

# Anti-Graphene

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### ABSTRACT

Another bluff wave called Graphene has rolled through modern Science. And it has once again confirmed that quasi-scientific speculations without taking into account the Fundamental Laws only lead to huge waste of effort and resources. But the wave itself was able to arise because it was not out of nowhere. Nobel laureates, who were in a hurry to get money, simply stated what was, in principle, expected, but from the prevailing erroneous Model of Graphite. And, thus, with their ignorant "proofs" they led the research of thin graphite layers down the wrong path. The analysis carried out in this article, using the example of the SIMPLE Graphite Material and its ultra-thin layers in a congruent matrix of boron nitride, shows how it is possible to create a whole class of fundamentally new, real materials. The ideal correct structure of thin layers of rhombohedral graphite, up to mono atomically thin, can be obtained not for a freely suspended (on sticky tape) film and not due to Van der Waals forces, as graphenologists claim, but in a congruent matrix - a crystal of rhombohedral boron nitride. And a radical improvement in the properties of materials can be obtained on the basis of truly unusual properties of such graphite layers with an undamaged surface, and in no way on the basis of a graphene that does not correspond to the real material.

**Keywords:** Van Der Waals Forces, Chemical Bond, Translational Invariance, Graphene, Real Characteristics of Materials

### Preamble

I feel partly guilty that the dirty graphene wave could have emerged at all.

On the one hand, during half a century of work at the Academy of Sciences, I saw its degeneration and that illiterate careerists were climbing into Russian academics, who supported the nomination of also illiterate Russian specialists in adhesive tape for the Nobel Prize.

On the other hand, it was our employee, being the author of a handbook on graphite and nitrides published in Springer, who did not even bother to look into the scientific journal of our institute, where our article with Sharupin, correcting the models of graphite and boron nitride, had long been published. And he inserted into the international handbook an ancient, completely useless

(as the authors themselves wrote in the conclusion) American article. So the general public had ideas about graphite from the beginning of the last century, which prompted graphenologists, who have little understanding of science, to childish fantasies on the topic of graphite. And on the third hand, the energetic careerist, the late director of our very own Ioffe Institute, Zhores Alferov, set an example for other swindlers of how to promote any nonsense for a Nobel Prize (as Academician Prokhorov, who deservedly received the Nobel Prize for LASER, said about the Alferov Prize at the National Conference on Crystal Growth in 2000: We know what Nobel Prizes are given for now).

I have already written a lot about the fact that graphene was the name given to speculations on graphite that are far from science in my popular science articles on the website of the Nanotechnology Society of Russia [1,2]. And in Wikipedia, in the article on Van der Waals forces, I also wrote that these forces, introduced for crystals formed from deeply cooled inert gases, cannot in any way be used to describe the properties of

refractory crystals and their monatomic films. But graphene speculations did not arise out of nowhere - graphite, a well-known layered mineral, has been studied for a long time. And it was these early studies, believing that it is the monatomic layers that slide in graphite, that Pauling used to construct a model of flat electron ( $\sigma$ ) orbitals that connect carbon atoms in graphite layers into hexagons [3]. But Pauling, as a chemist, could not ignore the fact that the carbon atom has 4 valence electrons and introduced an additional  $\pi$ -orbital, which he assumed to bind (weakly, slipperily, since the orbitals are blurred throughout the layer) the hexagons of different layers. But this crude model did not take into account the spatial distribution of interlayer bonds and their localization on carbon atoms, which also required their ordering (translation) in the crystal. Uniform blurring of interlayer electrons created the illusion of their uniform distribution throughout the layer, which led to a purely theoretical misconception that the bonds between atomic layers are formed due to van der Waals forces [4]. At the same time, the compilation works of Dreselhaus [5] also did a disservice to the science of graphite.

