JOURNAL OF MATERIALS SCIENCE **37** (2002) 2731 – 2736

Temperature and pressure dependences of the elastic properties of ceramic boron carbide (B_4C)

S. P. DODD, G. A. SAUNDERS
Department of Physics, University of Bath, Bath BA2 7AY, UK

B. JAMES
DERA, LSAB1, Chobham Lane, Chertsey, Surrey KT16 OEE, UK

Pulse-echo-overlap measurements of ultrasonic wave velocity have been used to determine the elastic stiffness moduli and related elastic properties of ceramic boron carbide (B_4C) as functions of temperature in the range 160–295 K and hydrostatic pressure up to 0.2 GPa at room temperature. B_4C is an elastically stiff but extremely light ceramic: at 295 K, the longitudinal stiffness (C_L), shear stiffness (μ), adiabatic bulk modulus (B^S), Young's modulus (E) and Poisson's ratio (σ) are 498 GPa, 193 GPa, 241 GPa, 457 GPa and 0.184, respectively. In general, the adiabatic bulk modulus B^S agrees well with both experimental and theoretical values determined previously and is approximately constant over the measured temperature range. Both E and μ increase with decreasing temperature and do not show any unusual effects. The values determined at 295 K for the hydrostatic-pressure derivatives $(\partial C_L/\partial P)_{P=0}$, $(\partial \mu/\partial P)_{P=0}$ and $(\partial B^S/\partial P)_{P=0}$ are 5.7 ± 0.3, 0.78 ± 0.4 and 4.67 ± 0.3, respectively. The hydrostatic-pressure derivative $(\partial B^S/\partial P)_{P=0}$ of the bulk modulus is found to be comparable with that estimated previously from dynamic yield strength measurements. The effects of hydrostatic pressure on the ultrasonic wave velocity have been used to determine the hydrostatic-pressure derivatives of elastic stiffnesses and the acoustic-mode Grüneisen parameters. The longitudinal (γ_L), shear (γ_S), and mean (γ^{el}) acoustic-mode Grüneisen parameters of B_4C are positive: the zone-centre acoustic phonons stiffen under pressure in the usual way. Knowledge of the elastic and nonlinear acoustic properties sheds light on the thermal properties of ceramic B_4C. Since the acoustic Debye temperature Θ_D (=1480 K) is very high, the shear modes provide a substantial contribution to the acoustic phonon population at room temperature. © *2002 Kluwer Academic Publishers*

1. Introduction

Boron carbide stands apart from many advanced ceramics although it has the usual refractory properties such as high melting point, high stability, outstanding hardness, low density and resistance to wear [1, 2], it also has a large neutron absorption cross-section [1, 3, 4] and semiconductor properties [1, 5–7]. These properties result in a range of applications from neutron control rods in fast breeder reactors [3], to light body armour [1], to sand blast nozzles [8] and could assist development of high temperature semiconductor technology [5].

The crystal structure of boron carbide is well documented [1, 8–10]; it consists of distorted $B_{11}C$ icosahedra located at the corners of a rhombohedral unit cell (point group: $R\bar{3}m$). Strong covalent bonds between icosahedra give the material its refractory properties [1]; it has been suggested that a chain of three atoms (C-B-C) links the icosahedra along the [111] direction. The carbides of boron exist as a single-phase materials over a wide range of compositions [11]. B_4C represents the carbon rich single-phase limit.

Measurements of elastic moduli as a function of temperature and pressure are important for engineering design purposes but to date only a limited number have been made on B_4C. Attention has been focused on the room temperature technological elastic moduli (Young's and shear moduli and Poisson's ratio) as a function of porosity and composition [1, 12–14]. Although high temperature data exist [4, 15], the low temperature dependences of the elastic moduli have not been reported previously. Only neutron diffraction data as a function of pressure [9] have been used to determine the bulk modulus B^S and its pressure derivative $\partial B^S/\partial P$ experimentally. The present high-pressure ultrasonic study of the elastic and non-linear acoustic properties of boron carbide has been motivated by the need for an accurate determination of longitudinal and shear ultrasonic waves propagated in B_4C, which is essential for engineering applications and investigations of dynamic response to applied pressure [9, 10, 16]. Ultrasonic wave velocities have been measured as a function of hydrostatic pressure up to 0.2 GPa at room temperature and the measurements have been extended from room temperature down to 160 K. The elastic stiffnesses of a solid determine the slopes of the acoustic-phonon dispersion curve in the long wavelength limit;

0022–2461

their hydrostatic pressure derivatives provide information on the shift of the mode energies with compression and hence are used here to determine the anharmonicity of the zone-centre acoustic phonons.

