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Report Title

DFT Study of BZY Cluster Model

ABSTRACT

Technical reqport for 2013-2014 (DFT modeling part)

Novel MC/BZY Proton Conductor: Materials Development, Device Evaluation, and Theoretical Exploration using CI and DFT Methods

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(DFT Modeling Part)

During this reporting period, our DFT efforts were focused on determining the surface energy of $BaZrO_3$ perovskite with different surface terminations. We first optimized the bulk structure of $BaZrO_3$ perovskite. Second, we cleaved the low index surface, namely {100}, {110} and {111} surfaces, and examined the stability of these surfaces by evaluating their surface energies. Third, we selected the most stable surface as the basis for constructing the super-surface, and then introduced the pairs of Y atoms and oxygen vacancies (one vacancy for each pair of Y) to build the surface of $BaZr_{0.8}Y_{0.2}O_{3-\delta}$. In the next reporting period, we will introduce the OH^- and CO_3^{2-} to the super-surface to simulate the proton conducting behaviors at the interface between $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ and carbonate.

I. The structural features of $BaZrO_3$ perovskite

The $BaZrO_3$ ceramic has an ideal cubic perovskite structure with a space group (Pm3m) and point-group symmetry (O_h). As shown in Figure 1, the barium atoms sit at the corners of a simple cubic unit cell, the oxygen atoms sit on the faces and the zirconium atom sits at the center. Moreover, Zr atoms are bonded to six O atoms which form an octahedral ZrO_6 while the Ba atoms are bonded to twelve O atoms with a cuboctahedral configuration which forms BaO_{12} cluster.

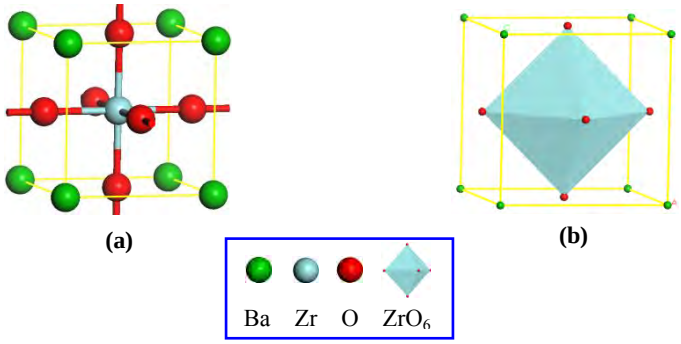


Figure 1. Crystal structure of $BaZrO_3$ showing (a) atomic positions of the unit cell and (b) structure depicting by ZrO_6 octahedra.

II. The parameters test and relaxation of $BaZrO_3$ structure

First, we tested the calculated parameters in our DFT model. It should be mentioned that the convergence of the cutoff energy, the number of *k*-points, and the size of the vacuum layer has been carefully checked. For all the calculations, we have used the VASP *ab initio* package [Phys. Rev. B 54:11169-11186, 1996], and the PBE functional [Phys. Rev. Lett. 77:3865, 1996] has been

employed. A cutoff energy of 500 eV and a 6×6×6 Monkhorst-Pack k-point mesh [Phys. Rev. B 13:5188-5192, 1976] for 1×1×1 unit cell have been determined. Spin-polarized calculations have been applied throughout. The $2s^2 2p^4$ of O, $4s^2 4p^6 5s^2 4d^2$ of Zr and $5s^2 5p^6 6s^2$ of Ba were treated as valence electrons in the DFT calculations. For optimization of the atomic structure, the Hellmann-Feynman forces have been minimized to the maximum value of 0.02 eV/ Å on each atom of the system.

To test the reliability of our theoretical level and parameters as mentioned above, the unit cell parameters, ion positions and electronic structures of the cubic $BaZrO_3$ were first calculated at the concerned levels, allowing both unit cell parameters and atomic positions to relax. Our optimized the lattice constant of $BaZrO_3$ is 4.25 Å, which is in good agreement with the experimental value of 4.20 Å [Dalton Trans. 3061–3066, 2004; New Physics: Sae Mulli, 63(8):939-944,2013] and the theoretical value of 4.24 Å [Phys. Rev. B 75: 155431, 2007], with less than 1% deviation in the cell parameters. Figure 2 shows the total density of states (TDOS) and the energy bands structure of the $BaZrO_3$. Our calculated the energy gap of $BaZrO_3$ is 2.78 eV, which is slightly smaller than previous value of 3.1 eV [Phys. Rev. B 75: 155431, 2007] and is significantly lower than the experimental value of 4.9 eV [New Physics: Sae Mulli, 63(8):939-944, 2013] or 5.33 eV [Sci. Technol. B 18:1785, 2000]. This difference is quite usual for DFT calculations and can be largely attributed to the underestimation of band gaps by DFT-LDA (local density approximation) or GGA (generalized gradient approximation). Figure 2 indicates that the $BaZrO_3$ is a wide band gap semiconductor.

