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Disclosure Document : Cover Letter

8-18-93

The Synthetic Carbon Allotrope Glitter and Related Synthetic Binary Compounds of Group 13 or Group 14 or Group 15 or Group 16 Elements Based Upon 1,4-Cyclohexadieneoid Unit Rings: Superhard Materials for Machining and Compression Applications and Applications Involving Diamond or Graphite

I, Michael John Bucknum, residing at 4 South Main Street, Moravia, NY, 13118 with the telephone number 315-497-0841; disclose the following invention entitled, "The Synthetic Carbon Allotrope Glitter and Related Synthetic Binary Compounds of Group 13, or Group 14 or Group 15 or Group 16 Elements Based Upon 1,4-Cyclohexadieneoid Unit Rings: Superhard Materials for Machining and Compression Applications and Applications Involving Diamond and Graphite". This attached disclosure has been made by me in front of witnesses on the 19th day of August, 1993.

This disclosure is made as an addendum to, or alternatively an independent and separate supplementary disclosure document to the previous disclosure document; Disclosure Document Number 336650 submitted by me to the U.S. Patent and Trademark Office in August, 1993.

Michael John Bucknum

Disclosure Document No.
337466
Filing Fee: \$10.00
Retained for 2 yrs.
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8/19/93

Virginia C. Moses

VIRGINIA C. MOSES
Notary Public, State of New York
No. 4975479
Qualified in Tompkins County
Commission Expires December 10, 1994



Nature Precedings : hdl:10101/npre.2008.1530.1 : Posted 22 Jan 2008

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I. Abstract of Invention

As previously described on 8-3-93 in Disclosure Document No. 336650 to the U.S. Patent and Trademark Office; this invention relates to the architecture of carbon materials and binaries of group 13 or group 14 or group 15 or group 16 elements, which contain 1,4-cyclohexadieneoid unit rings¹ in their structures. Specifically this invention claims the materials described in the next Section, the use of these materials for the applications described in Section IV, and the synthetic strategies for creating these materials as described in Section III.

Crystallographic aspects of the parent 3-dimensional structure^{ASB} which for the case of the pure carbon material is termed Glitter², are described in the next Section. Photographs of a prototype of this structure, that is of the same space group as the mineral cooperite, $P4_2/m\ mc$, are presented in Section II as well. The glitter structure forms the basis for a new class of materials claimed to be useful in applications that currently involve diamond or graphite or related periodic compounds³. Also the invention describes several different substructures implied by the glitter structure and claims related applications for these substructures.

Solid state chemical methods for diamond and related materials' synthesis⁴ and vapor deposition methods for diamond films and related thin films' synthesis⁵, that are well documented in the literature, are claimed as synthetic strategies for creating these materials, as is discussed in Section III. Of particular interest is the creation of alloys of carbon with either boron or silicon which possess the empirical formulas C_4B_2 , Si_4C_2 , Si_4B_2 , B_4C_2 , C_4Si_2 , B_4Si_2 which are discussed and claimed in Section V.

II. Structure of Glitter and Materials Based Upon this Lattice

Crystallographic analysis has shown that diamond is built from cyclohexaneoid unit rings which are connected in cyclohexaneoid layers that are stacked parallel to each

¹ see particularly #1 and #2 of the attached Glitter Drawings Form

² the name originates from the Shakespearean quote, 'All that glitters isn't gold.'

³ H.T. Hall, *Periodic Compounds: Syntheses at High Pressures and Temperatures*, **Science**, **148**, 1965

⁴ H.T. Hall, *Ultrahigh Pressures*, **Scientific American**, **201**, 5, 1959

⁵ R.C. DeVries, *Synthesis of Diamond Under Metastable Conditions*, **Ann. Rev. Mater. Sci.**, **17**, 1987

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other in the case of cubic diamond and antiparallel to each other in hexagonal diamond⁶. Similar analysis on the graphite allotrope of carbon has shown that it is built from benzeneoid layers stacked in an 'ababab' sequence to yield hexagonal graphite and an 'abcabcabc' sequence to give rhombohedral graphite⁷.

As described in this invention, 1-, 2- and 3-dimensional extended structures of carbon, or more generally of any binary combination of group 13 or group 14 or group 15 or group 16 elements; which are built from 1,4-cyclohexadieneoid unit rings, are claimed for the uses described. These structures are related to diamond and graphite, or related to their respective binary compounds adopting the diamond or graphite structures; like the BN phases, in that they involve a six-membered ring as a principal motif in their architecture. For the allotrope of carbon termed Glitter, the unit ring of its structure is pictured in #1 of the Glitter Drawings Form as is described in this Section. In the more general case of a binary material adopting the glitter structure, the unit ring of its structure is shown in #2 of the Glitter Drawings Form as described in this Section.

As molecular hydrocarbon fragments of their extended structures⁸, cyclohexane, 1,4-cyclohexadiene and 1,3,5-cyclohexatriene (benzene) are related to each other through the identical connectivity of the carbon atoms, forming a six-membered ring in each case. They differ from each other only in the degree of saturation of the carbon atoms. Cyclohexane is a fully saturated hydrocarbon molecule, six methylene (-CH₂-) groups linked together in a ring; in contrast benzene is an unsaturated hydrocarbon, six methylenidene (-CH=) groups linked together in a ring; between these two extremes 1,4-cyclohexadiene has 2 saturated hydrocarbon atoms forming methylene links, and 4 unsaturated hydrocarbon atoms forming methylenidene links. The structural formula⁹ for the prototypical 1,4-cyclohexadieneoid unit ring, 1,4-cyclohexadiene, is pictured in #1 of the attached Glitter Drawings Form. A generalization of 1,4-cyclohexadiene is pictured in #2 of

⁶ Spear, K.E., Phelps, A.W. and W.B. White, *Diamond Polytypes and Their Vibrational Spectra*, **J. Mater. Res.**, Vol. 5, No. 11, Nov 1990

⁷ Wilks, J. and E. Wilks, **Properties and Applications of Diamond**, Butterworth and Heinemann Ltd, 1991. and Bragg, L., **The Crystalline State-Vol. 1: A General Survey**, Cornell University Press, 1965.

