



IR-Raman of Silicon Carbide Nanocrystal Cluster and Vibrational Spectroscopy Properties at the *PBE/6–31G*

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Abstract

The IR and Raman spectra are implemented to investigate the vibrational properties for silicon carbide (SiC) by using the density functional theory (DFT) at the PBE/6–31G level and include the polarization functions basis. The vibrational spectrum frequencies were studied also for the reduced masses, force constants, vibration intensities and depolarization spectra. In the last section, a comparative account changes the size-related in certain frequencies of vibrational at SiC diamondoids with regards to the bulk in experimental.

All results showed decrease the energy gap and density of states with increasing the size from diamantane to octamantane while the highest peak of bond length has register at 1.93 Å in octamantane. The tetrahedral angles of octamantane is 109° then that is much closer to the ideal value 109.2°. The high reduced mass mode (HRMM) and high force constant mode (HFCM) were larger than of the diamondoids in tetramantane were found 465.11 cm⁻¹ and 864.40 cm⁻¹ respectively.

Introduction

The theoretical calculations of the infrared vibrational frequency and the Raman lines of SiC nanocrystal cluster and the variation in these vibrations from molecular to bulk size have been carried out earlier [1]. The cluster full geometrical optimization calculations are available to execute with DFT in Gauss View 05 program [2]. The present work is concerned with the theoretical calculations of infrared vibrational frequency lines of diamond nanocrystals and the variation in these vibrations from molecular to bulk size [3]. The variations appreciation in the dissimilar properties from the molecular to the bulk-scale through the nano is substantial in order to learn how to deal with these materials in their nanotechnology application.

Recently, diamondoids are the collection of molecules with an increasing number of atoms and of varying sizes, have been found to be the building blocks of nano materials [4].

Theory

All-electron density functional theory (DFT) at generalized gradient approximation level of Perdew, Burke, and Ernzerhof (PBE) is used. The PBE/6–31G basis set that contains the functions polarization are incorporated in the present calculations. At first, the geometrical optimization is performed followed by the frequency and vibrational analysis. The frequencies are multiplied by an appropriate scaling factor (0.986) usually assigned to present method and basis set (PBE/6–31G) [5]. All calculations are performed using Gaussian 09 program [6].

The nomenclature of the diamondoids follows the number of cages in each diamondoid. As an example, diamantane contains two cages while octamantane contains eight cages [7] shown in fig. (1) using the “GaussView05” software.

