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Doctoral School in Materials, Mechatronics and Systems Engineering

Thermal properties of polymer derived Si-O-C-N ceramics

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To my parents and my family...and a special dedication to my uncle Dr. R. Sridharan Pillai...

Abstract

The main objective of the thesis is to study the thermal properties of Si-based polymer derived ceramics (PDCs) at elevated temperatures and to classify the main factors affecting the thermal transport through these ceramics. The polymer derived ceramics with the chemistry Si-O-C-N were prepared starting from commercial polycarbosilane, polysiloxane, and polysilazane precursors. These precursors are cross-linked at room temperature to obtain the preceramic, followed by controlled pyrolysis (at different temperatures ranging from 1200 °C to 1800 °C in argon, nitrogen or carbon-di-oxide atmospheres), to get the final ceramic.

The first part of the thesis discusses on development and studies of dense polymer derived thin disks having a basic chemistry, Si-C, Si-O-C, and, Si-C-N-O, developed via a casting technique followed by specific pyrolysis cycles. Having a thickness in the range of 100 µm-300 um. these ceramic disks were studied to be nanocrystalline/amorphous at least up to a temperature of 1400 °C and were found to have a significant amount of Cfree phase existing in them along with the intended chemistry. The high-temperature thermal properties were primarily investigated on ceramics prepared at a pvrolvsis temperature of 1200 °C (ceramic still in nanocrystalline/amorphous glassy phase). The disks were found to have very low expansion coefficients (CTE) measured up to ~900 °C and the thermal diffusivity (κ) and thermal conductivity (λ) of these disks were also measured. An attempt to understand the influence of the different phases in a SiOC ceramic (mainly the Cfree phase, studied by enriching the carbon percentages using DVB) in determining the final thermal properties was also conducted. The influence of carbon enrichment on the mechanical properties of these disks is also studied as a sub-part of this work.

The second part of the work deals with testing the possibility to use these ceramics for high-temperature insulation applications. 'Reticulated' ceramic foams of relatively same chemistries as that of the disks were prepared by a template replica approach, using polyurethane (PU) foams (more open-celled to more closed-celled types of PU foams were used in the study) as the template. Porous structures having densities ranging from as low as 0.02 g.cm⁻³ to 0.56 $a.cm^{-3}$ and with a porosity ~ 80 % to ~99% were prepared and tested. The developed foams showed excellent thermal stability up to a temperature of 1400 °C and possessed very low thermal expansion. The thermal conductivity measured on them at RT gave values in the range 0.03 W.m⁻¹.K⁻¹- 0.25 W.m⁻¹.K⁻¹. A Gibson-Ashby modeling approach to explain the thermal conductivity of the porous ceramics was also attempted. The developed foams were also found to be mechanically rigid.

In a nutshell, the thesis work studies the thermal properties of Si-O-C-N ceramics in detail and probes into the possibility to develop these class of Si-O-C-N ceramics into promising high-temperature insulation material.

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Studying the thermal properties of polymer derived ceramics having basic chemistry of Si-O-C-N and further augmenting the possibilities of these ceramics by investigating the potentiality as hightemperature insulants (by developing porous artifacts) are the principal objectives of the thesis. The thesis is structured in such a way that the main contents would be divided into 6 chapters. Chapter 1 briefly introduces the basic concepts and terminologies that are essential to address the thermal properties of ceramic materials, thermal transport in ceramics, measurement methods, factors affecting the thermal properties, low conducting ceramics, and the prospects of porous ceramics in thermal transport. Chapter 2 gives the introduction to the field of 'Polymer Derived Ceramics (PDCs)'- explaining the transformation of organic polymeric precursors to functional ceramics. Further, the production viabilities, properties, and applications of PDCs are discussed with the support of the available literatures and the stateof-the-art on the thermal properties of the Si-based PDCs is presented. These introductory chapters are followed by the experimental part, Chapter 3 in which the materials used, methods adopted, the experimental setups, and characterization tools used are discussed in detail. In **Chapter 4**, the studies conducted and the measurements taken on the dense ceramics prepared are discussed. The studies are mainly envisioned to understand the thermal properties of the different chemistries investigated. In Chapter 5, highly porous ceramic structures having relative chemistries developed via classical approaches would be studied and discussed with the main emphasis on the thermal properties. The work is concluded with the Chapter 6 in which the main observations, outcomes and the conclusions drawn would be discussed along with the future prospects.

1.1 Thermal properties of ceramics-a brief outline

The versatility of the ceramics has earned it the title of being the most 'omnipotent' class amongst the material fraternity. In fact, they are the most ancient class of the materials which the mankind still depends on in his daily life [1,2]. Nowadays, ceramics are used everywhere, right from pavement tiles to spacecraft components. Further, the possibility to have ceramics in a wide variety of forms, like coatings, films, fibers, porous structures (aerogels, foams, etc.) has extended the domain of its applicability. Along with all the other virtues that ceramics possess [3–7], they are also well regarded as high temperature performance materials owing to their high thermal stability and decent mechanical properties (high specific strength) at elevated temperatures [3,8,9]. Ceramics are often considered for a wide range of heat related applications, from the era of traditional ceramics to the present age of advanced ceramics; as high temperature refractories, and in various fields of semiconductor, automobile, and aerospace industries [2,10,11]. It is always important to understand the thermal properties of the particular ceramic depending on the application for which it is envisioned for.

While addressing the thermal properties of a ceramic in general, the main terminologies to be focused are the thermal conductivity (λ), thermal diffusivity (κ), thermal expansion behavior, heat capacity (C_p), maximum service temperature, and thermal shock resistance of a ceramic [10,12–15]. Understanding these parameters are essential to make the best choice of the material.

So, in this introductory chapter, a brief overview on each of these parameters or terms, which have to be considered while defining the thermal properties of a material (ceramics mainly in this case), will be discussed followed by a briefing on the mechanisms of thermal transport in ceramics, different measurement techniques, the need for porous ceramics, and the motivation of the work.

1.1.1 Understanding the fundamentals: Thermal conductivity, thermal diffusivity, and specific heat capacity

Thermal conductivity (λ) is an intrinsic property of a material which refers to the measure of its capability to conduct heat [13–15]. It refers to the rate of heat transfer that can take place in a material (considering unit area, unit thickness, and unit temperature difference between the considered surfaces, see Figure 1.1).



Figure 1.1 Heat flux across a temperature gradient (adapted from [15]).

Heat conduction studies through solids started at a slow pace in the early days, when Johann Heinrich Lambert considered to re-probe into and correct Guillaume Amontons's experiments in the 18^{th} century, until the French mathematician and physicist Joseph Fourier in 1807 (published in *Théorie Analytique dela Chaleur*, 1822 [16]) came up with the classical Fourier's law in which, based on his inquiries and experimentations, he proposed a relationship between the heat flux (*q*) and the temperature gradient (∇T), using a thermal conductivity (λ) tensor [10,12,15–17], as shown below (eq. 1.1),

$$q = -\lambda \nabla T \qquad (\text{eq. 1.1})$$

Bearing in mind that heat or thermal flux (*q*) is a vector quantity which represents the rate of heat energy (*Q*) flow per unit area and the thermal gradient (∇T) is considered between two surfaces having a length difference of *l* and are at temperatures T_1 and T_2 (where, T_1 is at a higher temperature and T_2 at lower temperature), heat flux equation could be written as (eq. 1.2) [10,12,15,18],

$$q = -\lambda \frac{T1 - T2}{l} \qquad (eq. 1.2)$$

However, the Fourier's understanding of thermal conductivity was basically in a steady temperature gradient, meaning that the line of heat transfer is not expected to change with time [12,15,18].

According to the first law of thermodynamics¹ (eq. 1.3),

$$Q = \frac{dU}{dt} = mC\frac{dT}{dt}$$
 (eq. 1.3)

When combining the first law with the Fourier's law [10,12,15,16] we obtain the one-dimensional heat diffusion equation which is based on temperature distribution (eq. 1.4) rather than on heat flux.

$$\frac{\partial^2 T}{\partial x^2} = \frac{\rho C}{\lambda} \frac{\partial T}{\partial t} \equiv \frac{1}{\kappa} \frac{\partial T}{\partial t}$$
(eq. 1.4)

 $\frac{dU}{dt}$ refers to the rate of change of internal thermal energy (U) with time (t).

 $^{^1\,}Q=q.\,A,$ where the heat (Q) is equal to the product of heat flux (q) and area associated (A) and m=mass.

The substance undergoes an incompressible process (volume is a constant with pressure) hence the specific heats are the same; $C_p = C_v = C$.

Thus, the unsteady state of heat transfer/ the transient heat conduction could be defined using a term referred to as **thermal diffusivity** (κ). The thermal diffusivity is the property that determines how quickly a thermal front diffuses into/through a material. Thermal diffusivity not only addresses the heat transfer through a material but also considers the change in the temperature of the body due to this heat transfer [12]. The thermal diffusivity and thermal conductivity are related by the equation [10,12,13];

$$\kappa = \frac{\lambda}{\rho \, C_{\rm p}} \tag{eq. 1.5}$$

where, the ρ refers to the density of the material and C_p to the **specific heat capacity** of the materials (simply defined as, the amount of heat energy required to raise the temperature of a unit mass of a substance by a unit temperature). The term ' ρ C_p' represents the volumetric specific heat of the material, hence the thermal diffusivity of the material could also be defined as the 'ratio of the thermal conductivity of the material to the heat storage capacity of the material' [10,13]. It can also be defined as the measure of the rate at which a state of thermal equilibrium is achieved by a material, at a non-uniform temperature flow.

1.1.2 Convective and radiative heat transfers

The heat transfer through a material also occurs by convection and radiation mechanisms even though conduction is the main mode of transfer.

Convective transfer (λ_c) of heat usually occurs within a fluid (liquid or gas) or between a solid surface and a fluid by random molecular motions (diffusion) and/or as a result of a bulk movement of fluids (advection) in the form of currents or eddies as referred to. These

currents are often caused naturally (if these currents are from the same heat transfer process, due to density differences of the fluids and resultant buoyant forces) or can also be forced convectional currents (using any external agent to force the fluid to flow past a surface, transferring more heat at a particular temperature difference) [12,14,18].

As shown in Figure 1.2, when a fluid having a temperature, T_{∞} pass over a hot surface (T_{body}), often the heat is transferred on to a small region or a film of the fluid which comes near the hot surface and is referred to as the 'boundary layer'. Heat transfer happens in this small film region by conduction. This conduction and transfer of heat by the moving fluid can be called convection [10,12,15].



Figure 1.2 Convective flow over a hot body [12].

The conventional heat transfer rate could be explained using Newton's law of cooling (eq. 1.6).

$$q = h(T_{body} - T_{\infty}) \tag{eq. 1.6}$$

The term 'h' is referred to as the convective heat transfer coefficient (of the film). The value of h depends on factors like geometry, fluid motion and the thermodynamic properties of the fluid. The q refers to the heat flux and q = Q/A.

Radiative heat transfer (λ_r) or thermal radiation refers to the emitted portion of the heat energy. The intensity of the radiative energy

depends of the temperature of the radiating body and the surface nature. The heat energy is conveyed in the form of electromagnetic waves [12,14] even in absence of a medium. Electromagnetic waves in the wavelength 0.1 to 1000 μ m is usually considered to cause the thermal radiation among the electromagnetic spectrum. Even-though the radiation exists at room temperature conditions, the radiative heat transfer is usually considered important only at elevated temperatures (usually > 700 K).

Black bodies [12,14] are the perfect but conceptual thermal radiators. As per definition, it refers to a body that absorbs all the energy which falls on it and reflects literally nothing. As shown in Figure 1.3 normally when a radiative flux falls on a normal body (non-black body), a part of the total energy incident will be reflected, a part will be absorbed, and the remaining will be transmitted. The fraction of the incident energy that is absorbed is called absorptance (α), the fraction of the reflected energy is called the reflectance (ρ), and the third part transmitted is referred to as transmittance (τ). Since the total energy should be unity, the relation between the three is given by the eq. 1.7 [12,14,15];



Figure 1.3 Radiation flux on a non-black body [15].

$$1 = \alpha + \rho + \tau \qquad (eq. 1.7)$$

In case of a perfect black body, all the incident energy is absorbed, such that, $\rho = \tau = 0$ and $\alpha = 1$. In this context, the energy radiated

from a black body reaches a theoretical maximum, which could be explained using the Stefan-Boltzmann law.

According to the **Stefan-Boltzmann law**, the radiation emitted from the surface is caused by the thermal energy possessed by the body; the rate at which this energy is liberated per unit area is referred to as the surface emissive power (*E*). In the case of a perfect black body $E = E_b$, where E_b is (eq. 1.8) [14],

$$E_b = \sigma T^4 \tag{eq. 1.8}$$

Here, *T* is the absolute temperature of the surface (in kelvin), and σ is the Stefan-Boltzmann constant (σ = 5.67 X 10⁻⁸ W.m⁻².K⁻⁴). In case of real surfaces emitting heat, the surface emissive power is always less than that in a black body and is given by a modified equation (eq. 1.9) [14],

$$E = \varepsilon \sigma T^4$$
 (eq. 1.9)

where, ε (0 ≤ ε ≤1) is the **emissivity** of a material.

All materials are known to expand on heating and contract on cooling. Understanding the extent of this change in the dimensions with temperature is important as far as the design factors are concerned.

The change in the dimension with temperature is usually represented using a parameter, a material property termed as **thermal expansion coefficient** (α_L or α_V ; can be represented as both linear or volumetric expansion coefficients). It can be defined as the extent to which the material expands upon heating and can be represented by the equation (eq.1.10 and 1.11) [13];

$$\frac{\Delta L}{L} = \alpha_L \Delta T \qquad (\text{eq.1.10})$$

$$\frac{\Delta V}{V} = \alpha_V \Delta T \qquad (\text{eq.1.11})$$

where, *L* and ΔL are the actual length and the change in length (if linear expansion is considered; α_L is the linear thermal expansion coefficient for a temperature difference of ΔT). Similarly, *V* and ΔV represents the actual volume and the change in the volume of the material with a temperature change of ΔT (α_V is the volumetric coefficient of thermal expansion).



Figure 1.4 Potential energy (E) as a function of interatomic distance (r), showing the increase in the interatomic separation with a rise in temperature (bold line shows the real asymmetric trough of the potential energy curve and the dashed line shows the imaginary symmetric trough. The red arrow represents the shift in r_0) (adapted from [19]).

At an atomic level, the physical mechanism behind the thermal expansion can be understood from the potential energy (E) versus interatomic distance (r) plot, shown in Figure 1.4. The equilibrium interatomic position, r_0 at 0 K represents the minimum position on the

energy curve or it is the energy trough minimum. At r_0 , the atoms are at their minimum vibrational energy level and have the minimum vibrational amplitude, say x_0 (represented by the width of the energy trough at a particular energy value). On the application of heat to the solid, the vibrational energy of the atoms increases thereby increasing the vibrational amplitude. At low temperatures, even though the vibrational amplitude increases, the mean interatomic separation (r_0) remains the same. The same would have been the case in a solid at high temperatures if the potential energy trough was symmetric (which is not the case). In such a situation, there would be no thermal expansion happening to the solid with an increase in temperature. However, at the higher temperatures, the increase in the vibrational amplitude also increases the mean interatomic spacing owing to the asymmetric curvature of the potential energy trough. Thus, this asymmetry of the potential energy trough explains the thermal expansion in a solid with temperature (because of the shift in the mean interatomic spacing) [13,19].

Owing to the changes in the temperature, some stress (**thermal stress**) is usually generated in solid materials, which can often lead to fracture cracks or permanent deformations in them. The stresses developed in a constrained piece of rod (axial constrain) could be shown by the equation [13];

$$\sigma_T = E \alpha_L \Delta T \tag{eq.1.12}$$

where *E* represents the elastic modulus of the material, α_L the linear thermal expansion coefficient, and temperature difference of ΔT .



Figure 1.5 Linear expansion coefficient against the thermal conductivity, the λ/α_L shows the parameter, thermal distortion ² [20,21].

Figure 1.5 shows the variation in the thermal expansion coefficient of different materials with the thermal conductivity. The quantity λ/α represents an important design parameter while crafting against thermal distortion, where λ represents the thermal conductivity and α represents the thermal expansion coefficient of the material. Thermal gradients in a material often lead to deformations in them (distortions). Thus, while considering a material for mechanical design, with a specific geometry and heat flow, the thermal distortion occurring could be minimized by picking a material with a large λ/α (W.m⁻¹) value. Thus, from Figure 1.5 it is evident that the materials like diamond, SiC, and silicon have a low thermal expansion coefficient owing to the presence of less anharmonic covalent bonds in them and hence low thermal distortion [21]. Another design parameter considered is the sensitivity to vibration in the materials (more could be read from [21]).

 $^{^2}$ More representative and comparative graphs on λ are added in the Annexes.

Thermal stresses are also generated due to temperature gradients in the materials. Often, as described above, these gradients can lead to either plastic deformations (as in metals and polymers) or breakage/fracture (in case of ceramics that are brittle). This occurrences in brittle materials are normally referred to as **thermal shocks** and the ability of the material to withstand these flops are called thermal shock resistance (TSR) of a material [13], given by:

$$TSR = \frac{\sigma_f . \lambda}{E.\alpha_L}$$
 (eq.1.13)

where, σ_f is the fracture strength of the material, λ , *E*, α_L represent, the thermal conductivity, elastic modulus, and the linear thermal expansion coefficient of the material, respectively. So, a high TSR can be expected for a ceramic with high σ_t and λ ; and low *E* and α . Ceramics like SiC and Si₃N₄ have high TSR values and are usually used for high-temperature structural applications. Soda-lime glass has low TSR (owing to the high α) when compared to Pyrex (low α) which is more resistant to thermal shocks. Glass-ceramics also have very low α making it shock resistant to temperatures even above 1000 °C [13,19,21].

The chart presented in Figure 1.6 shows the plot between the normalized tensile strength (in ceramics, the tensile fracture strength, σ_f) and the linear coefficient of thermal expansion. The graph helps in the selection of materials that can resist damage with a rapid change in the temperature (ΔT). The TSR in ceramics can be presented as an index considering the λ as an internal constraint, say '*C*'. The rate of heat transfer in a material/surface determines how fast the material cools (when quenched) and this is often represented by the heat transfer coefficient (*h*).

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Figure 1.6 Normalized tensile strength (σ_t/E) versus linear coefficient of expansion, the contours show a measure of the thermal shock resistance (TSR) [21].

Considering a material with a low *h* and high λ , the thermal gradients would be reduced and hence the thermal stress (σ_f) will be less than the value calculated (from eq. 1.13) by a factor *A* (eq. 1.14) [21]:

$$A = \frac{th/\lambda}{1+th/\lambda}$$
 (eq.1.14)

where, A is the axial constraint; *t* is the sample dimension in the direction of the heat flow and hence the λ constraint will be reduced to *C*/*A*. Thus, eq. 1.13 could be modified as (eq. 1.15) [21]:

$$B\Delta T = \frac{\sigma_f}{E.\alpha_L}$$
(eq.1.15)

where,

$$B = \frac{c}{A}$$
 (eq.1.16)

and *B* is the factor which allows for constraint and accounts for the heat transfer considerations. The contours of the graph (Figure 1.6) show the values of the TSR index = $B\Delta T$ (see eq.1.15), with an appropriate correction for the constraint [21].

1.1.3 Thermal transport in ceramics

In most of the solids the heat transportation is mainly carried out by two modes (however, in addition to these two, other modes like electromagnetic and spin waves, and other excitations are also present [3,10]),

- (i.) by electrical carriage (electron/hole pairs) or/and,
- (ii.) by lattice vibrations (phonons)

In metals owing to their electron rich nature, electronic thermal conduction is the dominant mode of heat transfer, in which the free electrons actively transport the heat across (the kinetic energy gained by the electrons from a hot region is transferred to an atom/s in the cold region as a result of collisions), while in an insulator, the lattice vibrations (the solid atoms vibrate in their mean positions causing the propagation of wave packets called phonons, which are basically 'quanta of thermal energies') are the dominating heat carriers [3,10,22]. The thermal conductivities of some of the common materials are shown in the Figure 1.7.

Therefore, the total thermal conductivity could be represented as,

$$\lambda = \lambda_e + \lambda_p \tag{eq. 1.17}$$

where, λ_e and λ_p represents the conductivity contributions from the electrons and the phonons, respectively [14].





In the case of ceramics, due to the lack of availability of free electrons as in the case of metals (due to the formation of ionic-covalent bonds), phonons would be the main heat carriers (at high temperatures, the effect of electronic thermal conduction is considered in the case of semiconductors but is negligible in ceramic materials). Phonons are considered less effective in transferring heat when compared to the free electrons (in metals) owing to higher scattering rate [3,14]. On the contrary, some of the non-metals are exceptional and have comparable or even higher thermal conductivity than that of metals; like diamond, AIN, SiC, etc. (most of them having diamond like structure, with strong covalent bonds, hence with low scattering rates) [10,23].

In general, the thermal conductivity of ceramics decreases as temperature increases owing to the increase in the scattering and the resultant reduction in the mean free path of the phonons. But, as the temperature increases beyond a certain value the thermal conductivity shows a rising trend due to the radiant heat transfer coming into play (as can be seen in the Figure 1.8).

Basically, there are two branches of phonon conduction in solids, namely the acoustic phonon branch and the optical phonon branch. However, the low frequency acoustic phonons are the main heat conductors, while the high frequency optical phonons can significantly influence the heat conduction by interacting with the acoustic phonons [10]. The phonon conduction could be represented using the equation given below, which is derived from the kinetic theory of gases [24];

$$\lambda_p = \frac{1}{3} C_{\text{p. } \nu. \Lambda} \qquad (\text{eq. 1.18})$$

where, $_{\upsilon}$ and $_{\Lambda}$ are the phonon group velocity and phonon mean-free path (here, $_{\Lambda}$ = $_{\tau\cdot\upsilon}$ and $_{\tau}$ is the phonon relaxation time).



Figure 1.8 Thermal conductivities of selected ceramics [13].

Phonon heat transport systems are basically classified as diffusive and ballistic types. If the phonons are subjected to numerous scattering owing to the fact that the size of sample (D) is much larger (hence possessing lots of anharmonicities) than the mean free path of the phonon (Λ); such a thermal transport is referred to as a diffusive transport. On the other hand, if the phonons are able to travel without being scattered, they are said to be ballistically transporting heat. In such a situation it is essential that the D< Λ . However, the possibility of occurrence of a ballistic transport is always limited to nano/single crystal ceramics. In addition to the scattering happening due to the interactions like, with the other phonons, at imperfections (crystal defects), and with the impurities present [3,10,25] (see Figure 1.9) can

also cause the scattering of these phonons. All these, in effect, determine the final thermal conductivity of the ceramic material.



Figure 1.9 Scattering of phonons (adapted from [25,26]); (a) phonon-phonon interaction, (b) phonon-boundary interaction, (c) phonon-defect interaction, and (d) phonon-electron interaction.

At high temperatures, the main scattering mode of the phonon is the interaction with other phonons, resulting in an elastic thermal energy dissipation leading to a finite κ . Sir Rudolf Peierls classified the phonon scattering into two processes based on the momentum conservation principle (according to him the possibility to have a finite thermal conductivity for a material is difficult if the scattering phonons conserve momentum) [27]. He classified the process in which the phonon momentum is conserved as Normal process (N-process) and the one in which the momentum is not conserved; hence causing significant thermal resistance due to the effective participation in the phonon stream as **Umklapp process** (U-process). Figure 1.10, explains the sum of the momentum vectors reaching beyond the Brillouin zone [27].



Figure 1.10 Schematic showing the Normal and Umklapp scattering processes, in the classical way [28].

It is obvious that the presence of the anharmonicities in the medium is only triggering the phonons to come in contact with each other. The total scattering, meaning that the total phonon mean-free path (Λ) could be represented according to the Matthiessen rule as (eq. 1.19) [10,29];

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_{phonon}} + \frac{1}{\Lambda_{boundary}} + \frac{1}{\Lambda_{defect}}$$
(eq.1.19)

At lower temperatures, the majority of the phonon scattering are contributed by the extrinsic factors like the defects, boundaries, and impurities. However, in most of the ceramics Umklapp scattering owing to lattice imperfections is the main factor limiting the mean free path (Λ) of the phonons, even at low temperatures and the effect become more predominant at high temperatures (Figure 1.11) [3,27].

In **glasses**, due to their non-crystalline amorphous structure, the mean free path is drastically reduced to the order of interatomic distances [3,10]. This fixed value of Λ limits or lowers the thermal conductivity values in glasses further than that in the case of crystalline solids and

ceramics. Kittel [30] explained this behavior based on Debye's model of thermal conductivity in solids and he observed that the scale of the Λ is in the order of the scale of disorder in glasses (~70nm). The glasses were found to show a very typical thermal conductivity pattern, like a region with a sharp rise in the λ followed by a plateau region. The initial rise in the λ was explained owing to the scattering of the low energy state phonons and the reason for a constant λ (plateau) was rationalized owing to the synergy of several factors, viz. tunneling effects, structural disorder scattering, and resonance scattering modes [31–33]. This type of a thermal conductivity trend (steep curve followed by a plateau) is also observed in the case of quasi-crystalline materials [10].



Figure 1.11 Contribution of the various scattering processes on the lattice thermal conductivities with temperature increase (in the ceramic, CoSb₃); solid line denotes the experimental data and dashed line denotes the theoretical data (limits) considering the different scattering processes [10].

The thermal conductivity in glasses at higher temperatures are also reduced by series of random localized events of oscillations and were explained by different models (Cahill and Pohl model; Orbach model, etc. [34,35]).

1.1.4 Main factors affecting heat transfer in bulk ceramics

We have discussed about those factors which influence the conductivity at the atomic level. However, it is worth discussing certain important factors on a macroscopic scale, which are considered in bulk ceramics when we study the thermal conduction in them [3].

Primarily, the thermal conductivity of a ceramic depends on the **composition and the structure** of the material. Ceramics constituted of elements having greater difference in the atomic weights are found to possess low thermal conductivity. Complex ceramic structures tend to have a greater scattering of the lattice waves (phonons) hence lowering the thermal conductivity. For instance, MgAl₂O₄ (spinel) has lower thermal conductivity than the constituent ceramics (MgO and alumina) in spite of having most of the other properties the same. This reflects how the complexity in the composition can influence the thermal conductivity. **Impurities** and solid solutions in a way add to the complexity of the structures and thus increase the anharmonicity. In the case of solid-solution impurities, the effectiveness of lowering the thermal conductivity depends on factors like the size, mass, binding-energy, etc. of the impurity.

Crystallinity of the ceramic is an important factor influencing the thermal conductivity. Monocrystalline material will possess a higher thermal conductivity than polycrystalline material even with similar chemistry. This is obviously due to the scattering of phonons at the boundaries in the case of the polycrystalline ceramics (diffusive heat transfer), while in the case the mono-crystals, the phonon conduction

is more profound due to the absence of any hindrances (a ballistic type of heat transfer) [3].

Existence of **multiple phases in ceramics** can significantly affect the thermal conduction. In this context the porosities which are usually present in ceramics could be considered as a phase. **Porosities** forms a discontinuous phase in the ceramic which drastically affects the phonon conduction. Porosities are a kind of macroscopic defects, which act like scattering centers in the solid ceramic phase and even small percentages of porosities can significantly reduce the mean free path of the phonons, thus reducing the thermal conductivity. Numerous models are often discussed to address this effect of porosities on the thermal conductivity (*viz.* Maxwell-Eucken). At high temperatures, the radiative heat transfer across the pores also should be considered while addressing the thermal conductivity of the ceramics [3].

Some of the commonly used models to explain the thermal conductivity in porous ceramics (isotropic) are mentioned below [36]:

Simple models like the Series (where, the two components are arranged in series and the material with the lowest λ obstruct the thermal conduction, giving the lowest possible effective thermal conductivity (λ_E) for the combination of the two, for the given volume fraction. The λ_E in this case is represented by eq. 1.20) and Parallel (where, the two components are connected parallel and the component with the highest λ conducts the heat effectually. The highest possible λ_E for the combination of the two is obtained, as represented in eq. 1.21) models often serve as the lower and the upper bounds for the effective conductivity in heterogeneous materials, considering conduction as the only heat transfer mechanism.

Series:
$$\lambda_E = \frac{1}{\frac{1-\vartheta_2}{\lambda_1} + \frac{\vartheta_2}{\lambda_2}}$$
(eq.1.20)

Parallel:
$$\lambda_E = (1 - \vartheta_2)\lambda_1 + \vartheta_2\lambda_2$$
 (eq.1.21)

where, λ_E is the effective thermal conductivity (in W.m⁻¹.K⁻¹), λ_1 and λ_2 are the thermal conductivities of the two components in W.m⁻¹.K⁻¹ (in porous material one component is air) and ϑ_2 is the volume fraction, let us say of the solid phase (other being air in a porous ceramic).

Hashin and Shtrikman [37] came up with effective conductivity bounds for macroscopically homogenous, two-phase systems, derived from the volume fractions and the conductivities, which were mathematically equivalent to the Maxwell-Eucken model (see eqs.1.22 and 1.23).

Maxwell-Eucken 1:
$$\lambda_E = \lambda_1 \frac{2\lambda_1 + \lambda_2 - 2(\lambda_1 - \lambda_2)\vartheta_2}{2\lambda_1 + \lambda_2 + (\lambda_1 - \lambda_2)\vartheta_2}$$
 (eq.1.22)

Maxwell-Eucken 2:
$$\lambda_E = \lambda_2 \frac{2\lambda_2 + \lambda_1 - 2(\lambda_2 - \lambda_1)(1 - \vartheta_2)}{2\lambda_2 + \lambda_1 + (\lambda_2 - \lambda_1)(1 - \vartheta_2)} \quad (eq.1.23)$$

The symbols represent the same terms as in the above equations (eqs. 1.20 and 1.21).

The effective thermal conductivity of two-component systems, with a random distribution (with neither phase being essentially continuous or dispersed), was modeled from the Effective Medium Theory (EMT) theory equation (eq.1.24)

$$(1 - \vartheta_2)\frac{\lambda_1 - \lambda_E}{2\lambda_E + \lambda_1} + \vartheta_2 \frac{\lambda_2 - \lambda_E}{2\lambda_E + \lambda_2} = 0$$
 (eq.1.24)

The symbols represent the same terms as in the above equations (eqs. 1.20 and 1.21).
1.1.5 High and low thermally conducting ceramics

Ceramics having both high and low thermal conductivities are widely in demand for various applications. High conductivity in ceramics are needed for applications like micro-electronic packaging, semiconductor modules, wireless devices, laser (photonics), solar cells, and thermo-electrics, while low thermally conducting ceramics are used for applications like in thermal barrier coatings for various high temperature devices, furnaces, gas-turbines, in aerospace and also for applications like thermal insulation at elevated temperatures [38–41].

The thermal properties of some of the commonly used ceramics are enlisted on the Table 1.1.

Ceramics	Thermal Conductivity (W/m. K)	Thermal expansion (CTE) X10 ⁻⁶ /K	Specific heat capacity (J/g.K)	
Porcelain	1.05 -1.90	1.6-19.6	_	
FOICelain	(25 °C-1000 °C)	(200 °C)		
Clay	1.13-2.09	_	_	
	(100 °C-1000 °C)			
Soda-lime	0.72-1.75	>10	_	
glass	(RT-1500 °C)			
Borosilicate	0.85-1.7	4.7-9	_	
glass	(900 °C-1100) °C	(~400 °C)	-	
Graphite	50-3000< (// plane, upto ~700 °C)	1.8-5.3 (800 °C)	~ (0.7-1.9) (~900 °C)	

Table 1.1 Thermal properties of some commonly used ceramics and glasses [24,42,51–56,43–50].

	3-38 (⊥ plane, ~ 600		
	°C)		
Diamond	1-2300<	-	-
Amorphous carbon	0.1-3.5 (RT-1230 °C)	-	0.71-1.66 (RT-750 ℃)
	1.05-2.51 (fused SiO ₂	0.57 (Vitreous,	
SiO	glass, 200 °C-1600 °C)	RT-1250 °C)	~ 0.65 -1.23
5102	7.2-4.4 (quartz, 0-500	~14.6 (quartz,	(RT-1000 °C)
	°C)	RT-1050 °C)	
	25.1-7.1 (Al ₂ O ₃ , RT-		
	1600 °C)	8.58 (~1700 °C	0.72-1.25
Alumina	43.1-12.1 (single	(polycrystalline)	(900 °C)
	crystal, RT-800 °C)		
Creinel	14.7-5.4 (100 °C-1200	9.17	
Spiner	°C)	(RT-1500 °C)	-
AIN	30-17.6 (25 °C-800 °C)	6.09 (RT-1350 °C)	0.82-1.0 (600 °C)
TiN	28.9-56.9 (RT-2300 °C)	9.35	-
	196.6-15.6 (RT-2000	11.1	_
BeO	°C)	(RT-2000 °C)	-
TiC	30.0 5.6 (PT 2200 %C)	7.9	0.67-0.88
	30.9-3.0 (1(1-2300-0)	(RT-2500 °C)	(1100 °C)
	6.7-3.3 (100 °C-1200	9.5	_
TiO ₂	°C)	(RT-1500 °C)	
MgO	40.6-7.9 (RT-1800 °C)	15.89 (RT-1800 °C)	-

			0.66-1.25 (β
	114.0-26.3 ($lpha$ SiC, RT-	1.1-5.5	SiC, 120 °C-
SIC	1500 °C)	(RT-1500 °C)	800 °C)
310	178.2-1.3 (β SiC, 120	3.2-5.1	1.08-1.33 (α
	°C-1530 °C)	(RT-1000 °C)	SiC, RT-
			1500 °C)
	20 1 14 0 (PT 1200 °C)	~ 3.66	0.71
Si ₃ N ₄	30. 1-14.0 (R1-1200 °C)	(RT-1500 °C)	0.71
	2.3-2.21 (RT-800 °C)	5-11	-
Zirconia	,		
	53.9-17.2 (150 °C -	9.0-9.2	_
MoSi ₂	1100 °C)	(RT-1500 °C)	
BN	28.7-26.7 (// to 'a', 300		
	°C-1000 °C)	13.3	
	15.1-12.3 (// to 'c', 300	(RT-1350 °C)	-
	°C-1000 °C)		
ZnO	37-4 (RT -1000 °C)	-	-

1.1.6 Measurement techniques- thermal conductivity

There are different techniques used to measure the thermal conductivity of ceramic material (generally used for all the materials). The commonly used techniques could be basically divided into (see Figure 1.12) [10,57,58]:

(i.) Steady-state approach

In a steady-state approach, the thermal conductivity across a temperature difference (gradient) of ' Δ T' is stated, as the name suggests, considering a steady state heat flow 'Q' through them.

They are further classified into methods like:

- (a) Absolute technique
- (b) Comparative technique

- (c) Radial heat flow method
- (d) Parallel conductance method



Figure 1.12 A brief scheme depicting some of the basic approaches used for the thermal conductivity measurements; (a) Absolute, (b) Comparative, (c) Radial heat flow, (d) Maldonado technique, (e) Hot-wire method (adapted/ taken from the refs. [10,57]).

(ii.) Transient approach

Often steady state approaches are coupled with drawbacks like parasitic heat losses, contact resistance, and time delay. To overcome these shortcomings; instead of a steady 'Q', transitory heat sources are used, like laser pulses that generate transient temperature changes. There are different well-known standard techniques which use this approach like:

- (a) Pulsed power technique (Maldonado technique)
- (b) Hot-wire method (needle-probe method)
- (c) Laser-flash method ³

^{3,4} will be discussed in detail in the experimental part.

- (d) Transient plane source (TPS) method ⁴
- (e) 3ω method
- (f) FDTR technique
- (g) TDTR technique

1.1.7 Porous ceramics

Engineering the porosity in ceramics has been found to be beneficial for various industrial and domestic applications. The synergistic combination of the intrinsic boons of the ceramics (viz. high specific strength, high thermal, mechanical and chemical stability, good biocompatibility, etc.) and that imparted by the pores like, low density, low thermal conductivity, high surface area, etc. has fostered the interest in them than their dense counterparts [7,59,68,69,60–67].

The porosities in ceramics could be classified as micro, meso, and macro⁵, hence the corresponding ceramics could be named as micro-, meso-, and macro-porous ceramics, respectively.

Further, the pore morphology (open to closed pores) as well as the pore distribution can also significantly influence the properties. Numerous approaches are reported for the fabrication of porous ceramics (macro-porous), like partial sintering (classical approach), replica approach [64,65,69], fugitive templating approach [64–66,69], direct foaming techniques [62,66], and additive manufacturing [67] (pioneering approach), see Figure 1.13 [61,70].

 $^{^5}$ The IUPAC classification of porosity, < 2 nm (micro-pore), 2 nm-50 nm (meso-pore), and 50 nm < (macro-pore).



Figure 1.13 Common approaches to yield porous ceramics along with the corresponding typical applications and the pore type (classification) [70].

Porosity has been engineered in ceramics to get honey-comb structures, foams, aerogels, and 3D-printed lattices in most of the universally used sophisticated ceramics like Al_2O_3 [71,72], SiC [64], SiO₂ [73,74], YSZ [75,76], BN [77,78], MoS₂ [79], Si₃N₄ [80–84] and in various carbon [59,85–87] based ceramics.

The porosity inclusions in ceramics can significantly modify many of the properties of the corresponding dense ceramics in a way favoring or improving its applicability. In this context, the possibility to lower the thermal conductivity while increasing the resistance to thermal shock in a ceramic by pore inclusions are quite commendable [88,89]. This further favors the use of these porous ceramic artefacts for thermal insulation and related applications.

