Zirconia nanoparticles and nanostructured systems

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Abstract Stability of rhombic (tetragonal-like) and cubic-like zirconia nanoparticles is investigated using the density functional pseudopotential method in a general gradient approximation. The binding energy (E_b) increases with increasing of rhombic particles, but the cubic-like particle is more favorable than rhombic ones. All studied nanoparticles have non-zero energy distances (ΔE) between occupied and non-occupied states. A simple model of nanostructured zirconia has been constructed using a $Zr_{16}O_{32}$ cluster as a unit element for a three dimensional superlattice with cubic symmetry. This work was supported by the Russian Foundation of Basic Researches, the grant # 04-02-9700.

1. Introduction

Zirconia (ZrO_2) is interesting as a ceramic material with useful optical, electrical, thermal, hardness and other characteristics. A monoclinic (*m*) phase of pure ZrO_2 is stable below 1170°C. From 1170°C up to 2370°C pure ZrO_2 has a tetragonal structure, but at temperatures between 2370°C and 2706°C (the melting point) it exists as cubic [1,2]. The cubic phase can be stabilized (e.g. the temperature of the "$c \rightarrow t$" transition may be decreased), by inducing such additives as MgO, CaO, Y_2O_3 and so on.

One of the ways to construct stable ceramics on the base of high temperature phases of zirconia is the using of nanoparticles. There are few works on the formation of stable thin films and nanoparticles from pure (undoped) zirconia of tetragonal and cubic structure [3-11]. It has been shown [11] experimentally and theoretically that the tetragonal-cubic transition takes place (at low temperatures) at a particle size of about two nanometers. However, theoretical results of that investigation were obtained without taking into account of the relaxation of the atomic structures of nanoparticles. The goal of this work is to study equilibrium atomic and electronic structures of cubic and tetragonal zirconia nanoparticles. Besides, we have studied a model of a three-dimensional net constructed from cubic zirconia nanoparticles.

2. Methods and details of calculations

Calculations were realized using the FHI96md computer code [12] based on the density functional theory, the pseudopotential method and the plane wave basis. To calculate the exchange and correlation energies we used the generalized gradient approximation in the Perdew-Wang (PW91) approach [13]. Pseudopotentials were constructed following the Troullier-Martins technique [14]

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using the FHI98pp code [15]; they were tested for the ability to reproduce the basic characteristics of the bulk materials: namely, equilimrium lattice constants and bulk modules have been calculated.

The plane wave energy cutoff of 40 Ry was implemented. The maximal sizes of the investigated particles were about 1.5 nanometer; the distances between them were about 0.8 nm. A single k-point (0;0;0) of the Brillouin zone was used to study nanoparticles, while for modeling of bulk zirconia two special points (0.25;0.25;0.25) and (0.25;0.25;0.75) have been taken with the weights of 0.25 0.75, respectively.

3. Results and discussions

3.1. Nanoparticles

In contrast with Ref. 11 we concentrated our opinion on studying of stoichiometric particles of zirconia. To analyze the equilibrium geometry and energetics of nanoparticles we studied two types of particles: namely, the Zr_6O_{12}, $Zr_{10}O_{20}$ and $Zr_{14}O_{28}$ particles which are fragments of bulk lattice of cubic zirconia but have no cubic symmetry (figure 1), and a cubic-like $Zr_{19}O_{38}$ particle (figure 2).
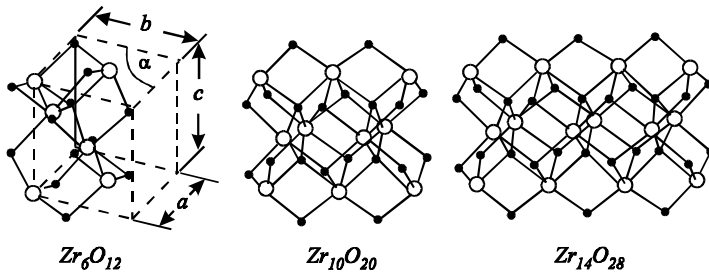

Figure 1. Nanoparticles Zr_6O_{12}, $Zr_{10}O_{20}$ and $Zr_{14}O_{28}$. White circles are Zr atoms, black circles are O atoms. A unit cell of the initial cubic phase is shown at the left image as a dashed cube ($a=b=c$ и $\alpha=90°$).
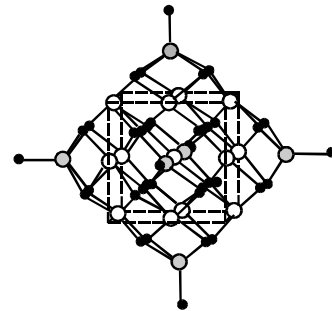
Figure 2. Atomic scheme of the relaxed $Zr_{19}O_{38}$ nanoparticle. Grey circles are Zr atoms added for saturation of outward oxygen atoms. A cubic unit cell is shown as dashed.