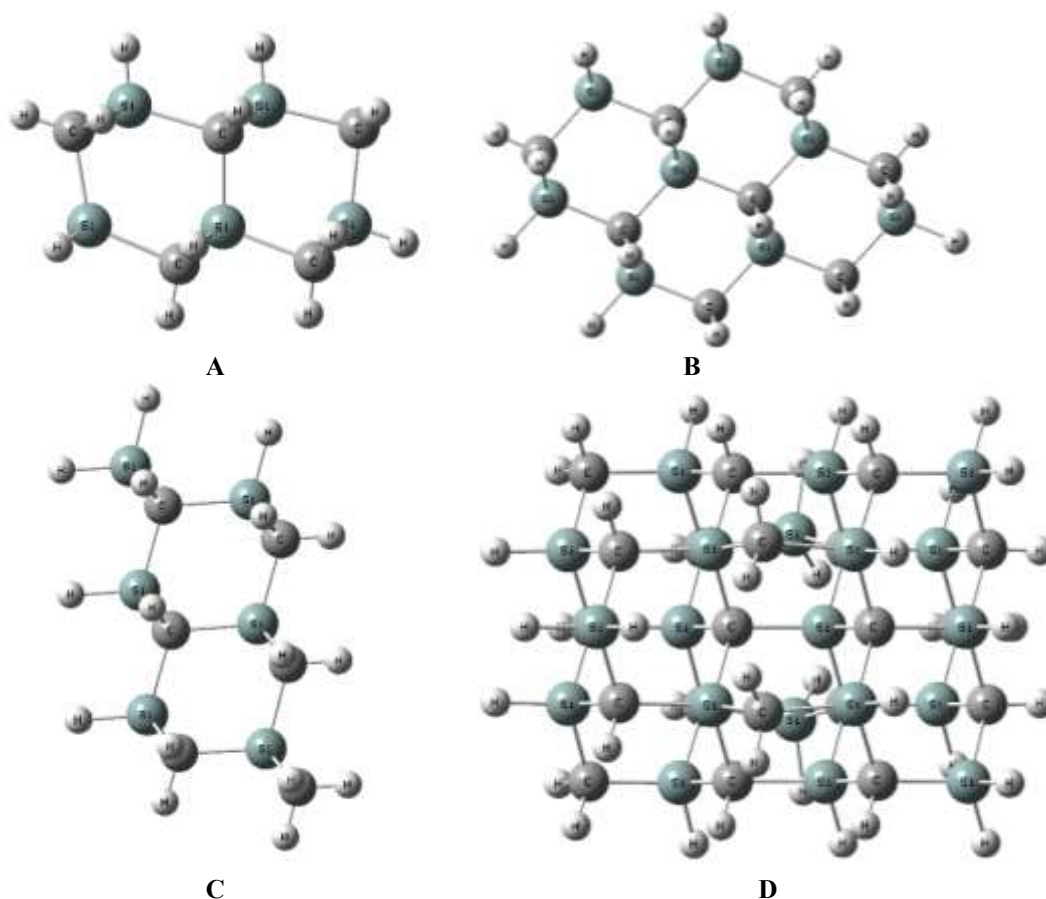


Fig (1). Shape of geometrically optimized of SiC- diamondoids of
A- diamantane $\text{Si}_7\text{C}_7\text{H}_{20}$ **B- tetramantane $\text{Si}_{11}\text{C}_{11}\text{H}_{28}$**
C- hexamantane $\text{Si}_{13}\text{C}_{13}\text{H}_{30}$ **D- octamantane $\text{Si}_{20}\text{C}_{20}\text{H}_{42}$**

Results and discussion

We can see the difference between the energy gap of the smallest diamondoids considered in the present work, i.e., SiC-diamantane and SiC-octamantane. The energy gap reduces from 5.71 eV in SiC-diamantane to 4.35 eV in SiC-octamantane shown in fig. (2). The smallest gap recorded in our calculations is 4.35 eV

for SiC-octamantane. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) have all negative values in fig. (3). These values show that extraction of an electron or addition of an external electron requires some external energy.

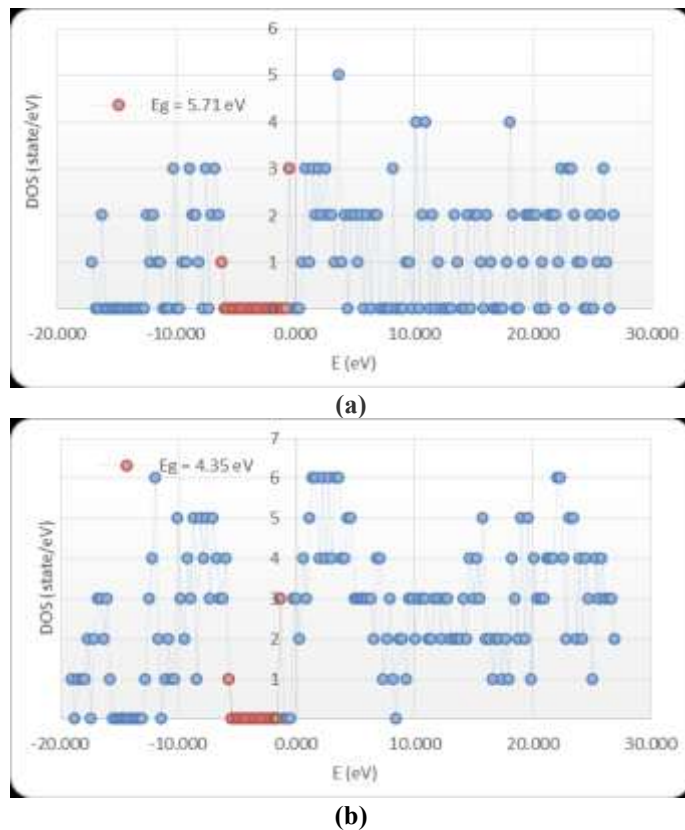


Fig. (2) The density of states (DOS) as a function of the energy level of: (a) SiC-diamantane and (b) SiC-octamantane

