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Theoretical calculations of the hexagonality influence on the mechanical and thermal properties of SiC polytypes

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Abstract:

Silicon carbide is one of the most important semiconductor materials in different science fields because of its ability to appear in different crystalline arrangements, which affects its properties. Therefore, Theoretical calculations based on density functional theory (DFT) that performed with CASTEP code were used to investigate the mechanical and thermal properties of four commonly known silicon carbide polytypes 3C, 2H, 4H, and 6H. The calculations were compared with the available data from the experiments and the other's theoretical studies. Accordingly, the polytypesim effect on these properties was evaluated. The results showed that the four SiC polytypes satisfy the mechanical stability conditions. In addition, the different stacking sequences of the SiC tetrahedron gave a rise of diversity in the structure parameters, which caused in variation in the configuration nature of the bilayers among those polytypes. This difference affected their mechanical and thermal properties. The calculations showed that the cubic polytype has higher hardness and better toughness followed by 4H polytype. The 6H-SiC appeared to be the most brittle polytype followed by 2H and 4H. In addition, the 6H and 2H polytypes showed a higher stiffness. The high Debye temperature of SiC polytypes referred to a high heat capacity, high chemical bonding, and low expansion coefficient. Generally, an inverse relationship appeared between the thermal properties of SiC polytypes and their hexagonality.

Keywords: DFT, *Sic* Polytypes, Mechanical and Thermal Properties, Hexagonality Arrangement.

الحسابات النظرية لتأثير الترتيب الشبكي السداسي على الخواص والحرارية للأنواع المتعددة لكربيد السيليكون

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الملخص

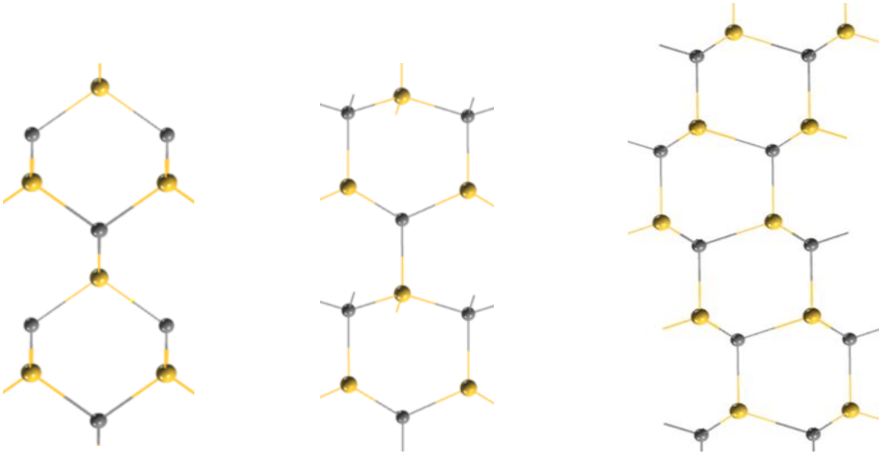
يعد كربيد السيليكون واحد من أهم المواد شبه الموصلة في مجالات العلوم المختلفة لقدرته على التشكل بترتيبات بلورية مختلفة مما يؤثر على خواصه. وعليه فقد تم استخدام نموذج البرمجة (CASTEP) والمعتمد على نظرية الكثافة الوظيفية (DFT) في اجراء بعض الحسابات النظرية للخواص الميكانيكية والحرارية لاكثر أربع ترتيبات بلورية معروفة لكربيد السيليكون وهي (C, 2H, 4H, 6H3)، ومن ثم مقارنتها مع بعض الدراسات النظرية والعملية السابقة. وفقا لذلك، تمت دراسة مدى تأثير نسبة الترتيب السداسي على خواص الأنواع المتعددة لكربيد السيليكون. النتائج أظهرت أن أنواع كربيد السيليكون الأربعة تحقق شروط الاستقرار الميكانيكي. من ناحية أخرى فإن الاختلاف في تسلسلات التراص لرباعي الاسطح في بلورات SiC أدى إلى تغير في المسافات البينية بين ذرات السيليكون والكربون في الشبكة البلورية لكربيد السيليكون مما نتج عنه اختلاف في ترتيب الطبقات الثنائية. هذه الاختلافات أثرت بدورها على الخواص الميكانيكية والحرارية لأنواع كربيد السيليكون الأربعة. أظهرت النتائج أن الترتيب الشبكي المكعب لكربيد السيليكون (C3) هو الأكثر صلابة ومتانة يليه الترتيب 4H. بالنسبة للترتيب السداسي فإن 6H هو الأكثر هشاشة يليه 2H ومن ثم 4H. كما أن 6H و H2 يتميزان بخاصية بلاستيكية أعلى من سواهما. بالإضافة إلى ذلك فإن درجة حرارة ديباي المرتفعة لانواع SiC والمتحصل عليها من الحسابات أشارت إلى سعة حرارية عالية وترابط كيميائي عالي ومعامل تمدد منخفض، كما أظهرت النتائج أن أدنى قيمة تم تسجيلها

