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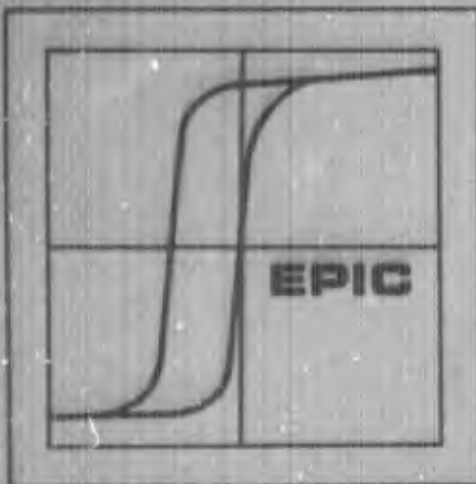
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BORON NITRIDE

M. NEUBERGER

DATA SHEET DS-158

NOVEMBER 1967



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FOREWORD

This report was prepared by Hughes Aircraft Company, Culver City, California, under Contract Number AF 33(615)-2460. The contract was initiated under Project No. 7381, "Materials Application," Task No. 738103, "Materials Information Development, Collection, and Processing." The work was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Mr. R. F. Klinger, Project Engineer.

The Electronic Properties Information Center conducts documentary research based on the collection, analysis, and review of the scientific and technical literature relevant to the electrical, electronic, and magnetic properties of materials. The primary objective of this program of evaluation and correlation is to provide a source of competent information to the DoD community. By means of several series of publications such as Data Sheets, Special Reports, Interim Reports, and several services such as Computer Bibliographies, technical question answering services, and special studies, research and development support is made available to this extended community.

The initial step in the preparation of this data sheet was retrieval, by means of a modified coordinate index, of all boron nitride literature in the EPIC file. Bibliographies were also reviewed to ensure the inclusion of all relevant literature. Papers containing primary experimental data were selected. Secondary reviews and evaluations were considered during the data analysis. In all, 52 references were used from EPIC holdings, totalling 132.

In general if data available from several sources are judged to be equally valid, then all are given. Data are considered questionable and are rejected for inclusion because of faulty or dubious measurements, unknown sample composition, or if more reliable and inclusive data are available from another source. Selection of data is based upon evaluation of that which is most representative, precise, reliable and inclusive over a wide range of parameters. In the case of boron nitride however, the paucity of data caused inclusion of all available information.

Within every property section we have tried to include every parameter and range of experimental condition found in the literature. Measurement environment and sample specification are included when available. Some alterations in units and presentation may be made to facilitate comparison with other experimental data.

This report consists of the compiled data sheets on boron nitride. A full list of EPIC publications to-date appears at the end of the report.

The author wishes to acknowledge the contribution of Dr. J. J. Grossman and Dr. Sheldon J. Welles in the review of the experimental data and the final compilation. The supporting assistance of another member of the EPIC staff, Mrs. Marjorie Dunn is gratefully acknowledged.

Acknowledgement is also made for the assistance of Dr. Y. S. Touloukian of the Thermophysical Properties Research Center at Purdue University in supplying some of the thermal conductivity information.

The assistance of Mr. R. C. Olsen and Mr. N. J. Norante of The Carborundum Company in supplying data on boron nitride is gratefully acknowledged.

ABSTRACT

These data sheets present a compilation over a wide range of electronic properties for Boron Nitride. These properties are compiled over the widest possible range of parameters and are then agglomerated in several large groups as follows: Optical Properties include absorption, reflection and refraction. Transport Properties include electrical conductivity and resistivity. Energy Band Structure includes energy gap values. Phonon Branch Distribution appears separately. Both Photon and Electron Emission data are represented including Spectral Emissivity. Thermal Properties include Debye temperature, thermal conductivity, and thermal emf. There are other individual properties and effects included, especially dielectric constant and dissipation factor.

The Introduction discusses the two polymorphic boron nitride forms; their crystal structure, lattice parameters and transition points. The isotropic and anisotropic boron nitride prepared by chemical vapor deposition is discussed from the mechanical and electrical standpoint. Information is given on a number of boron nitride devices and applications. A table of the best values available for physical and electronic properties is given.

This report has been reviewed and is approved for publication.

Sheldon J. Welles

Dr. Sheldon J. Welles, Head
Electronic Properties Information Center

E. F. Smith

E. F. Smith
Project Manager

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PHYSICAL AND ELECTRONIC PROPERTIES

Physical Properties	Symbol	Value	Unit	Temperature	Reference
Formula		BN			
Molecular Weight		10.82+14.008=24.828			
Density					
Hexagonal		2.25	g/cm ³	20°C	29709
Cubic		3.45	g/cm ³	25°C	
Color		White, transparent			
Melting Point					
(Commercial)		2730 (subl.)	°C & 1 atm.		12808
(Pure)		3000 (subl.)	°C & 1 atm.		12808
Lattice Symmetry (hexagonal)		C6m2(D ₃ ^{1h})Z=2			*26
Lattice Parameter					
Hexagonal	a ₀	2.51±0.02	Å	20°C	*1
	c ₀	6.69±0.04		20°C	*1
	B-N	1.446			22943
Cubic	a ₀	3.615±0.001		25°C	29709
	B-N	1.57		25°C	29709
Hardness, Mohs scale					
Hexagonal		2			29709 *3
Cubic		10			
Cubic (microhardness)		7300-10,000	kg/mm ²		
Specific Heat (hexagonal)					
CVD		0.24	cal/g/°C	20°C	26546
Pressed Powder		0.418	cal/g/°C	20-2200°C	12808
CVD - Specific Heat Coefficient					
0.214+5.25x10 ⁻⁴ T-2.59x10 ⁻⁷ T ²			cal/g/°C		21962
Coefficient of Thermal Expansion					
CVD Hexagonal	a ₀	-2.9x10 ⁻⁶	/°C	20°C	4878
	c ₀	+40.5x10 ⁻⁶	/°C	20°C	4878
Hot Pressed (hexagonal)		+10.2x10 ⁻⁶	/°C	25-350°C	*26
		+7.5x10 ⁻⁶	/°C	25-1000°C	*26
Cubic		+3.5x10 ⁻⁶	/°C	0-400°C	28367

Physical and Electrical Properties (continued)

Physical Properties	Symbol	Value	Unit	Temperature	Reference
Tensile Strength					
CVD		30×10^3	psi	20°C	22943
Hot Pressed		15×10^3	psi	20°C	22943
Electrical Properties					
Energy gap					
Hexagonal direct	Eg	7.533	eV	0°K	14587
indirect		2.7	eV	0°K	14587
Cubic		10	eV		22943
Electrical Resistivity	ρ				
Hot Pressed (hexagonal)		10^{13}	Ωcm	25°C	29802
CVD		10^{15}	Ωcm	25°C	22943
Dielectric Constant					
CVD Hexagonal	ϵ_0	5.12		20-500°C	22943
Cubic	ϵ_0	7.1			28367
Cubic	ϵ_∞	4.5			
Refractive Index					
Hexagonal Powder	ω	2.20 ± 0.05		300°K	29726
	ϵ	1.66 ± 0.02		300°K	
Cubic ($\lambda = 0.54\mu$)	n	2.117		300°K	28367
Debye Temperature	θ				
Hexagonal		598 \pm 7	°K		*28
Cubic		1973	°K		28367
Thermal Conductivity	k				
CVD		0.8	W/cm°K	200°C	22943
CVD		0.7		845°C	
Hot Pressed		0.2	W/cm°K	20°C	24396
Magnetic Susceptibility (gram)	χ	-0.4×10^{-6}	cgs		4878
Phonon Branch Distribution					
Cubic	TO	.132	eV		28367
	LO	.166	eV		
	TA	.043	eV		
	LA	.085	eV		

Physical and Electrical Properties (continued)

Electrical Properties	Symbol	Value	Unit	Temperature	Reference
Phonon Branch Distribution (continued)					
Hexagonal	LO	.199, .103	eV		25245
	TO	.169, .196, .097	eV		25245
Spectral Emission Coefficient					
Hot Pressed (hexagonal)	e	($\lambda=4-14\mu$) 0.8		600-1000°C to 2000°K	17412
CVD	e	($\lambda=6\mu$) ~1.0			30876
Electron Thermionic Emission		50	mAmp/cm ²	1700°C	15528

*References found on pages 20 and 21.

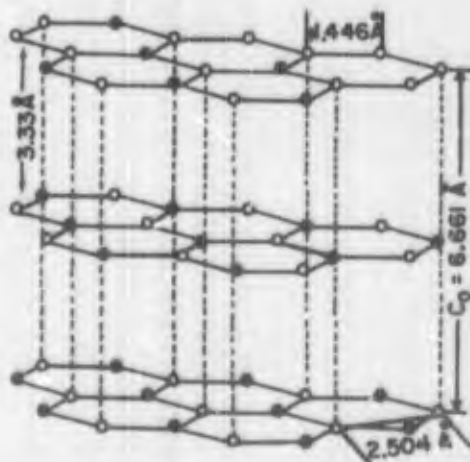
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INTRODUCTION

I. CRYSTAL STRUCTURE

a. Hexagonal and Cubic Boron Nitride

Although boron nitride has a much lower electrical conductivity and diamagnetic anisotropy than carbon, the resemblance between the two is strong. Like carbon, boron nitride occurs in two forms; the stable form is a white solid ("white graphite") with hexagonal symmetry, a density of 2.25 g/cm^3 at 20°C and a hardness of Mohs 2. The "diamond" or zincblende (fcc) form has a density of 3.45 g/cm^3 at 25°C and a hardness close to Mohs 10 [Ref. 29709].



Hexagonal Boron Nitride

[Ref. 22943]

Hexagonal boron nitride has lubricating properties based on cleavage and a crystal structure similar to that of graphite. The molecule comprises boron and nitrogen atoms alternating in stacked sheets of six-membered rings with:

$$a_0 = 2.50399 \pm 0.00005 \text{ \AA}$$

$$c_0 = 6.6612 \pm 0.0005 \text{ \AA}$$

These values are for 35 °C. Measurements are made on recrystallized commercial material, density = $2.29 \pm 0.03 \text{ g/cm}^3$ with about 0.6% by weight impurities. [Ref. 4878]

Later values are given by Donnay,¹ who quotes an average:

$$a_0 = 2.51 \pm 2 \text{ \AA}$$

$$c_0 = 6.69 \pm 4 \text{ \AA}$$

Other crystal structure parameters for hexagonal boron nitride are:

$$\text{B-N} = 1.446 \text{ \AA}$$

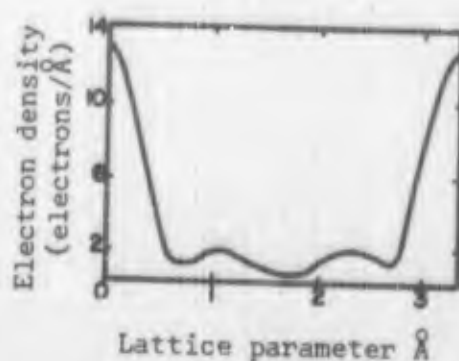
$$\text{Layer separation} = 3.33 \text{ \AA} \quad [\text{Ref. 22943}]$$

These values are confirmed by EPR measurements on sintered powder hexagonal boron nitride:

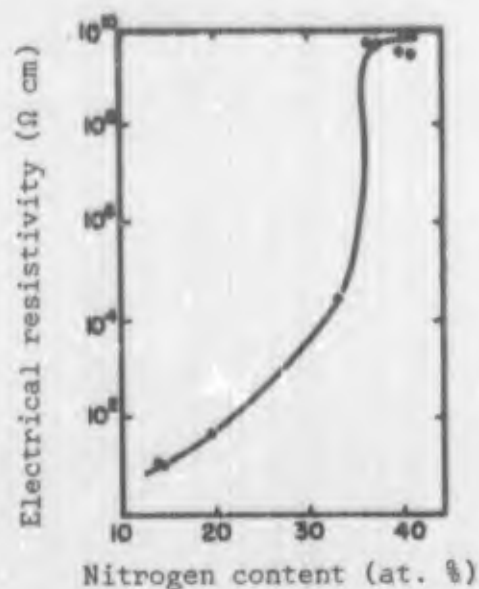
$$\text{B-N} = 1.45 \text{ \AA}$$

$$\text{Layer separation} = 3.35 \text{ \AA} \quad [\text{Ref. 27881}]$$

Efforts to obtain the molecular spectra by intense surface heating with a laser beam resulted in the boron oxide spectra and no boron nitride bands were seen.²



The above graph on the distribution of electron density in a boron nitride crystal indicates that 15 to 16 percent of the total electron density, corresponding to two electrons from each pair of boron-nitrogen atoms is found between the network layers. The bond between the boron and nitrogen atoms in the network is ionic rather than metallic which accounts for the fact that boron nitride is a typical semiconductor rather than a metal. The heat of formation from the elements is 60.7 kcal per mole²⁸ and this has led to the conclusion that there are double bonds between the boron and nitrogen layers.²⁶



Electrical resistivity as a function of excess nitrogen content in atomic percent.

Hexagonal boron nitride has a large region of homogeneity; the rearrangement of the boron lattice during nitrogenation leads to the formation of melts in the nitride homogeneity region with predominance of electron (n-type) conductivity. With an increase in the nitrogen content of the nitride, the electrical resistance of the compound increases sharply at first, but after reaching 35-38% nitrogen, resistance increases more slowly. It is believed that electron participation in conduction affects the bonds between the plane layers of atoms in the nitride structure.

[Ref. 30176]

Crystal structure parameters for the zincblende (fcc) form are:

$$a_0 = 3.615 \pm 0.001 \text{ \AA} \quad (25^\circ\text{C})$$

$$\text{B-N} = 1.57 \text{ \AA}$$

[Ref. 29709]

These cubic crystals have been studied by N.E. Filonenko et al.³ and show a primary habit of positive (111) and negative (1-11) tetrahedra. Their microhardness was 7300 to 10,000 kg/mm².

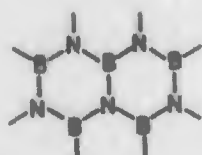
Kudaka et al.⁴ from observations of the crystal surfaces of the cubic form similarly conclude:

1. The (111) face is the most stable crystal plane.
2. Although (110) faces are rarely found in diamond, they appear more often than (100) faces in cubic boron nitride.
3. The triangular growth layers are positively oriented to etch pits on (111) faces in diamond, but are negatively oriented to etch pits in cubic boron nitride.
4. There are a variety of shapes of growth layers in cubic boron nitride.
5. There are two kinds of triangular pyramids positively and negatively oriented to (111) face in cubic boron nitride.
6. Spiral patterns have been observed on (111) face.

From the morphology of these features described above it is conjectured that the crystals of cubic boron nitride have been formed due to the growth of various shapes of layers or triangular pyramids on (111) faces.

The crystal characteristics and habits of the boron nitride forms, both cubic and hexagonal have been well studied. R. Sato⁵ in a discussion of stacking faults in the hexagonal form states that x-ray diffraction patterns indicate "displacement" stacking faults as well as the "turbostratic" faults reported by J. Thomas et al.⁶

This structure shows further analogies between boron nitride and carbon. It is synthesized by controlled reaction between fused urea-boric acid and ammonia at 500-950 °C.



The layers which comprise B-N rings, are stacked roughly parallel to each other but with random rotation and translation around the layer normal. The average stack height is 14 Å and the average layer diameter is 46 Å.

This turbostratic form may be transformed by heat in the presence of boron oxide in a nitrogen atmosphere between 1450 to 1850 °C, to the ordered layer-lattice hexagonal form in a "graphitization" process.

A pseudocubic hexagonal form is given for a boron nitride polymer (BN)_x:⁷

$$a_0 = 7.46 \text{ Å}$$

A semiconducting cubic form of boron nitride can be prepared by doping the hexagonal form. Several patents have been issued to R.H. Wentorf, Jr. for the process, (U.S. 3,192,015; 3,078,232).^{8,9}

Beryllium and lithium additions give p-type crystals, of deep blue color with resistivities as low as 200 ohm-cm at 25 °C; more typical is a resistivity of 10^3 ohm-cm. The conduction activation energy for these samples is about 0.2 eV and it is suggested that the beryllium forms acceptor levels. Sulfur additions yield n-type crystals of pale yellow color, resistivity about 10^4 ohm-cm at 25 °C and an activation energy of 0.05 eV. U.S. patent 3,142,595 describes bulk p-n and p-p boron nitride junctions that have excellent rectifying properties.¹⁰

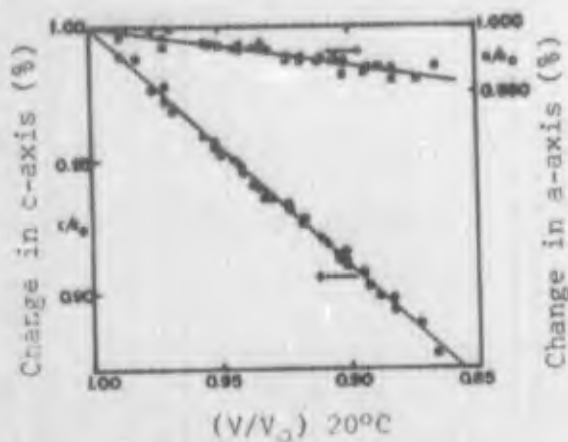
The reversible transformation between cubic and hexagonal boron nitride has been well investigated. The hexagonal form is heated from at least 1350 °C to 1800 °C under pressures of 62,000 to 85,000 atmospheres to yield the dark cubic form. With increase of temperature to 2500 °C and pressure increase to 50,000 atmospheres, the cubic substance reverts to the soft, white hexagonal boron nitride. [Ref. 29709]

In the cubic-hexagonal transformation, the following table is given by H.J. Milledge et al.¹¹

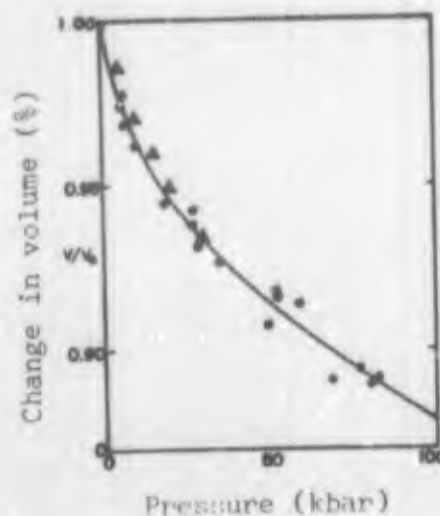
Temperature ($\pm 20^\circ\text{C}$)	Time (min.)	Effect on cubic boron nitride
1500 °C	5	no change
1650 °C	3	partial conversion to hexagonal
1800 °C	1	complete conversion to hexagonal
2000 °C	1	" " " "
2200 °C	instantaneous	" " " "

The hexagonal form so produced in vacuo is not the normal form, but rather a graphite form with a different x-ray diffraction pattern.

b. Effect of Pressure



Percentage change in c-axis and a-axis with volume change.



Percentage change in volume with pressure at 20 °C.

▲ 30

The effect of pressure has been measured on the lattice parameters and the volume of hexagonal boron nitride by x-ray diffraction method at 20 °C. The volume decrease with pressure comprises a large decrease in the c-axis and a small one in the a-axis as seen in the table below.

Lattice parameters and compressibility of BN.				
V/V_0	c/c_0^a	a/a_0^b	$(c/c_0)/(a/a_0)$	$P(\text{kbar})$
1.0	1.000	1.000	1.000	0
0.98	0.9821	0.9989	0.9832	4.5
0.96	0.9641	0.9979	0.9661	12.3
0.94	0.9461	0.9968	0.9491	25
0.92	0.9282	0.9956	0.9323	44
0.90	0.9102	0.9944	0.9153	68
0.88	0.8922	0.9931	0.8984	(100)
0.86	0.8743	0.9918	0.8815	
Markers Used				NaF, LiF MgO

^a $a_0 = 2.5040 \text{ \AA}$
^b $a_0 = 6.6612 \text{ \AA}$

The transition from hexagonal to cubic symmetry shown in the work of Wentorf [Ref. 29709] is seen at 68 kbar at which point the data is terminated.

[Ref. 24434]

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Solubility and x-ray diffraction studies by Kudaka and Konno¹²

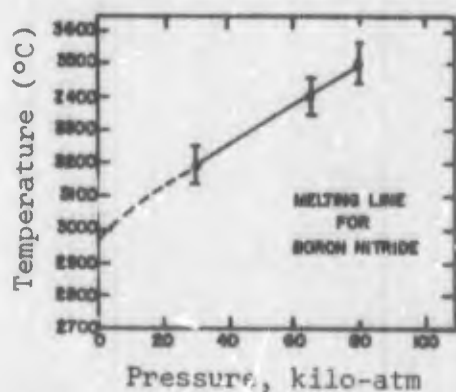
indicate that the structural change of boron nitride under high pressure is different from that of graphite. Using the following samples:

1. Untreated hexagonal boron nitride
2. Hexagonal boron nitride treated at 20 °C and 50 kbar pressure
3. Hexagonal boron nitride treated at 1500 °C and 50 kbar pressure

these investigators find that the 3-dimensional order of the crystal is lessened in sample 2, but sample 3 shows high order with residual stress along the c-axis.

