Elastic and structural instability of cubic Sn_3N_4 and C_3N_4 under pressure

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We use *in situ* high-pressure angle dispersive x-ray diffraction measurements to determine the equation of state of cubic tin nitride (γ-Sn_3N_4) under pressure up to 26 GPa. While we find no evidence for any structural phase transition, our estimate of the bulk modulus (B_0) is 149($\pm$1.2) GPa, much lower than the earlier theoretical estimates and that of other group IV-nitrides. We corroborate and understand these results with complementary first-principles analysis of structural, elastic, and vibrational properties of group IV-nitrides, and predict a structural transition of Sn_3N_4 at a higher pressure of 88 GPa compared to earlier predictions of 40 GPa [M. Huang and Y. P. Feng, J. Appl. Phys. **96**, 4015 (2004)]. Our comparative analysis of cubic nitrides shows that bulk modulus of cubic C_3N_4 is the highest (379 GPa) while it is structurally unstable and should not exist at ambient conditions.

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I. INTRODUCTION

Since the discovery of cubic spinel (γ) phases in group IV nitrides,[1–3] they have received a renewed interest in the past few years due to prediction of superhardness[4] in these class of materials. It is also expected that these spinel classes of nitrides will exhibit interesting electronic properties, such as varying electronic band-gap energies suitable for optoelectronic applications. So far, the binary nitrides of tin,[1] germanium,[2] and silicon[3] have been synthesized and shown to adopt the spinel structure under different experimental conditions. These new polymorphs have the dense spinel structure with silicon (Si)/Ge/Sn atoms in octahedral as well as tetrahedral coordination with nitrogen and the coordination of nitrogen is four. The crystal structure of γ-A_3N_4 (γ-A_3N_4, A=Si, Ge, and Sn) (space group $Fd\bar{3}m$, No. 227) can be described as a distorted close-packed lattice of nitrogen atoms at (u,u,u) positions with A atoms occupying 1/8 of the tetrahedral interstitial sites and 1/2 of the octahedral sites.[1–3] The anion arrangement produces a rigid-vertex linkage of A-filled regular tetrahedra (A^tN_4) and distorted octahedral (A^oN_6) sharing half of their edges. The cation sublattice can be described as an array of empty corner-sharing tetrahedra and A-filled truncated tetrahedra. Recent attempts to describe and predict mineral compression have led to the interpretation of the crystal bulk modulus in terms of the bulk moduli of the constituent cation-anion tetragonal and octahedral polyhedra.[5] The volume of the unit cell can also be partitioned into atomic compartments. In this ion-in-the-lattice model, recently suggested by Pend as *et al.*,[5] there is a direct relation between the local and bulk properties. Thus, the bulk compressibility can be expressed as a sum of the atomic compressibilites weighted by the corresponding fractional volume occupancies. This theory indicates that the high-pressure behavior of any cubic spinel is determined mainly by its anion sublattice. Moreover, in case of spinel nitrides, nitrogen is the most compressible ion whereas the metal cations generally are more difficult to compress. In terms of the ion-in-the-lattice equation of state (EOS), it is found that the nitrogen contribution to the compressibility is much larger than the cation contribution, and in fact almost identical with the observed bulk compressibility. As a result, the superhard behavior of γ-Si_3N_4 is determined mainly by the nitrogen anion sublattice, in agreement with the previous findings for the oxide and selenium spinels. Therefore, the bulk modulus of the spinel phase is expected to be high, primarily determined by the nitrogen sublattice but it should be influenced by the choice of cations. A very high-bulk modulus of 369 GPa (Ref. 6) has been predicted for the cubic phase of C_3N_4, without any success in synthesizing this material. Though both Si_3N_4 and Ge_3N_4 have similar bulk moduli, the same for Sn_3N_4 has been predicted to be significantly different. Also, from recent nanoindentation studies,[7] tin nitride spinel was found to be significantly softer and more plastic than its lighter congeners (Si_3N_4 and Ge_3N_4). Thus, the exact role of the cation in determining the stability and elastic properties is not yet completely understood.

