First-principles Calculations of The Elastic Properties, Electronic Structure and Optical Properties of Hexagonal Al₄SiC₄

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Abstract: The crystal structure, elastic constants, electronic structure and optical properties of Al₄SiC₄ have been systematically investigated using the first principles calculation method based on density functional theory. The calculated lattice constants and elastic constants are consistent with the experimental and calculated values, and it shows that the hexagonal Al₄SiC₄ crystal structure is stable. The calculated bulk, shear, Young’s modulus and Poisson’s ratio of hexagonal Al₄SiC₄ in the (100) and (001) directions with photon energy are calculated, including complex dielectric function, complex refractive in-dex, absorption spectrum and reflection spectrum. In the (100) and (001) directions, the static dielectric con-stants are 7.74 and 8.96, respectively, and the refractive indexes are 2.78 and 2.99, respectively. The calu-culated results can provide theoretical basis for related applications.

Keywords: Al₄SiC₄; Electronic structure; Optical properties; First-principles.

1. Introduction

Al₄SiC₄ ceramic is characterized by its low density (3.03 g/cm³), high melting point (> 2700°C), high chemical stability, high strength, low thermal expansion coefficient and excellent oxidation and hydration resistance. It has become a promising high-temperature structural material and high-performance refractory material to be developed, and has gradually attracted people's attention in the fields of aerospace structural ceramics and high-temperature electronic semiconductors. Since Barczak et al. first discovered Al₄SiC₄, several research groups have focused on the synthesis and preparation of Al₄SiC₄ (such as solid-state reaction sintering method, chemical vapor deposition). Experimental study on the properties and applications of volume-solid phase sintering method, hot pressing sintering method, high temperature self-spreading method, penetration method, mechanical alloying method, etc. have been completed on the Cambridge Sequential Total Energy Package(CASTEP)[29] module. In the calculation process, the interaction potential between ions and valence electrons is described by the mode conservation approximation (GGA) is selected for exchange correlation terms[30]. The interaction potential between ions and valence electrons is described by the mode conservation approximation (GGA) is selected for exchange correlation terms[30]. The interaction potential between ions and valence electrons is described by the mode conservation approximation (GGA) is selected for exchange correlation terms[30]. The interaction potential between ions and valence electrons is described by the mode conservation approximation (GGA) is selected for exchange correlation terms[30]. The interaction potential between ions and valence electrons is described by the mode conservation approximation (GGA) is selected for exchange correlation terms[30]. The interaction potential between ions and valence electrons is described by the mode conservation approximation (GGA) is selected for exchange correlation terms[30]. The interaction potential between ions and valence electrons is described by the mode conservation approximation (GGA) is selected for exchange correlation terms[30]. The interaction potential between ions and valence electrons is described by the mode conservation approximation (GGA) is selected for exchange correlation terms[30].
The valence electrons involved in the calculation are Al: 3s²3p¹, Si: 3s²3p², C: 2s²2p². The Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm was used to optimize the structure of the cell model, and the truncation energy was set to 750 eV. The self-consistent cyclic convergence accuracy is 5.0 × 10⁻⁶ eV/atom, the stress error between atoms is less than 0.02 GPa, the maximum displacement convergence error between atoms is less than 5.0 × 10⁻⁴ Å, and the total energy convergence standard of the system is 5.0 × 10⁻⁶ eV/atom. The k-point grid in Brillouin zone is 5 × 5 × 2.

3. Result and Discussion

3.1. Lattice parameter

Al₄SiC₄ is a hexagonal system with space group P6₃mc [1, 1], group number 186, lattice constant a = b = 3.2771 Å, c = 21.676 Å, V = 201.60 Å, α = β = 90°, γ = 120°. The crystal structure of Al₄SiC₄ is shown in Figure 1, where the purple is Al atom, the light gray is C atom, and the yellow is Si atom. Through the geometric structure optimization of Al₄SiC₄ cell, the lattice constant after optimization is obtained, as shown in Table 1. Compared with the experimental value [11], the difference between a and c is -0.63% and 0.31%, indicating that the model and calculation method adopted are credible.

