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Model and Properties of Fullerene-Like and Wurtzite-Like ZnO and Zn(Cd)O Clusters

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The electronic structure of the ground state of fullerene-like and wurtzite-like Zn_nO_n and $Zn_{n-x}Cd_xO_n$ clusters has been investigated by computer physics methods. A relative evaluation of the stability and band gap width of clusters depending on the number of atoms in the cluster and its geometry has been performed. The model of a fullerene-like $(ZnO)_{60}$ particle with a mixed sp^3/sp^2 type of bonds has been constructed. A $(ZnO)_{12}$ cluster of T_h symmetry was taken as a base of the model. Within the framework of the B3LYP electron density hybrid functional method with a set of 3-21G(d) split valence basis functions, a numerical investigation of the influence of the incorporation of cadmium (33%) into the ZnO matrix on the electronic structure and the band gap width has been performed.

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1. Introduction

In recent years, ZnO-based low-dimensional materials have aroused great scientific interest due to their promising applications in photocatalysis and nanoscale optoelectronic devices. In particular, ZnCdO ternary alloys have been attracting growing attention due to their tunable band-gap. Nevertheless, in spite of a great number of previous experimental studies, there are still many unsolved problems, such as low cadmium solubility, deviations from stoichiometry and optimal energetic configuration, etc. [1, 2]. In this regard, the computational study may be a useful and powerful instrument for overcoming the existing disadvantages of these semiconductor systems. Theoretical investigation of ZnO and ZnCdO clusters will provide vital information for not only experimental efforts to seek them, but also for understanding the growth mechanisms and stability of ZnO and ZnCdO clusters with the lowest energy of formation.

To study the aforementioned effects by the quantum-chemical methods, we propose to use fullerene-like and wurtzite-like clusters. We have previously revealed that the $A^{IV}B^{IV}$, $A^{III}B^{V}$, $A^{II}B^{VI}$ semiconductor compounds, including ZnO, exhibit a tendency to form fullerene-like structures [3]. For these structures, the cohesive energy is smaller than that for the basic structure of ZnO. Moreover, the energy of cohesion increases as the number of atoms in the cluster increases, i.e. larger clusters are more stable than smaller ones. Although no clear tendency to decrease the band gap with increasing cluster size is observed, the value of the band gap energy for all clusters not only depends on the size of the cluster, but also can be influenced by other factors, in particular, geometry [4, 5].

To determine the size dependence of the stability of the fullerene-like cluster (ZnO), a relative evaluation of the stability of the fullerene-like cluster $(ZnO)_n$ ($n = 12$, 36, 48) was performed. These clusters can serve as a structural unit of periodic structures. We also calculated the wurtzite-like $(ZnO)_n$ clusters for $n = 26$, 36, 48.

The modeling of structures that do not exhibit translation invariance, to which ZnCdO ternary alloys belong, is a rather complex problem and is critically important for the interpretation of the physicochemical properties of these compounds with the aim to develop materials with predetermined properties. In construction of these models, one can use structural fragments of known crystalline modifications of investigated matters. For instance, in [6, 7], fragments of diamond and lonsdeilite were used in construction of models of nanodiamond particles in which the local environment of carbon atoms hardly differed from that for diamond. Fullerene C_{20} was located at the center of the model. We used the approach described in [6, 7] to construct a model of a fullerene-like $(ZnO)_{60}$ particle with mixed sp^3/sp^2 bonds.

To study the influence of cadmium on the electronic structure, a $Zn_{36}O_{36}$ cluster with a cadmium content of 33% ($Zn_{24}Cd_{12}O_{36}$ with the initial T_d symmetry) was used.

2. Construction of the model and computational technique

Models of fullerene-like $(ZnO)_n$ clusters for $n = 12$, 36, 48 [3, 4] are shown in Fig. 1. A $(ZnO)_{12}$ cluster of T_h symmetry is formed by 6 squares and 8 hexagons,

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in which each zinc atom has an environment of three oxygen atoms and, vice versa, each oxygen atom has an environment of three zinc atoms. The characteristic feature of the $(ZnO)_{12}$ cluster is that it can serve as a structural unit of periodic zeolite-like structures with a cubic lattice, in which all the atoms are bound by sp^3 bonds. A $(ZnO)_{48}$ cluster of T_h symmetry has the shape of a tetragon and consists of 6 squares, located at the vertices of the tetragon, and 40 hexagons integrated into 8 plane fragments, each of which consists of 5 hexagons. A model of a fullerene-like $Zn_{24}Cd_{12}O_{36}$ cluster with the initial T_d symmetry was obtained by replacing twelve Zn atoms by twelve Cd atoms uniformly over the surface of a $(ZnO)_{36}$ cluster.