لحرارة ديباي كانت للترتيب المكعب 3C، أما بالنسبة للأنواع السداسية فإن حرارة ديباي تزداد كلما كانت نسبة الترتيب السداسي أقل مما يشير إلى علاقة عكسية بين الخواص الحرارية ونسبة الترتيب الشبكي السداسي لانواع SiC المتعددة.

الكلمات المفتاحية: DFT، أنواع SiC المتعددة، الترتيب الشبكي السداسي، الخواص الميكانيكية، الخواص الحرارية.

Introduction

Silicon carbide is a semiconductor compound of two group IV elements, silicon and carbon. The main block of SiC is a tetrahedron of Si (C) atom bonded to four C (Si) atoms where Si-Si (C-C) distance is 3.08 A$^\circ$ and Si-C bond length is 1.89 A$^\circ$. Silicon carbide crystallizes in different polytypes. The close packed structures of SiC crystals consist of bilayers of Si and C atoms, and each bilayer occupies one of three different positions. There are two ways to arrange two bilayers with respect to each other. As shown in figure (1), if the orientation of the tetrahedral in the top layer coincides with that of the bottom layer, then the stacking type will lead to cubic structure. Whereas if the tetrahedra of the bottom and the top layers are rotated by 60° with respect to each other, the stacking type will lead to hexagonal structure. Therefor the stacking sequences of these bilayers characterize the polytype from the other polytypes. Recently, more than 200 polytypes of SiC are known with a same chemical composition and different stacking sequence where the number of atoms in a unit cell varies from polytype to polytype influencing its physical and electrical properties. Among these polytypes, there are only few common polytypes such as 3C with pure cubic structure and 2H, 4H, and 6H with 100%, 50%, and 33% hexagonality respectively.



Pure Cubic Pure Hexagonal Mixed Cubic and hexagonal

Figure 1. The ways of SiC tetrahedrons to arrange together

Silicon carbide is one of the most intensively studied semiconductors experimentally and theoretically because of its unique properties. In addition to its ability to appear in different structures with variety in the electronic and optical properties, SiC polytypes have had a great attention as mechanical materials. To date, many experimental and theoretical studies were introduced to investigate the SiC properties in order to solve and overcome challenges that can restrict its applications in the engineering and scientific fields.

In recent years, ab initio calculations of mechanical properties of crystalline solids have reached to a high level of accuracy where the calculated parameters are very close to the experimentally measured values. Among these calculations, the elastic constants calculations are the most essential parameters that used to investigate the mechanical properties because many other mechanical parameters are related to these constants and can be derived from them [1][2][3].