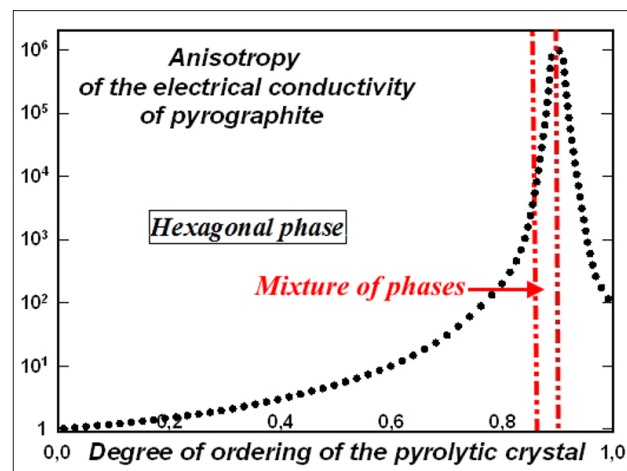
These abstract ideas about graphite, contradicting both the known relatively small anisotropy of its Debye temperature and the fact that graphite crystals do not collapse up to 3000 degrees, based on the primitive idea of the sliding of graphite layers (in reality, graphite flakes slide, not monoatomic layers in them) formed both the theoretical models of graphite energy bands and the drawn, free-hanging and in a vacuum monoatomic layers of graphite, called graphene. Although it is clearly visible, even in the example of a balloon, that without external support the film will shrink. It was also already known that pieces of graphite monoatomic film shrink into balls, called fullerenes. Landau's theorem also speaks about this, proving that purely one-dimensional and two-dimensional objects in a free state cannot exist. But this is not the first dirty wave in science, which has involved a lot of researchers – as they used to say at our Ioffe Institute – those who have done nothing worthwhile in science are rushing to jump on the dirty wave.

## C&BN

Unlike dreamers with sticky tape, we, together with B.N. Sharupin [6], who created the first boron nitride in the world, studied pyrocrystals of boron nitride and graphite with different degrees of ordering of the crystal lattice in parallel. In this case, it was verified that up to pressures of 60 kBar, liquid metals do not penetrate between monoatomic layers - the liquid metal enters only defects between graphite flakes. An increase in electrical conductivity along the C axis was also discovered with a high degree of ordering of graphite crystals (Figure 1), when graphite passes from the hexagonal phase with disordered interlayer bonds and with a translation period along the C axis equal to twice the interatomic distance into the rhombohedral phase with a strict translation period along the C axis equal to three times the interplanar distance. In this case, the degree of ordering of the crystal lattice in Figure 1 was determined, as described earlier, by the blurring of the translation parameters, both in the plane of the hexagons and along the C axis, which was supplemented by the dependences of the thermoelectric power of graphite pyrocrystals.

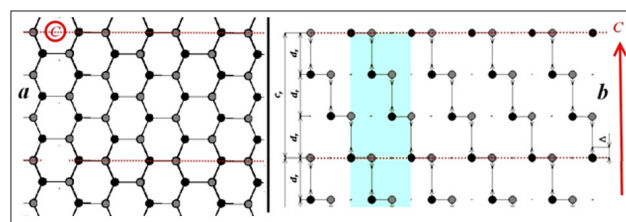
The pyrocrystals of the dielectric analogue of graphite, boron

nitride, grown by B. N. Sharupin were studied in parallel with graphite [7], which actually made it possible to obtain such highly ordered rhombohedral pyrocrystals that their properties were close to single-crystal ones. Thus, on the setup for measuring the temperature dependences of the electrical conductivity of metals, Dmitry Kolgunov discovered that there was an anomaly on the graphite samples, which, as he figured out, was due to the fact that the standard hundred-micron-thick graphite plates had a resistance lower than that of copper measuring wires.



**Figure 1:** Reduction of the anisotropy of electrical conductivity of graphite pyrocrystals during the transition from the hexagonal phase to the rhombohedral phase due to an increase in electrical conductivity across the monatomic layers of graphite.

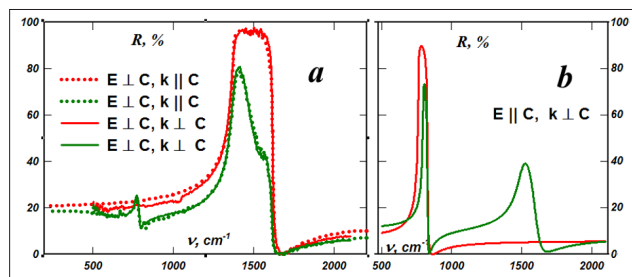
As our studies have shown, the decrease in anisotropy at a very high degree of ordering of graphite pyrocrystals is associated not with the ordering of their microstructure (which initially leads to an increase in anisotropy), but with a decrease in electrical resistance at the boundaries of packets perpendicular to the C axis and with the order-disorder transition in the distribution of interlayer bonds in the crystal lattice in packets [8]. The transition from chaotically distributed interlayer bonds to strictly ordered ones determines, both in graphite and in boron nitride, the phase transition from the hexagonal phase, with a period of translation of monoatomic layers along the C axis equal to twice the interatomic distance, to the highly ordered rhombohedral phase with a period of translation of monoatomic layers equal to three times the interatomic distance (Figure 2).