The large compressibility in the basal plane is about 10 times the theoretical, calculated from equations relating empirically the force constants of bonds to the bond length. It is suggested that the compression causes a change in the bond character. In boron nitride the bonds are between atoms of different electronegativity and there is an increase from 22% to 33% double-bond character for each bond.¹³

The increase in melting point of boron nitride with pressure indicates that molten boron nitride has lower density than either the solid hexagonal or cubic form.¹⁴



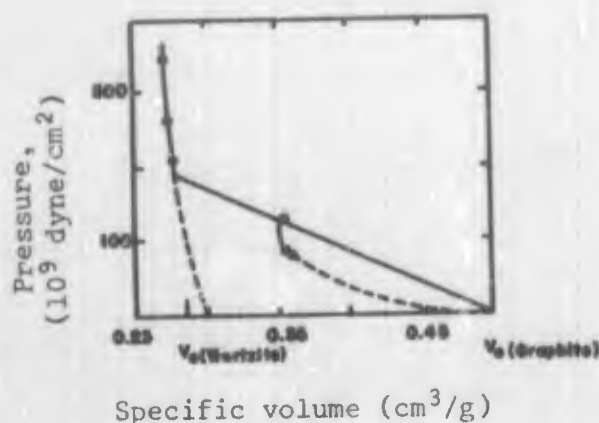
Melting Point
($\pm 100^\circ\text{C}$)

Pressure

3200 °C	30,000 atm
3400 °C	65,000 atm
3500 °C	80,000 atm
2730 °C (sublimes)	1 atm

The sublimation temperature for the pure material is 3000°C at one atmosphere but the usual commercial powder sublimes at about 2730°C. [Ref. 12808]

Recent work by G.A. Adadurov, et al., has produced a wurtzite modification of boron nitride by impact compression.



Shock adiabetic curve of boron nitride

The change in specific volume is shown as a function of static pressure. (Data taken from reflectivity measurements.) Phase transition is indicated at 128×10^9 dyne/cm² for a volume of $0.352 \text{ cm}^3/\text{g}$.

Shock wave propagation = 4.68 km/sec

Pressure = $128\text{-}192 \times 10^9$ dynes/cm²

The lower pressure limit marks a sharp discontinuity in the pressure-volume curve; an extrapolation to zero pressure gave a specific volume for the new phase of $0.3 \text{ cm}^3/\text{g}$, (specific volume of the cubic and hcp forms is $0.287 \text{ cm}^3/\text{g}$). The infrared absorption spectrum showed a change from two intense lines at 12.4 microns and 7.19 microns to weaker lines at 21.3, 19.6 and 9.1 microns.

[Ref. 30001]

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II. PYROLYTIC (CVD) BORON NITRIDE

The high thermal conductivity and low thermal expansion of hexagonal boron nitride, coupled with its high mechanical strength, give this material outstanding resistance to thermal shock. However, the hot-pressed powder requires binding and fluxing agents that decrease its purity, with a resultant property degradation.

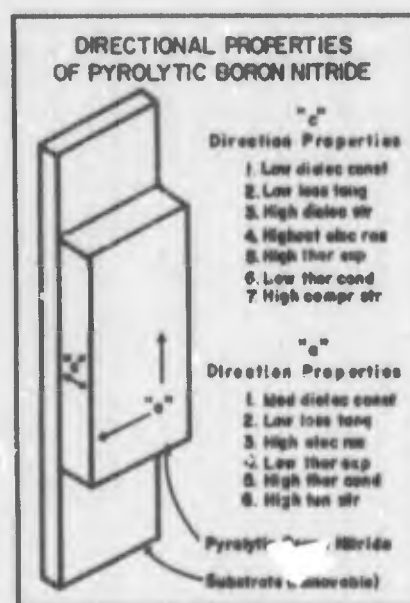
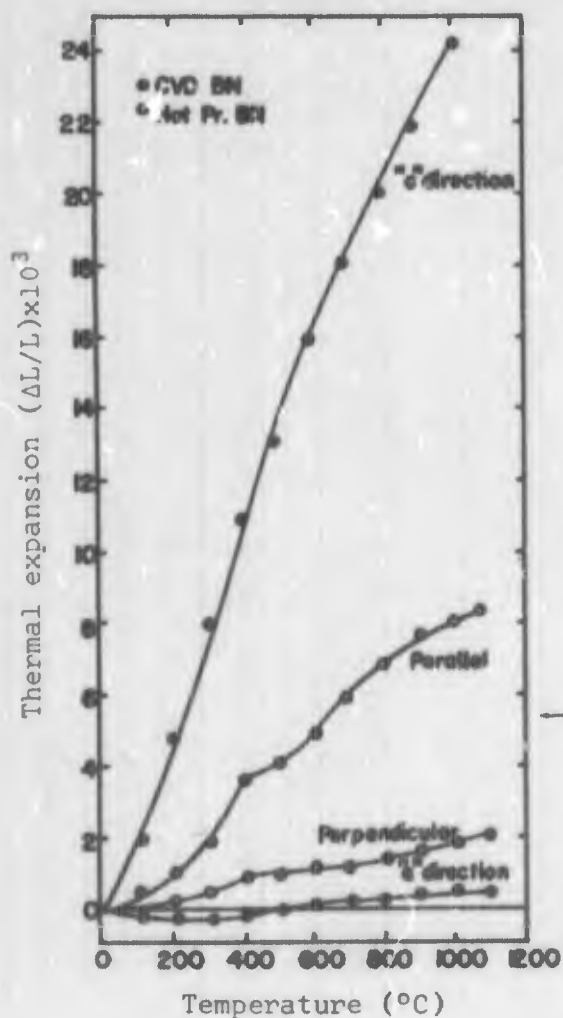
Recent developments in boron nitride research have replaced the hot-pressed powder form with chemical vapor-deposited (CVD) boron nitride, also called pyrolytic boron nitride.

The chemical vapor deposition method of boron nitride production yields bulk or film material of highly superior quality with the following advantages:

1. High purity
 2. High density
 3. High dielectric strength
 4. High temperature strength
 5. Microwave and infrared transmission
 6. Resistance to thermal shock
 7. High crystallite orientation
 8. Variety in shape and thickness
- ¹⁵ and [Ref. 21962]

This method yields all thicknesses from film to bulk of a non-porous material. With a Mohs hardness of 2, it machines easily to close tolerances with a smooth finish. It is much less brittle than the usual silica ceramics although its electrical resistivity is approximately that of porcelain. It has good oxidation resistance and is inert to almost all reagents even at high temperatures. Its excellent dielectric properties are discussed in the corresponding section of these data sheets.

The compound is prepared from the gas phase by the reaction between boron chloride and ammonia at 1900°C and 1 mm mercury pressure. The polycrystalline deposit is pure and highly oriented giving the anisotropic properties of single crystal material.¹⁶ As the temperature of the deposition increases, the nitride can change radically both in appearance and properties. At lower temperatures between 1000 and 1600°C, the material is hard, glassy, yellow-brown with some transparency but still crystalline with definite grain boundaries. Above 1600°C the material is white or cream-colored, dense and highly anisotropic. The a-direction of this form has minimum expansion.¹⁵

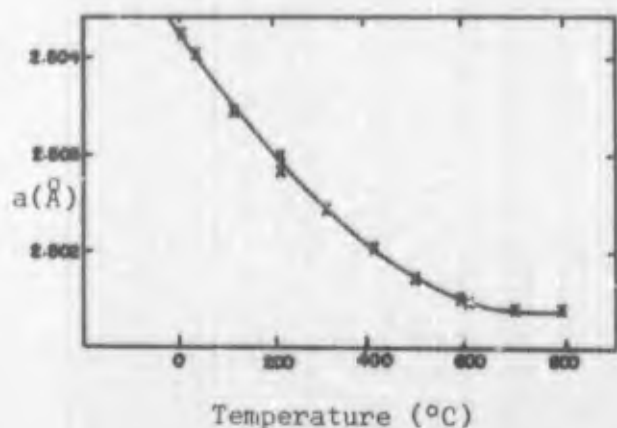


[Ref. 21962]

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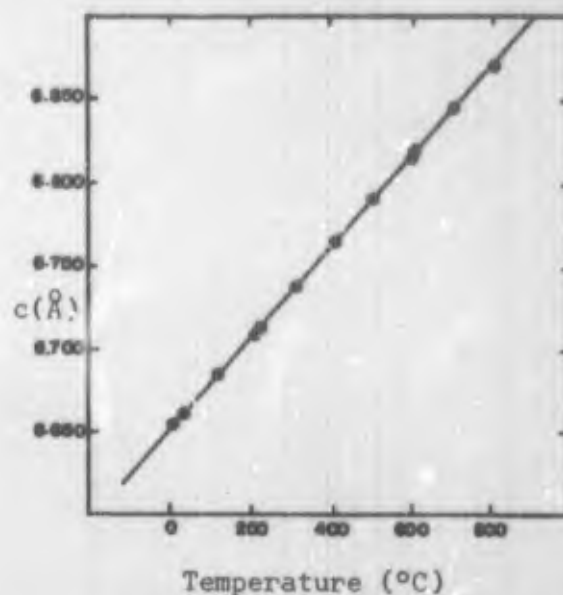
Thermal expansion of pyrolytic and hot-pressed boron nitride. For "c" or "a" direction, see adjoining graph. Parallel and perpendicular refer to orientation set up in the hot-pressing process.

[Ref. 22943]



Variation of a-dimension
with temperature.

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Variation of c-dimension
with temperature.

The variation in the a- and c-axis of hexagonal boron nitride with temperature is shown in commercial pyrolytic boron nitride disks by x-ray diffraction. The thermal coefficient of expansion for the lattice parameters:

$$a_0 = (2.50424 - 7.42 \times 10^{-6}T + 4.79 \times 10^{-9}T^2) \text{Å} = -2.9 \times 10^{-6}/^\circ\text{C at } 20^\circ\text{C}$$

The contraction is not linear and becomes constant at about 800°C.

$$c_0 = (6.6516 + 2.74 \times 10^{-4}T) \text{Å} = 40.5 \times 10^{-6}/^\circ\text{C} \quad [\text{Ref. 4878}]$$

The pyrolytic (CVD) boron nitride is far superior in high temperature behavior to the hot-pressed material as shown with regard to expansion [Ref. 22943] and deformation [Ref. 29924]. In this latter study, hot-pressed boron nitride deformed at 2200°C although the "melting point" was 2990°C. Material failure was seen far below the melting point although thermal treatment will raise the failure temperatures.

As mentioned on page 16, chemical vapor deposition at lower temperatures (1500°C) and higher deposition rates, results in a randomly oriented fine-grained material with a density of about 0.6 that of the high density oriented boron nitride. This polycrystalline material however, is not porous and its physical and electrical properties are isotropic. At 1065°C, the resistivity is 8×10^7 ohm cm and at 1355°C, the value drops to 1.6×10^6 ohm cm. [Ref. 30877]

The average dc dielectric breakdown strength of this material varies between 3 and 6.6 kV/mil, depending on the deposition temperature. [Ref. 30878]

Isotropic pyrolytic boron nitride is practically unaffected by humidity until temperatures above 800°C are reached; surface resistance measurements of 10^{10} ohms/sq. have been obtained after 24 hours exposure to 100% humidity. There is also no detectable helium permeability at 20°C. This material also has excellent shock resistance; samples at 1400°C are quenched in cold water without damage. Finally, electron irradiation by 4 kV in vacuo and at 1500°C showed no damage. [Ref. 30877]

This resistivity to irradiation damage is also true of commercial pressed powder boron nitride. Massive exposure to beta-particles caused only nominal decrease in resistivity. [Ref. 6138]

Boron isotope B^{10} is an effective absorber of thermal neutrons and is present as ~ 19% of boron compounds. It has an absorption cross section of 3990 barns and its low density makes it highly efficient on a weight basis.²⁷

III. APPLICATIONS

The major application of boron nitride is in electrical insulation but several other uses are to be found in the literature.

1. Infrared transmitting optical filter. Based on the IR Christian-sen Filter effect, selective transmission at 9-12 microns is possible with powder boron nitride in an IR-transparent matrix. [Ref. 29708] U.S. 2,986,527 ¹⁷ is a patent for such an optical device.

2. A boron nitride-octadecane slurry is a pressure transmitting medium for single crystals.¹⁸

3. U.S. 3,297,470 ¹⁹ gives a method of producing lubricating glass or quartz fibers that maintain 85% tensile strength at 1500°F.

4. High density boron nitride is used as an insulating sheath in a spiral high flux electric heater, in order to attain a low temperature difference between spiral and sheath.²⁰ However, efforts to deposit boron nitride as an insulating coating on metal wires have been unsuccessful. Both chemical vapor deposition and immersion coating yield layers that spall and react with the metal. They also oxidize at high temperatures.^{21, 22}

5. Fr. 1,440,917 outlines a production method for 0.07 mm. thick boron nitride sheets.²³

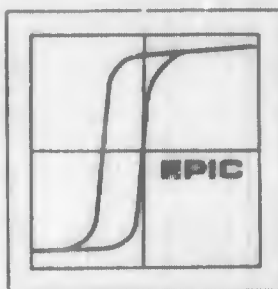
6. Fr. 1,196,188 is for an electroluminescent cell comprising zinc-doped, p-type boron nitride and tellurium-doped n-type boron nitride. This cell responds to continuous or direct current.²⁴ U.S. 3,278,815 is a recent patent for a capacitor, resistant to extremes in environment. This device can operate at less than 3 kv and below 500°C at a few microfarad capacitance.²⁵

U.S. 3,240,614 [Ref. 26645] is a modified boron nitride mixture comprising 40% boron nitride-60% silicon dioxide designed for electrical applications under severe moisture conditions. At a bulk density of 2.18 g/cc, there was no change in dissipation factor ($\sim 3 \times 10^{-4}$ at 1 kc) and the dielectric constant at that density showed an increase of less than 0.1.

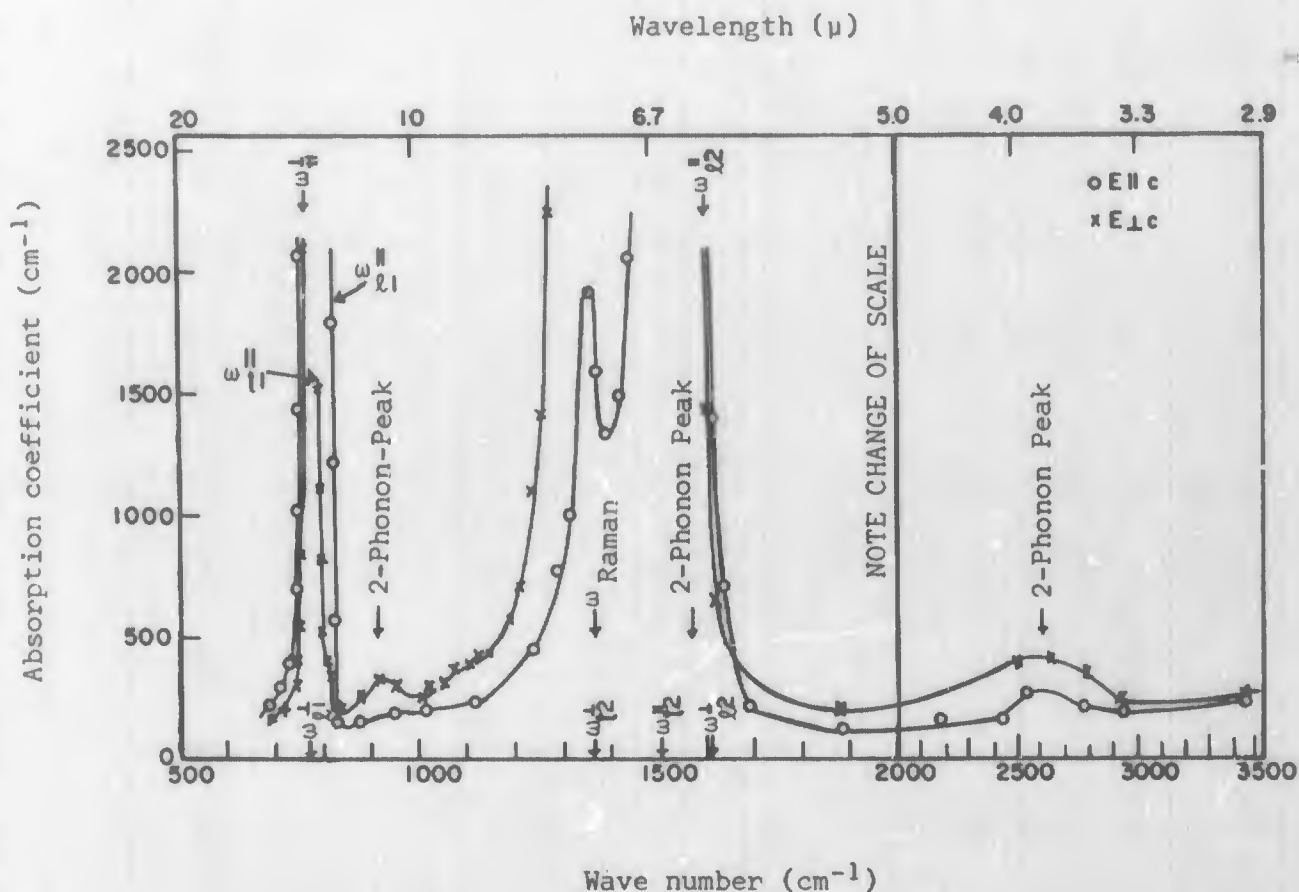
In the search for a radome material with acceptable dielectric properties in addition to an ability to withstand a severe thermal environment, engineers have turned to isotropic CVD boron nitride. In all respects, high thermal conductivity, low coefficient of thermal expansion, high thermal shock resistance and low loss dielectric stability, this material is apparently outstanding. Initial investigations indicate also, that this material can be made efficiently in the required size and shape for radome application.²⁹

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- ² FERGUSON, H.I.S., et al. Laser Excitation of Powdered Solids. NATURE, v. 204, no. 4965, Dec. 26, 1964. p. 1295.
- ³ FILONENKO, N.E., et al. Crystal Morphology of Cubic Boron Nitride. DOKL. AKAD. NAUK SSSR, v. 164, no. 6, 1965. p. 1286-1288.
- ⁴ KUDAKA, K., et al. Some Observations on the Crystal Surfaces of Cubic Boron Nitride. JAP. J. OF APP. PHYS., v. 4, no. 10, Oct. 1965. p. 767.
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- ⁶ THOMAS, J., et al. Turbostratic Boron Nitride, Thermal Transformation to Ordered - Layer - Lattice Boron Nitride. J. AM. CHEM. SOC., v. 84, no. 24, Jan. 25, 1963. p. 4619.
- ⁷ KNAGGS, I.E. "Tables of Cubic Crystal Structures." London, 1932.
- ⁸ WENTORF, R.H., JR. Growth of Large Crystals of Cubic Boron Nitride. U.S. 3,192,015, June 29, 1965.
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- ¹⁰ WENTORF, R.H., JR. Bulk p-n and p-p junctions of p-type diamond and n- or p-type Boron Nitride Crystals. U.S. 3,142,595, July 28, 1964.
- ¹¹ MILLEDGE, H.J., et al. Transformation of Cubic Boron Nitride to a Graphite Form of Hexagonal Boron Nitride. NATURE, v. 184, no. 4687, Aug. 29, 1959. p. 715.
- ¹² KUDAKA, K. and H. KONNO. Effect of Ultrahigh Pressure on Boron Nitride. KOGYO KAGAKU ZASSHI, v. 69, no. 12, 1966. p. 2260-2262.
- ¹³ PAULING, L. The Structure and Properties of Graphite and Boron Nitride. PROC. NATL. ACAD. SCI. U.S., v. 56, no. 6, 1966. p. 1646-1652.
- ¹⁴ WENTORF, R.H., JR. Condensed Systems at High Pressures and Temperatures. J. OF PHYS. CHEM., v. 63, no. 11, Nov. 18, 1958. p. 1939.
- ¹⁵ McMASTER, D.G. Preparation of Chemical Vapor-Deposited Materials for Use in Field-Enhanced Electron Emission Studies. Techn. Rept. ECOM-2681. Mar. 1966. 36p. AD 631 515.
- ¹⁶ STEELE, S.R., et al. Chemical Vapor Deposited Materials for Electron Tubes. Rept. No. 2, 2nd Quart. Rept., Aug. 15, 1965 to Nov. 14, 1965. Contract No. DA 28-043-AMC-01343(E). Jan. 1966. 46p. AD 477 126.

