

Study of the Effect of Selenium Doping on the Geometries and Electronic Characteristics of Germanium Clusters (SeGe_n , $n = 1-20$) Using DFT Calculations

I. Zitouni*, K.E. Aiadi, O. Bentouila, M. Benaida, Z. Ayat

Laboratory of New and Renewable Energy in Arid and Saharan Zones – LENREZA, Ouargla University,
30000 Ouargla, Algeria

(Received 05 March 2021; revised manuscript received 15 April 2021; published online 20 April 2021)

A theoretical systematic investigation based on the calculating geometrical structures, stability, and electronic characteristics of the system (SeGe_n clusters, $n = 1-20$) was presented within the framework of density-functional theory (DFT) as implemented in the SIESTA simulation code. All the ground-state isomers obtained have 3D structures. Big SeGe_n clusters of size $n \geq 16$ exhibit higher binding energy. Likewise, the obtained second-order energy difference $\Delta_2 E$ results show that the positive maximum peaks at $n = 2, 4, 8, 11, 14, 17$, and 19 have private stability. This signifies that they have a greater stability character than their neighbors. The results of calculations of electronic properties such as highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap, vertical ionization potential (VIP) and vertical electron affinity (VEA) reveal that the SeGe_1 dimer is more stable than neighboring clusters. On the other hand, according to the HOMO-LUMO gaps analysis, we conclude that the $\text{SeGe}_{2, 4, 6, 9, 11, 13, 17}$ clusters have lower HOMO-LUMO gap values than the corresponding pure germanium clusters, suggesting that the substitution of one Ge atom by a Se one enhances the chemical reactivity of the host germanium clusters, and thus increases the metallic character of relevant clusters. The results of this study are very important as they open us with good perspectives for the use of these candidate clusters in applications of nanotechnology and nanoelectronics.

Keywords: Selenium-doped germanium clusters, DFT calculations, Stability, Geometry, Electronic properties.

DOI: [10.21272/jnep.13\(2\).02027](https://doi.org/10.21272/jnep.13(2).02027)

PACS numbers: 36.40.Mr, 61.46.Bc

1. INTRODUCTION

Today, nanotechnology is one of the most active research areas. The mastery of the arrangements between atoms to form nanosystems, with new physical, chemical or biological properties, opens the way for applications that mark the beginning of an absolutely innovative technological era [1]. Germanium clusters are important in technical applications where they have characteristics different from those of bulk materials [2]. On the other hand, selenium clusters are among the most important clusters that have the ability to conduct electricity, which makes them a good candidate in the field of photovoltaic cells [3] and electrical converters [4]. Pure and doped germanium clusters have been studied and published intensively by several authors in both theoretical and experimental fields [5, 6]. On the theoretical aspect, the ground state structures and their electronic characteristics have been investigated for chromium doped germanium clusters ($n = 1-13$) by Kapila et al. [7]. It was found that the binding energy of chromium doped germanium clusters CrGe_n increases with the size of the cluster, indicating that the cluster can gain energy during the formation process. Shi et al. [8] demonstrated the effect of aluminum atom on the characteristics of pure Ge_{n+1} ($n = 1-9$) nanoclusters. The researchers found that the stability of Ge_{n+1} cluster was somewhat higher than that of AlGe_n .

Benaida et al. [9] proposed a computational study and performed it on AsGe_n and Ge_{n+1} clusters for $n = 1-20$. It was shown that the substitution of one Ge atom by an As one did not contribute to the reinforcement of the stability of the germanium framework. The effect of

niobium and tantalum doping on the characteristics of germanium clusters has been shown and discussed by Siouani et al. [10] and it was found that the Nb, TaGe_{15} and VGe_{14} isomers have higher stability.

From previous studies on doped germanium clusters, as far as we know, till now, there is no investigation on selenium doped germanium clusters in a large-size range ($1 \leq n \leq 20$).

The main objective of this work is to highlight the effect of the replacement of one Ge atom by a Se one on some properties, such as structural and electronic, of different isomers of Ge_{n+1} clusters.