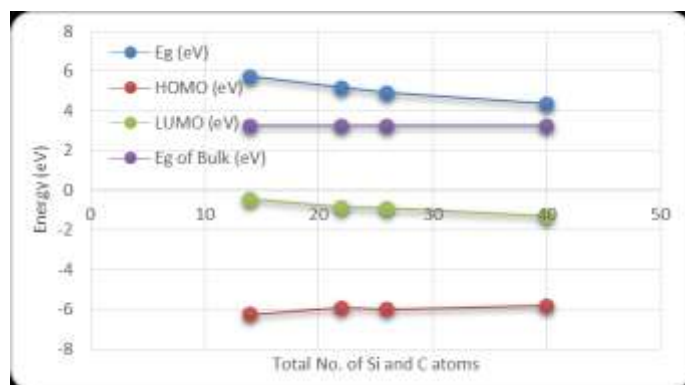
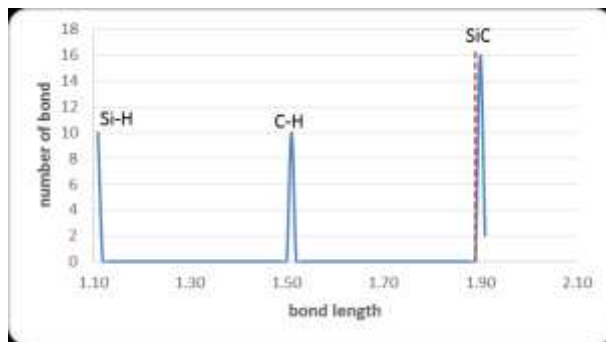


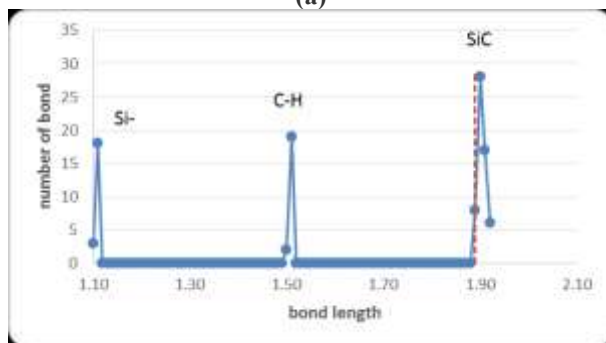
Fig. (3) Energy gap, HOMO, and LUMO levels as a function of the total number of Si and C atoms in SiC diamondoids using PBE/6–31G basis set

Regarding the bond lengths of SiC-diamantane and SiC-octamantane, the short bonds are Si-H and C-H, respectively. A small number of bonds in SiC-diamantane do not allow the true statistical features of these bonds. In SiC-octamantane, Si-H and C-H bonds show a high sharp peak. Si-N bond have many peaks depending on the number of hydrogen atoms attached to Si and C atoms. In SiC-diamantane, this bond value is smallest when both Si and C are linked to a single atom of hydrogen. It is about 1.89 Å and corresponds to the high peak for diamantane. The longest bond is 1.91 Å, which is near the far

diamantane molecule ends in which the core atoms (Si or C) is connected to two atoms of hydrogen. The location of the bond in the molecule affects its value that explains the several peaks for SiC-diamantane. SiC-octamantane, on the other hand, has a different situation that the spectrum of bonds in case of SiC-octamantane lies in the range of (1.91-1.93) Å with the highest peak at 1.93 Å. The experimental bond length of bulk SiC (1.89 Å) is within SiC-diamantane and SiC-octamantane bond distribution are shown in fig. (4).



(a)

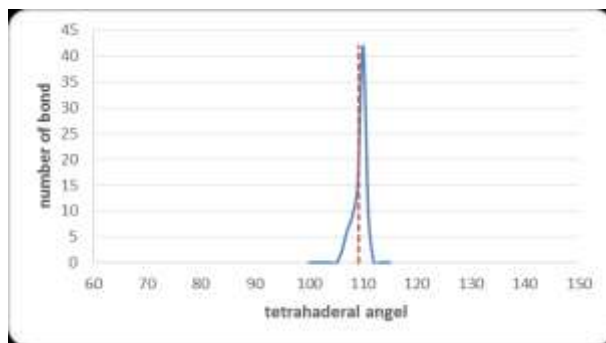


(b)