<table>
<thead>
<tr>
<th>Method</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pres.</td>
<td>3.2562</td>
<td>21.6097</td>
<td>198.427</td>
</tr>
<tr>
<td>Expt.</td>
<td>3.2771</td>
<td>21.676</td>
<td>201.60</td>
</tr>
<tr>
<td>Expt.</td>
<td>3.2812</td>
<td>21.7042</td>
<td>—</td>
</tr>
<tr>
<td>Calc.</td>
<td>3.277</td>
<td>21.74</td>
<td>201.60</td>
</tr>
<tr>
<td>Calc.</td>
<td>3.222</td>
<td>21.352</td>
<td>—</td>
</tr>
<tr>
<td>Calc.</td>
<td>3.282</td>
<td>21.796</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 1. Calculated lattice parameters a, c (in Å), and volume V (in Å³) with the literature results for comparison

For the hexagonal crystal phase Al₄SiC₄, there are five independent constants, respectively C₁₁, C₁₂, C₁₃, C₃₃, C₄₄, C₆₆ = (C₁₁−C₁₂)/2, and the calculation results are shown in Table 2. As can be seen from Table 2, C₁₁ > C₁₂ > C₄₄ > C₃₃ > C₁₃ > 0. According to the elastic stability criterion of hexagonal crystal structure [31]: C₁₁−|C₁₂| > 0, C₄₄ > 0, (C₁₁+C₁₂)C₃₃−2(C₁₃)² > 0, it can be seen that the calculated elastic constant of Al₄SiC₄ satisfies the above stability conditions, so the crystal structure of Al₄SiC₄ is stable.

Table 2. Calculated second order elastic constants (Cij in GPa) of Al₄SiC₄

<table>
<thead>
<tr>
<th>Method</th>
<th>C₁₁</th>
<th>C₁₂</th>
<th>C₁₃</th>
<th>C₃₃</th>
<th>C₄₄</th>
<th>C₆₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pres.</td>
<td>389.1</td>
<td>127.9</td>
<td>46.8</td>
<td>404.4</td>
<td>110.7</td>
<td>130.6</td>
</tr>
<tr>
<td>Calc.</td>
<td>386</td>
<td>118</td>
<td>50</td>
<td>409</td>
<td>122</td>
<td>134</td>
</tr>
<tr>
<td>Calc.</td>
<td>369.5</td>
<td>117</td>
<td>52.9</td>
<td>383.5</td>
<td>110.2</td>
<td>121.2</td>
</tr>
</tbody>
</table>

3.2. Elastic property

Based on the calculated elastic constant Cij, the volume modulus and shear modulus can be obtained according to the Reuss-Voigt-Hill [32] model:

\[
\begin{align*}
G &= \frac{1}{15} (2C_{11} + C_{33} - C_{12} - 2C_{13}) + \frac{1}{5} \left( \frac{C_{44}}{2} + C_{11} - C_{12} \right) \\
G &= 15 \left[ 2(S_{11} + S_{33}) - 4(S_{12} + 2S_{13}) + 6(S_{44} + S_{11} - S_{12}) \right]^{-1} \\
B &= \frac{1}{9} \left( 2C_{11} + C_{33} \right) + \frac{2}{9} \left( C_{11} + C_{12} + C_{13} \right) \\
B &= 3 \left( 2S_{11} + S_{33} \right) + 2 \left( S_{12} + 2S_{13} \right) \left[ -1 \right]^{-1} \\
\nu_x &= \frac{3B_x - 2G_x}{2(3B_x + G_x)} \\
E_x &= \frac{9G_xB_x}{3B_x + G_x}
\end{align*}
\]

Where Sij is the elastic flexibility tensor, Poisson’s ratio and Young’s modulus can then be calculated:

