0.03% of the sample. At the magnification employed, any hole larger than 300 A in diameter would have been noticed. Above this size, we conclude that the films are essentially continuous.

It will be noted that improved aperturing of the beam and the deliberate addition of a large incoming beam contamination, while radically changing the elastic distribution, have only minor effects on the characteristic distribution. Moreover, it appears that at angles beyond 4×10^{-3} radian the angular dependence of the elastically scattered electrons is less rapid than that of the characteristically scattered electrons.

The data for aluminum presented in Fig. 2 were analyzed in an attempt to confirm the dependence of the value of the characteristic energy loss, E, on the scattering angle, θ, reported by Watanabe[9] and attributed by him and others to the dispersion of plasma waves. The expected dependence is of the form $E=A\theta^2$. In a small region between 6 and 12 milliradians, our data show a θ^2 dependence, although the constant disagrees by 50% from that of Watanabe. Outside this region, neither the constant nor the exponent agrees with his values.

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[9] H. Watanabe, J. Phys. Soc. Japan 11, 119 (1956).

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Multiband Luminescence in Boron Nitride

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Boron nitride can be excited to luminesce by (1) alternating electric fields, (2) ultraviolet photons, or (3) cathode rays. The luminescence, in all cases, has a complex emission spectrum, extending from approximately 2950 A to 6500 A. The relative intensities of the bands in the fine structure are affected by current density with cathode-ray excitation, and by the energy (frequency) of the photons with ultraviolet excitation. The maximum of the photoluminescence emission intensity with temperature occurs at about 875°K, with the luminescence emission intensity falling to 50% of the maximum value at approximately 1375°K.

Correspondence of known infrared absorption bands with energy differences in the fine structure in the luminescence suggest vibrational origins for the fine structure. The identities of the excited electronic states have not yet been ascertained, although these may be due to exciton states, impurity states, or surface states.

INTRODUCTION

BORON nitride (BN) was first prepared by Balmain,[1] and some of the chemical properties of BN have been reviewed recently by Finlay and Fetterley.[2] The photoluminescence and cathodoluminescence of BN have been investigated previously by Tiede and his coworkers,[3,4] while alpha-particle excitation of BN has been reported by Kirkbride,[5] and electroluminescence from BN has been observed recently.[6] Luminescence from nitrides other than the boron compound has also been reported,[7] including beryllium nitride with aluminum activator, and aluminum nitride with silicon activator.

With the availability of purified BN,[8] the investigations of the luminescence properties of this material were extended by us to include field excitation, emission spectrum determination, especially in the near ultraviolet, and temperature dependence of the luminescence emission.

EXPERIMENTAL METHODS

Spectral Measurements

All spectral curves were obtained with a special automatic-recording spectroradiometer, using an RCA-1P28 as the radiation detector, and a grating. Since no intensity standard for the middle and far ultraviolet was available, all curves (with one exception) are shown as recorded without corrections for intensity. The dashed curve of Fig. 1 has been corrected with data extrapolated from measurements on a tungsten standard. However, since in the ultraviolet region, even the tungsten data are somewhat untrustworthy, this curve is shown only to emphasize the unusual type of spectral distribution obtained from BN. Measurements of other ultraviolet-

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[1] W. H. Balmain, J. Prakt. Chem. 27, 422 (1842); Phil. Mag. 21, 170 (1842).

[2] G. R. Finlay and G. H. Fetterley, paper presented at the 53rd annual meeting of the American Ceramics Society, April, 1951 (unpublished).

[3] E. Tiede and F. Buescher, Ber. deut. chem. Ges. 53B, 2206 (1920).

[4] E. Tiede and H. Tomaschek, Z. anorg. u. allgem. Chem. 147, 111 (1925).

[5] J. Kirkbride, Proc. Phys. Soc. (London) B68, 253 (1955).

[6] S. Larach and R. E. Shrader, Phys. Rev. 102, 582 (1956).

[7] S. Satoh, Sci. Papers Inst. Phys. Chem. Research, Japan 29, 41 (1936); E. Tiede, Ber. deut. chem. Ges. 61, 1568 (1928).

[8] Purified BN was obtained from the Norton Company and Carborundum Company.