2. COMPUTATIONAL METHODOLOGY

Our calculations are based on density functional theory (DFT) [11] within the generalized gradient approximation (GGA) formulated by Perdew-Burke-Ernzerhof [12]. All calculations were executed using the SIESTA code [13]. The norm-conserving Troullier-Martins pseudopotentials were used [14]. The k grid integration was conducted by using the Γ point approximation. In addition, the conjugated gradient (CG) method within Hellmann-Feynman forces was utilized and, after structural relaxation, all forces were less than 10^{-3} eV/Å. Based on the convergence criterion of 10^{-4} a.u. for the system total energy, the self-consistent calculations were conducted. In this calculation, we employed a cubic supercell of 40 Å, where the periodic boundary condition was considered to evade interactions among adjacent clusters. Furthermore, we used the double ζ (DZ) basis for both Se and Ge atoms with an energy shift equal to 50 meV.

* Z.ikram30@gmail.com

The putative configuration shape of SeGe_n was found in the relaxation process after the replacement of one Ge atom by a Se one in possible sites for the ground state of pure germanium Ge_{n+1} isomer which was obtained by Benaïda et al. [9].

The reliability of the calculation scheme was validated on Ge_2 and Se_2 clusters. Our calculation results show that the bond lengths for Ge_2 and Se_2 are estimated at 2.503 Å and 2.301 Å, respectively. These values correspond perfectly to both theoretical [15, 16] and experimental data of 2.57 Å for Ge_2 [17] and 2.17 Å for Se_2 [18]. Also, the vertical electron affinity is estimated at 1.473 eV for Ge_2 and 1.293 eV for Se_2 , and it also corresponds par excellence to theoretical and experimental data [18-20].

3. RESULTS AND DISCUSSION

3.1 Geometric Structures

In our discussion, we only consider clusters with the lowest energy when analyzing and discussing. The geometric structures of the ground-state isomers obtained are shown in Fig. 1.

The binding energy (per atom) of the most stable SeGe dimer is 2.471 eV. This value is large when compared to that of Ge_2 dimer (1.445 eV/atom) [9]. The calculated bond length for SeGe is 2.239 Å. SeGe_2 trimer has a triangular geometry with C_{2v} symmetry. The same geometry was obtained for Ge_3 trimer [9]. It has bond lengths of 2.659 Å and 2.495 Å for Ge–Ge and Se–Ge, respectively. The ground-state SeGe_3 cluster has a tetrahedral structure, where the lengths of Se–Ge and Ge–Ge bonds are 2.549 Å and 2.681 Å, respectively. The binding energy is 2.597 eV/atom, which is large compared to that of tetramer Ge_4 [9]. For the size $n = 4$, the most suitable structure is a pentagon constructed by three triangles with C_1 point group symmetry. It has bond lengths of 2.610 Å and 2.537 Å for Ge–Ge and Se–Ge, respectively. The most appropriate isomer SeGe_5 displays a distorted octahedron structure (C_{4v}), where the lengths of Se–Ge and Ge–Ge bonds are 2.761 Å and 2.801 Å, respectively. Its binding energy (2.758 eV/atom) is small than that found in earlier work for Ge_6 [9]. A bicapped pentagonal configuration is found to be the most favorable isomer with C_{2v} point group symmetry. The mentioned structure SeGe_6 has a binding energy equal to 2.859 eV/atom. As for $n = 7$, the

doping of one Se atom in a pure Ge_8 cage [9] gives the lowest-energy cluster SeGe_7 , which presents a capped pentagonal bipyramid shape. This shape is similar to the structure of Ge_8 [9]. For the next cluster size $n = 8$, a capped pentagonal bipyramid configuration was found. It has C_s symmetry and a calculated binding energy equal to 2.948 eV/atom. This structure is the same as that obtained in the Ge_9 frame [9]. Besides, the most favorable configuration for SeGe_9 can be characterized as a capped pentagonal geometry (C_s). The average distances are 2.749 Å and 2.770 Å for Ge–Ge and Se–Ge bonds, respectively. For the subsequent cluster size $n = 10$, a Se atom takes a peripheral position in the germanium cage. The mean Se–Ge and Ge–Ge bond lengths are 2.678 Å and 2.799 Å, respectively.

