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STRUCTURE AND PROPERTIES MODIFICATIONS IN BORON NITRIDE.
PART I: DIRECT POLYMORPHIC TRANSFORMATIONS MECHANISMS

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S-a efectuat o examinare aprofundată a structurii varietăților polimorfe ale nitrurii de bor BN şi a mecanismelor tranzițiilor polimorfe de la structurile hibridizate sp^2 *la structurile hibridizate* sp^3 *cu scopul de a explica pe baze cantitative modificarea dramatică a durității care face ca nitrura hexagonală de bor (grafitul alb) să fie un lubrifiant solid moale, în timp ce nitrura cubică de bor este un superabraziv situat al doilea după diamant ca duritate. In vederea scopului propus au fost luate în considerare numai transformările referitoare la tranzițiile polimorfe directe fără implicarea solvenților-catalizatori în cursul sintezei varietăților polimorfe hibridizate* sp^3.

A thorough examination of the structure of boron nitride (BN) polymorphs and of the polymorphic transition mechanisms from sp^2 *hybridized structures to* sp^3 *hybridized structures has been undertaken in view of explaining on quantitative bases the dramatic modification in hardness that makes hexagonal boron nitride (white graphite) a soft solid lubricant and cubic boron nitride (borazone) a superabrasive, second in hardness after diamond. Having in view this goal we have taken into consideration only the direct polymorphic transformations of BN that do not involve the participation of catalyst-solvent substances in the synthesis of* sp^3 *bonded polymorphs.*

Keywords: hBN, rBN, turbostratic BN, cBN, wBN structure, polymorphic transitions, puckering and buckling mechanisms

1. Introduction

Boron nitride (BN) is a modern man made compound that perfectly parallels the crystalline structure and properties of naturally occurring elementary carbon. Actually hexagonal boron nitride hBN (or white graphite) is a high performance lubricant similar to natural graphite, while cubic boron nitride cBN (or borazone) is second in hardness after diamond, both substances being classified as the best superabrasives. Even more, a perfect crystallographic analogy exists between the

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boron nitride polymorphs and the carbon allotropes: hBN (hexagonal boron nitride) has the same crystal lattice as graphite, rBN (rhombohedral boron nitride) has the same crystal lattice as rhombohedral graphite, cBN (cubic boron nitride) has the same crystal lattice as diamond, wBN (wurtzitic boron nitride) has the same crystal lattice as lonsdaleite (a wurtzitic variety of diamond). For boron nitride as well as for carbon the same distinction can be made between the *low density –low hardness polymorphs* and *high density – high hardness polymorphs.*

The present paper intends to make a close examination of the mechanisms by which the low density BN polymorphs transform into high density BN polymorphs. By considering hardness as an external expression of the interatomic forces acting in a specific crystallochemical structure, this structure analysis is a requisite for calculating the hardness modification during the polymorphic transformation processes.

2. Crystallochemical caracterisation of boron nitride polymorphs

Table 1, adapted from reference [1], shows the main crystallographic characteristics of the four BN polymorphs, indicating the space group to which the crystal lattice is belonging , the coordination number z, the lattice parameters a and c, the minimum interatomic spacing d (representing the length of the strong covalent bond), the interlayer spacing d_{002}, the roentgenographic density ϱ. Also indicated in Table 1 are some chemical characteristics that are of interest for calculating the theoretical hardness, namely the state of hybridization of the valence orbitals (sp^2 or sp^3) and the energy per interatomic bond (either strong covalent bond or weak van der Waals bond if it exists).

Table 1

Crystallographic characteristics for various boron nitride polymorphs

Hybrid. state	Phase	Space group	z	a (A^o)	c (A^o)	d (A^o)	d_{002} (A^o)	ϱ (g/cm^3)	bond energy (eV)	
									cov.	van der Waals
sp^2	hBN	$P6_3$/mmc	3	2,504	6,661	1.4457	3.3306	2,29	3.25	0.052
sp^2	rBN	R3m	3	2,504	10,010	1.4500	3.34	2,29	3.25	0.052
sp^3	cBN	Fd3m	4	3,615	-	1.5670	-	3,51	1.52	-
sp^3	wBN	$P6_3$mc	4	2,550	4,230	1.5760	2.20	3,50	1.52	-

Fig.1 depicts the crystal lattices of the four BN polymorphs. A common feature of all of them is the location of B and N atoms as nearest neighbours in alternate positions.

