Denser than diamond: *Ab initio* search for superdense carbon allotropes

Qiang Zhu,[1,*] Artem R. Oganov,[1,2] Miguel A. Salvadó,[3] Pilar Pertierra,[3] and Andriy O. Lyakhov[1]

[1]*Department of Geosciences, Department of Physics and Astronomy, and New York Center for Computational Sciences,*
Stony Brook University, Stony Brook, New York 11794, USA

[2]*Geology Department, Moscow State University, 119992, Moscow, Russia*

[3]*MALTA Consolider Team, Departamento de Química Física y Analítica, Universidad de Oviedo,*
ES-33006, Oviedo, Spain

Diamond has the highest number density (i.e., the number of atoms per unit volume) of all known substances and a remarkably high valence electron density ($r_{ws} = 0.697$ Å). Searching for possible superdense carbon allotropes, we have found three structures (hP3, tI12, and tP12) that have significantly greater density. The hP3 and tP12 phases have strong analogy with two polymorphs of silica (β-quartz and keatite), while the tI12 phase is related to the high-pressure SiS_2 polymorph. Furthermore, we found a collection of other superdense structures based on the motifs of the aforementioned structures, but with different ways of packing carbon tetrahedra, and among these the hP3 and tI12 structures are the densest. At ambient conditions, the hP3 phase is a semiconductor with the GW band gap of 3.0 eV, tI12 is an insulator with the band gap of 5.5 eV, while tP12 is an insulator, the band gap of which is remarkably high (7.3 eV), making it the widest-gap carbon allotrope. These allotropes are metastable and have comparable to diamond or slightly higher bulk moduli; their Vickers hardnesses are calculated to be 87.6 GPa for hP3, 87.2 GPa for tI12, and 88.3 GPa for tP12, respectively, thus making these allotropes nearly as hard as diamond (for which the same model gives the hardness of 94.3 GPa). Superdense carbon allotropes are predicted to have remarkably high refractive indices and strong dispersion of light.

Carbon is a unique element in that it adopts a wide range of structures, which range from superhard insulating (diamond and lonsdaleite) to ultrasoft semimetallic (graphite, an excellent lubricant) and even superconducting (doped diamond and fullerenes).[1–4] The number of all possible metastable phases is infinite, and much work both in experiment and theory has been done to search for the carbon phases with special properties (such as metallic conductivity, hardness, etc.).[5–11] Of all the physical characteristics, density is of fundamental interest because it could affect many other mechanical, electronic, and optical properties. Diamond is not only the hardest known material, but also has the highest number density of all known materials,[12] whereas the densest two-dimensional (2D) material is graphene. Such extremely high density, with uniquely high valence electron density (Wigner-Seitz radius $r_{ws} = 0.697$ Å) is a result of a compromise between electronic kinetic energy and exchange-correlation energy. Localizing electrons in such small volume is penalized by the kinetic energy, and to compensate for this penalty, extremely strong bonding (stemming from exchange correlation) is required. Although diamond is the densest known three-dimensional (3D) carbon allotrope in a wide range of pressures, theoretical studies proposed bc8 or R8 structures to be denser.[13–17] Whether there can be other carbon allotropes denser than diamond is still unknown, but the open topology of the diamond structure gives reasons for positive expectations. Here, we report three allotropes of carbon, which are denser than diamond and any previously proposed structures and possess remarkable physical properties.

