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Computational materials chemistry:  
from polymer precursors to ceramics  
and high-pressure materials

by

Shariq Haseen

DISSERTATION

Submitted in partial fulfillment of the requirements

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Supervising Committee:

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## ABSTRACT

With advances in computing power, the field of computational chemistry has flourished. Using current computational resources, atomistic simulations of billion atoms and trillions of atoms have been performed. Computational techniques can be used to support experimental investigations into new materials as well as independently predict the existence of new materials. Furthermore, computational techniques are becoming instrumental in investigations.

This work is split into two parts. Part I focuses on high-pressure and materials chemistry. We investigate the cristobalite-rutile transformation for  $\text{SiO}_2$ ,  $\text{GeO}_2$ , and  $\text{TiO}_2$ , and predict conditions at which cristobalite- $\text{GeO}_2$  and cristobalite- $\text{TiO}_2$  may be synthesized (Chapter 1), we provide supporting calculations for the discovery of two ternary compounds,  $\text{Sn}_2\text{N}_2\text{O}$  (Chapter 2) and Si-Ti-N (Chapter 3), synthesized at high pressure, and we investigate the work of adhesion in compound graphene- $\text{SiO}_2/\text{Si}_2\text{CO}_2$  systems (Chapter 4). Part II is focused on studying amorphous ceramics, including polymer-derived ceramics with classical methods. We calculate elastic properties of SiCO ceramics and determine the impact of free carbon content, density, and free carbon morphology (Chapter 1), we develop a new method to quantify the extent of the free carbon morphology in large atomistic systems (Chapter 2), and we develop a new parametrization of the reactive force field ReaxFF for simulations of the polymer-to-ceramic conversion process used to synthesize silicon carbonitride from polysilazanes (Chapter 3).

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## LIST OF ABBREVIATIONS

DFT: Density functional theory  
MD: Molecular dynamics  
ReaxFF: Reactive force field  
ccp: Cubic-closest packing  
hcp: Hexagonal closest packing  
VASP: Vienna ab initio Simulation Package  
PBE: Perdew, Burke, Ernzerhof generalized gradient approximation functional  
SCAN: Strongly Constrained and Appropriately Normed  
PAW: Projector-augmented wave  
SpGr/S.G.: Space group  
HV-HT: High-pressure, high-temperature  
LVP: Large volume press  
SnNO: Sn<sub>2</sub>N<sub>2</sub>O  
XRD: X-ray diffraction  
ADT: Automated diffraction tomography  
EDX: Energy-dispersive X-ray spectroscopy  
2D: Two-dimensional  
3D: Three-dimensional  
FWHM: Full width half maximum  
CN: Coordination number  
HSE06/HSE: Heyd-Scuseria-Ernzerhof exchange correlation functional  
PBE0: Mixture of Perdew, Burke, Ernzerhof exchange and correlation energies and Hartree-Fock exchange energy  
DAC: Diamond anvil cell  
CuK<sub>α</sub>: Copper K- $\alpha$   
NED: Nanoelectron-diffraction  
SiTiN: Silicon titanium nitride  
SSP: Single-source precursor  
PHPS: Perhydropolysilazane  
TDMAT: Tetrakis(dimethylamido)titanium

PHTiPS5: Polytitanosilazane

SEM-EDS: Scanning electron microscopy and energy dispersive X-ray spectroscopy

ADF-STEM: Annular dark-field imaging in scanning transmission electron microscope

EELS: Electron energy loss spectroscopy

STEM: Scanning transmission electron microscopy

STEM-EDX: Energy dispersive X-ray tomography in scanning transmission electron microscope

TEM: Transmission electron microscopy

SEM: Scanning electron microscopy

DFT-ulg: Universal low gradient van der Waals correction method

DFT-TS: Tkatchenko-Scheffler van der Waals correction method

DFT-vdW-DF: Nonlocal van der Waals density functional of Dion et al.

DFT-vdW-DF2-B86R: Nonlocal van der Waals density functional of Hamada

DFT-D2: Grimme's D2 van der Waals correction method

SiCO: Silicon oxycarbide

PDC: Polymer-derived ceramic

CMC: Ceramic matrix composite

$T_{\max}$  : maximum temperature used during simulation

WWW: Wooten, Winer, and Waire algorithm

aiMD: ab initio molecular dynamics

LAMMPS: Large-scale Atomic/Molecular Massively Parallel Simulator

## INTRODUCTION

With advances in computing power, the field of computational chemistry has flourished. Using current computational resources, atomistic simulations of billion atoms[1] and trillions of atoms[2] have been performed. Computational techniques can be used to support experimental investigations into new materials as well as independently predict the existence of new materials. Investigations with computations have been used to study a variety of different phenomena from the band structure of the tetracyanoplatinate chain[3] to DNA-carbon nanotube hybrids[4] to the F<sub>1</sub>-ATPase mechanism[5].

Density functional theory (DFT) is one of the most popular methods used in computational chemical physics[6]. DFT is an electronic structure theory formulated on the principle that the ground-state properties of a system are a function of its total electron density sidestepping the many-electron wave function[7]. Work by Car and Parrinello[8] paved the way for the use of DFT in molecular dynamics simulations.

In spite of DFT general's accuracy and its general applicability, the computational expense of DFT is substantial and simulations exceeding thousands of atoms are not routinely feasible. For investigations where the quantum chemical accuracy of DFT can or must be spared, classical potentials have been developed that can study system sizes up to millions of times larger than DFT. The Tersoff potential is a classical potential where bond order is dependent on the local environment[9]. Although the applications of the Tersoff potential are limited, it can be used to study several properties including mechanical properties[10] and thermal conductivity[11].

In order to perform simulations with quantum chemical accuracy using system sizes approaching those used in empirical potential simulations, the reactive force field ReaxFF[12] was developed. ReaxFF can be trained to reproduce DFT accuracy[13] and perform simulations with system sizes surpassing the practical size limit of DFT. Compared to other classical potentials and force fields, ReaxFF is quite complex. The



system energy calculated by ReaxFF can depend on multiple terms including bond energy, over-coordination energy, under-coordination energy, valence angle energy, torsion angle energy, conjugation energy, and van der Waals energy[12]. However, the central principle of ReaxFF is that (nearly) every term depends smoothly on the bond order. Thus, ReaxFF features bond-breaking allowing for the investigation of chemical reactions.

The first part of this work focuses on DFT calculations of materials synthesized at high pressures and the work of adhesion in compound graphene-SiO<sub>2</sub>/Si<sub>2</sub>CO<sub>2</sub> systems.

Stishovite is an SiO<sub>2</sub> mineral with the rutile structure-type that is ultrahard[14] but can only be synthesized at high pressures[15, 16]. To predict alternative routes to synthesize stishovite, we investigate energetics of the well-known transformation between  $\alpha$ -cristobalite, another SiO<sub>2</sub> mineral, and stishovite. By studying the reverse rutile-cristobalite transformation as well we also examine the formation of cristobalite forms of GeO<sub>2</sub> and TiO<sub>2</sub>. From calculation of the activation barriers of the cristobalite-rutile transformation, we predict conditions for the synthesis of stishovite and cristobalite GeO<sub>2</sub> and TiO<sub>2</sub>.

We also contribute to collaborations focused on synthesizing ternary materials in high-pressure experiments and characterizing them. Following the synthesis of a new *Pbcn*-Sn<sub>2</sub>N<sub>2</sub>O, we perform supporting enthalpy-pressure calculations in order to determine pressures at which *Pbcn*-Sn<sub>2</sub>N<sub>2</sub>O become favorable. Additionally, we contribute bulk modulus and band structure calculations of *Pbcn*-Sn<sub>2</sub>N<sub>2</sub>O. In the discovery of spinel-type ternary silicon titanium nitride, we provide calculations for elastic properties and electronic properties. Since the exact position of Si and Ti in spinel-type silicon titanium nitride is unknown, and Ti could occupy any of the Si sites from spinel-Si<sub>3</sub>N<sub>4</sub>, we used combinatorial analysis through DFT calculations to predict favorable sites for Ti placement. Using Bader charge analysis, we calculate Ti to be in two distinct oxidation states, Ti<sup>3+</sup> and Ti<sup>4+</sup>.

Two-dimensional (2D) materials are being studied for further development of complementary metal-oxide-semiconductor (CMOS) technology[17]. Graphene is a 2D material with interesting properties including high carrier mobility[18] and high reversible capacity as lithium anodes[19]. We study the work of adhesion in potential anode systems in lithium-ion batteries consisting of graphene and a second component, either a bilayer-SiO<sub>2</sub> or a (001) SiC surface terminated with oxygen.

Part II is about investigations of amorphous ceramics, including polymer-derived ceramics, with classical methods. Polymer-derived ceramics are a class of advanced ceramics materials that have been under investigation for the last half century[20]. The composition of the ceramic depends on the composition of the starting polymer precursor. For pyrolysis temperatures between 1073 – 1573 K, ceramics (with excess free carbon) produced by the polymer-to-ceramic conversion process can be described as a mixture of an amorphous SiBCNO phase with an embedded “free carbon” phase. Although, there have been several experimental studies[21-23] investigating structural features of polymer-derived ceramics, the amorphous nature of PDCs preclude definitive structural characterization.

We study elastic properties of SiCO ceramics through classical molecular dynamics with the Tersoff potential. We examine how the elastic properties of SiCO ceramics depend on a variety of factors, including composition of the glass, free carbon content, density, and morphology of the free carbon phase. By independently varying parameters, we predict how free carbon content and density separately impact elastic properties. Additionally, we determine how the morphology of the free carbon phase can impact elastic properties.

In order to quantify free carbon morphology exhibited in atomistic models of amorphous ceramics, we develop a three-coordinated carbon topological shell counting method. We demonstrate how the topological shell counting method can be used to

determine the extent of the free carbon network and differentiate between amorphous ceramics with different free carbon morphologies.

Since the composition of PDCs depend on the starting polymer precursor and the method of processing during synthesis, we realize the need for investigation of the polymer-to-ceramic conversion process. We develop a new ReaxFF parameter set to study the polymer-to-ceramic conversion process of polysilazanes into amorphous SiCN ceramics. We start from parameters from Kulkarni et al.[24] and Ponomarev et al.[25] and train them on DFT calculations and ab initio molecular dynamics. The resulting parameter set is evaluated for good reproduction of the DFT potential energy surface for Si-C-N-H materials and we perform simulations of the polysilazane Ceraset.

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PART I: HIGH-PRESSURE AND MATERIALS CHEMISTRY

CHAPTER 1: PAVING THE WAY FOR CRISTOBALITE  $\text{TiO}_2$  AND  $\text{GeO}_2$   
ATTAINABLE UNDER MODERATE TENSILE STRESS: A DFT STUDY OF  
TRANSFORMATION PATHS AND ACTIVATION BARRIERS IN CRISTOBALITE-  
RUTILE TRANSFORMATIONS OF  $\text{MO}_2$  (M = SI, GE, TI)

### **Motivation and Scope**

There are several different polymorphs of  $\text{SiO}_2$  including  $\alpha$ -quartz,  $\beta$ -quartz, coesite,  $\alpha$ -cristobalite, stishovite, and seifertite. Of the  $\text{SiO}_2$  polymorphs, stishovite is a high-pressure polymorph noted for being ultrahard[1]. The synthesis of stishovite requires significantly high pressures[2, 3]. We investigate the transformation between  $\alpha$ -cristobalite- $\text{SiO}_2$  and stishovite- $\text{SiO}_2$ , which exhibits the rutile-structure type.

Additionally, we extend the investigation to  $\text{GeO}_2$  and  $\text{TiO}_2$ , which are found in the rutile-type at ambient pressures. Using two different concerted mechanisms to describe the cristobalite-rutile transformation we calculate activation barriers between the two structure types for  $\text{SiO}_2$ ,  $\text{GeO}_2$ , and  $\text{TiO}_2$ . We assess the impact of external pressure on the activation energies associated with the cristobalite-to-rutile transformation.

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**Paving the way for cristobalite TiO<sub>2</sub> and GeO<sub>2</sub> attainable under moderate tensile stress: a DFT study of transformation paths and activation barriers in cristobalite-rutile transformations of MO<sub>2</sub> (M = Si, Ge, Ti)**

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**Abstract**

We investigate energetics of interconversions between cristobalite-type and rutile-type structures of SiO<sub>2</sub>, GeO<sub>2</sub>, and TiO<sub>2</sub> at different pressures within Density Functional Theory. Cristobalite-SiO<sub>2</sub> is succeeded by the rutile-type, stishovite-SiO<sub>2</sub>, at high pressures. The rutile-types of GeO<sub>2</sub> and TiO<sub>2</sub> are favored at ambient pressure, but small tensile stresses are sufficient to yield cristobalite-GeO<sub>2</sub> and TiO<sub>2</sub>. The transition from one structure-type into the other is modeled using collective movements of cations or anions with different degrees of freedom for the remaining structure parameters. We find that increasing the external pressure decreases activation barriers of the cristobalite-rutile transformation. Activation barriers of the reverse transformation from rutile to cristobalite decrease with decreasing pressure. If only a fraction of cations follows the collective movement we find even lower activation barriers. The final states are still tetrahedrally or octahedrally coordinated structures, albeit not the high-symmetry variants of cristobalite or rutile, respectively. The small tensile stresses needed to favor cristobalite-GeO<sub>2</sub> and TiO<sub>2</sub> over their respective rutile counterparts, and the low



activation barriers involved in their interconversion let us propose a simple route to synthesize cristobalite-GeO<sub>2</sub> and a new cristobalite-TiO<sub>2</sub>.

## **Introduction**

Transformations between structures described using the concepts cubic-closest packing (ccp) and hexagonal closest packing (hcp) are standard topics in metallurgy and crystal chemistry.[1] Many of them proceed or are activated at high temperature and/or high pressure. A particular example is the transformation between cristobalite-type and rutile-type structures. Anions in cristobalite are approximately ccp with cations filling tetrahedral interstitials while those in rutile are approximately hcp with cations in octahedral interstitials. The binary oxides silica (SiO<sub>2</sub>) and germania (GeO<sub>2</sub>) both exhibit cristobalite-type and rutile-type polymorphs.[2-7] SiO<sub>2</sub> α-cristobalite has many industrial uses[8] and stishovite is one of the hardest known oxides.[9] A natural source for GeO<sub>2</sub> cristobalite has not been discovered so far, but synthesis of GeO<sub>2</sub> cristobalite has been reported.[5-7] However, extensive characterization of GeO<sub>2</sub> cristobalite has not been reported, and its existence as a pure phase has even been disputed.[10] Rutile GeO<sub>2</sub> is the most stable GeO<sub>2</sub> polymorph at ambient conditions and has potentially useful optical properties.[11]. The eponymous rutile is a polymorph of titania (TiO<sub>2</sub>)[12] and well-known for its use as white pigment[13, 14] Additional applications range from (photo)catalysis to energy storage.[15, 16] A cristobalite-TiO<sub>2</sub> has not yet been synthesized or found in nature.

Previous studies investigated the transformation between SiO<sub>2</sub> cristobalite and stishovite. O’Keefe and Hyde proposed a reaction mechanism by which α-cristobalite transforms to rutile-type via rotation of SiO<sub>4</sub> tetrahedra and simultaneous displacement of cations and anions.[17] This path was studied later by Silvi et al. using Hartree-Fock calculations.[18] Klug et al. were the first to simulate the pressure-induced transformation from cristobalite to stishovite using ab initio constant pressure molecular

dynamics (MD).[19] Analysis of atomic trajectories during the transformation revealed a smooth structural evolution from cristobalite to stishovite similar to the transition path proposed by O’Keefe and Hyde. No intermediate structure of lower symmetry was reported. Huang et al. used a very similar method to study the transition in dynamic simulations.[20] Their study corroborated the transition path of O’Keefe and Hyde but indicated unquenchable intermediate structures along the pathway. Salvadó et al. followed the cristobalite-rutile transformation for SiO<sub>2</sub> within Density Functional Theory (DFT) using a common sub-group and applied a concerted movement of cations along the proposed transition path.[21] Their study yielded a smooth energy profile without intermediate local minima. We had previously performed a similar study of the cristobalite-rutile transition in SiO<sub>2</sub>, TiO<sub>2</sub>, and Cu<sub>2</sub>O (the anti-form) but followed a concerted movement of anions along the proposed transition path instead.[22]

The goal of this paper is to provide a comparative study of the transformation from cristobalite to rutile for SiO<sub>2</sub>, GeO<sub>2</sub>, and TiO<sub>2</sub>. We provide transition pressures and compare enthalpy profiles and activation energies for the concerted movements by cations and by anions. We indicate that intermediate structures may occur if only a fraction of cations move in a concerted way. Anticipating our results, we will show for both GeO<sub>2</sub> and TiO<sub>2</sub> that transformation from a rutile structure to cristobalite requires only moderate tensile stresses, and experimental realization should be feasible.

## **Method**

All calculations are done within Density Functional Theory as implemented in the Vienna *ab initio* Simulation Package (VASP).[23-26] For electron exchange and correlation we use the Generalized Gradient Approximation as parametrized by Perdew, Burke, and Ernzerhof (PBE).[27, 28] For comparison, we apply the Strongly Constrained and Appropriately Normed (SCAN) functional.[29] Atom cores are described through the projector augmented wave (PAW) method.[30, 31] A 4×4×4 mesh is used for all

structures to sample the Brillouin zone.[32] Energies are converged to 0.01 meV/atom and forces to 5 meV/Å.

After optimization of structures we compute the energy of each model for a series of volumes around the minimum configuration. At each step the structure is optimized under the constraint of constant volume. The resulting energy-volume data for each structure is transformed into enthalpy-pressure data by numerically differentiating a spline fit to the data. Points of equal enthalpy then define the transition pressure  $p_t$  of the transition from the  $\alpha$ -cristobalite-type to the rutile-type. In the case of  $\text{SiO}_2$ ,  $p_t$  is positive, while for  $\text{GeO}_2$  and  $\text{TiO}_2$   $p_t$  is negative.

### **Structures and Transition paths**

The structure of  $\alpha$ -cristobalite  $\text{MO}_2$  ( $M=\text{Si, Ge, Ti}$ ) is built up by corner-connected  $\text{MO}_4$  tetrahedra. Its topology resembles that of the diamond network, with two-connected O atoms bridging between vertices of the diamond structure. The O atoms in  $\alpha$ -cristobalite fall, approximately, on sites of a cubic-closest-packed structure. For  $\text{SiO}_2$  and  $\text{GeO}_2$  the optimized  $\alpha$ -cristobalite structure exhibits bending of the angle at O, while for  $\text{TiO}_2$  the bond angle is almost  $180^\circ$ . Hence,  $\text{TiO}_2$  optimizes towards the (ideal)  $\alpha$ -cristobalite structure.[33] The rutile structure, as realized in stishovite- $\text{SiO}_2$  as well as rutile- $\text{GeO}_2$  and  $\text{TiO}_2$ , comprises  $\text{MO}_6$ -octahedra sharing edges. O atoms are three-fold coordinated and fall, approximately, on sites of a hexagonal-closest packed structure.

With their resemblance to ccp (cristobalite) and hcp (rutile), a simple transformation path between cristobalite and rutile can be constructed following standard concepts of metallurgy and crystal chemistry.[17] Using a common space group  $C222_1$  (20), the two structures can be described using the parameters shown in Table 1.

Using the common space group representation with correspondence between the structure parameters, lattice parameters and coordinates, a transformation between

cristobalite and rutile is facilitated by interpolating the structure parameters between the two structures.

Table 1: Generic description of lattice parameters and coordinates of cristobalite-type and rutile-type structures using the common space group  $C222_1$  (20). The choice of parameters (e.g. 1 rather than 0) allows to describe the transition between of cristobalite and rutile by interpolation between the respective parameters.

$a,b,c$	$a_c$	$a_c$	$c_c$	$a_s$	$a_s$	$c_s$
	x	y	z	x	y	z
<b>Si1</b>	0	$y_c\text{Si}$	1/4	0	1/2	1/4
<b>Si2</b>	$y_c\text{Si}+1/2$	0	0	1	0	0
<b>O1</b>	$x_c\text{O}$	$y_c\text{O}$	$z_c\text{O}$	0	$y_s\text{O}$	1/2
<b>O2</b>	$y_c\text{O}$	$1/2-x_c\text{O}$	$z_c\text{O}-1/4$	$y_s\text{O}$	1/2	1/4

The interpolation can happen in different ways, for example by linear interpolation of all parameters simultaneously.[17] Two other modes of concerted movement of all atoms are studied here. In the “anion method,” positions of the anions as well as cell parameters are linearly interpolated between cristobalite and rutile. The cations are allowed to optimize, conforming to each new configuration. Previously, we had investigated this path for the transformation in  $\text{SiO}_2$ . [22] In the “cation method”, positions of cations are linearly interpolated between initial and final configurations, while the anions are allowed to optimize, conforming to each new configuration. In addition, at each intermediate step the cell parameters are allowed to optimize according to the given constraints. This approach has recently been investigated for transitions in  $\text{SiO}_2$  by Salvadó et al.[21] Note that the paths described above retain space group  $C222_1$  during the transformation. “Cation method” and “anion method” are barely distinguishable by looking at intermediate structure. However, the computed energy profiles are noticeably different as we will discuss further below. For both approaches we use 19 intermediate configurations. The small step size between intermediates guarantees a smooth connection and no significant jumps of atoms from one optimized step to the next one.

The concerted movement of atoms as described above causes a rotation of  $\text{MO}_4$  tetrahedra in cristobalite. This goes along with their slight deformation and, due to the volume contraction and increasing density, with the approach of two additional anions towards the cation center, see Figure 1. This forms  $\text{MO}_6$  octahedra characteristic for the rutile structure. Note that on the path from cristobalite to rutile no bond is broken, but two additional bonds per cation are formed. Conversely, the reverse path from rutile to cristobalite breaks two Si-O bonds.

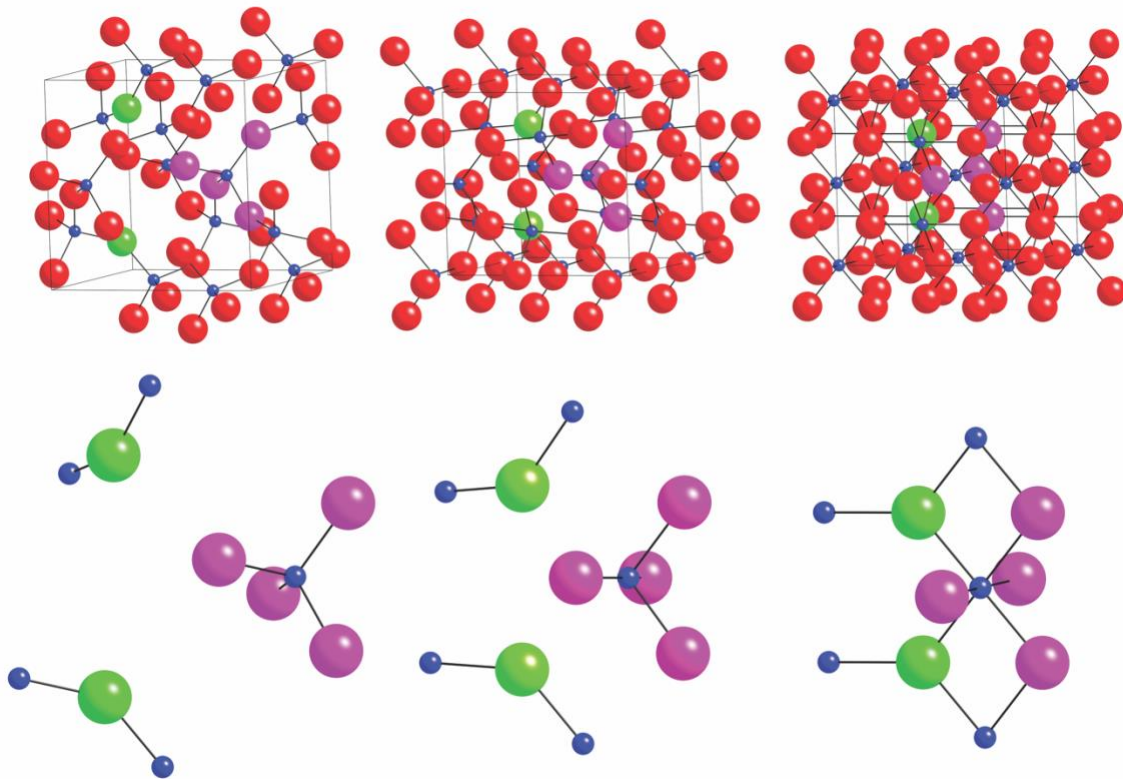


Figure 1: Initial (top left), intermediate (top middle) and final (top right) step of the transformation path from cristobalite to rutile. The orthorhombic common unit cell (SpGr.  $C222_1$ ) is outlined. Si atoms are blue and O atoms are red. For one Si we highlight its initially four (4) coordinating oxygen neighbors (purple) and the two additional oxygen (green) approaching it to form the final  $\text{SiO}_6$ -octahedron. Enlarged views of the forming octahedral  $\text{SiO}_6$  during the transformation are shown directly beneath the corresponding step in the transformation path.[34]

Table 2: Lattice parameters and internal parameters of  $C222_1$  cristobalite-type and rutile-type  $\text{SiO}_2$ ,  $\text{GeO}_2$ ,  $\text{TiO}_2$  from structures optimized with PBE and SCAN functionals.

<sup>a</sup>[35], <sup>b</sup>[36], <sup>c</sup>[37], <sup>d</sup>[38], <sup>e</sup>[39]

	<u>cristobalite-type</u>			<u>rutile-type</u>				
	Exp.	PBE	SCAN	Exp.	PBE	SCAN		
<u><math>\text{SiO}_2</math></u>	$a_c$ (Å)	7.0400 <sup>a</sup>	7.2270	7.0680	$a_s$ (Å)	5.9110 <sup>c</sup>	5.9900	5.9140
	$c_c$ (Å)	6.9321 <sup>a</sup>	7.1520	6.9580	$c_s$ (Å)	5.3338 <sup>c</sup>	5.3880	5.3400
	$y_{\text{cSi}}$	0.3008 <sup>a</sup>	0.2909	0.3000				
	$x_{\text{cO}}$	0.0680 <sup>a</sup>	0.0777	0.0679				
	$y_{\text{cO}}$	0.1719 <sup>a</sup>	0.1646	0.1714	$y_{\text{sO}}$	0.30613 <sup>c</sup>	0.3069	0.3064
	$z_{\text{cO}}$	0.4287 <sup>a</sup>	0.4207	0.4282				
<u><math>\text{GeO}_2</math></u>	$a_c$ (Å)	7.06 <sup>b</sup>	7.2240	7.0160	$a_s$ (Å)	6.2177 <sup>d</sup>	6.3690	6.2530
	$c_c$ (Å)	7.06 <sup>b</sup>	7.3870	7.1800	$c_s$ (Å)	5.7252 <sup>d</sup>	5.8580	5.7800
	$y_{\text{cGe}}$	0.328 <sup>b</sup>	0.3201	0.3291				
	$x_{\text{cO}}$	0.0445 <sup>b</sup>	0.0324	0.0244				
	$y_{\text{cO}}$	0.211 <sup>b</sup>	0.1945	0.2002	$y_{\text{sO}}$	0.3063 <sup>d</sup>	0.3067	0.3058
	$z_{\text{cO}}$	0.465 <sup>b</sup>	0.4562	0.4594				
<u><math>\text{TiO}_2</math></u>	$a_c$ (Å)		8.4740	8.4210	$a_s$ (Å)	6.49641 <sup>e</sup>	6.5980	6.5200
	$c_c$ (Å)		8.4680	8.4230	$c_s$ (Å)	5.91736 <sup>e</sup>	5.9390	5.9130
	$y_{\text{cTi}}$		1/2	1/2				
	$x_{\text{cO}}$		0.1203	0.1225				
	$y_{\text{cO}}$		0.1295	0.1274	$y_{\text{sO}}$	0.3048 <sup>e</sup>	0.3048	0.3042
	$z_{\text{cO}}$		0.3796	0.3775				

## Results and discussions

Optimizing the structures using PBE and SCAN functionals yields parameters listed in Table 2. Energy and energy differences between the optimized (local) ground state structures as well as computed transition pressures are given in Table 3.

Comparing results achieved with both functionals, we note that the SCAN functional appears to “favor” higher coordination of cations in the octahedrally coordinated structure. For instance,  $\alpha$ -cristobalite- $\text{SiO}_2$  is more favorable than stishovite (which is rutile- $\text{SiO}_2$ ). Within PBE the energy difference is 0.58 eV/ $\text{SiO}_2$ , while using SCAN this comes up to only 0.39 eV/ $\text{SiO}_2$ . For both  $\text{GeO}_2$  and  $\text{TiO}_2$  the rutile structure is more favorable than the cristobalite-type. Computed energy differences for  $\text{GeO}_2$  are

Table 3: Optimized energies of cristobalite-type and rutile-type SiO<sub>2</sub>, GeO<sub>2</sub>, and TiO<sub>2</sub> at ambient pressure, energy differences  $\Delta E$  from cristobalite-type to rutile-type, and computed transition pressures  $p_t$  found using PBE and SCAN functionals

	cristobalite-type (eV/f.u.)	rutile-type (eV/f.u.)	$\Delta E$ (eV/f.u.)	$p_t$ (GPa)
PBE				
SiO <sub>2</sub>	-23.74	-23.16	0.58	5.4
GeO <sub>2</sub>	-19.01	-19.17	-0.16	-1.4
TiO <sub>2</sub>	-26.32	-26.41	-0.09	-0.4
SCAN				
SiO <sub>2</sub>	-31.57	-31.21	0.36	3.2
GeO <sub>2</sub>	-36.52	-36.93	-0.41	-3.3
TiO <sub>2</sub>	-37.53	-38.05	-0.52	-1.9

-0.16 eV/GeO<sub>2</sub> (PBE) and -0.41 eV/GeO<sub>2</sub> (SCAN), and for TiO<sub>2</sub> they are -0.09 eV/TiO<sub>2</sub> (PBE) and -0.52 eV/TiO<sub>2</sub> (SCAN). Consequently, transition pressures  $p_t$  computed by computed using PBE are systematically 1.5 to 2 GPa higher than transition pressures SCAN (see Table 3).

The reason for reduced transition pressures is related to the (partial) inclusion of short range van-der-Waals interactions in SCAN.[40] This is corroborated by adding van-der-Waals interactions to the PBE functional. We choose the universal low gradient correction (ulg) together with the PBE functional, thus performing PBE+ulg calculations.[41] For the  $\alpha$ -cristobalite to stishovite of SiO<sub>2</sub> we then receive a transition pressure of 2.0 GPa, even lower than for SCAN (3.2 GPa) and significantly reduced in comparison to “standard” PBE calculations (5.4 GPa). Very similar trends are found for GeO<sub>2</sub> and TiO<sub>2</sub> as well.

We present the energy-volume graphs for SiO<sub>2</sub>, GeO<sub>2</sub>, and TiO<sub>2</sub> computed using PBE and SCAN in Fig. 2. It is apparent for each compound that the rutile-type structure has a higher curvature around the energy minimum than the cristobalite-type. Therefore, the rutile-type structure is less compressible. The very shallow E-V curve of the cristobalite-type is indicative of the shallow potential energy surface for bending the

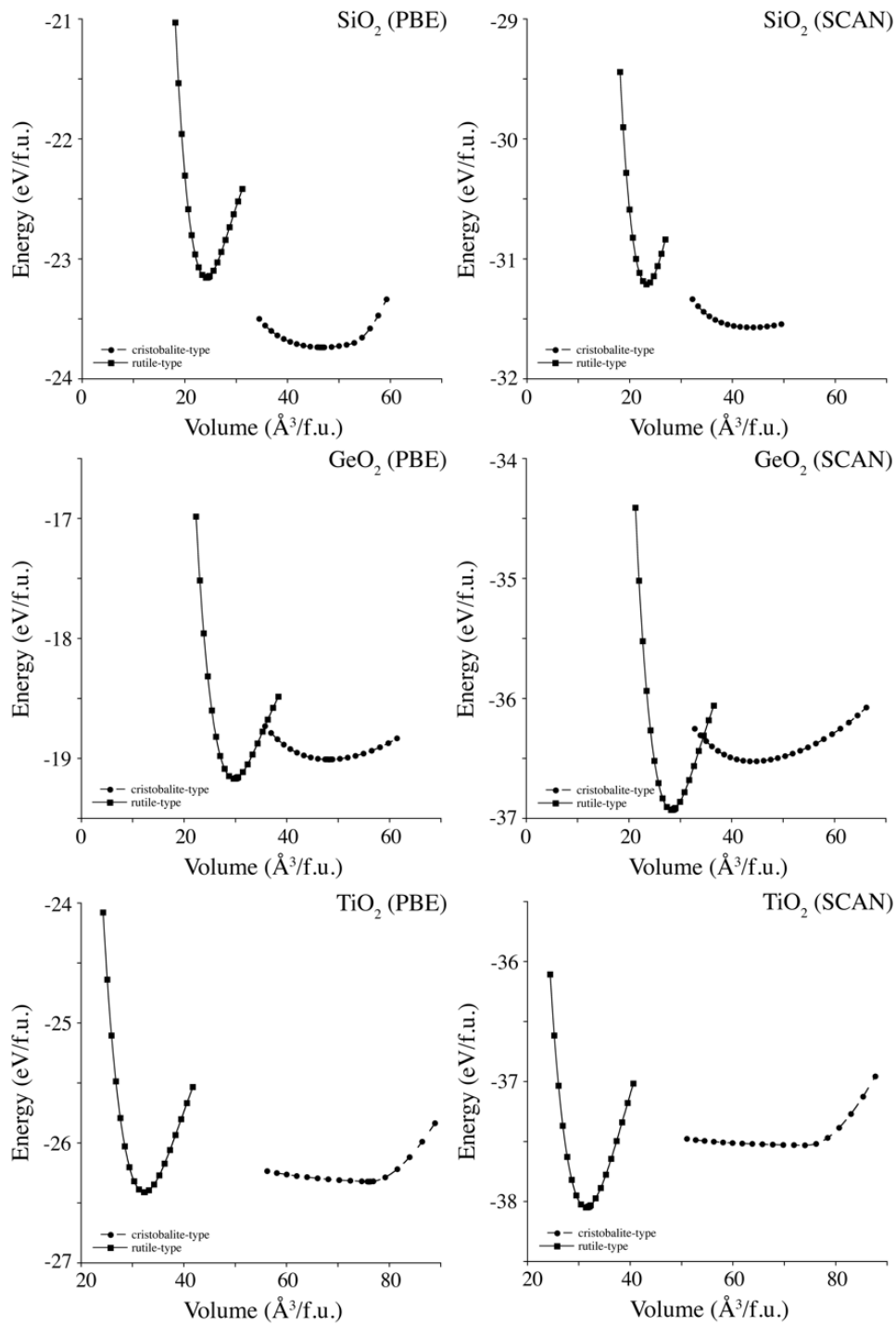


Figure 2: E-V diagrams with quantities given per formula unit (f.u.) for cristobalite-type and rutile-type SiO<sub>2</sub>, GeO<sub>2</sub>, and TiO<sub>2</sub> using PBE (left) and SCAN (right) functionals.