2. Experimental procedures

The B_4C ceramic used in this work was manufactured by Cercom (USA). The ceramic was essentially single phase. X-ray diffraction data indicated the presence of a very small proportion of an undetermined secondary phase and also gave no evidence of a preferred orientation. An electron microprobe analysis revealed the presence of a small proportion of impurity elements: oxygen (1.75 atom%) and aluminium (0.70 atom%). The sample density ρ ($=2514 \pm 15$ kgm^{-3}) was measured by Archimedes' method using acetone as a flotation fluid and was 99.7% of the theoretical density (2520 kgm^{-3}) of pure B_4C: the porosity was very small. A sample, which was large enough for precision measurements of ultrasonic wave velocities, was cut and polished with a pair of faces, flat to surface irregularities of about 3 μm and parallel to better than 10^{-3} rad. The sample thickness in the direction of ultrasonic wave propagation was 10.25 ± 0.009 mm.

To generate and detect ultrasonic pulses, X- or Y-cut (for longitudinal and shear waves, respectively) 10 MHz quartz transducers, operated in the 50 MHz overtone, were bonded to the specimen using Nonaq stopcock grease for low-temperature experiments. Dow resin was used as the bonding material for high-pressure experiments. Ultrasonic pulse transit times were measured using a pulse-echo-overlap system [17] capable of resolution of velocity changes to 1 part in 10^5 and particularly well suited to determination of pressure- or temperature-induced changes in ultrasound velocity. A correction was applied to the ultrasonic wave velocity for multiple reflections at the sample transducer interface [18]. The temperature dependences of ultrasound shear and longitudinal mode velocities were measured in the temperature range 160 to 295 K using a closed-cycle helium cryostat. At lower temperatures thermal expansion differences between sample, bond and transducer caused the ultrasonic signal to be lost; to overcome this a number of bonding agents were tried, but none gave satisfactory results. The dependence of ultrasonic wave velocity upon hydrostatic pressure was measured at room temperature (295 K). Hydrostatic pressure up to 0.2 GPa was applied in a piston-and-cylinder apparatus using silicone oil as the pressure-transmitting medium. Pressure was measured using a pre-calibrated manganin resistance gauge. Pressure-induced changes in the sample dimensions were accounted for by using the "natural velocity (W)" technique [19].

To further characterise the fundamental properties of this B_4C ceramic, the high temperature electrical resistivity (ρ) dependence was measured. A ceramic bar with approximate dimensions $1.5 \times 1.5 \times 15$ mm was cut from the same block as the ultrasonic sample; the density measured for this thin bar was the same as that given above. To measure the resistance of the sample, the standard 4-point probe method was used. Boron carbide is a p-type semiconductor [5]; good ohmic contacts, tested on a model Tektronix 577 curve tracer, were produced using germanium, a capping layer of titanium and then gold. The main error (about 2%) was that incurred in determining the contact separation. Errors in the resistivity calculations appearing because of contact placement and sample dimensions were tested by a Poisson equation calculation [20] but were found to be negligible. Other errors such as thermal voltages were removed by taking forward and reverse current (=1 mA) measurements. Resistance values were measured in the temperature range 300–900 K and in an atmosphere of flowing dry nitrogen.

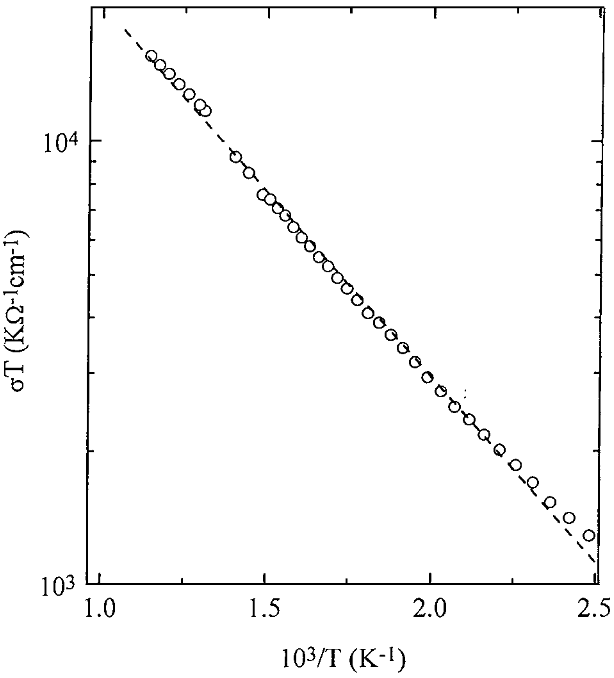


Figure 1 The temperature dependence of electrical conductivity for B_4C ceramic bar, plotted in accordance with an Arrhenius-type equation. The dashed line represents the least squares fit to the slope.