⁸ for discussion of this idea see A.F. Wells, **Structural Inorganic Chemistry**, 2nd ed, Oxford University Press, 1975.

⁹ taken from I.U.P.A.C. Nomenclature for Organic Compounds, **CRC Handbook of Chemistry and Physics, 71st ed.**, 1992, p.2-45.

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the Glitter Drawings Form, which is termed a 1,4-cyclohexadieneoid unit ring. Being a Markush structure, this ring represents all the possible combinations of 3-connected and 4-connected atoms taken from groups 13, 14, 15 and 16 of the periodic table with the connectivity implied by this drawing. This unit ring is the structural basis for the 1-, 2- and 3-dimensional structures pictured in #3, #4, #5, #6, #7 and #8 of the Glitter Drawings Form, as is described in this Section.

In the sense that 1,4-cyclohexadiene has methylenic links and methylene links, the 1,4-cyclohexadieneoid unit ring shares structural characteristics of both the benzeneoid unit rings of graphite and the cyclohexaneoid unit rings of diamond; or the analogous binary structures implied by #2 with their analogous diamond-like or graphite-like counterparts; for instance the BN phases. By retaining the six-membered unit ring motif that diamond and graphite both possess, it is clear from this perspective that structures built from 1,4-cyclohexadiene represent a hybridization of graphite and diamond structures; or the analogous binary structures implied by #2 with their analogous diamond-like or graphite-like counterparts; for instance the BN phases.

Extending #2, or #1 if A = B = carbon, by edge-sharing of the adjacent 3-connected vertices in the 1,4-cyclohexadieneoid unit ring, produces the 1-dimensional polyquinoid¹⁰ substructure of the glitter structure as shown in #3 of the Glitter Drawings Form. Extending #2, or #1 if A = B = carbon, by linking through the 4-connected vertices, produces a vertex sharing 1-dimensional polyspiroquinoid substructure of the glitter structure as shown in #4 of the Glitter Drawings Form. Linking 4-connected vertices of neighboring rings of #2, or #1 if A = B = carbon, produces 1-dimensional parallel, cyclopheneoid stacks of the 1,4-cyclohexadieneoid unit rings termed the polyparaquinoid substructure of the glitter structure as pictured in #5 of the Glitter Drawings Form.

Polyspiroquinoid chains are fused together through edge-sharing of the adjacent 3-connected points, labelled element 'B' in the Drawing Form, to produce a 2-dimensional substructure of the glitter structure, termed spirographite, as is pictured in #6 of the Glitter Drawings Form. By cross-linking the spirographite substructures through edge-sharing of the 3-connected points (B), as described for polyquinoid, and vertex-sharing of the 4-connected points (A), as described for polyspiroquinoid, the 3-dimensional glitter structure emerges. For the pure carbon

¹⁰ such structures are seen in B₂O phases as described in reference 2

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allotrope this is shown in #7 of the Glitter Drawings Form; the generalized structure which is produced by extension of the Markush ring, #2 in the Glitter Drawings Form, is shown in #8 of the Glitter Drawings Form and is termed the glitter structure. There are 20 possible allotropes of the group 13 or group 14 or group 15 or group 16 elements which would adopt the structure pictured in #7 of the Glitter Drawings Form, which is termed Glitter, and 380 binary compounds of group 13 or group 14 or group 15 or group 16 elements which would adopt the structure of #8 in the Glitter Drawings Form, which is termed the glitter structure. These structures possess the same space group symmetry as the mineral cooperite (platinum sulfide), $P4_2/m\ mc$ ¹¹. The 1- and 2-dimensional substructures will retain the respective symmetry elements of the glitter structure along their symmetry points, axes and planes, respectively.

A prototypical model of the glitter structure has been built and photographed and the photographs are attached to this document. Direct and stereoscopic views of this lattice are shown in the photographs. Connections between the 3-connected atoms, element B in #8 of the Glitter Drawings Form, are shown in red in the photographs while connections between the 3-connected and 4-connected atoms, element B to element A in #8 of the Glitter Drawings Form, are shown in black in the photographs. The unit cell of the glitter structure is outlined in each photograph by the beige cord. These models define the three-dimensional glitter structure, for the machining and compression and other applications described in Section IV, in the same way that models of well-characterized materials such as halite, fluorite or cooperite define these structures.

III. Synthesis of Materials Claimed In Section I Based Upon Glitter Structure

Standard methods of Chemical Vapor Deposition (CVD) described in the literature for the synthesis of diamond films¹², for creating layered cuprate superconductors¹³ and for other applications are claimed here as synthetic routes to the 20 Glitter allotropes and the 380 binary glitter structures and their respective substructures as

¹¹ Bragg, L., Claringbull, G.F. and W.H. Taylor, **The Crystalline State-Vol. IV: Crystal Structures of Minerals**, p. 65, 1965

¹² DeVries, R.C. *Synthesis of Diamond Under Metastable Conditions*, **Ann. Rev. Mater. Sci.**, **17**, 1991.

¹³ Chern, M.Y., Gupta, A. and B.W. Hussey, *Layer-by-layer deposition of $La_{1.85}Sr_{0.15}CuO_x$ films by pulsed laser ablation*, **Applied Physics Letters**, **60**, 1992.