The elastic constants and moduli give a great information about the bonding characteristic and interatomic interaction, structural stability of the material, phase transitions, and material strength, where, the elastic properties describe the nature of the operating forces that acting on the material. As known, there are only three elastic constants for the cubic structure of SiC, C_{11}, C_{12}, and C_{44}, while the crystals with a hexagonal structure have five independent elastic constants, C_{11}, C_{12}, C_{13}, C_{33}, and C_{44}. According to the obtained values of elastic constants, we can test the mechanical stability conditions of the crystals where:

The mechanical stability condition of the cubic structure [4][5] is:

$$C_{11}>0,\ C_{44}>0,\ C_{11}>C_{12},\ (C_{11}+2C_{12})>0$$

Whereas the mechanical stability condition of the hexagonal structure [6][7] is:

$$C_{44}>0,\ C_{11}>|C_{12}|,\ (C_{11}+2C_{12})\ C_{33}>2C_{13}^2$$

In addition, elastic constants are used to describe the elastic moduli as expressed in the Voigt- Reuss-Hill (VRH) approximations where the Voigt represents the upper limit of the polycrystalline constants obtained by assuming a uniform strain throughout the polycrystal, and the Reuss represents the lower limit of the constants obtained by assuming a uniform stress throughout the polycrystal. Therefore, the shear modulus is given by **$G = 1/2(G_V+G_R)$**, and Bulk modulus is given by **$B = 1/2(B_V+B_R)$**.

Young and shear moduli are considered as significant parameters and better correlated with hardness and stiffness than Bulk modulus, where, the material with low young modulus has low stiffness**.** The brittleness of the material can be characterized by Poisson's ratio, where the brittle material has a low Poisson's ratio. The ratio of the bulk modulus to the shear modulus (B/G) can characterize the ductility and brittleness of the material where the bulk modulus represents the resistance to fracture and the shear modulus represents the resistance to plastic deformation. In general, the material can be described as a brittle material when B/G is low (< 1.75) and a ductile material when B/G is high (> 1.75) [8][9][10][11]. Recently, the Cuchy Pressure (**$C.P. = C_{12} - C_{44}$**) was applied to identify the ductility where the positive value of C.P. refers to a ductile material while the negative value refers to a brittle material [12].

The thermal properties of SiC polytypes were evaluated by calculating Debye temperature (**Θ_D**). Debye temperature correlates the elastic properties of the crystal with its thermodynamic properties such as thermal conductivity, specific heat, lattice enthalpy, and thermal expansion coefficient.

Debye temperature of solids can be calculated from the averaged sound wave velocity that integrated over several crystal directions and obtained using the shear modulus and bulk modulus [13][14] where:

$$\Theta_D = 2\hbar V_m / (a_o K_B)$$

Where $\hbar$ and K_B are Plank's and Boltzmann's constants, a_o is the unit cell parameter, and V_m the speed of the sound which can be calculated from the relation:

$$V_m = \{ [1/3] [(2/V_t^3) + (1/V_l^3)]\}^{-1/3}$$

Where V_t and V_l are the transverse and longitudinal velocities respectively, and both can be calculated using Naviers' equations from bulk and shear moduli and the mass density [15] where:

$$V_t = (G/\rho)^{1/2} \qquad \text{and} \qquad V_l = [(3B + 4G)/3\rho]^{1/2}$$

The Computation Process

The present first-principles calculations were performed using the Cambridge Serial Total Energy Package (CASTEP) code within the plane-wave pseudopotential approach, and the exchange-correlation energy was approximated using Perdew-Burke-Ernzorhof generalized gradient approximation (PBE-GGA) functional. The calculations were performed for the contributions from valence electrons (2S2 and 2P2 for C, and 3S2 and 3P2 for Si) in order to achieve more accuracy and reduce the computational cost and complexity.

The Brillion zone (BZ) of these crystals was obtained using Monkhorst-Pack method where the cubic crystal (3C) SiC of (621) atoms with a 5x5x5 mesh was built with F43m space group while the hexagonal crystals (2H, 4H, and 6H) SiC of (525, 681, and 548) atoms respectively with a 5x5x2 mesh were built with P63mc space group. This method divides the Brillion zone into an equally spaced grid of K points, so the symmetry operation of the crystal reduces integrations in K space.

