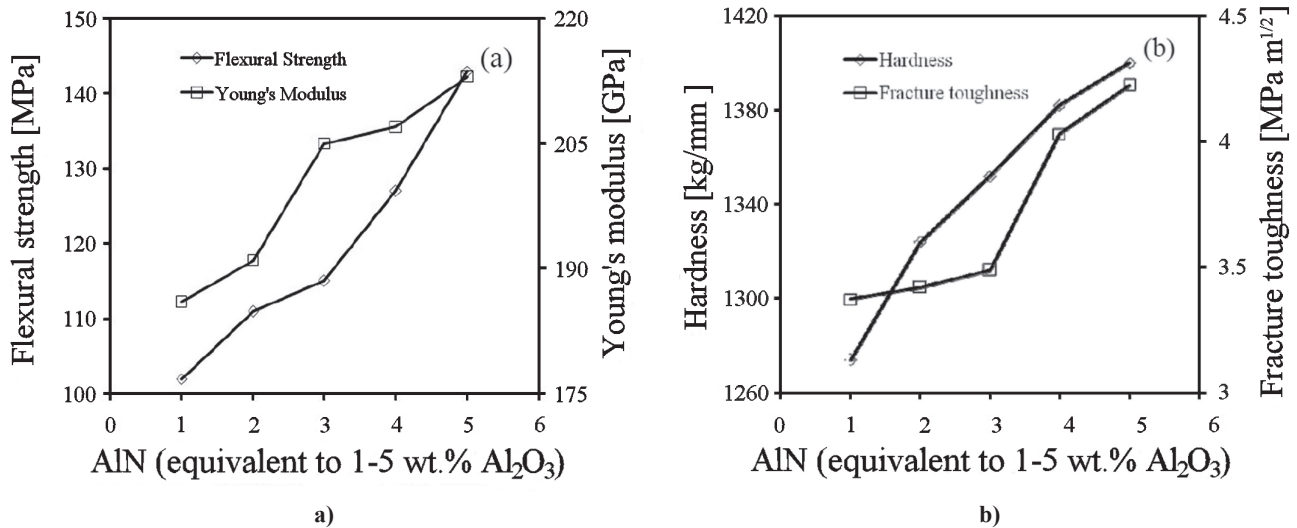


Figure 15. (a) Hardness and fracture toughness, and (b) flexural strength and Young's modulus of SSC40-1 to SSC40-5 sintered for 3 h at 1750°C (Table 9) [21]

pear to be very sensitive to the AlN concentration in the slurries. There is a significant difference between the apparent porosity and water absorption capacity values measured for SSC40, and SSC40-1 to SSC40-5, though all these samples have been sintered under identical conditions. Furthermore, there is a gradual increase in the values of bulk density, hardness, fracture toughness, flexural strength and young's modulus, and a concurrent decrease in the values of apparent porosity, water absorption capacity, linear shrinkage and mass loss of SSC40-1 to SSC40-5 with the increasing concentration of AlN in the slurry. There is an increase in the values of hardness from 1270 to 1390 kg/mm², of fracture toughness from 3.35 to 4.2 MPa·m^{1/2}, of flexural strength from 90 to 140 MPa and of Young's modulus from 184 to 213 GPa, and there is a decrease in the values of linear shrinkage from 22.5 to 18% and in the mass loss from 18 to 11%. The increased amounts of new alumino-silicate chemical bonds formed by the reactions between aluminium hydroxides derived from AlN and the Si₂N₂O (Fig. 13) could be responsible for the above mentioned changes in the sintered properties of SSC40-1 to SSC40-5.

