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Structural transition in Ba_nO_m clusters

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We have studied the atomic structures of small Ba_nO_m ($m \leqslant n \leqslant 9$) clusters, using the density functional theory with the generalized gradient approximation. A structural transition was found during the uptaking of oxygen atoms into Ba_n clusters. Initially, the frame of a Ba_n cluster is kept unchanged, while oxygen atoms occupy the tetrahedral positions. As the number of oxygen atoms exceeds a certain limit, a transition from the compact to cubiclike structure takes place, with an increasing highest occupied molecular orbital–lowest unoccupied molecular orbital gap. In contrast to other ionic clusters, segregation of Ba atoms was not observed in our calculations, in agreement with reported experiments.

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I. INTRODUCTION

One of the important issues in the study of cluster physics is the evolution of binding and structural properties from atomiclike to bulklike. Most metallic clusters with tens of atoms show a compact structure with icosahedronlike symmetry. Although bulklike structure can be developed in small clusters, the complete transformation to bulklike structure usually happens only in very large clusters. On the other hand, the binding properties approach the bulk much faster. A typical example is the alkaline-earth element cluster. The alkaline-earth element has a closed ns^2 shell. Clusters with two alkaline-earth atoms,[1–4] such as Mg_2 and Ba_2, are bound by the Van de Walls interaction, even though the alkaline-earth solids are metals. Theoretical calculations found that the transition from Van de Walls to metallic interaction among such clusters took place for quite small clusters.[2–5]

Both structure and bonding transitions can happen in alkaline-earth oxide clusters with increasing size. For the small $(BaO)_n$ clusters, we observed three growth modes for $n \leqslant 9$, among which the cubiclike growth mode is favored for large clusters.[6] However, compared to metallic clusters, much less is known about the structural properties of nonstoichiometric oxide clusters. For alkali oxide clusters, such as Li_nO_m, it was shown that the atomic structure could be viewed as $Li_{n-2m}(Li_2O)_m$. In other words, the excess alkali atoms aggregate among themselves to form a cluster, which is capped by a stoichiometric oxide cluster.[7,8] In the mass spectra of alkaline-earth oxide clusters, Martin and Bergmann[9] found that, the magic numbers for the icosahedral Ba_n clusters did not change upon uptake of up to five oxygen atoms, which implied that the structure of the icosahedral Ba_n could embed a few oxygen atoms. In terms of binding properties, the Ba clusters with a very small number oxygen atoms remain metallic. But as more oxygen atoms are added, there is a sudden change in the ionization potential (IP), which indicates a binding or structural transition. Very recently, IP measurements on barium oxide clusters Ba_nO_m (Refs. 10 and 11) show two such transitions. For small *m*, the IP remains roughly constant, which indicates that the energy required to ionize one electron is not sensitive to the number of oxygen atoms. For larger *m* with $n-m \leqslant 4$, the IP could decrease by 0.5 eV. However, going from Ba_nO_{n-1} to Ba_nO_n, a large increase of IP (<1.0 eV) suggests a complete transition to purely ionic binding in Ba_nO_n cluster, although the exact nature of the structural change is not clear.

In this paper, we report an extensive study on the structures and properties of Ba_nO_m to understand the structural changes in Ba_n clusters upon oxidization, using the *ab initio* molecular-dynamics method based on the discrete Fourier transform (DFT) theory. The change in cluster structures is followed carefully as oxygen atoms are added into Ba_n one by one. We find that at the initial stage of oxidization, the oxygen atom occupies the interstitial positions in Ba clusters without changing its structure. As more oxygen atoms are added into a Ba cluster, there is a transition to cubic structure. Such a change gives a good account for previously reported IP measurement.

II. DETAILS OF CALCULATIONS

Our calculations are based on density functional theory.[12–15] The structures of clusters are optimized by the *ab initio* molecular-dynamics method.[13,15] The clusters are placed in a simple cubic cell with a lattice constant of 18 Å. We chose a large size cell to make the interaction between a cluster and its periodic images negligible. The ultrasoft

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pseudopotential[16] is used to describe the interaction between the core and valence electrons. The wave functions are expanded in a plane wave base with an energy cutoff of 270 eV. The exchange and correlation energy is calculated within the generalized gradient approximation (GGA).[17] Only the Γ point is used in the summation of the Brillouin zone of the simulation cell.