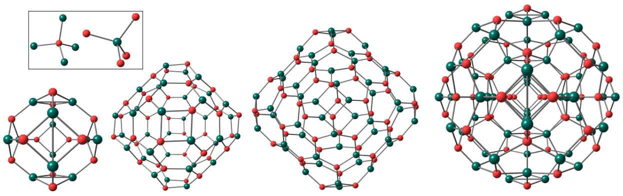

Fig. 1. Models of fullerene-like $(ZnO)_{12}$, $(ZnO)_{36}$, $(ZnO)_{48}$, and $(ZnO)_{60}$ clusters and structural units used in construction.

A model of the fullerene-like $(ZnO)_{60}$ particle with mixed sp^3/sp^2 bonds was constructed on the basis of a kernel of the hollow fullerene-like $(ZnO)_{12}$ cluster described above. In construction, structural fragments of ZnO wurtzite structure were also used. The kernel is decorated by structural fragments so that each atom of the kernel is the place of growth of the next wurtzite-like layer. In the obtained particle with two-layer packing of $(ZnO)_{60}$, among 120 constituent atoms, 48 internal atoms are bound by sp^3 bonds, and 72 surface atoms by bound by sp^2 bonds (the ratio of the atoms with sp^3 and sp^2 bonds is 48/72). It is assumed that the given technique will make it possible to construct a model of a particle with multilayer packing. The model of the fullerene-like $(ZnO)_{60}$ particle with mixed sp^3/sp^2 bonds and structural units used in construction are shown in Fig. 1.

Models of wurtzite-like $(ZnO)_{26}$, $(ZnO)_{36}$, and $(ZnO)_{48}$ clusters were constructed on the basis of [8] and are shown in Fig. 2. The shape of clusters is similar to the shape of a nanorod or a nanotube with a diamond-like wall. The cluster can be extended in the direction of growth of the nanotube. By this means a model of a $(ZnO)_{48}$ cluster was obtained by adding 12 atoms of the wurtzite layer to the $(ZnO)_{36}$ cluster. The atoms located at the center of the clusters have the sp^3 bonding configuration, the surface atoms have sp^2 bonds, and atoms with *sp* bonds are located on the end faces of the clusters. To improve the stability of the system, hydrogen atoms were added to atoms with *sp*-bonds on the end faces of the clusters.

Computations were performed within the framework of the B3LYP electron density hybrid functional method with a set of 3-21G(d) split valence basis functions. The geometry optimization was performed by the method of gradient descent. The cohesive energy of particles was computed as the difference between the total energy of the cluster and the total energy of noninteracting constituent atoms without regard for the energy of zero vibrations. In computations, a complex of GAMESS'09 programs [9], ChemCraft and Molekel 5.4 programs of visualization of computed results were used [10].

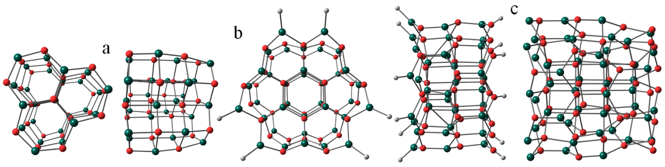

Fig. 2. Models of wurtzite-like clusters: (a) $(ZnO)_{26}$, (b) $(ZnO)_{36}$, (c) $(ZnO)_{48}$.

3. Results and analysis

The results of calculations are the optimized geometry and electronic structure of the investigated objects. Some results of calculation of the electronic structure, total energy, and cohesive energy per ZnO unit are presented in Table.

TABLE

Energy characteristics of the clusters: total energy per atomic pair, cohesive energy per ZnO atomic pair, energy band gap (calculation was performed by the RHF/MINI method).

