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Evidence about the hardness of hypothetical dense polymorphs of C_3N_4 relative to diamond

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Abstract (600 characters with space!)

An empirical linear correlation of hardness and shear modulus was revealed for the spinel nitrides of the group 14 elements, γ-M_3N_4 where M=Si, Ge, Sn, which also holds for the hexagonal α- and β-phases of Si_3N_4. The correlation, completed here by a careful measurement of the bulk modulus of γ-Sn_3N_4, was used to predict the hardness of hypothetical dense phases of C_3N_4 which elastic moduli we calculated. Our calculation approach was supported by the agreement with the experimental data for γ-M_3N_4. The hardness of all proposed dense polymorphs of C_3N_4 are predicted to be below that of diamond.

Keywords: spinel tin nitride, C_3N_4, hardness, elastic moduli, first-principles calculations, powder XRD, high-pressure equation of state

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I. INTRODUCTION

In the 1990's the excitement about materials harder than diamond was heated up after theoretical predictions of Liu and Cohen [1] that the hardness of the hypothetical carbon nitride β-C_3N_4 with the hexagonal structure, analogous to that of the well-known β-Si_3N_4 (Greek letters indicate in this work particular types of crystal structures described below), may be comparable with that of diamond. The Vickers hardness of H_V=100 GPa is adapted in the literature for the latter well known dense phase of carbon forming in the deep Earth at high pressures and temperatures [2]. The basis of this speculation was the assumption that hardness of a covalent solid can be reliably predicted from its bulk modulus B_0 at atmospheric pressure. The B_0 value of β-C_3N_4 was estimated from an empirical dependence of the bulk moduli of covalent solids on the interatomic bond length as described in Ref. [1]. Later on, Teter and Hemley [3] theoretically examined other hypothetical polymorphs of C_3N_4, among which the cubic c-C_3N_4 (derived from the Willemite-II structure of Zn_2SiO_4) was predicted to exhibit B_0=496 GPa, which is significantly higher than that of diamond (B_0 =442 GPa [4]), and to be stable at high pressures. The proposition that c-C_3N_4, if synthesized, could be harder than diamond heated up the search for dense forms of this hypothetical compound even further. For the next dense polymorphs such as α-C_3N_4 (hexagonal crystal structure analogous to that of α-Si_3N_4) and pseudo-cubic C_3N_4 (derived from the zinc-blende structure) B_0 above 400 GPa was predicted [3]. Similarly, further hypothetical polymorphs of C_3N_4 examined theoretically in multiple publications, such as γ-C_3N_4 having the cubic spinel structure and *zb*-C_3N_4 having the cubic zinc-blende structure showed bulk moduli comparable with that of diamond [5]. Theoretical studies on C_3N_4 were accompanied by multiple attempts to produce a dense form of this compound, but none of the reports about a successful synthesis could be reproduced so far e.g.[6,7]. Stabilization of the claimed C_3N_4 products by hydrogen (usually present in the starting reactants) was considered only sporadically; e.g.[8,9]. With the research extension in this field, doubts about the reliability of B_0 as a hardness predictor grew and empirical evidence was presented that the shear modulus G_0 should be used instead [10]. The theoretical justification of this statement can be summarized as follows [11]: Hardness (or yield stress) is a value describing material resistance to plastic deformations which occur only when shear stress is applied. According to the Frenkel analysis, the strength of an ideal crystalline solid is proportional to its G_0. The strength of a real crystal is significantly smaller than that of an ideal crystal and is controlled by movement and multiplication of lattice defects such as dislocations. The shear stress needed for activation of these processes is also proportional to G_0. Even though a correlation of hardness and G_0 is supported empirically, a significant scatter can be recognized if data for materials of different nature (e.g., ionic vs. covalent compounds) are compared. The attempts to establish empirical correlations for covalent compounds of one family (e.g. for the group 14 elements having diamond structure [12]) are rare because the number of such families, where G_0 and H extend over a reasonable range, is strongly limited. Another source of significant uncertainties is the fact that experimental G_0 and hardness of considered compounds are usually reported in distinct publications for samples of different origin with different or not described state of porosity, amount and nature of sintering additives *etc*. Up to very recently first-principles calculations provided rare and strongly deviating values of shear moduli of dense C_3N_4 polymorphs [3,13,14]. Extended calculations of their single crystal elastic moduli C_{ij} and then G_0 were presented in the last years [15,16], but without careful validation of the

calculation methods via comparison with experimental data for existing related compounds such as α-, β- or γ-Si_3N_4.