Since we have no *a priori* knowledge about the structures of these clusters, the structures of bare Ba_n clusters[2] are first optimized, and afterwards oxygen atoms are added one by one. For each $\mathrm{Ba}_n\mathrm{O}_m$ cluster, we have performed an extensive sampling of the potential surface by generating a large set of random structures as initial configurations. From each initial configuration, the structure is optimized by the conjugate gradient method, with a force convergence up to 2 meV/Å, i.e., the optimization stops when the largest force on all the atoms is smaller than 2 meV/Å. The structure with the lowest total energy is taken to be the ground-state structure.

To test the accuracy of the pseudopotentials, we have optimized interatomic distances of the Ba_2, BaO, and O_2 molecules. The interatomic distances obtained are 4.72 Å, 2.02 Å, and 1.28 Å, in comparison with experimental results of 4.6 Å, 1.94 Å, and 1.21 Å respectively.[1,10,18,19] The calculated lattice constants for Ba and BaO solids are 4.88 Å and 5.54 Å, respectively, which are in close with the experimental data 5.02 Å and 5.52 Å.[20,21]

III. RESULTS AND DISCUSSION

A. Structure of oxygen-poor $\mathrm{Ba}_n\mathrm{O}_m$ cluster

By adding oxygen atoms into the ground state structure of Ba_n clusters followed by further optimization, we obtain the structures of the $\mathrm{Ba}_n\mathrm{O}_m$ clusters, which are shown in Fig. 1.

For Ba_6, which is an octahedron,[2] one oxygen atom can be embedded without much distortion. Putting the oxygen atom inside the octahedron is energetically more favorable than leaving it outside. The oxygen atom could either be at the center of the octohedron or located asymmetrically on one side to bind with four Ba atoms in a tetrahedral unit as illustrated in Fig. 1(a). In terms of energy, the latter is more stable by just 0.03 eV, as the tetrahedral coordination of Ba atoms around O is favored, and the ionic interation between O and Ba atoms is stronger in the tetrahedral unit. If the oxygen atom is at the center of the octahedron, the unrelaxed Ba-O distance is 2.93 Å, which is too long for favorable ionic bonding. The optimized Ba-O distance, as shown in Fig. 1(a), is about 2.53 Å, 10% shorter than Ba-O distance in solid. Our calculation on $\mathrm{Ba}_4\mathrm{O}$ shows that its ground state structure is tetrahedral, in agreement with previous theoretical results.[10,11,22] It has also been noted before that the structure of $\mathrm{Ba}_5\mathrm{O}$ with the oxygen atom sitting at the tetrahedral position is about 0.25 eV more stable than the structure with the oxygen atom capped on a surface of the Ba_5 ground-state structure, which could be viewed as two tetrahedrons joined together sharing a surface.[2]

