

Structural Characterization and Material Property Evaluation in Polymer-Derived SiOC Ceramics and Ceramic Nanocomposites

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Abstract

The field of advanced ceramics will experience significant growth in the upcoming decade to address increasing demands for multifunctional temperature- and corrosion-resistant materials for aerospace, energy, and electronics sectors. Polymer-derived ceramics (PDCs) and specifically polymer-derived silicon oxycarbide (SiOC) are a promising and attractive material class to accommodate the need for novel ceramics with tailorable compositions and material properties. SiOC is a unique member of the PDC family as the polymer precursor route is the predominant fabrication and synthesis method. As the composition and properties of the evolved SiOC ceramic can be tuned by polymer chemistry and choice of additives, a variety of multifunctional SiOC ceramics have been prepared with additional electric, magnetic, or structural characteristics. However, SiOC microstructures have been difficult to resolve as the amorphous matrix that shows nanoscale heterogeneity has not been rigorously characterized due to instrument and detector limitations. Therefore, understanding phase evolution in SiOC is critical for further development and commercial application of SiOC ceramics and ceramic composites. This work focuses on fabrication and characterization of novel SiOC ceramics and ceramic nanocomposites to examine phase formation and functional material properties imbued by reinforcement phases. In particular, SiOC ceramic 2D nanocomposites will be fabricated with montmorillonite (MMT – a naturally-occurring clay comprised of stacked 2D nanosheets) and $\text{Ti}_3\text{C}_2\text{T}_x$ ‘MXene’ (a rapidly growing class of two-dimensional transition metal carbides/nitrides) to create nanostructured ceramic composites. Phase formation, porosity, and electrical conductivity will be analyzed to demonstrate attractive multifunctional capabilities of SiOC ceramics. In addition, thermodynamic modeling and advanced electron microscopy techniques will be utilized to better understand the locally-ordered amorphous SiOC matrix. The results and findings from this work will be among the first reported in the SiOC system and address limitations in the current state of knowledge.

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General Audience Abstract

The demand for advanced ceramics with multifunctional properties—such as temperature and corrosion resistance—across industries like aerospace, energy, and electronics is expected to grow significantly in the next decade. Polymer-derived ceramics (PDCs), particularly polymer-derived silicon oxycarbide (SiOC), represent a promising material class capable of meeting these demands due to their tunable composition and versatile material properties. SiOC ceramics, synthesized primarily through polymer precursor methods, offer unique advantages in tailoring their characteristics, including electrical, magnetic, and structural features. However, understanding the phase evolution and microstructure of SiOC remains challenging, as the material's amorphous matrix exhibits nanoscale heterogeneity that has not been fully characterized due to limitations in current analytical techniques. This work explores the fabrication and characterization of novel SiOC ceramics and nanocomposites, focusing on phase formation, porosity, and electrical conductivity. Specifically, 2D nanocomposites incorporating montmorillonite (MMT), a naturally occurring clay, and $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes, a class of 2D transition metal carbides, are examined to enhance the multifunctional properties of SiOC. Advanced electron microscopy and thermodynamic modeling are employed to gain deeper insights into the locally-ordered structures within the amorphous SiOC matrix. The findings from this study provide a critical step toward overcoming current limitations and advancing the development and application of SiOC-based materials in a wide range of industries.

Dedication

*To my mother Anu and my father Anand
To my brother Aaditya*

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Attribution

A brief description of the contributions of colleagues is provided as follows:

Chapter 2: A.V.R. performed all sample preparation, experiments, and characterization (except ^{29}Si NMR), data analysis, and main writing/editing in this manuscript. Mr. Kenneth Knott-Sharp (Virginia Tech Department of Chemistry) performed ^{29}Si NMR experiments and assisted with data analysis. Dr. Kathy Lu (Professor, Virginia Tech – now University of Alabama at Birmingham) served as the corresponding author and was involved in funding acquisition and editing of the manuscript.

Chapter 3: A.V.R. performed all sample preparation, experiments, and characterization, data analysis and main writing/editing. Dr. Kathy Lu served as the corresponding author and was involved in funding acquisition and editing of the manuscript.

Chapter 4: A.V.R. performed all sample preparation, experiments, and characterization (except ^{29}Si NMR), data analysis, and main writing/editing. Mr. Kenneth Knott-Sharp performed ^{29}Si NMR experiments. Dr. Kathy Lu served as the corresponding author and was involved in funding acquisition and editing of the manuscript.

Chapter 5: A.V.R. performed all sample preparation, experiments, and characterization, data analysis in this manuscript, and main writing/editing. Dr. Kathy Lu served as the corresponding author and was involved in funding acquisition and editing of the manuscript.

Chapter 6: A.V.R. performed all sample preparation, experiments, and characterization, data analysis, and main writing/editing. Dr. Kathy Lu served as the corresponding author and was involved in funding acquisition and editing of the manuscript.

Chapter 1: Introduction and Motivation

1.1. *Background on Advanced Ceramics*

Compared to traditional ceramics that have been long-produced from naturally-occurring minerals, advanced ceramics are interesting because of their higher strength and toughness, tailorable compositions, and higher operating temperatures. Containing classes of oxides, carbides, nitrides, and borides, engineering ceramics require advanced processing techniques to finely control composition, microstructure, crystallinity, and porosity compared to traditional ceramics such as porcelain, glass, and silica [1, 2]. With increasing demand for thermally-stable, chemically-resistant, and high-hardness materials for aerospace, energy, and corrosive applications, advanced ceramics have high potential for novel discovery and fabrication of multifunctional materials. The advanced ceramic market size is projected to nearly double within the next decade (**Figure 1.1.1**). While advanced ceramics are notable for their lightweight structural properties, increasingly complex material demands in high temperature or corrosive environments underscores the need for novel material discovery in functional advanced ceramics.

Advanced ceramics are fabricated either from ceramic powder or liquid precursors. Ceramic powder processing techniques such as ball milling, uniaxial or isostatic pressing, injecting molding, and tape casting are widely-used and well-established methods but can present several challenges that impact microstructure, material properties, and performance [1]. Densification and residual porosity remain critical issues due to incomplete sintering, powder size distribution, voids, or binder removal. Furthermore, furnace temperatures between ~50-75% of the ceramic melting temperature are required to adequately sinter advanced ceramics – ranging from 1200-1400°C for oxides to 1500-2000°C for nitrides and carbides [2]. While hot pressing, pressure sintering, spark plasma sintering, and microwave sintering have been shown to lower effective sintering temperatures and improve densification, these techniques limit the production of complex geometries and parts and require high equipment costs [3].

Technical ceramics are also produced through liquid-based precursor methods such as sol-gel or polymer-derived routes. Through hydrolysis and polymerization of organometallic or metal alkoxide precursors and sintering of the condensed gel, the sol-gel method produces ceramics with homogenous and controlled compositions and microstructures. a versatile method for synthesizing advanced ceramics with high purity and controlled microstructure [1, 2]. Polymer-derived ceramic

routes similarly proceed through polymerization, cross-linking, and pyrolysis of preceramic resins. Polymer-derived ceramics are particularly notable for their compositional control, near-net-shape ceramic fabrication, and amorphous microstructures [4-6]. Sol-gel and polymer-derived methods are limited by the material classes obtainable, precursor costs and hazards, and time-intensive processes; however, these methods typically exhibit exceptionally low porosity and controllable microstructures and are attractive routes for additive manufacturing of advanced ceramics [7]. The work in this dissertation will focus on polymer-derived ceramic fabrication, property analysis, and microstructural characterization.

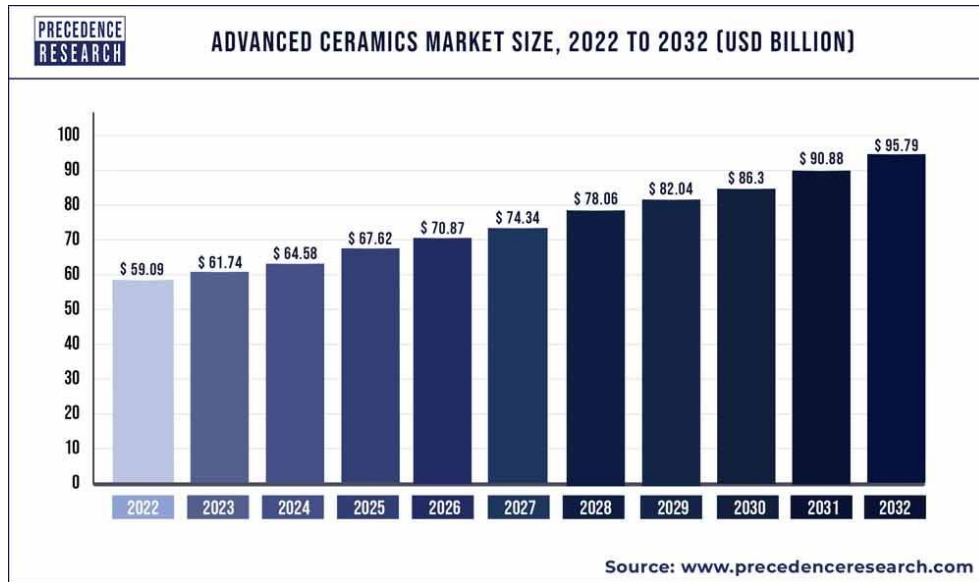


Figure 1.1.1: Projected market size for advanced ceramics from 2022 to 2032, depicting a projected double in market size and demand [8].

1.2. Functional Polymer-Derived Ceramics

Polymer-derived ceramics (PDCs) are an emerging and popular material class for ceramic fabrication with various microstructures and multifunctional properties by tailoring the polymer precursor chemistry and content as well as by addition of filler materials [5, 9-11]. The tailorable composition control as well as processability ease of the polymer precursors make PDCs an exciting material for synthesizing and fabricating novel materials with complex geometries generally unobtainable or difficult through conventional ceramic processing techniques. Silicon-based PDCs (e.g., SiC, SiOC, SiCN, SiN, SiON, etc.) are fabricated from organosilicon preceramic precursors that have adequately high molecular weights and polymeric structures with rings or cages to reduce volatilization of small polymer fragments during pyrolysis, in addition to high curing temperatures and tunable rheological characteristics for shaping and thermosetting capabilities [5, 11]. **Figure 1.1.(a)** summarizes the variety of Si-based ceramics obtainable through polymer precursor routes, with ternary ceramics (e.g., SiOC, SiON, SiCN, SiBC, etc.) possible by tailoring the precursor chemistry and architecture. **Figure 1.1.(b)** depicts typical PDC synthesis and processing methods: a crosslinked polymer is synthesized from silane monomers at slightly elevated temperatures less than 300°C. Pyrolytic decomposition above 400°C yields an amorphous ceramic matrix that inherits its microstructure from the disordered preceramic polymer. Higher sintering temperatures (>1200-1400°C) are required to induce crystallization, overcoming thermodynamic barriers for homogenous nucleation in the amorphous matrix.

Silicon oxycarbide (SiOC) ceramics are a unique subset of PDCs that evolve from carbon-rich polysiloxanes to yield an amorphous matrix in which carbon has been incorporated into silica networks [12]. Notably, PDC processing is the sole route for obtaining SiOC glasses due to the difficulty of substituting carbon-for-oxygen in silicate networks. SiOC ceramics exhibit higher hardness, Young's moduli, and crystallization temperatures than SiO₂ due to presence of Si-C bonds that provide structural and thermodynamic rigidity to the amorphous matrix [10, 12]. As a result, SiOC ceramics are popular materials for use in high/ultra-high temperature and corrosive environments due to their excellent creep resistance and oxidation-resistance. **Figure 1.1.(c)** depicts the typical route for SiOC fabrication in which the resulting ceramic can be described as a SiOC composite with SiO₂ and free carbon domains. SiOC ceramics are amorphous until 1200-1300°C after which SiC begins to crystallize – however, sintering temperatures above 1500-1600°C to obtain appreciable SiC content at the expense of significant pore formation, volumetric

shrinkage, and mass loss. Optical micrographs of typical PSO green bodies and pyrolyzed SiOC ceramics are provided in **Figure 1.1.(d)**, illustrating the characteristic volumetric shrinkage of PDC processing and the color change – the origin of the moniker ‘black glasses’ [9]. Near-net shaping of ceramics is also a promising advantage of PDC processing, leveraging advances in polymer lithography and additive manufacturing to produce complex SiOC parts and geometries (**Figure 1.1.(e)**) [12].

With the aforementioned properties, SiOC glasses are an attractive base for synthesis and fabrication of multifunctional advanced ceramics. Active and passive fillers incorporated in the preceramic phase imbue the resulting ceramic composite with magnetic [13, 14] and electric [15] properties, among others. Active fillers are additives that catalyze phase formation at high temperatures, while passive fillers generally are used to combat volumetric shrinkage and mass loss during pyrolysis [16]. Polymer-derived ceramics are a popular system for porous ceramic fabrication as pore structure, size, and distribution can be modified by methods such as use of sacrificial fillers [17, 18], phase separation from polymer precursors [19-21], replica templates [22, 23], incorporation of polymeric additives [24, 25], and selective etching of as-formed ceramic phases by controlling pyrolytic atmospheres and temperatures [25-28]. Porous SiOC ceramics have applications including catalyst supports, electrodes, gas separation membranes, thermal insulation, and lightweight structural materials [6, 29]. Engineering multifunctional properties in SiOC ceramics involves microstructural control of secondary phases that form in the amorphous matrix.

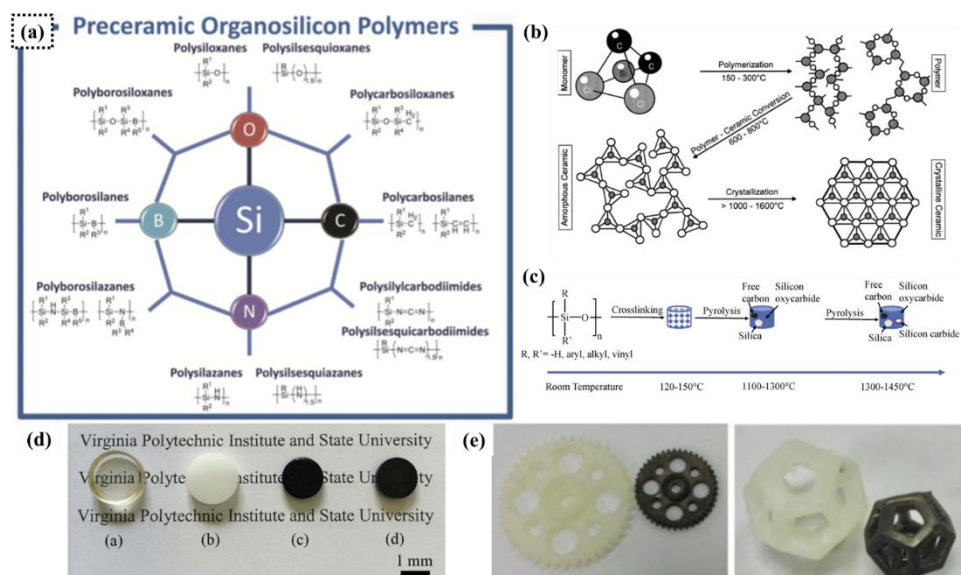


Figure 1.1.2: Overview of polymer-derived ceramic (PDC) and PDC-SiOC fabrication. (a) Variety of PDC classes that can be obtained through organosilicon preceramic polymers [11]; (b) general processing method for obtaining amorphous/crystalline ceramics from monomeric silane precursors [5]; (c) typical SiOC fabrication from a polysiloxane (PSO) precursor; (d) optical images of crosslinked PSO, crosslinked PSO with a SiO₂ filler, pyrolyzed SiOC, and pyrolyzed SiOC after HF etching. [9]; (e) SiOC ceramic parts produced by additive manufacturing of a modified PSO precursor. [12]

1.3. Two-Dimensional Nanomaterials

Classically defined with one physical dimension in the nanoscale, two-dimensional (2D) nanomaterials have unique properties compared to bulk analogs due to their high specific surface areas and inherent anisotropy [30]. Spurred by the discovery of graphene in the early 2000s, 2D nanomaterial research has expanded with the discovery of MXenes in the early 2010s and metal chalcogenides that have high electron mobility and high mechanical strength for potential applications in electronics and semiconductor industries. Top-down and bottom-up synthesis routes are used in 2D nanomaterial production with contrasting attributes. Top-down processing involves exfoliation or delamination of atomically-thin nanoflakes from a bulk precursor; common top-down methods include liquid-phase exfoliation, ion intercalation/exfoliation, and physical exfoliation [30]. While preferred for materials with weakly-held layers, top-down routes are hindered by lower control of nanoflake quality/morphology, low yield, and the introduction of different functional groups during processing. The primary advantage of bottom-up processing (e.g., molecular beam epitaxy, chemical vapor deposition, etc.) is the morphological and compositional control to yield atomically pure, defect-free, high quality 2D nanosheets. However, bottom-up fabrication methods have high material and equipment/capital costs and slow growth rates, which precludes further applications of 2D nanomaterials in bulk or composite materials. Two 2D nanomaterial systems are briefly discussed below: montmorillonite (a naturally-occurring clay that is comprised of stacked 2D nanolayers) and $\text{Ti}_3\text{C}_2\text{T}_x$ -MXene (a popular and emerging class of 2D transition metal carbides). Inherently ceramic materials, both montmorillonite and MXene nanosheets can be exfoliated through top-down methods and are interesting candidates as reinforcement phases in SiOC composites.

1.3.1. Montmorillonite (MMT)

First prominently utilized by the Toyota Research Group by incorporating into a nylon material to improve its thermal and mechanical properties [31, 32], montmorillonite (MMT) has been widely incorporated into polymer, carbon, and silica-based composites as an inexpensive nanostructured reinforcement. As shown in Figure 1.3.1(a), MMT is a naturally-occurring 2:1 layered aluminosilicate mineral, with stacked sheets of approximately 1 nm thickness comprising of an alumina octahedral sheet between two silica tetrahedral sheets [33-36]. Due to isomorphous substitutions of Mg^{2+} , Al^{3+} , and Fe^{2+} among the octahedral and tetrahedral sheets, the MMT layers

are inherently negatively-charged, and are balanced by low valence cations such as Na^+ and Ca^{2+} in the interlayer space [33, 35, 37]. As a result, MMT exhibits a well-known swelling capability in the presence of water through hydration of the interlayer cations [34-36, 38]. Furthermore, MMT sheets are held together only by weak electrostatic and van der Waals forces, so MMT is capable of exfoliating into distinct nanometer-thick sheets (Figure 1.3.1(b-c)) [35, 36]. MMT can be imbued with organic functionality [39-44] –contrasting from its inherent hydrophilic nature – through surface functionalization with long alkyl-chain surfactants [45-47] or silanes [40, 41, 48-50] of the terminal Si-O groups of the nanosheet. As an oxide material, MMT is a promising additive to SiOC due to the inherent material compatibility and the nanostructured morphology of both systems. Furthermore, the evolved oxide domains from high temperature decomposition of MMT can be selectively etched to yield templated porosity. However, methods for achieving exfoliated MMT nanocomposites are not completely reliable as the inherent MMT layer stacking tendencies yield agglomerated or intercalated structures.

In the automotive industry, MMT nanocomposites are used to improve the mechanical properties of plastics, providing materials that are lighter, stronger, and more durable. They are commonly employed in parts such as dashboards, door panels, and bumpers, where both strength and reduced weight are critical. MMT nanocomposites also show promise in improving barrier properties, making them ideal for packaging materials that need to resist oxygen, moisture, and other gases, extending the shelf life of food and pharmaceuticals. In the field of electronics, MMT nanocomposites have applications in conducting films, capacitors, and sensors. Their unique ability to modify the electrical conductivity of polymers opens up possibilities for flexible and lightweight electronic devices, such as wearable sensors and stretchable displays. In addition, their use in coatings provides protection against corrosion, electrical interference, and UV radiation, which is valuable in aerospace and marine applications. MMT nanocomposites are also being explored in environmental applications, such as water and air filtration systems, where their large surface area and high cation-exchange capacity allow for the adsorption of heavy metals, toxins, and pollutants.

1.3.2. MXene- $\text{Ti}_3\text{C}_2\text{T}_x$

Since its inception and discovery in 2011, the MXene class of 2D nanomaterials are promising materials due to their large specific surface areas, high electric conductivities, and

tunable characteristics through elemental engineering of evolved MXenes through the parent MAX phase [51-53]. With promising applications in energy storage [54-57], catalysis [58-61], water desalination [62, 63], sensing [64, 65], and electromagnetic shielding [66-68], MXenes are comprised of transition metal carbides (e.g., Ti_2CT_x , $\text{Ti}_3\text{C}_2\text{T}_x$, Nb_2CT_x , $(\text{V}_{0.5}\text{Cr}_{0.5})_3\text{C}_2\text{T}_x$), carbonitrides (e.g., Ti_3CNT_x) and nitrides (e.g., Ti_2NT_x , $\text{Ti}_4\text{N}_3\text{T}_x$), in which ‘M’ represents an early transition metal (e.g., Ti, V, Nb, Ta, Cr, Mo) and ‘X’ denotes carbon and/or nitrogen. Compositional control of MXene chemistry is directly imbued from the parent layered ternary MAX phases in which ‘A’ indicates a Group 13 or 14 element (e.g., Al, Si). MAX phases generally are of the form $\text{M}_{n+1}\text{AX}_n$ (space group $\text{P6}_3/\text{mmc}$), resulting in $\text{M}_{n+1}\text{X}_n\text{T}_x$ MXenes after selective chemical etching and exfoliation (Figure 1.3.1(d)) [51]. MXene nanosheets can be further exfoliated into $\sim 1\text{-}2$ nm thick sheets (Figure 1.3.1(e-f)). Of note in the latter formula, ‘ T_x ’ represents surface terminal groups (e.g., -O, -OH, -F) that emerge during chemical etching, impart hydrophilic functionality, and alter electronic and optical properties [69, 70]. Surface terminations offer potential sites for further modification or functionalization with intercalating agents [71-73], silanes [74-77], or metal nanoparticles [61, 78-81].

As the prototypical MXene, $\text{Ti}_3\text{C}_2\text{T}_x$ 2D nanomaterials are of particular significance due to their electrical conductivities reported from 1000 to 4000 S cm^{-1} [82, 83] and effective Young’s modulus of 0.33 TPa [84] for a single flake. In addition, thermal stability analysis of single-flake and multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ indicated that the two-dimensional morphology was retained up to 800°C, after which $\text{Ti}_3\text{C}_2\text{T}_x$ transformed to disordered carbon vacant cubic TiC_y [83, 85]. In the aforementioned study, $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets exhibited a significant increase in electrical conductivity from $\sim 800 \text{ S cm}^{-1}$ to $\sim 2000 \text{ S cm}^{-1}$ prior to and after calcination at 600°C in vacuum, respectively [83]. $\text{Ti}_3\text{C}_2\text{T}_x$ and other MXenes have enticing high temperature applications as either bulk materials or composite reinforcement, proving to be a popular and rapidly evolving research field. Apart from dedicated studies as nanoflakes, multilayered powders, or pressed discs, $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes are garnering interest as promising additive phases impart electronic [86, 87], photocatalytic [88, 89], electromagnetic shielding [90, 91], or sensing [92] attributes or improve corrosive resistance [77], flame retardancy/thermal stability [71, 93], or mechanical properties [94, 95] – among others – in a variety of ceramic [67, 88, 89, 92, 96] or polymer [86, 87, 94, 97-101] composite materials.

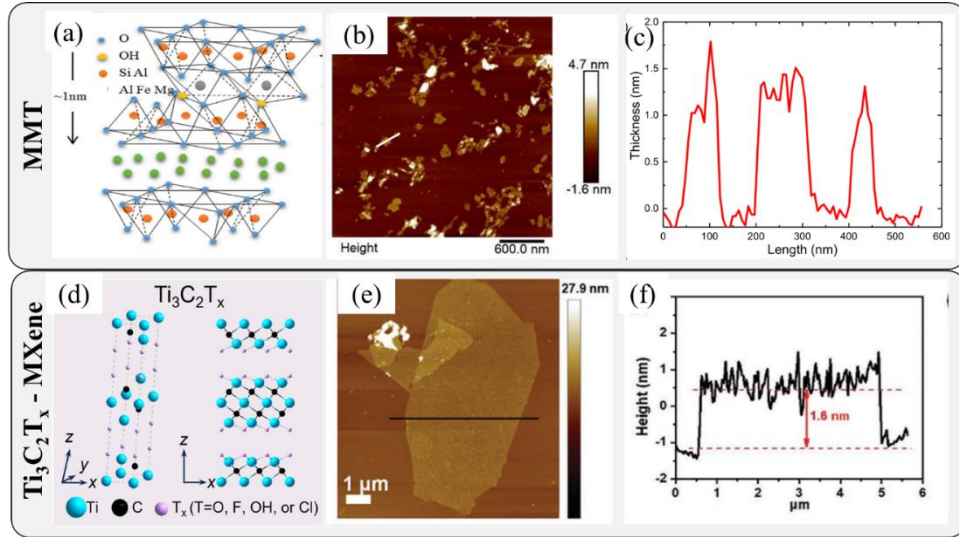


Figure 1.3.1: Crystallography and morphology of MMT and $\text{Ti}_3\text{C}_2\text{T}_x$ -MXene nanosheets. (a) crystallographic representation of MMT nanosheets indicating 2:1 stacking of SiO_2 and Al_2O_3 sheets with cations occupying the interlayer between nanosheets [102]; (b) AFM image of exfoliated MMT nanosheets [35]; (c) line profile of MMT nanosheets indicating $\sim 1\text{-}2\text{ nm}$ thickness and sheet widths from $50\text{-}100\text{ nm}$ [35]; (d) crystallographic representation of MXene nanosheets showing ordering of Ti, C, and surface group (T_x) atoms in both edge-on (left) and top-down (right) views; (e) AFM image of a delaminated MXene nanoflake [103]; (f) line profile from AFM image indicating sheet thickness of $\sim 1.6\text{ nm}$ and width of $\sim 4\text{ }\mu\text{m}$ [103].

1.4. Challenges

Further development and implementation of SiOC ceramics is limited by obtaining novel functionalities and understanding nanostructural phase formation and characteristics. While an amorphous ceramic, SiOC exhibits local (i.e., nanometer-scale) structural heterogeneity that has not been rigorously or thoroughly studied. Functional or novel nanocomposites have technical issues including agglomeration, material compatibility, and formation of by-products.

1.4.1. Functionality of SiOC Ceramics

Imbuing additional functionality in SiOC ceramics has been the focus of PDC-SiOC research over the last 30 years with active fillers; as such, there have been many published reports of *in-situ* 0D or quasi-1D nanostructured SiOC composites [104-107]. However, controlling *in-situ* phase formation is complicated by side-products formed thermodynamically during pyrolysis. For example, SiOC-Ni nanocomposites have promising catalytic and magnetic properties but only when containing Ni nanoparticle phases – the formation of nickel silicides (NiSi_y) has been shown to reduce SiC content and detract from the aforementioned properties [13]. Organometallic additives have been shown to yield metal oxide (ex. HfO_2), metal silicide (ex. Fe_3Si), or metallic (ex. Sn) nanoparticles dispersed in the SiOC matrix (Figure 1.4.1(a)). Organometallic additives to SiOC have been extensively studied ((Figure 1.4.1(b)) and either characterized or predicted to form their respective oxide, silicide, or metallic nanoparticle phases. The unique metallic phases present in these SiOC-M nanocomposites have been studied for improving magnetic, electric, or oxidative properties, among others. *Ex-situ* phases that do not contribute to phase evolution such as SiC, ZrO_2 , Al_2O_3 generally experience some size mismatch with the amorphous/nanocrystalline SiOC matrix. Figure 1.4.1(c) depicts cracks, pores, and material inhomogeneities in a SiOC-Al composite fabricated with 3 μm Al powder – typically forming due to an incoherent interface between the SiOC matrix and the bulk sized reinforcement phase. As a result, these phases act as inclusions rather than a homogenous continuous composite reinforcement. Nanosized fillers are available but at a much higher cost and with added complications of agglomeration and particle dispersion in the preceramic polymer. 2D nanomaterials are a promising candidate in PDC-SiOC ceramic composites as the intrinsic properties are retained (akin to *ex-situ* or passive fillers) but thermodynamically maintain some morphological coherency with the amorphous/nanocrystalline matrix (similar to active fillers) – however, to date there are practically no published findings of

2D SiOC ceramic nanocomposites. Novel material discovery and characterization of such nanocomposites would provide new insights and applications for SiOC ceramics.

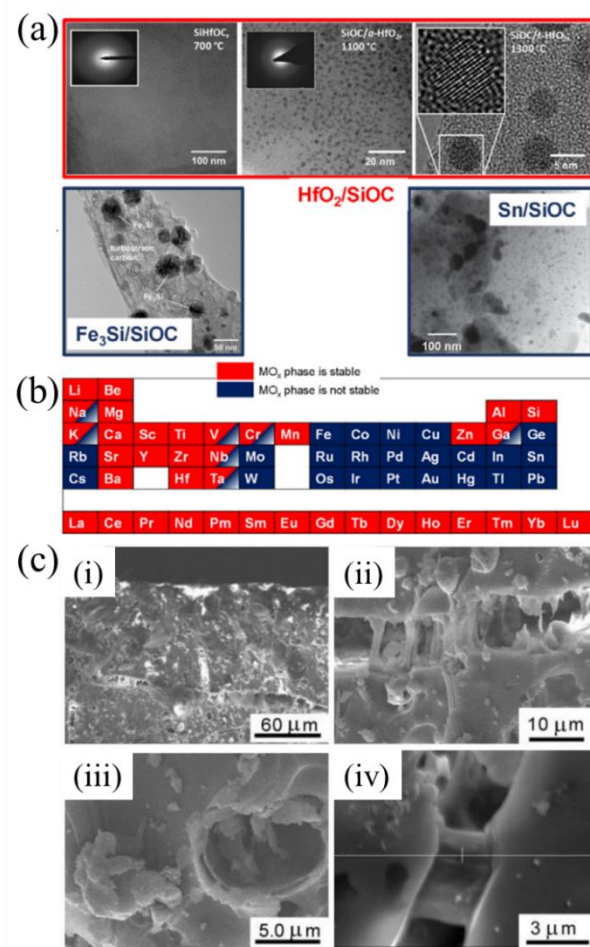


Figure 1.4.1: Overview of SiOC composites with nanostructured and bulk additives. (a) Example of SiOC-M composites prepared with organometallic precursors exhibiting *in-situ* formed nanosized metal oxide or silicide phases [12]; (b) table of studied metal additives in SiOC composites and classification of predicted stable MO_x (red) or M/MSi_y (blue) derived phases; (c) SiOC-Al composite prepared with bulk Al filler ($\sim 3 \mu\text{m}$) exhibiting pores, cracks, and other inhomogeneities [106].

1.4.2. Exfoliation and Dispersion of MMT and $\text{Ti}_3\text{C}_2\text{T}_x$ Nanoflakes

Emblematic of top-down processing, obtaining and retaining exfoliated nanoflake morphologies in MMT and $\text{Ti}_3\text{C}_2\text{T}_x$ remains a challenge for nanocomposite fabrication and characterization. Exfoliated nanocomposites are theorized to have higher mechanical strength as reinforcements are evenly distributed and do not behave as discontinuous inclusions in the matrix. Furthermore, the unique nanomaterial properties are lost in aggregated structures. MMT nanocomposite systems have long been studied but have not been reliably reported with exfoliated nanosheets but rather with intercalated or tactoid structures (Figure 1.5.1(a-b)). Commercially-available hydrophobic MMT is available that has been cation-exchanged with long alkyl-chain ammonium surfactants, but numerous studies have reported a mix of exfoliated and intercalated MMT in resulting composites. Little has been reported for colloidal processing of $\text{Ti}_3\text{C}_2\text{T}_x$ nanoflakes as most single-flake or “bulk” $\text{Ti}_3\text{C}_2\text{T}_x$ film studies have not utilized its exfoliated nature. For both MMT and $\text{Ti}_3\text{C}_2\text{T}_x$, improving the yield from a traditional top-down solution processing method is necessary to prepare enough sample for further bulk nanocomposite fabrication. With conventional yields of less than 10%, MMT and $\text{Ti}_3\text{C}_2\text{T}_x$ exfoliation needs to be optimized for better nanomaterial extraction as well as controlling the morphology for further surface functionalization. As MMT and $\text{Ti}_3\text{C}_2\text{T}_x$ are naturally hydrophilic, the surface chemistry needs to be modulated to promote re-exfoliation and dispersion in preceramic polymers which are predominantly hydrophobic. In preparing MMT and MXene composites, it is critical to obtain an exfoliated microstructure (Figure 1.5.1(c)) that fully utilizes the 2D nanostructured morphology; however, prior studies have been limited to intercalated or flocculated microstructure. This inherent material mismatch has precluded further examination and understanding of material properties in MMT/ $\text{Ti}_3\text{C}_2\text{T}_x$ nanocomposites.

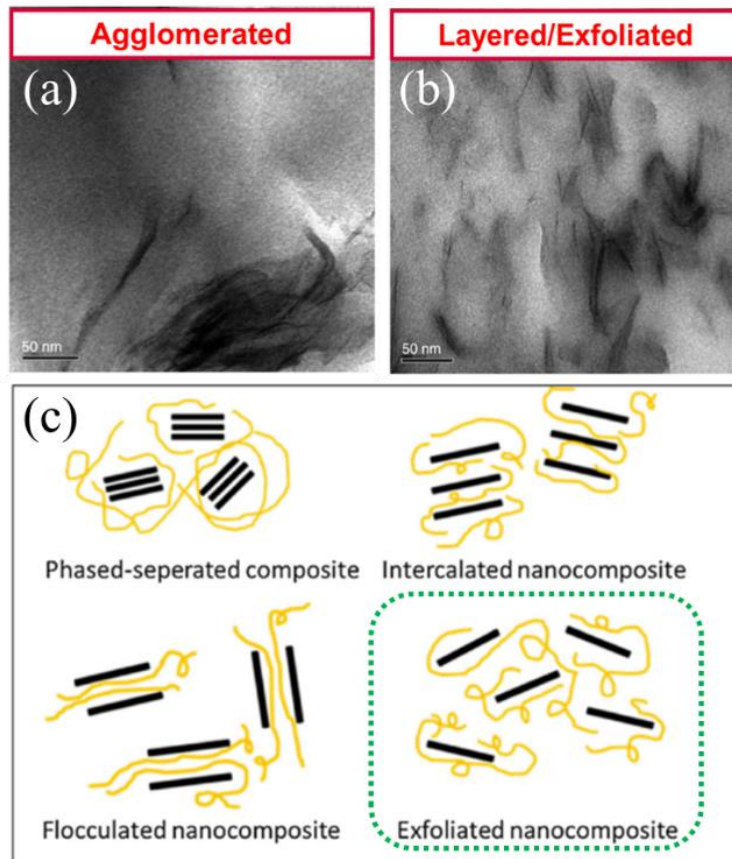


Figure 1.4.2: TEM micrographs of typical MMT nanocomposite morphologies showing (a) agglomerated and (b) layered/exfoliated MMT regimes in poly[(butylenesuccinate)-co-(butylene adipate)] composites [108]. (c) Overview of expected nanosheet composite morphologies showing a higher degree of nanoflake separation among phase-separated, intercalated, flocculated, and exfoliated nanocomposite microstructures [109].

1.4.3. Nanoscale Phase Evolution in SiOC Ceramics

While PDC development has existed for over 50 years, the phase evolution during the polymer-to-ceramic transition and the nanostructuring in the SiOC ceramic matrix is still not fully understood. Amorphous SiOC exhibits little electron contrast in typical SEM or TEM experiments. High-resolution electron microscopy capable of resolving sub-atomic phenomena is necessary to ascertain microstructural data; however, such technology is limited to the current state of detectors, cameras, and optics available. In addition, it has been postulated that SiOC ceramics may have some nanoscale heterogeneity due to ordering/clustering of Si tetrahedral units. As SiOC appears amorphous in most bulk characterization methods, this local amorphous ordering has not been appreciably studied or reported due to sub-nanometer resolution needed in electron microscopy experiments to deconvolute these features. There is also little examination of SiOC phase compositions as the matrix can be described as a mix of SiO₂, free carbon, SiC, and SiOC phases, in part due to lack of understanding of the governing thermodynamic phenomenon in SiOC phase evolution. Elucidating the nanostructural phase evolution in SiOC is important to enhancing the state of knowledge in PDC-SiOC systems and to improving the viability of SiOC in functional ceramic applications.

1.5. *Proposed Solution*

MMT-SiOC and Ti₃C₂T_x-SiOC are attractive high-temperature composite materials but little-to-no research has been published that has successfully integrated these nanoflakes into composite materials. In the case of MMT, the primary hindrance is to overcome the natural stacking tendency during composite preparation. While functionalization route with silanes and long-alkyl chain ammonium salt-exchanged bulk MMT have been shown to improve the concentration of exfoliated nanosheets, it still remains difficult to fully exfoliate these nanosheets from a bulk source solely through intercalation of organophilic functional groups.

In this dissertation, MMT-SiOC and Ti₃C₂T_x-SiOC composites were prepared by synthesizing organophilic nanoflakes through a novel exfoliation and twice-functionalization route (Figure 1.5.1(a)) that were studied as an additive phase to SiOC systems. In this method, nanoflakes were first isolated from their bulk/layered precursor through repeated cycles of freezing, thawing, and sonication (F/T/S). As MMT and Ti₃C₂T_x are both inherently hydrophilic and balanced by Na⁺ and Li⁺ cations, respectively, the F/T/S method leverages the swellability of MMT and Ti₃C₂T_x in

water through hydration shells and the volumetric expansion of water to saturate and separate layers from the bulk precursor. Exfoliated nanoflakes are isolated from layered analogs through centrifugation, and the colloidally-stable nanoflakes are subsequently treated with cetrilammonium bromide (CTAB) and 3-(2-aminoethyl)-aminopropyltrimethoxysilane (AEAPTMS) to create a covalently-bonded organophilic surface coating on the nanoflakes. As the nanoflakes are exfoliated in water and have high specific surface areas after exfoliation, the nanoflake surface energy is postulated to have too high to directly functionalize with AEAPTMS and may aggregate during reactions. CTAB is used akin to a capping agent for traditional nanoparticle synthesis to not only lower the surface energy for silane functionalization in organic media, but also prevent nanosheet agglomeration during processing. Silane grafting is not only predicted to promote nanoflake dispersion in the preceramic polymer, but also stabilize the nanosheet surface during pyrolysis of preceramic green bodies. The eventual SiOC-nanosheet composites are predicted to be dense with nanosheets stabilized in the SiOC matrix through an interfacial region (Figure 1.5.1(b)), which is theorized to bridge the coherency gap between the amorphous SiOC matrix and the crystalline nanosheets. Therefore, this dissertation will focus on synthesis and characterization of novel MMT-SiOC and $\text{Ti}_3\text{C}_2\text{T}_x$ ceramic nanocomposites to understand the effect of 2D nanoflake reinforcements on phase evolution and material properties.

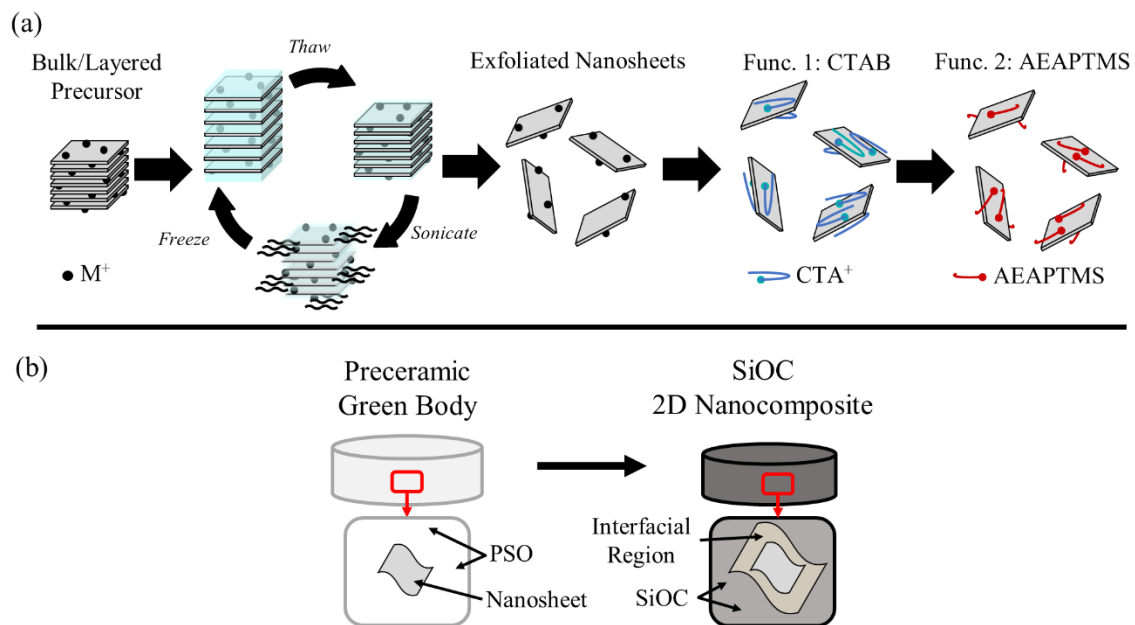


Figure 1.5.1: Schematic of proposed exfoliation and functionalization route for preparing organophilic nanoflakes with a covalently-bound silane surface group.

1.6. *Dissertation Objectives*

The aim of this work is the examination of microstructural evolution and material properties of SiOC ceramics and ceramic nanocomposites. The studies are predominantly experimental focusing on synthesis of novel SiOC composites with traditional fillers and novel MMT and $\text{Ti}_3\text{C}_2\text{T}_x$ 2D nanoflakes. In particular, this dissertation focuses on the synthesis of exfoliated and functionalized MMT and $\text{Ti}_3\text{C}_2\text{T}_x$ and subsequent MMT-SiOC and $\text{Ti}_3\text{C}_2\text{T}_x$ -SiOC nanocomposites and mechanistic understanding of phase evolution phenomenon. Specific aspects of the overall dissertation work are:

- (1) Improve fundamental understanding of phase evolution mechanisms in SiOC composites prepared with active and passive fillers. By examining the interactions between these fillers and the SiOC matrix, the goal is to identify the key factors that control phase stability, transformation temperatures, and the final material properties of the composite. In particular, the roles of Fe (active) and POSS (passive) in producing porous SiOC composites as a model system will be investigated. In addition, this work will develop thermodynamic models that correlate with phase content values obtained through elemental analysis techniques.
- (2) Develop methodology to synthesize exfoliated, organophilic MMT and $\text{Ti}_3\text{C}_2\text{T}_x$ nanoflakes for preparation of MMT-SiOC and $\text{Ti}_3\text{C}_2\text{T}_x$ -SiOC ceramic nanocomposites. As the SiOC matrix is amorphous/nanostructured, it is critical to produce additive phases that maintain size coherency with the evolving matrix. In course of developing these SiOC nanocomposites, a novel processing exfoliation and twice-functionalization route to exfoliate hydrophilic MMT and $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets from their respective bulk/layered precursors, and colloidally process the nanosheets to imbue organophilicity while maintaining the exfoliated structure, will be proposed and assessed with microstructural and chemical analysis techniques.
- (3) Investigate phase and microstructural evolution in MMT-SiOC and $\text{Ti}_3\text{C}_2\text{T}_x$ -SiOC nanocomposites, both during the polymer-to-ceramic transformation (400-800°C) and at elevated temperatures (900-1400°C). In particular, nanoscale interfacial phenomenon in both nanocomposite systems will be evaluated with advanced microstructural characterization techniques. In addition, MMT-SiOC ceramics will be assessed as potential candidates for porous ceramic applications through the effects of pyrolysis atmosphere

conditions (Ar vs. water vapor) on selectively-etched porosity. This dissertation will provide novel insight into synthesis and properties of MMT-SiOC and $\text{Ti}_3\text{C}_2\text{T}_x$ -SiOC nanocomposite systems, with further applicability in a wide range of polymer-derived ceramics.

Chapter 2: Porosity and Phase Content Modeling in SiOC-Fe Ceramics

2.1. *Abstract*

In this study, bulk and porous SiOC materials were synthesized via a polymer-derived ceramic (PDC) method from a base polysiloxane (PSO) precursor and an iron (Fe) catalyst under an inert pyrolytic atmosphere. Fe catalyzes not only the formation and nucleation of β -SiC at lower temperatures but also promotes phase separation of the amorphous SiO_xC_y phase, compared to PDCs without the Fe catalyst. Samples with Fe pyrolyzed at 1100°C have an appreciable β -SiC content compared to a negligible/unobservable β -SiC content in the corresponding Fe-less samples. Selective etching of the SiO_2 phase shows that Fe also induces segregation of the amorphous SiO_xC_y phase, yielding larger specific surface areas and gas sorption capability below 1300°C. At 1500°C, the pore structure changes to form interconnected networks due to the highly phase separated SiO_2 and β -SiC microstructure. A Gibbs free energy minimization method was used to determine the relative phase content of the pyrolyzed samples, with the effect of Fe quantified with simplified vapor-liquid-solid (VLS), solid-liquid-solid (SLS), and classical nucleation theories.

2.2. *Introduction*

Porous silicon oxycarbide (SiOC) ceramics have garnered interest for their excellent thermal stability [110-112], corrosion resistance [113], and thermomechanical properties [11, 114, 115] in potential high-temperature, aerospace, and abrasive applications [5, 11, 116]. In a typical PDC-SiOC synthesis method, the polymer-to-ceramic phase transformation initiates at 400°C with SiOC phases predominantly existing up to around 1300°C, which then gradually segregate to SiO_2 , β -SiC, and free carbon phases [117]. SiC prominently crystallizes at ~1500°C from the carbothermal reduction of SiO_2 and free carbon phases present in the SiOC matrix [117, 118] – these processing temperatures are generally needed to significantly realize a prominent SiC phase. Achieving bulk or porous SiC ceramics via PDCs thus remains an issue due to the high temperatures needed, low ceramic yield, and defect formation due to gas evolution and shrinkage during pyrolysis. The viability of bulk/porous SiC ceramics from polysiloxane precursors depends on the ability to lower the critical nucleation temperature for SiC.

Transition metal fillers have been shown to reduce the formation temperature of SiC through generation of transition metal carbides, silicides, and oxides. In addition to imparting ancillary properties for applications in catalysis [119, 120] and magnetism [121-123], transition metal active fillers such as Al [107, 124-127], Ce [120], Fe [14, 104, 121-123], Hf [105, 128-131], Ni [13], Ti [15, 16, 132-134], V [16, 104], and Zr [111, 135-137] have been incorporated into silicon-rich polymer precursors to improve or alter phase development. Based on some initial predictions by Ionescu et al. [104], these transition metal fillers can be further classified based on the metallic byproducts after pyrolytic conversion: metals that are reduced back to the elemental state, such as Au [104], Pd [138], Pt [119], and metals that form oxides, silicides, or carbides such as Fe [104, 121-123], Mg [139], Ni [13, 140], Ti [15, 132, 133], Hf [130], and Zr [136]. The relative stability of a metal oxide/silicide/carbide is dependent on the pyrolytic temperature and atmosphere as well as the precursor chemistry. In most of the mentioned systems, SiC nucleation was observed at lower temperatures than from an unmodified polymer system. Elucidation of the reaction pathways in which the nucleation temperature of SiC is reduced is critical. As of yet, understanding of the reaction steps and thermodynamic modelling has not yet been performed.

Fe is of interest for its ability to generate β -SiC at low temperatures, but previous studies used a relatively high weight content of Fe that led to higher iron silicide formation [121]. At high weight ratios of Fe to the base polymer, the catalytic effects of Fe were masked or overshadowed by secondary phase formation. By increasing the iron acetylacetonate ($\text{Fe}(\text{acac})_3$) concentration, SiC was shown to form at 1300°C with the simultaneous formation of iron silicides (Fe_xSi_y); Fe_xSi_y formation also induced magnetic functionality to the SiOC nanocomposite [121, 122]. The presence of Fe in the polymer precursor fostered the carbothermal reduction reaction by formation of Fe_xSi_y , Fe_xO_y , and Fe_xC_y crystallites in the SiOC matrix [141, 142]. It has also been reported that β -SiC is unstable in the presence of high concentrations of transition metals [140], which could be mitigated at a lower Fe content and has yet to be fully studied.

In addition to metallic fillers, organic fillers have been considered to mitigate processing issues common to PDCs including porosity, ceramic yield, and volume shrinkage. In general, the ceramic yield is on the order of 70%, which can hamper the viability of PDCs in large-scale applications. In a previous study, siloxane-based fillers were incorporated into a polysiloxane matrix to improve the ceramic yield [24]. Notably, octavinyl-polyhedral oligomeric silsesquioxane (POSS) – a caged siloxane additive – was shown to significantly improve the ceramic yield due to

enhanced SiO₂ nucleation and formation [24]. This SiO₂-rich precursor can be utilized in Fe-catalyzed systems to improve ceramic yield and drive β -SiC phase formation through carbothermal reduction of POSS-derived SiO₂ domains.

In this study, a low weight percent of Fe(acac)₃ was incorporated into a polysiloxane matrix along with a SiO₂-rich additive to investigate low temperature formation of SiC. Varying ratios of PSO to POSS were used to investigate and understand the catalytic effect of Fe in regard to β -SiC crystallization. The effects of composition and pyrolysis temperature were investigated using X-ray diffraction (XRD) and nuclear magnetic resonance (NMR) spectroscopy. The underlying thermodynamic and reaction pathways were proposed in order to predict the phase fractions in Fe-catalyzed SiOC systems and understand the mechanism of Fe-catalyzed β -SiC evolution. Phase content prediction from elemental composition was performed by a Gibbs free energy minimization program written in MATLAB.

2.3. *Experimental Methodology*

2.3.1. Materials and Methods

A commercially available polysiloxane Polyramic SPR-684 (PSO, [-Si(C₅H₆)₂O-]₃[-Si(CH₃)(H)O-]₂[-Si(CH₃)(CH=CH₂)O-]₂, Starfire Systems, Inc., Glenville, NY) was used as the base polymer precursor. Octavinyl-polyhedral oligomeric silsequioxane (POSS, OL1170, Hybrid Plastics, Hattiesburg, MS) was used as the additive in the base polymer, and iron (III) acetylacetonate (Fe(acac)₃, 97%, Sigma-Aldrich, St. Louis, MO) was chosen as the active filler. A 2.1% platinum-divinyltetramethyldisiloxane complex in xylene (Karstadt's catalyst, Gelest, Inc., Morrisville, PA) was used to crosslink the polymer precursor samples. Acetone (technical grade, Fisher Scientific, Waltham, MA) was used as a solvent to facilitate mixing and dispersion. Argon (Ar, Industrial Grade, AirGas, Radford, VA) was used as the pyrolysis atmosphere. Hydrofluoric acid (HF, 49% (aq), Avantor Specialty Materials Inc., Radnor, PA) was used as an etchant. Nanopure water (NP H₂O, 18.2 M Ω -cm) was used throughout the study. All chemicals were used as received without further purification.

Preceramic green bodies were prepared by mechanically stirring PSO with 0, 5, 10, or 15 wt% POSS (POSS content relative to total mass of PSO and POSS), 6.4 wt% Fe(acac)₃ (corresponding to 1 wt% Fe³⁺, and 100 pm of Karstedt's catalyst, and 5-10 mL of acetone until completely homogenous. A blank group without any Fe(acac)₃ or POSS was prepared similarly but without

acetone. The solutions were thoroughly degassed under vacuum, cast to $\Phi 12\text{mm} \times 5\text{ mm}$ cylindrical molds, degassed again, and cured at 60°C for 12 h and then 120°C for 12 h. The green bodies were polished and edges slightly beveled up to 1200 grit, and placed in a tube furnace (1830-12 Horizontal Tube Furnace, CM Furnaces, Inc., Bloomfield, NJ). Under an Ar atmosphere with a flow rate of $\sim 500\text{ cm}^3\cdot\text{min}^{-1}$, the green bodies were pyrolyzed at either 1100°C , 1300°C , or 1500°C by heating to the peak temperature at $2^\circ\text{C}\cdot\text{min}^{-1}$, holding for 2 h, and cooling to ambient temperature at $2^\circ\text{C}\cdot\text{min}^{-1}$. The pyrolyzed samples were denoted as xPOSS-1Fe or xPOSS-0Fe ($x = 0, 5, 10, \text{ or } 15$) for the samples with and without the Fe catalyst, respectively. The pyrolyzed samples were broken into $\sim 5\text{ mm}$ pieces and etched in a stirring 20% $\text{HF}_{(\text{aq})}$ solution at less than 10 wt% for at least 96 h until no mass loss was observed. Etched samples were thoroughly washed with NP H_2O and dried for 12 h at 120°C .

2.3.2. Characterization

The ceramic yield and volume shrinkage were calculated from changes in mass and volume, respectively, between the green bodies and pyrolyzed samples. Phase compositions were analyzed with an X'Pert PRO diffractometer (PANalytical B.V., EA Almelo, The Netherlands) with $\text{Cu K}\alpha$ radiation between $2\theta = 10\text{--}100^\circ$ with a scanning rate of $0.05^\circ/\text{s}$. Sample compositions were determined via combustion for C and optical emission spectroscopy (ICP-OES, Agilent 5110 ICP-OES, Agilent Technologies, Inc., Santa Clara, CA) for Si and Fe. Carbon combustion analysis was performed by Galbraith Laboratories, Inc. (Knoxville, TN). ICP-OES samples were prepared by borate fusion followed by acid digestion and dilution (Supporting Information I). The oxygen content was taken as the difference between the calculated masses for C, Si, and Fe and the total sample mass. The specific surface area, pore volume, and pore size distribution of the etched samples were evaluated by nitrogen adsorption at 77 K (Quantachrome Autosorb-1, Quantachrome Instruments, Boynton Beach, FL). Samples were degassed under vacuum at 300°C for 12 h prior to analysis. Non-Local Density Functional Theory (NLDFT) was applied to the adsorption branch with a cylindrical pore structure based on a silica adsorbate model. Single pulse MAS NMR spectra were measured using a Bruker Avance III NMR spectrometer at frequency of 59.627 MHz for ^{29}Si and a 4 mm rotor at MAS frequency of 10 kHz. The number of scans was 2500 or 5000. Single-pulse experiments used a $2.5\text{ }\mu\text{s}$ pulse width and 60 s recycle delay. ^{29}Si was calibrated by an external standard TMS (0 ppm).

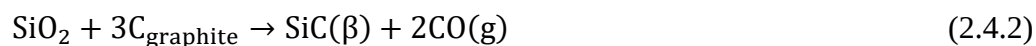
2.4. Results and Discussion

2.4.1. Phase evolution and physical properties

In pure SiOC systems, β -SiC formation has been postulated to occur through two processes: phase separation of amorphous SiOC or carbothermal reduction of phase separated SiO₂ and C [143]. In the former, phase separation of amorphous SiOC occurs from 1100°C to 1500°C to yield SiO₂, β -SiC, and graphitic/turbostratic C [121, 143, 144].



At higher pyrolytic temperatures than 1500°C, β -SiC is formed through carbothermal reduction of SiO₂ with evolution of CO [117, 118, 121, 143]:



The carbothermal reduction reaction proceeds through two steps, in which the second reaction is the rate-limiting step,



However, the presence of Fe lowers the critical temperature for β -SiC formation and has been postulated to occur through the formation of iron silicides (Fe_xSi_y). The pathway for Fe_xSi_y evolution – most prevalently Fe₃Si between 1000°C and 1300°C and Fe₅Si₃ above 1300°C – has been proposed to proceed through the phase separation and formation of FeO_x and Fe₃C intermediates [104, 121]. Upon pyrolytic conversion of the polymeric green bodies beginning at 600°C, a nominally single-phase SiFeOC undergoes phase separation into SiOC and FeO_x. In another study, Fe₃O₄ phases have been observed up to 600°C in an Fe-modified polycarbosilane system [123]. However, FeO_x is unstable in carbon-rich environments at this temperature and forms Fe₃C via carbothermal reduction. The conversion of Fe₃C to Fe₃Si occurs above ~770°C as Fe₃C is unstable in carburizing atmospheres [104, 145], and evolves into Fe₃Si upon reaction with SiO₂ and C:



Alternatively, it has been proposed that Fe₃C decomposes to elemental iron and graphite prior to formation of Fe₃Si [104]. As the Gibbs free energy change for the carbothermal reduction of FeO_x to Fe₃C is slightly lower than that of FeO_x to Fe [104, 121], it may be reasonably assumed that Fe₃C rather than elemental Fe is the ferrous intermediate generated prior to iron silicide formation.

The intrinsic decomposition of SiOC in Equation (2.1.3.1), removal of SiO₂ and C by-products in Equation (2.1.3.5), and added decomposition of the SiOC phase by Fe₃C can promote the growth of β -SiC. In the last scenario, such phase separation would also yield gaseous CO and SiO byproducts [122]. Above 1300°C, Fe₃Si can further induce crystallization of β -SiC through the following reaction [121]:



The effect of Fe and pyrolysis temperature are readily apparent in the XRD spectra (**Figure 2.4.1**). The spectra were normalized with respect to the $\sim 35.5^\circ$ peak, which was indexed as the (111) plane of β -SiC in order to qualitatively assess the effects of Fe and POSS contents and pyrolysis temperature. The peaks at 41° , 60° , and 72° were indexed as the (200), (220), and (311) planes of β -SiC, respectively. Broad graphite peaks were observed between 25° and 28° and at 44° . Minor reflections corresponding to iron silicides (Fe₃Si at 1100°C, Fe₅Si₃ at 1300°C and 1500°C) were observed in the Fe-containing samples between 45° and 47° . At 1100°C (**Figure 2.4.1(a)**), the catalyzing effect of Fe is immediately notable – the xPOSS-0Fe samples remain largely amorphous with little-to-no evidence of crystallized β -SiC, which agrees with prior studies [13, 24, 146]. The addition of Fe yields prominent crystallization of both graphite and β -SiC in all samples. At 1300°C (**Figure 2.4.1(b)**), β -SiC crystallization has initiated in the xPOSS-0Fe samples, as evidenced by broader peaks ($\sim 32^\circ$ - 38°) that are indicative of smaller crystallites. With the addition of Fe, the β -SiC phase is more prominent and the relative amorphous content decreases compared to the Fe-less samples. At 1500°C (**Figure 2.4.1(c)**), the sharpness and strength of the β -SiC peaks in the xPOSS-1Fe samples demonstrate substantial β -SiC crystallization as compared to unmodified samples. An amorphous SiO₂/SiO_xC_y/C halo in the 20° - 30° region is evident in the Fe-less samples at all temperatures and in the Fe-containing samples at 1100°C and 1300°C.

