

Topical Review

The atomic structure of ternary amorphous $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ hybrid oxides

M Landmann¹, T Köhler², E Rauls¹, T Frauenheim² and W G Schmidt¹¹ Lehrstuhl für Theoretische Physik, Universität Paderborn, 33095 Paderborn, Germany² Bremen Center for Computational Materials Science, Universität Bremen, 28359 Bremen, GermanyE-mail: landmann@mail.uni-paderborn.de

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Abstract

Atomic length-scale order characteristics of binary and ternary amorphous oxides are presented within the framework of *ab initio* theory. A combined numerically efficient density functional based tight-binding molecular dynamics and density functional theory approach is applied to model the amorphous (a) phases of SiO_2 and TiO_2 as well as the amorphous phase of atomically mixed $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ hybrid-oxide alloys over the entire composition range. Short and mid-range order in the disordered material phases are characterized by bond length and bond-angle statistics, pair distribution function analysis, coordination number and coordination polyhedra statistics, as well as ring statistics. The present study provides fundamental insights into the order characteristics of the amorphous hybrid-oxide frameworks formed by versatile types of TiO_n and SiO_m coordination polyhedra. In a- SiO_2 the fourfold crystal coordination of Si ions is almost completely preserved and the atomic structure is widely dominated by ring-like mid-range order characteristics. In contrast, the structural disorder of a- TiO_2 arises from short-range disorder in the local coordination environment of the Ti ion. The coordination number analysis indicates a large amount of over and under-coordinated Ti ions (coordination defects) in a- TiO_2 . Aside from the ubiquitous distortions of the crystal-like coordinated polyhedra, even the basic coordination-polyhedra geometry type changes for a significant fraction of TiO_6 units (geometry defects). The combined effects of topological and chemical disorder in a- $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ alloys lead to a continuous increase in both the Si as well as the Ti coordination number with the chemical composition x . The important roles of intermediate fivefold coordination states of Ti and Si cations are highlighted for ternary a- $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ as well as for binary a- TiO_2 . The continuous decrease in ring size with increasing Ti content reflects the progressive loss of mid-range order structure characteristics and the competing roles of network forming and network modifying SiO_m and TiO_n units in the mixed hybrid oxides.

Keywords: a- TiO_2 , a- SiO_2 , a- $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$, ternary amorphous oxides, DFT, molecular dynamics, coordination polyhedra

(Some figures may appear in colour only in the online journal)

1. Introduction

The catalytic and optical activity of solid-state materials strongly depends on diverse characteristics of the atomic structure. These are the crystal symmetry or rather the degree of structural disorder/amorphicity, as well as superordinate structural characteristics as grain size and pore size a.k.a. the effective

surface area, and further (artificial) nanostructuring of a particular sample. Commonly, the physico-chemical properties of pure materials limit the tunability of at least some of these properties. In order to overcome these kinds of limitations, the industrial need for new catalysts and optical materials drives the engineering of new, partially nanostructured, multi-component hybrid materials. Thereby, the fabrication of mixed and nanostructured

hybrid composites tries to meet two miscellaneous designing philosophies. On the one hand, systematic variation of the material composition as well as spatial structuring (e.g. quantum wells and superlattices) is used to benefit from synergetic effects between the physical properties (e.g. refractive indices, band gaps, band offsets) of the individual constituents. On the other hand, the synthesization of new hybrid materials is often motivated by the pursuit of novel physical material properties (e.g. electronic states within the band gaps or new active lattice sites for catalyzing chemical reactions) that cannot be realized by any of the alloy components.

One class of materials, that stands for the manifold of oxide alloys that have attracted considerable attention over the last years, are mixed $\text{TiO}_2/\text{SiO}_2$ (titania-silica) hybrid oxides, also termed $\text{TiO}_2/\text{SiO}_2$ binary oxides as well as ternary $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ oxides in the case of atomically mixed alloys. $\text{TiO}_2/\text{SiO}_2$ hybrid oxides take advantage of the catalytic properties of semiconducting TiO_2 and the high thermal stability and mechanical strength of SiO_2 . $\text{TiO}_2/\text{SiO}_2$ based compounds nowadays offer a promising engineering platform for new materials with wide area applicability in chemical industry and optoelectronics.

Many types of thin film, layered, and supported as well as nano- and mesostructured $\text{TiO}_2/\text{SiO}_2$ mixed oxides have been synthesized by electron-beam evaporation [1], vacuum deposition [2, 3], atomic layer deposition [4], liquid phase deposition [5], chemical vapour deposition [6–11], RF magnetron sputtering [14], ion-beam sputter deposition [15–17], plasma sputtering [18], and prevalently following sol-gel based preparation methods [19–29, 30, 32–34]. $\text{TiO}_2/\text{SiO}_2$ multilayer and thin films have been used in numerous coating applications like anti-reflective thin film coatings [1, 35], weather resistant thin film coatings [19], hydrophilic coatings [36], and implant coatings [32, 37]. Amorphous $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ thin films have also been deposited for the use as gate oxides in metal oxide semiconductor-field effect transistors [38]. Various optical devices as active and passive planar optical waveguides [20, 23, 27, 39], channel waveguides [21, 40], tailored periodically or gradually modulated refractive index devices (e.g. rugate filters) [41–43], and dielectric mirrors [17] especially benefit from the large differences in the refractive indices (~ 1.5 and ~ 2.5 for the bulk oxides of SiO_2 and TiO_2 [7, 9–11, 15, 44, 45]) and band gap energies (~ 8.5 and ~ 3.2 for the SiO_2 and TiO_2 bulk oxides [9, 15]) of $\text{TiO}_2/\text{SiO}_2$ hybrid materials.

Various studies have indicated that mixed $\text{TiO}_2/\text{SiO}_2$ binary oxides are more active catalysts than pure TiO_2 [29, 30] and a promising material for various catalytic applications. Comprehensive reviews on the structural as well as physico-chemical properties of mixed titania-silica oxide catalysts have been published by Davis and Liu [31] and Gao and Wachs [46]. In summary, the catalytic activity of $\text{TiO}_2/\text{SiO}_2$ compounds falls into three categories that reflect various characteristics of the utilized material. Photocatalytic properties are associated with band structure features as well as quantum size-effects due to particle size and nanostructuring. Based on the photocatalytic activity, the potential use of crystalline and amorphous $\text{TiO}_2/\text{SiO}_2$ nanocomposites for photocatalytic purification of contaminated (waste-) water [47, 48], exhaust gas [49], and textiles [50] has been discussed. Acid catalysis activity is generated by the character of

newly formed acid sites in mixed and nanostructured $\text{TiO}_2/\text{SiO}_2$ oxides that are not present in the pure material phases. The acidity [4, 31, 46] of $\text{TiO}_2/\text{SiO}_2$ mixed oxides has been discussed controversially in literature [22, 31]. The third category summarizes material related to supporting properties as porosity, surface area as well as thermal stability that are indirectly related to the catalytic activity of a material. Mixed amorphous and crystalline networks of micro- and mesoporous $\text{TiO}_2/\text{SiO}_2$ oxides are nowadays widely used as catalysts in chemical industry [25, 46, 51–64].

One prominent representative of the crystalline $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ structure family is the molecular sieve-type titanium-silicalite TS-1. TS-1 catalyzes several chemical reactions as phenol hydroxylation, cyclohexanone ammoximation, or propylene epoxidation at different stages of industrial application. In general, isolated fourfold coordinated Ti ions (Ti_{4c}) substituting Si_{4c} ions in the zeolite structure have been identified as the active sites in the mixed crystalline framework [51, 52, 54, 58, 65, 66]. TS-1 has been found to be a more active catalyst as amorphous $\text{TiO}_2/\text{SiO}_2$ itself. Hence, different species of Ti^{4+} ions in the crystalline TS-1 framework and in amorphous $\text{TiO}_2/\text{SiO}_2$ catalysts have been assumed [51].

The atomic structure of amorphous $\text{TiO}_2/\text{SiO}_2$ oxides has been investigated extensively over the last decades. Experimental studies [8] found no indication for substantial contributions from direct Si–Ti bonds in $\text{TiO}_2/\text{SiO}_2$ oxide films. Cross-linking between TiO_2 and SiO_2 domains in amorphous $\text{TiO}_2/\text{SiO}_2$ composites is rather found to be connected to the formation of bridging O ions in Ti–O–Si cross-linking bonds. The most common way to prove presence and amount of Ti–O–Si linkages is the identification by the intensity of an infrared (IR) absorption band between 900 and 965 cm^{-1} in IR spectroscopy [7–9, 11, 25, 34, 46, 54]. This absorption band has been associated with the motion of a bridging O ion in Ti–O–Si bonds, a Si–O vibrational mode disturbed by the presence of Ti ions, respectively. Further evidence on the formation of Ti–O–Si bonds in $\text{TiO}_2/\text{SiO}_2$ mixed oxides is given by Raman spectroscopy and the assignment of two frequency bands at 960 cm^{-1} and 1100 cm^{-1} to vibrational modes in Ti–O–Si linkages [46, 67]. Based on x-ray absorption spectroscopy (XAS) analysis of the electronic structure of the $\text{TiO}_2/\text{SiO}_2$ interface, Soriano *et al* [68] proposed the formation of Ti–O–Si cross-linking oxygen bonds that connect Ti_{6c} ions in octahedral TiO_6 units and Si_{4c} ions in SiO_4 tetrahedral units. Similar conclusions have been drawn from extended x-ray absorption fine structure (EXAFS) and x-ray absorption near-edge spectroscopy (XANES) analysis in a preceding study [69].

Experimental studies [7–13, 25, 26, 44, 46, 70, 71], focusing on details of the local atomic structure, have further indicated that Ti ions in a- $\text{TiO}_2/\text{SiO}_2$ show predominantly a partially distorted tetrahedral coordination of Ti ions by O ions at low Ti concentration between ~ 0.05 and 9 weight percent (wt%). Increasing the amount of Ti ions in the amorphous $\text{TiO}_2/\text{SiO}_2$ matrix up to ~ 15 wt% of TiO_2 leads to an increasing amount of octahedrally coordinated Ti_{6c} ions. Above ~ 15 wt% TiO_2 the segregation of TiO_2 as a second phase may occur. Phase separation has also been reported for high TiO_2 concentrations of ~ 41 molecular percent (mol%) [26, 72]. Orignac [73] reported coexisting and continuously increasing hetero-condensation (formation of SiO_2 and TiO_2 domain linking Ti–O–Si

bonds) and homo-condensation (formation of Si–O–Si and Ti–O–Ti bonds) for an increasing amount of Ti with a maximum fraction of Ti–O–Si bonds (coexisting with a local minimum of Ti–O–Ti bonds) at 20 mol% TiO₂ content. Based on EXAFS and XANES on TiO₂/SiO₂ mixed oxide glasses up to TiO₂ contents of 11.6 mol%, Henderson and Fleet [28] proposed the following scenario for the transition from a homogeneous mixed oxide to a phase separated heterogeneous composite upon an increasing TiO₂ content: The onset of phase separation is not the distortion of the SiO₄ tetrahedron network but the formation of sixfold coordinated Ti_{6c} ions. At low TiO₂ content the fourfold coordination of the tetrahedron network remains undisturbed. However, these larger TiO₄ tetrahedron building blocks put volume constraints on the glassy network whose relatively incompressible Si–O bonds only show a limited ability to adjust to the volume increase. From XAS studies [28, 74–76], also, the formation of larger TiO₄ tetrahedron building-block clusters seems highly unlikely. At some point it becomes more favorable for the strained TiO₂/SiO₂ framework to convert Ti_{4c} to Ti_{6c} rather than incorporating further fourfold coordinated Ti ions. Finally, the existence of crystal-like Ti_{6c} ions promotes the formation of a crystalline TiO₂ anatase phase.

Surprisingly, Gregeor *et al* [71] reported the existence of Ti_{6c} ions at very low TiO₂ concentrations below ~0.05 wt%. However, such observations seem inconsistent with various other studies and have not been confirmed experimentally or theoretically.

Very recently, the structure of low temperature (80 °C) prepared sol-gel TiO₂/SiO₂ composites has been extensively investigated by x-ray total scattering techniques [34]. For all TiO₂/SiO₂ samples (Ti concentrations of 20, 35, and 50 mol%) large fractions of both nanocrystalline anatase and amorphous TiO₂ have been reported.

In contrast to the reported phase-separation tendency upon increasing TiO₂ content, it has been reported [16, 17] that small amounts of SiO₂ enable TiO₂/SiO₂ mixed films to sustain higher annealing temperatures without TiO₂ phase transition from an amorphous state to polycrystalline anatase. While pure TiO₂ films exhibit a crystallization temperature of ~200 °C, the admixture of 5% SiO₂ increases the onset of crystallization to ~250 °C, the admixture of 9 % SiO₂ to ~300 °C, and the admixture of 17 % SiO₂ beyond 400 °C. Similarly, solid phase precipitation of crystalline TiO₂ has been found by Busani *et al* [11] in pure amorphous TiO₂ upon annealing to 400 °C while no phase segregation occurred for Ti_xSi_{1-x}O₂ oxide films even for TiO₂ fractions as high as 75%. Due to the nonfulfillment of the Bruggeman effective medium approximation for separated material phases of measured TiO₂/SiO₂ coating refractive indices, Larouche *et al* [8] excluded the formation of a heterogeneous mixture of SiO₂ and TiO₂ phases. Annealing to 400 °C induced TiO₂ crystallization in the high refractive index (TiO₂ rich) films while no crystal formation occurred in low refractive index (TiO₂ poor) mixtures. Therefrom, the necessity of TiO₂-rich regions as a seed for TiO₂ crystal growth has been deduced.

Gallas *et al* [2] studied the interface between SiO₂ and TiO₂. It has been shown that the growth of TiO₂ on SiO₂ begins with an amorphous interface layer even when the growth occurs at temperatures as high as 400 °C. Evidence for TiO₂–SiO₂ bonding by Ti–O–Si cross-linkages was given by x-ray photoemission spectroscopy (XPS) measurements. The possible fabrication of

well defined multilayer structures from amorphous SiO₂ and TiO₂ films has been demonstrated by Wang *et al* [45].

Gracia *et al* [9] reported the preparation of mixed TiO₂/SiO₂ optical thin films with Si/Ti ratios covering the total composition range from pure SiO₂ to pure TiO₂ by ion beam induced and plasma enhanced chemical vapor deposition (IBICVD and PECVD). By Fourier transform IR (FT-IR) spectroscopy the TiO₂/SiO₂ films have been characterized as homogenous a-Ti_xSi_{1-x}O₂ mixtures of the two binary oxides rather than a compound of separated SiO₂ and TiO₂ phases. From analysis of the crystal field splitting, Ti ions at low concentrations (2–10%) were attributed to TiO₄ building blocks. Upon TiO₂ content increase, the continuous increase in the crystal field splitting energies towards the value, representative for amorphous TiO₂, gives evidence for an increasing coordination number. Especially, the existence of an intermediate fivefold coordinated Ti species has been depicted as a likely coordination state at higher fractions of TiO₂ in a-Ti_xSi_{1-x}O₂ thin films.

While Ti ions in the two most common crystalline coordination states of SiO₂ (fourfold) and TiO₂ (sixfold) are repeatedly reported, fivefold coordinated Ti_{5c} ions in hexahedral TiO₅ building blocks represent a rarer coordination state that is only sporadically reported for pure TiO₂/SiO₂ mixed oxides [4, 9, 28, 31]. Besides, in several known crystalline oxides as K₂Ti₂O₅ [77] and silicates as fresnoite (Ba₂TiSi₂O₈) [78] or Na₂TiSiO₅ [79] the occurrence of TiO₅ units has been reported for ternary TiO₂/SiO₂ mixed oxides bearing fractions of alkali and alkaline-earth metal atoms that act as network modifiers [74–76, 80–83, 120].

In summary, the detailed analysis of existing literature shows that most experimental techniques have difficulties identifying fundamental correlations of material specific short-range order characteristics on the atomic level (within the first coordination shell) and the resulting trends in physical material properties on a mesoscopic or macroscopic length scale. Especially, the identification of possibly existing Ti_{5c} ions in a fivefold coordinated TiO₅ bonding environment and the differentiation of these ions from a superposition of Ti_{4c} ions in tetrahedral and Ti_{6c} ions in octahedral bonding environments demands a high accuracy of experimental techniques. Thus, finding fundamental structure-function relationships, that may support the engineering of advanced functional materials, can substantially benefit from modern high-performance computer simulations on the atomic structure of disordered solids. Recently, the structure and stability as well as the vibrational and excitation properties of numerous pure (SiO₂)_n and (TiO₂)_n as well as mixed Ti_mSi_{n-m}O_{2n} clusters with *n* between 2 and 5 and *m* between 1 and (*n*-1) have been investigated by Bandyopadhyay and Aikens in a combined density functional theory (DFT), time-dependent DFT, and coupled-cluster study. [84] Their results demonstrate that pure (SiO₂)_n favors linear chain-like structures with tetravalent states and (TiO₂)_n prefers compact three-dimensional configurations with hexavalent states. The structure of mixed Ti_mSi_{n-m}O_{2n} clusters shows a dependence on the compound stoichiometry with a stabilization of three-dimensional structures by incorporation of even small percentages of Ti. A theoretical study on larger scale models of titanium silicate glasses has been published by Rosenthal and Garofalini [85]. In their empirical potential MD study the structural properties of Ti_xSi_{1-x}O₂ compounds with

TiO₂ contents ranging from 2–15 mol% have been simulated using 360 atom unit cells. The influence of slower MD cooling rates on the Ti coordination state has been outlined. While a fast quenching rate promotes significant fractions of fivefold coordinated Ti ions for all TiO₂ concentrations, a lower cooling rate strongly favors tetrahedrally coordinated Ti at low TiO₂ contents ($\lesssim 10$ mol%). At higher TiO₂ content (~ 15 mol%), the slower quenching rate drastically reduces the occurrence of TiO₄ building blocks in favor of fivefold (53 %) and sixfold (28 %) coordinated Ti ions. In consideration of the strong dependence of the Ti coordination state on the cooling rate, the existence of TiO₅ building blocks in a-Ti_xSi_{1-x}O₂ mixed oxides remained still uncertain.

More recently, Bernard *et al* [121] studied the composition influence of undoped and Er doped TiO₂/SiO₂ mixed oxide glasses by large scale (5094 atom unit cells) empirical potential MD simulations for Ti concentrations ranging from 7.8 mol% up to 50 mol%. In all (pure) TiO₂/SiO₂ structure models, fourfold and fivefold coordinated Ti ions in TiO₄ and TiO₅ units represented the dominating structural building blocks. Already for the lowest simulated Ti concentration (7.8 mol% Ti), the formation of Ti_{4c} ions with 53% was only slightly favored over Ti_{5c} ions with a fraction of 42%. In the equimolar (50 mol% Ti) TiO₂/SiO₂ sample Ti_{5c} ions were found to be the dominant coordination state with a 60 % fraction while Ti_{4c} ions were limited to 30 %. Higher Ti coordination states were limited to minor percentages with a maximum of 10% of sixfold coordinated Ti_{6c} ions for the equimolar mixture. Based on a cluster analysis of Ti ions in the amorphous SiO₂ framework, the distribution of TiO₂ has been characterized to be neither homogeneous nor phase separated but rather random like. Even in the case of the equimolar TiO₂/SiO₂ structure model no evidence for the formation of a separated TiO₂ phase was found. Nevertheless, a general tendency to higher Ti coordination states upon increasing TiO₂ contents was interpreted as a favorable factor for the formation of a crystalline TiO₂ phase. Similar to the preceding work of Rosenthal and Garofalini [85] the quenching rate used in the MD simulations has been identified as the most crucial numerical parameter. In general, the time scales of the MD simulations might not have been sufficient to observe the possible occurrence of crystallization processes.

Aside from small cluster model *ab initio* calculations and the mentioned empirical potential MD studies, comprehensive numerical investigations of TiO₂/SiO₂ hybrid oxides are missing. The purpose of this study is to give new insights into the structural short-range and mid-range order characteristics of the pure binary phases of a-SiO₂ and a-TiO₂ as well as atomically mixed ternary a-Ti_xSi_{1-x}O₂ oxides over the entire composition range.

The paper is organized as follows: section 2 summarizes the underlying numerical framework for the MD simulations needed to generate the amorphous structure models. The basic ideas of structure analysis by (effective) coordination number analysis as well as coordination polyhedra and ring statistics are introduced in section 3. Section 4 provides presentation and discussion of physical trends in the structural material characteristics. Finally, section 5 summarizes the results and gives concluding comments and reasonings.

2. Methodology and numerical details

The structure formation of the amorphous oxides was simulated by performing combined self-consistent charge (SCC) density functional theory tight binding (DFTB) [86–88] MD simulated annealing (SA) and DFT [89, 90] calculations. SCC-DFTB based MD offers a good compromise between accuracy and computational efficiency for large-scale unit-cell simulations of the atomic and electronic structure of amorphous oxides [98, 99]. In the DFTB simulations, the Ti–O interaction parametrization of [93] was used. Within the MD-SA simulations, the Newton's equations of motion were solved using the Verlet-algorithm and the coupling to a heat-bath, according to a canonical (NVT) ensemble, was realized by an Anderson thermostat. The DFT structure relaxations and groundstate calculations have been performed using the projector-augmented wave (PAW) method [94, 95] as implemented in the Vienna *ab initio* simulation package (VASP) [96]. The generalized gradient approximation (GGA) according to Perdew, Burke, and Ernzerhof (PBE) [97] was applied to describe the exchange-correlation (XC) energy. In the DFT calculations, an energy cutoff of 400 eV was used to expand the wavefunctions into plane-wave basis sets. The *k*-point sampling was restricted to the Γ point and the DFTB optimized structure models were relaxed until a force convergence criterion of 0.001 eV Å⁻¹ was reached.

Initial structures, containing 216 atoms for the two binary oxides TiO₂ and SiO₂ and 300 atoms for the ternary Ti_xSi_{1-x}O₂ oxides (at composition parameters of $x = 0.2, 0.4, 0.6$, and 0.8) in a spatially and chemically randomized configuration, have been prepared as the starting point for the MD simulations. More abstractly speaking, the initial configurations have been prepared assuming the model of a hard sphere gas. All structure models considered in this study are strictly stoichiometric. The atoms are placed in fixed-volume rectangular cuboidal supercell arrangements of a size matching the microscopic mass densities of 4.20 g cm⁻³ for a-TiO₂ and 2.20 g cm⁻³ for a-SiO₂. Since experimental data on the mass densities of ternary a-Ti_xSi_{1-x}O₂ oxides over the entire composition range are limited and large variations in the atomic mass densities upon the sample preparation routes are reported in literature, we assume a mass-density dependence on the composition parameter following Vegard's law [91, 92]. Thus, the unit mass-density of the ternary oxides was linearly interpolated between the binary oxide mass densities.

As illustrated in figure 1, the amorphization starts with a short (500 time steps) equilibration phase at 5000 K that is followed by an exponential 23 000 time step cooling towards room temperature (300 K). The total duration of the cooling procedure amounts 23 ps. In general, For most structural features we report the structure statistics for both, the last DFTB-MD generated configuration (DFTB geometry) and the DFT post-relaxed VASP geometry. Detailed visualizations of the atomic structures of all VASP geometries are given in the figures 2, 3 and 4 as well as in figure 19.

The structure characterization in terms of coordination statistics, distribution function analysis and ring statistics has partially been done by the use of the structure analysis tools provided within the RINGS [100] and ISAACS [101] codes.

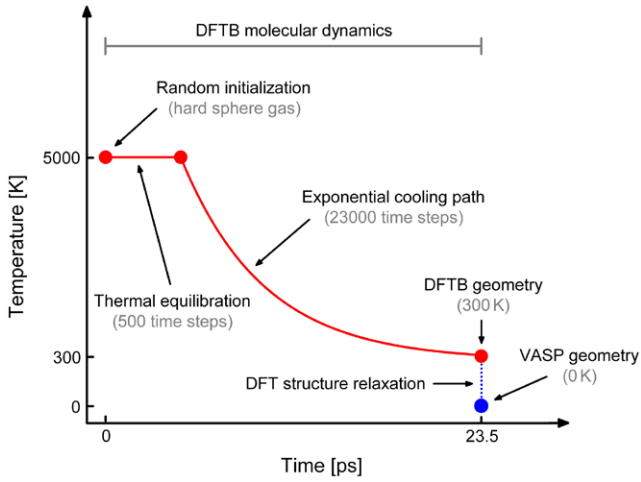


Figure 1. Schematic representation of the combined DFTB-MD and DFT amorphization approach applied for generating a-Ti_xSi_{1-x}O₂ structure models (see text for details).

3. Characterization of structural material properties

Crystalline materials are completely determined by their symmetry and chemical composition. A direct consequence of the lattice symmetry and translational invariance are long-range order attributes of the electronic wave function that are formally expressed in the validity of Bloch's theorem. In an amorphous solid the crystalline long-range order is completely lost due to random distortions in the atomic network. However, on a small length scale the atomic order in an amorphous solid partially commemorates the crystalline order characteristics. The existence of such short-range and in some cases also mid-range order characteristics is a material property that fundamentally distinguishes the class of amorphous solids from liquids. This paper especially focuses on the identification of the fundamental order characteristics of amorphous solids on an atomic length scale. While *nearest neighbor* bond lengths, bond angles and coordination characteristics are subsumed under the general term short-range order, mid-range order subsumes topological properties of the amorphous network. Characteristic examples of mid-range order are filament-like or ring-like structure elements. The type of order that is found in an amorphous solid strongly depends on the mass density, more precisely the density dependent ion-coordination states, of the considered material as exemplified by a-TiO₂ and a-SiO₂. Amorphous TiO₂ is known to be dominated by short-range order coordination characteristics [98], while the amorphous framework of a-SiO₂ predominantly shows ring-type mid-range order characteristics [100, 102–106]. Below, we will summarize the key concepts of the most important structure-analysis approaches that are required for an in-depth analysis of the mean local bonding environment and the topological network structure of the binary and multi-component amorphous oxides.

3.1. Short-range to mid-range order: pair distribution function analysis

Short-range as well as mid-range order characteristics of amorphous solids can be analyzed by interatomic correlation

functions [107–109]. The (partial) distribution $g_{\alpha\beta}(r)$ of interatomic distances between atom pairs of the chemical types α and β is given as a one-dimensional radial function quantifying the probability of finding an atom of type β within a radius r around an atom of type α at the origin:

$$g_{\alpha\beta}(r) = \frac{1}{4\pi r^2 \rho(r)} \frac{N}{N_\alpha N_\beta} \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} \delta(r - |\mathbf{r}_{ij}|). \quad (1)$$

Here, $\rho(r)$ is the real-space pair density function of the N atom containing system and N_α and N_β are the numbers of atoms of the chemical species α and β respectively. $|\mathbf{r}_{ij}|$ is the absolute value of the distance vector between an atom i of the chemical type α and an atom j of the chemical type β . The weighted sum of the partial pair distribution functions $g_{\alpha\beta}(r)$ with respect to the number concentrations $c_\alpha = N_\alpha/N$ and $c_\beta = N_\beta/N$ of chemical elements α and β gives the total (radial) pair distribution function $g(r)$.

$$g(r) = \sum_{\alpha,\beta} c_\alpha c_\beta g_{\alpha\beta}(r) \quad (2)$$

$$= \frac{1}{4\pi N \rho_0 r^2} \sum_{i=1}^N \sum_{j=1, j \neq i}^N \delta(r - |\mathbf{r}_{ij}|) \quad (3)$$

Instead of $g(r)$ and $g_{\alpha\beta}(r)$ themselves, we will make use of the reduced pair correlation functions

$$G_{\alpha\beta}(r) = 4\pi \rho_0 r [g_{\alpha\beta}(r) - 1] \quad (4)$$

and

$$G(r) = 4\pi \rho_0 r [g(r) - 1] \quad (5)$$

$$= 4\pi r [\rho(r) - \rho_0] \quad (6)$$

throughout this study.

Here, $\rho_0 = N/V$ is the average number density of N atoms in the unit cell of volume V and in the second step of equation (5) the relation $\rho(r) = \rho_0 g(r)$ between pair density function $\rho(r)$ and pair distribution function $g(r)$ has been used. In numerical simulations, the correlation functions $g(r)$ and $g_{\alpha\beta}(r)$ as well as the related reduced quantities $G(r)$ and $G_{\alpha\beta}(r)$ are directly accessible through real-space analysis of the generated atomic structure models. The total and partial pair distribution functions also give access to the total and partial coordination numbers and provide reasonable cutoff lengths for the coordination polyhedra analysis discussed below.

3.2. Short-range order: coordination number analysis

The most important short-range order information is given by the atomic coordination numbers, the mean atomic coordination numbers, respectively. For a monoatomic solid, the total (first) coordination number of an atom is defined as the average number of atoms within the first coordination spheres of radius $r_{\min}$

$$\begin{aligned} N_C &= 4\pi \int_0^{r_{\min}} \rho(r) r^2 dr \\ &= 4\pi \rho_0 \int_0^{r_{\min}} g(r) r^2 dr. \end{aligned} \quad (7)$$

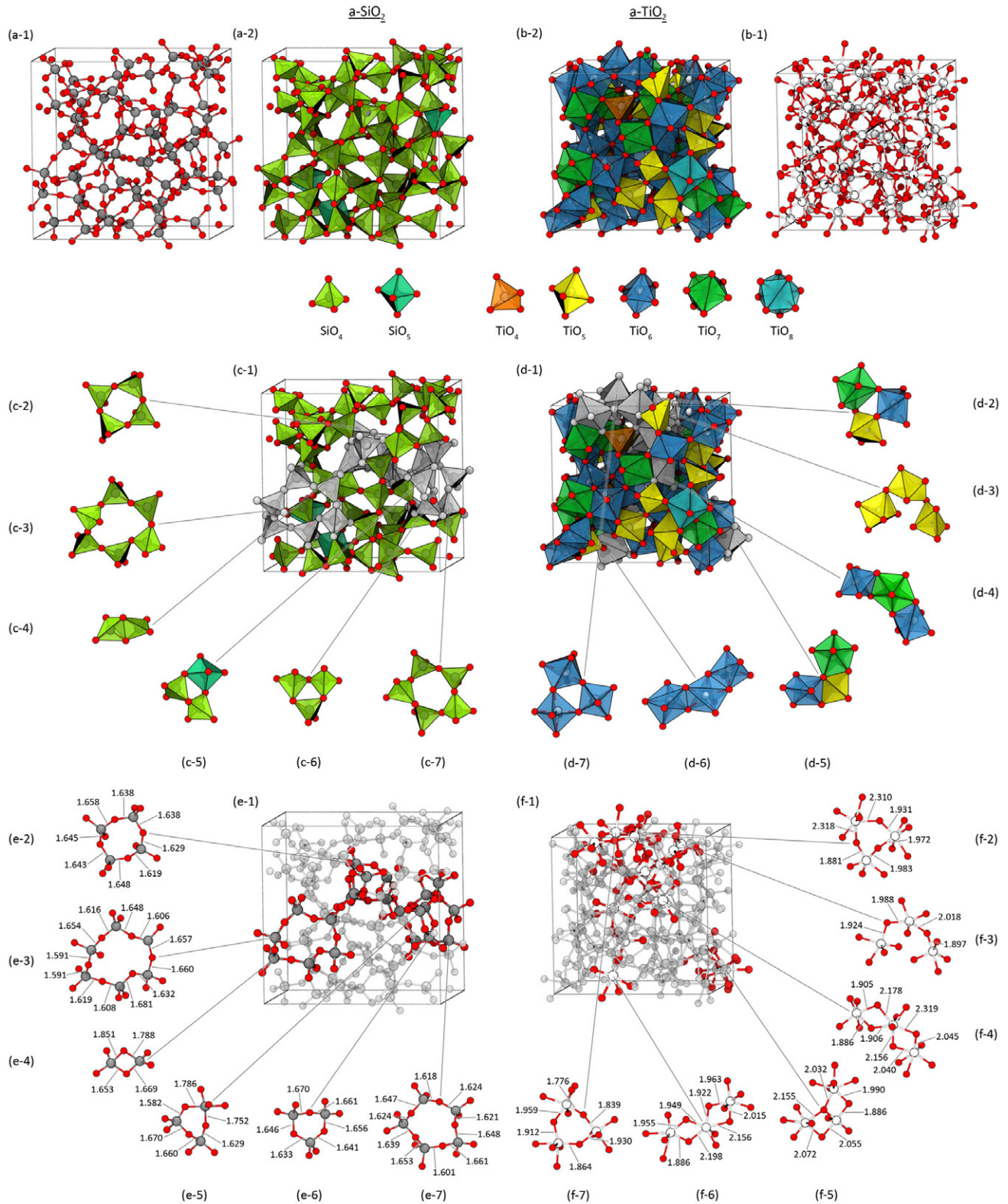


Figure 2. Ball and stick as well as coordination polyhedra representation for the $a\text{-SiO}_2$ (left) and $a\text{-TiO}_2$ (right) VASP geometries. Characteristic structure elements are visualized in the lower panels. The color coding indicates the local coordination states of the Ti and Si cations in TiO_n , $n = 4 \dots 8$ and SiO_m , $m = 4 \dots 5$ building blocks.