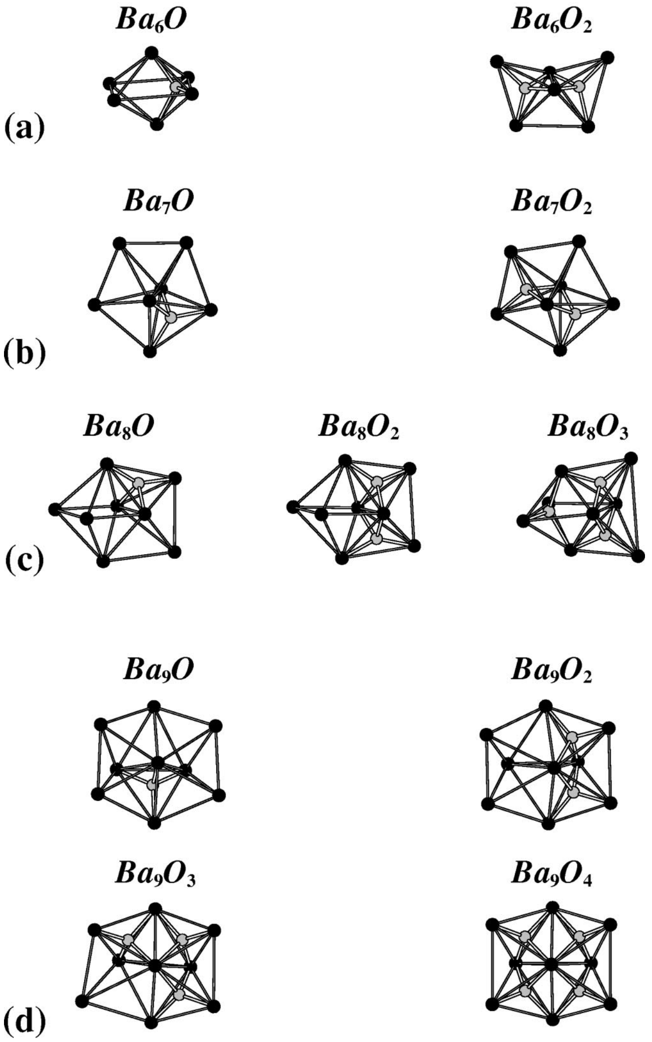

FIG. 1. The structure of $\mathrm{Ba}_n\mathrm{O}_m$ cluster with low concentration of O atoms. Dark circle for Ba atom and gray circle for oxygen atom. (a) $\mathrm{Ba}_6\mathrm{O}_m$ cluster, (b) $\mathrm{Ba}_7\mathrm{O}_m$ cluster, (c) $\mathrm{Ba}_8\mathrm{O}_m$ cluster, (d) $\mathrm{Ba}_9\mathrm{O}_m$ cluster.

The octahedral Ba_6 is not optimal for taking up two oxygen atoms, since it is too small to enclose both oxygen atoms. As a result, one oxygen atom has to be capped on the surface of the octahedron, and such a structure is not the most stable one. Instead, an isomer of Ba_6 with three adjacent tetrahedrons and a lower C_{2v} symmetry[2] is more favored, as it has enough tetrahedral positions to embed two oxygen atoms. As shown in Fig. 1(a), in such a structure, both oxygen atoms are at the tetrahedral positions. For the bare Ba_6, the energy difference between the structure with C_{2v} symmetry and the most stable octahedral structures is very small (0.03 eV), which is easily compensated by the energy gain in maximizing the number of O-Ba interaction upon embedding two oxygen atoms.

Figure 1(b) shows the structure of $\mathrm{Ba}_7\mathrm{O}_m$ $(m \leq 2)$ cluster. The ground-state structure of bare Ba_7 is pentagon bipyramid, which can embed up to two oxygen atoms in tetrahedral positions. However, it cannot accommodate three oxygen atoms in tetrahedral positions with sufficient O-O separation.

The structure of Ba_8 cluster can be considered as two Ba atoms capped on the adjacent faces of an octahedron, and there are three nonadjacent tetrahedral positions for oxygen atoms. As shown in Fig. 1(c), the first two positions are nearly ideal tetrahedron, but the third position is slightly distorted.

The structure of Ba_9 was found to be a C_{2v} geometry with two Ba atoms capped on adjacent faces of Ba_7 pentagon bipyramid structure. It can be also viewed as eight tetrahedrons joined together. However, the neighboring tetrahedral positions are too close, and Ba_9 can only accommodate four oxygen atoms as shown in Fig. 1(d).

B. Ba_nO_m cluster with cubiclike structures

BaO solid is a pure ionic solid, with cubic structure. We find that, as more oxygen atoms are added to Ba_n cluster and the number of ionic bonds increases, the Ba_n-like structure of Ba_nO_m clusters is suddenly changed to a cubiclike structure, which essentially consists of a cubiclike stoichiometric barium oxide cluster capped with a few Ba atoms, as shown in Fig. 2.

Although Ba_6O_3 is far from being stoichiometric, its structure becomes cubiclike and is totally different from the structure of pure Ba_6 cluster. As shown in Fig. 2(a), it can be considered as two Ba atoms capped on a Ba-O cube of Ba_4O_3, which is almost a cubic, albeit with one missing oxygen atom. For Ba_6O_4, a perfect cube of Ba_4O_4 has been formed and the two extra Ba atoms are again capped on two faces of the cube. It is interesting to note that the two extra Ba atoms are closely bonded to oxygen atoms. With one more oxygen atom in Ba_6O_5, the structure becomes more cubiclike and more compact. For Ba_6O_6, the structure is a perfect cuboid.

The structure of Ba_7O_3 is also cubiclike, bearing little resemblance to the structure of a bare Ba_7 cluster. Generally, the structures of Ba_7O_m ($m=3,4,5,6$) clusters can be viewed as a Ba atom capped on a corresponding Ba_6O_m cluster, as shown in Fig. 2(b). However, Ba_7O_7 cluster is an exception to this rule. The cubiclike structure with a BaO molecule capped on a Ba_6O_6 cuboid is an isomer, with a total energy about 0.5 eV higher than the ground-state structure. As discussed before,[6] the structure of Ba_7O_7 is based on an antitetragonal prism, because it cannot form a perfect cube. In such a compact structure, there are more O-Ba ionic bonds, which increases the binding energy and makes the structure more stable than the cubiclike structure.