In this work we unveil an empirical linear correlation of experimental values of G_0 and H_n (hardness measured using the nanoindentation testing) for dense nitrides of the group 14 elements (to which carbon belongs also) having spinel structure γ-M_3N_4 (where M = Si, Ge, and Sn). In particular, we made a selection of reliable experimental data on G_0 and H_n of the spinel nitrides and completed it by a thorough measurement of B_0 of γ-Sn_3N_4 permitting deriving of its G_0 from the earlier nanoindentation data [17]. The family of spinel nitrides, discovered in 1999 in the course of the search for a superhard C_3N_4 [18-22], is today well examined and measurements of elastic moduli and hardness for the same samples are available in the literature with one exception we remedy here. Spinel-nitrides are one of a few compound families having at least three members with a hardness spreading over a broad range. Obviously, three is the minimal number of data pairs needed to confirm empirically a linear relation between two physical values, e.g. H_n and G_0. Reliable data for G_0 and nanohardness H_n were obtained for γ-Si_3N_4 and γ-Ge_3N_4 from measurements of equations of state (EOS) on compression, $V(P)$, of the reduced elastic modulus E_r and H_n in nanoindentation tests, and of sound velocities via Brillouin spectroscopy [17,23,24]. The values of E_r and H_n were measured also for densified samples of γ-Sn_3N_4 [17] but the earlier experimental B_0, needed to derive G_0 from E_r using the well established approach [25,26], is less reliable: In only one work, B_0 of γ-Sn_3N_4 was obtained from $V(P)$ measured to relatively low pressures of 26 GPa and potentially systematically biased due to use of a methanol-ethanol-water pressure transmitting medium becoming non-hydrostatic above 11 GPa [27]. This shortcoming is remedied here: $V(P)$ of γ-Sn_3N_4 was accurately measured to much higher pressures under quasihydrostatic loading, and the G_0 value derived from the B_0 one that we have obtained, combined with the earlier reported E_r. The result permits us to confirm the reliability of a linear dependence of H_n on G_0 for the three spinel nitrides. Furthermore, we have performed first-principles calculations of single crystal elastic moduli C_{ij}, B_0, and G_0 for the existing γ-M_3N_4 in order to validate our calculation approach by comparison with the reliable experimental data. Then, C_{ij} values of all proposed dense polymorphs of C_3N_4 were calculated and G_0 values for the related isotropic polycrystalline bodies were derived. We used these values to estimate H_n of all proposed dense C_3N_4 polymorphs using the established here empirical correlation $H_n(G_0)$ for γ-M_3N_4 and, finally, to make a conclusion about the hardness of dense C_3N_4 materials.

II. METHODS

The sample of γ-Sn_3N_4 (γ indicates spinel structure described by the space group (S.G.) F$d\bar{3}m$ where 2/3 of cations are octahedrally coordinated and the remaining 1/3 is tetrahedrally coordinated by anions) used in this work was synthesized earlier [22]. It contained minor admixtures of SnO_2 and SnO (Figure 1) which, however, did not bias our measurement of B_0 and the first pressure derivative, B_0'. This is because X-ray diffraction (XRD) provides the unit cell volume (equivalent to the specific volume of a completely densified material) for each of the compounds independently. The unit cell parameter of γ-Sn_3N_4 at ambient conditions was measured using a standard diffractometer (Cu $K_{\alpha 1}$ radiation).

The EOS of γ-Sn_3N_4 was measured on compression in a diamond anvil cell (DAC) with anvils having culets of 350 μm in diameter. A platelet of the powder sample of about 50 μm in diameter and 10 μm in thickness (obtained by a preliminary compaction between the diamond anvils) was placed in the 120 μm hole in the pre-indented rhenium gasket of about 50 μm in thickness and embedded in condensed argon, which solidifies above 1.2 GPa [28,29]. Use of the argon pressure medium provided *quasi*-hydrostatic pressure conditions up to 50 GPa because the uniaxial stress in solid argon does not exceed, similar to solid neon, ~1% of the pressure value [30]. The pressure was determined from the earlier reported $V(P)$ of crystalline argon [29]. The unit cell volumes of both γ-Sn_3N_4 and argon were obtained from the angle-dispersive powder XRD patterns generated using a monochromatic X-ray synchrotron beam (wavelength 0.37380(4) Å) collimated to 20 μm (beamline ID27, ESRF, Grenoble, France). The two-dimensional XRD patterns were collected with an image-plate detector MAR345 and converted to 1D-diffractograms (Figure 1) using the Fit2D software [31].