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shown in the Glitter Drawings Form and described in Section II. Particularly of interest in this regard are the synthesis of the binaries of B, Si and C, by these methods, which adopt the glitter structure or its substructures, as described in Section II.

Standard solid state chemical synthetic methods including those described in any standard text of solid state chemistry¹⁴ involving the use of powdered materials containing the desired amounts of group 13 or group 14 or group 15 or group 16 elements as compounds or in any of their other forms as precursor to the structures claimed here as described in Section II, are claimed as synthetic strategies for these materials. Particularly of interest in this connection is the application of these methods in the synthesis of alloys of B, C or Si possessing the structures claimed here as described in Section II. Of special mention in this regard is the use of the Acheson Process or a modified Acheson Process for synthesis of binaries involving C and Si which is claimed as a synthetic strategy for the creation of these glitter structures.

A method of generating the structures claimed here of special ^{NTB} mention is the high pressure synthesis of the glitter structures or their respective substructures, as described in Section II, by static compression of single crystals of graphite or a graphite-like material (for example graphitic BN) along their basal plane by standard high pressure apparatus¹⁵. By orienting a single crystal of graphite or a graphite-like material (for example graphitic BN) so that its basal planes are parallel with the compression axis it is claimed here that sufficient pressure will disrupt the basal plane and rupture the graphitic sheets in such a manner to create instantaneously spirographitic sheets which simultaneously crosslink to produce the structures claimed in this invention as described in Section II.

Well characterized methods of synthesizing diamond or its periodic analogs¹⁶ by means of static high pressures and temperatures, or similar methods based upon shock compression synthesis¹⁷, possibly in the presence of a catalyst, are claimed here as synthetic strategies for creating the materials described in Section II and claimed in this invention.

¹⁴ West, A., **Solid State Chemistry**, 1990.

¹⁵ Timmerhaus, K.D. and M.S. Barber eds., **High Pressure Science and Technology-Vol. 1: Physical Properties and Materials Synthesis**, Plenum Press, 1979.

¹⁶ *ibid* 2, 3 and the references therein

¹⁷ *ibid* 12 and the references therein

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IV. Application of Materials Claimed in Section I Based Upon Glitter Structure

Applications of the glitter structures described in Section II for machining and for compression applications include application to machining of other very hard materials¹⁸, the creation of anvil materials for high pressure studies, and general claims as replacements to diamond or graphite wherever a glitter structure would be a convenient and viable replacement.

Further applications for these materials are claimed to include ¹⁹ use as materials to replace graphite or diamond wherever they are currently applied¹⁹ based upon the similarities such hybrid materials may share with graphite or diamond to make them convenient and desirable replacements. These replacement uses include needs for thermally and electrically conducting light weight materials as for example in electrochemical applications like those involving carbon electrodes or electrically conductive carbon-based materials, and as thermally conductive substrate material in the engineering of micro- and nanoprocessors in electronics and optics applications.

It is another claim of this invention that materials described in Section II which adopt the glitter structure and that empirically prove to be of the same magnitude of hardness as diamond be used as tools by which diamond and other hard materials are machined for use in their typical applications. Included among these applications is the use of these materials where they may prove useful for specialty machining of diamond anvils for use in high pressure cells and the use of the superhard materials possessing the glitter structure as components in high pressure cell equipment, including their use as materials for the anvils themselves.

Additionally claimed in this Section are the use of any of the substructures described in Section II, including the substructures pictured in the attached Glitter Drawings Form, for any applications where diamond or graphite are currently used

¹⁸ Boehler, R., High Precision Grinding of Diamond Anvils, Proceedings of the AIRAPT Conference, Denver, CO, 1993.

¹⁹ see reference 6 and Reynolds, W.N., **The Physical Properties of Graphite**, Elsevier Publishing Co. LTD, 1968 and Timmerhaus, K.D. and M.S. Barber eds., **High Pressure Science and Technology-Vol. 2: Applications and Mechanical Properties**, Plenum Press, 1979.

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such as those described in the previous paragraphs of this Section.

V. Creation and Uses of Binary Compounds C_4B_2 , Si_4C_2 , Si_4B_2 , B_4C_2 , C_4Si_2 , B_4Si_2

Of particular importance among the 380 possible binary materials described in Section II of this invention, the binary materials of B, C and Si which adopt the glitter structure are particularly claimed for use as superhard materials. It is well known that boron-carbides and silicon-carbides are the hardest materials known after diamond. It is also known that there are many different crystallographic environments in which B, C and Si are found, particularly of mention is the fact that B and C chemically bond both in tetrahedral and in trigonal planar configurations and Si nearly always occurs in a tetrahedral configuration. Therefore these materials are particularly claimed as superhard materials for machining and compression applications.

Appendix I: Calculation of Bulk Modulus of Glitter and Diamond

In support of the principal claim of this invention that materials ^{101B} adopting the glitter lattice composed of carbon with or without a binary element; particularly to include B or Si, are superhard materials ----- a standard semi-empirical formula for bulk modulus due to Cohen²⁰ is introduced here as:

$$B = \left[N_c / 4 \left((1972 - 220 \times I) / d^{3.5} \right) \right] \text{ GPa}$$

This simple expression is applicable to covalently bonded substances as defined for example by the electronegativity differences between the elements making up the material. In the glitter structures built from Group 13 or Group 14 or Group 15 or Group 16 elements, the equation is applicable. The term N_c refers to the weighted average coordination number for the atoms in the unit cell, I is a measure of the ionicity of the covalent bonds in the material and d is the weighted average of the bond distances in the material.