Throughout the calculations of the mechanical properties of the crystals, the cut-off energy was 310 eV, the maximum stress was zero GPa, the maximum displacement was 0.002 A°, and the maximum force was 0.05 eV/A°. Geometry optimizations were performed by the conjugate gradient method where all the atoms were allowed to relax during the optimization.

Focusing on the most common SiC polytypes (3C, 2H, 4H, & 6H), the elastic properties of the perfect SiC crystals were calculated, and then the effect of the hexagonality on the SiC polytypes properties was investigated.

Results And Discussion

The elastic constants, bulk modulus (B), young modulus (Y), shear modulus (G), Pugh's ratio (B/G), Poisson's ratio (v), and Debye temperature (θ_D) of SiC polytypes were computed (in GPa) and presented in table (1). The obtained values showed a reasonable agreement of the present calculations with the results estimated by experiments and theoretical computations. Experimentally, the present values of the elastic constants of 3C, 4H, and 6H were comparable of those of Feldman [16], Kamitani [17], and Djemia [18].

Table 1. The calculated elastic constants and moduli in (GPa) and Debye temperature of SiC polytypes using DFT

Elastic Constants	2H	4H	6H	3C
C_{11}	490	512	485	378
C_{12}	88	99	88	122
C_{13}	37	48	37	-
C_{33}	520	552	529	-
C_{44}	147	160	159	243
B	202	219	203	207
Y	472	290	466	318
G	188	197	192	179
B/G	1.074	1.112	1.057	1.156
ν	0.144	0.154	0.14	0.164
Θ_D	1145	1152	1168	1131

According to the obtained elastic constants and low Poisson's ratio, the four structures of SiC polytypes are stable and satisfy the mechanical stability conditions. The Poisson's ratio as shown in figure (2) refers to that the cubic polytype 3C has the highest ratio among the polytypes whereas the 6H-SiC has the lowest ratio which means that 6H-SiC is the most brittle polytype followed by 2H and 4H. The calculated values of Young, bulk, shear modulus, and the B/G ratio, as presented in figure (3), shows that the cubic polytype has somewhat the higher values, which indicates that it has higher hardness and better toughness followed by 4H polytype whereas the 6H and 2H polytypes show a higher stiffness with small differences. The shorter bonds, bigger bulk and shear modulus of 4H-SiC also indicate of its hardness comparing to the other hexagonal polytypes. The calculated bulk and shear modulus and Poisson's ratio showed a good agreement with those of Carnahan, R. D. [19] and Munro, R. G. [20]. Comparing to the others computations, our calculated values of elastic constants and moduli of 3C-SiC showed a reasonable agreement with Vashishta [21], Lu [22], Lebga [23], and Fan [24] results. The evaluated elastic constants and moduli of the hexagonal polytypes were found in great agreement with the obtained values of Huang [25], Umeno [26], Pizzagalli, L. [27], and Yao [28].

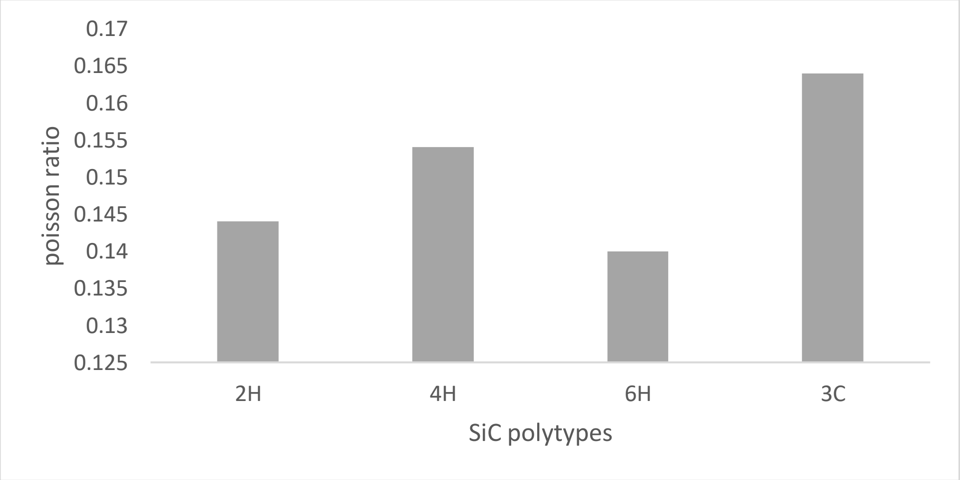


Figure 2. The calculated Poisson's ratio of the four SiC polytypes.