Tin nitrides are of special interest due to their promising semiconducting and electrochromic properties,[8,9] The feasibility of utilizing tin nitride thin film as write once, optical recording media has also been reported.[10] Therefore, the precise knowledge of the stability and mechanical properties of γ-Sn_3N_4 would be of great interest for several practical applications. Though the ambient bulk modulus (B_0) of γ-Si_3N_4 and γ-Ge_3N_4 has been intensively investigated,[11–13] there have been no experimental studies to determine the compressibility of tin nitride. With lack of experimental data, first-principles calculations have been used to investigate the properties of Sn_3N_4.[7,14–17] However, the predicted values of the bulk modulus appear to vary between 186 and 218 GPa.

In this work, we have performed high pressure x-ray diffraction (XRD) measurements on γ-Sn_3N_4 to determine the bulk modulus from the volume as a function of compression. We have also carried out first-principles density-functional theory (DFT) calculations in the generalized gradient approximation (GGA) to achieve a consistent understanding of our experimental findings. First-principles calculations have been carried out for other group-IV nitrides as well to (a) determine the stability of the spinel phase with respect to pressure and possible phase transitions and (b) understand the influence of cation on elastic behavior. Based on our calculations, we also discuss the stability of cubic phase of C_3N_4 at ambient conditions.

II. EXPERIMENTAL AND FIRST-PRINCIPLES CALCULATION DETAILS

Spinel tin nitride (γ-Sn_3N_4) was synthesized by high-pressure solid-state metathesis reactions where tin tetraiodide was reacted with lithium nitride and ammonium chloride in a piston-cylinder apparatus at 623 K and 2.5 GPa. γ-Sn_3N_4 was recovered at ambient conditions after quenching and subsequent release of pressure. Details of the synthesis procedure can be found elsewhere.[18] *In situ* high-pressure angle dispersive x-ray powder diffraction measurements (up to ~26 GPa) were performed using the monochromatic synchrotron radiation ($\lambda = 0.68881$ Å) at XRD1 beamline at ELETTRA synchrotron source, Italy. The choice of highest pressure of 26 GPa was deliberate to capture the discrepancy in bulk modulus. The two-dimensional XRD patterns were collected on a MAR345 imaging plate. The sample-to-detector (image plate) distance was calibrated by collecting the diffraction pattern of powdered Si at ambient conditions. The one-dimensional diffraction patterns were obtained by integrating along the Debye-Scherrer ring in the two dimensional image patterns using the FIT2D software.[19]

Polycrystalline Sn_3N_4 powder was placed together with gold into the 200 μm hole of a stainless steel gasket (T301), preindented to 60 μm, inserted between the diamonds of a Mao-Bell-type diamond anvil cell. The pressure was determined using the known equation of state of gold.[20] Methanol-ethanol-water (MEW) mixture (16:3:1) was used as pressure transmitting medium. To develop a microscopic understanding of the discrepancy between the calculated bulk modulus[7,14–17] earlier and our experimental estimate, we present different first-principles calculations based on DFT with GGA (Ref. 21) for the exchange correlation energy, as implemented in PWSCF (Ref. 22) package. We use ultrasoft pseudopotentials[23] to describe the interaction between the ionic core and valence electrons, and a plane-wave basis with energy cut-offs of 30 and 240 Ry in representation of wave functions and charge density, respectively. Integrations over Brillouin zone are sampled with an $8 \times 8 \times 8$ Monkhorst Pack Mesh.[24] Structural optimization is carried through minimization of energy using Hellman-Feynman forces in the Broyden-Fletcher-Goldfarb-Shanno-based method. Complete phonon dispersion is determined using DFT-linear response and $2 \times 2 \times 2$ mesh-based Fourier interpolation of interatomic force constants.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the XRD patterns of γ-Sn_3N_4 at various pressures. The cell parameters were obtained by analyzing the XRD profiles by Le-Bail profile fit using the GSAS software.[25] Ambient lattice parameter has been found to be $a = 9.0205(5)$ Å, which is in close agreement to earlier reported value.[18] Upon increasing the pressure, we did not observe any new diffraction peaks (see Fig. 1) or sudden discontinuity in the pressure dependences of the *d* values up to the maximum achieved pressure of ~26 GPa. This indicates that γ-Sn_3N_4 does not undergo any transition and remains in the cubic crystal structure up to the highest achieved pressure. Figure 2 shows pressure volume compression data. Using the second order Birch-Murnaghan (B-M) ($B_0' = 4$) EOS (Ref. 26) to fit the volume compression data in the whole pressure range (i.e., ~26 GPa), we found the bulk modulus (B_0) to be 145($\pm$1.7) GPa. However, it is known that beyond 11 GPa, use of MEW medium introduces nonhydrostaic stress environments[27,28] which in turn can impact the equation of state. In order to see the effect of nonhydrosta-

