

Chapter 1: Introduction

1.1 Background and Aim

Although diamond has sufficed as the hardest material known to man, its interaction with iron containing alloys at elevated temperatures limits its industrial application to machining of non-ferrous and non-metallic materials. In the 1960s a synthetic superabrasive cubic boron nitride (c-BN) was introduced on the market ⁽¹⁾. The value of c-BN as a superabrasive lies in its much higher oxidation stability compared to diamond and its nobility to iron attack at elevated temperatures ⁽¹⁾. However the hardness of c-BN is about half that of diamond. Over the years several attempts have been aimed at filling the hardness gap between the two traditional superabrasives. This has been driven by the need to obtain an all purpose, cost effective superabrasive with a wider range of applications. Furthermore, the need to find alternative superhard materials which compliment diamond in machining applications is not uncommon.

The B-C-N system has provided some of the most promising superhard materials which could address this problem ⁽²⁾. This emanates from the structural similarities (both low and high pressure polymorphs) and the slight atomic radii differences between carbon, boron and nitrogen. Thus it should be possible to obtain both binary and ternary solid solutions in this system with properties intermediate to those of the parent materials in the uncombined states. Technically, it would be right to assume that cubic BN-C materials would possess properties intermediate to those of diamond and c-BN. However the main challenges lie in

obtaining the most appropriate BN-C precursors and the prohibitively high pressures required to attain the phase transition. For instance, several methods have been used to obtain BN-C precursors in previous studies, but it still remains unclear whether these materials represent true solid solutions ⁽²⁾. Furthermore, the reported pressures for obtaining the cubic phases are prohibitively high for commercial production. However persistent research has proved the possibility of obtaining positive results over time and provides the basic knowledge to aid further development. This is the case with diamond and c-BN which are presently produced commercially in large quantities at relatively lower pressures than initially suggested by pioneering research ⁽³⁻⁴⁾. Considering this, the B-C-N system still remains promising in fulfilling the quest for alternative superhard materials.

In view of the above, the present work examined the possibility of obtaining B/C/N precursor materials using a solid state pyrolysis method. Sintering investigations were carried out under static high pressure and high temperature (HP/HT) firstly in a laser heated diamond anvil cell (LH-DAC) and a multi-anvil press. Additional studies were carried out under dynamic pressure conditions using shock compression technique with a gas-gun and column methods. It is envisaged that the knowledge generated in the present study will form a basis for future work in tailoring the synthesis conditions aimed at lowering the P, T requirements to commercially accessible values.

1.2 Project Overview

The present study was carried out with a view of investigating the possibility of obtaining a cubic BN-C material under HP/HT conditions from a polymer derived BN-C ceramic. Investigations were made under static and dynamic pressure conditions, with cubic phases being successfully obtained under static conditions. The research project is divided into six chapters. Chapter 1 presents the problem statement which has initiated this investigation. A theoretical background associated with superhard materials with particular emphasis on BN-C materials is presented in Chapter 2. Chapter 3 gives a summary of the experimental methods undertaken to achieve the goal of the project. The findings of the work are summarised and discussed in Chapters 4 & 5. Concluding remarks and comparisons with previous studies are made in Chapter 6.

CHAPTER 2: Literature Review

2.1: Superhard Materials: An Overview

A ‘superhard’ material by convention is one whose hardness exceeds 40GPa on the Vicker’s scale of hardness.⁽²⁾ In this regard, only diamond and cubic boron nitride (c-BN, *hereafter*) qualify for this title. However, over the years there have been tremendous efforts in the search for potential ‘superhard’ materials.⁽²⁻¹⁵⁾ This has been stimulated by the need to design materials which not only approach diamond in hardness but are more useful and complimentary to the traditional superhard materials.⁽²⁾ The B-C-N system is no exception in this regard. This system has generated some of the most promising ‘potential superhard’ materials for the future (e.g. the hypothetical C_3N_4 , BC_x phases, B_xN phases, and BC_xN phases). In particular, the metastable cubic BC_2N has been obtained under HP/HT conditions with Vickers microhardness of *ca.*76GPa being reported.⁽¹⁶⁾ Furthermore, it is expected that such alloys would possess mechanical and physical properties intermediate to those of diamond and c-BN.⁽¹⁷⁻²⁴⁾ For instance, these phases are expected to resist oxidation and graphitization to higher temperatures than diamond and remain strong for hardened steel cutting. This in a way gives them an edge over diamond in terms of range of applicability. However experimental results obtained so far are contradictory and it is not clear whether what has been claimed is from pure BC_2N solid solutions or mere mechanical mixtures of highly dispersed diamond and c-BN.^(8,9,11,22) In the case of the latter the full potential of c- BC_2N would not be realised. However despite this anomaly

a great deal of efforts are still being devoted towards obtaining these promising materials and as such this will keep the field energised for some time.

2.1.1: Designing Superhard Materials

The synthesis of materials with hardness comparable to diamond has gained fundamental technological interest over the years.⁽²⁴⁾ This has emanated from the need of obtaining materials which are more useful rather than ‘harder than diamond’ as highlighted earlier.⁽²⁾ This may include materials that are expected to be chemically and thermally more stable than diamond, and harder than c-BN. However to design new ‘superhard’ materials it must be understood what makes diamond special. It is a well known fact that the diamond crystal structure consists of tetrahedrally bonded sp^3 hybridised carbon atoms forming a rigid 3-dimensional covalent network of high symmetry with extreme resistance to shear.⁽²⁶⁾ There exist other carbon-based materials with shorter and stronger bonds than those in diamond (e.g. graphite) but these do not form a 3-dimensional covalent network as in diamond, rather these carbon networks are associated with bonding which is heterodesmic in nature, in which layers are linked by strong covalent bonds and separated by weak interlayer forces (Van-der Waal’s).⁽²⁶⁾ A 3-dimensional network composed of short, strong bonds is thus critical for hardness. The short bond length implies a high atomic and mass density comparable with diamond. Furthermore, a material is considered hard if it resists both elastic and plastic deformation.^(25,27) In principle, plastic deformation involves permanent and irreversible motion of atoms with respect to each other, often through the creation

and movement of dislocations.⁽²⁷⁾ This is in contrast with elastic deformation where atoms revert back to their initial positions after removal of load. Thus highly directional and strong bonding is of great importance in opposing or resisting such motions.

However microscopic parameters (i.e. type of atom, structure and atomic forces) alone do not govern the mechanical characteristics of a material but also the morphology of the material constituents, defects in the sample, methods of measurement and temperature play crucial roles.^(27, 28) In view of this, the strategic search for new superhard materials has also been directed towards modification of grain morphology and the state of defects to approach high hardness values.^(27, 28)

Another consideration in the designing of superhard materials is based on the stiffness of a material which is basically a measure of the resistance to volumetric compression (bulk modulus, B).^(25,27) Often materials with high bulk moduli values are seen to possess high hardness values.^(25,27-29) This is based on the fact that such materials would resist deformation when subjected to high loads owing to their high stiffness values. However it is a source of substantial confusion that high bulk modulus and high hardness are discussed together and many a time omitting the contribution by the shear modulus. In reality there exists a better correlation, with reasonable scatter between hardness and shear modulus, G . Furthermore plastic deformation is initiated when the shear component of the applied stress exceeds the yield stress.⁽³⁰⁾ Thus the prediction of hardness values

using the bulk moduli values alone may be misleading owing to this large scatter of the hardness-bulk modulus relationship.

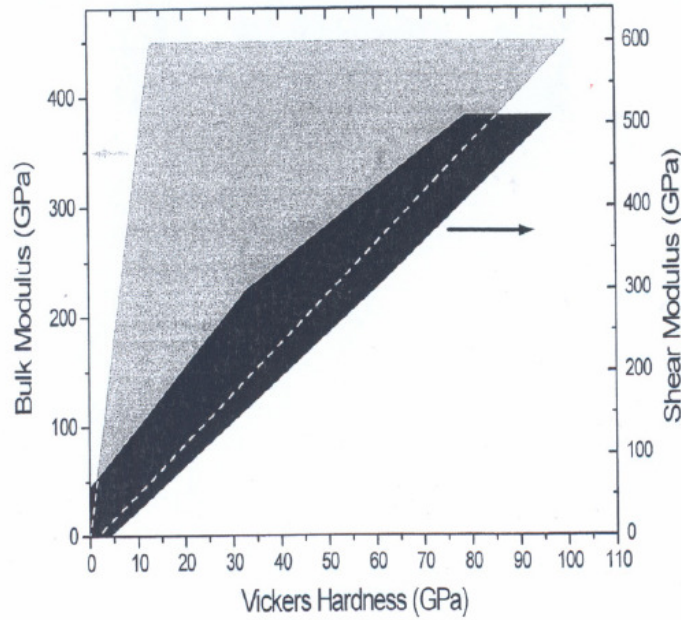


Figure 2.1: The general scattering of Vickers hardness as a function of shear modulus (dark region) and bulk modulus (grey region).⁽³⁰⁾

In view of this, these three main approaches have become the ‘radar’ to designing potential superhard materials. The first approach justifies the focus on the lighter elements boron, carbon, nitrogen and oxygen which form compounds with short covalent bonds. This has prompted research into three dimensional boron rich compounds (e.g. B_6O , $B_{22}O$, B_4C , $B_{25}N$ and $B_{53}N$)⁽³¹⁾, boroncarbonitrides ($B_xC_yN_z$)^(7-12, 16-24) and the hypothetical C_3N_4 .^(5, 6, 31) On the other hand the hardness values of existing superhard materials have been enhanced by manipulating the grain morphologies through various techniques. This second approach has led to a hybrid of nano-grained superhard materials with improved

mechanical properties.^(27, 28) The third approach focuses on achieving the goal through high bulk modulus elements. In this case the elements do not possess high enough hardness values to be considered ‘superhard’. Compounds have been tailored by alloying with small, covalent bond-forming atoms such as boron, carbon, nitrogen and oxygen structures with high packing indexes.⁽²⁸⁾ This has led to another hybrid of highly incompressible hard materials such as RuO_2 ⁽²⁹⁾ WC and $\text{Co}_6\text{W}_6\text{C}$ ⁽³²⁾, transition metal borides (TiB_2 , WB_4 , WB_2 and WB) and BeB_2 .⁽²⁸⁾ However despite the efforts, the first two approaches seem to have yielded materials with hardness values approaching that of diamond but not exceeding it. The progress in obtaining superhard materials using the third approach has somewhat been hindered by the fact that most of the compounds in this group possess some degree of ionicity (bonds not purely covalent) with low shear component values.⁽²⁷⁾ Figure 2.2 below shows details of the hardnesses of some superhard materials including several new materials prepared by high pressure synthesis.⁽³³⁾ Against this background, clearly it remains a challenge to experts in the materials science field to find substitute materials which fully complement diamond in this regard.

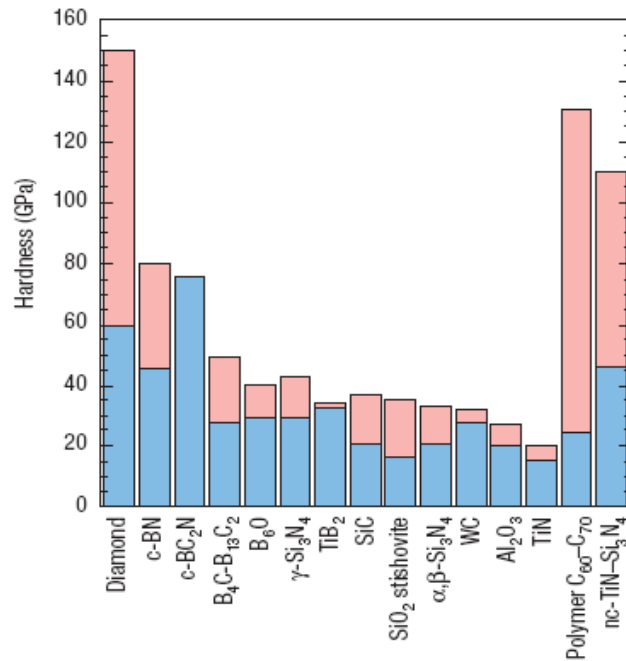


Figure 2.2: Typical hardness values of selected superhard, hard and several new materials prepared by high pressure synthesis showing both low-hardness (blue) and high-hardness (pink) values within a typically measured range. ⁽³³⁾

2.2: The Hardness Paradigm

Conventionally hardness is obtained by techniques that scratch or dent the surface. The scratch method is the longest established, known as the Mohs scale of relative hardness, with diamond ranked 10 as the hardest and talc ranked 1 as the least hard. However such a method excludes a lot of technologically important engineering materials hence its use is limited to the mineralogy field. The most commonly and more scientifically accepted is the indentation method. The hardness is deduced from the size of the indentation after an indenter has deformed a material. The size of the permanent deformation depends on several

factors such as pressure, temperature, porosity, impurities, dislocations and other defects.^(34, 35) In principle, the procedure measures the resistance of a material to the volume compression produced by pressure created by the indenter in a localised area.⁽²⁹⁾ Thus materials softer than the indenter tip material deform plastically and results can be interpreted easily. However for superhard materials where the hardness values approach those of diamond indentation no longer relies only on the plastic deformation but other factors such as brittle cracking and deformation of the indenting tip.⁽³⁵⁾ This makes hardness determinations of superhard materials a very difficult procedure.

In light of this, it is critical to provide details regarding the type of indenter, method used, applied loads, time of indentation, sample orientation and quality of tested surface when comparing the hardnesses of superhard materials.⁽³⁵⁾

2.2.1: Fracture Mechanics of brittle solids

Although ceramic materials have shown an unquestionable relevance to a diversity of technologies, their ability to resist crack propagation still remains a problem. Studies aimed at understanding the fracture phenomenon of ceramic materials are not uncommon.⁽³⁶⁻³⁸⁾ In practice fracture predictions are obtained from an experimentally determined fracture toughness value. Conceptually, this is a measure of a material's resistance to crack propagation and several methods can be used to determine it, details of which are presented in several publications.^(37, 39-41) A commonly used method is the hardness indentation method which yields

the fracture toughness component (K_{IC}) value. K_{IC} describes a critical value of the stress intensity factor, K_I which is a measure of the resistance to crack propagation initiated by stresses created near the crack tip during loading of a specimen.⁽⁴²⁾ K_I has been found to depend on the applied load, initial crack size and component geometry and its value increases until unstable crack propagation occurs at some critical value when; $K_I = K_{IC}$.^(42,43)

Three loading modes creating high stress at the crack tip have been identified as *Mode 1* (tension normal to crack plane); *Mode 2* (shear loading in crack direction) and *Mode 3* (out of plane shear loading).⁽⁴³⁾ *Mode 1* has been identified to be particularly the most useful for brittle materials with low fracture toughness values.⁽³⁸⁾ It has been reported earlier that the most problematic part in toughness determination is the creation of a crack and measuring its size.⁽⁴²⁾ This emanates from the fact that cracks are only initiated at loads in excess of a critical load, P_c .⁽³⁸⁾

The development of cracks in brittle solids occurs in a sequence of steps. Upon loading, the elastic limits of most ceramic materials are exceeded, a confined plastically deformed zone forms around any sharp points or corners of the indenter.^(37, 44) The indenter can be thought of as a wedge inducing tensile stresses in the surrounding material.⁽⁴⁵⁾ The tensile stresses overlap with the compressive stresses caused by the pressure applied by the indent thus restricting the mobility of the cracks formed.⁽⁴⁵⁾ This marks the initiation stage of ‘median vent’ cracks (Palmqvist cracks) which subsequently propagate radially outwards along suitable

planes of symmetry.^(37,46) Upon unloading, the compressive stress component ceases to exist and cracks formed assume their final length.⁽⁴⁵⁾ The crack will grow until a point at which the stress intensity is in equilibrium with the toughness of the material.⁽⁴⁵⁾

It has been observed that for highly brittle ceramics or at high indentation loads lateral vent cracks (half penny) initiate upon unloading and subsequently extend laterally from the deformation zone towards the specimen surface.⁽³⁷⁾ These cracks describe chipping phenomena in ceramic materials.

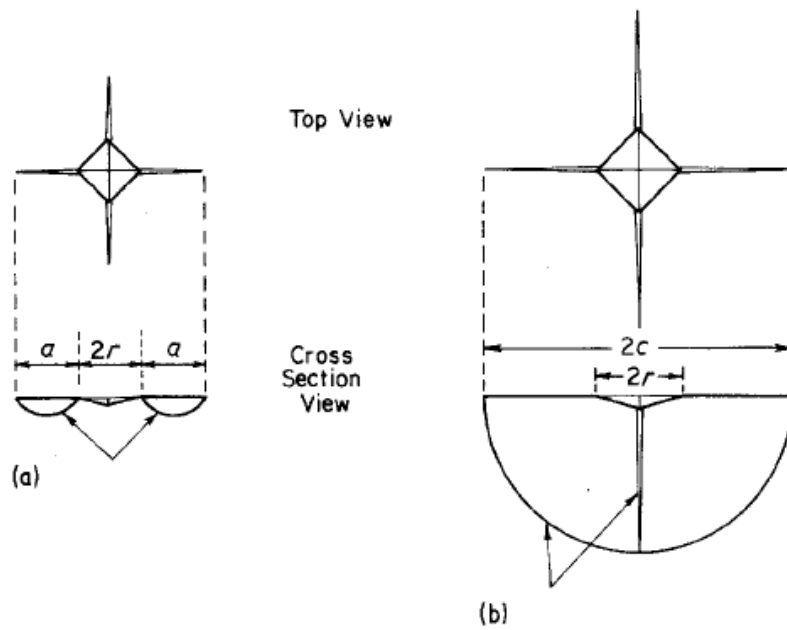


Figure 2.3: Schematic representation of (a) Palmqvist radial cracks and (b) median (half penny) cracks created by Vickers indentation as shown by the arrows.

(46)

2.2.2: Fracture Toughness determination of brittle materials

In view of the above a measure of the crack length generated during indentation would be a reasonable predictor of a material's crack stopping capability. Thus a tougher material would be expected to have a relatively shorter crack length in comparison to a weaker material. Evans and Charles *et al* ⁽³⁹⁾ developed a fracture determination method using cracks which develop during a Vickers hardness indentation test. Such a method consists of three basic steps namely;

- i) Crack generation in a test specimen.
- ii) Measurement of load of failure.
- iii) Determination of K_{IC} from failure load, failure stress and crack depth.

The standard method used for ceramic materials involves using Vickers indentation to initiate cracks which are later used to determine the K_{IC} from equation 2.1 below;

$$K_{IC} = 0.032H\sqrt{a}\left(\frac{E}{H}\right)^{\frac{1}{2}}\left(\frac{c}{a}\right)^{-\frac{3}{2}} \quad [2.1]$$

where H is the hardness; E is the Young's modulus; a is the half indent diagonal and c is the length of crack.

However the above formula is limited to materials whose Young's moduli values are well known. Shetty *et al* ⁽⁴⁶⁾ developed a relationship based on Palmqvist radial cracks which is independent of the Young's modulus E .

$$K_{IC} = 0.0889 \sqrt{\left(\frac{H * P}{4l} \right)} \quad [2.2]$$

where H is the Vickers hardness; P is the indent load; $l=c-a$ where $2a$ is the indent diagonal and $2c$ is the length of full crack.

Given the diverse cracking mechanisms associated with ceramic materials, both the stress field under load and residual stress are very complex.⁽⁴⁷⁾ The single edge V-notch method is a more reliable, albeit more reliable method.^(47b)

2.2.3: Elastic Properties of Materials

For years now the elastic properties of materials have become a standard formula in predicting the hardness values of potential ‘superhard’ materials. The most important being the bulk modulus, B and the shear modulus, G which are inturn correlated by the Poisson’s ratio, ν . The bulk modulus, B can be defined as the resistance of a material to volumetric compression through the expression derived by Cohen *et al*⁽⁴⁸⁾

$$B = -V \frac{\partial p}{\partial \nu} = \frac{V \partial^2 E}{\partial V^2} \quad [2.3]$$

where V , p and E are the volume, pressure and energy respectively.

The bulk modulus and the hardness of a material are closely related to the molar volume, nature of chemical bonding, and the crystal structure.⁽³¹⁾ M.Cohen *et al* further expanded his derivation to show the dependence of the bulk modulus B in (GPa) on the bond length d in (Å).^(31, 48)

$$B = \frac{1971 - 220\lambda}{d^{3.5}} \quad [2.4]$$

Where λ represents ionicity, $\lambda = 0$ for homopolar solids of G4 elements and $\frac{1}{2}, 1$ and 2 for heteropolar solids of group 3-4, 3-5 and 2-6 elements respectively.^(31, 48, 49) Clearly an increase in ionicity results in a decrease of B . This expression has been extended to account for non octet compounds where average coordination number $N_c \neq 4$ to give:

$$B = \frac{\langle N_c \rangle (1971 - 220\lambda)}{4d^{3.5}} \quad [2.5]$$

From another viewpoint, the bulk modulus B can be obtained from elastic constants through expression 2.6 below;^(27, 48)

$$B = \frac{(c_{11} + 2c_{12})}{3} \quad [2.6]$$

c_{ij} denotes an independent elastic constant in a specific direction i on plane j which determines the response of a crystal to external stresses and provides information about bonding characteristics between adjacent atomic planes, anisotropic bonding character and structural stability.

The above formula holds for isotropic materials. A superhard material should preferably be isotropic to prevent preferential deformation in a given direction.⁽²⁷⁾

The shear modulus, G describes a materials' resistance to elastic deformation by shear and is related to the bulk modulus through the expression below;

$$G = \left(\frac{3}{2}\right)B(1 - 3\nu) \quad [2.7]$$

where ν is the Poisson's ratio.

The value of ν is very small for covalently bonded materials (typically $\nu \sim 0.1$) in this case $G \sim 1.1B$. For ionic compounds $\nu \sim 0.25$ and $G \sim 0.6B$ and for metallic materials $\nu \sim 0.33$ and $G \sim 0.4B$.⁽²⁴⁾ The shear modulus can also be expressed in terms of the elastic constants;

$$G = \frac{(c_{11} - c_{12} + 3c_{44})}{5} \quad [2.8]$$

In the case where isotropy is observed ($c_{11} - c_{12} = 2c_{44}$) thus ($G \sim c_{44}$). Clearly, for high values of B and G , c_{11} and c_{44} must be high with low c_{12} value. Considering

the Cauchy relation, a central forces model, $c_{12} = c_{44}$, the condition described above is clearly the opposite of the Cauchy relation.⁽²⁷⁾ In view of this, two conditions satisfy the existence of high B and G values, that is, on the one hand v must be small and on the other, central forces must be absent.⁽²⁷⁾ This points to highly directional type bonding being most suitable, i.e., covalent type bonding. This also arises from the fact that materials that exhibit limited bond bending are those with directional bonds in high symmetry, 3-D lattice, with fixed atomic positions.⁽²⁷⁾ Purely covalent materials stand a better chance than materials with any other type of bonding in this regard. In the case of ionic or partially covalent materials the presence of electrostatic interactions induces non-directionality and yields low bonding force constants resulting in low shear moduli.⁽²⁷⁾ This explains the lower shear modulus values and consequently lower hardness values than expected possessed by ionic-covalent compounds. Thus the hardness of a material is properly studied by considering both the resistance to volumetric change (B) and shape deformation (G). Diamond for instance which is the hardest material known to man has a shear modulus value (540 GPa) which is greater than its bulk modulus value (442 GPa).⁽²⁷⁾

2.3: The B-C-N System

It is well known that the structural and electronic similarities between graphite and hexagonal boron nitride (h-BN) have stimulated the synthesis of solid solutions of the two materials. Such solid solutions are expected to possess a graphite like layered structure with a partial substitution of carbon by boron and

nitrogen.^(49,50) These hybrid materials are expected to possess tunable intermediate properties depending on the composition and structure of the resulting product. Furthermore, semiconducting properties are expected from the mixture of semimetallic graphite and the insulating h-BN and the cubic phase has been confirmed to possess a hardness value greater than that of c-BN and is presumed to compliment diamond with regards to oxidation resistance and reactivity with ferrous alloys in machining applications.^(11,12,16,51) For nearly two decades, much effort has been devoted to the theoretical design and experimental synthesis of the cubic superhard phases under *HP/HT* conditions.^(7-12,16) It has been observed that *HP/HT* synthesis of BC₂N materials strongly depends on the precursors used, not only their chemical composition, but also crystal structure and synthesis history which in turn determines the mechanism involved in the *HP/HT* phase transformation to the denser phase.^(7-12,16,22)

A wide range of synthesis methods have been used to obtain precursor materials these include the conventional mixing and ball-milling to the more complex chemical synthesis routes.^(11,52-61) This has resulted in a diverse range of compounds being obtained and hence physical and mechanical properties do differ as well. However what motivated most of investigations is the possibility of obtaining solid solutions in the B-C-N system. The study of solid solutions is a well known topic in the field of metallurgy. This field has yielded technologically important metallic alloys which find various industrial applications. However to achieve this, some basic principles need to be considered and understood in designing solid solutions in any other system including the non-metallic ones.

2.3.1: B-C-N Solid Solutions: An Insight

In accordance with the Hume-Rothery rules an extensive substitutional solid solution is only possible when certain conditions are met.⁽⁶²⁾ Among these are the size factor, crystal structure factor, difference in electronegativities and the valency factor. In principle, the atomic size difference should not exceed 15%, the components should possess similar crystal structures or there should be a reasonably negligible mismatch (such as in diamond and c-BN), electronegativity difference should be close to zero and valency difference should be minimum (thus minimising the formation of intermediate compounds) for complete solid solubility.⁽⁶²⁾ These rules have been applied extensively in metallic alloy systems however they also play a crucial role in non-metallic systems as mentioned earlier.
(62)

Carbon, boron and nitrogen which make up the B-C-N system follow each other in the periodic table with atomic size differences well below 15% and the resulting compounds formed possess similar ambient hexagonal type crystal structures and lattice parameters ($a = 0.2461(7)\text{nm}$; $c = 0.6710(6)\text{nm}$) for graphite (*ICDD NN.56-0159*)⁽⁶³⁾ and ($a = 0.2504(4)\text{nm}$; $c = 0.6656(2)\text{nm}$) for h-BN (*ICDD NN.34-0421*).⁽⁶⁴⁾ Furthermore, carbon and boron nitride possess similar phase diagrams and undergo similar phase transitions to form four coordinated sp^3 hybridised cubic and hexagonal phases under high pressure and high temperature conditions.

Investigations concerning the solubility of boron in carbon showed a maximum solubility of boron in carbon of *ca.* 2.35at% at 2350°C and that it is of substitutional type.⁽⁶⁵⁾ The solubility was found to decrease with decreasing temperature with a maximum solubility of *ca.* 1wt% at 1800°C being reported.⁽⁶⁵⁾ On the other hand, nitrogen which is also neighbouring to carbon was found to be substitutionally doped into graphite intralayers.^(48,66) Nitrogen concentrations of up to *ca.* 40wt% have been reported earlier.⁽⁶⁶⁾ A well known graphitic compound containing substitutional nitrogen is the hypothetical C₃N₄.⁽⁴⁸⁾ In recent years there has been increased interest in boron doping of diamond to produce several attractive properties.^(67,68) On the other hand nitrogen doping of diamond is not uncommon. Impurity nitrogen clusters are found in type 1a natural diamond and substitutional nitrogen is found in type 1b diamond with concentrations of *ca.* <1ppm to 1%.^(69,70) However only several hundreds of ppm of boron and nitrogen can be doped in diamond.⁽⁶⁸⁾ This is due to limited solubility of the dopants in diamond compared to graphite. Thus it would be reasonable to assume that the high pressure B-C-N phases will be more thermodynamically prone to dissociation because of the limited solubility. However in accordance with phase stability calculations by Lambrecht *et al* ⁽¹⁸⁾ the diamond/c-BN mixtures will appear like true solid solutions even though they are metastable. This is attributed to the much larger kinetic barriers required for bond breaking compared to driving force towards phase separation.⁽¹⁸⁾ Thus metastability of the B-C-N system should not be an impediment to further study as kinetic barriers towards phase separation even at fairly elevated temperatures are expected to be very significant.⁽¹⁸⁾

2.4: Crystal Structure and Properties of B-C-N Compounds

The structural similarity between graphite and h-BN forms the basis of BC_2N solid solutions. Conceptually, the B-C-N compounds are expected to possess a hexagonal type crystal structure and hexagonal BC_2N (h- BC_2N , *hereafter*) crystals have been synthesised under HPHT conditions with a proposed *ABAB...* type stacking.^(71,72) Theoretical propositions have been made concerning the stability of such a structure and always a problem arises in determining the most stable/preferred structure of the BC_2N monolayer.^(73,74) This has been shown to be due to the presence of an apparent competition between structural stress and chemical bond strength owing to different bond lengths present in the same structure i.e. C-C, B-N, B-C and C-N bonds.^(73,74) These calculations are based on the assumption that B-B and N-N interactions are kept to a minimum since they have a large formation energy.^(74, 75)

On the other hand most of the experimentally determined structures show turbostratic behaviour i.e. high degree of disorder along the c-axis, or are completely amorphous. This makes crystal structure determination difficult.⁽⁵²⁻⁶¹⁾ Naturally it is expected that a hexagonal to cubic transformation be induced under high pressure and temperature. The cubic phases reported so far are composed of aggregated submicron BC_2N crystallites.^(2,9,11,12,16) The synthesis of single crystals of adequate size has not been achieved so far owing to the metastability of the BN-C materials, which inhibits long holding times at high temperatures.⁽¹⁸⁾

In view of this, the BC₂N structures are still not well understood despite the many efforts to synthesise these solid solutions. There is still need to carefully relate what has been predicted from theoretical modelling to what is obtained experimentally to understand this area of study. Furthermore, the aspect of structural evolution under extreme conditions of pressure and temperature remains important in understanding the resulting structures.

2.4.1: Theoretical Structure Modelling of h-BC₂N

About sixteen possible geometries have been proposed for the BC₂N monolayer using methods such as pseudopotential local-orbital calculations, semi-empirical and classical methods based on an eight atom unit cell.^(49,50,73,76,77) In principle, the atomic arrangements in the proposed BC₂N structures have been investigated from a bond energy accounting viewpoint. As highlighted previously there is competition between bond strength and structural stress in the BC₂N structure thus the most stable structure would be one minimising structural stress. This means that the most stable structures are the ones with the lowest total energies and possess the highest chemical bond energies. It has been reported that models maximising the number of B-N and C-C bonds are the most stable among all homogeneous BC₂N systems.^(49,73) One such model was described by Liu *et al*⁽⁵⁰⁾ in which each C atom is bonded to two other C's and either one B or one N and every B atom has two N and one C nearest neighbours. Such coordination has been found to lead to C₂ and BN chains extending throughout the plane with few C-N and B-C bonds.^(49,50,73) Structural stresses are kept to a minimum since the

bond length difference between C-C ($1.44\text{\AA}$) and B-N ($1.45\text{\AA}$) is *ca.*1%. This difference is much smaller than in models consisting of more of B-C ($1.53\text{\AA}$) and C-N ($1.40\text{\AA}$) in the same monolayer. In that case a bond length difference of *ca.*13% is expected.^(49,73) These bond lengths are based on the predicted BC₂N structures under relaxation.⁽⁷³⁾

If the aforementioned theory holds then there is a possibility of phase separation into graphite-like and h-BN phases in the BC₂N system i.e. the BC₂N system is always thermodynamically stable towards segregation to graphite and h-BN.⁽⁴⁹⁾ This basically maximises the B-N and C-C bonding and in turn minimises the number of B-C and N-C type bonds. Luo *et al*⁽⁷⁷⁾ carried out calculations on the formation energies of sixteen of the supposedly stable modifications and showed that only one structure was stable. The energies of formation of the other fifteen structures were found to be positive with the exception of the alternate BN/C₂ layered structure. In this case the energy of formation was defined as;

$$\Delta E = E_{BC_2N} - \frac{1}{3}(2E_{\text{graphite}} + E_{h-BN}) \quad [2.9]$$

This result is consistent with several other calculations done earlier.^(21,22,73) A further classification based on this phase separation has been proposed by Nozaki *et al*⁽⁷³⁾ and Azevedo *et al*⁽⁷⁸⁾ consisting of segregated ‘striped’ and ‘island’ type systems mainly based on the layer configuration as shown in the figures below.^(73,78) In segregated systems the B-C and C-N bonds with smaller bond energies were assumed to be located only in the boundaries between C₂ and BN

layers.⁽⁷³⁾ A calculation of the cohesive energies using the semi-classical method have shown the striped pattern to be more stable than the island type for small unit cells.⁽⁷³⁾ This was attributed to the shorter boundaries between the two phases in the striped pattern compared to the island type.⁽⁷³⁾

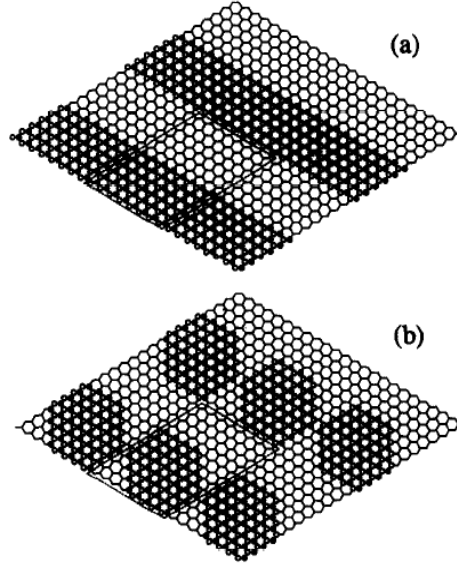


Figure 2.4: Topographical view of the predicted segregated type BC_2N monolayers with a) striped and b) island type configuration consisting of 192 atoms (*dark spots are graphite layers*).⁽⁷³⁾

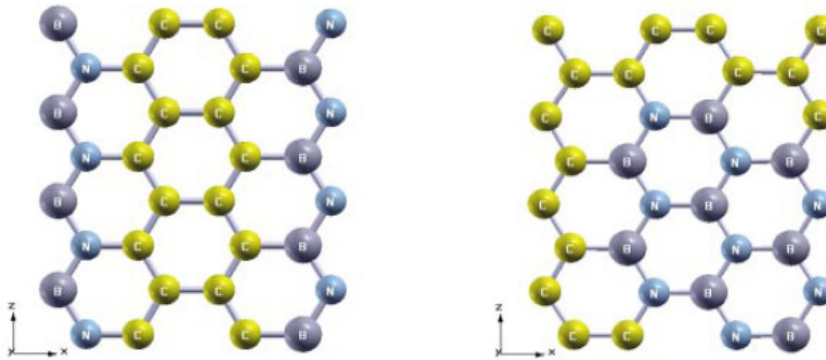


Figure 2.5: A topological view of the 'stripe like' (left) and 'island like' (right) B-C-N monolayer as described in [78].

Thus the number of B-C and C-N bonds in the striped pattern is less than in the island pattern. However in the case of large unit cells the difference between the cohesive energies of the two patterns becomes negligibly small.⁽⁷³⁾ Therefore, it is expected that the striped and island patterns actually co-exist as a quasi-stable state.^(73, 78) Furthermore, it is likely that the graphite and h-BN sheets are stacked alternately as segregated systems of BC₂N. In view of this, the synthesis of a homogenous BC₂N with a small sized unit cell is only possible through a well-controlled thermal method promoting high atomic mobility resulting in a B-C-N monolayer with all atoms in the same layer and minimum segregation. There are no experimental details on the crystal structure of h-BC₂N. This is due to lack of high quality h-BC₂N samples produced so far. However attempts have been made to synthesise h-BC₂N crystals under *HP/HT* conditions and the results on selected publications are summarised below;

Table 2.1: Summary of lattice parameter data (*a* and *c* values) for the graphite-like BN-C crystals in comparison to the theoretical values from ideal mixing.