- 17 RADFIELD, D. and R.L. BAUM. Infrared Transmitting Optical Filter. U.S. 2,986,527. May 30, 1961.
- 18 BROPHY, R.G., et al. Pressure Transmitting Medium for Fragile Structure or Single Crystal. REV. SCI. INSTRUM., v. 38, no. 1, 1967. p. 135-136.
- 19 MARTEL, R.A. Lubricating Glass or Quartz Fibers. U.S. 3,297,470. Jan. 10, 1967.
- 20 QUARRINGTON, J.A. and G.A. WIKHAMMER. An Improved Sheathed Electric Heater. ATOMIC ENERGY OF CANADA LTD. AECL 2592. July 1966.
- 21 GEN. ELECTRIC CO. KUHLMAN, W.C. Research and Evaluation of Materials for Thermocouple Application Suitable for Temperature Measurements up to 4500°F on the Surface Glide Re-Entry Vehicles. Final Rept. Tech. Doc. Rept. No. ASD-TDR-63-233. Contr. No. AF33(657)-8472. May 1963. 75p.
- 22 MELPAR, INC., FALLS CHURCH, VA. Investigation for 2000°F Power Wire. 3rd Quart. Rept. Dec. 28, 1965 - March 21, 1966. Contract No. AF33-615-2721. 39p. AD 480 628.
- 23 DIEFENDORF, R.J. Formation of Boron Nitride Sheets. FR. 1,440,917. June 3, 1966.
- 24 HANLET, J.M.N. Electroluminescent Cells. Societe d'electronique et d'automatisme. FR. 1,196,188, Nov. 23, 1959.
- 25 BOOE, J.M. and J.T. HOOD. Capacitor Resistant to Adverse Environmental Conditions. U.S. 3,278,815. Oct. 11, 1966.
- 26 SAMSONOV, G.V. et al. Boron, Its Compounds and Alloys. U.S. Atomic Energy Comm. Div. of Tech. Info. AEC tr. 5032, v. 1, 1960. p. 211.
- 27 FINLAY, G.R. Boron Compounds for Nuclear Applications. THE AMERICAN CERAMIC SOCIETY BULLETIN, v. 36, no. 3, Mar. 1957. p. 109-111.
- 28 DWORKIN, A.S. et al. The Thermodynamics of Boron Nitride; Low-Temperature Heat Capacity and Entropy; Heats of Combustion and Formation. J. OF CHEM. PHYS., v. 22, no. 5, May 1954. p. 837-842.
- 29 HOWE, R.O. Boron Nitride Utilization in Radomes. ELECTRICAL INSULATION CONFERENCE PROC. 7th, Oct. 15-19, 1967, Chicago, Ill. IEE Pub. no. 32C79. p. 175-178.
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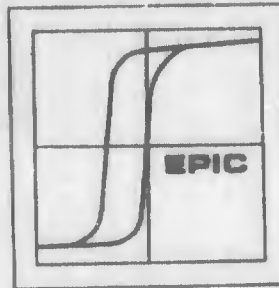


OPTICAL PROPERTIES - ABSORPTION COEFFICIENT (α)



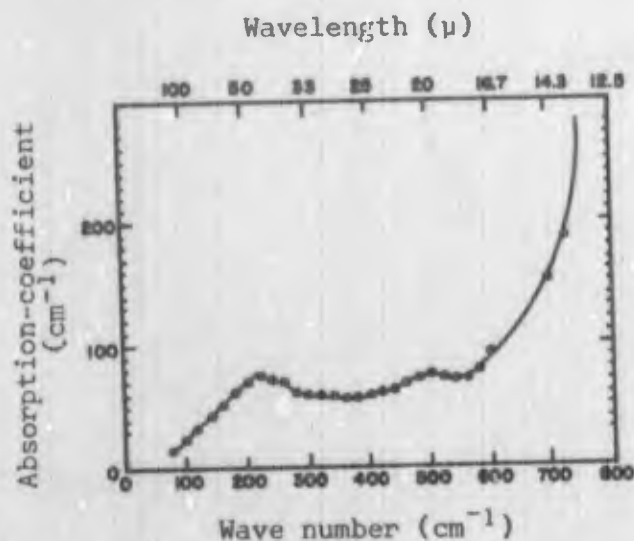
Absorption coefficient of polycrystalline hexagonal boron nitride samples with a preferential orientation of the c-axis. Data taken at 300°K, with linearly polarized light normal and parallel to the c-axis. Major peaks are seen near the infrared eigenfrequencies as determined from the reflectivity spectra on page 29. Minor peaks are attributed to high density of 2 phonon processes as indicated. These 2-phonon peaks are of greater intensity for illumination normal to the c-axis than for illumination parallel to the c-axis. (see page 29; discussion of reflectivity curves) Absorption curves for these same samples at wavelength from 14 to 100 microns is shown on following page.

[Ref. 25245]



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OPTICAL PROPERTIES - ABSORPTION COEFFICIENT (α)



Absorption coefficient of boron nitride samples as above, for polarized light normal to the c-axis, for a segment of the wavelength range from 12.5 to 100 microns. $T = 300^\circ\text{K}$.

[Ref. 25245]

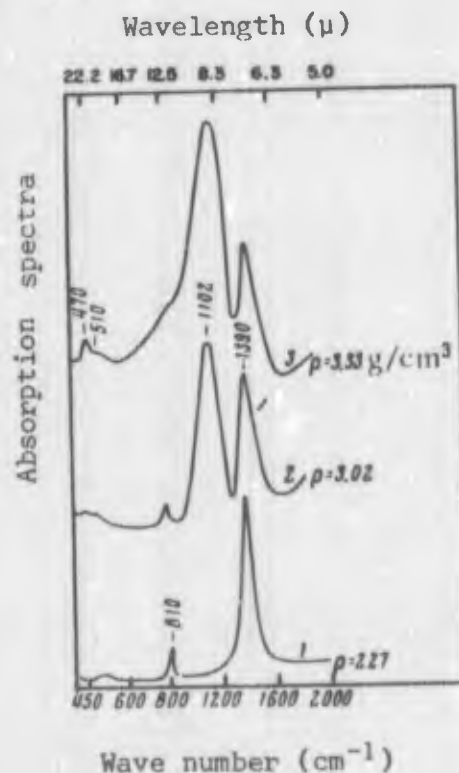
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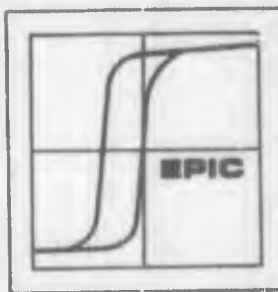
Absorption spectra as a function of wave number at 20°C for several samples of boron nitride under shock compression.

1. Initial substance, density = 2.27 g/cm^3 . Two intense bands are seen at 12.3 and 7.16μ , characteristic of the hexagonal boron nitride.
- 2, 3. In the shock-compressed samples, density rises with increase in the wurtzite form and new bands appear at 21.3 , 19.6 and 9.1μ which may be assigned to the wurtzite form.

[Ref. 30001]

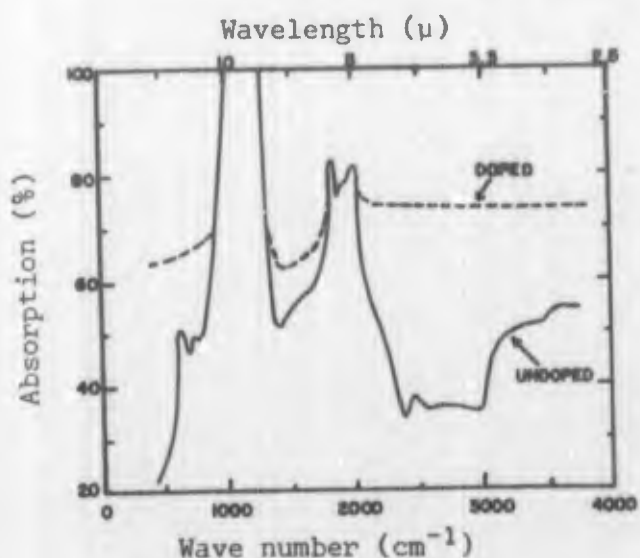
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OPTICAL PROPERTIES - ABSORPTION COEFFICIENT



Absorption in single crystal cubic boron nitride as a function of wavelength at 300°K.

— pure material, $p \sim 10^{10}$ ohm-cm
--- beryllium-doped, $p \sim 10^4$ ohm-cm

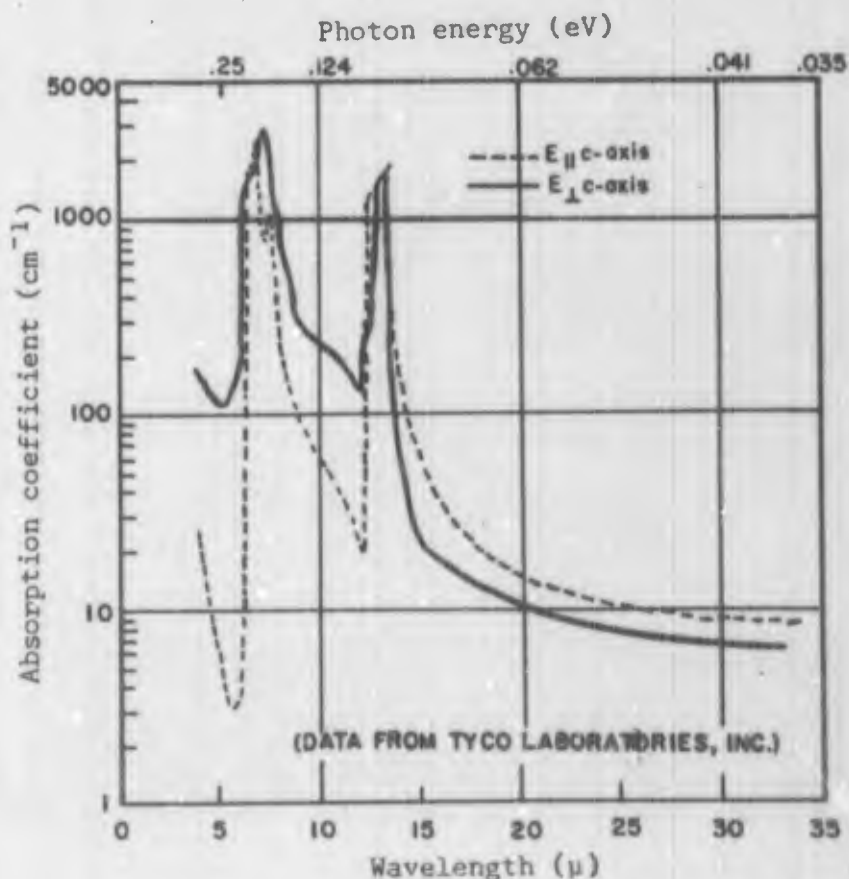
[Ref. 28367]

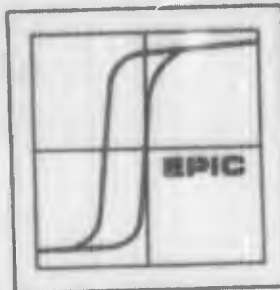
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Absorption coefficient as a function of wavelength for chemically vapor-deposited boron nitride at 300°K. The material is the hexagonal form and is polycrystalline, but the crystallite structure is highly oriented. This is evident in the anisotropy for incident light, normal and parallel to the c-axis.

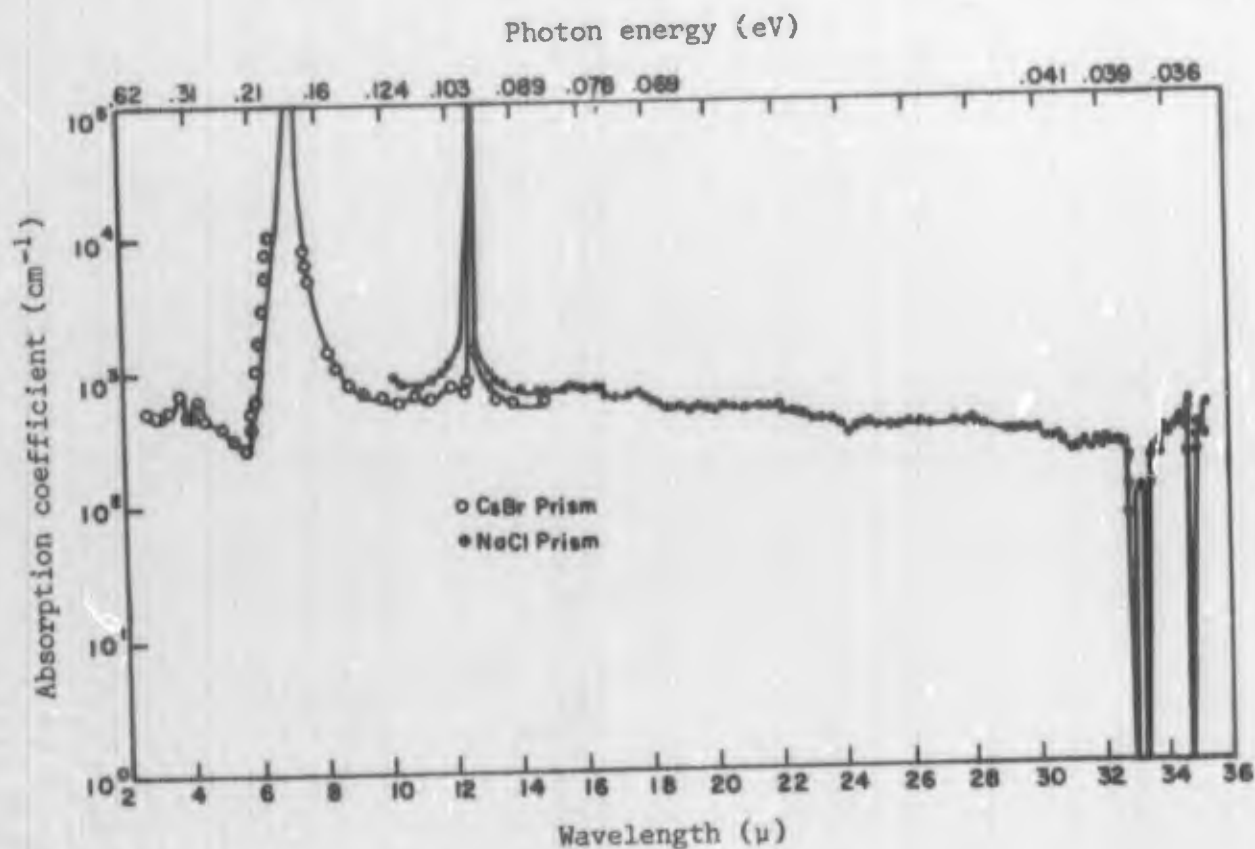
[Ref. 21962]

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OPTICAL PROPERTIES - ABSORPTION COEFFICIENT



Absorption coefficient as a function of wavelength for chemically vapour-deposited boron nitride at 300°K, 1 mil thick film, $p \sim 10^{15}$ ohm-cm. This process yields highly oriented films.

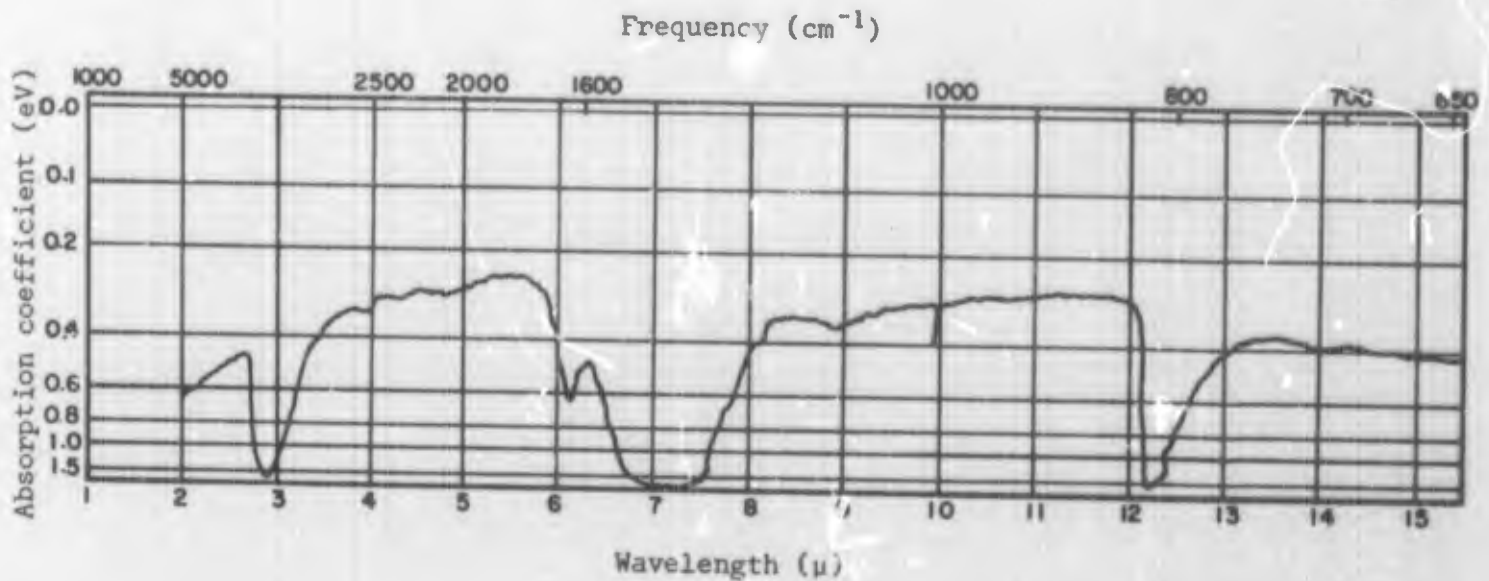
[Ref. 29402]

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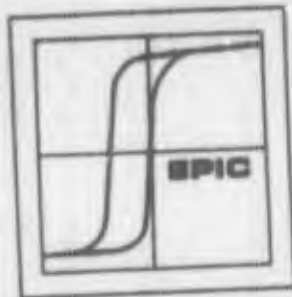
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OPTICAL PROPERTIES - ABSORPTION COEFFICIENT



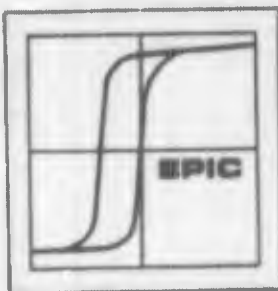
Absorption coefficient of a boron nitride film deposited on a tungsten substrate at 1950°C. The higher temperature of deposition yields a more crystalline film of appreciably higher hexagonal content

[Ref. 21330]

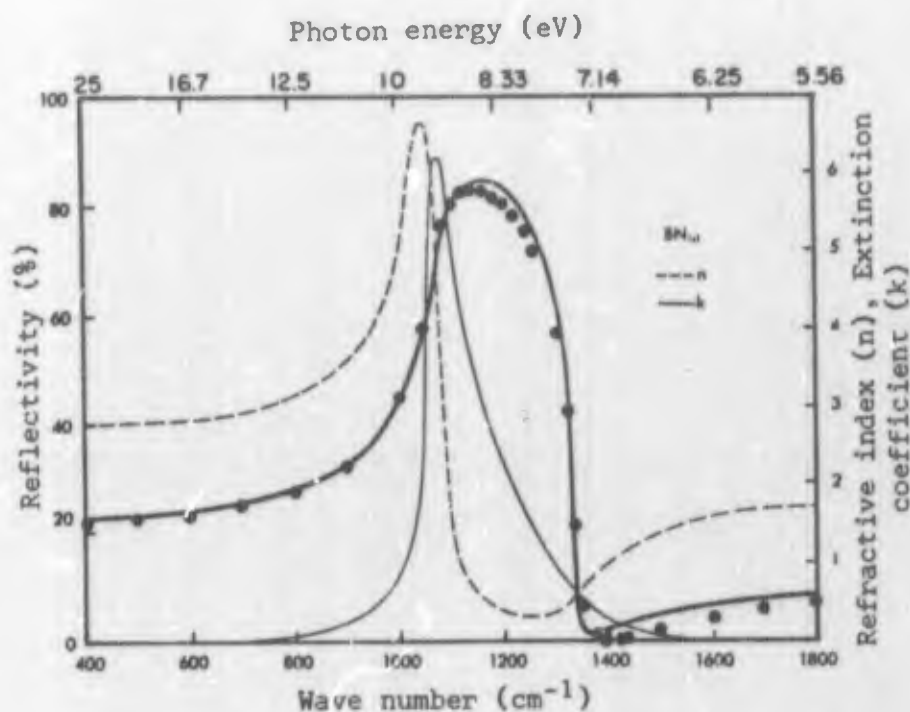


OPTICAL PROPERTIES - TRANSMISSION

Transmission measurements on high purity hexagonal boron nitride powder disks have been carried out by Brame et al. [Ref. 29728]. They report transmittance measurements in the wavelength range 2 to 16 microns at 300°K. Their results show a strong absorption band at 7.28 microns and a medium absorption band at 12.3 microns; transmittance drops to approximately 20% at 7.28 microns and to 60% at 12.3 microns. A region of high transmittance, greater than 90%, is observed in the range 4 to 6 microns.



OPTICAL PROPERTIES - REFLECTIVITY



Reflectivity and optical constants of cubic boron nitride as a function of wavelength at 300°K. The slope in the refractive index curve between 5.6 and 6.9 microns is seen on page 33.

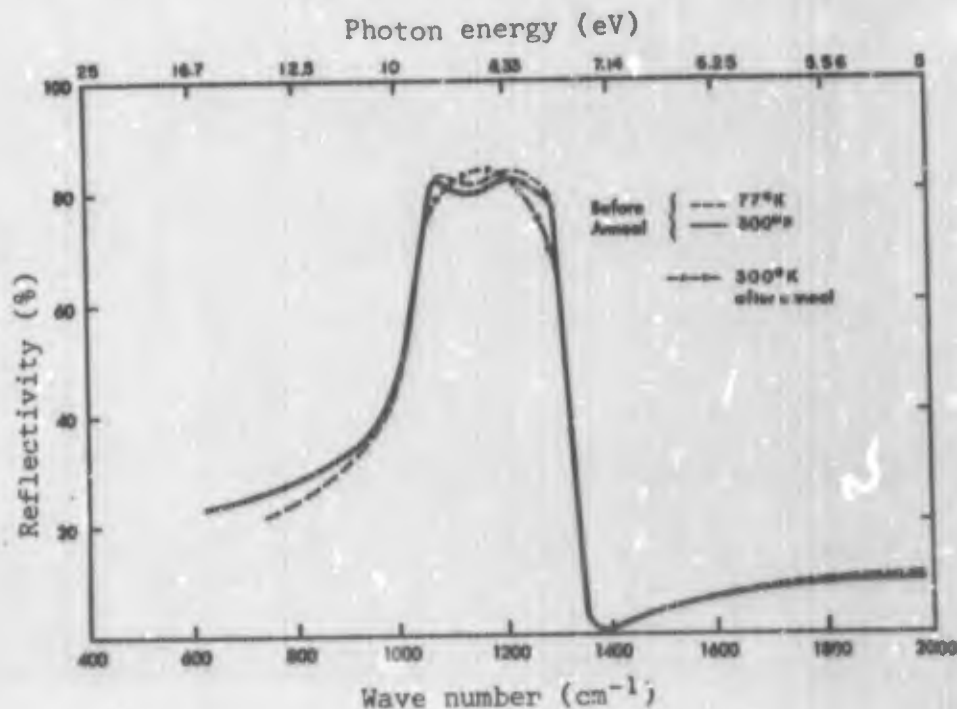
[Ref. 28367]

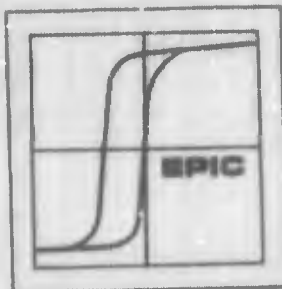
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Reflectivity of cubic boron nitride at 77 and 300°K. Measurement at low temperature shows very little change in reflectivity, indicating the strong bonding of the structure. Annealing eliminates surface conditions which caused the structure in the main band.

