U.P.B. Sci. Bull., Series B, Vol. 69, No. 2, 2007 ISSN 1454-2331

CRYSTALLOGRAPHIC FEATURES OF hBN AS A PRECURSOR IN THE cBN HIGH-TEMPERATURE-HIGH PRESSURE SYNTHESIS

Mădălina-Gabriela BALINT[1] , M.I. PETRESCU[2]

A fost efectuat un studiu comparativ pe 17 tipuri de pulberi de hBN cu diferite origini pentru a pune în evidenţă caracteristicile structurale ce influenţează comportarea acestora ca materie primă pentru sinteza catalitică a nitrurii de bor cubice superdure. Fiecare probă a fost caracterizată prin doi parametri structurali rezultaţi din prelucrarea unor informaţii diferite oferite de difractograma de raze X înregistrată experimental şi anume indicele de grafitizare G.I. şi parametrul p_3 *al ordinii tridimensionale indicând proporţia de defecte de împachetare turbostrat din structură. S-a făcut o încercare, neîntreprinsă până acum, de a stabili o corelaţie cantitativă liniară între aceşti parametri structurali aplicând un tratament statistic al datelor experimentale. Tentativa s-a dovedit interesantă, coeficienţii de corelaţie obţinuţi la un nivel de încredere de 95% fiind 0.8 când s-au luat în considerare toate probele investigate , respectiv 0.96 şi 0.88 când probele au fost considerate separat (cele comerciale produse de firme consacrate în domeniu, respectiv cele produse în scop de cercetare la Fabrica de diamante sintetice RAMI Dacia). Comportarea diferită a fost atribuită influenţei modului de fabricaţie asupra cantitaţii de defecte de împachetare a straturilor grafenice de tip turbostrat, şi eventual contribuţiei unor defecte de împachetare de tip politip.*

A comparative study was undertaken on 17 hBN types of powders of various origin in order to put in evidence the structural characteristics that are influential when hexagonal boron nitride is used as a raw material in the catalytic sythesis of the superhard cubic boron nitride. Each sample was characterized by two structural parameters obtained from different features of its recorded X-ray diffraction pattern, namely the graphitizing index G.I. and the three- dimensional order parameter p_3 *related to the concentration of the turbostratic stacking faults. An attempt was made to establish a quantitative linear correlation between these structural parameters by applying a statistical treatment to the experimental data. This attempt, not undertaken as yet, proved to be an interesting approach, because at a degree of confidence 0f 95% correlation coefficients were obtained as high as 0.8 when all investigated hBN powders were considered or 0.96 and 0.88 respectively when the group of commercial hBN powders produced by recognized companies in the field was considered separately from the powders of Romanian origin produced for research purposes at the RAMI Dacia Synthetic Diamond*

---

[1] Dr., RAMI Dacia Synthetic Diamond Factory, Bucharest, ROMANIA

[2] Reader, Dept. of Engineering and Management for Elaboration of Metallic Materials, University "Politehnica" of Bucharest, ROMANIA, ipetrescu@yahoo.com

Factory. This behavior was ascribed to the influence of the fabrication way on the amount of turbostratic stacking faults or to an eventual contribution of a different type of structural defects, namely the polytype stacking faults.

Keywords: hBN, X-ray diffraction, p_3 and G.I. structural parameters, quantitative correlation, turbostratic and polytype stacking faults

1. Introduction

As detailed in a previous paper [1] boron nitride (BN) is a man made material that is isoelectronic and isostructural with natural carbon and as a consequence it exhibits the same polymorphic varieties. Hexagonal boron nitride (hBN) is isostructural with graphite having the same layered structure, whilst cubic boron nitride (cBN) is isostructural with diamond.

