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Full Length Article

The electronic structures and work functions of (100) surface of typical binary and doped REB_6 single crystals

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ABSTRACT

The density function theory been used to calculate the electronic structures of binary and doped rare earth hexaborides (REB_6), which exhibits the large density of states (DOS) near Fermi level. The d orbital elections of RE element contribute the electronic states of election emission near the Fermi level, which imply that the REB_6 (RE = La, Ce, Gd) with wide distribution of high density d orbital electrons could provide a lower work function and excellent emission properties. Doping RE elements into binary REB_6 can adjust DOS and the position of the Fermi energy level. The calculated work functions of considered REB_6 (100) surface show that the REB_6 (RE = La, Ce, Gd) have lower work function and doping RE elements with active d orbital electrons can significantly reduce work function of binary REB_6. The thermionic emission test results are basically accordant with the calculated value, proving the first principles calculation could provide a good theoretical guidance for the study of electron emission properties of REB_6.

1. Introduction

REB_6 materials are being paid more and more attention for their complex physical properties [1–5]. For example, EuB_6 and YbB_6 have the properties of semiconductor, YB_6 is superconductors, SmB_6 has fluctuating valence, LaB_6 and CeB_6 are excellent electron emission materials. In addition, CeB_6 also has many unique properties, such as superconductivity, magnetic ordering and heavy fermion behavior, it is a typical of the Kondo effect materials. In recent years, SmB_6 and YbB_6 have attracted considerable interest as prospective topological insulator materials.

In the fields of electron emission, lanthanum hexaboride (LaB_6) and cerium hexaboride (CeB_6), are excellent thermionic and field election emission cathode materials which have extensive application in the civilian and national defense industry because of their especial mechanical, thermal and electrical properties [6–8]. The structure of the rare-earth hexaborides is special, such as LaB_6, which is composed of rare earth embedded inside a stable boron octahedron network. There are no hands combined between the B atoms and the rare earth mental atoms, and each B atom with other five B atoms together forming B_6. This arrangement allows a unique combination of all desired properties for an excellent electron emission material, such as low work function, high mechanical strength, high melting point, high conductivity, high Young's modulus, low volatility, high chemical resistance, which these properties seldom coexist in any other materials. So it is very meaningful to research the emission properties of hexaborides materials.

At present, LaB_6 and CeB_6 as excellent electron emission materials have been obtained a large numbers of verification by experiments and practical application. NdB_6 [9] and GdB_6 [10,11] have been extensively studied owing to their complicated magnetic transport properties. However, their electron emission properties have rarely been reported in the literature. Furthermore, it has been reported [12] that the La element doping into PrB_6 and NdB_6 leads to a reduction of work function. Moreover, these substituted multiple rare-earth hexaborides exhibit better emission performance than LaB_6. In our earlier works [16,17], the rare-earth hexaborides with doping suitable rare-earth elements showed better emission performance than binary REB_6.

In recent years, there have done lots of research work on theoretical calculations for optical properties of REB_6 [13,14], which have been rare reports on about its electron emission properties. Also, the experiments have shown that doping suitable rare-earth elements in the REB_6 can significantly improve their thermionic emission property [15–17], and there is still a lack of theoretical explanation for this phenomenon. To sum up, it is necessary to reveal the physical mechanism of REB_6 and doped REB_6 emission performance, and make theoretical and experimental guidance for

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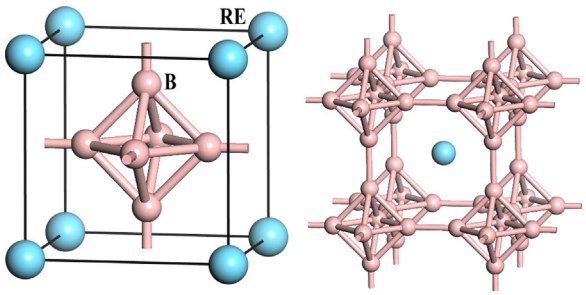

Fig. 1. The crystal structure of REB_6.

the applications of REB_6 materials in practice. Furthermore, it can provide guidance for the study of other system of cathode materials.

In this paper, we study the crystal electronic structure and work functions of typical binary and doped REB_6 (LaB_6, CeB_6, GdB_6, NdB_6, $La_{0.75}Ce_{0.25}B_6$, $La_{0.75}Nd_{0.25}B_6$, $La_{0.75}Gd_{0.25}B_6$, $Ce_{0.75}Gd_{0.25}B_6$, the single crystals were grown by the optical floating zone method) by the theoretical calculation combing thermionic emission experiment. Our work had shown that (100) surface of LaB_6 single crystals provide better emission performance [18], so the calculation and experiment of the work functions of binary and doped REB_6 were on the typical (100) surface.