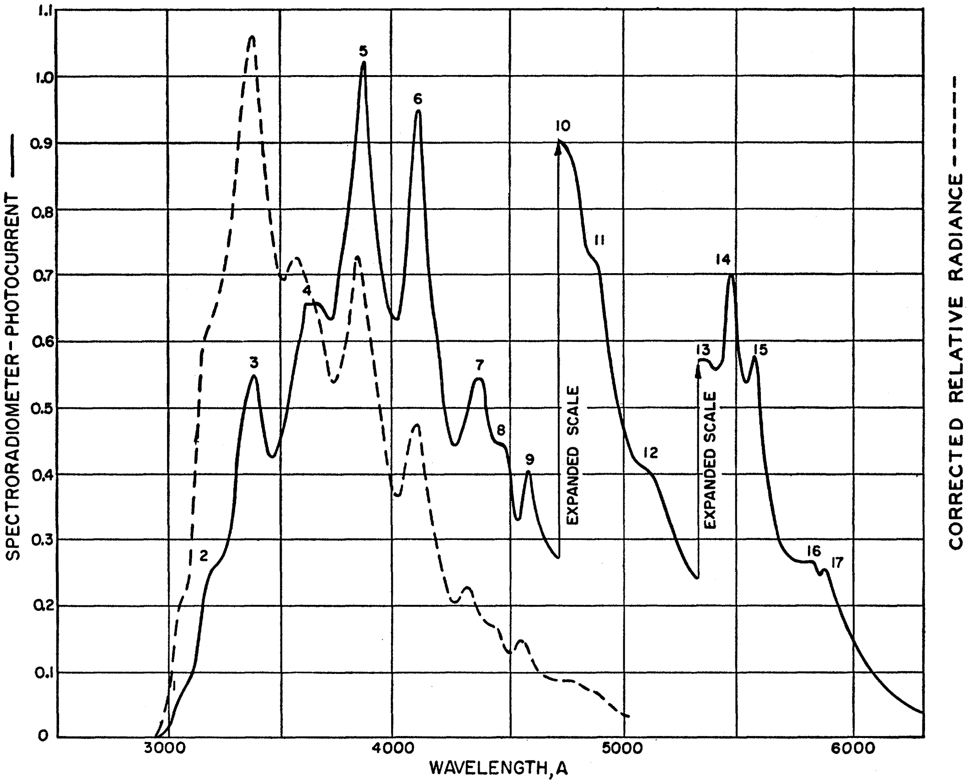

FIG. 1. Spectral distribution curve of the field-excited-emission from boron nitride; solid curve is uncorrected, dashed curve is corrected.

emitting phosphors indicate that the structure herein reported for BN is definitely a characteristic of the BN and is not the result of instrumental characteristics.

Field Excitation

All measurements of electroluminescence were made by first suspending BN powder in castor oil, using one gram of powder to two grams of the oil. Other dielectrics, such as silicones and plastics, could also be used. This suspension was placed between an opaque aluminum electrode and a transparent electrode (treated quartz), arranged to provide a stable gap (0.002 in. wide), as shown in Fig. 2. Each of the electrodes was capacitatively coupled to a plate of the output stage of a Fisher Model 50A amplifier. This provided sinusoidal, alternating voltages with low harmonic content for frequencies up to 30 kc/sec, and peak-to-peak voltages up to 1200 volts. A Hewlett-Packard Model 650A oscillator was used to drive the power amplifier.

Photoexcitation

A 500-mm Bausch and Lomb grating monochromator was used to separate the stronger mercury emission lines from a medium-pressure arc. These lines were used separately for photoexcitation over a temperature range, 77°K to 300°K.

Cathode-Ray Excitation

A special, demountable-type, cathode-ray tube was used for the electron excitation of BN. The cathode-ray tube was operated over a wide range of currents (up to 200 μa) and voltages (up to 15 kv). In addition, the beam was used focussed and defocused, as a steady spot and as a small raster.

Reflection Spectra

A Bausch and Lomb hydrogen-arc-lamp (Nestor type) was used as the source of light reflected from the surface of a pressed plaque of BN. The reflection was examined between 2200 A and 3200 A with the spectroradiometer.