When oxygen atoms are added into Ba_8 cluster, a cubiclike structure takes shape beginning at Ba_8O_4, with four Ba atoms capped on the faces of a Ba_4O_4 cube, as shown in Fig. 2(c). As more oxygen atoms added, the structure of Ba_8O_m can be viewed as an oxygen atom capped on the structure of Ba_8O_{m-1}. It is also interesting to note that for Ba_8O_6, the sixth O does not take the position to form a cubic Ba_6O_6 subunit within the cluster, but caps on the opposite side of cubic Ba_4O_4 unit to form a low symmetry structure [see Fig. 2(c)]. Nonetheless, these two structures are very close in binding energy with a difference of only 0.08 eV, as found in our calculations.

The equilibrium structures of Ba_9O_m ($5 \leqslant m \leqslant 9$) are presented in Fig. 2(d). As discussed in the previous section, the structure of Ba_9 cluster contains eight interstitial tetrahedral sites and can thus accommodate four oxygen atoms inside the cluster without distorting its basic structure framework. Beginning at Ba_9O_5, the structure of Ba_9O_m shows cubiclike features. Finally, the structure of Ba_9O_9 is a $3\times3\times2$ cuboid, as shown in Fig. 2(d).

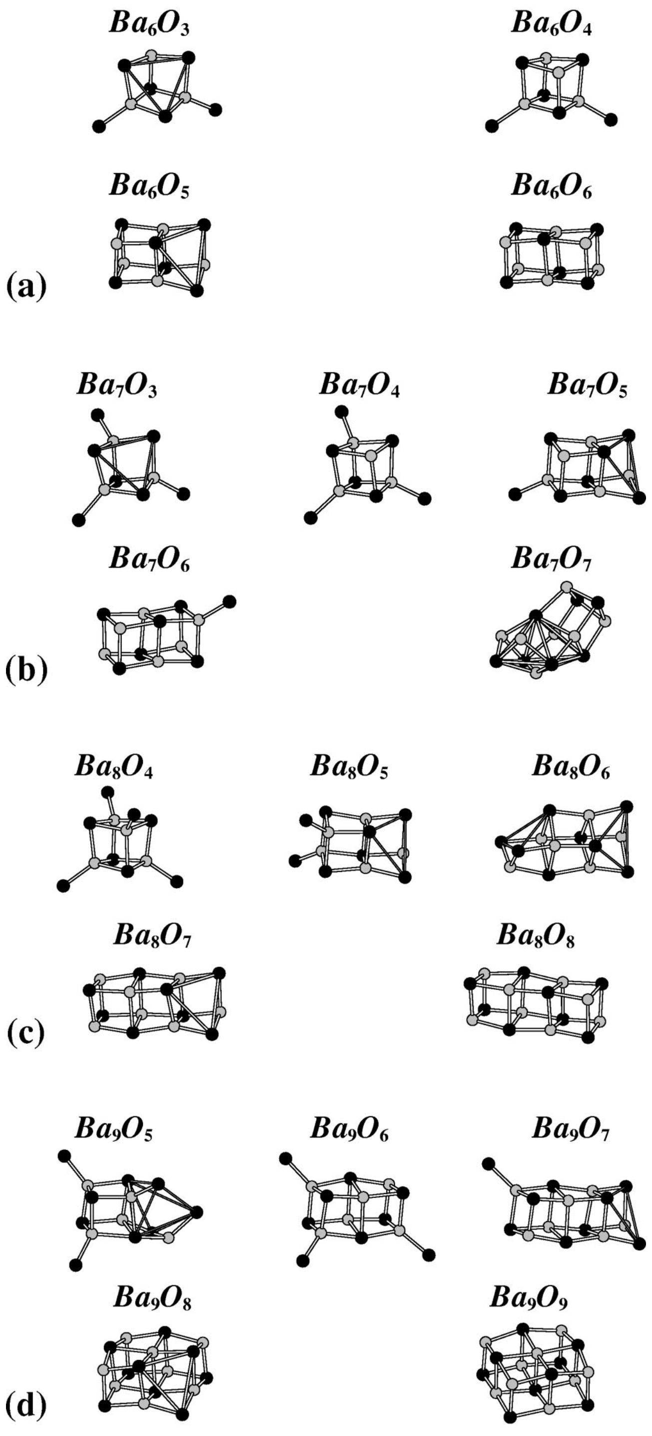

FIG. 2. The structure of Ba_nO_m cluster with cubiclike structure. Dark circle for Ba atom and gray circle for oxygen atom. (a) Ba_6O_m cluster, (b) Ba_7O_m cluster, (c) Ba_8O_m cluster, (d) Ba_9O_m cluster.