M-O-M bond angle at O.[42] Converting the energy-volume (E-V) data into relative enthalpy-pressure ( $\Delta H$ -p) diagrams computed yields the diagrams shown in Figure 3, from which we determine transition pressures as collected in Table 3.

Our results for the cristobalite-stishovite transition are aligned with previous studies, which found a transition pressure of 5–6 GPa.[18, 21, 22] Experimentally, a conversion from cristobalite to stishovite is feasible between 10 and 15 GPa, but intermediate phases may appear depending on exact temperature-pressure conditions.[43-45]

Since for both GeO<sub>2</sub> and TiO<sub>2</sub> the rutile structure is more favorable at ambient pressure, we compute negative pressures for a transition from rutile to cristobalite. In the case of GeO<sub>2</sub> values of  $p_t$  are -1.4 GPa (PBE) and -3.3 GPa (SCAN). Saito and Ono previously computed polymorphs of GeO<sub>2</sub> and their data yields  $p_t \approx -6$  GPa.[46] Yamaguchi et al. reported that cristobalite-GeO<sub>2</sub> transforms into rutile-GeO<sub>2</sub> through just grinding of the material.[7] On the other side, rutile-GeO<sub>2</sub> transforms into  $\alpha$ -quartz-GeO<sub>2</sub> at 1340 K at ambient pressure, supporting a small enthalpy difference between octahedral and tetrahedral polymorphs of GeO<sub>2</sub>. [47, 48] Given that for TiO<sub>2</sub> we compute even smaller transition pressures (PBE: -0.4 GPa; SCAN: -1.9 GPa) than for GeO<sub>2</sub>, a transition of rutile into a structure with tetrahedral TiO<sub>4</sub>-units should be feasible.

Negative pressures correspond to isotropic tensile stresses and have been realized by mixing materials with differing crystal structures.[49] Yet another approach is the synthesis of a material or composite under compressive stress and subsequent relaxation. This can be achieved, for instance, by thin film deposition on a bent substrate. Stress-relief of the substrate will in turn induce (negative) tensile stresses on the film. Stresses in the range of 5 GPa are quite commonly occurring in thin film depositions.[50, 51] The rate of a transition and, thus, whether the two polymorphs, cristobalite and rutile, can practically be converted into one another, depends on the activation energy required for

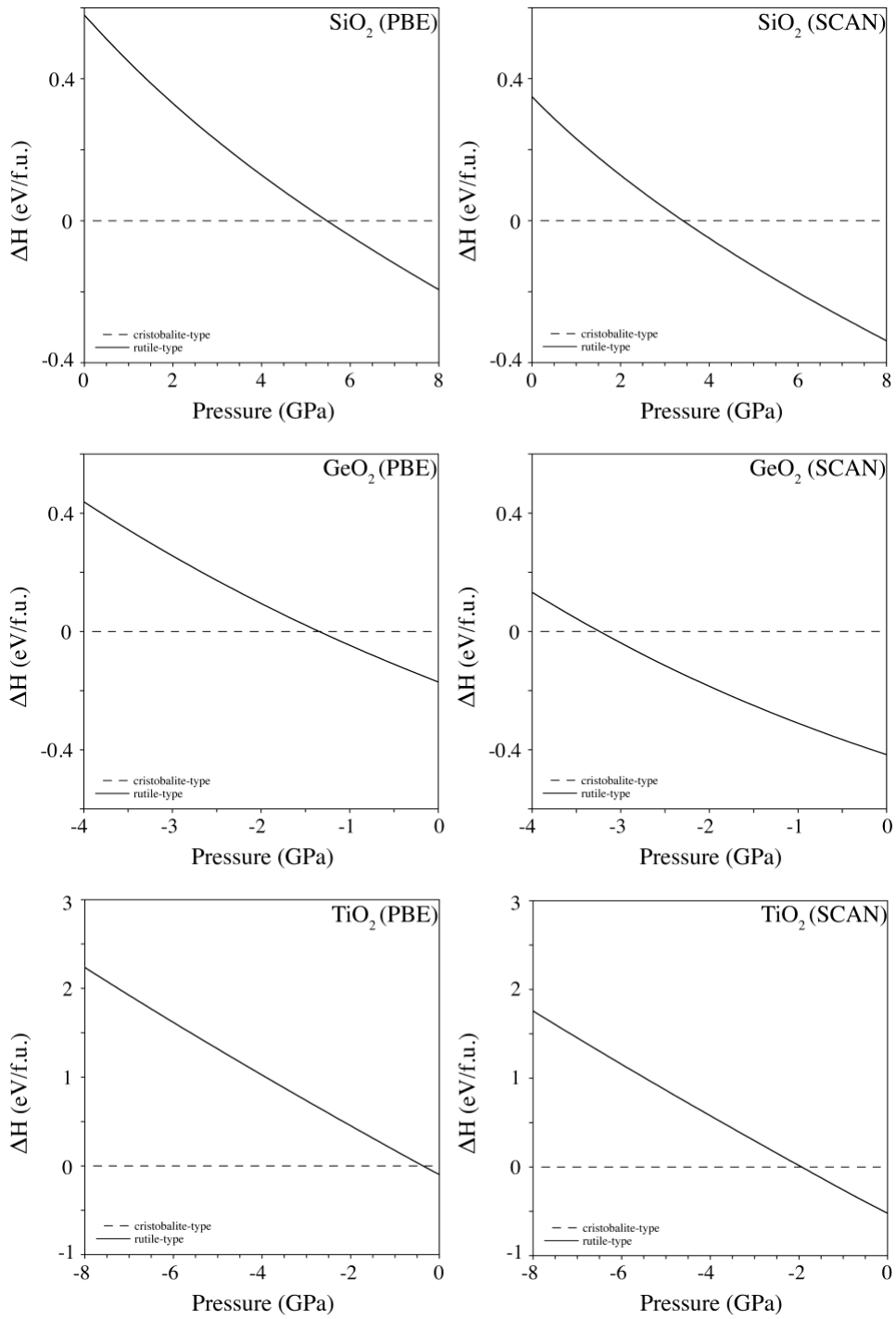


Figure 3: Enthalpy-pressure diagrams for  $MO_2$  ( $M=Si, Ge, Ti$ ) relative to enthalpy of corresponding cristobalite-type using PBE and SCAN functionals. Cristobalite-rutile transition pressures are found at intersections of enthalpy curves.

the process. Hence our further investigations address the energy profile of a transition between cristobalite- and rutile-type structures.

### **Transformation profiles between cristobalite and rutile at different pressures**

We then set out and computed the enthalpy profile for the transformation from cristobalite-type to rutile-types structure for each compound. The forward transition starts with the optimized structures of cristobalite-types of SiO<sub>2</sub>, GeO<sub>2</sub>, and TiO<sub>2</sub>, while the reverse transition starts with the rutile-type of each compound. We explicitly computed both directions of the transition path, forward and reverse, for each method and received matching energy profiles. We computed transition paths at ambient pressure (0 GPa), at the computed transition pressures (see Table 3), and at a few additional pressures to highlight trends. If a transition was performed at a given pressure, we selected optimized geometries of initial and final structures accordingly.

The enthalpy profile of a transition path reflects the enthalpy differences cristobalite- and rutile-type structures for a given MO<sub>2</sub> compound at a given pressure. Thus, at ambient pressure (0 GPa) initial and final state are energetically different according to the data of Table 3. At transition pressure  $p_t$ , however, cristobalite- and rutile-type have equal enthalpy and appear at level with each other. All transition paths provide a configuration with maximum enthalpy, the transition state. The activation barrier for the forward reaction,  $\Delta H_{a,fwd}$ , is defined as the enthalpy difference between cristobalite and the transition state. Conversely, the difference between rutile and the transition state constitutes the activation barrier for the reverse reaction,  $\Delta H_{a,rev}$ . We have chosen to plot the energy profiles relative to the structure with lowest energy at ambient pressure. Thus, for SiO<sub>2</sub> we plot the profile relative to cristobalite-type, while for GeO<sub>2</sub> and TiO<sub>2</sub> we plot all profiles relative to the rutile type.

## SiO<sub>2</sub>

The energy profiles for the two different paths to convert  $\alpha$ -cristobalite to stishovite are shown in Figure 4. Enthalpy barriers for the forward path,  $\Delta H_{a,fwd}$ , at different pressures are listed in Table 4. For paths computed at 0 GPa in both anion and cation method, we investigated the transition state in more detail and computed the Hessian matrix. It exhibits only a single imaginary eigenvalue, and the corresponding eigenvector aligns with conservation of space group symmetry  $C222_1$ . Overall we find that the cation

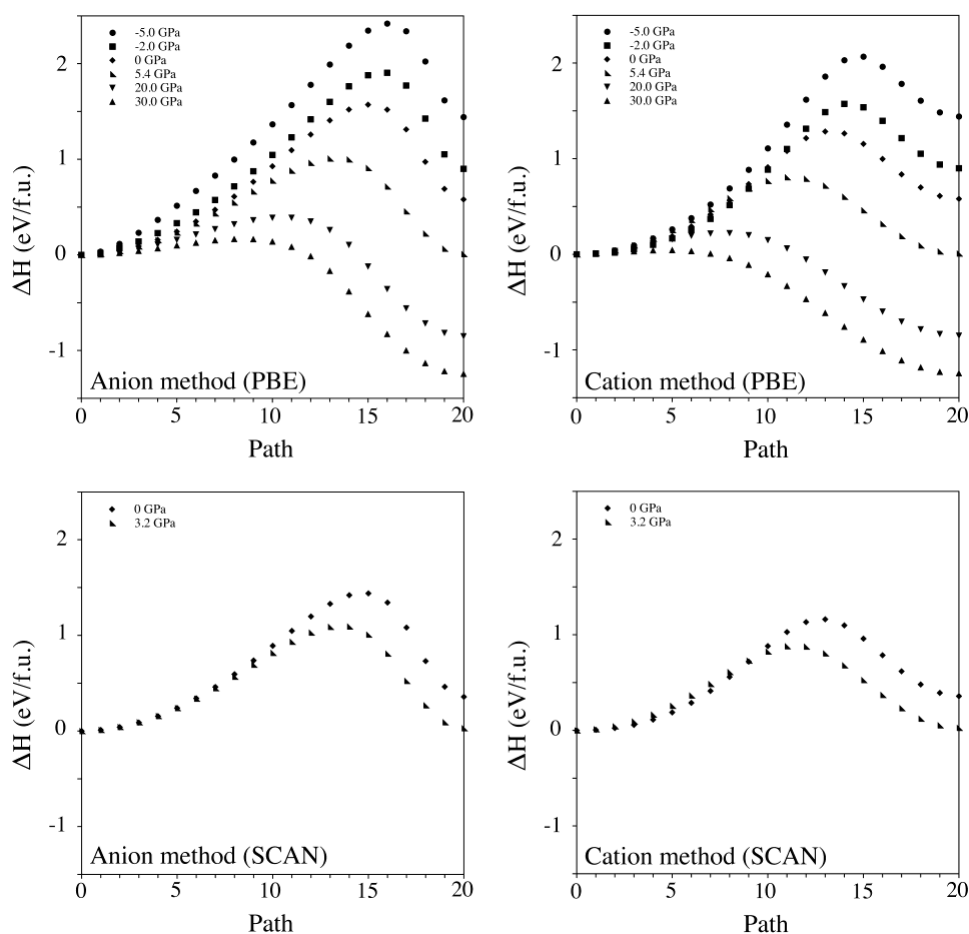


Figure 4: Enthalpy profiles of SiO<sub>2</sub>  $\alpha$ -cristobalite (step=0) to stishovite (step=20) transition at various pressures. PBE calculations for (top left) anion and (top right) cation method; SCAN calculations for (bottom left) anion and (bottom right) cation method. All enthalpies are given relative to  $\alpha$ -cristobalite SiO<sub>2</sub> at the corresponding pressure.

Table 4: Forward activation enthalpies  $\Delta H_{a,fwd}$  for SiO<sub>2</sub> cristobalite-rutile transformations. The asterisk (\*) indicates the transition pressure computed in the respective method.

Pressure (GPa)	Anion method $\Delta H_{a,fwd}$ (eV/f.u.)	Cation method $\Delta H_{a,fwd}$ (eV/f.u.)
PBE		
-5.0	2.42	2.07
-2.0	1.90	1.57
0	1.57	1.28
5.4*	1.01	0.81
20.	0.39	0.22
30.	0.17	0.04
SCAN		
0	1.44	1.16
3.2*	1.09	0.88

method produces slightly lower enthalpies, and consequently lower  $\Delta H_{a,fwd}$ , in comparison to the anion method. This occurs because more degrees of freedom, three position parameters and two cell parameters, are allowed to relax in this approach. In the anion method, we allow only one position parameter to optimize, while all other parameters are interpolated. We also observe that increasing pressure reduces the enthalpy barrier of the forward path,  $\Delta H_{a,fwd}$ , in either method and in both PBE and SCAN calculations.

Eventually the activation energy  $\Delta H_{a,fwd}$  approaches zero (0) at 30 GPa. In experiments,  $\alpha$ -cristobalite-SiO<sub>2</sub> completely amorphizes at about 28 GPa.[52] Comparing the two functionals we find that SCAN calculations yield slightly lower activation energies than their PBE counterparts; at ambient pressure  $\Delta H_{a,fwd}$  is about 10% lower. For the transition pressure  $p_t$  itself, however,  $\Delta H_{a,fwd}$  computed in SCAN is slightly higher,

because SCAN computes lower transition pressures in general. Conversely, the higher transition pressure  $p_t$  obtained with the PBE functional impacts the energy profile and yields a lower  $\Delta H_{a, fwd}$  at  $p_t$ .

## GeO<sub>2</sub>

The energy profiles for the transition paths from an  $\alpha$ -cristobalite-type to rutile-type GeO<sub>2</sub> are shown in Figure 5. Note that we depict enthalpy relative to rutile GeO<sub>2</sub> (see Table 5), since this is lower in energy at ambient pressure than cristobalite GeO<sub>2</sub>.

Consequently, we address  $\Delta H_{a, rev}$ , the enthalpy barrier for the reverse path. Again, the cation method yields

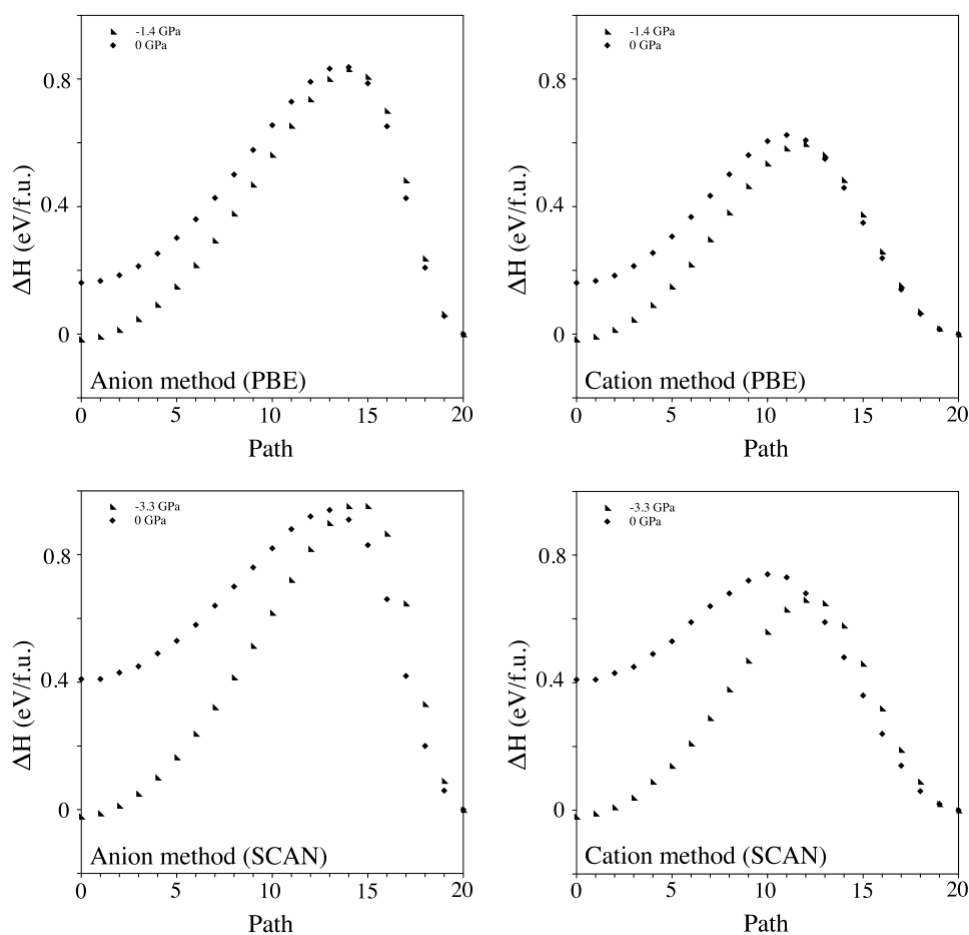


Figure 5: Enthalpy profiles of GeO<sub>2</sub> α-cristobalite (step=0) to rutile (step=20) transition at ambient and transition pressure p<sub>t</sub>. PBE calculations for (top left) anion and (top right) cation method; SCAN calculations for (bottom left) anion and (bottom right) cation method. All enthalpies are given relative to rutile GeO<sub>2</sub> at corresponding pressure.

Table 5: Reverse activation enthalpies  $\Delta H_{a,rev}$  for GeO<sub>2</sub> cristobalite-rutile transformations. The asterisk (\*) indicates the transition pressure computed in the respective method.

Pressure (GPa)	Anion method $\Delta H_{a,rev}$ (eV/f.u.)	Cation method $\Delta H_{a,rev}$ (eV/f.u.)
PBE		
0	0.84	0.62
-1.4*	0.83	0.60
SCAN		
0	0.94	0.74
-3.3*	0.95	0.66

lower enthalpy profiles and lower  $\Delta H_{a,rev}$  in comparison to the anion method. An impact of pressure on the energy profile is best seen within the cation method. Decreasing the pressure lowers the energy profile and, as a consequence, yields a lower  $\Delta H_{a,rev}$  at negative pressure. Comparing PBE and SCAN calculations we find that SCAN calculations in case of GeO<sub>2</sub> yield higher activation energies than their PBE counterparts, about 20% at ambient pressure. Even at the transition pressure, which SCAN locates at larger negative pressure than PBE, there is still a 10% difference.

## TiO<sub>2</sub>

The energy profiles for the transition paths from an α-cristobalite-type to rutile-type TiO<sub>2</sub> are shown in Figure 6. We depict enthalpy relative to rutile TiO<sub>2</sub> and address the enthalpy barrier  $\Delta H_{a,rev}$  of the reverse path (see Table 6). Once more, the cation

method yields lower enthalpy profiles and lower  $\Delta H_{a,rev}$  in comparison to the anion method. Reducing pressure significantly lowers the energy profile and, as a consequence, yields a lower  $\Delta H_{a,rev}$ .

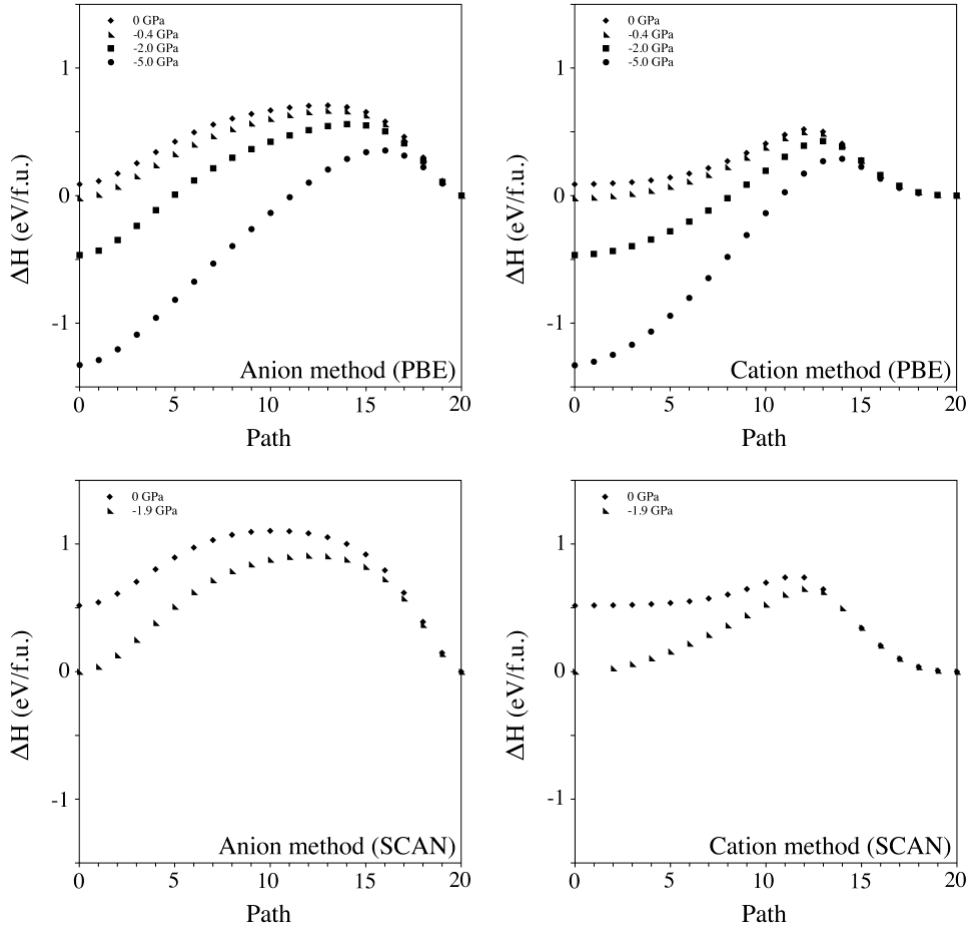


Figure 6: Enthalpy profiles of  $\text{TiO}_2$   $\alpha$ -cristobalite (step=0) to rutile (step=20) transition at ambient and transition pressure  $p_t$ . PBE calculations for (top left) anion and (top right) cation method; SCAN calculations for (bottom left) anion and (bottom right) cation method. All enthalpies are given relative to rutile  $\text{TiO}_2$  at corresponding pressure. Two points in the diagram for cation method with SCAN (step 1 at -1.9GPa and step 14 at 0 GPa) could not be optimized.

Like with  $\text{GeO}_2$ , SCAN calculations yield higher activation energies (about 40%) than their PBE counterparts. Independent of the path selected, however, going from ambient (0 GPa) to -5GPa essentially cuts the activation barrier in half. Thus, negative pressure



not only favors the cristobalite-type of  $\text{TiO}_2$ , but also makes it more easily accessible within this transformation.

Table 6: Reverse activation enthalpies  $\Delta H_{a,\text{rev}}$  for  $\text{TiO}_2$  cristobalite-rutile transformations. The asterisk (\*) indicates the transition pressure computed in the respective method.

Pressure (GPa)	Anion method $\Delta H_{a,\text{rev}}$ (eV/f.u.)	Cation method $\Delta H_{a,\text{rev}}$ (eV/f.u.)
PBE		
-5.0	0.35	0.29
-2.0	0.56	0.43
-0.4*	0.69	0.50
0	0.71	0.52
SCAN		
-1.9*	0.91	0.65
0	1.10	0.74

### Further reducing Degrees of Freedom during Transformations

The cation method and anion method are distinguished by the number of constraints implied and by the degrees of freedoms optimized at every step. Overall, the cation method yields lower activation barriers, because at every step more atom coordinates as well as the lattice parameters can relax. It is, therefore, of interest to see, if we can put even less constraints onto the transition and what enthalpy profile this would yield.

Starting with the same size of the simulation cell, 8 cations and 16 anions in space group  $C222_1$ , we extended the cation method in such a way as we did not impose any symmetry constraint ( $P1$ ) and, furthermore, allowed half of the cations to optimize during the transformation as well. Thus, a concerted motion is only provided by 4 cations, while all other atoms and cell parameters optimize in each intermediate step. We investigated the

path for SiO<sub>2</sub> at ambient pressure (0 GPa) with two different selections of a group of 4 cations, of which we will display the results of one only. The second choice had, essentially, very similar consequences.

Two energy profiles of this “half-cation method” are shown in Figure 7. One corresponds to a forward transition starting with  $\alpha$ -cristobalite SiO<sub>2</sub>. The value of the activation barrier,  $\Delta H_{a, fwd} = 1.17$  eV/f.u., is slightly lower than the 1.28 eV/f.u. we computed for the (regular) cation method. However, the forward transformation did not yield the expected stishovite SiO<sub>2</sub> structure. Instead, it left the C222<sub>1</sub> path early on, coinciding with a non-orthogonal cell at the transition point. Each Si atom still gained two additional bonds but from different O in comparison to the cation method. The final structure adopts monoclinic symmetry (SpGr. P2<sub>1</sub> (4))[53] with yet another ordered arrangement of SiO<sub>6</sub> octahedra. It bears resemblance to seifertite-SiO<sub>2</sub>,[44] although the agreement is not perfect. Its energy comes out as 0.1 eV/SiO<sub>2</sub> higher than that of seifertite-SiO<sub>2</sub>.

The second profile in Figure 7 corresponds to the reverse transition, starting with stishovite SiO<sub>2</sub>. The profile is noticeably different from the graph shown in Figure 6.

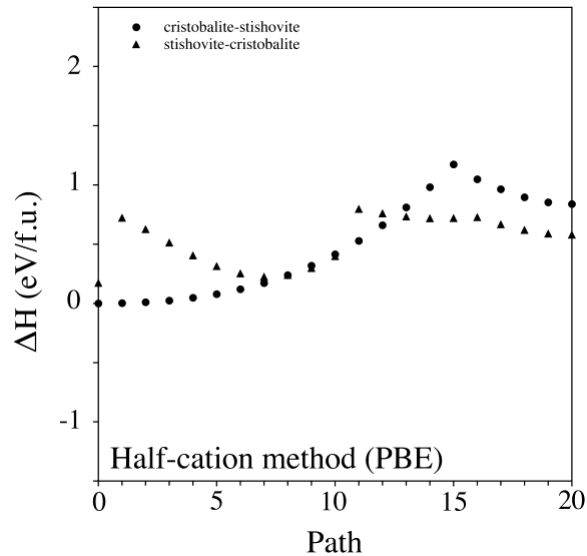


Figure 7: Enthalpy profiles of transformations from cristobalite-SiO<sub>2</sub> to stishovite-SiO<sub>2</sub> and stishovite-SiO<sub>2</sub> to cristobalite-SiO<sub>2</sub>; transformations were done at zero pressure with PBE using the half-cation method. Enthalpies are relative to the enthalpy of  $\alpha$ -cristobalite-SiO<sub>2</sub>.

Moreover, rather than an activation barrier of 0.71 eV/f.u.—the value of the reverse transformation from stishovite to cristobalite following the  $C222_1$  path in the cation method—we find that the stishovite structure ruptures with an activation of barely 0.22 eV/f.u. The outcome is not the cristobalite structure either but a disordered arrangement of four- and eight membered rings of corner-sharing SiO<sub>4</sub> tetrahedra in a non-rectangular cell. Its relation to the cristobalite structure is unclear to us. However, it may only take a relatively small amount of bond rearrangements to relate both structures. Such mechanisms are known among polymorphs of SiO<sub>2</sub>, for example, for the tridymite to keatite transition.[54]

The results above show, although the idealized structures were not reached, that cristobalite naturally transforms into a structure with SiO<sub>6</sub> octahedra upon compression. Indeed, ab-initio molecular dynamics simulation show that  $\alpha$ -cristobalite-SiO<sub>2</sub> transforms into stishovite-SiO<sub>2</sub> at high pressure, with intermediates described within  $C222_1$  symmetry.[19] We reproduced the results using the same small simulation cell as in the original study. However, extending the simulation cell to twice its size produced disordered models comprising SiO<sub>6</sub> octahedra rather than stishovite. Conversely, the transition paths show that upon expansion stishovite transforms into a structure with SiO<sub>4</sub> tetrahedra. Adding more degrees of freedom produced slightly lower activation barriers, indicating that our values we present in Tables 4, 5, and 6 can be considered as upper boundaries. Even though the idealized structures were not reached, it is conceivable that in an experiment further annealing of a disordered compound under compressive or tensile stress yields crystalline samples.

## Conclusions

Increasing pressure increases the relative stability of the rutile-type over the cristobalite-type for  $\text{SiO}_2$ ,  $\text{GeO}_2$ , and  $\text{TiO}_2$ . While for  $\text{SiO}_2$  the rutile-type succeeds the cristobalite-type at high pressures, we show that for  $\text{GeO}_2$  and  $\text{TiO}_2$ , where the rutile-type is an ambient pressure modification, the cristobalite-type is attainable at small negative pressures. Our investigation of transition paths show that increasing pressure yields lower activation barriers for a transformation from cristobalite-type to rutile-type. The activation barrier of the reverse transformation, from rutile-type into cristobalite-type, decreases with decreasing pressure. Following concerted movements of atoms, we show that the cation method of Salvadó et al.[21] yields lower activation barriers than a concerted movement of anions. Even smaller barriers are encountered if only a subset of cations is moved. The resulting structures in these “half cation methods” for both forward and reverse paths still display octahedral or tetrahedral coordination of all cations but may not match rutile or cristobalite structures.

Given that the magnitude of negative pressure at which cristobalite- $\text{GeO}_2$  and cristobalite- $\text{TiO}_2$  become thermodynamically stable is only 1 to 3 GPa, we propose to prepare experiments that utilize tensile stresses of this magnitude. For example, rutile-type  $\text{GeO}_2$  or  $\text{TiO}_2$  may be deposited as thin film on a curved substrate, which is then relaxed. Subsequent annealing at moderate temperatures may yield a crystalline tetrahedrally coordinated structure. Two new compounds with potentially interesting properties are in reach through relatively simple synthetic pathways.

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## Conflicts of interest

There are no conflicts to declare.

## Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

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## Summary

We investigated the cristobalite-rutile transformation in the forward and reverse directions for  $\text{SiO}_2$ ,  $\text{GeO}_2$  and  $\text{TiO}_2$ . Transformations between cristobalite-type and rutile-type structures were described using two different concerted mechanisms, an anion method and a cation method, which were named depending on which set of ions were moved in a concerted fashion during the transformation. We investigated the activation barriers of the forward and reverse transformations for a range of different external pressures, including negative pressures. Increasing pressure favored the rutile structure-type and resulted in a lowered activation barrier for the forward cristobalite-rutile transformation. Decreasing pressure favored the cristobalite structure-type and lowered the activation barrier of the reverse transformation, or the rutile-cristobalite transformation. At negative pressures, cristobalite-type  $\text{GeO}_2$  and  $\text{TiO}_2$  became thermodynamically stable and we predicted that the synthesis of cristobalite-type  $\text{GeO}_2$  and  $\text{TiO}_2$  may be possible with moderate tensile stresses.



## CHAPTER 2: A NOVEL HIGH-PRESSURE TIN OXYNITRIDE $\text{Sn}_2\text{N}_2\text{O}$

### Motivation and Scope

A new *Pbcn*  $\text{Sn}_2\text{N}_2\text{O}$  with all Sn six-fold coordinated is synthesized through high-pressure experiments. Ammonolysis is performed on  $\text{Sn}[\text{NMe}_2]_4$  mixed with tetrahydrofuran[1] and the resulting Sn-N-O precursors are then subjected to 20 GPa and 1200-1500°C. Characterization is done on the synthesized samples with powdered X-ray diffraction and automated diffraction tomography. Additionally, bulk modulus is experimentally determined. We contribute supporting DFT[2] calculations for elastic properties, including bulk modulus and shear modulus, and band gaps. We seek to rationalize the formation of *Pbcn*  $\text{Sn}_2\text{N}_2\text{O}$  by calculating the enthalpy of formation of *Pbcn*  $\text{Sn}_2\text{N}_2\text{O}$  from binary compounds at different pressures.

