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Structural evolution and stabilities of $(\text{PbTe})_n$ ($n = 1\text{--}20$) clusters



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ABSTRACT

The geometric and electronic structures of lead telluride clusters are investigated numerically. The result provided both vertical and adiabatic electron affinities (VEAs and AEAs) for these clusters, revealing a pattern of alternating values in which even n clusters exhibited lower values than odd n clusters up until $n = 8$ and beyond $n = 14$. Computations found lead telluride clusters with even n to be thermodynamically more stable than their immediate odd n neighbors, with a consistent pattern also being found in their HOMO-LUMO gaps. Analysis of cluster dissociation energies found at Pb_4Te_4 cube to be the preferred product of the queried fragmentation processes, consistent with our finding that Pb_4Te_4 cluster exhibits enhanced stability; it is a magic number species. Beyond $n = 10$, this study showed that the $(\text{PbTe})_n$ clusters in the size range $n = 11\text{--}20$, prefer two dimensional stacking of face-sharing lead telluride cubical units, where lead and tellurium atoms possess a maximum of fivefold coordination. The preference for sixfold coordination, which is observed in the bulk, was not observed at these cluster sizes.

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1. Introduction

In a number of scientific groups all over the world, special attention has been paid to investigations of IV-VI semiconductors. These semiconductors have some interesting characteristics, such as small energy gaps, low resistivities, large carrier mobilities, high dielectric constants and high melting points [1]. Lead telluride is well-known materials in this family since they have a high melting point, good chemical stability, low vapor pressure and good chemical strength, they are stable in a wide temperature range and have applications in the field of thermoelectrics power generation and refrigeration which is used for heating and cooling [2]. Lead is well known as a toxic metal which poses a great threat to the environment and human life, especially for children's neurological and physical development. The lead compounds should be an important topic in the lead pollution. The study of lead telluride clusters might provide useful information for material investigation and pollution control [3].

Despite the importance of lead telluride in the ultrasmall size regime, investigations of lead telluride molecules and clusters have been limited. Work which has been reported includes density functional study of structures and stabilities of Pb_mTe_n ($m + n \leq 6$) clusters [5], stoichiometric single-phase polycrystalline investigations of thermally evaporated nanocrystalline PbTe films [2], CdTe

matrix fabricated by ion implantation studied PbTe and SnTe quantum dot precipitates [5], a chemical vapor deposition technique investigations size-selective high yield growth of lead telluride (PbTe) nanocrystals [6].

However, despite much effort made in previous experimental studies on nanocrystals of lead telluride there is a lack of a systematical investigation of lead telluride clusters. It is well known that there are several lead telluride compounds with different chemical compositions. Moreover, clusters may not keep the bulk stoichiometry, especially for small clusters. To our knowledge, neither experimental nor theoretical studies of neutral lead telluride clusters exist in literature. In order to gain a better understanding of the structural evolution and electronic properties of small lead telluride clusters, we conducted a synergistic computational study.

2. Computational details

All the calculations described in this work are performed with the Vienna *Ab Initio* Simulation Package (VASP) [7]. The electron-ion interactions are described by ultrasoft pseudopotentials [8]. Based on a plane-wave expansion method employing the local density approximation (LDA) for exchange and correlation term [9]. The cutoff energy used in the plane wave expansion is 143.58 eV. Structural optimizations are performed using the conjugate gradient (CG) method where the components of forces on atoms are about 0.004 eV/Å, the structural optimizations are taken to be converged. The self-consistent field, SCF, calculations are

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carried out with a convergence in the total energy of 10^{-4} eV. The reciprocal space is sampled by the Γ point. A sufficiently large unit cell is chosen so that the minimum distance from the cluster boundary to cell boundary is about 5 Å. We use $20 \times 20 \times 20$ Å³ simulation box if the length of the cluster is less than 10 Å otherwise we use $30 \times 30 \times 30$ Å³ simulation box.

3. Results and discussion

We present the optimized geometries of neutral $(\text{PbTe})_n$ ($n = 1-20$) clusters along with their corresponding relative energies. The low-lying isomers of each size are labeled as a, b, c and d in energy order from low to high. It should be noted that only the low-lying isomers with total energies not more than 0.59 eV higher than that of the lowest-energy structure are presented and as far as possible we are trying to present a maximum four isomers to each cluster size for simplicity and clarity. The vertical electron affinities (VEAs) were calculated as the energy differences between the anion and neutral clusters at the same structures as those of the neutral. The adiabatic electron affinities (AEAs) were obtained as the energy differences between the cluster anions and the optimized neutral clusters using the neutral structures as initial structures [10]. We have computed our computations on neutral lead telluride clusters up to the nanometer-size regime (up to $n = 20$). Our aim was to examine the growth pattern of these clusters as a function of the number of PbTe molecular units.

3.1. Neutral $(\text{PbTe})_n$, ($n = 1-20$) clusters

3.1.1. PbTe dimer

The bond length between Pb and Te in neutral PbTe dimer is calculated to be 2.57 Å which is in excellent agreement with experimental value 2.59 Å [5] but it is different from the bulk value 3.23 Å [11]. The vertical electron affinities (VEA) and adiabatic electron affinities (AEAs) are calculated to be 1.77 eV and 1.89 eV, respectively.

3.1.2. $(\text{PbTe})_2$ cluster

Our calculations for these clusters revealed three stable and distinct structures: a non-planar bent structure, rhombus and tetrahedron (Fig. 1). In the first two structures, the Pb and Te atoms are arranged in an alternate fashion where Te atoms are doubly coordinated but, in the third structure every atom is found to be triply coordinated. The $(\text{PbTe})_2$ cluster prefers the bent structure with a dihedral angle of 30.45°. The Pb–Te bond length for this cluster is 2.83 Å, this bond length is longer than their corresponding PbTe dimer due to the doubly and triply coordinated of Te and Pb atoms. The separation between the Pb atoms is 3.46 Å. We calculated the VEAs/AEAs values for all the three isomers of as 2.34/2.62, 2.49/2.54 and 2.45/2.59 eV for the bent, rhombus and tetrahedron structures respectively.

3.1.3. $(\text{PbTe})_3$ clusters

For these clusters, two isomers were considered: a bridged trigonal bipyramidal and a folded structure which can also be viewed as an edge (PbTe) removed cubic structure (Fig. 1). Between these two isomers, the trigonal bipyramidal structure with a bridged Te atom is found to be the most preferred structure and it is obtained by adding of PbTe dimer on the convex face of the lowest energy structure of $(\text{PbTe})_2$ cluster (Fig. 1, 2a). The Pb–Te bond lengths in this isomer range from 2.84 to 3.05 Å. Interestingly, Pb–Pb interactions continue to be significant in this cluster as they did in the $(\text{PbTe})_2$ cluster (Fig. 1). The Pb–Pb bond length in the Te-capped edge of this isomer is 3.33 Å. We calculated the AEA and VEA values for both the isomers, the first one yields AEA and VEA values of

2.48 and 2.35 eV respectively. On the other hand, in the higher energy folded structure are 2.98 and 2.65 eV, respectively.