C. Structural Transition of Ba_nO_m clusters

Based on the results in the two previous sections, we can see that there are two distinct series of structures for Ba_nO_m

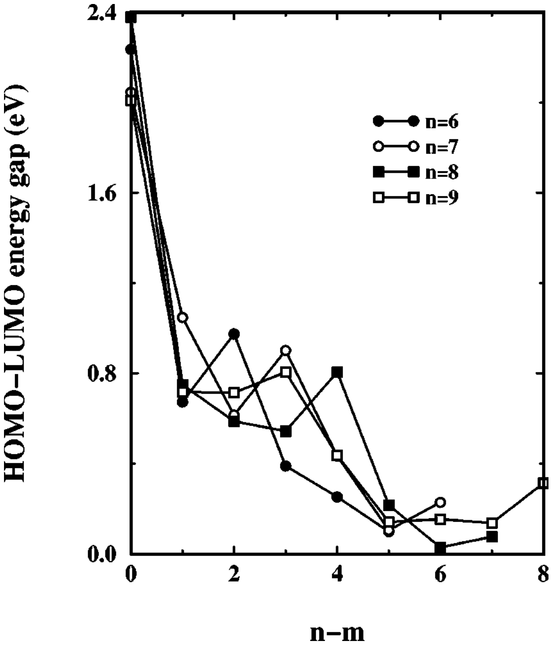

FIG. 3. The HOMO-LUMO energy gap of Ba_nO_m cluster. The sudden increase in the energy gap near $n-m=4$ indicates a transition of structure and binding behavior. The jump between $n-m=1$ and $n-m=0$ suggests that the binding becomes purely ionic.

clusters. The first one is based on the structure of pure Ba_n cluster, in which all the oxygen atoms are at the interstitial tetrahedron positions. The other one is the cubiclike structure, such as a fragment of Ba-O bulk solid, with some excessive Ba atoms capped on. A structural transition from the former to the latter takes place when there are not enough interstitial positions to embed oxygen atoms. When the number of oxygen atoms is small, the structural frame of a bare Ba_n cluster can provide enough interstitial positions for the oxygen atoms. Such accommodation is nonetheless limited by the fact that the interaction between Ba and oxygen atoms is ionic, and the interatomic distance between oxygen atoms should be as large as possible. In some cases, when every tetrahedron is filled with an oxygen atom, the distance between two neighboring oxygen atoms could become too close, with a value smaller than 2 Å. For instance, in Ba_7 the distance between two neighboring tetrahedral positions is only 1.8 Å. At such a distance, the ionic repulsion will be so strong as to make the structure unstable. As a result, not every interstitial position can embed one O atom. When an oxygen atom cannot find a proper interstitial position, the open structure with BaO bulklike geometry becomes more favorable.

Such a structural transition opens a small electronic energy gap in the Ba_nO_m cluster. Bare Ba_n cluster is metallic. After adding a small number of oxygen atoms to the Ba cluster, the gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) does not change much, as seen from Fig. 3. However, when the value of $n-m$ becomes smaller than $3\sim4$, an energy gap around 0.8 eV is observed, which suggests a change in the binding character from metallic to partially ionic. As the substoichiometric Ba_nO_{n-1} approaches stoichiometric Ba_nO_n cluster, all bonds become ionic, and the energy gap increases another ~1 eV. The valence charge density, defined as the sum of charge density from the first three wave functions below the Fermi level, qualitatively shows the changes of binding behavior from metallic to partially ionic, and finally ionic (see Fig. 4). In Ba_6, the valence charge density is homogeneously distributed in the whole cluster, which is a typical metallic binding. In Ba_6O_2, the valence charge density is also distributed in the whole cluster. However, in Ba_6O_4 where a HOMO-LUMO gap of ~0.9 eV appeared, the valence charge density is localized around two dangled Ba atoms. In the stoichiometric Ba_6O_6 cluster, the binding is purely ionic and the HOMO is the $2p$ orbitals of oxygen atom, which can be clearly observed in Fig. 4.