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## A Novel High-Pressure Tin Oxynitride $\text{Sn}_2\text{N}_2\text{O}$

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### Abstract

We report the first oxynitride of tin,  $\text{Sn}_2\text{N}_2\text{O}$  (SNO), exhibiting a  $\text{Rh}_2\text{S}_3$ -type crystal structure with space group  $Pbcn$ . All Sn atoms are in six-fold coordination, in contrast to Si in silicon oxynitride ( $\text{Si}_2\text{N}_2\text{O}$ ) and Ge in the isostructural germanium oxynitride

( $\text{Ge}_2\text{N}_2\text{O}$ ), which appear in four-fold coordination. SNO was synthesized at 20 GPa and 1200 – 1500°C in a large volume press. The recovered samples were characterized by synchrotron powder X-ray diffraction.

## Introduction

The Group 14 elements Si, Ge, and Sn form well-known nitrides[1] with exceptional thermomechanical and optoelectronic properties. Low compressibility and high hardness[1a,2] have been reported for spinel-type Si and Ge nitrides, and their solid solutions are predicted to form a new family of wide direct band gap semiconductors.[3] Hitherto, oxynitrides are known for Si and Ge, but not for Sn. Silicon oxynitride ( $\text{Si}_2\text{N}_2\text{O}$ ), named “Sinoite”, was discovered in a meteorite by Andersen et al.[1e] in 1962. At the same time, a synthetic  $\text{Si}_2\text{N}_2\text{O}$  was prepared by nitriding a mixture of silicon and quartz powder at 1450°C.[1f] It shows orthorhombic symmetry with space group  $Cmc2_1$ . [1f] Sinoite proved to be one of the most stable, oxidation resistant refractory oxynitrides.[4] Its formation and thermodynamic stability at ambient and high pressure have been investigated computationally previously.[1c] An isostructural germanium oxynitride  $\text{Ge}_2\text{N}_2\text{O}$  has been synthesized by ammonolysis of germanium oxides at temperatures above 850°C as well.[1d,5]

An oxynitride of tin is still unknown and has to the best of our knowledge not been reported as bulk material. There are a few reports on thin films of  $\text{SnO}_x\text{N}$ , [6] described as nitrogen-doped tin oxide with undetermined chemical composition and with a crystal structure related to  $\text{SnO}_2$ , either as rutile-type (mineral name cassiterite), or as pyrite-type high-pressure form.[6a,7] We did not find any computational studies related to tin oxynitrides.

Herein, we report the first tin oxynitride, exhibiting a  $\text{Rh}_2\text{S}_3$ -type crystal structure, which is known as a high-pressure modification of several oxides including  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ . All Sn atoms are in six-fold coordination, in contrast to the sinoite-type with only

four-fold metal coordination. We employed a high-pressure high-temperature (HP-HT) method, using a large volume press (LVP) for the synthesis of a novel  $\text{Sn}_2\text{N}_2\text{O}$  compound (SNO). Materials are characterized by elemental analysis, angle-dispersive XRD, TEM in combination with automated diffraction tomography (ADT), and energy-dispersive X-ray spectroscopy (EDX). We also determined the bulk modulus of SNO and used DFT calculations for structure modelling.

## **Results and Discussion**

### **Precursor and HP-HT synthesis**

The XRD pattern of the Sn-N-O precursor, prepared by low temperature ammonolysis, shows spinel-type  $\text{Sn}_3\text{N}_4$  (as the only crystalline phase) and an amorphous background (Figure S1, Supporting Information). Elemental analysis by the combustion method confirmed a content of 5.3(3) wt.% oxygen and 11.2(2) wt.% nitrogen in the synthesized compound. From these values, elemental contents of 18 (1) at.% O, 43.6 (8) at.% N, and 38(1) at.% Sn in the as-received compound can be calculated, which may be described as a mixture of tin nitride and tin oxide with a molar ratio of 1:1. This formally corresponds to a  $\text{Sn}_2\text{N}_2\text{O}$  stoichiometry. This precursor was subjected to HP-HT conditions (20 GPa and 1200–1500°C) in a Hall-type six-ram LVP (mavo press LPQ6 1500-100; Max Voggenreiter GmbH, Germany) installed at the P61B beamline at DESY, Hamburg. After HP-HT treatment, each recovered sample was dense and fine-grained in appearance (Figure S3, Supporting Information). EDX spectroscopy on the recovered samples confirms the presence of oxygen in addition to nitrogen and tin (Figure S4, Supporting Information) without other contamination. Quantification of O and N was not possible as EDX is not reliable for low Z elements.[8]

### **X-ray diffraction**

The XRD pattern of the HP-HT product measured with synchrotron radiation (Figure 1) shows a manifold of well resolved reflections—apart from a small fraction of spinel  $\text{Sn}_3\text{N}_4$ —which do not match to any known phase in the powder diffraction database (ICDD). They represent a novel phase, which (in the first approach) could be indexed by a primitive cubic lattice with  $a=7.831(2)$  Å.

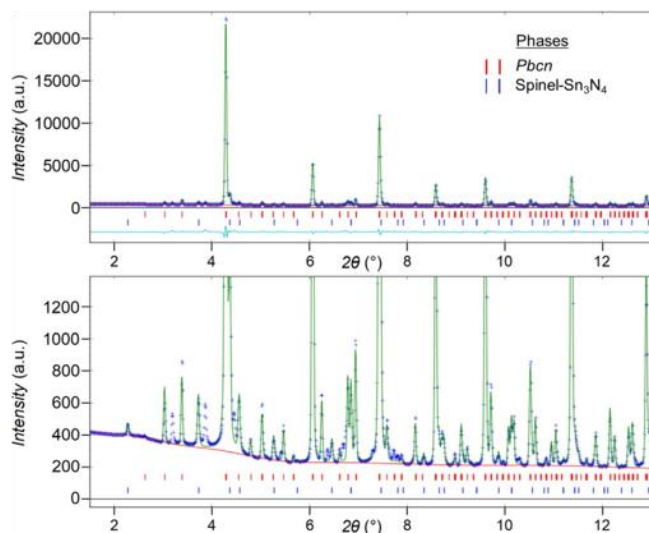


Figure 1. XRD pattern of SNO, in full (top) and magnified by a factor of  $\approx 20$  (bottom), with Rietveld refinement (green line) in space group  $Pbcn$  ( $\lambda=0.20736$  Å). The reflection markers show the calculated reflection positions of the SNO phase (upper row, in red online) and the spinel  $\text{Sn}_3\text{N}_4$  (lower row, in blue online).

A preliminary structure model of SNO could be deduced from the integrated intensities of the powder reflections, using direct methods (shelxs2013[9]). This model in space group  $Pa-3$  represents a double perovskite with two inequivalent Sn sites. One Sn shows a distorted octahedral coordination as usual in low-symmetry double perovskites. The other Sn resides in the centre of eight corner-linked octahedra, a position which in perovskites usually is occupied by atoms larger than those in the octahedral position. The cation to anion ratio of 2:3, implied by the structure model, is in accordance with the measured chemical composition  $\text{Sn}_2\text{N}_2\text{O}$  (for  $\text{Sn}^{4+}$ ,  $\text{N}^{3-}$ ,  $\text{O}^{2-}$ ). However, the model appears to represent only an averaged structure. No satisfying Rietveld refinement could be

achieved within the framework of the cubic unit cell. On the other hand, a possible splitting of X-ray reflections indicating a distortion of the cubic unit cell to lower symmetry seems to be too small to be detected in the XRD pattern.

### **Electron diffraction tomography (ADT)**

To elucidate the correct crystal symmetry of SNO, electron diffraction covering the 3D space was performed, namely automated diffraction tomography (ADT)[10] on a synthesized sample (run# HH148 at 20 GPa, 1500°C, Ta capsule). This sample contained only a very low fraction of spinel  $\text{Sn}_3\text{N}_4$  and no third phase, as confirmed by XRD ( $\text{CuK}\alpha$ ). ADT allows for collecting electron-diffraction intensities from single crystals as small as some tens of nm, and thus enables single-crystal structure determination from such small crystals. Crystals were used without any special orientation to the electron beam. The acquired off-zone diffraction patterns show reduced dynamical scattering effects and provide intensity data suitable for kinematical structure determination approaches like direct methods. For data acquisition a series of electron diffraction images (2D detector) are collected while tilting the crystal by  $1^\circ$  after every image. The wedges between the zones are integrated using electron beam precession. By processing these images afterwards, all patterns are reconstructed into a 3D diffraction space allowing visualization of the full diffraction information. More details are shown in the Supporting Information.

The unit-cell was derived from ADT data with lattice parameters  $a=7.80$ ,  $b=5.42$ ,  $c=5.52$  Å, which corresponds to an orthorhombic metric in the limit of expected errors of 1% for cell axes and  $1^\circ$  for angles. Two of the cell edges are approximately equal in length, and by a factor of  $\sqrt{2}$  shorter than the third one, in accordance with the pseudo-cubic unit cell from the XRD powder pattern. Inspection of the systematic extinctions leads to a match with space group (S.G.)  $Pbcn$ . The crystal structure was solved from 224 unique diffraction intensities at a resolution limit of 0.8 Å, using direct methods

(SIR2014).[11] For the further evaluation of the single-crystal ADT measurement, optimized lattice parameters from the synchrotron powder XRD data were used, as they are much more precise than those from electron diffraction.

### **Lattice parameters from XRD**

The lattice parameters of SNO were optimized by Rietveld refinement of the synchrotron powder data in S.G. *Pbcn*, with starting values from electron diffraction. In comparison with LaB<sub>6</sub>, only a small line broadening of the SNO reflections was observed, corresponding to a crystallite size of  $\approx 250$  nm. The refined lattice parameters are  $a=7.8257(8)$ ,  $b=5.5315(5)$ ,  $c=5.5438(4)$ , and  $V=239.98(4)$  Å<sup>3</sup> with ratios of  $a/b=1.4148=1.0004 \times \sqrt{2}$  and  $a/c=1.4116=0.9982 \times \sqrt{2}$ . The deviation of the unit-cell parameters from pseudo-cubic symmetry is so small, that the orthorhombic line splitting is less than the reflection width (FWHM) in the synchrotron powder diagram, as shown by the red tic marks in Figure 1. The upper figure shows the full XRD pattern with the profile calculated by Rietveld refinement in green colour and the difference curve in cyan. Below, an enlarged view of the same pattern is shown, magnified by a factor of  $\approx 20$  to enable visualization of the weak reflections. The structure model in space-group *Pbcn* was adopted from the crystal structure derived from ADT and not refined. The final  $wR$  is 7.5% and the phase fraction of spinel Sn<sub>3</sub>N<sub>4</sub> (blue tic marks) refined to 8.6 wt.%. There remain a few noninterpreted reflections belonging to a third, yet unknown phase (visible XRD data points without green calculated profile). These reflections cannot be explained by metallic tin or any of the reported Sn–O phases such as SnO<sub>2</sub> at ambient conditions (rutile-type *P4<sub>2</sub>/mnm*)[12] or at high-pressure (*Pnmm* and pyrite-type *Pa-3*),[7] or by Sn<sub>2</sub>O<sub>3</sub> (*P1*),[13] Sn<sub>3</sub>O<sub>4</sub> (*P2<sub>1</sub>/c*),[14] or SnO (litharge-type *P4/nmm*).[15]

### **Crystal structure from ADT**

The crystal structure was kinematically refined from 5176 single-crystal reflections measured as ADT data set up to a resolution of 0.5 Å. Averaging equivalent reflections in space group *Pbcn* resulted in 1046 unique reflections with  $R_{\text{int}}=0.21$ . The final residual is  $R1=0.26$ . Dynamical refinement reduced the residual further to  $R1=0.09$ . Dynamically derived atomic positions are shown in Table 1, all atomic positions are provided in the Supporting Information. Tin and nitrogen atoms are in general position (8d), whereas oxygen is positioned on the 2-fold axis (4c). The electron-scattering factors of nitrogen and oxygen are too similar to distinguish these elements from the diffraction data. However, only the chosen assignment of sites represents an ordered structure, as the amounts of nitrogen and oxygen have a ratio of 2:1 and also the numbers of atomic positions of the sites 8d and 4c have a ratio of 2:1. There is no reason to assume nitrogen and oxygen to be disordered over both sites. Optimization of *Pbcn*- $\text{Sn}_2\text{N}_2\text{O}$  at ambient pressure using DFT confirms the soundness of the proposed structure of SNO. The calculated lattice parameters are  $a=7.83010$ ,  $b=5.66335$ ,  $c=5.62591$  Å, (PBE values) and atomic coordinates are included in Table 1. The crystal structure of SNO is shown in Figure 2. All Sn atoms are symmetrically equivalent and have identical coordination, differing only by orientation or mirror symmetry. Within a single  $\text{SnN}_4\text{O}_2$  octahedron the Sn–N and Sn–O bond lengths from experiment and theory are compared in Table 2. In the dense SNO structure the octahedra share edges and even faces, leading to short Sn–Sn distances of 3.269(5) and 3.091(7) Å, respectively.



Table 1. Atomic positions of SNO in space group *Pbcn* (No. 60) from experiment and DFT calculations.

Table 1. Atomic positions of SNO in space group <i>Pbcn</i> (No. 60) from experiment and DFT calculations.				
Experiment (dynamical refinement)				
Atom	x	y	z	$U_{iso}$ [Å <sup>2</sup> ]
Sn1	0.11535(9)	0.24354(15)	0.52443(16)	0.0040(3)
N1	0.3507(5)	0.3841(7)	0.3952(9)	0.0012(8)
O1	0	0.4513(10)	0.25	0.0037(11)
DFT calculations				
Atom	x	y	z	
Sn1	0.1157	0.2376	0.5251	
N1	0.3507	0.3790	0.3954	
O1	0	0.4530	0.25	

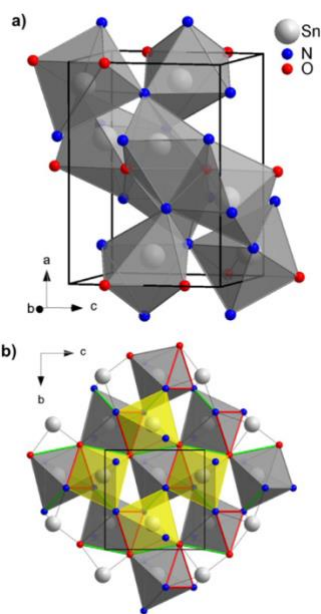
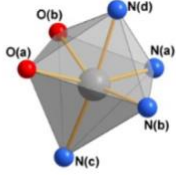


Figure 2. Crystal structure of SNO. a) Unit cell, showing the distorted octahedral coordination of Sn. b) View along the a-axis, showing grey and yellow coloured octahedra sharing faces (indicated as red triangles). Additional edge sharing (indicated as green lines) connects octahedra into chains running along the b-axis.

Table 2. Bond distances of Sn<sub>2</sub>N<sub>2</sub>O from experiment in comparison to DFT calculations.

Table 2. Bond distances of Sn <sub>2</sub> N <sub>2</sub> O from experiment in comparison to DFT calculations.			
Bond distance	DFT <i>d</i> [Å]	Experiment <i>d</i> [Å]	SnN <sub>4</sub> O <sub>2</sub> octahedron with labelling of atoms
Sn–O(a)	2.169	2.110(3)	
Sn–O(b)	2.343	2.286(4)	
Sn–N(a)	2.202	2.190(5)	
Sn–N(b)	2.174	2.130(4)	
Sn–N(c)	2.136	2.124(4)	
Sn–N(d)	2.223	2.233(4)	

### Equation of state

The bulk modulus of SNO  $B_0=193(5)$  GPa with pressure derivative  $B'=6.9(7)$  was determined from the pressure dependence of the unit-cell volume by fitting a 3rd order Birch–Murnaghan equation of state (EoS). The pressure dependence of the unit-cell volume is shown in Figure 3a, while the slope ( $3/2 B_0 (B' - 4) \neq 0$ ) of the linear  $\ln V$ -plot in Figure 3b clearly indicates the Birch–Murnaghan equation of state to be of 3rd order rather than 2nd order ( $B'=4$ ). The high value of the pressure derivative  $B'$  may be explained by deviatoric stress, which can evolve in dense sintered powders with submicron grain size at high pressure even under a neon pressure medium.[16] Deviatoric stress shows up in the  $\ln V$ -plot as a deviation of data points from a straight line in the high-pressure range. In our sample, however, such deviations are smaller than the experimental errors (cf. Figure 3b) and do not justify judging the highest-pressure data points as significantly affected by deviatoric stress.

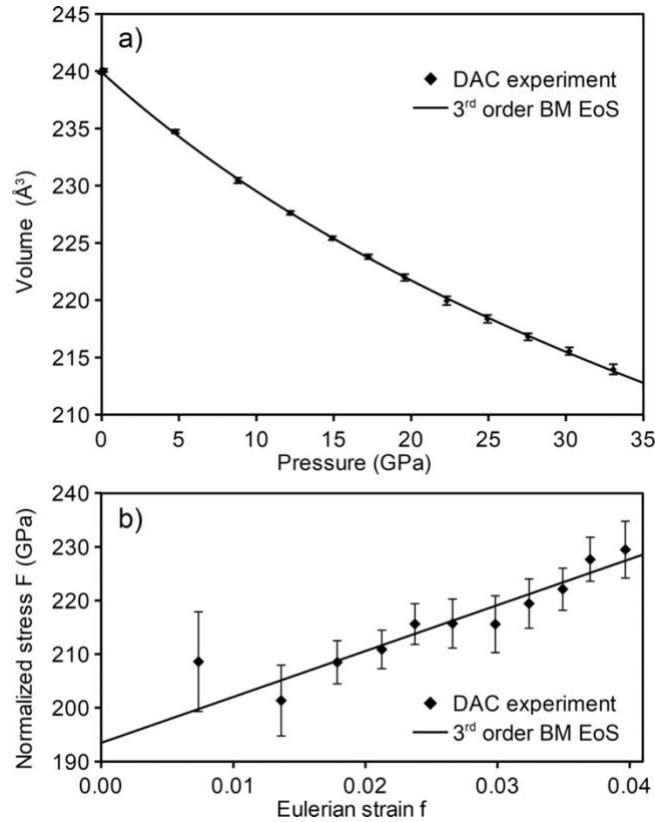


Figure 3. a) Pressure dependence of the unit-cell volume of SNO and the 3rd order Birch–Murnaghan EoS fitted to the data. b) The same EoS, rescaled to show the normalized stress  $F$  in dependence on Eulerian strain  $f$ . In the  $fF$  plot a 3rd order BM EoS displays as a straight line with  $y$ -axis intercept  $B_0$  and slope proportional to  $(B'-4)$ .

### DFT calculations

For  $\text{Sn}_2\text{N}_2\text{O}$ , we computed a bulk modulus  $B_0$  of 177 and 208 GPa by using the PBE and SCAN functional, respectively. The experimentally determined bulk modulus fits within this range. This is about 10% higher than  $B_0$  of spinel-type  $\text{Sn}_3\text{N}_4$ , which we computed to 164 GPa [SCAN: 191 GPa] (exp. 148: 1.2 GPa).[17] The shear modulus  $G$  is 95 GPa using the PBE functional [SCAN: 112 GPa], about 10% lower than  $G$  of  $\text{Sn}_3\text{N}_4$ .

Combining  $B_0$  and  $G$  yields a single-crystal hardness of  $\text{Sn}_2\text{N}_2\text{O}$  of 11–12 GPa.[18] Since  $G$  is lower and  $B_0$  is higher in comparison to  $\text{Sn}_3\text{N}_4$ , the hardness value of  $\text{Sn}_2\text{N}_2\text{O}$  can be expected to be 30–50% lower than the hardness of  $\text{Sn}_3\text{N}_4$  (14–17 GPa). Band structure

calculations for  $\text{Sn}_2\text{N}_2\text{O}$  by PBE and SCAN yield gaps of 0.3 and 0.6 eV, respectively. These values likely underestimate the true band gap. Using hybrid functionals we find a gap of 1.3 and 1.9 eV for HSE06[19] and PBE0[20] calculations, respectively. Thus, we expect that the gap of  $\text{Sn}_2\text{N}_2\text{O}$  single crystals will be close to that of  $\text{Sn}_3\text{N}_4$ , for which a value of 1.6 eV has been calculated[21] and 1.6:0.2 eV[3b] determined experimentally.

To rationalize the formation of  $\text{Sn}_2\text{N}_2\text{O}$  in the high-pressure experiment we computed its enthalpy of formation from the binaries  $\text{SnO}_2$  and  $\text{Sn}_3\text{N}_4$  as a function of pressure.  $\text{SnO}_2$  itself displays a rich high-pressure chemistry and has been subject of multiple experimental and computational studies.[7,22] At low pressure the rutile-type of  $\text{SnO}_2$  is most favourable. We compute the pressure at which it transforms into the pyrite-type of  $\text{SnO}_2$  to 9.6 GPa.  $\text{Sn}_3\text{N}_4$  adopts the spinel structure at ambient pressure and transforms into post-spinel phases only above 40 GPa. Huang et al.[23] predicted  $\text{CaTi}_2\text{O}_4$ - and  $\text{CaFe}_2\text{O}_4$ -type orthorhombic structures at 40 and 60 GPa, respectively. On the other hand, Kearney et al.[24] predicted structures with space groups  $P2_1/c$  and  $R-3c$  at pressures above 40 and 87 GPa, respectively. At ambient pressure, the enthalpy of formation  $\Delta H_f$  of  $Pbcn$ - $\text{Sn}_2\text{N}_2\text{O}$  from the binaries is +0.56 eV/ $\text{Sn}_2\text{N}_2\text{O}$ ; taking the more favourable (at zero pressure) defect-spinel-type of  $\text{Sn}_2\text{N}_2\text{O}$  the enthalpy difference is still +0.30 eV/ $\text{Sn}_2\text{N}_2\text{O}$ . This indicates that  $\text{Sn}_2\text{N}_2\text{O}$  is *meta*-stable with respect to decomposition into the binaries. Figure 4 shows that  $\text{Sn}_2\text{N}_2\text{O}$  will form at 12.0 GPa [SCAN: 14.3 GPa] and remains stable against decomposition at higher pressures.

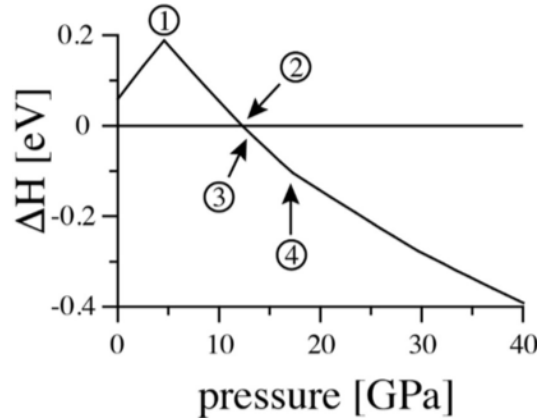


Figure 4. Reaction enthalpy (PBE results) of the reaction  $\text{SnO}_2 + \text{Sn}_3\text{N}_4 \rightarrow 2\text{Sn}_2\text{N}_2\text{O}$  as a function of pressure. The labels indicate (1) transformation of spinel-type  $\text{Sn}_2\text{N}_2\text{O}$  to *Pbcn*- $\text{Sn}_2\text{N}_2\text{O}$  (at 4.6 GPa), (2)  $\Delta H_f = 0$  (12.0 GPa), (3) transformation of rutile-type  $\text{SnO}_2$  to  $\alpha$ - $\text{PbO}_2$ -type  $\text{SnO}_2$  (12.5 GPa), and (4) transformation of  $\alpha$ - $\text{PbO}_2$ -type  $\text{SnO}_2$  to pyrite-type  $\text{SnO}_2$  (17.2 GPa).

Searching for alternative structures of  $\text{Sn}_2\text{N}_2\text{O}$  potentially appearing at low or high pressures, we found two relevant candidates. A “defect” spinel-type structure with disorder among the anions and vacancies on cation sites, constitutes the low-pressure modification of  $\text{Sn}_2\text{N}_2\text{O}$ . While we computed the lowest energy structure to adopt the ordered spinel  $\text{In}_2\text{S}_3$ -type structure, we found other “defective” variants of spinel (e.g. with S.G. *P32m1*) within a few meV/atom. All “defect” spinel-types exhibit tetrahedrally and octahedrally coordinated cations. At ambient pressure, the “defect” spinel-type of  $\text{Sn}_2\text{N}_2\text{O}$  is about 0.25 eV/ $\text{Sn}_2\text{N}_2\text{O}$  more favourable than the *Pbcn*-type. The transition to *Pbcn*- $\text{Sn}_2\text{N}_2\text{O}$  occurs at 5 GPa. The newly synthesized tin oxynitride remains the most favourable structure up to 95 GPa, when a new  $\text{Sn}_2\text{N}_2\text{O}$ -III with seven- and eight-fold coordinated cations (CN=7.5 at 100 GPa) and orthorhombic (*Pmn21*) symmetry becomes favoured by enthalpy.  $\text{Sn}_2\text{N}_2\text{O}$ -III distorts upon decompression into a monoclinic (*P21*) structure with reduced coordination.

Re-investigating the sequence of high-pressure structures of  $\text{Si}_2\text{N}_2\text{O}[1c]$  we find that a *Pbcn*- $\text{Si}_2\text{N}_2\text{O}$  will succeed the  $\text{Al}_2\text{O}_3$ -type only above 90 GPa. The  $\text{Rh}_2\text{S}_3$ -type

structure (sometimes addressed as  $\text{Rh}_2\text{O}_3$ -II type) with space group  $Pbcn$  is known as a high-pressure phase of  $\alpha\text{-Al}_2\text{O}_3$  (corundum,  $R\text{-}3c$ ) above 113 GPa,[25] or  $\alpha\text{-Fe}_2\text{O}_3$  (hematite,  $R\text{-}3c$ ) above 41 GPa,[26] or Bixbyite-type  $\text{In}_2\text{O}_3$  in the range of 10–25 GPa,[27] in which the latter compound shows also a metastable corundum-type phase at  $\approx 6$  GPa.

## Conclusions

In conclusion, the discovered tin oxynitride  $\text{Sn}_2\text{N}_2\text{O}$  with space group  $Pbcn$  ( $\text{Rh}_2\text{S}_3$ -type structure) is another example demonstrating the potential of high-pressure synthesis to access novel materials. Tin is in six-fold coordination in the  $\text{Rh}_2\text{S}_3$ -type structure in contrast to the sinoite-type oxynitrides of Si and Ge with four-fold metal coordination. Tin oxynitride was synthesized at high pressure and high temperature using a large volume press at beamline P61B, DESY, Hamburg. The compound forms from tin oxide and tin nitride only at high pressure and can be quenched to ambient pressure retaining its high-pressure structure. The crystal structure of the novel compound was determined using synchrotron powder XRD in combination with single-crystal electron diffraction tomography from a 200 nm sized single crystal. DFT calculations predicted this structure to be stable above 12 GPa and to remain the most favourable one up to 95 GPa. The calculations also confirmed the ordered distribution of nitrogen and oxygen. The synthesized tin oxynitride may be considered for applications, for example, in the field of low band-gap semiconductors. From the viewpoint of fundamental solid-state chemistry,  $\text{Sn}_2\text{N}_2\text{O}$  is a new member of inorganic compounds with the well-known  $\text{Rh}_2\text{S}_3$ -type structure. It is also the first evidence for the existence of a crystalline ternary oxynitride of tin and complements and extends the well-known Group 14 element oxynitrides of silicon and germanium.

## Experimental Section

## Synthesis

Oxygen-containing tin nitride precursors were synthesized from a  $\text{Sn}[\text{NMe}_2]_4$  complex using a two-stage ammonolysis procedure as described by Hector et al.[28] In the first stage, 7.93 mmol of  $\text{Sn}[\text{N}(\text{CH}_3)_2]_4$  was dissolved in 50 mL THF and cooled to  $-78^\circ\text{C}$ . Then, condensed ammonia was added by dropping method to the solution under constant stirring. A yellow powder was recovered after drying from the solvent and subsequently subjected to a second-stage standard ammonolysis at  $150^\circ\text{C}$  for 6 h and then to  $400^\circ\text{C}$  for 2 h (heating rate  $2^\circ\text{C min}^{-1}$ ; details are given in the Supporting Information). The product was characterized by XRD and elemental analysis using the combustion method (LECO tester). This precursor was subjected to HP-HT conditions (20 GPa and  $1200\text{--}1500^\circ\text{C}$ ) in a Hall-type six-ram LVP (mavo press LPQ6 1500-100; Max Voggenreiter GmbH, Germany) installed at the P61B beamline at DESY, Hamburg.

## XRD

X-ray diffraction of a crushed, synthesized sample (run# HH127, 20 GPa,  $1200^\circ\text{C}$ , Pt capsule) was performed using synchrotron radiation at the high-resolution powder beamline P02.1 of PETRA-III, DESY, Hamburg. The XRD pattern was quantitatively analysed by Rietveld refinement with the program GSAS-II[29] using instrumental profile parameters from a  $\text{LaB}_6$  standard measured on the same instrument. A second sample (run# HH148, 20 GPa,  $1500^\circ\text{C}$ , Ta capsule) was characterized with  $\text{CuK}\alpha$  radiation from a laboratory source. The pressure dependence of the unit-cell volume of SNO was measured in a diamond anvil cell (DAC) using synchrotron radiation at the extreme-condition beamline P02.2 of PETRA III, DESY, upon increasing the pressure from 0.14 to 33 GPa. The pressure in the DAC was measured with the ruby fluorescence method. The bulk modulus and its pressure derivative was determined by an equation of state fit [EoSFit v5.2].[30] The volume at ambient pressure,  $V_0=239.80(1) \text{ \AA}^3$ , was

determined from the Rietveld refinement of an X-ray pattern measured with  $\text{CuK}\alpha$  radiation using a sample from the same HP-HT run (#HH141, 20 GPa, 1300°C, Ta capsule) as for the DAC experiment.

### **Electron diffraction (ADT)**

Automated diffraction tomography (ADT) experiments[10] were carried out at the electron microscopy centre (EMC-M) of the Johannes Gutenberg-University Mainz. A TEM Tecnai F30 ST equipped with a field emission gun at 300 kV was used. Sample imaging for crystal tracking during stage tilt was performed in m-STEM mode with a HAADF detector. Diffraction measurements were performed using nanoelectron-diffraction (NED) mode with a 10  $\mu\text{m}$  C2 aperture leading to a semi-parallel illumination with a beam size of 200 nm. Electron diffraction patterns were acquired with a Gatan CCD US4000 using 2k x 2k images taken with 1 s exposure time for each pattern. To provide a high tilt range a Fischione tomography sample holder was used (tilt range of -45–60° due to limitations on the grid). ADT data were collected with electron beam precession (precession electron diffraction, PED) to improve reflection intensity integration quality using a Digistar unit developed by NanoMEGAS SPRL (precession angle 1°).[31] A fast acquisition module recently developed was used for diffraction data acquisition applying sequential tilts of 1°. The Fast-ADT acquisition is re-ported in more detail in the upcoming article of Plana-Ruiz et al.[32] Data processing, 3D reconstruction, cell parameter determination and space group analysis as well as diffraction intensity extraction were performed with ADT3D (eADT) software.[33] Ab initio structure solution assuming the kinematic approximation ( $\text{Int} \propto |F(\text{hkl})|^2$ ) was performed by direct methods implemented in the program SIR2014 including as well difference Fourier mapping and least-squares refinement.[11] Scattering factors for electrons were taken from Doyle and Turner.[34] Kinematical structure refinement was performed with



shelxl2013[9] and dynamical structural refinement with JANA2006[35] after data extraction with PETS.[36]

### **DFT calculations**

Calculations of total energy and volume were done within density functional theory as implemented in the Vienna ab initio simulation package (VASP).[37] The Generalized Gradient Approximation (GGA-PBE)[38] was used together with the projector-augmented-wave (PAW) method.[39] Consistency checks were done with the Strongly Conserved and Appropriately Normed (SCAN) function-al.[40] All results were obtained using a plane wave cut-off energy of 500 eV with forces converged to better than 1 meVÅ<sup>-1</sup>. The Brillouin zone of each structure was sampled by *k*-point meshes with grid sizes smaller than 0.03 Å<sup>-1</sup>. With the parameters above, enthalpy differences between structures are converged to better than 1 meV. Enthalpy and pressure of products and reactants are extracted from energy-volume data of corresponding structures. Computed elastic constants yield Young's modulus *E* and shear modulus *G* via the Voigt–Reuss–Hill approximation.[41] The approach of Chen et al.[18] was used to estimate single-crystal hard-ness. Searching for additional and alternative potential candidate structures of Sn<sub>2</sub>N<sub>2</sub>O we applied the USPEX code.[42] The code readily produced *Pbcn*-Sn<sub>2</sub>N<sub>2</sub>O and *Pmn*2<sub>1</sub>-Sn<sub>2</sub>N<sub>2</sub>O among a manifold of structures. Low-pressure modifications of defective spinel-types were taken from previous works[1c,43] and outperformed models provided by the search algorithm.

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### **Conflict of interest**

The authors declare no conflict of interest.

