Structural, Stabilities and Energetic properties of BGe_n clusters: A DFT Study

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***Abstract*— We present a systematic computational study based on the density functional theory (DFT) aiming tohigh light the possible effects of one B doping atom on the structural, energetic, and electronic properties of different isomers of Ge_{n+1} clusters in the atomic size range n = 1-5 atoms. By considering a large number of structures for each cluster size, the lowest-energy isomers are determined. The putative geometries show that the frameworks of the lowest-energy isomers are three-dimensional structures. The growth pattern behaviors and relative stabilities are analyzed from the binding energies, fragmentation energy and second-order difference of energies.**

Keywords*— *Ge Clusters, B atom, Density functional theory, Structural properties, energetic properties.

I. Introduction

Studying clusters of various chemical elements has become one of the modern research topics in both physical and chemical communities during the last four decades,[1,2]due to the size-dependent evolution of their fundamental properties and their technological applications in large variety of research fields going from catalysis to optoelectronics. Therefore, studying the changes in the structural and electronic properties of the cluster with its size become important.[3,4] Several theoretical calculations have been performed on pure and mixed neutral and charged clusters of group 14 elements [5,6]especially silicon and germanium.

Here, we report a systematic computational study based on the density functional theory (DFT) aiming to highlight the possible effects of one B atom on the structural and energetic properties of different isomers of Ge_{n+1} in the atomic size range n = 1-5 atoms.

II. Computational Methods

The electronic structure calculations of BGe_n (n = 1-5; q = 0, ±1) clusters were performed using the density functional theory (DFT)[7] as implemented in the SIESTA program.[8] The exchange correlation energy was evaluated using the generalized gradient approximation (GGA) parameterized by Perdew and Zunger[9]and by Perdew, Burke, and Ernserh of (PBE).[10]The self-consistent field (SCF) calculations were carried out with convergence criterion of $1x10^{-4}$ a.u. for total energy. The simulated clusters were placed in a big cubic supercell with a parameter of 40Å, including enough vacuums between neighboring clusters and periodic boundary conditions were imposed. To sample the Brillouin zone, only a single k-point centered at Γ was used because of the extended size of the supercell. Conjugated gradient method within Hellmann-Feynman forces was used and all the forces after structural relaxation were less than 10-3 eV/Å.

III. Results and Discussion

We report in Figure 1 the lowest-energy structures obtained for BGe_n (n = 1-5) and their corresponding isomers. Their energetic ordering is reported in Table 1. The BGe_n clusters adopt somehow similar structures than their corresponding Ge_{n+1}. In all cases, the arsenic atom is always located on the surface.

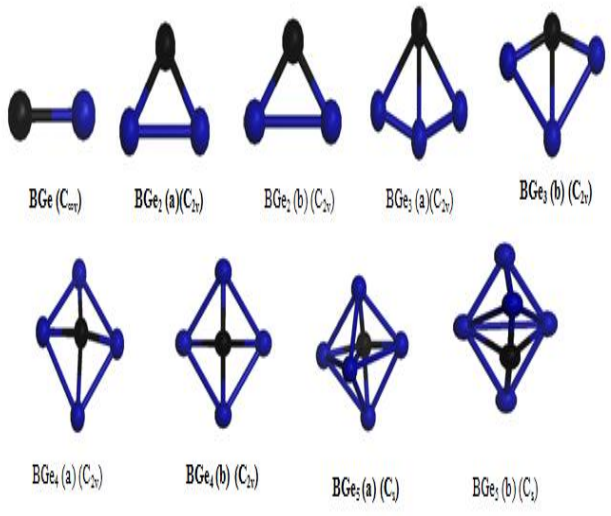

Fig 1.Most favorable structures and their corresponding isomers of BGe_n (n =1-5) clusters.

TABLE 1. Group of Symmetry, Binding Energ E_b (eV/atom) and Averaged Bond Length $a_{Ge\text{-}Ge}$ (Å), $a_{B\text{-}Ge}$ (Å) for BGe_n (n=1- 5) Clusters.

cluster size (n)	symmetry	E_b (eV/atom)	$a_{Ge\text{-}Ge}$ (Å)	$A_{B\text{-}Ge}$ (Å)
1	**(a)$C_{\infty v}$**	**1.748**	-	**2.052**
2	**(a)C_{2v}**	**2.464**	**2.788**	**1.965**
	(b)C_{2v}	2.464	2.788	1.964
3	(a) C_{2v}	2.769	2.577	2.105
	(b)C_{2v}	**2.769**	**2.577**	**2.105**
4	(a) C_{2v}	2.972	2.811	2.081
	(b)C_{2v}	**2.973**	**2.811**	**2.018**
5	**(a)C_{4v}**	**3.076**	**2.801**	**2.279**
	(b) C_{2v}	3.042	2.817	2.344

