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Research Article

ErB_6 and Ce doped ErB_6 hexaborides: A computational material study

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ABSTRACT

Erbiyum hexaboride is one of the heavy rare aearth hexaborides that indicate superior chemical and physical properties. In this study, Erbiyum hexaboride and Ce doped Erbium hexaboride crystal structures have been investigated systematically employing ab initio material modeling. The effects of Ce doping (wt.%10) on Erbiyum hexaboride structure in terms of optical, thermal, mechanical and electronic properties including band properties, enthalpy of formation energies and bulk modules were investigated. Results show that the Ce doping leads to an increase in the bandgap of the structure. Furthermore, the bulk modules calculations show that Ce doping to the structure leads to an increase in mechanical properties.

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Introduction

Metal Rare Earth Hexaborides (REB6) consisting of octahedral bor units are fascinating advanced materials due to their superior electrical[1], thermal[2], magnetic[3], optical[4, 5], and mechanical[6] properties. Thus, such properties have been used in a variety of applications, such as electron emitters[7], thermoelectric materials[8], coatings[9], single-photon detectors[10] and superconductors[11].

REB_6 are cubic crystal structures with the symmetry Pm3m (Oh). This type is under the group of the simple CsCl-type structure. Erbium atoms are located at the corners of the unit cell while an octahedral B cage occupies the center position of the structure. The superior properties of (Erbium hexaboride) ErB6 are mostly due to the three-dimensional boron-framework. The strong covalent bonding within the boron polyhedron leads to the range of homogeneity, stability, hardness, and high melting point[12, 13, 14, 15]. Baranovskiy et al.[12] studied the electronic structure, bulk and magnetic properties REB_6 and REB_{12}, including ErB_{12} materials based on the ab initio material modeling method. They calculated the elastic properties of some metal hexaborides and dodecaborides. Raymond[16] synthesized ErB_6 successfully. They found that ErB6 stayed stable for a limited temperature range. Gernhart et al. [17]produced ErB_6 nanowires via palladium nanoparticle-assisted chemical vapor deposition. They determine the length of the crystal structure.

