JOURNAL OF MATERIALS SCIENCE **36** (2001) 2557–2563

Ultrasonic study of the temperature and pressure dependences of the elastic properties of β-silicon nitride ceramic

S. P. DODD
Department of Physics, University of Bath, Bath BA2 7AY, UK
M. CANKURTARAN
Hacettepe University, Department of Physics, Beytepe, 06532 Ankara, Turkey
G.A. SAUNDERS
Department of Physics, University of Bath, Bath BA2 7AY, UK
B. JAMES
DERA, LSAB1, Chobham Lane, Chertsey, Surrey KT16 OEE, UK

Ultrasonic wave velocity measurements have been used to determine the elastic stiffness moduli and related elastic properties of high-purity, dense β-Si_3N_4 ceramic samples as functions of temperature in the range 150–295 K and hydrostatic pressure up to 0.2 GPa at room temperature. Due to its covalently bonded, rigid structural framework β-Si_3N_4 is an elastically stiff material; the elastic stiffness moduli of the ceramic at 295 K are: $C_L = 396$ GPa, $\mu = 119$ GPa, $B^S = 238$ GPa, $E = 306$ GPa, Poisson's ratio $\sigma = 0.285$. The longitudinal elastic stiffness C_L increases with decreasing temperature and shows a knee at about 235 K; the decrease in slope below the knee indicates mode softening. The shear elastic stiffness μ shows mode softening which results in a plateau centred at about 235 K and an anomalous decrease with further reduction in temperature. The hydrostatic-pressure derivatives of elastic stiffnesses at 295 K are $(\partial C_L/\partial P)_{P=0} = 4.5 \pm 0.1$, $(\partial B^S/\partial P)_{P=0} = 4.3 \pm 0.1$ and $(\partial \mu/\partial P)_{P=0} = 0.17 \pm 0.02$ (pressure < 0.12 GPa). An interesting feature of the nonlinear acoustic behaviour of this ceramic is that, in the pressure range above 0.12 GPa, the values obtained for $(\partial \mu/\partial P)_{P=0}$ and the shear mode Grüneisen parameter (γ_S) are small and negative, indicating acoustic-mode softening under these higher pressures. Both the anomalous temperature and pressure dependences of the shear elastic stiffness indicate incipient lattice shear instability. The shear $\gamma_S (=0.005)$ is much smaller than the longitudinal $\gamma_L (=1.18)$ accounting for the thermal Grüneisen parameter $\gamma^{th} (=1.09)$: since the acoustic Debye temperature $\Theta_D (=923 \pm 5$ K) is so high, the shear modes play an important role in acoustic phonon population at room temperature. Hence knowledge of the elastic and nonlinear acoustic properties sheds light on the thermal properties of ceramic β-Si_3N_4.

1. Introduction

Silicon nitride (Si_3N_4) is an important structural ceramic due to its high thermal resistance, strength and chemical stability, and a relatively low density. These properties have led to a variety of technological applications, especially in high-temperature and corrosive environments, as well as considerable scientific interest [1, 2]. There are two stable polymorphs of Si_3N_4 with trigonal (α phase) and hexagonal (β phase) lattice structures. The α-Si_3N_4 phase has a space group $P3_1c$ with two formula units in the unit cell, whereas the β-Si_3N_4 phase has a space group $P6_3/m$ with one formula unit in the unit cell [3]. Differing ceramic processing techniques result in varying proportions of the α and β phases typically being synthesised together and it can be difficult to determine the properties of either phase. Previously the elastic stiffness moduli of Si_3N_4 ceramics have been measured at room temperature by ultrasonic techniques [4–8] and in a temperature range from room temperature to about 1270 K at atmospheric pressure [9]. However, the effects of pressure on the elastic behaviour of Si_3N_4 are unknown. In the present work we investigate the elastic and nonlinear acoustic properties of ceramic β-Si_3N_4 prepared by hot pressing. The ultrasonic wave velocity measurements have been extended down to 150 K. To establish the nonlinear acoustic properties of β-Si_3N_4, ultrasonic wave velocities have been measured as a function of hydrostatic pressure up to 0.2 GPa at room temperature. The outcome of this experimental work has been the determination of second-order elastic stiffness moduli and related elastic properties and how they vary with temperature and hydrostatic pressure. The elastic stiffnesses of a material determine the slopes of the acoustic-phonon dispersion curves in long-wavelength limit; their hydrostatic-pressure dependences provide information on the shift of the mode energies with compression. The present results provide intriguing physical insight into the elastic and nonlinear acoustic properties of β-Si_3N_4 ceramic.

2. Experimental procedures

The β-Si_3N_4 ceramic was manufactured by Cercom (USA) using proprietary hot pressing technique. The material was formed from silicon followed by a conversion of the silicon to silicon nitride and then hot pressed. A number of techniques were used to characterise the material. First scanning electron microscope images of the grain structure were taken on suitably polished and thermally etched samples (Fig. 1). The grains are randomly oriented and have a range of sizes. To obtain a measure of average grain size, a lineal intercept analysis was performed: the intercept length for 1000 grains was measured. Actual grain sizes (d) were calculated using the expression:

$$d = 1.56L/m_{\mathrm{f}} \tag{1}$$

where L is the measured lineal intercept length and m_{f} is the magnification factor used in the scanning electron microscope. The factor 1.56 is an effective correction factor derived by Mendelson [10] for random slices through a model system consisting of space filling tetrakaidecahedrally shaped grains (truncated octahedrons) with a log-normal size distribution. All samples were considered to be single phase materials. This assumption is valid considering the very low secondary phase content and low porosity. The grain size distribution is shown in Fig. 2. Average grain size for this Si_3N_4 ceramic was calculated to be 0.98 ± 0.71 μm (median = 0.77 microns).

