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Equation of state of α-Si_3N_4

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X-ray diffraction at high pressures reveals that α-Si_3N_4 is metastable to at least 48 GPa when compressed statically at 295 K, and yields a zero-pressure bulk modulus of $K_0=228.5$ (±4) GPa, assuming a pressure derivative $K_0'=4$. The compression is nearly isotropic, but with the c direction being slightly more incompressible than the a direction, in good agreement with theory. [S0163-1829(97)04206-9]

INTRODUCTION

Due to their hardness, corrosion resistance, ability to withstand high temperatures, and relatively low density, ceramics play an important role in the modern development of materials. In particular, silicon nitrides show considerable potential for use in a wide variety of demanding applications.[1] Here we focus on α-Si_3N_4, which is closely related to the β phase, having the end member composition and prototype crystal structure for the sialons.[2,3]

Of the two known polymorphs of Si_3N_4, the α phase is recognized as being metastable relative to the β form.[4–6] Both crystal structures are hexagonal and consist of corner-linked SiN_4 tetrahedra, with the molar volume of α-Si_3N_4 being 0.2% larger than that of β-Si_3N_4.[5] Hence, the α phase is expected to become increasingly metastable relative to the β phase when taken to high pressures, and it has been suggested that the α–β transformation should take place by 3–6 GPa.[7] Previous static high-pressure work on α-Si_3N_4 has been limited to 5 GPa,[6–9] however, so we are motivated to characterize this phase to much higher pressures. We do this by x-ray diffraction using the diamond-anvil cell.

A more fundamental rationale for our work is that pressures in the 10–100 GPa range can be used to probe the strength and underlying bonding forces of materials.[10–12] For example, the equation of state obtained by high-pressure x-ray diffraction offers a powerful means of testing first-principles calculations of the ground-state properties of hard materials.[12] It is thus notable that an earlier neutron-diffraction study,[8,9] to a maximum pressure of 3.5 GPa yielded a bulk modulus ~15% higher than has recently been calculated by *ab initio* quantum chemical methods.[13]

EXPERIMENT

In a series of two separate experiments, α-Si_3N_4 (provided by Cercom Inc., Vista, CA)[14] with a particle size of ~70 nm was loaded into a modified Mao-Bell type diamond-anvil cell. We used spring-steel gaskets and diamond anvils with 350 μm culets. The structure of α-Si_3N_4 was determined from 0 to 48 GPa by means of energy-dispersive x-ray diffraction at beam line X17C at the National Synchrotron Light Source (NSLS). All data were collected at ~295 K with a scattering angle $2\theta=10.019°$ ($\pm0.004°$).

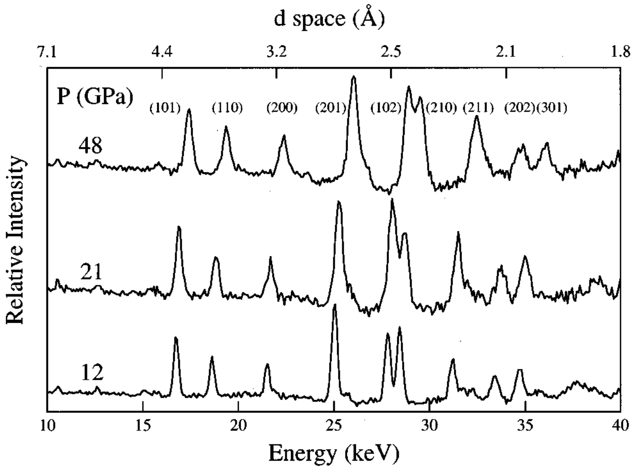

FIG. 1. Representative energy dispersive x-ray diffraction spectra of polycrystalline α-Si_3N_4 at 12, 21, and 48 GPa. Miller indices (hkl) are labeled, and $2\theta=10.020°$ ($\pm0.004°$).