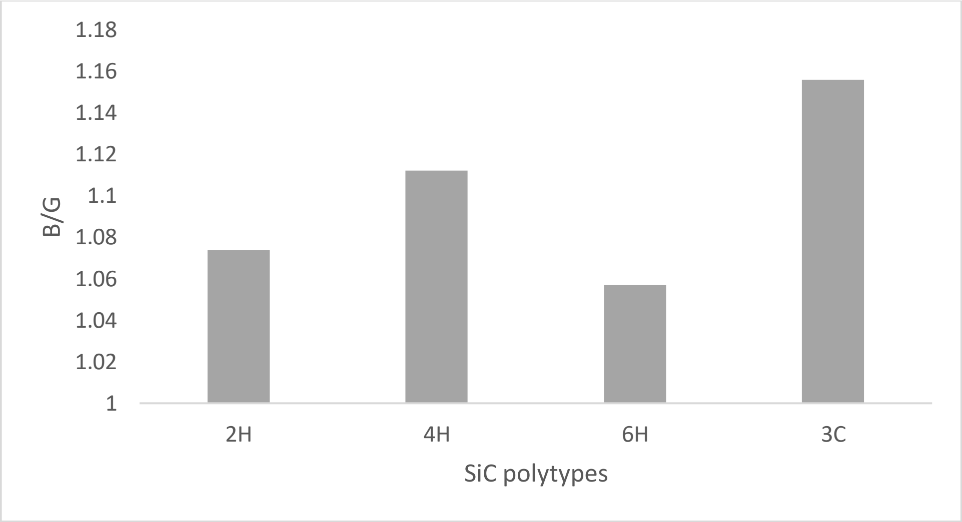


Figure 3. The calculated Pugh's ratio of the four SiC polytypes.

The thermal properties of the SiC polytypes can be evaluated from the Debye temperature. Debye temperatures of the most crystals are around 200-400K. The SiC polytypes showed high Debye temperatures, which implies to a high heat capacity, high thermal conductivity, and a high chemical bonding that refers to a hard material with a large wave velocity, and a low expansion coefficient. In addition, the calculated values imply to the inverse relationship between the hexagonality and the thermal properties of the hexagonal SiC polytypes as shown in figure (4) where the highest Debye temperature was obtained by 6H polytype.

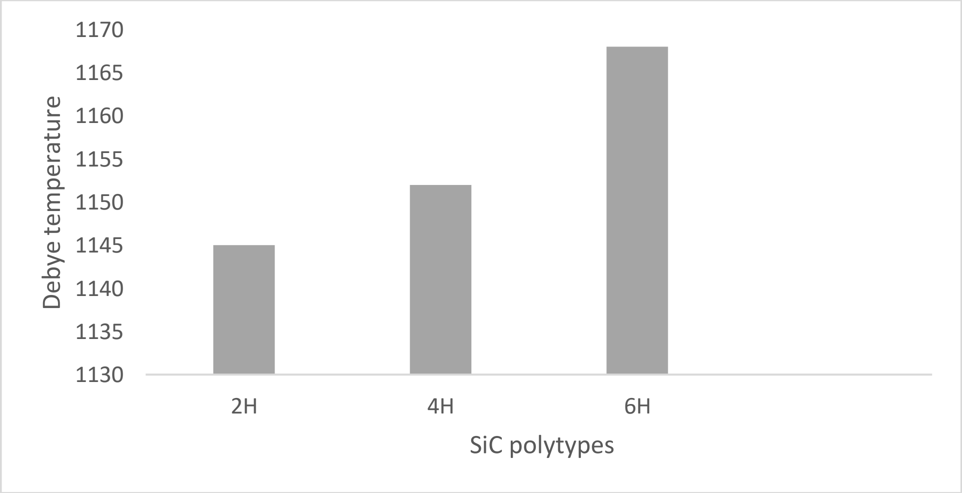


Figure 4. The relationship between Debye temperature and the hexagonality of SiC polytypes