Author	Composition	<i>a</i> (nm)	<i>c</i> (nm)	<i>Synthesis conditions</i>
Nicolich <i>et al</i> ⁽⁷¹⁾	BC _{1.65} N	0.248(2)	0.662(0)	Static HPHT
Yamada <i>et al</i> ⁽⁷²⁾	BC ₂ N	0.247(5)	0.676(2)	Shock wave
Komatsu <i>et al</i> ⁽⁵⁹⁾	CB _{0.49} N _{0.60}	0.244	0.681	HT- pyrolysis
Andreev <i>et al</i> ⁽⁵⁷⁾	BC ₂ N	0.249(7)	0.733(3)	HT- pyrolysis
ICDD no:56-0159	graphite	0.246(1)	0.671(1)	
ICDD no:34-0421	h-BN	0.250(4)	0.665(6)	Theoretical data
Ideal mixing	BC ₂ N	0.247(3)	0.669(3)	

HT: High Temperature, HPHT: High Pressure High Temperature.

Nicolich *et al* ⁽⁷¹⁾ proposed an orthorhombic type arrangement consisting of all three atoms present in the same monolayer as shown in Figure 2.7 below. However this structure contradicts the theoretical proposals above as it was found to be unstable. Thus it remains unclear what kind of structure is most stable and furthermore the final structure is governed by the precursors and synthesis method used. This area of study has remained inconclusive for some time and it is hoped that good quality, highly crystallised h-BC₂N samples will be produced in the near future.

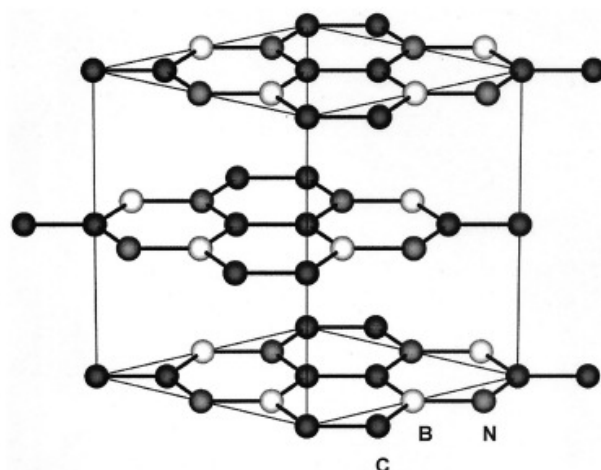


Figure 2.6: Proposed g-BC₂N crystal structure with atomic intermixing. ⁽⁷¹⁾

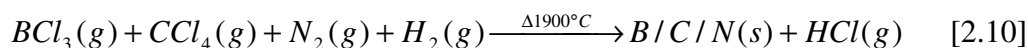
2.5: BN-C Precursor Synthesis Methods

There are several syntheses routes which can lead to BN-C phases, however the question whether the methods used in earlier works lead to complete solid solutions still remains open. As mentioned earlier several synthesis methods have

led to different modifications of BN-C materials and the precursor material remains key to the characteristic behaviour of the high pressure phase obtained. Thus it is important to consider and understand the basic science behind the most prominent synthesis techniques that lead to BN-C compounds.

2.5.1: Chemical Vapour Deposition (CVD)

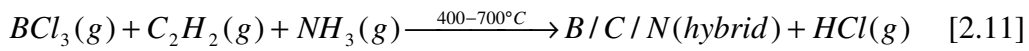
This technique is used extensively in the deposition of thin films from gaseous precursors on solid substrates.⁽⁷⁹⁾ It has been used successfully in the deposition of diamond and c-BN films of high technological importance.⁽⁷⁹⁾ This has prompted the synthesis of BN-C phases using gaseous mixtures and high volatility polymeric compounds containing all the three atoms.⁽⁸⁰⁻⁸⁸⁾ However the more atoms involved the more challenging the process becomes. This is evidenced by the results obtained so far. The success of deposition is depended on the statistical probability of obtaining BC₂N in favour of graphite and h-BN. The very first attempt by Badzian *et al*⁽⁸⁰⁾ was carried out using a gaseous mixture of BCl₃/CCl₄/N₂/H₂. At 1900°C, spheroidal polycrystalline (BN)_{0.26}C_{0.74} was deposited on a graphite rod in accordance with the reaction below.



However the products were obtained within a narrow reaction range with formation of some B₄C crystals below 1900°C and at temperatures above 1900°C Si contamination was observed.⁽⁸⁰⁾ The films were found to decompose to B₄C,

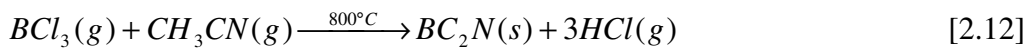
graphite and nitrogen at temperatures of 2200°C under argon atmosphere. Furthermore the BN-C solid solution decomposed to B₄C and graphite at a pressure of 3GPa and temperature of 2500°C in a Bridgeman press.⁽⁸⁰⁾

In a separate set of results Kaner *et al*⁽⁸¹⁾ prepared the B/C/N films on either quartz or pyrolytic BN substrate by reacting BCl₃, C₂H₂ and NH₃ gases at temperatures of 400°C and 700°C through the reaction below;



A dark grey to black solid was obtained with a turbostratic type structure. The products prepared at 400°C had a composition of B_{0.485}C_{0.07}N_{0.485} and that prepared at 700°C was B_{0.35}C_{0.30}N_{0.35}.⁽⁸¹⁾ Generally the final product stoichiometry becomes more difficult to control with increasing number of gaseous precursors owing to the fact mentioned earlier.

Further works by Kouvetakis and Sasaki *et al*⁽⁸⁹⁾ utilising only two gaseous reactants resulted in better ordering and more accurate compositions. Typical reactants used were boron trichloride (BCl₃) and acetonitrile (CH₃CN) at relatively lower temperatures *ca.* 800°C on quartz substrates via the reaction below;



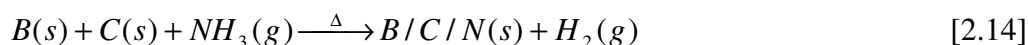
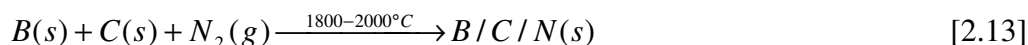
The films produced in this way had characteristic broad turbostratic reflections with no sheet to sheet registry.

Another interesting aspect is the use of highly volatile polymeric compounds such as alkylamineboranes, $R_3N \cdot BH_3$ containing all the three atoms. This has been made possible by the use of single reactants to replace a combination of reactants in earlier works described above. Typical examples of polymeric compounds used include dimethylamine-borane (DMAB, *hereafter*), $(CH_3)_2NH \cdot BH_3$ and trimethylamine-borane (TMAB, *hereafter*), $CH_3)_3N \cdot BH_3$.^(84, 85)

Although the above mentioned methods have yielded highly homogeneous materials, the difficulty in control of stoichiometries and low yields obtained are major constraints.

2.5.2: Solid Phase Nitriding

This is one of the oldest, simplest and still widely used method to mix together powdered reactants. A typical reaction is one used by Kosolapova *et al*⁽⁹⁰⁾ in which boron and carbon powders were heated at 1800-2000°C in N_2/NH_3 for prolonged periods promoting the reactions below;



In separate studies investigations have been done using mixtures of C_3N_4 nanospheres and elemental boron at high temperatures and pressure.⁽⁹¹⁾ In this case the aim was to induce both a chemical reaction to a BN-C phase and simultaneously to attain a phase transformation.

The formation of BC_2N in such reactions is diffusion controlled occurring at the solid (B/C or B/ C_3N_4) interfaces by a process of nucleation and growth. At elevated temperatures it is envisaged that the reactant atoms have enough energy to diffuse towards the interface forming the product. However the process slows down as the interface thickens and effectively the reactants are no longer in contact.⁽⁷⁹⁾ A complex diffusion process is therefore required in which solid ions diffuse towards the thick interface. Thus on the atomic level there is always some degree of inhomogeneity which renders the method ineffective for the formation of complete solid solutions.

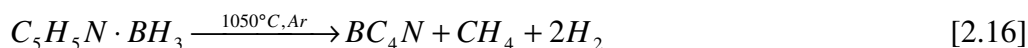
2.5.3: Solid-phase Pyrolysis

This process was developed in the mid 1970s initially with the aim of fabricating SiC inorganic fibers.⁽⁹²⁾ It has however been extended to the preparation of multi-component ceramics including BN-C ceramics and other nonoxide ceramics in relatively high yield.⁽⁹²⁾ Conceptually this method involves a 3-stage process involving thermal decomposition of organometallic preceramic polymers and can be summarised as follows;

- i) Polymer synthesis from low molecular weight compounds.
- ii) Thermal cross-linking to give a polymer derivative by release of volatiles.
- iii) Pyrolysis of the polymer derivative at higher temperatures resulting in the release of remaining volatile species leaving behind a ceramic residue.

It was observed earlier that the physical properties (i.e. melting point, viscosity and volatility) of an organometallic polymer determine their potential technical application.⁽⁹²⁾ Thus not all organometallic compounds are suitable for obtaining ceramics in good yield. The use of other alkylamine-boranes such as $\text{BH}_3\cdot\text{HN}(\text{CH}_3)_2$, $\text{BH}_3\cdot\text{N}(\text{CH}_3)_3$, $\text{BH}_3\cdot\text{N}(\text{C}_2\text{H}_5)_3$ or $\text{BH}_3\cdot\text{H}_2\text{NC}(\text{CH}_3)_3$ has been reported to result in distillation/evaporation and no significant polymers could be obtained. (54a,54b)

In the early 1990s Riedel *et al* ^(54a,54b) in his pioneering work reported on the synthesis of BC_2N and BC_4N compounds starting from piperazine borane and pyridine borane respectively as shown by the reactions below;



The ceramic yields reported using the piperazine borane precursor are in excess of 40wt%.^(53,55) The as-pyrolysed BC_2N materials were found to be amorphous with

intermixing of the B,C and N within the same basal plane as confirmed by Electron Spectroscopy for Chemical Analysis (ESCA). The BC_2N compound was found to crystallise at 2200°C under a pressure of 190MPa with slight decomposition into B_4C crystals.⁽⁵³⁾ However heat treatment below this temperature resulted in a turbostratic type structure with no sheet to sheet registry.^(53,54) An approximate nominal composition of BC_2N was obtained from bulk elemental analysis.⁽⁵³⁾

In 1995, Hubacek and Sato *et al* ⁽⁵²⁾ reported on a BC_4N compound which was obtained from the pyrolysis of a fused product of boric acid and saccharose dissolved in molten urea and heat treated. The B-C-N was turbostratic after heat treatment ($1300\text{-}2150^\circ\text{C}$ under N_2 atmosphere) composed of alternate C-C and B-N layers.⁽⁵²⁾ A similar method was used by He *et al* ⁽⁵⁸⁾ and he reported a highly ordered h-BCN single phase after heat treatment at 1600°C . However, some elemental B was observed besides the h-BCN and a stoichiometry of $(\text{B}_{0.82}\text{C}_{0.18})\text{N}$ was reported. The success of this method has been found to be highly controlled by the ratio of the precursor mixtures which inturn will determine the end product stoichiometry.

In another set of results, Komatsu *et al* ⁽⁵⁹⁾ reported on the pyrolysis of adducts formed from the reaction of BCl_3 and some nitrogen containing organic compounds such as heptazaphenalene derivatives, carbodiimides, amines, nitriles and cyanamides.⁽⁵⁹⁾ Of all the reactions studied two yielded a stoichiometry close to BC_2N ,i.e., melamine resin and BCl_3 adducts annealed at 1000°C under N_2

atmosphere resulted in a $\text{CB}_{0.49}\text{N}_{0.60}$ stoichiometry and a yield of 19% and one using BCl_3 and acetonitrile adducts gave a $\text{CB}_{0.5}\text{N}_{0.5}$ stoichiometry with a yield of 41%.⁽⁹³⁾ These adducts were polymerised at 500°C for 1hr and subsequently pyrolysed at 1000°C to remove volatiles, followed by annealing at 1500°C under N_2 atmosphere for 2hrs.⁽⁹³⁾ This resulted in a turbostratic B-C-N material composed of $(\text{BN})_y\text{CB}_x\text{N}_x$ segments confirmed by Fourier Transform Infrared (FTIR) Spectroscopy.

Although in some cases some of the precursors used resulted in inexact BC_2N stoichiometry, this method remains promising in terms of yield and controlling the end product stoichiometry.

2.5.4: Mechanical Mixing and Alloying

It has been established that metastable amorphous phases of BC_2N solid solutions can be formed by high energy ball milling of stoichiometric mixtures of graphite and h-BN.^(9,11,61,77,94,95) In principle, high energy milling induces several effects in the hexagonal planes of the precursors, such as slipping, fracture and intermixing and creation of non-six atomic rings related to deformation of these planes leading to nanostructures.^(11,94,95) This can be viewed as the breakdown of sp^2 bonding among the hexagonal rings of the graphite and h-BN thus introducing, to some extent, hybrid sp^3 bonding seeds.⁽¹¹⁾ This has been found to occur after several hours of milling, typically 34hrs or more resulting in some contamination. However this is not considered a serious problem owing to the lubricating nature

of both graphite and h-BN.⁽¹¹⁾ This method is quite attractive in terms of productivity and ease of composition control. However for BC₂N structural studies it may not be the best method for providing high quality samples.

2.6: Structural forms of c-BC₂N

A total of 420 different configurations of c-BC₂N have been predicted using *ab initio* pseudo potential local-density functional calculations on an eight atom zinc-blende structured unit cell.⁽²¹⁾ However, there are only seven topologically different structures reported owing to the high symmetry of the zinc-blende structured lattice. These structures have been shown to differ in bonding configurations thus giving them varying characteristic mechanical and physical properties.^(21, 96) Figure 2.8 below shows the seven calculated structures listed according to increasing numbers of B-B and N-N bonds as described in referenced literature⁽²¹⁾.

Structure 1 consists of separate BN and C layers with no B-B and N-N bonds and structure 2 has B, C and N atoms mixed in the same layer while no B-B and N-N bonds are present.⁽¹⁸⁾ These structures give rise to the lowest total energies and are the most stable. In structure 3, three C atoms occupy one sublattice, B and N occupy the other sublattice; structures 4 and 5 contain one B-B bond and one N-N bond respectively. The last two structures 6 and 7 have both B-B and N-N bonds with different atomic configurations where structure 7 has a distorted cubic

structure under relaxation. The expected physical and mechanical properties of the seven structures are given in Table 2.2 below.

In the BC_2N network there are 6-types of bonds expected i.e. C-C, B-N, C-N, B-C, B-B, N-N and all these bonds have been found to exist in the seven structures.^(18,93)

It has been observed that the general BC_2N -type bonding is not purely covalent but rather possesses some degree of ionicity as in BN.⁽⁹⁶⁾ This is a result of the expected surrounding chemical environment in the BC_2N matrix in other words the bond ionicity/polarisation is due to the differences in electronegativities of the atoms in its vicinity.⁽⁹⁶⁾

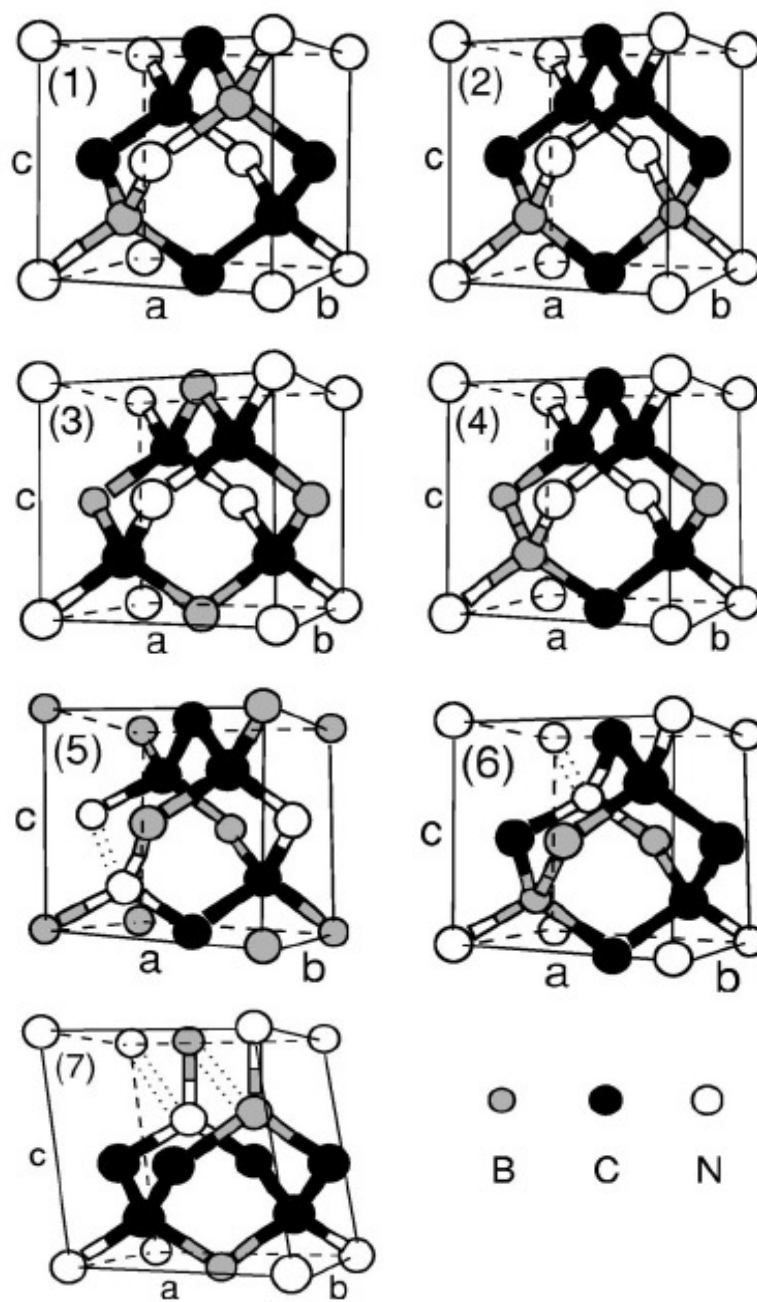


Figure 2.7: Proposed topologically different stable structures of $c\text{-BC}_2\text{N}$ starting from an eight atom zinc-blende unit cell as described in [21]. (dotted lines refer to broken bonds between N-N and B-B atoms)

Table 2.2: Calculated lattice parameters, bulk moduli and hardness values for the seven configurations of c-BC₂N (top) and experimentally determined values for various c-BC₂N samples (bottom) in comparison to diamond and c-BN parameters.

Theoretically determined Parameters:

<i>structure</i>	<i>a (nm)</i>	<i>b (nm)</i>	<i>c (nm)</i>	<i>α (°)</i>	<i>β (°)</i>	<i>γ (°)</i>	<i>V(nm³)</i>	<i>B(GPa)</i>	<i>H_v(GPa)</i>
BC ₂ N-1 [*]	0.3570	0.3570	0.3607	90	90	90	0.0459	402.1	70 ^{calc.}
BC ₂ N-2 [*]	0.3565	0.3568	0.3608	90	90	90	0.0459	380.7	72 ^{calc.}
BC ₂ N-3 [*]	0.3590	0.3590	0.3635	90	90	90	0.0468	362.9	72 ^{calc.}
BC ₂ N-4 [*]	0.3595	0.3597	0.3595	90.45	89.79	90.21	0.0465	355.9	70 ^{calc.}
BC ₂ N-5 [*]	0.3653	0.3679	0.3653	86.91	93.67	93.09	0.0489	263.5	-
BC ₂ N-6 [*]	0.3661	0.3661	0.3668	86.73	93.27	93.39	0.0489	249.5	-
BC ₂ N-7 [*]	0.3603	0.3603	0.4072	100.66	79.35	90.31	0.0510	302.8	-
β-BC ₂ N ^a	0.3577	0.3577	0.3577	89.38	90.62	90.62	0.0458	438.0	-
β-BC ₂ N ^b	0.3579	0.3579	0.3612	90	90	89.32	0.0463	383.3	-
1-BC ₂ N ^c	0.3554	0.3598	0.3553	90	90	90	0.0568	459.4	-
2-BC ₂ N ^d	0.2528	0.2502	0.3587	90	90	90	0.0567	408.9	-
ΦBC ₂ N ^e	0.2496		0.4192	90	90	120	0.0549	420.1	-

Experimentally determined parameters:

BC _{2.3} N ^f	0.3602	0.3602	0.3602	90	90	90	0.0467	355	-
BC ₂ N ^g	0.3642	0.3642	0.3642	90	90	90	0.0483	282	76
BC ₂ N ^h	0.3595	0.3595	0.3595	90	90	90	0.0465	-	62
BC ₂ N ⁱ	0.3605	0.3605	0.3605	90	90	90	0.0469	350	-
BC _{2.5} N ^j	0.3595	0.3595	0.3595	90	90	90	0.0465	401	-
diamond	0.3567	0.3567	0.3567	90	90	90	0.0454	442 ^k	115 [†]
c-BN	0.3617	0.3617	0.3617	90	90	90	0.0473	369 ^l	62 [†]

^a Reference [22]; ^b Reference [97]; ^{c,d} Reference [17]; ^e Reference [98]; ^f Reference [9]; ^g Reference [16]; ^h Reference [11]; ⁱ Reference [99]; ^j Reference [100]; ^{*} Reference [96]; ^{†,†} Reference [16]; ^k Reference [101]; ^l Reference [102]. V: unit cell volume; B: bulk modulus; H_v: Vickers microhardness; calc.: calculated.

Furthermore, all the seven structures were found to possess positive formation energies E_f defined as;

$$E_f = E_{BC_2N} - \frac{1}{3}(2E_{diamond} + E_{c-BN}) \quad [2.17]$$

This implies that cubic BC_2N is thermodynamically unstable and prone to decomposition into diamond and c-BN phases.^(24, 97, 103)

Zhang *et al* described a stable β - BC_2N phase possessing a cubic type structure with alternate layers of c-BN and diamond repeating in the (001) direction.⁽⁹⁷⁾ This is similar to structure 1 above and the β - BC_2N described by Tateyama *et al* below.⁽²²⁾ Several other modifications have been proposed consisting of rhombohedral type structures (1- BC_2N and 2- BC_2N) and hexagonal, similar to the diamond lonsdaleite structure (*see* Table 2.2).^(17, 97)

On the other hand there is no corresponding data on the crystal structures of the experimentally produced BC_2N samples.⁽¹⁰⁴⁾ Predictions have been made by attempting to link the cubic phases obtained with possible theoretical transformation mechanisms but however such findings will need supporting experimental evidence to be authentic.

2.6.1: Proposed Syntheses paths for cubic BC₂N

It has been shown earlier that different starting BN-C forms may lead to diverging synthesis routes and yield products of varying characteristic properties. There are several expected stable cubic phases in the BC₂N system.⁽²²⁾ Furthermore, it has been shown that cubic BC₂N is metastable and thermodynamically stable towards decomposition to diamond and c-BN. In view of this, it can be expected that several routes could lead to the cubic BC₂N phase depended on the aforementioned factors.

Four possible transformation paths leading to four different cubic BC₂N (referred to as α , β , γ , δ phases) have been predicted from theoretical modelling.⁽²²⁾ The investigations were based on the fact that the structures of the starting materials resemble the ‘striped’ and ‘island’ patterned graphitic or layered BC₂N structures mentioned earlier and that transformations are of diffusionless/martensitic type.⁽²²⁾ The same bond counting rules found in layered structures have been found to apply to cubic phases. Thus the more stable cubic structures are those which contain the maximum number of C-C and B-N bonds and contain no B-B and N-N interactions.⁽²²⁾ The two most stable structures would be structure 1 (referred to as β -BC₂N,*hereafter*) and γ -BC₂N, a rhombohedral modification suggested by Tateyama *et al*⁽²²⁾ β -BC₂N has been found to form from both graphitic BC₂N materials consisting of mixed B,C,N atoms (gr-BC₂N-1,*hereafter*) and layered structures consisting of alternate stacking of graphite and h-BN monolayers (sl-C₂/BN, *hereafter*).⁽²²⁾ The transformation has been found to be associated with the

formation of C-C and B-N interlayer bondings making this structure the most energetically favourable as shown in Figure 2.9 below;

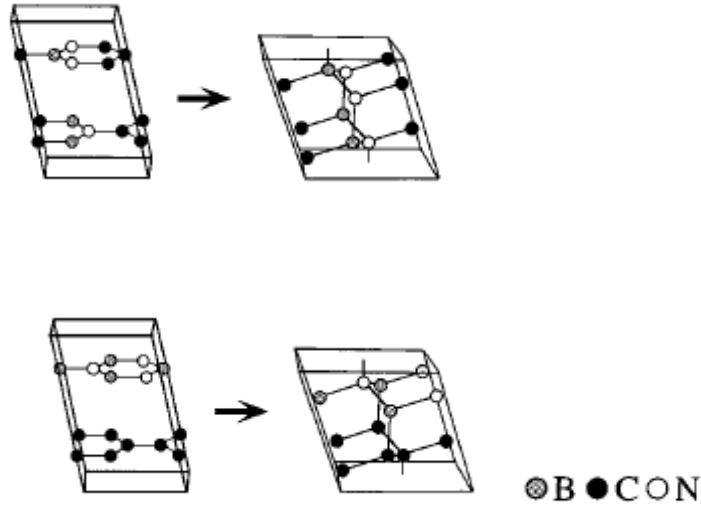


Figure 2.8: Proposed transformation paths from g-BC₂N-1 to β-BC₂N (top) and sl-BN/C₂ to β-BC₂N.⁽²²⁾

Another graphitic phase (gr-BC₂N-2, *hereafter*) with a different atomic configuration from gr-BC₂N-1 has been found to be compressed into γ-BC₂N by formation of C-N and B-C interlayer bondings as shown in Figure 2.10. An additional transformation route was found to occur by allowing the layers to slide during transformation, however this gives rise to a structure almost similar to γ-BC₂N.

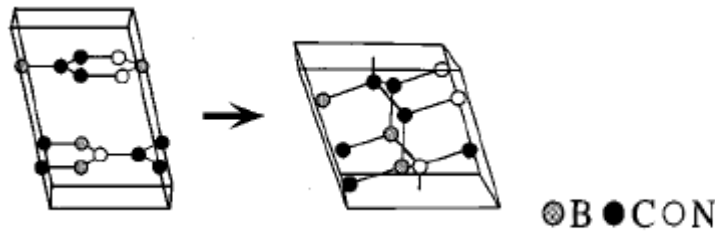


Figure 2.9: Proposed transformation path from g-BC₂N-2 to γ-BC₂N. ⁽²²⁾

Tateyama *et al* further calculated enthalpy stability values to ascertain the pressure dependence of the aforementioned phases (see Figure 2.11). Clearly from Figure 2.10 below γ-BC₂N becomes more stable than the gr-BC₂N above 11GPa and β-BC₂N is already stable at zero pressure. ⁽²²⁾ This means that gr-BC₂N can be transformed to γ-BC₂N at about 11GPa, and it is possible to obtain the β-BC₂N at nearly ambient pressure. Alternately, transformation can occur at about 16GPa into β-BC₂N starting from the stacked sl-C₂/BN material. It was concluded that β-BC₂N can be synthesised by compressing gr-BC₂N at near ambient pressure or compressing sl-C₂/BN at pressures of about 16GPa and low temperatures to avert decomposition into the thermodynamically favourable diamond and c-BN. ⁽²²⁾ This was confirmed by Nakano *et al* ⁽⁸⁾ who synthesised mixed crystals of diamond, c-BN and B-C-N at 7.7GPa and 2300°C using a graphitic B-C-N starting material obtained by CVD method. ⁽⁸⁾ In their conclusion they highlighted that cubic BC₂N crystals can be obtained at static pressures above 10GPa and temperatures below 2000°C to avert decomposition. This whole argument is based on the metastability factor.

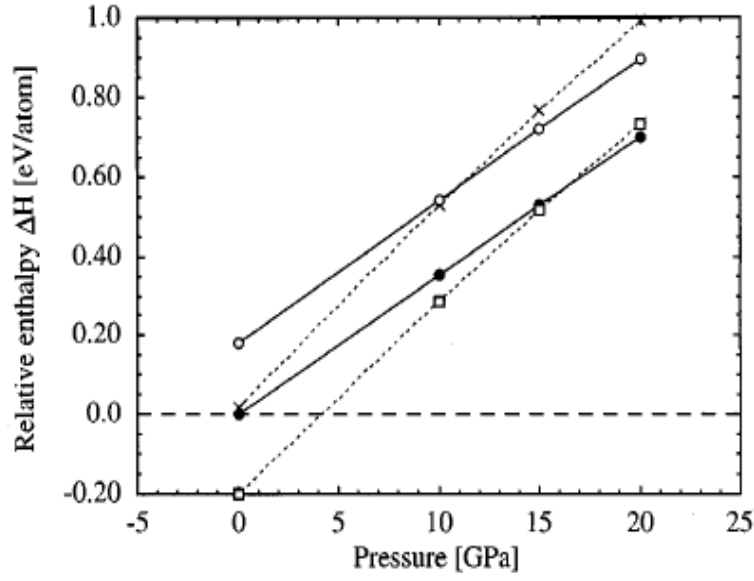


Figure 2.10: Pressure dependence of enthalpies relative to total energy for β -BC₂N at 0GPa; gr-BC₂N (crosses); β -BC₂N (filled circles); γ -BC₂N (open circles); sl-BN/C₂ (squares).⁽²²⁾

Experimentally synthesised c-BC₂N phases have been found to possess submicron-crystallites making it difficult to accurately determine the crystal structures and formation mechanism of these phases.^(9, 11, 12, 16) Thus the mechanism of transformation leading to c-BN-C materials is not well understood. Komatsu *et al*⁽¹⁰⁵⁾ attempted to explain transformation mechanism to cubic BN/C using a shock compressed BC_{2.5}N heterodiamond. In his conclusion he highlighted the transformation mechanism to be a result of three main mechanisms as observed from the morphology of crystallites obtained in transmission electron microscopy (TEM). In principle, the heterodiamond was found to deposit through rapid crystallisation from liquid phase (<0.1ns); rapid quenching from the liquid phase resulting in amorphous heterodiamond (*ca.*0.1ns)

and slow cooling resulted in rearranged heterodiamond ($>0.2\text{ns}$) these are more or less all diffusionless type reactions.⁽¹⁰⁵⁾ These reactions were found to occur simultaneously during transformation as confirmed by TEM results. However this is the only experimental attempt explaining the transformation mechanism and there is still need for extensive studies to investigate this section of study.

2.7: Diamond and c-BN Considerations

Diamond and c-BN are the building blocks of the B-C-N system and naturally it is expected that the BN-C phases would share certain characteristic properties with the constituent parent materials. As highlighted earlier the physical and chemical properties of BC_2N are expected to lie in between those of diamond and c-BN for ideal mixing (Vergad's Law). However this is not a rule but a generalisation and in reality some degree of deviation would be expected. Table 2.3 below highlights the known physical and mechanical properties of diamond and c-BN and what has been experimentally obtained for BC_2N .

The pioneering attempts to synthesise BC_2N were modelled on the well known diamond and c-BN catalytic transformations under *HP/HT*.^(7, 8, 106) However this did not yield the expected cubic BC_2N solid solutions but decomposition into diamond and c-BN was observed instead. Subsequent attempts to synthesise BC_2N without additives under static HPHT yielded some cubic phases at pressures of 20-25GPa and temperatures of 2100-2200K using turbostratic BN-C starting materials.^(11, 13) It is well known that the direct transformations from the

hexagonal to cubic phases for both diamond and c-BN are hindered by very high activation energy barriers.⁽¹¹²⁻¹¹⁵⁾ This explains the high thermobaric conditions required to obtain the cubic phases. By subjecting the low density hexagonal modifications to HP/HT conditions it is envisaged that the minimisation of the Gibb's free energy of the system can easily be achieved by structural transformations which favour reduction in the unit cell volume.⁽¹¹⁶⁾ In principle the transformation proceeds with change in dimensional order (sp^2 to sp^3 bonding) through bond breaking and subsequent bond reconstruction. Diamond is formed as a metastable phase and can be maintained under ambient conditions owing to the high energy required for graphitisation.⁽¹¹²⁾ However the major drawback is that the low pressure phases are persistent well in the diamond stability region at reasonably high thermobaric conditions (see Figure 2.11).

Table 2.3: A summary of selected properties for diamond and c-BN in comparison to those expected and experimentally obtained for c-BC₂N.

Property	Value			Remarks on BC ₂ N
	<i>diamond</i>	<i>c-BN</i>	<i>c-BC₂N</i>	
<i>Physical:</i>				
▪ density (g/cm ³) [†]	3.52	3.49	3.52 ^{calc.}	<i>Ideal mixing: 3.52gcm⁻³</i>
▪ lattice constant (nm) [†]	0.357	0.362	0.359(5) ^{calc.}	0.360(5) ^[12] ;0.364(2) ^[16] ;0.359(6) ^[11]
▪ Space group [†]	<i>Fd-3m</i>	<i>F-43m</i>	-	<i>intermediate</i> ^{[12],[106],[11]} <i>diamond-like</i> ^[16]
<i>Mechanical:</i>				
▪ Vickers har. (GPa) ^[105]	115 ^{s[109]}	62(3) ^s	76(4)	64 ^[11] ;see Table 2.2
▪ Knoop hard. (GPa) ^[105]	63 ^s	44(3) ^s	55(2)	-
▪ Young’s mo. (GPa) ^[105]	1141 ^{p[110]}	909 ^p	980(40) ^{calc.}	-
▪ Bulk modulus (GPa)	442 ^[98]	369 ^[102]	405 ^{calc.}	<i>Expt. Bulk moduli: 355(19)^[9];</i>
▪ Shear mod. (GPa) ^[108]	415-450	405	445 ^{calc.}	401(15) ^[12] ;
▪ Poisson’s ratio (ν) ^[108]	0.10-0.11	0.12	0.096 ^[108]	282(15) ^[16] ;350 ^[100]
▪ Fracture t.(MPa.m ^{1/2})	5 ^{s[109]}	3.0(3) ^{s[108]}	4.5(4) ^[108]	- -
<i>Thermal Properties:</i>				
▪ Conductivity (W/mK) [†]	2000	200 ^p ,1300 ^{calc.}	-	30wt% loss (700-900°C),
▪ Stability in air (°C) [†]	ca.627	ca.1300°C	700-900	stable up to 1300°C, the
▪ Linear expans. coeff. (x10 ⁻⁶ /K) at 300K [†]	0.81	1.15-1.9	ca.5.5 (1100-1300°C)	formation of protective B ₂ O ₃ coating prevented further oxidation of cubic BC _{2.5} N.
<i>Chemical:</i>				
▪ Reactivity [†]	low	low	low	expected to resist attack by

carbide formers and Fe
group metals.