3.1.4. $(\text{PbTe})_4$ clusters

The lowest energy geometry of this lead telluride clusters is a cube with alternating Pb and Te atoms. This is the smallest lead telluride cluster in which there is no Pb–Pb bonds and in which Pb–Te bonds govern the stabilization of the cluster. There is no other isomer presented in this cluster, all other structures have relative energy greater than 1.0 eV. The Pb–Te bond lengths in this cluster is 2.98 Å. It is evolved from the folded structure of $(\text{PbTe})_3$ clusters by adding of PbTe dimer on opposite of the fold. Our values of the AEA and VEA are 1.96 eV and 1.82 eV, respectively.

3.1.5. $(\text{PbTe})_5$ clusters

As shown in (Fig. 1, 5a–5c), our simulations found three low-lying isomers within an energy range of 0.43 eV for neutral $(\text{PbTe})_5$ cluster. A bi-capped non-planar octagonal structure is found as the lowest energy structure in this cluster, the Pb–Te bond lengths in this isomer range from 2.90 to 3.15 Å.

A derivative of the cubical structure observed in $(\text{PbTe})_4$ with a PbTe unit fused to one of the faces of the cube 0.18 eV higher in energy from the first and a little distortion of this structure make the third isomer 0.43 eV higher than the isomer 5a. In the isomer 5b and 5c there is a considerable interaction between two lead atoms with a Pb–Pb bond length of 3.26 Å and 3.20 Å. We calculate the AEAs/VEAs of all isomers and the values are 2.33/2.29, 2.64/2.33 and 3.02/3.00 eV respectively, for the structures in order of increasing energy.

3.1.6. $(\text{PbTe})_6$ clusters

Beyond $n = 5$, the geometries of lead telluride clusters evolve based on the $(\text{PbTe})_4$ cube cluster, where either lead telluride dimer or $(\text{PbTe})_2$ units are added to the cubic structure. The lowest energy geometry of the neutral $(\text{PbTe})_6$ cluster corresponds to two, face-sharing cubes (quadrangular Prism) (Fig. 1, 6a), while a drum structure made up of two hexagonal rings is found to be 0.44 eV higher in energy. In fact, there are four different Pb–Te bonds ranging from 2.93 to 3.17 Å. The longer bond lengths are observed when one of the Pb or Te atoms are fourfold coordinated, while the shorter bond length corresponds to threefold coordinated Pb and/or Te atoms. The calculated values of AEAs/VEAs for each isomer are 2.34/2.10 and 1.86/1.62 eV respectively.

3.1.7. $(\text{PbTe})_7$ clusters

On increasing the number of lead telluride units to seven, the formation of a symmetric linear array of face-sharing cubes, as was the case in the $(\text{PbTe})_6$ cluster, does not occur in $(\text{PbTe})_7$ cluster. Our calculations show that there are three stable isomers for the $(\text{PbTe})_7$ cluster. The lowest energy structure of $(\text{PbTe})_7$ corresponds to a more symmetric structure (Fig. 1, 7a), in which two cubes share an edge. A slightly distorted open-cage structure, which can also be described as two distorted cubes fused on the sides is found to be 0.14 eV higher in energy. The third structure is a cage containing six rhombuses and three hexagons. There are six different Pb–Te bonds ranging from 2.86 to 3.13 Å for this clusters. The calculated values of AEAs/VEAs for each isomer are 2.41/2.25, 2.50/2.33 and 2.16/1.73 eV respectively.

3.1.8. $(\text{PbTe})_8$ clusters

For this cluster, two isomers were considered. The lowest energy geometry of the $(\text{PbTe})_8$ cluster corresponds to a one-dimensional growth of the cubical units (a quadrangular prism), which can be obtained by stacking of three cubes (Fig. 1, 8a). This isomer can also be obtained by adding a $(\text{PbTe})_2$ unit to the lowest energy geometry of $(\text{PbTe})_6$ cluster in a linear fashion. On the other

