

# Isoglitter

Michael J. Bucknum<sup>1</sup>, Eduardo A. Castro<sup>1</sup> and Bin Wen<sup>2</sup>

<sup>1</sup>INIFTA, Theoretical Chemistry Division, Universidad Nacional de La Plata, La Plata 1900, Buenos Aires, Argentina

<sup>2</sup>State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, China, email:wenbin@ysu.edu.cn

**Abstract:** A novel orthorhombic lattice is described that is generated upon a 1,4-cyclohexadieneoid motif, and is a model of a potential allotrope of C. The orthorhombic lattice (Ammm, space group #65) that is described, is called isoglitter as it is a structural relative of the tetragonal glitter lattice ( $P4_2/mmc$ , space group #131) first proposed in 1994 by Bucknum et al. A geometrical optimization of the isoglitter lattice, employing the Cambridge Serial Total Energy Package (CASTEP) algorithm based upon density functional theory (DFT) was performed. The present report is an account of the CASTEP optimized isoglitter crystal structure, including an idealized drawing of the unit cell, and a set of optimized crystallographic coordinates for isoglitter. Results of an electronic band structure calculation, together with a density of states (DOS) profile for the lattice based upon CASTEP, are reported as well. The unit cell of isoglitter contains 8 C atoms and has a DFT modeled density of about  $3.009 \text{ g/cm}^3$ . Isoglitter is comprised entirely of planar and chair-like 6-gons in its structural pattern.. The Wells point symbol for the network is cited here as  $(6^6)(6^3)$  and it is thus a graphene-diamond hybrid, where this point symbol translates to a Schlaefli symbol given as (6, 3.5). The novel latticet is thus positioned midway between the grapheme sheet, located at (6, 3), and the diamond lattice, located at (6, 4), in the topology mapping of structures described earlier by Wells..

## 1. Introduction

This communication reports the structure of a novel 3-,4-connected network. Wells has presented a systematic survey of many 3-,4-connected networks in his important monograph [1]. Those 3-,4-connected networks constituted of coordinations grouped into trigonal planar atom pairs (3-connected component), and as tetrahedral vertices (4-connected component), comprise models of C allotropes. Still, there are other possible 3-,4-connected networks, including compositions patterned on the phenacite structure-type ( $\beta\text{-Ge}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ ) [2], which is comprised of isolated trigonal planar and tetrahedral vertices, as is shown in Figure 1. Yet another such 3-,4-connected pattern is the Waserite structure-type ( $\text{Pt}_3\text{O}_4$ ) [3], which is an anionic sublattice in charge balance with alkali metal cations, that is built from isolated square planar (Pt) and trigonal planar (O) vertices as shown in Figure 2.

**Figure 1****Figure 2**

Isoglitter as a structure-type that is reported in this paper, is a novel 3-,4-connected network [1] that is a model of a graphene-diamond hybrid. This paper describes the topology of the isoglitter structure-type, and its relationship to the glitter structure-type that has already been described previously [4]. The isoglitter and glitter structure-types are proposed as models of possible C allotropes. A CASTEP-DFT geometrical optimization of the isoglitter lattice is presented in this paper as well. [5] This geometrical optimization thus includes an identification of the symmetry space group of isoglitter as being in the orthorhombic system as Ammm (space group #65) [6]. Also, there is reported a table of optimized crystallographic coordinates for the 8 C atoms in the crystalline pattern, and its theoretical density is reported. Finally, a band structure and DOS generated by the CASTEP program are presented for the orthorhombic isoglitter structure-type as well. The band structure reveals the hypothetical orthorhombic C lattice is metallic, with a band crossing the Fermi level along the crystallographic *c*-axis in the unit cell in direct space.

**2. Isoglitter & Glitter**

The 3-,4-connected network described in this paper, called isoglitter, is a structural relative of another C allotrope built from 1,4-cyclohexadiene units called glitter. [4] Isoglitter, shown in Figure 3, is comprised of 1,4-cyclohexadiene building blocks coordinated to each other in a parallel fashion, while in contrast in the glitter structure-type the 1,4-cyclohexadiene rings are coordinated orthogonally to each other as shown in Figure 4.