Hexagonal boron nitride also termed white graphite has a set of properties that recommend it for a large variety of applications [2,3]. Due to the localized character of the π electrons involved in the van der Waals inter-layer bond hBN is an electrical insulator and has a white color in contrast with graphite. Due to its chemical inertness and high melting point associated with the strong σ type covalent intralayer bonds hBn is one of the most valuable refractory nitrides able to work up to 3000^{o} C. Similar to graphite it has a low density, it is a very good thermal conductor and has excellent lubrication properties. As a solid lubricant hBN is superior to graphite by the absence of water molecules between its graphene layers and by its resistance to oxidation and so it may work in a wide temperature range, from very low temperatures (as in cosmic space) up to 900^{o} C in oxidizing atmospheres. Such properties make hBN also useful as an additive in silicon liquids, in resins and other compounds in order to improve the thermal conductivity and diminish the thermal expansion. In composite ceramic materials an addition of hBN may improve the thermal shock resistance and help to control the electrical resistivity.

Perhaps the most exciting applications of hBN are found in high pressure technology and superhard materials synthesis. Without any doubt in this line the most prominent application consists in the key role played by hBN as a raw material for obtaining cBN, the latter being one of the most prized superabrasives second in hardness after diamond. Nevertheless other applications of hBN in high pressure- high temperature technology are to be taken into consideration as well [3]. For instance hBN is a useful gasket material and an excellent pressure transmitting material that may be used up to 3000^{o} C, in contrast with pyrophillite that is limited in such applications to 2500^{o} C. Recently hBN has been proposed as a pressure calibration material in diamond and cBN synthesis along with NaCl or MgO, because its compressibility depends on the degree of space order of the graphene layers.

All properties that recommend hBN for its large variety of applications are strongly dependent on its crystalline perfection. This is especially true when hBN is considered as the raw material in cBN synthesis. Indeed hBN has to accomplish at least three basic requirements for this application: high purity, good crystalline structure and easy compacting ability. The nucleation and growth rates of cBN during its high P-high T synthesis depend in a sophisticated manner on the hBN structural characteristics. So the selection of proper hBN materials for this application needs a thorough-going research.

In this paper we have focused on the crystallographic peculiarities required to make hBN an efficient precursor in the high P-high-T catalytic synthesis of cBN. In so doing a large number of hBN samples of various origin have been characterized by X-ray diffraction in order to put in evidence the degree of structural order and the types of defects that may be influential in the cBN synthesis.

2. Experimental methods and materials

A. Details on the X-ray techniques applied

The hBN powders for fabricating cBN have an intermediate structure between the hexagonal boron nitride and turbostratic boron nitride as defined in [1]. It is worthy to remind that in perfectly ordered hBN the hexagonal layers are coincident along the *c* axis (stacking sequence AA’AA’, polytype 1H). In turbostratic BN (tBN) the hexagonal layers are mostly parallel but each layer is randomly translated and rotated to the layer above and below it.

To investigate how far apart the hBN powder is from the turbostratic structure and how close it is to the perfectly ordered hexagonal structure we have made recourse to X-ray diffraction techniques and to special ways to interpret the obtained X-ray diffraction patterns

The three- dimensional order parameter p_3 and the concentration of the turbostratic stacking faults

As stated above there is limited three- dimensional order in tBN and so tBN may be considered as a very defective hBN material with a large amount of stacking faults.

The stacking faults that can be formed in the hBN structure are principally of two different types. The *polytype stacking faults* involve a shift of part of the hexagonal layers into positions equivalent to positions in the graphite structure (stacking sequence ABAB), with the Burgers vector of the corresponding partial dislocation $(1/3)\cdot a[10\bar{1}0]$. These stacking faults can be regularly distributed along the [0001] direction or *c* axis due to polytypism [4]. In contrast to graphite the occurrence of this type of stacking faults is considered to be poor in hBN. The *turbostratic stacking faults* are formed by a random displacement of the layers in their planes in such a way that there is no correlation between the neighboring layers in the defect region. Their concentration can reach unity when the structure is turbostratic. Accordind to Sato [5] polytype stacking faults give rise to broadening of the (hkl) diffraction lines with $l \neq 0$ and $h-k \neq 3n$ while turbostratic stacking faults broaden all (hkl) lines with $l \neq 0$.