Phonon Spectra:

▪ Raman (cm ⁻¹) [†]	1332	(LO) 1304	(LO) 1326 ^[112]	
		(TO) 1056	(TO) -	(LO) 1323 ^[9] ; TO missing in
▪ Infrared (cm ⁻¹) [†]	depends	(LO) 1340	1087	most samples.
	on purity	(TO) 1065		Broad reststrahlen band. ^[93]

[†] Reference [107]; s: single crystal (111); p: polycrystalline; calc.: calculated value

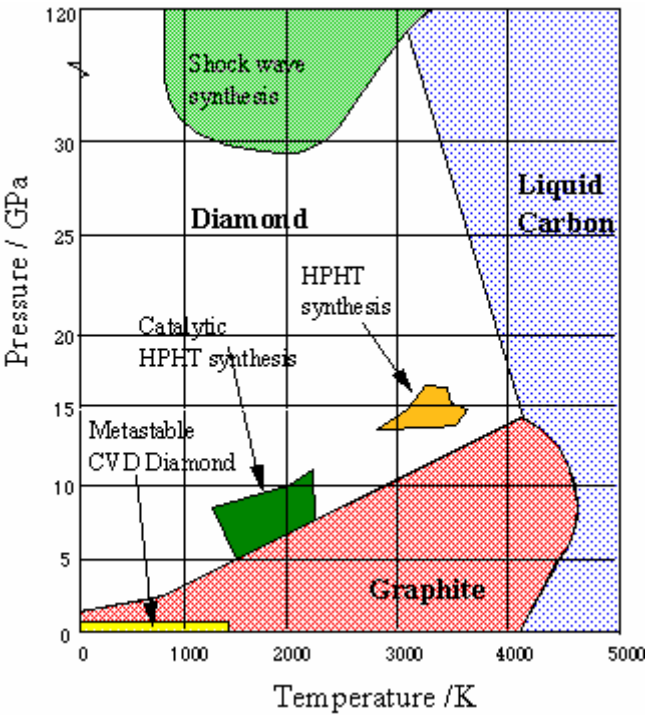


Figure 2.11: The carbon phase diagram adapted from [117] showing the various synthesis conditions used to obtain diamond commercially.

Effective synthesis of high dimensional cubic structures has been achieved by finding practical convenient pathways to avoid the high activation energy barriers.

^(27,112) A commercially viable method is the use of solvent catalysts which form eutectic alloys/ intermediate compounds which can be used to obtain the cubic phases under slightly lower thermobaric conditions.⁽²⁷⁾ In the case of diamond the reaction is enabled by the much lower solubility of diamond in the molten solvent metal than graphite thus ‘supersaturation’ is attained under optimal thermobaric conditions.⁽¹¹²⁾ Typical solvent catalysts used for diamond synthesis are iron group transition metals and their alloys such as Co, Co-Fe alloy, Fe-Ni alloy (*invar*).

The BN system behaves somewhat differently, intermediate compounds are formed instead which are themselves the solvent catalysts.⁽²⁷⁾ Typical catalytic compounds are composed of rare earth metal nitrides such as $\text{Mg}_3\text{B}_2\text{N}_4$, $\text{Ca}_3\text{B}_2\text{N}_4$, Li_3N and Mg-Al alloys have also been found to be effective.^(27,118) There are several other non-conventional catalysts which have been used details of which is published elsewhere.^(27,112,118) Effectively this has lowered the thermobaric conditions for the synthesis of both diamond (*ca.* 5.5-6 GPa and *ca.* 1500-1900 K) and c-BN (*ca.* 5.5-6 GPa and *ca.* 1950 K).⁽²⁷⁾

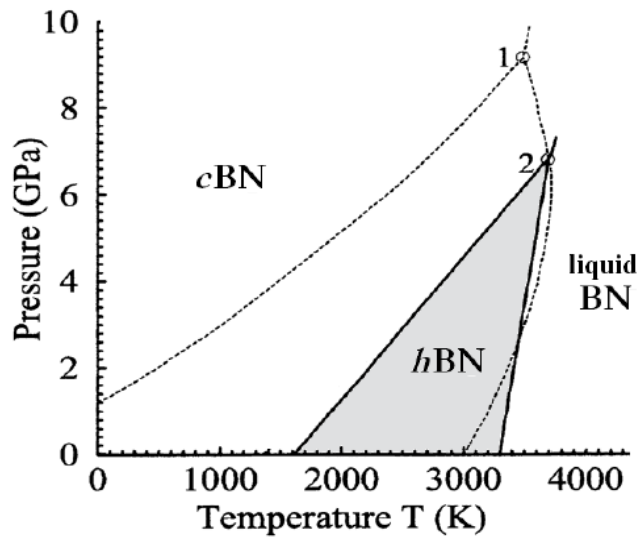


Figure 2.12: The BN phase diagram adapted from [119,120] showing the generally accepted phase diagram (1) and the Corrigan-Bundy phase diagram (2).

The use solvent catalyst in the BC_2N system has resulted in decomposition with Co and Mg_3BN_3 as catalysts in separate studies.^(7,118,122) Wedlake *et al*⁽¹⁰⁶⁾ patented work on the synthesis of a cubic type B-C-N phase using an Fe-Al alloy at 15GPa ; 3000°C in the belt press. However no experimental follow up was made in this work and it still remains unclear whether this is reproducible or not.

2.7.1: Transformation Mechanisms

The transformation mechanisms leading to diamond and c-BN are depended on several factors such as the mode of HPHT application (static/dynamic), the nature of starting material and other external factors such as use of a solvent catalyst. There are basically two possible mechanisms of direct transformation from the low to the high density phases namely diffusionless or martensitic-type and

diffusional or kinetically driven type transformations.^(32,52,54) The direct transformation of h-BN to c-BN has been achieved at high thermobaric conditions typically 12GPa and 2000K.⁽¹²³⁾ The diffusionless martensitic type transformation involves well crystallised starting materials h-BN (hexagonal BN) and r-BN (rhombohedral BN).⁽¹²³⁾ It has been shown experimentally that the hBN to w-BN (wurzitic BN) and rBN to zBN (zinc-blende BN) transitions occur by a puckering mechanism which involves rearrangement of whole atomic groups simultaneously.⁽¹²³⁾ In principle there is splitting of the (0001) basal planes into sublayers by means of B and N atomic displacements in opposite directions along the c axis.⁽¹²³⁾ On the other hand, disordered starting materials such as t-BN (turbostratic BN) and a-BN (amorphous BN) have been found to undergo diffusional type transformation to the higher density phases.⁽¹²⁴⁾ This involves atom by atom transitions.⁽⁵²⁾

The direct synthesis of diamond from graphite requires high thermobaric conditions of at least 10GPa and 3000K.⁽¹²⁵⁾ Thermodynamically this transition is possible at lower thermobaric conditions but fails owing to the high kinetic/activation energy barrier for the reorganisation of the graphitic structure into the diamond like structure.^(112,125) The catalytic transition of graphite to diamond has been found to be diffusion controlled, associated with diffusion of the metal atoms (clusters) along the graphite crystal planes resulting in a change in the nature of bonding between the carbon atoms.⁽¹²⁵⁾ Another diffusional mechanism in diamond synthesis has been observed and it involves nucleation and subsequent growth of diamond in a crystallisation medium, this is commercially used to grow

diamonds using initially some diamond seeds as nucleation sites in the temperature-gradient deposition method.^(125,128) A hexagonal modification of diamond (lonsdaleite) is known to form under a diffusionless process using pyrolytic graphite (disordered) under static HPHT conditions. Imperfect / low density graphite has been found to form cubic diamond structure through a martensitic type reaction under shock compression at pressures of up to 30GPa.⁽¹²⁷⁾ The use of perfect high density graphites was reported to require higher shock pressures (40-60GPa) for the transformation.⁽¹²⁸⁾

In view of the above it is clear that the direct synthesis of c-BN is relatively easier to attain compared to the graphite-diamond transition. As highlighted this is owing to the high activation energy barrier involved. This basically makes it difficult to predict the kind of mechanism that can lead to cubic BC₂N phases. However considering the fact that both graphitic and cubic BC₂N phases are metastable towards decomposition we are prompted to believe that the best route would be via a martensitic type reaction to avert decomposition. It must also be pointed that the structure of the starting BC₂N material also plays a crucial role in determining the transition type. Also considering the fact that most of the experimental starting materials used were turbostratic in nature, i.e. with disorder along the c axis, it would be expected that diffusionless type transition would result in random type bonding and possibly short range order in the cubic phases.

2.8: Boron Carbonitride: A Summary of Syntheses Methods

Clearly it has been shown that B-C-N alloys are expected to possess the same interesting properties as in diamond and c-BN i.e. high melting points, high hardness, high bulk moduli, low thermal expansion coefficients and wide band gaps. In light of this, there have been substantial advances in both theoretical modelling and experimental synthesis of B-C-N materials for nearly two decades as shown in the extensive studies highlighted in previous paragraphs. However, results on the attempted synthesis of cubic B-C-N dense phases reported by different authors are contradictory. It is a source of substantial confusion whether the obtained products are complete solid solutions or mere mechanical mixtures of highly dispersed diamond and c-BN which are difficult to distinguish with most characterisation techniques. Furthermore the full potential of c-BC₂N can only be realised if complete solid solutions are obtained as opposed to mixed crystals. However what is encouraging is the possibility of obtaining the cubic BC₂N phases under well controlled conditions. This in our opinion is going to open new avenues in the discovery of technologically important materials in the B-C-N system. In conclusion a summary of the obtained results since the first synthesis in 1979 is listed below to give an insight into the developments made so far;

Table 2.4: Summarised results of synthesised BN-C phases under HPHT conditions using various technologies.

Starting materials	HP apparatus	<i>P, T, t</i> conditions	Products and comments	Ref.
<i>Nitridation</i> B/C at 1800-2000 ⁰ C.	Belt press	5-10GPa/1300-2000 ⁰ C/ 10-60mins/ (Co/Ni/Fe): Al in the ratio (15:1 to 1:15) solvent catalyst.	c-BCN single crystals.	[106]
<i>Nitridation</i> B/C at 1900 ⁰ C.	Belt press	7.5GPa/1600 ⁰ C/40mins , Fe/Al (10:1)solvent catalyst.	c-BCN single crystals of up to 100µm in size.	[106]
<i>CVD method</i> BCl ₃ /CCl ₄ /N ₂ /H ₂	BA press	14GPa/3300K/no solvent catalyst.	BN _x C _{1-x} (0<x<1) mixed crystals with a sphalerite structure.	[7]
<i>CVD method</i> CH ₃ CN/BCl ₃ g-BC ₂ N produced.	Belt press	5.5GPa/1400- 1600 ⁰ C/20mins/Co solvent catalyst.	c-BN/diamond crystals.	[122]
		6GPa/1600 ⁰ C/Mg ₃ BN ₃ solvent catalyst.	no change.	[121]
<i>CVD method</i> CH ₃ CN/BCl ₃ g-BC ₂ N produced.	Belt press	7.7GPa/2000- 2400 ⁰ C/15-60mins/no solvent catalyst.	c-BN/diamond/BC _x N at T<2400 ⁰ C. Segregation to diamond/ c-BN at T=2400 ⁰ C.	[8 ,10]
<i>CVD method</i> CH ₃ CN/BCl ₃ / 1000 ⁰ C	SC	30-40GPa	Single phase c-(BN)C.	[129]

g-BC ₂ N.				
<i>Ball milled</i> mixture of graphite/h-BN.	SC	30-40GPa	Segregated phases of c- BN/diamond/w-BN	[129]
<i>Microcrystalline</i> & <i>Mechanical</i> <i>mixtures</i> g-C _x (BN) _{1-x} (x=0.3,0.5,0.6)	LH-DAC	T>1500K/30-50GPa/ no solvent catalyst.	Single phase c- C _{0.33} (BN) _{0.66}	[9]
<i>CVD method</i> g-BC ₂ N	MA press	18GPa/1250 ⁰ C/no solvent catalyst.	c-BC ₂ N + small amounts of diamond/c-BN. c-BC ₂ N separated at T>2000 ⁰ C.	[100]
<i>CVD method</i> g-BC ₂ N, /B _x C _{2(1-x)} N _x (x=0.34)	BA press (flash heating)	Laser heated for 10ms/15GPa	Single phase c- B _x C _{2(1-x)} N _x	[130]
<i>Mechanical</i> <i>mixture of C/h-BN</i> (1:1)	BA press (flash heating)	Laser heated for 10ms/15GPa	Diamond and w-BN.	[130]
<i>CVD method</i> CH ₃ CN/BCl ₃ g-BC _{2.5} N. <i>Solid pyrolysis of</i> BCl ₃ /CH ₃ CN adducts.	SC	35GPa/ca.3500°C	nano-crystalline c-BC _{2.5} N (5-20nm) with short range ordering. nano-c-BC ₂ N solid solution.	[12,60] [93]
amorphous h-C-B- N prepared by ball milling for 120hr (C _{0.65} (BN) _{0.35})	MF	Annealed 800- 900K/60mins in air.	Surface B ₂ O ₃ formed and weak XRD peaks of c-B- N solid solution observed, amorphous powder	[56]

			formed is highly reactive.	
<i>Solid pyrolysis of</i>	LH-DAC	P>18GPa/T>2000K.	18GPa/2000K nano-c-	[16]
fused B(OH) ₃ /			BC ₂ N forms in LH-DAC.	
sacharrose in	MA press	25GPa/2100K/30mins	c-BC ₂ N single phase.	
molten urea				
(BN) _{0.48} C _{0.52}	SC	30GPa/ca.3500K	c-B-C-N + g-BC ₂ N.	[131]
<i>Mechanical</i>	MA press	20GPa/2200K/5mins	c-BC ₂ N with a nano	[11]
<i>alloying C/h-BN</i>			graphitic matrix.	
(2:1) 34hrs.				
<i>Milled 50/50</i>	<i>Toroid press</i>	<i>8GPa/1500°C/5min</i>	<i>BC_{0.47}N_{0.85} (80wt %) +</i>	[91]
<i>mixture of C₃N₄</i>			<i>B₁₃C₂ (20wt %) refined</i>	
<i>nanospheres +</i>			<i>structure shows an F-43m</i>	
<i>boron.</i>			<i>phase space.</i>	

BA: Bridgeman Anvil; SC: Shock Compression; LH-DAC: Laser heated Diamond Anvil Cell; MA: Multi-Anvil.

Clearly there is no common agreement on the results compiled above partly owing to the different starting materials used. Several conclusions have been drawn from results obtained to date. These may provide research clues on the general experimental overview of the BC₂N synthesis:

- i.) c-BC₂N is thermodynamically metastable towards segregation into c-BN and diamond. It has been found to form at pressures P>18GPa and temperatures of T ≤ 2000°C under fast heating and quenching as in the laser heated Diamond Anvil Cells (DAC) and shock wave technologies with no solvent catalyst.

- ii.) Most of the starting materials used are thermally unstable at temperatures > 2000°C regardless of the pressure used.
- iii.) The use of solvent catalysts used for diamond and c-BN synthesis resulted in the segregation/decomposition of c-BC₂N into diamond and c-BN and some B-C-N phase in some cases.
- iv.) Mechanical mixtures of graphite and h-BN always result in mixed segregated products i.e. diamond, c-BN and w-BN regardless of the method used for synthesising the c-BC₂N phase. However mechanical alloying/milling for long periods (34hrs+) has been successfully used to synthesise single phase c-BC₂N containing some graphitic nanocomposite.
- v.) The physical and mechanical properties of c-BC₂N have not been unambiguously measured nor is the crystal structure well known. The stoichiometries reported by most authors are not exact.

Chapter 3

Experimental Procedure

3.1 Introduction

A BN-C ceramic with a turbostratic type structure was synthesised through a solid phase pyrolysis of a boron containing polymer derived from piperazine borane $C_4H_{10}N_2 \cdot BH_3$ at the Darmstadt University of Technology, Institute of Materials Science in Darmstadt, Germany. Piperazine borane was obtained by the reaction of piperazine (99%) with borane dimethyl sulphide complex in a molar ratio of 1:1. The reaction product, a fine white powder, was subsequently polymerised at 400°C for 10hr under Ar atmosphere forming a yellow coloured polymer derivative. A second step thermal treatment at 1050°C and 2 hours holding time under Ar flow resulted in a ternary B/C/N ceramic which was further heat treated at 1850°C for 2 hours under N_2 flow.

The ternary BN-C ceramics were studied under HPHT using both dynamic and static techniques. Shock-wave techniques using gas gun and column methods at the National Institute of Materials (NIMS) Japan and the University of Kumamoto respectively were utilised in this study. However no phase transitions were observed using these methods. This prompted an investigation using static HP/HT techniques. This was achieved by initially using a laser heated diamond anvil cell (LH-DAC) and a multi-anvil press to obtain bulk samples for physical and mechanical property characterisation. This work was conducted at the Bayrisches Geoinstitut, Bayreuth, Germany.

The precursor borane polymers were characterised by thermal analysis to ascertain the reaction products and yields during synthesis and IR spectroscopy to ascertain the nature of bonding. Furthermore, the obtained t-BN-C materials were thoroughly characterised by various techniques which include X-ray diffraction, Raman spectroscopy, Scanning electron microscopy, IR Spectroscopy, X-ray photoemission spectroscopy (XPS) and bulk elemental analysis. Due to the fine-grained structures obtained in the high pressure synthesised c-BN-C materials and the small size of samples produced specialised characterisation techniques were used in this thesis. The structural morphology was obtained by Transmission Electron Microscopy, and the microstructural evolution was obtained by synchrotron X-ray diffraction. The nature of the bonds present in the materials made was studied using Raman spectroscopy. The flow chart below summarises the synthesis procedure utilised in the present study.

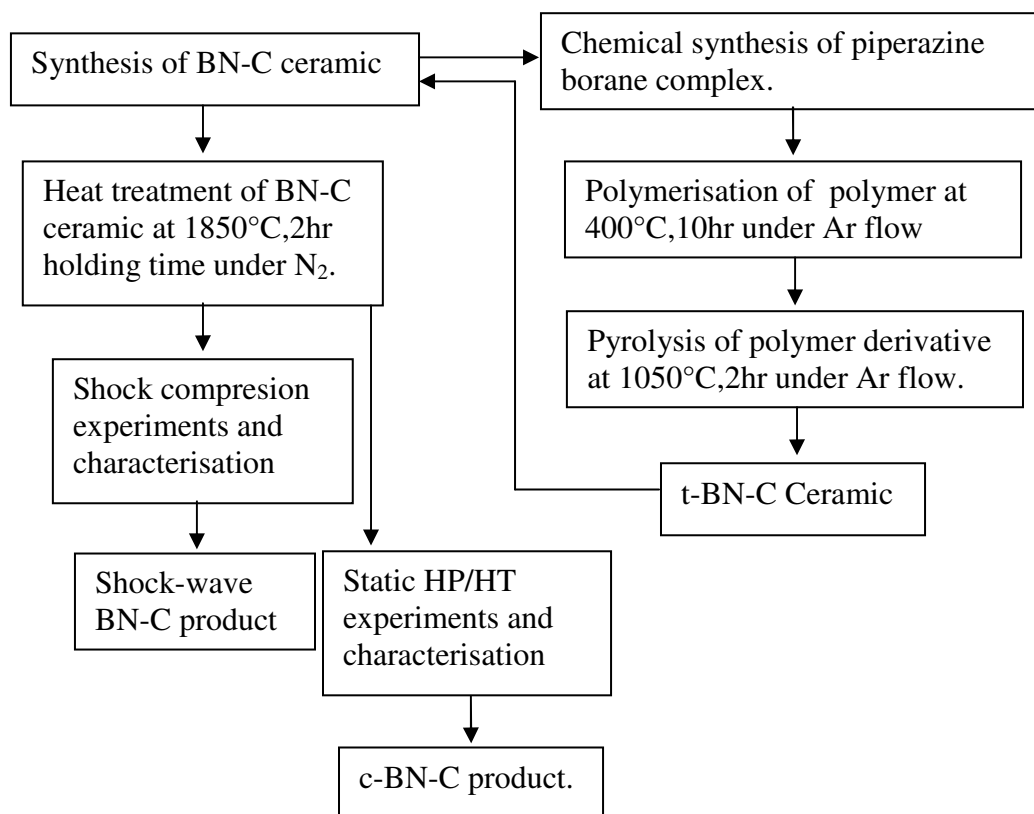


Figure 3.1: Summary of procedures used to synthesise the BN-C starting and final high pressure products.

3.2 Synthesis of Piperazine borane complex

A Schlenk technique ⁽¹³²⁾ useful in the handling of air sensitive compounds was used in the synthesis of piperazine borane. This apparatus consists of a double bank silica glass manifold with several ports to allow either vacuum or inert gas to be selected without the need of a separate line. Thus one of the banks is connected to a source of ultra pure inert gas which is vented through an oil bubbler to prevent air contamination. A high vacuum pump equipped with a digital meter

reading is connected on the other bank with a liquid nitrogen trap (cold trap) to prevent solvent vapours and gaseous products from contaminating the pump. The reaction vessels are connected to the banks through the ports by high pressure nylon tubing. This apparatus allows several reactions to be carried out simultaneously.

Piperazine borane ($\text{C}_4\text{H}_{10}\text{N}_2\cdot\text{BH}_3$) complex was obtained through a polyaddition reaction from piperazine ($\text{C}_4\text{H}_{10}\text{N}_2$) and borane dimethyl-sulfide ($\text{CH}_3\text{SCH}_3\text{-BH}_3$) complex mixtures with a ratio of 1:1 in a toluene solvent. Typically 0.23mol of piperazine were dissolved in 500ml of dry toluene and continuously stirred under Ar flow in a round bottom flask at room temperature until complete dissolution. The solution was placed in an ice bath, followed by addition of 0.28mol of borane dimethyl-sulfide complex by a dropwise injection method. A cloudy white solid was formed immediately and the apparatus was sealed and reaction allowed to go to completion under continuous stirring at 0°C and Ar flow for a period of 1hr. The reaction products were separated by applying vacuum of 5Pa under mild heating of 50°C . A white powder was obtained with an average yield of 87wt%. The only loss incurred is due to material sucked into the nylon pipes during extraction under high vacuum. The reaction was repeated several times to obtain the desired amounts of the piperazine borane complex.

3.3 Polymerisation and Pyrolysis Reactions

A vertical tube furnace was used for the polymerisation and pyrolysis reactions. This apparatus consists of molybdenum disilicide heating elements lined along the length of the furnace of 1200mm in height. The outside of the furnace is constructed from a perforated stainless steel sheet. Insulation is provided for by a hollow alumina tube placed at the centre of the furnace. A silica tube of 500mm in length and 40mm internal diameter was used to contain the sample. The inert gas (Ar) was allowed to flow through nylon tubing connected to the reaction chamber through glass connections. The outlet was vented through an oil bubbler. The heating/cooling cycles were programmed through a temperature controller connected to the furnace through a platinum-rhodium thermocouple.

The piperazine borane powder was heat-treated at 400°C for 10hrs in a vertical tube furnace using a silica tube as the reaction chamber (the powder was contained in the silica tube), a heating rate of 100°C/hr was used. A bright yellow powder was obtained (piperazine borane derivative); this describes the polymerisation stage. The infusible polymer derivative was subsequently pyrolysed at 1050°C for 2hr under Ar flow; a heating rate of 100°C/hr was used. A black powder was obtained with a yield of 44wt%. The ceramic powder was annealed at 1850°C maintained for 2hrs in a hot press furnace (*Thermal Technologies, USA*) using a graphite capsule coated with h-BN under N₂ flow with a heating rate of 600°C/hr. No substantial mass loss was observed during annealing. The furnace was allowed to cool at the same rate under N₂ flow.

3.4 High Pressure Shock-wave Experiments

The t-B/C/N materials were crushed using a pestle & mortar to 40 μ m in size as viewed under a light microscope. A portion of the powder was milled in a vibrator mill using a tungsten carbide lined rod and container for 20mins to a size of 10 μ m. The powders (10wt%) were mixed with copper powder (90wt%) of size 40 μ m and compressed inside a copper container with dimensions (30mm ht X 30mm OD) and a sample space of 2mm ht X 18mm diameter at the bottom of the container. A manually operated oil press was used to compress the powders into a pellet in the sample space, the pellet was kept in place by means of a threaded rod which was screwed in to touch the top of the pellet. The compressed densities of the powders were determined by measuring the masses and heights of the compressed pellets. The containers were loaded in a steel die and enclosed in a drum at one end of the gas gun apparatus which was evacuated and impacted with a projectile consisting a 3mm thick by 40mm diameter aluminium plate stuck to a thermosetting plastic containing a magnet inside for pressure estimations using the impedance match method ⁽¹⁾ for the velocity values. The projectile velocity is a function of the quantity of the propellant used; in the present study 100-200g propellant were used to simulate an effect on pressure variation.

The shock temperature is a function of the change in internal energy as described by the Renkin-Hugoniot shock-wave EOS (Equation of State) for internal energy summarised by equation [3.7] below;

¹ A method used to measure shock velocity in a conducting medium as described in [130].

$$\Delta E = \frac{1}{2} P(V_1 - V_0) \quad [3.7]$$

A material undergoing compression by a dynamic pressure P to a volume V_1 will experience a change in internal energy ΔE ⁽¹³¹⁻¹³²⁾. A larger fraction of this energy is dissipated as heat and the remainder stored in the material as lattice defects or distortions ⁽¹³¹⁻¹³²⁾. Thus more porous materials are accompanied by larger increase in internal energy as the starting volume V_0 is larger. In view of this powders were compacted to various final densities to simulate the effect of temperature variation.

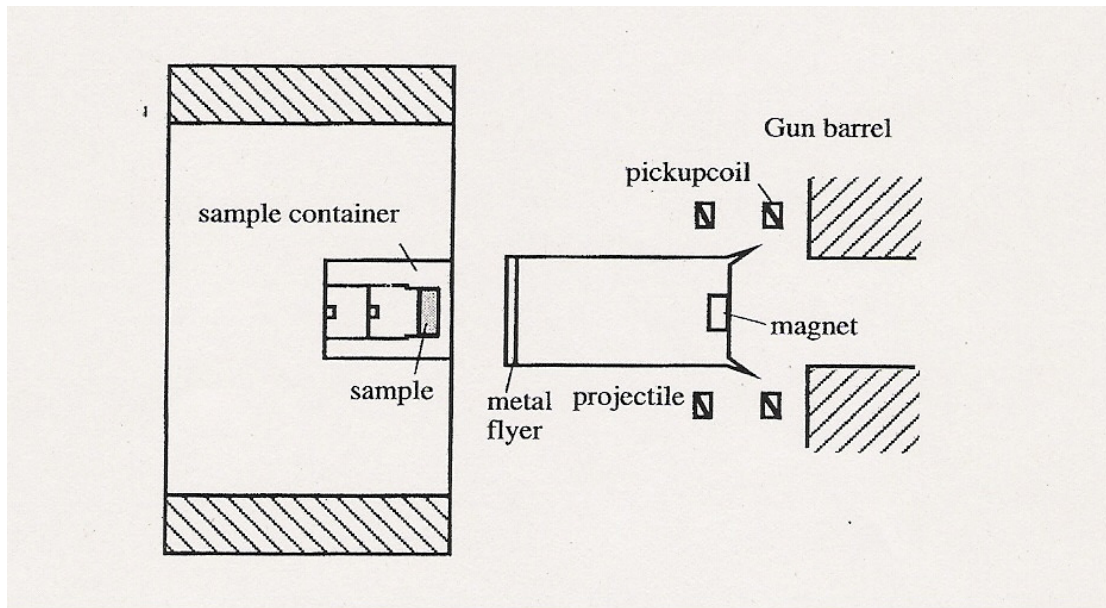
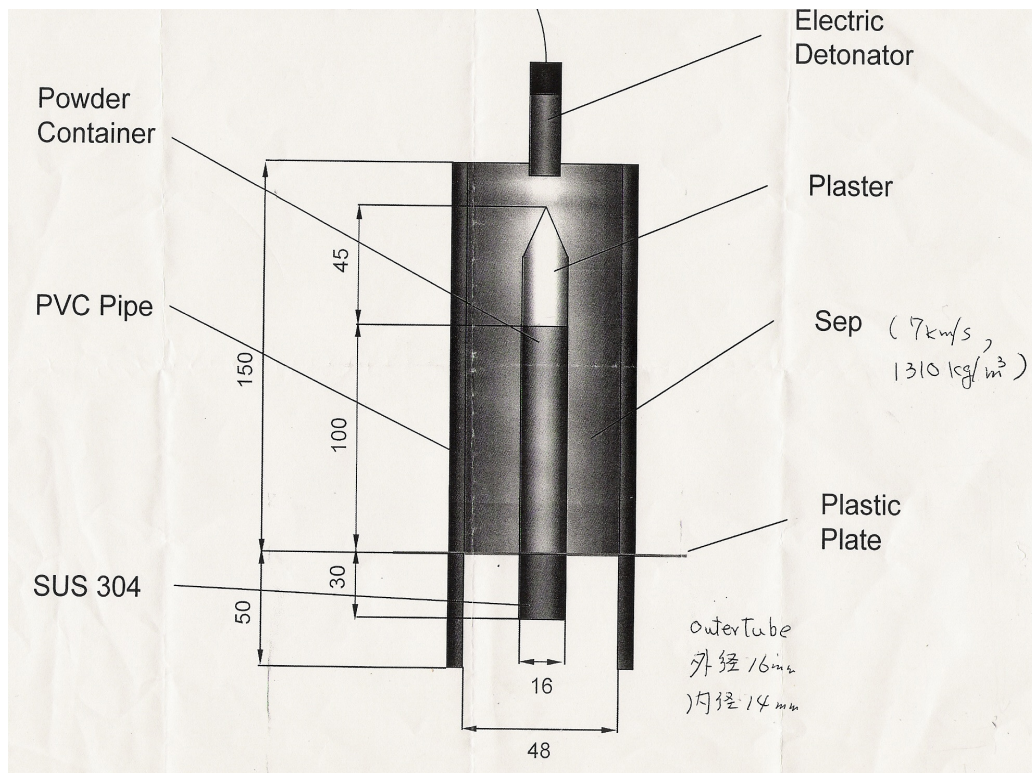


Figure 3.2: Exploded view of the shock recovery by gun accelerated projectile impact. The magnet embedded in the projectile is used to measure the projectile impact velocity with a series of pickup coils, this is used to estimate the impact pressure as described in [134].

The recovered samples were machined and immersed in 70% HNO_3 for 4hrs to remove the copper matrix. The powders were washed four times with distilled water in a Kubota (*Japan*) centrifugal machine, dried at 120°C and characterised by XRD using a RIGAKU RINT 2000. For comparison purposes h-BN was shock compressed at one of the shock conditions.



N.B: SUS 304 refers to a stainless steel grade 304; Sep refers to the explosive.

Figure 3.3: Schematic view of the column type shock recovery experiment (Sep and SUS denote the explosive and Stainless Steel Grade 304 respectively) (*Courtesy of Kumamoto University, Japan*).

Table 3.1: Summary of experimental parameters used in the shock wave experiments.

Shot no.	Initial density (gcm ⁻³)	Impact velocity (km/s)	Pressure (GPa)	Specimen thickness (mm)
WRM-1	5.50	1.456	32.5	1.90
WRM-2	4.84	1.440	32.1	2.20
WRM-3	5.90	1.426	31.7	1.35
WRM-4	5.50	1.670	38.5	1.40
WRM-5	4.50	1.418	31.5	1.70
WRM-6	4.50	1.670	38.5	2.00
WRM-7	4.59	1.700	38.2	1.70
WRM-8*	4.73	1.663	38.3	1.80
WRM-9(WRM-2 reshock)	5.24	1.670	38.5	1.30
WRM-10 (h-BN)	5.50	1.67	38.5	1.90
WRM-11(h-BN/C ₂)	5.57	1.671	38.5	1.80
WRM-12	6.25	1.674	38.6	1.3
WRM-13	6.53	1.92	46.2	1.25
SCE-1	2.90	7.0 ^a	30	8.14
SCE-2	4.03	7.0 ^a	30	8.31
SCE-3 (HT)	5.74	7.0 ^a	30	8.1
SCE-4 (NHT)	5.83	7.0 ^a	30	7.87

(* denotes 5wt% BN-C other samples are 10wt% BN-C; ρ_{Cu} samples WRM-7& 8 are from the non-heat treated BN-C material; SCE denotes products from column explosive shock compression HT-heat treated and NHT-non-heat treated,^a refers to detonation velocity)

3.5 Static High Pressure High Temperature (HP/HT) Synthesis

The phase transformation reactions were initially carried out in a laser heated Diamond Anvil Cell (LH-DAC) followed by bulk synthesis in the multi-anvil press using a 1200t *Sumitomo press* and the large volume 5000t *Zwick-Voggenreiter press* at the Bayrisches Geoinstitut, Bayreuth, Germany. Below is a brief description of the specialized High Pressure apparatus used.

3.5.1 HP/HT Laser Heated-Diamond Anvil Cell (LH-DAC)

Experiments

The HP/HT experiment was carried out using the ‘BGI hybrid’ DAC with diamond anvil tips of 450 μ m in size. The sample was loaded with an Ar pressure medium to generate a quasi-hydrostatic environment around the sample thus eliminating shear stresses and evenly distributing the pressure. A Re gasket of thickness 200 μ m pre-indented down to about 69 μ m with a 200 μ m hole drilled in the centre to contain the sample was used. The pressure exerted on the sample was determined insitu from the calibrated shift of the ruby R_1 fluorescent line using laser Raman. Raman measurements were carried out in the pressure range 0-25.8GPa with 5GPa increments for pressure calibration. The sample was subsequently heated under compression (25.8GPa) with a multimode Nd:YLF (yttrium lithium fluoride) CO₂ laser focused on the sample through the front diamond with a plano convex infrared lens. The average temperature in the laser heated spot was measured with an online designed optical system. The sample was successfully heated to temperatures of 1800°C and at 2000°C and heating to higher temperatures resulted in breaking of the diamonds.

3.5.2 Static HP/HT Multi-Anvil Experiments

The high pressure vessels used are of the “6-8” type configuration namely the 5000t *Zwick-Voggenreiter* press and the 1200t *Sumitomo* press. The “6-8” refers to two stages of anvils which are used to compress the high pressure assembly

containing the sample. The outer anvils consist of six hardened steel anvils attached to two guide blocks of a hydraulic press which applies uniaxial loads of up to 5000t for the *Zwick-Voggenreiter* press and 1200t for the *Sumitomo* press. The six anvils define a cubic cavity containing second stage (inner) anvils consisting of 8 WC cubes as shown in Figure 3.4 below.

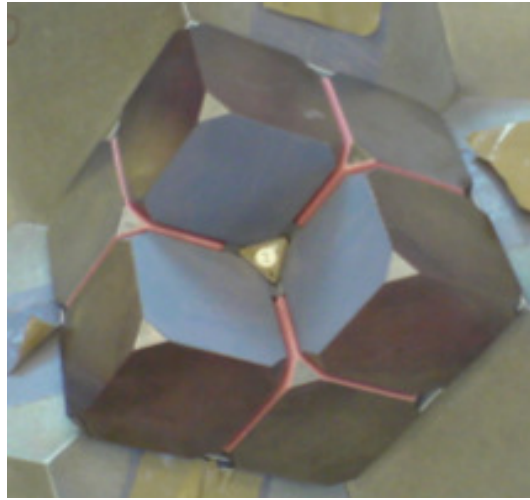


Figure 3.4: Exploded view of seven of the 8-WC cube assembly containing the sample cavity in the centre. The WC assembly is inside the lower 3 hardened steel assembly of the press.