To search for the densest structures, evolutionary structure prediction was performed using the USPEX code[18,19] in conjunction with *ab initio* structure relaxations using density functional theory[20] (DFT) within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA),[21] as implemented in the VASP code.[22] We used the all-electron projector-augmented wave (PAW) with [$1s^2$] core and plane-wave basis set with the 600-eV cutoff. Such calculations provide an excellent description of the density of tetrahedral phases of carbon; e.g., the computed densities are 3.504 g/cm^3 for diamond (3.52 g/cm^3 from experiment) and 3.496 g/cm^3 for lonsdaleite (3.52 g/cm^3 from experiment). The most significant feature of USPEX is the capability of searching for the global minimum according to the fitness function, given only the chemical composition. Here, we used the density as the fitness function, and all structures are fully relaxed at constant pressure. To ensure that the obtained superdense structures are dynamically stable, we calculated phonon frequencies across the Brillouin zone using the finite-displacement approach as implemented in the FROPHO code.[23]

We have performed structure searches at 0 GPa with up to 12 atoms in the unit cell. Our simulations produced the already known structures of diamond, hexagonal diamond (lonsdaleite), and the bc8 structure, but the highest density was indicated for two hitherto unknown structures, tI12 (with the tetragonal I-42d symmetry and 12 atoms per unit cell) and hP3 (chiral hexagonal structure with the $P6_222$ symmetry and three atoms per unit cell). The two structures have nearly the same density and, at 1 atm, are 3.2% denser than diamond and 2.2% denser than bc8. By using the chemical analogy approach, we explored the possibility for carbon to adopt the same structure as recently discovered for the new allotrope of germanium (tP12), and this gave us yet another superdense carbon allotrope, which is 1.1% denser than diamond.[24]

TABLE I. Crystallographic data for hP3, tI12, and tP12 structures of carbon at zero pressure.

hP3 Space group $P6_222$ $a = b = 2.605$ Å, $c = 2.801$ Å			
Atomic coordinates			
C	3c	0.5000	0.0000	0.0000

tI12 Space group I-42d $a = b = 2.705$ Å, $c = 8.989$ Å			
Atomic coordinates			
C1	4a	0.0000	0.0000	0.0000
C2	8d	0.8333	0.2500	0.6250

tP12 Space group $P4_32_12$ $a = b = 3.790$ Å, $c = 4.661$ Å			
Atomic coordinates			
C1	4a	0.0756	0.0756	0.0000
C2	8d	0.1668	0.3793	0.2171

Table I shows the structural data for the three superdense phases. As shown in Fig. 1, all of them have carbon atoms in the tetrahedral coordination (sp^3 hybridization). Interestingly, the structural motif of the hP3 phase has a binary counterpart in β-quartz SiO_2: in hP3, C atoms occupy the same positions as Si atoms in β-quartz. tI12, another superdense polymorph, is related to high pressure SiS_2 polymorph with both Si and S atomic positions occupied by C.[25] DFT calculation shows that tI12 is marginally denser than hP3. We found several β-quartz-like dense phases with different ways of packing of tetrahedra.[26] Since these structures share common features in topology, we refer to them as members of the same class of structures, with hP3 and tI12 as the end members. The crystal structure of tP12 is also related to the silicon sublattice in the SiO_2 modification keatite. Although diamond has the shortest average C–C bond length among sp^3 carbon allotropes, its density is not the highest. While in diamond, each carbon atom has 12 second nearest neighbors at 2.52 Å, the second nearest coordination sphere of C in hP3 has 14 carbon atoms in the range from 2.27–2.60 Å. This analogy with silica transpires again: quartz (analog of hP3) and keatite (analogy of tP12) are 13.7% and 7.7% denser than cristobalite (diamond form of SiO_2), respectively, while tridymite (lonsdaleite form of SiO_2) is 2.6% less denser than cristobalite.[27]

Are these allotropes totally hypothetical or they can be experimentally obtained? Their energies are high (0.89–1.14 eV/atom higher than diamond, as shown in Fig. 2(a), but the same is true for well-known low-density allotropes such as fullerenes (0.44–0.72 eV/atom higher than graphite[28]) and amorphous carbon (0.70–0.99 eV/atom higher than diamond[29]). Given that much greater density of the hP3, tP12, and tP12 allotropes predicted here, it is possible to obtain them by rapid dynamical compression of low-density forms of carbon. Alternatively, these allotropes can be synthesized by chemical-vapor-deposition (CVD) techniques on a suitable substrate. Their dynamical stability (i.e., there are no imaginary phonon frequencies[26]) indicates that, once synthesized, these allotropes can exist long at ambient conditions.