First-principles calculations of the stress-strain properties of the spinel nitrides and of a variety of dense C_3N_4 polymorphs were performed using density-functional theory (DFT). We employed the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) exchange-correlation functional [32], the improved Troullier-Martins norm-conserving pseudopotentials for core electrons and numerical atomic orbital basis set for valence electrons within the Kohn-Sham formalism of DFT [33]. Periodicity was enforced with a real-space mesh cut-off set to 200 Ry. Geometry optimizations were completed when the magnitude of forces on each atom is less than 0.008 eV/Å. All calculations were performed using the SIESTA simulation package [34].

For calculations of the elastic stress tensors of cubic crystals, we introduced a uniaxial strain ε_{xx} from 0.5 % to 5 % in 0.5% increments. C_{11} and C_{12} were then calculated from the resulting stress tensor σ_{xx}. While introducing shear strain by shifting the lattice angle φ from -6° to +6°, a pure shear strain ε_{xy} was produced and C_{44} was calculated from the resulting stress tensor σ_{xy}. To derive shear moduli for isotropic polycrystalline samples of the spinel nitrides, γ-M_3N_4 where M=Si, Ge, Sn, from our calculated C_{ij}, we used the Voigt-Reuss-Hill approach known to provide values (labeled as $G_{0H)}$ close to experiment. In the case of C_3N_4 polymorphs we calculated shear moduli using the Voigt approach (labeled as G_{0V}) which gives the upper limit for G_0 and, thus, provides the upper limit for H_n when a $H_n(G_0)$ systematics is applied.

III. RESULTS AND DISCUSSION

The cubic lattice parameter of γ-Sn_3N_4 at ambient conditions we measured to be a_0=9.033(6) Å, in agreement with the value a_0=9.037(3) Å reported in the original paper on its synthesis [22]. The latter value, measured with a higher precision, was used in our data treatment. XRD patterns of the sample compressed in a DAC up to 50 GPa showed ten or more diffraction peaks perfectly matching the spinel structure of γ-Sn_3N_4 (Figure 1) and up to five peaks of crystalline argon. From these patterns we determined the unit cell volume of γ-Sn_3N_4 as a function of pressure $V(P)$ (Figure 2) which showed a smooth decrease with pressure. No signs of a phase transition could be recognized. The third-order Birch-Murnaghan EOS was fitted to the experimental data points $V(P)/V_0$ and B_0 = 158(11) GPa and B' = 5.4(1.1) were obtained (Table I). A fit with B_0' fixed at 4 resulted in a slightly

higher B_0=174(3) GPa. The B_0 values we obtained for γ-Sn_3N_4 are ~17% higher than the only earlier reported experimental B_0=149 GPa (with fixed B_0'=4) [27] but still below the earlier predicted ones [17,35,36] (Table I). The significant discrepancy with the previous measurement we explain by use of a nonhydrostatic pressure medium and the short pressure range. Our experimental B_0=158 GPa significantly surpasses the earlier theoretical values calculated both using the LDA [35] and GGA [27,36] DFT approaches. In contrast, it perfectly agrees with our calculated B_0=169 GPa.

Applying our experimental B_0 and the earlier reported E_r=167(36) from the nanoindentation tests of a densified sample [17], we derived G_0 of γ-Sn_3N_4 to be 67(20) GPa (if B_0=158 GPa) or 65(19) GPa (if B_0=174 GPa) (Table I). The given error margins are mostly due to the uncertainty in E_r [17]. Surprisingly, a similar value of G_0=64 GPa was derived in Ref. [17] using the same E_r and a higher theoretical value of B_0=186 GPa. This indicates a weak influence of the approach on the bulk modulus uncertainty in contrast to uncertainties or errors in E_r [24]. Our experimental G_0=67(20) GPa agrees, within the experimental uncertainty, with our theoretical G_0=88 GPa derived from the calculated C_{ij} (see Table S-I in *Supplementary information*) applying the Voigt-Reuss-Hill (VRH) approach (Table I). Because we are not aware of any other calculation of C_{ij} or G_0 of γ-Sn_3N_4, a direct comparison with other theoretical methods is not possible. However, we could recognise that the elastic anisotropy of γ-Sn_3N_4 of $A=2\cdot C_{44}/(C_{11}-C_{12})$=2.1 is very similar to A=1.9-2.0 we have derived from the earlier calculated C_{ij} of γ-Ge_3N_4 and γ-Si_3N_4 [37,38].