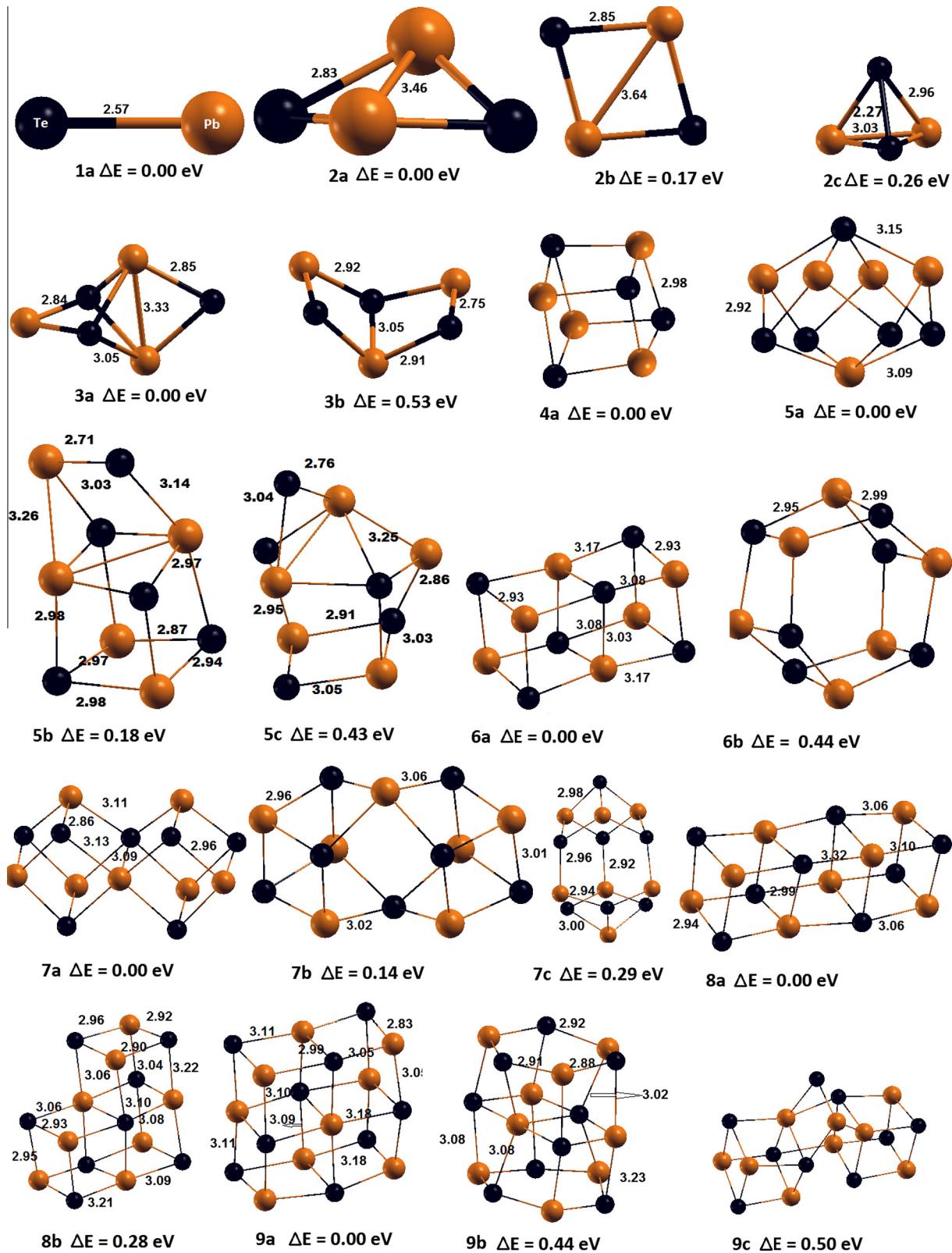


Fig. 1. Optimized geometry of $(\text{PbTe})_n$ ($n = 1\text{--}9$) with corresponding relative energy (ΔE), with respect to the lowest energy structure.

hand, if a $(\text{PbTe})_2$ unit were to be added on top of $(\text{PbTe})_6$, it would result in isomer 8b, which is 0.28 eV higher in energy than the isomer 8a. Isomer 8b can also be obtained by adding a PbTe unit to the edge-sharing $(\text{PbTe})_7$ cluster. There are five distinct Pb–Te bonds present in isomer 8a, with the Pb–Te bond length in the central

cube (3.32 \AA) being significantly longer than that of the other Pb–Te bonds in the cluster, but very close to the Pb–Te bond length in the bulk lead telluride crystal (3.23 \AA) [11]. In addition, the Pb–Te bond distances between fourfold coordinated lead and telluride atoms is larger (3.10 and 3.06 \AA) than that of the Pb–Te bond

distance between threefold coordinated lead and telluride atoms (2.94 \AA). Based on these bond lengths, the $(\text{PbTe})_8$ cluster can be visualized as two weakly interacting $(\text{PbTe})_4$ cubes. The calculated values of AEAs/VEAs for both isomers are $2.32/2.03$ and $2.47/2.04$ eV respectively.

3.1.9. $(\text{PbTe})_9$ clusters

The addition of a PbTe dimer unit on the two isomers of $(\text{PbTe})_8$ cluster results in three isomers of $(\text{PbTe})_9$ cluster (Fig. 1). The lowest energy geometry of $(\text{PbTe})_9$ cluster corresponds to the stacking of four cubes in two dimensions with Pb–Te bond lengths ranging from 2.83 to 3.18 \AA . This structure of $(\text{PbTe})_9$ cluster can be seen as an extension of isomer of $(\text{PbTe})_8$ cluster (Fig. 1, 8b). A tubular structure with three layers of hexagons (Fig. 1, 9b) is found to be 0.44 eV higher in energy, the third isomer being 0.50 eV higher in energy than the lowest energy geometry. The calculated values of AEAs/VEAs for each isomer are $2.35/2.32$, $2.56/2.44$ and $2.62/2.14$ eV respectively, in order of increasing energy difference.

3.1.10. $(\text{PbTe})_{10}$ clusters

Upon increasing the number of PbTe molecular units in the cluster to 10 , our calculations show three stable $(\text{PbTe})_{10}$ isomers within a maximum energy difference of 0.15 eV (Fig. 2). All three isomers correspond to periodic arrays of cubes stacked either in one or two dimensions. The lowest energy isomer of $(\text{PbTe})_{10}$ is a quadrangular prism structure (Fig. 2, 10a), obtained by a linear stacking of four cubes, with six distinct Pb–Te bonds ranging from 2.94 to 3.23 \AA . A symmetric structure exhibiting two-dimensional stacking of lead telluride cubical units (Fig. 2, 10b) is found to be 0.11 eV higher in energy than the lowest energy geometry. Another isomer with two-dimensional stacking of cubes, resulting in an L-shaped structure (Fig. 2, 10c), is found to be 0.15 eV higher in energy. The calculated values of AEAs/VEAs for each isomer are $2.48/2.43$, $2.41/2.26$ and $2.38/2.20$ eV respectively, in order of increasing energy.

3.1.11. $(\text{PbTe})_{11}$ clusters

As shown in (Fig. 2) our simulation found only two low-lying isomers for $(\text{PbTe})_{11}$ cluster within an energy range of 0.34 eV. The lowest energy structure for $(\text{PbTe})_{11}$ clusters is constructed by adding a PbTe unit to $(\text{PbTe})_{10}$ clusters (Fig. 2). The second isomer which is obtained by a three-dimensional stacking of cube on the lowest energy geometry of $(\text{PbTe})_9$ cluster is the smallest low energy lead telluride clusters where lead and tellurium atoms possess a six fold coordination. The Pb–Te bond lengths ranging from 2.93 to 3.17 \AA . The calculated values of AEAs/VEAs for both isomers are $2.34/2.10$ and $2.36/2.28$ eV respectively, in order of increasing energy.

3.1.12. $(\text{PbTe})_{12}$ clusters

For $(\text{PbTe})_{12}$ clusters, all the four isomers are within an energy range of 0.20 eV (Fig. 2). The lowest energy structure is obtained by adding a PbTe unit to the minimum energy structure of $(\text{PbTe})_{11}$ clusters and the other isomers are obtained by adding $(\text{PbTe})_2$ unit on $(\text{PbTe})_{10}$ isomers. The isomers (Fig. 2, 12a–12c) are almost energetically degenerates. The Pb–Te bond lengths ranging from 2.88 to 3.23 \AA . The calculated values of AEAs/VEAs for each isomer are $2.25/2.20$, $2.22/2.02$, $2.56/2.39$ and $2.20/2.03$ eV respectively, in order of increasing energy.

3.1.13. $(\text{PbTe})_{13}$ clusters

Similar to $(\text{PbTe})_{12}$ clusters, the four isomers lie within an energy range of 0.19 eV (Fig. 2). The lowest energy structure is obtained by adding a PbTe unit to $(\text{PbTe})_{12}$ cluster (Fig. 2, 12b). The Pb–Te bond lengths ranging from 2.84 to 3.34 \AA . The addition of a PbTe unit on highest energy isomer of $(\text{PbTe})_{12}$ (Fig. 2, 12d)

make the second isomer 0.06 eV higher in energy than the first isomer. The isomers (Fig. 2, 13a and 13b) are almost energetically degenerate. The calculated values of AEAs/VEAs for each isomer are $2.19/2.07$, $2.27/2.05$, $2.33/2.23$ and $2.21/2.10$ eV respectively, in order of increasing energy.