Table 10 presents the basic chemical composition, bulk density, elastic modulus, flexural strength, co-efficient of thermal expansion, dielectric permittivity, and $\tan \delta$ of SSC40-5 (Table 9) and of several other commercial radome materials. Materials trade names as well as the suppliers and their corresponding countries names are also summarized in this table. In general, all the radome materials exhibit reasonably low bulk density values (<3200 kg/m³), which are recommended for high-speed radome materials. It can be seen that among various materials, only the Si₃N₄ and β -SiAlON based materials exhibit higher elastic modulus and flexural strength values [79]. Except Cerablak™ (5.0×10⁻⁶/°C), Pyroceram 9606 (4.7×10⁻⁶/°C)

and β -SiAlON (4.1×10⁻⁶/°C), all other materials exhibited relatively low CTE values (<3.5×10⁻⁶/°C). As far as the important dielectric permittivity property is concerned, the fused silica appears to be best for as it has the value of only 3.3. The highest permittivity values are measured for β -SiAlON (7.4), and the Si₃N₄ based materials, IRBAS (7.6) and Ceralloy 147-31N (8) [79]. Nevertheless, all these materials exhibited considerably low $\tan \delta$ values (i.e. <0.003). When compared with other materials, the SSC40-5 possesses elastic modulus and flexural strength values that are almost three times higher than those of fused silica. The dielectric permittivity value of SSC40-5 was measured to be 5.896, which is less than that of β -Si₄Al₂O₂N₆ (7.4), IRBAS (7.6) and Ceralloy 147-31N (8). Based on these permittivity and strength properties together with the high temperature (>1300°C) withstanding and radome shape forming capability, this SSC40-5 can be considered for certain high speed radome applications [1–15].

IV. Conclusions

The following conclusions can be drawn from the above study:

1. Different types of dense β -Si_{6-z}Al_zO_zN_{8-z} (z = 1, 1.5, 2, 2.5, 3, 3.5 & 4) ceramics can be prepared following a conventional reaction sintering process at 1675–1700°C for 4 h under ~800 torr N₂ pressure using α -Si₃N₄, α -Al₂O₃, AlN and Y₂O₃ (3, 5 & 7 wt.%) as starting materials.
2. An increase in z value and sintering aid (Y₂O₃) concentration can cause an increase in bulk density, co-efficient of thermal expansion, grain size, fracture toughness, dielectric constant and phase formation of β -Si_{6-z}Al_zO_zN_{8-z} and as a consequence, the decrease of apparent porosity, water absorption capacity, hardness, 3-point bend strength.

3. A β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ ceramic formed at 1675°C for 4 h exhibits a bulk density of $\sim 3067 \text{ kg/m}^3$, AP of $\sim 0.012\%$, WA capacity of $\sim 0.004\%$, XRD phase of $\sim 94.43\%$, $\sim 1317 \text{ kg/mm}^2$, fracture toughness of $\sim 3.30 \text{ MPa}\cdot\text{m}^{1/2}$, 3-point bend strength of $\sim 226 \text{ MPa}$, coefficient of thermal expansion of $3.628 \times 10^{-6}/^\circ\text{C}$ between 30–700°C, and a dielectric constant of ~ 7.206 at 17 GHz. Furthermore, this material can also be prepared in the form of powder following a conventional extrusion process using the same precursor mixture in which the surface passivated AlN against hydrolysis needs to be utilized as one of the starting raw materials.
4. AlN powder can be successfully passivated against hydrolysis just by treating it in an ethanolic solution containing required amounts of ortho-phosphoric acid and aluminium di-hydrogen phosphate at 80°C for 24 h.
5. Dense ceramics of β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ can also be consolidated following various colloidal processing routes such as, aqueous gelcasting, hydrolysis assisted solidification and hydrolysis induced aqueous gelcasting (GCHAS) routes. Among various colloidal processing routes employed, the GCHAS was found to be superior for making thin wall β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ radomes and crucibles. Further, these green radome structures can be densified fully without the distortion of shape by following the conformal sintering and can be machined to obtain the desired finish using diamond tools.
6. Dense ceramic composites of β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ -fused silica with SiO_2 in the range of 20–80 wt.% can be prepared by sintering the dry-powder pressed composites of β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ and fused silica for 3–4 h at 1500–1750°C.
7. The $\text{Si}_2\text{N}_2\text{O}$ formed at 1750°C for 3 h from a powder mixture of 60 wt.% β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ and 40 wt.% fused silica exhibits flexural strength value more than three times of sintered bulk fused silica, and the dielectric constant value less than that of stoichiometric β - $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$.
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