[Ref. 28367]

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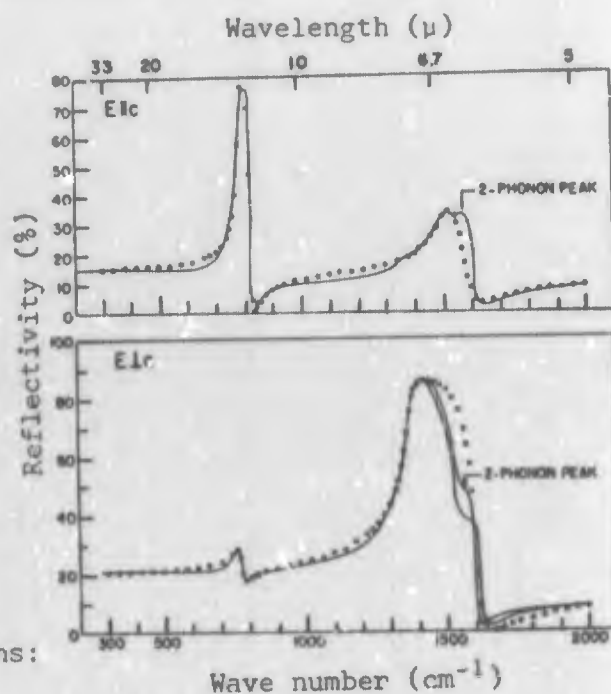


OPTICAL PROPERTIES - REFLECTIVITY

The reflectivity of polycrystalline hexagonal boron nitride samples with a preferential orientation of the c-axis. Data taken at 300°K, with linearly polarized light, normal and parallel to the c-axis. The spectra were analyzed by means of an optimum fit with the classical dispersion formula:

$$\epsilon = \epsilon' - i\epsilon'' = \epsilon_{\infty} + \frac{s_1^2}{\omega_1^2 - \omega^2 + i\omega\gamma_1} + \frac{s_2^2}{\omega_2^2 - \omega^2 + i\omega\gamma_2}$$

- ϵ_{∞} = optical dielectric constant
- ω = frequency of the incident light
- s_v = oscillation strength
- ω_v = eigenfrequency
- γ_v = damping constant of normal mode
- v = normal mode



The following values were used in the calculations:

$$\begin{aligned} \epsilon_{\infty} &= 4.10, & \epsilon_0 &= 5.09, \\ \omega_{11} &= 783 \text{ cm}^{-1}, & \omega_{12} &= 828 \text{ cm}^{-1}, & s_1^2 &= 3.26 \times 10^5 \text{ cm}^{-2}, & \gamma_1 &= 8.0 \text{ cm}^{-1}, \\ \omega_{21} &= 1510 \text{ cm}^{-1}, & \omega_{22} &= 1595 \text{ cm}^{-1}, & s_2^2 &= 1.04 \times 10^6 \text{ cm}^{-2}, & \gamma_2 &= 80.0 \text{ cm}^{-1}. \end{aligned}$$

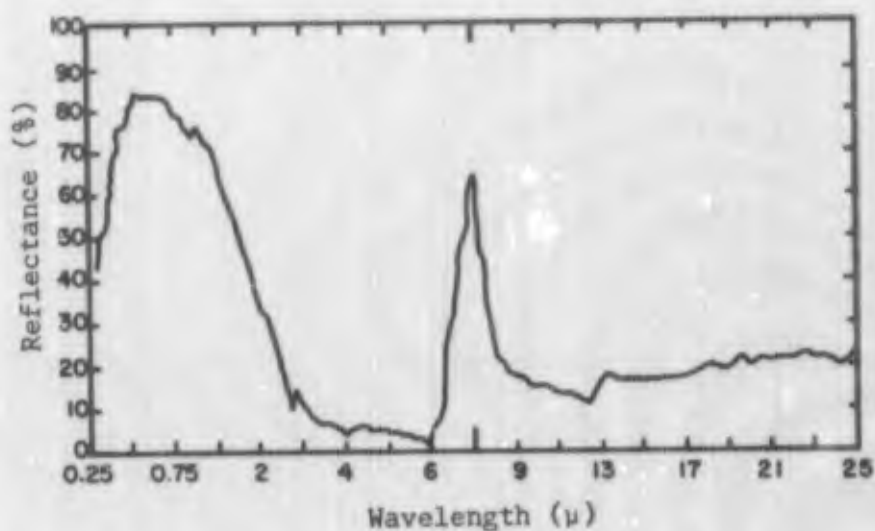
$$\begin{aligned} \epsilon_{\infty} &= 4.95, & \epsilon_0 &= 7.04, \\ \omega_{11} &= 767 \text{ cm}^{-1}, & \omega_{12} &= 778 \text{ cm}^{-1}, & s_1^2 &= 1.23 \times 10^5 \text{ cm}^{-2}, & \gamma_1 &= 35.0 \text{ cm}^{-1}, \\ \omega_{21} &= 1367 \text{ cm}^{-1}, & \omega_{22} &= 1610 \text{ cm}^{-1}, & s_2^2 &= 3.49 \times 10^5 \text{ cm}^{-2}, & \gamma_2 &= 29.0 \text{ cm}^{-1}. \end{aligned}$$

The longitudinal frequencies of the various lattice modes were derived from the poles of the complex dielectric constant of the classical oscillator fit. The highly anisotropic structure of the boron nitride requires highly anisotropic normal modes. Therefore, the modes with slightly different frequencies have to be considered as one normal mode of the lattice. The weaker modes in the infrared spectra are then probably due to the misorientation in the polycrystalline sample. The small shift in their frequencies, as compared to the stronger modes, may be due to the angular dependence of the extraordinary waves.

[Ref. 25245]



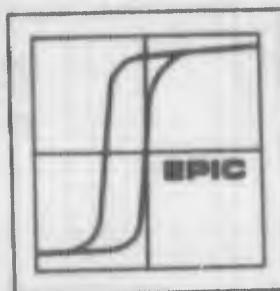
OPTICAL PROPERTIES - REFLECTIVITY



Reflectance as a function of wavelength for
pyrolytic boron nitride at 300°K.

α_s , the solar absorptance = 0.325

[Ref. 30876]



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OPTICAL PROPERTIES - REFRACTIVE INDEX

<u>Value</u>	<u>Sample</u>	<u>Temp.</u>	<u>Ref.</u>
$\omega = 2.20 \pm 0.05$	BN - hexagonal powder	300°K	29726
$\epsilon = 1.66 \pm 0.02$	< 10 μ size crystallites		

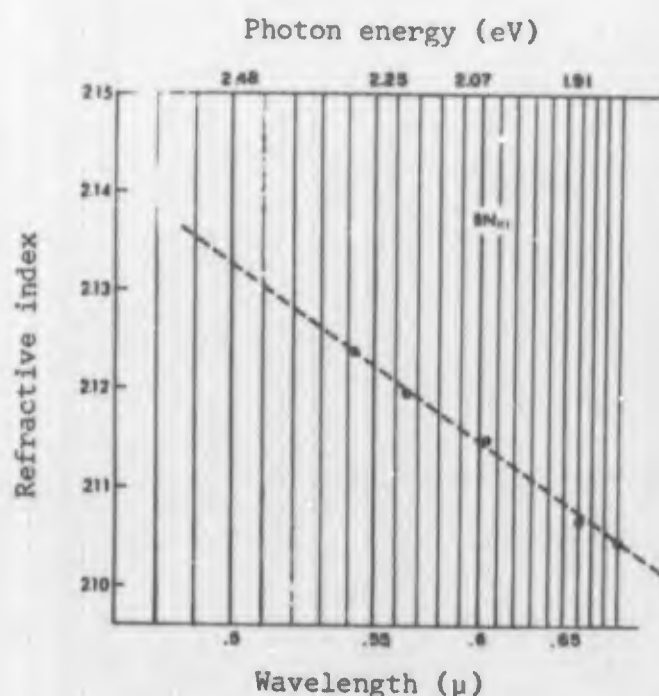
Birefringence = $\omega - \epsilon = 0.54 \pm 0.07$; uniaxial negative

$n = 2.22$	for cubic form		29702
2.117	Single crystal cubic $\rho \sim 10^{10} \Omega \text{ cm}$	1. Beche method (matching of indices with a standard) 2. Reflectivity meas. at $\lambda = 5-25 \mu$	300°K 28367



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OPTICAL PROPERTIES - REFRACTIVE INDEX



Refractive index as a function of wavelength at 300°K for single crystal cubic boron nitride. The dispersion is calculated and equals 0.0377, somewhat less than that of diamond.

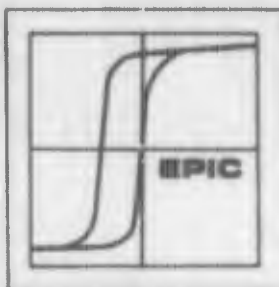
[Ref. 28367]

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Transmission spectra of the boron nitride showed a well defined peak near 5.5 microns, regardless of the preparation methods. However, when measured in a series of matrices, the peak wavelength varies from 4.89 to 10.15 microns. This is the Christensen Filter Effect and has device possibilities. (Patent U.S. 2,986,427)

Additional data from this paper gave refractive indices at 300°K for pressed and sintered hexagonal boron nitride in the infrared range, utilizing potassium halide matrices. The curve showed the 1.7 value at about 4 microns and two sharp minima at 6.5 and 12 microns. There are also two maxima at 8 and 13 microns.

[Ref. 29708]

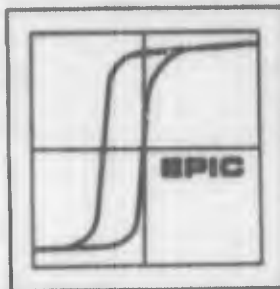


DIELECTRIC CONSTANT

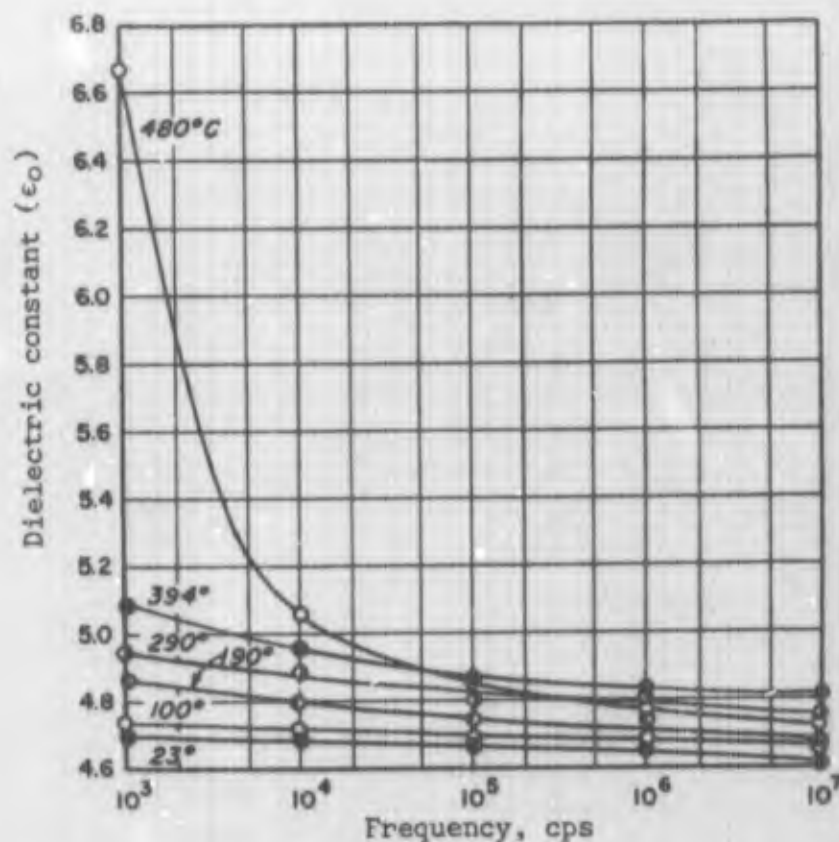
Symbol	Value	Sample	Measurement	Temp.	Ref.
ϵ_0	7.1	Single crystal $\rho \sim 10^{10} \Omega \text{ cm}$ cubic	Damped oscillator analysis	300°K	28367
ϵ_∞	4.5		Reflectivity $\lambda = 5\text{-}25 \mu$		
ϵ_0	5.12	CVD hexagonal	4.8 Gc E parallel to deposition plane	20-500°C	17357
$\tan \delta$	0.00014	"	"	20°C	17357
ϵ_0	4.777	hot-pressed	4.8 Gc	20°C	17357
$\tan \delta$	0.00033	hot-pressed	4.8 Gc		

ϵ_0 = Static dielectric constant

ϵ_∞ = High frequency (optical) dielectric constant



DIELECTRIC CONSTANT



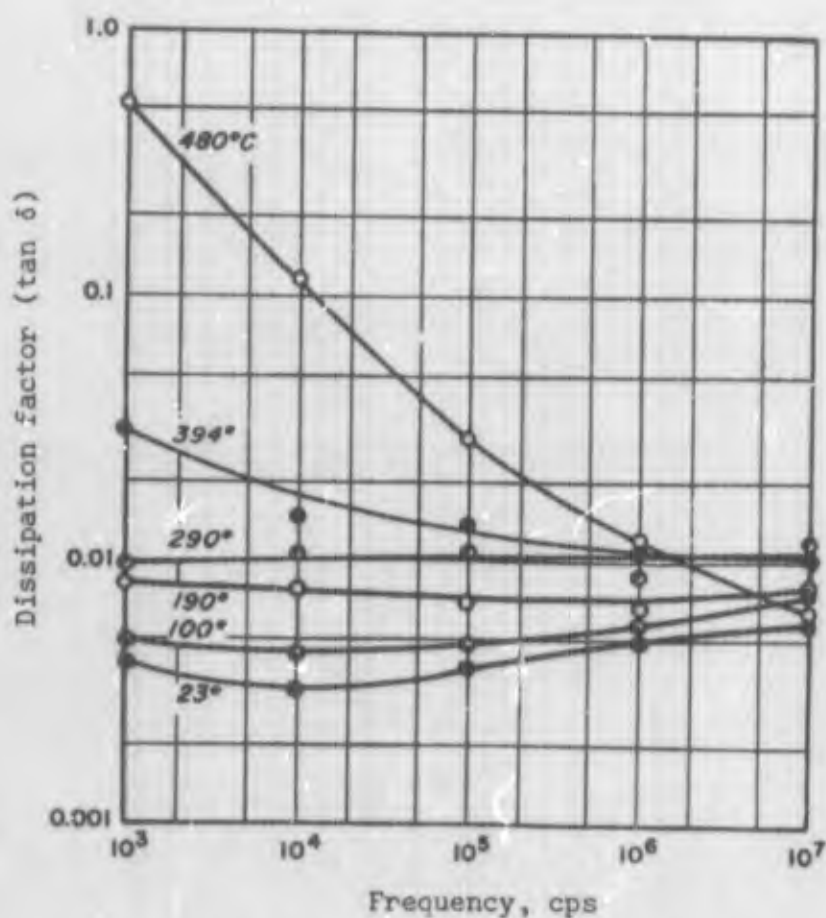
Dielectric constant as a function of frequency for several temperatures between 23 °C and 480 °C. The boron nitride samples are hot pressed disks.

[Ref. 12124]

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DIELECTRIC CONSTANT



Dissipation factor as a function of frequency for several temperatures between 23 °C and 480 °C. The boron nitride samples are hot pressed disks.

[Ref. 12124]

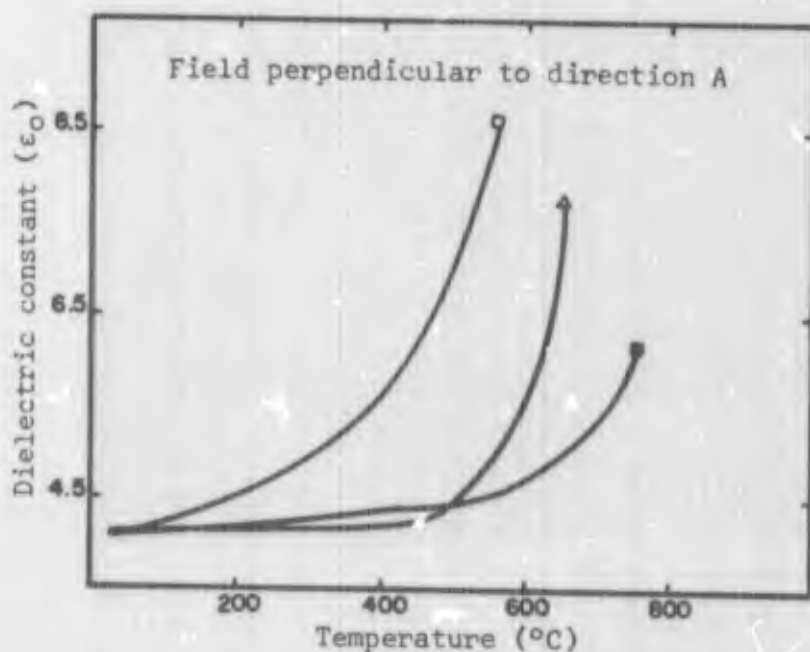
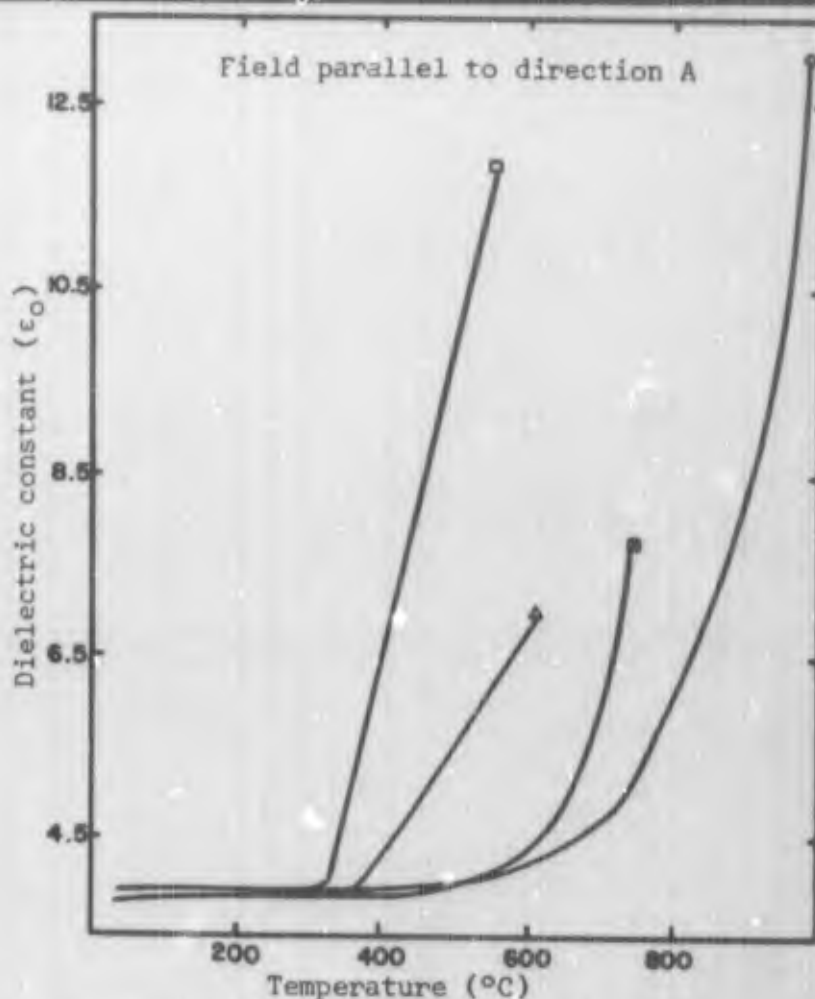
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DIELECTRIC CONSTANT

Dielectric constant as a function of temperature for commercial hot-pressed hexagonal boron nitride. The A-direction is the plane of deposition and is normal to the c-axis. The bulk material, therefore, is a highly oriented polycrystalline mass. Data taken at 4 frequencies as given.