Hence, $r_{\min}$ acts as a *static* cutoff parameter that determines the coordination number. A reasonable choice for $r_{\min}$ is given by the first minimum of the pair distribution function. Coordination numbers of higher coordination shells can be

obtained by integrating the atomic density within spherical shells whose limits are determined by higher local minima of the pair distribution function. Going to a multi-component system, the coordination number of an atom of chemical

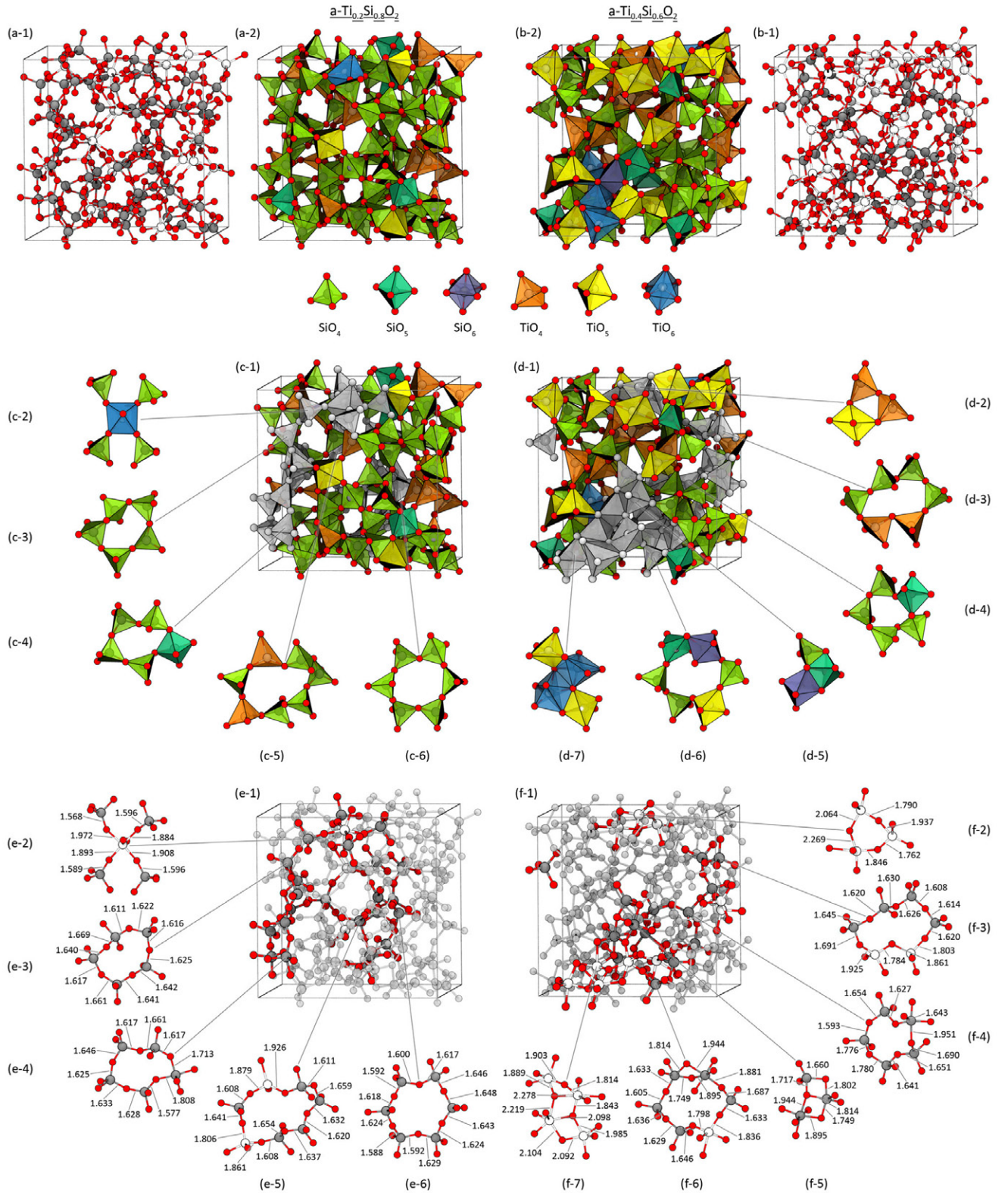


Figure 3. Ball and stick as well as coordination polyhedra representation for the $a\text{-Ti}_{0.2}\text{Si}_{0.8}\text{O}_2$ (left) and $a\text{-Ti}_{0.4}\text{Si}_{0.6}\text{O}_2$ (right) VASP geometries. Characteristic structure elements are visualized in the lower panels. The color coding indicates the local coordination states of the Ti and Si cations in TiO_n , $n = 4 \dots 6$ and SiO_m , $m = 4 \dots 6$ building blocks.

species α can also be decomposed into partial contributions $N_{\alpha\beta}$ from individual atom types β . $N_{\alpha\beta}$ is defined as the average number of atoms of type β within a spherical shell around an atom of type α

$$\begin{aligned}
 N_{C_{\alpha\beta}} &= 4\pi \int_0^{r_{\min}} \rho_{\alpha\beta}(r) r^2 dr \\
 &= 4\pi \rho_0 c_{\beta} \int_0^{r_{\min}} g_{\alpha\beta}(r) r^2 dr
 \end{aligned} \tag{8}$$

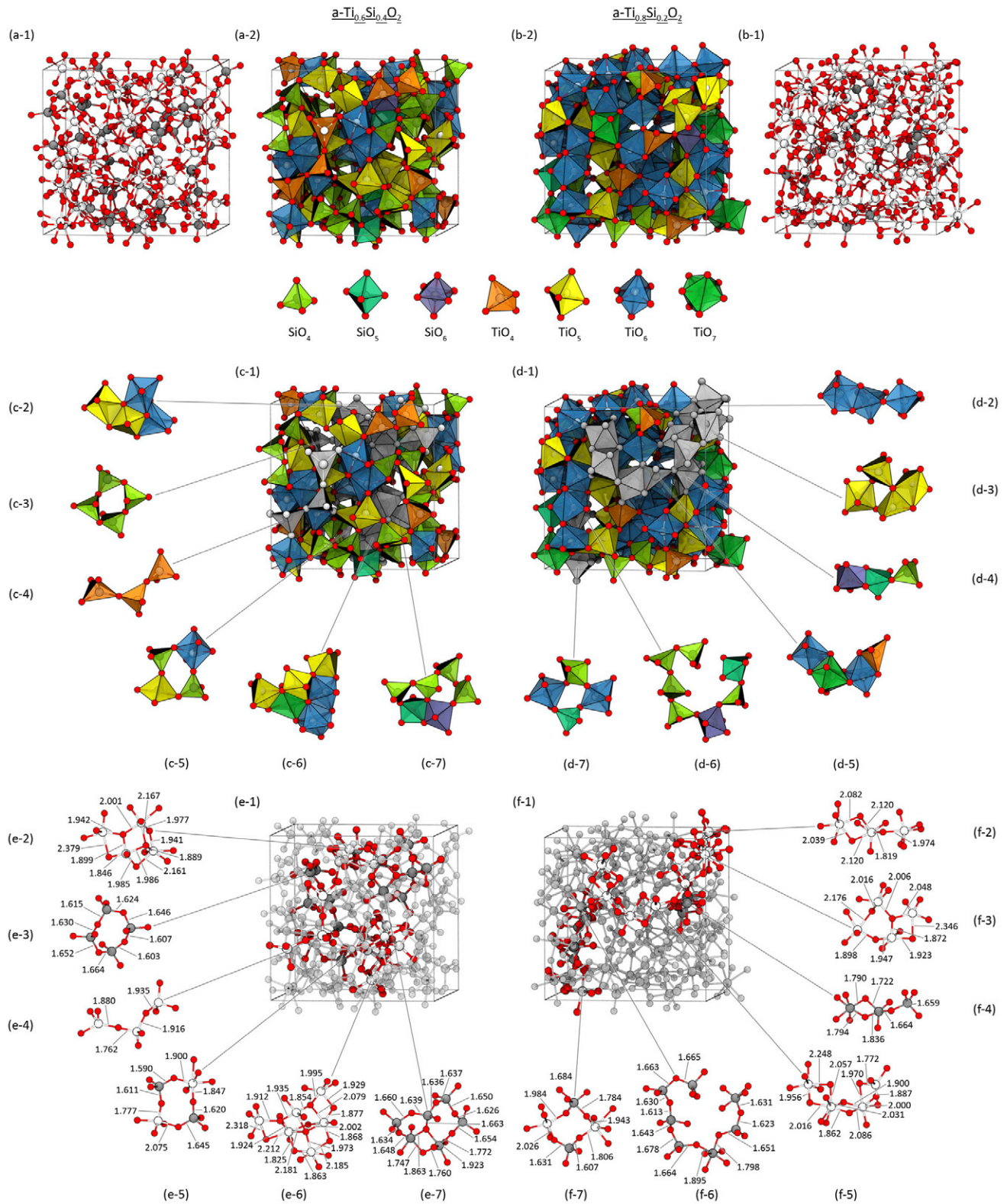


Figure 4. Ball and stick as well as coordination polyhedra representation for the $a\text{-Ti}_{0.6}\text{Si}_{0.4}\text{O}_2$ (left) and $a\text{-Ti}_{0.8}\text{Si}_{0.2}\text{O}_2$ (right) VASP geometries. Characteristic structure elements are visualized in the lower panels. The color coding indicates the local coordination states of the Ti and Si cations in TiO_n , $n = 4 \dots 7$ and SiO_m , $m = 4 \dots 6$ building blocks.

Necessarily, summation over all atomic species β provides the total coordination number of atom α by arbitrary atoms

$$N_{C\alpha} = \sum_{\beta} N_{\alpha\beta}. \quad (9)$$

A general shortcoming of this *conventional* approach to determine the (average) coordination state of an atom is a pronounced dependence on the choice of the cutoff parameters.

3.3. Short-range order: coordination polyhedra statistics

While the pair-distribution analysis is a powerful technique to analyze and compare averaged topological features on a short-range and the mid-range length-scale, it does not necessarily allow us to identify distinct characteristics of the short-range order within the first coordination shell. This shortcoming especially arises in amorphous structures due to the superposition of pair correlations from atoms in various coordination environments and through ubiquitous lattice distortions. In order to gain fundamental insights into the atomic structure within the first coordination shell, it is necessary to analyze the structural properties on the atomic level by splitting the solid into a set of simple geometric units that map the atomic structure characteristics of the solid and that appear repeatedly throughout the crystal. Besides strict mathematical decomposition schemes based on Voronoi tessellation and, complementary, Delaunay triangulation, one of the most useful and illustrative decomposition schemes is the description of the disordered atomic structure by coordination polyhedra as fundamental building blocks. These are constructed by considering the bonded atoms, the nearest neighbor atoms or ligands, respectively, within some specific cutoff range defining the actual coordination sphere, as the vertices of a geometrical object, more precisely an irregular polyhedron composed from differently shaped polygons. Such coordination polyhedra inherently combine the coordination number as a quantitative measure for the atomic environment with the topological information contained in the shape of a particular coordination polyhedron. In general, a coordination polyhedra will reflect a particular hybrid-orbital-type whose shape will be specified by a linear combination of the involved atomic orbitals. Hence, the diversity of coordination polyhedra is associated with the valence-orbital type of the involved chemical elements. In $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ compounds especially, the d electrons of Ti will increase the number of occurring coordination polyhedron-types.

Even if there are, strictly speaking, not two identical coordination polyhedra in an amorphous solid, it should be possible to assign the distorted polyhedra to a discrete number of fundamental *high symmetry* coordination polyhedra. Most likely, these fundamental structural units correspond to or at least include distorted elementary building blocks of crystalline material modifications with a comparable chemical composition and mass density. Many elements of coordination polyhedra statistics are also contained in the ideas of crystal field and ligand field theory that connect the local coordination geometry of molecules and solids to characteristic features, in particular the energy level splitting, of the electronic structure. The basic ideas of the coordination-polyhedra analysis, as well as the concept of coordination numbers itself, were brought up by Alfred Werner as early as 1893 [122] in the characterization of inorganic metal salts. Ever since, coordination number and polyhedra statistics have been proven to be important concepts to understand the atomic structure of crystalline solids [124]. Most notably, the topology of tetrahedrally [100, 106, 113] and octahedrally [98, 106] coordinated materials have been investigated. Both, SiO_2 and TiO_2 might

be seen as the archetypes of fourfold tetrahedral coordination (SiO_2) and sixfold octahedral coordination (TiO_2). The coordination polyhedra analysis especially illustrates the common short-range order features between crystalline modifications and amorphous phases of these oxides [98].

Idealized coordination polyhedra in a mathematical sense, exist in crystalline solids, but can not be found in an amorphous solid. In fact, an amorphous solid is formed by any number of randomly distorted polyhedron building blocks. Hence, we will label and subsume the distorted coordination polyhedra according to their basic high-symmetry structure types. In particular cases, prevalent at high coordination numbers, disorder induced distortions can severely handicap the assignment of a specific structure type to a particular coordination polyhedra. Also, the shape of coordination polyhedra can change continuously between various basic types. Nevertheless, in most cases the conserved short-range order allows the identification of various fundamental polyhedron-building block configurations for a given coordination number.

In order to unify the discussion, we will refer to all considered atomic building blocks as coordination polyhedra, including fundamental building blocks that are not a polyhedron in a mathematical sense or a polyhedron at all (i.e. simple polygons). Strictly speaking, there are only five regular polyhedra, the tetrahedron ($N_c = 4$), the octahedron ($N_c = 6$), the cube ($N_c = 8$), the dodecahedron ($N_c = 12$) and the icosahedron ($N_c = 20$), the Platonic solids. There are thirteen additional semi-regular polyhedra of the Archimedean solid family with $N_c > 12$ vertices. With respect to the coordination numbers, only the tetrahedron and the octahedron are found among the fundamental $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ building blocks. Single coordination polyhedra shapes can also be assigned to the infinite family of prisms. Further polyhedra types belong to the 92 membered family of Johnson solids [126], formed by non-uniform polyhedra ($N_c > 5$) constructed from regular polygons.

In order to define reasonable *convex* coordination polyhedra it is necessary to limit the radius of the coordination spheres around each atom. This is done by using the first minimum of the partial reduced pair distribution functions $G_{ij}(r)$ for each pair of chemical elements as cutoff radii. The applied cutoff radii for coordination-polyhedra statistics are 2.4 Å for Ti–O and 2.1 Å for Si–O pair correlations. The coordination polyhedra, that have been identified as structural building blocks of $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ mixed oxides, are discussed below and visualized in figure 5.

3.3.1. Threefold coordination ($N_c = 3$). Threefold coordinated AX_3 units, trigons respectively, occur in two basic configurations. In the trigonal pyramidal coordination type ([TPY-3]) the central atom is displaced along the surface normal from the ligand plane. The prototypical example for this coordination type is the C_{3v} symmetric NH_3 molecule. In the planar type the central atom is coplanar with its three ligands. The planar coordination type, splits into two subtypes, a regular trigonal plane type ([TP-3]) and a T-shaped ([TS-3]) configuration. Characteristic examples for threefold coordinated complexes are trifluoride molecules, with BF_3 showing a D_{3h}

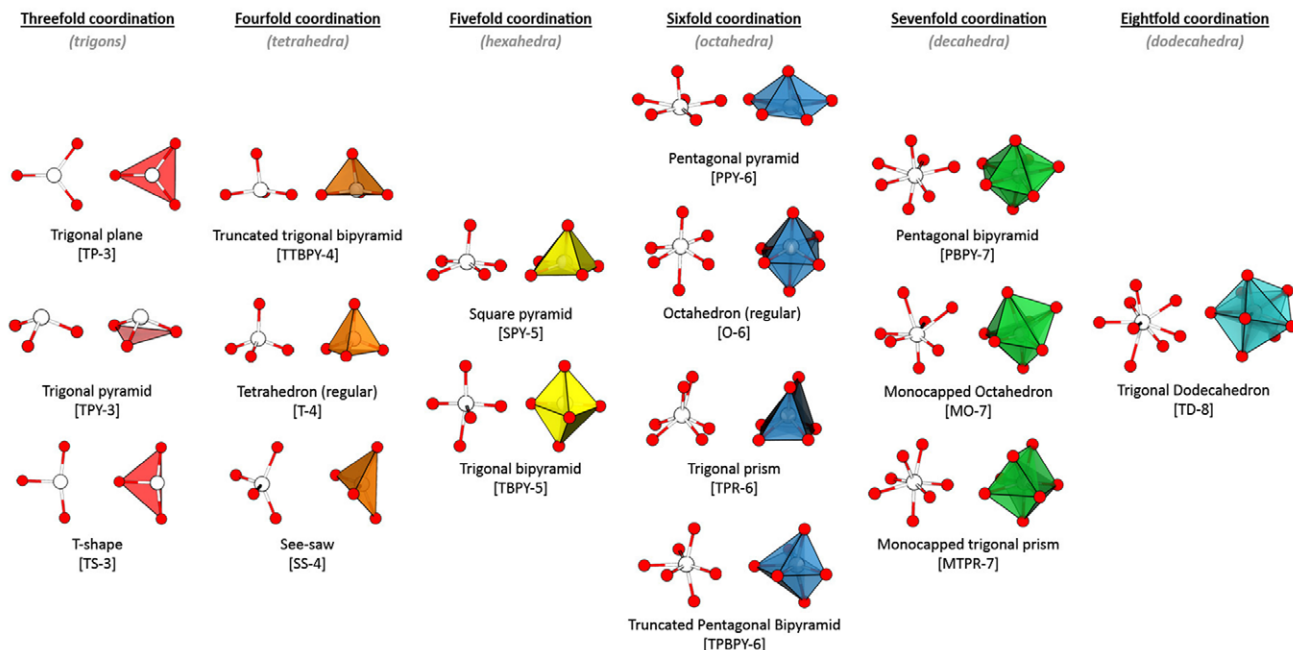


Figure 5. Coordination polyhedra for coordination numbers between three and eight. Characteristic examples are visualized of weakly distorted coordination polyhedra that can be found in the ternary $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ alloys. The polyhedra are labeled according to their corresponding high symmetry basic types, largely following the IUPAC recommended nomenclature [123].

symmetric [TP-3]-type structure and ClF_3 showing a C_{2v} symmetric [TS-3]-type structure.

A threefold planar coordination is the conventional coordination type of O ions in natural $c\text{-TiO}_2$ modification. Thereby, the OTi_3 units of rutile adopt a [TP-3]-shape and a [TS-3]-shape in anatase (see reference [125]). The more complex brookite phase combines [TP-3]-like and [TS-3]-like OTi_3 units. Consequently, both plane types also occur in the amorphous solid. Thereby, the disorder of the amorphous solid is reflected in an almost continuous variation of OTi_3 topologies between the [TP-3] and [TS-3] border cases. There are no pyramidal OTi_3 units in the three natural occurring TiO_2 polytypes rutile, anatase, and brookite. However, O ions in the metastable TiO_2 polymorphs hollandite and ramsdellite partially show a [TPY-3]-type coordination. Also, the threefold coordinated O_{3c} ions in the high pressure TiO_2 polytypes baddeleyite ($\text{TiO}_2(\text{MI})$), columbite ($\text{TiO}_2(\text{II})$) and the orthorhombic-type I ($\text{TiO}_2(\text{OI})$) show a weak displacement from the Ti ion plane. Ti ions are never found in a threefold coordination state, neither in crystalline nor in amorphous TiO_2 phases.

In SiO_2 threefold coordinated ions only occur in exceptional cases. The very dense SiO_2 polymorphs stishovite (rutile-like) and seifertite show fundamental [TP-3]-like OSi_3 building blocks. Also, $a\text{-SiO}_2$ threefold coordinated ions represent a very exceptional coordination state that can occur for both chemical elements in a very limited number of OSi_3 and O_3Si units.

3.3.2. Fourfold coordination ($N_c = 4$). There are four basic types of AX_4 coordination polyhedra, the square plane, the square pyramid, the tetrahedron and the see-saw type. Out of the four basic structure types, the square plane-type with the central atom coplanar with all four ligands and the

pyramidal-type with the central element A displaced from the ligand plane (i.e. square pyramid) is not found in the investigated $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ alloys or the pure crystalline phases of TiO_2 or SiO_2 . The regular [T-4] structure type with T_d symmetry is known among others from the CH_4 molecule and several tetrachlorides. The C_{2v} symmetric see-saw structure ([SS-4]) is a common geometry for tetrafluorides as SF_4 .

No O ion, neither in crystalline nor amorphous SiO_2 , shows a fourfold coordinated state. In contrast, a certain amount of O ions in $a\text{-TiO}_2$ forms [T-4]-type and [SS-4]-type coordination polyhedra. OTi_4 building blocks are also common for a fraction of O ions in crystalline bronze-type $\text{TiO}_2(\text{B})$ as well as for the crystalline TiO_2 high-pressure polytypes baddeleyite, orthorhombic-type I, fluorite (cubic TiO_2), and cotunnite ($\text{TiO}_2(\text{OII})$). Thereby, the OTi_4 units adopt a [SS-4]-type geometry in $\text{TiO}_2(\text{B})$, $\text{TiO}_2(\text{OI})$ and $\text{TiO}_2(\text{OII})$ and a [T-4]-type geometry in cubic TiO_2 .

The fourfold coordination state is by far the most common coordination of Si in SiO_2 and silicates in general. With exception of the extremely dense SiO_2 polytypes stishovite and seifertite, all SiO_2 crystal phases (α -quartz, β -quartz, α -tridymite, β -tridymite, α -cristobalite, β -cristobalite, keatite, moganite, and coesite) form more or less complex three-dimensional networks of corner connected [T-4]-type SiO_4 units.

The fourfold coordination state of Ti ions is rarely found in pure $a\text{-TiO}_2$, never found in pure crystalline TiO_2 , and sporadically found in the surface layers of low-index TiO_2 surfaces. Such surfaces are the rutile(001) surface [130], the anatase(110) surface and one coordination of the anatase(103) surface [131], as well as the brookite(010) surface [132]. In these surfaces the AX_4 coordination polyhedra adopt a [SS-4]-type geometry and form corner-linked rows. TiO_4 units are also repeatedly found in $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ alloys with low Ti

content and for Ti ions in titanium silicalites [51, 52, 54, 58, 65, 66]. A further fourfold coordination geometry, best characterized as a truncated trigonal bipyramid ([TTBPY-4]), can sometimes be found (mainly) for Ti ions. These coordination polyhedra may also be seen as a distorted regular polyhedron type in which the central atom is shifted into one of the faces, thus becoming the [TP-3]-type basis of a trigonal pyramid. Through atomic disorder in the amorphous alloys, the coordination geometry can change continuously between the [T-4] and the [TTBPY-4]-type.

3.3.3. Fivefold coordination ($N_c = 5$). The basic types of AX_5 coordination polyhedra are the square pyramid ([SPY-5]) and the trigonal bipyramid ([TBPY-5]), that represent the two five-vertex Johnson solids J_1 and J_{12} . Both structures are closely connected since the [TBPY-5]-type can be seen as an intermediate polyhedron occurring in the Berry pseudorotation-type interconversion [133, 134] (exchange of apical and equatorial ligands) between different [TBPY-5]-type isomers. Molecular examples for the basic C_{4v} and D_{3h} symmetries of [SPY-5]-type and [TBPY-5]-type coordination polyhedra are the pentafluorides ClF_5 and BrF_5 as well as the pentachlorides PCl_5 and $AsCl_5$. No pentagonal planar configuration was found in the $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ mixed-oxide alloys.

With the exception of the ultra-dense cotunnite polytype, no fivefold coordinated O ions are found in the pure and mixed ordered and disordered phases of TiO_2 and SiO_2 .

Si_{5c} ions in [SPY-5] and [TBPY-5]-type coordination polyhedra occur extremely rare in our structure models of pure $a\text{-SiO}_2$, but repeatedly in the ternary $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ mixed oxides. The occurrence of SiO_5 units under high pressure conditions has been reported experimentally in silicate liquids and glasses [127–129].

The possible occurrence of fivefold coordinated Ti_{5c} ions in hexahedral building blocks has already been discussed in the introductory section. In summary, a fivefold coordination seems to be a likely intermediate Ti coordination state especially in $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ thin-film alloys. Fivefold coordinated Ti_{5c} ions are also a common coordination state in low-index TiO_2 surface layers. Among these surfaces are the TiO_2 rutile surfaces (110), (100), and (101) [130], the TiO_2 anatase surfaces (101), (100), (001), and one of two possible coordinations of (103) [131], as well as the TiO_2 brookite surfaces (100) and (110) [132]. The fivefold coordinated Ti_{5c} surface ions show a characteristic alignment of edge-linked [SPY-5]-type coordination polyhedra in row-like structures with the square face oriented towards the vacuum.

3.3.4. Sixfold coordination ($N_c = 6$). There are three basic types of AX_6 coordination polyhedra. The regular O_h symmetric octahedron ([O-6]) that, together with the tetrahedron, is one of the occurring Platonic solid type polyhedra. Regular octahedral geometries are known in molecular form from hexachlorines (e.g. WCl_6) as well as hexafluorides (e.g. SF_6). The pentagonal pyramid type ([PPY-6]) as well as the trigonal prism type ([TPR-6]) represent less common representatives of AX_6 coordination polyhedra. The pentagonal pyramid is yet another example of a Johnson-type (J_2) coordination

polyhedron. Both the trigonal prism and the pentagonal pyramid in general are not octahedral solid figures. In fact, the D_{3h} symmetric regular trigonal prism is a pentahedron and the C_{5v} symmetric pentagonal pyramid is a hexahedron. However, both become octahedra in their distorted geometries. In some cases, molecular compounds as sixfold coordinated methyl complexes $[(CH_3)_nMX_{6-n}]$ tend to adopt a trigonal prismatic instead of an octahedral geometry [135]. A pentagonal pyramidal structure for instance occurs in the form of anionic $XeOF_5^-$ complexes [136]. A fourth structure type repeatedly found for sixfold coordinated Ti ions in $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ alloys can be described as a truncated pentagonal bipyramid ([TPBPY-6]) obtained through removal of one equatorial vertex. The [TPBPY-6]-type coordination state might also be considered a bicapped tetrahedron or even more obvious as a skewed trapezoidal bipyramid. In addition, [TPBPY-6]-like coordination polyhedra are characteristic intermediate states in the interconversion between octahedron and trigonal prism by a Bailar twist [138–141].

A sixfold coordination of Si ions occurs rarely in $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ alloy phases due to locally high coordinated ions in the vicinity of the Si ion. There is no indication of a Si coordination state with $N_c \geq 5$ in pure SiO_2 , although [O-6]-type Si_{6c} ions are known from the high density SiO_2 modifications stishovite and seifertite.

In contrast to the coordination states of the Si ion, a sixfold coordinated state represents the dominant coordination type of Ti ions in crystalline and amorphous TiO_2 . Besides the naturally occurring polytypes rutile, anatase, and brookite, also the metastable TiO_2 polymorphs $TiO_2(H)$, $TiO_2(R)$ and $TiO_2(II)$ belong to the class of octahedra network forming oxides. Also, pure $a\text{-TiO}_2$ shows Ti_{6c} ions as the dominant Ti coordination state.

The sixfold coordination of Ti ions in various $c\text{-TiO}_2$ modifications (with the exception of $TiO_2(B)$) commonly implies a threefold coordination of O ions. Thus, network forming TiO_6 as well as OTi_3 building blocks can be seen as complementary representations of the crystal structure of low-pressure $c\text{-TiO}_2$ polymorphs (see reference [125]).

3.3.5. Sevenfold coordination ($N_c = 7$). Sevenfold coordinated AX_7 geometries occur in three basic geometries. Among these polyhedra types the undistorted pentagonal bipyramidal geometry-type ([PBPY-7]) with D_{5h} symmetry shows the highest symmetry. The further sevenfold coordinated geometry types are monocapped versions of octahedral coordination polyhedra. They are monocapped, more precisely the square face is monocapped, trigonal prism ([MTPR-7]) with idealized C_{2v} symmetry and the monocapped octahedron ([MO-7]) with idealized C_{3v} symmetry. Both, the [PBPY-7] and the [MTPR-7] geometries belong to the Johnson type solids (J_{13} and J_{49}). A sevenfold coordination state represents a less common molecular coordination state. Nevertheless, there are experimentally verified molecular examples for all structure types. The [PBPY-7]-type coordination geometry is archetypically exemplified in iodine heptafluoride (IF_7) [142, 143]. Also, the simplest examples of monocapped trigonal prismatic type molecules are heptafluoride complexes as $[NbF_7]^{2-}$ and

[TaF₇]²⁻ [144]. A capped octahedral geometry has been reported for the chloride complex TaCl₄(PMe₃)₃ [145].

In a-Ti_xSi_{1-x}O₂ the sevenfold coordination state is reserved to a small number of Ti ions in the Ti-rich composition region and pure a-TiO₂. Thereby, the [PBPY-7]-type coordination polyhedra represent the most common coordination geometry. Also, the crystalline TiO₂ high pressure modifications TiO₂(MI) and TiO₂(OI) consist of fundamental [MO-7]-type TiO₇ building blocks.

3.3.6. Eightfold coordination ($N_c = 8$). There are several basic geometries of AX₈ complexes. The most important eightfold coordinated polyhedra are the trigonal irregular dodecahedron or snub disphenoid (Johnson solid J₈₄, D_{2d} symmetry), the cube (O_h), the square antiprism (D_{4d}), the hexagonal bipyramid (D_{6h}) as well as some capped octahedron and prism geometries. Eightfold coordinated ions are commonly found in cubic (ionic) binary solids and even the crystalline cubic fluorite-type high-pressure phase of TiO₂. Only the trigonal dodecahedral structure type [TD-8] is found as an extremely rare coordination state in the investigated a-Ti_xSi_{1-x}O₂ alloys, more precisely in pure a-TiO₂. An example of the rare case of [TD-8]-type molecular coordination geometry is the Na ion in the molecular Schiff base compound [(NiL)Na(NiL)]ClO₄ [146].

3.3.7. Further coordination states ($N_c = 1, 2$). Onefold coordinated or single bonded ([SB-1]) atoms, with the exception of the H atom, are typically found in small molecules, trivially in diatomic complexes. A onefold coordination in solids is typically connected to the formation of dangling-bond-type states at surfaces, around crystal defects and in amorphous solids and their saturation by a single bonded atom. To a large extent, a-Ti_xSi_{1-x}O₂ forms well connected network structures free of structural defects. However, sometimes a onefold coordination state is observed for O ions in the ternary a-Ti_xSi_{1-x}O₂ oxides. A prominent example for the fundamental importance of onefold coordinated states is hydrogenated amorphous silicon a-Si:H. In a-Si:H the hydrogen atoms occupy onefold coordinated sites in order to saturate dangling-bond type sites of under-coordinated Si ions. As a consequence, the high structural-defect density of pure a-Si is drastically reduced [147, 148].

Twofold coordinated atoms occur in a large number of molecular complexes. The two possible AX₂ type coordination geometries are a bend/angular configuration ([A-2]) and a linear alignment ([L-2]). There are two configurations for each geometry type, a homonuclear (XAX) and a heteronuclear (XAY) twofold coordination state. Examples for twofold coordinated atoms in linear molecules are the D_{∞h} symmetric CO₂ molecule for the homonuclear [L-2]-type ([HOL-2]) and the C_{∞h} symmetric HCN molecule for the heteronuclear [L-2]-type ([HEL-2]). The most prominent example of a homonuclear [A-2]-type coordination ([HOA-2]) is the C_{2v} symmetric H₂O molecule. A heteronuclear [A-2]-type complex ([HEA-2]) is exemplified in the C_s symmetric NOCl molecule.

In fact, a strictly linear coordination geometry does not occur in the amorphous solids. However, some configurations are very

close to the linear alignment and we will consider twofold coordinated complexes with an bonding angle $\geq 177^\circ$ as a distorted linear geometry of the [HOL-2] or [HEL-2]-type. In Ti_xSi_{1-x}O₂ only the O ion exists in a twofold coordinated state. In pure a-TiO₂ a notable fraction of [A-2]-type coordinated O ions exists next to an equal fraction of fourfold coordinated O ions and the dominant threefold coordination types. Besides sporadic examples of threefold coordinated O ions, the dominant fraction of O ions in pure a-SiO₂ shows a [A-2]-type coordination geometry and a very small fraction is found in an almost linear [L-2]-type coordination environment. Amorphous Ti_xSi_{1-x}O₂ alloys show, depending on the composition, all four possible twofold coordination types of the O ion by Si and Ti ions.