3.1.14. $(\text{PbTe})_{14}$ clusters

All isomers of $(\text{PbTe})_{14}$ clusters lie in the energy range of 0.22 eV (Fig. 3, 14a–14d) and obtained by adding a PbTe units on each isomers of $(\text{PbTe})_{13}$ clusters. The two isomers of $(\text{PbTe})_{14}$ clusters (14a and 14b) are almost energetically degenerate with an energy difference of 0.03 eV. The Pb–Te bond lengths ranging from 2.86 to 3.34 \AA . The calculated values of AEAs and VEAs for each isomer are $2.16/2.04$, $2.23/2.02$, $2.72/2.50$ and $2.49/2.45$ eV respectively, in order of increasing energy.

3.1.15. $(\text{PbTe})_{15}$ clusters

The lowest energy structure for $(\text{PbTe})_{15}$ c (Fig. 3, 15a) is constructed by adding a PbTe unit to all of the three isomers of $(\text{PbTe})_{14}$ clusters (Fig. 3, 14a, 14b and 14d). The Pb–Te bond lengths range from 2.80 to 3.36 \AA . The addition of a PbTe unit on high energy isomer of $(\text{PbTe})_{14}$ cluster (Fig. 3, 14c) make the second isomer 0.16 eV higher in energy than the lowest energy isomer. The highest energy isomers of this clusters are constructed by three-dimensional stacking of cubes on the lowest energy structure of $(\text{PbTe})_{11}$ and $(\text{PbTe})_{12}$ clusters. The calculated values of AEAs/VEAs for each isomer are $1.86/1.75$, $2.70/2.67$, $2.13/2.202$ and $2.17/2.11$ eV respectively, in order of increasing energy.

3.1.16. $(\text{PbTe})_{16}$ clusters

For the this cluster, three isomers are considered. The lowest energy structure of the $(\text{PbTe})_{16}$ cluster corresponds to a well symmetric two-dimensional growth of the cubical units, which can be obtained by adding of PbTe molecular units on the lowest energy geometry of $(\text{PbTe})_{15}$ cluster (Fig. 3, 15a). The addition of molecular unit on the highest energy isomers of $(\text{PbTe})_{15}$ clusters make the second isomer 0.48 eV higher in energy than the minimum energy geometry. The highest energy isomers of this clusters are constructed by three-dimensional stacking of cubes on the lower energy isomer of $(\text{PbTe})_{12}$ clusters (Fig. 2, 12b). The Pb–Te bond lengths range from 2.91 to 3.33 \AA . The calculated values of AEAs/VEAs for each isomer are $2.86/2.08$, $2.11/2.03$ and $2.98/2.84$ eV respectively, in order of increasing energy.

3.1.17. $(\text{PbTe})_{17}$ clusters

All isomers of the $(\text{PbTe})_{17}$ (Fig. 3) clusters lie in the energy range of 0.04 eV, so all the four isomers of this clusters are almost energetically degenerate. This is the smallest lead telluride neutral cluster where a six fold coordinated structure (Fig. 3, 17c) energetically degenerate to a five fold coordinated structures (Fig. 3). The lowest energy structure is obtained by adding a $(\text{PbTe})_2$ unit to the minimum energy geometry of $(\text{PbTe})_{15}$ cluster (Fig. 3, 15a). The Pb–Te bond lengths range from 2.86 to 3.39 \AA . The calculated values of AEAs/VEAs for each isomer are $2.01/1.96$, $2.07/1.97$, $2.08/1.87$ and $2.76/2.56$ eV respectively, in order of increasing energy.

3.1.18. $(\text{PbTe})_{18}$ clusters

All isomers of $(\text{PbTe})_{18}$ clusters lie in the energy range of 0.26 eV (Fig. 4, 18a–18d), the two isomers this clusters are almost energetically degenerate by an energy difference of 0.04 eV. The lowest energy structure of $(\text{PbTe})_{18}$ cluster is obtained by adding a dimer unit to the lowest energy geometry of $(\text{PbTe})_{17}$ cluster. The Pb–Te bond lengths ranging from 2.91 to 3.37 \AA . Both the isomers prefer two-dimensional stacking of cubes over the three dimensional stacking, there are no cluster posses six fold coordination of lead and tellurium atoms for all the four isomers. The calculated values