Keywords: density functional calculations · electron diffraction · high-pressure synthesis · synchrotron radiation · tin oxynitride

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## Summary

A new *Pbcn*-Sn<sub>2</sub>N<sub>2</sub>O with all Sn six-fold coordinated was synthesized through high-pressure experiments and characterized through powdered X-ray diffraction and automated diffraction tomography. The experimental bulk modulus of *Pbcn*-Sn<sub>2</sub>N<sub>2</sub>O was determined to be 193(5) GPa. Using DFT[1] we calculated the bulk modulus of *Pbcn*-Sn<sub>2</sub>N<sub>2</sub>O to be within a range of 177 – 208 GPa agreeing with experiment. Additionally, by calculating the single crystal hardness of *Pbcn*-Sn<sub>2</sub>N<sub>2</sub>O we estimated the hardness of *Pbcn*-Sn<sub>2</sub>N<sub>2</sub>O to be 30 – 50% lower than the hardness of spinel-type Sn<sub>3</sub>N<sub>4</sub>. Band gap calculations with hybrid functionals[2, 3] indicated that the band gap of *Pbcn*-Sn<sub>2</sub>N<sub>2</sub>O was in the range of the band gap of Sn<sub>3</sub>N<sub>4</sub>. In rationalizing the formation of *Pbcn*-Sn<sub>2</sub>N<sub>2</sub>O, we calculated  $\Delta H_f$  of *Pbcn*-Sn<sub>2</sub>N<sub>2</sub>O from the binaries to be positive at ambient pressure indicating that the experimentally recovered *Pbcn*-Sn<sub>2</sub>N<sub>2</sub>O is metastable with respect to decomposition into binary compounds at ambient pressures. Furthermore, calculations of enthalpy as a function of pressure showed that *Pbcn*-Sn<sub>2</sub>N<sub>2</sub>O becomes stable with respect to decomposition into binary compounds at 12 GPa and remains the most thermodynamically favored form of *Pbcn*-Sn<sub>2</sub>N<sub>2</sub>O until 95 GPa.

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## CHAPTER 3: DISCOVERY OF TERNARY SILICON TITANIUM NITRIDE WITH SPINEL-TYPE STRUCTURE

### **Motivation and Scope**

A new ternary Si-Ti-N compound with spinel-structure type is fortunately discovered during high-pressure experiments. Perhydropolysilazane and tetrakis(dimethylamido)titanium are reacted together to synthesize a single-source precursor which is converted into an amorphous Si-Ti-N ceramic under an ammonia atmosphere at 1000°C. Subjecting the amorphous ceramic to 15-20 GPa and 1800 – 2000°C results in a sintered sample that is a mixture of c-TiN and spinel-Si<sub>3</sub>N<sub>4</sub>, with ternary spinel-type (Si<sub>1-x</sub>,Ti<sub>x</sub>)<sub>3</sub>N<sub>4</sub> nanocrystals embedded in the spinel-Si<sub>3</sub>N<sub>4</sub>. We use DFT[1] to perform combinatorial analysis in order to determine the site preference of Ti in spinel-type (Si<sub>1-x</sub>,Ti<sub>x</sub>)<sub>3</sub>N<sub>4</sub>. From the most favorable structures of ternary spinel-type (Si<sub>1-x</sub>,Ti<sub>x</sub>)<sub>3</sub>N<sub>4</sub> that we find we compute the enthalpy of formation of the ternary compound from its binary phases. We use Bader charge analysis[2] to verify the experimental findings that Ti is present in spinel-type (Si<sub>1-x</sub>,Ti<sub>x</sub>)<sub>3</sub>N<sub>4</sub> in multiple oxidation states. Additionally, we compute elastic properties and band gaps.

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## Discovery of Ternary Silicon Titanium Nitride with Spinel-Type Structure

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### Abstract

Here we report on the discovery of a ternary silicon titanium nitride with the general composition  $(\text{Si}_{1-x}\text{Ti}_x)_3\text{N}_4$  with  $x = 0 < x < 1$  and spinel-type crystal structure. The novel nitride is formed from an amorphous silicon titanium nitride (SiTiN) precursor under high-pressure/high-temperature conditions in a large volume high-pressure device. Under the conditions of 15 – 20 GPa and 1800 - 2000°C, spinel-type  $\gamma\text{-Si}_3\text{N}_4$  and rock salt-type  $c\text{-TiN}$  are formed. In addition, crystals of the discovered nano-sized ternary phase  $(\text{Si}_{1-x}\text{Ti}_x)_3\text{N}_4$  embedded in  $\gamma\text{-Si}_3\text{N}_4$  are identified. The ternary compound is formed due to

kinetically-controlled synthesis conditions and is analyzed to exhibit the spinel-type structure with ca. 8 atom% of Ti. The Ti atoms occur in both  $Ti^{3+}$  and  $Ti^{4+}$  oxidation states and are located on the Si sites. The ternary nano-crystals have to be described as  $(Si,Ti)_3N_4$  with N-vacancies resulting in the general composition  $(Si^{4+}_{1-x} Ti^{4+}_{x-\delta} Ti^{3+\delta})_3N_4$ .

## Introduction

Spinel-type silicon nitride  $\gamma$ - $Si_3N_4$  is a high-pressure phase of silicon nitride and has been discovered in 1999[1]. In the same year, from the group 14 element, spinel type  $Ge_3N_4$  and  $Sn_3N_4$ [3] have been found afterwards. Based on these experimental findings, Ching

	C	Si	Ge	Sn	Ti	Zr	Hf
C	$C_3N_4$	$CSi_2N_4$	$CGe_2N_4$	$CSn_2N_4$	$CTi_2N_4$	$CZr_2N_4$	
Si	$SiC_2N_4$	$Si_3N_4$	$SiGe_2N_4$	$SiSn_2N_4$	$SiTi_2N_4$	$SiZr_2N_4$	
Ge	$GeC_2N_4$	$GeSi_2N_4$	$Ge_3N_4$	$GeSn_2N_4$	$GeTi_2N_4$	$GeZr_2N_4$	
Sn	$SnC_2N_4$	$SnSi_2N_4$	$SnGe_2N_4$	$Sn_3N_4$	$SnTi_2N_4$	$SnZr_2N_4$	
Ti	$TiC_2N_4$	$TiSi_2N_4$	$TiGe_2N_4$	$TiSn_2N_4$	$Ti_3N_4$	$TiZr_2N_4$	
Zr	$ZrC_2N_4$	$ZrSi_2N_4$	$ZrGe_2N_4$	$ZrSn_2N_4$	$ZrTi_2N_4$	$Zr_3N_4$	$ZrHf_2N_4$
Hf						$HfZr_2N_4$	$Hf_3N_4$

Figure 1: Overview of some high-pressure nitrides experimentally synthesized and theoretically predicted, after W.-Y. Ching et al.[4]



et al. predicted a variety of binary and ternary nitrides including nitrides of transition metal elements[4]. In Figure 1, an updated selection of prominent high-pressure nitrides experimentally accomplished (blue background) and those theoretically predicted (white background) but not achieved yet are listed.

According to their calculations, 39 spinel-type nitrides are characterized by interesting functional and structural features ranging from super-hardness via semiconducting to metallic properties[5]. Later on, it has been found experimentally, that the transition metal high-pressure nitrides of  $M = \text{Ti, Zr and Hf}$  with the stoichiometry  $M_3N_4$  do not show the spinel-type structure as forecasted, but appear in the cubic  $\text{Th}_3\text{P}_4$  structure-type[6]. Experimental studies verified that spinel nitride  $\gamma\text{-Si}_3\text{N}_4$  in particular, but also the transition metal nitrides  $M_3N_4$  with  $M = \text{Zr, Hf}$  combine ultra-high hardness with high thermal stability against decomposition in different environments. This suggests their promising use in potential applications such as cutting tools[7-9]. Due to their predicted semiconducting behaviour, calculations showed that spinel-type nitrides exhibit interesting optoelectronic properties, which may lead to applications such as light-emitting diodes[4,10].

Figure 1 impressively reveals that the majority of the predicted ternary nitrides have not been synthesized yet. To the best of our knowledge, the spinel-type  $\text{GeSi}_2\text{N}_4$  is the solitary ternary nitride successfully synthesized[11,12]. Other ternary nitrides remained unknown yet though projected in various studies. There are even more theoretical studies predicting the existence of ternary nitrides e.g. with perovskite-type-based structures[13] and others[14] which could further immensely extend the field of unknown nitrides. Recently, a few new ternary nitrides with different structure types were synthesized by Sun et al.[15,16] based on a calculated large stability map of the inorganic ternary metal nitrides. They reported thin films of Zn-based and Mg-based ternary nitrides with wurtzite-type and rock salt-type structures, respectively[16].

The forecasted ternary nitrides open up further numerous scientific questions related to synthesis, chemistry and properties of this interesting family of new materials. Novel synthesis approaches including high-pressure methods in combination with theoretical calculations offer a chance to find correct pressure/temperature conditions to realize the synthesis of the exemplarily mentioned and calculated nitrides[17].

In the present study, we report on a discovery of a ternary nitride formed between  $\text{Si}_3\text{N}_4$  and  $\text{Ti}_3\text{N}_4$  synthesized under high-pressure/temperature conditions, namely at pressures of 15 - 20 GPa and temperatures of 1800 - 2000°C in a large volume press. While the binary nitrides crystallize in different structure types (spinel-type for  $\text{Si}_3\text{N}_4$  and  $\text{Th}_3\text{P}_4$ -type for  $\text{Ti}_3\text{N}_4$ [18]), the formed ternary nitride reveals the spinel-type structure and it is, therefore, considered that Si in  $\gamma\text{-Si}_3\text{N}_4$  is substituted by Ti. In addition, the ternary  $(\text{Si,Ti})_3\text{N}_4$  crystals are nano-sized and are embedded in  $\gamma\text{-Si}_3\text{N}_4$  single crystals.

## **Results**

### **Single-source-precursor synthesis.**

High-pressure synthesis of inorganic metal nitrides requires appropriate precursor compounds, which contain all the elements of the targeted material to be obtained. In our study we first synthesized a single-source precursor (SSP) by the reaction of perhydropolysilazane (PHPS) with tetrakis(dimethylamido)titanium (TDMAT) according to the scheme given in Figure 2[19,20]. For this reaction, we set a Si:Ti atomic ratio of 5.

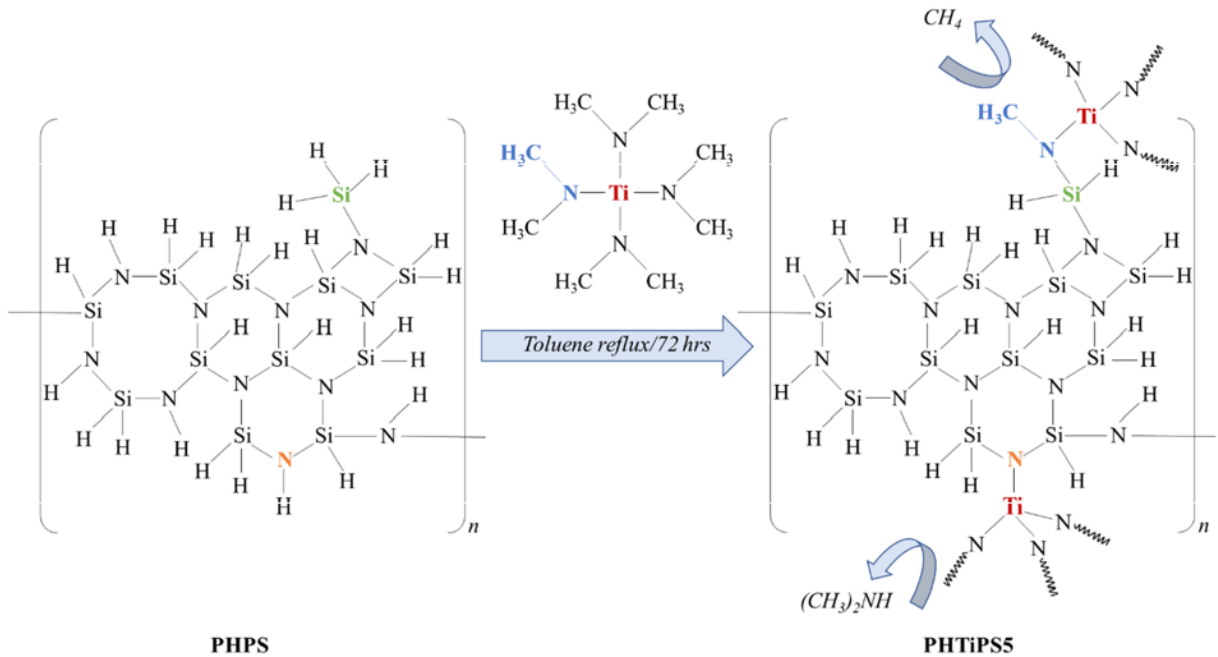


Figure 2: Synthesis procedure for the preparation of the SiTiN single-source precursor (SSP) according to reference[19].

The obtained SSP formed via the reaction of N-H- (dimethylamine release) and Si-H- (methane release) bonds from PHPS with the ligands of TDMAT is denoted as polytitanosilazane (PHTiPS5) and the following composition was obtained by chemical analysis: 38.4 wt% Si, 17.2 wt% Ti, 7.3 wt% H, 16.0 wt% N, 21.1 wt% C and 0.9 wt% O. By neglecting the oxygen contamination, a formal composition is derived from the analytical values:  $\text{Si}_{1.0}\text{Ti}_{0.25}\text{C}_{1.2}\text{N}_{0.8}\text{H}_{5.2}$ .

The SSP is finally converted to an amorphous/nanocrystalline SiTiN ceramic in ammonia atmosphere at 1000 °C with a ceramic yield of 73.25 wt%. Along with the amorphous background, the X-ray powder pattern of the synthesized SiTiN shows nanocrystalline features, which fit to the rock salt phase of TiN with a  $\sim 4.3 \text{ \AA}$  and a crystallite size of 2-3 nm. A quantitative elemental analysis of the SiTiN material revealed a composition of Si – 44.2 wt%; Ti – 18.9 wt%; N – 33.1 wt%; C – 0.02 wt% O – 3.8 wt%. The values are used to calculate a formal composition of the synthesized

powder by neglecting the carbon contamination:  $\text{Si}_{1.0}\text{Ti}_{0.2}\text{N}_{1.5}\text{O}_{0.15}$  that represents the presence of  $0.3 \text{ Si}_3\text{N}_4 + 0.2 \text{ TiN} + 0.07 \text{ SiO}_2$  of the respective thermodynamically phase compositions. Thus, the Si:Ti ratio in the ammonolyzed and pyrolyzed material amounts ca. 5 and reflects that of the molar ratio used for the synthesis of the SSP.

### High-pressure synthesis.

In the second step, the acquired SiTiN powder is subjected to a high-pressure/high-temperature treatment. The high-pressure experiments were performed in a large volume press under pressures between 16 and 20 GPa and temperatures between 1800 and 2000°C. After pressure release, a compact and sintered body is isolated from the reaction chamber. A SEM image of a fracture surface of the sample exhibits a composite microstructure with dark and bright contrasted nanocrystals (see Figure 7). X-ray diffraction analysis of the powdered sample revealed the presence of spinel-type  $\gamma\text{-Si}_3\text{N}_4$  and rocksalt-type c-TiN as well as some contamination with stishovite  $\text{SiO}_2$  (Figure 3).

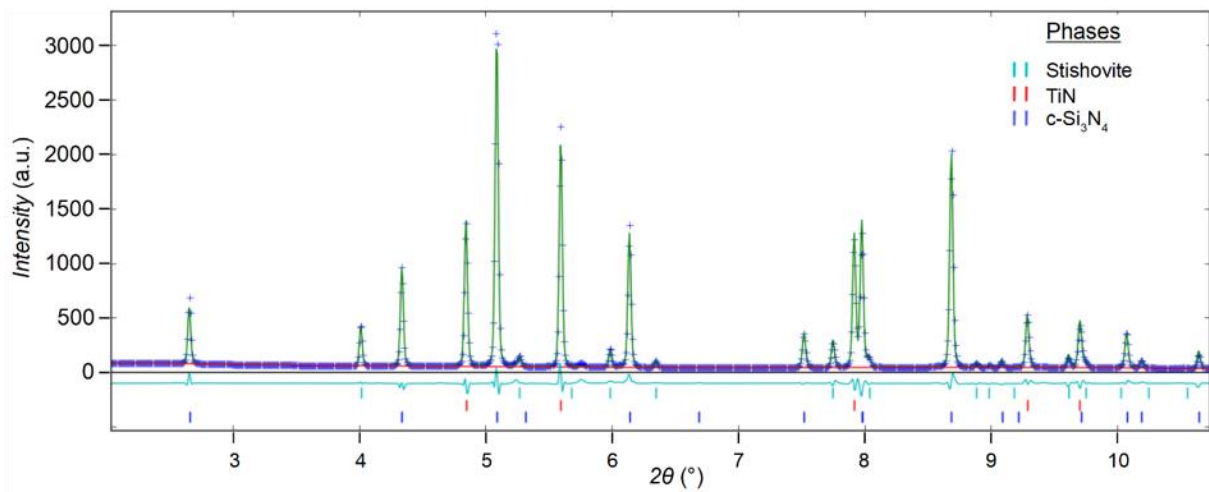


Figure 3: X-ray powder diffraction of SiTiN-run HH112 ( $\lambda = 0.207109 \text{ \AA}$ ) and Rietveld refinement.

The fraction of the crystalline phases was obtained by Rietveld refinement of the XRD data. The fractions were 72.6 wt%  $\gamma\text{-Si}_3\text{N}_4$ , 20.2 wt% of c-TiN and 7.1 wt% Stishovite

(SiO<sub>2</sub>) together with < 0.1 wt% Pt from the capsule material of the high- pressure experiment. The Si:Ti ratio thus remained ca. 5, and the bulk sample composition of the SiTiN starting material therefore did not significantly change during experimental high- pressure/temperature treatment.

### **Structural analysis via XRD and electron microscopy.**

The average sizes of the synthesized  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> and c-TiN were derived from the peak widths of the XRD pattern, and found both  $260 \pm 90$  nm. Since these grain sizes are too small for chemical composition analysis by SEM-EDS, the samples were observed using ADF-STEM. As shown in Figure 4(a), the sample consisted of two phases with different brightnesses. Since the brightness increases with increasing average atomic number, the brighter contrast grains should contain heavier elements, i.e. Ti. It is therefore concluded that the bright- and dark-contrast grains are c-TiN and  $\gamma$ -Si<sub>3</sub>N<sub>4</sub>, respectively. This evaluation was also confirmed by electron diffraction and EDX mapping (Figure 4b) of this region.

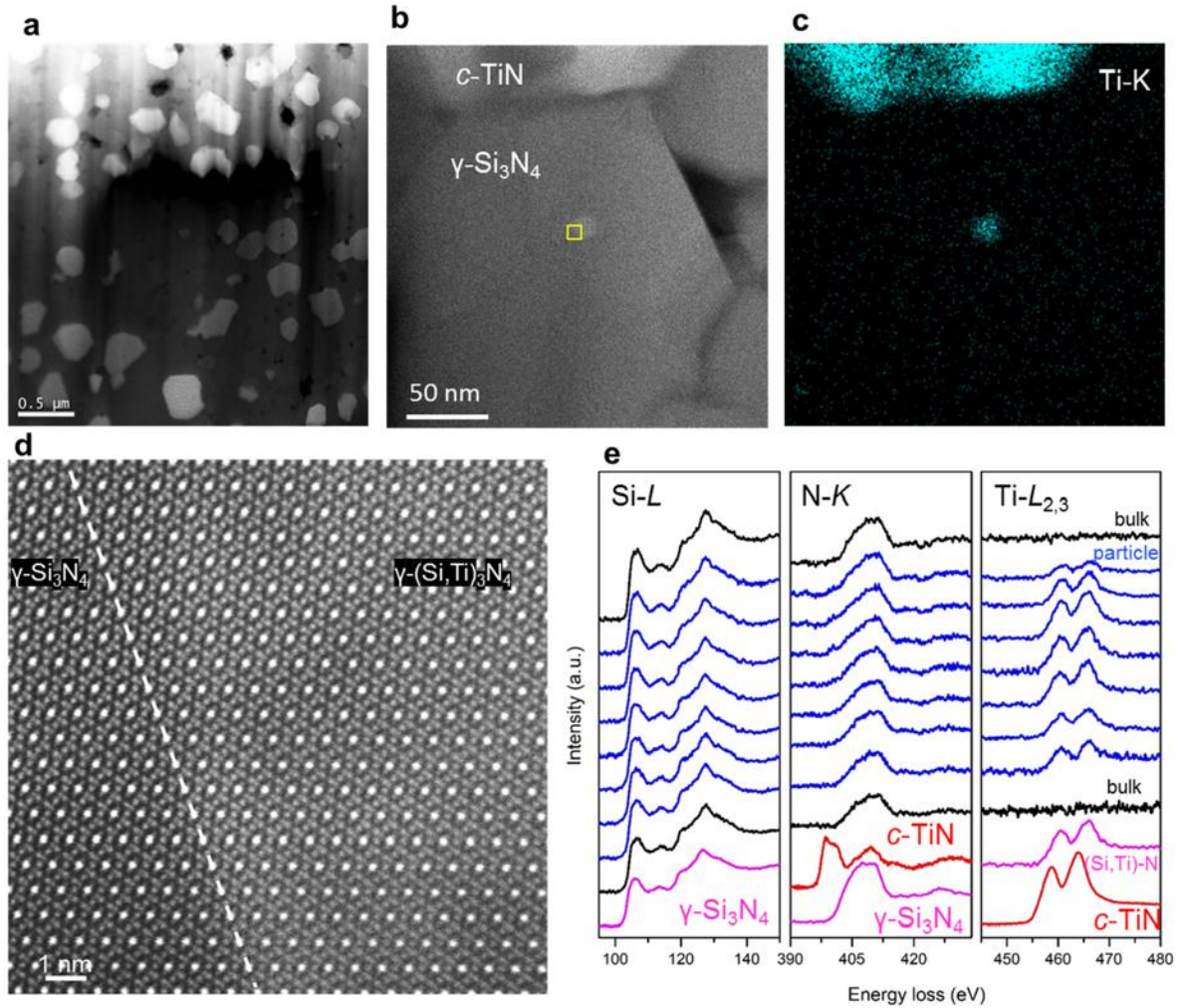


Figure 4: (a) Low-magnified ADF-STEM image, (b) ADF-STEM image obtained from a single grain, (c) Ti-K edge STEM-EDX mapping obtained from (b). (d) Atomic-resolution ADF-STEM image obtained from the yellow-framed section shown in (b). at the interface between  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> and ternary (Si,Ti)<sub>3</sub>N<sub>4</sub> particle (e) EELS profiles of Si-L, N-K and Ti-L<sub>2,3</sub> edges across the ternary (Si,Ti)<sub>3</sub>N<sub>4</sub> nano-particle, where the black, blue, pink and red-colored profiles correspond to the bulk material, the nano-particle,  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> and SiTiN, and c-TiN, respectively.

On the close inspection of the grains, we found a third type of nanocrystals inside of the  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> grains that can be seen as a brighter dot contrast in the ADF-STEM image of Fig. 4(b), suggesting that the nanocrystal should contain Ti atoms. The embedded nanocrystals are around 10 – 20 nm in size and occur in the majority of the silicon nitride

host crystals. The distribution of nanoparticles in  $\gamma$ - $\text{Si}_3\text{N}_4$  grain can be found in the low-magnification of annular bright-field (ABF) STEM image (see Supplementary Note 1). To directly confirm the validity of Ti-concentration at the nano-particle, we performed STEM-EDX mapping and the map of Ti- $K$  edge is shown in Fig. 4(c). On the basis of the STEM-EDX mapping, we elucidate that the nanocrystal contains Si, N and Ti atoms, and moreover the concentration of Si atoms is smaller than that in the vicinity of  $\gamma$ - $\text{Si}_3\text{N}_4$ . Thus, Ti atoms are considered to be in the substitutional form at Si atomic sites. It is important to note that no significant oxygen is found in the nanocrystals. Figure 4(d) shows an atomic-resolution ADF-STEM image viewed along the  $[110]$  orientation of  $\gamma$ - $\text{Si}_3\text{N}_4$ , including the interface between the nanocrystal and  $\gamma$ - $\text{Si}_3\text{N}_4$ . As indicated by the dotted line in Fig. 4(d), the nanocrystal (right-side) shows slightly brighter Z-contrast than that in the bulk of  $\gamma$ - $\text{Si}_3\text{N}_4$ , suggesting that the nanocrystal contains Ti atoms but the structure retains spinel-type with the coherent interface between the host  $\gamma$ - $\text{Si}_3\text{N}_4$  and the nanocrystal: the discovery of the ternary  $(\text{Si},\text{Ti})_3\text{N}_4$ . We note that although the boundary between the nanoparticle and  $\gamma$ - $\text{Si}_3\text{N}_4$  may be difficult to realize from the weak Z-contrast difference, it is the most evident in the Z-contrast intensity profile across the grain boundary and the simultaneously recorded ABF-STEM image (see Supplementary Note 2). For the further investigation, we performed EELS analysis across the nanocrystal as shown in Fig. 4(e), where the blue-, black- and red-colored profiles are related to the nanocrystal,  $\gamma$ - $\text{Si}_3\text{N}_4$ , and c-TiN, respectively. The pink colored profiles are obtained from the bulk of  $\gamma$ - $\text{Si}_3\text{N}_4$  and the nanoparticle (average for Ti- $L_{2,3}$  edge). The Si- $L$ , and N- $K$  edges of the nanocrystal are basically similar to those in  $\gamma$ - $\text{Si}_3\text{N}_4$ , which is well compatible with the observed atomic structure. The Ti- $L_{2,3}$  edges are localized within the nanocrystal, and the peak positions of the Ti- $L_{2,3}$  edge show slight upward shift compared with that in c-TiN, suggesting that Ti occurs in two oxidation states in the nanocrystal, namely  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$ . In spinel-type structure, there are two atomic sites for cations, namely octahedral and tetrahedral coordination, and the Ti oxidation states for the sites

have to be considered as  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$ . For the compensation of the total charge, the nanocrystal requires N vacancies, and we conclude that the formed ternary spinel structure has to be described as  $(\text{Si}^{4+}_{1-x}\text{Ti}^{4+}_{x-\delta}\text{Ti}^{3+\delta})_3\text{N}_{4-\delta}$ , where we could not determine the Ti content (x) because the experimental spectroscopic information (EDX and EELS) is in 2D projection (the nanocrystal is embedded in  $\gamma\text{-Si}_3\text{N}_4$  grain). However, from EELS we can roughly estimate the following ratio  $\text{Ti}^{4+}:\text{Ti}^{3+} = (x-\delta):\delta \sim 0.7 : 0.3$ , which leads to  $\delta \sim 0.3 x$ .

### Thermodynamic considerations.

The composition of the synthesized ternary silicon titanium nitride solid solution is located on the tie line between the binary subsystems  $\gamma\text{-Si}_3\text{N}_4$  and  $\text{Ti}_3\text{N}_4$  as illustrated in the isothermal section of the phase diagram shown in Figure 5.

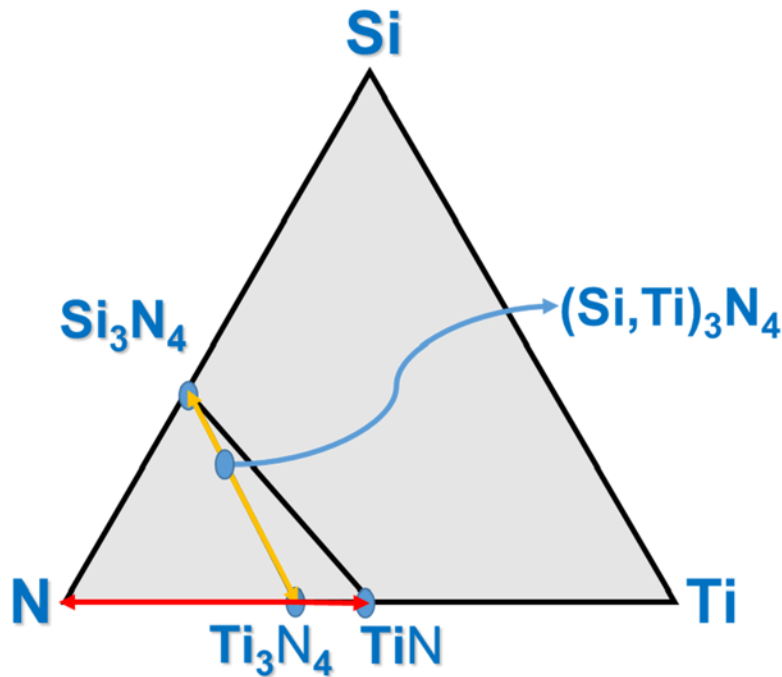
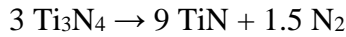


Figure 5: SiTiN ternary composition diagram with the known binary subsystems and the novel ternary SiTiN phase located on the tie line between  $\gamma\text{-Si}_3\text{N}_4$  and  $\text{Ti}_3\text{N}_4$ .



Accordingly, under the applied high-pressure/high-temperature conditions, amorphous SiTiN produced three phases, namely submicron-sized c-TiN with rocksalt-type structure and  $\gamma$ -Si<sub>3</sub>N<sub>4</sub>[1] grains with nano-sized inclusions of a ternary  $\gamma$ -(Si,Ti)<sub>3</sub>N<sub>4</sub> phase, both with spinel-type structure. With respect to the phase diagram we may hypothesize that the ternary  $\gamma$ -(Si,Ti)<sub>3</sub>N<sub>4</sub> phase partitions first into  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> and Ti<sub>3</sub>N<sub>4</sub> (along the yellow colored tie line in Figure 5). However, Ti<sub>3</sub>N<sub>4</sub> is thermodynamically unstable under our experimental conditions of 15-20 GPa and 1800-2000°C[21]. Thus, Ti<sub>3</sub>N<sub>4</sub> readily decomposes into the thermodynamically stable phases c-TiN and gaseous N<sub>2</sub> along the red colored tie line of the binary Ti-N subsystems presented in Figure 5 and according to the following reaction equation:



Moreover, crystalline Ti<sub>3</sub>N<sub>4</sub> cannot be recovered at ambient pressure[18,21], while the high-pressure phase of silicon-nitride shows an enormous metastability even at ambient pressure and can be heated up to 1400°C without any phase transformation[22]. Finally, once TiN is formed from the ternary  $\gamma$ -SiTiN phase, the resulting  $\gamma$ -Si<sub>3</sub>N<sub>4</sub>/c-TiN composite is thermodynamically stable at P > 10 GPa and metastable under ambient pressure.

### **Computation of Ti site preference and structure search.**

Guided by the experimental data we started exploring spinel-type SiTiN. A first task was to evaluate site preference of Ti<sup>4+</sup> substituting for Si<sup>4+</sup> in Si<sub>3</sub>N<sub>4</sub>. We chose to work in the conventional unit cell of the spinel structure comprising 56 atoms. In a structure model of Si<sub>23</sub>TiN<sub>32</sub> at ambient pressure, Ti prefers substitution of the octahedral site over a tetrahedral site. The energy difference we compute, however, is very small – only 0.01

eV. Increasing pressure increases slightly the preference for Ti to occupy the octahedral site to 0.07 eV at 15 GPa.

In a next step, we computed substitution of three Si by Ti simultaneously, still keeping  $\text{Ti}^{4+}$ . Thus, within the conventional unit cell we considered  $\text{Si}_{21}\text{Ti}_3\text{N}_{32}$  and performed a structure search over all possible combinations of three Ti on cation sites. The model with the lowest enthalpy that emerged displays three Ti in octahedral sites coordinating to the same N (see Figure 6a and 6b). The small cluster formed by three fused  $\text{TiN}_6$ -octahedra resembles a fragment of the rock-salt TiN structure, albeit in this case with  $\text{Ti}^{4+}$  rather than  $\text{Ti}^{3+}$  as in TiN. The next lowest enthalpy model, still containing only  $\text{Ti}^{4+}$  in octahedral sites is already 0.19 eV higher in energy (for the full 56 atom unit cell). The first model comprising Ti in a tetrahedral site comes out 0.28 eV higher in enthalpy than the ground state model of  $\text{Si}_{21}\text{Ti}_3\text{N}_{32}$ . Interestingly, the model of  $\text{Si}_{21}\text{Ti}_3\text{N}_{32}$  with highest enthalpy (about 3 eV higher than the ground state model) also comprises all Ti in octahedral sites, but arranged with maximum distance from each other.