Most of the approaches to yield porous ceramics usually start from the corresponding ceramic slurry. However, this approach has been found to have numerous shortcomings right from the processing stage to obtaining homogenous ceramic structures. The idea of starting the processing of porous ceramics from liquid molecular precursors, holding on to the typical processing techniques itself could be a more simple and efficient approach (see Figure 1.14).



Figure 1.14 Approaches to porous ceramics [69].

1.1.8 Porous ceramics *via* polymer derived approach for thermal insulation at elevated temperatures

The polymer derived approach to manufacture porous ceramics has been well documented [90–93]. The structural, thermal, and chemical stability of these molecular precursor derived ceramics are well studied, and their mechanical and electrical performances are also reported in detail. Advanced applications of this class of ceramics in various societal (thermal insulation, in the field of drug delivery, and as bio-scaffolds), environmental (water purification, filter supports, gas absorption, sensors), energy (Li-ion encapsulation, solar cells, etc.), and industrial (thermal shielding, in brake shoe composites, MEMS, etc.) fields are also reported [94–96].

Even though this class of materials is known to deliver ultra-high temperature performance [8], this possibility has not been exploited much to develop light and stable porous thermal insulators for applications at elevated temperatures. To understand the thermal performance of the ceramics, it is important to study the thermal properties of these ceramics at the anticipated conditions, which has not been documented well. The different parameters like the thermal conductivity and expansion coefficients of these ceramics are to be studied in correlation with the structural, chemical, and mechanical stability of these classes of materials.

Thus, in brief, the primary motivation of the work would be to clearly state, understand, and explain the thermal properties of selected polymer derived Si-based ceramics having a basic chemistry Si-O-C-N, and to further investigate the thermal performance of highly porous ceramics having relative chemistries for application as high-temperature insulators.

Chapter 2. Polymer Derived Ceramics (PDCs): Insights into the thermal properties of PDCsstate-of-the-art

2.1 Polymer Derived Ceramics (PDCs)- an introduction

Since 1960's significant advances have been achieved in this innovative field of processing, starting from a molecular precursor to yield a final ceramic. The developed ceramics were testified to be exceptionally functional, having improved thermal, chemical, and oxidational stability. Ceramics having different chemistries starting from organic, Si-based, B-based, and Al-based preceramics have been extensively studied and reported during the past decades [94–99]. The possibility to get wide range of morphologies and the opportunity to process them into numerous forms has further pushed the material community to explore the PDC approach. The availability of commercial precursors also helped to extend the domain of its application. The mechanical, oxidational resistance, thermal stability and performance, electrical properties, optical properties, magnetic properties, piezo resistive behavior, synergistic performances, etc. were of principal interest of exploration in the PDC research community, while the industries took them a level further to application in different fields including the automobile (brakes) and aerospace sectors (high-temperature coatings) [94–97,100]. Nowadays, many of the investigations are on integrating the concepts like MEMS and additive manufacturing techniques with the polymer derived ceramic (PDC) approach [93,94,101,102].

In this section of the chapter, a brief overview of this precursor derived ceramic approach would be discussed with particular focus on Sibased ceramics (Si-O-C-N-(M)) obtained from various organo-silicon based polymeric precursors. The processing of the ceramics would be

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discussed in particular along with a small section citing the properties and applications, and the possible future of this approach and ceramics.

2.1.1 Si based preceramic precursors (PP)

The selection of the precursor is one of the principle steps in the preparation of the polymer derived ceramics. The typical qualities that a polymer should poses, for it to be considered as an economic ceramic precursor are described in numerous reviews in the field [95,100]. The choice of the precursor would affect the composition, phase formations and phase distribution, microstructure, etc. [90,94-97,100]. Several organo-silicon polymers (considering a general equation, (R₁R₂-Si-X) _n) are available, having a Si-Si backbone (eventually deriving into Si-X backbone) to which the different organic substituents (R_1 and R_2) and the functional group (X) are attached [94]. The type of the functional group determines the class of the precursor and the functional groups significantly influence the various physio-chemical properties of the precursors like thermal stability. solubility, the elemental ratios (like, Si to C ratio), the ceramic yield, and the carbon content [94,95]. Some of the common preceramic precursors used for obtaining Si-based ceramics are shown in the Figure 2.1.

Polysilanes and **polycarbosilanes** (**PCSs**) are organo-silicon polymers usually used as precursors to yield nearly phase pure SiC ceramics. Polysilanes (general structure, $(R_1R_2-Si-)_n$) have a linear Sibackbone with the organic substituent side chain (alkyl, aryl, and silyl groups) [97]. Polysilanes are usually insoluble or could not be melted down, and most of their physiochemical properties depends on the molecular weight and the type of the organic side chain [97]. The preparation of the first polysilane dates back to 1921 with the

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preparation of poly(diphenylsilane) by the Wurtz-Fittig coupling reaction [95.97.100], which is still one of the most practiced synthesis approaches. However, Chang and Corev came up with a new dehydrocoupling approach (a catalyst assisted method), which gives higher yield as well as purer polysilanes [97]. The first synthesis of the polycarbosilane (general structure, (R₂Si-CH₂)_n) was explained by the famous Kumada rearrangement reaction, in 1958 [94,95,97,100], starting from the polysilane, poly(dimethylsilane). A methylene group is introduced on to the Si-backbone giving Si-CH₂-Si owing to the cleavage of the Si-Si bond and the formation of the silicon free radical. Thus, by this process, the non melt-able poly(dimethylsilane) is converted into soluble poly(methylsilylene-methylene) as explained by the Yajima process [103]. These class of polymers are often considered as the precursors for β -SiC ceramics. Other methods like coupling, cyclo-polymerization techniques, and thermolytic techniques are also reported for the synthesis of polycarbosilanes [95].



Figure 2.1 Silicon based organo-molecular precursors [104].

Polysiloxanes, also referred to as silicones, are a class of polymers $((R_2Si-O)_n))$ usually used as a precursor for silicon oxycarbide (SiOC) ceramics (by heat treatment in inert atmosphere). The simplest preparation approach is the reaction of the organic chlorosilanes with water (hydrolysis and polycondensation reactions). Another approach is the ring opening polymerization of cyclic silaethers [95,97]. Sol-gel approaches to prepare cross-linked polysiloxanes starting from hybrid alkoxides are also practiced and this approach also allows the introduction of metallic elements (B. Al. and. Ti) into the polymeric network by using corresponding alkoxides [94,95,97,98,100]. Polycarbosiloxanes also yield SiOC on controlled thermolysis. **Polysilsesquioxanes** ((RSi- $O_{1,5}$)_n) are another class of precursors for obtaining SiOC ceramics. The higher cross-linking degree in this case ensures better ceramic yield when compared to that of polysiloxanes. This class of precursors can also be modified using transition metal alkoxides to vield metal-containing silicon oxycarbide ceramics. Si-M-O-C, like SiHfOC and SiZrOC [97].



Figure 2.2 Preparation of various, typical organo-molecular precursors starting from organo-chlorosilanes or by other rearrangement techniques [94].

The ammonolysis/aminolysis of organosilicon chlorides yields **polysilazane** ($(R_2Si-NH)_n$ / $(R_2Si-NR)_n$), which are considered as the main precursors to get Si-C-N ceramics [94,97,100]. However, the polysilazanes like PHPS (considered carbon free precursor) gives Si-N bonds leading to the formation of silicon nitride ceramics, on thermolysis. The first synthesis of polysilazanes were reported in early 1960s by Kruger and Rochow [105,106]. Usually, the ceramic yield in polysilazanes is lower than the other classes of precursors because of the formation of low molecular weight polymers, which easily volatilize (proper crosslinking is always essential). Several researches attempted to increase the ceramic yield of this class of the precursors. Polysilsesquiazanes and Polysilylcarbodiimides ((R₂Si-N=C=N)_n) are also used as precursors for SiCN. Different approaches are explained in literature to synthesize polysilylcarbodiimides. However, the modified approach described in the patent by Murray and Klebe (1968) explained the most efficient approach (simple, with high vield) [96,97]. The first successful synthesis of SiCN ceramics from polysilylcarbodiimides was described in the work by Reidel et al. [107,108]. Normally, the binary phases – SiC and Si_3N_4 , are formed on the thermolysis of polysilylcarbodiimides in an inert atmosphere. The preparation of polysilylcarbodiimides by the non-oxide Stober's process also explained to yield ceramics with Si-C-N chemistry forming SiC₂N₄ (first crystalline ternary SiCN) [107]. Preparation of typical organo-molecular precursors starting from organo-chlorosilanes are shown in Figure 2.2.

It is quite important to have an oxygen-free processing environment while handling polycarbosilane and polysilazane precursors in order to avoid any undesired oxygen contamination in the final ceramics.

Several other precursors containing B and Al to obtain SiBCO, SiBCN, SiAION, SiAICN, and SiAICO ceramics [95,96,98,109–113] and different modified precursors and crosslinkers, giving novel compositions are also reported in literature [114–116].

2.1.2 Shaping and cross-linking of the precursors

The possibility to shape the polymeric precursor (into a thermoset by crosslinking), which could conceivably retain the form even after pyrolysis is one of the critical and the most advantageous stages in the processing of polymer derived ceramics. Different classical (casting, molding, pressing, coating, template replication, etc.) as well as advanced shaping approaches (additive manufacturing techniques) are employed to impart the final form to the ceramic (some of the common approaches are shown in the Figure 2.3).



Figure 2.3 Shaping of the polymeric precursors [117].

The shaping is usually conducted either followed by or along with the cross-linking of the polymers. Proper cross-linking of the preceramics often helps to attain higher ceramic yield after the pyrolysis. The

shaped thermosets formed are usually referred to as the monoliths or green bodies, which retain the shape in the final ceramics obtained after pyrolysis.

The presence of functional groups or by functionalizing a preceramic polymer to have groups like Si-H, Si-NH, or Si-OH helps to achieve an effective crosslinking of the preceramic *via* different reactions [94] to form the green body.

Under normal circumstances, in the presence of oxygen, the crosslinking of polycarbosilanes advances *via* a radical mechanism oxidizing the Si-H and Si-CH₃ bonds, which eventually results in the formation of Si-O-Si bonds (as shown in scheme 2.1) [95]. SiC ceramics with considerable percentages of oxygen (10-12% [95]) are formed after pyrolysis. On the other hand, Si-CH₂-Si bonds are formed in the absence of oxygen contamination due to the reaction between the Si-H and Si-CH₃ groups present, finally forming SiC with low oxygen percentages in them [94–96].

 $= Si-H \qquad \longrightarrow = Si \bullet$ $= Si \bullet + O_2 \qquad \longrightarrow = Si \bullet O-O \bullet$ $= Si-O-O \bullet + = Si-H \qquad \longrightarrow = Si-O-OH + = Si \bullet$ $= Si-O-OH + = Si-H \qquad \longrightarrow 2 = Si-OH$ $2 = Si-OH \qquad \longrightarrow = Si-O-Si = + H_2O$

Scheme 2.1 Crosslinking of PCS *via* radical mechanism in the presence of oxygen (shown for Si-H, adapted from [96]).

In the case of polysiloxanes, the two main mechanisms involved in the cross-linking process are the hydrosilylation reaction (catalyst-initiated addition reaction) and condensation-subsequent hydrolysis reactions. In addition to these, other mechanisms of crosslinking such as radial initiation reactions and vinyl polymerization reactions (at elevated temperatures) also occurs in polysiloxanes [94–97]. Hydrosilylation reactions can be initiated even at low temperatures, by instigating the

reaction of -Si-H functionalities with the available vinyl groups [94] using suitable catalysts. It is an effective method to get water-resilient and high-temperature stable ceramics with Si-C-Si entities [94]. The vinyl and methyl groups could be thermally cross-linked using peroxides [94,95], and silane crosslinkers, which are moisture sensitive. The silanol groups crosslink by condensation, followed by the hydrolysis of the hydroxy/alkoxy groups to form Si-O-Si units (catalysts can trigger reactions at room temperatures also).



Figure 2.4 Cross-linking in polysiloxanes and polysilazanes [94].

In polysilazanes, other mechanisms of crosslinking also exist like, transamination [95,96] and dehydro-coupling [95,96] reactions in addition to the hydrosilylation and vinyl polymerization reactions. Transamination reactions are often triggered at temperatures around 200 °C - 400°C and are always associated with mass losses (loss of ammonia, amines, etc. causing N yield loss). At around the same temperature ranges dehydrogenation (removal of hydrogen) reactions are also initiated owing to the reaction of Si-H groups with N-H/ other Si-H groups forming Si-N/Si-Si bonds, respectively. Volatizing of silane species also causes significant mass loss to polysilazanes (Si yield

loss) [94–97]. Figure 2.4 summarizes the general cross-linking mechanisms in polysiloxanes and polysilazanes.

2.1.3 Ceramics from the crosslinked polymer (polymer to ceramic transformation)- Structural evolutions and final compositions

In the present scenario, extensive studies have been conducted on developing new and advanced approaches [118–122] to the pyrolysis of the pre-ceramics into ceramics with diverse structures and microstructures in addition to the classical methods.

During the pyrolysis stage, the conversion of the polymeric thermoset into a ceramic occurs. The thermolysis of the preceramics involves several solid and vapour phase chemical reactions affecting the composition and the final microstructure of the ceramics formed [97]. The process also comprises of different gas volatizing steps, loss in masses (resulting in the reduction of the ceramic yield), pore formations, densification and associated shrinkage, and various ordering and rearrangements in the elemental network [95.96]. The transformation (polymer to ceramic) generally occurs in the temperature range of 300 °C - 800 °C, first forming amorphous ceramics, sometimes referred to as amorphous covalent ceramics [123,124]. With an increase in pyrolysis temperature (usually above ~1100 °C), the ceramics slowly start ordering along with various phase evolutions to form crystalline ceramics with specific phases. The addition of different fillers were identified to significantly influence the shrinkage and porous formations in these ceramics [125]. The different elemental presence (usually from the starting precursor), the carbon content, and the pyrolysis environment (different gas flows) also has been found to affect the crystallization behavior and the final composition [94,95,97,99]. Figure 2.5 shows the stages of transformation of a preceramic to a ceramic.

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Figure 2.5 Stages of transformation of the polymer to ceramic, on pyrolysis (as shown in ref. [125] for SiCN ceramics).

Cross-linked polycarbosilanes on pyrolysis, show a mass loss up to a temperature of ~850 °C due to the evaporation of the low molecular weight oligomers [123]. The preceramics transform in the temperature range of 550 °C and 800 °C [123,124] to give amorphous SiC/C or near stoichiometric SiC ceramics [123]. This transformation usually advances with the cleavage and the exclusion of Si-H, Si-CH₃, and Si-CH₂-Si bonds with the release of H₂ and methane gas (main mass loss involved) along with the formation of considerable amount of free carbon [123]. Further increase in the pyrolysis temperature initiates a crystallization of the SiC at around a temperature of ~1100 °C [123,126] and beyond 1400 °C (under normal conditions) often resulting in phase shifts and in silica consumption (from oxygen contamination) owing to the carbothermal reduction reactions with the carbot present [127–130].

Cured polysiloxanes on pyrolysis generally give amorphous SiOC ceramics along with a dispersed phase of free carbon (nanodomain models were illustrated by Saha *et al.* [131] and Widgeon *et al.* [132], as given in Figure 2.6). Mineralization reactions involving the evolution of gaseous components (mainly CH₄ and H₂ due to the cleavage of the

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Si-C and C-H bonds) occur at temperature in the range 700 °C -900°C. Below this range the redistribution reactions are active. Bevond 600 °C up to a temperature of 1000 °C. as documented in many literatures, the extensive cleavage process continues [97,133–135] until the formation of the SiOC/C phase. The nature of the bonds in the SiOC ceramics (mixed or non-mixed) could also be tuned by choosing the pyrolysis environment (see Figure 2.7(b)). Mixed bonds can be obtained in the final ceramics by pyrolysis in inert (Ar, He, N_2) environment or in H_2 (to obtain hydrogen-rich SiOC) while, pyrolyzing in CO₂ environment can give non-mixed bonds (due to the cleavage of the Si-C bonds) [136]. The crystallization in this class of ceramics was carefully studied by many researchers [96,133,134]. Basically, as reported by Saha and Raj [137] the crystallization advances in two ways; by the phase separation of the SiOC ceramics into amorphous SiO₂, β -SiC, and carbon at around ~1300 °C and/or the carbothermal reduction of SiO₂ with carbon decomposing to form β -SiC (onset in the temperature range of 1350 °C -1400 °C). However, the free carbon content is a decisive factor in determining the crystallization onset in these ceramics [138].



Figure 2.6 (a) Nano-domain model of SiOC by Saha *et al.* based on SAXS [131] and (b) Widgeon *et al.* [132] based on NMR.

Studies show that different polysilazanes show different pyrolytic behaviors. In the observation by Bill *et al.* [139] on polyhydridosilazane, above 550 °C Si-CH₂-Si units were formed owing to the reaction between Si-H and Si-CH₃, concurrently SiN₄ units were formed owing to the replacement of these methyl groups by N-H; both reactions cause significant release of methane. With further increase in the temperature Si-C and Si-N bonds were formed in them [139].



Figure 2.7 (a) The evolution of the different phases in SiOC and SiCN ceramics [140], (b) evolution of the different phases in SiOC with the pyrolysis conditions [94,140].

However, the vinyl containing silazanes (vinyl polymerization, forming sp^3 carbon chains at low temperatures) on pyrolysis at high temperatures were observed to give sp^2 hybridized carbon through a series of cleavage (Si-C), shifts, and elimination reactions along with formation of Si-H groups (at around 300 °C hydride shift and followed by the elimination of H₂) [97,109,139]. These Si-H participate either in hydrosilylation resulting in Si-C bonds (at lower temperatures) or mainly the de-hydrocoupling with available N-H bonds to form Si-N bonds. Cleavage of Si-C continues, finally leading to transformation of Si-C bonds to SiN₄ units[97].

In polysilsesquiazanes, transamination reactions occur at lower temperatures (200-500 °C) resulting in the release of ammonia and at higher temperatures Si-N bonds are formed (methane evolution) by the Si-C bond cleavage mechanism explained before. However, the transformation always shows anomalies and more can be read from the chapter by Weinmann *et al.* [97]. Generally, the final ceramics formed are having a chemistry Si₃N₄-C [97].

At the same time in polysilylcarbodiimides the Si-N bonds are not preserved as in the case of polysilazanes owing to the thermal breakdown of the Si-N=C=N skeleton. They show different thermal degradation mechanism through the formation of metastable structures. Unlike the polysilazanes, which usually give a mixed, single phase SiCN ceramics with a dispersed free carbon phase in them, the polysilylcarbodiimides, after pyrolysis, give a non-mixed bond (Figure 2.7 (a)) with separated domains. The final ceramics obtained from polysilylcarbodiimides often have a Si₃N₄-C/ Si₃N₄-C-SiC chemistry (more can be read from [97]).



Figure 2.8 SiCN, evolution of the particles with variation in the sintering temperature based on SAXS by Mera et al. [141].

The SiCN ceramics are known for their crystallization resistance and are amorphous to a minimum up to a temperature of 1450 °C [142]. However, after 1400 °C the carbothermal reduction of the SiO₂ phases are initiated [94] and at normal conditions, the carbothermal reduction of Si₃N₄ into SiC is initiated only >1480 °C [94] (the evolution was depicted by Mera *et al.* [141], as shown in Figure 2.8).

2.1.4 Properties and applications

Si-based polymer derived ceramics were extensively studied to elucidate the various application potentialities of this class of ceramics. As mentioned in the introduction part of this chapter, from the mechanical performance to the piezoelectric and magnetic properties of these ceramics have been studied and investigated in detail. The immense possibilities to shape the material, to control the chemistry, high temperature oxidation and creep resistance, and bioactivity are some of the advantages that could be listed. The amorphous nature along with the possibility to tune the properties (electrical, thermal, crystallization character) also add on to the multifunctionality of this class of ceramics. Numerous reports are available discussing the most modern and near future applications of the ceramics derived from this approach [90,91,100-102,104,117,125,143-146,92,147-154,93-99]. Most of the functionalities were found to be an outcome of the basic organization, crystallinity, and mostly the nature of the carbon phase in the matrix [94].

While some of the recent application interests on PDCs clearly show the versatility of these ceramics, the thermal stability and oxidation resistance of this class of material (especially, ceramics like Si-B-C-N are reported to be stable >1800 °C [98]) have boosted their choice for various high temperature applications like high temperature insulation systems (by engineering pores) [155], ceramic glow plugs [156], TBC's [113,157,158], etc. The possibility to have porous structures out of these ceramics has advanced its application further to different fields with immense societal importance like water purification [159,160], drug-delivery [161], catalysis [162,163], radiation shielding and absorption [151], etc. The ease of fabrication has pushed its application in the field of MEMS [102,164] and the possibility to club additive manufacturing techniques has facilitated the fabrication of micro components like micro-gears [154], micro-igniters [165], etc. with decent precision. The tunable electrical and thermal properties (often attained by controlling the phases and the carbon percentages) helps in attaining structures with engineered properties [158,164,166]. The high piezo-resistive values reported for SiCN chemistry along with high stability makes this class of ceramics an excellent candidate for various sensing-applications [167–169]. The thermo-electric character of these ceramics is also investigated with immense expectations [170]. Studies on the lithium-ion storage capacities has evidenced SiOC and SiCN ceramics/composites to be excellent anode materials with high cyclability [115,136,171]. The bio-activity of these ceramics are investigated nowadays. The SiOC/SiOC- based composites have been reported in numerous literatures to be bio-compatible with efficient antimicrobial characteristics [147]. Investigations suggest the use of these ceramics in various body-implants and bio-machineries (artificial-pacemakers) [172]. Numerous other applications like ceramic brake-shoes for bikes, coatings on launch vehicles, pump components, in membrane applications, etc. are also reported [94,96].

However, better understanding of the performances and the properties of these ceramics are essential to reach more realms of applications in the future.

2.2 Thermal properties of silicon (Si) based PDCs- an overview

Even though, the thermal stability, high-temperature performance, etc. of the Si based polymer derived ceramics are often referred to, nonetheless the thermal properties and the heat transport in PDCs are the least explored among the different investigated properties of these ceramics. In this section, the main motive is to compile the available reports on the thermal properties of mainly Si-O-C-N ceramics, considering each chemistry and to identify the gap in the understanding of the thermal properties.

The thermal properties of SiC ceramics are always of great interest. numerous literatures are available studying the thermal transport [56,173–179], however, the reports on the thermo-physical properties of precursor derived SiC are scarce. Primarily, the thermal conductivities (λ) were measured on β -SiC (with 77% theoretical density) with polycarbosilane based precursors as the binding phase (10 - 30 W.m⁻¹,K⁻¹) [180]. In a different work, SiC ceramic composites coated with polysilazane derived silicon-carbonitride ceramic were found to improve the interfacial adhesion and the thermal conductivity (1.2 - 4.6 W.m⁻¹.K⁻¹) of the composite due to the formation of conduction paths [181]. Still, the lowest λ value reported in literatures for amorphous SiC is ~4 W.m⁻¹.K⁻¹ [182]. Meanwhile, the thermal diffusivity and the specific heat values exclusively for polymer derived, dense (1.9 - 1.96 g.cm⁻³) SiC (from polydimethylsilane, microwave sintered at 1200 °C) were measured and the λ was calculated to be in the range 0.81 W.m⁻¹.K⁻¹ to 1.37 W.m⁻¹.K⁻¹ [183]. The polymer derived approach to modify the carbon percentages in the SiC, whereby tuning the thermal property of dense (2.2 - 2.4 g.cm⁻³) SiC was reported by Li et al. [184]. The ceramics pyrolyzed at 1300 °C showed a significant variation in the λ from 8.4 - 74.4 W.m⁻¹.K⁻¹ due to the influence of the carbon percentages and the crystal sizes [184]. Very recently, Balestrat et al. [185] reported the possibility to tune the thermal properties of AHPCS derived SiC ceramics by boron modification. The λ was found to decrease from 45.1 W.m⁻¹.K⁻¹ to 17.7 W.m⁻¹.K⁻¹ owing to the influence of the porosity and the oxygen concentration.

Incorporation of porosities into SiC was found to significantly decrease the λ values corroborating the possibility to develop high temperature thermal insulators. SiC powder along with PCS and other agents were also testified to get structures with porosity ~70% and with a TC ~0.5 W.m⁻¹. K⁻¹ [186]. Porous SiC ceramics were developed from an indigenously developed polycarbosilane (PCS) compact at different pyrolysis conditions and were measured to poses low thermal conductivity (0.5-1.6 W.m⁻¹. K⁻¹) and good oxidation resistance at a lower pyrolysis temperature (1200°C to 1500°C) when compared to a higher pyrolysis temperature (1800 °C. c.a. 3 W.m⁻¹, K⁻¹) [187]. A simple polymer derived replica approach to develop light, reticulated SiC ceramic foams using polyurethane (PU) foam as the template was reported by Jana et al. [155]. The attempt was found reasonably promising as solid strutted, stable, porous (up to 98%) SiC ceramics with variable densities (by controlling the precursor to the template ratio), good oxidation resistance up to 1500 °C and decent machinability were obtained. These open-celled foams were also found to have very low thermal conductivity values, in the range 0.05-0.12 W.m⁻¹. K⁻¹ (samples pyrolyzed at 1200 °C) and could be tuned by varying the bulk density. Polymer derived nanowire aerogels with ultralow thermal conductivity (0.025 W.m⁻¹. K⁻¹) and good fire-erosion resistance [188] were also reported recently. The SiC ceramics are reported to have very low coefficient thermal expansion (CTE), ~4.5 x 10⁻⁶ .K⁻¹ (upto ~1200 °C) [42,54].

To the best of our knowledge, the λ of SiOC ceramics was first reported by Gurlo *et al.* [189]. They observed that the λ of SiOC coincides the range of the λ reported for fused silica [190] and that of amorphous carbon at lower temperatures [191]. The porosities and the densification were found to have significant contribution on the final λ of these ceramics (Figure 2.9 (a)). The λ of dense, hot-pressed (@1600 °C) SiOC ceramics with significant free carbon percentage was measured (RT up to 1000°C) to be in the range from 1.4 to 1.75 W.m⁻¹. K⁻¹. The work also reported the possibility to adjust the λ using external phases (Hf and Zr oxidic phases) (Figure 2.9 (b)). Mazo and co-workers [121,192] also determined the λ of spark plasma sintered SiOC materials to be between 1.4 and 1.83 W.m⁻¹. K⁻¹. The CNF incorporation to these ceramics was found to improve the λ (to a maximum value of 2 W.m⁻¹. K⁻¹ @ 10% of CNF loading) (see Figure 2.10(a)) [193].



Figure 2.9 (a) Comparison of λ measured for SiOC with silica, a-carbon, and graphite (b) λ variation with external phase additions (as reported by Gurlo *et al.* in ref. [189]).

Recently, Eom *et al.* [194] reported that the λ values of SiOC were ranging from 1.3 to 1.8 W.m⁻¹. K⁻¹, depending on the processing temperature. The inclusion of barium (SiOC-Ba) was found to increase the λ (from 1.8 - 5.6 W.m⁻¹. K⁻¹). Fillers like h-BN also was found to increase the λ in SiOC [170].



Figure 2.10 (a) λ measured at different SPS sintering temperature for SiOC by Mazo *et al.* [192], (b) showing the influence of phases on the λ of SiOC, as reported by Stabler *et al.* in ref [195].

Stabler *et al.* [195] studied the effect of the phase compositions and microstructures on the thermal properties of SiOC ceramics and found

that increasing the amount of SiC nano-crystal content or precipitated C can lead to an increase of λ up to a maximum value of 2.7 W.m⁻¹.K⁻¹ (see Figure 2.10(b)).

Reticular macro-porous SiOC obtained from polysiloxanes having a porosity in the range of ~74% to ~89% was reported to give a λ in the range of ~0.04-0.08 W.m⁻¹. K⁻¹ [196]. The CTE of vitreous silica is reported to be very low, 0.57 x 10⁻⁶ .K⁻¹ [197]. However, the CTE of SiOC was recently reported 1.84-3.23 x 10⁻⁶ .K⁻¹ in the temperature range from 100 to 1000°C [195]. The higher CTE value in spite of having a SiO₂ matrix could be because of the presence of nano-SiC domains and continuous network of turbostratic carbon [195]. The CTE of Si(Al)OC ceramics was measured to give a value of ~1.56 x 10⁻⁶ .K⁻¹ (in the temperature range of RT- 1100 °C), higher than that reported for vitreous silica and lower than SiOC ceramics (showing significant influence of Al on the shrinkage characteristics) [198].

The λ of SiCN/SiCN(O) ceramics have been hardly reported. The thermal diffusivity was measured on SiCN ceramics by Janakiraman *et al.* [199]. There were random studies mentioning or measuring the λ of SiCN-O ceramics, to be in the range of other Si-based PDCs [157,181,200–203]. Also, the λ of these ceramics are reported to increase with inclusions of BN-nanotubes in them. However, an organized report of the properties, to the best of our knowledge, was not found. The reported CTE of SiCN(O) was in the range (2.15 - 2.69) x 10⁻⁶. K⁻¹ [204]. Recently, the λ of SiBN ceramics were calculated to be in the range 2.3-2.7 W.m⁻¹. K⁻¹ by applying computational approach (DFT calculations and MD based simulations) [205]. The λ of SiBCN (dense, films, and, foams) ceramics has been reported to be in the range of 0.40 - 3.6 W.m⁻¹. K⁻¹ [203,206–209] and the CTE reported is ~2 x 10⁻⁶. K⁻¹ [208].

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2.3 Thermal properties of Carbon

Significant presence of free-carbon (turbostratic carbon) are often reported along with PDCs [158,210–212]. The extent of this carbon dispersion is one of the significant factors influencing most of the properties of these classes of ceramics, including the thermal properties [158,164,171,195,212,213]. Hence, it is important to have an idea about the value of λ and the other thermal properties for this dispersed phase. Numerous literatures are available, studying the thermal properties of the different carbon polymorphs [214,215,224,216–223].



Figure 2.11 The λ measured for different carbon polymorphs and its derivatives as reported by Balandin [24].

However, the review by Balandin [24] gives a complete picture about the thermal transport in the different carbon-based materials, as shown in Figure 2.11. The λ of amorphous carbon from different literatures were measured to be in the range of 0.01- 3.48 W.m⁻¹. K⁻¹ (measured up to a temperature of ~1200 °C) [24,225,226] and 0.1-10 W.m⁻¹. K⁻¹ for diamond-like- carbon (DLC) [24]. Pyrolytic graphite on the other

hand was found to give a range of λ . The λ value was measured to be in the range from (~100 - ~450) W.m⁻¹. K⁻¹ (measured parallel to the basal plane) and (~0.62 - 2.92) W.m⁻¹. K⁻¹ (measured perpendicular to the basal plane) [53,227]. The thermal expansion in pyrolytic graphite often shown anisotropy. The reported CTE for pyrolytic graphite is around ~2 x 10⁻⁶. K⁻¹ (// to basal plane) and in the range of (24-29) x 10⁻⁶. K⁻¹ (\perp to basal plane) [227,228].

In spite of these recorded studies on understanding the thermal properties of polymer derived ceramics, there are scarce reports, apart from a few works, (namely the ones from Gurlo et al. [189] (in 2016), Mazo et al. [192] (in 2017), and those from Stabler et al. [195] and Eom et al. [194] (in 2018), restricted only to the study of the thermal properties of SiOC ceramics) which are systematically studying the thermal properties, especially that of the basic chemistries, Si-C, Si-O-C. and Si-C-N-O. The main objectives of this thesis work are scripted down with the motivation to analytically study the thermal properties of at least these basic chemistries (having mixed-bonds), considering the different factors that influence the property values. The work presented in the thesis is a contribution to the research community and an addon to the available literature, which is inadequate, in this regard. In addition to this, the possibility to develop thermally stable-highly porous structures (foams) out of these ceramics, exploiting the relative ease of fabrication for application as high temperatures insulators is also endeavored.

The methods of processing and the characterization techniques are discussed in the next chapter (Chapter 3).

Chapter 3. Experimental: Materials, Syntheses, and Characterization techniques

In this chapter, the materials used, the experimental techniques, and the different characterization tools used at various stages of the study are discussed.

3.1 Materials used

The processing of the ceramics starts from silicon based organomolecular precursors. Along with these precursors; carbon enrichers, catalysts, and different solvents were also used for the processing. Polymeric foam templates were also employed at a particular stage of the processing. In this part of the chapter, a briefing of the various chemicals, solvents, and template used will be given.

3.1.1 Preceramic precursors (PPs)

i.) SMP 10

StarPCS[™] SMP 10 (Starfire Systems Inc., Schenectady, NY, USA) is basically a commercially available, allyl-hydro-polycarbosilane and it was chosen as the one-component precursor for SiC ceramics. This precursor can give a near stoichiometric SiC and poses considerable ease in the handling.

The suppliers promise a ceramic yield of 72 -78% when pyrolyzed at a temperature range of 800 °C to 1200 °C forming amorphous SiC and with further increase in the temperature to >1250 °C, the crystallization reactions are initiated forming β -SiC. Some of the main properties of SMP 10 as given by the supplier are enlisted in the Table 3.1 [229].

StarPCS™ SMP 10		
Density (g.cm ⁻³)	0.998	
Appearance	Clear, amber liquid	
Viscosity (cPs)	40-100 @ 25 °C	
Solvents	Hexane, THF, Toluene	
Moisture	Low / inert or vacuum	
sensitivity/Storage	refrigerated	
Flash point (°C)	89	
Risks	Non-hazardous	

Table 3.1 Properties of StarPCS[™] SMP 10 [229].

ii.) SPR 036

Polyramic[®] SPR 036 (Starfire Systems Inc., Schenectady, NY, USA) is chosen as the polymeric precursor to yield SiOC ceramics. The presence of Si-C and Si-O bond structures in the organic framework and the possibility to cure at low temperature are its advantages. The suppliers promise a ceramic yield in the range of 60%-80% when pyrolyzed between 850 °C and 1100 °C. The ceramics from SPR 036 are also claimed to have high oxidation resistance. Some basic properties are given in the Table 3.2.

Polyramic [®] SPR 036		
Density (g.cm ⁻³)	1.1	
Appearance	Clear, slightly milky liquid	
Viscosity (cPs)	50-500 @ 25 °C	
Solvents	Hexane, THF, Toluene,	
	Acetone	
Moisture	Room temperature	
sensitivity/Storage		
Flash point (°C)	56	
Risks	Hazardous	

iii.) Durazane 1800

Durazane 1800 (CAS#: 503590-70-3; Merck Performance Materials GmbH, Wiesbaden, Germany), a commercially available oligosilazane, was used as the precursor to get SiCN/ SiCN(O) chemistry. The basic backbone is formed with silicon and nitrogen atoms, where one silicon atom is bonded to two separate nitrogen atoms and further each nitrogen to two other silicon atoms. The ceramic yield is reported to be in the range of 75% - 83% [231]. The artefacts made out of this precursor are claimed to be stable up to 1800 °C. Some basic properties are shown in the Table 3.3.

· · · · · · · · · · · · · · · · · · ·		
Durazane 1800		
Density (g.cm ⁻³)	~ 1.0	
Appearance	Clear liquid	
Viscosity (cPs)	<100 @ 20 °C	
Solvents	-	
Moisture	Moisture sensitive / Dry place-	
sensitivity/Storage	ventilated-in tightly closed	
	container	
Flash point (°C)	21	
Risks	Hazardous	

Table 3.3 Properties of Durazane 1800 [232] .

iv.) PHMS⁶

Poly hydrido-methyl-siloxane (PHMS, MW 1900, CAS#: 63148-57-2; Gelest, Morrisville, PA, USA) was another precursor used for obtaining the Si-O-C chemistry.

⁶ Sometimes referred to as PMHS, Poly-Methyl-Hydro-Siloxane
PHMS			
Density (g.cm ⁻³) 1.0			
Appearance	Clear transparent liquid		
Viscosity (cPs)	10-50 @ 20 °C		
Solvents	Acetone, Alcohols, Ethers, etc.		
Moisture	Moisture sensitive / Cool- Dry		
sensitivity/Storage	place		
Flash point (°C)	204		

Table 3.4 Properties of PHMS.

The crosslinked PHMS on pyrolysis usually gives SiOC and the percentage of carbon could be tuned using different carbon enrichers [171], which would be discussed in the next sections. Property details shown in Table 3.4.

3.1.2 Crosslinkers and carbon enrichers used

These organics are usually employed, on one side, for enhancing the crosslinking by increasing the amount of available vinyl moieties, thus expediting the hydrosilylation reactions while on the other side acting as carbon enhancing agents. Thus, they provide the opportunity to tune the final carbon content in the ceramics, which would cause significant property variations in them. Basically, DVB was used as the main carbon tuner (also as a crosslinker) in this work, and TVTMS was another crosslinking agent used, described as follows:

i.) DVB

Divinylbenzene (DVB, CAS#: 1321-74-0; Sigma-Aldrich, St. Louis, MO, USA) was used as one of the crosslinkers/carbon enrichers. These were used to obtain basically carbon rich samples of the different chemistries.

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ii.) TVTMS

1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (TVTMS, MW 345, CAS#: 2554-06-5; Gelest, Morrisville, PA, USA) was the other crosslinker basically used to obtain carbon poor or samples with less amount of free carbon in them when compared to that of DVB crosslinked samples.