Initial positions of atoms in the Zr_6O_{12}, $Zr_{10}O_{20}$ and $Zr_{14}O_{28}$ particles corresponded cubic phase, but symmetry of particles was not cubic. Symmetry of the given particles is symmetry of a rectangular parallelepiped which lateral surfaces are perpendicular to its bases.

Our calculations have shown that parameters a and b are equal to 0.46 nm in all studied particle. The c parameter is equal to 0.489 nm for Zr_6O_{12} and growths up to 0.503 nm for the $Zr_{14}O_{28}$. Thus, the c/a relation is growing from 1.063 up to 1.094. Perhaps, the reason is a special geometry of those particles: they have the same sizes at two directions corresponded to the a and b parameters and are different in the third direction that corresponds to the c parameter (see fig.2). The bond-bond angle α in the basis of the parallelepiped cell is not equal to 90° as is characteristic for a cubic phase. It is equal to 100° for the smallest particle (Zr_6O_{12}) and 92° for the largest one ($Zr_{14}O_{28}$). Thus, symmetry of relaxed Zr_6O_{12}, $Zr_{10}O_{20}$ and $Zr_{14}O_{28}$ particles is rhombic

Table I collects values of calculated geometry parameters for the Zr_6O_{12}, $Zr_{10}O_{20}$ and $Zr_{14}O_{28}$ particles compared with experimental ones for the bulk tetragonal phase. Parameters for the $Zr_{10}O_{20}$ and $Zr_{14}O_{28}$ particles have been averaged because they are different inside of particles and at their borders. It is necessary to note, that in all cases lateral surfaces of cells-parallelepipeds remain orthogonal to their bases, i.e. there is no tendency to occurrence of monoclinic symmetry. In order to speak about features of transitions between cubic and not cubic phases, it is necessary to study a relaxation of nanoparticles which starting geometry is cubic.

Table I. Geometry parameters for the Zr_6O_{12}, $Zr_{10}O_{20}$ and $Zr_{14}O_{28}$ nanoparticles comparing with experimental data for bulk tetragonal phase.

	Zr_6O_{12}	$Zr_{10}O_{20}$	$Zr_{14}O_{28}$	Bulk ZrO$_2$ (tetragonal)
A, nm	0.460	0.460	0.461	0.505
B, nm	0.460	0.460	0.461	0.505
c/a	1.063	1.080	1.094	1.026
A, °	100	96	92	90
Particle's size, nm×nm×nm	0.32×0.37×0.78	0.68×0.35×0.75	0.99×0.36×0.76	

We have chosen the particle $Zr_{19}O_{38}$ (fig. 3) as an example of such particle. This particle has been constructed by a cutting up of the $Zr_{16}O_{32}$ cluster from the lattice of cubic zirconia with addition of three zirconium atoms and six oxygen atoms.

The geometry optimization has shown that symmetry of the $Zr_{19}O_{38}$ particle remains cubic-like after its full relaxation. Parameter a (the cube edge shown by a dotted line in fig. 2) was found equal to 0.505 nm.

Table II contains the values of the binding energy E_b and the energy "gap" ΔE for zirconia particles investigated by us. Comparison of these data shows that the particle with cubic geometry is energetically more favorable, than particles which geometry is close to tetragonal.

Table II. Calculated energy characteristics for zirconia nanoparticles.

