JOURNAL OF MATERIALS SCIENCE **36** (2001) 3403–3407

Room temperature single crystal elastic constants of boron carbide

K. J. McCLELLAN, F. CHU, J. M. ROPER
Materials Science and Technology Division, Mail Stop G755, Los Alamos National Laboratory, Los Alamos, NM 87545, U.S.A.
E-mail: kmcclellan@lanl.gov

I. SHINDO
Crystal Systems Inc., 9633 Kobuchisawa, Kitakoma, Yamanashi, 408-0044 Japan

Single crystals of the high temperature ceramic boron carbide have been synthesized by the optical floating zone method. Room temperature elastic constants of a carbon-deficient boron carbide single crystal have been measured using the resonant ultrasound spectroscopy technique. Based upon density measurements, the single crystal stoichiometry was specified as $B_{5.6}C$. This crystal has room temperature single crystal elastic constants of $c_{11} = 542.81$, $c_{33} = 534.54$, $c_{13} = 63.51$, $c_{12} = 130.59$, and $c_{44} = 164.79$ GPa, respectively. Analysis of Cauchy's relationships, Poisson's ratios, and elastic anisotropic factors for the single crystal elastic constants indicates that it is more strongly anisotropic in elasticity and interatomic bonding than most solids. Room temperature isotropic elastic moduli of boron carbide show that its bulk, shear and Young's moduli are substantially higher than those of most solids, so that boron carbide belongs to the so-called "strong solids". Its Poisson's ratio is significantly lower than that of most solids. © *2001 Kluwer Academic Publishers*

1. Introduction

The boron-carbon binary system has one compound, boron carbide, which is typically labeled as B_4C although it has a large range of solubility on the boron-rich side [1–3]. Stoichiometric B_4C has a rhombohehral structure with lattice constants, $a = 5.19$ Å and $\alpha = 65°18'$. The corresponding hexagonal lattice constants are $a = 5.60$ Å and $c = 12.12$ Å, respectively [2, 3]. It has an ultra-high melting temperature, $T_m = 2450°C$ [1] and a significantly low mass density, $\rho = 2.52$ g/cm^3.

Boron carbide has a number of potential engineering applications because of its unique physical and mechanical properties [4, 5]. For instance, it is employed as light-weight armor plates for its ballistic properties, as wear-resistant components because of its tribological properties, and as abrasive grit. Boron carbide can also be used as a neutron absorber in nuclear reactors due to the nuclear characteristics associated with its high boron content. In order to evaluate and enhance the applications of boron carbide, it is desirable to obtain its fundamental physical properties as a baseline database.

Elastic properties of a solid are important because they relate to various fundamental solid-state phenomena such as interatomic potentials, equations of state, and phonon spectra. Elastic properties are also linked thermodynamically with specific heat, thermal expansion, Debye temperature, and the Grüneisen parameter. Most importantly, knowledge of elastic constants is essential for many practical applications related to the mechanical properties of a solid: load-deflection, thermoelastic stress, internal strain (residual stress), sound velocities and fracture toughness.

Although the isotropic elastic moduli of polycrystalline boron carbide have been obtained through mechanical testing [4–6], the complete set of single crystal elastic constants, which is more important for understanding the elastic properties of boron carbide, is still not available. In order to better understand the physical properties and mechanical behavior of B_4C, we have grown boron carbide single crystals and studied the single crystal elastic properties in this work. Boron carbide has a rhombohedral crystal structure and belongs to the R $\bar{3}$m space group [5], but for the simplicity of elastic property measurement and analysis, it is treated as a hexagonal structure in this study.

2. Experimental procedures

Fine powders of B_4C with nominal purity of 99.9 at.% were placed in a sealed rubber tube and isostatically pressed with water media at an applied force of approximately 100 MPa to form a rod of desired diameter (8 mm) and length (100 mm). These rods were then heated to 1500°C under an argon atmosphere to obtain sintered materials with an apparent density of 60–80 % of the theoretical value.