In all tetrahedrally coordinated crystalline SiO₂ modifications of the O ions show a twofold coordination by Si ions. Interestingly, also TiO₂(B), one of the lowest density polymorphs of crystalline TiO₂, contains some twofold coordinated O ions that interconnect more densely packed layers formed by threefold and fourfold coordinated O ions.

3.4. Short-range order: effective coordination numbers

One shortcoming of the conventional coordination-number analysis, introduced above, is the use of static cutoff parameters $r_{\text{cut}} \equiv r_{\text{min}}$. In general, the result of a coordination number as well as coordination polyhedra analysis will show a strong dependence on the choice of the cutoff parameter for disordered systems. Additionally, all bonded atoms are considered to contribute equally to the coordination of an atom. This approach corresponds to the use of equal bond-weighting functions, i.e. weights of $\omega_{ij} = 1$, for all atomic bonds between a central atom *i* and its surrounding neighbors *j*. While an equal weight of all interatomic bonds might be adequate for regular coordination polyhedra in crystalline systems with constant nearest neighbor distances, amorphous solids show a notable bond length disorder that is not reflected by the equal weights of the conventional coordination numbers analysis. In fact, an atom *j* with a larger bond-length distance d_{ij} from the considered atom *i* will show weaker bonding characteristics than an alternative atom *j* with smaller distance from atom *i*. In contrast, detailed information on bond length and bond angle disorder is contained in the geometrical shape of a particular coordination polyhedra, respectively its shape deviation from the idealized high-symmetry polyhedra geometry. Despite the comprehensive analysis of the local coordination environment by polyhedra building blocks, a complete coordination polyhedra analysis is an elaborate task resulting in a complex amount of data. A more straight forward way to consider the influence of short-range disorder in amorphous solids is given by the idea of using coordination numbers that rest upon the use of some kind of bond-weight function, i.e. weights of $\omega_{ij} \neq 1$, to account for different bonding distances between pairs *ij* of atoms. Such coordination numbers are called *weighted* or *effective* coordination numbers. In fact, all surrounding atoms *j* are considered with a fractional weight to calculate the effective coordination number of an atom *i*, thus eliminating the necessity of an initial bond-length cutoff parameter. The actual determination of appropriate bond

weights has a long standing history in coordination chemistry and various weighting concepts have been proposed (e.g. see reference [124] and references therein).

The concept of effective coordination numbers considered in this study is based on the concepts introduced by Hoppe *et al* in inorganic chemistry [149–151]. The effective coordination number η_c^i of an atom i is defined as a sum over bond-weight functions ω_{ij} for surrounding atoms j

$$\eta_c^i = \sum_j \omega_{ij}. \quad (10)$$

Commonly, an exponential bond-weight function is chosen in which the ratio of the actual pair distance d_{ij} and the average weighted bond length δ_{av}^i enters to the power of six.

$$\omega_{ij} = \exp \left[1 - \left(\frac{d_{ij}}{\delta_{av}^i} \right)^6 \right]. \quad (11)$$

In that way, the effective coordination numbers are actually parameter free. However, the result depends on a reasonable choice for the analytic form of the bond-weight function and a reasonable weighting function should recover the conventional coordination numbers of high-symmetry coordination polyhedra in crystals. The average weighted pair distance δ_{av}^i is defined individually for each atom i by

$$\delta_{av}^i = \frac{\sum_j d_{ij} \exp \left[1 - \left(\frac{d_{ij}}{\delta_{av}^i} \right)^6 \right]}{\sum_j \exp \left[1 - \left(\frac{d_{ij}}{\delta_{av}^i} \right)^6 \right]}. \quad (12)$$

Originally, the minimal bond distance $d_i^{\min}$ between atoms i and j instead of δ_{av}^i itself has been considered in the definition of δ_{av}^i . Due to the both-sided dependence, $d_i^{\min}$ needs to be calculated self-consistently for every atom. Following references [152–154] the δ_{av}^i self-consistency cycle is initialized to be the minimal bond distance $d_i^{\min}$ and iterated until self-consistency within an stopping condition of $|\delta_{av}^i[n+1] - \delta_{av}^i[n]| \leq 0.0001$ is reached. In practice δ_{av}^i converges rapidly within a few iteration steps. Effective coordination numbers defined in that way have recently been applied in the analysis of transparent conducting oxides [152], metal clusters [153, 154] and ternary telluride compounds [155]. In contrast to the conventional local coordination numbers n_c , the effective coordination numbers are, with exception of high symmetry polyhedra in crystalline systems, in general non-integer valued. The average weighted bond distances $\delta_{c(\alpha)}$ and effective coordination $\eta_{c(\alpha)}$ of a set of $N_{(\alpha)}$ atoms (of chemical species α) are given by

$$\delta_{c(\alpha)} = \frac{1}{N_{(\alpha)}} \sum_i \delta_{av}^i \quad (13)$$

and

$$\eta_{c(\alpha)} = \frac{1}{N_{(\alpha)}} \sum_i \eta_c^i. \quad (14)$$

Since the effective coordination numbers η_c^i and $\eta_{c(\alpha)}$ take into account deviations from an average bonding distance, they include effects of *radial disorder* that essentially reduce the value of the effective coordination numbers with respect

to the conventional local and total equal weight coordination numbers n_c and N_c . Consequently, the differences $n_c - \eta_c^i$ and $N_{c(\alpha)} - \eta_{c(\alpha)}$ are simple measures for the extent of short-range disorder of particular coordination polyhedra or ions of a chemical component in total, respectively.

3.5. Mid-range order: ring statistics

Even though some fundamental characteristics of the interconnectivity of coordination polyhedra are already contained in the pair distribution functions, the average radial character of the pair distribution functions is not sufficient to describe the distinct mid-range order features found in some amorphous oxides. The formation of extended ring-like structures throughout an amorphous solid is a distinct feature of low-density amorphous solids and has been discussed in literature predominantly for tetrahedrally coordinated materials as a-SiO₂ [100, 102–106]. Other amorphous materials whose atomic structures have been recently characterized by ring statistics are the amorphous binary antimonides GaSb [110] and InSb [111] as well as binary amorphous GeTe [113] and ternary amorphous GeSbTe alloys [112, 114].

In order to characterize the amorphous network, we define a ring as the *topologically shortest* closed path starting from one particular atom and returning to that atom by stepwise, going from one adjacent/bonded atom to another. In case of a crystalline structure, an adjacent atom is simply defined as a nearest neighbor of a particular atom. For an amorphous solid adjacent atoms are defined by the cutoff spheres for each element. Analog to the coordination polyhedra the cutoff parameters can be obtained from the RDFs. An n -fold ring represents a closed n step path within a crystal lattice or the disordered network of an amorphous solid. If the focus is directed mainly to the topological properties, it is common practice to use the terms vertices instead of atoms, and edges instead of bonds to characterize disordered network structure. In general there is no size limit for an n -fold ring. However, the requirement of a topological shortest path or *smallest* ring ensures that only rings are considered that cannot be decomposed into a *sum* of shorter closed paths by considering the path between any two atoms of the ring. Rings that fulfill the above requirements are called to be *primitive* or *irreducible* [100, 115–117]. By definition a primitive ring cannot be decomposed into smaller rings.

Besides the irreducibility criterion for primitive rings, different *shortest path* definitions for topological rings have been proposed in literature (see reference [100]). The most common definitions have been given by King [118] and Guttman [119]. In general, the characteristics of the ring size distribution in an amorphous solid will depend on the applied definition of topological rings and should be compared to ring distributions, obtained from differing definitions, with caution.

4. Results and discussion

4.1. Coordination numbers

The *average* coordination numbers of the investigated VASP as well as DFTB a-Ti_xSi_{1-x}O₂ structure models are visualized

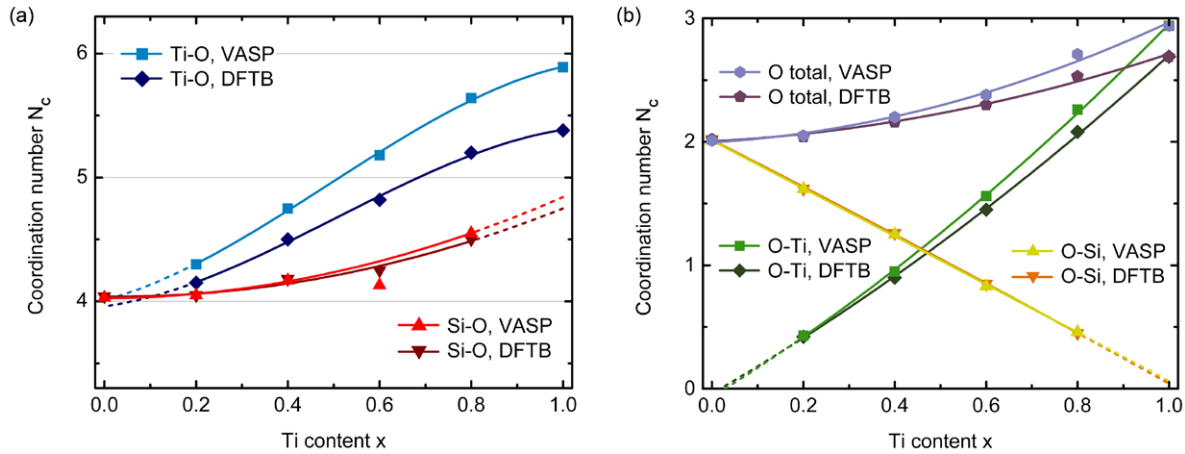


Figure 6. Conventional total and partial coordination numbers of Ti, Si, and O ions in $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ hybrid oxides (VASP and DFTB geometries). The trend lines were fitted by a third order polynomial for the Ti ion coordination by oxygen and by second order polynomials for all other coordinations. Dotted lines indicate extrapolations of the fitted trend lines.

in figure 6. Since all atomic bonds in the amorphous networks show an oxide-type cation-anion bonding behavior, i.e. the absence of cation-cation and anion-anion bonds, the total Ti and Si coordination numbers are given by their particular O coordination. The cutoff parameters of $r_{\text{cut}}[\text{Ti}] = 2.4 \text{ \AA}$ for Ti–O bonds and $r_{\text{cut}}[\text{Si}] = 2.1 \text{ \AA}$ for Si–O bonds, considered in the coordination number analysis, have been chosen based on the minima of the partial pair distribution functions discussed below. For the oxygen ions both the total as well as the partial coordinations by Ti and Si have been considered.

To begin with, we examine the coordination properties of the $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ VASP structure models. In pure $a\text{-SiO}_2$ the total Si coordination number of $N_{\text{CSi}} = 4.03$ indicates a virtually perfect tetrahedral coordination. At low Ti content ($\leq 20\%$) the average coordination number of the Si ions increases marginally. The Si coordination number increases nonlinear with the Ti content. In order to estimate the dependence of the coordination number on the composition parameter, we have fitted the Si coordination number by a second order polynomial. However, since the Si coordination number of the $a\text{-Ti}_{0.6}\text{Si}_{0.4}\text{O}_2$ VASP structure model seems to be artificially low ($N_{\text{CSi}}[0.6] = 4.13$) and no other anomalies with respect to the fitted trend lines has been observed, we have excluded this point from the data fitting. The data fitting results in a coordination number of $N_{\text{CSi}}[0.6] = 4.32$. The estimated coordination for an equimolar Ti/Si composition is $N_{\text{CSi}}[0.5] = 4.24$. For the highest calculated Ti content of $x = 0.8$ the Si coordination increases to 4.55 and the extrapolation towards a very dilute Si dispersion indicates a coordination number around ~ 4.8 at very high Ti content. However, it is not possible to estimate whether the higher coordination state of the Si ion is the result of a large fraction of locally fivefold coordinated Si ions or the results of averaging the coordination states of the tetrahedrally coordinated Si_{4c} ions and a small fraction of $c\text{-TiO}_2$ like sixfold coordinated Si_{6c} ions.

The Ti coordination in the $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ VASP structure models shows a qualitatively different trend than the Si coordination number. The overall dependence on the composition parameter x is nonlinear but rather cubic than quadratic. At

the lowest calculated Ti content the Ti coordination number is $N_{\text{CTi}}[0.2] = 4.30$. The extrapolation towards very dilute Ti concentrations indicate that a single Ti ion inserted into an $a\text{-SiO}_2$ matrix might preferably adopt a fourfold coordination state. For an equimolar composition the estimated coordination number of $N_{\text{CTi}}[0.5] = 4.97$ reflects almost the average of the tetrahedral and octahedral coordinations of crystalline TiO_2 and SiO_2 . However, similar to the Si ions, it is not clear to what extent this number represents a superposition of TiO_4 and TiO_6 building blocks or the formation of fivefold coordinated TiO_5 units. At very high Ti content, the coordination of the Ti ion tends to saturate below the crystalline sixfold coordination. The calculated coordination number of pure $a\text{-TiO}_2$ is $N_{\text{CTi}}[1.0] = 5.89$. Thus, the Ti coordination number almost covers the entire coordination range between the two crystalline coordination limits. The averaged coordination numbers clearly illustrate the existence of under-coordinated Ti ions even in pure $a\text{-TiO}_2$. Thereby, it is not indicated whether the lower coordination numbers are related to four- or fivefold coordinated Ti_{4c} or Ti_{5c} ions in general. Only for dilute Ti ion concentrations, the occurrence of fourfold coordinated Ti_{4c} ions has been confirmed without doubt by the analysis of the average coordination numbers.

The fact that Ti might reach a fourfold coordination state but not the sixfold coordination of the crystalline TiO_2 rutile phase, that exhibits the same mass density, points towards the qualitative different types of atomic order characteristics in TiO_2 and SiO_2 . The tetrahedral SiO_4 units in $a\text{-SiO}_2$ are sufficiently *stiff* to prevent a predominant fraction of Si ions from changing their coordination state by the influence of topological disorder. Therefore, in low Ti content $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ the Ti ion is preferably incorporated in form of TiO_4 units that, despite their larger size, can be incorporated into the relatively open-porous amorphous framework of the dominating SiO_2 component without the need for large readjustments of the amorphous network due to an increased connectivity of a higher coordinated cation. In the case of high Ti content $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ and pure $a\text{-TiO}_2$, that represent rather dense solid material phases, the topological disorder of the amorphous

network is predominantly mediated by changes in the local atomic coordination environment of the Ti ions, especially the occurrence of under-coordinated Ti ions, which basically prevents the reaching of a crystal-like coordination.

The total coordination number of oxygen changes nonlinear from an almost perfect ($N_{\text{Co}}[0.0] = 2.01$) twofold Si_{2c} crystal type coordination state in pure a- SiO_2 to $N_{\text{Co}}[1.0] = 2.94$ which is close to the O coordination in crystalline TiO_2 . However, equivalent to the Ti ions, the crystal-coordination state is not entirely reached. For a composition parameter of $x = 0.5$ the decomposition into partial contributions from Ti and Si ions indicates that this nonlinear behavior is due to changes in the partial coordination by Ti ions, while the O–Si coordination decreases linearly with the Ti content from $N_{\text{Co-Si}}[0.0] = 2.01$ to $N_{\text{Co-Si}}[0.8] = 0.46$ which practically extrapolates linearly to zero. An equal coordination of O ions by Ti and Si ions is observed slightly below an equimolar composition at $x = 0.46$. The nonlinear increase in the O coordination number might also be seen as a first fingerprint of edge-linked coordination-polyhedra building blocks that are formed progressively with increasing mass density between higher coordinated cations.

Qualitatively, the DFTB geometries show practically identical trends in the coordination numbers of a- $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$. Nevertheless, looking at the Ti–O coordination, the O–Ti coordination respectively, it is obvious that the DFTB structure models show substantial differences to the VASP post relaxed geometries. The DFTB coordination number of $N_{\text{CTi}}[1.0] = 5.38$ indicates half an electron less within the fixed cutoff radius around the Ti ions in pure a- TiO_2 . This difference reduces to ~ 0.15 at a Ti content of 20 mol%. Extrapolation further indicates a DFTB Ti–O coordination slightly below fourfold for a very dilute TiO_2 component. As a consequence of the reduced Ti–O coordination in the DFTB structure models, also, the O–Ti coordination is reduced compared to the VASP geometries. This reduction becomes observable around a Ti content of ~ 30 mol% and increases to 0.25 Ti ions in the first O coordination sphere in pure a- TiO_2 . In contrast to the Ti–O and the O–Ti coordination numbers, the Si ion related coordination numbers nearly agree for both numerical approaches. While the O–Si coordination is identical in both simulation approaches, the O–Si coordination tends to marginally lower values in the high Ti content regime. In turn, this effect seems to be related to the lower connectivity of the lower coordinated Ti ions in the DFTB geometries. The calculated difference between the VASP and DFTB geometries is 0.05 at a composition parameter of $x = 0.8$. The extrapolation towards pure a- TiO_2 indicates a maximum Si coordination around ~ 4.7 , which is only ~ 0.1 below the value estimated for the VASP post-relaxed model.

The differences between then VASP and DFTB structure models may have different origins. On the one hand, the DFTB structure models of a- $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ represent room temperature (300 K) geometries while the VASP post-relaxed structures formally represent the 0 K limit. Thus, the DFTB geometries are influenced by thermally induced fluctuations of the amorphous network, the local coordination state of Ti ions respectively. On the other hand, the structural properties are subject to the different numerical description within the VASP-DFT

and DFTB schemes. Differences in the DFTB approach most likely represent influences from the parametrization of interatomic pair interactions within Slater-Koster integral tables [93]. Since both, DFTB and VASP seem to describe different Ti coordination environments the question arises which unit-cell representations better reproduces the structural characteristics of a- $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ hybrid oxides. To answer this question, we have analyzed the coordination statistics of an a- TiO_2 structure model, that has been generated by DFT Car-Parrinello molecular dynamics (CPMD) under conditions similar to the DFTB molecular dynamics of this study.³

The properties of this CPMD structure model have been discussed in detail elsewhere. [98, 99] Adopting the same cutoff parameters used above, the coordination numbers of Ti and O ions in the CPMD structure model are 5.94 and 2.97 which is in excellent agreement to the respective VASP geometry coordination numbers of 5.89 and 2.94. Hence, it seems unlikely that the coordination number differences between the VASP and DFTB generated a- TiO_2 models are primarily related to temperature induced changes in the amorphous framework.

We further have to compare the generated structure models to published experimental data on a- TiO_2 . Published experimental coordination numbers depict a quite inconclusive picture on the a- TiO_2 coordination properties. Petkov *et al* [159] reported coordination numbers of sputtered a- TiO_2 layers as well as a- TiO_2 bulk powder samples. The Ti–O coordination number of amorphous bulk TiO_2 powders of 5.6 ± 0.4 is found to be in reasonable agreement with the calculated Ti–O coordination number of 5.89 for the VASP geometry. In contrast, the coordination number of 5.4 ± 0.4 for sputtered a- TiO_2 layers is in excellent agreement to the calculated DFTB geometry Ti–O coordination of 5.38. Thus, there is no distinct answer to the above question which approach is more suited to model the amorphous phases. In addition, some uncertainty remains due to missing information on the mass density of the prepared amorphous samples. Since the amorphous state of a solid is not defined by a specific atomic configuration, rather, from an experimental point of view, as the result of a samples preparation history, the direct comparison between experiment and theory might be seen as an ambiguous task, as long as preparation and simulation conditions do not match in detail. In fact, both simulation approaches seem to represent diverse facets of short-range disorder in the a- TiO_2 and in the same way the a- $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ networks.

The close agreement in Si–O and O–Si coordination numbers of VASP and DFTB geometries in low Ti content a- $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ clearly originates from the stiffness of the tetrahedral SiO_4 units that seem to be insensitive with respect to the applied simulation approach.

³ The CPMD calculations were performed using norm-conserving pseudo-potentials of the Troullier-Martins type [156, 157] and the Becke88 exchange functional [158]. The total simulation time of 8.6 ps was discretized by 51 000 steps to ensure energy convergence. At the beginning and the end of the cooling thermal equilibration phases of 4000 steps at 5000 K and 5000 steps at a room temperature of 300 K have been performed. In between an exponential-like cooling path, approximation by a suitable stepwise function was applied. A N ose–Hoover thermostat ensured the conditions of a canonical ensemble and the volume was kept constant.

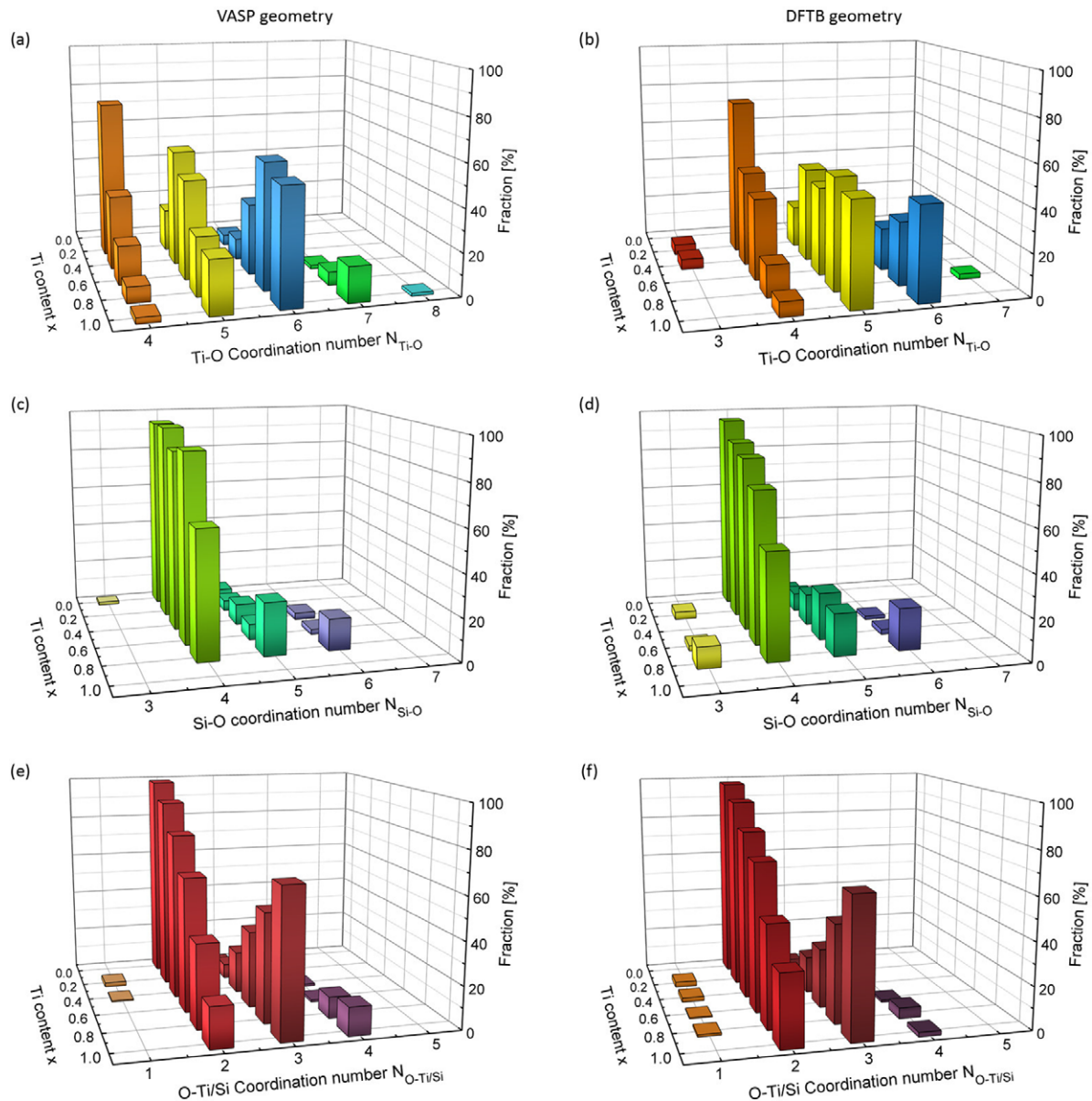


Figure 7. Bar diagram of the distribution of local coordination states in the $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ VASP (left) and the DFTB (right) geometries. See table 1 as well as figures 2, 3, and 4 for additional data.

In summary, the overall increase in the cation coordination-numbers, observed in both the VASP and the DFTB geometries, means that some of the Ti and Si ions experience a change in the local atomic O ion coordination state. This observation has led to the question; if the increase of the coordination numbers is the result of Ti in tetrahedral and Si in octahedral lattice sites or if considerable amounts of intermediate fivefold coordination states are formed in the disordered frameworks of $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ hybrid oxides. Since this information is not contained in the average coordination numbers, we have used the coordination polyhedra analysis to study the character of the local atomic coordination state in more detail.

4.2. Local coordination numbers

The fractional distributions of the local ion-coordination states in the $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ VASP and DFTB geometries are

illustrated in figure 7. Additionally, detailed coordination-polyhedra illustrations of the $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ VASP geometries are given in figures 2, 3, and 4. In contrast to the coordination number statistics above, the detailed analysis of the local atomic coordination states reveals short-range order features within the amorphous network that are commonly hidden by the averaging procedure.

Starting with the Ti-O coordination in the VASP geometry of pure $a\text{-TiO}_2$, the local coordination numbers indicate a much more diverse short-range order than might be expected from the Ti-O coordination number of ($N_{\text{Ti}}[1.0] = 5.89$). In fact, only slightly more than half of all Ti ions ($\sim 54\%$) preserve their crystalline coordination state. All other Ti coordination states arise from *coordination defects* that increase or decrease the local atomic coordination by ± 1 or ± 2 . Significant fractions of Ti ions are found in a fivefold (25%) and a sevenfold ($\sim 17\%$) coordination environment. Even $\sim 3\%$ and $\sim 1\%$

of the Ti ions respectively reside in TiO_4 and TiO_8 units. In sum, the slight prevalence for under-coordinated structural building blocks in the disordered polyhedra network results in the reduced coordination number of a- TiO_2 compared to TiO_2 in low-pressure crystal phases.

A similar distribution of local TiO_n coordination polyhedra in a- TiO_2 has been reported by Van Hoang [163, 164] on the basis of MD simulations using the Matsui and Akaogi (MA) force field [165] to simulate the structural properties of liquid and amorphous TiO_2 . At 4.20 g cm^{-3} (3000 atom unit cell, 350 K) TiO_5 , TiO_6 and TiO_7 fractions of 11%, 75%, and 14% have been observed. Even some minor contribution from TiO_8 units (<1%) has been reported. Tetrahedral TiO_4 building blocks were only reported at a lower mass density of 3.80 g cm^{-3} with a fraction <1%. In accordance with the higher fraction of sixfold coordinated units, the reported average Ti–O coordination number of 6.03 slightly overestimates the octahedral crystal limit and our value of 5.89.⁴

The a- $\text{Ti}_{0.8}\text{Si}_{0.2}\text{O}_2$ hybrid oxide structure model is characterized by a decrease of over-coordinated TiO_n structural units in favor of an increasing fraction of tetrahedrally coordinated Ti ions. However, the basic coordination-polyhedra distribution still resembles the distribution in pure a- TiO_2 . The minor fraction of TiO_8 building blocks vanishes completely and the fraction of the TiO_7 unit decreases from ~17% to ~6%. The TiO_4 building block fraction is found to increase to ~8%. For the two main-coordination states, sixfold and fivefold, a slight increase compared to pure a- TiO_2 is observed. The fraction of crystal-like coordinated Ti_{6c} ions increases to ~59% and the fraction of intermediate coordinated Ti_{5c} ions to ~28%. First qualitative differences in the distribution of TiO_n coordination polyhedra occur in the a- $\text{Ti}_{0.6}\text{Si}_{0.4}\text{O}_2$ oxide alloy. At this composition the ~47% fraction of TiO_5 building blocks becomes the predominant coordination state. Only one third of all structural units shows the sixfold coordination of TiO_2 crystals. TiO_7 building blocks are just found sporadically (~2%). The fraction of tetrahedrally coordinated structure units is more than doubled to ~18%. For a composition parameter of $x = 0.4$, the fivefold coordination reaches its maximum. 55% of all Ti ions show the intermediate coordination state. The fraction of TiO_4 building blocks increases to 35% while the sixfold coordinated crystal-type building blocks reduce to 10%. Finally, the 20 mol% Ti containing oxide alloy is dominated by the fourfold coordination state with a predominant fraction of 75%. The number of Ti ions in an intermediate fivefold coordination state collapses. Only 20% are incorporated into TiO_5 building blocks. The sixfold crystal coordination state becomes quite exceptional with a minor fraction of 5%.

Compared to empirical potential MD results of Bernard *et al* [120] for titania-silica glasses, the Ti coordination environment in our structure models stronger favors the fourfold coordination state at low Ti content (20 mol%). The reported

fractions of 42%, 54%, and 4% for locally fourfold, fivefold, and sixfold coordinated Ti ions indicate a slight preference for the formation of TiO_5 units over the tetrahedral coordination in TiO_4 building blocks while our data indicate TiO_4 , TiO_5 , and TiO_6 fractions of 75%, 25%, and 5%. This difference, in particular is, remarkable since the optimized density of the 20% Ti oxide alloy of 2.29 g cm^{-3} is notably smaller than our simulation density of 2.60 g cm^{-3} . Consequently, the average Ti coordination by O ions of 4.61 exceeds our calculated value of 4.3 significantly. A dominance of fourfold coordinated Ti_{4c} ions was observed for Ti concentrations as low as 7.8 mol%. An even more pronounced dominance of fivefold coordinated Ti_{5c} ions with a fraction of 60% over Ti_{4c} and Ti_{6c} ions with percentages of 30% and 10%, respectively, was observed at an equimolar Ti/Si alloy composition at a mass density of 2.50 g cm^{-3} . This distribution of local Ti coordination states closely resembles the coordination polyhedra distribution observed in the a- $\text{Ti}_{0.4}\text{Si}_{0.6}\text{O}_2$ VASP geometry. A general tendency towards the predominant formation of TiO_5 units (53%) at a composition close to $x = 0.2$ has also been reported in a preceding empirical potential MD study by Rosenthal and Garofalini for structure models generated with a low cooling rate [85]. At a higher cooling rate, a fourfold local coordination environment has been found to be the prevalent coordination state of Ti ions with a fraction of 55%.

In summary, the overall distribution of coordination polyhedra indicates a *richer*, more flexible Ti ion coordination environment in Ti-rich a- $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ hybrid oxides. With decreasing Ti content, the Ti ions progressively adapt the dominant fourfold coordination state of the amorphous matrix of the SiO_2 host material. In addition, an average Ti coordination number close to the sixfold crystalline coordination is by far no evidence for an amorphous network that is predominantly formed by (distorted) octahedron building blocks.

As already indicated in the average coordination number for pure a- SiO_2 , the predominant fraction of Si ions is fourfold coordinated. The dominant fraction of SiO_4 building blocks (~94%) is attended by minor fractions of under-coordinated Si_{3c} and over-coordinated Si_{5c} ions in SiO_3 (~1%) and SiO_5 (~4%) building blocks. Due to the small preference of over-coordinated Si_{5c} ions against under-coordinated Si_{3c} ions, the mean Si coordination exceeds the common fourfold crystal coordination marginally. Similar to the high Ti content ternary oxides, the high Si content a- $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ hybrid oxides ($x \leq 0.2$) show a coordination-polyhedra distribution similar to the pure amorphous phase. The crystal-type fourfold coordination remains almost constant at 95%. All remaining Si ions show the intermediate fivefold coordination state. For lower Si contents of 60% ($x = 0.4$) and 40% ($x = 0.6$) the fraction of SiO_4 building blocks decreases slightly, but not continuously, to ~87% ($x = 0.4$) and 90% ($x = 0.6$), respectively. Simultaneously, larger fractions of SiO_5 units (10% for $x = 0.4$ and ~8% for $x = 0.6$) are found. Furthermore, the incorporation of 40% and 60% Si ions, respectively, promotes the formation of a new highly coordinated Ti-like coordination state for Si ions. Approximately ~3% of the Si ions form octahedrally coordinated SiO_6 units. The lowest Si content a- $\text{Ti}_{0.8}\text{Si}_{0.2}\text{O}_2$ structure model is the only ternary oxide whose

⁴ The difference in the average coordination number is partially related to the applied cutoff parameter. In contrast to our study, a marginally larger Ti–O correlation cutoff was applied. Compared to our value of 5.89 reported above, a slightly larger coordination number of 5.96 is obtained using the same cutoff parameter of 2.5 Å to estimate the average Ti–O coordination state.

local coordination characteristics show notable differences in the Si coordination-polyhedra distribution. The crystal-type fourfold coordination is reduced abruptly from the ~90–95% in the Si richer ternary oxides to *only* 60%. In addition, the fractions of over-coordinated Si ions in SiO₅ and SiO₆ building blocks increase to 25% and 15%, respectively.

