



Analysis of compression and elasticity of the nanocrystalline cubic silicon nitride (γ - Si_3N_4) under high pressure

Monika Goyal & B.R.K.Gupta

Department of Physics, IAH

GLA University, Mathura-281406, (U.P.), India

Abstract: A simple theory based on Tait's equation of state is applied to predict the effect of pressure on nanomaterial (γ - Si_3N_4) which gets support from experimental and theoretical studies. We considered γ - Si_3N_4 to study the effect of pressure in the light of other formulations, viz. LDA and GGA. It is demonstrated that the spinal structure of Si_3N_4 nanocrystal initially exhibits an extremely high bulk modulus of 685 GPa but above 40 GPa, the bulk modulus is reduced to 415 GPa. Thus, a critical pressure of ~ 40 GPa, was determined that signifies the onset of size induced weakening of elastic stiffness in Si_3N_4 nanocrystal. The results obtained in the present study are found to present a good agreement with the experimental data as well as other formulations. A good agreement between theory and experiment demonstrates the validity of the Tait's equation of state in the present approach.

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I. Introduction

The nanomaterials are very sensitive to external parameters like pressure and temperature. The study of nanoparticles under high pressure is considered as a possible path to expand the range of available solid state materials. High pressure applications have the potential for the exploration of infinity of paths for nanoassembling or phase transformation in a controlled way and constitute a unique route for the elaboration of new materials. Over the past few years a large number of new materials with large hardness values have been fabricated [1,2]. A high shear modulus is related to high bond bending force constants and a small number of internal degrees of freedom [2]. Several candidate materials like boron nitride, silicon nitride and germanium nitride crystallize in a hexagonal structure before transforming into a spinel-type high pressure polymorph. Spinel may therefore be an important prototype for the design of novel materials of high hardness [3]. The expectation that high pressure may be a promising route to find novel super hard materials supported by volume elasticity systematics which show higher elastic moduli for matter volumes in an isochemical series of phases [4].

Silicon nitride is known to have excellent mechanical strength, low compressibility and high thermal stability [5]. Wang et al [6] have investigated the bulk modulus and some thermodynamic properties of γ - Si_3N_4 using the analytic mean field method. Kuwabara et al [7] have calculated the bulk moduli and thermal expansion coefficients of γ - Si_3N_4 using the theory of lattice dynamics. Recently Xu et al and Zerr et al [8, 9] have investigated α - γ and β - γ phase transitions for the Si_3N_4 polymorphs. They have calculated some of the thermodynamic properties such as thermal expansion coefficient, bulk modulus and Gruneisen parameters for Si_3N_4 crystal. The results obtained by these investigators are not, however, conformed with the experimental data. Therefore, more studies are required to evaluate the elastic and compressional properties of γ - Si_3N_4 with higher reliability. Pressure application, as for bulk materials allows the continuous modification of the interatomic interactions of the nano-object and constitutes a valuable tool to explore physic-chemical interactions at the nanoscale and their link with physical properties of interest. During the past years, several experimental studies have been performed to understand the high pressure behavior of nanomaterials including the cubic structure of γ phase of Si_3N_4 crystal which remains stable 15 GPa. However, the theoretical efforts are lacking. Thus, it is legitimate and may be useful to present a simple theoretical method to study the high pressure behavior of nanomaterials. In the present paper, we present a simple theoretical analysis to study compression and elastic behavior of γ - Si_3N_4 nanocrystal and compare it with some earlier formulations as an example. The method of analysis is given in section 2. The results and discussion is given in section 3.

II. Method of analysis

In the present study we have employed the usual Tait's equation of state to analyze the compressional and elastic behavior of γ - Si_3N_4 nanocrystal. The Tait's equation of state is obtained by assuming the fact that the product of thermal expansion coefficient (α_T) and bulk modulus (B_T) is constant under the effect of pressure [10], i.e.

$$\alpha_o B_o = \alpha_T B_T = \text{constant} \quad (1)$$

Differentiation of equation (1) with respect to volume at constant temperature gives

$$\alpha \left(\frac{dB}{dV} \right)_T + B \left(\frac{d\alpha}{dV} \right)_T = 0 \quad (2)$$

Anderson – Gruneisen parameter is defined as

$$\delta_T = \frac{V}{\alpha} \left(\frac{d\alpha}{dV} \right)_T \quad (3)$$

Where δ_T is Anderson – Gruneisen parameter at constant temperature T.