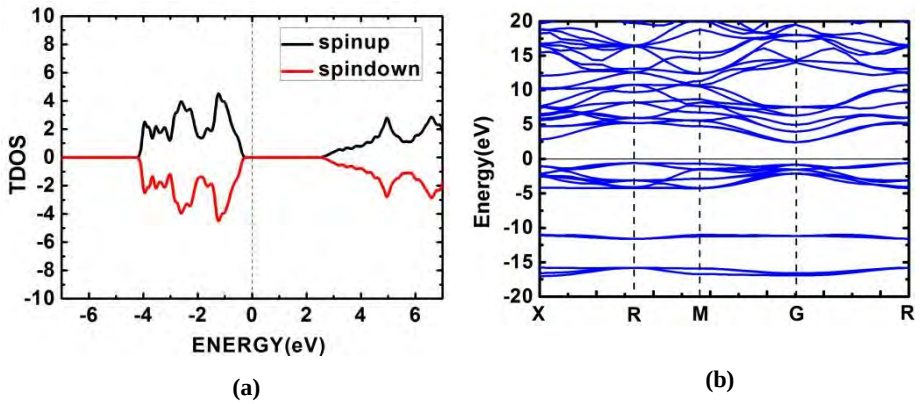


Figure 2. The total density of states (TDOS) of the $BaZrO_3$ (a) and the energy bands (b).

III. The stability of different surface

Second, we calculated the surface energies for different Miller indices in order to examine the stability of different surface for $BaZrO_3$. We have focused our attention on the low index surfaces of cubic $BaZrO_3$, namely {100}, {110} and {111}. In this part of calculations, a 2×1 super-surface and eight atom layers are performed. The vacuum layer of 15 Å has been assembled for our concerned surface relaxations. Cleavage of these three planes leads to two different dipolar surfaces for each Miller index. As a consequence, all the surfaces will have divergent surface energies in the macroscopic limit. However, the dipole and its associated divergent energy can be removed by surface reconstruction. As described in the early literature [J. Mater. Chem. 10:2298-2305, 2000], the simplest reconstruction involves transferring half the ions from one surface to the complementary surfaces. By using this strategy, we constructed the six surfaces and followed the

full optimization for each structure. The surface energy of the *i*th surface E_i has been calculated by

$$E_i = \frac{E_{surf} - E_{bulk}}{2S} \qquad (1)$$

Where E_{surf} and E_{bulk} are the total energy of the *i*th surface and the energy of bulk with the same number of ions, respectively. The *S* represents the reconstructed surface.

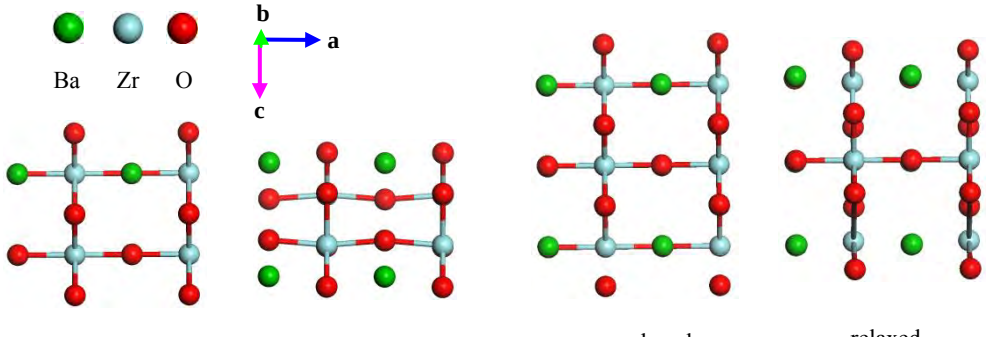
The calculated surface energies for the three surfaces of $BaZrO_3$ are sumarized in Table 1. From the surface energies listed in Table 1, it is predicted that the {100} surfaces will terminate with Ba and O ions, the {110} surface with an oxide layer, and the {111} surface with a Zirconium layer. It is clearly seen that the order of stability for the surfaces of $BaZrO_3$ is: {110} ≥ {100} > {111}. This trend was also observed in the $LaCoO_3$ perovskite [J. Mater. Chem. 10:2298-2305, 2000], where the {110} (O-terminating) surface is predicted to be the most stable. Furthermore, our results also suggest that the {110} and {100} surfaces are competitive. The highest stability of {110} agrees with the XRD patterns [Ceramics International 38: 2129–2138, 2012], where the intensity of the {110} peak is the highest.

Table 1. The calculated surface energies for different Miller index of $BaZrO_3$.