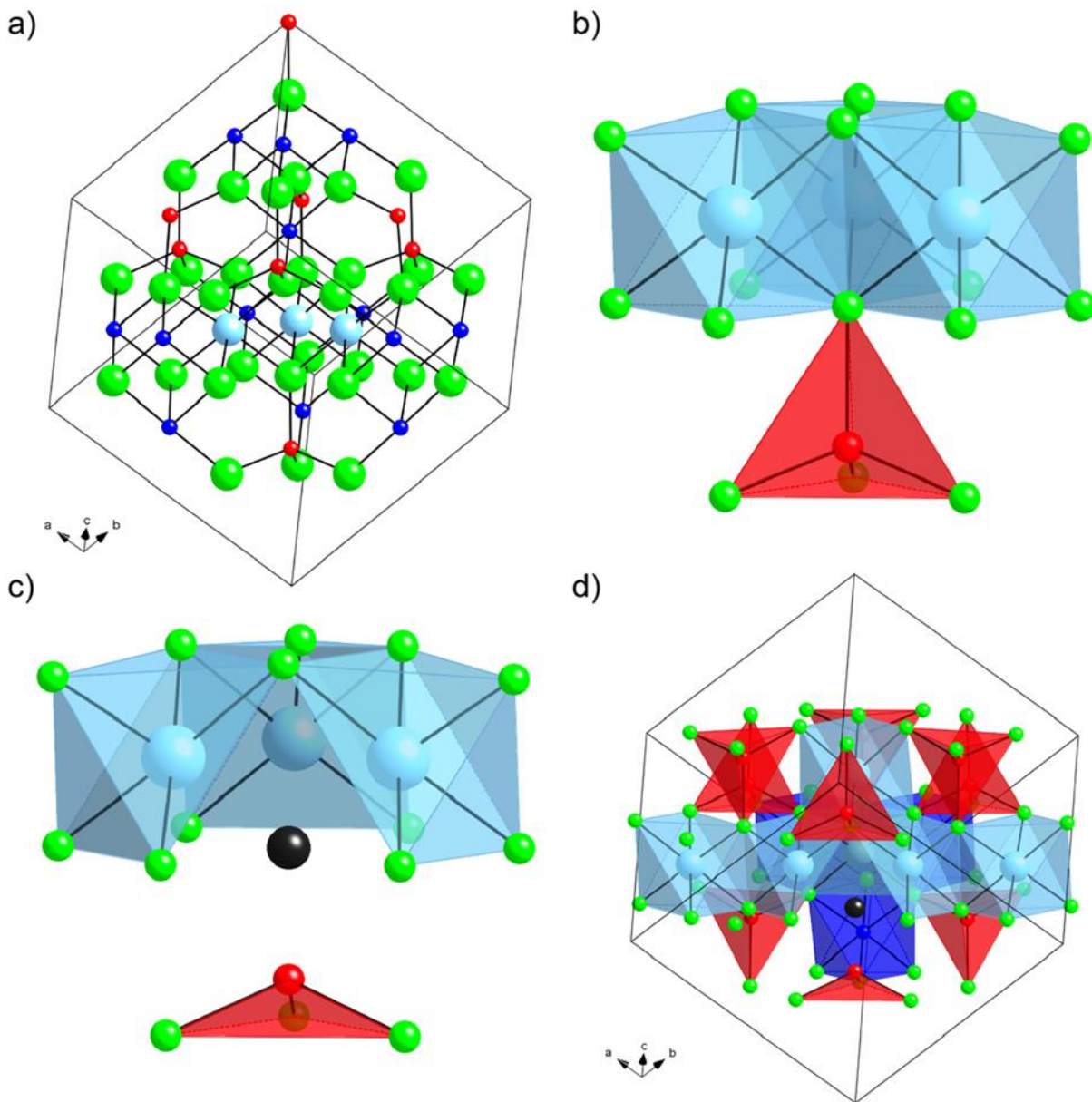


Figure 6: (a) Lowest-enthalpy structure of  $\text{Si}_{21}\text{Ti}_3\text{N}_{32}$  and (b) its arrangement of fused  $\text{TiN}_6$ -cluster. (c) Local environment of vacancy site in  $\text{Si}_{21}\text{Ti}_3\text{N}_{31}$  exhibiting  $\text{TiN}_5\text{V}$ -octahedra (d) Lowest-enthalpy structure of  $\text{Si}_{18}\text{Ti}_6\text{N}_{31}$  highlighting the chain of edge-sharing  $\text{TiN}_6$ -/ $\text{TiN}_5\text{V}$ -octahedra. Green spheres represent N, red and dark blue spheres tetrahedral and octahedral Si, respectively, and light blue (cyan) spheres Ti.

Introducing an anion vacancy does not change the picture of preferred cation arrangements in structures. Note that in models of  $\text{Si}_{21}\text{Ti}_3\text{N}_{31}$  all three Ti are (formally)  $\text{Ti}^{3+}$ . Again, we found that Ti prefers octahedral sites and tends to cluster. With the

vacancy in the model, the lowest enthalpy structure displays all Ti adjacent to the defect as  $\text{TiN}_5\text{V}$ -octahedra (see Figure 6c). Alternative arrangements are now a bit closer in energy, the second lowest-enthalpy structure is only 0.12 eV higher than the lowest-enthalpy model. Among all combinations, the highest enthalpy structure is still one in which all Ti are in octahedral, but maximally dispersed in the structure.

We finally expanded our search to  $\text{Si}_{18}\text{Ti}_6\text{N}_{31}$ . This model displays half of Ti as  $\text{Ti}^{4+}$  and the other half as  $\text{Ti}^{3+}$ . We limited our combinatorial search on Ti in octahedral sites, and computed only a few models explicitly considering tetrahedral Ti as well. The lowest enthalpy configuration of  $\text{Si}_{18}\text{Ti}_6\text{N}_{31}$  then shows only octahedral Ti, with three Ti in octahedral sites adjacent to the vacancy and the other Ti in different octahedral sites. Within the unit cell we considered, there now appears a chain of connected  $\text{TiN}_6$ - $\text{TiN}_5\text{V}$ -octahedra sharing edges along the [1 1 0] direction. Alternatives with more dispersed arrangements are less favorable in energy. This indicates once again the preference of Ti to cluster (see Figure 6d).

### **Enthalpy of formation.**

To compute enthalpies of formation,  $\Delta H_f$ , of the ternary SiTiN compounds we use  $\text{Si}_3\text{N}_4$ , TiN (for  $\text{Ti}^{3+}$ ), and spinel-type  $\text{Ti}_3\text{N}_4$  as reference models. Note that a spinel-type  $\text{Ti}_3\text{N}_4$  is not known, and only a  $\text{Th}_3\text{P}_4$ -type  $\text{Ti}_3\text{N}_4$  has been synthesized at 72 GPa in reference[18]. The lowest energy structure of  $\text{Ti}_3\text{N}_4$  comprising  $\text{Ti}^{4+}$  is predicted to adopt a monoclinic structure, as earlier studies have shown[23,24].

Despite the fact that spinel-type  $\text{Ti}_3\text{N}_4$  is not the ground state of  $\text{Ti}_3\text{N}_4$ , we nevertheless find only positive values for  $\Delta H_f$  of spinel-type SiTiN. This implies that its decomposition into binary compounds is favored by enthalpy. An anion vacancy and presence of some  $\text{Ti}^{3+}$  only increases the trend and so does pressure. With the  $\Delta H_f$  spinel-type SiTiN being positive, we turn to estimate the entropy of mixing,  $\Delta S_{\text{mix}}$ , arising from distributing Ti among the cation sites and a vacancy among anion sites[25,26].

Neglecting site preferences, which will only reduce our estimate of  $\Delta S_{\text{mix}}$ , we estimate an upper bound of  $\Delta S_{\text{mix}}$  of 749, 1160, 1430 J/(K·mol), for  $\text{Si}_{21}\text{Ti}_3\text{N}_{32}$ ,  $\text{Si}_{21}\text{Ti}_3\text{N}_{31}$ , and  $\text{Si}_{18}\text{Ti}_6\text{N}_{31}$ , respectively. Since less vacancies are present than Ti cations, the cation mixing contributes to the total entropy of mixing more than the anion mixing. With  $\Delta G = \Delta H_f - T\Delta S_{\text{mix}}$ , we estimate that it would require temperatures greater than 5000 K to “stabilize”  $\text{Si}_{21}\text{Ti}_3\text{N}_{31}$  and  $\text{Si}_{18}\text{Ti}_6\text{N}_{31}$  against decomposition into the ternary system  $\text{Si}_3\text{N}_4$ , TiN, and spinel-type  $\text{Ti}_3\text{N}_4$ . We also considered a superstructure of  $\alpha\text{-Si}_3\text{N}_4$  and substituted Si partially by Ti. This structure, thus, comprises tetrahedrally coordinated  $\text{Ti}^{4+}$  and may serve as a model for the precursor used during synthesis of spinel-type SiTiN. Not surprisingly, the lowest enthalpy structure of such a  $\text{Si}_{21}\text{Ti}_3\text{N}_{32}$  displays all Ti clustered and bonding to the same N. Moreover, we find that incorporation of Ti slightly reduces the pressure of the transition by 0.4 GPa, if we compare our models of  $\text{Si}_{21}\text{Ti}_3\text{N}_{32}$  and  $\text{Si}_{21}\text{Ti}_3\text{N}_{32}$  discussed above relative to pure  $\text{Si}_3\text{N}_4$  structures.

In summary, the occurrence of spinel-type SiTiN cannot be attributed to thermodynamical stability. A spinel-type  $(\text{Si},\text{Ti})_3\text{N}_4$  solid solution is less favorable than assemblages of separated phases of  $\text{Si}_3\text{N}_4$ , TiN, and  $\text{Ti}_3\text{N}_4$ . However, the spinel-type  $(\text{Si},\text{Ti})_3\text{N}_4$  solid solution is more favorable than the precursor system with tetrahedral  $\text{Ti}^{4+}$  mixed into a silicon nitride at 15 GPa. Therefore, formation of spinel-type  $(\text{Si},\text{Ti})_3\text{N}_4$  should be due to the sluggish kinetics, because formation of separate phases from the uniform precursor is a slower process than formation of a single phase of the spinel-type  $(\text{Si},\text{Ti})_3\text{N}_4$  solid solution.

### **Ti oxidation state.**

An interesting question is related to the different charge states identified for Ti in spinel-type  $(\text{Si},\text{Ti})_3\text{N}_4$ . The compound comprises both  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$ . For a characterization of charges, we compute the lowest energy configuration of  $\text{Si}_{21}\text{Ti}_3\text{N}_{32}$ ,  $\text{Si}_{21}\text{Ti}_3\text{N}_{31}$ , and  $\text{Si}_{18}\text{Ti}_6\text{N}_{31}$ , and use Bader charge analysis[27,28]. In  $\text{Si}_{21}\text{Ti}_3\text{N}_{32}$ , which displays  $\text{Ti}^{4+}$ , we

find 2.8 e<sup>-</sup> around the Ti according to the Bader charge analysis. On the other hand, Ti<sup>3+</sup> in Si<sub>21</sub>Ti<sub>3</sub>N<sub>31</sub> exhibits higher Bader charges of 3.2 e<sup>-</sup>. In Si<sub>18</sub>Ti<sub>6</sub>N<sub>31</sub>, which formally has equal proportions of Ti<sup>3+</sup> and Ti<sup>4+</sup>, we indeed find half of the Ti with Bader charges of 2.0 e<sup>-</sup>, while the other half displays Bader charges between 2.6 and 2.9 e<sup>-</sup>. This allows us to identify the two cohorts as Ti<sup>4+</sup> and Ti<sup>3+</sup>, respectively. Noteworthy is that Ti<sup>3+</sup> appears adjacent to the vacancy as TiN<sub>5</sub>V-octahedra, while Ti<sup>4+</sup> appears within TiN<sub>6</sub>-octahedra.

### Elastic properties.

We also computed elastic constants for all compounds and estimate elastic moduli ( $B$ ,  $G$ ) as well as Vickers hardness  $H_V$ , see Table 1. The Si<sub>3</sub>N<sub>4</sub> is a notably hard material[29], but adding Ti reduces elastic properties and decrease hardness. The estimated hardness of Si<sub>18</sub>Ti<sub>6</sub>N<sub>31</sub> comes out to be close of half of that of Si<sub>3</sub>N<sub>4</sub>.

Table 1: Bulk modulus  $B$ , shear modulus  $G$ , and Vickers hardness  $H_V$  of Si<sub>3</sub>N<sub>4</sub> and SiTiN compounds with the spinel structure type at ambient pressure using SCAN functional.

	<b>B (GPa)</b>	<b>G (GPa)</b>	<b>H<sub>V</sub> (GPa)</b>
<b>Si<sub>3</sub>N<sub>4</sub></b>	333	283	42
<b>Si<sub>21</sub>Ti<sub>3</sub>N<sub>32</sub></b>	327	248	33
<b>Si<sub>21</sub>Ti<sub>3</sub>N<sub>31</sub></b>	308	234	32
<b>Si<sub>18</sub>Ti<sub>6</sub>N<sub>31</sub></b>	292	204	26

### Electronic properties.

We compute the band gap of  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> to 4.95 eV using the screened hybrid HSE-functional[30]. This aligns with previous calculations and available experimental data[31]. Replacing Si<sup>4+</sup> by Ti<sup>4+</sup> introduces localized unfilled d-states below the conduction band, ultimately decreasing the width of the band gap. Introducing a single

nitrogen vacancy creates an odd number of  $\text{Ti}^{3+}$  and results in a partially filled band in the middle of the gap.

## Discussion

In summary, an amorphous SiTiN compound was synthesized by the reaction of perhydropolysilazane with tetrakis(dimethylamido)titanium and subsequent heat treatment in ammonia at  $1000^\circ\text{C}$ . The SiTiN was exposed to 15-20 GPa pressure and  $1800\text{-}2000^\circ\text{C}$  in a large volume press to form a high-pressure  $\gamma\text{-Si}_3\text{N}_4/\text{c-TiN}$  composite material for the first time. The special feature of the obtained composite is due to the discovery of an additional nanocrystalline ternary  $\gamma\text{-(Si,Ti)}_3\text{N}_4$  phase with spinel-type structure embedded within the majority of the submicron  $\gamma\text{-Si}_3\text{N}_4$  crystals. The  $\gamma\text{-(Si,Ti)}_3\text{N}_4$  phase was analyzed in detail by TEM and EELS and the results clearly showed the presence of two types of Ti atoms, namely  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$ , which in turn requires the formation of vacancies in the anion lattice. Therefore, the general formula of the discovered ternary spinel-type SiTiN has to be described as  $(\text{Si}^{4+}_{1-x}\text{Ti}^{4+}_{x-\delta}\text{Ti}^{3+\delta})_3\text{N}_{4-\delta}$ . According to theoretical calculations,  $\text{Ti}^{3+}$  appears adjacent to the vacancy as  $\text{TiN}_5\text{V}$ -octahedra, while  $\text{Ti}^{4+}$  appears within  $\text{TiN}_6$ -octahedra. Moreover, all of the ternary SiTiN compounds have been calculated to be thermodynamically unstable with respect to the binary phases, which is in accordance with the experimental result, that finally a binary  $\gamma\text{-Si}_3\text{N}_4/\text{c-TiN}$  high-pressure composite is formed.

In consequence, it has to be noted that the synthesis of the ternary spinel-type SiTiN phase is kinetically controlled and requires an appropriate precursor material (SSP) with  $\text{Ti}^{4+}$  atoms in tetrahedral coordination together with tetrahedrally coordinated Si in amorphous silicon nitride. A direct reaction of  $\text{Si}_3\text{N}_4$  with TiN to form a ternary high-pressure SiTiN phase is thermodynamically impossible and has not been observed yet experimentally. The present work encourages to study other SSP-derived Si-based

systems containing transition metal atoms other than Ti to form innovative high-pressure composite materials and novel inorganic ternary metal nitrides.

## **Methods**

### **Single-Source-Precursor Synthesis**

A single source precursor (SSP) of titanium-modified perhydropolysilazane (PHPS) was synthesized by a reaction between PHPS and tetrakis(dimethylamido)titanium (TDMAT) with a molar Si:Ti ratio 5:1 (labelled as PHPTiS5) according to our previous reports[19,20].

The manipulation of the PHPTiS5 sample was made in an argon-filled glove box (Jacomex, Campus-type; O<sub>2</sub> and H<sub>2</sub>O concentrations kept at 0.1 ppm and 0.8 ppm, respectively) to be ground in an agate mortar and then placed in alumina boats. Alumina boats containing the polymers were introduced in tubes under protective atmospheres (argon) to be transferred under argon flow into a silica tube inserted in a horizontal furnace [THERMOCONCEPT OS50/450/12]. After evacuation of the furnace under dynamic vacuum (0.1 mbar), the tube was refilled with ammonia up to atmospheric pressure and a continuous flow of ammonia was maintained through the tube. Subsequently, the samples were pyrolyzed at a heating rate of 5 °C min<sup>-1</sup> to 1000°C (dwell time for 2 h) in order to produce the SiTiN precursor (labelled as PHPTiS5\_1000). After cooling at a rate of 2°C min<sup>-1</sup> under nitrogen flow, the PHPTiS5\_1000 was used as a starting material for the subsequent high pressure synthesis.

The silicon and titanium contents of the synthesized SiTiN powders were measured by inductively coupled plasma/optical emission spectroscopy (ICP/OES) [Optima 8300 optical emission spectrometer Perkin Elmer, USA]. The carbon and the oxygen, nitrogen and hydrogen contents of the powders were determined by combustion elemental analysis [Carbon (EMIA-321V), O/N/H analyzer (EMGA-830) Horiba, Japan].



The phase composition of samples prepared at 1000°C was determined by powder X-ray diffraction (XRD) with a Bruker AXS D8 Discover and CuK $\alpha$  radiation. The scans were performed in the range of  $2\theta \in \langle 15^\circ; 90^\circ \rangle$  with a step of  $0.015^\circ$  and an exposure time of 0.7 s. The diffraction patterns were analyzed using the Diffrac + EVA software with the JCPDS-ICDD database.

### **High-Pressure Synthesis**

High-pressure high-temperature experiments were performed in a Hall-type six-ram LVP (mavo press LPQ6 1500-100; Max Voggenreiter GmbH, Germany) installed at the P61B beamline at DESY, Hamburg<sup>32</sup>. The samples were synthesized in a 14/7 or 10/4 assembly of eight tungsten carbide cubes (32 mm Fujilloy TF08) at the target pressures. A Cr<sub>2</sub>O<sub>3</sub>-doped MgO octahedron was used as the pressure-transmitting medium. The starting material was cold pressed into pellet form ( $h = 1.6$  mm,  $\phi = 1.9$  mm) using a platinum foil before placing in the MgO tube. The octahedral assembly was compressed to a pressure of 16 and 20 GPa and, at pressure, heated to a chosen temperature in the range of 1800 - 2000°C and held for 30 min. Pressure was calibrated at room temperature using the semiconductor to metal transition of GaP at 22 GPa<sup>[33]</sup>. Sample temperatures were estimated using power-temperature relations calibrated in a separate run using a W5%Re/W26%Re thermocouple (C-type). Overview of experimental conditions with the corresponding run numbers are given in Table 2.

Table 2: Overview of HP-HT experiments with run number, assembly, pressure, temperature, heating duration and capsule materials.

Run No	Sample	Assembly	Pressure (GPa)	Temperature (°C)	Heating duration (min)	Capsule material
HH113	SiTiN-II	14/7	16	1800	30	Pt
HH109	SiTiN-II	10/4	20	1800	30	Pt
HH112	SiTiN-II	10/4	20	2000	20	Pt

After recovery, each sample was found dense and fine-grained in appearance (see Figure 7).

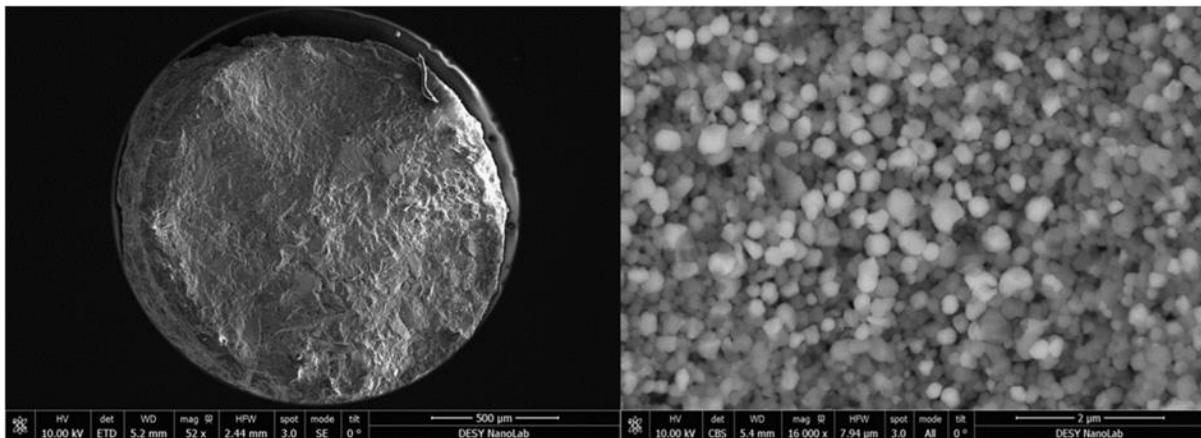


Figure 7: SEM micrographs (run# HH112) showing (left) an overview of the sample pellet after HP-HT and (right) a fracture surface with spinel-type  $\gamma$ - $\text{Si}_3\text{N}_4$  and rock salt-type  $c$ -TiN crystals. XRD of crushed samples was obtained using synchrotron radiation at the high-resolution powder diffraction beamline P02.1 of PETRA-III, DESY, Hamburg. The XRD pattern was quantitatively analyzed by Rietveld refinement with the program GSAS-II[34].

### Electron Microscopy

For the preparation of electron transparent thin specimen, the synthesized bulk sample was processed by focused ion beam (Helios G4, Thermo Fisher Scientific) and subsequently, to clean the specimen, Ar ion beam milling was performed at 0.5 kV in the final step. For the atomic and electronic structure analysis, we used an aberration-corrected STEM (JEM ARM-200CF, JEOL Ltd.), equipped with an annular dark-field (ADF) and annular bright-field (ABF) detectors, EEL spectrometer (Enfinium, Gatan Inc.) and dual electron dispersive X-ray (EDX) spectrometers. The electron microscope was operated at 200 kV. For atomic-scale imaging and spectroscopy, the illumination semi-angle was 24 mrad, and the ABF and ADF detectors span from 12 to 24 and 64 to 200 mrad, respectively, where a typical beam current was 20 pA.

### **Computational Method**

All calculations were performed using density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP).[35-38] For correlation and exchange we use the Strongly Conserved and Appropriately Normed (SCAN) functional together with the projector-augmented-wave (PAW) method.[39-41] Reported results were obtained using a plane wave cut-off energy of 500 eV. We sample the Brillouin zone of the conventional unit cell and all derived structures using a  $2 \times 2 \times 2$   $k$ -point mesh. With parameters reported above, enthalpy differences between structures are converged to better than 0.005 eV per conventional unit cell. Different models of spinel-type  $\text{Si}_{21}\text{Ti}_3\text{N}_{32}$  and  $\text{Si}_{21}\text{Ti}_3\text{N}_{31}$  were investigated by testing all the possible combinations of Ti at Si octahedral and tetrahedral sites. We first identified lowest enthalpy structures by static calculations without further relaxation. Structures with low enthalpies were further optimized until forces converged to 0.01 eV/Å and residual stresses are below 0.01 GPa. It turned out that this optimization does not change the ranking of the models to a significant extent. Lowest enthalpy models of each composition were further optimized

(forces converged to 5 meV/Å) and used for subsequent calculations. The lowest enthalpy model of  $\text{Si}_{18}\text{Ti}_6\text{N}_{31}$  attained monoclinic structure (SpGr.  $C1m1$  (8);  $a=7.905$  Å,  $b = 7.905$  Å,  $c=7.923$  Å,  $\alpha = 89.94^\circ$ ,  $\beta = 89.94^\circ$ ,  $\gamma = 89.68^\circ$ ), but displayed only small distortion away from a pseudo-cubic cell. Substituting Ti for Si increases the cell volume relative to spinel- $\text{Si}_3\text{N}_4$  even in models with a vacancy.

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## **Author contributions**

Abhijeet Lale and Samuel Bernard synthesized the single-source precursor and characterized the composition and molecular structure. Shrikant Bhat designed and performed the high-pressure experiments. Robert Farla supported and helped the high-pressure study. Ryo Ishikawa and Wei Zhang investigated the high-pressure samples by electron microscopic methods. Shariq Haseen and Peter Kroll worked on the computational part and Leonore Wiehl on the crystal structure analysis via Rietveld refinement. Ralf Riedel, Yuichi Ikuhara and Tomoo Katsura conceived the project and wrote the paper with input from the other authors.

## **Competing interests**

The authors declare no competing interests.



## Summary

A ternary spinel-type  $(\text{Si}_{1-x}, \text{Ti}_x)_3\text{N}_4$  compound with spinel-structure type is fortuitously discovered during high-pressure experiments as nanocrystals embedded in spinel- $\text{Si}_3\text{N}_4$  in a mixture of c-TiN and spinel- $\text{Si}_3\text{N}_4$ . In spinel-type  $(\text{Si}_{1-x}, \text{Ti}_x)_3\text{N}_4$ , Ti atoms are substituted at different Si sites found in spinel- $\text{Si}_3\text{N}_4$ . We perform combinatorial analysis with DFT[1] and find that Ti slightly prefers substitution of octahedral sites over tetrahedral sites in spinel-type  $(\text{Si}_{1-x}, \text{Ti}_x)_3\text{N}_4$ , though only with a small energy gain of -0.01 eV/56 atoms. In the lowest enthalpy structures of spinel-type  $(\text{Si}_{1-x}, \text{Ti}_x)_3\text{N}_4$  that we found, Ti occupied all octahedral sites and exhibited clustering behavior. Next, we computed the enthalpy of formation of the lowest enthalpy ternary compound from its binary phases. We found that the decomposition of spinel-type  $(\text{Si}_{1-x}, \text{Ti}_x)_3\text{N}_4$  into its binary phases is thermodynamically favored even if entropy of mixing is taken into account. However, because the precursor that led to the synthesis of spinel-type  $(\text{Si}_{1-x}, \text{Ti}_x)_3\text{N}_4$  contained tetrahedral Ti, which are highly disfavored in spinel-type  $(\text{Si}_{1-x}, \text{Ti}_x)_3\text{N}_4$  the formation of spinel-type  $(\text{Si}_{1-x}, \text{Ti}_x)_3\text{N}_4$  likely occurred due to sluggish kinetics. Bader charge analysis[2] indicated that both  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$  were present in structures of spinel-type  $(\text{Si}_{1-x}, \text{Ti}_x)_3\text{N}_4$  corroborating experimental results. Although, assigning the oxidation state of Ti atoms with Bader charge analysis alone was not possible. Additionally, we found that spinel-type  $(\text{Si}_{1-x}, \text{Ti}_x)_3\text{N}_4$  has lower bulk modulus, shear modulus, hardness than spinel- $\text{Si}_3\text{N}_4$  as well as having a smaller band gap.

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### Motivation and Scope

Graphene is a 2D material that has been intensely studied since Novoselov et al.[1, 2] first synthesized free graphene. Investigations suggest that the properties of graphene change if it is bonded to a substrate, and its properties also depend on the identity of the substrate[3, 4]. We study the work of adhesion in potential lithium-ion anode systems consisting of graphene and a second component, either a bilayer-SiO<sub>2</sub> or a (001) SiC surface terminated with oxygen. Additionally, we perform Bader charge analysis[5] to determine the impact of charge transfer on the work of adhesion of each system we study.

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## Work of adhesion in graphene-SiO<sub>2</sub> and graphene-SiCO

### Introduction

Graphene has been the focus of numerous investigations since it was first synthesized[1, 2]. The two-dimensional (2D) nature of graphene makes it a promising candidate for complementary metal-oxide-semiconductor (CMOS) design[3]. Additionally, graphene exhibits carrier mobility greater than 200,000 cm<sup>2</sup>/Vs[4] and reversible capacity between 540 – 835 mAh/g as an anode in lithium-ion batteries[5, 6]. As an anode, graphene has been combined with silicon, which by itself has a theoretical reversible capacity of 4200 mAh/g but undergoes volume expansion up to 400% during cycling[7] resulting in disintegration of the anode. Silicon-graphene composites have been synthesized and exhibited high capacity retention [8] and storage capacity up to 2200 mAh/g[9].

There have been several investigations of the work of adhesion between graphene and various systems[10, 11]. Additionally, substantial work has been done on the work of adhesion between SiO<sub>2</sub> and graphene. In 2011, Koenig et al.[12] measured the work of adhesion between monolayer graphene and a SiO<sub>2</sub>-substrate using a pressurized blister test and reported a value of  $0.45 \pm 0.02$  J/m<sup>2</sup>. In 2013, Boddeti et al[13] reported a work of adhesion value of 0.24 J/m<sup>2</sup> between graphene and SiO<sub>2</sub> by also performing pressurized blister tests. Meanwhile, Gao et al.[14] calculated 0.349 J/m<sup>2</sup> for work of adhesion associated with graphene and reconstructed silicon dioxide surfaces.

Considering the recent synthesis of a 2D bilayer of SiO<sub>2</sub> on graphene[15], we investigate potential anode materials consisting of a graphene-SiO<sub>2</sub>-bilayer system as well as additional graphene-Si<sub>2</sub>CO<sub>2</sub> systems. Through first-principles calculations, we calculate the work of adhesion between compound systems of graphene and SiO<sub>2</sub>/Si<sub>2</sub>CO<sub>2</sub>. Using Bader charge analysis[16], we determine the impact of charge transfer on calculated work of adhesion values.

## Method

Spin-polarized density functional theory calculations were carried out with the Vienna ab initio Simulation Package (VASP)[17-20]. Exchange-correlation was described by the PBE functional[21, 22], and calculations used the projector-augmented wave method (PAW)[23] with a  $E_{\text{kin}} = 500$  eV. Forces were converged to  $50$  meV/Å. Additionally, since PBE does not correctly describe dispersion interactions, calculations were done with the Tkatchenko-Scheffler method[24] (DFT-TS), the universal low gradient method[25] (DFT-ulg), and Hamada's nonlocal van der Waals density functional[26] (DFT-vdW-DF2-B86R). A  $k$ -point set of  $2 \times 2 \times 2$  was used for calculations of graphite and a  $k$ -point set of  $1 \times 1 \times 1$  was used for all other calculations when sampling the Brillouin zone[27]. Work of adhesion was calculated by taking the difference between the energy of an unrelaxed structure with "infinite" interlayer separation distance ( $d_{\infty} = 20$  Å) and the energy of an optimized structure with equilibrium interlayer separation distance ( $d_0$ ) and dividing by the cross-sectional area of the interface  $A$  (see Equation 1). Bader charge analysis was performed using the Bader Charge Analysis code[28, 29] developed by the Henkelman Group.

$$\text{Work of adhesion} = \frac{E_{d_{\infty}} - E_{d_0}}{A} \quad (1)$$

## Models

We investigated three different compound systems: graphene-bilayer-SiO<sub>2</sub>, graphene-15Si<sub>2</sub>CO<sub>2</sub>, and graphene-16Si<sub>2</sub>CO<sub>2</sub>. To model the graphene-bilayer-SiO<sub>2</sub> system we combined a supercell of graphene (150 atoms) with a bilayer of SiO<sub>2</sub> (64 SiO<sub>2</sub>). The bilayer-SiO<sub>2</sub> model itself was constructed of two layers of [SiO<sub>4</sub>]-tetrahedra.

Additionally, we constructed two graphene-Si<sub>2</sub>CO<sub>2</sub> models. Two (001) surfaces of SiC were terminated with oxygen and then extended into supercells of  $3 \times 5 \times 1$  and  $4 \times 4 \times 1$ . The

$3 \times 5 \times 1$  supercell had a composition of  $15\text{Si}_2\text{CO}_2$  and was combined with a supercell of graphene (48 atoms) to yield a graphene- $15\text{Si}_2\text{CO}_2$ . Meanwhile, the  $4 \times 4 \times 1$  supercell had a composition of  $16\text{Si}_2\text{CO}_2$  and was combined with a supercell of graphene (60 atoms) to yield a graphene- $16\text{Si}_2\text{CO}_2$  system. Lattice parameters are given in Table 1. For reference, we also performed calculations on graphite with 6 graphene layers with ABABAB-stacking (12 atoms).

Table 1: Lattice parameters a and b for graphene- $15\text{Si}_2\text{CO}_2$ , graphene- $16\text{Si}_2\text{CO}_2$ , and graphene-bilayer- $\text{SiO}_2$  optimized with different dispersion correction methods

	graphene- $15\text{Si}_2\text{CO}_2$		graphene- $16\text{Si}_2\text{CO}_2$		graphene-bilayer- $\text{SiO}_2$	
	<u>a (Å)</u>	<u>b (Å)</u>	<u>a (Å)</u>	<u>b (Å)</u>	<u>a (Å)</u>	<u>b (Å)</u>
DFT-ulg	8.6499	14.7040	12.1710	12.4442	21.2688	18.4193
DFT-TS	8.6612	14.7266	12.1851	12.4578	21.2736	18.4235
DFT-vdW-DF2 B86R	8.6735	14.7441	12.1989	12.4730	21.2959	18.4427

## Results

### Work of adhesion

Using different dispersion correction methods, we calculated work of adhesion (see Table 2). Calculations of the work of adhesion for graphite by the various dispersion correction methods generally agree with experiment[30]. Although DFT-DF functionals typically overestimate the equilibrium interlayer separation distance between layers  $d_0$ [31], the DFT-DF2-B86R functional calculates  $d_0$  close to those of the Tkatchenko-Scheffler and universal low gradient dispersion correction methods. Results from all van der Waals correction methods predict the work of adhesion between graphene for both  $\text{Si}_2\text{CO}_2$  slabs and the bilayer- $\text{SiO}_2$  slab to be lower than the work of adhesion of graphite. Work of

adhesion is higher for the graphene-Si<sub>2</sub>CO<sub>2</sub> systems than for the graphene-bilayer-SiO<sub>2</sub> system.