3.1.3 Catalyst

Karstedt's catalyst, Platinum (0)-1,3-divinyl-1,1,3,3 tetra-methyldisiloxane complex in xylene, having a platinum (Pt) content of ~2% (CAS#: 68478-92-2; Sigma–Aldrich, Saint Louis, MO, USA) was used as the hydrosilylation catalyst, further diluting it to a solution having 0.1% of Pt in the xylene. The basic chemical structures of the precursors, the Pt. catalyst, and the crosslinkers are shown in Figure 3.1.



Figure 3.1 Basic chemical structures of the precursors, cross-linkers, and the catalyst.

3.1.4 Template used (foams)

Polyurethane foams⁷ were used as templates for developing ceramic foams (processing will be discussed in detail in the methods part of this chapter). Two different types of polyurethane foams, PU, were used (ARE- S.r.I, Rosate, Milan, Italy) for the processing (see Figure 3.2) [233].

- i.) MTP-55 is a commercially available, polyester-based PU foam. The main feature of this kind of the PU foam is the partially closed cells. They are comparatively denser and have a density of 0.055± 5% g.cm⁻³. In most cases where we have used this foam, the abbreviation M would be used.
- ii.) PPI-60 is also a commercially available polyester-based PU foam with mostly open cells and having a density of 0.025± 8% g.cm⁻³. There are different variants of PPI viz. 10,30,60,90, etc. In this study we have chosen the PPI 60. It would be abbreviated as P generally.



Figure 3.2 Polyurethane (PU) foams used as templates; (M) MTP 55 with more closed pores, (P) PPI-60 with more open pores (as evident from the figure).

 $^{^{7}}$ More details of the PU templates could be read from the product brochure added as Annexes.

3.1.5 Solvents used

Several solvents like acetone (CAS#: 67-64-1; > 99% pure, Sigma– Aldrich), hexane (CAS#: 110-54-3), xylene (CAS#: 106-42-3, Sigma– Aldrich), and ethanol (CAS#: 64-17-5) were also used at different stages of the processing.

3.2 Methods and syntheses

In this section, the main methods for the preparation, processing conditions, and the set of samples prepared for the dense disks and the porous foams will be discussed.

3.2.1 Preparing thin, dense ceramic disks

Thin pore-free ceramic disks were prepared to study the dense properties. The disks were prepared by casting the precursor solution and the subsequent pyrolysis of the crosslinked preceramic disks punched out from the thin preceramic films formed. The processing steps are described below in detail:

i.) Preparation of the mould

The moulds were prepared by sticking a mylar sheet on a of flat plexiglass block. The surfaces of the PMMA block were initially cleaned properly to avoid any dirt or protrusions which can affect the surface flatness. A double-sided tape was used to stick the mylar film. It was taken care that while sticking the tape no air-bubbles got entrapped between the tape and the mylar film. The edges were folded up and taped or pinned to form of a small castable crucible/mould (see Figure 3.3).



Figure 3.3 Mylar lined mould used for casting the precursor.

ii.) Casting of the precursor solution

The precursor is often mixed with a solvent/s (acetone, acetone + hexane, etc. were used depending on the precursors, viscosity, and ability to dissolve, @1:1 ratio by wt. with the precursor). The cross-linker, carbon enhancers, and the catalyst were also added along with the solution and were blended with the help of a magnetic stirrer. However, it was made sure that no air-bubbles got entrapped during the processing, which would be difficult to remove later. The solution system was then slowly casted on the mould making sure no air bubbles are formed during the transfer. The moulds casted with the precursor solutions were left free for cross-linking and drying for a period of 2-3 days at RT conditions.

iii.) Precursor disks

Once the films were formed (see Figure 3.4(a)), thin disks were punched out from them before it becomes really brittle (see Figure 3.4(b)), to avoid the cracking while punching. The disks were punched out into different dimensions (diameters between 10 mm and 24 mm) depending on the requirement.

iv.) Ceramic disks by controlled pyrolysis

The preceramic disks were pyrolyzed in controlled atmosphere to obtain the final ceramic disk.

The pyrolyses, in this work, were carried out either in a tubular alumina furnace (Lindberg/Blue, USA) or in a graphite furnace (Astro furnace, model 1000-4560-FP30, Thermal Technology, Inc., Santa Barbara, CA). The tubular alumina furnace can operate up to a maximum temperature of 1600 °C. It was also possible to control the pyrolysis atmosphere (pyrolysis could be carried out in nitrogen, argon, air, and, CO_2 atmosphere) inside the furnace. While, the graphite furnace can be operated up to a temperature of *c.a.* 2000 °C. This furnace should be operated in an argon (inert) atmosphere and has an efficient water-cooling system. It is also possible to program both these furnaces to have different heating and cooling rates. Usually, very low heating and cooling rates, like 1-2 °C/min, were applied for pyrolyzing the disks in order to avoid cracks due to thermal stresses developed.

Here, the preceramic disks were pyrolyzed at different temperatures, from 1200 °C to 1800 °C. The alumina tubular furnace was used for the pyrolysis at the lower temperature range of 1200 °C-1600 °C and high temperature pyrolysis (> 1600 °C, upto 1800 °C) was carried out using the graphite furnace. The SPR 036 and PHMS (SiOC precursors) disks and SMP 10 (SiC) disks were pyrolyzed in argon atmosphere while the Durazane 1800 (SiCN(O) precursor) disks were pyrolyzed in N₂ atmosphere. The gas flow rate was fixed at constant value of 300 mL/min throughout the pyrolysis cycles in the alumina furnace and in the graphite furnace.



Figure 3.4 (a) Thin films formed, and (b) the preceramic disks punched out from the films formed and the final ceramic disks after pyrolysis.

The thermal cycle inside the furnace started with an initial 5 hours of keeping the preceramic disks at room temperature in the planned atmosphere (this was to make sure that the atmosphere around the samples is the controlled one and the possible reactive air, which was previously present in the tube, is totally purged out). Then the ramp starts to the maximum temperature (as mentioned before at a low heating rate, usually 1 °C/min) without any intermediate stops. The furnace will be held (dwell) at the maximum intended temperature for a period of 1-1.5 hour before starting the cooling ramp back to the room temperature (at a cooling rate of 1 °C/min). A brief scheme of the processing of ceramic thin disks could be seen in the Figure 3.5.



Figure 3.5 Scheme showing the preparation of the ceramic thin disks.

v.) Compositions prepared

Basically, 3 sets of samples were prepared to conduct different studies. The sets of samples prepared are given in Tables 3.5, 3.6, and 3.7.

Set 1, represented in the Table 3.5 were intended for the general studies of the thermal properties of the Si-O-C-N ceramics. These ceramic disks were prepared by pyrolysis at 1200 °C in inert atmosphere (most of the studies). Selected samples were pyrolyzed at other temperatures for certain studies (at 1500 °C and 1800 °C in SC 1 and SC 2 samples and at 1400 °C for the SO-1,2 and SN-1,2 samples). Set 2, represented in the Table 3.6 were devoted exclusively to study the influence of free-carbon on the thermal properties of SiOC ceramics, and set 3, represented in the Table 3.7 were for the studies to understand the influence of free carbon on the Young's modulus and the hardness of SiOC ceramics. For set 2 and 3, all samples were prepared by pyrolysis at 1200 °C.

Table 3.5 Set 1: Samples prepared for studying thermal properties of Si-O-C-N ceramics (with different DVB cross-linking).

Samples	SMP 10	SPR 036	Durazane 1800	DVB
	(g)	(g)	(g)	(g)
SC 1	2.0			0.15
SC 2	2.0			0.45
SO 1		1.5		0
SO 2		1.5		0.15
SN 1			1.5	0
SN 2			1.5	0.15

Samples	SPR 036 (g)	DVB (g)		
SO-S1	1.5	0.75		
SO-S2	1.5	1.5		
SO-S3	1.5	3		
SO-S4	1.5	6		

Table 3.6 Set 2: Samples prepared for studying the influence of different phases on the thermal properties.

Table 3.7 Set 3: Samples prepared for studying the influence of the carbon on the Young's modulus and hardness.

Samples	PHMS (g)	TVTMS (g)	DVB (g)
SiOC-1	1	2	-
SiOC-2	2	5	-
SiOC-3	1	-	1
SiOC-4	1	-	2
SiOC-5	1	-	4
SiOC-6	1	-	6

3.2.2 Processing reticulated foams by replica technique

Porous ceramic foams, which are replicas of PU foams, were prepared by controlled pyrolysis of the precursor impregnated PU porous structures. The detailed method is given below:

i.) Preparation of the monolith/preceramic foams

The preceramic foams were prepared upon impregnating PU foams with the commercial preceramic precursors. Acetone was used as the solvent for SPR 036 (SiOC precursor) and Durazane 1800 (SiCN(O) precursor) precursors while an acetone (50%) + hexane (50%) mixture was used for SMP 10 (SiC). The use of the solvent helps to decrease the viscosity of the polymeric precursor solutions, to cause a swelling

effect to the PU foams (as low viscosity is favorable for effective swelling of the polymer foam) as well as to provide suitable dissolution and homogeneous mixing of the used platinum (Pt) catalyst (100 μ L of 0.1% Pt solution per 1 g of polymer precursor). The amount of acetone used in the impregnation process was always 1/5th of the volume of PU template. The PU foams of the required dimensions were manually impregnated with this solution system. The process is repeated until visually all the solution has been taken-in by the PU foam, resulting in the swelling of the same. The impregnated PU foam is then left for drying usually for a period of 24 h at room temperature conditions before conducting the pyrolysis.

ii.) Impregnated PU foams to ceramic foams

The pyrolysis of the impregnated foams was carried out in the temperature range of 1200 °C -1800 °C, similar to that of the disks (low temperature range (1200 °C -1600 °C) pyrolysis was carried out in the alumina furnace and higher (>1600 °C, upto 1800 °C) in the graphite furnace). A heating rate of 5 °C/min was used at a gas flow rate of 300 mL/min (N2 was used for SiCN(O) samples, while Ar was used for the SiC and SiOC samples) with 5 h of gas purging before starting the heat treatment. Typically, one intermediate dwell step was applied, differently from that of the disks, at 600 °C for 0.5 h to ensure complete removal of the polyurethane template and then the dwell at the peak temperature lasting for 2 h. After this, the furnace was switched off to allow free cooling to room temperature.

iii.) Compositions prepared

The different ceramic foams, SiC, SiOC, and SiCN(O) were prepared by the pyrolysis of the polymeric precursor impregnated PU templates, as described in detail in the same section (3.2.2). As mentioned, basically two kinds of PU foam templates were used (**M** and **P**) and the ceramic foams were prepared by impregnating different amounts (by



Figure 3.6 Scheme showing the preparation of the ceramic reticulated foams.

weight) of the particular polymeric precursors onto the particular PU template and heat treating the same (the detailed processing scheme for the ceramic foams is shown in Figure 3.6).

Monoliths (polymeric precursor impregnated PU foams) with weight ratios of, polyurethane (PU); polymeric precursor (PP), 1:0.5, 1:1, 1:2, 1:3, 1:4, 1:5, and 1:6 were prepared for obtaining the three different final chemistries for the ceramics, starting from their respective precursors. The main studies were carried out on samples prepared by pyrolysis at 1200 °C. However, different studies were also conducted on samples prepared at other pyrolysis temperatures (up to a maximum of 1800 °C). The samples were labeled or named to include the information of the final chemistry, the type of the PU template used and the PU:PP ratio of the monolith used to get the ceramic. At in certain cases, the pyrolysis temperature would also be represented e.g., the ceramic sample prepared from a mixture with a 'M' type PU template: polycarbosilane (SMP 10), with a weight ratio of 1:4 and pyrolyzed at 1800 °C was named SiC-M4 1800 or a sample prepared from a mixture with 'P' type PU and polysiloxane (SPR 036) with a weight ratio of 1:2 pyrolyzed at 1200 °C would be labeled SiOC-P2 1200. In some cases, the samples were labelled only SiC, SiOC, and SiCN(O) in order to avoid complications. However, in these cases, the details of the sample chosen for that particular study will be clearly mentioned along with the associated text or figure.

3.3 Characterization techniques

In this section, the main characterization techniques employed to study the materials, starting from the precursor polymer to the final ceramics, will be discussed. A brief outline of characterizations conducted are depicted on the Figure 3.7.

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Figure 3.7 Characterization techniques, in a nutshell.

3.3.1 Density measurements

The bulk density (ρ_b), also known as the geometrical density of the material can be attained from the ratio of the measured mass and the volume computed (from the dimensions) of the material. This measured density also accounts for the porosities in the solid material.

3.3.1.1 Archimedes method

The apparent densities (ρ_t) of the dense ceramic disks could be obtained from the classical methods based on Archimedes' principle. A special setup is used to determine, basically three different weights of the disks, i.e. the dry weight (W_D, the weight of the dry sample), suspended (W_S, the suspended weight of the sample, in water), and the wet weight (W_w, the weight of the sample after filling the air-filled pores, if any). The densities could be calculated from the equations below;

$$\rho_b = \frac{W_D}{W_W - W_S} \tag{eq. 3.1}$$

$$\rho_t = \frac{W_D}{W_D - W_S} \tag{eq. 3.2}$$

However, this method was not suitable for the porous foams owing to their light nature.

3.3.1.2 Helium Pycnometry

Helium pycnometry was used to determine the skeletal density of the ceramics, which formed the porous network in the foams, considering there are no closed pores. At isothermal conditions, the volume occupied by the sample in a chamber of known volume, filled with helium gas, could be found out and by measuring the mass of the sample used, the density, which is the skeletal density (ρ_s) can be computed.

The skeletal density measurements were performed using a helium pycnometer (AccuPyc 1330 TC, Micromeritics, Norcross, GA, USA). The foam samples were properly packed in the 1.0 cc chamber so as to fill at least the 60-70% of the volume of the chamber. A total of 300 runs or cycles were made on one sample so as to obtain a stable value. The temperature was maintained at ~22.6 °C throughout the analysis.

The percent of pore volume can be calculated by the equation (eq. 3.3),

Porosity (%) =
$$\left(1 - \frac{\rho_b}{\rho_s}\right) X \, 100$$
 (eq. 3.3)

3.3.2 Thermo-gravimetric analysis (TGA)

The thermo-gravimetric analysis (Netzsch STA 409, Netzsch Gerätebau Gmbh, Selb, Germany) was used at different stages of the work; to study the thermal degradation of the template used, to comprehend the ceramic-yield of the different precursors, to determine the thermal stability of the final ceramics, etc. The thermo-gravimetry

was conducted at different controlled atmospheres like argon, nitrogen and in air (flow rate used was 50 mL.min⁻¹) depending on the requirement and type of study planned. The chamber is usually rinsed three times with the intended gas, before starting the thermal cycle so as to make sure that the chamber is free of any reactive gases. Nearly, 30-50 mg of the samples were used for each analysis. The thermal cycle was carried out at a heating rate of 10 °C.min⁻¹ up to 1550 °C (usual maximum temperature).

The DTA (differential thermal analysis) measurements coupled with the TG would also help to understand clearly the onset of various reactions and to detect various volatile expulsions at different stages of the thermal treatments on the precursor polymer.

3.3.3 X-ray diffraction (XRD)

The diffraction studies were conducted on the final ceramic powders (both dense disks and foams) to understand the phase evolutions. The analysis was carried out on different samples prepared by pyrolyzing at varying temperatures using a copper (Cu) K α radiation source (of wavelength, 1.541 Å) in a 2 θ angle ranging from 10 to 90°, with a step size of 0.05°, and the data were plotted after normalization.

In this study, the instrument Rigaku D / Max-B diffractometer (Rigaku, Tokyo, Japan) and Italstructures IPD3000 diffractometer (Italstructures, Arco, Italy) with the CPS120 detector on the diffracted beam were used.

The data analysis and the crystallite sizes determination were conducted with the help of the Material Analysis Using Diffraction (MAUD) software based on Rietveld approach.

3.3.4 Fourier transform infrared spectroscopy (FT-IR)

The structural nature of the PU templates and the knowledge regarding the type of bonds present in the preceramics were mainly gained from the FT-IR spectroscopic technique. The final ceramics were also studied using this technique (even though much information was not obtained). The spectra were acquired in transmission mode either using the KBr pellets or by directly using the powders (final ceramics) or small portions (PU template) operating in the instrument in ATR mode on the instrument Varian 4100 (Agilent Technologies, Inc., Santa Clara, CA, USA). An average of 32 scans with a resolution of 4 cm⁻¹ was conducted on each sample.

3.3.5 Raman spectroscopy

Raman spectroscopy was used as an effective tool to probe into the nature of the carbon in the final ceramics. The Raman spectra obtained from the Horiba HR800 micro-Raman spectrometer (Horiba Jobin Yvon GmbH, Bensheim, Germany, using Argon laser, wavelength = 514.5 nm) basically gave two main characteristic bands (peaks) [234,235];

'D'-band (usually at the position ~1360 cm⁻¹, due to the breathing modes of the sp^2 atoms in the rings), owing to the disorder induced vibrations, and

'G'-band (usually at the position ~1580 cm⁻¹, due to the bond stretching of all sp² atoms in the rings and chains) (see Figure 3.8).

In addition to this, the disordered carbon also shows some overtones and combinational modes of the D and G, observed at the positions, 2500-2800 cm⁻¹ (2D) and 2900 cm⁻¹ (D+G) [195].



Figure 3.8 Influence of clustering and bond ordering on the D and G bands in the Raman spectra[235].

Different information like the degree of clustering of the carbon in the material, the bond order, etc. can be obtained from the D and G bands. Also, the ratio of the intensities of the D and G bands (I_D/I_G) gives information regarding the crystallite size of the carbon [234,235]. The fitting of the curves, peaks intensities, and the integral area of the D and G bands were obtained using the spectroscopy software OPUS 7.2 (Bruker Corp., Billerica, MA, USA).

3.3.6 Scanning and transmission microscopy (SEM/TEM)

The scanning electron microscope (SEM) JEOL JSM 5500 (JEOL, Tokyo, Japan) was used to study the morphology of the PU template and to confirm that the final ceramics correctly replicated the structure and the cell features of the template. The SEM micrograph investigation of the fractured surfaces of the foams as well as the dense disks are also important, to understand the nature of the structs (in the case of the foams) and to confirm that the prepared ceramic disks are dense.

The scanning/transmission electron microscope, STEM Talos F200S (Thermo Fisher Scientific, Waltham, MA, USA) equipped with an EDS Super-X detector was used mainly to probe deep into the microstructural nature of the Si-O-C-N ceramics, and to understand the extent of the SiC nanocrystals and turbostratic carbon phase formation.

3.3.7 Nitrogen physisorption analysis

 N_2 physisorption measurements with an ASAP 2010 Micromeritics instrument (Micromeritics, Norcross, GA, USA) helps to estimate the pore size distribution in the ceramic samples. The N_2 gas is physically adsorbed on the surface owing to the forces acting between the solid and the gas (*'van der Waals'* forces). Normally, the quantity of gas adsorbed depends on the mass of the sample, the temperature, and the vapour pressure (P) of the gas. Considering 'n' as the quantity of the N₂ adsorbed (in moles per gram) on a given solid at a constant temperature (T),

$$\mathbf{n} = f(P)_{T,solid,N_2} \tag{eq. 3.4}$$

If the considered temperature is below the critical temperature of N₂, (eq. 3.4) can be modified as,

$$n = f(P/P_0)_{T,solid,N_2}$$
 (eq. 3.5)

where, P_0 is the saturation vapour pressure of the adsorptive gas (N₂). Thus, (eq. 3.5) represents the expression of an *adsorption isotherm*, where the amount of gas adsorbed at a constant temperature is related to the relative pressure of the gas.

The obtained isotherms were conveniently classified into 6 main groups (I to VI) according to IUPAC classification (see Figure 3.9), where group I represents micropores, group II and III represent non-porous material, group IV and V represent mesopores and VI represents macropores.



Figure 3.9 Classification of adsorption isotherms by IUPAC [236].

Hysteresis loops are often associated with the type IV and V isotherms. The lower branch of the loop represents the progressive addition of gas and the upper one shows the progressive removal of the gas from the material. They are also further classified into four types [237].

Different information like pore size distribution and the surface area available could be obtained from Brunauer, Emmett, Teller (BET) analysis [238] and in addition to this, this technique could also be used to confirm the dense, pore free samples. The BET model could be applied to obtain the specific surface area (SSA) by interpolating the volume adsorbed in the partial pressure range (P/P₀), 0.05-0.30. The BET model is represented as [238]:

$$\frac{V}{V_m} = \frac{C(\frac{P}{P_0})}{\left[1 + (C-1)\left(\frac{P}{P_0}\right)\right]\left[1 - \left(\frac{P}{P_0}\right)\right]}$$
(eq. 3.6)

where, P and P₀ represents the equilibrium and saturation pressure of the gas, V is the volume of gas adsorbed, V_m is the volume of molecules/atoms of the gas needed to form one monolayer of adsorbed gas on the solid surface and C is the BET constant. The obtained value of surface could be divided by the mass of the sample to get the SSA. The BJH (Barrett-Joyner-Halenda) method can be used to obtain the pore size distribution.

3.3.8 Chemical analysis

The chemical analysis helps to understand quantitatively the composition of the derived ceramics. The C, Si, and N contents were determined by the Mikroanalytisches Labor Pascher (Remagen, Germany). The amount of C was measured conductometrically after combustion and adsorption of CO₂ in a 0.1N NaOH solution. The Si determination was conducted by fusing the sample in a Pt-crucible with a mixture of Na₂CO₃/H₃BO₃. The Si content, after dissolution of the sample in acids, was measured using an inductively coupled plasma

atomic emission spectrometer, ICP-AES- iCap 6500 (Thermo Fisher Scientific, Waltham, MA, USA). N is measured with a Leco TCH 600 analyzer (Leco Corporation, Saint Joseph, MI, USA). The amount of oxygen in the ceramic samples was calculated as a difference to 100%.

3.3.9 Thermal characterizations

3.3.9.1 Thermal conductivity by Hot-disk apparatus

The room temperature (RT) thermal conductivity measurements on the ceramic foams and felts were performed by using a Hot Disk apparatus (Hot Disk TPS 2500 S, Kagaku Analys AB, Sweden).

The hot disk approach is also referred to as a transient plane source method. In this method an electrically insulated metal strip/disk is used both as a continuous plane heating source and also as the temperature sensor.

In the testing process, normally two slabs of the ceramic foams (each 40 mm X 40 mm X ~ 4.5 mm (t) and with flat, planar surfaces) would sandwich the metal strip sensor. A small constant current (10 mW for 10 s) applied to the metal strip would heat it up. The temperature rise on its surface depends on the nature of the two foams in contact with (sandwiching) it. The temperature increase on the surface is usually as low as 1-3 °C [57,58] and this is usually measured as a function of time (accuracy is usually ± 0.01 °C). The basic hot-disk setup for measuring the thermal conductivity is shown in Figure 3.10.



Figure 3.10 Hot-disk setup for measuring thermal conductivity [239].

The temperature fitting curves to the measured change in temperature (ΔT) gives the inverse of the thermal conductivity value (1/ λ). The mean value of the temperature rise, $\Delta T(\phi)$ is given by [240,241]:

$$\Delta T(\phi) = \frac{Q}{\pi^{1.5} r \lambda} D(\phi) \qquad (eq. 3.7)$$

$$\Phi = \sqrt{\frac{t\kappa}{r^2}} \qquad (eq. 3.8)$$

considering *Q* is the heat transferred, *r* as the sensor radius, $D(\phi)$ a dimensionless theoretical term, λ as the thermal conductivity, κ thermal diffusivity, and *t* the time.

3.3.9.2 Specific heat capacity

STA 449 F3 Jupiter (Netzsch Gerätebau, GmbH, Selb, Germany), equipped with a type-S thermocouple was used for measuring the specific heat capacity (Cp) of the prepared thin disks. The measurements were conducted in a constant argon flow in a Pt crucible upto a temperature of 1000 °C at a heating rate of 20 K/min. The standard used for the measurement was sapphire using the DIN standard 51007.

3.3.9.3 Thermal diffusivity by laser-flash technique (LFT)

The thermal diffusivity measurements at high temperatures were conducted on the thin disks and selected ceramic foams (only on the ones from the M-type, closed celled templates) using a Laser Flash LFA 1600 instrument (Linseis Messgeräte GmbH, Selb, Germany) equipped with a S-type thermocouple.

In the LF approach, samples having a diameter of 10 mm/12.7 mm (available slot sizes) and a thickness ~250 μ m (for dense disk samples) or ~ 2.5 mm (for the foam samples) were irradiated with high intensity short duration pulsed radiant energy [242,243]. To avoid reflection of the laser energy from the surfaces, both the surfaces were coated with graphite spray. The rise in temperature due to the absorbance of these energy pulses can be detected from the rear surface using a lens arrangement, which focuses it to the detector (the setup is shown in the Figure 3.11(a)). The samples are mounted using a special arrangement as shown in the Figure 3.11(b), where at a time more than one sample can be loaded.



Figure 3.11 (a) Laser-flash setup for measuring thermal diffusivity, (b) the samples mounting setup [243].

The thermal diffusivity value of the sample could be computed from the thickness of the sample and the time taken to heat up the rear surface of the sample to certain percentage of the maximum value. In the case of having a measurement at elevated temperatures, the set-up had a furnace, which helps to raise the temperature of the measurement environment. At least three measurements are recorded at a particular temperature of interest.

As per standard approach, at adiabatic conditions, thermal diffusivity could be determined from the eq. 3.9, where the relative increase in temperature is considered [243],

$$\kappa = \frac{0.1388.\ h^2}{t_{0.5}} \tag{eq. 3.9}$$

where, κ is the thermal diffusivity (cm²/s), h represents the thickness of the sample (in cm), and t_{0.5} is the time at which there is an increase of 50% of the maximum in temperature on the rear side of the sample

[243]. The main parameters measured would be time, change in temperature (Δ T), change in voltage (Δ V), and Δ V~ Δ T.

The thermal conductivity could be computed from the eq. 1.5 (chapter 1) by knowing the specific heat capacity (C_p), density of the material and the thermal diffusivity from LFT.

3.3.10 Dilatometry

The thermal expansion coefficients of the ceramic foams and the disks were determined using a L75 platinum series dilatometer (Linseis Messgeräte GmbH, Selb, Germany) up to a temperature of 950 °C using a quartz tube at a heating rate of 5 °C/min.

3.3.11 Compressive strength

The compressive strength of the foams was determined using Instron 4502 (Instron, Norwood, MA, USA) with a 10 kN load cell, on cubical samples having a dimension of (25X 25X25) mm³ (the measurements were taken on selected samples and for each composition 3 samples were tested) with a loading rate of 1mm/min.

3.3.12 Hardness

The hardness of the PHMS-(DVB/TVTMS) disks were determined using a nano-indentation device, iNano (Nanomechanics Inc, Oak Ridge, TN, USA). The indentations were made using a Berkovich indenter with a load of 40 mN. Tests were performed at two separate locations on each sample surface so as to accommodate the possible heterogeneities across the surface and 12 indentations in an array 4 × 3 (with a spacing of 20 μ m in each direction) were conducted at each location. While, the hardness of the Si-O-C-N ceramic system obtained from the precursors SPR 036, SMP 10, and Durazane 1800 were conducted using Microhardness tester FM 310 (Future-Tech Corp., Kanagawa, Japan) at different loads from100-500 gf.

3.4 Thermal conductivity estimation model: Gibson-Ashby approach

Gibson-Ashby model [88], a theoretical approach to estimate the thermal conductivity of the struts (material forming the strut) of the foams was attempted based on the input parameters like thermal conductivity of the bulk porous foams and the densities (bulk and skeletal densities).

The Gibson-Ashby equation is given as [88]:

$$\lambda_{Sf} = \frac{1}{3} \left(\frac{\rho_b}{\rho_s} \right) \lambda_{S^+} \left(1 - \frac{\rho_b}{\rho_s} \right) \lambda_{air}$$
 (eq. 3.10)

where, λ_{sf} is the thermal conductivity of the foam in W.m⁻¹.K⁻¹ (bulk, measured by the Hot-disk,), ρ_b and ρ_s represents the bulk density (by geometric method) and the skeletal density (from pycnometer), respectively, in g.cm⁻³. λ_s and λ_{air} are the thermal conductivities of the strut of the foam (to determine from the model) and that of air (0.025 W.m⁻¹.K⁻¹ at room temperature [244,245]) in W.m⁻¹.K⁻¹, respectively. The equation could be reordered in the form of an equation of a line, y = mx + C; where m is the slope of the line and C is the y intercept.

$$\lambda_{Sf} = \left(\frac{1}{3}\lambda_{S} - \lambda_{air}\right)\frac{\rho_{b}}{\rho_{s}} + \lambda_{air} \qquad (eq. 3.11)$$

The slope of the linear fit $\left(\frac{1}{3}\lambda_{s} - \lambda_{air}\right)$ can be used to estimate the thermal conductivity of the dense skeleton, which could be compared with the measurements on the dense films by LFT.

Chapter 4. Dense Si-O-C-N: Thermal studies on thin disks

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4.1 Introduction

This chapter is a compilation of the studies conducted on the different precursors and the corresponding final ceramics with the varied chemistries, Si-C, Si-O-C, and Si-C-N(O) (method as explained in the previous chapter (chapter 3)). The thermal properties measured on the ceramic disks are discussed as the main contribution. Two case-studies, investigating the influence of free carbon and other phases on a chosen chemistry (SiOC) are also discussed in separate sections.

4.2 Studies on the polymeric precursors

The three precursors, SMP 10 (for SiC), SPR 036 (for SiOC), and Durazane 1800 (for SiCN(O)) were cross-linked using the Pt catalyst (hydrosilylation catalyst).



Figure 4.1 Thermogravimetry (TG) of the precursors (in argon (SMP 10 and SPR 036) or nitrogen (Durazane 1800) atmosphere at a heating rate of 5°C/min and at a gas flow rate of 50 cc/min).

Cross-linking using Pt catalyst is expected to improve the final ceramic yield, which is a matter of great concern in the field of polymer derived ceramics. The TG curves of the precursors (cross-linked) are shown in Figure 4.1.

From the TG curves, it can be seen that the polymer precursors show a two-stage mass loss. The mass loss in the first stage, which generally lapses until at ~500 °C (around 350 °C in SMP 10, until at ~450 °C in SPR 036, and at ~520 °C in Durazane 1800) and can be attributed to the release of low molecular weight oligomers, while the second stage of mass loss in the temperature range between ~540 °C and ~900 °C (for SPR-036 and Durazane 1800) and ~400 °C to 1000 °C (for SMP 10) corresponds to the mineralization stage, where mainly methane and hydrogen are released [246–248]. The total mass losses at the temperature 1000 °C were *ca.* 27%, 21%, and 31% for SMP 10, SPR-036, and Durazane 1800, respectively. Cross-linking the preceramics with DVB could further improve the mass yield of these ceramics (as observed by Dalcanale *et al.* [164] on SMP 10) and can also significantly modify the carbon percentages in the final chemistry.

The TG of DVB modified precursors (~10% DVB added to the preceramic polymer) can be seen from the Figure 4.2. It is obvious that at a temperature of 1000 °C, the ceramic yield of all the three precursors increased. The yield of the polycarbosilane, SMP 10, increased from 73% (without DVB) to ~80% (with DVB), for the polysiloxane, SPR 036, the yield increased with the incorporation of DVB from 79% (without DVB) to ~88% (with DVB) and that of the polysilazane, Durazane 1800, the ceramic yield showed an improvement from 69% (without DVB) to 76% (with DVB). The chemical interactions could be better understood from the FT-IR analysis.



Figure 4.2 Thermogravimetry (TG) of the DVB-modified precursors (in argon (SMP 10 and SPR 036) or nitrogen (Durazane 1800) atmosphere at a heating rate of 5°C/min and at a gas flow rate of 50 cc/min).

The FT-IR analysis on the preceramic precursor SMP 10 (Figure 4.3), which is basically a polycarbosilane showed the main peaks at the positions, ~2120 cm⁻¹ (-Si-H stretching), ~1630 cm⁻¹ (C=C stretching), ~1030 cm⁻¹ (Si-CH₂-Si stretching), ~940 cm⁻¹ (-Si-H deformation), ~830 cm⁻¹ (-Si-CH₃ wagging), and, ~745 cm⁻¹ (Si-C deformation) [164,249]. While, in the case of Durazane 1800, characteristic silazane peaks at 3375 cm⁻¹ (N-H stretching), 2954 cm⁻¹ (C-H stretching), 2126 cm⁻¹ (Si-H stretching), 1252 cm⁻¹ (C-H deformation), 1163 cm⁻¹ (N-H deformation), and ~880 cm⁻¹ (Si-N-Si stretching) can be seen [250] and for polysiloxane precursor, a strong absorption band at ~1100 cm⁻¹ corresponding to the Si-O-Si stretching was observed, in addition to a band at *ca*. 2150 cm⁻¹ assigned to Si-H groups [251,252].



Figure 4.3 FT-IR spectrum of the precursors with and without DVB cross linking.

The FT-IR spectra of DVB added SMP 10 shows the remanence of Si-H as well as C=C peaks in spite of the expected hydrosilylation reactions, which should have obviously occurred. However, as observed by Dalcanale *et al.* [164] even at 12% by weight of DVB addition in SMP 10, Si-H and C=C bonds still persisted as the amount of DVB was not significant enough to show progression of the hydrosilylation (reduction of the Si-H and C=C).



Figure 4.4 FT-IR spectrum of DVB cross-linker (peaks were identified according to [253].

In DVB added SPR 036 and Durazane 1800, it was observed that not all the Si-H bonds have been consumed in the crosslinking reaction via hydrosilylation with the C=C groups [254,255] since SPR 036 and Durazane 1800 have only few C=C groups available, with a C=C/Si-H molar ratio in the range of 0.1 to 0.2. In SPR 036, the reduction of the Si-H peaks with DVB addition and absence of C=C peaks even for the only SPR 036 (no DVB added) samples shows the very intensive hydrosilylation reactions taking place in these polysiloxanes (in the presence of the Pt catalyst) [256]. While in DVB added Durazane 1800, the formation of a Si-O bond at ~1059 cm⁻¹ suggests also the possibility of de-hydrocoupling reactions (obvious due to the presence of moisture) taking place in this system [252].



Figure 4.5 Scheme of cross-linking (hydrosilylation), followed by pyrolysis at 1200 °C to get the different final chemistry.

Thus, to infer from the TG and FT-IR observations, higher rate of hydrosilylation reactions occur in all the three precursors with DVB addition, which results in increasing the network connectivity, and hence resulting in a higher ceramic yield (TG). The FT-IR of DVB is shown in Figure 4.4. The scheme showing the cross-linking of the three precursors *via* hydrosilylation, using DVB is shown in Figure 4.5. The cross-linked polymeric preceramic disks were pyrolyzed in inert conditions to obtain the ceramic disks (details could be read from chapter 3).

4.3 SiC dense thin disks

In this section, the studies conducted on the SiC ceramic disks obtained from the polycarbosilane precursor are presented. The evolution with the pyrolysis temperature, nature of the disks developed, and the thermal properties are discussed.

4.3.1 Composition and phase evolution

The set of SiC ceramic samples studied (pyrolyzed at 1200 °C) are shown in Table 4.1. The apparent densities measured for these disks were found to be in the range of 2.3-2.4 g.cm⁻³. These density values obtained were in the range of the reported densities of SiC PDCs [212.257]. From the elemental composition it could be seen that the major phase existing in these ceramics, obtained from a polycarbosilane precursor, is SiC. However, there is a significant presence of oxygen in the network for both the samples (SC1 and SC 2) studied, hence it would be more appropriate to consider them to have a SiC(O) chemistry rather than expecting only Si-C bonds to be present. The density measured were also comparable with the other expected phases in the matrix like the vitreous silica (~2.2 g.cm⁻³) and polymer derived Si-based glasses (like SiOCs) [258] [213.259] but was greater than that measured for pyrolytic carbon (1.8 - 2.0 g.cm⁻³ [260]). The density reported for crystalline β -SiC was much higher than the obtained value (3.2 g.cm⁻³) [261,262]. Nevertheless, the samples would be mentioned as only SiC in the further discussions in order to avoid confusion.

Samples	Density (g.cm ⁻³)	Chemical composition (wt.%)		SiO _x C _y + f C _{free}	
	(ρ _t ±0.1)	Si	C	0	Composition
SC 1 ⁸	2.3	52.14±	33.32±	14.54±	SiO _{0.49} C _{0.76} +
		0.1	0.03	0.03	$0.73C_{\text{free}}$
SC 2	2.4	53.09±	33.61±	13.30±	SiO _{0.44} C _{0.78} +
		0.1	0.01	0.01	$0.70C_{\text{free}}$

Table 4.1 Set of SiC thin disk samples studied (details mentioned in chapter 3).

Owing to the presence of oxygen in the final composition, the ceramic network could be considered similar to that of typical SiOC ceramic; built-up of mixed Si units sharing bonds simultaneously with O and C atoms and can be described by the formula: $SiC_xO_{2(1-x)}$, $0 \le x \le 1$ in which 'x' is the amount of substituted C. Hence, the composition would be represented as that for silicon oxycarbide glasses and is usually reported as: $SiC_xO_{2(1-x)} + f C_{free}$. Where, the 'f C_{free} ' represents the free carbon content, which is crucial in determining many properties. The ceramic samples, SC 1 and SC 2 were found to have nearly the same compositions and the free carbon contents were also comparable.