At 295 K, the electrical resistivity ρ ($=0.92 \pm 0.02$ Ωcm) for this B_4C ceramic was found to be slightly higher than previously measured values, which have a range: 0.3–0.8 [11, 21–23]. The present experimental results of conductivity (σ) as a function of temperature plotted in Fig. 1, as $\ln \sigma T$ against $1/T$ in accord with an Arrhenius-type equation ($\ln \sigma T = -E_A/k_B T$), obey a reasonably linear slope above 400 K. The activation energy (E_A) determined from the gradient is 0.17 eV, which is within the range 0.14–0.18 eV [23–25] previously measured. The temperature dependence of resistivity for B_4C was initially attributed to a small-polaron hopping mechanism (see for instance [24]); it is now, due to the lack of strong magnetic-field dependence on Seebeck coefficients and large paramagnetic susceptibility, believed to result from a small singlet bipolaron mechanism [26].

3. Temperature dependence of the elastic stiffness moduli

The velocities of longitudinal (V_L) and shear (V_S) ultrasonic waves propagated in the B_4C ceramic at 295 K are given in Table I. Shear wave velocities parallel and perpendicular to one principal axis were measured, the

TABLE I The ultrasonic wave velocities, adiabatic elastic stiffness moduli and their hydrostatic-pressure derivatives, and the acoustic-mode Grüneisen parameters of ceramic B_4C at 295 K, in comparison with data taken from literature. The sound velocities quoted in [16] were stated to have been accurate within about 2%

Description	This work	Ref. [16]	Ref. [11, 28]	Ref. [27]
Density ρ (kgm^{-3})	2514 ± 15	2500	2550	2510
Longitudinal velocity V_L (ms^{-1})	14086 ± 12	13780	14166–14205	
Shear velocity V_S (ms^{-1})	8766 ± 7	8540	8851	
Longitudinal stiffness C_L (GPa)	498 ± 4	475		
Shear stiffness μ (GPa)	193 ± 1	182	200	
Bulk modulus B^S (GPa)	240 ± 3	232	247	
Young's modulus E (GPa)	456 ± 4	434	472	461
Poisson's ratio σ	0.18 ± 0.004	0.188	0.18	0.178
Acoustic Debye temperature Θ_D (K)	1480 ± 3			
$(\partial C_L/\partial P)_{P=0}$	5.70 ± 0.3			
$(\partial \mu/\partial P)_{P=0}$	0.78 ± 0.04			
$(\partial B^S/\partial P)_{P=0}$	4.67 ± 0.3	$4.2 \pm 50\%$		
γ_L	1.21 ± 0.07			
γ_S	0.33 ± 0.02			
γ^{el}	0.62 ± 0.03			
γth	1.76			

results were identical: there is no indication of a preferred orientation. Since the ultrasonic wavelength is much larger than the average grain size, this small-grained polycrystalline ceramic can be treated as an isotropic material, which has two independent elastic stiffness moduli C_L $(=\rho V_L^2)$ and μ $(=\rho V_S^2)$. These elastic stiffness moduli, the adiabatic bulk modulus B^S, Young's modulus E, Poisson's ratio σ, and the acoustic Debye temperature Θ_D have been determined from the ultrasonic velocity data and sample density, using the standard relationships for an isotropic material. The results obtained at room temperature are compared where possible in Table I with those determined previously [11, 16, 27, 28] by ultrasonic velocity measurements made on hot-pressed B_4C ceramic samples of similar density. There is reasonable agreement between the present and previous data where it exists; the small discrepancies may be a result of differences in microstructure and purity of the samples used in each work.

The value determined for Young's modulus (Table I) lies within the range (432–480 GPa) of those found previously [3, 8, 12, 29–31]; techniques used by other researchers were strain gauge [13], resonance frequency technique [14], composite piezo-electric oscillator method [15] and the sonic method [32]. The spread in results are related to material properties, such as composition, purity and porosity. The corrections to Young's modulus for porosity [1, 13, 14] used a variety of methods, adding to inconsistencies between published values.