For the all carbon Glitter; $N_c = 3.33$, since 2/3 of the carbon atoms are 3-connected in the unit cell and 1/3 of the carbon atoms are 4-connected in the unit cell; $d = 1.45$ A, based upon the normal bond lengths observed in 1,4-cyclohexadiene of 1.51 A for the sp^3-sp^2 carbon-carbon bond and 1.33 A for the sp^2-sp^2 carbon-carbon

²⁰ M. Cohen, *Physical Review B* **32**, 7988, 1985

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bond²¹ a weighted average is $(1/3 \times 1.33 + 2/3 \times 1.51) = 1.45$ Å. Ionicity is zero for this lattice since there isn't any polarity in bonds between atoms of the same element. From these parameters a calculated value of $B = 447$ GPa is obtained.

For cubic diamond the coordination number, N_c , is 4 since all the carbon atoms are tetrahedral- sp^3 carbon atoms. Similarly all the carbon-carbon bond lengths are the standard sp^3 - sp^3 carbon bond length of 1.54 Å²², and the ionicity term is zero since all the atoms in the lattice are carbon. From these values a bulk modulus is calculated from the same equation as that used for Glitter; yielding $B = 435$ GPa for cubic diamond. From this simple analysis it is clear that Glitter is more than 12 GPa harder (resistant to deformation) than cubic diamond. The same will hold for any of the glitter allotropes as the coordination numbers, N_c , and the weighted average bond lengths should change in the same way as for carbon.

A similar calculation of the bulk moduli of a binary material adopting the cubic diamond structure (for example BN) and its respective glitter structure will show that the bulk modulus of the glitter structure is greater than that of the respective cubic diamond structure since the weighted average of the bond lengths is smaller for the 1,4-cyclohexadieneoid unit ring than for the corresponding cyclohexanoid unit ring. In the semi-empirical bulk modulus equation cited, the weighted average coordination number varies with the calculated bulk modulus linearly while the weighted average bond length varies with the calculated bulk modulus to an inverse $7/2$ power. The dominating factor in harder materials is shorter and stronger covalent bonds as is evidenced experimentally in the case of cubic diamond; a material less dense, yet harder than any of the transition elements.

Appendix II: Structures Derived from the Glitter Lattice--Hexagonite

Obvious structural variations from the Glitter lattice, which share the unique structural motif of extending 1,4-cyclohexadieneoid unit rings in 1-, 2- and 3- dimensions, can be imagined. These obvious structural variations of Glitter, or the glitter structures, are claimed here for the machining and compression applications already described for Glitter and the glitter structures in Section IV and Section V of this disclosure document. Further, the synthetic strategies for creating Glitter or any

²¹ taken from Bond Lengths and Angles in Molecules, **CRC Handbook of Chemistry and Physics, 71st ed.**, 1992, p.9-1.

²² *ibid* reference 20, p. 9-1

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of the glitter structures, that were described in Section III of this disclosure document, are claimed here for the creation of materials which are obviously structurally related to Glitter or any of the glitter structures described previously.

An important such structural variant of Glitter is Hexagonite²³ which is built from first linking 1,4-cyclohexadieneoid unit rings in 1-dimensional polyquinoid chains, as is the case in the Glitter lattice, and then cross-linking the polyquinoid chains through tetrahedral carbon atoms. In contrast, in the Glitter lattice the polyquinoid 1-dimensional chains are cross-linked by trigonal carbon atoms which then become part of the next chain of fused 1,4-cyclohexadieneoid unit rings in the adjacent polyquinoid chain (running perpendicular, or spiro, to the first polyquinoid chain) which results in the spirographite substructure of the Glitter lattice.

Cross-linking of the adjacent polyquinoid chains through tetrahedral carbon atoms produces cyclophaneoid stacks (called cyclopheneoid stacks in the case of the Glitter lattice) of 1,4-cyclohexadieneoid unit rings that extend in two dimensions; such a structure is called the paragraphite substructure of the Hexagonite lattice. By connecting the 2-dimensional paragraphite substructures to each other through cross-linking tetrahedral carbon atoms, an 'ababab' pattern of the cyclophaneoid stacks emerges in three dimensions with the alternating cyclophaneoid stacks being translationally displaced from each other by $(\cos 2/5\pi)r$ along the a-axis and $(\sin 2/5\pi)r$ along the c-axis, where r is the length of the sp^3 - sp^3 carbon-carbon single bond in Hexagonite. The Glitter lattice, in contrast, has cyclopheneoid stacks which run perpendicular, or spiro, to each other in all three directions.

Drawings of the 1-dimensional polyparaquinoid substructure of the Glitter lattice are shown in #5 of the Glitter Drawings Form, as has been described in Section II previously. By replacing the trigonal carbon atoms cross-linking adjacent 1,4-cyclohexadieneoid unit rings with tetrahedral carbon atoms, as is shown in #1 of the Hexagonite Drawings Form, the 1-dimensional cyclophaneoid stacks are produced. These stacks can themselves be cross-linked with tetrahedral carbon atoms again to produce the 2-dimensional paragraphite substructure of the Hexagonite lattice as is shown in #2 of the Hexagonite Drawings Form.

²³ the name originates from the hexagonal uniformity of this 3,4-connected three dimensional net as defined by A.F. Wells, **Three dimensional Nets and Polyhedra**, 1977, p.117

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From connecting together adjacent paragonite layers, the 3-dimensional Hexagonite lattice emerges as is shown in #3 of the Hexagonite Drawings Form. A generalized version of the Hexagonite lattice is shown in #4 of the Hexagonite Drawings Form in which A and B represent two different elements occupying 4-connected (tetrahedral) and 3-connected (trigonal) lattice points respectively; in a manner entirely analogous to the structures and substructures shown in the Glitter Drawings Form as discussed in Section II.