As mentioned in the experimental part of the thesis, the SC 1 and SC 2 samples were prepared (pyrolyzed) at 1200 °C and hence they are expected to be amorphous. But, as could be seen from the X ray diffractogram shown in the Figure 4.6 (a), clear and distinct peaks of β -SiC crystallization [155,263,264] become conspicuous in the amorphous network for both the SC 1 and SC 2 samples. The crystallite size of β -SiC of the samples pyrolyzed at 1200 °C were determined from the diffraction pattern with the help of MAUD, and was

⁸ The SC 1 samples would be represented as SC 1_1200 at times when the pyrolysis temperature has to be mentioned in the coming sections of the discussion.


Figure 4.6 (a) XRD, (b) FT-IR, (c) Raman analysis results on the SiC disks developed.

found to be ~3.2 nm. Hence it is appropriate to consider this SiC material to be a nanocrystalline one. The nanocrystalline nature is maintained also in samples pyrolyzed at 1500 °C, however the β -SiC peaks are seen more prominently with the increase in the pyrolysis temperature. The density (ρ_t) of the SiC disks prepared at 1500 °C was ~ 2.5 g.cm⁻³.

The FT-IR (Figure 4.6(b)) also shows peaks corresponding to Si-C and Si-O in the final ceramics. Raman analysis (Figure 4.6(c)) conducted on these samples confirms the presence of disordered carbon in the system. The lateral crystal size (L_a) of the carbon phase could be estimated from the approach presented by Cancado *et al.* [265], according to the equation (4.1);

$$L_{a} = (2.4X \ 10^{-10}) \cdot \lambda_{L}^{4} \cdot \left({I^{*}}_{D} / I^{*}_{G}\right)^{-1} \qquad (\text{eq. 4.1})$$

where, by knowing the λ_L (which represents the laser line wavelength, 514. 5 nm) and I_D^* and I_G^* (the integrated area of the D and G bands in the Raman Spectra), L_a could be calculated in nm. Table 4.2 shows these calculations from the Raman spectra for the SC 1 and SC 2 samples. It can be noted that the I_D/I_G ratio remains almost the same for both the samples. An increase in the crystallite size of SC 2, observed in spite of having only negligible variation in the composition from the SC 1 samples, could be attributed to the variation in the carbon cluster size [171].

Sample	D -	G -	I _D /I _G ⁹	I* _D /I* _G	La
	position	position			(nm)
	(cm⁻¹)	(cm ⁻¹)			
SC 1	1344.27	1603.49	1.96	5.99	2.8
SC 2	1347.36	1601.50	1.97	4.55	3.7

Table 4.2 Carbon crystallite size calculation from Raman spectrum for SiC

samples.

As mentioned before, increasing the pyrolysis temperature from 1200 °C to 1500 °C retains the nanocrystalline character in the SiC ceramics. However, the β -SiC peaks, which were clearly seen even after pyrolysis at 1200 °C, became more obvious and well distinct at 1500 °C (see Figure 4.7(a)). The clear peaks at 35°, 60°, and 72° are representative of cubic β -SiC crystallization [155,263,264]. The crystallite size, calculated (from MAUD), of β -SiC showed only a marginal increase of ~1 nm, i.e. from 3.2 nm (pyrolyzed at 1200 °C) to 4.3 nm (for the disks pyrolyzed at 1500 °C).

As the pyrolysis temperature was raised to 1800 °C the samples became well crystalized with β -SiC as the main crystalline phase (the maximum density achieved is ~2.7 g.cm⁻³ and the crystallite size determined from MAUD was ~41.4 nm), minor but prominent peaks of α -SiC (hexagonal polymorph) could also be seen from the XRD.

From Raman (Figure 4.7(b)) at 1500 °C the D and G peaks are still retained. As reported in a similar system by Chowdhury *et al.* [266] the evolution of nanocrystalline carbon occurs during this phase parallel with the β -SiC nanocrystalline formations. The lateral crystallite size (L_a) evaluated was found to increase from 2.8 nm (at 1200 °C) to 4.8 nm (at 1500 °C) showing a 2D growth of carbon from amorphous to

 $^{^9}$ I_D/I_G represents the intensity ratio of the bands D and G.



Figure 4.7 (a) XRD, (b) Raman of SiC sample prepared at different pyrolysis temperature.

free carbon phase and further to nanocrystalline graphite [257,266,267] in this temperature range. However, it can be seen that at 1800 °C, the graphitic (G band) and disordered carbon (D band) bands almost disappear, but prominent SiC bands appear, at 796 cm⁻¹ (TO) and 972 cm⁻¹ (LO) (also a small band at ~ 2700 cm⁻¹ is an overtone of 'D' band, usually referred to as '2D') [264,268,269]. The Raman confirms that in the SiC disks prepared at 1800 °C, the major phase would be β -SiC (3C) as evidenced from the TO (796 cm⁻¹) and LO (972 cm⁻¹) bands. However, it is hard to determine the possible mixing of α -SiC (6H) as the TO bands of α -SiC (6H) lies at ~ 797 cm⁻¹,

which makes it difficult to distinguish the two polytypes. But, the absence of an expected additional TO band for α -SiC (6H) at ~768 cm⁻¹ clearly reduces the chances of its dominance in these ceramics [263,270,271].

Owing to the significant amount of oxygen in the system, along with the crystallization in this temperature range, carbothermal reduction reactions also come into play in these matrices (>~1400 °C), i.e. silica scavenging on the available carbon giving rise to SiC. The reactions usually advance as shown in the equations 4.2 to 4.4.

$$SiO_{2(s)} + C_{(s)} \rightarrow SiO_{(g)} + CO_{(g)}$$

$$(4.2)$$

$$SiO_{(g)} + 2C_{(s)} \rightarrow SiC_{(s)} + CO_{(g)}$$

$$(4.3)$$

$$SiO_{2(s)} + 3 SiC_{(s)} \rightarrow 3 SiO_{(g)} + 2 CO_{(g)}$$

$$(4.4)$$

This will reduce the carbon percentages in the ceramics at a temperature greater than 1400 °C.

The turbostratic carbon can also be extensively studied using TEM imaging (an example is given in Figure 4.8, imaged from SC 1_1500 sample).



Figure 4.8 TEM showing the turbostratic carbon in the SiC (SC 1_1500 sample).

4.3.2 Dense thin disks: microstructure and pore formations



Figure 4.9 SEM fractographic images of SC 1 and SC 2.

Examinations using SEM on the fractured surfaces of the thin disks, SC 1 and SC 2 showed totally dense and pore free formations. This was very important since the presence of porosities could significantly influence the thermal measurements (thermal diffusivity, etc.), which were later conducted on these types of samples. The fractographic image also showed typical glassy fracture (Figure 4.9).



Figure 4.10 SEM fractographic images of SC 1_1500 (a, b, and c) and SC 1_1800 (d, e, and f).

However, pyrolyzing the samples at higher temperatures (>1400 °C) has found to initiate the formations of porosities in these structures. As can be seen from the Figure 4.10 (a-c), at 1500 °C the onset of microporous formations become evident on investigating the fracture surface. These pits and channels were formed as a result of the release of various gaseous components like CO and SiO from the disks at these temperature ranges [127,137]. At 1800 °C, the pore formations become more evident and also formation of nano-crystalline β -SiC

formed could also be seen from the micrographs (Figures 4.10 (d-f)) of the fractured surface.

However, the N₂ adsorption-desorption conducted on the SC 1_1200 as well for the SC 1_1500 showed totally flat isotherms (Figure 4.11), further validating the fact that the porosities are not conspicuous at least up to a temperature of 1500 °C, in spite of the fact that pits start appearing at 1500 °C, as can be seen from the SEM micrographs in the Figure 4.10 (a, b, and c).



Figure 4.11 N₂ adsorption-desorption isotherms for the SC series of disks.

From the SEM analysis it was obvious that the thin SiC disks obtained after pyrolysis at 1200 °C were dense and pore free, which was also confirmed from the flat isotherms obtained from the N_2 adsorption-desorption curves. Thus, the measurement of thermal properties on them would reflect the actual properties of the material without the interference of any other external impurities, in this case the pores. However, in the SC samples pyrolyzed at 1500 °C and 1800 °C the formation of porosities could influence the measurements recorded.

4.3.3 Thermal properties of the SiC disks

The linear thermal expansion (Figure 4.12) coefficients (CTE) measured for the SC 1 and SC 2 samples were determined to be 4.1 x 10^{-6} .K⁻¹ and 4.4 x 10^{-6} .K⁻¹, respectively, in the temperature range RT-950 °C. This CTE determined for the SC 1 and SC 2 were found to lie in the CTE range reported for β -SiC, i.e. 3.2×10^{-6} .K⁻¹ - 5.1×10^{-6} .K⁻¹, in the same temperature range [42]. The greater values of CTE obtained for the SC 1 and SC 2 samples when compared to that of vitreous silica (0.57 x 10^{-6} .K⁻¹[197]) and that reported for relatively similar SiOC ceramics (reported in the range of $1.84 - 3.23 \times 10^{-6}$.K⁻¹ [195]) clearly shows the higher fraction of Si-C bonds than Si-O present in the system. The relatively high CTE of these samples could also be explained by the presence of free C [272], which certainly would have a greater CTE compared to SiO₂ and SiC.



Figure 4.12 Thermal expansion of SiC (SC) samples pyrolyzed at 1200°C.

The specific heat capacity (Cp) of SC 1 and SC 2 samples were measured upto a temperature of 1000 $^{\circ}$ C (shown in Figure 4.13 (a)).

The obtained values were found to be in the range of 0.98 J.g⁻¹.K⁻¹ to 1.23 J.g⁻¹.K⁻¹. These values of Cp are almost at par with the Cp reported for SiOC ceramics and that of vitreous silica, i.e. in the range ~ 0.7 J.g⁻¹.K⁻¹ to 1.25 J.g⁻¹.K⁻¹ [273]. In case of the other phases which are present, such as β -SiC, the Cp reported is in the range of 0.65 J.g⁻¹.K⁻¹ to 1.2 J.g⁻¹.K⁻¹ [274] and would also contribute to the Cp value of the glassy ceramics. However, the presence of significant amount of carbon in the system can raise the Cp values since the Cp value reported for amorphous carbon is as high as 1.66 J.g⁻¹.K⁻¹ (at 750 °C) [195].

The results of the thermal diffusivity (κ) measured for these samples upto 1000 °C are given in Figure 4.13(b). The measured values were found to be in the range of the values measured for similar SiOC ceramics by Stabler *et al.* [195]. The κ value would be influenced by numerous factors like the volume fraction of β -SiC, extent of the segregated carbon phase, etc. Also, phonon scatterers like pores, impurities, grains etc. contribute immensely to the final κ of the ceramics [3]. The glass-like behavior of these ceramics at this pyrolysis temperature can significantly reduce the mean free path of the phonon conduction, hence drastically influencing the thermal diffusion through them.

The thermal conductivity (λ) of these disks could be computed by knowing the Cp, κ , and the density (ρ) values, using the equation (eq.1.5, Chapter 1);

$$\kappa = \frac{\lambda}{\rho C_{p}}$$
 Chap. 1, eq.1.5

The λ calculated for the SC 1 and SC 2 samples shows similar values upto a temperature of 1000 °C (are shown in the Figure 4.13 (c)). However, a small difference in the λ observed in the temperature range

from RT to 400 °C is not easy to be explained since both the samples have very close microstructure and composition. In the temperature



Figure 4.13 (a) The specific heat capacity (Cp), (b) thermal diffusivity (κ), and (c) thermal conductivity (λ) of the samples, SC 1 and SC 2.

range 100 °C - 1000°C, the average λ measured was ~ 1.5 W.m⁻¹. K⁻¹. This λ measured is much smaller than the λ reported for polycrystalline SiC at RT and this can be explained with the disordered nature of these materials. As a matter of fact, the λ reported for amorphous SiC is ~ 4 W.m⁻¹. K⁻¹ (at 100 °C) [182]. Also, the λ of the dense SiC discs at RT is in the same range as that of a-SiO₂ [189] and PDC-SiOC ceramics reported in the literature [189,192,195]. It could also be observed that the λ value was less influenced by the measurement temperature (temperature independent- λ). This observation was very similar to the one made by Gurlo et al. [189] on SiOC in the same temperature range. The Cp measured for the samples pyrolyzed at higher temperatures, SC 1 1500 and SC 1 1800 are shown in the Figure 4.14(a). We cannot observe a clear evolution of the Cp with the pyrolysis temperature. All the Cp values remain in the range corresponding to SiC [275]. The slight Cp decrease which may be observed in the sample treated at 1800°C could be tentatively assigned with the removal of Cfree and SiO₂ due the carbothermal reduction.

The thermal diffusivity (κ) measured on these disks shows that there is a significant increase in the diffusivity values as the pyrolysis temperature is raised to 1800 °C (Figure 4.14 (b)). This is obvious due to the crystallization of the amorphous matrix with formation of polycrystalline β -SiC. The diffusivity of the sample at 1500 °C does not change noticeably with the one at 1200°C. Another interesting observation is the evolution of the diffusivity with the temperature for the samples treated at 1800 °C: in this case the diffusivity decreases, suggesting a decrease of the λ typical of crystalline materials. The λ of the SC samples pyrolyzed at 1200, 1500 and 1800 °C are shown in Figure 4.14 (c). The λ of the 1800°C sample is very high and comparable to polycrystalline SiC, reflecting the microstructure of this sample. The λ value at 100°C is around 47 W.m⁻¹. K⁻¹ which is ~ 2/5th of the range reported in the literature (120-180 W.m⁻¹. K⁻¹ [45,56]) for crystalline SiC but still one or two orders of magnitude higher than the RT λ values of the samples prepared at 1200 °C. This lower value of λ , compared to the fully dense crystalline materials, could be ascribed to the presence of porosity in this sample, as shown before. With an increase in the measurement temperature, the λ decreases for the SC 1_1800 sample.



Figure 4.14 (a) The specific heat capacity (Cp), (b,c) thermal diffusivity (κ), and (d,e) thermal conductivity (λ) of the samples, SC 1_1200, SC 1_1500, and SC 1_1800.

This is well explained in previous literatures as due to the reduction in the mean free path caused by phonon scattering, which could be caused by phonon-phonon interaction, scattering at the grainboundaries, and, obviously due to phonon-pore interactions [24,29,276]. The RT λ value of the sample pyrolyzed at 1500°C is around 0.5 W.m⁻¹. K⁻¹, which is the lowest value measured in this study. The explanation for this result is not simple since at 1500 °C the SC is compositionally and structurally similar to the one at 1200°C with the only difference being the incipient carbothermal reduction which could lead to the formation of some porosity.

4.4 SiOC/SiCN(O) dense thin disks

In this section, the studies conducted on dense SiOC and SiCN(O) disks are presented. The studied samples were prepared by pyrolysis at 1200 °C. The evolution of the phases, microstructures and the thermal properties of these ceramics are discussed below.

4.4.1 Composition and phase evolution

Two set of samples each for SiOC (SO 1 and SO 2) and SiCN(O) (SN 1 and SN 2) ceramics were studied. The SiOC samples have slightly different composition with the SO 2 sample having higher free carbon content in it. In contrast, the SiCN(O) samples showed only marginal variation in the free carbon content, despite the fact that the composition varied, as can be seen from the Table 4.3.

Samples	Bulk	Chemical composition				SiO _x C _z N _y +
	Density		(wt	f C _{free}		
	(g.cm ⁻³)	SI C N O			Composition	
	(ρ _b ±0.1)					
SO 1	2.1	45.73	22.68	0	31.59	SiO _{1.21} C _{0.40} +
		±0.1	±0.08		±0.08	0.76C _{free}
SO 2	2.1	41.99	23.25	0	34.76	SiO _{1.45} C _{0.28} +
		±0.1	±0.51		±0.51	1.02C _{free}
SN 1	2.1	47.85	19.93	15.18	17.04	$SiO_{0.62}C_{0.21}N_{0.63}$
		±0.1	±0.07	±0.04	±0.09	+ 0.76C _{free}
SN 2	2.1	48.53	21.98	17.92	11.57	$SiO_{0.42}C_{0.24}N_{0.74}$
		±0.1	±0.03	±0.22	±0.28	+ 0.82C _{free}

Table 4.3 Set of SiOC and SiCN(O) thin disk samples studied (details mentioned in chapter 3).

The XRD analysis conducted on the SiOC and SiCN(O) glasses (shown in Figure 4.15 (a and b)) displayed that they are totally amorphous in nature at least upto 1400 °C and no sort of β -SiC crystallization was seen in them as in the case of the SiC samples studied in the previous section of the chapter. Also, in both SiOC and SiCN(O) samples, a small hump seen at around ~22° showed dominance of amorphous silica in the matrix of the ceramics. The FT-IR analysis on the SiOC glasses (Figure 4.15(c)) showed presence of Si-O and Si-C bonds while in the SiCN(O) system (Figure 4.15(d)), the region between 1100 cm⁻¹ and ~700 cm⁻¹ were overlapped with bonds of Si-O, Si-N, and, Si-C [277]. The Raman recorded on these materials also showed significant presence of free carbon in the system. The Raman spectra of the measurements on the SiOC and SiCN(O) can be seen on the Figures 4.15(e) and 4.15(f), respectively.



Figure 4.15 (a and b) XRD, (c and d) FT-IR, (e and f) Raman analysis, on the SiOC and SiCN(O) disks developed, respectively.

The crystalline sizes (L_a) were estimated [265] and tabulated in Table 4.4. For the SiOC ceramics, the L_a was found to decrease from 2.6 nm for SO 1 to 1.9 nm for SO 2 sample. Same was seen in the SiCN(O) samples, the L_a was found to decrease from 5.8 nm in SN 1 to 4.5 nm for SN 2. This possibly shows the higher clustering of the segregated carbon in the comparatively carbon rich compounds [171]. However, it can be noted that the lateral crystallite sizes (L_a) are more in the SiCN(O) samples than in the SiOC samples.

Sample	D -	G -	I _D /I _G	I* _D /I* _G	La
	position	position			(nm)
	(cm ⁻¹)	(cm ⁻¹)			
SO 1	1338.05	1608.96	1.70	6.52	2.6
SO 2	1332.58	1605.07	2.01	8.82	1.9
SN 1	1349.17	1605.08	1.67	2.90	5.8
SN 2	1333.65	1603.71	1.74	3.70	4.5

Table 4.4 Carbon crystallite size calculation from Raman spectrum for SiCN(O) and SiOC samples.

4.4.2 Microstructure analysis

The studies using SEM on the fractured surfaces of the SiOC and SiCN(O) disks are shown in Figure 4.16. The SO 1 and SO 2 samples, both prepared by pyrolysis at 1200 °C, were found to be dense and pore free (Figure 4.16 (a and b)). However, while examining a SO 1 sample pyrolyzed at 1400 °C (labelled as SO 1_1400, in Figure 4.16(c)) showed the onset of degradation of these classes of ceramics (SiOC) which were visible from the isolated pit formation on the surface of the fractured surface. While, in the case of the SiCN(O) samples, the SN 1 and SN 2 which were prepared at the 1200 °C (Figure 4.16(d and e)) also were totally dense and pore free and those pyrolyzed at 1400 °C (SN 1_1400, Figure 4.16(f)) was also observed to show no signs of degradation. The higher crystallization resistance of SiCN (onset, > 1500 °C) could be acknowledged in this context [278–280].



Figure 4.16 SEM fractographic images of: (a) SO 1, (b) SO 2, (c) SO 1_1400, (d) SN 1, (e) SN 2, (f) SN 1_1400.

Nevertheless, the N_2 adsorption-desorption, as can be seen from the Figure 4.17, presented totally flat isotherms validating the absence of any significant micro-meso pores on these disks.

The thermal studies were conducted mainly on the disks prepared at 1200 °C for both the SiOC and SiCN(O) disks studied.



Figure 4.17 $N_{\rm 2}$ adsorption-desorption isotherms for the SO and SN series of disks.

4.4.3 Thermal properties of SiOC disks



Figure 4.18 Thermal expansion of SiOC (SO) samples pyrolyzed at 1200°C.

The thermal expansion measured for the SiOC ceramics are given in the Figure 4.18. The CTE of SO 1 and SO 2 were determined to be ~2.9 x 10⁻⁶.K⁻¹ and 2.8 x 10⁻⁶.K⁻¹, respectively, in the temperature range from RT- 950 °C. The measured values were close to the range of the CTE reported for SiOC ceramics [195]. The values were lower than the CTE measured for the SC samples (discussed before) and that reported for β -SiC, showing the predominance of the silica (CTE= 0.57 x 10⁻⁶.K⁻¹[197]) in these set of ceramics.

The Cp measured for the SiOC disks. SO 1 and SO 2 are shown in Figure 4.19 (a). In case of the SiOC ceramics, the composition (SO 1 and SO 2) was found not to have much impact on the Cp value measured. The Cp values showed a rise upto a temperature of ~ 700 °C and then almost stabilized at higher measurement temperatures. The values obtained were slightly higher than that measured for SiC. The major fraction of the amorphous silica matrix, along with the β -SiC nanodomains and segregated carbon influence the Cp value in SiOC ceramics. The κ (thermal diffusivity) measured on SO ceramics (see Figure 4.19(b)) also gave comparable values as that of SiOC and related chemistries already reported in the literature [195]. The measured κ was used to calculate the λ for the SiOC (SO 1 and SO 2) and is presented in the Figure 4.19(c). The λ was found to increase with an increase in the measurement temperature. The SO 2, having higher segregated carbon was found to show a higher λ than SO 1. The SO 1 was measured to have a λ value from 1.1 W.m⁻¹. K⁻¹ to 2.76 W.m⁻¹. K⁻¹ (measured in the temperature range from 200 °C to 800 °C). While, the higher carbon containing counterpart (SO 2) presented a λ in the range of 1.92 W.m⁻¹.K⁻¹-3.3 W.m⁻¹.K⁻¹ (200 °C-800 °C). In the recent literatures by Gurlo et al. [189] and Stabler et al. [195], the main percolation phase present in these class of ceramics (SiOC) was identified to be the glassy silica matrix.



Figure 4.19 (a) The specific heat capacity (Cp), (b) thermal diffusivity (κ), and (c) thermal conductivity (λ) of the samples, SO 1 and SO 2.

However, an increase in the volume fractions of segregated carbon was found to cause a nonlinear increase in the λ owing to the formation of additional percolation paths [195]. Indeed, detailed investigations are required to have a clear conclusion of this hypotheses. A critical analysis to understand the influence of the different phases on the λ in a SiOC is presented as a case study (case study 1) in the section 4.6 of this chapter.

4.4.4 Thermal properties of SiCN(O) disks



Figure 4.20 Thermal expansion of SiCN(O) (SN) samples pyrolyzed at 1200°C.

For the SiCN(O) ceramics (see Figure 4.20), the values of CTE obtained (for both SN 1 and SN 2) was ~2.9 x 10^{-6} .K⁻¹. This CTE obtained was in the range of the reports available in literature for SiCN/SiCN(O) 2.69 x 10^{-6} .K⁻¹ [204] - 3.96 x 10^{-6} .K⁻¹ [281] and that of other relative chemistries, *viz.* SiOC[195]. The Cp measurements on the SiCN(O) ceramics also (see Figure 4.21(a)) showed a gradual increase in the value with an increase in the measurement temperature.



Figure 4.21 (a) The specific heat capacity (Cp), (b) thermal diffusivity (κ), and (c) thermal conductivity (λ) of the samples, SN 1 and SN 2.

The κ measured on the SiCN(O) samples were comparable to a similar report available on the diffusivity of SiCN ceramics by Janakiraman et al. [282]. The λ was calculated from the κ , and for the SN 1 sample (having lower segregated carbon) the λ obtained was in the range 0.95 W.m⁻¹ K⁻¹ -1.95 W.m⁻¹. K⁻¹ (200 °C-1000 °C) and for SN 2 (200 °C-1000 °C) the λ was calculated to be in the range 1.69 W.m⁻¹. K⁻¹ - 3.62 W.m⁻¹. K⁻¹. It is not easy to clearly identify the main percolation phase in the SiCN(O) system from the considered samples and the presence of any nano crystals of β -SiC would act as phonon scatterers inspite of the high conductivity of crystalline SiC. The λ values measured also evidence the importance of the segregated carbon in determining the final λ ; the extent of the segregated carbon network would determine the final λ of the system. Thus, the possibility to tune the λ by tuning the segregated carbon content is always available.

In Figures 4.22 (a) and 4.22 (b) the λ values of the three chemistries (SiC, SiOC and SiCN(O)) are compared with the literature data of similar PDCs and reference materials (Silica glass, amorphous carbon, pyrolytic graphite and amorphous SiC). It is quite apparent that our data fit quite well with those reported in the literature for similar Sibased polymer derived glasses/ceramics. Moreover, from the same figures it emerges that it is very difficult to differentiate, based on the λ values, the studied samples.



Figure 4.22 Comparison of the λ values of **SC 1**, **SO 1**, and **SN 1**: (a) with fused silica [190], amorphous carbon [226], pyrolytic carbon [226], and amorphous SiC [182] (amorphized *via.* neutron irradiation); (b) with available previous reports: SiOC 1 (SiO_{1.54}C_{0.53}[189]), SiOC 2 (SiO_{1.59}C_{0.66}[189]), SiOC 3 (sample C1[195]: SiO_{1.38} C_{0.32}), SiOC 4 (sample C17[195]: SiO_{0.94}C_{1.13}), and, SiBNC[209].

4.5 Vickers hardness measured on the Si-O-C-N disks

The hardness (Vickers hardness) was measured on these disks developed to understand the influence of the composition on the mechanical parameter (Figure 4.23). The SiOC and SiCN(O) samples gave H_V values in the range of 8.9 GPa - ~13.0 GPa which is in well agreement with the available reports. The H_V of SiOC ceramics are reported to be in the range 6.4 GPa to ~16 GPa [143,213] which is higher than that reported for vitreous silica (6-7 GPa [143]) owing to the higher bonding achieved due to the introduction of carbon into the network (sp³ hybridized). At the same time the H_V reported for SiCN lies in the range between 8 GPa and 26 GPa [259,282,283].

The SiC samples, SC 1 and SC 2 were measured to have higher H_V values, ~21.8±1.8 GPa (SC 1) and ~23.3±2.6 GPa (SC 2), respectively, when compared to the SiOC and SiCN(O) samples. Besides, the H_V of the SiC samples were measured only at lower loads as the samples were brittle; as cracks generated at higher loads (> 100 gf, as can be seen from the indentation images in the Figure 4.23). The H_V of polycarbosilane derived SiC are reported to be in the range 11 GPa to ~30 GPa from different literatures [119,284-286]. The value of H_V reported here for the SiC samples are obviously on the higher end due to the greater fraction of Si-C bonds (as evident from many of the analyses before) in this system and the prominence of Si-O bonds can cause a reduction in the H_V (from the indentation images, as can be seen from the Figure 4.23 showed no sort of crack initiation for the SiOC and SiCN(O) sample set, even at the highest load of measurement (500 g.f)). The fraction of segregated carbon in the system was also found to influence the hardness (H_V) of these ceramics. Considering the case of SiOC ceramics, it can be seen that the H_V decreased¹⁰ marginally from 10.2 GPa for SO 1 to 9.3 GPa SO

¹⁰ average value of the 3 loads considered, *viz.* 100,300,500 gfs.

2, where the segregated carbon amount is more for SO 2 than SO 1. A similar variation of H_V from 12.2 GPa for SN 1 to 11.8 GPa for SN 2 was also seen for the SiCN(O) sample pair. The observation underlines that, an increase in the amount of segregated carbon can cause a reduction in the H_V . However, the influence of this free carbon on the hardness and related mechanical properties would be studied as a separate case study, presented in Section 4.7 of this chapter.



Figure 4.23 Vickers hardness measurements on the Si-O-C-N disks (also showing selected images of the indentations, as labelled along with the respective images).

4.6 Case study-1: Influence of different phases on the thermal conductivity of silicon oxycarbide



Figure 4.24 Sketch showing the nanostructure of SiOC glasses having the amorphous $SiC_xO_{2(1-x)}$ network and the free carbon phase.

To study the influence of the different phases in SiOC (see the typical nanostructure in Figure 4.24) on the thermal conductivity (λ), 4 more samples (see Table 4.5) were prepared in addition to the SO 1 and SO 2 (Table 4.3) samples. The new set of samples were synthesized by the addition of higher weight percentages of DVB with the expectation of incorporating higher volume fractions of free carbon in the final SiOC ceramic (more details of the samples are given on the Table 3.6, in chapter 3). All the 6 samples, in total, were therefore prepared at the same pyrolysis conditions (at 1200 °C).

Samples	Bulk density (g.cm ⁻³)	$\begin{array}{c} \textbf{Composition}\\ SiO_{2(1-x)}C_x + f \ C_{free} \end{array}$
SO-S1	2.21±0.03	SiO _{1.12} C _{0.44} + 0.63C _{free}
SO-S2	2.26±0.01	SiO _{1.10} C _{0.45} + 0.76C _{free}
SO-S3	2.26±0.02	SiO _{0.99} C _{0.51} + 0.67C _{free}
SO-S4	2.33±0.03	SiO _{0.93} C _{0.53} + 1.16C _{free}

Table 4.5 Details of the new set of samples and the elemental analysis.



Figure 4.25 SEM images of, (a) SO-S1 and (b) SO-S4 ceramic thin disks prepared for the thermal measurements showing dense-pore free formations (representation of all the four samples, SO (S1-S4) considered), (c) The N_2 adsorption-desorption isotherms for the SO (S1-S4) series of disks.

The disks prepared were totally dense with no pore formations as evident from the SEM micrographs and the flat N_2 adsorption isotherms (see Figure 4.25). But, unfortunately, significant improvement in the carbon percentages was not obtained, as expected (as presented on the Table 4.5).

Table 4.6 Empirical formulae and the phase compositions of the samples u	used
for the critical analysis.	

Samples	Empirical Formulae	Vol.% of	Vol.% of	Vol.% of
		11 C _{free}	SiC	SiO ₂
SO 1	SiO _{1.21} C _{0.40} + 0.76C _{free}	22.1	17.9	59.9
SO 2	SiO _{1.45} C _{0.28} + 1.02C _{free}	25.9	11.0	63.1
SO-S1	SiO _{1.12} C _{0.44} + 0.63C _{free}	19.6	21.5	59.0
SO-S2	SiO _{1.10} C _{0.45} + 0.76C _{free}	22.8	21.1	56.2
SO-S3	SiO _{0.99} C _{0.51} + 0.67C _{free}	21.3	25.2	53.5
SO-S4	SiO _{0.93} C _{0.53} + 1.16C _{free}	32.3	23.3	44.4

Table 4.6 shows the volume percentages of each of the expected phases in the SiOC ceramics (data from the six samples *viz*. SO1 and SO2 from the sub-section 4.4.1 (see Table 4.3) and the SO-S1 to SO-S4 samples (see Table 4.5)), as computed from the empirical formula. The volume percentage of C_{free} was found to vary in the range 19.6 % - 32.3 %, SiC varied from 11.0 % - 25.2 %, and the volume percentage of the major phase, SiO₂, varied in the range 44.4 %- 63.1 %. However, these variations in the phases were not sufficient to clearly elucidate the influence of the different phases on the thermal conductivity (λ) of these ceramics. From the critical analysis conducted (using the data of the six SiOC samples, see Table 4.6) on the different phases, as shown

¹¹ The volume percentages were computed taking density values of 1.5 g.cm⁻

³, 3.2 g.cm⁻³, and 2.2 g.cm⁻³ for C_{free}, SiC, and SiO₂, respectively.



Figure 4.26 Critical analysis to understand the influence of the different phases (using the data from the six samples given on the Table 4.6), (a) $C_{free,}$ (b) SiO₂, (c) SiC on the thermal conductivity (λ) of SiOC ceramics at 100 °C.

in Figure 4.26, the only conclusions which could be drawn is that the λ values (at 100 °C) are in and around the reported values of amorphous silica [190] and that of the amorphous carbon [226], the two main phases present in these ceramics. The λ value available in literature for amorphous SiC at this temperature is ~4 W.m⁻¹. K⁻¹ [182] and the samples studied were found to exhibit a value much lower than the available reports.

Unfortunately, we were not able to significantly modify the free C content and therefore the variation of λ with the C_{free} (vol.%) could not be investigated. The influence of the silica matrix and that of the SiC fraction was also not properly understood. Further investigations are required to have a better understanding of the compositional influence on the thermal conductivity.

4.7 Case study-2: Influence of free carbon on the Young's modulus and hardness of silicon oxycarbide

The Figure 4.27(a) shows the typical cured resin samples and the corresponding SiOC glass obtained after pyrolysis at 1200°C in N₂ flow. After pyrolysis the samples showed shrinkage in the range 22% - 29% depending on the amount of TVTMS or DVB used in the synthesis (Table 4.6). The samples obtained using TVTMS as crosslinker, containing the lowest amount of free carbon after pyrolysis, were the ones which showed the highest tendency to crack. In contrast, the samples with high amount of DVB lead easily to un-cracked, monolithic SiOC discs.

The microstructural features of the SiOC samples were investigated by SEM. Accordingly, the SiOC samples have been fractured and the fracture surfaces were examined in search of a possible presence of porosity. SEM images reported in Figures 4.27(b) and 4.27(c) refer to SiOC-1 and SiOC-4 samples, however they are representative of all

the studied materials. The SEM investigation reveals a dense, porefree glass with a typical glassy fracture surface and characteristic twist hackle features. In order to investigate the presence of smaller, micromeso-pores a N₂ physisorption analysis was also performed which showed, for all samples, flat adsorption/desorption isotherms typical of non-porous materials, therefore confirming the formation of dense, pore-free SiOC glasses.



Figure 4.27 (a) The typical samples in the "as cured state" and after conversion into the SiOC glass; SEM fractographic image of (b) SiOC-1 and (c) SiOC-4 compositions showing the formation of dense, pore-free glasses (arrow pointer showing the twist-hackle marks on the fractographic image).

Table 4.7 reports the bulk density, pyrolysis shrinkage and the results of chemical analysis measured on the SiOC glass samples. In Table 4.7 the composition of the silicon oxycarbide glasses is also reported as $SiC_xO_{2(1-x)} + f C_{free}$. In order to express the composition of the SiOC samples as vol.% of the $SiC_xO_{2(1-x)}$ amorphous network and of the C_{free} , the density of the two phases has to be estimated. In the literature, the

density of SiC_xO_{2(1-x)} glassy phase with x ~ 0.37 has been reported in the range 2.3 – 2.4 g/cc [287,288] while for pyrolytic carbon obtained from a phenol-formaldehyde resin pyrolyzed at 1000°C the reported density is 1.45 – 1.55 g/cc [289,290]. Accordingly, we decided to estimate the vol.% of the two phases assuming density values for the amorphous silicon oxycarbide and C_{free} as 2.35 and 1.5 g/cc respectively.

Sample	Bulk	Shrinkage	Si	С	0	Composition
	Density	(%)	(wt.%)	(wt.%)	(wt.%)	$SiC_xO_{2(1-x)}$ + f C _{free}
	(g/cc)					
SiOC-1	2.32±0.1	22±2	46.8±0.1	19.9±0.1	33.4±0.2	SiC _{0.38} O _{1.25} +0.61C
SiOC-2	2.16±0.1	22±2	46.9±0.1	20.7±0.6	32.5±0.7	SiC _{0.39} O _{1.21} +0.63C
SiOC-3	1.95±0.1	23±2	38.4±0.2	38.4±0.3	23.3±0.2	SiC _{0.47} O _{1.06} +1.87C
SiOC-4	1.83±0.1	27±2	33.2±0.1	47.9±0.1	18.9±0.1	SiC _{0.50} O _{1.00} +2.86C
SiOC-5	1.82±0.1	29±2	29.3±0.1	51.0±0.1	19.8±0.1	SiC _{0.41} O _{1.18} +3.66C
SiOC-6	1.82±0.1	27±2	28.4±0.1	52.3±0.1	19.4±0.1	SiC _{0.40} O _{1.20} +3.90C

Table 4.7 Chemical composition, bulk density and pyrolysis shrinkage of the studied SiOC glasses.

The chemical composition of the amorphous phases indicates that the $SiC_xO_{2(1-x)}$ network in the studied samples has similar C content in the range ~0.4 – ~0.5 while the free carbon content spans from a minimum of ~18 vol.% up to a maximum of ~60 vol.% (from Table 4.8).

Sample	Composition	SiC _x	O _{2(1-x)}	C _{free}	
	SiC _x O _{2(1-x)} +f C _{free}	(wt.%)	(Vol.%)	(wt.%)	(Vol.%)
SiOC-1	SiC _{0.38} O _{1.25} +0.61C	87.8	82.1	12.2	17.9
SiOC-2	SiC _{0.39} O _{1.21} +0.63C	87.7	82.0	12.3	18.0
SiOC-3	SiC _{0.47} O _{1.06} +1.87C	69.4	59.1	30.6	40.9
SiOC-4	SiC _{0.50} O _{1.00} +2.86C	59.3	48.2	40.7	51.8
SiOC-5	SiC _{0.41} O _{1.18} +3.66C	47.3	43.0	52.7	57.0
SiOC-6	SiC _{0.40} O _{1.20} +3.90C	45.8	41.5	54.2	58.5

Table 4.8 The vol.% of the amorphous $SiC_xO_{2(1-x)}$ and C-free phases (calculated assuming the density of the two phases a described in the text).