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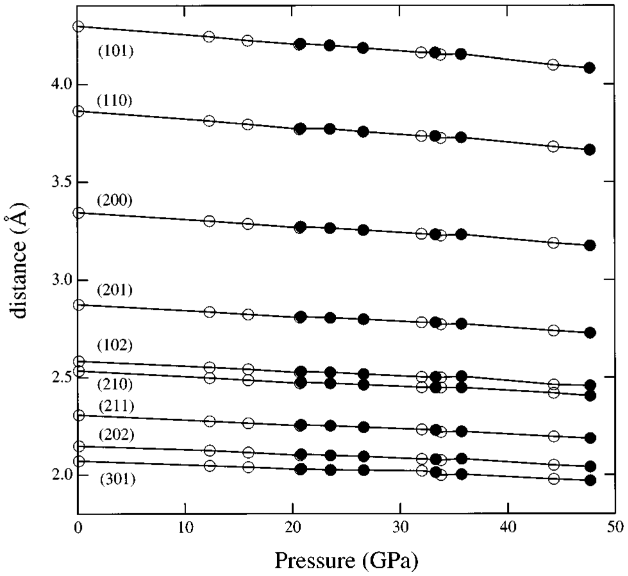

FIG. 2. Measured d spacings as a function of pressure. The closed symbols indicate data taken upon compression, while the open symbols are for data taken on decompression. The lines are guides.

For both loadings, 4:1 methanol:ethanol was mixed in with the α-Si_3N_4 in order to reduce the nonhydrostatic stresses present in the sample chamber. Less than 5% (by volume) of ruby powder was also dispersed across the sample, in order to determine the pressure at about five locations throughout the sample.[15]

DATA AND DISCUSSION

Typically, nine x-ray diffraction lines were obtained from α-Si_3N_4 at each pressure (Figs. 1 and 2): 101, 110, 200, 201, 102, 210, 211, 202, and 301. There is no evidence for hysteresis (i.e., a difference between data collected on compression and decompression). Also, we find no evidence for any phase transformations, in that the diffraction pattern of α-Si_3N_4 is retained with no new diffraction lines appearing to 48 GPa, the highest pressure of our study. A nonlinear, multivariate least-squares fitting procedure was used to determine the unit cell parameters of the P 31c crystal structure, a and c, and our zero-pressure measurements ($a = 7.757 \pm 0.001$ Å, $c = 5.623 \pm 0.001$ Å) are in good agreement with previously reported values (Table I).[8,16–19]

The pressure dependence of the unit cell volume (V), from 0–48 GPa, is summarized in Table I and Fig. 3. We use the Eulerian finite-strain formalism[20] to analyze the data because this approach has been empirically shown to be among the best for deriving an equation of state that is compatible with independently measured elastic moduli; that is, unlike pressure-volume polynomials (e.g., Slater expansion) or the Murnaghan equation of state, finite- and infinitesimal-compression measurements are reduced in a self-consistent manner.[21–23]

Taylor expansion of the Helmholtz free energy in terms of the Eulerian finite-strain parameter $f_\nu = (\frac{1}{2})[(V/V_0)^{-2/3} - 1]$ yields the following isothermal equation of state for the pressure (P):[20,23]

$$P = 3K_0 f_\nu (1 + 2f_\nu)^{5/2}[1 + af_\nu + bf_\nu^2 + \cdots], \qquad (1)$$

where K is the bulk modulus, the third order coefficient of energy in strain is given by

$$a = 3(K_0' - 4)/2, \qquad (2)$$

and the fourth-order coefficient b is a function of $K_0 K_0''$ as well as K_0'. Here, primes indicate differentiation with re-

TABLE I. Summary of zero and high-pressure diffraction measurements on α-Si_3N_4.