0022–2461

Single crystals of B_4C were grown by the optical floating zone technique [7] using sintered rods for both the feed and the seed rods. In the optical floating zone method, a four-mirror system with four 3 kW xenon lamps was used. The feed and seed rods were typically counter-rotated at 30–40 rpm, and the crystals were grown at a rate of 2 mm/hr under an argon atmosphere. Even though polycrystalline rods of B_4C were used as seed rods, a single grain was seen to dominate the solidified body after 30–40 mm of growth. Facets were seen on the growing crystal along with straight boundaries believed to demarcate twins in this system. Examination by both the back-reflection Laue and the precession techniques revealed that the growth facet was parallel to the $(11\,\bar{2}\,1)$ plane. Inversion twinning on the $(10\,\bar{1}\,1)$ plane was also observed.

The back-reflection Laue x-ray pattern along the growth direction, shown in Fig. 1, reveals that the boron carbide single crystals have a preferred orientation along the $c = [0001]$ direction in terms of the hexagonal cell, and also illustrates the quality of the crystal. The density of the specimen was determined using the water displacement method. Optical microscope observation of crystal sections revealed no evidence of internal porosity suggesting the crystal is ∼100% dense.

The room temperature single crystal elastic moduli of a boron carbide single crystal were measured by resonant ultrasound spectroscopy (RUS) [8]. A rectangular parallelepiped specimen was cut from a twin-free region of an as-grown single crystal and polished using diamond media to a 1 μm finish. The back-reflection Laue method was used to orient $\mathbf{x}_1$ parallel to $[10\,\bar{1}\,0]$, $\mathbf{x}_2$ parallel to $[\bar{1}\,2\,\bar{1}\,0]$ and $\mathbf{x}_3$ parallel to [0001]. The dimensions of the RUS sample were $x_1 = 5.425 \pm 0.001$ mm, $x_2 = 4.745 \pm 0.001$ mm, and $x_3 = 3.726 \pm 0.002$ mm. The room temperature single crystal elastic moduli were determined using 40 resonant frequencies from 0.70 MHz to 2.20 MHz. The software used to fit the RUS data can only be used with cubic, tetragonal, orthorhombic and hexagonal symmetry and can not be used directly for the rhombohedral structure of boron carbide. Therefore, two data fitting schemes were used for the RUS spectrum. One is to fit c_{11}, c_{33}, c_{44}, c_{12}, and c_{13} assuming the specimen is a hexagonal system. The other is to fit the c_{11}, c_{22}, c_{33}, c_{44}, c_{55}, c_{66}, c_{12}, c_{13}, and c_{23} assuming that the specimen is an orthorhombic system

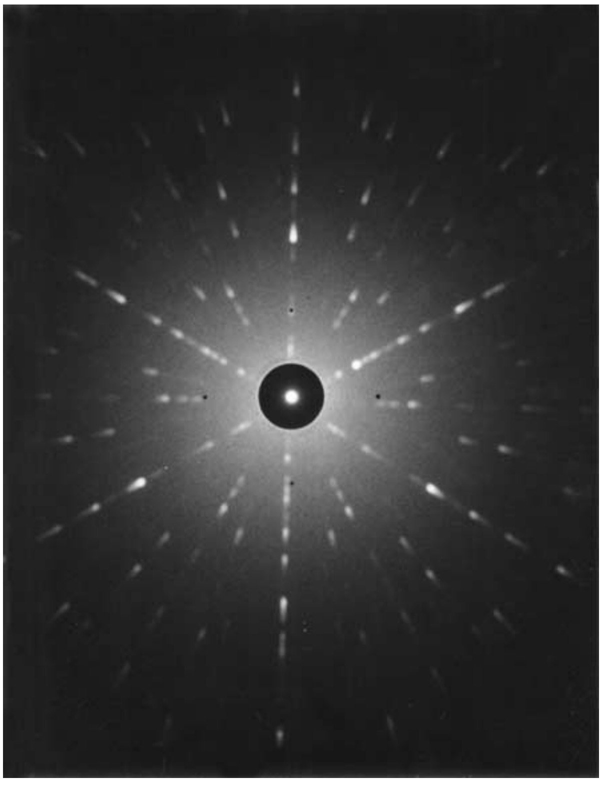

Figure 1 X-ray back-reflection Laue pattern along the growth direction of as-grown $B_{5.6}C$ single crystals, indicating that growth is along $\mathbf{c} = [0001]$.