Frequency

- 10² cps
- Δ 10³ cps
- 10⁴ cps
- 10⁵ cps

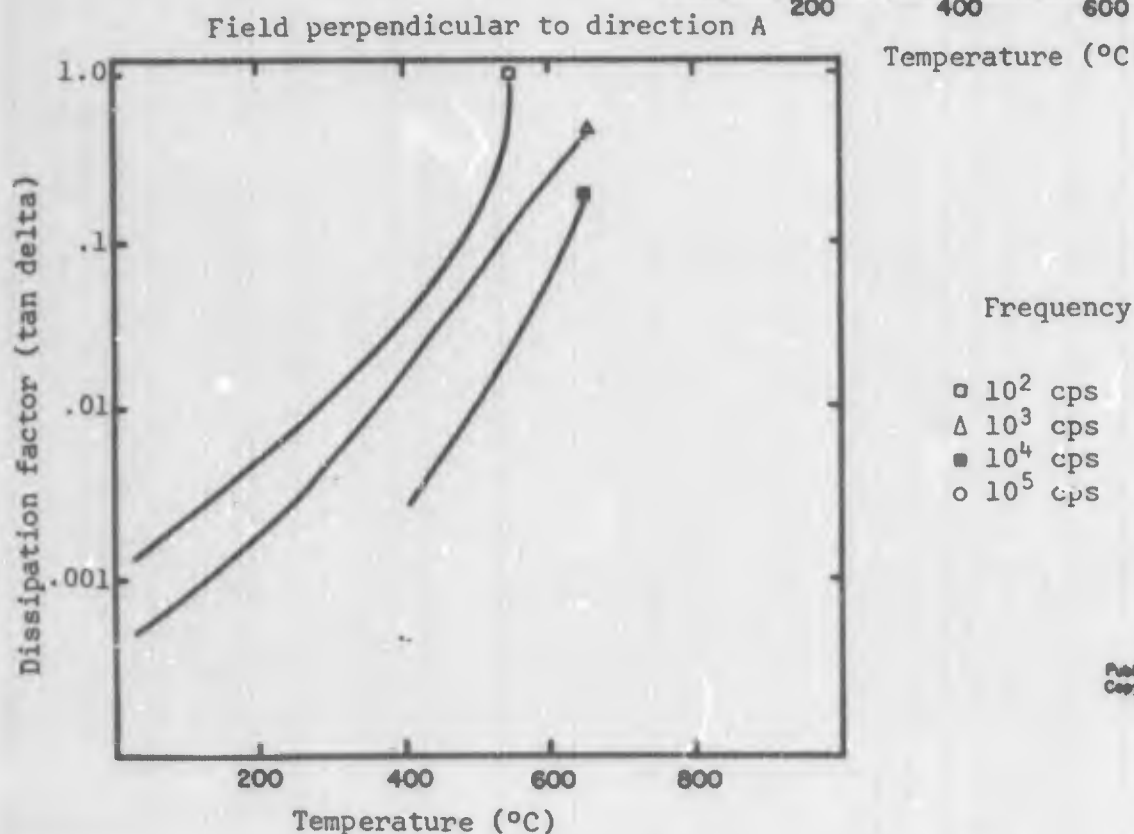
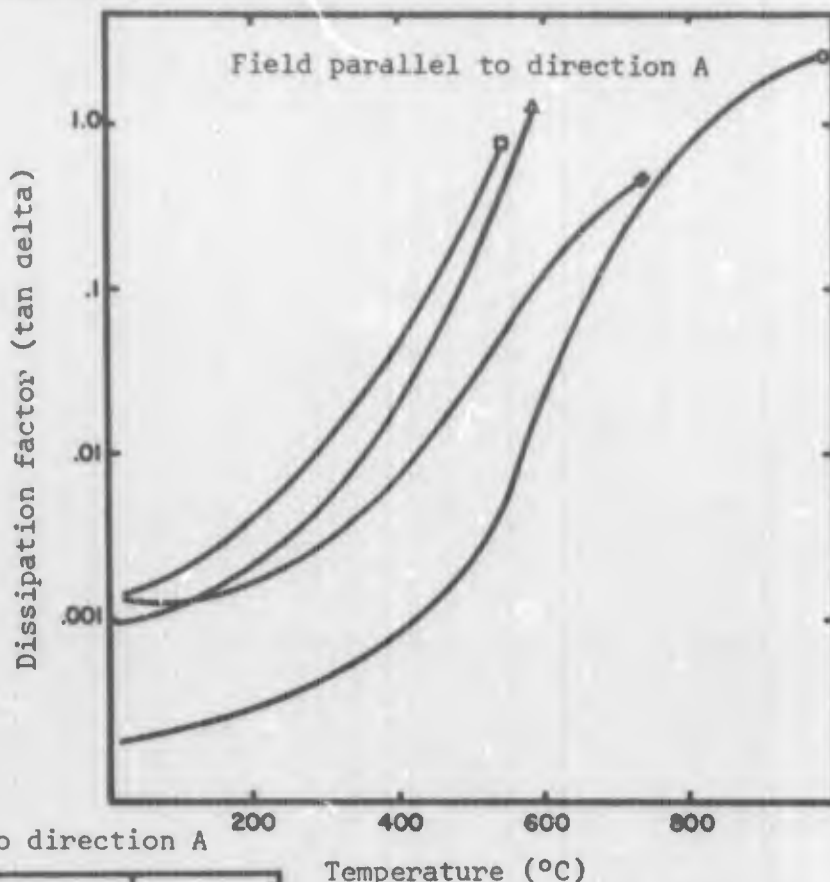
[Ref. 9178]

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DIELECTRIC CONSTANT

Dissipation factor as a function of temperature for commercial hot-pressed hexagonal boron nitride. The A-direction is the plane of deposition and is normal to the c-axis. The bulk material, therefore, is a highly oriented polycrystalline mass. Data taken at 4 frequencies as given.

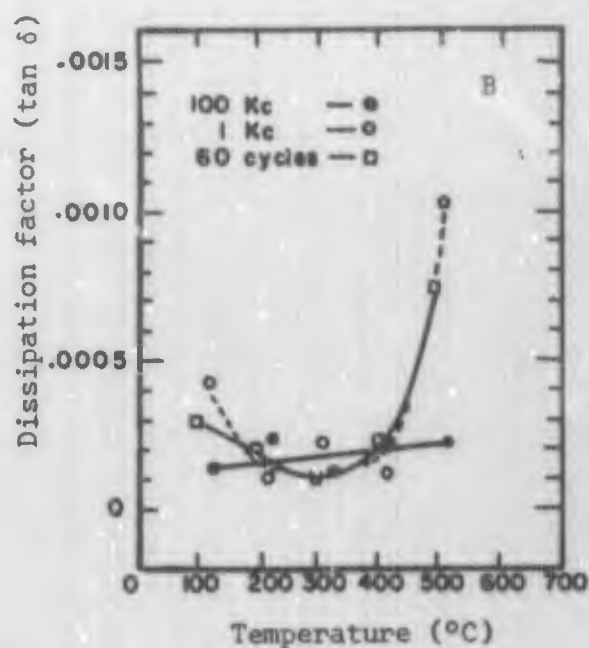
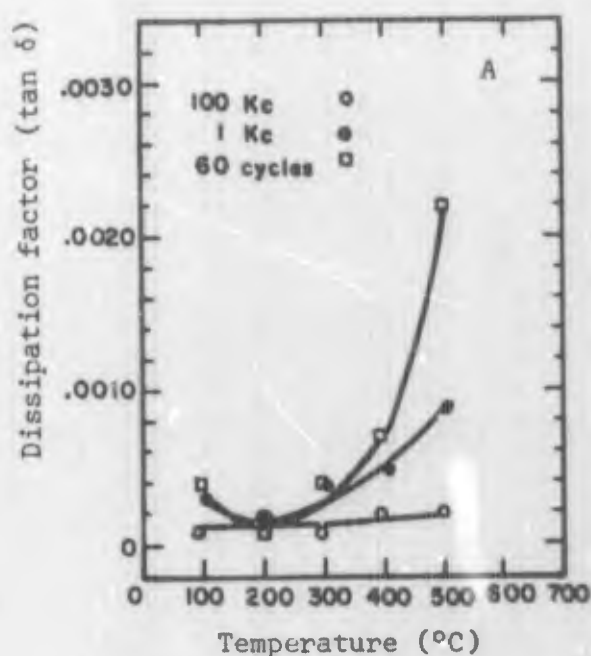


[Ref. 9178]

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DIELECTRIC CONSTANT



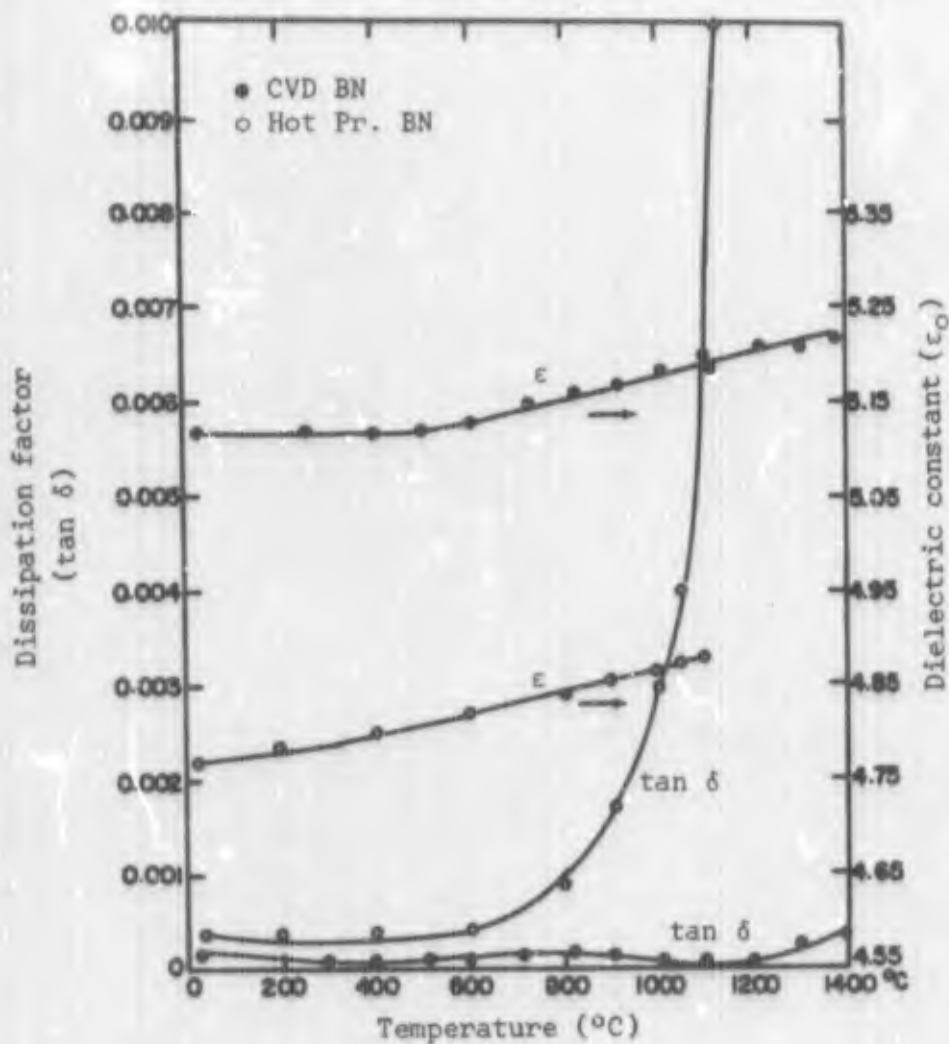
Dissipation factor as a function of temperature for hot pressed boron nitride at the three indicated frequencies. A and B are two disks from the same sample and indicate the inhomogeneity arising from this method of preparation. The powder was hot pressed at 1800 °C and 2000 psi for 125 minutes. This is apparently the optimum time, temperature and pressure. The heating volatilizes some of the impurities but also introduces others from the surrounding equipment.

[Ref. 4709]



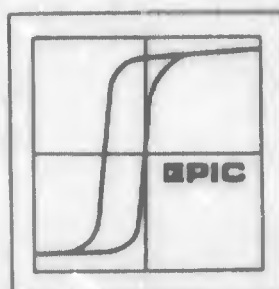
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DIELECTRIC CONSTANT



Dissipation factor and dielectric constant as a function of temperature for chemical vapor deposited and hot pressed boron nitride at 4.8 Gc. The field is parallel to the deposition plane of the highly oriented pure chemical vapor deposited material and therefore normal to the c-axis. The low, constant dissipation factor and the low temperature coefficient of the dielectric constant, indicate the superiority of the chemical vapor deposited material.

[Ref. 22943]



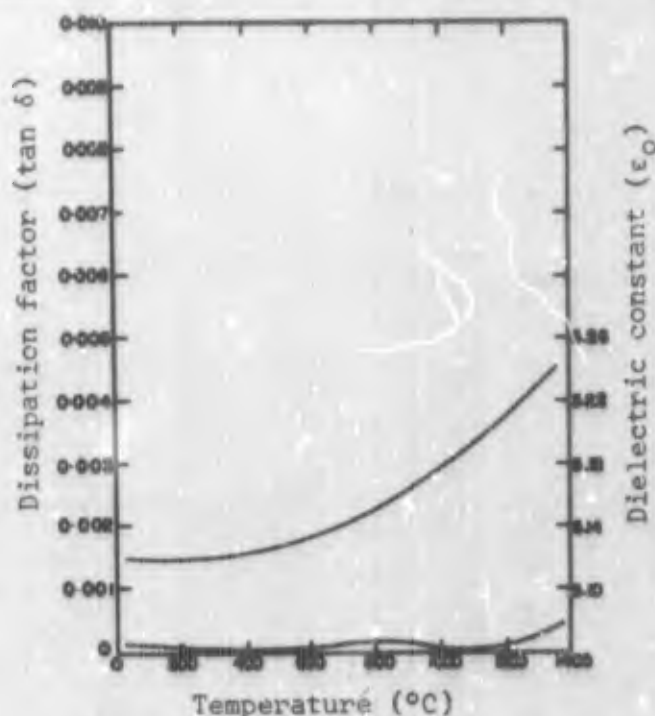
DIELECTRIC CONSTANT

Dissipation factor and dielectric constant as a function of temperature for chemical vapor deposited boron nitride. Electric field parallel to deposition plane and normal to c-axis.

Density = 2.135 g/cc

Frequency = 4.83 to 4.77 Gc

The low, constant dissipation factor and the low temperature coefficient of the dielectric constant are seen here as in [Ref. 22943].



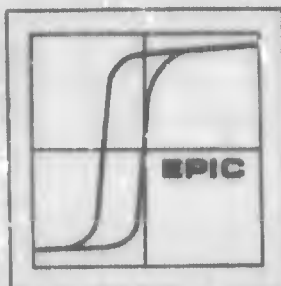
Electric field || deposition plane

T°C	ϵ	$\tan\delta$
25	5.12	0.00014
289	5.12	0.00008
392	5.12	0.00008
499	5.12	0.00009
600	5.14	0.00008
713	5.15	0.00012
835	5.16	0.00014
917	5.17	0.00015
1016	5.18	0.00005
1102	5.19	0.00005
1197	5.22	0.00005
1300	5.23	0.00027
1375	5.24	0.00039

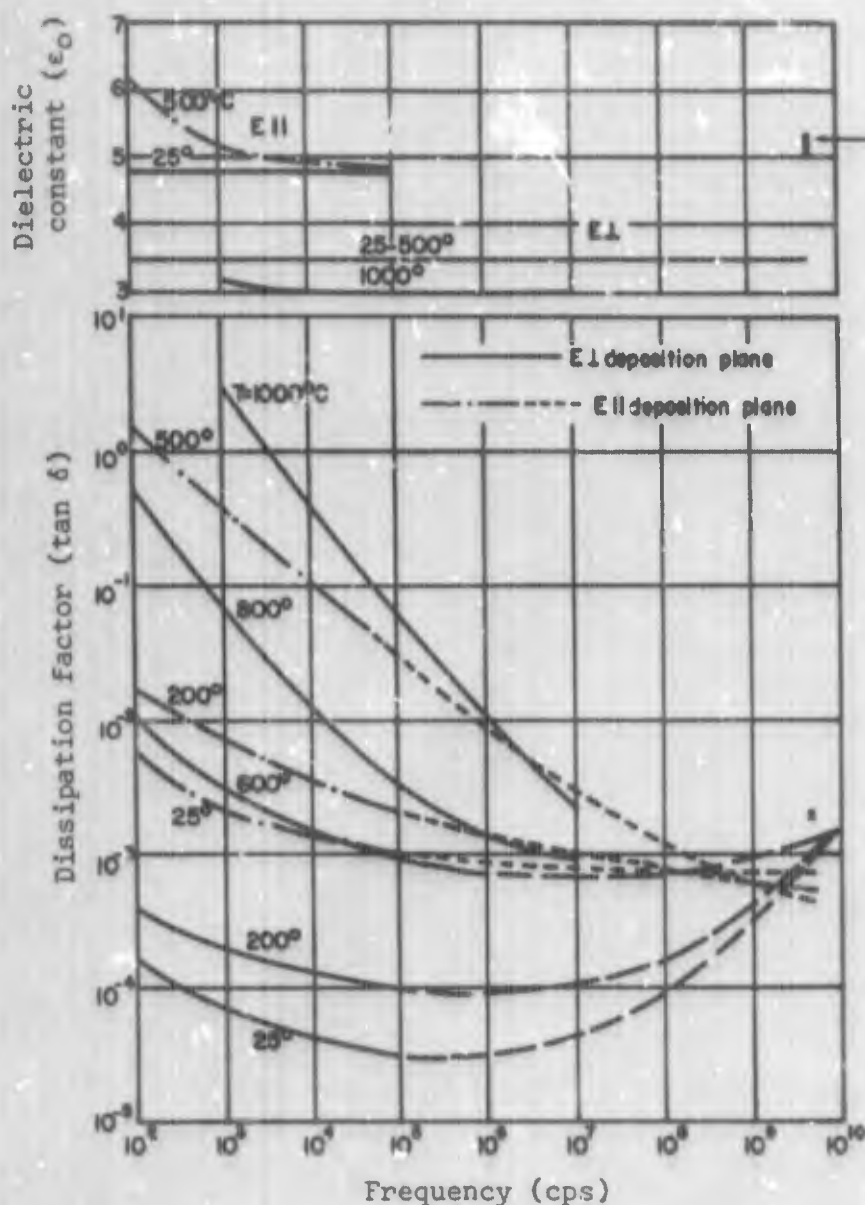
Electric field ⊥ deposition plane

25	3.50	0.0003
----	------	--------

[Ref. 22816]



DIELECTRIC CONSTANT



Anisotropy in chemical vapor deposited boron nitride is shown in curves of dielectric constant and dissipation factor as a function of frequency at several temperatures between 25°C and 1000°C. The electrical field is normal and parallel to the deposition plane. This latter is normal to the c-axis of the hexagonal boron nitride.

[Ref. 22816]



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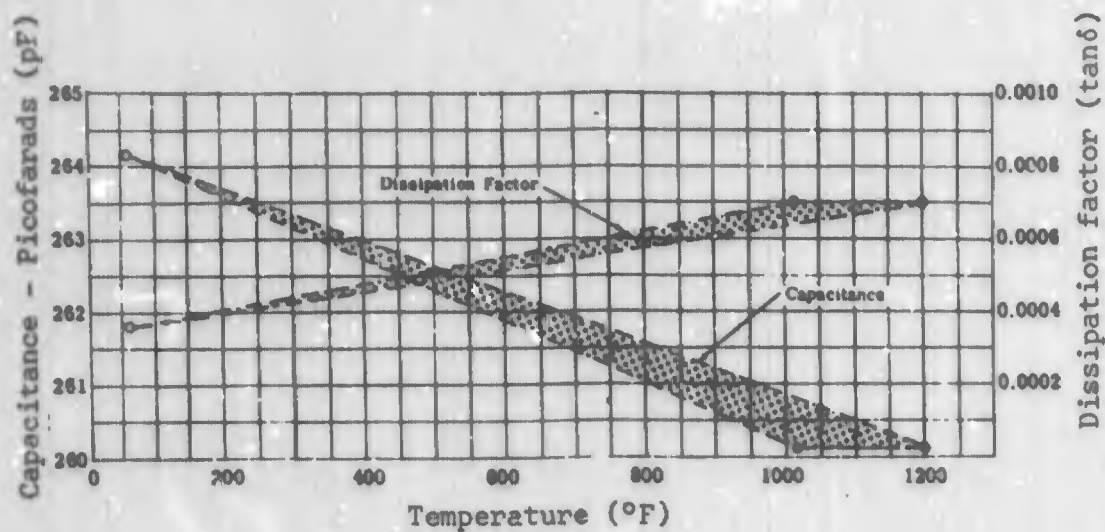
DIELECTRIC CONSTANT

ϵ_o		$\tan \delta$		Diel. Str. V/m		$\rho \Omega \text{ cm}$		Freq.	Temp.	Ref.
Cu	Mo	Cu	Mo	Cu	Mo	Cu	Mo			
5.7	4.4	.011	.003	3900	5000	10^{17}	10^{17}	1kc	25°C	17737
4.5	↓	.0045	—	2900	3800	10^{14}	10^{16}	↓	125°C	↓
4.4	↓	.0056	—	1500	3400	10^{13}	10^{15}	↓	175°C	↓
4.4	↓	.011	—	—	3000	—	10^{14}	↓	250°C	↓

Table shows dielectric properties of 0.5 micron thick boron nitride films, deposited on copper or molybdenum substrates by chemical vapor deposition. Films are deposited on the copper at 900-1000°C and on the molybdenum at 1400°C.

