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Empirical two-body potential for solid silicon nitride, boron nitride, and borosilazane modifications

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A short-ranged classical force-field for the modeling of silicon nitrides, boron nitrides, and borosilazanes (Si/B/N) has been derived on the basis of experimental and *ab initio* solid state and diatomic molecular data. The potential is a sum of pure two-body interaction terms with functional forms apt for fraction simulation. Structural parameters of hypothetical $Si_3B_3N_7$ polymorphs and crystalline boron and silicon nitrides containing threefold or fourfold coordinated boron and nitrogen and fourfold or sixfold coordinated silicon are well reproduced. The quality of second-order properties such as vibrational frequencies, bulk moduli, and elastic constants is more sensitive to the atomic coordination. Very good agreement with experiment is observed for BN and Si_3N_4 modifications with trigonal nitrogen coordination.

I. INTRODUCTION

Polycrystalline or amorphous boron nitrides and silicon nitrides are materials with a diversity of industrial applications.[1–5] A formal combination of both, an amorphous ceramic of nearly stoichiometric composition $Si_3B_3N_7$, was first synthesised from molecular precursors in Bonn in the 90 s.[6] This material is supposed to have great potential;[7,8] its temperature resistance, for example, exceeds that of silicon nitride. $Si_3B_3N_7$ does not show any tendency for crystallization—in fact crystalline modifications have not yet been detected.

For amorphous compounds, such as the above ones, structural data is extremely hard to extract from experiment. Theory can aid by constructing models which have to be validated by comparing calculated and experimental properties. Frequently employed models for amorphous networks are either isolated clusters or periodically repeated units (see, e.g., Refs. 9–18). In order to avoid artifacts due to the periodicity of solid state models, unit cells have to be large. Long-range order is not a problem for cluster models, but small aggregates easily suffer from surface effects. Thus, unit cells and clusters often comprise at least a thousand or more atoms. Despite the progress of *ab initio* molecular dynamics methods in this field, *ab initio* studies of $Si_3B_3N_7$ employing unit cells of this size are out of reach, at least with todays computer facilities.[19–21] Instead, phase space may be sampled by classical molecular dynamics (MD) or Monte Carlo simulations. Both approaches require the knowledge of the potential energy. Thus, if analytical interaction potentials are not available in the literature, one of the initial stages of such computer modeling is the parametrization of an appropriate classical force field. The parameters of the energy expressions may be fitted to reproduce the properties of molecules/crystals in a training set which ideally is sufficiently broad to yield transferable interaction potentials. In this work we report on the fitting and the performance of a force field tailored for ternary Si/B/N ceramics and their binary B/N and Si/N subsystems. Parameter sets for the modeling of silicon nitrides or boron nitrides have been reported earlier in the literature.[15,22–25] None of these are applicable to borosilazanes, however.

Boron, nitrogen, and silicon are typical network building elements. Bonding in solid boron nitride, silicon nitride, and borosilazane compounds exhibits partially ionic and partially covalent character. Ionic bonding is dominated by long-range Coulomb attraction and short-range Pauli repulsion. Both are isotropic in space, i.e., they do not depend on the spatial orientation of the two particles with respect to other particles, but only on their distance. Covalent bonding, on the other hand, involves angular correlation between forces. In a classical force field these are typically represented by three-body interaction terms.

In general, the presence of three-body potentials improves force constants and other second-order properties of covalent compounds. A complication arises when the number of bonded interactions varies for a pair of elements because three-body terms are biased towards a certain bond angle and concomitantly towards a particular atomic coordination number. It is thus extremely difficult to parametrize an interaction potential including three-body terms which simultaneously reproduces structures and second-order properties of differently coordinated modifications of a substance. For instance, a recently presented two- and three-body interaction potential yields structures and vibrational frequencies of Si/B/N compounds with threefold coordinated B and N and four-fold coordinated Si in excellent agreement with experiment but it fails in describing the zinc blende form of BN.[26]

TABLE I. Two-body potentials.