**Figure 3****Figure 4**

As can be traced from Figure 3, in the isoglitter structure-type the 3- and 4-connected constituent C atoms are linked into planar and chair-like hexagons. The Wells point symbol [7] for isoglitter is  $(6^6)(6^3)$ , and it is thus defined as a graphene-diamond hybrid structure [8]. Indeed the isoglitter lattice, being built as it is from 1,4-cyclohexadiene component substructures, is thus the first member of an infinite series of graphene-diamond hybrid networks in which all circuits are 6-gons, and in which all planar 6-gons in these networks are parallel to each other. [7-8] Isoglitter has the Schlaefli symbol of  $(6, 3.5)$ , and it is mapped exactly halfway between the locations for the graphene grid  $(6, 3)$  on the one hand, and the diamond lattice  $(6, 4)$  on the other hand, as is shown in the topology mapping of structures in Figure 5.

### Figure 5

By contrast, in the glitter structure-type the 3- and 4-connected constituent C atoms are linked into planar hexagons and puckered octagons. The Wells point symbol for glitter is  $(6^28^4)(6^28)_2$  and it is thus not a graphene-diamond hybrid structure. Glitter possesses the Schlaefli symbol of  $(7, 3^{1/3})$ , and it is mapped between the location of the  $(7, 3)$  series of networks [1], and the location for a heretofore unidentified structure-type with the topology  $(8, 4)$ .

### 3. Density Functional Theory (DFT) Geometry Optimization of Isoglitter

Table 1 contains the DFT optimized coordinates of the 8 C atoms in the isoglitter unit cell, also in Table 1 are the DFT optimized lattice parameters of isoglitter. The lattice parameters are thus given as  $\mathbf{a} = 2.502\text{\AA}$ ,  $\mathbf{b} = 2.716\text{\AA}$  and  $\mathbf{c} = 7.803\text{\AA}$ . The crystal cell parameters and atomic positions of the 8 C atoms in the isoglitter structure-type have been optimized by using density functional theory (DFT) based on the planewave pseudopotential technique implemented in the CASTEP package. [5, 9] The ion-electron interaction is modeled by using ultrasoft pseudopotentials. [10] The generalized gradient approximation (GGA) [11] with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [12] is used. The kinetic cutoff energy for plane waves is set as 800

eV. The  $\mathbf{k}$  point separation in the Brillouin zone of the reciprocal space is  $0.07 \text{ nm}^{-1}$ , resulting in a  $\mathbf{k}$  point mesh of  $5 \times 6 \times 2$  for isoglitter.

**Table 1**

From the DFT lattice parameters of isoglitter in Table 1, and the drawing of isoglitter in Figure 3, one can infer that the planar hexagons of the 1,4-cyclohexadiene substructures, from which the isoglitter lattice is generated, have a width across the  $\pi$  bonds of  $2.502 \text{ \AA}$ , which is only slightly distorted from the dimensions of the corresponding 1,4-cyclohexadiene hydrocarbon generating fragment at  $2.530 \text{ \AA}$ . [13] The  $\mathbf{b}$  lattice parameter at  $2.716 \text{ \AA}$  provides a measure of the stacking interaction between  $\pi$  bonds of the face-to-face, adjacent olefin units in the network. At this distance, the stacking interaction is minimal [14] and the network would be an insulator, were it not for the through-space interaction of p orbitals along the crystallographic  $\mathbf{c}$ -axis. These effects can be seen in the DFT electronic band structure shown in Figure 6, where one sees a band crossing the Fermi level from bonding states to antibonding states, that leads to a metallic status for the network in its corresponding DOS profile accompanying the band structure in Figure 6.