Figure 2(b) shows the equations of state of the hP3, tI12, tP12, bc8, R8, diamond, and several recently reported
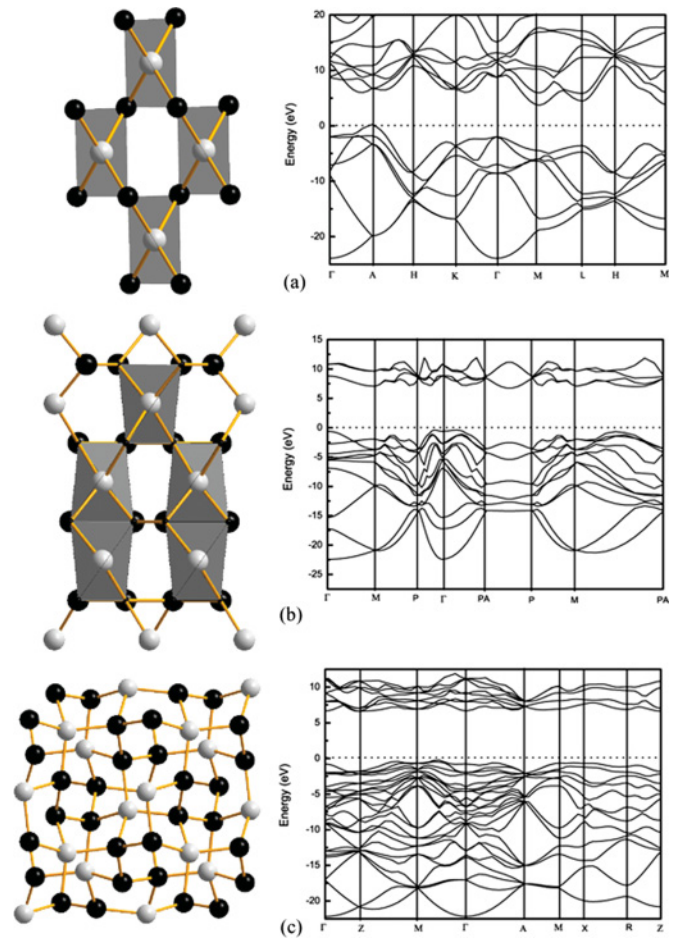

FIG. 1. (Color online) Crystal structures and hybrid functional band structures of (a) hP3, (b) tI12, and (c) tP12 allotropes. For carbon allotropes, hybrid-functional is believed to give the same level of accuracy as more rigorous GW quasiparticle calculations. The white (dark gray) spheres represent the different types of carbon atoms.

structures. The hP3 and tI12 allotropes have the most efficient packing of carbon atoms at all pressures up to 400 GPa, and at higher pressures bc8 and R8 will become denser. Remarkably, the computed equations of state indicate that hP3-carbon is even less compressible than diamond; parameters of the third-order Birch-Murnaghan equations of state are given in Table II.

We have also investigated the intrinsic hardness of these three materials using Gao's model.[30] The predicted hardness for hP3 is 87.6 GPa, which is quite comparable to that of diamond (theoretical hardness 94.3 GPa). Similarly, the theoretical hardnesses of tI12 and tP12 are 87.2 and 88.3 GPa, respectively. The reason why the hardness of hP3, tI12, or tP12 is lower than that of diamond is in the difference of bond strengths. While hP3, tI12, or tP12 have greater bond density than diamond, the bonds themselves are weaker and longer (e.g., the average C–C bond length in hP3 is 1.60 Å, i.e., significantly longer than 1.54 Å in diamond).

Greater density must impact the electronic structure and optical properties. It is well known that DFT underestimates band gaps by $\sim$30%, and therefore we employed both GW

TABLE II. Energy relative to diamond (δE), volume (V), bulk modulus (B_0), and its pressure derivative (B_0'), average bond length (d), hardness(H), static dielectric constant ϵ_s for the investigated structures. Experimental data are shown in parentheses, and GW band gaps and HSE dielectric constants are shown in curly brackets.