There are 20 possible allotropes of the group 13 or group 14 or ~~group 15~~ or group 16 elements which would adopt the structure pictured in #3 of the Hexagonite Drawings Form, which is termed Hexagonite, and 380 binary compounds of group 13 or group 14 or group 15 or group 16 elements which would adopt the structure of #4 in the Hexagonite Drawings Form, which is termed the hexagonite structure. These structures possess the same space group symmetry as the mineral nesquehonite (the trihydrate of magnesium carbonate), $Pmmm$ ²⁴. The 1- and 2-dimensional substructures will retain the respective symmetry elements of the hexagonite structure along their symmetry points, axes and planes, respectively.

As is apparent in the Hexagonite Drawings Form, the unit cell of Hexagonite has three trigonal carbon atoms and four tetrahedral carbon atoms, or a total of seven atoms in the unit cell. For the more general hexagonite structures, pictured in #4 of the Hexagonite Drawings Form, the presence of three trigonally coordinated atoms, B in drawing #4, and four tetrahedrally coordinated atoms, A in drawing #4, implies that the hexagonite structures will have the stoichiometry A_4B_3 to fit the $Pmmm$ hexagonite unit cell. Consequently the materials adopting the glitter structure and those adopting the closely related hexagonite structure will have the stoichiometries A_4B_2 and A_4B_3 , respectively. The structural motif that relates them to one another is the presence of 1,4-cyclohexadieneoid unit rings extended in 1-, 2- and 3-dimensions.

A prototypical model of the hexagonite structure has been built and photographed and the photographs are attached to this document. Direct and stereoscopic views of this lattice are shown in the photographs. Connections between the 3-connected atoms, element B in #4 of the Hexagonite Drawings Form, are shown in lavender in the photographs while connections between the 3-

²⁴ Powder Diffraction File Sets 1-5, Inorganic Volume, No. PD1S-5iRB, PDF Card Number 1-130, Joint Committee on Powder Diffraction Standards, Philadelphia, PA, L. Berry editor, 1967.

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connected and 4-connected atoms, element B to element A in #4 of the Hexagonite Drawings Form, are shown in white in the photographs. The unit cell of the hexagonite structure is outlined in each photograph by the red cord. These models define the three-dimensional hexagonite structure, for the machining and compression and other applications described in Section IV, in the same way that models of well-characterized materials such as halite, fluorite or cooperite define these structures.

Section V of this disclosure specifically claimed the creation and uses of the binary compounds C_4B_2 , Si_4C_2 , Si_4B_2 , B_4C_2 , C_4Si_2 , and B_4Si_2 which adopt the glitter structure; both the synthetic strategies to these binary compounds and the applications of these binary compounds as described in Sections III and IV. By analogy, the respective hexagonite structures described in this appendix, as shown in the Hexagonite Drawings Form, possessing the stoichiometries C_4B_3 , Si_4C_3 , Si_4B_3 , B_4C_3 , C_4Si_3 , and B_4Si_3 are claimed here for both the analogously worded synthetic strategies and applications as described in Section III and Section IV for the glitter structures.

Appendix III: Clarification on the Wording and Intent of this Disclosure

To be clear on the intent of Appendix II and this of this disclosure in general, the undersigned author, Michael John Bucknum, includes a generalized version of the wording in Section III and Section IV in which the wording, 'generalized glitter' can mean a hexagonite structure as described in Appendix II or any other obvious structural variation on the glitter structure as described in Section II:

III. Synthesis of Materials Claimed In Appendix II

Standard methods of Chemical Vapor Deposition (CVD) described in the literature for the synthesis of diamond films²⁵, for creating layered cuprate superconductors²⁶ and for other applications are claimed here as synthetic routes to the 20 Generalized Glitter allotropes and the 380 binary generalized glitter structures and their respective substructures as shown in the Generalized Glitter Drawings Form and described in Appendix II. Particularly of interest in this regard are the synthesis of the binaries of B, Si and C, by these methods, which adopt the generalized glitter structure or its substructures, as

²⁵ DeVries, R.C. *Synthesis of Diamond Under Metastable Conditions*, *Ann. Rev. Mater. Sci.*, **17**, 1991.

²⁶ Chern, M.Y., Gupta, A. and B.W. Hussey, *Layer-by-layer deposition of $La_{1.85}Sr_{0.15}CuO_x$ films by pulsed laser ablation*, *Applied Physics Letters*, **60**, 1992.

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described in Appendix II.

Standard solid state chemical synthetic methods including those described in any standard text of solid state chemistry²⁷ involving the use of powdered materials containing the desired amounts of group 13 or group 14 or group 15 or group 16 elements as compounds or in any of their other forms as precursor to the structures claimed here as described in Appendix II, are claimed as synthetic strategies for these materials. Particularly of interest in this connection is the application of these methods in the synthesis of alloys of B, C or Si possessing the structures claimed here as described in Appendix II. Of special mention in this regard is the use of the Acheson Process or a modified Acheson Process for synthesis of binaries involving C and Si which is claimed as a synthetic strategy for the creation of these generalized glitter structures.

A method of generating the structures claimed here of special mention is the high pressure synthesis of the generalized glitter structures or their respective substructures, as described in Appendix II, by static compression of single crystals of graphite or a graphite-like material (for example graphitic BN) along their basal plane by standard high pressure apparatus²⁸. By orienting a single crystal of graphite or a graphite-like material (for example graphitic BN) so that its basal planes are parallel with the compression axis it is claimed here that sufficient pressure will disrupt the basal plane and rupture the graphitic sheets in such a manner to create instantaneously quasigraphitic sheets which simultaneously crosslink to produce the structures claimed in this invention as described in Appendix II.