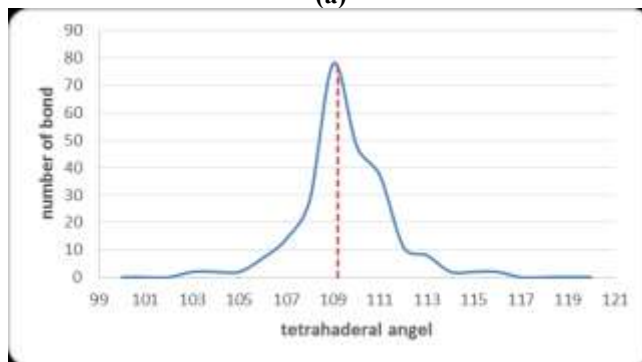
Fig. (4) The density of bonds: (a) SiC-diamantane, (b) SiC-octamantane. The experimental SiC bond length of (1.89) Å represents in dashed line

Fig. (5) shows the comparison between the density of tetrahedral angles in SiC-diamantane and the density of tetrahedral angles in SiC-octamantane. In a piece of bulk, far from the surface, all tetrahedral angles should have a value of 109.2° [8], the highest peak of SiC-diamantane is at 110°, while that of SiC-

octamantane is at 109°. The tetrahedral angles of diamantane and octamantane are much closer to the ideal value of 109.2°. This is due to the effect of surface reconstruction that has an effect on all atoms in SiC-diamantane and SiC-octamantane (all the atoms are bonded to hydrogen surface atoms).



(a)



(b)

Fig (5). The density of tetrahedral angles in SiC: (a) diamantine, (b) octamantane. The ideal value of zincblende structure at 109.2° represents in dashed line.

This might be true for the angles $\pm 180^\circ$ in SiC-diamantane, whereas in SiC-octamantane, all dihedral angles should have one of these values: -180° , -60° , 60° and 180° , in the bulk zincblende structure. It is

not completely true for the angles -60° and 60° . For SiC-octamantane, the situation improves for the angles near -59° and 59° that become closer to their ideal values in fig. (6).

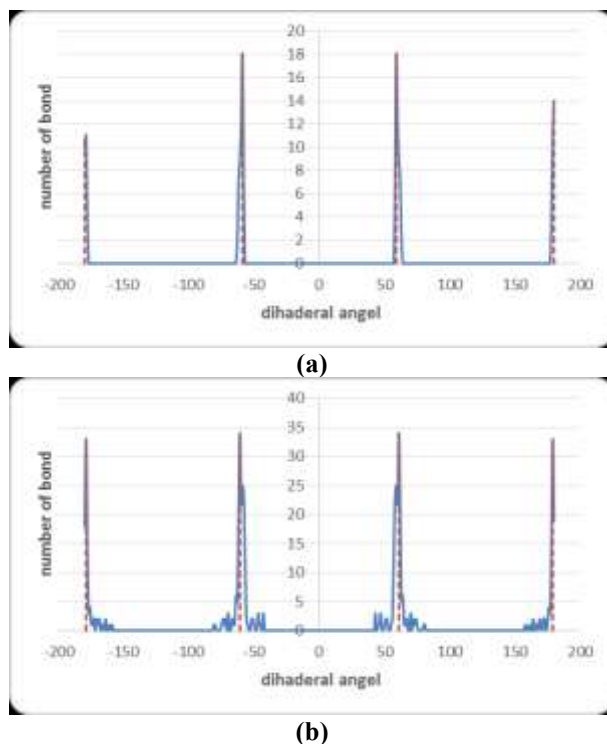


Fig (6). The density of dihedral angles in SiC (a) diamantane and (b) octamantane, in this case, PBE/6–31G basis sets are used. The dashed lines show the ideal value of this angle in bulk zincblende crystals, i.e., $\pm 60^\circ$ or $\pm 180^\circ$

The reduced masses of SiC-diamondoid vibrations, the left parts of Si-C vibrations are larger than the right parts of H vibrations and the right part is nearly

equal to 1 shown in fig. (7). The high reduced mass mode (HRMM) of tetramantane is larger than of the other diamondoids.