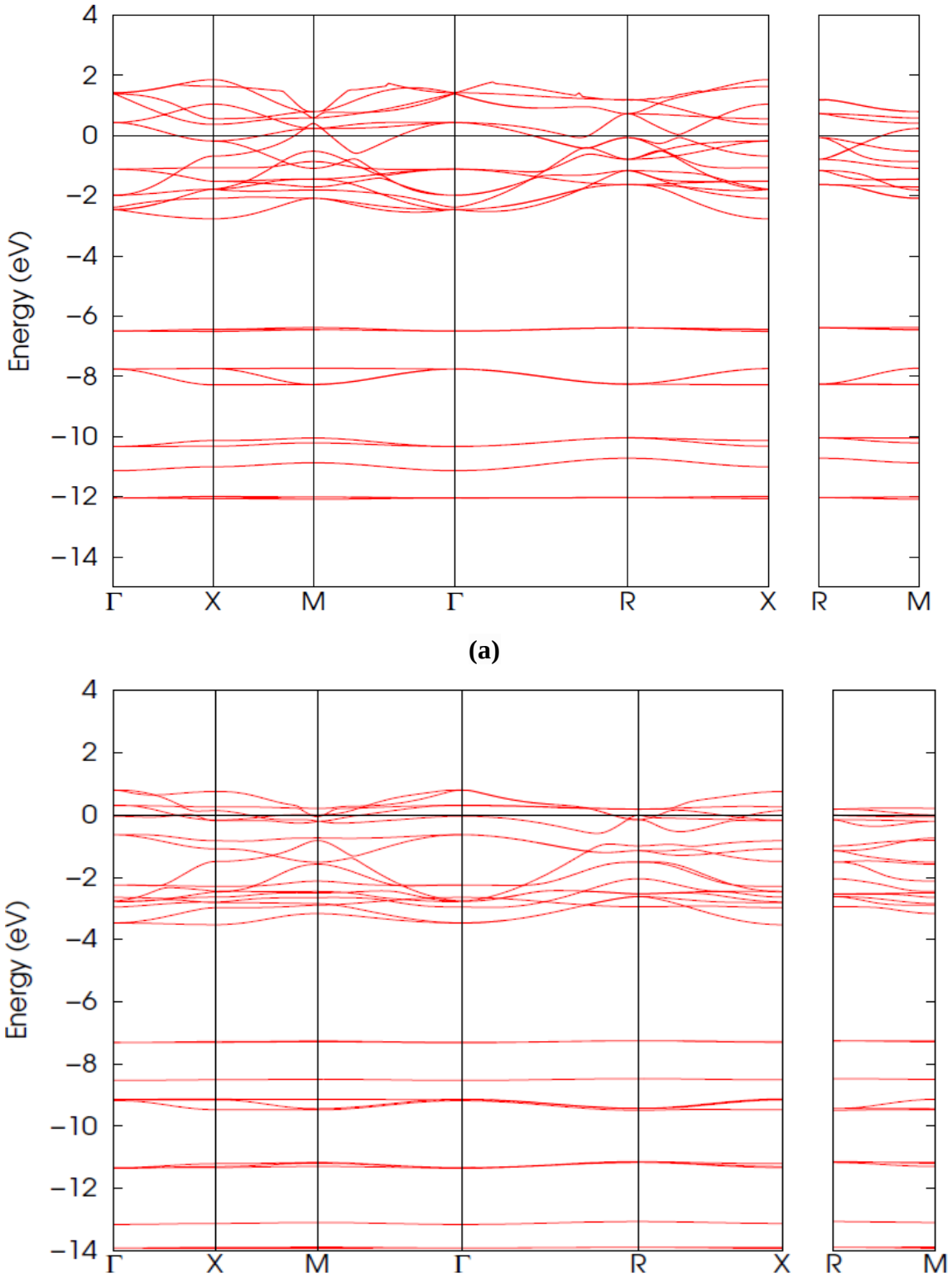
Due to the shared crystal structure, all rare-earth metal hexaborides including ErB_6 can form solid solutions, allowing for fine-tuning of electrical, optical and thermal properties with mixed-metals. This paper presents an overview of the electronic, magnetic, and optical properties of ErB_6 and Ce (wt.%10) doped ErB_6 rare-earth hexaboride crystals to guide researchers with the first step in pursuing these interesting and unique materials by ab initio material modeling. To the best of our knowledge, this is the first time ab initio material study related to the ErB_6 rare-earth hexaborides crystals. Like many other REB_6, ErB_6 presents certain synthesis and processing challenges. Hence, there exist a few experimental studies related to crystallized ErB_6 materials. We believe that this study enlightens future experiments as a preliminary process to a certain degree.

Materials and Methods

Density functional theory-based ab initio material modeling has been performed using Quantum Espresso Software (QE) packages based on the modeling of the material at the nanoscale or atomistic scale[18]. The generalized gradient approximations (GGA) of Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional and the projector augmented wave (PAW) method were preferred. The plane-wave basis set was determined by a kinetic energy cutoff of 500 R_y. The Brillion zone integration was performed at the 3×3×3 k mesh points using a methfessel-paxton smearing with a width of 0.02 Ry. For geometry optimization, all forces on the atoms were converged to less than 0.01 eVa_0^{-1}, the maximum ionic displacement was within 0.001 Å. Furthermore, Mechanical and thermal properties and band structures were calculated by thermo_pw software[19] that is used for the computation of material properties using QE routines.

Results and Discussion

For the evaluation of electronic band structures of ErB_6 and Ce doped ErB_6, the band structures along the high-symmetry directions of the cubic Brillion zone (BZ) are given in Figure 1. Figure 1 indicates the simple cubic BZ with Γ, X, M, and R high symmetry points.



(a)

(b)