Table 2: Work of adhesion (J/m<sup>2</sup>) for graphite, graphene-15Si<sub>2</sub>CO<sub>2</sub>, graphene-16Si<sub>2</sub>CO<sub>2</sub>, and graphene-bilayer-SiO<sub>2</sub>

	graphite	graphene- 15Si <sub>2</sub> CO <sub>2</sub>	graphene- 16Si <sub>2</sub> CO <sub>2</sub>	graphene- bilayer-SiO <sub>2</sub>
DFT-ulg	0.41	0.37	0.37	0.27
DFT-TS	0.58	0.46	0.45	0.33
DFT-vdW-DF2-B86R	0.39	0.29	0.29	0.25
Exp.	0.39 ± 0.02[30]	-	-	-

Generally,  $d_0$  of the graphene-Si<sub>2</sub>CO<sub>2</sub> systems is smaller than  $d_0$  of graphene-bilayer-SiO<sub>2</sub>. For graphene-16Si<sub>2</sub>CO<sub>2</sub> there are 16 O atoms on the relevant side of the Si<sub>2</sub>CO<sub>2</sub> slab interacting with 60 carbon atoms in the graphene layer leading to a 0.267 O: 1 C ratio (0.11 O atoms/Å<sup>2</sup> of graphene). Similarly, graphene-15Si<sub>2</sub>CO<sub>2</sub> has an oxygen surface density of 0.11 O atoms/Å<sup>2</sup> of graphene. Meanwhile, for graphene-bilayer-SiO<sub>2</sub> there are 48 O atoms on the relevant side of the bilayer-SiO<sub>2</sub> slab interacting with 150 C atoms in the graphene layer. Thus, there is a surface density of 0.12 O atoms/Å<sup>2</sup> of graphene. Considering the similar oxygen surface densities of each system, it is unlikely that repulsion between the surface O of each Si<sub>2</sub>CO<sub>2</sub>/bilayer-SiO<sub>2</sub> surface and graphene is responsible for the difference in  $d_0$  between the graphene-Si<sub>2</sub>CO<sub>2</sub> systems and graphene-bilayer-SiO<sub>2</sub>.

Table 3: Interlayer equilibrium separation distance ( $d_0$ ) in Å for graphite, graphene-15Si<sub>2</sub>CO<sub>2</sub>, graphene-16Si<sub>2</sub>CO<sub>2</sub>, and graphene-bilayer-SiO<sub>2</sub>

	graphite	graphene- 15Si <sub>2</sub> CO <sub>2</sub>	graphene- 16Si <sub>2</sub> CO <sub>2</sub>	graphene- bilayer-SiO <sub>2</sub>
DFT-ulg	3.34	3.10	3.08	3.20
DFT-TS	3.32	3.06	3.06	3.18
DFT-vdW-DF2- B86R	3.33	3.09	3.07	3.17
Exp.	3.34[32]	-	-	-

### Charge analysis

In order to determine the impact of charge transfer between the two components of the graphene-SiO<sub>2</sub>/Si<sub>2</sub>CO<sub>2</sub> systems on the work of adhesion, we calculate Bader charges for each component of the compound systems optimized with DFT-ulg (see Table 4). Bader charge analysis indicates charge transfer occurs between the two components of a compound model. Generally, the bilayer-SiO<sub>2</sub>/Si<sub>2</sub>CO<sub>2</sub> component of each compound model accumulates charge while the graphene component is depleted of charge. The magnitude of the largest charge transfer is between 0.0033 e<sup>-</sup>/Å<sup>2</sup> which is smaller than even the charge transfer between small organic molecules on an MoS<sub>2</sub> monolayer (0.005 – 0.025 e<sup>-</sup>/Å<sup>2</sup>)[33].

Table 4: Changes in Bader charges ( $e^-$ ) ( $q_{\text{compound}} - q_{\text{isolated-component}}$ ) for each component of the compound graphene-SiO<sub>2</sub>/Si<sub>2</sub>CO<sub>2</sub> systems optimized within DFT-ulg. Positive values indicate charge accumulation in the compound model and negative values indicate charge depletion

	bilayer-SiO <sub>2</sub> /Si <sub>2</sub> CO <sub>2</sub>	graphene
graphene-bilayer-SiO <sub>2</sub>	+0.00317	-0.00317
graphene-15Si <sub>2</sub> CO <sub>2</sub>	+0.00330	-0.00330
graphene-16Si <sub>2</sub> CO <sub>2</sub>	+0.00251	-0.00251

## Summary

We calculated the work of adhesion energies of interfaces formed between graphene and a bilayer-SiO<sub>2</sub> and graphene and Si<sub>2</sub>CO<sub>2</sub>. In order to correct for the poor description of dispersion interactions in standard PBE we performed calculations with several different van der Waals correction methods and functionals. Results produced by all dispersion correction methods generally agreed well with experiment for graphite. Although there is a large range of reported values for the work of adhesion between SiO<sub>2</sub> and graphene, our calculated work of adhesion value for graphene-bilayer-SiO<sub>2</sub> falls within that range.[12-14]

Work of adhesion values in the graphene-Si<sub>2</sub>CO<sub>2</sub> systems were significantly larger than work of adhesion in the graphene-bilayer-SiO<sub>2</sub> system. In order to determine why work of adhesion values differed between the graphene-Si<sub>2</sub>CO<sub>2</sub> systems and the graphene-bilayer-SiO<sub>2</sub> system we investigated the role charge transfer within the compound systems. While Bader charge analysis did indicate that there was charge transfer taking place from graphene to the Si<sub>2</sub>CO<sub>2</sub>/bilayer-SiO<sub>2</sub> surface in each system, the magnitude of the charge transfer is likely too small to explain the differences in the



work of adhesion between the graphene-Si<sub>2</sub>CO<sub>2</sub> systems and the graphene-bilayer-SiO<sub>2</sub> system.

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## Summary

We investigated the work of adhesion associated with interfaces formed between systems of graphene and a bilayer-SiO<sub>2</sub>, which has been recently synthesized[1], graphene and 15Si<sub>2</sub>CO<sub>2</sub>, and graphene and 16Si<sub>2</sub>CO<sub>2</sub>. Calculations were done with several different van der Waals correction methods and functionals to account for dispersion interactions. Results produced by all dispersion correction methods agreed well with experiment for our reference structure of graphite. Additionally, our calculated work of adhesion value for graphene-bilayer-SiO<sub>2</sub> agreed with experiment[2] We found that work of adhesion in graphene-Si<sub>2</sub>CO<sub>2</sub> was larger than work of adhesion in graphene-bilayer-SiO<sub>2</sub>. Consequently, we investigated the impact of charge transfer on the work of adhesion for our compound systems. Bader charge analysis[3] did indicate that there was charge depletion of graphene and charge increase on the Si<sub>2</sub>CO<sub>2</sub>/bilayer-SiO<sub>2</sub> surface in each system, but the magnitude of charge transfer was smaller than the charge transfer associated with the adsorption of small molecules on a surface.[4]

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## PART II: CALCULATION AND SIMULATION OF AMORPHOUS CERAMICS

CHAPTER 1: ANALYZING THE EFFECT OF COMPOSITION, DENSITY, AND  
THE MORPHOLOGY OF THE “FREE” CARBON PHASE ON ELASTIC MODULI IN  
SILICON OXYCARBIDE CERAMICS

Motivation and Scope

Several studies have been done on the mechanical properties of SiCO polymer-derived ceramics[1, 2]. Sorarù et al.[3] reported that Young’s modulus of SiCO with free carbon increases with increasing free carbon content but decreases with decreasing density. However, synthesis of the samples conflated free carbon content and density. Through molecular dynamics simulations, we compute elastic properties of SiCO with varying compositions of the glass, free carbon content, density, and free carbon structure. By independently varying free carbon content and density, we calculate how each quantity impacts elastic properties. Additionally, by varying the free carbon morphology while keeping composition and density constant, we assess the impact of free carbon morphology on elastic properties.

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## **Analyzing the Effect of Composition, Density, and the Morphology of the “free” Carbon Phase on Elastic Moduli in Silicon Oxycarbide Ceramics**

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### **Abstract**

We perform atomistic simulations to model structures and calculate elastic properties of silicon oxycarbide ceramics. We explore individual parameters – composition, density, carbon content – to disentangle mutual dependencies that are difficult to separate in experimental studies. Each parameter is studied through dynamic simulations at finite temperatures for a wide range of temperatures. With multi-million atom models in simulation boxes as large as 40 nm, we reveal a hitherto “hidden” parameter: the morphology of the “free” carbon phase. Embedding, distribution, and interconnection of the carbon phase inside the amorphous matrix of SiCO severely impact the material's mechanical properties. As a consequence, we call for the development of new characterization techniques that will quantify the morphology of carbon in this and similar systems.

### **Keywords**

silicon oxycarbide, free carbon morphology, elastic properties, molecular dynamics

## Introduction

Silicon oxycarbide (SiCO) ceramics have attracted much interest over the last decades[1]. They exhibit remarkable structural stability and chemical durability[2, 3], oxidation resistance[4, 5], and unusual creep resistance[6-8]. There are a variety of potential applications for SiCO ceramics, including usage as anode material in Li-ion batteries[9, 10], as heating elements for pencil-type glow plugs[11], and as coatings[12]. The properties and structural characteristics of SiCO ceramics depend on the precursor materials and processing conditions, particularly on the maximum temperature reached during the pyrolysis step of the precursor-to-ceramic conversion process. Pyrolysis temperatures must reach around 1273 K to yield a single-phase amorphous  $\text{SiC}_x\text{O}_y$ [13]. Meanwhile, pyrolysis between 1273 K and 1723 K results in phase separation of the amorphous SiCO ceramic into crystalline SiC and amorphous  $\text{SiO}_2$ [14, 15]. Furthermore, if the composition of the amorphous SiCO displays excess carbon besides SiC and  $\text{SiO}_2$ , then a “free” carbon phase  $\text{C}_{\text{free}}$ , with carbon bonding (almost) exclusively to carbon, forms. The resulting composition is  $\text{SiC}_x\text{O}_y = (y/2)\text{SiO}_2 + (1 - y/2)\text{SiC} + (x + y/2 - 1)\text{C}_{\text{free}}$ . Exceeding a pyrolysis temperature of 1723 K usually results in amorphous  $\text{SiO}_2$  and SiC nanocrystals encased by turbostratic carbon[14].

Multiple studies addressed the origin and structural evolution of the excess carbon phase[16, 17] A detailed summary of current understanding is presented in a recent review[18]. For pyrolysis temperatures lower than 1073 K, excess carbon has only begun to segregate and is amorphous, hydrogenated, and still dispersed in the ceramic matrix[19]. Increasing pyrolysis temperatures to 1073 K – 1273K results in a “free” carbon phase described as 2-3 layers thick turbostratic carbon saturated with hydrogen at the periphery[20]. Pyrolysis temperatures higher than 1273 K – 1473 K eliminate hydrogen from peripheral carbons and yield extended carbon layers. Above pyrolysis



temperatures of 1673 K, the excess carbon phase forms graphite nanocrystallites or an entangled network of single- or multi-layered graphene[18].

The mechanical properties of SiCO have been studied at ambient and elevated temperatures. Rouxel et al. were among the first to explore the high-temperature behavior of SiCO glasses[21]. They proposed that the Young's modulus of SiCO can be calculated using a simple rule of mixture using volume fractions of constituent phases. Since graphite has lower elastic moduli than SiC and SiO<sub>2</sub>, it is generally inferred that SiCO with high free carbon content displays low moduli when compared to SiCO with low free carbon content – provided that the ratio SiC to SiO<sub>2</sub> is comparable. This trend appears to be supported by a recent study by Sorarù et al., who synthesized SiCO glasses with varying amounts of free carbon and provided a thorough comparative study of Young's modulus and hardness[22]. The impact of the pyrolysis temperature on mechanical properties is also of interest for ceramic matrix composites (CMCs) that use a SiCO matrix and/or SiCO fibers embedded into a ceramic matrix[23, 24].

In contrast to many experimental studies, only a few computational investigations relate to SiCO. Early on, we used density functional theory (DFT) and ab initio molecular dynamics to investigate structure and elastic moduli of amorphous SiCO[25]. Subsequent work addressed interfacial bonding between glassy SiCO and the free carbon phase[26]. Further atomistic simulations with empirical potentials investigated some temperature-dependency of mechanical properties[27, 28].

In this study, we focus on the elastic properties of amorphous SiCO, including different amounts of “free” carbon,  $C_{\text{free}}$ . We perform atomistic simulations using an empirical potential to investigate how elastic moduli depend on various parameters, namely composition of the amorphous SiCO glass matrix, density,  $C_{\text{free}}$  content, and the particular morphology the  $C_{\text{free}}$  attains. We also study the temperature dependency of moduli. Significant computer resources facilitate us to examine each parameter individually, enabling us to disentangle dependencies that are difficult to separate in

experimental studies. Anticipating our results, we show that – for the same composition and density – the impact of carbon morphology on mechanical properties is considerable.

## **Method**

In previous work, we generated SiCO models using an approach based on the Wooten, Winer, and Waire (WWW) algorithm and optimized these models within density functional theory (DFT)[25, 26]. While DFT calculations are highly accurate, they are also computationally expensive, thus limiting the size of models and the extent of simulations. Calculations using the Tersoff potential, an empirical bond-order potential, are much faster than DFT calculations, and models can routinely be as large as millions of atoms. Simulations can extend for microseconds if needed. Models generated with the Tersoff potential, on the other side, display structural imperfections. Nevertheless, the Tersoff potential reproduces mechanical properties adequately[27, 28], even though the specific parametrization of the potential in some cases does impact the magnitude of trends[29].

Throughout this work, we perform molecular dynamics simulations implemented in the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)[30]. Interactions are described via the Tersoff potential[31, 32]. Si–Si, Si–C, and C–C interactions are parameterized by Tersoff[31-33]. Si–O interactions are parameterized by Munetoh et al.[34]. Similar to previous studies, we treat interactions between O atoms or between C and O as repulsive only, based on spectroscopic evidence[2]. We generate SiCO models through a melt-quench process: randomly positioned Si, C, and O atoms are heated from 0 K to temperature  $T_{\max}$  at a rate of 10 K/ps. For the critical parameter  $T_{\max}$ , we choose temperatures between 2000 and 8000 K. At  $T_{\max}$ , the system is equilibrated for 200 ps and then cooled to 300 K at a rate of 10 K/ps. All simulations are done at constant volume to fix density. We performed additional simulations using different equilibration times and cooling rates. Overall, we find that carbon morphology in models is almost

completely determined through  $T_{\max}$ . Longer equilibration times, we tested up to 100 ns at  $T_{\max}$ , have some impact. However, changes that occur when increasing  $T_{\max}$  by just 50 K are similar to an extension of equilibration time by a factor of 20 to 100. A slower cooling rate, e.g. 1 K/ps, does not change the morphology of carbon segregations but reduces the fraction of local defects in the final structure. Most importantly, it has a negligible impact on mechanical properties. Throughout our simulations, we use a time step of 1 fs to integrate the equations of motion.

In this study, we explore the impact of compositions and densities on the mechanical properties of SiCO. Addressing the composition of the stoichiometric SiCO glass matrix, we model three different compositions:  $\text{SiO}_2$ ,  $\text{Si}_5\text{CO}_8$  ( $=\text{SiC}_{0.2}\text{O}_{0.8}$ ), and  $\text{Si}_2\text{CO}_2$  ( $=\text{SiC}_{0.5}\text{O}$ ). This reflects 0, 20, and 50 mol-% SiC content, respectively. For each glass composition, we then build models with four different free carbon contents by adding as many C atoms as to achieve a ratio of  $C_{\text{free}}:\text{Si}$  of 0.5, 1, 2, and 3. Thus,  $\text{Si}_5\text{CO}_8$  with  $C_{\text{free}}$  corresponding to a ratio  $C_{\text{free}}:\text{Si} = 2$  has the composition  $\text{Si}_5\text{CO}_8:10 \cdot C_{\text{free}} = \text{Si}_5\text{C}_{11}\text{O}_8$ . Overall, this yields  $3 \cdot 4 = 12$  different compositions that we explore. Structures for each composition are then generated at five different densities (1.4–2.2 g/cm<sup>3</sup>). Furthermore, we generate models of each system for five different  $T_{\max}$ , 2000, 3000, 4000, 6000, and 8000K, to examine various free carbon morphologies. Finally, we generate three independent models by choosing different initial random numbers for each set of model parameters (glass composition,  $C_{\text{free}}$  content, density,  $T_{\max}$ ). In total, this yields  $(3 \cdot 4) \cdot 5 \cdot 5 \cdot 3 = 900$  models.

When developing models for this study, we realized that the simulation box size can constrain the morphology of the free carbon phase. This is particularly important for models with high carbon content and for models that display segregation. Modeling structural features of a particular dimension requires a simulation at a significantly larger length scale. For our study, models with a simulation box size between 7 and 10 nm are necessary to develop extended nano-sized carbon networks. Consequently, the models we

generate contain between 24,000 and 50,000 atoms in cubic boxes with side lengths between 7 and 10 nm. Figure 1 shows two models of  $\text{Si}_2\text{CO}_2 + \text{C}_{\text{free}}$  (24,576 atoms) with different densities. For each model, we display once all atoms (Figure 1 **a**, **b**) and then the C atoms only (Figure 1 **c**, **d**). Subsequent models' figures will display the C atoms only to highlight characteristics of carbon morphology. For consistency checks and to explore the impact of periodic boundary conditions, we modeled one composition,  $\text{Si}_5\text{CO}_8 + 10\text{C}_{\text{free}}$ , with a density of  $2.2 \text{ g/cm}^3$  in 8-fold and 64-fold sizes following the same simulation protocol as described above. The largest model, thus, comprises 2.52 million atoms and has a box length of  $\sim 40 \text{ nm}$ . We find through this scaling analysis that, albeit some subtle differences emerge and will be discussed, our choice of models is sufficient for exploring mechanical properties.

After model generation, we compute the elastic constants  $c_{ij}$  of each model through dynamic simulations at temperatures from 100 to 2000 K[35]. Temperatures for dynamic simulations of moduli are not to be confused with  $T_{\text{max}}$ , the temperature used for generating a particular model. For each model, 13 short simulations are performed: one for the initial state, six positive deformations, and six negative deformations. The first simulation is done to determine the initial state of the structure without deformation by equilibrating at a target temperature. During the other 12 simulations, models are deformed by 0.5% in a selected direction and equilibrated at the target temperature for 1.0 ps. Subsequently, the stress tensor is sampled 10 times every 0.1 ps within a 0.3 ps interval, and elastic constants are computed from the pressure tensor. The results of positive and negative deformations are averaged for each elastic constant. Application of the Voigt-Reuss-Hill approximation[36-38] to the calculated elastic constants yields values for bulk modulus,  $B_0$ , shear modulus,  $G$ , and Young's modulus,  $E$ . Using this method, we calculate the bulk modulus of cubic SiC to be 225 GPa at 300 K, which agrees with the value reported by Tersoff (220 GPa)[32].

## Results and Discussion

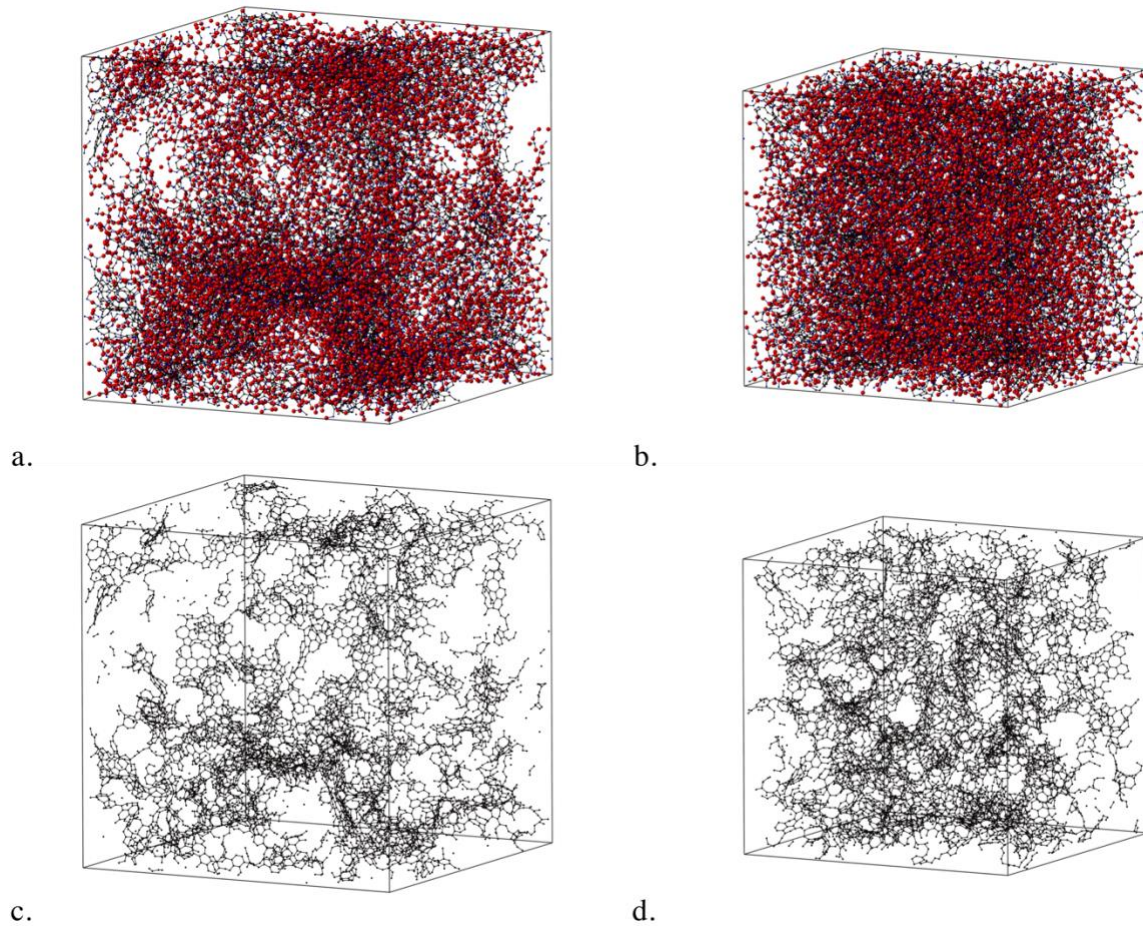


Figure 1: Models of  $\text{Si}_2\text{CO}_2 + \text{C}_{\text{free}}$  (24,576 atoms) generated at  $T_{\text{max}} = 4000$  K with a. density  $\rho = 1.4$  g/cm<sup>3</sup> and b.  $\rho = 2.2$  g/cm. Models from a. and b. shown without Si and O atoms and only C atoms with c.  $\rho = 1.4$  g/cm<sup>3</sup> and b.  $\rho = 2.2$  g/cm. C content  $\text{C}_{\text{free}}:\text{Si} = 0.5$ , density  $\rho$ ,  $T_{\text{max}} = 4000$  K. Si atoms are blue, O atoms are red, and C atoms are black.

### Impact of density

We start our investigation of the elastic properties of SiCO by comparing models with identical chemical compositions but different densities. Hence, in a system with the same glass composition and content  $\text{C}_{\text{free}}:\text{Si}$ , we only vary the volume of the simulation box.

Furthermore, we compare only data for models generated using the same  $T_{\text{max}}$ .

Comparison is also made only for data attained using the same simulation temperature

during dynamic simulations of moduli. Results are shown in Figure 2 for three selected compositions. In general, we find that the elastic response of  $\text{SiO}_2$  and  $\text{SiCO}$  is aligned with predictions of elastic medium theory: more dense models exhibit higher elastic moduli[39]. Similar trends were computed previously for stoichiometric  $\text{SiCO}$  glass using DFT calculations[25]. In fact, Colombo et al. observed that Young's modulus increased with increasing density for  $\text{SiCO}$  ceramic foams[40]. Without quantifying dependencies in greater detail, we find that the slope of the relation moduli versus density depends on the composition of the glass phase,  $T_{\text{max}}$  used for model construction, and the temperature used for the dynamic simulation of elastic moduli.

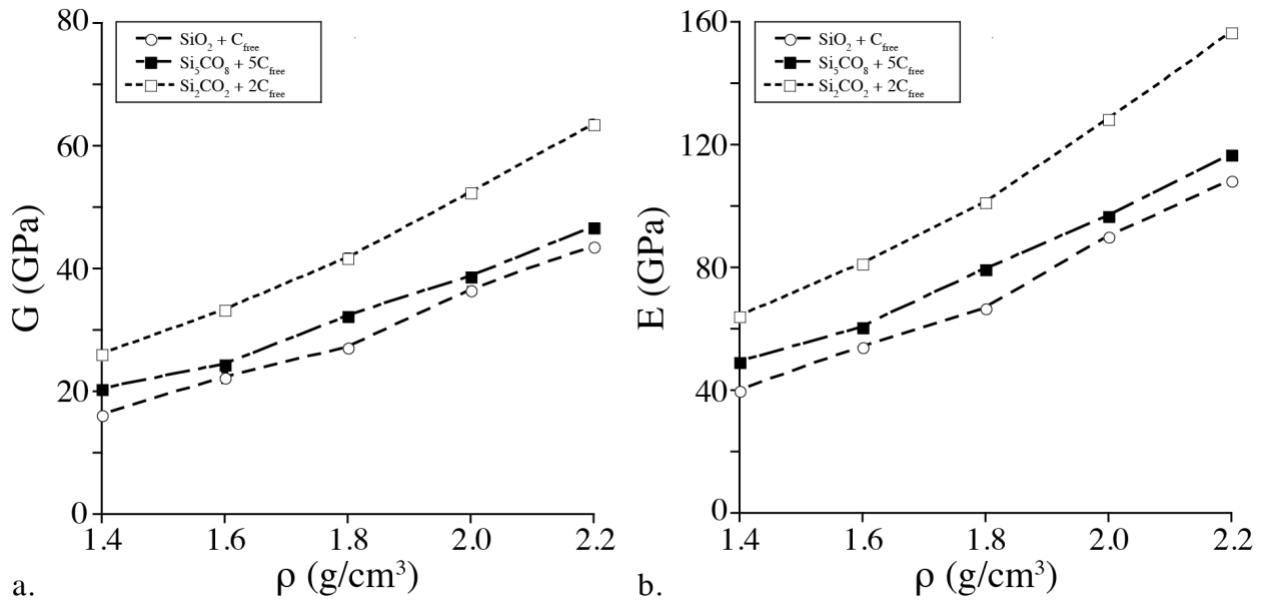


Figure 2: (Left) Shear modulus and (right) Young's modulus vs. density  $\rho$  for models with content  $\text{C}_{\text{free}}:\text{Si} = 1$  and composition  $\text{Si}_5\text{CO}_8 + 5\text{C}_{\text{free}}$ ,  $\text{SiO}_2 + \text{C}_{\text{free}}$ , and  $\text{Si}_2\text{CO}_2 + 2\text{C}_{\text{free}}$  generated at  $T_{\text{max}} = 3000$  K. Elastic constants are calculated in triplicate for each of 3 independently generated models. Error bars (if larger than the symbol used) represent standard error. Simulations are done at 300 K. Lines are provided to guide the eye.

### Impact of glass composition

We next assess the impact of the composition of the glass matrix in SiCO on its elastic properties. Thus, for models comprising the same free carbon content  $C_{\text{free}}:\text{Si}$  and density  $\rho$ , and generated using the same  $T_{\text{max}}$ , we analyze the dependency of elastic moduli on the composition of the glass matrix. In Figure 3, we show the temperature dependency of moduli (between 100 K and 2000 K) for models with a free carbon content  $C_{\text{free}}:\text{Si} = 0.5$ . Before discussing the trend, we note that the error margin increases significantly at higher temperatures. This error margin is considerably reduced in large models, as shown below.

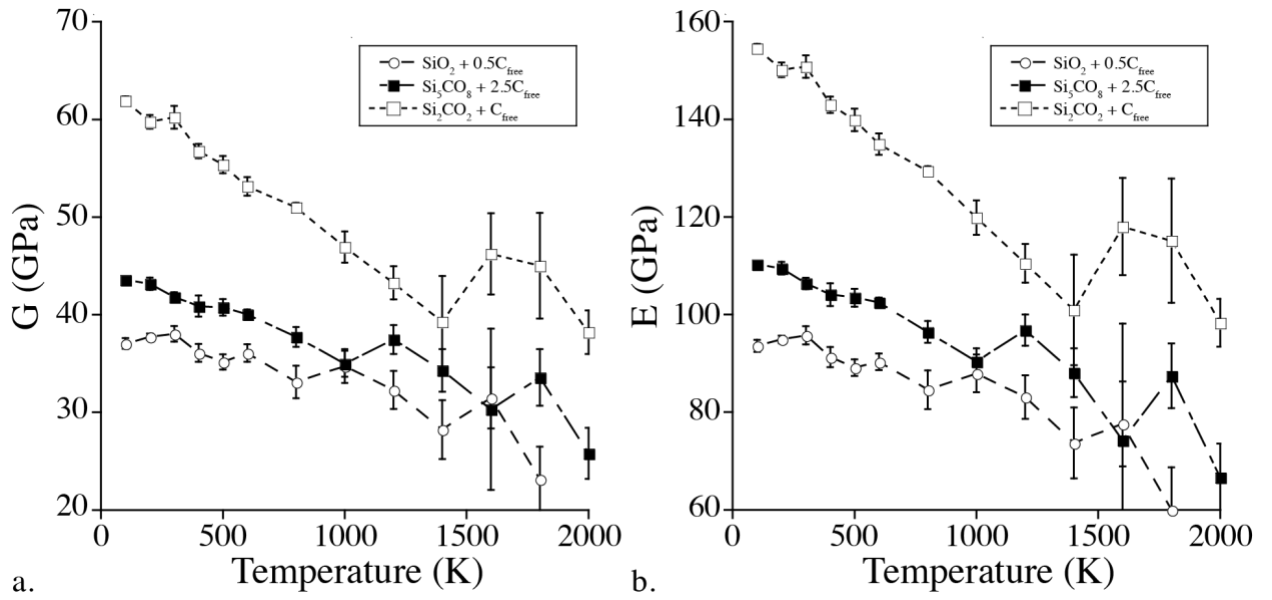


Figure 3: (a) Shear modulus and (b) Young's modulus for models with C content  $C_{\text{free}}:\text{Si} = 0.5$ , density  $\rho = 2.2 \text{ g/cm}^3$ , and composition  $\text{SiO}_2 + 0.5C_{\text{free}}$ ,  $\text{Si}_3\text{CO}_8 + 2.5C_{\text{free}}$ , and  $\text{Si}_2\text{CO}_2 + C_{\text{free}}$  generated using  $T_{\text{max}} = 4000 \text{ K}$ . Elastic constants are calculated in triplicate for each of 3 independently generated models. Error bars represent standard error. Lines are provided to guide the eye.

We observe that the higher the SiC content in the glass, the higher the elastic moduli. This trend is found for all combinations of C content, density, and  $T_{\text{max}}$ , albeit to a different extent in each case. The result is hardly surprising, given that both amorphous and crystalline SiC[41, 42] have higher elastic moduli than most amorphous and crystalline forms of  $\text{SiO}_2$ [43, 44]. The glass matrix of SiCO can be regarded as a solid

solution of both components. For models of glassy SiCO without free carbon, this trend was previously reported based on DFT calculations, albeit for much smaller models[25].

Experimentally, SiCO samples with very low amounts of excess carbon ( $\text{SiC}_{0.31}\text{O}_{1.39} + 0.07\text{C}$ ) have been synthesized and measured to have Young's modulus between 90 – 100 GPa[45]. The Young's moduli of SiCO samples with higher amounts of free carbon (12 – 54 wt%  $\text{C}_{\text{free}}$ ) are 77 – 108 GPa[22]. Under high load, the Young's modulus of SiCO with composition  $\text{SiC}_{0.8}\text{O}_{1.6}$  has been measured at  $180 \pm 30$  GPa[46]. Our computed values of Young's modulus for the selected SiCO compositions fall within experimental ranges. However, elastic moduli for the  $\text{Si}_2\text{CO}_2 + \text{C}_{\text{free}}$  are higher due to the high SiC content in the SiCO glass.

We observe that elastic moduli decrease with increasing simulation temperature for the selected SiCO compositions. Generally, elastic properties of materials decrease with increasing temperature[47, 48]. However,  $\text{SiO}_2$  glass displays a peculiar anomalous behavior since its moduli tend to increase with increasing temperature.[49, 50] Interestingly, work from Rouxel et al.[21] indicates a similar increase of Young's modulus of SiCO glass with increasing temperature.

### **Impact of free carbon content**

We then investigate models with different free carbon content  $\text{C}_{\text{free}}:\text{Si}$ , while keeping the model density and composition of the glass matrix identical. Results of shear modulus  $G$  and Young's modulus  $E$  for a series of such models generated at the same  $T_{\text{max}}$  are shown in Figure 4. We find that elastic moduli increase as the free carbon content increases as long as other parameters remain constant. The relation between modulus and carbon content appears approximately linear within the range of compositions studied here. These results seem to contradict recent experimental studies by Sorarù et al.[22]. The authors concluded that Young's modulus of SiCO ceramics decreases with increasing  $\text{C}_{\text{free}}$  content. We note, however, that the densities of the investigated samples decreased



with increasing  $C_{\text{free}}$  content. Therefore, their  $C_{\text{free}}$  content is strongly correlated to density, and the impact of one variable cannot be distinguished from the effects of the other. As we pointed out in the preceding section, decreasing density causes decreasing moduli, and the apparent disagreement can be remedied this way.