In order to further validate our theoretical approach, we calculated C_{ij} moduli of γ-Si_3N_4 and γ-Ge_3N_4, as well as their B_0 and G_0 using the VRH approach and compared with the existing reliable measurements (Table I). In the case of γ-Ge_3N_4 only one experimental B_0=295(5) from $V(P)$ was reported [19] and used in the unique nanoindentation work to derive G_0=124 GPa applying E_r=275 GPa [17,24]. This experimental B_0 is remarkably higher than our theoretical B_0=227 GPa (by ~25%) as well as the earlier one of B_0=242 GPa calculated using the LDA approach [38] (Table I). In contrast, our calculated G_0=168 GPa and the earlier LDA result [38] outperform (also by ~25%) the experimental G_0=124 GPa [17,24]. On the other hand, applying our calculated B_0 and G_0 for γ-Ge_3N_4 we obtain a theoretical value of E_r=308 GPa which is only ~10% above the measured one. This indicates a need of an independent measurement of B_0 and G_0 of γ-Ge_3N_4 and verification of a low porosity of samples used in the nanoindentation tests. It should be mentioned here that we did not consider for γ-Ge_3N_4, and below for γ-Si_3N_4, multiple first-principles calculations where only bulk moduli were reported because our work is focused on G_0 values needed to predict the hardness of γ-M_3N_4 and of hypothetical dense polymorphs of C_3N_4.

Despite a large number of measurements of B_0 for γ-Si_3N_4, only one very recent work reports both hardness and shear modulus (Tables I and II) for one and the same isotropic densified polycrystalline sample [23]. In this work both G_0=248(1) GPa and B_0=303(4) GPa were obtained using Brillouin light spectroscopy (BLS). This B_0 is slightly higher than B_0=290(5) GPa determined from the high-pressure EOS measurements [25]. In contrast, in the earlier nanoindentation tests E_r was measured and G_{0p}=148(16) derived for a sample with an unknown porosity [25]. Even though this G_{0p} is significantly lower than that of the dense sample, it was also considered here as an example of a porous sample. This could be done because above we have recognized that G_0 derived from E_r depends only weakly on

the bulk modulus. B_0 and G_0 of γ-Si_3N_4 obtained from the BLS measurements [23] agree very well with our present first-principles calculations which give B_0=285 GPa and G_{0H}=237 GPa (Table I). This agreement supports further the reliability of our calculation approach thus permitting its extension to C_3N_4 polymorphs. Previous theoretical works where all C_{ij} or the pairs B_0 and G_0 of γ-Si_3N_4 were calculated [37-39] show also a reasonable agreement with the most recent measurements [23] (Table I). However, these calculations were not validated for γ-Sn_3N_4 or γ-Ge_3N_4 and were not extended to dense C_3N_4 polymorphs.

In order to predict the hardness of dense C_3N_4 phases proposed in the literature, we first verified the empirical linear relation between G_0 (Table 1) and the hardness of the above considered dense spinel phases γ-M_3N_4 where M=Si, Ge, or Sn (Figure 3). In particular, we compared hardness values obtained in nanoindentation tests, H_n, (Table II) for the same samples for which elastic moduli, especially E_r or G_0, were measured simultaneously using the same technique [17,25] or BLS [23] (Figure 3). Moreover, we selected, if available, H_n values obtained for similar loads in order to exclude the biasing due to the indentation size effect e.g.[23]: If we consider only the H_n measured for γ-M_3N_4 with small indentation loads of 3-5 mN (Table II) then the linear relation between G_0 and H_n is described by the empirical equation $H_n(G_0)$=0.240(26)·G_0 (Figure 3). Taking into account of the H_n for a transparent γ-Si_3N_4 sample measured with a higher load of ~200 mN insignificantly changes the empirical relation (due to the indentation size effect) to $H_n(G_0)$=0.212(8)·G_0 (Figure 3). Interestingly, the result for one and the same sample of hexagonal α-Si_3N_4 (S.G. P$3_1/c$) reporting G_0 = 144(7) GPa (derived from the measured E_r = 289(7) GPa using the earlier reported B_0=248(10) GPa [40]) and H_n =34.5(2.0) GPa, obtained for a high indentation load of 700 mN [41], is located between these two lines. A good agreement with our steeper $H_n(G_0)$ empirical equation follows from the nanoindentation testing of a polycrystalline sample of β-Si_3N_4 (S.G. P$6_3/m$) where H_n =26(4) GPa was measured for the indentation load of 7.9 mN [42] and G_0 =101(21) GPa could be derived from E_r obtained for the same sample and the same load using the earlier reported B_0 =259 GPa [43].