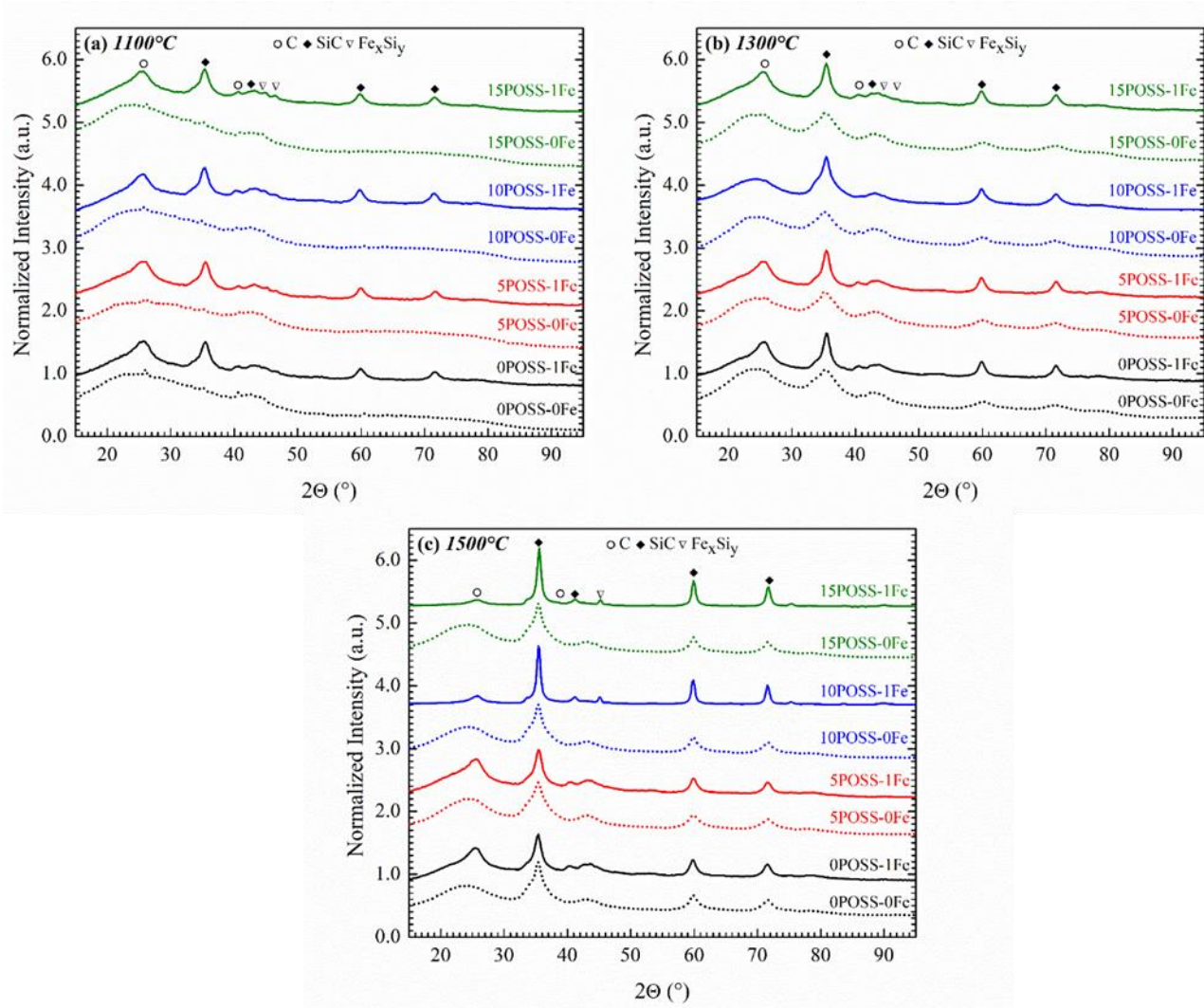


Figure 2.4.1: Normalized XRD spectra of pyrolyzed POSS-Fe samples in Ar at (a) 1100°C, (b) 1300°C, and (c) 1500°C of 0% (black), 5% (red), 10% (blue), and 15% (green) POSS-Fe samples. Solid lines refer to xPOSS-1Fe samples, dotted lines refer to xPOSS-0Fe samples. Spectra were normalized with respect to the intensity of the (111) β -SiC peak at $\sim 35.5^\circ$.

At both 1100°C and 1300°C, POSS does not influence β -SiC formation and predominantly contributes to more amorphous SiO₂ content. At 1500°C, POSS still remains a small contributor to amorphous SiO₂ formation in 0POSS-1Fe, 5POSS-1Fe, and all xPOSS-0Fe samples; however, in 10POSS-1Fe and 15POSS-1Fe samples, the β -SiC peak at $\sim 35.5^\circ$ is much sharper and stronger with a smaller graphitic carbon peak at $\sim 26^\circ$. At these POSS concentrations, the carbothermal reduction reaction of SiO₂ and C to β -SiC proceeds to a greater extent, potentially due to a higher probability of contact between SiO₂ and free C domains in the SiOC microstructure and the presence of better refined Fe-catalyzed β -SiC seeds/nucleation sites. Further β -SiC catalyzation from the conversion of Fe₃Si to Fe₅Si₃ also contributes to the enhanced phase refinement.

Compared to the spectra for the Fe-free samples, the graphite and β -SiC peaks are much sharper in the Fe-containing samples at each temperature, indicating a larger and more refined crystallite size. The sharpening of the graphitic peak at $\sim 26^\circ$ further indicates enhanced graphitization compared to the relatively disordered carbon in the Fe-less samples. The Scherrer equation can be used to estimate crystallite size (D) based on peak broadening (β):

$$D = \frac{0.9\lambda}{\beta \cos \theta_B} \quad (2.4.7)$$

in which λ is the wavelength of the incident Cu K α x-rays and θ_B is the diffraction Bragg angle. **Table 2.4.1** provides the mean crystallite size for β -SiC at 1100°C, 1300°C, and 1500°C for the different POSS concentrations. Little-to-no β -SiC could be detected at 1100°C in the xPOSS-0Fe samples, so the crystallite size is not calculated.

Table 2.4.1: Mean crystallite size (nm) of β -SiC after pyrolysis at 1100°C, 1300°C, and 1500°C. Average and standard deviation values were calculated from crystallite sizes determined from β -SiC peaks at 35.5°, 60°, and 72°.

Temp. (°C)	Mean β -SiC Crystallite Size (nm)							
	0POSS		5POSS		10POSS		15POSS	
	0Fe	1Fe	0Fe	1Fe	0Fe	1Fe	0Fe	1Fe
1100	---	5.2 $\pm$ 0.5	---	6.1 $\pm$ 0.6	---	6.0 $\pm$ 0.4	---	5.9 $\pm$ 0.3
1300	2.8 $\pm$ 0.3	7.2 $\pm$ 0.6	2.9 $\pm$ 0.2	6.9 $\pm$ 0.5	3.2 $\pm$ 0.5	7.2 $\pm$ 0.6	2.9 $\pm$ 0.3	6.6 $\pm$ 0.4
1500	5.4 $\pm$ 0.6	7.0 $\pm$ 0.4	4.3 $\pm$ 0.5	6.9 $\pm$ 0.5	5.6 $\pm$ 0.7	12.8 $\pm$ 0.6	5.8 $\pm$ 0.8	11.8 $\pm$ 0.6

The β -SiC mean crystallite size increases with the pyrolytic temperature in both Fe-containing and Fe-free samples as expected, due to the β -SiC formation from both SiO_xC_y phase separation and carbothermal reduction of SiO_2 . At all temperatures and POSS contents, the β -SiC crystallite size is larger in the Fe-containing samples. This further elucidates that Fe is responsible for β -SiC nucleation below 1100°C. These small nuclei in the Si-O-C microstructure provide energetically favorable sites for further nucleation/crystal growth and reduce the energetic barrier for β -SiC crystallization. At 1100°C and 1300°C, POSS does not appear to contribute to β -SiC crystallite growth. For the xPOSS-0Fe samples, the increase in the β -SiC crystallite size is mainly attributed to the SiOC phase separation and limited carbothermal reduction between 1100°C and 1500°C. For the xPOSS-1Fe samples, a relatively small change in the crystallite size between 1100°C and 1300°C indicates that the majority of the SiO_xC_y phase separation has occurred by 1100°C, with the process being nearly complete by 1300°C. Between 1300°C and 1500°C, the mean crystallite size for 0POSS-1Fe and 5POSS-1Fe is relatively constant; however, the crystallite size nearly doubles in the 10POSS-1Fe and 15POSS-1Fe samples. It is possible that the SiO_2 aggregation occurs due to a higher degree of proximity among SiO_2 domains evolved from either POSS degradation or SiO_xC_y phase separation. These larger domains could yield larger β -SiC crystallites upon carbothermal reduction. In a similar vein, the increased crystallite size could also occur from coarsening of β -SiC nanodomains formed after carbothermal reduction of SiO_2 nanodomains. As higher POSS content increases the contact probability between SiO_2 and free C and intrinsic proximity of SiO_2 nanodomains, the evolved β -SiC crystallites have a higher propensity to coalesce.

^{29}Si NMR was performed to quantitatively determine the relative amounts of SiO_2 , β -SiC, and amorphous SiO_xC_y (SiO_2 , $\text{SiO}_{3/2}\text{C}_{1/4}$, $\text{SiOC}_{1/2}$, $\text{SiO}_{1/2}\text{C}_{3/4}$) present in the pyrolyzed 0POSS-0Fe and 0POSS-1Fe samples. Due to the unique chemical environment around each Si nucleus, the amorphous SiO_xC_y phases can be differentiated. **Figure 2.4.2** depicts the ^{29}Si NMR spectra of the 0POSS-0Fe (dotted line) and 0POSS-1Fe (solid lines) samples pyrolyzed at 1100°C (black), 1300°C (red), and 1500°C (blue). The chemical shifts for SiO_2 , $\text{SiO}_{3/2}\text{C}_{1/4}$, $\text{SiOC}_{1/2}$, $\text{SiO}_{1/2}\text{C}_{3/4}$, and β -SiC of ~ -107 , -70 , -34 , 7 , and -11 ppm, respectively, were referenced from previous literature and studies [147-149]. At 1100°C, the 0POSS-0Fe sample (**Figure 2.4.2(a)**) has prominent amorphous SiO_2 and SiO_xC_y contents; however, upon addition of Fe (**Figure 2.4.2(b)**) there is notable phase separation to SiO_2 and β -SiC. At 1300°C, the Fe-less system (**Figure 2.4.2(c)**) has

undergone phase separation as well, but there is a higher proportion of β -SiC in the 0POSS-1Fe sample (**Figure 2.4.2(d)**) from growth of previously nucleated β -SiC seeds. At 1500°C, both samples are predominantly β -SiC but the 0POSS-0Fe sample (**Figure 2.4.2(e)**) still has some residual SiO₂.

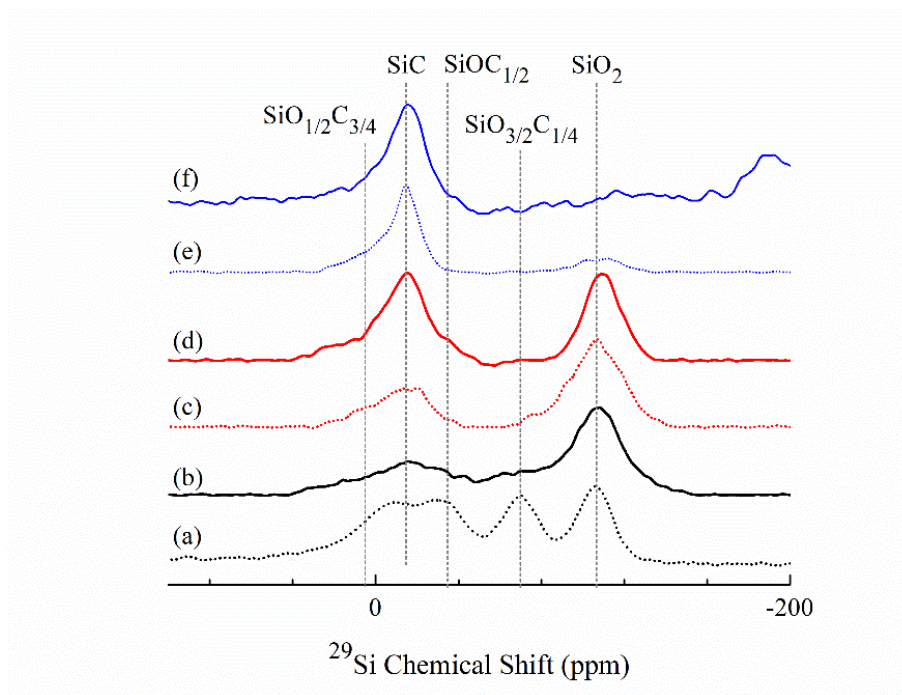


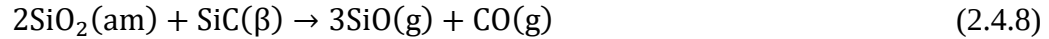
Figure 2.4.2: Normalized ^{29}Si NMR spectra of (a) 0POSS-0Fe (1100°C), (b) 0POSS-1Fe (1100°C), (c) 0POSS-0Fe (1300°C), (d) 0POSS-1Fe (1300°C), (e) 0POSS-0Fe (1500°C), and (f) 0POSS-1Fe (1500°C). Peaks I, II, III, IV, and V correspond to SiO_2 (-107 ppm), $\text{SiO}_{3/2}\text{C}_{1/4}$ (-70 ppm), $\text{SiOC}_{1/2}$ (-34 ppm), $\text{SiO}_{1/2}\text{C}_{3/4}$ (7 ppm), and SiC (-11 ppm) structural units, respectively. Spectra were normalized with respect to the most intense peak.

The relative phase fractions were obtained by fitting five Gaussian peaks to aforementioned chemical shifts to the experimental spectra (see Supporting Information S2) and are presented in **Table 2.4.2**. From the calculated phase fractions and qualitatively from the NMR spectra, Fe not only catalyzes β -SiC formation but also induces phase separation of the amorphous SiOC matrix, which has not been previously reported. In the unmodified SiOC systems, phase separation and carbothermal reduction are competing processes around 1300°C. With the addition of Fe, the decomposition of the amorphous SiOC matrix has nearly completed by 1300°C so there is more amorphous SiO₂ available to reduce to β -SiC. SiO₂ separation from the SiO_xC_y phase can also attribute to nanodomain aggregation to explain the larger β -SiC crystallite sizes in the 10POSS-1Fe and 15POSS-1Fe samples pyrolyzed at 1500°C. Therefore, Fe has been observed to not only lower the critical nucleation temperature of β -SiC and induce graphitization of free C, but also have an unexplored role in phase separation of amorphous SiO_xC_y. Because the concentration of Fe₃Si is very low, it could not be reasonably discerned in the ²⁹Si NMR spectra – this is corroborated by the low Fe content observed from elemental analysis. In the 0POSS-1Fe_1500 sample, the spectrum had high background noise that prevented more accurate peak fitting. While some of the SiO_xC_y intermediates are not expected to be appreciably present in this condition, fit peaks were forced through these peak centers as it was not readily apparent that these intermediates are present or absent.

Table 2.4.2: Calculated phase fractions of SiO_2 , $\text{SiO}_{3/2}\text{C}_{1/4}$, $\text{SiOC}_{1/2}$, $\text{SiO}_{1/2}\text{C}_{3/4}$, and $\beta\text{-SiC}$ from Gaussian peak fitting of ^{29}Si NMR spectra in **Figure 2.4.2** and the corresponding calculated (NMR) chemical composition.

Sample	Phase Content of SiO_xC_y Species (%)					Composition (Peak Fitting)
	SiO_2	$\text{SiO}_{3/2}\text{C}_{1/4}$	$\text{SiOC}_{1/2}$	$\text{SiO}_{1/2}\text{C}_{3/4}$	SiC	
0POSS-0Fe_1100	25.0	22.5	30.3	12.3	9.8	$\text{SiO}_{1.20}\text{C}_{0.40}$
0POSS-1Fe_1100	56.6	13.3	8.7	5.4	16.1	$\text{SiO}_{1.44}\text{C}_{0.28}$
0POSS-0Fe_1300	60	6.3	0.5	5.5	28.2	$\text{SiO}_{1.30}\text{C}_{0.33}$
0POSS-1Fe_1300	43.7	0.5	0.5	8.5	46.9	$\text{SiO}_{0.90}\text{C}_{0.52}$
0POSS-0Fe_1500	13.3	0.7	3.6	9.3	73.1	$\text{SiO}_{0.35}\text{C}_{0.79}$
0POSS-1Fe_1500	0.8	2.1	10.6	14.1	72.4	$\text{SiO}_{0.21}\text{C}_{0.85}$

Figure 2.4.3 depicts the ceramic yield (black) and volumetric shrinkage (blue) of the xPOSS-0Fe (dotted) and xPOSS-1Fe (solid) samples. The addition of POSS yields expected trends of increasing ceramic yield and decreasing volume shrinkage per an earlier study [24]. In general, the mass and volume losses of the Fe-containing samples are greater than those of the Fe-less samples. This may be attributed to CO evolution from the SiO₂ and C consumption in the Fe₃C to Fe₃Si conversion (Equation $\text{Fe}_3\text{C} + \text{SiO}_2 + \text{C}_{\text{graphite}} \rightarrow \text{Fe}_3\text{Si} + 2\text{CO(g)}$ (2.4.5) Between 1100°C and 1300°C, the yield remains relatively constant, indicating that any phase evolution is predominantly due to the phase separation of the amorphous SiOC matrix and there is no appreciable contribution from β-SiC formation via carbothermal reduction of SiO₂ and free C. However, at 1500°C, there is significant mass loss (yield decrease) in the presence of Fe while only a slight decrease is observed in the absence of Fe. As shown in **Figure 2.4.1**, the Fe-containing samples at 1500°C have more β-SiC phase so the mass loss should correspond to the crystallization and growth of β-SiC. The majority of β-SiC formation and mass loss is due to increased carbothermal reduction rate spurred by Fe-induced SiO₂ segregation. In addition to evolved CO (Equation $\text{SiO}_2 + 3\text{C}_{\text{graphite}} \rightarrow \text{SiC}(\beta) + 2\text{CO(g)}$ (2.4.2), additional mass loss above 1400°C may be attributed to the volatilization of SiO₂ and β-SiC phases [117]:



Saha et al. reported that crystallization kinetics and mass loss in SiOC systems are codependent and a function of the vapor pressure of CO in the system [117]. The higher β-SiC concentration at lower temperatures in the Fe-catalyzed samples can provide additional forward driving force for Equation $2\text{SiO}_2(\text{am}) + \text{SiC}(\beta) \rightarrow 3\text{SiO(g)} + \text{CO(g)}$ (2.4.8) and cause additional mass loss. Notably, the volumetric shrinkage of the Fe-containing sample does not significantly increase at 1500°C in a similar manner to the mass loss. These samples must then have pore formation as SiO and CO are evolved through Equations ($\text{SiO}_2 + \text{C}_{\text{graphite}} \rightarrow \text{SiO} + \text{CO(g)}$ (2.4.3) and ($2\text{SiO}_2(\text{am}) + \text{SiC}(\beta) \rightarrow 3\text{SiO(g)} + \text{CO(g)}$ (2.4.8) but the rigidity of the β-SiC network inhibits spontaneous sample shrinkage. Overall, the volumetric shrinkage for the Fe-containing samples is generally constant across the temperatures studied, indicating that any prominent mass loss events could yield some intrinsic porosity.

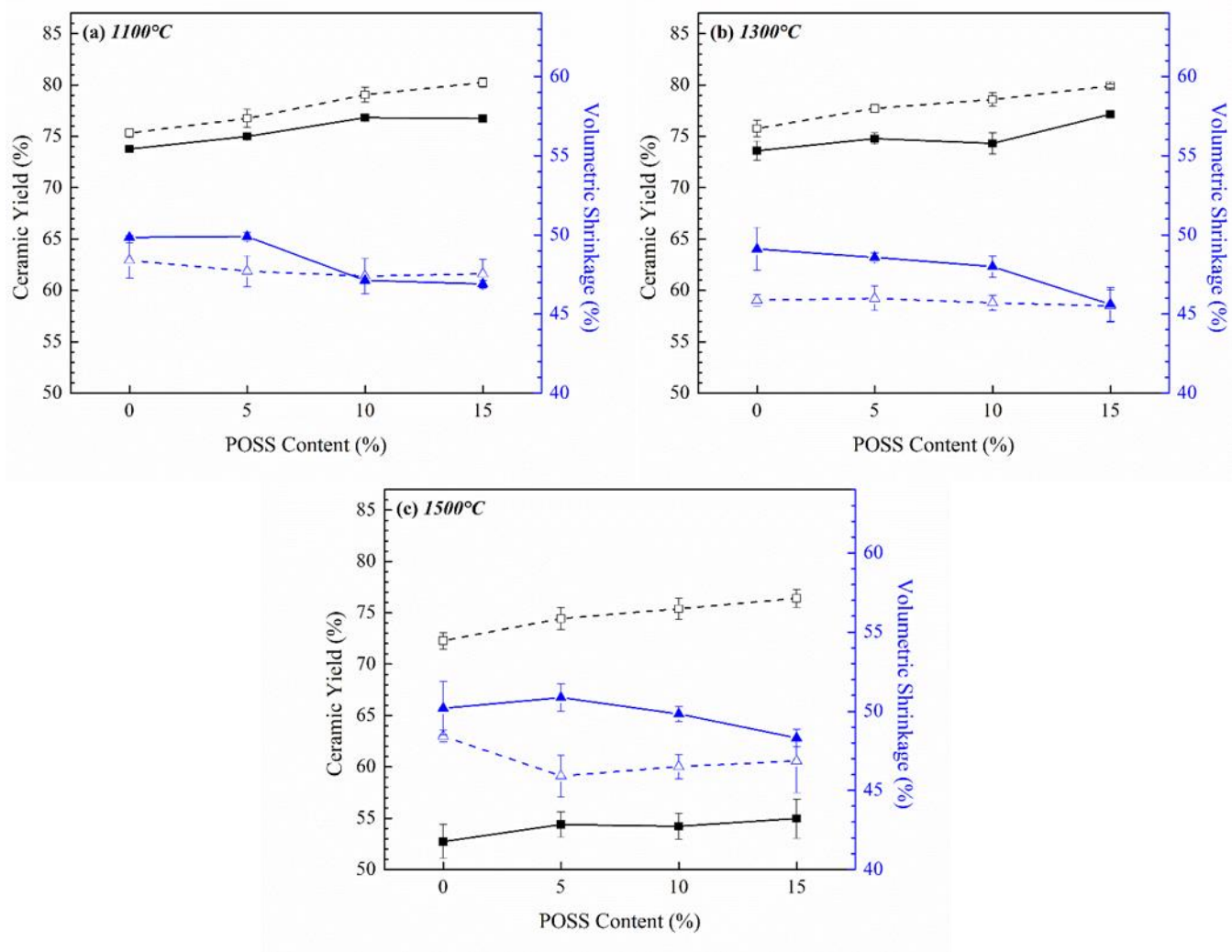


Figure 2.4.3: Ceramic yield (black) and volume shrinkage (blue) of pyrolyzed samples at (a) 1100°C, (b) 1300°C, and (c) 1500°C. Solid lines refer to xPOSS-1Fe samples, dotted lines refer to xPOSS-0Fe samples. Data points are averages of 4-6 samples and error bars indicate standard deviation.

2.4.2. Pore Size and Specific Surface Area of Porous SiOC/SiC

Porous SiOC/SiC structures are formed by selective etching of SiO₂ domains with HF. As SiO_xC_y and SiC (more specifically the Si-C bonds) are resistant to HF, mass loss and pore formation can be attributed to the size, concentration, and distribution of the SiO₂ domains, which are removed through the following reaction with a molar excess of HF:



Figure 2.4.4 shows the nitrogen sorption isotherms and pore size distributions for xPOSS-0Fe and xPOSS-1Fe pyrolyzed at 1100°C, 1300°C, and 1500°C after HF etching. The largest disparity is visible at 1100°C, with the HF-etched 0POSS-0Fe showing almost no adsorptive behavior (6.3 cm³/g at P/P₀ ~1) while the HF-etched 0POSS-1Fe has a gas adsorption volume of 206.7 cm³/g at P/P₀ ~ 1. Even though SiO₂ is present in the 0POSS-0Fe sample at 1100°C per the XRD and NMR results in Figures 2.1.3.1 and 2.1.3.2, the SiO₂ domains are most likely too small (less than 2-3 nm) to be accessed or etched by the HF solution. Due to the phase separation in the presence of Fe, the SiO₂ domains are more developed and thus can be successfully etched by HF. At 1300°C, phase separation has proceeded in the 0POSS-0Fe samples so sufficiently sized SiO₂ nanodomains can be etched. The gas adsorption volumes for 0POSS-0Fe and 0POSS-1Fe at 1300°C are 86.4 and 257.2 cm³/g, respectively, at P/P₀ ~ 1. At 1500°C, the gas adsorption volumes for 0POSS-0Fe and 0POSS-1Fe are 230.23 and 262.9 cm³/g, respectively. As expected, the gas adsorption volume increases with temperature in parallel with the growth of the amorphous SiO₂ phase. The volume adsorption difference between xPOSS-0Fe and xPOSS-1Fe samples decreases with increasing temperature, with nearly identical adsorption volumes at 1500°C although the pore structure is different. Up to 1300°C, Fe-catalyzed SiOC phase separation is the predominant mechanism for SiO₂ formation. From 1300°C-1500°C, intrinsic SiOC phase separation becomes more substantial and eventually the Fe catalyst effect becomes insignificant for SiO₂ formation. In addition, SiO₂ and C carbothermal reaction intensifies at high temperatures based on Equation (2.1.3.2), which can offset the Fe catalyst effect.

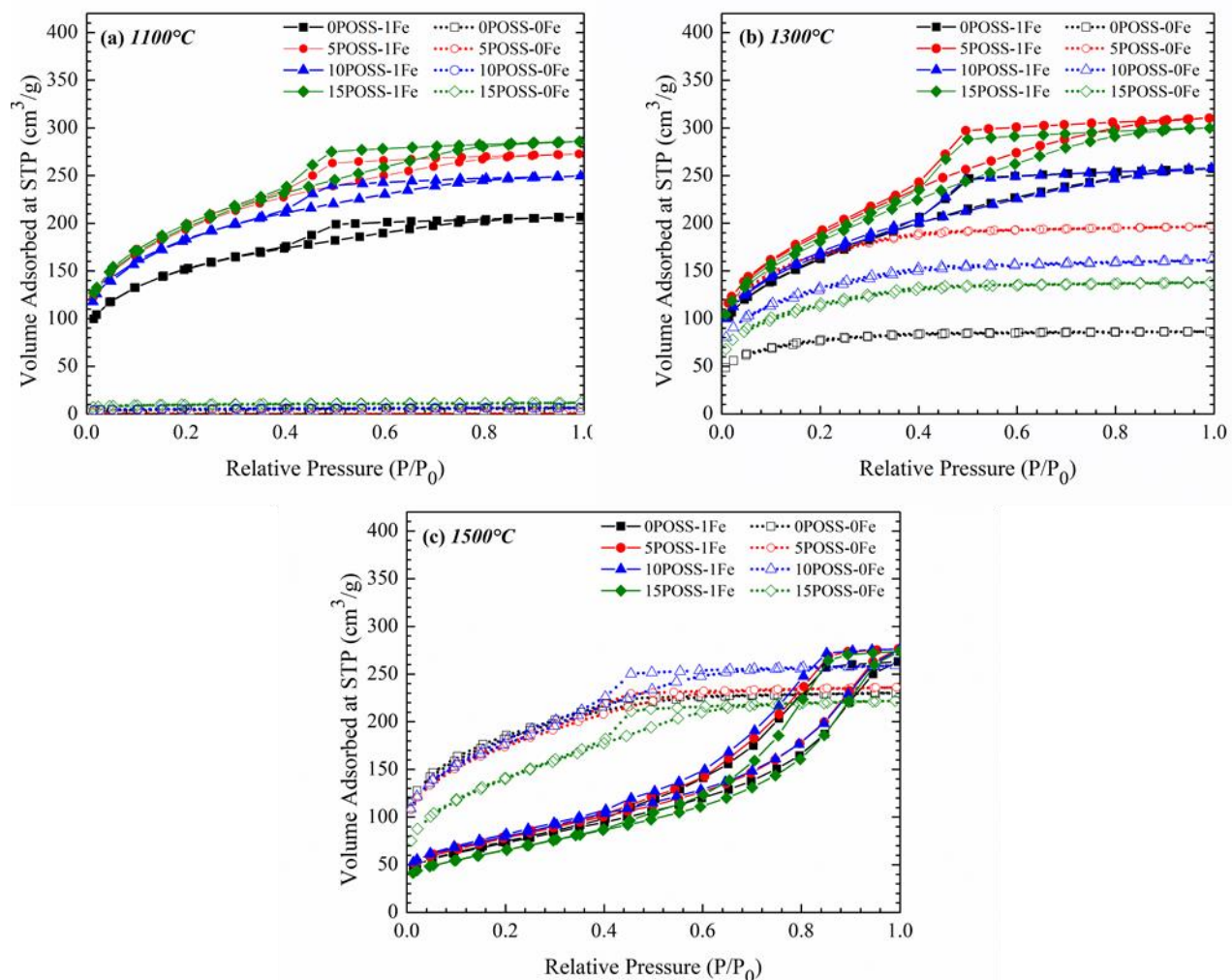


Figure 2.4.4: Nitrogen sorption isotherms of HF-etched 0% (black), 5% (blue), 10% (red), and 15% (green) POSS samples with Fe (solid line/solid symbols) and without Fe (dotted line/hollow symbols) at (a) 1100°C, (b) 1300°C, and (c) 1500°C.

In general, the addition of POSS increases the gas adsorption volume at 1100°C and 1300°C but with minimal difference at 1500°C for the samples with Fe. At 1100°C, the gas adsorption volumes of 0POSS-1Fe, 5POSS-1Fe, 10POSS-1Fe, and 15POSS-1Fe are 206.7, 272.6, 249.6, and 285.8 cm³/g, respectively. At 1300°C, the gas adsorption volumes of 0POSS-1Fe, 5POSS-1Fe, 10POSS-1Fe, and 15POSS-1Fe are 257.2, 310.3, 258.0, and 299.9 cm³/g, respectively. The decrease between 5% and 10% POSS could be due to the aggregation of either SiO₂ nanodomains from POSS or intrinsically formed SiO₂ domains [24]. At 1500°C, the gas adsorption volumes of 0POSS-1Fe, 5POSS-1Fe, 10POSS-1Fe, and 15POSS-1Fe are 262.9, 276.4, 276.2, and 274.1 cm³/g, respectively. Because the mesoporous structure observed at lower temperatures devolves into a wider pore distribution and forms interconnected channels due to SiO₂ domain aggregation, the overall gas sorption behavior becomes independent of the POSS content. Notably, the sorption curves for 0POSS-0Fe at all temperatures and 0POSS-1Fe at 1100°C and 1300°C show similar H4-type hysteresis behaviors, which is indicative of narrow slit-like pores. The sorption curve for 0POSS-1Fe at 1500°C shows H2-type hysteresis behavior, indicating there are both wide and narrow pores with possible interconnecting channels.

Pore size distributions are calculated from the adsorption branch, assuming cylindrical pore structures based on the NLDFT theory (Figure 2.1.5.2). While all samples except 0POSS-1Fe-1500°C exhibit slit-like pores, the small library of NLDFT on SiO₂ adsorbate models precluded analysis with either slit or hybrid slit/cylindrical pore structures. The pore sizes for xPOSS-0Fe at 1300°C and 1500°C and xPOSS-1Fe at 1100°C and 1300°C are all generally under 10 nm with most pores between 3-6 nm. As the SiO₂ nanodomains in the xPOSS-0Fe samples at 1100°C are sufficiently small/negligible to resist HF etching, no pores are detected through the NLDFT analysis. The xPOSS-1Fe samples at 1500°C lose the mesoporous structure observed in the other samples and have a wide distribution from 4 nm to over 20 nm, which leads to the degradation of the mesoporous network and formation of interconnected pore channels. In general, POSS appears to increase the concentration of pores between 4-10 nm.

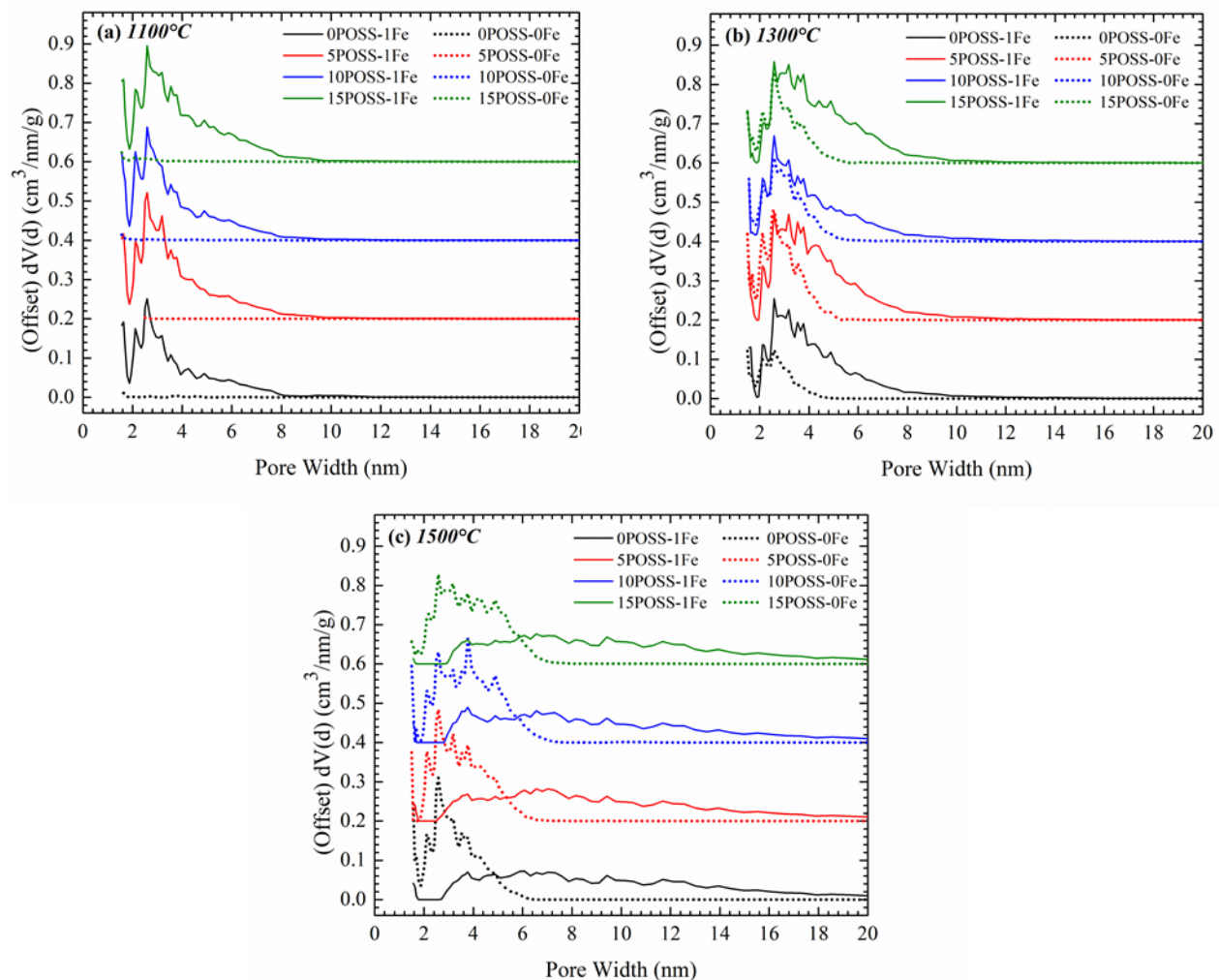


Figure 2.4.5: Pore size distributions of HF-etched 0% (black), 5% (blue), 10% (red), and 15% (green) POSS samples with Fe (solid line) and without Fe (dotted line) at (a) 1100°C, (b) 1300°C, and (c) 1500°C calculated from NLDFT theory. Distributions are offset for clarity.

The pore volumes and specific surface areas after HF etching are shown in Figure 2.1.5.3 as determined by the NLDFT theory. For the samples with Fe, the pore volume increases between 1100°C and 1300°C and is relatively constant from 1300°C to 1500°C. However, the specific surface area significantly decreases from 1300°C to 1500°C while remaining relatively constant from 1100°C to 1300°C. This phenomenon is also correlated to the formation of aggregated SiO₂ networks and domains that are removed after HF etching. For the xPOSS-0Fe samples, the pore volume and specific surface area all increase with temperature. In general, the pore volume of the xPOSS-1Fe samples remains relatively constant between 0.35-0.4 cm³/g between 1100°C and 1500°C, while the specific surface area decreases prominently between 1300°C and 1500°C from ~600 m²/g to ~250 m²/g. In the xPOSS-0Fe samples, the pore size generally increases from ~0.02 cm³/g at 1100°C, to ~0.12-0.3 cm³/g at 1300°C, and to ~0.35 cm³/g at 1500°C. Similarly, the specific surface area increases from ~40 m²/g, to ~300-600 m²/g, and to ~700 m²/g at 1100°C, 1300°C, and 1500°C, respectively. Notably, there is a much larger spread in pore volume and specific surface area values as a function of the POSS content in the xPOSS-0Fe samples at 1300°C compared to the xPOSS-1Fe samples. This can be attributed to the initial stages of SiO₂ phase separation from the amorphous SiOC matrix and agglomeration of POSS-derived SiO₂ nanodomains. At 1500°C, the xPOSS-0Fe samples generally have consistent pore volume and surface area values across the POSS values as the phase separated SiO₂ domains are more refined. POSS-derived SiO₂ nanodomain agglomeration at the 15POSS-0Fe condition could account for the observed decrease in specific surface area.

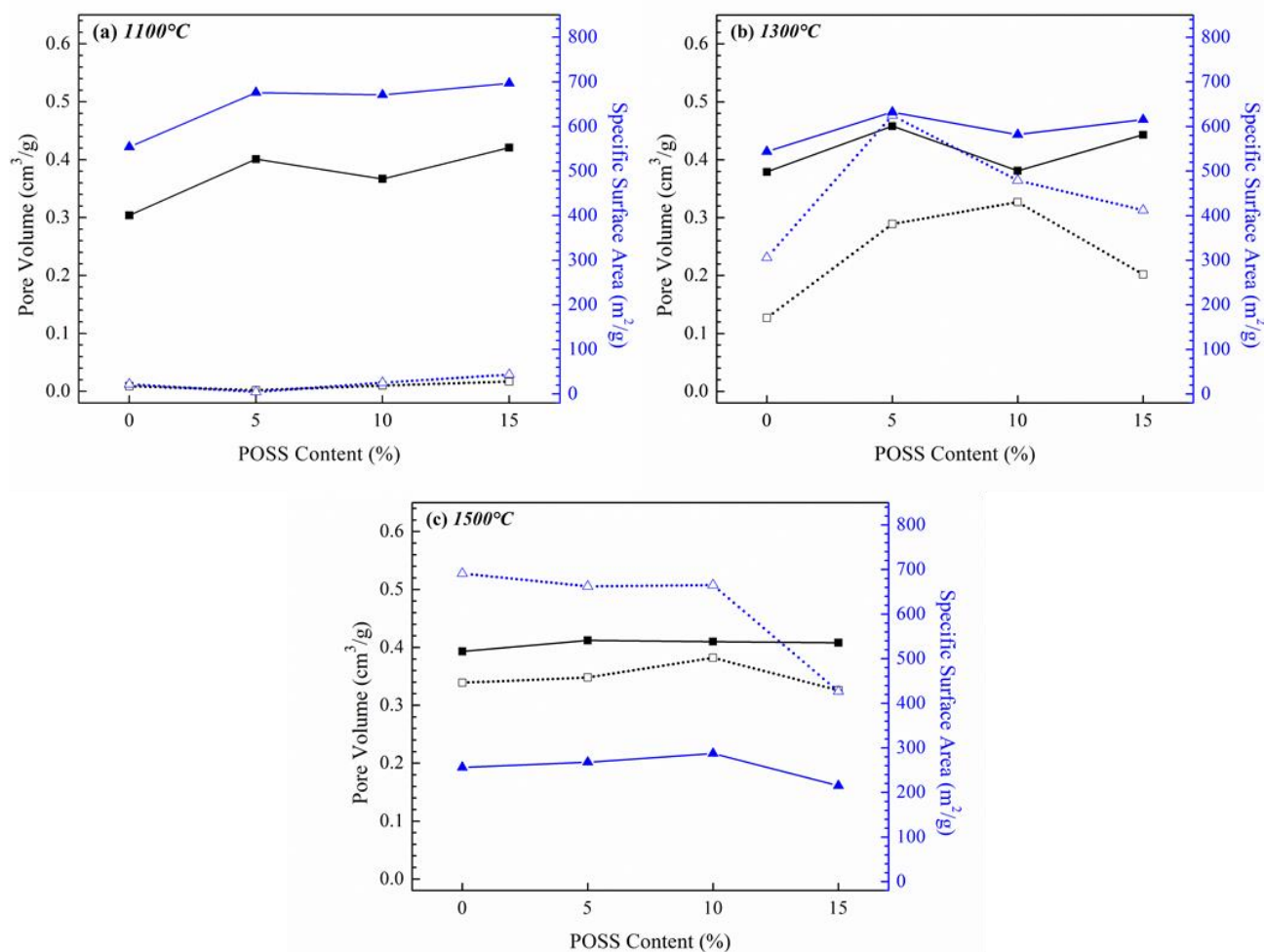


Figure 2.4.6: Pore volume (black) and specific surface area (blue) of HF-etched samples with Fe (solid line) and without Fe (dotted line) at (a) 1100°C, (b) 1300°C, and (c) 1500°C as a function of POSS content.

With the addition of POSS, the pore volume and specific surface area both increase. There is minimal change between 5% and 10% POSS concentrations for the Fe-containing samples and a decrease at 1300°C due to the aforementioned aggregation of the SiO₂ nanodomains prior to HF-etching. POSS content and temperature therefore have competing effects on pore characteristics, specifically in regard to the formation and distribution of SiO₂ nanodomains. At higher temperature and higher POSS content, SiO₂ nanodomains generated from POSS serve as the nucleation sites for the growth of the amorphous SiO₂ domains. However, these sites appear to lose coherency and begin aggregating at 10% POSS content, which contributes to the formation of pores between 5 and 10 nm per Figure 2.1.5.2a-b between 1100°C and 1300°C. In the samples without Fe, SiO₂ nanodomain formation in the absence of POSS only appreciably occurs above 1300°C, which explains why the sorption curves of Figure 2.1.5.2c show H4-type hysteresis instead of H2-type hysteresis as the interconnected pore network has yet to materialize.

2.4.3. Phase Content Modeling through Gibbs Free Energy Minimization

A computational model can be established to predict the relative phase content and understand the catalytic role of Fe in β -SiC nucleation and amorphous SiO_xC_y phase separation. Thermodynamic modeling of pure SiOC based on Gibbs free energy minimization has been performed in earlier work [143, 150] as well as in an analogous Si-C-N system [151]. In the current work, the catalytic generation of β -SiC by Fe is introduced. The goal of this model is to estimate the phase profile given the overall sample composition and the core thermodynamic phenomena. However, it should be noted that this model only considers phases between 1100°C and 1500°C pyrolysis temperatures and low Fe content (less than 5 mol%) as a higher Fe content would yield ancillary reactions and ferrous phase formation that requires more dedicated investigation into the relative reaction kinetics. Furthermore, this restriction keeps in line with the treatment of Fe as a catalyst—that does not appreciably contribute to the phase profile of the pyrolyzed ceramics. In addition, this model assumes that the system is sufficiently carbon-rich so Fe_xSi_y formation occurs via consumption of Fe₃C rather than FeO_x derivatives.

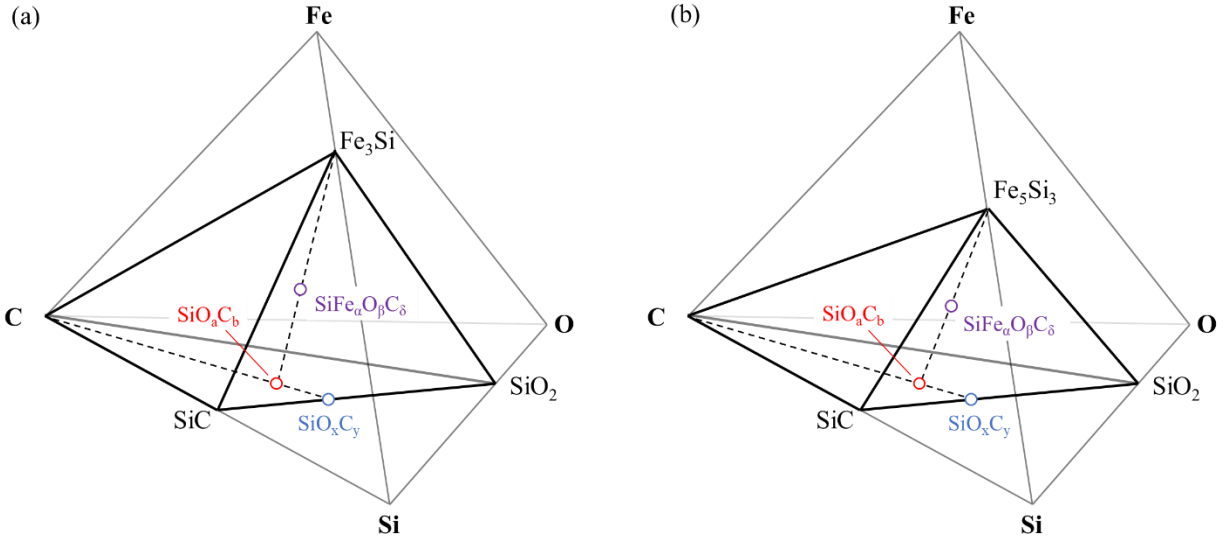


Figure 2.4.7: Schematic phase diagrams of Si-Fe-O-C quaternary system and phase separation of a nominal $\text{SiFe}_\alpha\text{O}_\beta\text{C}_\delta$ into (a) Fe_3Si , C, SiC, SiO_2 , and SiO_xC_y (1100-1300°C) or (b) Fe_5Si_3 , C, SiO_2 , SiC, and SiO_xC_y (1300-1500°C).

A sample with an overall composition of $\text{SiFe}_\alpha\text{O}_\beta\text{C}_\delta$ may be first treated as nominally-single phase, which then undergoes phase separation to yield $\text{Fe}_3\text{Si}/\text{Fe}_5\text{Si}_3$, C, SiC, SiO_2 , and SiO_xC_y phases. **Figure 2.4.7** gives schematic Si-Fe-O-C phase diagrams that show the bounds for the $\text{SiFe}_\alpha\text{O}_\beta\text{C}_\delta$ system such that Fe_3Si (a) or Fe_5Si_3 (b) exists in equilibrium with SiC, SiO_2 , SiO_xC_y , and free C phases. In either case, phase separation is modeled to proceed from the nominally-single phase $\text{SiFe}_\alpha\text{O}_\beta\text{C}_\delta$ to Fe_iSi_v and amorphous SiO_aC_b . SiO_aC_b further separates to free C and amorphous SiO_xC_y , here represented without excess C. Of note on the Si-O-C plane, the SiO_aC_b system is bounded by region C-SiO₂-SiC, and SiO_xC_y exists on the tie-line between SiC and SiO_2 . This final amorphous SiO_xC_y phase is the combination of SiC, SiO_2 , and intermediate $\text{SiO}_{(4-i)/2}\text{C}_{i/4}$ (for $i = 1$ to 3) phases along the SiC-SiO₂ tie-line. The relative amounts of each $\text{SiO}_{(4-i)/2}\text{C}_{i/4}$ phase along with SiC and SiO_2 are temperature-dependent.

The overall phase separation can be expressed as

$$\text{SiFe}_\alpha\text{O}_\beta\text{C}_\delta \Rightarrow f_M \text{Fe}_3\text{Si} + f_C \text{C}_{\text{free}} + (1 - f_M - f_C) \text{SiO}_x\text{C}_y \quad (2.4.10)$$

in which f_M and f_C refer to the fractions of the Fe_3Si and free C phases, respectively. For simplicity, only Fe_3Si is considered in the following derivation as the procedure is similar for Fe_5Si_3 and the phase fraction is expected to be quite low for either silicide. Since Si and O compositions along the C-SiO_xC_y tie-line are constant, it is evident that the O coefficient on either side of $\text{SiFe}_\alpha\text{O}_\beta\text{C}_\delta \Rightarrow f_M \text{Fe}_3\text{Si} + f_C \text{C}_{\text{free}} + (1 - f_M - f_C) \text{SiO}_x\text{C}_y$ (2.4.10) is the same:

$$\beta = x \quad (2.4.11)$$

As SiO_xC_y can be expressed as $\text{SiO}_{(4-i)/2}\text{C}_{i/4}$ to satisfy the stoichiometric constraints imposed on the SiC-SiO₂ tie-line, then the relationship between x and y can be identified as:

$$y = \frac{4-2x}{4} = \frac{4-2\beta}{4} \quad (2.4.12)$$

Therefore, the free C phase fraction is the stoichiometric difference between C in the SiO_xC_y and the nominal $\text{SiFe}_\alpha\text{O}_\beta\text{C}_\delta$ phases:

$$f_C = \frac{\delta - y}{1 + \alpha + \beta + \delta} = \frac{\delta - \frac{4-2\beta}{4}}{1 + \alpha + \beta + \delta} = \frac{0.5\beta + \delta - 1}{1 + \alpha + \beta + \delta} \quad (2.4.13)$$

Due to the restraint that only the Fe_3Si phase forms, then the phase fraction of Fe_3Si is

$$f_M = \frac{\frac{1}{3}\alpha}{1+\alpha+\beta+\delta} \quad (2.4.14)$$

The final phase separation event is SiO_xC_y along the SiO_2 -SiC tie-line into a combination of SiO_2 , SiC, and intermediate $\text{SiO}_{(4-i)/2}\text{C}_{i/4}$ (for $i = 1$ to 3) phases, in which f_0 , f_1 , f_2 , f_3 , and f_4 refer to phase fractions of SiO_2 , $\text{SiO}_{3/2}\text{C}_{1/4}$, $\text{SiOC}_{1/2}$, $\text{SiO}_{1/2}\text{C}_{3/4}$, and SiC, respectively:

$$\text{SiO}_x\text{C}_y \Rightarrow f_0 \text{SiO}_2 + f_1 \text{SiO}_{\frac{3}{2}}\text{C}_{\frac{1}{4}} + f_2 \text{SiOC}_{\frac{1}{2}} + f_3 \text{SiO}_{\frac{1}{2}}\text{C}_{\frac{3}{4}} + f_4 \text{SiC} \quad (2.4.15)$$

Whereas the phase fractions of Fe_3Si and free C are largely based on stoichiometric coefficients, the relative phase fractions of the five Si-O-C phases are codependent and should represent the most stable configuration based on the pyrolytic temperature. This configuration is related to the minimized Gibbs free energy of the total phase-separated amorphous system, represented as:

$$G_{\text{total}} = \sum_i [f_i(T) * G_i(T) + RT(f_i(T) * \ln(f_i(T)))] \quad (2.4.16)$$

in which $G_i(T)$ is the Gibbs free energy of amorphous phase i (for $i = 0$ to 4) as a function of temperature. The Gibbs free energy of amorphous SiC and SiO_2 is taken from available data [143, 151, 152] for the crystalline analogs and the vitrification energy, ΔE , to account for the loss of crystallinity:

$$G^{\text{am}}(T) = G^{\text{cr}}(T) + \Delta E \quad (2.4.17)$$

In order to account for the varied stoichiometries, a normalization factor n_{Form} equal to the number of atoms in the formula (e.g., $n_{\text{Form}}(\text{SiO}_2) = 3$, $n_{\text{Form}}(\text{SiC}) = 2$, etc.) is introduced, per an earlier analogous study [151]. In maintaining with prior convention, all Gibbs energies are expressed with units $[\text{kJ}/\text{M}_{\text{fu}}]$ obtained by $\frac{G_i}{n_{\text{Form}}}$. Then for ΔE of 6.9 and 54 kJ/mol for SiO_2 and SiC, respectively [143], the Gibbs free energies of amorphous SiO_2 and SiC as a function of temperature are

$$G_{\text{SiO}_2}^{\text{am}}(T) = G_0^{\text{am}}(T) = G_{\text{SiO}_2}^{\text{cr}}(T) + 2.3 \left[\frac{\text{kJ}}{\text{M}_{\text{fu}}} \right] \quad (2.4.18)$$

$$G_{\text{SiC}}^{\text{am}}(T) = G_4^{\text{am}}(T) = G_{\text{SiC}}^{\text{cr}}(T) + 27 \left[\frac{\text{kJ}}{\text{M}_{\text{fu}}} \right] \quad (2.4.19)$$

The Gibbs free energies of the intermediate amorphous SiO_xC_y phases are calculated as the summation of the number of constituting Si-O or Si-C bonds assuming a tetrahedral structure in the amorphous matrix and the energies of the constituting Si-O or Si-C bonds. These bond energies are approximated as a quarter of the total bonds about a Si atom in one tetrahedral unit of the respective crystalline form:

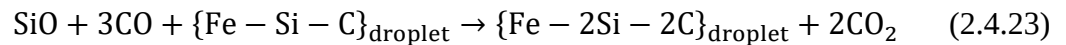
$$G_{\text{SiO}_3\text{C}_1}^{\text{am}}(T) = G_1^{\text{am}}(T) = \frac{1}{4}G_{\text{SiC}}^{\text{am}}(T) + \frac{3}{4}G_{\text{SiO}_2}^{\text{am}}(T) \quad (2.4.20)$$

$$G_{\text{SiOC}_1}^{\text{am}}(T) = G_2^{\text{am}}(T) = \frac{1}{2}G_{\text{SiC}}^{\text{am}}(T) + \frac{1}{2}G_{\text{SiO}_2}^{\text{am}}(T) \quad (2.4.21)$$

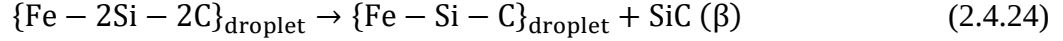
$$G_{\text{SiO}_1\text{C}_3}^{\text{am}}(T) = G_3^{\text{am}}(T) = \frac{3}{4}G_{\text{SiC}}^{\text{am}}(T) + \frac{1}{4}G_{\text{SiO}_2}^{\text{am}}(T) \quad (2.4.22)$$

The catalytic effect of Fe locally reduces the energetic barrier to β -SiC nucleation. In other Si-Fe-O-C systems, SiC nanowire growth has been observed with a Fe-Si droplet at the tip of the nanowire [153-160]. Fe was similarly observed to catalyze both HfC [161] and Si_3N_4 [162] nanowire formation with the presence of a Fe-rich droplet at the tip of each nanowire, which furthers the notion that an intermediate ferrous alloy generated in the matrix catalyzes metal carbide nucleation through the vapor-liquid-solid (VLS) mechanism. In other studies, energy dispersive X-ray spectroscopy (EDS) confirmed that the droplet at the tip of SiC nanowires was primarily comprised of Fe and Si [156-158]. However, in studies of Fe-catalyzed SiC nanowire growth, the nanowires were free to grow from a substrate – generally in chemical vapor deposition experiments [155] or porous media [153, 157] – and were not restricted by a solid matrix. As solid-state diffusion is slow and especially limited in the pyrolyzed SiFeOC ceramic samples, nanowire growth is neither expected nor observed in this study. This treatment assumes the β -SiC growth is from the very initial stages of VLS/SLS nanowire growth, but is restricted by both the dense microstructure and high solid-state diffusional barriers. Classical-nucleation and VLS/SLS growth theories can be approximated and adapted to model SiC formation.

In the carbon-rich SiOC matrix, Fe_3C nominally exists at $\sim 700^\circ\text{C}$ prior to conversion to Fe_3Si . In addition, Fe_3C was not observed in XRD spectra in a previous study [104] and EDS performed on Fe alloy droplets found on SiC nanowires only showed Fe and Si, as mentioned earlier. Therefore, the VLS mechanism most likely proceeds through a liquid Fe-C-Si alloy that quenches to Fe_3Si per Equation $\text{Fe}_3\text{C} + \text{SiO}_2 + \text{C}_{\text{graphite}} \rightarrow \text{Fe}_3\text{Si} + 2\text{CO}(\text{g})$ (2.4.5) after available reactants are consumed. The gaseous precursors for the VLS mechanism would be SiO and/or CO evolved from the reaction of SiO_2 and C (Equation $2\text{SiOC} \rightarrow \text{SiO}_2(\text{am}) + \text{SiC}(\beta) + \text{C}_{\text{graphite}}$ (2.4.1)). SiO and CO diffuse into the Fe-C-Si alloy droplet – denoted as $[\text{Fe-Si-C}]_{\text{droplet}}$ – leading to supersaturation of Si and C in the droplet.



SiC precipitation is then driven by the supersaturation of Si and C in the droplet.



It is also possible that some SiC is formed from the reduction of evolved SiO with C from Equation

$$\text{SiO} + 2\text{C}_{\text{graphite}} \rightarrow \text{SiC}(\beta) + \text{CO}(\text{g}) \quad (2.4.4)$$

and more CO is evolved from the reaction between CO₂ and C



This CO evolution also explains in part the origin to the ceramic yield discrepancies between Fe-containing and Fe-free samples. The corresponding SLS contribution could account for the enhanced phase separation of the amorphous Si-O-C matrix to yield SiO₂ and β -SiC. It is postulated that free C diffusion into the Fe_xSi_y droplet is more likely than SiO_xC_y diffusion due to the inherent stability of the amorphous ceramic. Sufficient C supersaturation is then thought to yield β -SiC, with the remnant Fe-C droplet quenching to Fe₃Si per Equation $\text{Fe}_3\text{C} + \text{SiO}_2 + \text{C}_{\text{graphite}} \rightarrow \text{Fe}_3\text{Si} + 2\text{CO}(\text{g})$ (2.4.5)

when the available reactants are depleted. However, dedicated atomistic modeling would be required to confirm or verify this process and what is presented is merely a potential mechanism. In practicality, the catalytic process is a hybrid of VLS and SLS mechanisms, with SLS believed to occur at lower temperatures in the dense microstructure and VLS occurring at higher temperatures as internal pores form due to gas evolution and transport.