**Figure 2:** Model of the crystal lattice of highly ordered rhombohedral boron nitride: a - plane perpendicular to the C axis, b - plane parallel to the C axis.

In this case, since the crystal lattice of boron nitride contains a dipole, its characteristic lattice vibrations are IR-active and the reflection spectra of boron nitride crystals clearly demonstrate in the reflection strongly damped lattice oscillators in the hexagonal phase with the creeping of orthogonal vibrations and

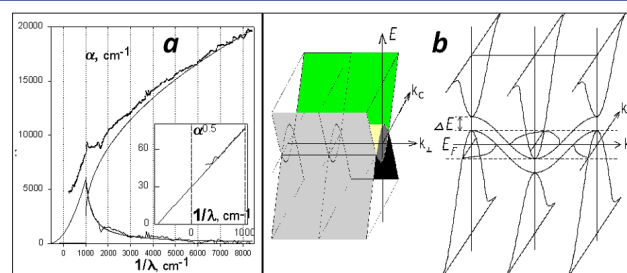
in the region of the same frequencies weakly damped lattice vibrations in the rhombohedral phase and without the creeping of orthogonal oscillators, i.e. practically the spectra of single crystals (Figure 3).



**Figure 3:** Lattice oscillators in the polarization reflection spectra of rhombohedral (red curves) and hexagonal (green curves) boron nitride.

Thus, in highly ordered rhombohedral boron nitride, weakly damped lattice oscillators are observed. In this case, for each polarization of IR radiation, there is only one, corresponding either to ion oscillations in the plane of the hexagons (Figure 3a), or to ion oscillations along the C axis - perpendicular to the plane of the hexagons (Figure 3b). And since the low-frequency edge of the oscillator corresponds to a transverse phonon and determines the rigidity of the bond between atoms in the crystal lattice, Figure 3 shows that the interlayer bond is only one and a half times weaker than the intralayer bond, which is in full agreement with the anisotropy of the Debye temperature. But, as was shown earlier, in the rhombohedral crystal lattice, there is one interlayer bond for every intralayer bond. Therefore, the rigidity of the boron nitride crystal along the C axis is only 4.5 times less than its rigidity perpendicular to the C axis, and not 1000 times, as follows from the Van der Waals forces [8]. So the crystal cannot be split with adhesive tape. The presence of a dipole in the boron nitride crystal lattice makes its oscillations IR-active and determines the width of the oscillator - its high-frequency edge corresponds to a longitudinal phonon that exists only in the boron nitride crystal, but the transverse phonons in the rhombohedral phases of boron nitride and graphite are close in frequency. In this case, graphite in the rhombohedral phase becomes a semi-metal with noticeable intrinsic electrical conductivity along the C axis, which, with a slight further increase in electrical conductivity along the graphite layers, determines the drop in the anisotropy of its electrical conductivity.

The obtained absorption spectra of pyrographites (Figure 4a) are well described by the additive contributions of two processes:  $\alpha \sim (\mathbf{E} - (\Delta E_1 + E_{ph}))^2$ , with the characteristic frequency  $(\Delta E_1 + E_{ph})/h = -640\text{cm}^{-1}$ , where  $E_{ph}$  is the phonon frequency, and direct allowed transitions:  $\alpha \sim (\mathbf{E} - \Delta E_2)^{1/2}$ , with  $\Delta E_2/h = +1000\text{cm}^{-1}$ . Considering that the maximum phonon frequency for graphite is about  $1400\text{cm}^{-1}$ , the obtained values of the edges of interband transitions correspond to a band structure with a direct gap near the Fermi level of about 0.125 eV and with an indirect anisotropic overlap of 0.25 eV (Figure 4b). From the above analysis it follows that with a decrease in the degree of disordering of pyrographites, the direct energy gap decreases, and the overlap of the bands increases [9].



**Figure 4:** Absorption spectrum of a film of finely dispersed pyrolytic graphite-pyrocarbon (a) and a model of the band structure of graphite (b).