Lastly, from the optimized lattice parameters for isoglitter cited in Table 1, one can calculate a theoretical density for the orthorhombic structure-type, and compare it to the DFT optimized density of glitter, using the same CASTEP method. [15, 16] With 8 C atoms in the orthorhombic cell, the density of isoglitter at  $3.009 \text{ g/cm}^3$  compares to the corresponding theoretical density of glitter at  $3.080 \text{ g/cm}^3$ . Thus the DFT theoretical densities of glitter and isoglitter are almost identical, with the glitter lattice being only very slightly denser, with a density difference of less than 1%. One might expect a significant difference in these theoretical densities, and this result is remarkable given that the spiroconjugation interactions known to be present in glitter [4], should confer a superior stability to glitter over isoglitter, where in isoglitter such stabilizing interactions are absent. [15, 16]

**Figure 6**

#### 4. Conclusions

As has been described in the preceding Sections, the isoglitter lattice represents an interesting and novel crystalline C allotrope of orthorhombic symmetry, that is the parent structure in an infinite family of para-(graphite-diamond) hybrid structures. As the progenitor structure for these para-(graphite-diamond) hybrid structures, it is an interesting result that the C network is metallic, where the metallic status is derived from the through-space interaction of p-orbitals at sites of C trigonal planar coordination (see Figure 3), along the crystallographic *c*-axis of the unit cell of the isoglitter material.

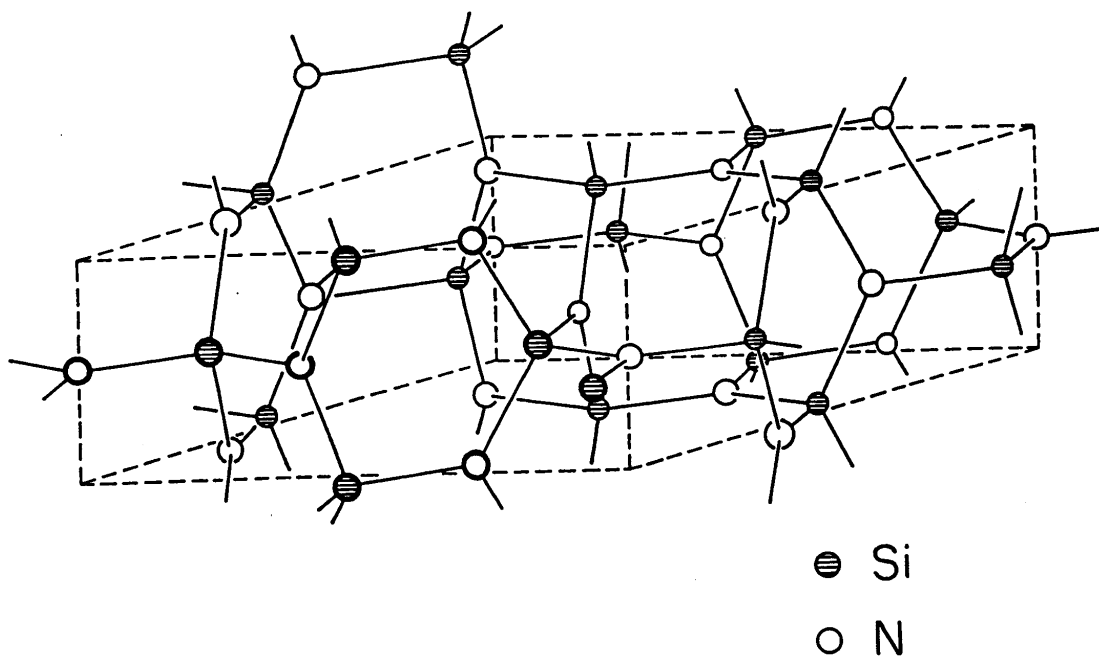
Figure 7 shows a graph of the relative stability of isoglitter at pressures to beyond 100 GPa, with respect to the corresponding stabilities of graphite (at the zero of the energy scale), and another novel hypothetical allotrope of C recently proposed by Wang et al., named as w-Carbon [17]. It is clear from the calculated data in Figure 7, that isoglitter becomes a structural-type more stable than the graphite structural-type beyond approximately 100 GPa. This result is intriguing from a synthetic perspective, and it thus suggests that perhaps a thermodynamic synthesis of isoglitter from graphite may be possible at synthesis pressures exceeding 100 GPa, as could be achieved in a conventional diamond anvil cell (DAC). The reader is left to speculate about the data on w-Carbon in Figure 7, and to consider the tantalizing possibility of a thermodynamic synthesis of this novel structural-type from graphite at considerably lower pressures near 20 GPa.