From classical nucleation theory, the steady-state nucleation rate (J_0) increases as energetic requirement for nucleation (ΔG_{Nucl}) decreases,

$$J_0 = A e^{-\frac{\Delta G_{\text{Nucl}}}{k_B T}} \quad (2.4.26)$$

in which A is a pre-exponential factor, k_B is Boltzmann's constant, and T is absolute temperature. The critical energy barrier can be further expressed as:

$$\Delta G_{\text{Nucl}} = \frac{16\pi\gamma_{LV}^3}{3(\Delta G_v)^2} \frac{2-3\cos\theta+\cos^3\theta}{4} \quad (2.4.27)$$

with γ_{LV} the interfacial surface energy between the liquid catalyst droplet and the precursor vapor/solid phase, θ the contact angle between the deposited solid phase and liquid catalyst droplet, and ΔG_v the Gibbs free energy change per unit volume of the solid phase. ΔG_v can be further defined as:

$$\Delta G_v = -\frac{k_B T}{\Omega \ln(1+\sigma)} \quad (2.4.28)$$

in which Ω is the molar volume, and σ the degree of supersaturation. Due to the lack of available data regarding solid-solid interfacial energies of Si-O-C derivatives and the thermodynamic complexity of the ternary Fe-Si-C liquid catalyst, several approximations are made to estimate the energetic contribution of VLS/SLS-mediated SiC formation, specifically that of the interfacial energy and supersaturation. A contact angle of 135° is assumed based on previous studies that investigated the wettability and interfacial energy of Cu and Ni on SiC [163] and microstructures of Fe_xSi_y -capped SiC nanowires. In the aforementioned system, Sn and Ni droplets were also studied on SiC with interfacial energies between 1.5 to 3.0 J m^{-2} . When computed for the SiC-liquid interface, the interfacial energy between the liquid droplet precursor vapor/solid phase is approximated as 1 J m^{-2} , as it is difficult to differentiate the prevailing growth mechanism. Furthermore, the surface energies of Au nanoparticles ($<10 \text{ nm}$) was computationally modeled and reported between 0.5 and 1 J m^{-2} [164], so such an approximation may be accepted for this nanoscale system.

While supersaturation is usually presented as the ratio of excess solute concentration to the equilibrium concentration, the complexity of simultaneous C and Si supersaturation in the alloy droplet (needed to nucleate SiC per the Fe-C-Si phase diagram near the liquidus temperature [165]) cannot be reasonably derived in available thermodynamic and kinetic models. For VLS nanowire systems, an estimated supersaturation has been postulated with regards to the critical nanowire (d_{cr}) and as-grown nanowire (d_{NW}) diameter [166]:

$$\Sigma \approx 2 \frac{\Omega_{at} \gamma_{SL}}{k_B T} \left[\frac{1}{d_{cr}} - \frac{1}{d_{NW}} \right] \quad (2.4.29)$$

in which Ω_{at} is the atomic volume of the nanowire and γ_{SL} is the interfacial energy between the nanowire and the liquid droplet. Similarly, for the nanoparticle system, γ_{SL} is assumed as 1 J m^{-2} . Based on the crystallite size in **Table 2.4.1** between 1100°C and 1300°C in the 0POSS-0Fe condition, the β -SiC nuclei that form intrinsically from phase separation can be roughly correlated as the critical size. In the 0POSS-1Fe condition, β -SiC nucleation has initiated at 1100°C with crystallite sizes of $\sim 5 \text{ nm}$ which indicates that the critical barrier had been surpassed at the initial stages of quasi-nanowire growth. For this analysis, the critical nuclei and observed nanoparticle sizes are roughly approximated as $d_{cr} \approx 2 \text{ nm}$ (all temperatures) and $d=d_{NW} \approx 5 \text{ nm}$ (1100°C) or 7 nm (1300 - 1500°C), respectively. However, in actuality the size may be lower but cannot be

verified due to instrument detection limits. Further nanostructure or atomistic modeling studies can be performed to refine these values, but are accepted with the intention of providing baseline model parameters. Then, the Gibbs free energy of the SiC phase is the combined contributions from SiC formed by phase separation and nucleation factors:

$$G'_4(T) = G_4^{\text{am}}(T) - n_{\text{Nucl}} \Delta G_{\text{Nucl}} \quad (2.4.30)$$

in which n_{Nucl} is a normalization factor to account for the molar ratio of Fe and the atomic units in stoichiometric $\text{SiFe}_\alpha\text{O}_\beta\text{C}_\gamma$ for the aforementioned unit convention.

$$n_{\text{Nucl}} = \frac{\alpha}{1+\alpha+\beta+\delta} \left(\frac{1}{1+\alpha+\beta+\gamma} \right) = \frac{\alpha}{1+\alpha+\beta+\delta} \left(\frac{1}{2+\alpha+0.5\beta} \right) \quad (2.4.31)$$

Here, MATLAB has been used to perform the Gibbs energy minimization calculation (See Supporting Information S4), and the predicted phase fractions based on the sample composition from elemental analysis (e.g., ICP-OES, carbon combustion) for 0POSS-0Fe and 0POSS-1Fe samples at 1100, 1300, and 1500°C are presented in **Table 2.4.3** (E.A. (calc)). In addition, the predicted phase fractions were generated from the calculated sample compositions from NMR analysis in **Table 2.4.2** (NMR (calc)). As neither Fe_3Si nor Fe_5Si_3 could be observed in the NMR spectra, the Fe content from the corresponding elemental analysis is used to generate the expected phase content. The corresponding phase fractions obtained from NMR peak fitting analysis (**Table 2.4.2**) are also presented for comparison (NMR (peak fit)). For the 0POSS-0Fe_1100 sample, the phase content from elemental analysis could not be calculated by this model due to an abnormally high O coefficient, which will be discussed later. The calculated phase content from both E.A. and NMR agree fairly closely with the phase fractions obtained from NMR peak fitting for the 0POSS-1Fe_1100 sample. In general, the phase profiles calculated from the NMR composition and observed via NMR peak fitting agree and follow expected trends. However, there is some difference in the expected SiO_2 and $\text{SiO}_{3/2}\text{C}_{1/4}$ content between the two NMR values, with peak fitting giving higher SiO_2 and lower $\text{SiO}_{3/2}\text{C}_{1/4}$ phase fractions than the calculated value. In these cases (specifically the 0POSS-0Fe_1300, 0POSS-1Fe_1300, and 0POSS-0Fe_1500 samples), it is interesting that the sum of the two phases from the calculated profile approximately equal that from the peak fit profile (e.g., for 0POSS-1Fe_1300 sample, SiO_2 (42.6%) + $\text{SiO}_{3/2}\text{C}_{1/4}$ (21.2%) $\approx$ SiO_2 (60.0%) + $\text{SiO}_{3/2}\text{C}_{1/4}$ (6.3%)). This indicates there is some intrinsic SiO_xC_y phase separation occurring in this regime, which can be implemented in future models upon study. The NMR peaks for SiO_2 (~107 ppm) and $\text{SiO}_{3/2}\text{C}_{1/4}$ (~64 ppm) are reasonably distinct so it is not believed that

peak deconvolution issues significantly caused this discrepancy. The phase content variations for the intermediate SiO_xC_y phases increase with temperature, and this may be attributed to detection limitations and high background noise present in the NMR spectra.

Table 2.4.3: Predicted phase content of SiO_xC_y species for 0POSS-0Fe and 0POSS-1Fe samples at 1100, 1300, and 1500°C calculated from Gibbs energy minimization performed in MATLAB. Calculated phase content is given for compositions obtained from elemental analysis (E.A.) and NMR. The phase content obtained from NMR peak fitting (Table 2) is provided for reference.

Sample	Composition		Phase Content of SiO_xC_y Species (%)				
			SiO_2	$\text{SiO}_{3/2}\text{C}_{1/4}$	$\text{SiOC}_{1/2}$	$\text{SiO}_{1/2}\text{C}_{3/4}$	SiC
0POSS-0Fe_1100	$\text{SiO}_{2.405 \pm 0.003} \text{C}_{3.259 \pm 0.004}$	E.A. (calc.)	--	--	--	--	--
	$\text{SiO}_{1.20}\text{C}_{0.40}$	NMR (calc.)	39.1	19.6	9.9	5.0	26.5
		NMR (peak fit)	25	22.5	30.3	12.3	9.8
0POSS-1Fe_1100	$\text{SiO}_{1.483 \pm 0.002} \text{C}_{4.924 \pm 0.006}$ ($\text{Fe}_{0.013}$)	E.A. (calc.)	54.0	26.7	7.9	3.0	14.5
	$\text{SiO}_{1.44}\text{C}_{0.28}$	NMR (calc.)	52.8	19.8	7.4	2.8	17.3
		NMR (peak fit)	56.6	13.3	8.7	5.4	16.1
0POSS-0Fe_1300	$\text{SiO}_{1.457 \pm 0.001} \text{C}_{4.489 \pm 0.003}$	E.A. (calc.)	50.7	21.9	9.5	4.1	13.9
	$\text{SiO}_{1.30}\text{C}_{0.33}$	NMR (calc.)	42.6	21.2	10.5	5.2	20.5
		NMR (peak fit)	60	6.3	0.5	5.5	28.2
0POSS-1Fe_1300	$\text{SiO}_{1.313 \pm 0.001} \text{C}_{4.436 \pm 0.002}$ ($\text{Fe}_{0.016}$)	E.A. (calc.)	43.9	20.9	9.9	4.7	20.7
	$\text{SiO}_{0.90}\text{C}_{0.52}$	NMR (calc.)	26.9	15.9	9.4	5.6	42.1
		NMR (peak fit)	43.7	0.5	0.5	8.5	46.9
0POSS-0Fe_1500	$\text{SiO}_{1.133 \pm 0.002} \text{C}_{4.439 \pm 0.006}$	E.A. (calc.)	33.7	20.2	12.1	7.2	26.9
	$\text{SiO}_{0.35}\text{C}_{0.79}$	NMR (calc.)	5.9	6.9	8.1	9.5	69.6
		NMR (peak fit)	13.3	0.7	3.6	9.3	73.1
0POSS-1Fe_1500	$\text{SiO}_{0.485 \pm 0.001} \text{C}_{3.310 \pm 0.001}$ ($\text{Fe}_{0.019}$)	E.A. (calc.)	10.2	9.7	9.2	8.7	62.2
	$\text{SiO}_{0.21}\text{C}_{0.85}$	NMR (calc.)	3.2	4.1	5.2	6.6	81.0
		NMR (peak fit)	0.8	2.1	10.6	14.1	72.4

While the overall phase content trends generally agree in **Table 2.4.3**, the difference between the NMR calculated and peak fit phase content for the 0POSS-0Fe_1100 sample is quite large and starkly different than the other samples. For the phase fractions calculated in **Table 2.4.3**, the Gibbs energy minimization program used reference values for amorphous SiO₂ ($G_{\text{SiO}_2}^{\text{am}}(T)$) and crystalline SiC ($G_{\text{SiC}}^{\text{cr}}(T)$), which are the prevailing phases in this temperature range. Per the XRD spectrum in **Figure 2.4.1(a)**, the 0POSS-0Fe_1100 sample is generally amorphous, so these assumptions may not truly apply. The phase content was recalculated using reference amorphous SiO₂ ($G_{\text{SiO}_2}^{\text{am}}(T)$) and SiC ($G_{\text{SiC}}^{\text{am}}(T)$) and presented in **Table 2.4.4**. As a result, the phase profile more closely matches the NMR peak fit profile but has slight deviations for the SiO_xC_y phases. Further model development is needed to determine the transition point between the applicability of either amorphous or crystalline SiC Gibbs energy reference values, but can be assumed that below 1100°C that the amorphous value better represents the SiOC system.

Table 2.4.4: Predicted phase content of SiO_xC_y species for 0POSS-0Fe_1100 using reference $G_{\text{SiO}_2}^{\text{am}}(\text{T})$ and $G_{\text{SiC}}^{\text{am}}(\text{T})$ values in the Gibbs energy minimization model. Phase contents calculated using reference $G_{\text{SiO}_2}^{\text{am}}(\text{T})$ and $G_{\text{SiC}}^{\text{cr}}(\text{T})$ values (Table 2.4.3) and from NMR peak fitting (Table 2.4.2) are provided as reference.

Sample	Composition	Reference Values	Phase Content of SiO_xC_y Species (%)				
			SiO_2	$\text{SiO}_{3/2}\text{C}_{1/4}$	$\text{SiOC}_{1/2}$	$\text{SiO}_{1/2}\text{C}_{3/4}$	SiC
0POSS-0Fe_1100	$\text{SiO}_{1.20}\text{C}_{0.40}$	SiO_2 (am) - SiC (am)	28.8	23.5	19.2	15.7	12.8
		SiO_2 (am) - SiC (cr)	39.1	19.6	9.9	5	26.5
		<i>NMR (peak fit)</i>	25	22.5	30.3	12.3	9.8

Although the initial results are promising, the discrepancies between NMR and elemental analysis compositions preclude a true direct comparison. Due to the low concentration, Fe_xSi_y content could not be discerned due to high signal-to-noise ratio. In this vein, low concentrations of any SiO_xC_y clusters may not be discernable or correctly modeled with the peak fitting algorithm. Significant peak broadening due to the nanodomain SiO_xC_y clusters can also mitigate proper peak fitting results. As Si NMR detects unique bonding environments, this might not directly correlate to truly realized or refined phases. Rather, the bonding environments in the amorphous structure most likely are a few nanometers of the Si atom. Furthermore, the C and Si contents in **Table 2.4.3** are measured using different techniques (ICP-OES and carbon combustion). Overall, **Table 2.4.3** shows that the calculated phase fractions for SiC are lower than those from the NMR characterization. In all samples except 0POSS-1Fe_110C, the O coefficient is larger than that obtained from NMR peak fitting, with the discrepancy increasing with temperature. In this model, a higher O coefficient yields more SiO_2 content generally at the expense of SiC. As the O coefficient was calculated as the residual from 100% from obtained Si, Fe, and C values, this corresponds to the Si amount from ICP being reported lower than expected (assuming the C values from combustion are true). While solutions were analyzed by ICP on the same day as preparation, it is believed that some amount of SiO_2 can polymerize and precipitate from the digestion solution even when CsCl and H_3BO_3 are used as ionization and SiO_2 stabilization compounds, respectively. For the 0POSS-0Fe_1100 sample, this is believed to inhibit similar phase prediction from the E.A. composition. In addition, this intrinsic issue causes the expected SiC content in the 0POSS-0Fe_1300, 0POSS-1Fe_1300, and 0POSS-0Fe_1500 samples to be far smaller than those from both NMR profiles. To further improve this method, there is a need for thermodynamic model refinement, accurate data input regarding solid-solid interfacial energies of Si-O-C derivatives, and thorough understanding of the thermodynamic complexity of the Fe-Si-C liquid catalyst. More importantly, accurate elemental composition analysis is a must, which is our ongoing effort. Dedicated atomistic modeling can also yield insight into both model parameters and mechanistic pathways for VLS/SLS-driven SiC formation. Overall, the Gibbs free energy model reliably predicts phase content in regards to observed trends from XRD and NMR across the studied temperatures, while presenting a more comprehensive, affordable, and fast method of calculating phase fractions of different amorphous SiOC clusters and evaluating the catalytic effect of active fillers in driving phase formation.

2.5. Conclusions

The effects of Fe and POSS on the phase formation of SiOC between 1100°C and 1500°C were studied. At 1100°C, Fe was sufficient to catalyze nucleation and growth of the SiC phase, which provides energetically favorable nucleation sites for further SiC growth at higher pyrolytic temperatures. At all temperatures, the SiC phase was more prevalent in the Fe-containing samples. In addition to reported SiC nucleation and graphitization, Fe induced phase separation of the amorphous SiOC phase, which yielded a higher SiO₂ content. Specific surface areas of etched Fe-containing samples were between 600-700 m²/g from 1100°C to 1300°C, but decreased to between 200-300 m²/g at 1500°C due to the growth and coalescence of the segregated SiO₂ phase. At 1100°C and 1300°C, the specific surface areas of the samples with Fe were larger than those of samples without Fe. Phase contents of the pyrolyzed samples were calculated based on a modified Gibbs free energy minimization method which utilizes a modified VLS/SLS mechanism to explain the role of Fe in catalyzation of SiC formation.

2.6. Supplementary Information

2.6.1. ICP-OES Experimental Methodology and Data Analysis

2.6.1.1 ICP-OES Materials

Calibration solutions were prepared from single-element standards of silicon (Si, 1000 µg/mL, ICP-014, Agilent Technologies Inc., Santa Clara, CA) and iron (Fe, 1000 µg/mL, 5190-8471, Agilent Technologies Inc., Santa Clara, CA). A commercial blank standard was used in the preparation of calibration curves (5190-7001, Agilent Technologies Inc., Santa Clara, CA). Lithium tetraborate (Li₂B₄O₇, >99.995%, Sigma-Aldrich, St. Louis, MO) and lithium metaborate (LiBO₂, 99.997%, Thermo Fisher Scientific, Ward Hill, MA) were used in the borate flux. Lithium bromide (LiBr, 99%, Thermo Fisher Scientific, Ward Hill, MA) was used as a non-wetting agent. Cesium chloride (CsCl, 99.99%, Thermo Fisher Scientific, Ward Hill, MA) and boric acid (H₃BO₃, 99.99%, Thermo Fisher Scientific, Ward Hill, MA) were used in the digestion solution to stabilize SiO₂. Concentrated nitric acid (HNO₃, Certified ACS Plus, Fisher Chemical, Hampton, NH) was used for digestion, dilution, and as a part of the analytical matrix. Nanopure water (NP H₂O, 18.2 MΩ·cm) was used throughout the experiments. All chemicals were used without further

purification. Polypropylene centrifuge tubes or beakers were used for solution preparation and storage.

2.6.1.2 ICP-OES Sample Preparation

In a typical fusion and digestion process, a pyrolyzed SiO_xC_y sample was powdered with a mortar and pestle, passed through a 45 μm sieve, and dried for 12 h at 120°C. The dried sample was thoroughly mixed with $\text{Li}_2\text{B}_4\text{O}_7$ and LiBO_2 in a 1:5:5 ratio by weight and charged to a platinum crucible with 0.5 mL of 0.2 M $\text{LiBr}_{(\text{aq})}$ solution. The platinum crucible was placed in a muffle furnace at 1000°C for 10 min, after which the fused bead was transferred to a 50 mL solution of 20% $\text{HNO}_{3(\text{aq})}$, 4 g/L $\text{CsCl}_{(\text{aq})}$, and 50 g/L $\text{H}_3\text{BO}_{3(\text{aq})}$ (volume ratio: 43:2:5) and vigorously stirred for 30 min. The solution was then sonicated (Cole-Parmer Model 08895-01, Vernon Hills, IL) until the bead was completely dissolved. Prior to analysis, 1 mL of the digested solution was diluted to 5 mL with 5% $\text{HNO}_{3(\text{aq})}$. A matrix blank was prepared with the same borate flux amounts and dilution protocol but without the powdered SiOC sample.

Si and Fe calibration solutions were prepared in the range of 1.0-100.0 mg/L and 1.0-20.0 mg/L, respectively. In general, 20 μL , 40 μL , 100 μL , 200 μL , 400 μL , 1000 μL , or 2000 μL of the respective stock solution (1000 $\mu\text{g/mL}$) was diluted with corresponding volumes of 4 g/L $\text{CsCl}_{(\text{aq})}$ (here, 160 μL) and 50 g/L $\text{H}_3\text{BO}_{3(\text{aq})}$ (here, 400 μL) to a total volume of 20 mL with 5% $\text{HNO}_{3(\text{aq})}$ to yield concentrations of 1.0, 2.0, 5.0, 10.0, 20.0, 50.0, and 100.0 mg/L, respectively. The volumes of 4 g/L $\text{CsCl}_{(\text{aq})}$ and 50 g/L $\text{H}_3\text{BO}_{3(\text{aq})}$ were calculated to replicate the concentrations in the ICP analytical solutions.

2.6.1.3 ICP-OES Analysis Conditions

The instrument settings for analysis of calibration solutions and the digested sample solutions are provided in Table 2.6.1. Emission spectra were collected at the following wavelengths: for Si, 251.611 nm, 288.158 nm, and 250.690 nm; for Fe, 238.204 nm, 259.940 nm, and 234.350 nm.

Table 2.6.2: Instrument parameters for Agilent 5110 ICP-OES.

ICP-OES Instrument Settings	
Plasma Flow	12.0 L/min
Auxiliary Flow	1.00 L/min
Nebulizer	0.70 L/min
Make-up	0.00 L/min
RF Power	1.2 kW
Pump Flow Rate	12 rpm
Sample Replicates	3
Sample Read Time	10 s
Sample Uptake Delay	25 s
Drift Correction	Ar and C Emission Lines
Plasma View	Axial
Stabilization Time	60 s

2.6.1.4 Si and Fe Calibration Data

The calibration curves for Si and Fe are presented in Figure 2.6.1. The linear regression parameters are provided in Table 2.6.3.

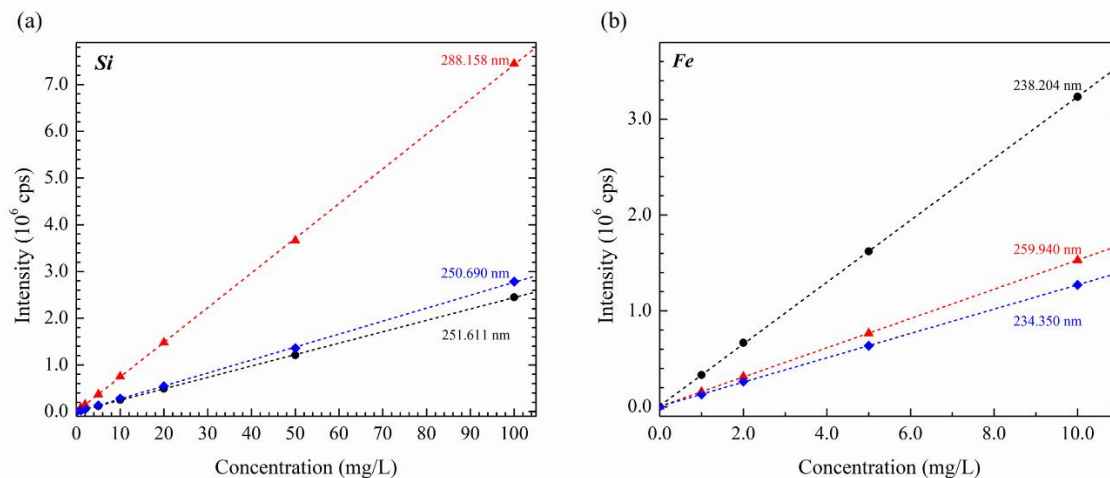
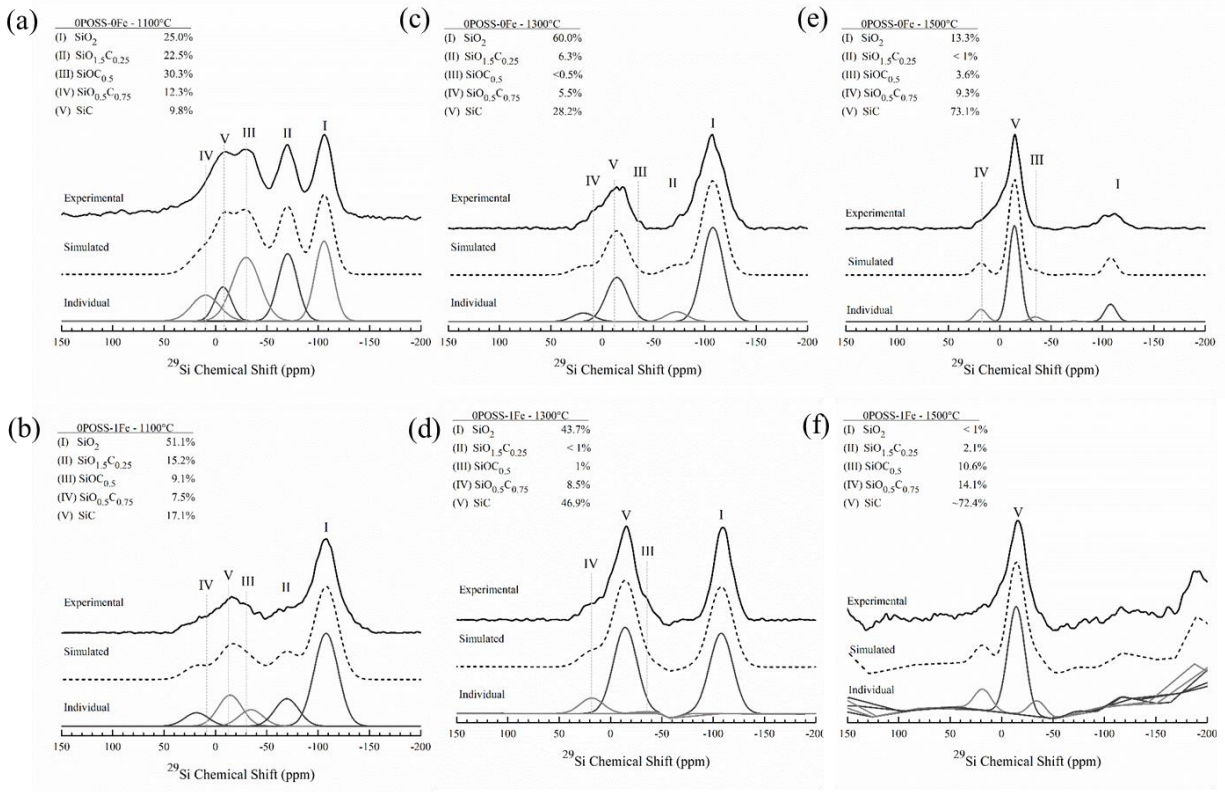


Figure 2.6.2: Linear fit data of (a) Si emission lines (250.690 nm (blue), 251.611 nm (black), and 288.158 nm (red)) and (b) Fe emission lines (238.204 nm (black), 259.940 nm (red), and 234.350 nm (blue)). The dotted lines represent the linear fit through the data points.

Table 2.6.4: Linear regression statistics for Si and Fe calibration curves in Figure S1.

Si and Fe Calibration Curve Data							
Element	Spectral Line (nm)	Linear Regression Statistics					
		m	s_m	b	s_b	R^2	s_y
Si	251.611	2440.18	6.71	77.54	270.76	0.99995	622.60
	288.158	7424.79	25.03	-47.40	1010.12	0.99993	2322.72
	250.690	2773.52	13.65	-370.20	550.83	0.99985	1266.60
Fe	238.204	32258.53	108.75	937.48	554.50	0.99997	878.10
	259.940	15257.22	59.58	475.61	303.78	0.99995	481.05
	234.350	12681.74	44.80	343.28	228.44	0.99996	361.75

2.6.2 ^{29}Si NMR Simulation and Peak Fitting



2.6.3 Gibbs Free Energy Minimization Code (MATLAB)

%% Gibbs Energy Minimization - Fe Catalyzed SiC Formation

%% Input Variables, Constants, and Reference Values

clear; close all;

% Input Temperature and Sample Composition

T_In = 1100; % Temperature (°C)

alpha = 0.016; % Mole/atom content of Fe (as decimal)

beta = 1.44; % Mole/atom content of O (as decimal)

delta = 0.28; % Mole/atom content of C (as decimal)

%FORMAT: Si Fe_alpha O_beta C_delta

T = T_In+273; % Temperature (K)

R = 0.008314; % Gas Constant (kJ mol⁻¹ K⁻¹)

NAv = 6.022E23; % Avogadro's Number (mol⁻¹)

K = R/NAv; % Boltzmann Constant (kJ K⁻¹)

% VLS/SLS Heterogenous Nucleation Parameters

GammaVL = 0.001; % Vapor/Solid-Liquid(Fe₃Si) Interfacial energy (kJ m⁻²)

```

GammaLS = 0.001;    % Liquid(Fe3Si)-Solid(SiC) Interfacial energy (kJ m^-2)
Vm = 40.096/(3.21*100^3); % SiC Molar Volume (m^3 mol^-1)
Theta = 135;    % Contact Angle (deg)
FTheta = (2-3*cos(deg2rad(Theta))+cos(deg2rad(Theta))^3)/4;
    % Contact Angle Parameter
d = [2 7]*1E-9;    % SiC Nuclei Size (m)
    % [1]: Critical Nuclei Size (nm)
    % [2]: Observed Nucleite Size (nm)
sigma = 2*(Vm/NAv)*GammaLS*(d(2)-d(1))/(d(1)*d(2)*K*T);
    % Supersaturation
gV = -K*T/(Vm*log(1+sigma));
    % GFE per Unit Volume (kJ mol m^-3)
gNucl = (16*pi*GammaVL^3)*FTheta/(3*gV^2*NAv);
    % GFE for Nucleation (kJ/mol)
nNucl = alpha/((1+alpha+beta+delta)*(2+alpha+0.5*beta));
    % Normalization Factor for gNucl related to Fe content and atomic
    % equiv in stoichiometric SiFeOC composition

% Gibbs Energy of Si-O-C Components ((kJ mol^-1 Mfu^-1)
Ga00 = -279.477 - 0.0436*T; % Amorphous SiO2
Gc00 = -281.777 - 0.0436*T; % Crystalline SiO2
Ga44 = 20.64 - 0.0445*T; % Amorphous SiC
Gc44 = -6.36 - 0.0445*T; % Crystalline SiC
G11 = 0.75*Ga00 + 0.25*Ga44; % Intermediate Si O1.5 C0.25
G22 = 0.5*Ga00 + 0.5*Ga44; % Intermediate Si O C0.5
G33 = 0.25*Ga00 + 0.75*Ga44; % Intermediate Si O0.5 C0.75

G0 = @(f0) Ga00*f0 + R*T*f0*log(f0); %f0: f(Si O2)
G1 = @(f1) G11*f1 + R*T*f1*log(f1); %f1: f(Si O1.5 C0.25)
G2 = @(f2) G22*f2 + R*T*f2*log(f2); %f2: f(Si O C0.5)
G3 = @(f3) G33*f3 + R*T*f3*log(f3); %f3: f(Si O0.5 C0.75)
G4 = @(f4) (Ga44-gNucl*nNucl)*f4 + R*T*f4*log(f4); %f4: f(Si C)
GTotal = @(f) G0(f(1))+G1(f(2))+G2(f(3))+G3(f(4))+G4(f(5));

%% Gibbs Free Energy Minimization Calculation
% fmincon Constraint Parameters
lb = zeros(1,5); % Lower bound values for f0,f1,f2,f3,f4
ub = ones(1,5); % Upper bound values for f0,f1,f2,f3,f4
Aeq = [2:-.5:0;0:0.25:1;ones(1,5)]; % Equality Constraint matrix for f0-f4 values
    % Row 1: Effective O coefficients in stoichiometric SiOxCy compositions

```

```

% Row 2: Effective C coefficients in stoichiometric SiOxCy compositions
% Row 3: Phase Fraction balance: sum of f0-f4 is 1.
options = optimoptions('fmincon','display','none');
fInitial = 0.2*ones(1,5); % Initial value for f = [f0,f1,f2,f3,f4]
warning('off','all'); % Suppress warning for poorly conditioned matrix, doesn't affect results

% Calculate phase fractions for sample based on stoichiometric coefficients
fSample = (3*beta)/(4+beta); % fSiO parameter for sample
fC = (0.5*beta+delta-1)/(1+alpha+beta+delta); % Phase fraction of free C
fM = (alpha/3)/(1+alpha+beta+delta); % Phase fraction of Fe3Si

phasesSample = zeros(8,1);
% Rows: f0,f1,f2,f3,f4,f_freeC, f_Fe3Si, Gmin
bSample = [beta; 1-0.5*beta;1];
[phasesSample(1:5), phasesSample(8)] =
fmincon(GTotal,fInitial,[],[],Aeq,bSample,lb,ub,[],options);
phasesSample(6) = fC;
phasesSample(7) = fM;
% phasesSample(1:5)=(1-phasesSample(6)-phasesSample(7))*phasesSample(1:5);
% Uncomment if want to normalize SiOC phases to all phases.
% Generate matrix of phase fractions at different fSiO values for plotting
% Plotting Parameters
x = 2:-0.05:0; % Range of O_x Values
y = 1-0.5*x; % Corresponding Range of C_y Values
fSiO = (3*x)/(2*(1+x+y)); % f(SiO) Parameter

phasesPlot = zeros(8,size(fSiO,2)); % Master matrix with minimization data.
% Rows: f0,f1,f2,f3,f4,f_freeC, f_Fe3Si, Gmin.
% Columns: fSiO
phasesPlot(7,:) = alpha/3; % Phase fraction of Fe3Si (constant)
bPlot = [x;y;ones(1,size(fSiO,2))]; % Equality Constraint matrix for f0-f4 values
% Row 1: x for O from 0-2 in stoichiometric SiOxCy
% Row 2: y for C from 1-0 in stoichiometric SiOxCy
% Row 3: Phase Fraction balance: sum of f0-f4 is 1.

for i=1:size(phasesPlot,2)

[phasesPlot(1:5,i),phasesPlot(end,i)]=fmincon(GTotal,fInitial,[],[],Aeq,bPlot(:,i),lb,ub,[],options)
;
freeC = (0.5*x(i)+delta-1)/(1+x(i)+delta+alpha);

```

```

phasesPlot(6,i)=(abs(freeC)+freeC)/2;
% Determine free C amount from delta at given x and y value. If free C < 0 then changes to 0.
% phasesPlot(1:5,i)=(1-phasesPlot(6,i))*phasesPlot(1:5,i);
% Uncomment if want to normalize SiOC phases to all phases
end
phasesPlot = round(phasesPlot,3);

%% Plotting
figure('Name','SiOxCy Composition vs. Phase Fraction')
hold on
plot(fSiO,phasesPlot(1:6,:))
plot([fSample fSample],[0,1],'k--')
plot(fSample, phasesSample(1:6),'rx')
xlabel('Composition of SiO_xC_y (f_S_i_O)')
ylabel('Phase fraction (f_i)')
legend('f_0(SiO_2)','f_1(SiO_1._.5,C_0._.2_5)','f_2(SiOC_0._.5)','f_3(SiO_0._.5C_0._.7_5)',
f_4(SiC)','f_5 (Free C)',")
hold off

```

Chapter 3: Twice-Functionalized Montmorillonite Nanosheets for Polymer-Derived MMT-SiOC Nanocomposites: Phase Formation and Porosity

3.1. Abstract

Clay-based reinforcements offer an inexpensive yet thermally compatible material for high-temperature ceramic systems, such as those in the silicon oxycarbide (SiOC) class of polymer-derived ceramics (PDCs). In this study, MMT nanosheets were purified and exfoliated from a crude clay source and further twice-functionalized with cetrirtrimethylammonium bromide and [3-(2-aminoethylamino)propyl]trimethoxysilane (AEAPTMS) to promote dispersion in the preceramic polymer. Phase profiles and compositions of MMT nanoflakes and MMT-SiOC were characterized with X-ray diffraction, infrared spectroscopy, and thermogravimetric analysis. The microstructures were examined by scanning and transmission electron microscopy. MMT nanoflakes were randomly dispersed in the SiOC matrix with α -quartz forming at the MMT-SiOC interface. Pyrolysis to 1400°C induced the formation of SiC nanowhiskers that were observed up to 20 μm in length and 200 nm in diameter. After selective etching of SiO₂ domains with HF, pore sizes and specific surface areas of MMT-SiOC were analyzed with nitrogen adsorption. The study provided a new fundamental understanding of MMT-SiOC interactions at different pyrolysis temperatures and also led to composites with specific surface areas reaching 120 $\text{m}^2\cdot\text{g}^{-1}$ up to 1200°C pyrolysis, and between 340 to 772 $\text{m}^2\cdot\text{g}^{-1}$ at 1400°C pyrolysis and pore size distributions between 2 and 5 nm. The methodology and results presented improve the understanding and viability of 2D nanomaterial-reinforced ceramic composites and MMT as a precursor for nanostructured SiC.

3.2. Introduction

Polymer-derived ceramics (PDCs) offer a novel yet facile method to fabricate complex ceramics with tailored microstructures and properties by choice of polymer precursor chemistry and filler materials [5, 9-11]. The tunable composition control and the processability ease of the polymer precursors make PDCs an exciting material for synthesizing and fabricating novel

materials with complex geometries generally unobtainable or difficult through conventional ceramic processing techniques. In particular, the silicon oxycarbide system (SiO_xC_y) has attracted interest for its high thermal stability and low thermal conductivity [15], excellent corrosion resistance [113], and attractive thermomechanical properties [115]. Beyond modifications of the polymer precursor chemistry, additional or secondary functionalities have been imbued through the incorporation of either active or passive fillers which can be incorporated into the pre-ceramic matrix. In particular, some additions are aimed at minimizing volume shrinkage and pore formation common in PDC systems. Both active fillers (e.g., Ti, TiSi_2 , Hf) and passive fillers (e.g., SiC, BN, ZrO_2 , Al_2O_3) have been utilized and shown to reduce volume shrinkage [133, 167-169], impart magnetic [13, 121], electric [15, 142], or catalytic [123] behavior, and improve high-temperature oxidation behavior [105, 170]. However, these fillers can potentially be expensive or yield the formation of undesirable secondary phases in the material. Analogous to applications in polymer composites, clay minerals can be a viable, inexpensive, and attractive option to improve the physical properties of SiOC ceramics, but as of yet have not been extensively studied.

Montmorillonite (MMT) is a naturally occurring 2:1 layered aluminosilicate mineral, with stacked sheets of approximately 1 nm thickness comprising of an alumina octahedral sheet between two silica tetrahedral sheets [33-36]. MMT composition is generalized as $\text{M}_{0.33}(\text{Al,Mg,Fe})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$, in which M represents intercalating cations (e.g., Na^+ , Ca^+), and some inherent water intercalation is present. Due to isomorphous substitutions of Mg^{2+} , Al^{3+} , and Fe^{2+} among the octahedral and tetrahedral sheets, the MMT layers are inherently negatively-charged and are balanced by low valence cations [33, 35, 37]. As a result, MMT exhibits a well-known swelling capability in the presence of water through the hydration of the interlayer cations [34-36, 38]. Furthermore, MMT sheets are held together only by weak electrostatic and van der Waals forces, so MMT is capable of exfoliating into distinct nanometer-thick sheets [35, 36].

Obtaining exfoliated microstructures in MMT-polymer composites remains an issue due to the inherent stacking tendencies of MMT layers to form intercalated, tactoid, or aggregated microstructures [102]. Serving as crack or defect initiation sites, agglomerated MMT has been observed to reduce composite mechanical properties. Twice-functionalized MMT of commercially available hydrophobic bulk MMT has been reported to improve dispersion, intercalation, and exfoliation in polymer matrices [108, 171, 172]. By utilizing long alkyl chain ammonium

surfactants to preemptively increase the MMT interlayer spacing, silane molecules are less hindered sterically and chemically from intercalating and grafting to the inner regions of MMT sheets [172]. Overcoming the intrinsic layering tendencies of MMT is tantamount to achieving a homogenous exfoliated microstructure in the preceramic green body and pyrolyzed ceramic nanocomposite. MMT nanosheets were reported to exfoliate into single-to-few layers by freezing, thawing, and sonicating an aqueous suspension of bulk MMT, which could be obtained after lyophilization [34-36]. The prominent volumetric expansion associated with water freezing provided adequate force to separate and exfoliate MMT nanosheets after only a few cycles and in conjunction with sonication. By initially exfoliating MMT layers, the nanosheets can be functionalized with colloidal and conventional nanomaterial processing techniques in order to retain the exfoliated microstructure in the preceramic green body and ceramic nanocomposite.

In this study, novel polymer-derived MMT-SiOC nanocomposites were fabricated with exfoliated and twice-functionalized MMT nanosheets obtained by freeze/thaw/sonication-assisted exfoliation of a naturally occurring MMT clay. MMT nanosheets were exfoliated and modified with cetyltrimethylammonium bromide (CTAB) and [3-(2-aminoethylamino)propyl]trimethoxysilane (AEAPTMS) to improve dispersion and exfoliation in the preceramic polymer. MMT content and pyrolytic processing temperature were varied to evaluate the effect of MMT on phase evolution and selectively etched porosity in MMT-SiOC nanocomposites.

3.3. *Experimental Methodology*

3.3.1. Materials

Naturally occurring montmorillonite clay (Crude MMT, 200 mesh powder, Alfa Aesar, Ward Hill, MA) was chosen as the crude clay precursor. Sodium hydroxide (NaOH, 50 wt% in H₂O, Sigma-Aldrich, Burlington, MA), acetic acid (CH₃COOH, glacial, Fisher Chemical, Waltham, MA), and silver nitrate (AgNO₃, ReagentPlus, ≥ 99.0%, Sigma-Aldrich, Burlington, MA) were used in washing and titrant solutions. Cetyltrimethylammonium bromide (CTAB, ≥ 98%, Sigma-Aldrich, Burlington, MA) and AEAPTMS (AEAPTMS, 98%, Gelest, Inc., Morrisville, PA) were chosen to surface functionalize the exfoliated MMT nanoflakes. A commercial polysiloxane Polyramic SPR-684 (PSO, [-Si(Ph)₂O-]₃[-Si(Me)(H)O-]₂[-Si(Me)(CH=CH₂)O-]₂, Starfire Systems, Inc., Glenville, NY) was chosen as the base preceramic

polymer, with a 2.1% platinum-divinyltetramethyldisiloxane complex in xylene (Karstedt's catalyst, Gelest, Inc., Morrisville, PA) selected to crosslink the preceramic green bodies. Concentrated hydrofluoric acid (HF, 49 wt%, Avantor Specialty Materials, Inc., Radnor, PA) was used to selectively etch SiO₂ from the MMT-SiOC ceramics. Acetone (technical grade, Fisher Scientific, Waltham, MA), dimethyl sulfoxide (DMSO, ≥ 99.9%, Sigma-Aldrich, Burlington, MA), hexanes (anhydrous, 95%, Sigma-Aldrich, Burlington, MA), methanol (MeOH, 200 proof, Fisher Scientific, Waltham, MA), toluene (≥99.5%, Fisher Scientific, Waltham, MA), and ultrapure water (NP H₂O, 18.2 MΩ-cm) were used throughout the experiment as general solvents. Argon (Ar, Industrial Grade, Airgas, Christiansburg, VA) was used for the pyrolysis atmosphere. All chemicals were used without further purification.

3.3.2. MMT purification and exfoliation

Exfoliated MMT nanosheets were collected through a modified procedure inspired by prior literature [35, 36]. A 5 w/v% suspension of crude MMT in 1.0 M NaOH_(aq) was mechanically stirred for 12 h, after which the alkalized MMT powders were washed with 0.05 M CH₃COOH_(aq) until the pH of the effluent was between 6-7. The purified MMT powder was collected over a 0.45 μm hydrophobic PVDF filter with 70% EtOH_(aq) and vacuum-dried (Fisher Isotemp Model 281A Vacuum Oven, Waltham, MA) at 70°C for 12 h. To exfoliate MMT nanosheets, a 0.5 w/v% suspension of purified MMT in NP H₂O was frozen at -20°C. The suspensions were thawed at room temperature and immersion bath-sonicated (Cole-Parmer Model 08895-01, 50W, Vernon Hills, IL) for 1 h; five cycles of freezing-thawing-sonication (F/T/S) were performed. The exfoliated MMT nanosheets were collected after centrifugation (Sorvall Legend X1R with FiberLite 8x50c rotor, Thermo Fisher Scientific, Waltham, MA) at 11000 x g for 15 min. The exfoliated MMT nanosheets (MMT-Na⁺) were collected after lyophilization (FreeZone Plus 2.5 L, Labconco Corp., Kansas City, MO) for 48-72 h and stored under vacuum.

3.3.3. Exfoliated MMT functionalization

Exfoliated MMT nanopowders were further surface functionalized with CTAB and AEAPTMS to improve dispersion in the preceramic polymer through modification and synthesis of prior reported procedures [74, 173, 174]. To a 0.5 w/v% suspension of MMT-Na⁺ in NP H₂O lightly stirring (<200 rpm) at 50°C, a 20 w/v% CTAB_(MeOH) was charged and stirred at 50°C for 3

h. The CTAB_(MeOH) solution corresponded to a 2X mass excess of CTAB to MMT-Na⁺. The CTAB-exchanged MMT nanosheets (MMT-CTA⁺) were washed repeatedly with MeOH until no halide ions were detected with 0.1 M AgNO_{3(aq)}, collected over a 0.45 µm hydrophilic PVDF filter with NP H₂O, and dried under vacuum at 100°C for 12 h.

MMT-CTA⁺ nanosheets were further functionalized with AEAPTMS to form a covalently bonded hydrophobic surface on the MMT nanosheets. A 0.5 w/v% suspension of MMT-CTA⁺ in 90% DMSO-10% MeOH was stirred in a 30°C water bath, and glacial CH₃COOH was slowly added to obtain a pH of 4. A 10 w/v% AEAPTMS_(EtOH) solution – corresponding to a 2X mass excess with respect to MMT-CTA⁺ – was added dropwise alternatively with additional glacial CH₃COOH to maintain a pH of 4, and stirred for 3 h at 30°C. The twice-functionalized silane-functionalized MMT nanoflakes (MMT-NH₂) were washed 5 times with 50% acetone-50% MeOH, collected over a 0.45 µm hydrophobic PVDF filter with hexanes, and vacuum-dried at 80°C for 12 h.

3.3.4. MMT-SiOC sample preparation

xMMT-PSO preceramic green bodies ($x = 0, 1, 2, 5$ wt%) were prepared by mixing PSO with toluene (~50 v/v% relative to PSO), 100 ppm of Karstedt's catalyst (relative to PSO), and the MMT-NH₂ nanoflakes. The suspension was stirred for at least 8 h under vacuum to remove residual solvent. The polymer suspensions were cast to Φ12 mm x 6 mm cylindrical silicone molds, degassed under vacuum, and cured at 60°C for 6 h and 120°C for 12 h. The green bodies were lightly ground and polished up to 1500 grit with SiC abrasive pads to remove any mold artifacts, and the edges were slightly beveled. To minimize potential surface oxidation, the green bodies were placed between two sheets of carbon felt in an alumina crucible. Under a flowing Ar environment (~500 mL·min⁻¹), the green bodies were pyrolyzed at 900°C, 1200°C, or 1400°C in a horizontal tube furnace (1830-12 Horizontal Tube Furnace, CM Furnaces, Inc., Bloomfield, NJ), with heating and cooling rates of 2°C min⁻¹ and soaking time of 2 h. The MMT-SiOC ceramic samples were denoted as xMMT-T_{pyr} with $x = 1, 2, 5$ wt% and T_{pyr} = 900, 1200, or 1400°C. The blank SiOC samples without MMT were similarly denoted SiOC-T_{pyr}.

3.3.5. Selective etching in MMT-SiOC ceramics

Pyrolyzed x MMT- T_{pyr} samples were lightly fractured into ~ 5 mm pieces and etched in a stirring 10% HF (aq) solution at less than 5 wt% for at least 96 h, or until no mass loss was observed. Samples were thoroughly washed with NP H_2O and dried under vacuum at 120°C for 12 h.

3.3.6. Characterization

Ceramic yield and volume shrinkage were calculated from changes in mass and sample volume, respectively, between green bodies and pyrolyzed samples. Reported values are averages of 4-6 replicates and corresponding errors indicate standard deviations. The densities of pyrolyzed x MMT-SiOC samples were measured using the Archimedes principle with EtOH as the immersion medium. The phase compositions of powdered samples were analyzed with an X-ray diffractometer (XRD, Empyrean, Malvern Panalytical Ltd., Almelo, The Netherlands) operated at 40 kV and 40 mA with Cu $K\alpha$ radiation between $2\theta=2$ - 90° and a scan rate of $0.02^\circ \text{ s}^{-1}$. Microstructures were observed with a scanning electron microscope at 10 kV (SEM, IT-500HR, JEOL USA, Peabody, MA, USA) and a transmission electron microscope (TEM, JEOL 2100, JEOL USA, Peabody, MA, USA) equipped with a LaB_6 filament operated at 200 kV. SiC nanostructure morphologies were observed with low voltage (700 V) imaging (LV-SEM, GeminiSEM 460, Carl Zeiss AG, Oberkochen, Germany). TEM lamella of 5MMT-SiOC ceramics were prepared by focused-ion beam liftout and thinning (FIB, Helios 5 UC, Thermo Fisher Scientific, Inc, Waltham, MA, USA). Thermogravimetric analysis (TGA, TGA 5500, TA Instruments, New Castle, DE, USA) of exfoliated/functionalized MMT nanoflakes was performed with a heating rate of 5°C min^{-1} from 50°C to 1000°C under argon flow of $40 \text{ mL}\cdot\text{min}^{-1}$. Bond characteristics in the functionalized MMT nanoflakes were analyzed by Fourier-transformed infrared spectroscopy (FTIR, Varian 670-IR, Agilent Technologies, Inc., Santa Clara, CA, USA) with the attenuated total reflectance (ATR) method between 4000 and 600 cm^{-1} with a resolution of 4 cm^{-1} and averaged over 128 scans. Pyrolytic mass loss and heat flow of x MMT-PSO green bodies were analyzed by a simultaneous thermal analyzer (SDT, SDT 650, TA Instruments, New Castle, DE, USA). Porosity and surface area characteristics were determined by nitrogen adsorption at 77 K (Quantachrome Autosorb-iQ C-XR, Quantachrome Instruments, Boynton Beach, FL, USA). Samples were degassed under vacuum at 250°C for 12 h prior to analysis. A

Non-Local Density Functional Theory (NLDFT) model was applied to the adsorption branch with a spherical/cylindrical pore structure based on a silica adsorbate model.

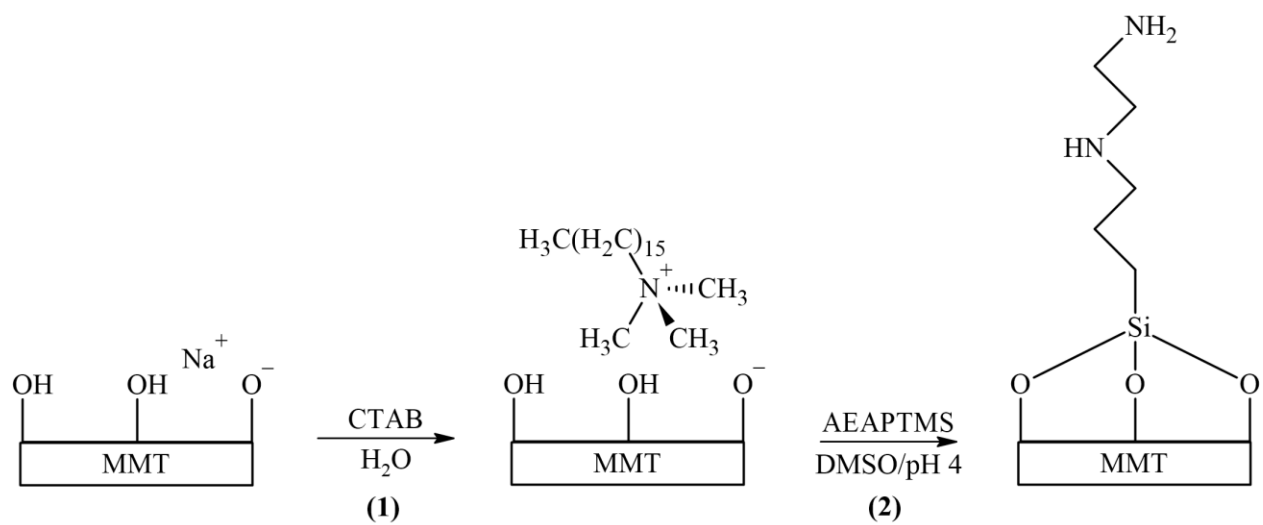
3.4. *Results and Discussion*

3.4.1. MMT nanosheet exfoliation and functionalization

Figure 3.4.1(a) depicts the synthesis of exfoliated, hydrophobic MMT through freeze/thaw/sonication (F/T/S)-mediated exfoliation and subsequent functionalization with CTAB and AEAPTMS. The F/T/S method leveraged the swellability of MMT due to interlayer Na^+ cations and the volumetric expansion of water upon freezing to separate and exfoliate MMT nanosheets. Further colloidal processing of the hydrophilic exfoliated MMT- Na^+ nanoflakes yielded organophilic, covalently-bonded functionality to the MMT nanoflakes. Crude MMT powders exhibited highly agglomerated yet sheetlike morphology as shown in Figure 3.4.1(b). MMT nanoflakes after exfoliation (Figure 3.4.1(c)) showed electron transparency in TEM, indicating single-to-few sheet thickness. Nanoflakes after exfoliation were generally 200 nm in length and 100 nm in width. MMT nanosheets obtained an exfoliated microstructure in the eventual MMT-SiOC ceramic (Figure 3.4.1(d)) as shown in the FIB lamella of 5MMT-900. MMT nanosheets were randomly oriented and distributed in the SiOC matrix, indicating complete exfoliation of functionalized MMT- NH_2 nanoflakes in the preceramic PSO green body.

In order to generate covalently-bonded silane surface groups, twice-functionalization was necessary with commercial MMT clays as the direct synthesis route yielded agglomerated MMT layers, interlayer bridging via silanes, or inadequate surface functionalization [49, 50]. While obtaining fully exfoliated polymer-clay microstructures remains difficult with twice-functionalized commercial MMT clays, the F/T/S exfoliation route was chosen to isolate and colloiddally process nanosheets to achieve proper dispersion in the preceramic polymer. Initial functionalization with CTAB occurred through the cationic exchange of CTA^+ with Na^+ at the MMT nanosheet surface (Scheme 1 – Reaction 1). While electrostatically coordinated, CTA^+ ligands imbued organic functionality that mitigated nanosheet agglomeration before colloidal suspension in the preceramic polymer. Silane functionalization of MMT- CTA^+ proceeded by removal of CTA^+ ligands in an acidic medium and subsequent grafting of AEAPTMS (Scheme 1 – Reaction 2). Acid-catalyzed AEAPTMS condensation was performed to imbue a near-monolayer organophilic coating without silane condensate by-products [74]. As the organic surface

functionalities were expected to evolve during PDC pyrolysis, excess silane molecules could contribute to additional mass loss and pore formation.



Scheme 1. Twice-functionalization of MMT nanosheets. (1) Cationic exchange of Na^+ with CTA^+ , (2) Acid-catalyzed silane (AEAPTMS) condensation.

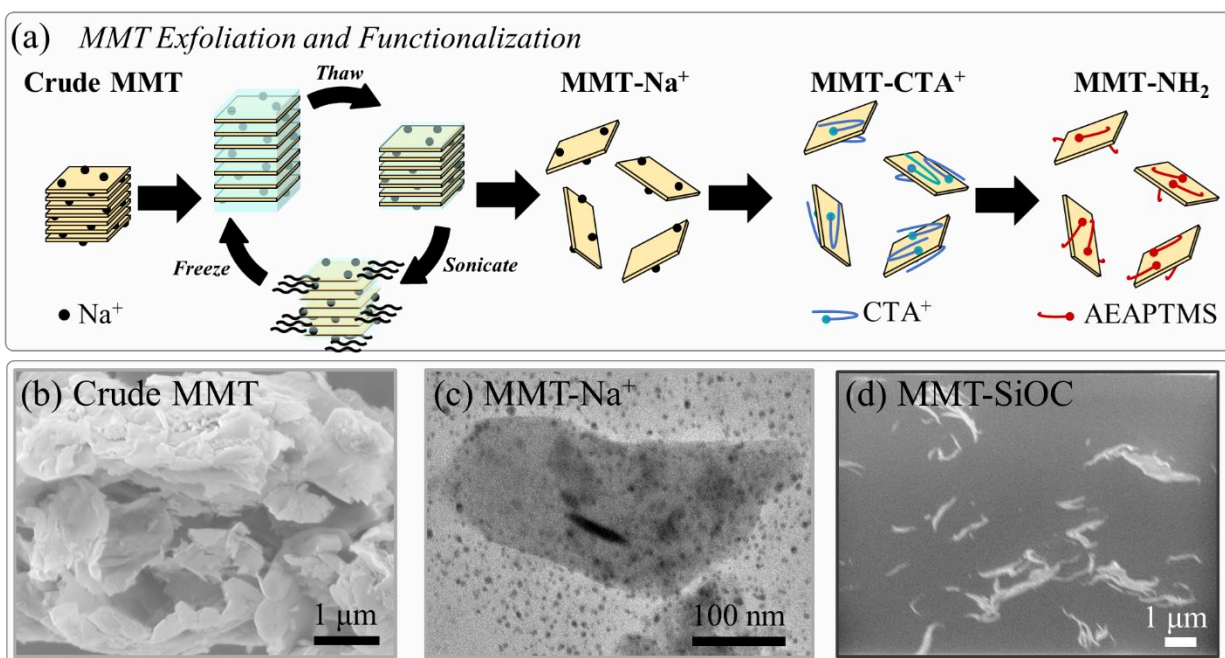


Figure 3.4.1: (a) Schematic of organophilic MMT nanoflakes synthesized with exfoliation via freeze/thaw/sonication and twice-functionalization with CTAB and AEAPTMS, (b) morphology of crude MMT powders before exfoliation (scale bar: 1 μm), (c) TEM micrograph of MMT-Na⁺ nanoflakes after exfoliation (scale bar: 100 nm), and (d) cross-section (prepared by FIB liftout) SEM micrograph of MMT nanoflakes in SiOC matrix after pyrolysis showing randomly exfoliated microstructure (scale bar: 1 μm).