Using these single crystal elastic constants, the elastic Debye temperature (Θ_D) of boron carbide can be calculated from the relationship [9]

$$\Theta_D = \frac{h}{k_B}\left(\frac{3N_o}{4\pi V}\right)^{1/3} \nu_m. \qquad (1)$$

Here, h and k_B denote the Planck and Boltzmann constants, N_0 is the number of independent three-dimensional oscillators in a volume V, and ν_m denotes the mean sound velocity defined by:

$$\nu_m^{-3} \frac{1}{M} \sum_{i=1}^{M} \frac{1}{3}\left(\nu_{li}^{-3} + 2\nu_{ti}^{-3}\right). \qquad (2)$$

where ν_{li} and ν_{ti} indicate longitudinal and transverse velocities in the ith propagating direction, respectively, and M is the number of all propagating directions. For this study, we chose $M = 70$. ν_l and ν_t can be determined from the measured c_{ij} and mass-density by solving the usual Christoffel equations [10] in the relevant propagation direction.

3. Results and discussion

The mass density of the as-grown boron carbide single crystal was measured as 2.495 g/cm^3, which is about 1% lower than the theoretical value of B_4C (2.52 g/cm^3). This is most probably caused by the substantial carbon loss in optical floating zone single crystal growth. Using the linear relationship between density and carbon content of boron carbide [5], the stoichiometry of the single crystals is calculated to be $B_{5.6}C$ or 15.2 atomic % C. This composition falls well within the phase stability regime of boron carbide, 8.8 to 20.0 atomic % C.

Fig. 2 shows a portion of the room temperature RUS spectrum of a $B_{5.6}C$ single crystal. The high signal-to-noise ratio and high-Q resonant peaks shown in Fig. 2 demonstrate the quality of the specimen and the RUS measurement. Table I tabulates the data fitting for four RUS peaks shown in Fig. 2. A total of 40 RUS peaks in the regime 0.70–2.20 MHz were fitted, and a r.m.s. error of 0.62% was obtained for the hexagonal fitting, indicating good agreement between the experimentally measured and calculated RUS peaks. The results of the orthorhombic fitting suggest that $c_{11} = c_{22}$, $c_{13} = c_{23}$,

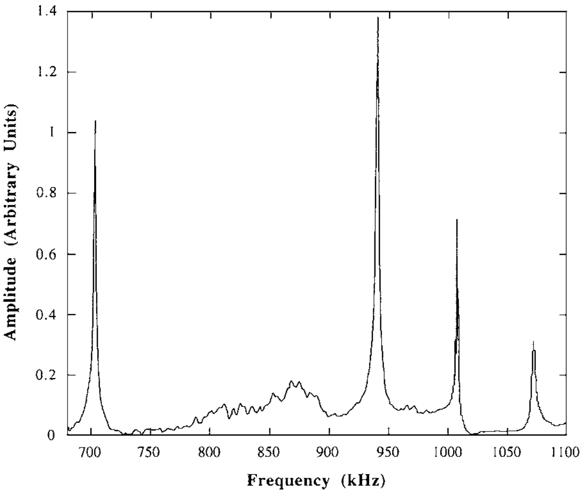

Figure 2 A portion of the room temperature RUS spectrum of single crystal $B_{5.6}C$.

