Electronic Structures and Work Function of Metallic Hexaboride Nanorods

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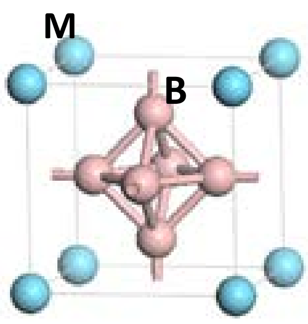
Abstract

Systematic modeling study has been performed to study the electronic properties and work functions of rare-earth hexaboride (MB_6) nanorods (M = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Ca, Ba, Y and Sr). Electronic structures of quasi one-dimensional MB_6 nanorods are studied to investigate metal element specificity and size-dependence of the electronic properties and work functions. Ensemble density functional theory (EDFT) was applied to facilitate convergence and optimization of the MB_6 nanorods and slab structures in the calculations. Our calculated partial density of states for these materials suggests that the low work functions of these MB_6 nanorods are closely related to the boron cage network.

Motivation



MB_6

- One dimensional metallic hexaboride nanorods have been proposed as efficient field emission materials because of their low bulk work functions (2.1 to 3.5 eV).
- A large range of work function values for MB_6 materials are reported due to different measurement conditions.
  ⇒ It is difficult to systematically study the field emission properties of these MB_6 nanorods.
- Goals:
  1. To understand the structural origin of the low work function and the electronic structure of MB_6
  2. To elucidate the effect of geometry on the work functions of different MB_6 nanorods

Method

Computation Theory:

- Density Functional Theory (DFT) within the local density approximation implemented in CASTEP codes
  Ensemble Density Functional Theory (EDFT) scheme applied to overcome the convergence problem inherited in the rare earth system

Calculation Criteria

- Plane wave basis set, with energy cutoff around 240 eV, and ultra-soft pseudo-potential with the local density approximation for the generalized gradient approximation (GGA) and Perdew-Burke-Ernzerhof PBE exchange and correlation functional till the force is lower than 0.03 eV/Å.

Construction of MB_6 Nanorod Models

- Basic unit cell: a thin infinitely long periodic MB_6 rod extended to two directions, i.e. n***a*** x n***b***, where ***a*** and ***b*** are unit vectors perpendicular to the rod, & n =1, 2, 3 & 4.
- (M = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Ca, Ba, Y and Sr)
- The nearest atomic distance between neighboring cells, which is size of the supercell, is chosen to be greater than 24 Å to ensure a good energy reference for work function calculations.

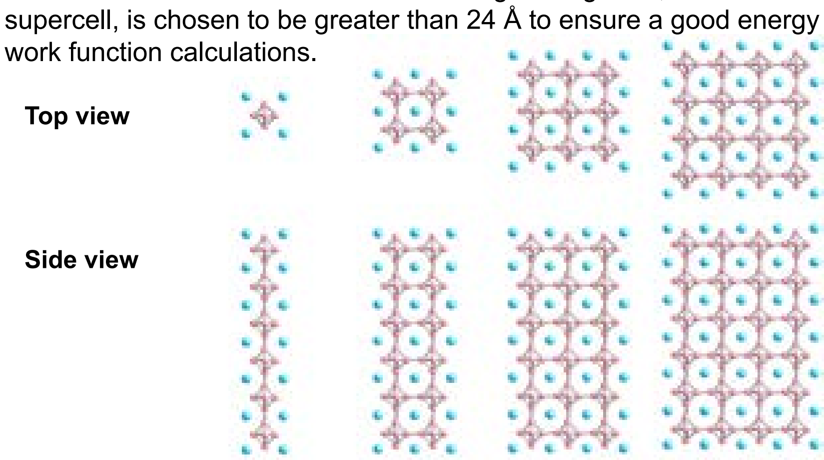


Figure 1. Optimized structures of (1x1), (2x2), (3x3) and (4x4) LaB_6 nanorods.

Calculation of Work Function

- The work function, *W*, in our calculations is defined as depth of Fermi level seen from the vacuum energy, expressed as $W = -\Phi(V_{ac}) - E_F$, where both Fermi energy E_F and $\Phi(V_{ac})$, the electrostatic potential at the lowest level inside the supercell, are results we compute. In our case the supercells are infinitely long squares of width about 35 Å and four infinitely long rods located at the corners.
- The work functions are calculated from the sides of the rods.

