



Mode Grüneisen parameters of boron carbide



Helmut Werheit ^{a,*}, Murli H. Manghnani ^{b,**}, Udo Kuhlmann ^{a,1}, Anwar Hushur ^{b,2},
Sulkhan Shalamberidze ^c

^a Experimental Physics, University Duisburg-Essen, 47048 Duisburg, Germany

^b Hawaii Institute of Geophysics and Planetology, University of Hawaii, Honolulu, HI 96822, USA

^c Institute of Stable Isotopes, Tbilisi 380086, Georgia

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ABSTRACT

IR- and Raman-active phonons of boron carbide and the mode Grüneisen parameters γ related are studied concerning their dependence on chemical composition, temperatures between 30 and 800 K and pressures up to ~70 GPa. Most bulk phonons yield γ between +1.5 and -1.5; those related to icosahedra yield $\gamma = 0.8(3)$. Surface phonons are distinguished by considerably higher γ . Negative γ of chain bending modes supports the assumption that the chain center buckles out under pressure. Some striking specific mode Grüneisen parameters are explained. Pressure-dependent bond lengths suggest the reversible high-pressure phase transition to be second order.

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1. Introduction

Boron carbide is characterized by an outstanding combination of properties like high melting point ($T_m > 2700$ K), extraordinary hardness ($H_K, H_V = 30\text{--}38$ GPa), low density ($d = 2.51$ g cm⁻³), high chemical stability, high neutron absorption cross section (¹⁰B isotope) and moreover a high Seebeck parameter ($S \sim 300$ μVK⁻¹) up to very high temperatures. These properties are promising for technical applications under exceptional conditions. For reviews see Refs. [1–4].

Currently, light-weight armor is one of the most important applications [5]. Relevant macroscopic solid state properties in this respect, describing the macroscopic deformability of solids, are the coefficient of linear expansion α , Bulk modulus B and specific heat c . They form the Grüneisen parameter

$$\gamma_G = \frac{3B\alpha}{c} \quad (1)$$

The alternative definition of mode Grüneisen parameters is based on microscopic properties, namely the effect of inharmonic atomic bonding potentials on vibrational properties [6]:

$$\gamma_G = \frac{V}{\omega} \frac{\partial \omega}{\partial V} \quad (2)$$

below approximated by

$$\gamma \approx \left(\frac{\Delta \omega}{\omega} \right) / \left(\frac{\Delta V}{V} \right) \quad (2a)$$

with phonon frequency ω , volume V of the unit cell and their changes.

In a detailed description from the viewpoint of applications [7], Harris and Avrami state the importance of the Grüneisen parameter γ in cases of rapid heating of materials by intense pulses of radiation. Their duration is small compared to relevant times of acoustic transport, and the resulting thermal pressure is directly proportional to γ . As in such cases the contribution of phonons dominates, determining the mode Grüneisen parameters is useful.

Hofmeister and Mao [8] pointed out that the definition by Grüneisen holds for monatomic solids only, where the atomic volume is proportional to the unit cell volume and to the molar volume, respectively. This does not hold in polyatomic structures, where specific bonding conditions of functional atomic groups

* Corresponding author.

** Corresponding author.

E-mail addresses: helmut.werheit@uni-due.de (H. Werheit), murli@soest.hawaii.edu (M.H. Manghnani).

¹ Present address: Pirelli Deutschland GmbH, Breunberg D-64747, Germany.

² Permanent address: Department of Physical Science and Technology, Xinjiang University, Shengli Road 14, Urumqi, Xinjiang, China.

determine the phonon frequencies. Equation (2) persists in such cases only, when the whole structure is periodically deformed like in the case of acoustic phonon modes. In contrast, optical IR- and Raman-active phonon modes interact with single atoms or small atomic groups, whose specific partial volumes are to be considered.

This is the case in boron carbide, whose complex structure is

composed of 12-atom icosahedra and three-atomic linear chains yielding a large variety of vibrational modes. An ab-initio calculation by Fan et al. [9] yields $\gamma = 1.5 \pm 1.0$ depending on temperature (0–2000 K) and pressure (0–90 GPa). Experimental results available from literature [2,5,10,11,13,14] are listed in Table 1. Properties at pressures up to 1.5 TPa are calculated by Shamp et al. [12].

Analyzing the pressure dependence of Raman spectra, Guo et al. [13] and Manghnani et al. [14] reported mode Grüneisen parameters of boron carbide. However, they did not consider that the Raman spectra of boron carbide depend qualitatively on the excitation energy of the Raman laser. The reason is sufficiently high reflectivity of the sample or sufficiently small penetration depth of the exciting radiation at the frequency of the exciting laser. This occurs for example below the plasma edge of hexaborides [15,49] or above the absorption edge of very strong interband transitions like in the case of boron carbide [16–19,49]. In that case, the signal originating from surface scattering exceeds that originating from bulk scattering by several orders of magnitude. Depending on the reflectivity R , largely pure Raman spectra of surface or bulk

Table 1
Experimental Grüneisen parameters of boron carbide.