Elasticity in the cubic diamond and tetragonal glitter C allotropes has been evaluated by Bucknum et al. previously. [18] In this analysis, Cohen's semi-empirical formula for estimating the static bulk modulus of these crystalline materials was employed. [19] From these results cubic diamond is estimated to have a static bulk modulus of about 435 GPa, while tetragonal glitter has a static bulk modulus of about 440 GPa by the same method. Because of the nearly identical DFT densities calculated for glitter and isoglitter, as reported in this paper, it is to be expected that isoglitter will have very similar elastic properties to glitter and that both structure-types, as C allotropes, would be expected to potentially surpass cubic diamond in their intrinsic strength.

## References

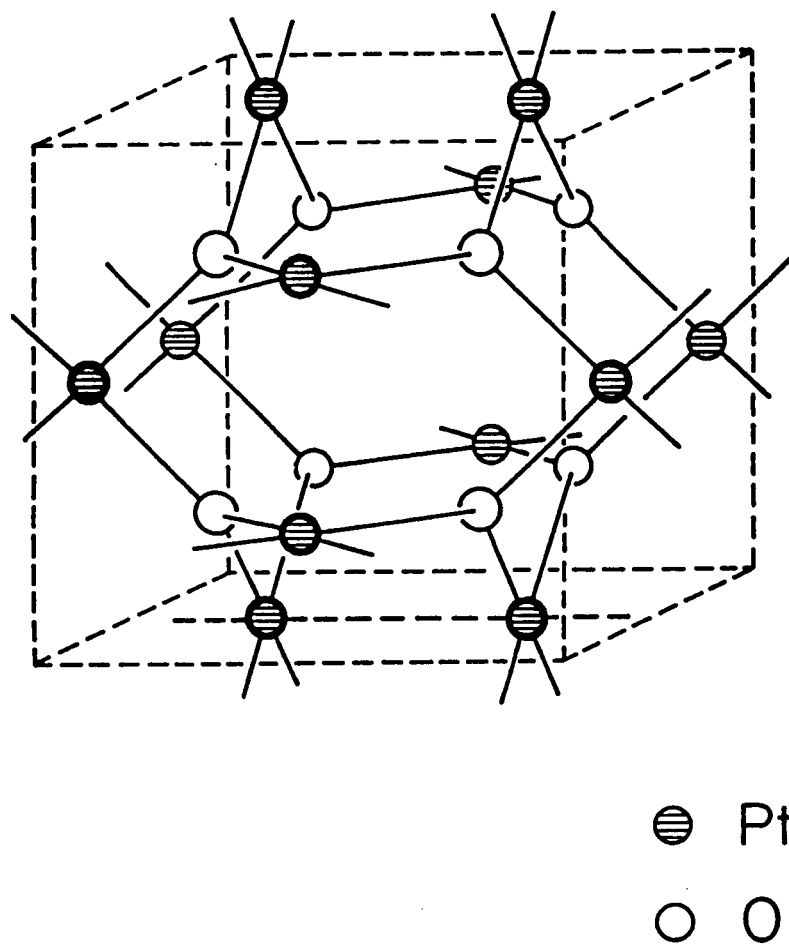
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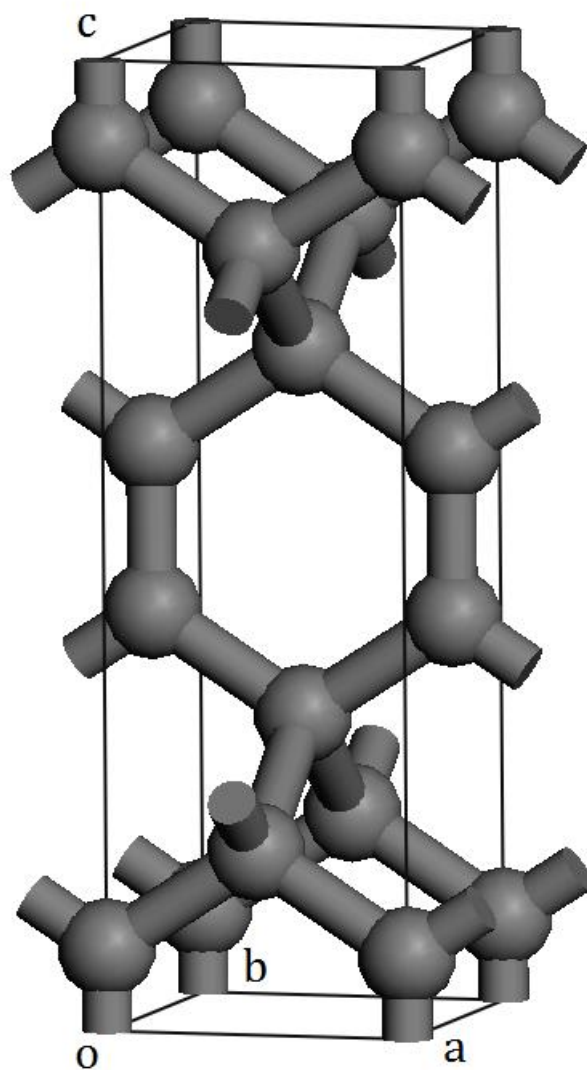