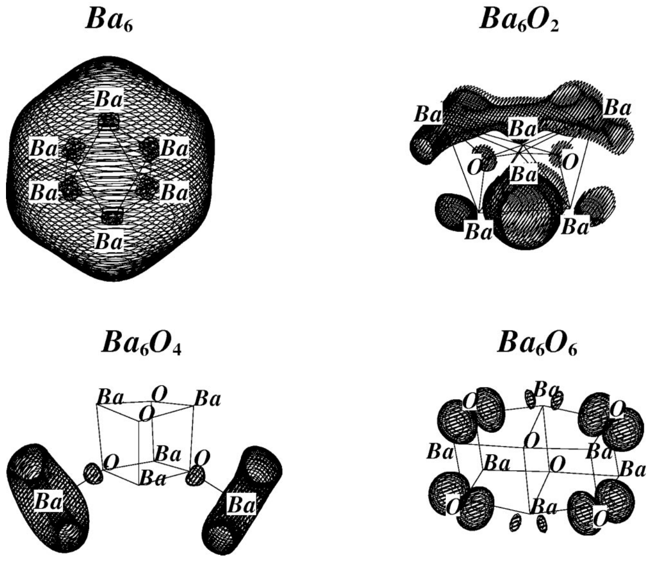

FIG. 4. Isodensity surface of the highest occupied states (HOMO) for Ba_6, Ba_6O_2 and Ba_6O_4 cluster. The delocalized, partially delocalized and localized charge density can be clearly observed in the Ba_6, Ba_6O_2, and Ba_6O_4 clusters, respectively.

The changes in cluster volume confirm the transition from the structure of a bare Ba cluster to a cubiclike structure, as shown in Fig. 5. We define the cluster volume as the volume of a polyhedron enclosed by the surface atom (nuclei). After the addition of a few oxygen atoms, these oxygen atoms are at the interstitial positions, and the volume of the cluster remains essentially the same. At the structure transition, with $n-m=3\sim4$, the cluster volume suddenly decreases by about 10.0 Å.[3] Afterwards, the cluster volume increases again with an increasing number of oxygen atoms. Such a difference before and after the transition suggests difference in the growth modes, as shown in Figs. 1 and 2. It is interesting to note that before the transition, the volume is slightly decreased with the increasing oxygen atoms. The reason is simply that the ionic bonding between O and Ba atoms makes Ba-Ba distance 0.5 Å, shorter than in a bare Ba_n cluster.

D. Discussions

It was generally believed that the ground-state structure of stoichiometric alkaline-earth oxide cluster is cubiclike, espe-

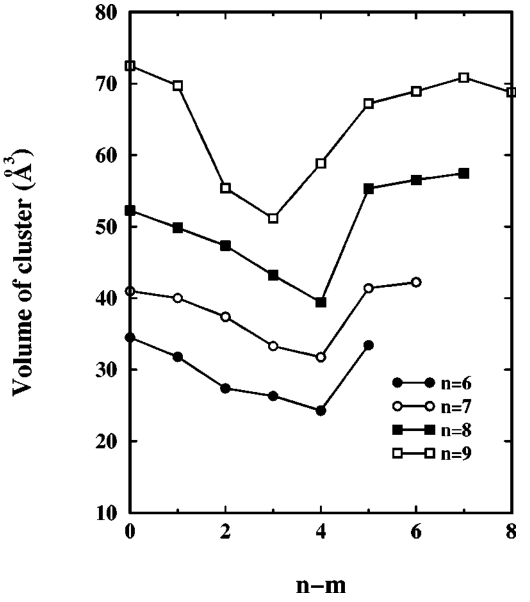

FIG. 5. The volume of $\mathrm{Ba}_n\mathrm{O}_m$ cluster as a function of O content. The dip near $n-m=4$ is an indication of structural transition.