A prolate geometry (C_s) is the ground state of SeGe_{11} cluster, where a Se atom is located on the surface of the cage. The mentioned geometry has a binding energy computed equal to 2.985 eV/atom. This value is somewhat smaller than the ground state geometry of SeGe_{10} . Furthermore, the (C_1) shape of SeGe_{12} was obtained by replacing the tetrahedrally coordinated capping Ge atom with a Se one. The mentioned shape has the lengths of Se–Ge and Ge–Ge bonds of 2.756 Å and 2.805 Å, respectively. The lowest-energy isomer for SeGe_{13} was achieved. It consists of a stack of two mis-represented rhombi and one fivefold ring capped with an atom. The mentioned isomer has C_s point group symmetry, where the lengths of Se–Ge and Ge–Ge bonds are 2.650 Å and 2.780 Å, respectively. In this case, both clusters with sizes $n = 14$ and 15 have a prolate configuration, so that the Se atom is located on the surface. The symmetry was obtained to be C_s and C_1 for SeGe_{14} and SeGe_{15} , respectively. The most appropriate configuration SeGe_{16} has an irregular cage-like shape (C_1). From our calculations, we found that the binding energy of this configuration equal to 0.003 eV/atom is somewhat larger than that of Ge_{17} [9]. The most suitable cluster SeGe_{17} gives a prolate geometry. It has C_1 point group symmetry. The average Ge–Ge and Se–Ge bond lengths are 2.816 Å and 2.648 Å, respectively.

For large clusters of sizes $n = 18, 19$ and 20, an irregular cage-like form is shown. In the case of these clusters, we note that the doping atom (Se) has a stable position on the surface. The binding energy calculated for $\text{SeGe}_{18, 19, 20}$ clusters is equal to 3.064, 3.057 and 3.090 eV/atom, respectively.

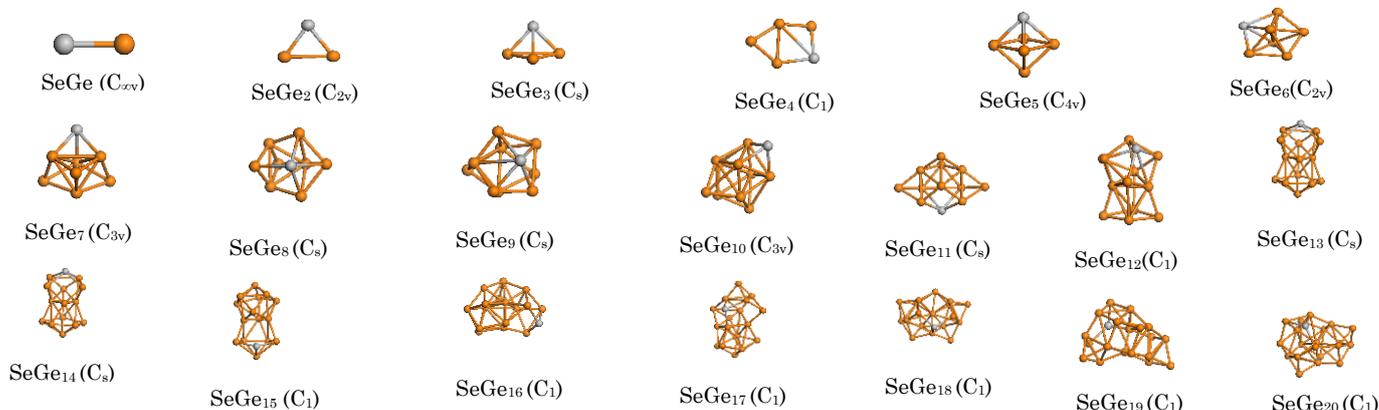


Fig. 1 – Most appropriate structures of SeGe_n ($1 \leq n \leq 20$) clusters

3.2 Relative Stability

In this section, we will discuss the relative stability of SeGe_n clusters ($0, \pm 1$) by studying the results of the parameters calculation (binding energy E_b and second-order energy difference $\Delta_2 E$) shown in Fig. 2 and Fig. 3. The evolution of the binding energy per atom E_b for both SeGe_n and Ge_{n+1} clusters in terms of cluster size n is plotted in Fig. 2.

At the beginning of the curve, we can notice that the small-size ($n \leq 3$) SeGe clusters have a higher binding energy than Ge_{n+1} . This signifies that doping with one Se atom reinforces the stability of pure germanium clusters. Besides, the E_b curve for Ge_{n+1} clusters augments rapidly with some oscillations, and this is in the size range $n = 3-14$, with the exception of cluster with $n = 7$, indicating a higher stability of the host clusters in this range. Moreover, it can also be observed that the SeGe_{20} cluster has the largest binding energy equal to 3.090 eV/atom.