**Figure 1:** Unit of pattern of hexagonal phenacite structure-type as a  $\beta$ - $\text{Si}_3\text{N}_4$  lattice in space group  $P6_3/mc$

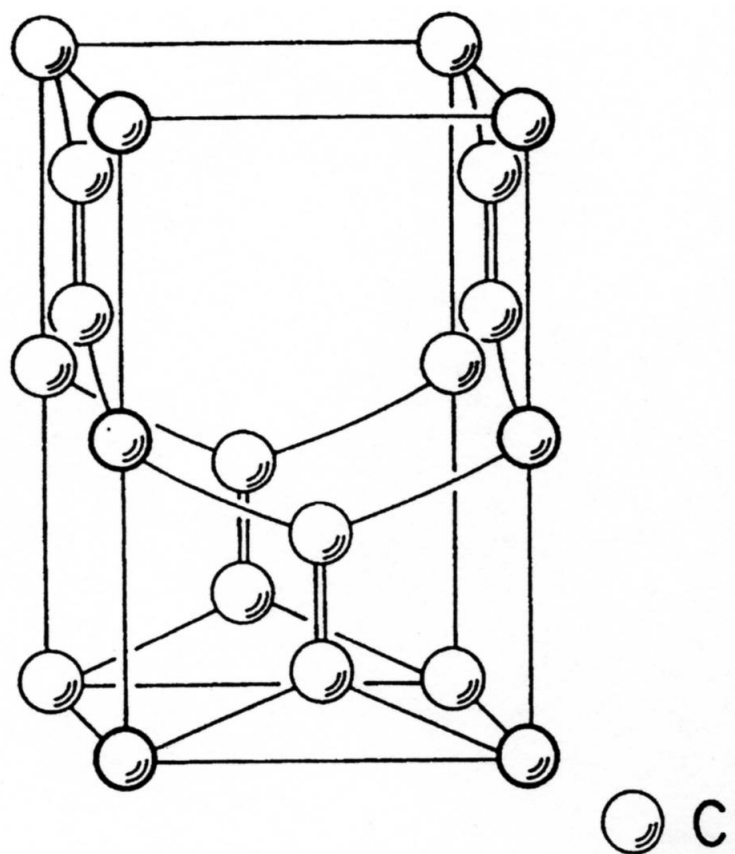




**Figure 2:** Unit of pattern of cubic Waserite structural type in space group  
Pm-3n