An X-ray diffraction study (Fig. 3) of the ceramic showed no α-phase lines; the material is β-phase except for a binding agent. Most of the unlabelled X-ray lines correspond to an impurity phase [11]. The X-ray diffraction data taken from three perpendicular faces of the sample indicated a slight preferred orientation. The sample density (3290 ± 10 kg m^{-3}) was measured by Archimedes' method using distilled water as a flotation fluid. A sample in the shape of a parallelepiped, 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 7.942 ± 0.002 mm.

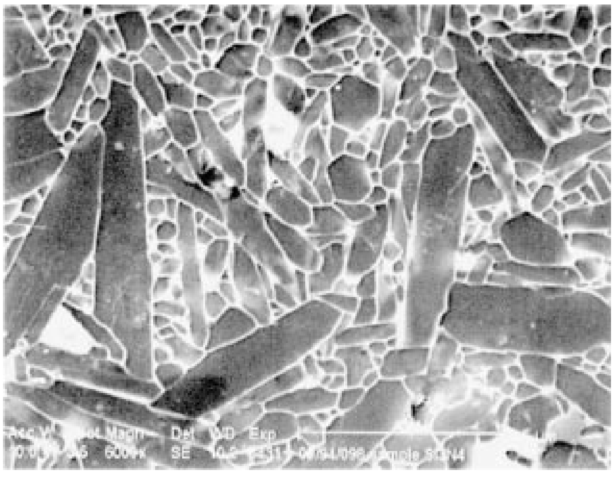

Figure 1 Scanning electron micrograph of β-Si_3N_4 ceramic.

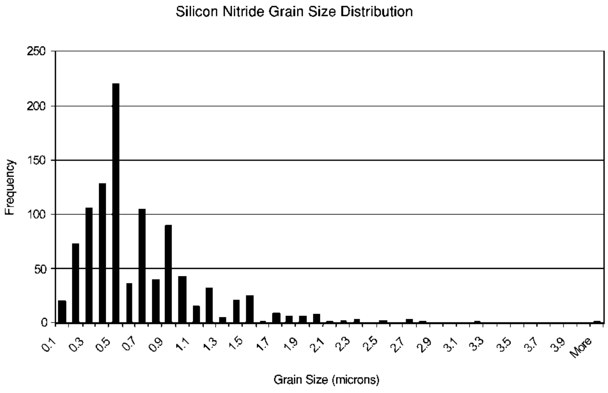

Figure 2 Grain size distribution of β-Si_3N_4 ceramic.

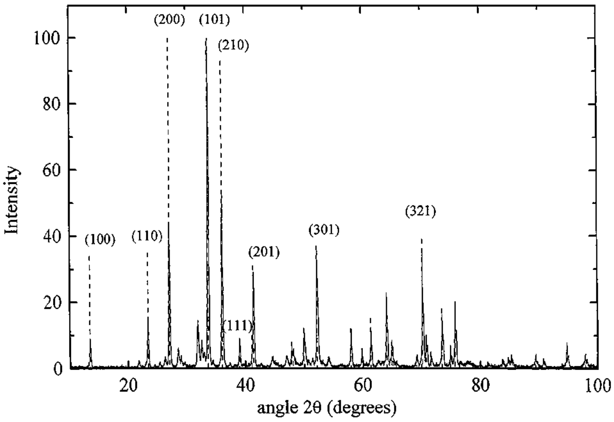

Figure 3 X-ray diffraction patterns of the β-Si_3N_4 ceramic. The β-phase lines are indicated by dashed lines; only lower index lines are labelled. Most of the other lines correspond to $Y_{20}N_4Si_{12}O_{48}$ formed during the hot pressing process of manufacture [11].

To generate and detect ultrasonic pulses, X- or Y-cut (for longitudinal and shear waves, respectively) 10-MHz quartz transducers were bonded to the specimen using Nonaq stopcock grease for low-temperature experiments. Dow resin was used as bonding material for high-pressure experiments. Ultrasonic pulse transit times were measured using a pulse-echo-overlap system [12], 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 velocity. To eliminate the error due to the finite time that it takes for the pulse to travel through the transducer and bonding material into the sample, the ultrasonic pulse transit time was corrected for transducer effects [13]. The temperature dependence of ultrasound velocity was measured between 150 and 295 K using a closed-cycle cryostat. At temperatures lower than about 140 K thermal expansion differences between sample, bond and transducer caused the ultrasonic signal to be lost. A number of bonding agents were tried, but none gave satisfactory results below this temperature. 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 [14].