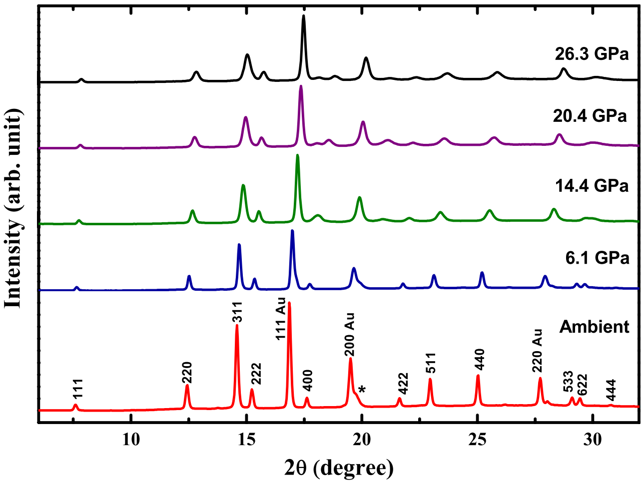

FIG. 1. (Color online) Pressure evolution of x-ray diffraction patterns of γ-Sn_3N_4 compressed quasihydrostatically in MEW up to 26 GPa. Diffraction lines due to gold (Au) (used for *in situ* pressure calibration) and stainless steel gasket (*) are also identified.

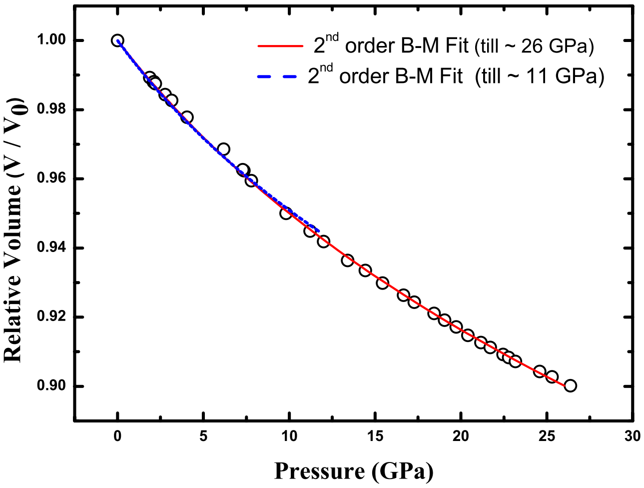

FIG. 2. (Color online) Relative volume change in γ-Sn_3N_4 as a function of pressure at ambient temperature [solid and the dashed lines are second-order Birch-Murnaghan fits to the experimental data (open symbols) till 26 GPa and 11 GPa, respectively].

TABLE I. Experimental and calculated equilibrium lattice constant (a_0) and bulk modulus (B) of the γ-phase of different group-IV nitrides.