From equation (2) and (3), we get

$$\delta_T = \frac{V}{\alpha} \left(\frac{d\alpha}{dV} \right)_T = - \frac{V}{B} \left(\frac{dB}{dV} \right)_T \quad (4)$$

Assuming δ_T to be independent of V,

$$\delta_T = \left(\frac{dB}{dP} \right)_T = B'_0 \quad (5)$$

Anderson- Gruneisen parameter δ_T and $\eta = V/V_0$ (where V_0 is the initial volume) are related by the following relation [11],

$$\left(\frac{\delta_T + 1}{\eta} \right) = A, \quad (6)$$

Where A is a constant for a given nanomaterial. In view of equation (6), equation (4) can be written as

$$\frac{dB}{B} = \left[\frac{-A}{V_0} + \frac{1}{V} \right] dV \quad (7)$$

Integrating eq. (7), we get

$$\frac{B}{B_0} = \frac{V}{V_0} \exp A \left[1 - \frac{V}{V_0} \right] \quad (8)$$

Where B is equal to

$$B = -V \left(\frac{dP}{dV} \right)_T \quad (9)$$

Using equation (8), equation (9) can be represented as

$$\frac{B}{B_0} \exp A \left[1 - \frac{V}{V_0} \right] dV = -dP \quad (10)$$

The integration of equation (10) gives

$$P = \frac{B_0}{A} \left[\exp A \left[1 - \frac{V}{V_0} \right] - 1 \right] \quad (11)$$

Here B_0 is the bulk modulus at zero pressure and the constant A is determined from the initial conditions, i.e. at $V = V_0$,

$$A = \delta_T^0 + 1$$

On substitution of constant A in equation (11) and taking natural log, we get the following final form of usual Tait's equation of state,

$$V(P, T_0) / V(0, T_0) = 1 - \frac{1}{B'_0 + 1} \log \left[1 + \left\{ \frac{B'_0 + 1}{B_0} \right\} P \right] \quad (12)$$

Where $V(P, T_0)$ is the volume of the material at pressure required to compress it, keeping the temperature constant. V_0 is the initial volume at room temperature T_0 . B_0 and B'_0 are the isothermal bulk modulus and its first pressure derivative at $T = T_0$.

The above equation (12) provides a simple and straight forward approach to predict the relative compression in γ - Si_3N_4 at high pressures. To analyse the elastic behavior we have assumed the approximation that Anderson-Gruneisen parameter δ is equal to the first order pressure derivative of bulk modulus as considered by Anderson [11]. In view of equations (4) and (5), Anderson-Gruneisen parameter δ may thus be written as:

$$\delta = - \frac{V}{B} \left(\frac{dB}{dV} \right)_T = B'_0 \quad (13)$$

The integration of equation (13) at constant temperature gives the following relation

$$\frac{B}{B_0} = \left(\frac{V}{V_0} \right)^{-B'_0} \quad (14)$$

It has been discussed [12] that equation (14) may be generalized likewise:

$$\frac{M}{M_0} = \left(\frac{V}{V_0} \right)^{-B'_0} \quad (15)$$

Where M represents any of the elastic moduli, such as C_{11} , C_{12} , C_{44} , $(C_{11}-C_{12})/2$, or $(C_{11}+2C_{12})/3$, M_0 refers to their initial values at zero pressure. On the basis of equation (15), the expressions relevant to C_{11} , C_{12} , and C_{44} can be written collectively as follows:

$$\frac{C_{ij}}{C_{0ij}} = \left(\frac{V}{V_0} \right)^{-\delta_{ij}} \quad (16)$$

Where (δ_{ij}) are the Anderson's constants corresponding to C_{ij} and defined as [10]:

$$\delta_{0ij} = \left(\frac{dC_{ij}}{dP} \right) \quad (17)$$

Equation (16) can be used to determine the pressure dependence of C_{ij} provided that the corresponding values of V/V_0 are known.