3. Temperature dependence of the elastic stiffness moduli

The velocities of longitudinal (V_L) and shear (V_S) ultrasonic waves propagated in the β-Si_3N_4 ceramic at 295 K are given in Table I. 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 $\mu(=\rho V_S^2)$, because the ultrasonic wavelength is about two orders of magnitude larger than the average grain size. The elastic anisotropy was checked by measuring both longitudinal and shear wave velocities in the sample at room temperature for different directions of wave propagation: the sample was found to be elastically isotropic. The longitudinal C_L and shear μ elastic stiffness moduli, adiabatic bulk modulus B^S, Young's modulus E, Poisson's ratio σ, and acoustic Debye temperature Θ_D, determined at room temperature and atmospheric pressure, from the ultrasonic velocity data and sample density, are compared, where possible, in Table I with those determined by other workers using ultrasonic techniques. Most of the data compiled in Table I are those measured for high-purity, dense β-Si_3N_4 produced by hot pressing. There is a general agreement between the present and previous data where it exists.

The bulk modulus of Si_3N_4 has been the subject of several experimental and theoretical investigations. An extrapolation of ultrasonic velocity measurements on Si_3N_4 with varying amounts of porosity and α/β ratios, gave a bulk modulus of 234 ± 5 GPa for fully dense, pure β-Si_3N_4 [5]; the present results (Table I) are in good agreement with this value. A high-pressure neutron diffraction study up to 3 GPa of the compression of β-Si_3N_4 yielded a bulk modulus of 256 GPa [3]. X-ray diffraction measurements [15] on β-Si_3N_4 under pressure up to 34 GPa at room temperature gave the values 273 ± 14 GPa and 266 ± 1 GPa for the bulk modulus by fitting the data to the Birch-Murnaghan equation of state and a "universal" equation of state, respectively. A value of 216 GPa has been estimated in the present work for the bulk modulus using the single-crystal elastic constants derived [16] from Young's modulus measurements of β-Si_3N_4 whisker-like grains by nano-indentation technique. Considerable effort has been devoted to determination of the bulk modulus of β-Si_3N_4 from model calculations (for a recent overview see Ref. [17]). For the sake of comparison, theoretical studies include: calculations using the orthogonalized linear combination of atomic orbitals (OLCAO) predicted 282 GPa for the bulk modulus [18], a method based on Hartree-Fock theory [19] led to a value of 264 GPa, a phenomenological model [20] based on short-range pair potentials estimated a bulk modulus of 258 GPa, neutron diffraction and inelastic scattering measurements combined with molecular-dynamics calculations gave a bulk modulus of 270 GPa [21], *ab-initio* total energy calculations gave 270 GPa [17]; Cohen's relationship [22] for bulk modulus as a function of nearest-neighbour separation yielded 270 GPa. These results obtained for the bulk modulus of β-Si_3N_4 are comparable to (at most 18% larger than) that found in the present ultrasonic study (Table I), and support the proposition [3] that a high value of the bulk modulus of silicon nitride is mainly due to its rigid framework structure.

The Young's modulus of Si_3N_4 has also been investigated extensively using various experimental methods including ultrasonic velocity measurements [4–9, 23, 24], a strain gauge technique [25, 26], vibration

TABLE I The ultrasonic wave velocities, adiabatic elastic-stiffness moduli and their hydrostatic-pressure derivatives, and the acoustic-mode Grüneisen parameters of ceramic β-Si_3N_4 at 295 K, in comparison with data taken from literature. The values quoted in brackets for $(\partial\mu/\partial P)_{P=0}$ and γ_S refer to the high-pressure region above 0.12 GPa

Description	Present work	Ref. [9]	Ref. [5]	Ref. [7]	Ref. [8]
Density ρ (kgm^{-3})	3290 ± 10	3180	Fully dense	3154	99% dense
Longitudinal wave velocity V_L (ms^{-1})	10971 ± 10				
Shear wave velocity V_S (ms^{-1})	6009 ± 10				
Longitudinal modulus C_L (GPa)	396 ± 2	330		383.6	
Shear modulus μ (GPa)	119 ± 1	118	122 ± 1	126.1	128
Bulk modulus B^s (GPa)	238 ± 2		234 ± 5	215.4	
Young's modulus E (GPa)	306 ± 3	290	312 ± 1	316.5	324
Poisson's ratio σ	0.285 ± 0.002	0.220	0.280	0.255	0.269
Acoustic Debye temperature Θ_D (K)	923 ± 5				
$(\partial C_L/\partial P)_{P=0}$	4.5 ± 0.1				
$(\partial\mu/\partial P)_{P=0}$	0.17 ± 0.02 (−0.08 ± 0.05)				
$(\partial B^S/\partial P)_{P=0}$	4.3 ± 0.1				
γ_L	1.18 ± 0.02				
γ_S	0.005 ± 0.006 (−0.25 ± 0.05)				
γ^{el}	0.40 ± 0.03				