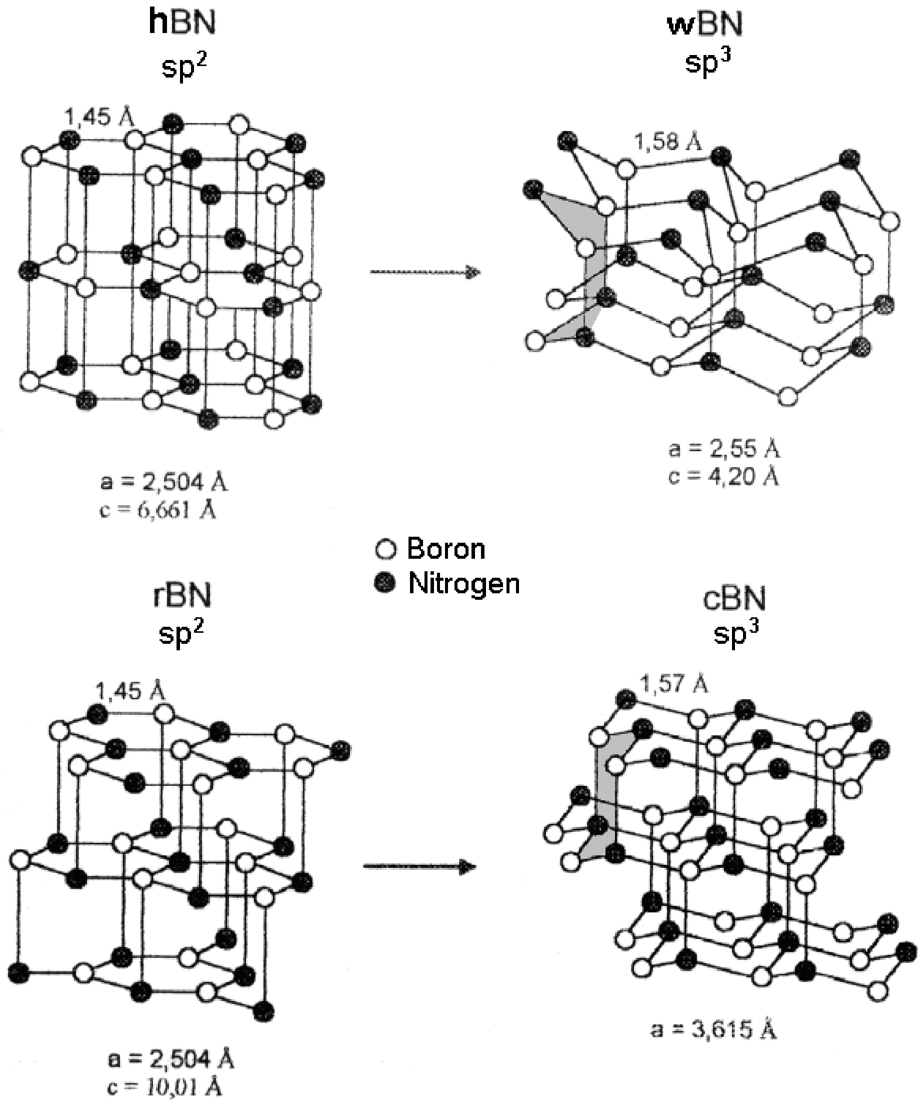

Fig.1 Crystal lattices of BN polymorphs and stacking sequence in the hexagonal lattices
- hBN: polytype 1H (stacking sequence of the hexagonal layers AA'AA'…)
- rBN: polytype 3R (stacking sequence of the hexagonal layers ABCABC…)
- wBN: polytype 2H' (stacking sequence of the hexagonal layers ABAB…)
- cBN : cubic

The crystal lattices of the low density BN (namely hBN and rBN) is built of planar layers consisting of B_3N_3 hexagons in which the sp^2 hybridized atomic orbitals result in three covalent bonds connecting each atom to its three nearest neighbours.