Finally, we performed calculations of C_{ij} of the five hypothetical dense carbon nitrides proposed in the literature [1,3,14]. In particular, we examined α-C_3N_4, β-C_3N_4 and γ-C_3N_4 having the same structures as the three well-known phases of Si_3N_4, namely, hexagonal low-pressure α- and β-phases (see above) and the γ-phase having the cubic spinel structure (S.G. F$d\bar{3}m$). We also considered two other cubic structures, namely the defect zink-blende *zb*-C_3N_4 (S.G. P$\bar{4}3m$) and the Willemite-II type c-C_3N_4 (S.G. I$\bar{4}3d$). The calculated C_{ij} moduli of these five phases of C_3N_4 are given in Table S-I of the *Supplementary Information*, and compared with earlier predictions. From our C_{ij} we calculated G_0 moduli of the C_3N_4 polymorphs using the Voigt approach, G_{0V} (Table I), and applied to them the empirical systematics $H_n(G_0)$ developed above for the spinel nitrides γ-M_3N_4 (Figure 3). The vertical bars in Figure 3 thus indicate our predicted upper limits for H_n for the considered here dense C_3N_4 phases (Table II). Furthermore, because H_n obtained for low loads in nanoindentation tests provide, in general, upper bounds for the standardized (micro)hardness values, such as H_V, due to the indentation size effect, our empirical H_n values for the C_3N_4 phases are well above their (micro)hardness. The highest shear modulus of G_{0V} = 386 GPa was calculated for *zb*-C_3N_4 (Table I). This value surpasses only insignificantly that of c-C_3N_4 calculated to be G_{0V} = 380 GPa. From our empirical

$H_n(G_0)$ systematics (Figure 3), we predict $H_n \leq 93(10)$ GPa for *zb*-C_3N_4, and thus for any other C_3N_4 phases considered here. This nanoindentation hardness value is well below the Vickers hardness of 100 GPa [2] adopted in the literature for diamond which shear modulus was measured to be G_0=536 GPa [44]. If we apply our systematics to the G_0 value of diamond then the nanoindentation hardness of diamond should be $H_n = 122(7)$ GPa, consistent with the concept of the indentation size effect. Therefore, we can conclude that all hypothetical dense C_3N_4 proposed in the literature will exhibit a hardness below that of diamond.

IV. CONCLUSIONS

We performed accurate measurements of B_0 and B' of γ-Sn_3N_4 via quasi-hydrostatic compression of a polycrystalline sample in a DAC up to 50 GPa. Combining earlier nanoindentation data for a densified sample with our B_0 value we determined the shear modulus of γ-Sn_3N_4. Selecting and analyzing the existing reliable data for the hardness and shear moduli of all known spinel nitrides, γ-M_3N_4, we revealed a linear correlation of their nanohardness and shear moduli. We performed calculations of elastic moduli of the same compounds and found good agreement with the trustworthiest experimental data. The confirmed reliability of our calculation approach permitted its extension to the proposed in the literature dense polymorphs of hypothetical C_3N_4. Applying the developed above correlation of hardness and shear moduli of γ-M_3N_4 we predicted the hardness of several dense C_3N_4 phases and found that all of them are well below the hardness of diamond. Although the prediction of a superhard C_3N_4 was disproved here via combined experimental and computational approaches, full experimental verification of the formation of a dense polymorph of this compound remains an exciting task for the field of solid-state chemistry.

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TABLE I. Parameters of the equation of state (B_0, B_0') and G_0 of γ-Sn_3N_4 measured here in comparison with the experimental data (Exp) for all existing γ-M_3N_4 (where M = Si, Ge, Sn) and calculated moduli (Calc) of γ-M_3N_4 and of the five dense polymorphs of C_3N_4 obtained using either the Generalized Gradient Approximation (GGA), the Local Density Approximation (LDA), or the Molecular Simulation Force Field (MSFF) approach. Our results are highlighted by bold fonts.