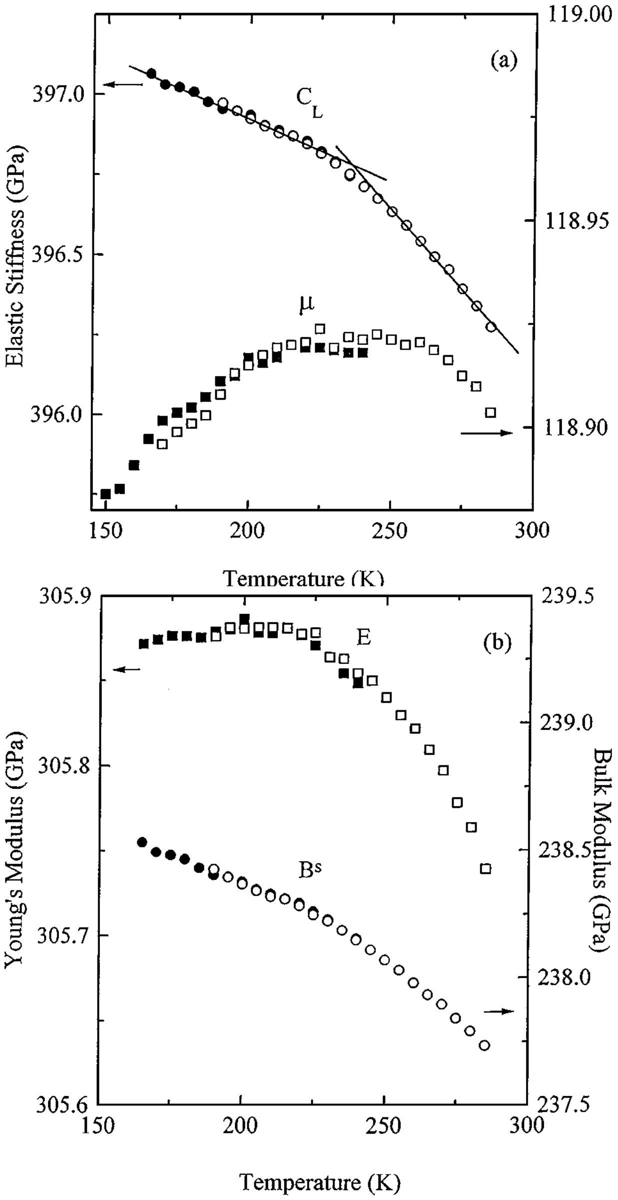

Figure 4 Temperature dependences of the elastic moduli of β-Si_3N_4 ceramic (a) C_L and μ, and (b) B^S and E. The filled symbols correspond to measurements made with decreasing temperature and the open symbols to data as the temperature was increased. The gradients $(\partial C_L/\partial T)_{P=0}$ (in units of GPa K^{-1}) of the temperature dependence of C_L are -0.0099 ± 0.0002 and -0.0038 ± 0.0001 above and below the knee at 235 K, respectively.

resonance methods [27–29], nano-indentation [16] and depth sensing indentation [30] techniques. The polycrystalline Young's moduli typically fall in the range 300–330 GPa, with the exact value depending on porosity, intergranular phase content, texture, and the relative amounts of α and β phases present in the specimen. Only a small anisotropy in Young's modulus has been observed in hot-pressed β-Si_3N_4 ceramic samples (see for instance Refs. [23, 24]). Nevertheless, Hay *et al.* [16] found a significant anisotropy in Young's modulus of whisker-like grains of β-Si_3N_4.

The temperature dependences of the longitudinal C_L and shear μ elastic stiffnesses, bulk modulus B^S and Young's modulus E are shown in Fig. 4. They were obtained from the sample density and the velocities of 30 MHz ultrasonic waves propagated in β-Si_3N_4 ceramic sample as it was cooled from 295 K down to about 150 K. Corrections on elastic moduli for sample length and density changes are expected to be negligible due to a small coefficient of thermal expansion [31, 32] and have not been made. When the sample was cycled between room temperature and 150 K, there was no thermal hysteresis in the ultrasonic wave velocities and no irreversible effects. The longitudinal elastic stiffness (Fig. 4a) increases with decreasing temperature and shows the unusual feature of a change in slope at about 235 K where there is a knee. There is a softening below the knee. The longitudinal modulus does not obey the conventional model [33] for vibrational anharmonicity.

The shear elastic stiffness μ shows even more unusual behaviour with temperature (Fig. 4a). It starts to increase as the temperature is lowered from room temperature but with a small gradient: $(\partial\mu/\partial T)_{P=0}$ is only about 0.001 GPa K^{-1} at 270 K. With further decrease in temperature $\mu(T)$ levels off at around 250 K and in a range centred on ~235 K the gradient of the elastic stiffness versus temperature curve is almost zero. Then below about 220 K the shear stiffness begins to decrease at a rate which becomes progressively larger as the temperature is reduced further, resulting in a relatively steep positive gradient in the range 200–150 K. This softening of the shear acoustic phonons emphasised below ~220 K implies incipient lattice instability at lower temperatures. It has been reported [9] that the shear stiffness of Si_3N_4 samples (with density 3180 kgm^{-3} and 3050 kgm^{-3}) determined at ~625 K is a few percent greater than the one derived from room temperature measurements: this is also anomalous and is consistent with mode softening.