Typical force-depth curves from the nanoindentation were reported and they showed good repeatability (Figure 4.28). The results also show that with a load of 40 mN, the observed depth of penetration is in the order of \sim 0.5µm.

The Young's modulus and the hardness values obtained from the nanoindentation experiments are reported in Table 4.9 and plotted in Figure 4.29(a) and 4.29(b), respectively as a function of the volume % of free carbon present in each sample. The reduced modulus of the samples was estimated using the software that is based on the standard procedure described in Oliver-Pharr [291]. The Poisson ratio of the studied SiOC glasses, which is required to estimate the Young's modulus according to the Oliver-Pharr model, is not available in literature. However, Poisson ratios of silica glass and of a SiOC glass having a composition of $SiC_{0.2}O_{1.6}$ + 0.6C_{free} are reported to be 0.15 and 0.11 respectively [292,293]. Consequently, we used an average value of Poisson ratio of 0.13 in the calculation of Young's modulus. It is worth mentioning that a ± 0.02 difference in the Poisson ratio would change the corresponding Young's modulus values less than 1%. Note that in the fits of Figure 4.28, we are neglecting the influences of the amount of carbon bonded to silicon, i.e. the x value in the SiC_xO_{2(1-x)} formula, on E and H due to its limited range (0.38-0.5). Moreover, in the literature there are no data reporting the elastic modulus and hardness of SiOC glasses having similar compositions.

The most important result, which clearly emerges from the nanoindentation data, is that both, the elastic modulus and the hardness decreases with increase in the volumetric fraction of free carbon. In both the cases these two properties show a linear relationship with the vol.% of free carbon suggesting that the nanocomposite follows reasonably well a simple rule of mixtures.



Figure 4.28 Typical force –depth curves from the indentation experiments of all the SiOC samples.
By extrapolating the linear fit to zero percent of free carbon, the Young's modulus of the "pure" SiC_xO_{2(1-x)}, x = -0.4 - -0.5 is found to be ~117 GPa, in good agreement with the Young's modulus values measured on SiOC glasses with negligible amount of free carbon and $x \sim 0.37$ [288]. The same fit extrapolated to 100% free carbon estimates an elastic modulus value of the free carbon phase ~63 GPa which is higher than the value reported for carbon materials derived from pyrolysis of organic resins, which is ~40 GPa [289,294]. The lower elastic modulus that the high-C samples display compared to the low-C ones could help in rationalizing the experimental evidence of the lower tendency to crack during pyrolysis shown by the high-C samples. Similar experimental evidence was also reported on C-rich SiC derived from polycarbosilane [164]. Accordingly, we consider that cracks during pyrolysis are generated from the development of stresses related to non-uniform shrinkage of the samples and they are proportional to the elastic modulus. Because the elastic modulus of the high-C content SiOC is up to 35% lower than the low-C content SiOC. it is reasonable to suggest that the high-C samples can be more easily pyrolyzed into a crack-free component due to their lower elastic modulus which prevents the formation of high stresses.

Extrapolation of the hardness fit to zero and 100% free carbon leads to values of 12.1 and 6 GPa, respectively. While the estimated value for the SiOC glass without free carbon (12.1 GPa) is slightly above the typical values reported in the literature, (~10 GPa) the hardness of the free carbon phase matched closely with the reported values (H = 5.5 - 6.0 GPa [294]).

We have observed that the E/H ratio is ~ 10 for all the SiOC compositions, independently from the amount of free C. According to Rouxel [295], glasses with E/H = 10 and with Poisson ratio lower than 0.19 should behave, under Vickers indentation, as 'anomalous glasses'

like silica with the formation of ring/con cracks instead of the radial/median cracks which form in "normal" soda-lime glasses. In an earlier study, it was reported that pure $SiC_xO_{2(1-x)}$ glasses with $y \approx 0$ show anomalous behavior, i.e. formation of Hertzian cone cracks during Vickers indentation, for low amount of substituted carbon and low pyrolysis temperature, while increasing these two parameters induce the transition from anomalous to normal behavior [287].

Sample	Location	Young's	Hardness ±	E/H
		Modulus \pm STD	STD	
		(GPa)	(GPa)	
SiOC-1	1	107.9 ± 4.4	11.0 ± 0.8	9.8
	2	105.7 ± 6.2	10.7 ± 1.0	9.9
SiOC-2	1	106.7 ± 3.4	10.8 ± 0.5	9.9
	2	110.0 ± 3.5	11.3 ± 0.9	9.7
SiOC-3	1	95.8 ± 5.2	9.7 ± 0.8	9.9
	2	92.9 ± 5.1	9.8 ± 0.9	9.5
SiOC-4	1	92.8 ± 3.4	9.4 ± 0.5	9.8
	2	83.3 ± 4.3	8.6 ± 0.9	9.7
SiOC-5	1	93.3 ± 5.2	8.4 ± 2.6	9.8
	2	88.5 ± 5.3	8.9 ± 0.7	10.2
SiOC-6	1	86.7 ± 3.9	8.8 ± 0.6	11.1
	2	$\textbf{76.9} \pm \textbf{4.7}$	7.5 ± 0.8	9.9

Table 4.9 Experimental Young's modulus and hardness values obtained from the nanoindentation tests.

Thus, silicon oxycarbide glasses with increasing amount of free C, from 18 vol.% up to 60 vol.%, show that both the elastic modulus and the hardness decrease with increase in the free carbon content and they follow a simple rule of mixtures. In particular the elastic modulus decreases linearly from ~106 GPa to ~80 GPa when the C-free content



increases from ~18 to ~60 vol.%. In the same C_{free} content range, the hardness decreased from ~11 to ~8 GPa.

Figure 4.29 Plots of the (a) Young's modulus and (b) hardness as a function of the vol.% of $C_{\mbox{\scriptsize free}}.$

4.8 Chapter summary

In this chapter, the three different precursors used to obtain the dense ceramics with the SiC, SiOC, and SiCN(O) chemistries were studied to elucidate their nature, ceramic yield, and processability using standard tools like FT-IR, TG, etc. The dense ceramics (thin disks, 100-300 µm) were obtained by simple casting of these preceramics and by subsequent pyrolysis of the same (preceramic disks). The evolution of different phases in the SiC ceramics obtained from a the polycarbosilane based precursor was studied and it was acknowledged that at a pyrolysis temperature of 1200 °C β-SiC nanocrystals appears. Further, the influence of the pyrolysis temperature on the composition and the morphology of the thin disks produced were studied. However, the SiOC and SiCN(O) ceramics from the polysiloxane and polysilazane preceramics, respectively were totally amorphous at least up to a temperature of 1400 °C. All the three systems were identified to also have significant fractions of segregated carbon in the matrix. These studies were followed by the thermal studies on these ceramics. The influence of the pyrolysis temperature on the SiC glassesceramics were studied to have an idea of its influence on the thermal properties. Nevertheless, the key thermal studies were conducted on samples prepared by pyrolysis at 1200 °C. The CTE measured was found to be ~4.0 x 10^{-6} .K⁻¹ for the SiC glasses while ~2.9 x 10^{-6} .K⁻¹ for the SiOC and SiCN(O). The λ was calculated to be ~1.5 W.m⁻¹. K⁻¹ for the SiC and in the range of 1.1 W.m⁻¹. K⁻¹ -3.3 W.m⁻¹. K⁻¹ for the SiOC and 0.95 W.m⁻¹. K⁻¹ – 3.62 W.m⁻¹. K⁻¹ for the SiCN(O), measured upto a maximum temperature of 1000 °C. Another observation is that the thermal properties of SiOC and SiCN(O) ceramics do not change by increasing the pyrolysis temperature up to 1400°C which is the onset for the thermal degradation of these two systems. The SiC system shows a clear and strong increase of λ when pyrolyzed at 1800°C. At this pyrolysis temperature λ value is *ca.* 2/5th of that reported for dense polycrystalline SiC and can be explained knowing that this sample has mesopores, which are formed during the evolution of SiO and CO occurring in the temperature range 1500 – 1800°C. The large presence of meso-porosity in the sample pyrolyzed at 1500°C combined with the amorphous (or nanocrystalline) matrix which still has not transformed into a well polycrystalline material (crystal size increases from ca. 4 nm at 1500°C up to ca. 41 nm at 1800°C) explain why, for pyrolysis temperature of 1500°C we have measured the lowest λ in whole this study ($\lambda = 0.5 \text{ W.m}^{-1}$. K⁻¹). These thermal properties measured were comparable with related chemistries and with the available literatures on similar materials. The hardness (Vickers microhardness) of these ceramics were also measured and were found to be comparable with the reports on similar materials. These studies were followed by two case studies on the SiOC system to systematically identify the influence of the different phases (especially the Cfree content) on various properties in these ceramics. Unfortunately, the influence of the different phases on the thermal conductivity of polymer derived silicon oxycarbide was not clearly understood. However, it was identified that the Young's modulus and the hardness of polymer derived silicon oxycarbide decreases with an increase in the vol.% of Cfree.

Chapter 5. Porous Si-O-C-N: Thermal studies on reticulated foams

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5.1 Introduction

In this chapter, the studies conducted on the highly porous, reticulated Si-O-C-N based ceramic foams developed from the pristine precursors *via* the modified template replica approach are reported in detail. The studies on the PU template used for the fabrication, followed by the various material characterizations and the thermal studies conducted on the porous ceramics are discussed.

5.2 Studies on the polyurethane (PU) templates

FT-IR analysis (as shown in the Figure 5.1) conducted on the PU foam templates indicate the presence of characteristic absorption bands for polyurethane at 3295 cm⁻¹ (N-H symmetric and asymmetric stretching. absorption band as a shoulder), at 2938 cm⁻¹, 2930 cm⁻¹, and 2864 cm⁻¹ ¹ (C-H stretching vibrations in methyl and methylene groups), as well as at 1723 cm⁻¹ and 1219 cm⁻¹ (sharp absorption peaks corresponding to the carboxy groups, i.e. stretching vibration of C=O and asymmetric vibration of C-O, respectively) [277][296]. The characteristic stretching peak at 1723 cm⁻¹ identifies the PU to be an ester-based one [296]. The TG analysis of both PU foams (shown in the Figure 5.2) shows the mass loss starting at around 240°C and reaching ca. 90 % at temperatures above 450 °C. Thus, the template loses 90 % of its mass during the pyrolysis and retains ~10 % of the mass fraction in the final ceramic, as carbon. The microstructures of the used PU templates are given in Figures 5.3 (a-d). As can be seen from the Figures 5.3 (a and b), the MTP-55 template (M-type) consists of partially closed cells with an average cell size of (580 ± 65) µm, while the cells of PPI-60 (P-type) are completely open porous with larger cells (Figures 5.3 (c and d)) with an average cell size of $(920 \pm 110) \mu m$.



Figure 5.1 FT-IR of the polyurethane (PU) templates (both M and P were of the polyester type).



Figure 5.2 Thermo-gravimetry of the polyurethane (PU) templates, MTP 55 and PPI 60.



Figure 5.3 SEM micrographs of the polyurethane (PU) templates, (a,b) MTP 55 (M), (c,d) PPI 60 (P).

5.3 Precursor-impregnated polyurethane (PU) template

The impregnation of the polymeric precursor (PP) on to the PU template was discussed in detail in Section 3.2.2 (Chapter 3) and process is depicted in Figure 3.6 (Chapter 3).

The precursor impregnated monoliths were studied to ensure that proper infiltration of the polymer solution was achieved. The FT-IR investigations helped to have a clear picture of the impregnation. In Figure 5.4, the impregnation of the polycarbosilane on to the PU template is illustrated with the help of FT-IR analysis. The FT-IR spectrum of the impregnated monolith shows the representative peaks of the polycarbosilane SMP 10 in them along with the characteristic peaks of the PU (the FT-IR recorded for the SMP 10 and PU is also shown along with to compare, in Figure 5.4). However, the impregnation of SMP 10 on similar template was systematically investigated previously by Jana *et al.* [155] of our group. Different tools

were effectively employed to state the impregnation of a similar system [155].



Figure 5.4 FT-IR analysis on the PU monolith impregnated with the polycarbosilane, SMP 10, data for impregnated samples were obtained from M-type foams with 1:2 ratio (the FT-IR of the PU and SMP 10 (shown in dashed lines) were presented before, however included for better clarity and for comparison).

While, the impregnation of the polysiloxane and polysilazane precursors on to PU were studied with the help of FT-IR and TGA and are presented in the Figure 5.5. From the FTIR analysis (Figure 5.5(a)) it can be read that the polymeric precursors were properly impregnated on to the PU template (characteristic FT-IR peaks of the precursors are seen along with that of the PU peaks). A marginal reduction in the Si-H stretching peaks shows the possible interaction of the precursor with the template [249]. The precursor-impregnated PU foams for both M-type and P-type showed, as expected, ceramic yields lying between

those of the pure PU templates and of the pure preceramic precursors, as can be seen from the Figure 5.5 (b).



Figure 5.5 (a) FT-IR spectrums of the prepared PU monolith impregnated with the polysiloxane, SPR 036 and the polysilazane, Durazane 1800. Data for impregnated samples were obtained from M-type foams with 1:2 ratio (the FT-IR of the PU and the precursors (SPR 036 and Durazane 1800) (shown in dashed lines) were presented before, however included for better clarity and for comparison) (b) TGA data for the impregnated PU templates (SPR 036 and

Durazane 1800), data from samples prepared from M-type foams impregnated with preceramic polymers in 1:1 weight ratio.

The infused PU foam monoliths were then pyrolyzed at the different temperatures (ranging from 1200 °C-1800 °C) to obtain the final ceramic foams (details addressed in Section 3.2.2 (Chapter 3)).

5.4 Reticulated ceramic foams

The studies on the ceramic foams are discussed in this section.

5.4.1 SiC foams – phases and microstructure

The SiC foams were prepared by pyrolysis at different temperatures (1200 °C,1500 °C, and 1800 °C) in argon atmosphere (preparation details could be read from Chapter 3). The bulk vs. skeletal densities of the SiC foams prepared by pyrolysis at 1200 °C are shown in Figure 5.6. The skeletal density (ρ_s) values were found to be *ca.* 2.20 g.cm⁻³ (more information in Table 5.2).



Figure 5.6 Skeletal density vs. bulk density of the prepared SiC foams prepared at 1200 °C.

This measured density matches well with the reported density of polymer derived amorphous SiC and that of other relative chemistries like SiOC and SiCN [123,184,266,297]. However, the density of β -SiC is higher, having a value of 3.2 g.cm⁻³ [261,262]. The amount of residual carbon from the template could also influence the density value of the final ceramic foam. The elemental analysis conducted on two selected foams (pyrolyzed at 1200 °C, shown in the Table 5.1), with different PU/PP ratios also showed significant oxygen fractions in the final ceramics. The oxygen fractions in the final ceramic show significant percentages of silica and it is quite possible that the oxygen contamination can also come from the PU template. At a temperature of 1200 °C, the amount of residual hydrogen content in these ceramics is negligible [298].

Samples	Bulk	Chemical composition (wt.%)		
	density (g.cm ⁻³)	Si	С	0
SiC -P3	0.11	51.85± 0.4	35.39± 0.07	12.76±0.4
SiC -M5	0.48	53.05± 0.07	35.38± 0.01	11.57±0.06

Table 5.1 Elemental analysis on selected SiC foams, prepared at 1200 °C.

Selected samples were prepared by pyrolysis at 1500 °C (the skeletal density was in the range 2.63 g.cm⁻³- 2.64 g.cm⁻³) and 1800 °C (the skeletal density was in the range 2.70 g.cm⁻³- 2.76 g.cm⁻³) (more details of the samples are given on the Table 5.3). Figure 5.7 shows an image of the SiC foams prepared at different temperatures.

The X-ray diffraction on the samples (shown in Figure 5.8 (a)) indicate that these SiC ceramics are mostly X-ray amorphous at 1200 °C. However, a clear onset of β -SiC crystallization can be seen even after pyrolysis at 1200 °C from the sprouting peaks at 2θ angle *ca*. 35°. The peaks become more obvious and well distinct as the pyrolysis

temperature is increased to 1500 °C (peaks at 35°, 60°, and 72° are representation of cubic β -SiC crystallization [155,263,264]). A small shoulder seen at around 33° corresponds to the possible crystallization



Figure 5.7 Showing an image of the SiC foams prepared at various pyrolysis temperatures (SiC-M and SiC-P represents the SiC foams made using M-type and P-type PU templates, respectively and the pictures are from the M3 and P3 sets).

of α -SiC (hexagonal polymorph) at this temperature [263,264]. Nevertheless, at 1800 °C, it is obvious that only the β -SiC is found to crystallize, showing stable nanocrystalline formation with literally no visible α -SiC crystalline formations. Raman spectroscopy gives a little more information regarding the evolution of the ceramics (see Figure 5.8(b)) [263]. The Raman analysis clearly showed that the segregated carbon phase is retained in the amorphous SiC system up to a pyrolysis temperature of 1500 °C (as seen from the characteristic 'D' and 'G' bands). At 1500 °C, the evolution of the SiC phase in the system become obvious. β -SiC starts evolving conspicuously, as evident from the peaks at 796 cm⁻¹ (TO) and 972 cm⁻¹ (LO) along with the '2D' band at 2700 cm⁻¹ [264,268,269]. At 1800 °C, it is obvious from the Raman spectrum that SiC is the dominant phase. The 'D' and 'G'

bands almost perished [263]; a significant fraction of C was eliminated, certainly via the carbothermal reduction reaction and also, at this temperature, the evolution of the nanocrystalline carbon into turbostratic carbon takes place [266].



Figure 5.8 (a) X-ray diffraction patterns and (b) Raman spectra of SiC foams at different pyrolysis temperatures (inset in (b) showing the magnified D and G bands of the SiC_1200 and SiC_1500 samples) (both the XRD and Raman were recorded from M3 set of the foam samples).

The microstructure of these porous structures can be corroborated from the SEM analysis. Figures 5.9 and 5.10 reports the SEM



Figure 5.9 SEM analysis on the SiC ceramic foams from the M-type template, prepared by pyrolysis at 1200 °C (a-c), 1500 °C (d-f), and, 1800 °C (g-i).

micrographs of the reticulated foams developed from the MTP and PPI PU templates, respectively, pyrolyzed at different temperatures, Figures 5.9(a-c), 5.9(d-f), and 5.9(q-i) corresponds to the SiC-M 1200. SiC-M 1500, and SiC-M 1800 samples, respectively. It is apparent that the struts formed are dense and the fractured surface of the struts has a smooth texture in the case of SiC-M 1200 and there aren't any sort of crack seen on the struts. However, with an increase of the temperature to 1500 °C, microcracks are formed and the fracture surface of the struts is not smooth anymore but shows a rough pattern. suggesting the presence of micro porosity (see Figure 5.9 (f)) [277,299]. On analyzing the samples pyrolyzed at 1800 °C (see Figures 5.9(g-i) it is evident that the microcracks are still present and the surface of the struts shows the homogeneous presence of nanocrystals (see the inset in the Figure 5.9(i)), which, based on the XRD results, can be identified as β -SiC [299]. In case of the SiC-P the microstructural evolution, reported in Figure 5.10, is similar to the one shown for SiC-M.

The N₂ adsorption-desorption on the foam (see Figure 5.11(a)) show that, the SiC foams prepared at 1200 °C (SiC-P_1200 and SiC-M_1200) are having totally dense struts, with literally zero pore formations on them, which is clear from the completely flat isotherms. As the pyrolysis temperature is increased to 1500 °C, from the isotherms it is obvious that pores are created owing to the liberation of SiO and CO gases during the carbothermal reduction reactions [277]. The pores are found to be in the mesoporous range (~3.7 nm (SiC-P_1500) and ~3.8 nm (SiC-M_1500)). While, in the samples pyrolyzed at 1800 °C, it was observed that there was gradual reduction in the pore volume when compared to the 1500 °C pyrolyzed ones. This could be due to the sintering of SiC at this temperature [300] which could result in the partial closure of the pores previously formed.



Figure 5.10 SEM analysis on the SiC ceramic foams from the P-type template, prepared by pyrolysis at 1200 °C (a-c), 1500 °C (d-f), and, 1800 °C (g-i).

However, the pore diameter in the SiC-P_1800 was still maintained at \sim 3.7 nm, while in the case of SiC-M_1800 the pore diameter reduced to \sim 2.9 nm.



Figure 5.11 (a) N₂ adsorption-desorption isotherms of the different foam samples, (b) the pore size distribution of these samples (all measurements taken on M3 set of samples).

The bulk and skeletal densities and the porosities of the SiC foams prepared at different pyrolysis conditions along with the λ measured on them are enlisted in Tables 5.2 (1200 °C), 5.3 (1500 °C), and 5.4 (1800 °C).

Table 5.2 The bulk density (ρ_b), skeletal density (ρ_s), porosity, and thermal conductivity (λ) values at RT of SiC ceramic foams pyrolyzed at 1200 °C¹².

Sample	Bulk	Skeletal	Porosity	Thermal
	density	density	(%)	conductivity
	(ρ _b ± 0.01)	$(\rho_s \pm 0.1)$		13
	(g.cm ⁻³)	(g.cm ⁻³)		$(\lambda \pm 0.01)$
				(W.m ⁻¹ . K ⁻¹)
SiC-M1/2	0.05	2.16	97.69	0.04
SiC-M1	0.11	2.19	94.97	0.06
SiC-M2	0.21	2.23	90.58	0.09
SiC-M3	0.33	2.28	85.53	0.10
SiC-M4	0.38	2.30	83.50	0.12
SiC-M5	0.48	2.35	79.53	0.16
SiC-P1/2	0.02	2.15	99.07	0.03
SiC-P1	0.04	2.16	98.15	0.04
SiC-P2	0.07	2.17	96.77	0.06
SiC-P3	0.11	2.19	94.97	0.05
SiC-P4	0.11	2.19	94.97	0.05
SiC-P5	0.12	2.19	94.52	0.06
SiC-P6	0.14	2.20	93.64	0.05

¹² SiC/SiOC/SiCN(O)-M or SiC/SiOC/SiCN(O)-P always represents a sample prepared at 1200 °C, if otherwise mentioned specifically the pyrolysis temperature along with it.

 $^{^{13}}$ The λ of SiC foams (1200 °C -1800 °C) would be discussed in the section 5.4.3 of this chapter.

Table 5.3 The bulk density (ρ_b), skeletal density (ρ_s), porosity, and thermal
conductivity (λ) values at RT of SiC ceramic foams pyrolyzed at 1500 °C.

Sample	Bulk	Skeletal	Porosity	Thermal
	density	density	(%)	conductivity
	(ρ _b ± 0.01)	$(\rho_s \pm 0.1)$		(λ)
	(g.cm ⁻³)	(g.cm ⁻³)		(W.m ⁻¹ . K ⁻¹)
SiC-M1/2_1500	0.04	2.64	98.62	0.06
SiC-M1_1500	0.07	2.64	97.48	0.08±0.01
SiC-M2_1500	0.18	2.63	93.28	0.11±0.01
SiC-M3_1500	0.26	2.63	90.19	0.16
SiC-P1_1500	0.03	2.64	98.84	0.06±0.01
SiC-P3_1500	0.09	2.64	96.42	0.08
SiC-P5_1500	0.15	2.63	94.21	0.10±0.04
SiC-P6_1500	0.19	2.63	92.65	0.11±0.03

Table 5.4 The bulk density (ρ_b), skeletal density (ρ_s), porosity, and thermal conductivity (λ) values at RT of SiC ceramic foams pyrolyzed at 1800 °C.

Sample	Bulk	Skeletal	Porosity	Thermal
	density	density	(%)	conductivity
	(ρ _b ± 0.01)	$(\rho_s \pm 0.1)$		(λ)
	(g.cm ⁻³)	(g.cm ⁻³)		(W.m ⁻¹ . K ⁻¹)
SiC-M1_1800	0.09	2.75	96.78	0.11±0.05
SiC-M2_1800	0.17	2.73	93.66	0.19±0.02
SiC-M3_1800	0.25	2.71	90.84	0.16±0.01
SiC-P1_1800	0.03	2.76	99.06	0.07
SiC-P3_1800	0.09	2.75	96.82	0.12
SiC-P5_1800	0.14	2.74	95.05	0.13±0.01
SiC-P6_1800	0.17	2.73	93.82	0.10±0.04

5.4.2 SiOC and SiCN(O) foams – phases and microstructure

SiCN(O) and SiOC ceramic foams with bulk densities ranging from 0.03 g.cm⁻³ to 0.56 g.cm⁻³ were prepared by altering the PU/PP weight ratio (see Figure 5.12). As expected, small ratios (i.e. high PP) resulted in relatively high ceramic foam densities; whereas the bulk densities were shown to decrease as the PU/PP ratio increases. The skeletal densities of the prepared ceramic foams were found not to vary significantly and showed values around 2.00 g.cm⁻³. The slight variation in the skeletal densities of the ceramic foams was also correlated to the PU/PP weight ratio, which influences the amount of residual carbon in the samples as seen previously in the case of SiC samples also (resulting from the decomposition of the PU template); consequently, it is expected that an increase in the residual carbon content in the ceramic foams will induce a slight decrease of their density (density of pyrolytic carbon is 1.8 - 2.0 g.cm⁻³ [260] while density of SiCN/SiOC is ca. 2.2 - 2.3 g.cm⁻³ [213,259], see Figure 5.12.



Figure 5.12 Skeletal density vs. bulk density of the prepared SiCN(O) and SiOC ceramic foams.



Figure 5.13 SEM analysis on the SiOC ceramic foams and the nature (microstructure) of the strut prepared at 1200 °C from the M-type PU template (a and b), and P-type PU template (c and d) (all images from M2 and P2 foams).



Figure 5.14 SEM analysis on the SiCN(O) ceramic foams and the nature (microstructure) of the strut prepared at 1200 °C from the M-type PU template (a and b), and P-type PU template (c and d) (all images from M2 and P2 foams).

It is clear from the micrographs given in Figures 5.13 and 5.14 that the SiOC and SiCN(O) ceramic foams retain the characteristic features of

the PU templates. The SiCN(O) and SiOC foams obtained from the Mtype PU foam, i.e. the SiCN(O)-M and SiOC-M ceramic foams, exhibit partially closed porosity, while those obtained from P-type foams, i.e. the SiCN(O)-P and SiOC-P ceramic foams show open pores. Significant difference related to the strut's morphology was observed between the ceramic foam series prepared from Durazane 1800 and SPR-036. The struts were dense for the silazane-derived samples and instead were hollow for the polysiloxane-derived ceramic foams. Such difference probably relates to two features: (i) the better affinity of polyurethane toward polysilazane compared to polysiloxane resulting into a better swelling of PU foam by Durazane¹⁴ and (ii) the different crosslinking kinetics of the polysiloxane and polysilazane precursors. i.e. SPR-036 showing much faster cross-linking than that of Durazane 1800. SPR-036 is thought to have cured on the PU template prior to complete swelling. Consequently, the ceramic struts are hollow after the PU was burnt out. Indeed, it was already reported that Pt is a very good catalyst for Si-H containing polysiloxane, while it is somehow less efficient if the Si-H groups are together with N-H groups such as in the case of polysilazane [256].

The chemical analysis (see Table 5.5) of the final SiOC and SiCN(O) ceramics was applied to the selected samples to understand the effect of the PU/PP weight ratio on the final ceramic composition. The foam type has almost no effect on the final chemical composition, as can be seen by comparing SiOC-P3 and SiOC-M3, which were prepared using the same PU/PP ratio of 1:3. However, the PU/PP weight ratio caused a clear effect on the chemical composition of the ceramic foams, as shown for the two SiCN(O) samples in Table 5.5. The nitrogen content increases with decreasing the PU/PP ratio, since the relative

¹⁴ The submersion of the PU foams into the pure (no solvent) liquid Durazane 1800 and liquid SPR-036 resulted into a volume increase, measured *in situ* in the liquid precursor, of 9.0% and 4.5% respectively unambiguously suggesting that polysilazane has a better affinity compared to polysiloxane for polyurethane.

importance of the ceramic residue from PP increases. Similarly, the oxygen contamination increases with increasing the PU/PP ratio, suggesting that such contamination comes more from the decomposition of the PU template during pyrolysis than from the reactivity of the polysilazane with the laboratory atmosphere during the impregnation/curing step.

Samples	Bulk	Chemical composition (wt.%)			
	density	Si	С	Ν	0
	$(\rho_b \pm 0.01)$				
	(g.cm ^{-s})				
SiOC-P3	0.11	43.50±	23.20±	0	33.30±
		0.4	0.08		0.3
SiOC-M3	0.24	43.95±	23.36±	0	32.69±
		0.2	0.1		0.3
SiCN(O)-P4	0.15	42.25±	26.79±	9.84±	21.13±
		0.4	0.06	0.5	0.2
SiCN(O)-M6	0.56	47.20±	23.03±	15.35	14.43±
		0.3	0.02	±0.4	0.1

Table 5.5 Elemental analysis on selected SiOC and SiCN(O) foams, prepared at 1200 °C.

The XRD patterns of the SiOC and SiCN(O) foams, pyrolyzed at different temperature are shown in Figures 5.15 (a) and 5.15(c). A hump in the range $20^{\circ} < 2\theta < 25^{\circ}$ shows the presence, for both systems, of an amorphous silica-based phase [121,192] thus confirming, also for the Durazane 1800-derived foams, the presence of oxygen in the SiCN network.



Figure 5.15 X-ray diffraction patterns and Raman spectra of SiOC ((a) and (b), respectively) and of SiCN(O) ((c) and (d), respectively).

The SiCN(O) foams remain amorphous up to 1400 °C while as the pyrolysis temperature is increased to 1500 °C, reflections associated to β -SiC start appearing around 35.6°, 61.0°, and 71.8° (see Figure 5.15(c)). The formation of SiC is due to the well-known decomposition occurring in SiCN-based ceramic systems exposed to temperatures above 1400 °C[301][302]. As for the SiOC system (Figure 5.15(a)), the samples remain amorphous up to 1300 °C. At temperatures above

1400°C, the diffraction peaks of β -SiC appear due to partitioning and subsequent carbothermal reaction of the silicon oxy-carbide[155,298,303]. The Raman spectra placed as inset in the XRD plots (see Figures 5.15(b) and 5.15(d)) shows the characteristic disordered (D) and graphitic (G) peaks of the sp²-hybridized residual carbon up to at least 1400 °C in both SiOC and SiCN(O) ceramics [235][304].

Table 5.6 The bulk density (ρ_b), skeletal density (ρ_s), porosity, and thermal conductivity (λ) values at RT of SiOC ceramic foams pyrolyzed at 1200 °C.

Sample	Bulk	Skeletal	Porosity	Thermal
	density	density	(%)	conductivity
	(ρ _ь ± 0.01)	$(\rho_s \pm 0.1)$		(λ ± 0.01)
	(g.cm ⁻³)	(g.cm ⁻³)		(W.m ⁻¹ . K ⁻¹)
SiOC-M1	0.09	2.03	95.6	0.05
SiOC-M2	0.18	2.10	91.4	0.08
SiOC-M3	0.24	2.14	88.8	0.08
SiOC-M4	0.37	2.24	83.5	0.12
SiOC-M5	0.40	2.27	82.4	0.13
SiOC-M6	0.47	2.32	79.7	0.16
SiOC-P1	0.03	1.98	98.5	0.03
SiOC-P2	0.06	2.01	97.0	0.04
SiOC-P3	0.11	2.04	94.6	0.04
SiOC-P4	0.13	2.06	93.7	0.04
SiOC-P5	0.18	2.10	91.4	0.07
SiOC-P6	0.21	2.12	90.1	0.06

Thermal conductivity (λ) measurements made on all the produced SiOC and SiCN(O) foams for which the details are given in Tables 5.6, 5.7, and 5. 8. The bulk density, skeletal density, porosity, and the thermal conductivity values measured at room temperature of the SiOC

and the SiCN(O) prepared at 1200 °C are tabulated in the Tables 5.6 and 5.7, respectively; while those of the selected SiOC and SiCN(O) foams prepared at 1400 °C for comparison study are given on the Table 5.8.

Table 5.7 The bulk density (ρ_b), skeletal density (ρ_s), porosity, and thermal conductivity (λ) values at RT of SiCN(O) ceramic foams pyrolyzed at 1200 °C.

Sample	Bulk	Skeletal	Porosity	Thermal
	density	density	(%)	conductivity
	(ρ _b ±0.01)	(ρ _s ±0.1)		(λ ± 0.01)
	(g.cm ⁻³)	(g.cm ⁻³)		(W.m ⁻¹ . K ⁻¹)
SiCN(O)-M1	0.10	2.04	95.1	0.05
SiCN(O)-M2	0.18	2.08	91.3	0.07
SiCN(O)-M3	0.26	2.13	87.8	0.10
SiCN(O)-M4	0.37	2.18	83.0	0.16
SiCN(O)-M5	0.42	2.21	81.0	0.15
SiCN(O)-M6	0.56	2.28	75.4	0.20
SiCN(O)-P1	0.05	2.02	97.5	0.03
SiCN(O)-P2	0.1	2.04	95.1	0.06
SiCN(O)-P3	0.1	2.04	95.1	0.07
SiCN(O)-P4	0.15	2.07	92.8	0.05
SiCN(O)-P5	0.16	2.07	92.3	0.07
SiCN(O)-P6	0.20	2.09	90.4	0.07

Table 5.8 The bulk density (ρ_b), skeletal density (ρ_s), porosity, and thermal conductivity (λ) values at RT of the SiOC and SiCN(O) ceramic foams pyrolyzed at 1400 °C.

Sample	Bulk density (ρ _b ± 0.01) (g.cm ⁻³)	Thermal conductivity (λ ± 0.01) (W.m ⁻¹ . K ⁻¹)
SiOC-M2_1400	0.17	0.08
SiOC-M4_1400	0.32	0.11
SiOC-P2_1400	0.07	0.04
SiOC-P4_1400	0.13	0.04
SiCN(O)-M2_1400	0.21	0.08
SiCN(O)-P2_1400	0.10	0.04

5.4.3 Thermal studies on SiC, SiOC, and SiCN(O) foams

The λ measured for the foams, having different morphology (M and P type), with different solid content (varying density), and prepared by pyrolysis at different temperatures are shown in Figure 5.16 and Figure 5.17. The different morphology obtained by using different replica templates were found not to have much impact on the λ , apart from the fact that the ceramic foams from the MTP template gave denser samples when compared to the ones from the PPI templates (this was obvious due to the higher density of the MTP PU foams than the PPI PU foams). The λ showed an increase with an increase in the bulk densities of the foams. Among the SiC foams prepared at 1200 °C, the lowest value of λ measured was for the sample SiC-P1/2 (0.03 W.m⁻¹. K⁻¹) having the bulk density, $\rho_b = 0.02$ g.cm⁻³ and the highest λ value obtained, at the same pyrolysis condition, was for the sample SiC-M5 (0.16 W.m⁻¹. K⁻¹) having a $\rho_b = 0.48$ g.cm⁻³. With an increase of pyrolysis temperature to 1500 °C, the ordering of these carbon increases and more importantly the extent of the nano crystalline SiC

domains also increase, this can cause an increase in the λ measured. However, the onset of the carbothermal reduction reactions at this temperature would cause the formation of pores on the solid struts of the foams, which in-effect lower the λ .

At 1800 °C, as observed from the XRD and the microstructural analyses, totally crystalline SiC phase is evolved, which would reflect in an increase in the λ of the foams. However, on the other side, the mesopores formed can lower the λ . Nevertheless, from the experimental results obtained it can be inferred that the influence of the crystallization (with removal of Si-O), which cause an increase in the λ is more decisive than the porosity which can cause a decrease in the final λ .



Figure 5.16 Thermal conductivity (λ) vs. bulk density (ρ_b) for the different SiC samples, prepared in the temperature range 1200 °C-1800 °C (values could be read from the Tables 5.2-5.4).



Figure 5.17 Thermal conductivity (λ) vs. bulk density (ρ_b) for the different, (a) SiCN(O) samples, (b) SiOC samples prepared in the temperature range 1200 °C-1400 °C (values could be read from the Tables 5.6-5.8).

Similar to the SiC foams discussed before, the λ of the SiOC and SiCN(O) foams also showed an increase as the bulk density increased. Among the SiCN(O) samples prepared at 1200 °C, the highest RT λ was measured for SiCN(O)-M6 (0.20 W.m⁻¹. K⁻¹), having a relative density of 0.25 and the lowest was from SiCN(O)-P1 (0.03 W.m⁻¹. K⁻¹) sample having a relative density of 0.02 (see Figure 5.17(a) and Tables 5.7-5.8). The highest value was recorded for the SiOC-M6 (0.16 W.m⁻¹. K⁻¹) and lowest was obtained for SiOC-P1 (0.03 W.m⁻¹. K⁻¹) (see Figure 5.17(b) and Table 5.6 and Table 5.8).



Figure 5.18 (a) Dilatometry and (b) TG curves of the SiC, SiOC, and SiCN(O) foams (measurements were taken on the M2 set of the foams).