	Calc. a_0 (Å)	Expt. a_0 (Å)	Calc. B (GPa)	Expt. B (GPa)	Band gap (eV)	Internal parameter (u)
γ-Sn_3N_4	9.136	9.0205 9.0144[a] 9.037[b]	158	149(±1.2)	0.2	0.2592
γ-Si_3N_4	7.792	7.7381(2)[c] 7.7339(1)[d]	292	308(±5)[c]	3.4	0.2575
γ-C_3N_4	6.796	Yet to be synthesized	379		1.02	0.2559

[a] Reference 18.

[b] Reference 1.

[c] Reference 12.

[d] Reference 11.

ticity, we have plotted the lattice parameter of gold obtained using the individual diffraction lines of gold.[29] However, surprisingly we did not find significant differences between the lattice constants obtained from individual gold lines though nonhydrostatic effects beyond 11 GPa are evident in our diffraction peak broadening. Hence, pressure-volume data below 11 GPa (hydrostatic regime) was further used to explore the compression behavior of the γ-Sn_3N_4 phase to obtain a more accurate equation of state. Using the same second-order Birch-Murnaghan ($B_0'=4$) equation of state (B-M EOS) (Ref. 26) we have fitted the volume compression data in the hydrostatic pressure regime (i.e., till 11 GPa) and we found an increase in 4 GPa in the bulk modulus (B_0) value (i.e., 149 ± 1.2) GPa. It is interesting to note that the bulk modulus value (i.e., 149 ± 1.2 GPa) thus obtained is much lower than the predicted bulk modulus values.[7,14–17] Thus, it was necessary to revisit the theoretical calculations.

Our theoretical estimate of the lattice constant of γ-Sn_3N_4 is 9.136 Å, within typical GGA errors of the experimental value of 9.0205 Å.[18] Bulk modulus estimated from first-principles energies as a function of volume is 158 GPa, in reasonable agreement with our measured value of 149 GPa reported here. The experimental value could be improved further by use of better hydrostatic medium such as neon or helium gas, inaccessible to us at present. We note that the earlier[17] theoretical estimate of the bulk modulus is within local-density approximation (LDA) (contrary to the claim of use of GGA in this paper; we have reproduced their result with the same code and LDA choice of exchange correlation function), and is overestimated to be 187 GPa. Thus, the observed softness of Sn_3N_4 reflected in the lower value of B_0 here should be reliable. With the same choice of density functional for exchange correlation energy, we systematically studied properties of other group IV nitrides in the spinel structure, and find that the bulk modulus (see Table I) reduces from 379 GPa of carbon nitride to 158 GPa of Sn_3N_4. While the lattice constant increases from carbon to tin by almost 30%, consistent with the size of the cation, the internal structural parameter (u) changes by only 2%.

The local stability of a structure can be confirmed through determination of the full phonon dispersion, and by verifying that there are no unstable modes in the structure. Our results (see Fig. 3) clearly show that C_3N_4 in the spinel structure is unstable with respect to both shear acoustic and optical modes, and should not form. This is consistent with the fact that there are no experimental reports so far on C_3N_4 in the spinel form. We also find that the frequency range (band