Where X = Reuss, Voigt or Hill. The calculation results are shown in Table 3. The calculated bulk moduli of Reuss, Voigt and Hill are 186.0, 179.7, 18.2 GPa, respectively, which are consistent with the calculated values (179 GPa [25], 171.9 GPa [30]) and experimental value (182.0 GPa [14]) agree well, indicating that the calculation method is reasonable. The shear modulus is 134.5, 129.3, 131.9 GPa, which is close to the value in the literature (140 GPa [25]). Bulk modulus B and shear modulus G represent the ability of materials to resist compressive deformation and shear strain, respectively. The ratio of shear modulus and bulk modulus G/B is widely used to characterize the ductility and brittleness of materials. According to an empirical criterion proposed by Pugh [33], when G/B > 0.57, the material is brittle, and when
G /B < 0.57, the material is ductile. In this paper, the G /B value of Al₄SiC₄ calculated by GGA-PBE method is 0.73, which is greater than the critical value of 0.57, indicating that Al₄SiC₄ is brittle, which is consistent with the predicted results of literature [26].

| Table 3. Calculated bulk modulus BX (X = V, R, H) (in GPa), shear modulus GX (in GPa), Young’s modulus EX (in GPa), Poisson’s Ratio νX with the literature results for comparison |
|-----------------|-----------------|-----------------|-----------------|
| Method          | BX (GPa)        | GX (GPa)        | EX (GPa)        |
| Pos.            | 180.6           | 179.7           | 180.2           |
| Calc.           | 172.0           | 171.7           | 179.0           |
| Exp.            | 182.0           | —               | —               |

3.3. Electronic property

Band structure is an important basis for material analysis. The band structure of Al₄SiC₄ is shown in Figure 2. The dotted line in the figure represents the Fermi level. It can be seen from the figure that the conduction band base of Al₄SiC₄ is located at the high symmetric point M in the first Brillouin region, and the valence band top is located at the high symmetric point G in the first Brillouin region, so Al₄SiC₄ has an indirect band gap, which is consistent with the results reported by Forster et al. [21]. The energy gap E_g = 1.076eV of Al₄SiC₄ is consistent with the calculated value (1.05eV [22], 1.12eV [26]), but lower than the experimental value (2-2.5eV [5]). Due to the deficiency of the calculation method in solving the excited state energy, the obtained band gap will be smaller than the experimental value, so the calculated value is smaller than the experimental value, but it does not affect the analysis of the band structure.

3.4. Optical property

3.4.1. Complex dielectric function

The macroscopic optical response of a solid can usually be described by the complex dielectric function ε(ω) = ε₁(ω) + iε₂(ω), where ε₁ and ε₂ are the real and imaginary parts of the complex dielectric function, respectively, and ω is the frequency of the photon. The calculated complex dielectric function curves of hexagonal crystal phase Al₄SiC₄ in the polarization direction of incident light along the a axis (100) and the c axis (001) are shown in Figure 4.

As can be seen from Figure 4, the static dielectric constant of Al₄SiC₄ in the direction of (100) and (001), that is, the value of zero frequency, is 7.74 and 8.96, respectively. In the direction of (100), in the low energy region, both the real and imaginary parts of the dielectric function increase with the increase of photon energy. The maximum value of the real part of the dielectric function at 4.38eV is 14, and the maximum value of the imaginary part at 5.86eV is 13.8, which is consistent with the results reported in the literature (the real part is 4.38eV [22], the imaginary part is 5.82eV [22]). Subsequently, the virtual part of the dielectric function decreases and approaches 0 after about 20 eV. The real part of the dielectric function decreases first and then rises, reaching the lowest value -4.12 at 9.07eV. The real part of the dielectric function increases slowly within the range of about 9 eV to
In the direction of (001), the real part of the dielectric function reaches a maximum of 15.7 at 3.71 eV, and the imaginary part reaches a maximum of 15.3 at 5.32 eV.

