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Structure of the boron nitride E-phase: Diamond lattice of $B_{12}N_{12}$ fullerenes

A.V. Pokropivny

Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, Krzhyzhanovsky str. 3, 03142, Kiev, Ukraine

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Abstract

The molecular and crystal structures of the boron nitride E-phase are determined. Analysis of all calculated for the first time main peaks of X-ray diffraction patterns (6.28, 3.85, 3.28, 2.72, 2.50, 2.22, 2.09, 1.92 Å) in comparison with experimental ones indicates that E-BN has the diamond-type lattice (the cell constant $a=10.877$ Å, the space group $Fd3m$ or O_h^7) formed with T_h symmetry $B_{12}N_{12}$ molecules copolymerized by the hexagonal faces. Hence we propose to mean "extradiamond" term instead of "explosion" term in the E-phase name. Extradiamond-$B_{12}N_{12}$ has a framework type of faujasite and can be referred to as $[B_{12}N_{12}]$-**FAU** zeolite. Ideal crystal of E-BN has 192 atoms per unit cell and theoretical density of 3.074 g/cm^3.

Keywords: Diamond-like boron nitride; Fullerene; Microstructure; X-ray diffraction

Boron nitride E-phase was synthesized for the first time in 1965 by Batsanov et al. [1]. The explosive shock compression of turbostratic boron nitride (t-BN) was found to result in the formation of transparent crystallites of a new phase with a density of 2.5–2.6 g/cm^3 and with the individual X-ray diffraction (XRD) pattern and IR spectrum [1–3]. This new phase was called the E-phase or E-BN owing to the method (explosion) by which it was synthesized. E-BN XRD pattern was interpreted in a rhombic syngony with the parameters: (i) $a=7.2$ Å, $b=8.1$ Å, $c=18.9$ Å [2], and (ii) $a=11.136$ Å, $b=8.058$ Å, $c=7.400$ Å [3].

Akashi et al. [4,5] obtained the E-phase with a twice repeated shock effect on hexagonal boron nitride (h-BN) [4] and with a once shock effect on wurtzite-type (w-BN) and zincblende-type (z-BN) boron nitride [5] using a plane-wave generator. E-BN was identified as a fcc structure with a lattice parameter of 8.405 Å [5].

Later E-BN was obtained with the several different non-explosive methods, namely by reactions with discharge [6,7] and laser [8–11] assistance, plasma- [12], photon- [13] and electric field- [14] assisted chemical vapor deposition, electrostatic acceleration of powders [15] and supercritical fluid [16] methods.

By that time, however, the molecular and crystal structures of E-BN were not yet clearly resolved. There were only several unsuccessful attempts to identify the crystal structure of E-phase from a XRD patterns analysis, as mentioned above [1–3,5]. But the authors [5] did not compare their XRD patterns with the full XRD pattern of E-BN [1] and the authors [1–3] interpreted E-phase rhombic cell by two different ways, which was incorrect.

Olszyna et al. [15] proposed the E-BN molecular structure as the cluster B_9N_9 with irregular hexagons. A theoretical distribution of the vibrational spectrum of the model cluster was calculated (902, 960, 1247, 1459 cm^{-1}) and compared with the IR spectrum, measured experimentally. But the authors [6] did not compare their IR spectrum with the full IR spectrum of the E-BN (450, 550, 700, 800, 940, 1030, 1110, 1200, 1260, 1400, 1650 cm^{-1} [1,2]), but only with its fragment, which was incorrect. Beside this, there was no analysis of the E-BN crystal structure.

It is necessary that the E-phase model adequately represents both the molecular and crystal structures. The new Batsanov's model [17] was the only one that had represented this. Batsanov noticed [17] that impulse methods of the E-BN synthesis [4–9], on a whole, were identical to the methods of carbon fullerenes synthesis. In his opinion, a 3D polymerization under high pressure is accompanied by a decrease of the fullerenes size and by origins of covalent bonds between

E-mail address: apokr@ipms.kiev.ua.

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fullerenes. As a result, an elemental rhombic cell of E-BN contains 3D polymerized BN-fullerenes of two types: on 60 and 24 atoms. Fullerenes are stabilized by an inclusion in their structures of oxygen atoms.

But it should be noted that Batsanov's model [17] do not represent the E-phase structure well. First of all, there are no accurate parameters of a rhombic cell. Next, there is no information on the structures of fullerenes and methods of their connection in a rhombic cell. And finally, a presupposition on the presence of oxygen in the E-BN structure is questionable, since other authors do not confirm this [4–16].