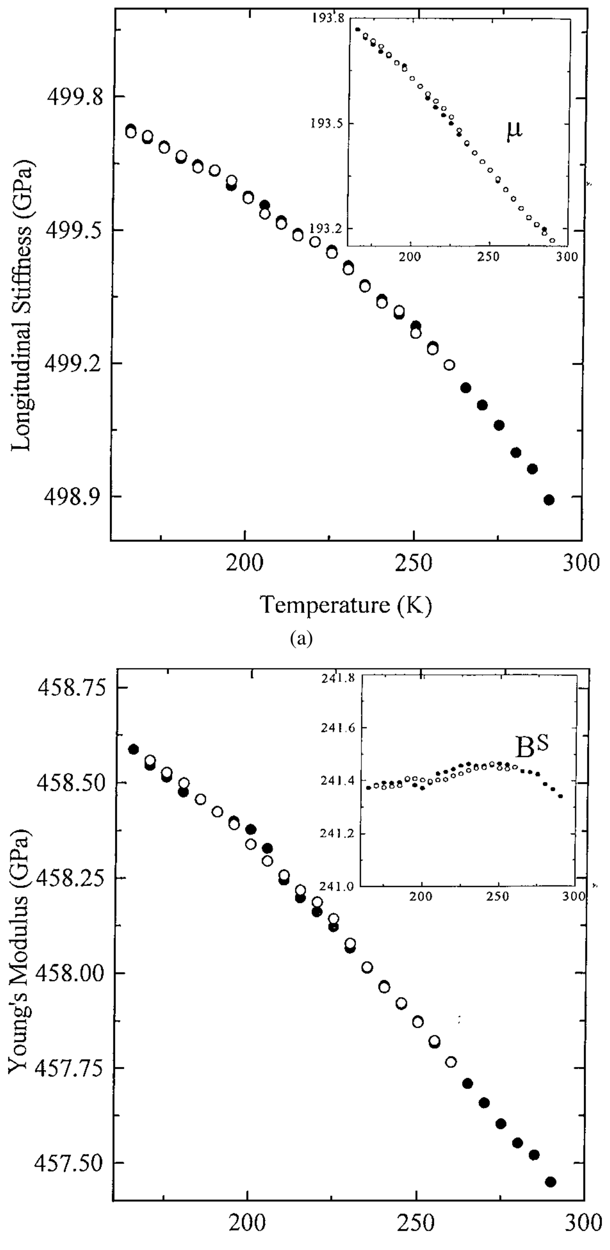
In general the bulk modulus is widely used as a parameter to examine interatomic binding forces in solids. The value for B^S measured here is in reasonable agreement with that measured experimentally by other workers seen Table I, Murthy [15] obtained 258 GPa. Theoretical calculations give a rather wider spread: a first-principle orthogonalised linear combination of atomic orbitals method gave 273 GPa [33] and a density-functional perturbation theory gave 240 GPa [10]. A calculation of the single crystal elastic constants, except C_{44}, for B_4C [34] using stress-strain relations under uniaxial loads has also been made and B computed using,

$$B = \frac{(C_{11} + C_{12})C_{33} - 2C_{13}^2}{C_{11} + C_{12} + 2C_{33} - 4C_{13}}. \tag{2}$$

Again the calculated value of 234 GPa is comparable with the experimental values including that of this study.

The large value of the shear modulus of the B_4C ceramic (Table I) is comparable with the data given in the literature [3, 8, 15, 32]. Liebling [14] measured μ (=205 GPa) and corrected for porosity yielding a larger value than obtained by other workers. The large value measured here for the shear modulus confirms that the ceramic does have large resistance to shear stress. The ultrasonic determinations of Poisson's ratio (Table I) all give values of 0.18, and other workers values cover a range for σ (0.14–0.21) [3, 8, 14]. Aselage *et al.* [11] calculated Poisson's ratio as a function of composition; at the low end of the carbon composition range the Poisson's ratio increased to 0.22, which may suggest that the elastic stiffnesses are influenced by non-central forces at the carbon rich limit [35]. The acoustic Debye temperature is very high (Table I), consistent it with the low specific density and strong bonding in the material.