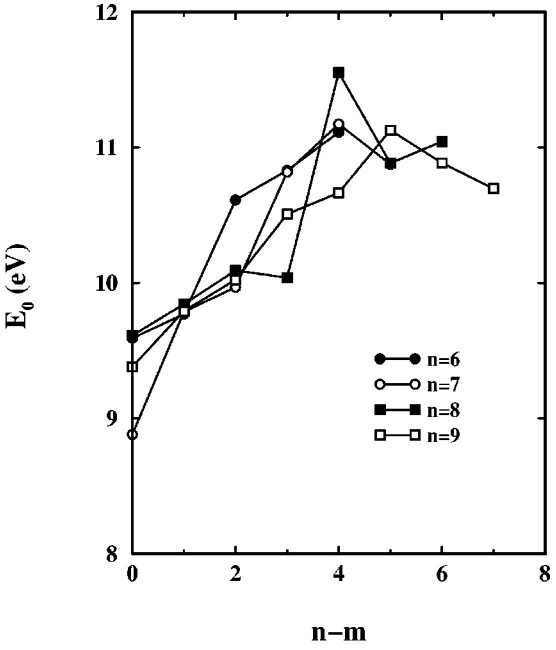

FIG. 6. The stepwise oxidization energy $[E_0=E_b(\mathrm{Ba}_n\mathrm{O}_m)-E_b(\mathrm{Ba}_n\mathrm{O}_{m-1})]$ as a function of $n-m$. For the $n-m\leqslant 4$, the binding energy increases with decreasing number of oxygen atoms. While for $n-m\geqslant 4$, E_0 does not change significantly with the content of oxygen atom, the change near $n-m=4$ suggests a phase transition.

cially for large clusters. We have shown previously that for small stoichiometric Ba-O clusters, there are three growth modes—cubiclike, ringlike, and tetragonal prism based. Although the cubiclike structure is prevailing, in terms of energy, its advantage over the other two growth modes is small.[6] On the other hand, much less is known about the structure of nonstoichiometric alkaline-earth oxide cluster. In the alkali-halide clusters.[23–25] and alkali-hydride clusters,[26,27] one can assume a simple segregation with a stoichiometric cluster and a pure metal cluster. Our calculations indicate that such a simple segregation scheme does not apply to the $\mathrm{Ba}_n\mathrm{O}_m$ cluster. Even for a cluster doped with just a few oxygen atoms, we do not observe any segregation to produce $\mathrm{Ba}_{n-m}(\mathrm{BaO})_m$, with Ba_{n-m} capped on $(\mathrm{BaO})_m$. Instead, the structural frame of the Ba_n cluster is kept, while the O atoms occupy the tetrahedral positions. This is quite different from the observation on the alkali-halide cluster. However, our results are in agreement with previous experimental observation.[9] which showed the conservation of magic number sequence for low O concentration in the icosahedral Ba clusters.

According to the IP measurement, Boutou *et al.*[10,11] suggested that a core of $\mathrm{Ba}_3\mathrm{O}_3$ or $\mathrm{Ba}_4\mathrm{O}_4$ was formed in $\mathrm{Ba}_n\mathrm{O}_m$ $(n\leqslant 8)$, although their speculation about the segregation of such a subunit from the other Ba atoms was not directly verified. We indeed find the formation of such cubiclike subunit as a core in the clusters, which indicates the transition from the compact structure of bare Ba_n to a cubiclike structure. However, no segregation among the rest of the Ba atoms is observed in our results. Our calculation clearly shows that in $\mathrm{Ba}_9\mathrm{O}_m$ clusters, a core with cubiclike structure appeared at $\mathrm{Ba}_9\mathrm{O}_5$, in close agreement with experimental observation. However, we do not see much difference in the transition for small $(n\leqslant 8)$ and large $(n>8)$ clusters.

The reason for the structural transition at different oxygen content can be attributed to the size effect. At the initial stage of oxygenation, the oxygen atoms occupy the interstitial positions of Ba_n cluster, and keep as far away from each other as possible due to strong repulsion of ions. In the small Ba_n clusters, the number of interstitial positions is limited. Thus as the number of oxygen atoms increases up to three or four, the transition to the cubiclike structure must take place. As the size of Ba_n cluster increases, more interstitial positions could be provided for oxygen atoms, and more oxygen atoms could be embedded. In agreement with experiment, our calculation suggests that the structure transition happens approximately at $n-m=4$.

Another indication of the phase transition is the energy gain when one oxygen atom is added to the cluster, we call it successive oxidization energy, defined here as $E_0=E_b(\mathrm{Ba}_n\mathrm{O}_m)-E_b(\mathrm{Ba}_n\mathrm{O}_{m-1})$. As shown in Fig. 6, when $n-m$ is larger than 4, i.e., in the first stage of oxygenation, all the oxygen atoms are embedded in the interstitial positions, and the energy gain by adding one O is almost the same, around 11 eV, while, as $n-m\leqslant 4$, the energy gain when adding one oxygen atom decreases linearly. The sudden change in the behavior of binding energy strongly suggests a phase transition near $n-m=4$.