B. Relative Stability

➢ *Binding Energy*

The size dependence on the binding energies per atom for the lowest energy structures of Ge_{n+1} and BGe_n (n= 1-5) clusters are shown in Figure 2. As expected, the bonding energy is gradually increasing with increasing size, and this can be associated to the average number of neighbours increase per atom. For BGe_n, we observe that the binding energies are larger than those for Ge_{n+1}. An increase in the binding energy is obtained with 1.748 eV for n=2 to 3.076 eV for n=5.

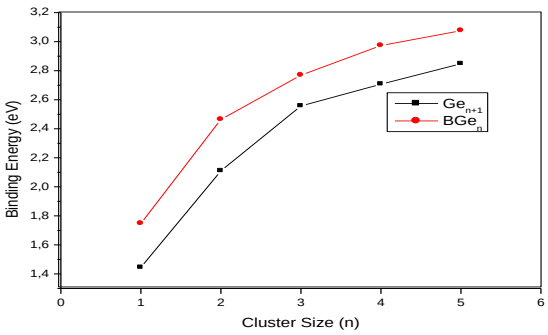

Fig 2. Evolution of the binding energy per atom for the lowest energy structures of Ge_{n+1} and BGe_n (n= 1-5) clusters as a function of cluster size.

➢ *Fragmentation Energy*

Figure 3 shows the plot of the size dependence on the fragmentation energies of Ge_{n+1} and BGe_n (n= 1-5) clusters. An oscillating behavior is observed. The clusters with large values of fragmentation energy are relatively stronger in thermodynamic stability than neighboring clusters. Consequently, the thermodynamic stabilities of Ge_4, BGe_2 and BGe_4 clusters are relatively strong.

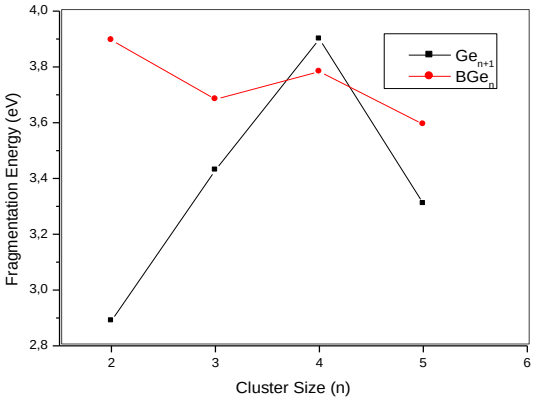

Fig 3. Evolution of the fragmentation energy of Ge_{n+1} and BGe_n (n= 1-5) clusters as a function of cluster size.

➢ *Second order difference*

The evolution of the second-order difference of energies for the most favorable structures of Ge_{n+1} and BGe_n (n=1-5) clusters as a function of the cluster size is plotted in Figure 4. The curve shows pronounced peaks for BGe_n at size n= 3 atoms. This suggests this cluster to be more favorable than their neighbors. It can also be seen that the curve of Ge_{n+1} clusters with range size n= 2, 3 and 5 exhibit higher stability than their neighbors.

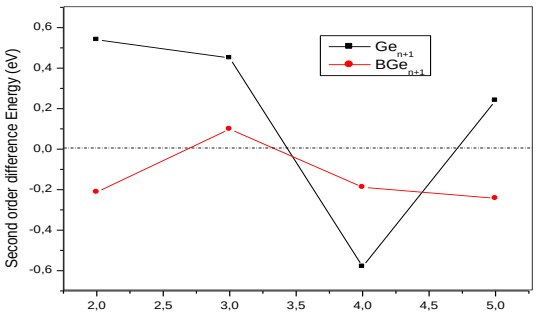

Fig 4. Evolution of the second-order difference of energy for the lowest energy structures of Ge_{n+1} and BGe_n (n=1-5) clusters as a function of cluster size.

IV. Conclusion

We have systematically investigated the structural and energetic properties of BGe_n (n = 1-5) clusters by means of DFT-based first principles quantum computations. The BGe_n clusters adopted somehow similar structures as those obtained for Ge_{n+1} .In all cases, the B-doping atom was found to always be located on the surface. Their relative stabilities have been examined through the calculated binding energies, fragmentation energies, and second-order difference of energies.

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