Altogether, the local Si coordination numbers indicate that tetrahedrally coordinated Si_{4c} ions are very robust with respect to changes in the chemical composition of SiO₂/TiO₂ hybrid oxides. Only in the presence of a large number of higher coordinated Ti ions and a significantly increased mass density of the hybrid-oxide alloy, the fractions of over-coordinated Si ions in an intermediate fivefold coordination state as well as a c-TiO₂ type sixfold coordination state increase notably. Up to now, preceding numerical studies on Ti containing SiO₂ glasses have paid less attention to the possible changes in the Si coordination environment that possibly might occur in Si rich a-Ti_xSi_{1-x}O₂ hybrid oxides.

The local coordination environment of O ions in the a-Ti_xSi_{1-x}O₂ VASP geometries shows a continuous transition of the predominant coordination state from a c-SiO₂ type twofold coordination to a c-TiO₂ type threefold coordination. In pure SiO₂, ~99% of the O anions are twofold coordinated as expected from the fourfold coordination of the Si cations. The fraction of twofold coordinated O ions decreases nonlinearly to ~19% in a-TiO₂. Simultaneously, the fraction of threefold coordinated O ions increases from ~1% in pure a-SiO₂ to ~68% in pure a-TiO₂. The crossing point of nonlinear (second order polynomial) fits for the fractions of two- and threefold coordinated O ions indicates equal contributions from O(Ti,Si)₂ and O(Ti,Si)₃ building blocks in the Ti rich regime around $x = 0.76$. While onefold coordination states of O ions are generally not observed in the two binary oxides, they occur in the lower Ti content VASP geometries. In the a-Ti_{0.2}Si_{0.8}O₂ hybrid oxide 2% of all oxygen atoms are onefold coordinated by a Ti ion. For a composition parameter of $x = 0.4$ this fraction reduces to <1%. In addition, the a-Ti_{0.4}Si_{0.6}O₂ alloy is the first structure that indicates the existence of a fourfold O ion coordination state with a fraction of 1%. The fraction of O(Ti,Si)₄ building blocks remains constant for 60 mol% of Ti ions, rises abruptly to 10% for an Ti content of 80 mol% and reaches ~13% in pure a-TiO₂.

In general, the local coordination of O ions gives a complementary view on the local coordination characteristics. Again, the fact that ~32% of O ions in a-TiO₂ differ from the threefold coordination state but only ~1% of O ions in a-SiO₂ deviates from a twofold coordination state implies a more flexible bonding environment in the denser and higher coordinated framework of a-TiO₂. The general occurrence of onefold Ti coordinated O states (O_{1c}) in the ternary oxides demonstrates that the disordered hybrid-oxide frameworks are locally limited in their ability to adapt completely to the higher connectivity of the Ti ion. Thus, a non-bridging O ion in the disordered hybrid-oxide network might be accepted, even if energetically unfavorable, in favor of the network connectivity and to sustain the mid-range order within the amorphous solids.

The coordination numbers of the a-Ti_xSi_{1-x}O₂ DFTB geometries indicated a substantially reduced average coordination

number for the Ti ion. Indeed, the local coordination environment of the Ti ion (see figure 7(b)) is the only element that shows pronounced coordination state changes in the DFTB structure models with respect to the VASP geometries.

While the main coordination type changes from fivefold to sixfold as a result of the increasing Ti content in the VASP geometries, all Ti containing DFTB structure models predict TiO₅ structure-building blocks as the largest coordination-polyhedra fraction. Even in pure a-TiO₂ a slight preference for fivefold coordinated TiO₅ units (~49%) over TiO₆ units (~44%) is observed. With decreasing Ti content the fraction of octahedrally coordinated Ti ions decrease almost linearly to 5% in a-Ti_{0.4}Si_{0.6}O₂. For a composition parameter of $x = 0.2$ no TiO₆ structure units are found. The fraction of intermediate fivefold coordinated states represents not only the largest structural building block in all ternary oxides but also remains roughly constant over a wide composition range with percentages of ~53% for $x = 0.8$, ~42% for $x = 0.6$, and 45% for $x = 0.4$. Between a Ti content of 40 and 20 mol% the fraction of intermediate coordinated Ti ions drops abruptly to 20%. This sharp drop in the fivefold coordination of Ti ions is connected to a simultaneous increase of tetrahedrally coordinated Ti_{4c} ions (75%), similar to the observations for the VASP geometries. In addition, pronounced differences between both approaches are found for the over and under-coordinated extreme coordination states, namely threefold, sevenfold and eightfold coordinated Ti ions and threefold and sixfold coordinated Si ions. The DFTB structure models indicate the possible occurrence of strongly under-coordinated Ti ions in TiO₃ building blocks at low Ti contents ($x = 0.2$ and $x = 0.4$) that could not be observed in the VASP geometries. Equally, characteristic differences occur for structurally highly coordinated Ti ions. Not only the exceptional eightfold coordination is absent also the sevenfold coordinated Ti_{7c} ions have almost completely vanished. Only the DFTB structure model of a-Ti_{0.8}Si_{0.2}O₂ contains a minor fraction of <3% of TiO₇ building blocks. The decrease of tetrahedrally coordinated Si ions with increasing Ti content is more continuous in the DFTB geometries. In addition, the percentage of SiO₄ building blocks in the Ti rich ternary oxides is stronger reduced. For $x = 0.8$ the fraction of SiO₄ units reduces to 50%. A stronger DFTB geometry preference for fivefold coordinated SiO₅ building blocks is indicated in the mean composition range with a maximum of ~23% SiO₅ units in a-Ti_{0.6}Si_{0.4}O₂. The distribution of c-TiO₂ like coordinated Si_{6c} ions is very similar in both numerical approaches. Only for a very high Ti content ($x = 0.8$) a slight increase of SiO₆ units to 20% is observed. Under-coordinated SiO₃ building blocks are not any longer limited to pure a-SiO₂. Threefold coordinated Si ions are contained in the DFTB geometries with a fraction of ~4% for $x = 0.2$ and ~3% for $x = 0.6$. In case of a-Ti_{0.8}Si_{0.2}O₂ an unexpected large fraction of 10% SiO₃ units is found. In sum, both the occurrence of threefold coordinated Si_{3c} ions at high Ti content and the larger percentage of octahedrally coordinated Si_{6c} give the picture of a more versatile Si coordination environment in the DFTB optimized geometries. The differences in the local coordination state occur despite the quite similar average coordination numbers (see figure 6).

Qualitatively similar to the VASP geometries, the fraction on twofold coordinated O_{2c} ions decreases nonlinearly from $\sim 98\%$ in pure a-SiO₂ to $\sim 33\%$ in pure a-TiO₂ and the percentage of threefold coordinated O_{3c} ions increases (non-linear) from $\sim 2\%$ in pure a-SiO₂ to $\sim 65\%$ in pure a-TiO₂. The transition point from a prevalently twofold coordination state to a prevalently threefold coordination state of O ions is estimated at a composition parameter of $x = 0.84$. Compared to the VASP geometries, the fraction of twofold coordinated O_{2c} ions is less strongly reduced in the DFTB geometries at high Ti content. In view of similar fractions of O_{3c} ions for both structure-model types, this difference is mainly due to the preference for twofold coordinated structural units against fourfold coordinated O_{4c} ions. The percentage of tetrahedrally coordinated O_{4c} ions is notably reduced in the DFTB structure models for high Ti contents. In pure a-TiO₂ only $\sim 2\%$ of the O ions show a fourfold coordination state compared to $\sim 13\%$ in the VASP structure. In contrast to the VASP geometries, all ternary oxide structure models show minor contributions from onefold coordinated (predominantly by Ti ions) O_{1c} ions. Thus, the existence of a onefold coordination state of the O anion is not necessarily limited to the low Ti content composition regime of a-Ti_xSi_{1-x}O₂ hybrid oxides.

As stated above, we expect that the VASP and DFTB structure models represent slightly different types of topological disorder in the a-Ti_xSi_{1-x}O₂ oxide alloys. In sum, both simulation approaches indicate a diverse coordination environment within the investigated binary and ternary oxides that is characterized by composition dependent variations of the local atomic coordination-defect states. Significant contributions from single and multiple over- and under-coordinated ions are found in all hybrid oxides. Even the binary amorphous oxides show large fractions of non-crystal-type coordination states. This is especially true for a-TiO₂ where the local coordination of roughly 50% of all ions shows an over- or under-coordinated state. In addition, the intermediate fivefold coordination state of Ti seems to be found as likely as a fourfold or sixfold Ti coordination state. Considering the entire composition range, Ti ions are found in a manifold of coordination states with local coordination numbers n_c ranging from 3 to 8. Less degrees of freedom are observed for the Si ions with coordination numbers of $n_c = 3 \dots 6$ and the local coordination numbers of O ions with $n_c = 1 \dots 4$. While the total *mean* coordination numbers vary continuously with the composition parameter, changes in the local coordination environment can be much more pronounced and volatile. It is not possible to deduce details of the local coordination environment and thus the atomic structure of the amorphous framework from a simple analysis of conventional averaged coordination numbers. The general existence of over and under-coordinated coordination-defect states indicates that the local coordination environment of a particular chemical component not only depends on the favorable crystal-type coordination number but also on the local availability of binding sites within the disordered atomic network. Especially in the presence of distinct mid-range order characteristics, the formation of a favorable local coordination state competes with the involved distortions of the amorphous framework.

4.3. Coordination polyhedra

The (local) coordination number statistics revealed that the crystalline coordination states (tetrahedrally for SiO₂ and octahedrally for TiO₂, respectively) in amorphous a-Ti_xSi_{1-x}O₂ hybrid oxides represent the main coordination states only for the pure binary oxides as well as for the limits of very dilute ion distributions in the disordered framework of the host oxide (Si ions in TiO₂ and Ti ions in SiO₂, respectively). In addition to a pure coordination number based analysis of the local coordination environment, the classification of coordination polyhedra according to their basic *symmetry* types provides additional structural information in order to characterize the oxide-network topology. The occurrence of alternative symmetry types for a given coordination number might be seen as a direct consequence of the competing short-range and mid-range order. Thereby, the existence of various polyhedra types allows local coordination units to adapt to the distorted atomic framework in a more efficient way, without changing their preferential coordination state. Changes of the basic symmetry types of a coordination polyhedra are of particular interest in order to discover basic correlations between the atomic structure of amorphous solids and the electronic and optical material properties as well as their fundamental deviations from crystalline material phases.

In table 1 the fractions of particular geometry types (see figure 5) of coordination polyhedra for the a-Ti_xSi_{1-x}O₂ VASP geometries are listed. Among the various chemical species, the Si ions show less distinct variations in the coordination-polyhedra geometry types. In agreement with the fundamental SiO₄ coordination-polyhedron type in SiO₂ crystals, fourfold coordinated Si_{4c} ions in the a-Ti_xSi_{1-x}O₂ oxides show an extreme preference for tetrahedral [T-4]-type coordination polyhedra (see figures 3(c-6), 3(d-4)). In addition, [SS-4]-type coordination polyhedra represent a geometry type occurring sporadically ($<2\%$) in pure a-SiO₂ and frequently ($\sim 17\%$) for a dilute distribution of SiO₄ units in an a-TiO₂ matrix at a composition of $x = 0.8$ (see figure 4(d-6)). In the Ti-rich alloys, the distortions of [T-4]-type coordination polyhedra into a [SS-4]-type geometry allow a better adaptation of SiO₄ building blocks to the, in general, larger TiO_n coordination polyhedra. With exception of a-Ti_{0.2}Si_{0.8}O₂, the coordination polyhedra of fivefold coordinated Si_{5c} ions show an approximate 1 : 2 partitioning between a [SPY-5]-type and [TBPY-5]-type polyhedron shape (see figures 3(d-4) and (d-5)). Due to the minor dependence of this partitioning ratio on the actual polyhedra fraction, both symmetry types need to be considered as fundamental units for highly coordinated Si ions in general. The SiO₆ building blocks exclusively belong to the class of octahedron type [O-6] polyhedra (see figures 4(c-7) and (d-6)). Thus, the sixfold coordination environment of Si ions is identical in a-Ti_xSi_{1-x}O₂ alloys and the ultra dense SiO₂ crystal phases stishovite and seifertite.

Considering the fourfold coordination state of the Ti ion, it is obvious that in the case of larger fractions of fourfold coordinated Ti ions ($>18\%$, $x \geq 0.4$) the main coordination-polyhedron type is the tetrahedron type [T-4] (see figures 3(c-5) and (d-3)). However, compared to Si_{4c} ions this preference

Table 1. Fractions of coordination polyhedra occurring in the $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ VASP geometries. Listed are the ion fractions that show a particular local coordination state of $n_c = 1 \dots 8$ (see figure 7). The fractions of a particular geometry type (see figure 5) are given with respect to the total number of n_c -fold coordinated ions.

Coordination	Ion	Polyhedron	Polyhedron fraction (%)					
			$x = 0.0$	$x = 0.2$	$x = 0.4$	$x = 0.6$	$x = 0.8$	$x = 1.0$
$n_c = 1$	O			2.0	0.5			
$n_c = 2$	O	[SB-1]-[Ti]		100	100			
			98.6	91.0	78.5	63.0	39.0	18.8
		[HOA-2]-[Ti]		5.0	22.3	30.2	62.8	100
		[HOL-2]-[Ti]				0.8		
		[HOA-2]-[Si]	97.9	67.6	43.3	31.0	11.5	
		[HOL-2]-[Si]	2.1	0.5				
		[HEA-2]		26.4	34.4	37.3	25.7	
$n_c = 3$	Si	[HEL-2]		0.5				
			1.4					
		[TP-3]	100					
	O		1.4	7.0	19.5	36.0	51.0	68.1
		[TP-3]	100	28.6	27.5	22.2	19.6	19.4
		[TPY-3]		71.4	70.0	69.5	77.5	76.5
		[TS-3]			2.5	8.3	2.9	4.1
$n_c = 4$	Ti			75.0	35.0	18.3	7.5	2.8
		[TTBPY-4]		6.7	14.3			50.0
		[T-4]		73.3	57.1	81.8	33.3	50.0
		[SS-4]		20.0	28.6	18.2	66.7	
	Si		94.4	95.0	86.7	90.0	60.0	
		[TTBPY-4]	1.5					
		[T-4]	97.0	100	100	100	83.3	
		[SS-4]	1.5				16.7	
	O				1.0	1.0	10.0	13.2
		[T-4]					60.0	57.9
		[SS-4]			100	100	40.0	42.1
$n_c = 5$	Ti			20.0	55.0	46.7	27.5	25.0
		[SPY-5]		50.0	45.4	35.7	50.0	61.1
		[TBPY-5]		50.0	54.5	64.3	50.0	38.9
	Si		4.2	5.0	10.0	7.5	25.0	
		[SPY-5]	33.3	75.0	33.3	33.3	40.0	
		[TBPY-5]	66.7	25.0	66.7	66.7	60.0	
$n_c = 6$	Ti			5.0	10.0	33.3	58.8	54.2
		[PPY-6]						2.6
		[O-6]		100	25.0	75.0	76.6	56.4
		[TPR-6]			50.0	15.0	17.0	25.6
	Si				25.0	10.0	6.4	15.4
		[TPBPY-6]			3.3	2.5	15.0	
		[O-6]			100	100	100	
						1.7	6.3	16.7
$n_c = 7$	Ti						100	83.3
		[PBPY-7]						16.7
		[MO-7]						
		[MTPR]				100		
$n_c = 8$	Ti							1.4
		[TD-8]						100

for [T-4]-type coordination polyhedra is much less pronounced. The ternary oxides exhibit notable polyhedra fractions of $\gtrsim 20\%$ of [SS-4]-type units in all oxide alloys (see figures 3(b-2) and 4(c-4)) that are less common for Si_{4c} ions. In addition, [SS-4]-type polyhedra actually represent the dominating Ti_{4c} coordination-polyhedron type in the Ti rich alloys ($x = 0.8$) with a fraction of $\sim 67\%$ (see figure 4(d-5)). Thereby, the function of the [SS-4]-type coordination polyhedra in the hybrid oxides of higher density ($\geq 3.80 \text{ g cm}^{-3}$) is basically the same for Si_{4c} and Ti_{4c} ions. In both cases the stronger geometry distortions of low coordinated polyhedra-building blocks are necessary in order to adapt to the surrounding larger polyhedra units of higher-coordinated ions. The [TTBPY-4]-type coordination state seems to be a sporadically occurring extreme distortion of the tetrahedral Ti coordination environment in the mixed alloys at lower mass

density ($\leq 3.00 \text{ g cm}^{-3}$). The coordination-polyhedra shapes of fivefold coordinated Ti_{5c} ions are roughly equally separated into [SPY-5]-type and [TBPY-5]-type coordination polyhedra. A slight prevalence for the trigonal bipyramidal [TBPY-5]-type is observed for $a\text{-Ti}_{0.6}\text{Si}_{0.4}\text{O}_2$ (see figure 4(c-6)) and for the truncated octahedron like [SPY-5]-type in pure $a\text{-TiO}_2$. The most common coordination type of Ti_{6c} ions is the crystal type [O-6] coordination polyhedron with a fraction of $\sim 56\%$ in pure $a\text{-TiO}_2$ (see figure 2(d-7)). In the low Si content $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ hybrid oxides ($x = 0.6, 0.8$) the fraction of [O-6]-type coordination polyhedra is usually even higher with a fraction of $\sim 75\%$. Sixfold coordinated Ti_{6c} ions at low Ti content always exhibit an octahedral crystal-like [O-6]-type coordination environment. With exception of a very dilute Ti distribution, also the distortion of TiO_6 building blocks into a trigonal prismatic geometry ([TPR-6]-type)

seems to be a fundamental but less frequently occurring ($\sim 26\%$ in pure a-TiO₂) structure characteristic of TiO₆ units (see figure 2(d-6)). Out of the two truncated pentagonal bipyramidal types [PPY-6] and [TPBPY-6] only the less symmetric second type (see figure 4(d-2)) occurs repeatedly for $x \geq 0.4$ with roughly half the frequency ($\sim 15\%$ in pure a-TiO₂) of [TPR-6]-type coordination polyhedra. [PPY-6]-type coordination polyhedra seem to be a rather exceptional structural unit that is only observed in the VASP optimized structure model of pure a-TiO₂. Altogether, sixfold coordinated Ti_{6c} ions show the most versatile coordination environments in a-Ti_xSi_{1-x}O₂ alloys and pure a-TiO₂. Sevenfold coordinated Ti_{7c} ions are predominantly found within [PBPY-7]-type geometrical units (100% in a-Ti_{0.8}Si_{0.2}O₂ and $\sim 83\%$ in pure a-TiO₂) (see figures 2(d-4) and (d-5)). The monocapped versions of the octahedron ([MO-7]-type) as well as the trigonal prism ([MTPR-7]-type) are significantly less frequently observed (see figure 4(d-5)). In pure a-TiO₂ the ratio of [PBPY-7]-type to [MO-7]-type coordination polyhedra is approximately 5 : 1. Only mono-capped prismatic [MTPR-7]-type coordination polyhedra are rather coincidentally observed for the 60 mol% Ti containing alloy. At all, only one (i.e. 1.4%) TiO₈ coordination-polyhedron building block, adopting a trigonal dodecahedron shape ([TD-8]-type), is observed for pure a-TiO₂.

The majority of twofold coordinated O_{2c} ions is arranged in homopolar angular [HOA-2] configurations. The sum of [HOA-2]-[Ti] and [HOA-2]-[Si] units is always $\geq 60\%$. Depending on the composition, notable fractions (between $\sim 26\%$ and $\sim 37\%$) of O_{2c} ions in the ternary oxides show a heteropolar twofold coordination environment. O_{2c} ions in more linear homopolar and heteropolar configurations (bonding angles $> 177^\circ$) are extremely rare structure elements within the disordered oxide framework. In case of threefold coordinated O_{3c} ions O(Ti,Si)₃ units typically show a $\geq 70\%$ fraction of pyramidal [TPY-3]-type coordination polyhedra. The corresponding close-to-planar structure type [TP-3] contributes with ~ 20 to $\sim 29\%$ to the TiO₃ coordination polyhedra, whereas the lower percentages are found in the Ti rich composition range. Also, some [TS-3]-type coordination polyhedra (one bonding angle $> 150^\circ$) are found at higher Ti content. The rarer O(Ti,Si)₄ coordination polyhedra exist in two configurations, the [T-4]-type and the [SS-4]-type. In the mid composition range ($x = 0.4$ and $x = 0.6$) the O(Ti,Si)₄ coordination polyhedra prefer the less symmetric [SS-4]-type shape. A percentage of 60% and $\sim 58\%$ [T-4]-type coordination polyhedra is characteristic for fourfold coordinated O_{4c} ions in the denser high Ti content ($x = 0.8$) ternary oxides and pure a-TiO₂, respectively. In general, the formation of [T-4]-type O(Ti,Si)_{4c} units necessitates a higher mass density than necessary for the formation [SS-4]-type O(Ti,Si)_{4c} coordination polyhedra. The existence of O_{4c} ions is an indication for the formation of local cluster-like entities governed by edge-linked coordination polyhedra. These structure units are almost exclusively formed by TiO_n coordination polyhedra. An characteristic example of such a TiO₂ cluster is visualized in figure 4(c-6).

In summary, the detailed analysis of the individual coordination polyhedra demonstrates that disorder in binary and

ternary a-Ti_xSi_{1-x}O₂ is not only related to changes in the local coordination numbers but also to variations in the basic coordination-polyhedron symmetry types for a given local coordination state. Thus, the shape information contained in the polyhedra geometries points towards an additional facet of topological disorder in amorphous oxides. Amorphous alloys do not necessarily contain only weakly distorted versions of a single crystal-like coordination polyhedron, rather various deformed polyhedra types coexist side by side. With respect to the well defined high-symmetry coordination polyhedra of the fourfold and sixfold coordinated cations in c-SiO₂ and c-TiO₂ these new polyhedra types might be characterized as *defective* coordination-polyhedra geometries. Thus, on an atomic level the topological disorder of an amorphous solid is not only visible as moderately distorted coordination polyhedra but also as a manifold of coordination and geometry defects as well as their hybrid forms. This observation indicates a rich structure polymorphism of coordination polyhedra even aside from coordination number changes that is of fundamental importance for the physical properties of materials.

Taking the example of TiO₂, the polyhedra geometry in c-TiO₂ leads to distinct crystal-field splitting related variations in the electronic density of states and the optical response [98, 125, 160, 161]. This is especially true for the TiO₆ coordination polyhedra in the natural occurring c-TiO₂ phases rutile, anatase, and brookite, whose TiO₆ units represent D_{2h}, D_{2d}, and even C₁ distorted versions of an idealized O_h symmetric TiO₆ octahedron (see TiO₂ coordination polyhedra in figure 11). These octahedral units typically show a splitting of electronic states into t_{2g} and e_g like states that are well separated in energy and reflected in the optical response [125, 137]. In amorphous solids the electronic structure reflects a superposition of the energy-level alignments in the diverse local coordination units. In general, the existence of alternative coordination-polyhedra geometry types will lead to distinct differences in the local electronic structure and the optical response. Especially the notable amount of trigonal prismatic D_{3h} like coordination units, whose energy level alignments substantially deviate from the octahedral type crystal-field splitting in O_h like coordination units [138], will change the electronic structure and optical functions of the amorphous phase from their characteristic form in the crystal phases. In contrast to a-TiO₂, a-SiO₂ is not only insignificantly affected by the formation of notable amounts of coordination defects, but also only weakly affected by coordination-polyhedra polytypism since the topological disorder is preferentially mediated through the amorphous framework itself. In ternary hybrid oxides as a-Ti_xSi_{1-x}O₂, the mixture of the different atomic-order types of the individual binary oxides results in a coordination-number and coordination-polyhedra distribution with features qualitatively different from the binary phases due to the formation and alignment of new fundamental structure-building blocks.

4.4. Bond length and bond angle distribution

We have analyzed the composition and coordination dependent distribution of bond lengths and bond angles in the VASP

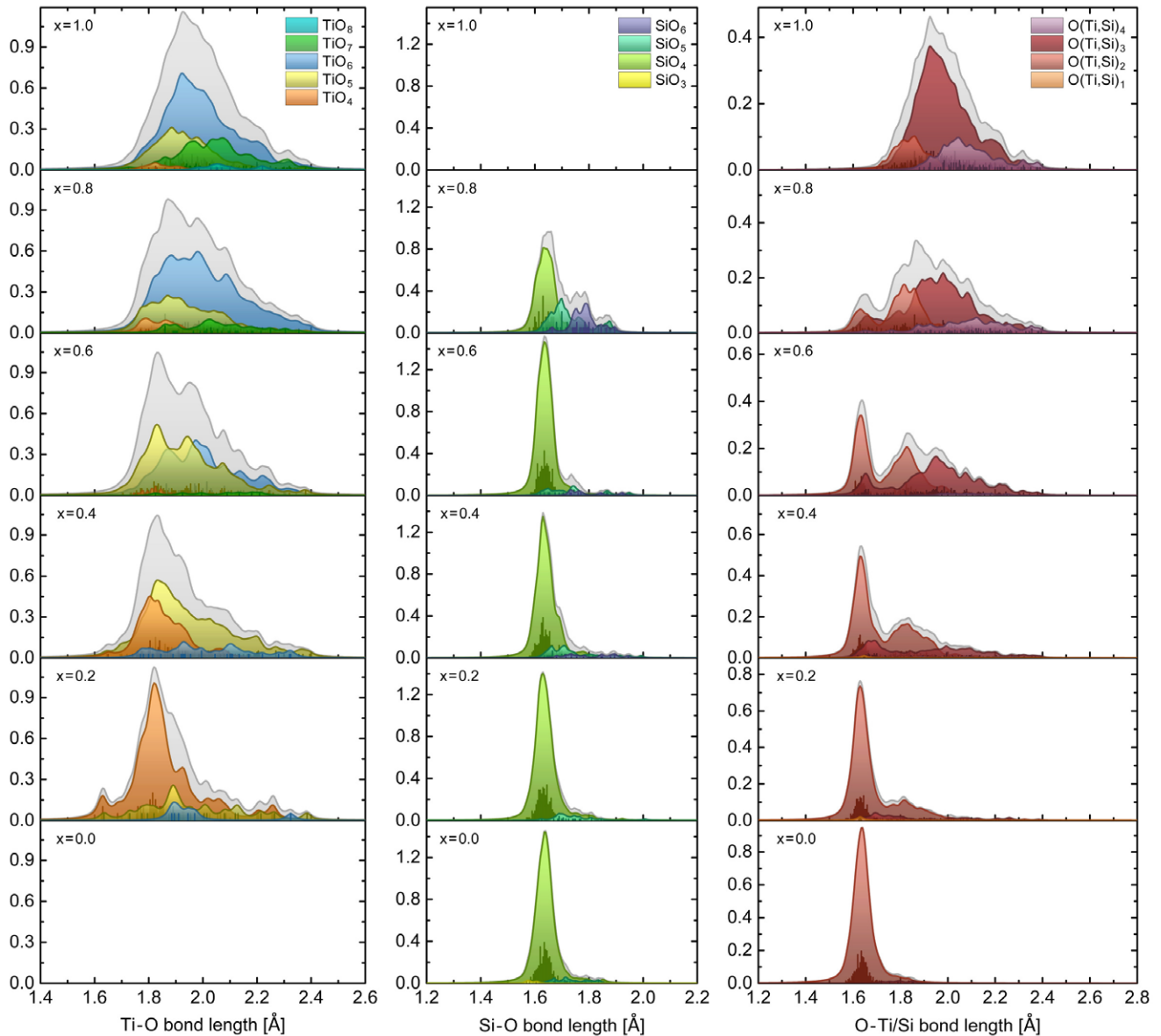


Figure 8. Total and local-coordination state decomposed Ti–O, Si–O and O–Ti/Si bond-lengths distributions in the $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ VASP geometries. The discrete line spectra are visualized as well as a continuous spectrum obtained by a Gaussian type line broadening.

relaxed structure models of $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$, in more detail, in order to discuss the various types of coordination polyhedra, quantitatively. The figures 8 and 9 show discrete line spectra and broadened spectra of the distribution of bond lengths and bond angles for all existing local coordination states. The average bond lengths and bond angles are visualized in figure 10 and tabulated in tables 2–4 for Si, Ti, and O ions. In addition, tables 2–4 list the minimal and maximal values of bond lengths and bond angles.

The extraordinary stability of the tetrahedral SiO_4 units is reflected in the extremely sharp distribution of Si–O bond lengths and bond angles over a wide alloy-composition range. Despite the occurrence of higher Si coordination states and some disorder induced broadening effects on the SiO_4 bond length and angle distributions, the position of the central peaks does not change notably up to the Ti richest alloy ($x = 0.8$). The average Si–O bond lengths of 1.639 ± 0.002 Å

and the average O–Si–O bond angles of $108.9^\circ \pm 0.3^\circ$ remain nearly constant over the entire composition range (see figures 10(b) and (e)). A similar independence on the Ti content, the alloy-mass density, is not observed for any other coordination state. It's interesting to note that the disorder induced distortions of tetrahedral SiO_4 units still increase the average Si–O bond length compared to the (average) Si–O bond length of 1.628 Å and 1.615 Å in the crystalline SiO_2 polytypes α -quartz and β -cristobalite (see figure 11). Nevertheless, individual Si–O bonds in the amorphous oxides can be significantly smaller than their crystal counterparts, as indicated by the minimal Si–O bond lengths of SiO_4 coordination polyhedra listed in table 2. In addition, the average SiO_3 unit bond length of 1.586 Å in pure $a\text{-SiO}_2$ is clearly smaller than the average bond length in any ordered or disordered fourfold coordinated polyhedron-building block. The average Si–O bond lengths of higher coordinated Si ions show a tendency to

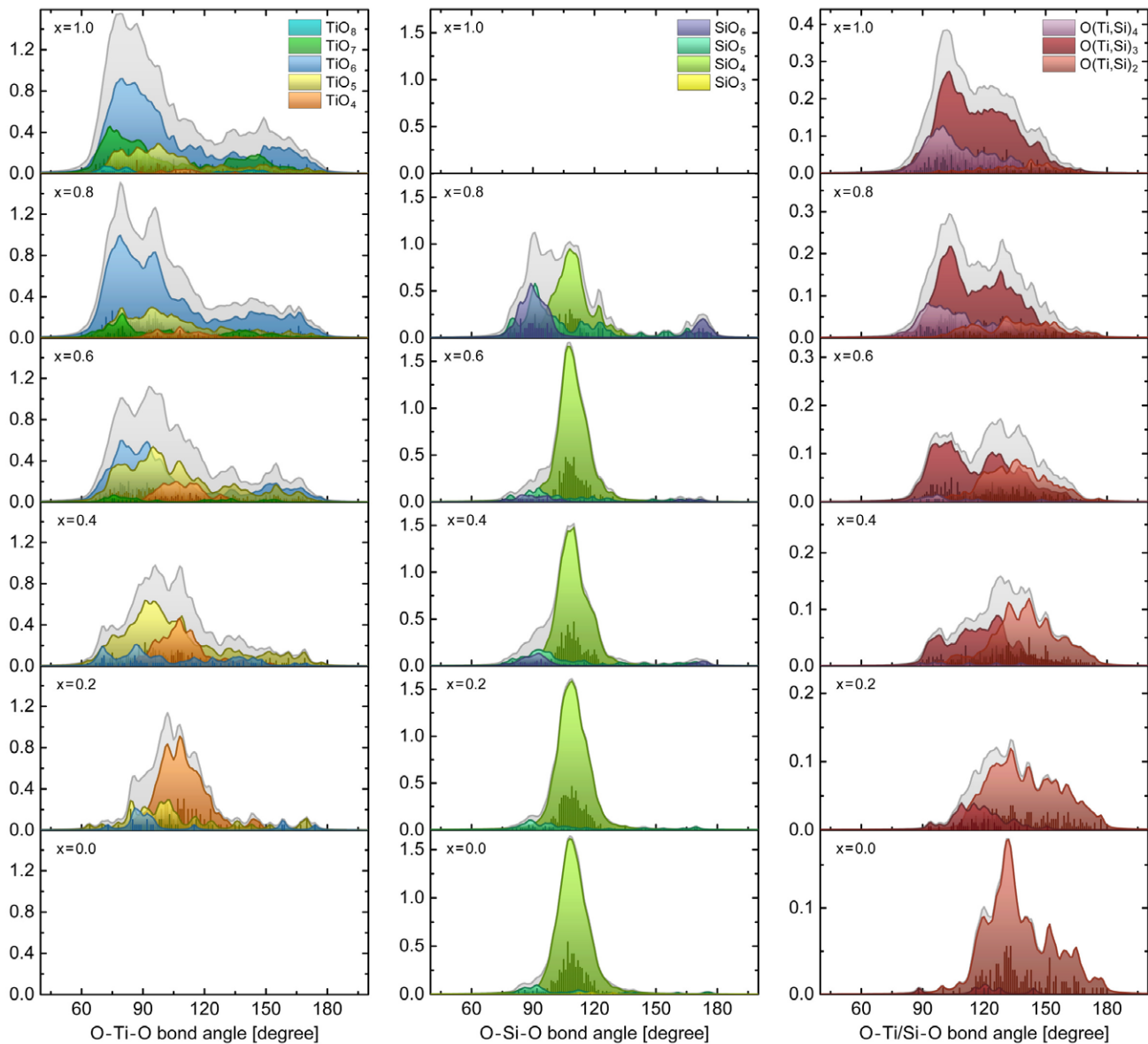


Figure 9. Total and local-coordination state decomposed O–Ti–O, O–Si–O and O–Ti/Si–O bond-angles distributions in the a-Ti_xSi_{1-x}O₂ VASP geometries. The discrete line spectra are visualized as well as a continuous spectrum obtained by a Gaussian type line broadening.

larger bond distances with both an increasing local coordination number and an increasing Si content. The average Si–O bond length in SiO₅ coordination polyhedra decreases from 1.737 Å in pure a-SiO₂ to 1.729 Å in a-Ti_{0.8}Si_{0.2}O₂ with a local maximum of 1.741 Å at a composition parameter of $x = 0.2$. For SiO₆ coordination polyhedra, the average Si–O bond length decreases almost linearly from 1.809 Å to 1.784 Å with increasing alloy-mass density. Altogether, the average bond lengths of Si–O bond pairs clearly separate the various local coordination states from each other (see figures 10(b)). In addition, this separation is nicely illustrated in figure 8 by the coordination dependent shift of the Si–O bond-length distribution peaks at a composition parameter of $x = 0.8$. The O–Si–O bond-angle distributions of high coordinated Si_{5c} and Si_{6c} ions, illustrated in figure 9, indicate that it might be quite difficult to separate angle contributions from fivefold coordinated units and a superposition of bond angles in tetrahedral

and octahedral building blocks. Compared to SiO₄ units, the most notable difference of the bond-angles distributions of SiO₅ and SiO₆ units is the presence of O–Si–O bond angles around 90°. Right angles are characteristic to the bond angles between an apical O ion, the central Si ion, and an O ion from the equatorial planes in [TBPY-5]-type SiO₅ and [O-6]-type SiO₆ coordination polyhedra. The average bond angles in SiO₅ building blocks show a slight continuous decrease from 107.3° to 106.7° with increasing alloy density up to a composition parameter of $x = 0.6$. At higher Ti content ($x = 0.8$), the average bond angle increases slightly to 107.0°. No definite trend is observed in SiO₆ units average O–Si–O bond angles between 106.4° and 105.3°. This might be due to the relatively small number of SiO₆ coordination polyhedra in the oxide alloys. Nevertheless, the minimal average bond angle is found for the a-Ti_{0.6}Si_{0.4}O₂ alloy for both fivefold coordinated Si_{5c} ions and sixfold coordinated Si_{6c} ions.