Material S.G.		B_0 **(GPa)**	B_0'	G_0 **(GPa)**	**Comment/Ref**
γ-Sn_3N_4 F$d\bar{3}m$	Exp	**158(11)** **174(3)** 149(1.2)	**5.4(1.1)** **4 (fixed)** 4 (fixed)	**67(20)** [a] **65(19)** [a] 	 [27]
	Calc	**169** 187 186 204	 4.34 4.53 4.98	**88** [b] 64 [c] 	**GGA** GGA [36] LDA [17] LDA [35]
γ-Ge_3N_4 F$d\bar{3}m$	Exp	295(5)	3.8(2)	124(17)	[19] & [17,24]
	Calc	**227** 242		**168** [b] 176 [b]	**GGA** LDA [38]
γ-Si_3N_4 F$d\bar{3}m$	Exp	290(5) 303(4)	4.9(6)	148(16) [d] 248(1)	[25] [23]
	Calc	**285** 273 284 311 305 312		**237** [b] 252 [b] 265 [b] 258 [b] 261	**GGA** GGA [37] GGA [38] LDA [37] LDA [38] [39]
α-C_3N_4 P$3_1/c$	Calc	**378** 388 191		**359** [e] 342 [e] 300 [e]	**GGA** GGA [16] MSFF [13]
β-C_3N_4 P$6_3/m$	Calc	**411** 408 252 433		**303** [e] 322 [e] 268 [e] 326 [e]	**GGA** GGA [16] MSFF [13] LDA [14]
γ-C_3N_4 F$d\bar{3}m$	Calc	**433** 442		**351** [e] 352 [e]	**GGA** LDA [15]
c-C_3N_4 I$\bar{4}3d$	Calc	**441** 441 487 496		**380** [e] 400 [e] 393 [e] 319 [e]	**GGA** GGA [16] LDA [15] LDA [3]
***z*b-C_3N_4** P$\bar{4}3m$ (P$\bar{4}2m$)	Calc	**395** 436 422 390		**386** [e] 409 [e] 397 [e] 388 [e]	**GGA** LDA [15] LDA [14] GGA [16]

[a] derived using our B_0 and E_r measured for a densified sample in Ref. [17]; [b] shear modulus derived from theoretical C_{ij} using the Voigt-Reuss-

Hill- or related approximation, G_{0H} [37,38]; [c] derived from experimental E_r using the theoretical B_0 reported in the same work; [d] derived using the E_r measured for a porous sample; [e] shear modulus derived from theoretical C_{ij} using the Voigt approximation, G_{0H}.

TABLE II. Nanoindentation hardness (H_n) of the dense C_3N_4 phases predicted in the present work using the experimental data for γ-M_3N_4 (where M = Si, Ge, Sn). The earlier measured and predicted H_V values of γ-M_3N_4 and of the dense C_3N_4 phases, respectively, are also shown for comparison.

Material S.G.	H_V **GPa**	**Ref.**	H_n **GPa**	**Load mN**	**Ref.**
γ-Sn_3N_4 F$d\bar{3}m$	11(2)	[17]	13(5)	3	[17]
γ-Ge_3N_4 F$d\bar{3}m$	28(5)	[17]	31(6)	5	[17]
γ-Si_3N_4 F$d\bar{3}m$	35(2) 34.9(7)	[45] [23]	36(5) [a] 52(2)	5 200	[25] [23]
α-C_3N_4 P$3_1/c$	84 [b]	[5]	**76-86** [b]	3-200	*This work*
β-C_3N_4 P$6_3/m$	85 [b]		**64-73** [b]	3-200	
γ-C_3N_4 F$d\bar{3}m$	59 [b]		**74-84** [b]	3-200	
c-C_3N_4 I$\bar{4}3d$	91 [b]		**81-91** [b]	3-200	
zb-C_3N_4 P$\bar{4}3m$	89 [b]		**82-93** [b]	3-200	