Based on the analysis of the broadening of the (hkl) lines with $l \neq 0$ Kurdyumov [6] has developed a method of estimating the concentration of turbostratic stacking faults. If this concentration is denoted γ one may calculate $p_3 = 1-\gamma$. The three-dimensional order parameter p_3 computed by Kurdyumov's method may be obtained by calculating γ from relationship (1):

$$\beta=0.03d^2_{hkl}l(\tan\theta).\gamma/(1-\gamma)^{-½} \tag{1}$$

where β is the half-width of the (hkl) line in the X-ray diffraction pattern, expressed in radian, d_{hkl} is the interplanar spacing between the (hkl) planes, and θ is the Bragg angle of the (hkl) reflection. In order to calculate the concentration γ of the turbostratic stacking faults it is convenient to use the (112) line whose broadening does not depend on the polytype stacking faults. To calculate the width β for the line (112) in relationship (1) it is appropriate to use the width B of the nearby (110) line because B_{hk0} includes both the instrumental width and the structural broadening due to the dispersed nature of the coherent scattering regions and the deformation of the lattice. The method for separating them depends on the functions that describe the profiles of the lines (either Gauss or Cauchy function)

The graphitizing index G.I.

The graphitizing index G.I., as defined by Thomas [7] is based on the modification of the X-ray diffraction patterns of boron nitride during the graphitizing process. The most significant evidence marking the onset of three-dimensional order is the resolution of the broad (10) reflection into the (100) and (101) reflections, accompanied by the sharpening of the (002) reflection and the appearance of the (004) reflection, as clearly depicted in the series of diffractograms in Fig.1 reproduced from reference [7]. As ordering proceeds, a new reflection appears and increases in intensity, namely the (102) reflection, whilst the resolution between the (100) and (101) peaks increases (see Fig.1).

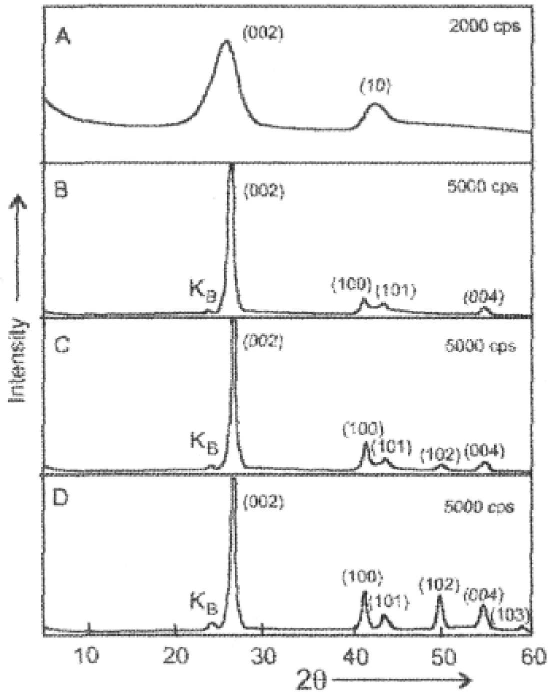

Fig.1. Diffraction patterns of boron nitride reproduced from [7]
A. turbostratic boron nitride,
B. partial three-dimensional ordering,
C. more advanced partial three-dimensional ordering,
D. complete three-dimensional ordering

To characterize the degree of three-dimensional ordering the graphitizing index G.I. is defined by relationship (2):

$$G.I.=[area_{(100)}+area_{(101)}]/area_{(102)} \qquad (2)$$

The areas involved in this definition are represented in Fig.2 by a hatch or a double hatch in the schematic illustration of an X-ray diffraction pattern.