This softening of the longitudinal and shear moduli is reflected in the technological moduli. The bulk modulus $B^S(=C_L - 4\mu/3)$ increases with decreasing temperature and shows a knee arising from the acoustic mode softening (Fig. 4b). The temperature dependence of Young's modulus E $[=\mu(3C_L - 4\mu)/(C_L - \mu)]$ exhibits similar features to those observed in the shear modulus (Fig. 4b). In its ceramic form β-Si_3N_4 is not as stiff at low temperatures as a theoretical lattice dynamical model developed without including mode softening would suggest. The acoustic mode softening indicates incipient lattice instability. A natural speculation follows: is this the source of the fact that typically α- and β-Si_3N_4 tend to be synthesised together?

The acoustic Debye temperature is exceptionally high, in accord with the large elastic stiffness and strong interatomic bonding; it has a value similar to that of high-density Al_2O_3 ceramic [34], and is essentially constant within the whole temperature range of measurements. Poisson's ratio increases slightly with decreasing temperature.

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

The effects of hydrostatic pressure on ultrasonic wave velocity in β-Si_3N_4 ceramic are small, in particular on the shear wave velocity (Fig. 5). The data for the pressure dependence of the velocities of both longitudinal

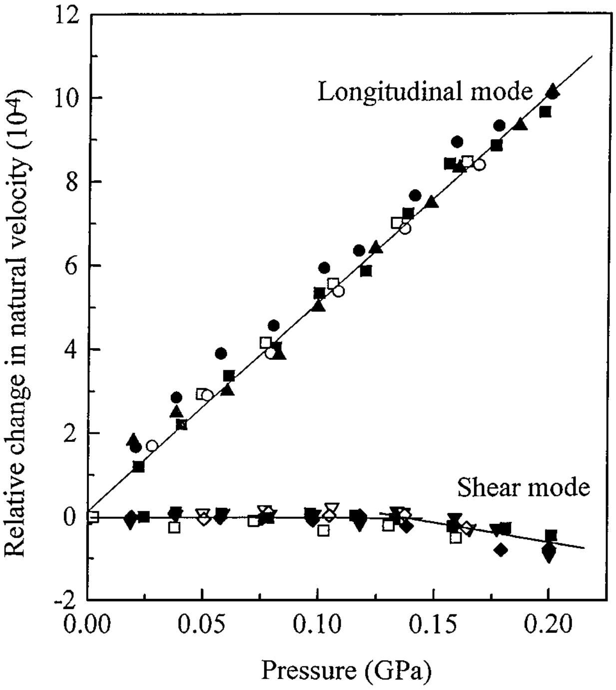

Figure 5 Hydrostatic-pressure dependence of the relative change in natural velocity measured at room temperature. The filled symbols correspond to measurements made with increasing pressure and the open symbols to data as the pressure was decreased. Different symbols refer to data collected during different runs. The solid lines are for visual guidance.

and shear ultrasonic waves are reproducible under pressure cycling and show no measurable hysteresis effects. This observation indicates that the β-Si_3N_4 ceramic does not alter under pressure cycling up to 0.2 GPa and that there is no relaxation of any residual stress. The velocity of the longitudinal ultrasonic waves increases approximately linearly with pressure. This is a normal behaviour: the long-wavelength longitudinal acoustic-modes stiffen under pressure. However, the behaviour under pressure of the velocity of shear ultrasonic waves is unlike that of the longitudinal mode. Two regions can be defined: in the low-pressure region up to 0.12 GPa, the shear wave velocity is practically independent of pressure and hence the pressure gradient $(\partial W_S/\partial P)_{P=0}$ of the natural velocity W_S is slightly positive; in the high-pressure region above 0.12 GPa, $\partial W_S/\partial P$ is negative, indicating shear acoustic-mode softening (Fig. 5). Increasing pressure has generally analogous effects on elastic stiffness to decreasing temperature; thus the shear acoustic-mode softening observed at low temperatures (Fig. 4a) may well be correlated to that found at high pressures: they may have the same origin. By using a phenomenological model to study the lattice dynamics of β-Si_3N_4, Mirgorodsky *et al.* [20] predicted a lattice instability under high pressure, namely, a pressure-induced softening of some low-frequency vibrational modes originating from out-of-plane motions of nitrogen atoms in silicon-nitrogen triangles. The interatomic forces arising in the material as a response to application of high pressure would alter the atomic force-constants matrix and soften certain vibrational modes of the lattice.

The hydrostatic-pressure derivatives $(\partial C_{IJ}/\partial P)_{P=0}$ of the elastic stiffnesses have been obtained from the ultrasonic velocity measurements under pressure by using [35]

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

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 B^T throughout the calculations, a procedure which introduces only a negligible error. The hydrostatic-pressure derivatives $(\partial C_L/\partial P)_{P=0}$ and $(\partial B^S/\partial P)_{P=0}$ determined for the β-Si_3N_4 ceramic have positive, normal values (Table I). Since the shear wave velocity data do not fit to a single straight line (see Fig. 5), the average value of $(\partial W_S/\partial P)_{P=0}$ has been used in the calculation of $(\partial B^S/\partial P)_{P=0}$. In Table I there are two values quoted for $(\partial \mu/\partial P)_{P=0}$, these relate to the low-pressure and high-pressure (values in brackets) regions. The longitudinal elastic stiffness and thus the slope of the corresponding acoustic-mode dispersion curve, at the long-wavelength limit, increase with pressure in the normal way. The same is true for the shear mode at low pressures. However, application of pressure to ceramic β-Si_3N_4 induces shear acoustic-mode softening at higher pressures as indicated by the small negative value of $\partial \mu/\partial P$ in the high-pressure region.