What is then the structure of E-phase?

There is unmistakable proof that the E-BN has a diamond-like crystal structure. The main idea of a nearness of E-phase to diamond lies in the next experimental fact. First four intensive peaks at the XRD pattern of E-BN [1], namely 6.28 Å, 3.85 Å, 3.22 Å and 2.686 Å are in an excellent agreement with those of diamond [18], namely (111), (211), (311) and (400) differing by factors of 3.063, 3.056, 3.003, 3.035, respectively, see columns 2 and 6 in Table 1. Only from this fact can one suppose that E-phase may be a material with the crystal structure of diamond and with a lattice parameter that ranged from $3.003a_0=10.72$ Å to $3.063a_0=10.93$ Å, where $a_0=3.57$ Å is a lattice parameter of diamond.

Three other intensive peaks at the XRD pattern of the E-BN, namely 2.201 Å, 2.076 Å and 1.955 Å, are in an excellent agreement with the (422), (333), and (440) diamond peaks, differing by factors of 3.053, 3.053, and 3.128. Only (331) diamond peak has no analogue at this E-BN XRD pattern. All of these main peaks are represented in Table 1 by a bold type font.

The parameter of a diamond cell of the E-BN calculated from the main (111) peak equals to $a=6.28*(1+1+1)^{1/2}=10.877$ Å. We proceed with the analysis, taking the value to be valid. Listed in column 4 of Table 1 are calculated values of the E-BN interplanar distances $d_{hkl}=a/(h^2+k^2+l^2)^{1/2}$, where h, k, and l are the Miller indices. Results of a comparison of the experimental and calculated interplanar distances indicate the most of calculated interplanar distances, namely 26 from 33 to be in an excellent agreement with experimental ones.

But the next question arises here: What is the molecular structure of diamond-like E-phase?

Table 1
Experimental and theoretical XRD patterns for E-BN and diamond (interlayer distances and intensities)

Indices	Extradiamond-$B_{12}N_{12}$ (E-BN)				Diamond			
hkl	Experiment [3]		Calculation		Experiment [18]		Calculation	
	d, Å	I/I_0, a.u.	*d*, Å	I/I_0, a	*d*, Å	I/I_0, a.u.	*d*, Å	I/I_0, a.u.
111	**6.28**	**100**	6.280	100	**2.05**	**100**	2.061	100
210	4.85	20	4.864	–	–	–	–	–
211	4.25	10	4.441	–	–	–	–	–
220	**3.85**	**50**	3.846	8.4	**1.26**	**80**	1.262	26
300, 221	3.54	20	3.626	–	–	–	–	–
310	3.36	10	3.440	–	–	–	–	–
311	**3.22**	**100**	3.280	3.3	**1.072**	**70**	1.076	8
222	3.04	20	3.140	–	–	–	–	–
320	2.983	10	3.017	–	–	–	–	–
321	2.784	20	2.907	–	–	–	–	–
400	**2.686**	**50**	2.719	0.27	**0.885**	**40**	0.893	16
411, 330	2.567	10	2.564	–	–	–	–	–
331	–	–	2.495	3.0	0.813	60	0.819	12
420	2.430	10	2.432	–	–	–	–	–
421	2.298	10	2.374	–	–	–	–	–
422	**2.201**	**50**	2.220	0.0001	**0.721**	**90**	–	–
333, 511	**2.076**	**50**	2.093	0.93	**0.680**	**60**	–	–
440	**1.955**	**50**	1.923	1.81	**0.625**	**40**	–	–
522, 441	1.901	10	1.893	–	–	–	–	–
531	–	–	1.839	0.098	0.597	60	–	–
532	1.769	10	1.764	–	–	–	–	–
620	1.696	20	1.720	0.00002	0.558	50	–	–
533	–	–	1.659	0.86	0.538	30	–	–
444	–	–	1.570	0.32	0.507	20	–	–
711, 551	1.544	20	1.523	0.006	0.496	40	–	–
642	–	–	1.454	0.14	0.473	70	–	–
731, 553	1.401	10	1.416	0.088	0.462	60	–	–
800	1.358	10	1.360	0.013	0.442	10	–	–
733	1.335	10	1.329	0.25	0.432	10	–	–
822, 660	–	–	1.282	0.17	0.417	50	–	–
751, 555	1.255	10	1.256	0.014	0.409	40	–	–
840	–	–	1.216	0.18	0.397	30	–	–
921, 761	1.172	10	1.173	–	–	–	–	–

Bold type peaks indicate propinquity of the crystal structures of E-BN and diamond.