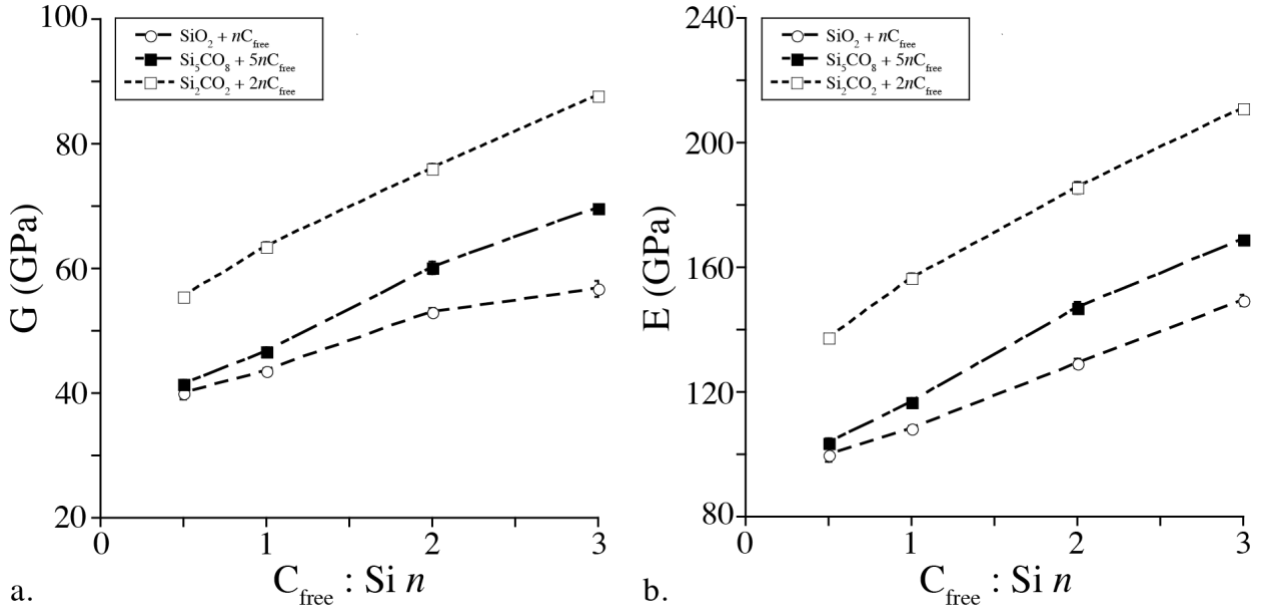


Figure 4: a. Shear modulus and b. Young's modulus vs free carbon content,  $C_{\text{free}}:\text{Si } n$ , for models of  $\text{Si}_5\text{CO}_8 + 5nC_{\text{free}}$ ,  $\text{SiO}_2 + nC_{\text{free}}$ ,  $\text{Si}_2\text{CO}_2 + 2nC_{\text{free}}$  generated at  $T_{\text{max}} = 3000 \text{ K}$  with  $\rho = 2.2 \text{ g/cm}^3$ .  $C$  content  $C_{\text{free}}:\text{Si } n$ , density  $\rho = 2.2 \text{ g/cm}^3$ ,  $T_{\text{max}} = 3000 \text{ K}$ . Elastic constants are calculated in triplicate for each of 3 independently generated models. Error bars (if larger than the symbol) represent standard error. Simulations are done at 300 K. Lines are provided to guide the eye.

To gain further insight into the impact of the free carbon on a modulus  $M$ , we seek the contribution of the carbon phase to moduli of the compound models. We analyze this through a simple mixing model:  $M_{\text{SiCO:Cfree}} = x_{\text{SiCO}} * M_{\text{SiCO}} + x_{\text{Cfree}} * M_{\text{Cfree}}$  ( $x_i$  is the mass fraction of glass and free carbon phase), into which we insert moduli for the SiCO glass to extract moduli of the carbon phase. To obtain moduli  $M_{\text{SiCO}}$  of SiCO glass phases, we extrapolate the data shown in Figure 4 to zero  $C_{\text{free}}$  content. For  $\text{SiO}_2$  this procedure yields  $B_0 = 64 \text{ GPa}$ ,  $G = 37 \text{ GPa}$ , and  $E = 89 \text{ GPa}$ . (each  $\pm 2 \text{ GPa}$ ) Performing simulations

for pure SiO<sub>2</sub> (24,600 atoms,  $T_{\max}=2000$  K,  $\rho = 2.2$  g/cm<sup>3</sup>) under conditions similar to those used for SiCO:C<sub>free</sub> models, we find  $B_0 = 58$  GPa,  $G = 34$  GPa,  $E = 85$  GPa (each  $\pm 2$  GPa). These results are well aligned with the extrapolation towards zero C content. We note that the computed bulk modulus for SiO<sub>2</sub> glass is considerably higher than experimentally reported ( $B_0 \approx 36$  GPa, [49]). A similar extrapolation analysis yields  $B$ ,  $G$ , and  $E$  of 66, 36, and 91 GPa, respectively, for Si<sub>5</sub>CO<sub>8</sub>. For Si<sub>2</sub>CO<sub>2</sub>, we obtain 84, 50, and 125 GPa for  $B$ ,  $G$ , and  $E$ , respectively. We then insert the extrapolated data into the mixing model and apply it to the data shown in Figure 4. The (hypothetical) moduli  $M_{Cfree}$  of the carbon phase are obtained through best fits. We obtain reasonable agreement for a bulk modulus of the carbon phase  $B_{Cfree}$  between 90 – 111 GPa, a shear modulus  $G_{Cfree}$  within 70 – 93 GPa, and a Young's modulus  $E_{Cfree}$  between 200 – 250 GPa. Note that these values are extracted under the assumption of a mixing model based on mass fraction. The moduli extracted from the compound models can then be compared to data computed through simulations of a large model of graphite:  $B = 55$  GPa,  $G = 87$  GPa, and  $E = 171$  (all  $\pm 1$  GPa). We also simulated (glass-free) models of amorphous carbon along the same protocol and received  $B = 166$  GPa,  $G = 176$  GPa, and  $E = 390$  GPa (all  $\pm 1$  GPa) – in agreement with recently reported values[51]. We find that – within a simple mixing model – the free carbon phase's impact on a compound model's elastic moduli is larger than expected from mixing graphite but smaller than expected by mixing pure amorphous carbon to glassy SiCO. Overall, its impact falls between contributions expected from adding graphite or amorphous carbon.

Increasing the simulation temperature at which elastic moduli are computed, we find that all moduli decrease with increasing temperature. This is shown in Figure 5 for shear modulus and Young's modulus of selected models of SiCO (compare Figure 3 as well). The trend holds regardless of the amount of free carbon, as simulation temperature does not change the impact of free carbon on elastic properties. Models with higher free carbon content generally have higher shear and Young's modulus for any given

temperature in the investigated range. Increasing the carbon content from  $C_{\text{free}}:\text{Si}$  ratio = 0.5 to  $C_{\text{free}}:\text{Si}$  ratio = 3 results in almost doubling shear and Young's modulus.

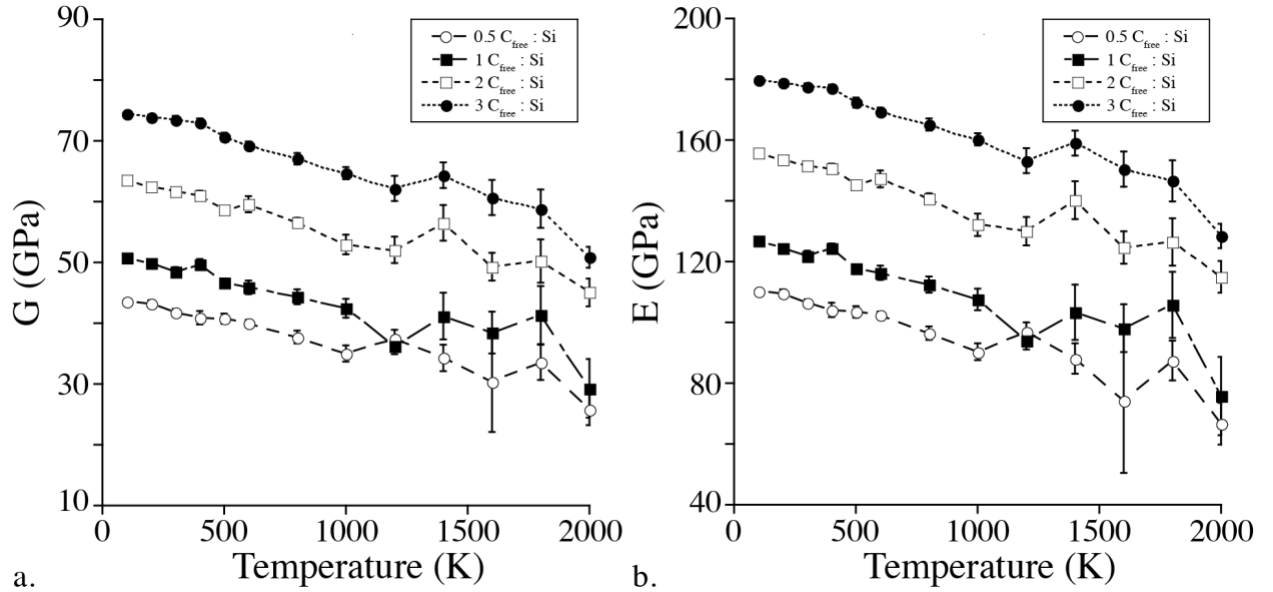


Figure 5: a. Shear modulus and b. Young's modulus of  $\text{Si}_5\text{CO}_8 + 10\text{C}_{\text{free}}$  models (39,360 atoms,  $a=7.9$  nm,  $2.2$  g/cm<sup>3</sup>) generated at  $T_{\text{max}} = 4000$  K. C content  $C_{\text{free}}:\text{Si} = 0.5, 1, 2, 3$ , density  $\rho = 2.2$  g/cm<sup>3</sup>,  $T_{\text{max}} = 4000$  K. Elastic constants are calculated in triplicate for each of 3 independently generated models. Error bars represent standard error. Lines are provided to guide the eye.

### Impact of carbon morphology

The most striking result we found in our investigation is the impact of the morphology of free carbon on elastic properties. Different carbon morphologies can be attained by using different maximum temperatures  $T_{\text{max}}$  during structure generation while keeping all other parameters (composition, density) identical. For instance, generating a structure at  $T_{\text{max}} = 2000$  K yields a model with small groups of carbon atoms, including  $\text{C}_6$ -rings (like benzene) and short chains, see Figure 6a. The groups are dispersed and isolated within the surrounding glass matrix. Thus, the carbon structure is not extended, and C-C bonds do not form a continuous path throughout the model. Increasing  $T_{\text{max}}$  to 4000 K yields an

extended C–C bond network with continuous paths connecting almost all C atoms. Only a minor portion of C atoms remain isolated. Indeed, most C atoms are three-connected ( $sp^2$ -like) and found within six-membered carbon rings, like aromatic carbon segregations (Figure 6b). The network is best characterized as “sheet-like”. Notably, small amounts of SiCO glass phase separate the curved 2D sheets of carbon from each other. Generating the structure at an even higher  $T_{\max}$  (6000 K or 8000 K) results in the formation of predominantly tubular networks (Figures 6c and 6d). Details of this “genesis” of the carbon structure within SiCO and how it depends on composition, heating rate, and other simulation parameters will be given elsewhere. Note that all models shown in Figure 6 have the same composition and density.

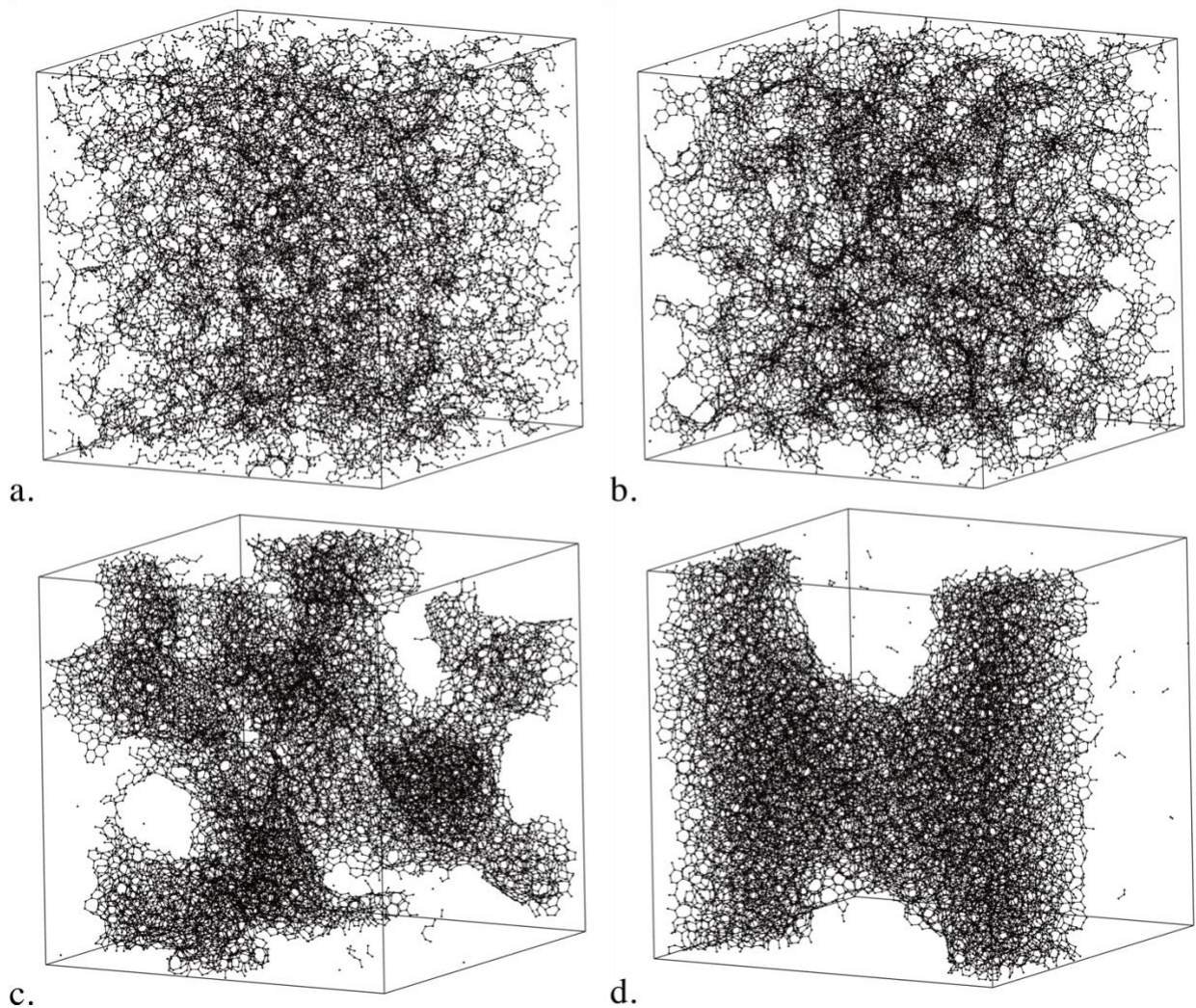


Figure 6:  $\text{Si}_5\text{CO}_8 + 10\text{C}_{\text{free}}$  models (39,360 atoms;  $a=7.9$  nm;  $2.2$  g/cm<sup>3</sup>) annealed at a. 2000 K, b. 4000 K, c. 6000 K, d. 8000 K. C content  $\text{C}_{\text{free}}:\text{Si} = 2$ , density  $\rho = 2.2$  g/cm<sup>3</sup>,  $T_{\text{max}}$ . Only C atoms (black) are shown.

We then computed elastic moduli for these models with identical composition, carbon content, and density but different carbon morphology (as directed via  $T_{\text{max}}$ ). Results, exemplified for structures with glass composition  $\text{Si}_5\text{CO}_8$  and different amounts of free carbon, are presented in Figure 7. The data shows that elastic moduli in SiCO structures can vary by up to 25% only by changing the morphology of the carbon segregation. The impact of morphology is more pronounced the higher the carbon content is. At low free carbon content,  $\text{C}_{\text{free}}:\text{Si} = 0.5$ , only minor differences in moduli appear; thus, the amorphous glass matrix dominates elastic properties. Conversely, at high free carbon content,  $\text{C}_{\text{free}}:\text{Si} = 3$ , the impact of free carbon morphology is substantial, with up to 25% difference (136 GPa vs. 172 GPa for C:Si=2; 157 GPa vs. 200 GPa for C:Si=3).

Therefore, at high  $\text{C}_{\text{free}}$  content – when a contribution of carbon to mechanical properties is more substantial – the spatial distribution of carbon and its morphology within the compound is essential. Overall, we find that amorphous SiCO –with identical composition and density – exhibits significant variation in its mechanical properties depending on the extent and morphology of carbon segregations.

Our results highlight that caution must be applied when using a “rule-of-mixture” to estimate or analyze properties in SiCO compound systems. Rouxel et al.[21] followed such an approach when comparing elastic properties of SiCO with a volume-weighted sum of elastic properties of constituent phases. Such an approach will yield only a rough approximation since it neglects a possible impact of the morphology of the phases. Our calculations predict that the morphology of the free carbon phase does have a significant effect on elastic properties. Therefore, even when model composition and density are identical, a simple rule-of-mixture may not be sufficient in estimating the elastic properties of SiCO.

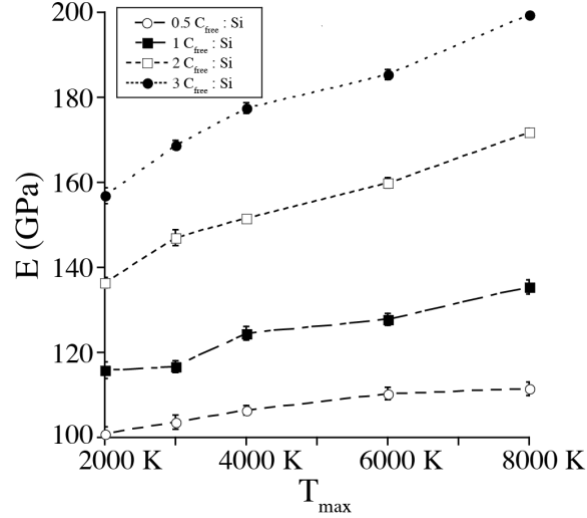


Figure 7: Young’s modulus plotted as a function of  $T_{\max}$  used in model generation.  $\text{Si}_5\text{CO}_8 + 5nC_{\text{free}}$  models with  $\rho = 2.2 \text{ g/cm}^3$  and  $C_{\text{free}}:\text{Si} = n$ , with  $n = 0.5, 1, 2$ , and  $3$ . Elastic constants are calculated in triplicate for each of 3 independently generated models. Error bars represent standard error. Simulations are done at 300 K. Lines are provided to guide the eye.

We also investigated the temperature dependence of elastic properties of models with different carbon morphology, see Figure 8. Consistent with the results shown above, we find that the moduli of SiCO generally decrease with increasing temperature. At low free carbon content, here  $C_{\text{free}}:\text{Si} = 0.5$ , elastic properties decrease by 10 – 40% when comparing data obtained at 300K to that computed at 2000K. At high free carbon content,  $C_{\text{free}}:\text{Si} = 3$ , elastic properties decrease between 20 – 40 % within the investigated temperature range. There is a subtle impact of carbon morphology, identified through  $T_{\max}$  (the temperature at which models have been generated), on the “consistency” or “thermal stability” of elastic moduli. Models generated at  $T_{\max} = 6000 \text{ K}$  and  $8000 \text{ K}$  have more consistent elastic properties and tend to decrease less at higher temperatures than models generated at  $T_{\max} = 2000 \text{ K}$ ,  $3000 \text{ K}$ , and  $4000 \text{ K}$ .

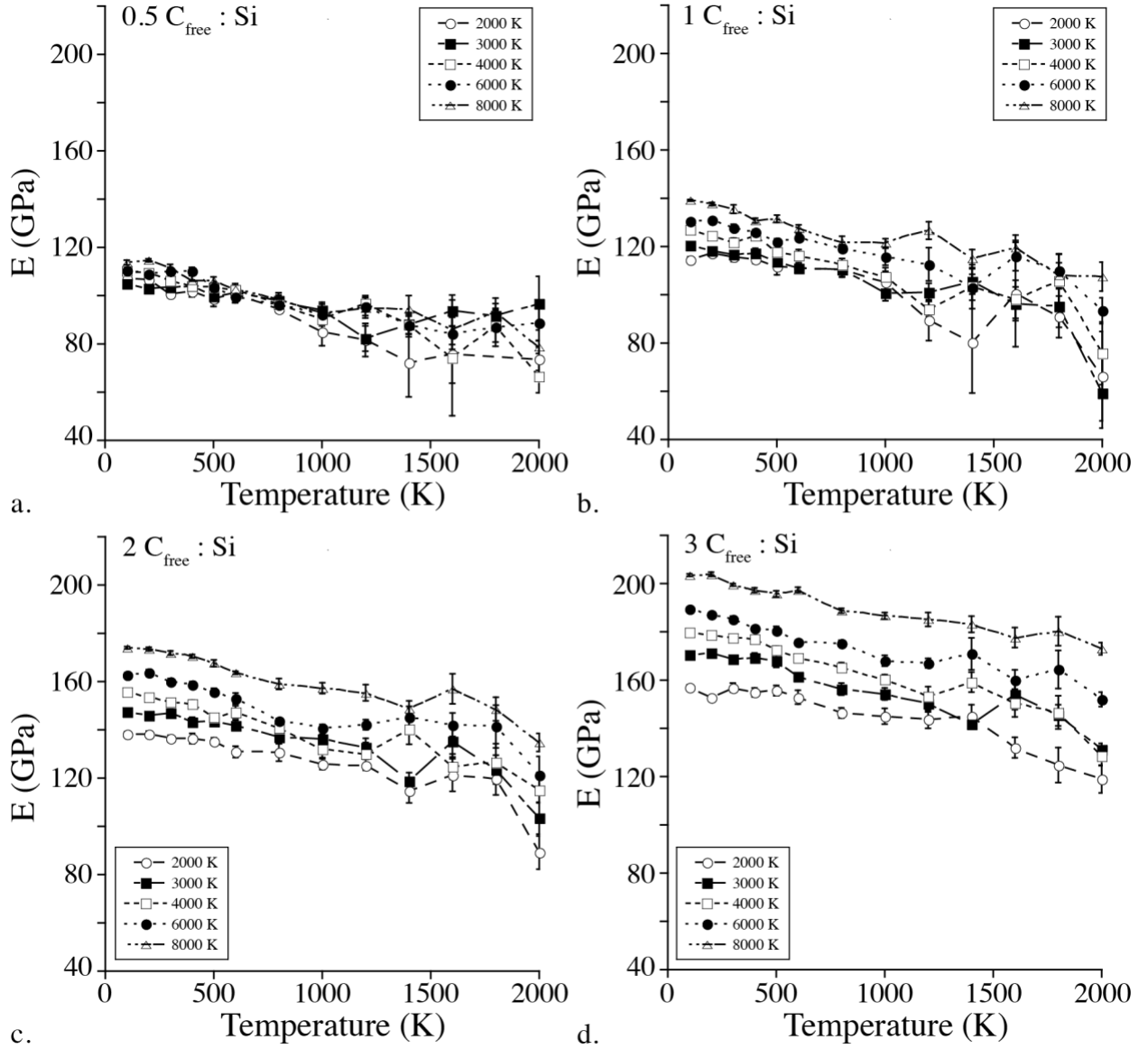


Figure 8: Young's modulus vs. simulation temperature for models of  $\text{Si}_5\text{CO}_8 + 5nC_{\text{free}}$  annealed between 2000 K – 8000 K with a.  $n = 0.5$ , b.  $n = 1.0$ , c.  $n = 2.0$ , d.  $n = 3.0$  where  $n = C_{\text{free}} : \text{Si}$ . density  $\rho = 2.2 \text{ g/cm}^3$ ,  $T_{\text{max}}$ . Elastic constants are calculated in triplicate for each of 3 independently generated models. Error bars represent standard error. Lines are provided to guide the eye.

### Finite-size effects

Our final investigation addresses the size of models used in this study. The initial series of our models had a characteristic unit cell extension (box dimension) of 10 nm and contained 24,000 – 50,000 atoms, depending on composition. A close look at the tubular segregations emerging for  $T_{\max}$  of 6000K and 8000K, see Figures 6c and 6d, shows that these segregations have diameters of about 2 nm and 4 nm, respectively. Since these fall well into the size of the simulation cell, the periodic boundary conditions are likely to impact structure generation and property calculations. To investigate such finite-size effects, we considered the composition  $\text{Si}_5\text{CO}_8 + 10\text{C}_{\text{free}}$  with a density of  $2.2 \text{ g/cm}^3$  and generated 8 times and 64 times larger models. These comprise simulation box dimensions of approximately 20 nm and 40 nm, respectively. Three different series of 20 nm models and one series of 40 nm models were generated. We maintained all procedural parameters, including heating rates, as outlined in the method section for these simulations. In Figure 9, we show 40 nm models generated at  $T_{\max} = 6000 \text{ K}$  and  $8000 \text{ K}$ . The model obtained at  $T_{\max} = 6000 \text{ K}$  still resembles its smaller counterpart in carbon morphology. The same trend holds for models obtained at even lower temperatures. On the other side, the 40 nm model generated at  $T_{\max} = 8000 \text{ K}$  exhibits a 3D tubular network, which is different from the 2D tubular networks the smaller 10 nm models generated at the same  $T_{\max}$  exhibit (see Figure 6d).



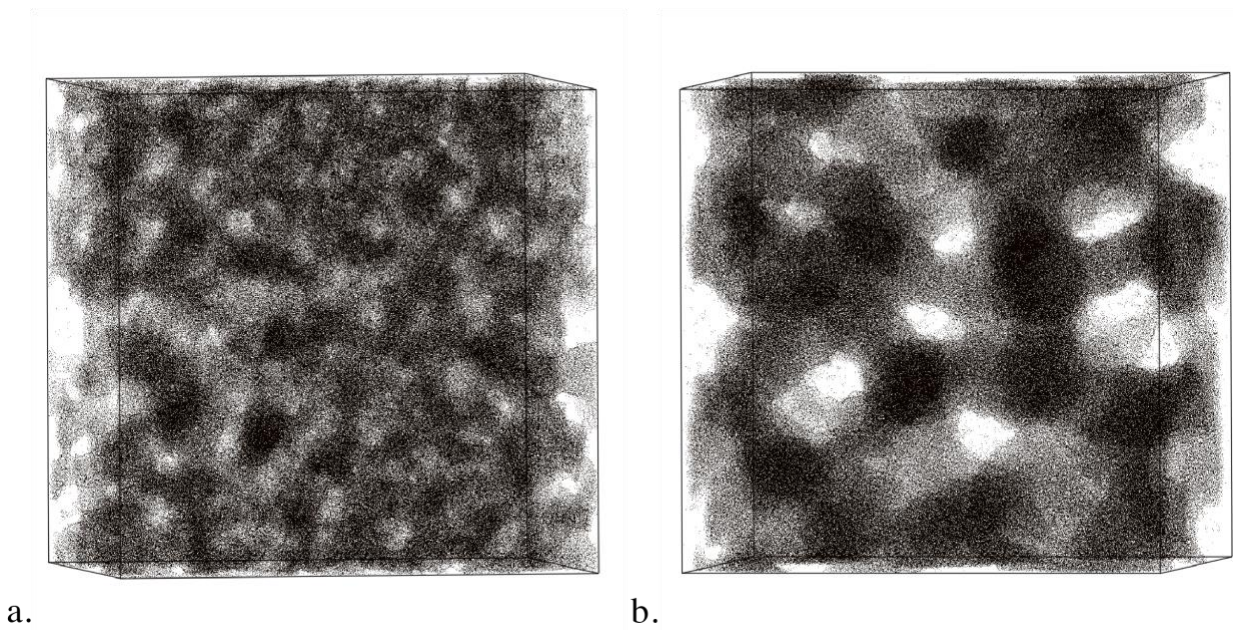


Figure 9:  $\text{Si}_5\text{CO}_8 + 10\text{C}_{\text{free}}$  with  $\text{C}_{\text{free}}:\text{Si} = 2$  and density  $\rho = 2.2 \text{ g/cm}^3$  generated at a.  $T_{\text{max}} = 6000 \text{ K}$  and b.  $T_{\text{max}} = 8000 \text{ K}$ . The models comprise about 2.5 million atoms within a simulation box of approximately 40 nm.

We computed Young's moduli of  $\text{Si}_5\text{CO}_8 + 10\text{C}_{\text{free}}$  models in three different sizes, 10, 20, and 40 nm, generated using  $T_{\text{max}} = 2000 \text{ K}$  and  $T_{\text{max}} = 8000 \text{ K}$  and compared them with each other, see Figure 10. Young's moduli calculated for 20 nm and 40 nm models agree with data previously obtained for the 10 nm model. We corroborate the ~20% difference in Young's moduli between models with identical composition and density but generated at different  $T_{\text{max}}$  (2000 K vs. 8000 K). Therefore, the impact of carbon morphology on elastic properties persists for models in larger simulation boxes. On the other side, a noticeable structural difference between the 10 nm and the larger models generated at  $T_{\text{max}} = 8000 \text{ K}$  relates to a 2D tubular network present in the former and 3D tubular networks found in the latter.

The most apparent benefit of simulating models of larger size emerges in simulations at elevated temperatures. The uncertainty obtained for data of a single model is much smaller, and the consistency between different models obtained through the same

protocol is much higher. The data shown in Figure 10 exemplifies this for a composition  $\text{Si}_5\text{CO}_8 + 10\text{C}_{\text{free}}$ : above 500 K. Young's moduli of 10 nm models generated with  $T_{\text{max}} = 2000$  K exhibit substantial uncertainty. In contrast, 20 nm models provide consistent results and agree with the data of the 40 nm model. Trends are similar for models generated at  $T_{\text{max}} = 8000$  K, which exhibit larger carbon segregations. Young's moduli computed for the larger models carry smaller errors and are consistent with each other. However, while the larger size models exhibit higher fidelity, we notice that all trends observed for small models are found in larger models as well – with the latter corroborating the results of the former.

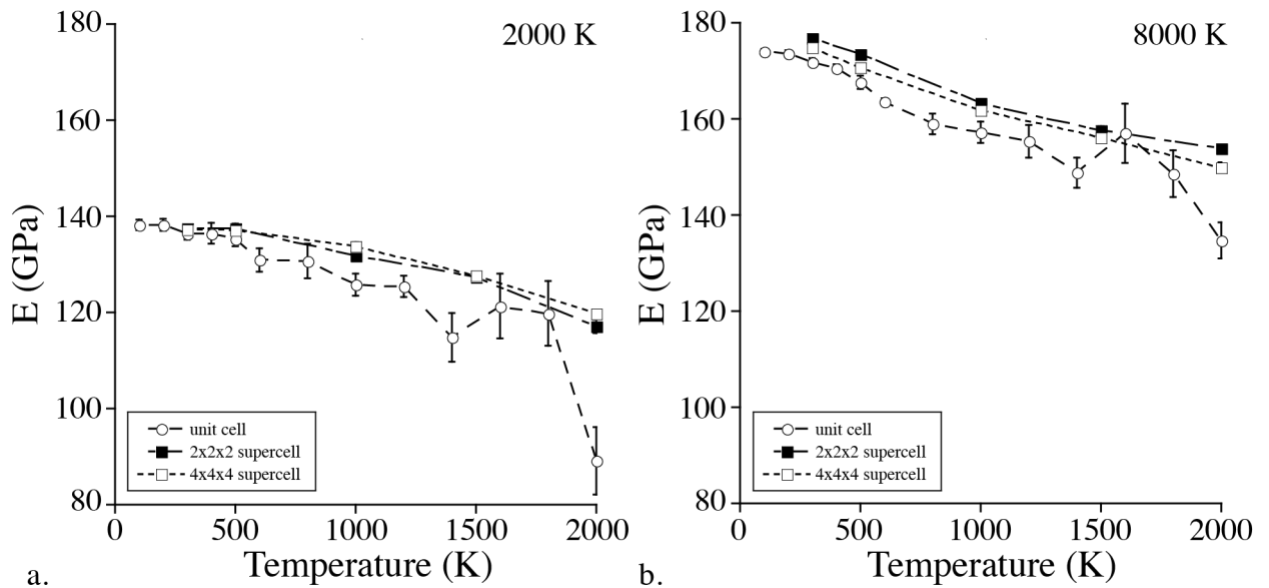


Figure 10: Young's modulus of  $\text{Si}_5\text{CO}_8 + 10\text{C}_{\text{free}}$  ( $C_{\text{free}}:\text{Si} = 2$ , density  $\rho = 2.2 \text{ g/cm}^3$ ) as a function of simulation temperature for models of different size attained at a.  $T_{\text{max}} = 2000$  K and b.  $T_{\text{max}} = 8000$  K. A unit cell of a 10 nm model contains 39,360 atoms, a 20 nm model contains 314,880 atoms, and a 40 nm model contains 2,519,040 atoms. Three models each are generated for 10 and 20 nm, while only a single model is generated with a size of 40 nm. Elastic constant calculations for all models are done in triplicate. Error bars represent standard error. Lines are provided to guide the eye.