Well characterized methods of synthesizing diamond or its periodic analogs²⁹ by means of static high pressures and temperatures, or similar methods based upon shock compression synthesis³⁰, possibly in the presence of a catalyst, are claimed here as synthetic strategies for creating the materials described in Appendix II and claimed in this invention.

IV. Application of Materials Claimed in Appendix II Based Upon Generalized Glitter Structure

Applications of the generalized glitter structures described in Appendix II for machining and for compression applications include application to machining of other very hard materials³¹, the creation of anvil materials for high pressure studies, and general claims as replacements to diamond or graphite wherever a generalized glitter structure would be a convenient and viable replacement.

²⁷ West, A., **Solid State Chemistry**, 1990.

²⁸ Timmerhaus, K.D. and M.S. Barber eds., **High Pressure Science and Technology-Vol. 1: Physical Properties and Materials Synthesis**, Plenum Press, 1979.

²⁹ *ibid* 2, 3 and the references therein

³⁰ *ibid* 12 and the references therein

³¹ Boehler, R., **High Precision Grinding of Diamond Anvils, Proceedings of the AIRAPT Conference**, Denver, CO, 1993.

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Further applications for these materials are claimed to include use as materials to replace graphite or diamond wherever they are currently applied³² based upon the similarities such hybrid materials may share with graphite or diamond to make them convenient and desirable replacements. These replacement uses include needs for thermally and electrically conducting light weight materials as for example in electrochemical applications like those involving carbon electrodes or electrically conductive carbon-based materials, and as thermally conductive substrate material in the engineering of micro- and nanoprocessors in electronics and optics applications.

It is another claim of this invention that materials described in Appendix II, which adopt a generalized glitter structure and that empirically prove to be of the same magnitude of hardness as diamond be used as tools by which diamond and other hard materials are machined for use in their typical applications. Included among these applications is the use of these materials where they may prove useful for specialty machining of diamond anvils for use in high pressure cells and the use of superhard materials possessing a generalized glitter structure as components in high pressure cell equipment, including their use as materials for the anvils themselves.

Additionally claimed in this Section are the use of any of the substructures described in Appendix II, including the substructures pictured in the attached Generalized Glitter Drawings Form, for any applications where diamond or graphite are currently used such as those described in the previous paragraphs of this Appendix II.

V. Creation and Uses of Binary Compounds C_4B_3 , Si_4C_3 , Si_4B_3 , B_4C_3 , C_4Si_3 , B_4Si_3

Of particular importance among the 380 possible binary materials described in Appendix II of this invention, the binary materials of B, C and Si which adopt a generalized glitter structure are particularly claimed for use as superhard materials. It is well known that boron-carbides and silicon-carbides are the hardest materials known after diamond. It is also known that there are many different crystallographic environments in which B, C and Si are found, particularly of mention is the fact that B and C chemically bond both in tetrahedral and in trigonal planar configurations and Si nearly always occurs in a tetrahedral configuration. Therefore these materials are particularly claimed as superhard materials for machining and compression application.

Inclusion of this generalized wording for Section III, Section IV and Section V should make very clear the intent of this disclosure to include any and all materials which share the structural motif of extending 1,4-cyclohexadieneoid unit rings in 1-, 2- and 3-dimensions to produce superhard materials or materials to replace graphite

³² see reference 6 and Reynolds, W.N., **The Physical Properties of Graphite**, Elsevier Publishing Co. LTD, 1968 and Timmerhaus, K.D. and M.S. Barber eds., **High Pressure Science and Technology-Vol. 2: Applications and Mechanical Properties**, Plenum Press, 1979.

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and diamond wherever they are currently applied.

Appendix IV: Physical Characteristics of Glitter and Related Structures

It is obvious from the bond lengths and bond angles published in any chemistry-physics reference book³³ that a theoretical density could be calculated for any of the 3-dimensional glitter structures or hexagonite structures described in this disclosure. Calculation of these and other properties, with the exception of the semi-empirical formula for bulk modulus used in Appendix I, won't change the essence of the disclosed ideas of this invention, though such calculated physical properties may be useful in the identification of phases in synthetic attempts at making these materials.

Theoretical x-ray diffraction patterns, such as those routinely calculated using coded algorithms³⁴, can readily be calculated for any of the glitter structures or hexagonite structures or any related structures based upon extension of 1,4-cyclohexadieneoid unit rings in 1-, 2- or 3-dimensions. Once the space group and the identity and position of the atoms in the unit cell are specified, as has already been definitively described in this disclosure document for the glitter structure and for the hexagonite structure; the process of computing a theoretical diffraction pattern involves determining the Bragg angles of the diffracted x-rays from the Bragg equation using the Miller indexed lattice spacings of the unit cell and the dimensions of the unit cell as implied by the bond lengths and bond angles assumed. The intensities, as well as the positions of the Bragg reflections, can also be calculated from the structure factors:

$$F(hkl) = \sum_{\text{unit cell}} f(e^{2\pi i(hx + ky + lz)})$$

Here the scattered amplitude of x-rays, proportional to the intensity of the given reflection, for a particular Bragg reflection, $F(hkl)$, is obtained by adding the product of the scattering factor, f , for a given atom in the unit cell (approximately the same as the atomic number) with the geometrical factor, $e^{2\pi i(hx + ky + lz)}$, which describes the differences in the path lengths of x-rays scattered by each atom in the unit cell for a particular (hkl) Bragg reflection. Taking $\text{Re}(F^*F) = I^2$ the intensity, I , can be