The samples were contained in either h-BN or Ta capsules to avoid chemical reactions at elevated temperatures. The sample assembly consisted of an MgO (5wt%Cr₂O₃) octahedron and a LaCrO₃ heater surrounding the sample capsule with Mo discs at both ends of the heater for electrical conductivity. The assembly was placed in an octahedron cavity created between eight 54mm or 34mm sided tungsten carbide anvils each with a truncation of 11mm or 5mm for the 5000t and

1200t assemblies respectively. The edges of the octahedral cavity were gasketed by means of pyrophyllite to avert metal to metal contact and to achieve the required sample compression. Each experiment consisted of compressing the assembly to the desired pressure followed by a stepwise temperature increase at a rate of 100°C/min to the target temperature and an isothermal holding time of 30s-5mins at the target temperature. The samples were subsequently quenched by switching off the heating power and slowly decompressed.

Table 3.2: Summary of synthesis parameters used in the static HP/HT experiments.

Sample	P/GPa	T/°C	holding time/s	Cooling mode	Capsule Material
Z608	20	2000	60	quench	h-BN
S4294	20	1500	120	quench	MgO
S4295	20	1920	300	quench	h-BN
S4306	20	2000	30	quench	Ta
S4316	20	2000	180	quench	h-BN
S4311	20	-	7200	-	h-BN

Samples designated S were synthesised in the 1200t Sumitomo press and Z in the 5000t Zwick-Voggenreiter press respectively.

3.5.3 Preparation Procedure

- i) Surfaces of the WC anvils were cleaned using a blade and acetone to remove sticking dirt from the surfaces.
- ii) The MgO, LaCrO₃ heater and capsule materials were dried in a muffle furnace at 1000°C for 1hr.

- iii) The WC cube assembly prepared by gluing pyrophyllite gaskets at all corners making up the inner octahedral. Additional gasket support was provided for by gluing manila paper behind the gaskets which also acted as an insulator.
- iv) Powder loaded and compacted in the capsule with the aid of an Al_2O_3 rod. Capsule closed and loaded inside the heater then MgO octahedral and closed at the ends with Mo discs.
- v) Capsule assembly glued and carefully loaded inside the WC assembly which was glued together. The electrical contacts were provided for by Cu plates placed on two opposite ends of the cube assembly.
- vi) Assembly loaded inside the press and compressed for 4hrs to the final pressure.
- vii) The assembly was heated by increasing the current on the controller at a rate of ca. $100^\circ\text{C}/\text{min}$ to the final temperature followed by an isothermal hold and quenching by switching off the furnace.

3.5.4 High Pressure/Temperature Studies in the Belt Press

A 30 000t “Kobelco” Belt Press was used to undertake studies on the crystallisation behaviour of the low pressure t-BN-C phase at the National Institute of Materials Science, Japan. The t-BN-C powders were loaded in a MgO capsule 10.6mm in height and 5.80mm internal diameter and compacted using a steel rod. The capsule was placed inside a graphite heater and the whole assembly was insulated from the pyrophyllite container by an h-BN lining. The assembly was loaded in the press and compressed at room temperature to the target pressure. The assemblies were heated to 2000°C and 3000°C and held at the target

temperatures for 5mins. Subsequent quenching was carried out by switching off the furnace and the assemblies were slowly decompressed at room temperature. The assemblies were carefully opened and cleaned by boiling in HCl for 4 hours. The samples were analysed by X-ray diffraction using a RIGAKU RINT 2000 powder diffractometer.



Figure 3.5: A schematic view of the 30 000t “Kobelco” belt press used for the high pressure studies. *(Courtesy of NIMS, Japan)*

3.6 Characterisation Techniques

The precursor ceramic powders and sintered compacts obtained by the aforementioned methods were characterised by various techniques to ascertain the properties possessed. Below is a summary of the characterisation techniques used in the present study.

3.6.1 Thermal gravimetric Analysis

An STA-429 (*Netzsch, Germany*) Thermal Analyser equipped with a heating furnace was used for thermal analysis and the evolved gases were detected insitu with a Balzers QMA 400 mass spectrometer coupled to the STA (Simultaneous Thermal Analyser) equipment. A representative piperazine borane derivative sample of *ca.*10mg was weighed in an alumina crucible and loaded inside the furnace. Thermal gravimetric analysis (TGA) was conducted at a heating rate of 5°C/min to a temperature of 1200°C and cooling to room temperature under Ar flow. The mass change with increasing temperature was noted and gaseous products produced were recorded with the mass spectrometer using appropriate software. The ceramic yield was estimated from the weight of the residue after cooling.

3.6.2 Elemental Analysis

Bulk elemental analyses of both the pyrolysed and heat-treated BN-C ceramics were obtained from LECO-CNO Analysers. An NO-Analyser Leco TC-436 was used to estimate the oxygen and nitrogen contents in the samples by an inert gas fusion method. Standards with known oxygen contents were measured and the equipment standardised prior to the sample measurements. The C content was obtained by a Leco C-200 through a combustion method i.e. a measure of the amount of oxidised C under high temperature heating in an oxygen environment. The reported elemental contents were obtained from an average of three different readings.

3.6.3 Fourier Transform Infrared (FT-IR) Analysis

Fourier transform infrared measurements were carried out using a Perkin Elmer 1750 FTIR Spectrometer. Conceptually such analyses provide details on the bonding nature in molecules. It is based on the principle that radiation absorption by a molecule occurs if the radiant energy (infrared radiation in the present case) matches the energy of a specific molecular vibration ⁽¹³⁶⁾. Thus absorption of radiant energy is represented by a 'trough' and zero transmittance corresponds to 100% light absorption at a particular wavelength. This means the IR spectra can be represented by absorbance (A) in the form of peaks as a function of wavenumbers. The absorbance (A) is related to the transmittance (T) through a logarithmic scale as follows;

$$A = \log_{10} \left(\frac{1}{T} \right) \quad [3.8]$$

Molecular vibrations are typically divided into two types i.e stretching and bending. It has been observed that only those molecules which possess a change in the dipole moment are IR active.

To enable measurements the samples were pulverised using a pestle and mortar mixed with KBr (*ca.*75wt%) powder and loaded in a 5mm diameter steel die pressed into a transparent pellet with a manually operated hand press. The pellet was subsequently loaded in the instrument for direct measurement in the mid infrared range (4000-400cm⁻¹) with a resolution of 4cm⁻¹ at 20 scans per run. A standard pure KBr pellet was used to scan and subtract the background prior to the actual measurement.

3.6.4 X-Ray Diffraction

X-ray powder diffraction of the ceramic powders was carried out using Cu-K α radiation with a step scan of 0.02° in the 2 θ regime of 10-80° with a Philips PW1780 diffractometer operated at 40kV and 60mA. The shock-wave synthesised materials were analysed using a RIGAKU RINT 2000 with Cu-K α radiation operated at 40kV and 60mA at NIMS, Japan. The high pressure phases were studied using a RIGAKU X-ray diffractometer with an FR-D high-brilliance source (Mo-K α radiation, $\lambda = 0.7108\text{\AA}$) operated at 55kV and 60mA and

synchrotron radiation facilities at APS, Argonne National Laboratory Chicago, USA ($\lambda = 0.3344\text{\AA}$) and the ESRF, Grenoble, France ($\lambda = 0.7693\text{\AA}$).

3.6.5 Raman Spectroscopy

Raman measurements for the precursor B/C/N materials were obtained using a multichannel Jobin-Yvon HR800 spectrometer at room temperature. Systematic observation of the selected area was made before each measurement using the charge coupled device (CCD) camera in order to assess the quality of the area to be studied. Argon ions with a wavelength of 514.5nm were used as the excitation source with an instrument resolution of 2cm^{-1} . The spectra for the high pressure samples were collected using both He-Ne laser and Ar ion laser using a Labram System with power outputs and wavelengths of 15mW, 632.8nm and 24mW, 514.5nm respectively. The laser was focused into the sample using an Olympus BX40 microscope to excite Raman effect in both cases. Spectra were collected over a frequency range of $200\text{-}4000\text{cm}^{-1}$ with 5 steps collected over 300s using the Labspec Software.

Raman scattering is a useful ‘finger printing’ technique based on the interaction of laser light with phonons or other excitations in a system. This results in the energy of the laser phonons being shifted which basically gives information on the phonon modes of a material. Thus “Raman shift” is an intrinsic property of a particular material.

3.6.5.1 Low Temperature Resistivity Studies

The electronic properties of sample Z608 were studied through the temperature dependence of the resistivity. The resistivity curve of Z608 was taken at zero field in a commercial ^4He cryostat ⁽¹³⁷⁾ using a standard 4-point AC resistance measurement technique. For this purpose the sample was connected to the apparatus with copper wires using graphite paste. The measurement was done at a current of $10\mu\text{A}$ and the resistivity was derived from resistance and sample geometry by application of the van-der-Pauw method as described in the literature.⁽¹³⁸⁾

3.6.6 X-ray Photoelectron Spectroscopy (XPS)

The powders to be analysed were loaded on sample holders and evacuated. The XPS spectra were collected at room temperature using a Thermo VG Scientific Escalab 250XL spectrometer with an Al-K α ($h\nu = 1486.6\text{eV}$) radiation in a vacuum of $\text{ca.}10^{-9}\text{mbar}$.

Conceptually, the XPS technique is based on the interaction of an X-ray photon ($h\nu$) with inner electrons of an atom. There is transfer of energy to the electron which causes it to escape from the atom with a specific kinetic energy (E_k). If this kinetic energy is measurable then the electron binding energy (E_b) can be obtained from;

$$E_b = h\nu - E_k \quad [3.9]$$

where h is the Plank's constant ($6.626 \times 10^{-34} \text{ m}^2 \text{ kg/s}$) and ν is the X-ray frequency.

Thus each element has a unique binding energy used to identify the elemental composition of a particular sample. ⁽⁷⁹⁾

3.6.7 Materialographic Preparation

The sintered BN-C materials were carefully removed from the octahedral capsule using a pair of pliers. The samples were mechanically cleaned in acetone using an ultrasonic bath for about 30mins. The recovered samples were mounted in a Lucite thermoplastic compressed under heating ca.150°C with subsequent water cooling. The samples were mechanically ground and polished with diamond paste to a mirror surface finish.

3.6.8 Scanning Electron Microscopy (SEM)

The surface morphology of both powders and diamond anvil cell synthesised materials were analysed using a LEO-1530 SEM (Scanning Electron Microscope). The powdered samples were mounted on aluminum studs and coated with a thin layer of carbon and the sintered samples were first mounted and polished and subsequently coated with carbon. The samples were loaded in the SEM chamber which was subsequently evacuated for 30mins. Both SE and BS images were

captured and stored using the online software. Energy dispersive spectroscopy (EDS) was used for chemical analysis of the samples.

3.6.9 Transmission Electron Microscopy (TEM)/ Electron Energy Loss Spectroscopy (EELS) Analysis

The t-BN-C and the c-BN-C materials were crushed between WC surfaces, dispersed in ethanol and loaded on copper grids coated with a holey carbon film. A Philips CM-20 FEG (Field Emission Gun) ATEM operated at 200kV was used in the present study. The textures were studied by both BF (bright field) and DF (dark field) imaging and HRTEM (High Resolution Transmission Electron Microscopy). Furthermore, SAED (Selected Area Electron Diffraction) was used to obtain interplanar spacings of the three strongest diffraction rings 111,220 and 311 which were subsequently used for lattice constant (a) determination. In an attempt to ascertain the nature of bonding in the cubic phases EELS spectra were collected for the B-K, C-K and N-K edges using a GATAN-PEELS 666 (parallel electron energy loss spectrometer) on a single crystal. The relative compositions (C_A/C_B) of the cubic B/C/N phases were estimated from the integrated intensities under the edge and above the background, collection angles β of 2.9mrad, 4.3mrad and convergence angle of 8mrad. The background was modelled by a power law function.

Chapter 4: Results

4.0 Introduction

A BN-C ceramic was obtained by a solid phase pyrolysis of a borane compound, $\text{C}_4\text{H}_{10}\text{N}_2\text{BH}_3$ with a yield of about 44wt%, a nominal composition of $\text{BC}_{1.97}\text{N}$ and oxygen content of about 0.438 (7) wt% after heat-treatment (1850°C , 2hr, N_2). Furthermore, the ceramic was found to possess a turbostratic type structure in which characteristic $(00l)$ and $(hk0)$ lines appear and general (hkl) and $(h0l)$ lines are missing in the XRD profile. Raman spectroscopy confirms existence of a microcrystalline graphitic type material with a high degree of disorder (confirmed by the presence of D and G bands). It was also shown that the same ceramic possesses IR-active BN-vibrations as observed in the Fourier Transform Infra red Spectroscopy (FT-IR) profile. A further investigation into the bonding properties by X-ray Photoemission Spectroscopy (XPS) however shows that bonding is mostly limited to C-C and B-N types which can be linked to the ‘stripped type’ models as described earlier by theoretical modellers.^(73, 78)

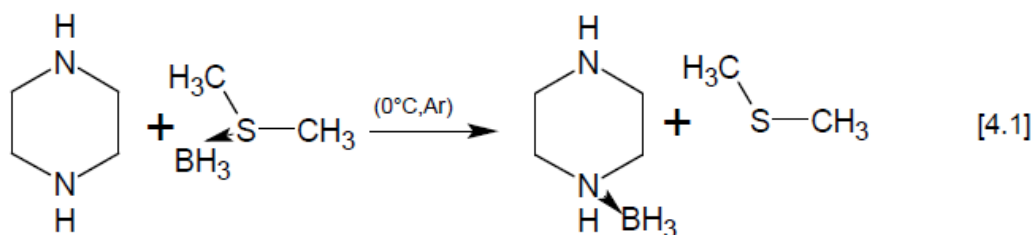
An investigation on the thermal stability of this polymer derived ceramic at 2GPa and temperatures of 2000°C and 3000°C in the belt press resulted in their decomposition into crystalline h-BN and graphite at about 2000°C . This process is more pronounced at 3000°C . Studies carried out at higher pressures under dynamic pressure conditions using a shock-wave technique resulted in decomposition into a mixture of BN-C and boron carbide materials at temperatures in excess of 2000°C and pressures of up to 30GPa. However no

phase transformation was observed at temperatures below 2000°C and pressures in excess of 30GPa. Investigations of the same BN-C precursors under static HPHT conditions in the multi-anvil press resulted in a cubic BN-C phase (20GPa, 2000°C, 30-60s holding time) as confirmed by XRD, Raman spectroscopy and TEM/EELS studies. Thus this chapter presents a confirmation on the successful synthesis of a polymer derived BN-C ceramic suitable for the synthesis of a cubic phase under static HPHT conditions.

4.1 Analysis of Starting Materials

4.1.1 Synthesis Results

The synthesis reaction can be assumed to proceed through polyaddition of an electron deficient $-BH_3$ molecule to the piperazine ring on nitrogen sites containing a free electron pair resulting in a monoborane as depicted by equation [4.1] below.



The yields of the piperazine borane were obtained from the balanced equation [4.1] which was used to derive modified equations [4.2] and [4.3] below:

$$M_{th(PB)} = \frac{M_{exp(PIP)}}{RMM_{(PIP)}} * RMM_{(PB)} \quad [4.2]$$

$$\eta(\%) = \frac{M_{\text{expt.}(PB)}}{M_{\text{th}(PB)}} * 100 \quad [4.3]$$

where $M_{\text{th}(PB)}$ is the theoretical mass of piperazine-borane as expected from the balanced equation, $M_{\text{expt}(PB)}$ is the experimental mass of piperazine-borane as obtained from the reaction, $RMM_{(PB)}$ ($=99.8\text{g/mol}$) is the relative molecular mass of piperazine-borane and η is the yield.

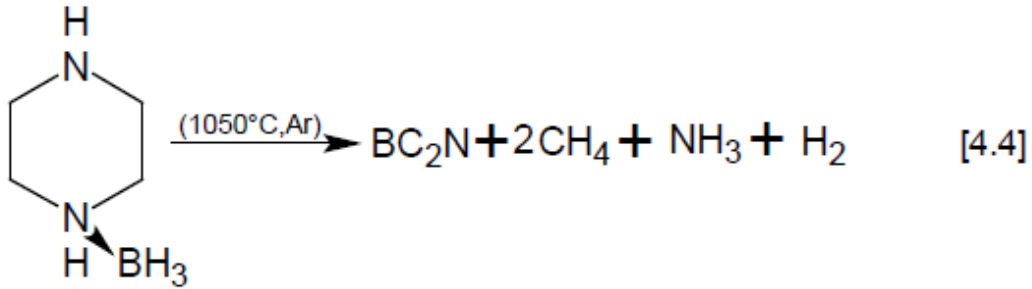
Table 4.1: Summary of experimental parameters used in the synthesis of piperazine borane complex.

Run	Piperazine/g ($\pm 0.0001\text{g}$)	Borane-dimethyl sulfide /ml ($\pm 0.1\text{ml}$)	Toluene/ml ($\pm 0.1\text{ml}$)	Piperazine-borane /g ($\pm 0.0001\text{g}$)	% yield
S1	20.052	26.7	500	20.5931	88.5
S2	15.327	20.0	400	14.9415	84.0
S3	35.1230	46.9	700	35.2974	86.6
S4	35.3429	46.8	700	35.1951	85.8
S5	36.6117	46.8	700	37.2711	87.7
S6	35.0511	46.8	700	35.9250	88.3
S7	47.5185	60.7	800	48.9192	88.7

An average yield of 87.0(9) % was obtained from the seven experiments listed in Table 4.1 above. The only losses recorded are due to slurry sucked into the nylon pipes during extraction of the dimethyl sulphide liquid under high vacuum which carried with it some of the piperazine borane powder.

The formation of BN-C from the piperazine-borane adduct compound, $\text{C}_4\text{H}_{10}\text{N}_2\cdot\text{BH}_3$, can be assumed to take place through a two stage process as already analysed and discussed in reference ^(54a,54b). The reaction involves the formation of an intermediate infusible bright yellow polymer derivative after heat

treatment at 400°C for 10hrs. This was enabled by loss of H₂ and rearrangement into a long chain polymer which was later broken down at higher temperatures (1050°C, 2hr, Ar) by the loss of predominately H₂, CH₄ and NH₃ to form the BC₂N ceramic as detected by simultaneous mass spectroscopy in the thermal gravimetric analysis (TGA/MS). Thus the formation of BC₂N from piperazine borane can be represented as shown in a simplified reaction [4.4] below.



The yields were obtained from the balanced equation [4.4] above which was used to derive modified equations [4.5] and [4.6] below:

$$M_{th(BC_2N)} = \frac{M_{\text{expt.}(P.B)}}{RMM_{(P.B)}} * RMM_{(BC_2N)} \quad [4.5]$$

$$\eta(\%) = \frac{M_{\text{expt.}(BC_2N)}}{M_{th(BC_2N)}} * 100 \quad [4.6]$$

where $M_{th(BC_2N)}$ is the theoretical mass of BC₂N as expected from the balanced equation, $M_{\text{expt.}(BC_2N)}$ is the experimental mass of BC₂N obtained from the present reaction, $RMM_{(BC_2N)}$ (= 48.8g/mol) is the relative molecular masses of BC₂N and η is the yield.

Table 4.2: Synthesis parameters of the pyrolysis reactions as observed in different trials.

Run	Piperazine mass/g (± 0.0001)	borane Mass of B/C/N ceramic /g (± 0.0001)	% yield
P1	18.9045	4.2984	46.5
P2	21.0867	4.5884	44.5
P3	19.7171	4.6627	48.4
P4	20.5949	5.2709	52.3
P5	25.4220	6.1222	49.3
P6	25.3000	5.5992	45.3
P7	8.4000	1.8220	44.4
P8	10.1866	2.2195	44.6
P9	12.9934	2.7676	43.6
P10	13.3343	2.8924	44.4
P11	12.6650	2.6784	43.3
P12	15.5830	3.3260	43.7
P13	20.8316	4.5461	44.6

An average yield of 45.7(6) % from a total of thirteen experiments recorded.

4.1.2 Characteristics of Starting Materials

4.1.2.1 FT-IR Results of Piperazine-Borane

The FT-IR spectrum of the piperazine borane was compared with that of piperazine. The main difference to note is the presence of a B-H bending mode ($2360\text{--}2250\text{cm}^{-1}$) in the piperazine borane complex (Figure 4.1) which is absent in the piperazine spectrum. The general profile differs from the one reported by Goto *et al*⁽⁵⁵⁾ for the piperazine-1N, 4N diborane complex confirming the formation of

a monoborane in the present study. Furthermore for a 1:1 molar ratio of piperazine vs. borane-methyl sulfide complex three N-H vibrations are expected in the wavenumber range 3300 to 3070 cm^{-1} ⁽⁵⁵⁾. In the present study three of these vibrations are found to exist at (3090, 3160, 3310 cm^{-1}) as stretching modes. Additionally other modes of vibration were observed as follows C-H stretching mode (2820-2990 cm^{-1}), N-H bending mode (688, 1470-1310 cm^{-1}), B-N bending mode (1190, 1060 cm^{-1}). The B-H vibration at 2250 cm^{-1} is broader than the one observed by Goto⁽⁵⁵⁾ possibly owing to hindrance by the piperazine ring.

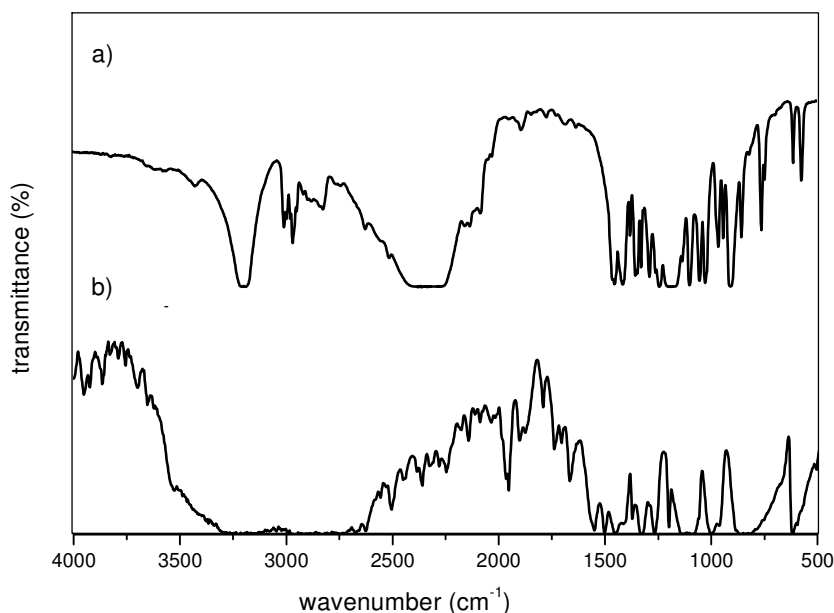


Figure 4.1: FTIR spectra of piperazine borane complex (a) in comparison with (99%) piperazine (b).

4.1.1.2 Thermal Treatment of polymer materials

A thermal gravimetric analysis of the borane derivative shows that weight loss of the piperazine borane is initiated at 250°C (see Figure 4.2). A maximum weight

change was observed at $T = 535^{\circ}\text{C}$ with no noticeable weight change beyond this temperature. The overall ceramic yield was found to be 40.5wt% from TGA at 1050°C comparable to the experimental yield of about 45wt%. Bill *et al*^(54a, 54b) reported a yield of 43wt% with piperazine borane at 1323K (1070°C) further confirming formation of a monoborane in the present study.

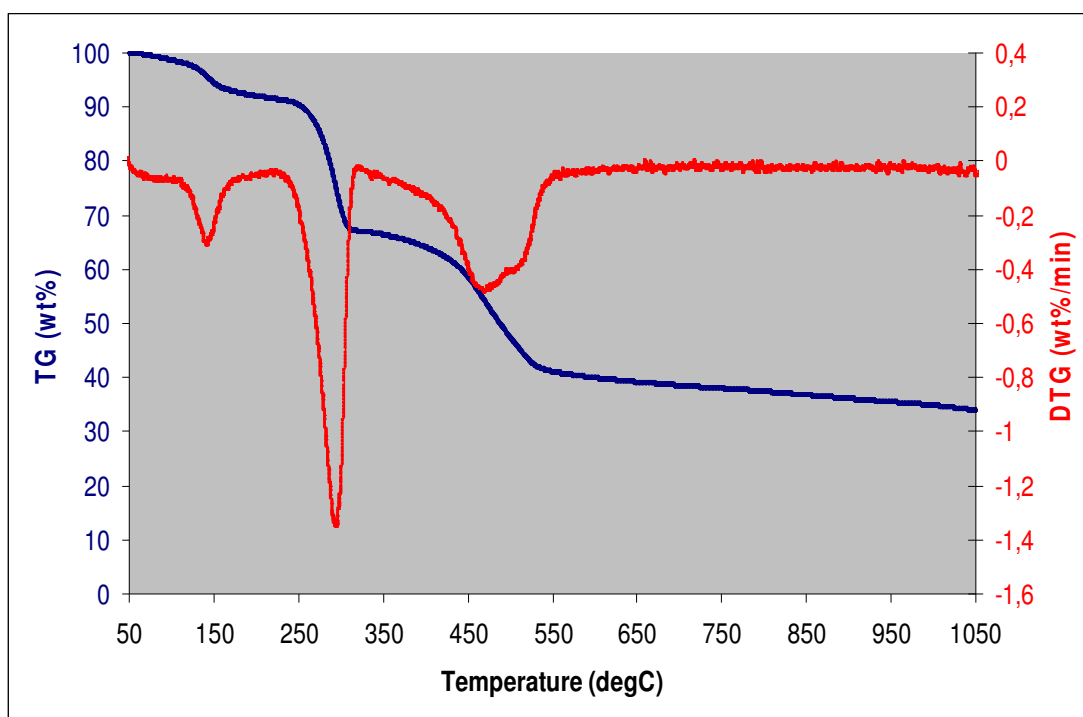


Figure 4.2: TGA /DTG curves of the piperazine borane complex up to the pyrolysis temperature.

The observed mass loss between $100\text{--}150^{\circ}\text{C}$ is related to loss of hydrogen with m/z (mass to electron charge ratio) of 1. A further mass loss in the range $250\text{--}600^{\circ}\text{C}$ is related to loss of hydrocarbons which correspond to the following m/z values with respective assignments given in brackets: $m/z = 15(\text{CH}_3^+)$, $16(\text{CH}_4^+)$, $27(\text{C}_2\text{H}_3^+)$, $29(\text{C}_2\text{H}_5^+)$ and ammonia based compounds with $m/z = 17(\text{NH}_3)$,

18(NH₄⁺). The loss of hydrogen, hydrocarbons and ammonia indicates the decomposition of the piperazine borane complex during the formation of the BN-C ceramic. The decomposition of the borane complex is assumed to proceed through equation 4.4.

4.1.3 Characteristics of the t-BN-C Ceramics

4.1.3.1 X-Ray diffraction Results

The X-ray diffraction patterns of the pyrolytic and heat treated samples are consistent with a turbostratic type structure revealing typical (*hk0*) and (*00l*) reflections with the general (*hkl*) lines missing.⁽¹²⁴⁾ The as-pyrolysed BN-C materials are clearly amorphous showing broad diffuse turbostratic lines. There is a marked decrease in the peak widths and increased intensities with increasing temperature but the ceramic material remains turbostratic even at higher temperatures as shown in Figure 4.3 below.

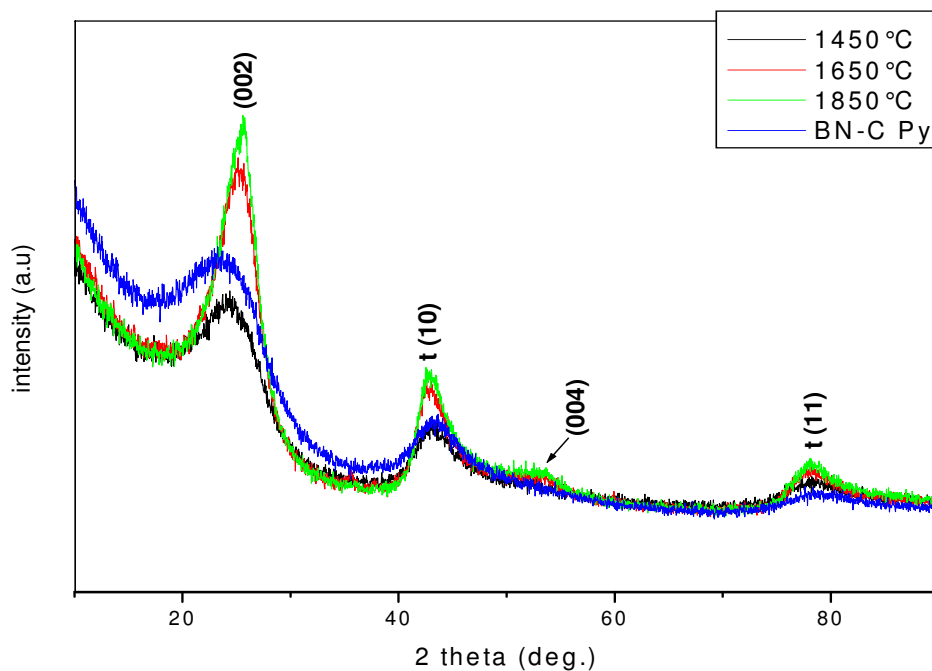


Figure 4.3: X-ray diffraction patterns of the BN-C materials heat treated to different final temperatures.

Furthermore a d_{002} value of 0.345nm was obtained from the heat-treated sample (1850°C). This is larger than those of crystalline graphite (0.335(5) nm) and h-BN (0.332(8) nm).⁽⁷¹⁾ This points to a loss of packing density within the layered structure and a turbostratic type structure is expected from such parameters i.e. structural disorder is expected to increase the interlayer spacing, $c^{(71)}$. The (002) reflection line is indexed in terms of hexagonal h-BC₂N and the index $t(hk)$ correlates with $(hk0)$ of the hexagonal BC₂N.

4.1.3.2 Elemental Analysis Results

Nominal compositions of BC_{1.75}N and BC_{1.97}N were obtained for the pyrolysed and heat treated (1850°C) powders respectively. This is in accordance with the

bulk elemental analysis in Table 4.3 below. The oxygen contamination observed is due to surface absorption which is drastically reduced by the heat treatment in N₂ atmosphere.

Table 4.3: Chemical composition of the as-pyrolysed (Pyro-BN-C) and the heat-treated (Heat-treat-BN-C) ceramic obtained by CNO elemental analysis.

<i>Sample</i>	<i>C (wt%)</i>	<i>N (wt%)</i>	<i>C/N ratio</i>	<i>O (wt%)</i>
Pyro-BN-C	40.0±0.4	22.9±1.1	1.75	4.2±0.3
Heat-treat-BN-C	46.4±0.6	23.5±2.0	1.97	0.4±0.2

4.1.3.3 FTIR-Results

The pyrolysed BN-C FT-IR spectrum was compared with that of the piperazine borane derivative to observe the major changes in the bonding nature associated with the heat treatment. The piperazine borane derivative shows a typical h-BN spectrum (Figure 4.4) with a broad B-N in-plane stretching mode with additional B-H bending mode in the range (2500-2375cm⁻¹), C-H stretching mode (2900-2875cm⁻¹) and a rather broad spectrum in the N-H vibration range assigned to N-H stretching mode. This is expected for the derivative since it still contains appreciable amounts of hydrogen atoms. The pyrolysed sample shows a broad peak at 1406cm⁻¹ assigned to in-plane sp² B-N stretching mode shifted ~33cm⁻¹ to a higher wavenumber from that of pure h-BN ⁽¹⁰⁴⁾ and weak peak at 791cm⁻¹ assigned to out of plane bending B-N mode. The N-H vibration is still present after heat treatment, this is due to the strength of the N-H bond which requires more energy to break. No C-C vibrations were observed within the whole spectrum range.

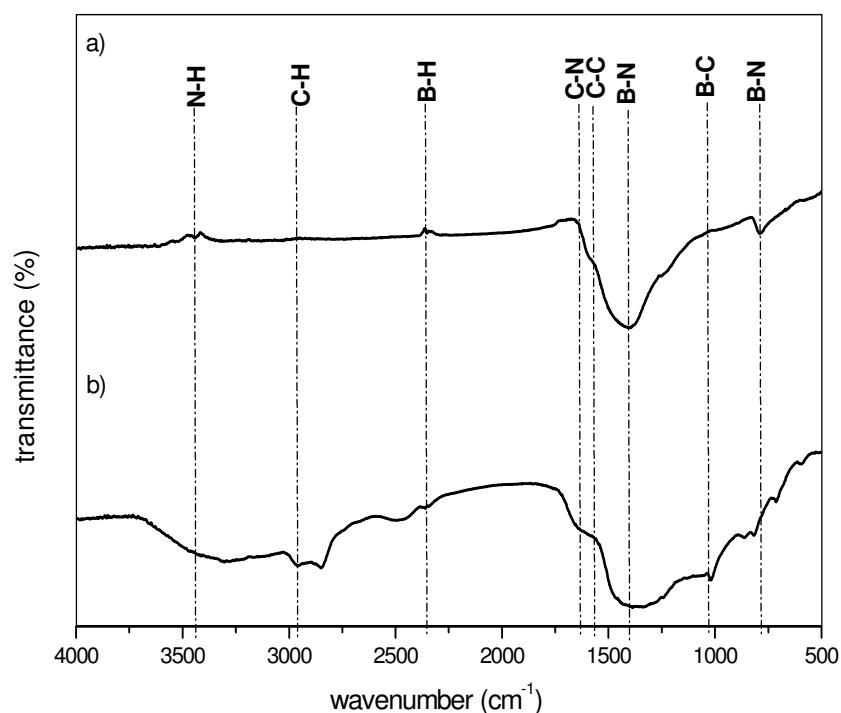


Figure 4.4: FT-IR spectra of the as-pyrolysed BN-C ceramic (a) in comparison with the piperazine borane derivative (b).

4.1.3.4 Raman Spectroscopy Results

The Raman spectra of the BN-C ceramics are characterised by broad D (1352cm^{-1}) and G (1600cm^{-1}) bands as shown in Figure 4.5 below. This is attributable to structural disorder on the one hand and presence of microcrystallites on the other hand, this is in accordance with observations made on graphitic materials in previous studies.⁽¹³³⁾ Furthermore, the intensity ratio is typical of glassy or amorphous carbon materials.⁽¹³⁴⁾ There is a marked difference between the two spectra, which could be a result of the amorphous (pyrolytic BN-C) to turbostratic (heat-treated BN-C) structural change and the crystallite growth associated with

the heat-treatment. Furthermore, a marked broadening and overlap of the G and D bands for the pyrolytic BN-C ceramic is observed. The range covered by these two bands covers both graphite and boron nitride Raman modes. However the bands become sharper and separate with increasing temperature to resemble the disordered graphite type spectrum which could mean a separation of the graphite and boron nitride layers within the system.