Name	Analytical form	Parameters	Units
Morse	$E=D_e\{(1-e^{-a(r-r_0)})^2-1\}$	D_e, a, r_0	eV, Å $^{-1}$, Å
General 1	$E=\frac{A}{r}e^{-r/\rho}$	A,ρ	eV Å , Å
Damped dispersion	$E=-\frac{C_6}{r^6}\left(1-e^{-b_6 r}\Sigma_{k=0}^{6}\frac{(b_6 r)^k}{k!}\right)$	C_6,b_6	eV Å ^{6}, Å $^{-1}$
Two-body taper	$P_5=(x_o-x_i)^{-5}$ $\times\{-6\cdot r^5$ $+15(x_i+x_o)r^4$ $-10(x_i^2+4x_ix_o+x_o^2)r^3$ $+30(x_i^2x_o+x_ix_o^2)r^2$ $-30x_i^2x_o^2r$ $+10x_i^2x_o^3+x_o^5-5x_ix_o^4\}$	x_i,x_o	Å, Å

Employing this force field the initially fourfold coordinated cubic structure of *c*-BN is transformed into the threefold coordinated rhombohedral form of BN when subjected to a geometry optimization.

In the molecular modeling of organic and biochemical compounds typically different parameter sets are utilized for different coordinations. This procedure implies that covalent bonds are neither broken nor made in the course of the simulation. The situation is different for ceramics; these materials are synthesized at high temperatures and bond breaking and bond formation therefore have to be part of the modeling. Further, in amorphous networks like borosilazanes irregularities may occur. Although there are indications from NMR spectra of amorphous $Si_3B_3N_7$ that the prevailing boron and nitrogen coordination is trigonal and that silicon is tetrahedrally surrounded in this material,[27] under and overcoordinations cannot be ruled out completely. Therefore, we would like to describe other coordinations at least qualitatively correctly.

II. FORCE FIELD

The current force field is a sum of two-body interaction terms only:

$$E_{\text{pot Si/N/B}}=E_{\text{N-Si}}+E_{\text{B-N}}+E_{\text{Si-Si}}+E_{\text{B-B}}+E_{\text{N-N}}+E_{\text{B-Si}}. \tag{1}$$

Analytical expressions for the potential energy terms are shown in Table I. In the following we shall discuss these expressions in some detail. Nearly all classical potentials for inorganic solids assign effective charges to the atoms. This is necessary for the determination of dipoles and associated properties, such as infrared intensities and splittings between longitudinal and transverse optical phonon dispersion curves. On the other hand, a full treatment of Coulomb interactions requires infinite summation techniques which add considerable complexity to a computer simulation and slow it down. Work on a charged model potential for Si/B/N compounds which enables us to compute such properties is in progress.[28] Here, we refrain from introducing explicit charges. Instead, Coulomb repulsions between Si-Si, B-B, N-N, and B-Si atomic pairs are mimicked by exponentially damped $1/r$-type potentials, denoted as General 1 in Table I. By construction these are short-ranged and avoid Ewald summation procedures. The potential energy functions acting between Si-N and B-N are expressed as Morse potentials. In the absence of Coulomb forces Morse potentials comply conveniently with the requirement of describing repulsion *and* attraction. Moreover, the parameters have a physical meaning, and diatomic molecules may thus serve as a good starting point for fitting. In order to obtain the proper layer structures of hexagonal and rhombohedral BN we included nitrogen-nitrogen dispersion interactions (damped dispersion). Herein, the negative singularity of the $1/r^6$ term at the origin is avoided by exponential damping according to the Tang-Toennies model of dispersion.[29] At large interatomic separations all two-body potentials are smoothly tapered to zero over a certain range such that the energy and its first and second derivatives with respect to the internuclear coordinate remain continuous. This is achieved by multiplying the two-body potential energy E by a fifth-order polynomial P_5 (two-body taper) for all interatomic distances which lie in the range between an inner (x_i) and an outer (x_o) cutoff radius.