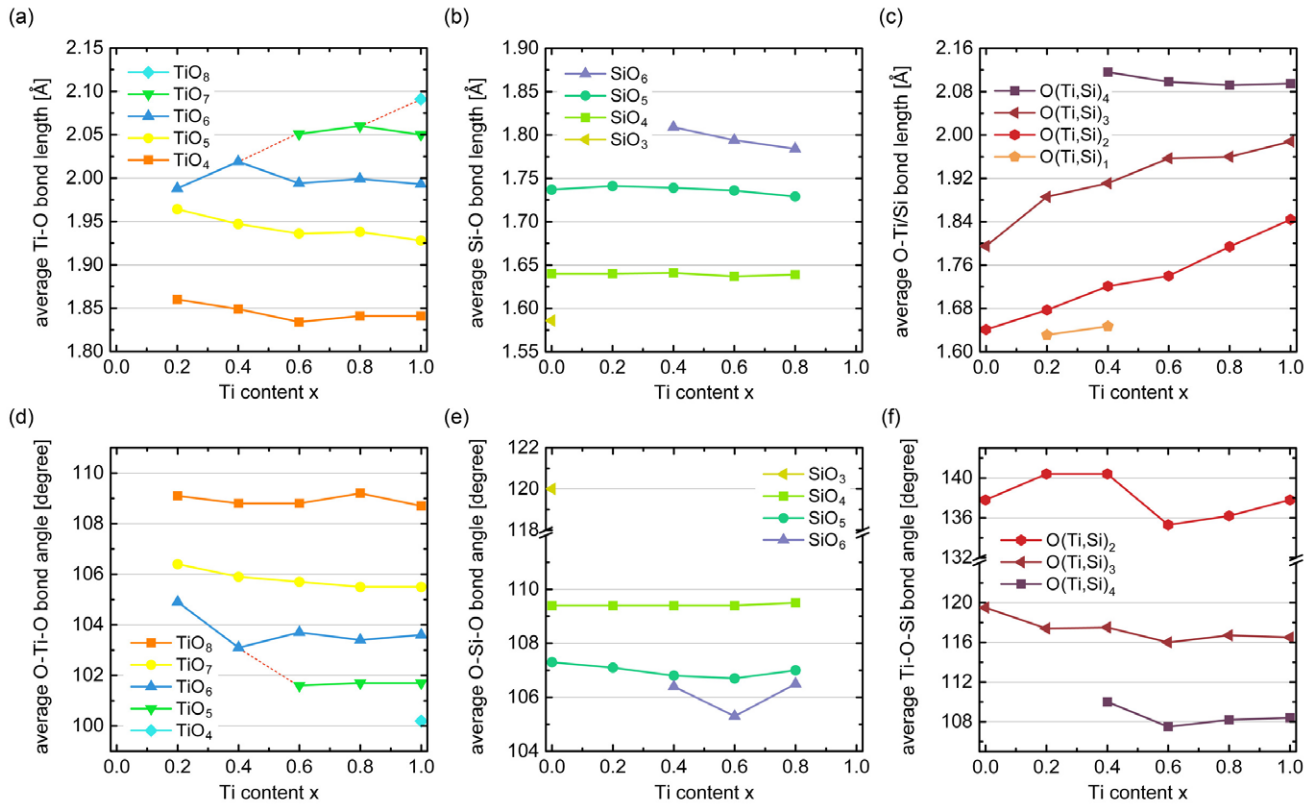


Figure 10. Average coordination polyhedra bond lengths (upper panels) and bond angles (lower panels) of the $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ VASP geometries. The dashed red lines in figures (a) and (d) are used to represent trends in the Ti–O bond length and O–Ti–O bond angles.

Table 2. Average Si–O bond lengths d_{ij}^{av} and O–Si–O bond angles φ_{ij}^{av} for the various coordination states of Si ions in the $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ VASP geometries. Values in brackets represent the corresponding minimal and maximal bond lengths and bond angles ($d_{ij}^{\text{min}} / d_{ij}^{\text{max}}$), ($\varphi_{ij}^{\text{min}} / \varphi_{ij}^{\text{max}}$), respectively.

Bond lengths d_{ij} (Å) and bond angles φ_{ij} (degree)						
Ion	$x = 0.0$	$x = 0.2$	$x = 0.4$	$x = 0.6$	$x = 0.8$	$x = 1.0$
Si3c	1.586Å (1.572Å/1.607Å) 120.0° (112.8°/128.8°)					
Si4c	1.640Å (1.572Å/1.855Å) 109.4° (83.3°/138.6°)	1.640Å (1.568Å/1.923Å) 109.4° (92.5°/135.2°)	1.641Å (1.582Å/1.792Å) 109.4° (85.5°/129.3°)	1.637Å (1.586Å/1.731Å) 109.4° (92.6°/128.9°)	1.639Å (1.581Å/1.718Å) 109.5° (94.5°/133.2°)	
Si5c	1.737Å (1.651Å/1.837Å) 107.3° (82.7°/176.3°)	1.741Å (1.624Å/2.007Å) 107.1° (79.7°/170.1°)	1.739Å (1.633Å/1.993Å) 106.8° (76.2°/169.9°)	1.736Å (1.622Å/1.948Å) 106.7° (78.3°/171.3°)	1.729Å (1.631Å/1.879Å) 107.0° (78.7°/175.1°)	
Si6c			1.809Å (1.681Å/1.944Å) 106.4° (76.3°/174.9°)	1.794Å (1.731Å/1.923Å) 105.3° (76.4°/172.2°)	1.784Å (1.663Å/1.895Å) 106.5° (78.4°/177.5°)	

In summary, the SiO_m coordination polyhedra seem to participate rather passively in the formation of the amorphous frameworks of $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ hybrid oxides. The individual coordination units do not absorb significant fractions of atomic short-range disorder by strong distortions into the direct coordination environment of Si ions and the generation of new coordination-polyhedra geometry types. However, under extreme conditions the Si ions will actually respond to the increased network connectivity by increasing their

coordination state in order to allow structure modifications of the amorphous framework on a mid-range order scale that affects the arrangement of coordination polyhedra over a few neighbor units.

Next, we consider the broader and substantially more complex distributions of Ti–O bond lengths and O–Ti–O bond angles (see figures 8 and 9). In general, the total distributions of Ti–O bond lengths and O–Ti–O bond angles closely follow the distributions of the dominant coordination

Table 3. Average Ti–O bond lengths d_{ij}^{av} and O–Ti–O bond angles φ_{ij}^{av} for the various coordination states of Ti ions in the a-Ti_xSi_{1-x}O₂ VASP geometries. Values in brackets represent the corresponding minimal and maximal bond lengths and bond angles ($d_{ij}^{min} / d_{ij}^{max}$), ($\varphi_{ij}^{min} / \varphi_{ij}^{max}$), respectively.

Ion	Bond lengths d_{ij} (Å) and bond angles φ_{ij} (degree)					
	$x = 0.0$	$x = 0.2$	$x = 0.4$	$x = 0.6$	$x = 0.8$	$x = 1.0$
Ti4c		1.860Å (1.627Å/2.260Å) 109.1° (86.4°/146.6°)	1.849Å (1.651Å/2.082Å) 108.8° (87.9°/152.1°)	1.834Å (1.747Å/1.945Å) 108.8° (84.3°/132.4°)	1.841Å (1.767Å/1.978Å) 109.2° (91.1°/147.0°)	1.841Å (1.774Å/1.917Å) 108.7° (88.5°/135.0°)
Ti5c		1.964Å (1.635Å/2.384Å) 106.4° (63.7°/170.0°)	1.947Å (1.643Å/2.393Å) 105.9° (62.8°/177.3°)	1.936Å (1.703Å/2.379Å) 105.7° (67.1°/172.1°)	1.938Å (1.732Å/2.383Å) 105.5° (67.0°/175.9°)	1.928Å (1.725Å/2.374Å) 105.5° (67.5°/177.6°)
Ti6c		1.988Å (1.884Å/2.325Å) 104.9° (72.7°/173.9°)	2.019Å (1.770Å/2.327Å) 103.1° (66.9°/169.5°)	1.994Å (1.728Å/2.344Å) 103.7° (64.9°/177.1°)	1.999Å (1.740Å/2.400Å) 103.4° (61.1°/178.5°)	1.993Å (1.759Å/2.388Å) 103.6° (64.7°/177.8°)
Ti7c				2.051Å (1.825Å/2.212Å) 101.6° (71.1°/155.3°)	2.060Å (1.858Å/2.355Å) 101.7° (61.5°/177.9°)	2.050Å (1.726Å/2.378Å) 101.7° (61.1°/175.2°)
Ti8c						2.091Å (1.985Å/2.219Å) 100.2° (67.2°/149.1°)

Table 4. Average O–Ti/Si bond lengths d_{ij}^{av} and Ti/Si–O–Ti/Si bond angles φ_{ij}^{av} for the various coordination states of O ions a-Ti_xSi_{1-x}O₂ VASP geometries. Values in brackets represent the corresponding minimal and maximal bond lengths and bond angles ($d_{ij}^{min} / d_{ij}^{max}$), ($\varphi_{ij}^{min} / \varphi_{ij}^{max}$), respectively.

Ion	Bond lengths d_{ij} (Å) and bond angles φ_{ij} (degree)					
	$x = 0.0$	$x = 0.2$	$x = 0.4$	$x = 0.6$	$x = 0.8$	$x = 1.0$
O1c		1.631Å (1.627Å/1.635Å) 167.7° (111.2°/177.2°)	1.647Å (1.643Å/1.651Å) 172.1° (98.4°/173.9°)			
O2c	1.641Å (1.572Å/1.837Å) 137.8° (99.5°/177.8°)	1.677Å (1.568Å/2.325Å) 140.4° (111.2°/177.2°)	1.721Å (1.582Å/2.119Å) 140.4° (98.4°/173.9°)	1.740Å (1.586Å/2.083Å) 135.3° (96.3°/176.0°)	1.794Å (1.581Å/2.065Å) 136.2° (99.2°/175.4°)	1.844Å (1.725Å/2.070Å) 137.8° (104.3°/161.6°)
O3c	1.795Å (1.722Å/1.855Å) 119.5° (88.3°/144.2°)	1.886Å (1.625Å/2.384Å) 117.4° (93.2°/150.7°)	1.911Å (1.619Å/2.393Å) 117.5° (91.1°/156.2°)	1.957Å (1.605Å/2.379Å) 116.0° (86.4°/160.6°)	1.960Å (1.604Å/2.400Å) 116.7° (82.4°/165.4°)	1.988Å (1.776Å/2.339Å) 116.5° (81.1°/167.0°)
O4c			2.116Å (1.889Å/2.278Å) 110.0° (89.0°/138.1°)	2.098Å (1.973Å/2.251Å) 107.5° (85.2°/162.9°)	2.092Å (1.646Å/2.397Å) 108.2° (78.3°/149.2°)	2.095Å (1.881Å/2.388Å) 108.4° (82.3°/150.4°)

state(s). Therefore, it might be rather difficult to identify contributions from non-dominant coordination states in experimental approaches. For example, the Ti–O bond length and O–Ti–O bond angles of under-coordinated Ti_{5c} ions and over-coordinated Ti_{7c} ions are completely enclosed by larger contributions from TiO₆ coordination polyhedra in pure a-TiO₂ and Ti rich a-Ti_xSi_{1-x}O₂ alloys ($x \geq 0.8$). It seems natural to assume that due to the similar coordination-environment characteristics to a superposition of under- and over-coordinated Ti ions, a-TiO₂ might have been sporadically misinterpreted as a purely octahedrally coordinated material. In the mid-composition range, comparable contributions to the bond lengths as well as bond-angles arise from differently coordinated Ti ions. At a composition parameter of $x = 0.4$ these are Ti ions located in TiO₄ as well as TiO₅ coordination polyhedra and for $x = 0.6$ Ti ions in TiO₅ as well as TiO₆ coordination units. The main peaks of the total

Ti–O bond length distributions show small variations in the Si rich regime ($x < 0.6$) but shift to higher bond length in the Ti rich hybrid oxides and pure a-TiO₂. The bond lengths as well as bond-angles distributions demonstrate that the individual TiO_n coordination states show slightly different distribution characteristics at various composition parameters. For example, the Ti–O bond length distribution of TiO₆ coordination polyhedra shows a two peak characteristic at a composition parameter of $x = 0.6$, a broadened multi-peak distribution at $x = 0.8$ and single broad main peak in pure TiO₂. Similarly, the O–Ti–O bond-angle distribution shows a two-peak characteristic between $\sim 70^\circ$ and $\sim 100^\circ$ at composition parameters of $x = 0.6$ and $x = 0.8$, while the bond-angle distribution of pure a-TiO₂ shows a broad single peak in this angle-size range. Qualitative differences are also observed for the distribution of bond lengths and bond angles of TiO₅ coordination polyhedra for Ti fractions of 40 and 60 mol%.

The qualitative differences in the distribution of bond lengths and bond angles clearly indicate that the TiO_n coordination polyhedra, all possibly occurring associated geometry types respectively, cannot be seen as rigid building blocks that assemble the amorphous solid. Rather, the TiO_n coordination units in $\text{a-Ti}_x\text{Si}_{1-x}\text{O}_2$ hybrid oxides show density dependent distortions for each alloy composition. It is particularly noteworthy that the average Ti–O bond lengths, and to a comparable extent the average O–Ti–O bond angles, presented in the figures 10(a) and (d), actually give some insights into the short-range order formation processes and the origin of higher coordinated TiO_n coordination polyhedra in a-TiO_2 and its amorphous alloys. The actual formation trends are most clearly observed for the octahedrally coordinated TiO_6 building blocks. The TiO_6 coordination polyhedra show an average Ti–O bond length of 1.988 Å at low Ti content ($x = 0.2$) and moderate alloy-mass density of 2.60 g cm^{-3} . This value is extremely close to the average Ti–O bond length of 1.981 Å in the C_1 symmetric TiO_6 octahedrons of crystalline TiO_2 in the brookite phase. With increasing mass density (3.00 g cm^{-3}) of the oxide alloys, a maximal average Ti–O bond length of 2.019 Å is reached for a composition parameter of $x = 0.4$. This point actually represents an extremum of absorbed short-range disorder through distortions of the TiO_6 building blocks. The extremal behavior is also reflected in the formation of alternative symmetry types for the TiO_6 coordination polyhedra (see table 1). While the TiO_6 coordination polyhedra exclusively show an [O-6]-type geometry at $x = 0.2$, only 25.0% of the TiO_6 coordination polyhedra can be attributed to this geometry type at the critical composition parameter of $x = 0.4$. 50.0% of TiO_6 coordination polyhedra are distorted to a [TPR-6]-type geometry. The remaining 25.0% are best characterized as a [TPBPY-6]-type coordination state. Thus, the increase in the average bond lengths is also related to massive changes in the geometry types of TiO_6 octahedrons, with which the local Ti ion coordination units try to diminish the tension within the amorphous framework. If the Ti content and for this reason the mass density is increased beyond 3.00 g cm^{-3} , $x = 0.4$ respectively, the individual TiO_6 building blocks cannot absorb anymore atomic disorder from the increasingly denser amorphous framework. Ultimately, at some point the system will spontaneously start to form sevenfold coordinated TiO_7 building blocks to increase the connectivity of the coordination polyhedra and to allow local relaxations of the distorted amorphous framework. The average bond length of 2.019 Å of maximal distorted TiO_6 coordination-polyhedra bonds is quite close to the average Ti–O bond length of 2.051 Å in the newly formed TiO_7 units, which actually facilitates the transition from a lower to a higher coordination state. The formation of the higher coordination complexes for the Ti ion actually takes away constraints of the amorphous framework onto the highest coordinated and likewise most flexible coordination unit that is present in the system at that time. After the formation of higher coordinated units the average bond length in TiO_6 building blocks relaxes to a value of 1.994 Å which is similar to the average Ti–O bond length at low alloy density. Subsequently, the

average TiO_6 coordination-polyhedra bond lengths remain roughly constant at high Ti contents and even in pure a-TiO_2 . Also, the number of crystal-like [O-6]-type coordination polyhedra increases abruptly and becomes the clearly dominant coordination-geometry state with fractions of 75.0% and 76.6% at compositions of $x = 0.6$ and $x = 0.8$. In complete analogy to the TiO_6 units, also the TiO_7 coordination polyhedra show a maximal average bond length of 2.060 Å at a composition parameter of $x = 0.8$ just before TiO_8 units are formed at even higher alloy density or in pure a-TiO_2 and the average Ti–O bond length of TiO_7 building blocks relaxes back to 2.050 Å. Similar transitions to higher coordinated units could not be observed for lower coordinated units in our data since TiO_4 and TiO_5 coordination polyhedra are present in any Ti containing $\text{a-Ti}_x\text{Si}_{1-x}\text{O}_2$ hybrid oxide. However, the trends in the average Ti–O bond length indicate that a transition from fivefold coordinated Ti_{5c} ions to sixfold coordinated Ti_{6c} ions as the highest coordination state might occur in $\text{a-Ti}_x\text{Si}_{1-x}\text{O}_2$ hybrid oxides for a composition parameter of $x \ll 0.2$. In addition, the average bond lengths within the TiO_5 building blocks show the strongest dependence on the Ti content. The average bond length decreases almost continuously from 1.964 Å in $\text{a-Ti}_x\text{Si}_{1-x}\text{O}_2$ to 1.928 Å in pure a-TiO_2 . The notable dependence of the TiO_5 polyhedra volume on the mass density hints to the role of TiO_5 units as some kind of transition state that mediate the transformation from fourfold coordinated Ti ions to a sixfold coordination state of Ti ions. TiO_5 coordination polyhedra show the distinct ability to adapt very flexible to the surrounding coordination polyhedra in size and shape alongside the density variations of the amorphous oxide alloy. Similar to the SiO_4 units, the TiO_4 coordination polyhedra units seem to be the most rigid coordination environment for Ti ions with variations in the average bond length between 1.860 Å in $\text{a-Ti}_{0.2}\text{Si}_{0.8}\text{O}_2$ and 1.834 Å in the $\text{a-Ti}_{0.6}\text{Si}_{0.4}\text{O}_2$ alloy. Especially at high Ti content, the average TiO_4 coordination bond length shows a constant value of 1.841 Å. The separation between the average Ti–O bond lengths of TiO_4 and TiO_5 coordination polyhedra of ~ 0.1 Å is quite large and remains constant for the largest part of the alloy composition range. Therefore, it seems unlikely that even for an ultra-low density oxide, that contains some amount of low coordinated TiO_n building blocks, a generation mechanism, similar to the the high coordination states might be observable. In light of existing TiO_9 coordination polyhedra in the ultra-dense cotunnite polytype of c-TiO_2 , higher TiO_n coordination states seem to be likely in amorphous oxides of high mass density or under significant pressure. However, since highly coordinated TiO_n units are formed locally, primarily due to disorder effects of the amorphous framework, and might be compensated by lower coordinated surrounding TiO_n coordination polyhedra (see figure 4(c-6)), there is a significantly higher probability of finding high Ti coordination states in an amorphous oxide phases than in a crystalline oxide phase under similar thermodynamical conditions.

The whole argumentation on the formation mechanism of higher coordination states might for the largest part be equivalently given in terms of the average O–Ti–O bond angles

(see figure 10(d)). However, instead of repeating the discussion itself, we will just shortly summarize the key data subsequently. The average O–Ti–O bond angle of TiO_6 coordination polyhedra exhibits a minimal value of 103.7° at a composition parameter of $x = 0.4$ and relaxes back to an average bond angle between 103.4° and 103.7° in the high Ti content alloys. With the increase of the coordination state, the average bond angle reduces successively to $101.7^\circ \pm 0.1^\circ$ in the TiO_7 coordination polyhedra and to 100.2° for the TiO_8 building blocks in pure a- TiO_2 . In case of fivefold coordinated Ti_{5c} ion, the average O–Ti–O coordination-polyhedra bond angle decreases continuously over the entire composition range from 106.4° at a composition parameter of $x = 0.2$ to 105.5° in pure a- TiO_2 . The tetrahedral TiO_4 coordination units are characterized by tetrahedron type average O–Ti–O bond angles of $109.0^\circ \pm 0.3^\circ$.

In summary, the formation of new high coordination states in a- $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ hybrid oxides shows a critical dependence on the Ti content, and therefore the mass density of the mixed oxides. As indicated by the average Ti–O bond lengths and O–Ti–O bond angles and their trends indicated in figures 10(a) and (b), the changes in the network topology due to the formation of new TiO_n coordination polyhedra closely resemble bifurcation-like changes of states in complex systems. Ultimately, the mass density acts as the critical system parameter for the spontaneous formation of new coordination units that itself is triggered by strong deformations in the direct coordination environment of existing coordination-polyhedra building blocks. It is obvious that all these complex trends seem to be restricted to the Ti coordination environment. Therefore, it seems reasonable to assume that disorder effects within the first Ti–O coordination shell play a fundamental and active role in the structure formation processes and, upon heat treatment, the crystallization dynamics in a- $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ hybrid oxides.

The distributions of the average O–Ti/Si bond lengths in figure 8(c) basically reflect the continuous transition from pure a- SiO_2 to pure a- TiO_2 . In pure a- SiO_2 , almost the entire amorphous network is connected by corner-linking Si–O–Si bonds between tetrahedral SiO_4 units with an O–Si average bond length of $1.641 \text{ \AA}$. In pure a- TiO_2 , in contrast, only a small number of O ions is actually twofold coordinated by Ti ions. The corresponding average O–Ti bond length is $1.844 \text{ \AA}$. With increasing Ti content, the bond length distribution of twofold coordinated O_{2c} ions in the oxide alloys shows a continuous transition between OSi_2 -like and OTi_2 -like coordination units and thus a two-peak characteristic (see figure 8). These two subpeaks at $\sim 1.64 \text{ \AA}$ and $\sim 1.84 \text{ \AA}$ do not show a notable dependence on the Ti concentration in the alloy. However, the peak heights change with the ratio of Ti and Si ions. Up to a composition parameter of $x = 0.4$, the total bond-length distribution closely follows the bond distribution of twofold coordinated O_{2c} ions. At composition parameters of $x = 0.6$ and $x = 0.8$ the total bond-length distribution is a superposition of contributions from $\text{O}(\text{Ti},\text{Si})_2$ and $\text{O}(\text{Ti},\text{Si})_3$ coordination units. In pure a- TiO_2 the total bond-length distribution is predominantly determined by contributions from threefold coordinated O_{3c} ions round an average O–Ti bond length of $1.988 \text{ \AA}$. Due to the various possible combinations

of O–Ti and O–Si bonds, a significant broadening, compared to the $\text{O}(\text{Ti},\text{Si})_2$ units, of the O–(Ti,Si)₃ bond-lengths distributions is observed. In the composition range between $x = 0.4$ and $x = 0.8$ a bond-length feature from short O–Si bonds remains identifiable. Higher bond length features originate from a mixture of elongated O–Si bonds and, prevalently, from the various types of O–Ti bonds. The new long-distance bond-length peak of threefold coordinated O_{3c} ions, located around $\sim 1.95 \text{ \AA}$, indicates substantially longer O–Ti bonds in $\text{O}(\text{Ti},\text{Si})_3$ complexes and, thus, different average O–Ti bond lengths in $\text{O}(\text{Ti},\text{Si})_2$ and $\text{O}(\text{Ti},\text{Si})_3$ coordination units. An even larger average bond length is indicated for tetrahedral $\text{O}(\text{Ti},\text{Si})_4$ coordination units in the Ti rich oxide alloys. In general, the average O–Ti/Si bond lengths (see figure 10) increase continuously from $1.641 \text{ \AA}$ to $1.844 \text{ \AA}$ for twofold coordinated O_{2c} and from $1.795 \text{ \AA}$ to $1.988 \text{ \AA}$ for threefold coordinated O_{3c} ions. Extremely short average O–Ti bond lengths of $1.631 \text{ \AA}$ and $1.647 \text{ \AA}$ are observed for onefold coordinated O_{1c} ions in the a- $\text{Ti}_{0.2}\text{Si}_{0.8}\text{O}_2$ and a- $\text{Ti}_{0.4}\text{Si}_{0.6}\text{O}_2$ alloys. In contrast, tetrahedral $\text{O}(\text{Ti},\text{Si})_4$ coordination polyhedra occur for the first time at a Ti content of 40 mol% with an extremely high average bond lengths of $2.116 \text{ \AA}$. The average O–(Ti,Si) bond length for fourfold coordinated O_{4c} ions is reduced to $2.092 \text{ \AA}$ in Ti rich mixed oxides ($x = 0.8$), which is almost identical to the value of $2.095 \text{ \AA}$ in pure a- TiO_2 . As might be expected from the large average bond length, the $\text{O}(\text{Ti},\text{Si})_4$ coordination polyhedra show a [SS-4]-type geometry at composition parameters of $x = 0.4$ and $x = 0.6$. In turn, the reduction of the average bond length for high Ti content alloys and pure a- TiO_2 is caused by the formation of an $\sim 60\%$ fraction of [T-4]-type $\text{O}(\text{Ti},\text{Si})_4$ coordination polyhedra.

The average O–Ti/Si–O bond angles of $\text{O}(\text{Ti},\text{Si})_2$ coordination units displayed in figure 10(f) indicate a rather complex dependence on the alloy composition. An identical average O–Si–O and accordingly O–Ti–O bond angle of 137.8° is observed for the two binary oxides. In the Si rich hybrid oxides the average O–Ti/Si–O bond angle increases to 140.4° . With Ti ions becoming the major cation type ($x > 0.5$), the O–Ti/Si–O angle drops considerably to 135.3° in a- $\text{Ti}_{0.6}\text{Si}_{0.4}\text{O}_2$ and increases slightly to 136.2° in a- $\text{Ti}_{0.8}\text{Si}_{0.2}\text{O}_2$. The average O–Ti/Si–O bond angle of $\text{O}(\text{Ti},\text{Si})_3$ units in pure a- SiO_2 decreases stepwise from 119.5° , indicating almost perfectly planar OTi_3Si_3 units, to 116.5° in a- TiO_2 , indicating a predominance of pyramidal distorted $\text{O}(\text{Ti},\text{Si})_3$ coordination polyhedra.

It is interesting to note that, compared to the higher coordination states, small coordination numbers (≤ 3) tend to result in a reversed density dependence of the bond lengths. This trend seems to reflect that the average bond length in $\text{O}(\text{Ti},\text{Si})_2$ and $\text{O}(\text{Ti},\text{Si})_3$ coordination units is actually the result of randomly arranged TiO_n and SiO_m coordination polyhedra of different size, of different coordination states n and m respectively, within the amorphous framework of the hybrid oxides. More or less, the continuous increase in the average bond length of both $\text{O}(\text{Ti},\text{Si})_2$ and $\text{O}(\text{Ti},\text{Si})_3$ coordination polyhedra is a first hint on the atomically mixed nature of the generated a- $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ structure models. In a phase separated oxide alloy, coordination units of O_{2c} and O_{3c} ions would reflect the bond

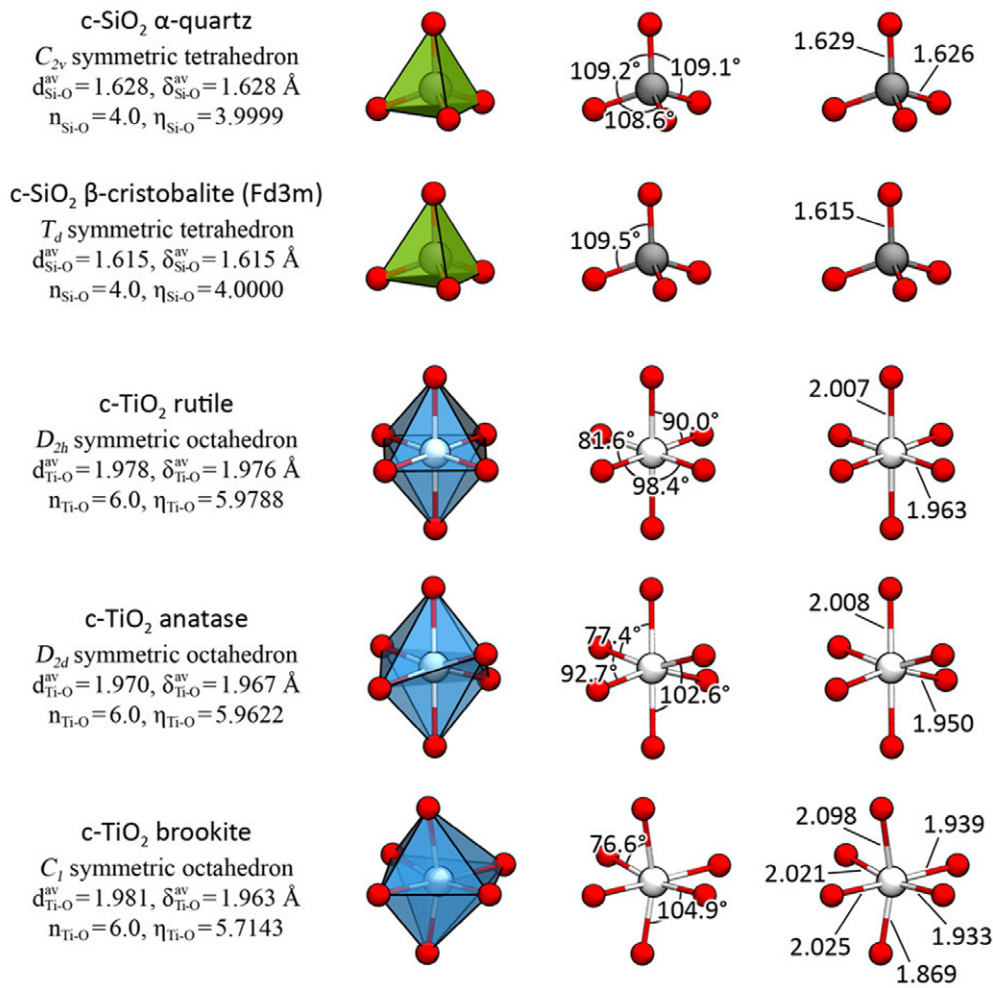


Figure 11. Overview on structural characteristics of the fundamental coordination polyhedra in crystalline TiO₂ and SiO₂ phases. Listed are the conventional and effective coordination numbers $n_{\text{Ti-O}}$ and $\eta_{\text{Ti-O}}$, as well as the average and weighted average coordination-polyhedra bond lengths d^{av} and δ^{av} . With the exception of the TiO₂ brookite phase, all different O–Ti–O bond angles and Ti–O bond lengths are given for the DFT-PBE optimized crystal structures. For brookite, only the minimal and the maximal O–Ti–O bond angles are documented.

length distribution in the binary-oxide domains of a-SiO₂ and a-TiO₂, respectively. In that case the average bond length of O(Ti,Si)₂ and O(Ti,Si)₃ coordination polyhedra should neither show a similar mass-density dependence nor a continuously increasing value over the entire composition range. However, the analysis of the average O–Ti/Si–O bond angles, and their less significant composition dependence, indicate that it might be difficult to deduce specific mid-range order characteristics solely from the analysis of the atomic structure within first cation-coordination shell of O ions.