IV. CONCLUSIONS

We have performed an extensive theoretical study on the structural evolution in the oxidization of barium clusters, with the atomic structure of $\mathrm{Ba}_n\mathrm{O}_m$ $(m\leqslant n\leqslant 9)$ clusters optimized by conjugate gradient method. The results show that in the initial stage of oxygenation, the O atoms favor tetrahedral positions. Due to the strong ionicity of the oxygen atom, not all the interstitial positions can be occupied as close contact between oxygen atoms must be avoided. Thus, a Ba_n cluster can only embed a small number of oxygen atoms. When more oxygen atoms are added, the structure of the Ba cluster becomes unstable. Instead, a cubiclike core can be formed, while the excessive Ba atoms are capped on the core. We do not observe any segregation, in contrast to the structure of alkali-halide clusters. We also find that, along with the structural transition, there is a noticeable change in the successive oxidation energy.

In summary, we have shown that oxidization can induce a structural transition at $n-m=4$, with an energy gap up to ~ 0.8 eV appeared. These results will shed light on understanding the microprocess of oxidization on the solid surface.

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[1] V. Boutou, A.R. Allouche, F. Spiegelmann, J. Chevaleyre, and M.A. Frécon, Eur. Phys. J. D **2**, 63 (1998).
[2] G. Chen, Z.F. Liu, and X.G. Gong, Eur. Phys. J. D **16**, 33 (2001).
[3] V. Kumar and R. Car, Phys. Rev. B **44**, 8243 (1991).
[4] R. Kawai and J.H. Weare, Phys. Rev. Lett. **65**, 80 (1990).
[5] X.G. Gong, Q.Q. Zheng, and Y.Z. He, Phys. Lett. A **181**, 459 (1993).
[6] G. Chen, Z.F. Liu, and X.G. Gong, J. Chem. Phys. **116**, 1339 (2002).
[7] P. Lievens, P. Thoen, S. Bouckaert, W. Bouwen, F. Vanhoutte, H. Weidele, R.E. Silverans, A. Navarro-Vázquez, and P. von R. Schleyer, J. Chem. Phys. **110**, 10 316 (1999).
[8] F. Finocchi and C. Noguera, Phys. Rev. B **57**, 14 646 (1998).
[9] T.P. Martin and T. Bergmann, J. Chem. Phys. **90**, 6664 (1989).
[10] V. Boutou, M.A. Lebeault, A.R. Allouche, C. Bordas, F. Paulig, J. Viallon, and J. Chevaleyre, Phys. Rev. Lett. **80**, 2817 (1998).
[11] V. Boutou, M.A. Lebeault, A.R. Allouche, F. Paulig, J. Viallon, C. Bordas, and J. Chevaleyre, J. Chem. Phys. **112**, 6228 (2000).
[12] N.D. Mermin, Phys. Rev. A **137**, 1141 (1965).
[13] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).
[14] M.C. Payne, M.P. Teter, D.C. Allan, T.A. Arias, and J.D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992).
[15] E.G. Moroni, G. Kresse, J. Hafner, and J. Furthmüller, Phys. Rev. B **56**, 15 629 (1997).
[16] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[17] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).
[18] Q. Wang, Q. Sun, J.-Z. Yu, B.-L. Gu, Y. Kawazoe, and Y. Hashi, Phys. Rev. A **62**, 063203 (2000).
[19] A.R. Allouche, M. Aubert-Frécon, G. Nicolas, and F. Spiegelmann, Chem. Phys. **200**, 63 (1995).
[20] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1976).
[21] R. W. G. Wyckoff, *Crystal Structures*, 2nd ed. (Wiley, New York, 1963 and 1964), Vols. 1 and 2.
[22] V. Bonačić-Koutecký, J. Pittner, R. Pou-Amerigo, and M. Hartmann, Z. Phys. D: At., Mol. Clusters **40**, 445 (1997).
[23] P. Labstie, J.M. Hermite, Ph. Poncharal, and M. Sence, J. Chem. Phys. **103**, 6362 (1995).
[24] G. Rajagopal, R.N. Barnett, A. Nitzan, U. Landman, E.C. Honea, P. Labastie, M.L. Homer, and R.L. Whetten, Phys. Rev. Lett. **64**, 2933 (1990).
[25] G. Rajagopal, R.N. Barnett, and U. Landman, Phys. Rev. Lett. **67**, 727 (1991).
[26] B. Vezin, Ph. Dugourd, D. Rayane, and M. Broyer, Surf. Rev. Lett. **3**, 171 (1996).
[27] B. Vezin, Ph. Dugourd, D. Rayane, P. Labasite, J. Chevaleyre, and M. Broyer, Chem. Phys. Lett. **206**, 521 (1993).