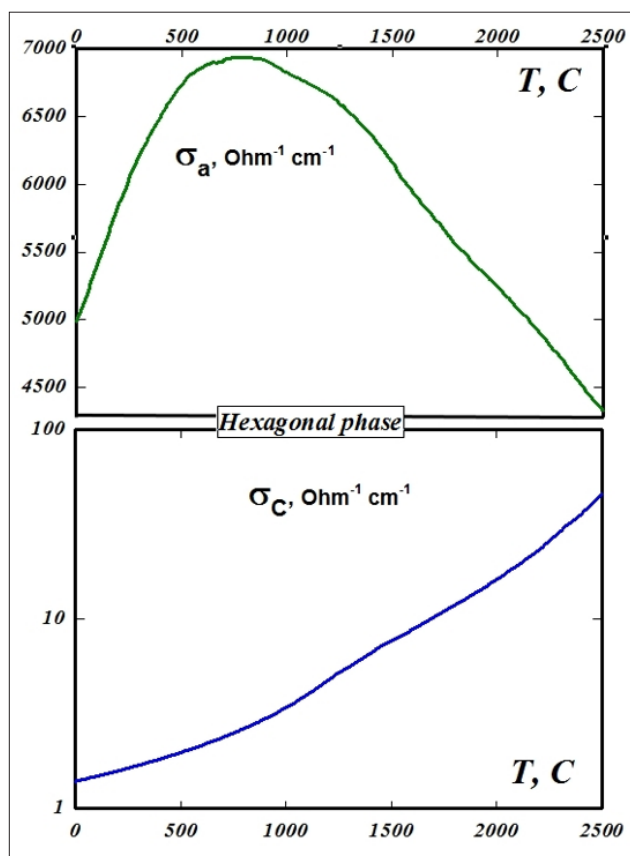
The presented zone model (Figure 4b) shows that to the normal, relatively small semi-metallic (zone) electrical conductivity of graphite (ordered) along the C axis, in the direction perpendicular to the C axis - in the plane of the hexagons, due to the minimal gap between the allowed zones by momentum, there is an addition in the form of "acoustic" electrical conductivity, which, in principle, makes the electrical conductivity of graphite hexagon layers related to superconductivity. But this large "acoustic" addition to the electrical conductivity at very low temperatures has a small "opening threshold" (minimum voltage, which is similar to the flow of superconducting bosons through a contact), corresponding to the gap by momentum between the allowed states, and with an increase in temperature it gives a large increase in electrical conductivity up to temperatures much higher than room temperature. And this is in good agreement in a wide temperature range with the anisotropy of the temperature dependence of the electrical conductivity of graphite, which manifests itself for the plane of hexagons in its purely semiconductor growth up to 800 C and in its metallic decline at a higher temperature (Figure 5, above). Although, as experiments on high-temperature annealing of highly ordered rhombohedral nitride samples have shown, during annealing a phase transition to the hexagonal phase occurs with a characteristic change in the lattice oscillators (Figure 3). The electrical conductivity along the C axis demonstrates a continuous exponential growth with increasing temperature (Figure 5, below), which is determined, in full accordance with the model of the band structure of graphite presented in Figure 4, by the increasing contribution of phonons to indirect transitions.

The damping of the lattice oscillators of the main orientation in the hexagonal phase of boron nitride, as can be seen from Figure 2, is accompanied by simultaneous excitation of the orthogonal: lower frequency in Figure 2a and higher frequency in Figure 2b. This excitation in the weakly ordered phase of orthogonal modes is associated with the fact that deviations of the C axes of crystallites in the hexagonal phase from the average axis of the pyrocrystal C, determined by the growth plane, are observed (Figure 6).

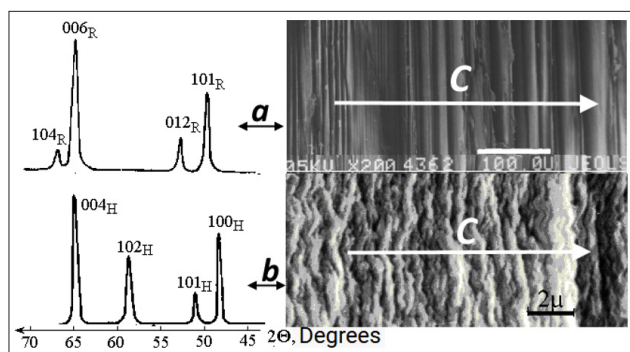
#### BN+C

Since the crystalline structures of graphite and boron nitride are similar, it seemed possible to grow graphite layers in boron nitride and boron nitride layers in graphite. Samples of graphite with boron nitride were analyzed for the purpose of obtaining composite thermoelectric material, but in the obtained non-order composite samples, only the diffusion thermoelectric mechanism operates and the thermoelectric figure of merit,

in accordance with the theory of flow in composites, did not increase significantly compared to the low thermoelectric figure of merit of pure graphite.