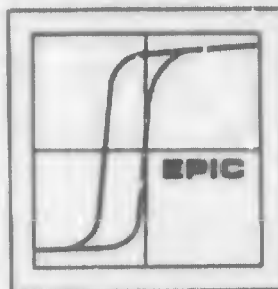


DIELECTRIC CONSTANT

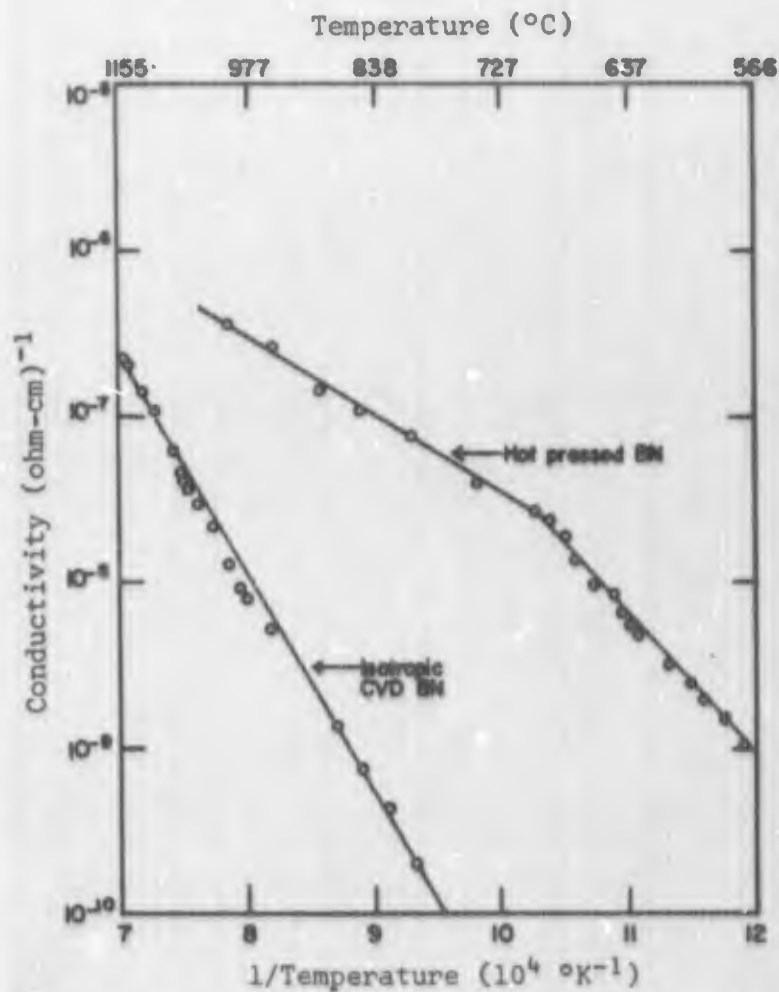


Capacitance and dissipation factor as a function of temperature for chemical vapor deposited boron nitride samples, 1.12 mil thick. Measured at 10^{-7} torr and 1 kc.

[Ref. 25502]



TRANSPORT PROPERTIES - ELECTRICAL CONDUCTIVITY



The dc bulk electrical conductivity of isotropic chemical vapor deposited boron nitride as a function of temperature. Comparison is made with a hot pressed sample.

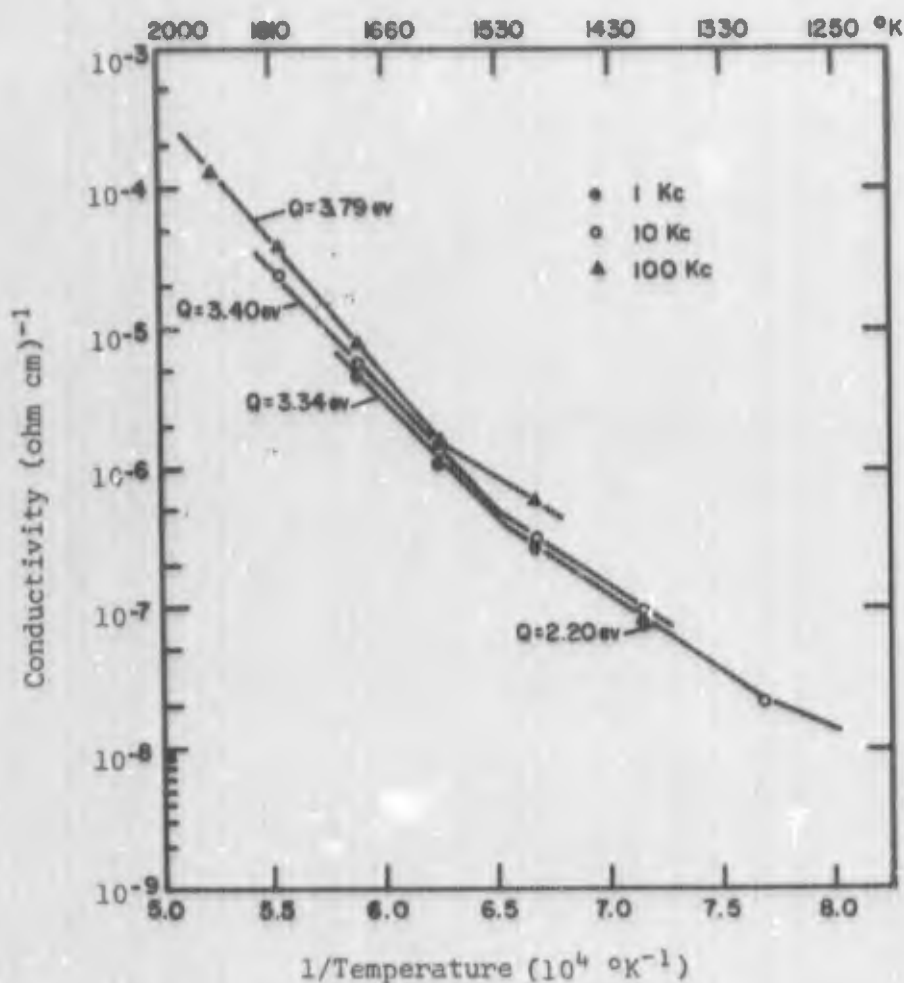
Density = (2.06 g/cc)

[Ref. 29976]



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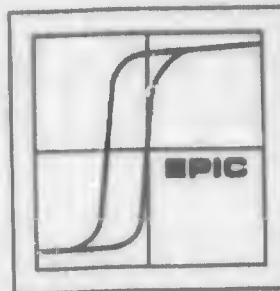
TRANSPORT PROPERTIES - ELECTRICAL CONDUCTIVITY



Electrical conductivity at three frequencies as a function of reciprocal temperature for pyrolytic boron nitride under an argon flow of 2.0 cfh (ft³/hr). CVD boron nitride is strongly oriented along the c-axis which was parallel to the deposition surface, and measurements were made in this direction.

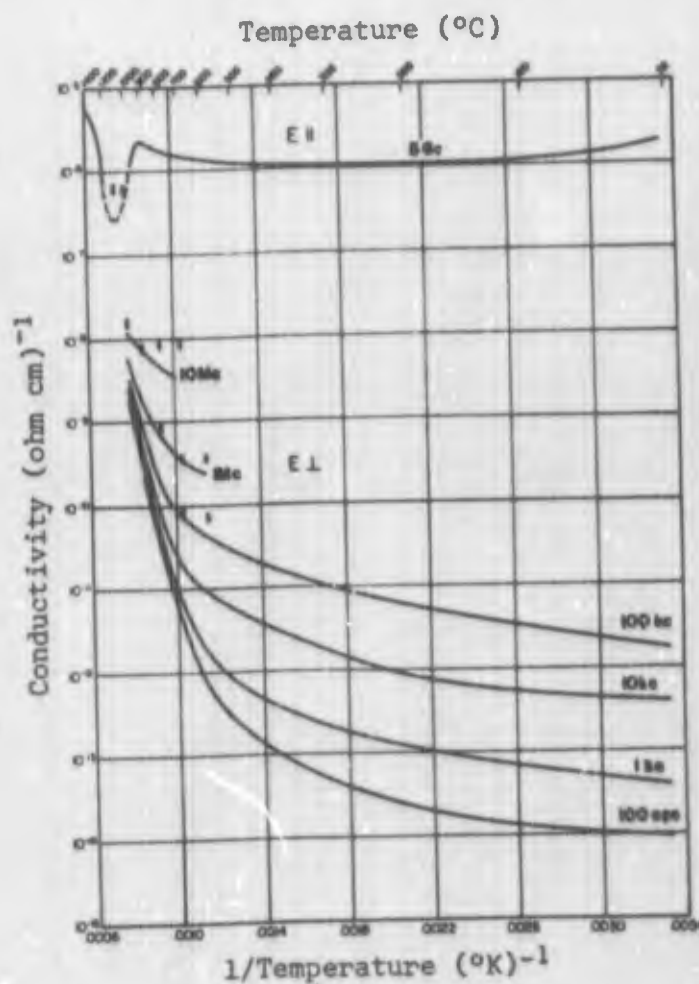
The sample had an impurity level of 113 ppm. Activation energies are shown, and the highest value of 3.79 eV corresponds to a band gap of 7.58 eV. It is suggested that intrinsic conduction sets in at 1500 °K as seen by the change in slope at that temperature.

[Ref. 29801]



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TRANSPORT PROPERTIES - ELECTRICAL CONDUCTIVITY

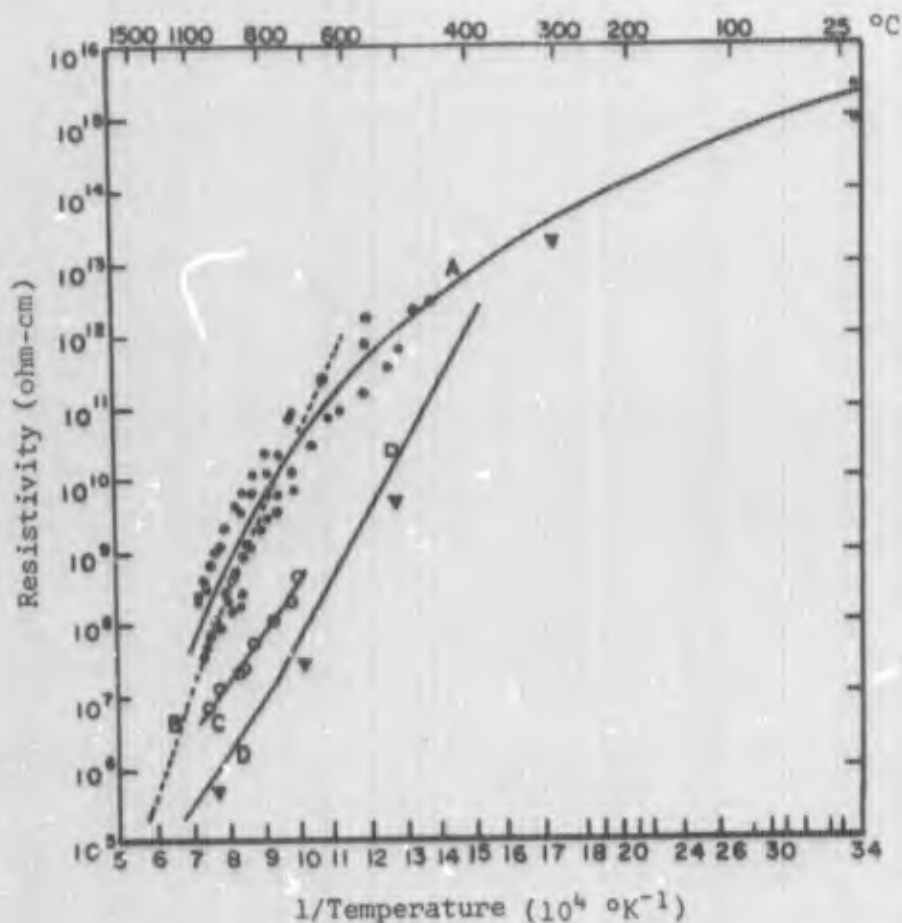


Electrical conductivity as a function of reciprocal temperature for pyrolytic boron nitride. The field is applied parallel and normal to the deposition plane which is the "a" direction (low resistivity). Data taken in a nitrogen atmosphere. Microwave data show a minimum probably due to some impurity loss.

[Ref. 17357]



TRANSPORT PROPERTIES - ELECTRICAL RESISTIVITY



Electrical resistivity as a function of reciprocal temperature in CVD (pyrolytic) boron nitride, measured parallel to the c-axis.

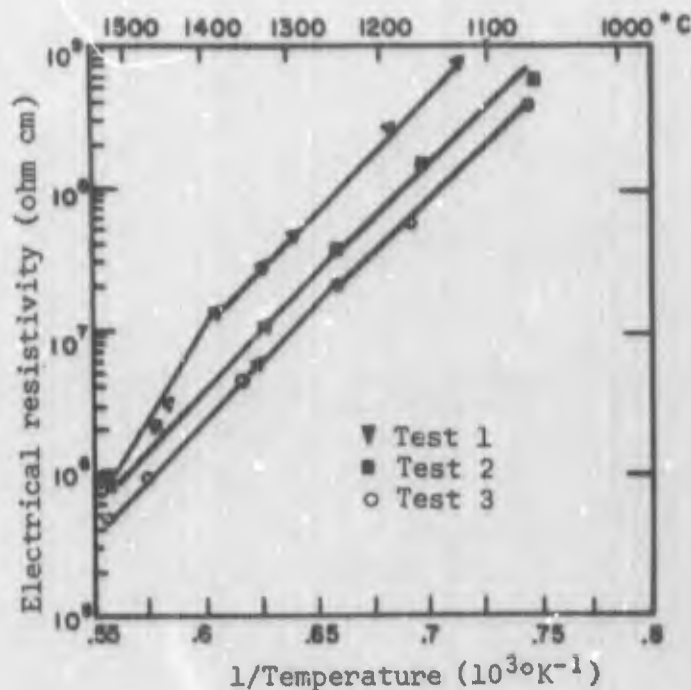
- A ● CVD boron nitride [Ref. 22943]
- B --- Pure, pressed powder boron nitride (Ingles & Popper)*
(Prepared by mixing boron nitride with 15% B_2O_3 and heating to 1800°C in nitrogen atmosphere for 4 hours)
- C ○ Hot pressed boron nitride [Ref. 22943]
- D — Hot pressed (900°C) boron nitride (Ingles & Popper)
- Δ Hot pressed boron nitride [Ref. 29802]

*INGLES, T.A. and P. POPPER. Special Ceramics.
Proceedings of a Symposium by the Br. Ceram.
Res. Assoc., Academic Press, Inc. New York,
1960. p. 144-169.

[Ref. 22943]



TRANSPORT PROPERTIES - ELECTRICAL RESISTIVITY



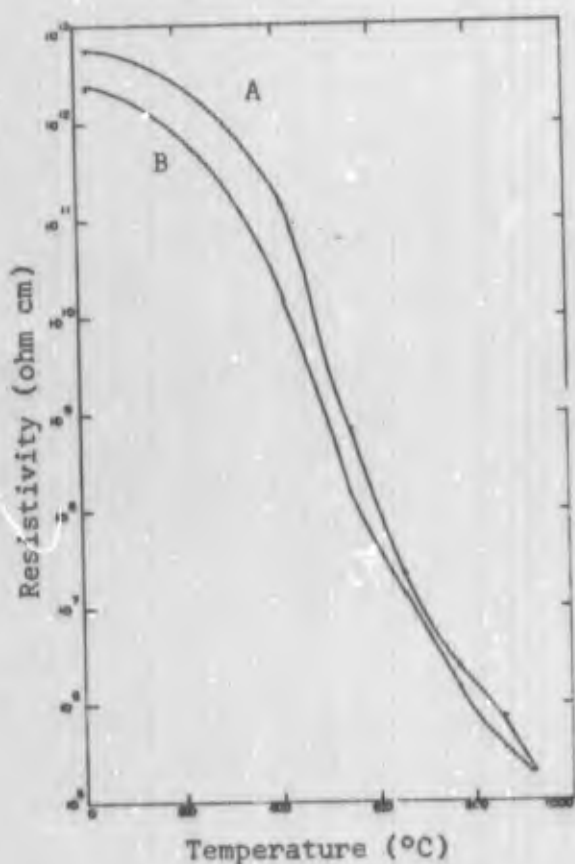
Electrical resistivity as a function of reciprocal temperature for hexagonal pyrolytic boron nitride discs, in nitrogen atmosphere containing 500 ppm hydrogen. Direct current parallel to the "c" or high resistivity direction. Cooling cycle curves.

Electrical resistivity measurements were made during heating and cooling cycles and tended to improve, probably as a result of decrease in impurity charge carriers. Various atmospheres (hydrogen, nitrogen, argon) had little effect on resistivity, it was rather the thermal treatment which affected the current voltage curves. These were linear for the first hours and at low voltages and temperatures, but above 1300°C the curves became non-linear as they did also above 180 volts.

[Ref. 27750]



TRANSPORT PROPERTIES - ELECTRICAL RESISTIVITY



- A Measured || to moulding pressure
B Measured ⊥ to moulding pressure

Electrical resistivity as a function of temperature in hot pressed boron nitride. This graph is drawn from data given in vendor literature of the Carborundum Co. Further data from the same company is seen in the table.

Volume Resistivity

(Measurements made with electric field parallel to pressing direction)

Temperature, °C	Resistivity, ohm-cm
25	1.7×10^{13}
500	2.3×10^{10}
1000	3.1×10^4
1500	6×10^2

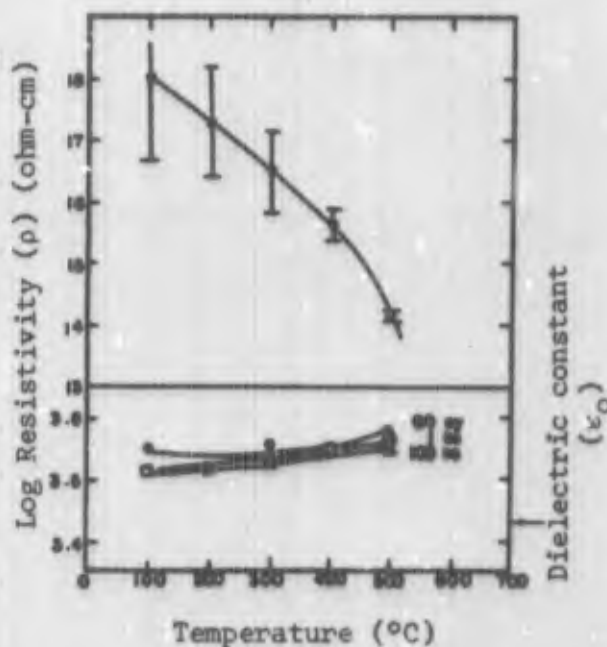
[Ref. 29802]

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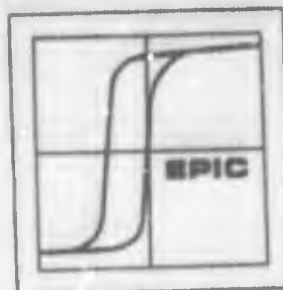
TRANSPORT PROPERTIES - ELECTRICAL RESISTIVITY



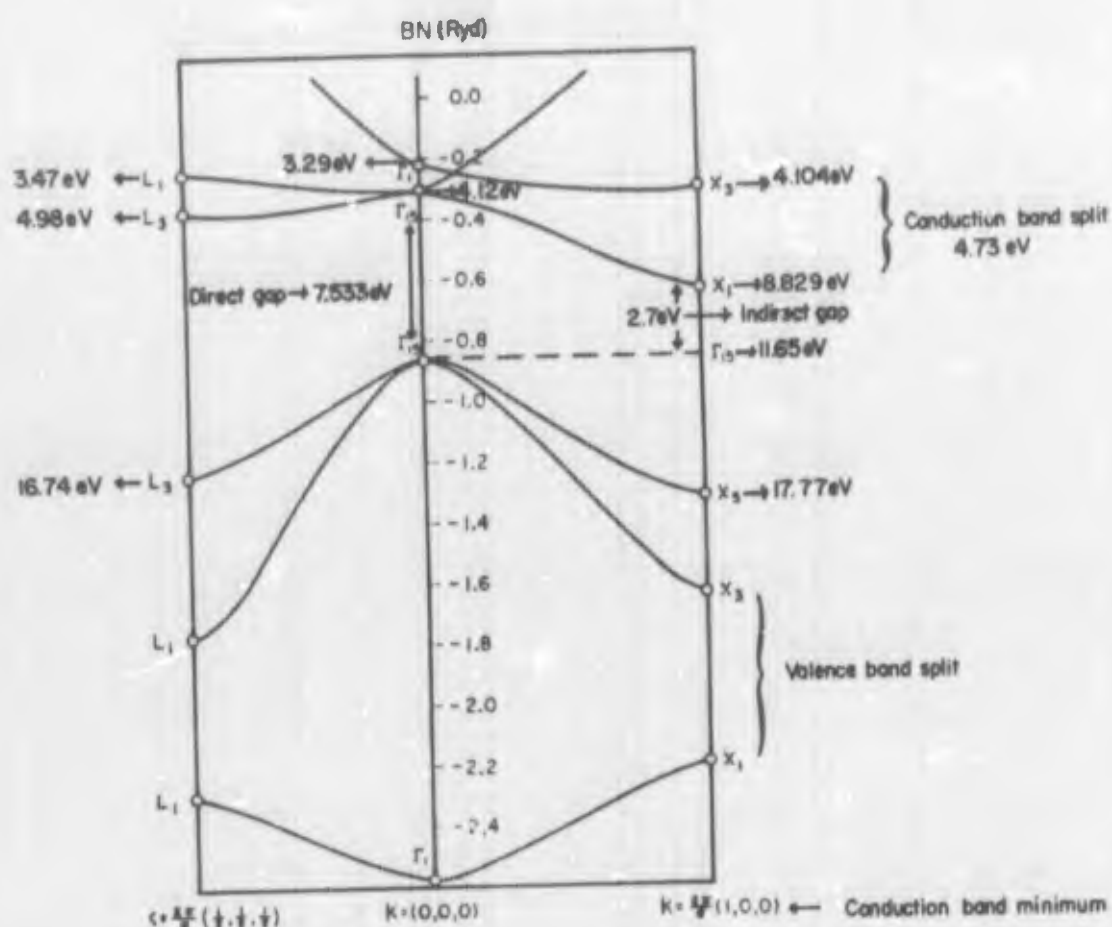
Optimum temperature, time and pressure parameters in the preparation of hot pressed boron nitride are seen in this curve of log electrical resistivity as a function of temperature.

The boron nitride is hot pressed in degassed graphite die at 1800°C and 2000 psi for 125 min.

[Ref. 4709]



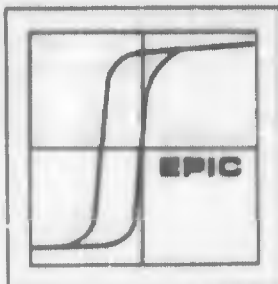
ENERGY BAND STRUCTURE



Band structure of boron nitride. Computed values are indicated by circles and result from OPW method applied to zincblende lattice. Split in X_1 state to X_1-X_3 is seen. Inserted values are given in (eV).