³³ see reference 21 or the references therein, for example

³⁴ for a discussion of structure factors calculated for a unit cell see Buerger, M.J., **Crystal Structure Analysis**, Wiley and Sons, 1960 or Azaroff, L., **Introduction to Solids**, Wiley and Sons, 1960

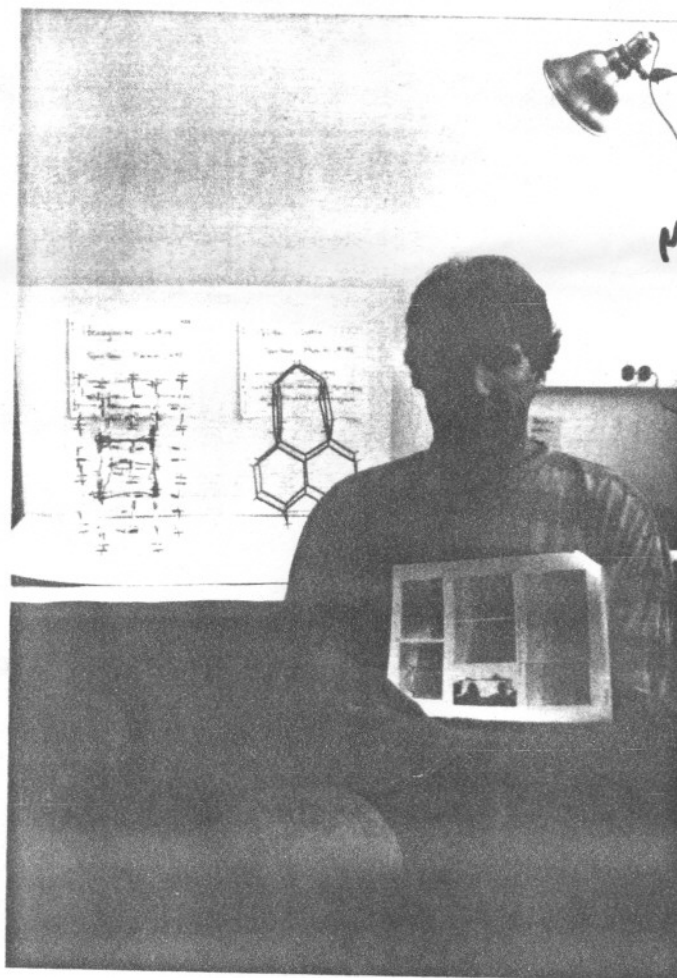
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determined from this equation.

Calculation of these theoretical diffraction patterns are dependent on the space group identity of the unit cell and the identity and position of the atoms in the unit cell, thus such calculated diffraction patterns won't change the essence of the disclosed ideas of this invention, though calculated diffraction patterns may be useful in the identification of phases in synthetic attempts at making these materials.

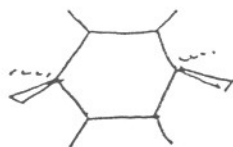
Other physical properties including thermal conductivity, heat capacity, electronic band structure, refractive index and chemical properties; which could be calculated approximately from various physical models, or inferred or estimated from chemical models: all of this information will ultimately be inferred for the purpose of identifying phases in synthetic attempts at making these materials. However in no case is the essence of the ideas described in this disclosure, based upon rigorous crystallographic concepts of symmetry and chemical concepts of bonding, changed by the absence or presence of information regarding physical or chemical properties of a glitter structure or an hexagonite structure or any obvious structural variations of these.

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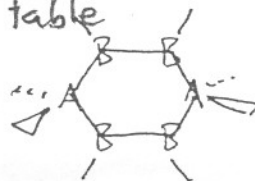


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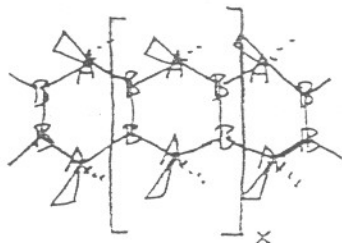
A, B are any of the Elements in Group 13, 14, 15 or 16 of the Periodic Table



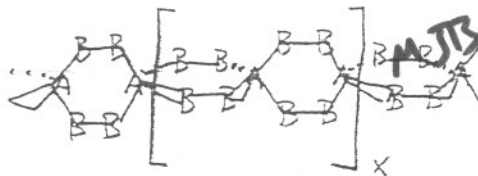
#1 1,4-cyclohexadieneoid unit ring



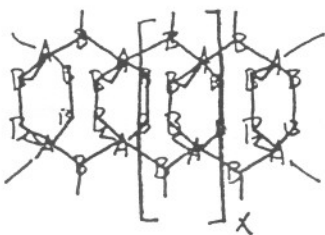
#2 Markush Structure for 1,4-cyclohexadieneoid unit ring



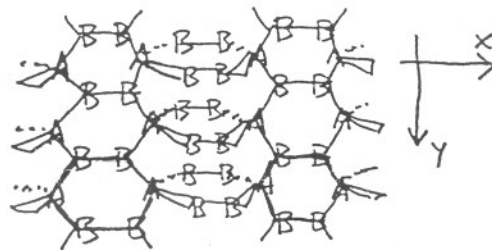
#3 polyquinoidal substructure of Glitter lattice ($x: 1 \rightarrow N_A$)



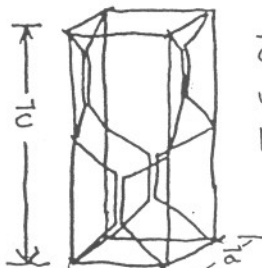
#4 polyspiroquinoidal substructure of Glitter lattice ($x: 1 \rightarrow N_A$)