4.5. Effective coordination numbers

In order to demonstrate the differences between the conventional coordination-number analysis and the effective coordination-number concept, we have calculated⁵ the Ti–O and Si–O coordination numbers of some crystalline TiO₂ as well as SiO₂ polymorphs (see figure 11). In the case of c-SiO₂, the crystalline phases α -quartz and β -cristobalite have been investigated. In detail, we have chosen the highest-symmetry

Fd3m-type polymorph from the theoretically proposed β -cristobalite structure models [162]. As characteristic for all c-SiO₂ low-pressure phases, α -quartz and β -cristobalite are composed of corner-sharing tetrahedral SiO₄ building blocks that form some kind of a regular three-dimensional network. For c-TiO₂ we have considered the three most common, naturally occurring, crystalline phases rutile, anatase, and brookite. These low-pressure polymorphs of c-TiO₂ are characterized by three-dimensional networks of edge as well as corner sharing TiO₆ octahedron building blocks [125].

The SiO₄ units in *Fd3m* β -cristobalite exhibit an idealized T_d symmetric tetrahedron shape that are characterized by idealized O–Si–O bond angles of $\sim 109.5^\circ$ and equal Si–O bond

⁵ The reported results refer to fully optimized DFT-PBE unit cells. In detail, a kinetic-energy plane-wave cutoff of 550 eV and k point samplings of $12 \times 12 \times 16$, $14 \times 14 \times 6$, and $6 \times 10 \times 10$ have been applied to the rutile, anatase, and brookite phases of c-TiO₂. In the case of the c-SiO₂ phases α -quartz and β -cristobalite, a k point mesh of $7 \times 7 \times 7$ has been used. The atomic position and unit cell volumes were relaxed until a force convergence criterion of $0.001 \text{ eV } \text{\AA}^{-1}$ was reached.

lengths of 1.615 Å. As expected for a high symmetry coordination state, both conventional and effective coordination numbers result in a coordination number of 4.0. In the most common c-SiO₂ polytype α -quartz, the tetrahedron symmetry of SiO₄ units is reduced to a C_{2v} symmetry due to two bond lengths pairs of 1.629 Å and 1.626 Å each and three slightly different O–Si–O bond angles between 108.6° and 109.2°. Since the SiO₄ tetrahedra turn out to be rather stiff and the bond-lengths variations are quite small, the α -quartz effective Si coordination number of $\eta_{\text{Si-O}} = 3.9999$ shows only marginal deviations from the conventional local coordination number of $n_{\text{Si-O}} = 4.0$. Also, differences between the average and the average weighted bond length are negligible (see figure 11).

In contrast to c-SiO₂, the effective coordination number differences of Ti ions in various TiO₂ crystal phases are much more obvious. In the c-TiO₂ rutile phase the TiO₆ octahedra-building blocks are slightly distorted with respect to the O_h symmetry of an ideal octahedron. The symmetry reduced octahedra are characterized by different in-plane (equatorial) and out-of-plane (apical) Ti–O bond lengths of 2.007 Å and 1.963 Å and two deformed O–Ti–O in-plane bond angles of 84.6° and 98.4°. The deviations from an ideal octahedron reduce the effective coordination number to $\eta_{\text{Ti-O}} = 5.9788$. In the c-TiO₂ anatase phase the O ions are displaced alternating below and above the equatorial octahedron plane, thus decreasing and increasing the ideal 90.0° out-of-plane O–Ti–O bond angles by 12.6°. The deformed in-plane bond angle is 92.7°. With respect to the rutile phase, the effective coordination numbers of the D_{2d} symmetric anatase TiO₆ coordination polyhedra are slightly reduced to $\eta_{\text{Ti-O}} = 5.9622$. Notable deviations from an idealized octahedral coordination are found for the TiO₆ building blocks of the c-TiO₂ brookite phase. In fact, the local coordination environment of brookite shows a complete loss of symmetry. The O–Ti–O bond angles of these C_1 symmetric coordination polyhedra vary between 76.6° and 104.9°. The Ti–O bond lengths of c-TiO₂ brookite span the range from 1.869 Å to 2.098 Å. In contrast to rutile and anatase, the notable distortions of the brookite coordination polyhedra lead to a much greater reduction of the effective coordination number to $\eta_{\text{Ti-O}} = 5.7143$. The calculated c-TiO₂ brookite average weighted bond length of 1.963 Å falls below the average bond length of 1.981 Å by ~1%. For rutile and anatase this difference is of the order of 1–2 per mill.

In sum, the effective coordination numbers prove to be quite sensitive to symmetry reductions of the local cation coordination environment and thus the particular shape and symmetry type of various coordination polyhedra. Thus, we expect the effective coordination numbers to be qualitative and, if compared to the conventional coordination numbers, quantitative measures for the degree of disorder within the first coordination shell around an atom. Notable deviations ($\geq 5\%$) from the conventional local coordination numbers, as observed for c-TiO₂ brookite, are a definite indicator for strongly distorted, non-crystalline coordination polyhedra, whose occurrence is characteristic to a-TiO₂ as indicated by the coordination polyhedra analysis above.

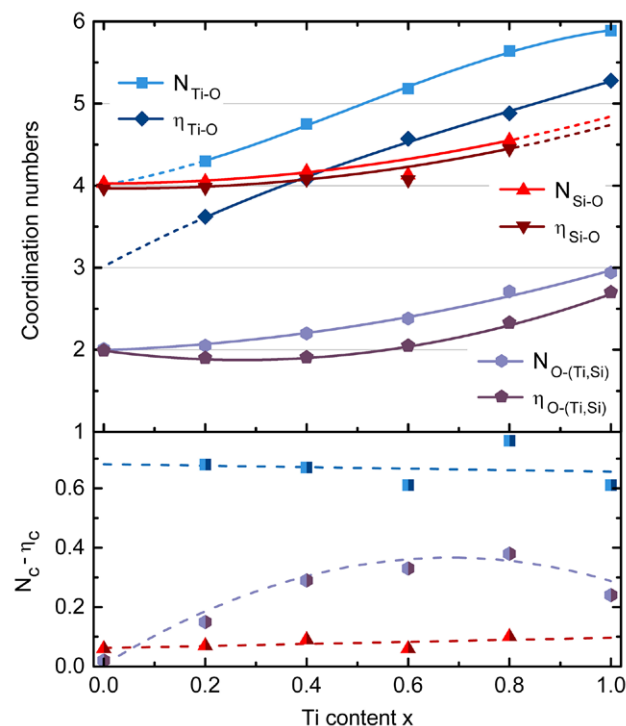


Figure 12. Upper panel: conventional (see figure 6) and effective coordination numbers N_c and η_c for the a-Ti_xSi_{1-x}O₂ VASP geometries. Solid lines refer to polynomial data fits (third order for Ti–O and second order for Si–O as well as O–Ti/Si coordination numbers). Dashed lines indicate data extrapolation towards the binary oxide limits. Lower panel: difference $N_{\text{Ti-O}} - \eta_{\text{Ti-O}}$ between the conventional and local coordination numbers. Dashed lines represent linear (Ti–O and Si–O coordination) and second order polynomial (O–Ti/Si coordination) fits.

The differences between the conventional and effective coordination numbers of each chemical component of the a-Ti_xSi_{1-x}O₂ hybrid oxides (VASP geometries) are illustrated in figure 12 over the entire composition range. Obviously, all chemical components show notable deviations from the conventional coordination numbers. The smallest coordination number differences are observed for the Si ion. The difference of $N_{\text{Si-O}} - \eta_{\text{Si-O}}$ between conventional and effective coordination numbers remains nearly constant over the entire composition range with variations between 0.06 and 0.1 (see lower panel of figure 12). In consideration of the rather stiff SiO₄ building blocks this is a notable change that reflects distortions of the Si coordination tetrahedra. Also in the case of the Ti ions, the difference between both coordination numbers remains almost constant over the entire composition range. Nevertheless, the degree of disorder in the O coordination environment of the Ti ion is much stronger as observed for the Si ion with difference variations between 0.61 and 0.76. Considering a difference of $N_{\text{Ti-O}} - \eta_{\text{Ti-O}} = 0.29$ in c-TiO₂ brookite, these values indicate substantial deviations from crystalline order in the binary and ternary amorphous oxides. This larger degree of disorder in the Ti coordination environment is in agreement with the larger number of possible coordination-polyhedra shapes that was observed above. While the effective coordination number of Ti as well as Si ions shows almost constant deviations from

the conventional coordination numbers, the coordination-number difference shows a more complex dependence on the alloy composition for O ions. The value of $N_{O-(Ti,Si)} - \eta_{O-(Ti,Si)}$ increases up to a composition parameter of $x = 0.8$ but with different slopes below $x = 0.4$ and between $x = 0.4$ and $x = 0.8$. For pure a-TiO₂ the data indicate a decrease of the coordination number difference compared to the Ti rich alloys. In general, the non-linear difference between conventional and effective coordination numbers arise from the mixing of short Si–O and long Ti–O bonds within particular coordination units. The coexistence of Si–O and Ti–O bonds necessarily increase the bond length deviations from the average coordination-polyhedron bond length. Considering the fact that the local coordination environment of the O ions reflects the linking between the various coordination polyhedra, the degree of disorder of the O ion coordination environment additionally represents *partial* information on the degree of disorder in the amorphous network while in the case of the Ti and Si ions the disorder *within* a particular coordination polyhedron is reflected. In fact, the information on the disorder is only given partially since a large part of the information on the network topology is contained in the bond angles of bridging O ions, Ti/Si–O–Ti/Si bond angles, respectively, rather than in the bond lengths variations. Nevertheless, some qualitative structure-formation trends are observable. While the effective coordination numbers show a constant degree of disorder within the cation-coordination polyhedra, smaller fractions of Ti ions act as a network modifying species. The differences in the coordination numbers indicate a notable influence of Ti ions on the mid-range ordered network topology of Si rich alloys up to a Ti concentrations of ~ 40 mol%. In the mid and high Ti content alloy-composition range between $x = 0.4$ and $x = 0.8$, the amorphous network shows smaller adaptations to a larger content of TiO₂ units indicating the successive transition towards a short-range ordered alloy. Finally, the formation of a pure a-TiO₂ phase slightly reduces the amount of disorder in the amorphous framework due to the absence of contributions from compositional disorder.

To put it in different words, the disorder of the amorphous network increases with increasing Ti content. A dominant but almost constant fraction of disorder is carried by the local Ti ion coordination environments and to a much smaller extend by the local Si ion coordination environments. Further disorder effects are projected onto the spatial arrangement of the coordination polyhedra, a.k.a. the amorphous network itself.

Further details on the effective coordination numbers are provided by the effective coordination-number distributions of the a-Ti_xSi_{1-x}O₂ VASP geometries illustrated in figure 13. The effective Ti ion coordination numbers indicate a complex spectrum of coordination states with several major and secondary features. Nevertheless, the basic characteristics of the distributions of conventional coordination numbers (see figure 7) are maintained. At low Ti content, large part of the Ti ions reside in distorted tetrahedral units. However, the broadening of this peak indicates notable disorder in the fourfold coordinated Ti units. The most notable differences to the conventional coordination numbers, that indicate TiO₄ units as the lowest coordination state, are effective coordination numbers

between 2.0 and 3.0. Obviously the bond length variations of some tetrahedral TiO₄ units seem to be of crucial size for the calculation of effective coordination numbers. At higher Ti contents, the effective coordination numbers reflect the distribution of conventional (local) coordination numbers. The fundamental transition from a predominant distorted fourfold coordination state at low Ti content to a broad a-TiO₂ coordination spectrum with significant contributions from distorted TiO₅ and TiO₆ as well as minor contributions from distorted under-coordinated TiO₄ units and over-coordinated TiO₇ and TiO₈ building blocks is also characteristic to the effective Ti coordination numbers. Thereby, the strong influence of atomic disorder is reflected by an increasing undervaluation of the corresponding conventional local coordination numbers. In the case of the Si ion, the SiO₄ coordination tetrahedra are clearly visible by the sharp peak close to the ideal tetrahedron coordination state of four. The heights of this peak remains almost constant over large part of the composition range and pronounced changes in the Si coordination environment do not occur until an alloy composition containing 80 mol% of Ti ions. At this composition, two distinct high coordination peaks at ~ 4.7 and ~ 5.8 represent distorted SiO₅ and SiO₆ coordination polyhedra. In agreement with the conventional local coordination numbers, weak indications of these high coordination states are already present from a composition parameter of $x = 0.4$ for distorted SiO₆ building blocks and throughout the entire composition range for distorted SiO₅ units. The effective coordination numbers of O ions nicely demonstrate the transition from a predominant twofold coordination in pure a-SiO₂ to a preferred threefold coordination type in pure a-TiO₂. The broader coordination number band between 2.5 and 3.0 for a-TiO₂ indicates notable disorder effects for threefold coordinated O ions. One interesting feature of the effective O ion coordination-number distributions is the occurrence of a low coordination-state tail in the ternary oxides that is not present in the pure amorphous phases of SiO₂ and TiO₂. This property agrees with the observed larger difference between conventional and effective O ion coordination numbers observed for the oxide alloys above (see figure 12). In the conventional coordination number analysis these coordination states are partially reflected by onefold coordinated O_{1c} ions in the low Ti content ternary oxides.

In order to compare further results from the local coordination-number analysis with the corresponding quantities from the effective coordination-number analysis, figure 14 illustrates the average effective coordination numbers for each conventional local coordination state in the a-Ti_xSi_{1-x}O₂ VASP geometries. The (average) effective coordination numbers of twofold coordinated O_{2c} ions of $\eta_{O_{2c}}[0.0] = 1.9787$ and $\eta_{O_{2c}}[1.0] = 1.9512$ in pure a-SiO₂ and a-TiO₂ indicate some degree of bond-length disorder in the binary amorphous oxides. In the amorphous alloys, the effective O_{2c} coordination numbers decrease depending on the cation ratio in the system. At composition parameters of $x = 0.2$ and $x = 0.8$, $\eta_{O_{2c}}$ reduces to ~ 1.893 . $\eta_{O_{2c}}$ reduces to ~ 1.867 for composition parameters of $x = 0.4$ and $x = 0.6$. Similar to the O_{2c} ions, threefold coordinated O_{3c} ions show a small degree of disorder in a-SiO₂ ($\eta_{O_{3c}}[0.0] = 2.9289$), a notable degree of disorder in a-TiO₂ ($\eta_{O_{3c}}[1.0] = 2.6965$) and strong disorder influences in

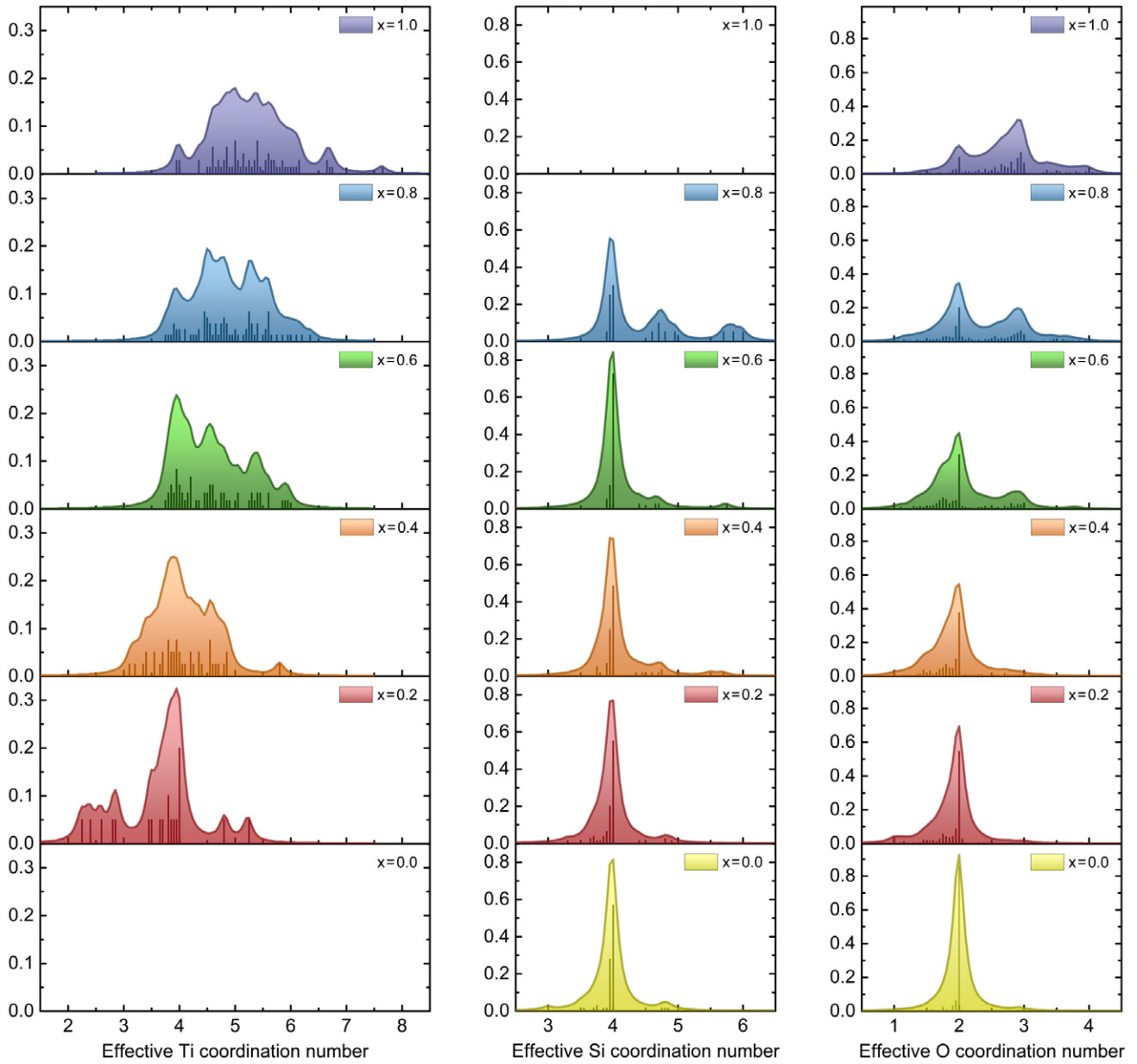


Figure 13. Effective coordination-number distributions of the various chemical components in the $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ VASP geometries. Illustrated are a discrete line spectrum as well as a continuous spectrum obtained by a gaussian type line broadening.

the alloys. The effective O_{3c} coordination number is reduced to its minimal value of $\eta_{\text{O}_{3c}}[0.4] = 2.1215$ at a composition parameter of $x = 0.4$. The effective O_{4c} coordination number varies between $\eta_{\text{O}_{4c}}[0.8] = 3.1671$ and $\eta_{\text{O}_{4c}}[0.6] = 3.7781$ indicating a notably distorted coordination environment. Compared to this strong variations in the coordination environment of O_{4c} ions, the average effective Si coordination numbers of $\sim 3.95 \pm 0.02$ for the dominant fourfold coordination state indicate just minimal distortions of the SiO_4 coordination units. In contrast, fivefold coordinated Si_{5c} and sixfold coordinated Si_{6c} ions show a notable degree of disorder. The effective Si_{5c} coordination number in pure $a\text{-SiO}_2$ of $\eta_{\text{Si}_{5c}}[0.0] = 4.8120$ decreases with increasing Ti content to $\eta_{\text{Si}_{5c}}[0.6] = 4.5880$. However, for the highest SiO_5 coordination polyhedra fraction of 25% at a composition parameter of $x = 0.8$ the effective coordination number increases to $\eta_{\text{Si}_{5c}}[0.6] = 4.7511$. Sixfold coordinated Si_{6c} ions show a quite

clear trend in the average effective coordination numbers. The $\sim 3\%$ of SiO_6 coordination polyhedra are strongly distorted in the mid-composition range ($x = 0.4$) as characterized by an average effective coordination of $\eta_{\text{Si}_{6c}}[0.4] = 5.5858$. A higher alloy density allows the octahedral SiO_6 units to reduce their strain deformations by relaxing to a shape with an effective coordination number of $\eta_{\text{Si}_{6c}}[0.8] = 5.8452$ that is actually closer to an idealized octahedral symmetry than the TiO_6 building blocks of the $c\text{-TiO}_2$ brookite phase (see figure 3). Altogether, it seems always possible to deduce the corresponding conventional local coordination state from the effective (average) Si coordination numbers. In some exceptional cases, this actually changes for the effective coordination number analysis of the Ti coordination environment. The average effective coordination number of fivefold coordinated Ti_{5c} ions of $\eta_{\text{Ti}_{5c}}[0.2] = 3.7074$ does not necessarily imply a locally fivefold coordinated Ti ion and points

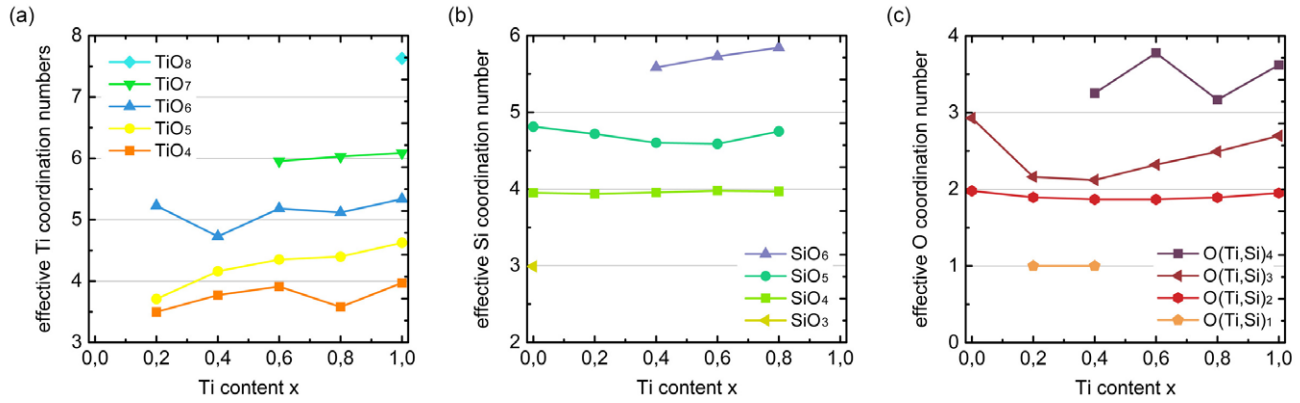


Figure 14. Average effective coordination numbers of all conventional cation and anion coordination-states (see figure 5) occurring in the $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ VASP geometries.

Table 5. Average effective coordination numbers of all coordination-polyhedra types (see figure 5) occurring in the $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ VASP geometries.

Coordination	Ion	Polyhedron	Effective coordination number					
			$x = 0.0$	$x = 0.2$	$x = 0.4$	$x = 0.6$	$x = 0.8$	$x = 1.0$
$n_c = 1$	O	[SB-1]-[Ti]		1.0000	1.0000			
$n_c = 2$	O	[HOA-2]-[Ti]		1.8006	1.8850	1.9186	1.9462	1.9512
		[HOL-2]-[Ti]				1.9290		
		[HOA-2]-[Si]	1.9784	1.9853	1.9902	1.9957	1.9886	
		[HOL-2]-[Si]	1.9936	1.9954				
		[HEA-2]		1.6830	1.6982	1.7192	1.7216	
		[HEL-2]		1.4992				
$n_c = 3$	Si	[TP-3]	2.9910					
	O	[TP-3]	2.9289	2.0607	2.0925	2.2821	2.5298	2.7411
		[TPY-3]		2.2033	2.1983	2.3108	2.4935	2.6791
		[TS-3]		2.0905	2.0905	2.5269	2.1872	2.8283
$n_c = 4$	Ti	[TTBPY-4]		2.8225	3.9174			3.9771
		[T-4]		3.4564	3.8314	3.9197	3.9364	3.9619
		[SS-4]		3.8610	3.5773	3.8689	3.3990	
	Si	[TTBPY-4]	3.4981					
		[T-4]	3.9587	3.9367	3.9565	3.9781	3.9649	
		[SS-4]	3.9434				3.9869	
$n_c = 5$	O	[T-4]					3.2215	3.6834
		[SS-4]			3.2531	3.7781	3.0857	3.5339
	Ti	[SPY-5]		3.0361	4.3998	4.3034	4.3825	4.6701
		[TBPY-5]		4.3787	3.9806	4.3727	4.4146	4.5531
		[SPY-5]	4.8071	4.6970	4.6630	4.6428	4.8344	
$n_c = 6$	Si	[TBPY-5]	4.8144	4.7815	4.4839	4.5606	4.6956	
		[PPY-6]						5.0139
		[O-6]		5.2284	5.7988	5.1275	5.0390	5.3283
	Ti	[TPR-6]			4.7070	5.5266	5.3068	5.3139
		[TPBPY-6]			3.7010	5.0681	5.5476	5.4598
		[O-6]			5.5858	5.7292	5.8452	
$n_c = 7$	Si	[PBPY-7]					6.0286	6.0722
	Ti	[MO-7]						6.1656
		[MTPR]				5.9560		
$n_c = 8$	Ti	[TD-8]						7.6298

towards strongly distorted TiO_5 coordination units in the low density $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ hybrid oxides. For higher Ti content and, with it, a notably higher fraction of TiO_5 coordination polyhedra in the alloy, the effective TiO_5 coordination number increases to $\eta_{\text{TiSc}}[0.4] = 4.1603$, still indicating strongly distorted TiO_5 units. Further increase of the Ti content successively raises the effective coordination to $\eta_{\text{TiSc}}[1.0] = 4.6246$ in pure $a\text{-TiO}_2$. Less distinct trends are observed for the effective coordination numbers of fourfold coordinated Ti_{4c} ions and sixfold coordinated Ti_{6c} ions. The average effective Ti_{4c} coordination numbers show strong oscillations between $\eta_{\text{Ti}_{4c}}[0.2] = 3.4951$ and $\eta_{\text{Ti}_{4c}}[1.0] = 3.9695$

. With exception of a composition parameter of $x = 0.4$, TiO_6 coordination polyhedra exhibit an average effective coordination number of $\sim 5.23 \pm 0.11$. For $x = 0.4$ a small effective coordination number of $\eta_{\text{Ti}_{6c}}[0.4] = 4.7285$ is obtained. This minimum directly correlates with the bond length maximum as well as bond angle minimum of TiO_6 units that is observed before the formation of higher coordinated TiO_n coordination polyhedra (see figures 10(a) and 10(b)). The average effective coordination number of over-coordinated Ti_{7c} ions remains close to six and shows a marginal increase from $\eta_{\text{Ti}_{7c}}[0.6] = 5.9560$ to $\eta_{\text{Ti}_{7c}}[0.6] = 6.0877$. These strong deviations from the

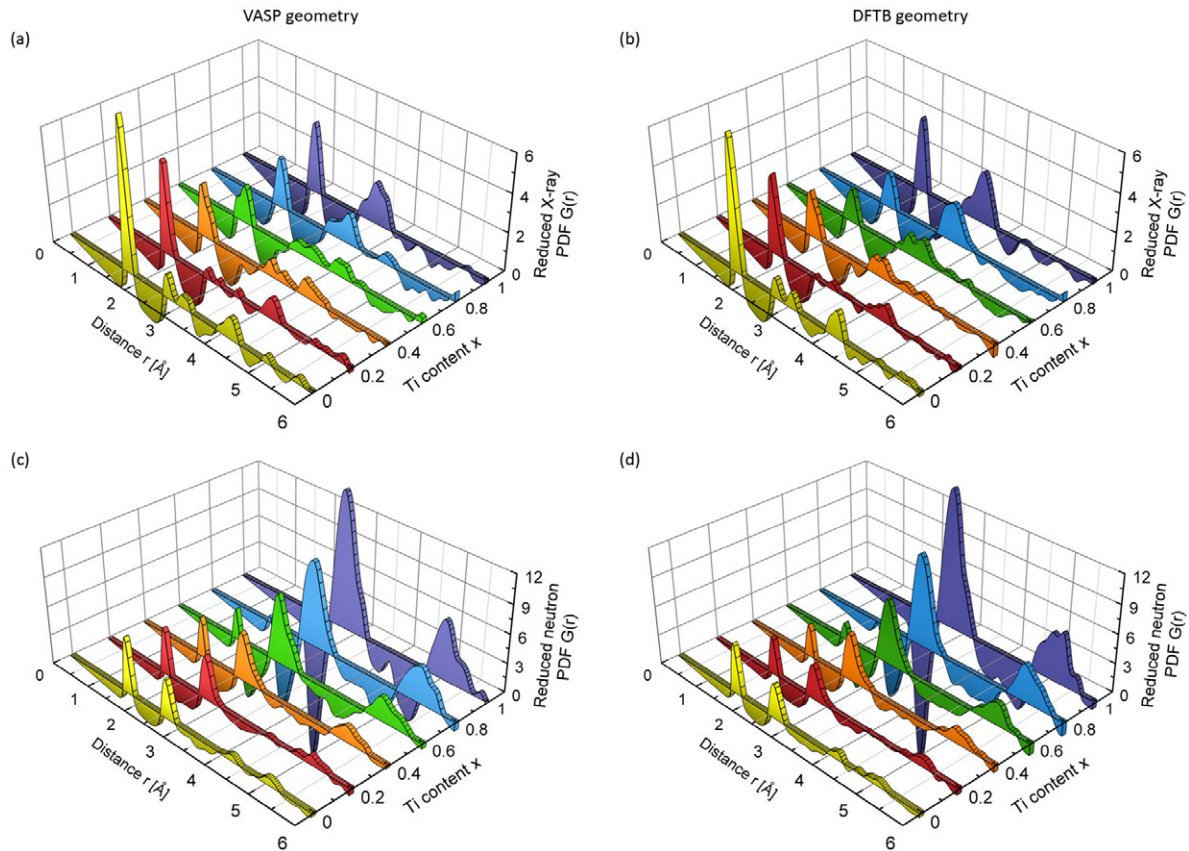


Figure 15. Reduced total x-ray (upper panels) and neutron (lower panels) pair distribution functions $G(r)$ for the $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ VASP (left) and DFTB (right) geometries.

conventional local coordination state indicate a strongly disordered coordination environment in TiO_7 coordination polyhedra. In contrast, smaller differences to the conventional coordination state are found by an average effective coordination number of $\eta_{\text{Ti}_{8c}}[1.0] = 7.6298$ of eightfold coordinated Ti_{8c} ions in pure $a\text{-TiO}_2$.