[a] porous sample, [b] predicted

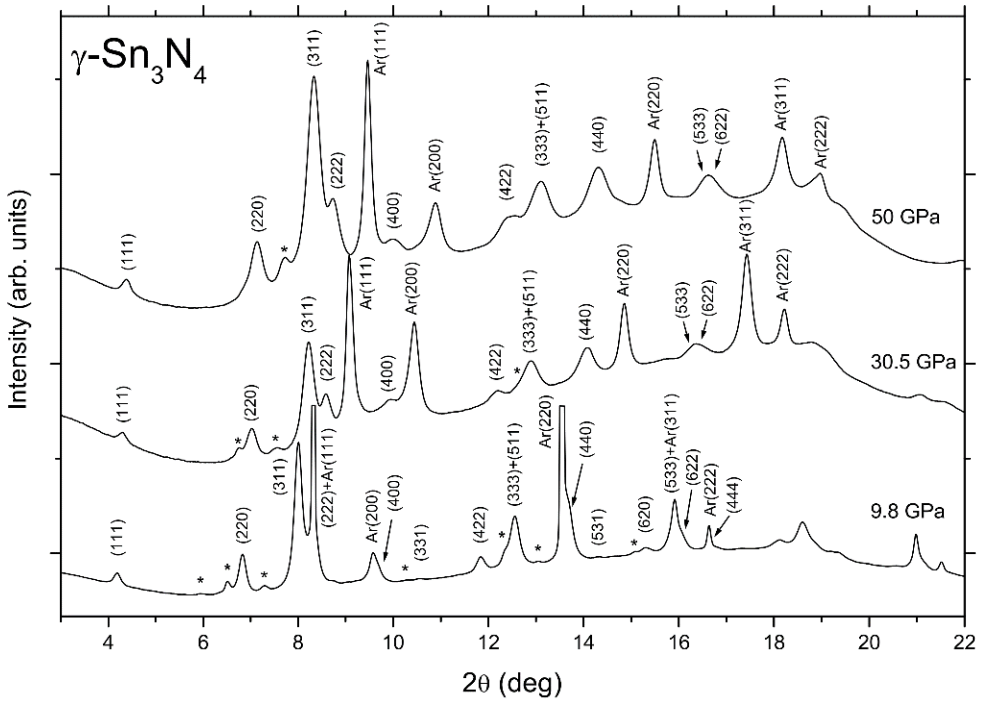

FIG. 1. Examples of powder diffraction patterns of γ-Sn_3N_4 embedded in a quasi-hydrostatic argon pressure medium, which is similarly soft as solid neon [30], and compressed in a DAC to high pressures. Asterisks indicate minor admixtures of SnO_2 and SnO present in the starting material [22].

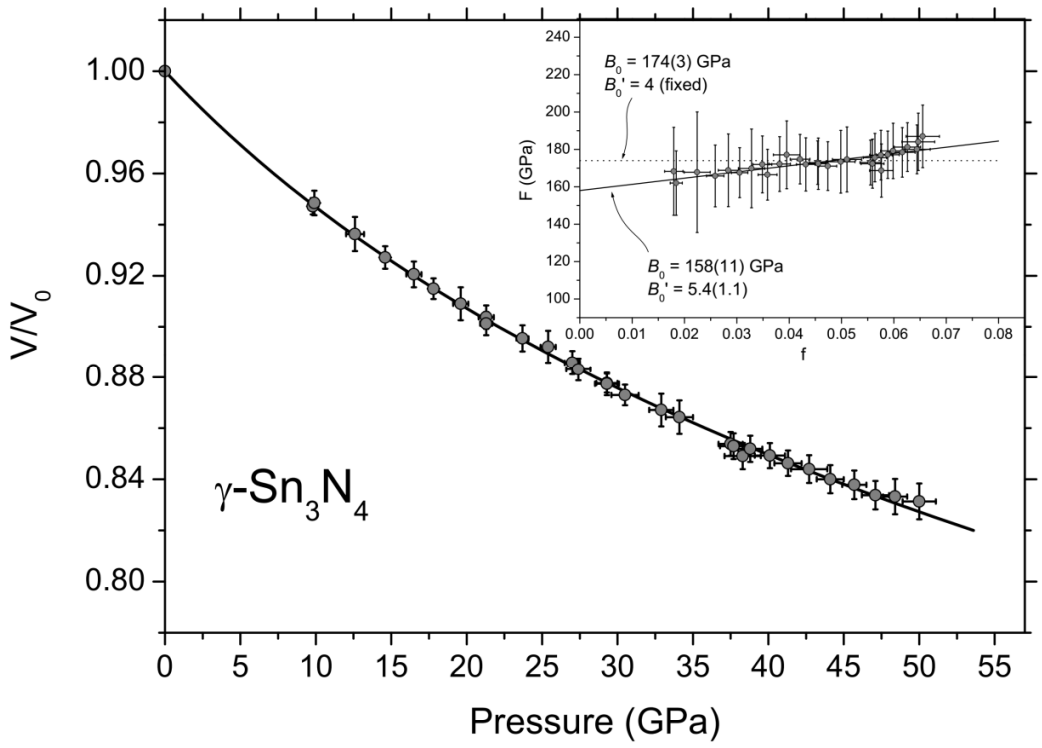

FIG. 2. Relative volume, V/V_0, of γ-Sn_3N_4 as a function of pressure: Solid symbols represent the experimental data-points while the solid line is the least-squares fit of the third order Birch-Murnaghan EOS to the data. **Insert:** compression data of γ-Sn_3N_4 in terms of normalized pressure $F = P/[3f(1+2f)^{5/2}]$ and Eulerian strain $f = [(V/V_0)^{-2/3} - 1]/2$. The solid and dotted lines represent the least-squares fits of the third- and second-order Birch-Murnaghan EOS, respectively.