Figure 3.4.2(a) depicts the phase profiles of MMT exfoliation and functionalization products from the crude clay source to twice-functionalized MMT. The evolution of exfoliated MMT nanoflakes that are single-to-few layers thick was indicated by the emergence of the (002) basal spacing peak at 7° and subsequent peak shift to smaller scattering angles. Retention of the exfoliated structure throughout the functionalization steps was imperative to preventing agglomeration and layering of the MMT nanoflakes in the preceramic green body. Crude MMT inherently exhibited a bulk, aggregated structure with naturally occurring impurities (e.g., quartz, carbonates, sediments, etc.). After purification and exfoliation of the crude clay, the exfoliated MMT- Na^+ nanosheets were characterized by the emergence and sharpening of the (001) diffraction peak at 7° and a general decrease in higher order (00n) peaks. A (002) basal spacing peak at 29° was observed in MMT- Na^+ that disappears upon further functionalization, and was attributed to inherent stacking tendencies after lyophilization due to van der Waals forces. Peaks characteristic to the MMT nanosheet (e.g., tetrahedral/octahedral layers) were identified at 20° , 35° , 54° , and 62° as (100), (105), (210), and (300) planes, respectively.

After CTAB functionalization, the (001) basal spacing peak in MMT- CTA^+ significantly increases in intensity and shifts from 7° to 4.9° , correlating to an increase in d-spacing from 12.6 Å to 18.0 Å, compared to MMT- Na^+ . Characteristic MMT diffraction peaks for (100), (105), (210), and (300) were retained at 20° , 35° , 54° , and 62° , respectively. Noting that the (002) basal spacing diffraction peak disappeared completely, the MMT nanosheets were determined to be predominantly monolayer and did not agglomerate. The basal spacing increase was induced by the successful grafting of CTAB to the MMT- Na^+ , as the hydrophobic tail provided a barrier against agglomeration. The two new diffraction peaks observed at 24.5° and 29° (denoted as CTA^+ in Figure 3.4.2(a)) were attributed to some coherent ordering of the CTA^+ ligands on the MMT nanoflake substrate when dried. Previous reports indicated that ordered states of intercalated alkyl chains have been observed due to inherent alkyl chain length, increasing chain interactions, and packing density of the alkyl ligands [33]. The corresponding d-spacings for the aforementioned CTA^+ diffraction peaks were 3.6 Å and 3.1 Å. While the total d-spacing contribution from CTA^+ (6.7 Å) was slightly larger than the change in (001) basal spacing (5.4 Å), this discrepancy was attributed to the loosely crystalline packing of CTA^+ ligands. Overall, the sole presence and refinement of the (001) diffraction and unique CTA^+ peaks indicated that the exfoliated

morphology was retained after CTAB functionalization and CTAB was properly grafted to the nanosheet surface.

Upon functionalization with AEAPTMS, the intensity of the (001) peak significantly increased with the absence of the (002) peak at 29° , indicating that the MMT-NH₂ nanoflakes were thoroughly exfoliated and predominantly single layer. In addition, the (002) peak shift from MMT-Na⁺ to twice-functionalized MMT-NH₂ of 7° to 5.5° corresponded to an increase of basal spacing from 12.6 Å to 16.0 Å, respectively. Intrinsic MMT nanoflake diffractions of (100), (105), (210), and (300) planes were similarly observed at 20° , 35° , 54° , and 62° , respectively. Notably, a new diffraction peak at 26° after AEAPTMS functionalization was attributed to the silane monolayer formed on the MMT nanosheet surface. As silane functionalization occurs through covalent linkage with the exposed Si-O groups of the MMT nanosheet, an effective siliceous layer forms through a bridging O atom between Si atoms of the MMT nanosheet and the silane. The d-spacing of the (101) SiO₂ peak was 3.4 Å, which directly correlates to the difference in (002) basal spacing between MMT-Na⁺ and MMT-NH₂. While the (002) basal spacing decreased from d-spacings of 18.0 Å to 16.0 Å from MMT-CTA⁺ to MMT-NH₂, the absence of higher order (00*n*) diffraction peaks indicated that the MMT monolayers were retained without agglomeration. The decrease in d-spacing was attributed to the difference in hydrophobic tail length between CTAB (18 C atoms) and AEAPTMS (5 C/2 N atoms). Not only was the exfoliated structure retained after functionalization, successful grafting of AEAPTMS to the MMT nanosheet surface increased the equilibrium spacing and mitigated nanoflake aggregation or stacking.

Bond formations in MMT-CTA⁺ and MMT-NH₂ were further elucidated with FTIR-ATR and XPS to observe CTAB or AEAPTMS motifs in the functionalized MMT products. Figure 3.4.2(b) depicts the FTIR spectra of MMT-Na⁺ (black), MMT-CTA⁺ (red), and MMT-NH₂ (blue) along with the reference spectra for CTAB (dashed blue) and AEAPTMS (dashed red). MMT-Na⁺, MMT-CTA⁺, and MMT-NH₂ all exhibited identical bands in the 1200-700 cm⁻¹ region that are due to stretching vibrations of Si-O(H), Al-O(H), Si-O-Si, and Si-O-Al groups in the MMT nanosheet [175]. For these samples, peak identification indicated these bands varied within ± 3 cm⁻¹ (within the resolution used in the analysis); for clarity, these vibrations were only noted in the MMT-NH₂ spectra but were identical among the three samples. Bands at 1116 and 1000 cm⁻¹ originated from Si-O stretching vibrations, and those at 914, 840, and 725 cm⁻¹ were attributed to Al-OH-Al, Si-O-Al, and O-(Al^{IV})-OH stretching vibrations in the interior and on the edges of

MMT nanosheets, respectively [175]. Absorption bands at 3624 cm^{-1} and 3428 cm^{-1} were due to stretching vibrations of O-H groups of structural -OH in the Al octahedral layer and hydrogen-bonded/intermolecular H_2O , respectively. The Al-OH vibration at 3624 cm^{-1} did not appreciably shift after functionalization, which could indicate these edge Al-OH groups in the octahedral layer were not involved in the reactions with CTAB or AEAPTMS. An O-H symmetric bending vibration was also observed at $\sim 1634\text{ cm}^{-1}$ and similarly attributed to adsorbed H_2O molecules. The intensity of the prior bands decreased after CTAB and AEAPTMS functionalization as few H_2O molecules could adsorb to the newly hydrophobic MMT surface. The band at 1365 cm^{-1} was assigned to O-H bending vibrations of structural -OH groups.

After CTAB functionalization, new adsorption bands were observed in MMT-CTA^+ at 2924 , 2850 , and 1487 cm^{-1} – the former two vibrations from alkyl C-H stretching and the latter from alkyl C-H bending modes. These alkane vibrations were from CTA^+ cations electrostatically bonded with the MMT nanosheet surface as the vibration frequencies and intensities matched closely with the prominent alkyl C-H bands of CTAB. Furthermore, the vibration at 3448 cm^{-1} shifted from 3428 cm^{-1} in MMT-Na^+ as fewer H_2O molecules could be adsorbed onto the hydrophobic MMT-CTA^+ nanosheet surface. This band indicated that any H_2O molecules present were generally hydrogen-bonded to exposed -OH structural groups on the octahedral sheet edges.

Twice-functionalized MMT-NH_2 clearly showed the lack of C-H vibrations characteristic of CTA^+ as the cation dissociated during AEAPTMS functionalization. Expanded views of the MMT-NH_2 FTIR spectra between $1700\text{--}1300\text{ cm}^{-1}$ and $3100\text{--}2700\text{ cm}^{-1}$ depicted the low-intensity bands from grafted AEAPTMS. The bands at 3411 cm^{-1} and 1630 cm^{-1} were attributed to N-H stretching and bending vibrations in the hydrophobic silane tail. The retained vibrations at 1413 cm^{-1} and 1375 cm^{-1} were assigned to structural -OH bending modes of the MMT nanosheet that were not involved in the functionalization. Alkyl C-H stretching vibrations from the hydrophobic tail were identified at 2949 , 2918 , 2875 , 2856 , and 2834 cm^{-1} , and bending vibrations at 1468 , 1462 , and 1452 cm^{-1} . Bands in the $1600\text{--}1500\text{ cm}^{-1}$ range were attributed to C=O vibrations from background or surface-adsorbed CO_2 . The N-H and C-H bands observed in MMT-NH_2 closely resembled those in native AEAPTMS.

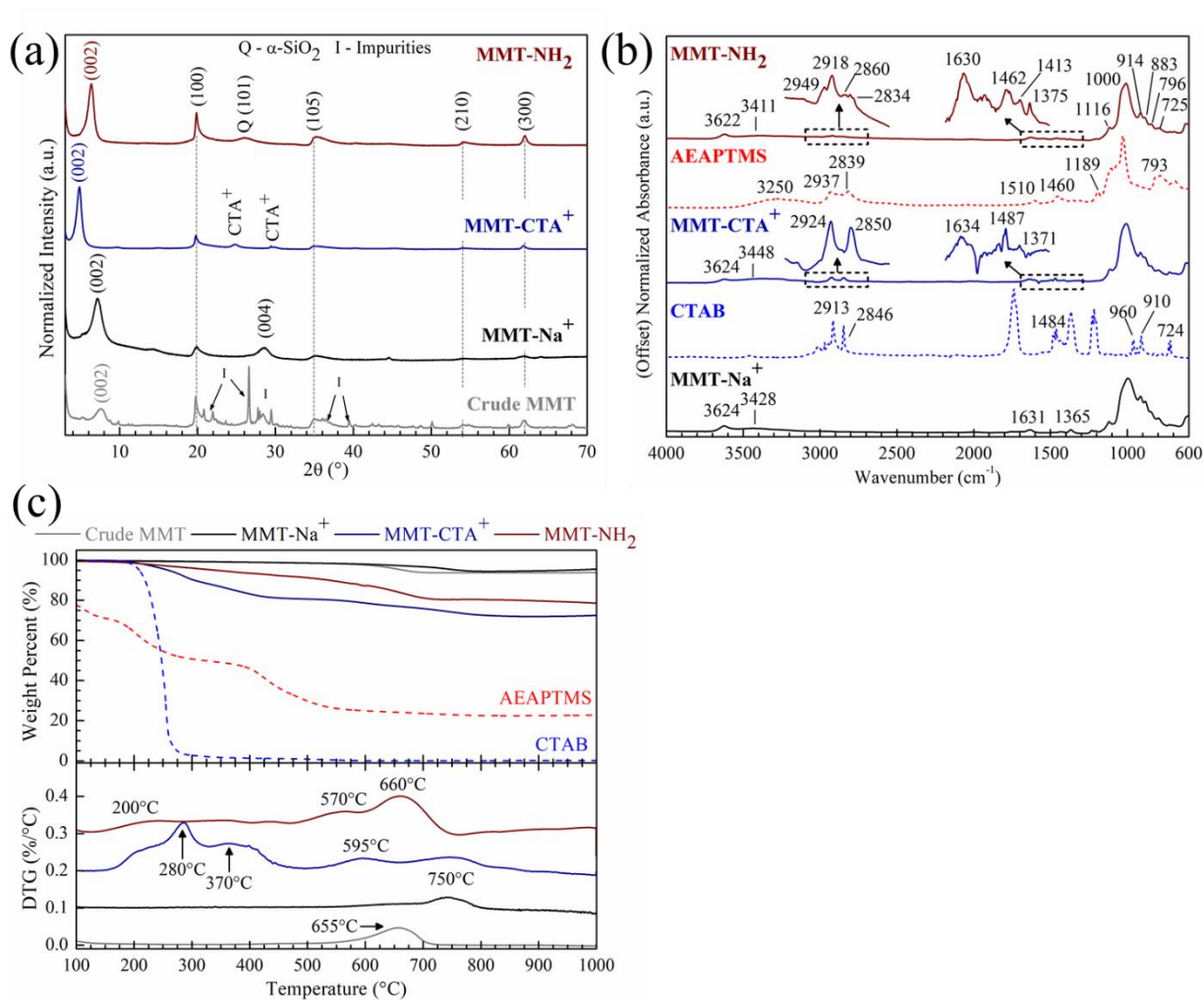


Figure 3.4.2: Structural and chemical characterization of exfoliated and functionalized MMT nanoflakes. (a) XRD spectra of crude MMT (gray), MMT-Na⁺ (black), MMT-CTA⁺ (blue), and MMT-NH₂ (red) nanoflakes, (b) FTIR spectra of MMT-Na⁺ (black), MMT-CTA⁺ (blue), and MMT-NH₂ (red) nanoflakes, (c) TG/DTG profiles of crude MMT (gray), MMT-Na⁺ (black), MMT-CTA⁺ (blue), and MMT-NH₂ (red). Reference spectra of CTAB (light blue) and AEAPTMS (light red) are provided for comparison in (b)/(c).

CTAB and AEAPTMS functionalization was further confirmed with TGA to identify mass loss events and signature functional groups present in MMT-CTA⁺ and MMT-NH₂. Figure 3.4.2(c) depicts the thermogravimetric (TG) and derivative (DTG) profiles of crude MMT (gray), MMT-Na⁺ (black), MMT-CTA⁺ (red), and MMT-NH₂ (blue) under Ar from 100°C to 1000°C. Both crude MMT and MMT-Na⁺ experienced ~5% mass loss and the primary mass loss event correlated to dehydroxylation of the MMT surface at ~655°C and ~750°C, respectively. While the decomposition temperature of crude MMT observed agreed with prior studies, the shift in dehydroxylation temperature for exfoliated MMT nanoflakes has not yet been reported.

The temperature shift is indicative that more energy is required to convert surface -OH groups as water after exfoliation. In a bulk/aggregated form, the closer stacking of MMT sheets is more conducive to dehydroxylation as more mass is available for H₂O evolution and the layered morphology stabilizes the decomposition of aluminosilicate product at lower temperatures. Upon exfoliation, the MMT nanosheets are sufficiently spaced to retard this decomposition event for an additional ~100°C, possibly as the surface energy of the surface -OH bonds increases with the larger exposed surface area.

After both functionalization with CTAB and AEAPTMS, MMT-CTA⁺ and MMT-NH₂ exhibited higher mass losses of 29% and 21%, respectively, compared to MMT-Na⁺ after heating to 1000°C. The reference spectra of CTAB (dashed red) and AEAPTMS (dashed blue) in Figure 3.4.2(a) indicated that CTAB fully decomposed by 300°C while AEAPTMS yielded a 15% mass residue of siliceous products. The corresponding DTG profiles of MMT-CTA⁺ and MMT-NH₂ illustrated additional gradual mass loss events between 200°C and 800°C, which can solely be attributed to grafted organic molecules after each functionalization step. The gradual mass loss observed in organically-modified MMT has been reported as the decomposition of hydrogen/electrostatically-bonded organic molecules between 200°C and 400°C and intercalated/covalently-bonded molecules above 450°C [49]. The DTG profile of MMT-CTA⁺ in Figure 3.4.2(b), the primary decomposition event between 200°C and 400°C, was attributed to CTA⁺ cations coordinated weakly to -OH/-O⁻ groups along the surfaces and edges of the MMT nanosheets. From 600°C to 800°C, tightly held CTA⁺ cations that formed an initial monolayer on the MMT surface finally evolved along with any remaining -OH surface groups.

Twice-functionalized MMT-NH₂ depicted a gradual yet distinct mass loss profile compared to MMT-CTA⁺, which indicated that CTA⁺ cations were sufficiently removed and

replaced with silane molecules. Compared to MMT-CTA⁺, there was significantly less mass loss observed below 400°C, which could indicate that the majority of silane molecules are covalently bonded to the MMT surface. The predominant mass loss in MMT-NH₂ occurred from 500°C to 750°C as the covalent bonds between MMT and silane were cleaved and residual -OH groups were evolved. Grafted AEAPTMS content on the MMT nanosheets was determined by TGA mass loss between 200°C and 600°C ($W_{200-600}$), as expressed in Equation (3.4.1).

$$\text{Silane Content (\%)} = \frac{100 \times W_{200-600}}{100 - W_{200-600}} \quad (3.4.1)$$

Neglecting dehydroxylation mass loss at 660°C intrinsic to MMT-Na⁺ decomposition (5.6%), $W_{200-600}$ was determined to be 19.8%, yielding a grafted silane content of 24.7%. The specific surface area (SSA) of MMT was also estimated from TGA silane mass loss, the surface density of O atoms on the crystalline MMT surface (σ_{O-MMT}), the grafting ratio of MMT surface O atoms to AEAPTMS Si atoms (N_{O-Si}), the molar mass of AEAPTMS ($\mu_{AEAPTMS}$), and Avogadro's number (N_a), as given in Equation (3.4.2).

$$\text{SSA} = \frac{\text{Silane Content}(\%)}{100} \times \frac{N_a}{\mu_{AEAPTMS}} \times \frac{N_{O-Si}}{\sigma_{O-MMT}} \quad (3.4.2)$$

σ_{O-MMT} was approximated as $\sim 1.629 \times 10^{19}$ atom·m⁻² from tetrahedrally-ordered O atoms on the MMT surface and a crystalline Si-O bond distance of 163 pm, and N_{O-Si} as 3, assuming complete grafting of the silane monolayer (Scheme 1 – Reaction 2). The SSA of MMT-NH₂ nanoflakes was calculated to be ~ 123 m²·g⁻¹ from Equation (3.4.2), which agreed with a reported value for exfoliated MMT similarly processed through F/T/S exfoliation [176]. While SSA values are lacking for MMT nanoflakes, bulk MMT SSA values were generally reported between 10-50 m²·g⁻¹ [176-179], which further pointed to the nanostructured/exfoliated morphology of the twice-functionalized MMT-NH₂ nanoflakes.

3.4.2. MMT-SiOC pyrolysis and properties

3.4.2.1. Phase evolution and physical properties

Preceramic xMMT-PSO green bodies (**Figure 3.4.3(a)**) exhibited colloidal dispersions of functionalized MMT-NH₂ nanoflakes, with the yellow color in 1MMT-PSO darkening to amber and brown in 2MMT-PSO and 5MMT-PSO, respectively. Notably, the loss of translucency in 5MMT-PSO implied that at such a high nanoflake content, MMT nanoflakes may exist as a few sheet-thick tactoids randomly dispersed in the matrix. Pyrolyzed 5MMT-900, 5MMT-1200, and

5MMT-1400 (**Figure 3.4.3(a)**) were dense and black from excess free C present in all silicon oxycarbide systems, and were representative of all pyrolyzed MMT-SiOC samples at the listed temperatures. Pyrolytic decomposition behaviors of xMMT-PSO to xMMT-SiOC were observed with TGA to 1500°C in Ar (**Figure 3.4.3(b)**) to determine the effect of MMT on SiOC phase evolution during the polymer-to-ceramic transformation (400-800°C) and up to SiOC carbothermal reduction to SiC domains (>1400°C). Native PSO yielded a ~72% residue upon pyrolysis to 1400°C and no appreciable mass loss was observed up to 1500°C. 1MMT-PSO exhibited a similar residue of ~72% at 1400°C but displayed additional mass loss (~1%) up to 1500°C. 2MMT-PSO and 5MMT-PSO yielded slightly higher ceramic residues (~74%) at 1400°C with a similar decomposition behavior as 1MMT-PSO between 1400°C and 1500°C. As not present in PSO, the high temperature decomposition event was not only due to MMT phase separation to cristobalite and mullite but also reactions with the SiOC matrix that would account for gas volatilization. While 1MMT-PSO and 2MMT-PSO showed similar DTG profiles to PSO, an additional event at ~370°C was revealed in 5MMT-PSO along with a reduction in mass loss at ~470°C. Increasing MMT content lowered the onset of the polymer-to-ceramic transition, most prevalently in 5MMT-PSO, pointing to a reaction between MMT nanosheets and the transforming SiOC matrix.

Pyrolytic decomposition events during the polymer-to-ceramic transformation were the combination of multiple individual kinetic processes that cannot be resolved solely with TGA. However, each event may be described by a rate-limiting step that ultimately drives volatilization reactions observable with TGA. Dedicated kinetic studies with TGA- mass spectrometry (MS) for evolved gas characterization would be needed for a more robust analysis of the polymer-to-ceramic transition, which was outside the scope of this study. The specific polysiloxane used in this study has not yet been analyzed with TGA-MS to characterize the evolved gaseous species, but overall similarities with previously studied PDC-SiOC/SiC systems sufficed for analysis of mass loss events in regards to underlying phase evolution [178-180]. DTG peak deconvolution for PSO and 5MMT-PSO (**Figure 3.4.3(c)**) revealed four decomposition events during the polymer-to-ceramic transition. In PSO, events I (448°C), II (475°C), III (547°C), and IV (662°C) contributed 28.5%, 8.8%, 48.6%, and 20.4% to mass loss during the polymer-to-ceramic transformation, respectively. A previous study correlating gas evolution with pyrolytic decomposition events in SiOC derived from 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane showed event I involved the release

of gaseous by-products from Si-OH and Si-H condensation [178]. While heavily overlapping with event I, event II involved the redistribution of Si-H, Si-O, and Si-C bonds and the release of some Si species in the process. Events III and IV were attributed to methane and hydrogen evolution from the cleavage of Si-Me, Si-H, Si-O, and Si-C bonds. DTG peak deconvolution for 5MMT-PSO revealed that event I (404°C) occurred earlier and contributed only 23.8% of total mass loss. Events II (482°C), III (546°C), and IV (643°C) proceeded similarly as in PSO but with respective mass loss contributions of 4.8%, 51.8%, and 19.6%. The improved ceramic yield in 5MMT-PSO originated from decreased mass loss during events I and II – the latter potentially indicating increased retention of Si in MMT-SiOC ceramics. Early-stage mass loss (event I) was correlated with higher SiO₂ content in the resultant SiOC ceramic [178].

The phenomenological origin of the observed mass loss profiles was believed to be related to how MMT nanosheets are incorporated into the SiOC matrix. It was not understood whether MMT nanoflakes were embedded in the amorphous SiOC matrix, served as discontinuous inclusions, or segregated into the free carbon phase that is intrinsic in carbon-rich PDC systems. Discontinuous inclusions can serve as defect or crack initiation sites and represent a common issue in MMT composite fabrication. If the MMT nanosheets were to behave as discontinuous inclusions, the MMT-SiOC ceramics were theorized to be incredibly brittle as the nanosheets would not be stabilized in the matrix or at high temperatures – the high nanosheet surface energy would cause MMT reinforcements as crack initiation sites to resolve this energy mismatch. Alternatively, if MMT nanosheets were to segregate to the free carbon phase – that is, unincorporated in the amorphous SiOC phase – there would be no significant difference in the TG/DTG profiles of PSO-xMMT green bodies compared to native PSO. In either scenario, MMT would not contribute to or affect SiOC phase formation, so the overall ceramic yield would be modeled as independent decomposition events of PSO-to-SiOC and MMT-NH₂ to kaolin. However, neither of these scenarios would yield the observed results presented in **Figure 3.4.3(b)**.

Crystalline MMT nanosheets were postulated to be embedded in the amorphous SiOC matrix through an interfacial zone that resolved the coherency mismatch. During the polymer-to-ceramic transformation, radical-mediated reactions among Si, C, and O atoms form the thermodynamically metastable amorphous SiOC matrix – in addition, reactions with MMT surface terminations either innate or residual from AEAPTMS were postulated to occur in conjunction with AEAPTMS decomposition in MMT-NH₂ as shown in Figure 3.4.2(c). This would have been

also necessary to stabilize the high surface energies of the MMT nanosheets as the silane functional groups volatilized. Therefore, it was believed that an interfacial zone between MMT nanosheets and the SiOC matrix evolved to stabilize the embedded nanosheets and resolve the material coherency mismatch. This interfacial region was theorized to transition from ordered Si-O/Si-C bonds near the crystalline MMT nanosheet to short-range/amorphous ordering of Si-O-C clusters towards the bulk SiOC matrix. SiOC phase formation is driven thermodynamically based on the preceramic polymer chemistry and pyrolytic atmosphere [139]. The MMT-SiOC system was inherently silica-rich as the nanosheets are comprised of 2 SiO₂ and 1 Al₂O₃ units. To maintain the overall ceramic composition, carbon may have been retained to compensate for the effective nanosized SiO₂ inclusions. Carbon was thought to be retained in this interfacial region between MMT and SiOC. While the MMT nanosheets were exfoliated, the interfacial zones may be sufficiently large— possible given the high specific surface area of the nanosheets – to coalesce above 1% MMT. As regions coalesce, less carbon may be required to resolve the crystalline/amorphous material boundary between MMT and SiOC compared to more dispersed nanosheets.

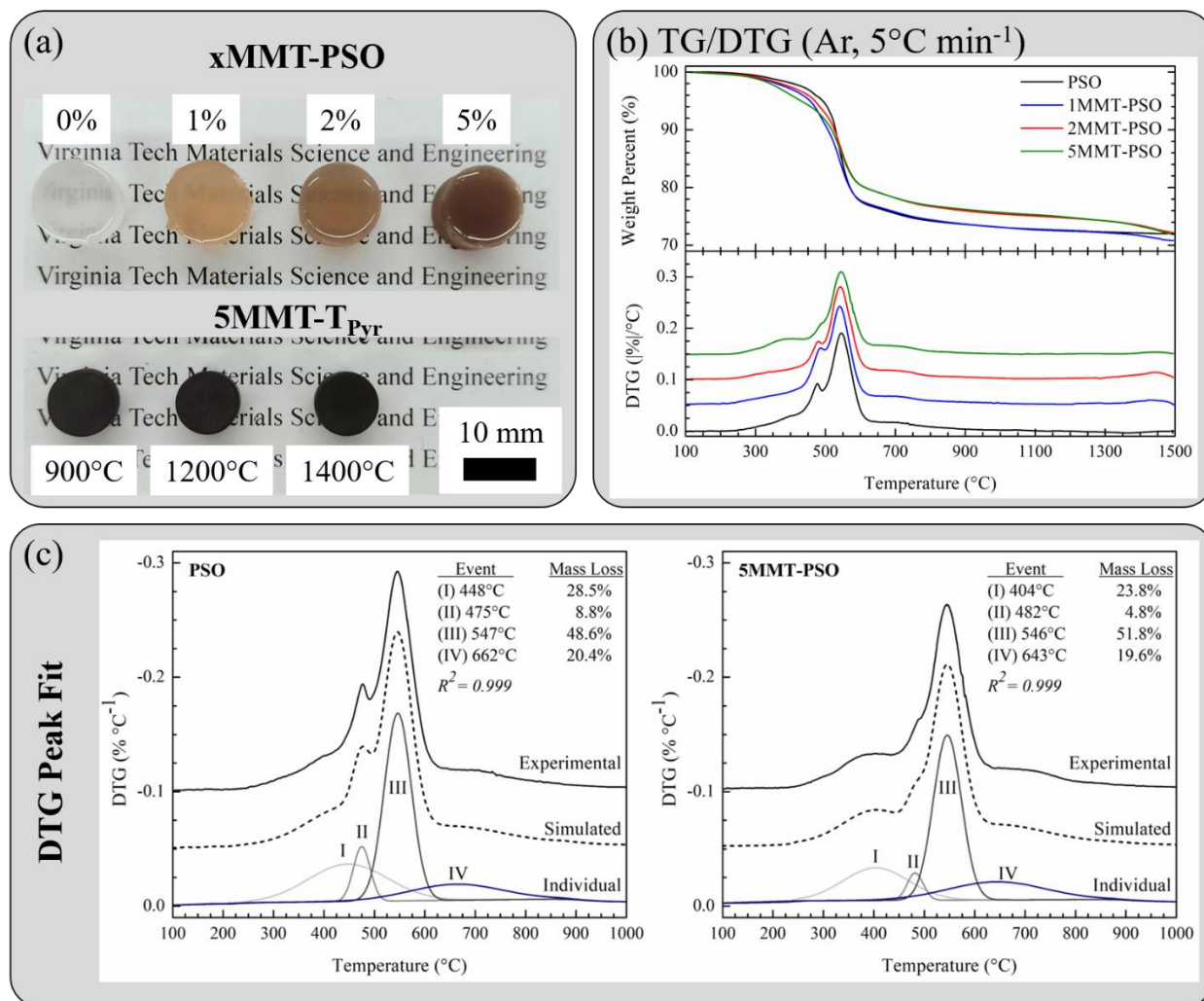


Figure 3.4.3: (a) Optical image of xMMT-PSO ($x = 0, 1, 2, 5$ wt%) preceramic green bodies (*top*) and pyrolyzed 5MMT-900, 5MMT-1200, and 5MMT-1400 ceramics (*bottom*); (b) TGA (*top*) and DTG (*bottom*) analysis of PSO-xMMT green bodies to 1500°C in Ar; (c) DTG peak fitting analysis of PSO and 5MMT-PSO between 100°C and 1000°C to evaluate effect of MMT during polymer-to-ceramic transformation..

Figure 3.4.4 depicts the phase compositions of xMMT-SiOC at (a) 900°C, (b) 1200°C, and (c) 1400°C as determined by XRD. SiOC-900 and SiOC-1200 samples were largely amorphous with the halo from ~10-40° attributed to amorphous SiOC, SiO₂, and C domains. A small α -quartz phase was detected in SiOC-900 but was attributed to unevolved Si-OH groups from the polymer-to-ceramic transition. At 1400°C (**Figure 3.4.4(c)**), poorly refined β -SiC (111), (220), and (311) diffraction peaks at 36°, 60°, and 72°, respectively, emerged from SiOC phase separation as the microstructure developed some nanocrystallinity. However, in the presence of MMT, two diffraction peaks at 20.7° and 26.5° corresponding to the (100) and (101) planes of α -quartz emerged and were retained in the 1/2/5MMT-SiOC samples at all temperatures. Overall, the 1/2/5MMT-SiOC samples were generally amorphous with no other crystalline contributions until 1400°C. Beyond β -SiC crystallization inherent to the SiOC matrix, a new cristobalite diffraction peak at 22° developed in the 1/2/5MMT-1400 samples, and its intensity increased with the MMT content. The MMT-SiOC samples were summarized as amorphous SiOC ceramics reinforced with nanocrystalline SiO₂ domains.

While no characteristic nanosheet diffraction peaks were detected, the MMT nanosheets were responsible for cristobalite and α -quartz crystalline phases present in the MMT-SiOC nanocomposites. Bulk MMT is known to decompose to metakaolin at around 650°C and cristobalite and mullite at about 1350°C. The cristobalite phases in 1/2/5MMT-1400 (**Figure 3.4.4(c)**) and the corresponding increase in the 22° peak intensity with increasing MMT content indicated that the cristobalite phase was MMT-derived rather than from the SiOC matrix. No prominent mullite peaks were observed or expected due to the low Al₂O₃ content in the MMT-SiOC system, but should be present in very low concentrations to satisfy the stoichiometric requirements of cristobalite formation from MMT. It was not evident that the nanosheet morphology inhibited or delayed MMT phase separation to cristobalite and mullite.

The absence of (100) and (101) α -quartz diffraction peaks in the SiOC-1200 and -1400 samples further indicated that the α -quartz phase was similarly MMT-derived. Notably, the intensities of the (100) and (101) α -quartz diffraction peaks in **Figure 3.4.4** were similar among all MMT-SiOC samples and therefore not dependent on the MMT content. However, α/β -quartz are not known products from SiOC phase separation or MMT decomposition even in bulk/layered studies. Furthermore, as the tendency for MMT to decompose to cristobalite and mullite was not suppressed even as a nanosheet, it should not be expected for nanostructured MMT to yield α -

quartz at 900°C. Neither originating from the nanomaterial reinforcement nor the ceramic matrix, the α -quartz phase was determined to form at the interface of the amorphous SiOC matrix and the crystalline MMT nanosheet, likely during the polymer-to-ceramic transition. From the XRD spectra of MMT-NH₂ in Figure 3.4.2, the SiO₂ monolayer that formed on the MMT nanosheet after AEAPTMS functionalization served as a potential surface for epitaxial SiO₂ formation to bridge the interface between the crystalline nanosheet inclusion and the amorphous SiOC matrix. As the organic moieties were thermally cleaved from MMT-NH₂ between 200°C and 700°C, the exposed siliceous MMT nanosheet surface was able to react with the pyrolytically-forming SiOC ceramic to form a homogenous microstructure. Without a proper interface, the MMT nanosheets would serve as inclusions rather than reinforcements and as a site for crack propagation and ceramic fracture/failure.

Above the $\alpha \rightarrow \beta$ quartz inversion at 573°C, the thermodynamically stable β -quartz phase had a hexagonal crystal structure that maintained coherency with the hexagonal crystal structure of the MMT nanosheets. These events occurred simultaneously with the radical-mediated polymer-to-ceramic transformation of the SiOC matrix and provided sites for interfacial bonding between exposed Si-O groups of MMT and the disordered Si tetrahedra of the evolving SiOC matrix. Furthermore, the high-symmetry β -quartz phase provided coherency to resolve the crystalline-to-amorphous microstructural transition at the interface. Further heating above 873°C would induce a phase transformation from β -quartz to tridymite depending on the presence of alkali/alkali earth metal impurities necessary to stabilize the tridymite phase, or to β -cristobalite at 1470°C through an intermediate amorphous phase [181]. It was not apparent that the MMT-SiOC interfacial regions transformed to β -cristobalite or accelerated the decomposition of the MMT regions to cristobalite and mullite as evidenced by the absence of the 22° α -cristobalite diffraction in the 1/2/5MMT-1200 samples (**Figure 3.4.4(b)**). Therefore, the interface was postulated to exist as an amorphous silica boundary bridging the MMT nanosheets and the SiOC matrix. Cristobalite phases were derived from MMT phase decomposition and increased with MMT content. Cristobalite crystallization was observed in SiO₂-based ceramic cores at the surface of quartz grains at 1380°C [182], and similarly proceeded in the 1/2/5MMT-1400 ceramics at the quartz interfaces between the MMT and SiOC matrix. Of note, both β -quartz and β -cristobalite undergo inversions to lower symmetry forms at 573°C and 250°C upon cooling, respectively, and may induce ceramic fracture at significant concentrations. The α -quartz phases identified in **Error!**

Reference source not found. formed during the quartz inversion upon cooling – therefore, it should be noted that the evolved α - quartz interphase may cause ceramic fracture due to significant volumetric reduction.

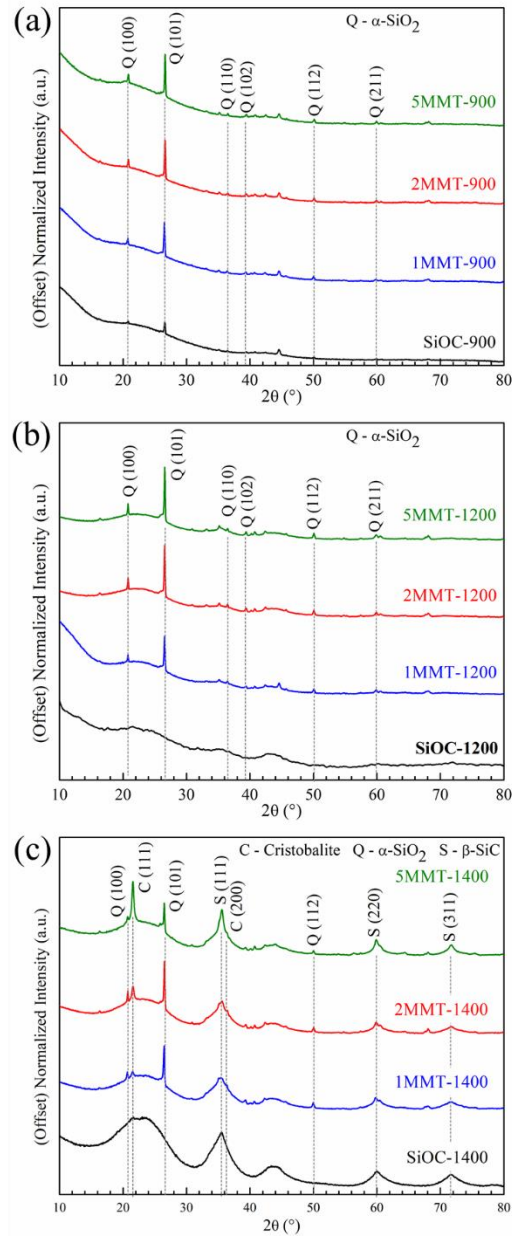


Figure 3.4.4: XRD spectra of xMMT-SiOC ceramic nanocomposites after pyrolysis at (a) 900°C, (b) 1200°C, and (c) 1400°C.

Table 3.4.1 summarizes the ceramic yield (C.Y.), volumetric shrinkage (V.S.), and density (ρ) of x MMT-SiOC ($x = 0, 1, 2, 5$) samples pyrolyzed at 900°C, 1200°C, and 1400°C in Ar. Ceramic yields of ~77%, volumetric shrinkages of ~39%, and densities of 1.58 g cm⁻³ were generally identical among SiOC-900, 1MMT-900, 2MMT-900, and 5MMT-900 samples and indiscernible within experimental standard deviation. Elevated pyrolytic temperatures of 1200°C and 1400°C yielded noticeable increases in ceramic yields and densities, and corresponding decreases in volumetric shrinkages, with the MMT content. SiOC-1200 exhibited a C.Y. of 73.5% while 1MMT-1200, 2MMT-1200, and 5MMT-1200 exhibited increased yields of ~75.3%. The V.S. of SiOC-1200, 1MMT-1200, and 2MMT-1200 were approximately ~48%, but 5MMT-1200 exhibited less shrinkage of 46% -- this was manifested in the slight increase in density from 1.73 g cm⁻³ in SiOC-1200 to 1.75 g cm⁻³ in 1/2/5MMT-1200. Similarly at 1400°C, 1/2/5MMT-1400 had slightly higher C.Y.s of ~74.5% compared to 73.2% for SiOC-1400. The decrease in V.S. from SiOC-1400 (47.4%) to 1/2MMT-1400 (~46.6%) was nominal but starker in 5MMT-1400 (45.6%). Densities slightly increased from 1.74 g cm⁻³ to 1.78 g cm⁻³ from SiOC-1400 to 5MMT-1400; however, all 1400°C samples exhibited some inherent porosity after pyrolysis, which can be attributed to CO gas evolution from the SiOC amorphous matrix carbothermal reduction to β -SiC above 1300°C. As a result, there was a slight decrease in V.S. from 1200°C to 1400°C in all samples. While the pure SiOC matrix primarily exhibited mass loss between 900°C and 1200°C and remained relatively constant to 1400°C, 1/2/5MMT-SiOC showed continued mass loss until 1400°C due to MMT phase decomposition and carbothermal synthesis of β -SiC nanowhiskers.

Table 3.4.1: Ceramic yield (C.Y./%), volumetric shrinkage (V.S./%), and density ($\rho/\text{g cm}^{-3}$) of xMMT-SiOC nanocomposites pyrolyzed at 900, 1200, and 1400°C in Ar. The error indicates the standard deviation of 4-5 replicates.

Ceramic Sample	900°C/Ar			1200°C/Ar			1400°C/Ar		
	C.Y. (%)	V.S (%)	ρ (g·cm ⁻³)	C.Y. (%)	V.S (%)	ρ (g·cm ⁻³)	C.Y. (%)	V.S (%)	ρ (g·cm ⁻³)
SiOC	77.1 ±	39.9 ±	1.58 ±	73.5 ±	48.3 ±	1.73 ±	73.2 ±	47.4 ±	1.74 ±
	0.8	0.6	0.02	0.3	0.7	0.01	0.6	0.5	0.01
1MMT	77.6 ±	40.0 ±	1.57 ±	75.5 ±	48.1 ±	1.75 ±	74.4 ±	46.7 ±	1.75 ±
	0.8	0.4	0.02	0.5	0.7	0.01	0.5	0.4	0.02
2MMT	76.9 ±	39.2 ±	1.58 ±	75.3 ±	47.3 ±	1.75 ±	74.7 ±	46.6 +	1.76 ±
	0.9	0.9	0.02	0.4	0.7	0.02	0.4	0.5	0.01
5MMT	77.7 ±	38.4 ±	1.58 ±	75.9 ±	46.3 ±	1.76 ±	74.4 ±	45.6 ±	1.78 ±
	0.7	0.7	0.02	0.3	0.2	0.01	0.6	0.5	0.02

3.4.2.2. Microstructural analysis

Fracture surface morphologies investigated by SEM (**Figure 3.4.5**) revealed that MMT contributed to increased faceting and the presence of crystallization fronts in 1/2/5MMT-900 and 1/2/5MMT-1200 samples. Compared to the smooth, featureless fracture surfaces of SiOC-900 and SiOC-1200, the crystallized facets indicated that the overall ceramic fracture mechanism was dominated by MMT-derived α - quartz domains rather than turbostratic C commonly present in PDC ceramics. Fracture surfaces of 1/2/5MMT-1400 ceramics revealed an additional coating of nanowhiskers that were embedded in the ceramic matrix. The nanowhiskers were intertwined and protruded from the fracture surface. Additionally, 5MMT-1400 ceramics exhibited slit-like pores on the fracture surface from the MMT phase decomposition, which mirrored fracture surface morphologies of MMT-SiOC prepared with 30-40 wt% bulk/calcined MMT as reported by Bernardo [183]. Unfractured nanowhiskers (**Figure 3.4.5(a)**) were able to reach at least 40 μm in length during pyrolysis at 1400°C but varied in diameter, especially towards the tip. Nanowhisker growth appeared to proceed in (i) steady-state and (iii) diffusion-limited regimes with (ii) transition between the regimes after $\sim 20\ \mu\text{m}$ of growth. Steady-state growth was initiated at a nodule in the MMT-SiOC matrix that was able to pull out from the matrix (**Figure 3.4.5(b)**) upon fracture. The nanowhiskers were typically 400-500 nm in diameter at the nodule and thinned to ~ 200 nm towards the transition regime. Diameters varied between 100 and 200 nm in the diffusion-limited growth regime, and the nanowhiskers were prone to fragmentation in this region. Nanowhisker growth appeared kinetically favorable at 1400°C due to prevalence on 1/2/5MMT-1400 fracture surfaces and continued non-steady state growth after the transition zone, so it was postulated the nanowhiskers are SiC and the concentration of reactive C species for carbothermal synthesis of β -SiC was insufficient for a high number of nanowhiskers present. This would further imply that the nanowhiskers are SiO₂-rich and originate from a SiO₂ nodule. Low-voltage SEM (LV-SEM) imaging of the nanowhiskers (**Figure 3.4.5(c)**) uncovered hexagonal nanowhisker morphology that was not resolvable with usual SEM imaging (5-15 kV), further proving that it was SiC. The nanowhiskers consistently exhibited faceted growth, and exposed interfaces between the nodule and whisker (**Figure 3.4.5 (d-e)**) show a clear hexagonal growth surface. LV-SEM of a pulled-out SiC nanowhisker and nodule (**Figure 3.4.5(f)**) revealed hexagonal structural features that were obscured with HV-SEM imaging (**Figure 3.4.5(b)**) from the conductive effects of SiC nanowhiskers.

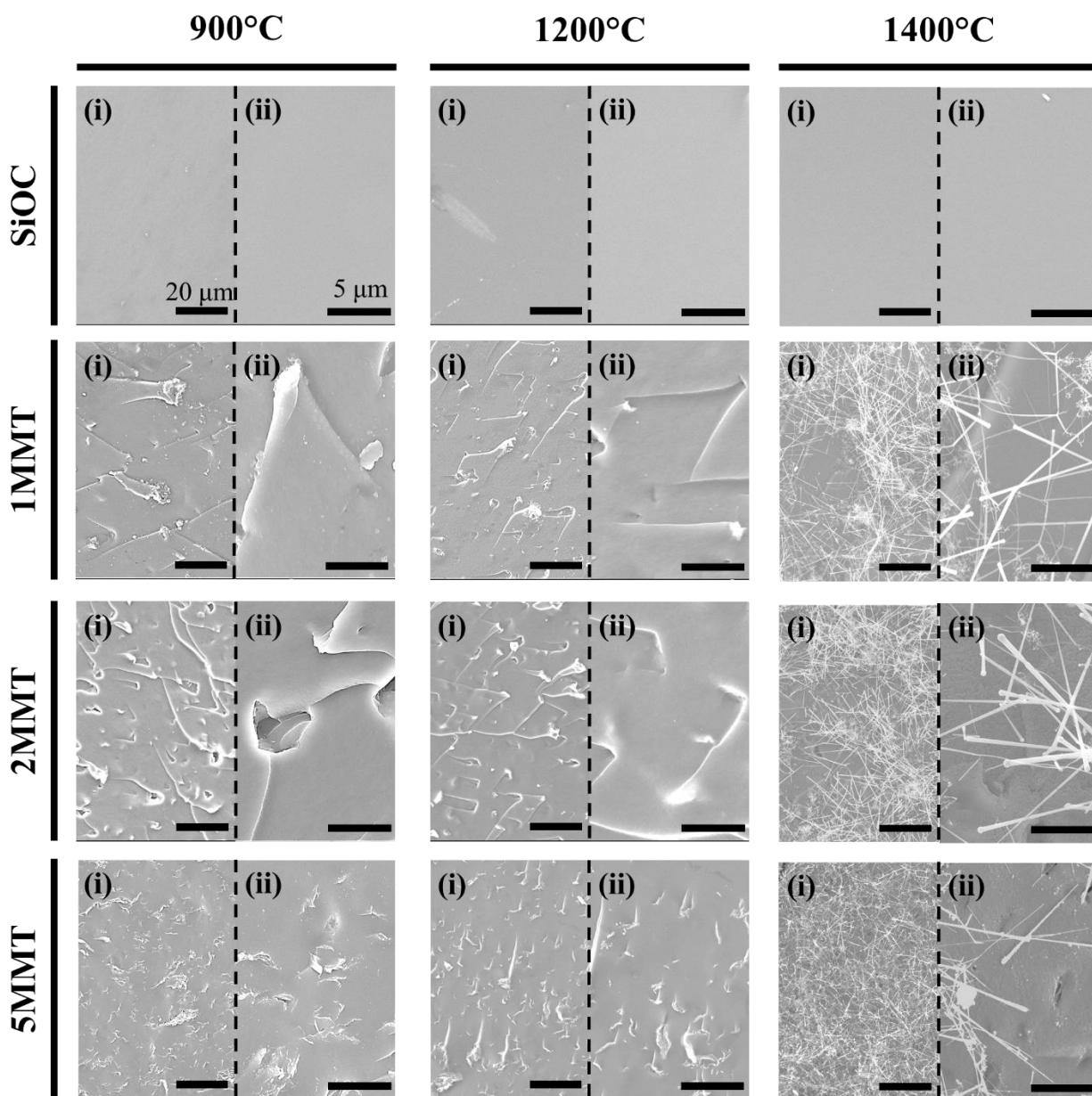


Figure 3.4.5: SEM micrographs of fracture surfaces of xMMT-SiOC ($x = 0, 1, 2, 5$ wt%) ceramics pyrolyzed to 900°C, 1200°C, and 1400°C. Scale bars in (i) and (ii) in all panels are 20 and 5 μm , respectively.

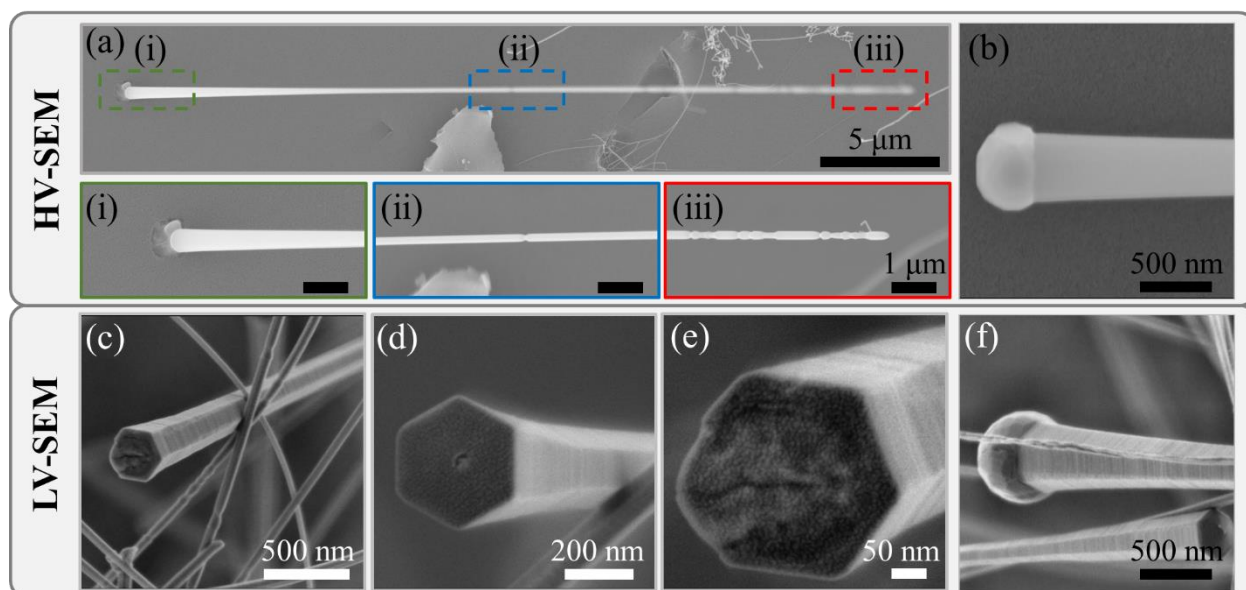


Figure 3.4.6. Morphology of β -SiC nanowhiskers in 1/2/5MMT-1400 ceramics observed with high voltage (10 kV – top) and low voltage (700V – bottom) SEM. (a) Unfractured nanowhisker grown from SiOC matrix with highlighted regions of (i) steady-state, (ii) transition, and (iii) diffusion-limited growth regimes. Scale bars in (i)-(iii) are 1 μm . (b) A pulled-out nanowhisker from the SiOC matrix illustrating a nodule that served as a nanowhisker growth site. (c)-(f) LV-SEM imaging of SiC nanowhiskers revealing hexagonal morphology that was not resolvable with HV-SEM.

The nanostructural evolution of the MMT regions was analyzed with TEM (**Figure 3.4.7**) in 5MMT-900, 5MMT-1200, and 5MMT-1400, and revealed MMT nanoflakes randomly distributed in the SiOC matrix and α -quartz nanoparticle evolution at the MMT-SiOC interface. As anticipated, MMT nanosheet stacking was attributed to the high MMT content in 5MMT-900/1200/1400 but the random dispersion of the nanosheets pointed to the intrinsically exfoliated nature of the MMT nanosheets in MMT-SiOC. As evidenced by XRD, α -quartz nanoparticles were observed at the MMT-SiOC interface and on the MMT nanoflakes in 5MMT-900 (**Figure 3.4.7(a-c)**), which indicated that the SiO₂ interlayer induced coherency between MMT regions and the SiOC matrix. α -quartz nanoparticles were generally about 5 nm in size and randomly dispersed on the MMT nanosheet surface. As α -quartz is a low temperature polymorph, nanoparticle size and distribution indicate crystallization from a high temperature polymorph such as the intermediate amorphous SiO₂ phase upon cooling.

In 5MMT-1200 (**Figure 3.4.7(d-f)**), the MMT nanosheets were covered with a higher concentration of α -quartz nanoparticles than at the interface with the SiOC matrix. As supported by XRD (**Figure 3.4.7(b)**), pyrolysis to 1200°C yielded a refined quartz phase; accordingly, the amorphous SiO₂ interlayer experienced further refinement during pyrolysis to yield the higher concentration of α -quartz nanoparticles. Kinetic analysis of quartz phase transformations revealed positive activation energies from quartz to intermediate amorphous SiO₂ which would spur amorphous phase refinement with higher pyrolysis temperatures [181]. The MMT nanosheets were more uniformly covered with α -quartz nanoparticles, pointing to further refinement of the amorphous SiO₂ interlayer. MMT phase decomposition and SiOC conversion to SiC at 1400°C were observed with slit-like pore formation from the MMT nanosheets and SiO₂ nucleation in the SiOC matrix (**Figure 3.4.7(g-i)**). Pore sizes obtained from TEM were not truly representative due to pore smearing during FIB thinning but regardless illustrated that the microstructural degradation in MMT-SiOC was primarily driven by MMT phase separation. Amorphous SiO₂ refinement at the MMT-SiOC interface predominantly occurred between 900°C and 1200°C, which yielded the increased α -quartz content observed in the XRD spectra of the MMT-SiOC ceramics. However, amorphous SiO₂ inherently present in SiOC did not undergo a similar phase transformation upon cooling, so the observed crystallization was assumed to be induced by the hexagonally-structured MMT surface serving as nucleation sites. In addition, at the expense of SiO₂ refinement, the interface was presumably carbon-deficient and may have less SiOC tetrahedra.

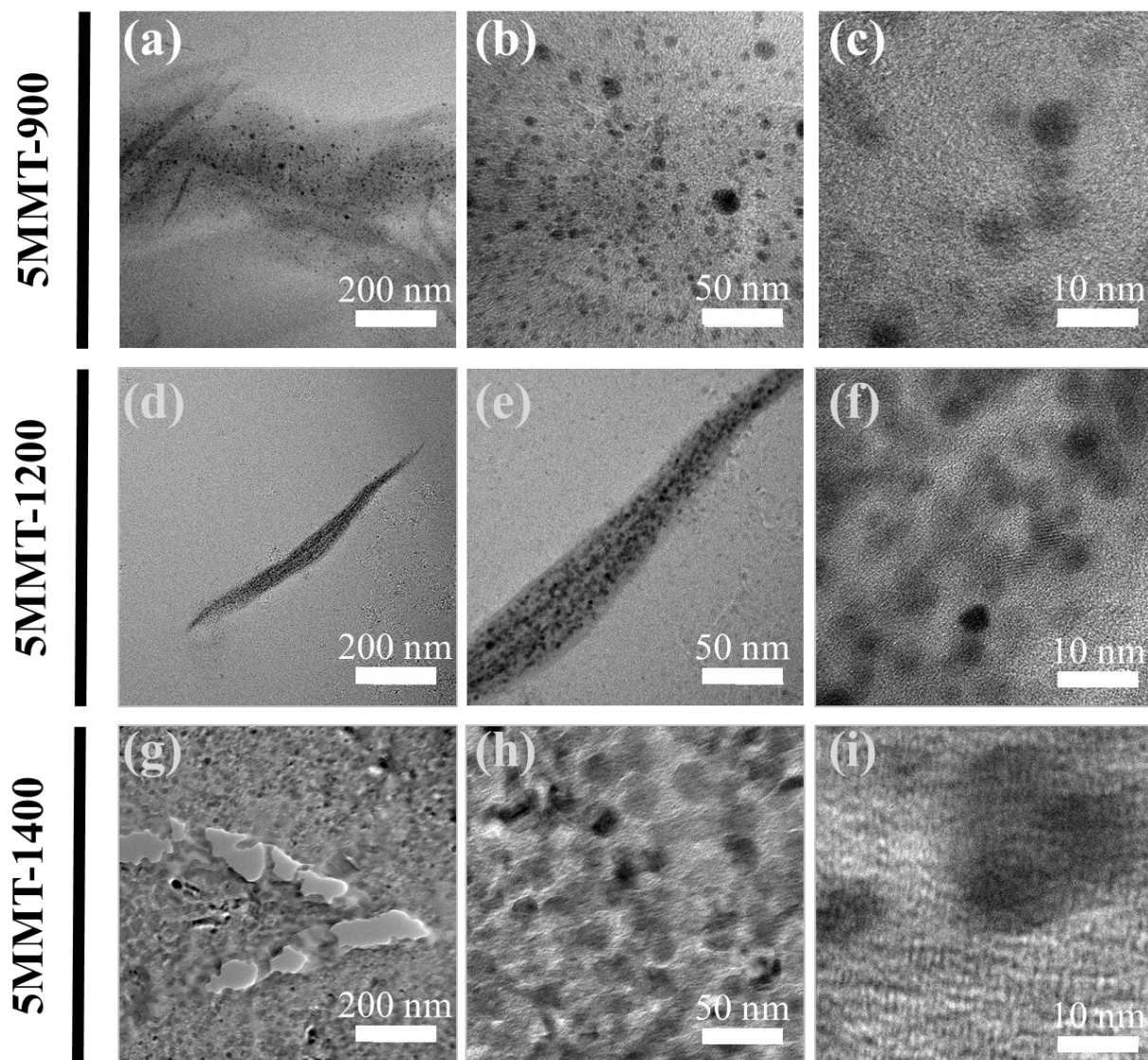


Figure 3.4.7: TEM micrographs illustrating nanostructural phase evolution of MMT nanosheets in 5MMT-900 (a-c), 5MMT-1200 (d-f), and 5MMT-1400 (g-i).

3.4.3. Etching-induced porous SiOC/SiC ceramics

Porous SiOC/SiC ceramics were prepared by etching of SiO₂ domains with excess HF (Equation 2.4.9), and the effect of MMT content on selectively-etched porosity and specific surface area (SSA) in xMMT-SiOC ceramics was determined with N₂ sorption experiments (Figure 3.4.8). As Si-C bonds are resistant to HF, selectively etched porosity was generally representative of the size and distribution of SiO₂ domains present in the MMT-SiOC ceramics.



SiOC-900-HF, 1MMT-900-HF, and 2MMT-900-HF ceramic samples exhibited very little porosity with nearly identical gas adsorption volumes of 8.0, 7.9, and 8.1 cm³ g⁻¹, indicating that the evolved SiO₂ domains from MMT were quite minimal and indiscernible from those present in SiOC-900. While 5MMT-900-HF exhibited increased gas sorption (28.1 cm³ g⁻¹), the HF-etched samples were quite brittle. Microstructural analysis (Figure 3.4.10(a)) revealed microcracks present after etching. The minimal porosity observed in SiOC-900-HF was attributed to the small α -quartz phase present from residual –OH groups, which were generally invariant with 1% and 2% MMT content. At 5% MMT content, microcracking may be due to residual stresses from coalesced α -quartz domains and gas release during etching. Specific surface areas (Figure 3.4.8(d)) of SiOC-900-HF, 1MMT-900-HF, and 2MMT-900-HF of 18, 18, and 23 m² g⁻¹, respectively, were indicative of poorly refined SiO₂ phases. The SSA of 5MMT-900-HF of 79 m²·g⁻¹ was reflective of microcracking and aggregated SiO₂ regions.