TABLE I Data fitting for the RUS peaks of $B_{5.6}C$ single crystals shown in Fig. 2. $f_{exp.}$ and $f_{cal.}$ are the experimentally measured and calculated frequencies, respectively

Number	$f_{exp.}$ (MHz)	$f_{cal.}$ (MHz)	Error (%)
1	0.705355	0.704346	−0.14
2	0.941491	0.945591	0.44
3	1.008610	1.008111	−0.05
4	1.073870	1.067511	−0.59

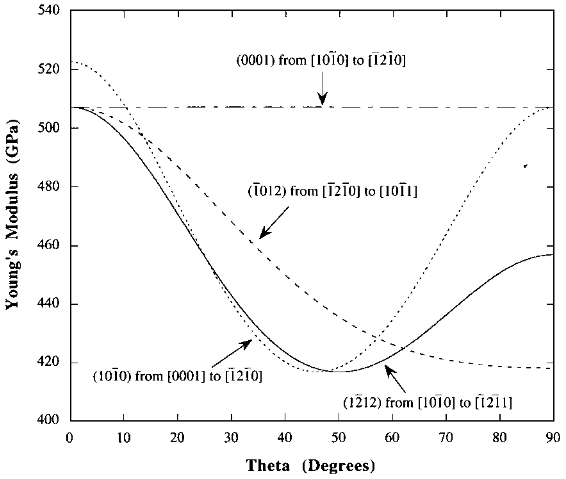

Figure 3 The orientation dependence of the Young's modulus of single crystal $B_{5.6}C$.

$c_{44} = c_{55}$ and $c_{66} = (c_{11} - c_{12})/2$, and c_{11}, c_{33}, c_{44}, c_{12}, and c_{13} are close to those obtained from the hexagonal fitting, indicating that the two results from the two different fitting schemes are consistent. The relationships, $c_{11} = c_{22}$, $c_{13} = c_{23}$, $c_{44} = c_{55}$ and $c_{66} = (c_{11} - c_{12})/2$, also are required for crystals such as boron carbide with rhombohedral structures belonging to the $\bar{3}$m laue class. It must be noted that, by approximating the rhombohedral boron carbide structure with the hexagonal lattice, c_{14} (and therefore c_{24} and c_{56}) are indeterminate. Therefore, except for c_{14}, the room temperature elastic parameters of $B_{5.6}C$ obtained from this study should be reliable.

3.1. Single crystal elastic parameters

TABLE II Room temperature elastic stiffness and compliance constants of $B_{5.6}C$ single crystals

(i,j)	11	33	13	12	44
c_{ij} (GPa)	542.8	534.5	63.5	130.6	164.8
s_{ij} (10^{-3} GPa^{-1})	1.972	1.914	−0.180	−0.453	6.068

Table II lists the room temperature single crystal elastic stiffness and compliance constants of boron carbide obtained from this study. Using these single crystal elastic parameters and formalism developed elsewhere [11, 12], the orientation dependence of the Young's modulus of $B_{5.6}C$ is plotted in Fig. 3. It can be seen from Fig. 3 that the Young's modulus is orientation-independent on the basal plane, and strongly orientation-dependent on the prismatic and the pyramidal planes. Fig. 3 also reveals that $B_{5.6}C$ is, in general, stiffer along any direction in the basal plane in response to tension or compression loading within the elastic regime. It was also found using these single crystal elastic parameters, Fig. 3, and analysis developed elsewhere [11] that: (a) the global maximum Young's modulus of $B_{5.6}C$ is along the $\mathbf{c} = [0001]$ direction, $E_{max} = E_{[0001]} = 1/s_{33} = 522.47$ GPa, (b) the global minimum Young's modulus of $B_{5.6}C$ is, $E_{min} = 64.37$ GPa, and (c) $E_{max}/E_{min} = 8.11$, indicating a significant anisotropy in elasticity. Therefore, boron carbide should be the stiffest along the $\mathbf{c} = [0001]$ direction in response to tension or compression loading within the elastic regime.

Similarly, the orientation dependence of the shear modulus of boron carbide is obtained and shown in Fig. 4. It can be seen from Fig. 4 that the shear modulus is orientation-independent and tends to be lowest on the basal plane; the shear modulus is orientation-dependent on the prismatic and pyramidal planes. It is interesting that the orientation-dependence of shear modulus on the (1 $\bar{2}$ 12) pyramidal plane is so weak that the shear modulus on this plane is approximately constant. Fig. 4