2. Experimental

The crystal electronic structure (band structure and density of states) of binary and ternary REB_6 (LaB_6, CeB_6, GdB_6, NdB_6, $La_{0.75}Ce_{0.25}B_6$, $La_{0.75}Nd_{0.25}B_6$, $La_{0.75}Gd_{0.25}B_6$, $Ce_{0.75}Gd_{0.25}B_6$) by the first-principles calculations based on density functional theory (DFT) [19]. The exchange correlation potentials were treated in the framework of Perdewe-Burkee-Ernzerhof (PBE) functional of the Generalized Gradient Approximation (GGA + U) [19–21]. The effect of on-site Coulomb interaction (U) under GGA + U formulation of the density-functional theory is considered in the calculations and can only be applied to localized electrons (4f). The cut-off energy for plane-wave basis set is chosen to be 380 eV. The k-point mesh of $24 \times 24 \times 24$ was employed in the calculation. The work function calculation were done using Vienna Ab-initio Simulation Package (VASP) [22]. The exchange correlation potentials were treated in the framework of Perdewe-Burkee-Ernzerhof (PBE) functional of the Generalized Gradient Approximation (GGA). The periodic lattice (slab) model were used to simulate the (100) surface of considered REB_6. The height of the vacuum region is 20 Å, which can ignore the interaction between different layers.

The typical considered REB_6 single crystal were grown by the floating zone method. The dense feed and seed REB_6 rods were firstly prepared by SPS method using the commercial REB_6 powder as starting material. Then the feed and seed rods on a vertical line were placed into the optical floating zone furnace to grow the large-sized single crystal REB_6 under the argon atmosphere. The quality of single crystals was examined by the 360° Phi scanning single crystal diffractometer, X-ray Laue diffraction, X-ray rocking curves and scanning electron microscope (SEM). The X-ray Laue diffraction was used to determine the (100) surfaces of considered REB_6 single crystal and then cut out this surfaces. The (100) surface area of the single crystal REB_6 were 1 mm^2 for thermionic emission measurement and the cathode test temperature was 1673 K, 1773 K and 1873 K under the vacuum of 2×10^{-5} Pa.

3. Results and discussion

The REB_6 crystal structure as shown in Fig. 1, which are composed of rare earth embedded inside a stable boron octahedron network, and each B atom with other five B atoms together forming B_6. RE-B atoms have weak binding power and B-B atoms have stable covalent bonds. The stable boron octahedron network result in stable physical and chemical properties and hard brittle mechanical properties of REB_6. There are no hands combined between the B atoms and the RE mental atoms, indicating the weak ionic nature of bonds between RE and B atoms. Those illustrate that the valence electrons of RE can freely travel in the crystal lattice, which causing REB_6 have metallic and electronic emission performances. Furthermore, there are difference for the valence electrons of different rare earth atoms, meaning the considered REB_6 single crystals have different emission performance. In short, those unique bonding between atoms of REB_6 could provide desired properties for an excellent electron emission material.

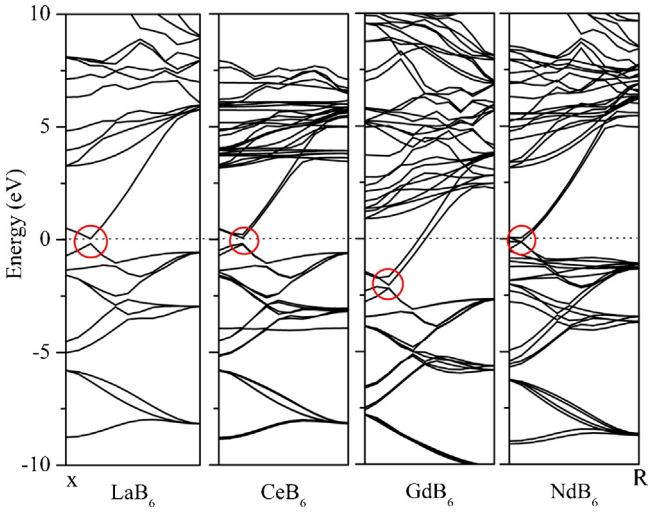

Fig. 2. The calculated electronic band structure of binary REB_6.

The calculated energy band structure of the typical REB_6 (RE = La, Ce, Gd, Nd) are shown in Fig. 2. The Fermi level is set to be 0 eV, other energy levels are determined comparing with the Fermi level. The red circle section in Fig. 2 show that the top of valence band (VB) and the bottom of conduction band (CB) at same points results in a direct band gap material for REB_6. Although the calculation underestimates the band gap of considered binary REB_6, the value of this gap turns out to be 0.038 eV, 0.064 eV for LaB_6 and CeB_6, respectively, this tiny band gap value accounts for its metallic behavior. A conduction band obviously crosses over the Fermi level along the X-R direction of the Brillouin zone, indicating more obvious metallic property of GdB_6 and NdB_6. The thermionic saturation emission current density (J) of REB_6 materials with metallic property could derived Richardson equation [23] as:

$$J = \frac{4\pi mek^2T^2}{h^3} \exp(-\Phi/kT) \quad (1)$$

Where e is elementary charge, h is Planck's constant, m is effective mass of charge carrier, T is the absolute temperature, k is the Boltzmann constant and Φ is work function. As can been seen from Fig. 2, the dispersion of the bands near the Fermi level fluctuate have wider energy region, meaning these relatively heavy bands have small effective mass which would favor to electron emission properties according this equation. Also, since electron emission properties of a material are closely related to its work function, and the work function Φ as a surface state property was classically defined as the minimal energy to bring an electron in the solid to a distance far away from the Fermi level, and its value can be obtained by the surface potential barrier minus Fermi level. So the position of Fermi level comparing the bottom of the conduction band or the top of valence band have an important impact on the work func-