Allotropes	δE eV/atom	V Å^3/atom	B_0 GPa	B_0'	d Å	H GPa	Band gap eV	ϵ_s
Diamond	0	5.70	431.1	3.74	1.545	94.3	4.2 {5.4}	5.83 {5.57}
	(0)	(5.68, Ref. 31)	(446, Ref. 31)		(1.54)	(96±5, Ref. 32)	(5.5)	(5.68)
Lonsdaleite	0.024	5.71	437.3	3.63	1.548	93.2	3.6 {5.0}	5.73 {5.52}
M-carbon (Ref. 6)	0.159	5.97	392.7	3.88	1.551	89.8	3.6 {5.0}	5.99 {5.52}
bct-4 (Ref. 9)	0.196	6.01	411.4	3.50	1.549	91.1	2.7 {3.8}	5.66 {5.42}
Chiral (Ref. 8)	0.112	6.22	389.0	3.72	1.555	86.5	4.1 {5.5}	5.26 {5.06}
bc8	0.697	5.60	389.6	4.03	1.588	88.8	2.7 {3.5}	7.07 {6.67}
hP3	1.113	5.49	432.7	3.71	1.603	87.6	2.0 {3.0}	8.35 {7.73}
tI12	1.140	5.48	425.0	3.83	1.603	87.2	4.1 {5.5}	8.49 {7.87}
tP12	0.883	5.64	396.0	3.79	1.583	88.3	5.4 {7.3}	7.58 {7.08}

and hybrid functionals as implemented in VASP (Refs. 33–35) to accurately estimate band gaps. From the data as shown in Table II, we found that the GW corrected band gap of diamond is 5.4 eV, which is close to the experimental value of

5.5 eV (however, that inclusion of band-gap renormalization due to electron-phonon coupling[36] would worsen the agreement). The electronic band structure of hP3 is shown in Fig. 1(a). It is a semiconductor with a band gap of 3.0 eV at ambient pressure. The value of the gap would mean intrinsic orange color, but since the band gap is indirect, the material is likely to be colorless. For tI12, the band gap is about 5.5 eV. Finally, electronic band structure of tP12 shows the typical characteristics of insulator. GW gives an indirect band gap of 7.3 eV. tP12 has the largest band gap among all forms of carbon, known or hypothetical.

Finally, we investigated dielectric and optical properties of carbon allotropes. We have computed static dielectric constants both in the standard DFT and hybrid-functional frameworks. Hybrid-functional HSE is believed to give the more reliable results.[35] Compared to diamond and other allotropes, it is clear that superdense phases have much higher dielectric constants due to their higher density. Refractive index n is important for optical applications, its high value
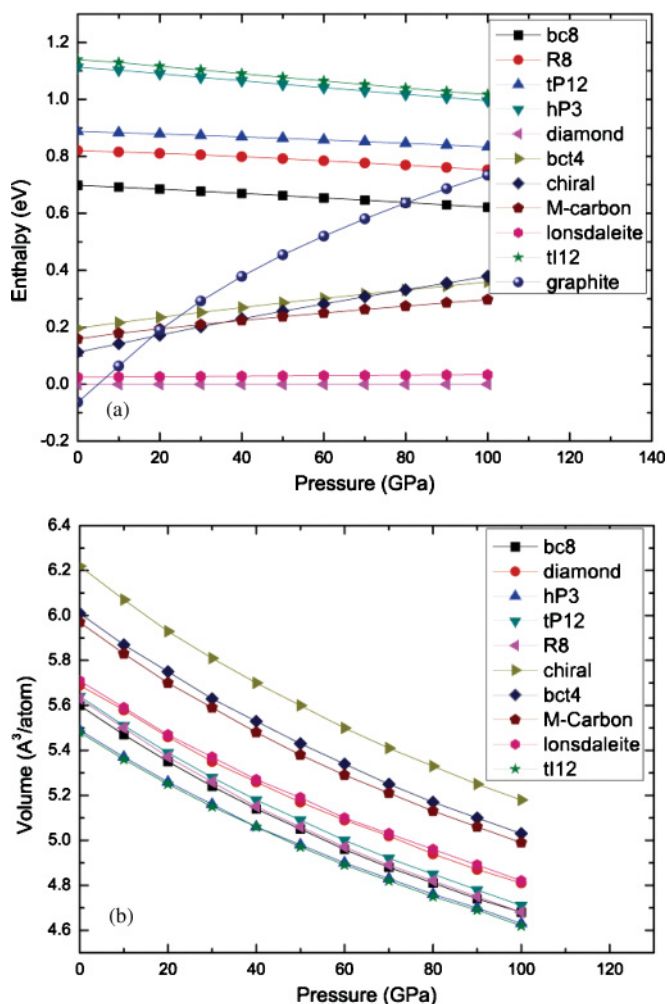