The second-order energy difference is shown in Fig. 3 as a function of cluster size for the most appropriate structures of Ge_{n+1} and SeGe_n ($n = 1-20$) clusters.

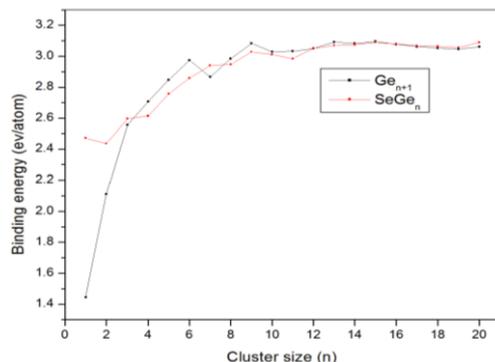


Fig. 2 – Binding energy for the most appropriate structures of Ge_{n+1} and SeGe_n clusters as a function of cluster size n

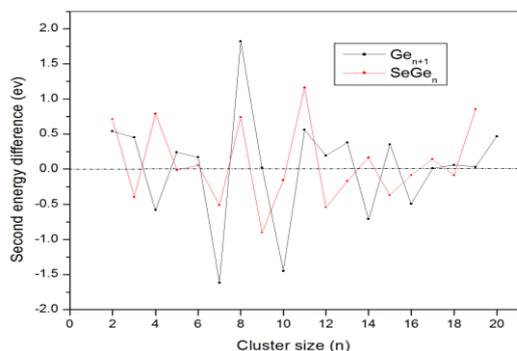


Fig. 3 – Second-order energy difference for the most appropriate structures of Ge_{n+1} and SeGe_n clusters as a function of cluster size n

In Fig. 3, through the curve of the second-order energy difference $\Delta_2 E$, we can see clearly prominent positive peaks at sizes $n = 2, 4, 8, 11, 14, 17$, and 19 . This signifies the special relative stability of SeGe isomers at these sizes. Likewise, we also note positive values at sizes $n = 2, 3, 5, 6, 8, 11, 12, 13, 15$, and 20 . This result is due to the relative stability of pure germanium cages at these sizes.

3.3 Electronic Properties

The HOMO-LUMO gap is a distinctive and important property that gives an idea about chemical activity and electronic stability of clusters. The results of HOMO-LUMO gaps for the most appropriate structures are presented in Fig. 4.

It can be seen that the HOMO-LUMO gap (ΔE) curve decreases gradually with some nonmonotonic oscillations. Besides, HOMO-LUMO gaps are also observed for SeGe clusters of sizes $n = 2, 4, 6, 9, 11, 13$, and 17 and they are less than those found in the corresponding pure germanium clusters, indicating an increase in the chemical activity of SeGe clusters of these sizes. The SeGe_1 structure records the highest peak of the HOMO-LUMO gap of 3.155 eV, which means that this structure is inert and has high chemical stability. Conversely, Ge_2 cluster has the lowest HOMO-LUMO gap value which is 0.265 eV.

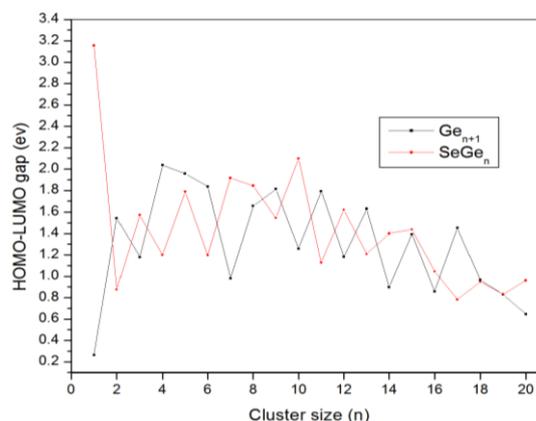


Fig. 4 – HOMO-LUMO gaps of Ge_{n+1} and SeGe_n ($n = 1-20$) clusters as a function of cluster size n

The vertical ionization potential (VIP) and vertical electronic affinity (VEA) are two very important criteria that are useful for predicting the stability of a cluster, as well as the cluster's ability to lose (VIP) or gain a valence electron (VEA). Fig. 5 and Fig. 6 illustrate, respectively, VIP and VEA changes relative to cluster size n for both Ge_{n+1} and SeGe_n clusters. The VIP curve takes an oscillating behavior. A decrease in the VIP values for SeGe clusters of sizes $n = 2-6$ was found. These five clusters can lose one or more electrons. In contrast, the large values of SeGe_{7-20} clusters suggest great stability. The SeGe_1 isomer is very stable because it has a prominent peak in the VIP (9.483 eV).