The temperature dependences of the adiabatic longitudinal and shear elastic stiffnesses, bulk and Young's moduli of B_4C ceramic at atmospheric pressure are shown in Fig. 2. They were obtained from the sample density ($=2514 \pm 15$ kgm^{-3}) and the measured velocities of 50 MHz ultrasonic waves propagated in the sample as it was cycled between room temperature and the lowest temperature of measurements. Corrections on elastic moduli for sample length and density changes are expected to be negligible due to the small thermal expansion values [1, 36, 37]. C_L, E and μ increase with decreasing temperature and do not show any unusual effects. There was no measurable thermal hysteresis in the ultrasonic wave velocities and no irreversible effects. The bulk modulus is approximately constant



(a)

(b)

Figure 2 Temperature dependences of the elastic moduli of B_4C ceramic: (a) longitudinal stiffness with the inset showing shear stiffness μ and (b) Young's modulus with the inset showing bulk modulus B^S. The filled circles correspond to measurements made with decreasing temperature and the open circles to data obtained as the temperature was increased.

over the temperature range seen Fig. 1b. The acoustic Debye temperature increases smoothly with decreasing temperature in accord with stiffening of both the longitudinal and shear wave velocities. Poisson's ratio increases very slightly and approximately linearly with increasing temperature. The results obtained for the temperature dependences of Young's and shear modulus are in line with and complement those reported previously [4, 15].

4. Hydrostatic-pressure dependences of ultrasonic wave velocity and elastic stiffness moduli

The effects of hydrostatic pressure on the ultrasonic wave velocity in B_4C ceramic are shown in Fig. 3. The data for the pressure dependence of the velocities of both longitudinal and shear ultrasonic waves are reproducible under pressure cycling and show no measurable hysteresis effects; the scatter in the data is negligible. This observation indicates that the ceramic does not alter in morphology under pressure cycling up to 0.2 GPa and that there is no relaxation of any residual stress. The velocities of both longitudinal and shear ultrasonic waves increase approximately linearly with pressure. This is a normal behaviour: both the long-wavelength longitudinal and shear acoustic-modes stiffen under pressure, the effect on the former being much the larger.

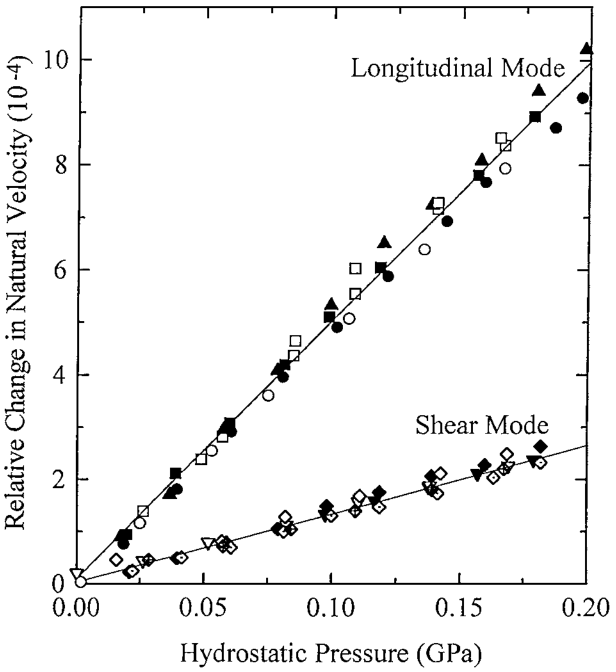


Figure 3 Hydrostatic-pressure dependence of the relative change in natural velocity of longitudinal and shear waves for B_4C ceramic measured at room temperature. The filled symbols correspond to measurements made with increasing pressure and the open symbols to data as the pressure was decreased (different symbols refer to different experimental runs). The straight lines are the least-squares fits to experimental data.

The hydrostatic-pressure derivative $(\partial M/\partial P)_{P=0}$ of each elastic stiffness M have been obtained from the ultrasonic velocity measurements under pressure by using [38]

$$\left(\frac{\partial M}{\partial P}\right)_{P=0} = (M)_{P=0}\left[\frac{2(\partial f/\partial P)}{f} + \frac{1}{3B^T}\right]_{P=0} \tag{3}$$