## Conclusions

Using molecular dynamics simulations with the Tersoff potential, we calculate elastic properties of SiCO models with different glass compositions, densities,  $C_{\text{free}}$  content, and carbon morphology. We examine each parameter individually and disentangle dependencies that are difficult to separate in experimental studies. In general, our results align well with expectations and previous experimental observations. In particular, higher elastic moduli are found for models with higher SiC content in the SiCO glass and for models with higher density. Dynamic simulations at finite temperatures show that for any given composition of SiCO, the elastic moduli decrease with increasing temperature. Our results then indicate that – when maintaining the density of a system – increasing the amount of  $C_{\text{free}}$  yields higher elastic moduli. While this appears to contradict previous experimental results[22], we show that density variations dominate the underlying experimental data in this study.

Finally, we uncover a “hidden” parameter – the morphology of the  $C_{\text{free}}$  phase – that impacts the mechanical properties of SiCO. Models with identical composition and density but different morphology of the same amount of  $C_{\text{free}}$  exhibit different mechanical properties. In general, models with dispersed small fragments of  $C_{\text{free}}$  have lower moduli than models with extended networks or tubular segregations of  $C_{\text{free}}$ . The effect can reach up to 25% of the mechanical property for models comprising large amounts of “free” carbon. As a consequence, caution has to be exerted if a simple rule-of-mixture based on the composition or volume content is used to predict the mechanical properties of SiCO. At this time, we are not aware of any experimental method that can quantify the morphology of “free” carbon embedded in the amorphous matrix of SiCO. Hence, we term it “hidden” and direct approaches for experimental characterization need to be developed to attain quantitative measures.

## **Acknowledgments**

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## Summary

Through finite temperature molecular dynamics simulations, we computed elastic properties of SiCO with varying compositions of the glass, free carbon content, density, and free carbon morphology. We found that increasing simulation temperature resulted in decreasing elastic moduli. By independently varying free carbon content and density, we calculated that elastic properties of SiCO generally increase when only free carbon content is increased and when only density is increased contradicting Sorarù et al.[1]. By varying the free carbon morphology while keeping composition and density constant, we calculated that elastic properties increase with increasing segregation of the free carbon phase. Models with small dispersed carbon fragments had lower elastic moduli than models with extended free carbon networks. Thus, controlling the morphology of the free carbon phase can be used to tailor elastic properties of SiCO PDCs. Finally, we verified our results using substantially larger, million atom models for the  $\text{Si}_5\text{CO}_8 + 10\text{C}_{\text{free}}$  composition, and we found that general trends agree with the trends we computed with smaller models.

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## CHAPTER 2: QUANTIFICATION OF FREE CARBON PHASE MORPHOLOGY

Substantial work has been done on investigating the structural evolution of “free” carbon in polymer-derived ceramics[1-3]. From our own work in Part II Chapter 1, we identify a need to quantify the free carbon phase morphology in amorphous SiCO/SiCN ceramics in atomistic systems used in computational investigations. So, we propose a method to quantify, in part, free carbon phase morphology. We develop our method to discriminate between different free carbon morphologies by calculating the “extent” of the 3-coordinated carbon network.

In order to differentiate between free carbon morphologies, we focus on a topological shell counting method. The topological shell counting method determines the 3-coordinated carbon character of “free” carbon structures. This method calculates the fraction of 3-coordinated carbons that are themselves coordinated to 3-coordinated carbon for  $n$ th successive fractions. Essentially, the topological shell counting method measures the topological shell to which the free carbon network extends to. Carbon allotropes, such as graphite and carbon nanotubes, which only consist of 3-coordinated carbons will always yield a value of unity (1) for the “ $n$ th fraction” as the counted topological shell approaches its maximal value; however, the “free” carbon phase in SiCO ceramics contains a mixture of differently coordinated carbons resulting in a decrease of the “ $n$ th fraction” to zero as the counted topological shell approaches larger values. The relationship between the “ $n$ th fraction” and the topological shell differs based on “free” carbon structure and, consequently, can provide limited differentiation between “free” carbon structures.

Models of SiCO are generated following the approach detailed in Part II Chapter 1. Molecular dynamics simulations are performed with LAMMPS[4] and interactions are described via the Tersoff potential[5, 6]. Si–Si, Si–C, and C–C interactions are parameterized by Tersoff[5-7] and Si–O interactions are parameterized by Munetoh et

al.[8] Based on spectroscopic evidence[9], interactions between O atoms and between C and O are left as repulsive only. We generate SiCO models through a melt-quench process where the parameter  $T_{\max}$ , the maximum temperature the system is exposed to, determines the morphology of the free carbon phase as long as composition and density are fixed. The system is equilibrated for 200 ps at  $T_{\max}$ , and then cooled to 300 K at a rate of 10 K/ps. All simulations are done at constant volume so models have fixed density.

We choose a composition of  $\text{Si}_5\text{CO}_8 + 10\text{C}_{\text{free}}$  and  $T_{\max}$  of 2000 K, 4000 K, 6000 K, and 8000 K to generate four models with over 300,000 atoms (see Figure 1) for each  $T_{\max}$  (12 models total). Models contain 144,320 carbon atoms. For lower  $T_{\max}$ , we observe more dispersed carbon chunks and carbon six-rings (see Figure 1a and Figure 1b). Increasing  $T_{\max}$  leads to the formation of extended tubular networks (see Figure 1c and Figure 1d).

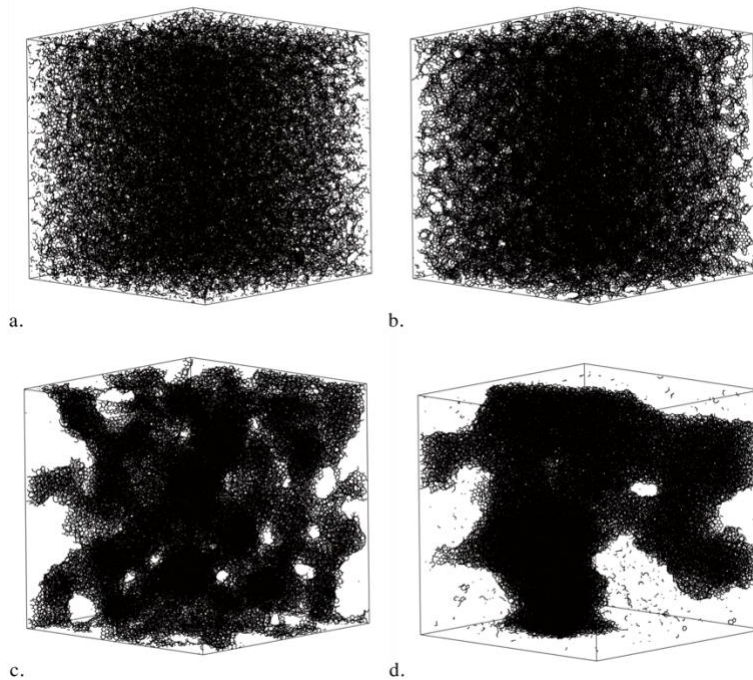


Figure 1:  $\text{Si}_5\text{CO}_8 + 10\text{C}_{\text{free}}$  (314,880 atoms; 144,320 C atoms;  $a = 15.8$  nm;  $\rho = 2.2$  g/cm<sup>3</sup>). Generated at  $T_{\max}$  equals a. 2000 K, b. 4000 K, c. 6000 K, and d. 8000 K. Only C atoms (black) are shown.

We apply our topological shell counting method on the free carbon phase of the 12 models we generated (see Figure 2). While models produced at  $T_{\max} = 2000$  K and  $T_{\max} = 4000$  K have  $C_{\text{free}}$  morphologies that appear visually similar, the extents of their free carbon networks differ substantially: the free carbon network of  $\text{Si}_5\text{CO}_8 + 10C_{\text{free}}$  generated with  $T_{\max} = 2000$  K does not extend past the 40<sup>th</sup> topological shell while the free carbon network of  $\text{Si}_5\text{CO}_8 + 10C_{\text{free}}$  generated with  $T_{\max} = 4000$  K extends past the 100<sup>th</sup> topological shell. Additionally, we find that models generated at  $T_{\max} = 6000$  K, and not at  $T_{\max} = 8000$  K, exhibit the most extended free carbon networks of the models investigated; however, it is likely that the “small” size of the box used to generate models inhibits the extent of the free carbon phase generated at  $T_{\max} = 8000$  K. Increasing the size of the simulation box could result in the true extent of the free carbon network being realized for models generated at  $T_{\max} = 8000$  K.

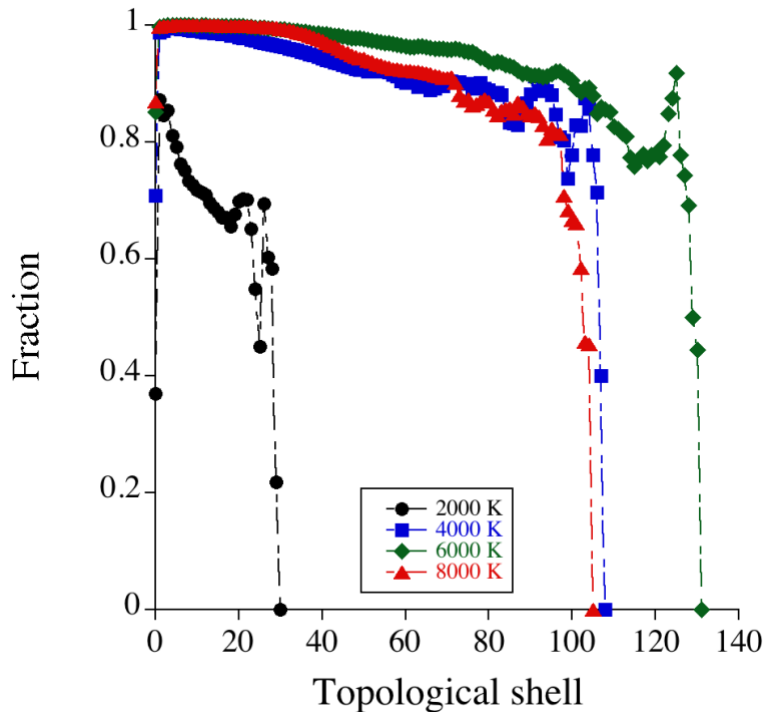


Figure 2: Topological shell counting method applied to carbon atoms in  $\text{Si}_5\text{CO}_8 + 10C_{\text{free}}$  generated at  $T_{\max} = 2000$  K, 4000 K, 6000 K, and 8000 K. The topological shell counting method is averaged over the results of three models for each  $T_{\max}$ .

In summary, we develop a method to partially quantify the free carbon phase morphology in carbon-containing amorphous materials by determining the extent of the three-coordinated carbon network. Using amorphous models of SiCO with different free carbon phase morphologies we demonstrate how much the extent of the free carbon phase can vary depending on the conditions used to produce the model. Our method may have application in quantitatively relating properties that depend on the free carbon phase, like elastic properties, to the morphologies of the free carbon phase.

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## CHAPTER 3: DEVELOPMENT OF A REACTIVE FORCE FIELD FOR SIMULATIONS OF SiCNH POLYMER-DERIVED CERAMICS

### **Motivation and Scope**

DFT calculations to study structural features of polymer-derived ceramics along with the polymer-to-ceramic conversion process can extend from months to year with current computational resources. Additionally, systems sizes are too limited by DFT in order to study and characterize the evolution of the free carbon phase during the polymer-to-ceramic conversion process which can require models tens of nanometers large. ReaxFF can be parametrized to have DFT-like accuracy for simulations with systems 10-100 times larger than currently possible in DFT. Previous work has been done parameterizing ReaxFF for investigating mechanical properties[1] and the polymer-to-ceramic conversion process involved in the synthesis of silicon oxycarbide[2, 3]. There are no complete parameter sets in literature for performing simulations of silicon carbonitrides, and existing SiCNH parameter sets were parameterized for studying different phenomena and are unsuitable for simulations of silicon carbonitride[4, 5]. We parameterize ReaxFF in order to investigate the polymer-to-ceramic conversion during the pyrolysis of polysilazanes.

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# DEVELOPMENT OF A REACTIVE FORCE FIELD FOR SIMULATIONS OF SiCNH POLYMER-DERIVED CERAMICS

## Introduction

SiCN polymer-derived ceramics (PDCs) exhibit interesting properties including corrosion resistance[1] and oxidation resistance[2]. Currently, SiCN ceramics are under investigation for a variety of applications including being used as anodes in lithium-ion batteries[3], as coatings with excellent mechanical properties[4, 5], and as low- $\kappa$  dielectric thin films serving as diffusion barriers for Cu in microelectronic devices[6]. SiCN ceramics can be synthesized through the polymer-to-ceramic conversion of polysilazanes. During the polymer-to-ceramic conversion process, if a pyrolysis temperature between 1073 – 1573 K is reached and the starting polymer precursors contain enough excess carbon then the resulting SiCN ceramic can be described as a mixture of  $\text{Si}_3\text{N}_4$ , SiC, and a “free” carbon phase,  $\text{C}_{\text{free}}$ , which consists of carbon that is almost completely bonded to other carbon. The composition of the SiCN ceramic is  $\text{SiC}_x\text{N}_y = (y/4)\text{Si}_3\text{N}_4 + (1 - 3y/4)\text{SiC} + (x + 3y/4 - 1)\text{C}_{\text{free}}$ .

Although, DFT has been instrumental in investigating the structural features of amorphous ceramics[7, 8], system sizes are limited to thousands of atoms and the computational expense and time of doing molecular dynamics simulations is extraordinary. Classical potentials, like the Tersoff potential[9], can perform molecular dynamics simulations for systems more than hundreds of millions of atom large and are useful in studying specific properties[10]; however, the outcome of empirical potential simulations can exhibit poor local bonding environments[11] and can lack proper description of bond breaking. The reactive force field ReaxFF[12] is meant to bridge the gap between the quantum chemical accuracy of DFT and the large system size limit of empirical potentials. ReaxFF can be parametrized to have quantum chemical accuracy[12, 13] while being able to simulate systems thousands of times the size of what

DFT can do. The principle on which ReaxFF is formulated is that all terms leading to the total ReaxFF energy of system depend on the bond order[12]. Thus, varying the bond order can result in the “formation” and “breaking” of bonds.

As far as we know, there exists no ReaxFF Si-C-N-H parameter set suitable for simulations involving the polymer-to-ceramic conversion of polysilazanes, but several ReaxFF parameter sets have been used to investigate SiCO PDCs which are similar to SiCN PDCs. Vashisth et al.[14] investigated mechanical properties of polymer-derived SiCO nanofibers within ReaxFF. Meanwhile, Gao et al.[15] studied the pyrolysis of the polymethylhydrosiloxane-hydridopolycarbosilane system using parameters developed by Newsome et al[16]. Ponomarev et al.[17] improved on the parameter set of Newsome et al.[16] and developed new ReaxFF parameters to study the pyrolysis of polysiloxanes into ceramics, including the pyrolysis of the cross-linked polymethylhydrosiloxane-divinylbenzene system.

Certain parameter sets in literature do contain Si-C-N-H parameters in various forms. Kulkarni et al.[18] developed ReaxFF parameters to study oxygen interactions with SiO<sub>2</sub> surfaces though their parameter set also happened to contain Si-N-H parameters. Meanwhile, a Si-C-N-O-H parameter set was trained to study carbon-based and silicon-based lubricating systems[19]. However, these parameter sets lack critical Si-C-N angle parameters.

We develop ReaxFF Si-C-N-H parameters in order to perform atomistic simulations of Si-C-N-H structures. Parameters are trained on a variety of SiC, Si<sub>3</sub>N<sub>4</sub>, SiCN, and SiCNH structures calculated with DFT total energy calculations and simulated with DFT ab initio molecular dynamics. The resulting parameters are used to investigate the polymer-to-ceramic conversion process of the polysilazane Ceraset.

## **Method**

### **Parameter fitting**



We started with the parameter set of Kulkarni et al.[18]. For C and Si atomic parameters and Si-C, C-C, and C-H parameters we substituted in parameters from Ponomarev et al.[17]. The training set consisted of amorphous and crystalline structures of Si<sub>3</sub>N<sub>4</sub>, SiC, C<sub>3</sub>N<sub>4</sub> and C<sub>2</sub>N, SiCN with and without C<sub>free</sub>, and SiCNH polymers. Additionally, NH<sub>3</sub>, SiH<sub>4</sub>, and CH<sub>4</sub> structures comprised part of the training set. A critical part of the training set were trajectories obtained from ab initio molecular dynamics.

DFT calculations were performed with VASP[20-23] with exchange-correlation described by the PBE functional[24, 25]. Calculations utilized the projector-augmented wave (PAW) method[26, 27] with a plane wave kinetic energy cutoff of 500 eV, and forces were converged to 5 meV/Å. ab initio molecular dynamics (aiMD) were performed within the NVT ensemble using a time step of 1.0 fs and a lower plane wave kinetic energy cutoff was used. Grimme's DFT-D2 method[28] was applied to describe dispersion interactions during aiMD .

ReaxFF parameters were optimized using a custom C-code following the approach of the ReaxFF FORTRAN program of the van Duin group[12]. Parameter fitting was done through a single-parameter search using parabolic interpolation[29]. ReaxFF energies differences were fit to corresponding DFT energy differences (see Equation 1). Additionally, ReaxFF atomic forces were fit to corresponding DFT atomic forces (see Equation 2) following the approach of Ercolessi et al.[30]. The error due to energy difference mismatch and the error due to force mismatch was added, in weighted manner, into a total objective error that was minimized (see Equation 3).

$$\text{energy error} = \sum_i \frac{(E_i^{\text{ReaxFF}} - E_i^{\text{DFT}})^2}{\text{weight}^2} \quad (1)$$

$$\text{force error} = \sum_j \frac{1}{3N_j} \sum_i \frac{(F_{x,i}^{\text{ReaxFF}} - F_{x,i}^{\text{DFT}})^2 + (F_{y,i}^{\text{ReaxFF}} - F_{y,i}^{\text{DFT}})^2 + (F_{z,i}^{\text{ReaxFF}} - F_{z,i}^{\text{DFT}})^2}{\text{weight}^2} \quad (2)$$

$$\text{total error} = 100 \times \text{energy error} + \text{force error} \quad (3)$$

ReaxFF is comprised of seven types of parameters: general parameters, atom parameters, bond parameters, off-diagonal terms, valence angle parameters, torsion angle parameters, and hydrogen bond parameters. For our purposes we only optimized Si and N atomic parameters, all bonding parameters and off-diagonal terms resulting from any combination of two elements in Si-C-N-H, and all valence angle parameters resulting from any combination of three elements in Si-C-N-H. Parameter fitting was done in batches by optimizing a subset of randomly chosen parameters along with a subset of the training set.

ReaxFF calculations and simulations were done in LAMMPS[31] using the USER-REAXC package[32]. Charge equilibration was done every step and momentum was rescaled every step. A time step of 0.4 fs was used for all calculations.

## **Results and Discussions**

### **Evaluation of the new parameter set**

We evaluate our final parameter set by determining how well ReaxFF energy differences correspond to DFT energy differences for a set of hypothetical crystalline Si-C-N structures (see Figure 1). Energy correspondence is examined for DFT-optimized structures by calculating the corresponding energies in ReaxFF before constant volume relaxation and after constant volume relaxation. A slope of 1 indicates ideal energy correspondence. Following our approach to fitting parameters, ReaxFF energies before constant volume relaxation exhibit strong correlation with DFT energies with slopes near or around 1. Even ReaxFF energies calculated after constant volume relaxation exhibit moderately strong correlation with DFT energies.

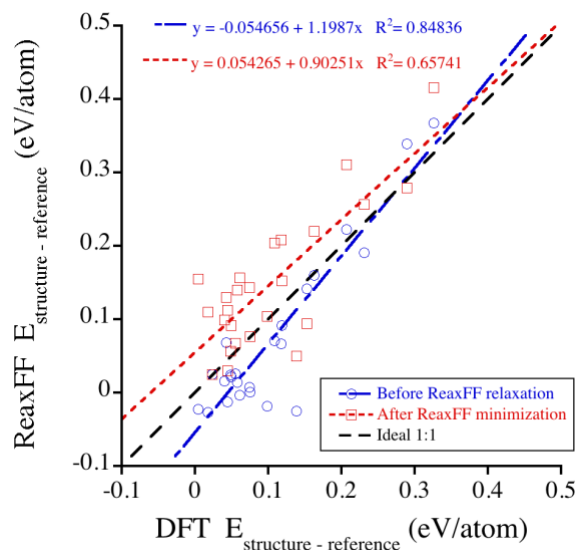


Figure 1: Energy correspondence between ReaxFF and DFT energy differences for 15SiC + 3Si<sub>3</sub>N<sub>4</sub> (Si<sub>3</sub>N<sub>4</sub>:SiC = 0.2). Static energies are calculated within ReaxFF without relaxation of DFT-optimized structures, and minimized energies are calculated within ReaxFF after constant volume optimization of DFT-optimized structures within ReaxFF. Energies are relative to the lowest energy Si-C-N structure calculated with the corresponding method (Reference structure ReaxFF energies before minimization: -6.07 eV/atom and after minimization: -6.38 eV/atom). The ideal 1:1 energy correspondence is indicated with a dashed line.

### Simulation of Ceraset

We perform a simulation of KiON Ceraset Polysilazane 20, or Ceraset for short, within ReaxFF. Ceraset consists of an alternating backbone of Si and N with vinyl and methyl groups on 20% of the silicon and methyl groups on the remaining 80% of silicon. Markel et al. [33] studied the pyrolysis of two Ceraset brands, PSZ10 and PSZ20, under inert atmosphere and found the primary gaseous products evolved are H<sub>2</sub> and CH<sub>4</sub> with a significant amount of N<sub>2</sub> being evolved above 1484°C due to the reaction between Si<sub>3</sub>N<sub>4</sub> and C.

We model Ceraset using an infinitely long strand (132 atoms) (see Figure 2a) and then create a 4×4×4 supercell of the single-strand model to get 64 infinitely long strands

(8448 atoms) for simulation purposes (see Figure 2b). Simulations are done with an NpT ensemble using a pressure of 2000 bar to prevent foaming of the polymer following the approach of Ponomarev et al.[17] The Ceraset system is equilibrated at 2000 K for 20 ps and the evolution of different gaseous species is observed.

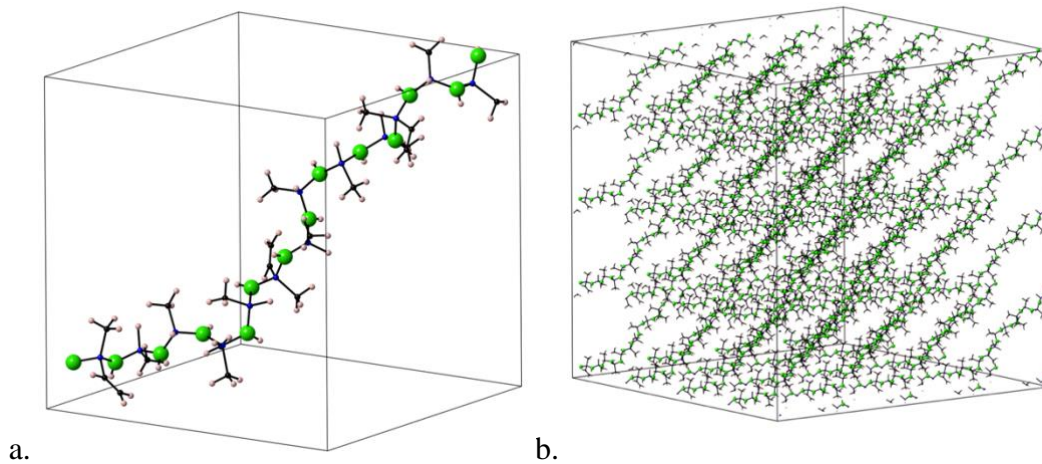


Figure 2: a. Infinite single strand of Ceraset  $\text{Si}_{15}\text{C}_{21}\text{N}_{15}\text{H}_8$  ( $a=21 \text{ \AA}$ ;  $\rho = 0.17 \text{ g/cm}^3$ ) b.  $4 \times 4 \times 4$  supercell of single strand of Ceraset  $\text{Si}_{960}\text{C}_{1344}\text{N}_{960}\text{H}_{5184}$  ( $a=84 \text{ \AA}$ ,  $\rho = 0.17 \text{ g/cm}^3$ ). Blue atoms are Si, green balls atom N, black atoms are C, and pink atoms are H. Models displayed with CrystalMaker[34].

We observe the formation of different gaseous species including  $\text{H}_2$ ,  $\text{CH}_4$ , and  $\text{NH}_3$ ; the most common abundant gaseous species evolved are  $\text{CH}_4$  and  $\text{H}_2$  similar to what Markel et al.[33] observed. After equilibration at 2000 K, the Ceraset system is heated to 3000 K at 10 K/ps and equilibrated for 400 ps in order to expedite reactions. Afterward, the system is cooled at 10 K/ps. The outcome of the simulation (see Figure 3) is a ternary spheroid structure with surrounding unreacted gaseous species. The spheroid structure is an agglomeration of Si-C-N-H and contains Si-Si, Si-C, Si-N, C-C, and C-N bonds (with H on the periphery) thus at least agreeing qualitatively with experiment[35] though there is an overabundance of single C-N bonds. Gaseous species formed during simulation at elevated temperatures mostly persist to the end of the simulation at 300 K.

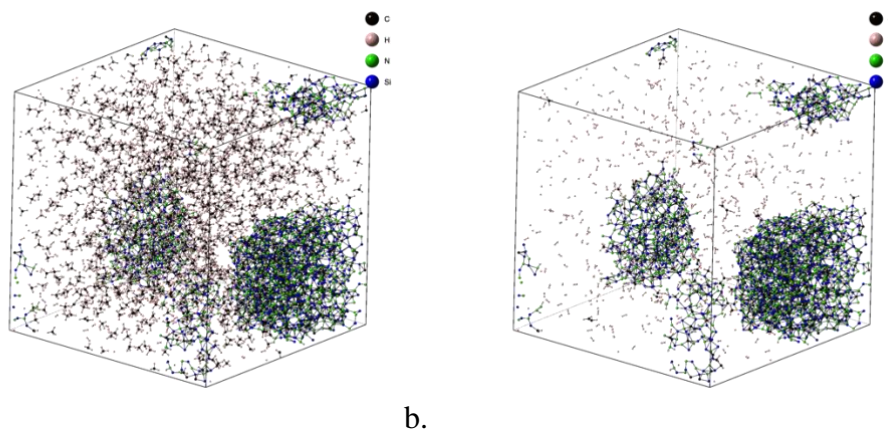


Figure 3: Ceraset  $\text{Si}_{960}\text{C}_{1344}\text{N}_{960}\text{H}_{5184}$  at 900 K after constant pressure simulation up to 3000 K ( $a=54.6 \text{ \AA}$ ,  $\rho = 0.63 \text{ g/cm}^3$ ) with a. all atoms displayed and b. methane removed from display. Models displayed with CrystalMaker[34].

## Summary

We optimize a new Si-C-N-H ReaxFF parameter set for simulation of the pyrolysis of polysilazane into amorphous SiCN ceramics. The new parameter set is trained on a diverse set of hypothetical and crystalline structures optimized in DFT. Upon evaluating the new parameter set, we find that ReaxFF and DFT energies are correlated, and energy correspondence is close to 1:1. Simulation of the polysilazane polymer Ceraset at elevated temperature is done in order to determine the types of gaseous species that evolve and what final structure may result. We find that the major gaseous species evolved during simulation of Ceraset,  $\text{CH}_4$  and  $\text{H}_2$ , agree with experiment[33].

Additionally, the resulting ternary agglomerate that forms at the end of the simulation exhibits bonding found in amorphous SiCN ceramics[35]. However, the abundance of C-N bonds indicates that further improvement of the parameters is required before meaningful results can be produced, including pyrolysis simulations with gas removal.

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## Summary

We optimized ReaxFF parameters for Si-C-N-H for simulation of the pyrolysis of polysilazane into amorphous SiCN ceramics. The new parameter set is evaluated on how well it reproduces the DFT potential energy surface in ReaxFF. We find that energy correspondence between ReaxFF and DFT energies is close to 1:1. Simulation of the polysilazane polymer Ceraset at elevated temperature is done and the evolution of different gaseous species is observed. The major gaseous species evolved during simulation of Ceraset are H<sub>2</sub>, CH<sub>4</sub>, and NH<sub>3</sub> to a lesser degree. While H<sub>2</sub> and CH<sub>4</sub> match what is produced in pyrolysis experiments[1], further work is needed to be sure that the quantity of each gaseous species agree with what should be produced in quantum chemical simulations. A ternary agglomerate is the outcome of simulation of Ceraset, and the agglomerate exhibits the type of bonding to what is expected in amorphous SiCN ceramics. Significant amounts of C-N bonding within the ternary agglomerate do indicate that further improvement of parameters is needed before any meaningful pyrolysis simulations can be done.

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## CONCLUSIONS

The first part of this work, Part I, focuses on high-pressure and materials chemistry. We investigate materials typically synthesized at high pressures and do calculations on the work of adhesion in compound graphene-SiO<sub>2</sub>/Si<sub>2</sub>CO<sub>2</sub> systems.

In Chapter 1, we study the transformation between  $\alpha$ -cristobalite-type and rutile-type for SiO<sub>2</sub>, GeO<sub>2</sub>, and TiO<sub>2</sub> using two different concerted mechanisms and conducting the transformation at different external pressures. Increasing external pressure favors the rutile-structure type while decreasing pressure favors the cristobalite structure-type. Based on the pressures at which the cristobalite structure-type of GeO<sub>2</sub> and TiO<sub>2</sub> becomes favorable, we predict that cristobalite-GeO<sub>2</sub> and cristobalite-TiO<sub>2</sub> can be synthesized with moderate tensile stresses.

Chapter 2 and Chapter 3 are dedicated to calculations supporting experimental discovery of structures in high pressure experiments. To rationalize the synthesis of *Pbcn*-Sn<sub>2</sub>N<sub>2</sub>O, we perform enthalpy-pressure calculations and determine that at ambient pressure *Pbcn*-Sn<sub>2</sub>N<sub>2</sub>O is thermodynamically favored to decompose into its binary phases. Thus, *Pbcn*-Sn<sub>2</sub>N<sub>2</sub>O must be metastable since it is experimentally recovered at ambient conditions. In the lucky discovery of spinel-type ternary silicon titanium nitride, we predict preferential sites where Ti would substitute in spinel-Si<sub>3</sub>N<sub>4</sub>. and determine that the lowest energy configurations of ternary silicon titanium nitride exhibit Ti in octahedral sites clustered together. Calculation of enthalpies of formation indicated that ternary silicon titanium nitride is thermodynamically favored to decompose into its binary phases at ambient conditions but was likely recovered in experiment due to kinetics.

In Chapter 4, we calculate the work of adhesion for compound graphene and bilayer-SiO<sub>2</sub> and graphene and Si<sub>2</sub>CO<sub>2</sub> systems. To get around the poor description of dispersion interactions in PBE[1, 2] we use different dispersion correction methods which

all yield results that agree with experiment for graphite. We find that the work of adhesion is much higher in graphene-Si<sub>2</sub>CO<sub>2</sub> systems than in the graphene-bilayer-SiO<sub>2</sub> system. Analysis of charges rules out charge transfer as significantly impacting work of adhesion in these systems, so we conclude that another phenomena is responsible for the different work of adhesion values.

Part II is about investigations of amorphous ceramics with a classical potential and force field.

Using the Tersoff potential[3] we calculate elastic properties of amorphous SiCO ceramics in Chapter 1. By independently varying parameters, we predict that increasing free carbon content increases elastic properties and increasing density also increases elastic properties contradicting Sorarù et al[4] who could not independently vary free carbon content and density. Additionally, we determine that the morphology of the free carbon phase can impact elastic properties, and when composition is fixed models with more segregated free carbon morphologies exhibit higher elastic moduli.

In Chapter 2, we develop a new method to quantify the morphology of free carbon in carbon-containing amorphous ceramics by counting the extent of three-coordinated carbon through topological shells. This topological shell counting method can be used to differentiate between amorphous ceramics containing different free carbon morphologies.

Chapter 3 involves the development of a new ReaxFF parameter set to study the polymer-to-ceramic conversion process of polysilazanes into amorphous SiCN ceramics. There are no complete SiCNH parameter sets in literature so we start from parameters from Kulkarni et al.[5] and Ponomarev et al.[6] and train them on DFT calculations and ab initio molecular dynamics. The resulting parameter set is evaluated for good reproduction of the DFT potential energy surface for Si-C-N-H materials and would likely perform well on simulations of SiCNH materials; however, issues observed during

simulation of Ceraset means that the parameter set must be improved before pyrolysis simulations, and essentially the polymer-to-ceramic conversion process, can be studied.

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## APPENDIX A

## PUBLICATION INFORMATION AND CONTRIBUTING AUTHORS

Material from this work is reproduced, in whole or in part, from several publications.

Part I Chapter 1 is reproduced in part from: S. Haseen, P. Kroll, Paving the way for cristobalite  $\text{TiO}_2$  and  $\text{GeO}_2$  attainable under moderate tensile stress: A DFT study of transformation paths and activation barriers in cristobalite-rutile transformations of  $\text{MO}_2$  ( $M = \text{Si}, \text{Ge}, \text{Ti}$ ), *Computational Materials Science* 170 (2019) 109170.

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Part II Chapter 1 is taken from a manuscript in preparation: Haseen, S.; Kroll, P. Analyzing the Effect Of Composition, Density, and the Morphology of the “Free” Carbon Phase on Elastic Moduli in Silicon Oxycarbide