Moreover, the VEA curve shows an oscillating and gradually increasing behavior. It was observed that SeGe clusters with $n = 2$ and 4 can capture an electron more easily with energy release.

4. CONCLUSIONS

A theoretical research aims to study the electronic properties and structural optimization of selenium-doped germanium clusters using DFT theory. The binding energy, second-order difference of energies, HOMO-LUMO energy gaps, vertical ionization potentials, vertical electron affinities, and chemical hardness were taken into consideration and therefore computed and

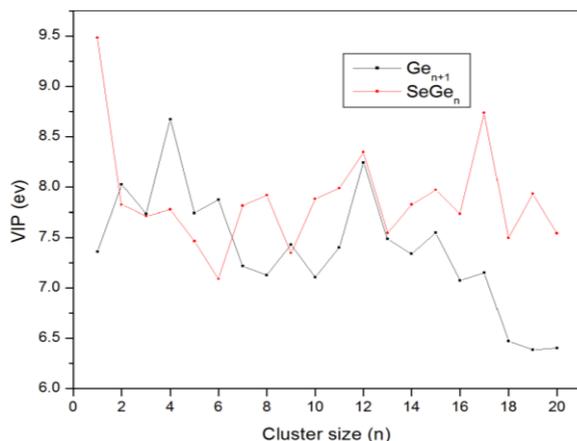


Fig. 5 – VIP for the most appropriate structures of Ge_{n+1} and SeGe_n ($n = 1-20$) clusters as a function of cluster size n

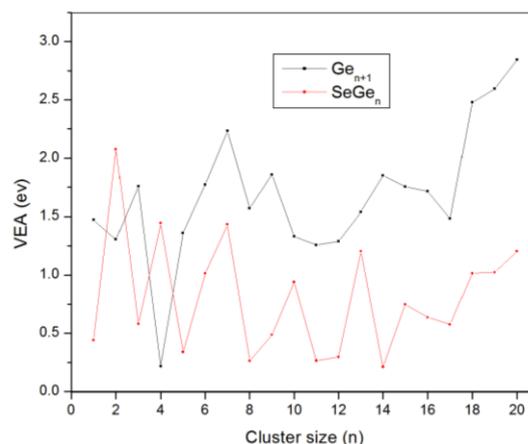


Fig. 6 – VEA for the most appropriate structures of Ge_{n+1} and SeGe_n ($n = 1-20$) clusters as a function of cluster size n

studied. The growth pattern of SeGe_n clusters shows that the Se atom favors stability on the germanium cage surface for most stable clusters, where the Se atom has an effect on improving the stability of large germanium clusters. Besides, the SeGe_{20} cluster shows high stability and can be considered as a good candi-

date for use in many nanotechnology applications.

ACKNOWLEDGEMENTS

The authors greatly thank the staff of LENREZA laboratory, Ouargla University, Algeria.