The thermal expansion of the foams was studied by dilatometry in the temperature range from 30 to 850 °C. The values of the coefficient of thermal expansion (CTE) were ca. 3.24 x 10⁻⁶.K⁻¹. 1.93 x 10⁻⁶.K⁻¹. and 1.72 x 10⁻⁶ .K⁻¹ for the investigated SiC, SiOC, and SiCN(O) foams, respectively (shown in Figure 5.18(a)). The CTE measured for the foams were found to be lower than that measured on the dense ceramics, reported in the previous chapter (Chapter 4). Obviously, the influence of the final composition (~10 wt.% of carbon from the PU template was also incorporated into the final ceramic foam) can also vary the CTE. However, the reported CTE is in the range reported for SiC ceramics. The SiOC sample mainly consists of amorphous silica phase and as described before in the previous chapter, the vitreous silica is known to have very low CTE of 0.57 x 10⁻⁶ .K⁻¹[197]. The reason for an increased CTE value for SiOC, compared to vitreous silica, might be the presence of free carbon and/or nano-crystalline SiC. The observed values were also in agreement with recently reported values of dense SiOC ceramics, e.g. 1.84-3.23 x 10⁻⁶ .K⁻¹ in the temperature range from 100 to 1000°C [195]. The measured CTE for the SiCN(O) foam was lower than the value reported in the literature for similar materials (2.69 x 10⁻⁶.K⁻¹[204]).The TG analysis on the ceramic foams up to a temperature of 1600 °C is shown in Figure 5.18(b). It can be seen that all the three types of ceramic foams, viz. SiC, SiOC, and SiCN(O) obtained are guite stable up to a temperature of at least 1400 °C, in Ar atmosphere and above 1500 °C the weight loss suggests a decomposition process.

With the aim of investigating the influence of the microstructure (open cells vs closed cells) on the λ of the ceramic foams (SiC, SiOC, and SiCN(O)), the experimental data have been plotted as a function of the relative density, differentiating between open vs closed cells for the samples prepared at 1200 °C (Figure 5.19).



Figure 5.19 RT thermal conductivity values measured on the: (a) SiC, (b) SiOC and, (c) SiCN(O) ceramic foams prepared at 1200 °C. Open symbols refer to the open cells, P-type, and solid symbols to the closed cells, M-type, ceramic foams.

The data shown in Figure 5.19 reveal that the P-type, open cells PU, in general leads to foams with lower relative density compared to the M-type PU. Indeed, PU foams with partially closed cells, retain more pre-ceramic polymer and form, after pyrolysis, a denser component. However, beside this obvious difference between the two types of templates, the dependence of the λ on the relative density is the same and all the data points, for each chemistry, fall into a master line.

The Gibson-Ashby model (using the λ values of the foams pyrolyzed at 1200 °C) developed to estimate the thermal conductivity (λ) for the solid (open cell) foams and is given as in the equations¹⁵ 3.10 and 3.11 (from chapter 3) [88]. Accordingly, the λ values of the SiC. SiOC, and SiCN(O) foam (pyrolyzed at 1200 °C) struts evaluated from the Gibson-Ashby model were found to be 1.9 W.m⁻¹. K⁻¹, 1.8 W.m⁻¹. K⁻¹, and 2.1 W.m⁻¹, K⁻¹, respectively at RT. The λ estimated for the struts of similar SiC foams (using the same approach) was ~1.7 W.m⁻¹. K⁻¹ [155]. The values for the silicon oxy-carbides struts are consistent with those previously reported for bulk SiOC [189,192,194,195] and also with polymer-derived Si-C based ceramics [155]. In case of SiCN(O), to the best of our knowledge, the λ value is the first one reported in the literature, still it falls well in the range of known λ value for the other Sibased PDC materials. These values also coincide with our reports on dense ceramics with relative chemistries, as discussed in the previous chapter (chapter 4) of the thesis.

The thermal diffusivity measurements performed from RT up to 1000°C, for the SiC, SiOC, and SiCN(O) ceramic foams prepared from

 $\begin{array}{l} ^{15} \lambda_{Sf} = \frac{1}{3} \left(\frac{\rho_b}{\rho_s} \right) \lambda_{S^+} \left(1 - \frac{\rho_b}{\rho_s} \right) \lambda_{air} & (eq. \ 3.10) \\ \lambda_{Sf} = \left(\frac{1}{3} \lambda_S - \lambda_{air} \right) \frac{\rho_b}{\rho_s} + \lambda_{air} & (eq. \ 3.11) \end{array}$
the M-type template is given in the Figure 5.20. We tried to use the LFA technique also on the P-type open cells foams however, due to insufficient absorption of the laser power of these samples the results were not reliable.



Figure 5.20 Thermal diffusivity vs. temperature data of SiC, SiOC, and SiCN(O)ceramic foams, by using laser flash technique (measured on M2 samples prepared at 1200 °C).

The thermal diffusivity values at RT for SiC and SiOC were measured to be 4.9 x 10^{-3} cm².s⁻¹ and 4.8 x 10^{-3} cm².s⁻¹ and for the SiCN(O) samples to be ~5.9 x 10^{-3} cm².s⁻¹. Recently, Stabler *et al.* [195] reported that the thermal diffusivity of dense SiOC obtained after pyrolysis at 1100 °C was ~ 6.75×10^{-3} cm². s⁻¹ at RT and also observed an increase in the diffusivity value with higher pyrolysis temperatures (1600 °C). Similarly, the thermal diffusivity of SiCN ceramics (dense) was reported to increase from 5.07 x 10^{-3} cm². s⁻¹ to 8.08 x 10^{-3} cm². s⁻¹ as the treatment temperature was raised from 800 °C to 1300 °C[199]. These reports match well with the diffusivity values measured in this work. As the measurement temperature is raised above 400 °C, there is a gradual increase in the diffusivity values. This could be attributed to the effect of the radiative component [189] in all the three foams of different chemistries considered.

5.4.4 Mechanical strength-Compressive test on foams

The crushing (compressive) strength of selected foams having varying chemistry were measured. The porous structures showed typical stress-strain pattern (as shown in Figure 5.21) similar to that observed in the case of elastic-brittle foams [155,305–307]. The characteristic stress-strain curve shows an elastic zone followed by a serrated plateau showing the continuing of the brittle crushing of the crumpled and not-crumpled regions of the cell walls and this stage is often followed by a densification [305,306]. The values of the measured compressive strength in MPa, of the respective foam samples are shown on the Table 5.9.



Figure 5.21 A typical stress-strain curve recorded for the foams developed (the depicted example, 1 and 2 were recorded from SiCN(O)-P4 sample).

Samples	Bulk density	Compressive strength
	(ρ _b ± 0.01)	
	(g.cm ⁻³)	(MPa)
SiOC-M2	0.18	1.36±0.18
SiOC-P4	0.13	0.20±0.06
SiCN(O)-M2	0.18	1.07±0.42
SiCN(O)-P4	0.15	0.32±0.08
SiC-P4	0.11	0.42±0.01
SiOC-M4	0.37	3.30±1.40
SiCN(O)-M4	0.37	2.64±1.27

Table 5.9 The compressive strength measured on selected foams, all prepared at 1200 °C.

It can be seen that the densification as well as the type of PU template (M-type, with more closed cells and P-type with more opened cells) from which the final ceramic foams were obtained determines the compressive strength. The ceramic foams from the M-type PU foams showed greater strength than that of a ceramic foam from a P-type PU, in spite of having comparable densities and similar chemistry (M2 and P4 pairs of both SiOC and SiCN(O) could be compared). The compressive strength measured for the different foams (see Table 5.9) ranged between ~0.2 MPa - ~3.3 MPa, which is at par with the compressive strength reports on similar polymer derived ceramics having Si-O-C and related chemistries [155,305,306]. It is also worth noting that the reasonably high crushing strength measured on these foams (>2.5 MPa, viz. the M4 set of both SiOC (λ = 0.12 W.m⁻¹. K⁻¹) and SiCN(O) (λ = 0.16 W.m⁻¹. K⁻¹) shown on the Table 5.9), was considerably higher than the strength measured for many of the commercially used high-temperature insulation panels (often reported in the range 0.04 W.m⁻¹. K⁻¹- ~ 0.2 W.m⁻¹. K⁻¹) in the market (<~1.0 MPa) despite having comparable or even lower λ with greater thermal stability [308,309]. Increase in the preparation (pyrolysis) temperature

was found to increase the λ as well as to make the struts, and ultimately the foams, weaker.

5.5 Chapter summary

In this chapter, studies on polymer derived reticulated SiC, SiOC and SiCN(O) ceramic foams, prepared by a replica method; i.e. by impregnating PU foam with preceramic precursors, followed by pyrolysis was discussed. The SiC and SiCN(O) reticulated ceramic foams from the polycarbosilane and polysilazane were found to exhibit dense struts, whereas the SiOC ceramic foams prepared with the polysiloxane had hollow struts. This result was related to the different swelling ability of the three Si-precursors in the PU stricture and to their different crosslinking kinetics. The linear thermal expansion coefficient values of the porous Si-O-C-N foams in the temperature range from 30 to 850 °C were measured to be in the range of \sim 1.72 x 10⁻⁶ .K⁻¹- \sim 3.24 x 10⁻⁶ .K⁻¹, depending on the different chemistry. The thermal conductivity analysis conducted at room temperature showed that the samples had conductivity in the range from 0.03 W.m⁻¹. K⁻¹ to 0.20 W.m⁻¹. K^{-1} for the SiCN(O) foams, and similarly in the range from 0.03 W.m⁻¹. K⁻¹ to 0.16 W.m⁻¹. K⁻¹ for the SiOC foams and in the range 0.03 W.m⁻¹. K⁻¹ to 0.19 W.m⁻¹. K⁻¹ for the SiC foams. A Gibson-Ashby model was used to estimate the thermal conductivity of the ceramic struts (i.e. dense material) which were found to be 1.9 W.m⁻¹. K⁻¹ for SiC, 1.8 W.m⁻ ¹.K⁻¹ for SiOC, and 2.1 W.m⁻¹. K⁻¹ for SiCN(O). The λ of the SiC and SiOC ceramic is in line with those already reported in the literature and with that measured on the dense material. While, the λ for the SiCN(O) material was never reported before but the values were comparable with the dense measurements. The crushing strength measured on these foams also showed that the foams from the P type PU templates are weaker than those from the M-type PU foam. The measured compressive strength of the foams were in the range 0.20±0.06 MPa -



Figure 5.22 (a) Thermal conductivity (λ) and Bulk density(ρ_b) vs. operational temperature, a comparison of the SiC, SiOC, and SiCN(O) foams developed (shown with * in the Figure) with selected commercial inorganic insulators (shown bold in the Figure) [308–310], and with some of the recent reports of similar materials [155,188,196,311–315], (b) and (c) shows the 2D-sections of the comparison plot represented in (a), at the different temperature ranges.

 3.30 ± 1.40 MPa. This low λ , high temperature stability, and reasonable strength endorses the possibility to use these reticulated ceramics for thermal insulation at elevated temperatures. A comparison of the λ and the density with the maximum working temperature of the developed foams having the compositions Si-O-C-N with some recent reports and some commercial inorganic insulators in the market are given on the Figure 5.22.

The thesis principally investigated the thermal properties and the thermal transport in polymer derived Si-based ceramics, mainly the chemistries SiC, SiOC, and SiCN(O). The thesis discusses the experimental work, starting from the fabrication of totally dense and highly porous ceramics (>75%) to the various systematic characterizations conducted on these developed materials.

Dense ceramics in the form of thin disks, having a thickness in the range of $100 \ \mu m$ - $300 \ \mu m$ was prepared by simple processes involving: (i) casting of the polymeric pre-ceramics onto specially prepared moulds, and (ii) sequentially conducting the pyrolysis of the monolithic-preceramic thin disks (punched out from the casted film). Some of the main conclusions drawn from our studies on the dense ceramic disks are summarized as follows:

K The microstructural investigations on these ceramic disks demonstrated that using this approach we were able to make totally pore-free samples when prepared at a moderate pyrolysis temperature of 1200 °C. This is important for ascertaining various intrinsic properties of the ceramic with the minimal influence of factors like pores on the measured properties, especially the thermal and micro-mechanical properties. However, our study has revealed that the pores starts forming on the prepared disks at higher pyrolysis temperatures, with SiCN(O) ceramics showing the highest thermal degradation stability (>1400 °C). The observations were further confirmed from the N₂ adsorption-desorption experiments, which resulted in totally flat isotherms.

K Among the three chemistries studied: the SiC showed nanocrystalline nature (as evident from the XRD analysis on these ceramic disks) even at the lowest preparation temperature of 1200 °C, which became more and more perceptible with an increase in the pyrolysis temperature (maximum temperature was 1800 °C). While, for the SiOC and SiCN(O), the amorphous network was found to be stable at least upto 1400 °C.

K The elemental analysis (conducted for the samples prepared at 1200 °C) showed significant oxygen contamination in both the SiC and SiCN(O) ceramics. It also indicated varying percentages of segregated carbon in all three chemistries, which was further confirmed by the Raman spectroscopic analysis of these ceramics.

The CTE measured on the disks pyrolyzed at 1200 °C were ~2.9 x 10⁻⁶.K⁻¹ for the SiOC and SiCN(O) systems, while they were slightly higher for the SiC system, i.e. ~4.0 x 10⁻⁶.K⁻¹. The measured values of CTE were found to be greater than the reported CTE of vitreous silica and lower than that of the β-SiC. However, the CTE values were found to be comparable to the reports on SiOC glasses.

The thermal conductivity (λ) was computed from the thermal diffusivity measurements (using a laser flash approach) and Cp values (from DSC) of the ceramic disks. The λ was calculated to be almost constant in the RT-1000 °C interval (~1.5 W.m⁻¹.K⁻¹) for the SiC pyrolyzed at 1200 °C. The increase in the pyrolysis temperature to 1500 °C was found to show a decrease in the λ to ~0.5 W.m⁻¹. K⁻¹. This could be explained with an increase in the scattering owing to the pore formations. SiC disks pyrolyzed at 1800 °C, show an increase of λ compared to the values obtained at lower temperatures. The λ pattern, in the measured temperature range, is similar to the one for β -SiC, i. e. it shows a decrease from RT to 1000°C. In the case of SiOC and SiCN(O) ceramics pyrolyzed at 1200 °C, the λ were in the range of 1.1 W.m⁻¹.K⁻¹- 3.3 W.m⁻¹.K⁻¹ and 0.95 W.m⁻¹.K⁻¹- 3.62 W.m⁻¹.K⁻¹, respectively in the measured temperature range of RT-1000 °C. For both these chemistries, the λ values measured at low temperature (100°C) are in the range 1- 2 W.m⁻¹.K⁻¹. These values compare well with those already reported in the literature for the SiOC system while for the SiCN(O) the λ was never reported before.

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▶ The Vickers hardness (H_V) measured on the disks prepared at 1200 °C were in the range of 8.9 GPa – 23.3±2.6 GPa. The hardness was measured to be higher for the polycarbosilane-derived SiC.

K The influence of the segregated carbon (C_{free}) content on the mechanical properties in SiOC ceramics was investigated and is reported. Increasing the amount of C_{free} in SiOC from 18 vol.% up to 60 vol.%, both the elastic modulus and the hardness were found to decrease in such a way that they followed the simple rule of mixtures.

ightarrow With the aim of investigating the relation between the amount of C_{free} and the λ dense SiOC disc samples were prepared starting from the SPR 036 resin and increasing amount of DVB. Unfortunately, we were not able to significantly modify the free C content and therefore the variation of λ with the C_{free} (vol.%) could not be investigated.

Apart from the dense ceramics, the thesis work involved the preparation of reticulated foams (porous ceramics). These were prepared by an improved sacrificial templating approach using PU foams as the template. The PU foams were impregnated with the different (polycarbosilane, polysiloxane, and polysilazane) pristine precursor complex followed by the controlled pyrolysis to get the final ceramic structure. The main aspects of the developed SiC, SiOC, and SiCN(O) foams are summarized as follows:

▶ The ceramic foams were prepared by simply tuning the precursor to the template ratio (PP/PU). The fabrication resulted in foams having varying cell features (totally opened to partially closed cell) and with density and porosity in the range of 0.02 g.cm⁻³ – 0.56 g.cm⁻³ and ~75% – ~99%, respectively.

The foams developed were found to show XRD patterns similar to that of the dense materials, i.e. they are amorphous at lower temperatures, while the β-SiC crystallizes with an increase in the pyrolysis temperature, typically in the temperature range of 1400 °C– 1500 °C.

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K The developed foams were found to be thermally stable at least up to a temperature of 1400 °C, measured in Ar atmosphere.

▶ The CTE values of the porous Si-O-C-N foams in the temperature range of 30 to 850 °C were measured to be in the range of ~ 1.72×10^{-6} .K⁻¹ - ~ 3.24×10^{-6} .K⁻¹.

Γ The RT λ measured on these foams using a Hot-Disk were found to be as low as 0.03 W.m⁻¹. K⁻¹. The measured λ was in the range of 0.03 W.m⁻¹. K⁻¹ to 0.19 W.m⁻¹. K⁻¹ for the SiC foams, 0.03 W.m⁻¹. K⁻¹ to 0.20 W.m⁻¹. K⁻¹ for the SiCN(O) foams, and 0.03 W.m⁻¹. K⁻¹ to 0.16 W.m⁻¹. K⁻¹ for the SiOC foams. The λ measurements did not appear to be affected by the cell features of the foams (apart from the fact that more closure lead to denser PU template in-effect resulting in denser ceramic foams).

Γ The Gibson-Ashby modelling approach was used to estimate the thermal conductivity of the ceramic struts (i.e. dense material) of the different foams. The λ was estimated to be 1.9 W.m⁻¹. K⁻¹ for the SiC foams, 1.8 W.m⁻¹.K⁻¹ for the SiOC, and 2.1 W.m⁻¹. K⁻¹ for the SiCN(O) foams studied.

The compressive strength of the foams was measured to be in the range of 0.20 ± 0.06 MPa – 3.30 ± 1.40 MPa. It was also observed that the foams derived from the P type PU templates are weaker than those from the M-type PU foam.

Future perspectives

➤ The thesis principally studied the thermal properties of SiC, SiOC, and SiCN(O) amorphous ceramics pyrolyzed at 1200 °C. In this work a brief examination was conducted to see the influence of the pyrolysis temperature on the thermal properties only for the SiC system, which need to be extended to the other systems in future studies. In order to have a complete picture of the thermal properties, detailed investigations are required *viz*. controlling the different processing parameters, tuning the existing and also by introducing new phases, varying the C_{free} percentages. Future investigations should be focused to better understand the thermal transport in these ceramics.

Apart from the possibility to tune or novelizing the composition, there is a possibility to extend the investigations on the fully dense ceramics developed to understand the electrical and thermo-resistive responses (not much explored on this class of materials).

> An extension of the studies on the developed foams coupled with a possible simulation approach could be helpful to further corroborate the thermal transport in these structures.

In this work, the investigations of the highly porous structures (foams) developed were mainly focused on the thermal aspects and its possible applications in the field of high-temperature insulation. However, the same structures can be exploited for a wider domain of applications, such as related to energy (as porous scaffolds for PCMs), as highly stable filters, as catalyst supports, and as possible bioscaffolds in future (recent studies show that Ca and Mg modifications on SiOC ceramics can provide bioactive nature [316,317]).

List of abbreviation and acronyms used

AHPCS	Allyl-Hydrido Polycarbosilane
BET	Brunauer-Emmett-Teller
CA	Chemical Analysis
CAS	Chemical Abstracts Service
C _{free}	Free carbon
CNF	Carbon-Nano Fiber
CTE	Coefficient of Thermal Expansion
DLC	Diamond-like Carbon
FDTR	Frequency-Domain Thermoreflectance
FT-IR	Fourier Transform Infrared (spectroscopy)
IUPAC	International Union of Pure and Applied Chemistry
LFT	Laser Flash Technique
MEMS	Micro-Electro-Mechanical Systems
MW	Molecular Weight
NMR	Nuclear Magnetic Resonance
NWAGs	Nano Wire Aerogels
PCM	Phase Change Materials
PCS	Polycarbosilane
PDC	Polymer Derived Ceramics
PMMA	Poly Methyl Methacrylate
PP	Polymeric Precursor
PS	Poly-styrene
PU	Polyurethane
RT	Room Temperature
SAXS	Small-angle X-ray Scattering
SEM	Scanning Electron Microscopy
SiC	Silicon Carbide
SiCN	Silicon Carbo-Nitride
SiCN(O)	Silicon Oxy-Carbo Nitride
SiOC	Silicon Oxy-Carbide

TBC	Thermal Barrier Coatings
TDTR	Time-Domain Thermoreflectance
ТЕМ	Transmission Electron Microscopy
TGA	Thermo-Gravimetric Analysis
TPS	Transient Plane source (method)
TSR	Thermal Shock Resistance
XRD	X-ray Diffraction
YSZ	Yttrium Stabilized Zirconia

List of main symbols used

q	Heat or thermal flux
Q	Heat
κ	Thermal diffusivity
λ	Thermal conductivity
Сp	Specific heat capacity
ρ	Density
∇T	Thermal gradient
λ_c	Convective heat transfer
h	Convective heat transfer coefficient
λ_r	Radiative heat transfer
α, τ, ρ	Absorptance, transmittance, and reflectance
Ε	Emissive power
E _b	Emissive power of a perfect black body
σ	Stefan-Boltzmann constant
ε	Emissivity
α_L	Linear thermal expansion coefficient
α_V	Volumetric thermal expansion coefficient
Δ	Change in
Τ	Temperature
σ_{f}	Fracture strength
Ε	Elastic modulus
λ_e	Conductivity contributions from the electrons
λ_p	Conductivity contributions from the phonons
υ	Phonon group velocity
٨	Phonon mean-free path
τ	Phonon relaxation time
λ_E	Effective thermal conductivity

- *θ* Volume fraction
- ρ_t Apparent density
- ρ_b Bulk density
- ρ_s Skeletal density
- Defined as $\sqrt{t\alpha} / r^2$ in transient plane source method
- t Time (s)

References

- [1] A. Bouquillon, History of Ceramics, Ceram. Mater. Process. Prop. Appl. (2010) 29–53. doi:10.1002/9780470612415.ch2.
- R.B. Heimann, R.B.H.M. Maggetti, Ancient and Historical Ceramics, 2014. http://www.schweizerbart.de//publications/detail/isbn/9783510652907 /Heimann_Maggetti_Ancient_and_Historica.
- [3] B. Kingery, H.K. Bowen, Uhlmann, introduction to Ceramics, 1976.
- [4] J.B. Wachtman, R.A. Haber, Ceramic Films and Coatings, Noyes Publications, 1993. https://books.google.it/books?id=ixJUAAAAMAAJ.
- [5] M. Berger, A. Bunsell, Fine Ceramic Fibers, Taylor & Francis, 1999. https://books.google.it/books?id=xH93Gn5plxQC.
- [6] R. Riedel, I.W. Chen, Ceramics Science and Technology, Volume 1: Structures, Wiley, 2008. https://books.google.it/books?id=I-WFvgkBiEMC.
- [7] M. Scheffler, P. Colombo, Cellular Ceramics: Structure, Manufacturing, Properties and Applications, Wiley, 2005. https://books.google.it/books?id=T6tRAAAAMAAJ.
- [8] E. Ionescu, S. Bernard, R. Lucas, P. Kroll, S. Ushakov, A. Navrotsky, R. Riedel, Polymer-Derived Ultra-High Temperature Ceramics (UHTCs) and Related Materials, Adv. Eng. Mater. 1900269 (2019) 1– 24. doi:10.1002/adem.201900269.
- [9] I.M. Low, Y. Sakka, C.F. Hu, MAX Phases and Ultra-High Temperature Ceramics for Extreme Environments, (2013) 1–679. doi:10.4018/978-1-4666-4066-5.
- [10] T.M. Tritt, Thermal Conductivity: Theory, Properties, and Applications, Springer US, 2005. https://books.google.it/books?id=whJNfKmziiIC.
- [11] R.H. Doremus, J.F. Shackelford, R.H. Doremus, Ceramic and glass materials: Structure, properties and processing, (2008).
- [12] J.H.L. IV, And, J.H.L. V, A H e a t T r a n s f e r T extbook, Phlogist. Press. Version 5. (2019). https://ahtt.mit.edu/wpcontent/uploads/2019/08/AHTTv500.pdf.
- [13] W. Callister, Fundamentals of Materials Science and Engineering, (2007) 713–729.
- [14] T.L. Bergman, F.P. Incropera, D.P. DeWitt, A.S. Lavine, Fundamentals of Heat and Mass Transfer, Wiley, 2011. https://books.google.it/books?id=vvyIoXEywMoC.
- [15] Introduction to Engineering Heat Transfer, (n.d.). https://ocw.mit.edu/courses/aeronautics-and-astronautics/16-050thermal-energy-fall-2002/lecture-notes/10_part3.pdf.
- [16] J.B.J. Fourier, The analytical theory of heat, Anal. Theory Heat. (2009) 1–466. doi:10.1017/CBO9780511693205.

- [17] T.N. Narasimhan, Thermal conductivity through the 19th century, Phys. Today. 63 (2010) 36–41. doi:10.1063/1.3480074.
- [18] G. Kaseb, S. & El-Hariry, Electronics Cooling : Basic Heat Transfer, Electron. Cool. (2003) 36–49.
- [19] C. Barry Carter, M. Grant Norton, Ceramic materials: Science and engineering, 2007. doi:10.1007/978-0-387-46271-4.
- [20] A. Fallis, Granta CES 2009 EDUPACK Chap 2, J. Chem. Inf. Model. 53 (2013) 1689–1699. doi:10.1017/CBO9781107415324.004.
- [21] M.F. Ashby, Materials Selection in Mechanical Design, Elsevier Science, 2016. https://books.google.it/books?id=K4h4CgAAQBAJ.
- [22] S. Kasap, R. Svoboda, Springer Handbook of Electronic and Photonic Materials, Springer Handb. Electron. Photonic Mater. (2017) 425–451. doi:10.1007/978-3-319-48933-9.
- [23] G.A. Slack, Nonmetallic crystals with high thermal conductivity, J. Phys. Chem. Solids. 34 (1973) 321–335. doi:https://doi.org/10.1016/0022-3697(73)90092-9.
- [24] A.A. Balandin, Thermal properties of graphene and nanostructured carbon materials, Nat. Mater. 10 (2011) 569–581. doi:10.1038/nmat3064.
- [25] Z.G. Chen, G. Hana, L. Yanga, L. Cheng, J. Zou, Nanostructured thermoelectric materials: Current research and future challenge, Prog. Nat. Sci. Mater. Int. 22 (2012) 535–549. doi:10.1016/j.pnsc.2012.11.011.
- [26] M. Asheghi, K. Kurabayashi, R. Kasnavi, K.E. Goodson, Thermal conduction in doped single-crystal silicon films, J. Appl. Phys. 91 (2002) 5079–5088. doi:10.1063/1.1458057.
- [27] R.E. Peierls, Quantum Theory of Solids, Clarendon Press, 1996. https://books.google.it/books?id=xCWQDwAAQBAJ.
- [28] Z. Ding, J. Zhou, B. Song, M. Li, T.H. Liu, G. Chen, Umklapp scattering is not necessarily resistive, Phys. Rev. B. 98 (2018) 1–6. doi:10.1103/PhysRevB.98.180302.
- [29] G. Amirthan, A. Udaya Kumar, M. Balasubramanian, Thermal conductivity studies on Si/SiC ceramic composites, Ceram. Int. 37 (2011) 423–426. doi:10.1016/j.ceramint.2010.09.003.
- [30] C. Kittel, Interpretation of the Thermal Conductivity of Glasses, Phys. Rev. 75 (1949) 972–974. doi:10.1103/PhysRev.75.972.
- [31] S. Kirkpatrick, Percolation and Conduction, Rev. Mod. Phys. 45 (1973) 574–588. doi:10.1103/RevModPhys.45.574.
- [32] M.C. Wingert, J. Zheng, S. Kwon, R. Chen, Thermal transport in amorphous materials: a review, Semicond. Sci. Technol. 31 (2016) 113003. doi:10.1088/0268-1242/31/11/113003.
- [33] D.B. Sirdeshmukh, L. Sirdeshmukh, K.G. Subhadra, Atomistic properties of solids, Springer Science & Business Media, 2011.
- [34] R.C. Zeller, R.O. Pohl, Thermal Conductivity and Specific Heat of Noncrystalline Solids, Phys. Rev. B. 4 (1971) 2029–2041.

doi:10.1103/PhysRevB.4.2029.

- [35] S. Alexander, C. Laermans, R. Orbach, H.M. Rosenberg, Fracton interpretation of vibrational properties of cross-linked polymers, glasses, and irradiated quartz, Phys. Rev. B. 28 (1983) 4615–4619. doi:10.1103/PhysRevB.28.4615.
- [36] J.K. Carson, S.J. Lovatt, D.J. Tanner, A.C. Cleland, Thermal conductivity bounds for isotropic, porous materials, Int. J. Heat Mass Transf. 48 (2005) 2150–2158. doi:10.1016/j.ijheatmasstransfer.2004.12.032.
- [37] Z. Hashin, S. Shtrikman, A variational approach to the theory of the effective magnetic permeability of multiphase materials, J. Appl. Phys. 33 (1962) 3125–3131.
- [38] S.L. Shinde, J. Goela, High Thermal Conductivity Materials, Springer, 2006. https://books.google.it/books?id=DPlqgGwTkcoC.
- [39] S. Caniglia, G.L. Barna, Handbook of Industrial Refractories Technology: Principles, Types, Properties and Applications, Elsevier Science, 1992. https://books.google.it/books?id=q-xxBAAAQBAJ.
- [40] R.C. Buchanan, Ceramic Materials for Electronics, Third Edition, Taylor & Francis, 2004. https://books.google.it/books?id=bLRf2l9itqsC.
- [41] W.G. Fahrenholtz, E.J. Wuchina, W.E. Lee, Y. Zhou, Ultra-High Temperature Ceramics: Materials for Extreme Environment Applications, Wiley, 2014. https://books.google.it/books?id=zF_KBAAAQBAJ.
- [42] Z. Li, R.C. Bradt, Thermal expansion of the cubic (3C) polytype of SiC, J. Mater. Sci. 21 (1986) 4366–4368. doi:10.1007/BF01106557.
- [43] H.O. Pierson, Handbook of Carbon, Graphite, Diamonds and Fullerenes, Handb. Carbon, Graph. Diamonds Fullerenes. (1993) 43– 69. doi:10.1016/B978-0-8155-1339-1.50008-6.
- [44] C.E. Weaver, Thermal properties of clays and shales, United States, 1976. http://inis.iaea.org/search/search.aspx?orig_g=RN:08322713.
- [45] J.F. Shackelford, Y.-H. Han, S. Kim, S.-H. Kwon, CRC Materials Science and Engineering Handbook, 2016. doi:10.1201/b18971.
- [46] J. Robertson, Advances in Physics Amorphous carbon, Adv. Phys. 35 (1986) 37–41. doi:10.1080/00018738600101911.
- [47] R. Taylor, The thermal conductivity of pyrolytic graphite, Philos. Mag. 13 (1966) 157–166. doi:10.1080/14786436608211993.
- [48] D.C. GINNINGS, R.J. CORRUCCINI, Enthalpy, specific heat, and entropy of aluminum oxide from 0 degrees to 900 degrees C., J. Res. Natl. Bur. Stand. (1934). 38 (1947) 593–600. doi:10.6028/jres.038.039.
- [49] J. Robertson, Properties of diamond-like carbon, Surf. Coatings Technol. 50 (1992) 185–203. doi:10.1016/0257-8972(92)90001-Q.
- [50] T. Olorunyolemi, A. Birnboim, Y. Carmel, O.C. Wilson, I.K. Lloyd, S. Smith, R. Campbell, Thermal Conductivity of Zinc Oxide: From Green to Sintered State, J. Am. Ceram. Soc. 85 (2004) 1249–1253.

doi:10.1111/j.1151-2916.2002.tb00253.x.

- [51] C.Y. Ho, R.W. Powell, P.E. Liley, Thermal Conductivity of Selected Materials, Part 2, Nsrds-Nbs 16. (1968) 168.
- [52] J.P. HOWE, Properties of Graphite, J. Am. Ceram. Soc. 35 (1952) 275–283. doi:10.1111/j.1151-2916.1952.tb13048.x.
- [53] G.A. Slack, Anisotropic thermal conductivity of pyrolytic graphite, Phys. Rev. 127 (1962) 694–701. doi:10.1103/PhysRev.127.694.
- [54] R.G. Munro, Material properties of a sintered α-SiC, J. Phys. Chem. Ref. Data. 26 (1997) 1195–1203. doi:10.1063/1.556000.
- [55] A.I. of Physics, D.E. Gray, A.A. Bennett, American Institute of Physics Handbook, McGraw-Hill, 1957. https://books.google.it/books?id=ymsGAQAAIAAJ.
- [56] K.J. Kim, K.Y. Lim, Y.W. Kim, Electrical and thermal properties of SiC ceramics sintered with yttria and nitrides, J. Am. Ceram. Soc. 97 (2014) 2943–2949. doi:10.1111/jace.13031.
- [57] D. Zhao, X. Qian, X. Gu, S.A. Jajja, R. Yang, Measurement techniques for thermal conductivity and interfacial thermal conductance of bulk and thin film materials, J. Electron. Packag. Trans. ASME. 138 (2016) 1–64. doi:10.1115/1.4034605.
- [58] N.Y.E.-A.A.E.-A. Almssad, The Review of Some Commonly Used Methods and Techniques to Measure the Thermal Conductivity of Insulation Materials, in: IntechOpen, Rijeka, 2016: p. Ch. 6. doi:10.5772/64157.
- [59] L. Borchardt, C. Hoffmann, M. Oschatz, L. Mammitzsch, U. Petasch, M. Herrmann, S. Kaskel, Preparation and application of cellular and nanoporous carbides, Chem. Soc. Rev. 41 (2012) 5053–5067. doi:10.1039/c2cs15324f.
- [60] A. Kelly, Why engineer porous materials?, Philos. Trans. R. Soc. A Math. Phys. Eng. Sci. 364 (2006) 5–14. doi:10.1098/rsta.2005.1686.
- [61] T. Ohji, Porous Ceramic Materials, Second Edi, Elsevier, 2013. doi:10.1016/B978-0-12-385469-8.00059-9.
- [62] A. Pokhrel, D.N. Seo, S.T. Lee, I.J. Kim, Processing of porous ceramics by direct foaming: A review, J. Korean Ceram. Soc. 50 (2013) 93–102. doi:10.4191/kcers.2013.50.2.093.
- [63] U.M.B. Al-Naib, Recent Advances in Porous Ceramics, IntechOpen, 2018. https://books.google.it/books?id=FReQDwAAQBAJ.
- [64] J.H. Eom, Y.W. Kim, S. Raju, Processing and properties of macroporous silicon carbide ceramics: A review, J. Asian Ceram. Soc. 1 (2013) 220–242. doi:10.1016/j.jascer.2013.07.003.
- [65] T. Fey, U. Betke, S. Rannabauer, M. Scheffler, Reticulated Replica Ceramic Foams: Processing, Functionalization, and Characterization, Adv. Eng. Mater. 19 (2017) 1–15. doi:10.1002/adem.201700369.
- [66] E.C. Hammel, O.L.R. Ighodaro, O.I. Okoli, Processing and properties of advanced porous ceramics: An application based review, Ceram. Int. 40 (2014) 15351–15370. doi:10.1016/j.ceramint.2014.06.095.

- [67] L.C. Hwa, S. Rajoo, A.M. Noor, N. Ahmad, M.B. Uday, Recent advances in 3D printing of porous ceramics: A review, Curr. Opin. Solid State Mater. Sci. 21 (2017) 323–347. doi:10.1016/j.cossms.2017.08.002.
- [68] R. Narayan, P. Colombo, S. Widjaja, D. Singh, Advances in Bioceramics and Porous Ceramics IV, Wiley, 2011. https://books.google.it/books?id=nlQF2AvJTEYC.
- [69] A.R. Studart, U.T. Gonzenbach, E. Tervoort, L.J. Gauckler, Processing routes to macroporous ceramics: A review, J. Am. Ceram. Soc. 89 (2006) 1771–1789. doi:10.1111/j.1551-2916.2006.01044.x.
- [70] T. Ohji, M. Fukushima, Macro-porous ceramics: Processing and properties, Int. Mater. Rev. 57 (2012) 115–131. doi:10.1179/1743280411Y.000000006.
- [71] K. Prabhakaran, N.M. Gokhale, S.C. Sharma, R. Lal, A novel process for low-density alumina foams, J. Am. Ceram. Soc. 88 (2005) 2600– 2603. doi:10.1111/j.1551-2916.2005.00446.x.
- [72] G. Zu, J. Shen, X. Wei, X. Ni, Z. Zhang, J. Wang, G. Liu, Preparation and characterization of monolithic alumina aerogels, J. Non. Cryst. Solids. 357 (2011) 2903–2906. doi:10.1016/j.jnoncrysol.2011.03.031.
- [73] Q. Yue, Y. Li, M. Kong, J. Huang, X. Zhao, J. Liu, R.E. Williford, Ultralow density, hollow silica foams produced through interfacial reaction and their exceptional properties for environmental and energy applications, J. Mater. Chem. 21 (2011) 12041–12046. doi:10.1039/c1jm12040a.
- [74] J.L. Gurav, I.K. Jung, H.H. Park, E.S. Kang, D.Y. Nadargi, Silica aerogel: Synthesis and applications, J. Nanomater. 2010 (2010). doi:10.1155/2010/409310.
- [75] W.L. Huo, X.Y. Zhang, Y.G. Chen, Y.J. Lu, W.T. Liu, X.Q. Xi, Y.L. Wang, J. Xu, J.L. Yang, Highly Porous Zirconia Ceramic Foams with Low Thermal Conductivity from Particle-Stabilized Foams, J. Am. Ceram. Soc. 99 (2016) 3512–3515. doi:10.1111/jace.14555.
- [76] Y. Dong, C.A. Wang, J. Zhou, Z. Hong, A novel way to fabricate highly porous fibrous YSZ ceramics with improved thermal and mechanical properties, J. Eur. Ceram. Soc. 32 (2012) 2213–2218. doi:10.1016/j.jeurceramsoc.2012.03.016.
- [77] W. Lei, D. Portehault, D. Liu, S. Qin, Y. Chen, Porous boron nitride nanosheets for effective water cleaning, Nat. Commun. 4 (2013) 1777. doi:10.1038/ncomms2818.
- [78] W. Lei, V.N. Mochalin, D. Liu, S. Qin, Y. Gogotsi, Y. Chen, Boron nitride colloidal solutions, ultralight aerogels and freestanding membranes through one-step exfoliation and functionalization, Nat. Commun. 6 (2015) 1–8. doi:10.1038/ncomms9849.
- [79] S.R. Kadam, U. V. Kawade, R. Bar-Ziv, S.W. Gosavi, M. Bar-Sadan, B.B. Kale, Porous MoS2 Framework and Its Functionality for Electrochemical Hydrogen Evolution Reaction and Lithium Ion Batteries, ACS Appl. Energy Mater. 2 (2019) 5900–5908. doi:10.1021/acsaem.9b01045.