- *Hexagonal boron nitride hBN (white graphite)* is the common low density polymorph. Its crystal lattice is the simplest among the layered type structures and is unique by the stacking sequence of the hexagonal layers, namely AA'AA'…, that is denoted polytype 1H.; it means that the hexagons are coincident in all layers along axis c. The strong σ covalent bond between B and N atoms within the hexagonal layers has however an ionic component due to the presence of two atomic species with different electronegativity. The interatomic bond between two successive hexagonal layers is extremely weak (a π bond, type van der Waals) and this explains its far higher length (3.3306 A^o in comparison with the short length (1.4457 A^o) of the strong covalent bond within the hexagonal layers . On account of the higher electronegativity of nitrogen the π electron is located closer to the N atom and this makes hBN to be an electrical insulator and to have a white colour.

- *Turbostratic boron nitride tBN* is similar to hBN but the order in the direction of axis *c* is disturbed. Actually each hexagonal layer may be twisted in a random way against its neighbour layers [2]. As a result the tridimensional order is limited and the spacing between the hexagonal layers is increased by 3-4% in comparison with a perfectly ordered structure. The structure may improve its order by high temperature compression when highly oriented pyrolytic boron nitride (hopBN) is obtained [3].

-*Rhombohedral boron nitride rBN* is a far less frequently encountered BN polymorph in which the packing sequence of the hexagonal layers [4] is ABCABC.. denoted as polytype 3R. It means that the hexagonal layers are no more coincident but are displaced in such a way that every fourth layer repeats the position of the first layer.

The two high density polymorphs (cBN and wBN) have tridimensional lattices in which each atom is in a sp^3 hybridization state and establishes four strong covalent σ bonds with its nearest neighbours that make up a tetrahedron around it. No more π electrons are available to give rise to a weak bond and this explains the high hardness and insulating character of the high density BN polymorphs.

The distinction between *cBN* and *wBN* lies in the fact that the tetrahedral topology is obtained in a different way in cBN whose lattice is cubic of sphalerite type (space group Fd3m) and in wBN whose lattice is hexagonal of wurtzite type (space group $P6_3$ mc).

3. Mechanisms of transformation between the low density sp^2 BN polymorphs and the high density sp^3 hybridized BN polymorphs

The phase equilibrium diagram depicted in Fig.2 reproduced from reference [3] shows that by acting on the external factors, temperature and pressure, one may promote phase transformations between various BN polymorphs. The diagram is valid for the direct transformations, not involving the participation of catalysts.

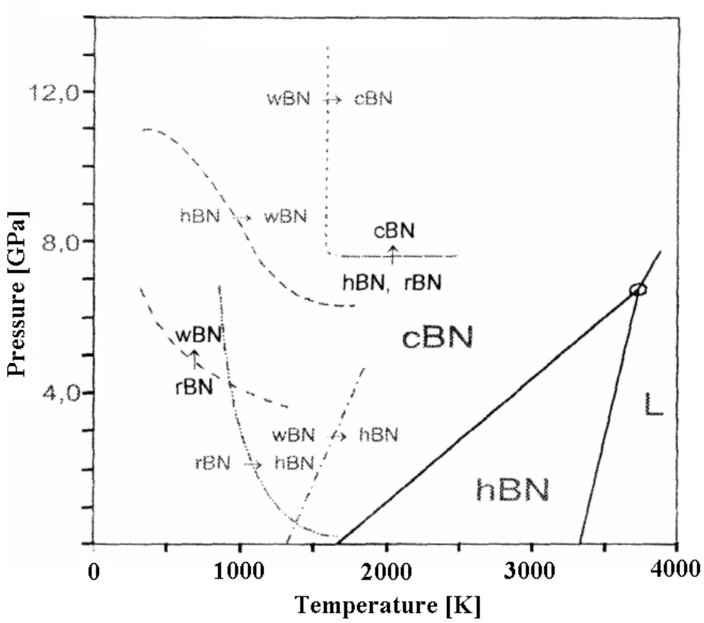

Fig.2. The P-T phase equilibrium diagram of boron nitride and the kinetic lines for the direct transformations between the BN polymorphs

Among the transformations indicated in Fig.2 the most interesting one from a practical standpoint is the hBN → cBN transformation intended to obtain borazone, the superabrasive that is not only in competition with diamond but also complements diamond in its applications [5].

From a crystallochemical standpoint what matters in this phase transformation is the fact that hBN has a planar distribution of the covalently bonded B and N atoms required by the sp^2 hybridization, whilst cBN has a tridimensional distribution of the covalently bonded B and N atoms required by the sp^3 hybridization.