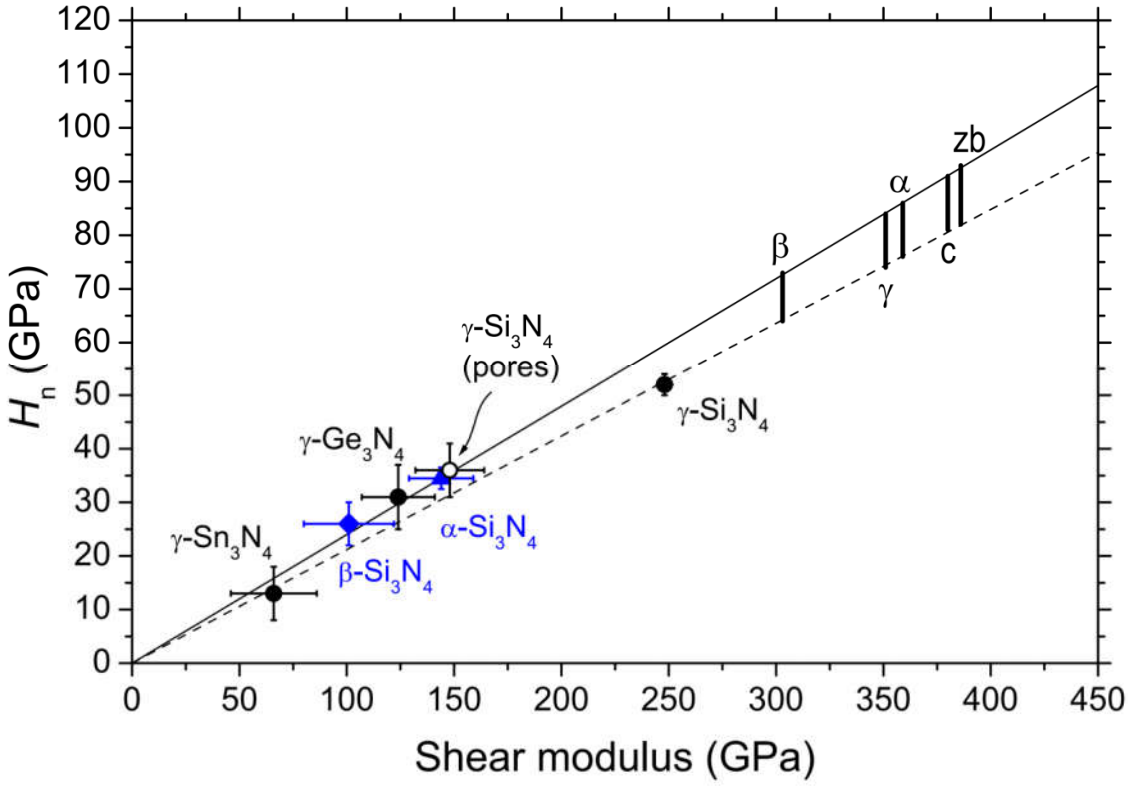

FIG. 3. Empirical relation between the nanohardness H_n and shear modulus G_0 of γ-M_3N_4 (where M = Si, Ge, Sn) where only experimental data-pairs obtained for one and the same sample were considered. Solid and open symbols indicate experimental H_n–G_0 data measured for densified and porous samples, respectively (Tables I and II). Error bars for the experimental G_0 of γ-Ge_3N_4 and γ-Si_3N_4 were calculated here using the literature data. The solid line indicates a linear fit to the data obtained for γ-M_3N_4 with low loads of 3-5 mN and the dashed one to all available data for γ-M_3N_4 (Table II). The H_n–G_0 data for α-Si_3N_4 and β-Si_3N_4 (blue solid triangle and rhombus, respectively) are shown for comparison. Vertical solid bars span the possible H_n values of dense C_3N_4 phases we predict applying our calculated G_0 values and the empirical linear relation $H_n(G_0)$ for γ-M_3N_4.

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