- [80] D. Yao, Y. Xia, Y.P. Zeng, K.H. Zuo, D. Jiang, Fabrication porous Si 3N 4 ceramics via starch consolidation-freeze drying process, Mater. Lett. 68 (2012) 75–77. doi:10.1016/j.matlet.2011.09.092.
- [81] H.L. Hu, Y.P. Zeng, Y.F. Xia, D.X. Yao, K.H. Zuo, High-strength porous Si3N4 ceramics prepared by freeze casting and silicon powder nitridation process, Mater. Lett. 133 (2014) 285–288. doi:10.1016/j.matlet.2014.06.176.
- [82] E.G. de Moraes, D. Li, P. Colombo, Z. Shen, Silicon nitride foams from emulsions sintered by rapid intense thermal radiation, J. Eur. Ceram. Soc. 35 (2015) 3263–3272. doi:10.1016/j.jeurceramsoc.2015.02.007.
- [83] Z. Du, D. Yao, Y. Xia, K. Zuo, J. Yin, H. Liang, Y.P. Zeng, The high porosity silicon nitride foams prepared by the direct foaming method, Ceram. Int. 45 (2019) 2124–2130. doi:10.1016/j.ceramint.2018.10.118.
- [84] K. Bodišová, M. Kašiarová, M. Domanická, M. Hnatko, Z. Lenčéš, Z.V. Nováková, J. Vojtaššák, S. Gromošová, P. Šajgalík, Porous silicon nitride ceramics designed for bone substitute applications, Ceram. Int. 39 (2013) 8355–8362. doi:10.1016/j.ceramint.2013.04.015.
- [85] M. Inagaki, J. Qiu, Q. Guo, Carbon foam: Preparation and application, Carbon N. Y. 87 (2015) 128–152. doi:10.1016/j.carbon.2015.02.021.
- [86] N.C. Gallego, J.W. Klett, Carbon foams for thermal management, Carbon N. Y. 41 (2003) 1461–1466. doi:10.1016/S0008-6223(03)00091-5.
- [87] J. Feng, J. Feng, Y. Jiang, C. Zhang, Ultralow density carbon aerogels with low thermal conductivity up to 2000 °C, Mater. Lett. 65 (2011) 3454–3456. doi:10.1016/j.matlet.2011.07.114.
- [88] L.J. Gibson, M.F. Ashby, Cellular Solids: Structure and Properties, 2nd ed., Cambridge University Press, Cambridge, 1997. doi:DOI: 10.1017/CBO9781139878326.
- [89] V.R. Vedula, D.J. Green, J.R. Hellman, Thermal Shock Resistance of Ceramic Foams, J. Am. Ceram. Soc. 82 (2004) 649–656. doi:10.1111/j.1151-2916.1999.tb01813.x.
- [90] J. Zeschky, F. Goetz-Neunhoeffer, J. Neubauer, S.H.J. Lo, B. Kummer, M. Scheffler, P. Greil, Preceramic polymer derived cellular ceramics, Compos. Sci. Technol. 63 (2003) 2361–2370. doi:10.1016/S0266-3538(03)00269-0.
- [91] C. Vakifahmetoglu, D. Zeydanli, P. Colombo, Porous polymer derived ceramics, Mater. Sci. Eng. R Reports. 106 (2016) 1–30. doi:10.1016/j.mser.2016.05.001.
- [92] P. Colombo, Engineering porosity in polymer-derived ceramics, J. Eur. Ceram. Soc. 28 (2008) 1389–1395. doi:10.1016/j.jeurceramsoc.2007.12.002.
- [93] T.A.S. Zak C. Eckel, Chaoyin Zhou, John H. Martin, Alan J. Jacobsen, William B. Carter, Additive manufacturing of polymerderived ceramics, Science (80-.). 351 (2016) 3–8.

- [94] G. Mera, E. Ionescu, Polymer-Derived Ceramics, Encycl. Inorg. Bioinorg. Chem. (2019) 1–26. doi:10.1002/9781119951438.eibc2705.
- [95] P. Colombo, G. Mera, R. Riedel, G.D. Soraru, Polymer-derived ceramics: 40 years of research and innovation in advanced ceramics, J. Am. Ceram. Soc. 93 (2010) 1805–1837.
- [96] P. Colombo, Polymer Derived Ceramics: From Nano-structure to Applications, DEStech Publications, 2010. https://books.google.it/books?id=k1uQFNpmwZQC.
- [97] M. Weinmann, E. Ionescu, R. Riedel, F. Aldinger, Precursor-Derived Ceramics, Second Edi, Elsevier, 2013. doi:10.1016/B978-0-12-385469-8.00056-3.
- [98] A. Viard, D. Fonblanc, D. Lopez-Ferber, M. Schmidt, A. Lale, C. Durif, M. Balestrat, F. Rossignol, M. Weinmann, R. Riedel, S. Bernard, Polymer Derived Si–B–C–N Ceramics: 30 Years of Research, Adv. Eng. Mater. 20 (2018) 1–31. doi:10.1002/adem.201800360.
- [99] R. Riedel, G. Mera, R. Hauser, A. Klonczynski, Silicon-Based Polymer-Derived Ceramics Synthesis, J. Ceram. Soc. Japan. 444 (2006) 33–38.
- [100] R. Riedel, G. Mera, R. Hauser, A. Klonczynski, Silicon-based polymer-derived ceramics: Synthesis properties and applications-A review, J. Ceram. Soc. Japan. 114 (2006) 425–444. doi:10.2109/jcersj.114.425.
- [101] X. Wang, F. Schmidt, D. Hanaor, P.H. Kamm, S. Li, A. Gurlo, Additive manufacturing of ceramics from preceramic polymers: A versatile stereolithographic approach assisted by thiol-ene click chemistry, Addit. Manuf. 27 (2019) 80–90. doi:10.1016/j.addma.2019.02.012.
- [102] M. Schulz, Polymer derived ceramics in MEMS/NEMS a review on production processes and application, Adv. Appl. Ceram. 108 (2009) 454–460. doi:10.1179/174367609X422171.
- [103] S. YAJIMA, J. HAYASHI, M. OMORI, K. OKAMURA, Development of a silicon carbide fibre with high tensile strength, Nature. 261 (1976) 683–685. doi:10.1038/261683a0.
- [104] G. Mera, M. Gallei, S. Bernard, E. Ionescu, Ceramic nanocomposites from tailor-made preceramic polymers, Nanomaterials. 5 (2015) 468– 540. doi:10.3390/nano5020468.
- [105] C.R. Krüger, E.G. Rochow, Polyorganosilazanes, J. Polym. Sci. Part A Gen. Pap. 2 (1964) 3179–3189. doi:10.1002/pol.1964.100020717.
- [106] C.R. Krüger, E.G. Rochow, Polymerisation of Cyclosilazanes, Angew. Chemie Int. Ed. English. 1 (1962) 458. doi:10.1002/anie.196204582.
- [107] R. Riedel, A. Greiner, G. Miehe, W. Dressler, H. Fuess, J. Bill, F. Aldinger, The First Crystalline Solids in the Ternary Si-C-N System, Angew. Chemie (International Ed. English). 36 (1997) 603–606. doi:10.1002/anie.199706031.
- [108] A.O. Gabriel, R. Riedel, S. Storck, W.F. Maier, Synthesis and

Thermally Induced Ceramization of a Non-oxidic Poly(methylsilsesquicarbodiimide) Gel, Appl. Organomet. Chem. 11 (1997) 833–841. doi:10.1002/(SICI)1099-0739(199710/11)11:10/11<833::AID-AOC643>3.0.CO;2-S.

- [109] J. Bill, T.W. Kamphowe, A. Müller, T. Wichmann, A. Zern, A. Jalowieki, J. Mayer, M. Weinmann, J. Schuhmacher, K. Müller, J. Peng, H.J. Seifert, F. Aldinger, Precursor-derived Si-(B-)C-N ceramics: Thermolysis, amorphous state and crystallization, Appl. Organomet. Chem. 15 (2001) 777–793. doi:10.1002/aoc.242.
- [110] G.D. Sorarù, M. Mercadini, R.D. Maschio, F. Taulelle, F. Babonneau, Si-Al-O-N Fibers from Polymeric Precursor: Synthesis, Structural, and Mechanical Characterization, J. Am. Ceram. Soc. 76 (1993) 2595–2600. doi:10.1111/j.1151-2916.1993.tb03986.x.
- [111] G. Parcianello, E. Bernardo, P. Colombo, Z. Lenčéš, M. Vetrecín, P. Šajgalík, M. Kašiarová, Preceramic polymer-derived SiAION as sintering aid for silicon nitride, J. Am. Ceram. Soc. 97 (2014) 3407– 3412. doi:10.1111/jace.13134.
- [112] B. Tang, Y. Zhang, S. Hu, B. Feng, A dense amorphous SiBCN(O) ceramic prepared by simultaneous pyrolysis of organics and inorganics, Ceram. Int. 42 (2016) 5238–5244. doi:10.1016/j.ceramint.2015.12.050.
- [113] Y. Wang, Y. Fan, L. Zhang, W. Zhang, L. An, Polymer-derived SiAICN ceramics resist oxidation at 1400 °C, Scr. Mater. 55 (2006) 295–297. doi:10.1016/j.scriptamat.2006.05.004.
- [114] C. Zhou, A. Ott, R. Ishikawa, Y. Ikuhara, R. Riedel, E. Ionescu, Single-source-precursor synthesis and high-temperature evolution of novel mesoporous SiVN(O)-based ceramic nanocomposites, J. Eur. Ceram. Soc. (2019) 0–1. doi:10.1016/j.jeurceramsoc.2019.11.021.
- [115] R.J.C. Dubey, P.V.W. Sasikumar, F. Krumeich, G. Blugan, J. Kuebler, K. V. Kravchyk, T. Graule, M. V. Kovalenko, Silicon Oxycarbide—Tin Nanocomposite as a High-Power-Density Anode for Li-Ion Batteries, Adv. Sci. 6 (2019). doi:10.1002/advs.201901220.
- [116] P. Taheri, A. Bokka, P. Asgari, J. Jeon, J.C. Lang, R. Campostrini, G.D. Sorarù, P. Kroll, Novel Sulfur-Containing Cross-Linking Agent for Si-Based Preceramic Polymers, Macromol. Chem. Phys. 3 (2019) 1–9. doi:10.1002/macp.201900380.
- [117] P. Greil, Polymer Derived Engineering Ceramics, Adv. Eng. Mater. 2 (2000) 339–348. doi:10.1002/1527-2648(200006)2:6<339::AID-ADEM339>3.0.CO;2-K.
- [118] M. Esfehanian, R. Oberacker, T. Fett, M.J. Hoffmann, Development of Dense filler-free polymer-derived SiOC ceramics by field-assisted sintering, J. Am. Ceram. Soc. 91 (2008) 3803–3805. doi:10.1111/j.1551-2916.2008.02730.x.
- [119] E. Bernardo, I. Ponsot, P. Colombo, S. Grasso, H. Porwal, M.J. Reece, Polymer-derived SiC ceramics from polycarbosilane/boron mixtures densified by SPS, Ceram. Int. 40 (2014) 14493–14500. doi:10.1016/j.ceramint.2014.07.008.
- [120] G.A. Danko, R. Silberglitt, P. Colombo, E. Pippel, J. Woltersdorf,

Comparison of Microwave Hybrid and Conventional Heating of Preceramic Polymers to Form Silicon Carbide and Silicon Oxycarbide Ceramics, J. Am. Ceram. Soc. 83 (2004) 1617–1625. doi:10.1111/j.1151-2916.2000.tb01440.x.

- [121] M.A. Mazo, C. Palencia, A. Nistal, F. Rubio, J. Rubio, J.L. Oteo, Dense bulk silicon oxycarbide glasses obtained by spark plasma sintering, J. Eur. Ceram. Soc. 32 (2012) 3369–3378. doi:10.1016/j.jeurceramsoc.2012.03.033.
- [122] R. Ma, D. Erb, K. Lu, Flash pyrolysis of polymer-derived SiOC ceramics, J. Eur. Ceram. Soc. 38 (2018) 4906–4914. doi:10.1016/j.jeurceramsoc.2018.07.010.
- [123] G.D. Soraru, F. Babonneau, J.D. Mackenzie, Structural evolutions from polycarbosilane to SiC ceramic, J. Mater. Sci. 25 (1990) 3886– 3893. doi:10.1007/BF00582455.
- [124] G.D. Soraru, F. Babonneau, J.D. Mackenzie, Structural concepts on new amorphous covalent solids, J. Non. Cryst. Solids. 106 (1988) 256–261.
- [125] G. Barroso, Q. Li, R.K. Bordia, G. Motz, Polymeric and ceramic silicon-based coatings-a review, J. Mater. Chem. A. 7 (2019) 1936– 1963. doi:10.1039/c8ta09054h.
- [126] C.L. Schilling, J.P. Wesson, T.C. Williams, Polycarbosilane Precursors for Silicon Carbide., J. Polym. Sci. Polym. Symp. 128 (1983) 121–128. doi:10.1002/polc.5070700110.
- [127] H.P. Martin, R. Ecke, E. Müller, Synthesis of nanocrystalline silicon carbide powder by carbothermal reduction, J. Eur. Ceram. Soc. 18 (1998) 1737–1742. doi:10.1016/s0955-2219(98)00094-6.
- [128] C. Vix-Guterl, P. Ehrburger, Effect of the properties of a carbon substrate on its reaction with silica for silicon carbide formation, Carbon N. Y. 35 (1997) 1587–1592. doi:10.1016/S0008-6223(97)00117-6.
- [129] D.H. Filsinger, D.B. Bourrie, Silica to Silicon: Key Carbothermic Reactions and Kinetics, J. Am. Ceram. Soc. 73 (1990) 1726–1732. doi:10.1111/j.1151-2916.1990.tb09820.x.
- [130] J.J. Biernacki, G.P. Wotzak, Stoichiometry of the C+ SiO2 reaction, J. Am. Ceram. Soc. 72 (1989) 122–129.
- [131] A. Saha, R. Raj, D.L. Williamson, A model for the nanodomains in polymer-derived SiCO, J. Am. Ceram. Soc. 89 (2006) 2188–2195. doi:10.1111/j.1551-2916.2006.00920.x.
- [132] S.J. Widgeon, S. Sen, G. Mera, E. Ionescu, R. Riedel, A. Navrotsky, 29Si and 13C Solid-state NMR spectroscopic study of nanometerscale structure and mass fractal characteristics of amorphous polymer derived silicon oxycarbide ceramics, Chem. Mater. 22 (2010) 6221–6228. doi:10.1021/cm1021432.
- [133] V. Belot, R.J.P. Corriu, D. Leclercq, P.H. Mutin, A. Vioux, Thermal redistribution reactions in crosslinked polysiloxanes, J. Polym. Sci. Part A Polym. Chem. 30 (1992) 613–623. doi:10.1002/pola.1992.080300413.

- [134] C.G. Pantano, A.K. Singh, H. Zhang, Silicon oxycarbide glasses, J. Sol-Gel Sci. Technol. 14 (1999) 7–25. doi:10.1023/A:1008765829012.
- [135] R. Raj, L. Pederiva, M. Narisawa, G.D. Soraru, On the onset of fracture as a silicon-based polymer converts into the ceramic phase, J. Am. Ceram. Soc. 102 (2019) 924–929. doi:10.1111/jace.16089.
- [136] M. Graczyk-Zajac, D. Vrankovic, P. Waleska, C. Hess, P.V. Sasikumar, S. Lauterbach, H.J. Kleebe, G.D. Sorarù, The Li-storage capacity of SiOC glasses with and without mixed silicon oxycarbide bonds, J. Mater. Chem. A. 6 (2017) 93–103. doi:10.1039/c7ta09236a.
- [137] A. Saha, R. Raj, Crystallization maps for SiCO amorphous ceramics, J. Am. Ceram. Soc. 90 (2007) 578–583. doi:10.1111/j.1551-2916.2006.01423.x.
- [138] C. Turquat, H.-J. Kleebe, G. Gregori, S. Walter, G.D. Sorarù, Transmission Electron Microscopy and Electron Energy-Loss Spectroscopy Study of Nonstoichiometric Silicon-Carbon-Oxygen Glasses, J. Am. Ceram. Soc. 84 (2001) 2189–2196. doi:10.1111/j.1151-2916.2001.tb00986.x.
- [139] J. Bill, J. Seitz, G. Thurn, J. Dürr, J. Canel, B.Z. Janos, A. Jalowiecki, D. Sauter, S. Schempp, H.P. Lamparter, J. Mayer, F. Aldinger, Structure analysis and properties of Si-C-N ceramics derived from polysilazanes, Phys. Status Solidi Appl. Res. 166 (1998) 269–296. doi:10.1002/(SICI)1521-396X(199803)166:1<269::AID-PSSA269>3.0.CO;2-7.
- [140] G. Mera, A. Navrotsky, S. Sen, H.J. Kleebe, R. Riedel, Polymerderived SiCN and SiOC ceramics-structure and energetics at the nanoscale, J. Mater. Chem. A. 1 (2013) 3826–3836. doi:10.1039/c2ta00727d.
- [141] G. Mera, A. Tamayo, H. Nguyen, S. Sen, R. Riedel, Nanodomain structure of carbon-rich silicon carbonitride polymer-derived ceramics, J. Am. Ceram. Soc. 93 (2010) 1169–1175. doi:10.1111/j.1551-2916.2009.03558.x.
- [142] G. Mera, R. Ishikawa, E. Ionescu, Y. Ikuhara, R. Riedel, Atomic-scale assessment of the crystallization onset in silicon carbonitride, J. Eur. Ceram. Soc. 35 (2015) 3355–3362. doi:10.1016/j.jeurceramsoc.2015.01.008.
- [143] C. Stabler, E. Ionescu, M. Graczyk-Zajac, I. Gonzalo-Juan, R. Riedel, Silicon oxycarbide glasses and glass-ceramics: "All-Rounder" materials for advanced structural and functional applications, J. Am. Ceram. Soc. 101 (2018) 4817–4856. doi:10.1111/jace.15932.
- [144] K. Lu, Porous and high surface area silicon oxycarbide-based materials - A review, Mater. Sci. Eng. R Reports. 97 (2015) 23–49. doi:10.1016/j.mser.2015.09.001.
- [145] R. Riedel, M. Seher, J. Mayer, D.V. Szabó, Polymer-derived Sibased bulk ceramics, part I: Preparation, processing and properties, J. Eur. Ceram. Soc. 15 (1995) 703–715. doi:10.1016/0955-2219(95)00041-R.

- [146] O. Flores, R.K. Bordia, D. Nestler, W. Krenkel, G. Motz, Ceramic fibers based on SiC and SiCN systems: Current research, development, and commercial status, Adv. Eng. Mater. 16 (2014) 621–636. doi:10.1002/adem.201400069.
- [147] M. Arango-Ospina, F. Xie, I. Gonzalo-Juan, R. Riedel, E. Ionescu, A.R. Boccaccini, Review: Silicon oxycarbide based materials for biomedical applications, Appl. Mater. Today. (2019) 100482. doi:10.1016/j.apmt.2019.100482.
- [148] A. Lale, M. Schmidt, M.D. Mallmann, A.V.A. Bezerra, E.D. Acosta, R.A.F. Machado, U.B. Demirci, S. Bernard, Polymer-Derived Ceramics with engineered mesoporosity: From design to application in catalysis, Surf. Coatings Technol. 350 (2018) 569–586. doi:10.1016/j.surfcoat.2018.07.061.
- [149] E. Bernardo, L. Fiocco, G. Parcianello, E. Storti, P. Colombo, Advanced ceramics from preceramic polymers modified at the nanoscale: A review, Materials (Basel). 7 (2014) 1927–1956. doi:10.3390/ma7031927.
- [150] E. Ionescu, H.-J. Kleebe, R. Riedel, Silicon-containing polymerderived ceramic nanocomposites (PDC-NCs): preparative approaches and properties, Chem. Soc. Rev. 41 (2012) 5032–5052. doi:10.1039/C2CS15319J.
- [151] W. Duan, X. Yin, Q. Li, L. Schlier, P. Greil, N. Travitzky, A review of absorption properties in silicon-based polymer derived ceramics, J. Eur. Ceram. Soc. 36 (2016) 3681–3689. doi:10.1016/j.jeurceramsoc.2016.02.002.
- [152] K. Lu, D. Erb, Polymer derived silicon oxycarbide-based coatings, Int. Mater. Rev. 63 (2018) 139–161. doi:10.1080/09506608.2017.1322247.
- [153] P. Colombo, J.R. Hellmann, Ceramic foams from preceramic polymers, Mater. Res. Innov. 6 (2002) 260–272. doi:10.1007/s10019-002-0209-z.
- [154] E. Ionescu, R. Riedel, Polymer Processing of Ceramics, Ceram. Compos. Process. Methods. (2012) 235–270. doi:10.1002/9781118176665.ch7.
- [155] P. Jana, E. Zera, G.D. Sorarù, Processing of preceramic polymer to low density silicon carbide foam, Mater. Des. 116 (2017) 278–286. doi:10.1016/j.matdes.2016.12.010.
- [156] L.A. Liew, V.M. Bright, R. Raj, A novel micro glow plug fabricated from polymer-derived ceramics: In situ measurement of hightemperature properties and application to ultrahigh-temperature ignition, Sensors Actuators, A Phys. 104 (2003) 246–262. doi:10.1016/S0924-4247(03)00027-X.
- [157] G.S. Barroso, W. Krenkel, G. Motz, Low thermal conductivity coating system for application up to 1000°C by simple PDC processing with active and passive fillers, J. Eur. Ceram. Soc. 35 (2015) 3339–3348. doi:10.1016/j.jeurceramsoc.2015.02.006.
- [158] K. Lu, D. Erb, M. Liu, Thermal stability and electrical conductivity of carbon-enriched silicon oxycarbide, J. Mater. Chem. C. 4 (2016)

1829-1837. doi:10.1039/c6tc00069j.

- [159] D. Zeydanli, S. Akman, C. Vakifahmetoglu, Polymer-derived ceramic adsorbent for pollutant removal from water, J. Am. Ceram. Soc. 101 (2018) 2258–2265. doi:10.1111/jace.15423.
- [160] M. Hojamberdiev, R.M. Prasad, K. Morita, M.A. Schiavon, R. Riedel, Polymer-derived mesoporous SiOC/ZnO nanocomposite for the purification of water contaminated with organic dyes, Microporous Mesoporous Mater. 151 (2012) 330–338. doi:10.1016/j.micromeso.2011.10.015.
- [161] C. Vakifahmetoglu, D. Zeydanli, V.C. Ozalp, B.A. Borsa, G.D. Soraru, Hierarchically porous polymer derived ceramics: A promising platform for multidrug delivery systems, Mater. Des. 140 (2018) 37–44. doi:10.1016/j.matdes.2017.11.047.
- [162] Z. Yu, P. Zhang, Y. Feng, S. Li, Y. Pei, R. Riedel, Template-Free Synthesis of Porous Fe3O4/SiOC(H) Nanocomposites with Enhanced Catalytic Activity, J. Am. Ceram. Soc. 99 (2016) 2615– 2624. doi:10.1111/jace.14305.
- [163] G. Glatz, T. Schmalz, T. Kraus, F. Haarmann, G. Motz, R. Kempe, Copper-containing SiCN precursor ceramics (Cu@SiCN) as selective hydrocarbon oxidation catalysts using air as an oxidant, Chem. - A Eur. J. 16 (2010) 4231–4238. doi:10.1002/chem.200902836.
- [164] F. Dalcanale, J. Grossenbacher, G. Blugan, M.R. Gullo, A. Lauria, J. Brugger, H. Tevaearai, T. Graule, M. Niederberger, J. Kuebler, Influence of carbon enrichment on electrical conductivity and processing of polycarbosilane derived ceramic for MEMS applications, J. Eur. Ceram. Soc. 34 (2014) 3559–3570. doi:10.1016/j.jeurceramsoc.2014.06.002.
- [165] F. Scientific, T. Report, A Novel Polymer-Derived-nanoCeramic for Ultrahigh Temperature MEMS Micro-igniter / Sensor Final Scientific and Technical Report, (2008).
- [166] G.D. Sorarù, G. Kacha, R. Campostrini, A. Ponzoni, M. Donarelli, A. Kumar, G. Mariotto, The effect of B-doping on the electrical conductivity of polymer-derived Si(B)OC ceramics, J. Am. Ceram. Soc. 100 (2017) 4611–4621. doi:10.1111/jace.14986.
- [167] R. Riedel, L. Toma, E. Janssen, J. Nuffer, T. Melz, H. Hanselka, Piezoresistive effect in SiOC ceramics for integrated pressure sensors, J. Am. Ceram. Soc. 93 (2010) 920–924. doi:10.1111/j.1551-2916.2009.03496.x.
- [168] L. Zhang, Y. Wang, Y. Wei, W. Xu, D. Fang, L. Zhai, K.C. Lin, L. An, A silicon carbonitride ceramic with anomalously high piezoresistivity, J. Am. Ceram. Soc. 91 (2008) 1346–1349. doi:10.1111/j.1551-2916.2008.02275.x.
- [169] K. Terauds, P.E. Sanchez-Jimenez, R. Raj, C. Vakifahmetoglu, P. Colombo, Giant piezoresistivity of polymer-derived ceramics at high temperatures, J. Eur. Ceram. Soc. 30 (2010) 2203–2207. doi:10.1016/j.jeurceramsoc.2010.02.024.
- [170] A.B. Kousaalya, X. Zeng, M. Karakaya, T. Tritt, S. Pilla, A.M. Rao, Polymer-Derived Silicon Oxycarbide Ceramics as Promising Next-

Generation Sustainable Thermoelectrics, ACS Appl. Mater. Interfaces. 10 (2018) 2236–2241. doi:10.1021/acsami.7b17394.

- [171] V.S. Pradeep, M. Graczyk-Zajac, R. Riedel, G.D. Soraru, New insights in to the lithium storage mechanism in polymer derived SiOC anode materials, Electrochim. Acta. 119 (2014) 78–85. doi:10.1016/j.electacta.2013.12.037.
- [172] J. Grossenbacher, M.R. Gullo, F. Dalcanale, G. Blugan, J. Kuebler, S. Lecaudé, H. Tevaearai Stahel, J. Brugger, Cytotoxicity evaluation of polymer-derived ceramics for pacemaker electrode applications, J. Biomed. Mater. Res. - Part A. 103 (2015) 3625–3632. doi:10.1002/jbm.a.35477.
- [173] X. Wu, H. Ma, X. Chen, Z. Li, J. Li, Thermal Conductivity and Microstructure Properties of Porous SiC Ceramic Derived from Silicon Carbide Powder, New J. Glas. Ceram. 03 (2013) 43–47. doi:10.4236/njgc.2013.31007.
- [174] D.M. Liu, B.W. Lin, Thermal conductivity in hot-pressed silicon carbide, Ceram. Int. 22 (1996) 407–414. doi:10.1016/0272-8842(95)00125-5.
- [175] S.R. Choi, D. Kim, S.H. Choa, S.H. Lee, J.K. Kim, Thermal conductivity of AlN and SiC thin films, Int. J. Thermophys. 27 (2006) 896–905. doi:10.1007/s10765-006-0062-1.
- [176] L.S. Sigl, Thermal conductivity of liquid phase sintered silicon carbide, J. Eur. Ceram. Soc. 23 (2003) 1115–1122. doi:10.1016/S0955-2219(02)00271-6.
- [177] H. Xie, J. Wang, T. Xi, Y. Liu, Thermal Conductivity of Suspensions Containing Nanosized SiC Particles, Int. J. Thermophys. 23 (2002) 571–580. doi:10.1023/A:1015121805842.
- [178] S. Chabi, V.G. Rocha, E. Garclá-TunÌón, C. Ferraro, E. Saiz, Y. Xia, Y. Zhu, Ultralight, Strong, Three-Dimensional SiC Structures, ACS Nano. 10 (2016) 1871–1876. doi:10.1021/acsnano.5b05533.
- [179] B. Zhu, R. Wang, S. Harrison, K. Williams, R. Goduguchinta, J. Schneiter, J. Pegna, E. Vaaler, X. Wang, Thermal conductivity of SiC microwires: Effect of temperature and structural domain size uncovered by 0 K limit phonon scattering, Ceram. Int. 44 (2018) 11218–11224. doi:10.1016/j.ceramint.2018.03.161.
- [180] M. Mehr, D.T. Moore, J.R. Esquivel-Elizondo, J.C. Nino, Mechanical and thermal properties of low temperature sintered silicon carbide using a preceramic polymer as binder, J. Mater. Sci. 50 (2015) 7000– 7009. doi:10.1007/s10853-015-9252-1.
- [181] Y. Hwang, K. Ahn, J. Kim, Silicon carbonitride covered SiC composites for enhanced thermal and electrical insulation, Appl. Therm. Eng. 70 (2014) 600–608. doi:10.1016/j.applthermaleng.2014.05.015.
- [182] L.L. Snead, S.J. Zinkle, Structural relaxation in amorphous silicon carbide, Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms. 191 (2002) 497–503. doi:10.1016/S0168-583X(02)00599-2.
- [183] X. Han, X. Xing, H. Cheng, J. Wang, Reducing thermal conductivity 198

of polymer derived SiC ceramics via microwave sintering processing, Adv. Mater. Res. 476–478 (2012) 932–935. doi:10.4028/www.scientific.net/AMR.476-478.932.

- [184] Z. Li, Y. Wang, L. An, Control of the thermal conductivity of SiC by modifying the polymer precursor, J. Eur. Ceram. Soc. 37 (2017) 61– 67. doi:10.1016/j.jeurceramsoc.2016.08.023.
- [185] M. Balestrat, E. Diz Acosta, O. Hanzel, N. Tessier-Doyen, R. Machado, P. Šajgalík, Z. Lenčéš, S. Bernard, Additive-free low temperature sintering of amorphous Si–B–C powders derived from boron-modified polycarbosilanes: Toward the design of SiC with tunable mechanical, electrical and thermal properties, J. Eur. Ceram. Soc. (2019). doi:10.1016/j.jeurceramsoc.2019.12.037.
- [186] B. Zhang, H. Huang, X. Lu, X. Xu, J. Yao, Fabrication and properties of SiC porous ceramics using a polyurethane preparation process, Ceram. Int. 44 (2018) 16589–16593. doi:10.1016/j.ceramint.2018.06.083.
- [187] S.S. Hossain, S. Sarkar, N.K. Oraon, A. Ranjan, Pre-ceramic polymer-derived open/closed cell silicon carbide foam: microstructure, phase evaluation, and thermal properties, J. Mater. Sci. 51 (2016) 9865–9878. doi:10.1007/s10853-016-0220-1.
- [188] D. Lu, L. Su, H. Wang, M. Niu, L. Xu, M. Ma, H. Gao, Z. Cai, X. Fan, Scalable Fabrication of Resilient SiC Nanowires Aerogels with Exceptional High-Temperature Stability, ACS Appl. Mater. Interfaces. (2019) acsami.9b16811. doi:10.1021/acsami.9b16811.
- [189] A. Gurlo, E. Ionescu, R. Riedel, D.R. Clarke, The Thermal Conductivity of Polymer-Derived Amorphous Si-O-C Compounds and Nano-Composites, J. Am. Ceram. Soc. 99 (2016) 281–285. doi:10.1111/jace.13947.
- [190] D.G. Cahill, Thermal Conductivity Data, (2014). doi:http://users.mrl.illinois.edu/cahill/tcdata/ tcdata.html.
- [191] C.Y. Ho, R.W. Powell, P.E. Liley, Thermal conductivity of the elements: a comprehensive review, Published by the American Chemical Society, for the National Bureau of Standards, 1974. https://books.google.it/books?id=JDvxAAAAMAAJ.
- [192] M.A. Mazo, A. Tamayo, A.C. Caballero, J. Rubio, Electrical and thermal response of silicon oxycarbide materials obtained by spark plasma sintering, J. Eur. Ceram. Soc. 37 (2017) 2011–2020. doi:10.1016/j.jeurceramsoc.2017.01.003.
- [193] M.A. Mazo, A. Tamayo, A.C. Caballero, J. Rubio, Enhanced electrical and thermal conductivities of silicon oxycarbide nanocomposites containing carbon nanofibers, Carbon N. Y. 138 (2018) 42–51. doi:10.1016/j.carbon.2018.05.075.
- [194] J.H. Eom, Y.W. Kim, K.J. Kim, W.S. Seo, Improved electrical and thermal conductivities of polysiloxane-derived silicon oxycarbide ceramics by barium addition, J. Eur. Ceram. Soc. 38 (2018) 487–493. doi:10.1016/j.jeurceramsoc.2017.09.045.
- [195] C. Stabler, A. Reitz, P. Stein, B. Albert, R. Riedel, E. Ionescu, Thermal properties of SiOC glasses and glass ceramics at elevated

temperatures, Materials (Basel). 11 (2018) 1–18. doi:10.3390/ma11020279.

- [196] L. Qiu, Y.M. Li, X.H. Zheng, J. Zhu, D.W. Tang, J.Q. Wu, C.H. Xu, Thermal-conductivity studies of macro-porous polymer-derived SiOC ceramics, Int. J. Thermophys. 35 (2014) 76–89. doi:10.1007/s10765-013-1542-8.
- [197] T. Rouxel, G. Massouras, G.D. Sorarù, High temperature behavior of a gel-derived SiOC glass: Elasticity and viscosity, J. Sol-Gel Sci. Technol. 14 (1999) 87–94. doi:10.1023/A:1008779915809.
- [198] R. Harshe, Synthesis and Processing of Amorphous Si (AI) OC Bulk Ceramics : High Temperature Properties and Applications, A Diss. Submitt. to Dep. Mater. Sci. Darmstadt Univ. Technol. - Degree Doktor-Ingenieur. (2004) 0–222.
- [199] N. Janakiraman, F. Aldinger, Fabrication and characterization of fully dense Si-C-N ceramics from a poly(ureamethylvinyl)silazane precursor, J. Eur. Ceram. Soc. 29 (2009) 163–173. doi:10.1016/j.jeurceramsoc.2008.05.028.
- [200] J. Yang, J. Sprengard, L. Ju, A. Hao, M. Saei, R. Liang, G.J. Cheng, C. Xu, Three-dimensional-linked carbon fiber-carbon nanotube hybrid structure for enhancing thermal conductivity of silicon carbonitride matrix composites, Carbon N. Y. 108 (2016) 38–46. doi:10.1016/j.carbon.2016.07.002.
- [201] Y. Jia, T.D. Ajayi, J. Morales, M.A.R. Chowdhury, G. Sauti, S.H. Chu, C. Park, C. Xu, Thermal properties of polymer-derived ceramic reinforced with boron nitride nanotubes, J. Am. Ceram. Soc. 102 (2019) 7584–7593. doi:10.1111/jace.16670.
- [202] P. Jianqiang, Thermochemistry and constitution of precursor derived Si-(B)-C-N ceramics, Diss. an Der Univ. Stuttgart. (2002) 1–139. doi:10.18419/OPUS-6503.
- [203] A.B. Kousaalya, R. Kumar, B.T.N. Sridhar, Thermal conductivity of precursor derived Si-B-C-N ceramic foams using Metroxylon sagu as sacrificial template, Ceram. Int. 41 (2015) 1163–1170. doi:10.1016/j.ceramint.2014.09.044.
- [204] Z.L. Sun, Y. Zhou, D.C. Jia, X.M. Duan, Z.H. Yang, D. Ye, P.F. Zhang, Q. Zhang, Mechanical and thermal physical properties of amorphous SiCN(O) ceramic bulks prepared by hot-press sintering, Mater. Lett. 72 (2012) 57–59. doi:10.1016/j.matlet.2011.12.053.
- [205] A. Dasmahapatra, P. Kroll, Computational study of impact of composition, density, and temperature on thermal conductivity of amorphous silicon boron nitride, J. Am. Ceram. Soc. 101 (2018) 3489–3497. doi:10.1111/jace.15470.
- [206] J. Martan, O. Herý, V. Lang, Two-detector measurement system of pulse photothermal radiometry for the investigation of the thermal properties of thin films, J. Appl. Phys. 102 (2007) 1–7. doi:10.1063/1.2778642.
- [207] J.J. Gengler, J. Hu, J.G. Jones, A.A. Voevodin, P. Steidl, J. Vlček, Thermal conductivity of high-temperature Si-B-C-N thin films, Surf. Coatings Technol. 206 (2011) 2030–2033.

doi:10.1016/j.surfcoat.2011.07.058.