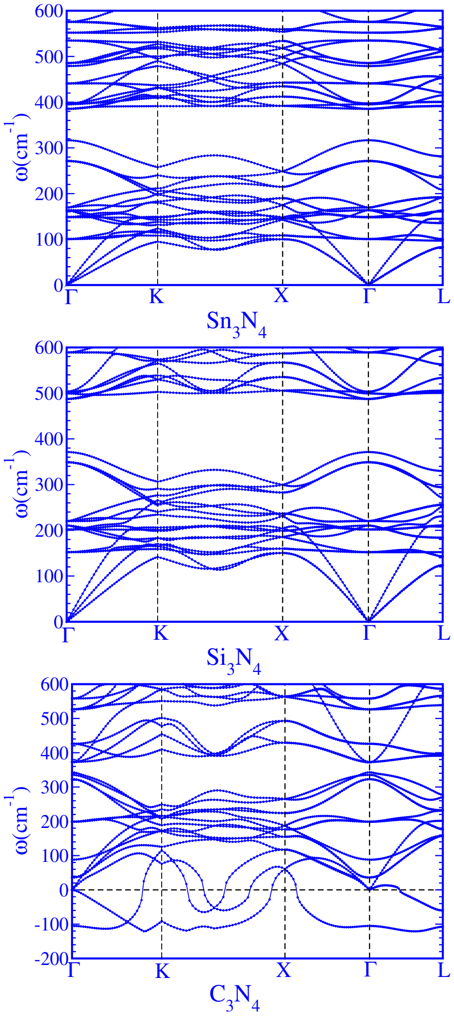

FIG. 3. (Color online) Phonon dispersion of γ-Sn_3N_4, γ-Si_3N_4, and γ-C_3N_4 at equilibrium lattice constant.

TABLE II. Calculated Born effective charges of the octahedral, tetrahedral coordinated cations, and N atoms and electronic dielectric constant in the γ phase of different nitrides.

	Z^* of tetrahedral cation	Z^* of octahedral cation	Z^* of N	Dielectric constant
γ-Sn_3N_4	3.90	4.17	−3.02	9.17
γ-Si_3N_4	3.59	3.70	−2.72	5.29
γ-C_3N_4	1.90	3.98	−2.45	8.99

width) of acoustic branches reduces from silicon to tin nitrides, confirming their increasing elastic softness. If K is the spring constant or the stiffness of a bond and a is the lattice constant, a simple analysis shows that the bulk or elastic modulus should scale as K/a. Although the slopes of the acoustic modes in these nitrides seem different in the phonon dispersion (see Fig. 3), variation in B_0 with $1/a$ is almost linear and has been found to fit the linear equation, $B_0 = (5857/a) - 475$. (In studying the variation in B_0 with $1/a$, the B_0 and a values for γ-Ge_3N_4 have been taken from the calculation done by Mori-Sánchez *et al.*[30]) This means that the bond-stiffness in the nitrides studied here is quite similar and it is the volume of the unit cell that is responsible largely for the monotonous decrease in the Bulk modulus from carbon to tin nitride. As the spinel structure contains cations with tetrahedral and octahedral coordination, it is not straightforward to describe it with a single type of a bond. Since all anions are symmetry equivalent, our reference to bond stiffness here is reasonable in the sense of average bond stiffness.

Our estimates of the Born effective charges (Z^*) also bear a similar feature (see Table II), with two types of effective charges of a cation and degenerate effective charges of N. While the effective charges of Si_3N_4 and Sn_3N_4 are similar, those of C_3N_4 are singularly different. We find that the effective charge of carbon is most anomalous (i.e., deviates most from its nominal charge of $Z^*=4$); this is not very surprising, as the anomalous charges (though larger than the nominal values) are known to correlate with structural instabilities (the presence of unstable vibrational modes) in the system.[31] We also note that the effective charges of carbon atoms with fourfold and sixfold coordination are rather different, in contrast to relatively similar charges of the two symmetry inequivalent cations in Si and Sn nitrides. We find that the band gap (see Table I) steadily increases from 0.2 eV in Sn_3N_4 to 3.4 eV in Si_3N_4 but reduces substantially to 1.02 eV in C_3N_4, confirming rather different nature of the electronic structure and bonding in C_3N_4 from the rest. Our analysis based on projection of energy eigenfunctions on the atomic orbitals shows that carbon in spinel-C_3N_4 is close to being sp^3 hybridized with covalent bonding with N while the cations in Si_3N_4 and Sn_3N_4 appear more ionic. In summary, the unexpectedly low measured bulk modulus of Sn_3N_4 does follow the trend in properties of the group IV-nitrides and seems to be readily understandable.

Our experiments show that Sn_3N_4 remains stable in the spinel structure up to 26 GPa. We now use first-principles simulations to explore its stability at much higher pressures.