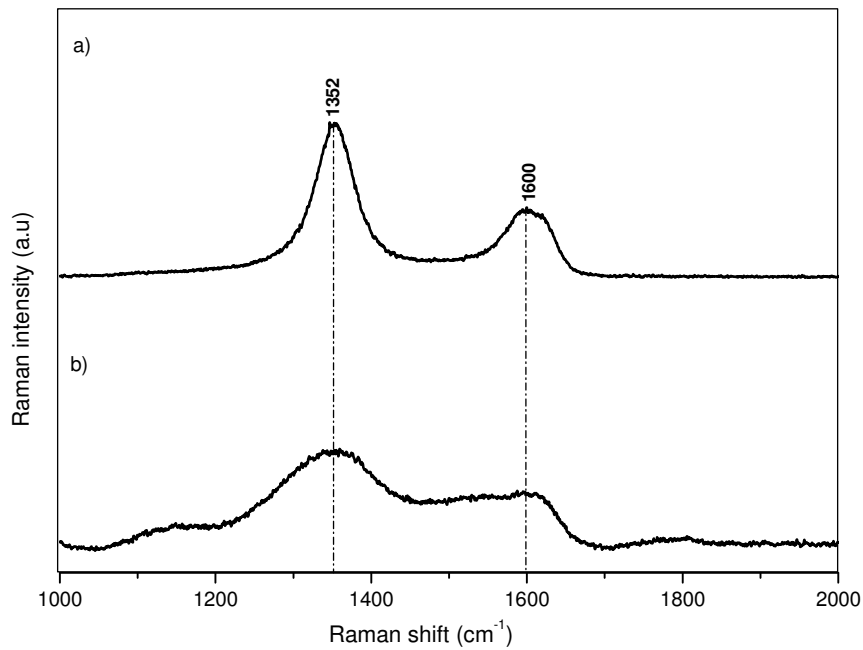


Figure 4.5: First order Raman spectra of the heat treated (a) in comparison with the as-pyrolysed (b) BN-C ceramic.

4.1.3.5 X-ray Photo-Spectroscopy Results

The B1s peaks of both the pyrolysed BC_2N (190eV) and the heat-treated BC_2N (190.5eV) are within the binding energy range of h-BN (190.5eV).⁽¹³⁵⁾ This suggests the dominant bonding in the boron and nitrogen atoms in the BN-C ceramics is largely due to the B-N type. Deconvolution of the peaks resulted in

small peaks centred at higher binding energies in the region of about 192-194eV. However since nitrogen is the most electronegative atom in this system, the peaks can only be due to B-N type bonding. Thus the broad B1s peaks for both BN-C ceramics are due to fully B-N type bonding. The C1s peaks are both symmetrical and centred at 284.5eV which is slightly lower than that of graphite (285eV).⁽¹³⁵⁾ Thus the bonding type is purely due to C-C type bonding as in graphite. The N1s peaks of the pyrolysed (398.3eV) and the heat-treated (398.1eV) BN-C ceramics are slightly larger than the binding energy of h-BN (395.8eV) but are within the B-N range.⁽¹³⁵⁾ Clearly the ESCA results show that the present BN-C ceramics are likely to consist of dominantly C-C and B-N type bonding. The likelihood of B-C (282.9-284.9eV)⁽¹³⁶⁾ and C-N (399.3eV)⁽¹³⁵⁾ type bonding is highly unlikely owing to the high symmetry and small FWHM (Full Width at Half Maximum) of the spectra collected.

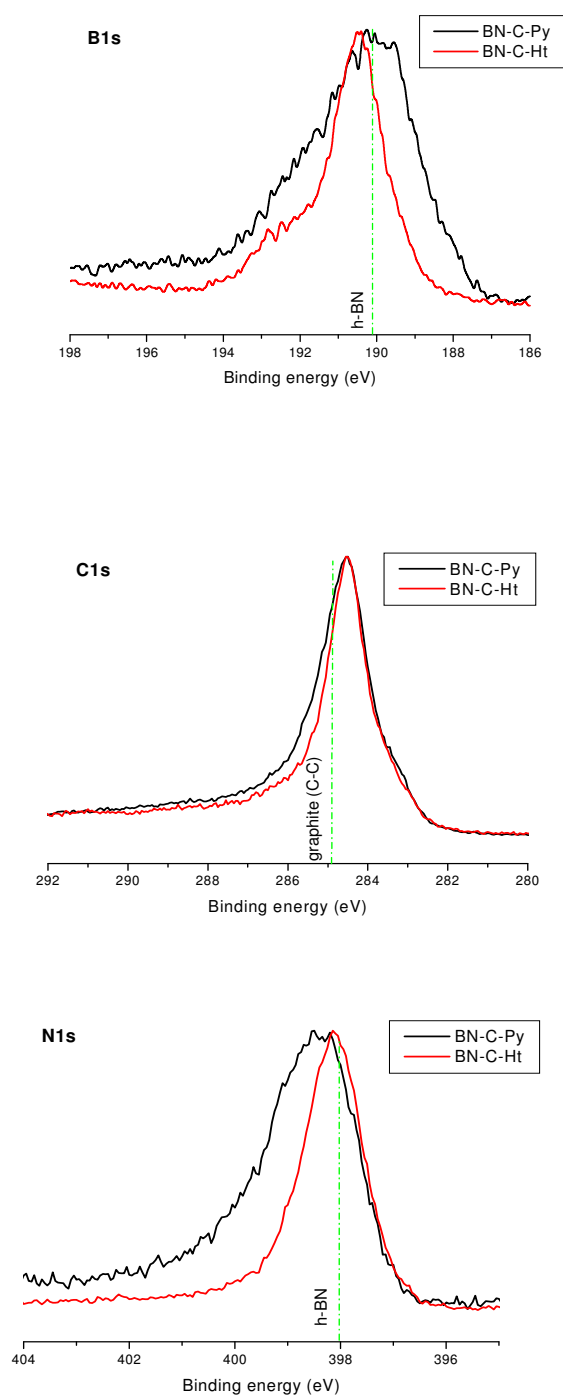


Figure 4.6: ESCA Spectra of the BN-C pyrolysed (Py) and heat treated (Ht) materials in comparison to those of standard materials graphite and h-BN.

4.1.3.6 SEM Results

The SEM images of the starting BN-C materials (Figures 4.7 and 4.8) show thin layered and elongated particles. The heat treated samples show some rounded features on the surfaces of the layered particles. The features depict escape of low melting phases and gases from the borane precursor leaving the ceramic residue particles to agglomerate and grow into the final shapes.

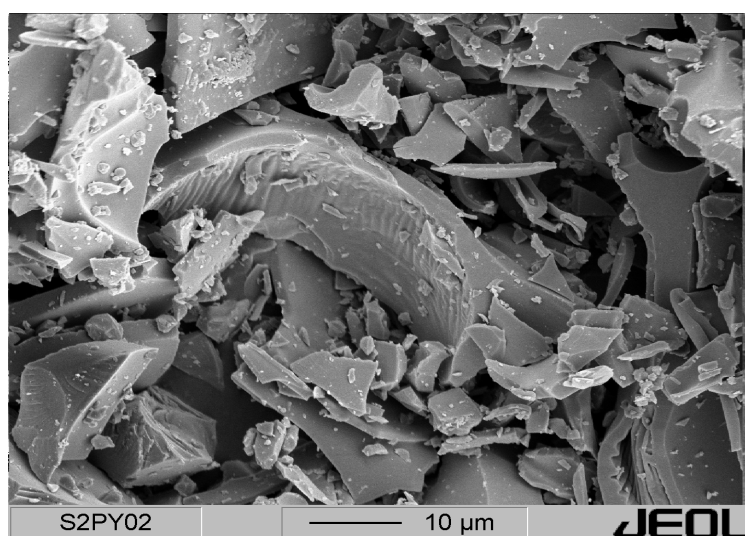


Figure 4.7: SEM image of the as-pyrolysed BN-C ceramic treated at 1050°C under Ar flow for 10hrs.

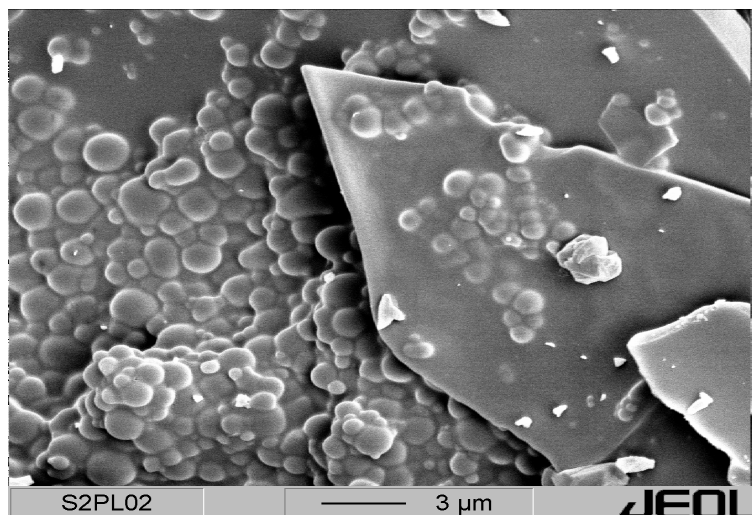


Figure 4.8: SEM image of the final BN-C ceramic heat treated at 1850°C, 2hrs under N₂ flow.

4.1.3.7 Electron Energy Loss Spectroscopy (EELS) Results

The EELS profile (Figure 4.9) of the heat treated starting BN-C ceramic shows the B-K, C-K and N-K edges appearing concurrently throughout the whole spectrum. Pre-edge features at 191.4eV and 197.7eV at the B-K edge, 285eV and 292.5eV at the C-K edge and 400eV and 407.7eV at the N-K edge were identified as transitions due to π^* (π^*) and σ^* (σ^*) molecular orbitals confirming sp^2 type bonding in the starting materials. The peaks occurring at higher energy loss values in each K-edge range are featureless.

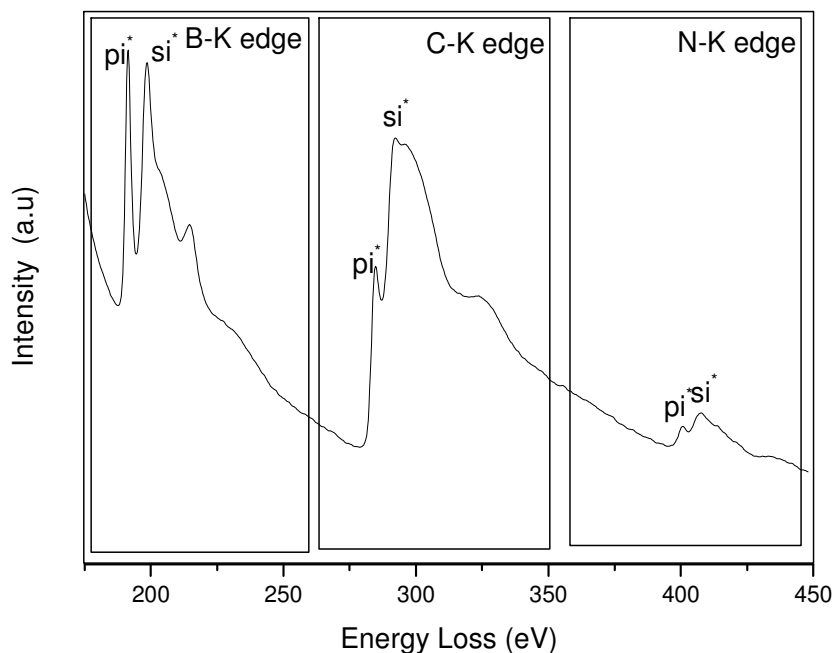


Figure 4.9: Electron Energy-Loss Spectrum (EELS) of the starting t-BN-C material.

4.2 Analysis of Shock synthesised Materials

Below is a summary of the shock compression results obtained at various P, T conditions using a 30mm bore single stage-propellant gun. The temperatures could not be accurately determined but were estimated from the initial densities, thus an initial density of 5.50gcm^{-3} was assumed to result in a temperature of about 1900°C from previous experiments. Thus a lower starting density resulted in a higher temperature and conversely a higher starting density will have a lower starting temperature.

Table 4.4: Summary of experimental parameters and results obtained in shock compression experiments.

Shot no.	Initial density (gcm ⁻³)	Impact velocity (km/s)	Pressure (GPa)	Specimen thickness (mm)	XRD Comment
WRM-1	5.50	1.456	32.5	1.90	t-BN-C
WRM-2	4.84	1.440	32.1	2.20	t-BN-C + B _x C _y
WRM-3	5.90	1.426	31.7	1.35	t-BN-C
WRM-4	5.50	1.670	38.5	1.40	t-BN-C
WRM-5	4.50	1.418	31.5	1.70	t-BN-C + B _x C _y
WRM-6	4.50	1.670	38.5	2.00	t-BN-C + B _x C _y
WRM-7	4.59	1.700	38.2	1.70	t-BN-C + B _x C _y
WRM-8*	4.73	1.663	38.3	1.80	t-BN-C + B _x C _y
WRM-9	5.24	1.670	38.5	1.30	t-BN-C + B _x C _y
WRM-10 (h-BN)	5.50	1.67	38.5	1.90	w-BN
WRM-11(h-BN/C ₂)	5.57	1.671	38.5	1.80	w-BN + graphite
WRM-12	6.25	1.674	38.6	1.3	t-BN-C
WRM-13	6.53	1.92	46.2	1.25	t-BN-C
SCE-1	2.90	7.0 ^a	30	8.14	t-BN-C + B _x C _y
SCE-2	4.03	7.0 ^a	30	8.31	t-BN-C + B _x C _y
SCE-3 (HT)	5.74	7.0 ^a	30	8.1	t-BN-C + B _x C _y
SCE-4 (NHT)	5.83	7.0 ^a	30	7.87	t-BN-C

(* denotes 5wt% BN-C other samples are 10wt% BC₂N; samples WRM-7& 8 are from the non-heat treated B-C-N material; SCE denotes products from column explosive shock compression HT-heat treated and NHT-non-heat treated, ^a refers to detonation velocity)

The results above show a clear trend on the heat stability of the BC₂N material under shock compression. For instance, a comparison of samples WRM-4,6 &12 which were shocked at the same pressure of 38GPa but different temperatures (starting densities different) show a phase change recorded for the lowest starting density of 4.5gcm⁻³ (WRM-6) with formation of a boron carbide compound. However the lower angle peaks for B₄C (2θ < 25°) were not observed this could be a result of the broad B/C/N peaks which mask the low intensity peaks. Also the peaks assigned to boron carbide did not exactly match those of pure B₄C (*ICDD No.*: 35-0798) possibly owing to the presence of the other forms of boron carbide such as B₁₃C₂ and B₁₃C₃. This trend is repeated with all the other samples with

starting density values in the range ($4.5\text{-}5.0\text{gcm}^{-3}$) irrespective how high the shock pressure used was.

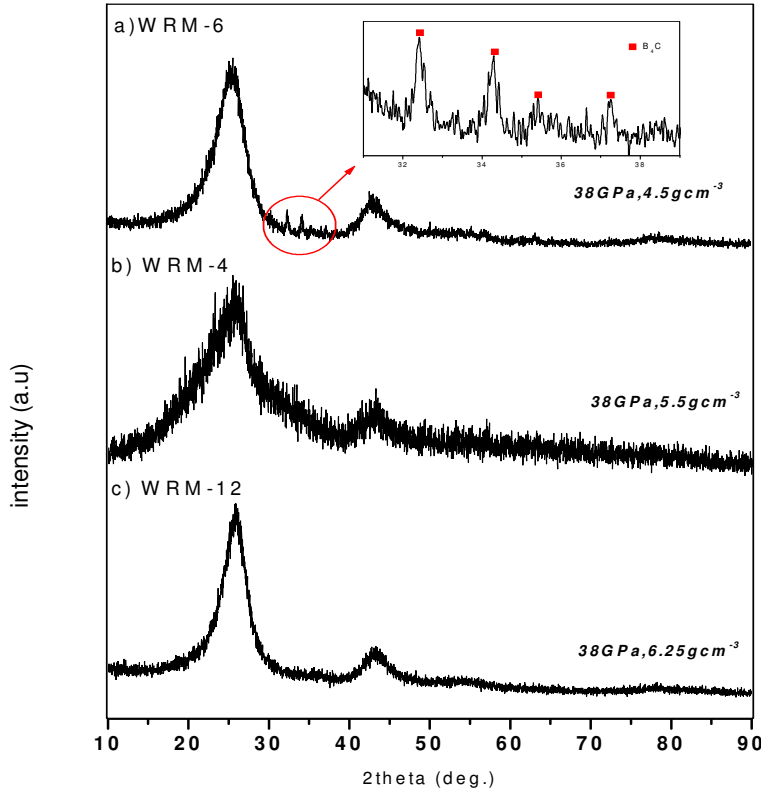


Figure 4.10: Effect of temperature at the same shock pressure using a heat treated BN-C starting material.

This points to instability of the present BN-C material at higher temperatures since the shock temperatures in this range are slightly above 2000°C . Therefore there exists a threshold stability temperature for the present BN-C material. This is also supported by the fact that at much higher densities $\geq 5.5\text{gcm}^{-3}$ (lower shock temperatures) no phase changes were observed despite the values in the shock pressure. An improved crystallisation behaviour was observed in these samples in

comparison to the starting material. The *101* peak progressively becomes more symmetrical with increasing pressure at lower temperature (Figure 4.10).

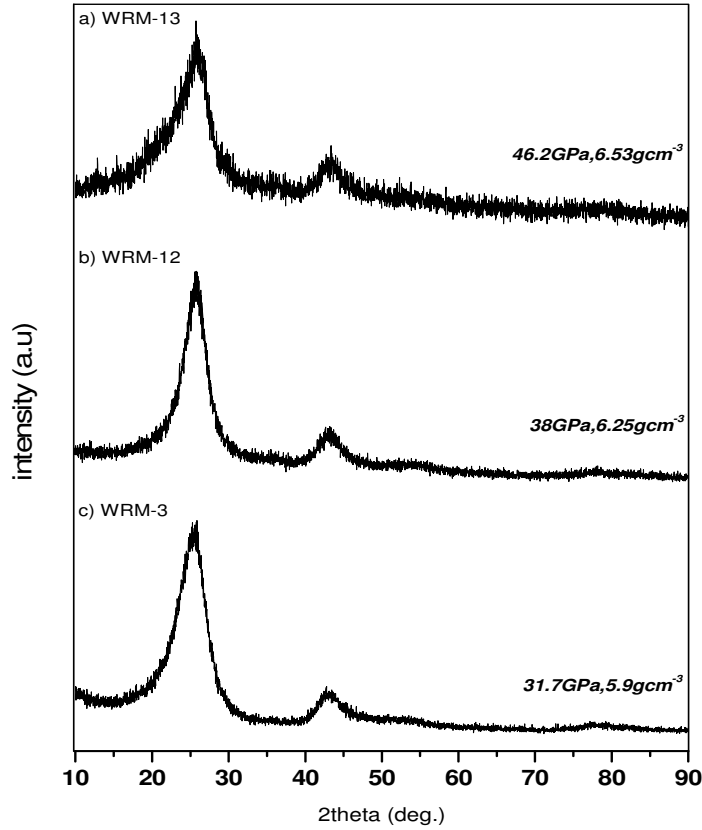


Figure 4.11: Effect of Pressure increase at almost constant shock-temperature values using a heat-treated BN-C starting material.

However no cubic phases were observed in the present study, in previous reports temperatures in excess of 2500°C were used which proved to be too high for the present BN-C material ^(99,105,131).

In another set of experiments utilising explosives (column method) SCE-1 to SCE-4, it was observed that SCE-1 & 2 experienced substantial decomposition.

SCE-1 has the lowest starting density (highest shock temperature) hence the relatively greater and sharper boron carbide peak observed.

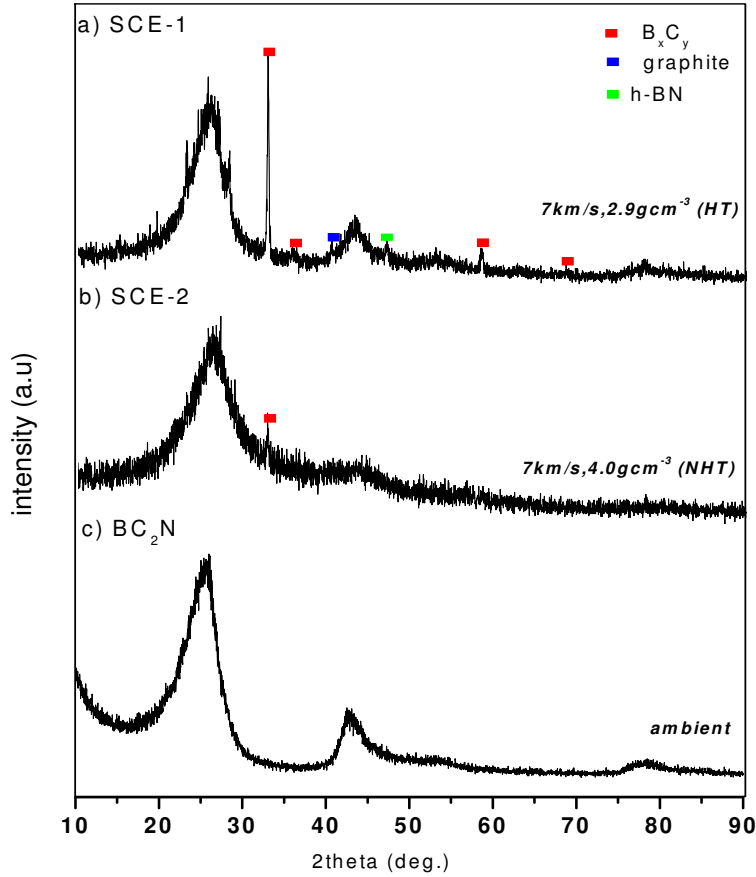


Figure 4.12: XRD patterns of the samples shocked with the column type method in comparison with the starting BN-C material.

For comparison an h-BN powder was shock compressed at 38GPa and ~2000°C and this led to the formation of wurtzite type BN. The line broadening is due to the small crystallite size obtained after shock compression. In another set of experiments h-BN and graphite powder milled for 50hrs was shock compressed at the same conditions. This resulted in a high pressure w-BN and graphite.

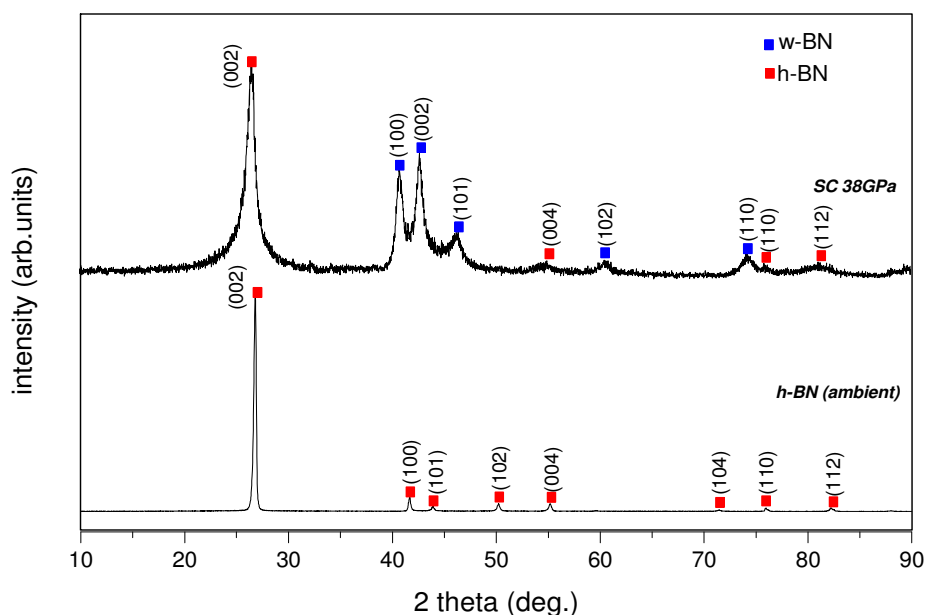


Figure 4.13: X-ray diffraction of h-BN shock compressed at 38GPa using the propellant gun method.

4.3 Static High Pressure High Temperature Results

4.3.1 Results on the HP/HT Studies in the Belt Press

A static high pressure study on the behaviour of the BN-C ceramic at pressures lower than the theoretical transition pressure were done with an aim of observing the low pressure phase characteristics. X-ray diffraction clearly reveals decomposition at temperatures of 2000°C and 3000°C (Figure 4.14). More pronounced decomposition occurs at the higher temperature (3000°C), this could imply existence of a threshold stability temperature. At 2000°C there is no splitting of the (002) peak however the appearance of a (100) h-BN peak at higher 2 theta values shows commencement of phase separation. This means that at

temperatures of 2000°C and above and 2GPa pressure the thermodynamically more stable low pressure phases in the B/C/N system are graphite and h-BN. A comparison of the lattice parameter d-spacing values at the conditions studied shows a trend towards a decrease in the d-value of the BC₂N with increasing temperature. The heat treated BC_{1.97}N starting material has a slightly larger d₀₀₂ value (0.343(7) nm) compared to the expected theoretical (0.343(5) nm) for a t-BC₂N (t-C (0.344(3) nm) and t-BN (0.343(2) nm)).⁽⁷¹⁾ Heat treatment at 2GPa and 2000°C led to partial decomposition into graphite and h-BN with the 002 peak showing no splitting.

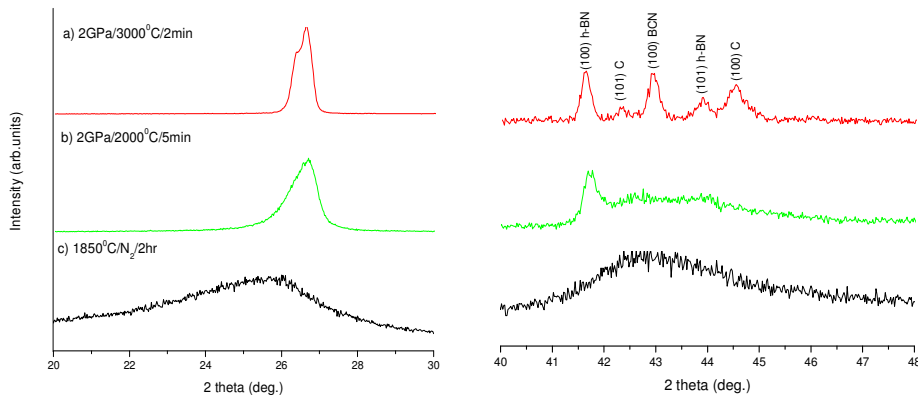


Figure 4.14: X-ray diffraction patterns of the materials treated in the belt press a) and b) in comparison with the starting material c).

4.4 Laser Heated-Diamond Anvil Cell Results

The results presented below are for the sample successfully synthesised at 25.8GPa and 1800°C using a laser-heated diamond anvil cell (LH-DAC). Synthesis at temperatures of 2000°C and above were not successful (anvils broke

at temperatures of 2000°C and above) thus no results are available for the experiments. No phase transformations were observed at 15GPa and 20GPa and 1800°C laser heating.

There is a clear indication of phase transformation from the XRD results obtained (Figure 4.15). Evolution of the 111 diffraction peak with a 2θ value of 19.72° and an average d spacing value of $0.207(8) \pm 0.003$ nm was obtained from an average of 3-separate readings. Additional peaks with 2θ values of 17.15° and d -spacing of $0.237(7) \pm 0.010$ nm and 24.09° with a d -spacing of $1.703(2)$ nm were also observed. The associated values of these peaks do not exactly match those of the graphitic BN-C phases. However owing to the HPHT conditions these peaks can be assumed to correspond to compressed graphitic phases 100 ($0.215(1)$ nm) and 004 ($0.167(1)$ nm) respectively. The whole XRD pattern could not be obtained owing to the small size of the sample and the large beam diameter obtainable from the RIGAKU X-ray diffractometer.

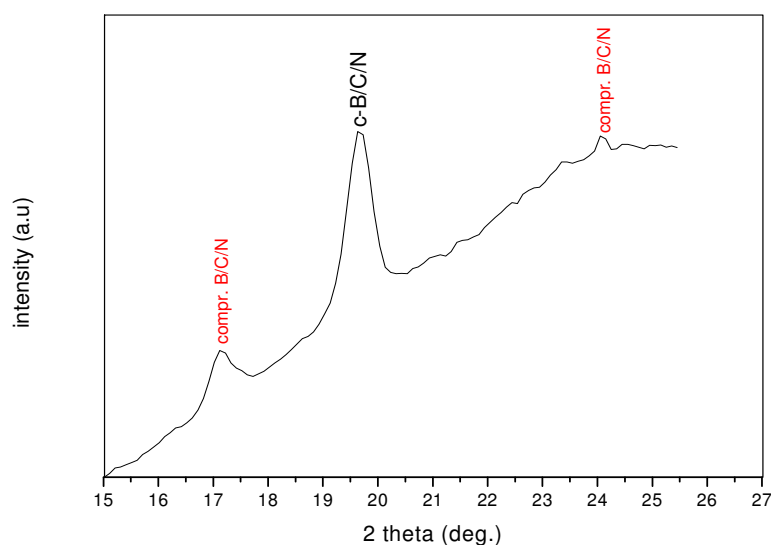


Figure 4.15: X-ray diffraction pattern of the sample obtained in the LH-DAC at 25.8GPa and 1800°C laser heating. The peaks labelled (compr.BN-C) may be due to compressed BN-C starting material and c-BN-C is the (111) cubic phase peak.

A further investigation by Raman spectroscopy revealed a characteristic broad band which was consistently observed at various spots of the sample occurring in the frequency range of 1100-1350 cm^{-1} . A distinguishable small sharp peak was observed at a wavenumber of about 1270 cm^{-1} . The spectrum has an additional peak coinciding with the low pressure phase G-band. This could be a result of incomplete transformation. The crystals were found to degrade upon irradiation with Ar^+ laser at higher power outputs (500mW). Thus the measurements were successfully taken at a power output of 24mW with no degradation.

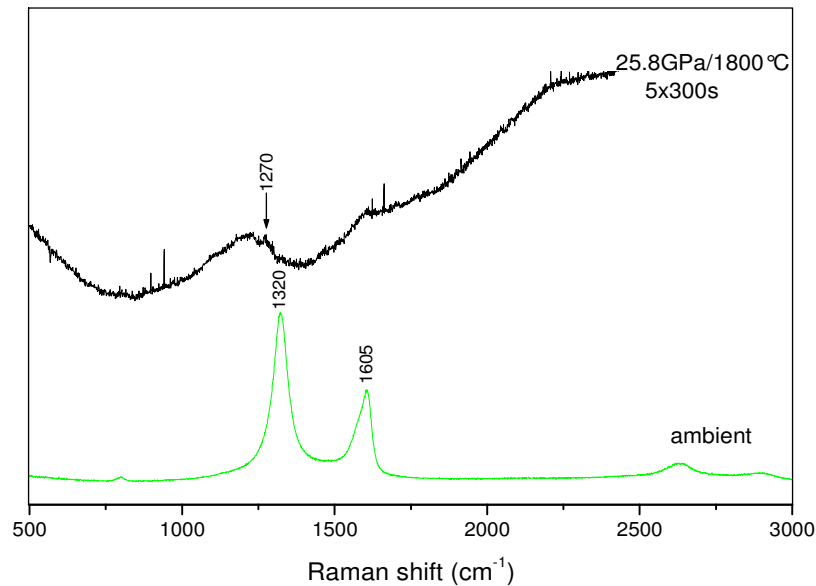


Figure 4.16: Raman Spectrum of the LH-DAC sample obtained at 2.8GPa, 1800°C laser heating, in comparison to that of the starting t-BN-C material at ambient conditions.

The morphology and chemical composition of the LH-DAC sample were observed with SEM and EDX (Energy Dispersive X-ray) respectively. There is no specific crystalline morphology observed with the synthesised material with most particles consisting of irregular shapes as observed in Figure 4.17 below. However there is a marked difference from the starting materials morphology as seen earlier. The LH-DAC synthesised particles are more massive as compared to the thin plate-like particles observed for the starting materials. There is a mixture of large and small particles ranging in size from 5-20 μm . The magnified image shows that the larger particles are in fact made up of smaller particles. EDX results reflect a reasonable consistence in the composition BC_2N although this is not accurate for (wt%) light metal determination.

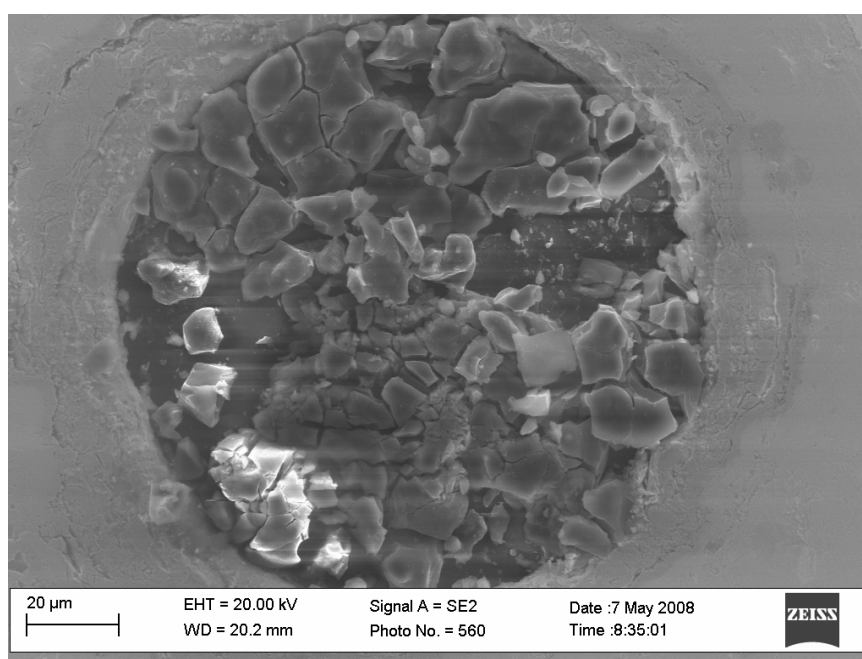


Figure 4.17: SEM micrograph of LH-DAC sample obtained at 25.8GPa, 1800°C laser heating. The particles are contained in a Re gasket hole.

In view of the above, partial transformation of the t-BN-C was observed under the present conditions. This could be a result of poor sample heat absorption also taking into consideration the short heating durations in such experiments. However the conditions used (25.8GPa, 1800⁰C) were found suitable for obtaining the cubic phase provided heat absorption is unlimited.

4.5 Results of HP/HT Materials Synthesised in the Multi Anvil Press

The results of the high pressure synthesised materials are summarised in Table 4.5 below. The present results were compared with results obtained in previous referenced studies. In the present study a well sintered black disc of size about 1.8mm in diameter and 1.2 mm in height was obtained for sample Z608 as shown in Figure 4.18 below. Sample S4306 consisted of black aggregated particles of size ca.200µm in size. No phase transformations were observed for Samples S4294 and S4311 which were synthesised at 1500°C and room temperature respectively. Sample S4295 however was partially transformed and the final product still contained a small quantity of compressed starting material.