Pressure (GPa)	a (Å)	c (Å)	Volume (Å^3)	Comments
0	7.7462(8)	5.619(1)	292.0(1)	Neutron (Ref. 8)
0	7.752(4)	5.618(5)	292.3(5)	Neutron (Ref. 8)
0	7.753(4)	5.618(4)	292.5(4)	X-ray (Ref. 16)
0	7.765(1)	5.622(1)	293.5(1)	X-ray (Ref. 17)
0	7.818(3)	5.591(4)	296.0(3)	X ray (Ref. 18)
0	7.748(1)	5.617(1)	292.02(9)	X-ray (Ref. 19)
		This study		
21(2)	7.553(3)	5.488(4)	271.1(3)	Compression
24(2)	7.540(1)	5.470(1)	269.3(1)	Compression
26.6(8)	7.516(3)	5.458(4)	267.0(3)	Compression
33(1)	7.470(4)	5.428(5)	262.3(4)	Compression
36(2)	7.456(4)	5.426(6)	261.3(4)	Compression
48(5)	7.330(2)	5.327(3)	247.9(2)	Compression
44(4)	7.364(5)	5.342(6)	250.9(4)	Decompression
34(3)	7.449(5)	5.416(7)	260.3(5)	Decompression
32(3)	7.476(7)	5.43(1)	262.7(7)	Decompression
21(1)	7.541(3)	5.478(4)	269.8(3)	Decompression
16(1)	7.588(2)	5.510(3)	274.7(2)	Decompression
12.3(8)	7.624(2)	5.536(2)	278.6(2)	Decompression
0	7.757(1)	5.623(1)	293.03(7)	Decompression

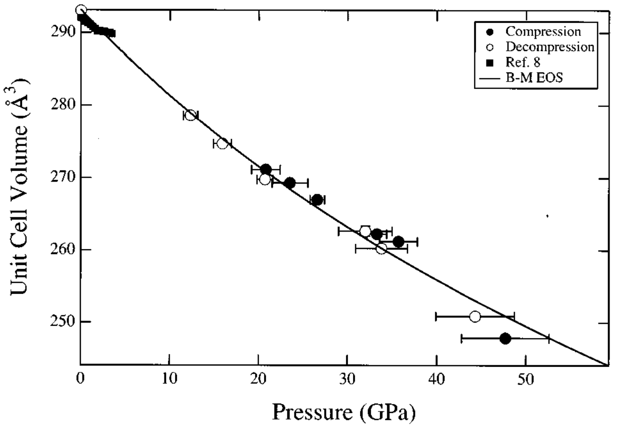

FIG. 3. Experimentally determined pressure dependence of the unit cell volume of α-Si_3N_4 at 295 K. Results from a previous neutron-diffraction study to 3.5 GPa (squares) (Ref. 9) are compared with the present x-ray diffraction measurements to 48 GPa (circles). For the present data, filled symbols are data taken on compression, and open symbols on decompression. The line indicates the best fit to the x-ray diffraction data using a second-order Eulerian finite strain equation of state (Birch equation), as described in the text, with bulk modulus $K_0=228.5$ (± 4.0) GPa, assuming a pressure derivative $K_0'=4$ (Ref. 22). The kink in the neutron diffraction data may be due to nonhydrostaticity.

spect to pressure, and the subscript zero refers to zero pressure ($T=295$–300 K) conditions. Defining the normalized pressure, F_v, as

$$F_v = P/[3f_v(1+2f_v)^{2.5}] \tag{3}$$

yields a third-order finite-strain equation of state that is linear in f_v:[20]

$$F_v = K_0[1-1.5(4-K_0')f_v]. \tag{4}$$

When the P-V data are recast into the form of Eq. (4), the intercept directly yields the bulk modulus, while the slope indicates the deviation of K_0' from a value of 4 (Fig. 4). As K_0' is close to 4 for most materials, a second-order equation of state (Birch equation) is often adequate;[20,23] K_0 is determined by a weighted average over the measured F, since the slope in Eq. (4) is zero in this approximation. Given the scatter in our data, we use the second-order equation of state ($K_0'=4$) to obtain a zero-pressure bulk modulus of $K_0=228.5$ (± 4) GPa. Fitting all of the present x-ray diffraction data, using a third-order equation of state yields $K_0=223.4$ (± 15) GPa and $K_0'=4.5$ (± 1.3). These values are in generally good agreement with estimates of the zero-pressure bulk modulus obtained by ultrasonic methods, $K_0=248$ (± 10) GPa. The reason that the ultrasonically determined value of K_0 has such a large uncertainty is that it is an extrapolation based upon measurements which were carried out on composite samples that were mixtures of α- and β-Si_3N_4 and having varying degrees of porosity.[24] A weighted, third-order fit to the x-ray diffraction data and the ultrasonically determined value of the bulk modulus yields $K=240.1$ (± 8) GPa, and $K'=3.1$ (± 0.7).