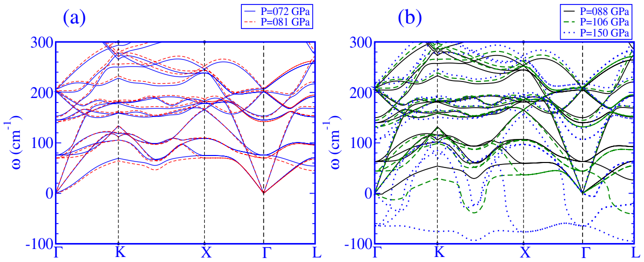

FIG. 4. (Color online) Phonon dispersion of γ-Sn_3N_4. as a function of pressure, (a) below the critical pressure ($P_c = 88$ GPa) and (b) on and above the critical pressure.

Since it is difficult to explore all possible structures as a function of pressure, we determine complete phonon dispersion of cubic Sn_3N_4 as a function of pressure. This is an efficient method to find unstable modes and detect any structural transition that the spinel structure would undergo with pressure, and is similar in spirit to approach used commonly in ferroelectric structural transitions.[32] Here, phonon spectrum is used to evaluate the local stability of a system. For materials which undergo second-order structural phase transformation (in the second-order transition there is no energy barrier between the two phases) as a function of pressure, transition pressure estimation using total-energy calculations and the unstable phonon mode analysis would be same. However, for materials undergoing first-order structural phase transformations (first-order transition is characterized by an energy barrier between the two phases), transition pressures estimation based on the total-energy calculation and the unstable phonon modes are expected to be different, the latter providing an upper bound to transition pressure. Estimation of the transition pressure from total energies requires energy curves for the two candidate structures [as done in Ref. 14]. In the present work we have restricted our self to the local stability of spinel structure establishing ultimate limit to its stability with respect to pressure. Our results (see Fig. 4) show that the Sn_3N_4 remains stable locally in the spinel structure up to pressures of 88 GPa, and develops an instability in the transverse acoustic branch along $\langle 111 \rangle$ direction. Thus, Sn_3N_4 in the spinel structure will distort with a shear-strain above 88 GPa suggesting a transition from cubic to low-symmetry phase. At higher pressures, we find that many more unstable modes develop that involve optical phonons as well, suggesting that the structures beyond 88 GPa are expected to be more complex. It has already been shown by Huang *et al.* [Ref. 14] that the possible high-pressure phases of Sn_3N_4 are $CaFe_2O_4$ and $CaTi_2O_4$-type structures. Electronic structure of Sn_3N_4 is also rather sensitive to pressure but exhibits an unusual trend: its band gap increases rather sharply from 0.2 eV at 0 pressures to about 2 eV at a pressure of 50 GPa. This was observed experimentally as a color change in the sample from dark brown to red at high pressures. This is indeed consistent with the trend in band gaps from Sn_3N_4 to Si_3N_4, where the pressure has chemical origin (i.e., the lattice parameter decreases with increasing pressure which is somewhat similar to substitution of cations with smaller ionic radius).

IV. CONCLUSION

In summary, *in situ* angle dispersive high pressure x-ray studies reveal that bulk modulus of γ-Sn_3N_4 is 149($\pm$1.2) GPa and is stable up to a pressure of 26 GPa. Our first-principles calculations are in excellent agreement with these results with an estimate of a bulk modulus of 158 GPa, well below the earlier calculations. Thus, we demonstrate that γ-Sn_3N_4 is highly compressible, compared to the lighter members (Si and Ge) in the family and hence cannot be used in mechanically demanding environments. We predict a structural phase transition in γ-Sn_3N_4 at 88 GPa based on phonon dispersion calculation as a function of pressure. While our calculations confirm a very high value of bulk modulus of C_3N_4 (as predicted earlier),[6] our finding of unstable phonon modes and anomalous Z^* values show that γ-C_3N_4 is unstable at ambient conditions. This is in agreement with no experimental reports so far on C_3N_4 synthesized in the cubic form.

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