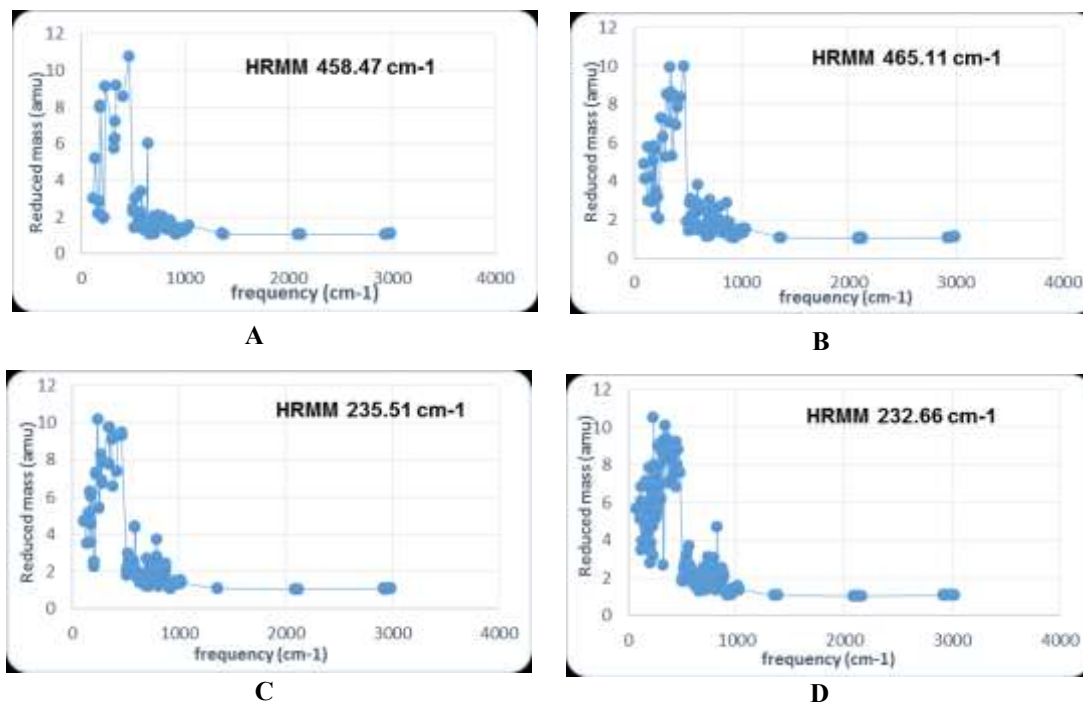


Fig. 7: SiC-diamondoids reduced mass as a function of vibration frequency of
A- diamantane $\text{Si}_7\text{C}_7\text{H}_{20}$ B- tetramantane $\text{Si}_{11}\text{C}_{11}\text{H}_{28}$
C- hexamantane $\text{Si}_{13}\text{C}_{13}\text{H}_{30}$ D- octamantane $\text{Si}_{20}\text{C}_{20}\text{H}_{42}$

SiC-diamondoid force constants as a function of vibrational frequency. As deduced from a part of the statistical difference between the numbers of vibration frequencies of all SiC-diamondoids, all shapes as shown in fig. (8) are nearly similar and

begin from approximately 0 cm^{-1} of Si-C vibrations and ends at less than 400 cm^{-1} , whereas right parts of H vibrations start at approximately 465 cm^{-1} and ends at nearly 2940 cm^{-1} .