Pyrolysis at 1200°C led to a refinement of α -quartz domains, and the 1/2/5MMT-1200-HF ceramics displayed improved pore characteristics compared to SiOC-1(Figure 3.4.8(b)). While SiO₂ clusters are present in SiOC ceramics when measured by ²⁹Si NMR [186, 187], these nanosized clusters (< 2 nm) were too small or inaccessible to be etched by HF. The small concentration of SiO₂ in SiOC-1200 was reflected in poor gas sorption volume (4.6 cm³·g⁻¹) and SSA (3 m²·g⁻¹) for SiOC-1200-HF. Improved porosities in 1/2/5MMT-1200-HF ceramics resulted from a refinement of MMT-derived α -quartz domains, with gas sorption volumes and SSAs increasing to 12.1, 26.5, and 30.6 cm³·g⁻¹ and SSA 20, 105, and 120 m²·g⁻¹, respectively. The effect of MMT on the porosity plateaued between 2% and 5% MMT content due to either limited diffusional lengths by interspersed turbostratic C or tactoid formation of MMT layers from increased MMT loading.

Pore characteristics increased by an order of magnitude between 1200°C and 1400°C inherently due to SiO₂ phase refinement from carbothermal reduction as shown by the amorphous SiO₂ halo emergence in **Figure 3.4.4(c)** and improved gas sorption volume of 109.9 cm³·g⁻¹ and SSA of 340 m²·g⁻¹ for SiOC-1400-HF (Figure 3.4.8(c)). While the MMT content improved selectively etched porosity in 1/2MMT-1400-HF with increased sorption volumes of 161.7 cm³·g⁻¹ and 252.5 m²·g⁻¹, 5MMT-1400-HF displayed a reduced sorption volume of 212.7 cm³·g⁻¹. The SSAs of 1/2/5MMT-1400-HF ceramics followed the same trend, increasing to 500 m²·g⁻¹ and 772 m²·g⁻¹ before decreasing to 574 m²·g⁻¹, respectively. The decrease in pore characteristics may be attributed to the inherent macroporosity visible on the fracture surface of 5MMT-1400 (**Figure 3.4.5**) due to tactoidal layering of MMT nanoflakes at 5 wt% loading and MMT decomposition above 1350°C. The observed increase in pore characteristics in 1/2/5MMT-1400-HF was a combination of inherent porosity from MMT decomposition in the unetched 1/2/5MMT-1400 ceramics (**Figure 3.4.7**) and etching of SiOC-derived and MMT-derived SiO₂ regions.

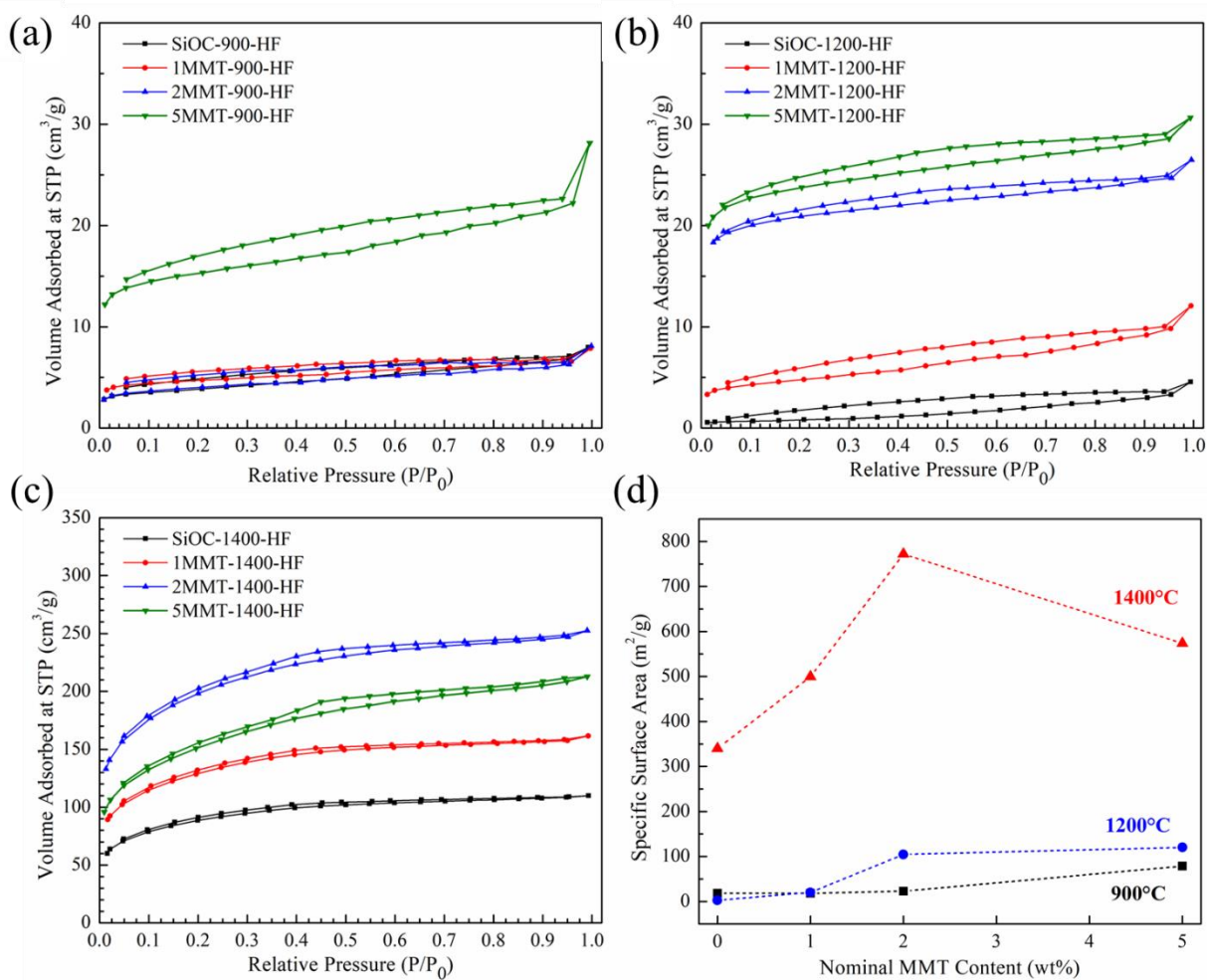


Figure 3.4.8. Nitrogen sorption isotherms of HF-etched xMMT-SiOC ceramics ($x = 0$ /black, 1/red, 2/blue, 5/green) pyrolyzed at (a) 900°C, (b) 1200°C, and (c) 1400°C. (d) SSAs of HF-etched xMMT-SiOC ceramics pyrolyzed at 900°C (black), 1200°C (blue), and 1400°C (red) as determined by NLDFT fitting.

Pore size distributions (Figure 3.4.9) were determined from a NLDFT model of the adsorption branch of N₂ isotherms assuming cylindrical and sphere pore structures. The minimal pore characteristics of xMMT-900-HF ceramics (Figure 3.4.9(a)) were primarily due to the underlying porosity from unresolved Si-OH bonds in the SiOC matrix, with the small concentration of pores in SiOC-900-HF sized between 3 to 10 nm. The addition of MMT generally increased the pore sizes between 2 to 5 nm although quite minimally at 900°C. Further pyrolysis at 1200°C coincided with a refinement of SiO₂ clusters (Figure 3.4.9(b)), yielding few ~5 nm pores upon pyrolysis that were representative of the SiO₂ phases inherently present in SiOC-1200. MMT content primarily increased pore concentrations between 2 to 5 nm in 1/2/5MMT-1200-HF with slight additional contributions to pore sizes from 6 to 10 nm, indicating that the selectively-etched porosity was primarily due to the inclusion of MMT nanosheets and independent of matrix effects.

Pore size distributions in xMMT-1400-HF ceramics (Figure 3.4.9(c)) showed that the porosity from MMT-derived SiO₂ domains augmented that intrinsic to SiOC-1400-HF ceramics. Carbothermal reduction above 1300°C decreases SiO₂ domains to 2 to 5 nm, which were shown to solely contribute to the pore size characteristics of SiOC-1400-HF. Pore size concentrations between 2 and 5 nm further increased in 1/2MMT-1400-HF from the additive effect of MMT-derived SiO₂ domains. Correlating with the decrease in gas sorption volume and SSA, pore size concentrations in 5MMT-1400-HF were generally similar to those in 1MMT-1400-HF and attributed to some loss of the nanostructured MMT-derived SiO₂ domains in the development of slit-like pores observed under SEM (**Figure 3.4.5**). While the microstructures of etched xMMT-SiOC ceramics were generally invariant of their pre-etched analogs, the morphologies of β -SiC nanowhiskers in all xMMT-1400-HF ceramics were affected by HF etching with the nodule present at the base of the nanowhiskers disappearing and the overall length refining to around 5 μ m (Figure 3.4.10(b-c)). The sharpened β -SiC nanowhiskers upon etching indicated that the original nanowhiskers originated from a SiO₂ nodule. The SiO₂-rich nature of the nanowhiskers was postulated to also contribute to non-steady state growth regimes observed as the lack of available reactive C species present during pyrolysis at 1400°C precluded continuous carbothermal reduction of SiO₂ for β -SiC crystallization.

xMMT-1200-HF ceramics displayed porosity indicative solely of MMT-derived SiO₂ domains, while the porosity in xMMT-1400-HF ceramics was developed from MMT phase decomposition and etching of intrinsic amorphous SiO₂ phase and residual MMT-derived SiO₂

domains. SSAs of x MMT-1200-HF ceramics remained below $100 \text{ m}^2\cdot\text{g}^{-1}$, so MMT-derived SiO_2 phase development may be diffusion-limited by turbostratic C barriers in the SiOC matrix. Reactive fillers or pyrolysis atmospheres may be required to augment or improve pore volumes. Overall, 1MMT-1200-HF and 2MMT-1200-HF ceramics serve as potential candidates in porous ceramic applications due to the controlled porosity achieved from the dispersion and etching of the MMT nanosheets.

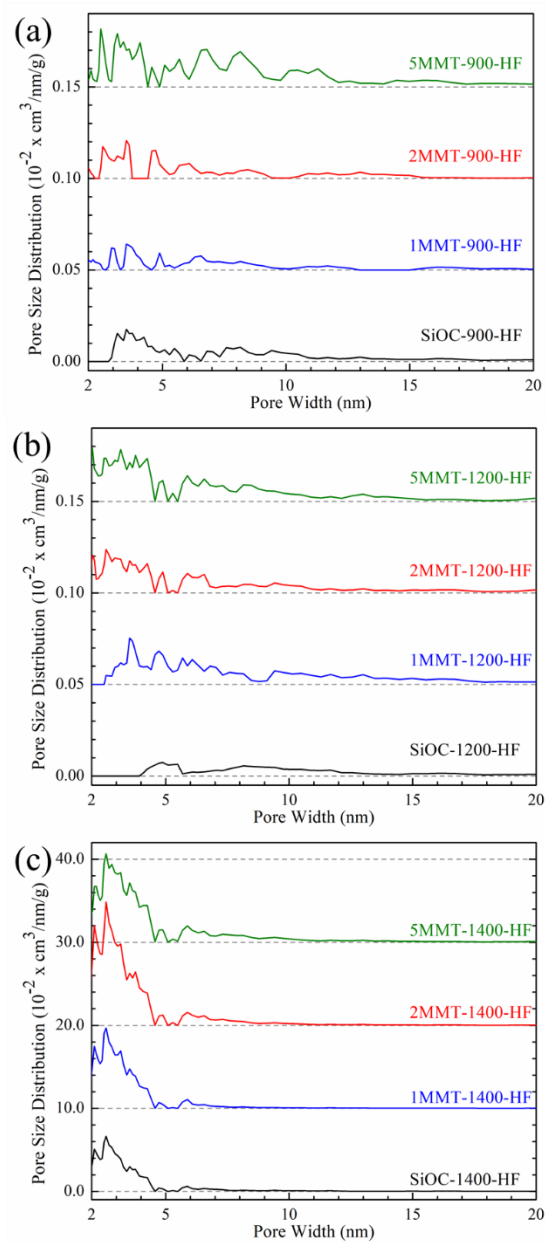


Figure 3.4.9. Pore size distributions of HF-etched MMT-SiOC ceramics pyrolyzed at (a) 900°C, (b) 1200°C, and (c) 1400°C. Curves were offset for clarity.

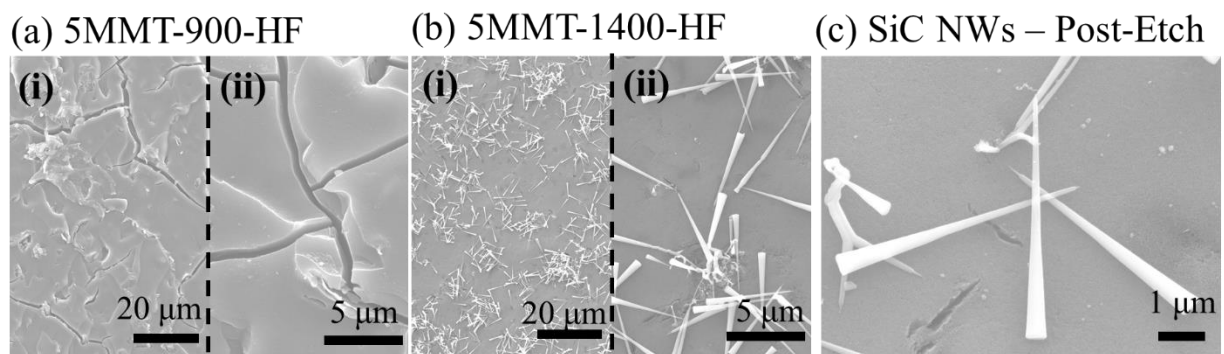


Figure 3.4.10. SEM micrographs of HF-etched (a) 5MMT-900 and (b) 5MMT-1400 ceramic samples. (c) SiC nanowhiskers on the surface of 5MMT-1400 after HF etching.

3.5. *Conclusion*

Organophilic MMT nanoflakes were synthesized by novel twice-functionalization of MMT nanosheets in order to promote exfoliation in the preceramic polymer matrix. Novel MMT-SiOC ceramic nanocomposites were prepared to investigate the effect of nanostructured MMT on phase evolution and selectively etched porosity between 900°C and 1400°C. xMMT-SiOC ceramic nanocomposites fabricated at 900°C and 1200°C showed growth and refinement of a crystalline α -quartz phase on the MMT nanoflakes that led to the formation of 2 to 5 nm pores upon etching. SSAs of HF-etched xMMT-1200 ceramics reached $\sim 100 \text{ m}^2 \cdot \text{g}^{-1}$ but the size of the SiO_2 domains appeared to be diffusion-limited by turbostratic C phases in the SiOC matrix. Further pyrolysis to 1400°C led to β -SiC nanowhisker formation in xMMT-1400 ceramics with structures observed up to 20 μm in length and 500 nm in diameter. Low voltage SEM imaging revealed hexagonal faceting during nanowhisker growth. The findings of this study offer novel fabrication of exfoliated MMT nanocomposites and show that nanostructured MMT and MMT-SiOC ceramics are attractive candidates for porous ceramics and precursors to nanostructured SiC.

Chapter 4: Nanostructural Phase Evolution in MMT-SiOC Ceramic Nanocomposites with Water Vapor-Assisted Pyrolysis

4.1. *Abstract*

Bulk montmorillonite-silicon oxycarbide (MMT-SiOC) ceramic nanocomposites were fabricated with either Ar or Ar-H₂O pyrolytic atmospheres to determine the effect of water vapor on SiO₂ phase evolution at the MMT-SiOC interface and selectively-etched porosity. While water vapor-assisted pyrolysis selectively removes free C in pure SiOC, surprisingly, MMT and water vapor in combination led to encapsulation, shielding, and retention of C as graphene oxide in MMT-SiOC-H₂O ceramics. Crystalline α -quartz phases in MMT-SiOC were converted to amorphous SiO₂ phases during water vapor-assisted pyrolysis, leading to 25-50% reductions in specific surface areas of HF-etched MMT-SiOC without changes to the intrinsic pore structure of water vapor-pyrolyzed SiOC. Further pyrolysis to 1400°C led to the dissolution of the aforementioned pore structure due to more extensive carbothermal reduction as well as refinement of β -SiC nanowhiskers. This work provides a new mechanistic understanding of phase/microstructure evolution and properties of MMT-SiOC nanocomposites as potential candidates in porous ceramic applications.

4.2. *Introduction*

Silicon oxycarbide (SiOC) is a promising class of polymer-derived ceramics (PDCs) with notable thermal stability, oxidation resistance, and thermomechanical properties that offer attractive applications for aerospace, thermal insulation, catalyst supports, and lightweight structures. Classically amorphous, SiOC glasses are comprised of disordered SiO_xC_{4-x} ($1 \leq x \leq 3$) tetrahedra interspersed with SiO₂, SiC, and free carbon (C) regimes, in which the composition of Si-O-C tetrahedra may be tailored from the preceramic polymer(s) and pyrolytic temperatures and atmospheres [9]. Inert atmosphere pyrolysis between 800°C and 1100°C yields an amorphous SiOC matrix with SiO₂ amorphous domains and turbostratic C regimes spreading between SiOC clusters. Pyrolysis to 1300°C induces crystalline β -SiC through carbothermal reduction and turbostratic/graphitic C. Continued β -SiC nucleation and growth proceeds above 1500°C from carbothermal reduction of amorphous SiO₂ and SiOC, but nuclei sizes are generally restricted to less than 5 nm [10].

While containing an amorphous SiO₂ phase, SiOC glasses intrinsically exhibit poor porosity after selective etching with HF as the SiO₂ phase is either sufficiently small (< 2 nm) or shielded by C and SiOC phases serving diffusional and chemical barriers [188]. Porous SiOC is generally obtained through sacrificial additives to impart rationally controlled pore structures either through self-foaming during pyrolysis or selective etching. For PDC systems, sacrificial additives generally must be chemically compatible with preceramic polymer(s) and the evolved ceramic; and maintain coherency with the amorphous/nanostructured SiOC matrix in order to serve as reinforcements rather than inclusions. Promising sacrificial additives for PDCs are then reduced to organic polysiloxane fillers or novel oxide nanoparticles, which may require higher material or production costs [24]. Montmorillonite (MMT) clay additives are popular reinforcements in polymer nanocomposites, leveraging the naturally occurring two-dimensional (2D) nanostructured morphology of ~1 nm layered aluminosilicate sheets to improve mechanical properties and gas permeability, among others [35]. MMT additives are also attractive high-temperature reinforcements due to the inherent stability of the aluminosilicate sheet structure up to 1300-1400°C before phase separation to cristobalite and mullite [185].

Novel MMT-SiOC ceramic nanocomposites were recently fabricated with twice-functionalized MMT nanoflakes to achieve an exfoliated 2D nanocomposite microstructure [189]. MMT nanoflakes were stabilized in the SiOC matrix through an interfacial α -quartz zone originating from the siliceous functional groups on the MMT surface. Selective etching of MMT-derived SiO₂ regimes indicated the emergence of small slit-like pores between 2 and 5 nm, but the relatively small specific surface areas (SSAs) of ~100 m²·g⁻¹ for MMT-SiOC ceramics pyrolyzed to 1200°C in Ar elucidated that SiO₂ phase evolution from MMT was diffusion limited by excess free/turbostratic C present in MMT-SiOC ceramics. MMT nanoflakes are a promising material for introducing anisotropic porosity owing to its 2D morphology but there is a need to improve the intrinsic porosity imbued by MMT structures and phase changes.

Reactive pyrolysis atmospheres (e.g., H₂O, H₂, CO) have been utilized to impart additional O, H, or C species and drive phase evolution in SiOC through radical-mediated reactions with Si during the polymer-to-ceramic conversion between 400°C and 800°C [148, 187, 190-194]. Notably, water vapor-assisted pyrolysis has been shown to preferentially induce the formation of free C, suppress the crystallization of C and SiC, and accelerate SiO₂ crystallization in SiOC [27, 187, 188] through an increase of Si-O-Si bonds and a decrease of Si-C bonds. As excess C is

evolved as CO gas in the presence of water vapor during the polymer-to-ceramic transition, any turbostratic C retained in the SiOC matrix is comprised of fewer graphitic layers and diminishes the barrier for atomic diffusion. Water vapor-assisted pyrolysis in SiOC yielded SSAs of $\sim 2000 \text{ m}^2\cdot\text{g}^{-1}$ with pore sizes generally between 2 and 5 nm [27], and thus is an attractive processing route for enhancing porosity in MMT-SiOC ceramic nanocomposites.

This study focused on the effect of water vapor-assisted pyrolysis on SiO_2 phase formation in MMT-SiOC ceramics to evaluate the role of MMT nanosheet reinforcements as SiO_2 growth sites within the amorphous SiOC matrix (900-1200°C) and SiC nanowhisker growth at higher pyrolytic temperatures (>1400°C). Water vapor-assisted pyrolysis further served to selectively remove excess C during the polymer-to-ceramic transition, and the role of C as a diffusional barrier to SiO_2 phase growth was investigated. MMT content and pyrolytic processing temperature were varied to evaluate phase evolution and selectively etched porosity in MMT-SiOC ceramic nanocomposites.

4.3. *Experimental Methodology*

4.3.1. Materials

The materials for MMT exfoliation and functionalization were provided in a prior study [189]. A commercially available polysiloxane Polyramic SPR-684 (PSO, $[-\text{Si}(\text{Ph})_2\text{O}-]_3[-\text{Si}(\text{Me})(\text{H})\text{O}-]_2[-\text{Si}(\text{Me})(\text{CH}=\text{CH}_2)\text{O}-]_2$, Starfire Systems, Inc., Glenville, NY) was chosen as the base preceramic polymer, with a 2.1% platinum-divinyltetramethyldisiloxane complex in xylene (Karstedt's catalyst, Gelest, Inc., Morrisville, PA) selected to crosslink the preceramic green bodies. Concentrated hydrofluoric acid (HF, 49 wt%, Avantor Specialty Materials, Inc., Radnor, PA) was used to selectively etch SiO_2 from the MMT-SiOC ceramics. Acetone (technical grade, Fisher Scientific, Waltham, MA), toluene ($\geq 99.5\%$, Fisher Scientific, Waltham, MA), and ultrapure water (NP H_2O , 18.2 $\text{M}\Omega\cdot\text{cm}$) were used throughout the experiment as general solvents. Argon (Ar, Industrial Grade, Airgas, Christiansburg, VA) was used for the pyrolysis atmosphere. All chemicals were used without further purification.

4.3.2. MMT-SiOC sample preparation and pyrolysis

Functionalized MMT nanoflakes were prepared following a prior procedure [189]. x MMT-PSO preceramic green bodies ($x = 0, 1, 2, 5$ wt%) were prepared by mixing PSO with toluene (~ 50 v/v% relative to PSO), 100 ppm of Karstedt's catalyst (relative to PSO), and functionalized MMT nanoflakes. The suspension was stirred under vacuum to remove residual solvent. The polymer suspensions were cast to $\Phi 12$ mm x 6 mm cylindrical silicone molds, degassed under vacuum, and cured at 60°C for 6 h, 120°C for 6 h, and 150°C for 12 h. The green bodies were lightly ground to 1500 grit with SiC abrasive pads to remove any mold artifacts, and the edges were slightly beveled. To minimize potential surface oxidation, the green bodies were placed between two sheets of carbon felt in an alumina crucible. The green bodies were pyrolyzed at 900°C, 1200°C, or 1400°C in a horizontal tube furnace (1830-12 Horizontal Tube Furnace, CM Furnaces, Inc., Bloomfield, NJ), with heating and cooling rates of 2°C·min⁻¹, soaking time of 2 h, and inflowing Ar of 500 cm³·min⁻¹. Water vapor was injected between 500°C and 700°C by flowing Ar through a water bath maintained at 60°C (corresponding to 80 vol% Ar-20 vol% H₂O). The temperature was held for 30 min at 500°C and 700°C to ensure a thorough changeover of Ar to Ar-H₂O and Ar-H₂O to Ar, respectively. MMT-SiOC ceramics prepared with water vapor-assisted pyrolysis were denoted as x MMT-T_{Pyr}-H₂O with $x = 1, 2, 5$ wt% and T_{Pyr} = 900, 1200, or 1400°C. Comparable MMT-SiOC ceramics were pyrolyzed without water vapor and denoted as x MMT-T_{Pyr}-Ar. Blank SiOC ceramics without MMT were similarly denoted SiOC-T_{Pyr}-Ar or SiOC-T_{Pyr}-H₂O.

4.3.3. Characterization

Ceramic yield and volume shrinkage were calculated from changes in mass and sample volume, respectively, between green bodies and pyrolyzed samples. Reported values are averages of 3-5 replicates and corresponding errors indicate standard deviations. The phase compositions of powdered samples were analyzed with an X-ray diffractometer (XRD, Empyrean, Malvern PANalytical Ltd., Almelo, The Netherlands) operated at 40 kV and 40 mA with Cu K α radiation between $2\theta=3-90^\circ$ and a scan rate of 0.02° s⁻¹. Microstructures were observed with a scanning electron microscope (SEM, JEOL IT-500HR, JEOL USA, Peabody, MA) and a transmission electron microscope (TEM, JEOL 2100, JEOL USA, Peabody, MA) equipped with a LaB₆ filament operated at 200 kV. Simultaneous differential scanning and thermogravimetric analysis (STA, SDT 650, TA Instruments, New Castle, DE) was performed with a heating rate of 5°C min⁻¹.

¹ to 1500°C under argon flow of 20 mL·min⁻¹. Single-pulse magic angle spinning (MAS) nuclear magnetic resonance (NMR, Bruker Avance II, Bruker Corp., Billerica, MA) spectra for ²⁹Si were collected with a frequency of 59.627 MHz, 2.5 μs pulse width, 60 s recycle delay, averaged over 5000 scans, and in a 4 mm rotor at a MAS frequency of 10 kHz. ²⁹Si was calibrated by an external TMS standard (0 ppm). Raman characterization (XploRA PLUS, Horiba Scientific, Piscataway, NJ) was performed with an Ar laser at 532 nm between 500-4000 cm⁻¹. Elemental analysis (E.A.) for Si (ICP-OES) and C (combustion) was performed by Galbraith Laboratories, Inc. (Knoxville, TN).

xMMT-SiOC ceramics were lightly fractured into ~5 mm pieces and etched in a 10% HF (aq) solution at 1 w/v% for at least 96 h. Samples were thoroughly washed with NP H₂O and EtOH and vacuum dried at 120°C for 12h. Porosity and surface area characteristics were determined by nitrogen adsorption at 77 K (Quantachrome Autosorb-iQ C-XR, Quantachrome Instruments, Boynton Beach, FL). Samples were degassed under vacuum at 300°C for 12 h prior to analysis. A Non-Local Density Functional Theory (NLDFT) model was applied to the adsorption branch with a spherical/cylindrical pore structure based on a silica adsorbate model.

4.4. *Results and Discussion*

4.4.1. Microstructural and phase evolution

Phase compositions of MMT-SiOC ceramics pyrolyzed in Ar and Ar-20%H₂O were analyzed with XRD and shown in **Figure 4.4.1**. SiOC pyrolyzed with Ar and Ar-20%H₂O were largely amorphous but with an increased SiO₂ halo between 22-24° in both SiOC-900-H₂O (**Figure 4.4.1(a)**) and SiOC-1200-H₂O (**Figure 4.4.1(b)**) samples. For the 1400°C pyrolyzed pure SiOC samples, SiO₂ crystallization is more pronounced for SiOC-1400-H₂O. All these observations are consistent with earlier studies [27, 143, 187, 188], indicating that water vapor pyrolysis accelerates SiO₂ formation and even SiO₂ crystallization in pure SiOC. However, in **Figure 4.4.1(a-b)**, SiOC-900 and SiOC-900-H₂O samples, along with xMMT-900-Ar and xMMT-1200-Ar ceramics exhibited α-quartz (100) and (101) reflections at 20.7° and 26.5°, respectively, from crystallized α-quartz. We believe such α-quartz formation is transient in pure SiOC, as this phase disappears in **Figure 4.4.1(b)** for the SiOC-1200 and SiOC-1200-H₂O samples and re-appears in **Figure 4.4.1(c)** for the SiOC-1400-H₂O sample. Amorphous SiO₂ and free turbostratic C phases likely

reacted at higher pyrolysis temperatures, which was elucidated through recent ReaxFF/LAMMPS simulation studies [195, 196].



However, for the xMMT-SiOC samples, such α -quartz crystallites are believed to be predominately at the interface between MMT nanosheets and the SiOC matrix, as they are persistent in the xMMT-SiOC samples, also consistent with that reported previously [189]. These α -quartz peaks are absent for the SiOC-1200 and SiOC-1200-H₂O samples, likely due to the consumption of α -quartz by conversion into SiOC through C diffusion. With water vapor-assisted pyrolysis, however, the surprising finding is that α -quartz reflections were less intense in 1MMT-900-H₂O, 2MMT-900-H₂O, 1MMT-1200-H₂O, and 2MMT-1200-H₂O. The intensities of α -quartz reflections in 5MMT-900 and 5MMT-1200 were identical for both Ar and Ar-20%H₂O pyrolysis conditions, potentially due to bulk MMT effects from nanosheet stacking at the high loading content. While all MMT-SiOC-H₂O samples pyrolyzed at 900°C and 1200°C exhibited a more pronounced amorphous SiO₂ halo, water vapor-assisted pyrolysis suppressed α -quartz crystallization at the MMT-SiOC interface. This is opposite to the general notion that water pyrolysis facilitates SiO₂ formation. Fracture surfaces observed with SEM (**Figure 4.4.2(a)**) were identical among 2MMT-900 and 2MMT-1200 samples pyrolyzed with either Ar or Ar-20% H₂O, illustrating dense microstructures with faceted features in MMT-SiOC samples due to fracture at or along MMT domains. No discernable differences in SEM were expected due to similar MMT content across pyrolysis environments and changes to SiO₂ content occurring at the nanoscale. Suppressed α -quartz crystallization, however, indicated that water vapor-assisted pyrolysis may have reduced overall SiO₂ content and even SiO₂ domain size in MMT-SiOC, contradicting the typical behavior of SiOC with water vapor-assisted pyrolysis.

Further pyrolysis to 1400°C (**Figure 4.4.1(c)**) corresponded to the increased presence of amorphous SiOC (~22° halo), turbostratic C (broad reflection at ~44°), and poorly crystallized β -SiC (broad reflections at 36°, 60°, and 72° for (111), (220), and (311) planes, respectively). While present in SiOC-1400-H₂O and 1/2/5MMT-1400-Ar, α -quartz was not observed in the XRD spectra of 1/2/5MMT-1400-H₂O, indicating that water vapor-assisted pyrolysis fully suppressed crystallization of the MMT-SiOC interface. The known increase in SiO₂ content in SiOC in the presence of water vapor seemingly contradicted the observed inhibition of α -quartz crystallization, alluding to the reduction of C as the driving mechanism to the displayed behavior. Free C in SiOC

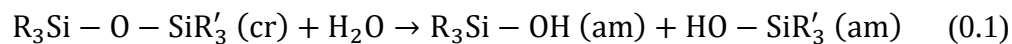
systems originates from excess C-rich functional groups in the preceramic polymer. In carbon-rich SiOC, free C regimes exist as a continuous network that encapsulates SiO₂ regimes with the SiOC tetrahedra at the interlayer [117]. α -quartz was theorized to form upon cooling from high temperature tridymite formed at the MMT-SiOC interface during the pyrolysis.

Identical emergence and strengthening of the 22° cristobalite reflection among 1/2/5MMT-1400-Ar and 1/2/5MMT-1400-H₂O was attributed to MMT decomposition, with the increasing reflection intensity correlating with MMT content. In addition, β -SiC formation was enhanced in 1/2/5MMT-1400-H₂O as indicated by the increased prominence of (111), (200), and (311) reflections in **Figure 4.4.1(c)**. MMT-SiOC pyrolyzed to 1400°C in Ar exhibited β -SiC nanowhisker growth (**Figure 4.4.2(b-e)**) from nanoflake MMT decomposition to cristobalite and mullite, of which the former formed β -SiC via carbothermal reduction with encapsulated and neighboring C regimes (Equation 2.4.2) β -SiC nanowhiskers were abundantly observed on xMMT-1400-Ar and xMMT-1400-H₂O fracture surfaces, randomly oriented and often protruding from the surface (**Figure 4.4.2(b)**). SiOC-1400-Ar and SiOC-1400-H₂O were similarly featureless and lacking β -SiC nanowhiskers, indicating that MMT addition primarily catalyzed nanowhisker growth (**Figure 4.4.2(a)**). We postulated that nanowhisker growth was spurred by the small amount of mullite from MMT present, because mullite was previously shown to exhibit needle-like morphologies in a variety of oxide ceramics. However, these β -SiC nanowhiskers exhibited higher dendritic and non-steady state growth features (**Figure 4.4.2(c-d)**) compared to those present in MMT-SiOC-Ar [187]. The forked and coiled β -SiC nanowhiskers indicated that there was a general dearth of reactive C species, but this created a stark dichotomy with XRD spectra showing enhanced β -SiC crystallization in MMT-1400-H₂O (**Figure 4.4.1(c)**). With water vapor-assisted pyrolysis, MMT-1400 ceramics formed more β -SiC, which required more C present as β -SiC formation proceeded purely through carbothermal reduction of SiO₂ in SiOC systems. Non-steady state growth observed at nanowhisker terminations was not attributed to the overall lack of reactive C, but to an insufficient amount relative to the higher concentration of β -SiC nanowhiskers formed near MMT flakes.

From the above observations, we believed that MMT and water vapor-assisted pyrolysis in conjunction both suppressed SiO₂ crystallization and retained C in MMT-SiOC-H₂O, which was further observed and confirmed with (HR)TEM and STEM-EDS nanostructural characterization (**Figure 4.4.3**) of 5MMT-1200-Ar and 5MMT-1200-H₂O. The MMT-SiOC interfacial region in

5MMT-1200-Ar (**Figure 4.4.3(a)**) was revealed from the crystalline MMT regimes peppered with α -quartz nanoparticles to the generally featureless SiOC matrix. Vein-like SiO₂ grains were observed to bridge the MMT-SiOC interface, which was further revealed (**Figure 4.4.3(b)**) to be comprised of both am-SiO₂ (white grains) and α -quartz (black particles). Crystalline α -quartz contributions were identified by minor diffraction spots in the FFT inset (yellow circles). MMT was shown previously to catalyze Si-O-Si condensation during pyrolysis of MMT-PSO around 400°C, a ~50°C earlier onset than in pure PSO, as the interfacial region between SiOC and MMT formed [187]. This interfacial region was theorized to comprise encapsulated C and SiOC clusters that bridged the coherency difference between crystalline MMT and amorphous SiOC. α -quartz nanoparticles on the MMT surface (**Figure 4.4.3(c)**) and in the interface (**Figure 4.4.3(d)**) were well-crystallized with lattice fringes measured as 4.6 Å and 1.9 Å and attributed to (100) and (112) planes, respectively.

While MMT-1200-H₂O exhibited a similar morphology between MMT domains and the SiOC matrix (**Figure 4.4.3(e)**), the interfacial regions characterized by loss of crystallinity from α -quartz and encapsulated SiOC/C regimes were observed within or between MMT domains. The MMT-SiOC interfacial region (**Figure 4.4.3(f)**) exhibited solely am-SiO₂ grains with no crystalline α -quartz present. Water vapor injection suppressed α -quartz crystallization through amorphization of crystallized Si-O-Si bonds (Equation 4.4.1), which were shown to exhibit high reactivity with water in *ab initio* molecular dynamic simulations [195]. While high pressures have been shown to spur SiO₂ amorphization [196, 197], water vapor injection between 500°C and 700°C generated •H and •OH radicals that reacted with strained Si-O-Si bonds. Amorphization of Si-O-Si bonds further relieved lattice strain between crystalline regimes and the amorphous SiOC matrix. In the presence of MMT that created α -quartz prior to water injection, water vapor promoted amorphous SiO₂ formation through vitrification of crystalline α -quartz, accounting for the suppressed reflections observed in XRD (**Figure 4.4.1**).



Furthermore, during water vapor injection between 500°C and 700°C, MMT regimes effectively shielded C from volatilizing as CO through encapsulation of SiOC/C regions, as indicated in **Figure 4.4.3(e)**. The lack of such encapsulated regions in 5MMT-1200-Ar indicated that water vapor not only promoted amorphization of Si-O-Si bonds but also C diffusion into SiO₂-rich regions. In this regard, water vapor may have led to additional SiOC clusters. HRTEM analysis

within encapsulated regions (**Figure 4.4.3(g)**) revealed turbostratic C diffused between am-SiO₂ grains and characterized by lattice fringe spacing of 4.4 Å corresponding to (001) C planes. Volatilization of C species (e.g., CH₄, H₂C=CH₂, H₃C-CH₂=CH₂) during Ar atmosphere pyrolysis is typical between 400°C and 700°C from excess C-rich functional groups in the preceramic polymer [179, 180], and water vapor-assisted pyrolysis further volatilizes free C as CO (Equation 4.4.2) [27, 186]. However, MMT domains shielded these encapsulated SiOC/C regimes from H₂O oxidation and C was retained in the matrix.



EDS elemental maps of 5MMT-1200-Ar (**Figure 4.4.3(i)**) and 5MMT-1200-H₂O (**Figure 4.4.3(j)**) further revealed encapsulated SiOC/C regimes within MMT domains. MMT domains in both 5MMT-1200-Ar and 5MMT-1200-H₂O are Si ((**Figure 4.4.3(i1)**)-(j1)) and O ((**Figure 4.4.3(i2)**)-(j2)) rich, with C ((**Figure 4.4.3(i3)**)-(j3)) generally segregated outside MMT domains. Al ((**Figure 4.4.3(i4)**)-(j4)) and Fe ((**Figure 4.4.3(i5)**)-(j5)) signatures were detected from the MMT nanosheet. However, as indicated in **Figure 4.4.3(j4)**, C was detected within MMT regimes in 5MMT-1200-H₂O; this further confirmed that C was retained within MMT regimes and protected from water vapor ingress. Overall, water vapor-assisted pyrolysis produced inverse effects in MMT-SiOC ceramics as MMT domains preferentially retained C and water vapor induced α -quartz amorphization. Encapsulated SiOC/C regimes further enhanced β -SiC nanowhisker growth in MMT-1400-H₂O ceramics due to the carbothermal reduction of nanosized SiO₂ and C phases.

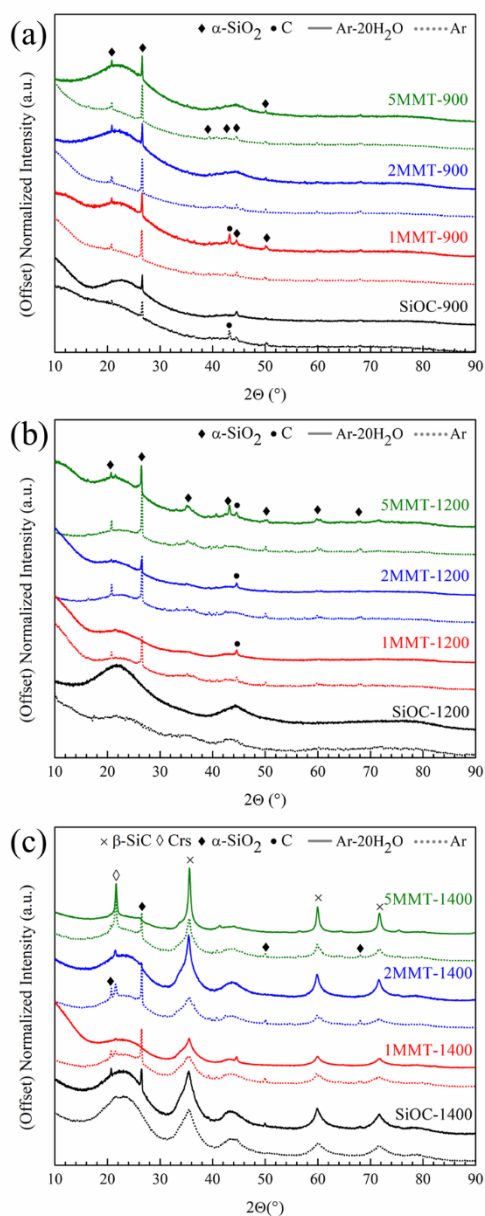


Figure 4.4.1. XRD spectra of xMMT-SiOC ceramics pyrolyzed at (a) 900°C, (b) 1200°C, and (c) 1400°C in Ar-20%H₂O (solid) and Ar (dashed). Spectra were normalized and offset for clarity. Reflections for α -quartz (filled diamond), C (filled circle), β -SiC (X), and cristobalite (Crs/hollow diamond) were indicated on the respective spectra.

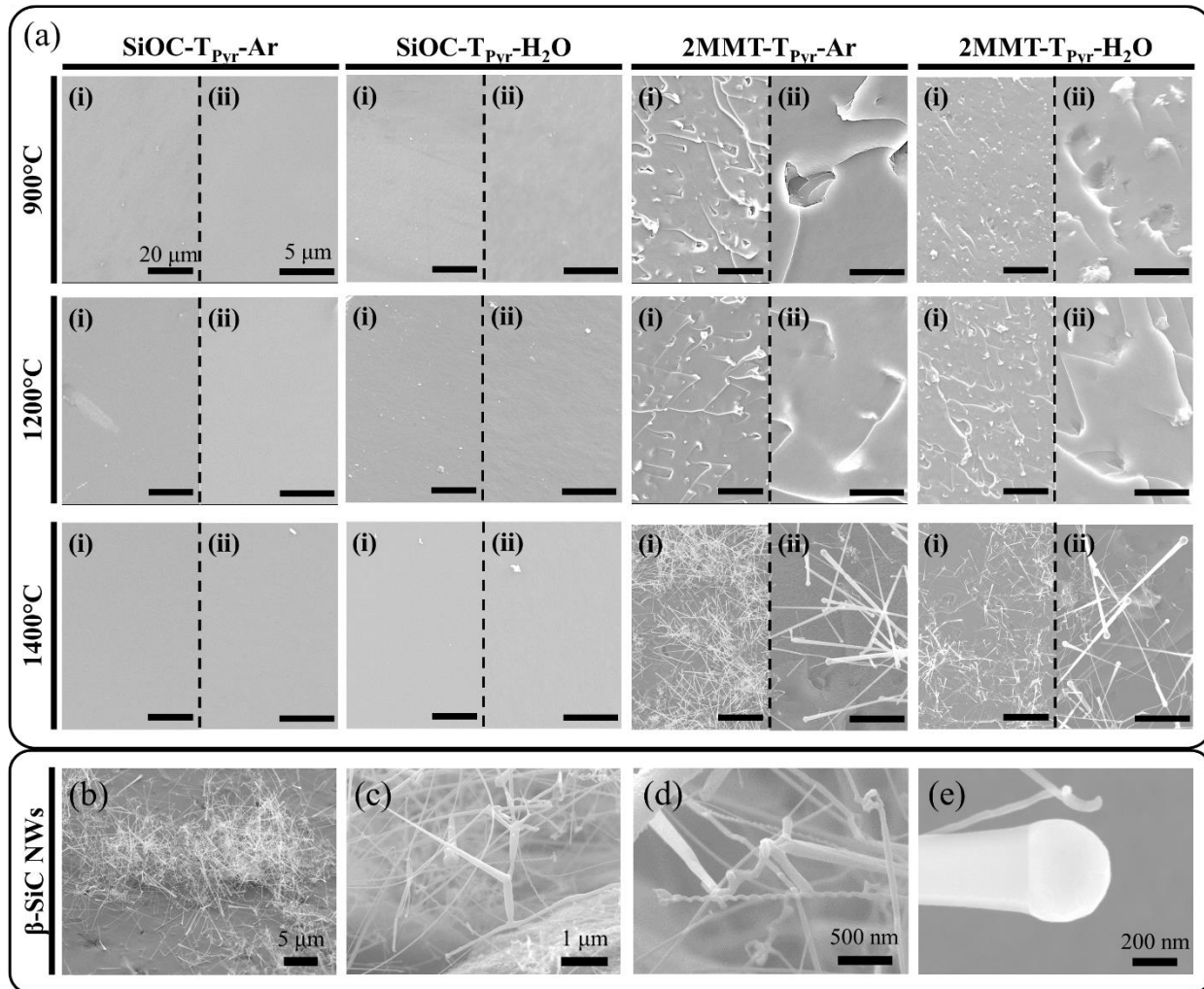


Figure 4.4.2. (a) Fracture surface morphologies of SiOC and 2MMT-SiOC ceramics pyrolyzed to 900°C, 1200°C, and 1400°C with Ar or Ar-20%H₂O. Scale bars in panels (i) and (ii) in all micrographs are 20 and 5 μm, respectively; (b)-(d) β-SiC nanowhisker structures formed during water vapor-assisted pyrolysis of 1/2/5MMT-SiOC to 1400°C illustrating a non-steady state and dendritic growth; (e) detached SiO₂ nodule from which β-SiC nanowhiskers form.

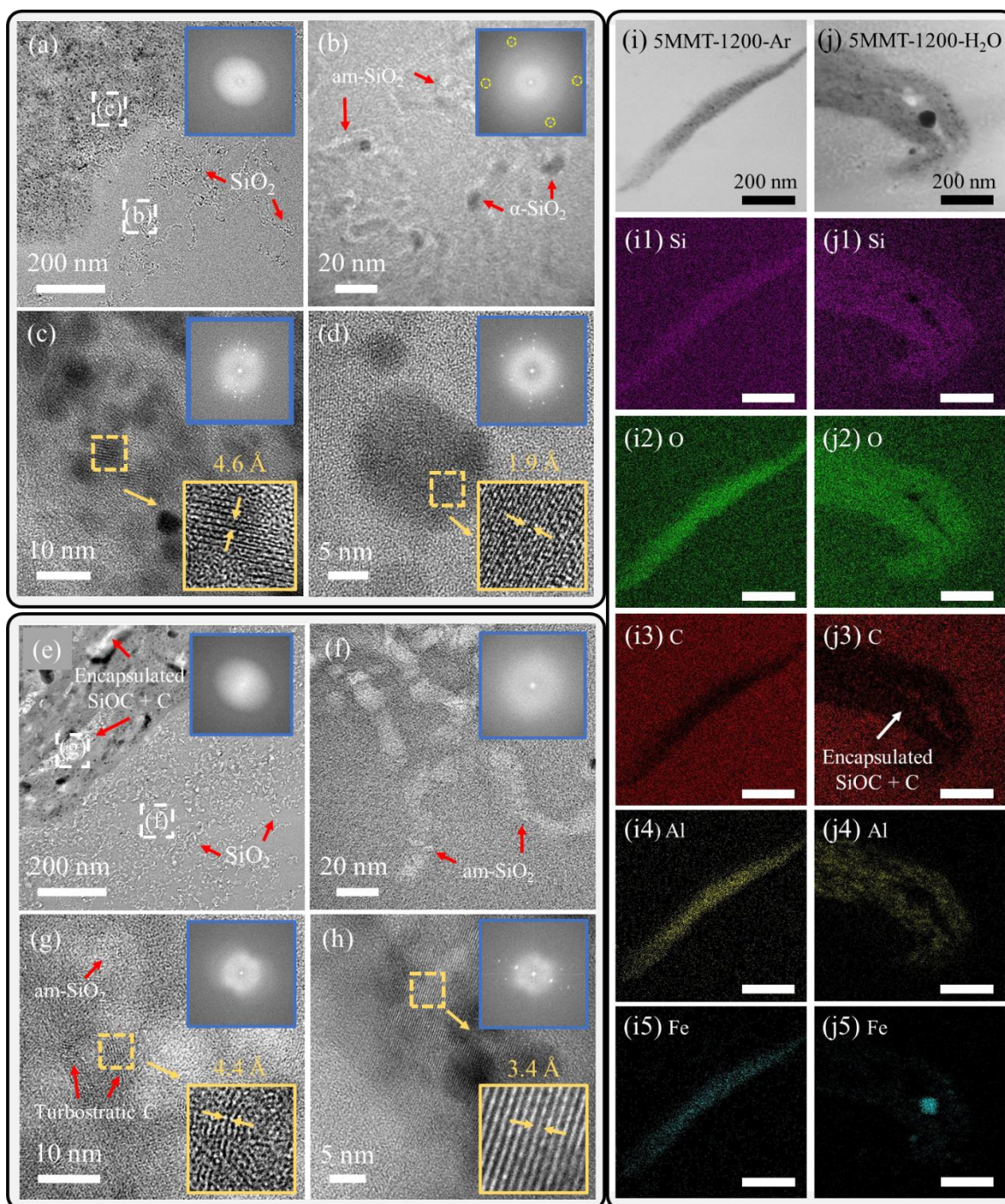


Figure 4.4.3. (HR)TEM characterization of (a)-(d) 5MMT-1200-Ar and (e)-(h) 5MMT-1200-H₂O cross-sections prepared by FIB lift-out. Blue insets show respective FFT patterns and orange insets show enhanced views of lattice fringes. STEM-EDS elemental maps for Si (1/purple), O (2/green), C (3/red), Al (4/yellow), and Fe (5/blue) of (i) 5MMT-1200-Ar and (j) 5MMT-1200-H₂O. Scale bars in all (i)/(j) panels are 200 nm.

4.4.2. Physical properties and selectively-etched porosity

Notably, water vapor-assisted pyrolysis produced MMT-SiOC-H₂O ceramics that showed a higher retention of C, which had further implications in overall physical properties.

Figure 4.4.4 summarizes the ceramic yield (CY, top panel/black) and volumetric shrinkage (VS, bottom panel/blue) of MMT-SiOC-Ar and MMT-SiOC-H₂O pyrolyzed at (a) 900°C, (b) 1200°C, and (c) 1400°C. Ceramic residues of MMT-SiOC-H₂O samples pyrolyzed at 900°C were 3-5% greater than corresponding MMT-SiOC-Ar ceramic yields. The ceramic yields of 1/2/5MMT-900-Ar (CYs: $\sim 77.7 \pm 0.8\%$) were not discernable from those of SiOC-900-Ar (CY: $77.0 \pm 0.8\%$) within experimental error. While water vapor-assisted pyrolysis improved the ceramic yield between SiOC-900-Ar and SiOC-900-H₂O (CY: $82.0 \pm 0.2\%$) by 5%, 1/2MMT-900-H₂O (CYs: $\sim 80.5 \pm 0.3\%$) and 5MMT-900-H₂O (CY: $81.7 \pm 0.5\%$) ceramics only showed a 3% improvement compared to 1/2/5MMT-900-Ar. Presumably, MMT inhibited reactions between water vapor and the transforming MMT-PSO/MMT-SiOC matrix, hence limiting C removal caused by water vapor pyrolysis. The observed higher CYs between 2MMT-900-H₂O and 5MMT-900-H₂O were attributed to the bulk MMT effects from coalesced MMT regimes. In addition, a slight net improvement in ceramic yields at 900°C was obtained, and water vapor-assisted pyrolysis did not affect volumetric shrinkage (**Figure 4.4.4(a)**) among SiOC-900-Ar (VS: $39.9 \pm 0.6\%$), SiOC-900-H₂O (VS: $40.9 \pm 0.3\%$) 1MMT-900-Ar (VS: $39.4 \pm 0.7\%$), and 1MMT-900-H₂O (VS: $40.0 \pm 0.4\%$). While causing an additional $\sim 2\%$ shrinkage difference between 2MMT-900-H₂O (VS: $41.6 \pm 0.4\%$) and 2MMT-900-Ar (VS: $39.2 \pm 0.9\%$), water vapor-assisted pyrolysis accentuated the expected bulk MMT effects at 5% MMT loading with a $\sim 4\%$ difference between 5MMT-900-H₂O (VS: $42.3 \pm 0.2\%$) and 5MMT-900-Ar (VS: $38.4 \pm 0.7\%$). Even though it induced notable changes to the pure SiOC matrix, water vapor pyrolysis was not sensitive to increasing MMT content up to 2% as the trends between SiOC-900, 1MMT-900, and 2MMT-900 were identical regardless of pyrolysis atmosphere. Therefore, water vapor pyrolysis of MMT-SiOC affected SiO₂ phase formation both in the matrix SiOC and in MMT domains, but with inverted effects.

Further pyrolysis to 1200°C generally exhibited $\sim 1.5\text{-}2\%$ greater ceramic yields (**Figure 4.4.4(b)**) in SiOC-1200-H₂O (CY: $74.5 \pm 0.5\%$) and 1/2/5MMT-1200-H₂O (CY: $\sim 76.9 \pm 0.6\%$) than for Ar-pyrolyzed SiOC-1200 (CY: $73.5 \pm 0.3\%$) and 1/2/5MMT-1200 (CY: $\sim 75.5 \pm 0.5\%$), which were expected from hindered carbon removal and oxygen/hydroxyl incorporation during water vapor-assisted pyrolysis. Ceramic yields among 1/2/5MMT-1200-H₂O and 1/2/5MMT-

1200-Ar were nearly identical and not discernable within experimental error. As shown in **Figure 4.4.4(b)**, the net mass increase corresponded with a general $\sim 2.5\text{-}3\%$ lower volumetric shrinkage across SiOC-1200 and 1/2/5MMT-1200 pyrolyzed with Ar-20% H_2O compared to the Ar-pyrolyzed analogs. Volumetric shrinkage in MMT-SiOC-1200 samples was primarily caused by matrix reactions with the water vapor pyrolysis environment: shrinkage lowered from $48.3 \pm 0.6\%$ in SiOC-1200- H_2O to $45.2 \pm 0.6\%$ in SiOC-1200-Ar. No significant differences were observed in 1MMT-1200- H_2O (VS: $48.1 \pm 0.8\%$) and 1MMT-1200-Ar (VS: $45.3 \pm 0.4\%$) compared to the corresponding SiOC-1200 samples. The samples with MMT content above 2% exhibited slight VS decreases of $\sim 1\text{-}1.5\%$ across either pyrolysis atmosphere, with 2MMT-1200- H_2O (VS: $43.8 \pm 0.8\%$) vs. 2MMT-1200-Ar (VS: $47.3 \pm 0.8\%$) and 5MMT-1200- H_2O (VS: $44.7 \pm 0.6\%$) vs. 5MMT-1200-Ar (VS: $46.3 \pm 0.5\%$), continuing the aforementioned trend between Ar-20% H_2O and Ar pyrolysis atmospheres. Notably, the increase in ceramic yield among xMMT-1200- H_2O was associated with the absence of α -quartz phases (**Figure 4.4.1(c)**). This indicated that water vapor-assisted pyrolysis of MMT-SiOC did not appreciably introduce SiO_2 around the MMT-SiOC interface but rather predominantly occurred in the SiOC matrix as suggested earlier. The associated mass gain was believed to originate from retained SiOC or C around the interface that was resistant to reactions with water vapor.

Carbothermal reduction at 1400°C accounted for the general decrease in CY and increase in VS through the formation of β -SiC phases and CO evolution in all MMT-SiOC ceramics across either pyrolysis atmosphere. Water vapor-assisted pyrolysis induced an additional $\sim 2\text{-}4\%$ mass loss in SiOC-1400- H_2O (CY: $71.1 \pm 0.8\%$), 1/2MMT-1400- H_2O (CYs: $\sim 72.2 \pm 0.6\%$), and 5MMT-1400- H_2O (CY: $70.5 \pm 0.4\%$) compared to SiOC-1400-Ar (CY: $73.2 \pm 0.6\%$) and 1/2/5MMT-1400-Ar (CYs: $\sim 74.5 \pm 0.5\%$). The observed trends were attributed to accelerated CO evolution from β -SiC formation as XRD (**Figure 4.4.1(c)**) revealed more prominent β -SiC reflections in 1/2/5MMT-1400- H_2O samples. While water vapor-assisted pyrolysis typically increases SiO_2 and decreases C contents, MMT domains and specifically MMT-SiOC interfaces appeared resistant to these effects. Anticipated bulk MMT effects such as nanosheet stacking and increased proximity of MMT regimes from high loading content manifested in a further 2% mass loss in 5MMT-1400- H_2O . Analogous behavior was not appreciably observed in 5MMT-1400-Ar presumably due to the abundance of free C. Volumetric shrinkages among the Ar- and water vapor-pyrolyzed MMT-SiOC-1400 samples were generally identical within experimental error, with a

slightly more shrinkage observed in SiOC-1400-H₂O (VS: $49.0 \pm 0.4\%$) and SiOC-1400-Ar (VS: $47.4 \pm 0.5\%$) than in MMT-containing ceramics. Among MMT-SiOC-1400 ceramics, pyrolysis atmosphere had little effect on volumetric shrinkage at corresponding MMT content as shown between 1/2MMT-1400-H₂O (VSs: $\sim 46.6 \pm 0.7\%$) and 1/2MMT-1400-Ar (VSs: $\sim 47.0 \pm 0.5\%$), and 5MMT-1400-H₂O (VS: $46.2 \pm 0.4\%$) and 5MMT-1400-Ar (VS: $45.6 \pm 0.7\%$). Above the stable temperature range of SiOC (from 1200-1300°C), xMMT-SiOC-1400 ceramics illustrated the thermal degradation behavior that would compromise MMT-SiOC microstructures, phase profile, and physical properties. Overall, while water vapor-assisted pyrolysis in pure SiOC induced physical property changes through reduction of C and incorporation of O, MMT-SiOC ceramics did not show appreciable changes with increasing MMT content. That is, the incorporation of C into partially ceramitized MMT domains produced net improvements in CY and VS among all MMT-SiOC ceramics.

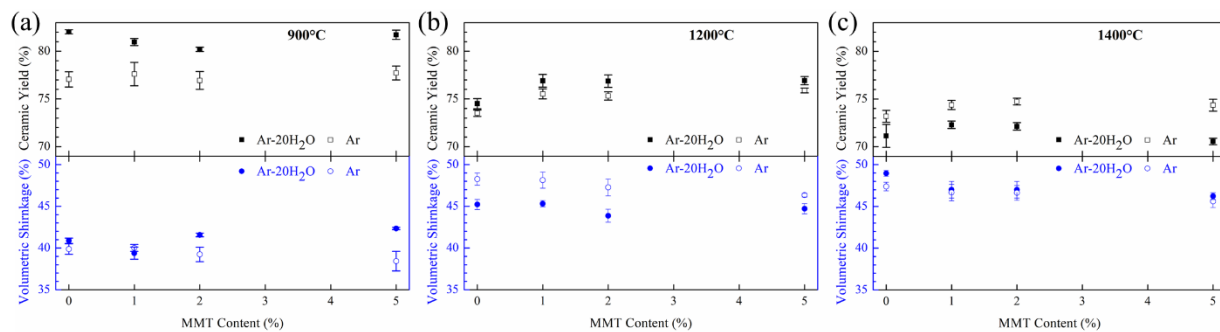


Figure 4.4.4. Ceramic yield (top panel/black) and volumetric shrinkage (bottom panel/blue) of MMT-SiOC ceramics pyrolyzed at (a) 900°C, (b) 1200°C, and (c) 1400°C in either Ar-20% H_2O (filled symbol) and Ar (unfilled). Error bars indicate a standard deviation of 3-5 samples.