REFERENCES

1. S. Chadha, *Int. J. Res. Agric. Food. Sci. Tech.* **4** No 10, 1011 (2013).
2. P.N. Samanta, K.K. Das, *Comput. Theor. Chem.* **980**, 123 (2012).
3. S.B. Ambade, R.S. Mane, S.S. Kale, S.H. Sonawane, Arif V. Shaikh, Sung-Hwan Han, *Appl. Surf. Sci.* **253** No 4, 2123 (2006).
4. R.S. Mane, S.P. Kajve, C.D. Lokhande, Sung-Hwan Han, *Vacuum* **80** No 6, 631 (2006).
5. S. Yoshida, K. Fuke, *J. Chem. Phys.* **111** No 9, 3880 (1999).
6. S. Bals, S. Van Aert, C.P. Romero, K. Lauwaet, M.J. Van Bael, B. Schoeters, B. Partoens, E. Yücelen, P. Lievens, G. Van Tendeloo, *Nat. Commun.* **3**, 897 (2012).
7. N. Kapila, I. Garg, V.K. Jindal, Hitesh Sharma, *J. Magn. Mater.* **324** No 18, 2885 (2012).
8. S. Shi, Y. Liu, C. Zhang, Banglin Deng, Gang Jiang, *Comput. Theor. Chem.* **1054**, 8 (2015).
9. M. Benaida, K.E. Aiadi, S. Mahtout, S. Djaadi, W. Rammal, M. Harb, *J. Semicond.* **40** No 3, 032101 (2019).
10. C. Siouani, S. Mahtout, F. Rabilloud, *J. Mol. Model.* **25** No 5, 113 (2019).
11. P. Ordejón, E. Artacho, J.M. Soler, *Phys. Rev. B.* **53** No 16, R10441 (1996).
12. J.P. Perdew, K. Burke Matthias Ernzerhof, *Phys. Rev. Lett.* **77** No 18, 3865 (1996).
13. J.M. Soler, E. Artacho, J.D. Gale, A. García, J. Junquera, P. Ordejón, D. Sánchez-Portal, *J. Phys. Condens. Matter.* **14** No 11, 2745 (2002).
14. N. Troullier, J.L. Martins, *Phys. Rev. B.* **43** No 3, 1993 (1991).
15. S. Mahtout, C. Siouani, Franck Rabilloud, *J. Phys. Chem. A* **122** No 2, 662 (2018).
16. J.X. Guo, S.Y. Wu, L. Peng, Li-Na Wu, Xiao-Hong Chen, *Phys. B: Condens. Matter.* **524**, 1 (2017).
17. S. Nagendran, S.S. Sen, H.W. Roesky, D. Koley, H. Grubmüller, A. Pal, R. Herbst-Irmer, *Organometallics.* **27** No 21, 5459 (2008).
18. C.-G. Li, J. Zhang, Y.-Q. Yuan, Y.-N. Tang, B.-Z. Ren, W.-G. Chen, *Physica E* **86**, 303 (2017).
19. J. Wang, J.G. Han, *J. Phys. Chem.* **112** No 14, 3224 (2008).
20. J.E. Kingcade, H.M. Nagarathna-Naik, I. Shim, K.A. Gingerich, *J. Phys. Chem.* **90** No 13, 2830 (1986).

Вивчення впливу легування селеном на геометрію та електронні характеристики кластерів германію (SeGe_n , $n = 1-20$) за допомогою розрахунків DFT

I. Zitouni, K.E. Aiadi, O. Bentouila, M. Benaida, Z. Ayat

Laboratory of New and Renewable Energy in Arid and Saharan Zones – LENREZA, Ouargla University, 30000 Ouargla, Algeria

Систематичне теоретичне дослідження на основі обчислення геометричних структур, стійкості та електронних характеристик системи (кластери SeGe_n , $n = 1-20$) було представлено в рамках теорії функціоналу густини (DFT) і реалізовано в код моделювання SIESTA. Всі отримані ізомери в основному стані мають тривимірні структури. Великі кластери SeGe_n розміром $n \geq 16$ демонструють більшу енергію зв'язку. Аналогічно, отримані результати різниці енергій Δ_2E другого порядку показують, що позитивні максимальні піки при $n = 2, 4, 8, 11, 14, 17$ та 19 мають деяку стабільність. Це означає, що вони мають більшу стабільність, ніж їх сусіди. Результати розрахунків електронних властивостей, таких як зона НОМО-LUMO (найвища зайнята молекулярна орбіталь-найнижча незайнята молекулярна

орбіталь), вертикальний потенціал іонізації (VIP) та вертикальна спорідненість до електронів (VEA), виявляють, що димер SeGe_1 є більш стабільним, ніж сусідні кластери. З іншого боку, згідно з аналізом зон НОМО-LUMO, можна зробити висновок, що кластери $\text{SeGe}_{2, 4, 6, 9, 11, 13, 17}$ мають менші значення зон НОМО-LUMO, ніж відповідні кластери чистого германію, що свідчить про те, що заміщення одного атома Ge одним атомом Se підвищує хімічну реакційну здатність германієвих кластерів-хазяїв і, отже, збільшує металевий характер відповідних кластерів. Результати цього дослідження дуже важливі, оскільки вони відкривають гарні перспективи для використання цих кластерів-кандидатів у додатках нанотехнологій та наноелектроніки.

Ключові слова: Леговані селеном кластери германію, Розрахунки DFT, Стабільність, Геометрія, Електронні властивості.