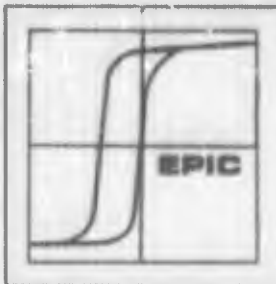
L		Γ		X	
(eV)	Ryd	(eV)	Ryd	(eV)	Ryd
3.469	0.257	3.288	0.243	4.104	0.304
4.982	0.369	4.188	0.305	8.829	0.654
16.74	1.24	11.651	0.863	17.766	1.316

[Ref. 14587]

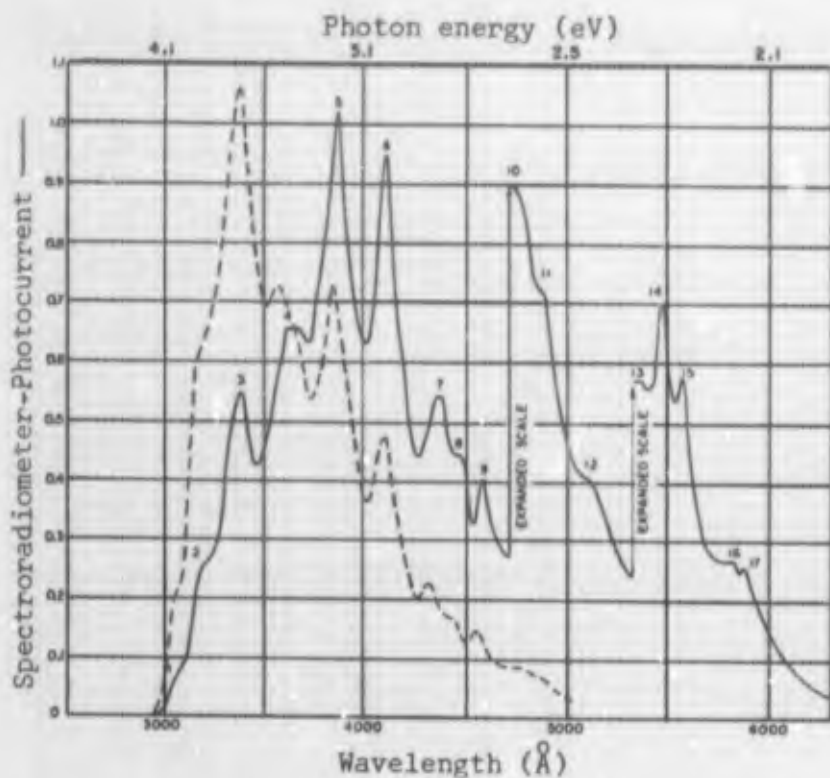


ENERGY BAND STRUCTURE - ENERGY GAP

Symbol	Assignment	Value (eV)	Determination	Ref.
E _g (direct)	$\Gamma_{15}-\Gamma_{15}$	7.533	OPW (calc.) for hexagonal boron nitride	14587
E _{g₁} (indirect)	$\Gamma_{15}-X_1$	2.7		
Conduction band splitting	X_1-X_3	4.73		
E _g (direct)		7.8	CVD sample electrical resistivity 1250°K-1800°K at frequencies of 1 to 100 kc	29801
E _g		~5	CVD (isotropic) electrical resistivity at 1065°C-1355°C	30877
E _g		10	Calc. for cubic boron nitride	452



PHOTON ELECTROLUMINESCENCE



Spectral distribution curve of the field-excited-emission from boron nitride. The powder is suspended in an oil medium. Voltage to 1200 volts. Frequencies to 30 kc. $T = 300^\circ K$. The bands are numbered in order of increasing wavelength from 1 through 17. Emission extends from 2950 Å to about 6500 Å.

— Uncorrected
--- Corrected

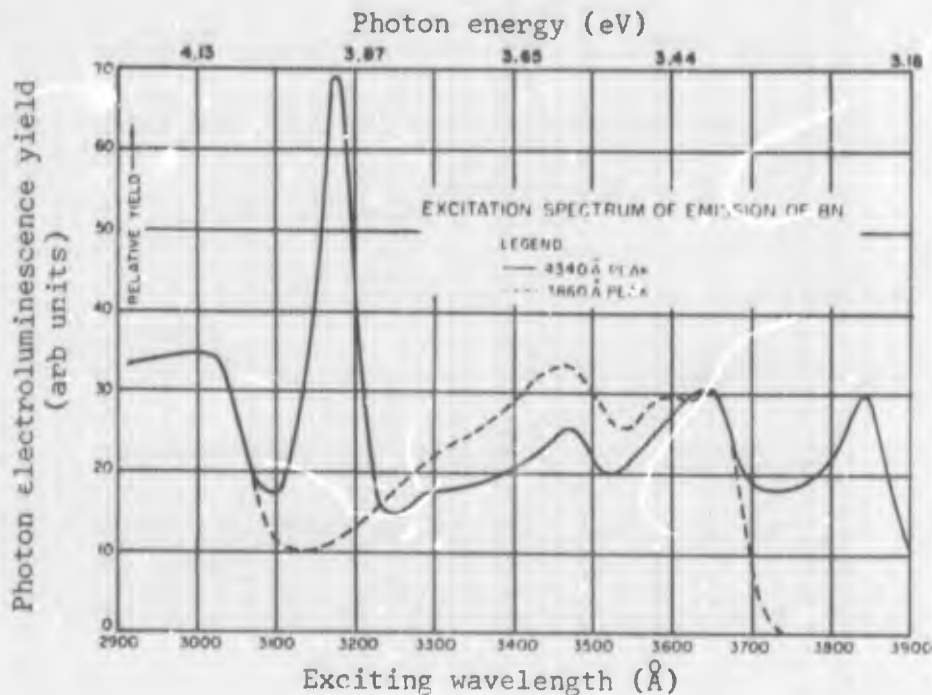
[Ref. 18594]

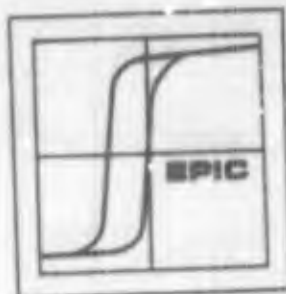
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Excitation spectra of two bands of the electroluminescence spectra of boron nitride shown above.

[Ref. 6446]

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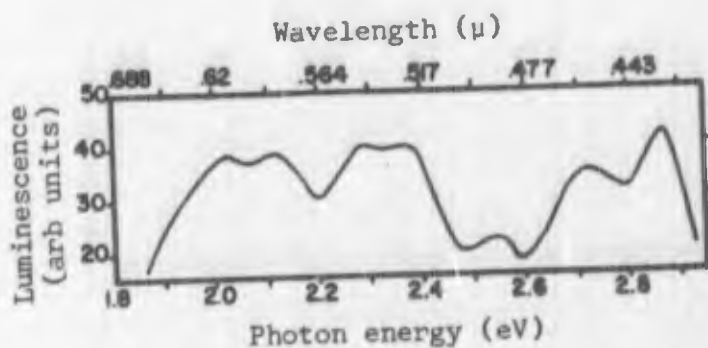
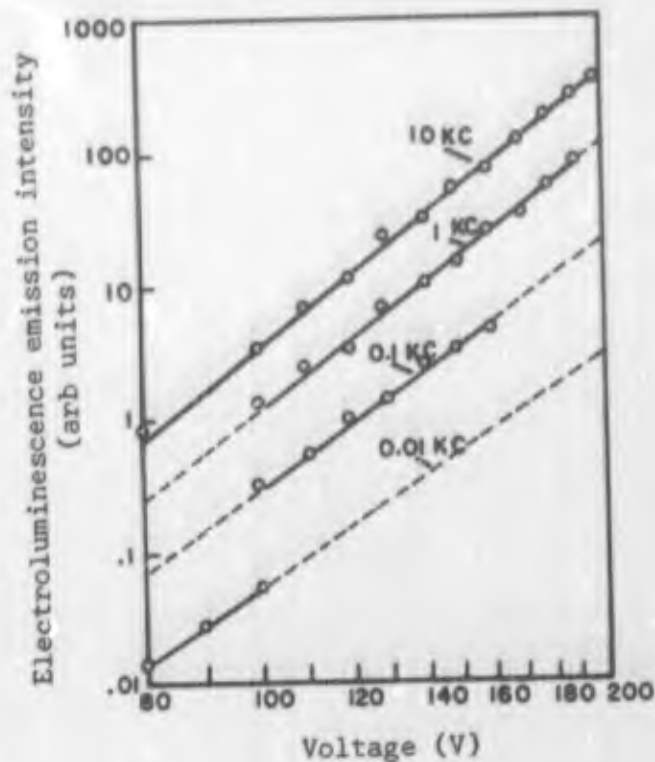


PHOTON ELECTROLUMINESCENCE

Brightness-voltage relationships at frequencies from 10 c/s to 10 kc for field excited emission from boron nitride powder at 300 °K.

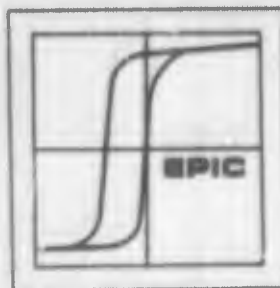
[Ref. 18594]

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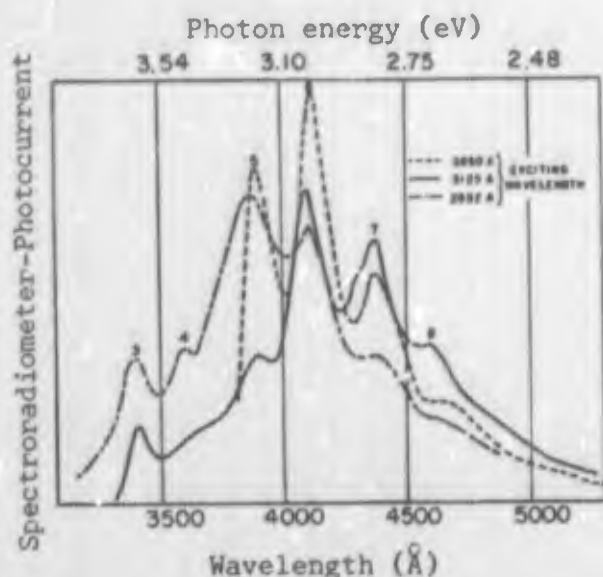
Cathodoluminescence intensity as a function of photon energy in boron nitride at 20 °C. Data taken from:

Tiede, E. and H. Tomaschek. Über das aktivierende Element im leuchtenden Borstickstoff. Zt. F. Anorg. Chemie, v. 147, 1925. p. 111-122.



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PHOTON LUMINESCENCE



Spectral distribution curves of the photoluminescence from boron nitride for various exciting ultraviolet-photon energies at 77 °K. The relative intensities of the photoluminescence bands from boron nitride are dependent on the energy of the exciting photons. The average radiance was maintained constant for each exciting wavelength.

Excitation (Å)	Band	Intensity
2652A	5	highest
	7	greatly reduced
3125A	5	greatly reduced
	6	highest
	7	shows additional structure
3650A	5	highest
	5-9	displaced to higher wavelengths.

Peak wavelength (in Å) of emission bands from boron nitride excited by ultraviolet photons at various wavelengths, at 77 °K. (Italics denote major bands.) Numbered bands on graph are indicated.

2650 Å	2990 Å	3125 Å	3349 Å	3650 Å
	3145			
3200	3200			
	3250			
3350	3350			
3400 (3)		3400 (3)		
3520	3520			
3555		3550		
3615 (4)	3620	3615		
3690	3680	3685		
3820		3830		
3870 (5)	3870	3870 (5)	3870	3870
3950		3955		3930 (5)
		4045		
4100 (6)	4100	4095 (6)	4110	4110 (6)
		4275		4230
4350 (7)	4360	4345 (7)	4350	
		4500		
		4610 (9)		
		4775	4665	
		4950	4775	
			5075	
		5150	5180	

The emission spectrum remains fairly invariant as to band position after treatment and as a function of type of excitation, indicating that the fine-structure emission is inherent to the boron nitride molecular layers.

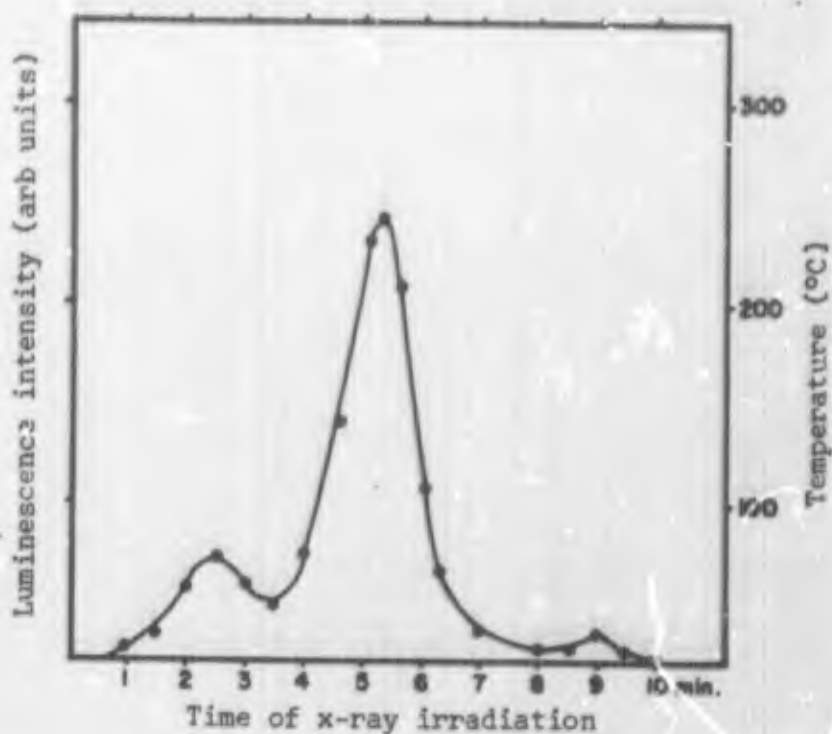
[Ref. 18594]



PHOTON LUMINESCENCE

Photon luminescence of boron nitride after x-ray irradiation. The powder was sintered at 2000°C. After irradiation, it shows intensive peak in the glow curve at 200°C.

Hanle, W. and H. Peter. Thermo-lumineszenz und Dosimetrie. Thermoluminescence and Dosimetry. Oberhessische Ges. f. Natur. u. Heilkunde, Ber.; Naturwiss. Abt., Giessen., v. 29, 1958. p. 105-110.



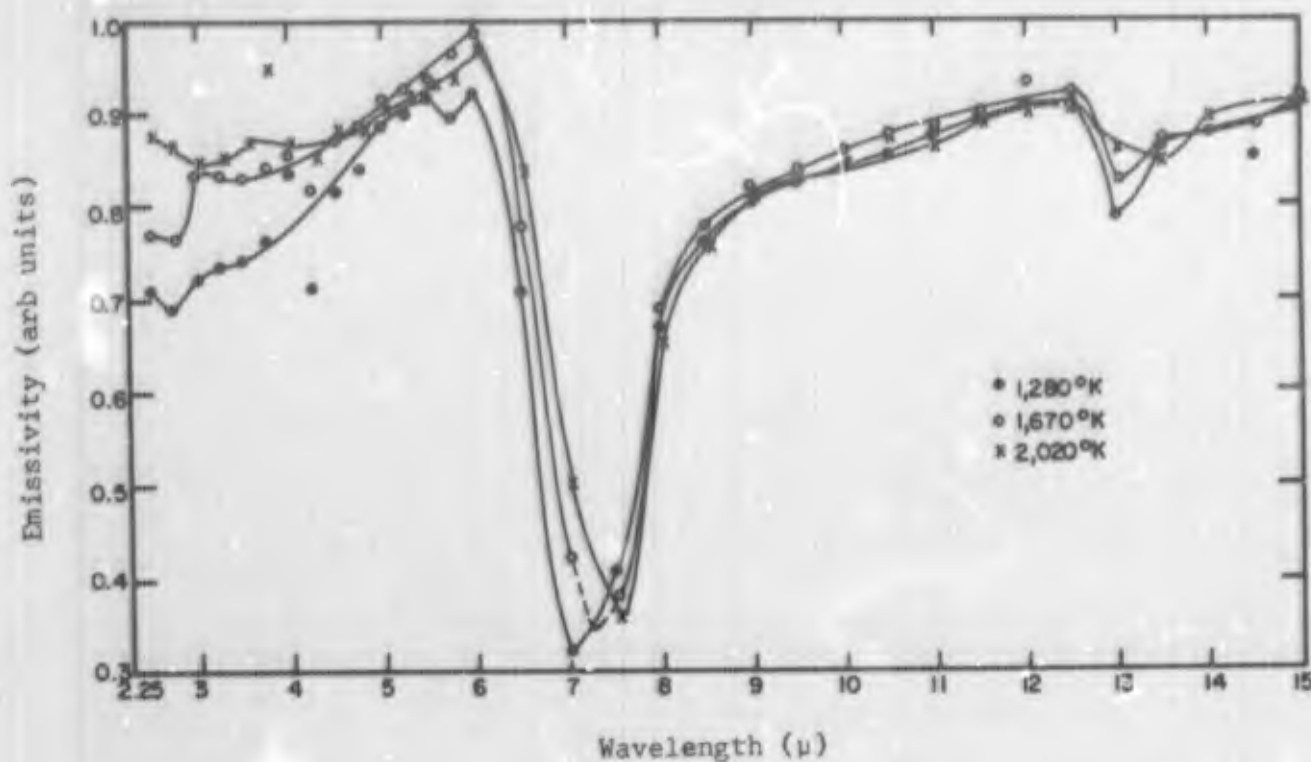
Some carbon-doping is apparently requisite for the luminescence which shifts in color from blue to a yellow green. The green band is always present and stable, the violet also, but the latter varies greatly in intensity.

[Ref. 11988]



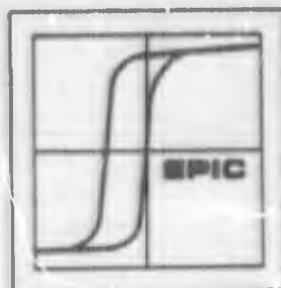
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SPECTRAL EMISSIVITY

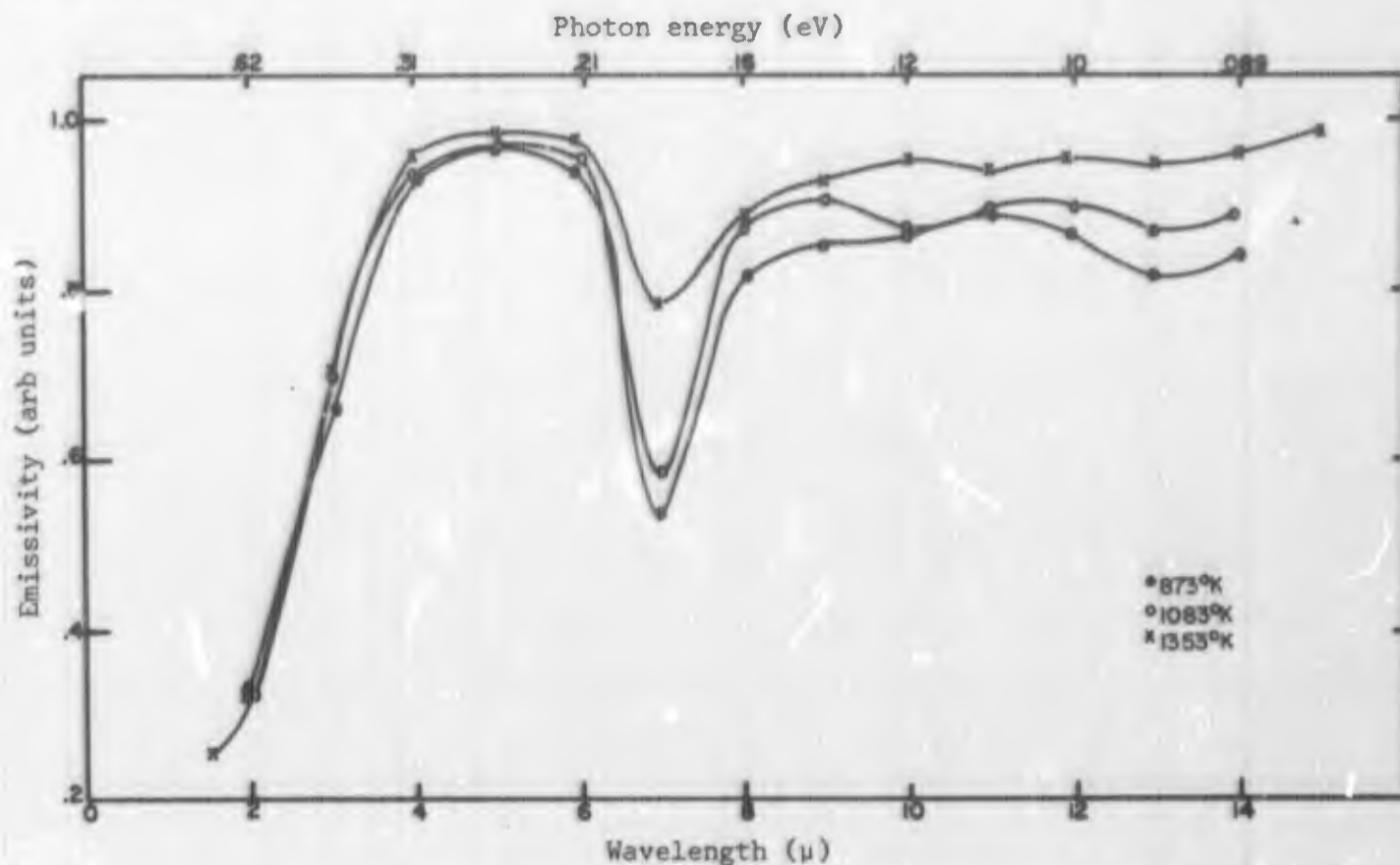


Spectral emissivity of anisotropic pyrolytic boron nitride heated in air. The intensity curves show the two parameters of sample temperature and emission wavelength. The deep minimum at about 7-8 microns is deeper for the pyrolytic material than for the hot-pressed and corresponds to an absorption band. It is evident that the emittance minimum shifts to longer wavelength with the temperature increase.