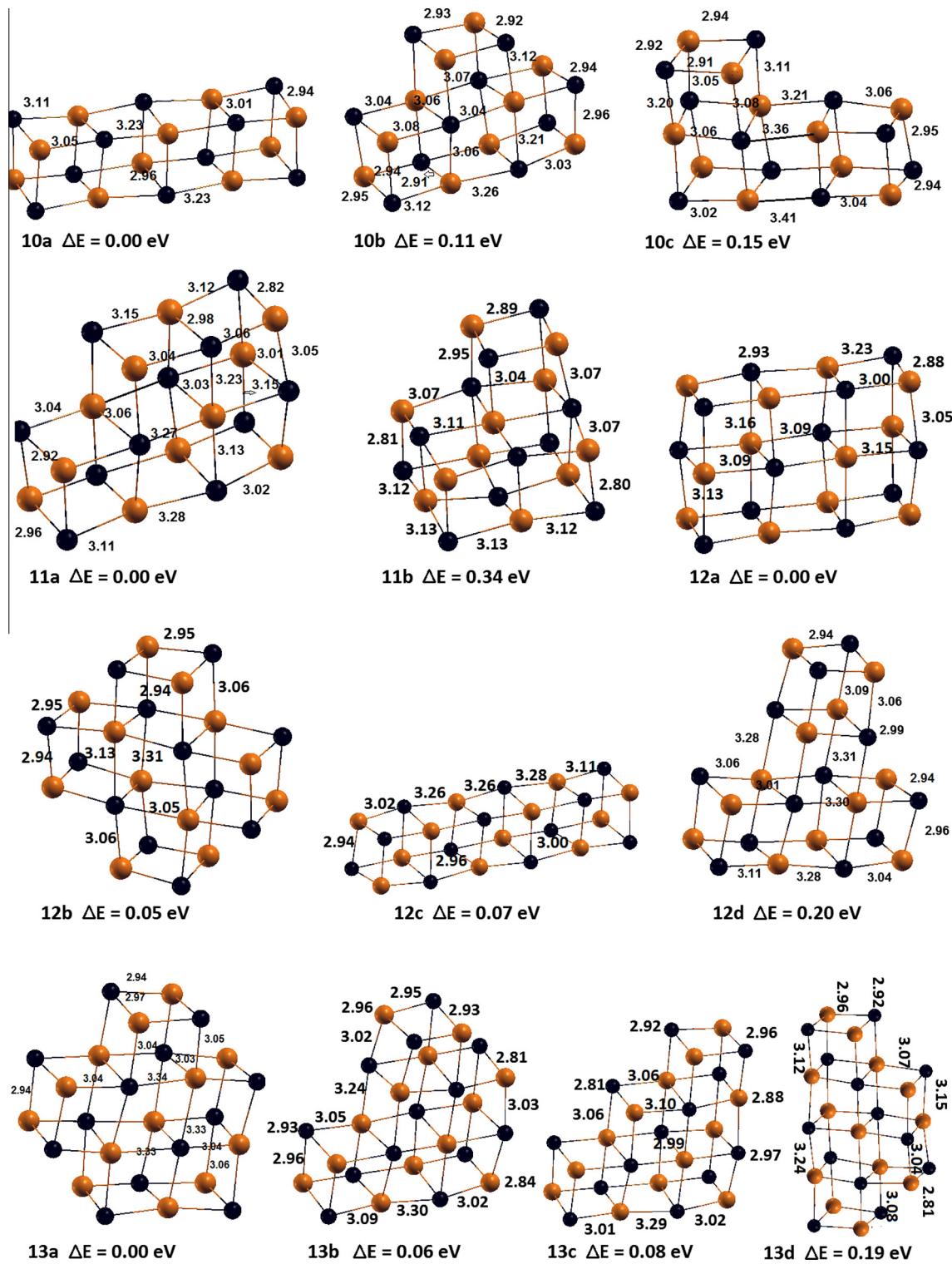


Fig. 2. Optimized geometry of $(\text{PbTe})_n$ ($n = 10-13$) with corresponding relative energy (ΔE), with respect to the lowest energy structure.

of AEAs/VEAs for each isomer are 1.94/1.83, 2.71/2.63, 2.68/2.51 and 2.61/2.43 eV respectively, in order of increasing energy.

3.1.19. $(\text{PbTe})_{19}$ clusters

For this cluster, four low-laying isomers are considered. The minimum energy geometry of the $(\text{PbTe})_{19}$ cluster (Fig. 4, 19a) prefer a two-dimensional growth of the cubical units, which can be obtained by adding of PbTe dimer units on all of the four isomers

of $(\text{PbTe})_{18}$ cluster. The stacking of two cubes on the two opposite face of the lowest energy isomers of $(\text{PbTe})_{15}$ cluster make the second and third isomers 0.32 eV and 0.46 eV higher in energy than the minimum energy geometry, both of these isomers contain a six fold coordination of lead and tellurium atoms. The $\text{Pb}-\text{Te}$ bond lengths ranging from 2.92 to 3.36 Å. The calculated values of AEAs/VEAs for each isomer are 1.89/1.77, 2.66/2.56, 2.69/2.60 and 2.70/2.54 eV respectively, in order of increasing energy.

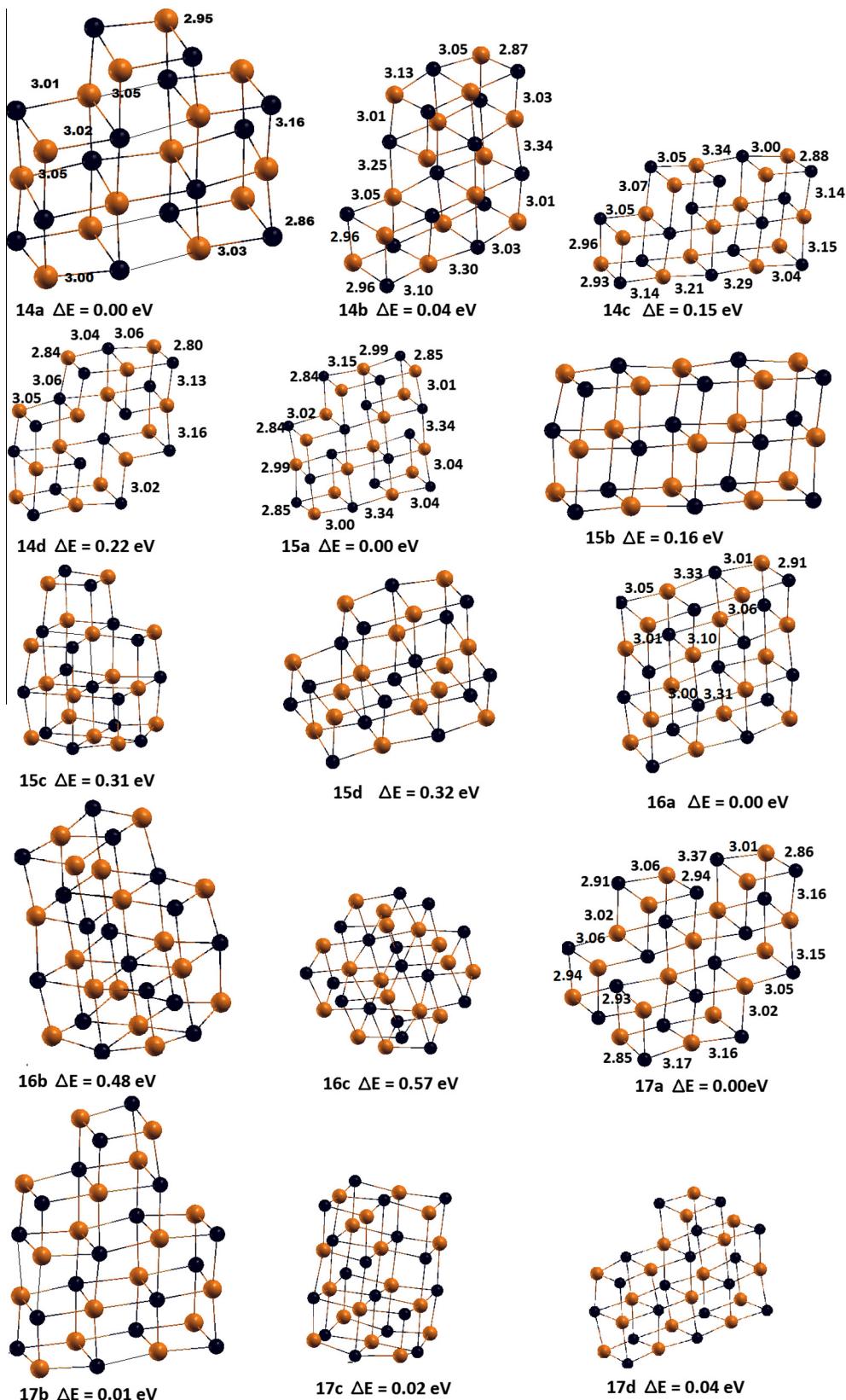


Fig. 3. Optimized geometry of $(\text{PbTe})_n$ ($n = 14-17$) with corresponding relative energy (ΔE), with respect to the lowest energy structure.