The obtained values of Debye temperature were comparable of the obtained values by Zywietz [29] and Islam [15].

Conclusion

The calculations based on Density functional theory were employed to investigate the mechanical and thermal properties of SiC polytypes, and the influence of the stacking sequence on these properties. The stacking sequence of the bilayers creates diversity in the bond's length and angles, which affects the lattice structures of the polytypes, and thus the mechanical and thermal features. The calculated elastic constants and modules referred to the high hardness and toughness of the cubic SiC comparing to the hexagonal SiC polytypes. Among the three SiC hexagonal polytypes, 4H-SiC with 50% hexagonality showed higher hardness and toughness whereas the other two polytypes showed a higher stiffness. According to the calculated values of Debye temperature, the SiC polytypes have great thermal properties. The concluded observations improve the dependence of the calculated mechanical and thermal properties of the SiC polytypes on the hexagonality. Our results showed a good agreement with the experimental results and other theoretical calculations. According to the achieved results, SiC polytypes have notable features and manufacturing ability with a high potential in devices applications.

References

1. Willardson, R. K., & Weber, E. R. (1998). *SiC materials and devices* (Vol. 52). Academic Press.
2. Saddow, S. E., & Agarwal, A. K. (2004). Advances in Silicon Carbide Processing and Applications. Artech House.
3. Fan, J., & Chu, P. K. (2014). General properties of bulk SiC. In *Silicon carbide nanostructures: fabrication, structure, and properties* (pp. 7-114). Cham: Springer International Publishing.
4. Wu, Z., Hao, X., Liu, X., & Meng, J. (2007). Structures and elastic properties of Os N 2 investigated via first-principles density functional calculations. *Physical Review B—Condensed Matter and Materials Physics*, *75*(5), 054115.
5. Ding, Y. C., Chen, M., Gao, X. Y., & Jiang, M. H. (2012). Theoretical investigation on the electronic structure, elastic properties, and intrinsic hardness of Si2N2O. *Chinese Physics B*, *21*(6), 067101.
6. Watt, J. P., & Peselnick, L. (1980). Clarification of the Hashin-Shtrikman bounds on the effective elastic moduli of polycrystals with hexagonal, trigonal, and tetragonal symmetries. *Journal of Applied Physics*, *51*(3), 1525-1531.
7. Wu, Z. J., Zhao, E. J., Xiang, H. P., Hao, X. F., Liu, X. J., & Meng, J. (2007). Crystal structures and elastic properties of superhard Ir N 2 and Ir N 3 from first principles. *Physical Review B—Condensed Matter and Materials Physics*, *76*(5), 054115.
8. Pugh, S. F. (1954). XCII. Relations between the elastic moduli and the plastic properties of polycrystalline pure metals. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, *45*(367), 823-843.
9. Ravindran, P., Fast, L., Korzhavyi, P. A., Johansson, B., Wills, J., & Eriksson, O. (1998). Density functional theory for calculation of elastic properties of orthorhombic crystals: Application to TiSi 2. *Journal of Applied Physics*, *84*(9), 4891-4904.
10. Liu, X. J., Li, L. F., & Lu, F. (2013). Optical properties and mechanical properties of C, Si, Ge and 3C-SiC materials calculated from first principles theory. *arXiv preprint arXiv:1301.1745*.
11. Fan, Q., Chai, C., Wei, Q., & Yang, Y. (2016). Two novel C3N4 phases: structural, mechanical and electronic properties. *Materials*, *9*(6), 427.