Furthermore, MMT-SiOC-H₂O ceramics showed a net reduction of crystallized α -quartz through XRD and TEM analysis, as water vapor produced sufficient $\bullet$ OH and $\bullet$ H radicals to vitrify crystalline Si-O-Si bonds. While producing a higher concentration of amorphous SiO₂, the total concentration and size of these SiO₂ domains were not apparent from the aforementioned analysis. To characterize SiO₂ content, porous ceramics were prepared by etching SiO₂ domains in MMT-SiOC-Ar and MMT-SiOC-H₂O with excess HF (Equation (2.4.9)), and the effect of water vapor-assisted pyrolysis on selectively-etched porosity and specific surface area (SSA) in MMT-SiOC was determined with N₂ sorption experiments (Figure 4.4.5(a-c)). The specific surface areas (SSAs) of HF-etched MMT-SiOC were reported in Table 4.4.1. Selectively etched porosity was representative of the concentration, size, and distribution of SiO₂ domains present in the MMT-SiOC ceramics as Si-C and C-C bonds were resistant to HF.



MMT-SiOC pyrolyzed in Ar-20%H₂O exhibited a marked enhancement in pore volumes after HF etching at both 900°C (Figure 4.4.5(a)) and 1200°C (Figure 4.4.5(b)), although porosity was primarily derived through the SiOC matrix. This was shown by marked increases in pore volumes between SiOC-900-Ar (8 cm³·g⁻¹) and SiOC-900-H₂O (309 cm³·g⁻¹), and between SiOC-1200-Ar (5 cm³·g⁻¹) and SiOC-1200-H₂O (505 cm³·g⁻¹). xMMT-900-Ar and xMMT-1200-Ar were previously shown to marginally yet incrementally enhance pore volumes between 2 and 5 nm after HF etching with 2MMT-1200-Ar and 5MMT-1200-Ar exhibiting the best improvements with pore volumes of 25 cm³·g⁻¹ and 30 cm³·g⁻¹, respectively [187]. However, MMT addition contributed to smaller pore volumes in all water vapor-pyrolyzed and HF-etched 1MMT-900-H₂O (55 cm³·g⁻¹), 2MMT-900-H₂O (202 cm³·g⁻¹), and 5MMT-900-H₂O (259 cm³·g⁻¹) ceramics compared to SiOC-900-H₂O. This trend continued in HF-etched 1MMT-1200-H₂O (150 cm³·g⁻¹), 2MMT-1200-H₂O (165 cm³·g⁻¹), and 5MMT-1200-H₂O (343 cm³·g⁻¹), indicating that MMT did not promote or accelerate pore formation with water vapor-assisted pyrolysis. The reduction in porosity again contradicted the expected effect of water vapor to grow SiO₂ regimes.

Pore size distributions obtained from NLDFT fitting (Figure 4.4.5(d-e)) revealed a near-unimodal distribution of about 2 nm but less than 3 nm in both SiOC-900-H₂O and SiOC-1200-H₂O. At both 900°C and 1200°C, 1 wt% and 2 wt% MMT content decreased the concentration of these pores before increasing in 5 wt% MMT samples, all without altering the intrinsic pore size

distribution of SiOC-900-H₂O and SiOC-1200-H₂O. Therefore, the observed reduction in pore volume in xMMT-900-H₂O and xMMT-1200-H₂O was not related to SiO₂ growth/coalescence but rather a decrease in SiO₂ content in MMT-SiOC compared to SiOC. Specific surface areas (SSAs) calculated from NLDFT fitting (Table 4.4.1) enumerated the decreased SiO₂ content in MMT-SiOC samples at 900°C, with SSAs decreasing nearly by half from SiOC-900-H₂O (1407 m²·g⁻¹) to 1MMT-900-H₂O (677 m²·g⁻¹) before incrementally increasing in 2MMT-900-H₂O (858 m²·g⁻¹) and 5MMT-900-H₂O (1055 m²·g⁻¹). The stark decrease in SSA between SiOC-1200-H₂O (2081 m²·g⁻¹) to 1MMT-1200-H₂O (656 m²·g⁻¹) further pointed to the reduction in HF-etchable SiO₂. The two-fold increase between 2MMT-1200-H₂O (707 m²·g⁻¹) and 5MMT-1200-H₂O (1441 m²·g⁻¹) was associated with additional α -quartz present in the latter (**Figure 4.4.1(c)**) presumably due to bulk effects from higher MMT content and excess evolved α -quartz at the MMT-SiOC interface that could not be incorporated within the amorphous SiOC matrix. Recalling that xMMT-1200-H₂O exhibited higher ceramic yields than xMMT-1200-Ar, the decrease in SiO₂ concentration was attributed to retention of SiOC phases and oxidation resistance of MMT domains in water vapor-pyrolyzed MMT-SiOC.

Pore volumes (Figure 4.4.5(c)) and pore size distributions (Figure 4.4.5(f)) of HF-etched xMMT-1400-Ar and xMMT-1400-H₂O indicate the dissolution of distinct pore structures of the analogous 1200°C samples. SiOC-1400-H₂O (239 cm³·g⁻¹), 1MMT-1400-H₂O (254 cm³·g⁻¹), 2MMT-1400-H₂O (228 cm³·g⁻¹), and 5MMT-1400-H₂O (218 cm³·g⁻¹) all displayed identical pore characteristics. Similarly observed in SiOC-1400-Ar and 1/2/5MMT-1400-Ar, the broadening of pore sizes between 2 and 5 nm illustrated the thermal degradation characteristics and the fate of the SiO₂ phase in MMT-SiOC upon pyrolysis above 1400°C. As a result, SSAs (Table 4.4.1) of SiOC-1400-H₂O (724 m²·g⁻¹), 1MMT-1400-H₂O (757 m²·g⁻¹), and 2MMT-1400-H₂O (657 m²·g⁻¹) were generally identical, with a further reduction in SSA in 5MMT-1400-H₂O (498 m²·g⁻¹) due to consumption of SiO₂ during carbothermal formation of β -SiC nanowhiskers. At all pyrolysis temperatures, MMT reduced the overall SiO₂ content in MMT-SiOC-H₂O ceramics compared to native SiOC, and the pore properties were primarily derived from the matrix SiOC, not from MMT regimes or the MMT-SiOC interface.

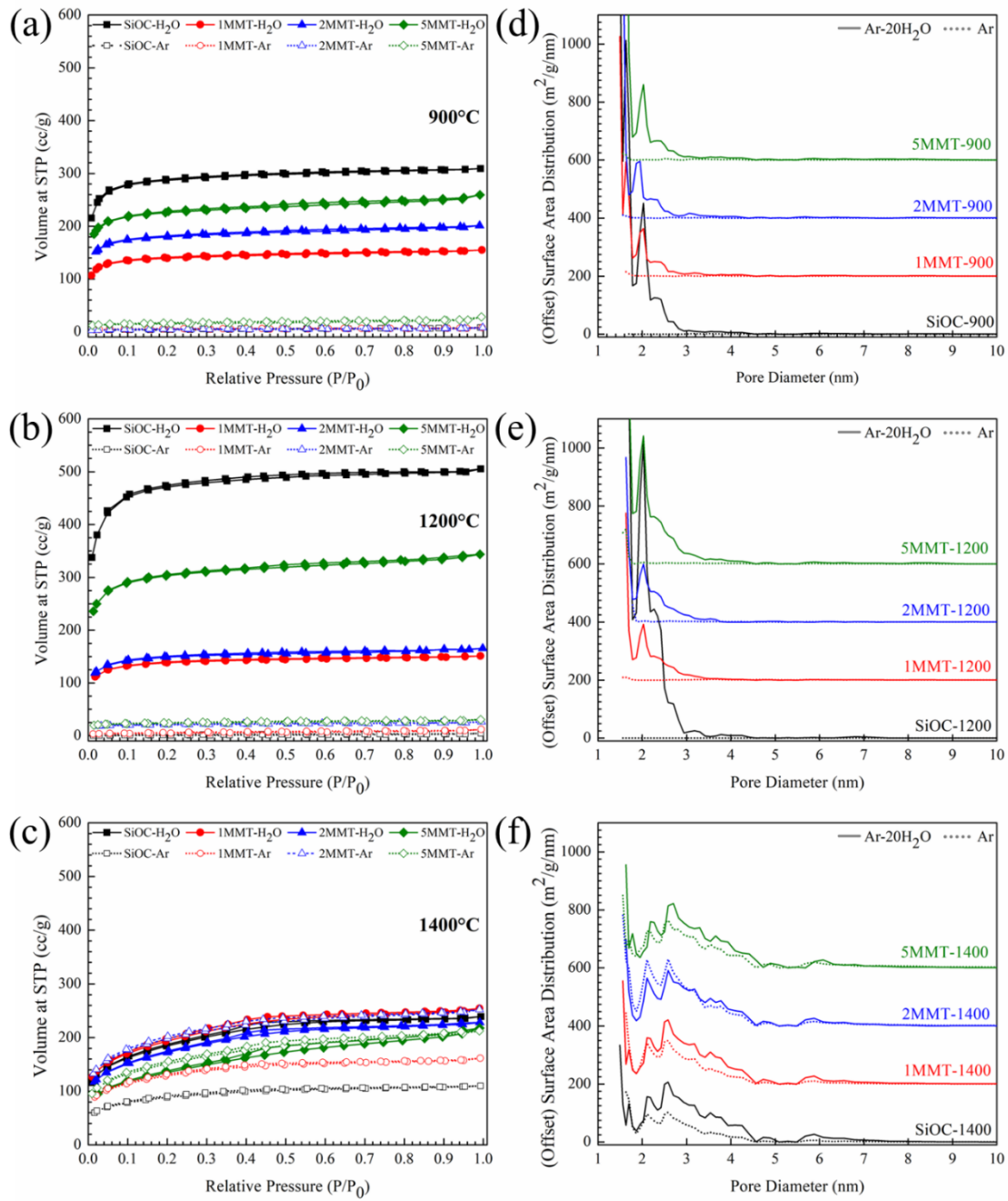


Figure 4.4.5. Porosity characterization in HF-etched MMT-SiOC-Ar (dashed) and MMT-SiOC-H₂O (solid) with N₂ sorption. N₂ sorption isotherms of HF-etched xMMT-SiOC ($x = 0/\text{black}$, $1/\text{red}$, $2/\text{blue}$, $5/\text{green}$) pyrolyzed at (a) 900°C, (b) 1200°C, and (c) 1400°C. Pore size distributions of HF-etched xMMT-SiOC ceramics pyrolyzed at (d) 900°C, (e) 1200°C, and (f) 1400°C as determined by NLDFT fitting. Pore size distributions were offset for clarity.

Table 4.4.1: Calculated specific surface areas (SSA/m²·g⁻¹) of etched xMMT-SiOC-Ar and xMMT-SiOC-H₂O ceramics. SSAs were determined by NLDFT fitting of adsorption branches using a silica adsorbate model with spherical/cylindrical pore structures.

Ceramic Sample	Specific Surface Area (m ² ·g ⁻¹)					
	900°C		1200°C		1400°C	
	Ar	H ₂ O	Ar	H ₂ O	Ar	H ₂ O
SiOC	18	1407	3	2081	340	724
1MMT	18	677	20	656	499	757
2MMT	23	858	105	707	772	657
5MMT	78	1055	120	1441	574	498

4.4.3. Compositional analysis and mechanistic understanding

Water vapor-assisted pyrolysis clearly did not enhance SiO_2 formation in MMT-SiOC, so compositional analysis was performed on SiOC-1200-Ar, SiOC-1200- H_2O , 2MMT-1200-Ar, and 2MMT-1200- H_2O to understand the distribution of SiO_xC_y and C phases. The concentration of amorphous SiO_xC_y (I- SiO_2 , II- $\text{SiO}_{1.5}\text{C}_{0.25}$, III- $\text{SiOC}_{0.5}$, IV- $\text{SiO}_{0.5}\text{C}_{0.75}$, V- SiC) phases was quantitatively analyzed with ^{29}Si NMR as the unique chemical environments about each Si nucleus may be differentiated. Figure 4.4.6(a) depicts the ^{29}Si NMR spectra of SiOC-1200-Ar (black dotted), SiOC-1200- H_2O (black solid), 2MMT1-1200-Ar (blue dotted), and 2MMT-1200- H_2O (blue solid) with the expected chemical shifts and Si tetrahedral structures of SiO_2 (-108 ppm), $\text{SiO}_{1.5}\text{C}_{0.25}$ (-68 ppm), $\text{SiOC}_{0.5}$ (-34 ppm), $\text{SiO}_{0.5}\text{C}_{0.75}$ (10 ppm), and SiC (-11 ppm) sourced from literature and indicated [186, 200, 201]. A small overtone peak (I') at ~ -125 ppm causing peak asymmetry of Peak I (SiO_2) was attributed to non-structural 5-coordinated SiO_4 from interactions with neighboring O atoms; while the authors could not find an appropriate reference for this peak in SiOC systems, a similar effect was observed in amorphous Si_3N_4 systems and the rationale was applied to this system [202]. This I' peak was not included in composition and phase fraction calculations because it did not represent a unique Si bonding environment – see the Supplementary Information for details.

SiOC-1200-Ar was revealed to contain SiO_2 , $\text{SiO}_{1.5}\text{C}_{0.25}$, $\text{SiOC}_{0.5}$, and SiC units that converted to predominantly SiO_2 upon water vapor-assisted pyrolysis in SiOC-1200- H_2O . Notably, 2MMT-1200-Ar showed the emergence of $\text{SiO}_{0.5}\text{C}_{0.75}$ clusters between 50 and 20 ppm, which were not present in SiOC systems and have been seldom reported. MMT generally provides characteristic peaks between -90 and -110 ppm as shown in previous ^{29}Si NMR characterization studies [203-205], so the new Si bonding environment in 2MMT-1200-Ar was not from MMT itself but $\text{SiO}_{0.5}\text{C}_{0.75}$ clusters presumably at the MMT-SiOC interface. Similar to SiOC-1200- H_2O , water vapor-assisted pyrolysis induced restructuring of Si tetrahedra in 2MMT-1200- H_2O to predominantly SiO_2 ; however, some $\text{SiO}_{0.5}\text{C}_{0.75}$ and SiC clusters were retained. While SiO_2 clusters in SiOC-1200- H_2O were completely removed with water vapor-assisted pyrolysis, some SiO_2 in 2MMT-1200- H_2O was oxidation resistant to water vapor ingress between 500°C and 700°C, indicating that these clusters may have formed during early stages of the polymer-to-ceramic transformation (300°C to 500°C).

Gaussian peak deconvolution (Figure 4.4.6(b)) further quantified these trends as the integrated area of each peak provided the relative phase fractions of SiO_xC_y phases and the calculated NMR composition of the SiOC matrix. Full Gaussian peak fitting details may be found in the Supplemental Information. Matrix compositions for SiOC-1200-Ar ($\text{SiO}_{1.06}\text{C}_{0.47}$) and 2MMT-1200-Ar ($\text{SiO}_{1.10}\text{C}_{0.45}$) were nearly identical but were comprised of unique distributions of SiO_xC_y phases. MMT addition primarily induced restructuring of $\text{SiO}_{1.5}\text{C}_{0.25}$ (11.4% in SiOC-1200-Ar to 6.4% in 2MMT-1200-Ar), $\text{SiOC}_{0.5}$ (13.8% to 4.7%), SiC (32.1% to 13.3%), to $\text{SiO}_{0.5}\text{C}_{0.75}$ (~0% to 36.5%). The slight increase in SiO_2 content (37.6% to 39.2%) upon MMT addition was attributed to interfacial α -quartz and MMT itself. It was postulated that the $\text{SiO}_{0.5}\text{C}_{0.75}$ existed at or near the MMT-SiOC interface, which bridged between crystalline MMT and amorphous SiOC. Furthermore, this could also imply that more C is retained around the MMT domains which can explain the accelerated β -SiC formation through carbothermal reduction observed in XRD spectra of MMT-SiOC ceramics at 1400°C (Figure 4.4.1(c)). This would further indicate that MMT was thoroughly incorporated and embedded in the SiOC matrix at the nanoscale as additional SiO_xC_y phases were formed to resolve the incoherency at the interface.

While water vapor-assisted pyrolysis significantly altered the matrix composition ($\text{SiO}_{1.93}\text{C}_{0.04}$) in SiOC-1200- H_2O to mainly SiO_2 (88.4%) with small amounts of $\text{SiO}_{1.5}\text{C}_{0.25}$ (7.3%) and $\text{SiOC}_{0.5}$ (4.2%), 2MMT-1200- H_2O ($\text{SiO}_{1.50}\text{C}_{0.25}$) was partially resistant to water vapor attack between 500°C to 700°C as SiC (8.3%) and $\text{SiO}_{0.5}\text{C}_{0.75}$ (17.9%) were retained in appreciable amounts and less SiO_2 (62.3%) was formed. This finding supported the observed decrease in pore volumes and SSA in xMMT-900- H_2O and xMMT-1200- H_2O ceramics after HF etching compared to SiOC-900- H_2O and SiOC-1200- H_2O (Figure 4.4.5(a-d)). The retained yet decreased SiC and $\text{SiO}_{0.5}\text{C}_{0.75}$ contents indicated that the domains around MMT or the MMT-SiOC interface were oxidation-resistant, but the size of the MMT-SiOC interface may have decreased upon water vapor pyrolysis. As the SiOC matrix is inherently SiO_2 -rich after water vapor pyrolysis, fewer SiO_xC_y clusters were necessary to bridge the coherency gap between crystalline MMT and amorphous SiOC, or amorphous SiO_2 in the case of SiOC-1200- H_2O . However, advanced nanoscale characterization such as synchrotron X-ray or 4D-STEM would be needed to discern changes in crystallinity and amorphous ordering across the MMT-SiOC interface.

As a carbon-rich SiO_xC_y phase, $\text{SiO}_{0.5}\text{C}_{0.75}$ clusters revealed in ^{29}Si NMR suggested higher C retention in MMT-SiOC at or near the interface. The nature of C in MMT-SiOC was

characterized by Raman spectroscopy (Figure 4.4.6(c)) and elemental analysis (Table 4.4.2) to ascertain the effect of MMT on C content and structure. Raman analysis revealed no significant differences in C ordering among SiOC-1200-Ar, SiOC-1200-H₂O, 2MMT-1200-Ar, and 2MMT-1200-H₂O as C appeared to be comparably disordered as evidenced by the D band at ~1330 cm⁻¹. The apparent G band at ~1600 cm⁻¹ was determined to have contributions from the actual G band (~1550 cm⁻¹) and an overtone D' band (~1620 cm⁻¹), the presence of the latter confirmed by D+D' (~2950 cm⁻¹) and 2D' (~3200 cm⁻¹) bands. Superposition of D' and G bands was commonly reported in disordered carbons, but the difference between apparent G (G_{app}) and the inferred D' (D'_{inf}) bands from the 2D' band was shown to provide more information about the state of C with respect to graphene, graphene oxide (GO), or reduced graphene oxide (rGO) [206, 207]. Graphene was characterized by a (D'_{inf} - G_{app}) difference greater than 25, rGO by a difference between 0 and 25, and GO by a difference less than 0 [206]. In all samples, 2D' was determined to be ~3180-3190 cm⁻¹, yielding D'_{inf} of ~1590-1595 cm⁻¹, and G_{app} was ~1605 cm⁻¹, indicating that C regimes existed primarily as GO phases with a high degree of disorder. Furthermore, a D+D'' overtone band at ~2450 cm⁻¹ revealed a D'' band at ~1180 cm⁻¹, originating from sp²-sp³ interactions.

Lorentzian peak deconvolution of D and G_{app} (Figure 4.4.6(d)) further confirmed the similarity of C regimes among the four ceramic samples with A_D/A_G ratios of 5.45, 5.59, 4.49, and 5.86 for SiOC-1200-Ar, SiOC-1200-H₂O, 2MMT-1200-Ar, and 2MMT-1200-H₂O, respectively. Full Lorentzian peak deconvolution and Raman peak information can be found in the Supplemental Information. Due to the significant overlap of D, D', and G bands, the typical I_D/I_G ratio to determine the degree of disorder was not valid for such disordered carbons so the integrated area ratio A_D/A_G was chosen to better quantify D and G contributions [208, 209]. The Tuinstra-Koenig equation (Equation 4.4.3) relating lateral crystalline size (L_α) to A_D/A_G, with λ the laser excitation wavelength (532 nm), yielded similar L_α values of 3.3, 3.2, 3.9, and 3.1 nm, respectively. The marginal increase in crystallize size at 2MMT-1200-Ar was not deemed significant. Overall, neither water vapor-assisted pyrolysis nor MMT addition altered C structuring in MMT-SiOC.

$$L_{\alpha} = (2.4 * 10^{-10}) \lambda^4 \left(\frac{A_D}{A_G} \right)^{-1} \quad (4.4.2)$$

Elemental analysis (E.A.) was performed to determine the total Si and C content in SiOC-1200-Ar, SiOC-1200-H₂O, 2MMT-1200-Ar, and 2MMT-1200-H₂O. O was determined as the residual from 100%. Some Si loss was observed during water vapor-assisted pyrolysis between

SiOC-1200-Ar (28.5 wt%) and SiOC-1200-H₂O (26.3 wt%), as well as between 2MMT-1200-Ar (27.8 wt%) and 2MMT-1200-H₂O (26.3 wt%). While this was attributed to a small amount of Si evolution during water vapor injection, the overall Si content was generally invariant. Agreeing with previous studies [27, 143, 188], water vapor pyrolysis aggressively removed C between SiOC-1200-Ar (31.7 wt%) and SiOC-1200-H₂O (20.6 wt%) through oxidation of free C. However, not only did MMT addition increase the C content by 15 wt% in 2MMT-1200-Ar (46.6 wt%), but also MMT addition proved to show resistance to water vapor ingress as the C content in 2MMT-1200-H₂O (43.9 wt%) did not decrease similarly as in SiOC-1200-H₂O.

From the overall (E.A.) composition calculated from Si, O, and C content (Table 4.4.2) and the matrix composition calculated from ²⁹Si NMR (Figure 4.4.6(c) and also provided in Table 4.4.2), the stoichiometric SiO_xC_y and free C phase compositions were described as SiO_xC_y + zC_{free}. In each sample, the O coefficient from E.A. was higher than the matrix O content from ²⁹Si NMR so the excess O was assigned to the free C phase in the form of GO following Raman analysis. While the relative free C to SiO_xC_y ratio in SiOC-1200-Ar (Si O_{1.06} C_{0.47} + 2.1 CO_{0.65}) did not appreciably decrease in SiOC-1200-H₂O (Si O_{1.93} C_{0.04} + 1.8 CO_{0.90}), the free C phase was more oxidized as was expected from prior studies. Not only did the free C phase content increase with MMT addition for both 2MMT-1200-Ar (Si O_{1.10} C_{0.45} + 3.5 CO_{0.15}) and 2MMT-1200-H₂O (Si O_{1.50} C_{0.25} + 3.7 CO_{0.13}), but also the phase was less oxidized. Overall, while MMT addition did not alter the size or bonding characteristics of the free C phase, it encapsulated more C within the MMT-SiOC interface that was resistant to water vapor oxidation during the polymer-to-ceramic transformation. Even if this retained C were potentially further oxidized, it was preferentially retained in the MMT-SiOC matrix as GO and not evolved as CO.

Figure 4.4.7 summarizes phase evolution mechanisms in MMT-SiOC-Ar and MMT-SiOC-H₂O ceramics from the preceramic MMT-PSO through stages before and after water vapor injection between 500°C and 700°C. During phase evolution in the polymer-to-ceramic transformation, MMT regimes retained more free C from the preceramic polymer within the interfacial region between 400°C and 500°C when silane condensation reactions occurred earlier with MMT addition as shown by TGA [180, 189]. In these regions of nascent SiOC, the matrix retained more C around MMT regimes acting as a SiO₂ source to maintain the overall matrix composition of the MMT-SiOC ceramics, which were shown earlier by ²⁹Si NMR to be identical between SiOC-1200-Ar and 2MMT-1200-Ar. As this event occurred prior to water vapor injection

in the 2MMT-SiOC samples, nascent SiOC regimes about MMT were not as susceptible to oxidation as similar phases forming in SiOC around 475-500°C [189]. While producing typical SiO₂ structures in the SiOC matrix, water vapor-assisted pyrolysis preferentially incorporated and retained C within amorphized α -quartz domains. In MMT-SiOC-Ar, α -quartz exists solely within the MMT interfacial region with a small concentration of SiO₂ clusters forming in the matrix. In the presence of H₂O, there is a higher concentration of am-SiO₂ in the SiOC matrix but α -quartz is transformed to am-SiO₂ with more C retained within the MMT-SiOC interface.

In SiOC systems, free C is modeled as surrounding and diffusing into SiO₂ clusters to form SiO_xC_y tetrahedra [117]. The emergence of the SiO_{0.5}C_{0.75} phase in 2MMT-1200-Ar supported this mechanistic explanation. In MMT-SiOC, additional C was retained to resolve structural incoherency between crystalline MMT and amorphous SiOC. Coherency and interfacial bonding occurred through SiO_{0.5}C_{0.75}, SiC, and SiOC_{0.5} phases, which formed through C diffusion into encapsulated regimes. Forming earlier in MMT-SiOC than in pure SiOC, these regimes were resistant to water vapor attack. The effects of water vapor on phase formation, composition, and selectively etched porosity were then only a function of the SiOC matrix with MMT decreasing total SiO₂ content.

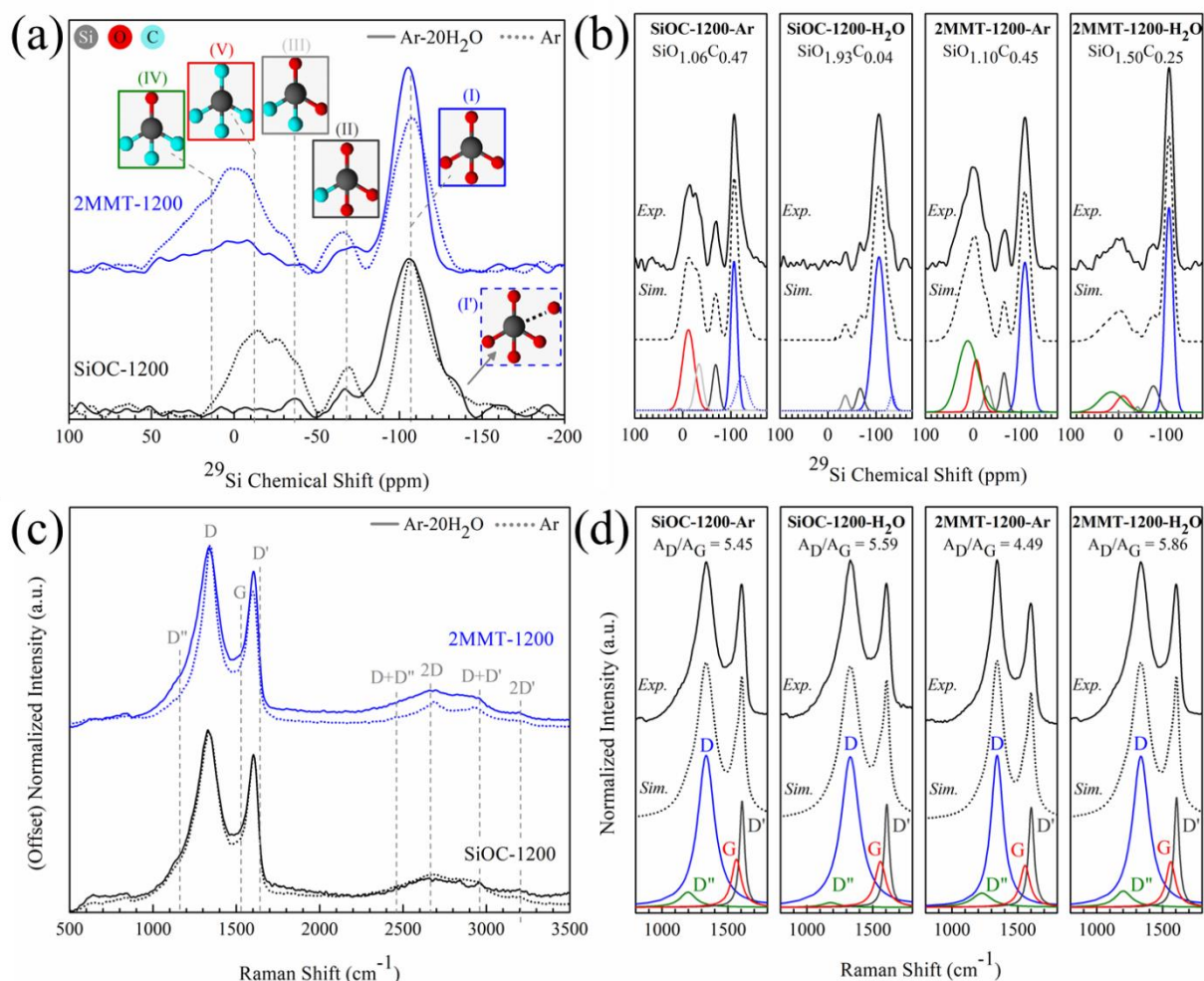


Figure 4.4.6. (a) ^{29}Si NMR spectra of SiOC-1200-Ar (black/dotted), SiOC-1200-H₂O (black/solid), 2MMT-1200-Ar (blue/dotted), and 2MMT-1200-H₂O (blue/solid). Peaks I-V indicate the chemical shifts and Si tetrahedral structure of SiO₂ (-108 ppm/blue), SiO_{1.5}C_{0.25} (-68 ppm/dark grey), SiOC_{0.5} (-34 ppm/light gray), SiO_{0.5}C_{0.75} (10 ppm/green), and SiC (-11 ppm/red), respectively; (b) deconvoluted and simulated ^{29}Si NMR spectra with calculated compositions. Full peak fitting details are provided in the Supplemental Information; (c) Raman spectra of SiOC-1200-Ar (black/dotted), SiOC-1200-H₂O (black/solid), 2MMT-1200-Ar (blue/dotted), and 2MMT-1200-H₂O (blue/solid); (d) D/G peak deconvolution and calculated A_D/A_G ratio for previous samples. Peak fitting details are provided in the Supplemental Information.

Table 4.4.2: Elemental analysis (E.A.), NMR, and calculated $\text{SiO}_x\text{C}_y + z\text{C}_{\text{free}}$ compositions of SiOC-1200-Ar, SiOC-1200-H₂O, 2MMT-1200-Ar, and 2MMT-1200-H₂O. As the NMR composition only considered C and O bonded to Si, the free C phase content and composition were extracted from the E.A. composition.

Sample	Elemental Analysis (E.A.)			E.A. Composition	NMR Composition	$\text{SiO}_x\text{C}_y + z\text{C}_{\text{free}}$
	Si (wt%)	O (wt%)	C (wt%)			
SiOC-1200-Ar	28.5	39.8	31.7	Si O _{2.45} C _{2.59}	Si O _{1.06} C _{0.47}	Si O _{1.06} C _{0.47} + 2.1 CO _{0.65}
SiOC-1200-H ₂ O	26.3	53.2	20.6	Si O _{3.54} C _{1.83}	Si O _{1.93} C _{0.04}	Si O _{1.93} C _{0.04} + 1.8 CO _{0.90}
2MMT-1200-Ar	27.8	25.7	46.6	Si O _{1.62} C _{3.92}	Si O _{1.10} C _{0.45}	Si O _{1.10} C _{0.45} + 3.5 CO _{0.15}
2MMT-1200-H ₂ O	26.3	29.8	43.9	Si O _{1.98} C _{3.90}	Si O _{1.50} C _{0.25}	Si O _{1.50} C _{0.25} + 3.7 CO _{0.13}

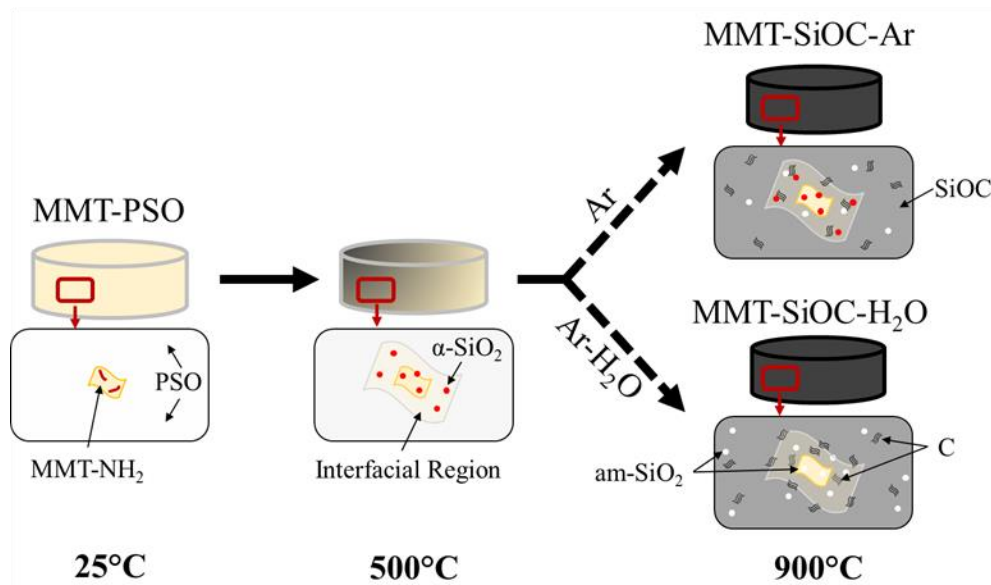


Figure 4.4.7: Schematic of phase evolution mechanisms in MMT-SiOC-Ar and MMT-SiOC-H₂O ceramics. With water vapor-assisted pyrolysis, α -quartz converted to am-SiO₂ and more free C was retained within the MMT-SiOC interfacial regime.

4.5. Conclusions

In this study, MMT-SiOC-Ar and MMT-SiOC-H₂O nanocomposites were prepared to determine the effect of water vapor on SiO₂ phase evolution and selectively etched porosity. While water vapor-assisted pyrolysis typically removes free C and drastically increases amorphous SiO₂ clusters between 2 nm and 5 nm in pure SiOC, MMT domains not only inhibited H₂O ingress but also encapsulated and shielded C from volatilization. Furthermore, while MMT produced crystalline α -quartz in Ar-pyrolyzed MMT-SiOC, water vapor-assisted pyrolysis selectively amorphized these domains through activation and vitrification of Si-O-Si bonds with H₂O. Nanostructural phenomena were confirmed with (HR)TEM analysis that showed the lack of α -quartz nanodomains in the MMT-SiOC interface and the presence of encapsulated C domains within or near MMT regimes. N₂ sorption experiments further confirmed the decreased SiO₂ content in MMT-SiOC-H₂O with pore structures between 2 nm and 5 nm were primarily derived from matrix SiOC but decreased with MMT content and water vapor-assisted pyrolysis. ²⁹Si NMR characterization revealed the emergence of SiO_{0.5}C_{0.75} clusters in MMT-SiOC that were postulated to form within the MMT-SiOC interface and were retained after Ar-H₂O pyrolysis. Encapsulated SiOC/C regimes further contributed to enhanced β -SiC nanowhisker growth as shown by SEM and XRD. This study provided new findings of encapsulation, shielding, and retention of C as graphene oxide in MMT-SiOC-H₂O ceramics under the simultaneous presence of MMT and water vapor and a mechanistic understanding of MMT-SiOC interfacial phenomenon and phase formation in MMT-SiOC ceramic nanocomposites.

4.6. Supplementary Information

4.6.1. ^{29}Si NMR Fitting Parameters

Table 4.6.1: Gaussian fitting parameters for peak deconvolution of ^{29}Si NMR spectra (x_0 – peak center; FWHM – full-width half-maximum; I/I_0 – peak intensity; A_{int} – integrated peak area (% of total integrated peak areas).

Sample	I - SiO ₄				I' - O--SiO ₄			
	x ₀ (ppm)	FWHM	I/I ₀ (a.u.)	A _{int} (%)	x ₀ (ppm)	FWHM	I/I ₀ (a.u.)	A _{int} (%)
SiOC-1200-Ar	-106.8	16.14	209.92	32.69	-123.7	27.52	49.23	13.07
SiOC-1200-H ₂ O	-106.3	30.27	216.87	85.16	-133.8	12.58	22.41	3.66
2MMT-1200-Ar	-107.5	25.07	210.98	39.16	---	---	---	---
2MMT-1200-H ₂ O	-105.2	20.19	288.49	62.23	---	---	---	---
Sample	II - SiO ₃ C				III - SiO ₂ C ₂			
	x ₀ (ppm)	FWHM	I/I ₀ (a.u.)	A _{int} (%)	x ₀ (ppm)	FWHM	I/I ₀ (a.u.)	A _{int} (%)
SiOC-1200-Ar	-68.6	16.00	64.32	9.93	-33.7	19.12	65.42	12.07
SiOC-1200-H ₂ O	-67.3	17.18	31.57	7.04	-36.1	14.46	21.69	4.07
2MMT-1200-Ar	-64.0	15.61	55.29	6.39	-29.5	17.10	36.83	4.66
2MMT-1200-H ₂ O	-72.7	27.11	37.23	10.78	-39.9	10.05	7.90	10.05
Sample	IV - SiOC ₃				V - SiC ₄			
	x ₀ (ppm)	FWHM	I/I ₀ (a.u.)	A _{int} (%)	x ₀ (ppm)	FWHM	I/I ₀ (a.u.)	A _{int} (%)
SiOC-1200-Ar	7.0	8.61	2.21	0.18	-11.7	29.28	113.49	32.06
SiOC-1200-H ₂ O	8.9	0.00	0.00	0.00	-15.1	0.86	7.07	0.08
2MMT-1200-Ar	11.5	49.13	100.32	36.48	-6.4	24.38	73.72	13.30
2MMT-1200-H ₂ O	14.5	58.21	28.75	17.88	-9.2	33.37	23.14	8.25

Sample	Relative Phase Fractions - I' Excluded (%)					SiOC Composition
	I - SiO ₂	II - SiO _{1.5} C _{0.25}	III - SiOC _{0.5}	IV - SiO _{0.5} C _{0.75}	V - SiC	
SiOC-1200-Ar	37.6	11.4	13.8	0	32.1	SiO _{1.06} C _{0.47}
SiOC-1200-H ₂ O	88.4	7.3	4.2	0	0	SiO _{1.93} C _{0.04}
2MMT-1200-Ar	39.2	6.4	4.7	36.5	13.3	SiO _{1.10} C _{0.45}
2MMT-1200-H ₂ O	62.3	10.8	0.9	17.9	8.3	SiO _{1.50} C _{0.25}

4.6.2. Raman Fitting Parameters

Table 4.6.2: Raman shifts (cm^{-1}) of D, G, and overtone bands determined by peak fitting analysis for SiOC-1200-Ar, SiOC-1200-H₂O, 2MMT-1200-Ar, and 2MMT-1200-H₂O.

Sample	Raman Band and Shift (cm^{-1})							
	D''	D	G	D'	D+D''	2D	D=D'	2D'
SiOC-1200-Ar	1197	1335	1565	1607	2519	2668	2889	3195
SiOC-1200-H ₂ O	1180	1329	1558	1606	2501	2647	2918	3201
2MMT-1200-Ar	1218	1343	1557	1603	2490	2671	2908	3198
2MMT-1200-H ₂ O	1202	1336	1562	1607	2540	2671	2889	3198

Table 4.6.3: Lorentzian fitting parameters for D, G, D', and D'' peak deconvolution of Raman spectra (x_0 – peak center; FWHM – full-width half-maximum; I/I_0 – peak intensity; A_{int} – integrated peak area). A_D/A_G ratio was calculated from integrated peak areas of D and G bands.

Sample	D (~1335 cm^{-1})				G (~1560 cm^{-1})				A_D/A_G
	x_0 (cm^{-1})	FWHM	I/I_0 (a.u.)	A_{int}	x_0 (cm^{-1})	FWHM	I/I_0 (a.u.)	A_{int}	
SiOC-1200-Ar	1335	155.0	0.878	213.8	1565	90.0	0.278	39.2	5.45
SiOC-1200-H ₂ O	1329	170.9	0.871	233.8	1558	100.3	0.265	41.8	5.59
2MMT-1200-Ar	1343	112.0	0.878	154.6	1557	90.6	0.242	34.4	4.49
2MMT-1200-H ₂ O	1336	153.7	0.873	211	1562	87.0	0.263	36	5.86
Sample	D'' (~1200 cm^{-1})				D' (~1605 cm^{-1})				
	x_0 (cm^{-1})	FWHM	I/I_0 (a.u.)	A_{int}	x_0 (cm^{-1})	FWHM	I/I_0 (a.u.)	A_{int}	
SiOC-1200-Ar	1197	147.0	0.087	20.1	1607	46.5	0.613	44.8	
SiOC-1200-H ₂ O	1180	154.0	0.027	6.6	1606	47.3	0.597	44.3	
2MMT-1200-Ar	1218	179.0	0.081	22.8	1603	51.2	0.577	46.4	
2MMT-1200-H ₂ O	1202	155.4	0.094	22.9	1607	47.6	0.635	47.5	

Chapter 5: Synthesis of Exfoliated, Silane Functionalized $\text{Ti}_3\text{C}_2\text{T}_x$ (MXene) and Microstructural Evolution in Novel Polymer-Derived $\text{Ti}_3\text{C}_2\text{T}_x$ -SiOC Ceramic Nanocomposites

5.1. Abstract

Two-dimensional $\text{Ti}_3\text{C}_2\text{T}_x$ (MXene) nanomaterials have gained popularity for their exceptional electrical conductivity as a potential material in electrodes and sensors. However, wider application in bulk composites is precluded by low exfoliated $\text{Ti}_3\text{C}_2\text{T}_x$ yield and surface chemistry constraints. The ceramic nanosheets are attractive filler materials in polymer-derived ceramic (PDC) systems due to the inherent compatibility of the ceramic matrix and ceramic nanomaterial. Exfoliated $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets were synthesized and incorporated into a preceramic polymer after surface functionalization with [3-(2-aminoethylamino)propyl]trimethoxysilane. Pyrolytic decomposition of the preceramic green bodies produced SiOC- $\text{Ti}_3\text{C}_2\text{T}_x$ ceramic nanocomposite, and the effect of MXene content on phase formation and electrical conductivity was studied as a function of pyrolytic temperature. SiOC- $\text{Ti}_3\text{C}_2\text{T}_x$ ceramic nanocomposites have potential in high temperature electrical and aerospace applications that leverage the structural and chemical stability of the ceramic constituents. The methodology for SiOC- $\text{Ti}_3\text{C}_2\text{T}_x$ fabrication can serve as a template for development of novel 2D nanomaterial modified ceramic composites.

5.2. Introduction

Polymer-derived silicon oxycarbide (SiOC) ceramics provide a potential solution of thermally stable yet electrically conductive materials for electrode materials, catalysts, and sensors [210, 211]. By leveraging advances in polymer processing and chemistry, novel SiOC ceramics can be obtained by tailoring polymer precursor chemistry and architecture, preceramic polymer processing/shaping, and pyrolytic conditions [5, 9, 11]. Pyrolytic decomposition of silicon-rich preceramic polymer yields an amorphous matrix of Si tetrahedral units with mixed Si-O and Si-C bonds that remains stable between 800°C to 1300°C – within this matrix, stoichiometric SiO_xC_y phases can be denoted as $\text{SiO}_{(4-i)/2}\text{C}_{i/4}$ for $i = 0-4$ (e.g., SiO_2 , $\text{SiO}_{3/2}\text{C}_{1/4}$, $\text{SiOC}_{1/2}$, $\text{SiO}_{1/2}\text{C}_{3/4}$, and SiC) [9, 10, 143, 212]. A free turbostratic carbon phase originates from excess carbon in the preceramic polymer which aids in crosslinking and generally provides the primary electronic conduction mechanism in SiOC ceramics [213]. However, increasing carbon content in SiOC

systems only results in generally unremarkable electrical conductivity (e.g. $10^{-3} - 10^{-2} \text{ S cm}^{-1}$) and also at the expense of thermal stability and oxidation resistance [213].

Enhancing electrical conduction in SiOC ceramics can be achieved through secondary phases classified as either active or passive fillers. Active fillers include organometallic or metal alkoxide precursors that spur or alter phase formation during pyrolysis through *in-situ* evolved metal or metal oxide/carbide/silicide phases [16, 104]. Ti-doped SiOC ceramics formed by the addition of titanium isopropoxide were shown to spur *in-situ* TiC evolution upon pyrolysis and improve the electrical conductivity of SiOC pyrolyzed between 1200°C and 1400°C [15]. Furthermore, the notable increase in electrical conductivity has also been leveraged for flash pyrolysis processing methods [214]. Passive fillers do not affect microstructural evolution in the ceramic matrix but can change bulk ceramic properties (e.g., porosity) or combat issues commonly encountered in PDC processing (e.g., ceramic yield, volumetric shrinkage) [6, 9]. Due to the amorphous-to-nanostructured nature of SiOC ceramics, filler choice has the added complication and dependency of size and material coherency with the matrix. Two-dimensional (2D) nanomaterials (e.g., graphene, boron nitride, MXenes, metal chalcogenides) are an interesting reinforcement choice as one dimension is classically defined to be nanometer-sized, and their large specific surface areas and anisotropic properties that vary starkly to their bulk analogs can spur novel material development and understanding in SiOC-based ceramic nanocomposites.

As the prototypical MXene, $\text{Ti}_3\text{C}_2\text{T}_x$ 2D nanomaterials are of particular significance due to their electrical conductivities reported from 1000 to 4000 S cm^{-1} [82, 83] and effective Young's modulus of 0.33 TPa [84] for a single flake. In addition, thermal stability analysis of single-flake and multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ indicated that the two-dimensional morphology was retained up to 800°C, after which $\text{Ti}_3\text{C}_2\text{T}_x$ transformed to disordered carbon vacant cubic TiC_y [83, 85]. In the aforementioned study, $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets exhibited a significant increase in electrical conductivity from $\sim 800 \text{ S cm}^{-1}$ to $\sim 2000 \text{ S cm}^{-1}$ prior to and after calcination at 600°C in vacuum, respectively [83]. $\text{Ti}_3\text{C}_2\text{T}_x$ and other MXenes have enticing high temperature applications as either bulk materials or composite reinforcement, proving to be a popular and rapidly evolving research field. Apart from dedicated studies as nanoflakes, multilayered powders, or pressed discs, $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes are garnering interest as promising additive phases impart electronic [86, 87], photocatalytic [88, 89], electromagnetic shielding [90, 91], or sensing [92] attributes or improve corrosive resistance [77], flame retardancy/thermal stability [71, 93], or mechanical properties [94,

95] – among others – in a variety of ceramic [67, 88, 89, 92, 96] or polymer [86, 87, 94, 97-101] composite materials.

However, MXene-based PDC composites have had little published research and are an exciting class for novel material development. Polymer-derived SiBCN-TiC ceramics with 3, 5, and 10 wt% $\text{Ti}_3\text{C}_2\text{T}_x$ were studied for use in electromagnetic shielding after pyrolysis between 1200°C and 1400°C [67]. While $\text{Ti}_3\text{C}_2\text{T}_x$ was synthesized by HF-etching of Ti_3AlC_2 , the study primarily focused on MXene-derived TiC rather than the imbued properties of $\text{Ti}_3\text{C}_2\text{T}_x$ in the SiBCN matrix. The phase profile of the pyrolyzed ceramic composites did not show any retained $\text{Ti}_3\text{C}_2\text{T}_x$, and any crystalline contributions were from TiC crystallites formed by transformation of $\text{Ti}_3\text{C}_2\text{T}_x$ at 1200°C. Furthermore, $\text{Ti}_3\text{C}_2\text{T}_x$ was prepared solely by HF etching and without subsequent delamination/exfoliation – this would yield an accordion-like layered structure and not discrete nanosheets. Some quasi-exfoliation may have been expected from powdering and cold-pressing the preceramic gelled powders, but overall the intrinsic effects of $\text{Ti}_3\text{C}_2\text{T}_x$ in the bulk SiBCN matrix were not investigated. However, a notable consequence was the degradation of $\text{Ti}_3\text{C}_2\text{T}_x$ into TiC above 1200°C, establishing a crude upper limit at which MXene morphology may expected to be retained when encapsulated by a bulk matrix. Recently, SiOC- Ti_3C_2 ceramics were prepared with a commercially-available $\text{Ti}_3\text{C}_2\text{T}_x$ powder that indicated the retention of the layered Ti_3C_2 morphology after pyrolysis at 1000°C [96]. However, the Ti_3C_2 nanosheets were generally agglomerated from the phase profile of the sintered ceramic, presumably due to impurities (i.e., unexfoliated Ti_3C_2) in the supplied MXene nanopowder or experimental methodology. While exfoliated $\text{Ti}_3\text{C}_2\text{T}_x$ layers were not reliably obtained, the addition of Ti_3C_2 was observed to augment the intrinsic electrical conductivity of the SiOC matrix up to 0.1 wt%. With 1 wt% of Ti_3C_2 , conduction was primarily driven by Ti_3C_2 pathways with no SiOC matrix contributions, indicating that there may exist a critical MXene loading content above which additive conduction pathways saturate. Overall, the field of PDC-MXene composites is at a nascent stage with existing studies not fully utilizing the nanomaterial properties of $\text{Ti}_3\text{C}_2\text{T}_x$ and rather multilayered/agglomerated analogs. Further improvements are contingent on understanding and controlling the surface chemistry and morphology of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets, and devising new methodology to overcome the material incoherency of an intrinsically hydrophilic ceramic reinforcing phase in a hydrophobic preceramic polymer matrix. In particular, the exfoliated (i.e.,

few layers thick) microstructure of $\text{Ti}_3\text{C}_2\text{T}_x$ should be retained as individual-to-few layers thick flakes in order to differentiate from bulk/agglomerated effects.

Polymer-derived SiOC- $\text{Ti}_3\text{C}_2\text{T}_x$ ceramic nanocomposites were prepared through complete synthesis of exfoliated $\text{Ti}_3\text{C}_2\text{T}_x$ nanopowder and incorporation into a hydrophobic preceramic polymer. $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets were exfoliated *via* a top-down synthesis method from the parent Ti_3AlC_2 (MAX) phase and further surface functionalized to promote dispersion in the preceramic polymer. Full-length production of exfoliated $\text{Ti}_3\text{C}_2\text{T}_x$ offered control of nanosheet surface chemistry, quality and yield, and processing parameters and methodology. The effects of $\text{Ti}_3\text{C}_2\text{T}_x$ content in SiOC- $\text{Ti}_3\text{C}_2\text{T}_x$ nanocomposites were studied as a function of pyrolytic temperature to understand phase evolution of both the ceramic bulk matrix and the retained 2D structure of $\text{Ti}_3\text{C}_2\text{T}_x$. Electrical properties were elucidated through impedance measurements of both direct and alternating current electronic conduction as a function of temperature. The methodology and findings offer a facile and reliable method for polymer or ceramic composites reinforced with 2D nanomaterials, broadening both the viability and utility of PDCs and MXenes in electronic, catalysis, shielding, and high temperature applications.

5.3. *Experimental Methodology*

5.3.1. Materials

Titanium carbide (TiC, 99.5% metals basis, 2 μm , Alfa Aesar, Haverhill, MA), titanium (Ti, 99.5% metals basis, 325 mesh, Thermo Scientific, Waltham, MA), and aluminum (Al, 99.5%, 325 mesh, Alfa Aesar, Haverhill, MA) powders were chosen as the precursors to synthesize the parent Ti_3AlC_2 (MAX) phase. Lithium fluoride (LiF, 300 mesh, Sigma-Aldrich, Burlington, MA), concentrated hydrochloric acid (HCl, 37 wt%, Certified ACS Plus, Fisher Chemical, Waltham, MA), and concentrated hydrofluoric acid (HF, 49 wt%, Avantor Specialty Materials, Inc., Radnor, PA) comprised the etchant solution. Lithium hydroxide (LiOH, $\geq 98\%$, Sigma-Aldrich, Burlington, MA), sodium bicarbonate (NaHCO_3 , Certified ACS, Fisher Chemical, Waltham, MA), and acetic acid (CH_3COOH , glacial, Fisher Chemical, Waltham, MA) were used in washing solutions. N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEAPTMS, 98%, Gelest, Inc., Morrisville, PA) was chosen to surface functionalize the exfoliated $\text{Ti}_3\text{C}_2\text{T}_x$ nanopowder. A commercially available polysiloxane Polyramic SPR-684 (PSO, $[-\text{Si}(\text{Ph})_2\text{O}-]_3[-\text{Si}(\text{Me})(\text{H})\text{O}-]_2[-\text{Si}(\text{Me})(\text{CH}=\text{CH}_2)\text{O}-]_2$, Starfire Systems, Inc., Glenville, NY) was chosen as the base preceramic

polymer, with a 2.1% platinum-divinyltetramethyldisiloxane complex in xylene (Karstedt's catalyst, Gelest, Inc., Morrisville, PA) selected to crosslink the preceramic green bodies. Acetone (technical grade, Fisher Scientific, Waltham, MA), ethanol (EtOH, 200 proof, Decon Laboratories, Inc. King of Prussia, PA), hexanes (anhydrous, 95%, Sigma-Aldrich, Burlington, MA), and dimethyl sulfoxide (DMSO, $\geq 99.9\%$, Sigma-Aldrich, Burlington, MA) were used as general solvents, and ultrapure water (NP H₂O, 18.2 M Ω cm) was used throughout the experiment. Argon (Ar, Industrial Grade, Airgas, Christiansburg, VA) was used for the pyrolysis atmosphere. All chemicals were used without further purification.

5.3.2. Ti₃C₂T_x synthesis and exfoliation

Ti₃C₂T_x (MXene) was exfoliated through modified procedures previously reported [53, 103]. The parent Ti₃AlC₂ (MAX) phase was prepared by homogenizing TiC, Al, and Ti powders in a 2:1.1:1 molar ratio with a high-energy ball mill (SPEX 8000M Mixer/Mill, SPEX SamplePrep, Metuchen, NJ) for 30 minutes and sintering at 1380°C in a tube furnace (1830-12 Horizontal Tube Furnace, CM Furnaces, Inc., Bloomfield, NJ) under Ar with 5°C min⁻¹ heating and cooling rates and 6 h soaking time. The sintered Ti₃AlC₂ was ground and passed through a 325-mesh sieve and dried under vacuum at 70°C for 12 h (Fisher Isotemp Model 281A Vacuum Oven, Waltham, MA). The Al layers of Ti₃AlC₂ were selectively etched by mechanically stirring a 5 w/v% suspension of Ti₃C₂T_x in a 2M LiF/1M HF/9M HCl (aq) etching solution at room temperature for 48 h. Ti₃AlC₂ was slowly introduced to the stirring etchant solution over 30 minutes to temper H₂ gas evolution and heat generation. The etched Ti₃C₂ (MX-Ti₃C₂-F) powder was washed with NP H₂O until the pH of the supernatant was between 6-7, collected over a 0.47 μ m hydrophobic PVDF filter with EtOH, and vacuum-dried at 70°C for 12 h. Residual -F surface groups were removed by stirring 1 w/v% suspension of MX-Ti₃C₂-F in a 5 wt% LiOH (aq) solution under continuous Ar bubbling at 50°C for 12 h. The alkalized Ti₃C₂ (MX-Ti₃C₂-OH) powder was neutralized to pH 6-7 with NP H₂O, collected over a 0.47 μ m hydrophobic PVDF filter with EtOH, and vacuum-dried at 70°C for 12 h.

Ti₃C₂T_x nanosheets were exfoliated using a freezing-thawing-sonication (F/T/S) method inspired by previous studies [103, 215]. A 0.5 w/v% suspension of MX-Ti₃C₂-OH in NP H₂O was mechanically stirred at room temperature for 12 h and then transferred to a -20°C freezer. The suspensions were thawed at room temperature and immersion-bath sonicated (Cole-Parmer Model

08895-01, 60W, Vernon Hills, IL) for 1 h under continuous Ar bubbling and bath temperature between 2-15°C. Five F/T/S cycles were performed, and the supernatant containing exfoliated $\text{Ti}_3\text{C}_2\text{T}_x$ nanoflakes was collected by centrifugation at 3400 rpm for 1 h. The exfoliated $\text{Ti}_3\text{C}_2\text{T}_x$ suspensions were reserved and frozen at -20°C, and exfoliated $\text{Ti}_3\text{C}_2\text{T}_x\text{-Li}^+$ nanopowder was collected after lyophilization (FreeZone Plus 2.5 L, Labconco Corp., Kansas City, MO) for 48 h. The nanopowders were vacuum-dried at 35°C for 12 h and stored under vacuum.

5.3.3. $\text{Ti}_3\text{C}_2\text{T}_x$ surface functionalization

To improve dispersion in the preceramic polymer, $\text{Ti}_3\text{C}_2\text{T}_x\text{-Li}^+$ was surface functionalized through a modified procedure inspired by prior literature [74]. To a 0.5 w/v% suspension of $\text{Ti}_3\text{C}_2\text{T}_x\text{-Li}^+$ in NP H_2O lightly stirring (<200 rpm) at 50°C, a 20 w/v% CTAB_(MeOH) was charged and stirred at 50°C for 3 h. The CTAB_(MeOH) solution corresponded to a 5X mass excess of CTAB to $\text{Ti}_3\text{C}_2\text{T}_x\text{-Li}^+$. The CTAB-exchanged $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets ($\text{Ti}_3\text{C}_2\text{T}_x\text{-CTA}^+$) were washed repeatedly with MeOH until no halide ions were detected with 0.1 M $\text{AgNO}_{3(\text{aq})}$, collected over a 0.47 μm hydrophilic PVDF filter with NP H_2O , and dried under vacuum at 100°C for 12 h.