All fitting has been performed using the GULP program.[30,31] We fit at constant-pressure and zero-temperature conditions using a weighted least-squares procedure. Observables are either physical properties like binding energies, vibrational frequencies, etc. or structural data. Wherever applicable, i.e., in cases in which a structural relaxation results in a positive definite Hessian, the relax fitting mechanism has been employed. In this fitting mode, crystalline or molecular structures are optimized at every step and coordinates are taken as observables instead of forces.[30]

A starting set of parameters for the Morse potentials describing the Si-N and B-N interactions, respectively, was obtained from structures, harmonic vibrational frequencies, and dissociation energies of the corresponding diatomic molecules. The diatomic SiN molecule has an electronic ground state of ${}^2\Sigma^+$ symmetry with an equilibrium bond distance of $r_e=1.572$ Å. Its harmonic vibrational frequency (ω_e) is equal to 1151.4 cm^{-1}.[32] An estimate of the molecular dissociation energy was obtained by adding $(1/2)\omega_e$ to the experimental value for D_0 (4.68 eV).[33] In case of BN, our first choice of reference state was the $X^3\Pi$ ground state. According to quantum chemical studies by Bauschlicher *et al.*[34] this state exhibits a bond order of roughly 2.5. In the course of our fitting procedure it turned out, however, that it is more

TABLE II. Parameter set.

Interaction partners	Type of potential	Parameter	Value
N-B	Morse	D_e	5.50007
		a	2.84990
		r_0	1.32521
N-Si	Morse	D_e	3.88461
		a	2.32660
		r_0	1.62136
N-N	damped dispersion	C_6	16691.4
		b_6	0.50328
N-N	general 1	A	2499.01
		ρ	0.36029
B-B	general 1	A	1231.52
		ρ	0.36119
Si-Si	general 1	A	177.510
		ρ	0.63685
B-Si	general 1	A	643.332
		ρ	0.43302
Two-body taper		x_i	4.30000
		x_o	5.80000

favorable to use the spectroscopic constants of the triply bonded first excited electronic state, $a^1\Sigma^+$, as input data. In the equilibrium region $a^1\Sigma^+$ and $X^3\Pi$ are nearly isoenergetic.[35] The physical data $\omega_e = 1705.4$ cm^{-1} and $r_e = 1.2745$ Å were taken from experimental work.[36] Unlike the $X^3\Pi$ state, $a^1\Sigma^+$ does not dissociate to atomic ground state products, $N(^4S_u) + B(^2P_u)$. Instead it correlates with the first excited channel, $N(^2D_u) + B(^2P_u)$. So, the D_e value of ≈ 6.66 eV was estimated on the basis of a theoretical value of 4.3 eV for the $X^3\Pi$ ground state[34] and an experimental value for the atomic excitation energy of $N(^4S_u) \rightarrow N(^2D_u)$.[37]

The most common crystal structures of silicon nitride (α-Si$_3$N$_4$ and β-Si$_3$N$_4$),[38,39] of hexagonal (h-BN) and rhombohedral (r-BN) boron nitride,[40,41] and two hypothetical polymorphs of Si$_3$B$_3$N$_7$ (β-2 and α-1) (nomenclature according to Kroll and Hoffmann[42]) served as solid state input data. In addition to structural data, properties such as elastic constants, bulk moduli, and phonon frequencies at the Γ point were chosen as observables in the fitting.[43–47] Further details on the selection of solid state properties may be found in Ref. 26. A newly detected cubic modification of Si$_3$N$_4$ (c-Si$_3$N$_4$),[48] the cubic zinc blende[49] (c-BN) and wurtzite[50] (w-BN) modifications of boron nitride, and further hypothetical modifications of Si$_3$B$_3$N$_7$ were not used for fitting, but were included later in the test set.