Temperature Dependence

Spectroradiometer measurements were made up to 850°C by placing a thin coating of BN on a stainless

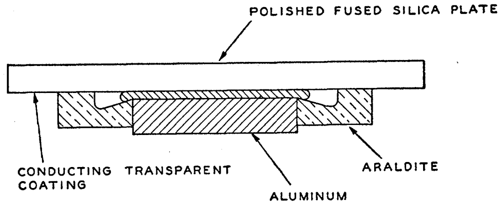

FIG. 2. Electroluminescence test cell.

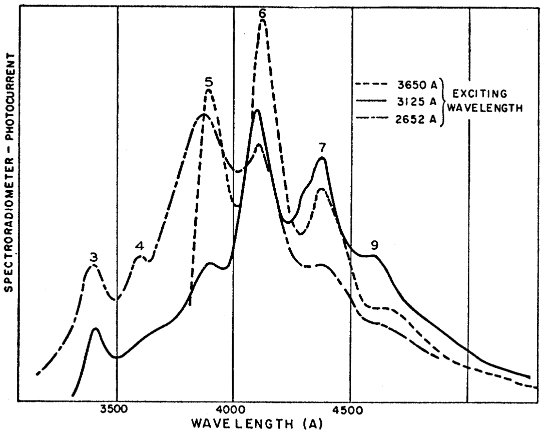

FIG. 3. Spectral distribution curve of the photoluminescence from boron nitride for various exciting ultraviolet-photon energies.

steel dish nested into the top of a "glo-coil" heater, which was in turn nested into a conical cavity in firebrick. The temperature was stabilized against convection cooling by covering the dish with another firebrick with a cavity cut out for clearance. A small window of fused silica provided optical access to the BN. Temperature was measured by a Cr-Al thermocouple welded to a small tab of Ni held in contact with the surface of the BN.

For measurements at higher temperature, some modification was necessary. The BN was held in a platinum boat heated by 60-cycle ac current. A Pt-13% Rh thermocouple was partially embedded in the BN. The assembly was held at the bottom of a conical cavity in firebrick and viewed through a fused silica window. The incandescence of the furnace and the incident exciting uv radiation (2967 A Hg line) caused some interference in the measurement of the luminescence. Moderate success was finally achieved by using a Corning 5860 filter which passes the central portion of the luminescence. Although this filter has low transmission in the red and infrared, it was found necessary to determine the luminescence by measuring the ac component of the photocurrent available from the 120-cycle excitation of the ac operated mercury arc. The thermal inertia of the furnace was sufficient to reduce any large ac component from the incandescence up to 1450°K.

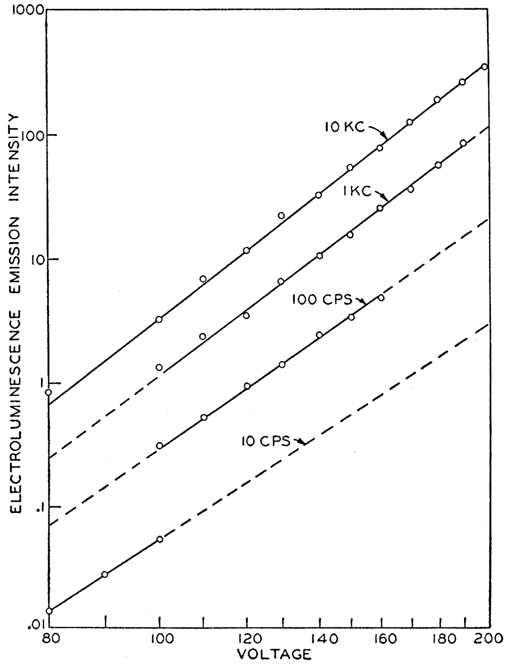

FIG. 4. Brightness-voltage relationships at various frequencies for field excited emission from boron nitride.

RESULTS

Emission Spectrum

The luminescence emission from BN is complex, with many narrow bands being present, for all the modes of excitation. Although the relative intensity of the fine structure differs with the type of excitation, the position of the fine structure is essentially invariant with excitation type.

Figure 1 is a spectral distribution curve of the electroluminescence from BN, with some of the more obvious bands being numbered (in order of increasing wavelength from 1 to 17). The emission extends from about 2950 A to about 6500 A. Tiede and Tomaschek[4] have reported multiband cathodoluminescence from BN, which extended from the blue to the blue-green region of the spectrum.