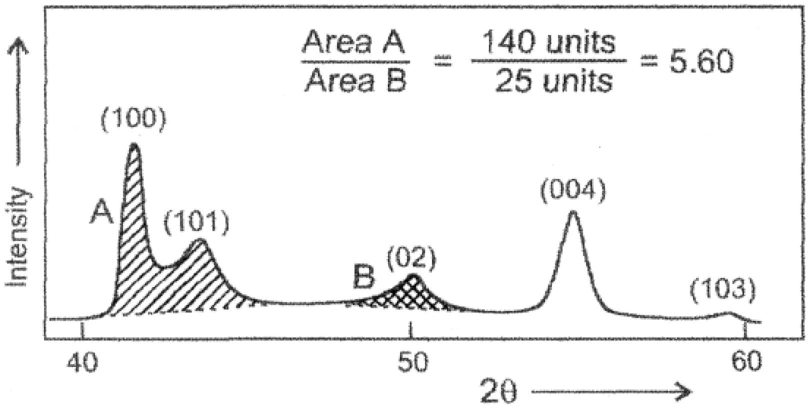

Fig.2 Illustration of the defined areas used in calculating the graphitizing index G.I. [7]

According to this definition a higher value of G.I. would mean less three-dimensional ordering in hBN because the denominator in eq. (2) namely area$_{(102)}$ is small. A lower value of G.I. means more three-dimensional ordering in hBN because the denominator in eq. (2) namely area$_{(102)}$ becomes larger (see Fig.1) Powders with a G.I. value of 1.6 are considered to have a perfect three-dimensional ordering in their hBN structure, whilst a value G.I. of about 50 is considered to be the upper limit for a disordered turbostratic structure. Experiments of cBN snthesis have imposed the criterion of a graphitizing index less than 7.5 for the hBN precursor.

B. Details on the investigated hBN powders

A number of 17 different hBN powders with various degrees of three-dimensional ordering of various origin have been investigated and characterized by the above mentioned structural parameters p_3 and G.I. Based on this structural characterization some of the investigated hBN powders have been selected for a further study concerning their behavior during the catalytic synthesis of cBN. Among the 17 investigated hBN powders, 6 were of Romanian origin produced for research purposes at the RAMI Dacia Synthetic Diamond Factory.; these samples were denoted by symbol A (namely A1, A2, A3, A4, A5, A6). The remaining 11 powders (denoted by symbol B (namely B1, B2, B3, B4, B5, B6, B7, B8, B9, B10, B11) were produced by recognized companies in the field: ESK-Elektroschmelzwerk Kempten GmnH, (samples B1-B4, B7), HCST (sample B5) Showa-Denko Japan (sample B6), UK Abrasives Inc.(sample B8), Advanced Ceramics Corp. (samples B9, B10).

3. Results

For all investigated hBN powders the X-ray diffraction patterns have been recorded by means of a Philips PW 1390 diffractometer that has been used in step by step mode ($40s/0.01^{o}\,2\theta$), employing filtered Cu Kα radiation (40 kV/20 mA).

A special attention was paid to sample preparation for avoiding the preferential orientation of the hBN crystallites. Indeed on account of their layer type structure the hBN crystallites have a tendency to arrange themselves with the *c* axis perpendicular to the free surface of the powder sample, and this tendency is more pronounced if the crystallites size is large. As a result there isn't an equal probability for all crystalline planes to be exposed to the X-ray beam, and this leads to a very high intensity for the (002) reflection at the expense of the reflections produced by the planes parallel to axis *c.* In these conditions the G.I. values calculated by means of relationship (2) are underestimated in comparison with the real ones.

In order to check the absence of the preferred orientation in the powder sample we have measured for each sample the intensity ratio of the (100) and (004) reflections that has a theoretical value equal to 15/ 6, and we have reiterated the sample preparation until the Thomas criterion [7] was satisfied. This criterion states that as long as the intensity of the (004) reflection is smaller than the intensity of the (100) reflection the graphitizing index G.I. is not appreciably influenced by the preferred orientation of the crystallites in the powder sample.

