Theoretical study on elastic properties of Si_2N_2O by ab-initio calculation
第一原理計算による酸窒化シリコンの弾性的性質の研究

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1. Abstract

The crystalline silicon oxynitride (Si_2N_2O) can be synthesized by heating silicon and quartz powder in nitrogen atmosphere at 1,450 °C[1]. Its crystal structure was discovered in 1960s[1], which is illustrated in **Fig. 1**(a).

Si_2N_2O has been studied as a favorable high-temperature structural ceramic because of its good heat characteristics. For example, it exhibits high oxidation resistance and high flexural strength up to 1400 °C[2]. In addition, it shows low thermal expansion coefficient (3.5×10^{-6} K^{-1}) and extraordinary thermal shock resistance[2]. On the other hand, its mechanical properties are hardly studied, including its elastic constants.

In this study, we determine all of the independent elastic constants of Si_2N_2O by *ab*-initio calculation. In parallel, we determine the elastic constants of crystalline SiO_2 (α-quartz) and β-Si_3N_4 for comparison. These three Si-O-N compounds have similar structures in terms of being made of tetrahedron centering around Si atoms.

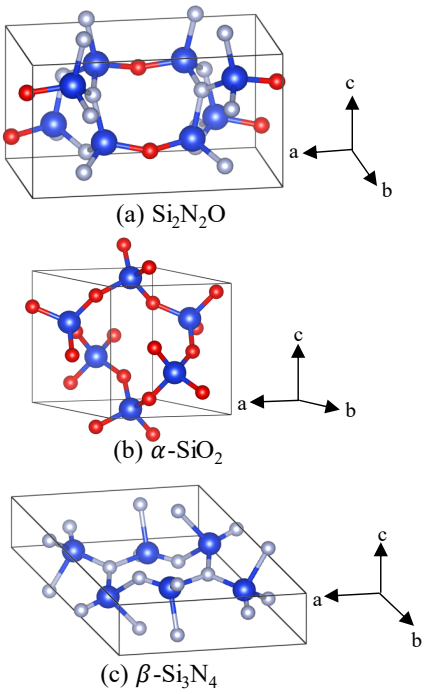
2. Materials

Si_2N_2O has an orthorhombic symmetry, belonging to the space group $Cmc2_1$[1]. As shown in **Fig. 1**(a), it consists of [SiN_3O] tetrahedron connecting with each other via shared vertices. Because of the symmetry, Si_2N_2O has nine independent elastic constants:

$$C_{ij} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ & C_{22} & C_{23} & 0 & 0 & 0 \\ & & C_{33} & 0 & 0 & 0 \\ & & & C_{44} & 0 & 0 \\ & sym. & & & C_{55} & 0 \\ & & & & & C_{66} \end{pmatrix} \quad (1)$$

SiO_2 has several crystal structures, and we chose α-SiO_2 as the comparison, because of its high stability at room temperature and atmospheric pressure. As shown in Fig. 1(b), crystalline α-SiO_2 has trigonal symmetry, showing six independent elastic constants. Its space group is $P3_121$.

Si_3N_4 has two principal types of crystal structures (α-Si_3N_4 and β-Si_3N_4), and here we chose β-Si_3N_4 as a calculation target. Its shows hexagonal symmetry with five independent elastic constants. Space group of β-Si_3N_4 is controversial and possibly be $P6_3/m$ or $P6_3$[3]. Here, we chose the $P6_3$ and performed the calculation, and we show its structure in Fig. 1(c).



(a) Si_2N_2O
(b) α-SiO_2
(c) β-Si_3N_4

Fig. 1 The crystal structures of (a)Si_2N_2O, (b)α-SiO_2 and (c)β-Si_3N_4. The blue, silver and red balls represent silicon, nitrogen and oxygen atoms, respectively.

2. Computational method

Here, we used the Vienna Ab initio Simulation Package (VASP) to determine the lattice constants and elastic constants[4]. The VASP employs the Projector Augmented Wave (PAW) method, which allows us to calculate all electrons (including core

electrons). As exchange correlation potentials, we used both Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA) to compare with the experimental values. The cutoff energy and k-point meshes are 1000 eV and 10×10×10 respectively.

