Structure and growth modes of $(BaO)_n$ ($n \leq 9$) clusters

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Using density functional theory with the generalized gradient approximation, we have studied the
structures of small $(BaO)_n$ ($n \leq 9$) clusters. We find that there are three different growth modes
(cubic-like, ring-like and anti-tetragonal prism based) for the $(BaO)_n$ clusters. Although the
cubic-like structure is prevailing for the clusters, the energy difference from other growth modes is
small. The anti-tetragonal prism based structures are found to be ground states for $(BaO)_5$ and
$(BaO)_7$. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1427716]

I. INTRODUCTION

One of the primary goals of cluster science is to study
the properties of small clusters as they evolve to those of the
bulk condensed state. For small clusters, structures are usu-
ally different from that of the bulk. Thus it is interesting to
know at which size the cluster shows the bulk-like structure.
Since there is no direct way to experimentally measure the
atomic structure of small clusters, numerous theoretical
works have been done. However, most of these works con-
centrated on the metallic and semiconductor clusters. It is
now clear that, the compact structure dominates most of the
small metallic clusters because of the geometric and elec-
tronic shell effect. The bulk-like structure usually appears in
the clusters with a few tens of atoms or even larger. In the
semiconductor-like clusters, the dangling bonds result in
very complicated structures of small clusters.

In contrast to metallic and semiconductor clusters, the
study of metal-oxide clusters has by far progressed much
less, despite their fundamental role in many physical pro-
cesses, such as heterogeneous catalysis, metal oxidation, etc.
In the large stoichiometric alkali-earth metal oxide clusters,
the structure is believed to be mostly cubic-like, which has
been confirmed by experimental observations[1–6] and also by
theoretical calculations based on model potentials.[4,5,8] En-
hanced stability of $(MgO)_n Mg^{2+}$ clusters were found for n
$= 8, 11, 13, 16, 19, 22, 25,$ and 27 in the mass spectrum,
which was explained in terms of a cubic-like cluster resem-
bling pieces of the MgO crystal lattice.[4,5,7] For very small
clusters with only a few molecules, the atomic structures
have been studied by the Hartree–Fock method,[5,7,9–12] and
density functional theory.[13–18] In the regime of large clusters,
calculations based on model potentials found that the struc-
ture is cubic-like, in agreement with results from the experi-
mental mass spectrum. While for the clusters containing

2–10 molecules, the model potential predicted that most of
the structures were spherical-like with squares and
hexagons.[5] However, in the regime of small cluster size,
quantum effect would be very important and the empirical
model will be invalid. For example, an experimental study
found that, the structures of small MgO and CaO clusters are
different. The building block of MgO cluster is $(MgO)_3$ and
the building block of CaO cluster is $(CaO)_2$,[6] which strongly
suggests that electronic effect in the small metal-oxide clus-
ters is important. But there are few systematic studies on the
structures of metal-oxide clusters from first principles.

In this paper, we have studied the atomic structure of
stoichiometric $(BaO)_n$ ($n \leq 9$) clusters, based on the density
functional theory. We find three growth modes, cubic-like
mode, ring-like mode and anti-tetragonal prism based mode.
The cubic-like structure appears in the very small BaO clus-
ters and dominates the whole series in the studied regime.
However, we predict a new anti-tetragonal prism based
growth mode which appears from $(BaO)_5$.

II. CALCULATION DETAILS

Our calculations are based on the density functional
theory,[19–21] with generalized gradient approximations
(GGA).[22] Since we have no *a priori* knowledge as to what
the structures of these clusters are, we have performed an
extensive sampling of the potential surface by generating a
large set of random structures as initial configurations for
each cluster ($n = 2–9$). From each initial configuration, we
optimize the structure by the conjugated gradient method,
with a force convergence up to 0.02 eV/Å. The clusters with
size $n = 2–8$ are placed in a simple cubic cell with a lattice
constant 14 Å, and a big cell with edge length 16 Å is used
in the calculation of $(BaO)_9$ cluster. The size of the cell is
large enough so that the interaction between a cluster and its

periodic images is negligible. Only the Γ point is used in the summation of the Brillouin zone of the simulation cell. We have used the ultrasoft pseudopotential[23,24] to describe the interaction between the valence electrons and the core. The wave functions are expanded in a plane wave basis with an energy cutoff 270.0 eV.

To test the accuracy of our methods, we have optimized interatomic distances of the Ba_2, BaO, and O_2 molecules. The obtained interatomic distances are 4.92, 2.25, and 1.32 Å, which are in agreement with previous theoretical results.[2,15,25,26]

III. RESULTS AND DISCUSSIONS

We have found three growth modes for the structures of the studied $(BaO)_n$ clusters. Figure 1 shows the obtained structures of $(BaO)_n$ clusters. Three different growth modes, the cubic-like structure, the ring-like structure and the anti-tetragonal prism based structure can clearly be observed. Although for most of the clusters, the cubic-like structure has the largest energy, some of the clusters with the anti-tetragonal prism based structures have larger energies. Most importantly, in those $(BaO)_n$ clusters, the energies for different structures are quite close.