For each sample we have calculated from the experimental diffraction pattern the parameter p_3 by means of eq.(1) according to Kurdyumov's method and parameter G.I. by means of eq.(2) according to Thomas's method. In order to separate the widths of the (112) and (110) lines we have used the following relationship for calculating β required in eq. (1):

$$\beta=B_{(112)}-[B^{2}_{(110}/B_{(112)}] \qquad (3)$$

which was valid because the line profiles are described by functions between the Gauss and Cauchy distributions

The values of the structural parameters, p_3 and G.I., that characterize the three-dimensional ordering in the investigated hBN powders are summarized in Table1. For sample B11 which has extremely large crystallites the obtained structural parameters have to be considered with caution because of the preferred crystallites orientation during sample preparation that was not possible to be avoided. Indeed the best intensity ratio for the reflection (004) towards (100) that was possible to be obtained for this sample was 3/2 and so an underestimated value for G.I. is likely to be obtained on account of the preferred crystallites orientation in the powder sample.

Table 1

Values of p_3 and G.I. structural parameters obtained for the investigated hBN samples

	A9	A3	A2	A4	A1	A5	B7	B1	B4	B3	B9	B6	B2	B5	B10	B8	B11
p_3	0.87	0.87	0.90	0.90	0.90	0.91	0.89	0.93	0.94	0.95	0.95	0.96	0.97	0.97	0.97	0.98	0.99
G.I.	7.50	4.95	3.88	3.65	2.66	2.27	7.50	4.45	4.05	3.11	1.98	1.56	1.96	1.96	1.41	1.39	0.99

The experimental data in Table 1 have been separated in two groups according to the origin of the investigated powders: group A (Romanian origin produced for research purposes at the RAMI Dacia Synthetic Diamond Factory) and group B (hBN powders produced by recognized companies in the field). The data in each group were arranged in a decreasing sequence for parameter p_3. With a few exceptions this was also the decreasing sequence for parameter G.I. Table 1 also shows that parameter G.I. seems to be more sensitive for characterizing the degree of structural order, because samples showing the same value for parameter p_3 may have a range of values for parameter G.I.

4. Discussion

The self-consistency manifested by the values of the two structural parameters p_3 and G.I. in Table 1 was considered to be worth of closer examination, especially when one has in mind that each of these structural parameters stems from different features of the recorded X-ray diffraction pattern, as indicated by eq.(1) and eq.(2). Indeed each of these two structural parameters p_3 and G.I. reflects distinct crystallographic characteristics of the hBN powder sample resulting from its specific way of fabrication. The relationship between these structural parameters for hBN has not been studied on a quantitative basis as yet

To this purpose a search of a possible correlation between these structural parameters was undertaken. To put in evidence a possible correlation between two experimentally measured parameters *x* and *y* we have applied the well known method of the correlation analysis [8] by supposing that both regression functions (empirical regression of *y* on *x,* as well and *x* on *y*) are linear functions. The degree of correlation between *x* and *y* was characterized by the correlation coefficient ρ according to relationship:

$$\rho = M\,[(x-a)/\sigma_x]\,[(y-b)/\sigma_y] \qquad (4)$$

where a = Mx *and* b= My represent the centers of repartition for the variables *x* and *y* , whilst σ_x and σ_y are their empirical dispersions. If there is no correlation between parameters x and y their correlation coefficient ρ equals zero. Increasing ρ means a tighter and tighter correlation between x and y.

The meaning of the correlation coefficient ρ between the structural parameters p_3 and G.I. was checked by comparing its absolute value multiplied by $(n-1)^{1/2}$ with its critical value H for the degree of confidence 95%. If for the experimental value of ρ the product $|\rho.(n-1)^{1/2}|$ is higher than the critical value H then one may consider that the two variables are correlated at a degree of confidence equal to 95%.

Fig.3 is a graphical representation of our experimental values p_3 versus G.I. By applying the above mentioned quantitative considerations a correlation coefficient ρ between these two parameters equal to -0.80 at a degree of confidence equal to 95% was obtained. Sign minus for the correlation coefficient ρ simply reflects the inverse proportionality between p_3 and G.I. Because this calculus was based on the supposition of a linear correlation between the investigated parameters we have also indicated in Fig.3 the equation of the straight line that correlates the parameters p_3 and G.I. obtained by the least squares method.

