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Theoretical study of hydrogen-sorption properties of lithium and magnesium borocarbides

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ABSTRACT

The statistical theory of hydrogen-sorption properties of compounds of alkaline and alkaline-earth metals $M(BC)_nH_x$ ($M = Li, Mg; 0 \leq x \leq 12, n = 1,2$) has been developed in this paper in the expectation that such hydrogenated boron carbides will be the reliable materials for the reversible accumulation and storage of hydrogen in large quantities in perspective. The calculation of free energy of these crystals has been performed on the basis of molecular-kinetic notions, the equation of thermodynamic equilibrium of such system, determining the P-T-c phase diagram, has been derived in the present paper. The hydrogen solubility in these compounds has been ascertained in dependence on temperature and external pressure, the possibility of manifestation of hysteresis effect has been justified. The derived formulae allow to establish the P, T-conditions of high hydrogen content in boron carbide systems and can permit to select the optimum composition of material choosing for hydrogen storage, the regime of technological process, to develop the experimental technology for solving of the practical problems, if in this case the energetic parameters of these materials are known from independent experiments.

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Introduction

Since the exciting discovery in 2001 of superconductivity in compound MgB_2 with an unusually high transition temperature ($T_c = 39$ K) [1], interest in simple compounds of boron and light elements has undergone a renaissance. Doping on both the Mg and B sites has led both theorists and experimentalists to the investigation of structurally related compounds [2]. The $M(BC)_n$ phases ($M =$ alkaline-earth or rare-earth metal, $n = 1,2$)

triggered an enormous interest as compounds with structurally similar features, namely graphite-like layers [3,4]. Although the physical properties of $M(BC)_n$ compounds family have been widely investigated, some of their structures are still debated, especially with respect to the position of B atoms versus C atoms.

In the case of MgB_2C_2 and LiBC compounds, for instance, the recent discovery of various potentially interesting properties [5–10] has revived the interest of the scientific community. The structure of the LiBC and MgB_2C_2 , both containing

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B–C layers isoelectronic to graphite, have been investigated in detail in many experimental and theoretical works [11–14].

Interest in the intercalated heterographites, as LiBC and MgB_2C_2 [15–17], has going to be renewed thanks to the considerable progress made in graphite research, whose lattice points might be entirely occupied by carbon (graphene layers) and stacked along the direction perpendicular to the layer plane (graphite) or alternatively substituting carbon by boron and adding a layer formed by electron-donor elements, as lithium and magnesium, between the heterographene layers.

For the first time LiBC compound was prepared in 1995 by Nesper's group [4, 18] who also determined some of their physical and chemical properties. LiBC is a layered boron carbide consisting of alternating graphene-like $(\text{BC})^-$ sheets [4, 19, 20] separated by intercalated Li^+ ions. It normally crystallizes in primitive hexagonal lattice with space group symmetry $P6_3/mmc$ (Fig. 1). LiBC borocarbide is structurally and electronically similar to the superconductor MgB_2 , except for the replacement of Mg by Li and by replacement of B by C at

every second position along in-plane covalent bonds as well as along the hexagonal axis, what leads to doubled unit cell along the hexagonal axis [8, 13, 16, 21–29]. LiBC was experimentally subjected to very high pressures [13, 24] and experiments revealed that crystal structure of LiBC remains stable up to 60 GPa. The B–C distance of 1589 Å in LiBC is comparable with that in MgB_2C_2 [29].

A related layered borocarbide MgB_2C_2 has been suggested [29–31]. Magnesium diboride dicarbide, MgB_2C_2 , compound made of alternate boron–carbon and metallic sheets constitute an important class of the alkaline-earth metal boron carbides. The structure of MgB_2C_2 contains analogously graphite-like but slightly puckered boron–carbon layers (formed nets of condensed six-membered rings) [29, 32–42] and for MgB_2C_2 a high-pressure Pnm phase was also synthesized and structurally characterized [14]. Yan and collaborators [43] have recently provided an extensive study of structural and thermodynamic properties of insulating MgB_2C_2 . The B–C distances within the layers range are from 1562 to 1595 Å [29].

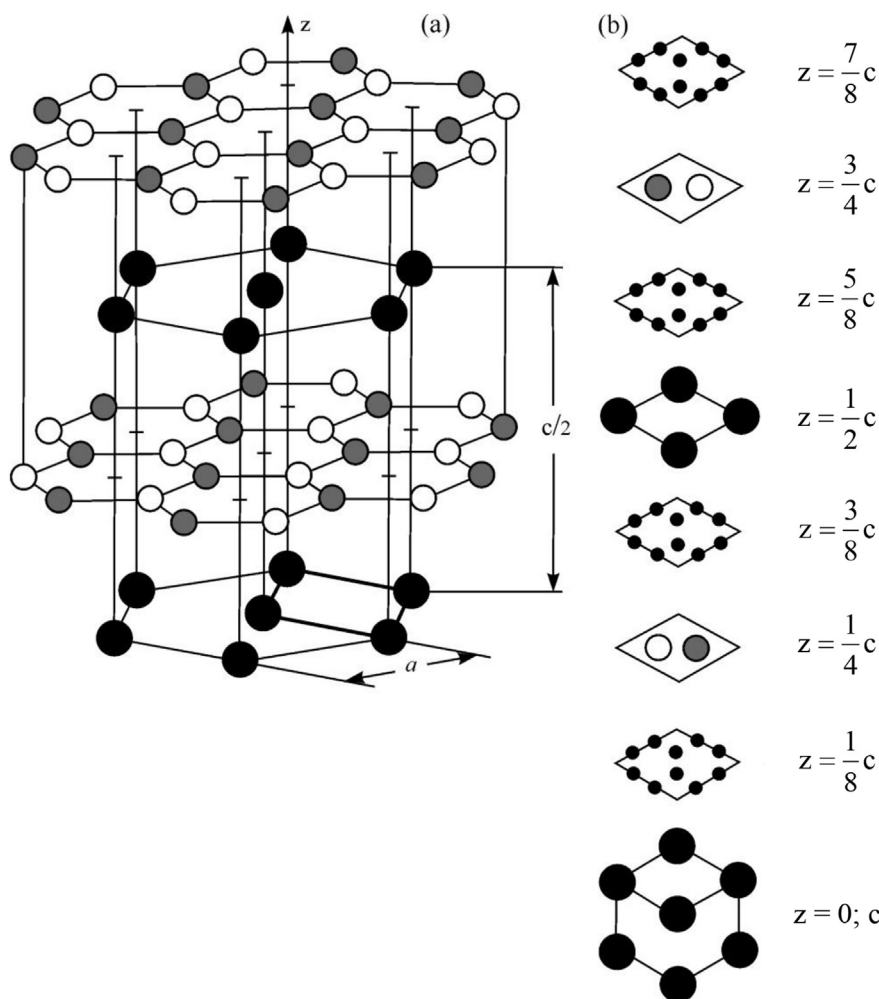


Fig. 1 – The hexagonal crystal structure of stoichiometric LiBC, illustrating the similarity to MgB_2 : (a) spatial projection and (b) its projection onto the planes perpendicular to the z axis at different z ; Sites of first type corresponding to lithium atoms (●), sites of second type corresponding to boron atoms (●) and carbon atoms (○) and triangular interstitial sites for hydrogen atoms (●). B and C alternate along the \bar{c} axis, doubling the unit cell.

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