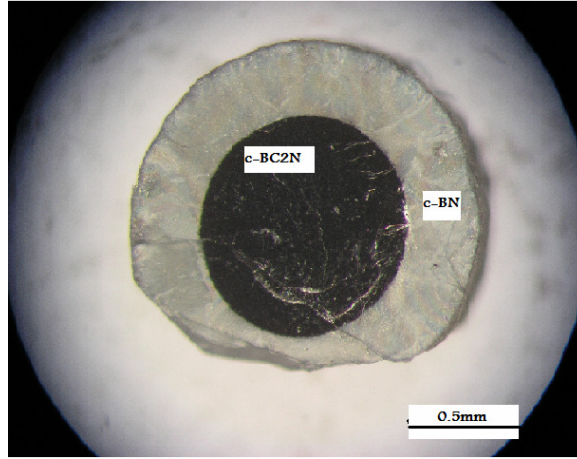


Figure 4.18: Optical micrograph of sample Z608 enclosed in the c-BN capsule.

Table 4.5: Summary of synthesis HP/HT conditions, structure of final product and refined lattice parameters (*GSAS Software Package*)⁽¹³³⁾ of the present BN-C materials in comparison to previously obtained BN-C materials.

Sample	P/GPa	T/°C	holding time/s	Product	Lattice parameter/Å
Z608	20	2000	60	c-BN-C+NanoD	3.555(2)
S4294	20	1500	120	t-BN-C	-
S4295	20	1920	300	t-BN-C+c-BC ₂ N	-
S4306	20	2000	30	c-BN-C	3.596(6)
S4311	20	25	7200	t-BN-C	-
Other Experimentally obtained c-BC₂N materials					
Author	Starting material	P,T,t conds	method	Product /XRD	Lattice Parameter/Å
Zhao ^[11]	milled BN/C ₂	20GPa/1927°C/5mins	MA	c-BC ₂ N	3.595(7)
Solozhenko ^[16]	gr-BC ₂ N	25GPa/1820°C/30mins	MA	c-B _{0.4} C _{1.1} N _{0.5}	3.642(2)
Komatsu ^[93]	gr-BC ₂ N	50GPa/3227°C/1μs	SC	c-BC _{2.5} N	3.605
Knittle ^[7]	milled BN/C ₂	30GPa/1727°C/5-10mi	LHDAC	c-(BN) _{0.67} C _{0.33}	3.613(3)
Nakano ^[9]	gr-BC ₂ N	7.7GPa/2300°C/15mins	BP	c-BN,Dia.,c-B/C/N mixture	-
Filonenko ^[91]	C ₃ N ₄ /B (HT)	8GPa/1500°C/5mins	TP	c-BC _{0.47} N _{0.85} + B ₁₃ C ₂ (ratio 4:1)	3.645

MA: Multi-Anvil; SC: Shock Compression; LHDAC: Laser Heated Diamond Anvil Cell; BP: Belt Press; TP: Toroidal Press; Dia: diamond; NanoD: nanodiamond-like material; HT: heat treated; gr: graphitic

4.5.1 Synchrotron Diffraction Results

The XRD profiles of the transformed material confirm the presence of a monophasic zinc-blende type structure with (111), (200), (220), and (311) and (400) reflections (Figure 4.20). Furthermore, two reflections at high d-values (0.219(7) nm and 0.188(5) nm) marked ss were observed in Figure 4.19 below. These reflections were observed from S4306 profile only. It is interesting to note that the lattice parameter for Z608 obtained by Rietveld refinement (*GSAS software package*)⁽¹³⁹⁾ is smaller than expected for an ideal BN-C solid solution (Table 4.5). This result could be due to a negative deviation from Vegard's Law with differences in the lattice constants b and c (up to 1% deviation permissible) as suggested by theoretical models^(21, 73, 98, 138). However it must be noted that the obtained results are a clear representation of a solid solution owing to the high resolution of the synchrotron beams used which can easily help identify a mixture of diamond and c-BN.

A (200) reflex was observed in all the transformed samples, which points to an $F\bar{4}3m$ space group (Figure 4.19). The XRD profile for sample S4306 shows greater broadening than sample Z608.

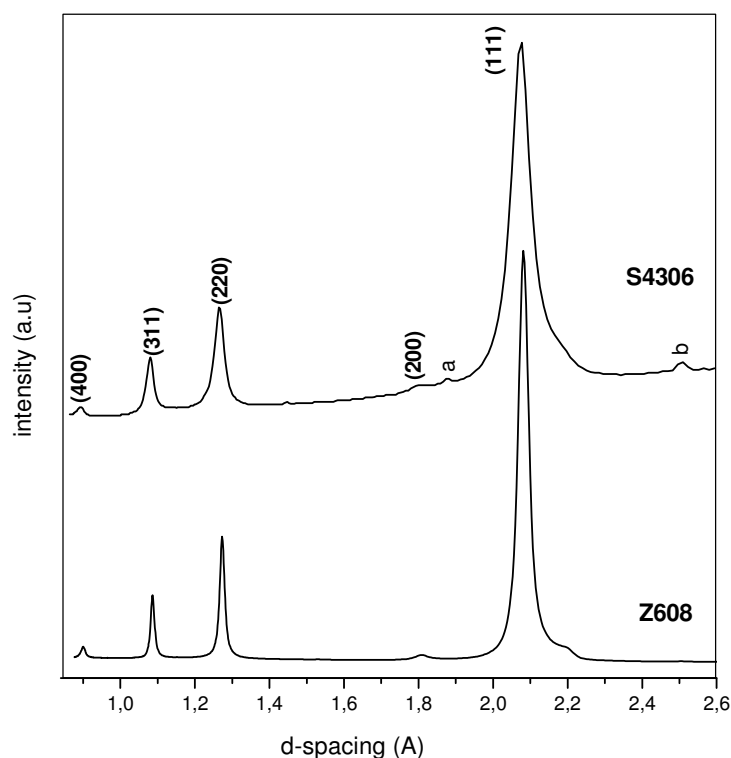


Figure 4.19: XRD patterns of samples S4306 (top) and Z608 (bottom) taken with monochromatic synchrotron radiation. Sample S4306 shows appreciable broadening owing to the smaller crystallite size (*ca.* 5-10 nm) in comparison to Z608 (*ca.* 50-100 nm) as analysed by TEM studies. Two minor reflexes labelled a and b do not correspond to the cubic peaks and could signify loss in the structure factor F .

Furthermore, the observed XRD profile for sample S4295 clearly highlights existence of the (002) starting material reflex signifying incomplete transformation.

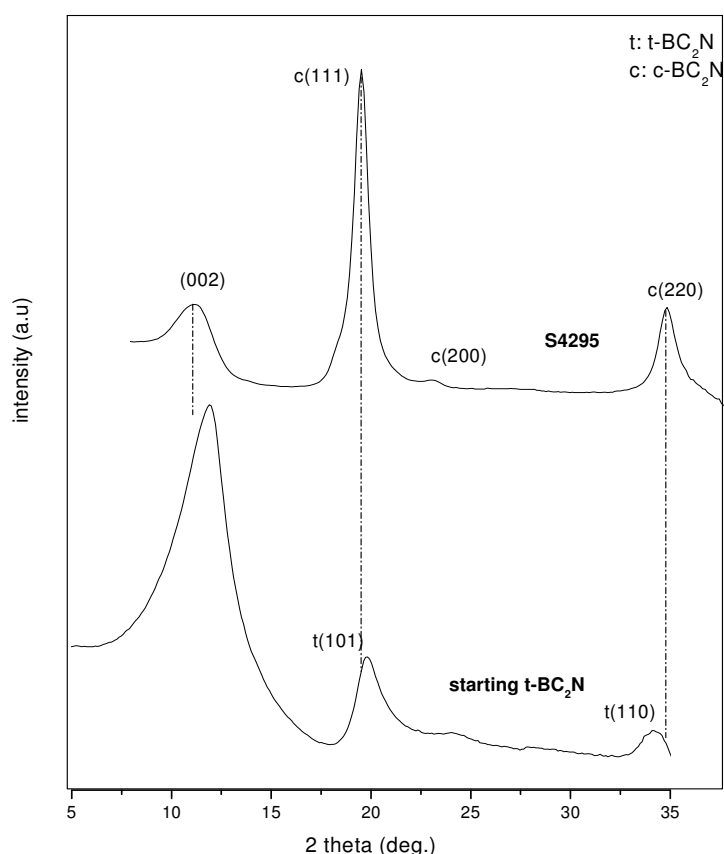


Figure 4.20: XRD patterns of sample S4295 (top) synthesised at 20 GPa, 1920 °C and 300 s holding time in comparison to the starting material (bottom).

4.5.2 Rietveld Refinement Results

Lattice parameter determination of the samples S4306 and Z608 were successfully carried out using the GSAS Software Package.⁽¹³⁶⁾ The refinement structure model consists of boron and nitrogen atoms occupying different lattice sites (as in c-BN) i.e. (000) and ($\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$) with carbon partially substituting for either. This is similar to the structure described by Filonenko *et al.*⁽⁹¹⁾ Effectively, this gives rise to embedded C-C and B-N layers half a lattice constant apart in the c-BC₂N lattice as suggested by theoretical modelling studies^(21,98,138). Table 4.6 below shows the atomic position coordinates used in the refinement.

Atom	x	y	z	$U_{\text{iso}}, \text{\AA}^2$
B	0	0	0	0.00100
N	0.25	0.25	0.25	0.02317
C1	0	0	0	0.04988
C2	0.25	0.25	0.25	0.00100

Table 4.6: Atomic position coordinates, site occupancies, and isotropic thermal parameters (U_{iso}) in the c-BN-C structure used for refinement.

The lattice parameter of Z608 (0.3555(2) nm) is smaller than expected for ideal mixing (0.3583 nm). This could be a result of lattice distortion owing to residual stresses imposed by the presence of B-N and C-C type bonds in the same structure or due to the decomposition experienced by the sample. On the other hand, the refined lattice parameter of S4306 (0.3596(6) nm) is within the expected range and satisfies Vegard's Law. Thus the conditions used for synthesising sample S4306 are most appropriate for obtaining a pure cubic BN-C from the polymer derived ceramic.

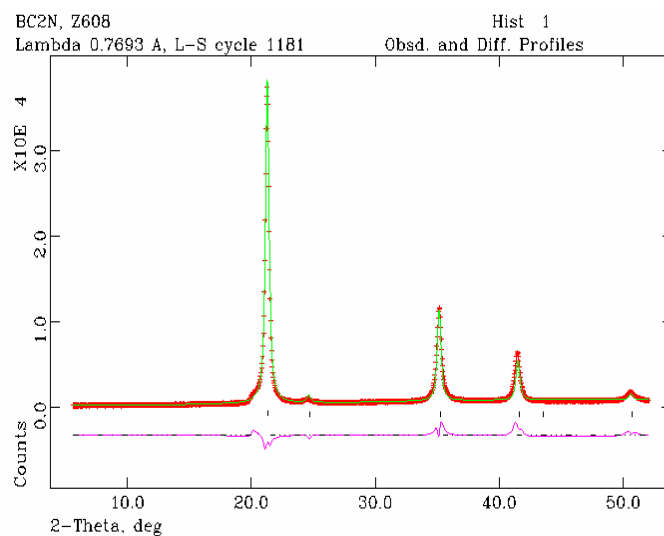


Figure 4.21: Rietveld refinement profile of sample Z608, the green profile represents the calculated profile red experimental profile and the pink is the difference plot of the two profiles, the vertical marks show the positions allowed reflections for the BC₂N phase (calculated).

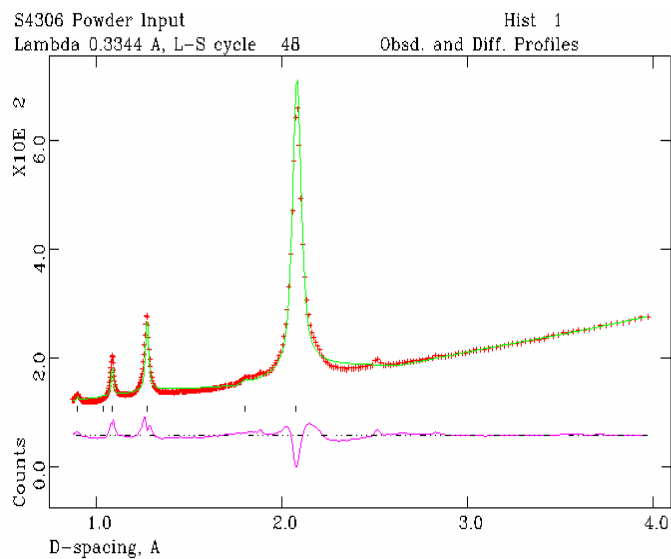


Figure 4.22: Rietveld refinement profile of sample S4306, the green profile represents the calculated profile red experimental profile and the pink is the difference plot of the two profiles, the vertical marks show the positions allowed reflections for the BC₂N phase.

4.5.3 Raman Spectroscopy Results

Raman excitation has been used as a finger printing technique for diamond and c-BN materials owing to the distinct optical modes characteristic of the bonding environments of the compounds. However for the c-BC₂N materials varying optical modes would be expected depending on the distribution of B, C and N in the unit cell. It is apparent that there is no comprehensive theoretical model relating the experimentally observed Raman bands with the structures and atomic distributions of the samples.⁽¹³⁹⁾ In the present study we observed two types of

spectra using Ar ion ($\lambda = 514.5$ nm) laser excitation at room temperature. The spectrum from sample Z608 (Figure 4.23) shows a stepped profile with a sharp band at about 1301 cm^{-1} , a small band at 1047 cm^{-1} , and a broad band centred at 497 cm^{-1} . No features were observed beyond 2000 cm^{-1} wave numbers. On the other hand samples S4295 and S4306 (Figure 4.24) show broad bands at 1446 cm^{-1} , a small band at 683 cm^{-1} and a broad band centred at about 405 cm^{-1} .

There is a significant difference between the present Raman results and the data published in previous studies ^(9, 139). However the observed spectra resemble those of boron-doped diamond samples as observed in references ⁽¹⁴²⁻¹⁴³⁾. A comparison was made with the spectra of nanocrystalline diamond and aggregated boron nitride nanocrystallites (ABNNC) as found in referenced literature ⁽¹⁴⁴⁻¹⁴⁵⁾. It is interesting to note that there is a general broadening, shifting and presence of additional Raman peaks associated with nanocrystalline materials as observed for ABNNC and nanocrystalline diamond ⁽¹⁴⁴⁻¹⁴⁵⁾ in comparison to those of c-BN and diamond respectively. Thus the present Raman profiles are a true representation of the present nanocrystalline c-BN-C materials. The exact significance of such a unique profile is not well known and it is assumed to be a result of the fine structure of the present materials as observed in ABNNC and nanocrystalline diamond materials ⁽¹⁴⁴⁻¹⁴⁵⁾. This finding has a practical implication for the present BN-C materials regarding for instance its semiconducting properties. In particular the electronic properties as a result of the doping effect imposed by boron and nitrogen in diamond. This effect has been observed for semiconducting boron

doped diamond materials synthesised under high pressure and high temperatures as explained in the referenced literature.⁽¹⁴²⁻¹⁴³⁾

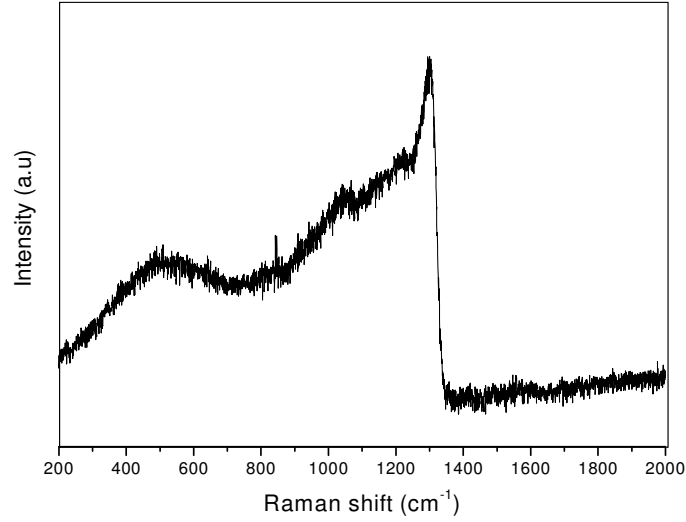


Figure 4.23: Raman spectrum of the BN-C material (Z608) measured with Ar ion laser excitation ($\lambda = 514.5$ nm).

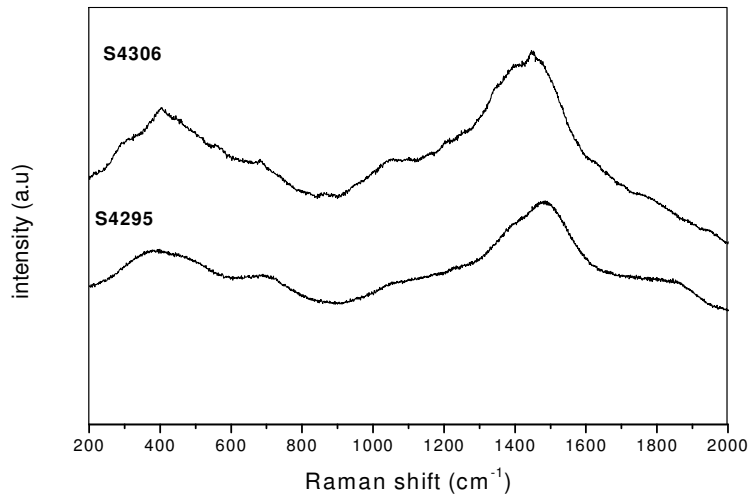


Figure 4.24: Raman spectrum of the BN-C phases S4306 (top) and S4295 (bottom) measured with Ar ion laser excitation ($\lambda = 514.5$ nm).

4.5.4 Temperature dependence of resistivity of sample Z608

The observed resistivity curve for sample Z608 shows a typical amorphous type semiconducting behaviour. According to the resistance vs. temperature measurements in the interval from room temperature down to 7K, the sample shows a semiconducting behaviour and the resistivity (ρ) decreases with increasing temperature.

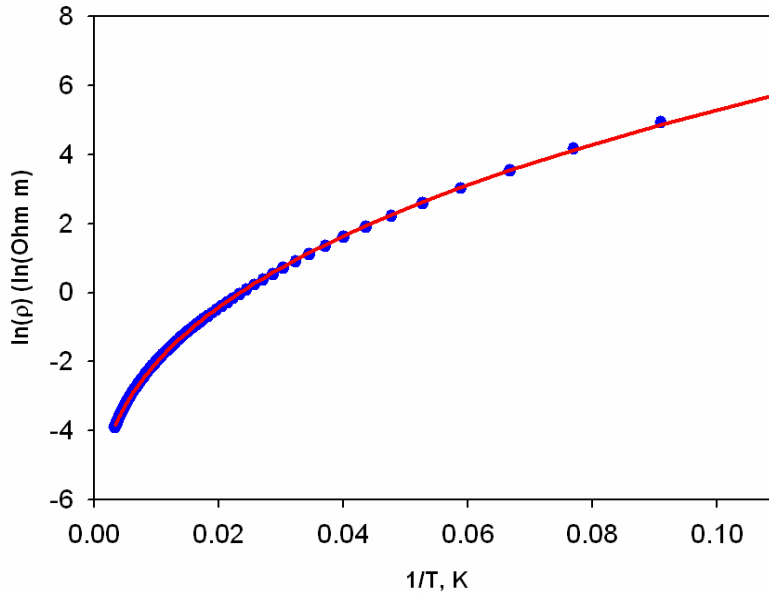


Figure 4.25: Plot of the temperature dependence of the resistivity of sample Z608.

However, the $\ln(\rho)$ vs. $1/T$ plot (Figure 4.25) does not show a straight line as expected for crystalline semiconductors, for which experimental data can be fitted according to the law described by equation [4.7] as described in literature. ⁽¹⁴⁶⁾

$$\rho(T) = \rho_0 * \exp\left[\left(\frac{T_0}{T}\right)^p\right] \quad [4.7]$$

$p = 1$.

The same equation, where the value of $p \neq 1$, is applied to amorphous semiconductors. For bulk materials $p = 1/4$ and $p = 1/3$ for two-dimensional amorphous semiconductors (thin films).⁽¹⁴⁷⁾ The fitting of the experimental data according to equation [4.7] gave $p = 0.374$ which is close to the value $p = 0.333$ predicted for two-dimensional amorphous semiconductors. However, considering a low temperature range (between 30K and 7K) separately and using a fixed value of $p = 0.25$ expected for the bulk amorphous material, the quality of the fit is not so different to that with $p = 0.333$.

4.5.5 TEM/EELS Results of HP BN-C phases

4.5.5.1 Sample Z608 TEM Results

In accordance with TEM observations the present cubic phases consists of aggregated nanocrystallites. Sample Z608 possesses relatively large nanocrystallites with up to 100 nm in size as confirmed by the dark field (DF) TEM micrograph below (Figure 4.26).

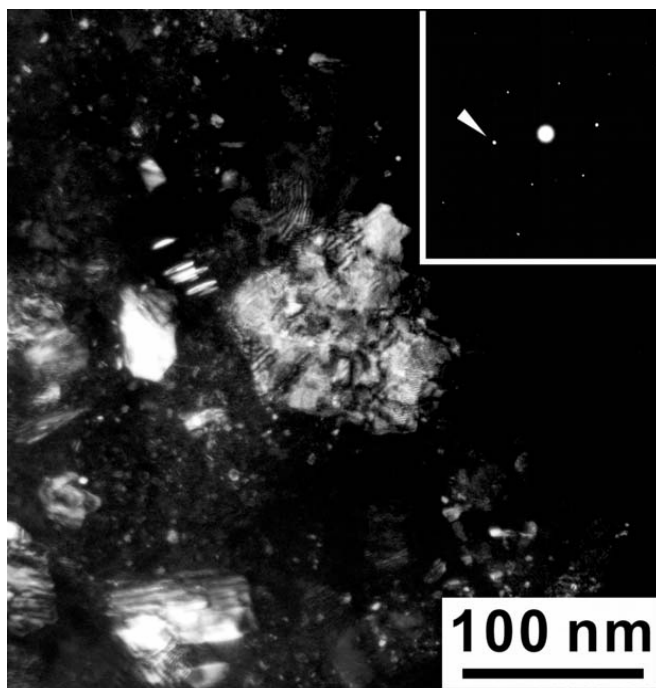


Figure 4.26: Dark Field TEM micrograph of sample Z608 sintered at 20GPa and 2000°C. The arrowed pattern was taken from the big crystal in the middle part using the diamond $\langle 110 \rangle$ zone axis ⁽²⁾.

Selected area electron diffraction (SAED) confirms the existence of a cubic type structure exhibiting 111, 220 and 311 rings with numerous discrete spots (Figure 4.27). This result is consistent with that observed in the XRD analysis. A lattice parameter measurement using diffraction spots resulted in values of (0.357 nm and 0.355 nm) which are smaller than the expected value for ideal mixing. However it must be noted that X-ray diffraction gives a more plausible lattice parameter value which was measured as 0.3555(2) nm with refinement by GSAS Software package.⁽¹³⁶⁾ Furthermore, the XRD profile shows sharp and symmetrical 111, 200, 220, 311 and 400 reflexes ruling out the existence of any other phases.

² Zone axis is parallel (or nearly parallel) to the electron beam.

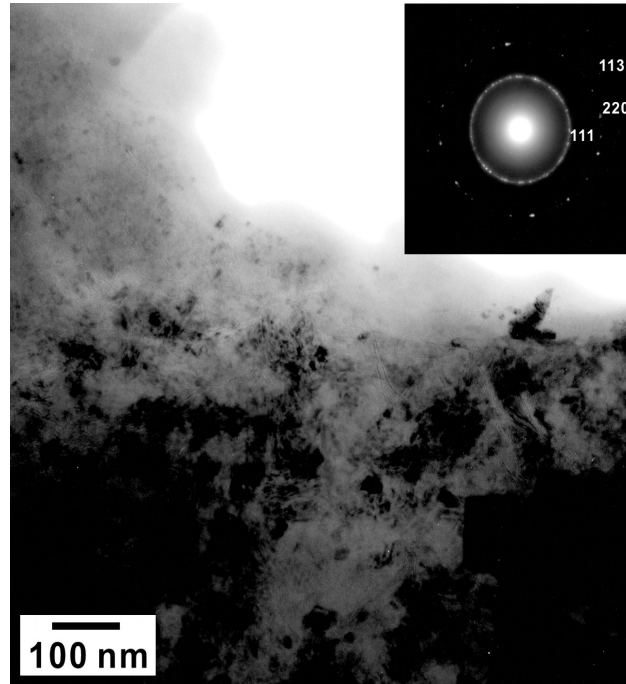


Figure 4.27: Selected Area Electron Diffraction (SAED) pattern of sample Z608.

A further study reveals that the diffraction pattern obtained from a specific crystal in Figure 4.26 above is indeed not indexed by a diamond, BN or 2H-BCN (a high pressure BN-C hexagonal modification analogous to lonsdaleite in diamond) structures. This further testifies to the existence of a structural distortion in the present BN-C material (Z608). Furthermore, interplanar angles as obtained from the arrowed spot and shown in Figure 4.26 were compared to those of diamond and 2H-BCN modification. The angle ρ between planes with reflections $h_1k_1l_1$ and $h_2k_2l_2$ was obtained from the equation 4.8 below where d_{hkl} represents the interplanar distance.⁽¹⁴⁸⁾

$$\cos \rho = \frac{d_{h_1 k_1 l_1} \cdot d_{h_2 k_2 l_2}}{|d_{h_1 k_1 l_1}| |d_{h_2 k_2 l_2}|} \quad [4.8]$$

this can be simplified to;

$$\cos \rho = \frac{h_1 h_2 + k_1 k_2 + l_1 l_2}{\sqrt{(h_1^2 + k_1^2 + l_1^2)(h_2^2 + k_2^2 + l_2^2)}} \quad [4.9]$$

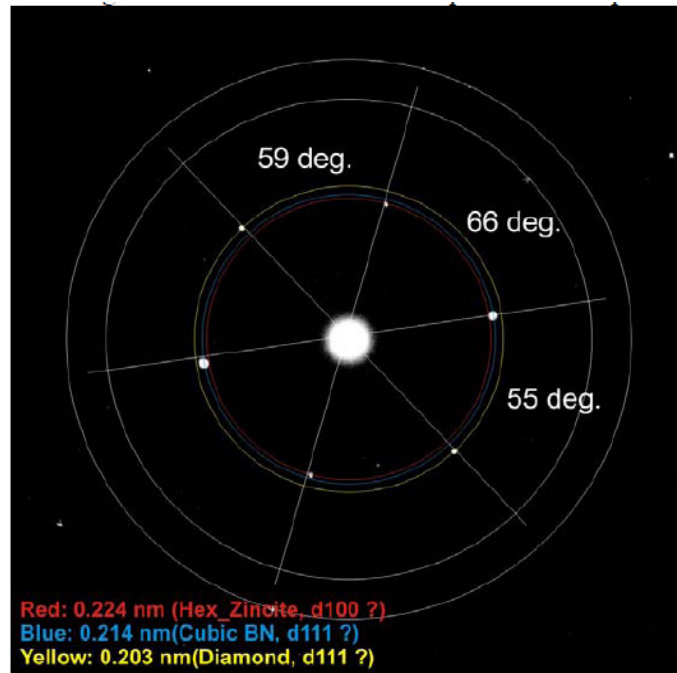


Figure 4.28: Diffraction pattern of arrowed part (insert in Figure 4.26) in comparison with the (111) planes of diamond and c-BN and (100) plane of hexagonal phase.

The spots of the present material (Z608) do not coincide with the expected diffraction spots of diamond-BN or hexagonal phase. Thus it is not indexed to any of these structures.

the fact that the interplanar angles for purely cubic phases should be the same as shown by the equations above. The anomaly observed clearly highlights a distortion in the present material. However it will be later shown by EELS analysis that the materials are actually sp^3 hybridised.

4.5.5.2 Electron Energy-Loss Spectroscopy (EELS) Results for Z608

The selected area EELS spectrum of Z608 (Figure 4.31) contains a complete B-C-N ternary system with B-K (196.9eV), C-K (292.7eV) and N-K (407.5eV) edges appearing concurrently with sp^3 type bonding only. The peaks are distinguishable from those of starting material which are characterised by π^* and σ^* transitions. A quantitative analysis of the spectrum gave an atomic composition of $B_{0.38}C_{1.00}N_{0.43}$ which is close to the ideal BC_2N stoichiometry. The C-K edge however contains a small portion covering the sp^2 region (285eV). HRTEM revealed the presence of a diamond like material with a darker contrast as shown in Figure 4.32 below.

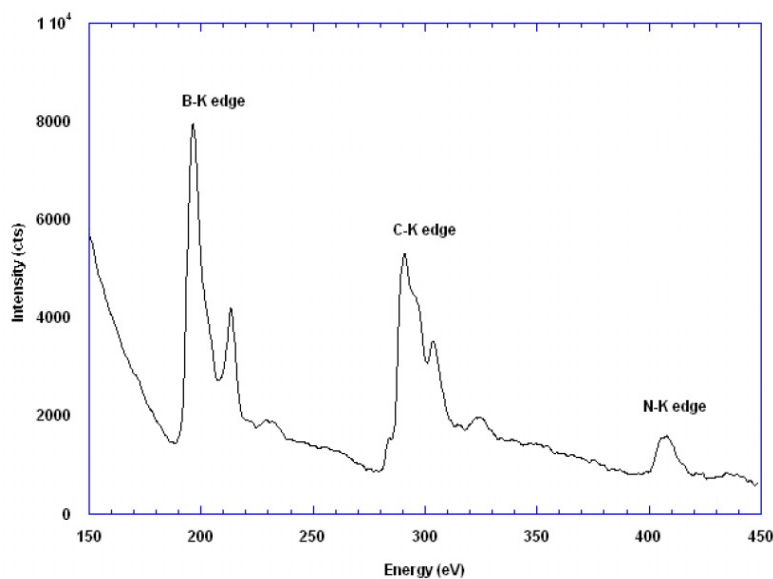


Figure 4.31: Electron Energy-Loss Spectrum (EELS) of sample Z608 showing the B-K, C-K and N-K ionisation energies.

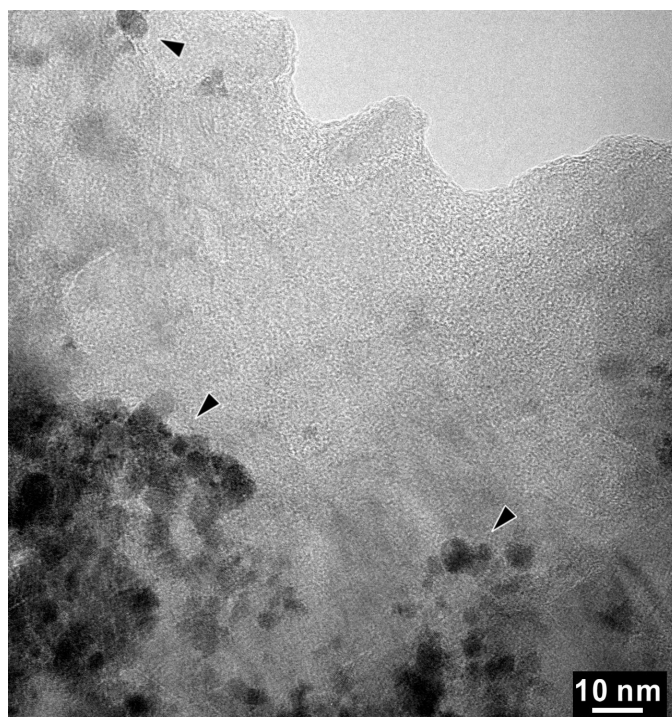


Figure 4.32: High Resolution TEM (HR-TEM) of a selected area of the BN-C domain of sample Z608. The arrowed regions with darker contrast were found to contain only C-K edges in EELS.

Furthermore, an EELS analysis of the diamond-like material showed a broad peak in the region 280-300eV. This result indicates the presence of a mixture of sp^2 and sp^3 hybridised carbon. In view of this, it is evident that there is slight decomposition of Z608 under the present conditions.

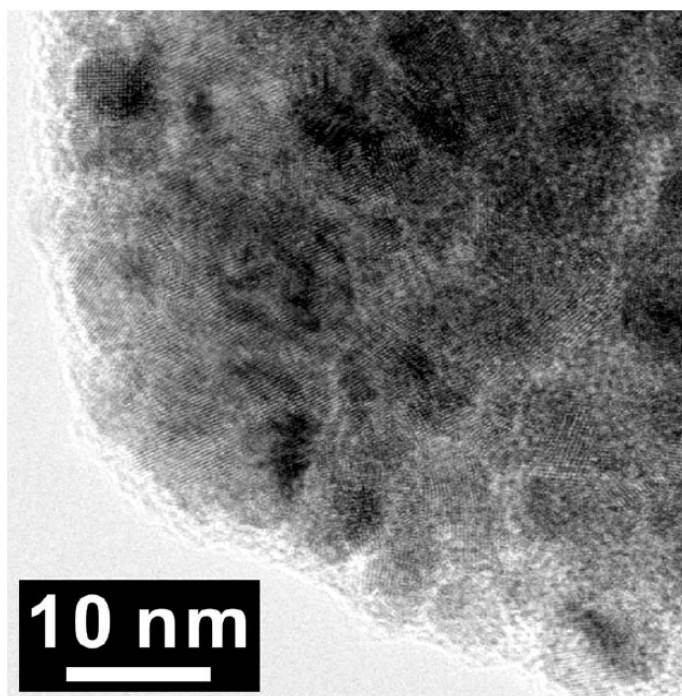


Figure 4.33: HRTEM of the arrowed region top left (Fig.4.32) showing the diamond nano-crystals (nanoD).

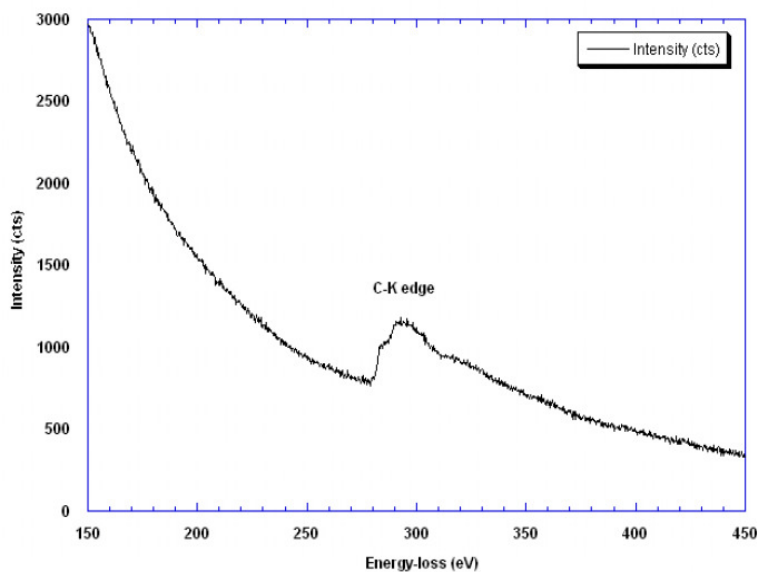


Figure 4.34: Electron Energy-Loss Spectrum collected from the arrowed region shown above (Fig.4.33).