III. Results and Discussion

A simple theory has been presented to predict the effect of pressure on γ - Si_3N_4 nanocrystal. In the present investigation the authors have determined the volume compression and elastic properties of γ phase of Si_3N_4 crystal under the effect of high pressure by making use of Tait's equation of state. The equation of state employed in the present study consists of only two input parameters, viz. $B_0 = 339$ GPa [13] and $B'_0 = 4$ [13]. We have compiled these data in table 1 along with their proper references [13, 15]. Since the studies on compression and elastic behavior of γ - Si_3N_4 nanocrystal have attracted much attention in experimental studies [5, 6], we have therefore considered γ - Si_3N_4 crystal as an example to test the validity of Tait's equation of state in the present study. Equation (12) is used to study the compression behavior of γ - Si_3N_4 nanocrystal. The calculated results are shown in figure 1 along with the experimental data for the sake of comparison. The results achieved by previous workers [13] using different methods are also shown in figure 1. It is found that the compression values (V/V_0) obtained by the authors presents a good agreement with available experimental data.

To analyze the elastic behavior of γ - Si_3N_4 nanocrystal, we have determined the values of elastic moduli, C_{11} , C_{12} , and C_{44} as a function of pressure. The calculated values are reported in figure 2 - 4 and compared with those determined by previous investigators using the different theoretical approaches. The trend of variation of elastic constants vs. pressure is found same as the previous results obtained by using the LDA and GGA theoretical approaches. It is noted from figure 2-4 that the calculated values of elastic constants follow the criteria of the mechanical stability of Si_3N_4 nanocrystal in γ -phase under the conditions [16,17]: (a) $\tilde{C}_{44} > 0$, (b) $\tilde{C}_{11} > \tilde{C}_{12}$, (c) $\tilde{C}_{11} + 2\tilde{C}_{12} > 0$, where $\tilde{C}_{\alpha\alpha} = C_{\alpha\alpha} - P$ ($\alpha=1,4$), $\tilde{C}_{12} = C_{12} + P$.

On the basis of overall descriptions, it may thus be emphasized here that a simple and straight forward theoretical method is capable of explaining the compressional and elastic properties of nanomaterials under high pressure satisfactorily. Due to simplicity and applicability, this may be of the current interest to the researchers engaged in the study of elastic properties of nanomaterials under high pressure. The high pressure study of nanomaterials is an appealing and highly expanding area of research for both applied sciences and nanotechnology.

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Table captions:

[1] Values of input parameters used in the present work for γ - Si_3N_4 nanocrystal

Figure captions:

[1] Figure 1: Variation of V/V_0 vs. P for γ - Si_3N_4 nanocrystal

[2] Figure 2: Variation of C_{11}/C_{011} vs. P for γ - Si_3N_4 nanocrystal

[3] Figure 3: Variation of C_{12}/C_{012} vs P for γ - Si_3N_4 nanocrystal

[4] Figure 4: Variation of C_{44}/C_{044} vs P for γ - Si_3N_4 nanocrystal

Table 1: Values of input parameters used in the present work for γ - Si_3N_4 nanocrystal

S.No.	Nanomaterial	B_0 [GPa]	B'_0	δ_{011}	δ_{012}	δ_{044}	Ref.
1.	γ - Si_3N_4	339[13]	4[13]	2.9	4.18	1.4	Present work
				2.7	4.12	1.2	[15]
				5.22	3.38	1.69	[13]
				5.24	3.42	2.11	[13]