Variations in Band Intensities

The relative intensities of the photoluminescence bands from BN are dependent on the energy of the exciting photons. Figure 3 shows the effect of different exciting ultraviolet-photon-energies on the relative intensities. Thus, with 2652 A excitation, band 5 is the most intense, while band 7 is greatly reduced in intensity. With 3125 A excitation, the short-wavelength emission bands are lower in intensity, the major band 5 greatly reduced with band 6 the most intense, and additional structure indicated in band 7. When 3650 A photons are used as the exciting source, bands 5 to 9 show slight displacements in peak wavelength to longer wavelength, band 5 becoming a band of major intensity once again. These effects are not a function of the intensity of the exciting radiation, and further, the average radiance was maintained constant for each exciting wavelength.

Voltage Dependence of Electroluminescence

Figure 4 is a plot of electroluminescence emission intensity as a function of applied voltage. For frequencies up to 1 kc/sec the emission intensity varies as the 6.5 power of the voltage. For excitation at 10 kc/sec, the power of the variation of brightness with voltage is even higher.

Brightness Wave Forms of Electroluminescence

The brightness wave form of electroluminescence from BN, for field excitation at 1 kc/sec, is shown in Fig. 5. It is interesting to note that fine structure was visible at the peaks of the brightness wave forms, and that no "secondary peaks" were noted.[9]

Temperature Dependence of Photoluminescence

Figure 6 is a plot of photoluminescence emission intensity as a function of temperature of the BN. An increase in emission intensity occurs from room temperature to about 875°K, after which there is a decrease in emission intensity with the increasing temperature. The emission intensity falls to 50% of the maximum value at about 1375°K. Zinc sulfide phosphors have temperature-break-points which range from 270°K for cub-ZnS:Ag to 490°K for cub-ZnS:Mn.[10]

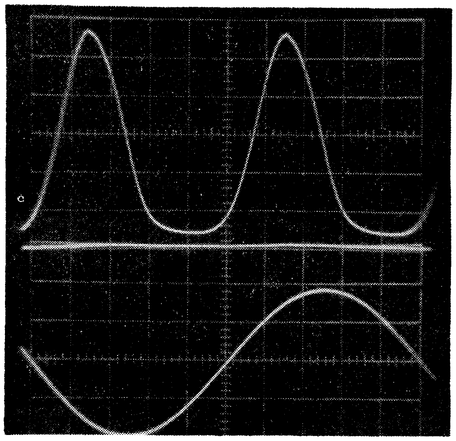

Fig. 5. Brightness wave form of field-excited boron nitride. Upper curve is cell-brightness; lower curve is applied cell-voltage.

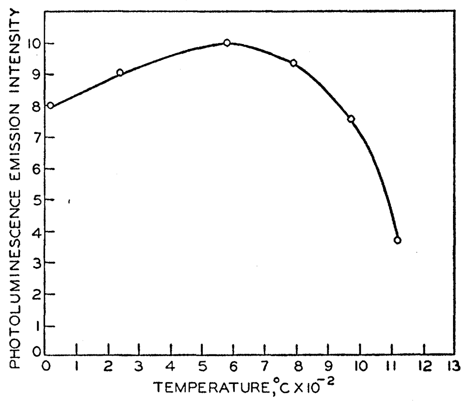

Fig. 6. Photoluminescence emission intensity of boron nitride as a function of temperature.

Cathodoluminescence

The emission spectrum of BN under cathode-ray excitation is shown in Fig. 7. Over a wide range of voltage and current, there is no essential difference in the nature of the emission, Fig. 7 being a typical experimental curve. The emission differs from the ultraviolet and field-excited spectra in the magnitude of the portion occurring at wavelengths shorter than 3500 A. The curve labeled "high density *CR* beam" shows a spectral distribution curve obtained by maintaining a sharply focused, stationary electron beam on the test sample. Although the beam voltage and current were sufficiently high to produce considerable heating at the focal spot, it is believed that the differences are probably caused by the high current density. An extremely long low-level persistence, possibly of the power-law type, was observed.

Reflection

Using the ultraviolet reflection method usually successful with powders,[11] an attempt was made to determine the absorption edge (band gap) of BN. However, comparison with the reflectivity from magnesium carbonate failed to indicate any reflection anomalies in the range 2200–3200 A. Because of the interference from

Fig. 7. Spectral distribution curves of cathodoluminescence emission from boron nitride at high and low current densities.