12. Jiang, M., Zheng, J. W., Xiao, H. Y., Liu, Z. J., & Zu, X. T. (2017). A comparative study of the mechanical and thermal properties of defective ZrC, TiC and SiC. *Scientific reports*, *7*(1), 9344.
13. Stephanos, J. J., & Addison, A. W. (2023). *Chemical thermodynamics and statistical aspects: questions to ask in fundamentals and principles*. Elsevier.
14. Clarke, D. R. (2003). Materials selection guidelines for low thermal conductivity thermal barrier coatings. *Surface and Coatings Technology*, *163*, 67-74.
15. Islam, M. (2024). A comprehensive investigation on the physical properties of SiC polymorphs for high-temperature applications: A DFT study based on GGA and hybrid HSE06 exchange correlation functionals. *Nuclear Materials and Energy*, *38*, 101631.
16. Feldman, D. W., Parker Jr, J. H., Choyke, W. J., & Patrick, L. (1968). Phonon dispersion curves by raman scattering in SiC, Polytypes 3 C, 4 H, 6 H, 1 5 R, and 2 1 R. *Physical Review*, *173*(3), 787.
17. Kamitani, K., Grimsditch, M., Nipko, J. C., Loong, C. K., Okada, M., & Kimura, I. (1997). The elastic constants of silicon carbide: A Brillouin-scattering study of 4H and 6H SiC single crystals. *Journal of applied physics*, *82*(6), 3152-3154.
18. Djemia, P., Roussigné, Y., Dirras, G. F., & Jackson, K. M. (2004). Elastic properties of β-SiC films by Brillouin light scattering. *Journal of applied physics*, *95*(5), 2324-2330.
19. Carnahan, R. D. (1968). Elastic properties of silicon carbide. *Journal of the American Ceramic Society*, *51*(4), 223-224.
20. Munro, R. G. (1997). Material properties of a sintered α-SiC. *Journal of physical and chemical reference data*, *26*(5), 1195-1203.
21. Vashishta, P., Kalia, R. K., Nakano, A., & Rino, J. P. (2007). Interaction potential for silicon carbide: A molecular dynamics study of elastic constants and vibrational density of states for crystalline and amorphous silicon carbide. *Journal of applied physics*, *101*(10).
22. Lu, Y. P., He, D. W., Zhu, J., & Yang, X. D. (2008). First-principles study of pressure-induced phase transition in silicon carbide. *Physica B: Condensed Matter*, *403*(19-20), 3543-3546.
23. Lebga, N., Bouamama, K., Djemia, P., & Chérif, M. (2022). Theoretical study of second and third order elastic constants of β-SiC. *Journal of Physical & Chemical Research*, *1*(2), 16-24.
24. Fan, Q., Chai, C., Wei, Q., & Yang, Y. (2016). The mechanical and electronic properties of carbon-rich silicon carbide. *Materials*, *9*(5), 333.
25. Huang, Z., Lü, T. Y., Wang, H. Q., & Zheng, J. C. (2015). Thermoelectric properties of the 3C, 2H, 4H, and 6H polytypes of the wide-band-gap semiconductors SiC, GaN, and ZnO. *AIP Advances*, *5*(9).

26. Umeno, Y., Kubo, A., & Nagao, S. (2015). Density functional theory calculation of ideal strength of SiC and GaN: Effect of multi-axial stress. *Computational Materials Science*, *109*, 105-110.
27. Pizzagalli, L. (2014). Stability and mobility of screw dislocations in 4H, 2H and 3C silicon carbide. *Acta Materialia*, *78*, 236-244.
28. Yao, H., Ouyang, L., & Ching, W. Y. (2007). Ab initio calculation of elastic constants of ceramic crystals. *Journal of the American Ceramic Society*, *90*(10), 3194-3204.
29. Zywietz, A., Karch, K., & Bechstedt, F. (1996). Influence of polytypism on thermal properties of silicon carbide. *Physical Review B*, *54*(3), 1791.