It is instructive to compare the value obtained in this work for $(\partial B^S/\partial P)_{P=0}$ of ceramic β-Si_3N_4 with those determined by other researchers using other methods. Li *et al.* [15] performed X-ray diffraction measurements on β-Si_3N_4 under pressure up to 34 GPa at room temperature (295 K) and analyzed the data on the pressure dependence of unit cell volume in terms of the Birch-Murnaghan equation of state and a "universal" equation of state: the former yielded 3.8 ± 1.6 for the pressure derivative $\partial B/\partial P$ of bulk modulus at zero pressure and the latter gave 4.3 ± 2.1 for $\partial B/\partial P$. From *ab-initio* total energy calculations Ching *et al.* [17] derived a value of 3.99 for the pressure dependence of the bulk modulus of β-Si_3N_4. Considering the fact that many factors such as porosity, microcracks, grain size and morphology, and secondary phases at grain boundaries affect the elastic moduli of polycrystalline samples and their behaviour under pressure, the value 4.3 ± 0.1 found for the pressure derivative $(\partial B^S/\partial P)_{P=0}$ of the adiabatic bulk modulus of ceramic β-Si_3N_4 in the present high-pressure ultrasonic study is in good agreement with the results of these recent high-pressure X-ray measurements [15] and theoretical calculations [17].

The measurements of the bulk modulus and its hydrostatic-pressure derivative have been used to calculate the volume compression $V(P)/V_0$ of ceramic β-Si_3N_4 up to very-high pressures, using an extrapolation method based on the Murnaghan's equation of state [36] in the logarithmic form. The calculation has been performed at room temperature and results are shown in Fig. 6. The comparatively small magnitude of the volume compression for ceramic β-Si_3N_4 is typical of that for silicon nitrides, in which the rigid framework

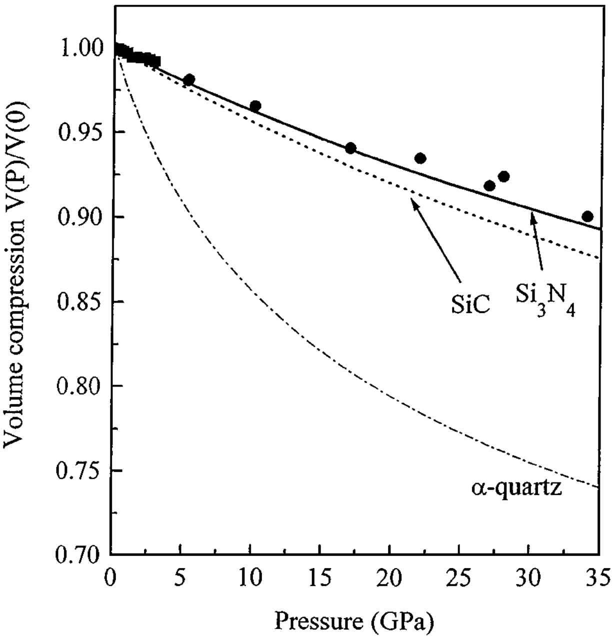

Figure 6 Volume compression of β-Si_3N_4 ceramic (full line) at room temperature extrapolated to very high pressures, using Murnaghan's equation of state, in comparison with the neutron diffraction data (filled squares) [3], X-ray diffraction data (filled circles) [15], SiC (dotted line) [37], and α-quartz SiO_2 (dash-dotted line) [36].

reduces the compressibility coefficients and hence increases the bulk modulus [3, 15]. A comparison of the volume compression of ceramic β-Si_3N_4 determined in this work with data taken from the literature [3, 15] and with those of α-quartz SiO_2 [37], SiC [38] is also given in Fig. 6. The remarkably incompressible behaviour of β-Si_3N_4 is consistent with its basic structure composed of irregular networks of SiN_4 tetrahedra which are unable to undergo cooperative reorientations. The SiN_4 tetrahedra are linked such that only distortions of the tetrahedra are permitted, hindering angle and bond length deformations. Neutron diffraction measurements [3] showed no change in the Si-N bond length and less than 2° change in the N-Si-N angle upon applying pressures up to 3 GPa to the β-Si_3N_4 crystal. This is in contrast with α-quartz SiO_2 in which the SiO_4 tetrahedra can easily undergo cooperative reorientations leading to a considerably larger compression (Fig. 6). High-pressure X-ray measurements [15] established that the a and c crystallographic lattice parameters of β-Si_3N_4 change at comparable rates with pressure (i.e., the linear compressibilities along the a- and c- directions are identical), with c/a ratio remaining constant over the compression region examined. Both the neutron [3] and X-ray diffraction [15] experiments confirmed the isotropic nature of the compression of β-Si_3N_4.