EDFT Calculation of Work Functions

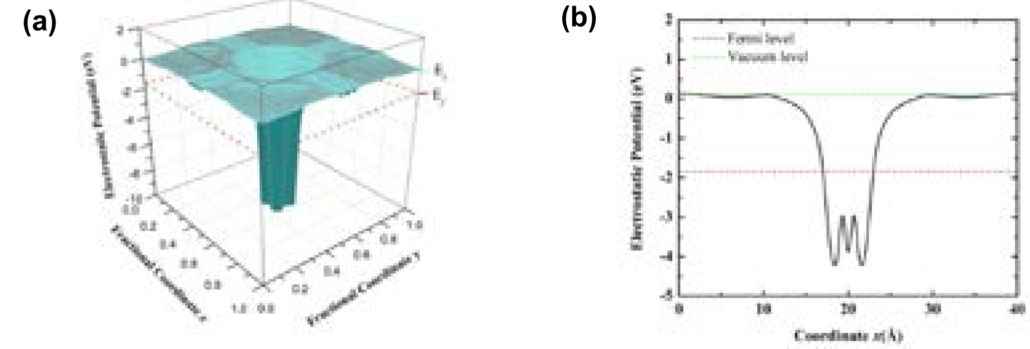


Figure 2. General electrostatic potential profile for the (1x1)-MB_6 rods. (a) average along z-axis and (b) average on yz-plane.

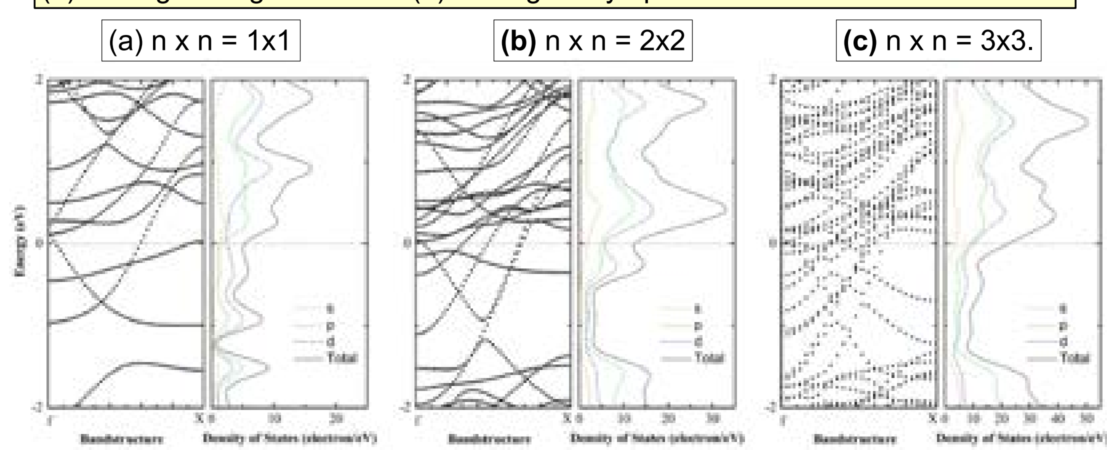


Figure 3. Band structures & density of states for LaB_6 nanorods.

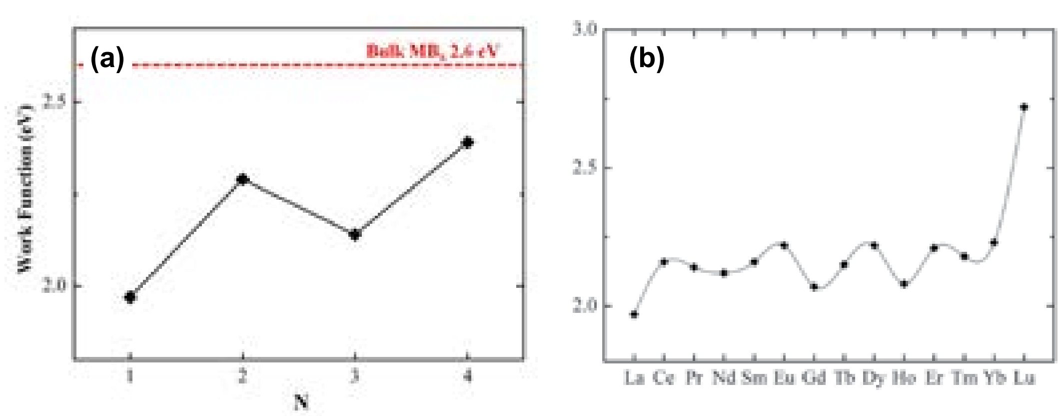
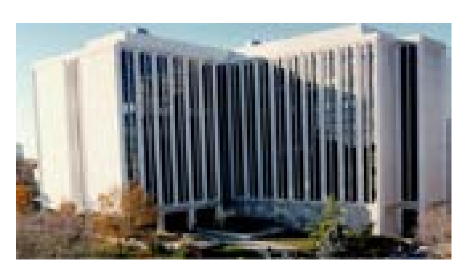


Figure 4. Comparative work function plots for (a) (n x n) unit cells of LaB_6 and (b) (1x1)-MB_6 nanorods.

Conclusions

- The low work function and high refractivity of MB_6 nanorods are related to their distinguished metal-like electronic properties of the born cage frame work and the abundant 5d and 6s states from the rare-earth metal atoms positioned the Fermi level.
- There is a weak dependence of the rare-earth metal to the corresponding work function of the MB_6 nanorods and slabs.
- Clear dependences of the working function of MB_6 on rod size were observed. These behaviors can be interpreted satisfactorily from the electronic calculations.



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