Theoretical study on elastic properties of Si$_2$N$_2$O by ab-initio calculation


1. Abstract

The crystalline silicon oxynitride (Si$_2$N$_2$O) 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$_2$N$_2$O 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$_2$N$_2$O by ab-initio calculation. In parallel, we determine the elastic constants of crystalline SiO$_2$ (α-quartz) and β-Si$_3$N$_4$ 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$_2$N$_2$O has an orthorhombic symmetry, belonging to the space group Cmc$_2$1[1]. As shown in Fig. 1(a), it consists of [SiN$_3$O] tetrahedron connecting with each other via shared vertices. Because of the symmetry, Si$_2$N$_2$O has nine independent elastic constants:

\[
C_\mu = \begin{pmatrix}
C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\
C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\
C_{13} & C_{23} & C_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & C_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{55} & 0 \\
0 & 0 & 0 & 0 & 0 & C_{66} \\
\end{pmatrix}
\]

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$_1$21.

Si$_3$N$_4$ has two principal types of crystal structures (α-Si$_3$N$_4$ and β-Si$_3$N$_4$), and here we chose β-Si$_3$N$_4$ as a calculation target. Its shows hexagonal symmetry with five independent elastic constants. Space group of β-Si$_3$N$_4$ 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).

(1) 

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 shape 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 is calculated as a function of the strain. The total energy can be written as follows, ignoring the higher order terms:

$$E(V, S) = E(V_0, 0) + V_0 \left( \sum_i \tau_i S_i + \sum_{i,j} C_{ij} S_i S_j \right)$$

Here, $V$, $\tau$ 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$_2$N$_2$O, compared experimental values with the calculations in this study, LDA calculation gives closer values and more appropriate than GGA.

<table>
<thead>
<tr>
<th></th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si$_2$N$_2$O</td>
<td>8.871</td>
<td>5.489</td>
<td>4.838</td>
</tr>
<tr>
<td>LDA</td>
<td>8.843</td>
<td>5.473</td>
<td>4.835</td>
</tr>
<tr>
<td>GGA</td>
<td>8.967</td>
<td>5.502</td>
<td>4.897</td>
</tr>
<tr>
<td>Experimental$^1$</td>
<td>8.871</td>
<td>5.489</td>
<td>4.838</td>
</tr>
<tr>
<td>α-SiO$_2$</td>
<td>4.882</td>
<td>$a=b$</td>
<td>5.381</td>
</tr>
<tr>
<td>LDA</td>
<td>5.037</td>
<td>$a=b$</td>
<td>5.525</td>
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<tr>
<td>GGA</td>
<td>4.913</td>
<td>$a=b$</td>
<td>5.405</td>
</tr>
<tr>
<td>Experimental$^5$</td>
<td>7.578</td>
<td>$a=b$</td>
<td>2.893</td>
</tr>
<tr>
<td>β-Si$_3$N$_4$</td>
<td>7.663</td>
<td>$a=b$</td>
<td>2.926</td>
</tr>
<tr>
<td>LDA</td>
<td>7.595</td>
<td>$a=b$</td>
<td>2.902</td>
</tr>
<tr>
<td>GGA</td>
<td>7.595</td>
<td>$a=b$</td>
<td>2.902</td>
</tr>
</tbody>
</table>

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, $C_{44}$=6.1, $C_{33}$=96.6 and $C_{44}$=52.2 GPa. Those of β-Si$_3$N$_4$ 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: $C_{11}$=105.41 and $C_{44}$=58.27 GPa$^7$. Those of β-Si$_3$N$_4$ 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$_2$N$_2$O are: $C_{11}$=312.4, $C_{12}$=82.5, $C_{13}$=53.8, $C_{22}$=244.8, $C_{33}$=36.8, $C_{44}$=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$_2$N$_2$O lays between those of α-SiO$_2$ and β-Si$_3$N$_4$. 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$_2$N$_2$O) 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$_3$N$_4$ crystals if we know the nitrogen content regardless of their different crystal structures.

![Fig.2 Nitrogen atoms concentrations dependence of averaged Young’s modulus.](image)

References