5. Grüneisen parameters and acoustic-mode vibrational anharmonicity

The hydrostatic-pressure dependences of ultrasonic wave velocities quantify to first order the vibrational anharmonicity of long-wavelength acoustic modes. Properties of a solid that depend upon thermal motion of the atoms are much influenced by anharmonicity. 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

$$\gamma_{\mathrm{p}} = -\left[\frac{\partial(\ln \omega_p)}{\partial(\ln V)}\right]_T, \tag{3}$$

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

$$\gamma_{\mathrm{L}} = -\frac{1}{6C_{\mathrm{L}}}\left[C_{\mathrm{L}} - 3B^{\mathrm{T}}\left(\frac{\partial C_{\mathrm{L}}}{\partial P}\right)_{p=0}\right] \tag{4}$$

and

$$\gamma_{\mathrm{S}} = -\frac{1}{6\mu}\left[\mu - 3B^{\mathrm{T}}\left(\frac{\partial \mu}{\partial P}\right)_{p=0}\right] \tag{5}$$

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

$$\gamma^{\mathrm{el}} = \frac{1}{3}(\gamma_{\mathrm{L}} + 2\gamma_{\mathrm{s}}). \tag{6}$$

This expression is strictly valid only at temperatures which are comparable with the acoustic Debye temperature. The results obtained for γ_{L}, γ_{S} and γ^{el} of ceramic β-Si_3N_4 at room temperature are included in Table I. Both γ_{L} and γ^{el} are positive. The shear-mode Grüneisen parameter γ_{S} is very small and positive in the low-pressure region; however, it is negative in the high-pressure region indicating shear acoustic-mode softening. Since β-Si_3N_4 has such a high acoustic Debye temperature $\Theta_{\mathrm{D}}(= 923 \pm 5\ \mathrm{K})$, longer wavelength acoustic phonons can be expected to dominate properties determined by vibrational anharmonicity even at room temperature. Although the thermal Grüneisen parameter γ^{th} includes the effects of all phonons in the Brillouin zone, contributions from optical phonons are expected to be negligible at room temperature. Small values for the acoustic-mode Grüneisen parameters and hence low vibrational anharmonicity are compatible with the low thermal expansion of β-Si_3N_4. The thermal Grüneisen parameter γ^{th} $(= 3\alpha V B^{\mathrm{S}}/C_{\mathrm{P}} = 1.09)$ has been obtained using the linear thermal expansion coefficient $\alpha(= 4.0 \times 10^{-6}\mathrm{K}^{-1})$ and specific heat $C_{\mathrm{P}}(= 795\ \mathrm{J\,kg^{-1}\,K^{-1}})$ data for β-Si_3N_4 quoted in Ref. [32]. Shear modes have a higher population density than the longitudinal modes. The shear acoustic-mode Grüneisen parameter γ_{S} $(= 0.005$, at low pressures) is much smaller than the longitudinal acoustic-mode Grüneisen parameter $\gamma_{\mathrm{L}}(= 1.18)$; this and their higher density accounts for the low thermal Grüneisen parameter γ^{th} estimated for this ceramic. Thus the higher population density of shear phonons at room temperature enhances their contribution to thermal expansion and specific heat-lowering the thermal expansion and hence the thermal Grüneisen parameter. In addition, both the anomalous temperature and pressure dependences of the shear elastic stiffness indicate incipient lattice shear instability. The low anharmonicity of long-wavelength acoustic modes of β-Si_3N_4 as quantified by the relatively small value of γ^{el}, which in part is due to the soft shear modes, is compatible with the small thermal expansion.

6. Conclusions

The velocities of longitudinal and shear 30 MHz ultrasonic waves propagated in ceramic β-Si_3N_4 have been measured as functions of temperature and hydrostatic pressure. There are several interesting features to note, which shed light on the elastic, nonlinear acoustic and lattice dynamical properties of this ceramic. They can be summarised as follows:

1. The ceramic β-Si_3N_4 is a comparatively stiff material elastically. Its volume-dependent elastic stiffness C_L and the bulk modulus B^S are large. The bulk modulus of β-Si_3N_4 is determined mainly by the rigid framework structure.
2. The temperature dependence of the longitudinal elastic stiffness shows a decrease in slope at about 235 K, which indicates acoustic mode softening. The shear elastic stiffness shows pronounced lattice shear softening in the temperature range below about 220 K at atmospheric pressure. The mode softening affects the bulk and Young's moduli. Although ceramic β-Si_3N_4 is a stiff material, nevertheless it is not quite as stiff, at low temperatures, as a theoretical lattice dynamical model developed without including mode softening would suggest.
3. The hydrostatic-pressure derivatives of the longitudinal elastic stiffness and bulk modulus have positive, normal values. However, the value obtained for the hydrostatic-pressure derivative of shear elastic stiffness is very small and positive in the low-pressure range, and becomes negative in the pressure range above 0.12 GPa indicating that application of hydrostatic pressure induces shear acoustic-mode softening.
4. The long-wavelength longitudinal and the mean acoustic-mode Grüneisen parameters are positive, whereas that for shear mode is slightly negative in the high-pressure range due to shear acoustic-mode softening. The thermal properties of β-Si_3N_4 are in accord with the low acoustic-mode vibrational anharmonicity.

Acknowledgements

G.A.S. and M.C. are grateful to NATO (Scientific and Environmental Affairs Division, Grant number CRG960584). B.J. is grateful to MOD for Corporate Research Programme funding. We would also like to thank E. F. Lambson, W. A. Lambson, B. Chapman and R. C. J. Draper for technical assistance.