where B^T is the isothermal bulk modulus, f is the pulse-echo-overlap frequency at atmospheric pressure and $\partial f/\partial P$ is its pressure derivative. The adiabatic bulk modulus B^S has been used rather than isothermal B^T throughout the calculations, a procedure, which introduces only a negligible error. The hydrostatic-pressure derivatives $(\partial C_L/\partial P)_{P=0}$, $(\partial \mu/\partial P)_{P=0}$ and $(\partial B^S/\partial P)_{P=0}$ determined for the B_4C ceramic have positive values (Table I) *typical of a normal solid material.* Both the longitudinal and shear elastic stiffnesses and thus the slopes of the corresponding acoustic-mode dispersion curves, at the long-wavelength limit, increase with pressure in the normal way. The value determined for the hydrostatic-pressure derivative $(\partial B^S/\partial P)_{P=0}$ of adiabatic bulk modulus of hot-pressed B_4C ceramic is larger than but comparable with that estimated from shock wave measurements [16] and included in Table I. The hydrostatic pressure derivative of bulk modulus was not directly measured: a fit of neutron diffraction versus pressure data to the Murnaghan equation of state produced the low value of 1 ± 2 [9]. A first principle calculation [10] generated a theoretical value for $(\partial B^S/\partial P)_{P=0}$ of 3.5, which is in better accord with the present value.

Measurements of the elastic moduli B^S of B_4C have been used to test the proposal that the icosahedra themselves could be more compressible than the structure between them; changes observed in the elastic stiffness of boron carbides as a function of carbon concentration were found to be in accord with this suggestion [11]. The same conclusion was reached from a consideration of the results obtained from neutron diffraction experiments, which gave a value of 169 GPa for the icosahedra while that for the total components of the unit cell was 220 GPa [9]. However a first principles calculation based on density-functional perturbation theory has suggested a contrary result, namely that the high bulk modulus of B_4C (and α-rhombohedral boron B_{12}) are mainly determined by stiff intramolecular bonding within the icosahedra [10]. The finding that the ultrasonic measurements give values for the bulk modulus and its pressure derivative that are close to those obtained from this theoretical calculation gives some experimental support to the model used in the theory.

Although the shock wave technique provides bulk modulus data at extreme pressures, it is not always reliable. In general pulse echo ultrasonic experiments are a more accurate way of obtaining elastic and non-linear acoustic properties, howbeit at much lower pressures. The bulk modulus and its hydrostatic-pressure derivative obtained here confirm the shock wave data [16] (see Table I). Both sets of values have been used to calculate the volume compression $V(P)/V_0$ of B_4C ceramic up to 12 GPa at room temperature, using an extrapolation method based on the Murnaghan's equation of state [39] in the logarithmic form. Results of the calculations are compared with those obtained by the diamond anvil technique [9] including that for the icosahedra in Fig. 4. The calculated volume compressions obtained using the data for the bulk modulus and its hydrostatic-pressure derivative (Table I) from the shock wave and ultrasonic experiments are nearly identical, as would be expected from the agreement found between the results of these techniques.

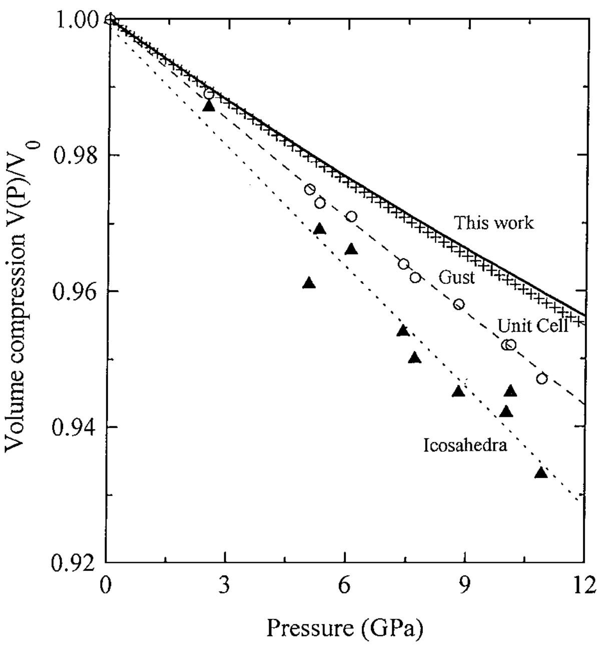


Figure 4 Volume compression of B_4C ceramic at room temperature (thick line), extrapolated to very high pressures using Murnaghan's equation of state. Comparison is made with data from [16] (crosses) and data extracted from [9]: dashed line is the equation of state fit to unit cell data (circles) and dotted line is a least squares fit to the icosahedra data (triangles).