Figure 1 *The band structure of (a) ErB_6 and (b) Ce doped ErB_6*

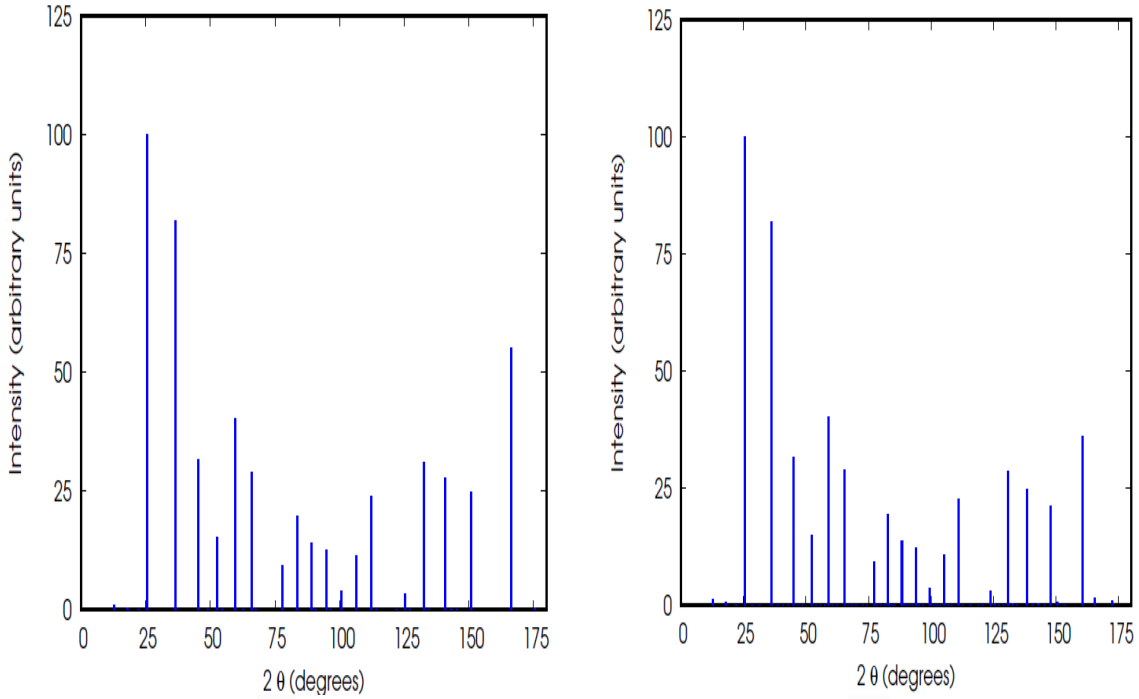


Figure 2 *The XRD structure of (a) ErB_6 and (b) Ce doped ErB_6 structures.*

For simplicity, the band structures along with high symmetry directions in the BZ were only plotted in this part. It can be concluded that Ce doping to the ErB_6 structure leads to an increase in bandgap (see Figure 1). Also, due to the Ce doping, the energy levels of the bands decreased.

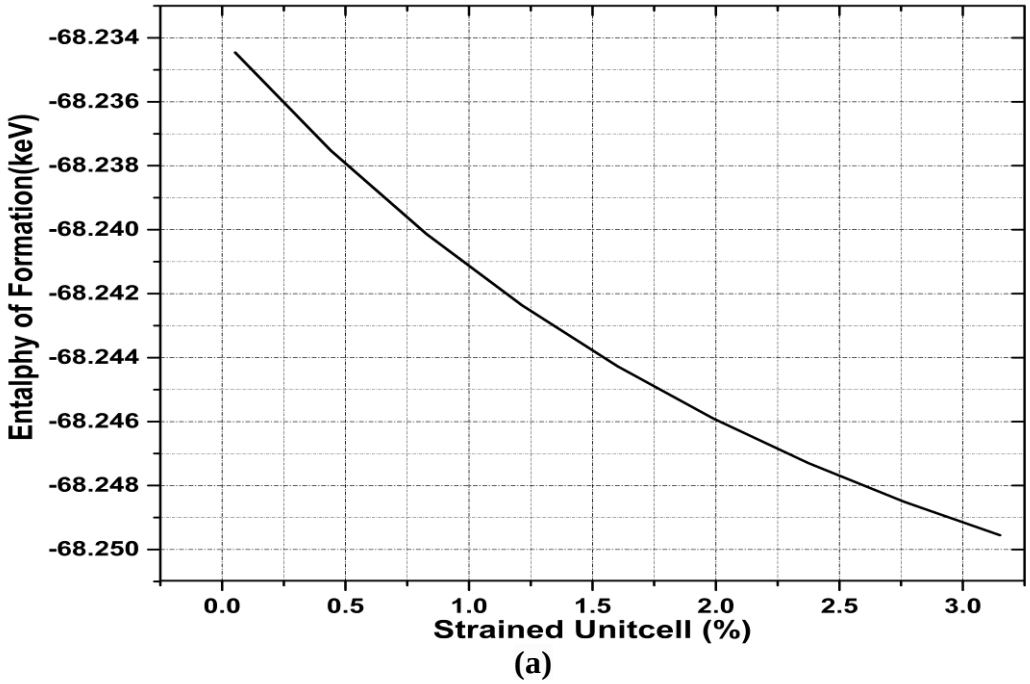
For the microstructural characterization, we calculated the XRD analyzes of the structures (see Figure 2). The peaks in the XRD pattern are indexed to the tetragonal system with the space group Pm3m-O. Ce peak was not observed in the Ce doped structure since the addition of one Ce atom by removing one Er atom does not lead to any differences in the geometry or crystallographic direction of the structure, i.e., Ce atom occupies the same position as the removed Er atom. Except for some peaks, the XRD results of ErB_6 are generally consistent with previous studies.