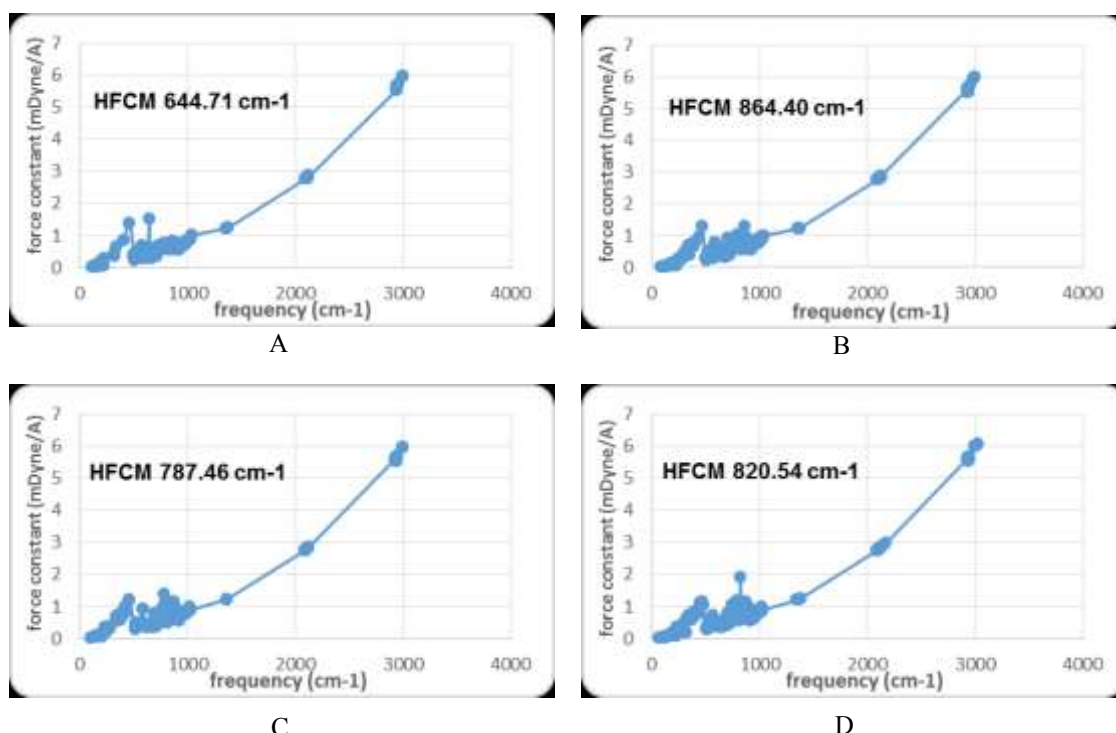


Fig. 8: Force constant of SiC- diamondoids as a function of frequency of
A- diamantane diamantane $\text{Si}_7\text{C}_7\text{H}_{20}$ B- tetramantane $\text{Si}_{11}\text{C}_{11}\text{H}_{28}$
C- hexamantane $\text{Si}_{13}\text{C}_{13}\text{H}_{30}$ D- octamantane $\text{Si}_{20}\text{C}_{20}\text{H}_{42}$

Table (1) gives the high reduced mass mode (HRMM) and high force constant mode (HFCM) with the differences SiC diamondoids. The (HRMM)

and (HFCM) of tetramantane is larger than that of the other diamondoids structures.

Table (1): high reduced mass mode and high force constant mode

SiC diamondoids	high reduced mass mode (HRMM) cm^{-1}	high force constant mode (HFCM) cm^{-1}
Diamantane $\text{Si}_7\text{C}_7\text{H}_{20}$	458.47	644.71
Tetramantane $\text{Si}_{11}\text{C}_{11}\text{H}_{28}$	465.11	864.40
Hexamantane $\text{Si}_{13}\text{C}_{13}\text{H}_{30}$	235.51	787.46
Octamantane $\text{Si}_{20}\text{C}_{20}\text{H}_{42}$	232.66	820.54

Conclusions

Diamondoids are the building blocks of SiC nanocrystals and bulk. These structures can be used to align the SiC properties nanocrystals and bulk with their corresponding molecular properties. The diamondoids exhibited minimal surface effects of relaxation, as deduced from their lengths of bond, angles of tetrahedral, angles of dihedral, energy gap and depolarization. SiC bond lengths were found to

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be affected by surface reconstruction. The shortest Si-C bond was noted between the atoms, not connected to the surface hydrogen atoms. Tetrahedral and dihedral angles showed a convergence to their ideal zincblende values when higher size diamondoids were obtained. The density of energy states also revealed the transition from single energy levels to band structure along with increasing higher size diamondoids.

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الخواص الطيفية التذبذبية (IR- Raman) للتركيب العنقودي النانوي لبلورة السيلكون كارباید

باستخدام PBE/6-31G

بلال كمال الراوي

قسم الفيزياء ، كلية التربية للعلوم الصرفة ، جامعة الانبار ، الانبار ، العراق

الملخص

في هذه الدراسة تم استخدام نظرية دالية الكثافة (DFT) في المستوى PBE/6-31G وتضمنت قواعد دوال الاستقطاب لايجاد طيفي IR- Raman للصفات التذبذبية للسيلكون كارباید.

الترددات الطيفية التذبذبية تم دراستها وتحليلها للكتل المختزلة ولثوابت القوى ولترددات التذبذبية وكذلك لطيف الاستقطاب.

كما تم مقارنة التغير بالاحجام المرتبطة بالترددات الاهتزازية في SiC-Diamondoids مع النتائج العملية.