[Ref. 30876]



SPECTRAL EMISSIVITY

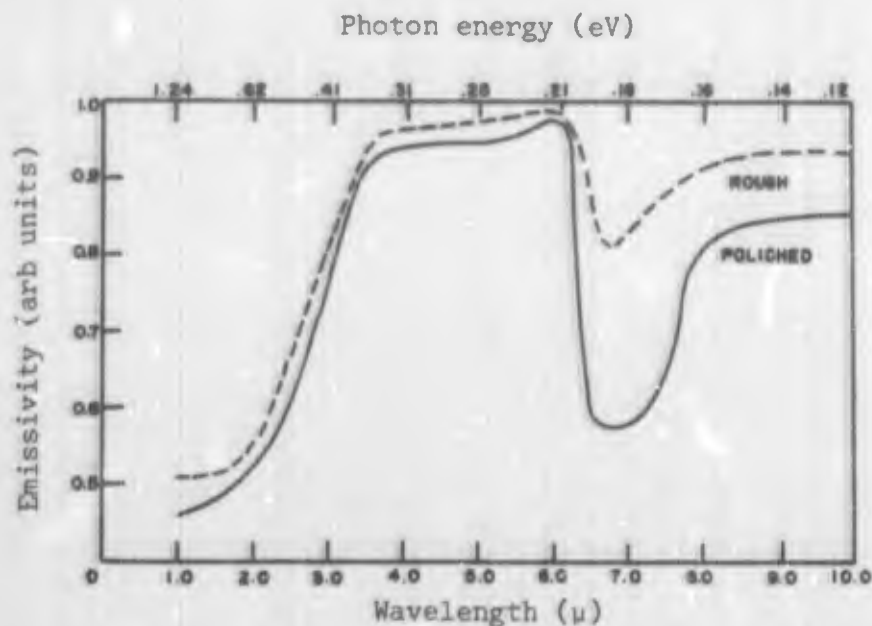


Spectral emissivity of bulk commercial boron nitride heated in air. The intensity curves show the two parameters of sample temperature and emission wavelength. The IR wavelength of the emission shows a sharp drop at about 7 microns, corresponding to a strong absorption band. This minimum is due to internal reststrahlen effects and depends on sample purity and temperature. [Ref. 17412]

[Ref. 18070]



SPECTRAL EMISSIVITY



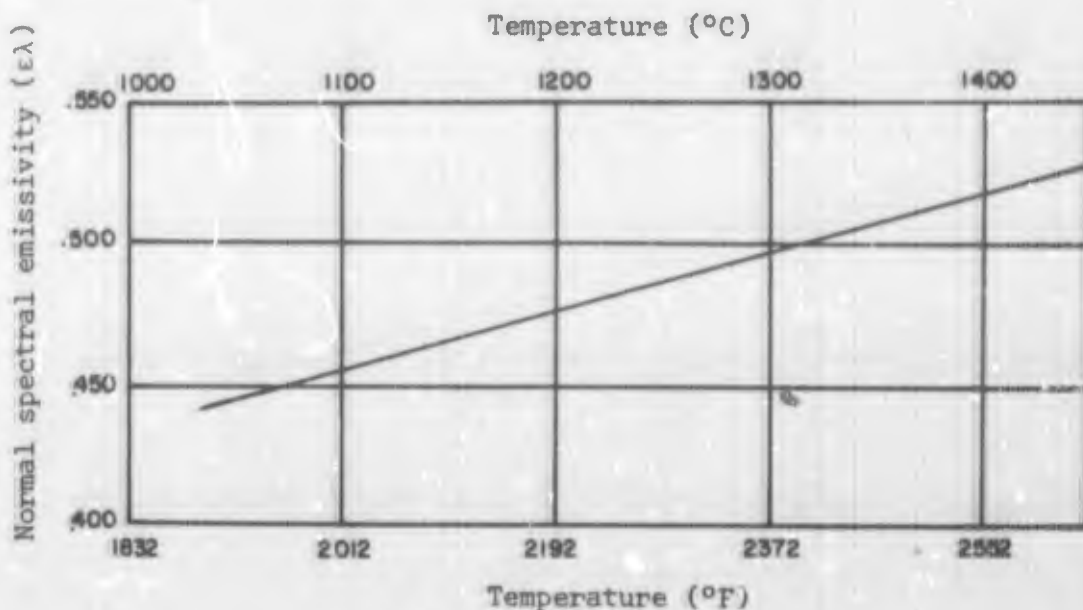
Spectral emissivity of polycrystalline, hexagonal boron nitride in bulk form. The samples included about 2.5% boron oxide. $T = 1300^\circ\text{K}$, 50 μ pressure. Measurements made in vacuum. Spectral emissivity runs parallel for rough and polished samples, with the former always the larger. The difference between the two samples, however, increases greatly in amount between 6 and 10 microns. Surface finish is 2.8 microns (110 micro-inches).

[Ref. 22695]



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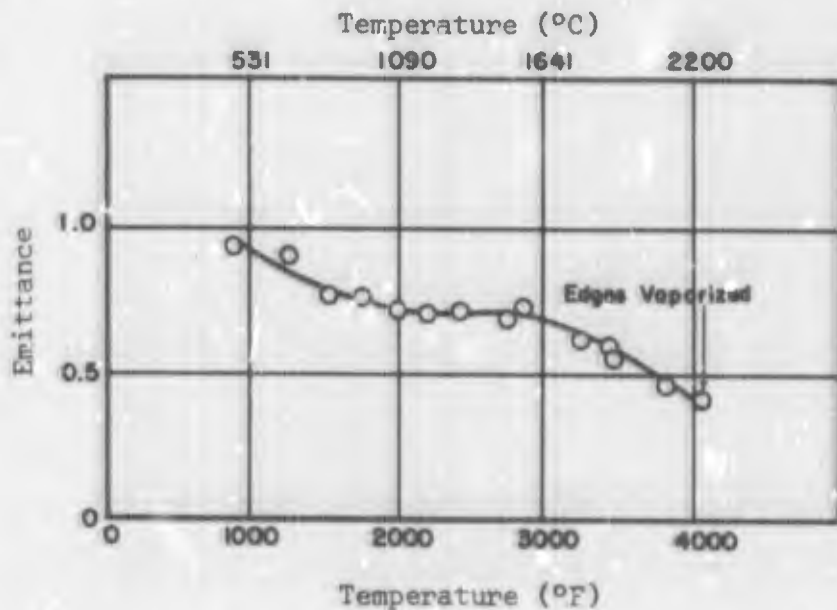
SPECTRAL EMISSIVITY



Spectral emissivity as a function of temperature in polycrystalline pure CVD boron nitride. The material is hexagonal with a high degree of crystallite orientation.

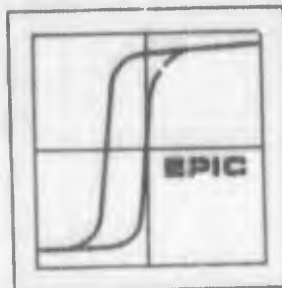
[Ref. 26546]

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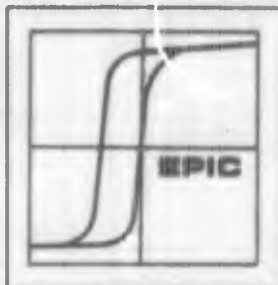
Total normal spectral emittance of polycrystalline bulk boron nitride polished to a 1 micron surface finish. The samples were heated in an Argon atmosphere with tantalum and tungsten contact discs (rather than inductively).

[Ref. 12808]



SPECTRAL EMISSION COEFFICIENT

<u>Value</u>	<u>Sample</u>	<u>Temp. °C</u>	<u>Ref.</u>
0.58	Powder paste applied to a tungsten cylinder in a thickness of $\sim 100\mu$ Emitted light had wave- length $\lambda = .65\mu$	850	29703
0.59		950	
0.59		1050	
0.59		1150	
0.60		1250	
↓		1350	
		1450	
		1550	
		1650	

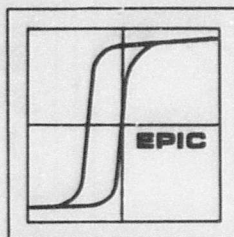


ELECTRON THERMIONIC EMISSION

<u>Value</u>	<u>Sample</u>	<u>Temp.</u>	<u>Ref.</u>
$\approx 0.04 \text{ amp cm}^{-2} \text{ } ^\circ\text{K}^{-2}$	Coating on a tungsten wire. Material evaporates rapidly at low emission temperature.	2000°K	15528
$\sim 50\text{mA/cm}^2$		1700°C	15528

* Saturation current

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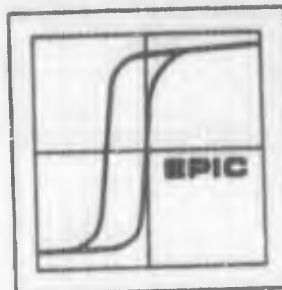


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SECONDARY ELECTRON EMISSION COEFFICIENT (δ)

<u>Value</u>	<u>Sample</u>	<u>Experimental Conditions</u>	<u>Temp.</u>	<u>Ref.</u>
2.9 at 600V (max)	hot pressed disk	$P=2 \times 10^{-9}$ torr	300°K	26078
1.7 at 300V				



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THERMAL PROPERTIES - DEBYE TEMPERATURE θ_D

<u>Value °K</u>		<u>Temp. °K</u>	<u>Ref.</u>
1700	Calculated from J.N. Plendl. Some New Interrelations in the Properties of Solids Based on Anharmonic Cohesive Forces. Phys. Rev., v. 123, no. 4, Aug. 15, 1961. p. 1172. (cubic boron nitride)	0°	28367
~1900	Calculated from Elastic constants for cubic material with $a_0 = 3.615 \text{ \AA}$ c_0 (elastic constant) = $3.83 \times 10^{12} \text{ dyne/cm}^2$	0°	29676
598±7	Hexagonal polycrystalline	0°	*28

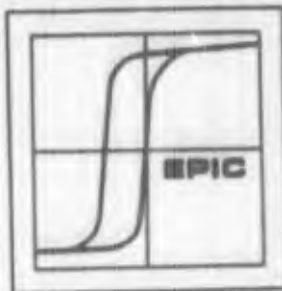
* Reference on page 21.



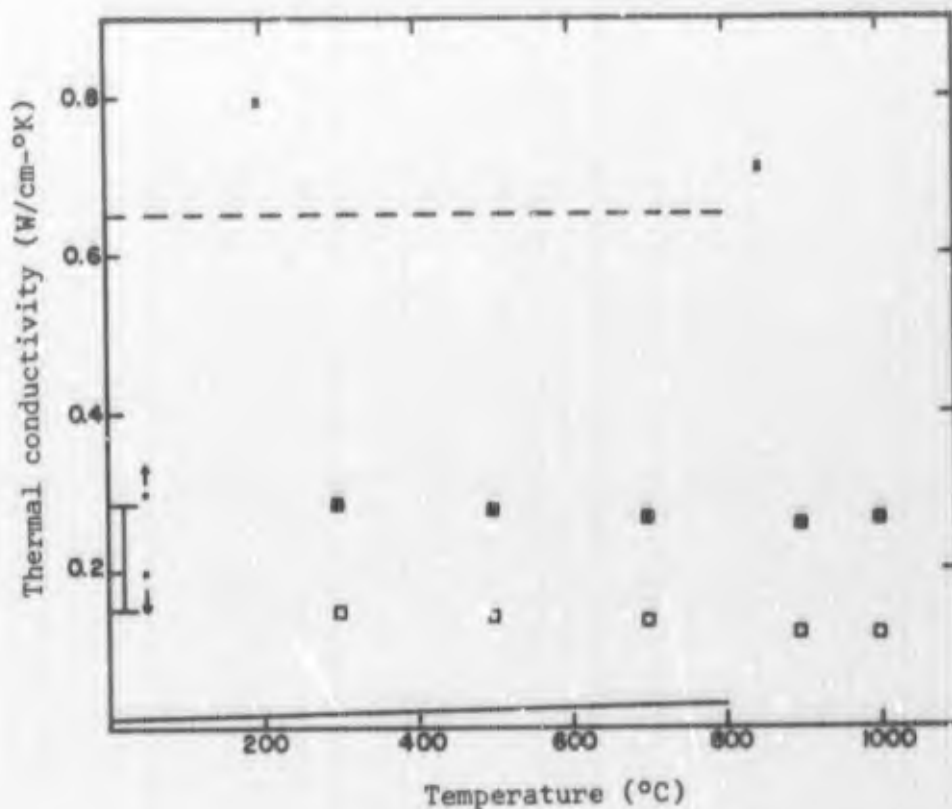
THERMAL PROPERTIES - THERMAL CONDUCTIVITY

Value W/cm ² K	Heat flow	Sample	Temp. (°C)	Symbol*	Ref.
0.150-0.285		$\rho \sim 10^{10} \Omega\text{-cm}$	20	I	17923
<0.2 >0.3	rod-axis ⊥ rod-axis	Hot-pressed rods, density = 2.14 g/cm ³	50	•	24396
0.015 0.030 0.65	⊥ a-axis a-axis	Hexagonal, polycrystalline, CVD commercial "Boralloy" (High Temperature Materials, Inc.), High crystalline orientation.	0 800 0-800	— ---	26546
0.795 0.711	a-axis	Hexagonal, CVD, highly oriented crystallites.	200 845	x	22943
0.151 0.142 0.134 0.126 0.121	moulding direction	Hot-pressed, commercial boron nitride (Carborundum Co.)	300 500 700 900 1000	□	29802
0.289 0.280 0.272 0.264 0.268	⊥ moulding direction		300 500 700 900 1000	■	

* Symbol on accompanying graph



THERMAL PROPERTIES - THERMAL CONDUCTIVITY



Higher temperature measurements of the thermal conductivity of polycrystalline rods of boron nitride show that the thermal conductivity varies from 0.262 W/cm-°K at 829°C to 0.194 W/cm-°K at 1853°C.

[Ref. 12808]

□ ● [Ref. 29802]

x [Ref. 22943]

● [Ref. 24396]

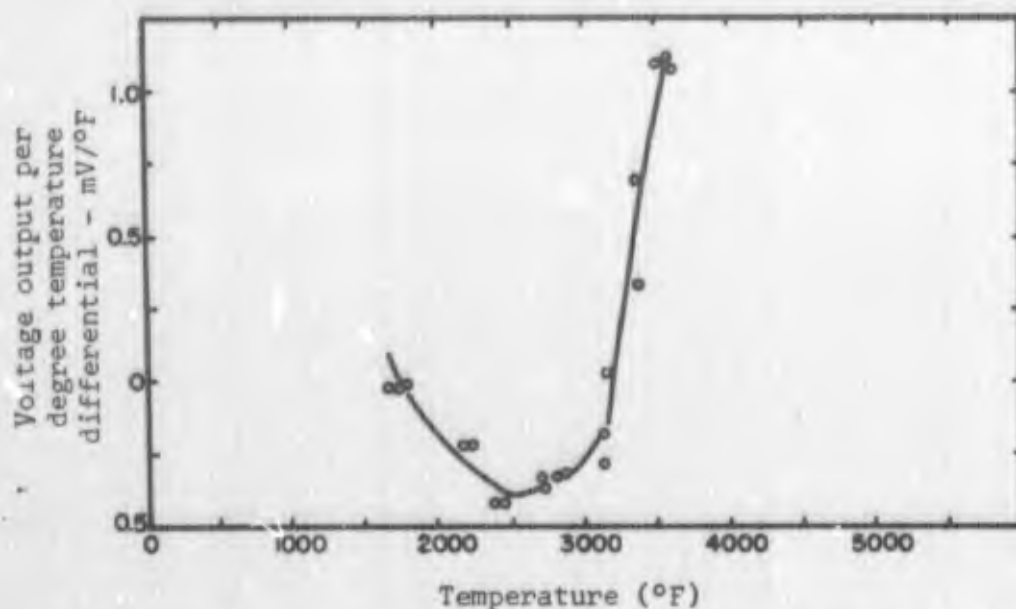
— [Ref. 26546]

--- [Ref. 26546]

I [Ref. 17923]



THERMAL PROPERTIES - THERMAL EMF



Thermoelectric emf measurements were made on polycrystalline boron nitride rods held between graphite rods. The voltage output was the sum of the Thompson effect plus the hot junction output and less the cold junction value. This voltage output was divided by the temperature difference between the two junctions and plotted as a function of the mean temperature. The high electrical resistivity indicates high internal power loss. At high temperature, the sample was blistered and split.

Electrical resistivity

Temperature

micro ohm-cm

°F °C

1.05×10^{10}

3330 1849

.94

3380 1860

.45

3490 1920

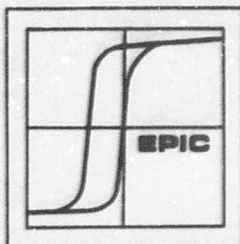
6.52×10^5

4100 2260

1.74×10^6

4100 2260

[Ref. 12808]



PHONON SPECTRUM

	<u>Value*</u>		<u>Sample</u>	<u>Method</u>	<u>Temp.</u>	<u>Ref.</u>
	<u>In plane</u>	<u>Out of plane</u>				
	<u>(cm⁻¹) (eV)</u>	<u>(cm⁻¹) (eV)</u>				
LO ₁	1610 (.199)		hexagonal	reflectivity	300°K	25245
LO ₃		828 (.103)	polycrystal	λ=3-20μ		
TO ₁	1367 (.169)					
TO ₂	1370 (.196)					
TO ₃		783 (.097)				
A,B	1300 (.161)					
C		680 (.084)				
optical or acoustical phonons						
D,E	240 (.029)					
F,G	100 (.0124)					

Photon Emission of several types (electro, cathodo- and photon luminescence) at 77° and 300°K at λ=.256-.6μ indicates a predominant differential between major emission bands of 1400 cm⁻¹ (.1736 eV) in boron nitride powder.

[Ref. 18594]

*Wave number in cm⁻¹ is given first, with equivalent photon energy (eV) in parenthesis.

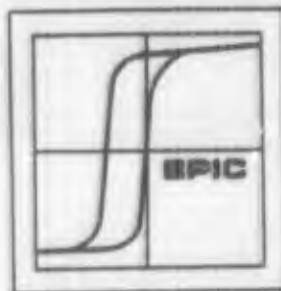


PHONON SPECTRUM

<u>Assignment</u>	<u>Value</u>		<u>Sample</u>	<u>Method</u>	<u>Temp.</u>	<u>Ref.</u>
	<u>wavenumber</u>	<u>photon energy</u>				
	<u>cm⁻¹</u>	<u>eV</u>				
LO	1232	.153	Cubic	Reflectivity	300°K	28367
LA	685	.085	Single	$\lambda=2.5-20\mu$		
TO	1000	.124	Crystal			
TA	348	.043				

<u>Assignment</u>	<u>Experimental Value</u>		<u>Calculated</u>	<u>Ref.</u>
	<u>cm⁻¹</u>	<u>eV</u>		
TO-TA	650	.081	652	28367
2TA	700	.087	696	
reststrahlen	1000-1260	.124-.156	...	
2LA(TO+TA)	1370	.170	1370(1348)	
LO+TA	1580	.196	1580	
...	1830	.227	...	
LO+LA	1920	.238	1917	
2TO	2000	.248	2000	
LO+TO	2230	.277	2232	
2LO	2465	.306	2464	
2TO+LA	2700	.335	2685	

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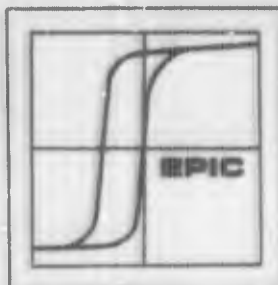


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MAGNETIC SUSCEPTIBILITY (χ)

<u>Value</u>	<u>Ref.</u>
$-0.4 \pm 0.1 \times 10^{-6}$ cgs (gram susceptibility)	4878
-9.9×10^{-6} cgs (mole susceptibility)	



GYROMAGNETIC PROPERTIES

<u>Value</u>	<u>Temp. °K</u>	<u>Sample</u>	<u>Method</u>	<u>Ref.</u>
2.0023 0.0010	1.7	Hexagonal: powder and sintered powder	*EPR at 9.4 Gc	27881
2.0052 0.0020	77	x-rays, UV and γ-radiation - also		
2.0027 0.0003	300	heating to 1850 °C yields EPR*-centers.		

* Electron Paramagnetic Resonance

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13. ABSTRACT These data sheets present a compilation over a wide range of electronic properties for Boron Nitride. These properties are compiled over the widest possible range of parameters and are then agglomerated in several large groups as follows: Optical Properties include absorption, reflection and refraction. Transport Properties include electrical conductivity and resistivity. Energy Band Structure includes energy gap values. Phonon Branch Distribution appears separately. Both Photon and Electron Emission data are represented including Spectral Emissivity. Thermal Properties include Debye temperature, thermal conductivity, and thermal emf. There are other individual properties and effects included, especially dielectric constant and dissipation factor. The Introduction discusses the two polymorphic boron nitride forms; their crystal structure, lattice parameters and transition points. The isotropic and anisotropic boron nitride prepared by chemical vapor deposition is discussed from mechanical and electrical standpoint. Information is given on a number of boron nitride devices and applications. A table of the best values available for physical and electronic properties is given. (1) →			

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	CVD Boron Nitride						
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