We have shown the cubic-like structures of $(BaO)_n$ clusters in Fig. 1(a). Since each Ba atom has two electrons which can be transferred to an O atom, forming a cubic structure as observed in BaO solid, it is not surprising to find the cubic-like structure for the $(BaO)_n$ clusters. The cubic-like growth mode starts at $(BaO)_4$ cluster. Clusters $(BaO)_6$, $(BaO)_8$, and $(BaO)_9$ also show cubic-like structures, corresponding to slightly distorted $2\times2\times3$, $2\times2\times4$, and $3\times3\times2$ rectangles, respectively. For $(BaO)_3$, $(BaO)_5$ and $(BaO)_7$ clusters, for which there is no way to form a rectangle, the obtained structures can be simply considered as a cubic-like structure with a BaO molecule missing, respectively.

Figure 1(b) shows the ring-like structures of $(BaO)_n$ clusters. We find that $(BaO)_n$ clusters with size $n=2-5$ are all two-dimensional ring structures, with a symmetry of D_{2h}, D_{3h}, D_{4h}, or D_{5h}, respectively. The structural transition from two-dimensional to three-dimensional structure occurs at $(BaO)_6$. The three-dimensional structure of $(BaO)_6$ consists of two $(BaO)_3$ hexagonal rings stacked together along the axial direction of the ring, as shown in Fig. 1(b). Obviously, the three-dimensional structure is more compact and has more bonds than the two-dimensional ring-like structure. One can obtain the structure of $(BaO)_7$ by capping the extra BaO molecule on the edge of $(BaO)_6$. The structure of $(BaO)_8$ consists of two $(BaO)_4$ rings stacked together along the axial direction of the $(BaO)_4$ ring, while $(BaO)_9$ can be considered as three $(BaO)_3$ rings stacked together. One could expect that a structure of $(BaO)_{10}$ could be formed by stacking two $(BaO)_5$ rings together. Thus, by using $(BaO)_3$, $(BaO)_4$ and $(BaO)_5$ as the building blocks, one can obtain the ring-like structure for an even larger cluster.

It is interesting to note that unlike the cubic-like structure, which can be considered as a fragment of solid structure, the ring structure has not been observed in the BaO solid phase. Thus, the ring-like structure can only be considered as a metastable structure which could exist only in small
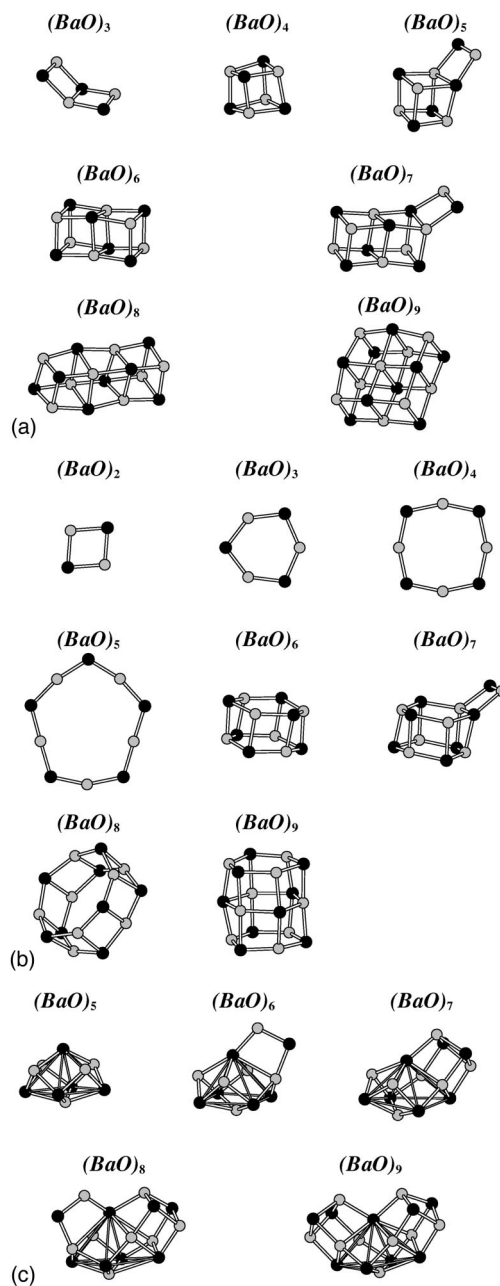

FIG. 1. Structures of $(BaO)_n$ ($2 \leq n \leq 9$) clusters. Dark circle for Ba atom and gray circle for O atom. (a) Cubic-like structure; (b) ring-like structure; and (c) anti-tetragonal prism based structure.