3.4.2. Complex refractive index

According to the relationship between dielectric function and complex refractive index: \( \varepsilon_1 = n^2 - k^2 \), \( \varepsilon_2 = 2nk \), (n is the refractive index, k is the extinction coefficient), the refractive index n and extinction coefficient k of the hexagonal crystal phase Al₄SiC₄ can be calculated along the polarization direction of the incident light along the a axis (100) and the c axis (001) with the photon energy. As shown in Figure 5.

As can be seen from Figure 5, the refractive index of Al₄SiC₄ at zero frequency in the direction of (100) and (001) is 2.78 and 2.99, respectively, which is consistent with the results reported in the literature (2.73 [22]). With the increase of photon energy, the refractive index first increases, then decreases and then increases. The refractive index along the direction (100) reaches a maximum value of 3.85 at 4.63 eV and a minimum value of 0.164 at 20.62 eV. The extinction coefficient starts to increase significantly at 2.02 eV, reaches a maximum value of 2.61 at 8.2 eV, and then decreases. The refractive index along the direction (001) reaches a maximum value of 4.06 at 3.94 eV and a minimum value of 0.159 at 19.58 eV. The extinction coefficient starts to increase significantly at 2.04 eV, reaches the first peak at 2.46 eV at 5.95 eV and then declines, then continues to rise to 8.43 eV, reaches the second peak at 2.50 eV, and then slowly decreases.

3.4.3. Absorption coefficient

Fig.6 shows the absorption coefficients of the hexagonal crystal phase Al₄SiC₄ along the polarization direction of the incident light along the a axis (100) and the c axis (001) with the photon energy. It can be seen that in the direction of (100) and (001), with the increase of photon energy, the absorption coefficient of Al₄SiC₄ first increases and then decreases, and the absorption coefficient is close to 0 after (0-2.5 eV) and 30 eV, respectively. The absorption coefficient reaches a peak value of \( 3.58 \times 10^5 / \text{cm} \) at 8.98 eV in the direction of (100), and \( 3.62 \times 10^5 / \text{cm} \) at 9.46 eV in the direction of (001).

3.4.4. Reflectance

Based on the relationship between reflectivity and rereflectivity [34]: \( R(\omega) = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2} \), n is refractive index, k is extinction coefficient. The reflectance curve of Al₄SiC₄ along the a axis (100) and c axis (001) of the incident light polarization direction along with the photon energy can be obtained, and the calculation results are shown in Fig.7. As can be seen from Fig.7, the reflectance of Al₄SiC₄ in the direction of (100) and (001) generally increases with the increase of photon energy, at first shows a wave rise and then a rapid decline, and reaches a maximum value of 0.642 and 0.628 at 18.0 eV and 17.8 eV, respectively. When the photon energy is greater than 22 eV, the reflectance in both directions is almost the same. In the visible light energy range of 1.6eV ~ 3.2eV, the reflectance of (100) direction is between 24% ~ 29%, and the reflectance of (001) direction is between 27% ~ 35%, but the latter is slightly larger than the former. Materials with reflectance greater than 25% are generally considered to have a metallic luster. As a result, Al₄SiC₄ has a metallic luster.

![Figure 4](image_url)

**Figure 4.** The complex dielectric functions of Al₄SiC₄

![Figure 5](image_url)

**Figure 5.** The complex refractive indexes of Al₄SiC₄

![Figure 6](image_url)

**Figure 6.** The absorption coefficients of Al₄SiC₄

![Figure 7](image_url)

**Figure 7.** The reflectivities of Al₄SiC₄
4. Conclusion

In this paper, the geometric structure parameters of the hexagonal crystal phase AlSiC4 are optimized by using the generalized gradient approximate mode conservation pseudopotential method based on the framework of density functional theory. The elastic constant, band structure, static density, complex dielectric constant, complex refractive index, absorption coefficient and reflectivity of the hexagonal crystal phase AlSiC4 are calculated and analyzed. It provides theoretical support for the practical application of hexagonal phase AlSiC4.

References