Boron and nitrogen atoms are threefold coordinated (120° bond angle) in hexagonal and rhombohedral BN crystals whereas they are tetrahedrally surrounded (109.47°) in the zinc blende and wurtzite forms.[40,41,50,51] In the well-known α- and β-Si$_3$N$_4$ modifications nitrogen is threefold coordinated whereas it exhibits a fourfold coordination in the newly detected cubic form.[38,39,48] In the latter, some of the silicon atoms adopt a sixfold coordination in an octahedral environment, while others are tetrahedrally surrounded. A collection of reference data is displayed in Tables III–V where a comparison with the corresponding results of force-field calculations is made.

Optimized force-field parameters for the energy expression in Eq. (1) describing the interactions in Si-N and B-N bonded networks are displayed in Table II. Merely 18 parameters are employed to fit 350 observables. We regard the number of parameters as very small—taking into account that we describe problems related to ternary compounds and the fact that the atoms do not bear charges and thus all interactions are parametrized explicitly.

III. PERFORMANCE OF THE FORCE FIELD

Applying the force field to the hexagonal and rhombohedral modifications of solid boron nitride yields results in very good agreement with experimental and *ab initio* data. As shown in detail in Table III this does not only apply to structural data but also to vibrational frequencies and elastic properties. Cell constants and bond distances are reproduced to within 0.02 Å. In spite of the fact that only two-body terms are employed in the construction of the force-field, zone-center frequencies of h-BN agree with experimental data to within roughly ten wave numbers. It has to be kept in mind, however, that most of these observables served as reference data in the fitting procedure. This is not the case for the vibrational frequencies of r-BN which nevertheless come out with an error of less than 20 cm^{-1}. We find h-BN to be energetically only slightly preferred over r-BN in agreement with the observation that h-BN can be used as a lubricant with easily relocatable layers. Both structures are true minima on the potential energy surface. Even total lattice energies compare remarkably well with the results of recent density functional theory (DFT) calculations by Albe.[52]

Also the structures of the four-fold coordinated cubic and wurtzite-like modifications of BN are reproduced very well. Note that we did not impose symmetry constraints. Like h-BN and r-BN they are true minima on the potential energy surface. This is a most remarkable result because the training set of the force field contained merely boron and nitrogen atoms with threefold coordination. Second-order properties

TABLE III. Empirically modeled vs measured and *ab initio* properties of crystalline boron nitride modifications. Cell constants a,b,c and internuclear separations in Å, cell angles α,β,γ in degrees, phonon frequencies ν_i at Γ point in cm^{-1}, total lattice energy E and zero-point vibrational energy $ZPVE$ per formula unit in eV, elastic constants c_{ij}, and bulk moduli B_0 in GPa.

Material	Included in fit	Property	Force-field value	Reference value	Literature (Ref.)
h-BN	yes	a,b	2.517	2.504	40
	yes	c	6.647	6.661	40
	yes	α,β	90.0	90.0	40
	yes	γ	120.0	120.0	40
	[a]	R_{NB}	1.453	1.446	
	[a]	$\sphericalangle$NBN	120.0	120.0	
	no	E	-11.491	-12.813	52
	no	$ZPVE$	0.225		
	yes	c_{33}	31.6	32.4	47
	no	B_0	30.9	36.7	55
	yes	ν_1	53.3	52.5	45
	no	ν_2	117.9		
	yes	ν_3	770.8	783	46
	no	ν_4	821.9	828	46
	yes	ν_5	1361.6	1367	46
	yes	ν_6	1361.8	1370	46
r-BN	yes	a,b,c	3.665	3.643	[b]
	yes	α,β,γ	40.159	40.235	[b]
	[a]	R_{BN}	1.453	1.446	
	[a]	$\sphericalangle$NBN	120.0	120.0	
	no	E	-11.487	-12.813	52
	no	$ZPVE$	0.217		
	no	B_0	32.7	33.4	56
	no	ν_1	774.4	794.1	57
	no	ν_2	1362.6	1374.5	57
c-BN	no	a,b,c	2.560	2.557	[c]
	no	α,β,γ	60.0	60.0	[c]
	no	R_{BN}	1.568	1.566	
	no	$\sphericalangle$NBN	109.47	109.47	
	no	E	-10.76	-13.2	58
				-12.94	52
				-16.30	59
	no	$ZPVE$	0.13		
	no	B_0	618	369–400	60,61
	no	c_{11}	920	820	60
	no	c_{12}	467	190	60
	no	c_{44}	450	480	60
	no	ν_1	699	1055	57,62,63
w-BN	no	a,b	2.567	2.553	50
	no	c	4.141	4.200	50
	no	α,β	90.0	90.0	50
	no	γ	120.0	120.0	50
	no	$R_{\mathrm{BN}}(3)$	1.564	1.566	
	no	$R_{\mathrm{BN}'}$	1.573	1.571	
	no	$\sphericalangle$NBN	110.45	109.75	
	no	$\sphericalangle$NBN	108.58	109.19	
	no	E	-10.83		