4.5.5.3 Sample S4306 TEM Results

The smaller crystallite size possessed by sample S4306 clearly highlights the effect of isothermal holding time on the growth rate of BN-C crystallites. Bright field (BF) and dark field (DF) imaging of the S4306 sample show relatively fine aggregated polycrystalline materials with approximate sizes of 5-10 nm (Figure 4.35). An HRTEM (High Resolution TEM) of the arrowed spot characterised by an FFT (fast fourier transformation) pattern shows discrete spots of approximately 0.2 nm in diameter further confirming the existence of extremely fine crystallites (Figure 4.36). Single crystal diffraction with such extremely small crystallites could not be obtained.

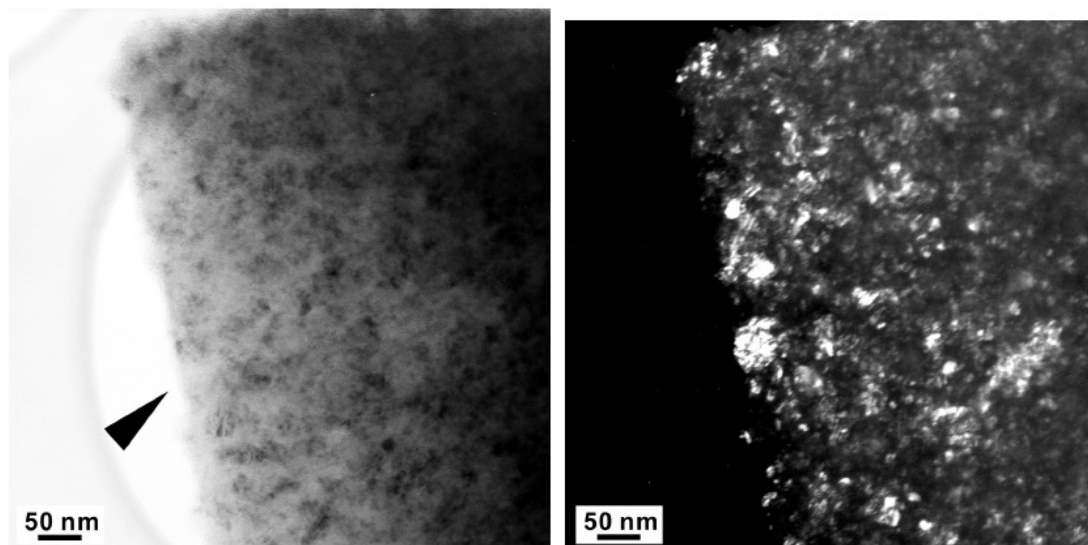


Figure 4.35: Bright field (BF) (left) and dark field (DF-right) images of sample S4306 showing nano-sized polycrystalline material.

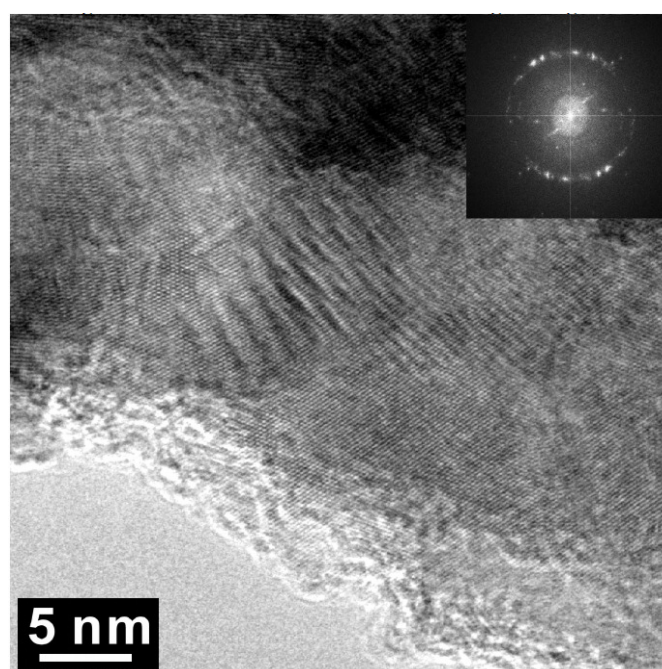


Figure 4.36: High Resolution-TEM micrograph of the arrowed region above. The insert is an FFT (fast fourier transform) pattern showing the approximate size of crystallites.

4.5.5.4 Electron Energy-Loss Spectroscopy (EELS) Results for S4306

The EELS spectrum from a selected area confirms the existence of a ternary BN-C phase with sp^3 hybridised bonds. The B-K (196.1eV), C-K (291.4eV) and N-K (407.7eV) edges are comparable to those of previously claimed c-BC₂N materials with appreciable broadening differentiating them from those of diamond and c-BN.⁽¹⁴⁹⁾ The quantitative analysis of the spectrum gave a nominal composition of B_{0.41}C_{1.00}N_{0.61} which is quite close to that of the ideal BC₂N stoichiometry.

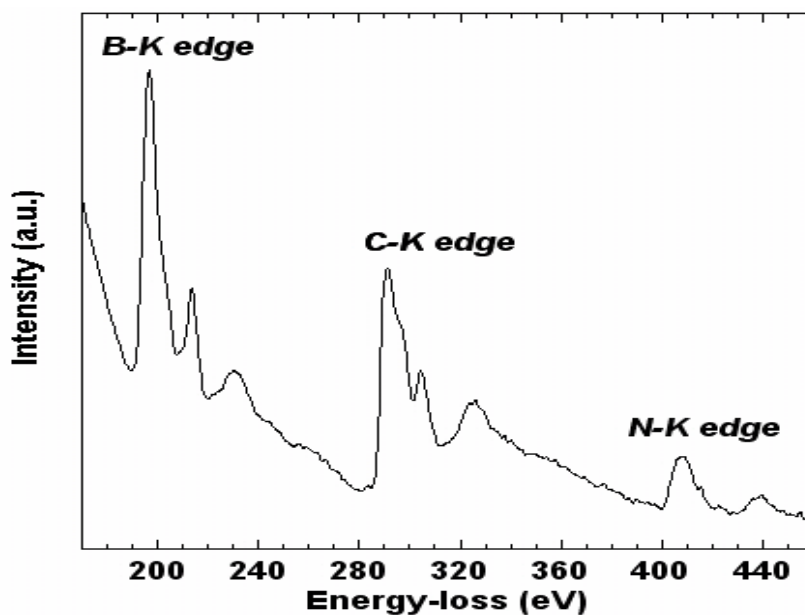


Figure 4.37: Electron Energy-Loss Spectrum (EELS) of S4306 showing the B-K, C-K and N-K ionisation energies.

Chapter 5: Discussion

5.1 Interpretation of Structure and Properties of the t-BN-C Ceramics

The t-BN-C ceramics were found to possess a turbostratic type structure which may be considered as an intermediate form between the amorphous and the crystalline states.⁽¹⁵⁰⁾ The stacking of layers in such structures is less periodic, in which there is random translation about the c-axis and sheets may be tilted or rotated about the normal. This lack of sheet-to-sheet registry accounts for the absence of general hkl or $h0l$ reflections in the XRD spectra of turbostratic materials.⁽¹⁵⁰⁾ The as-pyrolysed BN-C shows a typical amorphous type pattern with broad peaks and low intensities. Heat-treatment to higher temperatures resulted in reduced peak widths and increased intensities; this obviously resulted in a change in the interlayer spacing d_{002} . Thus it is envisaged that there is some dimensional change, however the overall structure remains turbostratic during heat treatment in the temperature range (1450-1850°C).

Owing to the presence of different bond types in BN-C materials it is apparent that there is competition between bond strength and structural stresses. This could lead to loss of packing density and 3D crystallinity.⁽⁷¹⁾ Thus the most stable structure would be one minimising structural stresses and favouring bond strength. Furthermore, annealing of the t-BN-C phase at higher temperatures leads to decomposition as observed in the static high pressure high temperature studies

where the t-BN-C phase started decomposing at a temperature of 2000°C and a pressure of 2GPa into graphite and h-BN. This implies that the low pressure phase is thermodynamically unstable and prone to decomposition into graphite and h-BN at temperatures of 2000°C or higher. This phenomenon has been observed in earlier studies.⁽⁷¹⁾ However B₄C has been found to be more stable in this temperature range under Ar atmosphere.⁽²⁵⁾

It is apparent that the structural properties of non-crystalline materials can not be well studied by X-ray diffraction alone. Spectroscopic studies do not rely on the crystallinity of materials thus they are most suitable for predicting structural properties of non-crystalline materials.⁽⁷⁹⁾ The Infrared (IR) spectra of BN-C compounds are closely linked to those of graphite and h-BN owing to the fact that most BN-C compounds are indeed made up of graphite and BN layers.⁽¹⁵¹⁾ Furthermore, it is possible to predict the general atomic arrangement of amorphous materials from the bonding nature as observed in spectroscopic studies.⁽⁷⁹⁾ Theoretical calculations show that the phonon modes for graphite and h-BN occur at wavenumbers of 1555cm⁻¹ and 1299cm⁻¹ respectively.⁽¹⁵¹⁾ The experimental data shows that the phonon modes for graphite and h-BN are 1600cm⁻¹ and 1366cm⁻¹ respectively as cited in reference.⁽¹⁵¹⁾ These phonon modes are doubly degenerate because of the threefold symmetry of both graphite and BN.⁽¹⁵¹⁾ In the case of BN-C materials a theoretical shear mode of g-BC₂N has been calculated to occur at 1394cm⁻¹ and an in-plane stretching mode at 1442cm⁻¹ both induced by splitting of the degenerate phonon modes at the Γ point

⁽³⁾ of h-BN or graphite respectively caused by lowered symmetry. This splitting has been found to be a good indication of the presence of g-BC₂N.⁽¹⁵¹⁾ These modes were predicted from a chemical structure composed of zig-zag arrays of C-C and B-N long chains.⁽¹⁵¹⁾ Thus the presence of only a single peak in this range indicates that the chemical structure of the present t-BN-C phase is not similar to the aforementioned zig-zag arrangement.

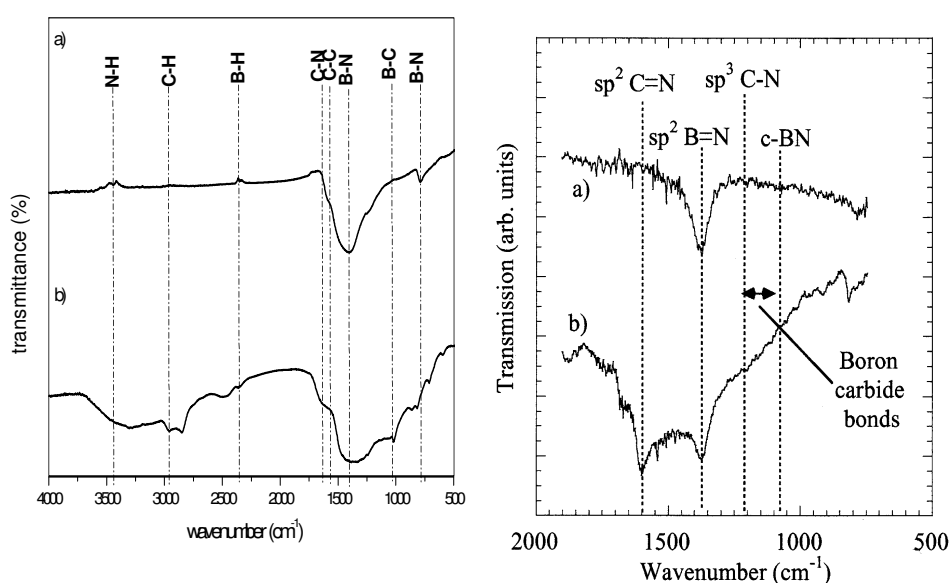


Figure 5.1: Fourier Transform Infrared spectrum of the t-BN-C starting material (a) corresponds to the heat treated sample and b) is the pyrolysed sample) in comparison with BN-C films deposited on various substrates as described in [152].

In the present study the t-BN-C was found to possess a spectrum similar to that of h-BN with slight shifting of the in-plane B-N stretching mode at 1406cm⁻¹ and an out of plane B-N bending mode at 791cm⁻¹. The absence of splitting of the degenerate modes as described by theoretical modellers signifies a deviation of

³ Γ point is defined as the centre of the Brillouin zone.

the present structure from the theoretically predicted one. A consideration of other spectroscopic studies would enable the prediction of present t-BN-C structure.

Raman spectroscopy has been found to be sensitive to the structure of C-based materials, hence its use as a diagnostic tool. The a- and c-axis, coherence lengths L_a and L_c and the d_{002} interplanar spacing all affect the Raman spectrum of graphitic materials.⁽¹⁵³⁾ It has been found that single crystal graphite has vibrational modes of the type $2E_{2g}$, $2B_{2g}$, E_{1u} and A_{2u} .⁽¹⁵³⁾ The $2E_{2g}$ modes are Raman active and occur at about 1582cm^{-1} and a low frequency scattering feature at 47cm^{-1} .⁽¹⁵³⁾ The E_{1u} (1568cm^{-1}) and A_{2u} (868cm^{-1}) are IR active and observable with IR reflectance. The B_{2g} modes are optically inactive.⁽¹⁵³⁾ Highly ordered pyrolytic graphite exhibits a sharp 1582cm^{-1} band between $1100\text{-}1700\text{cm}^{-1}$ (first order Raman region); also second order features are observable between $2400\text{-}3300\text{cm}^{-1}$.⁽¹⁵³⁾ A significant change has been found to occur for finite sized microcrystallites ($L_a < 100\text{nm}$) and with structures possessing a deviation from the ordered sp^2 hybridised graphitic structure such as glassy carbons (GC) and diamond-like-carbon (DLC). This is associated with the appearance of a band at about 1360cm^{-1} . The $1360/1582\text{cm}^{-1}$ intensity ratio has been found to increase with decreasing microcrystallite size. Thus the appearance of the 1360cm^{-1} band (referred to as D-band) is attributable to structural disorder on the one hand and presence of microcrystallites on the other. This is as a result of loss of packing density and loss in 3D crystallinity and in most cases such disordered materials are amorphous.⁽¹³³⁾ Raman spectrum of h-BN is associated with two E_{2g} modes at 52.5cm^{-1} and 1366cm^{-1} .⁽¹⁰⁷⁾ Clearly the Raman spectra of the present BN-C

materials were obtained in the vicinity of both pure h-BN and amorphous graphite. Hagio *et al* ⁽¹⁵³⁾ observed a widening of the 1582 band in graphite and a growth of the relative intensity of the 1360 band with increasing boron doping. An overlap of the two bands has been observed in BC₃ and BN-C materials. This has been attributed to boron substitution in the carbon lattice. ⁽¹⁵³⁾ In view of this, it is apparent that the as-pyrolysed BN-C in the present study shows the effect of boron doping in the carbon matrix. However the overlap is lost due to heat-treatment signifying separation of phases with the formation of a typical disordered graphitic spectrum. This can be attributed to graphitization of the BN-C leading to formation of an intimate mixture of disordered graphite and boron nitride. A consideration of the IR and Raman spectra is in support of this prediction.

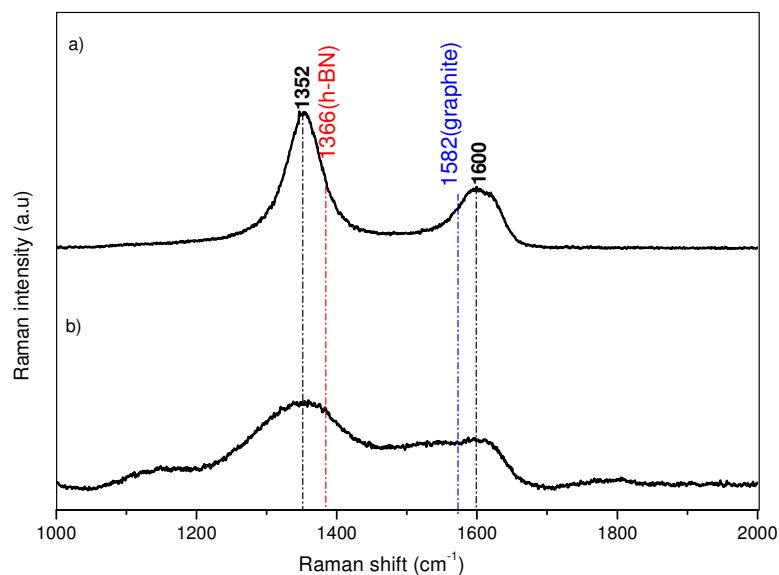


Figure 5.2: Raman spectra of the t-BN-C material in comparison to the graphite (gr.) and h-BN peak positions.

A further observation made in the X-ray photoemission spectra (XPS) confirms the aforementioned structural arrangement prediction. Clearly, the boron atoms are dominantly chemically bonded to the nitrogen atoms in a way similar to the ones in h-BN. The carbon atoms have been found to form only C-C type bonds similar to those in graphite. There is a general reduction in the spectra widths from the as-pyrolysed to the heat-treated samples. Effectively, separation is imminent at higher temperatures. These observations are in-line to what has been mentioned earlier using other spectroscopic techniques.

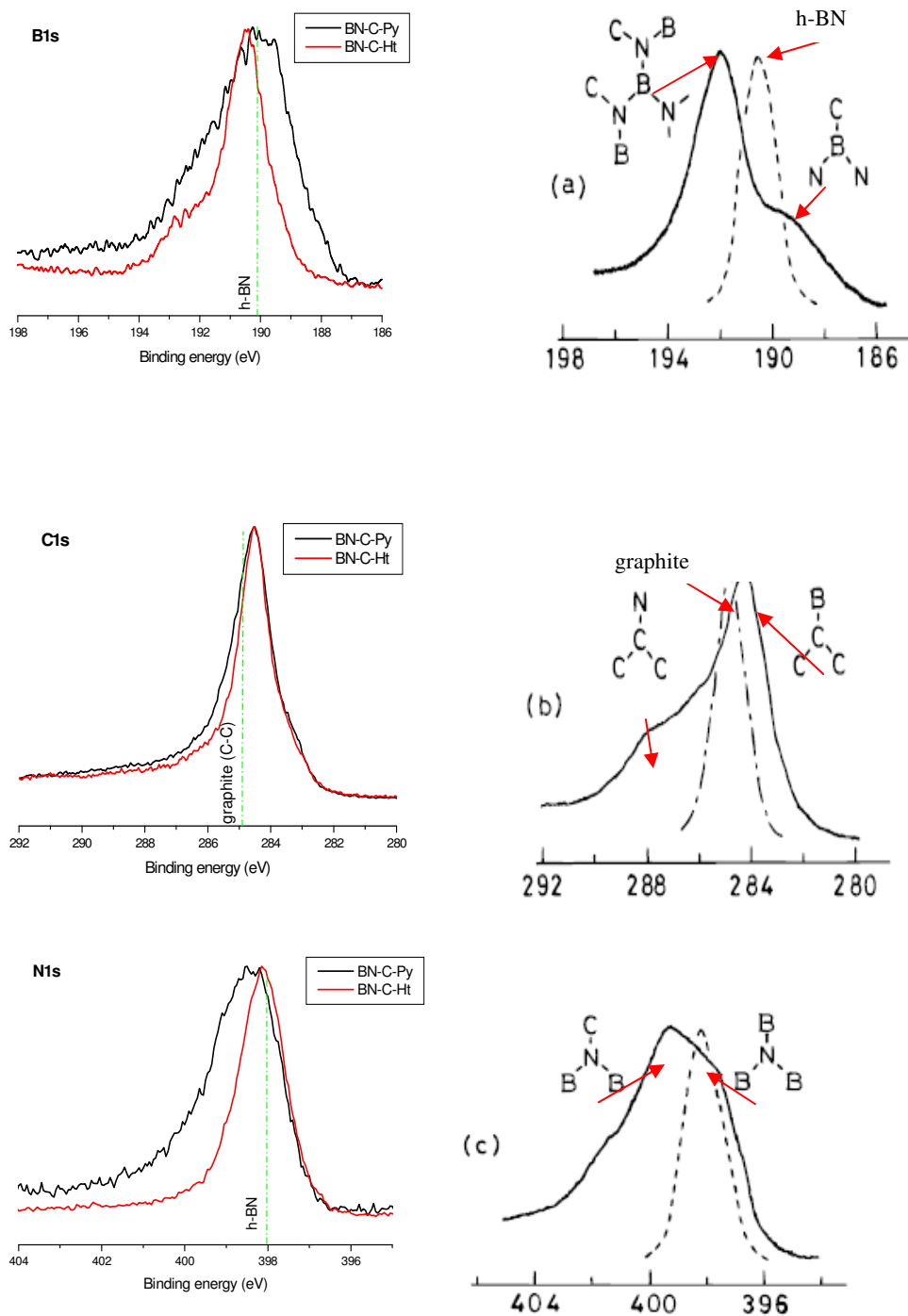


Figure 5.3: B1s, C1s and N1s spectra of the present t-BN-C (BN-C-Py and BN-C-Ht correspond to the pyrolysed and heat-treated samples respectively) in comparison with graphitic BCN phase produced by CVD [135] (a-c) showing the type of bonds expected in each region.

The electron energy loss spectrum (EELS) of t-BN-C shows information on local coordination environment. Clearly all the pre-edge EELS features are identified as transitions due to $\pi^*(\pi^*)$ and $\sigma^*(\sigma^*)$ molecular orbitals (MOs), indicating trigonal-planar sp^2 type bonding. The energy loss values of t-BN-C shown in Table 5.1 are clearly similar to those of pure h-BN and graphite materials. Furthermore, they compare very well with those of graphitic BC_2N materials. This suggests that the present t-BN-C are made up of an intimate mixture of h-BN and graphite layers or they form complete solid solutions with energy loss values similar to those of graphite and h-BN. However considering the fact that most boron carbonitride materials are metastable in nature and tend to decompose into graphite and h-BN on heat treatment at temperatures in the vicinity of 2000°C , the latter suggestion may not suffice.

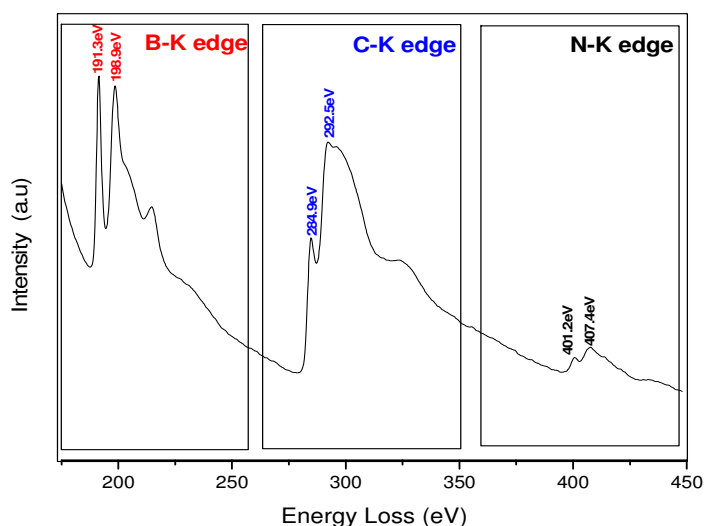


Figure 5.4: EELS spectra showing B-K,C-K and N-K edges of the present t-BN-C materials.

Table 5.1: A summary of the energy loss values of the present t-BN-C materials in comparison to those of pure h-BN, graphite and graphitic BC₂N.

Sample	B-K(eV)		C-K (eV)		N-K (eV)		Ref.
	π^*	σ^*	π^*	σ^*	π^*	σ^*	
t-BN-C	191.3	198.9	284.9	292.5	401.2	407.4	This study
h-BN	191.9	198.1			401.6	408.1	149a
graphite			285	291.7			149b
g-BC ₂ N	191.6	197.7	285	291.7	400.7	406.3	149a

In the case of an intimate mixture of graphite and h-BN, the exact arrangement of the C-C and B-N layers of the heat-treated sample is not easily predictable. Two possible arrangements have been theoretically predicted composed of alternate layers of B-N and C-C chains linked by C-N and B-C type bonds, this was named the striped type ^(73, 78). The other type consists of islands of C-C and B-N chains randomly distributed over the whole lattice named the ‘island type’, again the B-C and C-N bonds are confined to the boundaries of the islands. It was however shown through energy calculations that the striped type is more stable than the island type.^(73,78) Furthermore, the formation of B-C, C-C, C-N and B-N in the same monolayer is inhibited by the structural stresses imposed by the bond length differences as mentioned earlier.⁽⁷¹⁾ For brevity, the present BN-C materials can be assumed to be composed of a solid solution in the as-pyrolysed materials which is broken down to an intimate mixture, possibly the stripped type, with heat-treatment.

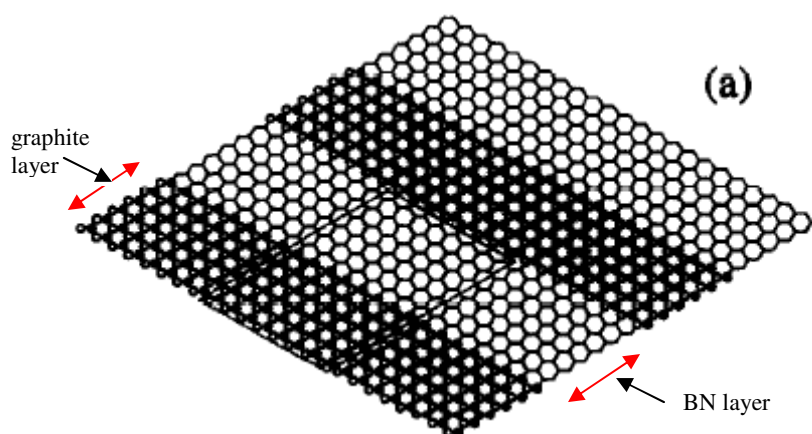


Figure 5.5: Predicted layered structure of the t-BN-C starting material as described in [73].

5.2 Shock Compressed BN-C Materials

Generally no phase transformation was observed at temperatures of less than about 2000°C despite the high pressure used in some cases. This is owing to the low reaction times involved in the shock experiments, limited to microseconds. There is either very little time for reaction to proceed successfully or the reverse reaction is more dominant. The latter is experienced in the case of high residual temperatures after the quenching stage. This would be expected at much higher synthesis temperatures of more than 2000°C. This is observed in the high temperature samples (above 2000°C) with decomposition into boron carbides. Alternatively, the yields of the cubic phases in shock compression may be very low such that all the cubic BN-C material is converted back to the low pressure phase during quenching. This is possible since the pressure is applied

instantaneously and the material is exposed to high temperatures at pressure release point since the quenching rate is not as fast as the pressure release.

5.3 Interpretation of Structure and Properties of the c-BN-C Materials

The high symmetry and lack of splitting observed in the Synchrotron diffraction profiles of the transformed phases Z608 (20GPa/2000°C/60s) and S4306 (20GPa/2000°C/30s) highlights the monophasic nature of the cubic B/C/N materials formed under the present HP/HT conditions. S4306 possesses relatively broader line widths signifying smaller crystallite size in comparison to Z608 as confirmed by DF (dark field) and BF (bright field) TEM imaging. This has a direct link to the isothermal holding time during high pressure synthesis. There are several anomalies which were observed in the XRD results. Firstly, the refined lattice parameter of Z608 (0.3555(2) nm) is smaller than expected for ideal mixing (0.3583 nm). This could be a result of lattice distortion leading to smaller lattice parameter values (up to 1% deviation permissible) as suggested by various theoretical models in referenced literature^(21,73,98,138,140). This may be induced by the slight differences in the B-N and C-C bond lengths which impose some residual stresses in the B/C/N lattice. Alternatively, this could be a result of the slight decomposition as observed in TEM which basically caused a carbon deficit and a deviation from the expected BC₂N stoichiometry in Z608. Furthermore, the observed two peaks at higher values (0.219(7) nm) and (0.188(5) nm) observed in the S4306 profile do not belong to the cubic phase with $a = 0.3596\text{\AA}$. This could

be a result of contamination from the Ta capsule used considering that these peaks are not present in the Z608 profile synthesised in an h-BN crucible.

It is clear from TEM investigations that the present cubic phases are polycrystalline in nature consisting of aggregated nanocrystallites. The formation of nano-diamond (nanoD) materials as observed in Z608 HRTEM is a clear sign of decomposition under the same P-T conditions as S4302 with double the isothermal reaction time of 60s signifying a narrow reaction time range. The EELS spectrum for Z608 showed inconsistent distribution of atoms owing to the decomposition, however S4306 showed good chemical homogeneity from different spots observed comparable to previously observed spectra.

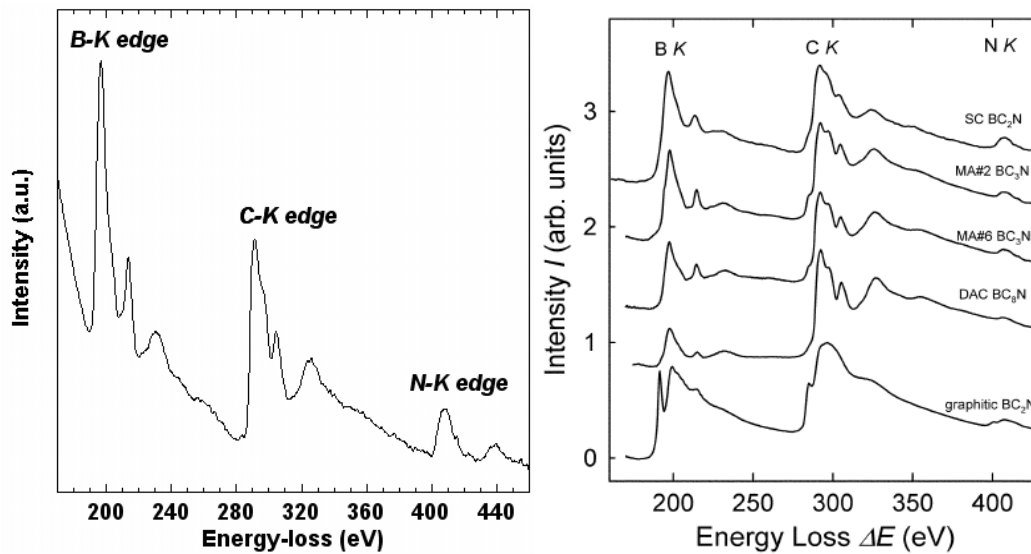


Figure 5.6: Electron Energy Loss Spectrum of sample S4306 (left) in comparison to cubic BN-C phases obtained in the diamond anvil cell (DAC), Multi anvil press

(MA) and under shock compression (SC) and the graphitic starting material as described in [149].

There is a significant difference between the present Raman results and the data published in previous studies.^(9,139) However the observed spectra resemble those of boron-doped diamond samples as observed in literature.⁽¹⁴²⁻¹⁴³⁾ A comparison was made with the spectra of nanocrystalline diamond and aggregated boron nitride nanocrystallites (ABNNC) as found in referenced literature.⁽¹⁴⁴⁻¹⁴⁵⁾ It is interesting to note that there is a general broadening, shifting and presence of additional Raman peaks associated with nanocrystalline materials as observed for ABNNC and nanocrystalline diamond⁽¹⁴⁴⁻¹⁴⁵⁾ in comparison to those of c-BN and diamond respectively.

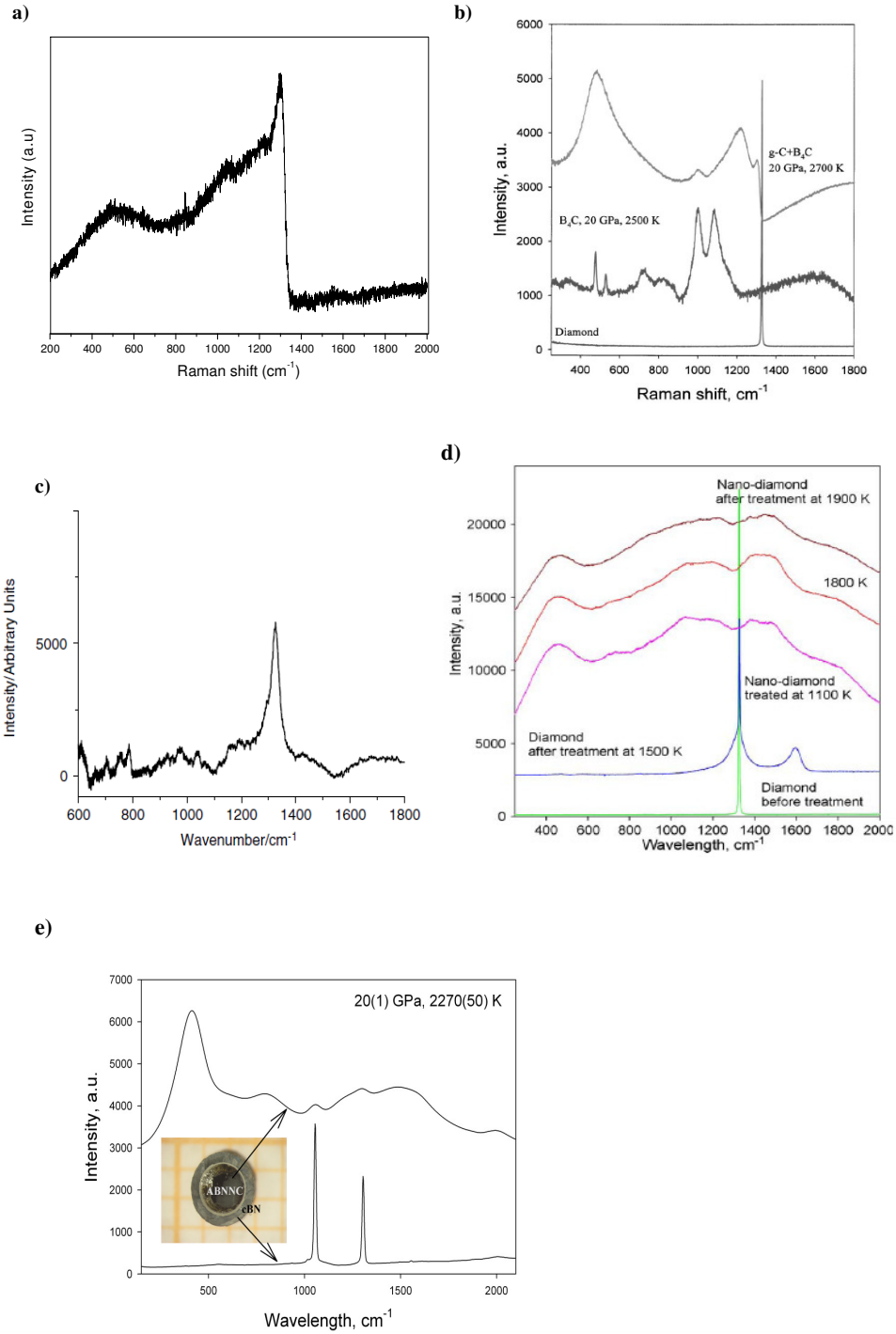


Figure 5.7: Raman spectrum of sample Z608 a) in comparison with b) boron-doped diamond, B_4C , diamond [Ref.142], c) $\text{c-BC}_2\text{N}$ [Ref.141], d) nano-diamond spectra as described in [144] and e) ABNNC and c-BN as described in [145] .