clusters. In fact, the metastability of the ring-like structure could be understood from the point view of bonds. It is known that the binding energy is proportional to the number of bonds in the ionic system. Thus, the ring-like structure, which has less bonds, would not be as stable as the cubic-like structure. One can easily get the cubic-like structure of $(BaO)_6$, $(BaO)_8$, and $(BaO)_9$ clusters by shrinking the rings to ladder-like structures in order to form more bonds. The ring-like structure for the other metal-oxide clusters, such as MgO clusters, has been predicted to be dominant in the small cluster region[9] by calculations based on model potentials, while in our first-principles calculations, those ring-like structures are only found to be metastable.
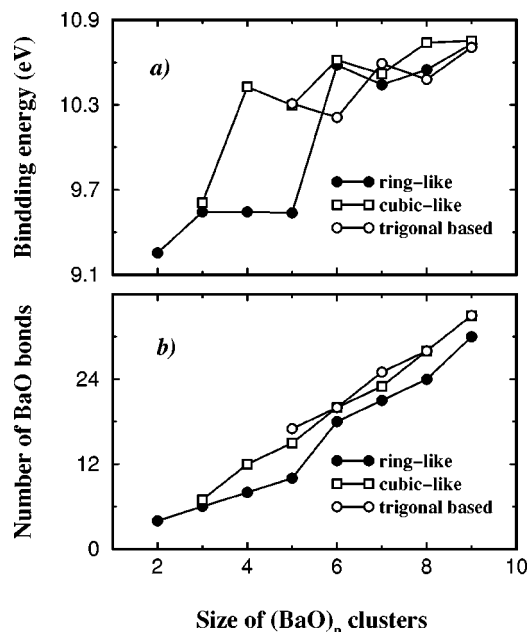
FIG. 2. The binding energy and the number of bonds for the $(BaO)_n$ cluster. (a) The binding energies, and (b) the number of Ba–O bonds for each calculated cluster. The binding energy and the number of bonds are well correlated, both of them suggest that cubic-like structure appears in the small $(BaO)_n$ cluster, while the anti-tetragonal prism based structures with more Ba–O bonds are stable for $(BaO)_5$ and $(BaO)_7$ clusters.

Our calculations predict that the most stable structure of $(BaO)_5$ cluster is an anti-tetragonal prism with one Ba and one O atom capped on either ends of the prism, as shown in Fig. 1(c). These structures are more compact than the cubic-like and ring-like structures. A similar structure has not been observed in previous model potential calculations. In fact, both LDA and GGA calculations show that this structure is more stable than any other structure. In comparison with other metastable structures, we find that this anti-tetragonal prism based structure has more Ba–O bonds, one bond more than the cubic structure and six bonds more than the ring-like structure. This might be one of the reasons that this structure is lower in energy. Starting from the compact structure of $(BaO)_5$ cluster, we can get structures for larger clusters by capping more BaO molecules [see Fig. 1(c)]. In this growth mode, the core of the structure is anti-tetragonal prism, and with more atoms capped on, the core does not change significantly. Since there is no favorable structure for $(BaO)_7$ cluster in both cubic-like growth mode and ring-like growth mode, we find that $(BaO)_7$ with anti-tetragonal prism based structure is the most stable, since again, this structure has more bonds than cubic-like and ring-like structure.

The upper panel of Fig. 2 shows the binding energies of $(BaO)_n$ clusters for all the three growth modes. One can see that, for most of these clusters, the cubic-like structure has the largest binding energy, but for $(BaO)_5$ and $(BaO)_7$ cluster, the anti-tetragonal prism based structures have larger binding energies, because they are more compact as discussed earlier. The figure shows that the ring-like structure of $(BaO)_3$ has similar binding energy as the cubic-like structure, but the ring-like structures of $(BaO)_4$ and $(BaO)_5$ have much smaller binding energies than those of cubic-like structures, while

the transition to three-dimensional structure at $(BaO)_6$ drives its binding energy close to that of cubic-like structure again. Although the ring-like structure always has smaller binding energy, for some clusters, the binding energy is very close to that of the cubic-like structure.

The binding energies of clusters are strongly correlated with the number of Ba–O bonds. As shown in the lower panel of Fig. 2, we can see that the number of bonds shows a similar trend as that for the binding energies. The ring-like structure always has the smallest number of bonds in all these clusters, and the sudden increase of bond number at $n=6$ suggests a structural transition from two dimension to three dimension. At $n=5,7$, the anti-tetragonal prism based structures have the largest number of bonds. Consequently these two clusters have larger binding energies. However, the number of bonds can't fully account for the stability of the cluster. For $n=6,8,9$, the numbers of bonds for both anti-tetragonal prism based structures and cubic-like structure are the same, but the binding energies are different, which indicates that the stability cannot be fully described by a very simple model based on the number of bonds.

IV. SUMMARY

In summary, we have systematically studied the structures of $(BaO)_n$ ($n \leqslant 9$) clusters within density functional theory with generalized gradient approximations. We find three structural growth modes for these clusters: cubic-like growth, ring-like growth, and anti-tetragonal prism based growth modes. Although the cubic-like growth mode dominates the whole series, the anti-tetragonal prism based structures have the largest binding energies at $n=5,7$, which has never be reported before. Above the size $n=6$, all three kinds of structures have similar binding energies, which suggests that all of them could be stable structures at different physical and chemical environments. The ring-like structure, which was predicted to be the ground state by model potential calculations in other metal-oxide clusters, is found to be metastable in our study.

ACKNOWLEDGMENTS

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