TABLE III. (*Continued*).

Material	Included in fit	Property	Force-field value	Reference value	Literature (Ref.)
	no	$ZPVE$	0.21		
	no	B_0	637	394	24
	no	$\nu_{\max}$	1299		

[a] Fractional coordinates were employed in the fitting rather than bond lengths and bond angles.

[b] Cell parameters correspond to a hexagonal unit cell with dimensions $a=b=2.506$ and $c=10.030$ Å as determined by Ueno *et al.* (Ref. 41).

[c] Cell parameters correspond to a cubic unit cell with dimensions $a=b=c=3.6715$ Å as determined by Solozhenko *et al.* (Ref. 51).

such as vibrational frequencies, elastic constants, and bulk moduli show larger deviations from experimental values than the corresponding properties in *h*-BN and *r*-BN though. Both the vibrational frequency and the total lattice energy of *c*-BN indicate that this modification of boron nitride is too loosely bound in our force-field calculations.

In the asymmetric part of the unit cell of α-Si_3N_4 four nonequivalent nitrogens are found. All of them are threefold coordinated to silicon with out-of-plane angles between 0° and 22° and Si-N bond lengths between 1.715 Å and 1.760 Å . As apparent from Table IV the structure of α-Si_3N_4 is well reproduced by the force field; deviations from the experimentally determined bond distances are smaller than 0.03 Å. Also bond angles and out-of-plane angles, not shown in the table, agree to within a few degrees. The quality of elastic properties may be judged by the good agreement of the bulk modulus with the most reliable experimental value which was not used as an observable during the parametrization. To our knowledge, the relative stability of α-Si_3N_4 and β-Si_3N_4 has not been determined experimentally. However, on the basis of experimental structural data Grün[39] estimated that β-Si_3N_4 is the more stable modification which is confirmed by our force-field calculations and is in accord with density functional calculations on the two polymorphs.[23,48] Also the total lattice energy of β-Si_3N_4 compares well with the result of a recent first principles calculation.[53]

Two symmetry nonequivalent nitrogens exist in β-Si_3N_4, both planar coordinated. It is generally agreed that one type of nitrogen atom lies on a threefold rotational symmetry axis and thus exhibits three equal bond lengths. These features are nicely reproduced by the force-field calculation in spite of the fact that no symmetry constraints have been imposed. Experimental bond distances relating to the other, symmetry inequivalent, nitrogen differ considerably in the experimental literature and even the space group of β-Si_3N_4 appears to be controversial ($P63$ vs $P63/m$). (As one example for a $P63/m$ structure, refer to Ref. 54.) We started the geometry optimization from the $P63$ structure as determined by Grün[39] which exhibits three different Si-N bond distances at the asymmetric site, i.e., 1.704 Å, 1.735 Å, and 1.760 Å. The present force-field parametrization reproduces the lower symmetry, though quantitatively the difference between the shortest and the longest Si-N is slightly underestimated.