Thus the present Raman profiles are a true representation of the present nanocrystalline c-BN-C materials. The exact significance of such a unique profile is not well known and it is assumed to be a result of the fine structure of the present materials as observed in ABNNC and nanocrystalline diamond materials⁽¹⁴²⁻¹⁴⁵⁾. This finding has a practical implication on the properties of the present BN-C materials. In particular, the electronic properties as a result of the doping effect imposed by boron and nitrogen in diamond. This effect has been observed for superconducting boron doped diamond materials synthesised under high pressure and high temperatures as explained in the referenced literature.⁽¹⁴²⁻¹⁴³⁾ Resistivity studies for sample Z608 show a characteristic behaviour typical of amorphous type semiconductors, but it can not be distinguished, if it is bulk or two-dimensional.

5.4 Overview

The successful synthesis of c-BN-C materials is highly depended on the microstructure of the starting materials used. An investigation on the starting materials revealed a disordered turbostratic layered type structure from X-ray diffraction. Furthermore, spectroscopic studies confirmed bonding to be predominantly C-C and B-N type with a typical disordered graphite type Raman spectrum. This result is consistent with the theoretical hypothesis that the most stable structures in the B-C-N system are the ones with the maximum number of C-C and B-N type bonds.⁽⁷³⁾ This basically minimises the residual stresses imposed by the bond length differences.⁽⁷³⁾ Thus it is presumed that the most likely

structure obtained is one consisting of carbon and B-N layers with B-C and C-N type bonds confined to the boundaries of the layers. This is known as the ‘striped’ type.⁽⁷³⁾ The thermal stability of the t-BN-C was found to be limited to a temperature of 2000°C and lower, this signifies a thermodynamic instability with phase separation into graphite and h-BN as highlighted in referenced literature.^(73, 77, 78) A comparison of the present materials with results from previous studies confirms a similarity in the structure and properties of the materials although the precursor syntheses methods are different. Thus the results obtained for the t-BN-C are consistent with the observations that these materials are indeed metastable.

It has been shown that c-BN-C is obtainable at 20GPa/2000°C/30s under static HP/HT conditions with no phase transition being observed under dynamic pressure conditions. The pressure is slightly higher than predicted by Tateyama *et al*⁽²²⁾. The phase transformation mechanisms from the hexagonal to the cubic phase are well known for both the carbon and boron nitride systems. A theoretical prediction has shown that starting with the layered type BN-C materials the transformation mechanism is most likely to be the diffusionless/martensitic type.⁽²²⁾ This is similar to the h-BN to c-BN transformation mechanism. The present synthesis conditions are characterised by a very short isothermal holding time (30s) and the resulting crystallite size is confined to the nanometer range. A more prolonged isothermal holding time (60s) resulted in the growth of crystals coupled with decomposition of the c-BN-C phase resulting in additional nano diamond material. This observation is consistent with the theoretical prediction on the thermodynamic instability of the c-BN-C materials.

Theoretically, the physical and mechanical properties of ideal c-BN-C materials are expected to lie between those of diamond and c-BN. Diffraction by Synchrotron radiation proves the existence of a monophasic material with a cubic type structure. The lattice parameter value of sample S4306 (20GPa/2000°C/30s) is very close to the expected from ideal mixing (Vergad's Law) of diamond and c-BN (3.591(3) Å) and negative deviation of sample Z608 is a result of the slight decomposition. A comparison of the synthesis conditions, final structures and lattice parameters shows that the result obtained is similar to that obtained by Zhao *et al*⁽¹¹⁾ (Table 5.1).

Table 5.2: A summary of the synthesis parameters and lattice parameter values in comparison to referenced results in previous studies.

Author	Starting material	P,T,t conds	meth.	Product	Lattice Parameter/Å
Zhao ^[11]	Milled a-BN/C ₂	20GPa/1927°C/5mins	MA	c-BC ₂ N	3.595(7)
Solozhenko ^[16]	gr-BC ₂ N	25GPa/1820°C/30mins	MA	c-B _{0.4} C _{1.1} N _{0.5}	3.642(2)
Komatsu ^[93]	gr-BC ₂ N	50GPa/3227°C/1μs	SC	c-BC _{2.5} N	3.605
Knittle ^[9]	milled BN/C ₂	30GPa/1727°C/5-10mi	LHD AC	c-(BN) _{0.67} C _{0.33}	3.613(3)
Nakano ^[10]	gr-BC ₂ N	7.7GPa/2300°C/15mins	BP	c-BN,Dia.,c-B/C/N mixture	-
Filonenko ^[91]	C ₃ N ₄ /B (HT)	8GPa/1500°C/5mins	TP	(80%)cBC _{0.47} N _{0.85} + (20%)B ₁₃ C ₂	3.645
S4306	t-BC _{1.97} N	20GPa/2000°C/30s	MA	c-BN-C	3.555(2)
Z608	t-BC _{1.97} N	20GPa/2000°C/60s	MA	c-BN-C+nanoD	3.596(6)

The nature of the observed Raman spectra have been linked to the crystallite size of the present materials. This is characterised by shifting and broadening in the Raman bands a phenomenon observed with nano diamond materials and attributed

to the breakdown of selection rules owing to the small crystallite size.⁽¹⁴⁴⁾ This has resulted in completely differently observations as obtained in previous studies.⁽¹⁴¹⁾ The semi-conducting properties of sample Z608 are consistent with the theoretical predictions for BN-C materials in referenced literature. In view of the above, the cubic BN-C phase was obtained under a diffusionless type mechanism and was found to be thermodynamically unstable at prolonged isothermal holding times.

Chapter 6: Conclusion

The aim of the present study was to develop a superabrasive alloy material between diamond and c-BN which could find potential use in the cutting tool industry. Theoretical hypotheses suggest that the BN-C solid solutions are thermodynamically unstable and prone to decomposition. This basically makes the development of BN-C solid solutions a challenging task which is not unambiguously solved yet. Also there exist a lot of inconsistent data regarding the stability properties of these solid solutions. Thus this investigation coupled with the theoretical background proved that indeed the BN-C phases are metastable. It has been highlighted that one of the most important factors in the successful synthesis of cubic BN-C phases is the formation and microstructural characteristics of the starting materials. It has been shown that better intermixing at the atomic level leads to better quality starting materials which are less prone to decomposition as opposed to mechanical mixing and milling.

The fact that most of these BN-C materials are not well crystallised makes it difficult to predict their crystal structures. Theoretically, the most stable structures would be the ones maximising the number of C-C and B-N bonds and possessing minimum residual stress owing to bond length differences. Thus the starting ceramics in the present study were predicted to have a turbostratic type structure with predominantly C-C and B-N type bonding as observed in spectroscopic studies.

A cubic BN-C phase was successfully obtained under static conditions in the multi anvil press at 20GPa/2000°C and 30s isothermal holding time. Instability was observed under the same P, T conditions with double the isothermal holding time and formation of nano diamond was observed by TEM. However synchrotron XRD could not identify the nano diamond phase, signifying a low quantity of this component (< 1wt%). A unit cell parameter of $a = 3.596(6) \text{ \AA}$ which is comparable to the expected value from ideal mixing between diamond and c-BN (*calculated* $a_{BC_2N} = 3.583(1) \text{ \AA}$) was obtained for sample S4306 produced at 20GPa/2000°C/30s. The existence of two weak peaks which did not corresponding to the cubic type structure in S4306 (20GPa/2000°C/30s) profile signifies possible contamination from the Ta capsule. Further studies using TEM and EELS confirm the existence of nanosized polycrystals with a size of 5-10nm and sp^3 hybridised bonds similar to those in diamond and c-BN. The prolonged heating of sample Z608 resulted in much larger crystallites of the BN-C solid solution with a size of 50-100nm. The EELS spectra of the high pressure samples are clearly distinguishable from those of the starting t-BN-C materials, showing a complete disappearance of the π^* transitions. Thus it is clear that the c.BN-C phases obtained under the present conditions are prone to decomposition at prolonged synthesis times signifying metastability of these phases. The existence of nanodiamond as observed by TEM has proved the above hypothesis.

Hardness measurements could not be done owing to the small size of samples. The samples were characterised by Raman spectra resembling those of boron doped diamond and dissimilar to the one observed for c-BN-C materials as

described in referenced literature ^(9,141). The profile details are characteristic those of nanosized materials as observed in nanodiamond materials which is directly linked to the scattering behaviour of nanostructured materials. This has also been partly attributed to breakdown of selection rules, however the exact significance of this is not well known. Furthermore, sample Z608 (20GPa/2000°C/60s) was found to be semiconducting with a typical amorphous type material behaviour.

In view of the above, it has been shown that polymer derived t-BN-C ceramics are suitable starting materials for the HP/HT synthesis of c-BN-C material under static high thermobaric conditions. The synthesis conditions used to obtain the present materials are comparable with previously used conditions as shown in Table 5.2 and Figure 6.1 below.

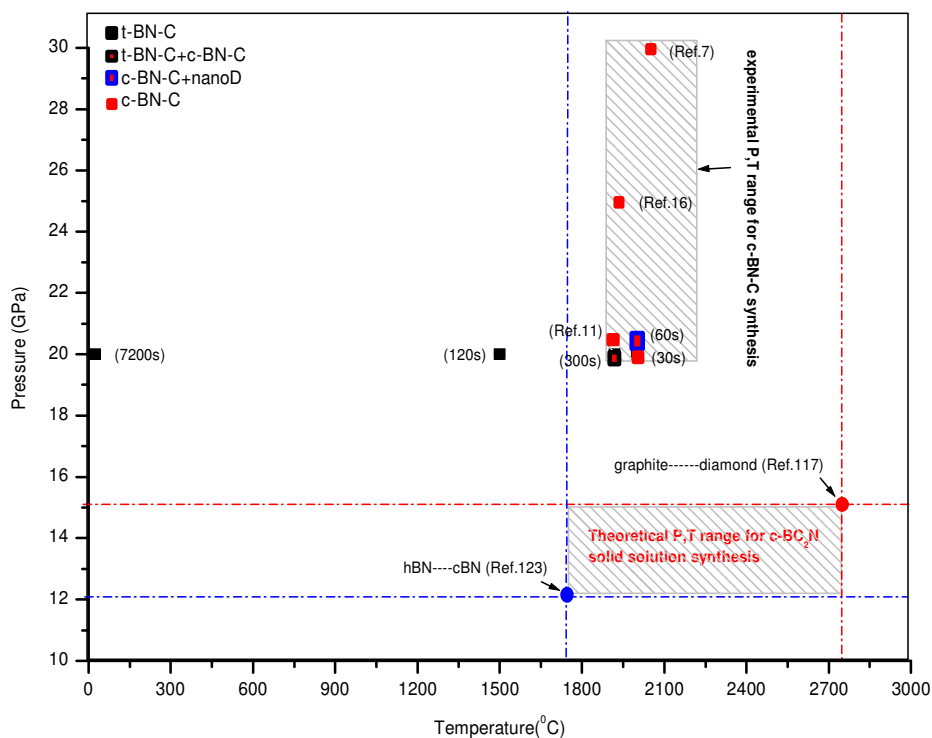


Figure 6.1: P-T conditions used in the present study and the BN-C products obtained in comparison to referenced literature and those of direct synthesis of diamond [117] and c-BN [123] The value in brackets represents the isothermal holding time.

It has been confirmed that the successful commercialisation of the direct synthesis of c-BN-C materials is not possible owing to the very high thermobaric conditions required i.e. pressures of up to 20GPa and temperatures of about 2000°C. However it may be of interest to study these materials using solvent catalysts in an attempt to reduce the high thermobaric conditions to commercially available values.

References

- 1) G.J. Davies in Handbook of Ceramic Hard Materials, edited by R. Riedel (Wiley-VCH Verlag GmbH, Weinheim, Germany 2000), *Cubic BN crystallisation*, vol 2, 510.
- 2) V.L. Solozhenko and E. Gregoryanz, *Materials Today*, 2005, 44-51.
- 3) F.P. Bundy, *Nature*, 1973, 241, 116-118.
- 4) T. Taniguchi, K. Watanabe and S. Koizumi, *phys.stat.sol (a)*, 2004, 201(11), 2573-2577.
- 5) D.M. Teter and R.J. Hemley, *Science*, 1996, 1, 161.
- 6) T. Malkow, *Materials Science and Eng. A302*, 2001, 311-324.
- 7) A.R. Badzian, *Mater. Res. Bull.*, 1981, 16(11), 1385-1393.
- 8) S. Nakano, M. Akaishi, T. Sasaki and S. Yamaoka, *Chem. Mater.* 1994, 6(12), 2246-2251.
- 9) E. Knittle, R.B. Kaner, R. Jeanloz and M.L. Cohen, *Phys. Rev. B*, 1995, 51(18), 12149.
- 10) S. Nakano, *In Proceedings of the 3rd NIRIM International Symposium for Advanced Materials, National Institute for Research in Inorganic Materials, Japan*, 1996, 287.
- 11) Y. Zhao, D.W. He, L.L. Daemen, T.D. Shen, R.B. Schwarz, Y. Zhu, D.L. Bish, J. Huang, J. Zhang, G. Shen, J. Qian, T.W. Zerda, *J. Mater. Res.*, 2002, 17(12), 3139-3145.
- 12) T. Komatsu, M. Nomura, Y. Kakudate, and S. Fujiwara, *J. Mater. Chem.*, 1996, 6(11), 1799-1803.
- 13) V.L. Solozhenko, N.A. Dubrovinskaya and L.S. Dubrovinsky, *Applied Phys. Letters.*, 2004, 85(9), 1508.
- 14) J.E. Lowther, *J. Phys. Condens.*, 2005, 17, 3221.
- 15) M.H. Manghnani, S. Tkachev, P.V. Zinin, X. Zhang, V.V. Brazhkin, A.G. Lyapin and A. Trojan, *Phys. Rev.*, 2001, 64(12), 121403.
- 16) V.L. Solozhenko, D. Andrault, G. Fiquet, M. Mezouar and D.C. Rubie, *Appl. Phys. Lett.*, 2001, 78(10), 1385.

- 17) M.Mattesini and S.F.Matar, *International J.Inorg.Mater.*, 2001, 3, 943-957.
- 18) W.R.L.Lambrecht and B.Segall, *Phys.Rev.B.*, 1993, 17(15), 9289-9296.
- 19) Z.Pan, H.Sun and C.Chen, *J.Phys.Condens.Mater.*, 2005, 17, 3211-3220.
- 20) Z.Pan, H.Sun, and C.Chen, *Phys.Rev.B.*, 2006, 73, 214111-4.
- 21) H.Sun, S-H.Jhi, D.Roundy, M.L.Cohen and S.G.Louie, *Phys.Rev.B.*, 2001, 64, 094108-6.
- 22) Y.Tateyama, T.Ogitsu, K.Kusakabe and S.Tsuneyuki, *Phys.Rev.B.*, 1997, 55(16), R10161-4.
- 23) J.Widany, W.S.Verwoerd, Th.Frauenheim, *Diamond & Related Mater.*, 1998, 7, 1633-1638.
- 24) J-C.Zheng, C.H.A.Huan, A.T.S.We, R-Z Wang and Y-M Zheng, *J.Phys. Condens. Mater.*, 1999, 11, 927-935.
- 25) R.Riedel, *Adv.Mater.*, 1992, 4(11), 759-761.
- 26) H.Pierson, *Handbook of Carbon, Graphite, Diamond and Fullerenes: Properties, Processing and Applications*, Noyes Publications, NJ USA, 1994, 30-39.
- 27) J.Haines, J.M.Leger and G.Bocquillon, *Annu.Rev.Mater.Res.*, 2001, 31, 1-23.
- 28) V.V.Brazhkin, *High Pressure Res.*, 2007, 27(3), 333-351.
- 29) J.M.Leger, J.Haines, B.Blanzat, *J.Mater.Sc.Letters.*, 1994, 13, 1688-1690.
- 30) A.Zerr and R.Riedel, in *Handbook of Ceramic Hard Materials vol.1*, ed. by R.Riedel, Wiley-VCH, Weinheim, 2000, 1.
- 31) R.Riedel, *Adv.Mater.*, 1994, 6(7/8), 549-560.
- 32) N.A.Dubrovinskaia, L.S.Dubronvinsky, S.K.Saxema, B.Sundman, *J.Alloys & Compounds.*, 1999, 285, 242-245.
- 33) P.F.McMillan, *Nature Materials*, 2002, 1, 19-25.
- 34) F.Gao, J.He, E.Wu, S.Liu, D.Yu, D.Li, S.Zhang and Y.Tian, *Phys. Rev. Lett.*, 2003, 91 (1), 015502-1.

- 35) V.Brazhkin, N.Dubronviskaia, M.Nicol, N.Novikov, R.Riedel, V.Solozhenko and Y.Zhang, *Nature Materials*, 2004, 3,576-577.
- 36) A.G.Evans and F.F.Lange, *J.Mater.Sc.*, 1975, 10, 1659-1664.
- 37) B.R.Lawn, M.V.Swain and K.Phillips, *J.Mater.Sc.Lett.*, 1975, 10, 1236-1239.
- 38) K.Niihara, R.Morena and D.P.H.Hasselmann, *J.Mater.Sc.Lett.*, 1982, 1, 13-16.
- 39) A.G.Evans and E.A.Charles, *J.Am.Cer.Soc.*, 1976, 59,371.
- 40) J.J.Petrovic, L.A.Jacobson, P.K.Talty and A.K.Vasudevan, *J.Am.Cer.Soc.*, 1975, 58, 113.
- 41) A.G.Evans, *Fracture Mechanics of Ceramics vol. I*, Ed.by R.C.Bradt, D.P.H. Hasselmann and F.F.Lange, Plenum Press, NY, 1974, 17.
- 42) D.Munz and T.Fett, *Ceramics: Mechanical properties, failure behaviour, materials selection vol.36*, Springer-Verlag, Berlin & Heidelberg GmbH Co., 1999.
- 43) C.Olagnon, J.Chevalier and V.Panchard, *J.Eur.Ceramic Soc.*, 2006, 1-9.
- 44) G.Elssner, H.Hoven, G.Kiessler, P.Wellner and R.Wert, *Ceramics and Ceramic Composites: Materialographic Preparation*, Elsevier, 1999, 144-158.
- 45) G.R.Anstis, P.Chantikul, P.Lawn and B.R.Marshall, *J.Amer. Cer .Soc.*, 1981, 64, 533-538.
- 46) D.K.Shetty, I.G.Wright, P.N.Mineer and A.H.Claner, *J.Mater.Sc.*, 1985, 20, 1873-1882.
- 47) a) R.Morrell, *Handbook of Properties of Technical Eng.Ceramics Part I: An Introduction for the Engineer and Designer*, HMSO London, 1985, 92-93. b) G.A.Gogotsi, *Strength of Materials*,200,32(1),81-85
- 48) M.L.Cohen, *Phys.Rev.B*, 1985, 32(12), 7988-7991.
- 49) S.Azevedo, *Phys.Letters A*, 2006, 351, 109-112.
- 50) A.Y.Liu, R.M.Wentzovitch and M.L.Cohen, *Phys.Rev.B*, 1989, 39(3), 1760-5.

- 51) Z.X.Cao and H.Olchsner, *J.Appl.Phys.*, 2003, 93(2), 1186-9.
- 52) M.Hubacek and T.Sato, *J.Solid State Chem.*, 1995, 114,258-264.
- 53) J.Bill, R.Riedel and G.Passing, *Z.anorg.allg.Chem.*, 1992,610, 83-90.
- 54) a) R.Riedel, J.Bill and G.Passing, *Adv.Mater.*, 1991, 3(11), 551-552. b)
J. Bill, M. Frieß, R. Riedel, *Eur. J. Solid State Inorg. Chem.*, 1992 29,
195-212.
- 55) Y.Goto, M.Sasaki and K.Mukaida, *Key Eng. Materials*, 1999, 159-160,
347-52.
- 56) B.Yao, L.Liu and W.H.Su, *J.Mater.Res.*, 1998, 13(7), 1753-56.
- 57) Y.G.Andreev, T.Lundström, R.K.Harris, Se-W.Oh, D.W.Apperley and
D.P.Thompson, *J.Alloys and Cmpnds.*, 1997,227, 102-8.
- 58) J.L.He, Y.J.Tian, D.L.Yu, T.S.Wang, R.Xiao, A.D.Li, D.C.Li,
Y.G.Peng, and L.Li, *J.Mater.Sc.Lett.*, 2000, 19, 2061-63.
- 59) T.Komatsu and A.Goto, *J.Mater.Chem.*, 2002, 12, 1288-93.
- 60) T.Komatsu, Y.Kakudate, and S. Fujiwara, *Rev.High Pressure Sci.
Technology.*, 1998, 7, 983-985.
- 61) Y.F.Zhang, Y.H.Tang, C.S.Lee, I.Bello and S.T.Lee, *Diamond and
Rel.Mater.*, 1999, 8, 610-13.
- 62) A.H.Cottrell, *An Introduction to Metallurgy*, Edward Arnold
publishers, London, 1967, 192.
- 63) J.Howe, C.Rawn, L.Jones, H.Ow, *Powder Diffraction*, 2003, 18, 159.
- 64) *Natl.Bur.Std (U.S) Monogr.*, 25,1984,20.
- 65) C.E.Lowell, *J.Amer.Cer.Soc*, 1967, 50(3), 142.
- 66) Th.Fraunheim, G.Jungnickel, P.Sitch, M.Kankonen, F.Weich,
J.Widany and D.Porezeg, *Diamond and Rel.Mater.*, 1998, 7,348-55.
- 67) N.A.Dubrovinskaia, L.Dubrovinsky, T.Papageorgiou, A.Bosak,
M.Krisch, H.F.Braun and J.Wosnitza, *Appl.Phys.Lett.*, 2008,
92,132506.
- 68) T.Borst and O.Weist, *phys.stat.sol (a)*, 1996,154,423.

- 69) J.Birrell, J.E.Gerbi, O.Auciello, J.M.Gibson, D.M.Gruen and J.A.Carlisle, *J. Appl. Phys.*, 2003, 93(9), 5606-12.
- 70) S.Dannefaer, *phys. stat. sol (c)*, 2007, 4(10), 3605-13.
- 71) J.P.Nicholich, F.Hofer, G.Brey and R.Riedel, *J.Amer.Cer.Soc.*, 2001, 84(2), 279-82.
- 72) K.Yamada, *J.Amer.Cer.Soc.*, 1998, 81(7), 1941-44.
- 73) H.Nozaki and S.Itoh, *J.Phys.Chem.Solids*, 1996, 57(1), 41-49.
- 74) H.Nozaki and S.Itoh, *Phys.Rev. B*, 1996, 53(21), 14161-70.
- 75) G.A.Barraff and M.Schlüter, *Phys.Rev.B*, 1986, 33, 7346.
- 76) X.Blase, J-Ch.Charlier, A.De Vita, R.Car, *Appl.Phys.A*, 1999, 68, 293-300.
- 77) X-G.Luo, Z-Y.Liu, X-J.Guo, J-L.He, D-L.Yu, Y-J.Tian, J.Sun and H-T.Wang, *Chin.Phys.Lett.*, 2006, 23(8), 2175.
- 78) S.Azedevio and R.De Paiva, *Europhys.Lett.*, 2006, 75(1), 126-132.
- 79) A.R.West, *Basic Solid State Chemistry*, Chichester, England & NY: John Wiley, 1988.
- 80) A.R.Badzian, T.Niemyski, S.Oppenheimer and E.Olkusnik, *Khim. Suyaz. Poluprov. Polumetall.*, 1972, 362.
- 81) R.B.Kaner, J.Kouvetakis, C.E.Warble, M.L.Sattler and N.Bartlett, *Mater. Res. Bull.*, 1987, 22, 399.
- 82) F.Saugnac, F.Teyssandier, A.Marchand, *J.Phys.4*, 1991, 1, C2-673.
- 83) A.W.Moore, S.L.Strong, G.L.Doll, M.S.Dresselhaus, I.L.Spain, C.W.Bowers, J.P.Issi, L.J.Piroux, *J.Appl.Phys.*, 1989, 65, 5109.
- 84) M.L.Kasinova, Yu.M.Runyantsev, A.N.Golubenko, N.I.Fainer, B.M.Ayupov, I.P.Dolgovesova, B.A.Kolesov, V.V.Kaichev and F.A.Kuznetsov, *Inorg.Mater.*, 2003, 39(4), 366-73.
- 85) M.L.Kasinova, Yu.M.Rumyantsev, N.I.Fainer, E.A.Maximovski, *Nuclear Instr. & Methods in Phys.Res.A.*, 2001, 470, 253-57.
- 86) C.Popov, K.Saito, B.Ivanov, Y.Koga, S.Fujiwara, V.Shanov, *Thin Solid Films*, 1998, 312, 99-105.

- 87) Y.Goto, M.Sasaki, M.Hashizume and M.Suzuki, *J.Eur.Ceramic Soc.*, 1999, 19, 2695-2700.
- 88) M.O.Watanabe, T.Sasaki, S.Itoh, K.Mizushima, *Thin solid Films*, 1996, 281-82, 334-36.
- 89) J.Kouvetakis, T.Sasaki, C.Shen, R.Hagiwara, M.Lerner, K.M.Krishnan, N.Bartlett, *Synth.Met.*, 1989,34,1.
- 90) T.Ya.Kosolapova, G.N.Makarenko, T.I.Serebryakova, E.V.Prilutskii, O.T.Khorphyakov, O.I.Chernysheva, *Poroshk.Metall.*, 1971,1,27.
- 91) V.P.Filoneko, V.N.Khabashesku, V.A.Davydov, I.P.Zibrov and V.N.Agafonov, *Inorg.Mater.*, 2008, 44(4), 395-400.
- 92) R.Riedel, *Naturwissenschaften*, 1995, 82, 12-20.
- 93) T.Komatsu, *J.Mater.Chem.*, 2004, 14, 221-227.
- 94) R.Torress, I.Caretti, R.Gago, Z.Martin and I. Jimenez, *Diamond & Rel. Mater.*, 2007, 16, 1450-54.
- 95) Y.H.Xiong, S.Yang, C.S.Xiong, H.L.Pi, J.Zhang, Z.M.Ren, Y.T.Mai, W.Xu, G.H.Dai, S.J.Song, J.Xiong, L.Zhang, Z.C.Xia and S.L.Yuan, *Physica B*,2006, 382,151-55.
- 96) X.Guo, Z.Liu, X.Luo, D.Yu, J.He, Y.Tian and H-T.Wang, *Diamond and Rel.Mater.*, 2007, 16, 526-30.
- 97) R.Q.Zhang, K.S.Chan, H.F.Cheung and S.T.Lee, *Apl.Phys.Lett.*, 1999, 75(15), 2259-61.
- 98) M.Mattesini and S.F.Matar,*Comp.Mater.Sc.*,2001, 20, 107-119.
- 99) T.Komatsu, M.Samedima, T.Awano, Y.Kakadate, S.Fujiwara, *J.Mater. Proc. Tech.*,1999, 85, 69-73.
- 100) W.Utsumi, S.Nakano, K.Kimoto, T.Okada, M.Isshiki, T.Taniguchi, K.Funakoshi, M.Akaishi and O.Shimomura,*In Proceedings of AIRAPT-18,Beijing*,2001,186.
- 101) H.J.McSkimin, P.J.Andreatch,*J.Appl.Phys.*,1972, 43, 2944.
- 102) R.C.De Vreis, *Cubic Boron Nitride: A Handbook of Properties GE Report*, 1972, 72, CRD178.

- 103) W.R.L.Lambrecht and B.Segall, *Phys.Rev.B*, 1989, 40(14), 9909-9919.
- 104) F.Gao, J.He, E.Wu, S.Liu, D.Yu, D.Li, S.Zhang and Y.Tian, *Phys. Rev. Lett.*, 91(1), 015502:1-4.
- 105) T.Komatsu, M.Nomura, Y.Kakudate and S.Fujiwara, *J.Chem. Soc. Faraday Trans.*, 1998, 94(11), 1649-55.
- 106) R.J.Wedlake, and A.L.Penny, *De-Beers Industrial Diamond Division Ltd, Ger. Pat.*, 2806070, 1979, 1.
- 107) [Landolt-Börnstein, Group VIII Advanced Materials and Technologies, Powder Metallurgy Data. Refractory, Hard and Intermetallic Materials](#), 2002, 13 91-13 112.
- 108) V.L.Solozhenko, S.N.Dub, N.V.Novikov, *Diamond and Rel. Mater.*, 2001, 10, 2228-2231.
- 109) N.V.Novikov, S.N.Dub, *J.Hard.Mater.*, 1991, 2, 3.
- 110) J.E.Field, in *J.E.Field Ed., The Properties of Natural and Synthetic Diamond*, Academic Press, London, 1992, 6678.
- 111) M.P.D'Evelin and K.Zgonc, *Diamond and Rel.Mater.*, 1997, 6, 812.
- 112) G.J Davies in *Handbook of Ceramic Hard Materials, Introduction: Novel Ultrahard Materials*, Wiley- VCH, vol 2, 485 (2000)
- 113) G.Demazeau, *J.Phys.:Condens.Matter*, 2002, 14, 11031-11035.
- 114) L.Vel, G.Demazeau and J.Etourneau, *Mater.Sc.Eng.B*, 1991, 10, 149.
- 115) J.Y.Huang, H.Yasuda and H.Mori, *J.Amer.Cer.Soc.*, 2000, 83, 403409.
- 116) V.Z.Turkevich, *J.Phys.:Condens.Mater.*, 2002, 14, 10963-68.
- 117) <https://www.bris.ac.uk/Depts/Chemistry/MOTM/diamond>.
- 118) S.K.Singhal, J.von der Gonna, G.Nover, H.J.Meurer and B.P.Singh, *Diamond & Rel.Mater.*, 2005, 14, 1389-94.
- 119) V.L.Solozhenko, *Diamond and Rel.Mater.*, 1994, 4, 1.
- 120) V.L.Solozhenko, *Doklady Phys.Chem.*, 1988, 301, 592.

- 121) S.Nakano, H.Ikawa, O.Fukunaga, *J.Amer.Cer.Soc.*, 1992, 75, 240.
- 122) T.Sasaki, M.Akaishi, S.Yamaoka, Y.Fujiki and T.Oikana, *Chem. Mater.*, 1993, 5, 695-699.
- 123) V.F.Britun, A.V.Kudymov, *J.Mater.Sc.*, 1999, 34, 5677.
- 124) T.Kobayashi, S.Tashiro, T.Sekine and T.Sato, *Chem.Mater.*, 1997, 233.
- 125) D.V.Fedoseev, N.G.Sanzharlinskii, N.V.Kirova and S.P.Vnukov, *Transl. from Akademii Nauk.SSSR, Seriya Khinicheskaya*, 1978, 11, 2647.
- 126) R.C.Burns and M.Sibanda, in *Handbook of Ceramic Hard Materials, Introduction: Novel Ultrahard Materials*, Wiley- VCH, vol 2, 496 (2000)
- 127) P.S.DeCarli and J.C.Jamieson, *Science*, 1961, 133, 1821.
- 128) B.J.Alder and R.H.Christian, *Phys.Rev.Lett.*, 1961, 7, 367.
- 129) Y.Kakudate, M.Yoshida, S.Usuba, H.Yokoi, S.Fujiwara, M.Kawaguchi, K.Sato and T.Sawai, *Trans.Mater.Res.Soc.Jpn*, 1994, 14B, 1447.
- 130) H.Kagi, I.Tsuchida, Y. Masuda, M. Okuda, K.Katsura, and M. Wakatsuki, in *Proceedings of the Fifteenth AIRAPT International Conference edited by W.A Tzreciakowski*, World Scientific, Singapore, 1996, 258-260.
- 131) A.V.Kurdyumov, V.L.Solozhenko, M.Gubachek, N.I.Borimchuk, V.B.Zelyavskii, N.F.Ostrovskaya and V.V.Yarosh, *Powder Metallurgy and Metal Ceramics*, 2000, 39(9-10), 467-73.
- 132) D.F.Shriver and M.A.Drezdon, *The Manipulation of Air Sensitive Compounds*, 2nd ed., Wiley: New York, 1986.
- 133) F.Tuinstra and J.Koenig, *J.Chem.Phys.*, 1970, 53(3), 1126-1130.
- 134) HORIBA Jobin Yvon, *Raman Application Note*, Carbon 01, 1-4.
- 135) M.Kawaguchi, T.Kawashima, T.Nakajima, *Chem.Mater.*, 1996, 8, 1197-1201.
- 136) H.Kunzle, P.Gantenbein, R.Steiner, P.Oelhafen, *J.Anal.Chem.*, 1993, 346, 41.

- 137) PPMS from Quantum Design, 6325 Lusk Boulevard, San Diego, CA 92121-3733, USA.
- 138) L.J.van der Pauw, *Phylips Res.Repts.*,1958, 13, 1-9.
- 139) A.C.Larson and R.B.VonDreele, GSAS, General Structure Analysis System (LANL, Los Alamos, New Mexico) 1986.
- 140) E.Kim, T.Pang, W.Utsumi, V.L.Solozhenko and Y.Zhao, Cubic phases of BC₂N: A first principles study, *Phys.Rev.B.*, 2007, 75, (2007) 184115.
- 141) H.W.Hubble, I.Kudryashov, V.L.Solozhenko, P.V.Zinin, S.K.Sharma and L.C.Ming, *J.Raman Spectrosc.*, 2004, 35, 822-825.
- 142) N.Dubrovinskaia, G.Eska, G.A.Sheshin, H.Braun,*J.Applied Physics.*, 2006, 99, 033903.
- 143) N.Dubrovinskaia, L.Dubrovinsky, T.Papageorgiou, A.Bosak, M.Krisch, H.F.Braun and J.Wosnitza, *Applied Physics Letters*, 2008, 92, 132506.
- 144) N.Dubrovinskaia, L.Dubrovinsky, F.Langenhorst, S.Jacobsen, C.Liebske, *Diamond and Related Materials*, 2005, 14, 16-22.
- 145) N.Dubrovinskaia, V.L.Solozhenko, N.Miyajima, V.Dmitriev, O.Kurakevych, L.Dubrovinsky, *Applied Physics Letters*, 2007, 90, 101912.
- 146) N.W.Ashcroft and N.D.Mermin, Solid State Physics, Saunders College Publishing, 1976.
- 147) N.F.Mott, *Phil.Mag.*, 1969, 19(160), 835.

- 148) D.B.Williams and C.B.Carter, *Transmission Electron Microscopy: A Textbook for Materials Science*, 1996, Plenum Press, NY.
- 149) a) F.Langenhorst and V.L.Solozhenko, *Phys.Chem.Chem.Phys.*, 2002,4 5183-5188. b) R.Arenal, M.Kociak and N.J.Zaluzec, High-angular-resolution electron energy loss spectroscopy of hexagonal boron nitride, *Applied Physics Letters.*,2009, 90,204105.
- 150) Y.G.Andreev and T.Lundström,*J.Appl.Cryst.*, 1994, 27, 767-771.
- 151) Y.Miyamoto, M.L.Cohen and S.G.Louie, *Phys.Rev.B*, 1995, 52(20), 14 971-14 975.
- 152) Y.K.Yap, Y.Wada, M.Yamaoka, M.Yoshimura, Y.Mori, T.Sasaki, *Diamond and Related Materials.*, 2007, 10, 1137-1141.
- 153) Y.Wang, D.C.Alsmeyer and R.L.McCreery, *Chem.Mater.*, 1990, 2, 557.