$\text{Ti}_3\text{C}_2\text{T}_x\text{-CTA}^+$ nanosheets were further functionalized with AEAPTMS to form a covalently bonded hydrophobic surface on the MXene nanosheets. A 0.5 w/v% suspension of $\text{Ti}_3\text{C}_2\text{T}_x\text{-CTA}^+$ in 90% DMSO-10% MeOH was stirred in a 30°C water bath, and glacial CH_3COOH was slowly added to obtain a pH of 4. A 10 w/v% AEAPTMS_(EtOH) solution – corresponding to a 2X mass excess with respect to $\text{Ti}_3\text{C}_2\text{T}_x\text{-CTA}^+$ – was pre-hydrolyzed with glacial CH_3COOH to pH 4, added slowly to the reaction mixture, and stirred for 3 h at 30°C. The twice-functionalized silane-functionalized $\text{Ti}_3\text{C}_2\text{T}_x$ nanoflakes ($\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2$) were washed 5 times with acetone, collected over a 0.45 μm hydrophobic PVDF filter with hexanes, and vacuum-dried at 80°C for 12 h.

5.3.4. $\text{Ti}_3\text{C}_2\text{T}_x\text{-SiOC}$ pyrolysis

$x\text{Ti}_3\text{C}_2\text{T}_x\text{-PSO}$ preceramic green bodies ($x = 0, 1, 2, 5$) were prepared by mixing PSO with toluene (~50 v/v% relative to PSO), 100 ppm of Karstedt's catalyst (relative to PSO), and functionalized $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2$ (100/0, 99/1, 98/2, 95/5 relative to PSO). The suspensions were stirred for at least 8 h under vacuum to remove residual solvent. The polymer suspensions were cast to $\Phi 12$ mm x 6 mm cylindrical silicone molds, degassed under vacuum, and cured at 60°C for 6 h

and 120°C for 12 h. The green bodies were lightly ground and polished up to 1500 grit with SiC abrasive pads to remove any mold artifacts, and the edges were slightly beveled. To minimize potential surface oxidation, the green bodies were placed between two sheets of carbon felt in an alumina crucible. Under a flowing Ar environment ($\sim 500 \text{ mL}\cdot\text{min}^{-1}$), the green bodies were pyrolyzed at 1000°C, 1200°C, or 1400°C in a horizontal tube furnace (1830-12 Horizontal Tube Furnace, CM Furnaces, Inc., Bloomfield, NJ), with heating and cooling rates of 2°C min^{-1} and soaking time of 2 h. The $\text{Ti}_3\text{C}_2\text{T}_x\text{-SiOC}$ ceramic samples were denoted as $x\text{Ti}_3\text{C}_2\text{T}_x\text{-T}_{\text{Pyr}}$ with $x = 1, 2, 5 \text{ wt\%}$ and $\text{T}_{\text{Pyr}} = 1000, 1200, \text{ or } 1400^\circ\text{C}$. The blank SiOC samples without MXene were similarly denoted SiOC- T_{Pyr} .

5.3.5. Characterization

Ceramic yield and volumetric shrinkage were calculated from changes in sample mass, diameter, and thickness between green bodies and pyrolyzed samples. Reported values are averages of 3-5 replicates and corresponding errors indicate standard deviations. Bulk densities were measured in triplicate by the Archimedes method with EtOH as the immersion medium. Skeletal densities were measured in replicate ($n > 5$) by helium gas pycnometry (AccuPyc II 1340, Micromeritics, Norcross, GA) with an outlet pressure of 19.5 psi in a 1 cc sample cell. The phase compositions of powdered samples were analyzed with an X-ray diffractometer (XRD, Empyrean, Malvern Panalytical Ltd., Almelo, The Netherlands) operated at 40 kV and 40 mA with Cu $K\alpha$ radiation between $2\theta = 2\text{-}90^\circ$ and a scan rate of $0.02^\circ\cdot\text{s}^{-1}$. Microstructures were observed with a scanning electron microscope (SEM, JEOL IT-500HR, JEOL USA, Peabody, MA) and a transmission electron microscope (TEM, JEOL 2100, JEOL USA, Peabody, MA) equipped with a LaB_6 filament operated at 200 kV. Thermogravimetric analysis (TGA, SDT 650, TA Instruments, New Castle, DE) was performed with a heating rate of $5^\circ\text{C}\cdot\text{min}^{-1}$ to 1500°C under an argon flow of $20 \text{ mL}\cdot\text{min}^{-1}$. Chemical compositions were examined by X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM, Physical Electronics USA, Inc., Chanhassen, MN) with an Al $K\alpha$ source (1486.6 eV). Spectra were shifted with respect to the C 1s emission line at 284.4 eV. Raman characterization (XploRA PLUS, Horiba Scientific, Piscataway, NJ) was performed with an Ar laser at 532 nm between $500\text{-}4000 \text{ cm}^{-1}$.

5.4. Results and Discussion

5.4.1. $\text{Ti}_3\text{C}_2\text{T}_x$ exfoliation and functionalization

In order to achieve an exfoliated microstructure in the eventual $\text{Ti}_3\text{C}_2\text{T}_x$ -SiOC ceramic composites, $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets were required to colloidally disperse in preceramic PSO. However, not only did this mean overcoming in the inherent material incoherency between hydrophilic $\text{Ti}_3\text{C}_2\text{T}_x$ and organophilic PSO, but also necessitated a novel production method to generate the proper yield of exfoliated $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets for bulk sample preparation and a facile functionalization route. Figure 5.4.1(a) summarizes the synthesis, exfoliation, and twice-functionalization route for organophilic $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. Layered MX- $\text{Ti}_3\text{C}_2\text{-OH}$ (Figure 5.4.1(c)) was prepared through a modified MILD etching route of MAX- Ti_3AlC_2 (Figure 5.4.1(b)) which was synthesized through sintering of TiC, Ti, and Al powders [53, 103], and LiOH alkalization. After LiOH alkalization, $\text{Ti}_3\text{C}_2\text{T}_x\text{-Li}^+$ nanosheets were obtained after F/T/S-assisted exfoliation (Figure 5.4.1(d)) that were generally 100 nm by 50 nm in lateral size and ranged up to 10-15 nm in thickness with AFM (Figure 5.4.1(e)). While some layer stacking was expected during sample preparation, this method generally yielded few-to-multilayered MXene. Not only did F/T/S exfoliation leverage greater yields of exfoliated $\text{Ti}_3\text{C}_2\text{T}_x$ comparable to prior reports [103], but also isolated nanosheets that were colloidally stable in H_2O and stabilized through hydration shells about $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets and Li^+ cations [216].

Due to the high nanosheet surface energy due to large specific surface areas and -OH terminations imbued after alkalization, a twice-functionalization approach with CTAB and AEAPTMS was needed to not only form a covalently-bonded organophilic functional group on $\text{Ti}_3\text{C}_2\text{T}_x$, but also to prevent nanosheet agglomeration. CTA^+ ligands first replaced Li^+ intercalating cations on the MXene surface through aqueous processing; while imparting hydrophobicity, CTA^+ ligands were electrostatically coordinated and could contribute to extraneous mass loss and pore formation during pyrolytic processing. Cationic exchange of Li^+ with CTA^+ also led to a decrease in nanosheet surface energy and promoted colloidal dispersion of $\text{Ti}_3\text{C}_2\text{T}_x\text{-CTA}^+$ in DMSO for further acid-catalyzed AEAPTMS functionalization. Acidic functionalization conditions not only inhibited self-condensation reactions among silane molecules, but also dissociated CTA^+ ligands from the nanosheet surface. Silanol condensation with -OH MXene surface terminations yielded a covalently-bonded organophilic surface that enabled colloidal dispersion of functionalized $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2$ in the preceramic polymer matrix.

Structural evolution during $\text{Ti}_3\text{C}_2\text{T}_x$ synthesis, exfoliation, and functionalization products from MAX- Ti_3AlC_2 to twice-functionalized $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2$ was evaluated with XRD (Figure 5.4.2(a)). In particular, emergence and refinement of the (002) reflection at $\sim 6\text{-}7^\circ$ pointed to the formation of layered Ti_3C_2 after MILD etching of MAX- Ti_3AlC_2 . The (002) reflection initially shifts from $\sim 9.5^\circ$ in MAX- Ti_3AlC_2 to 7° in MX- $\text{Ti}_3\text{C}_2\text{-OH}$ upon removal of Al interlayers and LiOH alkalization. Furthermore, the (002) reflection broadens upon etching and exfoliation due to a variety of single-to-few layer thick MXene nanoflakes. AEAPTMS functionalization led to refinement of the (002) reflection, indicating that $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2$ were predominantly monolayer. AEAPTMS functionalization also induced a (002) reflection shift to 5° , which was due to the grafted siliceous monolayer further separating MXene layers and minimizing restacking.

XPS and TGA analysis of $\text{Ti}_3\text{C}_2\text{T}_x\text{-Li}^+$, $\text{Ti}_3\text{C}_2\text{T}_x\text{-CTA}^+$, and $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2$ elucidated surface chemistry evolution during twice-functionalization of MXene nanosheets. XPS analysis (Figure 5.4.2(b)) of exfoliated $\text{Ti}_3\text{C}_2\text{T}_x\text{-Li}^+$ and functionalized $\text{Ti}_3\text{C}_2\text{T}_x\text{-CTA}^+$ and $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2$ confirmed CTA^+ ion exchange and AEATPMS grafting. $\text{Ti}_3\text{C}_2\text{T}_x\text{-Li}^+$ exhibited characteristic emission lines for Ti 2p_{1/2} (457.0 eV), Ti 2p_{3/2} (462.7 eV), C 1s (284.8 eV), O 1s (530.7 eV), and F 1s (685.2 eV). The small amount of F retained after LiOH alkalization was sufficiently negligible to achieve dense $\text{Ti}_3\text{C}_2\text{T}_x\text{-SiOC}$ ceramics after pyrolysis. In a separate study, F surface terminations of non-alkalized $\text{Ti}_3\text{C}_2\text{T}_x$ were shown to induce self-etching and significant pore evolution in $\text{Ti}_3\text{C}_2\text{T}_x\text{-SiOC}$ [217]. F surface groups were determined to electrostatically coordinate with AEAPTMS rather than covalently bond, and upon pyrolysis to 500°C began volatilizing and reacting with Si-H clusters in the transforming SiOC matrix. CTAB functionalization was confirmed by increased C 1s emission intensity as grafted CTA^+ ligands imbued long aliphatic functional groups on the MXene surface. After AEAPTMS grafting, Si 2s (153.2 eV), Si 2p (102.2 eV), and N 1s (400.2 eV) emission lines emerged from the covalently-bonded silane; in addition, the C 1s emission line decreased in intensity corresponding to the difference in functional group length between CTAB (16 C atoms) and AEAPTMS (5C/2N atoms).

TGA analysis (Figure 5.4.2(c)) further revealed that grafted AEAPTMS inhibited thermal degradation of MXene nanosheets up to $\sim 1100^\circ\text{C}$, as $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2$ yielded a residue of $\sim 82\%$ compared to the $\text{Ti}_3\text{C}_2\text{T}_x\text{-Li}^+$ residue of $\sim 50\%$. MXene thermal degradation was revealed through hot stage XPS experiments to occur through volatilization and restructuring of F and O functional groups [85, 218]. The covalent bond formed between AEAPTMS and O/OH MXene functional

groups restricted the mobility of these surface groups and mitigated thermal degradation of the MXene nanosheets. At 1500°C, $\text{Ti}_3\text{C}_2\text{T}_x\text{-Li}^+$ yielded a ~35% residue as the MXene nanosheets decomposed to $\text{TiC}_y/\text{TiO}_z$ with gradual mass loss above 1100°C. However, functionalized $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2$ exhibited accelerated decomposition at 1300°C to yield a ~24% residue at 1500°C due to reactions between $\text{Ti}_3\text{C}_2\text{T}_x$ and the effective SiO_2 monolayer formed after AEAPTMS decomposition. TiC and SiO_2 were shown in prior studies to react above 1000°C to form TiO_2 and SiC without gas evolution, but this would not account for the nearly 60% mass loss between 1100°C and 1500°C.. The mass loss was generally attributed to CO evolution but postulated to originate from decomposition to TiO_x , as only a small amount of AEAPTMS was grafted based on Si and N emission intensities in $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2$ (Figure 5.4.2(b)). Overall, twice-functionalization of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets with CTAB and AEAPTMS was shown to imbue organophilic surface functionality through covalent bonding of silane molecules with -O/-OH MXene functional groups, and also inhibited thermal degradation until 1300°C as MXene surface groups were stabilized by grafted AEAPTMS.

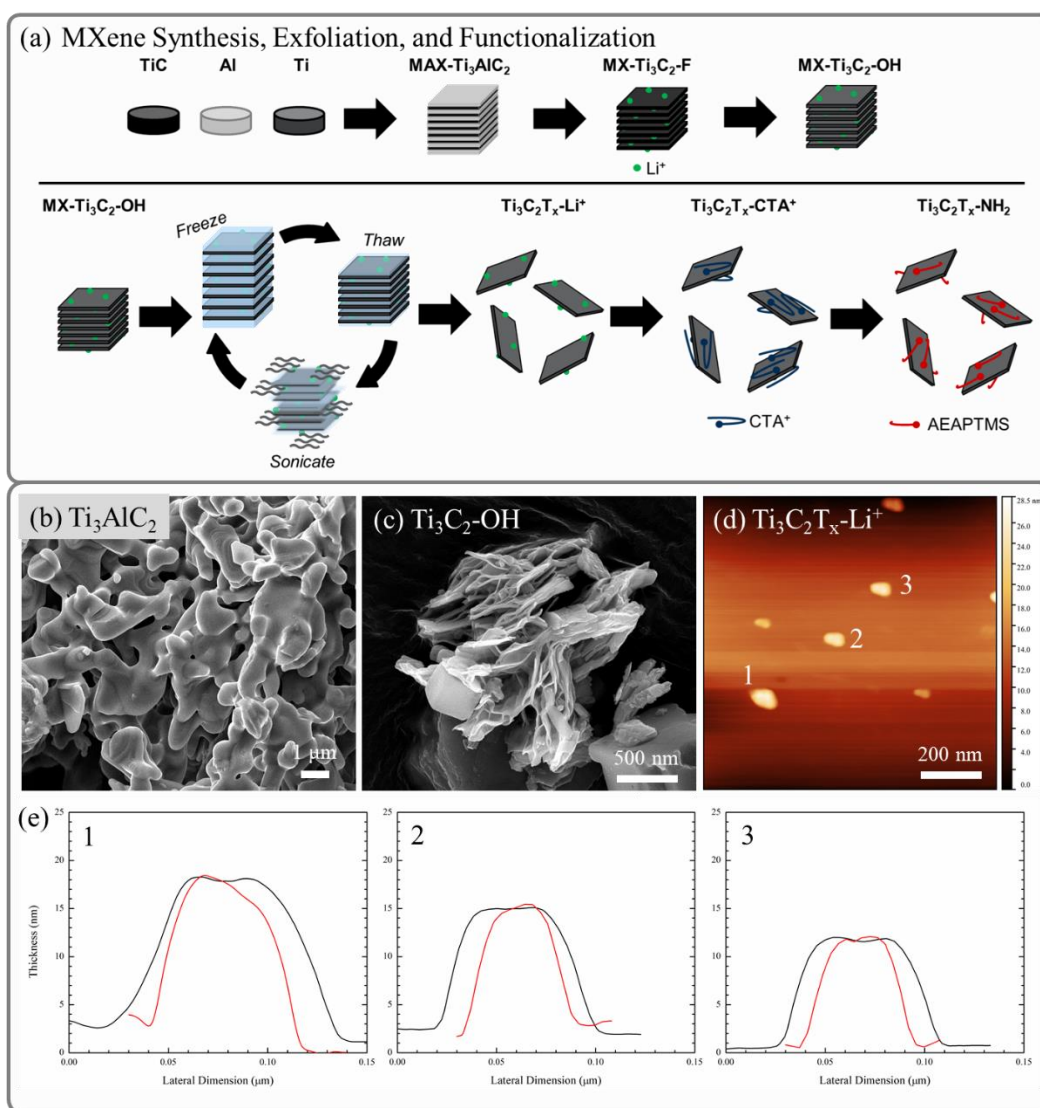


Figure 5.4.1: (a) Schematic of MXene synthesis and functionalization from MAX- Ti_3AlC_2 sintering to AEPTMS functionalization; SEM micrographs of (a) sintered MAX- Ti_3AlC_2 ; scale bar: 1 μm and (c) MX- $\text{Ti}_3\text{C}_2\text{-OH}$; scale bar: 500 nm; (d) AFM micrograph of $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2$.

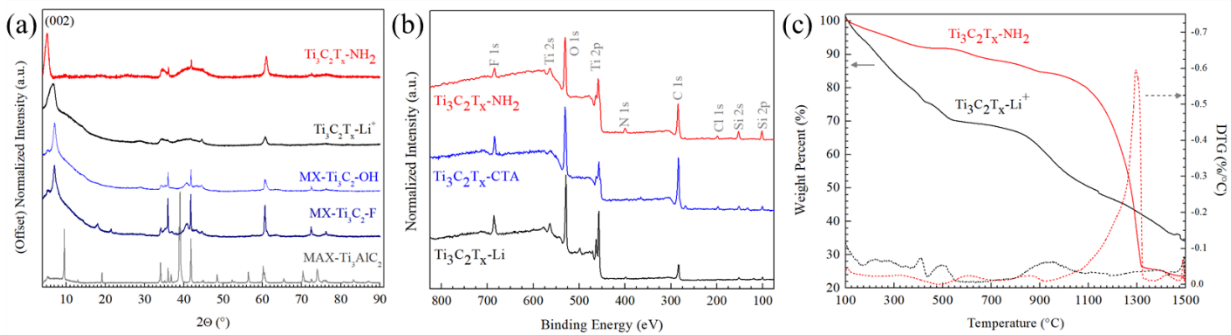


Figure 5.4.2: (a) XRD spectra of MXene precursors, exfoliated $\text{Ti}_3\text{C}_2\text{T}_x\text{-Li}^+$, and functionalized $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2$; (b) XPS spectra of $\text{Ti}_3\text{C}_2\text{T}_x\text{-Li}^+$, $\text{Ti}_3\text{C}_2\text{T}_x\text{-CTA}^+$, and $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2$; (c) TG/DTG profiles of $\text{Ti}_3\text{C}_2\text{T}_x\text{-Li}^+$ and $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2$ heated to 1500°C in Ar.

5.4.2. $\text{Ti}_3\text{C}_2\text{T}_x\text{-SiOC}$ pyrolysis and physical properties

Pyrolysis of $\text{Ti}_3\text{C}_2\text{T}_x\text{-PSO}$ green bodies was investigated with TGA (Figure 5.4.3(a)) up to 1500°C in Ar to ascertain key phenomenon during the polymer-to-ceramic transformation between $400\text{-}800^\circ\text{C}$ and up to SiOC carbothermal reduction to SiC regimes above 1400°C . PSO produced a 72.5% SiOC residue upon pyrolysis to 1400°C and no appreciable mass loss up to 1500°C . $1\text{Ti}_3\text{C}_2\text{T}_x\text{-PSO}$ exhibited a $\sim 1\%$ higher residue of 73.6% at 1400°C . Increased MXene content in $5\text{Ti}_3\text{C}_2\text{T}_x\text{-PSO}$ resulted in a $\sim 3\%$ improvement in ceramic residues (75.4%) at 1400°C compared to PSO. Both $1\text{Ti}_3\text{C}_2\text{T}_x\text{-PSO}$ and $5\text{Ti}_3\text{C}_2\text{T}_x\text{-PSO}$ exhibited a marginal $\sim 1\%$ mass loss up to 1500°C presumably from accelerated CO evolution. This high temperature decomposition event was attributed to carbothermal reduction reactions of TiO_y derived from MXene decomposition and turbostratic C from the SiOC matrix. DTG profiles (Figure 5.4.3(a)) clarified mass loss events during the polymer-to-ceramic transformation that provided insight to the retained mass in $\text{Ti}_3\text{C}_2\text{T}_x\text{-SiOC}$. While $1\text{Ti}_3\text{C}_2\text{T}_x\text{-PSO}$ and $5\text{Ti}_3\text{C}_2\text{T}_x\text{-PSO}$ showed overall similar DTG profiles to PSO, there was less mass loss observed at $\sim 475^\circ\text{C}$ and accelerated onset of a mass loss event at $\sim 375^\circ\text{C}$. Notably for the latter observation, the earlier onset pointed to reactions between $\text{Ti}_3\text{C}_2\text{T}_x\text{-nanosheets}$ and the transforming SiOC matrix during the polymer-to-ceramic transition.

Pyrolytic decomposition events during the polymer-to-ceramic transformation were the combination of multiple individual kinetic processes that cannot be resolved solely with TGA, which would require more dedicated kinetic studies with TGA-MS for evolved gas characterization. However, each event may be described by a rate-limiting step that manifested in the mass loss events observable with TGA, and while this specific polysiloxane used in this study has not yet been analyzed with TGA-MS to characterize the evolved gaseous species, overall similarities with previously studied PDC-SiOC/SiC systems sufficed for mass loss correlation with phase evolution [180-182]. A previous study correlating gas evolution with pyrolytic decomposition events in SiOC derived from a SiO_2 -rich 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane showed event I occurring at $\sim 425^\circ\text{C}$ involved Si-OH and Si-H condensation and release of gaseous by-products [180]. Event II ($\sim 475^\circ\text{C}$) was reported to heavily overlap with event I and corresponded to redistribution of Si-H, Si-O, and Si-C bonds and the release of some Si species in the process. Events III ($\sim 575^\circ\text{C}$) and IV ($\sim 700^\circ\text{C}$) were attributed with methane and hydrogen evolution from cleavage of Si-Me, Si-H, Si-O, and Si-C bonds. A similar TGA-MS study of C-rich AHPCS identified similar mass loss events but corresponding to

methane (event I), ethylene (event II), propylene (event III), and hydrogen (event IV) evolution [181, 182]. As the PSO used in this study is both a high C-containing preceramic resin and a siloxane, mass loss events in $\text{Ti}_3\text{C}_2\text{T}_x$ -PSO pyrolysis were a superposition of both mechanisms.

In both $1\text{Ti}_3\text{C}_2\text{T}_x$ -PSO and $5\text{Ti}_3\text{C}_2\text{T}_x$ -PSO, increased mass loss in and earlier onset of event I alluded to SiO_2 formation in MXene-SiOC interfacial regions from silane volatilization and nascent SiOC phase formation about MXene domains. The slight decrease in event I mass loss between $1\text{Ti}_3\text{C}_2\text{T}_x$ -PSO and $5\text{Ti}_3\text{C}_2\text{T}_x$ -PSO was attributed to expected bulk effects from high nanomaterial loading in the latter. Early stage mass loss (event I) was correlated with higher SiO_2 content in the resultant SiOC ceramic [180]. Event II mass loss sharply declined from PSO to $5\text{Ti}_3\text{C}_2\text{T}_x$ -SiOC; however, this event was postulated to involve primarily retention of C (as opposed to evolution as ethylene) rather than retention of Si. If MXene nanosheets acted as discontinuous inclusions in the evolving SiOC matrix, not only would the resulting $\text{Ti}_3\text{C}_2\text{T}_x$ -SiOC have been brittle, but also the thermal degradation profiles should have independently reflected PSO decomposition to SiOC and $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2$ decomposition shown in Figure 5.4.1(c). That is, there would be no appreciable reactions between SiOC and MXene, which was not evidenced by the TG/DTG profiles.

Alternatively, crystalline MXene was proposed to form a coherent interface with the evolving amorphous SiOC matrix that would be characterized with higher retained C and SiOC phases. During the polymer-to-ceramic transformation, the metastable amorphous SiOC matrix developed through radical-mediated reactions among Si, C, and O atoms; in addition, reactions with MXene surface terminations were believed to proceed simultaneously with AEAPTMS decomposition to stabilize the exposed nanosheet surface that have high surface energies. Therefore, it was believed that an interfacial zone between $\text{Ti}_3\text{C}_2\text{T}_x$ and the SiOC matrix evolved to stabilize the embedded nanosheets and resolved the material coherency mismatch by creating a transition from ordered Si-O/Si-C bonds near the crystalline MXene nanosheet to short-range/amorphous ordering of Si-O-C clusters towards the bulk SiOC matrix. Carbon was thought to be retained in this interfacial region between MMT and SiOC to account for SiO_2 formed in MXene domains and maintain a homogenous matrix composition. At high loading content, interfacial zones may be sufficiently large— possible given the high specific surface area of the nanosheets – to coalesce and require less C to resolve the crystalline/amorphous material boundary between MXene and SiOC.

Table 5.4.4 summarizes the ceramic yield (C.Y.) and volumetric shrinkage (V.S.) of $x\text{Ti}_3\text{C}_2\text{T}_x\text{-SiOC}$ ($x = 0, 1, 2, 5$) bulk samples pyrolyzed at 1000°C, 1200°C, and 1400°C in Ar. Ceramic yields of ~77% and volumetric shrinkages of ~43% were identical within experimental error in $1\text{Ti}_3\text{C}_2\text{T}_x\text{-1000}$, $2\text{Ti}_3\text{C}_2\text{T}_x\text{-1000}$, and $5\text{Ti}_3\text{C}_2\text{T}_x\text{-1000}$, yielding ~3% and ~1.5% improvements, respectively, compared to SiOC-1000 (C.Y.: $74.2 \pm 0.4\%$; V.S.: $45.5 \pm 0.3\%$). Correlating with the improved ceramic residue observed with TGA (Figure 5.4.3(a)), $\text{Ti}_3\text{C}_2\text{T}_x$ predominantly improved C retention in $\text{Ti}_3\text{C}_2\text{T}_x\text{-SiOC}$, attributing to the net improvement in ceramic yield. Similarly, ceramic residues of $1/2/5\text{Ti}_3\text{C}_2\text{T}_x\text{-1200}$ (C.Y.'s: $\sim 76.3 \pm 0.5\%$; V.S.'s: $\sim 46.3 \pm 0.5\%$) showed ~2% and ~1.5% improvements compared to SiOC-1200 (C.Y.: $73.9 \pm 0.8\%$; V.S.: $47.6 \pm 0.7\%$). This trend continued at 1400°C with similar differences between $1/2/5\text{Ti}_3\text{C}_2\text{T}_x\text{-1400}$ (C.Y.'s: $\sim 75.3 \pm 0.5\%$; V.S.'s: $\sim 45.6 \pm 0.3\%$) and SiOC-1400 (C.Y.: $73.5 \pm 0.5\%$; V.S.: $47.4 \pm 0.5\%$). Overall, the trends of decreasing ceramic yield and increasing volumetric shrinkage among all samples as function of temperature was expected from CO evolution, but the improved ceramic residues in $\text{Ti}_3\text{C}_2\text{T}_x\text{-SiOC}$ during the polymer-to-ceramic transformation were retained up to 1400°C and did not induce any further reactions between $\text{Ti}_3\text{C}_2\text{T}_x$ domains and SiOC above 1000°C. The observed bulk trends correlated with TGA results, indicating that the primary source of retained mass in $\text{Ti}_3\text{C}_2\text{T}_x\text{-SiOC}$ was from retention of C.

Phase profiles of pyrolyzed $\text{Ti}_3\text{C}_2\text{T}_x\text{-SiOC}$ (shown representatively with $5\text{Ti}_3\text{C}_2\text{T}_x\text{-SiOC}$) with XRD analysis (Figure 5.4.3(b)) primarily indicated the presence of α -quartz in $5\text{Ti}_3\text{C}_2\text{T}_x\text{-1000/1200/1400}$ with the (101) reflection at 26.5° . Both SiOC-1000 and $5\text{Ti}_3\text{C}_2\text{T}_x\text{-1000}$ exhibited similar amorphous profiles with the halo between $10\text{-}20^\circ$ corresponding to amorphous SiOC, $20\text{-}30^\circ$ to amorphous SiO_2 , and at $\sim 44^\circ$ to turbostratic C. However, $5\text{Ti}_3\text{C}_2\text{T}_x\text{-1000}$ contained a marginal amount of TiC_y from MXene, as evidenced by poorly refined, small reflections at $\sim 35^\circ$ and $\sim 62^\circ$ corresponding to (111) and (022) reflections, respectively. While pyrolysis to 1200°C produced a more prominent amorphous SiO_2 halo in SiOC-1200 , the XRD spectra of $5\text{Ti}_3\text{C}_2\text{T}_x\text{-1200}$ showed that MXene domains inhibited SiO_2 amorphization from SiOC and retained a strong amorphous SiOC halo between $10\text{-}20^\circ$. In addition, the weak TiC reflections disappeared as MXene nanosheets decomposed and formed mixed amorphous TiO_y/SiOC . While an amorphous TiOC phase has been reported in literature [219-221], these were generally obtained above 1500-1600°C pyrolysis and not believed to appreciably form at 1200°C. MXene domains further impeded amorphization of SiO_2 at 1400°C as the strong amorphous halo from $10\text{-}20^\circ$ was retained

and amorphous SiO_2 halo from $20\text{-}30^\circ$ was suppressed in $5\text{Ti}_3\text{C}_2\text{T}_x\text{-}1400$. $\text{SiOC-}1400$ was additionally characterized by poorly crystallized $\beta\text{-SiC}$ from carbothermal reduction of SiO_2 , with (111), (220), and (311) reflections emerging at 36° , 60° , and 72° , respectively. Similar crystalline reflections were observed in $5\text{Ti}_3\text{C}_2\text{T}_x\text{-}1400$ but attributed to a mix of SiC and TiC , the latter confirmed by the (200) reflection at $\sim 42^\circ$. SiC and TiC were both produced through carbothermal reduction of SiO_2 and TiO_2 , respectively, with free C. Overall, domains derived from $\text{Ti}_3\text{C}_2\text{T}_x$ decomposition effectively stabilized the amorphous SiOC structure and prevented growth of amorphous SiO_2 . The chemistry of the amorphous phase could not be ascertained with XRD, so it remained unclear whether the retained amorphous halo between $10\text{-}20^\circ$ was comprised of SiOC , TiO_y , TiOC , or some combination of the three potential phases.

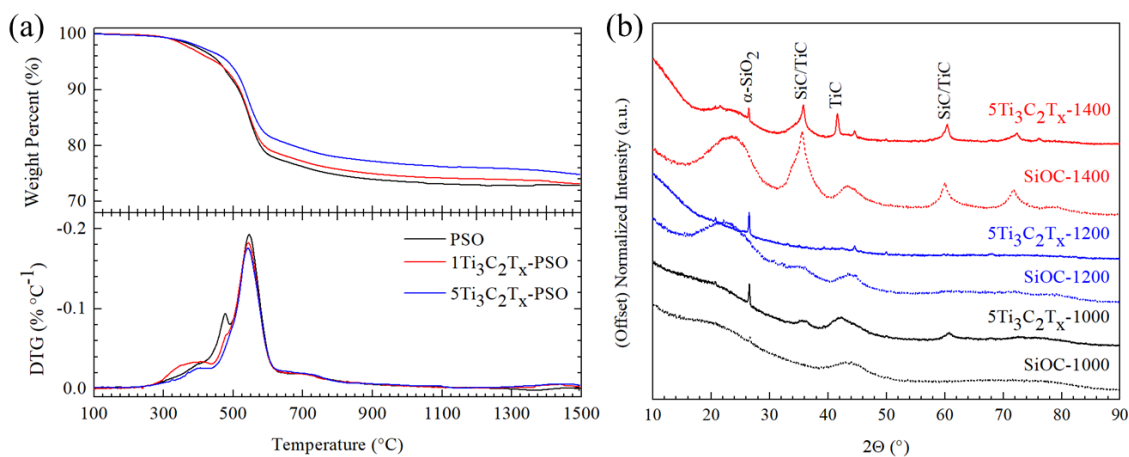


Figure 5.4.3: (a) TG/DTG profiles of PSO (black), 1Ti₃C₂T_x-PSO (red), and 5Ti₃C₂T_x-PSO (blue) to 1500°C in Ar; (b) XRD spectra of SiOC-T_{PyT} (dashed) and 5Ti₃C₂T_x-T_{PyT} (solid) ceramics pyrolyzed at 1000°C (black), 1200°C (blue), and 1400°C (red). Spectra were offset for clarity.

Table 5.4.4: Ceramic yield (%) and volumetric shrinkage (%) of $x\text{Ti}_3\text{C}_2\text{T}_x\text{-SiOC}$ ceramics pyrolyzed to 1000°C, 1200°C, and 1400°C. Error indicated the standard deviation of 3-5 samples.

Ceramic Sample	Ceramic Yield (%)			Volumetric Shrinkage (%)		
	1000°C	1200°C	1400°C	1000°C	1200°C	1400°C
SiOC	74.2 ± 0.4	73.9 ± 0.8	73.5 ± 0.5	45.5 ± 0.3	47.6 ± 0.7	47.4 ± 0.5
1Ti ₃ C ₂ T _x	77.0 ± 0.5	76.1 ± 0.4	75.3 ± 0.5	43.1 ± 0.6	46.1 ± 0.5	46.0 ± 0.4
2Ti ₃ C ₂ T _x	77.3 ± 0.5	76.0 ± 0.6	75.7 ± 0.4	42.9 ± 0.5	46.9 ± 0.3	45.3 ± 0.5
5Ti ₃ C ₂ T _x	77.1 ± 0.2	76.8 ± 0.5	75.1 ± 0.6	43.5 ± 0.3	45.9 ± 0.5	45.6 ± 0.5

5.4.3. Microstructural evolution

Fracture surface morphologies of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SiOC}$ assessed by SEM (Figure 5.4.4(a)) revealed the presence of crystalline artifacts imbued by the MXene nanosheets, shown representatively with $5\text{Ti}_3\text{C}_2\text{T}_x\text{-T}_{\text{pyr}}$ ceramics. SiOC-1000, SiOC-1200, and SiOC-1400 ceramics exhibited featureless and smooth fracture surfaces due to the lack of intrinsic crystallinity and high turbostratic C content that predominate fracture behavior along basal planes. However, $5\text{Ti}_3\text{C}_2\text{T}_x\text{-1000}$ exhibited clear faceted fracture surface features caused by crystallized fronts either from crystalline $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets or crystallized α -quartz in the interface as revealed by XRD (Figure 5.4.3(b)). Further pyrolysis to 1200°C not only corresponded with decreased concentration of crystallized fronts on the $5\text{Ti}_3\text{C}_2\text{T}_x\text{-1200}$ fracture surface, but also led to discrete phases present at residual crystallized fronts. The lack of faceted features indicated the loss of relative crystalline features in the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SiOC}$ matrix, alluding to MXene nanosheet decomposition into amorphous TiO_y analogs. Therefore, it was determined that 1000°C may be the maximum temperature limit at which MXene nanosheets are stable in SiOC composites. EDS analysis (Figure 5.4.4(b)) revealed that these nodules were derived from MXene decomposition and typically Ti (Figure 5.4.4(b4)) and O (Figure 5.4.4(b2)) rich. Notably, Si (Figure 5.4.4(b1)) and C (Figure 5.4.4(b3)) were deficient in these regimes, so these artifacts were confirmed to originate from MXene nanosheet decomposition. Fracture surfaces of $5\text{Ti}_3\text{C}_2\text{T}_x\text{-1400}$ ceramics (Figure 5.4.4(a)) revealed a similarly smooth fracture surface akin to SiOC-1400 but peppered with secondary phase particles ranging from 1 to 3 μm in cluster size. $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets completely decomposed by 1400°C into amorphous $\text{TiO}_2 + \text{SiO}_2$ domains as shown by EDS analysis (Figure 5.4.4(c)). The inclusions were clearly Si (Figure 5.4.4(c1)), O (Figure 5.4.4(c2)), and Ti ((Figure 5.4.4(c4) rich with a notable deficiency in C (Figure 5.4.4(c3)), indicating that C may have been removed from these MXene domains as CO. Microstructural analysis with SEM showed that phase evolution in $\text{Ti}_3\text{C}_2\text{T}_x\text{-SiOC}$ produced more amorphous domains with higher pyrolysis temperature, corresponding with MXene nanosheet decomposition above 1000°C .

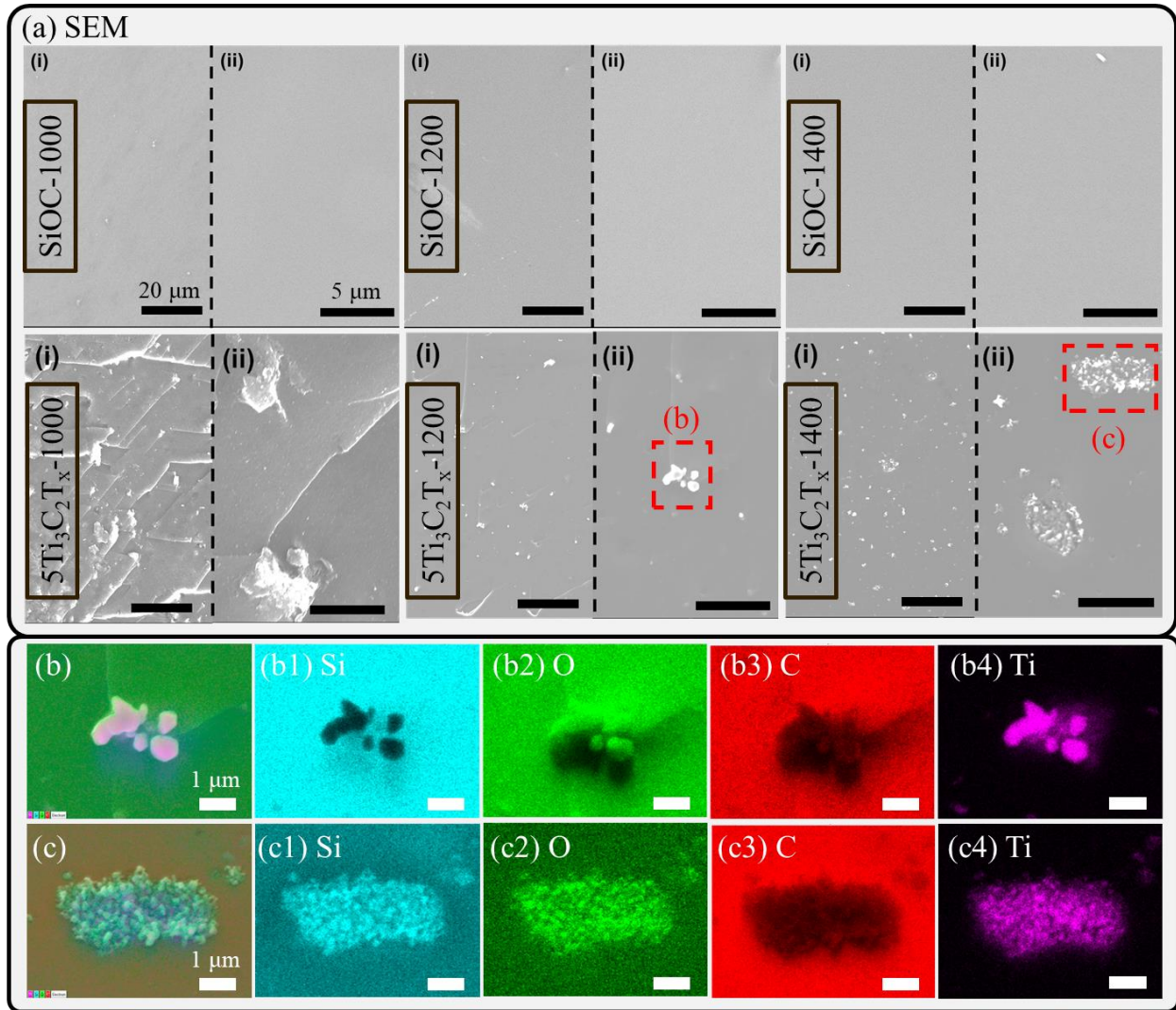


Figure 5.4.4: (a) Fracture surface morphologies of SiOC-1000/1200/1400 and $5\text{Ti}_3\text{C}_2\text{T}_x$ -1000/1200/1400. Scale bars in (i) and (ii) in all panels are 20 μm and 5 μm , respectively; Composite EDS and elemental (Si: 1/blue; O: 2/green; C: 3/red, Ti: 4/purple) maps of indicated regions for (b) $5\text{Ti}_3\text{C}_2\text{T}_x$ -1200 and (c) $5\text{Ti}_3\text{C}_2\text{T}_x$ -1400. Scale bars in all (b)/(c) panels are 1 μm .

Nanostructural morphology in $5\text{Ti}_3\text{C}_2\text{T}_x$ -1000/1200/1400 was investigated with TEM (Figure 5.4.5) to elucidate interfacial phenomenon and ascertain the nature of MXene domains. $\text{Ti}_3\text{C}_2\text{T}_x$ exhibited some slight clustering in $5\text{Ti}_3\text{C}_2\text{T}_x$ -1000 (Figure 5.4.5(a)); while this was to be expected given the high loading content in these composite samples, interfacial properties between MXene domains and SiOC would be representative of typical behavior in all MXene samples. $\text{Ti}_3\text{C}_2\text{T}_x$ domains in SiOC were roughly 200 nm in length and 100 nm in width, and coated with α -quartz (Figure 5.4.5(d)) nanoparticles from silane decomposition and early stage pyrolysis reactions. Similar morphologies were observed in $5\text{Ti}_3\text{C}_2\text{T}_x$ -1200 (Figure 5.4.5(b/e)) but the nanosheet structure decomposed at 1400°C to sub-100 nm nodules in $5\text{Ti}_3\text{C}_2\text{T}_x$ -1400 (Figure 5.4.5(c)). These nodules were determined to comprise of α -quartz and β -SiC ((Figure 5.4.5(f)), which indicated that MXene decomposition also led to dissolution of the MXene-SiOC interface. Elemental mapping with TEM-EDS (Figure 5.4.6) was performed to evaluate the distribution of Si, O, C, and Ti atoms in TEM foils of $5\text{Ti}_3\text{C}_2\text{T}_x$ -1000/1200/1400. In both $5\text{Ti}_3\text{C}_2\text{T}_x$ -1000 (Figure 5.4.6(a)) and $5\text{Ti}_3\text{C}_2\text{T}_x$ -1200 (Figure 5.4.6(b)), Si, O, and C atoms were distributed throughout the matrix while Ti was solely detected within the MXene domain. That is, the $\text{Ti}_3\text{C}_2\text{T}_x$ -SiOC interface was not only comprised of SiOC but also amorphous TiO_x . At 1200°C, the $\text{Ti}_3\text{C}_2\text{T}_x$ -SiOC interface is similarly distributed with Si, O, and C atoms, but there was a slightly higher concentration of O in MXene domains. Accordingly, this indicated that the MXene nanosheet structure decomposed primarily to TiO_y and potentially TiO_x . Correlating with SEM fracture morphology, this accounted for the decrease in observed crystallized fronts or faceted features. Pyrolysis to 1400°C (Figure 5.4.6(c)) corresponded with decomposition of the MXene nanosheet structure into TiO_y nodules – notably, Ti-rich domains were C deficient not only from MXene decomposition but also CO evolution. In addition, Si was highly clustered in the decomposed MXene domain, existing as a combination of SiOC and SiC. SiO_2 was not appreciably observed as Si-rich and O-rich domains had very little overlap, which agreed with the suppressed amorphous SiO_2 halo observed in the XRD spectra of $5\text{Ti}_3\text{C}_2\text{T}_x$ -1400 (Figure 5.4.3(b)). EDS analysis revealed that the MXene nanosheet structure was retained up to 1200°C with $\text{Ti}_3\text{C}_2\text{T}_x$ -SiOC interface comprised evenly of Si, O, and C as amorphous SiOC.

Given the apparent amorphous nature of $\text{Ti}_3\text{C}_2\text{T}_x$ -SiOC, TEM analysis could not characterize differences in amorphous ordering at the nanoscale. Advanced TEM characterization such as 4D-STEM or EELS or advanced diffraction techniques such as neutron diffraction would

be needed to fully deconvolute amorphous ordering in $\text{Ti}_3\text{C}_2\text{T}_x\text{-SiOC}$. 4D-STEM in particular provides the adequate point and spatial resolution to evaluate bonding characteristics within the MXene-SiOC interface. While such advanced nanoscale characterization would be the focus of separate dedicated study, TEM analysis however was critical in evaluating the state of MXene nanosheets and derived domains up to pyrolysis temperatures of 1400°C.

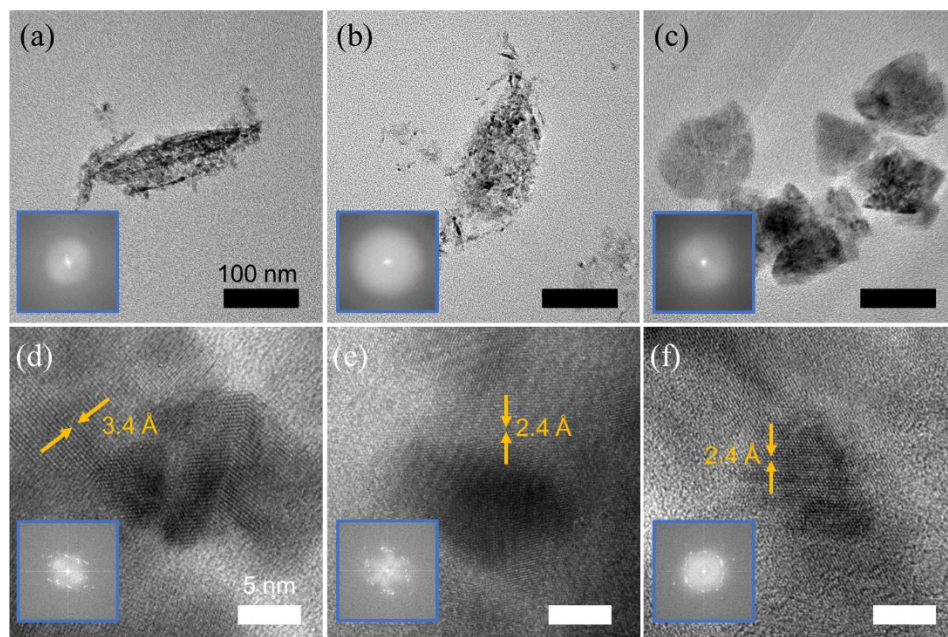


Figure 5.4.5: TEM micrographs of (a) 5Ti₃C₂T_x-1000, (b) 5Ti₃C₂T_x-1200, and (c) 5Ti₃C₂T_x-1400. Scale bars in (a)-(c) are 100 nm; HR-TEM micrographs of (d) 5Ti₃C₂T_x-1000, (e) 5Ti₃C₂T_x-1200, and (f) 5Ti₃C₂T_x-1400. Scale bars in (d)-(f) are 5 nm

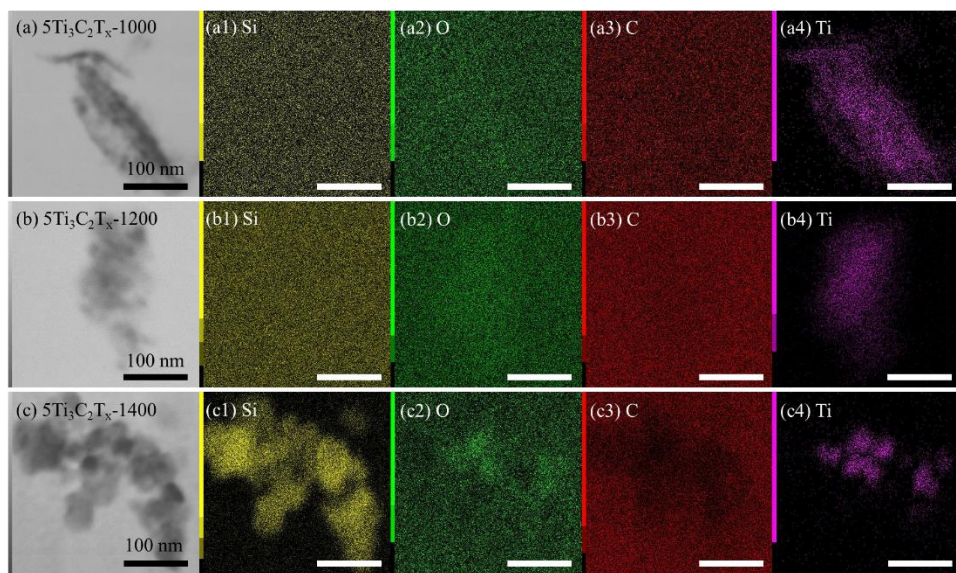


Figure 5.4.6: STEM-EDS elemental (Si: 1/blue; O: 2/green; C: 3/red, Ti: 4/purple) maps for (a) $5\text{Ti}_3\text{C}_2\text{T}_x-1000$, (b) $5\text{Ti}_3\text{C}_2\text{T}_x-1200$, and (c) $5\text{Ti}_3\text{C}_2\text{T}_x-1400$. Scale bars in all panels are 100 nm.

5.5. *Conclusions*

In this study, $\text{Ti}_3\text{C}_2\text{T}_x$ -SiOC ceramic nanocomposites were fabricated with organophilic MXene nanosheets prepared through a novel synthesis route of F/T/S-assisted exfoliation and twice-functionalization with CTAB and AEAPTMS. This route was developed to imbue a covalently-bonded silane functional group while as retaining the exfoliated nanosheet structure during processing and in the preceramic green bodies. $\text{Ti}_3\text{C}_2\text{T}_x$ -SiOC was pyrolyzed from 1000°C to 1400°C to investigate the effect of MXene nanosheets on phase evolution and ceramic properties. MXene nanosheets were determined to retain their 2D nanosheet morphology up to 1200°C before decomposing to TiO_y . $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets also stabilized the amorphous SiOC matrix, but full characterization of amorphous ordering in $\text{Ti}_3\text{C}_2\text{T}_x$ -SiOC remains a challenge and the subject of a future study. The findings of this study offer novel fabrication of exfoliated $\text{Ti}_3\text{C}_2\text{T}_x$ nanocomposites and fundamental understanding of phase evolution mechanisms in polymer-derived ceramic-MXene composite materials.

Chapter 6: Self-Etching $\text{Ti}_3\text{C}_2\text{T}_x$ -SiOC Ceramics: Effects of MXene Surface Terminations on High-Temperature Ceramic Nanocomposites

6.1. *Abstract*

$\text{Ti}_3\text{C}_2\text{T}_x$ (MXenes) are novel 2D nanomaterials with exceptional electrical conductivity. Their surfaces are covered with functional groups that may significantly affect material properties such as hydrophobicity, electrical conductivity, and oxidation resistance. The role of these terminations in high-temperature ceramic systems with regard to phase and microstructural evolution has not been investigated. In this study, $\text{Ti}_3\text{C}_2\text{T}_x$ -SiOC 2D nanocomposites were fabricated with -F and -OH terminated MXene to evaluate the role of surface terminations in silane coupling and phase formation during the polymer-to-ceramic transformation. X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS) identified self-etching mechanisms caused by F-terminated $\text{Ti}_3\text{C}_2\text{T}_x$ and revealed the retained F surface terminations are retained in the MXene structure until evolution at $\sim 550^\circ\text{C}$. Evolved F reacts with Si-H bonds in the transforming ceramic matrix, causing additional mass loss and volumetric deformation. LiOH alkalization was shown to suppress the self-etching phenomenon through the substitution of F groups with OH on the nanosheet surface. Furthermore, F terminations were determined to only engage in hydrogen bonding with silane molecules as opposed to covalent linkages with OH terminations, which accelerated silane removal and $\text{Ti}_3\text{C}_2\text{T}_x$ degradation. The study provides a fundamental understanding of the nature and behavior of MXene surface terminations in the context of high-temperature ceramic nanocomposite fabrication.

6.2. *Introduction*

Polymer-derived silicon oxycarbide (SiOC) is a potential high-temperature electroceramic material that leverages its inherent thermal stability, oxidation and corrosion resistance, and creep resistance with compositional, electrical, mechanical, and microstructural properties tunable from the preceramic polymer chemistry and architecture [4-6, 9, 10, 12, 222]. It is an amorphous ceramic comprised of disordered Si tetrahedra of mixed SiO_xC_y bonds and a free turbostratic C phase from excess polymeric C species typically present in preceramic SiOC polymers [143, 212, 223]. SiOC exhibits inherently poor electrical conductivity of $51\ \mu\text{S}\cdot\text{m}^{-1}$ at room temperature but

was shown to increase with C content, indicating that the primary conduction mechanism in SiOC ceramics proceeds through free C phases [213, 224]. However, as increasing C content affects oxidation resistance and mechanical strength, there is a need to improve the conductivity of the SiOC matrix to promote viable applications in sensors, MEMS devices, and energy materials.

Active and passive fillers are popular choices to enhance SiOC matrix conductivity by introducing conductive species either through *in-situ* phase formation or through retained conductive phases, respectively [16]. Active filler-controlled pyrolysis is typically preferred as the *in-situ* formed phases better maintain coherency with the SiOC matrix through thermodynamically controlled phase formation. Ni and Ti organometallic additives were shown to significantly enhance the elevated temperature conductivity of SiOC through active-filler catalyzed phase formation. Polymer-derived SiOC-Ni composites pyrolyzed up to 1100°C in Ar-20%H₂O improved room temperature and elevated temperature electrical conductivity through nucleation of metallic Ni nanoparticles in the SiOC matrix, with SiOC-Ni exhibiting conductivity values up to 247 S·m⁻¹ at 900°C compared to 62 S·m⁻¹ for pure SiOC [13]. Electrical conductivity values reached 1177 S·m⁻¹ at 950°C in SiOC-Ti nanocomposites through *in-situ* TiC phases produced during pyrolysis to 1400°C in Ar [15]. SiOC-Ti nanocomposites displayed sufficient conductivity for second-stage flash sintering, improving room temperature conductivity from 4.83 μS·m⁻¹ in pure SiOC to 2.12 S·m⁻¹ in SiOC-Ti with 20% Ti loading [214]. While improving conductivity, active organometallic fillers can form undesirable ancillary phases during pyrolysis such as NiO or NiSi_x in SiOC-Ni [13] or TiO_x in SiOC-Ti [15, 214] that may require alternative pyrolysis or sample preparation conditions to mitigate but not completely nullify due to an underlying thermodynamic phase formation phenomenon [104, 212]. Furthermore, high organometallic additive loading (>10%) was required to significantly enhance conductivity in the aforementioned studies. There is a need to improve electrical conductivity in SiOC ceramics while minimizing additive content to prevent ancillary phase formation and retain bulk properties of the ceramic matrix that may appreciably change at higher loading.

Part of a rapidly growing MXene family of 2D transition metal carbides and nitrides (among others), Ti₃C₂T_x is the most prominent and investigated MXene due to single-flake conductivity values reported ranging from 241 kS·m⁻¹ [83] to 460 kS·m⁻¹ [82] which potential applications in a variety of sensors [64, 65], energy materials [55, 57, 79, 80, 225, 226], and composite materials [67, 88, 95, 227-230]. Ti₃C₂T_x are primarily synthesized from selective

etching of MAX-Ti₃AlC₂ either through HF or LiF/HCl, with subsequent exfoliation of MXene nanosheets through intercalating agents such as TBAOH or Li⁺ [53]. With traditional HF etching, bulky intercalating agents such as TBAOH which contain large alkyl-substituted ammonium cations were necessary to physically separate and exfoliate MXene nanosheets. LiF/HCl (MILD) etching routes inherently generate Li⁺ intercalants in etched Ti₃C₂ as HF is formed *in-situ* from dissociation of LiF in HCl. Notably, Li⁺ intercalating cations were sufficient to exfoliate MXene nanosheets through sonication methods [53, 103]. Irrespective of the method, etching yields layered Ti₃C₂ with -F and -OH surface terminations that have been shown to affect electronic [73], optoelectronic [69], and oxidation-resistance [82] properties while also serving as potential sites for silane [74, 76, 231] or nanoparticle [61, 78, 79] functionalization.

The surface groups of Ti₃C₂T_x (-O, -F, -Cl, =O), intrinsically part of the MXene structure, have been shown to affect thermal and electronic properties. Thermal annealing of MXene films was shown to remove or reorganize -F and -O surface groups during annealing of single-flake Ti₃C₂T_x films above 500°C [85] with improvements in electrical conductivity from 85 S·m⁻¹ for native MXene to 241 kS·m⁻¹ after annealing at 500°C [83]. However, this generally coincided with rutile TiO₂ formation before nanosheet decomposition to TiC_y above 1000°C [83, 85]. The thermal stability of HF-etched Ti₃C₂ revealed the dissolution of the layered structure to form TiC upon heat treatment to 1200°C in Ar, with the transformation initiating at 900°C [232]. Notably, F content as detected by EDS decreased from 28 at% at 500°C to 14 at% at 900°C and 0 at% at 1200°C with O content increase (21 at%, 28 at%, and 33 at%, respectively) at the studied temperatures, indicating that intrinsic surface terminations were evolved during heat treatment and induced phase transformation from hexagonal/layered Ti₃C₂ to cubic TiC [232]. TiC formation from Ti₃C₂T_x has been observed at 1200°C in SiBCN/TiC ceramic composites, but may have been accelerated due to multilayered/agglomerated MXene domains in the microstructure [67]. Single-flake and multilayered Ti₃C₂T_x films annealed to 1000°C in Ar revealed higher refinement of TiC in multilayered films, indicating that the sheet-like morphology may be better retained with thorough exfoliation and separation of MXene nanosheets [85]. Whether the Ti₃C₂T_x nanosheet structure is retained or decomposes to TiC_y, surface terminations generally control phase formation between 500°C and 800°C, but the role of these terminations in high-temperature ceramic composites has not been appreciably studied.

There are very few studies of polymer-derived SiC/SiCN/SiOC/etc.-MXene composites presumably due to the low yield of the MXene exfoliation process and the need to devise functionalization strategies to promote colloidal MXene dispersion in the typically hydrophobic preceramic polymer. The aforementioned SiBCN/TiC study fabricated ceramics from ball-milled Ti_3C_2 and preceramic polymer powders, which may not have produced homogeneously dispersed single-flake MXene sheets, enhanced electromagnetic wave adsorption in the pyrolyzed ceramic composites [67]. SiOC- Ti_3C_2 composites prepared through HF etching, TBAOH intercalation, and APTES functionalization slightly enhanced the conductivity from $5 \text{ S}\cdot\text{m}^{-1}$ in pure SiOC at 1000°C to $18 \text{ S}\cdot\text{m}^{-1}$ in 0.1 wt% MXene composites, with conductivity of 1 wt% MXene composites generally invariant at $6 \text{ S}\cdot\text{m}^{-1}$ due to agglomerated MXene layers revealed in XRD [96]. In either case, no attention was paid to the role of MXene surface terminations in the preparation of the preceramic or the pyrolyzed ceramic composites.