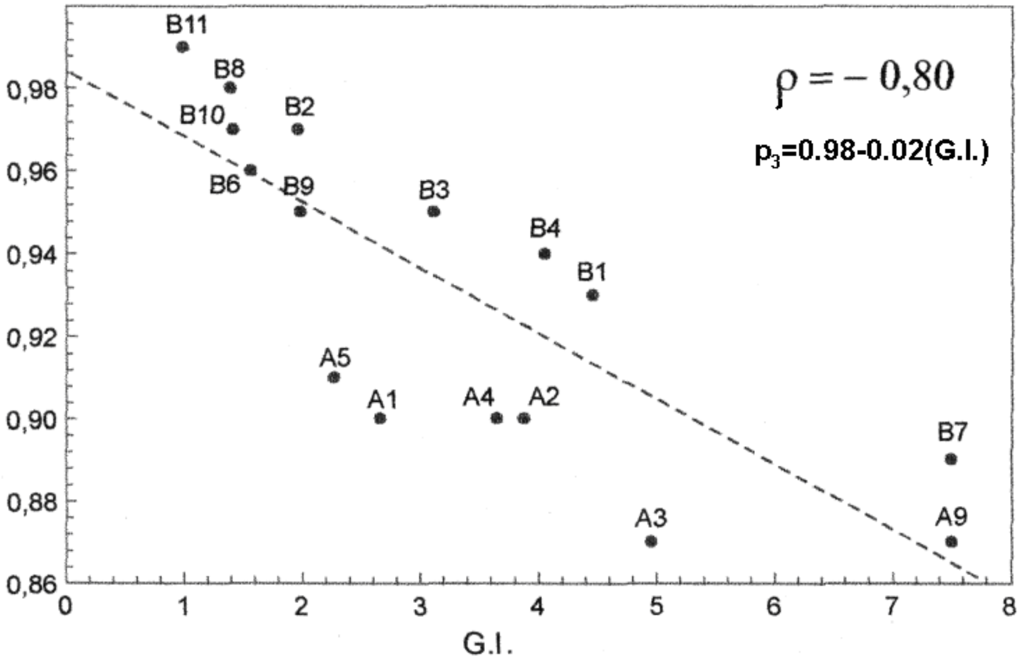

Fig.3 Calculated linear correlation between the experimental parameters p_3 and G.I. at a level of confidence equal to 95% for all hBN investigated samples

It is easy to see in Fig.3 that the points for the samples of Romanian origin produced for research purposes at the RAMI Dacia Synthetic Diamond Factory denoted by symbol A are located below the correlation straight line, whilst the points denoted by symbol B for the commercial hBN powders produced by recognized companies in the field are located above the correlation straight line. If the two groups of hBN powders were considered separately an improved correlation coefficient between the parameters p_3 and G.I. was obtained, namely $\rho = -0.88$ for the samples in group A and $\rho = -0.96$ for the samples in group B, respectively, at the same degree of confidence 95%. This behavior suggests a significant difference between the two groups of hBN powders.

A possible interpretation of this different behavior is that at the same value of the graphitizing index G.I. the hBN powders in group A contain a larger amount of turbostratic stacking faults than those in group B.

A second interpretation, which for the moment is just a supposition because it requires a more detailed investigation, is that polytype stacking faults have to be considered along with the turbostratic stacking faults when the three-dimensional ordering in hBN is described by the stacking sequence of the hexagonal crystallographic planes and associated defects. Such an approach may lead to a different correlation between the structural parameters G.I. and p_3 for hBN powders that contain and those that do not contain polytype stacking faults. It is true that for the moment the polytype staching faults are considered to be unlikely to occur in hBN. This statement is based on Kurdyumov's remark [6] that the rhombohedral modification of boron nitride (rBN) which involves the existence of an ordered arrangement of polytype stacking faults is very seldom encountered, in contrast with graphite which sometimes may contain as much as 20% rhombohedral phase. This difference between hBN and graphite concerning the likelihood of appearance of rhombohedral phases and associated polytype stacking faults is to be ascribed to differences between the interlayer bonds existing in the two substances and as a consequence between the energy of the corresponding phases. Indeed according to reference [9] the energies for the two graphite allotropes, -rhombohedral and hexagonal -, are the same (-1.19 kcal/mole), whilst for BN there is a notable difference between the energy of rhombohedral and hexagonal phases (-1.57 cal/mole and -1.75 cal/mole). However depending on the way of fabrication the existence of polytype stacking faults cannot be excluded in turbostratic boron nitride. Further results to be presented in a next to come paper concerning more extended correlations between p_3 and G.I on one side and structural parameters concerned with the crystallites size seem to bring support to this supposition.