References

1. F. L. RILEY, "Progress in Nitrogen Ceramics" (Martinus Nijhoff Publishers, Boston, 1983).
2. A. KELLY and N. H. MACMILLAN, "Strong Solids" (Clarendon Press, Oxford, 1986).
3. L. CARTZ and J. D. JORGENSEN, *J. Appl. Phys.* **52** (1981) 236.
4. O. YEHESKEL, Y. GEFEN and M. TALIANKER, *J. Mater. Sci.* **19** (1984) 745.
5. O. YEHESKEL and Y. GEFEN, *Mater. Sci. Eng.* **71** (1985) 95.
6. J. P. SINGH, K. C. GORETTA, D. S. KUPPERMAN and J. L. ROUTBORT, *Adv. Ceram. Mater.* **3** (1988) 357.
7. E. S. FISHER, M. H. MANGHNANI, J-F. WANG and J. L. ROUTBORT, *J. Amer. Ceram. Soc.* **75** (1992) 908.
8. A. R. DE ARELLANO-LÓPEZ, M. A. MCMANN, J. P. SINGH and J. MARTINEZ-FERNANDEZ, *J. Mater. Sci.* **33** (1998) 5803.
9. W. A. FATE, *J. Appl. Phys.* **46** (1975) 2375.
10. M. I. MENDELSON, *J. Amer. Ceram. Soc.* **52** (1969) 443.
11. F. F. LANGE, S. C. SINGHAL and R. C. KUZNICKI, *J. Amer. Ceram. Soc.* **60** (1977) 249.
12. E. P. PAPADAKIS, *J. Acoust. Soc. Am.* **42** (1967) 1045.
13. E. KITTINGER, *Ultrasonics* **15** (1977) 30.
14. R. N. THURSTON and K. BRUGGER, *Phys. Rev.* **133** (1964) A1604.
15. Y. M. LI, M. B. KRUGER, J. H. NGUYEN, W. A. CALDWELL and R. JEANLOZ, *Solid State Commun.* **103** (1997) 107.
16. J. C. HAY, E. Y. SUN, G. M. PHARR, P. F. BECHER and K. B. ALEXANDER, *J. Amer. Ceram. Soc.* **81** (1998) 2661.
17. W-Y. CHING, Y-N. XU, J. D. GALE and M. RÜLHE, *ibid.* **81** (1998) 3189.
18. Y. XU and W. Y. CHING, in "Silicon Dioxide and Its Interface," edited by S. T. Pantelides and G. Lucovsky (Materials Research Society, Pittsbhurgh, PA, 1988) p. 181.
19. J. A. WENDEL and W. A. GODDARD III, *J. Chem. Phys.* **97** (1992) 5048.
20. A. P. MIRGORODSKY, M. I. BARATON and P. QUINTARD, *Phys. Rev. B* **48** (1993) 13326.
21. C. K. LOONG, P. VASHISHTA, R. K. KALIA and I. EBBSJÖ, *Europhys. Lett.* **31** (1995) 201.
22. M. L. COHEN, *Phys Rev B* **32** (1985) 7988.
23. S. T. BULJAN, J. G. BALDONI and M. L. HUCKABEE, *Am. Ceram. Soc. Bull.* **66** (1987) 347.
24. F. LEE and K. J. BOWMAN, *J. Amer. Ceram. Soc.* **75** (1992) 1748.
25. F. F. LANGE, *ibid.* **56** (1973) 518.
26. S. R. CHOI and J. A. SALEM, *ibid.* **77** (1994) 1042.
27. G. HIMSOLT, H. KNOCH, H. HUEBNER and F. W. KLEINLEIN, *ibid.* **62** (1979) 29.
28. G. PEZZOTTI, I. TANAKA, T. OKAMOTO, M. KOIZUMI and Y. MIYAMOTO, *ibid.* **72** (1989) 1461.
29. I. TANAKA, S. NASU, H. ADACHI, Y. MIYAMOTO and K. NIIHARA, *Acta Metall. Mater.* **40** (1992) 1995.
30. J. GUBICZA, P. ARATÓ, F. WÉBER and A. JUHÁSZ, *Mater. Sci. Eng. A* **259** (1999) 65.
31. F. F. LANGE, in "1974 Annual Review of Materials Science," edited by R. A. Huggins (Annual Reviews, Inc., Palo Alto, CA) p. 365.
32. J. MIYAUCHI and Y. KOBAYASHI, SAE Technical Papers Series (Warrendale, Pa., Automotive Engineers, 1985) p. 31.
33. S. C. LAKKAD, *J. Appl. Phys.* **42** (1971) 4277
34. D. H. CHUNG and G. SIMMONS, *ibid.* **39** (1968) 5316.
35. R. N. THURSTON, *Proc. IEEE* **53** (1965) 1320.
36. F. D. MURNAGHAN, *Proc. Natl. Acad. Sci.* USA **30** (1944) 244.
37. Q. WANG, G. A. SAUNDERS, P. TSCHAUFESER, S. C. PARKER and B. J. JAMES, *Phys. Rev. B* **45** (1992) 10242.
38. H. LIU and G. A. SAUNDERS (1999) unpublished data.

Received 31 August 1999
and accepted 26 September 2000