3.1.20. $(\text{PbTe})_{20}$ clusters

As shown in (Fig. 4) our calculations found four low-lying isomers for $(\text{PbTe})_{20}$ cluster within maximum energy range of

0.36 eV. The two isomers of $(\text{PbTe})_{20}$ clusters (Fig. 4) lie in the energy range of 0.26 eV and they are obtained by adding a PbTe dimer unit on the lowest and the next higher energy isomer of

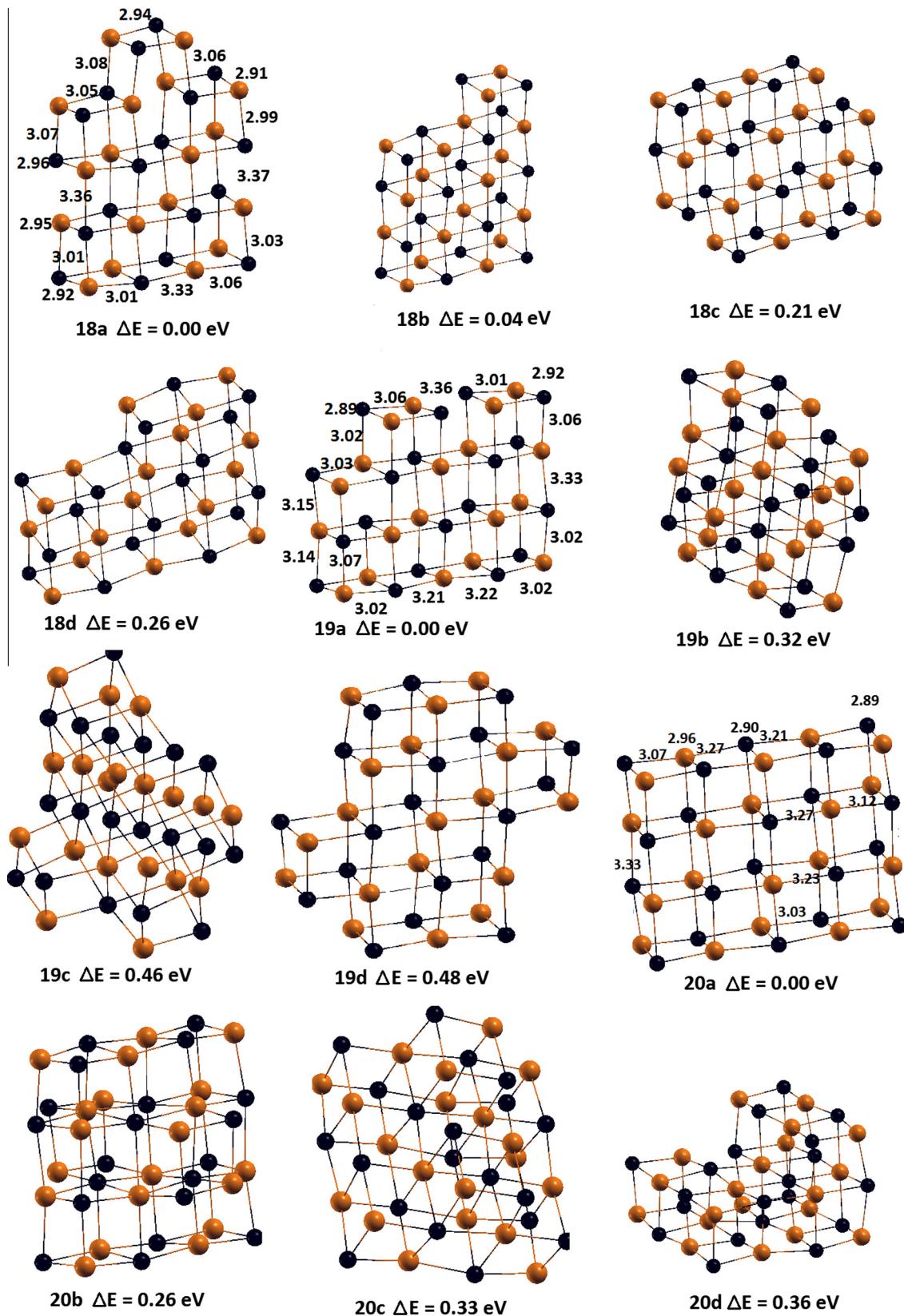


Fig. 4. Optimized geometry of $(\text{PbTe})_n$ ($n = 18-20$) with corresponding relative energy (ΔE), with respect to the lowest energy structure.

$(\text{PbTe})_{19}$ cluster respectively. The Pb–Te bond lengths range from 2.89 to 3.33 Å. The calculated values of AEAs/VEAs for each isomer

are 1.74/1.69, 2.03/1.94, 2.15/1.87 and 2.21/2.05 eV respectively, in order of increasing energy.

Hence, we infer that the structural evolution of lead telluride clusters follows a growth pattern of adding cubes in one or two dimensions. The growth pattern can be generalized as a two dimensional stacking of cubical units, such that they either share a face or an edge depending upon the number of lead telluride molecular units in a given cluster. While small lead telluride clusters adopt various distorted geometries (Fig. 1) as their sizes increase, from $n = 8$ on up in size, the lowest energy structures were dominated by cuboidal arrangements of lead telluride units. In addition, there are two other cluster types worth mentioning. First, there is the quadrangular prism (QP): which is a linear (one-dimensional) arrangement of cubes. As the size of the cluster increases, the preference for quadrangular prism steadily decreases. For example, for $n = 12, 14$, and 16 cluster sizes, the relative energy differences between the most stable structures and the QP structures are 0.07 eV, 0.28 eV, and 0.83 eV, respectively. This is understandable because as the sizes of the clusters increase, the preference for “clusterization” where more and more atoms attain higher coordination, also increases. The lowest energy isomers considered here have one thing in common; the maximum coordination number that all the lead and tellurium atoms adopt is five. In other words, all the isomers are either one or two-dimensional stacking of cubes.

What about clusters where at least some atoms are sixfold coordinated? Note that in the bulk all lead and tellurium atoms have hexa-coordination. In order to understand the energy preference for bulk-like clusters, we have studied isomers where at least one PbTe unit is hexa-coordinated, as in 11b, 15c, 16b, 17c, 19b and 20b shown in the previous figures. In all these isomers, the coordination around central PbTe unit is similar to that of the bulk structure. Our calculations indicate that these isomers are 0.34 eV, 0.31 eV, 0.48 eV, 0.02 eV, 0.32 eV and 0.26 eV respectively, higher in energy than their corresponding lowest energy structures. Although, the cluster size has reached nanometer scale (the diameter in $(\text{PbTe})_{20}$ is 1.2 nm) the geometrical strain, as reflected in Pb-Te bond lengths, associated in the formation of hexa-coordination is not sufficiently compensated for the cluster sizes considered in this study.