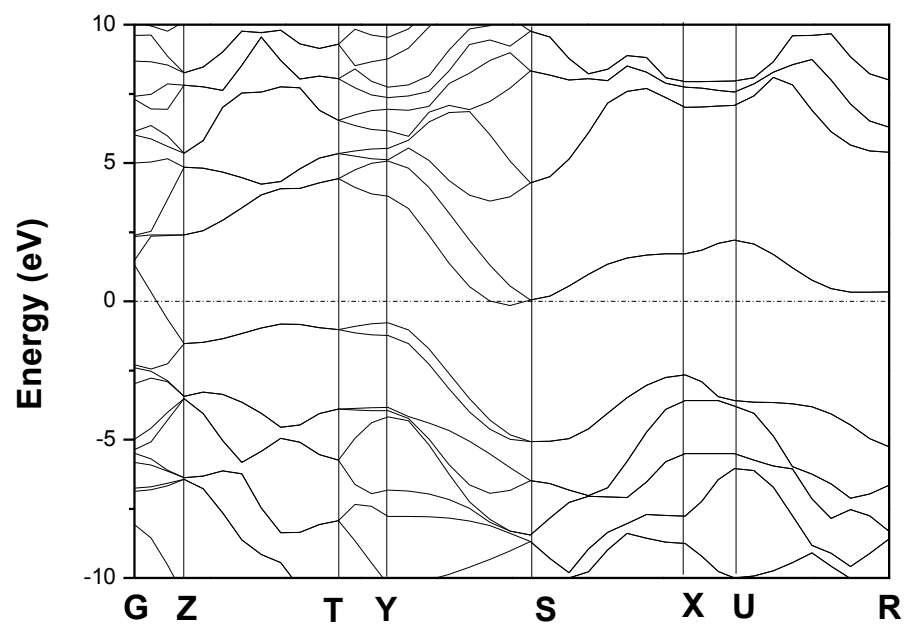
**Figure 3:** Unit of pattern of orthorhombic isoglitter C allotrope in space group Ammm



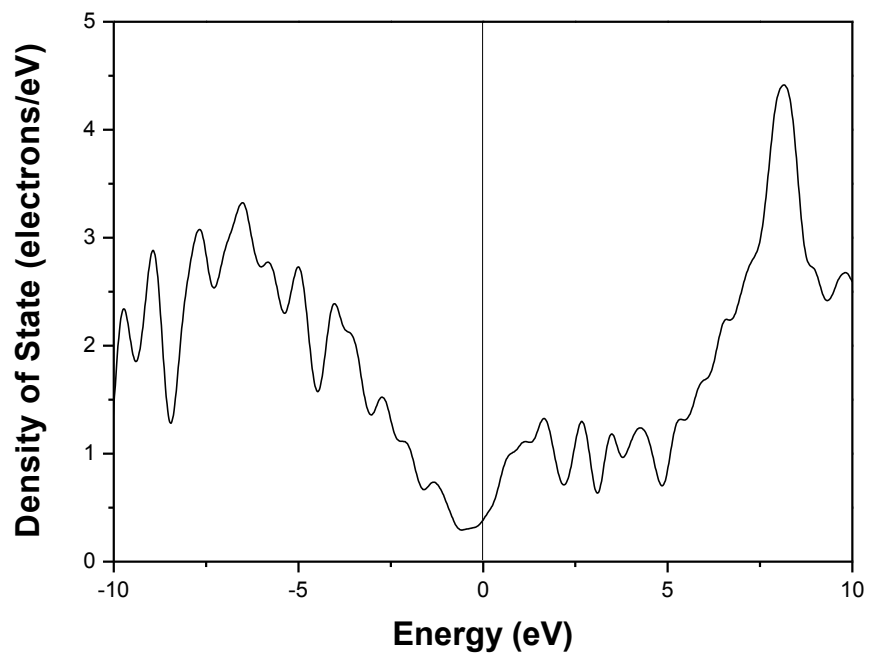
**Figure 4:** Unit of pattern of tetragonal glitter C allotrope in space group  $P4_2/mmc$