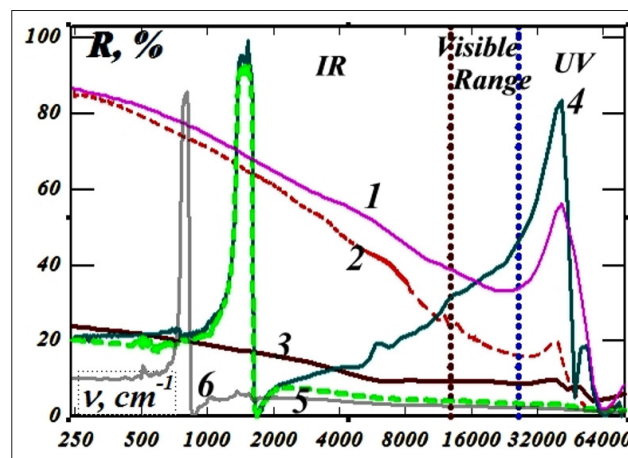
**Figure 5:** Temperature dependences of the specific electrical conductivity of ordered hexagonal graphite in the plane of the hexagons (a - from above) and along the C axis (from below)



**Figure 6:** Wulff-Bragg reflection (left) and microstructure (right) of rhombohedral (a) and hexagonal (b) pyrocrystals.

But since the parameters of the crystal lattices of the rhombohedral phases of boron nitride and graphite are very close, the highly ordered boron nitride of the rhombohedral phase is an ideal environment (support) for the existence of atomic-thick graphite layers. Boris Nikolaevich Sharupin grew crystals of highly ordered boron nitride containing very thin graphite layers [9,10]. The samples were slightly cloudy when viewed through the light, since the thinnest graphite layers in boron nitride were in the form of millimeter-diameter spots. Individual thin layers of graphite naturally transmitted visible light, but since the real part of the permittivity of graphite is much greater than its imaginary part, then in aggregate, due to the interference of

reflections of the thinnest layers of graphite, they give a mirror metallic reflection of visible light from the plane of the crystal, perpendicular to the C axis and practically did not reflect visible light from the plane parallel to the C axis - they were completely black for any polarization (Figure 7).



**Figure 7:** Polarization spectra of reflection from different faces of highly ordered graphite pyrocrystals and highly ordered boron nitride pyrocrystals with embedded thin graphite layers:

1 - graphite, E  $\perp$  C, k  $\parallel$  C, 2 - graphite, E  $\parallel$  C, k  $\perp$  C, graphite, 3 - graphite, E  $\parallel$  C, k  $\parallel$  C, 4 - BN, E  $\perp$  C, k  $\parallel$  C, 5 - BN, E  $\perp$  C, k  $\perp$  C, 6 - BN, E  $\parallel$  C, k  $\perp$  C.

This led to a gigantic spatial dispersion in the visible region of the spectrum. As shown in Figure 7, in the IR range, the lattice peaks of reflection of boron nitride with graphite inclusions with polarization perpendicular to the C axis are practically independent of the orientation of the wave vector (curves 4 and 5). And the anomalously large "silver" reflection in the visible range of the spectrum of boron nitride samples with graphite inclusions from the plane perpendicular to the C axis (Figure 7, curve 4) and, thus, the giant spatial dispersion (Figure 7, curve 5) are associated with a powerful diffraction maximum of reflection in the ultraviolet region of the spectrum, which, in frequency, corresponds to local plasma oscillations in graphite patches with a diameter of about 50 nm.