The multi-peak structure of several peaks in the distribution of effective coordination numbers in figure 13 suggests that effective coordination numbers might also be useful to estimate the number of various coordination-polyhedra geometry types that might exist for a given coordination state. In order to identify specific coordination polyhedra solely by their effective coordination number, the average effective coordination numbers for each coordination-polyhedra type, listed in figure 5, are summarized in table 5. With a few exceptions, it does not seem possible to find a unique mapping of coordination-polyhedra geometries onto the effective coordination numbers that applies to the entire composition range. For example, there seems to be a change in the effective coordination-number ratio for planar and pyramidal $\text{O}(\text{Ti},\text{Si})_3$ units. In Ti rich alloys ($x \geq 0.8$) as well as pure $a\text{-TiO}_2$, the planar $\text{O}(\text{Ti},\text{Si})_3$ units and $\text{O}(\text{Ti})_3$ units, respectively, exhibit larger effective coordination numbers than their pyramidal distorted counterpart. Lower Ti concentrations in the amorphous alloy result in a higher effective coordination number for [TPY-3]-type $\text{O}(\text{Ti},\text{Si})_3$ units. Based on the relatively small number of O_{3c} ions in the Si rich alloys, it is difficult to estimate if this behavior describes a basic trend or is the artifact of the partially small data basis for

evaluation of the effective coordination numbers. Observable trends are actually limited to the lower coordination states. The effective coordination numbers of twofold coordinated O_{2c} ions are highest ($\eta_{\text{OSi}_2} \leq 1.98$) for homopolar OSi_2 units, slightly smaller for homopolar OTi_2 units ($1.80 \leq \eta_{\text{OTi}_2} \leq 1.95$), and notably smaller for heteropolar $\text{O}(\text{Ti},\text{Si})_2$ coordination units ($1.50 \leq \eta_{\text{O}(\text{Ti},\text{Si})_2} \leq 1.72$). The effective coordination numbers of [T-4]-type coordination polyhedra clearly increase with the Ti content from $\eta_{\text{TiO}_4[\text{T}-4]}[0.2] = 3.4564$ in $a\text{-Ti}_{0.2}\text{Si}_{0.8}\text{O}_2$ to $\eta_{\text{TiO}_4[\text{T}-4]}[1.0] = 3.9619$ in pure $a\text{-TiO}_2$. For higher coordination states it becomes increasingly difficult to identify trends for a specific coordination-polyhedron geometry type.

In general, it seems difficult to extract clear trends from the effective coordination numbers of individual coordination-polyhedra types. This suggests that a purely exponential weighting function, defined according to equation 11, might not be an ideal choice to characterize the atomic short-range order in an amorphous solid. Especially, the more deformable coordination environment of the Ti ions shows strong variations in the effective coordination state. This shortcoming seems to be related to the extreme sensitivity of the weighting function against bond-length variations of distorted coordination polyhedra in the amorphous oxides. In order to extract well converged trends from an effective coordination number analysis it might be necessary to increase the analyzed data basis notably by increasing the structure models and/or performing averages over a large number of equilibrium MD configurations at fixed temperature. However, due to the general

density dependence of the coordination-polyhedra shapes, a unique identification of a specific coordination-polyhedron geometry-type by a single-number quantity, as the effective coordination number, might be out of reach even with an optimally chosen weighting function.

In sum, both the conventional and the effective coordination numbers provide fundamental information to characterize the short-range order in amorphous oxides. While an in depth coordination-polyhedra analysis remains an elaborate task and the conventional coordination numbers do not provide a measure for the degree of disorder within different coordination polyhedra, the effective coordination-number approach serves both purposes. Effective coordination numbers, as used in this study, are suited to determine the local coordination state of ions in the investigated amorphous hybrid oxides and to obtain information on the degree of disorder within the first coordination shell. Indeed, the possible existence of various geometry types for a particular coordination state is clearly indicated, whereas, a unique identification of the different polyhedra types at various alloy-mass densities remains ambiguous.

4.6. Radial distribution functions

The (radial) pair distribution functions are the most common tool to investigate the atomic structure of amorphous solids. Figure 15 illustrates the total reduced x-ray as well as neutron pair distribution functions for our generated VASP and DFTB structure models of $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ hybrid oxides. In case of the $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ VASP geometries (see figure 15(a)), the first x-ray pair correlation peak of Ti–O pairs and Si–O pairs nicely reflect the continuous transition between the pure binary oxides. The Si rich hybrid oxides show a sharp Si–O correlation peak around ~ 1.6 Å that decays linearly with the increasing Ti content. Analog, the sharp Ti–O correlation peak around ~ 1.9 Å of Ti rich oxide alloys decays linearly with the decreasing Ti content. The difference in the average Si–O and Ti–O correlation length allows the differentiation of both pair correlations in the mid composition range. Both the $a\text{-Ti}_{0.4}\text{Si}_{0.6}\text{O}_2$ and $a\text{-Ti}_{0.6}\text{Si}_{0.4}\text{O}_2$ VASP geometries show indications of this double peak substructure. Our calculated Si–O as well as Ti–O pair correlation length of ~ 1.6 Å and ~ 1.9 Å are in excellent agreement with experimental data. Wallidge *et al* [166] reported x-ray correlation lengths, and virtually identical neutron-correlation lengths, of 1.60 Å and 1.93 Å for sol-gel formed amorphous $(\text{TiO}_2)_x(\text{SiO}_2)_{1-x}$ samples (calcined to 250 °C) at a composition parameter of $x = 0.41$. Almost identical neutron correlation lengths for sol-gel derived $(\text{TiO}_2)_x(\text{SiO}_2)_{1-x}$ glasses have been reported by Rigden *et al* [72] as well as Pickup *et al* [167]. The clearly visible correlation features in the Ti rich composition range in the bond-length region between ~ 3.0 Å and ~ 4.0 Å belong to homonuclear correlations between Ti–Ti pairs. The characteristic two-peak substructure of this correlation peak can be assigned to different Ti–Ti distances of Ti ions in either corner-linked or edge-linked TiO_n coordination polyhedra. It proves to be quite difficult to identify the characteristic O–O correlation features in the total $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ pair-correlation

functions, that should be observable below ~ 3.0 Å. Similarly, the homonuclear Si–Si and heteronuclear Ti–Si pair correlations can hardly be separated from the low correlation lengths Ti–Ti pair correlations in the total correlation functions.

The reduced neutron pair distribution functions in figures 15(c) and (d) look qualitatively extremely different from the x-ray pair distribution functions. These differences are most pronounced in the case of the Ti rich oxide alloys as well as pure $a\text{-TiO}_2$ and a direct consequence of the notably negative neutron-scattering length of Ti ions. Therefore, Ti–O and Ti–Ti pair correlations are characterized by negative features in the distribution function and, thus, easily distinguishable from purely Si and O related correlations. Overall, the neutron pair distribution functions show three characteristic positive correlation features below a correlation length of 6.0 Å. The low distance feature around ~ 1.6 Å clearly arises from Si–O correlations and decays with increasing Ti content. In contrast to the total x-ray distribution functions, the homonuclear O–O pair-correlation peak appears prominently in the neutron pair distribution functions. The O–O pair-correlation peaks are located around ~ 2.7 Å and become the dominant positive correlation peaks in the Ti rich alloys and pure $a\text{-TiO}_2$. The long distance positive feature around 5 Å represents second coordination-shell pair correlations of O ions. The dominant negative feature of the reduced neutron pair-distribution functions around ~ 2.0 Å is associated to first coordination shell Ti–O pair correlations, as indicated by the strong increase with the Ti content in the amorphous alloy. Compared to the x-ray pair distribution functions, the neutron pair distribution functions strongly support the differentiation of the closely spaced Ti–O and Si–O pair correlations in the mid-composition range. The negative feature around ~ 4.2 Å can be attributed to second coordination shell Ti–O pair correlations. In general, it is quite difficult to identify the various contributions of homonuclear and heteronuclear cation–cation pair correlations in the distance range between ~ 3.0 Å and ~ 4.0 Å in the total neutron pair distribution functions.

The direct comparison of the total x-ray pair-correlation functions for the VASP and DFTB geometries indicates quite similar ordering characteristics for both numerical approaches. Merely, the separation between Ti–O and Si–O pair correlations is less distinct in the DFTB $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ geometries, which is best illustrated for the $a\text{-Ti}_{0.6}\text{Si}_{0.4}\text{O}_2$ alloy. Similar to the x-ray distribution functions, the neutron pair distribution functions of the VASP and DFTB geometries show qualitatively identical ordering characteristics. Slight differences seem to be present for the higher-order pair correlations in the Ti rich alloys.

Altogether, the total pair-correlation functions do not, per se, allow the identification of structure correlations between arbitrary pairs of chemical elements. Most problematic, short-range order differences within the first correlation shell, as indicated by the local coordination number differences for different composition parameters and between the VASP and DFTB geometries (see figure 7), are not resolved, or rather hidden in the total pair correlation functions.

Nevertheless, further insights into the atomic structure are provided by the partial reduced (x-ray) pair correlation functions $G_{\alpha\beta}(r)$ illustrated in figure 16 for the $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$

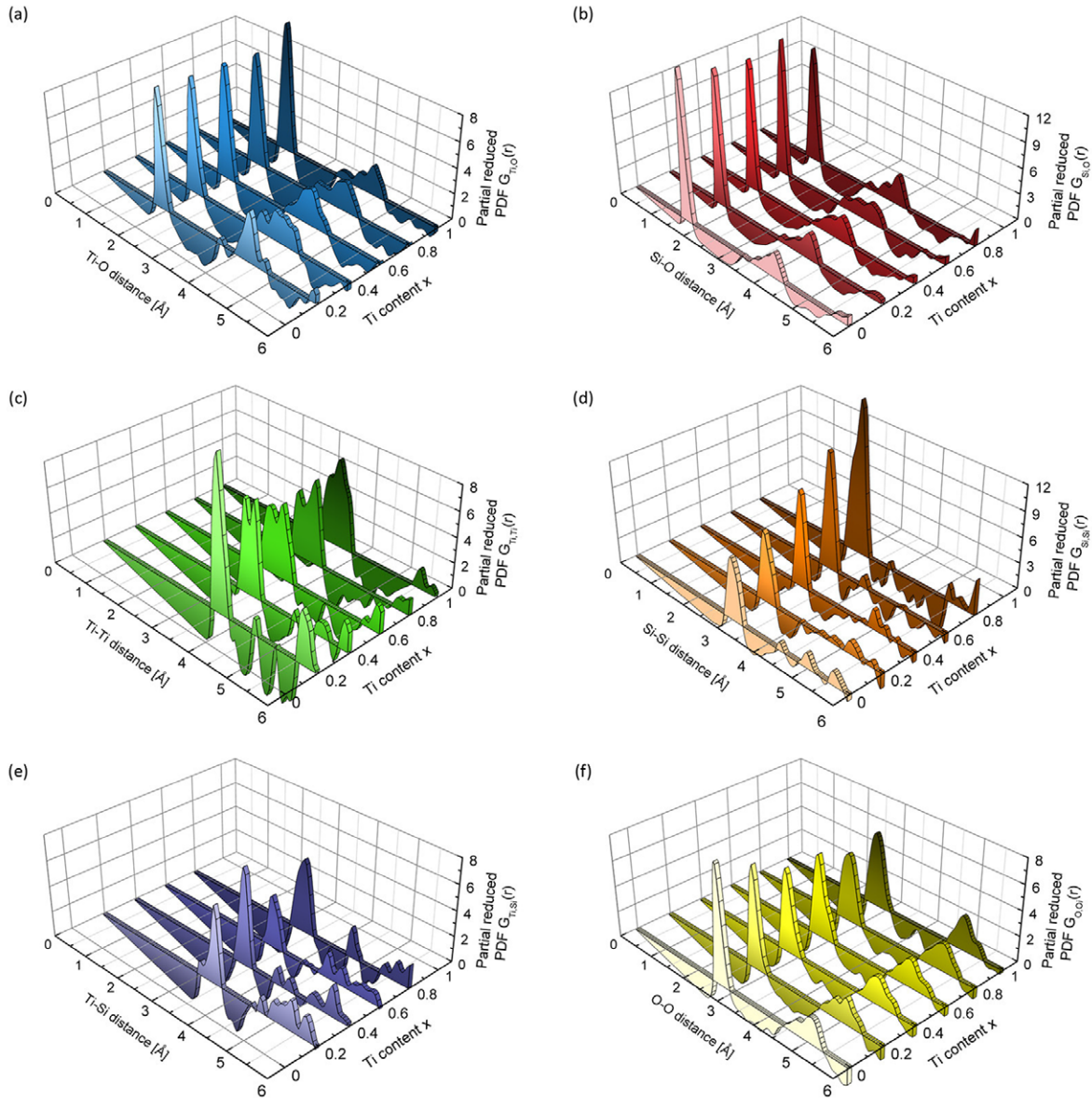


Figure 16. Reduced partial x-ray pair distribution functions $G_{\alpha\beta}(r)$ for the $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ VASP geometries.

VASP geometries. The first Ti–O pair-correlation peak in figure 16(a) shows some minor position dependence on the alloy composition. The central-peak position increases continuously from ~ 1.9 Å in $a\text{-Ti}_{0.2}\text{Si}_{0.8}\text{O}_2$ to ~ 2.0 Å in pure $a\text{-TiO}_2$. Since by trend, the individual coordination polyhedra show a decreasing average bond length with increasing alloy density (see figure 10), such an increase directly reflects the occurrence of increasingly higher coordinated TiO_n building blocks. Compared to the average Ti–O coordination-polyhedra bond length of 1.860 Å in table 3, the $a\text{-Ti}_{0.2}\text{Si}_{0.8}\text{O}_2$ Ti–O correlation peak position around ~ 1.9 Å indicates a dominant fourfold Ti coordination state with minor contributions from higher coordination states. This observation nicely agrees with the 75%, 20%, and 5% of Ti_{4c} , Ti_{5c} , and Ti_{6c} ions observed in the (conventional) coordination-polyhedra analysis above (see figure 7(a) and table 1). Due to an average TiO_6 coordination-polyhedra bond length of 1.993 Å, the Ti–O correlation-peak position around ~ 2.0 Å indicates that, at least by majority

(54.2%), $a\text{-TiO}_2$ is built from octahedral TiO_6 building blocks. Since the average Ti–O bond length of under-coordinated TiO_4 and TiO_5 building blocks are below the value of sixfold coordinated crystal-like coordination units and above this value for over-coordinated TiO_7 and TiO_8 building blocks, coordination defects in $a\text{-TiO}_2$ have to be a mixture of both defect types. In fact, our $a\text{-TiO}_2$ VASP structure model shows 27.8% of under-coordinated Ti ions and 18.1% of over-coordinated Ti ions (see table 1). Ti–O pair correlation of the second coordination shell are observed by a correlation feature located at a pair distances around ~ 4.3 Å. With increasing mass density the width of this correlation peak is increasingly broadened on the small correlation-length edge.

The first Si–O pair-correlation peak in figure 16(b) shows basically identical structure-correlation characteristics, just merely shifted to smaller correlation distances. The center of the first correlation-shell peak shifts from ~ 1.6 Å in pure $a\text{-SiO}_2$ to ~ 1.7 Å in $a\text{-Ti}_{0.8}\text{Si}_{0.2}\text{O}_2$. A correlation length around

~ 1.6 Å is an indication of predominantly fourfold coordinated Si ions in a-SiO₂ since the average bond length of SiO₄ coordination polyhedra is 1.639 ± 0.002 Å in the entire composition range (see table 2). Again, the fact that the first correlation peak shifts with increasing mass density, clearly indicates an increase in the fraction of over-coordinated SiO_{*n*} units in the Ti rich alloys since the average polyhedra-bond lengths remain only constant (SiO₄) or decrease (SiO₅ and SiO₆, see figure 10(b)) with increasing alloy-mass density. In contrast to the Ti–O correlation peak, the position shift does not depend linear on the Ti content. A notable peak shift is not notable until a composition parameter of $x = 0.8$ is reached. This observation is in close agreement with the observed fraction of SiO₄ coordination polyhedra which remains roughly constant at $90 \pm 4\%$ up to a composition parameter of $x = 0.6$ (see figure 7(c) and table 1). In the a-Ti_{0.8}Si_{0.2}O₂ alloy the fraction of tetrahedral coordination units is reduced to 60.0% and the remaining 40.0% are portioned into 25.0% of SiO₅ and 15.0% of SiO₆ coordination polyhedra with average Si–O coordination-bond lengths of 1.729 Å and 1.784 Å, respectively. Si–O pair correlations of the second correlation shell are observed between ~ 3.5 Å and ~ 4.5 Å over the entire composition range.

Ti–Ti pair correlations (see figure 16(c)) are observed as a broad feature around pair distances of 3.5 Å. The Ti–Ti pair correlation peaks show a qualitative transition from a single-peak characteristic at low Ti content ($x = 0.2$) to a double-peak characteristic in the mid-composition range and additional modifications in pure a-TiO₂. This transition reflects an important ordering characteristic of the Ti–O coordination polyhedra in the a-Ti_{*x*}Si_{1–*x*}O₂ hybrid oxides. The different Ti–Ti correlation distances originate from TiO_{*n*} coordination polyhedra sharing either a common oxygen ion, a polyhedron corner/vertex respectively (e.g. see figure 2(d-7)), or two common oxygen atoms, two polyhedron vertices or a common polyhedron edge respectively (e.g. see figure 2(d-6)). In general, the Ti–Ti correlation length is longer for corner-linked coordination polyhedra than for edge-linked coordination units. For our structure models, the single-peak characteristic of the partial Ti–Ti pair correlation functions is actually limited to the low Ti content regime. The Ti–Ti pair correlation peak is located around ~ 3.6 Å in a-Ti_{0.2}Si_{0.8}O₂. At low Ti content the Ti ions are incorporated into the almost perfectly corner-linked amorphous framework of a-SiO₂ (see figure 2(a-2)). The extreme predominance of corner-linking is the results of the relatively small tetrahedral coordination units. Edge-linking would cause a small and thus, energetically unfavorable distance between the central cations. Therefore, low-coordinated TiO_{*n*} units are exclusively interconnected with each other via bridging Ti–O–Ti bonds, with a single shared O ion. From the coordination-polyhedra analysis above, it is further known that 75% of the Ti ions adopt the fourfold coordination state of the Si ions. Due to the sparse distribution, the Ti ions will more often connect to the network by sharing common oxygen atoms with the surrounding SiO₄ coordination polyhedra (see figure 3(c-5)). Similarly, also the 20% and 5% of fivefold and sixfold coordinated Ti_{5c} and Ti_{6c} ions are almost exclusively incorporated into the a-SiO₂

matrix by sharing common corners with the neighboring SiO₄ coordination polyhedra (see figures 3(c-4) and (c-2) for examples of TiO₅ and TiO₆ coordination polyhedra corner-linked to SiO₄ coordination units). All in all, the single-peak characteristic of the partial Ti–Ti pair correlation peak indicates that the amorphous network remains virtually entirely corner-linked despite the presence of Ti ions. However, in order build in the 25% of non-tetrahedrally coordinated Ti_{5c} and Ti_{6c} ions, the amorphous framework needs to adapt to the higher connectivity of these coordination units. Since the Si–O coordination environment has repeatedly proven to be rather stiff and only 5% of the Si ions increase their local coordination number to five, the amorphous network itself needs to change its mid-range order characteristics in order to incorporate the Ti_{5c} and Ti_{6c} ions as discussed below. The increase of the Ti content beyond 20 mol% inevitably leads to the splitting of the Ti–Ti pair correlations peaks into two sub-peaks. More precisely, the occurrence of an additional smaller Ti–Ti correlation-lengths feature that merges with the Ti–Ti pair-correlation peak of the corner-linked coordination polyhedra. Thereby, the central positions of the corner-linked polyhedra peaks do not change notably throughout the entire alloy-composition range indicating a qualitatively equivalent type of Ti–O–Ti bridging oxygen bonds for all corner-linked TiO_{*n*} coordination polyhedra. The additional smaller correlation-length feature is observed around ~ 3.4 Å in a-Ti_{0.4}Si_{0.6}O₂ and caused by small entities of edge-linked TiO_{*n*} coordination polyhedra. These edge-linked entities are exclusively formed by a mixture of the higher fivefold and sixfold TiO_{*n*} coordination states whose fractions in a-Ti_{0.4}Si_{0.6}O₂ increased to 55.0 % and 10.0 %, respectively. However, the size of the new atomic cluster-type conglomerates is initially limited to a few (typically three to four) TiO_{*n*} coordination polyhedra as exemplified in figure 3(d-7). Increasing the Ti content to 60 mol% on the one hand increases the number of small edge-linked atomic clusters (see figure 4(c-2)). On the other hand, existing highly coordinated edge-linked atomic conglomerates favor the aggregation of additional TiO_{*n*} coordination polyhedra (see figure 4(c-6)). In addition, the high coordination clusters can be seen as local generators of new high coordination states as indicated by the TiO₇ coordination unit in the edge-linked cluster visualized in figure 4(c-6). Sporadically, the edge-linked TiO_{*n*} conglomerates starts to form chain-like fragments. The peak width and position of the Ti–Ti pair correlations of edge-linked TiO_{*n*} coordination polyhedra strongly depends on the Ti content for $x \leq 0.6$. The central peak position shifts notably from ~ 3.4 Å in a-Ti_{0.4}Si_{0.6}O₂ to ~ 3.2 Å in a-Ti_{0.6}Si_{0.4}O₂ and remains basically constant at even higher Ti percentages. This basically indicates that the TiO_{*n*} coordination polyhedra start to form well defined a-TiO₂ phases in all Ti rich a-Ti_{*x*}Si_{1–*x*}O₂ hybrid oxides. The smallest qualitative differences in the partial Ti–Ti pair correlation functions are observed between the amorphous 60 mol% and the 80 mol% containing oxides. Thereby, the a-Ti_{0.8}Si_{0.2}O₂ alloy shows the most distinct separation into the two sub-peaks around ~ 3.2 Å and ~ 3.6 Å. Compared to

the characteristic Ti–Ti distances in the naturally occurring c-TiO₂ phases, these correlation features closely resemble the Ti–Ti distances in long-range ordered networks of [O-6]-type TiO₆ coordination polyhedra. In c-TiO₂ rutile the Ti–Ti distance within the formed edge-linked TiO₆ polyhedra chains is 2.97 Å. These edge-linked polyhedra chains are interconnected by shared oxygen atoms and the corresponding Ti–Ti distance between Ti ions in neighboring chains is 3.61 Å. The three dimensional edge-linked octahedral coordination network of c-TiO₂ anatase shows Ti–Ti distances of 3.09 Å between all edge-linked TiO₆ coordination polyhedra. The Ti–Ti distances between TiO₆ coordination-polyhedra sharing a common oxygen atom are 3.81 Å. Since the c-TiO₂ brookite phase shows a combination of rutile and anatase features, the Ti–Ti distances of edge-linked TiO₆ polyhedra range from 2.97 Å to 3.12 Å, thus, covering the values of the higher symmetry crystal phases. Similarly, the Ti–Ti distances between Ti ions in corner-linked TiO₆ coordination polyhedra vary between 3.56 Å and 3.83 Å. In view of the highest fraction of octahedrally coordinated Ti ions among all a-Ti_xSi_{1-x}O₂ hybrid oxides of 58.8%, the a-Ti_{0.8}Si_{0.2}O₂ alloy has the strongest characteristics of a disordered octahedral TiO₂ phase. The actual distribution of edge-linked coordination units, and TiO_n coordination polyhedra in general, in a-Ti_{0.8}Si_{0.2}O₂ is quite isotropic without notable tendencies to form a fine grained mixture of larger clusters. Basically, the a-Ti_{0.8}Si_{0.2}O₂ alloy represents a low density amorphous phase of TiO₂ including fragments of the lower coordinated SiO₂ framework inside its cavities (see figure 19). In pure a-TiO₂ the sub-peaks around crystal-like Ti–Ti correlation lengths of ~3.2 Å and ~3.6 Å remain clearly visible. However, the main Ti–Ti pair-correlation sub-feature is located around ~3.5 Å and represents the typical Ti–Ti distance in corner-linked TiO₆ building-block units as visualized in figure 2(d-7), whereas, the ~3.6 Å feature seems to be related to Ti–Ti distances involving over-coordinated (n>6) TiO_n coordination polyhedra. In summary, the partial Ti–Ti pair-correlation peaks give deep insides to the incorporation characteristics of TiO_n coordination polyhedra into the disordered framework of a-SiO₂. In the Ti rich and high density a-Ti_xSi_{1-x}O₂ hybrid oxides the stepwise formation of isotropic amorphous TiO₂ phases is indicated by the formation of a characteristic double-peak distribution for Ti–Ti pair-correlation length.

The partial Si–Si pair-correlation features (see figure 16(d)) contain much less information on the amorphous oxide-ordering characteristics. The Si–Si pair correlation features are centered around ~3.0 Å in the entire alloy-composition range indicating the predominance of one single Si–O–Si bond type of corner-sharing SiO_m coordination polyhedra. Solely for a composition parameter of $x = 0.8$, notable pair correlations from higher-coordinated edge-linked SiO_m coordination units are weakly indicated by a small distance shoulder of the Si–Si pair correlation peak. A characteristic example of edge-linked SiO_m coordination polyhedra is visualized in figure 4(d-4) for a pair of SiO₅ and SiO₆ polyhedra. Nevertheless, identical pairs of edge-linked SiO_m coordination polyhedra units are likewise, but only

occasionally, present in the a-Ti_{0.4}Si_{0.6}O₂ (see figure 3(d-5)) and a-Ti_{0.6}Si_{0.4}O₂ (see figure 4(c-7)) oxide alloys.

Heteronuclear Ti–Si pair correlations functions (see figure 16(e)) show one dominant first correlation-shell feature around correlation lengths of ~3.3 Å for all mixed oxides. This value lies roughly half between the correlation lengths of homonuclear Si–Si pair correlations around ~3.0 Å and the homonuclear Ti–Ti pair correlations of corner-linked TiO_n coordination polyhedra. Thus, the observed Ti–Si pair correlation features can, most likely, be attributed to cross-linking Ti–O–Si bonds connecting corner-sharing TiO_n and SiO_m coordination polyhedra. The stronger developed pair-correlation lengths tail around ~3.0 Å at a composition parameter of $x = 0.2$ correlating with the high fraction (75.0%) of tetrahedrally coordinated Ti_{4c} ions in the a-Ti_{0.2}Si_{0.8}O₂ alloy and the formation of corner-linked TiO₄–SiO₄ pairs (see figure 3(c-5)). At higher composition parameters, the Ti–Si pair correlation functions show a broader single peak feature due to the larger number of available coordination states that allow a manifold of corner-linked TiO_n–SiO_m polyhedra pairs (e.g. see figure 4(d-7)). Finally, the partial O–O pair-correlation functions (see figure 16(f)) show a well defined first correlation-shell feature around ~2.7 Å throughout the entire alloy-composition range as well as the two binary oxides. The mass-density dependence of the O–O pair correlations is expressed by a successive broadening of the corresponding pair-correlation peak. This broadening directly originates from the transition from the twofold (98.6%) O–(Ti,Si)₂ coordination environment of pure a-SiO₂ to the predominantly threefold (68.1%) O–(Ti,Si)₃ coordination environment of pure a-TiO₂ (see figure 7(e)). Thereby, the higher O ion coordination state offers more degrees of freedom in shape and arrangement of the trigonal O(Ti,Si)₃ coordination units. Second coordination shell pair correlations are clearly visible in the distance range between ~4.5 Å and ~5.5 Å and show a similar position independence on the alloy composition.

In summary, the pair-distribution function analysis primarily allows to deduce ordering characteristics of the coordination polyhedra among themselves. Hints on extended mid-range ordering features within the amorphous hybrid oxides are given semi-indirectly in the partial pair-distribution functions. Deeper insights into the mid-range order of a-Ti_xSi_{1-x}O₂ oxide alloys require more specialized structure-analysis techniques.

4.7. Ring statistics

While we have repeatedly seen that a-TiO₂ is a material whose structure is governed by short-range order features, it is well known that a-SiO₂ is a prototypical Zachariasen glass characterized by ring-like structural-ordering features of the disordered oxide framework [100], [102–106]. As visualized in figure 17, well defined ring-like ordering features are also the fundamental structure characteristic of all tetrahedrally coordinated c-SiO₂ low-pressure phases. The most common α -quartz phase is constructed from 12 atom (see figure 17(a)) and 16 atom wide rings (see figure 17(b)) that are built by six

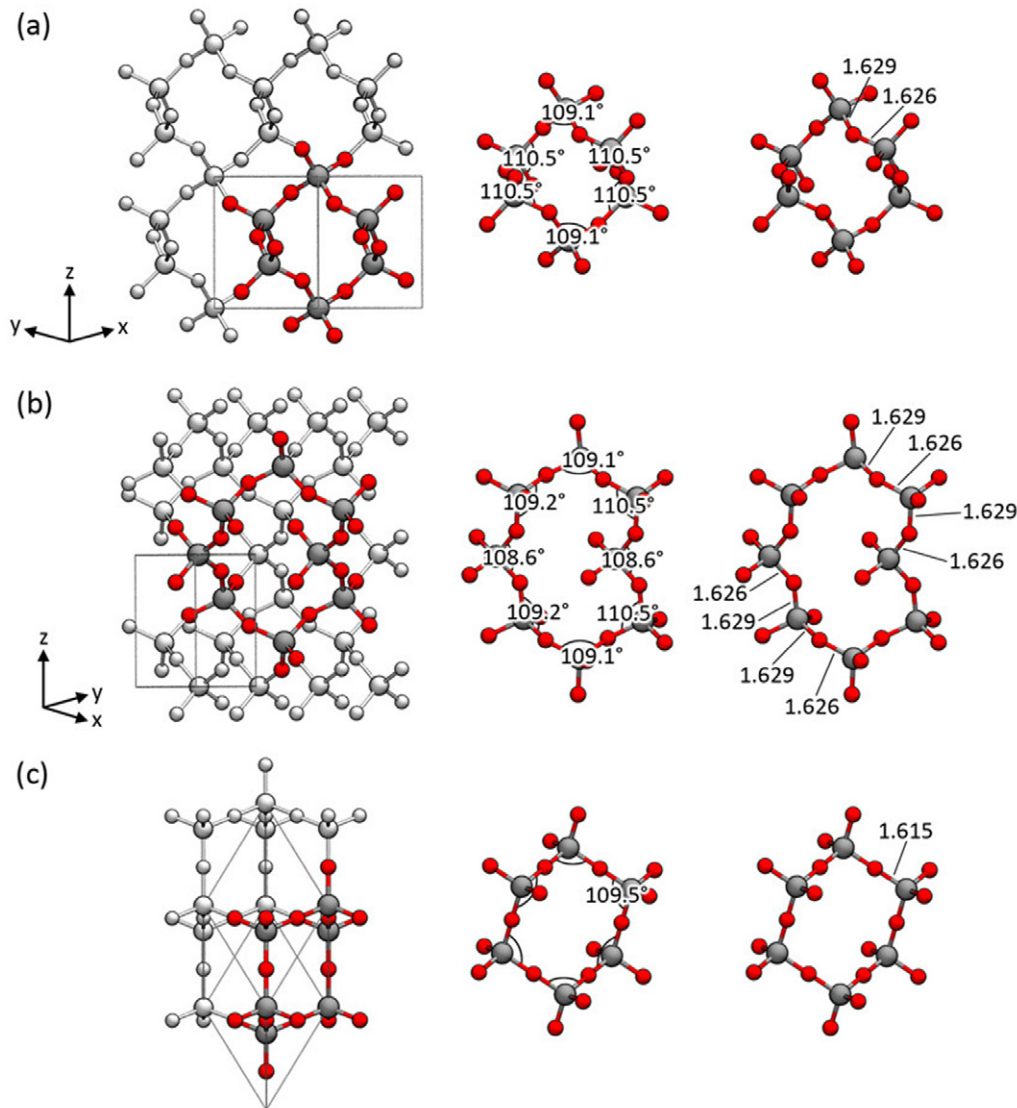


Figure 17. Illustration of ring-like structures in c-SiO₂ phases. Displayed are (a) the 12-atom (SiO₄)₆ and (b) the 16-atom (SiO₄)₈ rings of α -quartz as well as (c) the 12-atom (SiO₄)₆ rings of (Fd3m) β -cristobalite.

and eight SiO₄ coordination polyhedra, respectively. Besides, the high symmetry β -cristobalite phase of c-SiO₂ is completely composed from sixfold (SiO₄)₆ rings (see figure 17(c)). In addition, sixfold (SiO₄)₆ rings are, among others, found in the c-SiO₂ polymorphs cristobalite and moganite, while eightfold (SiO₄)₈ rings are present in keatite and coesite. Fourfold (SiO₄)₄ rings are found in the c-SiO₂ polymorph moganite and coesite as well as fivefold (SiO₄)₅ rings in the c-SiO₂ polymorph keatite and tridymite. Threefold (TiO₂)₃ rings are also found in the ultra-dense octahedrally coordinated c-SiO₂ polytypes seifertite and stishovite.