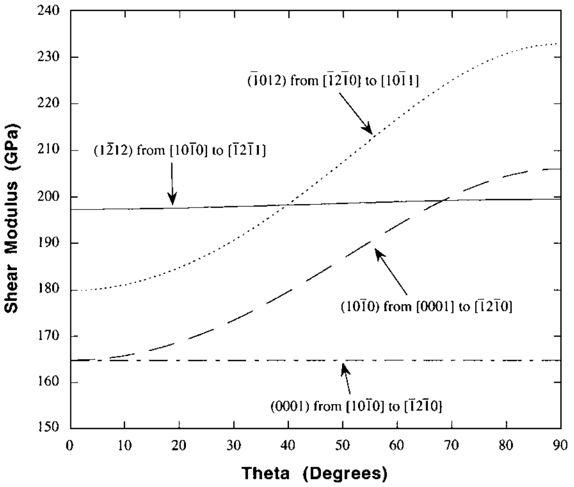

Figure 4 The orientation dependence of the shear modulus of single crystal $B_{5.6}C$.

also reveals that the shear modulus on the basal plane is, in general, lower than those on the prismatic and pyramidal planes. Therefore, it is plausible to expect the basal slip is one of the operating deformation systems of B_4C. Of course, this needs to be confirmed by a combination of mechanical testing and characterization of deformation modes of B_4C.

Single crystal elastic parameters can also provide valuable insight into the characteristics of interatomic bonding through certain criteria, e.g., Cauchy's relationships, elastic isotropic factors, Poisson's ratios, and c_{33}/c_{11} ratio. The Cauchy's relationships between the elastic stiffness constants for hexagonal solids with central forces are [12]

$$c_{13} = c_{44}, c_{11} = 3c_{12} \quad (\text{or } c_{12} = c_{66}). \tag{3}$$

The data in Table II indicate that the Cauchy's relationships do not hold true for $B_{5.6}C$ and this fact implies that the interatomic forces in boron carbide are non-central. Furthermore, Table II shows that the elastic stiffness constants can differ in $B_{5.6}C$ by more than a factor of 2 in some case (e.g., $c_{44}/c_{13} \sim 2.6$), indicating that the interatomic bonding in this system is highly directional.

The elastic anisotropy factors of $B_{5.6}C$ are tabulated in Table III. Table III suggests that most elastic anisotropy factors of boron carbide differ substantially from unity, indicating that it is significantly anisotropic in elasticity.

The Poisson's ratios of $B_{5.6}C$ are tabulated in Table IV, along with those of the typical hexagonal solids Ti and Zr. Table IV shows that ν_{31} is about the same as ν_{13} but significantly differs with ν_{12}. This can be understood through the interatomic bonding nature along $\mathbf{c} = [0001]$ and on the basal plane of boron carbide, as analyzed below. The data in Table IV clearly demonstrate that the Poisson's ratios of $B_{5.6}C$ single crystals are substantially smaller than those of common hexagonal solids ($\nu \sim 0.33$), indicating again that the interatomic bonding in boron carbide is strongly directional.

It is generally true for hexagonal systems that a quantitative comparison between c_{11} and c_{33} may provide a qualitative comparison between the bonding strength along $\mathbf{c} = [0001]$ and on the basal plane. It can be seen from Table I that c_{33} and c_{11} of $B_{5.6}C$ are close so that $c_{33}/c_{11} \sim 1$. The implication is that the atomic bonds along the $\mathbf{c} = [0001]$ direction between the nearest neighbors are about the same as those along any direction in the basal plane. Therefore, ν_{31} (the ratio of the contraction in the basal plane to the elongation along the c-direction) should be comparable to ν_{13} (the ratio of the contraction along the c-direction to the elongation along any direction in the basal plane). On the other hand, ν_{12} (the ratio of the contraction along one direction to the elongation along another perpendicular direction in the basal plane) should be different from ν_{13}.