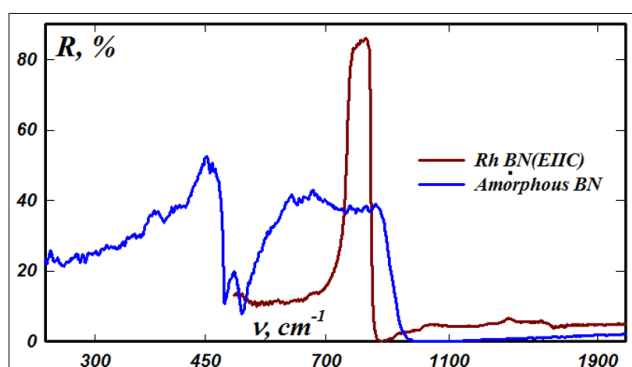
So, millimeter spots of graphite embedded in boron nitride consist of smaller nanoflakes of antigraphene - rhombohedral graphite with a minimum thickness equal to three times the interatomic distance. The large (approaching 100%) height of the diffraction reflection peak indicates a very high electron mobility along the graphite layer in the spot. Such a giant spatial dispersion was first discovered in the IR region in disproportionate quasicrystals of higher manganese silicide [11]. But boron nitride samples with graphite interlayers clearly demonstrated it in visible light: with polarization of the electric vector perpendicular to the C axis, a specular "silver" reflection from the plane of the crystal perpendicular to the C axis and complete non-reflection of visible light with the same polarization from a plane parallel to the C axis. This allowed us to understand that giant spatial dispersion cannot be described by the Landau smallness parameter and that these observed giant effects are described by models that are borderline between optical and radio engineering - waveguide models. And these models describe, taking into account the scale of the embedded graphite spots in boron nitride and the



gigantic spatial dispersion of boron nitride with graphite. In addition, a relatively small but significant spatial dispersion is also observed in samples of highly ordered graphite (Figure 4, curves 1 and 2) and also with the manifestation of a characteristic peak of ultraviolet reflection. Previously, it was associated with interband transitions in graphite, which is very strange with a semi-metallic overlap of energy bands. But judging by the spectra given, the graphite layers themselves consist of tightly folded 50 nano-flakes of antigraphene, electrically and mechanically contacting along the boundaries and forming packets of graphite layers with thicknesses of about 200 nm.

## Conclusion

Thus, the two-sided crystalline support of thin graphite layers by the crystal lattice of rhombohedral boron nitride congruent to graphite allows obtaining unusual, but real characteristics of ultra-thin layers of rhombohedral graphite - antigraphene. With one-sided application of graphite on crystals of rhombohedral boron nitride, even on the surface perpendicular to the C axis, led to amorphous graphite films. Neutron analysis of massive samples of amorphous graphite showed that they consist of graphite microcrystals 50 nm in size. But IR spectral analysis of similar amorphous boron nitride showed that the amorphous phase is its isotropic gamma phase in which "soft" interatomic bonds prevail, corresponding to interlayer bonds in the rhombohedral phase of boron nitride (Figure 8).



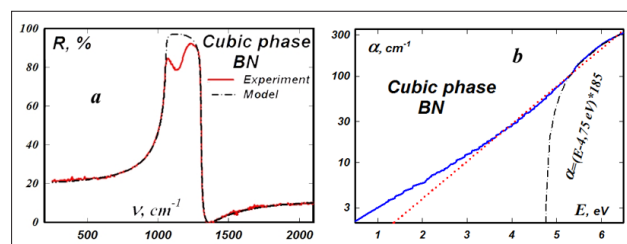
**Figure 8:** Reflectance spectrum of fine-crystalline, amorphous (gamma) phase of boron nitride (blue curve) and interlayer oscillator of rhombohedral boron nitride (brown curve).

Thus, it can be expected that breaking interlayer bonds and one free surface of the graphite film is sufficient for its amorphization to the gamma phase of graphite. Naturally, it can be expected that even greater amorphization of thin graphite films grown on other substrates with poorly matching crystal structure.

## Appendix

Highly ordered pyrocrystals of boron nitride with embedded thin layers of graphite were subjected to ultra-high pressure by explosion in a high-pressure chamber and thus transferred to the cubic phase (Figure 9a).

Uniformly weakly doped with carbon, greenish transparent crystals were obtained, the absorption spectrum of which corresponded to interband transitions with a band gap width of approximately 4.75 eV (Figure 9b). The crystals had very high hardness and strength. Their wear resistance was almost an order of magnitude greater than that of diamond.



**Figure 9:** Characteristic lattice oscillator of cubic boron nitride (a) and the spectrum of its absorption coefficient (b).

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