$n \backslash p$	3	4	5	6	7	8	...
3	t	o	i	(3,6)	(3,7)	(3,8)	
4	c	(4,4)	(4,5)	(4,6)	(4,7)	(4,8)	
5	d	(5,4)	(5,5)	(5,6)	(5,7)	(5,8)	
6	(6,3)	(6,4)	(6,5)	(6,6)	(6,7)	(6,8)	
7	(7,3)	(7,4)	(7,5)	(7,6)	(7,7)	(7,8)	
8	(8,3)	(8,4)	(8,5)	(8,6)	(8,7)	(8,8)	
⋮							

**Figure 5:** Chemical topology mapping of polyhedra, tessellations and networks in a Schlaefli space



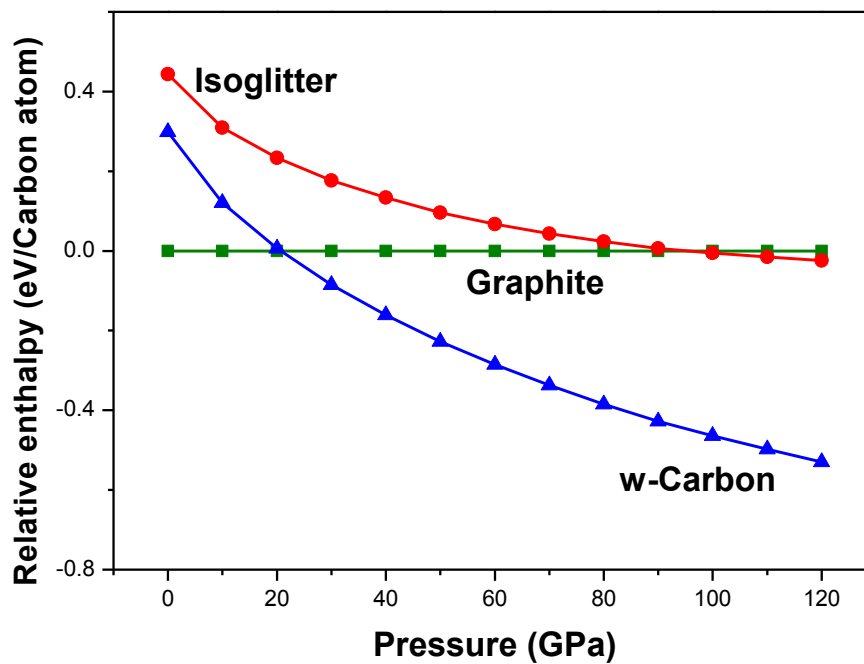
**Figure 6(a):** Electronic band structure of isoglitter C allotrope



**Figure 6(b):** Density of states (DOS) profile of the isogitter C allotrope

**Table 1:** Fractional orthorhombic crystallographic coordinates of the C isoglitter unit cell, with optimized lattice parameters **a**, **b** and **c** in Å units

Atom#	x/ <b>a</b>	y/ <b>b</b>	z/ <b>c</b>	<b>a</b>	<b>b</b>	<b>c</b>
1	0	0	0.08585	2.502, 2.716, 7.803		
2	0	1/2	0.1891	"		
3	1/2	1/2	0.3108	"		
4	1/2	0	0.4141	"		
5	1/2	0	0.5858	"		
6	1/2	1/2	0.6891	"		
7	0	1/2	0.8108	"		
8	0	0	0.9141	"		



**Figure 7:** Relative stability scale of isoglitter, w-Carbon and graphite carbon allotropes with pressure