This study investigates the effect of -F and -OH terminated $\text{Ti}_3\text{C}_2\text{T}_x$ on microstructural evolution in $\text{Ti}_3\text{C}_2\text{T}_x$ -SiOC polymer-derived ceramics up to 1000°C in Ar. F and O atoms are the primary MXene surface adatoms derived from the etching process. The majority of MXene synthesis research utilizes predominantly -F terminated MXene obtained after HF or LiF/HCl etching. LiOH alkalization was utilized to replace -F with -OH surface groups while maintaining the structural and colloidal properties of the MXene nanosheets. $\text{Ti}_3\text{C}_2\text{T}_x$ -SiOC composites were prepared with $\text{Ti}_3\text{C}_2\text{T}_x$ either untreated or alkalized with LiOH and functionalized with AEAPTMS and pyrolyzed to 1000°C . The effect, role, and fate of MXene surface terminations on densification and phase formation in the $\text{Ti}_3\text{C}_2\text{T}_x$ -SiOC ceramics were analyzed with X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS).

6.3. *Experimental Methodology*

6.3.1. Materials

The materials for $\text{Ti}_3\text{C}_2\text{T}_x$ synthesis, exfoliation, and functionalization are provided in Section 5.3.1. A commercially available polysiloxane Polyramic SPR-684 (PSO, $[-\text{Si}(\text{Ph})_2\text{O}-]_3[-\text{Si}(\text{Me})(\text{H})\text{O}-]_2[-\text{Si}(\text{Me})(\text{CH}=\text{CH}_2)\text{O}-]_2$, Starfire Systems, Inc., Glenville, NY) was chosen as the base preceramic polymer, with a 2.1% platinum-divinyltetramethyldisiloxane complex in xylene

(Karstedt's catalyst, Gelest, Inc., Morrisville, PA) selected to crosslink the preceramic green bodies. Acetone (technical grade, Fisher Scientific, Waltham, MA), ethanol (EtOH, 200 proof, Decon Laboratories, Inc. King of Prussia, PA), hexanes (anhydrous, 95%, Sigma-Aldrich, Burlington, MA), dimethyl sulfoxide (DMSO, $\geq 99.9\%$, Sigma-Aldrich, Burlington, MA) and ultrapure water (NP H₂O, 18.2 M Ω cm) were used as general solvents throughout the experiment. Argon (Ar, Industrial Grade, Airgas, Christiansburg, VA) was used for the pyrolysis atmosphere. All chemicals were used without further purification.

6.3.2. Ti₃C₂T_x-SiOC sample preparation

The methodology for preparing functionalized, -OH terminated Ti₃C₂T_x nanoflakes (Ti₃C₂T_x-NH₂-OH) is provided in the Section 5.3.2. Functionalized, -F terminated Ti₃C₂T_x nanoflakes (Ti₃C₂T_x-NH₂-F) were prepared identically but without LiOH alkalization. 1Ti₃C₂T_x-PSO preceramic green bodies were prepared by stirring PSO with toluene (50 v/v%), Karstedt's catalyst (10 ppm), and functionalized Ti₃C₂T_x nanoflakes (99:1 w/w relative to PSO). The suspension was stirred under vacuum to remove residual solvent. The polymer suspensions were cast to $\Phi 12$ mm x 6 mm cylindrical silicone molds, degassed under vacuum, and cured at 60°C for 6 h, 120°C for 6 h, and 150°C for 12 h. The green bodies were lightly ground and polished up to 1500 grit with SiC abrasive pads to remove any mold artifacts, and the edges were slightly beveled. Green bodies were denoted as 1Ti₃C₂T_x-PSO-F or 1Ti₃C₂T_x-PSO-OH for samples prepared with -F or -OH terminated Ti₃C₂T_x, respectively. To minimize potential surface oxidation, the green bodies were placed between two sheets of carbon felt in an alumina crucible. The green bodies were pyrolyzed at 1000°C in a horizontal tube furnace (1830-12 Horizontal Tube Furnace, CM Furnaces, Inc., Bloomfield, NJ), with heating and cooling rates of 2°C·min⁻¹, soaking time of 2 h, and flowing Ar (500 cm³·min⁻¹). The pyrolyzed Ti₃C₂T_x-SiOC ceramics were denoted as 1Ti₃C₂T_x-1000-F or 1Ti₃C₂T_x-1000-OH for samples prepared with -F or -OH terminated Ti₃C₂T_x, respectively. Blank SiOC ceramics without Ti₃C₂T_x were similarly denoted SiOC-1000.

6.3.3. Characterization

Ceramic yield and linear shrinkage were calculated from changes in mass, sample radii, and thickness between green bodies and pyrolyzed samples. Reported values are averages of 3-5 replicates and corresponding errors indicate standard deviations. Bulk densities were measured in

triplicate by the Archimedes method with EtOH as the immersion medium. Skeletal densities were measured in replicate ($n > 5$) by helium gas pycnometry (AccuPyc II 1340, Micromeritics, Norcross, GA) with an outlet pressure of 19.5 psi in a 1 cc sample cell. The phase compositions of powdered samples were analyzed with an X-ray diffractometer (XRD, Empyrean, Malvern Panalytical Ltd., Almelo, The Netherlands) operated at 40 kV and 40 mA with Cu K α radiation between $2\theta = 2-90^\circ$ and a scan rate of $0.02^\circ \cdot s^{-1}$. Microstructures were observed with an optical microscope (OM, VK-X3000, Keyence Corp., Osaka, Japan) or a scanning electron microscope (SEM, JEOL IT-500HR, JEOL USA, Peabody, MA). Thermogravimetric analysis (TGA, SDT 650, TA Instruments, New Castle, DE) was performed with a heating rate of $5^\circ C \cdot min^{-1}$ to $1500^\circ C$ under an argon flow of $20 mL \cdot min^{-1}$. Chemical compositions were examined by X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM, Physical Electronics USA, Inc., Chanhassen, MN) with an Al K α source (1486.6 eV). Spectra were shifted with respect to the C 1s emission line at 284.4 eV.

6.4. Results and Discussion

6.4.1. $Ti_3C_2T_x$ -SiOC microstructure and physical properties

Figure 6.4.1(a) depicts representative preceramic polymer green bodies of PSO, $1Ti_3C_2T_x$ -PSO-OH and $1Ti_3C_2T_x$ -PSO-F and analogous pyrolyzed ceramics SiOC-1000, $1Ti_3C_2T_x$ -1000-OH and $1Ti_3C_2T_x$ -1000-F. While their preceramic green bodies were indiscernible but lacking the translucency of PSO, $1Ti_3C_2T_x$ -1000-OH, and $1Ti_3C_2T_x$ -1000-F were starkly different as the latter endured significant volumetric deformation, pore formation, and cracking and was coated with a white layer along all surfaces and cracks (Figure 6.4.1(c-d)). SEM images in Figure 6.4.1(f-e-f) of lightly fractured $1Ti_3C_2T_x$ -1000-F further revealed a high density of coalesced pores distributed throughout the sample. Larger pores appeared to originate from generally symmetric dumbbell-shaped pores (Figure 6.4.1((g-h))). SiOC-1000 and $1Ti_3C_2T_x$ -1000-OH exhibited uniform reductions in sample thickness (ΔT) and radius (ΔR) consistent with PDC processing, as illustrated in Figure 6.4.1(b). $1Ti_3C_2T_x$ -1000-F experienced generally non-uniform changes in thickness due to volumetric expansion from gas evolution and pore formation; as such, the change in thickness was quantified by maximum sample thickness after pyrolysis, typically at the middle of the sample.

Table 6.4. summarizes the ceramic yields, ΔR , and ΔT for SiOC-1000, $1\text{Ti}_3\text{C}_2\text{T}_x$ -1000-OH, and $1\text{Ti}_3\text{C}_2\text{T}_x$ -1000-F. SiOC-1000 and $1\text{Ti}_3\text{C}_2\text{T}_x$ -1000-OH both exhibited reductions in sample dimensions typical with PDC processing, with $\Delta R/\Delta T$ of $-18.5 \pm 0.3\%/-18.0 \pm 0.3\%$ and $-17.5 \pm 0.3\%/-15.0 \pm 0.8\%$ respectively. $1\text{Ti}_3\text{C}_2\text{T}_x$ -1000-F also displayed a reduction in sample radius (ΔR : $-14.9 \pm 1.5\%$) with less contraction due to pore formation and volumetric expansion. However, as deformation primarily occurred axially (ΔT : $(+)22.4 \pm 3.1\%$), gas evolution/pore formation in $1\text{Ti}_3\text{C}_2\text{T}_x$ -1000-F may have occurred during the latter stages of the polymer-to-ceramic transition after some initial sample contraction at lower pyrolysis temperatures (400-500°C). Large variations of ΔR and ΔT in $1\text{Ti}_3\text{C}_2\text{T}_x$ -1000-F were representative of nonuniform radial and axial deformations observed. Volumetric expansion and pore formation in $1\text{Ti}_3\text{C}_2\text{T}_x$ -1000-F correlated with a lower ceramic yield of $66.0 \pm 0.2\%$ compared to $74.1 \pm 0.4\%$ and $77.0 \pm 0.5\%$ for SiOC-1000 and $1\text{Ti}_3\text{C}_2\text{T}_x$ -1000-OH, respectively. Increased mass loss and pore evolution in $1\text{Ti}_3\text{C}_2\text{T}_x$ -1000-F pointed to self-foaming or self-etching mechanisms imbued by -F terminated $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. The $\sim 3\%$ improved ceramic yield between SiOC-1000 and $1\text{Ti}_3\text{C}_2\text{T}_x$ -1000-OH further indicated that intrinsic MXene surface terminations produced the stark physical differences between $1\text{Ti}_3\text{C}_2\text{T}_x$ -1000-OH and $1\text{Ti}_3\text{C}_2\text{T}_x$ -1000-F.

Table 6.4. also provides experimental bulk density (ρ_{bulk}), skeletal density (ρ_{skeletal}), and close porosity values of the ceramic samples. Due to the accelerated mass loss and pore formation, ρ_{bulk} of $1\text{Ti}_3\text{C}_2\text{T}_x$ -1000-F ($1.12 \pm 0.04 \text{ g}\cdot\text{cm}^{-3}$) was lower than ρ_{bulk} values for both SiOC-1000 and $1\text{Ti}_3\text{C}_2\text{T}_x$ -1000-OH ($1.71 \pm 0.01 \text{ g}\cdot\text{cm}^{-3}$). ρ_{skeletal} measurements with helium pycnometry further indicated that SiOC-1000 and $1\text{Ti}_3\text{C}_2\text{T}_x$ -1000-OH were dense with measured ρ_{skeletal} values of $1.704 \pm 0.004 \text{ g}\cdot\text{cm}^{-3}$ and $1.700 \pm 0.008 \text{ g}\cdot\text{cm}^{-3}$ agreeing within experimental error of ρ_{bulk} and with negligible closed porosity. Experimental ρ_{skeletal} of $1.480 \pm 0.030 \text{ g}\cdot\text{cm}^{-3}$ for $1\text{Ti}_3\text{C}_2\text{T}_x$ -1000-F corresponded with a closed porosity of $24 \pm 4\%$. The closed porosity value understated the overall porosity in $1\text{Ti}_3\text{C}_2\text{T}_x$ -1000-F samples, but accurate apparent densities were difficult to obtain due to uneven sample deformation.

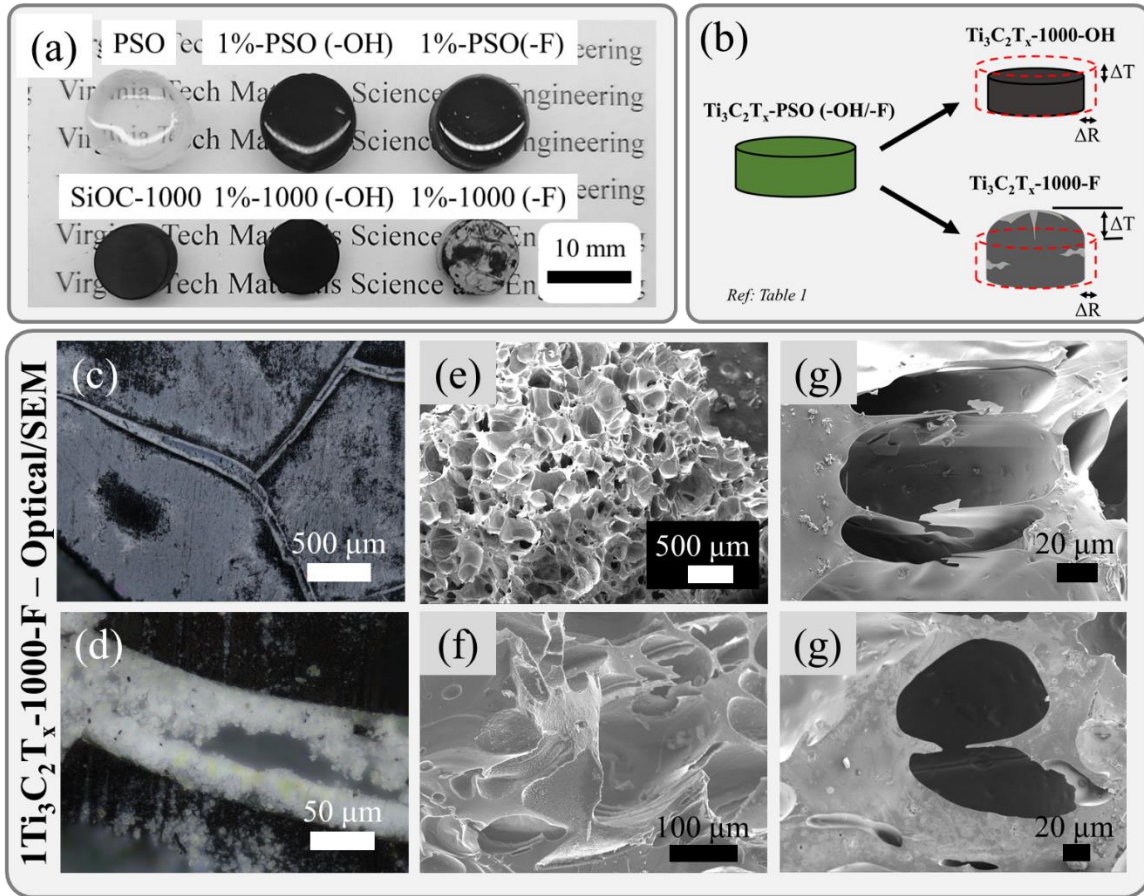


Figure 6.4.1: (a) Optical image of (top row, left to right) PSO, $1Ti_3C_2T_x-PSO-OH$, and $1Ti_3C_2T_x-PSO-F$ preceramic green bodies, and (bottom row) SiOC-1000, $1Ti_3C_2T_x-1000-OH$, and $1Ti_3C_2T_x-1000-F$ pyrolyzed ceramics. (b) Schematic of volumetric change during pyrolysis to 1000°C in Ar with ΔT and ΔR indicating change in sample thickness and radius (Table 6.4.). (c)/(d) Optical micrographs of $1Ti_3C_2T_x-1000-F$ sample surface illustrating cracking and material deposition on the surface and within cracks. Scale bars are 500 μm and 50 μm , respectively. (e)-(h) SEM micrographs of $1Ti_3C_2T_x-1000-F$ illustrating open/coalesced pore structures. Scale bars are 500 μm , 100 μm , 20 μm , and 20 μm , respectively.

Table 6.4.1: Ceramic yield (%), relative changes in sample radius ($\Delta R/\%$) and thickness ($\Delta T/\%$), densities ($\text{g}\cdot\text{cm}^{-3}$), and calculated closed porosity (%) of SiOC-1000, $1\text{Ti}_3\text{C}_2\text{T}_x$ -1000-OH, and $1\text{Ti}_3\text{C}_2\text{T}_x$ -1000-F. The error indicates a standard deviation of 5 replicates.

Ceramic Sample	Ceramic Yield (%)	ΔR (%)	ΔT (%)	ρ_{bulk} ($\text{g}\cdot\text{cm}^{-3}$)	ρ_{skeletal} ($\text{g}\cdot\text{cm}^{-3}$)	Closed Porosity (%)
SiOC-1000	74.1 ± 0.4	-18.5 ± 0.3	-18.0 ± 0.4	1.71 ± 0.01	1.704 ± 0.004	---
$1\text{Ti}_3\text{C}_2\text{T}_x$ -1000-OH	77.0 ± 0.5	-17.5 ± 0.4	-15.0 ± 0.8	1.71 ± 0.01	1.700 ± 0.008	---
$1\text{Ti}_3\text{C}_2\text{T}_x$ -1000-F	66.0 ± 0.2	-14.9 ± 1.5	$(+)22.4 \pm 3.1$	1.12 ± 0.04	1.480 ± 0.030	24 ± 4

XRD spectra of SiOC-1000 and $1\text{Ti}_3\text{C}_2\text{T}_x-1000\text{-OH}$ (Figure 6.4.2(a)) reveal predominantly amorphous phase profiles with large halos from $2\Theta=10\text{-}20^\circ$, $20\text{-}25^\circ$ and $40\text{-}50^\circ$ for amorphous SiOC, SiO_2 , and C, respectively. A small C (001) reflection was detected at $\sim 26^\circ$ in SiOC-1000 due to low concentrations of turbostratic C typically present in SiOC ceramics. $1\text{Ti}_3\text{C}_2\text{T}_x-1000\text{-OH}$ exhibited low intensity (101) and (100) α -quartz reflections at 26.7° and 21° , respectively, from the siliceous interface between the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet regimes and the SiOC matrix formed during pyrolysis. The self-etching effect in $1\text{Ti}_3\text{C}_2\text{T}_x-1000\text{-F}$ was apparent by the reduction of amorphous SiO_2 and C halos; however, the amorphous SiOC halo from $10\text{-}20^\circ$ was retained. Refined α -quartz reflections were observed as (110) and (112) reflections were additionally resolvable at 36.6° and 39.5° , respectively. F etching of Si was responsible for the decreased amorphous SiO_2 content.

SEM investigation of $1\text{Ti}_3\text{C}_2\text{T}_x-1000\text{-OH}$ (Figure 6.4.2(b,c)) and $1\text{Ti}_3\text{C}_2\text{T}_x-1000\text{-F}$ (Figure 6.4.2(d,e)) fracture surfaces revealed starkly differing microstructures, as the former possessed a dense fracture surface with faceting from crystalline α -quartz present at the $\text{Ti}_3\text{C}_2\text{T}_x\text{-SiOC}$ interface. Bulk pore structures in $1\text{Ti}_3\text{C}_2\text{T}_x-1000\text{-F}$ described earlier (Figure 6.4.1(e)) were comprised of coalesced, dumbbell-shaped pores that formed around a $<1\text{ }\mu\text{m}$ bridge. The pore structure elucidated that gas evolution occurred symmetrically, which could only occur at the exposed lateral surfaces of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. Specifically, gas and pore evolution in $1\text{Ti}_3\text{C}_2\text{T}_x-1000\text{-F}$ thus occurred at the MXene-SiOC interface through reactions of Si and F.

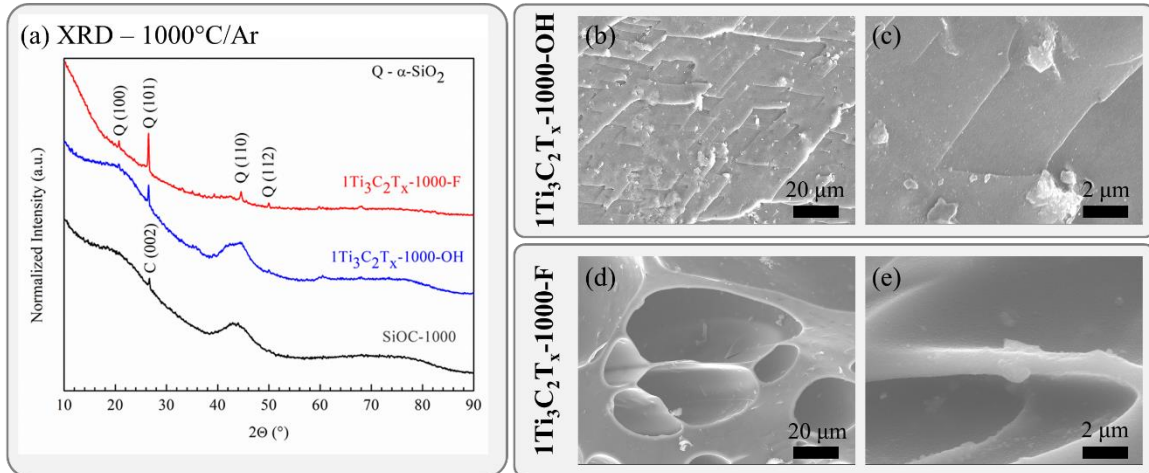


Figure 6.4.2: (a) XRD spectra of SiOC-1000 (black), $1\text{Ti}_3\text{C}_2\text{T}_x$ -1000-OH (blue), and $1\text{Ti}_3\text{C}_2\text{T}_x$ -1000-F (red) ceramics pyrolyzed at 1000°C in Ar; fracture surface micrographs of (b)/(c) $1\text{Ti}_3\text{C}_2\text{T}_x$ -1000-OH and (d)/(e) $1\text{Ti}_3\text{C}_2\text{T}_x$ -1000-F. Scale bars in (b)/(d) and (c)/(e) are 20 μm and 2 μm , respectively.

6.4.2. $\text{Ti}_3\text{C}_2\text{T}_x$ -PSO pyrolysis and polymer-to-ceramic transformation

Figure 6.4.3(a) shows thermogravimetric (TG) and derivative (DTG) profiles of PSO, $1\text{Ti}_3\text{C}_2\text{T}_x$ -PSO-OH, and $1\text{Ti}_3\text{C}_2\text{T}_x$ -PSO-F preceramic green bodies in Ar to 1000°C with a heating rate of 5°C min^{-1} . PSO, $1\text{Ti}_3\text{C}_2\text{T}_x$ -PSO-OH, and $1\text{Ti}_3\text{C}_2\text{T}_x$ -PSO-F yielded $\sim 74\%$, 76% , and 68% residues, respectively, at 1000°C , agreeing with the bulk ceramic yields presented in Table 6.4.. DTG profiles elucidated individual mass loss events during the polymer-to-ceramic transformation between 350°C and 800°C . It is noted while mass loss events during the polymer-to-ceramic transformation were the combination of multiple individual kinetic processes that cannot be isolated with TGA, the major processes were governed by some rate-limiting step that ultimately drove volatilization reactions observable with TGA. Dedicated kinetic studies with TGA-MS for evolved gas characterization would be needed for a more robust analysis of the polymer-to-ceramic transition, which was outside the scope of this study. The specific polysiloxane used in this study has not yet been analyzed with TGA-MS to characterize the evolved gaseous species, but overall similarities with previously studied PDC-SiOC/SiC systems sufficed for analysis of mass loss events in regards to underlying phase development [180-182].

Peak deconvolution of DTG profiles (Figure 6.4.3(b-d)) revealed four mass loss events (I-IV) common among PSO, $1\text{Ti}_3\text{C}_2\text{T}_x$ -PSO-OH, and $1\text{Ti}_3\text{C}_2\text{T}_x$ -PSO-F. In PSO (Figure 6.4.3b), events I (442°C), II (475°C), III (546°C), and IV (648°C) contributed 25.7% , 8.5% , 45.4% , and 20.4% to mass loss during the polymer-to-ceramic transformation, respectively. As reported by Garcia-Garrido et al. [180], event I correlated with gaseous by-products from condensation reactions of Si-H and Si-OH while event II – which the authors reported to heavily overlap with event I – involved some volatilization of Si species from redistribution of Si-O, Si-H, and Si-C bonds. Events III and IV were correlated with methane and hydrogen evolution from cleavage of Si-Me, Si-H, Si-O, and Si-C bonds in the final restructuring of the SiOC matrix. DTG peak deconvolution for $1\text{Ti}_3\text{C}_2\text{T}_x$ -PSO-OH elucidated four similar mass loss events, however with earlier onset for event I (384°C). Functionalized $\text{Ti}_3\text{C}_2\text{T}_x$ - NH_2 nanosheets were fabricated with a siliceous monolayer from AEAPTMS, which provided additional Si-OH/Si-H sites that promoted event I kinetically. Such condensation reactions may create additional SiO_2 in the evolving SiOC matrix as there was less overlap between events I and II in $1\text{Ti}_3\text{C}_2\text{T}_x$ -PSO-OH. Events I, II (480°C), III (545°C), and IV (615°C) corresponded with 18.9% , 6.7% , 48.4% , and 26.0% to mass loss, respectively. Events I and II induced less mass loss in $1\text{Ti}_3\text{C}_2\text{T}_x$ -PSO-OH than in native PSO,

which could indicate the source of the improved ceramic yield observed in Table 6.4.. Higher relative mass losses during events III and IV pointed to increased methane/hydrogen evolution and thus C removal from the SiOC/free C matrix.

While $1\text{Ti}_3\text{C}_2\text{T}_x\text{-PSO-F}$ retained events I-IV, an additional event (V – 527°C) was identified as the cause of the enhanced mass loss and pore formation observed. Events I (383°C), II (488°C), III (545°C), and IV (633°C) occurred similarly as in $1\text{Ti}_3\text{C}_2\text{T}_x\text{-PSO-OH}$ but with respective mass loss contributions of 21.2%, 4.4%, 47.0%, and 14.4%. Relative mass loss contributions from Event III were generally invariable across the ceramic samples, and thus may relate to the evolution of carbon species from the high C-containing preceramic polymer. Noting that event IV was not as prevalent in $1\text{Ti}_3\text{C}_2\text{T}_x\text{-1000-F}$, event V was thus attributed to Si and H evolution to account for the observed low ceramic yield. As an isolated phenomenon at 527°C as opposed to a uniform process, event V was then attributed to pore evolution and axial expansion discussed earlier as it occurred after some initial sample loss/contraction had occurred below 500°C . As the sole difference between $1\text{Ti}_3\text{C}_2\text{T}_x\text{-1000-OH}$ and $1\text{Ti}_3\text{C}_2\text{T}_x\text{-1000-F}$ was the presence of -OH or -F terminations on the MXene surface, event V could have only proceeded through reactions of Si in the matrix with retained -F surface groups. Typically such reactions involve the etching of Si/SiO₂ domains, further reinforcing the cause of the observed self-etching behavior to originate from reactions with F-terminated MXene. While Si-C bonds are chemically inert to HF, Si-H and Si-O bonds present in the evolving SiOC matrix were susceptible to etching.

Table 6.4. summarizes the bond dissociation (Equations A-E) and radical-mediated pyrolysis (Equations 1-5) reactions, with corresponding enthalpies of reaction (ΔH_{rxn}) pertinent to etching of Si-H and Si-O bonds with F. Si-H bonds were more susceptible to F attack than Si-O bonds owing to lower ΔH_{rxn} for Equations 1 ($-169.5 \text{ kJ mol}^{-1}$) and 2 (-98 kJ mol^{-1}) than Equation 3 ($-35.5 \text{ kJ mol}^{-1}$). Si-H reactions (Equations 4 and 5) with $\bullet\text{OR}$ ($\text{R} = \text{H, Si}$) radicals were not as favorable ($311\text{-}325 \text{ kJ mol}^{-1}$) due to the large dissociation energies for H-OR (Equation B) or Si-OR (Equation D) bonds. While Si species in Equations 1 and 3 were volatilized as Si-F, Si $\bullet$ radicals formed in Equation 2 exhibit favorable reactivity with $\bullet\text{OR}$ radicals to condense into Si-OR bonds (Equation C – reverse reaction). Similarly, H $\bullet$ not evolved as H₂ may condense with $\bullet\text{OR}$ radicals to form H-OR species (Equation B – reverse reaction). Therefore, it was determined that the primary etching mechanism occurred through F attack of Si-H bonds, yielding in volatilization of SiF₄ and H₂ species. H₂ evolution during event V at 527°C (**Figure 6.4.3(d)**) would account for

the decreased H_2 volatilization observed in event IV at 633°C in the DTG profile of 1Ti₃C₂T_x-PSO-F (Figure 6.4.3(d)), which supported the proposed etching mechanism. Condensation of •OR with Si• radicals yielding deposited Si-OR species may account for accelerated α -quartz crystallization observed in Figure 6.4.2(a) and the white coating observed on surfaces and cracks in Figure 6.4.1(c-d).

Table 6.4.2: Summary of radical-forming bond dissociation reactions (A-F), proposed radical-mediated pyrolysis reactions (1-5), and corresponding enthalpies of reaction (ΔH_{rxn}) for self-etching reaction mechanisms.

Equation	Reaction ($R = H, Si$)	$\Delta H_{\text{rxn}}^{\circ}(\text{kJ mol}^{-1})$	Ref.
(A)	$\text{H}_2 \rightarrow 2 \text{H} \bullet$	432	[233]
(B)	$\text{H} - \text{O} - \text{R} \rightarrow \text{H} \bullet + \bullet \text{O} - \text{R}$	459	
(C)	$\text{Si} - \text{H} \rightarrow \text{Si} \bullet + \text{H} \bullet$	318	
(D)	$\text{Si} - \text{O} - \text{R} \rightarrow \text{Si} \bullet + \bullet \text{O} - \text{R}$	452	
(E)	$\text{Si} - \text{F} \rightarrow \text{Si} \bullet + \text{F} \bullet$	565	
(F)	$\text{F}_2 \rightarrow 2 \text{F} \bullet$	155	
(1)	$\text{Si} - \text{H} + \text{F} \bullet \rightarrow \text{Si} - \text{F} + \text{H} \bullet$	-169.5	<i>This Work</i>
(2)	$\text{Si} - \text{H} + \text{H} \bullet \rightarrow \text{Si} \bullet + \text{H}_2$	-98	
(3)	$\text{Si} - \text{O} - \text{R} + \text{F} \bullet \rightarrow \text{Si} - \text{F} + \bullet \text{O} - \text{R}$	-35.5	
(4)	$\text{Si} - \text{H} + \bullet \text{O} - \text{R} \rightarrow \text{Si} \bullet + \text{HO} - \text{R}$	311-318	
(5)	$\text{Si} - \text{H} + \bullet \text{O} - \text{R} \rightarrow \text{Si} - \text{O} - \text{R} + \text{H} \bullet$	318-325	

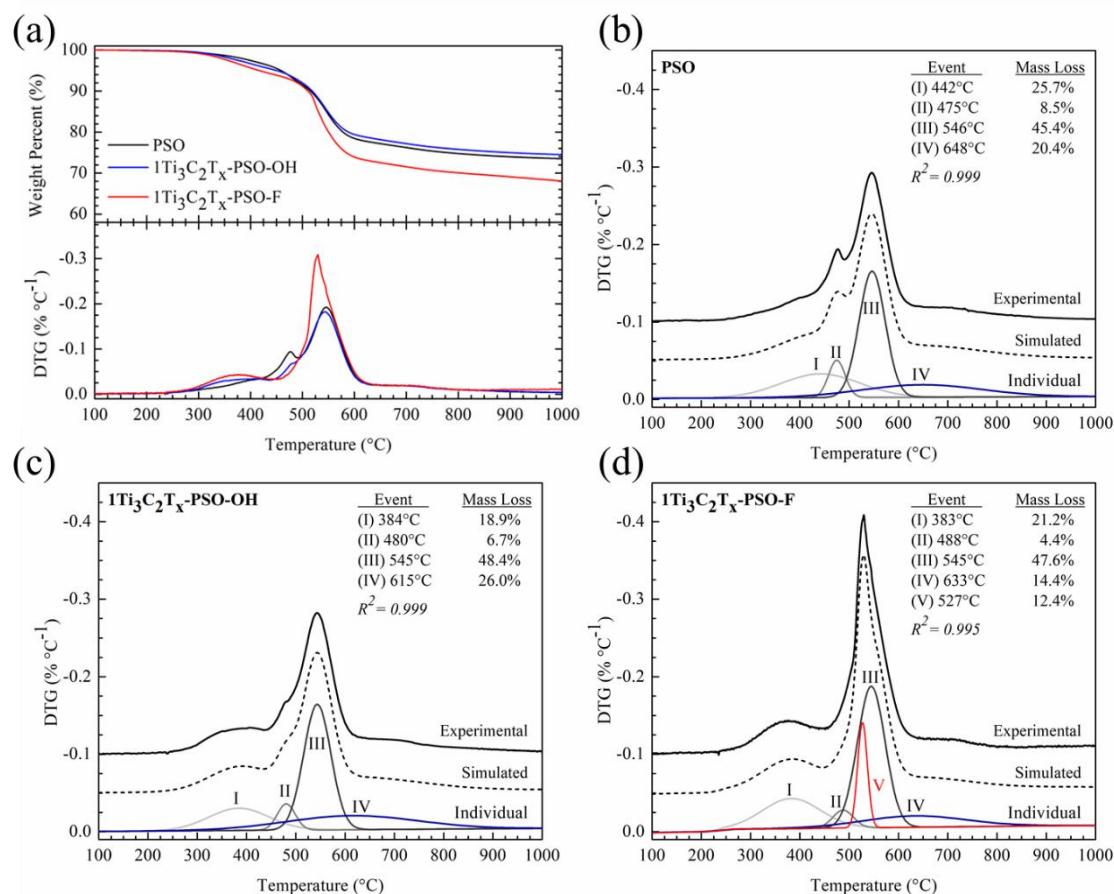


Figure 6.4.3: (a) TG (*top*) and DTG (*bottom*) profiles of PSO (black), 1Ti₃C₂T_x-PSO-OH (blue), and 1Ti₃C₂T_x-PSO-F (red) in Ar to 1000°C with 5°C min⁻¹ heating rate; DTG peak deconvolution and analysis for (b) PSO, (c) 1Ti₃C₂T_x-PSO-OH, and (d) 1Ti₃C₂T_x-PSO-F.

6.4.3. $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-F/-OH}$ characterization

The self-etching phenomenon in $1\text{Ti}_3\text{C}_2\text{T}_x\text{-1000-F}$ was related to the concentration of -F surface terminations on the $\text{Ti}_3\text{C}_2\text{T}_x$ retained after functionalization with CTAB and AEAPTMS, and indicated that LiOH alkalization sufficiently substituted -OH with -F terminations to produce dense microstructures in $1\text{Ti}_3\text{C}_2\text{T}_x\text{-1000-OH}$. Chemical analysis with XPS (Figure 6.4.4(a)) revealed a strong presence of -F surface groups (1s: 685.2 eV) in $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-F}$ with a small O contribution (1s: 530.7 eV) from any -OH MXene surface groups and Ti-O-Si bonds formed through acid-catalyzed AEAPTMS condensation. XPS spectra of LiOH-alkalized and AEAPTMS-functionalized $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-OH}$ showed an intensification of the O 1s peak with the F 1s peak nearly reduced. The small amount of remnant -F after LiOH alkalization did not affect densification in $1\text{Ti}_3\text{C}_2\text{T}_x\text{-1000-OH}$ ceramics and was deemed negligible. Intrinsic to both $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-F}$ and $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-OH}$, Ti (2p_{1/2}: 457.0 eV; 2p_{3/2}: 462.7 eV), C (1s: 284.8 eV), Cl (1s: 198.6 eV), Si (2s: 153.2 eV, 2p: 102.2 eV), and N (1s: 400.2 eV) emission lines were attributed to either the MXene nanosheet (Ti, C, Cl) or the silane functional group (C, Si, N). A marginal amount of retained -Cl terminations formed during MAX- Ti_3AlC_2 etching with LiF/HCl were responsible for the observed Cl 1s emission. Furthermore, smaller Si 2s/2p emission intensities in $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-F}$ compared to $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-OH}$ pointed to less grafted silane molecules as -F terminations were not involved in silane condensation reactions and may impart some inherent hydrophobicity. Overall, XPS analysis confirmed that the self-etching phenomenon in $\text{Ti}_3\text{C}_2\text{T}_x\text{-1000}$ ceramics was related to the concentration of -F and -O surface groups in $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-F}$ and $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-OH}$ was the primary chemical difference between the two functionalized MXene nanosheets.

Chemical differences between $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-F}$ and $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-OH}$ with regards to -F and -OH surface terminations manifested in distinct thermal degradation (TG/DTG) profiles (Figure 6.4.4(b)) that further pointed to retained -F groups as the source of the self-etching phenomenon. Both $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-F}$ and $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-OH}$ exhibited gradual mass loss between 100°C and 400°C from the evolution of adsorbed gas species and electrostatically bound silane molecules from the MXene nanosheet surface. As revealed in the DTG profiles, higher mass loss in $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-F}$ between 200°C and 350°C was attributed to a higher concentration of electrostatically bound silane molecules. However, $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-F}$ displayed a unique mass loss event at ~550°C that was assigned to the evolution of -F surface groups, which was shown through *in-situ* heated XPS

experiments by Persson et. al. of single-layer MXene nanosheets obtained after HF etching [218]. Furthermore, -F evolution at $\sim 550^{\circ}\text{C}$ in $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-F}$ correlated with mass loss event V (527°C) in the DTG profile of $1\text{Ti}_3\text{C}_2\text{T}_x\text{-PSO-F}$ (Figure 6.4.3(d)), confirming the source of mass loss, volumetric expansion, and pore formation in $1\text{Ti}_3\text{C}_2\text{T}_x\text{-1000-F}$ as the retained MXene -F terminations. While the evolution of covalently-bound silane groups contributed to mass between 550°C and 700°C in $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-OH}$, the lack of similar degradation in $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-F}$ further indicated that grafted AEAPTMS molecules were primarily electrostatically-linked through hydrogen bonding.

Further heating above 800°C induced TiC_y formation through the evolution of remaining -F or -O terminations from the decomposition of MXene nanosheet structure [85]. However, MXene decomposition was suppressed in $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-OH}$ ($\sim 4\%$ mass loss) due to the siliceous monolayer imbued by covalently grafted AEAPTMS which stabilized the 2D nanosheet structure. As hydrogen-bonded AEAPTMS molecules in $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-F}$ were released below 400°C and F terminations were cleaved at 550°C , the exposed MXene surface was more prone to degradation above 800°C ($\sim 18\%$ mass loss) without surface stabilization by AEAPTMS. While -O terminations were shown to redistribute upon F evolution in hot-stage XPS experiments [218], the relatively low concentration of intrinsic -O terminations after etching and low-temperature evolution of AEAPTMS in $1\text{Ti}_3\text{C}_2\text{T}_x\text{-PSO-F}$ may have accelerated MXene decomposition above 800°C .

XPS and TGA characterization of $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-F}$ and $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-OH}$ provided further insight into bonding characteristics between MXene and AEAPTMS. Silane evolution in TGA profiles (Figure 6.4.4(b)) indicated that AEAPTMS molecules were loosely coordinated (i.e., hydrogen-bonded) to MXene nanosheets and evolved at lower temperatures ($<400^{\circ}\text{C}$) in $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-F}$ while covalently-bonded AEAPTMS molecules in $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-OH}$ required higher temperatures ($>600^{\circ}\text{C}$) for volatilization. Thus, -F surface groups imbued after MAX etching were not involved in AEAPTMS condensation reactions with MXene, retained in $1\text{Ti}_3\text{C}_2\text{T}_x\text{-PSO-F}$ green bodies, and unfavorably reacted with the evolving SiOC matrix during pyrolysis. Persson et. al. elucidated with *in-situ* heated XPS and STEM-HAADF characterization that -F/-OH surface groups organized on 2 sites on the MXene surface – an energetically favorable ‘A’ site located above Ti atoms in the central layer of the MXene sheet and an alternative ‘B’ site located above central C atoms – but F atoms exhibited a sole preference for the ‘A’ site while O atoms occupied

‘B’ sites when no ‘A’ sites were available [218]. The authors proposed that O atoms at ‘B’ sites were bridging atoms, presumably bonded to 2 surface Ti atoms, and possessed less binding energy than ‘A’ site atoms due to the noted surface mobility of O adatoms [218]. Thus, ‘A’ site atoms were more favorable to engage in functionalization reactions than ‘B’ site atoms but the concentration of F and/or O atoms at ‘A’ sites dictated coupling reactions between MXene and AEAPTMS.

While all the ‘A’ sites in $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-F}$ were filled with F atoms, the non-reactivity of -F surface groups with condensable Si-OH groups of AEAPTMS yielded hydrogen bonding between -F terminations and -OH groups of AEAPTMS. After LiOH alkalization, F atoms in the ‘A’ sites were replaced with O atoms that displayed higher reactivity towards silane condensation, yielding a covalently bonded silane monolayer. It was not discerned whether ‘B’ site O bridging atoms were similarly reactive with silane, but given the aforementioned mobility of ‘B’ site atoms and the structural role coordinating with 2 Ti atoms, it was postulated that silane grafting reactions at ‘B’ sites were not as favorable as ‘A’ sites. It was further believed that any silane reactions with ‘B’ site O atoms were primarily through hydrogen bonding, but dedicated atomistic modeling and characterization would be necessary to confirm the reaction schemes. AEAPTMS functionalization reaction schemes with $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-F}$ and $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-OH}$ were summarized in Figure 6.4.4(c), depicting silane coordination with ‘A’ site F or O atoms through hydrogen and covalent bonding, respectively.

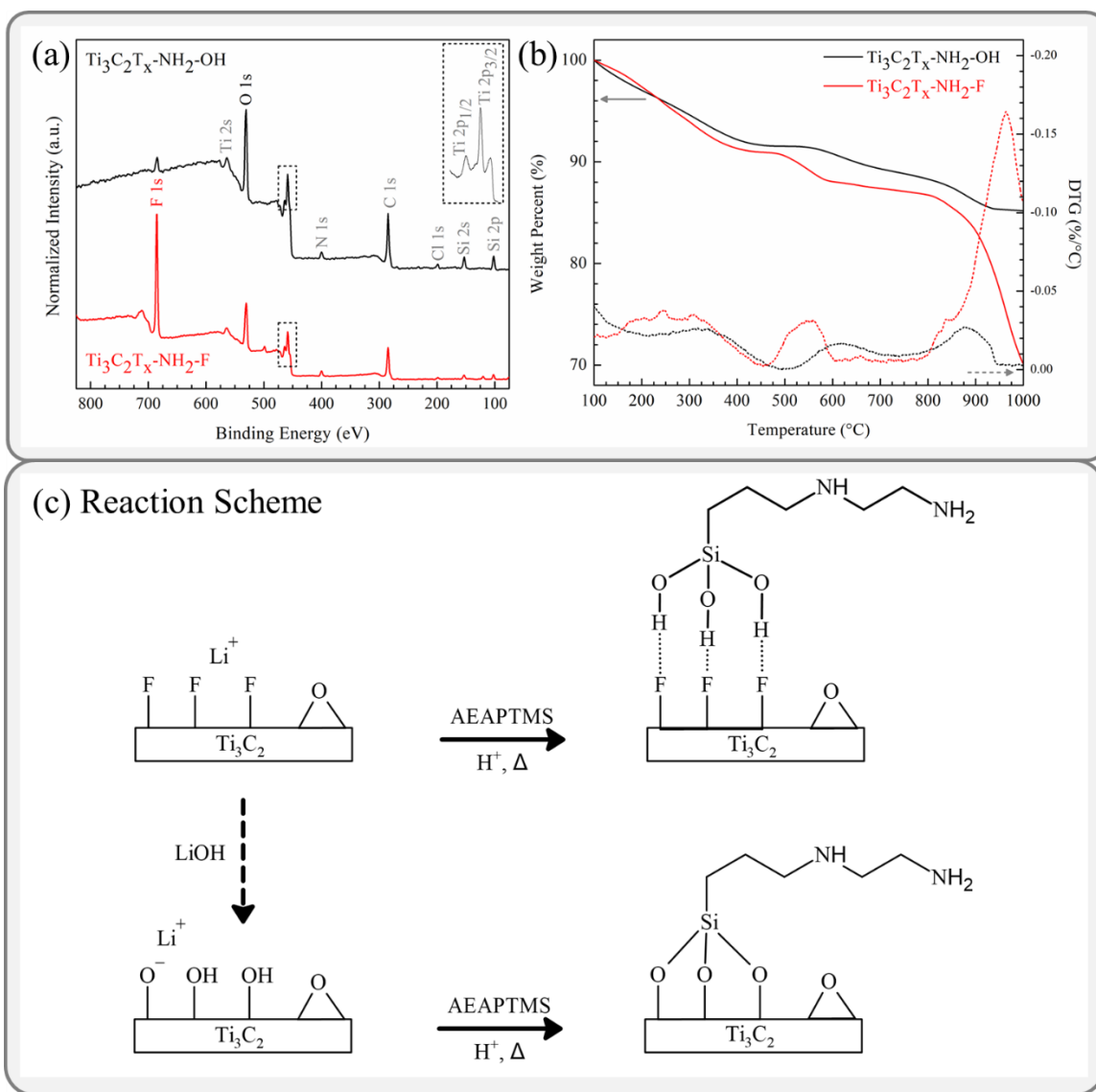


Figure 6.4.4: (a) XPS spectra of $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-OH}$ and $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-F}$; (b) TG/DTG profiles of $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-OH}$ and $\text{Ti}_3\text{C}_2\text{T}_x\text{-NH}_2\text{-F}$; (c) reaction schematic of AEAPTMS functionalization of -F and -OH terminated MXene.

6.5. Conclusion

This work evaluated the role of MXene surface terminations on phase and microstructural development of $\text{Ti}_3\text{C}_2\text{T}_x\text{-SiOC}$ nanocomposites. Through XRD, TGA, and XPS analysis, it was determined that -F surface terminations imbued during MAX- Ti_3AlC_2 etching were retained after AEAPTMS functionalization and primarily interacted through hydrogen bonding. $\text{Ti}_3\text{C}_2\text{T}_x\text{-SiOC}$ composites prepared with F-terminated MXene experienced significant pore evolution, volumetric deformation, and accelerated mass loss due to F evolution and self-etching with Si-H bonds at $\sim 550^\circ\text{C}$. LiOH alkalization sufficiently substituted -F with -O/-OH terminations that formed covalent bonds with AEAPTMS molecules during acid-catalyzed silane condensation. $\text{Ti}_3\text{C}_2\text{T}_x\text{-SiOC}$ ceramics prepared with LiOH-treated MXene exhibited dense microstructures and physical properties analogous to pure SiOC. LiOH alkalization was shown to mitigate the self-etching phenomenon induced by retained F terminations. The findings from this study provided novel insight into bonding and pyrolytic reaction mechanisms in $\text{Ti}_3\text{C}_2\text{T}_x\text{-SiOC}$ ceramic nanocomposites which can spur the development of novel exfoliated MXene-PDC nanocomposites.

Chapter 7: Conclusions and Future Work

7.1. *Summary of Dissertation Findings*

The dissertation focused on the fundamental understanding and characterization of processing-structure-property relationships in SiOC ceramics and in novel SiOC 2D nanocomposite systems. The goal of this work was to develop novel functional ceramic materials with potential applications in porous or electronic ceramics. Some of the important findings from this current work are listed:

- (1) Thermodynamic and mechanistic modeling of phase formation in SiOC-Fe ceramics revealed the catalytic effect of Fe₃Si nanoparticles in β -SiC nucleation and growth. Fe also induced coalescence of SiO₂ domains and led to highly porous SiOC ceramics. A Gibbs free energy minimization model was developed that quantified the catalytic role of Fe through quasi-1D nanowire growth equations. While there is still a need to refine the model to account for O present in the free C phase (as graphene oxide), predicted phase content from thermodynamic models generally agreed with elemental and compositional values.
- (2) A novel synthesis route for exfoliation and twice-functionalization of MMT and Ti₃C₂T_x nanosheets was developed in order to prepare bulk quantities of nanomaterial for producing MMT-SiOC and Ti₃C₂T_x-SiOC and to improve the degree of nanosheet exfoliation in the ceramic composites. In this method, exfoliated nanosheets were isolated from bulk/layered precursors through repeated cycles of freezing/thawing/sonication. Nanoflakes were twice-functionalized with CTAB and AEAPTMS not only to form an organophilic surface coating, but also prevent nanoflake agglomeration. Structural and chemical evolution was assessed to gauge the viability and efficacy of the proposed synthesis route.
- (3) Detailed microstructure analysis of MMT-SiOC and Ti₃C₂T_x-SiOC ceramic nanocomposites revealed exfoliation of both MMT and MXene nanoflakes in the SiOC matrix, but also the formation of a continuous interface between nanoflake regimes and SiOC. This interface was notable as it bridged between crystalline nanosheet domains and the amorphous SiOC matrix, and was generally characterized by the presence of α -quartz nanodomains. Furthermore, the MMT nanosheet morphology was retained up to 1200°C, above which MMT decomposed and formed β -SiC nanowhiskers that were

observed up to 20 μm in length and 200 nm in diameter. $\text{Ti}_3\text{C}_2\text{T}_x$ nanoflakes however were only stable up to 1000°C and transformed into TiO_y clusters.

- (4) Selectively-etched porosity characterization in MMT-SiOC ceramics revealed that MMT nanoflakes generally contributed to 2-5 nm pores and led to porous ceramics with specific surface areas up to 100 $\text{m}^2 \text{g}^{-1}$ for ceramics pyrolyzed up to 1200°C. However, with water vapor-assisted pyrolysis, MMT effectively reduced the total SiO_2 content and retained more free C in MMT-SiOC- H_2O ceramics compared to native SiOC- H_2O . In addition, water vapor led to amorphization of α -quartz nanodomains. Selectively-etched porosity showed a ~25-50% decrease in pore volume with both MMT and water vapor, indicating that MMT domains imbued resistance to water vapor ingress and mitigated SiO_2 evolution.
- (5) The role of nanosheet surface terminations was assessed between F-terminated and O-terminated MXene and densification/pore evolution in $\text{Ti}_3\text{C}_2\text{T}_x$ -SiOC nanocomposites. It was shown that F surface groups retained after initial MAX etching volatilized and reacted with nascent Si domains during pyrolysis, causing self-etching, significant pore evolution, and volumetric deformation in the prepared ceramics. Not only was LiOH alkalization shown to mitigate this effect, but also led to covalent bonds between O surface groups and AEAPTMS as opposed to electrostatic coordination in the case of F surface groups. This work illustrated that surface groups were non-trivial component of SiOC-2D nanosheet composite systems, but also provided vital information for further development of high temperature MXene composites.

7.2. *Overview of Scientific Contributions*

This dissertation focused on the microstructural and property analysis of SiOC and SiOC 2D nanocomposites, but the core findings and results can be transferred to other material systems or for designed applications. The overall scientific contributions of this work are listed:

- (1) Introduction of a novel synthesis and twice-functionalization route for producing exfoliated 2D nanomaterials, offering broad applicability to various polymer and ceramic nanocomposite systems. The method enables efficient exfoliation and surface modification of layered 2D materials, particularly those derived through top-down synthesis mechanisms and stabilized by interlayer cationic species. The proposed

methodology served to improve nanosheet dispersion which has generally been a limiting factor in prior studies due to agglomeration or layer restacking. This synthesis route produced well-exfoliated nanosheets, of which the nanostructural properties could be leveraged in the eventual ceramic composites.

- (2) Discovery of a novel interfacial phenomenon and phase evolution in ceramic 2D nanocomposite systems, characterized by the formation of quartz at the interface between nanosheet regimes and the ceramic matrix and retention of the nanosheet morphology up to 1200°C. Previously unreported, interfacial quartz formation was determined as key microstructural feature in the ceramic composite systems that bridged between crystalline nanosheets and the amorphous matrix. This work served as among the first to evaluate microstructural evolution in ceramic composites reinforced with 2D nanomaterials, and the results have pertinence in the design and application of engineering ceramic parts.
- (3) Evaluation of nanostructured MMT and $\text{Ti}_3\text{C}_2\text{T}_x$ as candidates in ceramic composites. The study demonstrated that MMT and $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet morphologies were retained up to 1200°C. MMT was shown to be a viable additive for porous ceramics and as a precursor to nanostructured SiC, while $\text{Ti}_3\text{C}_2\text{T}_x$ enhanced electrical conductivity. This work correlated microstructural features to material properties in both MMT and MXene composite systems, of which the main findings have pertinence for selecting 2D nanomaterials in ceramic systems for tailored or advanced properties.

7.3. *Future Perspectives*

The work presented in this dissertation may serve as inspiration for the study of a variety of MMT and $\text{Ti}_3\text{C}_2\text{T}_x$ nanocomposite systems beyond ceramic systems. Within the polymer-derived ceramic class, future work could focus on advanced nanostructural characterization techniques to further investigate the nature of the SiOC-nanoflake interface and other changes to amorphous ordering in SiOC ceramics, application of manufacturing processes to produce novel ceramic nanocomposite features, and further synthesis of novel SiOC hybrid materials.

- (1) Improve understanding of local nanostructural perturbations in amorphous ordering in interfacial regions in MMT-SiOC and $\text{Ti}_3\text{C}_2\text{T}_x$ -SiOC ceramics with advanced nanoscale characterization techniques. The interfacial region was uniquely critical in bridging the coherency mismatch between crystalline nanosheet domains and the amorphous SiOC

matrix. However, the TEM analysis methods used in this study were not able to elucidate changes to amorphous ordering due to the resolution limit of the TEM probe. Advanced characterization techniques such as 4D-STEM or neutron diffraction would have resolution needed to truly identify the bonding characteristics within the interface. Such techniques would reveal unique and important structural phenomenon that exist solely within this interfacial region.

- (2) Development of novel MMT-SiOC-metal hybrids that leverage the heavy metal ion absorption capability of functionalized MMT. It is predicted that during green body preparation, the addition of organometallic precursors will lead to clustering of metal cations to the MMT surface through electron-donating reactions between M^+ ions and amine groups of the grafted AEAPTMS functional group. This study would evaluate the effect of MMT nanoflakes in driving *in-situ* metallic nanoparticle formation for novel hybrid materials, which can be assessed for as candidate materials for porous ceramic, magnetic, or electronic applications. The methodology could also be applied to $Ti_3C_2T_x$ -SiOC ceramics, and would provide valuable insight into phase evolution mechanisms in PDC systems.
- (3) Implementation of polymer manufacturing processes for near-net-shaped ceramics. Polymer manufacturing processes (e.g., additive manufacturing, extrusion, electrospinning, etc.) are widely ubiquitous and would leverage preceramic polymer properties to produce near-net-shaped ceramics. This study would generally focus on the properties of MMT-PSO and $Ti_3C_2T_x$ -PSO preceramic resins such as rheology, UV-vis absorption, and reaction kinetics/mechanisms, among others. In particular, preceramic polymers are interesting materials for soft lithography additive techniques (e.g., SLA 3D printing) which would allow for production of a wide array of near-net-shaped green bodies and ceramics.
- (4) Evaluation of MMT and $Ti_3C_2T_x$ nanosheets as secondary phases in other polymer-derived ceramic systems (e.g., SiC, SiBC, Si_3N_4). The preceramic PSO polymer used in this study yields an SiOC residue that is C-rich but can be deemed slightly “oxidized” due to incorporation of O atoms into disordered Si tetrahedra. To further develop understanding in these nanocomposite systems, it would necessary to evaluate phase formation mechanisms in PDC systems that are not excessively C-rich but also in non-

oxidized systems such as SiC or Si₃N₄. In particular, the lack of O species may inhibit TiO_y formation observed in Ti₃C₂T_x-SiOC.

Scientific Communications

Publications

- (1) **Rau, A.V.**, Knott Jr, K., Lu, K. “Porous SiOC/SiC ceramics *via* an active-filler catalyzed polymer-derived method” ***Mater. Chem. Front.*** 2021, **5**, 6530-6545
- (2) Kong, L., **Rau, A.V.**, Yang, N., Lu, K. “Flexible ZnO Nanoparticle-Poly(methyl methacrylate) Hybrid Films and Their Ultraviolet Shielding Behaviors” ***JOM***, 2021, **73**, 432–440
- (3) Mondal, S., **Rau, A.V.**, Lu, K., Li, J., Viehland, D. “Multicomponent hexaborides with low work functions by ultra-fast high temperature sintering” ***Open Ceramics*** 2023, **16**, 100479.
- (4) **Rau, A.V.**, Lu, K. “Twice-Functionalized Montmorillonite Nanosheets for Polymer-Derived MMT-SiOC Nanocomposites: Phase Formation and Porosity” ***under review***
- (5) **Rau, A.V.**, Lu, K. “Self-Etching $\text{Ti}_3\text{C}_2\text{T}_x$ -SiOC Ceramics: Effects of MXene Surface Terminations on High-Temperature Ceramic Nanocomposites.” ***under review***
- (5) **Rau, A.V.**, Lu, K. “Nanoscale Phase Evolution in Montmorillonite-SiOC Ceramics with Water Vapor-Assisted Pyrolysis” ***under review***
- (5) **Rau, A.V.**, Lu, K. “Phase Evolution and High Temperature Electrical Conductivity in Novel Polymer-Derived $\text{Ti}_3\text{C}_2\text{T}_x$ (MXene)-SiOC Ceramic Nanocomposites” ***in preparation***

Conference Presentations

- (1) **Rau, A.V.** and Lu, K. “Porous SiOC/SiC ceramics *via* an active-filler catalyzed polymer-derived method”, MS&T 2021, Columbus, OH – Poster (Virtual)
- (2) **Rau, A.V.** and Lu, K. “Synthesis and Microstructural Evolution of Novel Polymer-Derived SiOC– Exfoliated Montmorillonite Ceramic Nanocomposites”, MS&T 2023, Columbus, OH – Presentation
- (3) **Rau, A.V.** and Lu, K. “Synthesis and Fabrication of Novel Polymer-Derived SiOC-Exfoliated $\text{Ti}_3\text{C}_2\text{T}_x$ ‘MXene’ Ceramic Nanocomposites”, MS&T 2023, Columbus, OH – Presentation
- (4) **Rau, A.V.** and Lu, K. “Polymer-Derived Silicon Oxycarbide – Exfoliated Montmorillonite Ceramic Nanocomposites for Porous Ceramics and SiC Formation”, MS&T 2024, Pittsburgh, PA, Presentation
- (5) **Rau, A.V.** and Lu, K. “Synthesis and Fabrication of Novel Polymer-Derived SiOC-Exfoliated $\text{Ti}_3\text{C}_2\text{T}_x$ ‘MXene’ Ceramic Nanocomposites”, MS&T 2024, Pittsburgh, PA, Presentation

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