3.2. Stability and energetics of $(\text{PbTe})_n$ ($n = 1–20$) clusters

The energy difference between the highest occupied and lowest unoccupied molecular orbital is a measure of the cluster stability with the higher the HOMO-LUMO (HL) gap suggesting a greater stability [13]. The calculated HOMO-LUMO (HL) gaps of $(\text{PbTe})_n$ ($n = 1–20$) neutral clusters are plotted in Fig. 5. For the most part, the HOMO-LUMO gaps of lead telluride clusters oscillate with size, although their values tend to decrease with increasing size, for example the HOMO-LUMO gap of PbTe dimer is 2.47 eV and that of $(\text{PbTe})_{18}$ cluster is 1.46 eV. Significantly, the PbTe dimer has the largest and $(\text{PbTe})_3$ cluster has the lowest HOMO-LUMO gap found in this study.

In an experimental study of quantum dots synthesized via electroporation of synthetic vesicles, exhibited time-dependent, oscillating red and blue shifts of their UV absorption bands [13]. In addition, beyond the size corresponding to $n = 8$ a monotonic redshift of the absorption band was observed. Our calculated results exhibit an oscillating trend in the HL gaps with a sharp drop in HL gap values beginning at ($n = 9$), and a minimal change in the HL gap observed at $n = 13–15$. Curiously, our theoretical results are similar with the above mentioned experimental results. Beside this what we observed from the optimization process is that a cluster that exhibit homonuclear (Pb-Pb or Te-Te) interaction have a very low HOMO-LUMO gap among the isomers example (Figs. 1, 2a–c and 3) and HL gap also depend on the number of coordination posses by each lead and tellurium atoms in the cluster, in general

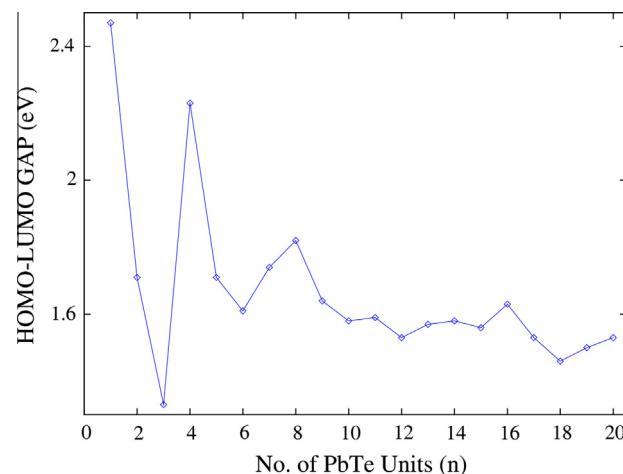


Fig. 5. HOMO-LUMO gap of $(\text{PbTe})_n$ clusters as a function of the number of PbTe units (n).

clusters that posses high coordination of atoms observed to have lowest HL gaps (Fig. 1).

Binding energy of the cluster is the mechanical energy required to disassemble a whole cluster into separate parts of atoms. It is the energy that keeps the atoms together in the cluster. The binding energy per atom, E_b , of $(\text{PbTe})_n$ ($n = 1–20$) clusters is calculated from the following equation:

$$E_b = \frac{-[E(\text{PbTe})_n - n(E(\text{Pb}) + E(\text{Te}))]}{2n} \quad (1)$$

These E_b values as a function of the number of PbTe molecule (n) are plotted in Fig. 6. The E_b values increase dramatically with the number of PbTe units between $n = 1–4$. Beyond $n = 4$, the change in binding energy per atom is minimal, with even n clusters exhibiting slightly larger binding energies than odd n clusters because the binding energy depend on the coordination number of the cluster and its symmetry. The nearly saturated binding energies beyond $n = 4$ may be due to structural similarities among larger $(\text{PbTe})_n$ clusters, possibly due to the presence of cubical $(\text{PbTe})_4$ motifs.

Another method to determine the relative stability is through electron affinity. Electron affinity is a measure of the energy change when an electron is added to a neutral atom to form a negative ion. The lead telluride clusters with smaller electron affinities are expected to be more stable than their neighbors. The vertical

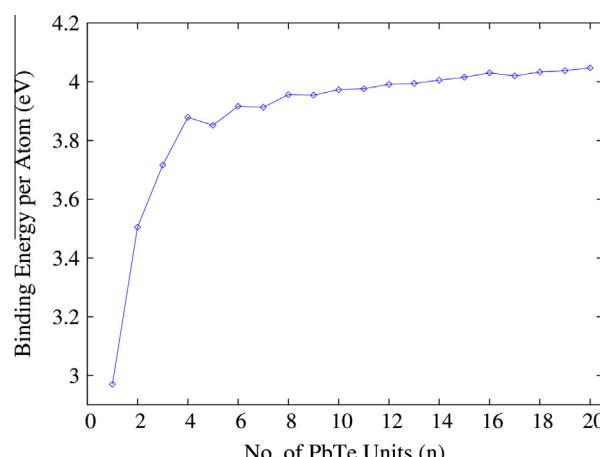


Fig. 6. Binding energy per atom of $(\text{PbTe})_n$ clusters as a function of the number of PbTe units (n).

electron affinity (VEA) and the adiabatic electron affinity energy (AEA) values as a function of the number of PbTe molecule (n) are plotted in Fig. 7. Vertical and adiabatic electron affinity (VEA and AEA) for the cluster, revealing a pattern of alternating values in which even n clusters exhibited lower values than odd n clusters up until $n = 8$ and beyond $n = 13$, although their values tend to decrease with increasing size, for example the VEA and AEA of $(\text{PbTe})_2$ cluster is 2.62/2.34 eV on the other hand for $(\text{PbTe})_{20}$ cluster is 1.74/1.69 eV. For relatively small clusters $(\text{PbTe})_4$ have a very low VEA and AEA values compare to its neighbors. It is observed that clusters with higher HOMO–LUMO gap have smaller vertical and adiabatic electron affinity and vice versa.