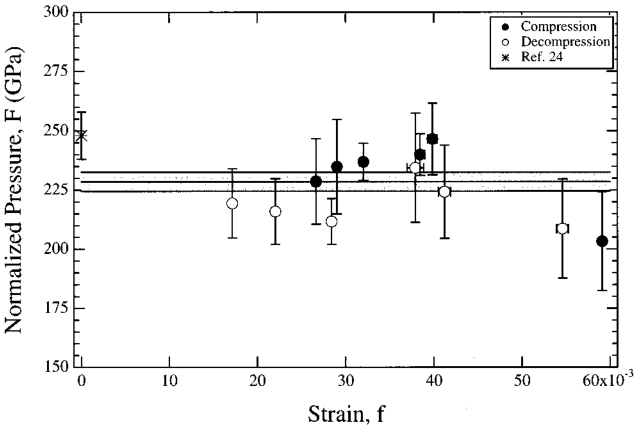

FIG. 4. Normalized pressure F as a function of the Eulerian strain measure f (see text and Ref. 22), with symbols as in Fig. 3. The asterisk at $f=0$ is from an ultrasonic study (Ref. 24).

The only other equation-of-state measurement known to us for α-Si_3N_4 was obtained by neutron diffraction over the pressure range 0–3.5 GPa.[8,9] The quoted bulk modulus is 282 (± 12) GPa obtained by taking the average of a linear, least-squares fit to the volumes as a function of pressure for $P<2$ and another fit for $2<P<3.5$ GPa. The authors' analysis was influenced by a change in slope they observed in the P-V data at 1.5 GPa. The raw data are compatible with our own measurements, particularly for pressures below 2 GPa (Fig. 3). We believe that the higher bulk-modulus value obtained in the neutron diffraction study may be due to nonhydrostaticity, and have found similar effects in our own work. Indeed, if taken at face value, some of our own highly nonhydrostatic measurements suggest a bulk modulus in excess of 300 GPa.[25] The reason that such anomalously high values can arise is due to the high strength of α-Si_3N_4 which is the very reason this material evokes interest.[11,26]

A theoretical calculation in which the force field was determined by *ab initio* Hartree-Fock calculations on $N(SiH)_3$ and $Si(NH_2)_4$ clusters and applied to a molecular dynamics simulation of α-Si_3N_4 yields a zero-pressure bulk modulus of $K_0=246$ GPa at $T=300$ K.[13] Alternatively, a relation derived by Cohen[27,28] for the bulk modulus as a function of nearest-neighbor separation (d) in angstroms and ionicity (λ) of the compound[27–29]

$$K_0 \ \ (\mathrm{GPa}) = (1971 - 220\lambda)/d^{3.5} \tag{5}$$

yields $K_0 \approx 270$ GPa. In light of the approximations involved, the theoretical values are in good accord with the range of experimental measurements obtained for the bulk modulus of α-Si_3N_4.

We can examine the changes in the a and c parameters in order to determine the anisotropy of the compression. Qualitatively, we note little change in crystallographic anisotropy under pressure, as all of our data between 0 and 48 GPa are compatible with a constant value of $c/a=0.726$ (± 0.001). Similarly, the neutron-diffraction results were interpreted in terms of an isotropic compression of the unit cell to 3.5 GPa.

In more detail, the Eulerian finite-strain analysis can be extended to obtain linear compressibilities.[30] We define the strain parameters f_a and f_c for the a and c directions, as well as the corresponding normalized pressures F_a and F_c:

$$f_a=\frac{1}{2}\left[\left(\frac{a_0}{a}\right)^2-1\right], \tag{6}$$

$$f_c=\frac{1}{2}\left[\left(\frac{c_0}{c}\right)^2-1\right], \tag{7}$$

$$F_a=\frac{P(ac_0/a_0c)^{2/3}}{f_a(1+2f_v)^{2.5}}, \tag{8}$$

$$F_c=\frac{P(a_0c/ac_0)^{4/3}}{f_c(1+2f_v)^{2.5}}. \tag{9}$$

The F_i and f_i (where i is either a or c) are then related by

$$F_i=K_{i0}[1-1.5(4-K'_{i0})f_i], \tag{10}$$

where K_{i0} is the linear incompressibility in the ith direction and the prime indicates pressure differentiation. The linear incompressibilities provide a quantitative measure of the degree to which compression is isotropic. The K_{i0} are related to the bulk modulus by