TABLE III Elastic anisotropy factors of boron carbide

Anisotropy factors	c_{33}/c_{11}	c_{13}/c_{12}	$2c_{44}/(c_{11}-c_{12})$
$B_{5.6}C$	0.98	0.49	0.80

TABLE IV The Poisson's ratios of boron carbide and some hexagonal solids

Poisson's Ratios	$B_{5.6}C$	Ti(*)	Zr(*)
$\nu_{31} = -s_{13}/s_{33}$	0.0940	0.265	0.300
$\nu_{12} = -s_{12}/s_{11}$	0.2297	0.486	0.396
$\nu_{13} = -s_{13}/s_{11}$	0.0912	0.188	0.238

*From [15].

Finally, the single crystal elastic constants of $B_{5.6}C$ can be used to determine its sound velocities, the mean sound velocity and the elastic Debye temperature (Θ_D) using Equations (1, 2). The longitudinal velocity along the $\mathbf{c} = [0001]$ direction, $v_L = (c_{33}/\rho)^{1/2}$, is 14849 m/s and transverse velocity along this direction, $v_T = (c_{23}/\rho)^{1/2}$, is 5118 m/s. The longitudinal velocity along any direction on the basal plane, $v_L = (c_{11}/\rho)^{1/2}$, is 14964 m/s, and the transverse velocity along any direction on the basal plane, $v_T = (c_{12}/\rho)^{1/2}$, is 7339 m/s. It is expected that the longitudinal velocities along $\mathbf{c} = [0001]$ and along any directions in the basal plane are close, because of the interatomic bonding along these directions, as analyzed above, and the nature of longitudinal sound wave. The mean sound velocity in $B_{5.6}C$ is about 9787 m/s, which is much higher than the mean sound velocity in common solids. The Debye temperature of $B_{5.6}C$ is 1501 K with a Θ_D/T_m ratio of 0.55.

3.2. Isotropic elastic moduli

The isotropic elastic moduli of boron carbide can be derived by the Voigt, Reuss, or Hill approximations from its single crystal elastic parameters, which are tabulated in Table V along with some previously published experimental results for polycrystalline materials. Table V shows that the data from this study are consistent with previously published experimental results of polycrystalline boron carbides. In addition, the isotropic Young's modulus from this study is consistent with the value of 462 GPa obtained from mechanical testing on polycrystalline $B_{5.5}C$ [6]. It can be seen from Table V that the derived isotropic elastic moduli from single crystal elastic constants of $B_{5.6}C$ in this study are 2–4% smaller than those from experimental results on polycrystalline B_4C, but are in good agreement with

TABLE V The room temperature isotropic elastic moduli of boron carbide. *K* is the bulk modulus, *G* the shear modulus, *E* the Young's modulus, and ν the Poisson's ratio

Methods	*K* (GPa)	*G* (GPa)	*E* (GPa)	ν
Derived from single crystal c_{ij}	236.84	195.56	460.07	0.176
Measured from polycrystalline B_4C*	247	200	472	0.18
Measured from polycrystalline $B_{5.5}C$*	236	197	462	0.17

* From [6].

those reported for polycrystalline $B_{5.5}C$. These data in Table V show also that the Poisson's ratio of boron carbide is considerably lower than those of common solids (i.e., $\nu \sim 0.33$). Since the Poisson's ratio of a solid is generally associated with its bonding directionality and a lower Poisson's ratio means higher directional bonds in general, this again indicates that the interatomic bonding in B_4C is highly directional. The other isotropic elastic moduli in Table V are substantially higher than those of common solids, but comparable with those of the so-called "strong materials" [13], e.g., diamond, SiC, Si_3N_4, BeO, etc. This suggests that the bonding strength in boron carbide is very high.

Finally, the isotropic elastic moduli of boron carbide can be used to estimate its mechanical behavior, for example, using the Pugh criterion [14] . Based on this criterion, a solid should be relatively ductile if it has a large K/G ratio. Boron carbide has a K/G value of 1.2, which is smaller than that of Si ($K/G = 1.4$) and significantly lower than those of most solids ($K/G > 2$). Although the Pugh criterion should be applied to solids with the same crystal structure, the comparison of these ratios indicates that B_4C may not possess promising mechanical behavior at low temperatures. Of course, the true mechanical properties of B_4C are determined by its deformation modes/mechanisms.