5. Grüneisen parameters and acoustic-mode vibrational anharmonicity

Properties of a solid that depend upon thermal motion of the atoms are much influenced by vibrational anharmonicity. The hydrostatic-pressure dependences of ultrasonic wave velocities *quantify to* first order the anharmonicity of long-wavelength acoustic modes. Common practice is to describe the anharmonic properties in terms of Grüneisen parameters, which quantify the volume or strain dependence of the lattice vibrational frequencies. The dependence of the acoustic-mode frequency ω_p in a phonon branch p on volume V can be expressed as a mode Grüneisen parameter

$$\gamma_p = -\left[\frac{\partial(\ln\omega_p)}{\partial(\ln V)}\right]_T, \tag{4}$$

which can be obtained from the measurements of the elastic stiffnesses and their pressure derivatives. The longitudinal (γ_L) and shear (γ_S) acoustic-mode Grüneisen parameters have been determined using

$$\gamma_L = -\frac{1}{6C_L}\left[C_L - 3B^T\left(\frac{\partial C_L}{\partial P}\right)_{P=0}\right] \tag{5}$$

and

$$\gamma_S = -\frac{1}{6\mu}\left[\mu - 3B^T\left(\frac{\partial \mu}{\partial P}\right)_{P=0}\right], \tag{6}$$

respectively. The mean acoustic-mode Grüneisen parameter (γ^{el}), which is a measure of the overall contribution of zone-centre acoustic modes to the lattice vibrational anharmonicity, has been obtained using

$$\gamma^{el} = \frac{1}{3}(\gamma_L + 2\gamma_S), \tag{7}$$

which is strictly valid only at temperatures comparable with the acoustic Debye temperature. The results obtained at room temperature for γ_L, γ_S and γ^{el} of B_4C are included in Table I. The shear acoustic-mode Grüneisen parameter γ_S is smaller than the longitudinal acoustic-mode Grüneisen parameter γ_L, which is usual. All acoustic-mode Grüneisen parameters have normal values. A value for the thermal Grüneisen parameter γth (=$3\alpha VB^{S}/C_{P}$) has been estimated (Table I), using thermal expansion α [37] and specific heat C_{P} [1] data from the literature. The larger value obtained for γth implies that the optic phonons, which contribute to this parameter in addition to the acoustic modes, have the larger Grüneisen parameters. Since B_4C has such a high acoustic Debye temperature (=1480 K), the long-wavelength acoustic phonons can be expected to dominate properties determined by vibrational anharmonicity at room temperature. (Table I). The shear modes, which have the lower energy, should play a more important role than longitudinal modes in the acoustic phonon population at room temperature; this enhances their contribution to thermal expansion and specific heat.

6. Conclusions

The velocities of longitudinal and shear 50 MHz ultrasonic waves propagated in hot-pressed B_4C ceramic have been measured as functions of temperature and hydrostatic pressure. The ceramic is a stiff material elastically: its elastic stiffness moduli and acoustic Debye temperature are large. The elastic stiffness moduli increase with decreasing temperature due to the usual vibrational anharmonicity of acoustic modes and show no unusual effects. The hydrostatic-pressure derivatives of the longitudinal and shear elastic stiffnesses and bulk modulus have positive values; hence, the long-wavelength longitudinal, shear and mean acoustic-mode Grüneisen parameters are positive.

Acknowledgements

B.J. is grateful to MOD for Corporate Research Programme funding. We would also like to thank J. Brace and E. Sherwood for assistance with measurement of electrical resistance.

