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Enhanced thermionic emission performance of LaB_6 by Ce doping

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Motivated by enhanced thermionic emission performance resulting from low work function, the work function of $Ce_xLa_{1-x}B_6$ is studied by first-principles calculation based on density functional theory. By calculation, the optimal Ce doping concentration is determined to be 0.25, and a very low work function Φ=2.04 eV is predicted on the (001) surface of $Ce_{0.25}La_{0.75}B_6$. High-quality $Ce_{0.25}La_{0.75}B_6$ single crystal was fabricated by optical floating zone technique. By the experimental measurement on the thermionic emission performance, the average work function of $Ce_{0.25}La_{0.75}B_6$ is about 2.61 eV, which is lower than the work function of both CeB_6 and LaB_6. By the combination of calculation and experiment, we concluded that Ce doping can reduce the work function of LaB_6 and enhance its thermionic emission performance.

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I. INTRODUCTION

All rare earth hexaborides LnB_6 (Ln=La-Lu) crystallize into simple cubic structure with space group Fm-3m. Although the crystal structure is very simple, rare earth hexaborides have attracted lots of research interest because of their rich magnetic and electronic transport properties.[1–5] All rare earth hexaborides are good conductors, except EuB_6. In the calculated band structure of EuB_6, there exits minute overlap between conducting and valence bands, which indicates that EuB_6 is semimetal.[6–8]

As a typical rare earth hexaboride, cerium hexaboride compound CeB_6 has attracted lots of research interests because of its special electronic and magnetic properties.[9–12] Metallic CeB_6 shares similar band structure with LaB_6, i.e., Fermi level lying on the d-orbital dominating conducting band. With a very high melting point ∼2823 K, CeB_6 has high chemical stability and excellent mechanical properties, such as high hardness. It also possesses high electronic emission and low volatility, as like lanthanum hexaboride LaB_6 which is widely used as thermionic emitter.[13,14] Furthermore, CeB_6 is also potential field emission material with excellent performance.[15,16]

The work function dependent saturated thermionic emission current density J is described by the Richardson equation which reads,

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

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 the work function.[17,18] The saturated thermionic emission current J is strongly dependent on the work function, i.e., minimum energy needed to remove an electron from a solid to a point in the vacuum immediately outside the solid surface. Under the same conditions of temperature and external electric field, emission current is increasing with the decrease of work function. In practical application, work function is one critical index to evaluate the performance of cathode candidate. Therefore, it is critical important to evaluate the work function of cathode candidates candidate by calculation before experimental research.

On the (001) surface of LaB_6, the work function is about 2.7 eV,[19–21] while other surfaces have higher work function. For CeB_6, the work function on (001) surface is about 2.7(±0.3) eV from the results of different groups.[22–28] It is significant to determine the work function of CeB_6 accurately. Because of the rather high work function of LaB_6, its working temperature is still very high. How to reduce the work function or lower the working temperature is critical for practical application.

In this work, we calculated the work function of CeB_6 on (001), (011), (111), (012) surfaces with Ce or B atoms on the termination by the first-principles calculation. Our calculation reveals that the (001) surface has the lowest work function Φ(001)=2.24 eV when the Ce atom is on the termination. Additionally, we further calculated the work function of Ce-doped $Ce_xLa_{1-x}B_6$ (x=0.0, 0.25, 0.5, 0.75, 1.0) on (001) surfaces. We predicted that $Ce_{0.25}La_{0.75}B_6$ processes a very low work function Φ=2.04 eV, which is even lower that the work function of typical thermionic emitter LaB_6. We also successfully fabricated high-quality $Ce_{0.25}La_{0.75}B_6$ single crystal and measured its thermionic emission performance at different temperature. By experimental measurement, the work function of $Ce_{0.25}La_{0.75}B_6$, LaB_6 and CeB_6, is de-

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