FIG. 2. (Color online) (a) Enthalpies of various carbon structures relative to diamond. (b) The equations of state of various carbon phases at 0 K.
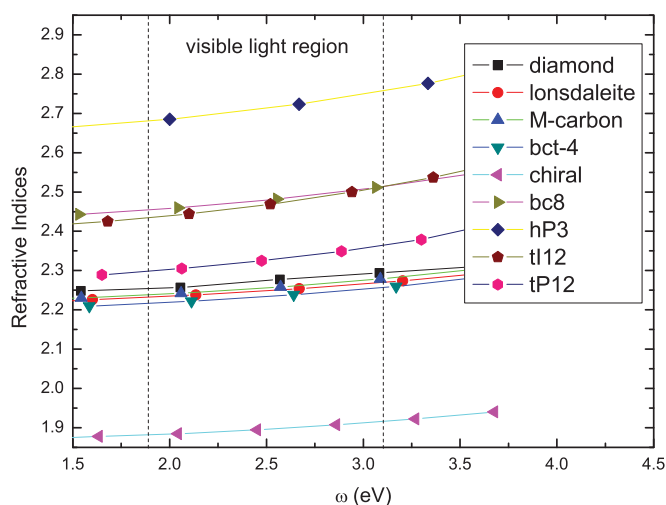

FIG. 3. (Color online) Refractive indices as a function of frequency for the investigated carbon allotropes.

for diamond determines its high brilliance, and it is calculated as[37]

$$n = \sqrt{\frac{\sqrt{\epsilon_1^2 + \epsilon_2^2} + \epsilon_1^2}{2}}, \tag{1}$$

where ϵ_1 and ϵ_2 represent the real and imaginary parts of the dielectric function, respectively. Figure 3 shows the frequency dependence of refractive indices of these dense sp^3 allotropes in the visible-light frequency range. It can be seen that all three superdense allotropes have significantly greater dispersion of light (i.e., the refractive index varies more with frequency) compared with diamond, i.e., if synthesized they will display not only a stronger luster (due to higher refractive index), but also stronger color effects (due to larger light dispersion).

In summary, a number of superdense carbon modifications have been predicted. Two of them, hP3 and tP12, have strong analogy with the silicon sublattices in two polymorphs of silica (β-quartz and keatite), while tI12 is analogous to the high-pressure polymorph of SiS$_2$. Global optimization with respect to density reveals that hP3 and tI12 carbon allotropes are the densest possible structures of carbon at ambient conditions. All of the structures possess high hardnesses and bulk moduli, comparable to those of diamond. Band gaps of these allotropes show large variability, while the dielectric constants, refractive indices, and light dispersion significantly exceed those of diamond or any other allotropes of carbon. It may be possible to synthesize them, e.g., by shock compression of amorphous carbon.

*qiang.zhu@stonybrook.edu

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