Two crystallographic mechanisms *puckering* and *buckling* have been proposed [6] for the analogous carbon transformations (namely graphite → lonsdaleite), to account for the carbon atoms displacement out of the graphitic plane. Due to the perfect similitude between carbon and BN crystallochemical structures, one is permitted to consider such mechanisms also valid for boron nitride transformations.

As depicted in Fig.3a the *puckering* mechanism transforms a planar hexagon into a tridimensional structure type *chair* simply by displacing upwards the atom in one corner of the hexagon and by displacing downwards the atom in the opposite corner of the hexagon. At its turn the *buckling* mechanism transforms the planar hexagon into a tridimensional structure type *boat* by displacing upwards both atoms located in opposite corners of the hexagon. By creating tridimensional structures the puckering and buckling mechanisms allow the formation of sp^3 covalent bonds between atoms coming from adjacent planar layers.

A structural feature implied in these mechanisms consists in the fact that during the process new hexagons are formed in a direction perpendicular to the original one. For cBN these new hexagons have a *chair* type structure, whilst for wBN these new hexagons have a *boat* type structure, as we have marked by a hatching in Fig.1 in the corresponding unit cells.

How these mechanisms are working during the direct polymorphic transformations of BN is worthy to be analyzed when we have in mind the accompanying drastic hardness modification.

According to [7] the direct transformations of sp^2 bonded BN polymorphs into sp^3 bonded BN polymorphs may be explained by analogy with the allotropic transformations of carbon. Nevertheless one has to take into account the bonding energies in BN being lower than in carbon due to the ionic bond component.

Based on the total energy involved in the process, a model has been calculated in 1986 by Fahy et al. [8] for the mechanism of the direct transformation rBN→ cBN as depicted in Fig.3b (right side). According to this model, the hexagonal layers in rBN come closer and closer under the action of the applied pressure. During this process they preserve their planar shape as long as the. interplanar spacing decreases from the original value (3.34 A^o) to a value equal to d= 2.5 A^o Further on, the hexagonal layers begin to lose their planar shape by undergoing a deformation type puckering and during this process the three covalent bonds specific to the sp^2 hybridization gradually increase their length. An energy barrier is created during this process, that attains its maximum when the spacing between the deformed layers approaches a value equal to 2.2 A^o (the interplanar spacing specific for wBN as reported in Table 1). At this moment there is a sudden change in the angle between the covalent bonds that attains the value 109.47^o specific for the tetrahedral coordination of the sp^3 hybridized atoms in cBN.

In the above model the sp^2 precursor for obtaining the sp^3 hybridized cBN structure (the borazone) is rBN. As specified earlier the latter is a rarely encountered BN polymorph, the usual sp^2 polymorph being hBN .

If hBN (white graphite) is taken into consideration as a precursor for obtaining high density sp^3 hybridized BN polymorphs, two opportunities arise.

The first opportunity, depicted in Fig.3b (left side) is a straightforward transformation hBN→ wBN. It involves a puckering mechanism resulting in the tridimensional structure of wBN that contains boat type deformed hexagons in the direction of axis *c* (see Fig.1 - the hatched boat type hexagon-). In contrast to this, the puckering mechanism involved in the rBN→ cBN transformation (that we have examined in detail) results in the tridimensional structure of cBN that contains chair type deformed hexagons in the direction of axis *c* (see also Fig.1 -the hatched chair type hexagon).