First, we performed the relaxation calculation to the atomic sites and lattice constants at the ground state. In this case, the volume, cell sharp and atomic position of unit cell are changed so that unit cell has the minimum total energy.

Next, the elastic constants C_{ij} are calculated. To determine them, strains are applied to the unit cell up to ±1%, and the total energy are calculated as a function of the strain. The total energy can be written as follows, ignoring the higher order terms;

$$E(V,S) = E(V_0,0) + V_0\left(\sum_I \tau_I S_I + \sum_{I,J} C_{IJ} S_I S_J\right) \quad \cdots(2)$$

Here, V, τ and S mean the cell volume, the residual stress and the engineering strain respectively. Finally, elastic constants can be determined by fitting a quadratic function.

3. Result

By the relaxation calculation, we obtained the lattice constants as shown in **Table 1.** About Si_2N_2O, compared experimental values with the calculations in this study, LDA calculation gives closer values and more appropriate than GGA.

Table 1 Lattice constants obtained by the relaxation calculation and experimental value. (Å)

		a	*b*	*c*
Si_2N_2O	LDA	8.871	5.489	4.838
	GGA	8.967	5.502	4.897
	Experimental[1]	8.843	5.473	4.835
α-SiO_2	LDA	4.882	*a*=*b*	5.381
	GGA	5.037	*a*=*b*	5.525
	Experimental[5]	4.913	*a*=*b*	5.405
β-Si_3N_4	LDA	7.578	*a*=*b*	2.893
	GGA	7.663	*a*=*b*	2.926
	Experimental[6]	7.595	*a*=*b*	2.902

Next, elastic constants of these three crystals were determined by the LDA calculation. Those of α-SiO_2 are: C_{11}=72.9, C_{12}=7.6, C_{13}=7.8, C_{14}=−0.1, C_{33}=96.6 and C_{44}=52.2 GPa. Those of β-Si_3N_4 are: C_{11}=422.9, C_{12}=199.3, C_{13}=117.7, C_{33}=553.9 and C_{44}=99.1 (in units of GPa).

Whereas, elastic constants of α-SiO_2 are known as: C_{11}=86.76, C_{12}=7.06, C_{13}=11.90, C_{14}=-17.98, C_{33}=105.41 and C_{44}=58.27 GPa[7]. Those of β-Si_3N_4 are also known as: C_{11}=433, C_{12}=195, C_{13}=127, C_{33}=574 and C_{44}=108 GPa[8]. There are only slight differences between experimental values and calculated values, thus calculations are sufficiently reliable.

The elastic constants of Si_2N_2O are: C_{11}=312.4, C_{12}=82.5, C_{13}=53.8, C_{22}=244.8, C_{23}=36.8, C_{33}=316.6, C_{44}=132.7, C_{55}=59.2 and C_{66}=76.9 GPa.

These compounds have different symmetry and we can't compare simply these values. We therefore apply the Hill approximation to calculate their direction-averaged (isotropic) elastic constants. After applying Hill approximation, we focus on Young's modulus (E). In Fig. 2, N/(O+N) represents atomic ratio of nitrogen. From Fig. 2, E of averaged Si_2N_2O lays between those of α-SiO_2 and β-Si_3N_4. In addition, these E nearly lay on a straight line (dash line in Fig. 2).

4. Conclusion

The elastic constants of crystalline silicon oxynitride (Si_2N_2O) were theoretically calculated. Its averaged Young's modulus shows strong correlation to the nitrogen concentration, and it will be estimated from Young's moduli of α-SiO_2 and β-Si_3N_4 crystals if we know the nitrogen content regardless of their different crystal structures.

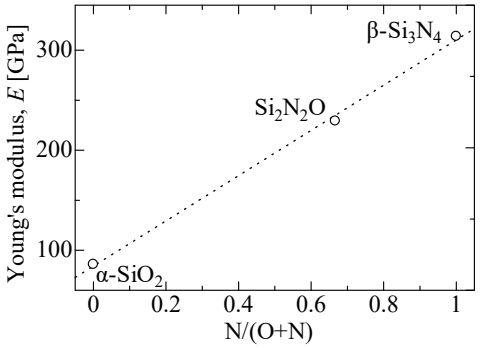


Fig.2 Nitrogen atoms concentrations dependence of averaged Young's modulus.

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