- [208] H.-P. Baldus, M. Jansen, Novel High-Performance Ceramics— Amorphous Inorganic Networks from Molecular Precursors, Angew. Chemie Int. Ed. English. 36 (1997) 328–343. doi:10.1002/anie.199703281.
- [209] A. Göbel, F. Hemberger, H.P. Ebert, M. Jansen, J. Wilfert, Thermophysical properties of an amorphous polymer-derived Si/B/N/C ceramic, Thermochim. Acta. 520 (2011) 20–24. doi:10.1016/j.tca.2011.03.001.
- [210] H.J. Kleebe, Y.D. Blum, SiOC ceramic with high excess free carbon, J. Eur. Ceram. Soc. 28 (2008) 1037–1042. doi:10.1016/j.jeurceramsoc.2007.09.024.
- [211] G. Mera, R. Riedel, F. Poli, K. Müller, Carbon-rich SiCN ceramics derived from phenyl-containing poly (silylcarbodiimides), J. Eur. Ceram. Soc. 29 (2009) 2873–2883.
- [212] Q. Wen, Z. Yu, R. Riedel, The fate and role of in situ formed carbon in polymer-derived ceramics, Prog. Mater. Sci. (2019) 100623. doi:10.1016/j.pmatsci.2019.100623.
- [213] G.D. Sorarù, L. Kundanati, B. Santhosh, N. Pugno, Influence of free carbon on the Young's modulus and hardness of polymer-derived silicon oxycarbide glasses, J. Am. Ceram. Soc. 102 (2019) 907–913. doi:10.1111/jace.16131.
- [214] Y. Zhang, Y. Heo, Y. Son, I. In, K. An, B. Kim, S. Park, Recent advanced thermal interfacial materials : A review of conducting mechanisms and parameters of carbon materials, Carbon N. Y. 142 (2019) 445–460. doi:10.1016/j.carbon.2018.10.077.
- [215] Y. Xie, S. Xu, Z. Xu, H. Wu, C. Deng, X. Wang, Interface-mediated extremely low thermal conductivity of graphene aerogel, Carbon N. Y. 98 (2016) 381–390. doi:10.1016/j.carbon.2015.11.033.
- [216] D. Liu, P. Yang, X. Yuan, J. Guo, N. Liao, The defect location effect on thermal conductivity of graphene nanoribbons based on molecular dynamics, Phys. Lett. Sect. A Gen. At. Solid State Phys. 379 (2015) 810–814. doi:10.1016/j.physleta.2014.12.050.
- [217] S. Ghosh, I. Calizo, D. Teweldebrhan, E.P. Pokatilov, D.L. Nika, A.A. Balandin, W. Bao, F. Miao, C.N. Lau, Extremely high thermal conductivity of graphene: Prospects for thermal management applications in nanoelectronic circuits, Appl. Phys. Lett. 92 (2008) 1–4. doi:10.1063/1.2907977.
- [218] Y.H. Zhao, Z.K. Wu, S.L. Bai, Study on thermal properties of graphene foam/graphene sheets filled polymer composites, Compos. Part A Appl. Sci. Manuf. 72 (2015) 200–206. doi:10.1016/j.compositesa.2015.02.011.
- [219] A.A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, C.N. Lau, Superior thermal conductivity of single-layer graphene, Nano Lett. 8 (2008) 902–907. doi:10.1021/nl0731872.
- [220] B. Wicklein, A. Kocjan, G. Salazar-Alvarez, F. Carosio, G. Camino, M. Antonietti, L. Bergström, Thermally insulating and fire-retardant lightweight anisotropic foams based on nanocellulose and graphene

oxide, Nat. Nanotechnol. 10 (2015) 277–283. doi:10.1038/nnano.2014.248.

- [221] W. Li, N. Mingo, L. Lindsay, D.A. Broido, D.A. Stewart, N.A. Katcho, Thermal conductivity of diamond nanowires from first principles, Phys. Rev. B - Condens. Matter Mater. Phys. 85 (2012) 1–5. doi:10.1103/PhysRevB.85.195436.
- [222] G. Fugallo, A. Cepellotti, L. Paulatto, M. Lazzeri, N. Marzari, F. Mauri, Thermal conductivity of graphene and graphite: Collective excitations and mean free paths, Nano Lett. 14 (2014) 6109–6114. doi:10.1021/nl502059f.
- [223] T.R. Anthony, W.F. Banholzer, J.F. Fleischer, L. Wei, P.K. Kuo, R.L. Thomas, R.W. Pryor, Thermal diffusivity of isotopically enriched C12 diamond, Phys. Rev. B. 42 (1990) 1104–1111. doi:10.1103/PhysRevB.42.1104.
- [224] Q. Zhang, M. Hao, X. Xu, G. Xiong, H. Li, T.S. Fisher, Flyweight 3D Graphene Scaffolds with Microinterface Barrier-Derived Tunable Thermal Insulation and Flame Retardancy, ACS Appl. Mater. Interfaces. 9 (2017) 14232–14241. doi:10.1021/acsami.7b01697.
- [225] A.J. Bullen, K.E. O'Hara, D.G. Cahill, O. Monteiro, A. von Keudell, Thermal conductivity of amorphous carbon thin films, J. Appl. Phys. 88 (2000) 6317–6320. doi:10.1063/1.1314301.
- [226] C.Y. Ho, R.W. Powell, P.E. Liley, Thermal conductivity of the elements, J. Phys. Chem. Ref. Data. 1 (1972) 279–421.
- [227] J. PAPPIS, S.L. BLUM, Properties of Pyrolytic Graphite, J. Am. Ceram. Soc. 44 (1961) 592–597. doi:10.1111/j.1151-2916.1961.tb11664.x.
- [228] R.H. KNIBBS, I.B. MASON, Thermal Expansion of Pyrolytic Graphite and its Variation due to Non-Alignment of the Crystallites, Nature. 203 (1964) 58–60. doi:10.1038/203058a0.
- [229] Starfire, StarPCS SMP-10, n.d. https://www.starfiresystems.com/wpcontent/uploads/2018/03/SMP-10.pdf.
- [230] Starfire, Polyramic SPR-036, n.d. https://www.starfiresystems.com/wp-content/uploads/2018/03/SPR-036.pdf.
- [231] T. Justus, P. Gonçalves, M. Seifert, M.L. Leite, S.M.H. Probst, C. Binder, G. Motz, A.N. Klein, Oxidation resistance and microstructure evaluation of a polymer derived ceramic (PDC) composite coating applied onto sintered steel, Materials (Basel). 16 (2019). doi:10.3390/ma12060914.
- [232] Merck, Durazane 1800, n.d. https://www.merckgroup.com/en/brands/pm/durazane.html.
- [233] B. Santhosh, C. Vakifahmetoglu, E. Ionescu, A. Reitz, B. Albert, G.D. Sorarù, Processing and thermal characterization of polymer derived SiCN(O) and SiOC reticulated foams, Ceram. Int. 46 (2020) 5594– 5601. doi:10.1016/j.ceramint.2019.11.003.
- [234] A.C. Ferrari, J. Robertson, Resonant Raman spectroscopy of disordered, amorphous, and diamondlike carbon, Phys. Rev. B -
Condens. Matter Mater. Phys. 64 (2001) 1–13. doi:10.1103/PhysRevB.64.075414.

- [235] J. Ferrari, A. C., & Robertson, Interpretation of Raman spectra of disordered and amorphous carbon. Physical Review B, 61(20), 14095–14107. doi:10.1103/physrevb.61.14095, Phys. Rev. B. 61 (2000) 14095–14107. doi:10.1007/BF02543693.
- [236] K.V. Kumar, S. Gadipelli, B. Wood, K.A. Ramisetty, A.A. Stewart, C.A. Howard, D.J.L. Brett, F. Rodriguez-Reinoso, Characterization of the adsorption site energies and heterogeneous surfaces of porous materials, J. Mater. Chem. A. 7 (2019) 10104–10137.
- [237] S.J. Gregg, K.S.W. Sing, Adsorption, surface area, and porosity, Academic Press, 1991. https://books.google.it/books?id=YhNRAAAAMAAJ.
- [238] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of Gases in Multimolecular Layers, J. Am. Chem. Soc. 60 (1938) 309–319. doi:10.1021/ja01269a023.
- [239] L. Gong, Y. Wang, X. Cheng, R. Zhang, H. Zhang, Porous mullite ceramics with low thermal conductivity prepared by foaming and starch consolidation, J. Porous Mater. 21 (2014) 15–21. doi:10.1007/s10934-013-9741-z.
- [240] A. Bouguerra, A. Aït-Mokhtar, O. Amiri, M.B. Diop, Measurement of thermal conductivity, thermal diffusivity and heat capacity of highly porous building materials using transient plane source technique, Int. Commun. Heat Mass Transf. 28 (2001) 1065–1078. doi:10.1016/S0735-1933(01)00310-4.
- [241] S.E. Gustafsson, Transient plane source techniques for thermal conductivity and thermal diffusivity measurements of solid materials, Rev. Sci. Instrum. 62 (1991) 797–804. doi:10.1063/1.1142087.
- [242] T.W. Lian, A. Kondo, M. Akoshima, H. Abe, T. Ohmura, W.H. Tuan, M. Naito, Rapid thermal conductivity measurement of porous thermal insulation material by laser flash method, Adv. Powder Technol. 27 (2016) 882–885. doi:10.1016/j.apt.2016.01.008.
- [243] L. Messger, G.V. Str, S. Phone, Instruction Manual LFA 1250 LFA 1600 Laser Flash Thermal Constant Analyzer, (n.d.) 1–44.
- [244] T.H. Laby, The thermal conductivity of air, Proc. R. Soc. London. Ser. A, Contain. Pap. a Math. Phys. Character. 144 (1934) 494–495.
- [245] H. Wu, S. Grabarnik, A. Emadi, G. De Graaf, R.F. Wolffenbuttel, Characterization of thermal cross-talk in a MEMS-based thermopile detector array, J. Micromechanics Microengineering. 19 (2009). doi:10.1088/0960-1317/19/7/074022.
- [246] A. Lavedrine, D. Bahloul, P. Goursat, N. Choong Kwet Yive, R. Corriu, D. Leclerq, H. Mutin, A. Vioux, Pyrolysis of polyvinylsilazane precursors to silicon carbonitride, J. Eur. Ceram. Soc. 8 (1991) 221– 227. doi:10.1016/0955-2219(91)90098-K.
- [247] M. Biesuz, P. Bettotti, S. Signorini, M. Bortolotti, R. Campostrini, M. Bahri, O. Ersen, G. Speranza, A. Lale, S. Bernard, G.D. Soraru, First synthesis of silicon nanocrystals in amorphous silicon nitride from a preceramic polymer, Nanotechnology. 30 (2019). doi:10.1088/1361-

6528/ab0cc8.

- [248] G.D. Sorarù, L. Pederiva, J. Latournerie, R. Raj, Pyrolysis kinetics for the conversion of a polymer into an amorphous silicon oxycarbide ceramic, J. Am. Ceram. Soc. 85 (2002) 2181–2187. doi:10.1111/j.1151-2916.2002.tb00432.x.
- [249] S. Kaur, G. Cherkashinin, C. Fasel, H.J. Kleebe, E. Ionescu, R. Riedel, Single-source-precursor synthesis of novel V 8 C 7 /SiC(O)based ceramic nanocomposites, J. Eur. Ceram. Soc. 36 (2016) 3553–3563. doi:10.1016/j.jeurceramsoc.2016.03.023.
- [250] P. Furtat, M. Lenz-Leite, E. Ionescu, R.A.F. MacHado, G. Motz, Synthesis of fluorine-modified polysilazanes: Via Si-H bond activation and their application as protective hydrophobic coatings, J. Mater. Chem. A. 5 (2017) 25509–25521. doi:10.1039/c7ta07687h.
- [251] M. Wójcik-Bania, A. Łącz, A. Nyczyk-Malinowska, M. Hasik, Poly(methylhydrosiloxane) networks of different structure and content of Si-H groups: Physicochemical properties and transformation into silicon oxycarbide ceramics, Polymer (Guildf). 130 (2017) 170–181. doi:10.1016/j.polymer.2017.10.020.
- [252] P. Dibandjo, S. Diré, F. Babonneau, G.D. Soraru, Influence of the polymer architecture on the high temperature behavior of SiCO glasses: A comparison between linear- and cyclic-derived precursors, J. Non. Cryst. Solids. 356 (2010) 132–140. doi:10.1016/j.jnoncrysol.2009.10.006.
- [253] E. Zera, Ceramic aerogels of the Si-C-N-O system from pre-ceramic polymer, Ph.D. Thesis , Univ. Trento, Italy. (2016).
- [254] Y. Blum, G.D. Sorarù, A.P. Ramaswamy, D. Hui, S.M. Carturan, Controlled mesoporosity in SiOC via chemically bonded polymeric "spacers," J. Am. Ceram. Soc. 96 (2013) 2785–2792. doi:10.1111/jace.12485.
- [255] E. Zera, R. Campostrini, P.R. Aravind, Y. Blum, G.D. Sorarù, Novel SiC/C aerogels through pyrolysis of polycarbosilane precursors, Adv. Eng. Mater. 16 (2014) 814–819. doi:10.1002/adem.201400134.
- [256] Z. Pan, M. Liu, C. Zheng, D. Gao, W. Huang, Study of Karstedt's Catalyst for Hydrosilylation of a Wide Variety of Functionalized Alkenes with Triethoxysilane and Trimethoxysilane, Chinese J. Chem. 35 (2017) 1227–1230. doi:10.1002/cjoc.201700024.
- [257] K. Wang, B. Ma, X. Li, Y. Wang, L. An, Effect of pyrolysis temperature on the structure and conduction of polymer-derived SiC, J. Am. Ceram. Soc. 97 (2014) 2135–2138. doi:10.1111/jace.12931.
- [258] G.M. Renlund, S. Prochazka, R.H. Doremus, Silicon oxycarbide glasses: Part II. Structure and properties, J. Mater. Res. 6 (1991) 2723–2734. doi:DOI: 10.1557/JMR.1991.2723.
- [259] S.R. Shah, R. Raj, Mechanical properties of a fully dense polymer derived ceramic made by a novel pressure casting process, Acta Mater. 50 (2002) 4093–4103. doi:10.1016/S1359-6454(02)00206-9.
- [260] J. Yin, S.H. Lee, L. Feng, Y. Zhu, X. Liu, Z. Huang, S.Y. Kim, I.S. Han, The effects of SiC precursors on the microstructures and mechanical properties of SiC f /SiC composites prepared via polymer

impregnation and pyrolysis process, Ceram. Int. 41 (2015) 4145–4153. doi:10.1016/j.ceramint.2014.11.112.

- [261] E.A. Burgemeister, W. Von Muench, E. Pettenpaul, Thermal conductivity and electrical properties of 6H silicon carbide, J. Appl. Phys. 50 (1979) 5790–5794. doi:10.1063/1.326720.
- [262] G.A. Slack, Thermal conductivity of pure and impure silicon, silicon carbide, and diamond, J. Appl. Phys. 35 (1964) 3460–3466.
- [263] F. Delobel, S. Lemonnier, É. Barraud, J. Cambedouzou, Influence of sintering temperature and pressure on the 3C-6H transition of silicon carbide, J. Eur. Ceram. Soc. 39 (2019) 150–156. doi:10.1016/j.jeurceramsoc.2018.09.010.
- [264] W. Li, J. Yuan, Y. Lin, S. Yao, Z. Ren, H. Wang, M. Wang, J. Bai, The controlled formation of hybrid structures of multi-walled carbon nanotubes on SiC plate-like particles and their synergetic effect as a filler in poly(vinylidene fluoride) based composites, Carbon N. Y. 51 (2013) 355–364. doi:10.1016/j.carbon.2012.08.064.
- [265] L.G. Cançado, K. Takai, T. Enoki, M. Endo, Y.A. Kim, H. Mizusaki, A. Jorio, L.N. Coelho, R. Magalhaes-Paniago, M.A. Pimenta, General equation for the determination of the crystallite size L a of nanographite by Raman spectroscopy, Appl. Phys. Lett. 88 (2006) 163106.
- [266] M.A.R. Chowdhury, K. Wang, Y. Jia, C. Xu, Semiconductorconductor transition of pristine polymer-derived ceramics SiC pyrolyzed at temperature range from 1200°C to 1800°C, J. Am. Ceram. Soc. n/a (2019). doi:10.1111/jace.16961.
- [267] F. Rosenburg, E. Ionescu, N. Nicoloso, R. Riedel, High-temperature Raman spectroscopy of nano-crystalline carbon in silicon oxycarbide, Materials (Basel). 11 (2018). doi:10.3390/ma11010093.
- [268] Y. Baek, Y. Ryu, K. Yong, Structural characterization of β-SiC nanowires synthesized by direct heating method, Mater. Sci. Eng. C. 26 (2006) 805–808. doi:10.1016/j.msec.2005.09.083.
- [269] T. Koyanagi, M.J. Lance, Y. Katoh, Quantification of irradiation defects in beta-silicon carbide using Raman spectroscopy, Scr. Mater. 125 (2016) 58–62. doi:10.1016/j.scriptamat.2016.08.004.
- [270] A. Cantarero, Raman Scattering Applied to Materials Science, Procedia Mater. Sci. 9 (2015) 113–122. doi:10.1016/j.mspro.2015.04.014.
- [271] N.W. Jepps, T.F. Page, Polytypic transformations in silicon carbide, Prog. Cryst. Growth Charact. 7 (1983) 259–307. doi:10.1016/0146-3535(83)90034-5.
- [272] R. Piat, E. Schnack, Identification of Coefficients of Thermal Expansion of Pyrolytic Carbon with Different Texture Degrees, Key Eng. Mater. 251–252 (2003) 333–338. doi:10.4028/www.scientific.net/KEM.251-252.333.
- H. Leffmann, The properties of silica. An introduction to the properties of substances in the solid non-conducting state: By Robert B. Sosman, Ph. D., Geophysical Laboratory, Carnegie Institution, Washington, DC 855 pages, 8vo, illustrated. New York, The

Chemical Cata, (1928).

- [274] M.W. Chase Jr, NIST-JANAF thermochemical tables, J. Phys. Chem. Ref. Data, Monogr. 9 (1998).
- [275] P.U.T.P.R. Center, Y.S. Touloukian, A.F.M.L. (U.S.), Thermophysical Properties of High Temperature Solid Materials: Elements, Macmillan, 1967. https://books.google.it/books?id=abxUgX0_3u4C.
- [276] L.G. Fave, Investigation of the thermal conductivity of SiC / SiC cladding before and after irradiation, 7378 (2017). https://infoscience.epfl.ch/record/224051/files/EPFL_TH7378.pdf.
- [277] V.L. Nguyen, E. Zera, A. Perolo, R. Campostrini, W. Li, G.D. Sorar??, Synthesis and characterization of polymer-derived SiCN aerogel, J. Eur. Ceram. Soc. 35 (2015) 3295–3302. doi:10.1016/j.jeurceramsoc.2015.04.018.
- [278] Y. Iwamoto, W. Völger, E. Kroke, R. Riedel, T. Saitou, K. Matsunaga, Crystallization Behavior of Amorphous Silicon Carbonitride Ceramics Derived from Organometallic Precursors, J. Am. Ceram. Soc. 84 (2004) 2170–2178. doi:10.1111/j.1151-2916.2001.tb00983.x.
- [279] H. Kleebe, D. Suttor, H. Müller, G. Ziegler, decompositioncrystallization of polymer-derived Si-C-N ceramics, J. Am. Ceram. Soc. 81 (1998) 2971–2977.
- [280] A. Badzian, Stability of Silicon Carbonitride Phases, J. Am. Ceram. Soc. 85 (2004) 16–20. doi:10.1111/j.1151-2916.2002.tb00031.x.
- [281] T. Nishimura, R. Haug, J. Bill, G. Thurn, F. Aldinger, Mechanical and thermal properties of Si-C-N material from polyvinylsilazane, J. Mater. Sci. 33 (1998) 5237–5241. doi:10.1023/A:1004440122266.
- [282] N. Janakiraman, F. Aldinger, Indentation analysis of elastic and plastic deformation of precursor-derived Si–C–N ceramics, J. Eur. Ceram. Soc. 30 (2010) 775–785.
- [283] G. Ziegler, H.J. Kleebe, G. Motz, H. Müller, S. Traßl, W. Weibelzahl, Synthesis, microstructure and properties of SiCN ceramics prepared from tailored polymers, Mater. Chem. Phys. 61 (1999) 55–63. doi:10.1016/S0254-0584(99)00114-5.
- [284] P. Šajgalík, J. Sedláček, Z. Lenčéš, J. Dusza, H.T. Lin, Additive-free hot-pressed silicon carbide ceramics-A material with exceptional mechanical properties, J. Eur. Ceram. Soc. 36 (2016) 1333–1341. doi:10.1016/j.jeurceramsoc.2015.12.013.
- [285] S.C. Zunjarrao, Polymer Derived Ceramics: Processing-Structure-Propertry Relationships, (2008).
- [286] K. V. Moraes, L. V. Interrante, Processing, fracture toughness, and vickers hardness of allylhydridopolycarbosilane-derived silicon carbide, J. Am. Ceram. Soc. 86 (2003) 342–346. doi:10.1111/j.1151-2916.2003.tb00020.x.
- [287] S. Walter, G.D. Soraru, H. Brequel, S. Enzo, Microstructural and mechanical characterization of sol gel-derived Si–O–C glasses, J. Eur. Ceram. Soc. 22 (2002) 2389–2400.
- [288] G.D. Sorarù, E. Dallapiccola, G. D'Andrea, Mechanical

Characterization of Sol–Gel-Derived Silicon Oxycarbide Glasses, J. Am. Ceram. Soc. 79 (1996) 2074–2080.

- [289] M. Šupová, J. Svitilova, Z. Chlup, M. Černý, Z. Weishauptova, T. Suchý, V. MACHOVIČ, Z. SUCHARDA, M. ŽALOUDKOVÁ, Relation between mechanical properties and pyrolysis temperature of phenol formaldehyde resin for gas separation membranes, Ceramics-Silikáty. 56 (2012) 40–49.
- [290] T. Ko, W. Kuo, Y. Chang, Microstructural changes of phenolic resin during pyrolysis, J. Appl. Polym. Sci. 81 (2001) 1084–1089.
- [291] W.C. Oliver, G.M. Pharr, An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments, J. Mater. Res. 7 (1992) 1564–1583.
- [292] C. Moysan, R. Riedel, R. Harshe, T. Rouxel, F. Augereau, Mechanical characterization of a polysiloxane-derived SiOC glass, J. Eur. Ceram. Soc. 27 (2007) 397–403.
- [293] T. Rouxel, Elastic properties and short-to medium-range order in glasses, J. Am. Ceram. Soc. 90 (2007) 3019–3039.
- [294] K. Jurkiewicz, M. Pawlyta, D. Zygadło, D. Chrobak, S. Duber, R. Wrzalik, A. Ratuszna, A. Burian, Evolution of glassy carbon under heat treatment: correlation structure-mechanical properties, J. Mater. Sci. 53 (2018) 3509–3523.
- T. Rouxel, Driving force for indentation cracking in glass:
 composition, pressure and temperature dependence, Philos. Trans.
 R. Soc. A Math. Phys. Eng. Sci. 373 (2015) 20140140.
- [296] L. Jiao, H. Xiao, Q. Wang, J. Sun, Thermal degradation characteristics of rigid polyurethane foam and the volatile products analysis with TG-FTIR-MS, Polym. Degrad. Stab. 98 (2013) 2687– 2696. doi:10.1016/j.polymdegradstab.2013.09.032.
- [297] G.M. Renlund, S. Prochazka, R.H. Doremus, Silicon oxycarbide glasses : Part II . Structure and properties, (1991) 2723–2734.
- [298] H. Brequel, J. Parmentier, S. Walter, R. Badheka, G. Trimmel, S. Masse, J. Latournerie, P. Dempsey, C. Turquat, A. Desmartin-Chomel, L. Le Neindre-Prum, U.A. Jayasooriya, D. Hourlier, H.-J. Kleebe, G.D. Sorarù, S. Enzo, F. Babonneau, S y s t e m a t i c S tr u c t u r a I C h a r a c t e r i z a t i o n o f t h e H i g h T e m p e r a t u r e B e h a v i o r o f N e a r ly S t o i c h i om e tr i c S i l i c o n O x yc a r b id e G I a sses, Chem. Mater. 16 (2004) 2585–2598.
- [299] J. Qian, J. Wang, Z. Jin, Preparation of biomorphic SiC ceramic by carbothermal reduction of oak wood charcoal, Mater. Sci. Eng. A. 371 (2004) 229–235. doi:10.1016/j.msea.2003.11.051.
- [300] B.K. Jang, Y. Sakka, Thermophysical properties of porous SiC ceramics fabricated by pressureless sintering, Sci. Technol. Adv. Mater. 8 (2007) 655–659. doi:10.1016/j.stam.2007.08.003.
- [301] R. Riedel, G. Mera, R. Hauser, A. Klonczynski, Silicon-based Polyemr-Derived Ceramics:Synthesis Properties and Applications-E Review, J. Ceram. Soc. Japan. 444 (2006) 33–38.
- [302] V.L. Nguyen, N.B. Laidani, G.D. Sorarù, N-doped polymer-derived

Si(N)OC: The role of the N-containing precursor, J. Mater. Res. 30 (2015) 770–781. doi:10.1557/jmr.2015.44.

- [303] G.T. Burns, R.B. Taylor, Y. Xu, A. Zangvil, G.A. Zank, High-Temperature Chemistry of the Conversion of Siloxanes to Silicon Carbide, Chem. Mater. 4 (1992) 1313–1323. doi:10.1021/cm00024a035.
- [304] S. Trassl, G. Motz, E. Rössler, G. Ziegler, Characterization of the free-carbon phase in precursor-derived Si-C-N ceramics: I, spectroscopic methods, J. Am. Ceram. Soc. 85 (2002) 239–244. doi:10.1111/j.1151-2916.2002.tb00072.x.
- [305] P. Colombo, M. Modesti, Silicon oxycarbide foams from a silicone preceramic polymer and polyurethane, J. Sol-Gel Sci. Technol. 14 (1999) 103–111. doi:10.1023/A:1008736100788.
- [306] G.D. Soraru, R. Campostrini, A.A. Ejigu, E. Zera, P. Jana, Processing and characterization of polymer derived SiOC foam with hierarchical porosity by HF etching, J. Ceram. Soc. Japan. 124 (2016) 1023– 1029. doi:10.2109/jcersj2.16072.
- [307] K. Schelm, E.A. Morales, M. Scheffler, Mechanical and surfacechemical properties of polymer derived ceramic replica foams, Materials (Basel). 12 (2019). doi:10.3390/ma12111870.
- [308] FOAMGLAS, FOAMGLAS ®, (n.d.). https://www.foamglas.com/enus.
- [309] GLAPOR, GLAPOR CELLULAR GLASS GRAVEL Technical Data SG 600 P, (n.d.). https://www.glapor.de/en/.
- [310] Promat, High temperature microporous insulation board 1000-1200°C, (n.d.). doi:10.1136/jnnp-2012-303898.
- [311] H. Wang, X. Zhang, N. Wang, Y. Li, X. Feng, Y. Huang, C. Zhao, Ultralight, scalable, and high-temperature–resilient ceramic nanofiber sponges, Sci. Adv. (2017) 1–10.
- [312] M. Koebel, A. Rigacci, P. Achard, Aerogel-based thermal superinsulation: An overview, J. Sol-Gel Sci. Technol. 63 (2012) 315–339. doi:10.1007/s10971-012-2792-9.
- [313] Y. Si, X. Wang, L. Dou, J. Yu, B. Ding, Ultralight and fire-resistant ceramic nanofibrous aerogels with temperature-invariant superelasticity, Sci. Adv. 4 (2018). doi:10.1126/sciadv.aas8925.
- F. Asdrubali, F. D'Alessandro, S. Schiavoni, A review of unconventional sustainable building insulation materials, Sustain. Mater. Technol. 4 (2015) 1–17. doi:10.1016/j.susmat.2015.05.002.
- [315] X. Xu, Q. Zhang, M. Hao, Y. Hu, Z. Lin, L. Peng, T. Wang, X. Ren, C. Wang, Z. Zhao, C. Wan, H. Fei, L. Wang, J. Zhu, H. Sun, W. Chen, T. Du, B. Deng, G.J. Cheng, I. Shakir, C. Dames, T.S. Fisher, X. Zhang, H. Li, Y. Huang, X. Duan, Double-negative-index ceramic aerogels for thermal superinsulation, Science (80-.). 363 (2019) 723–727. doi:10.1126/science.aav7304.
- [316] F. Xie, I. Gonzalo Juan, M. Arango-Ospina, R. Riedel, A.R. Boccaccini, E. Ionescu, Apatite Forming Ability and Dissolution Behavior of Boron- And Calcium-Modified Silicon Oxycarbides in

Comparison to Silicate Bioactive Glass, ACS Biomater. Sci. Eng. 5 (2019) 5337–5347. doi:10.1021/acsbiomaterials.9b00816.

[317] E. Ionescu, S. Sen, G. Mera, A. Navrotsky, Structure, energetics and bioactivity of silicon oxycarbide-based amorphous ceramics with highly connected networks, J. Eur. Ceram. Soc. 38 (2018) 1311– 1319. doi:10.1016/j.jeurceramsoc.2017.10.002.



Annex Figure 1 Thermal conductivity vs. Thermal diffusivity for the different materials (Chapter 1) [Source: Granta CES 2009 EDUPACK].

The chart helps the choice of the right thermal insulant. The thermal conductivity (λ) is more important when the heat flow is steady and the thermal diffusivity (κ) through a material is considered when the heat flow is transient. The contours of the chart define a parameter called volumetric specific heat (λ/κ).



Annex Figure 2 Strength vs. Maximum service temperature for the different materials (Chapter 1) [Source: Granta CES 2009 EDUPACK].

The temperature can cause degradation, decomposition, and/or creeping in a material, leading to the decline of its strength. Hence it is important to have a clear know-how of the appropriate temperature beyond which it is unsafe to use a particular material, often referred to as the T_{max} (maximum operating temperature). Ceramics top the list with a possibility to have a T_{max} >1500 °C and in the case of polymers the T_{max} is often <200 °C.



Annex Figure 3 Thermal conductivity spectrum of different materials (Chapter 1).



Annex Figure 4 Types of fillers and their effects in the PDC systems (Chapter 2) [Source: Barroso et al., J. Mater. Chem. A, 2019, 7, 1936].



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PPI 60 (S 28089)				
Caratteristiche	Norme	Unità di misura	Valori	Tolleranze
Densità	UNI EN ISO 845	Kg/m3	23 - 27	
Colore			nero	
Compression resistance 40% Resistenza alla compressione	ISO 3386/1	kPa	2.5 - 4.5	
Diametro Cellulare	SS/T.013.4	micron	740 - 1040	
JItimate elongation / Allungamento massimo	ISO 1798	%	300	
Tensile strength/ Resistenza alla trazione	ISO 1798	kPa	150	
Schiuma di poliuretano reticolata a b Prodotto ideale per la filtrazione dell'ar delle polveri etc.	ase poliestere, proge ia nell'industria autor	ettata per svariate a nobilistica, condizio	applicazioni nella namento dell'aria,	filtrazione. filtrazione

Annex Figure 5 Datasheet of the PU foam template used, type PPI 60 (Chapter 3).



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		MTP 55		
Caratteristiche	Norme	Unità di misura	Valori	Tolleranze
Densità*	UNI EN ISO 845	Kg/m3	55	± 5%
Colore			antracite	
Sforzo in compensazione, CV40*	UNI EN ISO 3386-1	KPa	6.0 (2.7-3.7)	± 15%
Resistenza alla trazione	UNI EN ISO 1798	kPa	180	MIN
Allungamento a rottura	UNI EN ISO 1798	%	170	MIN.
Deformazione residua dopo compressione	UNI EN ISO 1856 Metodo A	%	50%, 22h, 70°C 4.0	MAX.
Porosità	ESAME VISIVO	n. celle /cm	20	± 2

Schiuma di poliuretano flessibile a base poliestere. Il prodotto ha una struttura cellulare regolare ed una buona resistenza al passaggio dell'aria e quindi un buon potere di assorbimento acustico e termico. Ha un elevata resistenza meccanica e maggiore resistenza ai solventi organici.

Non sono disponibili dati relativi all'assorbimento acustico del materiale in quanto le diverse geometrie delle lastre come le diverse bugnature influiscono in modo importante sul dato. Sono valori che vanno verificati sul prodotto finito.

Principali applicazione nel settore automobilistico, calzature, acustica, igiene della casa, imballaggio, isolamento termico etc.

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Annex Figure 6 Datasheet of the PU foam template used, type MTP 55 (Chapter 3).

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	PPI 90 (S 3	1048)		
Caratteristiche	Norme	Unità di misura	Valori	Tolleranze
Densità	UNI EN ISO 845	Kg/m3	26 - 30	
Colore			nero	
Compression resistance 40% Resistenza alla compressione	ISO 3386/1	kPa	2.0 - 4.0	
Diametro Cellulare	SS/T.013.4	micron	440 – 520	
Iltimate elongation/ Illungamento massimo	ISO 1798	%	350	
ensile strength/ Resistenza alla trazione	ISO 1798	kPa	200	
Schiuma di poliuretano reticolata a b Prodotto ideale per la filtrazione dell'a delle polveri etc.	ase poliestere, proge ria nell'industria autor	ettata per svariate nobilistica, condizio	applicazioni nella namento dell'aria	filtrazione , filtrazione

CODICE DOGANALE : 39211310

Annex Figure 7 Datasheet of the PU foam template used, type PPI 90 (Chapter 3).



Annex Figure 8 Image showing a SiCN(O) foam developed and GLAPOR®, both machined using conventional tools.

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Curriculum vitae

Education

Ph.D. 2017 -2020	Doctoral school in Materials, Mechatronics and Systems Engineering (MMSE), Department of Industrial Engineering, University of Trento, Trento (Italy). Thesis : Thermal properties of polymer derived Si-O-C-N ceramics.
Master's degree (M.Tech) 2011-2013	Production and Industrial Engineering (PIE), Mahatma Gandhi University, Kottayam, India. Thesis : Nano-layered ceramic fillers for functional polymer application (CSIR-NIIST, Thiruvananthapuram, India).
Bachelor's degree (B.Tech) 2007-2011	Mechanical Engineering, Mahatma Gandhi University, Kottayam, India.

Research Experience

Research-Intern February, 2019	TU Darmstadt, Germany.
DRDO-Senior Research Fellow (SRF) 2015- 2016	Amrita University, TN, India.
Research fellow 2013-2015	CSIR-NIIST, Thiruvananthapuram, India.

Publications

• G. D. Sorarù, L. Kundanati, **B. Santhosh**, N. Pugno, Influence of free carbon on the Young's modulus and hardness of polymer-

derived silicon oxycarbide glasses, J. Am. Ceram. Soc. 2019, 102, 907–913.

- Balanand Santhosh, Cekdar Vakifahmetoglu, Emanuel Ionescu, Andreas Reitz, Barbara Albert, Gian Domenico Sorarù, 'Processing and thermal characterization of polymer derived SiCN(O) and SiOC reticulated foams', Ceram. Int. 2020,46, 5594– 5601.
- Mattia Biesuz, Michele Tomasi, Balanand Santhosh, Vincenzo M. Sglavo, Gian D. Sorarù, Polymer-derived Si₃N₄ nanofelts as a novel oil spills clean-up architecture, J. Environ. Chem. Eng. 2020, 8,104134.
- Balanand Santhosh, Emanuel Ionescu, Francesco Andreolli, Mattia Biesuz, Andreas Reitz, Barbara Albert, Gian Domenico Sorarú, Effect of pyrolysis temperature on the microstructure and thermal conductivity of polymer-derived porous and dense SiC ceramics (article to be submitted).
- Influence of carbon enrichment on the thermal properties of polymer derived, dense Si-C-N-O ceramics. (article under preparation).

Conferences and schools

- Balanand Santhosh, Prasanta Jana, Emanuele Zera, and Gian Domenico Sorarú, MSE 2018 -Materials Science and Engineering congress, September 26-28, 2018, Darmstadt, Germany. Presented work: Thermal properties of Ultra-light, Polymer derived SiC, SiOC, and SiCN reticulated foams.
- Balanand Santhosh and Gian Domenico Sorarú, XVI European Ceramic Society (EcerS) Conference -2019, June 16-20, 2019, Torino, Italy. Presented work: Thermal properties of dense and porous, Si-based polymer derived ceramics.
- Prasanta Jana, Emanuele Zera, Balanand Santhosh, and Gian Domenico Sorarú, 42nd International Conference on Advanced Ceramics & Composites, January 21-26, 2018, Daytona Beach, FL, USA. Work: Low Density Reticulated Polymer Derived SiC, SiCN and SiOC foams
- Balanand Santhosh and Gian Domenico Sorarú, Autumn career day- 2019, November 2019, Department of industrial engineering University of Trento, Italy. Presented work: Thermal properties of polymer derived SiC, SiOC, and SiCN(O) dense disks and reticulated foams.

- TOPSTARS-2018, EIT Raw Materials Summer school, Achievement: Member of the group winning the Innovando Challenge, organized as part of the school.
- Other seminars and schools organized by the DII department.