The bulk modulus of the structures has also been calculated. The values of ErB_6 and Ce doped ErB_6 are 149 GPa and 154 GPa respectively. The results show that doping to the ErB_6 leads to an increase in the mechanical properties of the ErB_6.

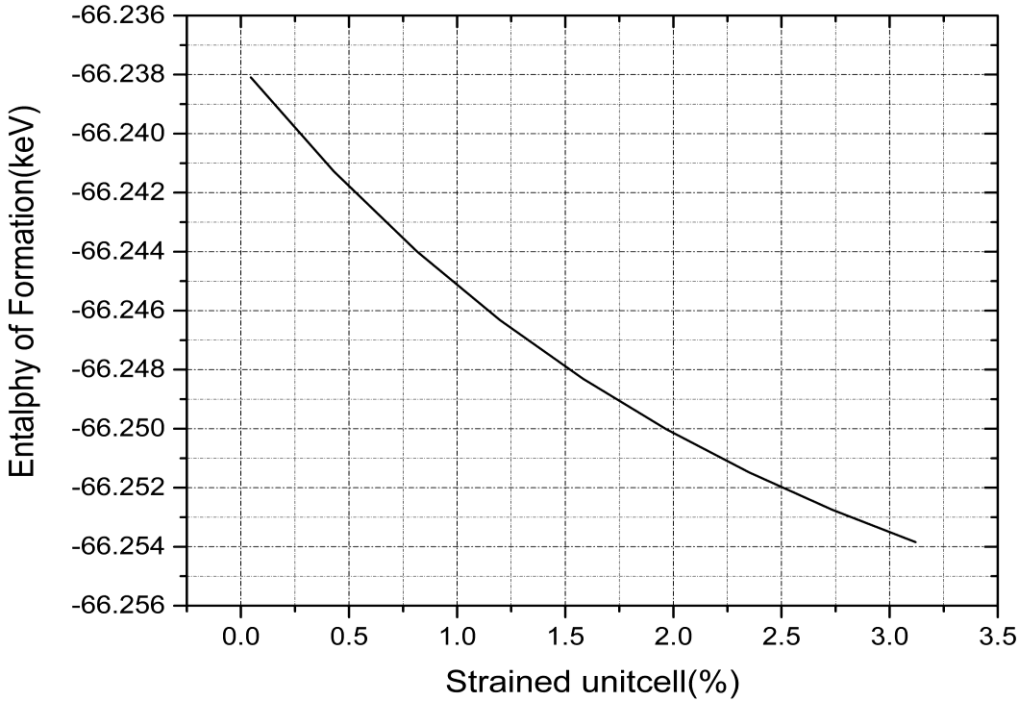
The relationship between thermal stability and mechanical properties has been investigated. Various ranges of elongated structures to examine the degree of thermal stability were calculated by applying tensile forces on doped and undoped ErB_6 nanocrystal structures. Figure 3 indicates the relation between enthalpy energy and elongation percentages of the structures. As the ratio of elongation increases, the thermal stability of both structures increases according to the enthalpy energy calculations. For a comparison of doped and undoped ErB_6 crystal structure, the applied tensile stress leads to more effect on Ce doped ErB_6 than pure ErB_6 in terms of stability.

Conclusions

A computational material study of ErB_6 crystal structures within the framework of ab initio material modeling at the level of DFT has been investigated. The Ce doped ErB_6 structures were also investigated. The optical properties calculations indicate that alloying of ErB_6 with Ce leads the material to have



(a)



(b)

Figure 3 *The Enthalpy formation energies of (a) ErB_6 and (b) Ce doped ErB_6 structures concerning the elongated volume.*

more insulating properties. Furthermore, the XRD of the structures was computed for microstructural evaluation. The XRD analyses support the studied crystal structures having the space group Pm3m-O. The enthalpy calculations show that the enthalpy energies of undoped ErB_6 are higher values than doped ones.

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