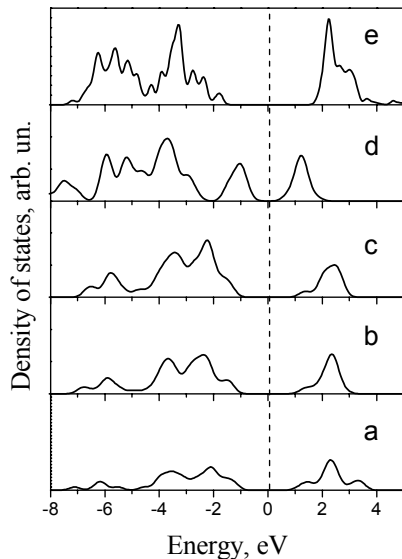|	Rhombic geometry			Cubic-like geometry	Bulk cubic ZrO$_2$ (calculations)	
	Zr_6O_{12}	$Zr_{10}O_{20}$	$Zr_{14}O_{28}$	$Zr_{19}O_{38}$	Our data	Published data [17]
E_b, eV	-23.09	-23.49	-23.81	-24.15	-25.91	-26.20
ΔE, eV	2.5	2.7	2.6	1.5	3.5	3.07

Figure 3. Calculated densities of electronic states for Zr_6O_{12} (a), $Zr_{10}O_{20}$ (b), $Zr_{14}O_{28}$ (c) and $Zr_{19}O_{38}$ (d) nanoparticles and for bulk cubic zirconia (e).

It must be noted that positions of oxygen atoms in the $Zr_{19}O_{38}$ particle do not precisely correspond to the perfect cubic positions, therefore their deviation from equilibrium places do not generate a tendency of the oxygen subsystem to distortion. In other words, a small disordering of cubic symmetry caused by dimensional effect stabilizes a cubic-like symmetry of the particle without it's doping.

Calculated values of the energy "gap" (even for bulk zirconia) are rather less than the experimental value of 6 eV [16]. This is a common problem for calculations based on the one-particle approach (see Ref. 17).

In order to compare the electronic structures of nanoparticles and bulk zirconia in details we constructed densities of states (DOS) using 0.2 eV wide Gaussian broadening functions centered on each electron level. These DOS are plotted in fig. 3. One can see that DOS plots for the Zr_6O_{12}, $Zr_{10}O_{20}$ and $Zr_{14}O_{28}$ particles arrive to the DOS for bulk zirconia with increasing of a particle size.

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3.2. A model of nanostructured zirconia

A simple model of nanostructured zirconia can be constructed using the $Zr_{16}O_{32}$ cluster as a unit element of the three dimensional superlattice with cubic symmetry. Figure 4 demonstrates the planar projection of this superlattice. The equilibrium binding energy is –24.61 eV per ZrO_2 unit that lays between -24.15 eV obtained for the $Zr_{19}O_{38}$ cubic-like nanoparticle and -25.91 eV calculated for the bulk cubic ZrO_2. Thus, a stable nanostructured porous zirconia can be formed from cubic-like nanoparticles with the energy gain of 0.5 eV per ZrO_2 unit.
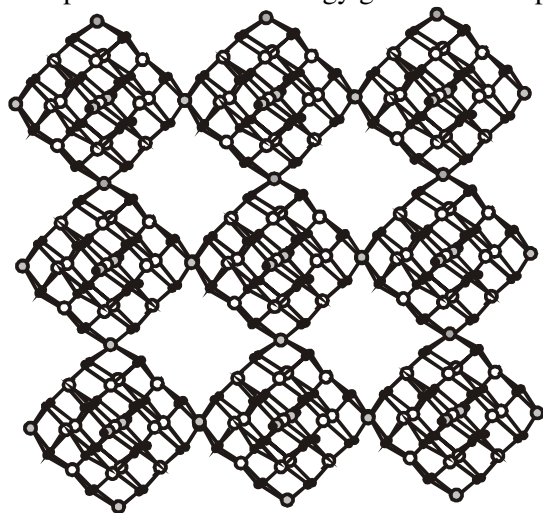

Figure 4. Fragment of nanostructured zirconia constructed from cubic-like particles.
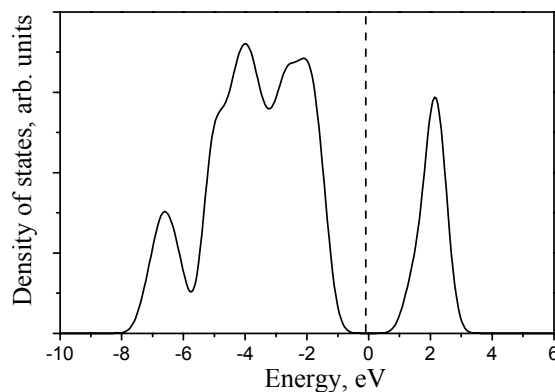
Figure 5. The DOS for nanostructured zirconia constructed from cubic-like particles.

The plot of DOS for the porous nanostructured zirconia is shown at figure 5. It demonstrates a rather wide energy gap of 2.6 eV between occupied and no occupied states.

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