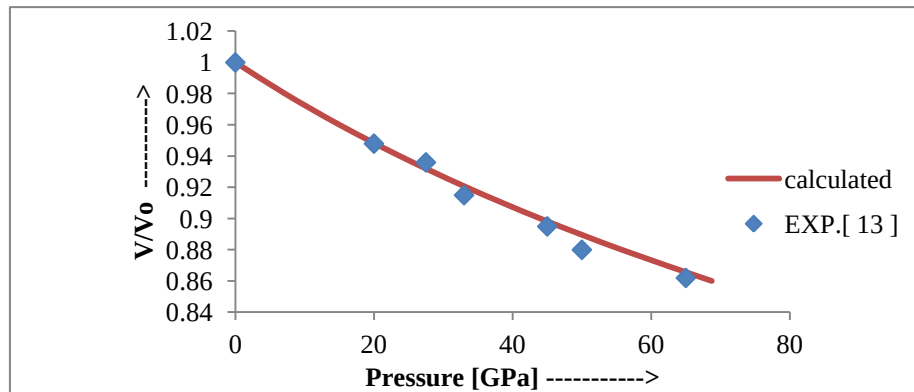


Figure 1: Variation of V/V_0 vs P for γ - Si_3N_4 nanocrystal

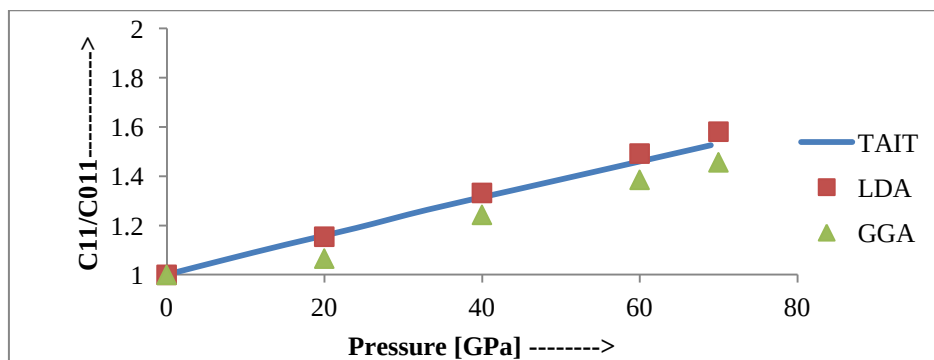


Figure 2: Variation of C_{11}/C_{011} vs. P for γ - Si_3N_4 nanocrystal

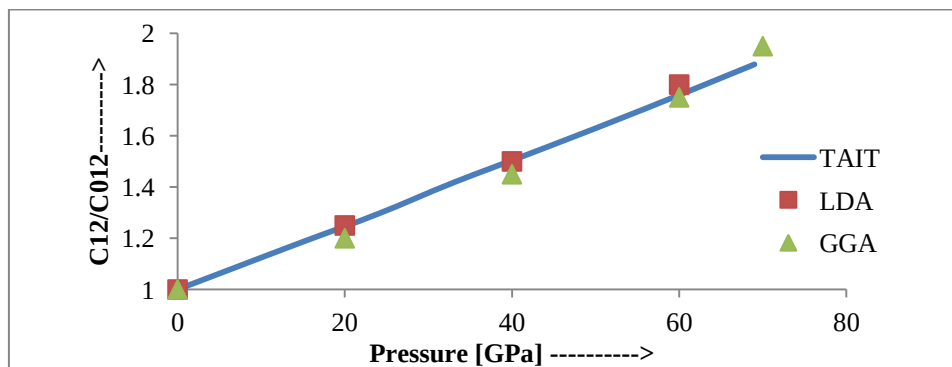


Figure 3: Variation of C_{12}/C_{012} vs P for γ - Si_3N_4 nanocrystal

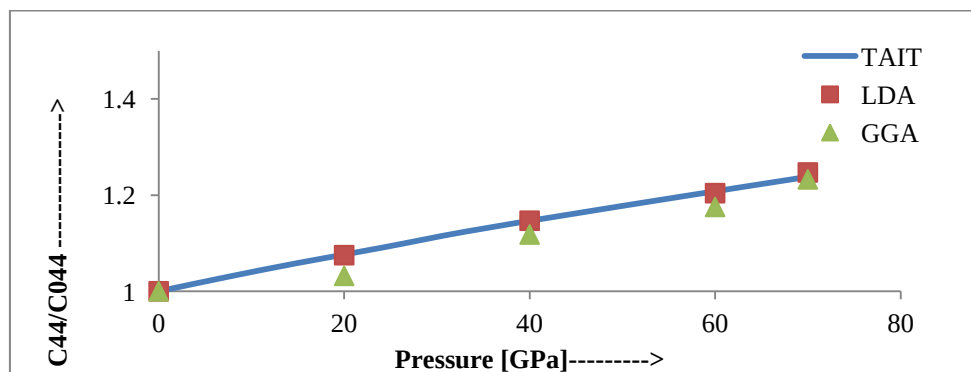


Figure 4: Variation of C_{44}/C_{044} vs P for γ - Si_3N_4 nanocrystal