Miller index	{100}OZr	{100}BaO	{110}O	{110}BaOZr	{111}Zr	{111}BaO_3
Surface Energy (Jm^{-2})	1.25	1.11	1.10	Non-convergence	1.99	2.30

IV. The thickness test of {110}O surface

Next, we took the {110}O and the {100}BaO surface as examples to construct the super-surface. First, the {110}O surface was used as an example to calculation since it has the most stability. Primarily, in order to balance the calculation accuracy and the time cost, we needed to estimate the suitable thickness of the {110}O surface. So, we relaxed the {110}O surface with 4-layers, 6-layers, 8-layers and 10-layers slab, respectively. The structures of unrelaxed and relaxed are displayed in Figure 3. The calculated surface energies as the function of the number of atomic layers are plotted in Figure 4. From the relaxed structures and the surface energy, we found in particular that the 6- or 8-layers slabs are thick enough for simulation of {110}O surface with surface energy convergence.



(a) 4-layers **(b) 6-layers**

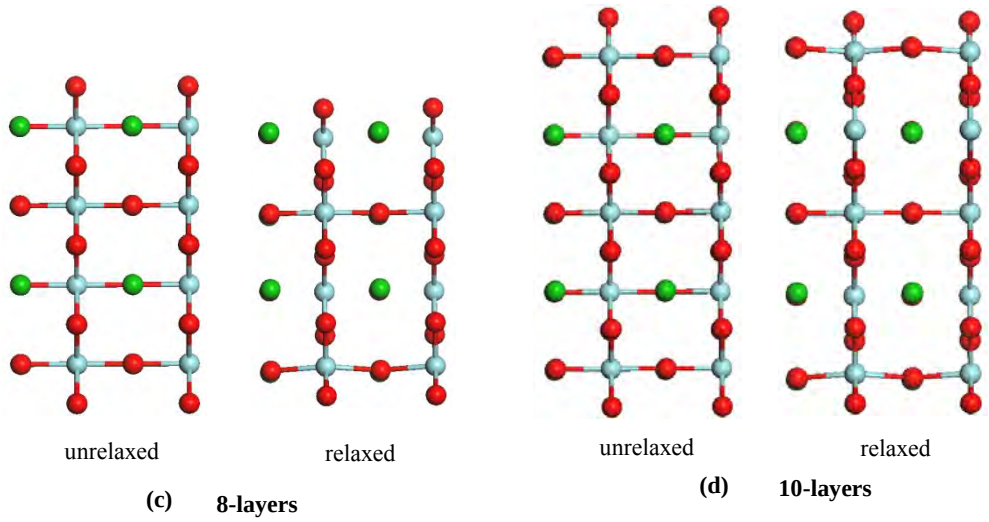


Figure 3. The unrelaxed and relaxed surface structures (side view) for 4-layers (a), 6-layers (b), 8-layers (c) and 10-layers (d) of the {110}O termination surface of the $BaZrO_3$.

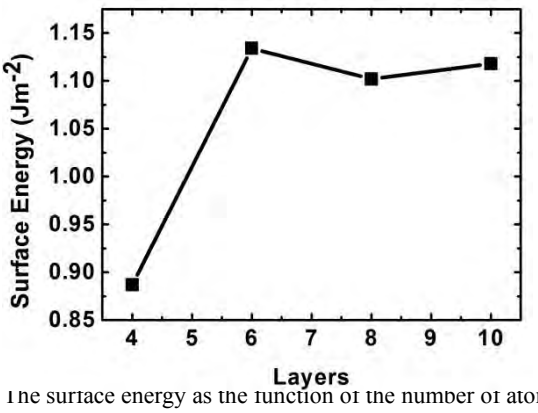


Figure 4. The surface energy as the function of the number of atomic layers.

V. Future work

In the near future, we will construct the super-surface with the {110} oxygen termination, as shown in Figure 5, where a 7-layers slab terminated on both sides with an oxygen plane will be used. Use of such symmetrical slab permits to avoid a problem of the surface dipole moment.

We will then relax the super-surface of {110}O (structure in Figure 5), introduce the defects by incorporation of pairs of Y atoms and O vacancies (one O vacancy for each pair of Y). In this effort, there will be a few variations, such as O vacancies locate at the surface and subsurface, the distribution of Y atoms in the {110}O slab and so on. Next, we will construct the models of interface between the $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ and the carbonate by introducing the carbonate ions on the surface. Finally, we will simulate the proton conduction at the interface by introducing the OH^- group to occupy the oxygen vacancy of a $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ slab.

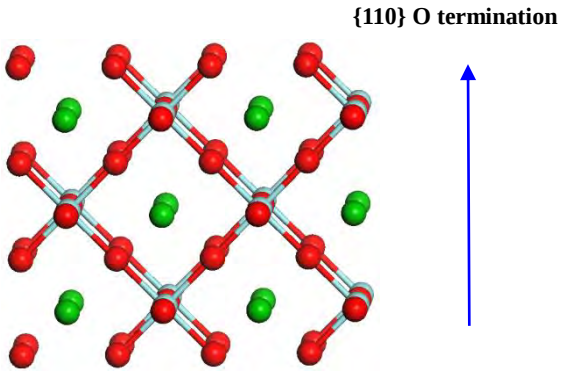


Figure 5. Super-surface of 7-layers {110} oxygen termination.