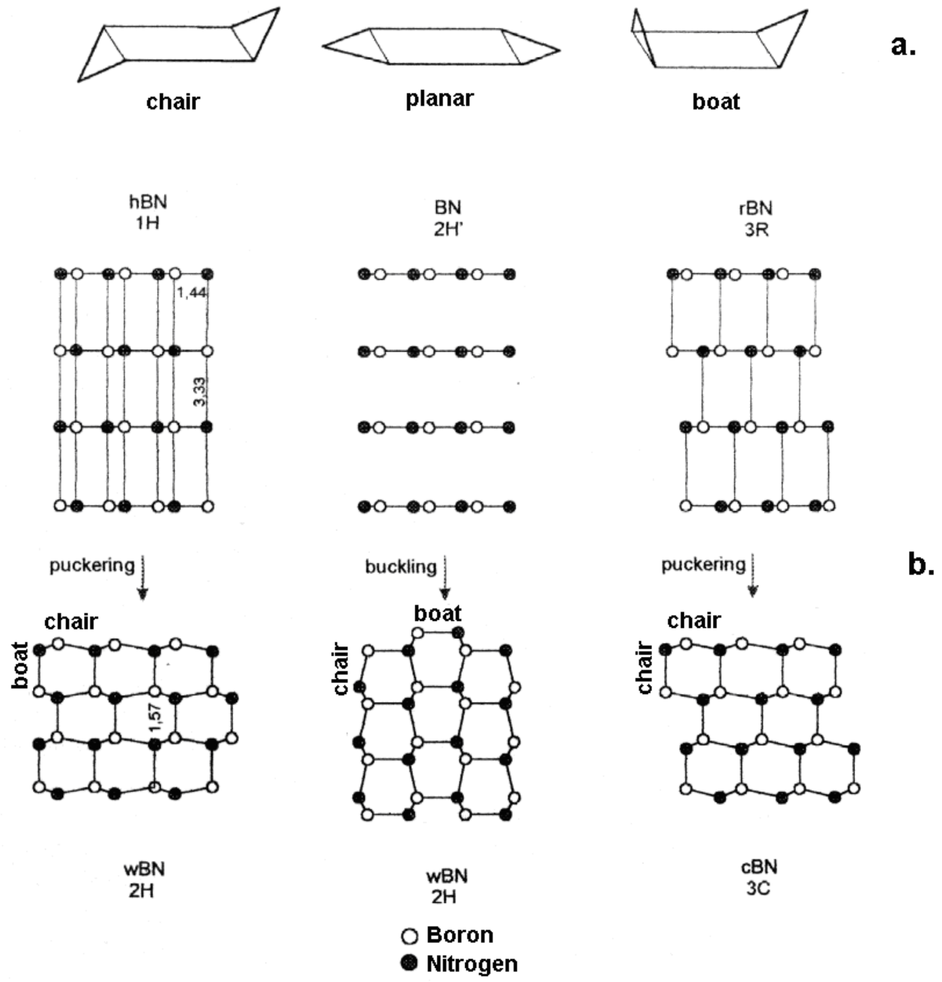

Fig.3. The puckering and buckling mechanisms

a. schematic representation of the ways to transform a planar hexagon into a *chair* type structure or a *boat* type structure

b. involvement of the puckering and buckling mechanisms in the polymorphic transformations of sp^2 hybridized BN polymorphs (hBN and rBN) into sp^3 hybridized BN polymorphs (wBN and cBN) - views along the *c* axis-

The second opportunity is the most interesting from a practical point of view because it is concerned with the transformation hBN (white graphite)→ cBN (boraxone) in a two stage process. In the first stage hBN transforms itself in rBN at high temperature and pressure. Further on, in the second stage, rBN transforms in cBN through the puckering mechanism already analyzed (Fig.3b, right side).

The transformation occurring in the first stage is considered to be of martensitic type [9], a diffusionless transformation involving the translation of the hexagonal layers on a distance equal to the length of the covalent interatomic bond. This stage is easily accomplished because it implies only the breaking of the weak van der Waals bonds between the layers. The second stage involving the puckering mechanism is again a diffusionless transformation that implies the atoms translation in a direction perpendicular to the hexagonal layers.

For sake of completeness we have indicated in Fig.3b (middle sketch) a transformation involving the buckling mechanism. Such a transformation has been put in evidence in pyrolytic boron nitride (pBN) obtained by the shock compression technique; it actually has the hBN structure (1H polytype) but with a strong preferred orientation of the crystallites. During the deposition process the 1H polytype of pBN may change its packing sequence from 1H to 2H' that is specific to graphite; later on the 2H' polytype transforms into wBN (2H polytype) by the buckling mechanism.

4. Conclusions

The examination of the mechanisms through which the low density-low hardness BN polymorphs transform into high density-high hardness polymorphs clearly demonstrates the reconstructive character of these phase transformations. The involved crystallographic mechanisms alter profoundly the atoms coordination and compactness as well as the nature and length of the atomic bonds. Such structural information on the reconstructive polymorphic transformations in boron nitride offer a quantitative base for evaluating the accompanying hardness modification. Even more it offers the possibility to discern between the role played by the crystallographic factors and the role played by the chemical factors in hardness modification.

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