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[9] Fine structure is not discernible in the figure because of loss of resolution in the reproduction process.

[10] H. W. Leverenz, *Introduction to Luminescence of Solids* (John Wiley and Sons, Inc., New York, 1950), pp. 126–127.

[11] Bube, Larach, and Shrader, Phys. Rev. **92**, 1135 (1953).

TABLE I. Peak wavelength (in A) of emission bands from boron nitride excited by ultraviolet photons at various wavelengths, at 77°K. (Italics denote major bands.)[a]

2650 A	2990 A	3125 A	3340 A	3650 A
	3145			
3200	*3200*			
	3250			
3350	*3350*			
3400		*3400*		
3520	*3520*			
3555		*3550*		
3615	3620	3615		
3690	*3680*	*3685*		
3820		3830		
3870	*3870*	*3870*	*3870*	3870
3950		3955		3930
		4045		
4100	*4100*	*4095*	*4110*	4110
			4170	4180
		4275		
4350	*4360*	*4345*	*4350*	
		4500		
		4610		
			4665	
		4775	4775	
		4950		
			5075	
		5150	5180	

[a] Error in assigning peak wavelengths is about 5 A because of the difficulty in resolving closely occurring components.

the luminescence itself, reflection in the emission region has not yet been investigated.

DISCUSSION

Radiative transitions have been reported for silicon carbide,[12] cadmium sulfide,[13] and for germanium.[14] With group III-V compounds, Braunstein[15] has observed radiative transitions from gallium antimonide, gallium arsenide, and indium phosphide. The emissions observed in the aforementioned materials are believed to occur mainly by carrier injection followed by electron-hole recombination, either directly or through bound states. In the above experiments, the electrodes were in contact with the materials, whereas the present results with boron nitride are found with alternating-field excitation even when the phosphor is separated from the electrodes by mica insulators.

Tiede and Buescher[3] have attributed the emission from BN to traces of carbon acting as an activator. In the present investigation, samples of BN, fired at 1400°C, in atmospheres of oxygen and of other gases, showed no change in emission spectra. If interplanar carbon were the activator, emission changes might well be expected after such treatment. The fact that the emission spectrum remains fairly invariant as to band position after treatment, or as a function of type of excitation can be taken as an indication that the fine-structure emission is inherent to the boron nitride molecular layers.

Band Gap

The boron nitride structure is of the graphitic type, consisting of parallel planes, with the boron and nitrogen atoms alternating in an hexagonal lattice. The interatomic spacing has been reported as 1.45 A, and the interplanar spacing is about 3.3 A.[16,17] Taylor and Coulson[18] have estimated from theoretical considerations that the band gap in BN is about 4.6 ev although the present findings failed to show a band gap less than 5.5 ev. However, the intrinsic band gap of BN may be difficult to determine (1) because the extremely small (approximately 1000 A) particle size of the powder may decrease the reliability of the reflection method, and (2) the effect of particle size on the band gap is unknown.[19]

Transitions in BN

Table I lists the peak wavelengths of the emission bands of BN, with excitation by ultraviolet photons of different energies, at 77°K, italics denoting major bands. Table II shows the energy differences (in cm^{-1}) between

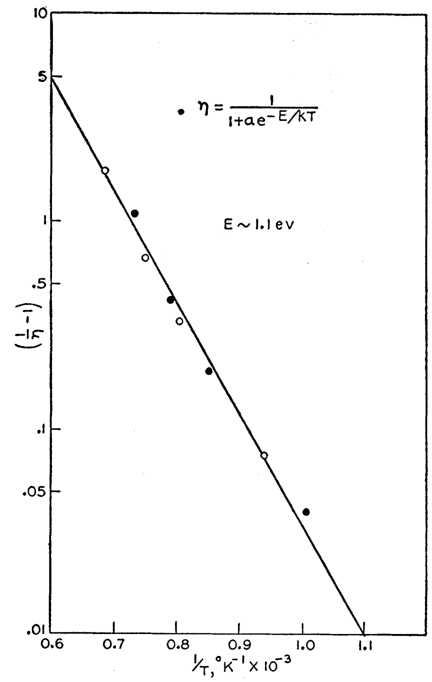

FIG. 8. (Reciprocal luminance −1) as a function of reciprocal temperature. Open circles are observed points. Closed circles are interpolated points from Fig. 6.