References

1. F. THÉVENOT, *J. Eur. Ceram. Soc.* **6** (1990) 205.
2. R. THOMPSON, "The Physics and Chemistry of Carbides; Nitrides and Borides," edited by R. Freer (Kluwer Academic Publishers, Netherlands, 1990) p. 113.
3. R. A. MURGATROYD and B. T. KELLY, *Atomic Energy Review* **15** (1977) 1.
4. G. W. HOLLENBERG, *Am. Ceram. Soc. Bull.* **59** (1980) 538, 548.
5. D. EMIN, *Physics Today* **40** (1987) 55.
6. H. WERHEIT, "The Physics and Chemistry of Carbides; Nitrides and Borides," edited by R. Freer (Kluwer Academic Publishers, Netherlands, 1990) p. 677.
7. D. EMIN, "The Physics and Chemistry of Carbides; Nitrides and Borides," edited by R. Freer (Kluwer Academic Publishers, Netherlands, 1990) p. 691.
8. K. A. SCHWETZ and W. GRELLNER, *J. Less-Common Metals* **82** (1981) 37.
9. R. J. NELMES, J. S. LOVEDAY, R. M. WILSON, W. G. MARSHALL, J. M. BESSON, S. KLOTZ, G. HAMEL, T. L. ASELAGE and S. HULL, *Phys. Rev. Lett.* **74** (1995) 2268.
10. N. VAST, J. M. BESSON, S. BARONI and A. DAL CORSO, *Comp. Mat. Sci.* **17** (2000) 127.
11. T. L. ASELAGE, D. R. TALLANT, J. H. GIESKE, S. B. VAN DEUSEN and R. G. TISSOT, "The Physics and Chemistry of Carbides; Nitrides and Borides," edited by R. Freer (Kluwer Academic Publishers, Netherlands, 1990) p. 97.
12. G. W. HOLLENBERG and G. WALTHER, *J. Amer. Ceram. Soc.* **63** (1980) 610.
13. B. CHAMPAGNE and R. ANGERS, *ibid.* **62** (1979) 149.
14. R. S. LIEBLING, *Mat. Res. Bull.* **2** (1967) 1035.
15. S. R. MURTHY, *J. Mater. Sci. Lett.* **4** (1985) 603.
16. W. H. GUST and E. B. ROYCE, *J. Appl. Phys.* **42** (1971) 276.
17. E. P. PAPADAKIS, *J. Acoust. Soc. Am.* **42** (1967) 1045.
18. E. KITTINGER, *Ultrasonics* **15** (1977) 30.
19. R. N. THURSTON and K. BRUGGER, *Phys. Rev.* **133** (1964) A1604.
20. M. YAMASHITA, *J. Phys. E: Sci. Instrum.* **20** (1987) 1457.
21. P. T. B. SHAFFER, "High Temperature Materials" (Plenum Press, 1964).
22. T. L. ASELAGE, D. EMIN, G. A. SAMARA, D. R. TALLANT, S. B. VAN DEUSEN, M. O. EATOUGH, H. L. TARDY, E. L. VENTURINI and S. M. JOHNSON, *Phys. Rev.* B **48** (1993) 11759.
23. M. BOUCHACOURT and F. THEVENOT, *J. Mats. Sci.* **20** (1985) 1237.
24. C. WOOD and D. EMIN, *Phys. Rev.* B **29** (1984) 4582.
25. G. A. SAMARA, D. EMIN and C. WOOD, *ibid.* **32** (1985) 2315.
26. T. L. ASELAGE, D. EMIN and S. S. McCREADY, *Phys. Stat. Sol.* B **218** (2000) 255.
27. G. DE WITH, *J. Mater. Sci.* **19** (1984) 457.
28. J. H. GIESKE, T. L. ASELAGE and D. EMIN, "Boron Rich Solids," edited by D. Emin, T. Aselage, C. L. Beckel, A. C. Switendick and B. Morosin, AIP Conf. Proc. No. 231 (American Institute of Physics, New York, 1991) p. 377.
29. D. L. ARENBERG, Final report Contract NONR 734 (00) (1955), tabulated in "Solid State Physics," Vol. 7, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1958) p. 316.
30. I. A. BAIRAMASHVILI, G. I. KALANDADZE, A. M. ERISTAVI, J. SH. JOBAVA, V. V. CHOTULIDI and YU. I. SALOEV, *J. Less-Common Metals* **67** (1979) 455.
31. R. N. KATZ and W. A. BRANTLEY, *Mat. Sci. Res.* **5** (1971) 271.
32. S. M. LANG, National Bureau of Standards Monograph, Vol. 6 (1960).
33. D. LI. and W. Y. CHING, *Phys. Rev.* B **52** (1995) 17073.
34. S. LEE, D. M. BYLANDER and L. KLEINMAN, *ibid.* **45** (1992) 3245.
35. K. SHIRAI, *J. Solid State Chem.* **133** (1997) 215.
36. J. J. GANGLER, *J. Amer. Ceram. Soc.* **33** (1950) 367.
37. G. V. TSAGAREISHVILI, T. G. NAKASHIDZE, J. SH. JOBAVA, G. P. LOMIDZE, D. E. KHULELIDZE, D. SH. TSAGAREISHVILI and O. A. TSAGAREISHVILI, *J. Less-Common Metals* **117** (1986) 159.
38. R. N. THURSTON, *Proc. IEEE* **53** (1965) 1320.
39. O. L. ANDERSON, *J. Phys. Chem. Solids* **24** (1963) 909.

Received 1 June 2001
and accepted 7 February 2002