#5 polycyclopheneoid substructure of Glitter lattice ($x: 1 \rightarrow N_A$)

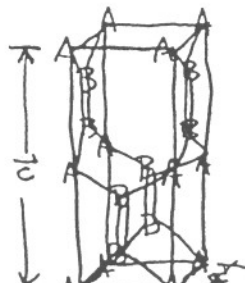


#6 spingraphite substructure of Glitter lattice ($x, y: 1 \rightarrow N_A$)



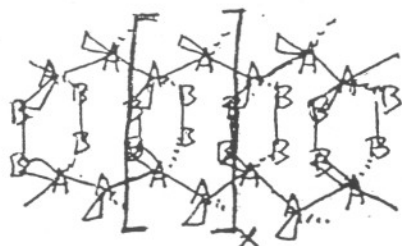
\vec{a} & \vec{c} are based upon published bond lengths & angles; see reference 21 of the disclosure

#7 Glitter Lattice, $P4_2/mmc$



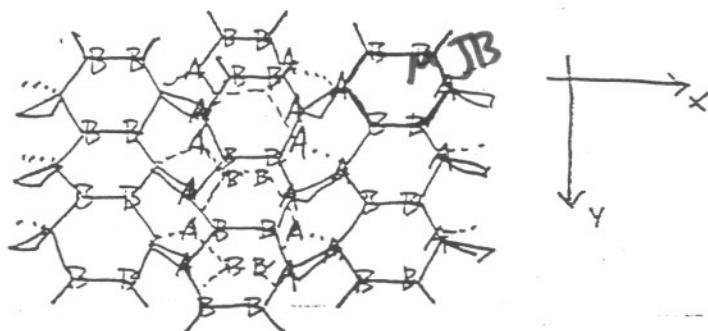
#8 Markush Structure: Glitter

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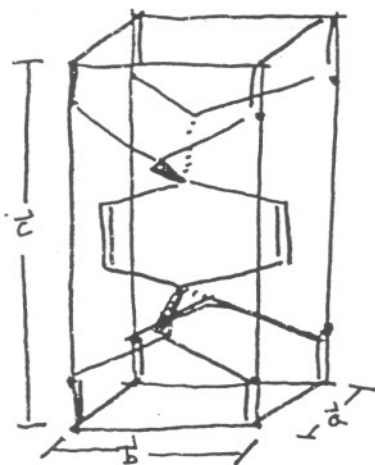


A and B can be any of the Group 13, 14, 15 or 16 Elements in Periodic Table

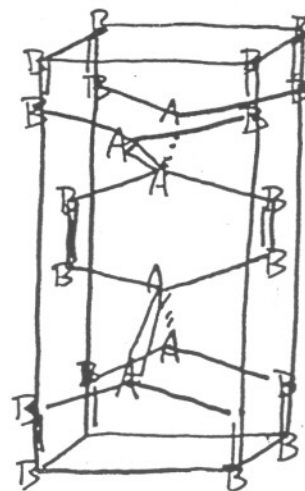
#1 polycyclophaneoid substructure of Hexagonite lattice (x: 1 → N_A)



#2 paragrafite substructure of the Hexagonite lattice (x,y: 1 → N_A)



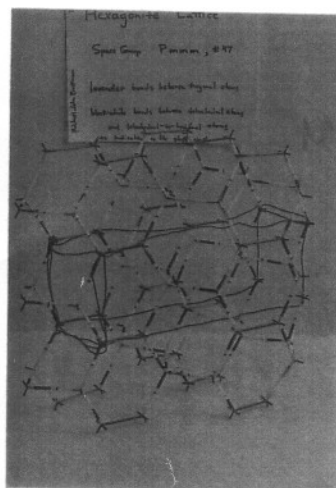
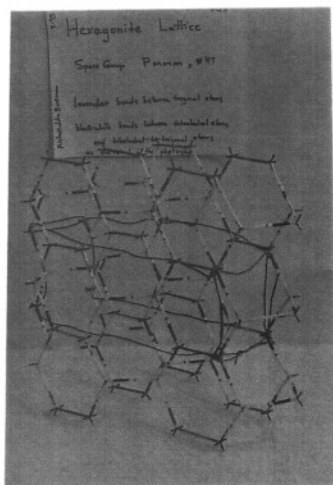
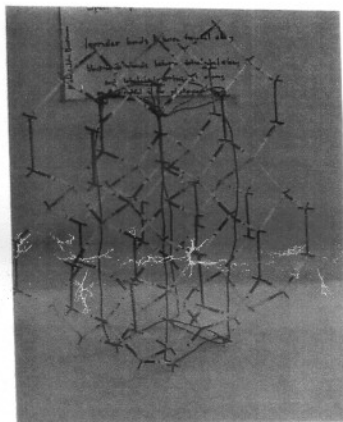
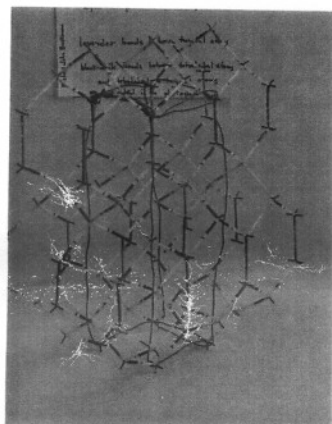
\bar{a} , \bar{b} & \bar{c} are based upon published bond lengths & angles; see reference 21 of the disclosure



#3 Hexagonite Lattice, Pmmm

#4 Markush Structure; Hexagonite

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JB