In contrast to the above mentioned hexagonal α and β modifications of Si_3N_4, the recently detected cubic form exhibits a fourfold coordination of nitrogen and both tetrahedral and octahedral silicon environments. Although neither fourfold coordinated nitrogens nor an octahedral surrounding of silicon has been part of the training set, *c*-Si_3N_4 is modeled astoundingly well (cf. Table IV). Its geometrical structure is retained while cell dimensions and bond distances are somewhat underestimated.

We optimized thirteen different polymorphs of the ternary $Si_3B_3N_7$, starting from the DFT geometries given by Kroll and Hoffmann.[42] All of them are found to be true minima on the model potential hypersurface. The results for the two most stable conformations, (β-2)-$Si_3B_3N_7$ and (α-1)-$Si_3B_3N_7$, are shown in detail in Table V. An overall good agreement between structural properties obtained from force-field and DFT calculations is observed. Cell dimensions and bond distances are slightly larger than the corresponding DFT values employing an SVWN functional.[42] We suppose that our force-field optimized structural constants are closer to the truth. This judgement is based on a remark by Kroll and Hoffmann according to which Si-N bond lengths come out somewhat too short in corresponding SVWN calculations on Si_3N_4.[42] The same is probably true for B-N internuclear separations since LDA is known to systematically overbind. In our force-field calculations this tendency should at least partially be compensated for since we included experimentally determined structural constants of BN and Si_3N_4 in the fitting procedure.

IV. SUMMARY

On the basis of experimental and *ab initio* data, we have derived a classical two-body potential for boron/silicon nitrides. The present force field can be applied to boron nitrides, silicon nitrides, and borosilazanes with varying atomic coordination. By design it cannot be used for the modeling of structures containing direct N-N, B-B, Si-Si, or Si-B bonds. Further, the model cannot be used to evaluate infrared and Raman intensities directly, because of the absence of charges or atomic polarizabilities. However, effective charges could be derived using electronegative equalization methods and combined with the eigenvectors from the model to give a first estimate of IR intensities. Simplistically this could be done by taking the charges as being fixed based on the equilibrium geometry or more rigorously by taking derivatives of

TABLE IV. Modelled vs measured properties of crystalline silicon nitride modifications. Cell constants a,b,c and internuclear separations in Å, cell angles α,β,γ in degrees, phonon frequencies ν_i at Γ point in cm^{-1}, total lattice energy E and zero-point vibrational energy $ZPVE$ per formula unit in eV, bulk moduli B_0 in GPa.

Material	Included in fit	Property	Force-field value	Reference value	Literature (Ref.)
α-Si$_3$N$_4$	yes	a	7.754	7.818	38
	yes	c	5.630	5.591	38
	yes	α,β	90.0	90.0	38
	yes	γ	120.0	120.0	38
	no	E	-35.08	$>\beta$-Si$_3$N$_4$ [a]	
	no	$ZPVE$	0.76		
	[b]	R_{NSi}	1.727	1.715	
			1.739	1.740	
			1.743	1.746	
	[b]	$R_{\mathrm{N'Si}}$	1.732	1.736	
			1.741	1.744	
			1.745	1.760	
	[b]	$R_{\mathrm{N''Si}}(3)$	1.737	1.746	
	[b]	$R_{\mathrm{N'''Si}}(3)$	1.729	1.759	
	no	B_0	242.5	228.5	43
	yes	$\nu_{\max}$	1017	1040[c]	44
β-Si$_3$N$_4$	yes	a,b	7.593	7.595	39
	yes	c	2.921	2.902	39
	yes	α,β	90.0	90.0	39
	yes	γ	120.0	120.0	39
	no	E	-35.14	-37.15	53
	no	$ZPVE$	0.72		
	[b]	R_{NSi}	1.734	1.704	
			1.735	1.728	
			1.738	1.766	
	[b]	$R_{\mathrm{N'Si}}(3)$	1.734	1.730	
	no	B_0	262.1	258.0	64
	yes	$\nu_{\max}$	1010	1047	44
cub-Si$_3$N$_4$	no	a,b,c	5.425	5.501	48
	no	α,β,γ	90.0	90.0	48
	no	E	-35.69		
	no	$ZPVE$	0.76		
	no	$R_{\mathrm{SiN}}(4)$	1.752	1.784	
	no	$R_{\mathrm{Si'N}}(6)$	1.867	1.889	
	no	B_0	411.9	310 ± 5	65
	no	$\nu_{\max}$	1119		