4. Conclusion

The high temperature ceramic boron carbide has been studied by single crystal growth and elastic property measurement. Five primary conclusions have been reached:

1. Single crystals can be synthesized by the optical floating zone technique. The preferred single crystal growth direction is $\mathbf{c} = [0001]$.
2. Using the hexagonal structure, $B_{5.6}C$ has room temperature single crystal elastic constants of $c_{11} = 542.81$, $c_{33} = 534.54$, $c_{44} = 164.79$, $c_{12} = 130.59$, and $c_{13} = 63.51$ GPa. The Young's modulus is orientation-independent on the basal plane and strongly orientation-dependent on the prismatic and pyramidal planes. The shear modulus is basically orientation-independent on the basal and the $(1\bar{2}12)$ pyramidal plane and strongly orientation-dependent on the prismatic and other pyramidal planes. Analysis of the Cauchy's relationships, Poisson's ratios, and elastic anisotropy factors indicates that boron carbide is more strongly anisotropic in elasticity and interatomic bonding than most solids.
3. The elastic, interatomic bonding and sound propagation characteristics along the $\mathbf{c} = [0001]$ direction and any directions on the basal plane are similar for boron carbide, although these properties are in general highly anisotropic.
4. $B_{5.6}C$ has a mean sound velocity of 9788 m/s and a Debye temperature of 1501 K (i.e., a Θ_D/T_m ratio of 0.55).
5. Room temperature isotropic elastic moduli of single crystal $B_{5.6}C$ are $K = 236.84$ GPa, $G = 195.56$ GPa, $E = 460.07$ GPa and $\nu = 0.176$. Its K, G and E are substantially higher than those of most solids, so that boron carbide belongs to the so-called "strong solids". Its Poisson's ratio is significantly lower than that of most solids.

Acknowledgments

The authors thank Dr. Ming Lei of DRS Inc. for his technical help and useful discussion. Work at Los Alamos National Laboratory was supported by the U. S. Department of Energy and administered by the University of California.

References

1. H. BAKER, "Alloy Phase Diagrams" (ASM International, 1992).
2. H. K. CLARK and J. L. HOARD, *J. Am. Chem. Soc.* **65** (1943) 2115.
3. T. L. ASELAGE and R. G. TISSOT, *J. Amer. Ceram. Soc.* **75** (1992) 2207.
4. G. W. HOLLENBERG and G. WALTHER, *ibid.* **63** (1980) 610.
5. F. THÉVENOT, *J. Eur. Ceram. Soc.* **6** (1990) 205.
6. J. H. GIESKI, T. L. ASELAGE and D. EMIN, in Proceedings of the Boron-Rich Solids, Albuquerque, NM, 1990, edited by D. Emin, T. L. Aselage, A. C. Switendick, B. Morosin and C. L. Beckel (American Institute of Physics, 1991) p. 675.
7. T. AKASHI, K. MATUMI, T. OKADA and T. MIZUTANI, *IEEE Trans. Magn.* **5** (1969) 285.
8. A. MIGLIORI, J. L. SARRAO, W. M. VISSCHER, T. M. BELL, M. LEI, Z. FISK and R. G. LEISURE, *Physica B* **183** (1993) 1.
9. M. BLACKMAN, in "The Specific Heat of Solids" (Springer-Verlag, 1955) p. 325.
10. B. A. AULD, "Acoustic Fields and Waves in Solids" (Krieger Publishing Co., 1990).
11. Y. HE, R. B. SCHWARZ, A. MIGLIORI and S. H. WHANG, *J. Mater. Res.* **10** (1995) 1187.
12. F. CHU, M. LEI, S. A. MALOY, J. J. PETROVIC and T. E. MITCHELL, *Acta Mater.* **44** (1996) 3035.
13. A. KELLY and N. H. MACMILLAN, "Strong Solids" (Clarendon Press, 1986).
14. S. F. PUGH, *Phil. Mag.* **45** (1954) 822.
15. E. A. BRANDES and G. B. BROOK, "Smithells Metals Reference Book" (Butterworth-Heinemann, 1992).

Received 28 June 2000
and accepted 16 January 2001