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[12] O. B. Lossev, Phil. Mag. **6**, 1024 (1928); Lehovec, Accardo, and Jamgochian, Phys. Rev. **82**, 330 (1951); **83**, 603 (1951).

[13] R. W. Smith, Phys. Rev. **93**, 347 (1954).

[14] J. R. Haynes and H. B. Briggs, Phys. Rev. **86**, 647 (1952).

[15] R. Braunstein, Phys. Rev. **99**, 1892 (1955).

[16] R. S. Pease, Nature **165**, 722 (1950).

[17] X-ray analyses (unpublished) by Dr. J. A. Amick of these Laboratories showed for BN: $a_0 = 2.508$ A, $c_0 = 6.674$ A, interplanar distance 3.337 A.

[18] R. Taylor and C. A. Coulson, Proc. Phys. Soc. (London) **A65**, 834 (1952).

[19] See E. E. Loebner on graphite [Phys. Rev. **102**, 46 (1956)].

major emission bands, for field excitation at room temperature, and ultraviolet excitation at 77°K. The energy between major emission bands which occurs most frequently is that of 1400 cm^{-1}. If successive energy differences are taken between all bands, major and minor, energy differences of the order of 100, 400, 500, and 800 cm^{-1} are obtained, in addition to the 1400 cm^{-1} difference. Such energy differences are usually associated with vibrational spectra. Miller and Wilkins[20] have investigated the infrared spectrum of BN and report findings at 1390 cm^{-1} (strong) and at 810 cm^{-1} (weak). The smaller energy differences can be ascribed to out-of-plane vibrations.

It would appear therefore that the fine structure luminescence spectrum from BN may be accounted for on vibrational grounds, the emission being due to transitions from vibrational levels in an excited electronic state to those in a ground state. The excited electronic states may be due to excitons, impurities or surface states, the identity of which have not yet been ascertained.

Temperature Quenching

If P_R is the probability of radiative transitions, P_N is the probability of nonradiative transitions, and η is the luminescence emission intensity, then

$$\eta = P_R/(P_R+P_N). \qquad (1)$$

Assuming that P_R is practically independent of temperature and that

$$P_N = Ke^{-E/kT}, \qquad (2)$$

we arrive at the expression

$$\eta = 1/(1+ae^{-E/kT}). \qquad (3)$$

TABLE II. Energy differences (in cm^{-1}) between major emission bands of boron nitride.

Field excitation (300°K)	3125 A excitation (77°K)
1500	1200
2300	1050
1400	1350
1800	1000
1400	1400
1000	
	3340 A excitation (77°K)
	1400
	1400
2650 A excitation (77°K)	
1800	
1700	
1900	
1400	
1400	
2990 A excitation (77°K)	
1400	
1400	
1250	
1350	
1400	
1450	

An estimate of the activation energy of the quenching process may be obtained from a plot of $[(1/\eta)-1]$ *versus* $1/T$, where η is the luminescence efficiency (radiance) and T is absolute temperature at which η is measured. Figure 8 is such a plot, covering the temperature range after the break-point. An activation energy of 1.08 ev is obtained for the quenching process, although there is as yet no indication as to the actual mechanism of the quenching.

ACKNOWLEDGMENTS

The authors wish to acknowledge valuable discussions with R. H. Bube, M. A. Lampert, and E. E. Loebner.

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[20] F. A. Miller and C. H. Wilkins, Anal. Chem. **24**, 1253 (1952).

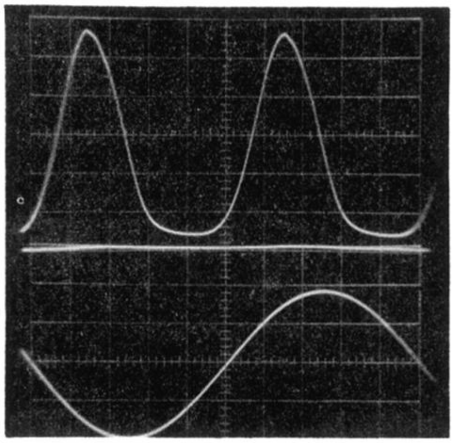

Fig. 5. Brightness wave form of field-excited boron nitride. Upper curve is cell-brightness; lower curve is applied cell-voltage.