TiO₂ is commonly not characterized in terms of rings due to its higher connectivity and the resulting ordering characteristics. Nevertheless, ring statistics are easily applied to crystalline and amorphous TiO₂ materials. Two edge-linked TiO_n coordination polyhedra always form an four-atomic ring. Thus, twofold (TiO₆)₂ rings are present in all octahedral c-TiO₂ phases that contain edge-linked TiO₆ coordination polyhedra. Corner-linked TiO₆ coordination polyhedra

in c-TiO₂ rutile form six-atomic (TiO₆)₃ rings. The regular arrangement of four TiO₆ coordination polyhedra leads to the formation of eight-atomic (TiO₆)₄ rings in the rutile as well as anatase phases. Again, the c-TiO₂ brookite phase unifies structural ordering features from rutile and anatase with twofold, threefold, and fourfold (TiO₆)_n rings. Eight-atomic (TiO₆)₄ rings are also present in the columbite-type TiO₂(II) phase. In addition, c-TiO₂ phases with lower mass-densities show even more extended ring like complexes. 12-atomic (TiO₆)₆ rings are present in ramsdellite-type TiO₂(R) and hollandite-type TiO₂(H) even shows 16-atomic (TiO₆)₈ rings. Ring-like structures are also present in non-octahedrally coordinated high-pressure polymorphs of c-TiO₂. Six-atomic (TiO₇)₃ and eight-atomic (TiO₇)₄ rings are found in the sevenfold coordinated c-TiO₂ baddeleyite-type TiO₂(MI) and orthorhombic TiO₂(OI) phases.

It is a central question in the structure analysis of amorphous solids in general, and more specifically glasses, to what extent the regular mid-range order characteristics of perfectly

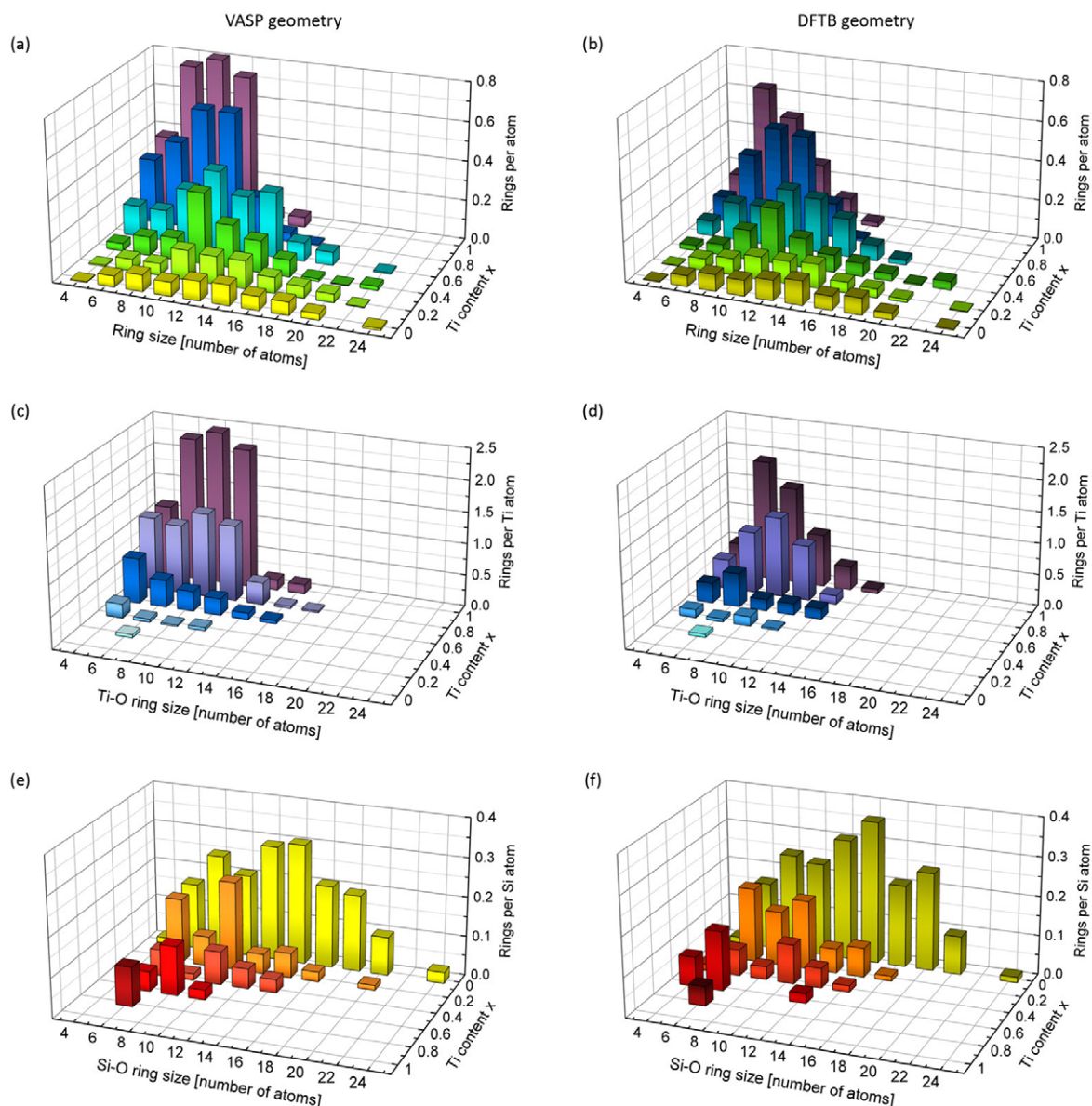


Figure 18. Total distribution of oxide type Ti/Si-O (upper panels), Ti-O (middle panels), and Si-O (lower panels) rings in the $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ VASP (left) and DFTB (right) geometries.

long-range ordered crystalline oxides are preserved, modified respectively, in the disordered material phases.

The total as well as TiO_2 -type and SiO_2 -type ring size distributions of the $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ VASP and DFTB geometries are visualized in figure 18. As discussed above, the generated amorphous structures virtually show a perfect oxide-like atomic structure free of homonuclear cation-cation or anion-anion bonds. Consequently, there are no relevant contributions from rings with an odd number of atoms. The binary amorphous oxides clearly illustrate the various connectivities of Ti and Si ions as well as the resulting short-range and mid-range order characteristics. The ring-size distribution of pure $a\text{-TiO}_2$ is centered around eight-atom rings. Almost identical contributions from six-atomic and 10-atomic rings are observed. Only very small fractions of larger 12 and 14 atom wide rings are present in the system. The sharp drop in

the number of 12-atomic and larger rings seems to be quite characteristic to the short-range ordered atomic structure of $a\text{-TiO}_2$. Compared to the ring-like features of the crystalline TiO_2 phases rutile and columbite-type $\text{TiO}_2(\text{II})$, that roughly show the same mass densities of 4.2 g cm^{-3} , mainly the existence of a large number of 10-atomic rings distinguishes the crystalline and disordered TiO_2 phases. 10-atomic rings in pure $a\text{-TiO}_2$ might be seen as a reminiscence to larger $(\text{TiO}_6)_n$ rings in low-density $c\text{-TiO}_2$ phases. The relative frequency of small four-atomic rings from edge-linked TiO_n coordination polyhedra is roughly half as much as the occurrence of the three dominating ring types. According to figure 18(c) every Ti ion participates in the formation of approximately one four-atomic ring. In other words, every TiO_n coordination polyhedron shares statistically at least one common edge with another TiO_n coordination polyhedron. Moreover, the

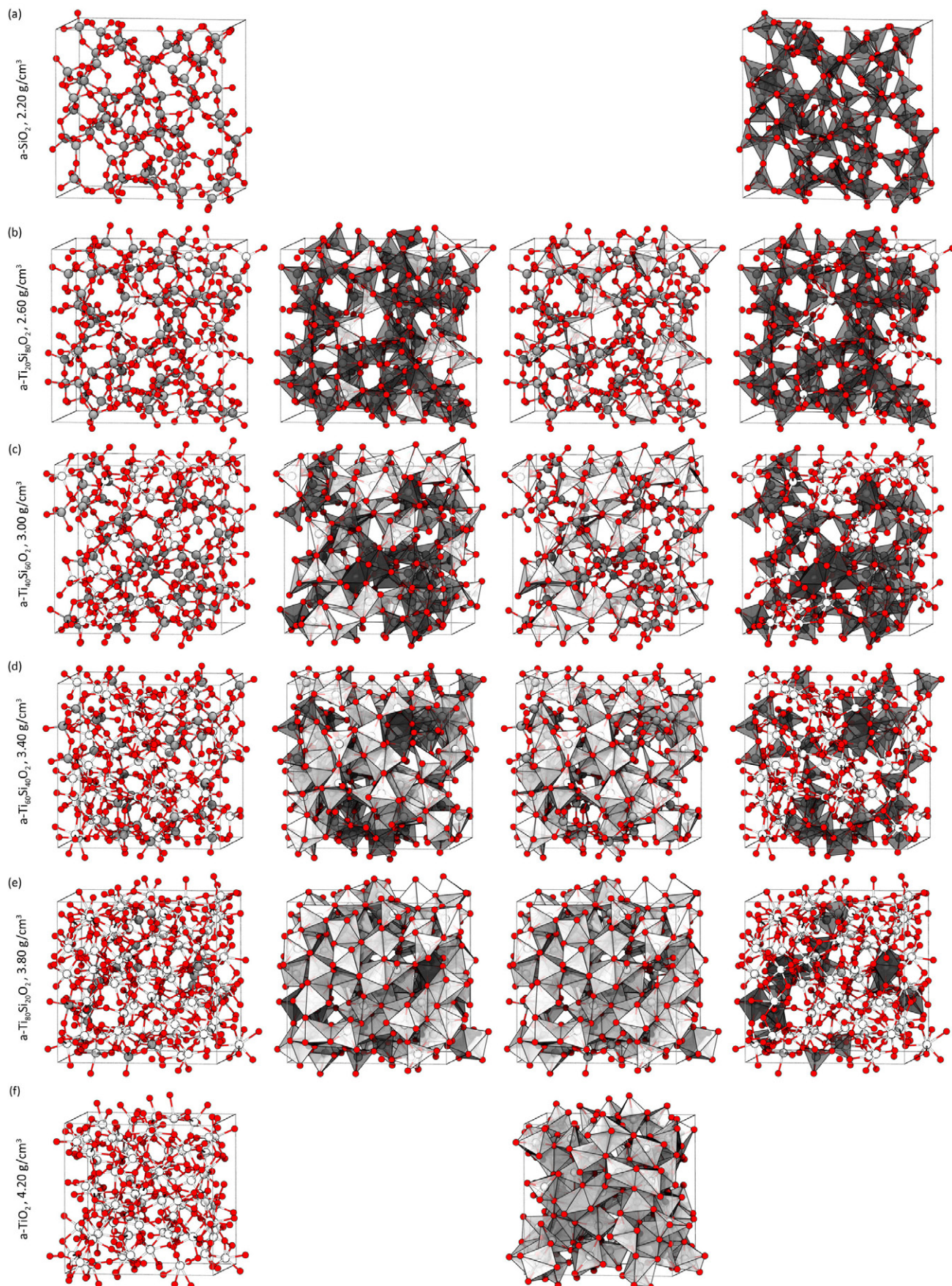


Figure 19. Ball and stick as well as coordination polyhedra representation (Ti: white, Si: dark gray and O: red) of the $a\text{-Ti}_x\text{Si}_{1-x}\text{O}_2$ VASP geometries.

statistics suggest that every Ti ion, on average, contributes equally to the formation of two six-atomic, eight-atomic, and 10-atomic TiO_2 rings.

In contrast to the ring-size distribution of pure a- TiO_2 , that remains quite similar to the ring sizes observed in the crystal phases, the ring-size distribution of pure a- SiO_2 shows stronger deviations from the characteristic ring sizes in c- SiO_2 phases. While the tetrahedrally coordinated c- SiO_2 phases, including very low density phases, typically show 8, 10, 12 and 16 atom wide ring-like features, the more flexible amorphous framework of a- SiO_2 allows the formation of several new ring types. The SiO_2 rings in a- SiO_2 show a continuous distribution between four-atomic and 24-atomic rings which is located around a weakly pronounced maximum of 14 atoms wide. Thus, the absence of crystal-like long-range order allows the disordered SiO_4 coordination-polyhedra network to adopt new structural features on a mid-range order length scale as one might expect from a good glass forming material. An identical range of ring-like features has been reported recently by Kohara *et al* [106] for a DFT optimized structure model of a- SiO_2 whereas the ring-size maximum is slightly shifted to 12-atom wide rings. Slightly narrower size distributions ranging from six-atomic to 20-atomic rings as well as six to 18 atom wide rings have been published by Rino *et al* [102] from empirical potential MD as well as Pasquarello *et al* [103] and Giacomazzi *et al* [104] on the basis of DFT simulations, respectively.

The ring distributions of the a- $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ oxide alloys illustrates the continuous decay of mid-range order features upon increasing Ti content. According to the total ring distribution of a- $\text{Ti}_{0.2}\text{Si}_{0.8}\text{O}_2$ (see figure 18(a)), low fractions of Ti ions do not dramatically change the qualitative mid-range order characteristics of the a- SiO_2 matrix. The integration of 20 mol% Ti into the amorphous framework basically produces the same distribution width of ring sizes. Additionally the number of *medium-sized* 10, 12, and 14 atom wide rings increases notably. This increase is obviously not related to binary TiO_2 type rings (see figure 18(b)) since pure TiO_2 type rings remain extremely exceptional in the a- $\text{Ti}_{0.2}\text{Si}_{0.8}\text{O}_2$ alloy. Similarly, the larger numbers of rings do not originate from binary SiO_2 type rings (see figure 18(c)). In fact, with exception of 6-atomic and 10-atomic rings, whose fractions remain almost constant, the number of all pure SiO_2 rings breaks down. The large majority of the SiO_2 type rings is just slightly modified by the incorporation of TiO_n coordination polyhedra (e.g. see figures 3(c-4) and (c-5)). The majority of TiO_4 coordination units, despite their larger size, simply replace tetrahedral SiO_4 units within ring structures. In addition, the 25.0% of non-tetrahedrally coordinated Ti_{5c} and Ti_{6c} ions not only replace tetrahedral SiO_4 polyhedra, rather these non-tetrahedral units add new bonding sites to the existing SiO_2 rings without destroying them. The additional bonding sites of the TiO_5 and TiO_6 coordination polyhedra connect to the amorphous SiO_4 network and promote the formation of additional 14, 12, and, especially, 10 atom wide rings. Thus, low amounts of Ti ions in a- SiO_2 actually act as a network forming and a network modifying species that selectively support the additional formation of certain ring sizes, thereby, strengthening the mid-range

order within the amorphous oxide alloy. Similar qualitative trends in the modification of the network-order characteristics are observed in the mid composition range at composition parameters of $x = 0.4$ and $x = 0.6$. In a- $\text{Ti}_{0.4}\text{Si}_{0.6}\text{O}_2$ the higher number of non-tetrahedrally coordinated Ti ions promotes the formation of medium-sized rings. Thereby, 10-atomic rings are more and more favored over other ring types. Due to the formation of further medium sized rings, the number of large rings (>18 atoms) starts to decay successively. In agreement with the first observation of a Ti-Ti pair-correlation double peak, that indicates the existence of edge-linked TiO_n coordination polyhedra, the first formation of four-atomic TiO_2 type rings is observed in the ring distribution of the a- $\text{Ti}_{0.4}\text{Si}_{0.6}\text{O}_2$ alloy. Binary SiO_2 type rings are observed less frequent and are restricted to ring sizes of six and 14 atoms. In a- $\text{Ti}_{0.6}\text{Si}_{0.4}\text{O}_2$ the number of four-atomic TiO_2 type rings increases notably. In general, the contributions from smaller ring sizes are enhanced by the progressively increasing number of c- TiO_2 characteristic ring sizes. Medium-sized rings of 12 and 14 atom width are also observed more frequently. Altogether, all a- $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ oxides with Ti contents ≤ 60 mol% show a similar width of their ring-size distribution and might be characterized as mid-range ordered oxide alloys. Looking back to the local coordination numbers, a common feature of all these mid-range ordered oxides is that a majority of $90 \pm 4\%$ of Si ions remains tetrahedrally coordinated (see figure 7(c)). In addition, the strong increase of medium sized rings directly correlates with TiO_5 coordination polyhedra as the main Ti coordination state (see figure 7(a)). The most distinct changes in the alloy-ordering characteristics are observed between composition parameters of $x = 0.6$ and $x = 0.8$. This is quite relevant, since the analysis of the partial pair-correlations, especially between homonuclear Ti pairs, did not indicate notable changes in the atomic structure. Amorphous $\text{Ti}_{0.8}\text{Si}_{0.2}\text{O}_2$ is the first alloy that shows a clear predominance of smaller rings and that, thus, might be characterized as a short range ordered material. Contributions from ring sizes above 12 atoms are notably reduced due to the high Ti content and rings larger than 16 atoms have vanished completely. The number of rings containing 10 or less atoms is roughly doubled. It is quite obvious that these changes correlate with octahedral TiO_6 coordination units becoming the dominant coordination-polyhedra type in the a- $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ alloys (see figure 7(a)). The complete loss of the remaining 20 mol% of Si ions weakly affects the qualitative ring-size distribution characteristics. Most notable, the amount of c- TiO_2 type rings, containing six to 10 atoms, increases significantly, while the number of edge linked TiO_n coordination polyhedra remains constant. Therefore, the notable increase of over-coordinated TiO_7 coordination polyhedra favors corner-linkages between TiO_n coordination units and the additional formation of c- TiO_2 like ring structures in the disordered framework of pure a- TiO_2 . The comparison of the ring-size distribution in the VASP and DFTB geometries indicates extremely similar ring-size distributions in the Si-rich a- $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ hybrid oxides. However, the mid-range order characteristics are partially affected by the structure-simulation approach. On the one hand, four-atomic rings, edge linked TiO_n coordination polyhedra, occur

less frequently. The smaller number of edge-linked coordination units is a consequence of general preference for a fivefold Ti_{5c} ion coordination state over the octahedral Ti_{6c} coordination state at all compositions (see figure 7(b)). On the other hand, the number of eight-atomic and 10-atomic rings in pure a-TiO_2 is significantly reduced. Again, this underestimation is a consequence of the, in general, smaller average Ti coordination number in the DFTB geometries. However, the actual width of the total ring-size distribution is just marginally narrower for the Ti-rich oxides.

In summary, ring statistics allow for the clear identification of mid-range order features that characterize the atomic structure of a-SiO_2 . Even if not commonly applied to this material class, ring statistics reveal a narrow ring-size distribution in a-TiO_2 . In the $\text{a-Ti}_x\text{Si}_{1-x}\text{O}_2$ oxide alloys the ring distribution reflects the competitive nature of both structure-ordering types. The mid-to-short-range order transition between pure a-SiO_2 and pure a-TiO_2 is less continuous as might be expected, for instance, from the various pair-distribution functions. In fact, the pair distribution functions predominantly reflect short-range order features of the atomic structure. In the case of the partial cation-correlation functions, this implies some information on the bonding characteristics of coordination polyhedra to their nearest-neighbor coordination units, whereas, it is not trivially possible to relate higher-order pair correlations to distinct mid-range order features. This causes some *insensitivity* of the atomic pair-correlation functions to actual mid-range order characteristics as the atomic rings of a glassy multi-component oxide network. Doping a-SiO_2 with minor fractions of Ti seem to increase the network connectivity without destroying, shorten respectively, existing rings. Thus low concentrations of Ti in a-SiO_2 glass act as both a glass forming and a glass modifying species that partially enhance the connectivity of the amorphous framework. This observation is quite consistent with the usage of low Ti content $\text{SiO}_2\text{-TiO}_2$ glass as an ultra-low thermal expansion material [168–171]. In the mid-range order regime, the additional, predominantly fivefold coordinated, Ti ions enhance the formation of medium-size rings without narrowing the ring-size distribution notably. At high Ti content ($x \geq 0.8$) the amorphous oxide alloys lose their mid-range order characteristics which indicates the formation of a low-density a-TiO_2 phase that is weakly disturbed by the presence of small amounts of Si ions.

4.8. Nanoscale phase separation

Finally, we address the question of phase separation in amorphous $\text{a-Ti}_x\text{Si}_{1-x}\text{O}_2$ hybrid oxides. It is quite obvious that our structure models describe rather the atomically mixed amorphous oxides than a phase separated material with notable domains of pure binary amorphous, or even crystalline, oxides. The chemically decomposed polyhedra representations of the $\text{a-Ti}_x\text{Si}_{1-x}\text{O}_2$ VASP geometries in figure 19 clearly show that the generated structure models are atomically mixed and no phase separation, phase segregation of a TiO_2 rich phase respectively, occurs throughout the entire composition range. As discussed above, cluster-like TiO_2 conglomerates are restricted to the mid-composition range and the size

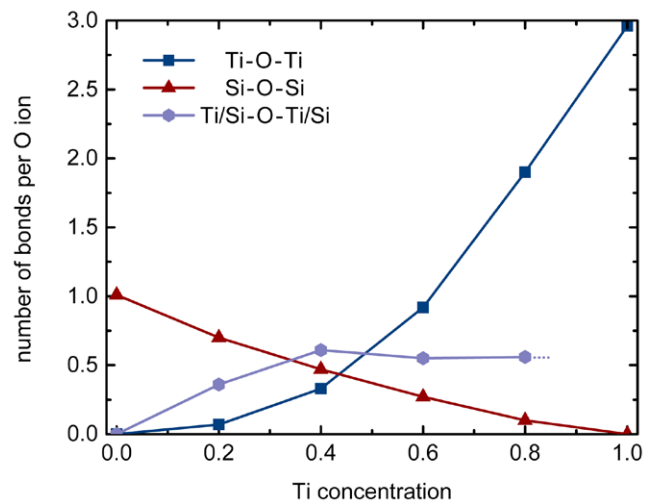


Figure 20. Number of homonuclear Ti–O–Ti and Si–O–Si as well as heteronuclear Ti/Si–O–Ti/Si cross linking bonds between various coordination polyhedra in the $\text{a-Ti}_x\text{Si}_{1-x}\text{O}_2$ VASP geometries.

of a few TiO_n coordination units (see figure 4(c–6)). The Ti rich $\text{a-Ti}_x\text{Si}_{1-x}\text{O}_2$ alloys systematically form mixed edge and corner-linked a-TiO_2 phases of diverse mass-density.

Some additional insights into the mixing properties are provided by the amount of homopolar Ti–O–Ti and Si–O–Si as well as heteropolar Ti/Si–O–Ti/Si bonds linking various coordination polyhedra illustrated in figure 20. Amorphous SiO_2 type network features dominate the ordering characteristics of the alloy below a composition of $x \approx 0.3$. With the beginning of edge-linking between TiO_n coordination polyhedra (see figure 18), Ti–O–Ti linkages become the dominant type of polyhedra bonds above a composition parameter of $x \approx 0.5$. In the small window between $x \approx 0.3$ and $x \approx 0.5$, mixed heteronuclear polyhedra linkages become the dominating bonding type. In pure a-SiO_2 the number of Si–O–Si bonds per O ion decrease slightly nonlinear from a value of 1.01, that is characteristic to an almost perfectly tetrahedrally coordinated SiO_4 network, to zero. Due to the higher connectivity of Ti ions, the number of Ti–O–Ti bonds increases quadratically to a value of 3.02 indicating, on average, an octahedral TiO_2 network. For both types of homopolar bonds the observed dependence on the Ti content, mass density respectively, indicates a continuous transition between the binary oxides. In contrast to homonuclear O ion linkages, the number of heteronuclear polyhedra-linking Ti/Si–O–Ti/Si bonds shows an discontinuous dependence on the Ti content. Up to 40 mol% of Ti ions, the number of Ti/Si–O–Ti/Si bonds per O ion increases to a value of 0.61 indicating that more than every second O ion in the $\text{a-Ti}_{0.4}\text{Si}_{0.6}\text{O}_2$ alloy interlinks a TiO_n coordination polyhedron with a SiO_m coordination polyhedron. Above a composition parameter of $x = 0.4$ the number of polyhedra-linking Ti/Si–O–Ti/Si bonds per O ion remains approximately constant. The constant number of Ti/Si–O–Ti/Si bonds per O ion indicates an increasing Si coordination state since the number of the Si ions decrease continuously and, thus, the connectivity of SiO_m coordination polyhedra has to increase to enhance the number of Ti/Si–O–Ti/Si bonds. This strongly suggest that the Si ions

are isotropically distributed in the Ti rich alloys and increase their coordination states in response to the surrounding higher coordination states of Ti ions. If SiO_2 would exist phase separated from TiO_2 only the coordination state of Si ions at the domain boundaries might change with variations in the alloy composition. Similarly, the formation of a separate TiO_2 phase should be reflected in the number of Ti–O–Ti linkages. Assuming the commonly reported coordination model of TiO_2 doped SiO_2 glasses, Ti ions are commonly fourfold coordinated at low Ti content and adopt a octahedral coordination state somewhere above 20 to 40 mol% of Ti ions. This would suggest that also the number of Ti–O–Ti polyhedra linkages should show indications of the tetrahedral-octahedral Ti coordination transition.

Altogether, no explicit indications of phase separation are given in our structure models indicating the general possibility of atomically mixed $\text{a-Ti}_x\text{Si}_{1-x}\text{O}_2$ hybrid oxides even at high Ti concentrations. However, it cannot be excluded that reheating beyond the crystallization temperature in successive MD runs favors the formation of a c-TiO_2 phase, most likely anatase or rutile, over an atomically mixed alloy phase.

5. Summary and conclusion

To conclude our study on the atomic structure of ternary $\text{a-Ti}_x\text{Si}_{1-x}\text{O}_2$ hybrid oxides, we briefly summarize our key results:

- Short and mid-range order in the amorphous phases of $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ hybrid oxides are comprehensively characterized by bond length and bond-angle statistics, pair distribution function analysis, coordination number and coordination polyhedra statistics, as well as ring statistics.
- The fundamental composition dependences of the cation-coordination numbers, observed in both the VASP and the DFTB geometries, mean that notable fractions of the Ti and Si ions experience a change in their local atomic coordination states with respect to their predominant coordination in crystalline binary (di)oxides.
- The average Si coordination number of $N_{\text{CSi}} = 4.03$ indicates a virtually perfect tetrahedral coordination in pure a-SiO_2 . The extrapolation towards a very dilute Si dispersion indicates a coordination number around ~ 4.8 at very high Ti contents.
- The average Ti coordination number shows a cubic dependence on the composition parameter and an extrapolated fourfold coordination state in the limit of a very dilute distribution of Ti ions in the disordered framework of a-SiO_2 . The average coordination number of pure a-TiO_2 of $N_{\text{CTi}}[1.0] = 5.89$ remains slightly below the crystal-coordination limit.
- The total coordination number of O ions changes nonlinear from an almost perfect ($N_{\text{CO}}[0.0] = 2.01$) crystalline Si_{2c} coordination state in pure a-SiO_2 to $N_{\text{CO}}[1.0] = 2.94$ which is close to the O coordination in crystalline TiO_2 .
- An average Ti coordination number close to the sixfold crystalline coordination is by far no evidence for a dis-

ordered a-TiO_2 network that is predominantly formed by (distorted) octahedron building blocks. Just slightly more than half of all Ti ions ($\sim 54\%$) preserve their crystalline coordination state. All other Ti coordination states arise from coordination defects that increase or decrease the local atomic coordination number by ± 1 or ± 2 .

- The intermediate fivefold Ti coordination state contributes notably to the $\text{a-Ti}_x\text{Si}_{1-x}\text{O}_2$ coordination characteristics. In the $\text{a-Ti}_{0.6}\text{Si}_{0.4}\text{O}_2$ oxide alloy TiO_5 building blocks even become the predominant coordination-polyhedra type.
- With progressively decreasing Ti content, the Ti ions tend to adopt the dominant fourfold coordination state of Si ions in a-SiO_2 .
- The local Si coordination numbers indicate that SiO_4 coordination polyhedra are very robust with respect to changes of the chemical composition parameter in $\text{a-Ti}_x\text{Si}_{1-x}\text{O}_2$. The fraction of SiO_4 coordination polyhedra remains roughly constant at $90 \pm 4\%$ up to a composition parameter of $x = 0.6$.
- The fractions of over-coordinated Si ions increase for a notable fraction of SiO_m coordination polyhedra only in the presence of a large number of higher coordinated Ti ions ($x \geq 0.8$).
- The detailed analysis of the coordination-polyhedra shapes demonstrates that disorder in binary and ternary $\text{a-Ti}_x\text{Si}_{1-x}\text{O}_2$ oxides is not only related to changes in the local coordination numbers but also to variations in the basic coordination-polyhedra symmetry types. Amorphous alloys do not necessarily contain only weakly distorted versions of a single crystal-like coordination polyhedron, rather various deformed polyhedra types coexist side by side.
- Bond lengths and bond-angles distributions indicate that the SiO_m coordination polyhedra participate rather passively in the formation of the amorphous frameworks of $\text{a-Ti}_x\text{Si}_{1-x}\text{O}_2$ hybrid oxides. Individual coordination units do not absorb significant fractions of atomic short-range disorder by being distorted into new coordination-polyhedra geometry types.
- The formation of new high Ti coordination states in $\text{a-Ti}_x\text{Si}_{1-x}\text{O}_2$ hybrid oxides depends critically on the Ti content. The average bond lengths and bond angles indicate that the formation of new TiO_n coordination polyhedra closely resembles bifurcation-like changes in a complex system. The mass density acts as the critical system parameter for the spontaneous formation of new coordination units that itself is triggered by strong deformations in the coordination environment of existing coordination-polyhedra building blocks.
- Effective coordination numbers prove to be quite sensitive to symmetry reductions of the local cation coordination environment and thus, the particular shape and symmetry type of a coordination polyhedron. Thus, the effective coordination numbers might be used as qualitative and, if compared to the conventional coordination numbers, quantitative measures for the degree of disorder within the first coordination shell around an atom.

- The disorder of the amorphous network increases with increasing Ti content. A dominant but almost constant fraction of disorder is carried by the local Ti ion coordination environments, and to a much smaller extent by the local Si ion coordination environments. Further disorder effects are projected onto the spatial arrangement of the coordination polyhedra, a.k.a. the amorphous network itself.
- Both the conventional and the effective coordination numbers provide fundamental information on the short-range order in amorphous oxides. While an in depth analysis of coordination-polyhedra remains an elaborate task and the conventional coordination numbers do not provide a measure for the degree of disorder within different coordination polyhedra, the effective coordination-number approach serves both purposes. Effective coordination numbers, as used in this study, are suited to determine the local coordination state of ions in the investigated amorphous hybrid oxides and to obtain information on the degree of disorder within the first coordination shell.
- It seems difficult to extract clear trends from the effective coordination numbers of individual coordination-polyhedra geometry types. This observation suggests that a purely exponential weighting function, might not be an ideal choice to characterize the atomic short-range order in an amorphous solid.
- Total pair-correlation functions do not, per se, allow us to identify structure correlations between arbitrary pairs of chemical elements. In addition, short-range order differences within the first correlation shell, that are indicated in the local coordination number analysis, are not resolved, or rather hidden, in the total pair correlation functions.
- Coordination polyhedra show a decreasing average bond length with increasing alloy density, thus the observed first correlation-shell shift of Ti–O and Si–O pair correlations to higher bond lengths with increasing Ti content necessitates the occurrence of successively higher coordinated TiO_n as well as SiO_m building blocks.
- The Ti–Ti pair correlation peaks show a qualitative transition from a single-peak characteristic at low Ti content ($x = 0.2$) to a double-peak characteristic in the mid-composition range. The different Ti–Ti correlation lengths originate from TiO_n coordination units connected by sharing either a common corner or a common edge with a neighboring TiO_n coordination polyhedron.
- The analysis of the partial pair-distribution functions allows us to deduce ordering characteristics of the coordination polyhedra among themselves. Hints on extended mid-range ordering features within the amorphous oxides are given indirectly. Deeper insights into the mid-range order of $\text{a-Ti}_x\text{Si}_{1-x}\text{O}_2$ oxide alloys require more specialized structure-analysis techniques as ring statistics.
- Even if not commonly applied to this material class, ring statistics reveal a quite narrow ring-size distribution in a-TiO_2 with predominant ring sizes below 12 atoms. In the $\text{a-Ti}_x\text{Si}_{1-x}\text{O}_2$ oxide alloys the ring distribution reflects the competitive nature of both short-range and mid-range types of atomic order.

- At low concentrations, Ti in a-SiO_2 glass acts as both a glass forming and a glass modifying species that partially enhances the connectivity of the amorphous framework without destroying existing rings.
- No explicit indications of phase separation are found in our structure models indicating the general capability of $\text{a-Ti}_x\text{Si}_{1-x}\text{O}_2$ hybrid oxides to form atomically mixed alloys even at high Ti concentrations.

The present study provides a comprehensive database for the characterization and interpretation of experimental data on short-range and mid-range order characteristics for the wide class of technologically important a-TiO_2 and a-SiO_2 containing amorphous and nano-structured oxides. The potential of various structure analysis approaches to describe atomic ordering features on various atomic length scales is comprehensively demonstrated for the disordered atomic frameworks of ternary $\text{a-Ti}_x\text{Si}_{1-x}\text{O}_2$ hybrid oxides. The results of this analysis will serve the future understanding of structure related electronic and optical properties of $\text{a-Ti}_x\text{Si}_{1-x}\text{O}_2$ alloys and disordered material phases in general.

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