[a] Madelung calculations by Grün: $\Delta G_{\alpha\rightarrow\beta}\approx-0.31$ eV; Ref. 23: E_{tot} of β-Si$_3$N$_4$ lies ≈1.63 eV below the one of β-Si$_3$N$_4$.

[b] Fractional coordinates were employed in the fitting rather than bond lengths and bond angles.

[c] The two highest (very weak) Raman lines have been omitted because the experimental spectrum (Ref. 43) contains eight peaks in access to those predicted by group theory.

the charge distribution projected along the eigenvector of each mode.

The model performs very well for structural properties of crystalline solids containing threefold coordinated boron and nitrogen atoms and tetrahedrally surrounded silicon. For compounds in this class, second-order properties such as vibrational frequencies, bulk moduli, and elastic constants are also very well reproduced. Although not being members of the training set, the structures of crystals with a fourfold coordination of boron and nitrogen or with an octahedral surrounding of silicon are described almost equally well. The description of second-order properties is less satisfactory in these cases, however.

The energy expression is very fast to evaluate because the

TABLE V. Classically vs quantum chemically modeled properties of the two most stable hypothetical $Si_3B_3N_7$ modifications (Ref. 42). Cell constants a,b,c and internuclear separations in Å, cell angles α,β,γ in degrees, total lattice energy E and zero-point vibrational energy $ZPVE$ per unit formula in eV, bulk moduli B_0 in GPa.

Material	Included in fit	Property	Force-field value	Reference value	Literature (Ref.)
β-2-$Si_3B_3N_7$	yes	a,b	7.495	7.488	65
	yes	c	5.372	5.292	65
	yes	α,β	90.0	90.0	42
	yes	γ	120.0	120.0	42
	no	E	−70.57	x	
	no	$ZPVE$	1.75		
	[a]	R_{NSi}	1.753	1.725	
	[a]	R_{NB}	1.445	1.432	
			1.458	1.472	
	[a]	$R_{\mathrm{N'Si}}$	1.729	1.704	
			1.760	1.720	
	[a]	$R_{\mathrm{N'B}}$	1.429	1.437	
	[a]	$R_{\mathrm{N''Si}}(3)$	1.726	1.716	
	no	B_0	170.1	200.0	42
α-1-$Si_3B_3N_7$	yes	a,b	7.455	7.395	65
	yes	c	5.241	5.239	65
	yes	α,β	90.0	90.0	42
	yes	γ	120.0	120.0	42
	no	E	−70.03	$x+0.2$	42
	no	$ZPVE$	1.72		
	[a]	R_{NSi}	1.747	1.727	
	[a]	R_{NB}	1.473	1.486	
			1.473	1.492	
	[a]	$R_{\mathrm{N'Si}}$	1.716	1.684	
			1.716	1.689	
	[a]	$R_{\mathrm{N'B}}$	1.436	1.427	
	[a]	$R_{\mathrm{N''Si}}(3)$	1.732	1.713	
	no	B_0	290.9	240.0	42

[a] Fractional coordinates were employed in the fitting rather than bond lengths and bond angles.

potential is a sum of two-body potentials only and all terms are short-ranged. Furthermore, the two-body potentials are free of singularities and are smoothly tapered to zero at large interatomic separations. Because of these properties the present force field constitutes an ideal tool for large-scale molecular dynamic simulations of structural properties of nitridic ceramic materials.

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