$$\frac{1}{K_v}=\frac{2}{K_a}+\frac{1}{K_c}. \tag{11}$$

Determination of the K_{i0} from the present study yields $K_{a0}=654$ (± 31) GPa and $K_{c0}=711$ (± 31) GPa, whereas the neutron diffraction work led to $K_{a0}=847.5$ (± 29) GPa and $K_{c0}=877.2$ (± 46) GPa.[8,9] Accepting the quantitative disagreement as most likely due to nonhydrostaticity in the previous work, both studies show that the compression is similar along the a and c directions, with the latter being about 5–10 % more incompressible than the former. In fact, the quantum-chemical calculation also yields a c axis that is slightly more incompressible: $K_{a0}=714$ GPa and $K_{c0}=819$ GPa.[13]

On the basis of infrared measurements, it has been inferred that pressure drives the $\alpha\rightarrow\beta$ transition at room temperature.[7] This conclusion stems from measuring the intensity ratio of the 685 cm^{-1} band characteristic of the α phase and the 578 cm^{-1} band that is characteristic of both phases.[7,31] In that work, the starting material was 86% α-Si_3N_4, with the remaining 14% in the β-phase.[7] When this material was subjected to a pressure of 1.84 GPa, it was interpreted that the starting material was converted to 31% β phase (69% α phase) based on the changes in the infrared spectra, and the speculation was that pressure-induced distortion of the Si-N α-phase tetrahedra produces the β phase even at room temperature. A linear extrapolation of these results would indicate that α-Si_3N_4 should convert completely to the β-phase by a pressure of ~14 GPa.

Although the structures are similar, and there are a number of d- spacings that nearly match, the α and β- phases have distinct x-ray diffraction patterns. Thus, the conversion of the α to the β phase can be monitored using x-ray diffraction, although it must be pointed out that the diffraction patterns may not yield quantitative values for the abundances of the two phases due to the effects of preferred orientation. Still, there is no evidence from our experiments for any increase in the amount of β phase with pressure. Our findings are in good agreement with a previous x-ray diffraction study, in which the authors took α-Si_3N_4 to 4→5 GPa and 1500→1800 °C but did not observe any transformation from the $\alpha\rightarrow\beta$ phase, although at 2000 °C a transformation to the β- phase was observed.[6]

Simply put, x-ray diffraction does not support the interpretation of the infrared intensity measurements, but instead shows that at room temperature, the α-phase is metastable to at least 48 GPa, the highest pressure of our study. Therefore, we suggest alternative explanations to the pressure-induced changes in the infrared absorption spectrum of α-Si_3N_4:

(1) There may be differences in the changes in absorption for each of the bands with pressure, with the intensity of the 685 cm^{-1} band decreasing more rapidly with pressure than the intensity of the 578 cm^{-1} band. This would result in a pressure-dependent ratio of band intensities, even though the α-β ratio is unchanged.

(2) Pressure may distort the α tetrahedra toward a more β-like tetrahedral structure, while not changing the long-range order of the crystal. Thus, although pressure causes the α phase to structurally resemble the β phase on a local level, it retains the long-range structure of the α phase.

CONCLUSION

Using synchrotron x-ray diffraction, we have found that α-Si_3N_4 is stable to nearly 50 GPa when compressed quasihydrostaticaly in a diamond-anvil cell. This is in sharp contrast to previous studies suggesting that α-Si_3N_4 undergoes the $\alpha\rightarrow\beta$ transformation at low pressure. We have measured the isothermal equation of state of α-Si_3N_4 by means of high-pressure x-ray diffraction, determining the bulk modulus and the linear incompressibilities along the a and c directions. Our peak pressure represents nearly a tenfold increase in applied pressure when compared with previous work, and the measurements are in general agreement with the results of a previous neutron diffraction experiment as well as with theoretical estimates.

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