Cluster	$-E_{\mathrm{total}}$/ZnO [eV]	E_{c}/ZnO [eV]	E_{g} [eV]
w-$(ZnO)_{26}$	50187.716	1.05	7.3
w-$(ZnO)_{36}$	50187.602	0.94	6.2
w-$(ZnO)_{36}H_{12}$	≈ 50197	≈ 10	8.9
w-$(ZnO)_{48}$	50187.897	1.23	6.5
f-$(ZnO)_{48}$	50187.73	1.07	7.0

The optimized geometries of the $(ZnO)_{36}$ and $Zn_{24}Cd_{12}O_{36}$ clusters are shown in Fig. 3. Our calculations showed that the band gaps of the $(ZnO)_{36}$ cluster and $Zn_{24}Cd_{12}O_{36}$ cluster are, respectively, ≈ 2.97 eV and 2.39 eV. The incorporation of cadmium (33%) into the ZnO matrix leads to a decrease in the energy gap by 0.58 eV.

Preliminary calculations carried out by the Hartree–Fock method with a minimal basic set (RHF/MINI) for the fullerene-like and wurtzite-like $(ZnO)_{48}$ clusters showed an advantage in stability of the wurtzite-like cluster over the fullerene-like analog. For the wurtzite-like $(ZnO)_{48}$ cluster, the obtained minimum of the total energy in the ground state (-50187.897 eV) is deeper than that for the fullerene-like cluster (-50187.73 eV), and the

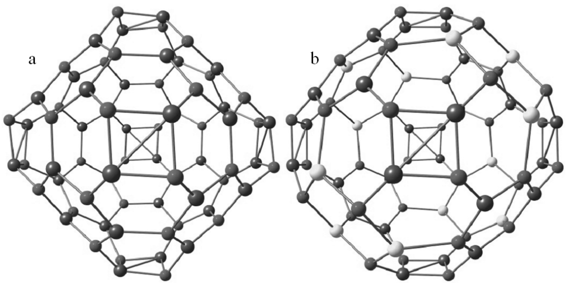

Fig. 3. Optimized geometries of nanoparticles: (a) $(ZnO)_{36}$, (b) $Zn_{24}Cd_{12}O_{36}$; black balls correspond to Zn, gray balls correspond to O, and light balls correspond to Cd.

cohesive energy per ZnO atomic pair of the wurtzite-like cluster is larger by 0.16 eV.

The wurtzite-like w-$(ZnO)_{36}$ cluster was found to be the least stable, and in the process of optimization, some of sp^3 bonds transformed into sp^2 ones. However, the saturation of sp bonds on the end faces of the cluster by hydrogen atoms led to an increase in its stability. As a result, the cohesive energy attained $\approx$ 10 eV. The presented values somewhat exceed true values because the cohesive energy of hydrogen atoms was not taken into account in the calculation.

Let us note that the obtained results (Table) due to lack of consideration of the correlation and overestimation of the energy gap were used only for qualitative analysis. Subsequent computations are being performed by the B3LYP electron density hybrid functional method with a set of 3-21G(d) split valence basis functions.

4. Conclusion

Models of the fullerene-like and wurtzite-like ZnO and Zn(Cd)O clusters with sp^2 and mixed sp^3/sp^2 bonds are proposed for study of the influence of the cadmium incorporation into the ZnO matrix on the electronic structure and the band gap of ZnCdO ternary alloys. For the first time, a model of a fullerene-like particle of cubic symmetry with a mixed sp^3/sp^2 type of bonds based on a $(ZnO)_{12}$ cluster of T_h symmetry has been constructed.

Calculations showed that cadmium incorporation (33%) into ZnO matrix of the fullerene-like clusters $(ZnO)_{36}$ leads to a decrease in the energy gap by 0.58 eV and the band gap equal to 2.4 eV.

Preliminary calculations showed also an advantage in stability of the wurtzitic-like cluster over fullerene-like analogue. Therefore the wurtzitic-like cluster as a model for the study the influence of the cadmium incorporation into the ZnO matrix can be perspective. However, such clusters need satiation of sp-bonds on the end faces of the cluster by the hydrogen atoms and they possess lower symmetry than fullerene-like clusters, that results in inaccuracy in the estimation of cohesion energy and increase of requirements to the computational resources accordingly. These questions require further research.

The presented investigation and its development can enable one to influence the goal-directed synthesis of new, stable and uniform ZnO-based materials with a required band gap.

Acknowledgments

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