5. Conclusions

1. The comparative study undertaken in this paper by X- diffraction on the structural parameters that characterize the three- dimensional ordering in hexagonal boron nitride (17 powder samples of various origin) have put in evidence notable differences induced by the degree of graphitization of hBN as a result of the way of fabrication.

2. The turbostratic disorder in the stacking of the hexagonal crystallographic planes in the investigated hBN powders was characterized by two structural parameters. The three-dimensional order parameter $p_3 = 1-\gamma$ (where γ is the concentration of the turbostratic stacking faults) was derived by a precision procedure from the structural broadening (as distinct from the instrumental broadening) of the (hkl) reflections with $l \neq 0$ in the X-ray diffraction pattern of the hBN powders. Values for p_3 have been obtained in the range 0.87- 0.98 indicating a concentration γ of the turbostratic stacking faults from 13% down to 2%

3. In a distinct estimation of the three-dimensional ordering in the investigated hBN powders the graphitizing index G.I. was calculated from different features of the experimental X-ray diffraction pattern, namely from the relative importance of the areas under selected recorded diffraction lines profiles. Values for G.I. in the range 1.39 -7.5 have been obtained, whose significance may be better seized if one has in mind that G.I.= 1.6 characterizes a well crystallized hBN powder, whilst G.I. = 50 is the upper limit for a disordered turbostratic structure.

4. An attempt, not tried before in the field, to establish a quantitative correlation between parameters p_3 and G.I. proved to be a successful one. Indeed a correlation coefficient $\rho = -0.80$ at a degree of confidence equal to 95% was obtained if all 17 investigated hBN powders were considered. However if the hBN samples denoted A (of Romanian origin produced for research purposes at the RAMI Dacia Synthetic Diamond Factory) and the hBN samples denoted B (commercial hBN powders produced by recognized companies in the field) were considered separately improved correlation coefficients were obtained ($\rho = -0.88$ for the samples in group A and $\rho = -0.96$ for the samples in group B).

5. The clear distinction between hBN powders of different origin attested by distinct linear correlations between the structural parameters p_3 and G.I. was ascribed in this paper either to a different amount of turbostratic stacking faults or to an eventual contribution of a different type of structural defects, namely the polytype stacking faults.

R E F E R E N C E S

[1]. *M.I.Petrescu, Mădălina- Gabriela.Balint,* U.P.B. Sci. Bull., series B, 63 (1), 2007, p.35- 52

[2]. *R.Haubner, M.Wilhelm, R..Weissenbacher, B.Lux,* Structure and bonding, 102, 2002, p.1

[3]. *J.H.Kim,* Journal Sci. Instruments, 42,1965, p.374

[4]. *K.Yagodzinskii,* Kristallografiya, 16, 1971, p.1235

[5]. *R. Sato,* Journal Phys.Soc. Japan, 21, 1966, p.1623

[6] *A.V.Kurdyumov,* Kristallografiya, 20, 1975, p.969

[7]. *J.Thomas, N.E.Weston, T.E.Connor,* Journal Amer. Chem.Soc.,84, 1963, p.4619

[8]. *I.Z.Rumshisk,* Matrematical treatment of experimental data, (in Romanian), Technical Publ.House, Bucharest, 1974

[9].*I.V.Nikolskaya, L.M.Prezman, V.M.Zorkii, L.B.Nepomnyanskaya, L.F.Vereshchagin, Ya.A. Kalashnikov, E.M.Feklichev,* Zh.Fiz.Khim., 43,1969, p.2614