Lead telluride semiconductors applied in the field of thermoelectric, infrared detection and thermal imaging all these applications need the thermodynamic properties of $(\text{PbTe})_n$ clusters. In order to study the thermodynamic stability of $(\text{PbTe})_n$ clusters, we have calculated the dissociation energies along different pathways such as fragmentation losing PbTe, $(\text{PbTe})_2$, $(\text{PbTe})_4$ and $(\text{PbTe})_8$ using the following equations [14]:

$$E_1 = -[E(\text{PbTe})_n - E(\text{PbTe})_{n-1} - E(\text{PbTe})] \quad (2)$$

$$E_2 = -[E(\text{PbTe})_n - E(\text{PbTe})_{n-2} - E(\text{PbTe})_2] \quad (3)$$

$$E_4 = -[E(\text{PbTe})_n - E(\text{PbTe})_{n-4} - E(\text{PbTe})_4] \quad (4)$$

$$E_8 = -[E(\text{PbTe})_n - E(\text{PbTe})_{n-8} - E(\text{PbTe})_8] \quad (5)$$

The fragmentation energies are calculated by considering the total energies of both the parent and the product clusters. The fragmentation energies calculated here provide us with a gauge of the stabilities of these clusters. In Fig. 8, we show fragmentation energies as a function of number of PbTe molecule (n) for the above four product outcomes. It is evident that $(\text{PbTe})_4$ exhibits unusually high stability compared to its neighboring clusters (more difficult to fragment). In addition, the fragmentation/dissociation resulting in $(\text{PbTe})_4$ as a product cluster is found to be consistently the most preferred fragmentation pathway for all of the $(\text{PbTe})_n$ clusters in the present study. This can also be seen from the HOMO–LUMO energy gap and binding energy curves. Among all the clusters, $(\text{PbTe})_8$ requires the least amount of energy (1.24 eV) to dissociate into two $(\text{PbTe})_4$ clusters. This scenario is consistent with the structure of $(\text{PbTe})_8$ discussed earlier, where the lowest energy geometry of $(\text{PbTe})_8$ can be seen as two weakly interacting $(\text{PbTe})_4$ cubic units. The fragmentation pathway leading to PbTe and $(\text{PbTe})_{n-1}$ units exhibits an odd–even alteration, with clusters comprising even numbers of PbTe units being more stable than

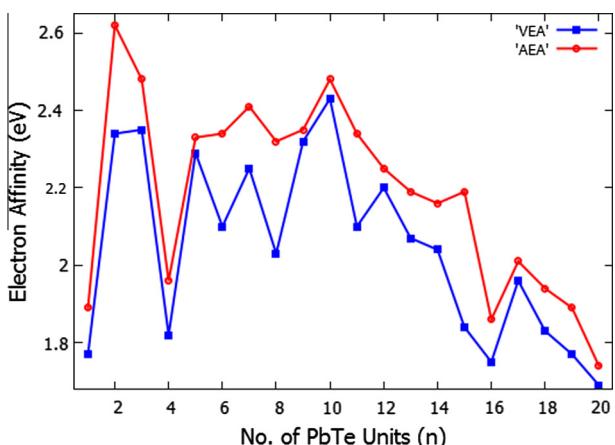


Fig. 7. Vertical and adiabatic electron affinities of $(\text{PbTe})_n$ clusters as a function of the number of PbTe units (n).

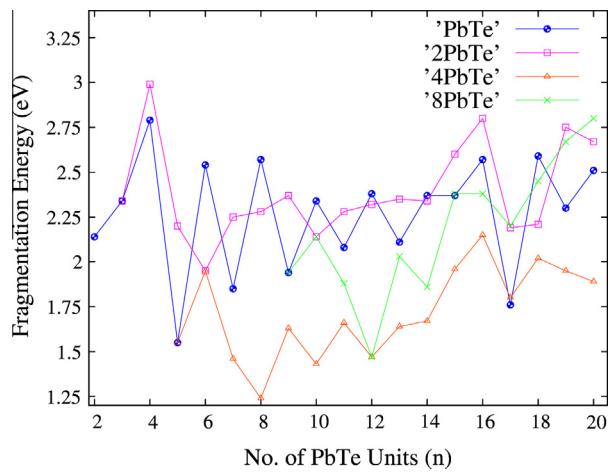


Fig. 8. Fragmentation energy losing of PbTe, $(\text{PbTe})_2$, $(\text{PbTe})_4$ and $(\text{PbTe})_8$ units of $(\text{PbTe})_n$ clusters as a function of the number of PbTe units (n).

clusters with odd values, indicating that the PbTe units prefer to add in pairs (i.e., Pb_2Te_2) and the lowest value is observed in the cage structure $(\text{PbTe})_5$ cluster. This is also consistent with the odd–even alteration observed in the electron detachment energy values, where the clusters with even n have a lower AEA than the clusters with odd n .

It is well known in cluster physics [14] that during the fragmentation of larger clusters, the most preferred fragmentation pathway often leads to the most stable species, i.e., a magic number cluster. A magic cluster is typically characterized by unusually high stability compared to its immediate neighbors, a large HL gap, and a smaller EA value than that of its immediate neighbors. The $(\text{PbTe})_4$ cluster satisfies all these criteria and can be classified as a magic cluster.

Both lead and tellurium atoms possess even number of valence electrons therefore the odd clusters contains unbalanced (unpaired) electrons, so they considered as immobilized free radical, the presence of these unpaired electrons in the odd clusters responsible for the formation of a number of dangling valence bonds, a chemical bond associated with an atom in the surface layer of a cluster that does not join the atom with a second atom but extends in the direction of the cluster's exterior. The origin of even–odd oscillations in the energetic properties of these clusters is the instability of odd clusters due to the presence of dangling bonds. In computational chemistry, a dangling bond is an error in structure creation, in which an atom is inadvertently drawn with too few bonding partners, or a bond is mistakenly drawn with an atom at only one end.

4. Conclusion

In the $(\text{PbTe})_n$ clusters, the observed electron attachment energies of these clusters show an odd–even alteration up to $n = 8$. Among the clusters considered in this study, $(\text{PbTe})_4$ has low AEA of 1.96 eV. For small clusters ($1 \leq n \leq 5$), our calculations revealed that the structures with Pb–Pb bonds were either lowest energy geometries or energetically competitive. Beyond $n = 5$, isomers containing Pb–Te bonds were found to be preferred. As a general rule, for any given neutral lead telluride cluster, the peripheral Pb–Te bonds are shorter and the interior bonds longer. This is due to the high coordination and the increased geometrical strain at the interior of the cluster. In addition, the energetics (binding, fragmentation, HL gaps) pertaining to the structural evolution of these clusters indicate that the $(\text{PbTe})_4$ is a magic cluster. Further-

more, in neutral $(\text{PbTe})_n$ ($n = 11\text{--}20$) nanoclusters, there is a strong preference for forming structures based on the two-dimensional stacking of cubes, in which the Pb and Te atoms prefer a maximum of fivefold coordination. The transition from one-dimensional stacking to two-dimensional stacking of cubes starts at $(\text{PbTe})_{11}$ clusters. This observation raised an important question: At what cluster size of $(\text{PbTe})_n$ does the transition to bulk-like structures occur, i.e., where the Pb and Te atoms have a sixfold coordination. Thus, one might expect a change in the optical properties of $(\text{PbTe})_n$ clusters when they undergo a structural transition from a two-dimensional layered structure to a bulk-like structure. A systematic study focusing on the structural evolution of $(\text{PbTe})_n$ nanoclusters with size is vital for understanding their size-dependent optical and electronic properties.

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