Raman Spectra of Boron Carbide $B_{4.3}C$ from first principles

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Despite decades of investigations, the atomic structure of boron carbide below 20% atomic carbon concentration is still subject to debates. For instance, the experimental Raman spectra of $B_{4.3}C$ is not yet understood: while most of the peaks have for long been explained by the theoretical ground state structure B_4C with 20% atomic carbon concentration [1], two large peaks remain unexplained even when common point defects are introduced in the structure [2,3]. Moreover, these two peaks have been measured under high pressure [4] and exhibit uncommon behavior of their Grüneisen parameters. Finding a theoretical explanation of this behavior certainly requires a detailed knowledge of the atomic structure.

Beside the B_4C unit cell that consists of one ($B_{11}C^p$) icosahedron and one C-B-C chain, new building blocks such as C-B-C-B chains and B<B_2>B pantograph-like intericosahedral blocks have been identified with HRTEM [5], and two crystalline unit-cells with either building blocks have been confirmed theoretically to be part of the B-C phase diagram at respectively 13.0% ($B_{6.7C}C$, named OPO_2) and 8.7% ($B_{10.5}C$, named OPO_1) atomic C concentrations [6].

We will review which modifications of these phases enable us to explain the phase diagram between 20% and 13.0%, and between 13.0% and 8.7% and how the theoretical 20% concentration is lowered to $B_{4.3}C$ at finite temperature. We will then show the lattice vibrations computed with density functional perturbation theory and Raman spectra computed with the 2nd order response [7]. The unexplained Raman peaks will be discussed in light of calculations under pressure. Finally, by showing the characteristics of the disorder, we will discuss the symmetry of the material and the large broadening of the two low frequency peaks.

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