γ	method	Ref.
1.282		[5]
$\gamma_L = 1.21 \pm 0.07$	Longitudinal acoustic mode	[10]
$\gamma_S = 0.33 \pm 0.02$	Shear acoustic mode	
$\gamma_{el} = 0.62 \pm 0.03$	Mean acoustic mode	
$\gamma_{th} = 1.76$	thermal	
0.26–1.38	Raman modes; pressure dependence. (surface phonons not identified)	[13,2]
0.3–0.9	Eulerian sound speed, 300–800 GPa	[11]
0.14–1.05	Raman modes (surface phonons not identified)	[14]

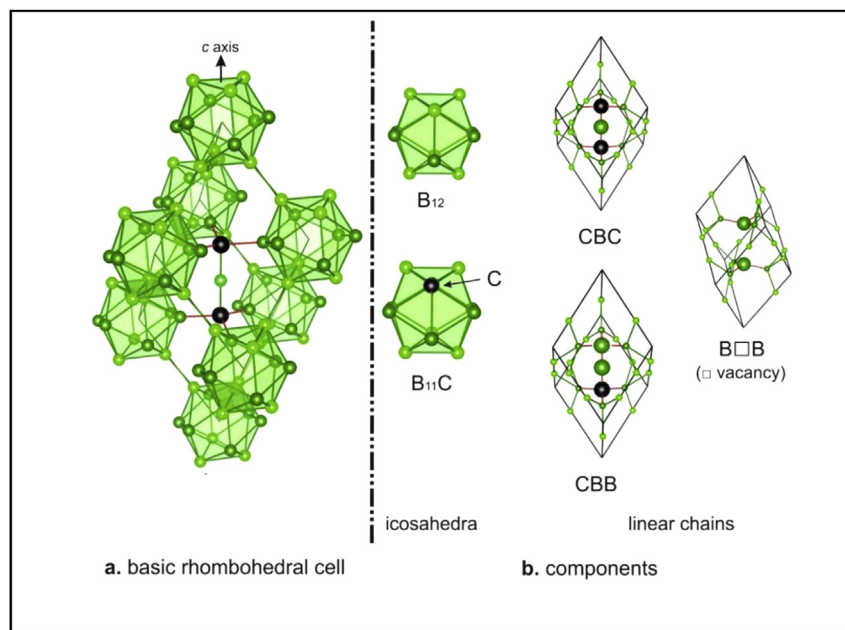


Fig. 1. Structure of boron carbide. Depending on chemical composition, the rhombohedral unit cell (left) contains randomly distributed variant concentrations of B_{12} or $B_{11}C$ icosahedra, CBC, CBB and $B\Box B$ (\Box , vacancy) linear chains. Visualization by VESTA [4].

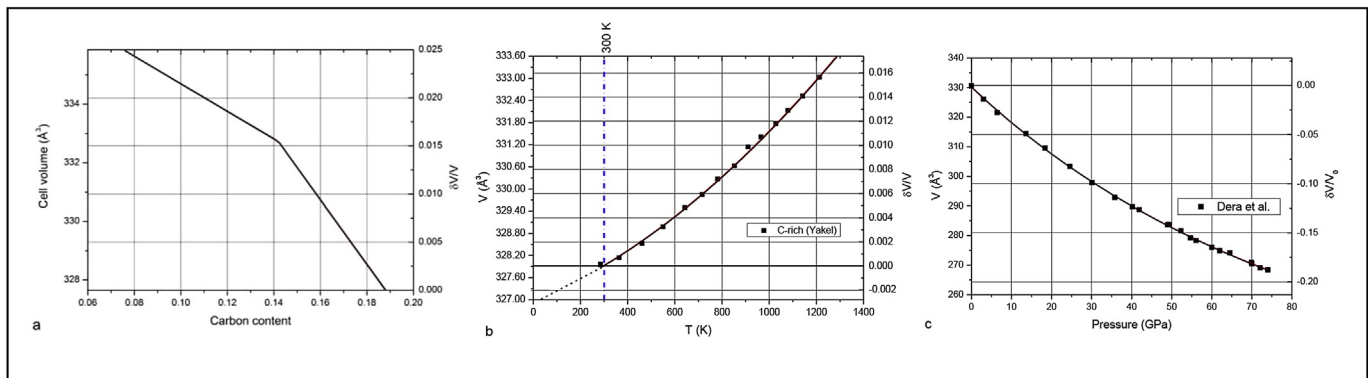


Fig. 2. Unit cell volume of boron carbide depending on various parameters. a. Chemical composition. Lattice parameters taken from Ref. [23], b. Temperature. Taken from Ref. [24] “carbon-rich boron carbide”; range of low T extrapolated. c. Pressure. Taken from Ref. [26].

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